tween copper(II) ions and ethylenediamine have been re-investigated over the visible range of the spectrum by the method of continuous variations and other physical methods.

2. In solutions over the concentration range studied it has been shown that both mono-ethylenediamine and bis-ethylenediamine copper(II) ions are present.

3. Water solutions of the crystalline complex compounds $Cu\,enCl_2$ and $Cu(en)_2Cl_2 \cdot H_2O$ show marked difference in absorption characteristics.

NEW ORLEANS, LOUISIANA RECEIVED DECEMBER 2, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Investigations on the Mechanism of Hydrogen Overvoltage. The Salt Effect[1]

BY ANDRÉ J. DE BÉTHUNE[2]

When the electrolysis of aqueous solutions of electrolytes is conducted in such a manner that hydrogen is evolved at the cathode, the electromotive force (with its sign[3]) of the cell

$$\text{cathode} \mid \text{solution} \mid \text{reversible hydrogen electrode} \quad (1)$$

is known as *the hydrogen overvoltage* η *of the cathode*. It is also convenient to define the cathode potential V as the e. m. f. (with its sign) of the cell

$$\text{constant reference electrode} \parallel \text{solution} \mid \text{cathode} \quad (2)$$

where the constant reference electrode may be, *e. g.*, a calomel electrode or a standard hydrogen electrode, and the liquid junction potential is eliminated as well as possible.[4] The relation between cathode potential and overvoltage is

$$V = V_e - \eta \quad (3)$$

where V_e is the equilibrium cathode potential (*i. e.*, the cathode potential at zero current, provided the electrochemical reaction remains the same in the measurement of V_e as in the measurement of V). The measured overvoltage defined above always includes a fraction of the Ohmic potential drop in the solution. This must be suitably eliminated or corrected for to obtain the "true" overvoltage. Overvoltage measurements can have meaning only within the current density range in which a single reaction occurs at the cathode (except at a dropping cathode). When several reactions occur at once, not only do the observed overvoltages and currents become very unsteady but they become difficult to interpret.

The overvoltage may be considered as an e. m. f. localized at or near the cathode surface, and needed to drive the chemical reaction at the cathode at a finite rate. The overvoltage vanishes at zero current, and is, in general, a monotonously increasing function of the current density I (in amperes $cm.^{-2}$). On several metals and in moderately acid solutions, the overvoltage can be represented over a fairly wide range of current densities by the Tafel equation

$$\eta = b \log I/I_0 \quad (4)$$

where b and I_0 are empirical constants.[5] At low overvoltages, this equation breaks down since η and I must approach zero together. The constant b is proportional[6,7] to the absolute temperature T, and at 25° often has the value 0.12 volt, which is $2\,(\ln 10)kT/e$, where k is the Boltzmann constant and e the electronic charge. This value of b has been confirmed by numerous workers and observed on different metals.[8] The constant I_0 is very dependent on the metal used; its temperature dependence is given by the Arrhenius equation (with an energy of activation of 18 kcal. on mercury in 0.2 N sulfuric acid.[6])

The dependence of I_0 on the composition of the solution has been investigated by Bowden,[9] Frumkin and co-workers[10] and Béthune and Kimball,[11] who all used mercury cathodes. Bowden discovered that, in dilute acids and in buffers containing 0.1 M potassium chloride, I_0 is constant throughout the entire pH range covered (from 0.8 to 6.6) ($\log I_0 = -11.5 \pm 0.2$ at 18°). This result was confirmed by the Russian workers for dilute solutions of *pure acids*. Béthune and Kimball extended Bowden's work to more concentrated acids and found that I_0 remains constant in sulfuric acid up to a concentration of 3 M. Above 3 M, there is a gradual decrease in overvoltage as the acid concentration is increased. In acid solutions containing salts, the Russian measurements seemed to indicate a salt effect, which, in the case of sulfates, raised the overvoltage (*i. e.*, lowered

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[1] Presented before the symposium on Galvanic Cells and Batteries, at the 113th National Meeting of the American Chemical Society, in Chicago, Ill., in April, 1948.

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[3] We are here adhering to the Lewis and Randall convention which makes the e. m. f. E of a cell positive when the + terminal is on the right.

[4] As here defined, the cathode potential is usually a negative quantity, while the overvoltage is always positive.

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

[6] F. P. Bowden, *Proc. Roy. Soc. (London)*, **A126**, 107 (1929).

[7] A. Frumkin, *Acta physico-chimica U.R.S.S.*, **18**, 45 (1943).

[8] S. Glasstone, *Ann. Reports Chem. Soc.*, **34**, 107 (1937); F. P. Bowden and J. N. Agar, *ibid.*, **35**, 90 (1938); K. Wirtz, *Z. Elektrochem.*, **44**, 303 (1938); S. Glasstone, "Introduction to Electrochemistry," Chapter XIII, Van Nostrand Co., Inc., New York, N. Y., 1942.

[9] F. P. Bowden, *Trans. Faraday Soc.*, **24**, 473 (1928).

[10] Papers by A. Frumkin, S. Levina, W. Sarinsky, S. Jofa, B. Kabanov, E. Kuchinski and F. Chistiakov, *Acta physico-chimica U. R. S. S.*, **6**, 491 (1937); **7**, 485 (1937); **10**, 317, 903 (1939); **18**, 23, 183 (1943).

[11] A. J. de Béthune and G. E. Kimball, *J. Chem. Phys.* **13**, 53 (1945).

I_0) and in the case of chlorides, bromides and iodides caused deviations from the Tafel relation, with an increase in overvoltage at the higher current densities, a decrease at the lower current densities, and evidence of hysteresis in the intermediate region. *That the overvoltage–current density-relation is independent of the hydrogen-ion concentration in dilute solutions of pure acids seems fairly well established.* A few scanty data on the effect of hydrogen pressure indicate that the cathode potential–current density relation is almost unaffected by variations in pressure in the range 0.1 to 10 atmospheres.[12]

Theoretical Developments

All recent theories[8] of hydrogen overvoltage are based on a mechanism, first proposed by Erdey-Grúz and Volmer,[13] which postulates that the slow step is the discharge of the hydrogen ion or proton

$$H^+ + e^- = H \qquad (5)$$

This mechanism gives a reasonable explanation for the observed value of b. Eyring, Glasstone and Laidler[14] (EGL) first attempted to explain why I_0 should be independent of the hydrogen ion concentration when it is the measure of the rate of a reaction involving hydrogen ions. They postulated that the protons discharged at the cathode come from *water* molecules rather than from *hydronium ions,* thus providing a reactant of essentially constant concentration. Unfortunately, this very attractive theory led to an erroneous conclusion, *viz.*, that the I *vs.* V relation should be independent of pH, rather than the I *vs.* η relation as observed experimentally. Since V_e decreases with increasing pH, this would have led to the conclusion that the overvoltage decreased with decreasing hydrogen ion concentration.[15]

To resolve the difficulties of the EGL theory, Kimball, Glasstone and Glassner[16] (KGG) postulated that the electrical double layer at the electrode surface, composed of the adsorbed ions and their electrical image in the electrode, extends outward from the electrode into the solution far enough to include *at least* two layers of adsorbed ions, so that a proton crossing the double layer must pass over at least two potential energy barriers before it reaches the electrode. KGG showed that the charge density in the inner ion layer increases with hydrogen ion concentration, hydrogen pressure and overvoltage, but that at reasonably high values of these variables, it becomes essentially "saturated," and then shields the inner half of the double layer from any further electrical disturbances in the outer half, and *vice versa.* That part of the reversible potential which varies with pH is then set up across the outer half of the double layer, while that part which varies with hydrogen pressure operates across the inner half. *If the slow step is the passage of a proton across the inner energy barrier,* the overvoltage is also set up across the inner half of the double layer. The cathode potential[17] V may be assumed to be localized across the double layer. It can then be written as the sum of an inner and an outer potential term

$$V = V_i + V_o \qquad (6)$$

If $(H_3O^+)_a$ is the activity of the hydronium ions adsorbed in the inner ion layer, and (H_3O^+) that in the solution, we have

$$V_o = (kT/e) \ln (H_3O^+)/(H_3O^+)_a \qquad (7)$$

$$V_i = (kT/e) \ln (H_3O^+)_a/p_{H_2}^{1/2} - \eta \qquad (8)$$

If hydronium ions are the only ions present in the inner ion layer, their activity is proportional to the charge density, to a first approximation. Thus $(H_3O^+)_a$ becomes essentially equal to a constant Q in the region where electrical saturation takes place. This conclusion had already been reached intuitively by Frumkin.[18]

For the rate of the cathode reaction, KGG write the equation[16,19]

$$I = Pa_0 \exp(-\alpha e V_i/kT) \qquad (9)$$

where α is the fraction of the inner potential operating between the inner ion layer and the top of the potential energy barrier, a_0 is the activity of the source of protons in the inner ion layer, and P is a rate constant. Substitution of (8) into (9) gives the relation between current density and overvoltage

$$I = Pa_0 (H_3O^+)_a^{-\alpha} p_{H_2}^{\alpha/2} \exp(+\alpha e\eta/kT) \qquad (10)$$

Volmer[13] pointed out that when α is set equal to 1/2, the correct value is obtained for b. The coefficient of the exponential is I_0. Its dependence on the hydrogen pressure is consistent with the few experimental results available. KGG retained the EGL postulate that the protons discharged come from water molecules, and they set a_0 equal to the activity of water in the inner ion layer. This is essentially constant, so that I_0 is independent of pH, in agreement with experiment. The EGL postulate, however, is not necessary to account for the observations. It is possible to set a_0 equal to the activity of hydronium ions in the inner ion layer and still obtain an expression for I_0 that is independent of pH. Thus the question is still open as to which molecular species, water or hydronium ions, is the source of the protons involved in the slow step.

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(12) S. J. Bircher and W. D. Harkins, THIS JOURNAL, **45**, 2890 (1923); M. Knobel, *ibid.*, **46**, 2751 (1924); H. M. Cassel and E. Krumbein, *Z. physik. Chem.*, **A171**, 70 (1935).

(13) T. Erdey-Grúz and M. Volmer, *Z. physik. Chem.*, **A150**, 203 (1930).

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

(15) A. Frumkin, *Acta physico-chimica U. R. S. S.*, **12**, 481 (1940).

(16) G. E. Kimball, S. Glasstone and A. Glassner, *J. Chem. Phys.*, **9**, 91 (1941).

(17) For theoretical purposes, the cathode potential V, defined as the e. m. f. of cell (2), is referred to the standard hydrogen electrode, with the liquid junction potential eliminated. Failure to define the reference electrode explicitly has led to much confusion in overvoltage theories.

(18) A. Frumkin, *Z. physik. Chem.*, **A164**, 121 (1933).

(19) G. E. Kimball, *J. Chem. Phys.*, **8**, 199 (1940).

KGG made another assumption, *viz.*, that the charge in the inner ion layer is due entirely to the hydronium ions, since other ions could come in only at the expense of some of their hydration energy. When this assumption is modified to permit the entrance of other positive ions, the theory predicts a "salt" effect on the overvoltage.

Theory of the Salt Effect. Monovalent Ions.—Let us assume that the solution contains monovalent cations M^+ in addition to hydronium ions. If these cations can penetrate into the inner ion layer and, by their charge, contribute to its electrical saturation, they will displace hydronium ions from this layer and decrease their activity $(H_3O^+)_a$ below its value Q in pure acid solutions. This should affect the overvoltage–current density relation given by (10). It is easy to see qualitatively the direction in which the overvoltage should be displaced. If we follow the EGL postulate, and set a_0 equal to the activity of water, the factor $(H_3O^+)_a$ comes in to the $-\alpha$ (or $-{}^1/_2$) power. Any lowering in $(H_3O^+)_a$ will therefore mean an increase in I_0, *i. e., a decrease in overvoltage at constant current density.* On the other hand, if a_0 is set equal to $(H_3O^+)_a$, this factor comes in to the $1 - \alpha$ (or $+{}^1/_2$) power, so that a lowering in $(H_3O^+)_a$ will mean a decrease in I_0, *i. e., an increase in overvoltage at constant current density,* Therefore, the salt effect, if it exists at all and is big enough to be observed, should settle the question as to the source of protons involved in the slow step.

KGG assumed that the ions M^+ could not enter the inner ion layer without losing so much of their energy of hydration as to be practically excluded. We shall go to the opposite extreme and neglect completely this effect of size difference. *We shall assume that the two ionic species penetrate into the inner ion layer in the same ratio in which they are present in the solution, i. e.,* that[20]

$$(M^+)_a/(H_3O^+)_a = (M^+)/(H_3O^+) \qquad (11)$$

With this assumption, it is possible to calculate the change in overvoltage expected from the addition of salt. The constant charge density Q needed to saturate the inner ion layer must now be set equal to the sum $(H_3O^+)_a + (M^+)_a$. In view of (11), this yields the result

$$(H_3O^+)_a = Q/[1 + (M^+)/(H_3O^+)] \qquad (12)$$

i. e., the activity of hydronium ions adsorbed in the inner ion layer is cut down by the addition of salt by a factor of $1 + (M^+)/(H_3O^+)$.

To determine the effect of this change in $(H_3O^+)_a$ on the overvoltage, let us rewrite (10) in the logarithmic form

$$\ln I = \ln P\, p_{H_2}^{\alpha/2} + \ln a_0 - \alpha \ln (H_3O^+)_a + \alpha e\eta/kT \qquad (13)$$

If a_0 is taken as the activity of water, the change in overvoltage, at constant current density and hydrogen pressure, should be

$$\Delta\eta = -(kT/e) \ln [1 + (M^+)/(H_3O^+)] \qquad (14)$$

If, however, a_0 is taken as the activity of hydronium ions, the change in overvoltage should be

$$\Delta\eta = [(1 - \alpha)/\alpha]\,(kT/e) \ln [1 + (M^+)/(H_3O^+)] \qquad (15)$$

If we take the experimental value of $\alpha = {}^1/_2$, these two expressions reduce to the same form and differ only in sign. From them we can calculate the magnitude of the salt effect. For a salt:acid concentration ratio of 1:1, $\Delta\eta$ should amount to ±0.018 volt at 25°; for a ratio of 10:1, ±0.062 volt; of 100:1, ±0.119 volt; of 1000:1, ±0.178 volt. Here the + sign applies if the protons are postulated to come from hydronium ions, and the − sign if they come from water. These $\Delta\eta$'s are certainly observable within the precision of most overvoltage measurements.

The salt effect, however, need not be as big as predicted here. KGG excluded it by assuming that the hydrated metal ions were too big to penetrate into the inner ion layer. Here, the assumption has been made that both ions could penetrate equally easily. If there is a partial restriction to the penetration of the metal ions, the salt effect may be smaller than predicted above.

Divalent Ions.—Let us now assume that the solution contains divalent cations M^{++} in addition to hydronium ions. Let us also assume, as before, that *the two ions, apart from their charge, can penetrate into the inner ion layer with equal facility, i. e.,* there are no specific restrictions due to water of hydration or any other cause. Then the potential across the outer half of the double layer, at equilibrium, must satisfy the equations

$$V_o = (kT/e) \ln (H_3O^+)/(H_3O^+)_a = (kT/2e) \ln (M^{++})/(M^{++})_a \qquad (16)$$

The distribution equation, analogous to (11), now takes the form

$$(H_3O^+)_a/(H_3O^+) = [(M^{++})_a/(M^{++})]^{1/2} \qquad (17)$$

The constant charge Q which saturates the inner ion layer must now be set equal to $(H_3O^+)_a + 2(M^{++})_a$. By means of (17), $(M^{++})_a$ can be eliminated and the resultant quadratic in $(H_3O^+)_a$ solved to yield the result

$$\ln (H_3O^+)_a/Q = -(1/2) \ln 2Q(M^{++})/(H_3O^+)^2 \qquad (18)$$

The absolute value of this expression cannot be calculated because of the constant Q whose value is unknown. Consequently it is not possible to predict exactly to what extent an *initial addition* of divalent ion will lower the activity of hydronium ions in the inner ion layer. However the fractional lowering of this activity for every *subsequent addition* of divalent ion can easily be calculated from (18) and is given by

$$\Delta \ln (H_3O^+)_a = -(1/2)\, \Delta \ln (M^{++})/(H_3O^+)^2 \qquad (19)$$

If we take $\alpha = 1/2$, the corresponding change in overvoltage can be expressed from (13) as

$$\Delta\eta = \pm (kT/2e)\, \Delta \ln (M^{++})/(H_3O^+)^2 \qquad (20)$$

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[20] Here and throughout the remainder of this paper, the assumption will be made that the activities of all species may be taken proportional to their concentrations.

where the + and − signs have the same meaning as before.

We have seen that the KGG theory accounts for the lack of variation of the η *vs.* I relation with *p*H by concluding that there exists, adjacent to a cathode on which hydrogen is being evolved, an "electrically saturated" layer of hydronium ions whose activity is virtually independent of *p*H. However, KGG left two points unsettled, *i. e.*, whether the protons discharged come from water molecules or from hydronium ions, and whether or not metallic ions are excluded from the saturated layer by their water of hydration.

If metallic ions can penetrate into the saturated layer and contribute to its electrical charge, they will displace hydronium ions from it and there will be a salt effect on the overvoltage. This salt effect, if it exists, should cause a rise in overvoltage if the protons come from hydronium ions, and a lowering if they come from water. The magnitude of the effect can be calculated if the size difference between the ions is neglected. If this size difference cannot be neglected, the salt effect may be smaller than the value predicted. It is therefore of interest to determine *experimentally* whether the salt effect exists, and, if so, its direction and magnitude, since such measurements will throw light on the two unsettled points of the KGG theory.

Since Bowden's[9] measurements in buffer solutions did not seem to indicate any salt effect, and since the Russian[10] results were inconclusive, an experimental investigation of these points was undertaken. Measurements were made on four different solutions of hydrochloric acid, three of hydrochloric acid–potassium chloride, and two of hydrochloric acid–calcium chloride at 25° and atmospheric pressure.

Experimental

The cell used is sketched in perspective in Fig. 1. It is made of Pyrex glass, and consists of three compartments: the anode A, the cathode C and the reference hydrogen electrode H. The tube connecting the anode and cathode compartments contains a fritted glass plate to prevent convection. The solution to be electrolyzed is admitted into the cell in an atmosphere of hydrogen through the two inlet tubes at the rear of A and H. At the rear of C is the mercury reservoir and inlet tube. At the front of A, C and H are three outlet tubes of similar design (only that at A is sketched in full, that at C is made of capillary tubing) through which the solution and the mercury cathode can be run out by excess hydrogen pressure. Compartments A and C are fitted with outlets to the hydrogen exit line leading out of the window. All ground glass joints and stopcocks are lubricated with distilled water, and held in place by rubber bands. The cell is mounted in a thermostat whose temperature can be controlled to 25.00 ± 0.02°.

The anode A is a large piece of platinized platinum foil which can be made to function satisfactorily in an atmosphere of hydrogen as a hydrogen anode, except at high currents ($>$ 100 to 500 μa) where it begins to function as a chlorine anode in the chloride solutions used. To prevent vitiation of the overvoltage measurement at the cathode by the presence of chlorine as a reducible impurity in the solution, the measurements at high currents are generally reserved to the end of each run, after which the solution is discarded and the cell cleaned out. It was observed that the presence of chlorine in the cell does depress the overvoltage upon return to the low currents. Electrical contact with the anode is made through mercury and a platinum in uranium glass seal.

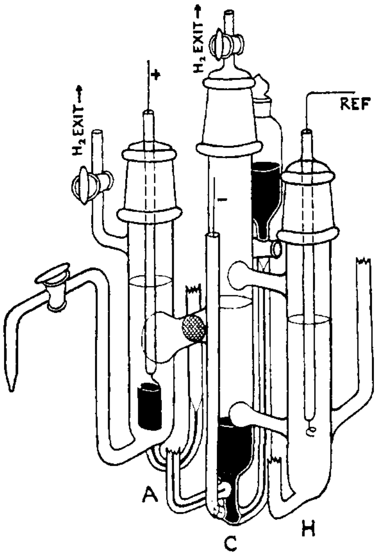

Fig. 1.—Apparatus.

The reference electrode H is the short end of a long piece of 0.35 mm. platinum wire wealed into a Pyrex glass tube. Electrical contact is made directly to the other end of this wire at the top of the tube. (Mercury contacts at this electrode always leaked mercury into the cell, and had to be eliminated.) This electrode, when platinized, functions as a very satisfactory reversible hydrogen electrode in an atmosphere of hydrogen. Continuous hydrogen bubbling is not necessary. Its potential (and also that of the hydrogen anode A) can be checked against that of a saturated calomel electrode (not shown in the figure) through the outlet tube at the front of H (or A). It was found that the optimum practice is to clean the two platinum electrodes in *aqua regia* and replatinize them afresh, at the beginning of each run. The useful life of the hydrogen reference electrode does not in general exceed twenty-four to forty-eight hours.

The cathode C, of redistilled mercury, is run in from the reservoir into the bottom of C up to the level of the side-arm to H. The cross-sectional area of the cathode, determined by measuring the height corresponding to a given volume of water pipetted into the cathode chamber, is 1.10 cm.^{2} ± 5% (log = 0.04 ± 0.02). The optimum practice is to run the cathode into the cell after drying the cell by passage of dry hydrogen for several hours. Wetting of the cathode walls leads to a depression of the overvoltage at low currents, which is more marked the higher the chloride ion concentration. This depression is *attributed* to the local formation along the cathode walls of mercurous chloride which migrates up to the cathode surface and there acts as a reducible impurity. Wetting of the cathode walls inevitably occurs during the course of a run so that the best results at low currents are obtained at the beginning of each run. This depression can also be observed temporarily by jarring the cathode or stirring it by violent bubbling of hydrogen through the solution. Electrical contact with the cathode is made through mercury and a platinum-in-Pyrex seal.

The solution to be electrolyzed is placed in the 1-liter flask F (Fig. 2) and the air removed by bubbling purified hydrogen through the solution for twelve hours (overnight) or longer. It is well known that oxygen, as a reducible impurity, exerts a depolarizing action on hydrogen cathodes and depresses the overvoltage. The precautions recommended by all workers in this field for the *stringent removal of oxygen cannot be too strongly emphasized.* When the removal of oxygen from the solution is incomplete, the overvoltage is low at the beginning of a run, and slowly rises in the course of a few hours to its steady value[10,11] as the last traces of oxygen are being gradually reduced at the cathode. In the present series of experiments, this difficulty was not encountered, the overvoltage generally being at its steady value at the beginning of a run, from which it was concluded that the oxygen removal is sufficiently complete. The depressions in overvoltage mentioned in the preceding paragraph, which were at first attributed to insufficient oxygen removal, later had to be attributed to the reason given above.

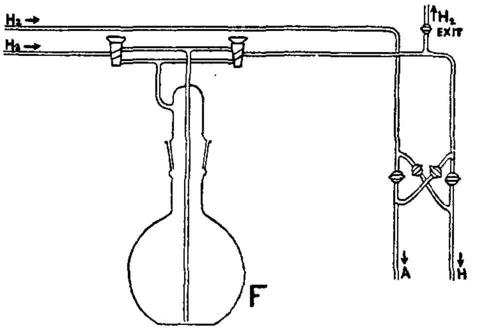

Fig. 2.—Apparatus.

Electrolytic tank hydrogen is purified by passage over a palladinized asbestos catalyst (made by soaking Gooch asbestos in a palladium chloride solution, drying, and reducing with hydrogen *in situ*), at the temperature of 450° recommended by Professor Beattie. It is dried over a long bed of calcium chloride and of calcium oxide. The hydrogen stream is then divided between the two hydrogen lines shown in Fig. 2, and the pressure on each line can be regulated independently by stopcocks (greased) and safety bubblers not shown in the diagram.

Figure 2 shows the apparatus used for admitting both dry hydrogen gas, and solution in an atmosphere of hydrogen, to the electrolytic cell, through the inlet tubes at the back of compartments A and H. All the stopcocks and ground joints shown in Fig. 2 are lubricated with distilled water except that to the hydrogen exit line which is greased.

The wiring diagram is schematically the same as that given before.[11] The polarizing e. m. f. is derived from three 6-volt lead storage batteries in series, and is adjusted by a voltage divider consisting of four rheostat potentiometers of 1000, 10, 2 and 100 ohms in series in that order. The two voltage taps are located at the center of the 1000 and 100 ohm rheostats, the 10 and the 2 being used as variable resistors. This makes it possible to go from a very coarse to a very fine adjustment of the applied e. m. f., which is essential for measurements at currents of 1 μa., or less.

The current is measured with a sensitive multi-scale d. c. microammeter, Type 501, number 9918, manufactured for us by the Rawson Electrical Instrument Company of Cambridge, Mass. This instrument has a selector for eight scales: 0–2, 6, 20, 60, 200, 600 μa., 2 and 6 ma., and a "short" position to protect the meter when not in use. The 5″ scale is divided into 100 parts on the 0–2 ranges, and into 120 parts on the 0–6 ranges. Calibration showed it to be good within the stated precision of 0.5% of full scale. By means of an external shunt, currents up to 1.12 amps. can be read. At high currents (> 1 ma.), the instrument is overdamped and is extremely sluggish. This, however, is not a disadvantage in overvoltage measurements where the steady state condition is of interest.

The electromotive force is measured with a Leeds and Northrup Type K potentiometer number 9043. The null-point is obtained with a Leeds and Northrup table galvanometer having a sensitivity of 0.16 mv./mm., and for the fine adjustment, with a Rubicon Spotlight galvanometer number 7462 with a sensitivity of 1.2 μ v./mm. or 0.0085 μa./mm. An auxiliary student potentiometer can be brought into the circuit to measure e. m. f.'s exceeding 1.6 volts. In this apparatus, the overvoltage is measured directly as the e. m. f. between the cathode C and the hydrogen reference electrode H.

The hydrochloric acid solutions electrolyzed were prepared by dilution of du Pont C. P. concentrated solution with conductivity water. C. P. potassium chloride was recrystallized once and used in the preparation of the hydrochloric acid–potassium chloride solutions, except in some of the final runs in which Merck Reagent grades potassium chloride was used directly. The hydrochloric acid–calcium chloride solutions were prepared by weighing out Merck Reagent grade calcium carbonate and adding the necessary amount of standard hydrochloric acid to the carbonate.

At the beginning of each run, the cell is flushed thoroughly with dry hydrogen for two or three hours, then some mercury is run into the dry cathode chamber, discarded, and the mercury cathode run in. The polarizing e. m. f. is turned on between A and C. The cell is filled quickly with solution, rinsed through with about 100 to 200 ml. (2 to 4 times the cell capacity), refilled, all the stopcocks are shut, and the measurements are begun. At the conclusion of a run, the optimum practice is to discard the solution, rinse the cell several times with distilled water, run out the cathode and dry the cathode chamber by letting dry hydrogen leak out for one or two hours through the outlet tube at C, remove the two platinum electrodes, clean them in *aqua regia*, replatinize them and return them to the cell, and flush the air out to make the cell ready for the next run. If this routine functions smoothly (!), about a week's time is spent on one run: one or two days in preparation, one or two days taking the measurements, and one or two days cleaning the cell and plotting the data.

Correction for *iR* Drop.—The operation of this cell proved very satisfactory except in one respect. The side-arm between C and H is made of 8 mm. tubing. Consequently, the equipotential surface in the solution which crosses the entire length of this side-arm from C to H does not lie at the cathode surface but at a point *ca.* 4 mm. above the cathode surface. The measured overvoltage then also includes the ohmic drop in this 4 mm. layer of solution. At high currents, when the polarizing e. m. f. exceeds 10 volts, and the field in the solution approaches 1 volt cm.$^{-1}$, this ohmic drop can amount to as much as 0.4 volt, a non-negligible quantity, for which it is necessary to make a correction. It would be desirable to redesign the cell so as to decrease this distance from 4 mm. to less than 1 mm., and so decrease the magnitude of the correction.

The effect of this ohmic drop on the measured overvoltage is illustrated in Fig. 3, which is a Tafel plot of the data for 0.01 *M* hydrochloric acid. Here the solid curves give the locus of the experimental points. The sharp upward deviation of the curves from the Tafel straight line at the high currents is caused by the ohmic drop. To prove that this is actually the case, an experiment was run in which the mercury level of the cathode was purposely left at a point about 7–8 mm. below the side-arm, and the measurements made. Then more mercury was run in to bring the cathode to its normal level, and the measurements repeated. The data showed a much sharper upward curvature when the cathode was low than when it was at its normal level. The difference between the two measured overvoltages turned out to be directly proportional to the current, and to have exactly the value expected from Ohm's law and the known conductivity of the electrolyte.

To correct for the ohmic drop, the following procedure was devised. The linear portion of the Tafel plot in the low current region is extended upwards, as a first approximation to the "correct" curve in the high current region (dotted line in Fig. 3). The difference between the measured overvoltage η and this extended straight line, which we shall call $\Delta\eta_1$, is plotted against the current i. It usually turns out that $\Delta\eta_1$ is a linear function of i, which,

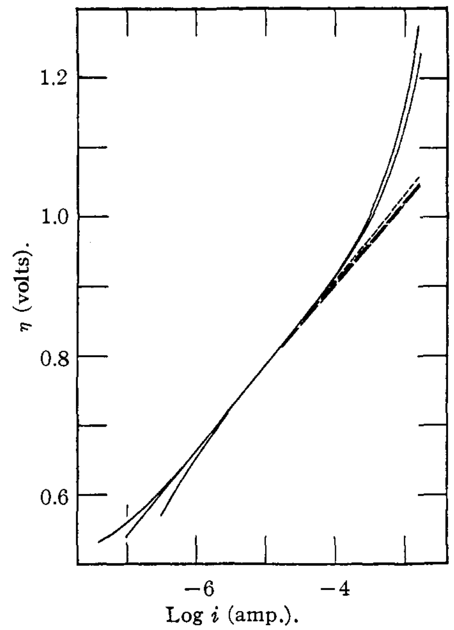

Fig. 3.—Hydrogen overvoltage on mercury in 0.01 *M* hydrochloric acid at 25° illustrating the correction for *iR* drop at high currents.

however, does not pass through the origin. The slope of the $\Delta\eta_1$ *vs.* i plot gives a first approximation R_1 to the resistance of the solution layer for which the ohmic correction has to be made. The measured overvoltage η is then corrected by subtracting iR_1, and the resulting points constitute the second approximation to the "correct" curve on the Tafel plot. A "best" straight line is drawn through these points, and the difference between η and this second line, which we shall call $\Delta\eta_2$, is plotted against i. This plot again usually turns out to be a straight line which passes much closer to the origin than the plot of $\Delta\eta_1$ *vs.* i. The slope of the $\Delta\eta_2$ *vs.* i plot gives a second approximation R_2 to the resistance of the solution layer, by means of which the above procedure can be repeated, if necessary, to a third approximation, etc. This procedure is repeated until *a straight line* is obtained on the Tafel plot which has the following property, *viz.*, that the difference $\Delta\eta$ between the measured overvoltage and *this straight line* gives a linear $\Delta\eta$ *vs.* i plot which passes through the origin. *This straight line* on the Tafel plot is then adopted as the "correct" overvoltage curve in the high current region. The slope of its $\Delta\eta$ *vs.* i plot gives the resistance R of the solution layer, from which the thickness of the layer can be calculated. The calculated thicknesses usually came out between 3 and 6 mm., which are reasonable values in view of the geometrical construction of the cell.

The two dashed lines in Fig. 3 correspond to the two experimental curves, when corrected for ohmic drop in this way. It is interesting to note that the difference between the two experimental curves amounts to as much as 50 mv. at the highest current which could be obtained. This difference corresponds to a shift of about 1.4 mm. in the level of the cathode in the two experimental runs. After correction, the difference between the two curves is reduced to 4 mv., a value which is well within the precision of the measured overvoltages in the low current region where the ohmic drop is negligible, *viz.*, ±3 mv. for 0.01 *M* hydrochloric acid.

It is also interesting to note that the best value of the slope of the Tafel plot for this solution, as obtained from the uncorrected curve in the current region: $-6 < \log i < -4.5$, is $b = 124 \pm 2$ mv. This corresponds to an α value of 0.48. However, the high current data, when corrected for ohmic drop, in nearly every run with every solution tested, give values of b in the range 118 ± 2 mv., corresponding to an α value of exactly 0.50. The reason why the slope of the uncorrected Tafel plot should be higher than that of the corrected Tafel plot is not far to see. At very low currents, traces of reducible impurities (whether oxygen, or as was suspected in these experiments, the local formation along the cathode walls of a surface film of calomel) exert a depolarizing action on the cathode and depress the overvoltage, causing the curve to bend downward as is usually observed. (A curve which bends upward at low currents, as it theoretically should, is the exception rather than the rule. Figure 3 gives examples of both types.) At high currents, the Tafel plot is bent upward by ohmic drop. The combined effect of the downward curvature at low currents, and of the upward curvature at high currents, causes the increase in the slope of the uncorrected Tafel plot.

Calculation of the Current Density.—In Figs. 3 to 6, the scale of abscissae is $\log i$, the common logarithm of the current expressed in amperes. To convert to the current density, it is necessary to divide the current by the cathode area of 1.10 cm.^{2} ± 5%. We can therefore obtain the logarithm of the current density I from the relation

$$\log I = \log i - 0.04 \qquad (21)$$

The uncertainty of 5% in the cathode area introduces an uncertainty of ±0.02 in $\log I$.

Results

Hydrochloric Acid Solutions.—The overvoltage was measured as a function of the current in hydrochloric acid solutions in the concentration range 1 molar to 10^{-3} molar. The results are given in a Tafel plot in Fig. 4 and are corrected for *iR* drop. Each curve represents a visual average of several hundred experimental points obtained in several parallel runs. The precision is about ±5 mv. in 1 *M* and 0.1 *M* solutions, ±3 mv. in 0.01 *M* solution, and ±12 mv. in 0.001 *M* solution. These

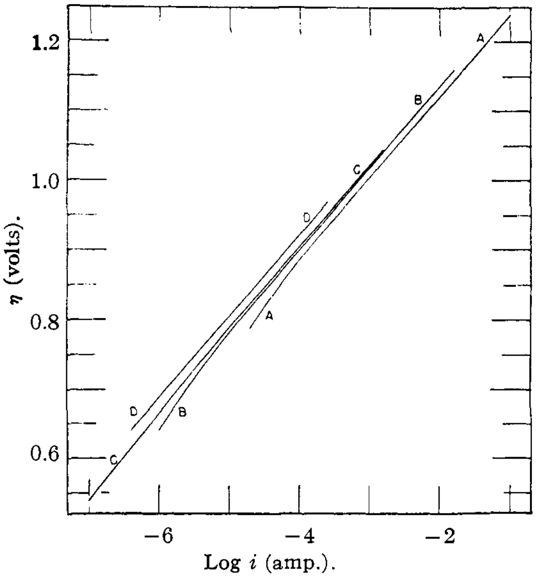

Fig. 4.—Hydrogen overvoltage on mercury in hydrochloric acid solutions at 25°: curve A, 1.005 *M*; B, 0.1 *M*; C, 0.01 *M*; D, 0.001 *M*.

results confirm the observation of previous workers that the hydrogen overvoltage–current density relation is practically independent of *p*H in dilute acids. They are interesting, however, in that, for the first time, they show a trend in the relation between overvoltage and *p*H. The overvoltage is nearly 40 mv. higher in 10^{-3} *M* hydrochloric acid than in 1 *M* hydrochloric acid, and this difference is well beyond the experimental uncertainty. This trend also manifests itself in the values of the Tafel constant I_0 whose logarithms are given in Table I.

The characteristics of these four solutions and of their η *vs.* I curves are summarized in Table I. The *p*H values are an average of glass electrode measurements, and of hydrogen electrode measurements made directly in the overvoltage cell. The values of the slope b of the Tafel plot are given, in millivolts, both for the uncorrected curves and for the curves corrected for iR drop. The corrected b's all came so close to 118 mv. that this value was adopted for all the solutions. This was done to provide a uniform basis of comparison for the Tafel I_0's (given in amp.cm.$^{-2}$), since the value of I_0 is affected by the particular choice of b.

TABLE I

OVERVOLTAGE MEASUREMENTS ON Hg IN HCl AT 25°

Molarity	*p*H	b (uncor.)	b (cor.)	log I_0 (cor.)
1.005	0.12	120 ± 2	118 ± 2	−11.53 ± 0.05
0.1	1.11	121 ± 2	118 ± 2	−11.67 ± .05
0.01	2.05	124 ± 2	118 ± 2	−11.71 ± .04
0.001	3.05	123 ± 3	118 ± 2	−11.84 ± .10

Hydrochloric Acid–Potassium Chloride.—The first solution investigated was 0.001 *M* hydrochloric acid–1 *M* potassium chloride, in which the concentration ratio of potassium to hydrogen ions is 1000:1. This high ratio was purposely chosen since it was expected that, if a salt effect exists, it would certainly show up in such a solution. The change in overvoltage anticipated theoretically was about 180 mv. When the measurements were attempted, with a polarizing current of several milliamperes, it was found that the salt effect not only did exist, but that it was so large that the measured overvoltage exceeded 1.6 volts, the maximum range of the Type K potentiometer. An auxiliary student potentiometer was brought into the circuit, and "overvoltages" of 1.65 and 1.71 volts were recorded on two successive runs in the same solution. These overvoltages were practically independent of the current, in fact, they even maintained their value with reverse currents of 0.1 μa. At high currents (>1 ma.), however, and up to the maximum attainable current of 30 ma., the overvoltage rose sharply (this may have been an iR effect, or the approach to a limiting diffusion current, or both). A remarkable feature of this electrolysis was the absence of gas evolution on the cathode, except at the very highest currents (>1 ma.), in contrast to that in the corresponding pure acid, where gas bubbles were present at all current densities. This result led to the conclusion that potassium ions were being reduced rather than hydrogen ions. This conclusion was confirmed by the fact that, after the electrolysis was stopped, and the cell had been rinsed with distilled water, the cathode was found to react with the water with a steady stream of very tiny bubbles. This first experiment indicated the existence of a salt effect much higher than that anticipated in that it actually blocked off completely the access of hydrogen ions to the electrode.

In an attempt to get a salt effect that would be more reasonable, the lower salt-to-acid concentration ratio of 100:1 was chosen, and the solution 0.001 *M* hydrochloric acid–0.1 *M* potassium chloride was investigated next. By keeping the initial polarizing current low (*ca.* 10 μa.), it was possible to obtain an overvoltage only 140 mv. higher than in the corresponding pure acid, and gas bubbles did appear on the cathode, indicating the evolution of hydrogen. This result proved very satisfactory in that the observed change was of the predicted order of magnitude (120 mv.). The addition of salt here caused an *increase* in the overvoltage. However, as the polarizing current was increased beyond 60 μa., the overvoltage began to jump erratically upward, and the electrode passed through a whole series of non-reproducible non-steady states whose points often gave negative slopes on the Tafel plot, until, at currents in excess of 1 ma., the overvoltage had risen to 1.6 volts and bubbles were no longer observed. At the maximum attainable current of 4.4 ma. the overvoltage rose to 1.78 volts. Then, as the current was lowered, the overvoltage decreased asymptotically to a constant value of 1.65 volts which it maintained as the current decreased through zero to a reversed value of 10 μa. Here was a repetition of the behavior observed with the previous solution. The cathode which had begun to function as a hydrogen electrode with a low initial polarizing current, was now functioning as a potassium-amalgam electrode. On standing overnight with a polarizing current which went from 14 to 22 μa., the overvoltage gradually decreased to 1.15 volts, a value about 200 mv. higher than the normal hydrogen overvoltage at this point in this solution.

The remaining measurements in 0.001 *M* hydrochloric acid—0.1 *M* potassium chloride solution were concentrated in the low current region where the cathode functions as a hydrogen electrode. The results of nine different runs on five samples of liquid are represented by curve E in Fig. 5. The results are not nearly as nicely reproducible as with the pure acid solutions, and the curves for the different runs fall in a band about 60 mv. wide. Line E in Fig. 5 represents a visual estimate of the center of gravity of this band, and the vertical lines give the spread of the points. At currents from 60 to 500 μa., the upward drift in the overvoltage described in the preceding para-

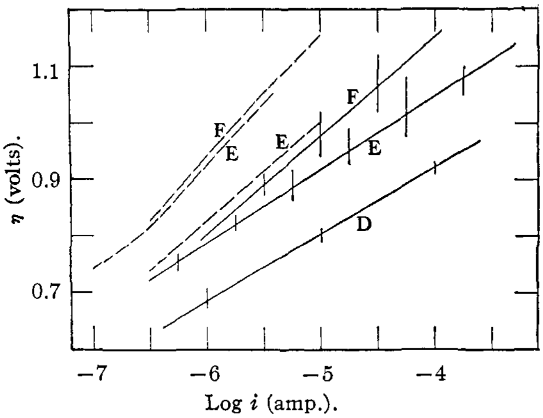

Fig. 5.—Hydrogen overvoltage on mercury at 25°: curve D, 0.001 *M* hydrochloric acid; E, 0.001 *M* hydrochloric acid–0.1 *M* potassium chloride; F, 0.001 *M* hydrochloric acid–1 *M* potassium chloride.

graph begins to set in. The two dotted curves marked E in Fig. 5 represent curves obtained on returning to low currents after this upward drift has set in. They are very reminiscent of the "upper branches" in Bowden's overvoltage curves,[9] which were also obtained in solutions containing 0.1 *M* potassium chloride. At low currents (from 3 μa. on down), depressions in the overvoltage begin to set in, so that the curves bend downward. These depressions have been attributed, as noted before, to the local formation along the cathode walls of calomel which migrates up to the cathode surface where it acts as a reducible impurity. These depressions are very noticeable in solutions containing appreciable concentrations of chloride ions.

The solution 0.001 *M* hydrochloric acid–1 *M* potassium chloride was then re-investigated in the low current region, where the cathode could be made to function as a hydrogen electrode. The results of eight runs on two samples of liquid are represented by curve F in Fig. 5. The hysteresis is more pronounced than for curve E, as indicated by the vertical lines. The upward drift at the upper end of the curve sets in at a lower current, and the depressions at the lower end come in at a higher current, so that the resulting curve is markedly steeper than curve E. Nevertheless, it is interesting to note that, when curves E and F are compared with the curve D for the corresponding pure acid, the rise in overvoltage is in each case of the magnitude predicted theoretically (Table II).

One more solution was investigated in this group, 0.1 *M* hydrochloric acid–0.1 *M* potassium chloride, with a salt-to-acid ratio of 1:1, to find out whether an increase in hydrogen ion concentration at a constant potassium ion concentration of 0.1 *M* would bring the overvoltage down. This solution was as well behaved as the corresponding pure acid. There was no marked hysteresis, and the results (corrected for iR drop) are well represented by curve G of Fig. 6 with a precision of ±6 mv. The overvoltage is considerably lower than in curve E of Fig. 5, and is only slightly higher than for the pure acid (curve B, Fig. 6) as anticipated theoretically (Table II).

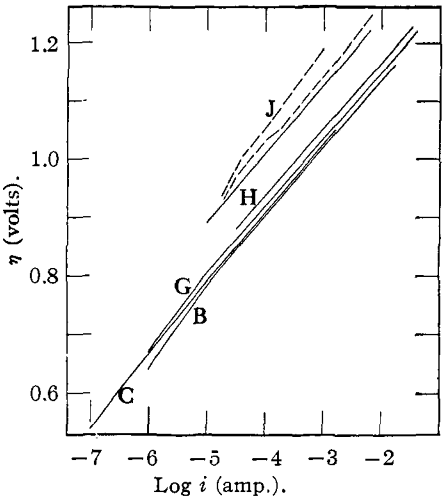

Fig. 6.—Hydrogen overvoltage on mercury at 25°: curve B, 0.1 *M* HCl; C, 0.01 *M* HCl; G, 0.1 *M* HCl–0.1 *M* KCl; H, 0.1 *M* HCl–0.05 *M* $CaCl_2$; J, 0.01 *M* HCl–0.05 *M* $CaCl_2$.

The results on hydrochloric acid–potassium chloride solutions are summarized in Table II. For those solutions which gave bands of points, it is impossible to assign definite values of the Tafel parameters b and I_0, and the values given correspond to the line chosen as the center of gravity of the band. These values are consequently very uncertain. The last two columns give, respectively, the observed increment in overvoltage due to the salt effect, and the increment calculated theoretically from eq. (15). The salt effect is here seen to cause an *increase* in the overvoltage, which can be well represented by eq. (15) within the rather large experimental uncertainty.

TABLE II

OVERVOLTAGE MEASUREMENTS ON Hg IN HCl–KCl AT 25°

Molarity HCl	Molarity KCl	pH	b	log I_0	$\Delta\eta$ (obs.)	$\Delta\eta$ (calcd.)
0.1	0.1	1.12	117 ± 1[a]	−11.87 ± 0.06[a]	14 ± 9	18
.001	0.1	3.09	130[b]	−12.1[b]	120 ± 50	119
.001	1.0	3.075	170[b]	−10.7[b]	200 ± 60	177

[a] For the uncorrected and corrected curves, both. If $b = 118$, $\log I_0 = -11.80 \pm 0.06$. [b] Approximate values for the center of gravity of the experimental bands.

Hydrochloric Acid–Calcium Chloride Solutions.—Two solutions were run as a test of eq. (20). The first of these 0.1 *M* hydrochloric acid–0.05 *M* calcium chloride, was well behaved at currents above 100 μa. where it gave well defined overvoltage curves which could be corrected for iR drop. The results are represented by curve H in Fig. 6 with a precision of about ±8 mv. As the polarizing current was decreased below 30 μa., there was a drop in overvoltage to a value about 100 mv. below the linear extension of the Tafel curve. Upon a return to higher polarizing currents, the overvoltage remained low up to currents of about 100 μa., and then jumped up to the curve again. In the low current region, the overvoltage data correspond then to a broad hysteresis band, 100 to 150 mv. wide, whose center lies about 150 mv. below the linear extension of the Tafel curve. No attempt is made to reproduce the low current data in Fig. 6, where curve H represents only the well behaved points at high currents.

The second solution investigated, 0.01 *M* hydrochloric acid–0.05 *M* calcium chloride, was ill-behaved at all currents. The downward deviation in overvoltage set in as the polarizing current was decreased below 10 μa. On increasing the polarizing current again, this downward deviation persisted up to currents in the entire range 10 μa. to 1 ma. At high currents, an upward drift sets in, analogous to that observed in solutions containing a large excess of potassium ions, and causing an upward deviation in the overvoltage (dotted curves J in Fig. 6) on returning to low currents. Nevertheless, from this large accumulation of amorphous data, there did emerge four or five well defined overvoltage curves, which could be corrected for *iR* drop, and which are represented by curve J in Fig. 6 with a precision of about ±5 mv. This well-behaved curve was adopted as representative of the hydrogen overvoltage in this solution.

The characteristics of these two solutions, and of their well-behaved overvoltage curves are summarized in Table III. The last column gives the observed increment in overvoltage due to the salt effect, *i. e.*, the difference between curves H and B, and curves J and C, respectively. These $\Delta\eta$'s cannot be calculated theoretically. Of greater interest is the difference between the two hydrochloric acid–calcium chloride solutions themselves (*i. e.*, between curves J and H) which amounts to about 75 ± 15 mv. The value anticipated from eq. (20) is 59 mv. The agreement here is about as good as may be expected, in view of the uncertainties in both the theory and the experimental results. It is interesting to note that the addition of calcium chloride also causes a *rise* in the overvoltage.

TABLE III

OVERVOLTAGE MEASUREMENTS ON Hg IN HCl–$CaCl_2$ AT 25°

Molarity HCl	Molarity $CaCl_2$	*p*H	*b* (uncor.)	*b* (cor.)	log I_0 (cor.)	$\Delta\eta$ (obs.)
0.1	0.05	1.11	115 ± 2	118 ± 2	—11.92 ± 0.07	30 ± 10
.01	.05	2.06	118 ± 2	118 ± 2	−12.60 ± .05	100 ± 10

Discussion

The experimental data reported here for nine solutions of hydrochloric acid with, or without, addition of potassium and calcium chlorides, were taken over a period of ten months' time. *They confirm the fact that, in pure acids, the hydrogen overvoltage is independent of pH, although the present data do indicate, for the first time, a slight trend in the relation between overvoltage and pH, i. e.*, the overvoltage is nearly 40 mv. higher in 0.001 *M* than in 1 *M* hydrochloric acid.

When salts are added, the overvoltage is markedly *increased.* From this fact, we conclude, on the basis of an extension of the KGG theory, that the protons discharged at a hydrogen cathode come from *hydronium ions* and not from *water molecules.* With potassium chloride, the increase in overvoltage agrees well with the value predicted by equation (15). With calcium chloride, there is also an increase in overvoltage, except at low currents where large hysteresis effects were noticeable. Although the rise in overvoltage upon the initial addition of calcium ion to the solution cannot be calculated theoretically,[21] the further rise upon the subsequent addition of calcium ion can be calculated from the ratio of the expressions $(Ca^{++}):(H_3O^+)^2$ in the two solutions, by equation (20). Here the observed difference between the two solutions investigated comes out in fair agreement with the theoretical value.

The fact that the observed salt effects are of the magnitude predicted theoretically is a justification of the assumption made, *viz.*, *that metallic ions and hydronium ions can penetrate into the innermost ion layer adsorbed on the electrode surface with equal facility*, *i. e.*, that there are no specific effects (hydration, or specific adsorption) tending to favor or hinder the penetration of one ion rather than the other. There are no good *a priori* reasons why this assumption should be valid, and it is undoubtedly true that hydration effects do play a role in determining the relative ease of penetration of different ions into the adsorbed ion layers. Therefore it would be of interest to investigate the effect of sodium and of lithium ions, which, because of their higher degree of hydration, would presumably penetrate less easily into the inner ion layer, and would therefore cause a smaller overvoltage rise than potassium ions. The attention of the reader is again called to the fact that Bowden's overvoltage measurements apparently showed no salt effect. The experimental re-investigation of Bowden's systems, and their correlation with the systems studied here would do much to clarify this point.

It is interesting to note that the slight increase in overvoltage with *p*H in pure acid solutions, first discovered in the present work, can also be interpreted as a substantiation of the postulate that the discharged protons come from hydronium ions rather than from water molecules. In the KGG theory, the activity $(H_3O^+)_a$ of hydronium ions in the inner ion layer is not rigorously a constant but rather a very slowly increasing function of the hydronium ion activity (H_3O^+) in the solution. Thus, on the basis of equation (13), the overvoltage should increase slightly with increasing hydrogen ion concentration if a_0 is taken as the activity of water, but it should decrease slightly if a_0 is

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[21] From the two observed rises in overvoltage, it is possible to estimate that the constant Q in equation (18) has a value close to unity.

taken as the activity of hydronium ions in the inner ion layer. The latter is the case actually observed.

Acknowledgment.—The author would like to express his indebtedness and his sincere gratitude to the National Research Council for the grant of a Fellowship which made this research possible, and to Professor George Scatchard of M. I. T. for his inspiring guidance, help and encouragement during the prosecution of this problem. He would also like to express his appreciation to Professors Isadore Amdur and Walter Stockmayer of M. I. T., George Kimball of Columbia, and Samuel Glasstone of Boston College for valuable discussions.

Summary

The KGG theory, which accounts for the lack of variation of hydrogen overvoltage with *p*H by means of an "electrically saturated" layer adjacent to the electrode surface in which the concentration of hydronium ions is practically independent of *p*H, has been extended to the case where the solution contains salt as well as acid. If the metallic ions can penetrate into the "saturated" layer and contribute to its electrical charge, they displace hydronium ions from it and cause a rise, or drop, in the overvoltage depending on whether the protons discharged are postulated to come from hydronium ions or from water molecules. The magnitude of the rise (or drop) can be calculated on the simple assumption that the two species of ions penetrate into the saturated layer with equal freedom (apart from any differences in charge). If there is a restriction to the penetration of metallic ions (*e. g.*, because of their hydration shell), the salt effect may be smaller than predicted.

The hydrogen overvoltage has been measured as a function of current density on a mercury cathode at 25° in solutions of hydrochloric acid with, and without, additions of potassium and calcium chlorides. In the pure acid, the overvoltage is almost independent of *p*H in the range 0 to 3, although the present data do indicate a slight increase in overvoltage with *p*H. With addition of potassium chloride, there is a *rise* in overvoltage of the magnitude predicted theoretically. With addition of calcium chloride, there is also a *rise* in overvoltage, at least at high current densities. At low current densities, the latter solutions show marked hysteresis and depression of the overvoltage below the pure acid values. These results are interpreted to mean that the protons discharged at a hydrogen cathode come from *hydronium ions* and not from *water molecules*. The slight variation of overvoltage with *p*H in pure acids is also consistent with this interpretation.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 23, 1948

[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXIX. Conductance of Several Salts in Ammonia at -34° by a Precision Method[1]

BY VINCENT F. HNIZDA[2] AND CHARLES A. KRAUS

I. Introduction

The purpose of the present investigation was: first, to develop a method for measuring the conductance of solutions of salts in liquid ammonia with a precision comparable with that of solutions in water; and, second, to measure the conductance of several salts in liquid ammonia, which measurements might serve as reference standards in evaluating the precision of other methods when such were found necessary or desirable.

The chief sources of error in conductance measurements in liquid ammonia are: (1) uncertainties as to the concentration of solutions measured, particularly at low concentrations; (2) lack of control of solvent purity and uncertainty as to the correction to be applied for solvent conductance; (3) lack of proper temperature control; (4) uncertainties in resistance measurements owing to capacitance effects due to leads.

(1) **Concentration Errors.**—In all measurements hitherto carried out in liquid ammonia, the dilution method has been employed. This method consists essentially in adding a known amount of salt to a known quantity of solvent, withdrawing a known amount of solution and replacing it by a known amount of fresh solvent. This procedure is repeated until the desired low concentration has been reached.

Two methods have been employed for determining the amount of solvent: (a) The volume of the solution is measured in the conductance cell before and after each withdrawal of solution and addition of solvent. This method was employed by Franklin and Kraus[3] in their earliest measurements; a similar method was employed by Monosson and Pleskov[4] in their more recent measurements. (b) The volume of solvent introduced is measured in a special pipet external to the con-

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[1] This paper is based on a portion of a thesis presented by Vincent F. Hnizda in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1935.

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[3] Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900).

[4] Monosson and Pleskov, *Z. physik. Chem.*, **156A**, 176 (1933).