125. *The Potential and Rate of Solution of Magnesium in Deuterochloric Acid.*

By G. E. Coates.

The potential and corrosion rate of pure magnesium have been measured in solutions of deuterochloric acid and of sodium chloride in deuterium oxide, and compared with its behaviour in similar aqueous solutions of hydrochloric acid and sodium chloride. The potential is 0·11—0·22 volt more negative in the deuterium oxide solutions; this indicates that the potential contains an overvoltage term. The acid corrosion rates are very similar in the two solvents; this suggests a diffusion control mechanism. The saline (alkaline) corrosion rate is about 30 times faster in deuterium oxide than in water.

An apparatus is described for the preparation and manipulation of small quantities of deuterochloric acid.

The most recent value for the standard electrode potential of magnesium, $-2{\cdot}375$ volts (preceding paper), has been shown to support Gatty and Spooner's mechanism for the corrosion of magnesium ("The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions," Oxford, 1938), and to exclude the other theories. The basis of their theory is that the self-polarisation of the corroding metal is almost entirely *anodic* and that the potential is determined by hydrogen overvoltage. It must be realised, of course, that the existence of hydrogen overvoltage itself implies a state of *cathodic* polarisation in that the electrode potential is more negative than that of a *reversible* hydrogen electrode. Gatty and Spooner could not test their theory since they had no information about the overvoltage behaviour of magnesium, but they endeavoured to do so by the use of overvoltage–current density relations which have since been shown (Hickling and Salt, *Trans. Faraday Soc.*, 1942, **38**, 474) not to have general validity. One part of their theory, *viz.*, that the corroding metal is under high anodic polarisation, follows from the large difference between the potential of the corroding metal ($-1{\cdot}5$ to $-1{\cdot}6$ volts in most solutions) and its standard potential ($-2{\cdot}375$ volts). The other part, *viz.*, that the potential of the corroding metal is equal to the reversible hydrogen electrode potential of the corroding solution plus the hydrogen overvoltage of the metal, was not so certain. This aspect is now examined.

Bowden and Kenyon (*Nature*, 1935, **135**, 105) found that, although reversible electrode processes took place in deuterium oxide at very nearly the same potentials as in water (see also Drucker, *Trans. Faraday Soc.*, 1937, **33**, 660; Novak, *Coll. Czech. Chem. Comm.*, 1937, **9**, 207), yet the irreversible discharge of hydrogen ions on mercury proceeded over a range of current densities at a potential 0·13 volt more negative in deuterium oxide than in water. Blokker (*Rec. Trav. chim.*, 1936, **55**, 979) found that for iron cathodes deuterium overvoltages in deuterium oxide were about 0·05—0·1 volt greater than hydrogen overvoltages in water. It is in the highest degree improbable that this effect is confined to iron and mercury, which are electrode materials of widely different properties. Its generality is suggested by the fact that considerable hydrogen–deuterium separation factors, which are certainly related to overvoltages, are observed at all cathodes examined. Consequently the effect is to be expected for magnesium, *i.e.*, its deuterium overvoltage should be greater than its hydrogen overvoltage for similar current densities. Hence, if the potential of corroding magnesium does involve hydrogen overvoltage—on Gatty and Spooner's theory—then it should be decidedly more negative in deuterium oxide solutions than in ordinary aqueous solutions. Similarly, if the potential be governed by some other processes, no appreciable difference would be anticipated.

Since the corrosion of magnesium in saline solutions, which rapidly become alkaline, is complicated by the formation of obstructive hydroxide films and current densities are therefore unknown, most of the work described below was carried out with acid solutions in which the corrosion of magnesium is uniform.

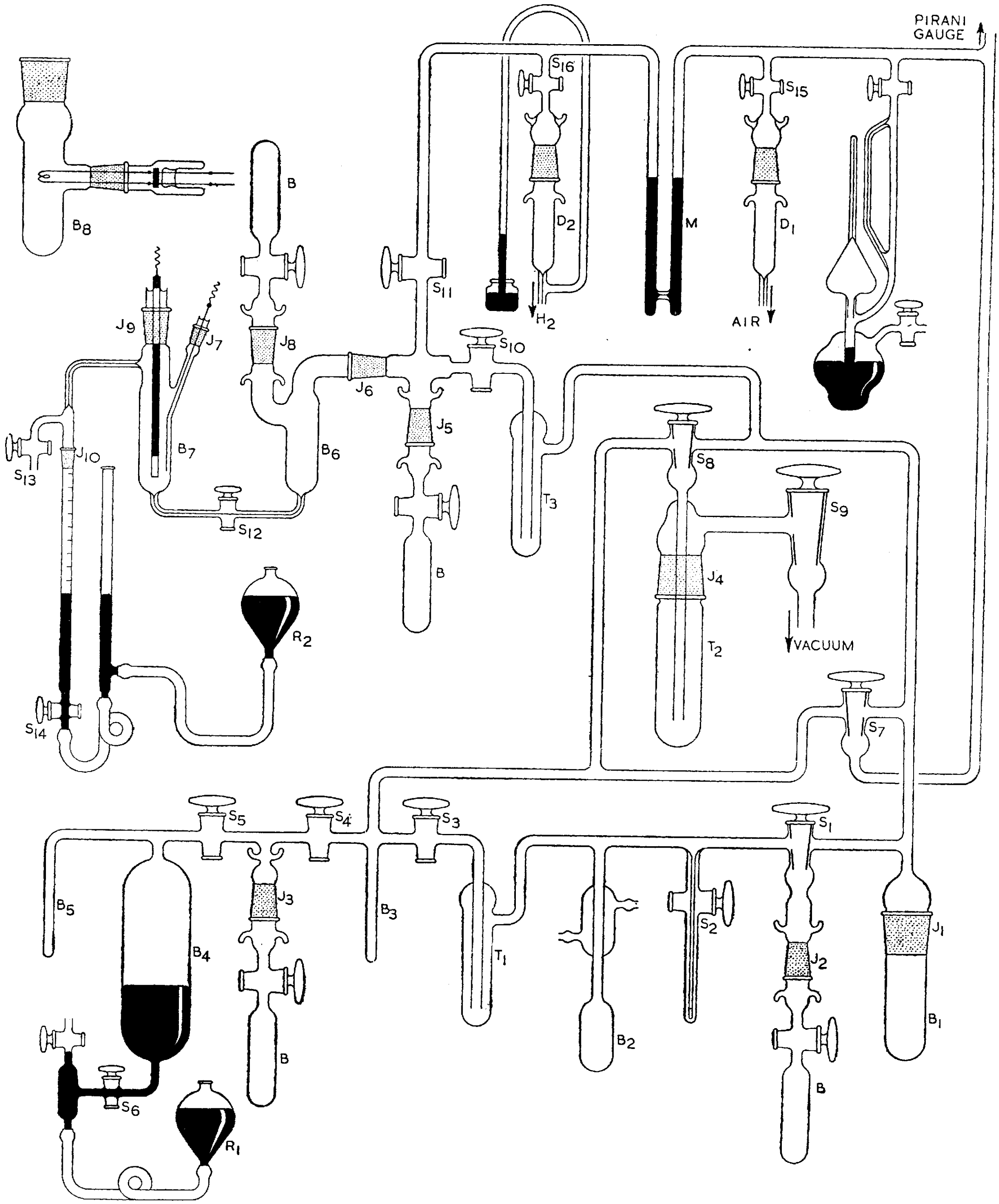
The object of this work was to compare the potentials of magnesium corroding in solutions of deuterochloric acid in deuterium oxide and of hydrochloric acid in water, these acids being chosen since deuterochloric acid is prepared more readily than other deutero-acids. To obtain further information about the corrosion mechanism, corrosion rates were measured in addition to potentials. Some additional measurements were made with solutions of sodium chloride in light and in heavy water.

Experimental.

1. *Preparation of Solutions.*—The apparatus (Fig. 1) was built of Pyrex glass with the extensive use of standard ground joints. Deuterium chloride was prepared, by a modification of Brown and Groot's method (*J. Amer. Chem. Soc.*, 1942, **64**, 2223), from deuterium oxide and benzoyl chloride. This method has the great advantage that both deuterium atoms in deuterium oxide are converted into deuterium chloride, with the formation of benzoic anhydride. The deuterium oxide (at least 99·9% pure; obtained from the Stuart Oxygen Co., San Francisco) was contained in a sealed tube holding 10 g. The latter was opened in the following way to avoid contamination with atmospheric moisture. The neck was scratched with a diamond and the tube placed in B8 (top left) which was attached to J1 (bottom right); B8 and the 22-c.c. bulb B (J2) were evacuated through S8 and S9 by an oil-diffusion and rotary pump, and with S7, 8, 9, and 10 closed, the neck of the deuterium oxide bulb (previously frozen in a carbon dioxide–ether bath) was cracked off by the hot wire device of B8. After the gas thus set free had been pumped off, the heavy water was distilled into the bulb B (J2) by cooling the latter, which could be detached and weighed. About 0·2 c.c. of deuterium oxide was transferred to the calibrated capillary S2, the section S1–S3 having been previously evacuated. "A.R." Benzoyl chloride, previously distilled (b.p. 26°/1 mm.) to remove hydrogen chloride, was sublimed through J2 into B2 (about 15 g.). Before the actual preparation of deuterium chloride, the reservoir B4 was evacuated, together with the rest of the apparatus, and the deuterium oxide in S2 was condensed on the benzoyl chloride in B2. Pure hydrogen was then admitted through the drying tube D2 (magnesium perchlorate) to a pressure of about 500 mm.; this was necessary since deuterium oxide and benzoyl chloride do not react at an appreciable rate at the low b.p. of benzoyl chloride at lower pressures. The benzoyl chloride and deuterium oxide were heated to boiling, with reflux from the water-cooled condenser above B2. When the total pressure (H_2 + DCl) had risen to about 1 atm., the heating was stopped, the trap T1 cooled to $-80°$,

T2 to −196°, and the gases slowly evacuated; some benzoyl chloride condensed in T1 and the deuterium chloride all condensed in T2. More hydrogen was admitted, and the above procedure repeated until all the deuterium chloride available had been collected in T2. The apparatus was then pumped out, S3 closed, B3 cooled to −196°, and T2 warmed to −80°. The deuterium chloride, then in B3, was transferred to B5 by cooling the latter to −196° and warming B3,

FIG. 1.

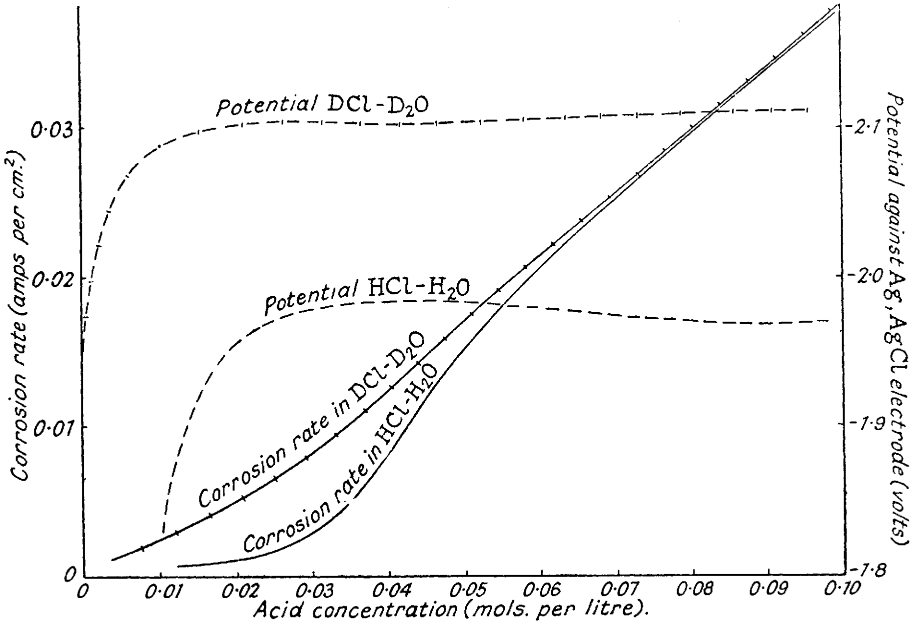


S8 having been closed and S4 and S5 opened. At this stage the Pirani gauge (communication through S7) indicated a pressure of 0·005 mm. of uncondensed gas, which was pumped off. Finally, with S5 closed, the deuterium chloride was allowed to evaporate into the storage vessel B4 (about 300 c.c.).

Solutions of deuterochloric acid in deuterium oxide were prepared by dissolving a known volume of the former (at known temperature and pressure) in a weighed quantity of the latter. The volume of each of the bulbs B was measured (including the tap bore); they were each about 22 c.c. and therefore contained about 1 millimole of gas at N.T.P. One of these weighed and evacuated bulbs was attached to J3 and filled with deuterium chloride at atmospheric pressure (R1 being levelled against B4), and the temperature noted. After the stopcock above the bulb B had been closed (S4 being closed), the deuterium chloride in B4 and in the space between S4 and S5 was condensed in B5 (−196°), S5 closed, and the deuterium chloride allowed to expand into B4. The bulb B was then transferred to J5, frozen in liquid nitrogen, and put into communication with another similar bulb attached to J2 and containing a weighed quantity of deuterium oxide, which condensed on the frozen deuterium chloride under J5. Finally, hydrogen was admitted to 500—600 mm. The discrepancy between the final weight of acid solution and the calculated weight of its components was usually about 1 in 10^4. Molar concentrations were calculated from molal on the assumption that the apparent molar volume of deuterium chloride is the same as that of hydrogen chloride at similar concentrations. The acid was always about 0·1N. The apparatus was degassed by being heated in a flame as far as possible; the large number of lubricated joints and stopcocks rendered this method somewhat ineffective, however, and further (surface) degassing was carried out by the passage of an electric discharge through the apparatus in the presence of about 0·05 mm. of hydrogen.

2. *Corrosion Experiments.*—The magnesium electrodes were prepared from pure distilled metal with the object of avoiding contamination with iron (the most objectionable impurity with regard to corrosion); a special casting method resulted in iron contents from 0·0003 to 0·0007%. The electrode areas, measured with a travelling microscope, were about 1 cm.^{2}, the remainder of the rod being coated with Edwards's Wax "W" except for the electrical connection at the top. The magnesium and the silver chloride electrode were mounted in ground joints J9 and J7. Preliminary experiments confirmed that the dry silver chloride electrode reached equilibrium within about 1 mv. a minute after immersion. Potentials were measured with a Cambridge vacuum tube potentiometer. The progress of corrosion was followed by the evolution of hydrogen or deuterium measured in the 25-c.c. gas burette, with levelling tube and finely adjustable reservoir R2. The mercury in both burette and levelling tube was lubricated with butyl phthalate to prevent sticking. The whole corrosion test unit was immersed in a water thermostat at 25°±0·05°, and was easily demounted for cleaning.

FIG. 2.



Potential and corrosion rate of magnesium in dilute solutions of HCl *in* H_2O *and* DCl *in* D_2O (*derived curves*).

The bulb B containing $DCl-D_2O$ of known concentration was attached to J8, and J5 was closed with a ground stopper. For experiments with aqueous solutions, the bulb was filled with de-aerated 0·1N-hydrochloric acid saturated with hydrogen. The mercury in the gas burette was brought to the zero mark, and S13 and S14 closed, then, with S11 and S12 open, the apparatus was evacuated until thoroughly dry. Hydrogen was admitted through D2 and S16 to atmospheric pressure, and S12 closed. The hydrogen pressure in the rest of the apparatus was reduced to about $\frac{1}{3}$ atm., and with S10 closed the acid was allowed to flow into B6. The hydrogen pressure in B6 was increased to 1 atm. and the acid allowed to reach thermal equilibrium. Since the right-hand side of the mercury manometer M was evacuated, the mercury level on that side was about 75 cm. higher than on the other side; the acid was driven into B7 by opening S12, S13, S14, and S15, whereupon the rise of mercury in the left-hand limb of M forced hydrogen into B6 and acid into B7. Then S12 and S13 were immediately closed and readings were taken on the gas burette and the potentiometer. It was necessary to know exactly how much acid was in B7 by measuring the quantity remaining in the bulb B over J8 and in B6. During the later stages of the corrosion experiment this part was evacuated, and any acid condensed in T3 at −80°. This was transferred to an evacuated bulb under J2 and weighed; hence the amount of acid in B7 was known accurately. At the end of the run the deuterium oxide was recovered in a very similar way, any acid left being removed by prolonged contact with magnesium turnings (in B1).

Results.—The experimental results were plotted as graphs showing the potential and volume of gas evolved (corrected to N.T.P.) as a function of time. From the total volume of hydrogen or deuterium evolved, the concentration of acid remaining in the corrosion cell was calculated, and the slope of the volume–time curve gave the corrosion rate. The latter was finally plotted against the acid concentration (Fig. 2). This graph does not show experimental points since it is derived from a smoothed curve of the tangents of the experimental curves; it shows the mean results of three runs with $HCl–H_2O$ and two with $DCl–D_2O$. Potentials were measured every few minutes at the beginning of the experiments with acid solutions, and at longer intervals towards the end when the corrosion rate became very slow. The experiments were continued for between 4 and 24 hours. Some additional experiments were carried out with 3% (by weight) solutions of sodium chloride in water and deuterium oxide.

DISCUSSION.

Potentials.—The potential of the corroding metal, measured against a silver chloride reference electrode without liquid junction, remained sensibly constant until the acid concentration dropped to about 0·02N in aqueous and 0·01N in deuterium solutions. At lower acid concentrations the potentials were changing rapidly (with concentration, though slowly with time) and the graph is less accurate in this range. The most significant result, however, was that in the deuterium solutions the potentials were 0·115—0·14 volt more negative than in the (hydrogen) aqueous solutions. This difference is similar to that observed by Bowden and Kenyon (*loc. cit.*) for mercury, *viz.*, 0·13 volt. At the beginning of the experiments the potentials were approximately $-2·11$ volts in 0·1N-$DCl–D_2O$, and $-1·97$ volts in 0·1N-$HCl–H_2O$. On the convention that the potential of the silver chloride electrode on the hydrogen scale is $0·222 - (\boldsymbol{RT}/\boldsymbol{F})\ln m_{\mathrm{Cl}'}\gamma_{\pm\mathrm{HCl}}$, the potentials of the magnesium on the same scale become $-1·82$ and $-1·68$ volts, respectively. The error in assuming equality between the potentials of the silver chloride reference electrode in the two solutions is negligible on account of the small difference of 3·4 mv. found by Abel, Bratu, and Redlich (*Z. physikal. Chem.*, **1935**, *A*, **173**, 353) between the e.m.f. of the cell $Pt,H_2|HCl|AgCl,Ag$ in light and in heavy water.

In a 3% (by wt.) solution of sodium chloride in water, the potential of pure magnesium, against a silver chloride reference electrode, was about $-1·70$ to $-1·71$ volts at 25°, and was steady within about 0·02 v. In a 3% (by wt.) solution of sodium chloride in deuterium oxide, the potential fell after immersion from $-2·08$ to $-1·93$ or $-1·92$ volts, remaining constant after about 20 hours. Hence the steady potential in deuterium oxide salt solution is about 0·22 volt more negative than in aqueous salt solution; this is a greater difference than in acid solutions.

For the reasons already given, these results indicate that the potentials of corroding magnesium in both acid and alkaline solutions are determined by hydrogen overvoltage, or at least that they contain an overvoltage term.

Corrosion Rates.—Fig. 2 shows that in strongly acid solutions the corrosion rates in light and heavy water are identical within the experimental error (estimated at ±15%). At acid concentrations below 0·05N, however, the deuterium oxide rate was significantly higher than the water rate. In a 3% solution of sodium chloride the corrosion rate in deuterium oxide, observed over a period of 72 hours, was very nearly constant at 6·2 mg. of magnesium per cm.^{2} per day, or a mean current density of 0·58 mA. per cm.^{2} This is very much greater than the rate in aqueous 3% salt solution, 0·23 mg. of metal per cm.^{2} per day. Hanawalt, Nelson, and Peloubet (*Metals Technology T.P.* 1353, Sept. 1941) found a mean corrosion rate of about 0·2 in the same units for magnesium of similar purity.

Two points arise from these results. The standard potential is $-2·38$ volts, and the actual potential is $-1·82$ volts in 0·1N-$DCl–D_2O$ and $-1·68$ volts in 0·1N-$HCl–H_2O$. It might perhaps be expected that the logarithm of the " driving force " causing corrosion would be proportional to the difference between the two. On the supposition that the corrosion rate is proportional to this " driving force " (Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," Chap. X, McGraw-Hill, 1941), the rate in deuterium oxide should be

$$I_{\mathrm{D_2O}} = \text{const. } \mathrm{e}^{-(1·82-2·38)2\boldsymbol{F}/\boldsymbol{RT}}$$

and in water,

$$I_{\mathrm{H_2O}} = \text{const. } \mathrm{e}^{-(1·68-2·38)2\boldsymbol{F}/\boldsymbol{RT}}$$

Hence

$$I_{\mathrm{H_2O}}/I_{\mathrm{D_2O}} = \mathrm{e}^{0·28\boldsymbol{F}/\boldsymbol{RT}} = 54,000$$

The observed *similarity* between the two rates strongly suggests that the actual potential of the metal is not a major factor in determining the corrosion rate. The alternative possibility is that the corrosion rate is limited almost entirely by diffusion, *viz.*, the diffusion of hydrogen ions to the metal surface. That the rate of ionic migration is not an important factor is suggested by the contrast between the similarity of corrosion rates in the two media and the considerable difference between the mobilities of hydrogen and deuterium ions in water and in deuterium oxide, respectively. If, then, the corrosion rates are controlled by diffusion, the rate in deuterium oxide should be about 12% less than in water on account of the difference in viscosity. This was not observed, but an effect of this magnitude would probably be lost in the experimental error of ±15% mentioned above. No satisfactory interpretation has yet been found for the faster corrosion in very dilute acid and saline solutions in deuterium oxide.

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