124. *The Standard Electrode Potential of Magnesium.*

By G. E. Coates.

The standard electrode potential (E_0) of magnesium has an important bearing on the various proposed corrosion mechanisms. A new value, $-2{\cdot}375\pm0{\cdot}005$ volts, has now been calculated from precise thermal data and from the activity product of magnesium hydroxide.

Three radically different mechanisms have been proposed for the corrosion of magnesium in aqueous solutions. In the first (Whitby, *Trans. Faraday Soc.*, 1933, **29**, 1318) the potential of the corroding metal in saline solution is interpreted in terms of preferential discharge of hydroxide ions, this theory being based on a value for the standard electrode potential of magnesium of $E_0 = -1{\cdot}85$ volts, obtained by Beck (*Rec. Trav. chim.*, 1922, **41**, 353) by direct measurements with magnesium and magnesium amalgam electrodes. The second mechanism (Gatty and Spooner, " The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions," Oxford, 1938) is derived from various thermodynamically calculated values for E_0 ranging from $-2{\cdot}35$ to $-2{\cdot}54$ volts, and this choice necessarily implies that corroding magnesium is in a state of high anodic polarisation, since the potential of the corroding metal is generally about $-1{\cdot}5$ to $-1{\cdot}6$ volts on the hydrogen scale. The third mechanism (Hanawalt and McNulty, *Trans. Amer. Electrochem. Soc.*, 1942, **81**, 423) is based on a value $-1{\cdot}55$ volts for E_0, which is found in many chemical textbooks. According to this mechanism the corroding metal is barely anodically polarised.

A reliable decision on the correct value for E_0 has clearly become a matter of some importance. Fortunately, some precise thermal data have recently been published which allow E_0 to be calculated thermodynamically with fair accuracy. The result of this calculation, *viz.*, $E_0 = -2{\cdot}375\pm0{\cdot}005$ volts, shows clearly that the corrosion mechanism proposed by Gatty and Spooner is to be preferred to the others. In particular, it is quite certain that in contact with aqueous solutions magnesium is always in a state of considerable anodic polarisation, since its potential on the hydrogen scale is always much more positive than $-2{\cdot}375$ volts.

Previous thermodynamically calculated values (in volts) are : $-2{\cdot}512$ (Makishima, *Z. Elektrochem.*, 1935, **41**, 697), $-2{\cdot}353\pm0{\cdot}05$ (Devoto, *ibid.*, 1928, **34**, 21), $-2{\cdot}34$ (Latimer, " Oxidation Potentials," Prentice-Hall, 1938), $-2{\cdot}54$ (Wilsmore, *Z. physikal. Chem.*, 1900, **35**, 310).

Data.—All data refer to 25° ($298{\cdot}1_6$° K.) and energies are given in international joules. Published values in calories at 15° were converted into these units by the factor 4·1833 (Rossini, *J. Res. Nat. Bur. Stand.*, 1939, **22**, 407).

1. *Heats of formation.* Units : int. j. mole^{-1}

$Mg_{(c)} + \frac{1}{2}O_{2(g)} = MgO_{(c)}$; $\Delta H_1^0 = -601{,}726\pm210$ (Shomate and Huffman, *J. Amer. Chem. Soc.*, 1943, **65**, 1625). $MgO_{(c)} + H_2O_{(l)} = Mg(OH)_{2(c)}$; $\Delta H_2^0 = -40{,}741\pm20$ (Giauque and Archibald, *ibid.*, 1937, **59**, 561). $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(l)}$; $\Delta H_3^0 = -285{,}795\pm40$ (Rossini, *loc. cit.*).

2. *Entropies.* Units : int. j. mole^{-1} degree^{-1}.

$Mg_{(c)}$: $S_1^0 = 32{\cdot}50 \pm 0{\cdot}4$ (Clusius and Vaughen, *J. Amer. Chem. Soc.*, 1930, **52**, 4696; Kelley, *Bull. Bur. Mines*, No. 350, 1932, p. 31).
$MgO_{(c)}$: $S_2^0 = 27{\cdot}86 \pm 0{\cdot}04$ (estimated uncertainty) (Giauque and Archibald, *loc. cit.*).
$Mg(OH)_{2(c)}$: $S_3^0 = 63{\cdot}13 \pm 0{\cdot}04$ (estimated uncertainty) (*idem, ibid.*).
$H_{2(g)}$: $S_4^0 = 130{\cdot}644 \pm 0{\cdot}02$ (Rossini, *loc. cit.*).
$O_{2(g)}$: $S_5^0 = 205{\cdot}090 \pm 0{\cdot}04$ (*idem, ibid.*).
$H_2O_{(l)}$: $S_6^0 = 70{\cdot}081 \pm 0{\cdot}08$ (*idem, ibid.*).

3. *Free energies.* Units : int. j. mole^{-1}.

$H_2O_{(l)} = H^+ + OH^-$ (free energy of ionisation of water) ;
$\Delta G_1^0 = 79{,}879 \pm 3$ (Harned and Owen, *Chem. Rev.*, 1939, **35**, 36).
$Mg(OH)_{2(c)} = Mg^{++} + 2OH^-$ (free energy of solution of magnesium hydroxide) ;
$\Delta G_2^0 = -\boldsymbol{R}T \ln$ (activity product).

Kline (*J. Amer. Chem. Soc.*, 1929, **51**, 2093) found $5{\cdot}5 \times 10^{-12}$ for the activity product. The possible range of values for this quantity is $3{\cdot}5$—8×10^{-12} (it is rather difficult to measure). Hence $\Delta G_2^0 = 64{,}260 \pm 1000$.

Calculation of E_0.—The standard potential of magnesium, E_0, is related to the standard partial free energy of the magnesium ion $\overline{G^0_{Mg^{++}}}$ by the equation $2E_0\boldsymbol{F} = \overline{G^0_{Mg^{++}}}$. The latter may be calculated from the free energy of formation of magnesium hydroxide and its free energy of solution (ΔG_2^0), since

$$G^0_{Mg(OH)_2(c)} = \overline{G^0_{Mg^{++}}} + 2\overline{G^0_{OH^-}} - \Delta G_2^0$$

Of these quantities, $G^0_{Mg(OH)_2(c)}$ may be calculated from the heat of formation of $Mg(OH)_2$, ΔG_2^0 is known from its activity product, and $\overline{G^0_{OH^-}}$ may be calculated from the known thermodynamic properties of water. These are considered in turn.

$$G^0_{Mg(OH)_2(c)} = (\Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0) - T(S_3^0 - S_1^0 - S_4^0 - S_5^0)$$

ΔG_2^0 is given above. $\overline{G^0_{OH^-}}$ is equal to the sum of the free energy of formation of liquid water and its free energy of ionisation (ΔG_1^0), since

$$\overline{G^0_{OH^-}} + \overline{G^0_{H^+}} = G^0_{H_2O} + \boldsymbol{R}T \ln K_w, \text{ and } \overline{G^0_{H^+}} = 0$$

by definition of the scale of ionic partial free energies. Hence

$$\begin{aligned} \overline{G^0_{OH^-}} &= \Delta H_3^0 - T(S_6^0 - S_4^0 - \tfrac{1}{2}S_5^0) + \Delta G_1^0 \\ \text{Now } \overline{G^0_{Mg^{++}}} &= G^0_{Mg(OH)_2(c)} - 2\overline{G^0_{OH^-}} + \Delta G_2^0 \\ &= (\Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0) - T(S_3^0 - S_1^0 - S_4^0 - S_5^0) - 2\Delta H_3^0 + 2T(S_6^0 - S_4^0 - \tfrac{1}{2}S_5^0) - 2\Delta G_1^0 + \Delta G_2^0 \\ &= (\Delta H_1^0 + \Delta H_2^0 - \Delta H_3^0) - T(S_3^0 + S_4^0 - S_1^0 - 2S_6^0) - 2\Delta G_1^0 + \Delta G_2^0 \\ &= -\,458{,}470. \end{aligned}$$

The uncertainty may be computed on a root mean square basis. The R.M.S. error of the H terms amounts to ± 215, that of the TS terms to ± 135, and that of the ΔG_2^0 term to ± 1000 j. mole^{-1}. Hence, it is clear that by far the largest part of the uncertainty in $\overline{G^0_{Mg^{++}}}$ is due to the uncertainty in the activity product of magnesium hydroxide.

Hence, $\overline{G^0_{Mg^{++}}} = -458{,}470 \pm 1030$ int. j. mole^{-1}.

A recent survey (Manov, Bates, Hamer, and Acree, *J. Amer. Chem. Soc.*, 1943, **65**, 1765) of fundamental constants gives $(9{\cdot}650 \pm 0{\cdot}001) \times 10^4$ int. coulombs g.-equiv.$^{-1}$ for $\boldsymbol{F}$, hence $E_0 = -(458{,}470 \pm 1030)/2 \times 96{,}500 = -2{\cdot}375 \pm 0{\cdot}005$ volts.

All the data of the above calculation are the results of modern precision thermochemical methods, with the sole exception of the activity product of magnesium hydroxide. In order that a more accurate value for E_0 may readily be calculated if a better determination of solubility is made, the following formula is given :

$$E_0 = -\frac{394{,}210 \pm 260 + \boldsymbol{R}T \ln \text{(act.prod.)}}{193{,}000}$$

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