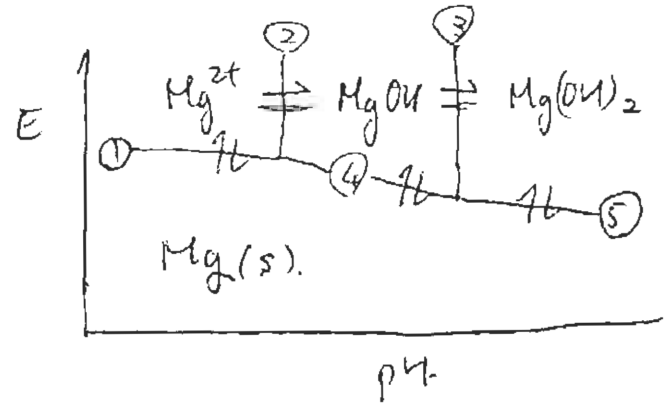
第11回　クイズ解答

Mg^{2+} の水酸化物生成及びそれらの還元を示す電位-pH図では次の①〜⑤の境界の式を調べれば良い



① Mg^{2+}/Mg 境界

$$Mg^{2+} + 2e^- \rightleftharpoons Mg, \quad E^0 = -2.37V$$

Nernst 式より、

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{Mg^{2+}}}{a_{Mg(s)}}$$

$$= E^0 + \frac{0.0592}{2} \log a_{Mg^{2+}} \quad (\because a_{Mg(s)} = 1)$$

$$= -2.37 + 0.0296 \log 10^{-8} \quad (\because a_{Mg} = 10^{-8} M)$$

$$= -2.61V$$

② $Mg^{2+}/MgOH^+$ 境界

$$Mg^{2+} + OH^- \rightleftharpoons MgOH^+$$

$$K_1 = \frac{a_{MgOH^+}}{a_{Mg^{2+}} \cdot a_{OH^-}} = 10^{2.58} \quad (I=0, \text{see p182})$$

$K_w = a_{H^+} \cdot a_{OH^-}$ をかけると

$$K_1 \cdot K_w = \frac{a_{MgOH^+}}{a_{Mg^{2+}}} a_{H^+}$$

$$= a_{H^+} \quad (\because a_{MgOH^+} = a_{Mg^{2+}} = 10^{-8} M)$$

$$\therefore pH = -\log a_{H^+} = -\log K_1 \cdot K_w$$

$$= -\log 10^{2.58-14} = 11.42$$

③ $Mg(OH)^+ / Mg(OH)_2$

$$MgOH^+ + OH^- \rightleftharpoons Mg(OH)_2 \quad ; K_{③}$$

$$K_{sp} = a_{Mg^{2+}} \cdot a_{OH}^2 = 1.1 \times 10^{-11}.$$

$$K_1 = \frac{a_{Mg(OH)}}{a_{Mg^{2+}} \cdot a_{OH}}$$ より.

$$K_{③} = \frac{1}{a_{MgOH} \cdot a_{OH}} = \frac{1}{K_1 \cdot K_{sp}}$$

$K_w = a_H \cdot a_{OH}$ より.

$$\frac{a_{H^+}}{a_{MgOH}} = \frac{K_w}{K_1 \cdot K_{sp}}.$$

$$\therefore \ pH = -\log a_{H^+}$$

$$= -\log \frac{K_w \cdot a_{MgOH}}{K_1 \cdot K_{sp}}.$$

$$= -(-14.0 - 8 - 2.58 + 11.0) \quad \because a_{MgOH} = 10^{-8} M.$$

$$= -13.6$$

④ $MgOH^+/Mg$..

$$MgOH + 2e \rightleftharpoons Mg + OH^-.$$

① で使用した Nernst の式

$$E = E^\circ_{Mg} + 0.0296 \log a_{Mg^{2+}}$$

に. $a_{Mg^{2+}} = \dfrac{a_{MgOH} \cdot a_{H^+}}{K_1 \cdot K_w}$ を代入して.

$$E = E^\circ_{Mg} + 0.0296\left(\log \frac{1}{K_1 \cdot K_w} + \log a_{MgOH} - pH\right)$$

$$= -2.27 - 0.0296 pH$$

⑤ $Mg(OH)_2/Mg$

$$Mg(OH)_2 + 2e \rightleftharpoons Mg$$

$$K_{sp} = a_{Mg} \cdot a_{OH}^2$$
$$K_w = a_{H^+} \cdot a_{OH}$$
より

$$a_{Mg^{2+}} = \frac{K_{sp}}{K_w^2} a_H^2$$

これを Mg^{2+}/Mg の Nernst 式に代入して.

$$E = E^\circ_{Mg} + 0.0296 \log\left(\frac{K_{sp}}{K_w^2} a_H^2\right)$$

= (中略)

$$= -1.87 - 0.0592pH$$

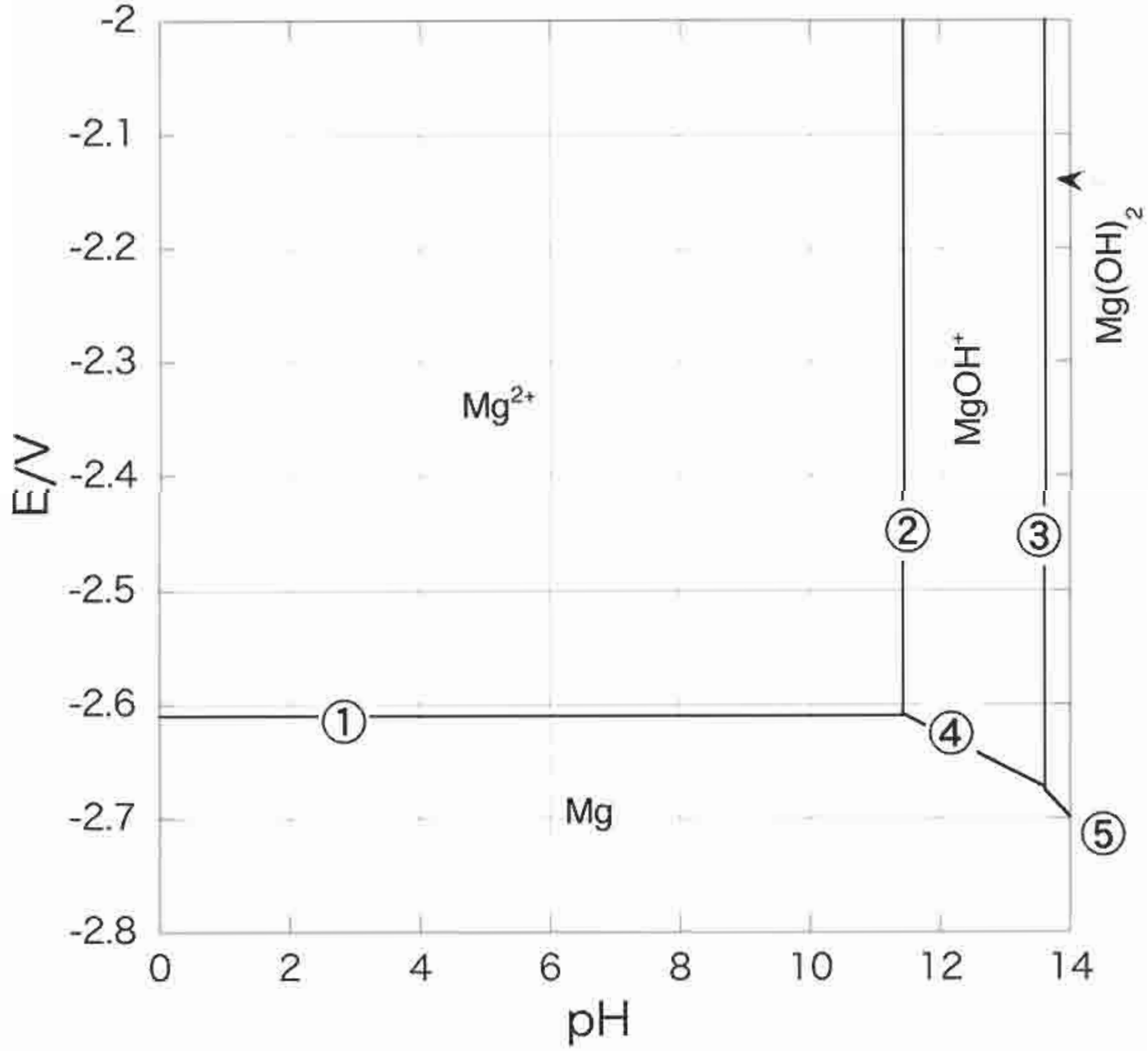


Fig. Potential-pH diagram for Mg(II) system ($a = 10^{-8}$ M)