

12章 問題解答

予習

1.



2.

- (1) Cu:還元 (酸化数減少 +2→0)
 (2) S:酸化 (酸化数増加 -2→+4)
 (3) O:還元 (酸化数減少 0→-1)

演習問題 A

12-A1

- ①還元, ②アノード, ③酸化, ④正極, ⑤負極, ⑥高い, ⑦還元, ⑧酸化, ⑨陰極, ⑩陽極, ⑪還元

12-A2

半電池	電極反応	標準電極電位 ϕ^0	ΔG^0
$\text{Cu}^{2+} \text{Cu}$	$1/2\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}$	$\phi^0_{20} = +0.340\text{V}$	ΔG_{20}
$\text{Cu}^+ \text{Cu}$	$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	$\phi^0_{10} = +0.520\text{V}$	ΔG_{10}
$\text{Cu}^{2+}, \text{Cu}^+ \text{Pt}$	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	ϕ^0_{21}	ΔG_{21}

標準ギブスエネルギー変化は加性があるので,

$$2\Delta G_{20} = \Delta G_{10} + \Delta G_{21}$$

また, $\Delta G = -nFE$ で, ここではいずれも $n=1$ であるから,

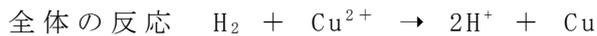
$$2E_{20} = E_{10} + E_{21} \quad (\text{すなわち, } 2\phi^0_{20} = \phi^0_{10} + \phi^0_{21})$$

よって, $E_{21} = 2E_{20} - E_{10} = 2(+0.340\text{V}) - (+0.520\text{V}) = +0.160\text{V}$ [答]

12-A3

(1)

左側, 酸化	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\phi^0_{\text{L}} = 0.0000\text{V}$
右側, 還元	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$\phi^0_{\text{R}} = +0.340\text{V}$



$$E^0 = \phi^0_{\text{R}} - \phi^0_{\text{L}} = (+0.340) - (0.0000) = +0.340\text{V} \quad [\text{答}]$$

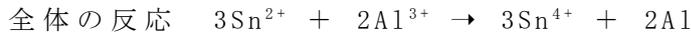
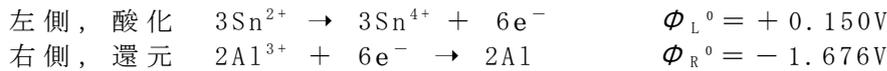
(2)

左側, 酸化	$2\text{Na}^+ \rightarrow 2\text{Na} + 2\text{e}^-$	$\phi^0_{\text{L}} = -2.714\text{V}$
右側, 還元	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	$\phi^0_{\text{R}} = -2.84\text{V}$



$$E^0 = \phi^0_{\text{R}} - \phi^0_{\text{L}} = (-2.84) - (-2.714) = -0.126 = -0.13\text{V} \quad [\text{答}]$$

12-A4



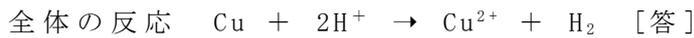
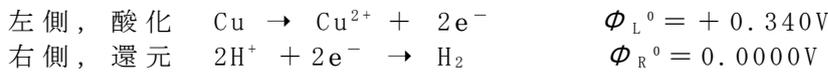
$$E^0 = \phi_{\text{R}}^0 - \phi_{\text{L}}^0 = (-1.676) - (0.150) = -1.826\text{V}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{(a_{\text{Sn}^{4+}})^3 (a_{\text{Al}})^2}{(a_{\text{Sn}^{2+}})^3 (a_{\text{Al}^{3+}})^2}$$

$$E = -1.826 - \frac{8.314 \times 298.15}{6 \times 96485} \ln \frac{(0.05)^3 (1.0)^2}{(0.2)^3 (0.1)^2} = -1.8279 = -1.828\text{V} \quad [\text{答}]$$

12-A5

(1)



$$E^0 = \phi_{\text{R}}^0 - \phi_{\text{L}}^0 = (0.0000) - (+0.340) = -0.340\text{V}$$

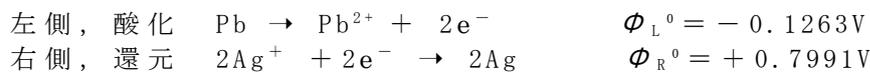
(2)
$$E = E^0 - \frac{RT}{nF} \ln \frac{(a_{\text{Cu}^{2+}})(a_{\text{H}_2})}{(a_{\text{Cu}})(a_{\text{H}^+})^2}$$

$$E = -0.340 - \frac{8.314 \times 298.15}{2 \times 96485} \ln \frac{(0.01)(0.8)}{(1.0)(0.07)^2} = -0.346\text{V} \quad [\text{答}]$$

(3) $\Delta G = -nFE = -2 \times 96485 \times (-0.346) = 6.68 \times 10^4 \text{J} \cdot \text{mol}^{-1}$ [答]

(4) ΔG が正であり, 自発的変化とならない。 [答]

12-A6



$$E^0 = \phi_{\text{R}}^0 - \phi_{\text{L}}^0 = (+0.7991) - (-0.1263) = +0.9254\text{V} \quad [\text{答}]$$

題意 $E = 0.9320\text{V}$ より, まず, ΔG を求めると,

$$\Delta G = -nFE = -2 \times 96485 \times (+0.9320) = -1.798 \times 10^5 \text{J} \cdot \text{mol}^{-1} \quad [\text{答}]$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p = 2 \times 96485 \times (0.000240) = 46.3 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad [\text{答}]$$

$$\Delta H = \Delta G + T \Delta S = -1.798 \times 10^5 \text{J} \cdot \text{mol}^{-1} + (298.15\text{K}) \times (46.3 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -1.66 \times 10^5 \text{J} \cdot \text{mol}^{-1} \quad [\text{答}]$$

12-A7

- (1) 25°Cにおける標準モルエントロピー S_m° は, $S_m^\circ(\text{H}_2, \text{g}) = 130.575 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$,
 $S_m^\circ(\text{O}_2, \text{g}) = 205.029 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $S_m^\circ(\text{H}_2\text{O}, \text{l}) = 69.91 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ である。
したがって, 標準反応エントロピー変化 ΔS_r° は,

$$\Delta S_r^\circ = 2S_m^\circ(\text{H}_2\text{O}, \text{l}) - \{2S_m^\circ(\text{H}_2, \text{g}) + S_m^\circ(\text{O}_2, \text{g})\} = 2 \times (69.91 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) - \{2 \times (130.575 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + (205.029 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\} = -326.4 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \text{ [答]}$$

- (2) $\text{H}_2\text{O}(\text{l})$ の標準生成エンタルピー $\Delta H_f^\circ(\text{H}_2\text{O}, \text{l})$ は, 25°Cで $-285.83 \text{kJ} \cdot \text{mol}^{-1}$ である。
よって, 標準反応熱 ΔH° は,

$$\Delta H^\circ = 2 \times (-285.83 \times 10^3 \text{J} \cdot \text{mol}^{-1}) - \{2 \times (0) + (0)\} = -571.66 \times 10^3 \text{J} \cdot \text{mol}^{-1}$$

一方, $\Delta S_r^\circ, \text{sur} = \frac{\Delta H^\circ, \text{sur}}{T} = \frac{-\Delta H^\circ}{T}$ である。

したがって, 外界の25°Cにおける標準反応エントロピー変化 $\Delta S_r^\circ, \text{sur}$ は,

$$\Delta S_r^\circ, \text{sur} = \frac{-\Delta H^\circ}{T} = \frac{-(-571.66 \times 10^3)}{298.15} = +1.917 \times 10^3 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \text{ [答]}$$

- (3) $\Delta S_r^\circ, \text{total} = \Delta S_r^\circ + \Delta S_r^\circ, \text{sur} = -326.4 + 1.917 \times 10^3 = +1.591 \times 10^3 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [答]

- (4) $\Delta S_r^\circ, \text{total} > 0$ より, この反応は自発的に起こる。[答]

- (5) 標準自由エネルギー変化 ΔG_r° は,

$$\Delta G_r^\circ = T \Delta S_r^\circ, \text{total} = (-298.15 \text{K}) \times (1.591 \times 10^3 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -474.4 \text{kJ} \cdot \text{mol}^{-1} \text{ [答]}$$

また, 水の25°Cでの標準生成自由エネルギーの値 ($\Delta G_f^\circ = -237.178 \text{kJ} \cdot \text{mol}^{-1}$) を使えば, 同じ値が得られる。すなわち,

$$\Delta G^\circ = 2 \times (-237.178 \text{kJ} \cdot \text{mol}^{-1}) - \{2 \times (0) + (0)\} = -474.4 \text{kJ} \cdot \text{mol}^{-1}$$

演習問題 B

12-B1

- (1) 次式のような一般的な化学平衡の式を考える。



溶質 A, B, L, M の化学ポテンシャルは

$$\mu_{\text{A}} = \mu_{\text{A}}^\circ + RT \ln a_{\text{A}}$$

$$\mu_{\text{B}} = \mu_{\text{B}}^\circ + RT \ln a_{\text{B}}$$

$$\mu_{\text{L}} = \mu_{\text{L}}^\circ + RT \ln a_{\text{L}}$$

$$\mu_{\text{M}} = \mu_{\text{M}}^\circ + RT \ln a_{\text{M}}$$

次に, 反応に伴うギブスエネルギー変化 ΔG は,

$$\begin{aligned} \Delta G &= (l\mu_{\text{L}} + m\mu_{\text{M}}) - (a\mu_{\text{A}} + b\mu_{\text{B}}) \\ &= l(\mu_{\text{L}}^\circ + RT \ln a_{\text{L}}) + m(\mu_{\text{M}}^\circ + RT \ln a_{\text{M}}) - a(\mu_{\text{A}}^\circ + RT \ln a_{\text{A}}) - b(\mu_{\text{B}}^\circ + RT \ln a_{\text{B}}) \end{aligned}$$

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{a_{\text{L}}^l \cdot a_{\text{M}}^m}{a_{\text{A}}^a \cdot a_{\text{B}}^b} \right)$$

ここで, $\Delta G^\circ = l\mu_{\text{L}}^\circ + m\mu_{\text{M}}^\circ - a\mu_{\text{A}}^\circ - b\mu_{\text{B}}^\circ$

平衡状態では， $\Delta G = 0$

$$\Delta G^\circ = -RT \ln \left(\frac{a_L^l \cdot a_M^m}{a_A^a \cdot a_B^b} \right)_{\text{平衡}}$$

$$\Delta G^\circ = -RT \ln K \quad [\text{答}]$$

(2) 次に，電池反応を考えると，

$$\Delta G = -nFE, \quad \Delta G^\circ = -nFE^\circ$$

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{a_L^l \cdot a_M^m}{a_A^a \cdot a_B^b} \right) \quad \text{ネルンストの式} \quad [\text{答}]$$

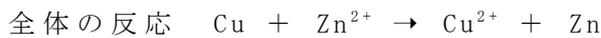
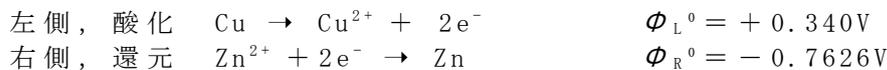
平衡状態では， $\Delta G = 0, \quad E = 0$

$$E^\circ = \frac{RT}{nF} \ln \left(\frac{a_L^l \cdot a_M^m}{a_A^a \cdot a_B^b} \right)_{\text{平衡}}$$

$$E^\circ = \frac{RT}{nF} \ln K \quad [\text{答}]$$

12-B2

(1)



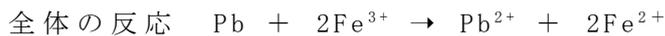
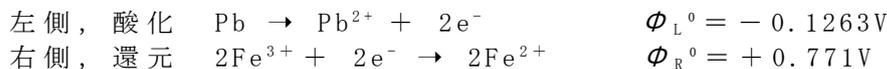
$$E^\circ = \phi_R^\circ - \phi_L^\circ = (-0.7626) - (+0.340) = -1.1026\text{V}$$

$$E^\circ = \frac{RT}{nF} \ln K$$

$$\ln K = E^\circ \times \frac{nF}{RT} = (-1.1026) \times \frac{2 \times 96485}{8.314 \times 298.15} = -85.83$$

$$K = 5.30 \times 10^{-38} \quad [\text{答}]$$

(2)



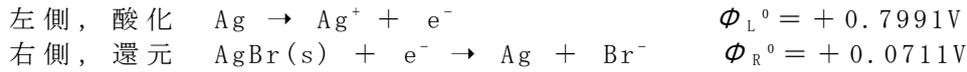
$$E^\circ = \phi_R^\circ - \phi_L^\circ = (+0.771) - (-0.1263) = +0.8973\text{V}$$

$$E^\circ = \frac{RT}{nF} \ln K$$

$$\ln K = E^\circ \times \frac{nF}{RT} = (+0.8973) \times \frac{2 \times 96485}{8.314 \times 298.15} = 69.85$$

$$K = 2.17 \times 10^{30} \quad [\text{答}]$$

12-B3



全体の反応 $\text{AgBr(s)} \rightarrow \text{Ag}^+ + \text{Br}^-$
 $E^0 = \Phi_{\text{R}}^0 - \Phi_{\text{L}}^0 = (+0.0711) - (+0.7991) = -0.7280\text{V}$

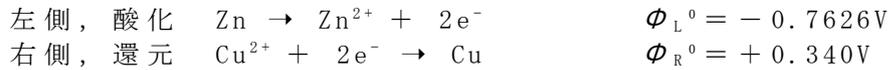
$$E^0 = \frac{RT}{nF} \ln K$$

$$\ln K = E^0 \times \frac{nF}{RT} = (-0.7280) \times \frac{1 \times 96485}{8.314 \times 298.15} = -28.34$$

$$K = K_{\text{sp}} = 4.92 \times 10^{-13} \quad [\text{答}]$$

12-B4

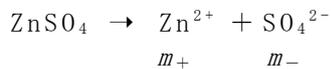
(1)



全体の反応 $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
 $E^0 = \Phi_{\text{R}}^0 - \Phi_{\text{L}}^0 = (+0.340) - (-0.7626) = +1.1026\text{V}$

$$E = E^0 - \frac{RT}{nF} \ln \left(\frac{a_{\text{Zn}^{2+}} \cdot a_{\text{Cu}}}{a_{\text{Zn}} \cdot a_{\text{Cu}^{2+}}} \right)$$

ここで, ZnSO_4 の電離を考えると (電離度 1 と考える),



ZnSO_4 の最初の質量モル濃度を m とすると,

$$m_+ = m, \quad m_- = m \quad \text{となる。}$$

また, $\gamma_{\pm} = \gamma_+ = \gamma_-$ と仮定する。

硫酸銅水溶液の場合も同様になる。

$$a_{\text{Zn}^{2+}} = \gamma_+ m_+ = \gamma_{\pm} m = 1 \times 0.5 = 0.5$$

$$a_{\text{Cu}^{2+}} = \gamma_+ m_+ = \gamma_{\pm} m = 1 \times 0.1 = 0.1$$

$$E = E^0 - \frac{RT}{nF} \ln \left(\frac{a_{\text{Zn}^{2+}} \cdot a_{\text{Cu}}}{a_{\text{Zn}} \cdot a_{\text{Cu}^{2+}}} \right) = 1.1026 - \frac{8.314 \times 298.15}{2 \times 96485} \ln \left(\frac{0.5 \times 1.0}{1.0 \times 0.1} \right) = 1.082\text{V} \quad [\text{答}]$$

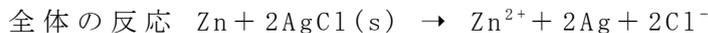
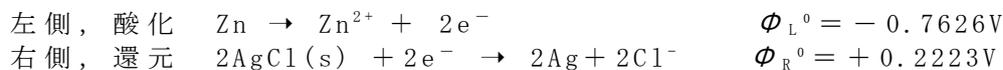
(2)

$$a_{\text{Zn}^{2+}} = \gamma_+ m_+ = \gamma_{\pm} m = 0.5 \times 0.5 = 0.25$$

$$a_{\text{Cu}^{2+}} = \gamma_+ m_+ = \gamma_{\pm} m = 0.15 \times 0.1 = 0.015$$

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{a_{\text{Zn}^{2+}} \cdot a_{\text{Cu}}}{a_{\text{Zn}} \cdot a_{\text{Cu}^{2+}}} \right) = 1.1026 - \frac{8.314 \times 298.15}{2 \times 96485} \ln \left(\frac{0.25 \times 1.0}{1.0 \times 0.015} \right) = 1.066\text{V} \quad [\text{答}]$$

12-B5



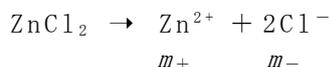
$$E^0 = \phi_{\text{R}}^0 - \phi_{\text{L}}^0 = (+0.2223) - (-0.7626) = 0.9849\text{V}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(a_{\text{Zn}^{2+}})(a_{\text{Ag}})^2(a_{\text{Cl}^-})^2}{(a_{\text{Zn}})(a_{\text{AgCl}(\text{s})})^2} = E^\circ - \frac{RT}{nF} \ln(a_{\text{Zn}^{2+}})(a_{\text{Cl}^-})^2$$

$$a_{\text{Zn}^{2+}} = \gamma_+ m_+$$

$$a_{\text{Cl}^-} = \gamma_- m_-$$

一方， ZnCl_2 の電離を考えると（電離度 1 と考える），



ZnCl_2 の最初の質量モル濃度を m とすると，

$$m_+ = m, \quad m_- = 2m \quad \text{となる。}$$

$$(a_{\text{Zn}^{2+}})(a_{\text{Cl}^-})^2 = (\gamma_+ m_+)(\gamma_- m_-)^2 = (\gamma_+ m)(\gamma_- 2m)^2 = \gamma_+ \cdot \gamma_-^2 \cdot 4m^3 = \gamma_{\pm}^3 \cdot 4m^3$$

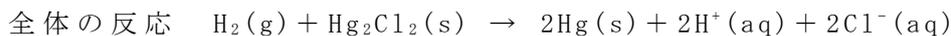
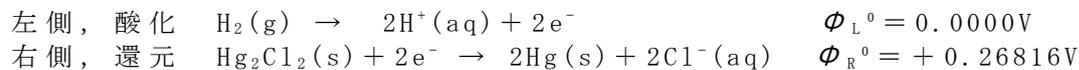
ここで， $\gamma_{\pm}^3 = \gamma_+ \cdot \gamma_-^2$ と仮定する。

$$E = E^\circ - \frac{RT}{nF} \ln(a_{\text{Zn}^{2+}})(a_{\text{Cl}^-})^2 = E^\circ - \frac{RT}{nF} \ln(\gamma_{\pm}^3 \cdot 4m^3)$$

$$1.1566 = 0.9849 - \frac{8.314 \times 298.15}{2 \times 96485} \ln(\gamma_{\pm}^3 \times 4 \times 0.0102^3)$$

これより， $\gamma_{\pm} = 0.717$ を得る。 [答]

12-B6



$$E^0 = \phi_{\text{R}}^0 - \phi_{\text{L}}^0 = (+0.26816) - (0.0000) = 0.26816\text{V}$$

$$(a_{\text{H}^+})^2 \cdot (a_{\text{Cl}^-})^2 = (a_{\text{H}^+})^4 \quad [\text{ここで，}(a_{\text{H}^+}) \approx (a_{\text{Cl}^-})]$$

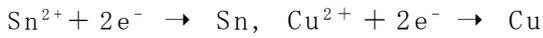
Nernst の式より，

$$E = E^\circ - \frac{RT}{2F} \ln(a_{\text{H}^+})^4 = E^\circ - \frac{2RT}{F} \ln(a_{\text{H}^+}) = E^\circ + (2) \times (2.303) \times \frac{RT}{F} \times \text{pH}$$

従って，

$$\text{pH} = \frac{(E - E^\circ)}{2 \times 2.303RT/F} = \frac{(E - 0.26816\text{V})}{0.1183\text{V}} = \frac{(0.7820\text{V} - 0.26816\text{V})}{0.1183\text{V}} = 4.344 = 4.34 \quad [\text{答}]$$

12-B7



10 分間に流れた電気量を電流値 $i[\text{A}]$ として求める。

$$Q = i \times t = i \times 10 \times 60 = 600i [\text{C}]$$

スズの 1 グラム当量 (M/z) は,

$$118.7/2 = 59.35\text{g}$$

スズめっきの重量増加は 3.278g である。このときの通過した電気量 Q_1 は,

$$Q_1 = \frac{F \times m}{(M/z)} = \frac{96485 \times 3.278}{59.35} = 5329\text{C}$$

次に, 銅電量計を考える。

銅の 1 グラム当量 (M/z) は,

$$63.55/2 = 31.78\text{g}$$

銅電量計での重量増加は 1.834g である。

このときの通過した電気量 (全通過電気量) Q_2 は,

$$Q_2 = \frac{F \times m}{(M/z)} = \frac{96485 \times 1.834}{31.78} = 5568\text{C}$$

電流効率 (C. E.) を求めると,

$$\text{C. E.} = Q_1/Q_2 = (5329\text{C}/5568\text{C}) \times 100 = 95.7 \% \quad [\text{答}]$$

銅電量計の通過した電気量より, 電流値を求めると次のようになる。

$$i = Q/t = 5568\text{C}/600\text{s} = 9.28\text{A}$$