

QUIZ CH104 Basic Electrochemistry

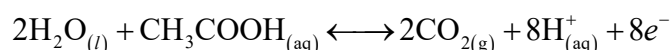
Lucas Montogue

► PROBLEMS

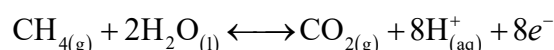
► Problem 1

Using the Gibbs free energy data in the Additional Information section, determine the standard potential for the following redox reactions:

1. Formation of CO_2 from carbon monoxide and water.
2. Chlor-alkali process to produce hydrogen and chlorine from a brine of NaCl (aqueous salt solution).
3. Acetic acid/oxygen fuel cell with acidic electrolyte, where the acetic acid reacts to form liquid water and carbon dioxide. The reaction at the negative electrode is



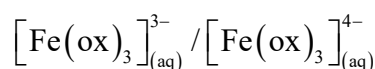
4. Oxidation of methane under acidic conditions. The anodic reaction is



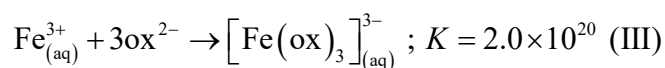
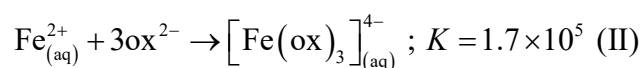
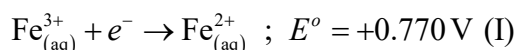
Reaction	E° (V)
1	
2	
3	
4	

► Problem 2

Calculate the standard electrode potential for the aqueous couple



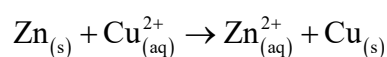
from the following data (298 K), where ox^{2-} refers to the oxalate anion, $\text{C}_2\text{O}_4^{2-}$.



- A) $E^\circ = -0.301 \text{ V}$
B) $E^\circ = -0.123 \text{ V}$
C) $E^\circ = +0.123 \text{ V}$
D) $E^\circ = +0.301 \text{ V}$

► Problem 3

Consider the global reaction



Given the standard potentials $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$ and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$, answer: is the reaction spontaneous? Also calculate the change in Gibbs free energy.

→ Problem 4.1

During electrolysis of a solution of AgNO_3 , 12,000 coulombs of charge pass through the electroplating bath. The mass of silver deposited on the cathode will be:

- A) $m = 4.12 \text{ g}$
- B) $m = 7.71 \text{ g}$
- C) $m = 13.4 \text{ g}$
- D) $m = 18.8 \text{ g}$

→ Problem 4.2

Aluminum oxide may be electrolyzed at 1000°C to furnish Al metal. How much electric charge is required to produce 5.12 kg of aluminum by electrolysis?

- A) $q = 2.75 \times 10^6 \text{ C}$
- B) $q = 5.50 \times 10^6 \text{ C}$
- C) $q = 2.75 \times 10^7 \text{ C}$
- D) $q = 5.50 \times 10^7 \text{ C}$

→ Problem 4.3

One gram of a certain metal was deposited after being subjected to the passage of 1.81×10^{23} electrons. The molar mass of the metal is:

- A) $M = 6 \text{ g/mol}$
- B) $M = 8 \text{ g/mol}$
- C) $M = 10 \text{ g/mol}$
- D) $M = 12 \text{ g/mol}$

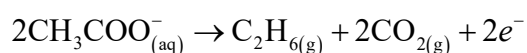
→ Problem 5.1

A 600 mL solution of NaCl was electrolyzed for 8 min. If the pH of the final solution was 12.2, calculate the average current used.

- A) $i = 1.90 \text{ A}$
- B) $i = 3.80 \text{ A}$
- C) $i = 5.52 \text{ A}$
- D) $i = 7.14 \text{ A}$

→ Problem 5.2

The electrolysis of acetate solution produces ethane according to the reaction



The current efficiency of the process is 80%. What volume of gases would be produced at 27°C and 740 torr, if a current of 0.5 A is passed through the system for 96.45 min?

- A) $V = 0.454 \text{ L}$
- B) $V = 0.908 \text{ L}$
- C) $V = 1.82 \text{ L}$
- D) $V = 3.21 \text{ L}$

→ Problem 5.3

A layer of chromium metal 0.25-mm thick is to be plated on an auto bumper with a total area of 0.32 m^2 from a solution containing CrO_4^{2-} . What current flow is required for this electroplating if the bumper is to be plated in 60 seconds? The density of chromium metal is 7.20 g/cm^3 .

- A) $i = 6.14 \times 10^3 \text{ A}$
- B) $i = 1.07 \times 10^4 \text{ A}$
- C) $i = 6.14 \times 10^4 \text{ A}$
- D) $i = 1.07 \times 10^5 \text{ A}$

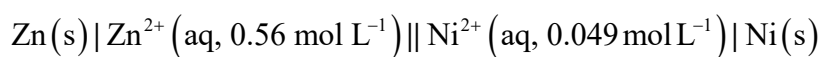
→ Problem 5.4 (Modified from Compton et al., 2011)

A British penny is manufactured by electroplating of copper onto mild steel. A steel coin with diameter ($2r$) of 2 cm and thickness (h) 1.5 mm is electroplated with copper using a solution of Cu^{2+} . A reductive charge of 29.4 C is passed. What thickness, t , of Cu has been deposited, given that the density of Cu is 8930 kg/m^3 and its molar mass is 63.5 g/mol ?

- A) $t = 0.882 \mu\text{m}$
- B) $t = 1.49 \mu\text{m}$
- C) $t = 2.13 \mu\text{m}$
- D) $t = 3.31 \mu\text{m}$

→ Problem 6.1

Determine the potential of the following cell at a temperature of 25°C.

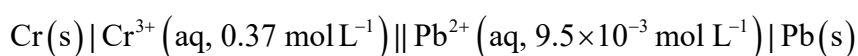


Use $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ and $E^\circ(\text{Ni}^{2+}/\text{Ni}) = -0.23 \text{ V}$.

- A) $E = +0.244 \text{ V}$
- B) $E = +0.332 \text{ V}$
- C) $E = +0.499 \text{ V}$
- D) $E = +0.530 \text{ V}$

→ Problem 6.2

Determine the potential of the following cell at 25°C.

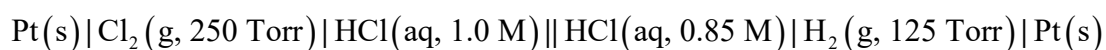


Use $E^\circ(\text{Cr}^{3+}/\text{Cr}) = -0.74 \text{ V}$ and $E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.13 \text{ V}$.

- A) $E = +0.284 \text{ V}$
- B) $E = +0.559 \text{ V}$
- C) $E = +0.844 \text{ V}$
- D) $E = +0.912 \text{ V}$

→ Problem 6.3

Determine the potential of the following cell at 25°C.

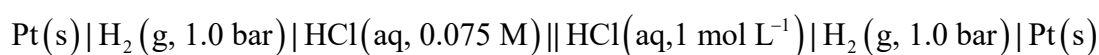


Use $E^\circ(\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$ and $E^\circ(\text{H}^+/\text{H}_2) = 0 \text{ V}$.

- A) $E = -2.44 \text{ V}$
- B) $E = -1.33 \text{ V}$
- C) $E = -0.871 \text{ V}$
- D) $E = -0.442 \text{ V}$

→ Problem 6.4

Determine the potential of the following cell at 25°C.

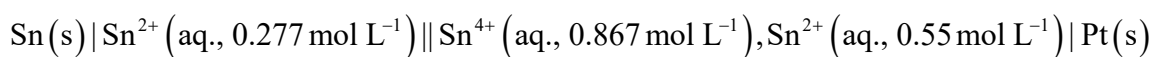


Use $E^\circ(\text{H}^+/\text{H}_2) = 0 \text{ V}$.

- A) $E = +0.0665 \text{ V}$
- B) $E = +0.202 \text{ V}$
- C) $E = +0.314 \text{ V}$
- D) $E = +0.406 \text{ V}$

→ Problem 6.5

Determine the potential of the following cell at 25°C.

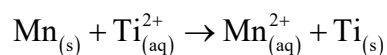


Use $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+}) = +0.15 \text{ V}$ and $E^\circ(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$.

- A) $E = +0.0871 \text{ V}$
- B) $E = +0.114 \text{ V}$
- C) $E = +0.312 \text{ V}$
- D) $E = +0.471 \text{ V}$

→ Problem 7.1

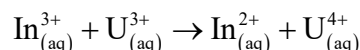
Given the standard potentials $E^\circ(\text{Ti}^{2+}/\text{Ti}) = -1.63 \text{ V}$ and $E^\circ(\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V}$, determine the equilibrium constant under standard conditions for the redox reaction



- A) $K_{\text{eq}} = 6.0 \times 10^{-20}$
- B) $K_{\text{eq}} = 6.0 \times 10^{-16}$
- C) $K_{\text{eq}} = 6.0 \times 10^{-12}$
- D) $K_{\text{eq}} = 6.0 \times 10^{-8}$

→ Problem 7.2

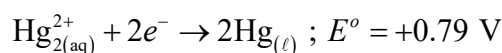
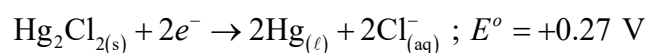
Given the standard potentials $E^\circ(\text{In}^{3+}/\text{In}^{2+}) = -0.49 \text{ V}$ and $E^\circ(\text{U}^{4+}/\text{U}^{3+}) = -0.61 \text{ V}$, determine the equilibrium constant under standard conditions for the redox reaction



- A) $K_{\text{eq}} = 1.34$
- B) $K_{\text{eq}} = 10.8$
- C) $K_{\text{eq}} = 107$
- D) $K_{\text{eq}} = 1100$

→ Problem 8.1

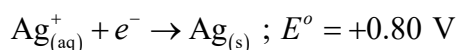
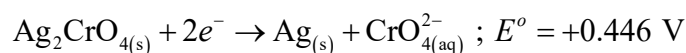
Using the data below, compute the solubility product of mercury(II) chloride, Hg_2Cl_2 .



- A) $K_{\text{sp}} = 2.58 \times 10^{-33}$
- B) $K_{\text{sp}} = 2.58 \times 10^{-28}$
- C) $K_{\text{sp}} = 2.58 \times 10^{-23}$
- D) $K_{\text{sp}} = 2.58 \times 10^{-18}$

→ Problem 8.2

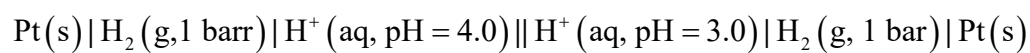
Using the data below, compute the solubility product of silver chromate, Ag_2CrO_4 .



- A) $K_{\text{sp}} = 1.03 \times 10^{-22}$
- B) $K_{\text{sp}} = 1.03 \times 10^{-17}$
- C) $K_{\text{sp}} = 1.03 \times 10^{-12}$
- D) $K_{\text{sp}} = 1.03 \times 10^{-7}$

► Problem 9

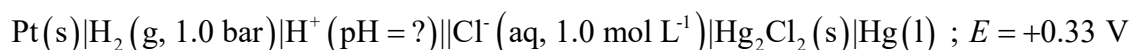
Determine the potential for the following concentration cell at 25°C .



- A) $E = +0.0114 \text{ V}$
- B) $E = +0.0591 \text{ V}$
- C) $E = +0.0912 \text{ V}$
- D) $E = +0.142 \text{ V}$

→ Problem 10.1

Determine the unknown quantity in the following cell.

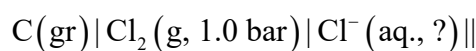


Use $E^\circ(\text{Hg}_2\text{Cl}_2/\text{Hg}, \text{Cl}^-) = +0.27 \text{ V}$.

- A) pH = 1.02
- B) pH = 3.31
- C) pH = 5.09
- D) pH = 6.11

→ Problem 10.2

Determine the unknown quantity in the following cell.



Use $E^\circ(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V}$ and $E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.51 \text{ V}$.

- A) $[\text{Cl}^-] = 0.00812 \text{ mol/L}$
- B) $[\text{Cl}^-] = 0.0112 \text{ mol/L}$
- C) $[\text{Cl}^-] = 0.0439 \text{ mol/L}$
- D) $[\text{Cl}^-] = 0.100 \text{ mol/L}$

→ Problem 11.1

A tin electrode in 0.015 M $\text{Sn}(\text{NO}_3)_2(\text{aq})$ is connected to a hydrogen electrode in which the pressure of H_2 is 1.0 bar. If the cell potential is 0.061 V at 25°C, what is the pH of the electrolyte at the hydrogen electrode? Use $E^\circ(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}$.

- A) pH = 0.106
- B) pH = 2.26
- C) pH = 4.92
- D) pH = 6.05

→ Problem 11.2

A lead electrode in 0.010 M $\text{Pb}(\text{NO}_3)_2(\text{aq})$ is connected to a hydrogen electrode in which the pressure of H_2 is 1.0 bar. If the cell potential is 0.057 V at 25°C, what is the pH of the electrolyte at the hydrogen electrode? Use $E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.13 \text{ V}$.

- A) pH = 0.101
- B) pH = 2.41
- C) pH = 4.99
- D) pH = 6.00

→ Problem 12.1

A galvanic cell has an emf of +1.1 V at 298 K, and the temperature coefficient of voltage for the cell is +6 mV K^{-1} . The cell reaction involves exchange of two electrons. True or false?

- 1. () The absolute value of the variation in Gibbs free energy is greater than 240 kJ/mol.
- 2. () The absolute value of the variation in entropy is greater than 1000 $\text{J K}^{-1}\text{mol}^{-1}$.
- 3. () The absolute value of the variation in enthalpy is greater than 600 kJ/mol.

→ Problem 12.2

For the electrochemical cell



the EMF at temperatures near the EMF obeys the following equation:

$$E[\text{V}] = -0.00614 + (2.71 \times 10^{-3})T - (8.40 \times 10^{-6})T^2 + (5.87 \times 10^{-9})T^3$$

where T is the temperature expressed in K. True or false?

- 1. () The absolute value of ΔG for this cell at 298 K is greater than 18 kJ/mol.
- 2. () The absolute value of ΔS for this cell at 298 K is greater than 80 $\text{J K}^{-1}\text{mol}^{-1}$.
- 3. () The absolute value of ΔH for this cell at 298 K is greater than 0.5 kJ/mol.

▶ ADDITIONAL INFORMATION

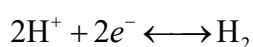
Table 1 Gibbs free energies of formation for use with Problem 1

Compound	ΔG_f° (kJ/mol)
C ₂ H ₆	-32.9
CH ₃ COOH	-389.0
CH ₄	-50.5
CO	-137.3
CO ₂	-394.4
H ₂ O	-237.2
NaCl	-393.1
NaOH	-419.2

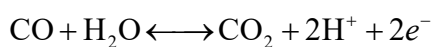
▶ SOLUTIONS

P.1 → Solution

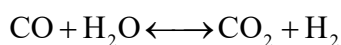
Part 1: In this case, the cathodic reaction is the formation of hydrogen gas,



while the anodic reaction is



Combining the two reactions gives



The reaction change in Gibbs free energy is determined as

$$\Delta G^\circ = \Delta G_f^\circ [\text{CO}_2] - \Delta G_f^\circ [\text{H}_2\text{O}] - \Delta G_f^\circ [\text{CO}]$$

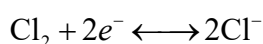
$$\therefore \Delta G^\circ = -394.4 - (-237.2) - (-137.3) = -19.5 \text{ kJ/mol}$$

The standard potential associated with the reaction is then

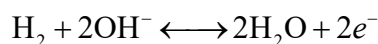
$$\Delta G^\circ = -nFE^\circ \rightarrow E^\circ = -\frac{\Delta G^\circ}{nF}$$

$$\therefore E^\circ = -\frac{(-19,500)}{2 \times 96,500} = \boxed{+0.101 \text{ V}}$$

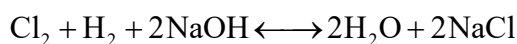
Part 2: The cathodic reaction is



while the anodic reaction is



The overall reaction is then



The reaction change in Gibbs free energy is determined as

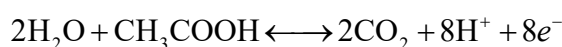
$$\Delta G^\circ = 2\Delta G_f^\circ [\text{NaCl}] + 2\Delta G_f^\circ [\text{H}_2\text{O}] - 2\Delta G_f^\circ [\text{NaOH}]$$

$$\therefore \Delta G^\circ = 2 \times (-393.1) + 2 \times (-237.2) - 2 \times (-419.2) = -422.2 \text{ kJ/mol}$$

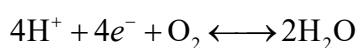
and the standard potential follows as

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{(-422,200)}{2 \times 96,500} = \boxed{+2.19 \text{ V}}$$

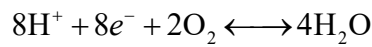
Part 3: We were given the anodic reaction



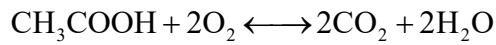
The cathodic reaction is, in turn,



We multiply the latter equation by 2 to balance electrons,



so that



The reaction change in Gibbs free energy is then

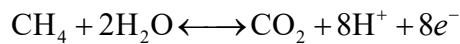
$$\Delta G^\circ = 2\Delta G_f^\circ[\text{H}_2\text{O}] + 2\Delta G_f^\circ[\text{CO}_2] - \Delta G_f^\circ[\text{CH}_3\text{COOH}]$$

$$\therefore \Delta G^\circ = 2 \times (-237.2) + 2 \times (-394.4) - (-389.0) = -874.2 \text{ kJ/mol}$$

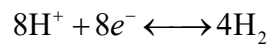
Lastly, the standard potential is calculated to be

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{(-874,200)}{8 \times 96,500} = \boxed{+1.13 \text{ V}}$$

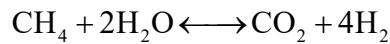
Part 4: We were given the anodic reaction,



The cathodic reaction is the evolution of hydrogen gas,



and the overall reaction is



The standard change in Gibbs free energy is then

$$\Delta G^\circ = \Delta G^\circ[\text{CO}_2] - 2\Delta G^\circ[\text{H}_2\text{O}] - \Delta G^\circ[\text{CH}_4]$$

$$\therefore \Delta G^\circ = -394.4 - 2 \times (-237.2) - (-50.5) = 130.5 \text{ kJ/mol}$$

Finally, the standard potential is calculated to be

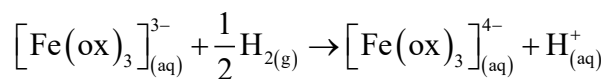
$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{130,500}{8 \times 96,500} = \boxed{-0.169 \text{ V}}$$

The results are summarized below.

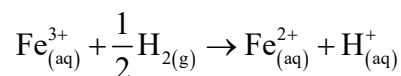
Reaction	E° (V)
1	+0.101
2	+2.19
3	+1.13
4	-0.169

P.2 → Solution

The standard electrode potential required can be found from ΔG for the reaction



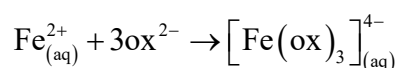
This reaction can be obtained if we combine some of the half-reactions we were given. The first reaction is



which, given the fact that the hydrogen reaction has a standard potential of zero, should have the same potential as reaction (I), or +0.770 V. The corresponding change in Gibbs free energy is then

$$\Delta G_1^\circ = -nFE^\circ = -1 \times 96,500 \times 0.770 = -74.3 \text{ kJ/mol}$$

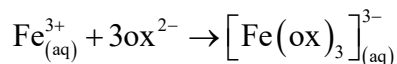
Likewise, the reaction



has a ΔG° of

$$\Delta G_2^\circ = -RT \ln K = -8.314 \times 298 \ln(1.7 \times 10^5) = -29.8 \text{ kJ/mol}$$

Next, we consider the reaction



which has a ΔG° of

$$\Delta G_3^\circ = -RT \ln K = -8.314 \times 298 \times \ln(2.0 \times 10^{20}) = -116 \text{ kJ/mol}$$

Lastly, the ΔG we aim for is given by

$$\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ - \Delta G_3^\circ = -74.3 - 29.8 - (-116) = 11.9 \text{ kJ/mol}$$

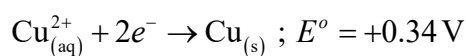
and the corresponding standard potential is

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{11,900}{1 \times 96,500} = \boxed{-0.123 \text{ V}}$$

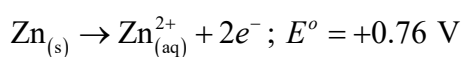
◆ The correct answer is **B**.

P.3 → Solution

In the present system, the cathodic reaction is



while the anodic reaction is



The potential of the global reaction is simply the sum of the potentials of the half-reactions,

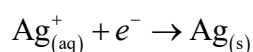
$$E^\circ = 0.34 + 0.76 = +1.1 \text{ V}$$

Since the voltage of the global reaction is positive, we surmise that the reaction is spontaneous. The change in Gibbs free energy – which should be negative in view of the fact that the reaction is spontaneous – follows as

$$\Delta G = -nFE = -2 \times 96,500 \times 1.1 = \boxed{-212 \text{ kJ/mol}}$$

P.4 → Solution

Part 1: In accordance with the cathodic reaction

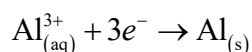


one mole of electrons, or 96,500 C, is required to produce one mole of silver. With 12,000 C, the mass of silver deposited will be

$$\frac{108 \text{ g Ag}}{96,500 \text{ C}} = \frac{m}{12,000 \text{ C}} \rightarrow \boxed{m = 13.4 \text{ g}}$$

◆ The correct answer is **C**.

Part 2: Aluminum cations are reduced to aluminum metal following the reaction

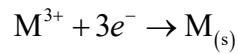


Accordingly, one mole of aluminum, or 27 g, is produced with three moles of electrons, or $3 \times 96,500 = 290,000$ C. The charge needed to produce 5.12 kg = 5120 g of aluminum is then

$$\frac{27 \text{ g Al}}{290,000 \text{ C}} = \frac{5120 \text{ g Al}}{q} \rightarrow \boxed{q = 5.50 \times 10^7 \text{ C}}$$

◆ The correct answer is **D**.

Part 3: The metal in question is deposited in the reduction reaction



which implies that one mole of metal is produced by 3 moles of electrons, or $3 \times (6.02 \times 10^{23}) = 18.06 \times 10^{23}$ electrons. The number of moles of metal obtained with the passage of 1.81×10^{23} electrons is then

$$\frac{1 \text{ mol metal}}{18.06 \times 10^{23} \text{ elec}} = \frac{M}{1.81 \times 10^{23} \text{ elec}} \rightarrow M = 0.1 \text{ mol}$$

This amount of moles corresponds to one gram of metal. The mass contained in one entire mole – that is, the molar mass – follows as

$$\frac{0.1 \text{ mol}}{1 \text{ g}} = \frac{1 \text{ mol}}{M} \rightarrow \boxed{M = 10 \text{ g/mol}}$$

◆ The correct answer is **C**.

P.5 → Solution

Part 1: Upon electrolysis, NaCl is converted into NaOH and H₂ at the cathode and Cl₂ at the anode. From the pH, we can determine the amount of NaOH formed and, from there, the average current. Now, if the pH of the solution is 12.2, the pOH must be $14 - 12.2 = 1.8$, and the concentration of NaOH formed follows as

$$[\text{NaOH}] = 10^{-1.8} = 0.0158 \text{ M}$$

The amount of NaOH in 600 mL of solution is

$$[\text{NaOH}] = 0.0158 \times 0.6 = 0.00948 \text{ mol}$$

which corresponds to a mass $m = 0.00948 \times 40 = 0.379 \text{ g}$. From Faraday's law, we have

$$m = zi\Delta t \rightarrow 0.379 = \left(\frac{40}{1 \times 96,500} \right) \times i \times (8 \times 60)$$

$$\therefore 0.379 = 0.199i$$

$$\therefore i = \frac{0.379}{0.199} = \boxed{1.90 \text{ A}}$$

◆ The correct answer is **A**.

Part 2: The amount of useful charge involved in the process is $0.8 \times 0.5 \times (96.45 \times 60) = 2310 \text{ C}$. From the stoichiometry of the reaction, two moles of electrons lead to the production of 3 volume-equivalents of gases (one of which comes from ethane, two of which from carbon dioxide). The amount of volume-equivalents formed from 2310 C is then

$$\frac{2 \times 96,500 \text{ C}}{3 \text{ moles gas}} = \frac{2310 \text{ C}}{x} \rightarrow x = 0.0359 \text{ moles gas}$$

The molar volume of an ideal gas at $27^\circ\text{C} = 300 \text{ K}$ and 740 torr is

$$\bar{V} = \frac{RT}{P} = \frac{62.4 \times 300}{740} = 25.3 \text{ L/mol}$$

The volume of gas produced in the reaction is then

$$V = 25.3 \frac{\text{L}}{\text{mol}} \times 0.0359 \text{ mol} = \boxed{0.908 \text{ L}}$$

◆ The correct answer is **B**.

Part 3: The volume of chromium required is $(0.25 \times 10^{-3}) \times 0.32 = 8 \times 10^{-5} \text{ m}^3$, which corresponds to a mass of $8 \times 10^{-5} \times 7200 = 0.576 \text{ kg} = 576 \text{ g}$. One mole of chromium, or 52 g, is produced by 6 moles of electrons. The amount of charge required to produce $576/52 = 11.1$ moles of chromium metal is

$$\frac{1 \text{ mol Cr}}{6 \times 96,500 \text{ C}} = \frac{11.1 \text{ mol Cr}}{q} \rightarrow q = 6.43 \times 10^6 \text{ C}$$

Since the plating process must be completed within 60 seconds, the current intensity required is

$$i = \frac{6.43 \times 10^6 \text{ C}}{60 \text{ s}} = \boxed{1.07 \times 10^5 \text{ A}}$$

◆ The correct answer is **D**.

Part 4: Deposition of 1 mole of copper requires 2 moles of electrons, or $2 \times 96,500 \text{ C}$. With a charge of 29.4 C , the amount of copper deposited is given by

$$\frac{1 \text{ mol Cu}}{2 \times 96,500 \text{ C}} = \frac{x}{29.4 \text{ C}} \rightarrow x = 1.52 \times 10^{-4} \text{ mol Cu} = 0.00965 \text{ g}$$

This corresponds to a volume

$$V = \frac{0.00965 \text{ g}}{8.93 \frac{\text{g}}{\text{cm}^3}} = 0.00108 \text{ cm}^3$$

The surface area of a penny, which may be regarded as a cylinder, is

$$A = 2\pi rh + 2\pi r^2 = 2\pi \times 1 \times 0.15 + 2 \times \pi \times 1.0^2 = 7.23 \text{ cm}^2$$

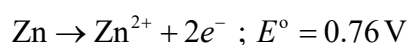
Dividing V by A , the thickness of the copper layer is calculated to be

$$t = \frac{V}{A} = \frac{0.00108}{7.23} = 1.49 \times 10^{-4} \text{ cm} = \boxed{1.49 \text{ }\mu\text{m}}$$

◆ The correct answer is **B**.

P.6 → Solution

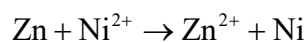
Part 1: The reaction at the anode is



while the reaction at the cathode is



The global reaction is then

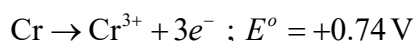


and the standard potential is $E^\circ = 0.76 - 0.23 = 0.53 \text{ V}$. Appealing to the Nernst equation, we have

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = 0.53 - \frac{8.314 \times 298}{2 \times 96,500} \ln \frac{0.56}{0.049} = \boxed{0.499 \text{ V}}$$

◆ The correct answer is **C**.

Part 2: The reaction at the anode is



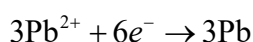
or, equivalently,



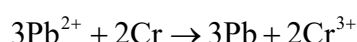
while the reaction at the cathode is



or, equivalently,



The global reaction is

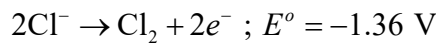


and the standard potential is $E^\circ = -0.13 + 0.74 = 0.61$ V. Resorting to the Nernst equation, we have

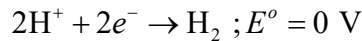
$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Cr}^{3+}]^2}{[\text{Pb}^{2+}]^3} = 0.61 - \frac{8.314 \times 298}{6 \times 96,500} \ln \left[\frac{0.37^2}{(9.5 \times 10^{-3})^3} \right] = \boxed{0.559 \text{ V}}$$

◆ The correct answer is **B**.

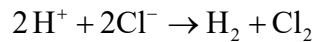
Part 3: The reaction at the anode is



while the reaction at the cathode is



The global reaction is then



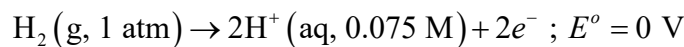
and the standard potential is $E^\circ = -1.36 + 0 = -1.36$ V. With reference to the Nernst equation, we have

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{P_{\text{H}_2} P_{\text{Cl}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right) =$$

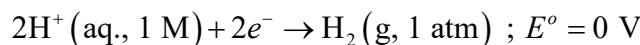
$$\therefore E - 1.36 - \frac{8.314 \times 298}{2 \times 96,500} \ln \left[\frac{(125/760) \times (250/760)}{0.85^2 \times 1.0^2} \right] = \boxed{-1.33 \text{ V}}$$

◆ The correct answer is **B**.

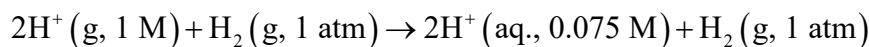
Part 4: The reaction at the anode is



Likewise, the reaction at the cathode is



The global reaction is



and the associated potential is $E^\circ = 0$ V. Invoking the Nernst equation, we have

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{[\text{H}^+, 0.075 \text{ M}]^2 \times P_{\text{H}_2}}{[\text{H}^+, 1.0 \text{ M}]^2 \times P_{\text{H}_2}} \right)$$

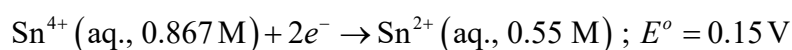
$$\therefore E = 0 - \frac{8.314 \times 298}{2 \times 96,500} \ln \left(\frac{0.075^2 \times 1}{1.0^2 \times 1} \right) = \boxed{0.0665 \text{ V}}$$

◆ The correct answer is **A**.

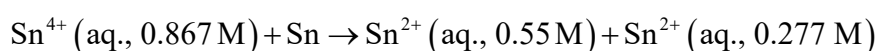
Part 5: The reaction at the anode is



and the reaction at the cathode is



The global reaction is



and the associated potential is $E^\circ = 0.14 + 0.15 = 0.29$ V. Appealing to the Nernst equation, we have

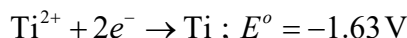
$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Sn}^{2+}, 0.55 \text{ M}][\text{Sn}^{2+}, 0.277 \text{ M}]}{[\text{Sn}^{4+}]}$$

$$\therefore E = 0.29 - \frac{8.314 \times 298}{2 \times 96,500} \ln \left(\frac{0.55 \times 0.277}{0.867} \right) = \boxed{0.312 \text{ V}}$$

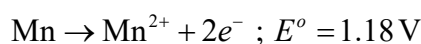
◆ The correct answer is **C**.

P.7 → Solution

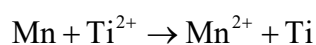
Part 1: Given the half-reactions



and



the potential for the global reaction



is determined to be $E^\circ = -1.63 + 1.18 = -0.45 \text{ V}$. The equilibrium constant can be obtained with the Nernst equation,

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

observing that, at equilibrium, $E = 0$ and $Q = K_{\text{eq}}$, so that

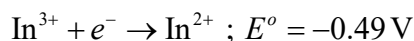
$$0 = E^\circ - \frac{RT}{nF} \ln K_{\text{eq}} \rightarrow \ln K_{\text{eq}} = \frac{nFE^\circ}{RT}$$

$$\therefore K_{\text{eq}} = \exp \left(\frac{nFE^\circ}{RT} \right)$$

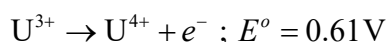
$$\therefore K_{\text{eq}} = \exp \left[\frac{2 \times 96,500 \times (-0.45)}{8.314 \times 298} \right] = \boxed{6.0 \times 10^{-16}}$$

◆ The correct answer is **B**.

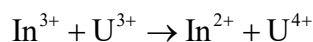
Part 2: Given the half-reactions



and



the potential for the global reaction



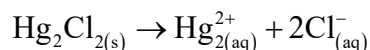
is determined to be $E^\circ = -0.49 + 0.61 = 0.12 \text{ V}$. The equilibrium constant can be obtained with the formula

$$K_{\text{eq}} = \exp \left(\frac{nFE^\circ}{RT} \right) = \exp \left(\frac{1 \times 96,500 \times 0.12}{8.314 \times 298} \right) = \boxed{107}$$

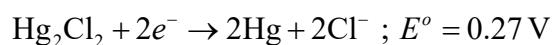
◆ The correct answer is **C**.

P.8 → Solution

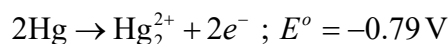
Part 1: The dissolution of Hg_2Cl_2 is represented by the reaction



This reaction can be obtained if we add the half-reactions



and



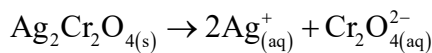
The standard potential of the dissolution reaction is then $E^\circ = 0.27 - 0.79 = -0.52 \text{ V}$. Noting that $\Delta G^\circ = -RT \ln K = -nFE^\circ$, we can determine the solubility product as

$$\ln K_{sp} = \frac{nFE^{\circ}}{RT} = \frac{2 \times 96,500 \times (-0.52)}{8.314 \times 298} = -40.5$$

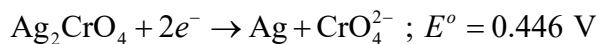
$$\therefore K_{sp} = 2.58 \times 10^{-18}$$

◆ The correct answer is **D**.

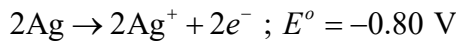
Part 2: The dissolution of silver chromate is represented by the reaction



This reaction can be obtained if we add the half-reactions



and



The standard potential of the dissolution reaction is then $E^{\circ} = 0.446 - 0.80 = -0.354 \text{ V}$. The solubility product follows as

$$\ln K_{sp} = \frac{nFE^{\circ}}{RT} = \frac{2 \times 96,500 \times (-0.354)}{8.314 \times 298} = -27.6$$

$$\therefore K_{sp} = 1.03 \times 10^{-12}$$

◆ The correct answer is **C**.

P.9 → Solution

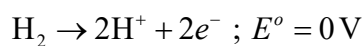
At pH = 3.0, $[\text{H}^+] = 10^{-3} \text{ M}$, while, at pH = 4.0, $[\text{H}^+] = 10^{-4} \text{ M}$. For electrodes involving evolution of gaseous hydrogen, the standard potential is $E^{\circ} = 0$. Appealing to the Nernst equation, we have

$$E = E^{\circ} - \frac{RT}{nF} \ln Q = 0 - \frac{8.314 \times 298}{1 \times 96,500} \ln \left(\frac{10^{-4}}{10^{-3}} \right) = 0.0591 \text{ V}$$

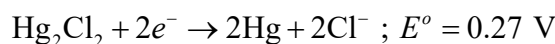
◆ The correct answer is **B**.

P.10 → Solution

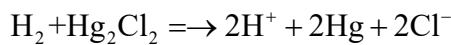
Part 1: The anodic reaction is



while the cathodic reaction is



The global reaction is



and the associated potential is $E^{\circ} = +0.27 \text{ V}$. With reference to the Nernst equation, we have

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{[\text{H}_2]} \rightarrow 0.33 = 0.27 - \frac{8.314 \times 298}{2 \times 96,500} \ln \frac{[\text{H}^+]^2 \times 1.0^2}{1.0}$$

$$\therefore 0.33 = 0.27 - 0.0128 \ln [\text{H}^+]^2$$

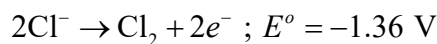
$$\therefore 0.33 - 0.27 = -0.0256 \times 2.303 \log [\text{H}^+]$$

$$\therefore 0.06 = 0.0590 (-\log [\text{H}^+])$$

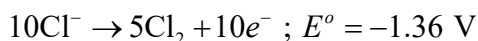
$$\therefore \text{pH} = \frac{0.06}{0.0590} = 1.02$$

◆ The correct answer is **A**.

Part 2: The anodic reaction is



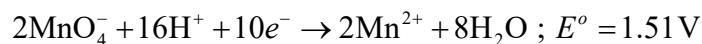
or, equivalently,



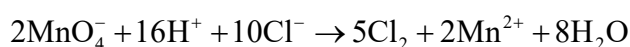
The cathodic reaction, in turn, is



or, equivalently,



Adding the anodic and cathodic reactions, we get the global reaction



which is associated with a standard potential $E^\circ = -1.36 + 1.51 = +0.15 \text{ V}$. We can now apply the Nernst equation and find the concentration of chloride ion,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Cl}_2]^5 [\text{Mn}^{2+}]^2}{[\text{MnO}_4^-]^2 [\text{H}^+]^{16} [\text{Cl}^-]^{10}}$$

$$\therefore -0.30 = +0.15 - \frac{8.314 \times 298}{10 \times 96,500} \ln \frac{1.0^5 \times 0.1^2}{0.01^2 \times (10^{-4})^{16} \times [\text{Cl}^-]^{10}}$$

$$\therefore -0.45 = -0.00257 \ln \frac{10^{66}}{[\text{Cl}^-]^{10}}$$

$$\therefore 175 = \ln 10^{66} - 10 \ln [\text{Cl}^-]$$

$$\therefore 175 = 152 - 10 \ln [\text{Cl}^-]$$

$$\therefore -10 \ln [\text{Cl}^-] = 23$$

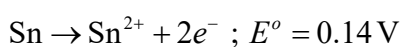
$$\therefore \ln [\text{Cl}^-] = -2.3$$

$$\therefore [\text{Cl}^-] = \exp(-2.3) = \boxed{0.10 \text{ mol/L}}$$

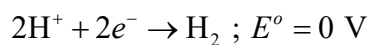
◆ The correct answer is **D**.

P.11 → Solution

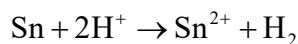
Part 1: The anodic reaction is



while the cathodic reaction is



Adding these reactions gives the global reaction



which has a standard potential $E^\circ = +0.14 \text{ V}$. With reference to the Nernst equation, we can determine the pH,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Sn}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2} \rightarrow 0.061 = 0.14 - \frac{8.314 \times 298}{2 \times 96,500} \ln \left(\frac{0.015 \times 1.0}{[\text{H}^+]^2} \right)$$

$$\therefore 0.061 = 0.14 - 0.0128 \ln \left(\frac{0.015}{[\text{H}^+]^2} \right)$$

$$\therefore -0.079 = -0.0128 \ln \left(\frac{0.015}{[\text{H}^+]^2} \right)$$

$$\therefore 6.17 = \ln 0.015 - 2 \ln [\text{H}^+]$$

$$\therefore 6.17 = -4.20 - 2 \ln [\text{H}^+]$$

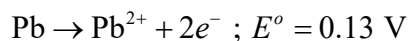
$$\therefore 10.4 = -2 \times 2.303 \log [\text{H}^+]$$

$$\therefore 2.26 = -\log [\text{H}^+]$$

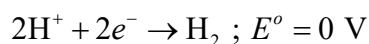
$$\boxed{\text{pH} = 2.26}$$

◆ The correct answer is **B**.

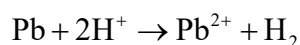
Part 2: The anodic reaction is



while the cathodic reaction is



Adding these reactions gives the global reaction



which has a standard potential $E^\circ = +0.13 \text{ V}$. Appealing to the Nernst equation, we can establish the pH,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Pb}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2} \rightarrow 0.057 = 0.13 - \frac{8.314 \times 298}{2 \times 96,500} \ln \left(\frac{0.01 \times 1.0}{[\text{H}^+]^2} \right)$$

$$\therefore 0.057 = 0.14 - 0.0128 \ln \left(\frac{0.01}{[\text{H}^+]^2} \right)$$

$$\therefore -0.083 = -0.0128 \ln \left(\frac{0.01}{[\text{H}^+]^2} \right)$$

$$\therefore 6.48 = \ln 0.01 - 2 \ln [\text{H}^+]$$

$$\therefore 6.48 = -4.61 - 2 \ln [\text{H}^+]$$

$$\therefore 11.1 = -2 \times 2.303 \log [\text{H}^+]$$

$$\therefore 2.41 = -\log [\text{H}^+]$$

$$\therefore \boxed{\text{pH} = 2.41}$$

◆ The correct answer is **B**.

P.12 → Solution

Part 1:

1.False. The change in Gibbs free energy is given by

$$\Delta G_{\text{cell}} = -nFE = -2 \times 96,500 \times 1.1 = \boxed{-212 \text{ kJ/mol}}$$

2.True. The change in entropy is given by

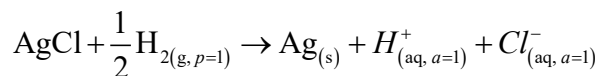
$$\Delta S_{\text{cell}} = nF \left(\frac{\partial E}{\partial T} \right)_P = 2 \times 96,500 \times (6 \times 10^{-3}) = \boxed{1160 \text{ J K}^{-1} \text{ mol}^{-1}}$$

3. False. The change in enthalpy is given by

$$\Delta H_{\text{cell}} = \Delta G_{\text{cell}} - T \Delta S_{\text{cell}} = -212 - 298 \times 1.16 = \boxed{-558 \text{ kJ/mol}}$$

Part 2:

1.True. The global reaction is



and involves exchange of one electron. The cell voltage at 298 K is

$$E = -0.00614 + (2.71 \times 10^{-3}) \times 298 - (8.40 \times 10^{-6}) \times 298^2 + (5.87 \times 10^{-9}) \times 298^3$$

$$\therefore E = 0.211 \text{ V}$$

The change in Gibbs free energy is calculated as

$$\Delta G = -nFE = -1 \times 96,500 \times 0.211 = \boxed{-20.4 \text{ kJ/mol}}$$

2.False. We first obtain the derivative $\partial E/\partial T$,

$$\left(\frac{\partial E}{\partial T}\right)_p = 2.71 \times 10^{-3} - 16.8 \times 10^{-6} T + 17.6 \times 10^{-9} T^2$$

Then, with $T = 298 \text{ K}$, we determine ΔS ,

$$\Delta S = nF(2.71 \times 10^{-3} - 16.8 \times 10^{-6} T + 17.6 \times 10^{-9} T^2)$$

$$\therefore \Delta S = 1 \times 96,500 \times (2.71 \times 10^{-3} - 16.8 \times 10^{-6} \times 298 + 17.6 \times 10^{-9} \times 298^2) = \boxed{-70.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

The negative sign of this entropy change reflects the loss of gaseous hydrogen in the cell reaction.

3.True. The heat of the cell reaction at 298 K is

$$\Delta H = \Delta G - T\Delta S = -20,400 - 298 \times (-70.8) = \boxed{698 \text{ J/mol}}$$

➤ ANSWER SUMMARY

Problem 1		Open-ended pb.
Problem 2		B
Problem 3		Open-ended pb.
Problem 4	4.1	C
	4.2	D
	4.3	C
Problem 5	5.1	A
	5.2	B
	5.3	D
	5.4	B
Problem 6	6.1	C
	6.2	B
	6.3	B
	6.4	A
	6.5	C
Problem 7	7.1	B
	7.2	C
Problem 8	8.1	D
	8.2	C
Problem 9		B
Problem 10	10.1	A
	10.2	D
Problem 11	11.1	B
	11.2	B
Problem 12	12.1	T/F
	12.2	T/F

► REFERENCES

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