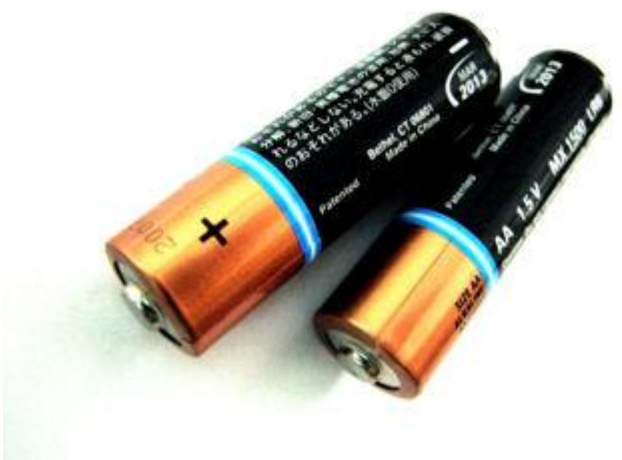
Thermodynamics tutorhour 4

Electrochemistry

Electrochemical cells

Nernst Equation



Electrochemical cell p,T constant: $\mathbf{\Delta_r \mathit{G} = -\nu F \Delta \mathit{E}_{cell}}$

ν: number of transferred electrons (according to the chemical equation)

F: Faraday constant = 96 485 C/mol

ΔE_{cell}: electromotive force of the cell

If a process is spontaneous then: $\mathbf{\Delta_r \mathit{G} \leq 0}$ (p,T constant)

So for a battery:

$\mathbf{\Delta \mathit{E}_{cell} \geq 0}$ (p,T constant)

Standard conditions

$$\Delta_r G^\ominus = -\nu F \Delta E_{cell}^\ominus$$

oxidizing agent		reducing agent	$E^\ominus$ (V)
$Cu^{2+} + 2\ e^-$	→	Cu	+ 0.34
$2\ H^+ + 2\ e^-$	→	H_2	0.000000
$Zn^{2+} + 2\ e^-$	→	Zn	- 0.76

Redox table
T = 298 K, $p = p^\ominus$ and
all activities a = 1

Standard Daniell cell: Zn(s) | Zn^{2+} || Cu^{2+} | Cu(s)

$$\Delta E_{cell}^\ominus = 0.34 - (-0.76) = 1.10\ \text{V}$$
$$\Delta_r G^\ominus = -2 \cdot 96485 \cdot 1.10 = -2.12 \cdot 10^5\ \text{J mol}^{-1} < 0$$

Non-standard conditions

If $p \neq p^{\Theta}$ and/or $a \neq 1$, apply a correction:

For each electrode: Ox + ν e^- $\longrightarrow$ Red

$$E = E^{\Theta} - \frac{RT}{\nu F} \ln Q$$

E: potential of the electrode

Q refers to the half-reaction of the cell

For overall potential:

$$\Delta E_{cell} = \Delta E^{\Theta}_{cell} - \frac{RT}{\nu F} \ln Q$$

Q: reaction quotient

(similar to concentration quotient)

Example: the nickel chromium battery

$$Ni^{2+} + 2e^- \rightarrow Ni \qquad 3x$$

$$Cr \rightarrow Cr^{3+} + 3e^- \qquad 2x$$

ν = 6 and $$Q = \frac{a_{Ni}^3 \cdot a_{Cr^{3+}}^2}{a_{Cr}^2 \cdot a_{Ni^{2+}}^3} = \frac{a_{Cr^{3+}}^2}{a_{Ni^{2+}}^3}$$

If the activities are known you can calculate the potential by:

$$\Delta E_{\mathrm{cell}} = \Delta E_{\mathrm{cell}}^{\Theta} - \frac{\mathrm{R}T}{\nu \mathrm{F}} \ln Q$$

see last slide for explanation

How to construct a chemical half reaction yourself

- put the formula of the particle that reacts on the left hand side, and the formula of the particle that appears on the right hand side of the equation
- put coëfficiënts in front of these formulas, to make sure all elements - except H and O - are equally present before and after the arrow
- equal the missing **O-atoms** with **H_2O**
- equal the missing **H-atoms** with **H^+**
- equal the **charge** with **e^-**
- check the environment:
  - if it is neutral, there can't be any **H^+ ions** present on the left hand side of the equation
  - if it is basic, there can't be any **H^+ ions** present on any side of the equation

In both cases, add as much **OH^- ions** as you need to neutralize the **H^+ ions** to form **H_2O**. Don't forget to add the same amount of **OH^- ions** on the other side of the equation!

Answers

Question 1

$Cu^{2+} + Zn(s) \longrightarrow Cu(s) + Zn^{2+}$

$$\Delta E_{\text{cell}} = \Delta E^{\Theta}_{\text{cell}} - \frac{RT}{\nu F}\ln Q = 0.34 - (-0.76) - \frac{RT}{\nu F}\ln\frac{a_{Cu}\cdot a_{Zn^{2+}}}{a_{Zn}\cdot a_{Cu^{2+}}}$$

$$\approx 1.10 - \frac{RT}{\nu F}\ln\frac{1\cdot[Zn^{2+}]}{1\cdot[Cu^{2+}]} = 1.14\ V$$

Question 2

$H_2(g) \longrightarrow 2\ H^+ + \cancel{2e^-}$ $E^{\Theta} = 0.00$ V

$2\ Ag^{2+} \cancel{+ 2e^-} \longrightarrow \cancel{2\ Ag^+}$ $E^{\Theta} = 1.98$ V

$\cancel{2\ Ag^+} + \cancel{2e^-} \longrightarrow \cancel{2\ Ag}$ $E^{\Theta} = 0.80$ V

$\cancel{2\ Ag} + CrO_4^{2-} \longrightarrow Ag_2CrO_4 + \cancel{2e^-}$ $E^{\Theta} = -\ 0.45$ V (reversed!)

$H_2(g) + CrO_4^{2-} + 2\ Ag^{2+} \longrightarrow Ag_2CrO_4 + 2\ H^+$ $\Delta E_{cell}^{\Theta} = 2.33$ V

Question 3

$2\ AgCl + 2e^- \rightarrow 2\ Ag + 2\ Cl^-$ $\quad E^\Theta = 0.22\ V$

$H_2(g) \rightarrow 2\ H^+ + 2e^-$ $\quad E^\Theta = 0.00\ V \quad +$

$H_2(g) + 2\ AgCl \rightarrow 2\ H^+ + 2\ Ag + 2\ Cl^-$ $\quad \Delta E_{cell}^\Theta = 0.22\ V$

$$\Delta E_{cell} = \Delta E_{cell}^{\theta} - \frac{RT}{\nu F} \ln Q \qquad Q = \frac{a_{H^+}^2 \cdot a_{Ag}^2 \cdot a_{Cl^-}^2}{a_{H_2} \cdot a_{AgCl}^2} = \frac{a_{H^+}^2 \cdot 1 \cdot a_{Cl^-}^2}{1 \cdot 1^2} \approx a_{H^+}^4$$

$$0.322 = 0.22 - \frac{8.3145 \cdot 298}{2 \cdot 9.6485 \cdot 10^4} \ln a_{H^+}^4$$

:

$$\ln a_{H^+} = \frac{0.22 - 0.322}{4 \cdot 0.0128} = -\ 1.986 \qquad => \quad a_{H^+} = e^{-\ 1.986} = 0.1372$$

$$=> \quad pH = -\log a_{H^+} = -\log 0.1372 = 0.86$$

Question 4

a. $\Delta E^{\theta}_{cell} = E^{\theta}_{+pole} - E^{\theta}_{-pole} =$ 1.685 − (− 0.356) = 2.041 V

$\Delta E^{\theta}_{EMF} = 6 * 2.041 = 12.246$ V

b. Per cell: $\Delta E_{cell} = \frac{\Delta E_{EMF}}{6} =$ 12.06 / 6 = 2.01 V and $\Delta E_{cell} = \Delta E^{\theta}_{cell} - \frac{RT}{\nu F} \ln Q$

$PbO_2(s) + Pb(s) + 2\ H_3O^+ + 2\ HSO_4^- \longrightarrow 2\ PbSO_4(s) + 4\ H_2O(l)$

$$Q = \frac{a^2_{PbSO_4} \cdot a^4_{H_2O}}{a_{PbO_2} \cdot a_{Pb} \cdot a^2_{H_3O^+} \cdot a^2_{HSO_4^-}} = \frac{1^2 \cdot 1^4}{1 \cdot 1 \cdot (10^{-pH})^2 \cdot a^2_{HSO_4^-}} = \frac{1}{(10^{-0,5})^2 \cdot a^2_{HSO_4^-}} = \frac{10}{a^2_{HSO_4^-}}$$

$$\Delta E_{cell} = \Delta E^{\theta}_{cell} - \frac{RT}{\nu F} \ln Q \quad \Leftrightarrow \quad 2{,}01 = 2{,}041 - \frac{8.3145 \cdot 298}{2 \cdot 9.6485 \cdot 10^4} \ln \frac{10}{a^2_{HSO_4^-}}$$

$$\Rightarrow \quad a_{HSO_4^-} = \sqrt{\frac{10}{11.18}} = 0.946$$

Explanation for nickel chromium battery

fill in for the reduction reaction:

the terms together and because

$y \cdot \ln(b) - y \cdot \ln(c) = y \cdot \ln(b/c)$

By changing the quotients the

$-\ln$ becomes $+\ln$

Fill in $\Delta E_{cell} = E_{+pole} - E_{-pole}$

$\{ y \cdot \ln(x) = y/2 \cdot \ln(x^2) \}$

$$E = E^{\Theta} - \frac{RT}{\nu F}\ln Q \qquad \Delta E_{cell} = E_{+pole} - E_{-pole}$$

$$E_{+pole} = E^{\Theta}_{+pole} - \frac{RT}{\nu F}\ln\frac{a_{red}}{a_{ox}} = -0.25 - \frac{RT}{2F}\ln\frac{1}{a_{Ni^{2+}}}$$

$Ni^{2+} + 2e^- \rightleftarrows Ni$

$$E_{-pole} = E^{\Theta}_{-pole} - \frac{RT}{\nu F}\ln\frac{a_{red}}{a_{ox}} = -0.74 - \frac{RT}{3F}\ln\frac{1}{a_{Cr^{3+}}}$$

$Cr^{3+} + 3e^- \rightleftarrows Cr$

$$\Delta E_{cell} = \left(-0.25 - \frac{RT}{2F}\ln\frac{1}{a_{Ni^{2+}}}\right) - \left(-0.74 - \frac{RT}{3F}\ln\frac{1}{a_{Cr^{3+}}}\right)$$

$$\Delta E_{cell} = \left(-0.25 + \frac{RT}{2F}\ln a_{Ni^{2+}}\right) - \left(-0.74 + \frac{RT}{3F}\ln a_{Cr^{3+}}\right)$$

$$\Delta E_{cell} = -0.25 + 0.74 - \left(\frac{RT}{6F}\ln a^2_{Cr^{3+}} - \frac{RT}{6F}\ln a^3_{Ni^{2+}}\right)$$

$$\Delta E_{cell} = 0.49 - \frac{RT}{6F}\ln\frac{a^2_{Cr^{3+}}}{a^3_{Ni^{2+}}}$$

$$\Delta E_{cell} = \Delta E^{\Theta}_{cell} - \frac{RT}{\nu F}\ln Q$$

$Ni^{2+} + 2e^- \rightarrow Ni$ 3x

$Cr \rightarrow Cr^{3+} + 3e^-$ 2x

$3\,Ni^{2+} + 2\,Cr \rightarrow 3\,Ni + 2\,Cr^{3+}$