CHEMICAL EQUILIBRIUM

Chapter 6 Outline

HW: Questions are below. Solutions are in separate file on the course web site.

Sect.	Title and Comments	Required?
1.	The Gibbs Energy Minimum	YES
2.	The Description of Equilibrium Skip Subsections 2.c (The relation between equilibrium constants) and 2.d (Equilibria in biological systems)	YES
3.	How Equlibria Respond to Pressure	YES
4.	The Response of Equilibria to Temperature	YES
Equilibrium Electrochemistry (Sections 5-9)		
5.	Half-Reactions and Electrodes	YES
6.	Varieties of Cells	YES
7.	The Cell Potential	YES
8.	Standard Elecrtrode Potentials We will cover Reduction Potentials, but will take the more straightforward approach of assuming ideal solutions. We will notpresent them in terms of ionic activities and activity coefficients.	YES
9.	Applications of Standard Potentials We will emphasize Sect. 6.9c (The determination of equilibrium constants) and Sect. 6.9d (The determination of thermodynamic functions). However, we will not cover Sect. 6.9b (The determination of activity coefficients)	MOST

Additional Related Material

(a) We will cover Solubility Equilibria, emphasizing Selective Precipitation of salts and determining whether a precipitate will form from mixing two soluble salts.

(b) In electrochemistry, we will cover Concentration Cells and their applications to determine trace concentrations and Solubility Products (Ksp).

Chapter 6 Homework Questions

6.1 The standard Gibbs Energy of the reaction, $H_2(g) + 3\ N_2(g) \rightleftharpoons 2\ NH_3(g)$, is -32.9 kJ/mol at 25 °C. Calculate the value of ΔG for the following values of the reaction quotient, Q:
(a) 0.01 , (b) 1.0 , (c) 10.0 , (d) 100, 000 , (e) 1,000,000
Estimate the value of the equilibrium constant, K, from the above data, and calculate the actual value of K.

6.2 Consider the gas phase reaction, $2\ H_2O(g) \rightleftharpoons 2\ H_2(g) + O_2(g)$. At 2257 K and p = 2.0 bar, H_2O is 1.77% dissociated. Calculate the equilibrium constant for this reaction.

6.3 Consider the reaction, $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$. The Gibbs Energy of Formation of $NH_3(g)$ is -16.5 kJ/mol at 298 K.

Calculate the reaction Gibbs Energy for the above reaction (at 298 K) when the partial pressures of the gases are; $p_{N2} = 3.0$ bar , $P_{H2} = 1.0$ bar , $P_{NH3} = 0.50$ bar. What is the spontaneous direction of the reaction under these conditions?

6.4 Consider the gas phase equilibrium, $3\ A(g) \rightleftharpoons B(g) + 2\ C(g)$. At 50 ^{O}C, the Gibbs Energy change for the reaction is -2.50 kJ/mol when the component pressures are:
$P_A = 2.0$ bar , $P_B = 4.0$ bar, P_C - 0.50 bar,

Calculate the value of the equilibriaum constant, K, at 50 °C.

6.5 Consider the gas phase dissociation equilibrium, $A(g) \rightleftharpoons B(g) + 3\ C(g)$. At 25 ^{O}C, the percent dissociation is 30% at a total pressure of 2 bar. Calculate the equilibrium constant, K.

6.6 Consider the dissociation equilibrium, $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$. At 25 °C and p = 1 bar, N_2O_4 is 18.46% dissociated. The reaction enthalpy is constant at $\Delta H^o = +56.2$ kJ/mol.
(a) Calculate the equilibrium constant, K, at 25 °C
(b) Calculate K at 100 °C

6.7 For the gas phase reaction, $2\ A + B \rightleftharpoons 3\ C + 2\ D$, it was found that when 1.00 mol of A, 2.00 mol of B, and 1.00 mol of D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.90 mol of of C at a total pressure of 4.0 bar.

(a) Calculate the equilibrium contant, K, for this reaction
(b) Calculate the Reaction Gibbs Energy, $\Delta_r G^o$, for this reaction at 25 °C.

6.8 The standard reaction enthalpy for the reaction, $Zn(s) + H_2O(g) \rightleftharpoons ZnO(s) + H_2(g)$, is approximately constant at 224. kJ/mol. The standard reaction Gibbs energy is +33 kJ/mol at 1280 K.

Determine the temperature at which the Equilibrium Constant for this reaction becomes greater than 1.

6.9 The equilibrium constant for the reaction, $A(g) \rightleftharpoons B(g)$, is temperature dependent and follows the equation:

$$\ln K = A + \frac{B}{T} + \frac{C}{T^2} \text{ , } A = -1.0 \text{ , } B = -1100 \text{ K , } C = 1.5\text{x}10^5 \text{ K}^2$$

Calculate

(a) the Reaction Enthalpy, ΔH^o (in kJ/mol) at 180 ^oC

(b) the Reaction Entropy, ΔS^o (in J/mol K) at 180 ^oC

6.10 For the gas phase equilibrium, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant is $K = 4.5$ at 150 ^OC.

(a) If one puts PCl5(g) into a container with an initial pressure of P_O = 3.0 bar, what are the pressures of PCl5(g) and PCl3(g) at equilibrium.

(b) Determine the Gibbs energy change for the when the partial pressures of the three gases are: P(PCl5) = 0.8 bar and P(PCl3) = 2.2 bar and P(Cl2) = 2.2 bar?

6.11 For the gas phase equilibrium, $2A(g) + B(g) \rightleftharpoons 2C(g)$, the equilibrium constant is $K = 1\text{x}10^{-3}$. If one puts A and B into a vessel with initial pressures, Pinit(A) = Pinit(B) = 3. bar, determine the pressure of C at equililbrium?

NOTE**:** You may assume that very little A and B react.

6.12 Consider the equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The value of the equilibrium constant is K= 337 at 100 ^CC and $K = 7.1\text{x}10^{-5}$ at 500 ^CC

(a) Determine the enthalpy (ΔH^O) and entropy (ΔS^O) changes for this reaction.

(b) Determine the value of the equilibrium constant at 300 ^OC.

(c) At 500 ^OC, the initial pressures (before reaction to form NH_3) of N_2 and H_2 are 3.0 bar and 2.0 bar, respectively. Calculate the pressure of NH_3 at equilibrium [Note: You can make the assumption that very little NH3 is formed relative to the initial pressures of N2 and H2 to simplify your calculation].

(d) Determine the Gibbs energy change for the reaction at 500 ^OC for $P_{N2} = P_{H2} = 0.2$ bar and $P_{NH3} = 2.5$ bar

6.13 Use the Reduction Potential Table below to calculate the equilibrium constants for the following two reactions:

(a) $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2\ Sn^{2+}(aq)$

(b) $Sn(s) + 2\ AgCl(s) \rightleftharpoons SnCl_2(aq) + 2\ Ag(s)$

Reduction Reaction	E_{red}^{o}
$Sn^{4+}(aq) + 2\ e^- \rightarrow Sn^{2+}(aq)$	+0.15 V
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	-0.14 V
$2\ AgCl(s) + 2\ e^- \rightarrow 2\ Ag(s) + 2\ Cl^-(aq)$	+0.22

6.14 The solubility products of two sparingly soluble Bromide (Br^-) salts are: AgBr - Ksp = 5.4×10^{-13} , $HgBr_2$ - Ksp = 6.2×10^{-20}

Consider a solution which initially contains 5.0×10^{-5} M $Ag^+(aq)$ and 5.0×10^{-5} M $Hg^{2+}(aq)$. KBr (a strong electrolyte) is added until $[Br^-] = 2.0 \times 10^{-8}$ M. Which of the above salts (AgBr and $HgBr_2$) will precipitate?

6.15 Mercury(I) Sulfate, Hg_2SO_4 , is a sparingly soluble salt with Ksp = 6.5×10^{-7}.

If 1200 mL of 0.010 M $K_2SO_4(aq)$ is mixed with 800 mL of 0.020 M $HgNO_3(aq)$, calculate the concentrations of $[Hg^+]$ and $[SO_4^{2-}]$ in the resulting solution and **determine whether or not** $Hg_2SO_4(s)$ will precipitate.

6.16 The standard reduction potentials of $Br_2(l)$ and $Hg^{2+}(aq)$ are +1.07 V and +0.86 Volts, respectively Consider the electrochemical cell,

$Br^-(0.005\ M)|Br2(l)||Hg^{2+}(2.5\ M)|Hg(l)$.

(a) Write the balanced equation for this reaction, and indicate the number of electrons transfered.

(b) Calculate the standard cell potential, E^o_{cell}, for the reaction.

(c) Calculate the equilibrium constant for the reaction at 25 ^oC.

(d) Calculate the cell potential under the conditions shown above.

6.17 The standard reduction potentials of $Mg^{2+}(aq)$ and $Al^{3+}(aq)$ are -2.37 V and -1.66 Volts, respectively. Consider the electrochemical cell,

$Mg(s)|Mg^{2+}(1.8\ M)||Al^{3+}(0.001\ M)|Al(s)$.

(a) Write the balanced equation for this reaction, and indicate the number of electrons transfered.

(b) Calculate the standard cell potential, E^o_{cell}, for the reaction.

(c) Calculate the equilibrium constant for the reaction at 25 ^oC.

(d) Calculate the cell potential under the conditions shown above.

6.18 The EPA recommended maximum concentration of Zn^{2+} [M(Zn) = 65.4 g/mol] in drinking water is 5. mg/L. The amount of Zn in a sample of water can be determined by measuring the voltage of an electrochemical cell in which the reference electrode (cathode) has a standard concentration [say, 0.20 M Zn(NO3)2] and the sample electrode (anode) has the water sample. This cell can be designated as: $Zn(s)|Zn^{2+}(xx\ M)||Zn^{2+}(0.20\ M)|Zn(s)$.

The cell potential was measured as +0.078 V. Determine the concentration of Zn^{2+} in the sample, in mg/L.

6.19 An electrochemical cell is prepared with 0.50 M Pb(NO3)2(aq) in the reference compartment (cathode) and a saturated solution of lead iodate, Pb(IO3)2(aq), in the sample compartment (anode). The measured cell voltage is: 0.120 V.

Calculate the Solubility Product, Ksp, of Pb(IO3)2.

6.20 An electrochemical cell is prepared with 0.25 M $AgNO_3(aq)$ in the reference compartment (cathode) and a saturated solution of silver phosphate, Ag3PO4(aq), in the sample compartment (anode). The measured cell voltage is: 0.195 V.

Calculate the Solubility Product, K_{sp}, of Ag_3PO_4.

6.21 Consider the electrochemical cell reaction: $Hg_2Cl_2(aq) + H_2(g) \rightleftharpoons 2\ Hg(l) + 2\ HCl(aq)$.
The standard cell potential is temperature dependent and given by:
$E^o_{cell} = a - b/T^2$ where a = 0.313 V and b = $5.0x10^7$ V/K^2. , T is temperature in Kelvins.

For this reaction, calculate: (a) Δ_rG^o , (b) Δ_rS^o , (c) Δ_rH^o

Chapter 6

Chemical Equilibrium

Spontaneous Chemical Reactions

The Gibbs Energy Minimum

Consider the simple equilibrium reaction: $A \rightleftharpoons B$

The equilibrium concentrations (or pressures) will be at the extent of reaction at which the Gibbs function of the system will be at a minimum.

The equilibrium may lie:

(1) Close to pure A: The reaction "doesn't go"

(2) Close to pure B: The reaction "proceeds to completion"

(3) At a point where there are finite concentrations of both A and B (equilbrium)

Extent of Reaction (ξ): This parameter is a measure of how far the reaction has proceeded from reactants towards products.

$\xi = 0$: Reactants only

$\xi = 1$: Products only

The change in ξ may be related to the change in the number of moles of 'reactants and products.

For the simple reaction: A ⇌ B

$dn_A = -d\xi$ and $dn_B = +d\xi$ or $\Delta n_A = -\Delta\xi$ and $\Delta n_B = +\Delta\xi$

Let's say the stoichiometry is different; i.e. A ⇌ 2 B In this case:

$dn_A = -d\xi$ and $dn_B = +2d\xi$ or $\Delta n_A = -\Delta\xi$ and $\Delta n_B = +2\Delta\xi$

Back to: A ⇌ B

We showed in Chapter 3 that for a system with two species, the infinitesimal change, dG is given by:

$$dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B$$

For processes at constant T and p (e.g. many reactions), this reduces to:

$$dG = \mu_A dn_A + \mu_B dn_B$$

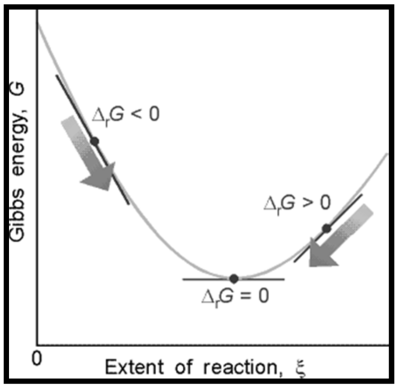
For the simple reaction: A ⇌ B $dn_A = -d\xi$ and $dn_B = +d\xi$

$$dG = \mu_A dn_A + \mu_B dn_B \longrightarrow dG = -\mu_A d\xi + \mu_B d\xi = \left(\mu_B - \mu_A\right) d\xi$$

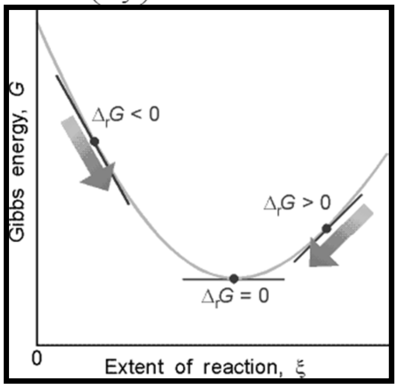
From this, one gets: $\left(\frac{\partial G}{\partial \xi}\right) = \mu_B - \mu_A = \Delta_r G$

Note: $\Delta_r G$ is a function of the mixture's composition (relative amounts of A and B)

Implications:



$$\left(\frac{\partial G}{\partial \xi}\right) = \mu_B - \mu_A = \Delta_r G$$



If: $\Delta_r G < 0$, the forward reaction is spontaneous The reaction is **exergonic**

$\Delta_r G > 0$, the reverse reaction is spontaneous The reaction is **endergonic**

$\Delta_r G = 0$, the reaction is at equilibrium

The Description of Equilibrium

Let's first reconsider the simple equilibrium, A ⇌ B , and assume that A and B are both Perfect Gases.

We learned in Chapter 5 that for a mixture of Perfect Gases, the chemical potential of each component is given by:

$$\mu_A = \mu_A^o + RT\ln\left(p_A/p^o\right) = \mu_A^o + RT\ln p_A$$ p^o is the reference state, 1 bar

$$\mu_B = \mu_B^o + RT\ln\left(p_B/p^o\right) = \mu_B^o + RT\ln p_B$$

We then have:

$$\Delta_r G = \mu_B - \mu_A = \left(\mu_B^o + RT\ln p_B\right) - \left(\mu_A^o + RT\ln p_A\right)$$

$$\Delta_r G = \left(\mu_B^o - \mu_A^o\right) + \left(RT\ln p_B - RT\ln p_A\right) = \left(\mu_B^o - \mu_A^o\right) + RT\ln\left(\frac{p_B}{p_A}\right)$$

Therefore: $\Delta_r G = \Delta_r G^o + RT\ln Q$

where $\Delta_r G^o = \mu_B^o - \mu_A^o$ and $Q = \dfrac{p_B}{p_A}$

Therefore: $\Delta_r G = \Delta_r G^o + RT \ln Q$

where $\Delta_r G^o = \mu_B^o - \mu_A^o$ and $Q = \frac{p_B}{p_A}$

Equilibrium

At equilibrium, $\Delta_r G = 0$.

$$\Delta_r G = 0 = \Delta_r G^o + RT \ln Q_{eq} \longrightarrow \Delta_r G^o = -RT \ln Q_{eq} = -RT \ln K$$

The equilibrium constant is: $K = Q_{eq} = \left(\frac{p_B}{p_A}\right)_{eq}$

We have developed the expression, $\Delta_r G = \Delta_r G^o + RT \ln Q$ for the simplest of equilibria.

However, as we'll see, one gets the same expression for more complex equilibria.

The General Case

Here, we will: (1) Use activities, rather than pressures
(2) Consider a more general reaction

$$aA + bB \rightarrow cC + dD$$

$$\mu_A = \mu_A{}^o + RT\bullet\ln(a_A) \qquad \mu_C = \mu_C{}^o + RT\bullet\ln(a_C)$$

$$\mu_B = \mu_B{}^o + RT\bullet\ln(a_B) \qquad \mu_D = \mu_D{}^o + RT\bullet\ln(a_D)$$

$$\Delta_r G = \{c\mu_C + d\mu_D\} - \{a\mu_A + b\mu_B\}$$

It can be shown that:

$$\boxed{\begin{gathered}\Delta_r G = \Delta_r G^o + RT\bullet\ln(Q) \\ \Delta_r G^o = \{c\mu_C{}^o + d\mu_D{}^o\} - \{a\mu_A{}^o + b\mu_B{}^o\} \\ Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}\end{gathered}}$$

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r G = \Delta_r G^o + RT \bullet \ln(Q) \qquad Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Standard Gibbs Energy Change ($\Delta_r G^o$)

$$\Delta_r G^o = \{c\mu_C^o + d\mu_D^o\} - \{a\mu_A^o + b\mu_B^o\}$$

$\Delta_r G^o$ is the Gibbs Energy change when reactants and products are in the standard state.

$$aA + bB \rightarrow cC + dD$$

Gas Phase: 1 bar 1 bar 1 bar 1 bar

Solution: 1 M 1 M 1 M 1 M

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b} = 1$$ in the standard state

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$$aA + bB \rightarrow cC + dD$$

$$\Delta_r G = \Delta_r G^o + RT \bullet \ln(Q)$$

Reaction Quotient (Q)

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Gas Phase

$$Q = \frac{\left(\frac{P_C}{P^o}\right)^c \left(\frac{P_D}{P^o}\right)^d}{\left(\frac{P_A}{P^o}\right)^a \left(\frac{P_B}{P^o}\right)^b} = \frac{P_C^c\, P_D^d}{P_A^a\, P_B^b}$$

Ref. State: $P^o = 1$ bar

Solution

$$Q = \frac{\left(\frac{[C]}{c_o}\right)^c \left(\frac{[D]}{c_o}\right)^d}{\left(\frac{[A]}{c_o}\right)^a \left(\frac{[B]}{c_o}\right)^b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Ref. State: $c_o = 1$ M

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r G = \Delta_r G^o + RT \bullet \ln(Q)$$

Reaction Quotient (Q)

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Standard State:	All a_J=1	$Q = 1$	$\Delta_r G = \Delta_r G^o$
Reactants Only:	$a_C = 0$ $a_D = 0$	$Q = 0$	$\Delta_r G = -\infty$
Products Only:	$a_A = 0$ $a_B = 0$	$Q = +\infty$	$\Delta_r G = +\infty$

$aA + bB \rightarrow cC + dD$ $\quad \Delta_r G = \Delta_r G^o + RT \bullet \ln(Q)$ $\quad Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$

General Notation

Reaction: $0 = \sum_J \nu_j J$

J is a chemical component (rct. or prod.)
ν_j is the stoichiometric coefficient
$\nu_j < 0$ for reactant
$\nu_j > 0$ for product

Gibbs Energy: $\Delta_r G = \sum_j \nu_j \mu_j = \Delta_r G^o + RT \sum_j \nu_j \ln a_j = \Delta_r G^o + RT \ln\left(\prod_j a_j^{\nu_j}\right)$

$\Delta_r G = \Delta_r G^o + RT \ln Q$ where $Q = \prod_j a_j^{\nu_j}$

Equilibrium: $\Delta_r G^o = -RT \ln Q_{eq} = -RT \ln K$ where $K = \left(\prod_j a_j^{\nu_j}\right)_{eq}$

FYI Only: You might see this notation in research or other courses.

An Illustrative Example

Consider: A(g) → B(g) + C(g) $\Delta_r G = \Delta_r G^o + RT \bullet \ln(Q)$ $Q = \frac{p_B p_C}{p_A}$

T = 298 K $\Delta_r G^o = +4430$ J

Calculation of K

$$\Delta_r G^o = -RT \ln Q_{eq} = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^o}{RT} = -\frac{+4430\,J}{(8.31\,J/mol \cdot K)(298\,K)} = -1.79$$

$$K = e^{-1.79} = 0.167 = \left(\frac{p_B p_C}{p_A}\right)_{eq}$$

Δ_rG under various conditions

$\Delta_r G = \Delta_r G^o + RT \bullet \ln(Q)$ $Q = \frac{p_B p_C}{p_A}$ $K = e^{-1.79} = 0.167 = \left(\frac{p_B p_C}{p_A}\right)_{eq}$

Standard State:	P_A=1 bar P_B=P_C=1 bar	Q = 1	$\Delta_r G = \Delta_r G^o = +4430$ J Reaction proceeds to Left
Reactant Only:	P_A=2 bar P_B=P_C=0	Q = 0	$\Delta_r G = -\infty$ Reaction proceeds to Right
Products Only:	P_A= 0 P_B=P_C=2 bar	Q = +∞	$\Delta_r G = +\infty$ Reaction proceeds to Left
Reactants and Products:	P_A=1.5 bar P_B=P_C=0.5 bar	Q = 0.167	$\Delta_r G = 0$ Reaction at Equilibrium

Some Equilibrium Calculation Examples

$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$

(a) The Gibbs Energies of formation of NO_2 and N_2O_4 are 51.3 kJ/mol and 97.9 kJ/mol, respectively. Calculate the equilibrium constant, K, at 25 ^oC

$\Delta G^o = -4.7\ kJ = -4700\ J \rightarrow K = 6.7$

(b) If the initial pressures of NO_2 and N_2O_4 are both 10^4 Pa (= 0.1 bar), calculate the direction of spontaneity under these conditions.

$\Delta G = -4700\ J + 5700\ J = +1000\ J$: Spontaneous to Left

(c) Calculate the pressures of NO_2 and N_2O_4 at equilibrium.

$26.8x^2 + 3.68x - 0.033 = 0$
x = 0.00845
$p(NO_2) = 0.1169$ p(N2O4) = 0.09155
Check: K = 6.70

Some Equilibrium Calculation Examples

$H_2O(g) \rightleftharpoons H_2(g) + (1/2)\ O_2(g)$

(a) ΔG^o for the dissociation of water vapor at 2300 K is +118.1 kJ/mol
Calculate K for this reaction.

$K = 2.07x10^{-3}$

(b) The fraction dissociation, α, is defined as the fraction of molecules which which have dissociated at equilibrium; i.e. $\alpha = 1 - n_{eq}/n$, where n is the initial amount of reactant prior to dissociation, and n_{eq} is the amount of reactant present at equilibrium.

Calculate α for H_2O gas at equilibrium at 2300 k and a total pressure of 1 bar. You may assume that $\alpha << 1$.

Some Equilibrium Calculation Examples

$H_2O(g) \rightleftharpoons H_2(g) + (1/2)\ O_2(g)$ K = 2.07x10-3

(b) The fraction dissociation, α, is defined as the fraction of molecules which have dissociated at equilibrium; i.e. $\alpha = 1 - n_{eq}/n$, where n is the initial amount of reactant prior to dissociation, and n_{eq} is the amount of reactant present at equilibrium.

Calculate α for H_2O gas at equilibrium at 2300 k and a total pressure of 1 bar. You may assume that α << 1.

Strategy:
1. Express number of moles of reactants and products in terms of α.
2. Determine mole fraction of each component.
3. Use Dalton's law to determine partial pressures of the components.
4. Calculate α from the equilibrium expression.

$\alpha = 0.0205 \approx 0.021$

Some Equilibrium Calculation Examples

$A(g) \rightleftharpoons 2\ B(g)$

The equilibrium constant for the gas phase dissociation above is:
K = 2.0

If one introduces pure A(g) into a vessel, calculate the fraction dissociation, α, and the partial pressures of A(g) and B(g) at a total pressure of 5. bar. Note: You may NOT assume that α << 1.

Strategy:
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Some Equilibrium Calculation Examples

$A(g) \rightleftharpoons 2\,B(g)$

The equilibrium constant for the gas phase dissociation above is:
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If one introduces pure A(g) into a vessel, calculate the fraction dissociation, α, and the partial pressures of A(g) and B(g) at a total pressure of 5. bar. Note: You may NOT assume that α << 1.

$$K = \frac{4\alpha^2}{1-\alpha^2}p$$

$$\alpha = \sqrt{\frac{K}{K+4p}} = \sqrt{\frac{2.0}{2.0+4\cdot 5.0}} = 0.302$$

$$p(A) = \frac{1-\alpha}{1+\alpha}p = 2.68\,bar$$

$$p(B) = \frac{2\alpha}{1+\alpha}p = 2.32\,bar$$

Some Equilibrium Calculation Examples

$A(g) \rightleftharpoons B(g) + C(g)$

HOMEWORK: The equilibrium constant for the gas phase dissociation above is: K = 2.0

If one introduces pure A(g) into a vessel, calculate the fraction dissociation, α, and the partial pressures of A(g), B(g) and C(g) at a total pressure of 5. bar. Note: You may NOT assume that α << 1.

$$K = \frac{\alpha^2}{1-\alpha^2}p$$

$$\alpha = \sqrt{\frac{K}{K+p}} = \sqrt{\frac{2.0}{2.0+5.0}} = 0.535$$

$$p(A) = \frac{1-\alpha}{1+\alpha}p = 1.52\,bar$$

$$p(B) = p(C) = \frac{\alpha}{1+\alpha}p = 1.74\,bar$$

Some Equilibrium Calculation Examples

Example: (Similar to HW #6.7) Consider the gas phase equilibrium:

$$\mathbf{A(g) + 3\,B(g) \rightleftharpoons C(g) + 2\,D(g)}$$

For the above gas phase reaction at 25 ^{o}C, it is found that if one mixes 1.0 mol A, 4.0 mol B and 3.0 mol D in a vessel, and the reaction is allowed to come to equilibrium, the mixture contains 0.60 mol C at a total pressure of 2.0 bar.

Calculate the following quantities for this equilibrium:

(A) the mole fraction of each species

n(A) = 0.40 mol x(A) = 0.054
n(B) = 2.20 mol x(B) = 0.297
n(C) = 0.60 mol x(C) = 0.081
n(D) = 4.20 mol x(D) = 0.568

n(tot) = 7.40 mol

Some Equilibrium Calculation Examples

Example: (Similar to Text Exer. 6.8a). Consider the gas phase equilibrium:

$$\mathbf{A(g) + 3\,B(g) \rightleftharpoons C(g) + 2\,D(g)}$$

For the above gas phase reaction at 25 ^{o}C, it is found that if one mixes 1.0 mol A, 4.0 mol B and 3.0 mol D in a vessel, and the reaction is allowed to come to equilibrium, the mixture contains 0.60 mol C at a total pressure of 2.0 bar.

Calculate the following quantities for this equilibrium:

(B) the equilibrium constant, K

x(A) = 0.054 p(A) = x(A) p = 0.108 bar
x(B) = 0.297 p(B) = x(B) p = 0.594 bar
x(C) = 0.081 p(C) = x(C) p = 0.162 bar
x(D) = 0.568 p(D) = x(D) p = 1.136 bar

$$K = \frac{p_C p_D^2}{p_A p_B^3} = \frac{(0.162)(1.136)^2}{(0.108)(0.594)^3} = 9.24$$

Some Equilibrium Calculation Examples

Example: (Similar to Text Exer. 6.8a). Consider the gas phase equilibrium:

$$A(g) + 3\,B(g) \rightleftharpoons C(g) + 2\,D(g)$$

For the above gas phase reaction at 25 °C, it is found that if one mixes 1.0 mol A, 4.0 mol B and 3.0 mol D in a vessel, and the reaction is allowed to come to equilibrium, the mixture contains 0.60 mol C at a total pressure of 2.0 bar.

Calculate the following quantities for this equilibrium:

(C) $\Delta_r G^o$

K = 9.24

$$\Delta_r G^o = -RT\ln K = -(8.31\,J/mol-K)(298\,K)\ln(9.24)$$
$$= -5500\,J/mol = -5.5\,kJ/mol$$

The Response of Equilibrium to Pressure

Condensed Phase Reactions: The external pressure has no effect.

Gas Phase Reactions: Upon increase in the external pressure, the equilibrium will shift in the direction of fewer moles of gas.

However, the equilibrium constant is unchanged!!

The above trend for gas phase reactions is an example of LeChatelier's Principle.

In the slides below, we will:
1. Present a quantitative treatment of the effect of pressure on amount of reactants and products.
2. Present some qualitative examples

The Response of Equilibrium to Pressure

Quantitative Treatment

Among the previous examples, we analyzed the dissociation equilibrium:

$$\mathbf{A(g) \rightleftharpoons 2\,B(g)}$$

We found that the equilibrium constant is a function of
(a) the fraction dissociation, α
(b) the total pressure, p

$$K = \frac{4\alpha^2}{1-\alpha^2}p$$

This equation was solved for α:

$$\alpha = \sqrt{\frac{K}{K+4p}}$$

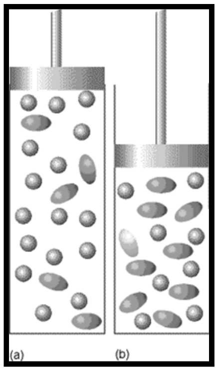
$\mathbf{A(g) \rightleftharpoons 2\,B(g)}$ $\quad K = \frac{4\alpha^2}{1-\alpha^2}p \quad$ $\alpha = \sqrt{\frac{K}{K+4p}}$

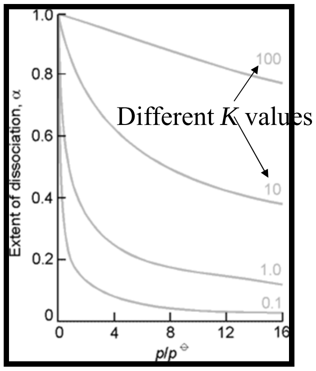
Let's apply this to the gas phase equilibrium, $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
K = 0.146 at 25 ^oC

p	**α**
0.1 bar	0.52
0.5	0.26
1.0	0.19
10.0	0.06

Notice that the equilibrium moves to the left (i.e. the fraction dissociation decreases) with an increase in the total pressure. This is consistent with LeChatelier's Principle.

$A(g) \rightleftharpoons 2\,B(g)$ $K = \frac{4\alpha^2}{1-\alpha^2}p$ $\alpha = \sqrt{\frac{K}{K+4p}}$





The graph above shows that the same trend holds for different values of the equilibrium constant, K.

The Response of Equilibrium to Pressure

Qualitative Examples

Consider the equilibrium: $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$

What happens to the equilibrium when:

(a) The volume is decreased:

The equlibrium is shifted to the right

(b) $NO_2(g)$ is added at constant volume:

There is no effect on the equilibrium

(c) $NO_2(g)$ is added at constant total pressure:

The equlibrium is shifted to the left

Note: In all cases, the equilibrium constant, K, is unchanged

The Response of Equilibrium to Pressure

Qualitative Examples

Consider the equilibrium: $H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$

What happens to the equilibrium when:

(a) The volume is decreased:

There is no effect on the equilibrum

(b) $Cl_2(g)$ is added at constant volume:

There is no effect on the equilibrium

(c) $Cl_2(g)$ is added at constant total pressure:

There is no effect on the equilibrium

Note: In all cases, the equilibrium constant, K, is unchanged

The Response of Equilibrium to Pressure

Qualitative Examples

Consider the equilibrium: $H_2(g) + I_2(s) \rightarrow 2\ HI(g)$

What happens to the equilibrium when:

(a) The volume is decreased:

The equilibrium is shifted to the left

(b) $Cl_2(g)$ is added at constant volume:

There is no effect on the equilibrium

(c) $Cl_2(g)$ is added at constant total pressure:

The equilibrium is shifted to the right

Note: In all cases, the equilibrium constant, K, is unchanged

The Response of Equilibrium to Temperature

Qualitative Considerations

Le Chatelier's Principle

The equilibrium constant, K, and hence the ratio of products to reactants, shifts in the ***endothermic*** direction as the as the temperature is increased

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta_r H^o = +57.2$ kJ

With rising temperature, K increases and the ratio of NO_2 to N_2O_4 increases; i.e. equilibrium shifts towards right.

$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta_r H^o = -92.0$ kJ

With rising temperature, K decreases and the ratio of NH_3 to N_2/H_2 decreases; i.e. equilibrium shifts towards left.

The Response of Equilibrium to Temperature

Quantitative Treatment: The van't Hoff Equation

In Chapter 3, when discussing the effect of temperature on the Gibbs Energy, we derived the formula:

$$\frac{d\left(\Delta_r G^o/T\right)}{dT} = -\frac{\Delta_r H^o}{T^2}$$ Gibbs Helmholtz Equation

We also have: $\Delta_r G^o = -RT\ln K$

Therefore: $$\frac{d\left(\left[-RT\ln K\right]/T\right)}{dT} = -\frac{\Delta_r H^o}{T^2}$$

Which yields: $$\boxed{\frac{d(\ln K)}{dT} = \frac{\Delta_r H^o}{RT^2}}$$

van't Hoff Equation

$$\frac{d(\ln K)}{dT} = \frac{\Delta_r H^o}{RT^2}$$

Alternate form of the van't Hoff Equation

Consider that: $\frac{d(1/T)}{dT} = \frac{d(T^{-1})}{dT} = -1 \cdot T^{-2} = \frac{-1}{T^2}$

Now: $\frac{d(\ln K)}{dT} = \frac{\Delta_r H^o}{RT^2} = \frac{d(\ln K)}{d(1/T)} \cdot \frac{d(1/T)}{dT} = -\frac{1}{T^2}\frac{d(\ln K)}{d(1/T)}$

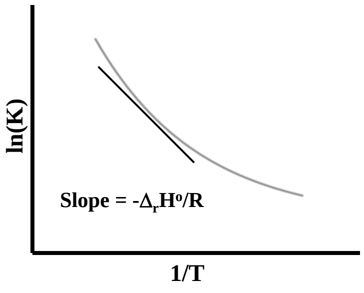
Therefore: $\frac{d(\ln K)}{d(1/T)} = -T^2 \cdot \frac{\Delta_r H^o}{RT^2}$

or: $\frac{d(\ln K)}{d(1/T)} = -\frac{\Delta_r H^o}{R}$

Alternate form

$$\frac{d(\ln K)}{dT} = \frac{\Delta_r H^o}{RT^2} \qquad \frac{d(\ln K)}{d(1/T)} = -\frac{\Delta_r H^o}{R}$$

The second form of the van't Hoff equation illustrates that if one plots ln(K) vs. 1/T, the tangent at a given point can be used to calculate $\Delta_r H^o$ at that temperature.



Application: Calculation of K at a second temperature

For a given reaction, A → B, the equilibrium constant is 0.05 at 25 °C. $\Delta_r H^o$ for the reaction is given by:

$\Delta_r H^\circ = a + b / T$ a = 125 kJ/mol and b = 2x10^4 kJ-K/mol

Calculate the value of the equilibrium constant at 75 °C

K = 2600 at 75 °C

HOMEWORK

For a given reaction, C → D, the equilibrium constant is 200. at 25 °C. $\Delta_r H^o$ for the reaction is given by:

$\Delta_r H^\circ = a + bT$ a = -80 kJ/mol and b = 0.12 kJ/mol-K

Calculate the value of the equilibrium constant at 75 °C

K = 18 at 75 °C

Integrated van't Hoff Equation with constant $\Delta_r H^o$

$$\frac{d(\ln K)}{dT} = \frac{\Delta_r H^o}{RT^2} \longrightarrow \int d\ln K = \int \frac{\Delta_r H^o}{RT^2} dT = \frac{\Delta_r H}{R} \int \frac{1}{T^2} dT$$

This integrates to: $\ln K = -\frac{\Delta_r H^o}{RT} + C$

Identification of the Integration Constant, C

$$\Delta_r G^o = -RT \ln K = \Delta_r H^o - T\Delta_r S^o$$

$$\ln K = \frac{\Delta_r H^o - T\Delta_r S^o}{-RT} = -\frac{\Delta_r H^o}{RT} + \frac{\Delta_r S}{R}$$

In a plot of lnK vs. 1/T, (a) the slope is $-\Delta_r H/R$
(b) the intercept is $+\Delta_r S/R$

$$\ln K = -\frac{\Delta_r H^o}{RT} + \frac{\Delta_r S}{R}$$

If one measures the equilibrium constant at two temperatures, K_1 at T_1 and K_2 at T_2 , the data can be used to determine $\Delta_r H$ and $\Delta_r S$

$$\ln K_2 = -\frac{\Delta_r H^o}{RT_2} + \frac{\Delta_r S}{R} \quad \text{and} \quad \ln K_1 = -\frac{\Delta_r H^o}{RT_1} + \frac{\Delta_r S}{R}$$

Subtraction of the second equation from the first equation (to eliminate $\Delta_r S$) yields:

$$\ln\left(K_2/K_1\right) = -\frac{\Delta_r H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation can be used to determine $\Delta_r H$ and then either of the first two equations can be used to calculate $\Delta_r S$.

Application: The Dissociation of $N_2O_4(g)$

For the equilibrium reaction, $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$, the equilibrium constant is 0.0176 at 0 °C and 15.05 at 100 °C.

(a) Calculate Δ_rH and Δ_rS for this reaction.

$\Delta_rH = +57.1$ kJ/mol

$\Delta_rS = +\ 176$ J/mol-K

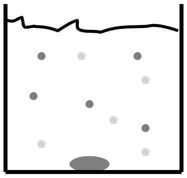
(b) Calculate the equilibrium constant at 25 °C

K = 0.146

(c) Calculate the temperature, in °C, at which the equilibrium constant is K = 100.

T = 143 °C

Solubility Product and Selective Precipitation



When an insoluble (actually “sparingly” soluble) salt is placed in water, a small amount dissolves.

Solubility (S) [aka Molar Solubility]

S is the number of moles of salt which will dissolve in 1 Liter of solution.

Solubility Product (K_{sp})

$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$ $AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^-(aq)$

$K_{sp} = [A^+][B^-]$ $K_{sp} = [A^{2+}][B^-]^2$

Note that these are like any equilibrium involving a pure solid:
The concentration of the solid is not included in the equilibrium expression.

Some Examples

(A) $Fe(OH)_2$ $K_{sp} = [Fe^{2+}][OH^-]^2$

(B) $AuBr_3$ $K_{sp} = [Au^{3+}][Br^-]^3$

(C) Ag_3PO_4 $K_{sp} = [Ag^+]^3[PO_4^{3-}]$

The General Case

$$A_mB_n(s) \underset{}{\overset{K_{sp}}{\rightleftarrows}} mA^{n+}(aq) + nB^{m-}(aq)$$

$$K_{sp} = \left[A^{n+}\right]^m \left[B^{m-}\right]^n$$

Precipitation: Will it Occur?

We can decide whether or not ions will precipitate to the solid by comparing the magnitude of the Ion Product**, Q, to the Solubility Product, K_{sp} .

$$A_mB_n(s) \overset{K_{sp}}{\rightleftarrows} mA^{n+}(aq) + nB^{m-}(aq) \qquad K_{sp} = \left[A^{n+}\right]^m \left[B^{m-}\right]^n$$

If $Q < K_{sp}$: No solid will precipitate

If $Q > K_{sp}$: Some of the salt ions will precipitate to form the solid

If $Q = K_{sp}$: We have an equilibrium between the solid and the ions in solution

The Ion Product is closely analogous to the Reaction Quotient used earlier in the Chapter, recognizing that the “concentration” of the solid does not appear in the expression for Q.

Let's consider the solubility of AgCl(s) in water:

$$AgCl(s) \xrightleftharpoons{K_{sp}} Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.8x10^{-10} = \left[Ag^+\right]\left[Cl^-\right]$$

If we mix two solutions, one of which contains Ag^+(aq) and the other contains Cl^-(aq), we would like to know whether or not any AgCl(s) precipitates from the final solution.

Example: If 25.0 mL of 0.0025 M HCl are mixed with 10.0 mL of 0.010 M $AgNO_3$, will AgCl(s) precipitate? $K_{sp} = 1.8x10^{-10}$.

1. Calculate moles of Ag^+ and Cl^-

$$n_{Cl^-} = M_{Cl^-}V_{Cl^-} = (0.0025M/L)\cdot(0.025L) = 6.25x10^{-5}\text{ mol}$$

$$n_{Ag^+} = M_{Ag^+}V_{Ag^+} = (0.010M/L)\cdot(0.010L) = 1.0x10^{-4}\text{ mol}$$

Example: If 25.0 mL of 0.0025 M HCl are mixed with 10.0 mL of 0.010 M $AgNO_3$, will AgCl(s) precipitate? $K_{sp} = 1.8x10^{-10}$.

2. Calculate concentrations, $[Ag^+]$ and $[Cl^-]$

$$V = 0.025L + 0.010L = 0.035L \qquad [Cl^-] = \frac{n_{Cl^-}}{V} = \frac{6.25x10^{-5}\text{ mol}}{0.035L} = 1.79x10^{-3}\text{ mol/L}$$

$$[Ag^+] = \frac{n_{Ag^+}}{V} = \frac{1.0x10^{-4}\text{ mol}}{0.035L} = 2.86x10^{-3}\text{ mol/L}$$

3. Determine Q and compare to K_{sp}

$$Q = [Ag^+][Cl^-] = (1.79x10^{-3})(2.86x10^{-3}) = 5.1x10^{-6}$$

Because $Q > K_{sp}$, some AgCl(s) will precipitate

Selective Precipitation

Consider two salts dissolved in solution.

If they share a common cation or anion and their solubilities are sufficiently different, the the less soluble salt can be selectively precipitated by adding a strong electrolye with the common ion.

Two examples are:

1. CuCl(aq): $K_{sp} = 1.9\text{x}10^{-7}$
   PbCl$_2$(aq): $K_{sp} = 1.7\text{x}10^{-5}$

   Either CuCl(s) or PbCl$_2$(s) or both can be precipitated by the addition of a strong electrolyte such as NaCl.

2. AgCl(aq): $K_{sp} = 1.8\text{x}10^{-10}$
   Ag$_2$CrO$_4$(aq): $K_{sp} = 9.0\text{x}10^{-12}$

   Either AgCl(s) or Ag$_2$CrO$_4$(s) or both can be precipitated by the addition of a strong electrolyte such as AgNO$_3$.

---

2. AgCl(aq): $K_{sp} = 1.8\text{x}10^{-10}$
   Ag$_2$CrO$_4$(aq): $K_{sp} = 9.0\text{x}10^{-12}$

   Either AgCl(s) or Ag$_2$CrO$_4$(s) or both can be precipitated by the addition of a strong electrolyte such as AgNO$_3$.

Consider a solution containing 0.02 M Cl$^-$(aq)* and 0.01 M CrO$_4$ $^{2-}$ **.

If a strong electrolyte such as AgNO$_3$ is added to the solution, which salt will precipitate out first, AgCl(s) or Ag$_2$CrO$_4$?

Strategy: Determine the Ag$^+$ concentration required to precipitate each salt.

Answer: AgCl(s) will precipitate out when $[Ag^+] > 9.0\text{x}10^{-9}$ M
Ag$_2$CrO$_4$(s) will precipitate out when $[Ag^+] > 3.0\text{x}10^{-5}$ M
Therefore, AgCl(s) will precipitate out first.

* e.g. from KCl(aq)

** e.g. from Na$_2$ CrO$_4$(aq)

Equilibrium Electrochemistry

Redox Reactions and Half-Reactions

Oxidation-Reduction (Redox) reactions are important in many areas of Chemistry. One particularly useful application is to harness spontaneous redox reactions to provide electric energy in an electrochemical cell.

Consider the reaction:

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

This can be split into:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$: Oxidation Half-Reaction

$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$: Reduction Half-Reaction

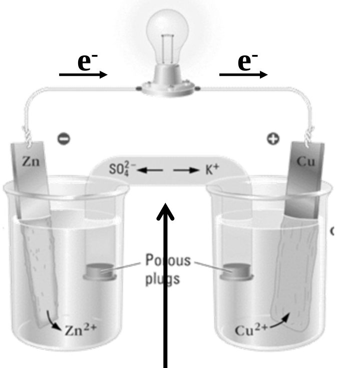
A useful pneumonic is:

OIL: Oxidation Is Loss (of electrons)

RIG: Reduction Is Gain (of electrons)

Electrochemical Cell

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



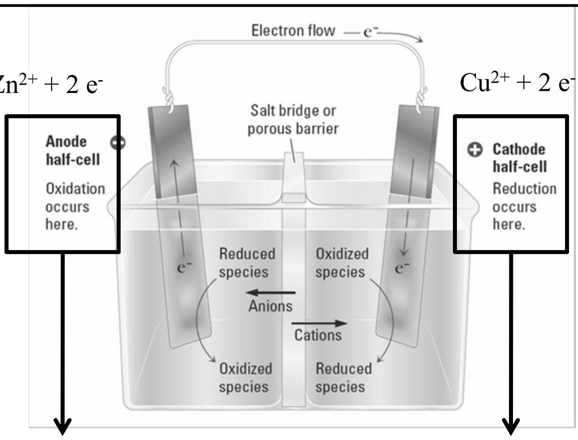
Oxidation:
$Zn \rightarrow Zn^{2+} + 2\ e^-$

Reduction:
$Cu^{2+} + 2\ e^- \rightarrow Cu$

K_2SO_4 "Salt Bridge": Flow of K^+ and SO_4^{2-} into the half-cells keeps the two halves electrically neutral.

$Zn \rightarrow Zn^{2+} + 2\ e^-$

$Cu^{2+} + 2\ e^- \rightarrow Cu$



Anode
Oxidation
Negative (-) Charge
Anions flow towards anode
Electrons leave anode

Cathode
Reduction
Positive (+) Charge
Cations flow towards cathode
Electrons enter cathode

Mneumonic:
Both A and O are vowels

Mneumonic:
Both C and R are consonants

Electrochemical Cells: Compact Notation

$$\underbrace{Zn(s)\ |\ Zn^{2+}(aq)}_{\text{anode cell}}\ ||\ \underbrace{Cu^{2+}(aq)\ |\ Cu\ (s)}_{\text{cathode cell}}$$

Current Flow

$$\longrightarrow$$

Current flows from anode to cathode.

| = phase boundary

|| = salt bridge

Details (e.g. concentration) are listed after each species.

Write the half-cell reactions and balanced redox equation for the reaction characterized by: $Cu(s)|Cu^{2+}(aq)||Fe^{3+}(aq)|Fe(s)$

Anode (Oxid): $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$

Cathode (Red): $Fe^{3+}(aq) + 3\ e^- \rightarrow Fe(s)$

Overall Rxn: $3\ Cu(s) + 2\ Fe^{3+}(aq) \rightarrow 3\ Cu^{2+}(aq) + 2\ Fe(s)$

The Cell Potential

Standard Cell Potential

The voltage of an electrochemical cell varies with the conditions (i.e. state of reactants and products, concentrations, etc.)

The cell potential has a *standard voltage* (E^o or E^o_{cell}) if:

Solute concentrations are 1 M

Gases have a pressure of 1 bar

Solids are pure

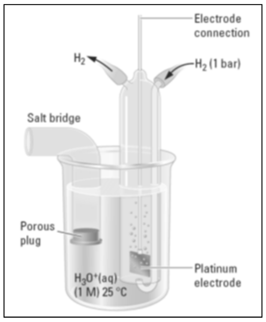
Sign of the Cell Potential (by convention)

If a reaction is Spontaneous, $E^o_{cell} > 0$

If a reaction is Non-Spontaneous, $E^o_{cell} < 0$

Note: Absolute Cell Potentials of a half-cell cannot be measured.
They are measured relative to a standard,
the **Standard Hydrogen Electrode**

Standard Hydrogen Electrode



Hydrogen gas at 1 bar, H_2 (g, 1 bar), is bubbled over a platinum electrode immersed in 1 M aqueous acid solution.

The cell potential for this half-reaction, is defined as 0 (for either oxidation or reduction).

Reduction: $2\ H_3O^+\ (aq, 1\ M) + 2\ e^- \rightarrow\ H_2(g, 1\ bar) + 2\ H_2O(l)\quad E^o(red) = 0$

Oxidation: $H_2(g, 1\ bar) + 2\ H_2O(l) \rightarrow 2\ H_3O^+\ (aq, 1\ M) + 2\ e^-\quad E^o(oxid) = 0$

The reduction potentials of other half-cell reactions can be determined with this convention, by measuring the voltage of a cell containing the standard hydrogen electrode (or indirectly)

Using the above convention, extensive tables of reduction potentials for many species have been derived. A partial list is given on the next slide.

Reduction Half-Cell Potentials (Partial List)

Easier to reduce than H_3O^+	$F_2(g) + 2\,e^-$	$\rightarrow 2\,F^-(aq)$	+2.87
	$H_2O_2(aq) + 2\,H_3O + 2\,e^-$	$\rightarrow 4\,H_2O(l)$	+1.77
	$MnO_4^-(aq) + 8\,H_3O^+ + 5\,e^-$	$\rightarrow Mn^{2+}(aq) + 12\,H_2O(l)$	+1.51
	$Cl_2(g) + 2\,e^-$	$\rightarrow 2\,Cl^-(aq)$	+1.36
	$Br_2(g) + 2\,e^-$	$\rightarrow 2\,Br^-(aq)$	+1.07
	$Ag^+(aq) + e^-$	$\rightarrow Ag(s)$	+0.80
	$Cu^{2+}(aq) + 2\,e^-$	$\rightarrow Cu(s)$	+0.34
	$2\,H_3O^+(aq) + 2\,e^-$	$\rightarrow H_2(g) + 2\,H_2O(l)$	0.00
Harder to reduce than H_3O^+	$Ni^{2+}(aq) + 2\,e^-$	$\rightarrow Ni(s)$	-0.25
	$Fe^{2+}(aq) + 2\,e^-$	$\rightarrow Fe(s)$	-0.44
	$Zn^{2+}(aq) + 2\,e^-$	$\rightarrow Zn(s)$	-0.76
	$Al^{3+}(aq) + 3\,e^-$	$\rightarrow Al(s)$	-1.66
	$Li^+(aq) + e^-$	$\rightarrow Li(s)$	-3.05

Using Standard Reduction Potentials

Consider the reaction: $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$ (I am leaving out the "aq" and "s" for convenience)

The two half-cell reactions are:

Reduction (Cathode): $Cu^{2+} + 2\,e^- \rightarrow Cu$ $E^o_{Red}(Cu^{2+}) = +0.34$ V

Oxidation (Anode): $Zn \rightarrow Zn^{2+} + 2\,e^-$ $E^o_{Oxid}(Zn) = -E^o_{Red}(Zn^{2+}) = +0.76$ V

Therefore, the overall cell potential is:

$E^o_{cell} = E^o_{Red}(Cu^{2+}) + E^o_{Oxid}(Zn) = +0.34 + 0.76 = +1.10$ V

Equivalently, one could write:

$E^o_{cell} = E^o_{Red}(Cu^{2+}) - E^o_{Red}(Zn^{2+}) = +0.34 - (-0.76) = +1.10$ V

Because $E^o_{cell} > 0$, this reaction is spontaneous.

The two half-cell reactions are:

Reduction (Cathode): $Cu^{2+} + 2\ e^- \rightarrow Cu$ $E^o_{Red}(Cu^{2+}) = +0.34$ V

Oxidation (Anode): $Zn \rightarrow Zn^{2+} + 2\ e^-$ $E^o_{Oxid}(Zn) = -E^o_{Red}(Zn^{2+}) = +0.76$ V

Therefore, the overall cell potential is:

$E^o_{cell} = E^o_{Red}(Cu^{2+}) + E^o_{Oxid}(Zn) = +0.34 + 0.76 = +1.10$ V

Equivalently, one could write:

$E^o_{cell} = E^o_{Red}(Cu^{2+}) - E^o_{Red}(Zn^{2+}) = +0.34 - (-0.76) = +1.10$ V

In general, one can calculate E^o_{cell} as either:

$E^o_{cell} = E^o_{Red}(\text{Cathode}) + E^o_{Oxid}(\text{Anode})$ or

$E^o_{cell} = E^o_{Red}(\text{Cathode}) - E^o_{Red}(\text{Anode})$

Review Example

The standard reduction potentials of Sn^{2+} and Al^{3+} are -0.14 V and -1.66 V, respectively.

Write the balanced redox equation and determine the cell potential for the reaction, $Al(s)|Al^{3+}(aq)||Sn^{2+}(aq)|Sn(s)$

$2\ Al(s) + 3\ Sn^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Sn(s)$

$E^o_{cell} = +1.52$ V

How many electrons are transfered in this reaction?

6 electrons

Note that even though the Al half-reaction was multiplied by 2 and the Sn^{2+} reaction was multiplied by 3, the cell potentials were NOT multiplied by any factor.

The Nernst Equation

It can be shown that the Gibbs Energy change, $\Delta_r G$, for a reaction is related to the cell potential, E_{cell}, by the equation:

$$\Delta_r G = -nFE_{cell}$$

n is the number of electrons transfered in the reaction.*

* The text uses the symbol, ν, to represent the number of transfered electrons.

F is Faraday's Constant.

This is the charge, in Coulombs (C) of one mole of electrons.

$F = 96{,}485$ C/mol ≈ 96,500 C/mol

We learned earlier in this chapter that the Gibbs Energy change for a reaction depends upon the reactant and product concentrations (or pressures for gases) and can be determined from the equation:

$$\Delta_r G = \Delta_r G^o + RT\ln(Q)$$

$\Delta_r G^o$ is the Standard Gibbs Energy change (concentrations = 1 M), and
Q is the reaction quotient.

It is straightforward to use the above equation, with the relations $\Delta_r G = -nFE_{cell}$ and $\Delta_r G^o = -nFE^o_{cell}$ to derive the following relationship between cell potential and concentrations:

$$-nFE_{cell} = -nFE^o_{cell} + RT\ln(Q)$$

which yields: $$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln(Q)}$$

Nernst Equation

$$\boxed{E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\ln(Q)}$$

Nernst Equation

Alternate Form

In classical Analytical texts, it is common to rewrite the Nernst Equation at the specific temperature of 25 ^{o}C (=298.15 K) in terms of base 10 logarithms [ln(x) = 2.303 log(x)]. In this case, the equation is commonly written:

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log(Q)$$

I'll use the more general form (which allows for variable temperature).

Example

The standard reduction potentials of Al^{3+} and Zn^{2+} are -1.66 V and -0.76 V, respectively.

Consider the electrochemical cell, Al(s)|Al^{3+}(5.0 M)||Zn^{2+} (0.02 M)|Zn(s)

(A) Write the oxidation and reduction half-reactions + the balanced overall reaction.

Oxidation: $Al(s) \rightarrow Al^{3+}(5.0\ M) + 3\ e^-$

Reduction: $Zn^{2+}(0.02\ M) + 2\ e^- \rightarrow Zn(s)$

Overall: $3\ Zn^{2+}(0.02\ M) + 2\ Al(s) \rightarrow 3\ Zn(s) + 2\ Al^{3+}(5.0\ M)$

(B) Determine the Standard Cell Potential, E^{o}_{cell}.

$$E^{o}_{cell} = E^{o}_{oxid}(Al) + E^{o}_{red}(Zn^{2+}) = +1.66 + (-0.76) = +0.90\,V$$

Example

The standard reduction potentials of Al^{3+} and Zn^{2+} are -1.66 V and -0.76 V, respectively.

Consider the electrochemical cell, $Al(s)|Al^{3+}(5.0\ M)||Zn^{2+}\ (0.02\ M)|Zn(s)$

Overall: $3\ Zn^{2+}(0.02\ M) + 2\ Al(s) \rightarrow 3\ Zn(s) + 2\ Al^{3+}(5.0\ M)$

(C) Determine the Cell Potential at 25 °C under the given conditions

$$Q = \frac{[Al^{3+}]^2}{[Zn^{2+}]^3} = \frac{(5.0)^2}{(0.02)^3} = 3.13x10^6$$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln(Q)$$

$$= +0.90V - \frac{(8.31C\cdot V/mol\cdot K)(298K)}{(6)(96,500C/mol)}\ln(3.13x10^6)$$

$$= +0.90V - 0.064V \approx 0.84V$$

$E^o_{cell} = 0.90$ V

R = 8.31 J/mol-K

= 8.31 C-V/mol-K

T = 298 K

F = 96,500 C/mol

Note: You get the same answer if you use the alternate form of the Nernst Equation:

Concentration Cells

One can have the same species being oxidized and reduced in the two half-cells, and there will be a voltage if the concentrations differ.

Consider: $Zn(s)|Zn^{2+}(0.01\ M)||Zn^{2+}(1.0\ M)|Zn(s)$

The half-cell reactions are:

Oxidation (Anode): $Zn(s) \rightarrow Zn^{2+}(0.01\ M) + 2\ e^-$

Reduction (Cathode): $Zn^{2+}(1.0\ M) + 2\ e^- \rightarrow Zn(s)$

The net reaction is: $Zn^{2+}(1.0\ M) \rightarrow Zn^{2+}(0.01\ M)$

The standard voltage, $E^o_{cell} = 0$. However, there will be a voltage given by:

$$E_{cell} = E^o_{cell} - \frac{0.0592\ V}{2}\log\left(\frac{[0.01M]}{[1.0M]}\right) = 0 - (-0.0592V) \approx +0.06V$$

Applications of Concentration Cells: pH Measurement

Because the cell potential depends upon the solute concentration, in principle, one can determine the [H^+] concentration in a cell by the use of $H_2|H^+$ half-cells.

Consider the concentration cell: $H_2(g)|H^+(xx\ M)||H^+(1.00\ M)|H_2(g)$

sample **reference**

The net reaction in this cell is: $H^+(1.00M) \rightarrow H^+(xx\ M)$

The cell potential will be dependent upon [H^+] in the sample cell:

$$E_{cell} = 0 - \frac{0.0592\ V}{1}\log\left(\frac{[xx\ M]}{[1.0\,M]}\right)$$

For example, if the concentration in the sample is [H^+] = $1\text{x}10^{-4}$ M (pH = 4.0), the voltage would be 4 x 0.0592 = +0.237 V

pH Measurement

Consider the concentration cell: $H_2(g)|H^+(xx\ M)||H^+(1.00\ M)|H_2(g)$

sample **reference**

$$E_{cell} = 0 - \frac{0.0592\ V}{1}\log\left(\frac{[xx\ M]}{[1.0\,M]}\right)$$

As a practical matter, it is inconvenient to use $H_2|H^+$ electrodes because of the requirement to continually flow in $H_2(g)$ at a constant pressure of 1 bar.

However, commercial pH meters work on the same principle.

The voltage in a sample cell containing H^+ is measured against a standard reference electrode (built into the pH meter).

After calibration, the measured voltage is used to determine [H^+] and, thus, the solution pH

Applications of Concentration Cells: Impurity Determination

Concentration cells can be used to measure the impurity levels of toxic metals (and other species) in aqueous solution.

One example is the determination of $Cu^{2+}(aq)$ levels in drinking water.

The EPA has set an upper safe limit of Cu^{2+} as 1.3 mg/L in water.
At higher levels, copper can be toxic, and has been linked to vomiting, hypotension, jaundice, gastrointestinal distress. Recently, it has also been determined that Alzheimer's patients have elevated levels of copper in their blood.

We will demonstrate how a concentration cell can be used to measure the levels of $Cu^{2+}(aq)$ in water.

One begins by preparing an electrochemical cell with a reference solution [e.g. 0.100 M $Cu(NO_3)_2$] as the cathode and the drinking water with the unknown Cu^{2+} concentration (xx M) as the anode.

$$Cu(s)|Cu^{2+}(xx\ M)||Cu^{2+}(0.100\ M)|Cu(s)$$

sample **reference**

$$Cu(s)|Cu^{2+}(xx\ M)||Cu^{2+}(0.100\ M)|Cu(s)$$

sample **reference**

The chemical reaction is: $Cu^{2+}(0.100\ M) \rightarrow Cu^{2+}(xx\ M)$

The measured cell potential is related to the Molarity of the impurity by:

$$E_{cell} = 0 - \frac{0.0592\ V}{n}\log\left(\frac{[xx\ M]}{[0.100\,M]}\right) = -\frac{0.0592\ V}{2}\log\left(\frac{[xx\ M]}{[0.100\,M]}\right)$$

The electrochemical cell potential of a water sample of unknown Cu^{2+} potential was measured relative to that of a standard 0.100 M $Cu(NO_3)_2$ solution, and was found to be: $E_{cell} = +0.082$ V

M(Cu) = 63.5 g/mol

What is the Cu^{2+} concentration in the water sample, in mg/L?

Cu(s)|Cu^{2+}(xx M)||Cu^{2+}(0.100 M)|Cu(s)

sample **reference**

1. Calculate Cu^{2+} Molarity (i.e. xx)

$$0.082 = -\frac{0.0592\ V}{2}\log\left(\frac{[xx\ M]}{[0.100\,M]}\right)$$

$$\log\left(\frac{[xx\ M]}{[0.100\,M]}\right) = \left(-\frac{2}{0.0592}\right)\cdot 0.082 = -2.77$$

$$\frac{[xx\ M]}{[0.100\,M]} = 10^{-2.77} = 0.00170 \longrightarrow \left[Cu^{2+}\right] = xx = (0.00170)\cdot(0.10) = 1.70x10^{-4}\ M$$

2. Convert to mg/L

$$1.70x10^{-4}\ mol\ /\ L\cdot\frac{63.5\ g}{1mol} = 0.0108\ g\ /\ L\cdot\frac{1mg}{10^{-3}\ g} = 10.8\ mg\ /\ L$$

Note that the Cu^{2+}(aq) level in the water sample is significantly above the safety limit of 1.3 mg/L set by the EPA.

Applications of Concentration Cells: Solubility Equilibria

Earlier in this chapter, we discussed solubility equilibria and Solubility Products (K_{sp}).

A very effective method for experimentally determining the Solubility Product for a sparingly soluble salt is through the application of concentration cells.

As an example, consider the dissociation equilibrium of Silver Sulfite:

$$Ag_2SO_3(s) \overset{K_{sp}}{\rightleftharpoons} 2\,Ag^{+}(aq) + SO_3^{2-}(aq) \quad K_{sp} = \left[Ag^{+}\right]^2\left[SO_3^{2-}\right]$$

As shall be demonstrated, if one determines the Ag^+ concentration in a saturated solution of Ag_2SO_3 by comparing the voltage to a reference sample (e.g. $AgNO_3$) of known concentration, then it is straightforward to determine K_{sp}.

Consider an electrochemical cell, in which a reference solution of 0.20 M $AgNO_3$(aq)is placed in the cathode compartment, and a saturated solution of Ag_2SO_3(aq) is placed in the anode compartment.
The cell is designated as:

$Ag(s)|Ag^+(xx\ M)||Ag^+(0.20\ M)|Ag(s)$

sample **reference**

The chemical reaction is: $Ag^+(0.20\ M) \rightarrow Ag^+(xx\ M)$

The measured cell potential is related to the Molarity of the Ag^+ in the sample cell by:

$$E_{cell} = 0 - \frac{0.0592\ V}{n}\log\left(\frac{[xx\ M]}{[0.20\,M]}\right) = -\frac{0.0592\ V}{1}\log\left(\frac{[xx\ M]}{[0.20\,M]}\right)$$

The electrochemical cell potential of the saturated Ag_2SO_3(aq) relative to the 0.20 M reference solution was found to be: $E_{cell} = +0.226$ V

Calculate the solubility product, K_{sp}, of Ag_2SO_3.

$Ag(s)|Ag^+(xx\ M)||Ag^+(0.20\ M)|Ag(s)$

sample **reference**

The electrochemical cell potential of the saturated Ag_2SO_3(aq) relative to the 0.20 M reference solution was found to be: $E_{cell} = +0.226$ V

Calculate the solubility product, K_{sp}, of Ag_2SO_3.

1. Calculate Ag^+ Molarity (i.e. xx)

$$0.226 = -\frac{0.0592\ V}{1}\log\left(\frac{[xx\ M]}{[0.200\,M]}\right)$$

$$\log\left(\frac{[xx\ M]}{[0.200\,M]}\right) = \left(-\frac{1}{0.0592}\right)\cdot 0.226 = -3.82$$

$$\frac{[xx\ M]}{[0.200\,M]} = 10^{-3.82} = 1.52x10^{-4}\ M$$

$$\left[Ag^+\right] = xx = \left(1.52x10^{-4}\right)\cdot\left(0.20\right) = 3.04x10^{-5}\ M$$

$Ag(s)|Ag^+(xx\ M)||Ag^+(0.20\ M)|Ag(s)$

sample **reference**

The electrochemical cell potential of the saturated $Ag_2SO_3(aq)$ relative to the 0.20 M reference solution was found to be: $E_{cell} = +0.226$ V

Calculate the solubility product, K_{sp}, of Ag_2SO_3.

$$\left[Ag^+\right] = 3.04x10^{-5}\ M$$

2. Calculate s and $[SO_3^{2-}]$

$$Ag_2SO_3(s) \overset{K_{sp}}{\rightleftarrows} 2\,Ag^+(aq) + SO_3^{2-}(aq)$$

$[Ag^+] = 2s$

$[SO_3^{2-}] = s$

Therefore: $s = ½[Ag^+] = ½(3.04x10^{-5}\ M) = 1.52x10^{-5}$ M

and: $[SO_3^{2-}] = s = 1.52x10^{-5}$ M

$$\left[Ag^+\right] = 3.04x10^{-5}\ M$$

Therefore: $s = ½[Ag^+] = ½(3.04x10^{-5}\ M) = 1.52x10^{=5}$ M

and: $[SO_3^{2-}] = s = 1.52x10^{=5}$ M

3. Calculate K_{sp}

$$Ag_2SO_3(s) \overset{K_{sp}}{\rightleftarrows} 2\,Ag^+(aq) + SO_3^{2-}(aq) \qquad K_{sp} = \left[Ag^+\right]^2\left[SO_3^{2-}\right]$$

$$K_{sp} = \left[Ag^+\right]^2\left[SO_3^{2-}\right] = \left(3.04x10^{-5}\right)^2\left(1.52x10^{-5}\right) = 1.4x10^{-14}$$

Cell Potential and the Equilibrium Constant

One interesting application of electrochemical cell potentials is to calculate the equilibrium constant for a reaction.

Remember from earlier in the chapter that, at equlibrium:

$$\Delta_r G = 0 = \Delta_r G^o + RT \ln Q_{eq} \longrightarrow \Delta_r G^o = -RT \ln Q_{eq} = -RT \ln K$$

Because the reaction Gibbs Energy change is related to the cell potential, $\Delta_r G = -nFE_{cell}$, one also has that, at equilibrium:

$$-nFE_{cell} = 0 = -nFE^o_{cell} + RT \ln Q_{eq}$$

$$E_{cell} = 0 = E^o_{cell} - \frac{RT}{nF} \ln Q_{eq} \longrightarrow E^o_{cell} = \frac{RT}{nF} \ln Q_{eq} = \frac{RT}{nF} \ln K$$

Example

The standard reduction potentials of Fe^{2+} and Cd^{2+} are -0.44 V and -0.40 V, respectively.

Determine the equilibrium constant, at 25 °C for the reaction:

$Fe(s) + Cd^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cd(s)$

R = 8.31 J/mol-K
= 8.31 C-V/mol-K
T = 298 K
F = 96,500 C/mol

$$E^o_{cell} = E^o_{oxid}(Fe) + E^o_{red}(Cd^{2+}) = +0.44V + (-0.40V) = +0.04V$$

$$E^o_{cell} = \frac{RT}{nF} \ln K \rightarrow \ln K = \frac{nF}{RT} E^o_{cell}$$

$$\ln K = \frac{(2)(96,500\,C/mol)}{(8.31\,C \cdot V/mol \cdot K)(298\,K)}(0.04V) = 3.12$$

$$K = e^{3.12} = 22.6 \approx 23$$

The Determination of Thermodynamic Functions

Gibbs Energy Change ($\Delta_r G^o$)

One can use standard cell potentials to calculate the standard Gibbs Energy change for a reaction from the formula:

$$\Delta_r G^o = -nFE^o_{cell}$$

As we see below, the dependence of cell potential on temperature can be used to determine the Entropy change, $\Delta_r S^o$, and Enthalpy change, $\Delta_r H^o$, of the reaction.

Entropy Change ($\Delta_r S^o$)

Remember that the total differential for dG is:

$$dG = -SdT + Vdp = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

This leads to: $S = -\left(\frac{\partial G}{\partial T}\right)_p$

Entropy Change ($\Delta_r S^o$)

This leads to: $S = -\left(\frac{\partial G}{\partial T}\right)_p$

For a reaction under standard conditions, one can write $\Delta_r G^o = G^o(\text{Prod}) - G^o(\text{Rct})$ and $\Delta_r S^o = S^o(\text{Prod}) - S^o(\text{Rct})$

Thus, for a reaction, the above equation can be rewritten as:

$$\Delta_r S^o = -\left(\frac{\partial \Delta_r G^o}{\partial T}\right)_p = -\frac{d\left[-nFE^o_{cell}\right]}{dT} = +nF\frac{dE^o_{cell}}{dT}$$

Therefore, $\Delta_r S^o$ for a reaction can be determined from the measured temperature dependence of the standard electrochemical cell potential.

Enthalpy Change ($\Delta_r H^o$)

We have already seen that the Gibbs Energy change and the Entropy change for a reaction are related to the electrochemical cell potential by:

$\Delta_r G^o = -nFE^o_{cell}$ and $\Delta_r S^o = +nF\dfrac{dE^o_{cell}}{dT}$

We recall from Chapter 3 that the relation between the Enthalpy, Entropy and Gibbs Energy changes for a reaction is:

$\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o$ which yields: $\Delta_r H^o = \Delta_r G^o + T\Delta_r S^o$

If we wish, we can plug in the expressions for $\Delta_r G^o$ and $\Delta_r S^o$ to get:

$$\Delta_r H^o = -nFE^o_{cell} + nFT\frac{dE^o_{cell}}{dT}$$

Alternately, we can first calculate $\Delta_r G^o$ and $\Delta_r S^o$ and then insert the numerical values into the equation: $\Delta_r H^o = \Delta_r G^o + T\Delta_r S^o$

Example (similar to Text Example 6.5)

Consider the electrochemical cell reaction:
$AgBr(s) + \frac{1}{2}H_2(g) \rightarrow Ag(s) + HBr(aq)$

The standard cell potential is temperature dependent and is given by:

$E^o_{cell} = a + \dfrac{b}{T}$ a = -0.0884 V , b = +47.6 V-K , T = temperature in K

Calculate $\Delta_r G^o$, $\Delta_r S^o$ and $\Delta_r H^o$ for this reaction at 25 ^{o}C = 298 K

n = 1

F = 96,500 C/mol
1 C-V = 1 J

(A) $\Delta_r G^o$

$$E^o_{cell} = a + \frac{b}{T} = -0.0884 + \frac{47.6}{298} = +0.0713V$$

$$\Delta_r G^o = -nFE^o_{cell} = -(1)(96500C/mol)(0.0713V) = -6880C\cdot V/mol$$
$$= -6880J/mol \approx -6.9kJ/mol$$

Example (similar to Text Example 6.5)

Consider the electrochemical cell reaction:
$AgBr(s) + \frac{1}{2} H_2(g) \rightarrow Ag(s) + HBr(aq)$

The standard cell potential is temperature dependent and is given by:

$E^o_{cell} = a + \frac{b}{T}$ a = -0.0884 V , b = +47.6 V-K , T = temperature in K

Calculate $\Delta_r G^o$, $\Delta_r S^o$ and $\Delta_r H^o$ for this reaction at 25 ^oC = 298 K

n = 1

F = 96,500 C/mol
1 C-V = 1 J

(B) $\Delta_r S^o$

$$\Delta_r S^o = nF\frac{dE^o_{cell}}{dT} = nF\left[0-\frac{b}{T^2}\right] = 1\left(96,500\,C/mol\right)\left[-\frac{47.6\,V\cdot K}{\left(298\,K\right)^2}\right]$$
$$= -51.7\,C\cdot V/mol\cdot K = -51.7\,J/mol\cdot K \approx -52\,J/mol\cdot K$$

Example (similar to Text Example 6.5)

Consider the electrochemical cell reaction:
$AgBr(s) + \frac{1}{2} H_2(g) \rightarrow Ag(s) + HBr(aq)$

The standard cell potential is temperature dependent and is given by:

$E^o_{cell} = a + \frac{b}{T}$ a = -0.0884 V , b = +47.6 V-K , T = temperature in K

Calculate $\Delta_r G^o$, $\Delta_r S^o$ and $\Delta_r H^o$ for this reaction at 25 ^oC = 298 K

n = 1

F = 96,500 C/mol
1 C-V = 1 J

(C) $\Delta_r H^o$

$\Delta_r G^o$ = -6880 J/mol
$\Delta_r S^o$ = -51.7 J/mol-K

$$\Delta_r H^o = \Delta_r G^o + T\Delta_r S^o = -6880\,J/mol + (298\,K)(-51.7\,J/mol\cdot K)$$
$$= -22,300\,J/mol \approx -22.3\,kJ/mol$$