REDOX REACTIONS 100/100 OIL RIG (Oxidation is Loss Reduction is Gain)

GHW#7

CHEM 281(01) Winter 2014. Chapter 5. HOMEWORK 7. Name :

1) Which of the following reactions are redox?

a) $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$ — percipitation - oxidation #s stay the same

b) $NaOH + HCl \rightarrow NaCl + H_2O$ — not redox - simple acid-base rxn

c) $Zn + 2HCl \rightarrow ZnCl_2 + H_2$ — redox - single displacement

d) $2Cr + 6HCl \rightarrow 2CrCl_3 + 3H_2$ — redox - Cr is oxidized

e) $MnO_2 + 4HBr \rightarrow Br_2 + MnBr_2 + 2H_2O$ — redox

2) Separate the reduction and oxidation half reactions in following chemical equations.

a) $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

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

RHR: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

b) $MnO_2 + 4HBr \rightarrow Br_2 + MnBr_2 + 2H_2O$

OHR: $2Br^- \rightarrow Br_2 + 2e^-$

RHR: $4H^+ + MnO_2 + 2e^- \rightarrow Mn^{2+} + H_2O$

c)

c) $10K + 2KNO_3 \rightarrow N_2 + 6K_2O$

OHR: $10K \rightarrow K^+ + 10e^-$

RHR: $2NO_3^- + 10e^- \rightarrow N_2 + 3O_2^-$

3) Balance following reactions that take place and give the sum of stoichiometric coefficients.

a) $Cr_2O_7^{2-}(aq) + Cl^-(aq)$ ----- $Cr^{3+}(aq) + Cl_2(g)$ (acid solution)

OHR: $3(2Cl^- \rightarrow Cl_2 + 2e^-)$

RHR: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

net ionic: $Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$

molecular: $K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

b) $Br^-(aq) + MnO_4^-(aq)$ ----- $Br_2(g) + Mn^{2+}(aq)$ (acid solution)

OHR: $5(2Br^- \rightarrow Br_2 + 2e^-)$

RHR: $2(8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O)$

net ionic: $10Br^- + 16H^+ + 2MnO_4 + 10e^- \rightarrow 5Br_2 + 10e^- + 2Mn^+ + 8H_2O$

Net ionic: $10Br^- + 16H^+ + 2MnO_4 \rightarrow 5Br_2 + 2Mn^+ + 8H_2O$

Molecular Equation: $16HBr + 2KMnO_4 \rightarrow 2MnBr_2 + 5Br_2 + 2KBr + 8H_2O$

c) $Al(s) + MnO_4^-(aq)$ ----- $MnO_2(s) + Al(OH)_4^-(aq)$ (basic solution)

OHR: $(Al \rightarrow Al^{3+} + 3e^-)$

RHR: $(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-)$

net ionic: $MnO_4^- + Al(s) + 2H_2O \rightarrow Al^{3+} + MnO_2 + 4OH^-$

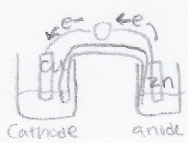
Molecular: $K^+MnO_4^- + Al(s) + 2H_2O \rightarrow K^+Al(OH)_4^- + MnO_2$

4) Construct a Galvanic cellemploying following reations:

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

$Cu^{2+} + 2e^- \rightarrow Cu$ $E_{1/2} = 0.34$

$Ni \rightarrow 2e^- + Ni^{2+}$ $E_{1/2} = -0.77$



b) $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

$2H^+ + e^- \rightarrow H_2(g)$ $E_{1/2} = 0.0$ (cathode)

$Zn(s) \rightarrow e^- + Zn^{2+}$ $E_{1/2} = -0.77$ (anode)

electrons flow from anode (oxidation) to cathode (reduction)

★ $\Delta G^\circ = -nFE^\circ_{cell}$ $E^\circ_{cell} = E_{cat} - E_{anode}$

Cell with lower E° is anode

Cell with higher E° is cathode

Nernst equation

$E = E^\circ + \frac{RT}{nF} \ln \frac{aA^a}{aB^b}$

NOT ON TEST

E° - standard electrode potential

R = gas constant, 8.314 J/mol

T = absolute temperature

F = Farday's constant

n = # of e^- involved

a = activity

(2) ox. half reaction : $Zn^0 \rightarrow Zn^{2} + 2e^-$
a) red. half reaction : $2H^+ + 2e^- \rightarrow H_2$

b) ox. half : $2Br^- \rightarrow Br_2 + 2e^-$
red. half : $MnO_2^+ + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

c) ox half : $10K \rightarrow 10K^+ + 10e^-$
red half : $2NO_3^- + 10e^- \rightarrow N_2 + 6O_2^-$

(3) a) $Cr_2O_7^{2-} + Cl^- \rightarrow Cr^{3+} + Cl_2$ (acid solution)

rhr $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

ohr $(2Cl^- \rightarrow Cl_2 + 2e^-) \times 3$

$6Cl^- \rightarrow 3Cl_2 + 6e^-$

net ionic: $Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$

$KCr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

b) $Br^- + MnO_4^- \rightarrow Br_2 + Mn^{2+}$ (acid solution)

rhr $(MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O) \times 2$

ohr $(2Br^- \rightarrow Br_2 + 2e^-) \times 5$

$2MnO_4^- + 10e^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O$

$10Br^- \rightarrow 5Br_2 + 10e^-$

$2MnO_4^- + 16H^+ 10Br^- \rightarrow 5Br_2 + 2Mn^{2+} + 8H_2O$

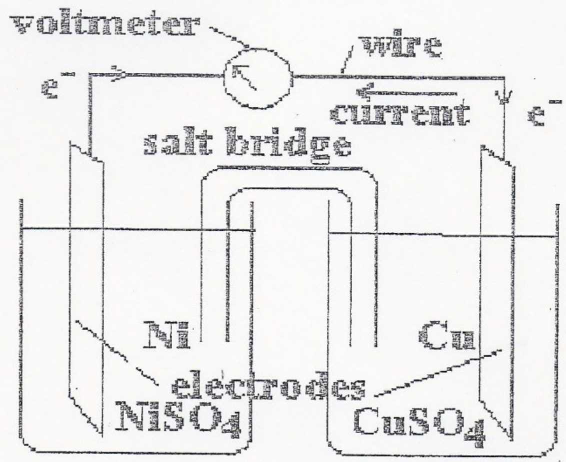
$16HBr + 2KMnO_4 \rightarrow 2MnBr_2 + 2KBr + 5Br_2 + 8H_2O$

c) $Al + MnO_4 \rightarrow MnO_2 + AlOH_4$ (basic solution)

rhr $MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$

ohr $Al \rightarrow Al^{3+} + 3e^-$

$2H_2O + KMnO_4 + Al \rightarrow MnO_2 + KAl(OH)_4^-$



To complete the galvanic cell a salt bridge, external wire and a voltmeter is used as show below:

5) Using the E^0 values given in the table calculate the E^o_{cell} for reactions in problem 4 and identify following:
a) two half reactions; b) anode; c) cathode; d) direction of electron flow through the external wire.

a) two half reactions b) anode c) cathode d) the direction of electron flow through the external wire.

a) Two half- reactions

$Ni(s) + Cu^{2+} (aq) \text{------>} Ni^{2+}(aq) + Cu$

Reduction Half Reaction(RHR): $Ni(s) \text{------>} Ni^{2+}(aq) + 2e-$

Oxidation Half Reaction(OHR): $Cu^{2+} (aq) + 2e- \text{------>} Cu$

Two half reactions written as reduction reactions:

$Ni(s) \text{------>} Ni^{2+}+(aq) + 2e-$;$E^o_{half\text{-}cell} = -0.23V$(anode)

$Cu \text{------>} Cu^{2+} (aq) + 2e-$;$E^o_{half\text{-}cell}= +0.34V$(cathode)

Cathode is the half cell where the **reduction** is taking place and the **anode** is where **oxidation** is taking place.

Cathode -Reduction

Anode-Oxidation (Remember vowels goes together)

As a general rule cathode has a higher value of Eohalf-cell than the anode. E.g.

$E^o_{Ni/Ni2+}$=-0.23V(lower value- anode) $E^o_{Cu/Cu2+}$=+0.34V(higher value-cathode).

$E^o_{cell} = E^o(catode) - E^o(anode)$

$E^o_{cell} = E^o_{Cu/Cu2+} - E^o_{Ni/Ni2+}$

$E^o_{cell} = 0.34 -(-0.23) = 0.34 + 0.23$

E^o_{cell} =0.57 Volts

b) Anode

$Ni(s) + Cu^{2+} (aq) \text{------>} Ni^{2+}(aq) + Cu$

Reduction Half Reaction(RHR): $Ni(s) \text{------>} Ni^{2+}(aq) + 2e-$

Oxidation Half Reaction(OHR): Cu^{2+} (aq) + 2e- ------> Cu

Cathode is the half cell where the **reduction** is taking place and the **anode** is where **oxidation** is taking place.

Cathode -Reduction

Anode-Oxidation (Remember vowels goes together)

Anode: Ni(s) ------> Ni^{2+}(aq) + 2e-

Anode is the Ni/Ni^{2+} -Ni electrode.

c) Cathode

Ni(s) + Cu^{2+} (aq) ------> Ni^{2+}(aq) + Cu

Reduction Half Reaction(RHR): Ni(s) ------> Ni^{2+}(aq) + 2e-

Oxidation Half Reaction(OHR): Cu^{2+} (aq) + 2e- ------> Cu

Cathode is the half cell where the **reduction** is taking place and the **anode** is where **oxidation** is taking place.

Cathode -Reduction

Anode-Oxidation (Remember vowels goes together)

Cathode: Cu^{2+} (aq) + 2e- ------> Cu

Catode is the Cu/Cu^{2+} -Cu electrode.

d) the direction of electron flow through the external wire.

Ni(s) + C^{2+}+ (aq) ------> N^{2+}+(aq) + Cu

Reduction Half Reaction(RHR): Ni(s) ------> Ni^{2+}(aq) + 2e-

Oxidation Half Reaction(OHR): Cu^{2+} (aq) + 2e- ------> Cu

As a general rule cathode needs electrons and anode has extra electrons. In this process electrons flow from anode to cathode through the external wire completing the circuit required for the current flow.

The direction of electron flow through the external wire: From Anode(Ni/Ni^{2+} -Ni electrode) to catode(Cu/Cu^{2+} -Cu electrode).

6) Calculate the ΔG^0 value for reactions in problem 4.

ΔGo= -nFE^o_{cell},

F= 96,485 c/mol e-

E^o_{cell}=0.57 volts

n = 2 electrons transferred in the redox reaction

ΔG^o= -(2 x 96,485 x 0.57) = - 1.09 x 10^5 (coulombs/volt) ; coulombs/volt= J

ΔG^o= - 1.09 x 10^5 J

The cell is spontaneous in the direction written in the net ionic equation since the ΔG is negative for the reaction.

7) Using Ellingham diagram find out the minimum temperature required for the reduction of SiO_2 by C. Please write the redox reactions involved.

The extraction of Si is more difficult than that of Fe Cu. Ellingham diagram shows that minimum Temperature is at about 1500°C where C → CO line and MO → M+O lines cross.

The total Redox Reaction:

$$SiO_2(s) + 2C(s) \xrightarrow{1500^\circ C} Si(s) + 2CO(g)$$

Half reactions

$$4e^- + \overset{4+}{Si}O_2 \rightarrow Si^0 + 2O^{2-}$$

$$2C + 2O^{2-} \rightarrow 2\overset{+2}{C}O + 2e^-$$

$$SiO_2 + 2C \rightarrow Si + 2CO$$

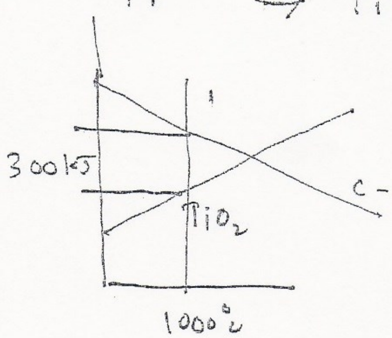
8) Estimate the potential difference required to reduce TiO_2 to metal at 1000°C.

$TiO_2 \rightarrow Ti + O_2$ $\Delta G = -nEF$

$Ti^{+4} \rightarrow Ti$ $E = -\frac{\Delta G}{nF} = \frac{-300 kJ}{4 \times 9649 kC}$

$= \frac{-300 kJ}{4 \times 96.49 kC}$

$= 2.07 V$



potential difference that need to be applied is 2.07 V

9) Using Lattimer diagram(Appendix 2) calculate the E^0 for the reduction of $HClO_3$ to HClO in aqueous acidic solution.

$$ClO_4^- \xrightarrow{1.2} ClO_3^- \xrightarrow{1.18} ClO_2^{-} \xrightarrow{1.7} HClO \xrightarrow{1.63} Cl_2 \xrightarrow{1.36} Cl^-$$

+7 +5 +3 +1 0 -1

$ClO_3^- \xrightarrow{1.18} ClO_2^-$ $(2e^-)$

$ClO_2 \xrightarrow{1.7} HClO$ $(2e^-)$

$E = \frac{n_1E_1 + n_2E_2}{n_1 + n_2}$

$E = \frac{2(1.18) + 2(1.7)}{4}$

$E = 1.44$