Exam 4
Chem 1142
Fall 2008

Name:_____ KEY _____

MULTIPLE CHOICE. [4 pts ea.]

Q1. $6I^-$(aq) + $2MnO_4^-$(aq) + $4H_2O$(l) → $3I_2$(s) + $2MnO_2$(s) + OH^-(aq)

(handwritten above terms:) (-1) (+7)(-2) (+1)(-2) (0) (+4)(-2) (-2)(+1)
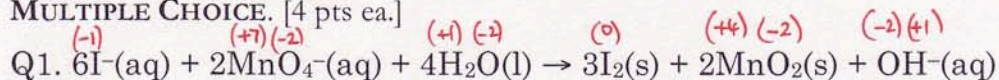
Which of the following statements regarding the reaction represented by the equation above is correct?

a) Iodide ion is oxidized by hydroxide ion. ✗ *I⁻ is ox. by MnO₄⁻!*
b) MnO_4^- is oxidized by iodide ion. ✗ *MnO₄⁻ is red. by I⁻*
c) The oxidation number of manganese changes from +7 to +2. *+7 → +4*
d) The oxidation number of manganese remains the same. *+7 → +4*
e) The oxidation number of iodine changes from −1 to 0. ✓ YES.

(answers a, b, c, d circled/crossed; e circled)

Q2. __ $Cr_2O_7^{2-}$ + **6** e^- + **14** H^+ → **2** Cr^{3+} + **7** H_2O(l)
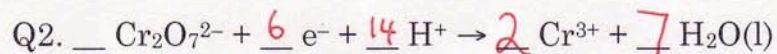
When the equation for the half reaction above is balanced with the lowest whole-number coefficients, the coefficient for H_2O is

a) 2   b) 4   c) 6   (d) 7   e) 14

(d circled)

Q3. Which of the following must be true for a reaction that proceeds spontaneously from initial standard state conditions?

a) $\Delta G° > 0$ and $K_{eq} > 1$ b) $\Delta G° > 0$ and $K_{eq} < 1$ c) $\Delta S° < 0$ and $K_{eq} > 1$
d) $\Delta G° < 0$ and $K_{eq} > 1$ e) $\Delta G° = 0$ and $K_{eq} = 1$

(d circled)

Q4. Which of the following produces an INCREASE in entropy of the system?

a) H_2O(l) → H_2O(s)   b) $2O_2$(g) + $2SO$(g) → $2SO_3$(g)
c) $2CH_3OH$(g) + $3O_2$(g) → $2CO_2$(g) + $4H_2O$(l)   d) I_2(s) → I_2(l)
e) None of the above.

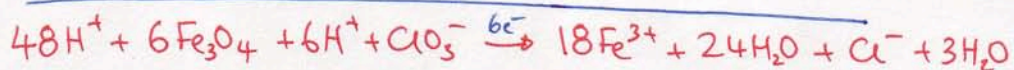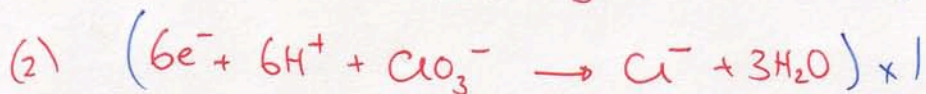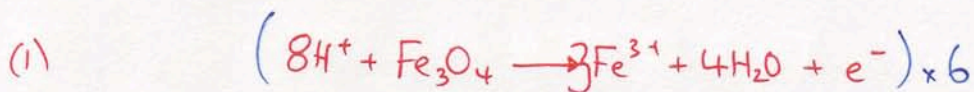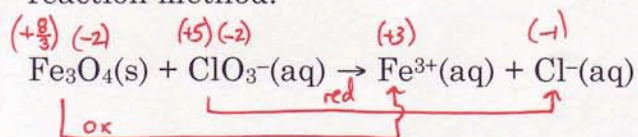*(d circled)*

liquids are "more disordered" than solids.

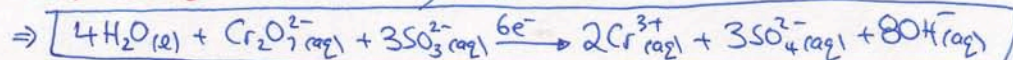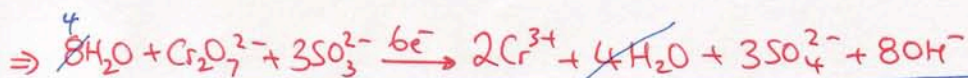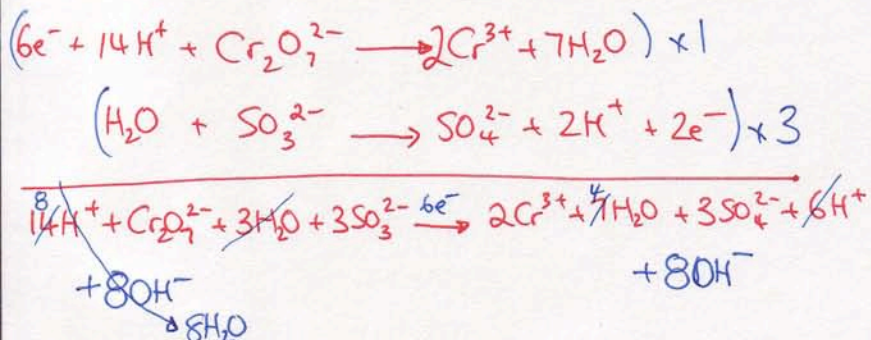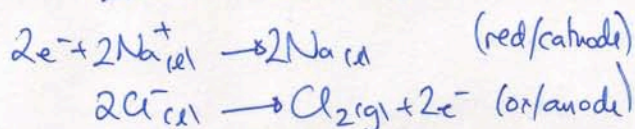Q5. When a reaction is at equilibrium, which of the following statements is TRUE?

a) $\Delta G = \Delta G°$ b) $\ln K_{eq} = 0$ c) $\Delta G° = 0$ d) $Q = 0$ (e)) $\Delta G = 0$

Q6. Which of the following statements about a salt bridge in a voltaic cell is TRUE?

a) Free electrons flow through the salt bridge to maintain electrical neutrality in the two half-cells.
b) The salt bridge allows the ions present in the two half-cells to mix extensively.
c) The wire must be connected directly to the salt bridge in order for the salt bridge to be able to maintain electrical neutrality in the two half-cells.
d) In some cases, a salt bridge functions as the anode.
(e)) Ions from the electrolyte in the salt bridge flow into each half-cell to maintain *neutrality.*

Q7. [10 pts.] Balance the following redox reaction in acidic solution using the half-reaction method:

$(+\frac{8}{3})\ (-2)$ $(+5)(-2)$ $(+3)$ (-1)
$Fe_3O_4(s) + ClO_3^-(aq) \rightarrow Fe^{3+}(aq) + Cl^-(aq)$
red
ox

(1) $\left(8H^+ + Fe_3O_4 \longrightarrow 3Fe^{3+} + 4H_2O + e^- \right) \times 6$

(2) $\left(6e^- + 6H^+ + ClO_3^- \longrightarrow Cl^- + 3H_2O \right) \times 1$

_____

$48H^+ + 6Fe_3O_4 + 6H^+ + ClO_3^- \xrightarrow{6e^-} 18Fe^{3+} + 24H_2O + Cl^- + 3H_2O$

$\Rightarrow$ $\boxed{54H^+_{(aq)} + 6Fe_3O_{4(s)} + ClO_3^-{}_{(aq)} \xrightarrow{6e^-} 18Fe^{3+}{}_{(aq)} + 27H_2O_{(\ell)} + Cl^-{}_{(aq)}}$

Q8. [10 pts.] Balance the following redox reaction in basic solution using the half-reaction method:

$$\overset{(+6)}{Cr_2O_7^{2-}}\overset{(-2)}{(aq)} + \overset{(+4)}{SO_3^{2-}}\overset{(-2)}{(aq)} \rightarrow \overset{(+3)}{Cr^{3+}}(aq) + \overset{(+6)}{SO_4^{2-}}\overset{(-2)}{(aq)}$$

(red) (ox)

$$(6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O) \times 1$$

$$(H_2O + SO_3^{2-} \longrightarrow SO_4^{2-} + 2H^+ + 2e^-) \times 3$$

$$\overset{8}{\cancel{14}H^+} + Cr_2O_7^{2-} + 3\cancel{H_2O} + 3SO_3^{2-} \overset{6e^-}{\longrightarrow} 2Cr^{3+} + \overset{4}{\cancel{7}H_2O} + 3SO_4^{2-} + \cancel{6}H^+$$

$$+8OH^- \qquad\qquad\qquad +8OH^-$$
$$\searrow 8H_2O$$

$$\Rightarrow \overset{4}{\cancel{8}}H_2O + Cr_2O_7^{2-} + 3SO_3^{2-} \overset{6e^-}{\longrightarrow} 2Cr^{3+} + 4H_2O + 3SO_4^{2-} + 8OH^-$$

$$\Rightarrow \boxed{4H_2O(l) + Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \overset{6e^-}{\longrightarrow} 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 8OH^-(aq)}$$

Q9. [10 pts.] Molten NaCl is electrolysed for 3.0 hours using an electrical current of 120 A. How many moles of $Cl_2(g)$ are formed?

$$2NaCl \rightarrow 2Na + Cl_2$$

$$2e^- + 2Na^+_{(l)} \rightarrow 2Na_{(l)} \quad (red/cathode)$$
$$2Cl^-_{(l)} \rightarrow Cl_2(g) + 2e^- \quad (ox/anode)$$

$$Q = I \cdot t = 120\tfrac{C}{s} \times 3.0h\left|\frac{60min}{1h}\right|\frac{60s}{1min} = 1.30 \times 10^6 C$$

#mol

$$\frac{1.30 \times 10^6 C}{} \left|\frac{1 mol\ e^-}{96,500\ C}\right|\frac{1\ mol\ Cl_2}{2\ mol\ e^-} = 6.7\ mol\ Cl_2$$

Q10. [6 pts.] Calculate $E°$ for the following cell: $Mg(s)|Mg^{2+}(aq)||Ag^+(aq)|Ag(s)$

$$E°_{cell} = E°_{RHS} - E°_{LHS} = E°_{Ag^+/Ag} \ominus E°_{Mg^{2+}/Mg}$$

(Table 19-1 was provided on this exam!)

$$= +0.80V \ominus -2.37V$$

$$= +3.17V$$

Q11. [10 pts.] Write the cell reaction for the following cell:
$Mg(s)\,|\,Mg^{2+}(aq)\,|\,|\,Ag^{+}(aq)\,|\,Ag(s)$

$\underbrace{\qquad\qquad}_{\text{ANODE (OX)}}$ $\underbrace{\qquad\qquad}_{\text{CATHODE (RED)}}$

Ox: $\left(Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^{-}\right) \times 1$

red: $\left(Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}\right) \times 2$

$Mg_{(s)} + 2Ag^{+}_{(aq)} \xrightarrow{\;2e^{-}\;} Mg^{2+}_{(aq)} + 2Ag_{(s)}$
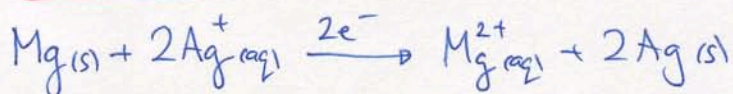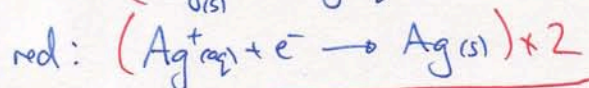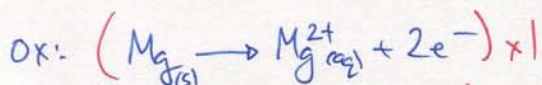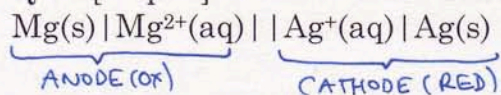
Q12. [10 pts.] A reaction has $\Delta H° = +30.3$ kJ/mol and $\Delta S° = +320$ J/mol·K. Calculate $\Delta G°$ at 25°C, and 75 °C. At what temperature will the reaction become spontaneous?

$\Delta G° = \Delta H° - T\Delta S°$ $\qquad T_1 = 25 + 273 = 298K \qquad T_2 = 75 + 273 = 348K$

$\Delta G_{25°c} = +30.3\frac{kJ}{mol} - 298K \times \frac{320\,J}{mol\cdot K} \times \frac{1kJ}{10^3 J} = -65.06\frac{kJ}{mol}$

$\Delta G_{75°c} = +30.3\frac{kJ}{mol} - 348K \times \frac{320\,J}{mol\cdot K} \times \frac{1kJ}{10^3 J} = -81.06\frac{kJ}{mol}$
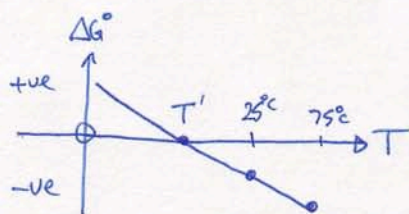
Spont when $\Delta G° = 0$

$\Rightarrow 0 = \Delta H° - T\Delta S°$

$\Rightarrow T = \frac{\Delta H°}{\Delta S°} = \frac{+30.3\ ^{kJ}/_{mol}}{+0.320\ ^{kJ}/_{mol\cdot K}} = 94.7K$

$(-178.3°C)$

Q13. [10 pts.] Predict the sign of $\Delta S°$ (+ve, −ve, ≈0) for the following chemical reactions:

a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ −ve (3 mol gas → 1 mol gas)

b) $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g)$ +ve (0 mol gas → 1 mol gas)

c) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ ≈0 (2 mol gas → 2 mol gas)
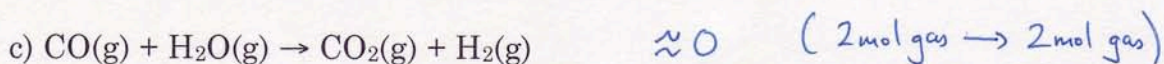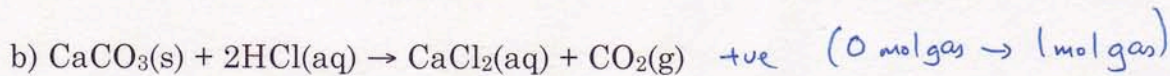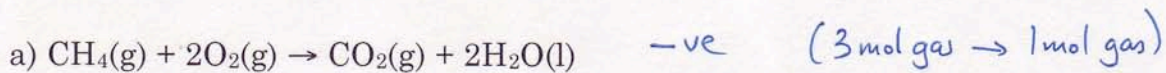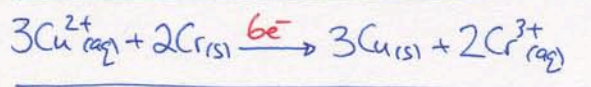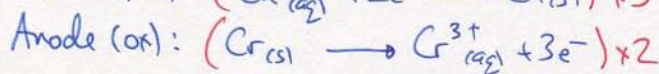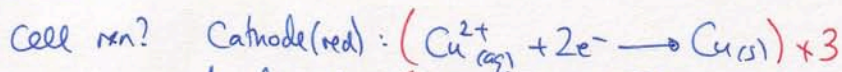
Q14. [10 pts.] Determine the cell voltage produced by the following cell *(where the reactants and products are not in their standard states!)* at 298 K:

Useful Information: $E°_{Cr^{3+},Cr} = -0.74$ V, $E°_{Cu^{2+},Cu} = +0.34$ V

$Cr(s)\,|\,Cr^{3+}(aq,\,0.045\,M)\,\|\,Cu^{2+}(aq,\,0.85\,M)\,|\,Cu(s)$ $E°_{cell} = E°_{RHS} - E°_{LHS} = +0.34V \ominus -0.74V$
$\qquad\qquad = +1.08V$

Nernst eq: $E_{cell} = E°_{cell} - \frac{RT}{nF}\ln Q$

$\Rightarrow$ need n, Q.

Cell rxn? Cathode (red): $\left(Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}\right) \times 3$

Anode (ox): $\left(Cr_{(s)} \longrightarrow Cr^{3+}_{(aq)} + 3e^-\right) \times 2$

$\rule{8cm}{0.4pt}$

$3Cu^{2+}_{(aq)} + 2Cr_{(s)} \xrightarrow{6e^-} 3Cu_{(s)} + 2Cr^{3+}_{(aq)}$

$\rule{8cm}{0.4pt}$

$\Rightarrow n=6 \quad \Rightarrow Q = \dfrac{[Cr^{3+}]^2}{[Cu^{2+}]^3} = \dfrac{0.045^2}{0.85^3} = \underline{0.003297}$

$\Rightarrow E_{cell} = +1.08V - \dfrac{8.3145\frac{J}{mol\cdot K} \times 298K}{6 \times 96,500\frac{C}{mol}} \times \ln\left(0.003297\right)$

$= \quad +1.10V \qquad\qquad \left(1V = 1\frac{J}{C}\right)$

BONUS QUESTION: A chemical reaction has $\Delta G° = -3.4$ kJ/mol at 25 °C. What is its equilibrium constant?

$\Delta G° = -RT\ln K$

$\Rightarrow K = e^{-\Delta G°/RT}$

$= e^{-\frac{-3400\,J/mol}{8.3145\frac{J}{mol\cdot K} \times 298K}}$

$= e^{+1.3722}$

$= 3.9$

$\left(\text{note: } \Delta G° = -ve \text{ implies } K > 1 \text{ and } E°_{cell} = +ve\right)$