AP Chemistry – Thermodynamics / Electrochemistry Exam

Name: Key Date: 75 points possible Period:

ThermoelectroExam1011.docx

Show all work to receive credit. Circle the letter corresponding to the best choice on multiple choice questions. There are 15 questions.

$\Delta S^\circ_{univ} = \Delta S^\circ_{surr} + \Delta S^\circ_{sys}$ | $\Delta S^\circ_{sys} = \Sigma m S^\circ_{prod} - \Sigma n S^\circ_{react}$ | $R = 8.3145 J/molK$

$\Delta S^\circ_{surr} = -\Delta H^\circ_{sys}/T$ | $\Delta H^\circ = \Sigma m \Delta H_f^\circ{}_{prod} - \Sigma n \Delta H_f^\circ{}_{react}$ | $\Delta G^\circ = \Delta H^\circ_{sys} - T\Delta S^\circ_{sys}$

$\Delta G^\circ = \Sigma m \Delta G_f^\circ{}_{prod} - \Sigma n \Delta G_f^\circ{}_{react}$ | $\Delta G = \Delta G^\circ + RT \ln Q$ | $K = {}^\circ C + 273.15$

$\Delta G^\circ_{rxn} = -RT \ln K$ | $\Delta G = \Delta H_{sys} - T\Delta S_{sys}$ | $F = 96{,}485 C/mol\ e^-$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ | $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$ | $E_{cell} = E^\circ_{cell} - (0.0592V/n)\log Q$

$E = E^\circ - (0.0257/n)\ln Q$ | $\ln K = nE^\circ/(0.0257)$ | $E^\circ_{cell} = (RT/nF)\ln K_{eq}$

$\Delta G^\circ = -nFE^\circ$ | $I = q/t$ | 1Volt = 1joule/coulomb

$V = IR$ | $N_A = 6.022 \times 10^{23}$

1. Estimate the boiling point of carbon tetrachloride given the following thermodynamic parameters.

	ΔH°_f(KJ/mol)	S°(J/Kmol)	ΔG°_f(kJ/mol)
$CCl_{4(l)}$	-128.4	214.4	-57.6
$CCl_{4(g)}$	-96.0	309.7	-53.6

$\Delta H^\circ_{rxn} = 32.4 kJ$

$\Delta S^\circ_{rxn} = 95.3 J/K$

$\Delta^\circ G_{rxn} = 0$ @ equilibrium

Work Area:

$CCl_{4(l)} \longrightarrow CCl_{4(g)}$

$0 = 32.4 - T(.0953)$

$T = 339.979 - 273.15 = 24.86$

$T = 66.829\ ^\circ C$

x5

Answer: 66.8 (67) °C

2. Use the following thermodynamic data

	ΔH_f° (kJ/mol)	S° (J/Kmol)
$H_2O_{2(l)}$	-187.78	109.6
$H_2O_{(l)}$	-285.83	69.91
$O_{2(g)}$	0	205.14

To calculate ΔS°_{univ} for the decomposition of hydrogen peroxide at 25.0°C.

$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

Work Area:

$2(-285.83) - 2(-187.78) = \Delta H^\circ_{rxn} = -196.1 kJ$

$[2(69.91) + 1(205.14)] - 2(109.6) = \Delta S^\circ_{sys} = 125.76 J/K$

$\Delta S^\circ_{univ} = \frac{-\Delta H^\circ_{sys}}{T} + \Delta S^\circ_{sys}$

$= \frac{196{,}100 J}{298.15 K} + 125.76 J/K = 783.48$

x5

Answer: 783.5 J/K

3. Consider the reaction

$2POCl_{3(g)} \rightarrow 2PCl_{3(g)} + O_{2(g)}$

a. Calculate ΔG° for this reaction. The ΔG°_f values for $POCl_{3(g)}$ and $PCl_{3(g)}$ are -502kJ/mol and -270.kJ/mol, respectively.

$2 mol(-270. kJ/mol) - 2 mol(-502 kJ/mol) = 464 kJ$

Work Area:

x5

Answer: 464 kJ

x15

b. The value of ΔS° for this reaction is 179J/K. What is the threshold temperature (in K) at which this reaction becomes spontaneous at standard conditions? Assume that ΔH° and ΔS° do not depend upon temperature.

Work Area:

When does ΔG° become negative

① $464\text{kJ} = \Delta H^\circ - 298.15\text{K}(.179\text{kJ/K})$

$464\text{kJ} = \Delta H^\circ - 53.36885\text{kJ}$

$\Delta H = 517.36885$ when $\Delta G^\circ = 0$ System is @ equilibrium

② $0 = 517.37\text{kJ} - T(.179\text{kJ/K})$

$T = 2890$

+5

Answer: $T > 2890$ K

4. Ethanethiol (C_2H_5SH; also called ethyl mercaptan) is commonly added to natural gas to provide the "rotten egg" smell of a gas leak. The boiling point of ethanethiol is 35.0°C and its heat of vaporization is 27.5kJ/mol. What is the entropy of vaporization for this substance?

Work Area:

$\Delta H_{vap} = 27.5\text{ kJ/mol} = 27{,}500\text{ J/mol}$

$35.0 + 273.15 = 308.15\text{ K}$

$\Delta G = \Delta H - T\Delta S$ @ equilibrium $\Delta G = 0$

$0 = \Delta H - T\Delta S$ $\quad \Delta H = T\Delta S$

$\Delta S_{sys} = \Delta H/T = \frac{27{,}500\text{J/mol}}{308.15\text{K}} = 89.2\text{ J/mol K}$

+5

Answer: 89.2 J/molK

5. Cells use the hydrolysis of adenosine triphosphate, abbreviated as ATP, as a source of energy. Symbolically, this reaction can be written as

$$ATP_{(aq)} + H_2O_{(l)} \rightarrow ADP_{(aq)} + H_2PO_4^-{}_{(aq)}$$

Where ADP represents adenosine diphosphate. For this reaction $\Delta G^\circ = -30.5$kJ/mol.

a. Calculate K at 25.0°C.

Work Area:

$\Delta G^\circ_{rxn} = -RT\ln K$

$-30{,}500\text{J} = -(8.314\text{ J/mol K})(298.15\text{K})\ln K$

$12.30 = \ln K$

$K = e^{12.30} = 2.21 \times 10^5$

+5

Answer: 2.21×10^5

b. If all the free energy form the metabolism of glucose ($C_6H_{12}O_{6(s)}$)

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

goes into forming ATP from ADP, how many ATP molecules can be produced for every molecule of glucose? (Standard Gibbs free energy of formation (kJ/mol): $C_6H_{12}O_{6(s)} = -911$; $CO_{2(g)} = -394$; $H_2O_{(l)} = -237$)

Work Area:

$\Delta G^\circ_{rxn} = [6(-237) + 6(-394)] - (-911) = -2875\text{ kJ}$

$\frac{-2875}{-30.5} = 94.3$ molecules

+5

Answer: 94.3 (94) ATP molecules

6. Calculate E for the following electrochemical cell at 25°C

$$Pt_{(s)} \mid Sn^{2+}{}_{(aq,\ 0.50\ M)}, Sn^{4+}{}_{(aq,\ 0.50\ M)} \parallel I^-{}_{(aq,\ 0.15\ M)} \mid AgI_{(s)} \mid Ag_{(s)}$$

given the following standard reduction potentials.

$2AgI_{(s)} + 2e^- \rightarrow 2Ag_{(s)} + 2I^-_{(aq)}$ $\quad E^\circ = -0.15$ V ← ox — +0.15 V $\quad$ 0.30 V ↑

$Sn^{4+}{}_{(aq)} + 2e^- \rightarrow Sn^{2+}{}_{(aq)}$ $\quad E^\circ = +0.15$ V ← red

Work Area:

$E = E^\circ - \left(\frac{.0257}{n}\right)\ln Q$ $\quad E = 0.30\text{V} - \left(\frac{.0257}{2}\right)\ln 44.44 = 0.25\text{V}$

Remember The tin (Sn) should be reduced but it's shown at the anode in the cell diagram so the voltage will be negative.

$Q = \frac{[Sn^{2+}_{aq}]}{(I^-_{aq})^2(Sn^{4+}_{aq})} = \frac{[.50\text{M}]}{[0.15\text{M}]^2[0.50\text{M}]} = 44.44$

+5

Answer: -0.25 V

+5

7. What is the pH (pH = -log[H_3O^+]) of the solution at the cathode if E_{cell} = –0.174 V for the following electrochemical cell at 25 °C?

$Pt \mid H_{2(g,\ 1.0\ atm)} \mid H^+_{(aq,\ 1.00\ M)} \parallel H^+_{(aq)} \mid H_{2(g,\ 1.0\ atm)} \mid Pt$

Work Area:

$-0.174V = 0 - \left(\frac{0.0257}{2}\right) \ln \frac{(1.00M)^2(1.0atm)}{(1.0atm)(x)^2}$

$13.54 = \ln\left(\frac{1}{x^2}\right)$ $759834.58 = \frac{1}{x^2}$

$x^2 = 1.316 \times 10^{-6}$

$x = .001147\ M\ H_3O^+$

$pH = -\log(.001147) = 2.94$

Answer: 2.94

8. Calculate ΔG° for the disproportionation reaction of Cu^+ at 25 °C,

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

given the following thermodynamic information.

$Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$ $E^\circ = +0.518$ V .518

$Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$ $E^\circ = +0.337$ V .337

Work Area:

$\Delta G^\circ = -nFE^\circ_{cell} = -2(96,485)(.181V)$

$= -34,927.57\ J$

$= -34.9\ kJ$

Answer: -34.9 kJ

9. Calculate the equilibrium constant for the following reaction at 25°C,

$Co^{2+}_{(aq)} + 2\ Cr^{2+}_{(aq)} \rightarrow Co_{(s)} + 2\ Cr^{3+}_{(aq)}$

given the following information.

$Co^{2+}_{(aq)} + 2\ e^- \rightarrow Co_{(s)}$ $E^\circ = -0.28$ V (ox)

$Cr^{3+}_{(aq)} + e^- \rightarrow Cr^{2+}_{(aq)}$ $E^\circ = -0.41$ V

Work Area:

$E^\circ_{cell} = .41 - .28 = .13$

$\ln k = nE^\circ/0.0257 = \frac{(2)(.13V)}{(0.0257)}$

$\ln k = 10.1167$ $k = e^{10.1167} = 24753.7$

Answer: 2.5×10^4

10. One kind of battery used in watches contains mercury(II) oxide. As current flows, the mercury oxide is reduced to mercury.

$HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$

If 2.5×10^{-5} amperes flows continuously for 1095 days, what mass of $Hg_{(l)}$ (in grams) is produced?

Work Area:

$1095 days \left(\frac{24 hrs}{1 day}\right)\left(\frac{3600 s}{1 hr}\right) = 9.46 \times 10^7 s$

$2.5 \times 10^{-5} \frac{C}{s}\ (9.46 \times 10^7 s) = 2365.2 C$

$2365.2 C / 96,485 C/1 mol e^- = .0245 mol\ e^-$

$.0245 mole \left(\frac{1 mol\ Hg}{2 mole^-}\right) = .01226 mol$

$.01226 mol \times 200.6 \frac{g}{mol} = 2.46 g$

Answer: 2.5 g

11. Write a balanced half-reaction for the reduction of $ClO_3^-{}_{(aq)}$ to $Cl_{2(g)}$ in an acidic solution.

Answer: $12H^+_{(aq)} + 2ClO_3^-{}_{(aq)} + 10e^- \rightarrow Cl_{2(g)} + 6H_2O_{(l)}$

12. For a chemical system, ΔG° and ΔG are equal when
a. the system is in equilibrium
b. the reactants and products are in standard state conditions
c. the equilibrium constant, K, equals 0
d. the reaction quotient, Q, is less than 1
e. the reactants and products are in the gas phase

Based on $\Delta G = \Delta G^\circ + RT \ln Q$

13. The following reaction is endothermic

$$3O_{2(g)} \rightarrow 2O_{3(g)}$$

The reaction is
a. spontaneous at all temperatures
b. non-spontaneous at all temperatures
c. spontaneous at low temperatures
d. spontaneous at high temperatures

endothermic implies $\Delta H_{rxn} > 0$
Reduction in moles of gas implies $\Delta S < 0$
$\Delta G = \Delta H - T\Delta S$
$>0 \quad <0$ ΔG always >0

14. With respect to electrolytic and galvanic cells, which of the following statements about these cells is correct?
a. The anode will gain weight in a voltaic cell.
b. Oxidation occurs at the cathode of both cells.
c. The free energy change, ΔG, is negative for the voltaic cell.
d. The current flows from cathode to anode in an electrolytic cell.

must be to be spontaneous

15. Use the standard reduction potentials below to determine which element or ion is the best reducing agent?

$Pd^{2+}_{(aq)} + 2e^- \rightarrow Pd_{(s)}$ $\quad E^\circ = +0.90V$
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $\quad E^\circ = -0.14V$
$Cr^{2+}_{(aq)} + 2e^- \rightarrow Cr_{(s)}$ $\quad E^\circ = -0.91V$

a. $Pd^{2+}_{(aq)}$
b. $Pd_{(s)}$
c. $Sn^{2+}_{(aq)}$
d. $Cr^{2+}_{(aq)}$
e. $Cr_{(s)}$