

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.

$$\Delta S^{\circ}_{\text{univ}} = \Delta S^{\circ}_{\text{surr}} + \Delta S^{\circ}_{\text{sys}}$$

$$\Delta S^{\circ}_{\text{surr}} = -\Delta H^{\circ}_{\text{sys}}/T$$

$$\Delta G^{\circ} = \sum m\Delta G^{\circ}_{\text{f, prod}} - \sum n\Delta G^{\circ}_{\text{f, react}}$$

$$\Delta G^{\circ}_{\text{rxn}} = -RT \ln K$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$E = E^{\circ} - (0.0257/n)\ln Q$$

$$\Delta G^{\circ} = -nFE^{\circ}$$

$$V = IR$$

$$\Delta S^{\circ}_{\text{sys}} = \sum mS^{\circ}_{\text{prod}} - \sum nS^{\circ}_{\text{react}}$$

$$\Delta H^{\circ} = \sum m\Delta H^{\circ}_{\text{f, prod}} - \sum n\Delta H^{\circ}_{\text{f, react}}$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}}$$

$$\ln K = nE^{\circ}/(0.0257)$$

$$I = q/t$$

$$N_A = 6.022 \times 10^{23}$$

$$R = 8.3145 \text{ J/molK}$$

$$\Delta G^{\circ} = \Delta H^{\circ}_{\text{sys}} - T\Delta S^{\circ}_{\text{sys}}$$

$$K = e^{-(\Delta G^{\circ}/RT)}$$

$$F = 96,485 \text{ C/mol } e^{-}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592 \text{ V}/n)\log Q$$

$$E^{\circ}_{\text{cell}} = (RT/nF)\ln K_{\text{eq}}$$

$$1 \text{ Volt} = 1 \text{ joule/coulomb}$$

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

	$\Delta H^{\circ}_{\text{f}}$ (kJ/mol)	S° (J/Kmol)	$\Delta G^{\circ}_{\text{f}}$ (kJ/mol)
$\text{CCl}_4(\text{l})$	-128.4	214.4	-57.6
$\text{CCl}_4(\text{g})$	-96.0	309.7	-53.6

Work Area:



$$\Delta H^{\circ}_{\text{rxn}} = 32.4 \text{ kJ}$$

$$\Delta S^{\circ}_{\text{rxn}} = 95.3 \text{ J/K}$$

$$\Delta G^{\circ}_{\text{rxn}} = 0 \text{ equilibrium}$$

$$0 = 32.4 - T(0.0953)$$

$$T = 339.979 - 273.15 = 66.83$$

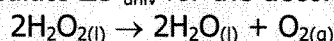
$$T = 66.829^{\circ}\text{C}$$

Answer: 66.8 (67) $^{\circ}\text{C}$

2. Use the following thermodynamic data

	$\Delta H^{\circ}_{\text{f}}$ (kJ/mol)	S° (J/Kmol)
$\text{H}_2\text{O}_2(\text{l})$	-187.78	109.6
$\text{H}_2\text{O}(\text{l})$	-285.83	69.91
$\text{O}_2(\text{g})$	0	205.14

To calculate $\Delta S^{\circ}_{\text{univ}}$ for the decomposition of hydrogen peroxide at 25.0°C .



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

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

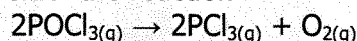
Work Area:

$$\Delta S^{\circ}_{\text{univ}} = \frac{-\Delta H^{\circ}_{\text{sys}}}{T} + \Delta S^{\circ}_{\text{sys}}$$

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

Answer: 783.5 J/K

3. Consider the reaction



a. Calculate ΔG° for this reaction. The $\Delta G^{\circ}_{\text{f}}$ values for $\text{POCl}_3(\text{g})$ and $\text{PCl}_3(\text{g})$ are -502 kJ/mol and -270 kJ/mol , respectively.

Work Area:

$$2 \text{ mol}(-270 \text{ kJ/mol}) - 2 \text{ mol}(-502 \text{ kJ/mol}) = 464 \text{ kJ}$$

Answer: 464 kJ

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:

$$\textcircled{2} -517.37 = -T(.179)$$

$$T = 2890$$

When does ΔG° become negative

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

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

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

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

Answer: $T > 2890$ K

4. Ethanethiol ($\text{C}_2\text{H}_5\text{SH}$; 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 27.5 kJ/mol . What is the entropy of vaporization for this substance?

Work Area:

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

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

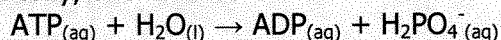
$$\Delta G = \Delta H - T\Delta S \text{ @ equilibrium } \Delta G = 0$$

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

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

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



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

a. Calculate K at 25.0°C .

Work Area:

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

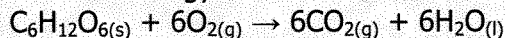
$$-30,500 \text{ J} = -(8.314 \text{ J/mol K})(298.15 \text{ K}) \ln K$$

$$12.30 = \ln K$$

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

Answer: 2.21×10^5

b. If all the free energy from the metabolism of glucose ($\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$)



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): $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) = -911$; $\text{CO}_2(\text{g}) = -394$; $\text{H}_2\text{O}_{(\text{l})} = -237$)

Work Area:

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

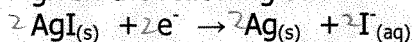
$$\frac{-2875}{-30.5} = 94.3 \text{ molecules}$$

Answer: 94.3 (94) ATP molecules

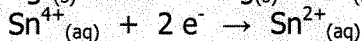
6. Calculate E for the following electrochemical cell at 25°C



given the following standard reduction potentials.



$$E^\circ = -0.15 \text{ V} \leftarrow \text{ox} \rightarrow +0.15 \text{ V} \quad 0.30 \text{ V} \text{ TL}$$



$$E^\circ = +0.15 \text{ V} \leftarrow \text{red}$$

Work Area:

$$E = E^\circ - \left(\frac{0.0257}{n} \right) \ln Q$$

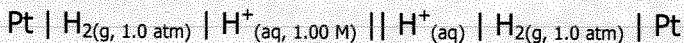
$$E = 0.30 \text{ V} - \left(\frac{0.0257}{2} \right) \ln 44.44 = 0.25 \text{ V}$$

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

$$Q = \frac{[\text{Sn}^{2+}]}{[\text{I}^{-}]^2 [\text{Sn}^{4+}]} = \frac{[0.50 \text{ M}]}{[0.15 \text{ M}]^2 [0.50 \text{ M}]} = 44.44$$

Answer: -0.25 V

7. What is the pH ($\text{pH} = -\log[\text{H}_3\text{O}^+]$) of the solution at the cathode if $E_{\text{cell}} = -0.174 \text{ V}$ for the following electrochemical cell at 25°C ?



Work Area:

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

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

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

Answer: 2.94

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



given the following thermodynamic information.



Work Area:

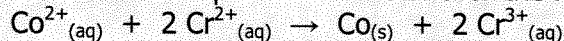
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -2(96,485)(.181 \text{ V})$$

$$= -34,927.57 \text{ J}$$

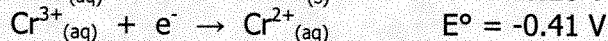
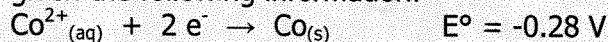
$$= -34.9 \text{ kJ}$$

Answer: -34.9 kJ

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



given the following information.



Work Area:

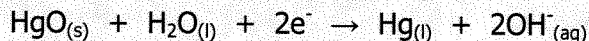
$$E_{\text{cell}}^\circ = .41 - .28 = .13$$

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

$$\ln K = 10.1167 \quad K = e^{10.1167} = 24753.7$$

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.



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

Work Area:

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

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

$$2365.2 \text{ C} / 96,485 \text{ C/mole} = .0245 \text{ mole}$$

Answer: 2.5 g

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

$$= .01226 \text{ mol}$$

$$.01226 \text{ mol} \times 200.6 \frac{\text{g}}{\text{mol}}$$

$$= 2.46 \text{ g}$$

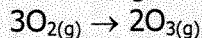
11. Write a balanced half-reaction for the reduction of $\text{ClO}_3^-(\text{aq})$ to $\text{Cl}_2(\text{g})$ in an acidic solution.

Answer: $12\text{H}^+(\text{aq}) + 2\text{ClO}_3^-(\text{aq}) + 10\text{e}^- \rightarrow \text{Cl}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

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



- The reaction is
- spontaneous at all temperatures
 - non-spontaneous at all temperatures
 - spontaneous at low temperatures
 - spontaneous at high temperatures

endothermic implies $\Delta H_{\text{rxn}} > 0$

Reduction in moles of gas implies $\Delta S < 0$

$$\Delta G = \Delta H - T\Delta S$$

$> 0 \quad < 0 \quad \Delta G \text{ always } > 0$

14. With respect to electrolytic and galvanic cells, which of the following statements about these cells is correct?

- The anode will gain weight in a voltaic cell.
- Oxidation occurs at the cathode of both cells.
- The free energy change, ΔG , is negative for the voltaic cell.
- 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?



- $\text{Pd}^{2+}_{(aq)}$
- $\text{Pd}_{(s)}$
- $\text{Sn}^{2+}_{(aq)}$
- $\text{Cr}^{2+}_{(aq)}$
- $\text{Cr}_{(s)}$

x/2