

Ch ~~16~~ 17

$$pH = pK_a + \log \frac{[B]}{[A]}$$

$$pH = \text{or } pK_a + \log \frac{[A^-]}{[HA]}$$

Same thing!

Ch ~~17~~ 18

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

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

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

$$\ln K = -\frac{\Delta H}{R} \left( \frac{1}{T} \right) + \frac{\Delta S}{R}$$

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

NAME Key

Su2014/CHEM1451/Exam 4/Dooley

August 1, 2014

125 Points Total

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Multiple Choice: (4 Points Each) Place the letter corresponding to the correct answer to the left of each problem number. <sup>3</sup>

- C 1. When titrating a weak acid with NaOH, the
- pH will be less than 7 at the equivalence point.
  - pH will be equal to 7 at the equivalence point.
  - pH will be greater than 7 at the equivalence point.
  - titration will require more moles of base than acid to reach the equivalence point.
  - titration will require more moles of acid than base to reach the equivalence point.

- A 2. In a weak acid titration with a strong base, the equivalence point is found to occur at 60 mL of added base. What did the pH equal after only adding 30 mL of base?
- The  $pK_a$  of the weak acid
  - The  $pK_b$  of the weak acid
  - The pH varies depending on the base you are using
  - pH = 7
  - pH = 3.5
- half-way*

- B 3. A 60 mL sample of 0.400M hypochlorous acid ( $K_a = 2.9 \times 10^{-8}$ ) is titrated with 0.100M NaOH. What is the pH of the sample before any base is added?
- 1.95
  - 3.97
  - 10.03
  - 7.00
  - None of the above
- $[H_3O^+] = .000108 M$   
 $pH = 3.97$

- C 4. When you compare the titration curves of several weak acids of the same molarity with a strong base, which of the following indicates that you are looking at the curve for the weakest of the acids?
- The pH jump at the equivalence point is the largest
  - The initial pH is the lowest, and it takes more base to neutralize.
  - The pH in the buffer region is the highest and the pH at the equivalence point is the highest. ✓
  - The equivalence point occurs with less base added.
  - You can't tell the strength of the acid from its titration curve.

- B 5. Which of the following compounds will be more soluble in acidic solution than in pure water?
- $\text{PbCl}_2$
  - $\text{FeCO}_3$  ←  $\text{CO}_3^{2-}$  is a WB
  - $\text{Ca}(\text{NO}_3)_2$
  - $\text{CuI}$
  - None of the above will be more soluble in acidic solution.

- B 6. Determine the molar solubility of  $\text{PbSO}_4$  in pure water.  $K_{\text{sp}}(\text{PbSO}_4) = 1.82 \times 10^{-8}$ .
- $1.82 \times 10^{-8} \text{ M}$
  - $1.35 \times 10^{-4} \text{ M}$
  - $9.1 \times 10^{-9} \text{ M}$
  - $3.31 \times 10^{-16} \text{ M}$
  - $4.48 \times 10^{-4} \text{ M}$

- B 7. Write the reaction associated with the solubility product of  $\text{Pb}(\text{CO}_3)_2$ .
- $\text{Pb}^{4+}(\text{aq}) + 2\text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{Pb}(\text{CO}_3)_2(\text{s})$
  - $\text{Pb}(\text{CO}_3)_2(\text{s}) \rightleftharpoons \text{Pb}^{4+}(\text{aq}) + 2\text{CO}_3^{2-}(\text{aq})$
  - $\text{Pb}^{4+}(\text{aq}) + 2\text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{Pb}(\text{CO}_3)_2(\text{aq})$
  - $\text{Pb}(\text{s}) + \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Pb}(\text{CO}_3)_2(\text{s})$
  - None of the above

- B 8. Write the expression for the solubility product for  $\text{Pb}(\text{CO}_3)_2$ .
- $K_{\text{sp}} = [\text{Pb}(\text{CO}_3)_2]$
  - $K_{\text{sp}} = [\text{Pb}^{4+}][\text{CO}_3^{2-}]^2$
  - $K_{\text{sp}} = \frac{[\text{Pb}^{4+}][\text{CO}_3^{2-}]^2}{[\text{Pb}(\text{CO}_3)_2]}$
  - $K_{\text{sp}} = \frac{[\text{Pb}(\text{CO}_3)_2]}{[\text{Pb}^{4+}][\text{CO}_3^{2-}]^2}$
  - None of the above

- A 9. If an ionic compound is dissolved in an unsaturated solution, how does Q compare with  $K_{\text{sp}}$ .
- $Q < K_{\text{sp}}$
  - $Q > K_{\text{sp}}$
  - $Q = K_{\text{sp}}$
  - Q is totally unrelated to  $K_{\text{sp}}$ , so there is no way to tell
  - Q is related to K, but doesn't tell you if a solution is saturated

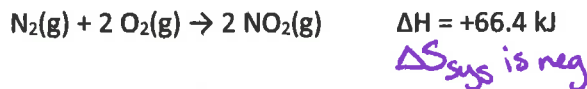
- C 10. Which of the following processes have a  $\Delta S > 0$ ?
- $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{s})$  ✗
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$  ✗
  - $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$  ✓
  - $\text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \rightarrow 2\text{NaHCO}_3(\text{s})$  ✗
  - All of the above processes have a  $\Delta S > 0$ .

- B 11. Which of the following statements is TRUE?
- a. Entropy is ~~not~~ a state function.
  - b. Endothermic processes decrease the entropy of the surroundings, at constant T and P. ✓
  - c. Endothermic processes are never spontaneous. *— they can be either*
  - d. Exothermic processes are always spontaneous.
  - e. None of the above are true.

- B 12. Consider a reaction that has a negative  $\Delta H$  and a positive  $\Delta S$ . Which of the following statements is TRUE?
- a. This reaction will be spontaneous only at high temperatures.
  - b. This reaction will be spontaneous at all temperatures.
  - c. This reaction will be nonspontaneous at all temperatures.
  - d. This reaction will be nonspontaneous only at high temperatures.
  - e. It is not possible to determine without more information.

- A 13. Consider a reaction that has a positive  $\Delta H$  and a positive  $\Delta S$ . Which of the following statements is TRUE?
- endo*  
*good. At high T this will overcome +ΔH*
- a. This reaction will be spontaneous only at high temperatures.
  - b. This reaction will be spontaneous at all temperatures.
  - c. This reaction will be nonspontaneous at all temperatures.
  - d. This reaction will be nonspontaneous only at high temperatures.
  - e. It is not possible to determine without more information.

- B 14. Consider the following reaction at constant P. Use the information here to determine the value of  $\Delta S_{\text{surr}}$  at 298 K. Predict whether or not this reaction will be spontaneous at this temperature based on what you know about the  $\Delta S_{\text{sys}}$ .



$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{-66.4 \text{ kJ}}{298 \text{ K}} = -223 \text{ J/K}$$

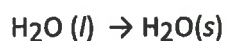
- a.  $\Delta S_{\text{surr}} = +223 \text{ J/K}$ , reaction is spontaneous
- b.  $\Delta S_{\text{surr}} = -223 \text{ J/K}$ , reaction is not spontaneous
- c.  $\Delta S_{\text{surr}} = -66.4 \text{ J/K}$ , reaction is spontaneous
- d.  $\Delta S_{\text{surr}} = +66.4 \text{ kJ/K}$ , reaction is not spontaneous
- e.  $\Delta S_{\text{surr}} = -66.4 \text{ J/K}$ , it is not possible to predict the spontaneity of this reaction without more information

$$\Delta S_{\text{Tot}} = -223 \text{ J/K} + -\Delta S_{\text{sys}}$$

*must be neg., so Non-spon.*

- E 15. What is the sign for  $\Delta G$  and  $\Delta S_{\text{univ}}$  for a spontaneous process?
- a. Both are positive
  - b. Both are negative
  - c.  $\Delta G$  is positive, and you must calculate  $\Delta S_{\text{univ}}$  to determine its sign
  - d.  $\Delta G$  is positive and  $\Delta S_{\text{univ}}$  is negative
  - e.  $\Delta G$  is negative and  $\Delta S_{\text{univ}}$  is positive

- A 16. For the following example, identify the following.



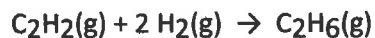
exothermic  $\Delta H^-$   
more ordered  $\Delta S^-$

- a negative  $\Delta H$  and a negative  $\Delta S$
- a positive  $\Delta H$  and a negative  $\Delta S$
- a negative  $\Delta H$  and a positive  $\Delta S$
- a positive  $\Delta H$  and a positive  $\Delta S$
- It is not possible to determine without more information.

- A 17. Choose the reaction that illustrates  $\Delta H^\circ_f$  for  $\text{Ca}(\text{NO}_3)_2$  which is a solid in its standard state.

- $\text{Ca}(s) + \text{N}_2(g) + 3\text{O}_2(g) \rightarrow \text{Ca}(\text{NO}_3)_2(s)$
- $\text{Ca}^{2+}(aq) + 2\text{NO}_3^-(aq) \rightarrow \text{Ca}(\text{NO}_3)_2(aq)$
- $\text{Ca}(s) + 2\text{N}(g) + 6\text{O}(g) \rightarrow \text{Ca}(\text{NO}_3)_2(s)$
- $\text{Ca}(\text{NO}_3)_2(aq) \rightarrow \text{Ca}^{2+}(aq) + 2\text{NO}_3^-(aq)$
- $\text{Ca}(\text{NO}_3)_2(s) \rightarrow \text{Ca}(s) + \text{N}_2(g) + 3\text{O}_2(g)$

- D 18. Calculate  $\Delta S^\circ_{\text{rxn}}$  for the following reaction. The  $S^\circ$  for each species is shown below the reaction.



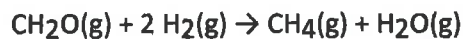
$S^\circ(\text{J/mol}\cdot\text{K})$       200.9      130.7      229.2

- +303.3 J/K
- +560.8 J/K
- 102.4 J/K
- 233.1 J/K
- 229.2 J/K

$$229.2 - [130.7 \times 2 + 200.9]$$

$$= -233.1 \text{ J/K}$$

- A 19. Calculate  $\Delta G^\circ_{\text{rxn}}$  for the following reaction at 449.0 K.



$\Delta H^\circ = -94.9 \text{ kJ}$ ;  $\Delta S^\circ = -224.2 \text{ J/K}$

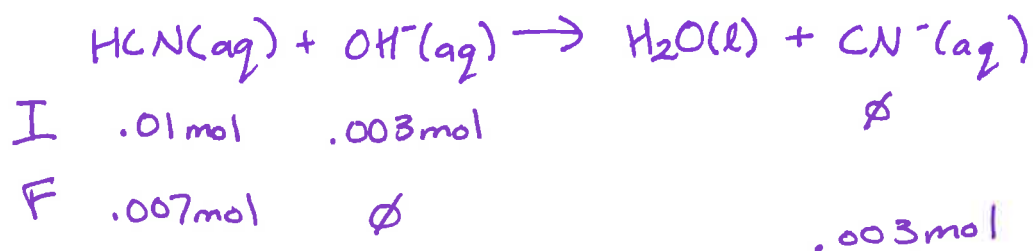
- +5.8 kJ
- +12.9 kJ
- 101 kJ
- +1.4 kJ
- 4.2 kJ

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

$$= -94.9 \text{ kJ} - 449.0 \text{ K} (-.2242 \text{ kJ/K})$$

$$= 5.8 \text{ kJ}$$

2. (15 Points) A 50.0 mL sample of 0.200 M HCN is titrated with 0.10M NaOH. Determine the pH of the solution after the addition of 30.0 mL of NaOH. (The  $K_a$  of HCN is  $4.9 \times 10^{-10}$ )



$$\text{pH} = \text{p}K_a + \log\left(\frac{.003}{.007}\right)$$

$$\boxed{= 8.94}$$

3. (10 Points) Above what temperature does the following reaction become nonspontaneous?

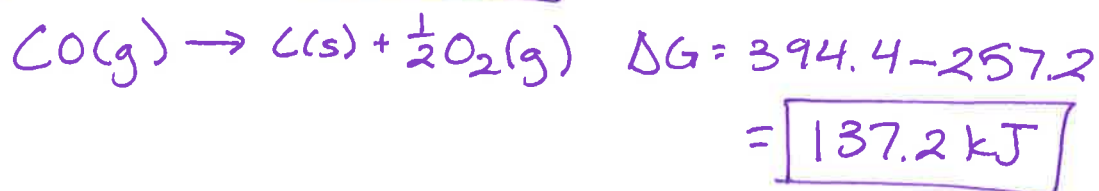
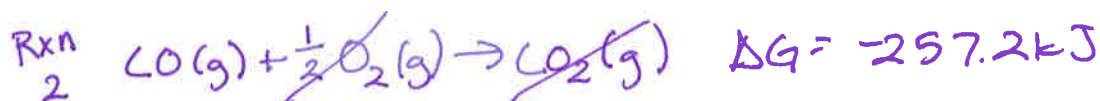
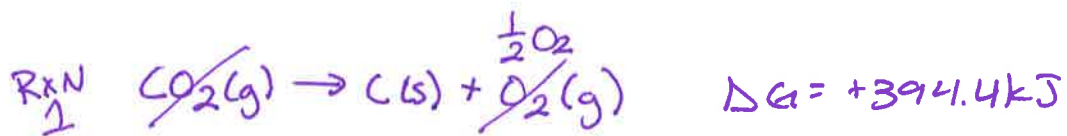
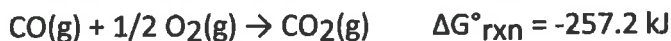
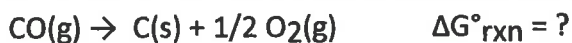


$$\Delta H = -1036 \text{ kJ}; \Delta S = -153.2 \text{ J/K}$$

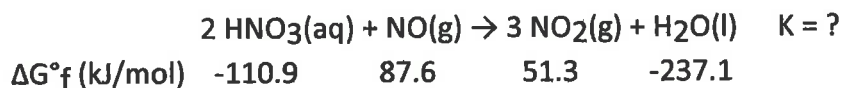
$$\Delta G = 0 = -1036 \text{ kJ} - T\left(-.1532 \frac{\text{kJ}}{\text{K}}\right)$$

$$\boxed{T = 6762 \text{ K}}$$

4. (12 Points) Use Hess's law to calculate  $\Delta G^\circ_{\text{rxn}}$  using the following information.



5. (8 Points) Use the free energies of formation given below to calculate the equilibrium constant (K) for the following reaction at 298 K.



$$\Delta G^\circ = [3(51.3 \text{ kJ}) + 1(-237.1 \text{ kJ})] - [2(-110.9 \text{ kJ}) + 1(87.6 \text{ kJ})]$$

$$= 51 \text{ kJ}$$

$$\Delta G^\circ = -RT \ln K$$

$$\frac{-51000}{8.314 \cdot 298} = -20.58 = \ln K$$

$$K = \boxed{1.15 \times 10^{-9}}$$