

CHM2046 S10: Exam #3 (2010.04.07)

**MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.**

- 1) This is FORM A. There were also forms B, C, D, and E on this exam.
- 2) Determine the molar solubility of AgBr in a solution containing 0.150 M NaBr.  $K_{sp}$  (AgBr) =  $7.7 \times 10^{-13}$ . Answer: B
- A)  $8.8 \times 10^{-7}$  M  
B)  $5.1 \times 10^{-12}$  M  
C) 0.150 M  
D)  $5.8 \times 10^{-5}$  M  
E)  $3.9 \times 10^{-13}$  M

This is relatively simple. The solubility of AgBr is just the concentration of the  $\text{Ag}^+$  ion. So,  $[\text{Ag}^+] = K_{sp}/[\text{Br}^-] = 7.7 \times 10^{-13}/0.150 = 5.1 \times 10^{-12}$  M.

- 3) (DIFFICULT) Calculate the  $\Delta G^\circ_{\text{rxn}}$  using the following information. Answer: C



$\Delta H^\circ_f$ (kJ/mol)	-207	91.3	33.2	-285.8
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$S^\circ$ (J/mol·K)	146	210.8	240.1	70.0
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- A) -85.5 kJ  
B) +222 kJ  
C) +50.8 kJ  
D) -151 kJ  
E) -186 kJ

This is not so much difficult as it is tedious! All you need to do is follow the First Law to get your answer:

$$\Delta H^\circ = 3(33.2) + (-285.8) - \{2(-207) + 91.3\} = +136.5 \text{ kJ}$$

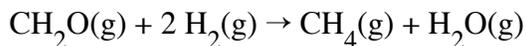
$$\Delta S^\circ = 3(240.1) + 70.0 - \{2(146) + 210.8\} = 287.5 \text{ J/K} = 0.2875 \text{ kJ/K}$$

$$T = 298.15 \text{ (by definition)}$$

$$\Delta G^\circ = +50.8 \text{ kJ ("C" appeared as +58.0 on the original exam; however, this is close enough to the original answer so as to be the best choice.)}$$

- 4) (DIFFICULT) Determine the equilibrium constant for the following reaction Answer: E

at 549 K.



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

- A)  $1.94 \times 10^{-12}$
- B) 481
- C)  $9.35 \times 10^{-10}$
- D)  $1.07 \times 10^9$
- E)  $2.08 \times 10^{-3}$

First, calculate  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -94.9 + (549)(0.2242) = +28.19 \text{ kJ} = -RT \ln K$ .  
 $\ln K = 28.19 / (-0.0083124472 \times 549) = -6.176$ ; thus  $K = 0.00208$ .

5) Give the expression for the solubility product constant for  $\text{Cr}_2(\text{CO}_3)_3$ . Answer: B

- A)  $\frac{[\text{Cr}^{3+}]^3[\text{CO}_3^{2-}]^2}{\text{Cr}_2(\text{CO}_3)_3}$
- B)  $[\text{Cr}^{3+}]^2[\text{CO}_3^{2-}]^3$
- C)  $\frac{\text{Cr}_2(\text{CO}_3)_3}{[\text{Cr}^{3+}]^2[\text{CO}_3^{2-}]^3}$
- D)  $[\text{Cr}^{3+}]^3[\text{CO}_3^{2-}]^2$
- E)  $\frac{[\text{Cr}^{3+}]^2[\text{CO}_3^{2-}]^3}{\text{Cr}_2(\text{CO}_3)_3}$

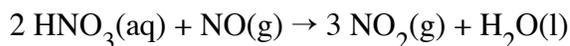
This is just a simple application of the definition for  $K_{\text{sp}}$ .

6) Which of the following does not have  $\Delta G_f^\circ = 0$ ? Answer: C

- A)  $\text{O}_2(\text{g})$
- B)  $\text{Fe}(\text{s})$
- C)  $\text{H}_2\text{O}(\text{l})$
- D)  $\text{I}_2(\text{s})$
- E)  $\text{He}(\text{g})$

All but (C) are *elements* in their free, most stable, states.

7) Below what temperature does the following reaction become nonspontaneous? Answer: A

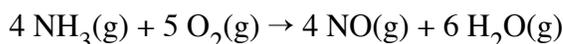


$$\Delta H = +136.5 \text{ kJ}; \Delta S = +287.5 \text{ J/K}$$

- A) 475 K
- B) 39.2 K
- C) 151 K
- D) This reaction is nonspontaneous at all temperatures.
- E) This reaction is spontaneous at all temperatures.

This is a simple division:  $T = 136.5/0.2875 = 475\text{K}$ . Note that the entropy was converted into kJ/K first!

- 8) Calculate  $\Delta S^\circ_{\text{rxn}}$  for the following reaction. The  $S^\circ$  for each species is shown **Answer: C** below the reaction.



$S^\circ(\text{J/mol}\cdot\text{K})$       192.8      205.2      210.8      188.8

- A) -401.2 J/K
- B) +287.4 J/K
- C) +178.8 J/K
- D) +160.0 J/K
- E) -336.6 J/K

This is a simple application of the First Law:

$$\Delta S^\circ = 6(188.8) + 4(210.8) - \{4(192.8) + 5(205.2)\} = +178.8 \text{ J/K}.$$

- 9) **(DIFFICULT)** A 100.0 mL sample of 0.20 M HF is titrated with 0.10 M **Answer: B** KOH. Determine the pH of the solution after the addition of 200.0 mL of KOH. The  $K_a$  of HF is  $3.5 \times 10^{-4}$ .

- A) 10.54
- B) 8.14
- C) 7.00
- D) 3.46
- E) 9.62

We have  $100.0(0.20) = 20$  mmol of acid and  $200.0(0.10) = 20$  mmol of base. **Thus, we are at the equivalence point and this is just a solution of the salt.** The total volume is just 300.0 mL. Thus, the concentration of the salt (conjugate base) is just  $20/300 = 0.0667\text{M}$ . For the conjugate, base,  $K_b = 2.86 \times 10^{-11}$ . So,  $[\text{OH}^-] \approx \sqrt{(2.86 \times 10^{-11} \times 0.0667)} = 1.38 \times 10^{-6}$ . Then,  $14.00 + \log(1.38 \times 10^{-6}) = 8.14$ .

- 10) A 1.0 L buffer solution is 0.250 M  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.050 M  $\text{LiC}_2\text{H}_3\text{O}_2$ . Which **Answer: B** of the following actions will destroy the buffer?
- A) adding 0.050 moles of  $\text{HC}_2\text{H}_3\text{O}_2$

- B) adding 0.050 moles of HCl
- C) adding 0.050 moles of NaOH
- D) adding 0.050 moles of  $\text{LiC}_2\text{H}_3\text{O}_2$
- E) None of the above will destroy the buffer.

We have 0.250 moles of acid and 0.050 moles of conjugate base here. So, either adding 0.250 moles of strong base or 0.050 moles of strong acid will destroy the buffer. The latter case is the answer, B. Adding more weak acid (A) or conjugate base (D) will certainly not destroy the buffer. Also, (C) has too little strong base to carry out the destruction. B is the obvious correct answer!

- 11) What effect will the addition of the reagent in each of the following have on the pH of a  $\text{CH}_3\text{COOH}$  solution, respectively? **Answer: E**

Flask 1: Addition of  $\text{NaCH}_3\text{CO}_2(\text{aq})$

Flask 2: Addition of  $\text{Ca}(\text{CH}_3\text{CO}_2)_2(\text{aq})$

- A) no change, increase
- B) no change, decrease
- C) decrease, no change
- D) decrease, decrease
- E) increase, increase

Both solutions are simply solutions of the conjugate base. Adding *any* base will increase the pH! Also, adding conjugate base--which enters into the numerator of the logarithmic term of the HH equation would also increase the pH. So, (E) should be obvious!

- 12) Determine the molar solubility of  $\text{Fe}(\text{OH})_2$  in pure water.  $K_{\text{sp}}(\text{Fe}(\text{OH})_2) = 4.87 \times 10^{-17}$ . **Answer: C**

- A)  $2.44 \times 10^{-17} \text{ M}$
- B)  $3.65 \times 10^{-6} \text{ M}$
- C)  $2.30 \times 10^{-6} \text{ M}$
- D)  $1.62 \times 10^{-17} \text{ M}$
- E)  $4.03 \times 10^{-9} \text{ M}$

This is a 1:2 electrolyte. For such,  $s = (K_{\text{sp}}/4)^{1/3}$ . Thus,  $s = (4.87 \times 10^{-17}/4)^{1/3} = 2.30 \times 10^{-6} \text{ M}$ .

- 13) **(DIFFICULT)** Consider the following reaction. Use the information here to determine the value of  $\Delta S_{\text{surr}}$  at 355 K. Predict whether or not this reaction will be spontaneous at this temperature. **Answer: E**



- A)  $\Delta S_{\text{surr}} = +114 \text{ kJ/K}$ , reaction is spontaneous
- B)  $\Delta S_{\text{surr}} = +114 \text{ kJ/K}$ , reaction is not spontaneous
- C)  $\Delta S_{\text{surr}} = -321 \text{ J/K}$ , reaction is not spontaneous
- D)  $\Delta S_{\text{surr}} = +321 \text{ J/K}$ , reaction is spontaneous
- E)  $\Delta S_{\text{surr}} = +321 \text{ J/K}$ , it is not possible to predict the spontaneity of this reaction without more information.

The reaction is exothermic. Thus,  $\Delta S_{\text{surr}} = 114000/355 = +321 \text{ J/K}$ . *However*, you were *not* given the entropies of the compounds. You need these to determine if  $\Delta S_{\text{univ}} > 0$ . That is, you cannot get  $\Delta S_{\text{sys}}$  and, thus, cannot complete the calculation. Hence, (E) is the correct answer.

- 14) Calculate the pH of a solution formed by mixing 100.0 mL of 0.20 M HClO with 200.0 mL of 0.30 M KClO. The  $K_a$  for HClO is  $2.9 \times 10^{-8}$ . Answer: E

- A) 7.71
- B) 5.99
- C) 7.54
- D) 6.46
- E) 8.01

This is a straight Henderson-Hasselbalch calculation. You have 60 mmol of conjugate base and 20 mmol of acid.  $\text{p}K_a = -\log(2.9 \times 10^{-8}) = 7.54$ . So,  $\text{pH} = 7.54 + \log(60/20) = 8.01$ .

- 15) Which of the following processes have a  $\Delta S > 0$ ? Answer: C

- A)  $2 \text{HBr}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{Br}_2(\text{l})$
- B) lithium fluoride forms from its elements
- C) sodium chloride dissolves in pure water.
- D)  $2 \text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{NH}_2\text{CONH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- E) All of the above processes have a  $\Delta S > 0$ .

(C) is the clearest choice since the ions are dispersed into a larger volume and a crystal is dissolved. All the other processes have either a negative or nearly zero entropy.

- 16) Which ONE of the following statements is TRUE? Answer: A

- A) A buffer resists pH change by reacting with both acids and bases.

- B) A buffer does not change pH when strong acid or base is added.
- C) A buffer can absorb an unlimited amount of acid or base.
- D) A buffer is an aqueous solution composed of two weak acids.
- E) None of the above are true.

(A) should be obvious. (B) is false since that could contradict the HH equation. (C) is absurd.

(D) would simply be an acidic solution with no buffer properties.

17) Which of the following compounds will have the highest molar solubility in pure water? Answer: A

- A)  $\text{MgCO}_3$ ,  $K_{\text{sp}} = 6.82 \times 10^{-6}$
- B)  $\text{PbS}$ ,  $K_{\text{sp}} = 9.04 \times 10^{-29}$
- C)  $\text{FeS}$ ,  $K_{\text{sp}} = 3.72 \times 10^{-19}$
- D)  $\text{AgI}$ ,  $K_{\text{sp}} = 8.51 \times 10^{-17}$
- E)  $\text{PbSO}_4$ ,  $K_{\text{sp}} = 1.82 \times 10^{-8}$

All these are 1:1 electrolytes; that is they are all the same type of electrolyte. Thus, the largest

$K_{\text{sp}}$  value would correspond to the greatest solubility. Thus, (A) should be obvious!

18) Consider a reaction that has a positive  $\Delta H$  and a negative  $\Delta S$ . Which of the following statements is TRUE? Answer: A

- A) This reaction will be nonspontaneous at all temperatures.
- B) This reaction will be spontaneous at all temperatures.
- C) This reaction will be spontaneous only at high temperatures.
- D) This reaction will be nonspontaneous only at high temperatures.
- E) It is not possible to determine without more information.

$\Delta G = \Delta H - T\Delta S > 0$  for all possible values of T here. Thus, (A) should be obvious!

19) Place the following in order of increasing molar entropy at 298 K. Answer: E

- NO   CO   SO
- A)  $\text{SO} < \text{CO} < \text{NO}$
  - B)  $\text{CO} < \text{SO} < \text{NO}$
  - C)  $\text{SO} < \text{NO} < \text{CO}$
  - D)  $\text{NO} < \text{CO} < \text{SO}$
  - E)  $\text{CO} < \text{NO} < \text{SO}$

All of these are diatomic oxides. Thus, the only determiner of S here would be the size.

So, the ordering by MW gives (E) as the obvious answer. Alternatively, CO, NO, and SO have 12, 13, and 24 electrons, respectively.

- 20) If the  $pK_a$  of  $\text{HCHO}_2$  is 3.74 and the pH of an  $\text{HCHO}_2/\text{NaCHO}_2$  solution is 3.74, which of the following is TRUE? **Answer: A**
- A)  $[\text{HCHO}_2] = [\text{NaCHO}_2]$
  - B)  $[\text{HCHO}_2] < [\text{NaCHO}_2]$
  - C)  $[\text{HCHO}_2] < < [\text{NaCHO}_2]$
  - D)  $[\text{HCHO}_2] > [\text{NaCHO}_2]$
  - E) It is not possible to make a buffer of this pH from  $\text{HCHO}_2$  and  $\text{NaCHO}_2$ .

When  $\text{pH} = pK_a$ , it should be obvious that  $[\text{HCHO}_2] = [\text{NaCHO}_2]$ . This is about as simple as an HH problem can get.

- 21) A 100.0 mL sample of 0.10 M  $\text{Ca}(\text{OH})_2$  is titrated with 0.10 M HBr. **Answer: D**  
Determine the pH of the solution before the addition of any HBr.
- A) 1.00
  - B) 13.00
  - C) 12.86
  - D) 13.30
  - E) 0.70

**Before** the addition of any acid, the hydroxide ion concentration is 0.20 M. (Please remember that 0.10 moles of calcium hydroxide would release 0.20 moles of hydroxide ion--simple stoichiometry.) So,  $\text{pH} = 14.00 + \log(0.20) = 13.30$ .

- 22) When titrating a weak monoprotic acid with NaOH at 25°C, the **Answer: E**
- A) pH will be less than 7 at the equivalence point.
  - B) titration will require more moles of base than acid to reach the equivalence point.
  - C) pH will be equal to 7 at the equivalence point.
  - D) titration will require more moles of acid than base to reach the equivalence point.
  - E) pH will be greater than 7 at the equivalence point.

At the equivalence point, you have the salt of a weak acid with a strong base. Strong beats weak! Thus,  $\text{pH} > 7$ . None of the other answers can be true.

- 23) (**DIFFICULT**) A solution is made to be  $2.2 \times 10^{-3}$  M in  $\text{Cu}^{2+}$  and 0.33 M in  $\text{LiCN}$ . If the  $K_f$  for  $\text{Cu}(\text{CN})_4^{2-}$  is  $1.0 \times 10^{25}$ , how much copper ion remains at equilibrium? **Answer: C**
- A)  $3.8 \times 10^{-24}$  M
  - B)  $4.6 \times 10^{-25}$  M

- C)  $2.1 \times 10^{-26}$  M
- D)  $2.9 \times 10^{-27}$  M
- E) 0.0 M

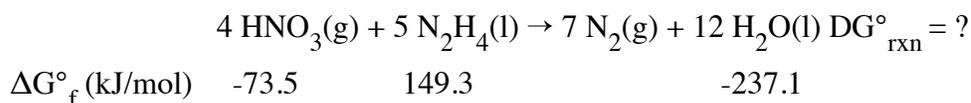
This is a problem involving a large  $K$ . Thus, it is best to first run the reaction to completion. When you do, stoichiometry says that you would have  $[\text{Cu}^{2+}] = 0$ ,  $[\text{Cu}(\text{CN})_4^{2-}] = 0.0022\text{M}$  and  $[\text{CN}^-] = 0.33 - 4(0.0022) = 0.32$  M. Then, since the amount of copper(II) ion would be small, it is easy to rearrange the equation to get  $[\text{Cu}^{2+}] = 0.0022 / (1.0 \times 10^{25} \times (0.32)^4) = 2.1 \times 10^{-26}$  M.

You can check this answer by reverse engineering:  $K_f = 0.0022 / \{2.1 \times 10^{-26} \times 0.32^4\} = 1.0 \times 10^{25}$ .

- 24) Which of the following statements is TRUE? Answer: C
- A) Exothermic processes are always spontaneous.
  - B) Endothermic processes are never spontaneous.
  - C) Endothermic processes decrease the entropy of the surroundings.
  - D) Entropy is not a state function.
  - E) None of the above are true.

Only (C) is always true!

- 25) Calculate the  $\Delta G^\circ_{\text{rxn}}$  using the following information. Answer: B



- A) +110.7 kJ
- B)  $-3.298 \times 10^3$  kJ
- C) -312.9 kJ
- D)  $+2.845 \times 10^3$  kJ
- E) -954.7 kJ

This is a straightforward application of the First Law. For this problem,

$$\Delta G^\circ_{\text{rxn}} = 12(-237.1) + 7(0) - \{4(-73.5) + 5(149.3)\} = -2845.2 - (+452.5) = -3297.7 \text{ kJ}$$