Vers. A

CHEM 1423 - Exam 4 – April 20, 2017

Name Solutions

The Gas Constant is: R = 8.31 J/mol-K = 8.31×10^{-3} kJ/mol-K

(76) **PART I. MULTIPLE CHOICE (Circle the ONE correct answer)**

1. The solubility of lead (II) arsenate, $Pb_3(AsO_4)_2$, in pure water is 3.3×10^{-8} M. The solublility product, K_{sp}, of lead (II) arsenate is approximately:

   (A) 1.4×10^{-36} (B) 3.9×10^{-38} (C) 2.8×10^{-36} (D) 4.2×10^{-36}

For #2 - #3: consider the slightly soluble compound, $PbI_2(s)$. The solubility product (aka solubility constant) is $K_{sp} = 1.4 \times 10^{-8}$.

2. What is the Iodide concentration, $[I^-]$, when PbI_2 is dissolved in water?

   (A) 3.0×10^{-3} M (B) 1.2×10^{-4} M (C) 4.8×10^{-3} M (D) 1.5×10^{-3} M

3. What is the solubility of $PbI_2(s)$ in a 0.01 M solution of the strong electrolyte, $Pb(NO_3)_2(aq)$?

   (A) 1.2×10^{-3} M (B) 5.9×10^{-4} M (C) 1.2×10^{-2} M (D) 7.3×10^{-8} M

4. The solubility products of two sparingly soluble Bromide (Br^-) salts are:
   AgBr - $K_{sp} = 5.4 \times 10^{-13}$, $HgBr_2$ - $K_{sp} = 6.2 \times 10^{-20}$.

   Consider a solution which initially contains 5.0×10^{-5} M $Ag^+(aq)$ and 4.0×10^{-5} M $Hg^{2+}(aq)$. KBr (a strong electrolyte) is added until $[Br^-] = 5.0 \times 10^{-8}$ M. Which of the above salts will form any solid precipitate?

   (A) AgBr only (B) $HgBr_2$ only (C) Both AgBr and $HgBr_2$

   (D) Neither AgBr nor $HgBr_2$

5. Which of the following statements is/are correct?

   (1) The entropy change on condensing a gas is negative
   (2) The entropy usually decreases when a gas is dissolved in a liquid
   (3) The entropy of $CaCO_3(s)$ is higher than the entropy of CaO(s)
   (4) The entropy generally decreases when a solid dissolves in a liquid

   (A) 2 & 3 & 4 (B) 1 & 3 (C) 1 & 2 & 3 (D) 1 & 2 & 4

6. The normal melting point of toluene is -95 °C. The Enthalpy of Fusion of toluene is 6.6 kJ/mol. What is the entropy change of the **surroundings** when one mole of liquid toluene crystallizes to solid toluene at -95 °C?

   (A) -48.3 J/mol-K (B) +37 J/mol-K (C) +69 J/mol-K (D) -37 J/mol-K

Vers. A

7. Consider the reaction: $2\ Ca(s) + O_2(g) \rightarrow 2\ MgO(s)$, $\Delta H^o < 0$. This reaction is:

   (A) Reactant Favored at all temperatures

   (B) Product Favored at all temperatures

   (C) Product Favored at low temperature

   (D) Product Favored at high temperature

For #8 - #9: Consider the reaction: $2\ SO_3(g) \rightarrow 2\ SO_2(g) + O_2(g)$ at 25 °C

	$SO_2(g)$	$SO_3(g)$	$O_2(g)$
S_m^o(25 °C)	248 J/mol-K	257 J/mol-K	205 J/mol-K
ΔG_f^o(25 °C)	-297 kJ/mol	-396 kJ/mol	

8. What is ΔG^o for the above reaction [at 25 °C] ?

   (A) +198 kJ (B) +99 kJ (C) -198 kJ

   (D) Insufficient data is available

9. What is ΔH^o for the above reaction [at 25 °C]?

   (A) -142 kJ (B) +254 kJ (C) +142 kJ

   (D) Insufficient data is available

10. For the hypothetical reaction, $A \rightleftharpoons B$, $\Delta H^o = +50$ kJ/mol (independent of temperature). The equilibrium constant for the reaction at 400 °C is 1.0×10^{-8}. What is the entropy change, ΔS^o for this reaction?

    (A) -28 J/K (B) +79 J/K (C) -42 J/K (D) -79 J/K

11. The reaction A → B is **exergonic** at 25 °C and the enthalpy change is +45 kJ. What can be concluded about the entropy change for this reaction?

    (A) $\Delta S < -70$ J/K (B) $\Delta S > +150$ J/K

    (C) $\Delta S < -150$ J/K (C) $\Delta S = \frac{\Delta H}{T}$

12. For the **endergonic** reaction, C → D, $\Delta S = +50$ J/K For this reaction,

    (A) $\Delta G>0$ & $\Delta H>0$ (B) $\Delta G>0$ & $\Delta H<0$

    (C) $\Delta G<0$ & $\Delta H>0$ (D) $\Delta G<0$ & $\Delta H<0$

13. Consider the reaction, $2\ HI(g) \rightleftharpoons H_2(g) + I_2(s)$ at 25 °C. The Gibbs Free Energy of Formation of HI(g) is +1.70 kJ/mol. Therefore, the equilibrium constant for the above reaction at 25 °C is approximately:

    (A) 0.25 (B) 2.0 (C) 3.9 (D) 2.4

Vers. A

14. For the reaction, 2 $C_2H_2(g)$ + 4 $H_2(g)$ → 2 $C_2H_6(g)$, ΔS° = -470 J/K and ΔH° = -620 kJ. What is the entropy change of the **system**, ΔS_{sys}, for the related reaction, $C_2H_6(g) \rightarrow C_2H_2(g) + 2\ H_2(g)$ at 25 °C?

(A) +235 J/K (B) +1040 J/K (C) +470 J/K (D) -1040 J/K

For #15 - #16: The Enthalpy of Fusion of I_2(sol) is 7.80 kJ/mol. The Entropy of Fusion of I_2(sol) is 19.6 J/mol-K.

15. The Entropy change of the universe, ΔS_{univ}, when one mole of I_2(liq) crystallizes to I_2(sol) at 80 °C is approximately:

(A) -2.5 J/mol-K (B) +7.7 J/mol-K (C) +2.5 J/mol-K

(D) None of the above

16. The Gibbs Energy Change, ΔG°, when 1 mole of I_2(liq) crystallizes to I_2(sol) at 150 °C is approximately:

(A) -0.5 kJ/mol (B) -4.9 kJ/mol (C) +4.9 kJ/mol (D) +0.5 kJ/mol

17. In class we discussed the transformation of a protein (e.g. Ribonucleus) between the Native and Random Coil forms with variation in temperature. Consider a hypothetical protein with two native forms, α and β. For the transition from the α to the β structure, $\alpha \rightarrow \beta$, the enthalpy and entropy changes are: ΔH° = -140 kJ/mol and ΔS° = -420 J/mol-K. For this protein, the _____ form is the more stable one at all temperatures **above** _____ °C.

(A) α , 60 °C (B) α , 333 °C (C) β , 47 °C (D) β , 60 °C

18. In class, we discussed the thermodynamics involved in Base Pairing in the formation of Doubly-Coiled DNA from the individual DNA strands. Consider the denaturation of a DNA double coil. This involves the breaking of base pairs such as Cytosine-Guanine (C-G). For the **breaking** of one of these base pairs, i.e. C-G → C + G, the process is _____ by ΔH° and _____ by ΔS°.

(A) favored, favored (B) favored, disfavored

(C) disfavored, favored (D) disfavored, disfavored

19. Regarding the following reaction, which of the statements below is/are correct?

$$Fe_2S_3(s) + 3\ GeS(g) \rightarrow 2\ Fe + 3\ GeS_2(g)$$

✓(1) Fe_2S_3 is the oxidizing agent ✗(2) GeS_2 is oxidized

✗(3) 3 electrons are transfered ✗(4) GeS is reduced

(A) 2 & 4 (B) 1 & 3 (C) 1 & 2 & 3 (D) 1 only

PART II. TWO (2) PROBLEMS : REMEMBER TO SHOW WORK FOR CREDIT

The Gas Constant is: R = 8.31 J/mol-K = 8.31×10^{-3} kJ/mol-K

Vers. A

$T = 50^\circ C = 323 K$

(14) 1. For the reaction, $2\ NH_3(g) \rightleftharpoons N_2(g) + 3\ H_2(g)$, $\Delta H^\circ = +92$ kJ and $\Delta S^\circ = +360$ J/K.

(6) (a) Calculate the equlibrium constant, K, for this reaction at 50 °C, **in kJ**.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +92,000\ J - (323\ K)(360\ J/K) = -24,280\ J$

$\Delta G^\circ = -RT\ln K \rightarrow \ln K = -\frac{\Delta G^\circ}{RT} = -\frac{-24,280}{(8.31)(323)} = +9.05$

$K = e^{9.05} = \boxed{8.48 \times 10^3}$

(4) (b) Calculate the value of ΔG for this reaction at 50 °C when the pressures are: $P(N_2) = P(H_2) = 15.0$ bar, $P(NH_3) = 0.10$ bar.

$Q = \frac{P_{N_2} P_{NH_3}^3}{P_{NH_3}^2}$

$= \frac{(15)(15)^3}{(0.1)^2}$

$= 5.063 \times 10^6$

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

$= -24280 + (8.31)(323)\ln(5.063 \times 10^6)$

$= -24,280 + 41,440\ J$

$= \boxed{17,160\ J = 17.2\ kJ}$

(4) (c) Calculate the temperature, **in °C**, at which reactants and products are in equilibrium under standard conditions. Is the reaction **Reactant favored** or **Product favored** at temperatures higher than this.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$

$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{92,000\ J}{360\ J/K}$

$= 256\ K - 273 = \boxed{-17^\circ C}$

Product favored at higher T.

Vers A & B

(10) 2. Balance the following oxidation-reduction reaction in **aqueous Basic** solution.

$$\underset{+6}{Mo_2O_7^{2-}} + \underset{+4}{SO_2} \rightarrow \underset{+3}{Mo^{3+}} + \underset{+6}{SO_4^{2-}}$$

Oxid: $SO_2 \rightarrow SO_4^{2-}$

Red. $Mo_2O_7^{2-} \rightarrow Mo^{3+}$ ← need Mo^{3+} by 2

Ox: Add: $2H_2O$ to left, $4H^+$ to right; $2e^-$ to right

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Red. Add $7H_2O$ to right, $14H^+$ to left, $6e^-$ to left

$$Mo_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Mo^{3+} + 7H_2O$$

(3 x Ox) + (1 x Red.)

$$3SO_2 + 6H_2O + Mo_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 3SO_4^{2-} + 12H^+ + 6e^- + 2Mo^{3+} + 7H_2O$$

Cancel H^+, H_2O, e^-

$$3SO_2 + Mo_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Mo^{3+} + H_2O$$

Add $2OH^-$ to each side & cancel H_2O's.

$$3SO_2 + Mo_2O_7^{2-} + H_2O \rightarrow 3SO_4^{2-} + 2Mo^{3+} + 2OH^-$$

Vers. B

CHEM 1423 - Exam 4 – April 20, 2017

Name Solutions

The Gas Constant is: R = 8.31 J/mol-K = 8.31×10^{-3} kJ/mol-K

(76) **PART I. MULTIPLE CHOICE (Circle the ONE correct answer)**

For #1 - #2: consider the slightly soluble compound, $PbI_2(s)$. The solubility product (aka solubility constant) is $K_{sp} = 1.4 \times 10^{-8}$.

1. What is the Iodide concentration, $[I^-]$, when PbI_2 is dissolved in water?

   (A) 4.8×10^{-3} M (B) 1.2×10^{-4} M (C) 3.0×10^{-3} M (D) 1.5×10^{-3} M

2. What is the solubility of $PbI_2(s)$ in a 0.01 M solution of the strong electrolyte, $Pb(NO_3)_2(aq)$?

   (A) 1.2×10^{-3} M (B) 7.3×10^{-8} M (C) 1.2×10^{-2} M (D) 5.9×10^{-4} M

3. The solubility of lead (II) arsenate, $Pb_3(AsO_4)_2$, in pure water is 3.3×10^{-8} M. The solublility product, K_{sp}, of lead (II) arsenate is approximately:

   (A) 4.2×10^{-36} (B) 3.9×10^{-38} (C) 2.8×10^{-36} (D) 1.4×10^{-36}

4. The solubility products of two sparingly soluble Bromide (Br^-) salts are:
   AgBr - $K_{sp} = 5.4 \times 10^{-13}$, $HgBr_2$ - $K_{sp} = 6.2 \times 10^{-20}$.

   Consider a solution which initially contains 5.0×10^{-5} M $Ag^+(aq)$ and 4.0×10^{-5} M $Hg^{2+}(aq)$. KBr (a strong electrolyte) is added until $[Br^-] = 5.0 \times 10^{-8}$ M. Which of the above salts will form any solid precipitate?

   (A) AgBr only (B) $HgBr_2$ only (C) Neither AgBr and $HgBr_2$
   (D) Both AgBr and $HgBr_2$

5. The normal melting point of toluene is -95 °C. The Enthalpy of Fusion of toluene is 6.6 kJ/mol. What is the entropy change of the **surroundings** when one mole of liquid toluene crystallizes to solid toluene at -95 °C?

   (A) -48.3 J/mol-K (B) +37 J/mol-K (C) +69 J/mol-K (D) -37 J/mol-K

6. Which of the following statements is/are correct?

   (1) The entropy change on condensing a gas is negative
   (2) The entropy usually decreases when a gas is dissolved in a liquid
   (3) The entropy of $CaCO_3(s)$ is higher than the entropy of $CaO(s)$
   (4) The entropy generally decreases when a solid dissolves in a liquid

   (A) 2 & 3 & 4 (B) 1 & 3 (C) 1 & 2 & 3 (D) 1 & 2 & 4

Vars. B

For #7 - #8: Consider the reaction: $2\ SO_3(g) \rightarrow 2\ SO_2(g) + O_2(g)$ at 25 °C

	$SO_2(g)$	$SO_3(g)$	$O_2(g)$
$S_m°$(25 °C)	248 J/mol-K	257 J/mol-K	205 J/mol-K
$\Delta G_f°$(25 °C)	-297 kJ/mol	-396 kJ/mol	

7. What is $\Delta G°$ for the above reaction [at 25 °C] ?

   (A) -198 kJ (B) +99 kJ (C) +198 kJ

   (D) Insufficient data is available

8. What is $\Delta H°$ for the above reaction [at 25 °C]?

   (A) +254 kJ (B) -142 kJ (C) +142 kJ

   (D) Insufficient data is available

9. Consider the reaction: $2\ Ca(s) + O_2(g) \rightarrow 2\ MgO(s)$, $\Delta H° < 0$. This reaction is:

   (A) Reactant Favored at all temperatures

   (B) Product Favored at all temperatures

   (C) Product Favored at high temperature

   (D) Product Favored at low temperature

10. Consider the reaction, $2\ HI(g) \rightleftharpoons H_2(g) + I_2(s)$ at 25 °C. The Gibbs Free Energy of Formation of HI(g) is +1.70 kJ/mol. Therefore, the equilibrium constant for the above reaction at 25 °C is approximately:

    (A) 0.25 (B) 3.9 (C) 2.4 (D) 2.0

11. For the **endergonic** reaction, C → D, ΔS = +50 J/K For this reaction,

    (A) $\Delta G<0$ & $\Delta H<0$ (B) $\Delta G>0$ & $\Delta H<0$

    (C) $\Delta G<0$ & $\Delta H>0$ (D) $\Delta G>0$ & $\Delta H>0$

12. The reaction A → B is **exergonic** at 25 °C and the enthalpy change is +45 kJ. What can be concluded about the entropy change for this reaction?

    (A) $\Delta S > +150$ J/K (B) $\Delta S < -150$ J/K

    (C) $\Delta S < -70$ J/K (C) $\Delta S = \frac{\Delta H}{T}$

13. For the hypothetical reaction, A ⇌ B, $\Delta H° = +50$ kJ/mol (independent of temperature). The equilibrium constant for the reaction at 400 °C is 1.0×10^{-8}. What is the entropy change, $\Delta S°$ for this reaction?

    (A) -28 J/K (B) +79 J/K (C) -42 J/K (D) -79 J/K

Vers. B

For #15 - #16: The Enthalpy of Fusion of I_2(sol) is 7.80 kJ/mol. The Entropy of Fusion of I_2(sol) is 19.6 J/mol-K.

15. The Entropy change of the universe, ΔS_{univ}, when one mole of I_2(liq) crystallizes to I_2(sol) at 80 °C is approximately:

(A) +2.5 J/mol-K (B) +7.7 J/mol-K (C) -2.5 J/mol-K

(D) None of the above

16. The Gibbs Energy Change, ΔG^o, when 1 mole of I_2(liq) crystallizes to I_2(sol) at 150 °C is approximately:

(A) -0.5 kJ/mol (B) -4.9 kJ/mol (C) +0.5 kJ/mol (D) +4.9 kJ/mol

14. For the reaction, 2 C_2H_2(g) + 4 H_2(g) → 2 C_2H_6(g), ΔS^o = -470 J/K and ΔH^o = -620 kJ. What is the entropy change of the **system**, ΔS_{sys}, for the related reaction, C_2H_6(g) → C_2H_2(g) + 2 H_2(g) at 25 °C?

(A) +1040 J/K (B) +235 J/K (C) +470 J/K (D) -1040 J/K

18. In class, we discussed the thermodynamics involved in Base Pairing in the formation of Doubly-Coiled DNA from the individual DNA strands. Consider the denaturation of a DNA double coil. This involves the breaking of base pairs such as Cytosine-Guanine (C-G). For the **breaking** of one of these base pairs, i.e. C-G → C + G, the process is _____ by ΔH^o and _____ by ΔS^o.

(A) favored, favored (B) disfavored, favored

(C) favored, disfavored (D) disfavored, disfavored

17. In class we discussed the transformation of a protein (e.g. Ribonucleus) between the Native and Random Coil forms with variation in temperature. Consider a hypothetical protein with two native forms, α and β. For the transition from the α to the β structure, $\alpha \rightarrow \beta$, the enthalpy and entropy changes are: ΔH^o = -140 kJ/mol and ΔS^o = -420 J/mol-K. For this protein, the _____ form is the more stable one at all temperatures **above** _____ °C.

(A) β , 60 °C (B) α , 333 °C (C) β , 47 °C (D) α , 60 °C

19. Regarding the following reaction, which of the statements below is/are correct?

$$Fe_2S_3(s) + 3\ GeS(g) \rightarrow 2\ Fe + 3\ GeS_2(g)$$

(1) Fe_2S_3 is the oxidizing agent (2) GeS_2 is oxidized

(3) 3 electrons are transfered (4) GeS is reduced

(A) 2 & 4 (B) 1 & 2 & 3 (C) 1 only (D) 1 & 3

PART II. TWO (2) PROBLEMS : REMEMBER TO SHOW WORK FOR CREDIT

The Gas Constant is: R = 8.31 J/mol-K = 8.31×10^{-3} kJ/mol-K

$T = 60 + 333\,K$ Ver. B

(14) 1. For the reaction, $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$, $\Delta H^o = +92$ kJ and $\Delta S^o = +360$ J/K.

(6) (a) Calculate the equlibrium constant, K, for this reaction at 60 °C, **in kJ**.

$\Delta G^o = \Delta H^o - T\Delta S^o = +92{,}000 - (333)(360) = -27{,}880\ J$

$\Delta G^o = -RT\ln K \rightarrow \ln K = -\frac{\Delta G^o}{RT} = \frac{-(-27880)}{(8.31)(333)} = 10{,}08$

$K = e^{10{,}08} = \boxed{2.37 \times 10^4}$

(4) (b) Calculate the value of ΔG for this reaction at 60 °C when the pressures are: $P(N_2) = P(H_2) = 12.0$ bar, $P(NH_3) = 0.10$ bar.

$Q = \frac{P_{N_2} P_{H_2}^3}{P_{NH_3}^2}$

$= \frac{(12)(12)^3}{(0.1)^2}$

$= 2.074 \times 10^6$

$\Delta G = \Delta G^o + RT\ln Q$

$= -27{,}880 + (8.31)(333)\ln(2.074 \times 10^6)$

$= -27{,}780 + 40{,}250$

$= \boxed{+12{,}470\ J = 12.5\ kJ}$

(4) (c) Calculate the temperature, **in °C**, at which reactants and products are in equilibrium under standard conditions. Is the reaction **Reactant favored** or **Product favored** at temperatures higher than this.

$\Delta G^o = \Delta H^o - T\Delta S^o = 0$

$T = \frac{\Delta H^o}{\Delta S^o} = \frac{92{,}000\ J}{360\ J/K}$

$= 258\,K - 273 = \boxed{-17^oC}$

Product favored at high Temp.

Vers A & B

(10) 2. Balance the following oxidation-reduction reaction in **aqueous Basic** solution.

$$\underset{+6}{Mo_2O_7^{2-}} + \underset{+4}{SO_2} \rightarrow \underset{+3}{Mo^{3+}} + \underset{+6}{SO_4^{2-}}$$

Oxid: $SO_2 \rightarrow SO_4^{2-}$

Red. $Mo_2O_7^{2-} \rightarrow Mo^{3+}$ ← multiply by 2

Ox: Add: $2H_2O$ to left, $4H^+$ to right; $2e^-$ to right

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Red. Add $7H_2O$ to right, $14H^+$ to left, $6e^-$ to left

$$Mo_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Mo^{3+} + 7H_2O$$

(3 x Ox) + (1 x Red.)

$$3SO_2 + 6H_2O + Mo_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 3SO_4^{2-} + 12H^+ + 6e^- + 2Mo^{3+} + 7H_2O$$

Cancel H^+, H_2O, e^-

$$3SO_2 + Mo_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Mo^{3+} + H_2O$$

Add $2OH^-$ to each side & cancel H_2O's.

$$3SO_2 + Mo_2O_7^{2-} + H_2O \rightarrow 3SO_4^{2-} + 2Mo^{3+} + 2OH^-$$