

The Gas Constant is: $R = 8.31 \text{ J/mol-K} = 8.31 \times 10^{-3} \text{ kJ/mol-K}$

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

1. The solubility of lead (II) arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, in pure water is $3.3 \times 10^{-8} \text{ M}$. The solubility 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, $\text{PbI}_2(\text{s})$. The solubility product (aka solubility constant) is $K_{sp} = 1.4 \times 10^{-8}$.

2. What is the iodide concentration, $[\text{I}^-]$, when PbI_2 is dissolved in water?
- (A) $3.0 \times 10^{-3} \text{ M}$ (B) $1.2 \times 10^{-4} \text{ M}$ (C) $4.8 \times 10^{-3} \text{ M}$ (D) $1.5 \times 10^{-3} \text{ M}$
3. What is the solubility of $\text{PbI}_2(\text{s})$ in a 0.01 M solution of the strong electrolyte, $\text{Pb}(\text{NO}_3)_2(\text{aq})$?
- (A) $1.2 \times 10^{-3} \text{ M}$ (B) $5.9 \times 10^{-4} \text{ M}$ (C) $1.2 \times 10^{-2} \text{ M}$ (D) $7.3 \times 10^{-8} \text{ M}$
4. The solubility products of two sparingly soluble Bromide (Br) salts are:
 $\text{AgBr} - K_{sp} = 5.4 \times 10^{-13}$, $\text{HgBr}_2 - K_{sp} = 6.2 \times 10^{-20}$.

Consider a solution which initially contains $5.0 \times 10^{-5} \text{ M Ag}^+(\text{aq})$ and $4.0 \times 10^{-5} \text{ M Hg}^{2+}(\text{aq})$. KBr (a strong electrolyte) is added until $[\text{Br}^-] = 5.0 \times 10^{-8} \text{ M}$. 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 $\text{CaCO}_3(\text{s})$ is higher than the entropy of $\text{CaO}(\text{s})$
 ✗(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 $-95 \text{ }^\circ\text{C}$. 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 $-95 \text{ }^\circ\text{C}$?
- (A) -48.3 J/mol-K (B) $+37 \text{ J/mol-K}$ (C) $+69 \text{ J/mol-K}$ (D) -37 J/mol-K

U.S. A

7. Consider the reaction: $2 \text{Ca}(s) + \text{O}_2(g) \rightarrow 2 \text{MgO}(s)$, $\Delta H^\circ < 0$. 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: $2 \text{SO}_3(g) \rightarrow 2 \text{SO}_2(g) + \text{O}_2(g)$ at 25 °C

	$\text{SO}_2(g)$	$\text{SO}_3(g)$	$\text{O}_2(g)$
$S_m^\circ(25^\circ\text{C})$	248 J/mol-K	257 J/mol-K	205 J/mol-K
$\Delta G_f^\circ(25^\circ\text{C})$	-297 kJ/mol	-396 kJ/mol	

8. What is ΔG° 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° 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, $A \rightleftharpoons B$, $\Delta H^\circ = +50 \text{ kJ/mol}$ (independent of temperature). The equilibrium constant for the reaction at 400 °C is 1.0×10^{-8} . What is the entropy change, ΔS° for this reaction?
- (A) -28 J/K
 - (B) +79 J/K
 - (C) -42 J/K
 - (D) -79 J/K
11. The reaction $A \rightarrow B$ is **exergonic** at 25 °C and the enthalpy change is +45 kJ. What can be concluded about the entropy change for this reaction?
- (A) $\Delta S < -70 \text{ J/K}$
 - (B) $\Delta S > +150 \text{ J/K}$
 - (C) $\Delta S < -150 \text{ J/K}$
 - (C) $\Delta S = \frac{\Delta H}{T}$
12. For the **endergonic** reaction, $C \rightarrow D$, $\Delta S = +50 \text{ J/K}$ 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, $2 \text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(s)$ at 25 °C. The Gibbs Free Energy of Formation of $\text{HI}(g)$ 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, $2 \text{C}_2\text{H}_2(\text{g}) + 4 \text{H}_2(\text{g}) \rightarrow 2 \text{C}_2\text{H}_6(\text{g})$, $\Delta S^\circ = -470 \text{ J/K}$ and $\Delta H^\circ = -620 \text{ kJ}$. What is the entropy change of the **system**, ΔS_{sys} , for the related reaction, $\text{C}_2\text{H}_6(\text{g}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + 2 \text{H}_2(\text{g})$ 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 $\text{I}_2(\text{sol})$ is 7.80 kJ/mol . The Entropy of Fusion of $\text{I}_2(\text{sol})$ is 19.6 J/mol-K .

15. The Entropy change of the universe, ΔS_{univ} , when one mole of $\text{I}_2(\text{liq})$ crystallizes to $\text{I}_2(\text{sol})$ at 80°C is approximately:

(A) -2.5 J/mol-K (B) $+7.7 \text{ J/mol-K}$ (C) $+2.5 \text{ J/mol-K}$
(D) None of the above

16. The Gibbs Energy Change, ΔG° , when 1 mole of $\text{I}_2(\text{liq})$ crystallizes to $\text{I}_2(\text{sol})$ at 150°C is approximately:

(A) -0.5 kJ/mol (B) -4.9 kJ/mol (C) $+4.9 \text{ kJ/mol}$ (D) $+0.5 \text{ kJ/mol}$

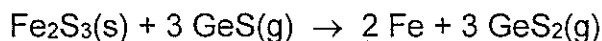
17. In class we discussed the transformation of a protein (e.g. Ribonucleus) between the Native and Random Coil forms with variation in temperature. Consider a hypothetical protein with two native forms, α and β . For the transition from the α to the β structure, $\alpha \rightarrow \beta$, the enthalpy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

(A) $\alpha, 60^\circ \text{C}$ (B) $\alpha, 333^\circ \text{C}$ (C) $\beta, 47^\circ \text{C}$ (D) $\beta, 60^\circ \text{C}$

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. $\text{C-G} \rightarrow \text{C} + \text{G}$, 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?



✓(1) Fe_2S_3 is the oxidizing agent. ✗(2) GeS_2 is oxidized
✗(3) 3 electrons are transferred ✗(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: $R = 8.31 \text{ J/mol-K} = 8.31 \times 10^{-3} \text{ kJ/mol-K}$

Vers. A

$$T = 50^\circ\text{C} = 323\text{K}$$

(14) 1. For the reaction, $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$, $\Delta H^\circ = +92\text{ kJ}$ and $\Delta S^\circ = +360\text{ J/K}$.

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

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

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

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

(4) (b) Calculate the value of ΔG for this reaction at 50°C when the pressures are:
 $P(\text{N}_2) = P(\text{H}_2) = 15.0\text{ bar}$, $P(\text{NH}_3) = 0.10\text{ bar}$.

$$Q = \frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

$$= \frac{(15)^1 (15)^3}{(0.1)^2}$$

$$= 5.063 \times 10^6$$

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

$$= -24,280 + (8.31)(323) \ln(5.063 \times 10^6)$$

$$= -24,280 + 41,440\text{ J}$$

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

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

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

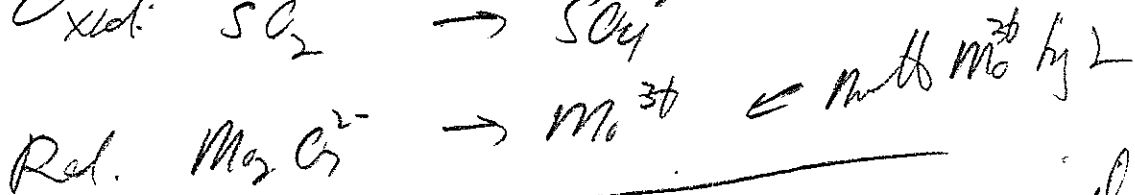
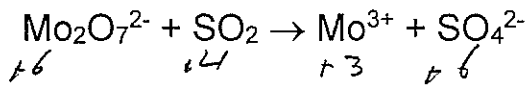
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{92,000\text{ J}}{360\text{ J/K}}$$

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

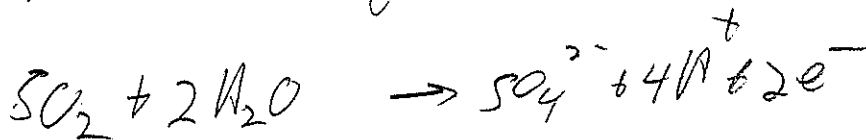
Product favored at high T .

Vars A/B

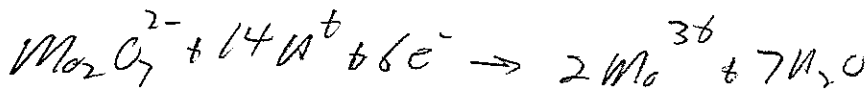
(10) 2. Balance the following oxidation-reduction reaction in **aqueous Basic** solution.



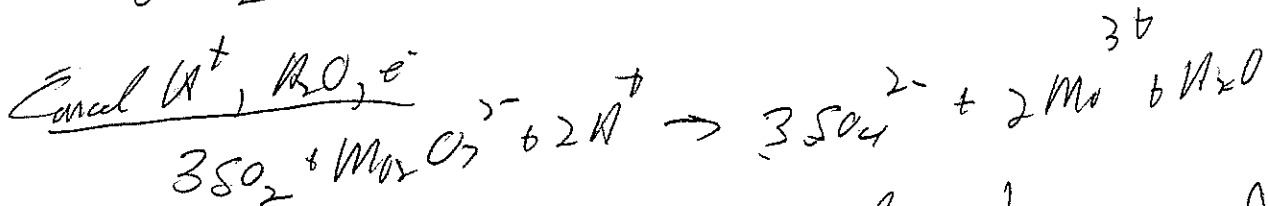
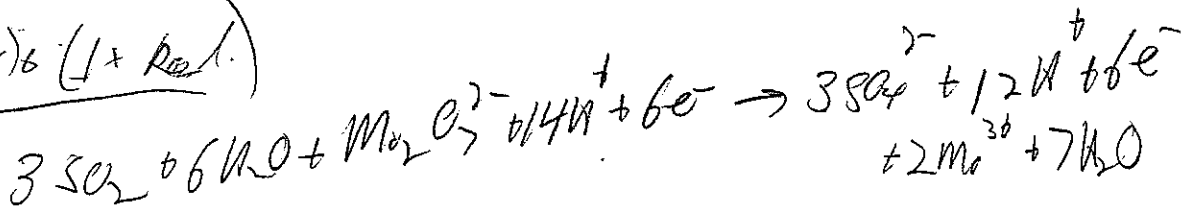
Ox: Add: 2H₂O to left, 4H⁺ to right, 2e⁻ to right



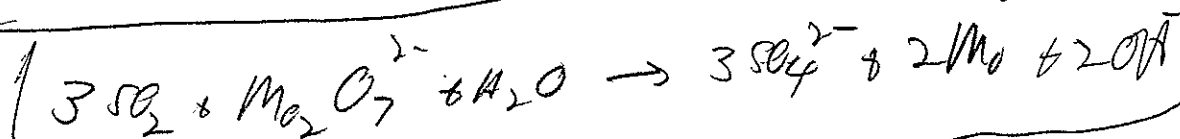
Red: Add 7H₂O to right, 14H⁺ to left, 6e⁻ to left



(3x Ox) + (1x Red)



Add 2OH⁻ to each side & cancel H₂O's



The Gas Constant is: $R = 8.31 \text{ J/mol-K} = 8.31 \times 10^{-3} \text{ kJ/mol-K}$

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

For #1 - #2: consider the slightly soluble compound, $\text{PbI}_2(\text{s})$. The solubility product (aka solubility constant) is $K_{\text{sp}} = 1.4 \times 10^{-8}$.

- What is the iodide concentration, $[\text{I}^-]$, when PbI_2 is dissolved in water?
 (A) $4.8 \times 10^{-3} \text{ M}$ (B) $1.2 \times 10^{-4} \text{ M}$ (C) $3.0 \times 10^{-3} \text{ M}$ (D) $1.5 \times 10^{-3} \text{ M}$
- What is the solubility of $\text{PbI}_2(\text{s})$ in a 0.01 M solution of the strong electrolyte, $\text{Pb}(\text{NO}_3)_2(\text{aq})$?
 (A) $1.2 \times 10^{-3} \text{ M}$ (B) $7.3 \times 10^{-8} \text{ M}$ (C) $1.2 \times 10^{-2} \text{ M}$ (D) $5.9 \times 10^{-4} \text{ M}$
- The solubility of lead (II) arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, in pure water is $3.3 \times 10^{-8} \text{ M}$. The solubility 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}
- The solubility products of two sparingly soluble Bromide (Br) salts are:
 $\text{AgBr} - K_{\text{sp}} = 5.4 \times 10^{-13}$, $\text{HgBr}_2 - K_{\text{sp}} = 6.2 \times 10^{-20}$.
 Consider a solution which initially contains $5.0 \times 10^{-5} \text{ M Ag}^+(\text{aq})$ and $4.0 \times 10^{-5} \text{ M Hg}^{2+}(\text{aq})$. KBr (a strong electrolyte) is added until $[\text{Br}^-] = 5.0 \times 10^{-8} \text{ M}$. 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
- The normal melting point of toluene is $-95 \text{ }^\circ\text{C}$. 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 $-95 \text{ }^\circ\text{C}$?
 (A) -48.3 J/mol-K (B) $+37 \text{ J/mol-K}$ (C) $+69 \text{ J/mol-K}$ (D) -37 J/mol-K
- 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 $\text{CaCO}_3(\text{s})$ is higher than the entropy of $\text{CaO}(\text{s})$
 (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

Vans. B

For #7 - #8: Consider the reaction: $2 \text{SO}_3(\text{g}) \rightarrow 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ at 25 °C

	$\text{SO}_2(\text{g})$	$\text{SO}_3(\text{g})$	$\text{O}_2(\text{g})$
$S_m^\circ(25 \text{ }^\circ\text{C})$	248 J/mol-K	257 J/mol-K	205 J/mol-K
$\Delta G_f^\circ(25 \text{ }^\circ\text{C})$	-297 kJ/mol	-396 kJ/mol	

7. What is ΔG° for the above reaction [at 25 °C] ?
(A) -198 kJ (B) +99 kJ (C) +198 kJ
(D) Insufficient data is available
8. What is ΔH° 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: $2 \text{Ca}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO}(\text{s})$, $\Delta H^\circ < 0$. 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, $2 \text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{s})$ at 25 °C. The Gibbs Free Energy of Formation of $\text{HI}(\text{g})$ 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, $\text{C} \rightarrow \text{D}$, $\Delta S = +50 \text{ J/K}$ 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 $\text{A} \rightarrow \text{B}$ is **exergonic** at 25 °C and the enthalpy change is +45 kJ. What can be concluded about the entropy change for this reaction?
(A) $\Delta S > +150 \text{ J/K}$ (B) $\Delta S < -150 \text{ J/K}$
(C) $\Delta S < -70 \text{ J/K}$ (C) $\Delta S = \frac{\Delta H}{T}$
13. For the hypothetical reaction, $\text{A} \rightleftharpoons \text{B}$, $\Delta H^\circ = +50 \text{ kJ/mol}$ (independent of temperature). The equilibrium constant for the reaction at 400 °C is 1.0×10^{-8} . What is the entropy change, ΔS° for this reaction?
(A) -28 J/K (B) +79 J/K (C) -42 J/K (D) -79 J/K

Wers. 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° , 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, $2 C_2H_2(g) + 4 H_2(g) \rightarrow 2 C_2H_6(g)$, $\Delta S^\circ = -470 J/K$ and $\Delta H^\circ = -620 kJ$. 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) +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. $C-G \rightarrow C + G$, the process is _____ by ΔH° and _____ by ΔS° .
(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: $\Delta H^\circ = -140 kJ/mol$ and $\Delta S^\circ = -420 J/mol-K$. 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 transferred ✗ (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: $R = 8.31 J/mol-K = 8.31 \times 10^{-3} kJ/mol-K$

$$T = 600 = 333 \text{ K}$$

Verse. B

(14) 1. For the reaction, $2 \text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g})$, $\Delta H^\circ = +92 \text{ kJ}$ and $\Delta S^\circ = +360 \text{ J/K}$.

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

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

$$\Delta G^\circ = -RT \ln K \rightarrow \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-27880)}{(8.31)(333)} = 10.08$$

$$K = e^{10.08} = \boxed{2.37 \times 10^4}$$

(4) (b) Calculate the value of ΔG for this reaction at 60°C when the pressures are:
 $P(\text{N}_2) = P(\text{H}_2) = 12.0 \text{ bar}$, $P(\text{NH}_3) = 0.10 \text{ bar}$.

$$Q = \frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2} = \frac{(12)(12)^3}{(0.1)^2} = 2.074 \times 10^4$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -27,880 + (8.31)(333) \ln(2.074 \times 10^4) \\ &= -27,780 + 40,250 \\ &= \boxed{+12,470 \text{ J}} = 12.5 \text{ kJ} \end{aligned}$$

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

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

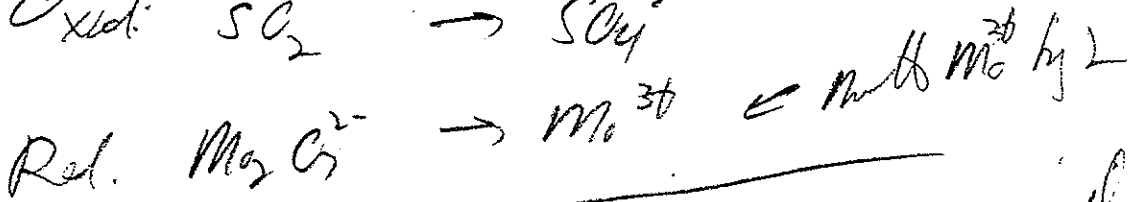
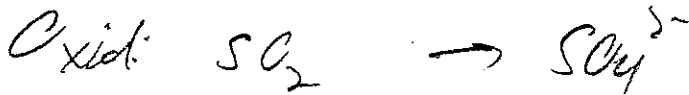
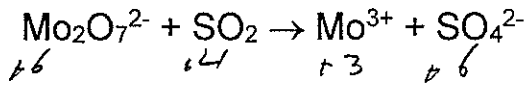
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{92,000 \text{ J}}{360 \text{ J/K}}$$

$$= 257 \text{ K} - 273 = \boxed{-17^\circ \text{C}}$$

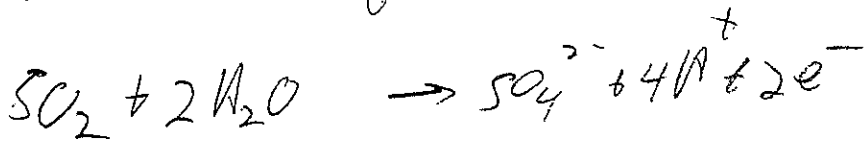
Product favored at high Temp.

Vars A/B

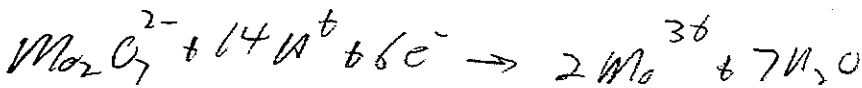
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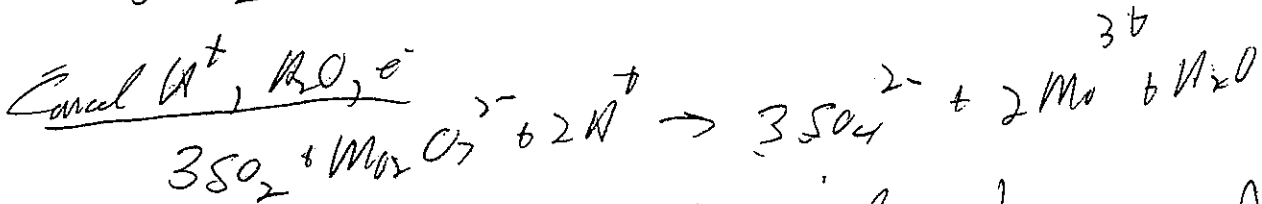
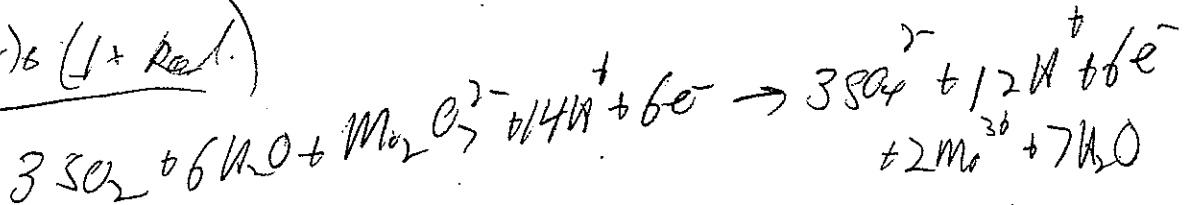
Ox: Add: 2H₂O to left, 4H⁺ to right, 2e⁻ to right



Red: Add 7H₂O to right, 14H⁺ to left, 6e⁻ to left



(3x Ox) + (1x Red)



Add 2OH⁻ to each side & cancel H₂O's

