Part 1: Multiple Choice. (4 pts each, 44 pts total)

Instructions: Bubble in the correct answer on your ScantronTM form AND circle the answer on your exam. Each question has one correct answer.

- **1.)** The answer to question 1 is **A**. Bubble in **A** on your ScantronTM form.
- 2.) Consider the sublimation of dry ice:

$$CO_2(s) \Longrightarrow CO_2(g)$$

If K_1 is the equilibrium constant at 300 K, and K_2 is the equilibrium constant at 400 K, which of the following inequalities must be true?

A.) $K_1 = K_2$ B.) $K_1 = K_2^{-1}$ C.) $K_1 K_2 = 0$ D.) $K_1 > K_2$ E.) $K_1 < K_2$

3.) For the vaporization of methanol

$$CH_3OH(l) \Longrightarrow CH_3OH(g),$$

 $\Delta H^{\circ} = 38.0 \text{ kJ mol}^{-1}$ and $\Delta S^{\circ} = 112.9 \text{ J K}^{-1} \text{ mol}^{-1}$. What is the boiling point of methanol at sea level? Assume ΔH° and ΔS° are independent of T.

A.) 64 K B.) 237 K C.) 273 K D.) 337 K E.) 373 K

4.) Consider the reaction:

$$N_2(g) + 3H_2(g) \implies 2NH_3(g)$$

at equilibrium. What would be the reaction quotient immediately following the reduction of volume by two at constant temperature before any reaction occurs?

A.)
$$Q = \frac{1}{4}K$$
 B.) $Q = \frac{1}{2}K$ C.) $Q = K$ D.) $Q = 2K$ E.) $Q = 4K$

5.) One mole of an ideal gas expands *isothermally* against a constant pressure of 1 atmosphere. Which of the following inequalities is true?

A.)
$$\Delta P > 0$$
 B.) $q > 0$ C.) $\Delta S < 0$ D.) $\Delta V < 0$ E.) $\Delta T < 0$

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6.) One mole of an ideal gas expands *adiabatically* against a constant pressure of 1 atmosphere. Which of the following inequalities is true?

- A.) $\Delta P > 0$ B.) q > 0 C.) $\Delta S < 0$ D.) $\Delta V < 0$ E.) $\Delta T < 0$
- 7.) At what temperature does K = 1, $\Delta G^{\circ} = 0$ for the reaction H₂O (l) \Longrightarrow H₂O (g)?
 - A.) –273 °C B.) 0 °C C.) 100 °C D.) 273 °C E.) 373 °C
- **8.)** How many different ways can you distribute six distinguishable stones between two boxes with five in the first box and one in the second box?
 - A.) 1 B.) 3 C.) 6 D.) 9 E.) 15
- **9.)** The caloric content of 10 little cookies can heat up 10 kg of water by 10 °C. What would be the change in temperature if 1 little cookie was used to heat up 1 kg of water?
 - A.) 0.1 °C B.) 1.0 °C C.) 10 °C D.) 100 °C E.) 1000 °C

For each of the problems 10-12, select the graph that best describes the behavior listed.



- **10.)** $P_{N_2O_4}$ as a function of $(P_{NO_2})^2$ for N_2O_4 (g) \Longrightarrow 2NO₂ (g), at constant T.
- 11.) $\ln(K)$ as a function of $\frac{1}{T}$ for a the combustion of liquid methanol (CH₃OH).

A or B

C

12.) ΔG° as a function of T for the vaporization of water, H₂O (l) \Longrightarrow H₂O (g).

E

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Part 2: Short Answer Problems (101 pts total)

Instructions: Enter answers in the boxes provided. Show your work. Explain your answer when requested in 15 words or less.

(30 pts)

1.) The reaction

 $SO_2Cl_2(g) \implies SO_2(g) + Cl_2(g)$

is endothermic with $\Delta H = 4.6 \text{ kJ/mol}$. SO₂Cl₂ (g) and SO₂ (g) are placed in a bulb at a fixed temperature with partial pressures of 3.0 atm each.

Answers:

 $\mathbf{Q} = \mathbf{P}_{SO2} \times \mathbf{P}_{C12} / \mathbf{P}_{SO2C12}$ $\mathbf{Q} = \mathbf{0}$

a) Write the expression for reaction quotient (Q) and calculate its value before any reaction occurs.

b) After equilibrium is reached in the bulb at the same fixed temperature, the partial pressure of Cl_2 (P_{Cl_2}) is found to be 1.0 atm. What are the partial pressures of SO₂Cl₂ and SO₂ ($P_{SO_2Cl_2}$ and P_{SO_2})?

	SO_2Cl_2	SO_2	Cl_2		
Init:	3	3	0		Answers:
Change	X	$+_{\mathbf{X}}$	$+_{\mathbf{X}}$		$P_{SO2C12} = 2 \text{ atm}$
	_	_			$P_{SO2} = 4 \text{ atm}$
Final	3–x	3+x	Х	(x = 1)	
	2	4	1		

c) Calculate the value of the equilibrium constant for the reaction in part b).

K	=	$P_{SO2} \times P_{C12} / P_{SO2C12}$
	=	$4 \times 1 / 2 = 2$

Same

Answer:		
	K = 2	

d) If some Cl₂ is added to the equilibrium mixture, will the pressure of SO₂ increase, decrease, or stay constant as the system approaches the new equilibrium state? Circle the answer and explain.

Decrease

Increase

Explanation: When more product is added, reaction goes backwards, producing reactants and eliminating products like SO₂. Page 5 of 6

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(18 pts)

2.) Consider the reaction of silver chloride (AgCl) dissolving in water.

AgCl (s)
$$\longrightarrow$$
 Ag⁺ (aq) + Cl⁻ (aq)

a) Dissolving 14.3 g of AgCl (s) consumes 6.5 kJ of heat. What is the temperature change if 14.3 g of AgCl(s) totally dissolves in 1.00 L of water initially at 20 °C?

$$\Delta T = q / m c_p$$

= (-6500 J) / (1000 g) (4.184 J g⁻¹ K⁻¹)
= -1.6 K

Answer:		
	–1.6 K	

b) In actuality the equilibrium constant (K) for this reaction is very small (1.6×10^{-10} at 25.0 °C). How will this affect the temperature change predicted in part (a)? Explain.

Answer: K is very small, less product is formaed, the temperature change is smaller than in (a)

(23 pts)

3.) A study of the geology of the earth shows that rocks older than 2 billion years contain iron in the form of FeS_2 . In rocks less than 2 billion years old, iron appears mostly as the oxide Fe_2O_3 (hematite).

 $4 \text{ FeS}_2(s) + 8 \text{ H}_2\text{O}(l) + 15 \text{ O}_2(g) \longrightarrow 2 \text{ Fe}_2\text{O}_3(s) + 8 \text{ H}_2\text{SO}_4(l)$

a) Calculate ΔH° for the above reaction.

 $q = m c_{\rm p} \Delta T$

 $\Delta H^{\circ} = [2 H^{\circ}_{Fe2O2} + 8 H^{\circ}_{H2SO4}]$ $- [4 H^{\circ}_{FeS2} + 8 H^{\circ}_{H2O} + 15 H^{\circ}_{O2}]$ = 2(-824.2) + 8(-814.0)- [4(-178.2) + 8(-285.8) + 15(0)] kJ= -5161.2 kJ

Answer: $\Delta H^{\circ}_{\text{reaction}} = -5161.2 \text{ kJ}$

b) Calculate ΔS° for the above reaction.

 $\Delta S^{\circ} = \begin{bmatrix} 2 \ S^{\circ}_{Fe2O2} + 8 \ S^{\circ}_{H2SO4} \end{bmatrix} \\ - \begin{bmatrix} 4 \ S^{\circ}_{FeS2} + 8 \ S^{\circ}_{H2O} + 15 \ S^{\circ}_{O2} \end{bmatrix} \\ = 2(87.4) + 8(156.9) \\ - \begin{bmatrix} 4(52.93) + 8(69.91) + 15(205.03) \end{bmatrix} J/K \\ = -2416.45 \ J/K$

Answer: $\Delta S^{\circ}_{\text{reaction}} = -2416.45 \text{ J/K}$

c) Over what temperature range is this reaction spontaneous? As always, show your calculations.

 $\begin{array}{l} 0 > \Delta G^{\rm o} = \Delta H^{\rm o} - T \Delta S^{\rm o} < 0 \\ T < \Delta H^{\rm o} / \Delta S^{\rm o} \ (\text{for } \Delta S^{\rm o} < 0) \\ T < (-5161.2 \times 10^3 \text{ J}) / (-2416 \text{ J/K}) = 2136 \text{ K} \end{array}$

Answer: T < 2136 K

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(23 pts)

4.) Consider the hydrogenation of formaldehyde ($H_2C=O$) to form methanol (CH_3OH).

 $CH_2O + H_2 \longrightarrow CH_3OH$

-				
Average Bond Energy				
(kJ/mol)				
H-H	436	C-0	360	
H-C	413	C=O	743	
Н-О	463	C-C	348	
0-0	146	C=C	612	
0=0	497	C≡C	838	
			H	

H-C=O	+	H-H	>	н-С-О-Н
Н				Н

a) Estimate ΔH^{o} for this reaction.

bonds broken: 2 C-H + 1 C=O + 1 H-Hbonds made: 3 C-H + 1 C-O + 1 O-H $\Delta H^{\circ} = 743 + 436 - (413 + 360 + 463) = -57 \text{ kJ}$ Answer: $\Delta H^{\circ} = -57 \text{ kJ}$

b) The *formation* of which species, formaldehyde or methanol, is more exothermic (i.e. has the lower ΔH_{f}°)?

 $\Delta H^{o}_{f}(CH_{3}OH) = 2 C-C + \frac{1}{2} O=O + 2 H-H$ - [3 C-H + 1 C-O + 1 O-H] = -246 kJ $\Delta H^{o}_{f}(CH_{2}O) = 2 C-C + \frac{1}{2} O=O + H-H$ - [2 C-H + 1 C=O] = -188 kJ

Answer: methanol (CH₃OH)

c) The *combustion* of which species, formaldehyde or methanol, produces more heat per mole?

CH₂O + O₂ → CO₂ + H₂O $\Delta H = 2 C-H + 1 C=O + 1 O=O$ - [2 C=O + 2 O-H] = -346 kJCH₃OH + ³/₂ O₂ → CO₂ + 2 H₂O $\Delta H = 3 C-H + 1 C-O + 1 O-H + ³/₂ O=O$ - [2 C=O + 4 O-H] = -530 kJ

Answer:

methanol (CH₃OH)