Chemistry 1A, Spring 2008

Midterm Exam III, Version A April 14, 2008 (90 min, closed book)

Name:___KEY____

SID:_____

TA Name:_____

- 1.) Write your name on every page of this exam.
- 2.) This exam has 15 multiple-choice questions and 3 short answer questions. Fill in the Scantron form AND circle your answer on the exam.
- 3.) There is no penalty for guessing, so answer every question.
- 4.) Select **one** answer for each multiple choice question.
- 5.) Show all work to receive credit on short answer questions.

Question	Page	Points	Score
Multiple Choice	3-5	60	
16) Phase Changes	6-7	14	
17) Thermodynamics	8	14	
18) Equilibria	9	12	
Total		100	

Name_

$$E = hv
\lambdav = c
\lambda_{deBroglie} = h / p = h / mv
E_{kin} (e) = hv - \Phi = hv - hv_0
E_n = $-\frac{Z^2}{n^2} R_{\infty}$

$$E_{i \to f} = -R_{\infty} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)
\Delta x \Delta p \ge h/4\pi
p = mv
Particle in a box (1-D Quantum):
E_n = h^2 n^2/8mL^2; n = 1, 2, 3...
PV = constant
PV = nRT
E_{kin} = $\frac{3}{2}RT$
 $v_{rms} = \sqrt{\frac{3RT}{M}}$
 $\Delta E = q + w$
 $w = -P_{ext}\Delta V$
 $\Delta E = \frac{3}{2}nR\Delta T$
N₀ = 6.02214 x 10²³ mol⁻¹
R<sub>\overline{\overline{A}}} IS
N₀ = 6.02214 x 10¹⁸ J
R<sub>\overline{\overline{A}}} IS
m_e = 9.101939 x 10⁻³¹ kg
c = 2.99792 x 10⁸ m s⁻¹
Gas Constant:
R = 8.31451 J K⁻¹ mol⁻¹
R = 8.20578 x 10⁻² L atm K⁻¹ mol⁻¹
T (K) = T (C) + 273.15
F = 96,485 C / mol
1 V = 1 J / C 1 nm = 10⁻⁹ m
1 kJ = 1000 J
1 atm = 760 mmHg = 760 torr = 101,325 Pa
1 atm L = 101.3 J</sub></sub>$$$$



$$\Delta G^{\circ} = - \operatorname{RTln} K$$
$$\ln K = -\frac{\Delta H^{\circ}}{R} \frac{1}{T} + \frac{\Delta S^{\circ}}{R}$$
$$\Delta G^{\circ} = - \operatorname{nF}\Delta C^{\circ}$$

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

Heat Capacity of $H_2O(l) = 4.184 \text{ Jg}^{-1}\text{K}^{-1}$ Density of water = 1.00 g/mL

For y =
$$ax^2+bx+c$$
, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Multiple Choice Questions (4 points each)

- Which of the following gases would you expect to behave least like an ideal gas?
 A) He
 - B) CO₂
 C) H₂O
 D) Xe
 E) Pa
 - E) Br_2
- 2) Using the diagram below, which of these is a plot of the vapor pressure of water vs. temperature?



- A system absorbs 716 kJ of heat and does 598 kJ of work on the surroundings. What is the change in internal energy of the system?
 A) 1314 kJ
 B) 118 kJ
 C) -118 kJ
 D) -1314 kJ
 E) 598 kJ
- 4) When breathing, the average human lung expands by 0.50 L. If this expansion occurs against an external pressure of 1.0 atm, how much work is done by the system?

 A) - 51 J
 B) 0.51 J
 C) 0 J
 D) -0.51 J
 E) 51 J

5) For which of the following is ΔS° expected to be positive?

A) $H_2O(g) \rightarrow H_2O(l)$ B) $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ C) $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$ D) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$ E) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

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10000 1000 solid liquid 100 a Pressure (atm) 10 0.1 0.0 gas 0.001 -40 -20 -140 -120 -100 -80 -60 0 20 40 60 80 100 Temperature (°C)

Use the phase diagram of CO₂ below to answer the next *three* questions:

- 6) Which phases are present at point 'a'?
 - A) Supercritical Fluid
 - B) Solid and Liquid
 - C) Liquid and Gas
 - D) Solid and Gas
 - E) Solid, Liquid and Gas
- 7) At sea level, what is the approximate temperature at which CO₂ sublimes (solid to gas phase change)?

A) 0°C B) 30°C <u>C) -78°C</u> D) -55°C E) -115°C

- 8) What does point 'b' represent in the phase diagram?
 - A) Triple Point
 - B) Condensation
 - C) Vaporization
 - D) Critical Point
 - E) Sublimation
- 9) The decomposition of H_2O_2 is exothermic:

 $H_2O_2(g) \rightarrow H_2O + \frac{1}{2}O_2$

	Average Bond Enthalpies (kJ mol ⁻¹)
O-H	463
0-0	146
O=O	497

Using the bond energy data above, what is the molecular structure of H_2O_2 ?



t be E) None of these

10) Which of the following *cannot* occur at the same time?

A) $\Delta S_{sys} > 0$ and $\Delta S_{surr} < 0$ B) $\Delta S_{sys} < 0$ and $\Delta S_{surr} < 0$ C) $\Delta S_{sys} > 0$ and $\Delta S_{surr} > 0$ D) $\Delta S_{sys} < 0$ and $\Delta S_{surr} > 0$

- E) All of these can occur at the same time.
- **11**) A reaction will occur spontaneously at standard conditions if: A) $\Delta H > 0$ B) $\Delta S > 0$ C) $\Delta G > 0$ D) K > 1 E) $\Delta H < 0$
- 12) Consider the following exothermic reaction at equilibrium in a sealed container: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Which of the following conditions will result in the reaction favoring products?

A) High temperature

B) Low Pressure

- C) Thermal Insulation
- D) High Pressure
- E) None of these
- **13**) Which of the following correctly represents the Ksp expression for this reaction: $K_2CO_3(s) \leftrightarrows 2K^+(aq) + CO_3^{2-}(aq)$
 - A) $[K^+] [CO_3^{2^-}]/[K_2CO_3]$ B) $[K_2CO_3]/[K^+] [CO_3^{2^-}]$ C) $[K^+]^2 [CO_3^{2^-}]/[K_2CO_3]$ D) $[K_2CO_3]/[K^+]^2 [CO_3^{2^-}]$ E) $[K^+]^2 [CO_3^{2^-}]$
- 14) A 30.0 g bar of iron (Fe) is heated to 106.0°C and then placed in a calorimeter with 100.0 g of 20.8°C water. The final temperature of the water is 23.4°C. What is the heat capacity of the Fe in J g⁻¹ K⁻¹?
 - A) 439 B) -439 C) -0.439 D) 0.439 E) -39.9
- **15**) In the presence an acid solution, chromate and dichromate exists in equilibrium with a moderate equilibrium constant.

$$2H^{+}(aq) + 2CrO_{4}^{2-}(aq) \leftrightarrows Cr_{2}O_{7}^{2-}(aq) + H_{2}O(l)$$

The chromate ion (CrO_4^{2-}) is yellow in color, while the dichromate $(Cr_2O_7^{2-})$ anion is orange. If we add potassium chromate (K_2CrO_4) , a very soluble salt, what would happen to the color of the solution as it regains equilibrium?

A) The color will not change.

B) The solution will become more orange.

- C) The solution will become more yellow.
- D) The solution will become transparent.
- E) The color change cannot be determined from the data given.

Short Answer Questions

16) Phase Diagrams (14 points)

A bottle contains 166 g of ethanol (molecular formula of ethanol is CH_3CH_2OH) at 1 atm. Consider the heating curve and data below for ethanol to answer the following questions.



Thermodynamic data for ethanol		
	Ethanol	
$\Delta H_{fus} (kJ mol^{-1})$	4.9	
$\Delta H_{vap} (kJ mol^{-1})$	38.6	
C_s , liquid (J mol ⁻¹ K ⁻¹)	112.4	
C_s , gas (J mol ⁻¹ K ⁻¹)	78.3	
$\Delta H_{\rm f}$, liquid (kJ mol ⁻¹)	-277.6	
$\Delta H_{\rm f}$, gas (kJ mol ⁻¹)	-234.8	

A) What happens to the ethanol in going from point B to point D? Circle your answer(s). (2 pts)

Heating	Cooling	Melting	Vaporization	Freezing
	-		=	

How much energy is required to make this transition from point B to point D? Clearly show all work for credit. (4 pts)

B → C:
$$q = n\Delta H_{fus}$$

 $q = (3.61mol)(4.9kJmol^{-1})$
 $q = 17.7kJ$
C → D: $q = nC\Delta T$
 $q = (3.61mol)(112.4Jmol^{-1}K^{-1})(78.4K - (-114.3K))$
 $q = 78.0kJ$
Total E = (78.0 + 17.7) kJ
 $= 95.7$ kJ

B) Calculate the enthalpy of sublimation. Show all work for credit. (4 pts)

Can use Hess' Law: $CH_3CH_2OH (s) \rightarrow CH_3CH_2OH (l), \Delta H_{fus} = 4.9 \text{ kJ/mol}$ $CH_3CH_2OH (l) \rightarrow CH_3CH_2OH (g), \Delta H_{vap} = 38.6 \text{ kJ/mol}$ Final equation: $CH_3CH_2OH (s) \rightarrow CH_3CH_2OH (g), \Delta H_{vap} = 43.5 \text{ kJ/mol}$

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16) Phase Diagrams (continued)

C) Does ethanol in the vapor or liquid state at 78.4°C pose more of a hazard? (1pt)

Vapor	Liquid	They're the same
Explain your answer. (3 pts)		

Ethanol in the vapor state poses more of a hazard as compared to the liquid state because the vapor state has 42.8 kJ more of energy per mole.

17) Thermodynamics (14 points)

Consider the following reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$.

	$\mathbf{H}_{2}\left(\mathbf{g}\right)$	O ₂ (g)	$H_2O(g)$
ΔH°_{f} (kJ mol ⁻¹)	0	0	-241.8
S° (J mol ⁻¹ K ⁻¹)	130.7	205.2	188.8

Table 17.1. ΔH°_{f} and S° values at 25°C.

A) Calculate ΔH°_{rxn} (in kJ), ΔS° (in J/K) and ΔG° (in kJ) for the indicated reaction at 25°C using the values in the table above. (**6pts**)

$$\begin{split} \Delta H_{rxn}^{\circ} &= (-241.8 k J mol^{-1})(2 mol) - 0 = -483.6 k J \\ \Delta S_{rxn}^{\circ} &= (188.8 J mol^{-1} K^{-1})(2 mol) - [(130.7 J mol^{-1} K^{-1})(2 mol) + (205.2 J mol^{-1} K^{-1})(1 mol) \\ &= -89.6 J K^{-1} \\ \Delta G_{rxn}^{\circ} &= -483.6 k J - (298 K)(-0.0896 k J K^{-1}) = -456.9 k J \end{split}$$

B) What conditions are optimal to make this reaction product favored? (Circle your answer) (1 pt)

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High T
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(Low T)

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never favorable always favorable
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At what temperature (in K) does the sign of ΔG° change? What is the significance of this temperature? Explain and show all work for credit. (**3pts**)

T when $\Delta G^{\circ} = 0$ is the temperature when the reaction changes from being product favored to being reactant favored. $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 0$ $T = \Delta H^{\circ} / \Delta S^{\circ} = -483.6 kJ / - 0.0896 kJ K^{-1}$ T = 5397 K

Above this temperature, the reaction would not proceed spontaneously.

C) Consider the following statement: If $\Delta G^{\circ} < 0$, then products are always favored for the reaction regardless of the initial conditions. Is this a true statement? Circle your answer. (1 pt)



 ΔG° only describes a system at standard conditions, 1M and 1atm. However for a system at non-standard condition we must look at $\Delta G = \Delta G^{\circ} + RT \ln(Q)$. Here the initial conditions are accounted for in the reaction quotient, Q.

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18) Equilibrium (12 points)

Consider the dissociation of the poisonous gas phosgene, COCl_2 . At 425 K it will dissociate to establish the following equilibrium: $\text{COCl}_2(g) \leftrightarrows \text{CO}(g) + \text{Cl}_2(g)$. The equilibrium constant, K, is 1.00 x 10⁻⁴.

A) What is the equilibrium constant expression for the dissociation reaction of phosgene? (2 pts)

 $K = \frac{P_{CO}P_{Cl}}{P_{COCl_2}} = \frac{[CO][Cl_2]}{[COCl_2]} = 10^{-4}$

B) At equilibrium, what is the partial pressure of CO (g), P_{CO} ? Justify any approximations used. Assume the initial pressure of $COCl_2$ is 5 atm and initially there are no products. (**4pts**)

$$K = \frac{P_{CO}P_{Cl}}{P_{COCl_2}} = 10^{-4}$$

$$K = \frac{(x)(x)}{(5-x)} = 10^{-4}, \text{ where } x \text{ is } P_{CO} \text{ and } P_{Cl2}$$

Assuming that x is negligible compared to 5 atm since K ~ 10⁻⁴, the equation becomes:

$$K \approx \frac{(x)(x)}{(5)} = 10^{-4}$$

Solving for x, x = P_{CO} = 0.0224 atm

C) Now we take the equilibrated system from part (B) and double the volume of the container the reaction is contained in. Immediately following this change, what is the reaction quotient, Q? (4 pts)

As in class, if we double the volume, the pressure is reduced by a factor of 2. From part (B) we know that the P_{CO} and $P_{Cl2} = 0.0224$ atm at equilibrium and $P_{COCl2} \sim 5$ atm.

So
$$Q = \frac{(\frac{0.0224}{2} atm)(\frac{0.0224}{2} atm)}{\frac{5}{2} atm} = 5.02 \times 10^{-5}$$

D) To regain equilibrium from part (C), the reaction will proceed towards: (Circle one) (1 pt)

Reactants

Products

No Change

Explain your choice. (1 pt)

The reaction will regain equilibrium by proceeding towards products. We know this because Q is less than K. An explanation along the lines of stoichiometrically there are more gas molecules on the products side, so an increase in volume would favor products is also acceptable.