S17 Exam4

Tuesday, April 18, 2017 10:46 AM

Chem 105 Exam 4 Name _______________

This exam is schedule for 75 minutes and I anticipate it to take the full time allotted. You are free to leave if you finish. In multiple part problems, points awarded will not be penalized for incorrect answer on previous parts, so simply **move on if you get stuck on one part**. If you need to, make up an answer for the previous part. Always neatly show work for partial credit.

1. Define the first and second laws of thermodynamics and explain what impact they have on the important concepts of thermodynamics that we have discussed in class.

   First Law - heat must be conserved. This is the origin of enthalpy during our discussion (ΔH)

   Second Law - The universe tends toward disorder. This was our introduction to entropy and it allows us to understand how entropy relates to spontaneity and ΔG.

2. Coal power plants are not 100% efficient; that is, not all of the energy produced from the combustion reaction results in usable energy.

   a. The combustion of coal is shown below. Is this reaction endothermic or exothermic? Explain your choice.

      $C\ (s) + O_2\ (g) \rightleftharpoons CO_2\ (g)$

      Exothermic. Two bonds are being made and only one broken. Making bonds is exothermic.

b. What happens to the rest of the energy?

It is transferred to the surroundings as heat.

c. Clearly explain how this is related to thermodynamics.

$\Delta U = q + w$

The work done by the system is the usable energy. The heat lost is shown as q. The total energy exchange is ΔU

3. $\Delta S_{vaporization} > \Delta S_{fusion}$; Explain why this statement is true. Liquid --> gas creates much more disorder

4. Which direction does a reaction "shift" when Q > K. **You must clearly explain your choice to receive full credit.**

Reactants Products

If Q > K, this means that there are more products and less reactants than are needed at equilibrium.

What is the sign of ΔG when Q < K ? positive negative

5. Explain why each of the following statements are false.
   a. A spontaneous reaction occurs when energy is consumed by a system. Spontaneous reactions do not require energy.
   b. Liquid water has a formation enthalpy of zero ($\Delta H_f^0 = 0$). Only elements in their most stable form have values of zero.
   c. Br_2 (*l*) has a standard molar entropy of zero ($S^0 = 0$) This violates the 3rd law of thermodynamics
   d. Endothermic reactions are never spontaneous. They can be if there is a strong entropic favorability
   e. Equilibrium occurs when the concentration of products and reactants are equal. Equilibrium occurs when the rate of the forward are reverse reactions are equal, not when the concentrations are equal.

6. Consider the following reactions. Which is most likely to have a **negative** ΔS? You must clearly explain your answer to receive credit.

$CO_2 (g) + H_2O (l) \rightleftharpoons H_2CO_3 (aq)$ $2\ C_8H_{18} (l) + 25\ O_2 (g) \rightleftharpoons 16\ CO_2 (g) + 18\ H_2O (g)$

The other reaction is creating more gas molecules. The highlighted reaction is consuming a gas, producing an aqueous compound, AND it is making one molecule from two. All of these things suggest it will be unfavorable.

7. The synthesis of NO occurs according to the following reaction where Kc = $7.5 \times 10^{-9}\ M^{-1}$ at 1000 K.

$N_2 (g) + 2\ O_2 (g) \rightleftharpoons 2\ NO_2 (g)$

   a. If 1 M of each gas is mixed together at 1000 K, would the synthesis of NO_2 be spontaneous?

   No $K < 1$

   b. Determine Kc for this related reaction: $2\ NO_2 (g) \rightleftharpoons N_2 (g) + 2\ O_2 (g)$

   reversed $K^{-1} = \frac{1}{7.5\times10^{-9}} = 1.3\times10^{8}\ M$

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c. Calculate Kp at 1000 K. Include the correct units.

$\Delta n = -1 \quad K_p = K_c(RT)^{\Delta n_{gas}}$

$K_p = 7.5\times10^{-9}(0.08206 \cdot 1000)^{-1}$

8. Consider the following reaction:

$K_p = 9.14\times10^{-11}\ atm^{-1}$

6 HCl (g) + 2 As (s) ⇌ 2 $AsCl_3$ (l) + 3 H_2 (g)

a. For each of the following, determine if the equilibrium will shift. If so, determine if products or reactants will be formed.

   i. ~~Magnesium~~ arsenic is added — no change

   ii. HCl is added. products

   iii. The volume of the flask is decreased. more gas as reactants ... more impact products

b. Using the information available at the back of the exam, calculate ΔG° and ΔH°.

ΔG° = 305.2 kJ/mol

ΔH° = 49.6 kJ/mol

$6HCl(g) + 2As(s) \rightleftharpoons 2AsCl_3(l) + 3H_2(g)$

ΔH_f°: -110, ∅, -305.2, ∅

ΔG_f°: -137.2, ∅, -259.0, ∅

$\Delta H = 2(-305.2) - 6(-110) = 49.6$

$\Delta G = 2(-259) - 6(-137.2) = 305.2$

c. What is the equilibrium constant at 25 °C?

$305{,}200 = -8.314(298.15)\ln K$

$K = 3.38\times10^{-54}$

d. Calculate ΔS°

$305{,}200 = 49{,}600 - 298.15\,\Delta S$

$\Delta S^\circ = -857.3\ J/mol\cdot K$

e. Calculate ΔG if 0.4 atm of CO, 2.5 atm of CO_2, 14 g of S, and 0.98 atm of CS_2 are added to a reaction flask at 25 °C.

$\Delta G = 305200 + 8.314(298.15)\ln Q$

9. Consider the following reaction.

3 F_2 (g) + N_2 (g) ⇌ 2 NF_3 (g)

a. 2 atm of F_2 and 1 atm of N_2 are combined in a sealed reaction flask at 100 °C. Once equilibrium has been reached, the pressure is the flask is 1.706 atm. Determine the equilibrium constant at this temperature.

	$3F_2$	+ N_2	⇌ $2NF_3$
I	2	1	∅
C	-3x	-x	2x
E	2-3x	1-x	2x

$2 - 3x + 1 - x + 2x = 1.706$

$3 - 2x = 1.706$

$x = 0.647$

$P_{NF_3} = 1.294$

$P_{N_2} = 0.353$

$P_{F_2} = 0.059$

$K = \frac{(1.294)^2}{(0.353)(0.059)^3}$

$K = 2.31\times10^{4}$

b. When the temperature is raised to 200 °C, the pressure of F_2 decreases to 0.01 atm.

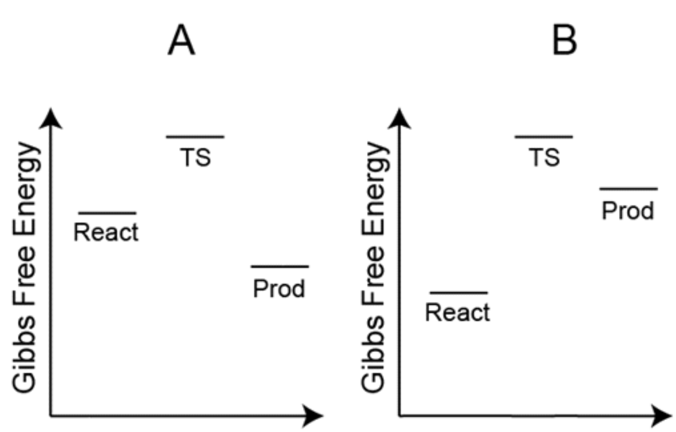
i. Is this reaction endothermic or exothermic? Justify your selection.

F_2 decrease, so products form   K increases as T increases

ii. Optional (bonus): calculate ΔH.

$\Delta H > 0$

10.



Consider the two reaction coordinates below. Answer each of the following questions. **If it is not possible to determine, say that. Partial credit will be considered if your answer is explained.**

a. Which reaction is spontaneous?

A

b. Which reaction has a larger equilibrium constant?

A

c. Which reaction has a larger rate constant?

A

d. Which of these reactions is endothermic?

can't tell

e. Which reaction might have $\Delta H > 0$ and $\Delta S < 0$?

B

11. **Complete one of the problems on this page**. You can answer more for extra credit. Please use the next page to show your work if you need more space.

a. Determine the total pressure at equilibrium if 14 grams of carbon, 1.82 atm of H_2, and 2.33 atm of CH_4 are added to a reaction flask at 500 °C. 3.26 atm

$8910.4 - 19583.2x + 10760x^2 = 2.33 + x$

$C(s) + 2\ H_2\ (g) \rightleftharpoons CH_4\ (g)$ Kp = 2690 atm^{-1} at 500 °C

1.82 2.33 $Q = 0.7$ $2690 = \frac{2.33+x}{(1.82-2x)^2} \Rightarrow$ $10760x^2 - 19584.2x + 8908.07$

-2x +x

1.82-2x 2.33+x

b. Using the information in the table below, determine the heat capacity of solid CS_2 if 2.34 kJ of heat is released when 10 grams of liquid CS_2 is cooled from 46.3 °C to -150 °C. $\Delta H = 78.99(-110.8 - 46.3)$ $x = 0.893$

0.131 mol 46.3 → -110.8 $\Delta H = -12,409$ kJ(.131) ~ -1.626 kJ

c. ΔS_{vap} of CS_2 is 86.55 J mol^{-1} K^{-1}. Using the information in the table below, determine the boiling temperature.

$\Delta G = 0 = \Delta H - T\Delta S$ $T_b = \frac{\Delta H}{\Delta S} = \frac{27650}{86.55} = 319.5$ K

$\Delta H = T\Delta S$

Thermodynamic values for CS_2						
T_b (˚C)	T_m (˚C)	ΔH_{fusion} (kJ/mol)	$\Delta H_{vaporization}$ (kJ/mol)	C (solid) J / (mol K)	C (liquid) J / (mol K)	C (gas) J / (mol K)
	-110.8	4.39	27.65		78.99	46.55

$\Delta H_2 = -4.39(.131)$

$\Delta H_2 = -0.575$

$\Delta H_1 + \Delta H_2 = -2.2$ kJ

$-2.34 + 2.2 = -0.139 = \Delta H_3$

$\Delta H_3 = 0.131\ (C)(-150 - -110.8)$

$\boxed{C = 27.05\ J/mol \cdot K}$

d. 1368 kJ of heat is required to decompose 112.04 grams of CO (g). Noting that the bond enthalpy of a CO triple bond is 1072 kJ mol^{-1}, calculate the bond enthalpy of a CO double bond.

$2\ CO\ (g) \rightleftharpoons C(s) + CO_2\ (g)$

e. Incomplete combustion of natural gas produces carbon monoxide and water vapor (see unbalanced reaction below).

$CH_4\ (g) + O_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$

Determine $\Delta H°$ for this reaction from the data below:

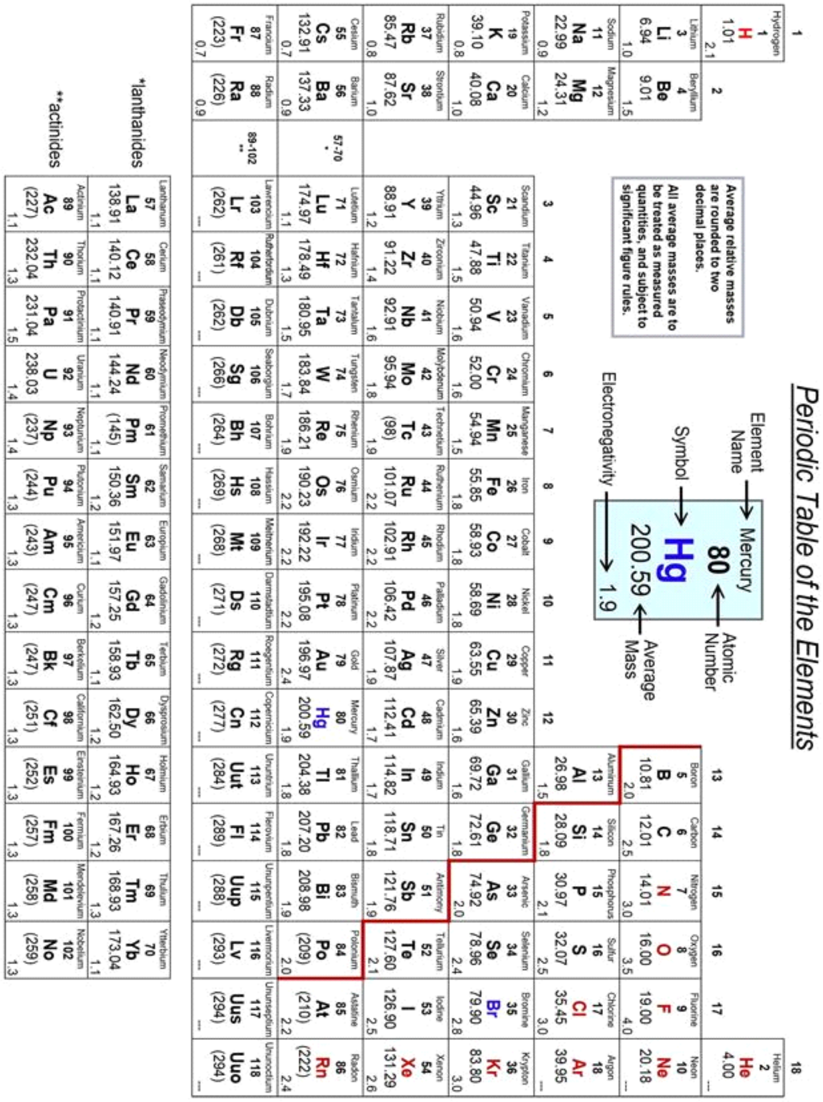
$CH_4\ (g) + 2\ O_2\ (g) \rightleftharpoons CO_2\ (g) + 2\ H_2O\ (g)$ $\Delta H° = -802$ kJ mol^{-1}

$2\ CO\ (g) + O_2\ (g) \rightleftharpoons 2\ CO_2\ (g)$ $\Delta H° = -566$ kJ mol^{-1} everyone gets credit

mistake

f. Using the information at the back of the exam, determine the temperature that is needed to make this reaction spontaneous.

$6\ HCl\ (g) + 2\ As\ (s) \rightleftharpoons 2\ AsCl_3\ (s) + 3\ H_2\ (g)$



	ΔH_f^0 kJ mol^{-1}	ΔG_f^0 kJ mol^{-1}
$AsCl_3$ (l)	-305.2	-259.0
HCl (g)	-110.5	-137.2

Equations

$\Delta G = \Delta H - T\Delta S$ $\quad \Delta G^0 = -RTlnK$ $\quad \Delta G = \Delta G^o + RTlnQ$

$\Delta U = q + w$ $\quad w = -p\Delta V$ $\quad \Delta G = -T\Delta S_{universe}$

$\Delta H = C_p\Delta T$ $\quad ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ R = 0.08206 L atm mol^{-1} K^{-1} R = 8.314 J mol^{-1} K^{-1}

Kp = Kc (RT)$^{\Delta ngas}$ $\quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$