CHEM 202H – 12,13,14

EXAM 2, Spring 2016

Name______________________________

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SCORED GRADE (100 max.)____________

CIRCLE YOUR COURSE SECTION IN THE LIST BELOW

202-12 W 10-12:50 202-13 W 2-2:50 202-14 W 3-3:50

Section 1. Entropy, Enthalpy, and Gibb's Energy under Standard Conditions (16 pts)

1. Identify the compound in each series with the largest *S*°.

A. $Hg_{(l)}$ $Br_{2(l)}$ $CCl_{4(l)}$ $CS_{2(l)}$

_______________ $CCl_{4(l)}$ ___________________

B. $CH_3CH_2OH_{(g)}$ $CH_3CH_2OH_{(l)}$ $CH_3CH_2OH_{(s)}$ $CH_3CH_2OH_{(aq)}$

__________ $CH_3CH_2OH_{(g)}$ _________________

For questions 2 – 3, identify the reaction as: A) Spontaneous at all T; B) Non-spontaneous at all T; C) Spontaneous at low T, but non-spontaneous at high T; or D) Non-spontaneous at low T, but spontaneous at high T.

2. $2\ C_4H_{10(g)} + 13\ O_{2(g)} \rightarrow 8\ CO_{2(g)} + 10\ H_2O_{(g)}$ (HINT: This is a combustion reaction)

________________ A) Spontaneous at all T ____

3. The sublimation of CO_2.

_____________________D) Non-spontaneous at low T, but spontaneous at high T ______________________________

4. Select the thermodynamic value on the left with the appropriate term on the right. (NOTE: not all terms on the right will be used, a term may be used more than once)

	A. endothermic
___E____ $\Delta G_{sys} = 0$	B. exothermic
___ C____ $\Delta S_{univ} < 0$	C. endergonic
___B ___ $\Delta S_{surr} > 0$	D. exergonic
	E. equilibrium

Section 2. Entropy, Enthalpy, and Gibb's Energy under General Conditions (14 pts)

5. Write a reaction quotient for the following reactions:

A. $2\ NO_{(g)} + 2\ Cl_{2(g)} \rightarrow 2\ Cl_2O_{(g)} + N_{2(g)}$

$$\boxed{Q = \frac{P_{N_2} P^2_{Cl_2O}}{P^2_{NO} P^2_{Cl_2}} or \frac{[N_2][Cl_2O]^2}{[NO]^2[Cl_2]^2}}$$

B. $PbSO_{4(s)} \rightarrow Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$$\boxed{Q = [SO_4^{2-}][Pb^{2+}]}$$

6. Select the thermodynamic condition on the left with the appropriate term on the right. (NOTE: Some terms may be used more than once and some terms may not be used at all.)

___D____ Q = K

___C ___ Q/K > 1

___A ____ Q = 1

___B____ Q < K

A. standard conditions

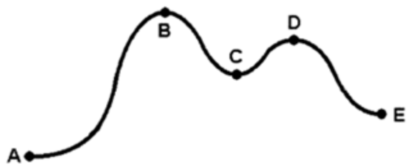
B. spontaneous

C. non-spontaneous

D. equilibrium

Section 3. Fundamentals of Reaction Mechanisms (12 pts)

7. Use the following Reaction Energy Diagram to the answer the following questions:



What is the spontaneity of this reaction under standard conditions?	_non-spontaneous_ _(endergonic)_ _endothermic is ok_
What point(s) represents the transition state(s)?	___B, D________________
How many chemical steps are involved in this reaction?	___2__________________
What value can be calculated by subtracting the energy at A from that at B?	_Activation energy_ _(fwd step1)_

8. For the elementary reaction A + B → products, what two conditions must be met for the reaction to occur?

A&B must collide with the proper orientation and sufficient energy

Section 4. Rates and Rate Laws (10 pts)

9. Consider the following 2 step-reaction:

$$A_{(aq)} + H_2O_{(l)} \rightarrow B_{(aq)} + C_{(aq)}$$

$$B_{(aq)} \rightarrow D_{(aq)}$$

A. Write the overall reaction.

________ $A_{(aq)} + H_2O_{(l)} \rightarrow C_{(aq)} + D_{(aq)}$________________________________

B. Identify any intermediates in the reaction.

_____________ $B_{(aq)}$ ____________________________________

C. Write the rate law assuming the first step is the slow step.

Rate = k_1[A]

D. If the first step is fast and reversible and that the second step is slow, the rate law is:

$$rate = \frac{k_1 k_2 [A]}{k_{-1}[C] + k_2}$$

Under what conditions would this reaction appear first-order overall?

Low [C] such that $k_{-1}[C] << k_2$

Section 5. General Equilibrium (10 pts)

10. The following reaction is at equilibrium. Indicate if the following changes to the system will:
A) shift reaction towards products; B) shift reaction towards reactants; or C) no shift the equilibrium.

$$HNO_{3(l)} + ClF_{(g)} \rightarrow ClONO_{2(g)} + HF_{(g)}$$

A. Addition of $HF_{(g)}$ _ B) shift reaction towards reactants _

B. Addition of $HNO_{3(l)}$ _ C) no shift the equilibrium _

C. Increasing P by addition of $N_{2(g)}$ _ C) no shift the equilibrium _

D. Increasing P by reducing reactor V _ B) shift reaction towards reactants _

Section 6. Calculations (30 pts). YOU MUST SHOW YOUR WORK FOR CREDIT.

11. The degradation of SO_2Cl_2 occurs via a single elementary step with a rate constant of $2.2 \times 10^{-5}\ s^{-1}$. If the initial concentration of SO_2Cl_2 is 0.0040 M, what is the concentration of SO_2Cl_2 after 1.00 hour?

$$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$$

0.0037 M

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12. The rate constant for 2 A → B is $1.8 \times 10^{-2}\ M^{-1}\ s^{-1}$. Calculate the half-life when the concentration of A is 0.35 *M*.

79 s

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13. The standard Gibb's energy ($\Delta G°$) for the following reaction at 298 K is -141.8 kJ/mol.

$$COCl_{2(g)} + H_2O_{(l)} \rightarrow CO_{2(g)} + 2\ HCl_{(g)}$$

What is ΔG for the reaction 298 K when: $P_{COCl2} = 0.3$ atm; $P_{CO2} = 0.6$ atm; and $P_{HCl} = 0.2$ atm.

-148.1 kJ/mol

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14. The equilibrium vapor pressure of H_2O at 20 °C is 2.30×10^{-2} atm. Calculate the standard Gibb's energy ($\Delta G°$) for the vaporization of H_2O at this temperature. (HINT: How is the EVP related to K?)

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

9.19 kJ/mol

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15. At 425 °C, the K_p for the following reaction is 4.18×10^{-9}. At this temperature, if the initial HBr pressure is 1.5 atm, what is the partial pressure of H_2 at equilibrium?

$$2\ HBr_{(g)} \rightarrow H_{2(g)} + Br_{(g)}$$

9.7×10^{-5} atm

Section 7. Essay (8 pts). Answer in paragraph form comprised of 4-6 full sentences.

16. The combustion of methane gas is a spontaneous process, but the reaction requires a spark to ignite the gas. Explain this observation in terms of *thermodynamics* and *kinetics.*

The combustion reaction is spontaneous, but it requires a spark of energy to overcome the activation barrier before the reaction can begin. The spontaneity of a reaction is a thermodynamic concept that compares the energy of the reactants and the products. If the products are lower in energy than the reactants, the reaction is spontaneous but this does not indicate anything about how the reaction will proceed. The rate of a reaction is a kinetic concept that depends on the pathway between reactants and products. The pathway includes a barrier associated with the activation energy. The spark in this example provides the energy for reactants to overcome the barrier and proceed to products.

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USE THE BACK FOR SCRATCH PAPER IF NEEDED

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

$S = k \ln W$

$k = 1.381 \times 10^{-23}$ J/K

$R = 8.314$ J/mol K = 0.08206 L atm/mol K

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

$$K = e^{-\Delta G^\circ/RT}$$

$$\ln \frac{[A]_0}{[A]_t} = akt$$

$$\frac{[A]_0}{[A]_t} = e^{akt}$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = akt$$

$$t_{1/2} = \frac{\ln 2}{ak}$$

$$t_{1/2} = \frac{1}{ak\,[A]_0}$$

$$k = A\, e^{-E_a/RT}$$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$