# **Chemistry 210**

Exam 2

Be sure to put your name on each page. This page can be removed from your exam so that you will have a Periodic Table handy throughout the exam, it does not need to be turned in. Show all your work for problems which require any sort of calculation, no credit will be given for answers without work shown. If you have shown a significant amount of work or multiple drawings for a problem, draw a box around what you consider your final answer.

Avogadro's Number =  $6.022 \times 10^{23}$  units/mol  $32.00^{\circ}F = 0.000^{\circ}C = 273.15K$ Density of Water =  $1.000^{g}/_{mL}$   $R = 0.08206^{L \cdot atm}/_{mol \cdot K} = 8.314^{J}/_{mol \cdot K}$ PV=nRT  $\Delta T_{fp/bp} = k_{fp/bp} \cdot m \cdot i$ For water:  $k_{fp} = -1.86^{\circ C}/_{m}$   $k_{bp} = 0.512^{\circ C}/_{m}$   $P_{1} = X_{1}P_{1}^{\circ}$   $\Pi = MRTi$   $C_{1}V_{1} = C_{2}V_{2}$ Quadratic formula:  $x = \frac{-b \pm \sqrt{b^{2} - 4ac}}{2}$ 

$$\begin{split} &\text{Integrated Rate Laws:} \\ &0^{\text{th}} \text{ order } \quad [A]_t = -kt + [A]_o \\ &1^{\text{st}} \text{ order } \quad \ln[A]_t = -kt + \ln[A]_o \\ &2^{\text{nd}} \text{ order } \quad 1/[A]_t = kt + 1/[A]_o \\ &k = Ae^{-Ea/RT} \\ &\ln(k) = \left(\frac{-E_a}{R}\right) \left(\frac{1}{T}\right) + \ln(A) \\ &\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right) \end{split}$$

$E_{cell} = E_{cell}^{o} - {RT \choose nF} \ln Q$
$E_{cell}^{o} = {RT \choose nF} ln K^{o}$
$K^{o} = e^{(nF)}_{RT} E^{o}_{cell}$
$F = 96485  \text{J}_{\text{V-mol of electrons}}$
$\Delta G^{o} = \Delta H^{o}_{system} - T\Delta S^{o}_{system}$
$\Delta G^{o} = -nFE^{o}_{cell} = -RTlnK^{o}$
$\Delta G = \Delta G^{o} + RT lnQ$
$F = 96485$ $^{\rm C}/_{\rm mol\ electrons}$
1A = 1 C / sec

1																	2
H																	He
1.0079	4	1										5	6	7	8	9	4.0026
												5 <b>D</b>	6	, <b>N</b> T	-		
Li	Be											В	C	N	О	F	Ne
6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
22.990	24.305											26.982	28.086	30.974	32.066	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	$\mathbf{V}$	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	$\mathbf{A}\mathbf{g}$	Cd	In	Sn	Sb	Te	I	Xe
85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	$\mathbf{W}$	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.91	137.33	138.91	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
87	88	89	104	105	106	107	108	109	110	111	112		114		116		
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									
(223)	226.03	227.03	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)	(277)						

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.91	144.24	(145)	150.36	151.97	157.25	158.93	162.50	164.93	167.26	168.94	173.04	174.97
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	$\mathbf{U}$	Np	Pu	Am	Cm	$\mathbf{B}\mathbf{k}$	Cf	Es	Fm	Md	No	Lr
232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(258)	(258)	(259)	(260)

## Multiple Choice: Circle the letter of the most correct response. (3pts per question)

- 1. Which of the following does *not* affect the rate of a reaction?
  - a. The coefficients of the reactants in the balanced equation
  - b. The temperature of the system
  - c. The energy of collisions between reacting particles
  - d. The frequency of collisions between reacting particles
  - e. The orientation of colliding particles
- 2. For the generic equation:

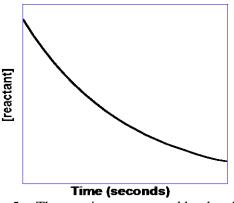
$$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$$

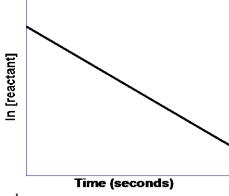
Which of the following is a correct expression of the rate of the reaction:

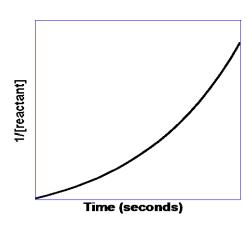
- a.  $\frac{1}{a} \frac{\Delta[A]}{A}$
- b. k[A]<sup>a</sup>[B]<sup>b</sup>
- c.  $\frac{-1}{d} \frac{\Delta[D]}{\Delta t}$
- $\underline{d}$ .  $k[C]^{c}[D]^{d}$
- e.  $^{-1}/_{\mathrm{b}}$   $^{\Lambda[\mathrm{B}]}/_{\Lambda}$
- 3. If the rate of a reaction increases by a factor of 4 when the initial concentration of reactant "A" is increased by a factor of 4, the reaction must be:
  - a. Oth order with respect to [A]<sub>o</sub>
  - b. 1st order with respect to [A]<sub>o</sub>
  - c. 2nd order overall
  - d. 2nd order with respect to [A]<sub>o</sub>
  - e. The order of the reaction depends on the balanced chemical equation
- 4. For a second order reaction:

### a. The slope of the integrated rate law plot is equal to k

- b. The slope of the integrated rate law plot is equal to  $(-E_a/R)$
- c. The intercept of the integrated rate law is equal to the ln of the initial concentration
- d. The intercept of the integrated rate law plot is equal to the initial concentration
- e. The slope of the integrated rate law is equal to the frequency factor, A.







- 5. The reaction represented by the plots above:
  - a. Is zero order

#### b. Is first order

- c. Is second order
- d. Is third order
- e. The order can't be determined by these graphs

- 6. Which of the following is *false* regarding reaction mechanisms?
  - a. The observed rate law is equal to the sum of the rate laws from all steps
  - b. The observed rate law must agree with the rate law of the slowest step
  - c. The steps of the mechanism can contain chemical species that do not appear in the overall correctly balanced chemical equation
  - d. Catalysts can appear in the steps of a mechanism
  - e. A mechanism must be composed of elementary reactions
- 7. Which of the following is *true* regarding catalysts and catalyzed reactions?
  - a. The presence of a catalyst does not change the mechanism of a reaction
  - b. The presence of a catalyst changes the equilibrium constant for a reaction
  - c. The presence of a catalyst changes the activation energy for a reaction
  - d. The presence of a catalyst changes the energy of the products and reactants in a reaction
  - e. The concentration of a catalyst cannot appear in the rate law for a reaction
- 8. For a reaction at equilibrium:
  - a. The reactants and products must be in the gas phase.
  - b. The concentration of reactants is equal to the concentration of products.
  - c. The reaction has stopped.
  - d. The mass of reactants is equal to the mass of products.
  - e. The rate of the forward reaction is equal to the rate of the reverse reaction.
- 9. Which of the following is *false* regarding equilibrium?
  - a. The concentrations of products and reactants does not change once the reaction has reached equilibrium
  - b. Equilibrium can often be shifted by changing pressure or temperature
  - c. The rates of the forward and reverse reactions are equal
  - d. Equilibrium concentrations do not depend upon whether you approach equilibrium from the left or the right
  - e. The forward and reverse reactions stop when a system reaches equilibrium
- 10. For the generic equation

$$aA(g) + bB(g) = cC(g) + dD(g)$$

The value of the equilibrium constant, K<sub>c</sub>:

- a. Is not affected by temperature
- b. Is equal to  $([A]^a[B]^b)/([C]^c[D]^d)$
- c. Is equal to k[A]<sup>a</sup>[B]<sup>b</sup>

### d. Is equal to $([C]^c[D]^d)/([A]^a[B]^b)$

- e. Must be measured, it cannot be derived from the balanced equation
- 11. Which of the following is *true* regarding equilibrium reactions?
  - a. If K < 0, the reaction reaches equilibrium very quickly.
  - b. If K > 1, the reaction is reactant-favored.
  - c. If K = 1, the reaction has stopped.
  - d. If K > 1, the reaction is product-favored.
  - e. If K is very small, the limiting reactant is very nearly used up.
- 12. Considering the reaction given, all of the following stresses will shift the equilibrium to the right except:

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \qquad \Delta H_{rxn} = 131 \text{ }^{kJ}/_{mol}$$

- a. Removing carbon dioxide from the system
- b. Increasing the temperature of the system
- c. Adding carbon monoxide to the system
- d. Increasing the pressure on the system
- e. Removing hydrogen from the system

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*Name*:\_\_\_\_\_

- 13. All of the following can be explained by LeChatelier's Principle except:
  - a. Removing a gaseous product will shift the equilibrium right.
  - b. Adding more of an aqueous reactant will shift the equilibrium right.
  - c. Increasing the temperature of an endothermic reaction will shift the equilibrium right.
  - d. Increasing the pressure will shift an equilibrium toward the side that has more gas particles.
  - e. Removing a gaseous reactant will shift the equilibrium left.
- 14. The reaction quotient for a reaction:
  - a. Tells you how fast the reaction happens
  - b. Is usually a negative number
  - c. Is a constant
  - d. Tells you what direction the reaction must shift to reach equilibrium
  - e. Is the concentration of reactants divided by the concentration of products
- 15. Which of the following statements is *false* regarding the reaction quotient, Q?
  - a. It tells the direction that the reaction must shift to reach equilibrium
  - b. If  $Q < K_c$ , the system needs to shift toward the products to reach equilibrium
  - c. If  $Q=K_c$ , the system is at equilibrium
  - d. If  $Q>K_c$ , the system needs to shift toward the products to reach equilibrium
  - e. It has the same mathematical form as the equilibrium constant

#### **Problems:** Show your work.

- 16. Ammonia gas (NH<sub>3</sub>) reacts with fluorine gas to form trifluoroamine gas (NF<sub>3</sub>) and hydrogen gas. Under some set of conditions at some point in time, you find that 0.147mols of fluorine react every minute in a 1.643L vessel. (20pts)
  - a. What is the rate of florine consumption?
  - b. What is the rate of NH<sub>3</sub> consumption?
  - c. What is the rate of NF<sub>3</sub> production?
  - d. What is the rate of hydrogen production?
  - e. What is the rate of the *reaction*?

$$\begin{array}{l} 2 \ NH_3(g) \ + \ 3 \ F_2(g) \ \ \rightarrow \ \ 2 \ NF_3 \ (g) \ + \ 3 \ H_2(g) \\ Rate_{F2} \ = \ ^{\Delta[F2]}/_{\Delta t} \ = \ (0.147 mols/1.643 L) \ / \ 1 \ minute \ = \ 0.0895^{M}/_{min} \\ Rate_{NH3} \ = \ ^{\Delta[NH3]}/_{\Delta t} \ = \ \{\ ^{(2mol\ NH3)}/_{(3mol\ F2)} \} (\ ^{\Delta[F2]}/_{\Delta t}) \ = \ \{\ ^{(2mol\ NH3)}/_{(3mol\ F2)} \} (0.0895^{M}/_{min}) \ = \ 0.0596^{M}/_{min} \\ Rate_{NF3} \ = \ ^{\Delta[NF3]}/_{\Delta t} \ = \ \{\ ^{(2mol\ NF3)}/_{(3mol\ F2)} \} (\ ^{\Delta[F2]}/_{\Delta t}) \ = \ \{\ ^{(2mol\ NF3)}/_{(3mol\ F2)} \} (0.0895^{M}/_{min}) \ = \ 0.0596^{M}/_{min} \\ Rate_{H2} \ = \ ^{(3mol\ H2)}/_{(2mol\ F2)} \} (\ ^{\Delta[F2]}/_{\Delta t}) \ = \ \{\ ^{(3mol\ H2)}/_{(3mol\ F2)} \} (0.0895^{M}/_{min}) \ = \ 0.0895^{M}/_{min} \\ Rate_{rxn} \ = \ \{\ ^{(1mol\ rxn)}/_{(3mol\ F2)} \} (\ ^{\Delta[F2]}/_{\Delta t}) \ = \ \{\ ^{(1mol\ rxn)}/_{(3mol\ F2)} \} (\ 0.0895^{M}/_{min}) \ = \ 0.0298^{M}/_{min} \\ \end{array}$$

17. A reaction is found to be first order with respect to reactant A and zero order with respect to reactant B. If  $[A]_o = 0.193M$ ,  $[B]_o = 0.482M$  and  $k = 8.61 \times 10^{-3} \text{ sec}^{-1}$ , what is the initial rate of the reaction? (15pts)

Rate<sub>o</sub> = 
$$k[A]_o^{-1}[B]_o^{-0} = k[A]_o^{-1} = (8.61 \times 10^{-3} \text{sec}^{-1})(0.193 \text{M})^1 = 1.66 \times 10^{-3} \text{ M/sec}$$

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#### 18. For the reaction:

$$2 \text{ NO}_2(\text{aq}) + \text{F}_2(\text{aq}) \rightarrow 2 \text{ NOF}(g) + \text{O}_2(g)$$

You have collected the following data at 12.68°C:

Experiment	$[NO_2]_o$	$[F_2]_o$	Rate <sub>observed</sub>
1	1.28 M	0.334 M	$2.08 \times 10^{-4} \text{ M/}_{min}$
2	2.56 M	0.334 M	$2.08 \times 10^{-4} \text{ M/}_{min}$
3	1.28 M	0.167 M	$5.41 \times 10^{-5} \text{ M/}_{\text{min}}$

What are the rate law and the value of the rate law constant, k, for this reaction?

If you redo Experiment 2 at 37.81°C, the rate is  $1.48 \times 10^{-3}$  M/<sub>min</sub>. What is the activation energy for this reaction? (20pts)

Comparing Exp't 1 & 2,  $[NO_2]_0$  doubles, Rate is unchanged  $\rightarrow$  rxn is 0<sup>th</sup> order with respect to  $[NO_2]_0$ Comparing Exp't 3 & 1,  $[F_2]_0$  doubles, Rate is changed by a factor of  $4 \rightarrow rxn$  is  $2^{nd}$  order w.r.t.  $[F_2]_0$ 

Rate<sub>0</sub> =  $k[F_2]_0^2$ 

Plugging in data from Exp't 1 to calculate  $k \rightarrow 2.08 \times 10^{-4} \,\mathrm{M}_{\rm min} = k(0.334 \mathrm{M})^2$ 

 $k = 1.86 \times 10^{-3} \,\mathrm{M}^{-1} \mathrm{min}^{-1}$ 

Plugging in the data from the high T Exp't 2 to calculate a new k  $\rightarrow$  1.48x10<sup>-3 M</sup>/<sub>min</sub> = k(0.334M)<sup>2</sup>  $k = 1.33 \times 10^{-2} \,\mathrm{M}^{-1} \mathrm{min}^{-1}$ 

Plugging in to the comparative Arrhenius equation  $\rightarrow \ln (k_1 / k_2) = (E_a / R)(^1/_{T2} - ^1/_{T1}) \rightarrow$  $\ln \left(1.86 \times 10^{-3} \text{ M}^{-1} \text{min}^{-1} / 1.33 \times 10^{-2} \text{ M}^{-1} \text{min}^{-1}\right) = \left(E_a / 8.314^{J} / \text{mol.K}\right) \left(\frac{1}{310.96 \text{K}} - \frac{1}{285.83 \text{K}}\right)$ 

 $E_a = 57700 \, J_{mol} = 57.7 \, J_{mol}$ 

19. A reaction is found to be second order with respect to phosphate ion, a reactant. If  $[PO_4^{-3}]_0 = 1.39M$  and  $k = 3.16 \times 10^{-3}$ min<sup>-1</sup>, how much time must pass before the concentration of phosphate ions falls to 1.03M? (15pts)

This is an integrated rate law problem (trying to relate concentration and time)  $1/[SO_4^{-2}]_t = kt + (1/[SO_4^{-2}]_o) \rightarrow 1/1.03 = (3.16x10^{-3} min^{-1})(t) + (1/1.39M)$ 

$$1/[SO_4^{-2}]_t = kt + (1/[SO_4^{-2}]_0) \rightarrow 1/1.03 = (3.16x10^{-3} min^{-1})(t) + (1/1.39M)$$
  
 $t = 79.6min$ 

20. For the reaction:

$$2 \text{ NH}_2\text{OH}(g) + \text{CH}_4(g) \iff \text{H}_2\text{C}(\text{OH})_2(g) + 2 \text{ NH}_3(g) \qquad \Delta H = +683.2 \text{ }^{kJ}/_{mol}$$

The following equilibrium concentrations are observed:  $[NH_2OH]_{eq} = 2.28 \times 10^{-2} M$ ,  $[CH_4]_{eq} = 0.304 M$ ,  $[H_2C(OH)_2]_{eq} = 0.304 M$ 0.291 M,  $[NH_3]_{eq} = 4.82 \times 10^{-3} \text{ M}$ . What is the equilibrium constant value for this reaction? Is the reaction productfavored or reactant-favored? (15pts)

$$K = [H_2C(OH)_2]^1[NH_3]^2 / [NH_2OH]^1[CH_4]^1 = (0.291M)^1(4.82x10^{-3}M)^2 / (2.28x10^{-2}M)^2(0.304M)^1 = 4.28x10^{-2}M^2(0.304M)^2 = 4.$$

K is less than 1 so the equilibrium is reactant-favored

- 21. When 0.183mols of carbon dioxide  $\{CO_2(g)\}$  and 0.208mols of hydrogen gas  $\{H_2(g)\}$  are sealed together in a 1.500L vessel, they reach equilibrium with methane  $\{CH_4(g)\}$  and oxygen  $\{O_2(g)\}$ . The equilibrium concentration of  $CO_2(g)$  is found to be 0.0792 M. (20pts)
  - a. What are the equilibrium concentrations of all products and reactants?
  - b. What is the value of  $K_c$ ?
  - c. Is the reaction product-favored or reactant-favored?

	CO <sub>2</sub> (g) +	2 H <sub>2</sub> (g) ⇔	$CH_4(g) +$	$O_2(g)$
[ ]initial	0.183mols/1.500L 0.1220M	0.208mols/1.500L 0.1387M	0 <b>M</b>	ОМ
Δ[]	-x	-2x	+x	+x
[]equilibrium	(0.1220 - x)M	(0.1387 - 2x)M	х М	х М

$$[CO_2]_{eq} = 0.0792M = (0.1220 - x)M$$
  
 $x = 0.0428M$ 

Plugging in to get all the concentrations:

 $[H_2]_{eq} = 0.1387 - 2(0.0428) = 0.0531M; \ [CH_4]_{eq} = 0.0428M; \ [O_2]_{eq} = 0.0428M \\ K_c = [CH_4]_{eq} [O_2]_{eq} / [CO_2]_{eq} [H_2]_{eq}^2 = (0.0428)(0.0428) / (0.0792M)(0.0531M)^2 = 8.20 \\ K_c \text{ is greater than 1, so the equilibrium is product-favored}$