

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 = 6.022×10^{23} units/mol

$32.00^\circ\text{F} = 0.000^\circ\text{C} = 273.15\text{K}$

Density of Water = $1.000^{\text{g}}/\text{mL}$

$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} = 8.314 \text{ J}/\text{mol}\cdot\text{K}$

$PV = nRT$

$\Delta T_{\text{fp/bp}} = k_{\text{fp/bp}} \cdot m \cdot i$

For water: $k_{\text{fp}} = -1.86^\circ\text{C}/m$
 $k_{\text{bp}} = 0.512^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

Quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Integrated Rate Laws:

0th order $[A]_t = -kt + [A]_o$

1st order $\ln[A]_t = -kt + \ln[A]_o$

2nd order $1/[A]_t = kt + 1/[A]_o$

$k = Ae^{-E_a/RT}$

$$\ln(k) = \left(\frac{-E_a}{R} \right) \left(\frac{1}{T} \right) + \ln(A)$$

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

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \right)$$

$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$

$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K^\circ$

$K^\circ = e^{(nF/RT) E^\circ_{\text{cell}}}$

$F = 96485 \text{ J}/\text{V}\cdot\text{mol of electrons}$

$\Delta G^\circ = \Delta H^\circ_{\text{system}} - T\Delta S^\circ_{\text{system}}$

$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K^\circ$

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

$F = 96485 \text{ C}/\text{mol electrons}$

$1A = 1 \text{ C} / \text{sec}$

1 H 1.0079																	2 He 4.0026				
3 Li 6.941	4 Be 9.0122															5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305															13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80				
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29				
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)				
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)	114		116							

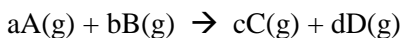
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.94	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)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



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

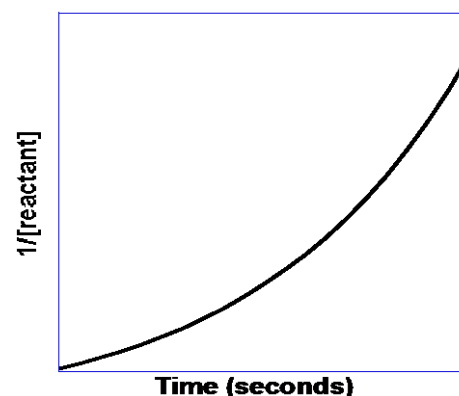
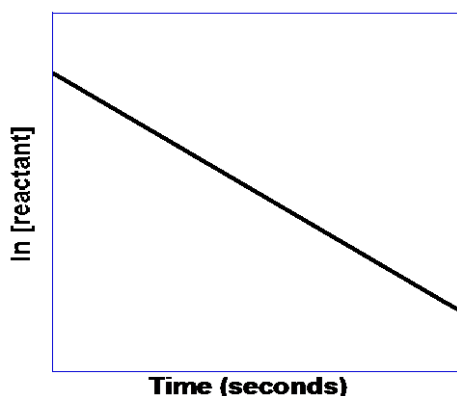
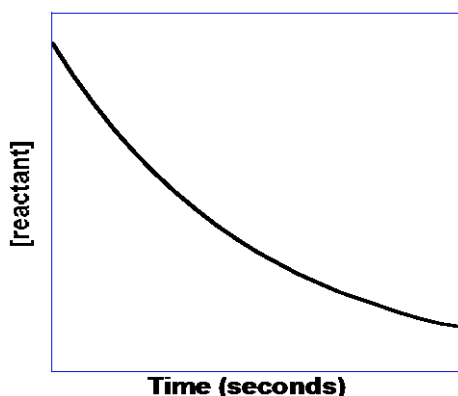
- a. $\frac{1}{a} \frac{\Delta[A]}{\Delta t}$
- b. $k[A]^a[B]^b$
- c. $-\frac{1}{d} \frac{\Delta[D]}{\Delta t}$
- d. $k[C]^c[D]^d$
- e. $-\frac{1}{b} \frac{\Delta[B]}{\Delta t}$**

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. 0th order with respect to $[A]_0$
- b. 1st order with respect to $[A]_0$**
- c. 2nd order overall
- d. 2nd order with respect to $[A]_0$
- 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?
- The observed rate law is equal to the sum of the rate laws from all steps**
 - The observed rate law must agree with the rate law of the slowest step
 - The steps of the mechanism can contain chemical species that do not appear in the overall correctly balanced chemical equation
 - Catalysts can appear in the steps of a mechanism
 - A mechanism must be composed of elementary reactions
7. Which of the following is *true* regarding catalysts and catalyzed reactions?
- The presence of a catalyst does not change the mechanism of a reaction
 - The presence of a catalyst changes the equilibrium constant for a reaction
 - The presence of a catalyst changes the activation energy for a reaction**
 - The presence of a catalyst changes the energy of the products and reactants in a reaction
 - The concentration of a catalyst cannot appear in the rate law for a reaction
8. For a reaction at equilibrium:
- The reactants and products must be in the gas phase.
 - The concentration of reactants is equal to the concentration of products.
 - The reaction has stopped.
 - The mass of reactants is equal to the mass of products.
 - The rate of the forward reaction is equal to the rate of the reverse reaction.**
9. Which of the following is *false* regarding equilibrium?
- The concentrations of products and reactants does not change once the reaction has reached equilibrium
 - Equilibrium can often be shifted by changing pressure or temperature
 - The rates of the forward and reverse reactions are equal
 - Equilibrium concentrations do not depend upon whether you approach equilibrium from the left or the right
 - The forward and reverse reactions stop when a system reaches equilibrium**
10. For the generic equation
- $$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$
- The value of the equilibrium constant, K_c :
- Is not affected by temperature
 - Is equal to $([A]^a[B]^b)/([C]^c[D]^d)$
 - Is equal to $k[A]^a[B]^b$
 - Is equal to $([C]^c[D]^d)/([A]^a[B]^b)$**
 - Must be measured, it cannot be derived from the balanced equation
11. Which of the following is *true* regarding equilibrium reactions?
- If $K < 0$, the reaction reaches equilibrium very quickly.
 - If $K > 1$, the reaction is reactant-favored.
 - If $K = 1$, the reaction has stopped.
 - If $K > 1$, the reaction is product-favored.**
 - 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:
- $$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \quad \Delta H_{rxn} = 131 \text{ kJ/mol}$$
- Removing carbon dioxide from the system
 - Increasing the temperature of the system
 - Adding carbon monoxide to the system
 - Increasing the pressure on the system**
 - Removing hydrogen from the system

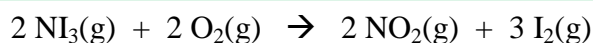
13. All of the following can be explained by LeChatelier's Principle except:
- Removing a gaseous product will shift the equilibrium right.
 - Adding more of an aqueous reactant will shift the equilibrium right.
 - Increasing the temperature of an endothermic reaction will shift the equilibrium right.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

True/False: For each of the following statements, circle T for true and F for false. For all false statements, give a brief explanation of *why* the statement is false. (3pts each row)

		Statement	If false, explain why (briefly)
16.	T F	The observed rate law is equal to the sum of the rate laws from all steps	Observed rate law is consistent with the slowest rate/slowest step
17.	T F	Catalysts can appear in the steps of a mechanism	
18.	T F	The presence of a catalyst changes the equilibrium constant for a reaction	Equilibrium is thermodynamics, catalysts only change the kinetics of a rxn
19.	T F	Equilibrium can often be shifted by changing pressure or temperature	
20.	T F	At equilibrium, the concentration of reactants and products are equal	@Equilibrium, the concentrations do not change, but they may or may not be equal
21.	T F	If $K > 1$, the reaction is reactant-favored.	$K < 1$ is reactant-favored $K > 1$ is product-favored
22.	T F	The reaction quotient indicates the direction that the reaction must shift to reach equilibrium	
23.	T F	If $Q < K_c$, the system needs to shift toward the products to reach equilibrium	

Problems: Show your work.

24. Triiodoamine (NI₃) reacts with oxygen to form nitrogen dioxide and iodine. Under some set of conditions at some point in time, you find that 0.183mols of oxygen react every minute in a 900.0mL vessel. (15pts)
- What is the rate of oxygen consumption?
 - What is the rate of NI₃ consumption?
 - What is the rate of nitrogen dioxide production?
 - What is the rate of iodine production?
 - What is the rate of the *reaction*?



$$\text{Rate}_{\text{O}_2} = \frac{\Delta[\text{O}_2]}{\Delta t} = (0.183 \text{mols}/0.9000\text{L}) / 1 \text{ minute} = 0.203 \text{M}/\text{min}$$

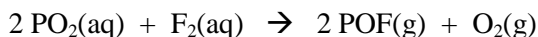
$$\text{Rate}_{\text{NI}_3} = \frac{\Delta[\text{NI}_3]}{\Delta t} = \left\{ \frac{2 \text{mol NI}_3}{2 \text{mol O}_2} \right\} \left(\frac{\Delta[\text{O}_2]}{\Delta t} \right) = \left\{ \frac{2 \text{mol NI}_3}{2 \text{mol O}_2} \right\} (0.203 \text{M}/\text{min}) = 0.203 \text{M}/\text{min}$$

$$\text{Rate}_{\text{NO}_2} = \frac{\Delta[\text{NO}_2]}{\Delta t} = \left\{ \frac{2 \text{mol NO}_2}{2 \text{mol O}_2} \right\} \left(\frac{\Delta[\text{O}_2]}{\Delta t} \right) = \left\{ \frac{2 \text{mol NI}_3}{2 \text{mol O}_2} \right\} (0.203 \text{M}/\text{min}) = 0.203 \text{M}/\text{min}$$

$$\text{Rate}_{\text{I}_2} = \frac{\Delta[\text{I}_2]}{\Delta t} = \left\{ \frac{3 \text{mol I}_2}{2 \text{mol O}_2} \right\} \left(\frac{\Delta[\text{O}_2]}{\Delta t} \right) = \left\{ \frac{2 \text{mol NI}_3}{2 \text{mol O}_2} \right\} (0.203 \text{M}/\text{min}) = 0.305 \text{M}/\text{min}$$

$$\text{Rate}_{\text{rxn}} = \left\{ \frac{1 \text{mol rxn}}{2 \text{mol O}_2} \right\} \left(\frac{\Delta[\text{O}_2]}{\Delta t} \right) = \left\{ \frac{1 \text{mol rxn}}{2 \text{mol O}_2} \right\} (0.203 \text{M}/\text{min}) = 0.102 \text{M}/\text{min}$$

25. For the reaction:



You have collected the following data at 18.68°C:

Experiment	[PO ₂] _o	[F ₂] _o	Rate _{observed}
1	1.43 M	0.882 M	2.08x10 ⁻⁴ M/min
2	2.86 M	0.882 M	2.08x10 ⁻⁴ M/min
3	1.43 M	0.441 M	5.41x10 ⁻⁵ M/min

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

If you redo Experiment 3 at 33.81°C, the rate is 1.48x10⁻⁴ M/min. What is the activation energy for this reaction? (15pts)

Comparing Exp't 1 & 2, [PO₂]_o doubles, Rate is unchanged → rxn is 0th order with respect to [PO₂]_o

Comparing Exp't 3 & 1, [F₂]_o doubles, Rate is changed by a factor of 4 → rxn is 2nd order w.r.t. [F₂]_o

$$\text{Rate}_o = k[\text{F}_2]_o^2$$

$$\text{Plugging in data from Exp't 1 to calculate k} \rightarrow 2.08 \times 10^{-4} \text{ M}/\text{min} = k(0.882 \text{M})^2$$

$$k = 2.67 \times 10^{-4} \text{ M}^{-1} \text{min}^{-1}$$

$$\text{Plugging in the data from the high temperature Exp't 3 to calculate a new k} \rightarrow 1.48 \times 10^{-4} \text{ M}/\text{min} =$$

$$k(0.441 \text{M})^2$$

$$k = 7.61 \times 10^{-4} \text{ M}^{-1} \text{min}^{-1}$$

$$\text{Plugging in to the comparative Arrhenius equation} \rightarrow \ln(k_1/k_2) = (E_a/R)(1/T_2 - 1/T_1) \rightarrow$$

$$\ln(2.67 \times 10^{-4} \text{ M}^{-1} \text{min}^{-1} / 7.61 \times 10^{-4} \text{ M}^{-1} \text{min}^{-1}) = (E_a / 8.314 \text{ J}/\text{mol.K})(1/306.96\text{K} - 1/291.83\text{K})$$

$$E_a = 51600 \text{ J}/\text{mol} = 51.6 \text{ kJ}/\text{mol}$$

26. A reaction is found to be second order with respect to reactant A and first order with respect to reactant B. If $[A]_0 = 0.334\text{M}$, $[B]_0 = 0.482\text{M}$ and $k = 5.18 \times 10^{-4} \text{M}^{-2}\text{sec}^{-1}$, what is the initial rate of the reaction? (12pts)

$$\text{Rate}_0 = k[A]_0^2[B]_0 = (5.18 \times 10^{-4} \text{M}^{-2}\text{sec}^{-1})(0.334\text{M})^2(0.482\text{M}) = 2.79 \times 10^{-5} \text{M}/\text{sec}$$

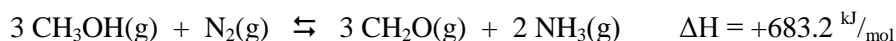
27. A reaction is found to be first order with respect to sulfate ion, a reactant. If $[\text{SO}_4^{2-}]_0 = 1.67\text{M}$ and $k = 3.63 \times 10^{-2} \text{min}^{-1}$, how much time must pass before the concentration of sulfate ions falls to 1.03M ? (12pts)

This is an integrated rate law problem (trying to relate concentration and time)

$$\ln [\text{SO}_4^{2-}]_t = -kt + \ln [\text{SO}_4^{2-}]_0 \rightarrow \ln(1.03\text{M}) = -(3.63 \times 10^{-2} \text{min}^{-1})(t) + \ln(1.67\text{M})$$

$$t = 13.3\text{min}$$

28. For the reaction:



The following equilibrium concentrations are observed: $[\text{CH}_3\text{OH}]_{\text{eq}} = 8.34 \times 10^{-3}\text{M}$, $[\text{N}_2]_{\text{eq}} = 0.118\text{M}$, $[\text{CH}_2\text{O}]_{\text{eq}} = 0.186\text{M}$, $[\text{NH}_3]_{\text{eq}} = 1.02 \times 10^{-4}\text{M}$. What is the equilibrium constant value for this reaction? (12pts)

$$K = [\text{CH}_2\text{O}]^3[\text{NH}_3]^2 / [\text{CH}_3\text{OH}]^3[\text{N}_2]^1 = (0.186\text{M})^3(1.02 \times 10^{-4}\text{M})^2 / (8.34 \times 10^{-3}\text{M})^3(0.118\text{M})^1 = 9.78 \times 10^{-4}$$

29. When 0.183mols of nitrogen dioxide $\{\text{NO}_2(\text{g})\}$ and 0.208mols of hydrogen gas $\{\text{H}_2(\text{g})\}$ are sealed together in a 1.500L vessel, they reach equilibrium with ammonia $\{\text{NH}_3(\text{g})\}$ and oxygen $\{\text{O}_2(\text{g})\}$. The equilibrium concentration of $\text{NO}_2(\text{g})$ is found to be 0.0412M . (15pts)

- What are the equilibrium concentrations of all products and reactants?
- What is the value of K_c ?
- Is the reaction product-favored or reactant-favored?

	$2 \text{NO}_2(\text{g}) +$	$3 \text{H}_2(\text{g}) \rightleftharpoons$	$2 \text{NH}_3(\text{g}) +$	$2 \text{O}_2(\text{g})$
$[\]_{\text{initial}}$	$0.183\text{mols}/1.500\text{L}$ 0.1220M	$0.208\text{mols}/1.500\text{L}$ 0.1387M	0M	0M
$\Delta [\]$	$-2x$	$-3x$	$+2x$	$+2x$
$[\]_{\text{equilibrium}}$	$(0.1220 - 2x)\text{M}$	$(0.1387 - 3x)\text{M}$	$2x \text{M}$	$2x \text{M}$

$$[\text{NO}_2]_{\text{eq}} = 0.0412\text{M} = (0.1220 - 2x)\text{M}$$

$$x = 0.0404\text{M}$$

Plugging in to get all the concentrations:

$$[\text{H}_2]_{\text{eq}} = 0.1387 - 3(0.0404) = 0.0175\text{M}; [\text{NH}_3]_{\text{eq}} = 2(0.0404) = 0.0808\text{M}; [\text{O}_2]_{\text{eq}} = 2(0.0404) = 0.0808\text{M}$$

$$K_c = [\text{NH}_3]_{\text{eq}}^2[\text{O}_2]_{\text{eq}}^2 / [\text{NO}_2]_{\text{eq}}^2[\text{H}_2]_{\text{eq}}^3 = (0.0808)^2(0.0808)^2 / (0.0412\text{M})^2(0.0175\text{M})^3 = 4690$$

K_c is greater than 1, so the equilibrium is product-favored