

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							

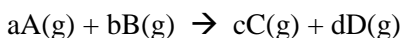
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.94	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)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

Multiple Choice: Circle the letter of the most correct response. (5pts 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:

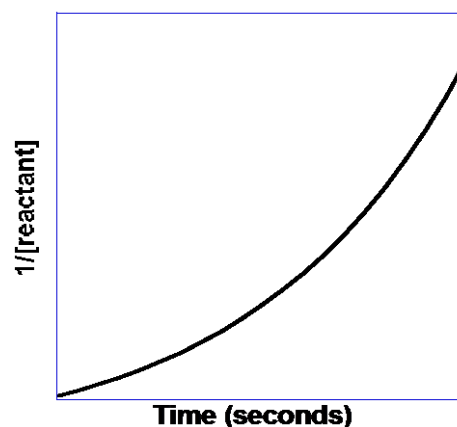
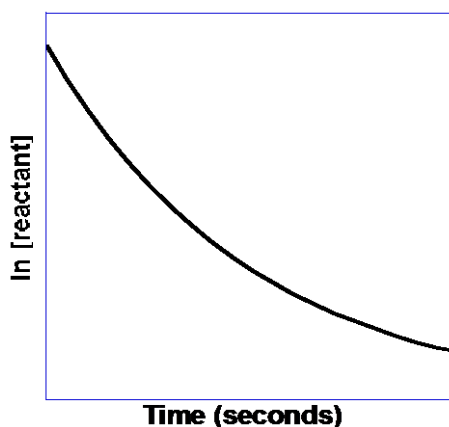
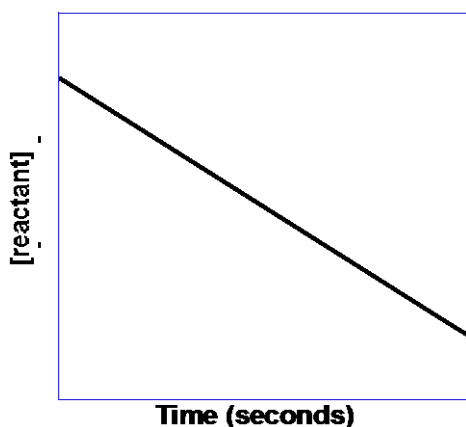
- a. $1/a \Delta[A]/\Delta t$
- b. $k[A]^a[B]^b$
- c. $-1/d \Delta[D]/\Delta t$
- d. $k[C]^c[D]^d$
- e. $-1/b \Delta[B]/\Delta t$**

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 2, 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 first 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.

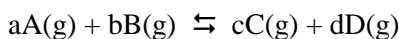


5. The reaction represented by the plots above:

- 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

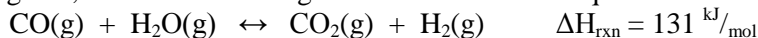
6. Which of the following is **false** regarding reaction mechanisms?
- a. **The observed rate law is equal to the sum of the rate laws from all steps**
 - b. The observed rate law must agree with the rate law of the slowest step
 - c. The steps of the mechanism can contain chemical species that do not 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. 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**

9. For the generic equation



The value of the equilibrium constant, K_c :

- a. Is not affected by temperature
 - b. Is equal to $([A]^a[B]^b)/([C]^c[D]^d)$
 - c. Is equal to $k[A]^a[B]^b$
 - d. **Is equal to $([C]^c[D]^d)/([A]^a[B]^b)$**
 - e. Must be measured, it cannot be derived from the balanced equation
10. 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.
11. Considering the reaction given, all of the following stresses will shift the equilibrium to the right except:



- 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

12. Which of the following statements is **true** regarding the reaction quotient, Q ?
- a. It indicates how quickly a reaction will reach equilibrium
 - b. **If $Q > K_c$, the system needs to shift toward the reactants to reach equilibrium**
 - c. If $Q = K_c$, the reaction has stopped
 - 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 rate law expression

Problems: Show your work.

13. A reaction is found to be second order with respect to reactant A and zero order with respect to reactant B. If $[A]_o = 0.351\text{M}$, $[B]_o = 0.442\text{M}$ and $k = 5.18 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$, what is the initial rate of the reaction? (12pts)

The rate law is:

$$\text{Rate}_o = k [A]_o^2 [B]_o^0 = k [A]_o^2$$

Plugging in the numbers from the problem:

$$\text{Rate}_o = (5.18 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}) (0.351\text{M})^2 = 6.38 \times 10^{-4} \text{ M}/\text{sec}$$

14. For the reaction:



The equilibrium concentrations are observed: $[\text{CH}_3\text{OH}]_{\text{eq}} = 0.291\text{M}$, $[\text{F}_2]_{\text{eq}} = 0.118\text{M}$, $[\text{CF}_3\text{OH}]_{\text{eq}} = 7.72 \times 10^{-2} \text{ M}$, $[\text{H}_2]_{\text{eq}} = 0.834 \text{ M}$. What is the equilibrium constant for this reaction? (12pts)

Plugging the numbers from the problem into the equilibrium constant expression:

$$K_c = \frac{[\text{CF}_3\text{OH}]_{\text{eq}}^2 [\text{H}_2]_{\text{eq}}^3}{[\text{CH}_3\text{OH}]_{\text{eq}}^2 [\text{F}_2]_{\text{eq}}^3} = \frac{(7.72 \times 10^{-2})^2 (0.834)^3}{(0.291)^2 (0.118)^3} = 24.8$$

15. A reaction is found to be zero order with respect to carbonate ion, a reactant. If $[\text{CO}_3^{2-}]_o = 3.94\text{M}$ and $k = 6.81 \times 10^{-2} \text{ M} \cdot \text{min}^{-1}$, how much time must pass before the concentration of carbonate ions falls to $1.54 \times 10^{-3} \text{ M}$? (12pts)

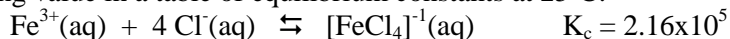
This problem uses the zeroth order integrated rate law:

$$[\text{CO}_3^{2-}]_t = -kt + [\text{CO}_3^{2-}]_o$$

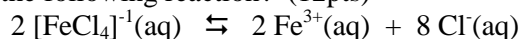
Plugging in the numbers from the problem:

$$(1.54 \times 10^{-3} \text{ M}) = -(6.81 \times 10^{-2} \text{ M}/\text{min})(t) + (3.94\text{M})$$
$$t = 57.8 \text{ minutes} = 3470 \text{ seconds} = 0.964 \text{ hours}$$

16. You have found the following value in a table of equilibrium constants at 25°C:



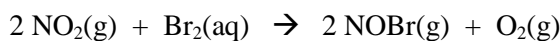
What is the equilibrium constant for the following reaction? (12pts)



To get from the first equation to the second equation, we need to reverse it and double it. Therefore, the new equilibrium constant value is:

$$K_{\text{new}} = \left(\frac{1}{K_c} \right)^2 = \left(\frac{1}{2.16 \times 10^5} \right)^2 = 2.14 \times 10^{-11}$$

17. For the reaction:



You have collected the following data at 46.92°C:

Experiment	[NO ₂] _o	[Br ₂] _o	Rate _{observed}
1	1.38 M	1.62 M	1.37x10 ⁻² M/min
2	2.76 M	1.62 M	1.37x10 ⁻² M/min
3	1.38 M	3.24 M	5.48x10 ⁻² 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 16.31°C, the rate is 7.53x10⁻⁴ M/min. What is the activation energy for this reaction? (21pts)

Comparing Exp't 1 and 2, the NO₂ concentration doubles, but the rate is unchanged, so the reaction must be zero order with respect to [NO₂]_o.

Comparing Exp't 1 and 3, the Br₂ concentration doubles and the rate increases by a factor of 4 {that's 2²}, so the reaction must be 2nd order with respect to [Br₂]_o.

Plugging in to the rate law expression:

$$\begin{aligned} \text{Rate}_o &= k [\text{NO}_2]_o^0 [\text{Br}_2]_o^2 = k [\text{Br}_2]_o^2 \\ (1.37 \times 10^{-2} \text{ M/min}) &= k (1.62 \text{ M})^2 \\ k &= 5.22 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1} \end{aligned}$$

To determine activation energy, we need to calculate k at the new temperature, plugging in the concentrations from Exp't 3 and solving gives k_{16.31°C} = 7.17x10⁻⁵ M⁻¹min⁻¹

Plugging in to the comparative form of the Arrhenius equation:

$$\ln\left(\frac{k_1}{k_2}\right) = \ln\left(\frac{5.22 \times 10^{-3}}{7.17 \times 10^{-5}}\right) = \left(\frac{E_a}{8.314 \text{ J/mol}\cdot\text{K}}\right) \left(\frac{1}{(16.13 + 273.15)\text{K}} - \frac{1}{(46.92 + 273.15)\text{K}}\right) = \left(\frac{E_a}{R}\right) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solving, E_a = 1.07x10⁵ J/mol = 107 kJ/mol

18. When 0.267mols of sulfur dioxide {SO₂(g)} and 0.338mols of fluorine gas {F₂(g)} are sealed together in a 1.500L vessel, they reach equilibrium with thionyl fluoride {SOF₂(g)} and oxygen {O₂(g)}. The equilibrium concentration of F₂(g) is found to be 0.193 M. (21pts)

- 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 SO ₂ (g) +	2 F ₂ (g) ↔	2 SOF ₂ (g) +	O ₂ (g)
Initial	$\frac{0.267 \text{ mols SO}_2}{1.500 \text{ L}} = 0.178 \text{ M}$	$\frac{0.338 \text{ mols F}_2}{1.500 \text{ L}} = 0.225 \text{ M}$	0 M	0 M
Δ	- 2x	- 2x	+ 2x	+ x
@ Equil.	(0.178 - 2x) M	(0.225 - 2x) M	2x M	x M

The problem gives the equilibrium concentration of F₂(g), so we can solve for "x" by:

$$\begin{aligned} 0.225 \text{ M} - 2x &= 0.193 \text{ M} \\ x &= 0.016 \text{ M} \end{aligned}$$

Plugging in "x", we can solve for all the equilibrium concentrations.

$$\begin{aligned} [\text{SO}_2]_{\text{eq}} &= 0.178 - 2(0.016) = 0.146 \text{ M} & [\text{F}_2]_{\text{eq}} &= 0.193 \text{ M (from problem);} \\ [\text{SOF}_2]_{\text{eq}} &= 2(0.016) = 0.032 \text{ M} & [\text{O}_2]_{\text{eq}} &= 0.016 \text{ M} \end{aligned}$$

Plugging the equilibrium concentrations into the equilibrium constant expression:

$$K_c = \frac{[\text{SOF}_2]_{\text{eq}}^2 [\text{O}_2]_{\text{eq}}^1}{[\text{SO}_2]_{\text{eq}}^2 [\text{F}_2]_{\text{eq}}^2} = \frac{(0.032)^2 (0.016)^1}{(0.146)^2 (0.193)^2} = 0.0206$$

The value of K_c is less than 1, so the equilibrium is reactant-favored. (Although not by a lot...)