

# 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

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

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

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

$1\text{atm} = 760\text{torr} = 760\text{mmHg} = 101.325\text{kPa}$

$PV = nRT$

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

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:

0<sup>th</sup>  $[A]_t = -kt + [A]_o$

1<sup>st</sup>  $\ln[A]_t = -kt + \ln[A]_o$

2<sup>nd</sup>  $1/[A]_t = kt + 1/[A]_o$

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

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

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

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

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

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

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

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

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

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

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

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

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

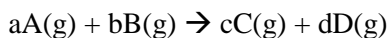
1 <b>H</b> 1.0079																	2 <b>He</b> 4.0026				
3 <b>Li</b> 6.941	4 <b>Be</b> 9.0122															5 <b>B</b> 10.811	6 <b>C</b> 12.011	7 <b>N</b> 14.007	8 <b>O</b> 15.999	9 <b>F</b> 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305															13 <b>Al</b> 26.982	14 <b>Si</b> 28.086	15 <b>P</b> 30.974	16 <b>S</b> 32.066	17 <b>Cl</b> 35.453	18 <b>Ar</b> 39.948
19 <b>K</b> 39.098	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.956	22 <b>Ti</b> 47.88	23 <b>V</b> 50.942	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.938	26 <b>Fe</b> 55.847	27 <b>Co</b> 58.933	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.61	33 <b>As</b> 74.922	34 <b>Se</b> 78.96	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.80				
37 <b>Rb</b> 85.468	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.906	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.906	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53 <b>I</b> 126.90	54 <b>Xe</b> 131.29				
55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.33	71 <b>Lu</b> 174.97	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.95	74 <b>W</b> 183.84	75 <b>Re</b> 186.21	76 <b>Os</b> 190.23	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.97	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.38	82 <b>Pb</b> 207.2	83 <b>Bi</b> 208.98	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)				
87 <b>Fr</b> (223)	88 <b>Ra</b> 226.03	103 <b>Lr</b> (260)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 <b>Ds</b> (269)	111 <b>Rg</b> (272)	112 <b>Cn</b> (277)	113	114	115	116	117	118				

57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.97	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.93	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.93	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.94	70 <b>Yb</b> 173.04
89 <b>Ac</b> 227.03	90 <b>Th</b> 232.04	91 <b>Pa</b> 231.04	92 <b>U</b> 238.03	93 <b>Np</b> 237.05	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (258)	101 <b>Md</b> (258)	102 <b>No</b> (259)

**Multiple Choice:** Circle the letter of the most correct response. (4pts per question)

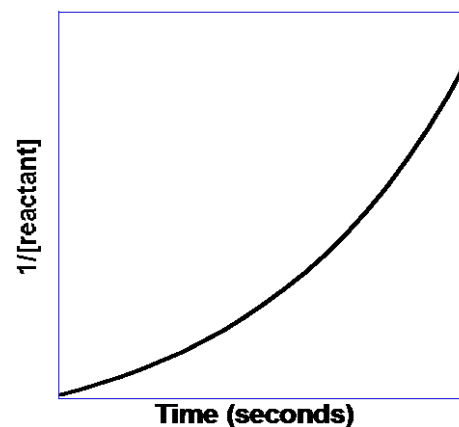
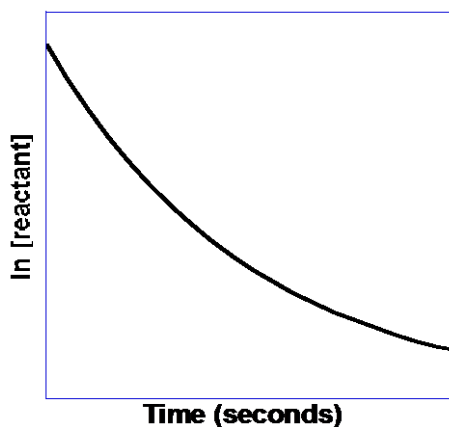
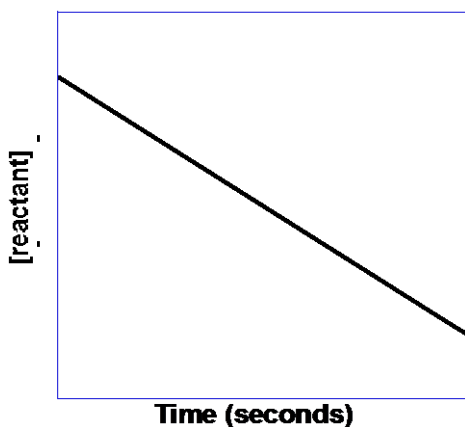
- Which of the following does **not** affect the rate of a reaction?
  - The orientation of colliding particles
  - The coefficients of the reactants in the balanced equation**
  - The temperature of the system
  - The energy of collisions between reacting particles
  - The frequency of collisions between reacting particles

- For the generic equation:



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

- $k[C]^c[D]^d$
  - $^{-1/b} \Delta[B]/\Delta t$**
  - $^{1/a} \Delta[A]/\Delta t$
  - $k[A]^a[B]^b$
  - $^{-1/d} \Delta[D]/\Delta t$
- If the rate of a reaction increases by a factor of 9 when the initial concentration of reactant “A” is increased by a factor of 3, the reaction must be:
    - 0th order with respect to  $[A]_0$
    - 1st order with respect to  $[A]_0$
    - 2nd order overall
    - 2nd order with respect to  $[A]_0$**
    - The order of the reaction depends on the balanced chemical equation
  - For a zero order reaction:
    - The intercept of the integrated rate law is equal to the  $\ln$  of the initial concentration
    - The intercept of the integrated rate law plot is equal to the initial concentration**
    - The slope of the integrated rate law is equal to the frequency factor, A.
    - The slope of the integrated rate law plot is equal to k
    - The slope of the integrated rate law plot is equal to  $(-E_a/R)$

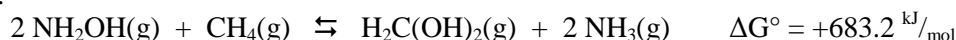


- The reaction represented by the plots above:
  - Is zero order**
  - Is first order
  - Is second order
  - Is third order
  - The order can't be determined by these graphs

6. Which of the following is **false** regarding reaction mechanisms?
- 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
  - A mechanism must be composed of elementary reactions
  - The observed rate law is equal to the sum of the rate laws from all steps
7. For a reaction at equilibrium:
- The rate of the forward reaction is equal to the rate of the reverse reaction.
  - 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.
8. Which of the following is **false** regarding equilibrium?
- 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
  - The concentrations of products and reactants does not change once the reaction has reached equilibrium
  - The rates of the forward and reverse reactions are equal
9. 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
10. Which of the following is **true** regarding equilibrium reactions?
- 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.
  - If  $K < 0$ , the reaction reaches equilibrium very quickly.
  - If  $K > 1$ , the reaction is reactant-favored.

**Problems:** Show your work.

11. For the reaction:



The following equilibrium concentrations are observed:  $[\text{NH}_2\text{OH}]_{\text{eq}} = 9.13 \times 10^{-2} \text{ M}$ ,  $[\text{CH}_4]_{\text{eq}} = 0.284 \text{ M}$ ,  $[\text{H}_2\text{C}(\text{OH})_2]_{\text{eq}} = 0.257 \text{ M}$ ,  $[\text{NH}_3]_{\text{eq}} = 3.84 \times 10^{-3} \text{ M}$ . What is the equilibrium constant value for this reaction? Is the reaction product-favored or reactant-favored? (10pts)

Equilibrium constant expression:

$$K_c = \frac{[\text{H}_2\text{C}(\text{OH})_2]_{\text{eq}}^1 [\text{NH}_3]_{\text{eq}}^2}{[\text{NH}_2\text{OH}]_{\text{eq}}^2 [\text{CH}_4]_{\text{eq}}^1} = \frac{(0.257 \text{ M})^2 (3.84 \times 10^{-3} \text{ M})^2}{(9.13 \times 10^{-2} \text{ M})^2 (0.284 \text{ M})^1} = 1.60 \times 10^{-3}$$

$K < 1$ , reactant-favored

12. A reaction is found to be zero order with respect to ethane (C<sub>2</sub>H<sub>6</sub>), a reactant. If [C<sub>2</sub>H<sub>6</sub>]<sub>0</sub> = 2.95M and k = 7.81x10<sup>-2</sup> M<sup>-1</sup>min<sup>-1</sup>, how much time must pass before the concentration of ethane falls to 0.227M? (15pts)

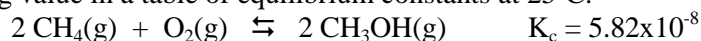
Zero-order integrated rate law:

$$[C_2H_6]_t = -kt + [C_2H_6]_0$$

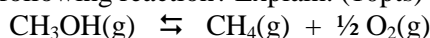
$$(0.227M) = -(7.81 \times 10^{-2} \text{ M}^{-1}\text{min}^{-1})t + (2.95M)$$

$$t = 34.9\text{min}$$

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



What is the equilibrium constant for the following reaction? Explain. (10pts)



Rxn is reversed and multiplied by 1/2, so the value of K should be inverted and raised to the 1/2 power.

$$(1 / 5.82 \times 10^{-8})^{1/2} = 4.15 \times 10^3$$

14. A reaction is found to be first order with respect to reactant A and second order with respect to reactant B. If [A]<sub>0</sub> = 0.128M, [B]<sub>0</sub> = 0.215M and k = 4.37x10<sup>-5</sup> M<sup>-2</sup>sec<sup>-1</sup>, what is the initial rate of the reaction? (10pts)

$$\text{Rate}_0 = k[A]_0^1[B]_0^2$$

$$\text{Rate}_0 = (4.37 \times 10^{-5} \text{ M}^{-2}\text{sec}^{-1})(0.128\text{M})^1(0.215\text{M})^2 = 2.59 \times 10^{-7} \text{ M/sec}$$

15. Chlorine gas reacts with water gas to form chlorine dioxide gas (ClO<sub>2</sub>) and hydrogen gas. Under some set of conditions at some point in time, you find that 0.124mols of chlorine react every minute in a 1.882L vessel. (15pts)
- What is the rate of chlorine consumption?
  - What is the rate of water consumption?
  - What is the rate of ClO<sub>2</sub> production?
  - What is the rate of hydrogen production?
  - What is the rate of the *reaction*?

$$\text{Cl}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{ClO}_2(\text{g}) + 4 \text{H}_2(\text{g})$$

$$\text{Rate}_{\text{Cl}_2} = \{0.124\text{mols Cl}_2 / 1.882\text{L}\} / 1.000\text{min} = 0.0659 \text{ M}/\text{min}$$

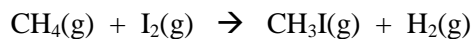
$$\text{Rate}_{\text{H}_2\text{O}} = (0.0659 \text{ M}/\text{min}) (4\text{mol H}_2\text{O} / 1\text{mol Cl}_2) = 0.264 \text{ M}/\text{min}$$

$$\text{Rate}_{\text{ClO}_2} = (0.0659 \text{ M}/\text{min}) (2\text{mol ClO}_2 / 1\text{mol Cl}_2) = 0.132 \text{ M}/\text{min}$$

$$\text{Rate}_{\text{H}_2} = (0.0659 \text{ M}/\text{min}) (4\text{mol H}_2 / 1\text{mol Cl}_2) = 0.264 \text{ M}/\text{min}$$

$$\text{Rate}_{\text{rxn}} = (0.0659 \text{ M}/\text{min}) (1\text{mol rxn} / 1\text{mol Cl}_2) = 0.0659 \text{ M}/\text{min}$$

16. For the reaction:



You have collected the following data at 14.22°C:

Experiment	[CH <sub>4</sub> ] <sub>0</sub>	[I <sub>2</sub> ] <sub>0</sub>	Rate <sub>observed</sub>
1	1.39 M	0.243 M	3.19x10 <sup>-6</sup> M/min
2	2.78 M	0.243 M	6.38x10 <sup>-6</sup> M/min
3	1.39 M	0.486 M	1.28x10 <sup>-5</sup> M/min

What is the rate law for this reaction (including the value & units of k)? Show your work/explain your answers.

If you redo Experiment 3 at 4.86°C, the rate is 5.18x10<sup>-6</sup> M/min. What is the activation energy for this reaction? (20pts)

Comparing Exp't 1 & 2, [CH<sub>4</sub>]<sub>0</sub> doubles and rate doubles → 1<sup>st</sup> order with respect to [CH<sub>4</sub>]<sub>0</sub>

Comparing Exp't 1 & 3, [I<sub>2</sub>]<sub>0</sub> doubles and rate increases by a factor of 4 → 2<sup>nd</sup> order with respect to [I<sub>2</sub>]<sub>0</sub>

$$\text{Rate}_0 = k [\text{CH}_4]_0^1 [\text{I}_2]_0^2$$

Plugging in the values from Exp't 1:

$$(3.19 \times 10^{-6} \text{ M/min}) = k (1.39 \text{ M})^1 (0.243 \text{ M})^2$$

$$k = 3.88654 \times 10^{-5} \text{ M}^{-2} \text{ min}^{-1}$$

Plugging in the values from Exp't 3 at the new temperature:

$$(5.18 \times 10^{-6} \text{ M/min}) = k (1.39 \text{ M})^1 (0.486 \text{ M})^2$$

$$k = 1.577765 \times 10^{-5} \text{ M}^{-2} \text{ min}^{-1}$$

Using the comparative form of the Arrhenius Equation:

$$\ln \left( \frac{3.88654 \times 10^5}{1.577765 \times 10^5} \right) = \frac{E_a}{8.314 \text{ J/mol.K}} \left( \frac{1}{278.01 \text{ K}} - \frac{1}{287.37} \right)$$

$$E_a = 64.0 \text{ kJ/mol}$$

17. When 0.183mols of nitrogen dioxide {NO<sub>2</sub>(g)} and 0.208mols of hydrogen gas {H<sub>2</sub>(g)} are sealed together in a 1.500L vessel, they reach equilibrium with ammonia {NH<sub>3</sub>(g)} and oxygen {O<sub>2</sub>(g)}. The equilibrium concentration of NO<sub>2</sub>(g) is found to be 0.0592 M. (20pts)

- What are the equilibrium concentrations of all products and reactants?
- What is the value of K<sub>c</sub>?
- Is the reaction product-favored or reactant-favored?

	2 NO <sub>2</sub> (g)	+ 3 H <sub>2</sub> (g)	⇌ 2 NH <sub>3</sub> (g)	+ 2 O <sub>2</sub> (g)
[ ] <sub>initial</sub>	0.183mol/1.500L = 0.1220 M	0.208mol/1.500L = 0.1387 M	0 M	0 M
Δ [ ]	-2x M	-3x M	+ 2x M	+ 2x M
[ ] <sub>equilibrium</sub>	(0.1220 - 2x) M	(0.1387 - 3x) M	2x M	2x M

Since we know that [NO<sub>2</sub>]<sub>equilibrium</sub> = 0.0592 M, we can determine "x"...

$$0.1220 - 2x = 0.0592$$

$$x = 0.0314$$

Plugging in:

$$[\text{NO}_2]_{\text{equilibrium}} = 0.1220 - 2x = 0.0592 \text{ M}$$

$$[\text{H}_2]_{\text{equilibrium}} = 0.1387 - 3(0.0314) = 0.0445 \text{ M}$$

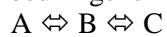
$$[\text{NH}_3]_{\text{equilibrium}} = 2(0.0314) = 0.0628 \text{ M}$$

$$[\text{O}_2]_{\text{equilibrium}} = 2(0.0314) = 0.0628 \text{ M}$$

$$K_c = \frac{[\text{NH}_3]_{\text{eq}}^2 [\text{O}_2]_{\text{eq}}^2}{[\text{NO}_2]_{\text{eq}}^2 [\text{H}_2]_{\text{eq}}^3} = \frac{(0.0628)^2 (0.0628)^2}{(0.0592)^2 (0.0445)^3} = 50.4$$

Product-favored (although not by all that much...)

18. You have been studying a reaction that can be described in generic terms as:



By studying the thermodynamics of these reactions, you find:  $\Delta G^\circ (A \rightarrow B) = +25 \text{ kJ/mol}$ ,  $\Delta G^\circ (B \rightarrow C) = -14 \text{ kJ/mol}$ .

Exploration of the kinetics of this system revealed that the activation energy barrier for the reaction  $A \rightarrow B$  is  $+31 \text{ kJ/mol}$  and the activation energy barrier for the reaction  $B \rightarrow C$  is  $+14 \text{ kJ/mol}$ .

- Draw a **quantitatively correct** reaction coordinate diagram for this overall process.
- Is the overall reaction ( $A \rightarrow C$ ) spontaneous (exergonic) or non-spontaneous (endergonic)?
- Is the first step of this reaction the rate-determining step or is the second step the rate-determining step?
- Is the equilibrium  $A \rightleftharpoons C$  product-favored or reactant-favored?

Explain all of your answers completely. (15pts)