CH102 Spring 2019
Discussion #13
Chapter 17 $\Delta G = -nFE = RT\ln\left(\frac{Q}{K}\right)$

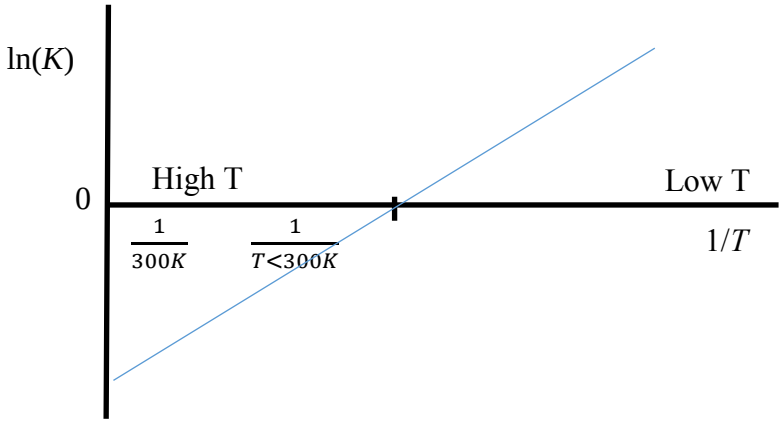
Student name_____ TA name_____ Section_____

Important equation for this packet:

1. A 0.01 M solution of an acid has pH = 4 at 300 K. At a lower temperature, the pH of the acid solution is 3. On the graph below, sketch the line of ln(K) versus (1/T) for this acid.

HA(aq) + H_2O(l) ⇔ H_3O^+(aq) + A^-(aq)

   a. pH↓ this means [H_3O^+]↑ when T↓ Process is exothermic this means that slope is positive.
   b. **K**↓ when T↑
   c. **K(300K)**=[H_3O^+][A^-] / [HA]=$1\cdot10^{-6}$
      K(T↓)= $1\cdot10^{-4}$
   d. We are dealing with the week acid with the K_a<1 so ln*K*<0 ;
   e. Since lnK<0 the line has to cross at the negative scale.
   f. Line crosses at the T where K=1



2. A fuel cell is made based on the combustion of ethanol. The fuel cell gas pressures are $p_{O_2} = 31.5$ bar and $p_{CO_2} = 0.0200$ bar. For this combustion, $\Delta_r H° = -1367.51$ kJ/mol and $\Delta_r S° = -138.58$ J/(mol·K). Calculate the total energy available for useful work from the complete combustion of 1.00 kg of ethanol (46.06 g/mol) in this fuel cell at 25°C.

$$CH_3CH_2OH(l) + 3\,O_2(g) \rightleftarrows 2CO_2(g) + 3\,H_2O(l)$$

$\Delta G° = \Delta H°_{sys} - T\Delta S°_{sys} = -1367.51\ \frac{kJ}{mol} - 298.15K \cdot \left(-138.48\frac{J}{mol\cdot K}\right)\frac{1kJ}{1000J} = -1326.19\frac{kJ}{mol}$

$Q=\frac{(CO_2)^2}{(O_2)^3}=1.28\cdot10^{-8}$

$\Delta G = \Delta G° + RT\ln Q == -1326.19\frac{kJ}{mol} + R\cdot 298.15K lnQ = -1371.24\frac{kJ}{mol}$

Total Energy$== -1371.24\frac{kJ}{mol}\cdot\frac{1000.0g}{46.06^{g}/_{mol}}$=*-29770.79kJ=-29800kJ*

3. The pH of water is 7.27 at 10.0°C and 6.77 at 40.0°C. Calculate the molar standard enthalpy and entropy change for the autoionization of water.
At T_1=283.15K $K_{W1}=(10^{-7.27})^2=10^{-14.54}$; At T_2=313.15K $K_{W2}=(10^{-6.77})^2=10^{-13.54}$;
Expecting an Endothermic.

$-RT_1 \ln K_{w1} = \Delta H°_{sys} - T_1\Delta S°_{sys}$
$-RT_2 \ln K_{w2} = \Delta H°_{sys} - T_2\Delta S°_{sys}$

$-RT_1 \ln K_{w1} + RT_2 \ln K_{w2} = -T_1\Delta S°_{sys} + T_2\Delta S°_{sys}$; $\Delta S°$=-78.52J/mol·K

And then solve for $\Delta H°_{sys}$; $\Delta H°_{sys}$ =56.58kJ/mol

Important information in chapter 18:

2. Rate $= \frac{[A]}{\Delta t}$; units $= \frac{\text{concentration (M)}}{\text{time (sec)}}$
3. Rate of chemical reactions depends on:
    a. Temperature
    b. Catalysts
    c. Initial concentrations
    d. Magnitude of the rate constant
4. Initial Reaction Rates:
    a. For a reaction: aA + bB → cC + dD
    b. Initial Reaction Rate $= -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$
    c. Where $\frac{\Delta[A]}{\Delta t}$ is an individual rate of loss of A,
    $\frac{\Delta[B]}{\Delta t} = \frac{b}{a} \cdot \frac{\Delta[A]}{\Delta t}$ $\frac{\Delta[C]}{\Delta t} = \frac{c}{a} \cdot \frac{\Delta[A]}{\Delta t}$
5. Rate Law:
    a. Differential rate law: rate vs. concentration
    aA + bB ⇄ cC + dD
    Rate = k $[A]^x[B]^y$ Where k is a rate constant $k = \frac{\text{rate}}{[A]^x \cdot [B]^y}$
    Where x is the order of the reaction with respect to species A, and y is the order of the reaction with respect to species B.
    b. Comparing initial rates:
    $\frac{rate\ 1}{rate\ 2} = \frac{k[A]_1^x[B]_1^y}{k[A]_2^x[B]_2^y}$
    c. Units of the rate constant depend on over all reaction order.
    $k = \frac{\left(M/s\right)}{M^x \cdot M^y} = \frac{M^{1-(x+y)}}{s}$ where (x+y) is the order of the overall reaction.
6. Integrated Rate Laws: see attached table for more information
    a. Zero−Order: $[R]_t - [R]_0 = -kt$
    b. First-Order: $\ln\frac{[R]_t}{[R]_0} = -kt$; $t_{1/2} = \frac{ln2}{k}$
    c. Second-Order: $\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$
7. Half Life $\frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n$; $t_{pass} = n \cdot t_{½}$; $t_{½} = \frac{0.693}{k}$;

1. A study of the reaction belo gave the data shown in the table. Fill in the missing information in the table.

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

	[NO]	$[O_2]$	$-\frac{d[NO]}{dt}$ [M/s]	Reaction rate
Ex1	0.0125	0.0185	0.020	
Ex2	0.0250	0.0185	0.080	
Ex3	0.0250	0.0370	0.160	
Ex4	0.0125	0.0370	0.040	

a. What order is the reaction with respect to [NO]?

b. What order is the reaction with respect to $[O_2]$?

c. Write the rate law: rate $= k[\quad]^x[\quad]^y$

d. Overall rate order =

e. What are the units of the rate constant *k*?

f. Calculate rate constant: $k =$

g. What is the reaction rate when $[NO] = [O_2] = 0.020M$

h. For each reactant, circle which plot correlating concentration with time will give you a **straight line,** and what the **sign of the slope** will be.

[NO] vs. time 1/[NO] vs. time ln[NO] vs. time

Slope: positive negative zero

$[O_2]$ vs. time 1/ $[O_2]$ vs. time ln$[O_2]$ vs. time

Slope: positive negative zero

2. A study of the reaction below gave the data shown in the table. Fill in the missing information in the table and answer questions below.

$2NO_{(g)} + Cl_{2\,(g)} \rightarrow 2NOCl_{\,(g)}$

	[NO]	$[Cl_2]$	$-\frac{d[NO]}{dt}$ [M/s]	RXN rate
Ex1	1.2	2.5		0.3
Ex2	4.8	2.5		0.15
Ex3	1.2	5.0		0.9

a. What order is the reaction with respect to [NO]
To find x we need to compare the rate of experiment 1 to the rate of experiment 2:
NOTE: The rate constant does not change with experimental conditions: it is a constant.
Concentration of NO changes but concentration of Cl_2 stays the same. $[Cl_2]_1=[Cl_2]_2$

$$\frac{rate1}{rate2}=\frac{0.3}{0.15}=\frac{k[NO]_1^x[Cl_2]_1^y}{k[NO]_2^x[Cl_2]_2^y}=\left(\frac{[NO]_1}{[NO]_2}\right)^x=\left(\frac{1.2}{4.8}\right)^x$$

$$\mathbf{2=\left(\frac{1}{4}\right)^x \quad log2=x\,log(1/4) \quad x=\left(\frac{\log 2}{\log 1-\log 4}\right)=\left(\frac{0.3}{-0.6}\right)=-\left(\frac{1}{2}\right)=-0.5}$$

b. What order is the reaction with respect to $[Cl_2]$
To find y we need to compare the rate of experiment 1 to the rate of experiment 3:
NOTE: The rate constant does not change with experimental conditions: it is constant.
Concentration of Cl_2changes but concentration of NO stays the same. $[NO]_3=[NO]_2$

$$\frac{rate3}{rate1}=\frac{0.9}{0.3}=\frac{k[A]_3^x[B]_3^y}{k[A]_1^x[B]_1^y}=\left(\frac{[B]_3}{[B]_1}\right)^y=\left(\frac{5.0}{2.5}\right)^y;\ \mathbf{3=2^y;\ log(3)=y\,log2;\quad y=1.6}$$

Fill in the table for reaction rate with respect to NO
Write the rate law: **rate = $k[NO]^{-0.5}[Cl_2]^{1.6}$**

c. Overall rate order: **x + y= 1.6+(-0.5)= 1.1**

d. What are the units of *this* k? $\frac{\left(M/s\right)}{M^x\cdot M^y}=\frac{M^{1-(x+y)}}{s}=M^{-0.1}/s$

3. Consider the chemical reaction: 3A + 4B → 2C + 2D. The experimentally determined rate law is Rate = $k[A]^2[B]$. When the initial concentrations are $[A]_i = 0.5$ M and $[B]_i = 0.01$ M, the rate of consumption of B is 8 x 10^{-5} M/s. Give the value of the rate constant, *k*, including the units.

$$Rate = -\frac{1}{4}\frac{d[B]}{dt}=k[A]^2[B]$$

$$-\frac{1}{4}*\left(-\frac{8x10^{-5}M}{s}\right)=k[5x10^{-1}M]^2[1x10^{-2}M]$$

$$k=\frac{2x10^{-5}M/s}{25x10^{-4}M^3}=\frac{8x10^{-3}}{M^2s}$$

4. Consider the reaction A + 2 B → D + C. Three experiments were conducted, and the initial reaction rate of each reaction was determined. For each of the reactants, find the appropriate order.

	Initial conc. (mol/L)		Initial Rate
Exp	[A]	[B]	(mol/L·sec)
#1	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	$3.2 \cdot 10^{-7}$
#2	$1.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$9.6 \cdot 10^{-7}$
#3	$4.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$1.9 \cdot 10^{-6}$

5. Consider the chemical reaction: 3A + 4B → 2C + 2D. The experimentally determined rate law is Rate = k[A] [B]^2. When the initial concentrations are $[A]_i = 0.3$ M and $[B]_i = 0.01$ M, the rate of consumption of B is $6 \cdot 10^{-4}$ M/s. Give the value of the rate constant, k, including the units.

6. Consider the comproportionation reaction of bromate and bromide to make bromine gas. Four experiments were conducted, and the initial reaction rate was determined.

$$12\ H_3O^+\ (aq) + 2\ BrO_3^-\ (aq) + 10\ Br^-\ (aq) \leftrightarrows 6\ Br_2\ (g) + 18\ H_2O\ (l)$$

a. Using the data, determine the order of the reaction with respect to H_3O^+.

	Initial Concentrations (mol/L)			Initial Reaction
Exp	$[BrO_3^-]$	$[Br^-]$	$[H_3O^+]$	Rate (mol/L·sec)
#1	0.10	0.10	0.01	1.0
#2	0.20	0.10	0.01	2.0
#3	0.10	0.30	0.01	3.0
#4	0.20	0.10	0.02	8.0

b. What is the initial rate of formation of bromine gas in experiment #1?

7. In a first order chemical reaction, the concentration of a reactant is observed to fall from 1.000 M to 0.250 M between $t = 6$ s and $t = 10$ s. What is the concentration (in M) at $t = 12$ s?

Solution:

One half-life 1M→0.5M

Two half life's 0.5M →0.250M time spend was 10s-6s=4s for 2 half life's

$t_{½}$ = 2s at time 12s one more half-life must pass so the concentration is 0.125M

8. The first order reaction is 60.% complete after 100. seconds. What is rate constant k and $t_{½}$ for this reaction?

Solution:

$$\frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n \quad \frac{40}{100} = \left(\frac{1}{2}\right)^n \quad \frac{4}{10} = \left(\frac{1}{2}\right)^n \quad \mathbf{n=1.32} \quad \mathbf{;\ t_{½} = t/n = 75.65\ s;} \quad \mathbf{k} = \frac{0.693}{t_{1/2}} \mathbf{= .009161\ 1/s}$$

9. Fluorine−18 (^{18}F) has a half-life of 110. minutes. After 4 half-lives, how much time has elapsed? What percentage of your original ^{18}F remains? What percentage has decayed?

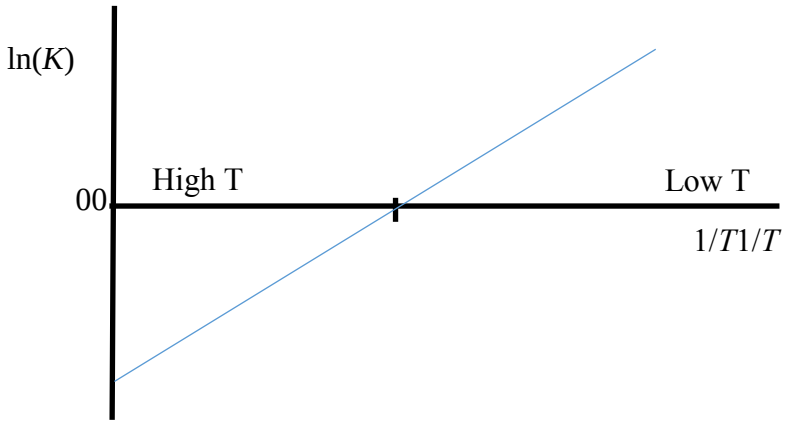
10. You are trying to find the half-life of a new, meta-stable compound (X) created in your lab. You analyze the amount of X you have 30 minutes after initial production of X. You find you have 20% of the original amount. Approximately, what is $t_{½}$?

    6 m. $<t_{½}<$ 7.5 m. 7.5 m. $<t_{½}<$ 10 m. 10 m. $<t_{½}<$ 15 m. 15 m. $<t_{½}<$ 30 m.

11. For another compound (Y), 94% of an original 100.0 g has decayed in 60.0 minutes. Express your answer to **one significant figure.**
    a. How many grams of Y is remaining?
    b. How many half-lives have elapsed?
    c. What is the half-life of this compound?

Answers Chapter 17:

1.
2. -29800kJ
3. 56.58kJ/mol; -78.5J/molK



Answers Chapter 18:

1.
   a.
   b. 2
   c. 1
   d. rate = $k[NO]^2[O_2]^1$
   e. 3
   f. $1/M^2s$
   g. 3.5×10^3
   h. 2.8×10^{-2}
   i. 1/[NO] vs. time, positive = 2k, $ln[O_2]$ vs. time, negative = -k
2.
   a. -0.5
   b. 1.6
   c.
   d. rate = $k[NO]^{-0.5}[Cl_2]^{1.6}$
   e. 1.1
   f. $M^{-0.1}/s$
3. 8.0×10^{-3} $1/M^2s$
4. 1, 0.5

	Initial conc. (mol/L)		Initial Rate (mol/L·sec)
Exp	[A]	[B]	
#1	$1.0\cdot10^{-3}$	$1.0\cdot10^{-3}$	$3.2\cdot10^{-7}$
#2	$1.0\cdot10^{-3}$	$3.0\cdot10^{-3}$	$9.6\cdot10^{-7}$
#3	$4.0\cdot10^{-3}$	$3.0\cdot10^{-3}$	$1.9\cdot10^{-6}$

5. $5\ M^{-2}s^{-1}$

6.

	Initial Concentrations (mol/L)			Initial Reaction Rate (mol/L·sec)
Exp.	$[BrO_3^-]$	$[Br^-]$	$[H_3O^+]$	
#1	0.10	0.10	0.01	1.0
#2	0.20	0.10	0.01	2.0
#3	0.10	0.30	0.01	3.0
#4	0.20	0.10	0.02	8.0

   a. 2
   b. 6 mol/L·sec
7. 0.125 M
8. k= 0.009161 1/s; t= 75.65 s
9. 6.25% remains, 93.75% decayed
10. 10 m. $<t_{½}<$ 15 m.
11.
   a. 6 g
   b. 4
   c. 15 mins

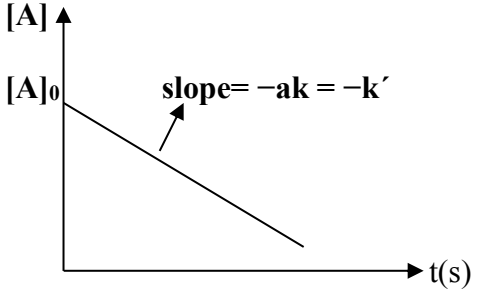
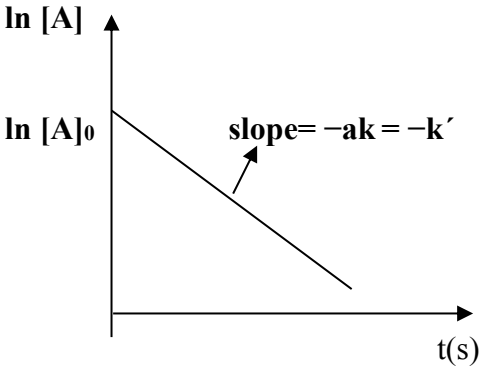
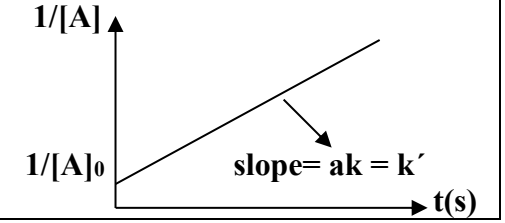
Next week's discussion section will be optional (last day of classes, May 2nd, is a Thursday). All sections held on Thursday will be available to attend for the students that have discussion on Fridays. The Thursday schedule (rooms and times) will be posted on the class webpage.

Exam 3 Answers:

1. $2Ag^+(aq) + 3H_2O(l) + CH_2O(aq) \rightleftarrows 2Ag(s) + CH_2O_2(aq) + 2H_3O^+(aq)$
2. $2 \cdot 10^{45}$
3.
   a. 0
   b. 1
   c. $Pt(s)|H_2(g) \mid H_3O^+(aq, 10^{-7}M)|| H_3O^+(aq, 10^{-6}M) \mid H_2(g) \mid Pt(s)$
   d. 0.05912
4. 3
5. a→b and c→b
6.
   a. -85.2J/molK
   b. 29.8kJ/mol
7.
   a. Q>1; Q<K
   b. n=2
   c. 1.095
8.
   a. None
   b. Ag, O_2
9. Q<K; E=9V
10.
   a. $4H^+(aq) + O_2(g) + 4\,e^- \rightarrow 2H_2O(l)$
   b. $H_2(g) \rightarrow 2H^+(aq) + 2e^-$
   c. E will be more positive

Chem 102 Spring final exam review will be on
Monday May 6th from 10am-12pm and 1pm-3pm

ROOM	TOPIC
CAS 211	Counting Arrangements, Entropy, (Q, K, ΔG, S), Colligative properties
CAS 313	Equilibrium, Acid/Base, Buffers, Ksp, Solubility, Exam 2
CAS 216	Electrochemistry and Redox, Exam 3
CAS 522	Kinetics, Half-Life, Mechanisms
CAS 203	Gas Laws, KMT, Phase diagrams, Solution Enthalpy, Exam1
CAS 213	Molecular orbitals

Reaction Order	Differential Rate Law Conc. Dependence	Units of the rate constant, k, depend on the reaction order.	Half life, $t_{1/2}$, Integrated Rate Law	Graph Concentration versus time $[A]_0$ is [A] at t = 0
Zero order reaction x = 0, y = 0, x + y = 0	**Rate = k$[A]^0[B]^0$** **Rate = k** Rate is Constant Rate is independent of initial concentration.	**(M/s) =** units of k **k = (M/s)** are the units of the rate In general the units of **k** are a good indicator of the reaction order.	**$[A]_{final} = [A]_{initial} - akΔt$** **When:** **$[A]_{final} = \frac{[A]_{initial}}{2}$** $\frac{[A]_{initial}}{2} = [A]_{in} - akt_{1/2}$ $t_{1/2} = \frac{[A]_{initial}}{2ak}$	
First order reaction Example: x = 1, y = 0, x + y = 1	**Rate = k$[A]^1[B]^0$** **Rate = k[A]** Rate depends linearly on initial concentration (ex. doubling [A] doubles the rate)	**(M/s) =** units of k *** (M)** **k = (1/s)**	**$\ln [A]_{final} = \ln [A]_{initial} - akΔt$** $\ln \frac{[A]_{final}}{[A]_{initial}} = -akΔt$ **When:** **$[A]_{final} = \frac{[A]_{initial}}{2}$** $t_{1/2} = \frac{ln2}{ak}$ (half life is independent of initial concentration) $t_{1/2}$ is constant	
Second order reaction Example: x = 2, y = 0, x + y = 2	**Rate = k$[A]^2[B]^0$** **Rate = k$[A]^2$**	**(M/s) = units of k * $(M)^2$** $k = \left(\frac{1}{M \cdot s}\right)$	**$1/[A]_{final} = 1/[A]_{initial} + akΔt$** **When :** **$[A]_{final} = \frac{[A]_{initial}}{2}$** $t_{1/2} = \frac{1}{ak[A]_{initial}}$	

aA + bB → cC **rate(M/s) =** $-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t}$ **= k $[A]^x [B]^y$**

x and y are independent of stoichiometry and can only be determined from experimental data