

## AP Chem Unit Review

### Kinetics, Equilibrium, Electrochemistry, Thermodynamics, Nuclear Chemistry

#### Kinetics

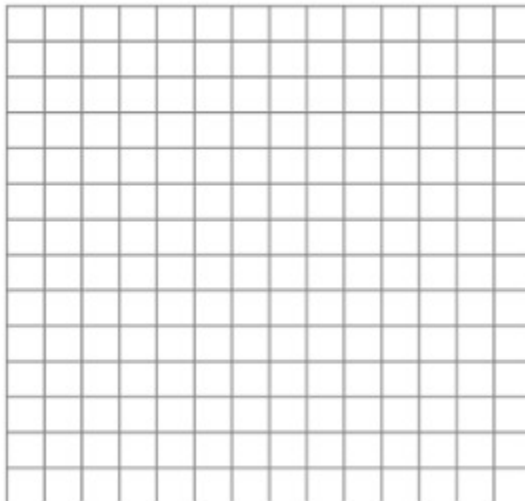
1) Discuss the steps required for a reaction to initiate. Include a molecular diagram and energy change diagram to support your answer.

2) Show how an energy diagram for a spontaneous reaction would look versus a nonspontaneous reaction. (hint: high energy to low energy is favorable)

3) Demonstrate how rate changes over the course of a 150 second reaction by comparing the initial reaction rate of the decomposition of nitrogen dioxide to the final given the following data.

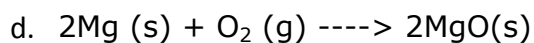
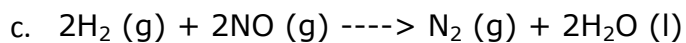
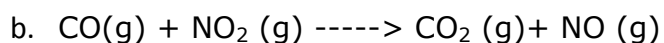
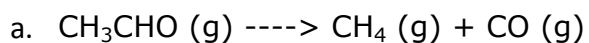
Time (sec)	NO <sub>2</sub> (mol/L)
0	0.0100
50	0.0079
100	0.0065
150	0.0055

- 4) Graph the data from question 3 and show how you can determine the instantaneous rate at any given moment using concentration versus time data. Explain the directional slope.



- 5) Write the decomposition reaction for nitrogen dioxide, producing nitrogen monoxide and oxygen. Discuss how the rates of production of nitrogen monoxide and oxygen will compare.

- 6) Initial reaction rates allow us to ignore the influence of products on reaction rates. Write the initial rate law for the following reactions.

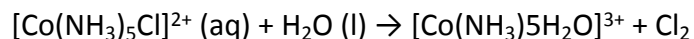


- 7) Given the following reaction data for reaction "c" from #6.: determine the rate constant and the overall rate order of reaction "c" from #6.

[H <sub>2</sub> ]	[NO]	Rate
0.1	0.1	1.0×10 <sup>-1</sup>
0.2	0.1	2.0×10 <sup>-1</sup>
0.1	0.4	4.0×10 <sup>-1</sup>

- Determine the rate constant
- Determine the overall rate order
- Predict the rate of the reaction if you start under the conditions [H<sub>2</sub>] = 2.5M and [NO] = 0.95M

- 8) Determine the rate order and rate constant for the following reaction:



Exp.	Initial Concentration (mol/L)	Initial rate of [Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup> mol/(L• min)
	1.0 × 10 <sup>-3</sup>	1.3 × 10 <sup>-7</sup>
	2.0 × 10 <sup>-3</sup>	2.6 × 10 <sup>-7</sup>
	3.0 × 10 <sup>-3</sup>	3.9 × 10 <sup>-7</sup>
	1.0 × 10 <sup>-3</sup>	1.3 × 10 <sup>-7</sup>

- 9) Explain how the manipulation of experimental conditions can allow us to determine the pseudo rate law for a reaction.

10) Write out the integrated rate laws for zero order, first order and second order reactions and identify how to determine the rate constant from concentration over time data.

11) The decomposition of  $\text{N}_2\text{O}_5$  in the gas phase was studied at constant temperature.



The following results were collected:

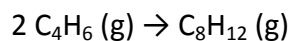
<u>[N<sub>2</sub>O<sub>5</sub>]</u>	<u>Time (s)</u>
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Determine the rate law and calculate the value of k.

What is the concentration of  $\text{N}_2\text{O}_5(\text{g})$  at 600 s?

At what time is the concentration of  $\text{N}_2\text{O}_5(\text{g})$  equal to  $0.00150 \text{ M}$  ?

12) Butadiene reacts to form its dimer according to the equation



The following data were collected for this reaction at a given temperature:

<u><math>[\text{C}_4\text{H}_6]</math></u>	<u>Time (<math>\pm 1 \text{ s}</math>)</u>
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

a. What is the order of this reaction? Explain. Sketch your graph as part of your explanation.

Write the rate law expression:

b. What is the value of the rate constant for this reaction?

13) What are the rules that a proper chemical mechanism for a reaction must meet?

14) Discuss the influence a proposed mechanism has on the rate law for a reaction if the first reaction is the slow step, versus when the second step is the slow step. Support your discussion with an example problem from your notes.

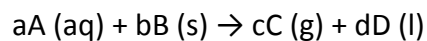
15) Explain the role of catalysts and show their influence on a reaction using an energy versus reaction progression diagram.

## Equilibrium

1) Discuss what chemical equilibrium represents by comparing the forward and reverse reactions for the ionization of water into hydronium and hydroxide ions.

2) Write the general equilibrium expression for a reaction  $aA + bB \rightarrow cC + dD$

3) Rewrite the equilibrium expression given the following phases. Explain your answer.



4) Use your understanding of the equilibrium expression to discuss the following:

- a. What does a large K value ( $K > 1$ ) represent?
- b. What does a small K value ( $K < 1$ ) represent?
- c. What does it mean when  $K = 1$ ?

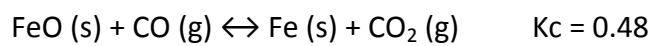
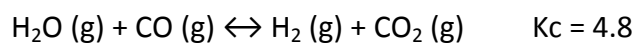
5) Compare and contrast  $K_p$  and  $K_c$ .

6)  $C(s) + 2H_2O(g) \leftrightarrow CO(g) + H_2(g)$  has a value of  $K_c = 2.5 \times 10^{-6}$ .

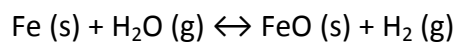
a. What is the  $K_c$  value for  $2C(s) + 4H_2O(g) \leftrightarrow 2CO(g) + 2H_2(g)$ ?

b. What is the  $K_p$  of the original reaction at  $32C$ ?

7) Given the following equations:



Calculate the  $K_c$  value for:





8) For the reaction:  $2 \text{NO}_2 (\text{g}) \leftrightarrow \text{N}_2\text{O}_4 (\text{g})$

At equilibrium  $[\text{N}_2\text{O}_4] = 0.25 \text{ M}$  &  $[\text{NO}_2] = 0.175 \text{ M}$ . Calculate  $K_c$ .

9) Compare and contrast the equilibrium constant ( $K$ ) and the reaction quotient ( $Q$ ).  
Discuss what  $K > Q$ ,  $K < Q$ , and  $K = Q$  represent.

10) For the equation:  $\text{N}_2 (\text{g}) + \text{O}_2 (\text{g}) \leftrightarrow 2\text{NO} (\text{g})$ ,  $K_c = 0.527$ . If you mix equal volumes of  $0.20 \text{ M}$   $\text{N}_2$ ,  $0.35 \text{ M}$   $\text{O}_2$ , and  $0.10 \text{ M}$   $\text{NO}$ , are you at equilibrium? If not, which direction will the reaction progress and what will be the final concentrations for each species?

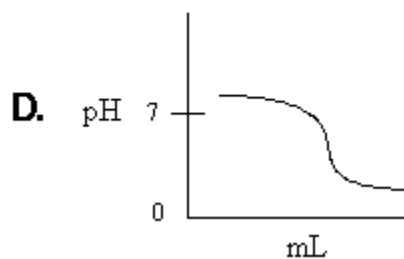
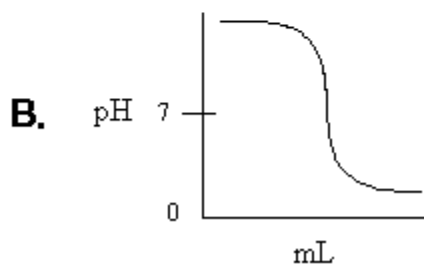
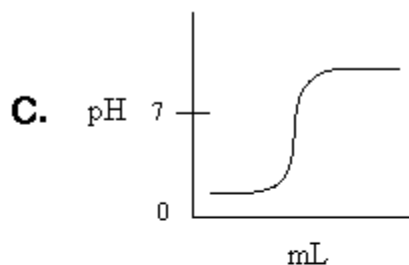
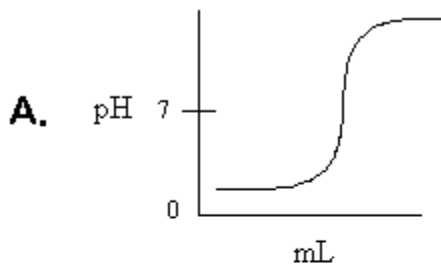
11) Discuss the affect each scenario will have on the equilibrium of the reaction from #10.

- a. Adding  $\text{NO}(\text{g})$
- b. Adding heat (assume this is an exothermic reaction)

12) Write the general equilibrium expression for the following:

- a. Dissociation of a strong acid
- b. Dissociation of a strong base
- c. Dissociation of a weak acid
- d. Dissociation of a weak base
- e. Reaction of a strong acid and a strong base
- f. Reaction of a strong acid and a weak base
- g. Reaction of a weak acid and a strong base

13) Identify the type of neutralization each titration curve represents



14) Discuss what the half-way point and equivalence point represent regarding acid/base concentration and pH/pKa.

15) A titration of a 25mL of nitric acid requires 54mL of 0.40M ammonia ( $pK_b = 4.74$ ) to reach the equivalence point. What is the concentration of the nitric acid?

16) Calculate the pH of solution upon mixing 15mL of 0.20M potassium hydroxide and 25mL of 0.40M acetic acid ( $pK_a = 4.75$ )

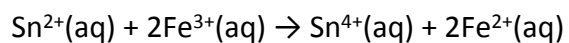
17) Review how to calculate the pH of a weak acid/strong base titration at any given time:

- a. Before adding any base
- b. Before the equivalence point
- c. At the equivalence point
- d. After the equivalence point

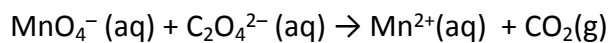
## Electrochemistry

1) Write out a general equation that shows oxidation and one that shows reduction.

2) Identify the species being oxidized and the species being reduced in the following reaction and write out the proper half-reactions:



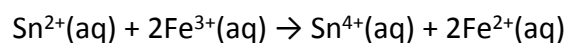
3) Write out the complete balanced equation for the following redox reaction:



4) Discuss the difference between galvanic and electrolytic cells.

5) Draw a diagram of an electrochemical cell. Identify the reaction that occurs at the anode and the reaction that occurs at the cathode, the charge each electrode takes on, the change in mass expected at each electrode, and the direction of electron flow.

6) Determine the standard cell potential for the following reaction:



7) Calculate the change in cell potential if the tin solution is 0.35M and the iron solution is 1.34M at a temperature of 39C.

8) Is the cell in #7 spontaneous? Would it be a galvanic or electrolytic cell? Support your answer with a discussion of both cell potential and Gibbs free energy.

9) How much voltage can be obtained from a concentration cell of magnesium in a magnesium sulfate solution if one half-cell has a concentration 0.21M and the other a concentration of 3.1M?

10) Review the construction of common rechargeable and alkaline batteries and the chemical reactions that take place in each.





4) Review the ways enthalpy ( $\Delta H$ ) can be determined for a reaction or process overall.

- a. Bond dissociation energy
- b. Summation of enthalpy of formation values ( $\Delta H_f$ )
- c. Hess's law

5) Review how entropy (S) can be determined for a reaction or process overall.

- a.  $\Delta S = q/T = -\Delta H/T$
- b. Summation of  $\Delta S$  values

6) Review how free energy (G) can be determined for a reaction or process overall.

- a. Summation of  $\Delta G$  values
- b. Hess' Law
- c.  $\Delta G = \Delta H - T\Delta S$
- d.  $\Delta G = \Delta G^\circ + RT\ln Q$
- e.  $\Delta G^\circ = -RT\ln K$
- f.  $\Delta G^\circ = -nFE^\circ$

7) Discuss how nonspontaneous reactions can be driven by coupling them with other reactions and the importance of this process to biological systems.

8) Explain the difference between spontaneous and instantaneous. Relate the terms to free energy and activation energy.

9) Predict the spontaneity of the following reactions by looking up their standard enthalpy and entropy values.

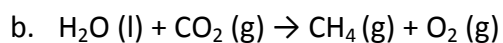
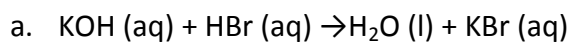


Table A-6

Thermodynamic Properties (at standard states)							
$\Delta H_f^\circ$ in kJ/mol		$\Delta G_f^\circ$ in kJ/mol		$S^\circ$ in J/mol·K			
concentration of aqueous solutions is 1 M							
Substance	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$S^\circ$	Substance	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$S^\circ$
Ag	0	0	42.7	H <sub>3</sub> PO <sub>3</sub>	-972	—	—
AgCl	-127	-110	96.1	H <sub>3</sub> PO <sub>4</sub>	-1280	-1120	110
AgCN	-146	-164	83.7	H <sub>2</sub> S	-20.1	-33.0	206
Al	0	0	28.3	H <sub>2</sub> SO <sub>3</sub> (aq)	-614	-538	232
Al <sub>2</sub> O <sub>3</sub>	-1670	-1580	51.0	H <sub>2</sub> SO <sub>4</sub> (aq)	-908	-742	17.2
BaCl <sub>2</sub> (aq)	-873	-823	121	HgCl <sub>2</sub>	-230	-177	—
BaSO <sub>4</sub>	-1470	-1350	132	Hg <sub>2</sub> Cl <sub>2</sub>	-265	-211	196
Be	0	0	9.54	Hg <sub>2</sub> SO <sub>4</sub>	-742	-624	201
Be <sub>3</sub> N <sub>2</sub>	-568	-512	—	I <sub>2</sub>	0	0	117
Bi	0	0	56.9	K	0	0	63.6
BiCl <sub>3</sub>	-379	-319	190	KBr	-392	-379	96.4
Bi <sub>2</sub> S <sub>3</sub>	-183	-164	146	KMnO <sub>4</sub>	-813	-714	172
Br <sub>2</sub>	0	0	152	KOH	-426	—	—
CH <sub>4</sub>	-74.8	-50.8	186	LiBr	-350	—	—
C <sub>2</sub> H <sub>4</sub>	+52.3	+68.1	219	LiOH	-487	-444	50.2
C <sub>2</sub> H <sub>6</sub>	-84.7	-32.9	229	Mn	0	0	32.0
C <sub>4</sub> H <sub>10</sub>	-125	-15.7	310	MnCl <sub>2</sub> (aq)	-555	-491	38.9
CO	-111	-137	198	Mn(NO <sub>3</sub> ) <sub>2</sub> (aq)	-636	-451	218
CO <sub>2</sub>	-393.5	-394.4	214	MnO <sub>2</sub>	-521	-466	53.1
CS <sub>2</sub>	+87.9	+63.6	151	MnS	-214	—	—
Ca	0	0	41.6	N <sub>2</sub>	0	0	192
Ca(OH) <sub>2</sub>	-987	-897	—	NH <sub>3</sub>	-46.2	-16.6	193
Cl <sub>2</sub>	0	0	223	NH <sub>4</sub> Br	-270	-175	113
CoCO <sub>3</sub>	-723	-650	—	NO	+90.4	—	211
CoO	-239	-213	43.9	NO <sub>2</sub>	+33.8	+51.8	240
Cr <sub>2</sub> O <sub>3</sub>	-1130	-1050	81.2	Na	0	0	51.0
CsCl(aq)	-415	-371	188	NaBr	-360	—	—
Cs <sub>2</sub> SO <sub>4</sub> (aq)	-1400	-1310	283	NaCl	-411	-384	72.4
CuI	-67.8	-69.5	96.7	NaNO <sub>3</sub> (aq)	-447	—	—
CuS	-53.1	-53.7	66.5	NaOH	-427	—	—
Cu <sub>2</sub> S	-79.5	-86.2	121	Na <sub>2</sub> S(aq)	-437	—	—
CuSO <sub>4</sub>	-770	-662	113	Na <sub>2</sub> SO <sub>4</sub>	-1380	-1270	149
F <sub>2</sub>	0	0	203	O <sub>2</sub>	0	0	205
FeCl <sub>3</sub>	-405	—	—	P <sub>4</sub> O <sub>6</sub>	-1640	—	—
FeO	-267	—	—	P <sub>4</sub> O <sub>10</sub>	-2980	-2700	229
Fe <sub>2</sub> O <sub>3</sub>	-822	-741	90.0	PbBr <sub>2</sub>	-277	-260	162
H	+218	—	115	PbCl <sub>2</sub>	-359	-314	136
H <sub>2</sub>	0	0	131	S	0	0	31.9
HBr	-36.2	-53.2	198	SO <sub>2</sub>	-297	-300	249
HCl	-92.3	-95.3	187	SO <sub>3</sub>	-438	-368	95.6
HCl(aq)	-167	-131	56.5	SrO	-590	-560	54.4
HCN(aq)	+151	+172	94.1	Ti	0	0	30.3
HF	-269	-271	174	TiO <sub>2</sub>	—	-853	50.2
HI	+25.9	+1.30	206	TiI	-50.2	-83.3	236
H <sub>2</sub> O(l)	-286	-237	70.0	UCl <sub>4</sub>	-1050	-962	198
H <sub>2</sub> O(g)	-242	-229	189	UCl <sub>5</sub>	-1100	-993	259
H <sub>2</sub> O <sub>2</sub>	—	-118	110	Zn	0	0	41.6
H <sub>3</sub> PO <sub>2</sub>	-609	—	—	ZnCl <sub>2</sub> (aq)	-487	-410	3.72
				ZnSO <sub>4</sub> (aq)	-1063	-892	-92.0

10) Show how an increase in temperature influences free energy for the reactions in #9.

## Nuclear Chemistry

1) List and describe the types of nuclear decay.

2) Review isotopic symbols and the information they provide. For example:



3) Use isotopic symbols to show how a Uranium-238 isotope changes when undergoing alpha decay followed by beta decay.

4) Explain why gamma decay is almost always happens simultaneously with alpha and beta decay.

5) Discuss the processes of fission and fusion and use Einstein's equation to explain how large amounts of energy can be gained from these processes.

6) The half-life of tritium ( $^3\text{H}$ ) is 12.3 years. What mass of tritium will be left after 35 years following a nuclear accident if 75 mg is released?

7) Relate the concepts of half-life, radioactivity, and stability.

8) Be able to discuss how elements formed during the formation of the universe and why radioactive isotopes are now rare.