Chemistry 10123, **Exam 2**   **Answer Key**
February 20, 2019

1. (9 points) **SHOW ALL WORK.** At 50 °C, the ion product (K_w) for water is 5.48×10^{-14}. Determine the pH of a 0.0025 M $Ba(OH)_2$ solution at this temperature. Include a *balanced chemical equation* for the relevant *equilibrium reaction*.

$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ $K_w = [H^+][OH^-] = 5.48 \times 10^{-14}$

$[OH^-] = (0.0025 \text{ mole } Ba(OH)_2 / L)(2 \text{ mole } OH^- / 1 \text{ mole } Ba(OH)_2) = 0.0050 \text{ M}$

$[H^+] = K_w / [OH^-] = (5.48 \times 10^{-14}) / 0.002550 = 1.096 \times 10^{-11}$

$pH = -\log(1.096 \times 10^{-11}) = 10.96$

2. (2 points) Among the following, circle the *strongest acid*.

$HBrO_3$ $HClO_2$ H_2SO_3 $HBrO_2$ $HClO_3$ H_2SeO_3

3. (2 points) Among the following, circle the *weakest acid*.

H_2Se HBr HF H_2O H_2S HCl

4. (9 points) **SHOW ALL WORK.** At 100 °C, a reaction has an activation energy (E_a) of 165 kJ/mole. When a catalyst is added (at the same temperature), the reaction rate increases by a factor of 10 billion (i.e., 1.00×10^{10} times faster). Determine the activation energy of the catalyzed reaction.

let k_1 = rate constant for un-catalyzed Rx and let k_2 = rate constant for catalyzed Rx

$k_1 = Ae^{-E_{a1}/RT}$ where $E_{a1} = 165$ kJ/mole

$k_2 = Ae^{-E_{a2}/RT}$ where E_{a2} = activation energy of catalyzed Rx

$k_2 / k_1 = (e^{-E_{a2}/RT}) / (e^{-E_{a1}/RT})$

$\ln(k_2 / k_1) = -E_{a2}/RT - (-E_{a1}/RT) = (E_{a1} - E_{a2}) / RT$

$\ln(1.00 \times 10^{10}) = (165 \text{ kJ/mole} - E_{a2}) / (8.314 \times 10^{-3} \text{ kJ/mole·K})(373 \text{ K})$
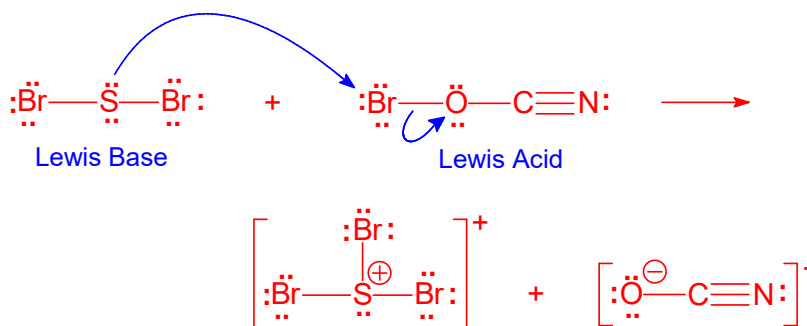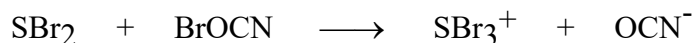
$23.026 = (165 - E_{a2}) / 3.101$

∴ $E_{a2} = 93.6$ kJ/mole

5. (4 points)   (a) The conjugate acid of $HAsO_4^{2-}$ is $H_2AsO_4^-$.
          (b) The conjugate base of HSF_3 is SF_3^-.

6. (2 points) A molecule or ion that can function as both an acid and a base is described as being amphoteric. An excellent example of such a species is H_2O.

7. (4 points) Which one of the following molecules or ions behaves as a *weak base* in aqueous solution? Circle your answer and then write a balanced chemical equation for this process.

HN_3 NH_4^+ N_2O_5 NO_2^- OH^- N_2

$NO_2^-{}_{(aq)} + H_2O \rightleftharpoons HNO_2{}_{(aq)} + OH^-{}_{(aq)}$
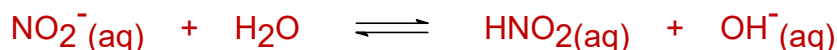
8. (10 points) Consider the following reaction in terms of the Lewis Acid-Base concept. Write *complete Lewis electron dot formulas* for all reactants and products. *Clearly indicate which reactant is the Lewis acid and which is the Lewis base*. Use arrows to illustrate the formation and breaking of any bonds as the reaction proceeds from left to right.

$$SBr_2 \; + \; BrOCN \; \longrightarrow \; SBr_3^+ \; + \; OCN^-$$

:Br—S̈—Br: + :Br—Ö—C≡N: ⟶

     Lewis Base   Lewis Acid

$$\begin{bmatrix} :\ddot{B}r: \\ | \\ :\ddot{B}r\!-\!\overset{\oplus}{S}\!-\!\ddot{B}r: \end{bmatrix}^+ \; + \; \begin{bmatrix} :\overset{\ominus}{\ddot{O}}\!-\!C\!\equiv\!N: \end{bmatrix}^-$$

9. (8 points) For two solutions, **A** and **B**, fill in the missing values (at 25 °C) in the table below. *Pay attention to significant figures*.

Solution	pH	$[H_3O^+]$	pOH	$[OH^-]$
A	- 1.04	11	15.04	9.1×10^{-16}
B	10.725	1.88×10^{-11}	**3.275**	5.31×10^{-4}

10. (10 points) **SHOW ALL WORK.** As the TA for a Gen Chem lab, you are required to prepare 50.0 L of aqueous HBr with a pH of 2.50. In the chemistry storeroom, you find a bottle of stock solution that is 48.0 % HBr by weight and has a density of 1.50 g/mL. Determine the volume (in mL) of stock solution that you will need in order to prepare 50.0 L of HBr solution with pH = 2.50. (molar mass: HBr = 80.9, H_2O = 18.0)
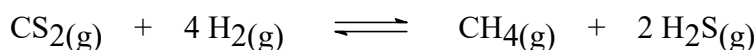
molarity of HBr = $[H^+]$ = $10^{-2.50}$ = 0.00316 mole/L

(50.0 L) (0.00316 mole HBr / L) (80.9 g/mole) = 12.78 g HBr

(12.78 g HBr) (100 g soln / 48.0 g HBr) = 26.63 g soln

(26.63 g soln) (1 mL / 1.50 g) = 17.8 mL

11. Consider the following gas-phase reaction for which $K_c = 8.30 \times 10^5$ at 500 °C.

$$CS_{2(g)} + 4 H_{2(g)} \rightleftharpoons CH_{4(g)} + 2 H_2S_{(g)}$$

(a) (4 points) How will the equilibrium amount of $CS_{2(g)}$ be affected by each of following changes? Indicate your answer by writing the appropriate letter.

[**I** = increase, **D** = decrease, **N** = no change]

Change	moles $CS_{2(g)}$
add some $CH_{4(g)}$	I
add a catalyst	N
increase the pressure	D
remove some $H_2S_{(g)}$	D

(b) (2 points) When the temperature of the above equilibrium system is increased, the value of K_c decreases. This observation indicates that the enthalpy change for the reaction is (circle one):

positive   zero   negative

(c) (10 points) **SHOW ALL WORK.** At 500 °C, a 2.00 L container was filled with 0.0200 moles of $CS_{2(g)}$ and 0.150 moles of $H_{2(g)}$. Calculate the molar concentration of CS_2 in this system after the above equilibrium is established. ***Clearly state and justify any assumptions that you may make.*** ($K_c = 8.30 \times 10^5$)

	$CS_{2(g)}$	+	$4 H_{2(g)}$	$\rightleftharpoons$	$CH_{4(g)}$	+	$2 H_2S_{(g)}$
I	0.0100 M		0.0750 M		0		0
C	- 0.0100		- 0.0400		+ 0.0100		+ 0.0200
"E"	0		0.0350		0.0100		0.0200
C	+ x		+ 4x		- x		- 2x
E	x		0.0350 + 4x		0.0100 - x		0.0200 - 2x

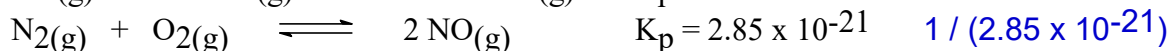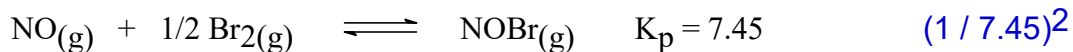Since K_c is very large, the reaction goes essentially to completion. The actual equilibrium concentration of the limiting reactant CS_2 should be very small. So, we can assume x << 00.0100, 2x << 0.0200, and 4x << 0.0350.
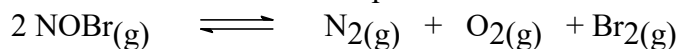
$K_c = [CH_4][H_2S]^2 / [CS_2][H_2]^4$

$8.30 \times 10^5 = (0.010 - x)(0.020 - 2x)^2 / (x)(0.035 + 4x)^4 \approx (0.01)(0.02)^2 / (x)(0.035)^4$

$x = [CS_2] \approx 3.2 \times 10^{-6}$ M   assumption is OK

12. (4 points) **SHOW ALL WORK.** Consider the following reactions and their equilibrium constants.

$$NO_{(g)} + 1/2\ Br_{2(g)} \rightleftharpoons NOBr_{(g)} \qquad K_p = 7.45 \qquad (1 / 7.45)^2$$
$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2\ NO_{(g)} \qquad K_p = 2.85 \times 10^{-21} \qquad 1 / (2.85 \times 10^{-21})$$

From this information, determine K_p for the reaction below.

$$2\ NOBr_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)} + Br_{2(g)}$$

We need to reverse both of the above equations and multiply the first one by 2. This means inverting both K_p values and squaring the first.

$K_p = (1 / 7.45)^2 / (2.85 \times 10^{-21}) = 6.32 \times 10^{18}$

13. (10 points) The following gas-phase reaction is found experimentally to be "first order in H_2 and first order in BrCl." Write the experimental rate law and *propose* a reasonable *two-step mechanism* for this reaction. *Briefly explain* (30 words max) how your mechanism is consistent with the experimental rate law. Clearly indicate which step in your mechanism is the rate-determining step. If your proposed mechanism contains an intermediate, circle it.
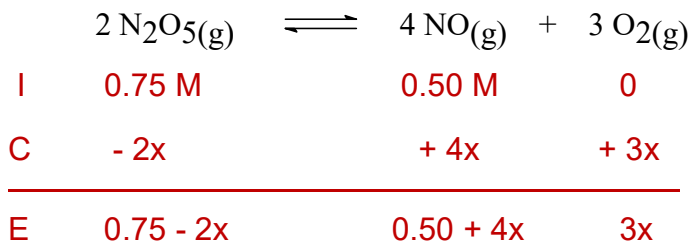
$$H_{2(g)} \; + \; 2\,BrCl_{(g)} \; \longrightarrow \; 2\,HCl_{(g)} \; + \; Br_{2(g)}$$
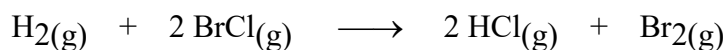
Expt: rate = k[H_2][BrCl]

This rate law is consistent with the following proposed mechanism if the first step is rate-determining and the intermediate is HBr.

| slow: | H_2 + BrCl $\longrightarrow$ HBr + HCl |
| fast: | HBr + BrCl $\longrightarrow$ Br_2 + HCl |

$$H_2 \; + \; 2\,BrCl \; \longrightarrow \; Br_2 \; + \; 2\,HCl$$

Based on the slow step, the predicted rate law is: rate = k[H_2][BrCl]

14. (10 points) **SHOW ALL WORK.** At 300 K, the following reaction has K_c = 1.75 x 10^{-10}. At this temperature, 0.75 moles of N_2O_5 and 0.50 moles of NO are combined in a 1.00-L container. Determine the molar concentration of O_2 after equilibrium is achieved.

$$2\,N_2O_{5(g)} \; \rightleftharpoons \; 4\,NO_{(g)} \; + \; 3\,O_{2(g)}$$

	2 N_2O_5	4 NO	3 O_2
I	0.75 M	0.50 M	0
C	- 2x	+ 4x	+ 3x
E	0.75 - 2x	0.50 + 4x	3x

K_c = 1.75 x 10^{-10} = [NO]^4 [O_2]^3 / [N_2O_5]^2 = (0.50 + 4x)^4 (3x)^3 / (0.75 - 2x)^2

Since K_c is very small, not much O_2 should be produced.
    Assume: 4x << 0.50 and 2x << 0.75

$$1.75 \times 10^{-10} \approx (0.50)^4 (3x)^3 / (0.75)^2$$

[O_2] = 3x ≈ 1.2 x 10^{-3} M   assumption is OK