Chemistry 10123 & 10125, **Exam 2** **Answer Key**
February 16, 2011

1. (8 points) Complete the following table of values for two solutions **A** and **B** (at 25 °C).

Solution	**[H_3O^+]**	**pH**	**[OH^-]**	**pOH**
A	7.25	- 0.86	1.38×10^{-15}	14.86
B	2.24×10^{-11}	10.65	4.47×10^{-4}	3.35

2. (6 points) **SHOW ALL WORK.** At 50 °C, a sample of pure water has a pH of 6.63. Determine the value of K_w at this temperature. Include a balanced chemical equation for the relevant equilibrium reaction.

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$$

In pure water (at 50 °C), $[H_3O^+] = [OH^-] = 10^{-6.63} = 2.34 \times 10^{-7}$ M

$K_w = [H_3O^+][OH^-] = (2.34 \times 10^{-7})^2 = 5.50 \times 10^{-14}$

3. (4 points) In aqueous solution, cyanide ion (CN^-) behaves as a *weak base*. Write a balanced chemical equation to illustrate this behavior.

$$CN^-_{(aq)} + H_2O \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

4. (2 points) Among the following, circle the *weakest* Brønsted-Lowry base.

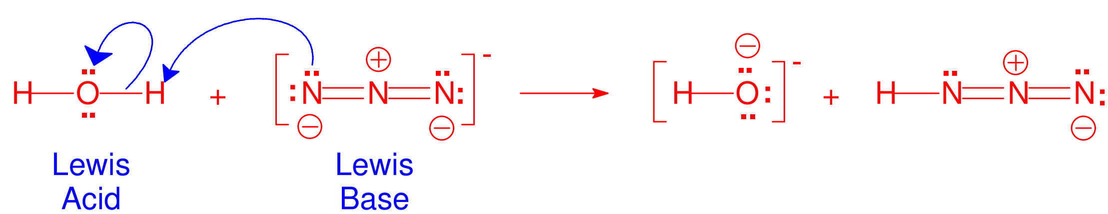
ClO_3^- ClO_4^- BrO_2^- BrO_4^- BrO_3^-

5. (2 points) The conjugate acid of HNO_3 is $H_2NO_3^+$

The conjugate base of H_2CF_2 is HCF_2^-

6. (10 points) Consider the following reaction in terms of the Lewis Acid-Base concept. Write ***Lewis electron dot formulas*** (including formal charges and/or resonance forms if needed) 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 goes from left to right. (Recall that azide ion has a linear skeletal structure.)

$$H_2O + N_3^- \longrightarrow OH^- + HN_3$$



7. Coal can be used to produce hydrogen (a potential fuel) by the following reaction ($\Delta H° = 90$ kJ).

$$C_{(s)} + 2\,H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 2\,H_{2(g)}$$

(a) (4 points) Complete the equilibrium constant expression for this reaction.

$K_c = [CO_2]\,[H_2]^2 / [H_2O]^2$

(b) (10 points) At equilibrium, how will the molar concentration of $H_{2(g)}$ and/or the value of K_c be affected by each of following changes? Indicate your answers by writing the appropriate letter.

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

Change	**[H_2]**	**K_c**
increase the pressure	D	N
add more coal, $C_{(s)}$	N	N
increase the temperature	I	I
add a catalyst	N	N
remove some $CO_{2(g)}$	I	N

8. (2 points) Among the following, circle the *strongest* Brønsted-Lowry acid.

CH_4 H_2S SiH_4 PH_3 H_2O NH_3

9. (10 points) **SHOW ALL WORK.** Many "insoluble" metal salts, e.g., $Co(OH)_{2(s)}$, are often more soluble in solutions containing Lewis bases (e.g. NH_3). This is illustrated by the following reaction for which $K_c = 7.70 \times 10^{-10}$. Determine the equilibrium concentration of the complex ion, $Co(NH_3)_4^{2+}$, in a solution that is initially 0.50 M $NH_{3(aq)}$. (***Clearly state and justify any assumptions that you wish to make.***)

	$Co(OH)_{2(s)}$ +	$4\,NH_{3(aq)}$ $\rightleftharpoons$	$Co(NH_3)_4^{2+}{}_{(aq)}$ +	$2\,OH^-{}_{(aq)}$
I		0.5 M	0	0
C		- 4x	+ x	+ 2x
E		0.5 - 4x	x	x

$K_c = [Co(NH_3)_4^{2+}]\,[OH^-]^2 / [NH_3]^4$

$7.70 \times 10^{-10} = (x)\,(2x)^2 / (0.5 - 4x)^4$

Since K_c is very small, there will be only small amounts of products at equilibrium.
Thus, assume $4x << 0.50$

$7.70 \times 10^{-10} \approx 4x^3 / (0.5)^4$

$x \approx 2.3 \times 10^{-4}$ (Assumption OK!)

10. (10 points) **SHOW ALL WORK.** A sample of pure $NO_{2(g)}$ (molar mass = 46.0) is heated to 378 °C at which temperature it partially decomposes according to the following reaction. At equilibrium, the density of the gas mixture is 0.575 g/L and the total pressure is 0.961 atm. Determine K_c for the reaction.

	$2\,NO_{2(g)}$	$\rightleftharpoons$	$2\,NO_{(g)}$	+	$O_{2(g)}$
I	0.0125 M*		0		0
C	- 2x		+ 2x		+ x
E	0.0125 - 2x		2x		x

*Reactions don't create matter (mass),

∴ total mass of products = initial mass of reactant = 0.575 g/L

initial conc of NO_2 = (0.575 g/L) (1 mole / 46.0 g) = 0.0125 M

let n = total moles of gas (per liter) at equilibrium

n = PV/RT = (0.961 atm) (1 L) / (0.0821 L·atm/mole·K) (650 K) = 0.0180 mole

n = moles NO_2 + moles NO + moles O_2

0.0180 = (0.0125 - 2x) + 2x + x ∴ x = 0.0055

$[NO_2]$ = 0.0125 - 2(0.0055) = 0.0015

[NO] = 2(0.0055) = 0.011 $[O_2]$ = 0.0055

$K_c = [NO]^2 [O_2] / [NO_2]^2 = (0.011)^2 (0.0055) / (0.0015)^2 = 0.30$

11. The following two-step mechanism was proposed for the reaction of silyl bromide (H_3SiBr) with cyanide ion (CN^-).

$$H_3SiBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \boxed{H_3Si^+} + Br^- \quad \text{fast}$$

$$\boxed{H_3Si^+} + CN^- \xrightarrow{k_2} H_3SiCN \quad \text{slow}$$

(a) (3 points) Write the overall net reaction.

$H_3SiBr + CN^- \longrightarrow H_3SiCN + Br^-$

(b) (2 points) Circle the intermediate(s), if any, in the above mechanism.

(c) (7 points) **SHOW ALL WORK.** Determine the ***predicted rate law*** for the reaction based on the above mechanism.

slow step: rate = $k_2 [H_3Si^+] [CN^-]$

fast equilibrium step: $rate_1 = rate_{-1}$

$k_1 [H_3SiBr] = k_{-1} [H_3Si^+] [Br^-]$

$[H_3Si^+] = k_1 [H_3SiBr] / k_{-1} [Br^-]$

substituting this expression for $[H_3Si^+]$ in the $rate_2$ equation above yields the overall rate law:

rate = $(k_1 k_2 / k_{-1}) [H_3SiBr] [CN^-] / k_{-1} [Br^-]$

12. (10 points) **SHOW ALL WORK.** At a certain temperature, the following reaction has $K_c = 36$. The reaction was started initially with 2.0 M Br_2 and 1.0 M Cl_2. After the reaction proceeded for several minutes, the concentration of BrCl was found to be 1.60 M. Determine whether or not the system has reached equilibrium by calculating the appropriate quantity. (***Hint***: It is not necessary to determine any equilibrium concentrations nor is the quadratic formula required!)

	$Br_{2(g)}$	+ $Cl_{2(g)}$	$\rightleftharpoons$	$2\ BrCl_{(g)}$
I	2.0 M	1.0 M		0
C	- 0.80	- 0.80		+ 1.60
E	1.20	0.20		1.60 M

As shown above, if 1.6 moles/L of BrCl is formed, then 0.80 moles each of Br_2 and Cl_2 must have been consumed, leaving 1.20 mole Br_2 and 0.20 moles Cl_2.

The "appropriate" quantity is the reaction quotient, Q.

$$Q = [BrCl]^2 / [Br_2]\,[Cl_2] = (1.60)^2 / (1.2)\,(0.20) = 10.7$$

Since Q and K_c are not equal, the reaction is not at equilibrium!

Since Q is less than K_c, the reaction must shift further forward to reach equilibrium.

13. (2 points) A chemical species that can function as both an acid and a base is described as being amphoteric. A very good example of such a species is H_2O (or HCO_2^-, HSO_4^-, etc.)

14. (8 points) **SHOW ALL WORK.** Consider the following reactions and their equilibrium constants.

$$NO_{(g)} + 1/2\ Br_{2(g)} \rightleftharpoons NOBr_{(g)} \qquad K_p = 5.3$$

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2\ NO_{(g)} \qquad K_p = 4.8 \times 10^{-31}$$

From this information, determine K_p for the reaction below.

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

Reverse eq 1 and multiply by 2, reverse eq 2, then add the equations together.

$$2\ NOBr \rightleftharpoons \cancel{2\ NO} + Br_2 \qquad K_p = 1 / (5.3)^2 = 3.56 \times 10^{-2}$$

$$\cancel{2\ NO} \rightleftharpoons N_2 + O_2 \qquad K_p = 1 / (4.8 \times 10^{-31}) = 2.08 \times 10^{30}$$

$$2\ NOBr \rightleftharpoons N_2 + O_2 + Br_2$$

$$K_c = (3.56 \times 10^{-2})\,(2.08 \times 10^{30}) = 7.4 \times 10^{28}$$