# CHEM 36
General Chemistry
## EXAM #2

March 13, 2002

Name: _____ *Key* _____

INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself! Circle your final answer to numerical questions.

The entire exam is worth a total of 150 points. Attached are a periodic table and a formula sheet jam-packed with useful stuff. Good Luck!

Page	Possible Points	*Points Earned*
2	25	*25*
3	30	*30*
4	25	*25*
5	45	*45*
6	25	*25*
TOTAL:	*150*	*150*
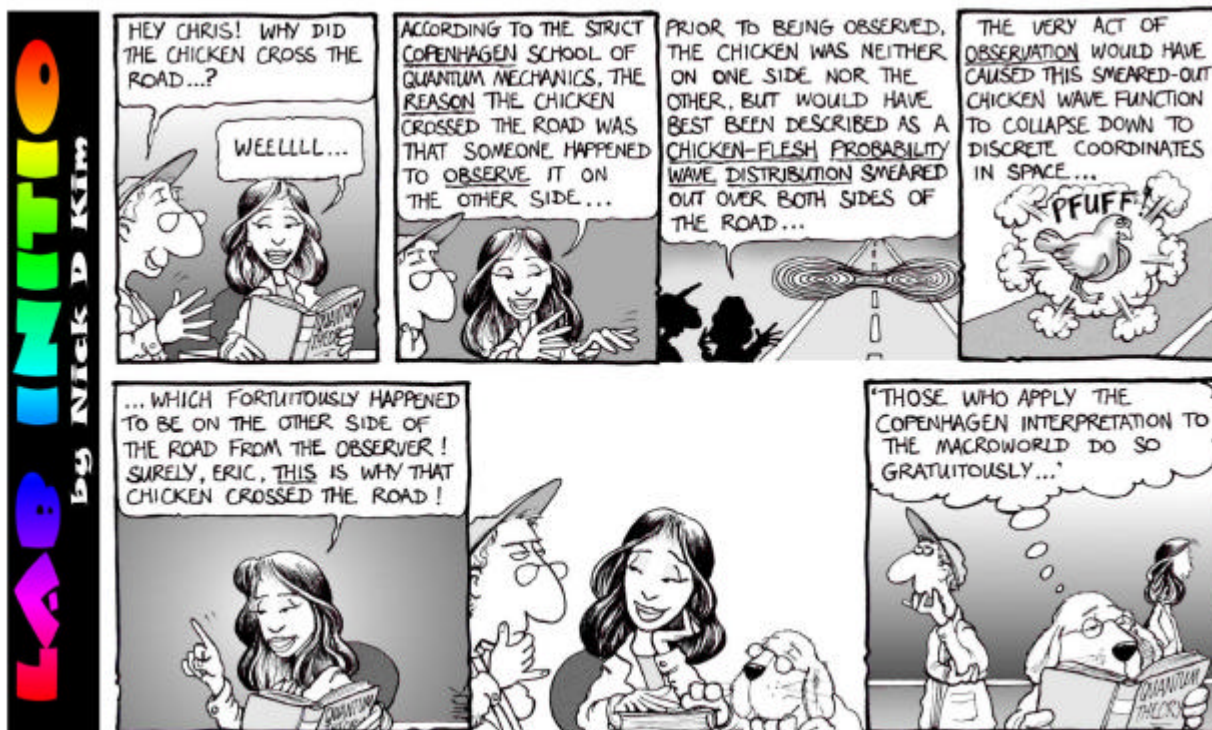
1. For the dissociation of acetic acid in water:

$$CH_3COOH\ (aq) \leftrightarrows H^+\ (aq) + CH_3COO^-\ (aq)$$
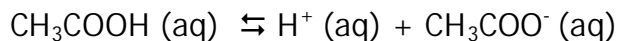
   at 25.0°C, $K_a = 1.76 \times 10^{-5}$.

   a. **[10 pts]** Calculate ΔG^0 (kJ/mol) for this reaction.

   $$\mathbf{\Delta G^0 = -RTLnK}$$
   $$\mathbf{= -(8.3145\ J/mol\text{-}K)(298.15\ K)Ln(1.76 \times 10^{-5})}$$
   $$\mathbf{= 2.7139 \times 10^4\ J/mol \times 10^{-3}\ kJ/J = \boxed{27.139\ kJ/mol}}$$

   b. **[5 pts]** At equilibrium, what is the value of ΔG?

   $$\boxed{\text{For \textit{any system} at equilibrium: } \mathbf{\Delta G = 0}}$$

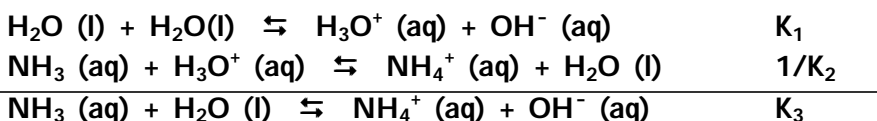2. **[10 pts]** Calculate the *molarity* of an aqueous acetic acid solution that is 36.0% acetic acid (by mass). The density of the solution is 1.045 g/mL and the molecular weight of acetic acid is 60.05 g/mol.

$$\frac{36.0\ g\ HAc}{100.0\ g\ soln} \times \frac{1\ mol\ HAc}{60.05\ g\ HAc} \times \frac{1.045\ g\ soln}{mL\ soln} \times \frac{1000\ mL}{L} = \textit{6.2648 mol HAc/L}$$

$$= \boxed{\textit{6.26 M HAc}}$$

3. **[15 pts]** Given equilibrium constants for reactions 1 and 2, compute K_3:

(1) H_2O (l) + H_2O(l) $\leftrightarrows$ H_3O^+ (aq) + OH^- (aq) K_1 = 1.0 x 10^{-14}

(2) NH_4^+ (aq) + H_2O (l) $\leftrightarrows$ NH_3 (aq) + H_3O^+ (aq) K_2 = 5.7 x 10^{-10}

(3) NH_3 (aq) + H_2O (l) $\leftrightarrows$ NH_4^+ (aq) + OH^- (aq) K_3 = ???
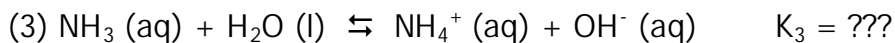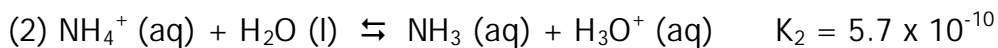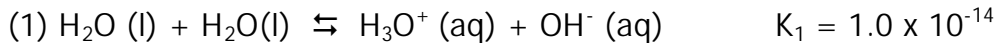
Reaction (1) – Reaction (2) = Reaction (3)

H_2O (l) + H_2O(l) $\leftrightarrows$ H_3O^+ (aq) + OH^- (aq)	K_1
NH_3 (aq) + H_3O^+ (aq) $\leftrightarrows$ NH_4^+ (aq) + H_2O (l)	$1/K_2$
NH_3 (aq) + H_2O (l) $\leftrightarrows$ NH_4^+ (aq) + OH^- (aq)	K_3

So: K_3 = K_1 $(1/K_2)$ = 1.0 x 10^{-14}/5.7 x 10^{-10} = *1.754 x 10^{-5}* = 1.8 x 10^{-5}

4. Chloroacetic acid dissociates in aqueous solution to produce the chloroacetate and hydronium ions:

$$CH_2ClCOOH \text{ (aq)} + H_2O \text{ (l)} \leftrightarrows CH_2ClCOO^- \text{ (aq)} + H_3O^+ \text{ (aq)}$$
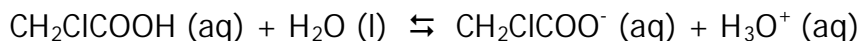
a. **[10 pts]** Compute K at 25.0 °C. given the following set of equilibrium concentrations:

[$CH_2ClCOOH$] = 0.0888 *M*
[CH_2ClCOO^-] = 0.0112 *M*
[H_3O^+] = 0.0112 *M*

K = [CH_2ClCOO^-][H_3O^+] = **(0.0112)(0.0112)** = *1.4126 x 10^{-3}* = 1.41 x 10^{-3}
     [$CH_2ClCOOH$]   **(0.0888)**

b. **[5 pts]** Calculate the pH of this solution.

pH = –Log[H_3O^+] = –Log(0.112) = *1.95078* = 1.95

5. Consider the following endothermic (ΔH° = 41.18 kJ/mol) reaction:

$$CO_2 \text{ (g)} + H_2\text{(g)} \rightleftharpoons CO \text{ (g)} + H_2O \text{ (l)}$$
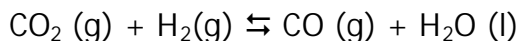
At 25.0 °C, K = 3.2 x 10^{-4}.

If we start with 1.0 atm of each of the gas phase species in a closed vessel containing some water:

a. **[10 pts]** Is the system at equilibrium? If not, will the reaction proceed to the *left* or to the *right* in order to reach equilibrium?

$$Q = \frac{P_{CO}}{P_{CO_2} \, P_{H_2}} = \frac{(1.0)}{(1.0)(1.0)} = 1.0 \gg K$$

If Q > K, then there is an excess of CO and reaction will shift to the:

(Left)   **Right**   **No Change**   (circle one)

b. **[15 pts]** Calculate the partial pressure of H_2 (g) for the system at equilibrium.

	CO_2 (g)	+ H_2(g)	$\rightleftharpoons$	CO (g)	+ H_2O (l)
Initial	1.00	1.00		1.00	
Change	+x	+x		-x	
Equilibrium	1.00+x	1.00+x		1.00-x	

$$3.2 \text{ x } 10^{-4} = \frac{(1.00 - x)}{(1.00+x)(1.00+x)}$$

A quadratic: 3.2 x 10^{-4} x^2 + 1.00064 x – 9.9968 x 10^{-1} = 0

x = 0.998714

P_{H_2} = 1.00 + x = *1.998714* = **2.0 atm**

4

c. **[5 pts each]** How will the equilibrium partial pressure of H_2 (g) be affected by the following:

i. CO_2 (g) is added to the system (at constant volume).

    Increase   (***Decrease***)   ***No Change***   (circle one)

ii. The volume of the reaction vessel is halved.

    Increase   (***Decrease***)   ***No Change***   (circle one)
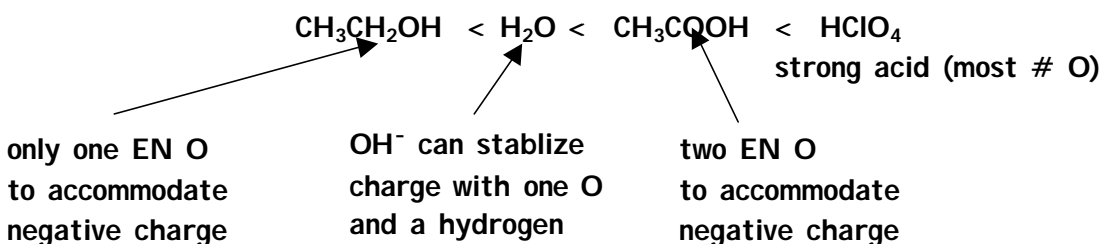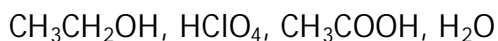
iii. Argon gas is added to the system (at constant volume).

    Increase   ***Decrease***   (***No Change***)   (circle one)

iv. The temperature of the system is increased.

    Increase   (***Decrease***)   ***No Change***   (circle one)
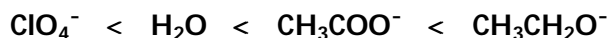
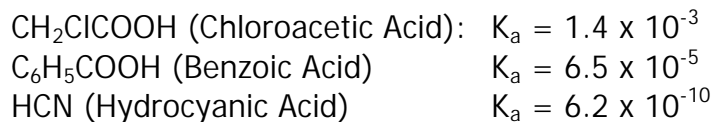6a. **[10 pts]** Arrange the following acids in order of increasing strength (briefly explain your reasoning):

$$CH_3CH_2OH, HClO_4, CH_3COOH, H_2O$$

$$\textbf{CH}_3\textbf{CH}_2\textbf{OH} \ < \ \textbf{H}_2\textbf{O} < \ \textbf{CH}_3\textbf{COOH} \ < \ \textbf{HClO}_4$$

strong acid (most # O)

only one EN O
to accommodate
negative charge

OH⁻ can stablize
charge with one O
and a hydrogen

two EN O
to accommodate
negative charge

b. **[10 pts]** Identify the corresponding conjugate bases for these acids:

Acid	Conjugate Base
CH_3CH_2OH	$\textbf{CH}_3\textbf{CH}_2\textbf{O}^-$
$HClO_4$	$\textbf{ClO}_4^-$
CH_3COOH	$\textbf{CH}_3\textbf{COO}^-$
H_3O^+	$\textbf{H}_2\textbf{O}$

c. **[5 pts]** Arrange the conjugate bases in order of increasing strength.

$$\textbf{ClO}_4^- \ < \ \textbf{H}_2\textbf{O} \ < \ \textbf{CH}_3\textbf{COO}^- \ < \ \textbf{CH}_3\textbf{CH}_2\textbf{O}^-$$

7. **[5 pts each]** Given the K_a values for the following acids:

$CH_2ClCOOH$ (Chloroacetic Acid): $K_a = 1.4 \times 10^{-3}$
C_6H_5COOH (Benzoic Acid) $K_a = 6.5 \times 10^{-5}$
HCN (Hydrocyanic Acid) $K_a = 6.2 \times 10^{-10}$

a. Which acid is the weakest?

HCN has the *smallest* K_a, so it is the weakest acid

b. Write the acid dissociation equilibrium reaction for the acid you identified in part a.

HCN (aq) + H_2O (l) $\leftrightarrows$ CN^- (aq) + H_3O^+ (aq)
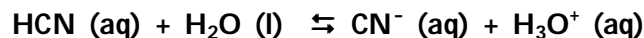
c. Which of the conjugate bases for these acids is the weakest?

The conjugate base of the *strongest acid* will be the weakest:
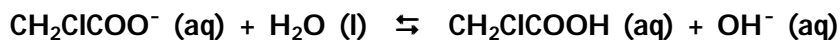
$CH_2ClCOOH$ is the strongest acid,

so CH_2ClCOO^- is the weakest conjugate base

d. Calculate the value of K_b for the base you identified in part c.

**For a conjugate acid/base pair: $K_aK_b = K_w$**

So: $K_b = K_w/K_a = 1.0 \times 10^{-14}/1.4 \times 10^{-3}$
= 7.14 x 10^{-12}
= 7.1 x 10^{-12}

e. Write the base dissociation (K_b) equilibrium reaction for the base you identified in part c.

CH_2ClCOO^- (aq) + H_2O (l) $\leftrightarrows$ $CH_2ClCOOH$ (aq) + OH^- (aq)
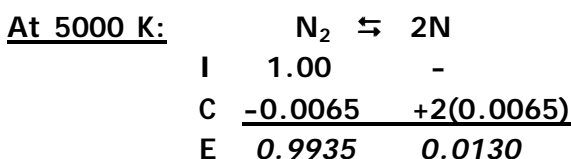
Extra Credit! -- 10 pts

The triple bond in the N_2 molecule is very strong, but at high enough temperatures even it breaks down. At 5000 K, when the total pressure exerted by a sample of nitrogen is 1.00 atm, N_2 (g) is 0.65% dissociated at equilibrium:
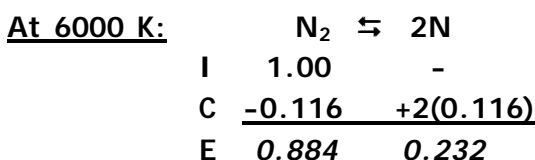
$$N_2 \text{ (g)} \leftrightarrows 2 N \text{ (g)}$$
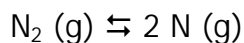
At 6000 K, with the same total pressure, the proportion of N_2 (g) dissociated at equilibrium rises to 11.6%. Calculate the ΔH of this reaction.

We need K at 5000 K (T_1) and at 6000 K (T_2):

At 5000 K: $N_2 \leftrightarrows 2N$

I   1.00   –

C   –0.0065   +2(0.0065)

E   *0.9935*   *0.0130*

So: $K_1 = \dfrac{(P_N)^2}{P_{N2}} = \dfrac{(0.0130)^2}{0.9935} = $ *1.70×10^{-4}*

At 6000 K: $N_2 \leftrightarrows 2N$

I   1.00   –

C   –0.116   +2(0.116)

E   *0.884*   *0.232*

So: $K_2 = \dfrac{(P_N)^2}{P_{N2}} = \dfrac{(0.232)^2}{0.884} = $ *6.09×10^{-2}*

Now, plug into Van't Hoff equation and solve for ΔH:

$$Ln(K_2/K_1) = -(\Delta H^o/R)[(1/T_2) - (1/T_1)]$$

$$5.8812 = -\Delta H^o \, (-4.0091 \times 10^{-6})$$

$\Delta H^o = 1.467 \times 10^6$ J   ® $\boxed{\textit{1.5} \times 10^3 \textit{ kJ}}$