CH302H – Principles of Chemistry II: Honors
Spring 2014, Unique 51880

Exam 2
6 March 2014

Name: Key

You may use any material you wish provided it does not have a heartbeat nor does it connect to a wireless or cellular network.

Honor Code:

"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

Signature Date

1. (15 points) Determine whether the following statements are true or false.

a. True (False) $S^0_m(Cl_2(g)) > S^0_m(I_2(g))$ FW(I_2) > FW(Cl_2)

b. True (False) The "white" part of a newly laid egg contains a significant concentration of $CO_2(g)$ dissolved in water. Over the first 1-2 days after the egg is laid, this $CO_2(g)$ escapes through the shell of the egg. The pH of the egg whites thus decreases. CO_2 dissolved in water makes H_2CO_3, as $[CO_2]\downarrow$, $[H_2CO_3]\downarrow$, pH↑

c. True (False) If one mole of a gas decomposes to 2 moles of a gaseous product, when the pressure inside the reaction vessel increases, K_p of the reaction will decrease.

d. True (False) It is not possible for a solution to have a pH < 0. $\frac{dK_p}{dP} = 0$

e. (True) False A weak acid must have a strong conjugate base.

2. (15 points) The following table shows the equilibrium constant for the autoionization of water as a function of temperature (this is a copy of Table 15.1 in your textbook, if that is easier for you to examine):

T (°C)	K_w	pH of water
0	0.114×10^{-14}	7.47
10	0.292×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.47×10^{-14}	6.63
60	9.61×10^{-14}	6.51

Explain the observed trend using any combination of clear and concise English, equations, and figures that may be necessary. Be sure to state all assumptions explicitly.

As T increases, K_w increases as well. This means that the autoionization of water must be endothermic ($\Delta H^\circ_{rxn} > 0$). To confirm:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

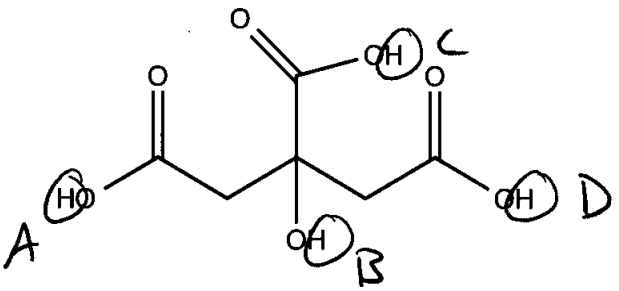
ΔH_f°: -285.8 kJ/mol $\quad -285.8$ kJ/mol $\quad -230.0$ kJ/mol

$$\Delta H^\circ_{rxn} = \Delta H_f^\circ(OH^-) + \Delta H_f^\circ(H_3O^+) - 2\Delta H_f^\circ(H_2O)$$

$$= -230.0 \text{ kJ/mol} + -285.8 \text{ kJ/mol} - (2)(-285.8 \text{ kJ/mol})$$

$$\boxed{\Delta H^\circ_{rxn} = 56 \text{ kJ/mol}}$$

3. (15 points) The structure of citric acid is given below:



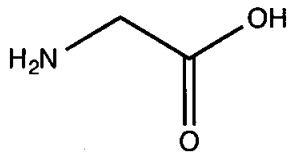
a) How many acidic protons does citric acid contain?

4

b) Rank all of citric acid's acidic protons in order of increasing pK_a. (Make clear how you are identifying each proton, by for example labeling it on the figure (A, B, etc.)

The carboxylic acid protons are all approximately the same. All are easier to deprotonate than the alcohol group. In order of increasing pKa: $A \approx C \approx D < B$

4. (20 points) The structure of glycine, the simplest amino acid, is given below:



a) Glycine undergoes two independent chemical reactions with water, one with a pK_a of 9.6 and the other with a pK_a of 2.3. Identify the reaction taking place at these two pK_a values and determine the equilibrium constant of the reaction.

pka 9.6: H_2N–CH$_2$–C(=O)–OH + H_2O ⇌ H_3N^+–CH$_2$–C(=O)–O$^-$ + OH^- $\quad K_b = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{10^{-9.6}} = 4.0\times10^{-5}$

pka 2.3: H_2N–CH$_2$–C(=O)–OH + H_2O ⇌ H_2N–CH$_2$–C(=O)–O$^-$ + H_3O^+ $\quad K_a = 10^{-2.3} = 5.0\times10^{-3}$

b) Determine the ~~pH~~ concentration of all species in solution of a 0.10 M aqueous solution of glycine.

Consider each rxn separately

Deprotonation: $Gly + H_2O \rightleftharpoons Gly^- + H_3O^+$ $\quad K_a = \frac{[H_3O^+][Gly^-]}{[Gly]} = 5.0\times10^{-3}$

	Gly	Gly^-	H_3O^+
I:	0.10 M	0	≈0
Δ:	−x	+x	+x
E:	0.10 M − x	x	x

$K_a = \frac{x^2}{0.10}$ $\quad x = 0.022 = [Gly^-] = [H_3O^+] = 0.022\,M$

→

Scratch paper

4b) cont.

Protonation: $Gly + H_2O \rightleftharpoons Gly^+ + OH^-$ $\quad K_b = 4.0\times10^{-5}$

I:	0.1M	0	≈ 0
Δ:	$-x$	$+x$	$+x$
E:	$0.1-x$	$+x$	$+x$

$K_b = \frac{x^2}{0.1}$; $x = 0.002 = [Gly^+] = [OH^-] = 0.002M$

AND: The autoionization of H_2O:

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l) \qquad K = K_w^{-1} = 1.0\times10^{14}$$

I 0.022 0.002

We will consume all of our available OH^- to neutralize the H_3O^+:

~~EH~~ -assume 1L H_2O, $n(H_3O^+)_{remaining} = (0.022-0.002)mols = 0.020M$

$[H_3O^+] = 0.020\,M$

So:

$[Gly^+] = 0.0020M$
$[Gly^-] = 0.002M$
$[H_3O^+] = 0.020M$
$[OH^-] \approx 0$

* as an aside, even though this molecule is acting as both an acid and a base, the final solution is acidic (pH=1.7), which is why these molecules are called "amino acids."

5. (20 points) Solid ammonium carbonate, $(NH_4)_2CO_3$, decomposes to form ammonia, carbon dioxide, and water gases at 150°C.

a) A certain amount of the solid decomposes, resulting in a total pressure of products of 0.12 atm. Determine the equilibrium constant for this reaction.

First balance the rxn: $(NH_4)_2CO_{3(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)} + H_2O_{(g)}$

If $P_{TOT} = 0.12$ atm, $P_{H_2O} = P_{CO_2} = 0.030$ atm, $P_{NH_3} = 0.060$ atm

$K_p = P_{NH_3}^2 P_{CO_2} P_{H_2O} = (0.060)^2(0.030)(0.030) = \boxed{3.2\times10^{-6} = K_p}$

b) A certain amount of the solid is added to a reaction vessel maintained at 150°C with a partial pressure of water is 0.20 atm. What is the partial pressure of all decomposition products under these condition?

K_p remains constant!

	$2NH_3$	CO_2	H_2O
I:	0	0	0.20
Δ:	+2x	+x	+x
E:	2x	x	0.2+x ≈ 0.2

$K_p = (2x)^2(x)(0.2)$

$x = \left(\frac{K_p}{0.8}\right)^{1/3} = 0.016$

$P_{NH_3} = 0.032$ atm $P_{H_2O} = 0.2$ atm

$P_{CO_2} = 0.016$ atm

6. (15 points) Which of the following solutions will result in a buffer of pH 5.0 if made in water?

a) 1.2 M H_2CO_3 + 0.051 M $NaHO_3$ $pH = 6.37 - \log\frac{[1.2]}{[0.051]} = 5.0$ ✓

In all cases: $pH = pka - \log\frac{[HA]}{[A^-]}$

b) 0.35 M $NaHC_2O_4$ + 2.3 M CaC_2O_4 $pH = 4.19 - \log\frac{(0.35)}{(2.3)} = 5.0$ ✓

c) 0.3 M CH_3COOH + 0.7 M $NaCH_3CO_2$ $pH = 4.75 - \log\frac{(0.3)}{(0.7)} = 5.1$ X

d) 1.0×10^{-5} M HCl Strong acid - not a buffer

e) 1.0 M $NaNH_4$ + 0.7 M NH_3

$pH = 9.25 - \log\frac{[1.0]}{(0.7)} = 9.1$ X