## CHEM102 Exam II (Jul 31 2009).

 $33\frac{1}{3}$  points / problem with maximum of 100 points.

1.

a)  $P_{\text{H}_2\text{S}}^{ini} = 100.0 \text{ torr} = 0.1316 \text{ atm}; P_{\text{H}_2\text{O}}^{eq} = 99.803 \text{ torr} = 0.1313 \text{ atm};$  $P_{\text{O}_2}^{ini} = 200.0 \text{ torr} = 0.2632 \text{ atm} (4 \text{ sig. figs.}).$  Write ICE table as follows:

	$H_2S$	$O_2$	$SO_2$	$H_2O$
Ι	$0.1316 \mathrm{atm}$	$0.2632 \mathrm{~atm}$	0  atm	0  atm
-	-x	$-\frac{3}{2}x$	+x	+x
Ε	0.1316 - x  atm	$0.\bar{2}632 - \frac{3}{2}x$ atm	$x \operatorname{atm}$	$x \operatorname{atm}$

The equilibrium pressure of water gives x = 0.1313 atm. Write the expression for  $K_p$ :

$$K_p = \frac{P_{\rm SO_2}^{eq} \cdot P_{\rm H_2O}^{eq}}{P_{\rm H_2S}^{eq} \cdot \left(P_{\rm O_2}^{eq}\right)^{3/2}} = \frac{(0.1313)^2}{(0.1316 - 0.1313) \cdot (0.2632 - \frac{3}{2} \cdot 0.1313)^{3/2}} = 3370.0$$

- b)  $K_p = K_c (RT)^{\Delta n} \Rightarrow K_c = K_p (RT)^{-\Delta n}$ .  $\Delta n = \text{products} \text{reactants} = 2 2.5 = -0.5$ . Must use  $R = 0.08206 \frac{\text{L atm}}{\text{mol K}}$  because this is compatible with the atm units used for  $K_p$  and L for  $K_c$ . Plugging in the numbers gives  $K_c = 1.667 \times 10^4$  (with T = 298 K).
- c) The new equation is rearranged by multiplying both sides by 2 and then reversing the reactants and products. The first step corresponds to squaring  $K_p$  and the second taking  $1/K_p$ . Thus the new  $K'_p = 1/K_p^2 = 8.8052 \times 10^{-8}$ .
- d)  $Q_p = \frac{P_{\text{SO}_2} \cdot P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}} \cdot P_{\text{O}_2}^{3/2}} = \frac{(0.1313 + 0.013158)(0.1313)}{(0.0003)(0.06625)^{3/2}} = 3708$ . Since  $Q_p > K_p$ , the reaction proceeds from right to left to reach the new equilibrium.
- e)  $\Delta G_{rxn}^{\circ} = -RT \ln (K_p) = -(8.314 \frac{\text{J}}{\text{mol K}}) \times (298 \text{ K}) \ln (3370) = -21.12 \text{ kJ/mol.}$

2.

- a) It can donate 1, 2, or 3 protons depending on the conditions (acceptor).
- b)  $pK_a = -\log(K_a) \Rightarrow K_a = 10^{-pK_a}$ . Inserting the  $pK_a$  values:  $K_{a1} = 10^{-3.13} = 7.4 \times 10^{-4}, K_{a2} = 1.7 \times 10^{-5}, K_{a3} = 4.0 \times 10^{-7}$ .

- c)  $K_a \cdot K_b = 10^{-14}$  (at room temperature). Thus  $K_b = \frac{10^{-14}}{K_a}$  and  $K_{b1} = \frac{10^{-14}}{7.4 \times 10^{-4}} = 1.7 \times 10^{-11}$ ;  $K_{b2} = 5.9 \times 10^{-10}$ ;  $K_{b3} = 2.5 \times 10^{-8}$ .
- 3.
  - a) Denote benzoic acid (weak acid) by BZH. To find out the pH, construct ICE table:

101	BZH	$H_2O$	$\mathrm{BZ}^-$	$H_3O^+$			
Ι	1.0 M	_	0 M	0 M			
С	-x	—	+x	+x			
Ε	(1.0 - x) M	—	x M	$x \mathrm{M}$			
$K_a = \frac{x^2}{1-x} \approx x^2 \Rightarrow x = \sqrt{2.5 \times 10^{-5}} = 5.01 \times 10^{-3}$ (less than 5%)							
of 1; approximation OK). Since $[H_3O^+] = x = 5.01 \times 10^{-3} \text{ M}$ then							
$pH = -\log\left(\left[\mathrm{H}_{3}\mathrm{O}^{+}\right]\right) = 2.3.$							

- b)  $pH + pOH = 14 \Rightarrow pOH = 14 pH$  (at room temperature). This gives pOH = 14 2.3 = 11.7.
- c) Note that H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> are "synonyms" in water solutions. From the above  $[H^+] = 5.01 \times 10^{-3} \text{ M}$  and  $[OH^-] = 2.00 \times 10^{-12} \text{ M}$  because  $K_w = [H_3O^+] \cdot [OH^-] = 10^{-14}$  (room temperature).