PRINCIPLES OF GEOCHEMISTRY
GEOL 423
PROBLEM SET 3 – ANSWERS
Fall 2009

Problem 1:

1) Species: H^+, OH^-, HAc^0, Ac^-

2) Mass Action Expressions:

$$HAc^0 \leftrightarrow Ac^- + H^+ \qquad K_1 = \frac{[H^+][Ac^-]}{[HAc^0]} = 10^{-4.75}$$

$$H_2O(l) \leftrightarrow OH^- + H^+ \qquad K_w = [OH^-][H^+] = 10^{-14}$$

3) Mass-balance Expression:

$$0.05 \text{ mol L}^{-1} = [HAc^0] + [Ac^-]$$

4) Charge-balance Expression:

$$[H^+] = [Ac^-] + [OH^-]$$

5) Make Reasonable Assumptions:

a) HAc^0 is an acid so $[H^+] >> [OH^-]$
b) HAc^0 is weak acid so $[HAc^0] >> [Ac^-]$

Therefore, the mass-balance equation becomes 0.05 mol $L^{-1} \approx [HAc^0]$, and the charge-balance becomes $[H^+] \approx [Ac^-] = x$.

$$K_1 = 10^{-4.75} = \frac{x^2}{0.05}$$

$$x^2 = 8.89\text{x}10^{-7}$$

$$x = 9.43\text{x}10^{-4}$$

$$[H^+] \approx [Ac^-] = 9.43\text{x}10^{-4} \text{ mol L}^{-1}$$

$$pH = 3.03$$

$[HAc^0] = 0.05 - 9.43\text{x}10^{-4} = 0.0491$ mol L^{-1} or 1.9% error so assumption b) is OK.

$[OH^-] = 10^{-14}/10^{-3.03} = 1.07\text{x}10^{-11}$ mol L^{-1} so assumption a) is also OK.

Problem 2:

1) Species: H^+, OH^-, $H_3AsO_4^0$, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}

2) Mass-action Expressions:

$$H_3AsO_4^0 \leftrightarrow H_2AsO_4^- + H^+ \qquad K_1 = 10^{-2.2} = \frac{[H_2AsO_4^-][H^+]}{[H_3AsO_4^0]}$$

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+ \qquad K_2 = 10^{-7.0} = \frac{[HAsO_4^{2-}][H^+]}{[H_2AsO_4^-]}$$

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+ \qquad K_3 = 10^{-11.5} = \frac{[AsO_4^{3-}][H^+]}{[HAsO_4^{2-}]}$$

$$H_2O(l) \leftrightarrow OH^- + H^+ \qquad K_w = [OH^-][H^+] = 10^{-14}$$

3) Mass-balance Expression:

$$0.2 \text{ mol L}^{-1} = [H_3AsO_4^0] + [H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}]$$

4) Charge-balance Expression:

$$[H^+] = [H_2AsO_4^-] + 2[HAsO_4^{2-}] + 3[AsO_4^{3-}] + [OH^-]$$

5) Reasonable Assumptions:
   a) $H_3AsO_4^0$ is an acid so $[H^+] >> [OH^-]$
   b) According to the dissociation contants, we can expect that
$$[H_3AsO_4^0] > [H_2AsO_4^-] >> [HAsO_4^{2-}] >> [AsO_4^{3-}]$$

So the charge-balance becomes: $[H^+] \approx [H_2AsO_4^-] = x$
And the mass-balance becomes:

$$0.2 \text{ mol L}^{-1} = [H_3AsO_4^0] + [H_2AsO_4^-]$$
$$[H_3AsO_4^0] = 0.2 - x$$

$$K_1 = 10^{-2.2} = \frac{x^2}{0.2 - x}$$
$$1.26\text{x}10^{-3} - 6.31\text{x}10^{-3}x - x^2 = 0$$

$$x = \frac{6.31\times10^{-3} \pm \sqrt{\left(-6.31\times10^{-3}\right)^2 - 4(-1)\left(1.26\times10^{-3}\right)}}{2(-1)}$$

$x_1 = -0.0388$ (unreal root)

$x_2 = 0.03248$

$[H^+] \approx [H_2AsO_4^-] = 0.03248 \text{ mol L}^{-1}$

pH = 1.49

$[H_3AsO_4^0] = 0.2 - 0.03248 = 0.1675 \text{ mol L}^{-1}$ (16% dissociated)

$$K_2 = 10^{-7.0} = \frac{[HAsO_4^{2-}]0.03248}{0.03248}$$

$[HAsO_4^{2-}] = 10^{-7.0}$ mol L^{-1}

$$K_3 = 10^{-11.5} = \frac{[AsO_4^{3-}]0.03248}{10^{-7.0}}$$

$[AsO_4^{3-}] = 9.74x10^{-18}$ mol L^{-1}

It is quite clear that assumption b) is good.

$[OH^-] = 10^{-14}/10^{-1.49} = 3.09x10^{-13}$ mol L^{-1} so assumption a) is also OK.

Problem 3:

1) Species: CO_2(g), $H_2CO_3^0$, HCO_3^-, CO_3^{2-}, H^+, OH^-

2) Mass-action Expressions:

$CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3^0$ $$K_H = 10^{-1.5} = \frac{[H_2CO_3^0]}{P_{CO_2}}$$

$H_2CO_3^0 \leftrightarrow HCO_3^- + H^+$ $$K_1 = 10^{-6.3} = \frac{[HCO_3^-][H^+]}{[H_2CO_3^0]}$$

$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ $$K_2 = 10^{-10.3} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

$H_2O(l) \leftrightarrow OH^- + H^+$ $$K_w = [OH^-][H^+] = 10^{-14}$$

3) Partial Pressure Constraint: $P_{CO_2} = 10^{-2.0}$ atm.

4) Charge-Balance Expression:

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

5) Reasonable Assumptions:
   a) $H_2CO_3^0$ is an acid so $[H^+] >> [OH^-]$
   b) Also, according to the dissociation constants, we have $[HCO_3^-] >> [CO_3^{2-}]$

So the charge-balance becomes: $[H^+] \approx [HCO_3^-] = x$.

From the Henry's Law mass-action expression we get:

$$[H_2CO_3^0] = K_H P_{CO_2} = (10^{-1.5})(10^{-2.0}) = 10^{-3.5} \text{ mol } L^{-1}$$

$$K_1 = 10^{-6.3} = \frac{x^2}{10^{-3.5}}$$
$$x^2 = 10^{-9.8}$$
$$x = 10^{-4.9}$$
$$[H^+] \approx [HCO_3^-] = 10^{-4.9}$$
$$pH = 4.9$$

$$K_2 = 10^{-10.3} = \frac{[CO_3^{2-}]10^{-4.9}}{10^{-4.9}}$$
$$[CO_3^{2-}] = 10^{-10.3}$$

so assumption b) is OK.

$[OH^-] = 10^{-14}/10^{-4.9} = 7.94x10^{-10}$ mol L^{-1}, so assumption a) is also OK.

Note that, as shown in class, when $P_{CO_2} = 10^{-3.5}$ atm we get pH = 5.65, but when $P_{CO_2} = 10^{-2.0}$ atm we get pH = 4.9, so increasing P_{CO_2} results in a decreasing pH of rain water.

Problem 4:

1) Species: SO_2(g), $H_2SO_3^0$, HSO_3^-, SO_3^{2-}, H^+, OH^-

2) Mass-action Expressions:

$SO_2(g) + H_2O(l) \leftrightarrow H_2SO_3^0$	$K_H = 2.0 = \frac{[H_2SO_3^0]}{P_{SO_2}}$
$H_2SO_3^0 \leftrightarrow HSO_3^- + H^+$	$K_1 = 2 \times 10^{-2} = \frac{[HSO_3^-][H^+]}{[H_2SO_3^0]}$
$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$	$K_2 = 10^{-6.91} = \frac{[SO_3^{2-}][H^+]}{[HSO_3^-]}$
$H_2O(l) \leftrightarrow OH^- + H^+$	$K_w = [OH^-][H^+] = 10^{-14}$

Partial Pressure Constraint: $P_{SO_2} = 10^{-8.0}$ atm.

Charge-Balance Expression:

$$[H^+] = [HSO_3^-] + 2[SO_3^{2-}] + [OH^-]$$

Reasonable Assumptions:
$H_2SO_3^0$ is an acid so $[H^+] >> [OH^-]$
Also, according to the dissociation constants, we have $[HSO_3^-] >> [SO_3^{2-}]$

So the charge-balance becomes: $[H^+] \approx [HSO_3^-] = x$.

From the Henry's Law mass-action expression we get:

$$[H_2SO_3^0] = K_H P_{SO_2} = (2)(10^{-8}) = 2x10^{-8} \text{ mol L}^{-1}$$

$$K_1 = 2 \times 10^{-2} = \frac{x^2}{2 \times 10^{-8}}$$
$$x^2 = 4x10^{-10}$$
$$x = 2x10^{-5.0}$$
$$[H^+] \approx [HSO_3^-] = 2x10^{-5.0}$$
$$pH = 4.70$$

$$K_2 = 10^{-6.91} = \frac{[SO_3^{2-}]10^{-4.7}}{10^{-4.7}}$$
$$[SO_3^{2-}] = 10^{-6.91}$$

so assumption b) is OK.

$[OH^-] = 10^{-14}/10^{-4.7} = 5x10^{-10}$ mol L^{-1}, so assumption a) is also OK.

Note that, as shown in class, when $P_{SO_2} = 5x10^{-9}$ atm we get pH = 4.85, but when $P_{SO_2} = 10^{-8.0}$ atm we get pH = 4.7, so increasing P_{SO_2} also results in a decreasing pH of rain water.

Problem 5:

Because H_2SO_4 is a strong acid, the $[H^+]$ of rain containing will be $[H^+] = 2C_{H_2SO_4}$. The factor of 2 is because $2H^+$ ions are produced for every H_2SO_4 molecule dissociated. Also, H_2SO_4 is very soluble in water, so we can assume that all the sulfuric acid produced will dissolve into the rain. So the problem comes down to determining $C_{H_2SO_4}$.

At $P_{SO_2} = 10^{-8.0}$ atm, 1 m^3 of atmosphere contains $10^{-8.0}$ m^3 of SO_2. To convert to moles, we need to know how much volume 1 mole of gas occupies at 15°C and 1 atm. To calculate this, we use the ideal gas law!

$$V = \frac{nRT}{P} = \frac{(1\text{ mol})(0.08206\text{ atm L mol}^{-1}\text{ K}^{-1})(288.15\text{ K})}{(1\text{ atm})}$$
$$V = 23.65 \text{ L} = 23.65x10^3 \text{ cm}^3 (1 \text{ m}/100 \text{ cm})^3 = 0.02365 \text{ m}^3$$

Thus, 1 m^3 of air contains 10^{-8} $m^3/0.02365$ m^3 $mol^{-1} = 4.23x10^{-7}$ mol of SO_2. If all this is completely oxidized to H_2SO_4, and then dissolved in 0.001 dm^3 = 0.001 L of water, this would yield $4.23x10^{-4}$ mol L^{-1} of H_2SO_4, or $8.46x10^{-4}$ mol L^{-1} of H^+ or pH = 3.07.