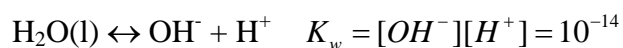
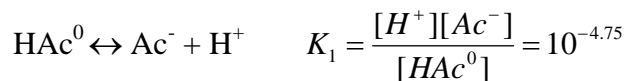


PRINCIPLES OF GEOCHEMISTRY
GEOL 423
PROBLEM SET 3 – ANSWERS
Fall 2009

Problem 1:

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

2) Mass Action Expressions:



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 $[H^+] \gg [OH^-]$

b) HAc^0 is weak acid so $[HAc^0] \gg [Ac^-]$

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

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

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

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

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

$$\text{pH} = 3.03$$

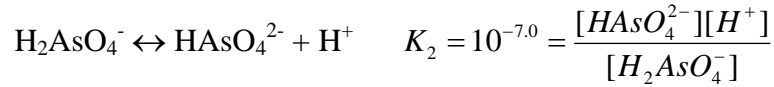
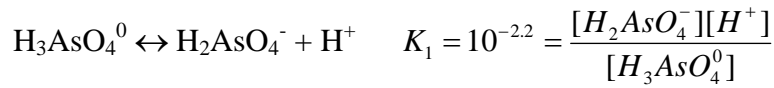
$[HAc^0] = 0.05 - 9.43 \times 10^{-4} = 0.0491 \text{ mol L}^{-1}$ or 1.9% error so assumption b) is OK.

$[OH^-] = 10^{-14} / 10^{-3.03} = 1.07 \times 10^{-11} \text{ mol L}^{-1}$ 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:



3) Mass-balance Expression:

$$0.2 \text{ mol L}^{-1} = [\text{H}_3\text{AsO}_4^0] + [\text{H}_2\text{AsO}_4^-] + [\text{HAsO}_4^{2-}] + [\text{AsO}_4^{3-}]$$

4) Charge-balance Expression:

$$[\text{H}^+] = [\text{H}_2\text{AsO}_4^-] + 2[\text{HAsO}_4^{2-}] + 3[\text{AsO}_4^{3-}] + [\text{OH}^-]$$

5) Reasonable Assumptions:

a) H_3AsO_4^0 is an acid so $[\text{H}^+] \gg [\text{OH}^-]$

b) According to the dissociation constants, we can expect that

$$[\text{H}_3\text{AsO}_4^0] > [\text{H}_2\text{AsO}_4^-] \gg [\text{HAsO}_4^{2-}] \gg [\text{AsO}_4^{3-}]$$

So the charge-balance becomes: $[\text{H}^+] \approx [\text{H}_2\text{AsO}_4^-] = x$

And the mass-balance becomes:

$$0.2 \text{ mol L}^{-1} = [\text{H}_3\text{AsO}_4^0] + [\text{H}_2\text{AsO}_4^-]$$

$$[\text{H}_3\text{AsO}_4^0] = 0.2 - x$$

$$K_1 = 10^{-2.2} = \frac{x^2}{0.2 - x}$$

$$1.26 \times 10^{-3} - 6.31 \times 10^{-3}x - x^2 = 0$$

$$x = \frac{6.31 \times 10^{-3} \pm \sqrt{(-6.31 \times 10^{-3})^2 - 4(-1)(1.26 \times 10^{-3})}}{2(-1)}$$

$$x_1 = -0.0388 \text{ (unreal root)}$$

$$x_2 = 0.03248$$

$$[\text{H}^+] \approx [\text{H}_2\text{AsO}_4^-] = 0.03248 \text{ mol L}^{-1}$$

$$\text{pH} = 1.49$$

$$[\text{H}_3\text{AsO}_4^0] = 0.2 - 0.03248 = 0.1675 \text{ mol L}^{-1} \text{ (16\% dissociated)}$$

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

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

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

$$[AsO_4^{3-}] = 9.74 \times 10^{-18} \text{ mol L}^{-1}$$

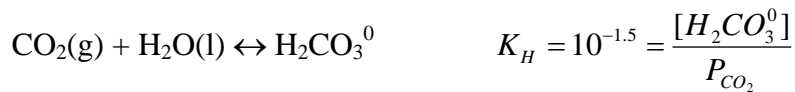
It is quite clear that assumption b) is good.

$[OH^-] = 10^{-14}/10^{-1.49} = 3.09 \times 10^{-13} \text{ mol L}^{-1}$ 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:



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

4) Charge-Balance Expression:

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

5) Reasonable Assumptions:

a) $H_2CO_3^0$ is an acid so $[H^+] \gg [OH^-]$

b) Also, according to the dissociation constants, we have $[HCO_3^-] \gg [CO_3^{2-}]$

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.

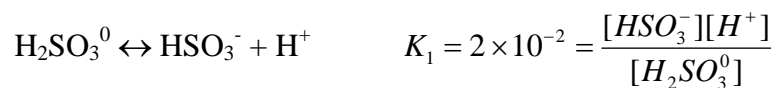
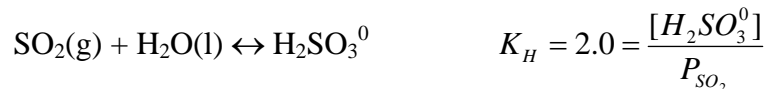
$[OH^-] = 10^{-14}/10^{-4.9} = 7.94 \times 10^{-10} \text{ mol L}^{-1}$, so assumption a) is also OK.

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:



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 $[H^+] \gg [OH^-]$

Also, according to the dissociation constants, we have $[HSO_3^-] \gg [SO_3^{2-}]$

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

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

$$[\text{H}_2\text{SO}_3^0] = K_H P_{\text{SO}_2} = (2)(10^{-8}) = 2 \times 10^{-8} \text{ mol L}^{-1}$$

$$K_1 = 2 \times 10^{-2} = \frac{x^2}{2 \times 10^{-8}}$$

$$x^2 = 4 \times 10^{-10}$$

$$x = 2 \times 10^{-5.0}$$

$$[\text{H}^+] \approx [\text{HSO}_3^-] = 2 \times 10^{-5.0}$$

$$\text{pH} = 4.70$$

$$K_2 = 10^{-6.91} = \frac{[\text{SO}_3^{2-}][\text{H}^+]}{[\text{HSO}_3^-]}$$

$$[\text{SO}_3^{2-}] = 10^{-6.91}$$

so assumption b) is OK.

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

Note that, as shown in class, when $P_{\text{SO}_2} = 5 \times 10^{-9}$ atm we get pH = 4.85, but when $P_{\text{SO}_2} = 10^{-8.0}$ 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 $[\text{H}^+]$ of rain containing will be $[\text{H}^+] = 2C_{\text{H}_2\text{SO}_4}$. 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 $C_{\text{H}_2\text{SO}_4}$.

At $P_{\text{SO}_2} = 10^{-8.0}$ atm, 1 m^3 of atmosphere contains $10^{-8.0} \text{ m}^3$ 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!

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(288.15 \text{ K})}{(1 \text{ atm})}$$

$$V = 23.65 \text{ L} = 23.65 \times 10^3 \text{ cm}^3 (1 \text{ m}/100 \text{ cm})^3 = 0.02365 \text{ m}^3$$

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