

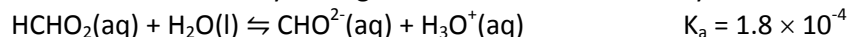
## Chem1B, General Chemistry II

1.) Both  $\text{H}_2\text{PO}_4^-$  ( $K_a = 4.2 \times 10^{-13}$ ) and  $\text{HSO}_3^-$  ( $K_a = 6.2 \times 10^{-8}$ ) are amphiprotic (amphoteric). Write out the expected equilibrium formed between these compounds, clearly indicating which will behave as the acid and which as the base.

Since  $\text{HSO}_3^-$  has a higher  $K_a$ , it is the stronger acid and will donate the proton to  $\text{H}_2\text{PO}_4^-$



2.) Consider a buffer solution created by mixing formic acid with formate by the following equilibrium.



- a.) Calculate the grams of magnesium formate ( $\text{Mg}(\text{CHO}_2)_2$ , 114.35 g/mol) needed to be dissolved in 1.50 L of 0.25 M formic acid to obtain a pH of 4.23.

$$4.23 = -\log(1.8 \times 10^{-4}) + \log([\text{base}]/0.25 \text{ M})$$

$$0.4852 = \log([\text{base}]/0.25)$$

$$[\text{base}] = 0.7642 \text{ M}$$

$$0.7642 \text{ mols/L} \times (1.50 \text{ L}) = 1.146 \text{ moles formate}$$

$$1.146 \text{ mols formate} \times \frac{1 \text{ mole Mg}(\text{CHO}_2)_2}{2 \text{ moles CHO}_2^-} \times \frac{114.35 \text{ g Mg}(\text{CHO}_2)_2}{1 \text{ mole Mg}(\text{CHO}_2)_2} = 65.54 \rightarrow \mathbf{65.5 \text{ g Mg}(\text{CHO}_2)_2}$$

- b.) To the buffer solution in (a), 0.125 moles of sodium hydroxide (NaOH) are added without changing the volume of the solution. Calculate the new pH of the buffer.

NaOH is a strong base and will reduce the acid and add to the conjugate base.

$$\frac{0.25 \text{ moles acid}}{1 \text{ L solution}} \times 1.50 \text{ L solution} = 0.375 \text{ moles HCHO}_2 \text{ initially}$$

$$0.375 \text{ moles HCHO}_2 \text{ initially} - 0.125 \text{ moles NaOH} = 0.250 \text{ moles HCHO}_2 \text{ in excess}$$

$$0.125 \text{ moles NaOH} \times \frac{1 \text{ mole formate}}{1 \text{ mole NaOH}} = 0.125 \text{ moles formate produced}$$

$$1.146 \text{ moles CHO}_2^- \text{ initially} + 0.125 \text{ moles CHO}_2^- \text{ produced} = 1.271 \text{ moles CHO}_2^-$$

$$\text{pH} = -\log(1.8 \times 10^{-4}) + \log\left(\frac{\frac{1.271 \text{ moles formate}}{1.50 \text{ L solution}}}{\frac{0.250 \text{ moles acid}}{1.50 \text{ L solution}}}\right)$$

$$\text{pH} = -\log(1.8 \times 10^{-4}) + 0.7062 = 4.4509 \rightarrow \mathbf{4.451} \text{ (should be higher than (a))}$$

- c.) To the buffer solution in (a), 0.135 moles of hydrobromic acid (HBr) are added without changing the volume of the solution. Calculate the new pH of the buffer.

HBr is a strong acid and will reduce the amount of conjugate base and add to the acid.

$$1.146 \text{ moles CHO}_2^- \text{ initially} - 0.135 \text{ moles HBr} = 1.011 \text{ moles CHO}_2^- \text{ excess}$$

$$0.135 \text{ moles HBr} \times \frac{1 \text{ mole acid produced}}{1 \text{ mole HBr}} = 0.135 \text{ moles acid produced}$$

$$0.375 \text{ moles HCHO}_2 \text{ initially} + 0.135 \text{ moles HBr} = 0.51 \text{ moles HCHO}_2$$

$$\text{pH} = -\log(1.8 \times 10^{-4}) + \log\left(\frac{\frac{1.011 \text{ moles formate}}{1.50 \text{ L solution}}}{\frac{0.51 \text{ moles acid}}{1.50 \text{ L solution}}}\right)$$

$$\text{pH} = -\log(1.8 \times 10^{-4}) + 0.2971 = 4.0419 \rightarrow \mathbf{4.042} \text{ (should be lower than (a))}$$

3.) Consider the following compounds all at 0.100 M:  $\text{HNO}_3$ , NaOH,  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ),  $\text{HClO}_2$  ( $K_a = 1.1 \times 10^{-2}$ ).

- a.) Arrange the above in order of **increasing pH**, from lowest to highest.



- b.) Arrange the above in order of **increasing % ionization**, from lowest to highest.



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4.) Should a precipitate of  $\text{Mg}(\text{OH})_2(\text{s})$  form in a solution made from 0.010 M  $\text{MgCl}_2$  and 0.10 M  $\text{NH}_3$ ? The  $K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ , and the  $K_{sp}$  for  $\text{Mg}(\text{OH})_2$  is  $1.8 \times 10^{-11}$ .

$$[\text{Mg}^{2+}] = 0.010 \text{ M } \text{MgCl}_2 \times \frac{1 \text{ mole } \text{Mg}^{2+}}{1 \text{ mole } \text{MgCl}_2} = 0.010 \text{ M } \text{Mg}^{2+}$$

	$\text{NH}_3(\text{aq}) +$	$\text{H}_2\text{O}(\text{aq}) \leftrightarrow$	$\text{NH}_4^+(\text{aq}) +$	$\text{OH}^-(\text{aq})$
I	0.10 M		0	0
C	-x		+x	+x
E	0.10 - x		x	x

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.10} \quad (\text{ignoring } -x \text{ due to low \% ionization})$$

$$x^2 = 1.8 \times 10^{-6} \rightarrow x = 1.34 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

$$Q = (0.010 \text{ M})(1.34 \times 10^{-3})^2 = 1.8 \times 10^{-8}, Q > K_{sp} \text{ so } \mathbf{yes}, \text{ the salt will precipitate.}$$

5.) Consider the titration of a 30.0 mL portion of 0.20 M HF ( $K_a = 6.6 \times 10^{-4}$ ) with 0.10 M NaOH.

a.) Calculate the initial pH of the solution when 0 mL of NaOH has been added.

	$\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow$	$\text{H}_3\text{O}^+(\text{aq}) +$	$\text{F}^-(\text{aq})$
I	0.20	0	0
C	-x	+x	+x
E	0.20 - x	x	x

$$6.6 \times 10^{-4} = \frac{x^2}{0.20} \quad (\text{ignoring } -x \text{ due to low \% ionization})$$

$$x^2 = 1.32 \times 10^{-4} \rightarrow x = 0.0114 = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.0114) = 1.939 \rightarrow \mathbf{1.94}$$

b.) Calculate the pH of the solution after 10.0 mL of NaOH have been added.

$$10.0 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.10 \text{ moles NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol HF}}{1 \text{ mol NaOH}} = 1.0 \times 10^{-3} \text{ moles HF used}$$

$$30.0 \text{ mL HF initial} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.20 \text{ moles HF}}{1 \text{ L}} = 6.0 \times 10^{-3} \text{ moles HF initial}$$

$$6.0 \times 10^{-3} \text{ initial} - 1.0 \times 10^{-3} \text{ used} = 5.0 \times 10^{-3} \text{ moles HF in excess}$$

$$\text{moles NaOH added} = \text{moles } \text{F}^- \text{ produced, so moles } \text{F}^- = 1.0 \times 10^{-3} \text{ moles}$$

$$[\text{HF}] = (5.0 \times 10^{-3} \text{ moles}) / (0.030 \text{ L} + 0.010 \text{ L}) = 0.125 \text{ M}$$

$$[\text{F}^-] = 1.0 \times 10^{-3} \text{ moles} / (0.030 \text{ L} + 0.010 \text{ L}) = 0.025 \text{ M}$$

$$\text{pH} = -\log(6.6 \times 10^{-4}) + \log(0.025/0.125) = 2.481 \rightarrow \mathbf{2.48}$$

c.) Calculate the pH of the solution at equivalence point.

$$6.0 \times 10^{-3} \text{ moles HF initial} = 6.0 \times 10^{-3} \text{ moles NaOH added} = 6.0 \times 10^{-3} \text{ moles } \text{F}^- \text{ present}$$

$$6.0 \times 10^{-3} \text{ moles NaOH} \times (1 \text{ L} / 0.10 \text{ moles NaOH}) = 0.06 \text{ L added to reach equiv.}$$

$$[\text{F}^-] = 6.0 \times 10^{-3} \text{ moles} / (0.06 \text{ L} + 0.030 \text{ L}) = 0.0666 \text{ M}$$

	$\text{F}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow$	$\text{HF}(\text{aq}) +$	$\text{OH}^-(\text{aq})$
I	0.066	0	0
C	-x	+x	+x
E	0.066 - x	x	x

$$K_b = (1.0 \times 10^{-14}) / (6.6 \times 10^{-4}) = 1.51 \times 10^{-11} = \frac{x^2}{0.066} \quad (\text{ignoring } -x \text{ term due to low \% ion})$$

$$x^2 = 1.0 \times 10^{-12} \rightarrow x = 1.0 \times 10^{-6} = [\text{OH}^-] \text{ so } \text{pOH} = -\log(1.0 \times 10^{-6}) = 6.00$$

$$\text{pH} = 14 - 6.00 = \mathbf{8.00}$$

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6.) Calculate the total change in entropy ( $\Delta S_{\text{total}}$ ) for 18.3 g of  $\text{H}_2\text{O(s)}$  (18.016 g/mol) at 273 K to melt in a container held at 315 K, given that the heat of fusion ( $\Delta H_{\text{fus}}$ ) for water is 6.02 kJ/mol at 0 K. Assume complete heat transfer from the ice to the surrounding air.

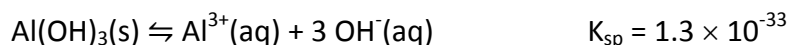
$$18.3 \text{ g ice} \times \frac{1 \text{ mole ice}}{18.016 \text{ g ice}} \times \frac{6.02 \text{ kJ}}{1 \text{ mole ice}} = 6.114 \text{ kJ absorbed by system, lost by surroundings}$$

$$\Delta S_{\text{sys}} = (6.114 \text{ kJ})/273 \text{ K} = 0.02239 \text{ kJ/K}$$

$$\Delta S_{\text{surr}} = (-6.114 \text{ kJ})/315 \text{ K} = -0.01941 \text{ kJ/K}$$

$$\Delta S_{\text{total}} = 0.02239 \text{ kJ/K} - 0.01941 \text{ kJ/K} = 2.977 \times 10^{-3} \text{ kJ/K} \times 1000 \text{ J/kJ} \rightarrow \mathbf{2.98 \text{ J/K}}$$

7.) Consider the following equilibrium:



A solution has  $[\text{Al}^{3+}] = 0.075 \text{ M}$  and  $[\text{HC}_2\text{H}_3\text{O}_2] = 1.00 \text{ M}$ . What is the maximum quantity, in g, of  $\text{NaC}_2\text{H}_3\text{O}_2$  (82.03 g/mol) that can be added to 250.0 mL of this solution before precipitation of  $\text{Al(OH)}_3(\text{s})$  begins?  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .

$$K_{\text{sp}} = 1.3 \times 10^{-33} = [\text{Al}^{3+}][\text{OH}^{-}]^3 = (0.075 \text{ M})(x)^3 \rightarrow x = 2.58 \times 10^{-11} = [\text{OH}^{-}]$$

$$\text{pOH} = -\log(2.58 \times 10^{-11}) = 10.587, \text{ so } \text{pH} = 14 - 10.587 = 3.412 \text{ at saturation}$$

$$3.412 = -\log(1.8 \times 10^{-5}) + \log(x/1.00)$$

$$-1.331 = \log(x/1.00)$$

$$10^{-1.331} = 0.0465 = x/1.00 \rightarrow x = 0.0465 = [\text{C}_2\text{H}_3\text{O}_2^{-}]$$

$$0.0465 \text{ moles } \text{C}_2\text{H}_3\text{O}_2^{-}/1 \text{ L} \times 0.2500 \text{ L solution} = 0.0116 \text{ moles } \text{C}_2\text{H}_3\text{O}_2^{-}$$

$$0.0116 \text{ moles } \text{C}_2\text{H}_3\text{O}_2^{2-} \times \frac{1 \text{ mole sodium acetate}}{1 \text{ mole acetate}} \times \frac{82.03 \text{ g}}{1 \text{ mole sodium acetate}} = 0.955$$

$$\rightarrow \mathbf{0.96 \text{ g NaC}_2\text{H}_3\text{O}_2}$$