

AP Unit 10: Manipulating K_{sp} 's when Adding Reactions and Finding pH for Amphoteric Acids

Find the K for the reaction of lead II chloride reacting with iodide ion, if the K_{sp} of PbI_2 is 1.4×10^{-8} and the K_{sp} of $PbCl_2$ is 1.6×10^{-5} .

Write the reaction: $PbCl_{2(s)} + 2 I^{-1}_{(aq)} \leftrightarrow PbI_{2(s)} + 2 Cl^{-1}_{(aq)}$

For PbI_2 : $PbI_{2(s)} \leftrightarrow Pb^{2+}_{(aq)} + 2 I^{-1}_{(aq)}$ $K_{sp} = 1.4 \times 10^{-8}$

$$K_{sp} = [Pb^{2+}]^1 [I^{-1}]^2$$

This reaction needs to be flipped for our overall reaction, so



The K of this reaction = $1 / [Pb^{2+}]^1 [I^{-1}]^2$, which equals $1 / K_{sp}$.
(The old products are now the reactants, so the K equation is upside down.)

****Reversing a reaction, equals 1 / K.****

For $PbCl_2$: $PbCl_{2(s)} \leftrightarrow Pb^{2+}_{(aq)} + 2 Cl^{-1}_{(aq)}$ $K_{sp} = 1.6 \times 10^{-5}$

Adding the reactions $PbCl_{2(s)} + 2 I^{-1}_{(aq)} \leftrightarrow PbI_{2(s)} + 2 Cl^{-1}_{(aq)}$
and canceling Pb^{2+}

$$\text{The K of this reaction is: } = \frac{[Cl^{-1}]^2}{[I^{-1}]^2}$$

****Adding the reactions, the K's are multiplied.****

$\frac{1}{K_{sp} \text{ of } PbI_2} \cdot K_{sp} \text{ of } PbCl_2 = \frac{1}{[Pb^{2+}] [I^{-1}]^2} \cdot [Pb^{2+}] [Cl^{-1}]^2 = \frac{[Cl^{-1}]^2}{[I^{-1}]^2}$ This equals the K of the above reaction.

$$\frac{1}{K_{sp} \text{ of } PbI_2} \cdot K_{sp} \text{ of } PbCl_2 = \frac{1}{1.4 \times 10^{-8}} \cdot 1.6 \times 10^{-5} = 1.1 \times 10^3$$

Finding pH for Amphiprotic Acids

Amphoteric substances can act as either Acids or Bases.

Examples are water

or polyprotic acids, which have lost a H^+ , but still have another H^+ , they can lose.

Ex.1) Find the pH of 0.100 M $NaHCO_3$.

For H_2CO_3 : $K_{a1} = 4.3 \times 10^{-7}$, $K_{a2} = 5.6 \times 10^{-11}$

For **amphiprotic** acids (acids that can act as either acids or bases):

pH = the average of the 2 pK_a values involved in the acid base reactions.

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

$$= \frac{(-\log 4.3 \times 10^{-7}) + (-\log 5.6 \times 10^{-11})}{2} \quad \text{Adding powers is like multiplying the numbers.}$$

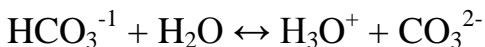
$$= \frac{-\log [(4.3 \times 10^{-7}) (5.6 \times 10^{-11})]}{2} \quad \frac{1}{2} \text{ of a power is the square root of the number.}$$

$$= -\log \sqrt{(4.3 \times 10^{-7}) (5.6 \times 10^{-11})} = \mathbf{8.31}$$

$$\text{so } pH = \frac{pK_{a1} + pK_{a2}}{2} = -\log \sqrt{K_{a1} \cdot K_{a2}}$$

Proof (There are different ways to derive these equations. If you look in other sources, you will find other ways to get to the same place.):

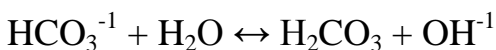
As an Acid:



$$K_{a2} = 5.6 \times 10^{-11} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^{-1}]}$$

$$[HCO_3^{-1}] = \frac{[H_3O^+][CO_3^{2-}]}{5.6 \times 10^{-11}}$$

As a Base:



Since $K_a \times K_b = K_w$, so $K_b = K_w / K_{a1}$ (K_{a1} of H_2CO_3)

$$K_b = \frac{1 \times 10^{-14}}{4.3 \times 10^{-7}} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^{-1}]}{[\text{HCO}_3^{-1}]} \quad \text{Substitute in } \text{HCO}_3^{-1} \text{ from the acid reaction.}$$

$$K_b = \frac{1 \times 10^{-14}}{4.3 \times 10^{-7}} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^{-1}]}{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}] / 5.6 \times 10^{-11}}$$

$$\frac{1 \times 10^{-14}}{4.3 \times 10^{-7}} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^{-1}](5.6 \times 10^{-11})}{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]} \quad \text{Solve for } \text{H}_3\text{O}^+.$$

$$[\text{H}_3\text{O}^+] = \frac{[\text{H}_2\text{CO}_3][\text{OH}^{-1}](5.6 \times 10^{-11})(4.3 \times 10^{-7})}{[\text{CO}_3^{2-}](1 \times 10^{-14})}$$

$$K_w = 1 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^{-1}]$$

$$\frac{1}{[\text{H}_3\text{O}^+]} = \frac{[\text{OH}^{-1}]}{(1 \times 10^{-14})} \quad \text{Substitute } 1/\text{H}_3\text{O}^+ \text{ for } \text{OH}^{-1}/K_w$$

$$[\text{H}_3\text{O}^+] = \frac{[\text{H}_2\text{CO}_3] \cdot 1}{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]} (5.6 \times 10^{-11})(4.3 \times 10^{-7})$$

$$[\text{H}_3\text{O}^+]^2 = \frac{[\text{H}_2\text{CO}_3](5.6 \times 10^{-11})(4.3 \times 10^{-7})}{[\text{CO}_3^{2-}]}$$

**If $[\text{HCO}_3^{-1}]$ is larger than K_{a1} and $[\text{HCO}_3^{-1}] \cdot K_{a2}$ is larger than K_w , then $[\text{H}_2\text{CO}_3]$ and $[\text{CO}_3^{2-}]$ are assumed to have similar concentrations, so they can be cancelled out. This generally works for concentrations of 1 M or 0.1 M for the original amphiprotic acid, but then as the concentration decreases, the calculated pH starts to vary from the experimental pH and this assumption no longer works!

So then, $[\text{H}_3\text{O}^+]^2 = (5.6 \times 10^{-11})(4.3 \times 10^{-7})$

$$[\text{H}_3\text{O}^+] = \sqrt{(5.6 \times 10^{-11})(4.3 \times 10^{-7})}$$

$$-\log [\text{H}_3\text{O}^+] = -\log \sqrt{(5.6 \times 10^{-11})(4.3 \times 10^{-7})}$$

$$\text{pH} = -\log \sqrt{K_{a1} \cdot K_{a2}}$$

End of Notes