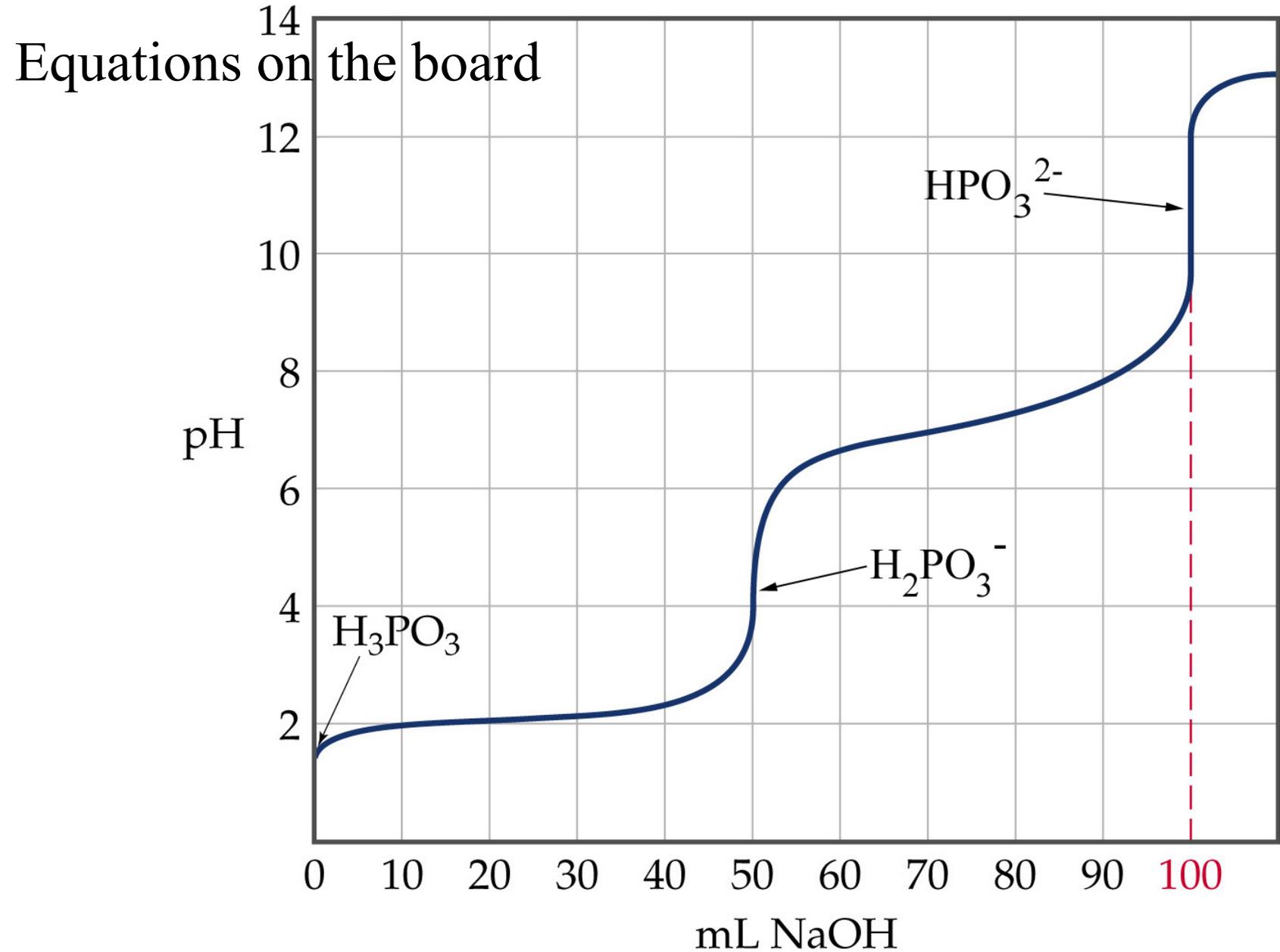


## Titration of Polyprotic Acids

- In polyprotic acids, each ionizable proton dissociates in steps.
- Therefore, in a titration there are  $n$  equivalence points corresponding to each ionizable proton.
- In the titration of  $\text{H}_3\text{PO}_3$  with  $\text{NaOH}$ .
  - The first proton dissociates to form  $\text{H}_2\text{PO}_3^-$ .
  - Then the second proton dissociates to form  $\text{HPO}_3^{2-}$ .

Titration of 50.0 mL of 0.10 - M  
phosphorous acid with 0.10 - M NaOH



# Solubility Equilibria

## The Solubility-Product Constant, $K_{sp}$

- Consider



- for which

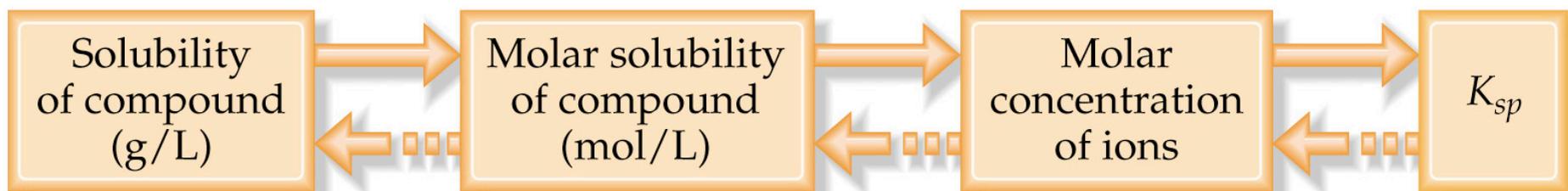
$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

- $K_{sp}$  is the solubility product. ( $\text{BaSO}_4$  is ignored because it is a pure solid so its concentration is constant.)

- In general: the solubility product is the molar concentration of ions raised to their stoichiometric powers.
- Solubility is the amount (grams) of substance that dissolves to form a saturated solution.
- Molar solubility is the number of moles of solute dissolving to form a liter of saturated solution.

## Solubility and $K_{sp}$

- To convert solubility to  $K_{sp}$
- solubility needs to be converted into molar solubility (via molar mass);
- molar solubility is converted into the molar concentration of ions at equilibrium (equilibrium calculation),
- $K_{sp}$  is the product of equilibrium concentration of ions.



## Examples

1. The solubility of calcium carbonate in water at 25°C is  $6.7 \times 10^{-3}$  g/L. Calculate the molar solubility and  $K_{sp}$ .
2. The solubility of manganese (II) hydroxide in water at 25°C is  $3.42 \times 10^{-5}$  mol/L. Calculate the solubility in g/L and calculate  $K_{sp}$ .
3.  $K_{sp}$  for  $PbF_2$  at 25°C is  $3.6 \times 10^{-8}$ . Calculate the molar solubility and the solubility in g/L.
4.  $K_{sp}$  for  $Ca_3(PO_4)_2$  is  $2.0 \times 10^{-29}$ . Calculate the molar solubility and the solubility in g/L.

## Examples

1. The solubility of calcium carbonate in water at 25°C is  $6.7 \times 10^{-3}$  g/L. Calculate the molar solubility and  $K_{sp}$ .

$$6.7 \times 10^{-5} \text{ M}, K = 4.5 \times 10^{-9}$$

2. The solubility of manganese (II) hydroxide in water at 25°C is  $3.42 \times 10^{-5}$  mol/L. Calculate the solubility in g/L and calculate  $K_{sp}$ .

$$K = 1.6 \times 10^{-13}, 3.0 \times 10^{-3} \text{ g/L}$$

# Factors that Affect Solubility

## The Common Ion Effect

- Solubility is decreased when a common ion is added.
- This is an application of Le Châtelier's principle:



- as  $\text{F}^{-}$  (from NaF, say) is added, the equilibrium shifts away from the increase.
- Therefore,  $\text{CaF}_2(s)$  is formed and precipitation occurs.
- As NaF is added to the system, the solubility of  $\text{CaF}_2$  decreases.

## Examples

1. Calculate the solubility of  $\text{Ag}_2\text{SO}_4$  ( $K_{\text{sp}} = 1.5 \times 10^{-5}$ )
  - a. In water
  - b. In 0.25 M  $\text{AgNO}_3$  solution
  - c. In 0.20 M  $\text{K}_2\text{SO}_4$  solution

## Examples

1. Calculate the molar solubility of  $\text{Ag}_2\text{SO}_4$  ( $K_{\text{sp}} = 1.5 \times 10^{-5}$ )
- In water 0.016 M
  - In 0.25 M  $\text{AgNO}_3$  solution  $2.4 \times 10^{-4}$  M
  - In 0.20 M  $\text{K}_2\text{SO}_4$  solution  $4.3 \times 10^{-3}$  M



## Solubility and pH

- Again we apply Le Châtelier's principle:



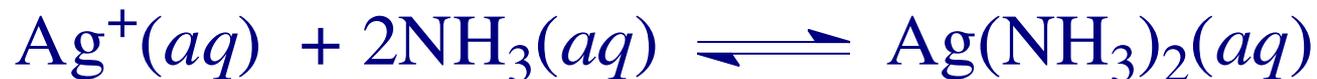
- If the  $\text{F}^{-}$  is removed, then the equilibrium shifts towards the decrease and  $\text{CaF}_2$  dissolves.
- $\text{F}^{-}$  can be removed by adding a strong acid:



- As pH decreases,  $[\text{H}^{+}]$  increases and solubility increases.
- The effect of pH on solubility is dramatic.
  - Acidic salts are more soluble in basic solution and less soluble in acidic solution
  - Basic salts are more soluble in acidic solution and less soluble in basic solution.

## Formation of Complex Ions

- Consider the formation of  $\text{Ag}(\text{NH}_3)_2^+$ :



- The  $\text{Ag}(\text{NH}_3)_2^+$  is called a complex ion.
- $\text{NH}_3$  (the attached Lewis base) is called a ligand.
- The equilibrium constant for the reaction is called the formation constant,  $K_f$ :

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2]}{[\text{Ag}^+][\text{NH}_3]^2}$$

## Formation of Complex Ions

- Consider the addition of ammonia to AgCl (white precipitate):



- The overall reaction is



- Effectively, the  $\text{Ag}^+(aq)$  has been removed from solution.
- By Le Châtelier's principle, the forward reaction (the dissolving of AgCl) is favored.