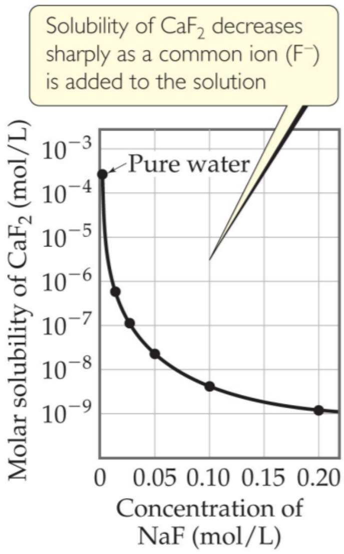
7.沉淀-溶解平衡与沉淀滴定Precipitation-Dissolution Equilibrium and Precipitation Titration

- 沉淀溶解平衡Precipitation-Dissolution Equilibrium
  - Solubility Equilibria 溶解度平衡
    - 因为离子化合物是强电解质，它们完全解离到溶解的程度Because ionic compounds are strong electrolytes, they dissociate completely to the extent that they dissolve.
    - 当写平衡方程时，固体是反应物，溶液中的离子是生成物When an equilibrium equation is written, the solid is the reactant and the ions in solution are the products.
    - KSP
      - 平衡常数表达式称为溶度积常数，用Ksp表示The equilibrium constant expression is called the **solubility-product constant**. It is represented as Ksp

        $$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

      - Ksp和溶解度不一样Ksp is not the same as solubility.
        - 溶解度是物质溶解形成饱和溶液的量Solubility is the quantity of a substance that dissolves to form a saturated solution
        - 溶解度常用单位Common units for solubility
          - Grams per liter (g/L)
          - Moles per liter (mol/L)
- 影响溶解度的因素Factors Affecting Solubility
  - 同离子效应The Common-Ion Effect
    - 如果溶液平衡中的一个离子已经溶解在溶液中，盐的溶解度就会降低If one of the ions in a solution equilibrium is already dissolved in the solution, the solubility of the salt will decrease.
    - 如果存在钙离子或氟离子，那么氟化钙的可溶性就会降低If either calcium ions or fluoride ions are present, then calcium fluoride will be less soluble



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$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Example: adding sulfuric硫磺的 acid $H_2SO_{4\,(aq)}$ to a solution of barium sulfate 硫酸钡, will increase the concentration of $SO_4^{\ 2-}$ ions. The equilibrium above shifts left to remove the excess sulfate and $BaSO_4$ precipitates out沉淀.

Notice: as concentrated acid H_2SO_4 is added, white $BaSO_4$ precipitates 沉淀

$BaSO_4$ (s) ← Ba^{2+} + SO_4^{2-}

- pH
  - 如果一种物质有碱性阴离子，它在酸性溶液中更容易溶解If a substance has a basic anion, it will be more soluble in an acidic solution.
    - 阳离子kation 阴离子anion
  - 记住，缓冲液控制ph值，当使用缓冲液时，氢氧根离子的浓度没有变化Remember that buffers control pH. When a buffer is used, there is no change in concentration of hydroxide ion!
- 形成络离子Complex Ion Formation
  - 金属离子可作为路易斯酸，在溶剂中与路易斯碱形成络合离子Metal ions can act as Lewis acids and form complex ions with Lewis bases in the solvent.
  - 这些络合离子的形成增加了这些盐的溶解度The formation of these complex ions increases the solubility of these salts.

Table 17.1 Formation Constants for Some Metal Complex Ions in Water at 25 °C

Complex Ion	K_f	Equilibrium Equation
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+\,(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-\,(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2\,S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}\,(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4^{2-}\,(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4\,OH^-(aq) \rightleftharpoons Cr(OH)_4^-\,(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4\,SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}\,(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4\,NH_3\,(aq) \rightleftharpoons Cu(NH_3)_4^{2+}\,(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}\,(aq) + 4\,CN^-(aq) \rightleftharpoons Cu(CN)_4^{2+}\,(aq)$
$Ni(NH_3)_6^{2+}$	1.2×10^9	$Ni^{2+}\,(aq) + 6\,NH_3\,(aq) \rightleftharpoons Ni(NH_3)_6^{2+}\,(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}\,(aq) + 6\,CN^-\,(aq) \rightleftharpoons Fe(CN_3)_6^{4-}\,(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^{3+}\,(aq) + 6\,CN^-\,(aq) \rightleftharpoons Fe(CN)_6^{3-}\,(aq)$

- e.g.
  - 氯化银是不溶的，它的Ksp为1.6 × 10^ -10Silver chloride is insoluble. It has a Ksp of 1.6 × 10^−10
  - 在NH3存在下，银离子与NH3形成络合离子，溶解度大大提高In the presence of NH3, the solubility greatly increases because Ag+ will form complex ions with NH3
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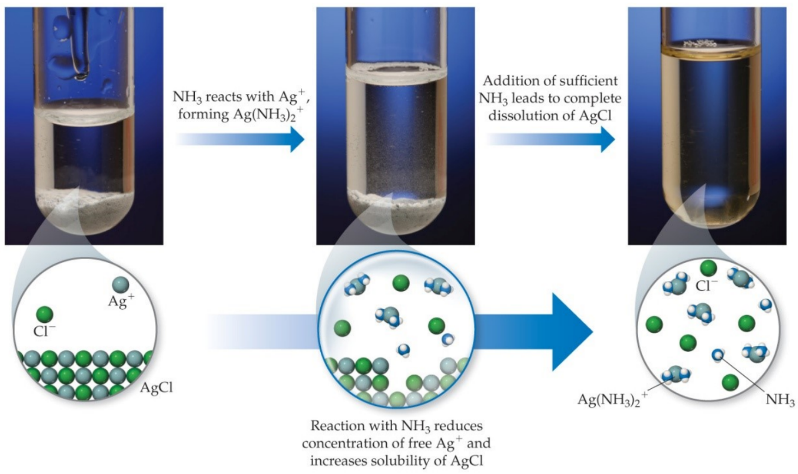

- 沉淀滴定Precipitation Titrations
  - 分析物和滴定剂形成不溶性沉淀物的反应也可以作为滴定的基础
  - A reaction in which the analyte被分析物 and titrant滴定液 form an insoluble precipitate also can serve as the basis for a titration.
  - 计算滴定曲线

1.Calculating the precipitation Titration Curve

Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Because the reaction's equilibrium constant is so large,

$$K = (K_{sp})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9$$

we may assume that Ag^+ and Cl^- react completely.

Step 1: Calculate the volume of Ag^+ needed to reach the equivalence point;

$$\text{mol } Ag^+ = M_{Ag}V_{Ag} = M_{Cl}V_{Cl} = \text{mol } Cl^-$$

Solving for the volume of Ag^+

$$V_{eq} = V_{Ag} = \frac{M_{Cl}V_{Cl}}{M_{Ag}} = \frac{(0.0500\text{ M})(50.0\text{ mL})}{0.100\text{ M}} = 25.0\text{ mL}$$

Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Step 2: Before the equivalence point the titrand到达滴定点前, Cl^-, is in excess. The concentration of unreacted Cl^- after we add 10.0 mL of Ag^+,

$$[Cl^-] = \frac{(\text{mol } Cl^-)_{initial} - (\text{mol } Ag^+)_{added}}{\text{total volume}} = \frac{M_{Cl}V_{Cl} - M_{Ag}V_{Ag}}{V_{Cl} + V_{Ag}}$$

$$[Cl^-] = \frac{(0.0500\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 2.50 \times 10^{-2}\text{ M}$$

$$pCl = 1.60$$

Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Step 3: At the titration's equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal;

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = 1.8 \times 10^{-10}$$

$$x = [Cl^-] = 1.3 \times 10^{-5}\text{ M}$$

$$pCl = 4.89$$

Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Step 4: After the equivalence point, the titrant is in excess. We first calculate the concentration of excess Ag^+ and then use the K_{sp} expression to calculate the concentration of Cl^-; For example, after adding 35.0 mL of titrant- $AgNO_3$

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$$[Ag^+] = \frac{(\text{mol } Ag^+)_{added} - (\text{mol } Cl^-)_{initial}}{\text{total volume}} = \frac{M_{Ag}V_{Ag} - M_{Cl}V_{Cl}}{V_{Ag} + V_{Cl}}$$

$$[Ag^+] = \frac{(0.100\text{ M})(35.0\text{ mL}) - (0.0500\text{ M})(50.0\text{ mL})}{35.0\text{ mL} + 50.0\text{ mL}} = 1.18 \times 10^{-2}\text{ M}$$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8}\text{M}$$

$$pCl = 7.81$$

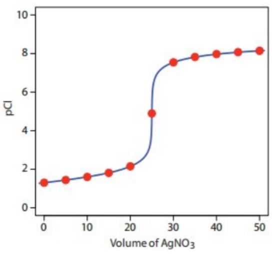
Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

Volume of $AgNO_3$ (mL)	pCl	Volume of $AgNO_3$ (mL)	pCl
0.00	1.30	30.0	7.54
5.00	1.44	35.0	7.82
10.0	1.60	40.0	7.97
15.0	1.81	45.0	8.07
20.0	2.15	50.0	8.14
25.0	4.89		

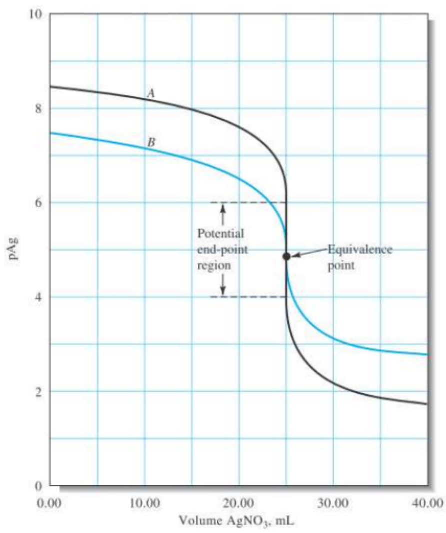
The **red** points corresponds to the data in Table. The **blue** line shows the complete titration curve.



- 稀释对滴定曲线的影响Diluting effect of the titration curves

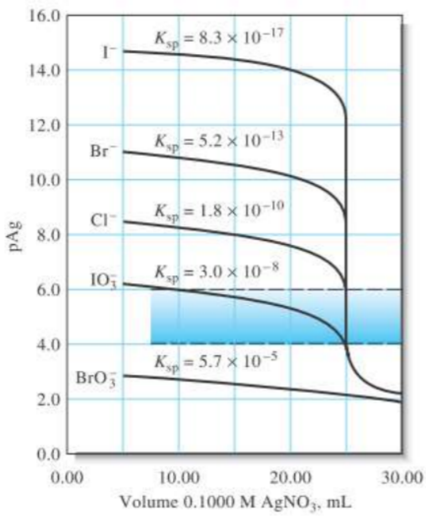
Titration curve for (A), 50.00 mL of 0.05000 M NaCl titrated with 0.1000 M $AgNO_3$ and (B), 50.00 mL of 0.00500 M NaCl titrated with 0.01000 M $AgNO_3$.

Note the increased sharpness of the break at the end point with the more concentrated solution.



- Ksp对滴定曲线的影响Ksp effect of the titration curves

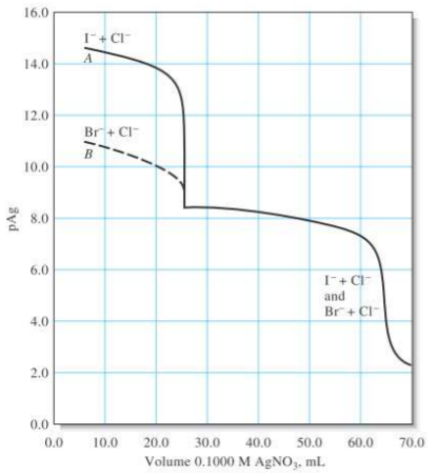
50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M $AgNO_3$.



- 滴定混合物Titration of a mixture

Titration curves for 50.00 mL of a solution **0.0800 M in Cl^-** and **0.0500 M in I^- or Br^-**.

K_{sp} for
AgCl = 1.82×10^{-10}
AgBr = 5.0×10^{-13}
AgI = 8.0×10^{-17}



Example 17-2A Titration of a mixture

A 25.00 mL solution containing Br^- and Cl^- was titrated with 0.03333 M $AgNO_3$. $K_{sp}(AgBr)=5.0 \times 10^{-13}$, $K_{sp}(AgCl)=1.82 \times 10^{-10}$.

(a) Which analyte is precipitated first?

(b) The first end point was observed at 15.55 mL. Find the concentration of the first that precipitated (Br^- or Cl^-?).

(c) The second end point was observed at 42.23 mL. Find the concentration of the second that precipitated (Br^- or Cl^-?).

Solution

(a)

$Ag^+_{(aq)} + Br^-_{(aq)} \leftrightarrows AgBr_{(s)}$ $K_f = 1/K_{sp}(AgBr) = 2 \times 10^{12}$

$Ag^+_{(aq)} + Cl^-_{(aq)} \leftrightarrows AgCl_{(s)}$ $K_f = 1/K_{sp}(AgCl) = 5.6 \times 10^{9}$

AgBr precipitated first

(b)

$$\frac{15.55\,\text{mL}\,Ag^+}{1} \times \frac{1\,\text{L}\,Ag^+}{1000\,\text{mL}\,Ag^+} \times \frac{0.03333\,\text{mol}\,Ag^+}{1\,\text{L}\,Ag^+} \times \frac{1\,\text{mol}\,Br^-}{1\,\text{mol}\,Ag^+} \times \frac{1}{25\,\text{mL}} \times \frac{1000\,\text{mL}}{1\,\text{L}} = 0.02073\,\text{M}\,Br^-$$

(c)

$$\frac{(42.23-15.55)\,\text{mL}\,Ag^+}{1} \times \frac{1\,\text{L}\,Ag^+}{1000\,\text{mL}\,Ag^+} \times \frac{0.03333\,\text{mol}\,Ag^+}{1\,\text{L}\,Ag^+} \times \frac{1\,\text{mol}\,Cl^-}{1\,\text{mol}\,Ag^+} \times \frac{1}{25\,\text{mL}} \times \frac{1000\,\text{mL}}{1\,\text{L}} = 0.03557\,\text{M}\,Cl^-$$