Ministry of Higher Education
and Scientific Research
Alrasheed college university
Pharmacy department

Lecture (5)

- Gravimetric Analysis
- The Solubility of Precipitates
- Common Ion Effect on Solubility

Gravimetric Analysis

Gravimetric analysis is a method whereby analytes or solutes are converted to insoluble species (precipitates).These precipitates are separated, dried and finally weighed. From the weight and chemical content, the weight of analyte in the sample can be calculated.

✓ Properties of precipitates and precipitating reagents

The precipitating agent must be:

1-React **specifically** or, if not that, at least **selectively** with the analyte.

Specific reagents (react only with a single chemical species).

Selective reagents (react with limited number of species).

2. React with the analyte and give a product that is:

- ✓ Readily filtered and washed free of contaminants.
- ✓ Of low solubility so that no significant loss of the solid occurs during filtration and washing.
- ✓ Unreactive with constituents of atmosphere.
- ✓ Of known composition after it is dried or ignited.

➢ Calculations in Gravimetric Analysis:

The results of a gravimetric analysis are generally computed from two experimental measurements, the weight of sample and the weight of a product of known composition.

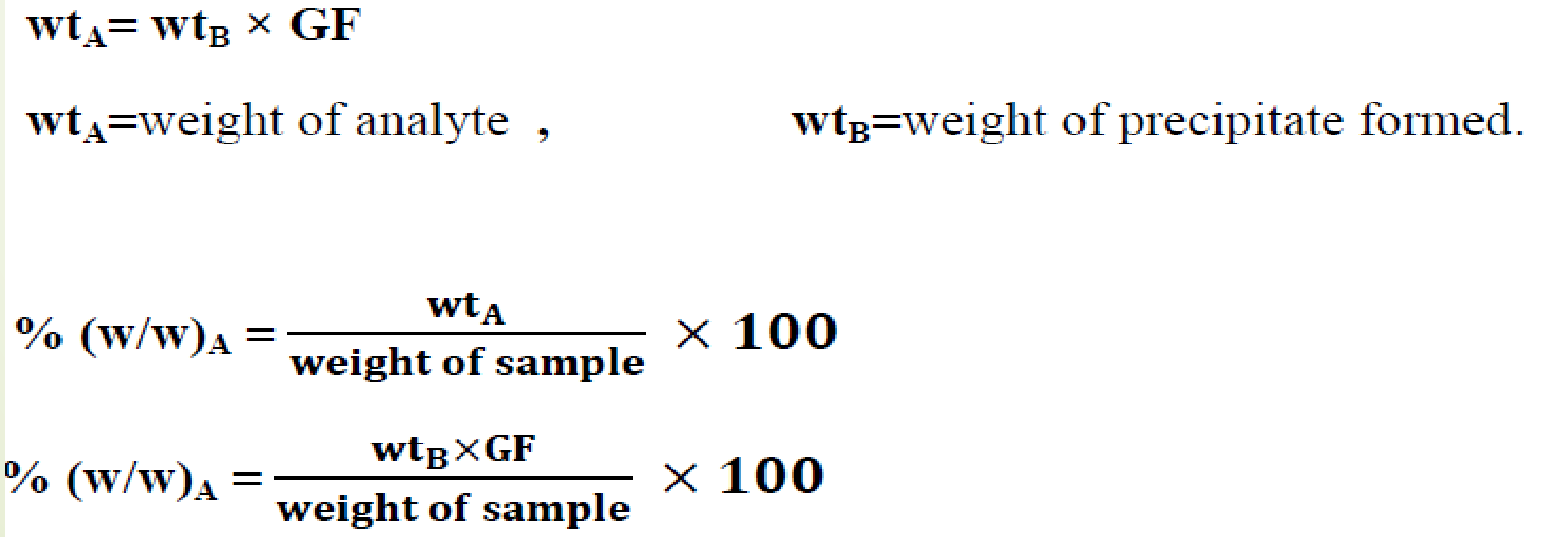
Calculation of the percentage of analyte (A) in the sample using gravimetric analysis is based on :

$$\boxed{\%\,(\mathrm{w/w})_A = \frac{\text{weight of analyte (g)}}{\text{weight of sample (g)}} \times 100}$$

The weight of analyte obtains by multiplying the weight of precipitate formed by a constant. This constant is called the gravimetric factor (GF).

$$\mathbf{GF} = \frac{a \times \text{M.mass of substance analyzed (A)}}{b \times \text{M.mass of precipitate (B)}}$$

Where a and b are small whole numbers that have values such that the number of molecular weights in the numerator and denominator are chemically equivalent.



$$wt_A = wt_B \times GF$$

wt_A=weight of analyte , wt_B=weight of precipitate formed.

$$\%\ (w/w)_A = \frac{wt_A}{\text{weight of sample}} \times 100$$

$$\%\ (w/w)_A = \frac{wt_B \times GF}{\text{weight of sample}} \times 100$$

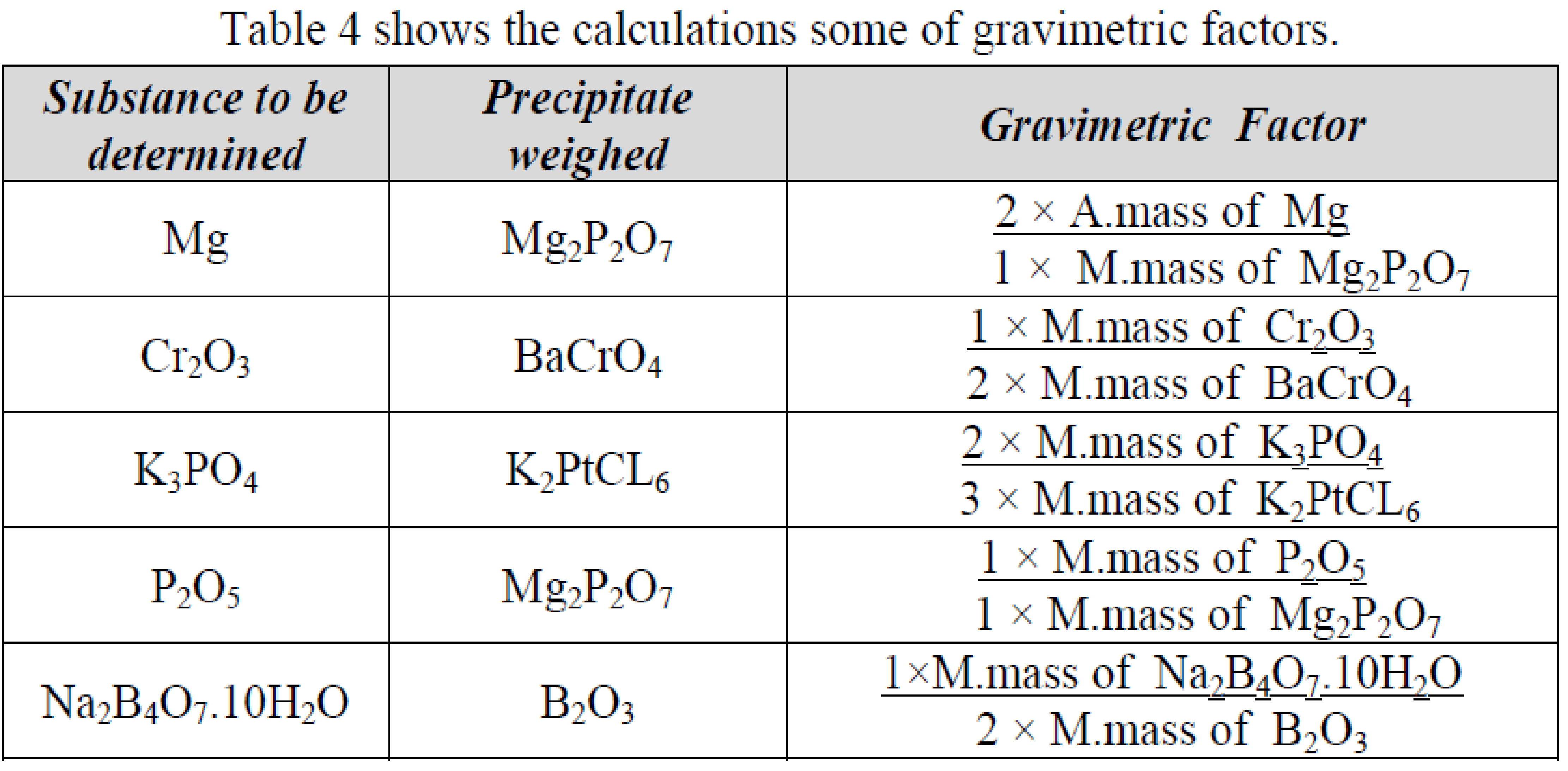


Table 4 shows the calculations some of gravimetric factors.

Substance to be determined	***Precipitate weighed***	***Gravimetric Factor***
Mg	$Mg_2P_2O_7$	$\frac{2 \times \text{A.mass of Mg}}{1 \times \text{M.mass of } Mg_2P_2O_7}$
Cr_2O_3	$BaCrO_4$	$\frac{1 \times \text{M.mass of } Cr_2O_3}{2 \times \text{M.mass of } BaCrO_4}$
K_3PO_4	K_2PtCL_6	$\frac{2 \times \text{M.mass of } K_3PO_4}{3 \times \text{M.mass of } K_2PtCL_6}$
P_2O_5	$Mg_2P_2O_7$	$\frac{1 \times \text{M.mass of } P_2O_5}{1 \times \text{M.mass of } Mg_2P_2O_7}$
$Na_2B_4O_7.10H_2O$	B_2O_3	$\frac{1 \times \text{M.mass of } Na_2B_4O_7.10H_2O}{2 \times \text{M.mass of } B_2O_3}$

Example 1:-

A sample of ore weighing 1.2504 g contains sulphur is treated with HNO_3 and $KClO_3$ to convert sulphur to $BaSO_4$.After treating with HCl, chlorate and nitrate are removed and $BaSO_4$ is precipitated, weighing 0.5473 g. Calculate the percentage of sulphur in the sample (A.wt of S=32.064 and M.wt of $BaSO_4$= 233.40 g mol^{-1}).

Solution:

$S \longrightarrow BaSO_4\downarrow$

1 mol of S is equivalent to 1 mol of $SO_4^{=}$ as $BaSO_4$

$$GF= \frac{1\ \text{mol} \times \text{A.mass S}}{1\ \text{mol} \times \text{M.mass } BaSO_4} = \frac{1\ \text{mol} \times 32.064\ \text{g/mol}}{1\text{mol}\times 233.4\ \ \text{g/mol}} = 0.1374\ \frac{g\ S}{g\ BaSO_4}$$

$wt_A = wt_B \times GF$

$\text{wt S} = \text{wt } BaSO_4 \times GF$

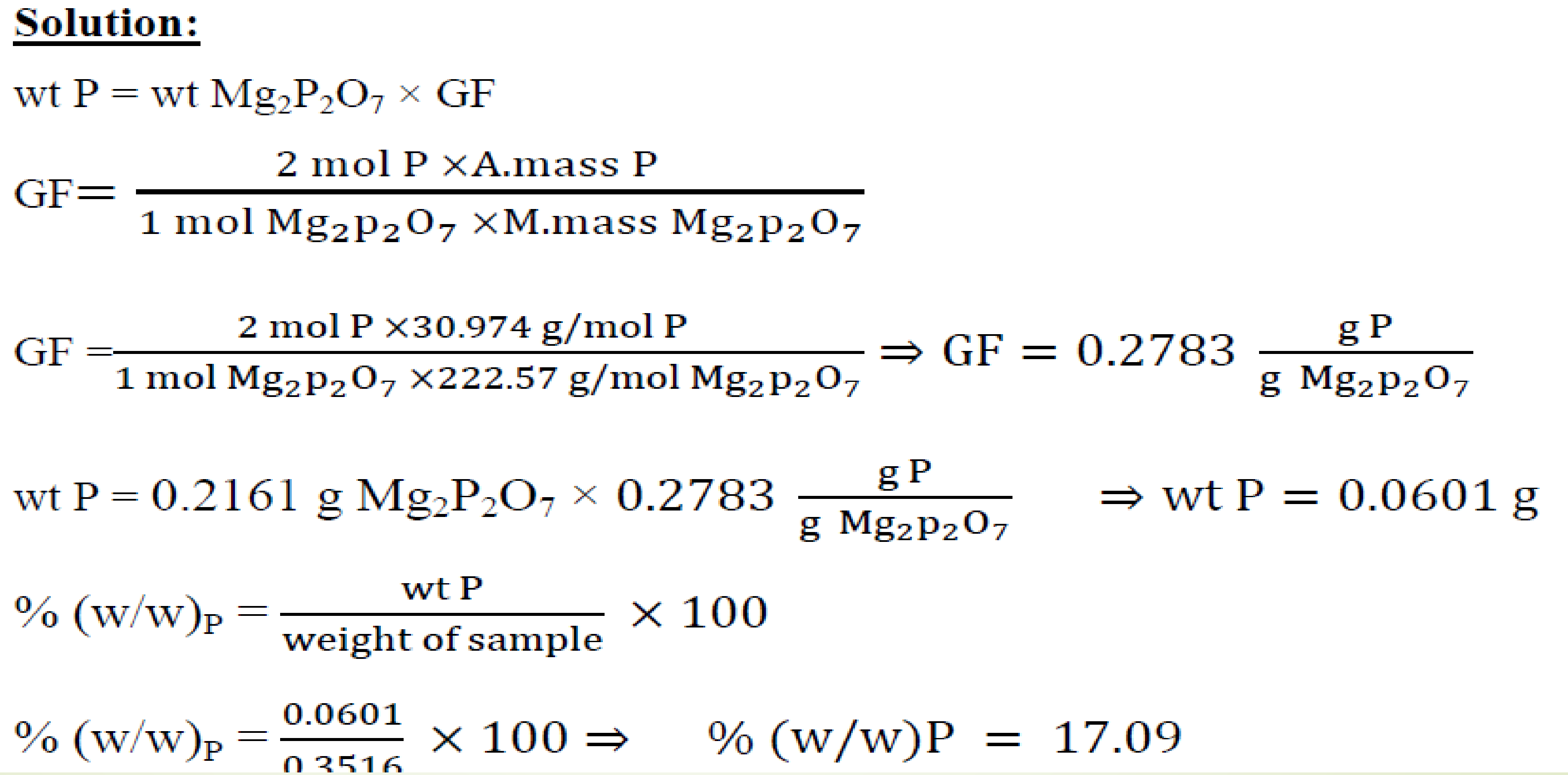
$$\text{wt S} = 0.5473\ \text{g } BaSO_4 \times 0.1374\ \frac{\text{g S}}{\text{g } BaSO_4} \Rightarrow 0.0752\ \text{g}$$

$$\%\,(w/w)_S = \frac{\text{wt S}}{\text{weight of sample}} \times 100$$

$$\%\,(w/w)_S = \frac{0.0752\ \text{g}}{1.2504\ \ \text{g}} \times 100 \Rightarrow \qquad \%\,(w/w)_S = 6.010\%$$

Example 2:-

A 0.3516 g sample of a commercial phosphate detergent was ignited at a red heat to destroy the organic matter. The residue was then taken up in hot HCl, which converted the P to phosphoric acid. The phosphate was precipitated by addition of Mg^{2+} followed by aqueous NH_3.After being filtered and washed, the precipitate was converted to $Mg_2P_2O_7$ (222.57 g/mol) by ignition at 1000°C. This residue weighed 0.2161g. Calculate the percent P (30.974 g/mol)in the sample.



Solution:

$$\text{wt P} = \text{wt } Mg_2P_2O_7 \times GF$$

$$GF = \frac{2 \text{ mol P} \times \text{A.mass P}}{1 \text{ mol } Mg_2p_2O_7 \times \text{M.mass } Mg_2p_2O_7}$$

$$GF = \frac{2 \text{ mol P} \times 30.974 \text{ g/mol P}}{1 \text{ mol } Mg_2p_2O_7 \times 222.57 \text{ g/mol } Mg_2p_2O_7} \Rightarrow GF = 0.2783 \ \frac{\text{g P}}{\text{g } Mg_2p_2O_7}$$

$$\text{wt P} = 0.2161 \text{ g } Mg_2P_2O_7 \times 0.2783 \ \frac{\text{g P}}{\text{g } Mg_2p_2O_7} \quad \Rightarrow \text{wt P} = 0.0601 \text{ g}$$

$$\% \, (w/w)_P = \frac{\text{wt P}}{\text{weight of sample}} \times 100$$

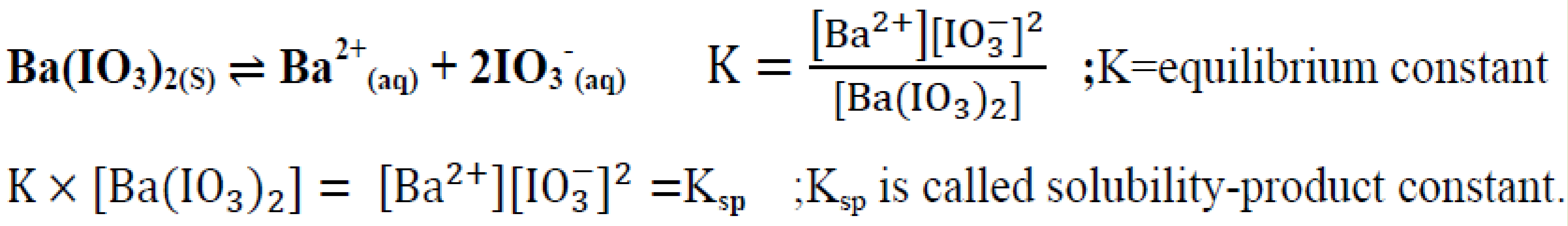
$$\% \, (w/w)_P = \frac{0.0601}{0.3516} \times 100 \Rightarrow \quad \% \, (w/w)P = 17.09$$

The Solubility of Precipitates

The ultimate accuracy of a gravimetric analysis may be limited by the losses of precipitate due to its solubility in the reaction medium and in the wash liquid employed for purification.

✓ **The common variables that influence the solubility of precipitate**

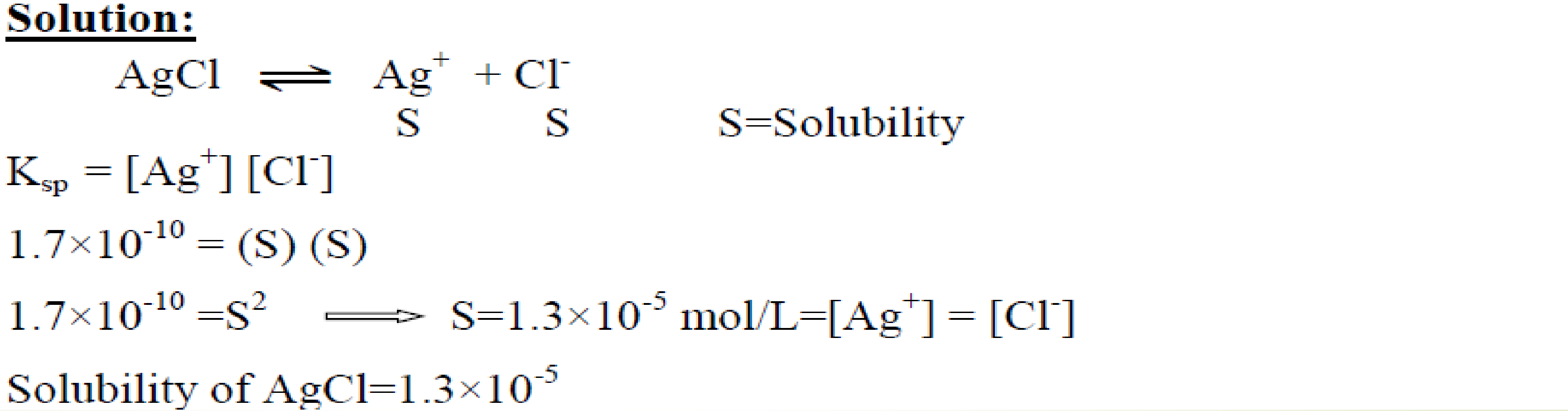
1. Temperature
2. pH
3. Reagent concentration
4. Salt concentration
5. Solvent concentration.



$\mathbf{Ba(IO_3)_{2(S)} \rightleftharpoons Ba^{2+}_{(aq)} + 2IO_3^{-}{}_{(aq)}}$ $K = \frac{[Ba^{2+}][IO_3^-]^2}{[Ba(IO_3)_2]}$;K=equilibrium constant

$K \times [Ba(IO_3)_2] = [Ba^{2+}][IO_3^-]^2 = K_{sp}$;K_{sp} is called solubility-product constant.

Example 3:- Calculate the concentration of Ag^+ and Cl^- and the solubility of AgCl if K_{sp} of AgCl is 1.7×10^{-10} mol^2/L^2.



Solution:

$$AgCl \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{Cl^-}$$

S=Solubility

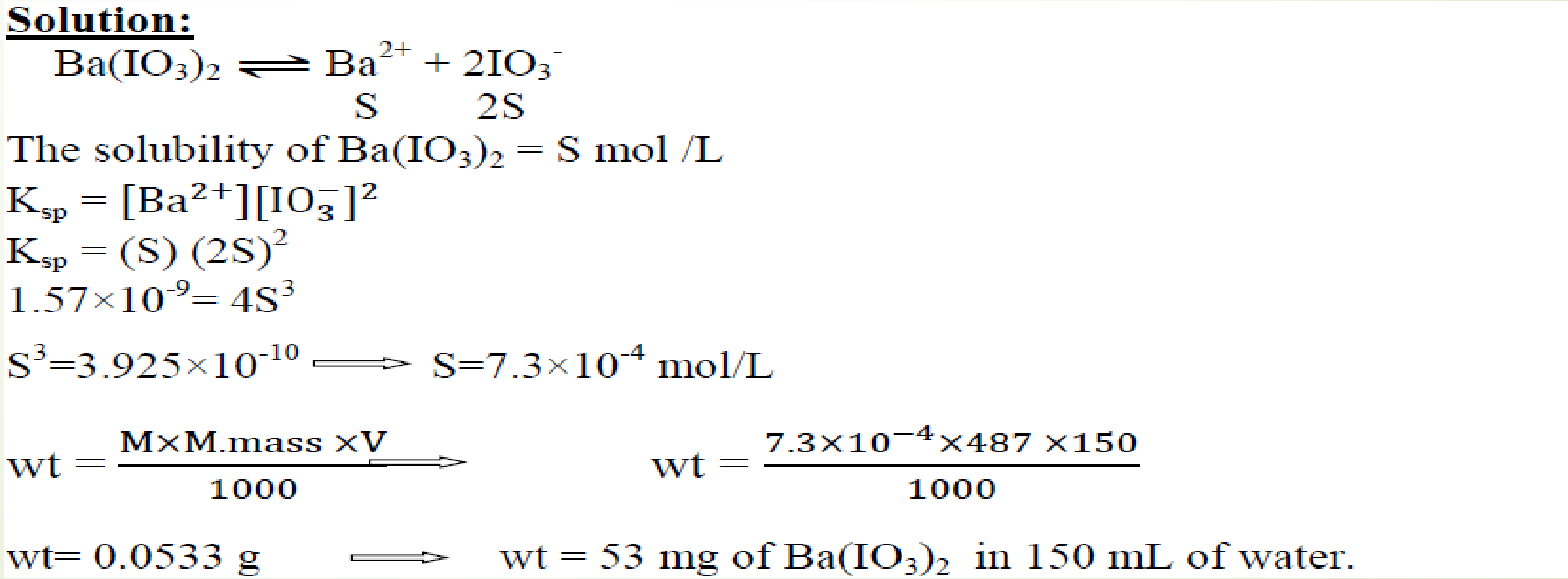
$K_{sp} = [Ag^+]\,[Cl^-]$

$1.7\times10^{-10} = (S)\,(S)$

$1.7\times10^{-10} = S^2 \Longrightarrow S=1.3\times10^{-5}\ mol/L=[Ag^+] = [Cl^-]$

Solubility of AgCl=1.3×10^{-5}

Example 4:- How many milligrams of $Ba(IO_3)_2$ (487 g /mol) can be dissolved in 150 mL of water at 25˚C. $K_{sp}=1.57\times10^{-9}\ mol^3/L^3$.



Solution:

$$Ba(IO_3)_2 \rightleftharpoons \underset{S}{Ba^{2+}} + \underset{2S}{2IO_3^-}$$

The solubility of $Ba(IO_3)_2$ = S mol /L

$K_{sp} = [Ba^{2+}][IO_3^-]^2$

$K_{sp} = (S)\,(2S)^2$

$1.57\times10^{-9}= 4S^3$

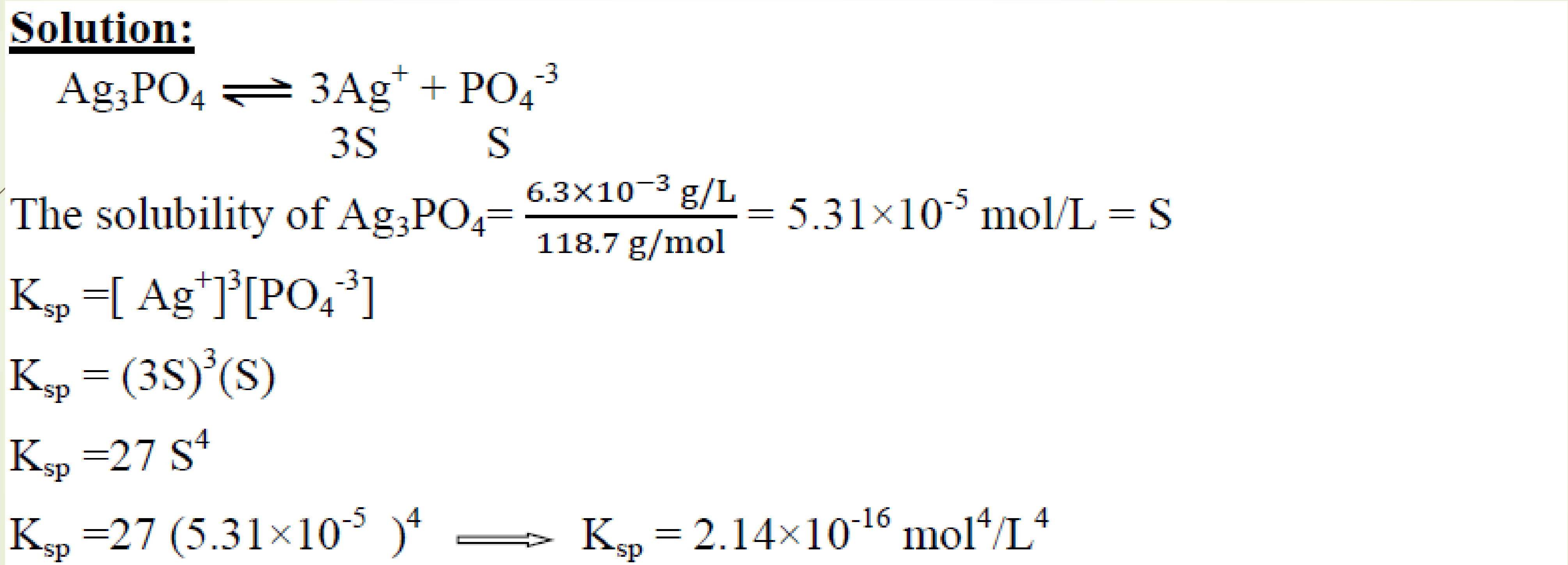
$S^3=3.925\times10^{-10} \Longrightarrow S=7.3\times10^{-4}\ mol/L$

$$wt = \frac{M\times M.mass\times V}{1000} \Longrightarrow wt = \frac{7.3\times10^{-4}\times487\times150}{1000}$$

wt= 0.0533 g $\Longrightarrow$ wt = 53 mg of $Ba(IO_3)_2$ in 150 mL of water.

Example 5:-

The solubility of Ag_3PO_4=6.3×10^{-3} g/L. Calculate the K_{sp} of Ag_3PO_4 (M.wt=118.7 g/mol).



Solution:

$$\underset{}{Ag_3PO_4} \rightleftharpoons \underset{3S}{3Ag^+} + \underset{S}{PO_4^{-3}}$$

The solubility of Ag_3PO_4= $\frac{6.3\times10^{-3}\ g/L}{118.7\ g/mol}$ = 5.31×10^{-5} mol/L = S

K_{sp} =[$Ag^+]^3[PO_4^{-3}]$

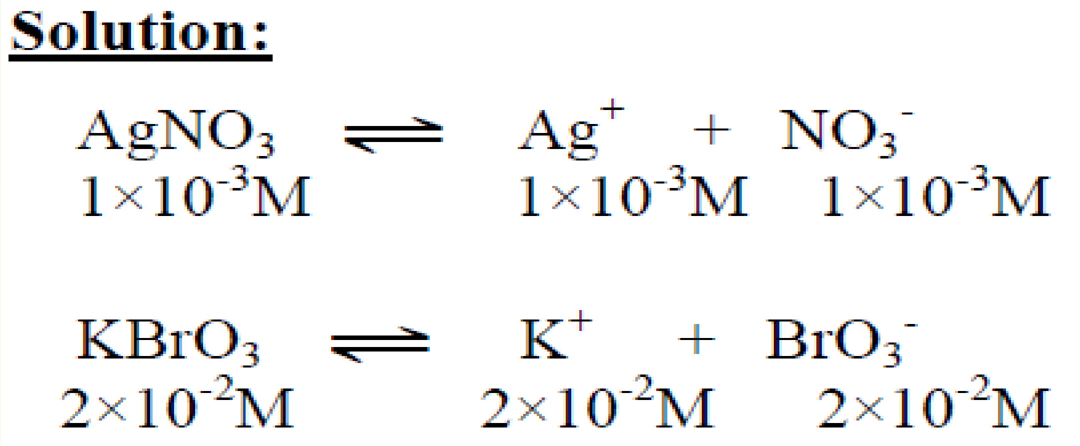
K_{sp} = $(3S)^3(S)$

K_{sp} =27 S^4

K_{sp} =27 $(5.31\times10^{-5}\ )^4$ $\Longrightarrow$ K_{sp} = 2.14×10^{-16} mol^4/L^4

Example 6:-

Explain a precipitate of $AgBrO_3$ ($K_{sp}=6\times10^{-5}$ mol^2/L^2) will form or not when equal volumes of a 1×10^{-3} M $AgNO_3$ solution and 2×10^{-2} M $KBrO_3$ solution are mixed?



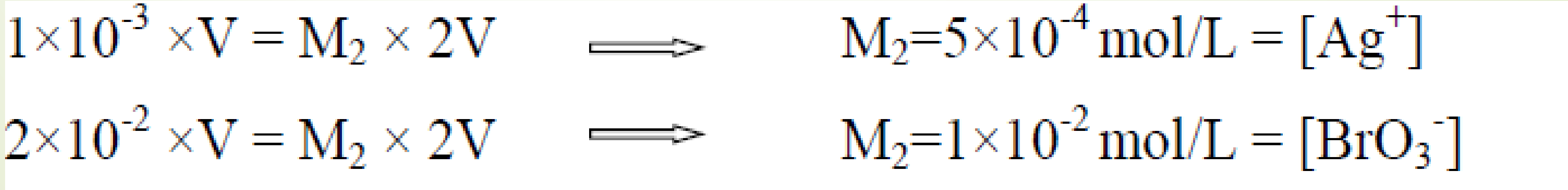
Solution:

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$
$$1\times10^{-3}M \quad 1\times10^{-3}M \quad 1\times10^{-3}M$$

$$KBrO_3 \rightleftharpoons K^+ + BrO_3^-$$
$$2\times10^{-2}M \quad 2\times10^{-2}M \quad 2\times10^{-2}M$$

In this example, dilution occurred in the mixing, therefore the initial concentration of Ag^+ and BrO_3^- are:

$$M_1 \times V_1 = M_2 \times V_2$$



$$1\times10^{-3} \times V = M_2 \times 2V \Longrightarrow M_2=5\times10^{-4}\,mol/L = [Ag^+]$$

$$2\times10^{-2} \times V = M_2 \times 2V \Longrightarrow M_2=1\times10^{-2}\,mol/L = [BrO_3^-]$$

- The precipitation reaction will occur only if the product of the initial Ag^+ and BrO_3^- concentrations exceeds the solubility product constant.
- The product of these concentrations is given by

$$\begin{aligned}\text{Ionic product (IP)} &= [Ag^+]\,[BrO_3^-]\\ &= (5\times10^{-4})\,(1\times10^{-2})\\ &= 5\times10^{-6}\ \text{mol}^2/\text{L}^2\end{aligned}$$

- The solubility product for $AgBrO_3$ is larger than the concentration product obtained ($K_{sp}=6\times10^{-55} > IP=5\times10^{-6}$).Therefore that precipitation will not occur.

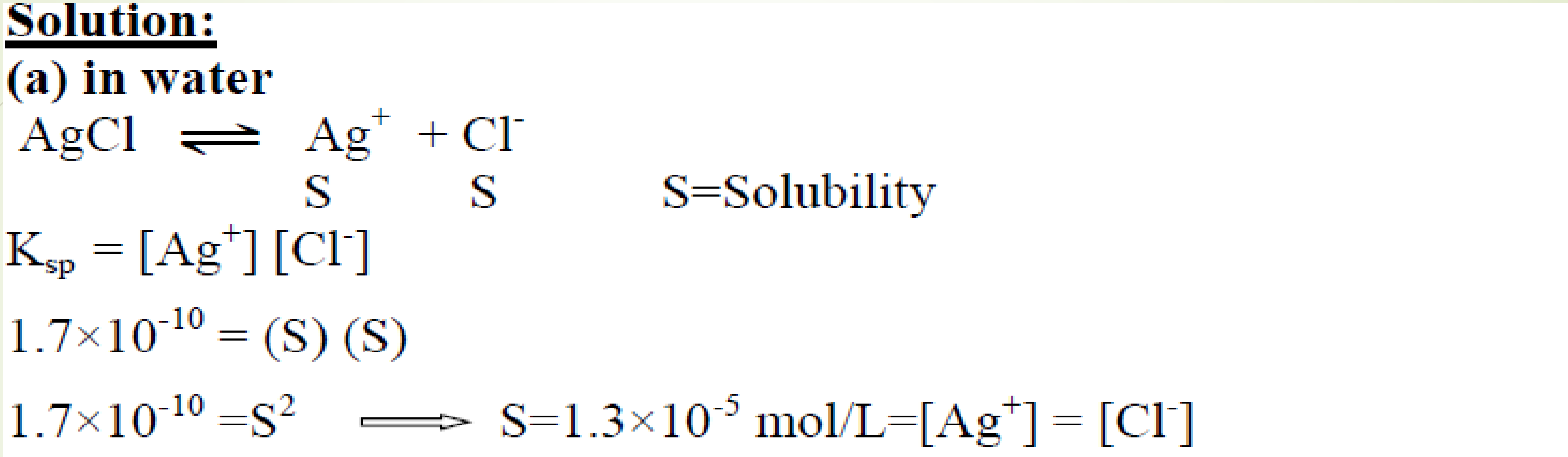
Common Ion Effect on Solubility

The effect of common ion on solubility will take place if in the solution there exists an excess of one of the ions which is the same as the ion from the precipitate, therefore causing the solubility to be less.

Example: $AgBr \rightleftharpoons Ag^{+} + Br^{-}$

With addition Ag^{+} into the solution, the equilibrium position will move to the left causing solubility of AgBr to be less follows the **Le Chatelier's** principle.

Example 7:- **Calculate the molar concentrations of AgCl in (a)water and (b)in 0.1M KCl solution. K_{sp} of AgCl is 1.7×10^{-10} mol^2/L^2.**



Solution:

(a) in water

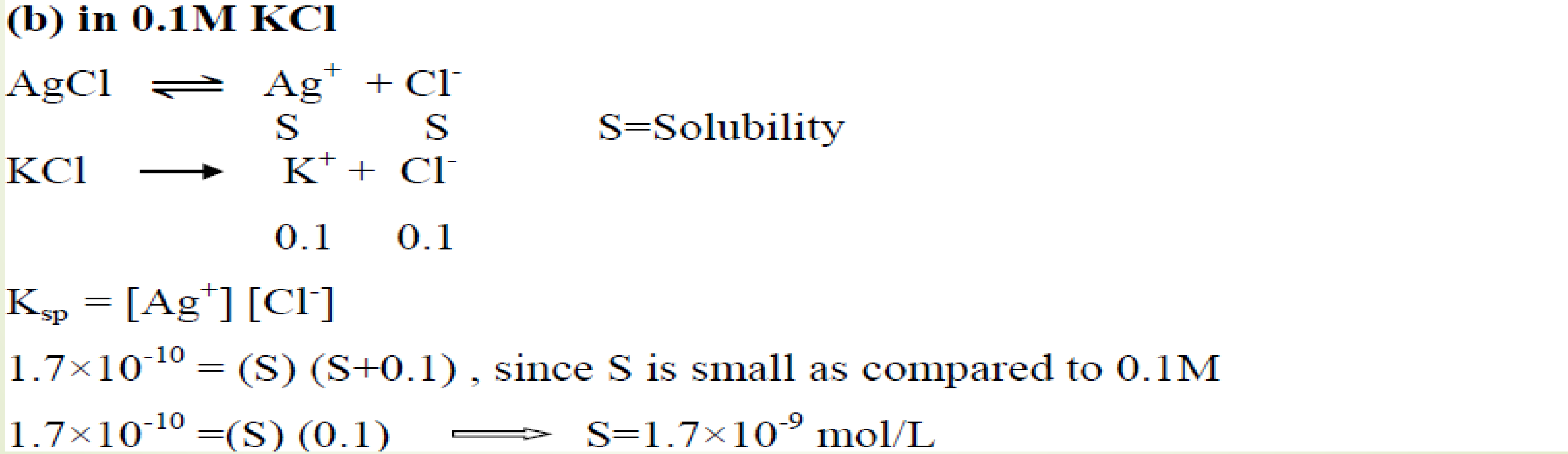
$AgCl \rightleftharpoons Ag^+ + Cl^-$

$\qquad\qquad S \qquad S \qquad$ S=Solubility

$K_{sp} = [Ag^+][Cl^-]$

$1.7\times10^{-10} = (S)(S)$

$1.7\times10^{-10} = S^2 \Longrightarrow S=1.3\times10^{-5}$ mol/L$=[Ag^+] = [Cl^-]$



(b) in 0.1M KCl

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$\qquad\qquad S \qquad S \qquad$ S=Solubility

$KCl \longrightarrow K^+ + Cl^-$

$\qquad\qquad 0.1 \qquad 0.1$

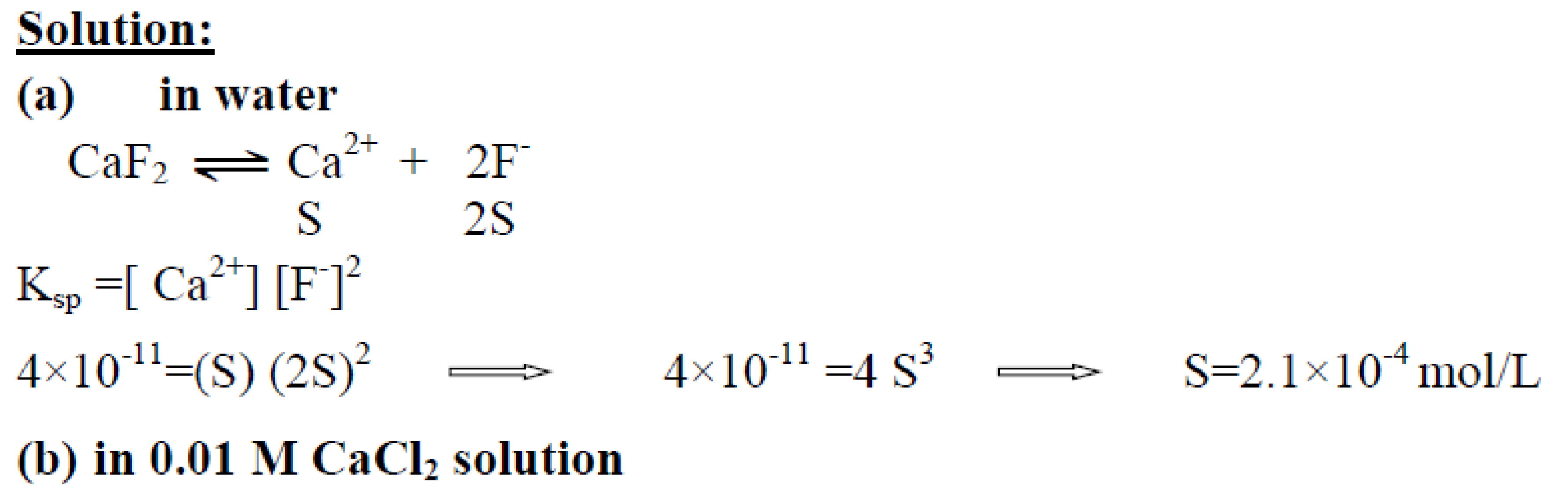
$K_{sp} = [Ag^+][Cl^-]$

$1.7\times10^{-10} = (S)(S+0.1)$, since S is small as compared to 0.1M

$1.7\times10^{-10} = (S)(0.1) \Longrightarrow S=1.7\times10^{-9}$ mol/L

Example 8:-

Calculate the solubility of CaF_2 ($k_{sp} = 4\times10^{-11}$ mol^3/L^3) in:(a) water, (b) in 0.01M $CaCl_2$ solution, (c) in 0.01 M NaF solution.



Solution:

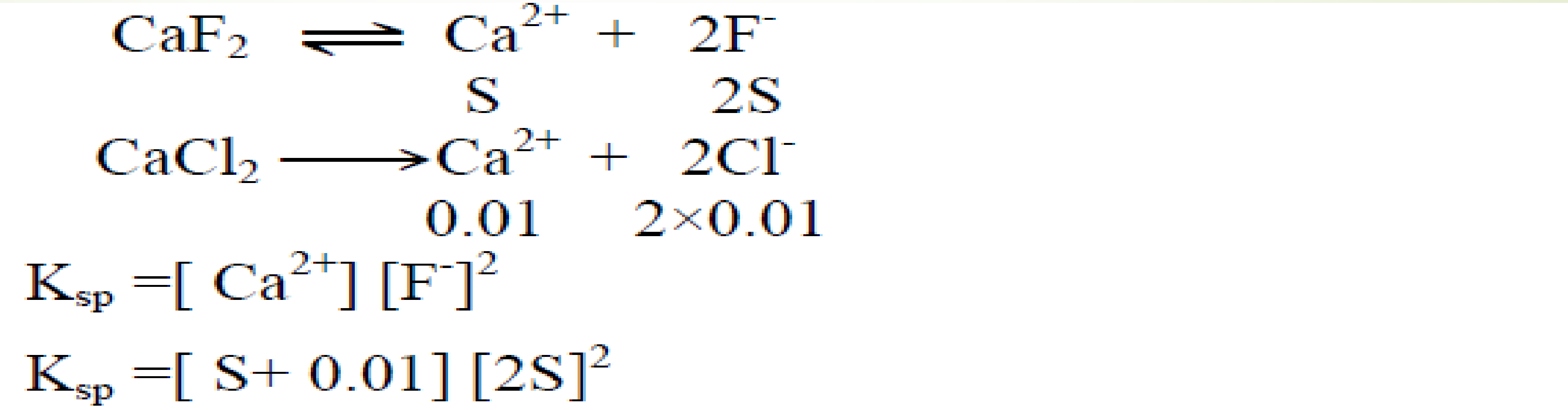
(a) in water

$$\begin{matrix} CaF_2 \rightleftharpoons & Ca^{2+} & + & 2F^- \\ & S & & 2S \end{matrix}$$

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$4\times10^{-11} = (S)(2S)^2 \Longrightarrow 4\times10^{-11} = 4S^3 \Longrightarrow S = 2.1\times10^{-4}\ mol/L$$

(b) in 0.01 M $CaCl_2$ solution



$$\begin{matrix} CaF_2 \rightleftharpoons & Ca^{2+} & + & 2F^- \\ & S & & 2S \end{matrix}$$

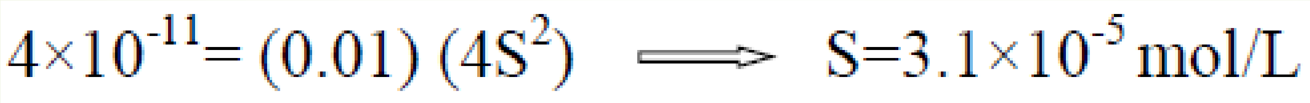
$$\begin{matrix} CaCl_2 \longrightarrow & Ca^{2+} & + & 2Cl^- \\ & 0.01 & & 2\times0.01 \end{matrix}$$

$$K_{sp} = [Ca^{2+}][F^-]^2$$

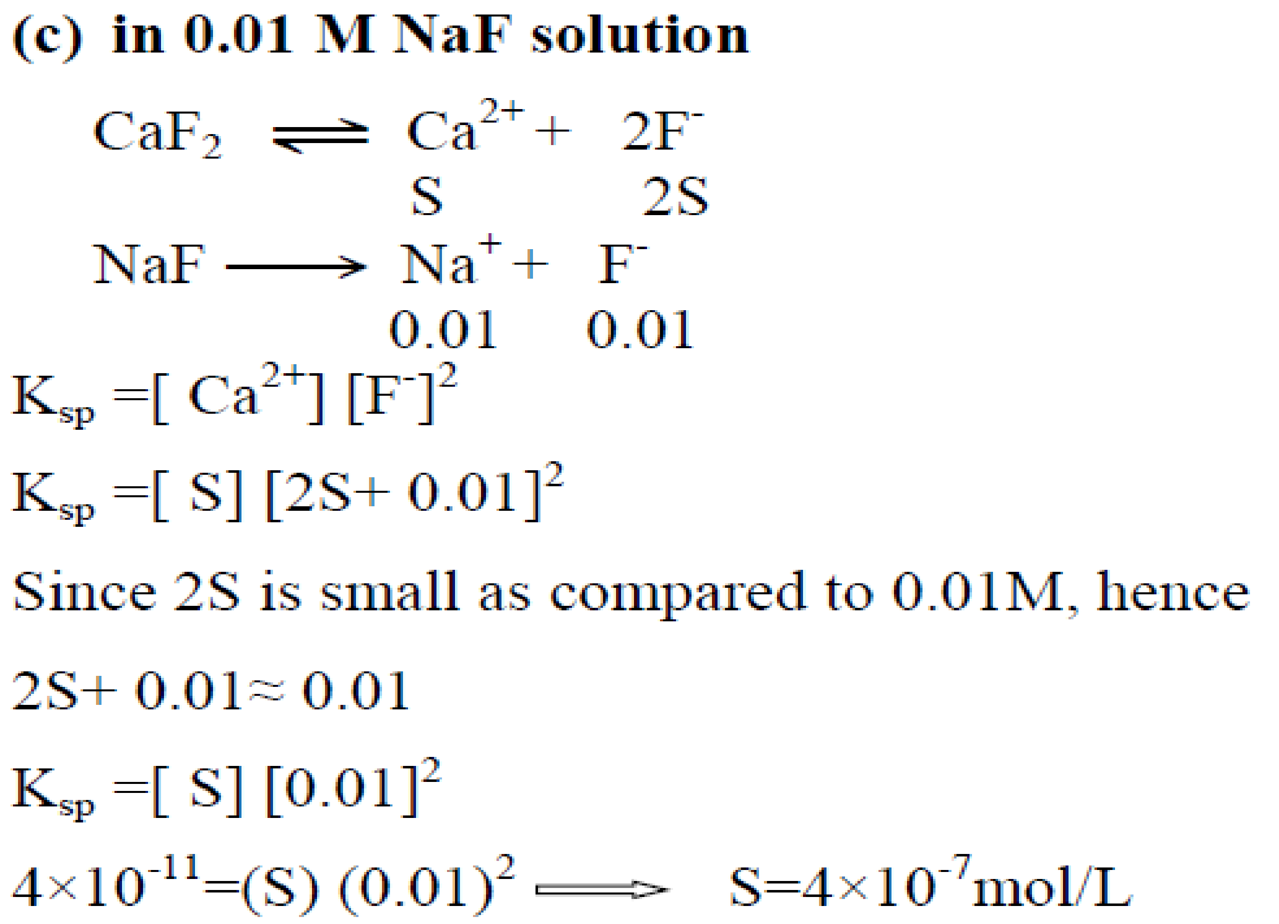
$$K_{sp} = [S + 0.01][2S]^2$$

- Since S is small as compared to 0.01M (solubility constant is small, therefore the Ca^{2+} formed from solubility is also small), hence

$$K_{sp} = [0.01]\,[2S]^{2}$$



$$4\times10^{-11} = (0.01)\,(4S^{2}) \Longrightarrow S = 3.1\times10^{-5}\ \text{mol/L}$$



(c) in 0.01 M NaF solution

$$CaF_2 \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2F^-}$$

$$NaF \longrightarrow \underset{0.01}{Na^+} + \underset{0.01}{F^-}$$

$$K_{sp} = [Ca^{2+}]\,[F^-]^2$$

$$K_{sp} = [S]\,[2S + 0.01]^2$$

Since 2S is small as compared to 0.01M, hence

$$2S + 0.01 \approx 0.01$$

$$K_{sp} = [S]\,[0.01]^2$$

$$4\times10^{-11} = (S)\,(0.01)^2 \Longrightarrow S = 4\times10^{-7}\ \text{mol/L}$$

Thank you