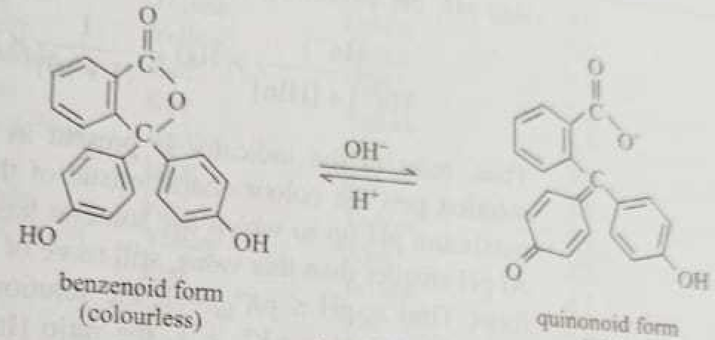
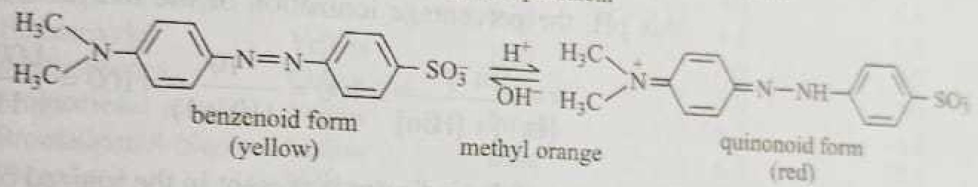
4.24 ACID-BASE INDICATORS

Indicators, in general, are either organic weak acids or weak bases with a characteristic of having different colours in the ionized and unionized forms. For example, phenolphthalein is a weak acid (ionized form is pink and unionized form is colourless) and methyl orange is a weak base (ionized form is red and unionized form is yellow).



phenolphthalein



methyl orange

ndicator Constant The equilibrium between ionized and unionized forms of an indicator can be treated like that of any other weak electrolyte. Considering an acid indicator HIn, the equilibrium involving it and its conjugate base In⁻ can be represented as

$$\mathrm{HIn} \rightleftharpoons \mathrm{H}^+ + \mathrm{In}^-$$

Its equilibrium constant K_{In} is given by

$$K_{\mathrm{In}} = \frac{[\mathrm{H}^+][\mathrm{In}^-]}{[\mathrm{HIn}]} \qquad (4.24.1)$$

This K_{In} is known as the *indicator constant* and like any other dissociation constant, its value depends only on the temperature and not on individual concentrations of H⁺, In⁻ and HIn. These are usually tabulated as $\mathrm{p}K^\circ_{\mathrm{In}}$ $\{= -\log (K_{\mathrm{In}}/\mathrm{M})\}$.

icator Range Rewriting Eq. (4.24.1), we get

$$[\mathrm{H}^+] = K_{\mathrm{In}} \frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \quad \text{or} \quad \mathrm{pH} = \mathrm{p}K^\circ_{\mathrm{In}} + \log \frac{[\mathrm{In}^-]}{[\mathrm{HIn}^-]} \qquad (4.24.2)$$

In general, the intensity of a coloured solution depends on the concentration of the colour imparting species. If the solution contains two coloured species, say In^- and HIn, the colour of the solution depends on the relative amounts of the two species. On an average, the solution acquires a distinct colour characteristic of In^- if the concentration of the latter is approximately 10 (or more) times greater than that of HIn and vice versa. Thus, we have

(a) At $pH = pK^{\circ}_{In} - 1$, the ratio $[In^-]/[HIn]$ in the solution is (1/10). For this pH, the percentage ionization of the indicator is

$$\frac{[In^-]}{[In^-]+[HIn]} \times 100 = \frac{1}{(1+10)} \times 100 = \frac{100}{11} \approx 9.1$$

Thus, most of the indicator is present in the unionized acid form HIn and the solution gets the colour characteristic of this form. In fact, $pH = pK^{\circ}_{In} - 1$ is the maximum pH up to which the solution has a distinct colour characteristic of HIn. At pH smaller than this value, still more of the indicator is present in the unionized form. Thus at $pH \leq pK^{\circ}_{In} - 1$, the solution has a colour characteristic of HIn.

(b) At $pH = pK^{\circ}_{In} + 1$, the ratio $[In^-]/[HIn]$ in the solution is (10/1). For this pH, the percentage ionization of the indicator is

$$\frac{[In^-]}{[In^-]+[HIn]} \times 100 = \frac{10}{(10+1)} \times 100 = \frac{1000}{11} \approx 91$$

Thus, most of the indicator is present in the ionized base form In^- and the solution gets the colour characteristic of this form. In fact, $pH = pK^{\circ}_{In} + 1$ is the minimum pH up to which the solution has a distinct colour characteristic of In^-. At pH greater than this value, still more of the indicator is present in the ionized form. Thus at $pH \geq pK^{\circ}_{In} + 1$, the solution has a colour characteristic of In^-.

In between the pH range $pK^{\circ}_{In} - 1$ to $pK^{\circ}_{In} + 1$, transition of colour takes place. A list of indicators is given in Table 4.24.1 which also includes the colours of acid and base forms of each indicator and the pH value at which one or the other form is sufficiently predominant to impart its colour to the solution.

ection of cators

Near the equivalence point of acid-base titration, the pH value of the solution changes steeply and the pH range of this steep change depends on the nature of the acid-base pair being titrated. The centre of this steep change lies at pH = 7 only when a strong acid is titrated with a strong base. For any other titration involving either weak acid or base, the salt formed undergoes hydrolysis and therefore, gives a pH value either greater than or less than 7. The selected indicator should be such that it offers a colour change near the vicinity of the pH of the solution at the equivalence point. Thus, the selection of indicator must satisfy the following two points:

(i) The steep section of the titration curve at the equivalence point must encompass an interval of pH values at least as large as the pH transition range of an indicator.

(ii) The pH transition range of the indicator must coincide with the steep portion of the titration curve.

Table 4.24.1 Acid-Base Indicators

Indicator	Colour change		pH transition range	
	Acid form	*Base form*	*Acid form predominate at pH*	*Base form predominate at pH*
Picric acid	Colourless	Yellow	0.0	1.2
Malachite green	Yellow	Green	0.0	2.0
Methyl violet	Yellow	Violet	0.1	3.2
m-Cresol purple	Red	Yellow	1.2	2.8
Thymol blue	Red	Yellow	1.2	2.8
Bromophenol blue	Yellow	Blue	3.0	4.6
Congo red	Blue	Red	3.0	5.0
Methyl orange	Red	Yellow	3.1	4.4
Bromocresol green	Yellow	Blue	3.8	5.4
Methyl red	Red	Yellow	4.2	6.3
Litmus	Red	Blue	4.5	8.3
Propyl red	Red	Yellow	4.6	6.4
Chlorophenol red	Yellow	Red	4.8	6.4
Hematoxylin	Yellow	Red	5.0	6.0
p-Nitrophenol	Colourless	Yellow	5.0	7.0
Bromocresol purple	Yellow	Purple	5.2	6.8
Bromothymol blue	Yellow	Blue	6.0	7.6
Phenol red	Yellow	Red	6.8	8.4
m-Cresol purple	Yellow	Purple	7.4	9.0
Thymol blue	Yellow	Blue	8.0	9.6
Phenolphthalein	Colourless	Red	8.3	10.0
Thymolphthalein	Colourless	Blue	9.3	10.5
Alizarin yellow R	Yellow	Lavender	10.0	12.1
Alizarin blue S	Green	Blue	11.0	13.0
Malachite green	Green	Colourless	11.4	13.0
Trinitrobenzene	Colourless	Orange	12.0	14.0

Indicators in Some Typical Titrations

The following is a brief summary of the choice of indicators employed in different types of titrations:

Strong acid and strong base The pH at the equivalence point is 7 and slightly before and after the equivalence point, it encompasses an interval from pH = 3 to pH = 11 (Fig. 4.24.1). Therefore, any indicator whose pH range is within this interval can be used. Any of the indicators from bromophenol blue to thymolphthalein listed in Table 4.24.1 can be used. However, *the range of the steep change of* pH *at the equivalence point depends upon the concentrations of acid and base being titrated.* For dilute solutions, the corresponding pH change is less as compared to that of concentrated solutions. Hence, the most ideal indicator is that which changes its colour (base form) near pH = 7. Methyl orange, methyl red and phenolphthalein, the common laboratory indicators, can be used for this purpose. The usual choice, however, is phenolphthalein because the colour change in this case is from colourless to a slight pink colour— change which can be easily detected.

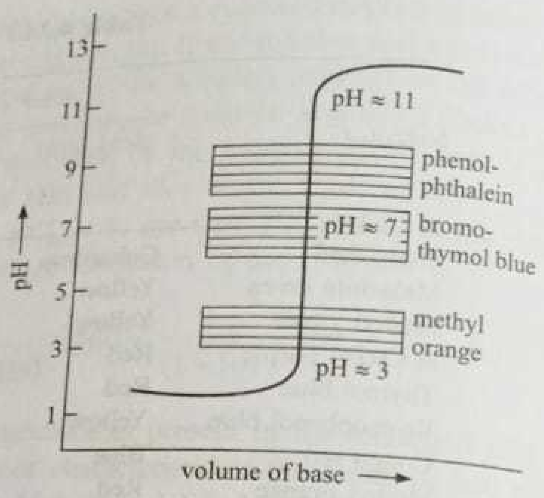


Fig. 4.24.1 Titration curve (only schematic) of a strong acid with a strong base

Weak base and strong acid The pH of the solution at the equivalence p lies slightly in the acidic range. For example, pH of the solution at equivalen point when 0.1 M NH_4OH is titrated with 0.1 M HCl is 5.3; the presence a slight excess of the acid lowers the pH further down to between 4 and (Fig. 4.24.2). Obviously the use of phenolphthalein as an indicator is ruled o Methyl red or methyl orange can be used as an indicator for this titration.

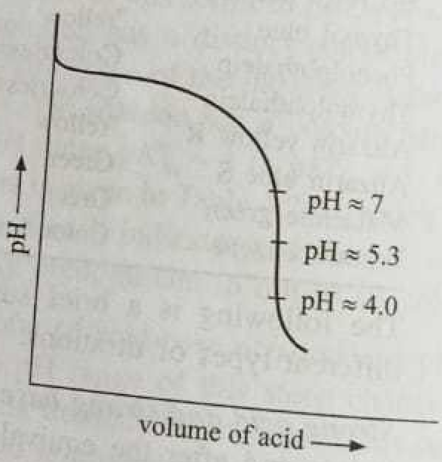


Fig. 4.24.2 Titration curve (only schematic) of a weak base (NH_4OH) with a strong acid (HCl)

Weak acid and strong base The pH of the solution at the equivalence poi lies on the alkaline side. For example, when 0.1 M HAc is titrated with 0.1 M NaOH, its pH is 8.7 (Fig. 4.24.3). A slight excess of base brings the pH up t 9 or 10 and hence phenolphthalein can be used as the indicator in this titration

Weak acid and weak base In this particular case, neither the steep rise of pH near the equivalence point occurs nor the rise of pH encompasses an interval equal to the pH transition range of any of the indicators. Hence, no suitable indicator can be employed to detect the end point as it will cause much error

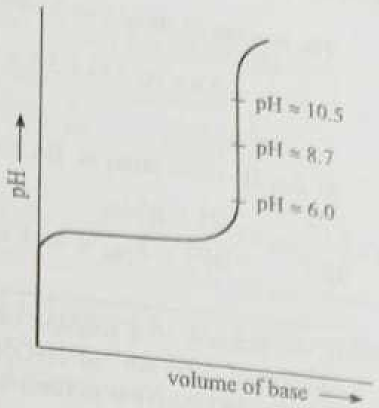


Fig. 4.24.3 Titration curve (only a schematic) of a weak acid (HAc) with a strong base (NaOH)

Example 4.24.1

For the indicator thymol blue, the value of pH is 2.0 when half of the indicator is present in the unionized form. Calculate the percentage of the indicator in the unionized form in a solution of 4.0×10^{-3} M hydrogen ion concentration.

Solution

Since at pH = 2.0, half of the indicator is present in the unionized form, therefore

$$[\mathrm{HIn}] = [\mathrm{In}^-]$$

Using $\mathrm{pH} = \mathrm{p}K^\circ_{\mathrm{In}} + \log \dfrac{[\mathrm{In}^-]}{[\mathrm{HIn}]}$, we have

$$\mathrm{p}K^\circ_{\mathrm{In}} = \mathrm{pH} = 2.0$$

pH of the solution containing 4.0×10^{-3} M of H^+ is

$$\mathrm{pH} = -\log(4.0 \times 10^{-3}) = 2.4$$

Thus, $\log\left(\dfrac{[\mathrm{In}^-]}{[\mathrm{HIn}]}\right) = \mathrm{pH} - \mathrm{p}K^\circ_{\mathrm{In}} = 2.4 - 2.0 = 0.4$

or $\dfrac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = 2.5$

Adding 1 on both sides, we get

$$\frac{[\mathrm{In}^-] + [\mathrm{HIn}]}{[\mathrm{HIn}]} = 3.5 \quad \text{or} \quad \frac{[\mathrm{HIn}]}{[\mathrm{In}^-] + [\mathrm{HIn}]} = \frac{1}{3.5} = 0.286$$

Thus, the percentage of indicator in the unionized form = 28.6

Example 4.24.2

An indicator is a weak acid and the pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the centre of the hydrogen ion concentrations corresponding to given pH range, calculate the ionization constant of the indicator.

Solution

The hydrogen ion concentrations of the given pH range are

$$\mathrm{pH} = 3.1 = -\log\{[\mathrm{H}^+]/\mathrm{M}\} \quad \text{i.e.} \quad \log\{[\mathrm{H}^+]/\mathrm{M}\} = -3.1 = \bar{4}.9$$

Hence, $[\mathrm{H}^+] = 7.9 \times 10^{-4}$ M

$$\mathrm{pH} = 4.5 \quad \text{i.e.} \quad \log\{[\mathrm{H}^+]/\mathrm{M}\} = -4.5 = \bar{5}.5$$

Hence, $[\mathrm{H}^+] = 3.2 \times 10^{-5}$ M

The average of these two hydrogen ion concentrations is

$$\frac{7.9 \times 10^{-4}\ \text{M} + 3.2 \times 10^{-5}\ \text{M}}{2} = 4.11 \times 10^{-4}\ \text{M}$$

At this H^+ concentration, $[In^-] = [HIn]$. Therefore,

$$\text{pH} = \text{p}K^{\circ}_{HIn}$$

or $$[H^+] = K_{HIn} = 4.11 \times 10^{-4}\ \text{M}$$

Example 4.24.3 In the titration of a solution of a weak acid, HX with NaOH, the pH is 5.8 the addition of 10.0 cm^3 of NaOH solution and is 6.4 after the addition of 20.0 NaOH solution. What is the ionization constant of the HX?

Solution Let x be the initial amount of the acid HX and let y be the amount of base NaOH per dm^3 of the solution. Let the volume of the acid being titrated be V.

(i) *After the addition of 10.0* cm^3 *of the base* (pH = 5.8):

Amount of salt = Amount of NaOH added

$$= \left(\frac{y}{1\ \text{dm}^3}\right)(10\ \text{cm}^3) = \left(\frac{y}{1\ \text{dm}^3}\right)(10^{-2}\ \text{dm}^3) = y \times 10^{-2}$$

$$\text{Amount of acid left} = \left(\frac{x}{1\ \text{dm}^3}\right)(V) - y \times 10^{-2}$$

(ii) *After the addition of* 20.0 cm^3 *of the base* (pH = 6.4):

$$\text{Amount of salt} = \left(\frac{y}{1\ \text{dm}^3}\right)(2 \times 10^{-2}\ \text{dm}^3) = 2y \times 10^{-2}$$

$$\text{Amount of acid left} = \left(\frac{x}{1\ \text{dm}^3}\right)(V) - 2y \times 10^{-2}$$

Using the Henderson's equation, we have

$$5.8 = \text{p}K^{\circ} + \log\left(\frac{y \times 10^{-2}}{x\,(V/\text{dm}^3) - y \times 10^{-2}}\right)$$

$$6.4 = \text{p}K^{\circ} + \log\left(\frac{2y \times 10^{-2}}{x\,(V/\text{dm}^3) - 2y \times 10^{-2}}\right)$$

Subtracting Eq. (1) from Eq. (2), we get

$$0.6 = \log\left\{\frac{2y \times 10^{-2}}{x(V/\text{dm}^3) - 2y \times 10^{-2}} \times \frac{x(V/\text{dm}^3) - y \times 10^{-2}}{y \times 10^{-2}}\right\}$$

Simplifying, we get

$$\frac{x(V/\text{dm}^3)}{y} = 3 \times 10^{-2}$$

Substituting this in either Eq. (1) (or Eq. 2), we get

$$5.8 = \mathrm{p}K^\circ + \log\left\{\frac{y\times10^{-2}}{3\times10^{-2}\,y - y\times10^{-2}}\right\}$$

i.e. $5.8 = \mathrm{p}K^\circ + \log\left(\frac{1}{2}\right)$ or $\mathrm{p}K^\circ = 5.8 - \log\left(\frac{1}{2}\right) = 6.1$

Universal Indicators A mixture of the following indicators can be used to determine the approximate pH of the solution in the range 4 to 11.

Methyl red, α-naphtholphthalein, thymolphthalein, phenolphthalein and bromothymol blue.

This mixture gives different colours at different pH values of the solution. These are

pH	4	5	6	7	8	9	10	11
Colour	Red	Orange red	Yellow	Green yellow	Green	Blue green	Blue violet	Red violet

4.25 TITRATION OF A STRONG MONOPROTIC ACID WITH A STRONG BASE

At the Start of Titration If n_0 is the amount of acid present in the volume V_a of the solution, then

$$[\mathrm{H_3O^+}] = \frac{n_0}{V_a}$$

Before the Equivalence Point If c_a and c_b are the concentrations of acid and base, respectively, then after the addition of the volume V_b of the base, the amount of $\mathrm{H_3O^+}$ left is

$$n_a = n_0 - c_b V_b \qquad (4.25.1)$$

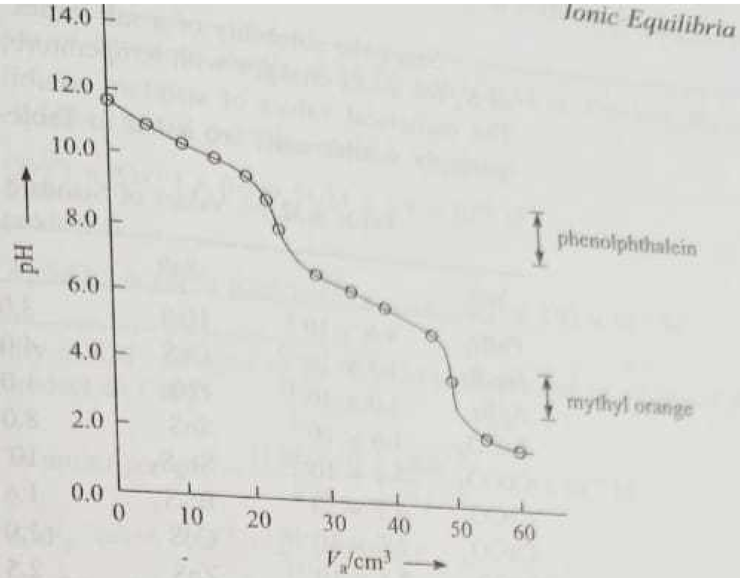
Total volume of the solution = $V_a + V_b$

Hence, the concentration of remaining $\mathrm{H_3O^+}$ in solution is

$$[\mathrm{H_3O^+}] = \frac{n_0 - c_b V_b}{V_a + V_b} \qquad (4.25.2)$$

This expression will not be applicable very near to the equivalence point since the concentration of $\mathrm{H_3O^+}$ from the remaining acid becomes comparable with the $\mathrm{H_3O^+}$ concentration due to the dissociation of water. In this case, we use the expression

$$\begin{aligned}[\mathrm{H_3O^+}]_{\text{total}} &= [\mathrm{H_3O^+}]_{\text{acid}} + [\mathrm{H_3O^+}]_{\text{water}} \\ &= [\mathrm{H_3O^+}]_{\text{acid}} + [\mathrm{OH^-}]_{\text{water}} \\ &= \frac{n_0 - c_b V_b}{(V_a + V_b)} + \frac{K_w}{[\mathrm{H_3O^+}]_{\text{total}}} \qquad (4.25.3)\end{aligned}$$



4.31.1 **Titration** of sodium onate wtih ochloric acid

SOLUBILITY PRODUCT

finition

If a slightly soluble salt is placed in water, a dynamic equilibrium is established where the rate of dissolution of ions from the solid equals the rate of precipitation of ions from the saturated solution. For example, in AgCl, we have the following equilibrium

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

with the equilibrium constant

$$K' = \frac{[\mathrm{Ag^+}][\mathrm{Cl^-}]}{[\mathrm{AgCl}]}$$

Since the concentration of a pure solid is a constant, [AgCl] may be combined with K' to give a new constant, called the *solubility product*:

$$K_s = K'\,[\mathrm{AgCl}] = [\mathrm{Ag^+}]\,[\mathrm{Cl^-}]$$

Thus, the solubility product is equal to the product of the ionic concentrations present in a saturated solution. When the salt dissolves to give unequal numbers of positive and negative ions, each concentration term must be raised to a power equal to the coefficient of the ion in the chemical equation. For example:

Salt	*Reaction*		*Solubility product expression*	
F_2	$CaF_2(s)$	$\rightleftharpoons Ca^{2+} + 2F^-$	$K_s(CaF_2)$	$= [Ca^+]\,[F^-]^2$
I_2	$PbI_2(s)$	$\rightleftharpoons Pb^{2+} + 2I^-$	$K_s(PbI_2)$	$= [Pb^{2+}]\,[I^-]^2$
Cl_2	$Hg_2Cl_2(s)$	$\rightleftharpoons Hg_2^{2+} + 2Cl^-$	$K_s(Hg_2Cl_2)$	$= [Hg_2^{2+}]\,[Cl^-]^2$
$OH)_3$	$Al(OH)_3(s)$	$\rightleftharpoons Al^{3+} + 3OH^-$	$K_s\{Al(OH)_3\}$	$= [Al^{3+}]\,[OH^-]^3$
$PO_4)$	$Ag_3(PO_4)(s)$	$\rightleftharpoons 3Ag^+ + PO_4^{3-}$	$K_s\{Ag_3(PO_4)\}$	$= [Ag^+]^3\,[PO_4^{3-}]$
$PO_4)_2$	$Ca_3(PO_4)_2(s)$	$\rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$	$K_s\{Ca_3(PO_4)_2\}$	$= [Ca^{2+}]^3\,[PO_4^{3-}]^2$
$SO_4)_2$	$KAl(SO_4)_2$	$\rightleftharpoons Al^{3+} + K^+ + 2SO_4^{2-}$	$K_s\{KAl(SO_4)_2\}$	$= [K^+]\,[Al^{3+}]\,[SO_4^{2-}]^2$

Since the solubility of a salt varies with temperature, the numerical value of K_s for a salt changes with temperature; values are usually recorded at 25 °C. The numerical values of standard solubility product for some of the common sparingly soluble salts are listed in Table 4.32.1.

Table 4.32.1 Values of Standard Solubility Products at 25 °C†

Salt	K_s°	*Salt*	K_s°	*Salt*	K_s°
$PbBr_2$	4.6×10^{-6}	HgS	3.0×10^{-53}	$Pb(OH)_2$	4.2×10[illegible]
Hg_2Br_2	1.3×10^{-22}	CuS	4.0×10^{-38}	$Mg(OH)_2$	8.9×10[illegible]
AgBr	5.0×10^{-13}	PbS	1.0×10^{-29}	$Mn(OH)_2$	2×10[illegible]
$BaCO_3$	1.6×10^{-9}	SnS	8.0×10^{-29}	$Ni(OH)_2$	1.6×10[illegible]
$CdCO_3$	5.2×10^{-12}	Sb_2S_3	10^{-80}	$Sr(OH)_2$	3.2×10[illegible]
$CaCO_3$	4.7×10^{-9}	Bi_2S_3	1.6×10^{-72}	$Sn(OH)_2$	3×10[illegible]
$CuCO_3$	2.5×10^{-10}	CdS	1.0×10^{-28}	$Zn(OH)_2$	4.5×10[illegible]
$FeCO_3$	2.1×10^{-11}	ZnS	2.5×10^{-22}	PbI_2	8.3×10[illegible]
$PbCO_3$	1.5×10^{-15}	CoS	7×10^{-23}	Hg_2I_2	4.5×10[illegible]
$MgCO_3$	1×10^{-5}	NiS	3×10^{-21}	AgI	8.5×10[illegible]
$MnCO_3$	8.8×10^{-11}	MnS	5.6×10^{-16}	AgCN	1.6×10[illegible]
Hg_2CO_3	9.0×10^{-17}	FeS	1.0×10^{-19}	AgCNS	1.0×10[illegible]
$NiCO_3$	1.4×10^{-7}				
Ag_2CO_3	8.2×10^{-12}	BaF_2	2.4×10^{-5}	BaC_2O_4	1.5×10[illegible]
$SrCO_3$	7×10^{-10}	CaF_2	3.9×10^{-11}	CaC_2O_4	1.3×10[illegible]
$ZnCO_3$	2×10^{-10}	PbF_2	4×10^{-8}	PbC_2O_4	8.3×10[illegible]
		MgF_2	8×10^{-8}	MgC_2O_4	8.6×10[illegible]
$PbCl_2$	1.6×10^{-5}	SrF_2	7.9×10^{-11}	$Ag_2C_2O_4$	1.1×10[illegible]
Hg_2Cl_2	1.1×10^{-18}			SrC_2O_4	5.6×10[illegible]
AgCl	1.7×10^{-10}	$Al(OH)_3$	5×10^{-33}	$Ba_3(PO_4)_2$	6×10[illegible]
		$Ba(OH)_2$	5×10^{-3}	$Ca_3(PO_4)_2$	1.3×10[illegible]
$BaCrO_4$	8.5×10^{-11}	$Cd(OH)_2$	2×10^{-14}	$Pb_3(PO_4)_2$	1×10[illegible]
$PbCrO_4$	2×10^{-16}	$Ca(OH)_2$	1.3×10^{-6}	$Ag_3(PO_4)$	1.8×10[illegible]
Hg_2CrO	2×10^{-9}	$Cr(OH)_3$	6.7×10^{-31}	$Sr_3(PO_4)_2$	1×10[illegible]
Ag_2CrO_4	1.9×10^{-12}	$Co(OH)_2$	2.5×10^{-16}		
$SrCrO_4$	3.6×10^{-5}	$Co(OH)_3$	2.5×10^{-43}	$BaSO_4$	1.5×10[illegible]
		$Cu(OH)_2$	1.6×10^{-19}	$CaSO_4$	2.4×10[illegible]
		$Fe(OH)_2$	1.8×10^{-15}	$PbSO_4$	1.3×10[illegible]
		$Fe(OH)_3$	6×10^{-38}	Ag_2SO_4	1.2×10[illegible]
				$SrSO_4$	7.6×10[illegible]

---

† In the expression of standard solubility product, c is replaced by c/c°, where c° is the standard concentration of 1 M.

and Product

The numerical value of the solubility product for a salt can be determined from its molar solubility and vice versa. The following problems illustrate the procedure.

Example 4.32.1

The solubility of strontium oxalate at 20 °C is 0.000 54 M. Calculate the solubility product.

Solution

Since SrOx $\rightleftharpoons$ $Sr^{2+} + Ox^{2-}$, therefore

$$[Sr^{2+}] = [Ox^{2-}] = 0.000\ 54\ M = 5.4 \times 10^{-4}\ M$$

Solubility product is

$$K_s(SrOx) = [Sr^{2+}]\,[Ox^{2-}] = (5.4 \times 10^{-4}\ M)^2 = 2.92 \times 10^{-7}\ M^2$$

Example 4.32.2

The solubility of CaF_2 in water at 20 °C is 15.6 mg per dm^3 of solution. Calculate the solubility product of CaF_2.

Solution

$$\text{Solubility in moles per } dm^3 = \frac{(15.6 \times 10^{-3}\ g\ dm^{-3})}{(78\ g\ mol^{-1})} = 2.0 \times 10^{-4}\ M$$

Since $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$, therefore

$$[Ca^{2+}] = 2.0 \times 10^{-4}\ M \quad \text{and} \quad [F^-] = 2 \times 2.0 \times 10^{-4}\ M$$

Hence, the solubility product is

$$K_s = [Ca^{2+}]\,[F^-]^2 = (2.0 \times 10^{-4}\ M)\,(4.0 \times 10^{-4}\ M)^2 = 32 \times 10^{-12}\ M^3$$

Example 4.32.3

What is the solubility of $Ag_2(CrO_4)$ in water if the value of solubility product is $K_s = 1.3 \times 10^{-11}\ M^3$?

Solution

Since $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$, therefore

$$[Ag^+] = 2[CrO_4^{2-}]$$

Let s be the solubility of Ag_2CrO_4, then

$$[Ag^+] = 2s \quad \text{and} \quad [CrO_4^{2-}] = s$$

Hence, $K_s = [Ag^+]^2\,[CrO_4^{2-}] = (2s)^2\,(s)$ i.e. $4s^3 = 1.3 \times 10^{-11}\ M^3$

Therefore, $s = \{3.25 \times 10^{-12}\ M^3\}^{1/3} = 1.48 \times 10^{-4}\ M$

Example 4.32.4

A mixture of solid $SrSO_4$ and solid $BaSO_4$ is shaken up with water until saturation equilibrium is established. Given that $K_s(SrSO_4) = 7.6 \times 10^{-7}\ M^2$ and $K_s(BaSO_4) = 1.5 \times 10^{-9}\ M^2$, calculate the concentrations of Sr^{2+}, Ba^{2+} and SO_4^{2-}.

Solution

If x and y are the respective concentrations of $SrSO_4$ and $BaSO_4$ in the solution, then

$$[Sr^{2+}] = x; \qquad [Ba^{2+}] = y; \qquad [SO_4^{2-}] = x + y$$

Thus, $K_s(SrSO_4) = [Sr^{2+}]\,[SO_4^{2-}] = x(x + y) = 7.6 \times 10^{-7}\ M^2$

$$K_s(BaSO_4) = [Ba^{2+}]\,[SO_4^{2-}] = y(x + y) = 1.5 \times 10^{-9}\ M^2$$

Solving for x and y, we get

$$x = [Sr^{2+}] = 8.7 \times 10^{-4}\ M \quad \text{and} \quad y = [Ba^{2+}] = 1.7 \times 10^{-6}\ M$$

$$x + y = [SO_4^{2-}] = 8.717 \times 10^{-4}\ M$$

Factors Affecting Solubility of Salt

There is evidence that some salts ionize in steps. For example, lead chloride

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_s = [Pb^{2+}][Cl^-]^2$$

is thought to ionize according to the expressions

$$PbCl_2(s) \rightleftharpoons PbCl_2(aq) \qquad K_1 = [PbCl_2(aq)]$$

$$PbCl_2(aq) \rightleftharpoons PbCl^+(aq) + Cl^-(aq) \qquad K_2 = \frac{[PbCl^+][Cl^-]}{[PbCl_2(aq)]}$$

$$PbCl^+(aq) \rightleftharpoons Pb^{2+}(aq) + Cl^-(aq) \qquad K_3 = \frac{[Pb^{2+}][Cl^-]}{[PbCl^+]}$$

The product of the constants K_1, K_2 and K_3 is

$$K_1K_2K_3 = [PbCl_2(aq)]\left(\frac{[PbCl^+][Cl^-]}{[PbCl_2(aq)]}\right)\left(\frac{[Pb^{2+}][Cl^-]}{[PbCl^+]}\right)$$
$$= [Pb^{2+}][Cl^-]^2 = K_s$$

In these expressions, $PbCl_2(aq)$ is an undissociated molecule in solution.

Thus, the principle of solubility product applies to all solutions of slightly soluble materials whether they dissociate in steps or not. However, the K_s of salts that dissociate in steps must be carefully interpreted. For example, in a saturated solution of $PbCl_2$, the concentration of Cl^- is not twice the concentration of Pb^{2+} as the expression for the K_s might lead one to expect; such an erroneous deduction ignores the dissociation of the salt in steps. The value of K_s applies only if the actual concentrations of Pb^{2+} and Cl^- are employed, and the stepwise mechanism is taken into account in order to deduce the correct concentration terms.

Other factors such as complex formation, hydrolysis, etc., introduce errors into solubility calculations for certain salts. For example, the solubility of lead chloride is enhanced in a moderately concentrated solution of chloride ions because of the formation of the complex ion $PbCl_3^-$, so that

$$PbCl_2(s) + Cl^-(aq) \rightleftharpoons PbCl_3^-(aq)$$

Also, the hydrolysis of the Pb^{2+} ions according to the reaction

$$Pb^{2+}(aq) + 2H_2O \rightleftharpoons Pb(OH)^+(aq) + H_3O^+(aq)$$

reduces the concentration of Pb^{2+} ions so that the solubility of $PbCl_2$ is actually higher than the value obtained from the calculation that ignores hydrolysis

Example 4.32.5 What is the solubility of PbS: (a) ignoring the hydrolysis of ions, and (b) including the hydrolysis of ions (assume pH of the solution to be equal to 7)? Given that $K_s(\text{PbS}) = 7.0 \times 10^{-29}\ \text{M}^2$, $K_{b2}(\text{Pb(OH)}^+) = 1.5 \times 10^{-8}$ M, $K_a(\text{H}_2\text{S}) = 1.0 \times 10^{-7}$ M and $K_{a2}(\text{HS}^-) = 1.0 \times 10^{-14}$ M.

Solution ***Ignoring hydrolysis*** Let s be the concentration of PbS in the solution, then

$$K_s(\text{PbS}) = [\text{Pb}^{2+}]\,[\text{S}^{2-}] = 7.0 \times 10^{-29}\ \text{M}^2$$

Hence, $(s)\,(s) = 7.0 \times 10^{-29}\ \text{M}^2$ or $s = 8.4 \times 10^{-15}$ M

Including hydrolysis The given assumption that pH of the solution to be taken equal to 7 is justified on the basis that any H^+ or OH^- obtained through the hydrolysis of very low concentrations of Pb^{2+} and S^{2-} (of the order of 8.4×10^{-15} M) may be ignored in comparison to that derived from the ionization of water. The solubility of PbS including hydrolysis of ions may be calculated as follows:

The various equilibria are

$$\text{Pb}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pb(OH)}^+ + \text{H}_3\text{O}^+ \qquad K_{b1} = \frac{[\text{Pb(OH)}^+][\text{H}_3\text{O}^+]}{[\text{Pb}^{2+}]} \tag{1}$$

$$\text{S}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^- + \text{OH}^- \qquad K_{b2} = \frac{[\text{HS}^-][\text{OH}^-]}{[\text{S}^{2-}]} \tag{2}$$

$$\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + \text{OH}^- \qquad K_{b3} = \frac{[\text{H}_2\text{S}][\text{OH}^-]}{[\text{HS}^-]} \tag{3}$$

The values of K_{b1}, K_{b2} and K_{b3} are

$$K_{b1} = \frac{[\text{Pb(OH)}^+]}{[\text{Pb}^{2+}][\text{OH}^-]}[\text{H}_3\text{O}^+][\text{OH}^-]$$

$$= \frac{K_w}{K_{b2}(\text{Pb(OH}^+)} = \frac{1.0 \times 10^{-14}\ \text{M}^2}{1.5 \times 10^{-8}\ \text{M}} = 6.7 \times 10^{-7}\ \text{M} \tag{4}$$

$$K_{b2} = \frac{[\text{HS}^-]}{[\text{S}^{2-}][\text{H}_3\text{O}^+]}[\text{OH}^-][\text{H}_3\text{O}^+]$$

$$= \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}\ \text{M}^2}{1.0 \times 10^{-14}\ \text{M}} = 1.0\ \text{M} \tag{5}$$

$$K_{b3} = \frac{[\text{H}_2\text{S}]}{[\text{HS}^-][\text{H}_3\text{O}^+]}[\text{OH}^-][\text{H}_3\text{O}^+]$$

$$= \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}\ \text{M}^2}{1.1 \times 10^{-7}\ \text{M}} = 9.1 \times 10^{-8}\ \text{M} \tag{6}$$

Mass-balance expressions are

$$[\text{Pb}^{2+}]_0 = [\text{Pb}^{2+}] + [\text{Pb(OH)}^+] \tag{7}$$

$$[\text{S}^{2-}]_0 = [\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}] \tag{8}$$

Making use of Eq. (1) in Eq. (7), we have

$$[\text{Pb}^{2+}]_0 = [\text{Pb}^{2+}] + \frac{K_{b1}[\text{Pb}^{2+}]}{[\text{H}_3\text{O}^+]} \tag{9}$$

$$[\text{Pb}^{2+}] = \frac{[\text{Pb}^{2+}]_0}{1 + \dfrac{K_{b1}}{[\text{H}_3\text{O}^+]}}$$

Making use of Eqs (2) and (3) in Eq. (8), we have

$$[S^{2-}]_0 = [S^{2-}] + K_{h2}\frac{[S^{2-}]}{[OH^-]} + K_{h2}\,K_{h3}\frac{[S^{2-}]}{[OH^-]^2}$$

or

$$[S^{2-}] = \frac{[S^{2-}]_0}{1 + \dfrac{K_{h2}}{[OH^-]} + \dfrac{K_{h2}K_{h3}}{[OH^-]^2}} \qquad (10)$$

Now the expression of solubility product of PbS is

$$K_s(PbS) = [Pb^{2+}]\,[S^{2-}]$$

Substituting $[Pb^{2+}]$ and $[S^{2-}]$ from Eqs (9) and (10), we get

$$K_s(PbS) = \frac{[Pb^{2+}]_0\,[S^{2-}]_0}{\left(1 + \dfrac{K_{h1}}{[H_3O^+]}\right)\left(1 + \dfrac{K_{h2}}{[OH^-]} + \dfrac{K_{h2}K_{h3}}{[OH^-]^2}\right)}$$

If y is the concentration of PbS in the solution, then it is obvious that

$$[Pb^{2+}]_0 = [S^{2-}]_0 = y$$

With this, the previous expression gives

$$y^2 = K_s(PbS)\left(1 + \frac{K_{h1}}{[H_3O^+]}\right)\left(1 + \frac{K_{h2}}{[OH^-]} + \frac{K_{h2}K_{h3}}{[OH^-]^2}\right)$$

Substituting the values of $K_s(PbS)$, K_{h1}, K_{h2}, K_{h3}, $[H_3O^+]$ and $[OH^-]$, we have

$$y^2 = (7.0 \times 10^{-29}\ M^2)\left(1 + \frac{6.7 \times 10^{-7}\ M}{10^{-7}\ M}\right)\left(1 + \frac{1.0\ M}{10^{-7}\ M} + \frac{9.1 \times 10^{-8}\ M^2}{(10^{-7}\ M)^2}\right)$$

$$= (7.0 \times 10^{-29}\ M^2)\,(7.7)\,(1.91 \times 10^7) = 1.029\,5 \times 10^{-20}\ M^2$$

Hence, $y = 1.014\,6 \times 10^{-10}$ M

Thus, the solubility of PbS including hydrolysis is $1.014\,6 \times 10^{-10}$ M. Comparing this with that obtained ignoring hydrolysis indicates that the solubility has been increased by a factor

$$\frac{1.014\,6 \times 10^{-10}}{8.4 \times 10^{-15}} = 12\,078$$

mple 4.32.6

Calculate the molar solubility of AgCN in water. Given:

$$K_s(AgCN) = 2.3 \times 10^{-16}\ M^2 \text{ and } K_b(CN^-) = 1.7 \times 10^{-5}\ M.$$

tion

Material-balance expression of the dissolved salt is

$$[Ag^+] = [CN^-] + [HCN] \qquad (1)$$

Charge-balance expression is

$$[Ag^+] = [CN^-] + [OH^-] \qquad (2)$$

From these two expressions, we get

$$[\mathrm{OH^-}] = [\mathrm{HCN}]$$

The base reaction of $\mathrm{CN^-}$ is

$$\mathrm{CN^- + H_2O \rightleftharpoons HCN + OH^-} \qquad (3)$$

Hence, $$K_\mathrm{b} = \frac{[\mathrm{HCN}][\mathrm{OH^-}]}{[\mathrm{CN^-}]}$$

Using Eq. (3), we get

$$K_\mathrm{b} = \frac{[\mathrm{HCN}]^2}{[\mathrm{CN^-}]} \quad \text{or} \quad [\mathrm{HCN}] = \sqrt{K_\mathrm{b}[\mathrm{CN^-}]}$$

Substituting this in Eq. (1), we get

$$[\mathrm{Ag^+}] = [\mathrm{CN^-}] + \sqrt{K_\mathrm{b}[\mathrm{CN^-}]}$$

With the use of solubility-product expression of AgCN, this becomes

$$[\mathrm{Ag^+}] = \frac{K_\mathrm{s}}{[\mathrm{Ag^+}]} + \left(\frac{K_\mathrm{b}\,K_\mathrm{s}}{[\mathrm{Ag^+}]}\right)^{1/2}$$

or $$[\mathrm{Ag^+}]^2 = K_\mathrm{s} + (K_\mathrm{b}\,K_\mathrm{s}\,[\mathrm{Ag^+}])^{1/2} \qquad (4)$$

Assuming $K_\mathrm{s} << (K_\mathrm{b}\,K_\mathrm{s}\,[\mathrm{Ag^+}])^{1/2}$, we get

$$[\mathrm{Ag^+}]^2 = (K_\mathrm{b}K_\mathrm{s}\,[\mathrm{Ag^+}])^{1/2}$$

or $$[\mathrm{Ag^+}]^4 = K_\mathrm{b}K_\mathrm{s}\,[\mathrm{Ag^+}]$$

or $$[\mathrm{Ag^+}] = (K_\mathrm{b}K_\mathrm{s})^{1/3}$$

Substituting the values of K_b and K_s, we get

$$\begin{aligned}[\mathrm{Ag^+}] &= [(1.7 \times 10^{-5}\ \mathrm{M})\ (2.3 \times 10^{-16}\ \mathrm{M^2})]^{1/3} \\ &= 1.58 \times 10^{-7}\ \mathrm{M}\end{aligned}$$

In order to check the assumption we made, let us calculate $\sqrt{K_\mathrm{b}K_\mathrm{s}[\mathrm{Ag^+}]}$ and then compare it with K_s

$$\begin{aligned}\sqrt{K_\mathrm{b}K_\mathrm{s}[\mathrm{Ag^+}]} &= [(1.7\times10^{-5}\ \mathrm{M})\,(2.3\times10^{-16}\ \mathrm{M^2})\,(1.58\times10^{-7}\ \mathrm{M})]^{1/2} \\ &= 2.48\times10^{-14}\ \mathrm{M^2}\end{aligned}$$

which is about 100 times greater than K_s justifying the assumption made to simplify the computations.

(Alternatively, Eq. (4) may be solved for $[\mathrm{Ag^+}]$ by the successive approximation method with initial concentration of $\mathrm{Ag^+}$ equal to $\sqrt{K_\mathrm{s}}$.)

Common-ion Effect on Solubility

The common-ion present in the solution decreases the solubility of a given compound, e.g., the solubility of $\mathrm{BaSO_4}$ in $\mathrm{Na_2SO_4}$ solution is smaller than that in an aqueous solution.

Example 4.32.7 At 25 °C, a saturated solution of $BaSO_4$ is 3.9×10^{-5} M. What is its solubility in 0.1 M Na_2SO_4 solution?

Solution In an aqueous solution $[Ba^{2+}] = [SO_4^{2-}] = 3.9 \times 10^{-5}$ M

$$K_s(BaSO_4) = [Ba^{2+}]\,[SO_4^{2-}] = (3.9 \times 10^{-5}\ M)^2 = 1.5 \times 10^{-9}\ M^2$$

In 0.1 M Na_2SO_4 solution, the concentration of $SO_4^{2-} = 0.1$ M. Hence,

$$[Ba^{2+}] = \frac{K_s(BaSO_4)}{[SO_4^{2-}]} = \frac{1.5 \times 10^{-9}\ M^2}{(0.1\ M)} = 1.5 \times 10^{-8}\ M$$

Thus, the solubility of $BaSO_4$ is reduced from 3.9×10^{-5} M to 1.5×10^{-8} M by the common-ion effect.

Example 4.32.8 Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol L^{-1} of ammonium chloride and 0.05 mol L^{-1} of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution. Given: $K_b^\circ(NH_4OH) = 1.8 \times 10^{-5}$, $K_s^\circ(Mg(OH)_2) = 8.9 \times 10^{-12}$ and $K_s^\circ(Al(OH)_3) = 6 \times 10^{-32}$.

Solution To start with, we have a buffer solution containing 0.25 mol L^{-1} of NH_4Cl and 0.05 mol L^{-1} of NH_4OH. In the equilibrium reaction

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-; \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

we have $[NH_4OH] = 0.05$ mol L^{-1} and $[NH_4^+] = 0.25$ mol L^{-1}

The dissolution of $Mg(OH)_2$ and $Al(OH)_3$ generates extra OH^- ions which causes the replacement of NH_4^+ by NH_4OH in the buffer solution. In the final solution, we will have

$$\text{(i)}\ \underset{c_1+\alpha}{NH_4OH} \rightleftharpoons \underset{c_2-\alpha}{NH_4^+} + \underset{z}{OH^-}; \qquad K_b = 1.8 \times 10^{-5}\ M$$

where $c_1 = 0.05$ mol L^{-1} and $c_2 = 0.25$ mol L^{-1}.

The concentration of NH_4^+ ions replaced by NH_4OH is α and z is the final concentration of OH^- in the solution. Besides this equilibrium, we also have

$$\text{(ii)}\ Mg(OH)_2 \rightleftharpoons \underset{x}{Mg^{2+}} + \underset{z}{2OH^-}; \qquad K_{s1} = 8.9 \times 10^{-12}\ M^3$$

$$\text{(iii)}\ Al(OH)_3 \rightleftharpoons \underset{y}{Al^{3+}} + \underset{z}{3OH^-}; \qquad K_{s2} = 6 \times 10^{-32}\ M^4$$

Finally, $$[\mathrm{Mg}^{2+}] = \frac{K_s(\mathrm{Mg(OH)_2})}{[\mathrm{OH}^-]^2} = \frac{8.9\times10^{-12}\ \mathrm{M}^3}{(1.45\times10^{-5}\ \mathrm{M})^2} = 0.0423\ \mathrm{M}$$

$$[\mathrm{Al}^{3+}] = \frac{K_s(\mathrm{Al(OH)_3})}{[\mathrm{OH}^-]^3} = \frac{6\times10^{-32}\ \mathrm{M}^4}{(1.45\times10^{-5}\ \mathrm{M})^3} = 1.97\times10^{-17}\ \mathrm{M}$$

Precipitation and Solubility Product

The numerical value of solubility product of a salt provides its maximum solubility in water. *For a solution of a salt at a specified concentration, the product of the concentrations of the ions, each raised to the proper power, is called the ionic product. Thus, for a saturated solution in equilibrium with excess solid, the ionic product is equal to its solubility product.* If the ionic product of the solution is less than the corresponding solubility product, it means that the solution is unsaturated and thus more salt can dissolve in it. On the other hand, if the ionic product exceeds the solubility product, the solution is holding more salt that can dissolve in it; therefore, precipitation takes place which continues till the ionic product becomes equal to the solubility product.

Example 4.32.9

Will a precipitate form if 20 cm^3 of 0.01 M $AgNO_3$ and 20 cm^3 of 0.000 4 M NaCl are mixed? Given: $K_s(\mathrm{AgCl}) = 1.7 \times 10^{-10}\ \mathrm{M}^2$.

Solution

Total volume of the solution after mixing is 40 cm^3, thus the concentrations of ions in the solution are decreased to half the values, i.e.

$$[\mathrm{Ag}^+] = 5.0 \times 10^{-3}\ \mathrm{M} \quad \text{and} \quad [\mathrm{Cl}^-] = 2.0 \times 10^{-4}\ \mathrm{M}$$

The ionic product is

$$[\mathrm{Ag}^+]\,[\mathrm{Cl}^-] = (5.0 \times 10^{-3}\ \mathrm{M})\ (2.0 \times 10^{-4}\ \mathrm{M}) = 1.0 \times 10^{-6}\ \mathrm{M}^2$$

This ionic product is larger than K_s (= $1.7 \times 10^{-10}\ \mathrm{M}^2$) and thus precipitation of AgCl will occur.

ample 4.32.10

At 25 °C, will a precipitate of $Mg(OH)_2$ form in a 0.000 1 M solution of $Mg(NO_3)_2$ if pH of the solution is adjusted to 9.0? ($K_s(\mathrm{Mg(OH)_2}) = 8.9 \times 10^{-12}\ \mathrm{M}^3$). At what minimum value of pH will precipitation start?

lution

If pH = 9.0, $[\mathrm{H_3O^+}] = 1.0 \times 10^{-9}$ M, then $[\mathrm{OH}^-] = 1.0 \times 10^{-5}$ M

The ionic product of $Mg(OH)_2$ in the solution

$$= [\mathrm{Mg}^{2+}]\,[\mathrm{OH}^-]^2 = (1.0 \times 10^{-4}\ \mathrm{M})\ (1.0 \times 10^{-5}\ \mathrm{M})^2$$

$$= 1.0 \times 10^{-14}\ \mathrm{M}^3$$

Since this value is smaller than $8.9 \times 10^{-12}\ M^3$, no precipitate will form. The concentration of OH^- required to precipitate Mg^{2+} from the solution is

$$\sqrt{\frac{K_s}{[Mg^{2+}]}} = \sqrt{\frac{8.9 \times 10^{-12}\ M^3}{1.0 \times 10^{-4}\ M}} = \sqrt{8.9 \times 10^{-8}\ M^2}$$
$$= 2.983 \times 10^{-4}\ M$$

Thus, $\quad pOH = -\log\{[OH^-]/M\} = -\log(2.983 \times 10^{-4}) = 3.54$

and hence, $pH = 14 - pOH = 10.46$

Preferential Precipitation of Salts

Frequently, a solution contains more than one ion capable of forming precipitates with another ion which is added to the solution. For example, in a solution containing Cl^-, Br^-, and I^- ions, if Ag^+ ions are added, then out of the three, the least soluble silver salt is precipitated first. If the addition of Ag^+ ions is continued, eventually a stage is reached when the next lesser soluble salt starts precipitating along with the least soluble salt and so on. If the stoichiometry of the precipitated salts is the same, then the salt with the minimum solubility product (and hence also the minimum solubility) will precipitate first followed by the salt of next higher solubility product and so on.

If the stoichiometry of the precipitated salts is not the same, then, from the solubility product data alone, we cannot predict which ion will precipitate first. Take, for example, a solution containing Cl^- and CrO_4^{2-}. Both these ions form precipitates with Ag^+. Though the solubility product of AgCl is larger than that of Ag_2CrO_4, yet it is AgCl (lesser soluble) which precipitates first when Ag^+ ions are added to the solution. In order to predict which ion (Cl^- or CrO_4^{2-}) precipitates first, we have to calculate the concentration of Ag^+ ions needed to start the precipitation through the solubility product data and the given concentration of Cl^- or CrO_4^{2-}. Since square root is involved in the expression for computing Ag^+ for silver chromate, the quantity of Ag^+ needed to start the precipitation of CrO_4^{2-} is larger than that for Cl^-. Hence, as $AgNO_3$ is added to the solution, the minimum of the two concentrations of Ag^+ to start the precipitation will be reached first and thus the corresponding ion (Cl^- in this case) will be precipitated in preference to the other. During the course of precipitation, concentration of Cl^- decreases and the corresponding concentration of Ag^+ to start the precipitation increases. Its concentration eventually becomes equal to the value required for the precipitation of CrO_4^{2-}. At this stage, practically whole of the Cl^- ions has been precipitated. The addition of more of $AgNO_3$ causes the precipitation of both the ions together.

The following problems illustrate the principle of preferential precipitation.

Example 4.32.11 A solution is 0.1 M in Cl$^-$, 0.1 M in Br$^-$ and 0.1 M in I$^-$. Solid AgNO$_3$ is added to this solution. Assuming that the addition of AgNO$_3$ does not change the answer the following:

(a) What concentration of Ag$^+$ ions will be required to start precipitation of the three ions?

(b) Which ion will precipitate first?

(c) What will be the concentration of this ion when the second ion starts precip

(d) What will be the concentration of both the ions when the third ion precipitating? Given:

$$K_s(\text{AgCl}) = 1.7 \times 10^{-10}\ \text{M}^2;$$

$$K_s(\text{AgBr}) = 5.0 \times 10^{-13}\ \text{M}^2$$

and $$K_s(\text{AgI}) = 8.5 \times 10^{-17}\ \text{M}^2$$

Solution (a) The concentration of Ag$^+$ ions to start the precipitation can be computed solubility product data.

Since $K_s = [\text{Ag}^+]\,[\text{X}^-]$, therefore

$$[\text{Ag}^+] = \frac{K_s}{[\text{X}^-]}$$

(where X$^-$ = Cl$^-$, Br$^-$

For chloride: $$[\text{Ag}^+] = \frac{1.7 \times 10^{-10}\ \text{M}^2}{(0.1\ \text{M})} = 1.7 \times 10^{-9}\ \text{M}$$

For bromide: $$[\text{Ag}^+] = \frac{5.0 \times 10^{-13}\ \text{M}^2}{(0.1\ \text{M})} = 5.0 \times 10^{-12}\ \text{M}$$

For iodide: $$[\text{Ag}^+] = \frac{8.5 \times 10^{-17}\ \text{M}^2}{(0.1\ \text{M})} = 8.5 \times 10^{-16}\ \text{M}$$

(b) Since [Ag$^+$] required to precipitate I$^-$ is minimum, therefore it is AgI which first. The same conclusion can also be reached from the solubility product data.

(c) The second ion Br$^-$ will be precipitated only when [Ag$^+$] ion in the solution reached to 5.0×10^{-12} M. Therefore, the concentration of remaining I$^-$ is

$$[\text{I}^-] = \frac{K_s(\text{AgI})}{[\text{Ag}^+]} = \frac{8.5 \times 10^{-17}\ \text{M}^2}{(5.0 \times 10^{-12}\ \text{M})} = 1.7 \times 10^{-5}\ \text{M}$$

(d) The third ion Cl$^-$ will be precipitated only when [Ag$^+$] in the solution has to 1.7×10^{-9} M. Therefore, the concentrations of remaining I$^-$ and Br$^-$ are:

$$[\text{I}^-] = \frac{K_s(\text{AgI})}{[\text{Ag}^+]} = \frac{8.5 \times 10^{-17}\ \text{M}^2}{(1.7 \times 10^{-9}\ \text{M})} = 5.0 \times 10^{-8}\ \text{M}$$

Percentage of I^- remaining in the solution when AgBr starts precipitating

$$= \frac{(1.7 \times 10^{-5}\ \mathrm{M})}{(0.1\ \mathrm{M})} \times 100 = 1.7 \times 10^{-2} = 0.017$$

Percentage of Br^- remaining in the solution when AgCl starts precipitating

$$= \frac{(3.0 \times 10^{-4}\ \mathrm{M})}{(0.1\ \mathrm{M})} \times 100 = 3.0 \times 10^{-1} = 0.3$$

Thus, we see that the precipitation of one ion is almost complete when the second starts precipitating. With a suitable method (*potentiometrically* or *conductometrically*), the concentrations of the individual ions can be determined without involving much error.

4.32.12

A solution is 0.1 M in Cl^- and 0.001 M in CrO_4^{2-}. If solid $AgNO_3$ is gradually added to this solution, which will precipitate first, AgCl or Ag_2CrO_4? Assume that the addition causes no change in volume. Given:

$$K_s(\mathrm{AgCl}) = 1.7 \times 10^{-10}\ \mathrm{M}^2$$

and $$K_s(\mathrm{Ag_2CrO_4}) = 1.9 \times 10^{-12}\ \mathrm{M}^3$$

When a precipitate begins to form, the ionic product of the substance just exceeds the corresponding K_s. Therefore, we calculate the $[Ag^+]$ needed to precipitate AgCl and Ag_2CrO_4:

$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-}$$

$$K_s = [\mathrm{Ag^+}]\,[\mathrm{Cl^-}] = 1.7 \times 10^{-10}\ \mathrm{M}^2$$

$$[\mathrm{Ag^+}] = \frac{1.7 \times 10^{-10}\ \mathrm{M}^2}{0.1\ \mathrm{M}} = 1.7 \times 10^{-9}\ \mathrm{M}$$

$$\mathrm{Ag_2CrO_4} \rightleftharpoons 2\mathrm{Ag^+} + \mathrm{CrO_4^{2-}}$$

$$K_s = [\mathrm{Ag^+}]^2\,[\mathrm{CrO_4^{2-}}] = 1.9 \times 10^{-12}\ \mathrm{M}^3$$

$$[\mathrm{Ag^+}] = \sqrt{\frac{1.9 \times 10^{-12}\ \mathrm{M}^3}{0.001\ \mathrm{M}}} = 4.4 \times 10^{-5}\ \mathrm{M}$$

Since the amount of Ag^+ needed to precipitate AgCl is less, this value will, therefore, be reached first in the solution and hence it is the AgCl which will be precipitated first.

ple 4.32.13

In Example 4.32.12, what will be the concentration of Cl^- when Ag_2CrO_4 begins to precipitate? At this point, what percentage of the Cl^- originally present remains in the solution?

Ag^+ required for the precipitation of Ag_2CrO_4 is 4.4×10^{-5} M. At this point, the concentration of Cl^- ion in the solution can be calculated from K_s(AgCl).

$$K_s = [\mathrm{Ag^+}]\,[\mathrm{Cl^-}] = 1.7 \times 10^{-10}\ \mathrm{M}^2$$

Therefore,

From Example 4.32.13 it may be concluded that virtually whole [illegible] precipitated when CrO_4^{2-} ion starts precipitating. Thus, the use of [illegible] as the precipitating indicator in the titration of Cl^- versus Ag^+ is [illegible] colour of Ag_2CrO_4 is red and hence the end-point of the above titration [illegible] by the appearance of a red precipitate. In actual practice, the concentration [illegible] CrO_4^{2-} used is much less and hence a higher concentration of Ag^+ is [illegible] start precipitation of Ag_2CrO_4. Consequently, much less of the Cl^- will [illegible] untitrated when Ag_2CrO_4 begins to precipitate.

Qualitative Analysis Qualitative analysis of cations is largely based on the principle of [illegible] product. Cations are separated into six groups depending upon the [illegible] of their salts. A brief description of the scheme of qualitative analysis [illegible] below.

Group I

Insoluble chlorides Only Ag^+, Hg_2^{2+} and Pb^{2+} form insoluble chlorides [illegible] they have low values of solubility products.

$$K_s(PbCl_2) = 1.6 \times 10^{-5}\ M^3$$

$$K_s(Hg_2Cl_2) = 1.1 \times 10^{-18}\ M^3$$

$$K_s(AgCl) = 1.7 \times 10^{-10}\ M^2$$

Group II

Insoluble sulphides in acidic medium The sulphide-ion concentration [illegible] solution that has been saturated with H_2S is given by

$$[S^{2-}] = \frac{K_1K_2\,[H_2S]}{[H^+]^2} = \frac{1.1 \times 10^{-21}\ M^2}{[H^+]^2}[H_2S]$$

In an acidic solution, the $[H^+]$ is large and thus $[S^{2-}]$ is low. For [illegible] in 10 cm^3 of a saturated H_2S solution that has been made 0.3 M in H^+ [illegible] approximately seven S^{2-} ions. Thus, when H_2S is passed in acidic [illegible] a solution containing several cations, only for least soluble sulphides [illegible] Bi^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Sb^{3+}, As^{3+} and Sn^{2+}, the ionic products become [illegible] than the corresponding solubility products which, therefore, are precipitated. [illegible] other cations such as Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}, etc., the ionic products [illegible] smaller than their respective solubility products and thus are not precipitated, i.e. their sulphides are soluble.

It is possible to compute the minimum pH of the solution at which [illegible] cation will form an insoluble sulphide when the solution is saturated with [illegible] This can be computed as follows:

The minimum concentration of sulphide ion necessary to start [illegible] precipitation of cation M^{2+} is

$$[S^{2-}] = \frac{K_s(MS)}{[M^{2+}]}$$

The hydrog [illegible] (maximum) of a solution having the above minimum $[S^{2-}]$ can be computed using the expression

$$[H^+] = \sqrt{\frac{(1.1\times10^{-21}\ M^2)[H_2S]}{[S^{2-}]}}$$

In an aqueous solution that is in equilibrium with H_2S gas at 101.325 kPa, $[H_2S] = 0.1$ M; hence

$$[H^+] = \sqrt{\frac{(1.1\times10^{-22}\ M^3)}{[S^{2-}]}}$$

$$= \sqrt{\frac{(1.1\times10^{-22}\ M^3)[M^{2+}]}{K_s(MS)}}$$

The minimum $[S^{2-}]$ and the maximum $[H^+]$ along with pH values for various sulphides ($[M^{2+}] = 0.01$ M) are being given in Table 4.32.2.

Table 4.32.2 Condition for the Precipitation of Various Sulphides

Solid		K_s^o	$[S^{2-}]_{min}/M$	$[H^+]_{max}/M$	*Min pH*
HgS	Gp. II	3.0×10^{-53}	3×10^{-51}	$\approx 2 \times 10^{14}$	≈ -14.3
CuS		4.0×10^{-38}	4×10^{-36}	$\approx 5 \times 10^{6}$	≈ -6.7
PbS		1.0×10^{-29}	1.0×10^{-27}	$\approx 3 \times 10^{2}$	≈ -2.5
SnS		8.0×10^{-29}	8.0×10^{-27}	$\approx 1 \times 10^{2}$	≈ -2.0
Sb_2S_3		10^{-80}	10^{-25}	$\approx 3 \times 10$	≈ -1.5
Bi_2S_3		1.6×10^{-72}	2.5×10^{-23}	≈ 2	≈ -0.3
CdS		1.0×10^{-28}	1.0×10^{-26}	$\approx 1.0 \times 10^{2}$	≈ -2.0
CoS		7×10^{-23}	7×10^{-21}	≈ 0.13	≈ 0.9
NiS		3×10^{-21}	3×10^{-19}	$\approx 2 \times 10^{-2}$	≈ 1.7
ZnS		2.5×10^{-22}	2.5×10^{-18}	$\approx 6 \times 10^{-2}$	≈ 1.2
FeS		1.0×10^{-19}	1.0×10^{-17}	$\approx 3 \times 10^{-3}$	≈ 2.5
MnS		5.6×10^{-16}	5.6×10^{-14}	$\approx 4 \times 10^{-5}$	≈ 4.4

The data in Table 4.32.2 reveal how cations of Group II could be separated from the rest of cations. The concentration of H^+ less than that listed (or pH greater than the listed value) yields sufficient sulphide ions to cause precipitation for each case. Thus, if in an acidic solution containing $[H^+]$ between 0.13 to 2 M (or pH < 0.9) H_2S is passed, only sulphides of Group II are precipitated.

Insoluble hydroxides in ammoniacal solution containing ammonium chloride

The concentration of OH^- in an ammoniacal solution decreases when NH_4Cl is added to it, because of the common-ion effect. Thus only for least soluble hydroxides of Fe^{3+}, Al^{3+} and Cr^{3+}, the ionic products exceed the corresponding solubility products. Therefore, only these three ions are precipitated; for other cations (Co^{2+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, etc.), the respective ionic product is smaller than the corresponding solubility product and thus they remain in the solution. In fact, cations such as Co^{2+}, Ni^{2+}, Mg^{2+}, etc., form complexes with ammonia and thus the amounts of free ions in the solution are decreased to a very large extent.

Consequently, a larger concentrations of OH^- is required to ions from the solution as compared to those required for the (*see* Section 4.33).

Group IV

Insoluble sulphides in ammoniacal medium In ammoniacal concentration of S^{2-} becomes larger when H_2S is passed through This is because of the formation of ammonium sulphide. The Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} are precipitated here.

Group V

Insoluble carbonates in ammoniacal solution containing ammonium The carbonates of Ba^{2+}, Ca^{2+} and Sr^{2+} are precipitated here, while not precipitate due to the low concentration of CO_3^{2-} caused by equilibrium

$$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$$

to the right side in the presence of ammonium salt.

Group VI

This contains the remaining cations, viz., Mg^{2+} and K^+.

Example 4.32.14

A solution that is 0.30 M in H^+, 1.0 M in Pb^{2+} and 1.0 M in Fe^{2+} is saturated should PbS and/or FeS precipitate? The K_s of PbS is 7×10^{-29} M^2 and K_s of is 4×10^{-19} M^2.

Solution

For any saturated solution of H_2S

$$[H^+]^2 [S^{2-}] = 1.1 \times 10^{-22}\ M^3$$

Since this solution is 0.30 M in H^+, therefore,

$$(0.3\ M)^2 [S^{2-}] = 1.1 \times 10^{-22}\ M^3$$

$$[S^{2-}] = 1.2 \times 10^{-21}\ M$$

Ionic product of either of the two sulphides

$$= (1.0\ M)(1.2 \times 10^{-21}\ M) = 1.2 \times 10^{-21}\ M^2$$

This ionic product is greater than the K_s of PbS; therefore PbS will precipitate. However, the ionic product is less than the K_s of FeS; the solubility of FeS is not exceeded; no FeS precipitate will form.

Example 4.32.15

A solution that is 0.1 M in Cd^{2+} and 0.1 M in H^+ is saturated with H_2S. What concentration of Cd^{2+} remains in solution after CdS has precipitated? The K_s of CdS is

Solution

For each Cd^{2+} ion precipitated, two H^+ ions are added to the solution according to the following reaction:

$$Cd^{2+}(aq) + H_2S(aq) \rightleftharpoons CdS(s) + 2H^+(aq)$$

We shall assume that virtually all Cd^{2+} ions precipitate as CdS. Hence, the precipitation introduces 0.20 mol of H^+ per dm^3 of solution, and the final H^+ is 0.30 M. The

$$[S^{2-}] = \frac{1.1 \times 10^{-22}\ M^3}{[H^+]^2} = \frac{1.1 \times 10^{-22}\ M^3}{(0.30\ M)^2}$$

$$= 1.22 \times 10^{-21}\ M$$

The concentration of Cd^{2+} after CdS has precipitated may be derived from the K_s of CdS:

$$[Cd^{2+}]\,[S^{2-}] = 1.0 \times 10^{-28}\ M^2$$

or $$[Cd^{2+}] = \frac{1.0 \times 10^{-28}\ M^2}{1.22 \times 10^{-21}\ M} = 8.2 \times 10^{-8}\ M$$

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mple 4.32.16 A solution containing zinc and manganese ions each at a concentration of 0.01 M is saturated with H_2S. If the K_s of ZnS is $1.0 \times 10^{-22}\ M^2$ and the K_s of MnS is $5.6 \times 10^{-16}\ M^2$, what is the pH at which the manganous sulphide will form a precipitate? Under these conditions, what will be the concentration of remaining zinc ions? Given: $[H_2S] = 0.10$ M.

Solution The minimum of concentration S^{2-} ion to start the precipitation is obtained from the K_s with $[Mn^{2+}] = 0.01$ M. Therefore, we have

$$[S^{2-}] = \frac{K_s(MnS)}{[Mn^{2+}]} = \frac{5.6 \times 10^{-16}\ M^2}{(0.01\ M)} = 5.6 \times 10^{-14}\ M$$

The H^+ concentration of the solution having the above $[S^{2-}]$ can be computed from the expression of H_2S equilibrium:

$$\frac{[H^+]^2\,[S^{2-}]}{[H_2S]} = \frac{[H^+]^2\,(5.6 \times 10^{-14}\ M)}{(0.10\ M)} = 1.1 \times 10^{-21}\ M^2$$

This gives

$$[H^+] = 4.43 \times 10^{-5}\ M \quad \text{or} \quad pH = 4.35$$

If the $[H^+] > 4.43 \times 10^{-5}$ M, then the $[S^{2-}]$ will be less than 5.6×10^{-14} M and MnS will no longer precipitate from the solution.

The concentration of Zn^{2+} ion remaining in the solution can be calculated from the solubility product of ZnS:

$$[Zn^{2+}] = \frac{K_s(ZnS)}{[S^{2-}]} = \frac{1.0 \times 10^{-22}\ M^2}{(5.6 \times 10^{-14}\ M)} = 1.79 \times 10^{-9}\ M$$

Thus, by properly adjusting the $[H^+]$ in the solution, it is possible to precipitate effectively all of zinc ions from the solution without precipitating any Mn^{2+} ion.

EQUILIBRIA INVOLVING COMPLEX IONS

A complex ion is an aggregate consisting of a metal ion surrounded by ligand
The latter may be an ion, molecule or a combination of the two. An essenti
feature of a ligand is that it must have an unshared pair of electrons with whi
l ion. A few examples are

$:\ddot{\underset{..}{Cl}}:^-$