EWC 105
Environmental Chemistry

Lecture 13

Instructor

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Lecture Outlines

Topics	Sub-Topics	References
Solids Dissolution and Precipitation	• Application of dissolution-precipitation principle • Dissolution- precipitation kinetics • Solubility of salts • Solubility of oxides and hydoxides	**1. *Chemistry for Environmental Engineering*** Authors: Clair N. Sawyer, Perry L. McCarty and Gene F. Parkin

Solid Dissolution - Precipitation

- Minerals in rock dissolve in or react with water.

- Approximately 0.5g/L of weathered continental rock is transported by rivers to oceans, roughly 80% as suspended solids and 20% as dissolved solids.

Application of Dissolution – Precipitation Principle

- Composition of natural water systems

- Drinking water treatment
  - ✓ Lime-soda softening (Ca and Mg removal by precipitation)
  - ✓ Scale formation (deposits of $CaCO_3$)
  - ✓ Iron and Mn removal
  - ✓ Coagulation with metal salts (for As removal)

- Wastewater treatment
  - ✓ Phosphorus removal
  - ✓ Heavy metal removal

Kinetics of Dissolution – Precipitation

$$A_mB_n\,(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} m\,A^{n+} + n\,B^{m-}$$

- The solubility is characterized by solubility product as follows:

$$K_{so} = \{A^{n+}\}^m \{B^{m-}\}^n$$

- Example 1: $CaCO_3\,(s) = Ca^{2+} + CO_3^{2-}$

$$K_{so} = \{Ca^{2+}\}\{CO_3^{2-}\}$$

- Example 2: $Ag_2CrO_4\,(s) = 2Ag^{2+} + CrO_4^{2-}$

$$K_{so} = \{Ag^{+}\}^2\{CrO_4^{2-}\}$$

Kinetics of Dissolution – Precipitation

K_{so} values for some common salts:

- $CaSO_4$ ($pK_{so} = 4.6$), $SrSO_4$ ($pK_{so} = 6.2$)
- $BaSO_4$ ($pK_{so} = 9.7$), $AgCl$ ($pK_{so} = 10.0$)
- $PdCl_2$ ($pK_{so} = 4.8$), Ag_2CrO_4 ($pK_{so} = 12.0$)
- MgF_2 ($pK_{so} = 8.1$), CaF_2 ($pK_{so} = 10.3$)

Solubility of Salts

- If a salt is dissolved in pure water (distilled water), the solubility may be given by the electroneutrality requirement, considering $(H^+) = (OH^-)$

- For example:

✓ For $CaSO_4$ (s) : $(Ca^{2+}) = (SO_4^{2-})$

✓ For MgF_2 (s) : $2(Mg^{2+}) = (F^-)$

✓ For Ag_2CrO_4 (s) : $(Ag^+) = 2(CrO_4^{2-})$

Solubility of Salts

Example:

$CaSO_4(s)$ ($pK_{so} = 4.6$) is in equilibrium with water. Calculate the concentration of Ca^{2+} and SO_4^{2-}.

Solution:

$$CaSO_4\ (s) = Ca^{2+} + SO_4^{2-}$$

Now, electroneutrality equation is

$$2\ (Ca^{2+}) + (H^+) = 2(SO_4^{2-}) + (OH^-)$$

Considering, for pure water, $(H^+) = (OH^-)$, then we have,

$$(Ca^{2+}) = (SO_4^{2-})$$

Then, $(Ca^{2+}) = (Ca^{2+}) = 10^{-4.6}$

Therefore, $(Ca^{2+}) = (SO_4^{2-}) = 10^{-2.3}$

However, such simple solutions are seldom encountered.

Solubility of Oxides and Hydroxides

$$Me(OH)_2\ (s) = Me^{2+} + 2OH^- \ldots\ldots\ldots (1)$$

$$MeO\ (s) + H_2O = Me^{2+} + 2OH^- \ldots\ldots\ldots (2)$$

$$\text{Therefore, } K_{so} = (Me^{2+})\ (OH^-)^2 \ldots\ldots\ldots (3)$$

Sometimes it is more appropriate and convenient to express solubility in terms of reactions with H^+. Thus equations (1) and (2) can be written as follows:

$$Me(OH)_2\ (s) + 2H^+ = Me^{2+} + 2H_2O \ldots\ldots\ldots (4)$$

$$MeO\ (s) + 2H^+ = Me^{2+} + H_2O \ldots\ldots\ldots (5)$$

In this case, solubility product is given by:

$$*K_{so} = (Me^{2+}) / (H^+)^2 \ldots\ldots\ldots (6)$$

Solubility of Oxides and Hydroxides

Previously we got,

$$K_{so} = (Me^{2+})\,(OH^{-})^2 \ldots\ldots\ldots (3)$$

Now, $(Me^{2+}) = K_{so} / (OH^{-})^2$

$$(Me^{2+}) = K_{so} \times K_w^2 / (H^{+})^2$$

Therefore, $\log (Me^{2+}) = \log K_{so} + 2\,pK_w - 2\,pH \ldots\ldots\ldots (7)$

Again, $^*K_{so} = (Me^{2+}) / (H^{+})^2 \ldots\ldots\ldots (6)$

Therefore, $\log (Me^{2+}) = \log {}^*K_{so} - 2\,pH \ldots\ldots\ldots (8)$

Now, $d \log (Me^{2+}) / d\,pH = -2$,

i.e., a plot of $\log (Me^{2+})$ vs pH will have a slope of -2.

Solubility of Oxides and Hydroxides

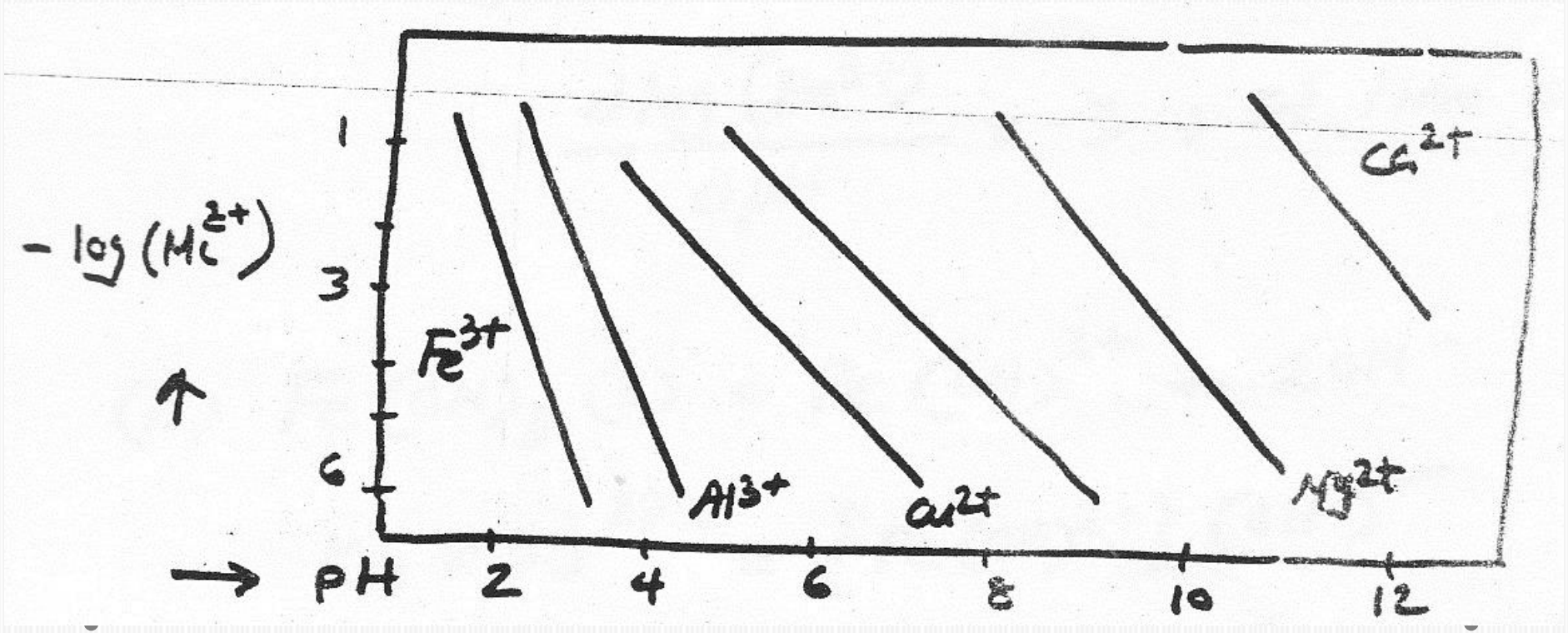
Now the general expressions are:

$$\log (Me^{z+}) = \log K_{so} + z\, pK_w - z\, pH \ldots\ldots\ldots (9)$$

$$\log (Me^{z+}) = \log {}^{*}K_{so} - z\, pH \ldots\ldots\ldots (10)$$

Now, $d \log (Me^{2+}) / d\, pH = -z \ldots\ldots\ldots (11)$

i.e., a plot of $\log (Me^{z+})$ vs pH will have a slope of -z.



Solubility of Oxides and Hydroxides

Some general observations from Log (Me^{z+}) vs pH plot shown before are as follows:

- As pH is raised, at first Fe^{3+} will precipitate, then Al^{3+} and so on.

- Precipitation of Mg^{2+} (and also Ca^{2+}) needs a pH of about 12 (even higher pH needed for Ca^{2+}). To raise pH, the cheapest available source is lime, $Ca(OH)_2$, used in water softening process.

- For water softening (hardness removal), we have to remove Ca^{2+} and Mg^{2+}. Addition of lime raises pH and Mg^{2+} is removed as $Mg(OH)_2$. At the same time Ca^{2+} is precipitated as $CaCO_3$ (s). If there is not enough CO_3^{2-}, soda ash (Na_2CO_3) is added (lime-soda softening process)