Chem 115

Instrumental Analysis and Bioanalytical Chemistry

Lecture 4: Concepts and analysis

What's in this lecture?

- Solubility calculations
- Solution activity

Where's the water?

$$2\ H_2O \leftrightarrow H_3O^+ + OH^-$$

Why:

$$K_w = [H_3O^+][OH^-]$$

Not:

$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Solubility in pure water

How many grams of $Ba(IO_3)_2$ can be dissolved in 500 mL of water at 25°C?

The common ion effect

What is the molar solubility of $Ba(IO_3)_2$ in a solution that is 2.00×10^{-2} M in $Ba(NO_3)_2$?

Large errors can occur from poor assumptions

What is the hydronium ion concentration in a solution that is 2.0×10^{-4} M in aniline hydrochloride?

Method of successive approximations

An iterative process that is suited for using computers to solve cubic (or higher order) equations.

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Multiple equilibria can occur

What is the concentration of Ba^{2+} when water is saturated with $BaSO_4$?

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

The equilibrium state, revisited

$$H_3AsO_4 + 3I^- + 2H^+ \leftrightarrow H_3AsO_3 + I_3^- + H_2O$$

After reaching equilibrium, what happens if we add $NaClO_4$?

$$\text{ionic strength} = \mu = \tfrac{1}{2}([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + ...)$$

where [A], [B], & [C] represent the molar concentrations of ions A, B, and C, and Z_A, Z_B, and Z_C are their charges.

The equilibrium state, revisited

If:

wW + xX ↔ yY + zZ

Then:

$$K = \frac{[Y]^y [Z]^z}{[W]^w [X]^x}$$

$$K = \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$$

Activity coefficients

$$K = \frac{a_{\mathrm{Y}}^{y} a_{\mathrm{Z}}^{z}}{a_{W}^{w} a_{\mathrm{X}}^{x}}$$

$$a_X = \gamma_x [X]$$

$$K = \frac{\gamma_{Y}^{y} \gamma_{Z}^{z} [Y]^y [Z]^z}{\gamma_{W}^{w} \gamma_{X}^{x} [W]^w [X]^x} = \frac{\gamma_{W}^{w} \gamma_{X}^{x}}{\gamma_{Y}^{y} \gamma_{Z}^{z}} K'$$

Activity coefficients properties

1. The activity coefficient is a measure of the effectiveness with which that species influences an equilibrium in which it is a participant.
2. In solutions with low concentration, the activity coefficient depends only upon the ionic strength.
3. For a given ionic strength, the activity coefficient of an ion departs farther from unity as the charge carried by the species increases.
4. At any given ionic strength, the activity coefficients of ions of the same charge are approximately equal.
5. The activity coefficient of a given ion describes its effective behavior in all equilibria in which it participates.

Debye-Hückel equation

$$-log\gamma_X = \frac{0.51Z_X^2\sqrt{\mu}}{1 + 3.3\alpha_X\sqrt{\mu}}$$

where

μ = ionic strength of the solution

Z_x = charge on species X

γ_x = activity coefficient of the species X

α_x = effective diameter of the hydrated ion X in nanometers

Activity coefficients at 25˚ C

Ion	α_x, nm	0.001	0.005	0.01	0.05	0.1
H_3O^+	0.9	0.967	0.933	0.914	0.86	0.83
Li^+, $C_6H_5COO^-$	0.6	0.965	0.929	0.907	0.84	0.80
Na^+, IO_3^-, HSO_3^-, $H_2PO_4^-$, $H_2AsO_4^-$, OAc^-	0.4	0.964	0.928	0.902	0.82	0.78
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-	0.35	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, $HCOO^-$	0.3	0.964	0.925	0.899	0.80	0.76
Rb^+, Cs^+, Tl^+, Ag^+, NH^{4+}	0.25	0.964	0.924	0.898	0.80	0.75
Mg^{2+}, Be^{2+}	0.8	0.872	0.755	0.69	0.52	0.45
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}	0.6	0.870	0.749	0.675	0.48	0.40
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5	0.868	0.744	0.67	0.46	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, $C_2O_4^{2-}$,	0.45	0.868	0.742	0.665	0.46	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}	0.40	0.867	0.740	0.660	0.44	0.36
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}	0.9	0.738	0.54	0.44	0.24	0.18
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4	0.725	0.50	0.40	0.16	0.095
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	0.5	0.57	0.31	0.20	0.048	0.021