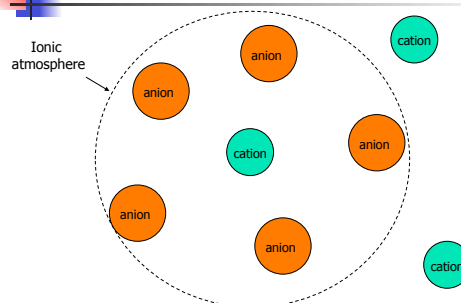


Ionic Solutions

- In the past we have assumed that ions dissolved in aqueous solution behave as if no other ions were present—ideal solutions
- This allowed us to use concentrations to calculate important quantities such as solubility products, pH, concentrations, etc.
- Real ionic solutions have interactions between anions and cations that affect the behavior

Ionic Solutions



Ionic Solutions

- The ionic atmosphere around an ion tends to reduce the charge of that particular ion seen by counter ions in solution
- Suppose we have a dilute solution of Ag^+ and Cl^- ions

$$K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$$
- If we add NaNO_3 , what will happen to the solubility of AgCl ?

Ionic Solutions

- NaCl and AgNO_3 are completely soluble salts, so they will not precipitate out
- Na^+ ions will tend to gather around the Cl^- ions, and NO_3^- will tend to gather around Ag^+ creating stronger ionic atmospheres around each
- NO_3^- surrounding Ag^+ will tend to mask the positive charge of Ag seen by the Cl^- anion reducing the attraction between the two

Ionic Solutions

- Consequently, the solubility of AgCl will increase with the presence of spectator ions
- NaNO_3 increases the *ionic strength* of the solution— Na^+ and NO_3^- do not participate in any chemistry, but they affect the chemistry of other ionic species
- The behavior of any ionic solution depends on the ionic strength of the solution

Ionic Solutions

- Ionic strength, μ , is defined as:

$$\mu = \frac{1}{2} (c_1 Z_1^2 + c_2 Z_2^2 + c_3 Z_3^2 + \dots) = \frac{1}{2} \sum_i c_i Z_i^2$$

where c_i is the concentration of species i , and Z_i is its ionic charge

When determining ionic strength, you use all ions present in the solution, not just those participating in chemistry

Ionic Solutions

- Determine the ionic strength of a solution that is 0.0250 M NaCl and 0.00750 M $\text{Pb}(\text{NO}_3)_2$
- Ions present in solution:

$$[\text{Na}^+] = 0.0250 \text{ M} \quad [\text{Pb}^{2+}] = 0.00750 \text{ M}$$

$$[\text{Cl}^-] = 0.0250 \text{ M} \quad [\text{NO}_3^-] = 0.0150 \text{ M}$$

$$\mu = \frac{1}{2} [0.0250(+1)^2 + 0.0250(-1)^2 + 0.00750(+2)^2 + 0.0150(-1)^2]$$

$$= 0.0475$$

Ionic Solutions

- For real solutions (not ideal behavior) the chemistry of the ionic species strictly depends on their *activity*, not their concentration
- Activity is defined as:

$$A_C = [C]\gamma_C$$

$$\gamma_C \text{ is the activity coefficient of C}$$

Ionic Solutions

- The activity coefficient can be calculated using different theoretical models
- Extended Debye-Hückel Theory gives

$$\log \gamma = \frac{-0.51 Z^2 \sqrt{\mu}}{1 + \frac{a\sqrt{\mu}}{305}} \quad \text{at } 25^\circ \text{C}$$

a is the ionic size in pm (see Table 8-1)

Ionic Solutions

- As a solution becomes more dilute, the activity and molar concentration become the same:

$$\lim_{[C] \rightarrow 0} \gamma_C = 1$$

$$\lim_{[C] \rightarrow 0} A_C = [C]$$

Ionic Solutions

- We use activities in the same manner as we use concentrations for equilibrium expressions:
- For $aA + bB \leftrightarrow cC + dD$

$$K_{\text{eq}} = \frac{A_C^c A_D^d}{A_A^a A_B^b} = \frac{(\gamma_C [C])^c (\gamma_D [D])^d}{(\gamma_A [A])^a (\gamma_B [B])^b}$$

Ionic Solutions

- Calculate the solubility of CaF_2 in a solution of 0.050 M NaF

$$K_{\text{sp}}(\text{CaF}_2) = 3.9 \times 10^{-11}$$

$$[\text{Na}^+] = 0.050 \text{ M}$$

$$[\text{F}^-] = 0.050 \text{ M (contribution from CaF}_2 \text{ is negligible)}$$

$$\mu = \frac{1}{2} [0.050(+1)^2 + 0.050(-1)^2] = .050$$

(contribution by Ca^{2+} is negligible)

Ionic Solutions

Calculate the solubility of CaF_2 in a solution of 0.050 M NaF

$$\gamma_{\text{Ca}} = 0.485$$

$$\gamma_{\text{F}} = 0.81$$

$$K_{\text{sp}} = [\text{Ca}^{2+}]_{\gamma_{\text{Ca}}}[\text{F}^-]_{\gamma_{\text{F}}}^2 = 3.9 \times 10^{-11}$$

$$[\text{Ca}^{2+}](.485)(.050)^2(.81)^2 = 3.9 \times 10^{-11}$$

$$[\text{Ca}^{2+}] = 4.9 \times 10^{-8} \text{ M}$$

$$[\text{Ca}^{2+}] = 1.6 \times 10^{-8} \text{ M neglecting activities}$$

Ionic Solutions

- pH is defined as:

$$\text{pH} = -\log(A_{\text{H}^+}) = -\log([\text{H}^+]_{\gamma_{\text{H}^+}})$$

Find pH of a 1.00 M NaCl solution

$$[\text{Na}^+] = 1.00 \text{ M}$$

$$[\text{Cl}^-] = 1.00 \text{ M}$$

$$\mu = \frac{1}{2}[1.00(+1)^2 + 1.00(-1)^2] = 1.00$$

$$\gamma_{\text{H}^+} = 0.743$$

$$\gamma_{\text{OH}^-} = 0.579$$

Ionic Solutions

Find pH of a 1.00 M NaCl solution

$$K_{\text{W}} = [\text{H}^+]_{\gamma_{\text{H}^+}}[\text{OH}^-]_{\gamma_{\text{OH}^-}} = 1.0 \times 10^{-14}$$

$$x = [\text{H}^+] = [\text{OH}^-]$$

$$x^2 = \frac{1.0 \times 10^{-14}}{\gamma_{\text{H}^+}\gamma_{\text{OH}^-}} = \frac{1.0 \times 10^{-14}}{(.743)(.579)} = 2.32 \times 10^{-14}$$

$$x = 1.52 \times 10^{-7}$$

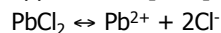
$$\text{pH} = -\log\{(1.52 \times 10^{-7})(.743)\} = 6.95$$

Ionic Solutions

Calculate $[\text{Pb}^{2+}]$ in a saturated solution of PbCl_2

$$K_{\text{sp}}(\text{PbCl}_2) = 1.7 \times 10^{-5}$$

Step 1: assume ideal behavior to determine approximate $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$



$$K_{\text{sp}} = (x)(2x)^2 = 1.7 \times 10^{-5}$$

$$x = 1.62 \times 10^{-2} \text{ M}$$

Ionic Solutions

Calculate $[\text{Pb}^{2+}]$ in a saturated solution of PbCl_2

$$K_{\text{sp}}(\text{PbCl}_2) = 1.7 \times 10^{-5}$$

Step 2: using approximate values, calculate γ 's for Pb^{2+} and Cl^- and new $[\text{Pb}^{2+}]$, $[\text{Cl}^-]$

$$\mu = \frac{1}{2} [.0162(+2)^2 + .0324(-1)^2] = 0.0486$$

$$\gamma_{\text{Pb}^{2+}} = .458$$

$$\gamma_{\text{Cl}^-} = .808$$

Ionic Solutions

Calculate $[\text{Pb}^{2+}]$ in a saturated solution of PbCl_2

$$K_{\text{sp}}(\text{PbCl}_2) = 1.7 \times 10^{-5}$$

Step 2: using approximate values, calculate γ 's for Pb^{2+} and Cl^- and new $[\text{Pb}^{2+}]$, $[\text{Cl}^-]$

$$1.7 \times 10^{-5} = [\text{Pb}^{2+}]_{\gamma_{\text{Pb}^{2+}}}[\text{Cl}^-]_{\gamma_{\text{Cl}^-}}^2$$

$$[\text{Pb}^{2+}] = .0242 \text{ M}$$

$$[\text{Cl}^-] = .0484 \text{ M}$$

Ionic Solutions

Calculate $[\text{Pb}^{2+}]$ in a saturated solution of PbCl_2

$$K_{\text{sp}}(\text{PbCl}_2) = 1.7 \times 10^{-5}$$

Step 3: using new values of $[\text{Pb}^{2+}]$ and $[\text{Cl}^-]$,
find improved μ , γ 's, and concentrations

Repeat this process until the calculated
concentrations do not change from one
iteration to the next

Ionic Solutions

Calculate $[\text{Pb}^{2+}]$ in a saturated solution of PbCl_2

$$K_{\text{sp}}(\text{PbCl}_2) = 1.7 \times 10^{-5}$$

Iteration	μ	$\gamma_{\text{Pb}^{2+}}$	γ_{Cl^-}	$[\text{Pb}^{2+}]$
0	--	1	1	.0162 M
1	.0486	.458	.808	.0242 M
2	.0726	.404	.779	.0259 M
3	.0777	.395	.773	.0262 M
4	.0786	.394	.773	.0262 M