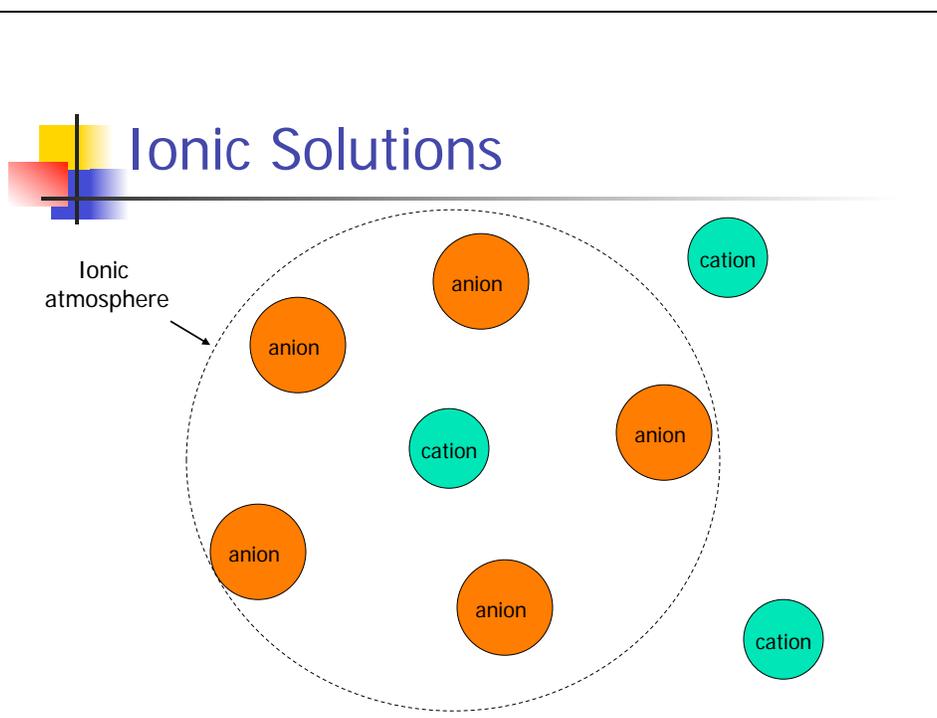




Ionic Solutions

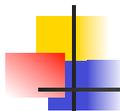
- In the past we have assumed that ions dissolved in aqueous solution behave as if no other ions were present—ideal solutions
- This allowed us to use concentrations to calculate important quantities such as solubility products, pH, concentrations, etc.
- Real ionic solutions have interactions between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





Ionic Solutions

- 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
- NaNO₃ increases the *ionic strength* of the solution—Na⁺ and NO₃⁻ 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

$$\log \gamma = \frac{-.51 Z^2 \sqrt{\mu}}{1 + \frac{a\sqrt{\mu}}{305}} \quad \text{at } 25 \text{ } ^\circ\text{C}$$

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

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

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

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

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

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



Ionic Solutions

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

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

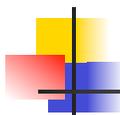
$$\gamma_{\text{F}} = 0.81$$

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

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

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

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



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

$$K_W = [H^+] \gamma_{H^+} [OH^-] \gamma_{OH^-} = 1.0 \times 10^{-14}$$

$$x = [H^+] = [OH^-]$$

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

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

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



Ionic Solutions

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

$$K_{sp}(PbCl_2) = 1.7 \times 10^{-5}$$

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



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

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



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 $[\text{Pb}^{2+}]$, $[\text{Cl}^-]$

$$\mu = \frac{1}{2} [0.0162(+2)^2 + 0.0324(-1)^2] = 0.0486$$

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

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



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 $[\text{Pb}^{2+}]$, $[\text{Cl}^-]$

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

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

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



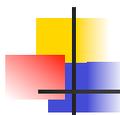
Ionic Solutions

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				