Analytical Chemistry

CHEM 311

Outline for Today’s Class

- Course website
- Syllabus and course structure
- Warning and Survival Advice
- Blackboard Vista and On-line weekly Quizzes
- First third of course, Equilibrium, solubility, acid-base, EDTA
- Start Chapter 6

Chapter 6
Equilibrium

$$A \leftrightarrow B$$

Forward rate = -d[A]/dt = kf[A]

Reverse rate = -d[B]/dt = kr[B]

At equilibrium, forward rate = reverse rate (both reactions **are occurring** at the same rate).

$$K = [B]_{eq}/[A]_{eq}$$

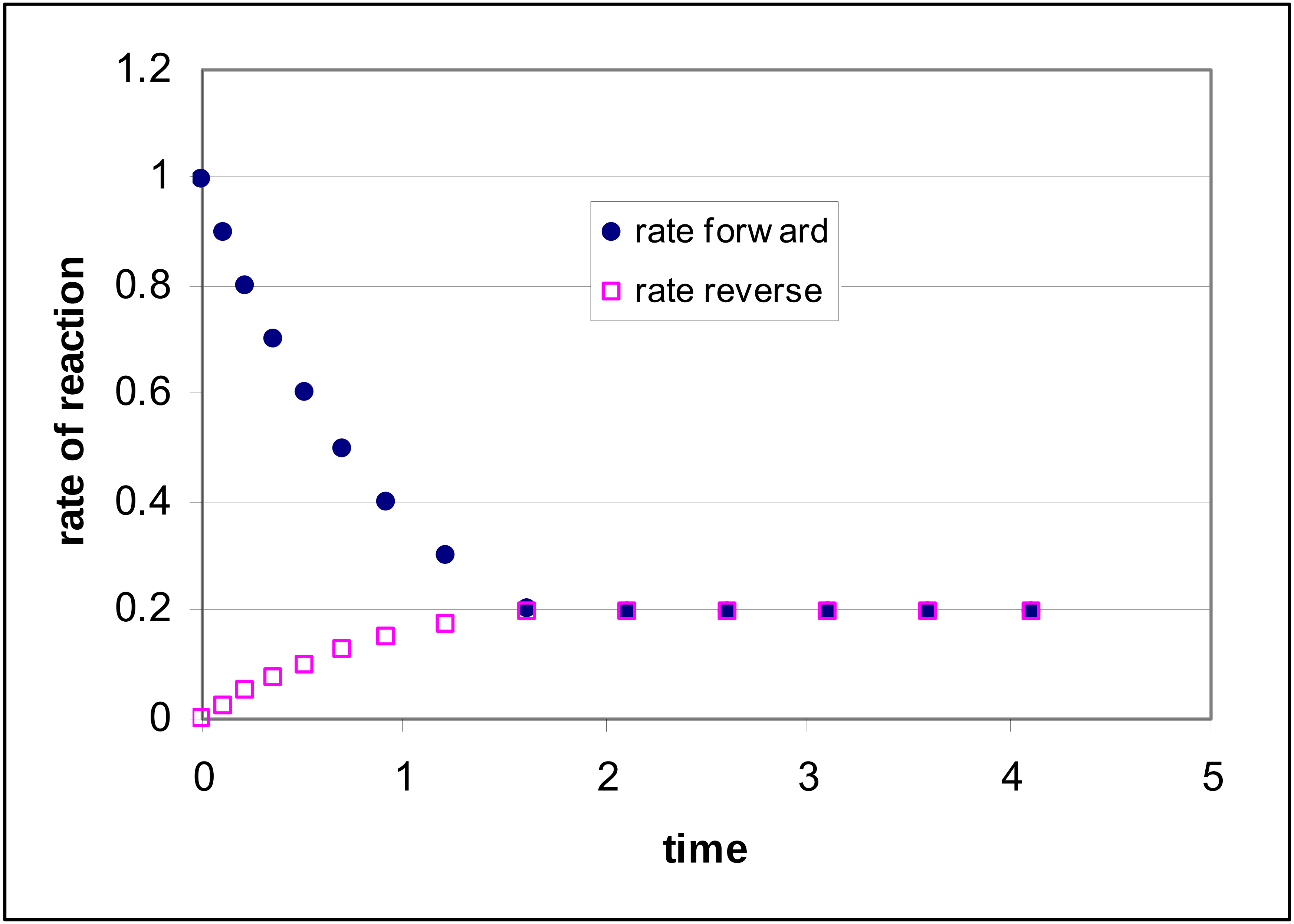
Reaching Equilibrium

Let K = 4.

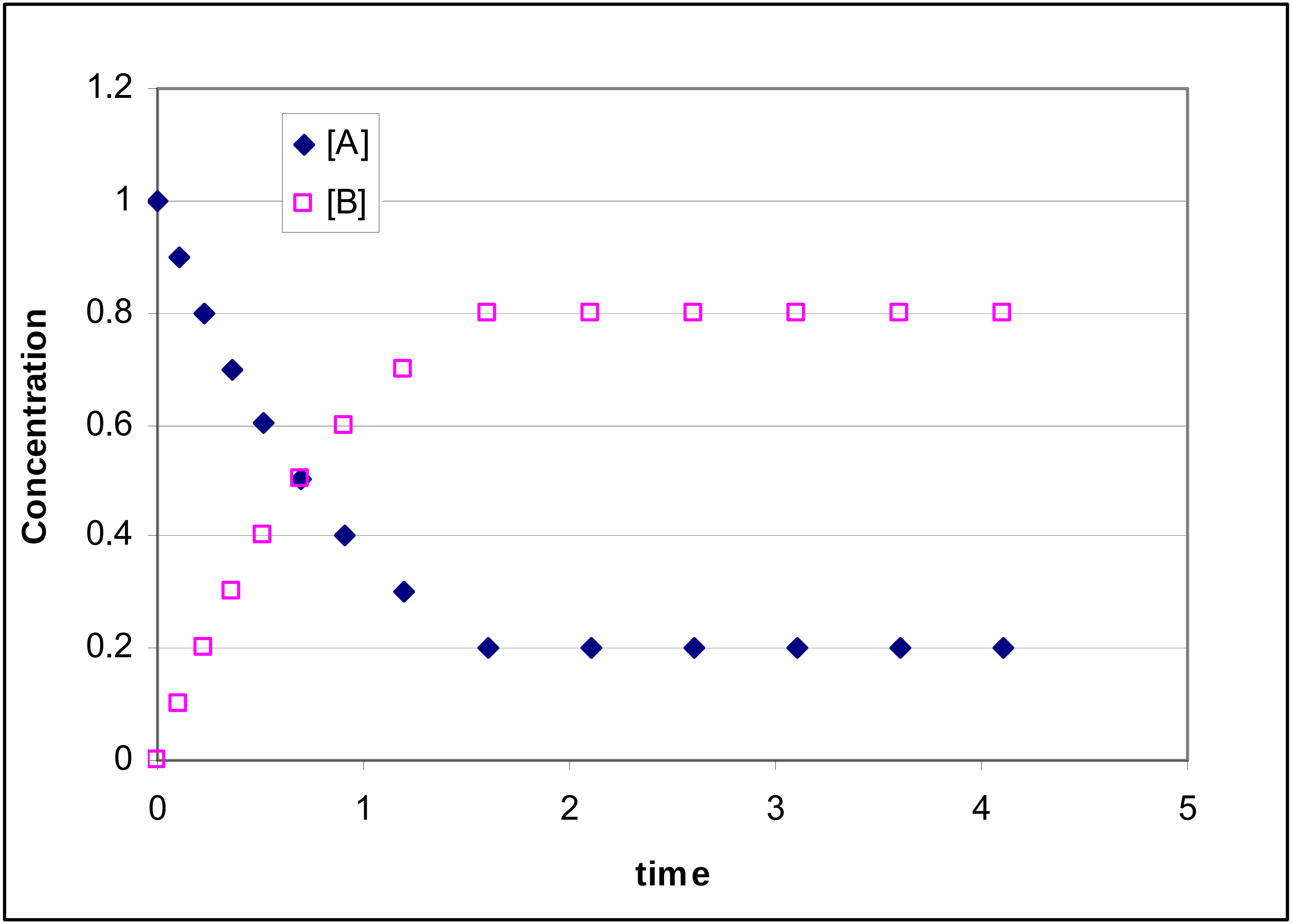
$K = [B]_{eq}/[A]_{eq}$ at equilibrium

Start with all A

- Plots of reaction rates and concentrations vs. Reaction Time



rate forw ard
rate reverse
rate of reaction
time
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5



1.2
1
0.8
0.6
0.4
0.2
0
Concentration
0
1
2
3
4
5
time
[A]
[B]

More General Form of K

$$aA + bB \overset{K}{\leftrightarrow} cC + dD,$$

where a, b, c, and d are stoichiometric coefficients

forward rate = $k_f[A]^a[B]^b$, where kf is the forward rate constant

reverse rate = $k_r[C]^c[D]^d$, where kr is the forward rate constant

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

$$K = k_f/k_r = [C]^c[D]^d / [A]^a[B]^b$$

Manipulating the Equilibrium Constant

$$HA \leftrightarrow H^+ + A^- \qquad K_1 = [A^-][H^+]/[HA]$$

$$+ \quad H^+ + C \leftrightarrow HC^+ \qquad K_2 = [HC^+]/[H^+][C]$$

$$HA + C \leftrightarrow A^- + HC^+ \qquad K_3 = [A^-][HC^+]/[HA][C]$$

$$K_3 = K_1K_2 = \{[A^-][H^+]/[HA]\}\{[HC^+]/[H^+][C]\}$$

$$HA \leftrightarrow H^+ + A^- \qquad K_1 = [A^-][H^+]/[HA]$$

$$H^+ + A^- \leftrightarrow HA \qquad 1/K_1 = [HA]/[A^-][H^+]$$

Free Energy and Equilibrium

$\Delta G \quad = \quad \Delta H \quad - \quad T\Delta S$

free energy — enthalpy — temperature (K) — entropy

$\Delta G = \Delta G^\circ + RT\ln Q$, where Q is the reaction quotient (K, but at non-equilibrium concentrations)

ΔG° - reactants and products in their standard states (1 bar (1.01325 atm), 1 M)

$\Delta G = \Delta G^\circ + RT\ln Q$, where Q is the reaction quotient ($[C]^c[D]^d / [A]^a[B]^b$)

when Q = 1 (standard state), $\Delta G = \Delta G^\circ$ (this defines ΔG°)

when $\Delta G = 0$, the reaction is at equilibrium, Q = K and,

$\Delta G^\circ = -RT\ln K$

$K = e^{-\Delta G^\circ/RT}$

R = 8.314 J/Kmol

Interpretation of $\Delta G°$

- When $\Delta G°$ is negative, the reaction is favorable (product will form) under standard state conditions
- When $\Delta G°$ is positive the reaction will proceed in the reverse direction (reactants will form) under standard state conditions.

But standard states are usually not that interesting!

- **How do we predict the direction in which the reaction is favored under any given set of concentrations?**
- By comparing the reaction quotient, Q, to the equilibrium constant. Q is the same expression written above for K, but it is at any given state, not necessarily at equilibrium.
- If $Q<K$, the reaction has to proceed to right to form more product until equilibrium is reached ($Q=K$)
- If $Q>K$, the reaction has to proceed to left to form more reactant until equilibrium is reached ($Q=K$)
- **Let’s apply this by perturbing an equilibrium and letting the reaction reach a new equilibrium position.**

Le Chatelier's Principle

- When an equilibrium is disturbed, the position of the equilibrium must shift in the direction that partially offsets the disruption
- Example:

$$A \leftrightarrow B, K=2$$

INITIALLY, [A] = 2.00 M and [B] = 4.00 M at equilibrium in 1.00 L

– ADD 0.50 mol of A (assuming negligible volume change)

$Q_{t=0} = [B]_0/[A]_0 = 4.00/2.50 = 1.60$

Q < K, so the reaction must shift toward the formation of more product to re-establish equilibrium

Set up your ICE (initial, change equilibrium) Table!!!

	[A]	[B]
I	2.50	4.00
C	x	-x
E	2.50-x	4.00+x

K = 2.00 = (4.00+x)/(2.50- x), solve for x

The x represents the number of moles/L of A that react to form B upon reaching the new equilibrium.

X = 0.33333333 M

At the new equilibrium position

[A] = 2.50 – 0.333333 = 2.17 M

[B] = 4.00 + 0.333333 = 4.33 M

Try this two part question

A + 2B ↔ C + 3D K = 2.3E-2

Part 1:

100 mL sample of a 0.10 M solution of A is mixed with a 100 mL sample of a 0.10 M solution of B, calculate the equilibrium concentrations of A, B, C, and D.

Part 2:

A 10 mL sample of 0.50 M D is added to this mixture. Determine the new equilibrium concentrations.

Part 1

- A + 2B $\leftrightarrow$ C + 3D
- Dilution by a factor of two (mixing to 100 mL solutions)
- Set up the ICE

	[A]	[B]	[C]	[D]
I	0.050	0.050	0	0
C	-x	-2x	x	3x
E	0.050-x	0.050-2x	x	3x

$$K = 2.3E\text{-}2 = [C][D]^3/[A][B]^2$$

$$= \{(3x)^3 x\} / \{(0.050-x)(0.050-2x)^2\}$$

This is difficult to solve by hand but it is easy by successive approximation using Excel.

$$x = 0.012_{105}\ M$$

$$[A] = 0.038\ M$$

$$[B] = 0.026\ M$$

$$[C] = 0.012\ M$$

$$[D] = 0.036\ M$$

Part 2

$$A + 2B \leftrightarrow C + 3D$$

- Addition of D, slightly diluted A and B

[A] = 0.0379(200/210) = 0.036_1 M

[B] = 0.0258(200/210) = 0.024_5 M

[C] = 0.0121(200/210) = 0.011_5 M

[D] = {0.036(200)+0.50(10)}/210 = 0.058_4 M

Part 2

- A + 2B $\leftrightarrow$ C + 3D
- Addition of D, slightly diluted A and B
- Set up the ICE

	[A]	[B]	[C]	[D]
I	0.0361	0.0254	0.0115	0.0584
C	x	2x	-x	-3x
E	0.0361+x	0.0254+2x	0.0115-x	0.0584-3x

$K = 2.3E\text{-}2 = [C][D]^3/[A][B]^2$

$= \{(0.0584\text{-}3x)^3\,(0.0115\text{-}x)\}\ /\{0.0361+x)(0.0254+2x)^2\}$

AGAIN, this is difficult to solve by hand but it is easy by successive approximation using Excel.

$x = 0.00344$ M

[A] = 0.039 M

[B] = 0.031 M

[C] = 0.008 M

[D] = 0.048 M

Solubility Product Constant

Solids are not included in the equilibrium expression. This is because the concentration (mass/volume) of a solid is its density, which is a constant. Since it remains constant throughout the course of a reaction it is incorporated into the equilibrium constant.

Example:

$$PbCO_{3(s)} \leftrightarrow Pb^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)}$$

$$Ksp = [Pb^{2+}][CO_3{}^{2-}] = 7.4 \cdot 10^{-14}$$

Experiment 1:

- Add some solid lead carbonate into a beaker of water. What will be the equilibrium concentrations of Pb^{2+} and CO_3^{2-}?
- $[Pb^{2+}]$ must equal $[CO_3^{2-}]$, because their only source is from $PbCO_{3(s)}$

$$7.4 \cdot 10^{-14} = [Pb^{2+}][CO_3^{2-}], = [Pb^{2+}]^2 = x^2$$

$$x = [Pb^{2+}] = [CO_3^{2-}] = 2.7 \cdot 10^{-7}\ M$$

Experiment 2:

Add some lead carbonate and 0.10 mol of sodium carbonate into a beaker and add water until volume is 1.00 L.

$K_{sp} = [Pb^{2+}][CO_3^{2-}]$, $= [Pb^{2+}]\ (0.10 + [CO_3^{2-}]_{(lead\ carb)}$

Let $x = [Pb^{2+}] = [CO_3^{2-}]_{(lead\ carb)}$, so

$$K_{sp} = x(0.1+x) = 7.4 \cdot 10^{-14}$$

It is EASIEST to make the assumption that 0.1 >>> x, and then check to make sure that it is according to your answer.

$$K_{sp} = x(0.1) = 7.4 \cdot 10^{-14}$$

$x = [Pb^{2+}] = 7.4 \cdot 10^{-13}$ M, assumption was valid

- **This illustrates the common ion effect!!!!**
- The addition of sodium carbonate to the water supply dramatically reduces the level of soluble lead that can come from lead plumbing.

Complex Ion Formation

- For any real system there are many reactions that involve the same species and these reactions all reach equilibrium. **All equilibrium conditions must be satisfied simultaneously (very important concept!!!!!)**

Example1:

Place lead iodide in water

* Without considering other soluble lead iodide species, we can say $2[Pb^{2+}] = [I^-]$, and let $x = [Pb^{2+}]$

$$Ksp = x(2x)^2 = 4x^3$$

$$x = [Pb^{2+}] = 0.001255\ M$$

- However, Life is not always this simple!!

Write the pertinent reactions.

(1) $PbI_{2(s)} \leftrightarrow Pb^{2+} + 2I^-$	$Ksp = 7.9 \cdot 10^{-9} = [Pb^{2+}][I^-]^2$
(2) $Pb^{2+} + I^- \leftrightarrow PbI^+_{(aq)}$	$K_1 = 100 = [PbI^+_{(aq)})]/[Pb^{2+}][I^-]$
(3) $Pb^{2+} + 2I^- \leftrightarrow PbI_{2(aq)}$	$\beta_2 = 1400 = [PbI_{2(aq})]/[Pb^{2+}][I^-]^2$
(4) $Pb^{2+} + 3I^- \leftrightarrow PbI_3^-{}_{(aq)}$	$\beta_3 = 8300 = [PbI_3^-{}_{(aq})]/[Pb^{2+}][I^-]^3$
(5) $Pb^{2+} + 4I^- \leftrightarrow PbI_4^{2-}{}_{(aq)}$	$\beta_4 = 30000 = [PbI_4^{2-}{}_{(aq})]/[Pb^{2+}][I^-]^4$

$[Pb^{2+}]$ is the same in all six of these equilibrium expressions. There can only be one $[Pb^{2+}]$ and one $[I^-]$ concentration.

Approach: We need more relationships

- Define soluble lead (S) – any soluble species containing lead contributes to the total concentration of soluble lead.

6) $S = [Pb^{2+}] + [PbI^{+}_{(aq)}] + [PbI_{2(aq)}] + [PbI_3^{-}{}_{(aq)})] + [PbI_4^{2-}{}_{(aq)})]$

Let $x = [Pb^{2+}]$, then

$S = [Pb^{2+}] + K_1[Pb^{2+}][I^-] + \beta_2[Pb^{2+}] [I^-]^2 + \beta_3[Pb^{2+}] [I^-]^3 + \beta_4[Pb^{2+}] [I^-]^4$

$S = x(1 + K_1[I^-] + \beta_2[I^-]^2 + \beta_3[I^-]^3 + \beta_4[I^-]^4$

- $Ksp = [Pb^{2+}][I^-]^2 = 7.9 \cdot 10^{-9}$
- Mass balance: 2(mol Pb) = mol I

(7) $$2S = [I^-] + [PbI^+_{(aq)}] + 2[PbI_{2(aq)}] + 3[PbI_3{}^-{}_{(aq)}] + 4[PbI_4{}^{2-}{}_{(aq)}]$$

$$2S = [I^-] + [PbI^+_{(aq)}] + 2[PbI_{2(aq)}] + 3[PbI_3^-{}_{(aq)}] + 4[PbI_4^{2-}{}_{(aq)}]$$

$$2S = [I^-] + K_1[Pb^{2+}] [I_-] + 2\beta_2[Pb^{2+}] [I^-]^2 + 3\beta_3[Pb^{2+}] [I^-]^3 + 4 \beta_4[Pb^{2+}] [I^-]^4$$

$$2S = [I^-] + xK_1[I_-] + 2x\beta_2[I^-]^2 + 3x\beta_3[I^-]^3 + 4x\beta_4[Pb^{2+}] [I^-]^4$$

$$2x(1 + K_1[I^-] + \beta_2[I^-]^2 + \beta_3[I^-]^3 + \beta_4[I^-]^4 =$$

$$[I^-] + xK_1[I_-] + 2x\beta_2[I^-]^2 + 3x\beta_3[I^-]^3 + 4x\beta_4[Pb^{2+}] [I^-]^4$$

- Substitute $(Ksp/x)^{1/2}$ for $[I^-]$ and then you have one equation with one unknown

Result

So, using Excel and successive approximations (more on this in a little bit)

$[I^-]$ =0.0023971 M

$[Pb^{2+}]$ = 0.0013746 M

S = 0.001715329 M

Example 2:

- Place lead iodide in water and add sodium iodide, such that $[I^-]$ = 100. mM
- S = x + 100(0.100)x + 1400(0.100)2x + 8300(0.100)3x + 30000(0.100)4x

  = 2.8677E-05 M

This is the common ion effect!

Example 3

- Place lead iodide in water and add sodium iodide, such that $[I^-] = 0.10$ M

  S = x + 100(1.0)x + 1400(1.0)2x + 8300(1.0)3x + 30000(1.0)4x

  = 0.000314 M
- This is the complex ion effect!

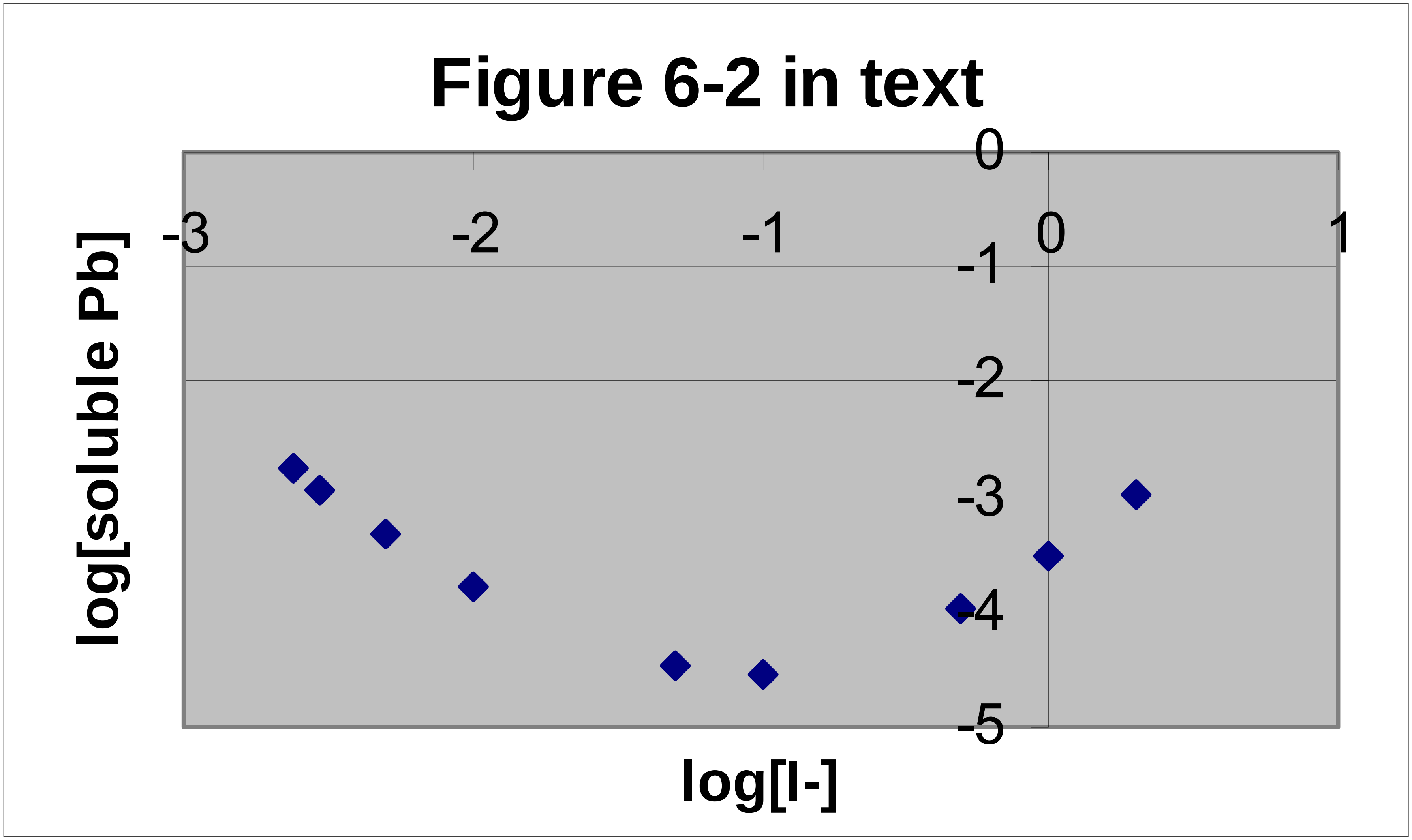


Figure 6-2 in text
log[soluble Pb]
log[I-]
-3
-2
-1
0
1
0
-1
-2
-3
-4
-5

Expressing Solubility

- Solubility – the amount of solid that dissolves in 1 L of solution
  - Molarity
  - ppm (mg/L)
  - ppb (μg/L)
  - ppt (ng/L)

Solubility of lead carbonate in water

$$7.4 \cdot 10^{-14} = [Pb^{2+}][CO_3^{2-}], = [Pb^{2+}]^2 = x^2$$

$$x = [Pb^{2+}] = [CO_3^{2-}] = 2.7 \cdot 10^{-7}\ M$$

MM (267.21 g/mol)

$(2.7 \cdot 10^{-7}$ mol/L)(267.21 g/mol)(10^6 mg/1 L)

= 72.1 ppm