CHEM 191

Energetics & Equilibria in Biological Systems

Module 1 Lecture 4

Equilibria and Solubility

Brown (15th) Chapter 17.4, 17.5

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Module 1 Lecture 4

Learning objectives

- to understand how a system at equilibrium responds to change

- to be able to write down correctly the expression for K_{sp} and Q_{sp} for an ionic solid

- to be able to solve problems involving K_{sp} and s

- to be able to predict whether or not a precipitate will form

- to be able solve problems involving common ions

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Response to change

- How does a system at equilibrium respond to change in

    - amounts of reactants or products
    - pressure

- Can use **Le Châtelier's principle** to determine these:
    - "if a system at equilibrium is disturbed, it will move in such a way to counteract the disturbance and restore equilibrium"

- But this can sometimes be misleading - best to do these types of problems in terms of a comparison of Q and K.

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Response to change

$$\text{A} \rightleftharpoons \text{B} \qquad Q = \frac{[B]}{[A]} \qquad K = \frac{[B]_e}{[A]_e}$$
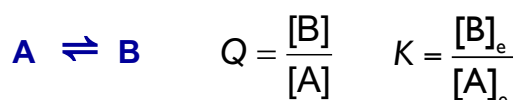
If more A is added, if **$Q < K$** $\longrightarrow$ eqbm position moves to the right, reducing [A] and increasing [B] until eqbm is again reached. (ie $Q = K$)

If some A is removed, **$Q > K$** $\longleftarrow$ eqbm position moves to the left, increasing [A] and decreasing [B] until eqbm is again reached. (ie $Q = K$)

REMEMBER: K does not change

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Changing amounts

- Consider   **PCl$_3$(g) + Cl$_2$(g) ⇌ PCl$_5$(g)**

- How will the equilibrium position change if we add some PCl$_3$(g) to a system at equilibrium?

- Start at equilibrium, therefore $Q = K$. Look at what happens to Q when we add PCl$_3$(g)

$$Q_c = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

- Adding PCl$_3$(g) will instantaneously *decrease Q* and the system will no longer be at equilibrium. Need to therefore *increase Q* to return to equilibrium. Can do this by making more PCl$_5$ and using up PCl$_3$ and Cl$_2$

- Equilibrium position will move to the *right*

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Changing pressure

- Can change pressure by changing volume, or by adding an inert gas.

CaCO$_3$(s) ⇌ CaO(s) + CO$_2$(g)

- Write the Q_c expression, remembering that $c = \dfrac{n}{V}$

$$Q_c = [CO_2] = \frac{n(CO_2)}{V} = n(CO_2) \times \frac{1}{V}$$

- This shows that Q_c is proportional to $1/V$. Thus if V increases, Q_c decreases. If we increase the volume, will have $Q_c < K_c$, and so the equilibrium position will move to increase Q_c. Equilibrium position will move to the *right*.

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Changing pressure

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Can show (exercise) that changing the pressure by changing the volume will have no effect on an equilibrium with equal numbers of moles of gas on either side of the equilibrium arrow, as the V terms cancel out in the expression for Q.

Changing the pressure by adding an inert gas (e.g. helium) will have no effect on the position of equilibrium, as there is no term for the inert gas in the expression for Q – it is not involved in the reaction.

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Solubility

- Solubility **(s)** is a measure of how much solute will dissolve in a given volume of solvent
- A ***saturated solution*** is formed when the maximum amount of solute is dissolved in a particular volume of solvent at temperature T. The following equilibrium exists in a saturated solution:

$$solute(s) \rightleftharpoons solute(aq)$$

- The solubility ***(s)*** of a solute is the amount of the solute that will dissolve in 1 L of water
- Solubility depends on:

    chemical nature of solute and solvent

    temperature, T

    pressure, p (for gaseous solutes)

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How soluble?

- Can dissolve 35.9 g NaCl in 100 mL water at 25 ^{o}C. We say that NaCl is soluble in water

- Can only dissolve 0.00019 g AgCl in 100 mL water at 25 ^{o}C. We *usually* say that AgCl is insoluble in water, but it isn't! It is slightly (sparingly) soluble. An equilibrium between undissolved solid and dissolved ions is reached.

- K_{sp}, **the Solubility Product**, is the equilibrium constant for the dissolution (dissolving) of a slightly soluble salt in water

The solubility product

- Consider a saturated solution of AgCl. The equilibrium for the dissolution of AgCl(s) is written as

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

- For this, $K_{sp} = [Ag^+]_e[Cl^-]_e = 1.8 \times 10^{-10}$ *(can look this up in tables)*

- Remember that ***pure solids*** do not appear in an equilibrium constant expression. Therefore, K_{sp} expressions are always just the products of the ions, each raised to the power of their stoichiometric coefficients.

Example

- Calculate K_{sp} for AgBr given that the solubility of AgBr in water is 6.9×10^{-7} mol L^{-1} at 25 $^{\circ}$C

$$\textbf{AgBr(s)} \rightleftharpoons \textbf{Ag}^+\textbf{(aq) + Br}^-\textbf{(aq)}$$

- $s = 6.9 \times 10^{-7}$ mol L^{-1} means that when 6.9×10^{-7} mol of AgBr has dissolved in 1 L of water, equilibrium is reached. At that point $[Ag^+]_e$ and $[Br^-]_e = 6.9 \times 10^{-7}$ mol L^{-1}

- $K_{sp} = [Ag^+]_e[Br^-]_e = (6.9 \times 10^{-7})(6.9 \times 10^{-7}) = 4.8 \times 10^{-13}$

- Remember that equilibrium constants have no units.

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K_{sp} and solubility (s)

- Can derive a relationship between K_{sp} and s. Three steps.

    1) Write the expression for K_{sp}
    2) Express the concentration of ions in terms of s
    3) Substitute (2) into (1)

- Example

    $$\textbf{AgCl(s)} \rightleftharpoons \textbf{Ag}^+\textbf{(aq) + Cl}^-\textbf{(aq)} \qquad K_{sp} = [Ag^+]_e[Cl^-]_e$$
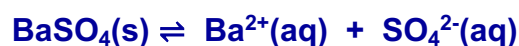
    s, the solubility, is equal to the amount of solid than can dissolve in 1L of water. So, if s mole AgCl(s) dissolves, there will be s mole each of Ag$^+$(aq) and Cl$^-$(aq)

    So $[Ag^+]_e = [Cl^-]_e = s$

    and therefore, for this 1:1 electrolyte, $\textbf{\textit{K}}_{\textbf{sp}} = \textbf{\textit{s}} \times \textbf{\textit{s}} = \textbf{\textit{s}}^2$

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Calculating s from K_{sp}

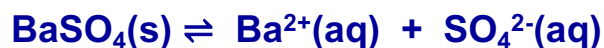### $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

- Ba^{2+} ions are highly toxic. However, $BaSO_4$ is used extensively as an X-ray contrast agent and is administered orally as a 'barium meal'.

- $K_{sp}(BaSO_4) = 1.1 \times 10^{-10}$. Only slightly soluble and the resulting $[Ba^{2+}]$ is too low to be dangerous
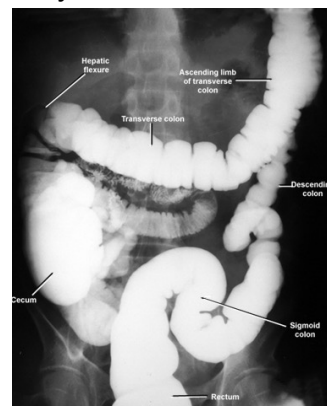
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Calculating s from K_{sp}

- Calculate the solubility of barium sulfate, $BaSO_4$, in water given $K_{sp} = 1.1 \times 10^{-10}$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp} = [Ba^{2+}]_e[SO_4^{2-}]_e = s^2 = 1.1 \times 10^{-10}$

$s = 1.0 \times 10^{-5}$ mol L^{-1}

- EPA recommends for drinking water that $[Ba^{2+}] < 1.46 \times 10^{-5}$ mol L^{-1} (< 2 mg L^{-1})

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Will a precipitate form?

- A comparison of Q_{sp} and K_{sp} can tell us whether or not a precipitate will form on mixing aqueous solutions of ions.

If Q_{sp} < K_{sp} no precipitate will form.
If Q_{sp} > K_{sp} precipitation will occur.

- Q_{sp} is therefore sometimes called the ***ionic product***

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Example

- In the US the EPA has set the maximum level for barium (Ba^{2+}) ions in drinking water at 2 mg L^{-1} (1.46 $\times$ 10^{-5} mol L^{-1}).
- Ba^{2+} ions can be removed in the environment or water treatment plants with sulfate (SO_4^{2-}) ions.

- Will a precipitate of $BaSO_4$(s) form in water with a [Ba^{2+}] of 1.46 $\times$ 10^{-5} mol L^{-1} and a [SO_4^{2-}] of 4.16 $\times$ 10^{-3} mol L^{-1}?
- Need to calculate Q_{sp} for the solution

$$Q_{sp} = [Ba^{2+}][SO_4^{2-}] = (1.46 \times 10^{-5})(4.16 \times 10^{-3}) = 6.07 \times 10^{-8}$$

- Now we compare:

Q_{sp} (= 6.07 $\times$ 10^{-8}) > K_{sp} (= 1.1 $\times$ 10^{-10})

therefore a precipitate **will** form removing Ba^{2+} from the water.

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The common ion effect

- The presence of a common ion will always *decrease* the solubility of an ionic solid.

- e.g. what is the solubility of $BaSO_4$ in 0.30 mol L^{-1} aqueous Na_2SO_4 solution? K_{sp} ($BaSO_4$) = 1.1×10^{-10}

- Sulfate (SO_4^{2-}) anion is essential for cell growth and other important physiological processes that are critical for the life of organisms.

- The concentration of sulfate is maintained at high levels (~0.30 mol L^{-1}) and is the fourth abundant anion in the plasma.

- Does this make the "barium meal" even safer?

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The common ion effect (cont)

- The balanced equation is

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$
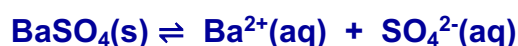
with

$$K_{sp} = [Ba^{2+}]_e[SO_4^{2-}]_e$$

- We solve this by setting up a concentration table and taking into account the 0.30 mol L^{-1} SO_4^{2-}(aq) already present in the solution.

	$BaSO_4(s)$	Ba^{2+}(aq)	SO_4^{2-}(aq)
Initial (mol L^{-1})		0.00	0.30
Change (mol L^{-1})		s	s
Equilm (mol L^{-1})		s	0.30 + s

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The common ion effect (cont)

- Substituting the equilibrium concentrations into K_{sp} gives

  $K_{sp} = [Ba^{2+}]_e[SO_4^{2-}]_e = s(0.30 + s) = 1.1 \times 10^{-10}$

- **Can assume that $(0.30 + s) \approx 0.300$ because of the small value of K_{sp}**

- $s(BaSO_4)$ in pure water is 1.0×10^{-5} mol L^{-1} (so **s** very small cf 0.30 mol L^{-1}).

- $K_{sp} = s(0.30) = 1.1 \times 10^{-10}$

  $s = 3.67 \times 10^{-10}$ mol L^{-1}

- Solubility is much lower in the presence of additional SO_4^{2-}.

- Barium meal even safer due to SO_4^{2-} concentration of plasma.

Kidney stones

- Consist of calcium oxalate

  $CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$ $K_{sp} = 4 \times 10^{-9}$

- Range in size from a grain of sand to a golf ball.

- Oxalate comes from breakdown of dietary protein

✳ Homework ✳

Brown (15th)

Problems 17.79, 17.80, 17.107

Answers on Blackboard

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