

Chemical Equilibria

General representation



Where uppercase letters are chemical species
and lowercase letters are coefficients
(i.e. # of atoms or moles)

Equilibrium Constant

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where [] = concentration, usually molar

True Thermodynamic Equilibrium Constant

$$K^{\circ} = \frac{(a_{\text{C}})^c (a_{\text{D}})^d}{(a_{\text{A}})^a (a_{\text{B}})^b}$$

For



K° Defined for standard conditions of 25 °C,
1 atm pressure and $I = 0$ (infinite dilution)

Equilibrium Constant

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where [] = concentration, usually molar

Many types of K's (equilibrium constants)

K_a for acid dissociation

K_b for base hydrolysis

K_w for water auto ionization

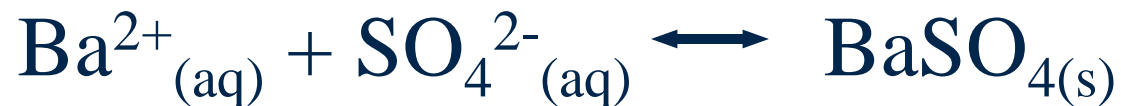
K_{sp} for solubility product

K_f for a formation constant

$K_1, K_2, K_3, \text{ etc.}$ for stepwise formation constants

$\beta_1, \beta_2, \beta_3, \text{ etc.}$ for overall formation constants

Solubility Equilibria



or by convention



We can write an equilibrium constant for rxn

Solubility Product (equilibrium constant)

$$K_{sp} = \frac{[\text{Ba}^{2+}] [\text{SO}_4^{2-}]}{1} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$

$$K_{sp} = \frac{a_{\text{Ba}} a_{\text{SO}_4}}{1} = a_{\text{Ba}} a_{\text{SO}_4}$$

activity of solid is defined as = 1

Solubility Calculated

Solubility (S) is the concentration of individual ions generated from an insoluble compound



$$S = [\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$$

Solubility Calculation (continued)

Given $K_{SP} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 2.0 \times 10^{-10}$

Then $S = \sqrt{K_{SP}} = \sqrt{2.0 \times 10^{-10}} = 1.4 \times 10^{-5} \text{ M}$

So $S = [\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 1.4 \times 10^{-5} \text{ M}$

Activity Correction

$$K_{SP} = \frac{a_{Ba} a_{SO_4}}{1} = a_{Ba} a_{SO_4}$$

Since

$$a_{Ba} = \gamma_{Ba} [Ba^{2+}] \quad \& \quad a_{SO_4} = \gamma_{SO_4} [SO_4^{2-}]$$

Substituting

$$K_{SP} = a_{Ba} a_{SO_4} = \gamma_{Ba} [Ba^{2+}] \gamma_{SO_4} [SO_4^{2-}]$$

Solubility Calculation (completed)

Since

$$K_{SP} = \gamma_{Ba} [Ba^{2+}] \gamma_{SO_4} [SO_4^{2-}] \quad \& \quad \gamma_{Ba} = \gamma_{SO_4}$$

Then

$$S = \sqrt{\frac{K_{SP}}{\gamma^2}}$$

To determine solubility of $BaSO_4$ in a solution containing other ions (as in SW), you must calculate the activity coefficient (γ)

Two ways to correct for activity

1) Correct each ion as discussed

$$K_{SP} = a_{Ba} a_{SO_4} = \gamma_{Ba} [Ba^{2+}] \gamma_{SO_4} [SO_4^{2-}]$$

2) Correct the equilibrium constant K

$$K' = \frac{K_{SP}}{\gamma^2} = [Ba^{2+}] [SO_4^{2-}]$$

Common Ion Effect

In seawater the total concentration of sulfate is 2.86×10^{-2} moles/kg \rightarrow must use here



$$K_{SP} = a_{Ba} a_{SO_4} = \gamma_{Ba} [Ba^{2+}] \gamma_{SO_4} [SO_4^{2-}]$$

$$K' = \frac{K_{SP}}{\gamma^2} = [Ba^{2+}] [SO_4^{2-}]$$

Water Hydrolysis (very important)



Applying same rules for K expressions

$$K_w = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{1} = a_{\text{H}^+} a_{\text{OH}^-}$$

Where H_2O (the solvent) is assigned activity = 1

Remember pH

pH is defined as the negative logarithm of the hydrogen ion activity

$$\text{pH} = -\log a_{\text{H}^+}$$

Given the numerical value $K_w = 1 \times 10^{-14}$

& $K_w = a_{\text{H}^+} a_{\text{OH}^-}$ then we can always calculate OH^- from the pH

pH Examples

At neutral pH $\mathbf{a_{H^+} = a_{OH^-}}$ and

$$\mathbf{a_{H^+} = \sqrt{K_w} = 1 \times 10^{-7} = \text{pH } 7.00}$$

At seawater pH (e.g., 8.2)

$$\mathbf{a_{H^+} = 1 \times 10^{-8.2} = 6.31 \times 10^{-9} \text{ M}}$$

$$\mathbf{a_{OH^-} = \frac{K_w}{a_{H^+}} = \frac{1 \times 10^{-14}}{6.31 \times 10^{-9}} = 1.58 \times 10^{-6} \text{ M}}$$

Hydronium Ion

Water actually hydrolyses to form a hydronium ion (H_3O^+) rather than the lone proton (H^+)

(Once again an ion-water interaction akin to those discussed previously)

For the sake of simplicity, we will refer to this species as H^+ which is common practice

A Note on Strong & Weak Electrolytes

Salts, Acids & Bases are all ionic compounds that dissociate (i.e., form ions) in water either partially or completely

Complete dissociation = a strong electrolyte



Partial dissociation = a weak electrolyte



Two step equilibrium = forward & back reactions

Acid-Base Equilibria

Fictitious Weak Acid (HA)



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad \frac{\mathbf{a}_{\text{H}^+} \mathbf{a}_{\text{A}^-}}{\mathbf{a}_{\text{HA}}}$$

The smaller the K_a the weaker the acid

Strong acids have no K_a it approaches infinity

Acid-Base Equilibria

Fictitious Weak Base (B)

Capable of accepting a proton (H^+)



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad \text{or} \quad \frac{a_{\text{BH}^+} a_{\text{OH}^-}}{a_{\text{B}}}$$

The smaller the K_b the weaker the base

Strong bases have no K_b it approaches infinity

Ion Pair or Complex Formation Equilibria

Dozens of Ion Pairs form in SW & even
more complexes – deal with them the same way



$$K_f = \frac{a_{\text{MgSO}_4}}{a_{\text{Mg}} a_{\text{SO}_4}}$$

Larger K_f = stronger formation – reaction \longrightarrow

Typical Problem in SW

Find Various Forms or Species

Given total concentration data for certain constituents in SW, find % of species

Example: If total Mg is $C_{\text{Mg}} = 5.28 \times 10^{-2}$ mol/kg

and total SO_4 is $C_{\text{SO}_4} = 2.82 \times 10^{-2}$ mol/kg

knowing that



and the value of the K_f or $K_{\text{MgSO}_4} = 2.29 \times 10^2$

Steps in the Manual Solution of Simple Equilibrium Problems

1) Start with a recipe: $C_{\text{Mg}} = 5.28 \times 10^{-2} \text{ mol/kg}$

$$C_{\text{SO}_4} = 2.82 \times 10^{-2} \text{ mol/kg}$$

2) List the species: Mg^{2+} , SO_4^{2-} , MgSO_4

3) List reaction(s): $\text{Mg}^{2+} + \text{SO}_4^{2-} \longleftrightarrow \text{MgSO}_4$

4) Write Mass Balance equations:

$$C_{\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgSO}_4] = 5.28 \times 10^{-2} \text{ mol/kg}$$

$$C_{\text{SO}_4} = [\text{SO}_4^{2-}] + [\text{MgSO}_4] = 2.82 \times 10^{-2} \text{ mol/kg}$$

Steps in the Manual Solution of Simple Equilibrium Problems

5) Write a Charge Balance equation:

$$\text{☞ } \sum Z_{i+}[i^+] = \text{☞ } \sum Z_{i-}[i^-]$$

6) Write equilibrium constant expression(s):

$$K_f = \frac{a_{\text{MgSO}_4}}{a_{\text{Mg}} a_{\text{SO}_4}} \quad \text{or} \quad \frac{[\text{MgSO}_4]}{[\text{Mg}^{2+}] [\text{SO}_4^{2-}]}$$

There are 3 species or 3 unknown concentrations

There are also 3 equations (actually 4) to solve

We can solve the 3 equations simultaneously to get an answer

Solve for free Mg concentration first = $[\text{Mg}^{2+}]$

Rearrange the mass balance equations:

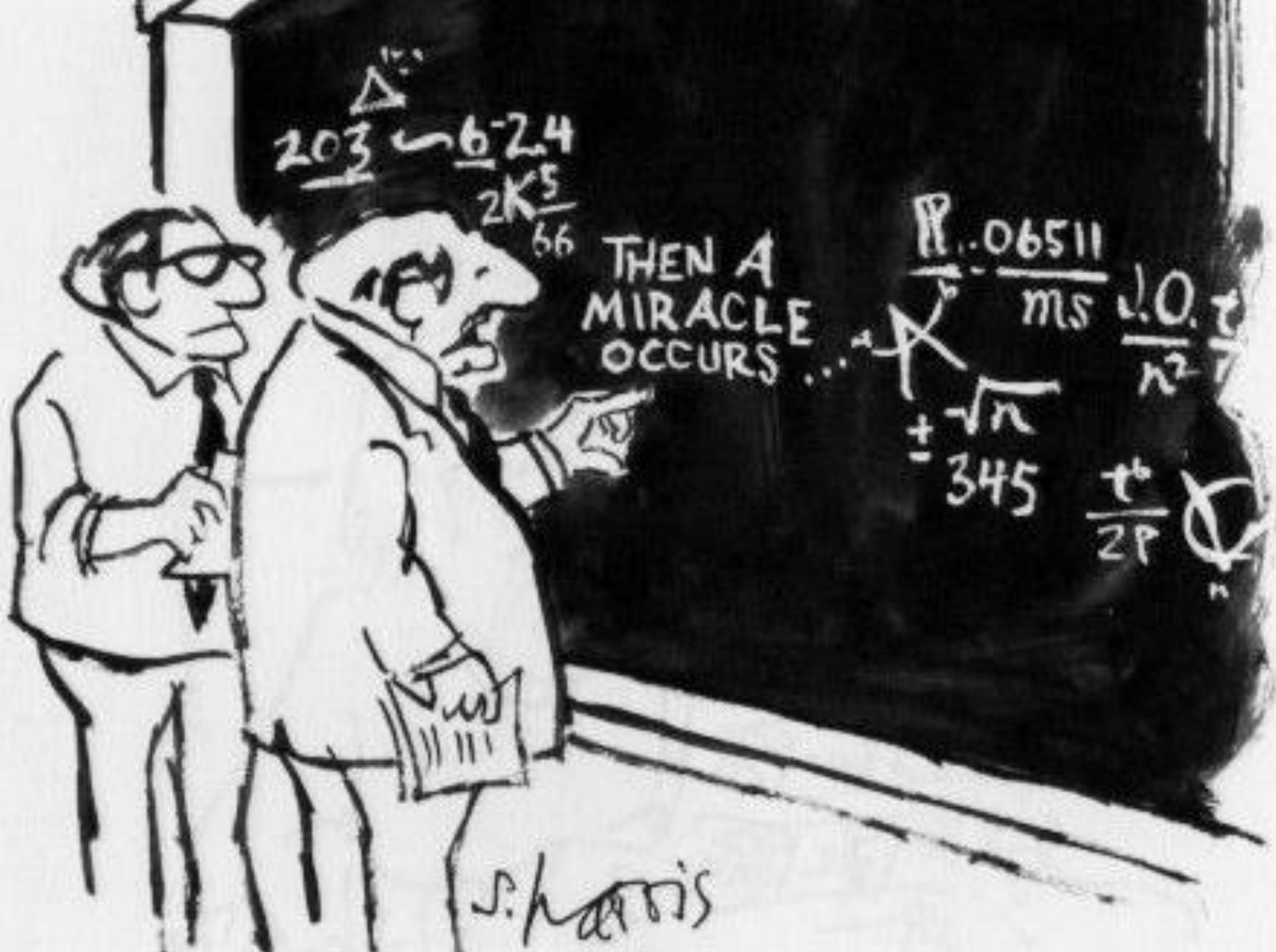
$$C_{\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgSO}_4] \quad \text{rearranges}$$

to give $[\text{MgSO}_4] = C_{\text{Mg}} - [\text{Mg}^{2+}]$

$$C_{\text{SO}_4} = [\text{SO}_4^{2-}] + [\text{MgSO}_4] \quad \text{rearranges}$$

giving $[\text{SO}_4^{2-}] = C_{\text{SO}_4} - [\text{MgSO}_4]$

We must also substitute the 1st into the 2nd



$$\Delta$$
$$203 \sim 6.24$$
$$2K^5$$
$$66$$

THEN A
MIRACLE
OCCURS...

$$\frac{R \cdot 0.06511}{ms}$$
$$\frac{1.0 \cdot t}{n^2}$$
$$\pm \sqrt{n}$$
$$345$$
$$\frac{t}{2P}$$
$$\phi$$

S. Harris

$$C_{\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgSO}_4] \quad \text{rearranges}$$

to give $[\text{MgSO}_4] = C_{\text{Mg}} - [\text{Mg}^{2+}]$

$$C_{\text{SO}_4} = [\text{SO}_4^{2-}] + [\text{MgSO}_4] \quad \text{rearranges}$$

giving $[\text{SO}_4^{2-}] = C_{\text{SO}_4} - [\text{MgSO}_4]$

Substituting the 1st into the 2nd for $[\text{MgSO}_4]$

Gives $[\text{SO}_4^{2-}] = C_{\text{SO}_4} - (C_{\text{Mg}} - [\text{Mg}^{2+}])$

Now we can

Substitute into K

$$K_f = \frac{[\text{MgSO}_4]}{[\text{Mg}^{2+}] [\text{SO}_4^{2-}]}$$

Our resulting equation looks like

$$K_{\text{MgSO}_4} = \frac{C_{\text{Mg}} - [\text{Mg}^{2+}]}{[\text{Mg}^{2+}] (C_{\text{SO}_4} - (C_{\text{Mg}} - [\text{Mg}^{2+}]))}$$

Be careful of signs in denominator

$$K_{\text{MgSO}_4} = \frac{C_{\text{Mg}} - [\text{Mg}^{2+}]}{[\text{Mg}^{2+}] (C_{\text{SO}_4} - C_{\text{Mg}} + [\text{Mg}^{2+}])}$$

Cast in the form of a quadratic

$$K[\text{Mg}^{2+}]C_{\text{SO}_4} - K[\text{Mg}^{2+}]C_{\text{Mg}} + K[\text{Mg}^{2+}]^2 = C_{\text{Mg}} - [\text{Mg}^{2+}]$$

Set equal to zero and solve with the quadratic formula

Equation from previous slide

$$K[Mg^{2+}]C_{SO_4} - K[Mg^{2+}]C_{Mg} + K[Mg^{2+}]^2 = C_{Mg} - [Mg^{2+}]$$

Set equal to 0 & rearrange in form for quadratic formula

$$K[Mg^{2+}]^2 + K[Mg^{2+}]C_{SO_4} - K[Mg^{2+}]C_{Mg} + [Mg^{2+}] - C_{Mg} = 0$$

Gather terms

$$K[Mg^{2+}]^2 + (KC_{SO_4} - KC_{Mg} + 1)[Mg^{2+}] - C_{Mg} = 0$$

Remember the quadratic formula ?

Equation from previous slide

$$\mathbf{K[Mg^{2+}]^2 + (KC_{SO_4} - KC_{Mg} + 1)[Mg^{2+}] - C_{Mg} = 0}$$

Quadratic formula

$$\mathbf{x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}$$

Solve for **x** which for us is $[Mg^{2+}]$ where

$$\mathbf{a = K}$$

$$\mathbf{b = (KC_{SO_4} - KC_{Mg} + 1)}$$

$$\mathbf{c = -C_{Mg}}$$

Solving this problem with the quadratic formula

And substituting in the known values for:

K_f' which equals $K_f \gamma^2$

Where $K_f = K_{MgSO_4} = 2.29 \times 10^2$ and $\gamma = 0.23$

$C_{Mg} = 5.28 \times 10^{-2}$ mol/kg

$C_{SO_4} = 2.82 \times 10^{-2}$ mol/kg

The answer is: $x = [Mg^{2+}] = 4.35 \times 10^{-2}$ mol/kg

Since $C_{Mg} = 5.28 \times 10^{-2}$ mol/kg then $[Mg^{2+}] = 82 \%$

Activity Coefficient

At typical ionic strengths for SW $I = 0.5$ to 0.7

From Davies Equation Mg^{2+} activity coefficient

$$\ln \gamma = - A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

If $Z = 2$ & $A = 1.17$ then $\ln \gamma = - 1.47$ & $\gamma = 0.23$

Calculate All Species

Given $C_{\text{Mg}} = 5.28 \times 10^{-2}$ mol/kg

and $C_{\text{SO}_4} = 2.82 \times 10^{-2}$ mol/kg

We calculated $[\text{Mg}^{2+}] = 4.35 \times 10^{-2}$ mol/kg or **82 %**

By difference $[\text{MgSO}_4] = 9.30 \times 10^{-3}$ mol/kg or **18 %**

We can likewise calculate $[\text{SO}_4^{2-}]$ concentration & %

$C_{\text{SO}_4} - [\text{MgSO}_4] = [\text{SO}_4^{2-}] = 1.89 \times 10^{-2}$ mol/kg

Problems

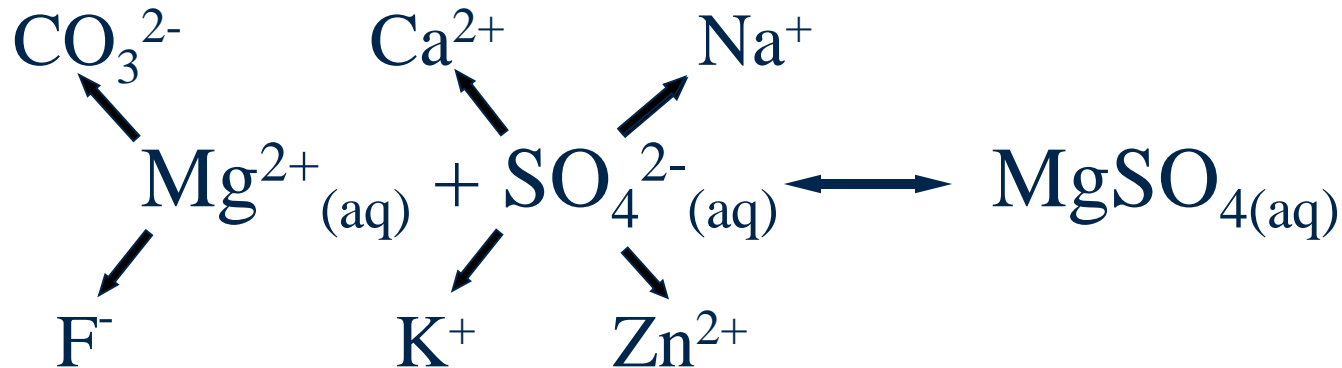
- # Went through a moderately difficult calculation & only calculated species for 1 reaction in SW
- # If considered more complicated equilibria where several reactions were going on, the math would quickly get out of hand
- # Didn't consider any other reactions involving Mg or SO_4 that might influence our results

Other Problems

- # Equilibrium constants can vary as much as 5% depending on the source
- # Concentration data vary as well
- # Activity corrections can also vary depending on the method used
- # We only considered activity corrections for charged species, while neutral species may also have γ 's that are non unity (e.g., MgSO_4)

Problems Mentioned

- # Only 1 reaction, 1 set of species, simple equilibrium
- # Didn't consider any other reactions involving Mg or SO_4 that might influence our results

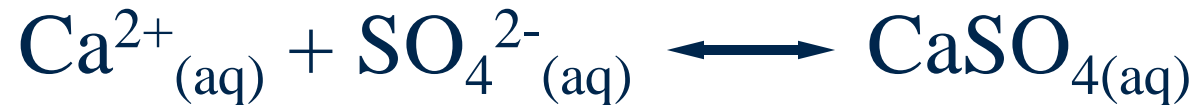


Other reactions influence amount of MgSO_4 produced

Must Consider Other Reactions



There are also



and



as well as others

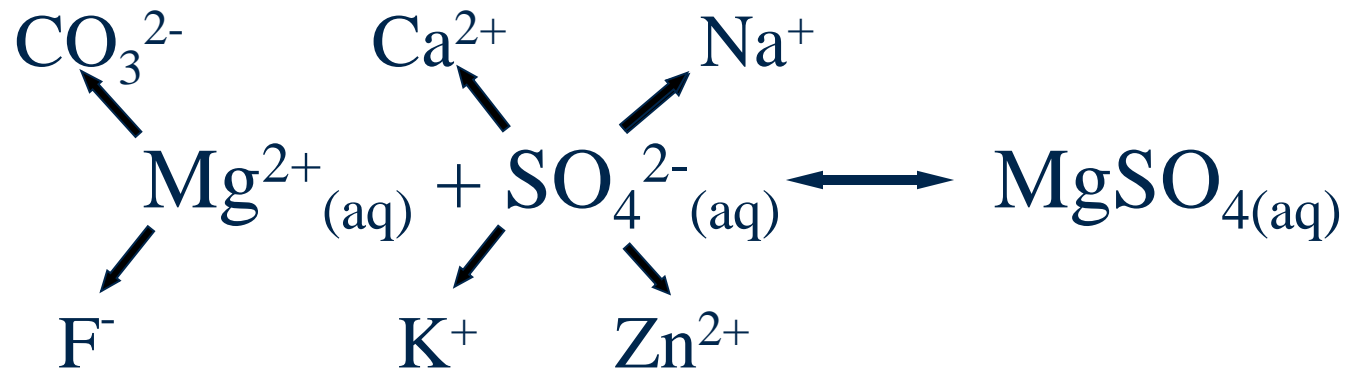
Several Questions to Ponder

- 1) Based on the knowledge that there are other competing reactions in SW, is our calculation accurate? (82 % free Mg^{2+} ?)
- 2) How do we know what other reactions are going on in SW that we should consider?
- 3) How do we include all the other equilibrium reactions that we might consider important?
- 4) How do we deal with the increased complexity of the mathematics?
- 5) Why did I take this course?

Answers to Question #1

Based on the knowledge that there are other competing reactions in SW, is our calculation accurate? (82 % free Mg^{2+} ?)

The calculation is only an estimate because we did not consider the formation of other species



their influence on the amount of MgSO_4 produced

Answers to Question #2

How do we know what other reactions are going on in SW that we should consider?

We will largely rely on the literature for known reactions in SW (e.g., books & papers such as the handout provided this week).

Chemical Intuition also helps

Answers to Question #3

How do we include all the other equilibrium reactions that we might consider important?

Using our manual approach to solving equilibrium problems, we would have to expand our mass balance equations as well as add additional equilibrium constant expressions

The number of species for which the concentration is unknown & the number of equations grows rapidly as we add equilibria.

Answers to Question #4

How do we deal with the increased complexity of the mathematics?

Solving 5 or more equations simultaneously can only be handled in two ways:

- 1) Assumptions or approximations can be made to simplify the equations to something more manageable
- 2) Computer programs designed to solve ionic equilibrium problems can be used

Computer programs

MINEQL+ – we will use this exclusively

<http://www.mineql.com/>

MINTEQA2 – EPA DOS version of MINEQL

<http://www.epa.gov/ceampubl/mmedia/minteq/index.htm>

GEOCHEM – geochemical modeling software

<http://envisci.ucr.edu/downloads/parker/geochem.zip>

Visual MINTEQ – user friendly MINTEQA2

www.lwr.kth.se/english/OurSoftware/vminteq/index.htm

PHREEQC – USGS modeling software

wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

Computer programs (continued)

HYDRA/MEDUSA

<http://w1.156.telia.com/%7Eu15651596/>

PHRQPITZ – USGS, for high ionic strength

<http://water.usgs.gov/software/phrqpitz.html>

WinHumicV – Includes humic binding model

<http://www.lwr.kth.se/english/OurSoftware/WinHumicV>

CHEAQS

<http://home.tiscali.nl/cheaqs/>

Handout

Marine Chemistry, 21 (1987) 101–116

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SPECIATION OF METALS IN THE OCEANS. I. INORGANIC COMPLEXES IN SEAWATER, AND INFLUENCE OF ADDED CHELATING AGENTS

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Motekaitis & Martell (1987) Table I

Note molar concentration units (M) & multiplier

Major and some minor constituents of seawater used in this study

Ion	Concentration, $M \times 10^3$	Trace Element	Concentration, $M \times 10^9$
Na^+	479	Mn	4
Mg^{2+}	54.5	Fe	8
Ca^{2+}	10.5	Ni	5
K^+	10.4	Cu	4
Cl^-	559	Zn	5
SO_4^{2-}	28.9	Cd	0.1
HCO_3^- , CO_3^{2-}	2.35	Hg	0.02
Br^-	0.86	Pb	0.05
F^-	0.075	U	14

Motekaitis & Martell (1987) Table I, Major Ions

Major and some minor constituents of seawater

Ion	Concentration, $M \times 10^3$
Na^+	479
Mg^{2+}	54.5
Ca^{2+}	10.5
K^+	10.4
Cl^-	559
SO_4^{2-}	28.9
HCO_3^- , CO_3^{2-}	2.35
Br^-	0.86
F^-	0.075

Note: These numbers have been multiplied by 10^3 or 1000 so they are millimolar (mM) or 479 is really 0.479 M or 4.79×10^{-2} M

Motekaitis & Martell (1987) Table I, Trace Ions

**Trace
Element**

**Concentration,
 $M \times 10^9$**

Mn

4

Fe

8

Ni

5

Cu

4

Zn

5

Cd

0.1

Hg

0.02

Pb

0.05

U

14

Note: These numbers have been multiplied by 10^9 and are nanomolar (nM) or 4 is really 4 nM or 4×10^{-9} M

Motekaitis & Martell give a long list of species with equilibrium constants

TABLE II

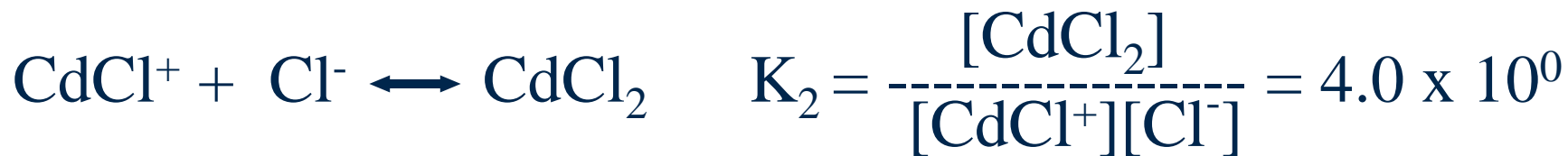
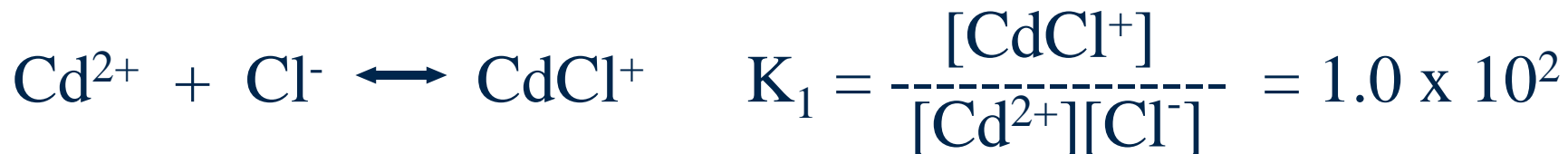
Note: Values are Log β not K, also $I(\mu) = 0.70$

Log overall stability constants for soluble components of seawater

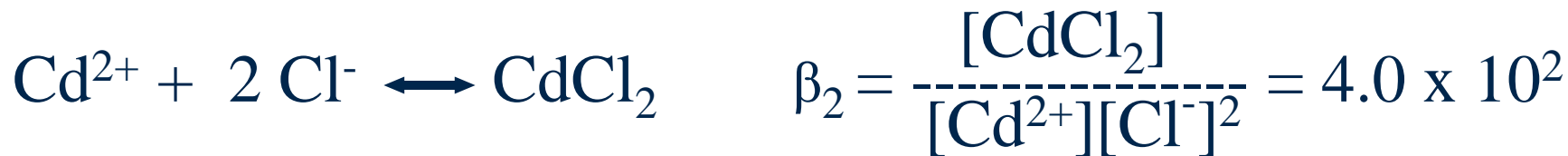
Species	Log β	Species	Log β
CaCO_3	2.21	FeH^+_{-2}	- 5.88
CaHCO_3^+	9.90	FeH^-_{-4}	- 20.76
CaSO_4	1.03	$\text{Fe}_2\text{H}^{4+}_{-2}$	- 3.08
CaF^+	0.60	MnHCO_3^+	10.00
CaH^+_{-1}	- 12.20	MnSO_4	0.80
MgCO_3	2.05	MnCl^+	- 0.20
MgHCO_2^+	9.80	MnCl_2	- 0.3
MgSO_4	0.90	MnCl_3^-	- 0.50
MgF^+	1.30	MnH^+_{-1}	- 10.80

The difference between β & K

K is a stepwise formation constant



β is an overall formation constant



Notes on β & K

$K_1 = \beta_1$ (from previous slide)

K_2 is not equal to β_2 (note denominators of each expression)

$\beta_2 = K_1 \times K_2$

$$\beta_2 = \frac{[\text{CdCl}_2]}{[\text{Cd}^{2+}][\text{Cl}^-]^2} = \frac{[\text{CdCl}^+]}{[\text{Cd}^{2+}][\text{Cl}^-]} \times \frac{[\text{CdCl}_2]}{[\text{CdCl}^+][\text{Cl}^-]}$$

$\beta_3 = K_1 \times K_2 \times K_3$ (etc.)

Motekaitis & Martell (1987)

TABLE VII

(values expressed as %)

Seawater speciation in the absence of added ligands at pH 8.1.

Metal ion	Cl ⁻	Br ⁻	F ⁻	SO ₄ ²⁻	(H)CO ₃ ^a	OH ⁻	Uncomplexed
Ca ²⁺			0.01	9.8	0.54		79.0
Mg ²⁺			0.07	8.4	0.45	0.02	91.1
K ⁺				2.2			97.8
Na ⁺				2.4	0.01		97.6
Mn ²⁺	34.4		0.01	4.4	0.15	0.12	60.9
Cd ²⁺	96.8	0.08		0.3		0.05	2.9
Hg ²⁺	99.9	0.05					
Fe ³⁺						1.71	
Cu ²⁺	1.9			0.2	22.4	73.6	1.85
Zn ²⁺	41.2	0.02		4.86	0.40	0.47	53.0
Pb ²⁺	22.32	0.02		0.3	71.9	3.9	1.5
Ni ²⁺	29.6	0.01		3.1		0.67	66.6
UO ₂ ²⁺					100.0		

Computer programs

MINEQL+ – we will use this
exclusively

<http://www.mineql.com/>


Program still requires setting up the Equilibrium Problem

- Must list species of interest
- Must have total concentration data for each constituent

Other needed information may include

- Ionic strength
- pH
- CO₂/Carbonate

Steps in the MINEQL+ Solution of Simple Equilibrium Problems

- 1) Start with a recipe: $C_{\text{Mg}} = 5.28 \times 10^{-2}$ mol/kg
 $C_{\text{SO}_4} = 2.82 \times 10^{-2}$ mol/kg
- 2) List the species: Mg^{2+} , SO_4^{2-} , MgSO_4

- 3) Run the program
- 4) Interpret the results