

Chemical Oceanography

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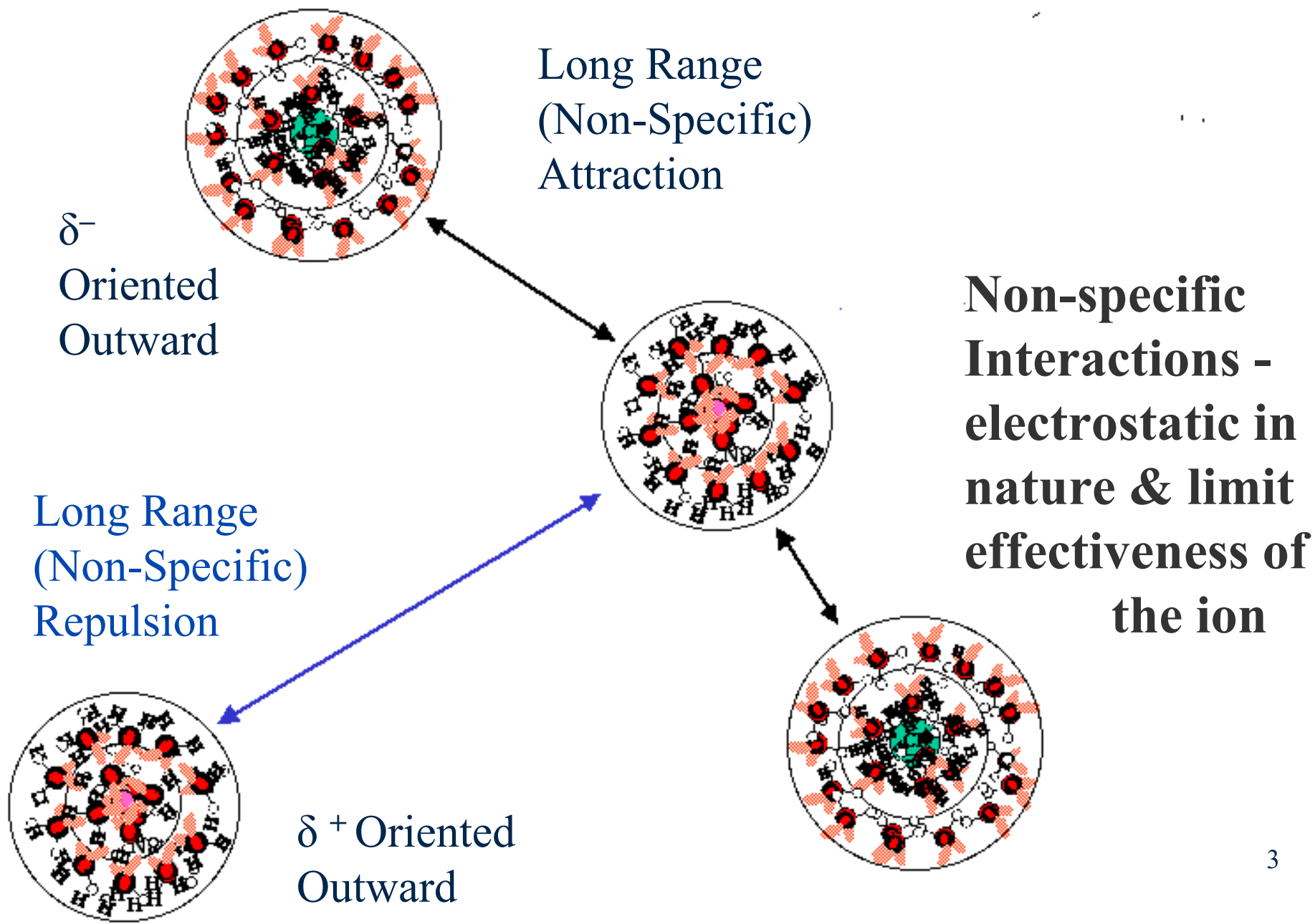
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http://faculty.uml.edu/David_Ryan/84.653

Ion-Ion Interactions

- # Many types – non-specific, bonding, contact, solvent shared, solvent separated
- # Non-specific i.e., long range interactions and the concepts of ionic strength, activity & activity coefficient
- # Specific interactions e.g. complexation, ion pairing (strong or weak)
- # Millero cartoons

<http://fig.cox.miami.edu/~lfarmer/MSC215/MSC215.HTM>



Non-specific Interaction

- # Electrostatic in nature
- # Limits effectiveness of ion in solution
- # Use concept of **activity** to quantify effect

(accounting for non-ideal behavior in solution)

$$\mathbf{a}_i = [\mathbf{i}]_F \gamma_F(\mathbf{i}) \quad \text{where } a_i = \text{activity of ion } i$$

$[\mathbf{i}]_F = \text{free ion conc. (m or M)}$
 $\gamma_F(\mathbf{i}) = \text{activity coefficient of ion } I \quad (\leq 1)$

In short

$$\mathbf{a} = [\mathbf{i}] \gamma$$

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

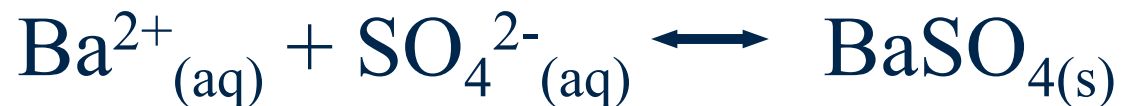
K_{sp} for solubility product

K_f for a formation constant

$K_1, K_2, K_3,$ etc. for stepwise formation constants

$\beta_1, \beta_2, \beta_3,$ 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

$$K_{\text{SP}} = a_{\text{Ba}} a_{\text{SO}_4} = \gamma_{\text{Ba}} [\text{Ba}^{2+}] \gamma_{\text{SO}_4} [\text{SO}_4^{2-}]$$

2) Correct the equilibrium constant K

$$K' = \frac{K_{\text{SP}}}{\gamma^2} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$

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^+)



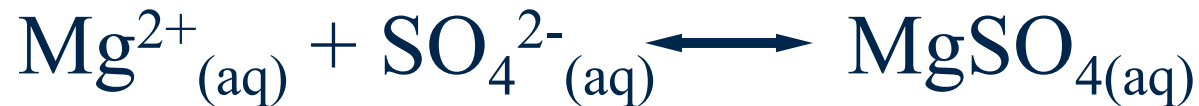
$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad \text{or} \quad \frac{a_{\text{BH}^+} a_{\text{OH}^-}}{a_{\text{B}}}$$

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:

$$\Sigma Z_{i+}[i^+] = \Sigma Z_{i-}[i^-]$$

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:

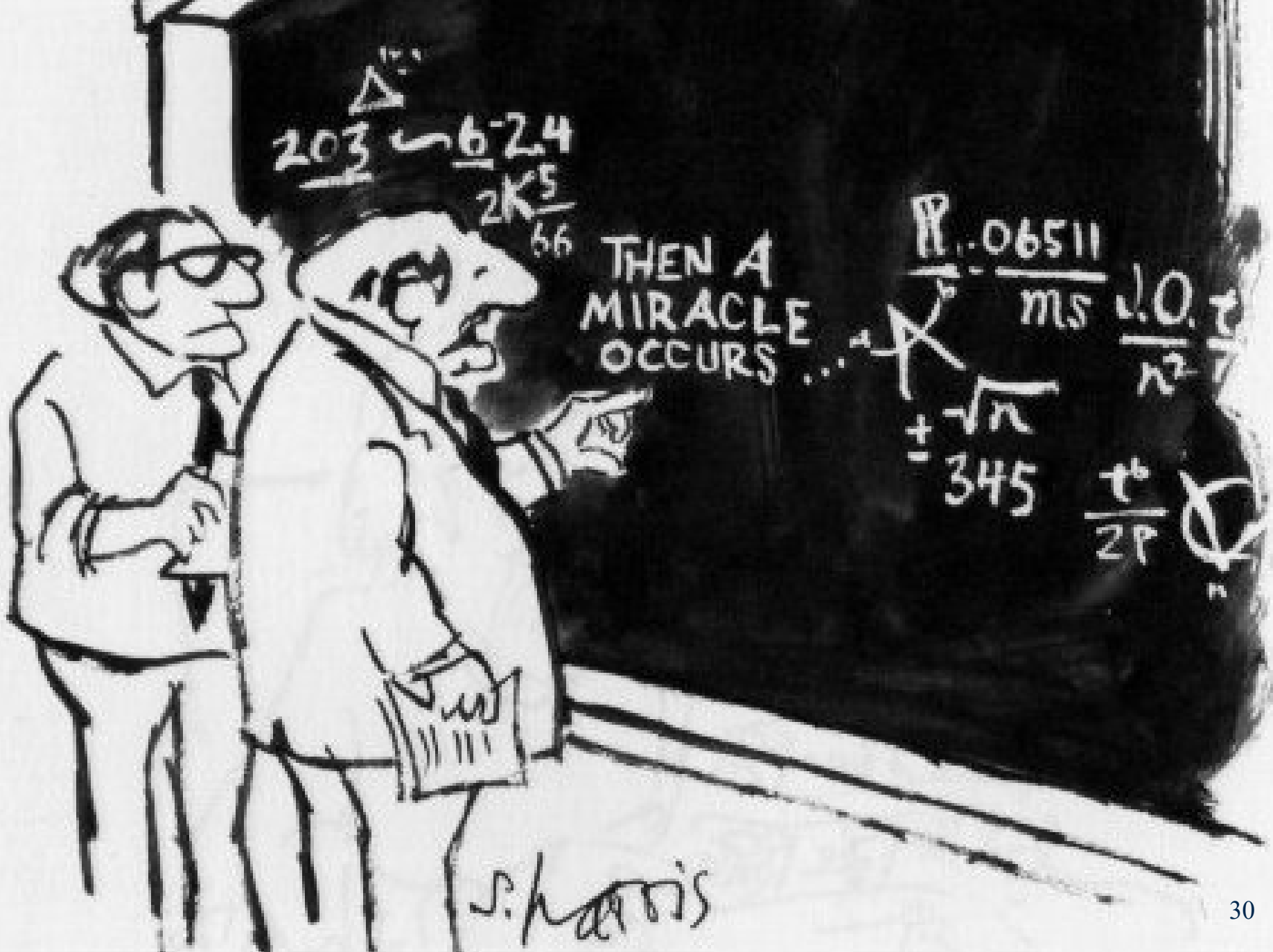
$$C_{\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgSO}_4] \quad \text{rearranges}$$

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



$$\begin{array}{l} \triangle \\ \hline 203 \\ \hline 6.24 \\ \hline 2K5 \\ \hline 36 \end{array}$$

THEN A
MIRACLE
OCCURS...

$$\begin{array}{l} \frac{.06511}{ms} \\ \sqrt{\quad} \\ +\sqrt{n} \\ 345 \end{array} \quad \frac{1.0. t}{n^2-7} \quad \frac{t^2}{2P} \quad \textcircled{D}$$

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

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

Substitute into K

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

$$\mathbf{a = K} \qquad \mathbf{b = (KC_{SO_4} - KC_{Mg} + 1)} \qquad \mathbf{c = -C_{Mg}}$$

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