Chemical Oceanography

Ryan Lecture 3

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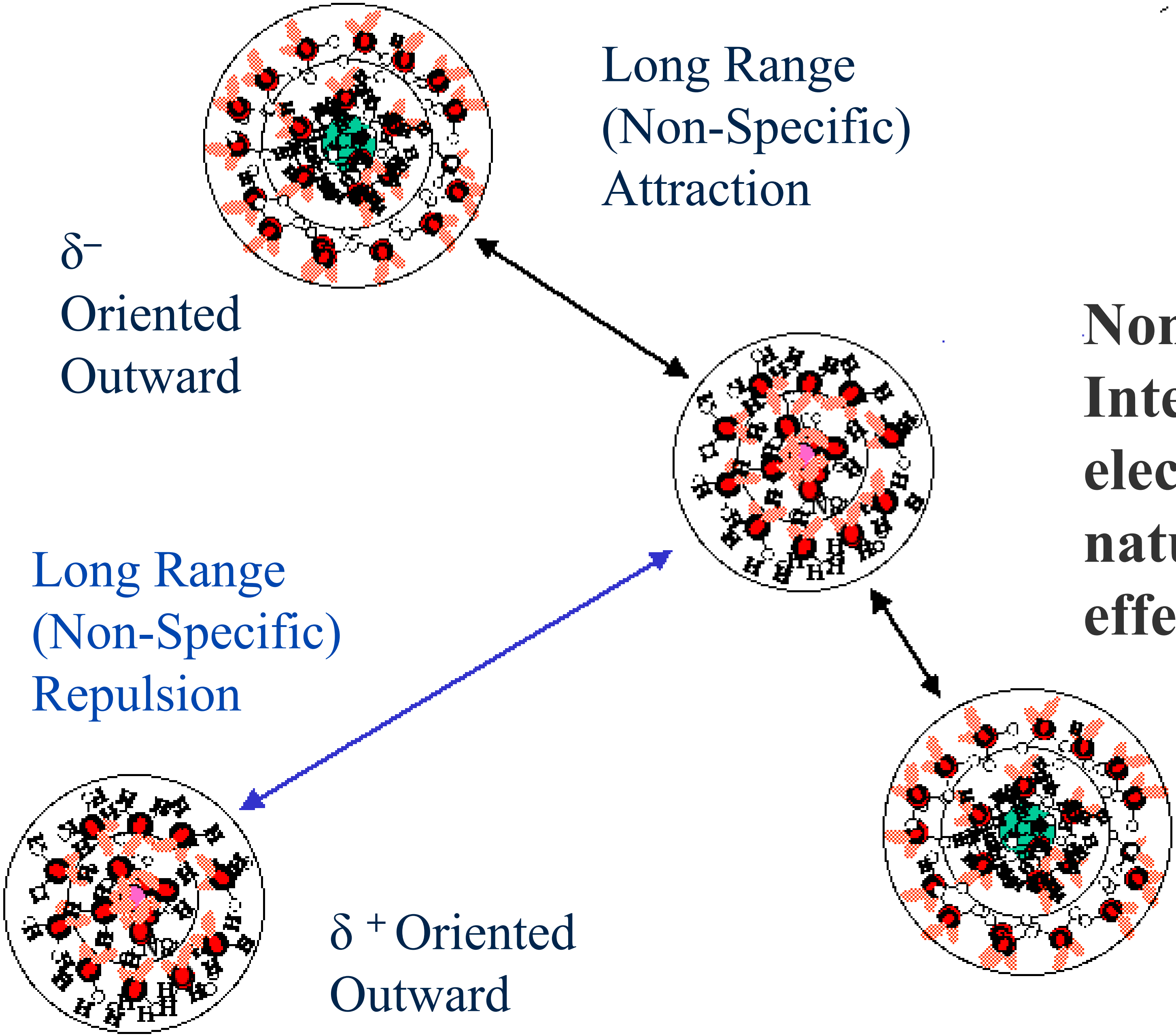
Ion-Ion Interactions

- 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



Long Range
(Non-Specific)
Attraction

δ⁻
Oriented
Outward

Long Range
(Non-Specific)
Repulsion

δ ⁺ Oriented
Outward

Non-specific Interactions - electrostatic in nature & limit effectiveness of the ion

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)

$\mathbf{a_i = [i]_F \, \gamma_F(i)}$

where a_i = activity of ion i

$[i]_F$ = free ion conc. (m)

$\gamma_F(i)$ = activity coefficient of ion I ($\leq$ 1)

In short $\boxed{\mathbf{a = [i] \, \gamma}}$

Activity of Individual Ion Influenced by Other Ions

- Ionic Strength of solution

$\mathbf{I = 0.5\ \Sigma\ Z^2\ m}$ where I = ionic strength

Z = charge on ion

m = molal conc.

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

Activity Coefficient (γ)

- Debye-Huckel Theory is starting point

(Primarily for very low ionic strength)

$$\ln \gamma\underline{+} = - A Z^2 I^{0.5} \qquad \text{original D.H.}$$

or

$$\ln \gamma\underline{+} = - S_f I^{0.5} /(1 + A_f a I^{0.5}) \qquad \text{extended}$$

Where $\gamma\underline{+}$ is the mean ion activity coefficient

S_f, A & A_f are constants related to temperature

I is ionic strength & a is the ion size parameter in Å

Z is the charge on the ion

Activity Coefficient (γ)

- Guntelberg Approximation

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

Where $\gamma\underline{+}$ is the mean ion activity coefficient

A is a constant

I is ionic strength

Z is the charge on the ion

Useful for $I \geq 0.1$

Activity Coefficient (γ)

- Davies Equation

$$\ln \gamma_{\pm} = -A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.3 I]$$

Where $\gamma_{\pm}$ is the mean ion activity coefficient

A is a constant (= 1.17)

I is ionic strength

Z is the charge on the ion

Useful for
$I \leq 0.5$

Activity Coefficient (γ)

- Bronsted-Guggenheim

$$\ln \gamma_{\pm} = \ln \gamma_{DH} + \sum_{j} B_{ij}[j] + \sum_{j} \sum_{k} C_{ijk}[j][k] + \ldots$$

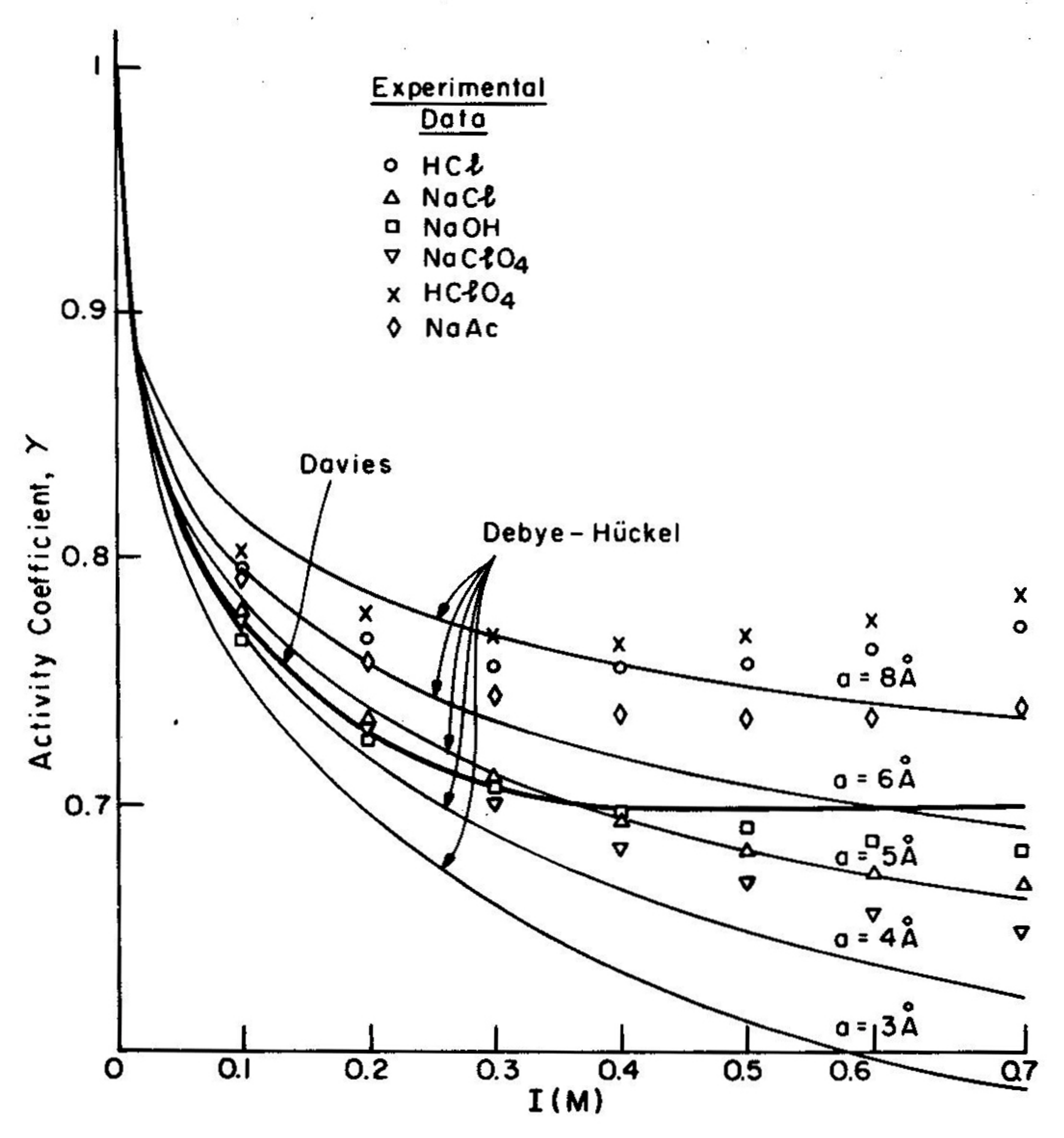
Where $\gamma_{\pm}$ is the mean ion activity coefficient

γ_{DH} is the γ from Debye-Huckel

B_{ij} is a virial coefficient for ion pairs

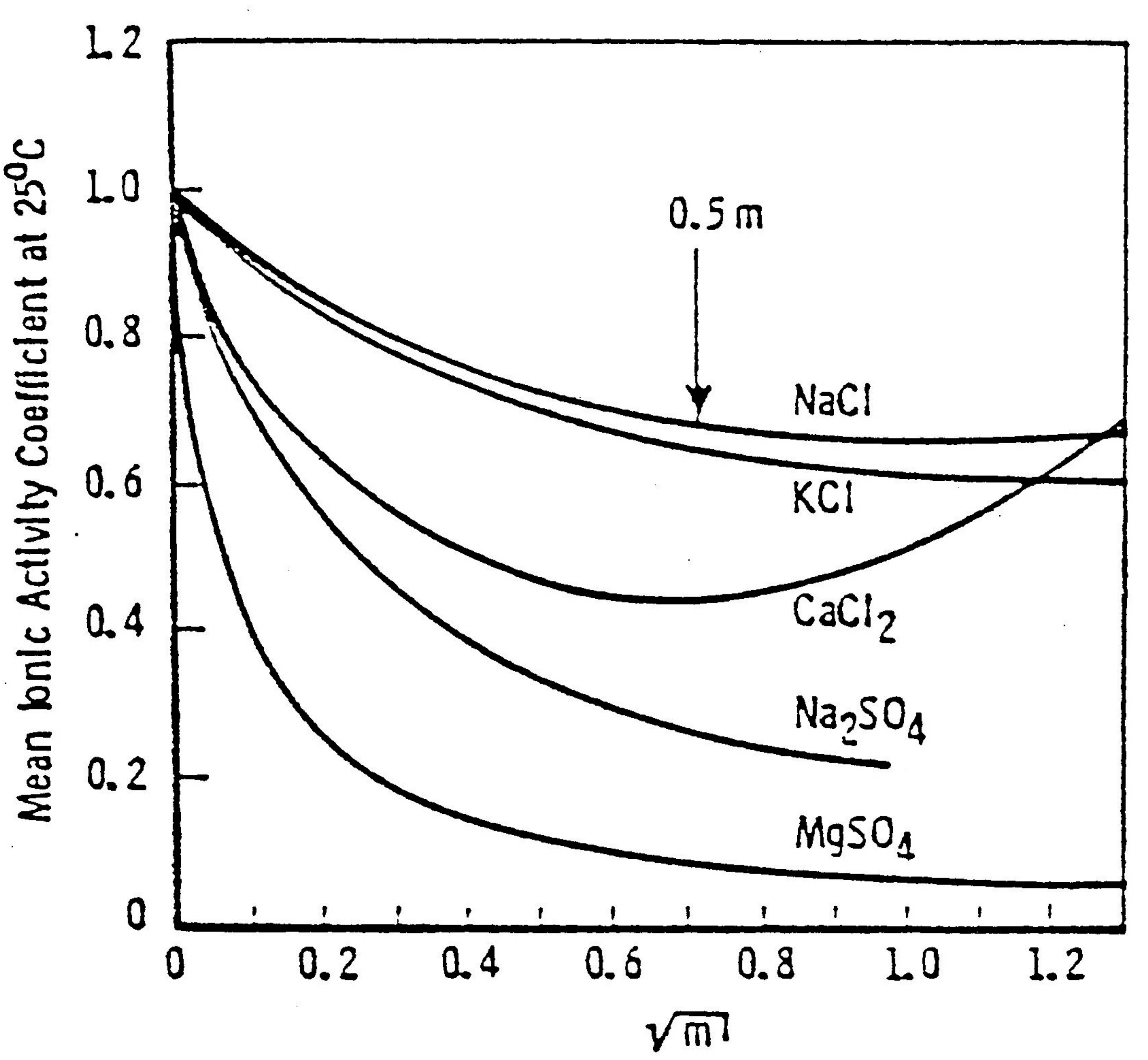
C_{ijk} is a virial coefficient for three ions

Useful at any I



Comparison of Davies Equation & Debye-Huckel for monovalent Ions

Morel & Hering 1993



Activity Coefficient vs. Conc., Monovalent & Divalent Systems

Activity Coefficient vs. Conc., Ideal, Monovalent & Divalent Systems

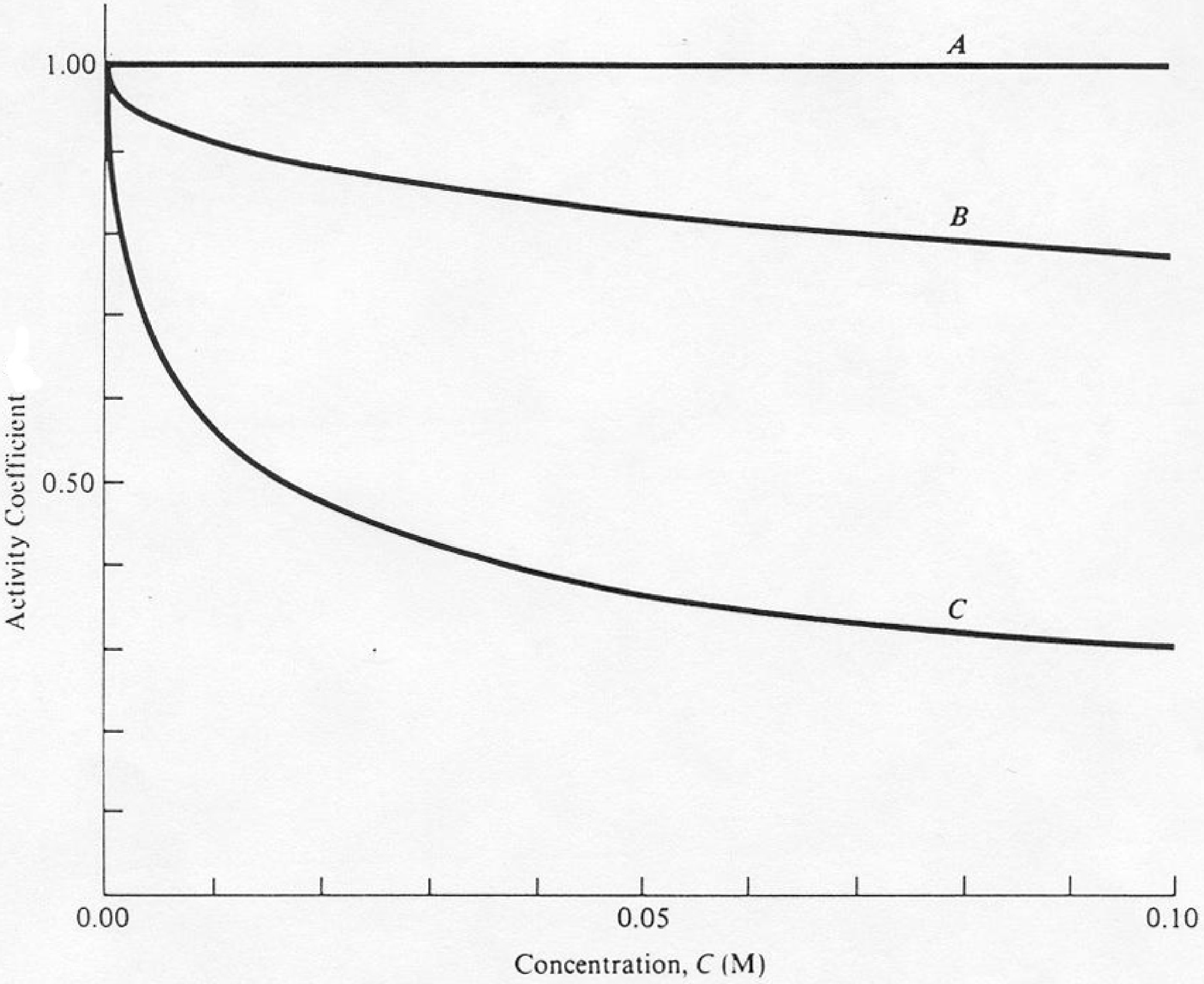


FIGURE 4-2 Activity coefficient as a function of concentration in the solution: (*A*) ideal solution for which $\gamma = 1.00$ at all concentrations: (*B*) activity coefficient for Na^+ in NaCl solutions; (*C*) activity coefficient for Ca^{2+} in $CaCl_2$ solution.

(Kennedy 1990)

Activity Coefficient vs. Conc., Ideal, Monovalent & Divalent Systems

(Kennedy 1990)

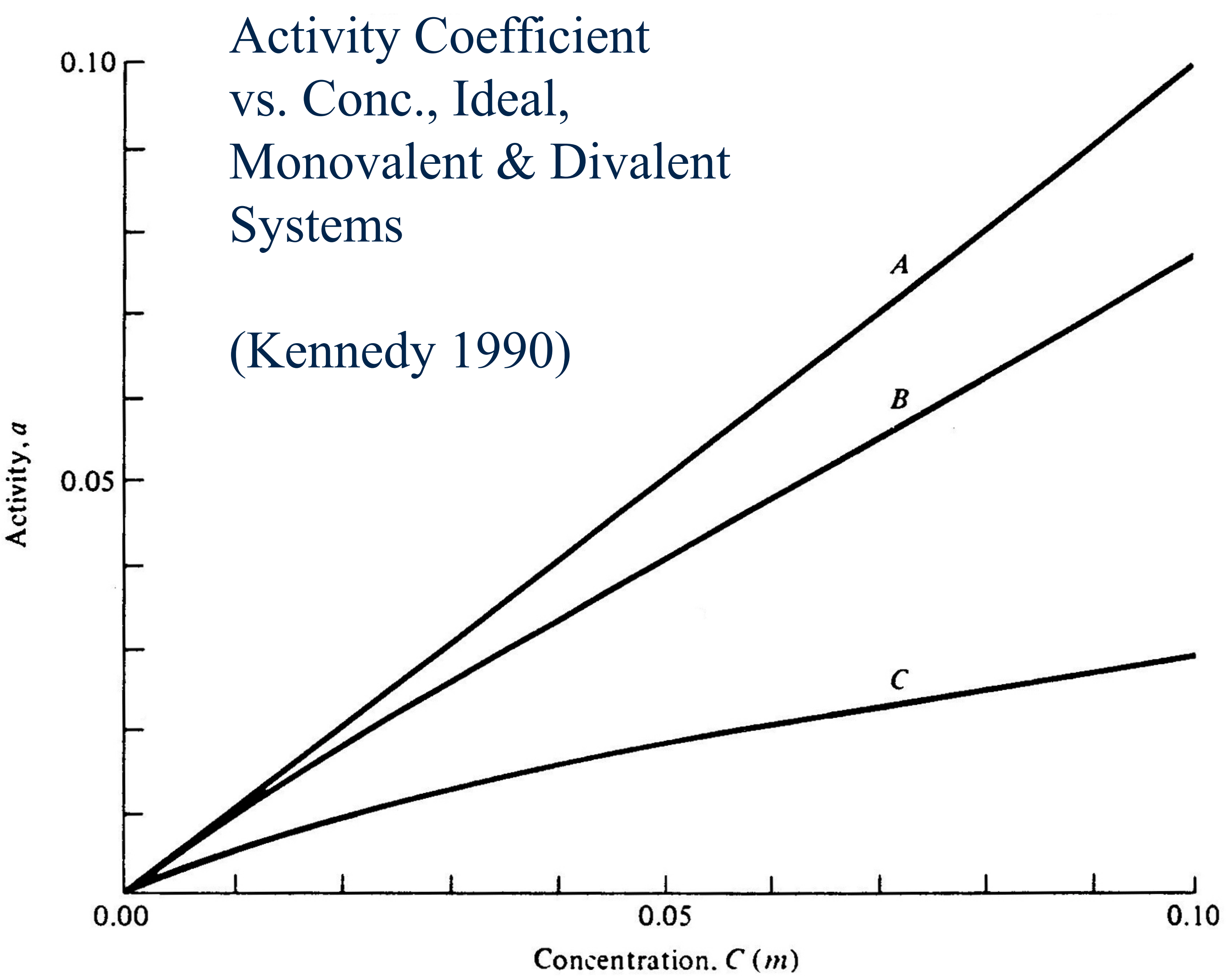


FIGURE 4-1 Activity as a function of concentration: (A) ideal solution for which $a = C$; (B) Na^+ activity in NaCl; (C) Ca^{2+} activity in $CaCl_2$.

Putting It All Together

- Calculate ionic strength from concentrations of all ions in solution using $\mathbf{I = 0.5\ \Sigma\ Z^2\ m}$
- Use Davies Equation to calculate activity coefficients for all ions of interest (Z = 1,2,3,4)

$$\ln \gamma\underline{+} = - A\ Z^2\ [I^{0.5}/(1 + I^{0.5}) - 0.3\ I]$$

- Calculate activity of the ions of interest using their concentrations and activity coefficients

$$a = [i]\ \gamma$$

Example: pH of SW

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

$$\mathbf{pH = -log\ a_{H+}}$$

At a typical ionic strength of seawater **$I = 0.7$**

From Davies Equation H^+ activity coefficient

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

If $Z = 1$ & $A = 1.17$ then $\ln \gamma = -0.37$ & **$\gamma = 0.69$**

(using 0.3 in the Davies Equation gives $\gamma = 0.75$)

Example: pH (cont.)

If a typical seawater pH is 8.2

Then H^+ activity is $1 \times 10^{-8.2}$ or 6.31×10^{-9} M

From $\mathbf{a = [i]\gamma}$ or $a_{H+} = [H^+]\gamma_{H+}$ & calculated $\gamma = 0.69$

$$6.31 \times 10^{-9}\ M = [H^+] \times 0.69$$

$$[H^+] = 9.14 \times 10^{-9}\ M$$

Activity of H^+ is 31% lower than it's concentration

Effectiveness of H^+ is 31% lower due to crowding

This phenomenon is greater for divalent ions

Composition of SW

- To Date We Have Covered:
    - Descriptive Oceanography (Millero chapter 1)
    - Special Properties of H_2O (Millero chapter 4)
    - Ion-Water & Ion-Ion Interactions (Millero chap. 4)
- Continuing Coverage
    - Major Components of SW (Millero chapter 2)
    - Salinity (Millero chapter 2)
    - Minor Components of SW (Millero chapter 3)
    - Ionic Equilibria (Millero chapter 4)

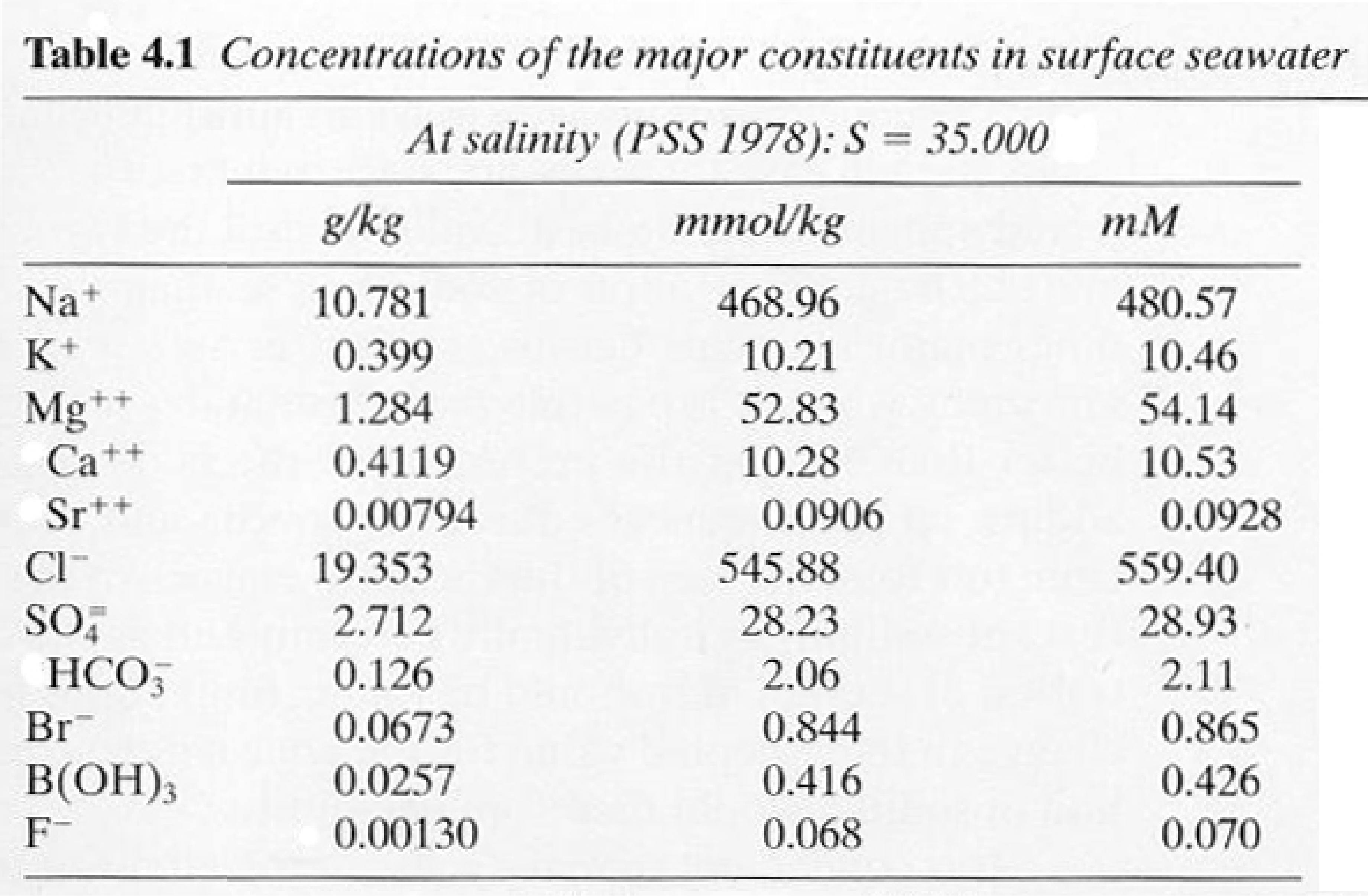


Table 4.1 *Concentrations of the major constituents in surface seawater*

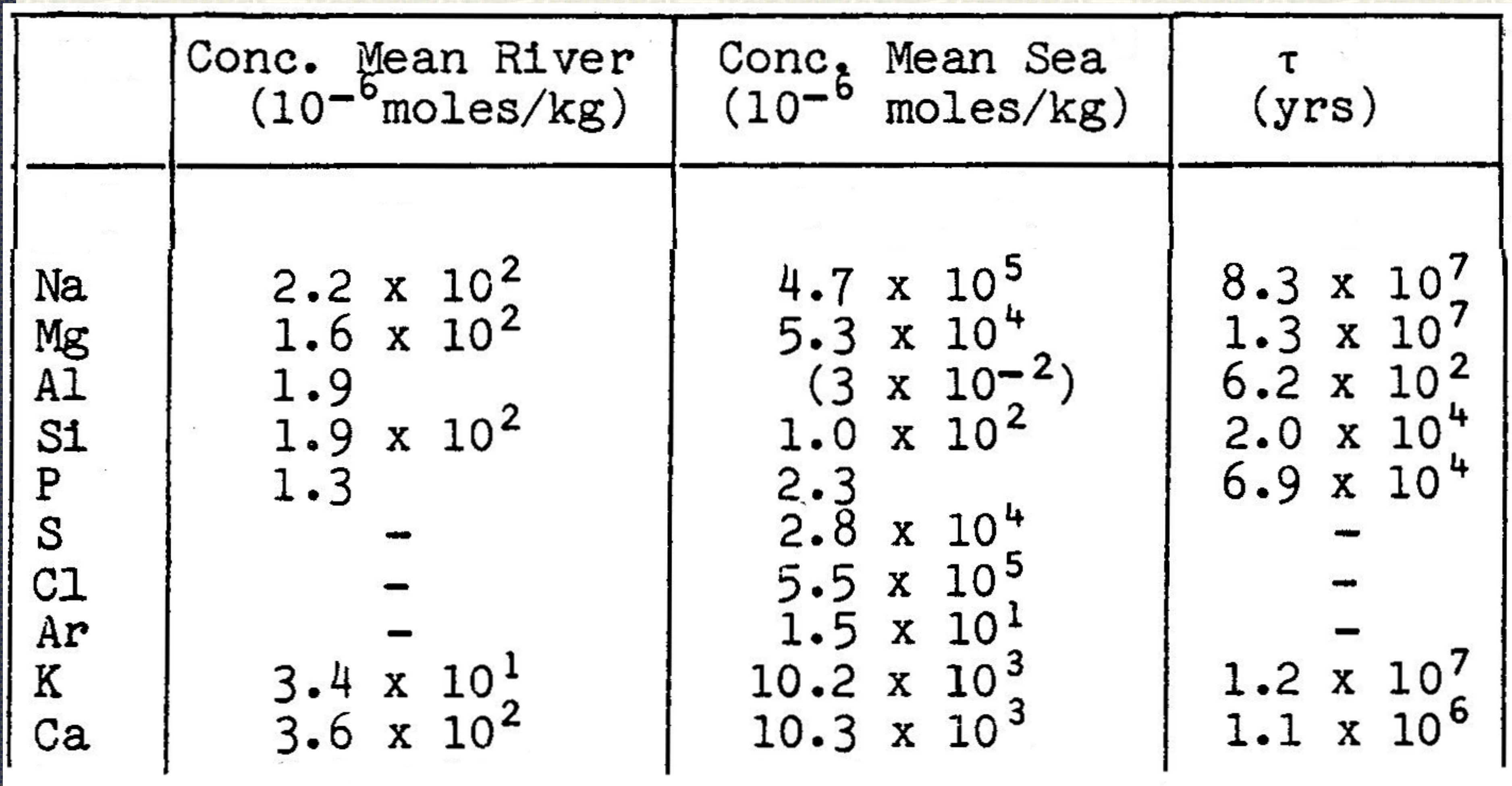
	At salinity (PSS 1978): S = 35.000		
	g/kg	*mmol/kg*	*mM*
Na^+	10.781	468.96	480.57
K^+	0.399	10.21	10.46
Mg^{++}	1.284	52.83	54.14
Ca^{++}	0.4119	10.28	10.53
Sr^{++}	0.00794	0.0906	0.0928
Cl^-	19.353	545.88	559.40
$SO_4^=$	2.712	28.23	28.93
HCO_3^-	0.126	2.06	2.11
Br^-	0.0673	0.844	0.865
$B(OH)_3$	0.0257	0.416	0.426
F^-	0.00130	0.068	0.070

SW Density = 1.024763 kg/L at 20 °C (Pilson 1998)

Major Components of SW

- Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} are most abundant
- Account for 98.5 % of dissolved species in SW
- Have major influence on SW density
- Have long residence time in the ocean
- Generally exhibit conservative behavior
  - Concentration influenced by physical processes such as evaporation & precipitation, not chemical or biological processes
- Discussing completely dissolved species

Element Concentrations in Average River & Average Ocean Water with Residence Times



	Conc. Mean River (10^{-6} moles/kg)	Conc. Mean Sea (10^{-6} moles/kg)	τ (yrs)
Na	2.2×10^2	4.7×10^5	8.3×10^7
Mg	1.6×10^2	5.3×10^4	1.3×10^7
Al	1.9	(3×10^{-2})	6.2×10^2
Si	1.9×10^2	1.0×10^2	2.0×10^4
P	1.3	2.3	6.9×10^4
S	-	2.8×10^4	-
Cl	-	5.5×10^5	-
Ar	-	1.5×10^1	-
K	3.4×10^1	10.2×10^3	1.2×10^7
Ca	3.6×10^2	10.3×10^3	1.1×10^6

Broecker and Peng (1982)

Cycling of SW Components

"The sea is a way station for the products of continental erosion. All substances received by the sea are ultimately passed along to the sediment…tectonic forces…eventually push the material buried in this way back above sea level where it becomes subject to erosion. Then another trip through the sea begins."

Broecker and Peng (1982)

Cycling of SW Components

- Most components are recycled many times within SW by a variety of processes
- Can determine residence times (τ) in ocean
- Constituents can be classified as:
  - Biolimiting – totally depleted in surface water
  - Biointermediate – partially depleted
  - Biounlimited – no measurable depletion
  - Noncycling – reactive & removed

Broecker and Peng (1982)

SW Composition

The composition of SW generally reflects two factors:

1) The relative abundance of the substance in river water (i.e., the input)
2) The presence of removal mechanisms that result in entrapment of the material in sediments (i.e., the output)