Chemical Oceanography 2022

Dr. David K. Ryan
Department of Chemistry
University of Massachusetts Lowell
&
Intercampus of Marine Sciences Program

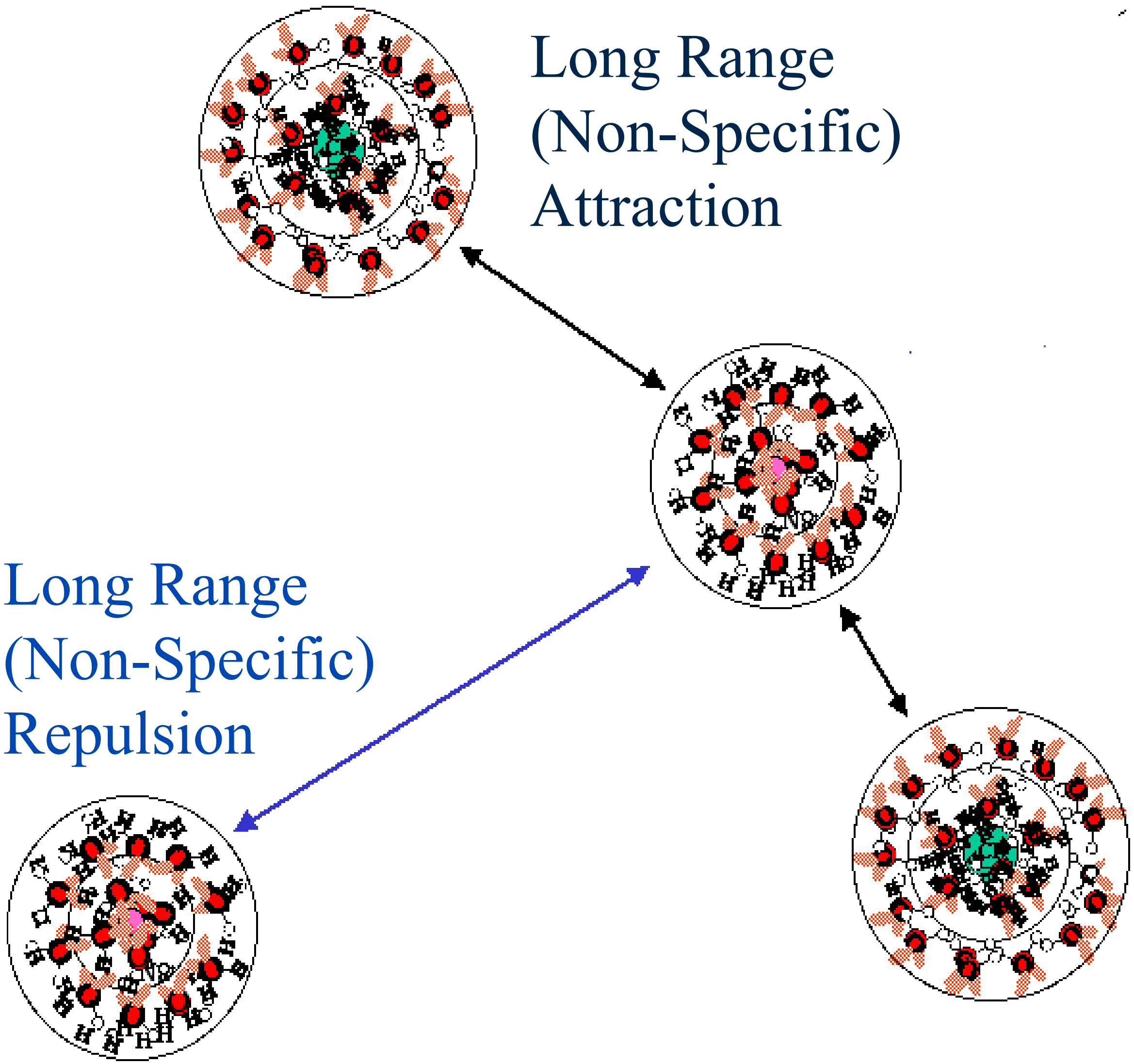
http://faculty.uml.edu/David_Ryan/84.653

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

Long Range Non-Specific Interactions



Electrostatic effects also occur for specific interactions (i.e. chemical reactions)

Non-specific Interaction

(When a particular ion of interest is affected by other ions)

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

(activity = effective concentration, accounts for non-ideal behavior)

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

where a_i = activity of ion i

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

$\gamma_F(i)$ = activity coefficient of ion i

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

Activity of Individual Ion Influenced by Other Ions

- Ionic Strength of solution

$$I = 0.5\ \Sigma\ Z^2\ m$$

where I = ionic strength

Z = charge on ion

m = molal conc.

(molarity or molinity can also be used)

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

Activity Coefficient (γ)

- Debye-Huckel Theory is starting point

  (Primarily for very low ionic strength)

$$\ln \gamma_{\pm} = - A Z^2 I^{0.5} \qquad \text{original D.H.}$$

or

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

Where $\gamma_{\pm}$ 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

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

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

A is a constant

I is ionic strength

Z is the charge on the ion

Useful for $I > 0.1$

Activity Coefficient (γ)

- Davies Equation

$$\ln \gamma_{\pm} = - A\, Z^2 \left[I^{0.5}/(1 + I^{0.5}) - 0.2\, I \right]$$

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

$\boxed{\text{Useful for } I \sim 0.5}$

Activity Coefficient (γ)

- Bronsted-Guggenheim

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

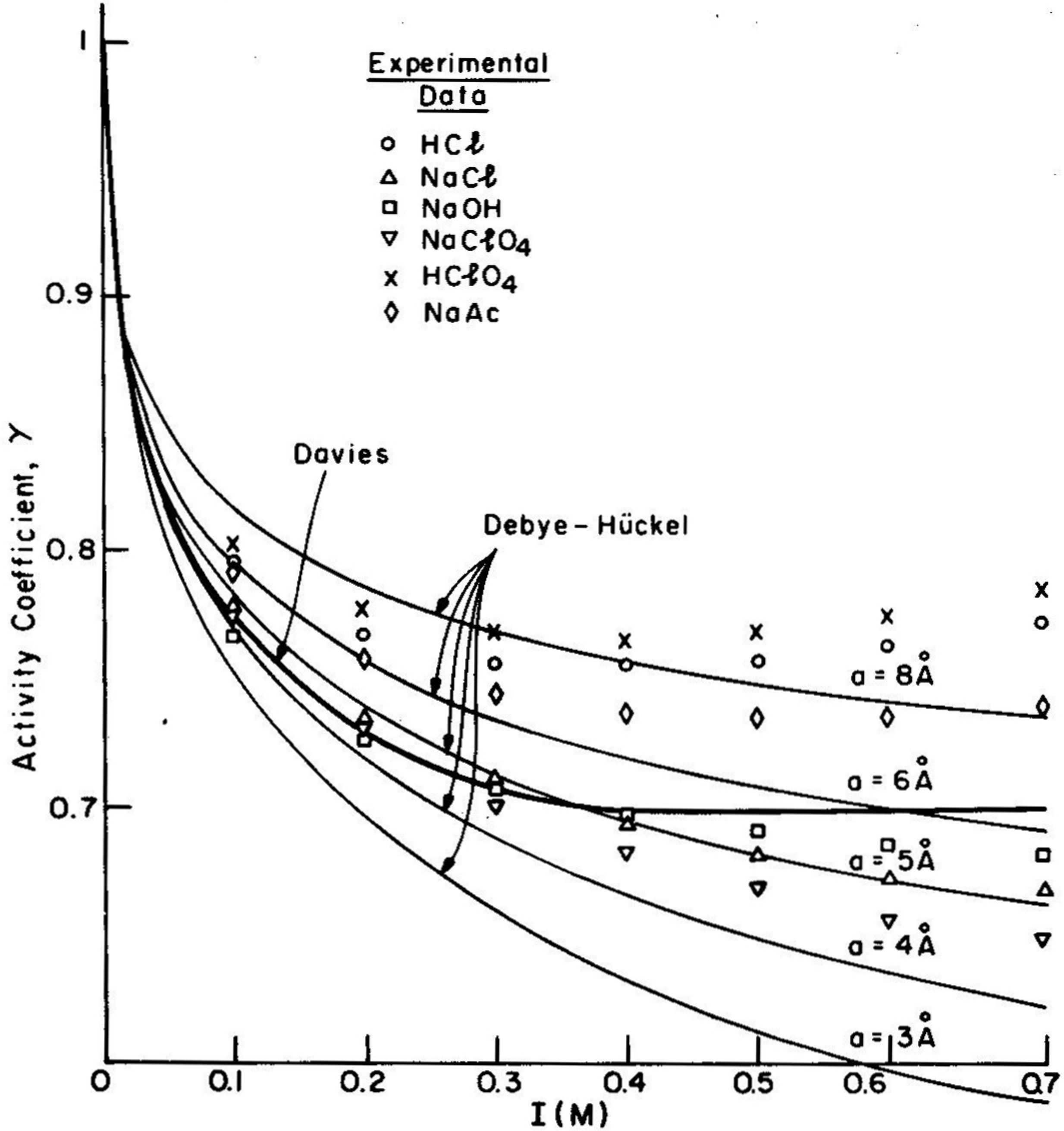
Where $\gamma_{\pm}$ is the mean ion activity coefficient

γ_{DH} is the γ from Debye-Huckel

B_{ij} is a virial coefficient for ion pairs

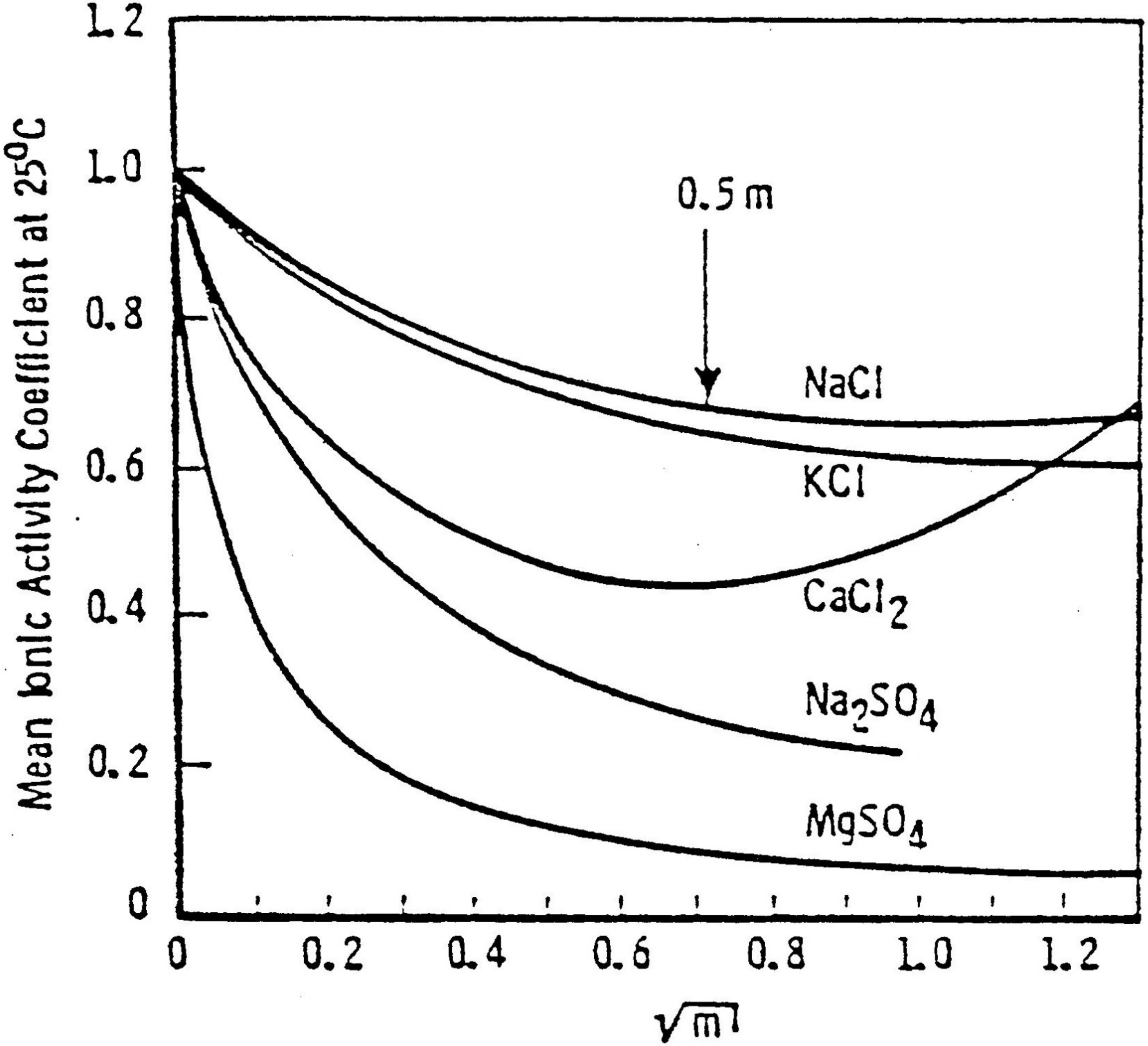
C_{ijk} is a virial coefficient for three ions

Useful at any I



Comparison of Davies Equation & Extended Debye-Huckel for monovalent Ions

Morel & Hering 1993



Activity Coefficient vs. Conc., Monovalent & Divalent Systems

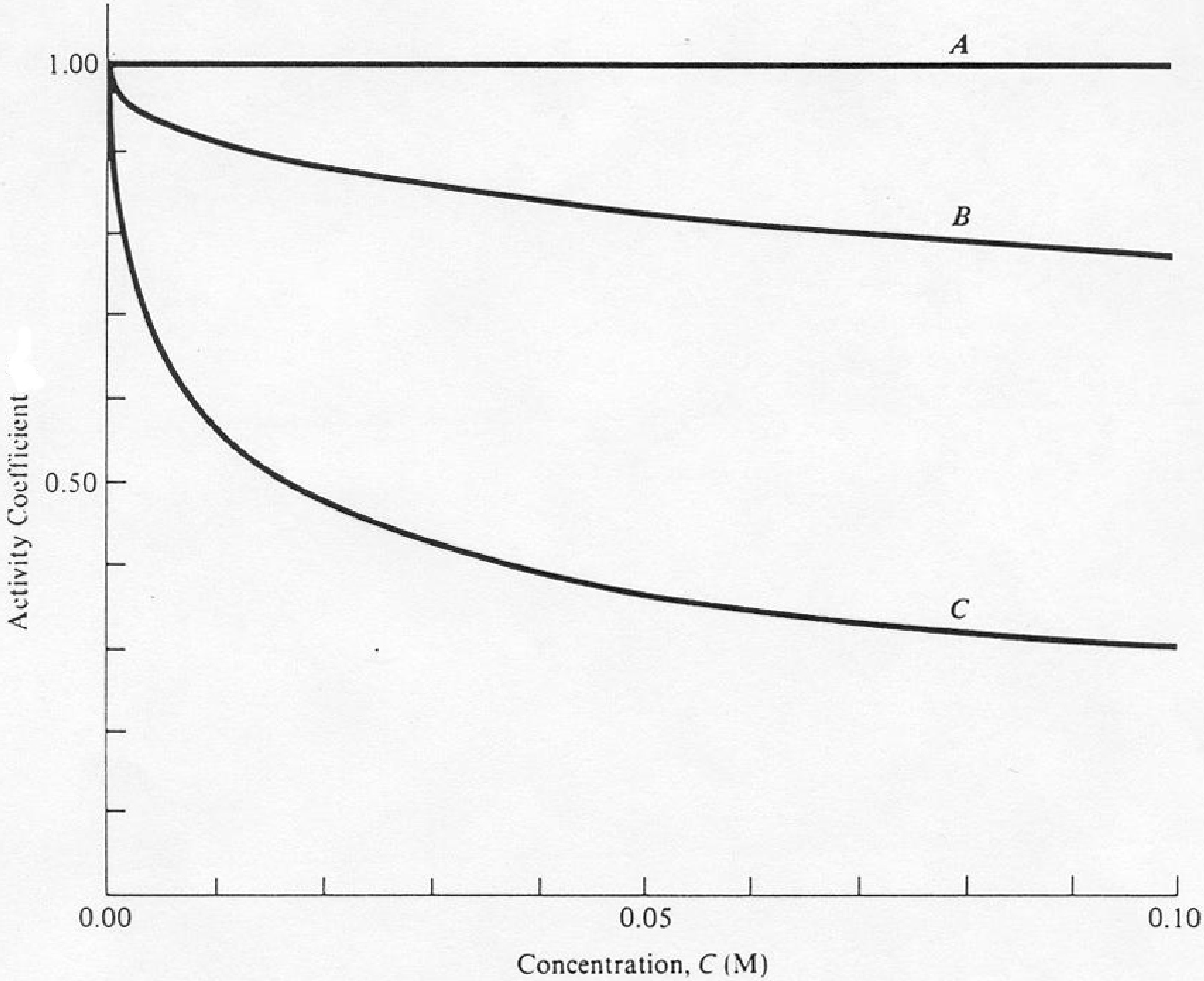


FIGURE 4-2 Activity coefficient as a function of concentration in the solution: (*A*) ideal solution for which $\gamma = 1.00$ at all concentrations: (*B*) activity coefficient for Na^+ in NaCl solutions; (*C*) activity coefficient for Ca^{2+} in $CaCl_2$ solution.

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

(Kennedy 1990)

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

(Kennedy 1990)

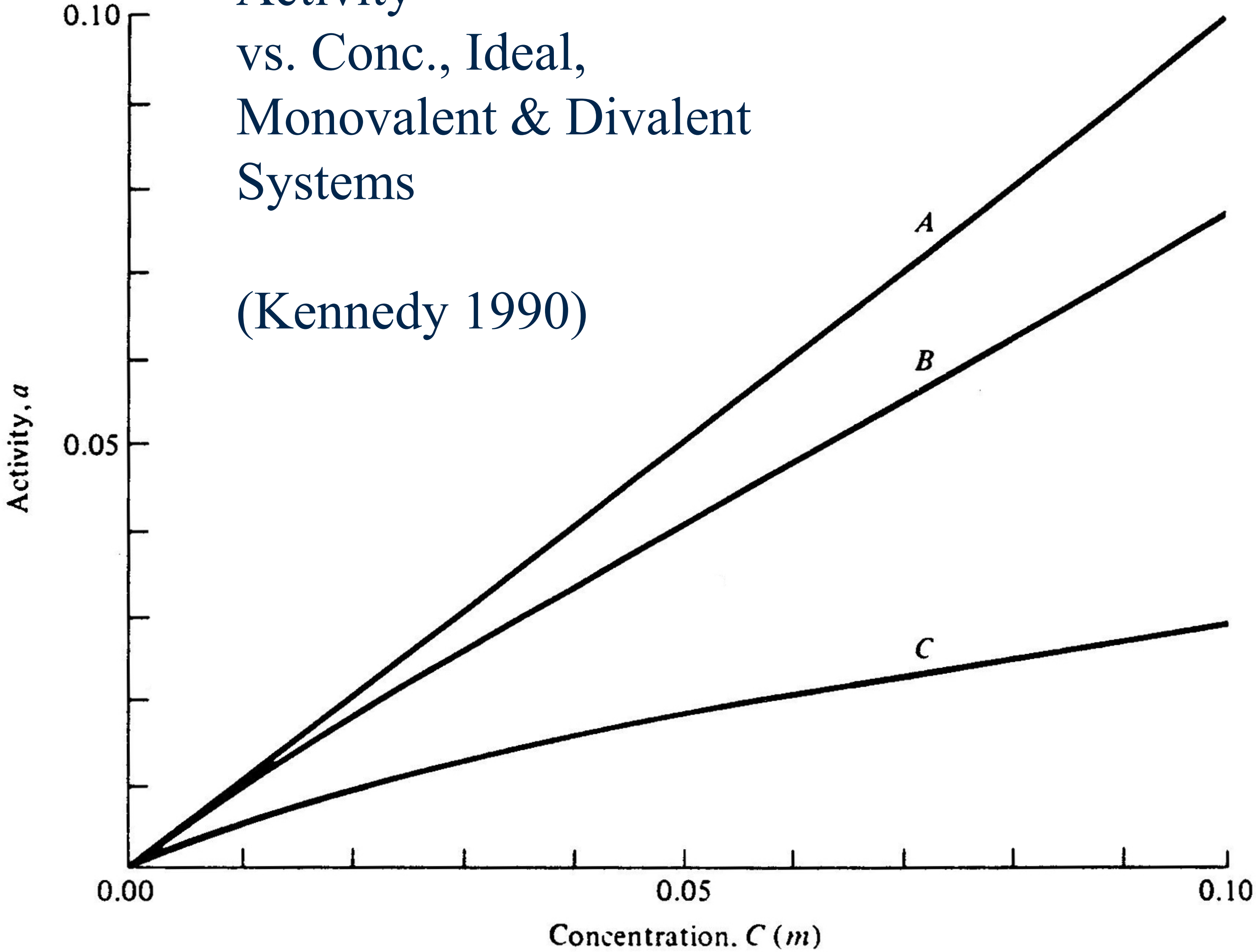


FIGURE 4-1 Activity as a function of concentration: (*A*) ideal solution for which $a = C$; (*B*) Na^{+} activity in NaCl; (*C*) Ca^{2+} activity in $CaCl_2$.

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)

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

- 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

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

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

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 $\gamma = 0.69$

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

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

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

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 ^oC (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

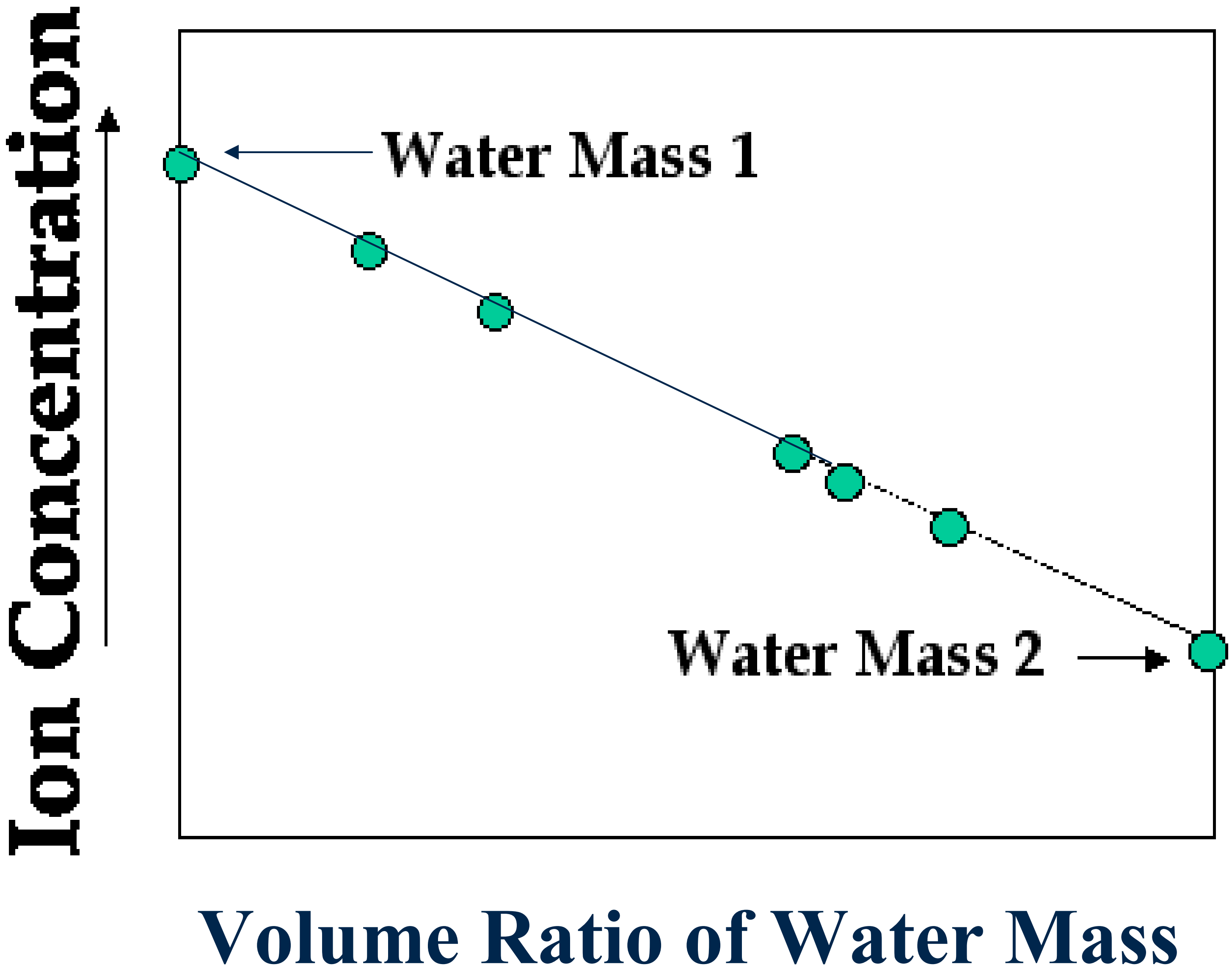
The composition of SW generally reflects two factors:

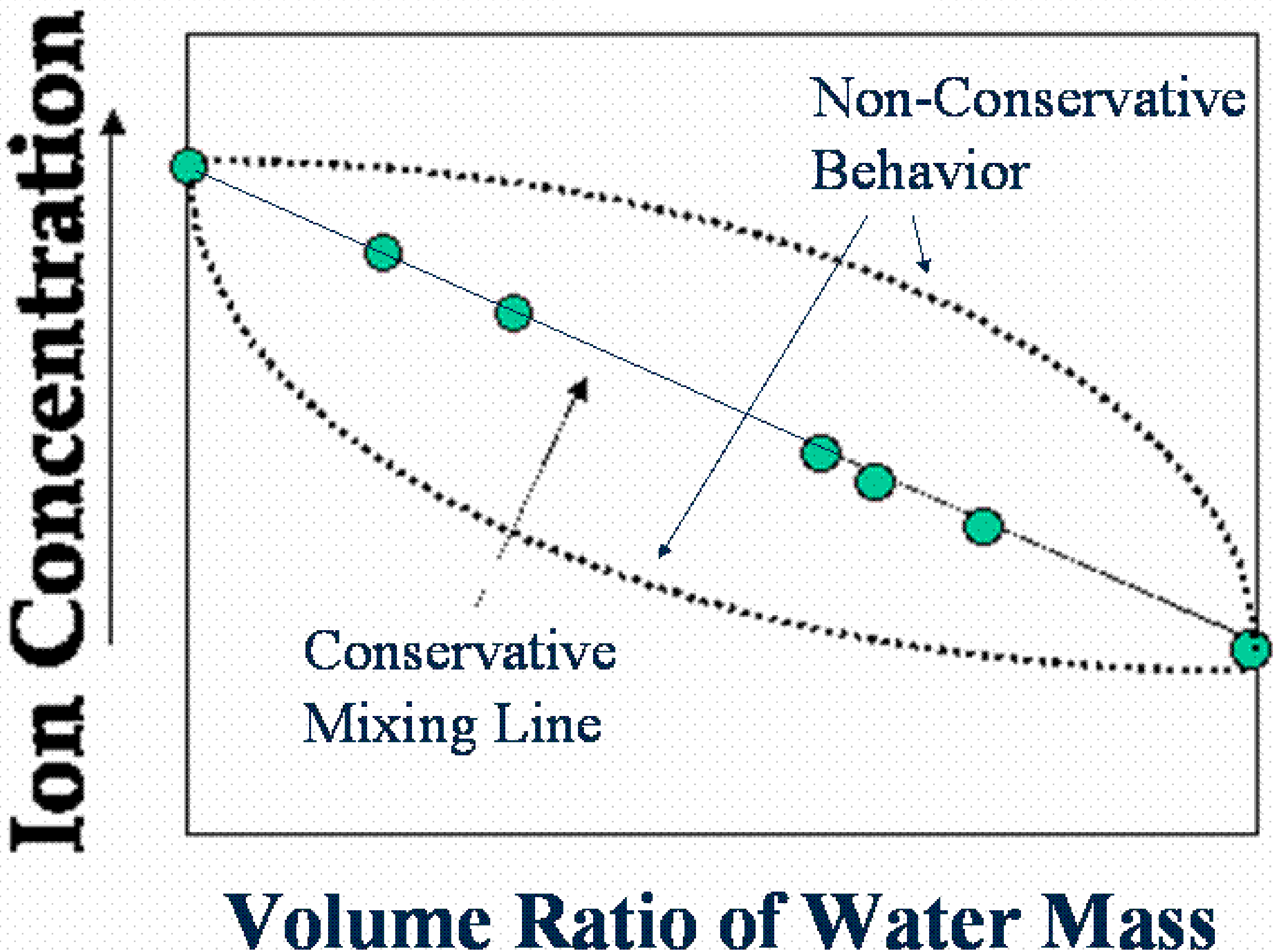
1) The relative abundance of the substance in river water (i.e., the input)
2) The presence of removal mechanisms that result in entrapment of the material in sediments (i.e., the output)

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 only by physical processes such as evaporation & precipitation, not chemical or biological processes
- Discussing completely dissolved species

Conservative Mixing




Non-Conservative
Behavior
Conservative
Mixing Line
Ion Concentration
Volume Ratio of Water Mass

Marcet Principle (1819)

- Relative composition of sea salt is nearly the same worldwide, i.e., major constituents are conservative
- Constancy of Composition
- Principle of Constant Composition (Pilson)
- Rule of Constant Proportions (Libes)
- First Law of Chemical Oceanography (Kester)
- Several exceptions to the rule

Exceptions to the Rule
(or non-conservative behavior)

- Caused by processes such as: Reduction, Dissolution, Evaporation, etc.
- Estuaries & Marginal Seas – largely input of river water of different composition & other processes also (e.g., Baltic Sea)
- Evaporation in Isolated Basins – evaporites
- Hydrothermal Vents – brines high in salt
- Precipitation & Dissolution – aragonite & calcite dissolution in deep ocean increase Ca^{2+} levels with precipitation elsewhere

Exceptions to the Rule
(continued)

- Anoxic Basins – bacterial reduction of SO_4^{2-} to S^{2-}
- Exchange at the Air-Sea interface – causes fractionation of many components
- Freezing – sea ice can be deficient in one or more constituents causing local concentration anomalies
- Interstitial Waters or Pore Waters – variety of processes many related to high surface areas in contact with water & anoxia

Cl^- has been Described as the Ultimate Conservative Tracer

- Highest concentration in SW
- Not biologically depleted
- Not chemically limited
- One of the longest Residence Times (1×10^8 yr)
- Generally pretty boring
- Oceanographers have used Cl^- concentration to define the concentration of ocean water masses
- Concept of Chlorinity = Cl^- (+ Br^-) content of SW

Chlorinity (Cl)

- Amount of Cl^-, Br^- and I^- in grams, contained in 1 kg of seawater assuming Br^- and I^- replaced by Cl^-
- The number giving chlorinity in per mille of a seawater sample is by definition identical with the number giving the mass with unit gram of atomic weight silver just necessary to precipitate the halogens in 0.3285234 kg of the seawater sample (Jacobsen & Knudsen, 1940).

Salinity (S)

- Historical Definition - Total amount of solid material, in grams, contained in 1 kg of seawater when all carbonate has been converted to oxide, the bromide and iodine replaced by chlorine, and all organic matter completely oxidized
- Practical Salinity Scale – Conductivity of seawater compared to KCl at 32.4356 g/kg (15 ^{o}C)

Practical Salinity Scale (PSS 1978)

- R_T = C (sample)/C (std seawater)
- C = conductivity at specified temp. & pressure
- Formerly used units of parts per thousand ($^{o}/_{oo}$)
- Unitless since based on a ratio
- Often see PSU or practical salinity units
- Calibrate instrumentation with SW standard

Absolute Salinity (S_R)

- SCOR/IAPSO

Scientific Committee on Oceanic Research

International Agency for the Physical Sciences of the Oceans

  - WG 127 Thermodynamics & Equations of State of SW
  - Density, Enthalpy, Entropy, Potential temp.,Freezing temp.,
  - Dissolved oxygen, Alkalinity, TCO_2 , Ca, Silica

$$S_R = (35.16504 / 35) \text{ g/kg} \times S$$

Precision in Salinity by Various Methods

1) Composition Studies of major components	± 0.01
2) Evaporation to dryness	± 0.01
3) Chlorinity	± 0.002
4) Sound Speeds	± 0.03
5) Density	± 0.004
6) Conductivity	± 0.001
7) Refractive index	± 0.05
8) Inductive Salinometer	

Relationship between Salinity & Chlorinity

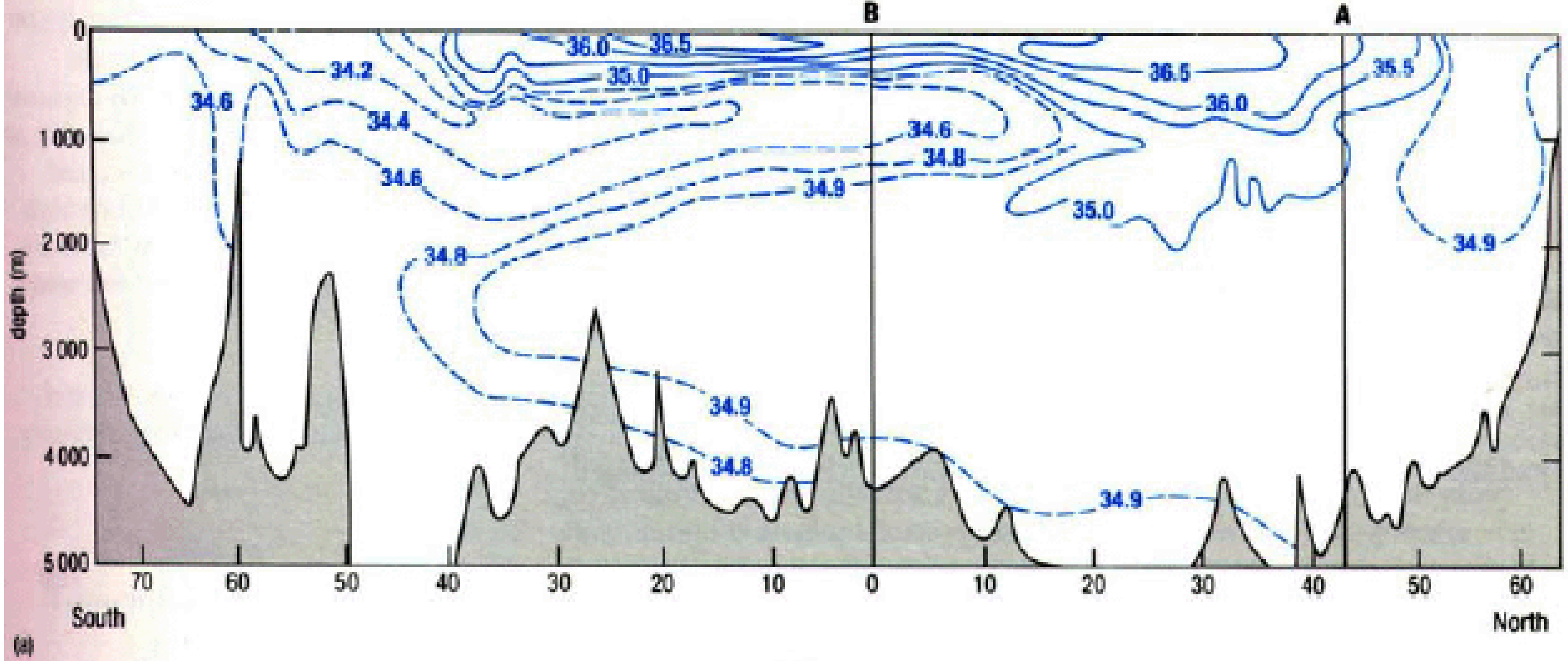
$$S = 1.80655\ Cl$$

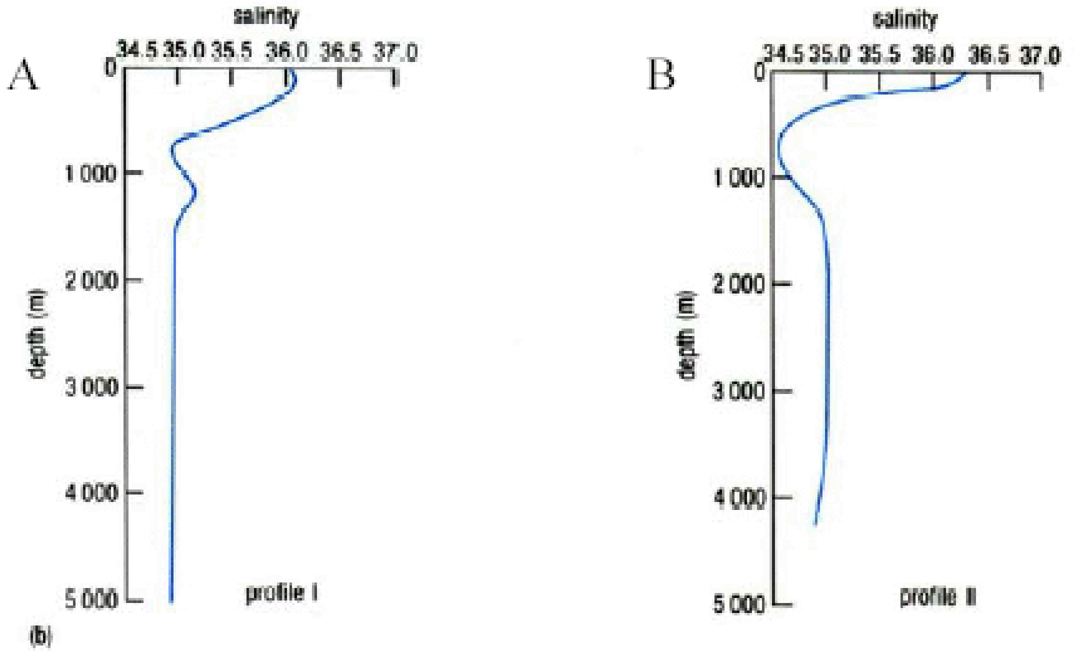
See Website for Salinity Handouts 1 - 4

CTDs

www.seabird.com

www.valeport.co.uk





A vertical section showing the mean distribution of salinity in the western Atlantic Ocean, and two salinity depth profiles corresponding to locations A and B.

Chemical Equilibria

General representation

$$a\,\mathbf{A} + b\,\mathbf{B} \rightleftharpoons c\,\mathbf{C} + d\,\mathbf{D}$$

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

Solubility Equilibria

$$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longleftrightarrow BaSO_{4(s)}$$

or by convention

$$BaSO_{4(s)} \longleftrightarrow Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Solubility Product (equilibrium constant)

$$K_{sp} = \frac{[Ba^{2+}]\,[SO_4^{2-}]}{1} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$K_{sp} = \frac{a_{Ba}\quad a_{SO4}}{1} = a_{Ba}\quad a_{SO4}$$

activity of solid is defined as = 1

Solubility Calculated

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

$$BaSO_{4(s)} \longleftrightarrow Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$$S = [Ba^{2+}] = [SO_4{}^{2-}]$$

Solubility Calculation (continued)

Given $K_{SP} = [Ba^{2+}][SO_4^{2-}] = 2.0 \times 10^{-10}$

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

So $S = [Ba^{2+}] = [SO_4^{2-}] = 1.4 \times 10^{-5}$

Activity Correction

$$K_{SP} = \frac{a_{Ba}\, a_{SO4}}{1} = a_{Ba}\, a_{SO4}$$

Since

$$a_{Ba} = \gamma_{Ba}[Ba^{2+}] \quad \& \quad a_{SO4} = \gamma_{SO4}[SO_4^{2-}]$$

Substituting

$$K_{SP} = a_{Ba} a_{SO4} = \gamma_{Ba}[Ba^{2+}]\gamma_{SO4}[SO_4^{2-}]$$

Solubility Calculation (completed)

Since

$$K_{SP} = [Ba^{2+}][SO_4^{2-}] \quad \& \quad \gamma_{Ba} = \gamma_{SO4}$$

Then

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

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