

Chemical Oceanography 2022



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Table 4.1 *Concentrations of the major constituents in surface seawater**At salinity (PSS 1978): $S = 35.000$*

	<i>g/kg</i>	<i>mmol/kg</i>	<i>mM</i>
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

- # 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

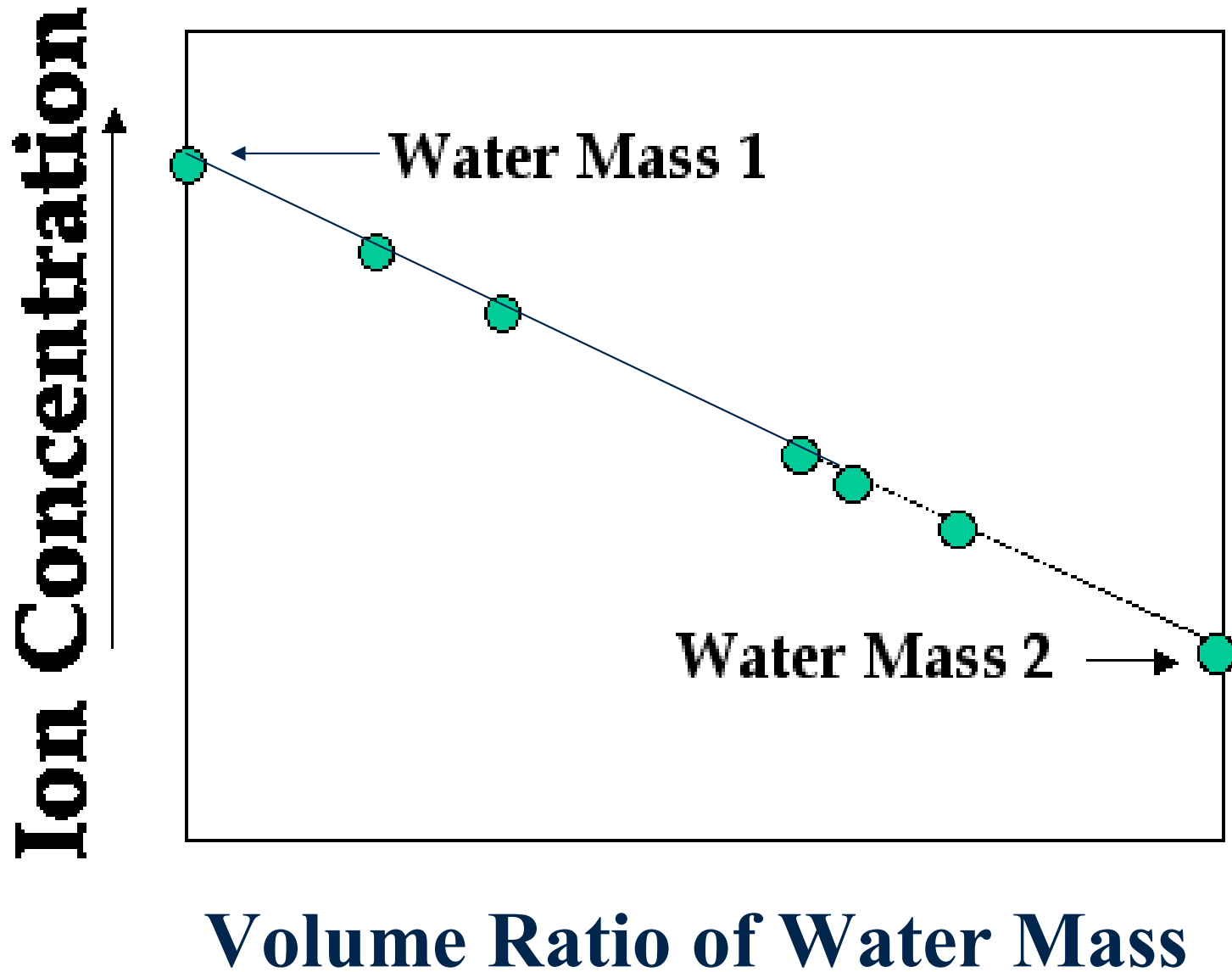
The composition of SW generally reflects two factors:

- 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)

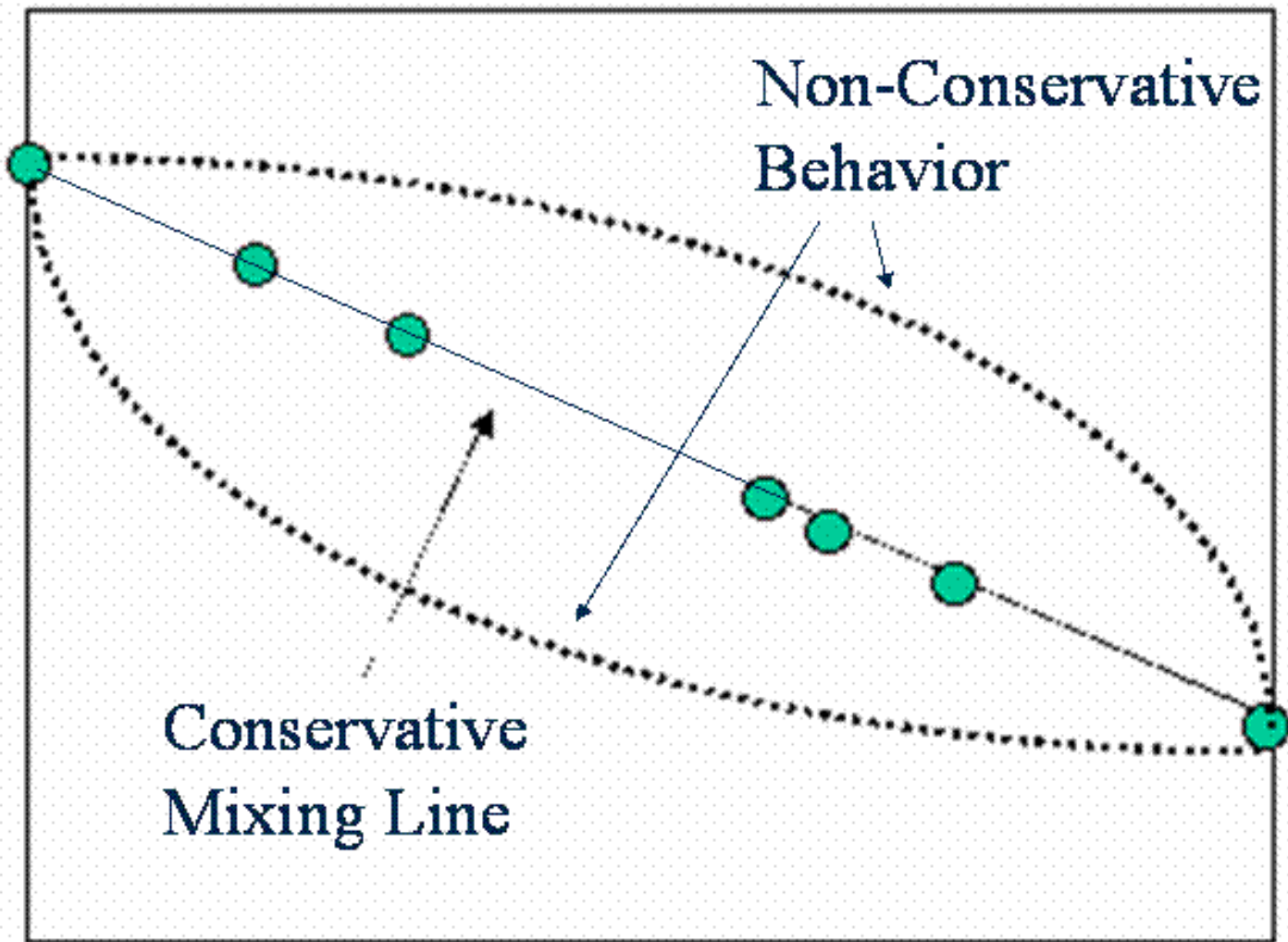
Major Components of SW

- # 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



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 – large 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 °C)

Practical Salinity Scale (PSS 1978)

- # $R_T = C(\text{sample})/C(\text{std seawater})$
- # $C =$ conductivity at specified temp. & pressure
- # Formerly used units of parts per thousand (‰)
- # 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

$$S = 1.80655 Cl$$

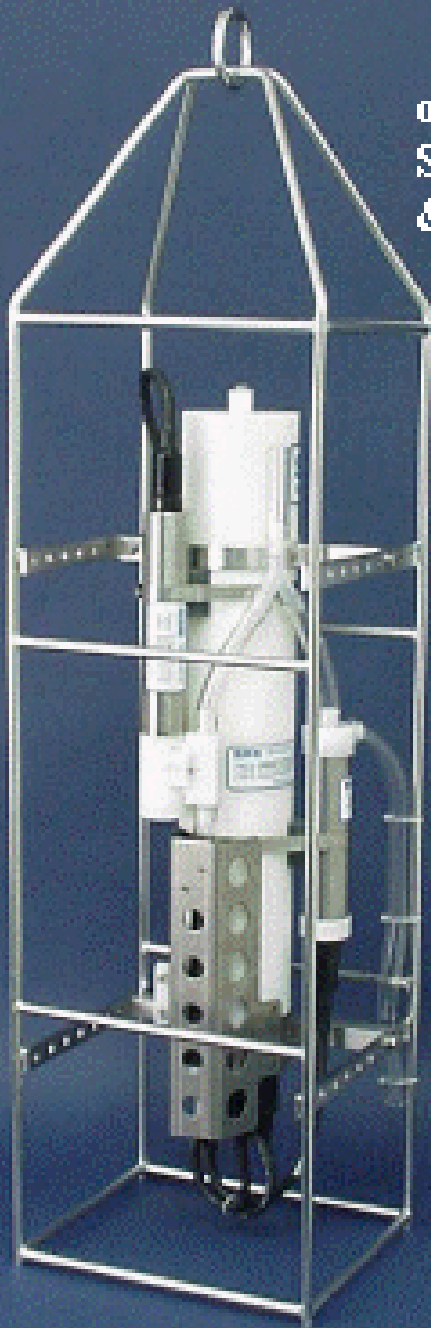
See Website for Salinity Handouts 1 - 4

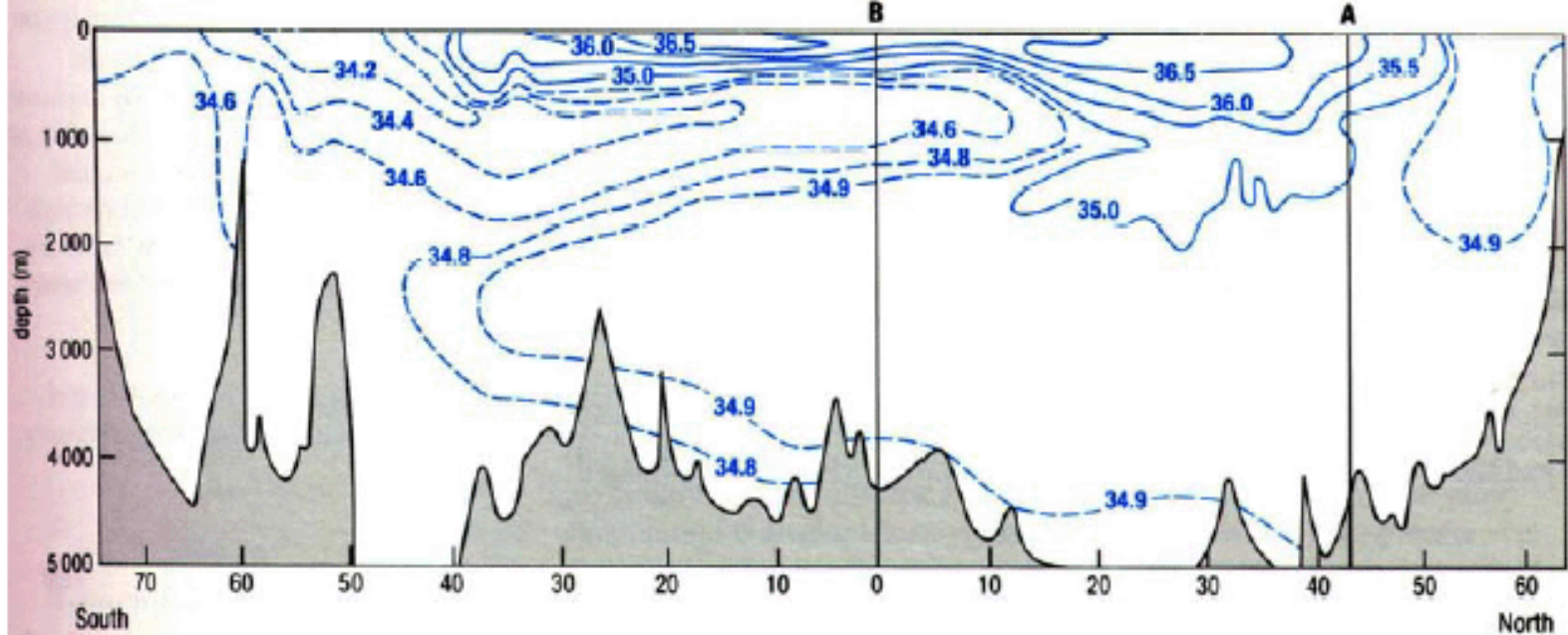
CTDs

Shown with
optional cage,
SBE 5T pump,
& SBE 43 DO
sensor

www.seabird.com

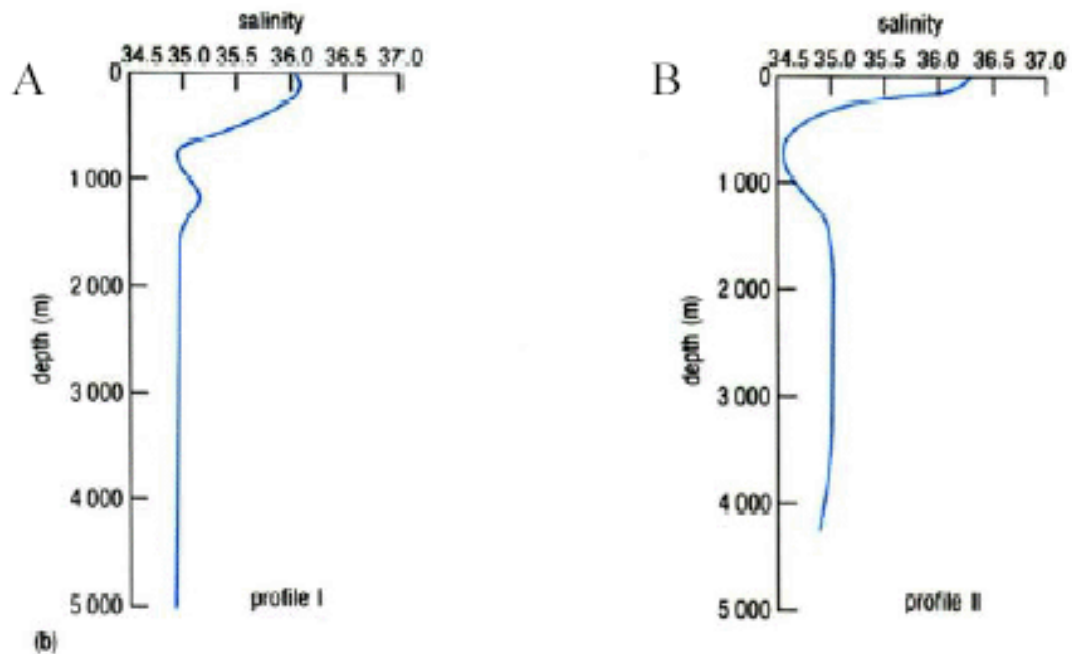
www.valeport.co.uk





(a)

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



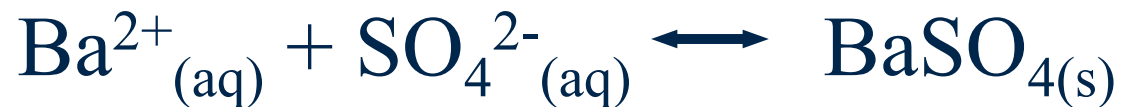
Where uppercase letters are chemical species
and lowercase letters are coefficients
(i.e. # of atoms or moles)

Equilibrium Constant

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

where [] = concentration, usually molar

Solubility Equilibria



or by convention



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

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

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

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

Then

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

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