

Lecture 4: Major Ions, Conservative Elements and Dissolved Gases in Seawater

Major Ions

Major ions are defined as those elements whose concentration is greater than 1 ppm. One reason this definition is used is because Salinity is reported to ± 0.001 or 1 ppm. Thus, the major ions are those ions that contribute significantly to the salinity. According to this definition there are **11 major ions**, all other elements in seawater are present in concentrations less than 1ppm ($<1\text{mg/kg}$) and are called minor or trace constituents. At a salinity of $S = 35.000$ seawater has the following composition.

The **major ions** ($>1\text{mg/kg}$ seawater) at $S = 35.000$ (from Pilson)

Ion	Formula	g/Kg	mmol/Kg
Sodium	Na^+	10.781	468.96
Magnesium	Mg^{2+}	1.284	52.83
Calcium	Ca^{2+}	0.4119	10.28
Potassium	K^+	0.399	10.21
Strontium	Sr^{2+}	0.00794	0.0906
Chloride	Cl^-	19.353	545.88
Sulfate	SO_4^{2-}	2.712	28.23
Bicarbonate	HCO_3^-	0.126	2.06
Bromide	Br^-	0.067	0.844
Borate	H_3BO_4^-	0.0257	0.416
Fluoride	F^-	0.00130	0.068
Totals	11	35.169	1119.87

Using the concentrations units of g kg^{-1} allows us to determine the contribution to salinity. Chemists prefer to use moles for units. mmol kg^{-1} are preferred (e.g. rather than mmol l^{-1}) because one kg of seawater is the same at all values of temperature and pressure.

Na^+ and Cl^- account for $>86\%$ of the salt content. The order of dominance of the other cations is $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Sr}^{2+}$. The anion Cl^- is approximately equal to the sum of the cations. The other anions are barely significant in the charge balance of seawater.

Seawater contains 300 times more dissolved salts than average river water and the mix of elements dissolved in river water is very different form that in seawater. In the marine environment substantial amounts of HCO_3^- , Ca^{2+} , and SiO_2 are removed from solution. The dissolved constituents in river water come from chemical weathering of rocks and from recycled sea salts via aerosols and rainfall. The average Cl^- content of continental rocks is in the order of 0.01% so only a minute fraction of river Cl^- could come from weathering. Most of the Cl^- in rivers is from recycled salts; similarly other sea salts contribute to river water in proportion to their abundance in the ocean. **If rivers are the chief source of the dissolved salts in seawater, why is seawater not simply concentrated river water?** The reason lies in the chemical behavior of dissolved constituents as they circulate through the hydrological cycle.

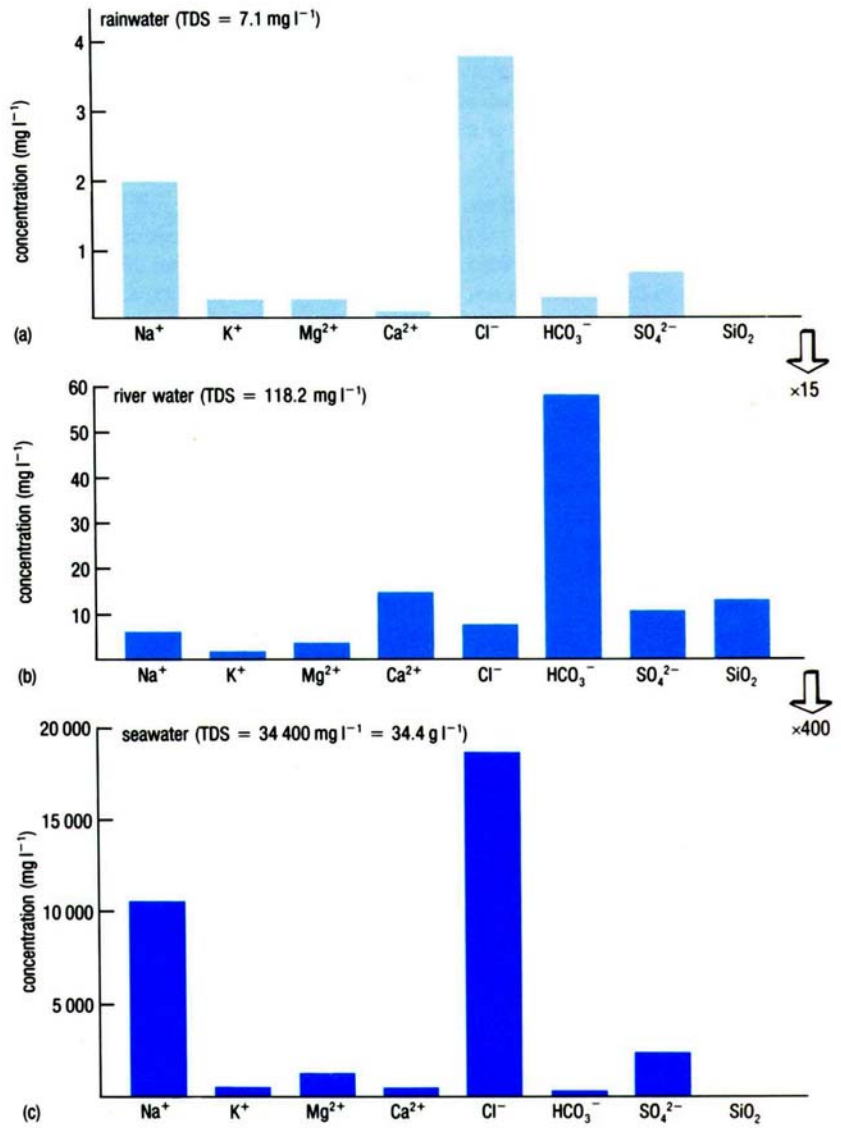


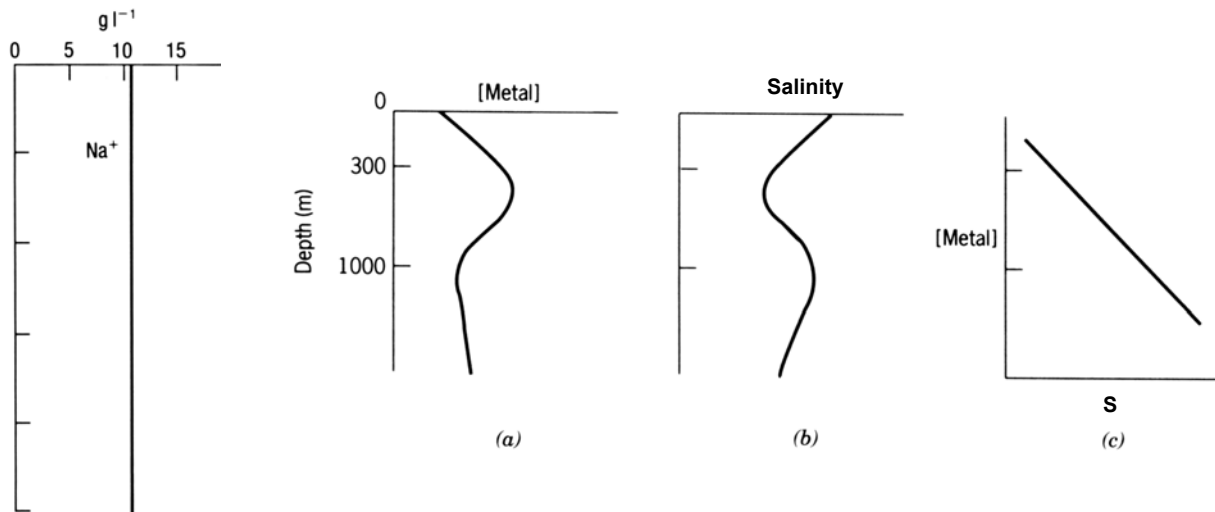
Figure 6.8 The average chemical composition of seawater, river water and rainwater for up to eight dissolved constituents, some at concentrations too low to appear (TDS = total dissolved salts). Note that total concentrations increase from rainwater to river water to seawater, also the scale change (arrows) of $\times 15$ from (a) to (b) and $\times 400$ from (b) to (c).

The abundance and distribution of elements in the ocean is a function of their solubility in seawater and their reactivity or their degree of involvement in biological and chemical processes and oceanic circulation.

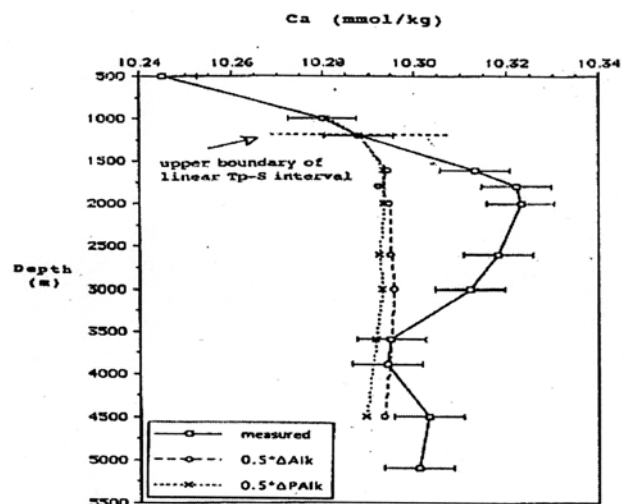
First of all, the degree of solubility for different minerals that are weathered and carried to the ocean are different. Many of the elements common in rocks (Si, Al) are not very soluble, so they are transported and deposited mainly as solid particles of sand and clay carried in rivers or as wind borne dust particles. Another example is Fe, in the oxic conditions of the present day atmosphere and oceans it is present in the Fe⁺³ state, which binds with oxygen to form oxide and hydroxide minerals that are very insoluble. But in past geological periods iron might have been mostly in the soluble Fe²⁺ form, thus it might have been very abundant in the oceans.

In order to efficiently summarize the major processes controlling the composition and distribution of elements in the ocean we will classify (group) the elements according to their distribution in seawater. We can broadly classify the elements in seawater into 4 groups: **conservative elements, dissolved gases, recycled elements and scavenged elements.**

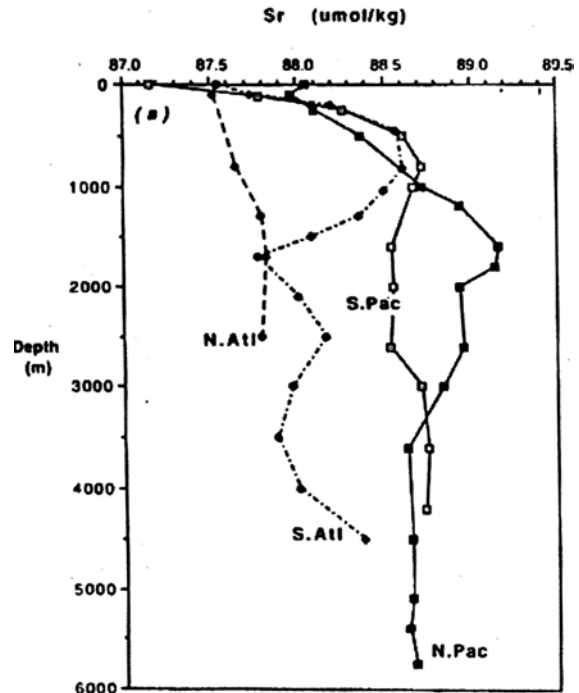
The **conservative elements**: These include most of the major ions in seawater and a few other elements and complexes (Li^+ , Rb^+ , Cs^+ , MoO_4^{2-} and $\text{UO}_2(\text{CO}_3)_3^{4-}$). The solubility of the minerals providing these elements is high (we can dissolve a lot of NaCl , KCl , MgSO_4 and CaSO_4 in seawater). Other non-major elements in this group interact only weakly with biological or other particles and are relatively soluble. The concentration of these elements **normalized to salinity** is constant with depth and in the different oceans. In other words, they are uniformly distributed. The ratio of one conservative element to another will also be constant. One way to establish if an element of unknown reactivity is conservative is to plot it versus another conservative element or against potential temperature or salinity (see figures below).



- Na, K, SO_4 , Br, B and F have constant ratios to Cl and each other, everywhere in the ocean. These elements are conservative.
- Ca has small ($\sim 0.5\%$) but systematic variations within the ocean. Probably due to formation and dissolution of CaCO_3 particles. A small hydrothermal input signal has also been observed. Vertical profiles of dissolved Ca (normalized to salinity) in the ocean, from DeVilliers (1999).



- Sr also increases from the surface to the deep water and from the north Atlantic to the north Pacific. The deep water is about 2% enriched relative to the surface water. The zooplankton, Acantharia make their shells out of Celestite (SrSO_4) and may be responsible for this variability. Dissolved Sr depth profiles normalized to salinity from DeVilliers (1999).



- Until recently, Mg was thought to be conservative. Recently, local Mg anomalies were found in deep waters located over mid-ocean ridges. Mg is known to be totally removed in high temperature hydrothermal vent solutions.

- Dissolved Inorganic Carbon, DIC ($\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$) varies by ~ 20% due to vertical transport and remineralization of both CaCO_3 and organic matter.

- SO_4^{2-} is conservative in oxic oceans but not in anoxic basins or within sediments. Sulfate is used by sulfate reducing bacteria to form HS^- or H_2S .

The elements colored in green are considered conservative (accumulating) the hatched green marks elements that have minor non-conservative behavior.

Group	1	2	Transition Elements										13	14	15	16	17	18					
1	H 1.008																	2 He 4.003					
2	Li 6.941	Be 9.012																5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	Na 22.99	Mg 24.30																13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80					
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3					
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 183.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)					
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104	105	106	107																
			Lanthanides																				
			58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0							
			Actinides																				
			90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (239)	95 Am (241)	96 Cm (244)	97 Bk (249)	98 Cf (252)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)							

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Gases and Gas Exchange

There are several reasons for studying gas exchange, important ones are:

1. The ocean is a sink for anthropogenic CO₂ and one of the major transfer modes of CO₂ to the ocean from the atmosphere is by gas exchange.
2. Oxygen is a chemical tracer for photosynthesis. The gas exchange flux of O₂ is an important parameter for calculating net biological production.
3. Gas exchange is the process by which O₂ is transported into the ocean and is thus a control on aerobic respiration.
4. Some gases can act as tracers for ocean circulation (CFCs, SF₆).

Fundamental Properties of Gases

The relative composition of the main gases in the atmosphere (ratio of one gas to another) is nearly constant horizontally and vertically to almost 95 km (the atmosphere is well mixed). Atmospheric water (H₂O) is highly variable. Some trace gases involved in photochemical reactions can also be highly variable.

Composition of the Atmosphere

More than 95% of all gases except radon reside in the atmosphere. The atmosphere controls the oceans gas contents for all gases except radon, CO₂ and H₂O, which are more abundant in seawater.

	Gas	Mole Fraction in Dry Air (f _G)	Henry's Law Constant (mol/kg at 35‰, 760 mm Hg)	
			K _H (10 ⁻³) 0°C	K _H (10 ⁻³) 24°C
N ₂	Nitrogen	78.084 %	0.80	0.51
O ₂	Oxygen	20.952 %	1.69	1.03
Ar	Argon	0.934 %	1.83	1.13
CO ₂	Carbon Dioxide	350 ppm	63	29
Ne	Neon	18 ppm	0.44	0.37
He	Helium	5 ppm	0.34	0.32
Kr	Krypton	1 ppm	3.8	2.1
Xe	Xenon	0.08 ppm	8.4	4.3
CH ₄	Methane	2 ppm		
H ₂	Hydrogen	0.5 ppm		
N ₂ O	Nitrous Oxide	0.3 ppm		
CO	Carbon Monoxide	0.05-0.2 ppm		
O ₃	Ozone	0.02-10 ppm		
NH ₃	Ammonia	4 ppb		
NO ₂	Nitrogen Dioxide	1 ppb		
SO ₂	Sulfur Dioxide	1 ppb		
H ₂ S	Hydrogen Sulfide	0.05 ppb		

See also Broecker and Peng 1982, p112.

Some comments about units of gases:

-Units
in air partial pressure of gas i (atm) = (pressure of gas i) / (total gas pressure)
one atmosphere = 760 mm Hg
partial pressure = (liters gas / liter air) = atm.; ppm = $\mu\text{l} / \text{l}$
in water volume gas / volume or weight seawater
liters gas (STP) / kg. Seawater [STP = standard T and P => 1 atm, 0 °C]

@ STP, 1 mole gas = 22.414 liters

The pressure and volume units are the same at 760 mm Hg

Dalton's Law

Gas concentrations are expressed in terms of pressures.

Total Pressure = ΣP_i = Dalton's Law of Partial Pressures

$$P_{\text{TOTAL}} = P_T = P_{\text{N}_2} + P_{\text{O}_2} + P_{\text{H}_2\text{O}} + \dots\dots\dots$$

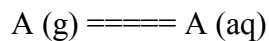
Dalton's Law implies ideal behavior -- i.e. all gases behave independently on one another. Gases are dilute enough that this is a good assumption.

Variations in partial pressure (P_i) result from:

- 1) variations in P_T (atmospheric pressure highs and lows)
- 2) variations in water vapor ($P_{\text{H}_2\text{O}}$)

Solubility

The exchange or chemical equilibrium of a gas between gaseous and liquid phases can be written as:



At equilibrium

$$K = [\text{A(aq)}] / [\text{A(g)}] \quad (\text{K is the equilibrium constant})$$

There are two main ways to express solubility.

Henry's Law:

We can express the gas concentration in terms of partial pressure using the ideal gas law:

$$PV = nRT$$

so that the number of moles n divided by the volume is equal to $[\text{A(g)}]$

$$n/V = [\text{A(g)}] = P_A / RT \quad \text{where } P_A \text{ is the partial pressure of A}$$

$$\text{Then } K = [\text{A(aq)}] / P_A / RT$$

$$\text{or } [\text{A(aq)}] = (K/RT) P_A$$

K/RT is defined as Henry's Law Constant (K_H)

This constant changes with temperature and salinity some values are listed above.

$$[A(aq)] = K_H P_A$$

Units for K are $\text{mol kg}^{-1} \text{ atm}^{-1}$; for P_A are atm ; and for $[A(aq)]$ mol kg^{-1}

Henry's Law states that the solubility of a gas is proportional to its overlying partial pressure.

Example: The value of K_H for CO_2 at 24°C is $29 \times 10^{-3} \text{ moles kg}^{-1} \text{ atm}^{-1}$. The partial pressure of CO_2 in the atmosphere is 350 ppm, or $350 \times 10^{-6} \text{ atm}$. The concentration of CO_2 in water in equilibrium with that partial pressure is: $[\text{CO}_2(aq)] = K_H \times P_A$

$$K_H \times P_A = 29 \times 10^{-3} \text{ moles kg}^{-1} \text{ atm}^{-1} \times 350 \times 10^{-6} \text{ atm} = 10.15 \times 10^{-6} \text{ moles kg}^{-1} = 10.15 \mu\text{M}$$

Bunson Coefficients

Since oceanographers frequently deal with gas concentrations not only in molar units but also in ml / l , we can also define

$$[A(aq)] = \alpha P_A$$

where $\alpha = 22,400 \times K_H$ (e.g., one mol of gas occupies $22,400 \text{ cm}^3$ at STP)

α is called the Bunsen solubility coefficient. Its units are $\text{cm}^3 \text{ mol}^{-1}$.

Solubility of gases is a function of their molecular weight, temperature and salinity.

Summary of trends in solubility:

1. Type of gas: K_H goes up as molecular weight goes up (note that CO_2 is anomalous)
2. Temperature: solubility goes up as temperature goes down
3. Salinity: solubility goes up as S goes down

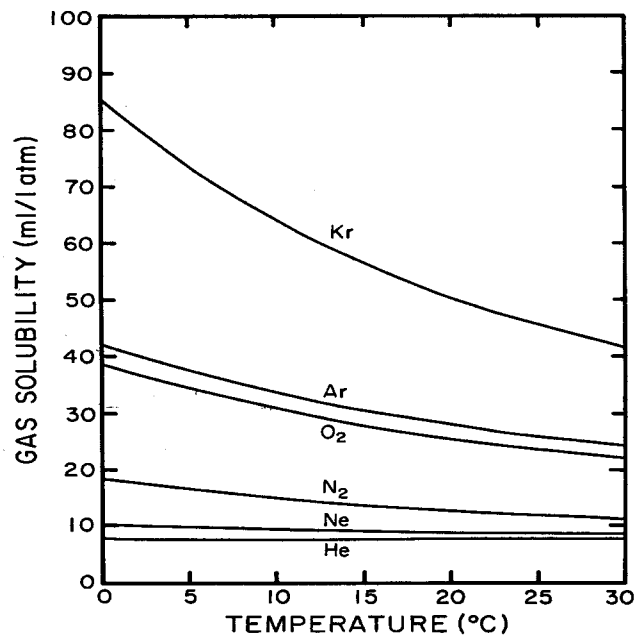


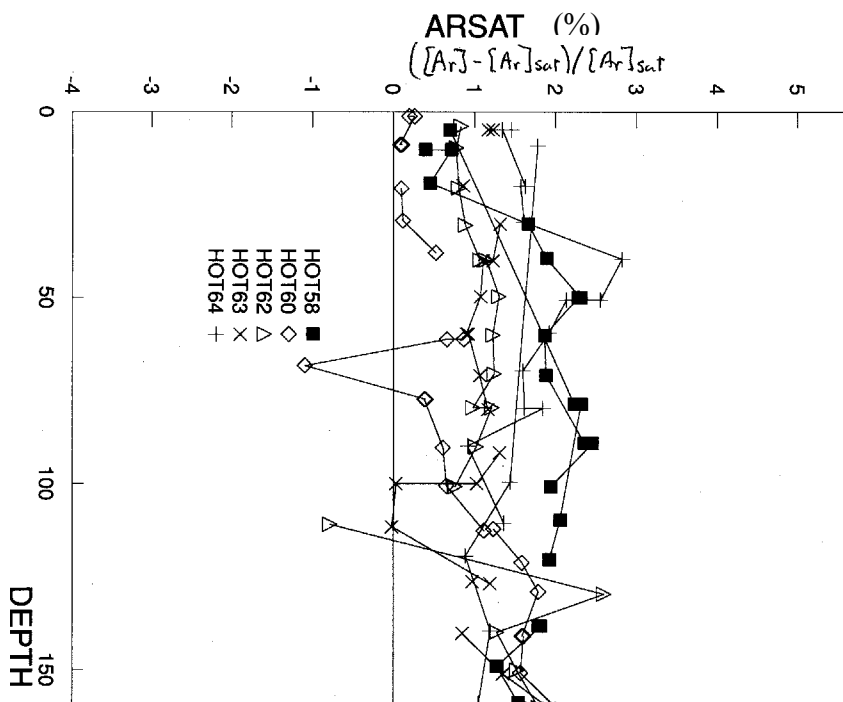
Figure 3-1. The solubilities of various gases in sea water as a function of temperature. The units are standard cubic centimeters of gas contained by a liter of water per atmosphere of pressure exerted by the gas.

Causes of deviations from Equilibrium:

The ocean may be out of equilibrium with respect to gas solubility. If the water is super saturated the gas flux will be out of the water, and if it is under saturated gas flux will be into the water.

Deviations from saturations could be caused by:

1. Non-conservative behavior, *in situ* consumption or production (e.g. photosynthesis, respiration, or denitrification)
2. Bubble or air injection; air injection by bubbles that are brought below the ocean surface by breaking waves. When bubbles are transported to several tens of cm, they collapse and supersaturate the water with atmospheric gases. The gas concentration ratios in the fraction added by bubbles is like in the air.
3. If temperatures change faster than the gases can re-equilibrate with the atmosphere, then the surface ocean will be supersaturated.
4. Subsurface mixing – This may result in possible super saturation or under saturation due to non-linearity of K_H vs. T .
5. Change in atmospheric pressure - if this happens quickly, surface waters cannot respond quickly enough to re-equilibrate.



If the *in situ* gas concentration is less than that of its normal atmospheric equilibrium concentration (NAEC), it is said to be under-saturated. If the observed gas exceeds its NAEC, the seawater is super-saturated with respect to that gas. The degree of gas saturation is expressed as:

$$\% \text{ Saturation} = \{ [A] \text{ in situ} / \text{NAEC for A} \} \times 100$$

Rates of Gas Exchange

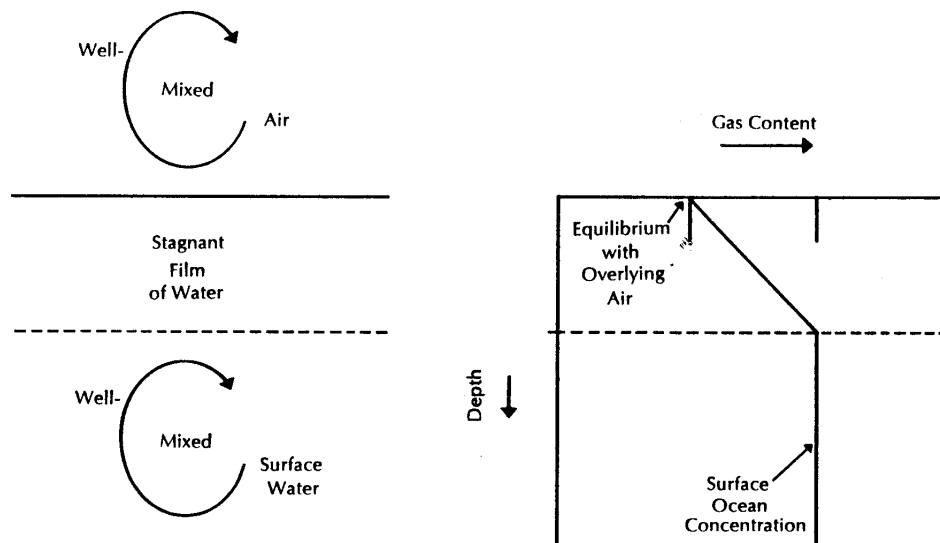
There are many situations for which we'd like to know the rate of gas exchange to estimate the time for gases to reach equilibrium.

The transfer of gases between the ocean and atmosphere is important for understanding:

- The influence of the ocean on atmospheric chemistry
- The fate of anthropogenic gases and their utility as tracers of ocean circulation
- The relationships between heat transfer and gas transfer

There are many models of gas transfer, and most assume that the final process of exchange is governed by molecular diffusion across a thin layer at the air-water interface. The simplest physical paradigm is **The Stagnant Film Model**

It assumes that the atmosphere is well mixed and that the surface ocean is well mixed. Transport is controlled by turbulent diffusion separated by a stagnant film on the water side of the interface where transport is controlled by molecular diffusion.



The stagnant film is the limiting factor to gas exchange and transfer is by molecular diffusion through the layer.

The gas concentration at the Air-water interface $[C_s]$ is assumed to be in saturation equilibrium with the atmosphere, via the Henry's Law coefficient, K_H ($\text{mol l}^{-1} \text{atm}^{-1}$).

The rate of transfer across this stagnant film occurs by molecular diffusion from the region of high concentration to the region of low concentration. Transport is described by Fick's First Law that states simply that the flux is proportional to concentration gradient.

$$F = -D \delta [A] / \delta Z$$

Where D is the molecular diffusion coefficient for the specific gas at the appropriate temperature ($\text{cm}^2 \text{sec}^{-1}$). δZ is the thickness of the stagnant film in centimeters (Z_{film}), $\delta [A]$ is

the concentration difference across the film. The water at the top of the stagnant film is assumed to be in equilibrium with the atmosphere (C_{eq}). We can calculate this value using the Henry's Law equation. The bottom of the film has the same concentration as the mixed-layer (C_s)

$$\text{Thus: } F = -D/Z_{\text{film}} (C_{eq} - C_s) = -D/Z_{\text{film}} (K_H P_A - C_s)$$

Gas	Diffusion Coefficient ($\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	
	0°C	24°C
H ₂	2.3	4.9
He	3.0	5.8
Ne	1.4	2.8
N ₂	1.1	2.1
O ₂	1.2	2.3
Ar	0.8	1.5
CO ₂	1.0	1.9
Rn	0.7	1.4

Because D/Z has velocity units, it has been called the **Piston Velocity** or mass transfer velocity.

Typical values for are $D = 1 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ and for $Z_{\text{film}} = 10$ to $60 \mu\text{m}$

Example: $D = 1 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, $Z_{\text{film}} = 17 \mu\text{m}$ ($= 17 \times 10^{-6} \text{ m} = 1.7 \times 10^{-3} \text{ cm}$)

$$\text{The piston velocity} = D/Z = 1 \times 10^{-5} / 1.7 \times 10^{-3} = 0.59 \times 10^{-2} \text{ cm sec}^{-1} \sim 5 \text{ m day}^{-1}$$

Each day a 5 m thick layer of water will exchange its gas with the atmosphere. For a 100 m thick mixed layer the exchange will be completed every 20 days.

The idea is that even when there is gaseous equilibrium, e.g. there is no gradient ($C_{eq} = C_s$), there is still exchange of gases at the rate of the piston velocity. Think of two imaginary pistons: one moving upward through the water pushing ahead of it a column of gas with the concentration of gas in the upper ocean (C_s) and one moving down into the sea carrying a column of gas with the concentration of gas in the top of the stagnant film (C_{eq}). Even if the ocean and atmosphere are in gaseous equilibrium the transfer of gas continues but the amount "pushed in" just equals the amount "pushed out".

Correlation of Gas exchange Rate and Wind Speed

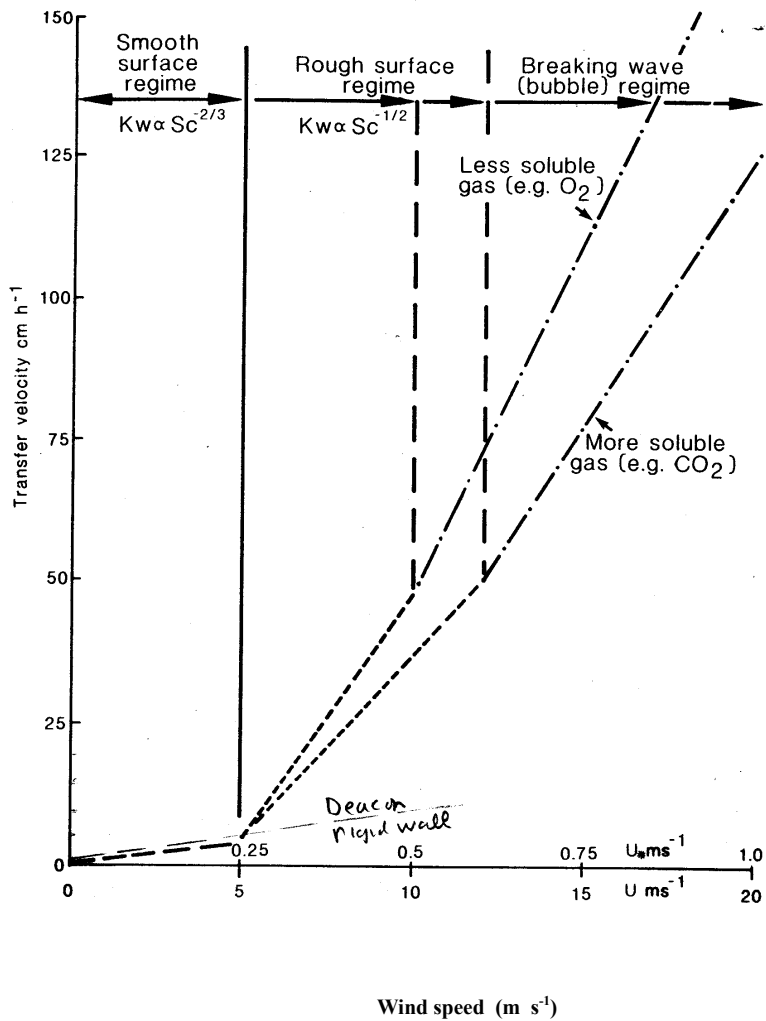
The parameter that is most easily measured that correlates with surface agitation of the water is wind speed. Liss and Merlivat (1986) pieced together a relationship between gas exchange rate and wind speed based on a series of gas exchange measurements in wind tunnels and tracer releases in lakes.

The Liss and Merlivat relationship has three regimes where the exchange rate is linear with wind speed – smooth surface, rough surface and breaking waves. The first two relationships are based

on tracer release in a small lake. The third comes from studies of gas exchange in a very large wind tunnel.

The transfer velocity ($G = \text{cm h}^{-1}$) in this description is dependent on the diffusion coefficient to the 2/3 power in region 1 and to the 1/2 power in regions two and three. Sc in the figure is the Schmidt number, which is the viscosity divided by the molecular diffusion coefficient.

Many of the field measurements done so far seem to agree with the Liss and Merlivat relationship.



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