Dissolved gases and Air-Sea Exchange

- -Dissolved gases are important biogeochemically
  - =dissolved oxygen and CO_2
    - =necessary for life
  - =signatures of biological processes
- -We can use gas concentrations as tracers for circulation
  - -esp Helium 3
- -What about CO_2?
  - =the oceans are a huge carbon reservoir
  - =the oceans takes up >25% of anthropogenic CO_2
  - = it gets there by air-sea gas exchange...

Dalton's Law of Partial Pressures, and Mole Fractions

In any sample of mixed gases, individual pressures are additive (so gases behave independently):

$$p_T = pp(\mathrm{N_2}) + pp(\mathrm{O_2}) + pp(\mathrm{Ar}) + pp(\mathrm{H_2O}) + ...$$

where p_T = total pressure
         pp (gas) = partial pressure

For any gas, the Ideal Gas Law, relates pressure, volume, temperature and number of moles of a gas (partial pressures are proportional to molar conc. (volume)):

$$p \cdot V = n \cdot R \cdot T$$

with   p the pressure of the gas
            V the volume of the gas
            n the number of moles of gas present
            T the absolute temp. in °K (=°C + 273.15)
            R is the gas constant

e.g. $R = 8.314\ \mathrm{L} \cdot \mathrm{kPa} \cdot \mathrm{K^{-1}} \cdot \mathrm{mol^{-1}}$
or $R = 0.08314\ \mathrm{L} \cdot \mathrm{bar} \cdot \mathrm{K^{-1}} \cdot \mathrm{mol^{-1}}$
or $R = 0.08206\ \mathrm{L} \cdot \mathrm{atm} \cdot \mathrm{K^{-1}} \cdot \mathrm{mol^{-1}}$

Relation between partial pressure and mole fraction

$$pp(\text{gas}) = P_{tot} \cdot x(\text{gas})$$

partial pressure = (total pressure) * (mole fraction)

Partial pressures and mole fractions are often quoted with the following units:

μatm $\rightarrow$ microatmospheres (partial pressure or fugacity) e.g. pCO_2 or fCO_2

ppm or ppt $\rightarrow$ volume fraction parts per million (10^6) or trillion (10^{12}) BY VOLUME

mole fraction $\rightarrow$ e.g. $x(O_2)$ units such as pmol mol^{-1} often used

Generally, volume fraction = mole fraction (non-ideal effects small)

Tropospheric Gas Composition

Conservative Gases

Air Composition
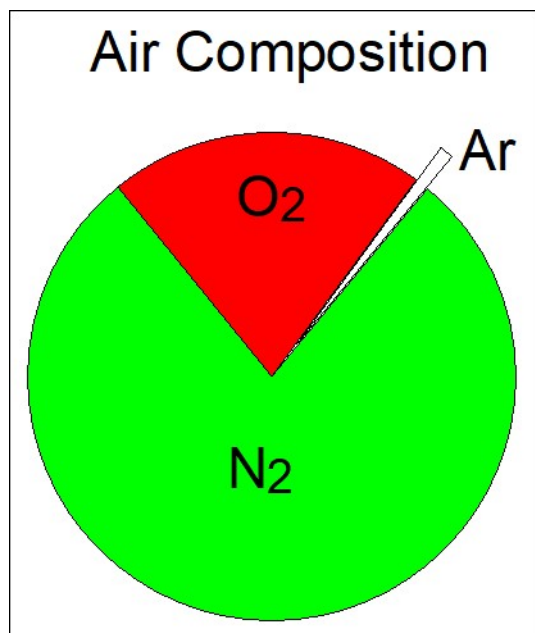
1 bar = 100 kPa.

1 std. atmosphere =
101.325 kPa

* pure water solubilities
(S=0) under pure gas

Gas	Mole Fraction (Dry Air)	Solubility at 20°C * (μmol kg^{-1} bar^{-1})
Nitrogen (N_2)	0.7808	688.7
Oxygen (O_2)	0.2095	1373
Argon (Ar)	0.00934	1503
Neon (Ne)	1.82×10^{-5}	458.5
Helium (He)	5.24×10^{-6}	385.6
Krypton (Kr)	1.14×10^{-6}	2765
Xenon (Xe)	8.7×10^{-8}	5109

Solubility of gases in seawater

Henry's Law

The amount of a gas dissolved in water at equilibrium is directly proportional to the pressure of that gas.

$$[G] = H_G \cdot pp(G)$$

Where:

[G]   is the concentration of the gas, G, in solution (should have units of mol kg-sw^{-1})

pp(G)   is the partial pressure* of gas G

H_G is the Henry's Law constant for gas G, (dependent on T and S)

*For thermodynamic correctness, the 'fugacity' rather than the partial pressure of the gas should be used, but for most oceanographic applications this distinction makes little difference.

Solubility varies from gas to gas

- Solubilities of different gases vary widely

- Gas solubility increases with increasing molecular weight of the gas

- Heavier, more polar gases are more soluble

- More soluble gases have greater temperature dependence
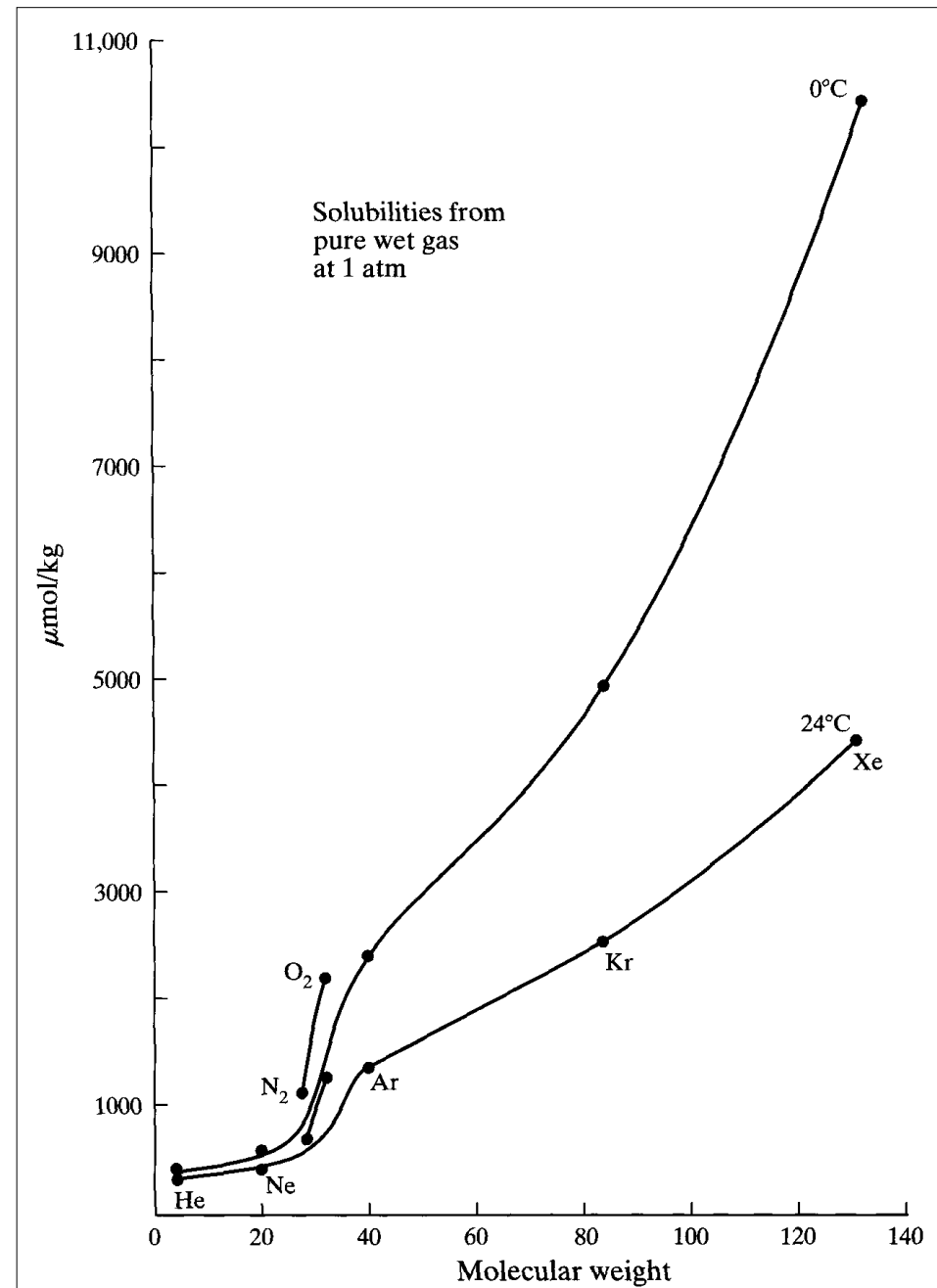
Solubility varies as *f*(T).
The T-dependence varies from gas to gas (more soluble the gas,
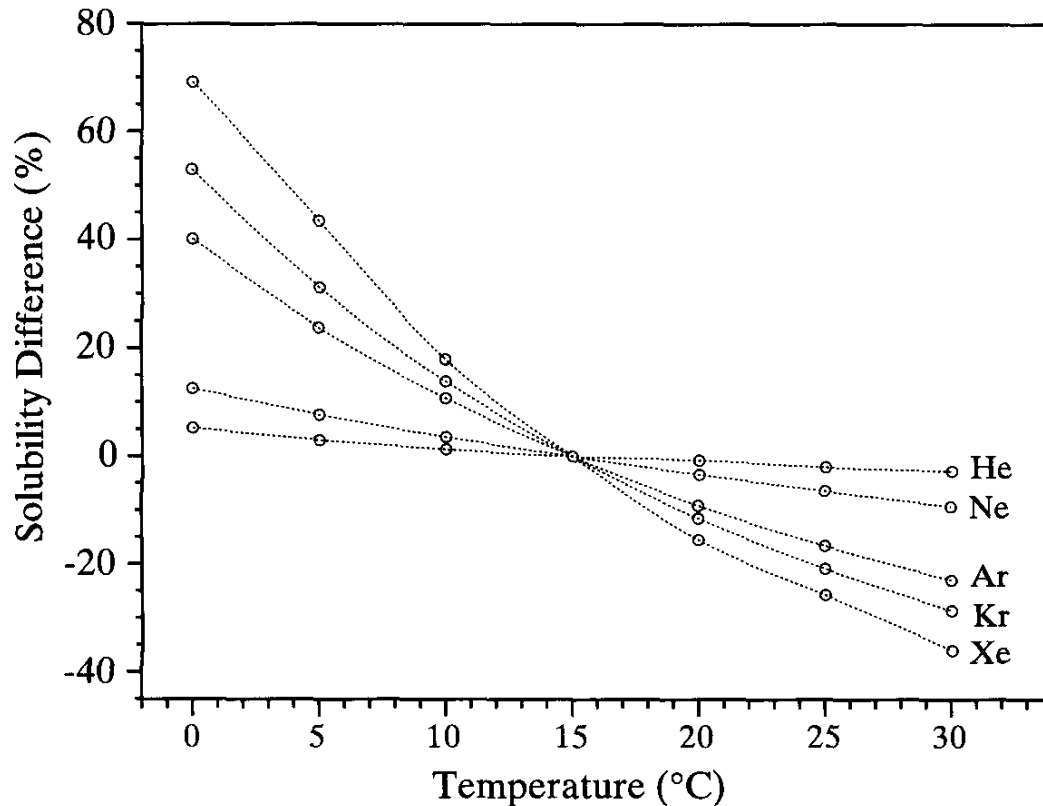   **greater T dependence)**

Figure 5.2 *Effect of temperature on the solubilities of the noble gases in seawater at a salinity of 35‰, expressed as the % change from the solubility for each gas at 15°C.* (Data from Appendix D.)

- Gas solubility decreases with increasing temperature
- Ar and O_2 have quite similar solubility behaviour

Solubility varies as *f*(S)
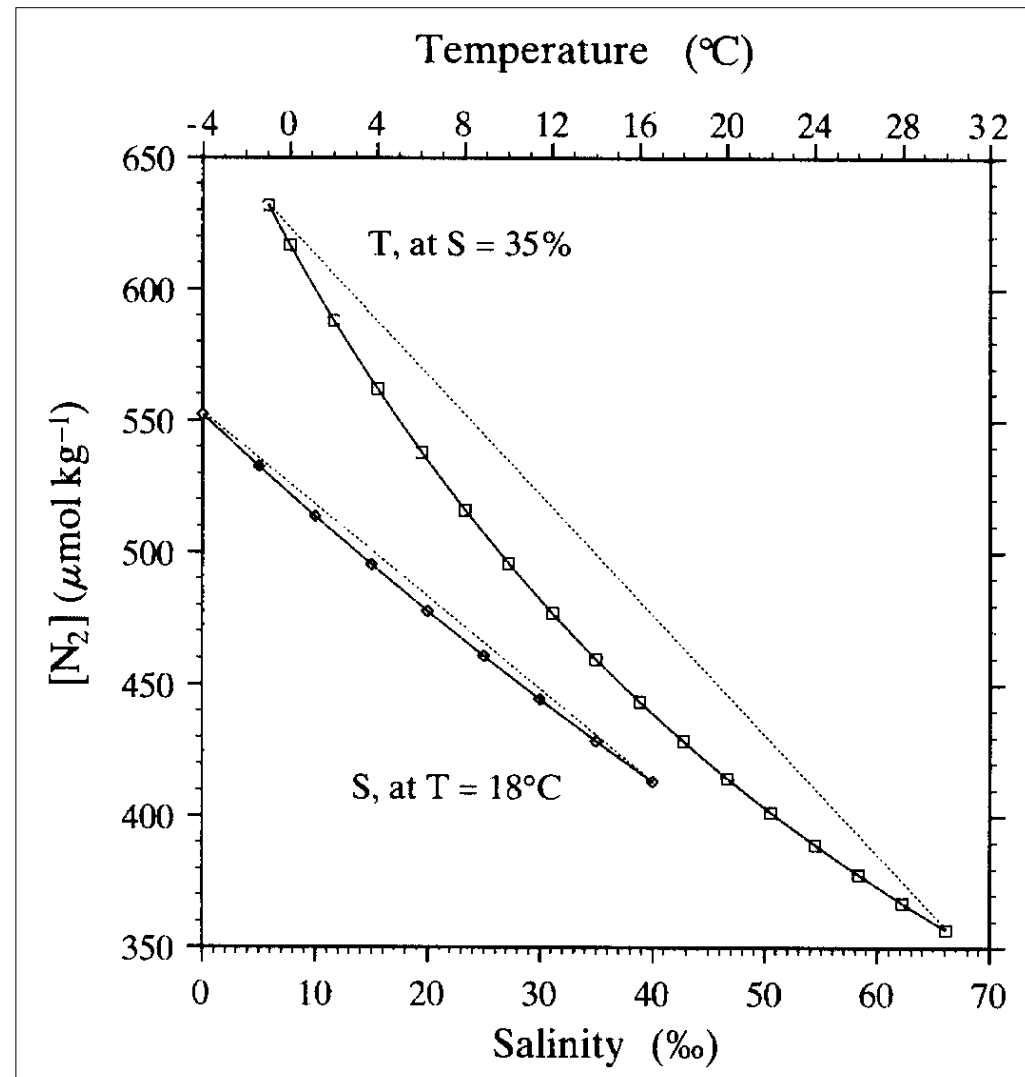
- Solubility of a gas decreases with increasing salinity

Figure 5.3 *Solubility of N₂ in seawater as a function of temperature at S = 35‰ (upper curve) and of salinity at 18°C (lower curve), relative to wet air. The dotted lines show the concentrations that would be found if two water masses, with the characteristics of the end members and saturated against air, mixed in various proportions without any opportunity to re-equilibrate with air. (Data from Appendix D.)*

<u>Pressure effects gas concentrations</u>

- Deep ocean waters only equilibrate (exchange gases) with the atmosphere at the sea-surface. Therefore concentrations of non-reactive gases are established at pressures that are close to atmospheric pressure

- Some gas exchange takes place between seawater and air within bubbles that have been transported to depths of ~10 m. This exchange takes place at elevated pressures (hydrostatic pressure and surface tension effects)

Seawater gas composition

Determined by atmospheric concentration and gas solubility
  (at Temperature and salinity of the surface ocean)
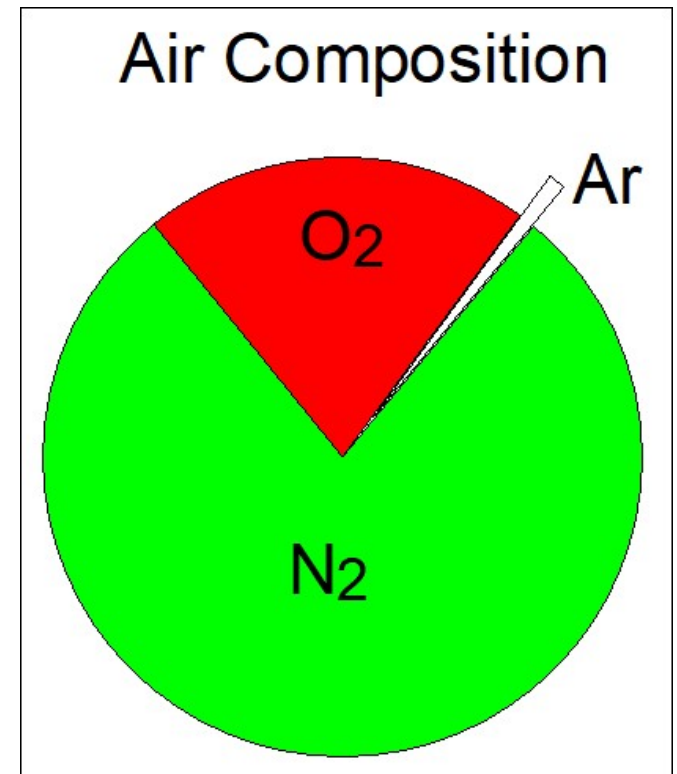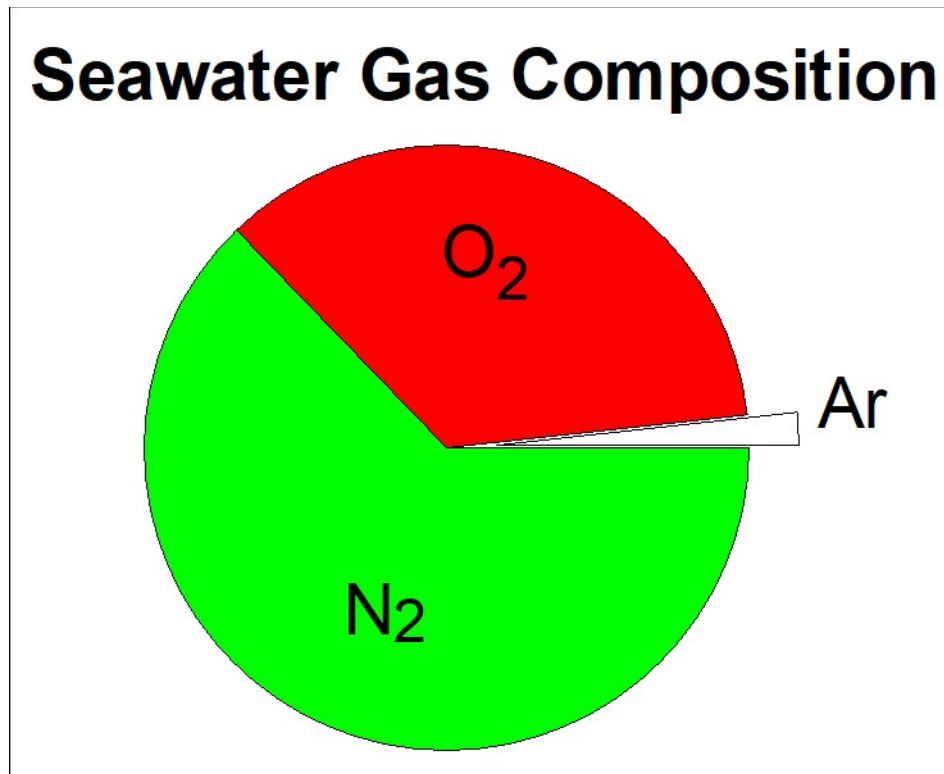
Sources and Sinks of 'Simple' Gases Processes Affecting Concentrations

1. Exchanges at ocean boundaries

Air-sea fluxes

- surface concentrations move towards equilibrium with atmosphere
  (i.e. $pp_w = pp_a$)

- equilibrium concentration is function of:
  gas solubility (temperature, salinity), atmospheric partial pressure

$$[G]_{eq} = pp_a . H_G (T,S)$$

- 'exact' equilibrium is rarely attained due to ocean and atmospheric sources and sinks, variability + kinetic effects (finite gas exchange)

Global balances

- Some gases tend to leave the ocean across the air-sea interface Ocean is a SOURCE (for the atmosphere)
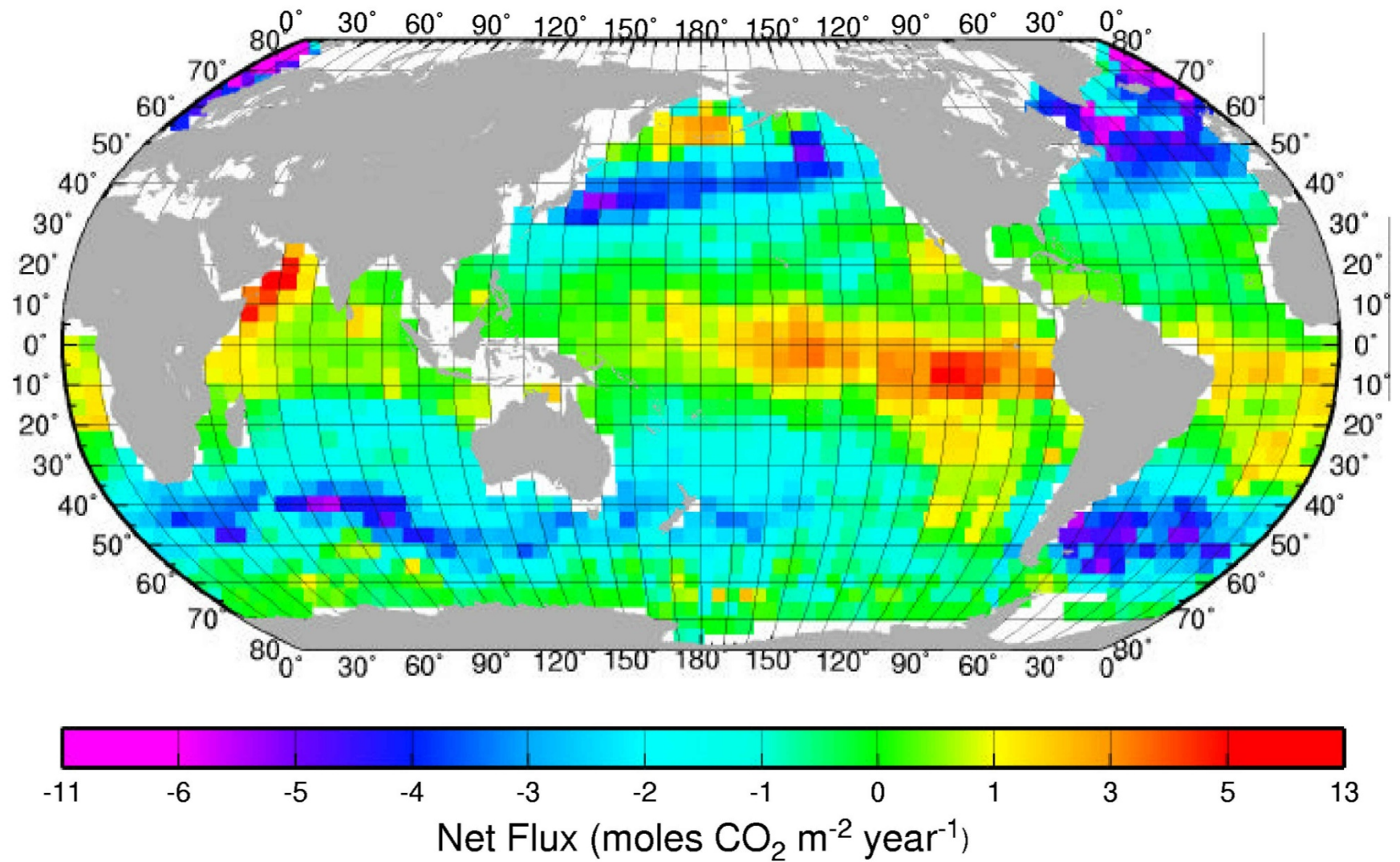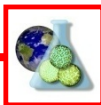
$$(\textbf{Supersaturated}) \quad pp_w > pp_a$$

- Some tend to enter the ocean Ocean is a SINK

$$(\textbf{Undersaturated}) \quad pp_w < pp_a$$

Examples
net flux out: radon (Rn), dimethyl sulfide $(CH_3)_2S$, halocarbons
net flux in: CO_2 (now), ^{39}Ar
flux in = flux out: oxygen (?), many noble gases (Xe, Kr)

Net Flux (moles CO_2 m^{-2} year^{-1})

Fluxes across sea floor or sediment-water interface

Sediments and ocean floor can act as source or sink for gases.

Examples

- N_2 produced by denitrification in sediments ($NO_3 \Rightarrow N_2$)

- O_2 consumed due to sediment respiration

- CH_4 produced from methanogenesis

- ^{3}He from mantle released by hydrothermal fluids

- ^{222}Rn from radioactive decay in sediments

2. Within-Ocean processes

N$_2$O-Konzentration

1. Radioactive decay:

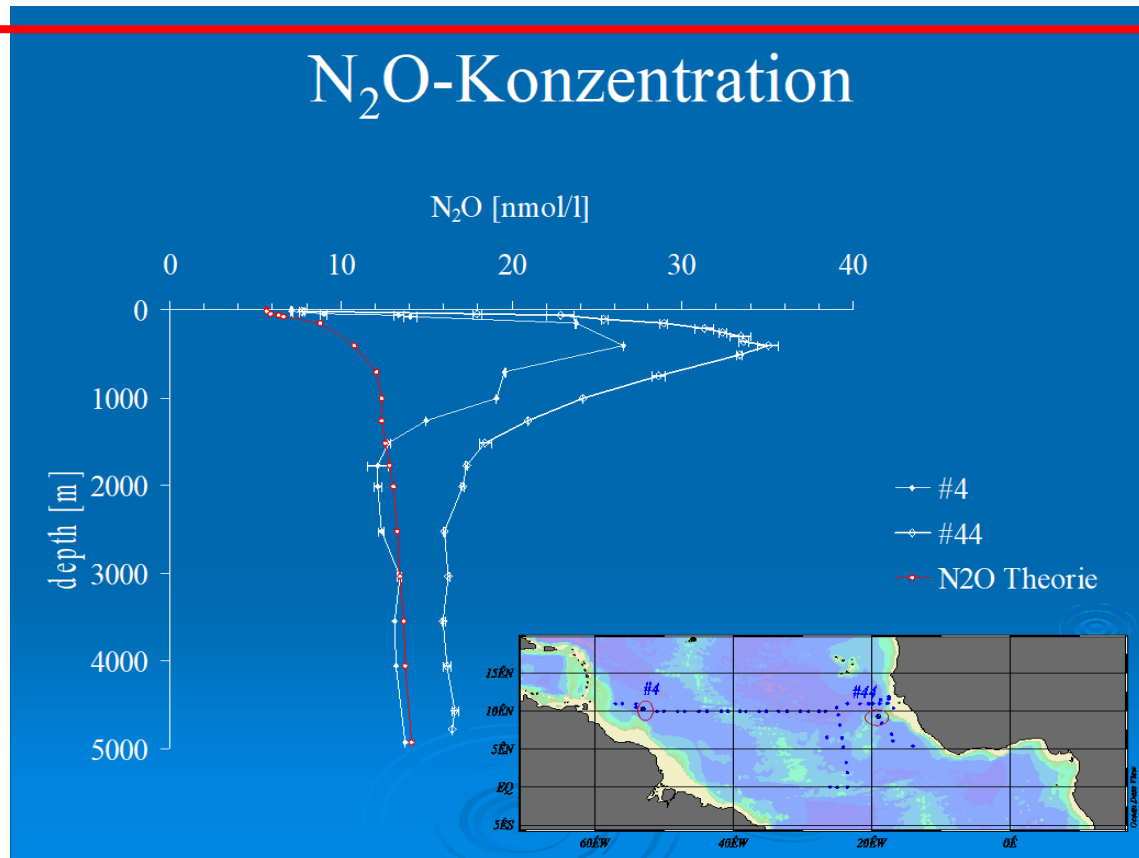 ^{222}Rn from Uranium decay series,

   ^{40}Ar from ^{40}K, ^{3}He from ^{3}H

2. Biological processes:

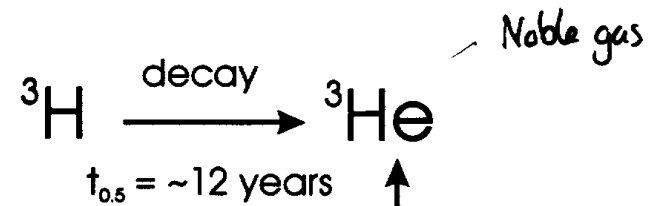   O$_2$, CO$_2$ from photosynthesis and respiration

   N$_2$O from nitrification, denitrification reactions

   Dimethylsulfide and halocarbons

Tritium – Helium Dating

Noble gas

$$^3H \xrightarrow{\text{decay}} {}^3He$$

$$t_{0.5} = \sim 12 \text{ years}$$
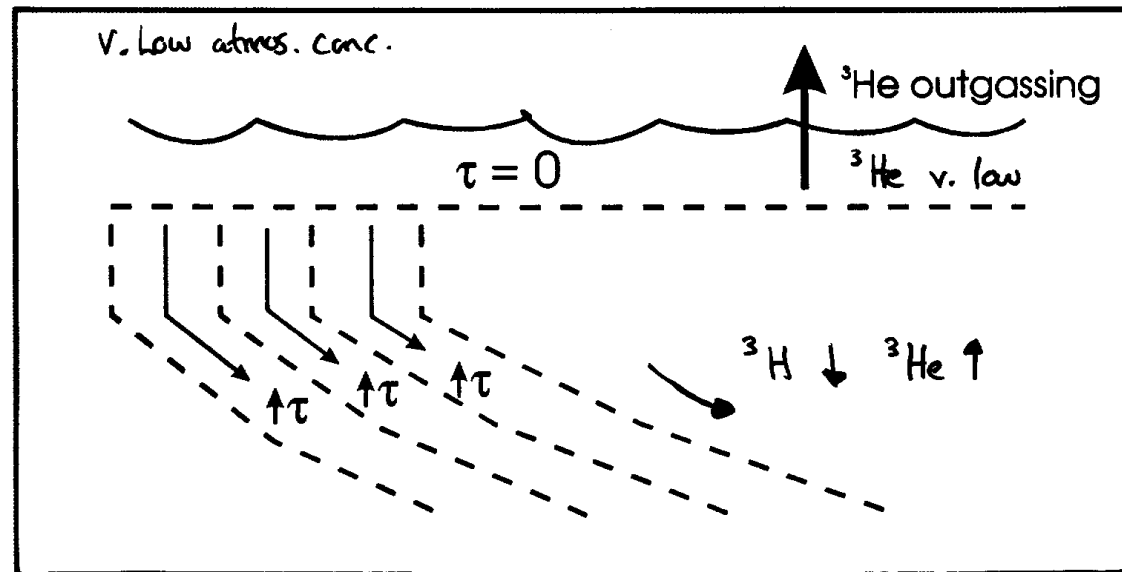
reset to zero at sea surface in most regions due to gas exchange

$$\tau \text{ (years)} = \lambda^{-1} \log (1 + ({}^3He)/({}^3H))$$

(where λ is the tritium decay constant)

v. Low atmos. conc.

^3He outgassing

$\tau = 0$ ^3He v. low

$^3H \downarrow \quad ^3He \uparrow$

$\uparrow\tau \quad \uparrow\tau \quad \uparrow\tau$

Factors affecting gas exchange rates

♦ Chemical reaction:
- *in situ* reactions could increase gradients

♦ Sea state
- near surface turbulence
- surface area/roughness
- bubbles produced by waves
- sea spray

♦ Organic films
- concentrated near surface
- affect turbulence and wave spectra

♦ The molecular size and so gas diffusivity in water (D)
- => Dependence on the *Schmidt number*

Kinetics of Air-Sea Gas Exchange

Idealised Model

- Turbulent bulk phase in surface ocean and lower atmosphere (well-mixed).

- Boundary layer close to the interface with only molecular diffusion. Molecular diffusion is SLOW compared to mixing by turbulent eddies

- For almost all gases, molecular diffusion across the boundary layer in the water is the rate-limiting process for air-sea gas exchange
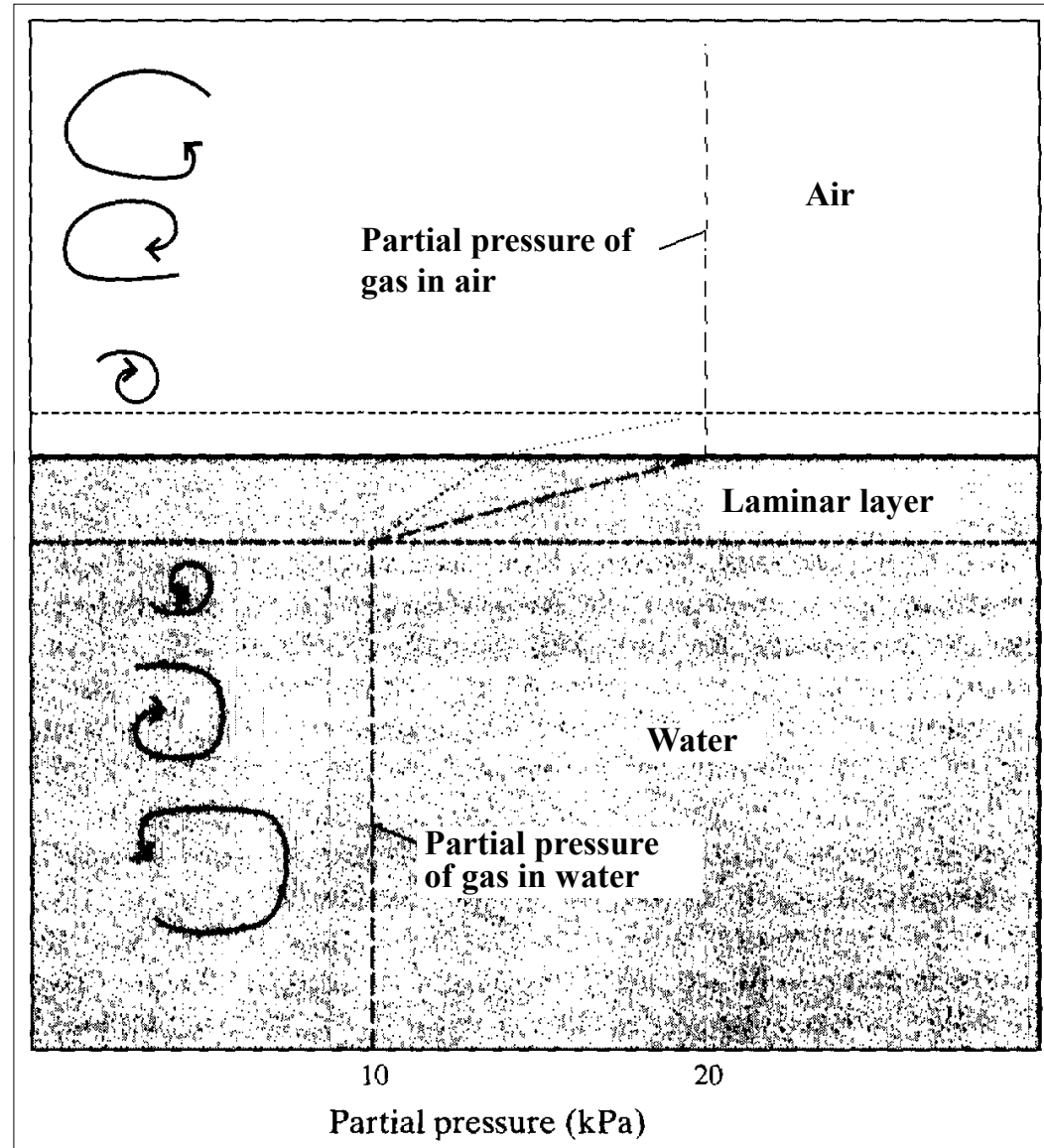
Reality (or: Where's the interface?)

- At equilibrium there is no net flux of gas between atmosphere and ocean

A net flux of a gas is driven by a partial pressure difference between atmosphere and ocean

$$Flux = e_G \cdot \left([G]_l - [G]_w \right)$$

where:

Flux is the rate of gas transfer per unit area per unit time (mol m^{-2} s^{-1})

e$_G$ is the gas exchange coefficient (transfer velocity, piston velocity, m s^{-1})

[G]$_l$ is the (calculated) gas concentration right at the air-sea interface (assumed to be in equilibrium with the atmospheric partial pressure) From Henry's Law, [G]$_l$ = H$_G$ x pp$_G$ (mol m^{-3}). (H$_G$ is a function of temperature and salinity).

[G]$_w$ is the measured gas concentration in the bulk liquid phase (mol m^{-3}). This is the surface water concentration of the dissolved gas.

Stagnant Film Model

If gas transfer is by molecular diffusion across a stagnant boundary layer:

$$Flux = \frac{D_G}{z} \cdot \left([G]_l - [G]_w\right) = e_G \cdot \left([G]_l - [G]_w\right)$$

where:

D_G is the molecular diffusion coefficient for the gas (m^2 s^{-1}). (For O_2, D= 2 x 10^{-9} m^2 s^{-1})

z   is the stagnant layer thickness (m). Rough estimates of z for typical ocean conditions range from 30 to 70 µm (thicker at lower wind speeds).

This simplistic, stagnant-film model predicts:

$$e_G \propto D, \; e_G \propto \frac{1}{z}$$

Variations of z
(thickness of laminar boundary layer)

Dependence on Wind Speed

- z becomes smaller as turbulence increases

- turbulence in ocean surface layer depends on energy supplied by the wind

- increased wind leads to increased surface area by waves, thinning of surface layer by turbulence

Figure 5.6 *Some of the gas transfer coefficients measured in ocean regions, collected from the literature by Wanninkhof (1992). These include several measurements of the loss of radon from surface waters, and experiments obtained by injection of gas tracers. The solid circle is the global average uptake of bomb-produced $^{14}CO_2$, and the open circle is for $^{14}CO_2$ uptake into the Red Sea. The estimated uncertainties of the oceanic ^{14}C inventories are indicated. Several published formulations to predict the rate of gas exchange are also on the graph. The exchange velocities are normalized to a Schmidt number of 600 to allow comparison between observations. The wind speeds are all normalized to the standard height of 10 m above the water surface. The dotted line is an equation with an assumed zero exchange at zero wind speed, and an assumed relation to the square of the wind speed, passed through the ocean $^{14}CO_2$ uptake rate. The solid line is the relationship developed by Wanninkhof to allow for the nonlinearity of the relationship and the statistical distribution of wind speeds. The latter line has the equation*
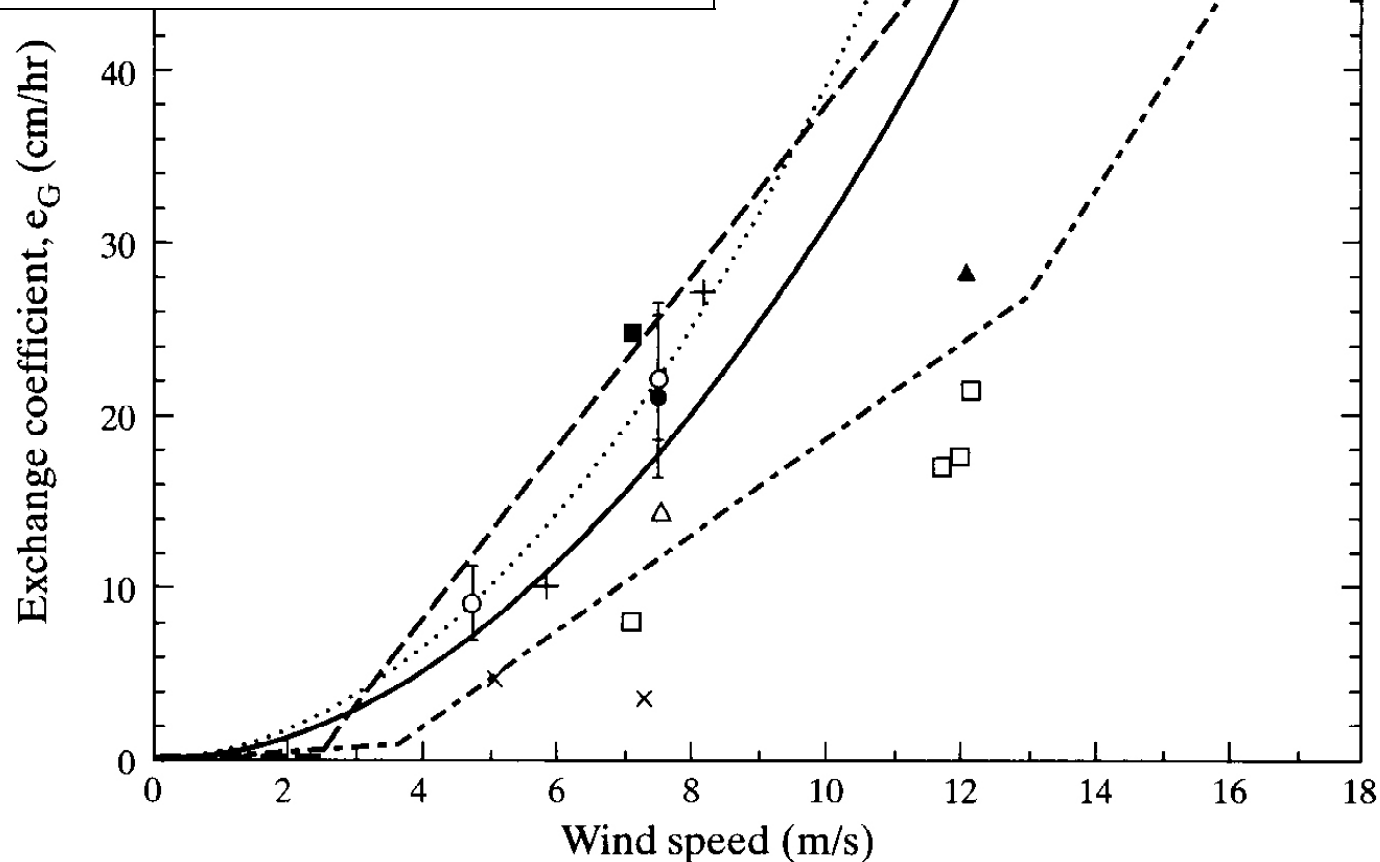
Variations of D
(molecular diffusion coefficient)

D varies for each individual gas and is temperature-dependent.

Table D.8 *Diffusion coefficients of some gases in water (10^{-9} m^2 s^{-1})*

Gas	Salinity	−1	0	5	10	15	18	20	25	30	35
						Temperature (°C)					
He	0	—	4.74	5.20	5.68	6.19	6.51	6.73	7.29	7.89	8.50
	35	4.37	4.46	4.90	5.37	5.87	6.18	6.39	6.94	7.52	8.13
Ne	0	—	2.34	2.63	2.94	3.28	3.5	3.65	4.04	4.46	4.91
Kr	0	—	0.88	1.03	1.20	1.39	1.52	1.61	1.85	2.11	2.41
Xe	0	—	0.66	0.79	0.93	1.09	1.2	1.27	1.47	1.70	1.96
Rn	0	—	0.57	0.68	0.81	0.96	1.07	1.14	1.34	1.56	1.81
H_2	0	—	2.83	3.22	3.64	4.10	4.39	4.59	5.13	5.71	6.33
	35	2.70	2.77	3.11	3.49	3.89	4.15	4.33	4.80	5.30	5.84
CH_4	0	—	0.94	1.09	1.25	1.43	1.55	1.63	1.85	2.09	2.35
CO_2	0	—	0.93	1.09	1.26	1.46	1.59	1.68	1.92	2.18	2.47

We had previously assumed that gas transfer is by simple molecular diffusion across a stagnant boundary layer. In this case, theory predicts that:

$$Flux = \frac{D_G}{z} \cdot \left([G]_l - [G]_w\right)$$

IN FACT: the way in which turbulence transfers momentum from the bulk fluid to the boundary layer in the real ocean cause the exchange coefficient to be less dependent on D than predicted by this simple model. So that:

$$e_G \propto D^{0.5}(rough\,water)\ to\ D^{0.67}(smooth\,water)$$

Why does the dependence on D matter?

- Gas exchange coefficients in the ocean are usually determined empirically using specific gases under specific conditions (e.g. wind-speed and temperature)

- We need a way to extrapolate estimates from these situations to other gases and other conditions

This requires a 'parameterization' of the gas-exchange coefficient e_G!

The Schmidt Number

The kinematic viscosity of water is also important in affecting the transfer of momentum within the water, and this is also a strong function of temperature.

The combined effects of temperature on the gas exchange coefficient through both the viscosity and the gas-diffusivity effects are PARAMETERISED by using the so-called Schmidt number:

$$Sc = \frac{v}{D}$$ (dimensionless)

where:

υ is the kinematic viscosity of seawater (units $m^2\ s^{-1}$)

Sc is characteristic for each gas and is temperature dependent

The gas exchange coefficient (e_G) is therefore inversely proportional to Sc

$$Flux = \frac{f}{\sqrt{Sc}} \cdot \left([G]_l - [G]_w \right)$$

where f is some function of the wind-speed, and the exponent 0.5 could be as high as 0.67 in quiet conditions.

Wanninkhof (1992) suggested the following:

$$Flux = \frac{8.0\,u^2}{\sqrt{Sc}} \left([G]_l - [G]_w \right)$$

where u is the wind-speed measured 10 m above the sea-surface in m/s
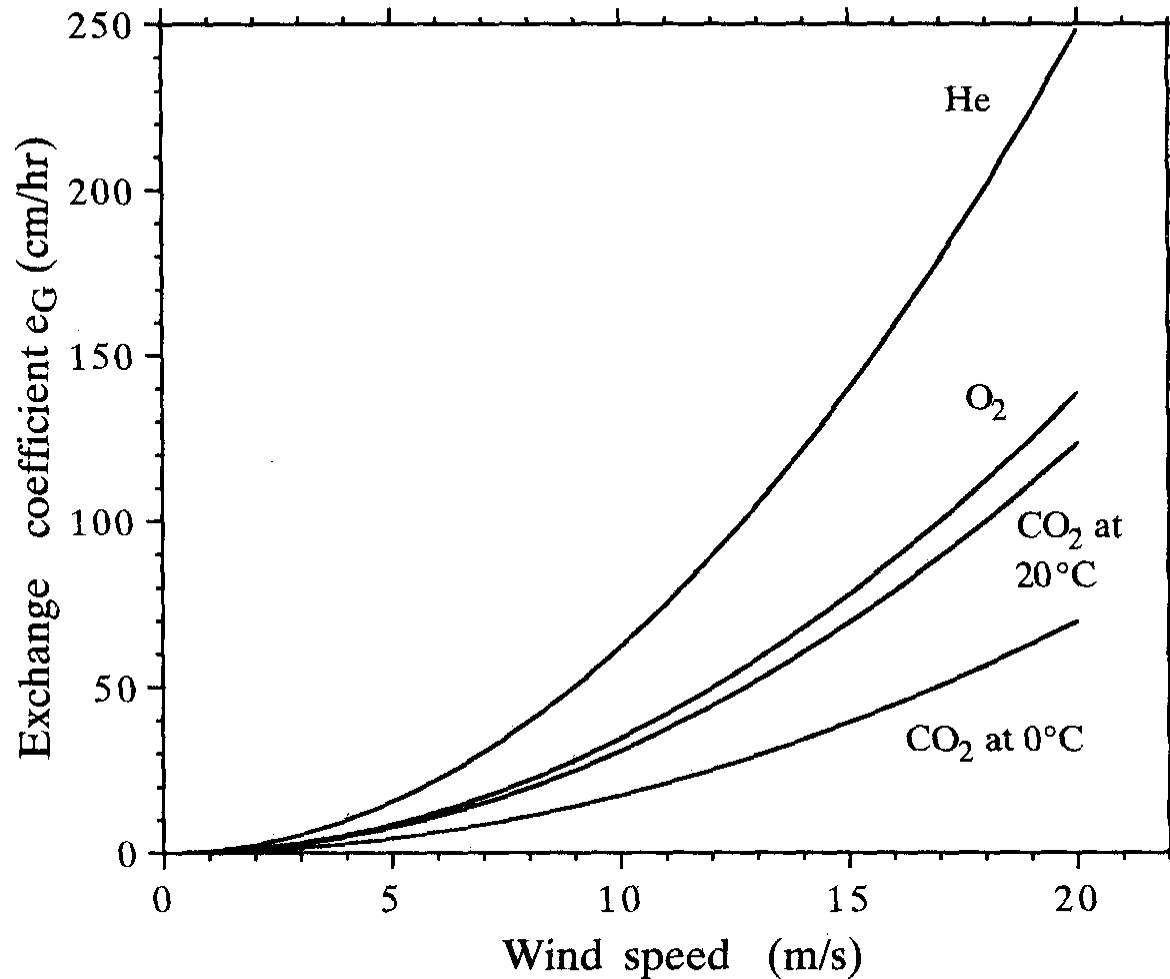(There are more recent *parameterizations*)

Figure 5.7 *Calculated values of the exchange coefficient for several gases as a function of wind speed at the standard height of 10 m above the water surface, according to Eqn. (5.10). The values for He, O_2, and CO_2 are calculated for a temperature of 20°C, and values for CO_2 are also calculated for 0°C. The values are plotted up to a wind speed of 20 m/s, but observational support for any relationships in the ocean does not extend above 15 to 18 m/s.*

How are Gas Exchange Coefficients Determined?

- Radon method

$(^{226}Ra$ $(t_{0.5} = 1620$ y$)$
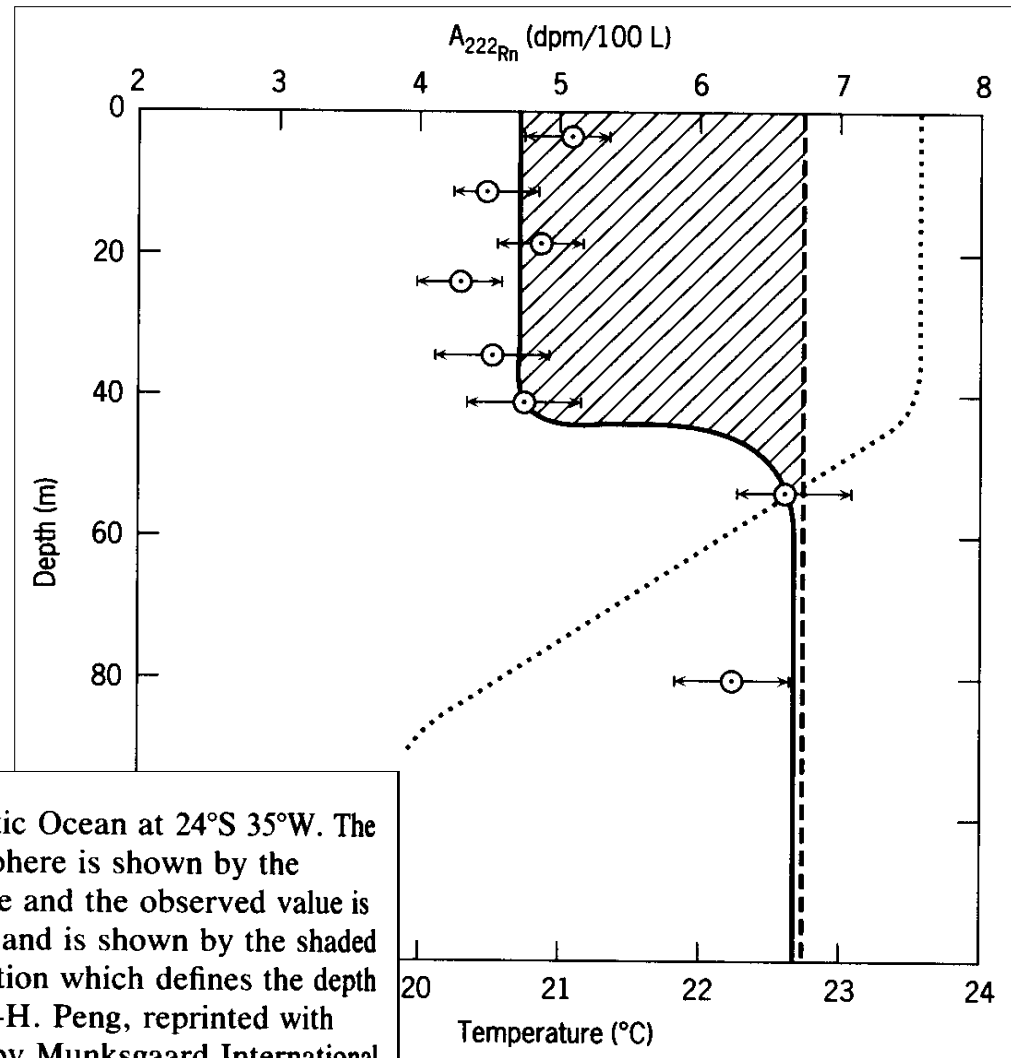
$\Rightarrow$ ^{222}Rn $(t_{0.5} = 0.01$y$)$

FIGURE 28.16. $A_{222_{Rn}}$ as a function of depth in the Atlantic Ocean at 24°S 35°W. The activity expected if no radon were escaping to the atmosphere is shown by the dashed line. The difference between this equilibrium value and the observed value is a measure of the amount of radon lost to the atmosphere and is shown by the shaded area. The dotted line is the temperature profile at this station which defines the depth of the mixed layer. *Source*: From W. S. Broecker and T.-H. Peng, reprinted with permission from *Tellus*, vol. 26, p. 30, copyright © 1974 by Munksgaard International Publishers, Ltd., Copenhagen, Denmark.

- Global ^{14}C Inventories

  natural ^{14}C inventories ($t_{0.5}$ = 5730 y)

  ^{14}C *from nuclear weapons tests*

  See: Broecker and Peng, Tracers in the Sea Chapter 3

- Deliberate tracer experiments

  SF_6 and ^3He injection

- Direct Flux Measurements

  eddy correlation etc.

http://www.pmc.noaa.gov/rb/project/gasex-98.htm

Concentration versus Saturation

- Concentration in seawater C (e.g. mol kg^{-1})

- %-saturation = C / C_{eq} * 100

- saturation anomaly in % = $100 \cdot (C / C_{eq} - 1)$

<u>where:</u>

C_{eq} is the concentration of the gas in equilibrium* with the atmospheric partial pressure of the gas

* for the temperature and salinity of the water, and for a total atmospheric pressure of 1 atmosphere (101.3 kPa) of water-saturated air

This refers to equilibrium at the air-sea interface. (For deep-water use the potential temperature of the water mass and 1 atmosphere pressure to calculate C_{eq}.

- **What drives the system away from equilibrium**

- Changes in T and S at the sea-surface over time

- Atmospheric pressure changes (up to 12% in storms, 3-4% seasonally)

- Air Injection (bubbles)

- Biological processes (e.g. respiration)

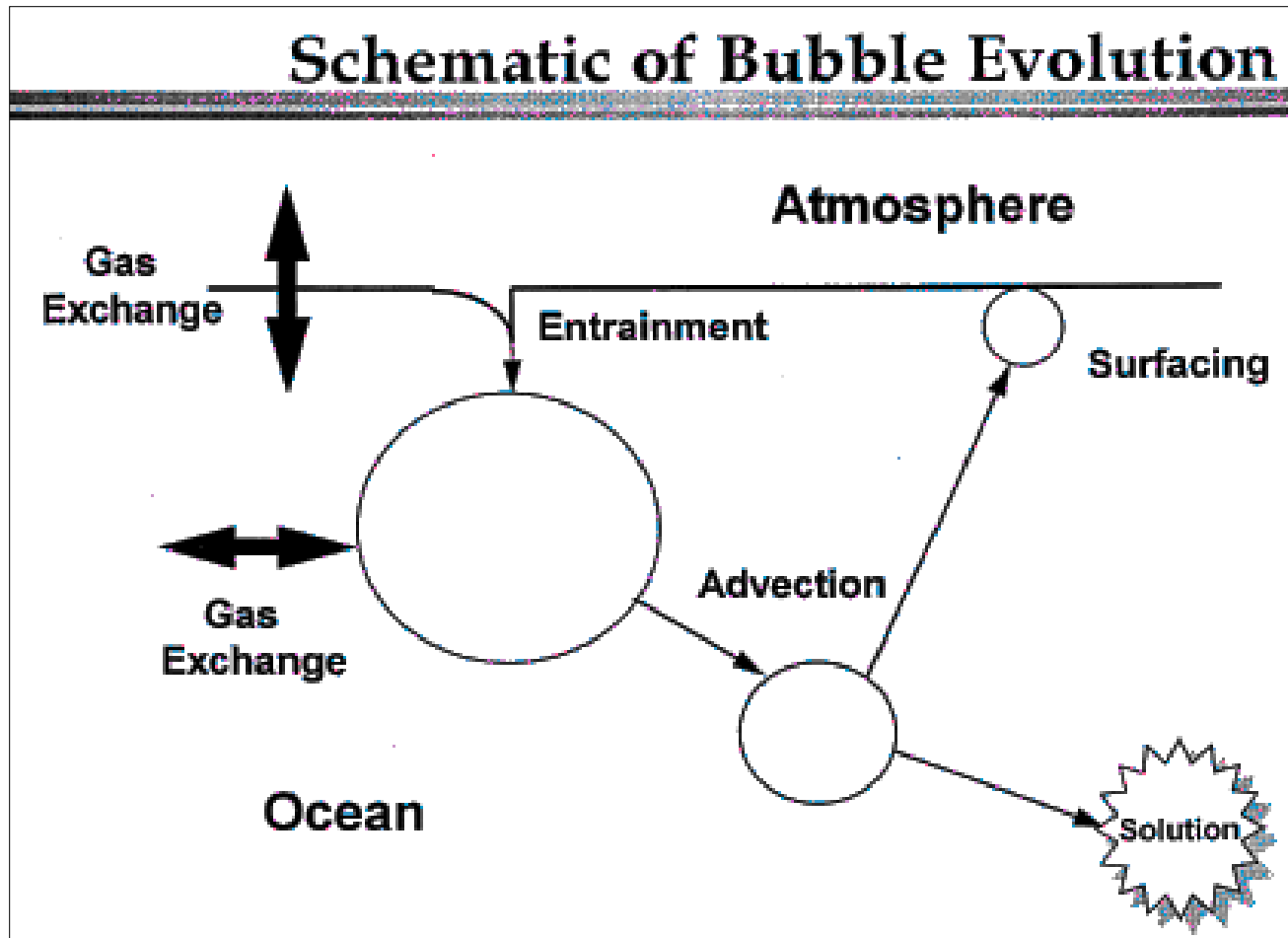- Mixing of water masses (solubility non-linear f(T,S))
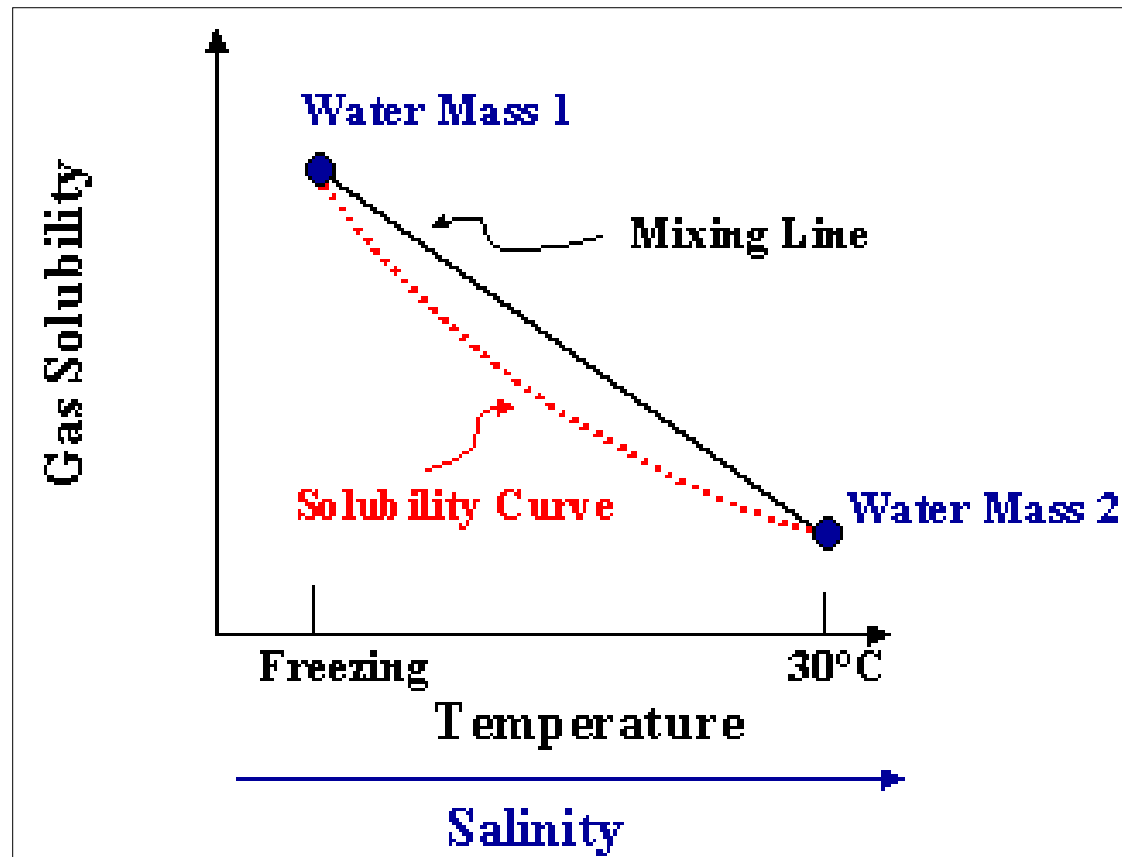
Air Injection

Hydrostatic pressure in the oceans increases with depth.
    10m = 1 bar = 0.99 atmospheres = 100 kPA

Bubbles are transported in storms to > 10m depth.

Schematic of Bubble Evolution

Atmosphere

Gas Exchange

Entrainment

Surfacing

Gas Exchange

Advection

Ocean

Solution

Pressure of air in a bubble is due to:

- atmospheric pressure

- hydrostatic pressure (depth)

- pressure due to surface tension effects

Higher pressure forces gases into solution. Can cause significant supersaturation of dissolved gases (relative to equilibrium at 1 atmosphere pressure)

Two extreme cases:

- Some bubbles collapse / dissolve completely

- Some bubbles dissolve partially

Complete injection of air from bubbles (bubbles collapse)

Change in water **conc.** reflects abundance of gases in the air.

Not related to gas solubility.

%-Saturation increase is highest for least soluble gases (e.g. He)

Gas	f_{air}	f_{sw}	Δ_{air}
N_2	0.7808	0.626	7.7%
O_2	0.2095	0.343	3.8%
Ar	0.00934	0.016	3.5%
Ne	18.2×10^{-6}	9.7×10^{-6}	11.6%
He	5.24×10^{-6}	2.3×10^{-6}	13.8%
Kr	1.14×10^{-6}	3.8×10^{-6}	1.8%
Xe	0.087×10^{-6}	0.54×10^{-6}	1.0%
CO_2	0.00034	0.014	0.1%

Δ_{air} (= % increase in concentration) resulting from the injection of 1 cm³ of air at STP into 1 kg of seawater at 15°C, S = 35.
Derived from Kester 1975.

Table 5.4 *Mole fraction (f) of gases in dry air and dissolved in air-saturated seawater, and the saturation anomaly*

Departures from Equilibrium: Conservative Gases

- Given sufficient time, (in the absence of air injection), surface layers of the ocean will reach equilibrium with the atmosphere

How much time is required?

- A characteristic timescale for equilibration of the ocean mixed layer can be derived from:

➢ the depth of the surface mixed layer z_M; say 100 m (units: LENGTH)

➢ the gas exchange coefficient, e_G (units LENGTH / TIME)

z_M / e_G has units of TIME

Examples:

wind speed at 10 m height   = 10 m s^{-1}

temperature   = 20°C

e_G (O$_2$)   = 40 cm / hr = 9.6 m day^{-1}

e_G (He)   = 80 cm / hr = 19.2 m day^{-1}

Equilibration time (O$_2$) = 100 m / 9.6 m day^{-1} = **10 days**

Equilibration time (He) = 100 m / 19.2 m day^{-1} = **5 days**

- He equilibrates faster than O$_2$

- Equilibration Time strongly dependent on wind speed (and mixed-layer depth)