

Gas solubility and exchange

Learning objectives:

- Familiarity with gas/pressure units
- Convert / calculate between concentration in water, mole fraction in air, partial pressure, etc.
- Understand how to adjust for water vapor content in the atmosphere
- Basic appreciation for the complexities of air-sea gas fluxes
- Ability to use a simple gas flux parameterization equation

Gas solubility and exchange

Learning objectives:

- Familiarity with gas/pressure units
- Convert / calculate between concentration in water, mole fraction in air, partial pressure, etc.
- Understand how to adjust for water vapor content in the atmosphere
- Basic appreciation for the complexities of air-sea gas fluxes
- Ability to use a simple gas flux parameterization equation

Outline:

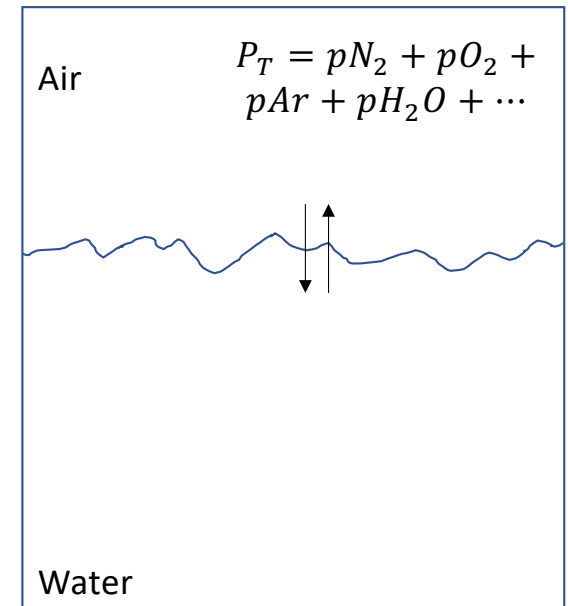
- Gas composition, units, laws
 - Dalton's law, ideal gas law, partial pressure vs. fugacity, water vapor, Henry's law
- Gas solubility and example calculations
- Examples of mechanisms that cause anomalies in saturation
- Basic theory of gas exchange
- Empirical gas exchange experiments
- Current (and simplified) flux parameterizations

Why are gases useful?

- Tracers for physical processes:
 - mixing, deep water formation, air-sea exchange, circulation
- Biological processes: biological production, respiration, oxygen deficient zones
- Atmospheric chemistry/global climate change
- Tracers of large-scale ocean changes

What controls gas concentrations?

- Air-sea gas exchange + solubility
- Mixing in the ocean
- Production and removal within the ocean



Composition of the atmosphere

Table 1.5. *The major gases of the atmosphere excluding water vapor, which has a concentration of a few percent at saturation in the atmosphere*

Seawater equilibrium concentrations were calculated from the Henry's Law coefficients at 20 °C and $S = 35$.

Gas	Atmospheric mole fraction (atm)	Seawater equilibrium concentration ($\mu\text{mol kg}^{-1}$)
N ₂	7.808×10^{-1}	4.18×10^2
O ₂	2.095×10^{-1}	2.25×10^2
Ar	9.34×10^{-3}	1.10×10^1
CO ₂	3.65×10^{-4}	1.16×10^1
Ne	18.2×10^{-6}	7.0×10^{-3}
He	5.24×10^{-6}	2.0×10^{-3}
Kr	1.14×10^{-6}	2.0×10^{-3}
Xe	0.87×10^{-7}	3.0×10^{-4}

Mole fraction is the amount (atm or moles) of a gas relative to atmosphere as a whole

Often denoted using X_i (e.g. X_{O_2})

Pressure units

In the **atmosphere**:

(Std) atmospheric pressure: **1 atm** or **1013.25 mb**
(varies by ~15%)

$$1 \text{ pascal} = 1 \text{ N m}^{-2}$$

$$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mmHg} (29.92 \text{ in Hg}) \\ = 1.013 \times 10^5 \text{ N m}^{-2} = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 100,00 \text{ Pa} \\ = 1.013 \text{ bar} = 1013.25 \text{ mb (millibar)} \\ = 14.7 \text{ lbs in}^{-2}$$

In the **ocean**:

$$0.1 \text{ bar} = 1 \text{ decibar} = \sim 1 \text{ m in seawater}$$

An increase in depth of **1000 m** in seawater increases the pressure by ~100 bar (or **1000 db**)

Pressure units

In the **atmosphere**:

(Std) atmospheric pressure: **1 atm** or **1013.25 mb**
(varies by ~15%)

1 pascal = 1 N m⁻²

1 atm = 760 torr = 760 mmHg (29.92 in Hg)
= 1.013 × 10⁵ N m⁻² = 1.013 × 10⁵ Pa

1 bar = 100,00 Pa
= 1.013 bar = 1013.25 mb (millibar)
= 14.7 lbs in⁻²

In the **ocean**:

0.1 bar = **1 decibar** = ~1 m in seawater

An increase in depth of **1000 m** in seawater increases the pressure by ~100 bar (or **1000 db**)

Gas units

Mole fraction, **X_c**: **ppm**

- Gas in a gas mixture or a liquid
- $X_c = \frac{n_c}{n_t} = \frac{p_c}{P_T}$, where n_c is the number of moles of gas C (i.e. the mole fraction gives the fraction of the total pressure that each gas contributes to dry air)

Partial pressure, **p_c**: **μatm** (micro atmospheres)

Fugacity, **f_c**: **μatm**

- like partial pressure, but accounts for non-ideality

Molar: **mol kg⁻¹**

- moles of gas per kg seawater

Volumetric: **L kg⁻¹**

- liter of gas @ STP per kg seawater

Working with gases:

Table 1.5. *The major gases of the atmosphere excluding water vapor, which has a concentration of a few percent at saturation in the atmosphere*

Seawater equilibrium concentrations were calculated from the Henry's Law coefficients at 20 °C and $S=35$.

Gas	Atmospheric mole fraction (atm)	Seawater equilibrium concentration ($\mu\text{mol kg}^{-1}$)
N ₂	7.808×10^{-1}	4.18×10^2
O ₂	2.095×10^{-1}	2.25×10^2
Ar	9.34×10^{-3}	1.10×10^1
CO ₂	3.65×10^{-4}	1.16×10^1
Ne	18.2×10^{-6}	7.0×10^{-3}
He	5.24×10^{-6}	2.0×10^{-3}
Kr	1.14×10^{-6}	2.0×10^{-3}
Xe	0.87×10^{-7}	3.0×10^{-4}

- Let's say we know the mole fraction of gases in the atmosphere, how do we, for instance, calculate an air-sea flux of a particular gas?
 - Mole fraction** → ratio of gas to atmosphere in dry air
 - Water vapor pressure** → amount of total atmospheric pressure that is made up by water vapor
 - Partial pressure** → portion of total atmospheric pressure
 - Fugacity → same as partial pressure, but for non-ideal gases
 - Solubility** → Concentration of gas water can hold at a given temperature and salinity
- Air-sea fluxes will (generally) act to reduce the difference between the partial pressure (gas pressure exerted on the surface of the ocean) and the solubility (how many moles of gas the water can hold at a given pressure)

Dalton's law of partial pressures

- Partial pressure (p_i) = Mole Fraction (X_i)* P_T
- Total pressure in a fixed volume is equal to the sum of the partial pressures of the components of the mixture

$$P_T = \sum p_G = p_{N_2} + p_{O_2} + p_{Ar} + p_{H_2O} + \dots$$

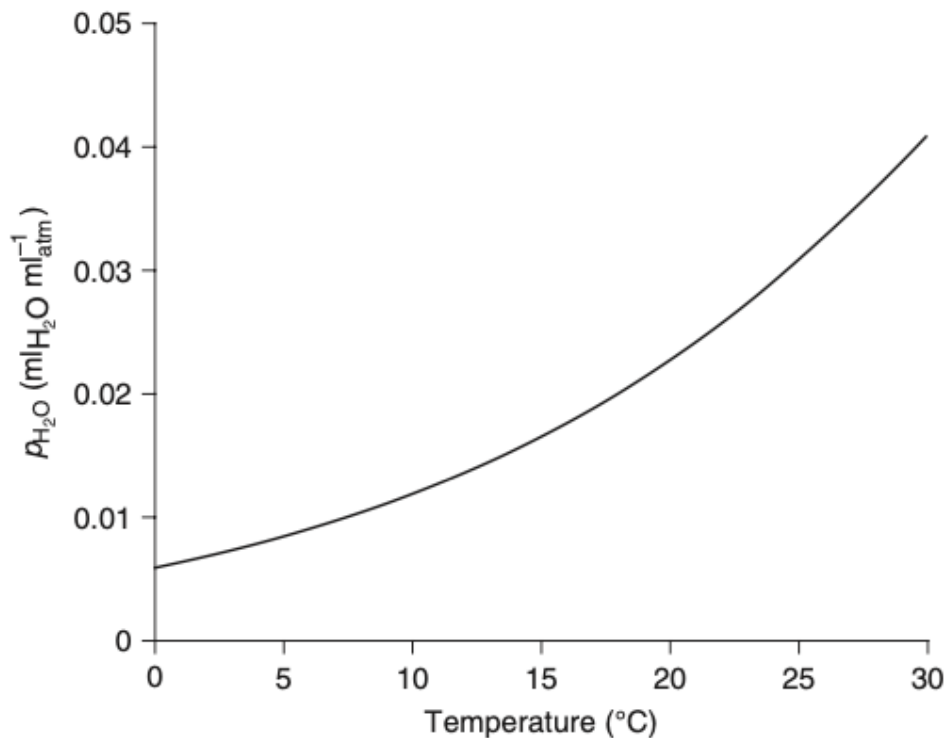
- Dalton's Law implies ideal behavior, i.e. all gases behave independently of one another.
- Gases are dilute enough that this is a pretty good assumption (~1% errors in the surface ocean)

Ideal gas law

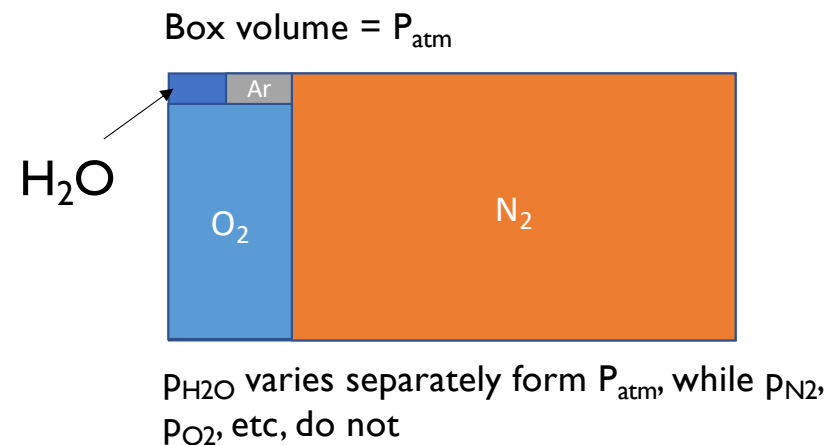
$$P_c V = n_c R T$$

- P_c = pressure exerted by gas c
 - V = volume
 - T = temperature in K
 - n_c = # mol of gas l
 - R = ideal gas constant
-
- At STP (i.e. 273.15 K and 1013.25 hPa), volume of a gas = 22.414 L mol⁻¹
 - STP for gases is 0C, not 25C!

Water vapor: Clausius-Clapeyron relation



- Water vapor is different than other gases in the atmosphere
- Water vapor is between ~0.6 and 4 % of total atmospheric pressure
- Must be accounted for when determining saturation concentrations from the mole fraction of atmospheric gases



Water vapor correction

- Mole fractions in the atmosphere are given in dry air
- Total atmospheric pressure includes the partial pressure of water vapor (p_{H_2O})
- To calculate the partial pressure that a gas exerts on the surface of the water, we must remove the water vapor pressure
- $p_c = X_c(P_T - p_{H_2O})$
 - p_c = partial pressure of gas C
 - X_c = mole fraction of gas in dry air
 - P_T = Total atmosphere pressure
 - $p_{H_2O} = (h/100) \times p_0$, where h is % relative humidity and p_0 is the saturation vapor pressure of water

Composition of the atmosphere is generally homogenous for major constituents and trace gases, except for H_2O , CO , N_2O , CO_2 , and CH_4 .

where p_G = partial pressure of gas G
 x_G = mole fraction of gas in dry air
 P_T = Total atmospheric pressure
 h = % relative humidity
 p_0 = saturation vapor pressure of water = $f(T)$

Fugacity (f)

- Some gases act differently than you would expect based on their partial pressure.
 - These are “non-ideal” gases
- Fugacity of a gas (f_i) corrects the partial pressure for non-ideal behavior
- f_i and p_i have units of “atm” (atmospheres)
- The fugacity of a gas is analogous to the activity of a solute
 - Unlike solutes: common elemental gases (e.g., O_2 , N_2 , Ar) deviate from ideal behavior by $<0.1\%$, so we can use fugacity (f) and partial pressure (p) interchangeably
 - Some molecular gases (e.g. N_2O , CO_2) have a larger non-ideal behavior ($<1\%$) and it is usually important to correct for this

Gas solubility

- The solubility of a gas determines its partitioning between the atmosphere and water
 - The amount of a gas that will be present in water at a given T and P_T (total atmospheric/headspace pressure)
- Solubility coefficients are a type of chemical equilibrium constant that defines the solubility of a gas in water
- Solubility coefficients can be expressed for water in equilibrium with Earth's atmosphere, or with a theoretical atmosphere of a pure gas of interest – need to be careful of what coefficients you use
 - Converting between them can be confusing
 - In this class I will give you solubility information, but if you are performing your own calculations be careful that you are consistent and use published values to check your work

Henry's Law

- The amount of gas that will dissolve in water at thermodynamic equilibrium is described by Henry's Law:

$$[C] = K_{H,C} f_c$$

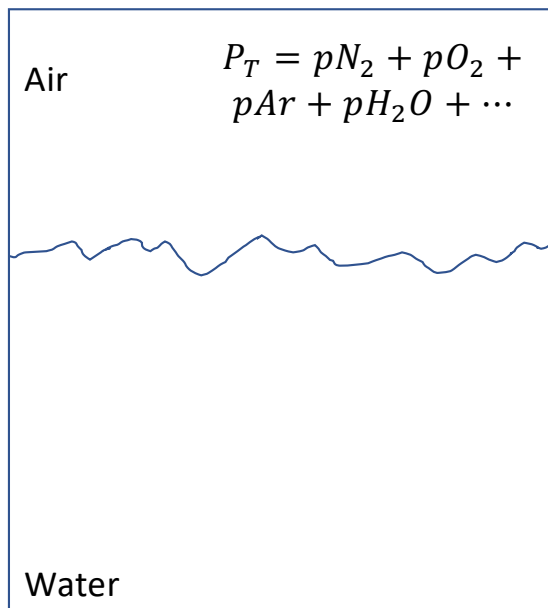
$[C]$ = the gas concentration mol kg⁻¹ atm⁻¹

$K_{H,C}$ = Henry's law solubility coefficient (mol kg⁻¹ atm⁻¹)

$f_c = p_c$ = fugacity or partial pressure of a gas

Henry's law coefficients are empirically determined and a function of temperature and salinity.

Saturation: Chemical equilibrium



- At equilibrium, the $[C]_{\text{obs.}} = [C]_{\text{sat}}$, which is determined by pC

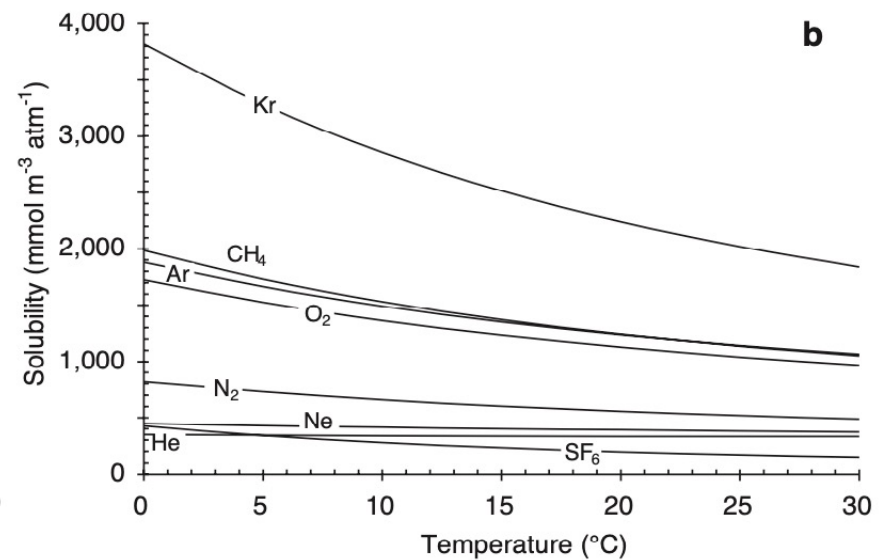
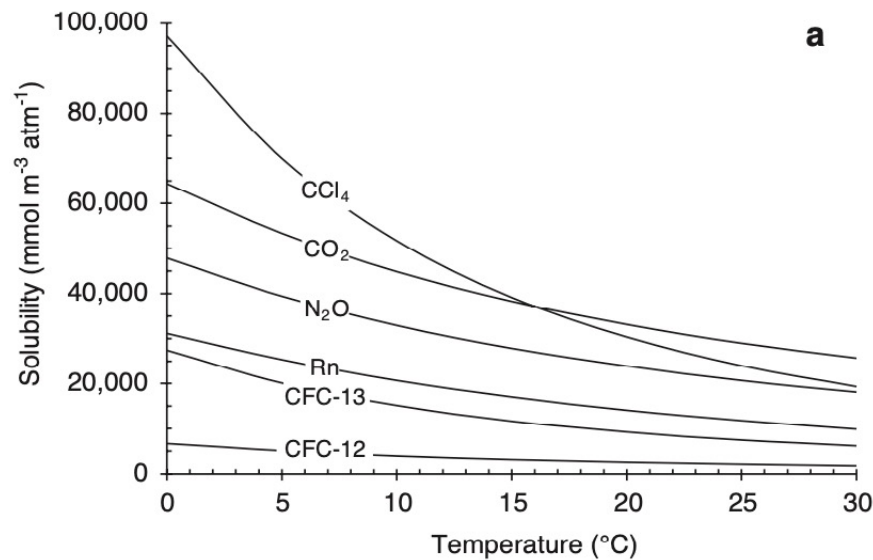
$$pC = P_T X_c (1 - p_{H_2O})$$

$$[C]_{\text{sat}} = K_{H,C} p_c$$

P_T =atmospheric pressure
 X_c =atmos. mole fract.
 p_c = partial pressure of gas C

- Supersaturated water: $[C]_{\text{obs.}} > [C]_{\text{sat}}$
 - Gas will tend to move from the water to the atmosphere
- undersaturated water: $[C]_{\text{obs.}} < [C]_{\text{sat}}$
 - Gas will tend to move from the atmosphere to the water

Gas solubility as a function of temperature



Note the change in scale

Example calculation

What is the saturation concentration of oxygen at 20°C? How about 5°C?

Example calculation

What is the saturation concentration of oxygen at 20°C? How about 5°C?

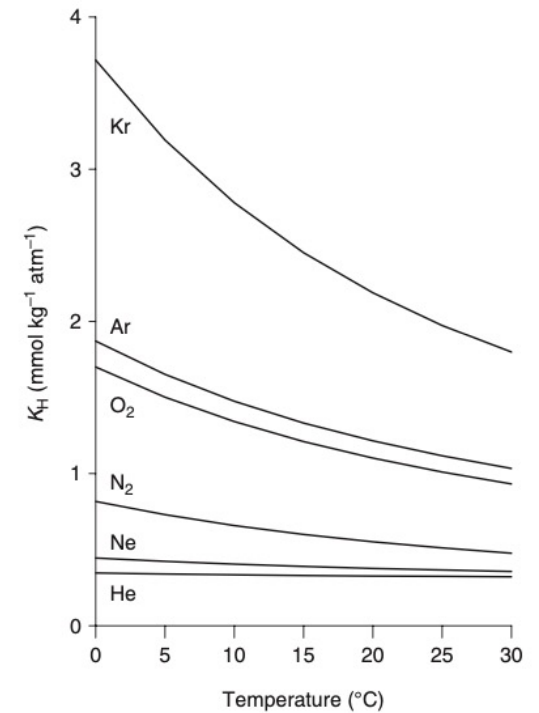
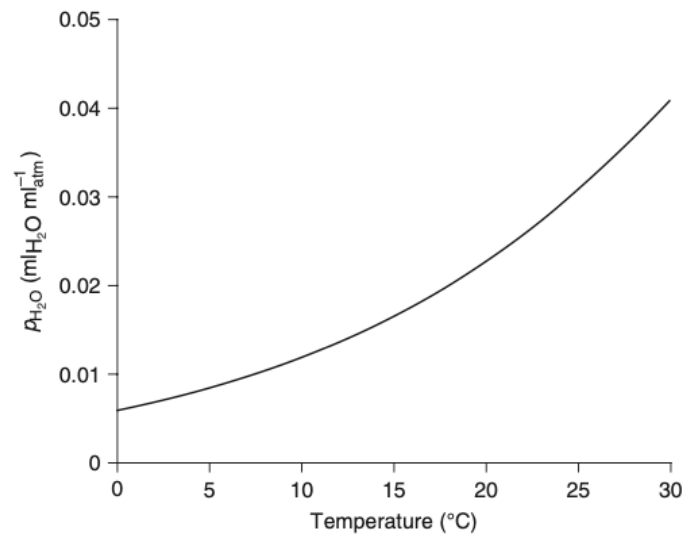
$$pC = P_T X_c (1 - p_{H_2O}) \quad [C]_{sat} = K_{H,c} p_c$$

Example calculation

What is the saturation concentration of oxygen at 20°C? How about 5°C?

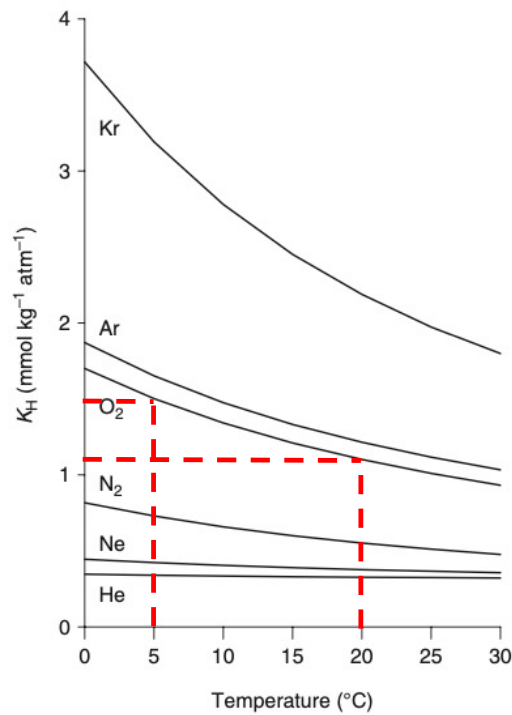
$$pC = P_T X_c (1 - p_{H_2O}) \quad [C]_{sat} = K_{H,c} p_c$$

Gas	Atmospheric mole fraction (atm)
N ₂	7.808×10^{-1}
O ₂	2.095×10^{-1}



Emerson and Hedges, at 1atm and S=35

Example calculation



What is the saturation concentration of oxygen at 20 $^{\circ}\text{C}$? How about 5 $^{\circ}\text{C}$?

$$p\text{O}_2 = P_T X_{\text{O}_2} (1 - p_{\text{H}_2\text{O}})$$

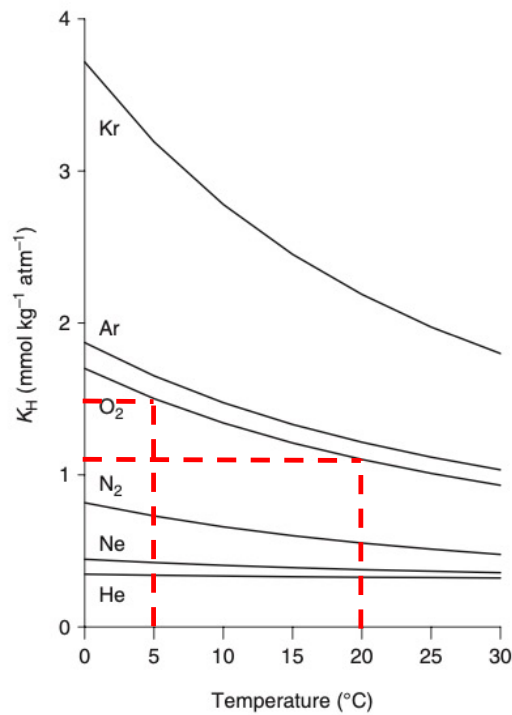
$X_{\text{O}_2} = 0.20946$ – that is the mole fraction in dry air

$p_{\text{H}_2\text{O}}(20^{\circ}\text{C}, S=35) = 0.0226$ (i.e. ~2 % of the total atmospheric pressure is water vapor)

So at 1atm, 20 $^{\circ}\text{C}$ the $p\text{O}_{2\text{atm}} = 1 * 0.20946 * (1 - 0.0226) = 0.2030 \text{ atm}$

Emerson and Hedges, at 1atm and S=35

Example calculation



What is the saturation concentration of oxygen at 20 $^{\circ}\text{C}$? How about 5 $^{\circ}\text{C}$?

$$p_{\text{O}_2} = P_T X_{\text{O}_2} (1 - p_{\text{H}_2\text{O}})$$

$X_{\text{O}_2} = 0.20946$ – that is the mole fraction in dry air

$p_{\text{H}_2\text{O}}(20^{\circ}\text{C}, S=35) = 0.0226$ (i.e. ~2 % of the total atmospheric pressure is water vapor)

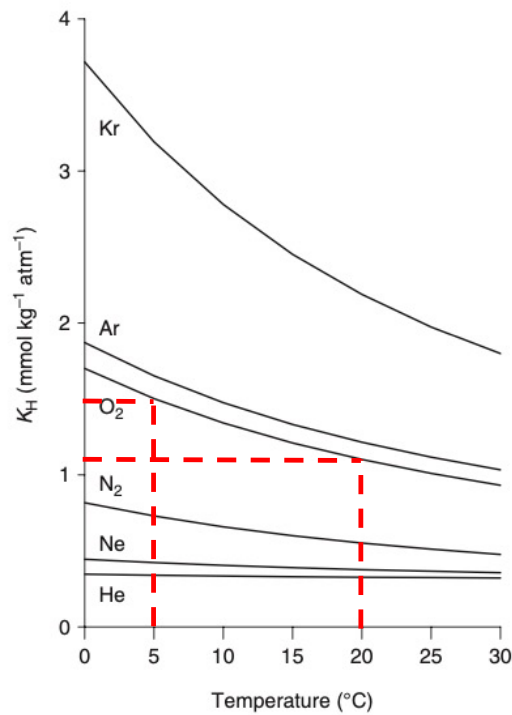
So at 1atm, 20 $^{\circ}\text{C}$ the $p_{\text{O}_2\text{atm}} = 1 * 0.20946 * (1 - 0.0226) = 0.2030 \text{ atm}$

$$[\text{O}_2]_{\text{sat}} = K_{H,\text{O}_2} p_{\text{O}_2}$$

$$[\text{O}_2]_{\text{sat},25^{\circ}\text{C}} = 1.1 \frac{\text{mmol}}{\text{kg atm}} 0.2030 \text{ atm} = 0.2233 \frac{\text{mmol}}{\text{kg}} = 223.3 \frac{\mu\text{mol}}{\text{kg}}$$

Emerson and Hedges, at 1atm and S=35

Example calculation



What is the saturation concentration of oxygen at 20°C? How about 5°C?

$$pO_2 = P_T X_{O_2} (1 - p_{H_2O})$$

$X_{O_2} = 0.20946$ – that is the mole fraction in dry air

$p_{H_2O}(20^\circ\text{C}, S=35) = 0.0226$ (i.e. ~2 % of the total atmospheric pressure is water vapor)

So at 1atm, 20°C the $pO_{2atm} = 1 * 0.20946 * (1 - 0.0226) = 0.2030 \text{ atm}$

$$[O_2]_{sat} = K_{H,O_2} p_{O_2}$$

$$[O_2]_{sat,25C} = 1.1 \frac{\text{mmol}}{\text{kg atm}} 0.2030 \text{ atm} = 0.2233 \frac{\text{mmol}}{\text{kg}} = 223.3 \frac{\mu\text{mol}}{\text{kg}}$$

$$pO_{2atm} = 1 * 0.20946 * (1 - 0.0084) = 0.2077 \text{ atm}$$

Note the lower p_{H_2O}

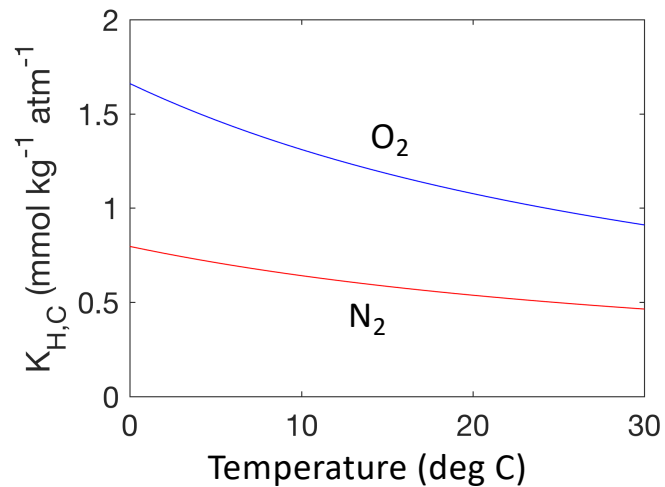
$$[O_2]_{sat,5C} = 1.5 \frac{\text{mmol}}{\text{kg atm}} 0.2077 \text{ atm} = 0.3115 \frac{\text{mmol}}{\text{kg}} = 311.5 \frac{\mu\text{mol}}{\text{kg}}$$

Emerson and Hedges, at 1atm and S=35

Solubility vs. partial pressure: O₂ and N₂

- Oxygen: ~20 % of the atmosphere
Partial pressure ($p_{O_2}=f_{O_2}$) = 0.209
- Nitrogen: ~78 % of the atmosphere
Partial pressure = 0.781

Solubility vs. Temperature

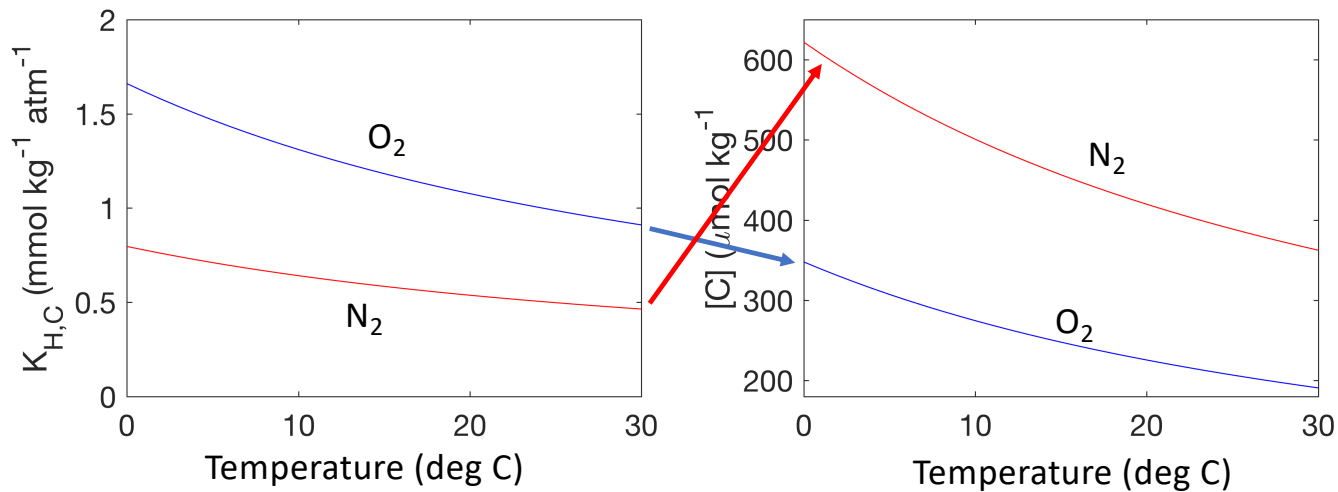


Solubility vs. partial pressure: O₂ and N₂

- Oxygen: ~20 % of the atmosphere
Partial pressure ($p_{O_2}=f_{O_2}$) = 0.209
- Nitrogen: ~78 % of the atmosphere
Partial pressure = 0.781

N₂ is 4x more plentiful in the atmosphere,
but only half as soluble as oxygen, so
saturation concentration is ~2x oxygen

Solubility vs. Temperature



Saturation anomalies: Mechanisms

Causes of deviation from equilibrium:

1. Warming or cooling of the sea surface (gas exchange is not instantaneous)
2. Bubble injection from winds/breaking waves
3. Mixing of different water masses
4. Biological activity (e.g. denitrification, photosynthesis/respiration)
5. Change in atmospheric pressure (again, gas exchange is not instantaneous)

Saturation anomalies: Mechanisms

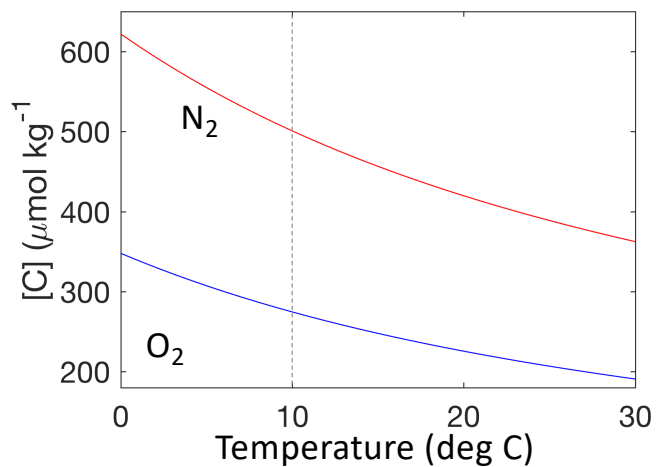
Causes of deviation from equilibrium:

1. **Warming or cooling of the sea surface (gas exchange is not instantaneous)**
2. Bubble injection from winds/breaking waves
3. **Mixing of different water masses**
4. Biological activity (e.g. denitrification, photosynthesis/respiration)
5. Change in atmospheric pressure (again, gas exchange is not instantaneous)

Saturation anomalies: Temperature change

Saturation anomalies can either be expressed in concentration or percent

$$\Delta[C] = [C] - [C]_{sat} \qquad \% \text{ sat} = \frac{[C]}{[C]_{sat}} \times 100 \qquad \% \text{ supersaturation} = \left(\frac{[C]}{[C]_{sat}} - 1 \right) \times 100$$

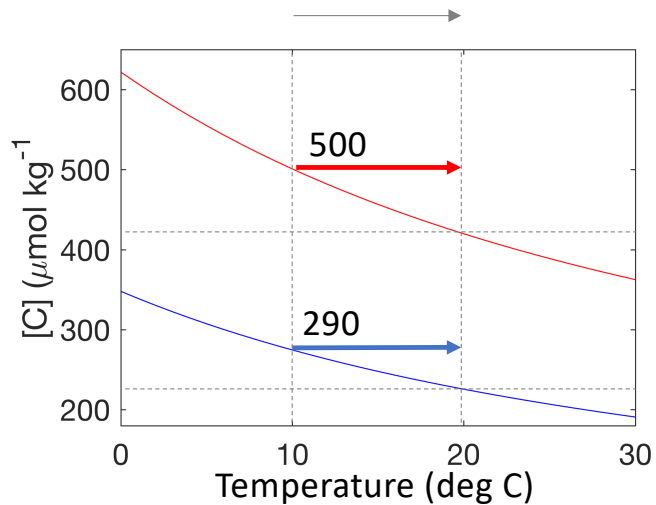


Saturation anomalies: Temperature change

Saturation anomalies can either be expressed in concentration or percent

$$\Delta[C] = [C] - [C]_{sat} \qquad \% \text{ sat} = \frac{[C]}{[C]_{sat}} \times 100 \qquad \% \text{ supersaturation} = \left(\frac{[C]}{[C]_{sat}} - 1 \right) \times 100$$

Water is warmed by 10 deg, no gas exchange allowed

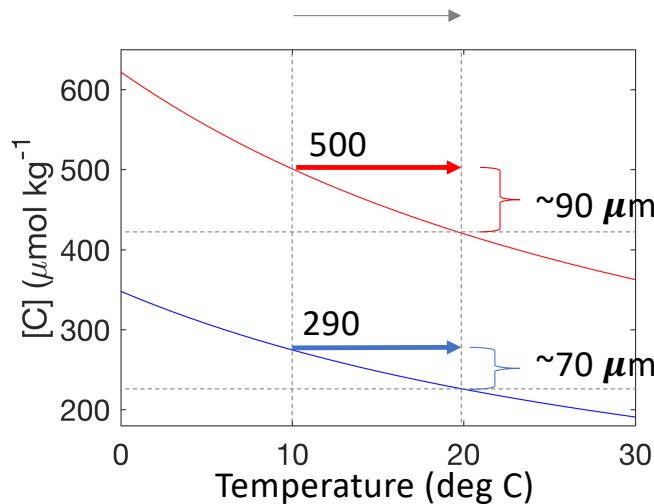


Saturation anomalies: Temperature change

Saturation anomalies can either be expressed in concentration or percent

$$\Delta[C] = [C] - [C]_{sat} \qquad \% \text{ sat} = \frac{[C]}{[C]_{sat}} \times 100 \qquad \% \text{ supersaturation} = \left(\frac{[C]}{[C]_{sat}} - 1 \right) \times 100$$

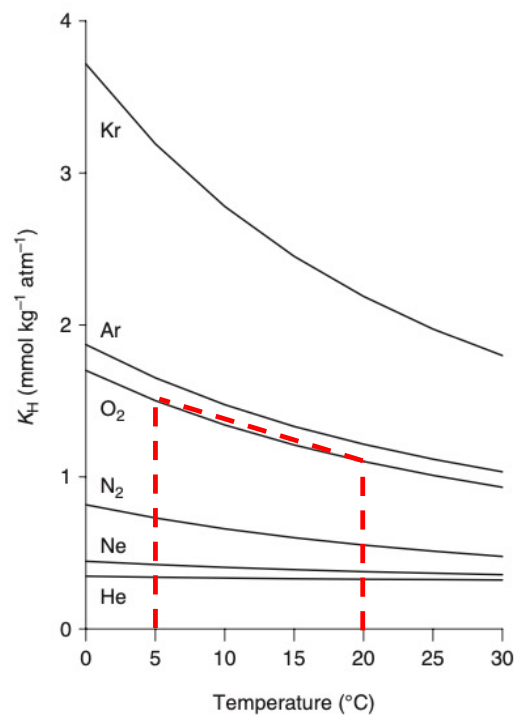
Water is warmed by 10 deg, no gas exchange allowed



$$\sim 90 \mu\text{mol}; \quad \Delta N_2 = 500 - 410 = 90 \frac{\mu\text{mol}}{\text{kg}} \text{ or } \frac{500}{410} \times 100 \approx 122\%$$

$$\sim 70 \mu\text{mol/kg}; \quad \Delta O_2 = 290 - 200 = 90 \frac{\mu\text{mol}}{\text{kg}} \text{ or } \frac{290}{200} \times 100 \approx 145\%$$

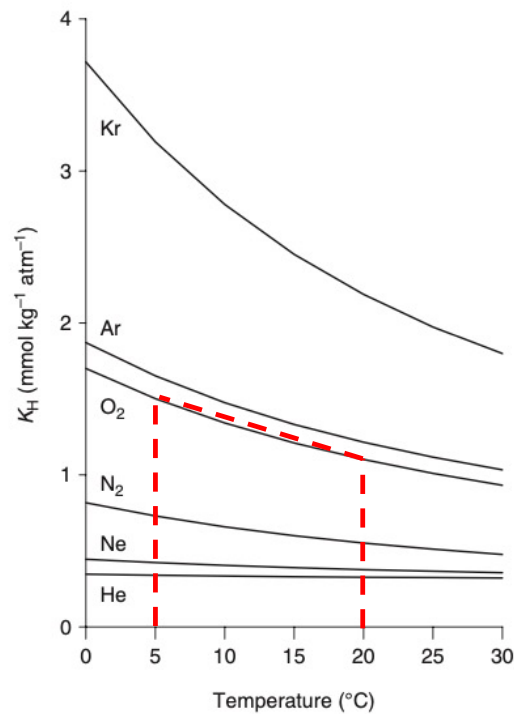
Saturation anomalies: Mixing



What happens when you mix two equal size water masses with different concentrations?

Temperature?
Concentration?
Saturation?

Saturation anomalies: Mixing



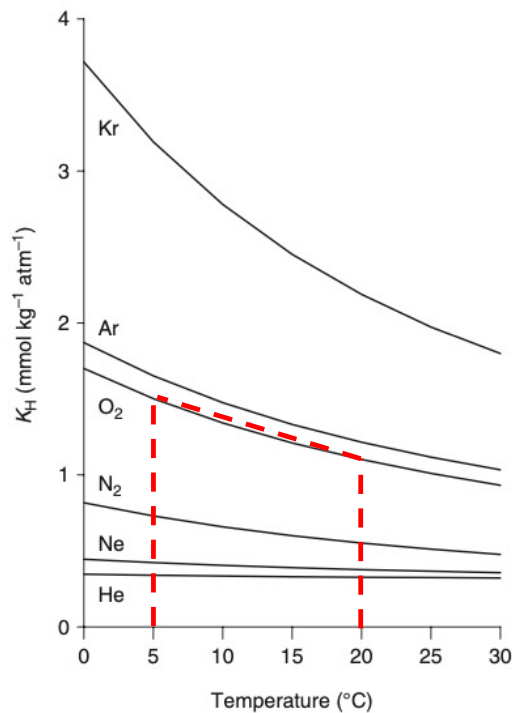
What happens when you mix two equal size water masses with different concentrations?

Temperature? – Conservative (i.e. $T_{\text{new}} = 12.5^{\circ}\text{C}$)

Concentration?

Saturation?

Saturation anomalies: Mixing



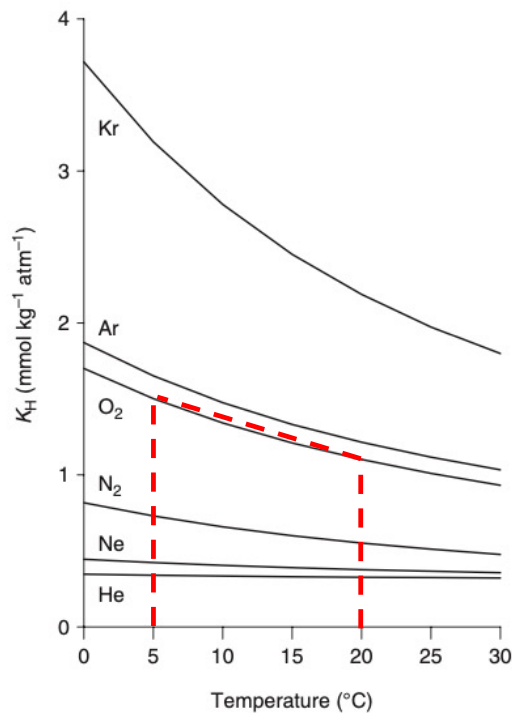
What happens when you mix two equal size water masses that are both equilibrated with the atmosphere?

Temperature? – Conservative (i.e. $T_{\text{new}} = 12.5^{\circ}\text{C}$, halfway between 20 and 5 $^{\circ}\text{C}$)

Concentration? – Conservative (i.e. $C_{\text{new}} = 268 \mu\text{mol/kg}$)

Saturation?

Saturation anomalies: Mixing



What happens when you mix two equal size water masses that are both equilibrated with the atmosphere?

Temperature? – Conservative (i.e. $T_{\text{new}} = 12.5^{\circ}\text{C}$, halfway between 20 and 5 $^{\circ}\text{C}$)

Concentration? – Conservative (i.e. $C_{\text{new}} = 268 \mu\text{mol/kg}$)

% Saturation? – non-conservative

$$C_{\text{sat},12.5} = 260 \mu\text{mol/kg}$$

The water is now supersaturated by $8 \mu\text{mol/kg}$ or $\sim 3\%$