

## Formulas/Constants, PHYC/OCEA 4595/5595 Atmospheric Chemistry

### Helpful Constants:

pptv = part per trillion ( $1 \times 10^{-12}$ )

ppbv = part per billion ( $1 \times 10^{-9}$ )

ppmv = part per million ( $1 \times 10^{-6}$ )

Surface area of a sphere:  $A = 4\pi r^2$

$1 \text{ m}^3 = 1000 \text{ l}$

$1 \text{ hPa} = 100 \text{ Pa} = 100 \text{ N/m}^2$

Gravitational acceleration  $g = 9.80 \text{ m/sec}^2$

Radius of the earth  $R = 6400 \text{ km}$

Mean molecular mass of air  $M_a = 28.96 \text{ g/mole}$

Molecular mass of  $\text{CO}_2$ :  $M_{\text{CO}_2} = 44 \text{ g/mole}$

$\text{N}_2$  mixing ratio in the atmosphere  $C_{\text{N}_2} = 0.78 \text{ mol/mol}$

$\text{O}_2$  mixing ratio in the atmosphere  $C_{\text{O}_2} = \text{oxygen} = 0.21 \text{ mol/mol}$

Dobson Unit (DU) =  $2.69 \times 10^{20} \text{ molec/m}^2$

Mass of the atmosphere:  $m_a = 4\pi R^2 P_s / g = 5.2 \times 10^{18} \text{ kg}$  (surface pressure  $P_s$  in  $\text{N/m}^2 = \text{Pascals}$ )

Avogadro's number  $A_v = 6.02 \times 10^{23}$  (number of molecules in a mole)

Ideal gas constant:  $R = 8.31 \text{ J/molK}$

### Ideal Gas Law:

Mixing ratio:  $C_x = p_x/p = n_x/n_a$  (pressure, molar, or number density fraction)

Moles of air in the atmosphere  $N_a = m_a/M_a$  ( $m_a$ : atmospheric mass, units consistent with  $M_a$ )

Moles of  $\text{CO}_2$  atmosphere  $N_{\text{CO}_2} = C_{\text{CO}_2} N_a$  ( $N_a$  number of moles in the atmosphere)

Mass of  $\text{CO}_2$  in the atmosphere:  $m_{\text{CO}_2} = N_{\text{CO}_2} M_{\text{CO}_2}$

Atmospheric column of x:  $\int n_x dz$  (molecules/area)

Ideal gas law:  $PV = NRT$  (Pressure  $P$  Pa ( $\text{N/m}^2$ ), Volume  $V$  ( $\text{m}^3$ ), moles  $N$ , temperature  $T$  (K))

Number density of air:  $[M] = n_a = A_v N/V = A_v P/RT$  (in  $\text{molec/m}^3$ ,  $V$  in  $\text{m}^3$ ,  $N$  is moles,  $A_v$ : Avogadro's number).

Number density of air:  $n_a = P/(1.38 \times 10^{-19} T)$  ( $n_a$  in  $\text{molec/cm}^3$ ,  $P$  in hPa and  $T$  in K).

Species number density:  $n_x = C_x A_v P/RT = C_x n_a$ .

Saturated water vapor pressure  $P_{\text{H}_2\text{O},\text{sat}}(T) = 6.112 \times e^{22.49 - (6142/T)}$  (in hPa,  $T$  in K).

$RH(\%) = 100 \times P_{\text{H}_2\text{O}}/P_{\text{H}_2\text{O},\text{sat}}(T)$

### Simple Models:

$dm/dt = F_{in} + E + P - F_{out} - D - L$

If sources constant and all losses first order, can write:  $dm/dt = S - km$ , which has the solution,  $m(t) = m(0)e^{-kt} + \frac{S}{k}(1 - e^{-kt})$ .

If loss of mass  $m$  is linear (first order):  $L = km$ .

Lifetime with respect to some first order loss process:  $\tau = \text{mass}/(\text{loss rate}) = 1/k$ .

Mass per unit area between pressure levels  $p_1$  and  $p_2$ ,  $M = (p_2 - p_1)/g$  ( $p_1$  and  $p_2$  in Pa)

Puff model of a pollution plume:  $d[X]/dt = E + P - L - D - k_{dil}([X] - [X]_b)$  where  $k_{dil}$  is a dilution rate constant, and  $[X]_b$  is the concentration of  $X$  in the background air.

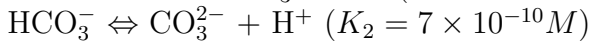
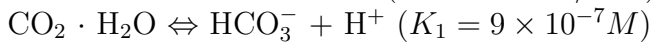
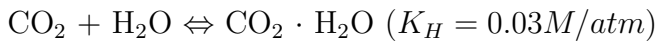
### Biogeochemical cycles:

Photosynthesis:  $\text{CO}_2 + \text{H}_2\text{O} + h\nu \rightarrow \text{CH}_2\text{O} + \text{O}_2$ , where  $\text{CH}_2\text{O}$  represents biomass material.

Burning, respiration, or decay:  $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

Total Dissolved Inorganic Carbon:  $[\text{CO}_2(\text{aq})] = [\text{CO}_2 \cdot \text{H}_2\text{O}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$

Henry's Law:  $[X]$  is the molar concentration in water and  $P_X$  the pressure:  $[X] = K_H P_X$ .



Molar fraction  $F$  of  $\text{CO}_2$  that is in the atmosphere:  $F = N_{\text{CO}_2(g)} / (N_{\text{CO}_2(g)} + N_{\text{CO}_2(aq)})$ , where  $N_{\text{CO}_2(g)}$  is the number of moles in the atmosphere and  $N_{\text{CO}_2(aq)}$  the number of moles of inorganic carbon in the ocean.

Number of moles dissolved inorganic carbon in the ocean:  $N_{\text{CO}_2(aq)} = V_{oc}[\text{CO}_2(aq)]$

### Radiative Transfer:

optical depth:  $\delta = n\sigma L = N\sigma$  Here  $N$  is the "column" in molecules/area,  $n$  the concentration in molecules/volume, and  $\sigma$  the absorption coefficient of the molecule (or more generally, any absorber or scatterer, such as an aerosol).

Fractional Transmission  $T = e^{-\delta/\cos\theta}$  (where  $\delta$  is the optical depth in the vertical, and  $\theta$  the angle from the vertical).

$$F(x + dx) = F(x) - dF_{abs} - dF_{scat}$$

$dF_{abs}$ : absorbed flux, the photon goes into the internal energy of the absorber

$dF_{scat}$ : scattered flux, the photon bounces off in the forward or backward direction

$$dF_{abs} = n\sigma_{abs}F(x)dx$$

$$dF_{scat} = n\sigma_{scat}F(x)dx$$

$$dF = F(x + dx) - F(x) = -n(\sigma_{scat} + \sigma_{abs})F(x)dx$$

$$F(L) = F(0)e^{-n(\sigma_{abs} + \sigma_{scat})L}$$

$$\delta = \ln \frac{F(0)}{F(L)}$$

photolysis rate:  $k = \int_{\lambda} q_x(\lambda)\sigma_x(\lambda)I_{\lambda}d\lambda$ , where  $I_{\lambda}$  is the actinic flux as a function of wavelength.

### Chemical Kinetics:

Standard bimolecular reaction:  $X + Y \rightarrow P + Q$ ,  $d[X]/dt = -k[X][Y]$  where  $[X] = n_x$  and  $k$  is the rate constant. Standard Arrhenius form of reaction constant:  $k = k_0e^{-E_a/RT}$ .  $E_a$  is the activation energy;  $R$  the gas constant;  $T$  the temperature in Kelvin.

Pressure dependent reaction:  $A + B + M \rightarrow AB + M$

$$\text{Low Pressure Limit: } \frac{d[AB]}{dt} = \frac{k_3k_5}{k_4}[A][B][M] = k_o[A][B][M]$$

$$\text{High Pressure Limit: } \frac{d[AB]}{dt} = k_3[A][B] = k_{\infty}[A][B]$$

$$\text{Both Limits: } \frac{d[AB]}{dt} = \frac{k_o[A][B][M]}{1 + \frac{k_o}{k_{\infty}}[M]}$$