



CHANGE IN EQUILIBRIUM COMPOSITION OF DRY AIR WITH HEIGHT

Statement

Evaluate the change in equilibrium composition of dry air with height.

🇪🇸 Estimar la variación de composición del aire con la altura, suponiendo equilibrio.

Solution. Assume that sea-level equilibrium is at $T_0=288$ K, $p_0=100$ kPa, $x_1=0.78$, $x_2=0.21$ and $x_3=0.01$, where 1 refers to nitrogen, 2 to oxygen and 3 to argon. The question is to evaluate dx_i/dz by knowing that at equilibrium $dT/dz=0$, $d\bar{v}/dz=0$ and $d(\mu_i+M_i gz)/dz=0$, or:

$$\frac{d\mu_i}{dz} + M_i g = 0$$

Substituting the above equilibrium conditions on the Gibbs-Duhem equation $0=SdT-Vdp+\sum n_i d\mu_i$ one gets the hydrostatic equation:

$$0 = -Vdp - \sum n_i M_i g dz = -Vdp - n \sum x_i M_i g dz = -Vdp - n M_m g dz = -Vdp - mg dz \Rightarrow \frac{dp}{dz} = -\rho g$$

where M_m is the molar mass of the mixture, and $\rho=m/V$. For each of the species:

$$0 = \frac{d\mu_i(T, p, x_i)}{dz} + M_i g = \frac{\partial \mu_i}{\partial p} \frac{dp}{dz} + \frac{\partial \mu_i}{\partial x_i} \frac{dx_i}{dz} + M_i g$$

and, recalling the dependence of the chemical potential with pressure and composition, for ideal mixtures:

$$\frac{\partial \mu_i}{\partial p} = v_i \quad \text{and} \quad \frac{\partial \mu_i}{\partial x_i} = \frac{R_u T_0}{x_i}$$

one gets:

$$0 = v_i \frac{dp}{dz} + \frac{R_u T_0}{x_i} \frac{dx_i}{dz} + M_i g = -v_i \rho_m g + \frac{R_u T_0}{x_i} \frac{dx_i}{dz} + M_i g \stackrel{\text{IGM}}{=} -M_m g + \frac{R_u T_0}{x_i} \frac{dx_i}{dz} + M_i g$$

that can be easily integrated in the limiting cases of an ideal gas mixture (IGM) and an ideal liquid mixture (ILM).

For a liquid mixture:

$$0 = -\frac{M_i}{\rho_i} \rho_m g + \frac{R_u T_0}{x_i} \frac{dx_i}{dz} + M_i g \rightarrow \frac{d \ln x_i}{dz} = \frac{M_i g}{R_u T_0} \left(\frac{\rho_m}{\rho_i} - 1 \right) \rightarrow \frac{x_i}{x_{i0}} = \exp \left[\frac{M_i g z}{R_u T_0} \left(\frac{\rho_m}{\rho_i} - 1 \right) \right]$$

For a gas mixture:

$$0 = -M_m g + \frac{R_u T_0}{x_i} \frac{dx_i}{dz} + M_i g \rightarrow \frac{d \ln x_i}{dz} = \frac{M_i g}{R_u T_0} \left(\frac{M_m}{M_i} - 1 \right) \rightarrow \frac{x_i}{x_{i0}} = \exp \left[\frac{M_i g z}{R_u T_0} \left(\frac{M_m}{M_i} - 1 \right) \right]$$

For the numerical computation, taking the standard troposphere ($z-z_0=11$ km), for the composition of the dry air considered, with $R_u=8.3$ J/(mol·K), $T_0=288$ K, $M_m=0.029$ kg/mol and $g=9.8$ m/s², one gets:

$$x_{N_2,11km} = 0.78 \exp \left[\frac{0.028 \cdot 9.8 \cdot 10000}{8.3 \cdot 288} \left(\frac{0.029}{0.028} - 1 \right) \right] = 0.81$$

$$x_{O_2,11km} = 0.21 \exp \left[\frac{0.032 \cdot 9.8 \cdot 10000}{8.3 \cdot 288} \left(\frac{0.029}{0.032} - 1 \right) \right] = 0.186$$

$$x_{Ar,11km} = 0.01 \exp \left[\frac{0.040 \cdot 9.8 \cdot 10000}{8.3 \cdot 288} \left(\frac{0.029}{0.040} - 1 \right) \right] = 0.006$$

i.e. the lighter component, nitrogen, increases from 78% at sea level to 81% at 11 km high, oxygen decreases from 21% at sea level to 19% at 11 km, and argon fraction nearly halves.

Comments. We assumed the atmosphere was in equilibrium and it is not so in practice, because it is not isolated; it is really permanently subjected to a bottom heating due to sun radiation absorption at the surface, that causes permanent temperature gradients and convective currents and instabilities, all tending to decrease the small concentration gradient found at equilibrium.

Stratification in a gas mixture can always be neglected at equilibrium in engineering problems. The first to realise that was Berthollet (~1800) who made the experiment of letting H₂ and CO₂ from two gas bottles at room temperature and pressure, mix within a long narrow vertical tube (H₂ up, CO₂ down), finding a 50/50 volumetric fraction in the tube (by sampling and CO₂ absorption) after some days.

Another way to compute the segregation in a gas mixture is by means of the following partial-pressure artifice: first consider two separated columns, 11 km high, one of oxygen and the other of nitrogen; if they have the same pressure at sea-level, at height z the O₂-column would have a smaller pressure (e.g. 24 kPa at 11 km for an isothermal column) than the N₂-column (28 kPa), so that if the two columns were proportionally joined and the total pressure were the sum (e.g. 21%·24+79%·28=27 kPa), the partial pressure would give the result wanted: 21%·24/(21%·24+79%·28)=18 kPa, i.e. 18% O₂ at 11 km.

Similarly to the atmospheric segregation analysed above, ocean salinity should have a gradient at equilibrium such that if the mass fraction of NaCl is 3.5% at sea-level, at the deepest trench in the ocean it would be $y=y_0\exp(-M_i g z(\rho_m/\rho_i-1)/(R_u T))=3.5\cdot\exp(-0.056\cdot 9.8\cdot 11000(1025/1500-1)/(8.3\cdot 288))=8\%$, were a constant density of sea-water 1025 kg/m^3 , and a representative density for NaCl in the liquid state (1500 kg/m^3 for molten NaCl) have been taken. Again, as for the general wind circulation, salinity is very homogeneous in the oceans, particularly below surface waters, because of the permanent ocean currents that continuously mix surface waters with deep waters (although ocean currents are slower than atmospheric currents).

[Back](#)