Workshop -3d

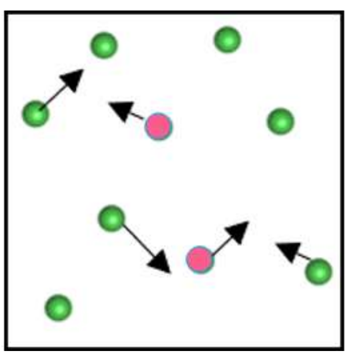
Physical Chemistry II

Exercises and Homework Set 5

Conceptional Review

- **i.** Discuss meaning of probabilistic (fractional) population of states, cells in phase space, transition probabilities, mass flux
- **ii.** General validity of classical Master Equation, quantum modifications.
- **iii.** Ergodic theorem
- **iv.** Biased and unbiased random walk, probability distribution in displacement, mean and variance, reflection and absorption at walls.
- **v.** Relation between drift and diffusion, diffusion equation
- **vi.** Reduction to Fick's diffusion laws.
- **vii.** Normal distribution, error and gamma functions.

1. Molecular Collisions in Air



Consider the motion of oxygen and nitrogen molecules in air (78% $\boldsymbol{N}_2$, 21% $\boldsymbol{O}_2$, density $\rho = 1.204$ kg/m^3) at normal pressure (p=*1*atm=*101.325* kPa) and temperature (*25*^{0}C). Approximate air as an ideal gas mixture. The molecular motion is dominated by collisions between oxygen and nitrogen molecules. The mean geometric cross section for collisions between these molecules is $\sigma \approx 0.42$ nm^2.

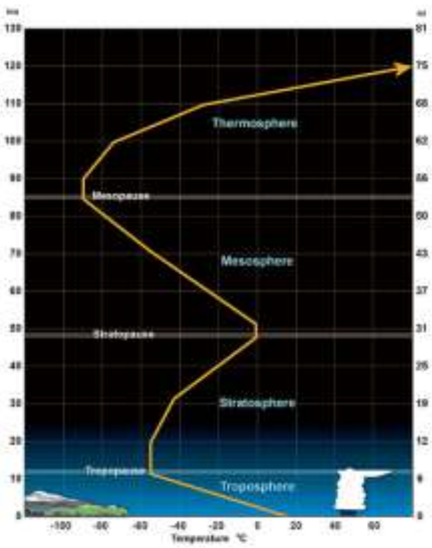
a) Calculate the numbers of oxygen and nitrogen molecules in a volume of $\boldsymbol{V} = 1$cm^3 of air.

b) Calculate the mean speeds $\langle u_O(T)\rangle$ and $\langle u_N(T)\rangle$ of oxygen and nitrogen molecules, respectively, in units of m/s (and km/hr).

c) Calculate the number of collisions between oxygen and nitrogen molecules within the volume of 1cm^3 air per second.

d) Calculate the mean free path of oxygen molecules in air.

2. Thermal Speed Distributions



The speed that a body of any mass must have to escape from Earth is $u = 1.07 \cdot 10^4\ m/s$. Since the temperatures of the upper atmosphere are quite moderate, air molecules exceed this value in the tail of the thermal speed distribution and may escape into space.

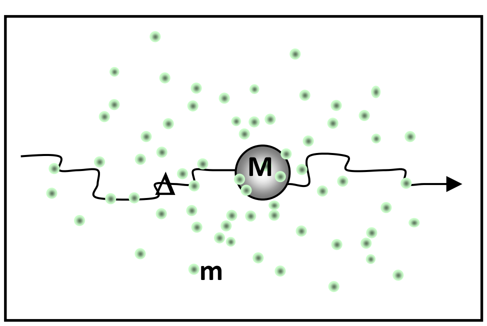
a) Derive an expression for the fraction of the atmospheric gas molecules that would have sufficient speeds to escape at a temperature of *T=293K*. (**Math Hint:** Gaussian integral with finite integration limits can be expressed in terms of the Error or Gamma functions, which are available in MS-Excel)

b) Calculate the fraction of the upper atmosphere hydrogen supply with speeds above the escape velocity.

Is Earth likely to lose a higher fraction of its atmospheric hydrogen or a higher fraction of its oxygen at altitude?

($m(H_2) = 3.3 \cdot 10^{-27} kg;\quad m(O_2) = 5.3 \cdot 10^{-26} kg$)

3. Random Walk and Brownian Motion



Thermal motion of small (mass ***m***) particles of an invisible medium at some temperature ***T*** can be made visible by their effects on the random motion of a visible, larger and heavier ($\boldsymbol{M} \gg \boldsymbol{m}$) "Brownian" test particle injected into the medium with some low initial velocity $\boldsymbol{u}_M$. In an experiment, a series of individual displacements $\Delta \boldsymbol{x_i}$ and $\Delta \boldsymbol{y_i}$ are measured of a Brownian polystyrene particle ($\boldsymbol{M=6 \cdot 10^{-13} g}$) relative to the starting point $\{x_i=0, y_i=0\}$ as functions of time $\boldsymbol{t}$.

a) Which observables can be used to determine the frictional (viscous) drag force on the Brownian particle and the temperature of the medium?

b) Determine the particle diffusivity D_M from the experimental data of mean-square displacement $\langle R_i^2(t) \rangle = \langle x_i^2(t) \rangle + \langle y_i^2(t) \rangle$ vs. time. The data show a linear dependence with a slope of $\boldsymbol{s}$ = *1.8* μm²/s.
(Modified after Nakroshis et al., 2002)

4. <u>Diffusion of Solids in Solids</u>

The diffusion coefficient for carbon in α-*Fe* is $D = 2.9 \cdot 10^{-8} cm^2 s^{-1}$ $(T = 773K)$.

Consider an exposure time of *t* = *1 year* of an α-*Fe* structure to carbon.

a) Define an observable that would be a good measure for the (average) progress of diffusion of a solute substance injected into a solid solvent.

b) How far has carbon diffused in 1 year?