Duration : 2 h 30. The use of a calculator or calculating device is forbidden. Any affirmation must be justified.

I - Diffusion of a perfume

After initially applying perfume locally on the skin in a surface $2x_0 \times L$, we model here 1D diffusion of perfume molecules in air. Let n(x,t) be the number of perfume molecules per volume of air. Due to slow evaporation the deposit of perfume liberates perfume molecules within the air on top of the $2x_0 \times L$ surface. We note α the constant number of perfume molecules added per unit of volume and per unit of time within the air layer of $-x_0 \ge x \le x_0$.

We note D the diffusion coefficient of perfume in air, and $\vec{j}_N(x,t)$ the diffusion flux density. We assume that the plane $(O, \vec{e_y}, \vec{e_z})$ is Π^+ , that is plane of symmetry, for n and for \vec{j}_N .



Q1. Define Fick's law, then justify that $\overrightarrow{j_N}(x,t) = j_N(x,t)\overrightarrow{e_x}$ with $j_N(x,t) = \overrightarrow{j_N}(x,t).\overrightarrow{e_x}$.

Q2. Establish rigorously the material balance for a layer of air between x and x + dx between t and t + dt, first within $x \in [-x_0, x_0]$, then for $x \in \mathbb{R} \setminus [-x_0, x_0]$.

We now study the diffusion in steady-state.

Q3. Establish the expression of n(x), with 4 unknowns that we leave undetermined for now.

We note $n(0) = n_0$, and in $x = \pm x_0$ there is no membrane that could constrain molecule movement.

Q4. State the boundary conditions in x = 0 and $x = x_0$, to demonstrate rigorously the following :

$$\begin{cases} \text{if } x \in [0, x_0] \quad n(x) = n_0 - \frac{\alpha}{2D}x^2 \\ \text{else if } x \ge x_0 \quad n(x) = n_0 + \frac{\alpha}{2D}x_0^2 - \frac{\alpha x_0}{D}x \end{cases}$$

A typical bottle of perfume contains 50 mL of liquid perfume of molar mass $M \simeq 100$ g.mol⁻¹ and volumetric mass $\mu \simeq 10^3$ kg.m⁻³. Such a bottle lasts about 6 months, for 2 sprays a day, each spray lasting around 5 hours before completely evaporating.

Q5. Establish an order of magnitude for α using the given data.

The diffusion coefficient of perfume within air is $D \simeq 3 \times 10^{-5} \text{ m}^2.\text{s}^{-1}$.

Q6. Estimate the time Δt for perfume molecules to diffuse over 1 meter of air. Relate your result to everyday life observations, and to other physical phenomenons.

(33% of the points)

II - Scuba diving accident : growth of gas bubbles

The 3 subpart of this problem are independent.

When scuba diving, the body is exposed to increasing hydrostatic pressure as depth increases. At higher pressures, more gases dissolve within the living tissues. If a diver then reaches the surface very quickly, gas trapped within the tissues does not have time to diffuse back to the blood and lungs, and instead grows into gas bubbles that can become mortal.

Throughout this study, we suppose that at equilibrium the concentration $c_{N_2, eq}$ (in mol/L) of dissolved N₂ within a living tissue is proportional to the **partial** pressure P_{N_2} in N₂ surrounding this tissue according to Henry's law : $c_{N_2, eq} = H \times P_{N_2}$ with $H = 6 \times 10^{-4} \text{ mol.L}^{-1}$.

II.1 First estimation of the danger

Q7. Recall the approximate value of the molar fraction of N_2 in air, then deduce the approximate value of $c_{N_2, eq}(z=0)$ for atmospheric pressure $P_0 = P(z=0)$.

Q8. Recall without any demonstration the hydrostatic pressure profile P(z) within water. Determine the approximate value of $c_{N_2, eq}(z_0)$ with $z_0 = 30$ m.

We imagine that the diver, initially at equilibrium at $z_0^{=30}$ m of depth, suddenly emerges at z = 0. The total volume of blood of a human being is about V = 5 L.

Q9. Determine the amount (in moles) of N_2 gas that appears within the diver's blood if it instantaneously reaches its new equilibrium. Using ideal gas law, convert this amount of N_2 gas into a volume of gas at atmospheric pressure, is this volume enough to obstruct a blood vessel?

II.2 Avoid the accident : the slow diffusion of dinitrogen in living tissues

Usually gas bubbles do not emerge in the blood, which circulates very often through the lungs and thus adapts quickly its concentration with the pressure P(z) within the lungs. Therefore we suppose that in blood for each depth z the concentration in N₂ is the one at equilibrium stated by Henry's law : $c_{N_2, eq} = 5 \times 10^{-4}$ mol/L.

blood

cartilage

blood

However, in tissues such as cartilage, diffusion limits the transport of N_2 : it takes time for it to diffuse and reach new equilibrium. Note that N_2 is **not** produced nor consumed by cartilage or any living tissue. We call n(x, t) the number of gas N_2 molecules per m³, and name D the diffusion coefficient of N_2 in cartilage.

Q10. By continuity of n(x) in 0 and L, determine the numerical values of n(0) and n(L).

Q11. Without any demonstration, express the differential equation that n(x, t) follows here for $x \in [0, L]$.

We look for stationary solutions for n(x,t). The plane at $x = \frac{L}{2}$ is Π^+ (a symmetry plane) for both n(x,t) and \vec{j}_{N_2} .

Q12. Demonstrate rigorously that n(x,t) can be written as :

 $n(x,t) = n(0) + Ae^{-q_n^2 Dt} \sin(q_m x)$ with $q_m = \frac{m\pi}{L}$ for $m \in \mathbb{N}$ and A an unknown.

Q13. Determine the only value for m that makes sense physically, and justify why by representing graphically n(x,t) for different m.

At t = 0, the maximum of concentration in N₂ within the cartilage $c_{N_2, eq, z=z_0} = 2 \times 10^{-3} \text{ mol/L}$. The diffusion coefficient of N₂ in cartilage is $D = 2 \times 10^{-9} \text{ m}^2 \text{.s}^{-1}$ and L = 1 cm.



(67% of the points)

 P_0

Q14. Determine the numerical value of A, then define a characteristic time τ for the decay of this excess of concentration in N₂ within cartilage : how long should a diver typically take to reach the surface after diving at 30 meters?

II.3 Growth of dinitrogen bubbles in living tissues

We study an isolated bubble of pressure P_{0N_2} and radius R(t). The evolution of the radius R(t) of the N₂ bubble is slow enough for the diffusion of N₂ in the liquid to be in steady-state. n is the number of dissolved molecules of N₂ per m³ within the living tissue(\sim water) $n(r) \xrightarrow[r\to\infty]{} n_{\infty}$. D is the diffusion coefficient of the gas in the liquid and V_n the molar volume of the gas, **supposed to be constant**. To study R(t) we neglect surface tension and give the following law : \circ Henry's law : $n(R) = HP_{0N_2}$ with $H = 3, 6 \times 10^{22} \text{ kg}^{-1}.\text{s}^2.\text{m}^{-2}$

In spherical coordinates for a scalar field n(r) the gradient and Laplacian are written as such :

$$\overrightarrow{\text{grad}} c = \frac{\partial c}{\partial r} \overrightarrow{e_r} \qquad \qquad \Delta c = \frac{1}{r} \frac{\partial^2}{\partial r^2} (rc)$$

Q15. Determine n(r) using r, R, n(R) and n_{∞} .

Q16. Using Fick's law, determine the volume variation rate \dot{V} of the bubble per unit of time.

Q17. Show that along these assumptions the bubble's radius follows :

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{HDV_n P_{0N_2}}{R(t)} \left(\frac{n_\infty}{HP_{0N_2}} - 1\right)$$

Here $n_{\infty} = 1.1 \times 10^{27}$, T = 310 K, $D = 2 \times 10^{-9}$ m².s⁻¹, $R_{ig} = 8.3$ J.K⁻¹.mol⁻¹ and $P_{0N_2} = 0.8$ bar.

Q18. Demonstrate that the bubble will indeed grow, then define and determine the value of the duration Δt for it to grow to $R_0 = 1$ mm. Comment your result in regards of previous results for diffusion of dissolved N₂ in cartilage.

The diver suddenly reached the surface : the concentration of dissolved N_2 initially remained the one at equilibrium for $z = z_0$ (before the diffusion of the II.2 significantly occurs), but the partial pressure P_{0N_2} in N_2 dropped causing this rapid bubble growth.



Written exam n°P, elements of correction: Q1. Fick's law states that $\overline{y_N} = -D \overrightarrow{P}n$ Since n = n(x, t), $\overline{\nabla}n = \frac{\partial n}{\partial x} \overline{e_x} + \frac{\partial n}{\partial y} \overline{e_y} + \frac{\partial n}{\partial z} \overline{e_z}^2$ Q2. Let us count d²N d²N = dN(t+dr) - dN(t) the variation of the number hill. of perfune molecules >c >c+d>c hetween x and x + dx between instants t and t+ dt. $-3d^2N = dN(t+dt) - dN(t) = hLdsc[n(x+dx,t+dt)-n(x+dx,t)]$ -> d²N = dt x x x Lhdsc + dt ff jn d Sin $= \alpha Lh dx dt + dt \int JN \cdot dS_{in, tar} + dt \int JN (x, t \cdot d\frac{t}{2}) \cdot dS_{i} + dt \int JN (x + dx, x) + dt \int JN ($ = $Lh dx dt \left[x - \frac{d j N}{d s c} \left(s + d \frac{t}{2} \right) \right]$ Hence $\frac{\partial n}{\partial t} (x + \frac{\partial x}{2}, t) = \alpha - \frac{\partial j N}{\partial s c} (x, t + \frac{\partial t}{2})$ Since $\frac{dx - sO}{dt - sO} = \left| \frac{\frac{dx}{2} \frac{\partial^2 n}{\partial x \partial t} (x, t)}{\left| \frac{\partial n}{\partial t} (x, t) \right|} \right| \ll 1$ and $\left| \frac{\frac{dt}{2} \frac{\partial^2 j N}{\partial x \partial t} (x, t)}{\left| \frac{\partial n}{\partial x} (x, t) \right|} \ll 1$ How $\frac{\partial n}{\partial t} + \frac{d j N}{d j c} = x$

For $x \in \mathbb{R} \setminus [-x_0, x_0] \quad x = 0$ hence $\frac{\partial n}{\partial t} + \frac{\partial j v}{\partial x} = 0$

Q3. The diffusion equation is lusing
Fick's law + material balance):
$x \in [-x_0; x_0]$ $x \in \mathbb{R} \setminus [-x_0; x_0]$
$\frac{\partial n}{\partial t} - D \frac{\partial^2 n}{\partial x^2} = \alpha \qquad \qquad$
Q4. By symmetry $(x=0,t)=\vec{o}$ Vt hence $\vec{1}$
$K_{\lambda} = 0$. $K_{2} = n(0)$. $n(+x) = n(-x)$ $\forall x \in \mathbb{R} = > \begin{cases} K_{4} = K_{6} \\ K_{3} = -K_{5} \end{cases}$
Material balance in $x = \pm x_0$ implies $j_N(x_0) = j_N(x_0^+)$ and $j_N(-x_0^-) = j_N(-x_0^+)$ $-\alpha = K_s = -K_3$ $K_3 = -\alpha = D^0$
Without membrane n is continuous
hence $\int n(0) - \frac{\alpha x_0}{z_0} = -\frac{\alpha x_0}{0} + K_4$

$$\begin{cases} 2D \\ n(0) - \frac{\alpha x_0^2}{2D} = -\frac{\alpha x_0^2}{D} + K_6 \end{cases}$$

$$K_{4} = n(0) + \frac{\alpha x_{0}^{2}}{20}$$



Q7. $T \sim \frac{L^2}{D} \sim \frac{1}{3 \times 10^{-5}} = 3 \times 10^4 \text{ s} \simeq 8 \text{ h or so.}$ Convection obviously dominates at these scales as far as the flow is free. Q8. Air contains a mober fraction of Nz of around 0,8 = 80%. Since $P_0 = 1 \text{ bar}$, $P_{N_2}(z=0) = 0.7 \text{ bar}$ and $C_{N_{2},eq}(z=0) = 4,8 \times 10^{-4} mol/L$ Q9. $P(z) = P_0 + \mu g z$ and $C_{N_2, eq}(z_0) = HP_{N_2}(z_0)$ and $\gamma g z_0 = 3 \times 10^5 P_a = 3 bar that is$ $P(z_0) = 4$ bar and $P_{N_2}(z_0) = 3.2$ bar hence $C_{N_2,eq}(z_0) = -19, 2 \times 10^{-4} \text{ mol}/L = 2 \times 10^{-3} \text{ mol}/L$ Q10. Initially at eq. CNZ, eq (20) = 2mmol/L within the blood. The new equilibrium requires (N2, eq (0) = 0, Smmol/L, that is n=7,5×10⁻³ mol of Nz are liberated. That is a volume $V = \frac{nRT}{P} = \frac{7,5\times10^{-3}\times8\times310}{10^5}$ $V = 15 \times 10^{-5} \text{ m}^3 = 0,15 \text{ L}$, that is about the volume (in gas) of a glass of water. Within a blood vessel of radius R = 3mmthat is a length $L = \frac{V}{\Pi R^2} = \frac{1.5 \times 10^{-4}}{3 \times 10^{-5}} = 5$ meters

long of bubble ! needles to say that this
is far from neglectable for the organism.
Q 11. The concentration of Nz in blood is

$$(N_{L,eq} = 5 \times 10^{-4} \text{ mol}/L$$
, that is $n(0) = n(L) = CN_{2,ea}NA$
 $= 5 \times 10^{-4} \text{ mol}/L$, that is $n(0) = n(L) = CN_{2,ea}NA$
 $n(0) = n(L) = 3 \times 10^{23} \text{ m}^{-3}$
Q 12. $\frac{\partial n}{\partial t} = 0 \frac{\lambda^2 n}{\partial x^2}$
Q 13. stationnary solutions are such that
 $n(x,t) = f(x_0) \times g(t)$ hence $\left[\frac{f'}{f}\right](t) = D\left[\frac{g''}{g}\right](t) = A$
with A a constant : $\int f' = Af$
 $g'' = \frac{A}{D}g$
 $f = foe$ and :
 $A > O$ $g(k) = x e^{-\int D^{k} + \beta e^{-\int D^{k} x} will satisfy$
 $g(\frac{L}{L} - x) = g(\frac{L}{L} + x)$ only for $(x, \beta) = (0, 0)$
 $A = O$ same .
Hence $A = O$ $g(k) = x \cos(\sqrt{\frac{A}{D}} x + 4)$

$$\begin{aligned} xnd \quad g(\frac{L}{2}-x) &= g(\frac{L}{2}+x) = y \\ \cos(\sqrt{-\frac{A}{D}}\frac{L}{2}+y)\cos x + \sin(\sqrt{-\frac{A}{D}}\frac{L}{2}+y)\sin x = \cos(\sqrt{-\frac{A}{D}}\frac{L}{2}+y)\cos x \\ &- \sin(\sqrt{-\frac{A}{D}}\frac{L}{2}+y)\sin x \\ = y \quad \sin(\sqrt{-\frac{A}{D}}\frac{L}{2}+y) = 0 \quad = y \quad y_{k} = k\pi - \sqrt{-\frac{A}{D}}\frac{L}{2} \\ &\quad k \in \mathbb{N} \end{aligned}$$

How
$$g(x) = \alpha (-1)^{k} \cos \left(\sqrt{\frac{A}{D}}(x - \frac{L}{2})\right)$$
.
Ac O thus $f(t) \rightarrow O$ yet $n(x,t) \rightarrow no$,
to the surrounding blood. $n(x,t)$
satisfying boundary condition here is the
superposition of no the uniform prefile in
stendy state + the stationary function that
one builds here: $n(x,t) = no + f_{0} e^{-At} \alpha (-1)^{k} \cos \left(\sqrt{\frac{A}{D}}(c, \frac{L}{2})\right)$
and $\binom{n(o,t) = n(0)}{(n(L,t) = n(L) = n(0)}$ impose:
 $\cos \left(\sqrt{\frac{A}{D}}\frac{L}{2}\right) = O$ thus $\sqrt{-\frac{A}{D}}\frac{L}{2} = \frac{\pi}{L} + \rho \pi$
hence $g(x) = x(-1)^{k} \cos \left(\left(\frac{\pi}{L} + 2\frac{\rho\pi}{L}\right)(x - \frac{L}{2})\right)$
 $= \alpha(-1)^{k} \sin \left(\frac{\pi \alpha}{L} + 2\frac{\pi \rho \alpha}{L}\right)$
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 $= \alpha(-1)^{k} \sin \left(\frac{\pi \alpha}{L} + 2\frac{\pi \rho \alpha}{L}\right)$



=> A?O and m = O since 9mx must be smaller than T Vx E [O; L] yer qmL ≤ TT => TT (1+2m) ≤ TT => M ≤ 0 Q15. $C_{N_{2},eq,z=20} = 2 \text{ mol} \cdot m^{-3}$ A + n(0) = MA× Cz, eq, 2=20 $A = (12-3) \times 10^{23} = 9 \times 10^{23} \text{ m}^{-3}$ The exponential decay suggests to define $C = \frac{L^2}{\pi^2 D} = \frac{25 \times 10^{-6}}{9 \times 2 \times 10^{-9}} \simeq 1.4 \times 10^3 = 4$ that is about 23 minutes : clearly it is necessary to be autionous. Q16. Without source term the diffusion

Q 16. Without source Vern the diffusion equation states for steady-state: n(r) and dr = 0 hence $r^2 \frac{dn}{dr} = \alpha$ thus $n = -\frac{\alpha}{r} + \beta$ $r = n \infty$ and $n(R) = -\frac{\alpha}{R} + n \infty$ hence $n(r) = -\frac{n(R) - n \infty}{r} R + n \infty$ Q 17. Using V_n , we can compute Vusing the quantity of N_2 diffusing

within the bubble per unit of time, that we all
$$\dot{N}$$

 $\dot{N} = \iint_{J} \vec{J}(R) \cdot d\vec{J}_{in}$
pointing inward, that is
 $d\vec{S}_{in} = -R^{2} \sin \Theta d\theta dP e^{-3}$
and $\vec{J} = D^{n} \frac{(R) - n\omega}{R} e^{-3}$ hence
 $\dot{N} = 4\pi\pi D (n\omega - n(R))R$ and $\dot{V} = \frac{4\pi V_{n} D(n\omega - n(e))R}{N/n}$
Qub. Geometrically $dt \dot{V} = V(t + dt) - V(t)$
 $= \frac{4\pi V_{n} R^{2}(t + dt) - R^{3}(t)$
Hence $\frac{dR}{dT} = \frac{V_{n} D}{W_{n}R} (n\omega - n(R))$
Hence $\frac{dR}{dT} = \frac{V_{n} D}{W_{n}R} (n\omega - n(R))$
Hence $n\omega = 1.4 \times 10^{23} \text{ m}^{-3}$
 $n(R) = 8 \times 10^{4} \times 3.6 \times 10^{47} = 3 \times 10^{22} \text{ m}^{-3}$
 $n\omega - n(R) > 0$ indeed.
 $R_{0}^{2} = \frac{2V_{n} D}{V_{A}} (n\omega - H_{0}N_{c}) \Delta t$
 $\Delta t = \frac{R_{0}^{2} N_{A}}{2 \sqrt{n} D(n\omega - H_{0}N_{c})} = \frac{R_{0}^{4} M_{n}^{4} P_{0}N_{c}}{2 R_{3}^{4} T (n\omega - H_{0}N_{c})} (n^{-2} - 1)^{2} S$

That is 10 millise conds only, dearly a let faster than the tens of minutes required to get rid of it via blood flow redirecting the excess Nz towards the longs! In reality such growth reglects the {mechanical constraints of {diffusion living tissue for which bubbles rather significantly grow in a few tens of seconds.