Problem III.5 ... drunken chamber

10 points

A closed Petri dish with a radius of 2.0 cm *containing* 6.0 ml *of ethanol is placed into a high-vacuum chamber with a volume of* 30 l*. The dish is then opened, exposing the surface of the ethanol. How much will the ethanol level drop after a long period, and how will the height of the ethanol change over time? The temperature of the chamber and ethanol is* 20 °C.

The pressure was way too high for Jarda.

We denote the saturated ethanol vapor pressure as p_v. For a temperature of 20 °C, it is $p_\mathrm{v} \doteq 5.95\,\mathrm{kPa}$. The pressure above a large ethanol surface stabilizes at this value because the evaporation rate equals the rate at which particles from the gas phase strike the surface.

The number of particles striking a unit area per unit time can be derived as

$$\varphi = \frac{1}{4} n v_\mathrm{a} = \frac{p}{\sqrt{2\pi m k\,T}}\,,$$

where $n = p/kT$ is the particle concentration in the gas phase, $v_\mathrm{a} = \sqrt{8kT/(\pi m)}$ is the mean arithmetic speed of the gas particles, m is their mass, k is the Boltzmann constant, and T is the temperature.

In deriving this relation, we start from the Maxwell–Boltzmann distribution, which gives the number of particles with a given speed as

$$f(v) = \frac{4}{\sqrt{\pi}} \frac{v^2}{c^3} \exp\left(-\frac{v^2}{c^2}\right)\,,$$

where we introduce $c^2 = 2kT/m$. During a time τ, particles that are at a distance $v\tau$, have the appropriate speed, and have the appropriate direction strike a surface element of area $\mathrm{d}S$.

Consider particles at a distance r from the surface element and with a polar angle θ. These particles can move in all directions; thus, only a fraction is directed toward our surface element. We express this fraction as the projection of the area $\mathrm{d}S \cos\theta$ to the total sphere area $4\pi r^2$.

The volume in the given direction from which the particles arrive can be written as $\mathrm{d}V = r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}r$, where we also introduce the azimuthal angle. The number of particles with a given speed in the given direction and volume is therefore

$$\mathrm{d}N = n\,\mathrm{d}V\ \frac{\mathrm{d}S\ \cos\theta}{4\pi r^2} f(v)\,\mathrm{d}v\,.$$

We must now integrate over all angles and distances. The angular part is straightforward:

$$\int_0^{2\pi}\int_0^{\pi} \sin\theta\cos\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi = \int_0^{2\pi}\mathrm{d}\varphi \frac{1}{2}\int_0^{\pi}\sin 2\theta\,\mathrm{d}\theta = \pi\,.$$

The next part is the integration over distance:

$$\int_0^{v\tau} \frac{1}{4\pi r^2} r^2\,\mathrm{d}r = \frac{v\tau}{4\pi}\,.$$

Finally, we must integrate over the speed distribution (to determine how many particles have the appropriate speed), which yields

$$\int_0^{\infty} v\ \tau f(v)\,\mathrm{d}v\ = \tau v_\mathrm{a}\,,$$

where the mean speed v_a is introduced above. To obtain the particle flux, we divide the number of particles N by the time τ, which poses no difficulty:

$$\Phi = \frac{N}{\tau} = \frac{1}{\tau} n\pi \frac{\tau}{4\pi} v_\mathrm{a} = \frac{1}{4} n v_\mathrm{a}\,.$$

Thus, we have outlined the derivation of the number of particles striking a unit area per unit time under the assumption that the particles do not collide with one another.

Let us now continue with our problem.

If the pressure above the surface p equals the saturated vapor pressure p_v, the particle arrival rate φ equals the evaporation rate R. We can therefore find this evaporation rate as

$$R = \frac{p_\mathrm{v}}{\sqrt{2\pi mk\,T}}\,.$$

This value does not depend on the pressure above the surface; it is determined solely by the temperature and the properties of the substance. From a dish placed in the apparatus, the amount that evaporates is therefore

$$\Phi_\mathrm{out} = R\pi r^2 = \pi r^2 \frac{p_\mathrm{v}}{\sqrt{2\pi mk\,T}}\,,$$

where r is the dish radius. However, the incoming flux is

$$\Phi_\mathrm{in} = \pi r^2 \frac{p}{\sqrt{2\pi mk\,T}}\,.$$

At equilibrium, the two fluxes must be equal, $\Phi_\mathrm{in} = \Phi_\mathrm{out}$, from which $p = p_\mathrm{v}$.

From the ideal gas equation of state, we can compute the number of evaporated ethanol particles as

$$N = \frac{p_\mathrm{v} V}{kT}$$

and their total mass as

$$m_\mathrm{v} = M_\mathrm{m} \frac{p_\mathrm{v} V}{RT} \doteq 3.4\,\mathrm{g}\,,$$

where R is the gas constant and $M_\mathrm{m} \doteq 46\,\mathrm{g\cdot mol^{-1}}$ is the molar mass of ethanol. For an ethanol density $\rho \doteq 789\,\mathrm{kg\cdot m^{-3}}$, this corresponds to an evaporated volume

$$V_\mathrm{v} = \frac{m_\mathrm{v}}{\rho} \doteq 4.3\,\mathrm{cm^3}\,.$$

This value is smaller than the initial $V_0 = 6.0\,\mathrm{ml}$, so the ethanol does not evaporate completely. The liquid level decreases by

$$\Delta h = \frac{V_\mathrm{v}}{\pi r^2} \doteq 3.4\,\mathrm{mm}\,.$$

We are now prepared to compute the time dependence of the liquid level in the dish. We know the evaporation rate Φ_out, which we consider constant. In contrast, the condensation rate Φ_in is proportional to the chamber pressure. The change in the number of particles ν in the dish is therefore

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = \Phi_\mathrm{in} - \Phi_\mathrm{out} = \pi r^2 \frac{p - p_\mathrm{v}}{\sqrt{2\pi mk\,T}}\,.$$

However, we must not forget that the total number of particles is conserved:

$$\nu_0 = \nu + N = \nu + \frac{pV}{kT}\,,$$

where ν_0 is the initial number of particles in the dish. Substituting for ν into the differential equation and multiplying by kT/V, we obtain

$$\frac{kT}{V}\cdot\frac{\mathrm{d}}{\mathrm{d}t}\left(\nu_0 - \frac{pV}{kT}\right) = -\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{kT}{V\sqrt{2\pi mk\,T}}\pi r^2\left(p - p_\mathrm{v}\right)\,.$$

We solve this equation by separation of variables and integration:

$$-\frac{\mathrm{d}p}{p - p_\mathrm{v}} = \frac{kT\pi r^2}{V\sqrt{2\pi mk\,T}}\,\mathrm{d}t \quad\Rightarrow\quad p = p_\mathrm{v}\left(1 - \exp\left(-\frac{kT\pi r^2}{V\sqrt{2\pi mk\,T}}t\right)\right)\,,$$

where we choose the integration constant so that the chamber pressure is zero at time $t = 0$.

Now that we know the time evolution of the pressure, we can also determine the time evolution of the particle number:

$$\nu(t) = \nu_0 - \frac{V}{kT}p_\mathrm{v}\left(1 - \exp\left(-\frac{kT\pi r^2}{V\sqrt{2\pi mk\,T}}t\right)\right)\,,$$

which we convert, using the properties of ethanol, to the liquid level height:

$$h(t) = \frac{M_\mathrm{m}\nu(t)}{N_\mathrm{A}\rho\pi r^2} = \frac{V_0}{\pi r^2} - \frac{M_\mathrm{m}V}{RT\rho\pi r^2}p_\mathrm{v}\left(1 - \exp\left(-\frac{kT\pi r^2}{V\sqrt{2\pi mk\,T}}t\right)\right)\,,$$

which is the solution to our problem.

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