Problem IV.S ... heating and explosions 10 points; průměr 5,54; řešilo 48 studentů

1. *Consider a thin-walled glass container of volume $V_1 = 100\,\text{ml}$, the neck of which is a thin and long vertical capillary with internal cross-section $S = 0.20\,\text{cm}^2$, filled with water at temperature $t_1 = 25\,°\text{C}$ up to the bottom of the neck. Now submerge this container in a larger container filled with a volume $V_2 = 2.00\,\text{l}$ of olive oil at a temperature $t_2 = 80\,°\text{C}$. How much will the water in the capillary rise?*

2. *In a closed container with a volume of $11.0\,\text{l}$ there is a weak solution containing sodium hydroxide with $p\text{H} = 12.5$ and a volume of $1.0\,\text{l}$. We burn $100\,\text{mg}$ of powdered carbon in the region above the surface. Determine the pressure value in the container a few seconds after burning out, after half an hour, and after one day. Before the experiment, the vessel contained air of standard composition at standard conditions; similarly, we maintained a standard temperature around the vessel in the laboratory.*

3. *Describe three different ways in which the temperature of stars can be determined. What basic physical principles are they based on, and what do we need to be careful of?*

Dodo remembered highschool chemistry.

Task 1

The first step is determining the temperature of the two liquids in the thermal equilibrium. We will use the calorimetry formula

$$\rho_1 V_1 c_1 t_1 + \rho_2 V_2 c_2 t_2 = (\rho_1 V_1 c_1 + \rho_2 V_2 c_2)\, t_3\,,$$

where $\rho_1 = 0.98\,\text{kg·L}^{-1}$ is the density of water and $\rho_2 = 0.91\,\text{kg·L}^{-1}$ is the density of oil, $c_1 = 4.2\,\text{kJ·kg}^{-1}\text{·K}^{-1}$ is the specific heat capacity of water, $c_2 = 1.97\,\text{kJ·kg}^{-1}\text{·K}^{-1}$ is the specific heat capacity of oil. However, these values depend on temperature. The previous formula also neglects density and heat capacity changes relative to temperature. It is, therefore, only a solution with an accuracy of at most two significant digits. After substituting in the values, we get the temperature $t_3 \doteq 74\,°\text{C}$.

Next, we have to calculate the expansion of the water column. The coefficient of volume expansion for water $\gamma = 2.6 \cdot 10^{-4}\,\text{K}^{-1}$ gives us

$$\Delta V_1 = V_1 \gamma\,(t_3 - t_1) = S\Delta h\,,$$

and after adjustments

$$\Delta h = \frac{V_1 \gamma\,(t_3 - t_1)}{S} = 6.4\,\text{cm}\,.$$

However, the volume of water is not linearly dependent on temperature, so we have to use the exact densities of water at two different temperatures to obtain the correct result: $\rho_1(t_1) = 997\,\text{kg·m}^{-3}$ a $\rho_1(t_3) = 975\,\text{kg·m}^{-3}$. We get

$$\Delta V_1 = V_1 \left(\frac{\rho_1(t_1)}{\rho_1(t_3)} - 1 \right),$$

$$\Delta h = \frac{V_1}{S} \left(\frac{\rho_1(t_1)}{\rho_1(t_3)} - 1 \right) \doteq 11\,\text{cm}\,.$$

The shift of water's surface height in the capillary due to capillary action and temperature-dependent change of surface tension is in the order of millimeters, so we neglect it in our solution.

Task 2

Let's begin by calculating how much of each compound we have in our closed system. If we subtract the volume of the solution from the volume of the container, we get a volume of $10\,l$ of air. At around $100\,kPa$ and $25\,°C$ that equals to the molar volume of $V_m = 24.5\,l$, which corresponds to $n_{vz} \doteq 0.41\,mol$. Air contains 21% of oxygen. Therefore, we have $n_{O_2} = 0.086\,mol$ of oxygen molecules. The question is whether this is sufficient to achieve complete combustion of $m_C = 100\,mg$ of carbon. Using the molar mass of atomic carbon $M_m(C) = 12.0\,g\cdot mol^{-1}$, we get the chemical amount $n_C = 0.008\,33\,mol$. Carbon burns according to the reaction

$$C + O_2 \rightarrow CO_2\,,$$
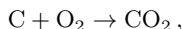
so complete combustion consumes $n_C \ll n_{O_2}$ of oxygen to produce the same amount of carbon dioxide.

In addition, the reaction releases heat of combustion equal to $H = 37.2\,kJ\cdot g^{-1}$, so $Q = mH = 3.72\,kJ$ per one hundred milligrams of carbon. Let's also look at the solution at the bottom of the container. Sodium hydroxide fully dissociates in water to create

$$NaOH \rightarrow Na^+ + OH^-\,,$$

so the concentration of hydroxide anions is pretty much the same as the concentration of sodium hydroxide[1]. We can approximately determine this concentration as

$$c = c_0 10^{pH-14} = 0.032\,mol\cdot l^{-1}\,,$$

where $c_0 = 1\,mol\cdot l^{-1}$. Thus, in total, we have $n_{NaOH} = 0.032\,mol$ in solution (roughly $1.3\,g$). For the sake of rigorousness, we add that there is $m_{H_2O} = 1\,kg/(18.0\,g\cdot mol^{-1}) \doteq 56\,mol$ of water in the container. The carbon dioxide released by burning will slowly be absorbed by this alkaline solution according to the equation

$$CO_2 + OH^- \rightarrow HCO_3^-$$
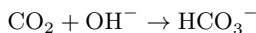
to form a bicarbonate anion. Again, $n_{CO_2} \ll n_{OH^-}$, and the reaction will run until there is no carbon dioxide left.

We can proceed to calculate the pressures. A few seconds after burning out, the amount of gas will be the same as in the beginning, but its temperature will be higher as energy got released. Because of the turbulent flow in the container, we can assume a rapid setting of the thermal equilibrium in the gas. If we consider the specific heat capacity of an ideal diatomic gas at a constant volume $c_V = 5R/2 = 20.8\,J\cdot mol^{-1}\cdot K^{-1}$, the gas will heat up by

$$\Delta T = \frac{Q}{c_V\,n_{vz}} \doteq 440\,K\,.$$

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[1]Indeed, besides the concentration of hydroxide anions, water dissociation also contributes to the concentration of hydroxide ions. However, in our current scenario, this contribution is negligible.

so the pressure increases, as predicted by Charles' law for isochoric processes, to

$$p_1 = p_0 \frac{T_0 + \Delta T}{T_0} \doteq 250 \,\text{kPa} \,.$$

Consequently, the gas in the container cools down to its original ambient temperature, and the pressure gets reduced. Given that the gas amount, temperature, and volume remain constant from the outset, the pressure must also remain unchanged. Therefore, $p_2 = p_0 = 100 \,\text{kPa}$.

Following this, carbon dioxide is gradually absorbed into the solution. Consequently, the gas quantity decreases to $n_C = 0.008\,33 \,\text{mol}$. To describe this process, we combine the gas laws for constant volume and temperature, resulting in the relation

$$\frac{p_3}{p_0} = \frac{n_{\text{vz}} - n_C}{n_{\text{vz}}} \,.$$

As a result, the pressure drops slightly to $p_3 \doteq 98 \,\text{kPa}$.

Task 3

When determining the temperature of cosmic bodies, we encounter one fundamental problem – we cannot touch them and stick a thermometer in them. We have to measure the temperature of stars remotely by using the information contained in the light they emit. In the previous episode of the series, we discussed black-body radiation and the distribution of its radiated energy into different wavelengths. We can easily derive From Planck's law, Wien's displacement law can be derived

$$\lambda_{\max} T = \text{const} \,,$$

which describes how the peak wavelength of the energy curve $\lambda_{\max}$ shifts with temperature T. In simple terms, we can determine the temperature of an object by observing its color. In practice, we achieve this by measuring the object's brightness through two different filters and applying a calibrated relationship between luminance difference and temperature that is widely recognized. The second possibility is to use the integral form of Planck's law – Stefan-Boltzmann law

$$L = 4\pi R^2 \sigma T^4 \,,$$

where L is the star's luminosity, R its radius and T its temperature. To apply this method, we need information about the star's radius, a value typically accessible only in eclipsing binary star systems. Interestingly, this relationship is often employed in reverse to estimate the radius of solitary stars. The problem, however, is that stars are not ideal black bodies. Their spectra contain spectral lines arising in stellar atmospheres[2] A more accurate method is, thus, the so-called Spectral Energy Distribution Modeling, which uses theoretically estimated spectra of stars of different radii, temperatures, masses, and chemical compositions and attempts to find the best match to the energy fluxes measured in various photometric filters from the ultraviolet to the infrared region of the spectrum.

A fundamentally different option is to look directly at the spectral lines. Particles in the atmosphere have thermal velocities according to Maxwell-Boltzmann distribution, causing the

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[2]Furthermore, researchers frequently conduct observations from the Earth's surface, which means that absorption within the Earth's atmosphere affects the measured spectrum. Additionally, interstellar dust along the path between the star and Earth may absorb light.

spectral lines to broaden due to Doppler phenomenon. Many other processes also affect the width of the spectral lines – particle collisions, the intrinsic lifetime of the transition levels, the rotation of the star itself, ... For thermal motion, the most important is the dependence of the broadening $\Delta\lambda$ on the mass of the atom m

$$\Delta\lambda = \sqrt{\frac{8kT\ln 2}{mc^2}}\lambda\,.$$

Therefore, the lines of hydrogen and then helium will be the widest, and the lines of heavier elements will be significantly narrower.

We can also use the intensity of the lines. The depth of the lines[3] depends, among other things, on the occupation of the levels of a given ion and the ionization state of a given nucleus. Let's consider, for example, the lines of helium with an ionization energy 24.6 eV and hydrogen with an ionization energy 13.6 eV. In very hot stars, most of the hydrogen is ionized into protons, resulting in faint hydrogen lines. Additionally, extremely hot stars contain a fraction of ionized helium He$^+$, leading to the appearance of lines in both neutral and ionized helium spectra. As stars cool down, the spectra begin to show lines from easily ionizable elements, and in very cool stars, molecular lines become visible. Conversely, lines from other ions fade as they return to their ground states, making transitions to higher states less likely. The presence of spectral lines in stellar spectra forms the basis of the Harvard classification system. Modern models allow for the calculation of line depths, enabling more accurate temperature determination. For instance, comparing the depths of lines from two different ionization stages of an element like iron can provide a more precise temperature estimate.

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[3]More precisely, we determine the so-called equivalent width by dividing the spectrum by the continuum spectrum and then calculating the area between the line progression and the continuum level 1.