PHY5524
STATISTICAL MECHANICS
Problem Set 2

Due on Monday, February 5, 2018

1.1:
Calculate the work performed by 10grams of oxygen (gas) expanding isothermally at 20°C from 1 to 0.3 atmospheres of pressure. Approximate the gas as ideal and state your answer in Joules (note that 4184Joules corresponds to 1Cal used in US nutrition labels.)

Starting from the expression:

$$W = \int_{V_i}^{V_f} P \mathrm{d}V$$

Since temperature is constant, pressure can be replaced by the familiar expression:

$$P = \frac{nRT}{V}$$

$$\begin{aligned} W &= nRT \int_{V_i}^{V_f} \mathrm{d}V \\ &= nRT \ln\left(\frac{V_f}{V_i}\right) \end{aligned}$$

Where $R = 8.314\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$, $T = 20 + 273.15 = 293.15\mathrm{K}$, and $n = \frac{10}{16 \cdot 2} = 0.3125\mathrm{mol}\ O_2$, $1\mathrm{atm} = 101325\mathrm{Pa}$, $0.3\mathrm{atm} = 30397.5\mathrm{Pa}$.

$$\begin{aligned} W &= (0.3125)(8.314)(293.15) \ln\left(\frac{101325}{30397.5}\right) \\ &\approx \boxed{916.99J} \end{aligned}$$

1.2:
a) What is the heat capacity at constant volume of a (classical) ideal diatomic gas?

First the classicla Maxwell-Boltzmann distribution will be used to find the average velocity of a single particle in an isolated system. The normalization constant must be found:

$$
\begin{aligned}
f(E) &= Ae^{-E/k_BT} \\
&\Rightarrow A\sqrt{\frac{2k_BT}{m}}\int_{-\infty}^{\infty} e^{-\frac{mv^2}{2k_BT}}\sqrt{\frac{m}{2k_BT}}\mathrm{d}v = 1, \quad \left(\mathrm{d}x = \sqrt{\frac{m}{2k_BT}}\mathrm{d}v\right) \\
&= A\sqrt{\frac{2k_BT}{m}}\sqrt{\pi} = 1, \quad \left(\int_{-\infty}^{\infty} e^{-x^2}\mathrm{d}x = \sqrt{pi}\right) \\
A &= \sqrt{\frac{m}{2\pi k_BT}}
\end{aligned}
$$

$$
\therefore \quad f(E) = \sqrt{\frac{m}{2\pi k_BT}}\exp\left[-\frac{mv^2}{2k_BT}\right]
$$

The average velocity can be computed:

$$
\begin{aligned}
\langle v^2\rangle &= \sqrt{\frac{m}{2\pi k_BT}}\int_{-\infty}^{\infty} v^2 e^{-\frac{mv^2}{2k_BT}}\mathrm{d}v \\
&= \sqrt{\frac{m}{2\pi k_BT}}\frac{\sqrt{\pi}}{2}\left(\frac{2k_BT}{m}\right)^{3/2}, \quad \left(\int_{-\infty}^{\infty} x^2 e^{-x^2}\mathrm{d}x = \frac{\sqrt{\pi}}{2}a^{3/2}\right) \\
&= \frac{k_BT}{m}
\end{aligned}
$$

The average kindetic energy in one dimension is therefore KE= $\frac{1}{2}m\left(\frac{k_BT}{m}\right) \rightarrow \frac{1}{2}k_BT$. Each translational degree of freedom is independent, which means the average kinetic energy in three dimensions is $\frac{3}{2}k_BT$ for each direction of velocity, (v_x, v_y, v_z). Extending this analogy to rotational degrees of freedom for the case of a diatomic molecule and by the equipartition theorem of energy, the internal energy is $U = \frac{3}{2}Nk_BT + \frac{2}{2}Nk_BT \rightarrow \frac{5}{2}NK_BT$.

b) Consider a reversible adiabatic process. If the pressure (P) of such an ideal di-atomic gas decreases by a factor of λ, by what factor does the temperature (T) change?

$$
\begin{aligned}
\mathrm{d}U &= \cancel{Q} - P\mathrm{d}V, \quad Q = 0 \\
C_V \mathrm{d}T &= -\cancel{P}\left[\frac{nR\mathrm{d}T - V\mathrm{d}P}{\cancel{P}}\right] \\
\int \frac{\mathrm{d}P}{P} &= \left(\frac{C_V}{nR} + 1\right)\int \frac{\mathrm{d}T}{T} \\
e^{\ln P} &= e^{\left(\frac{C_V}{nR}+1\right)\ln T + c_1} \\
P &= c_2 T^{\frac{C_V}{nR}+1} \\
&= c_2 T^{7/2}, \quad \left(C_V = \frac{5}{2}nR)\right)
\end{aligned}
$$

Therefore if $P \to \lambda P$ then,

$$
T = \left(\frac{\lambda P}{c_2}\right)^{2/7} \quad \text{or } T \propto \lambda^{2/7}
$$

c) Considering a column of such a gas in the gravitational field of Earth close to Earths surface. By mechanically balancing the effects of gravity and pressure changes, find the dependence of $\mathrm{d}P/\mathrm{d}z$ on P and T, where z is the altitude (height). Express your answer in terms of the Earths gravitational acceleration g, molar mass of the gas M, and the gas constant R.

$$
\begin{aligned}
mg\mathrm{d}z &= -V\mathrm{d}P \\
\frac{\mathrm{d}P}{\mathrm{d}z} &= -\frac{mg}{V} \\
&= -\frac{nMg}{V} \\
&= -\frac{P\cancel{V}Mg}{RT\cancel{V}}
\end{aligned}
$$

$$
\therefore \quad \frac{\mathrm{d}P}{\mathrm{d}z} = -\frac{PMg}{RT}
$$

d) Assuming the air changes its pressure and temperature adiabatically, find the rate of change of temperature with the altitude, $\mathrm{d}T/\mathrm{d}z$. Using $R = 8.314\frac{J}{\text{mol } K}$, $g = 9.8m/s^2$, and the molar mass of air $M = 28g/\text{mol}$, express the change of temperature in Kelvin per kilometer. Find the actual data in the literature and compare with your answer. Using the relation from part b:

$$
\begin{aligned}
\frac{\mathrm{d}P}{P} &= \left(\frac{C_V}{nR} + 1\right)\mathrm{d}T = -\frac{Mg\mathrm{d}z}{R} \\
\frac{\mathrm{d}T}{\mathrm{d}z} &= -\left(\frac{C_V}{nR} + 1\right)^{-1}\frac{Mg}{R} \\
&= -\frac{2}{7}\left(\frac{28 \cdot 9.8}{8.314}\right) \\
&\approx -9.43\mathrm{K} \cdot \mathrm{km}^{-1}
\end{aligned}
$$

The dry adiabatic lapse rate (DALR) is $9.8\mathrm{K} \cdot \mathrm{km}^{-1}$ which agrees well with calculated value.