Problem set 4

Due April 11, 2024

1. Using the solution to Problem 1 of Problem set 3, compute the average energy of the mixture of photochlorination products of isobutane at $t = 50°\text{C}$. The energy of 2-chloro-isobutane, $(CH_3)_3CCl$, (E_I) is the origin of the energy scale $(E_I = 0)$.

2. The partition function of a gas consisting of N rigid diatomic molecules at low pressure (so that intermolecular interactions do not need to be considered) and with volume V and absolute temperture T (a canonical ensemble) in the classical limit is expressed as given below

$$Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \left(\frac{Ve}{N}\right)^N \frac{T}{\Theta_r}$$

where m is the mass of a gas molecule, Θ_r is the characteristic rotational temperature of the molecule, \$$k_B$ is the Boltzmann constant, h is the Planck constant, and $e = 2.718\ldots$ is the Euler number.

   (a) Derive the formulas for (i) the energy and (ii) the pressure of the gas.

   Hint: Obtain a formula for $\ln Q$, use the formulas for the logarithms of product, the quotient, and exponential expressions to separate the respective terms of $\ln Q$ that depend only on one variable of state and then use the formulas learned in lecture 4 to compute the respective derivatives of $\ln Q$.

   (b) Compare formula (i) with that for the average energy of an ideal gas from the kinetic theory of gases.

   (c) Based on formula (ii) derive the equation of state (the Clapeyron equation) of an ideal gas.