Physics 201 Day 25

Last time, trying to find:

$$\frac{dT}{dz} = \underbrace{\frac{dT}{dP}}_{?} \; \underbrace{\frac{dP}{dz}}_{-\rho g} \text{ from last time.}$$

"Dry" Atmosphric Lapse Rate

$$\gamma P dV = V dP$$

$$\gamma \frac{P}{dP} = \frac{V}{dV} \quad \text{or} \quad \gamma \frac{dV}{V} = \frac{dP}{P}$$

$$\frac{f+2}{f} = \text{adiabatic exponent} = \frac{C_p}{C_v}$$

$$N k_B T = PV$$

$$\underbrace{N k_B dT}_{n c_v dT} = P dV = \frac{V dP}{\gamma}$$

$$n c_v dT = \frac{V dP}{\gamma}$$

$$\frac{dT}{dP} = \frac{V}{\gamma n c_v} = \frac{V}{n c_p} = \frac{V}{n (\underbrace{f}_{\#\text{ d.o.f.}}+2) \cdot R}$$

$$\frac{dT}{dz} = \left(\frac{\cancel{V}}{n\cancel{m}(f+2)R}\right)\left(-\cancel{\rho}\, g\right) = \frac{-g}{(f+2)R}\cdot\frac{m}{n}\ \left(\frac{kg}{mol}\right)\ \checkmark$$

$\rho \to \frac{m}{V}$

per mol

$$\rho = \frac{m}{V} =$$

mass density ~~per mol~~

$$\frac{dT}{dz} = \frac{-g\cdot m}{(f+2)Rn}$$

g units: $\frac{m}{s^2}$

R units: $\frac{J}{mol\cdot{}^\circ C} = \frac{kg\,\frac{m^2}{s^2}}{mol\cdot{}^\circ C}$

$$\frac{V}{n} = \frac{V}{m}\cdot\frac{m}{n}\ \checkmark$$

$$\frac{dT}{dz} = \frac{-g}{(f+2)R}\left(\frac{mass}{1\,mol}\right) = \frac{-9.8\frac{m}{s^2}\left(29\frac{gram}{mol}\right)}{7R}$$

R: $8.315\ \frac{J}{mol\cdot K}$

$$= -9.8\times10^{-3}\ \frac{{}^\circ C}{m} \approx -10\ \frac{{}^\circ C}{km}$$

monatomic

$f = 3$

diatomic

$N\equiv N = N_2$

$3 + 2 = 5$

u $\quad E_R = \frac{1}{2}I\omega^2$

$$\frac{1}{2}mv^2 = \frac{1}{2}m\left(V_x^2 + V_y^2 + V_z^2\right)$$

microscopic model:

like derivation of ideal gas

micro → in large numbers → macro prediction (average value)

$$\text{Probability} \propto \underbrace{e^{-E/k_B T}}_{\text{Boltzmann Factor, unit-free}}$$

$k_B = 1.38 \times 10^{-23} \frac{J}{K}$

Consider 2 level system:

E_1 and E_2 and no other options.

what is probability of finding system in state 1? State 2?

$P_1 \propto e^{-E_1/k_B T}$ $\quad P_2 \propto e^{-E_2/k_B T}$

Note: $\beta = \frac{1}{k_B T}$

$P_1 = C\, e^{-\beta E_1}$ $\quad P_2 = C\, e^{-\beta E_2}$

$$P_1 + P_2 = 1 = C e^{-\beta E_1} + C e^{-\beta E_2}$$

solve for C

$$C = \frac{1}{\underbrace{e^{-\beta E_1} + e^{-\beta E_2}}_{\text{The Partition Function}}}$$

$$Z = e^{-\beta E_1} + e^{-\beta E_2} + \dots \quad \Big\} \text{ sum over } \underline{\text{all}} \text{ states}$$

$$C = \frac{1}{Z}$$

<u>units</u>: $k_B = 1.38 \times 10^{-23} \ \frac{J}{K}$ ← energy E of <u>one</u> particle

<u>Can</u> do it per mol instead.

$$k_B = 0.00199 \ \frac{\text{kcal}}{\text{mol} \cdot K}$$

$$k_B \underbrace{(300K)}_{T_{room}} \simeq 0.6 \ \frac{\text{kcal}}{\text{mol}}$$

The zero of energy is arbitrary:
example:

2 states: $E_1 = 5.55 \frac{\text{Kcal}}{\text{mol}}$

$E_2 = 6.55 \frac{\text{Kcal}}{\text{mol}}$

Ⓐ Compute P_1 and P_2

Ⓑ and show get same result if

$E_1 = 0 \quad E_2 = 1 \frac{\text{Kcal}}{\text{mol}}.$

Given: $T = 300K \qquad k_B = 0.002 \frac{\text{Kcal}}{\text{mol} \cdot K}$

$k_B T = 0.6 \frac{\text{Kcal}}{\text{mol}}$

Ⓐ: $$C = \frac{1}{e^{-5.55/0.6} + e^{-6.55/0.6}}$$

$$C = 8752$$

$$P_1 \propto e^{-5.55/0.6} = 9.61 \times 10^{-5}$$

$$P_2 \propto e^{-6.55/0.6} = 1.815 \times 10^{-5}$$

$$P_1 = C e^{-5.55/0.6} = 0.84$$
$$P_2 = C e^{-6.55/0.6} = 0.16$$

(13): $E_1 = 0 \quad E_2 = 1 \frac{\text{Kcal}}{\text{mol}}$

$$P_1 \propto e^{0} = 1$$

$$P_2 \propto e^{-1/0.6} = 0.1889$$

$$C = \frac{1}{e^{0} + e^{-1/0.6}} = 0.841$$

$P_1 = 0.84$

$P_2 = 0.16$ about the same (check rounding).

Example 2: At room T, one state is twice as likely as another. Find difference in energies between states.

$1 = P_1 + P_2$

call ① the more likely state. (lower energy).

$P_1 = 2P_2$

$$1 = 2P_2 + P_2 = 3P_2 \Rightarrow P_2 = \frac{1}{3}$$

$$P_1 = \frac{2}{3} = 1 - P_2 .$$

Set $E_1 \rightarrow 0$ (by subtract E_1 from all energies)

$$E_2 \longrightarrow E_2 - E_1 = \Delta E$$

$$P_1 = \frac{e^0}{C} \qquad P_2 = \frac{e^{-\Delta E \cdot \beta}}{C}$$

$$P_1 = \frac{1}{C} = \frac{2}{3} \rightarrow C = \frac{3}{2}$$

$$P_2 = \frac{1}{3} = \frac{e^{-\Delta E \cdot \beta}}{3/2}$$

$$\frac{1}{2} = e^{-\Delta E \cdot \beta}$$

$$\ln\left(\tfrac{1}{2}\right) = \ln\left(e^{-\Delta E \cdot \beta}\right) = -\Delta E \cdot \beta$$

$$-0.693 = -\frac{\Delta E}{(k_B T)} = -\frac{\Delta E}{\left(0.6 \frac{\text{Kcal}}{\text{mol}}\right)}$$

$$0.693 \times 0.6 \frac{\text{Kcal}}{\text{mol}} = \boxed{\Delta E = 0.416 \frac{\text{Kcal}}{\text{mol}}}$$

Can find average values from probability.

average # devices =

# dev.	# stu.
0	0
1	7
2	21
3	6

$$\frac{\#\text{dev}}{\text{student}} = \frac{0\cdot 0 + 1\cdot 7 + 2\cdot 21 + 3\cdot 6}{0+7+21+6} \quad 0+7+21+6 = N$$

$$= 0\cdot\frac{0}{N} + 1\cdot\frac{7}{N} + 2\cdot\frac{21}{N} + 3\cdot\frac{6}{N}$$

dev.

Prob. of having that # of devices.

$$\overline{X} = \sum_i x_i P_i$$

for stat mech, consider $\overline{E}$

$$\overline{E} = \sum_i E_i \frac{e^{-E_i\beta}}{Z} = \frac{1}{Z} \sum_i E_i e^{-\beta E_i}$$

specific heat $= \dfrac{d\overline{E}}{dT}$