

1. 60 pts

- (a) Calculate the temperature at which 2.00 mol of an ideal gas occupies 40.0 L at a pressure of 1.50 bar. **Solution:**

$$PV = nRT \quad T = \frac{PV}{nR} = \frac{(1.50)(40.0 \text{ L})}{(2.00 \text{ mol})(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})} = \boxed{361 \text{ K}}$$

- (b) According to the equipartition principle, what is the molar heat capacity at constant pressure (in **SI** units) for tetrachloroethene (C_2H_4) in the limit that $k_{\text{B}}T$ is less than the lowest vibrational constant.

$$N_{\text{ep}} = 3 + 3 + 2 \times (3 \cdot 6 - 6) = 30$$

$$C_{Pm} = C_{Vm} + R = R \left[\frac{30}{2} + 1 \right] = 16R = \boxed{133.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

- (c) The mean free path of N_2 at 1.00 bar and 288 K is 790 Å. What is the mean free path at 0.020 bar and 298 K?

$$\lambda_2 = \frac{1}{\sqrt{2}\rho_2\sigma} = \frac{RT_2}{\sqrt{2}\mathcal{N}_A P_2\sigma} = \frac{R(298/288)T_1}{\sqrt{2}\mathcal{N}_A(0.020/1.00)P_2\sigma} = \frac{(298)(1.00)}{(288)(0.020)}\lambda_1 = \boxed{4.09 \cdot 10^4 \text{ Å}}$$

- (d) The Maxwell-Boltzmann distribution for CO at 300 K is labeled below. Which of the curves a–d gives the distribution for the Maxwell-Boltzmann distribution of C_2O_2 at 150 K? **Solution:** a. The v value of the curve's peak (like all of the characteristic speeds) is proportional to $\sqrt{T/m}$, so if $T_2 = T_1/2$ and $m_2 = 2m_1$, then the peak position should decrease by a factor of $\sqrt{(1/2)(1/2)} = 1/2$.

- (e) Which of the following approximations did we use to obtain the van der Waals equation for non-ideal gases starting from the intermolecular potential energy function? There may be more than one correct answer.

- The magnitude of the repulsive potential energy is less than the thermal energy. N
- The magnitude of the attractive potential energy is less than the thermal energy. Y
- The total potential energy of the N molecules is the sum of all the pair potentials. Y
- The potential energy at interaction distances less than R_{LJ} is essentially infinite. Y
- The integral of the product of $N(N-1)/2$ integrands can be set equal to the a one-dimensional integral raised to the $N(N-1)/2$ power. Y

- (f) Complete the Maxwell relation which is started below:

$$-\left(\frac{\partial S}{\partial n}\right)_{T,V} = \left[\frac{\partial}{\partial n}\left(\frac{\partial F}{\partial T}\right)_{V,n}\right]_{T,V} = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial n}\right)_{T,V}\right]_{V,n} = \boxed{\left(\frac{\partial \mu}{\partial T}\right)_{V,n}}$$

2. Shown below is the ensemble used in Fig. 2.5, showing three fluorine atoms, one of them in an excited electronic state, in four different translation states. The electronic energy of the one excited fluorine atom is 404 cm^{-1} above the ground state.

(a) Calculate the Boltzmann entropy of this system in SI units. **Solution:**

$$\Omega = 12 \quad S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega = (1.381 \cdot 10^{-23} \text{ J K}^{-1}) \ln(12) = \boxed{3.43 \cdot 10^{-23} \text{ J K}^{-1}}$$

(b) Calculate the Gibbs entropy of this system in SI units. **Solution:** There are two degrees of freedom: translational and electronic. There are only two electronic states, with probabilities of $\mathcal{P}(J = 3/2) = 2/3$ and $\mathcal{P}(J = 1/2) = 1/3$, and there are four translational states each with a probability of $1/4$. We add these two contributions to the entropy to get the total entropy for the ensemble. Using J to label the electronic states and k to label the translational states, we have

$$\begin{aligned} S_{\text{Gibbs}} &= -Nk_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i) = -Nk_{\text{B}} \left[\sum_{J=1/2}^{3/2} \mathcal{P}(J) \ln \mathcal{P}(J) + \sum_{k=1}^4 \mathcal{P}(k) \ln \mathcal{P}(k) \right] \\ &= -3(1.381 \cdot 10^{-23} \text{ J K}^{-1}) \left[\frac{1}{3} \ln \frac{1}{3} + \frac{2}{3} \ln \frac{2}{3} + 4 \frac{1}{4} \ln \frac{1}{4} \right] = \boxed{8.38 \cdot 10^{-23} \text{ J K}^{-1}} \end{aligned}$$

(c) Using the energy and entropy, estimate the temperature of this system. **Solution:** The only lower energy state is the one where all three particles are in the $J = 3/2$ electronic state, and that leaves four possible (degenerate) translational states. For that state, $\Omega = 4$ and $S_{\text{Boltzmann}} = 1.91 \cdot 10^{-23} \text{ J K}^{-1}$. Using the Boltzmann entropy, this predicts a temperature of

$$T \equiv \left(\frac{\partial E}{\partial S} \right)_{V,N} \approx \frac{\delta E}{\delta S} = \frac{(404 \text{ cm}^{-1})(1.986 \cdot 10^{-23} \text{ J/cm}^{-1})}{(3.43 - 1.91) \cdot 10^{-23} \text{ J K}^{-1}} = \boxed{530 \text{ K}}$$

3. If $d\rho/dt = D\rho/a$ at a point Z_0 in our system, where a is a distance, then find an expression for the flux at that point. **Solution:**

$$\begin{aligned} \frac{d\rho}{dt} &= D \frac{d^2\rho}{dZ^2} = D \frac{\rho}{a} & \rho &= \rho_0 e^{-\sqrt{D/a}Z} \\ \frac{d^2\rho}{dZ^2} &= \frac{\rho}{a} \\ J(Z_0) &= -D \left(\frac{d\rho}{dZ} \right) \Big|_{Z_0} = -D \int_0^{Z_0} \frac{d^2\rho}{dZ^2} dZ = -D \int_0^{Z_0} \frac{\rho}{a} dZ = -\frac{D\rho_0}{a} e^{-\sqrt{D/a}Z} \end{aligned}$$

4. A gas-phase sample of a diatomic molecule is placed in a chamber at 298 K. Spectroscopy determines the populations of vibrational and rotational states graphed below. Use the data to *roughly* estimate the values of the rotational and vibrational constants. **Solution:** We can estimate q from the number of states occupied, and then use the expressions for q_{rot} and q_{vib} to estimate the rotational and vibrational constants. The rotational levels have significant population up to roughly $J = 100$. Because each J level has $2J + 1$ states, that's $\sum_{J=0}^{100} (2J + 1) = (100^2) = 10^4$ rotational states. So we set $q_{\text{rot}} \approx 10^4$. On the other hand, only 1 or 2 vibrational states see significant population, so $q_{\text{vib}} \approx 1.5$.

$$\begin{aligned} q_{\text{rot}} &= \frac{k_{\text{B}}T}{B} \\ B &= \frac{k_{\text{B}}T}{q_{\text{rot}}} \approx \frac{(0.6950 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}{10^4} = \boxed{0.0207 \text{ cm}^{-1}} \\ q_{\text{vib}} &= \frac{1}{1 - e^{-\omega_e/(k_{\text{B}}T)}} \\ \omega_e &= -k_{\text{B}}T \ln \left(1 - \frac{1}{q_{\text{vib}}} \right) = (0.6950 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln \left(1 - \frac{1}{1.5} \right) = \boxed{227 \text{ cm}^{-1}} \end{aligned}$$

The populations are based on calculations for IBr, with $B_e = 0.0559 \text{ cm}^{-1}$ and $\omega_e = 268.71 \text{ cm}^{-1}$. Clearly, a broad range of answers is possible.

5. Imagine a blackbody composed of rigid, rotating molecules, so that the emission arises from **rotational** transitions rather than vibrational transitions. To find the average energy $\langle \epsilon_{\text{rot}} \rangle$ (in order to get its contribution to ρ_{rad}), we must use a sum over all the states, rather than an integral (otherwise we have the same problem as in the case of classical vibrations). Write $\langle \epsilon_{\text{rot}} \rangle$ for a linear molecule as a power series in x , where $x = e^{-B/(k_{\text{B}}T)}$. Treat q_{rot} as a constant that can be factored out. **Solution:**

$$\begin{aligned} \langle \epsilon_{\text{rot}} \rangle &= \sum_{J=0}^{\infty} \mathcal{P}(J) \epsilon_{\text{rot}}(J) &= \sum_J = 0^{\infty} [BJ(J+1)] \frac{(2J+1)e^{-BJ(J+1)/(k_{\text{B}}T)}}{q_{\text{rot}}} \\ &= \sum_J = 0^{\infty} [BJ(J+1)] \frac{(2J+1)(e^{-B/(k_{\text{B}}T)})^{J(J+1)}}{k_{\text{B}}T/B} \\ &= \frac{B^2}{k_{\text{B}}T} \sum_J = 0^{\infty} J(J+1)(2J+1)x^{J(J+1)} \end{aligned}$$

6. Sodium chloride is a relatively compressible solid, and has an internal pressure $\left(\frac{\partial E}{\partial V}\right)_{T,n} = 83 \text{ kbar}$, a density of 2.16 g cm^{-3} , and a coefficient of thermal expansion $39.8 \cdot 10^{-6} \text{ K}^{-1}$. Use these data to calculate the total work w **in kJ** when 50.00 g of solid NaCl is warmed from 285.0 K to 335.0 K at a constant pressure of 1.00 bar . Assume the molar heat capacity $C_{Pm} = 50.50 \text{ J K}^{-1} \text{ mol}^{-1}$ is constant over this temperature range. **Solution:** The idea is that NaCl (unlike the ideal gas) has a non-zero internal pressure, so work has to be done not only on the surroundings but also within the substance itself to allow for the expansion. If the internal pressure is non-zero, then it takes energy even to expand against a vacuum.

$$\begin{aligned} \Delta V &= V\alpha\Delta T = \left(\frac{50.0 \text{ g}}{2.16 \text{ g cm}^{-3}}\right) (39.8 \cdot 10^{-6} \text{ K}^{-1})(50 \text{ K}) = 0.215 \text{ cm}^3 \\ w &= -\left(\frac{\partial E}{\partial V}\right)_{T,n} \Delta V - P_{\text{min}} \Delta V = -\left[\left(\frac{\partial E}{\partial V}\right)_{T,n} + P_{\text{min}}\right] \Delta V \\ &= -(83 \cdot 10^3 \text{ bar} + 1.00 \text{ bar})(0.215 \text{ cm}^3)(10^{-3} \text{ L/cm}^3) [(100 \text{ J}/(\text{bar} \cdot \text{L}))] = \boxed{1.78 \text{ kJ}} \end{aligned}$$