

1. 40 points.

- (a) The diffusion constant of a lysozyme in water is $1.11 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and the diffusion constant of propane in water at the same temperature is $1.21 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. If we let propane diffuse in water for $3.60 \cdot 10^3 \text{ s}$ and measure the rms diffusion distance, how long would it take the lysozyme to reach the *same* rms diffusion distance? **Solution:** The Einstein equation for diffusion, $r_{\text{rms}} = \sqrt{6Dt}$, tells us that the products Dt must be equal for the two substance in order to achieve the same rms distance, so

$$t_{\text{lysozyme}} = \frac{D_{\text{propane}} t_{\text{propane}}}{D_{\text{lysozyme}}} = \frac{(1.21 \cdot 10^{-5})(3.60 \cdot 10^3 \text{ s})}{1.11 \cdot 10^{-6}} = \boxed{3.92 \cdot 10^4 \text{ s.}}$$

- (b) For the isobaric heating of an ideal gas, indicate whether each of the following is positive (“+”), negative (“-”), or zero (“0”):

- ΔE
- q because we are adding heat to the sample
- ΔP by definition of “isobaric”
- ΔT because temperature increases with energy for ideal gas
- ΔV by the ideal gas law, $V = nRT/P$ with P constant

- (c) Write a Maxwell relation based on taking the second derivative of E with respect to V and n . **Solution:**

$$dE = TdS - PdV + \mu dn$$

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial n} \right)_{S,V} \right]_{S,n} = \left[\frac{\partial}{\partial n} \left(\frac{\partial E}{\partial V} \right)_{S,n} \right]_{S,V}$$

$$\left(\frac{\partial \mu}{\partial V} \right)_{S,n} = - \left(\frac{\partial P}{\partial n} \right)_{S,V}$$

- (d) According to the Einstein equation for heat capacity, what is the numerical value of the heat capacity of a crystal of quartz at

- 1000 K (assume the high temperature limit) **Solution:** $3R = \boxed{24.94 \text{ J K}^{-1} \text{ mol}^{-1}}$.
- 0 K .

2. The Fe(III) - ferrozine complex has an extinction coefficient or molar absorptivity of $2.8 \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

- (a) What concentration would give an absorbance of 0.01 in a 1.0 cm pathlength cuvette? **Solution:**

$$c = \frac{A}{\epsilon l} = \frac{0.01}{(2.8 \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})(1/0 \text{ cm})} = \boxed{3.6 \cdot 10^{-7} \text{ M.}}$$

- (b) At this concentration, what percent of the incident light is *absorbed*? **Solution:** The fraction of light transmitted I/I_0 is given by $10^{-A} = 10^{-0.01} = 0.977$. That means that $1 - 0.977 = 0.023$ or 2.3% of the light is absorbed.
3. The heat capacity C_{Pm} for 1,2-dibromoethane gas is $96.8 \text{ J K}^{-1} \text{ mol}^{-1}$ at 383 K and 1.00 bar.

(a) As we heat the substance from 382 K to 384 K, how much heat (in J mol^{-1}) is transferred into each of these three degrees of freedom?

i. translation **Solution:** $3R\Delta T/2 =$ 24.9 J mol^{-1} .

ii. rotation **Solution:** $3R\Delta T/2 =$ 24.9 J mol^{-1} .

iii. vibration **Solution:** For the ideal gas, $C_{Pm} = C_{Vm} + R = \frac{1}{2}nRN_{\text{ep}} + R$. The translations and rotations add up to $3nRT$ in energy. Taking the derivative with respect to T and dividing by n to get the molar quantity gives a contribution of $3R$ to the heat capacity. The remaining degrees of freedom contributing to the heat capacity should come from vibration. We multiply that by ΔT to get the energy added into vibrations:

$$\Delta E_{\text{vib}} = \frac{1}{2}nR[N_{\text{ep}} - 3 (\text{trans}) - 3 (\text{rot})] \Delta T = (C_{Pm} - R - 3R)\Delta T =$$
 127 J mol^{-1} .

(b) Based on your results, roughly how many vibrational modes appear to be absorbing energy at this temperature? **Solution:** Each vibration that absorbs energy at the equipartition level will contribute $R\Delta T$ to the energy absorbed, so we have roughly $(127 \text{ J mol}^{-1})/(R\Delta T) = 7.6$ vibrational modes absorbing energy: 7 or 8 modes out of the 18 modes in the molecule. This accounts for all the vibrations of the two bromine atoms, plus one or two others.

4. Find what thermodynamic parameters are represented by X , Y , and Z in the equation

$$\kappa_S = \frac{C_V}{VT} \left(\frac{\partial T}{\partial X} \right)_Y \left(\frac{\partial T}{\partial X} \right)_Z.$$

Solution: We look ahead and see that in order to convert κ_S to C_V , we have to convert the derivative of V and P to a derivative of S and T . First we convert the derivative of V with S constant to a derivative of S with V constant:

$$\kappa_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad \text{definition of } \kappa_S$$

$$\left(\frac{\partial V}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P \left(\frac{\partial S}{\partial P} \right)_V \quad \text{use the derivative identity}$$

then convert the entropy derivative to the heat capacity derivative $\partial S/\partial T$:

$$\left(\frac{\partial S}{\partial P} \right)_V = \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_V \quad \text{another derivative identity}$$

$$\left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S \quad \text{Maxwell relation.}$$

Combining these, we obtain

$$\kappa_S = \frac{1}{VT} C_V \left(\frac{\partial T}{\partial P} \right)_S \left(\frac{\partial T}{\partial P} \right)_V,$$

so $\boxed{X = P, Y = S, Z = V.}$