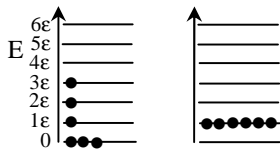


Constants: $R = 8.314$ or 0.08206 you know the units. $1 \text{ atm} = 1.0135 \times 10^5 \text{ Pa}$

Part 1: Answer 3 of the following 4 questions. If you answer more than 3 cross out the one you wish not to be graded. Otherwise only the first 3 will be graded. 8 points each.

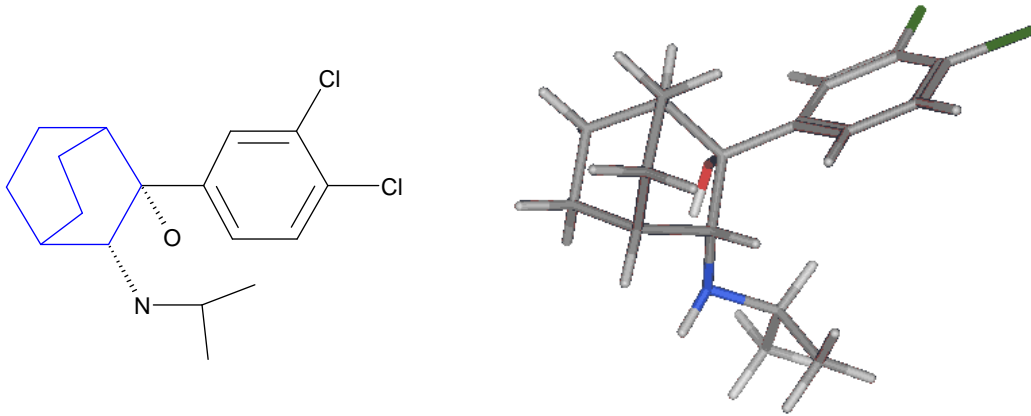
1. (a) What single thermodynamic parameter characterizes the most probable distribution?
(b). Which set of distribution numbers, below, is closer to equilibrium?



2. Use equipartition theory to predict the constant volume heat capacity of a diatomic gas, neglecting the vibrational degree of freedom.

3. When 3.00 mol of O_2 is heated at constant pressure of 3.25 bar, its temperature increases from 260.K to 285.K. Given that the molar heat capacity of O_2 at constant pressure is $29.4 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q and ΔH .

4. Cilobamine is an antidepressant produced by Merrell Pharmaceuticals. The MMFF force field steric energy terms are listed below using MOE. What would be a good molecule to compare with cilobamine to assess the ring strain? Get the printout for this molecule from the instructor. Which term in the force field dominates the strain energy (for credit give the full name for the force field term—not just the acronym)?



Cilobamine MMFF results:

| | E | str | ang | stb | oop | tor | vdw | ele |
|------|--------|-------|-------|-------|-------|--------|--------|--------|
| ALL: | 86.853 | 8.944 | 5.509 | 0.661 | 0.003 | -2.109 | 49.365 | 24.480 |

Part 2: Answer 5 of the following 7 questions. If you answer more than 5 cross out the ones you wish not to be graded. Otherwise only the first 5 will be graded. 15 points each.

5. A sample of 1.0 mol of an ideal diatomic gas with $C_p = \frac{7}{2} nR$ is initially at 1.00 bar and 298.15 K and has a volume of 24.80 L. The gas undergoes reversible adiabatic expansion until its pressure reaches 0.500 bar. Calculate q , w , and ΔU .

6. Consider the reaction: pyruvic acid \rightarrow acetaldehyde + CO₂ (g)
 (which is catalyzed by the enzyme pyruvate decarboxylase.) Calculate $\Delta_r S^\circ$ for this reaction for the system and the surroundings at 298.2 K. The values in the table below are at 298.2 K.

| substance | $\Delta_f H^\circ$ (kJ mol ⁻¹) | S° (J K ⁻¹ mol ⁻¹) |
|-----------------|--|--|
| acetaldehyde | -192.30 | 160.2 |
| CO ₂ | -393.51 | 213.74 |
| pyruvic acid | -584.5 | 179.5 |

7. We derived in class the second order correction for the volume of a substance as a function of temperature from α : $V - V_o = V_o \alpha (T - T_o) + \frac{V_o \alpha^2}{2} (T - T_o)^2$. (Remember the good, better, best discussion.) Derive the similar equation including the second order correction for the volume as a function of pressure from κ_T .

8. The enthalpy of combustion of lactic acid, $C_3H_6O_3$, is $-1343.9 \text{ kJ mol}^{-1}$. Given that $\Delta_f H^\circ$ for $CO_2 = -393.5 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ$ for $H_2O = -285.8 \text{ kJ mol}^{-1}$, calculate the enthalpy of formation of lactic acid.

9. Assume that the *gauche*-energy states for a 1,2-disubstituted ethane, $X-CH_2-CH_2-Y$, are at energy ϵ above the *anti*-state. The *anti*-state is set at the reference state. Show that the conformational entropy for the C–C bond in disubstituted ethane compounds is given by:

$$S = -\frac{R}{(1 + 2 e^{-\epsilon/RT})} \left[\ln\left(\frac{1}{1 + 2 e^{-\epsilon/RT}}\right) + 2 e^{-\epsilon/RT} \ln\left(\frac{e^{-\epsilon/RT}}{1 + 2 e^{-\epsilon/RT}}\right) \right]$$

10. Show that $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$.

[Show all your work with reasons for each step. For example: "since H is a state function" , "from the definition of heat capacity", or "dividing by dP". If you use a partial derivative relationship that has a name, if you choose not to derive the relationship, just state the corresponding relationship name. (e.g. "from the chain rule" or "from the Euler chain rule")

11. The most probable distribution maximizes the entropy. Starting with $S = -k \sum_i p_i \ln p_i$ show that $dS = -k \sum_i \ln p_i dp_i = 0$ maximizes the entropy, using the following steps. Show that in turn:

(a). $dS = -k \sum_i (p_i d \ln p_i + \ln p_i dp_i)$

(b). $dS = -k \sum_i dp_i - k \sum_i \ln p_i dp_i$

(c). $dS = -k \sum_i \ln p_i dp_i$

(d). $dS = -k \sum_i \ln p_i dp_i = 0$ maximizes the entropy

Since the intermediate results are given, give the reasons as well as any manipulations to derive each intermediate result (no credit for just giving the answer).