HW9

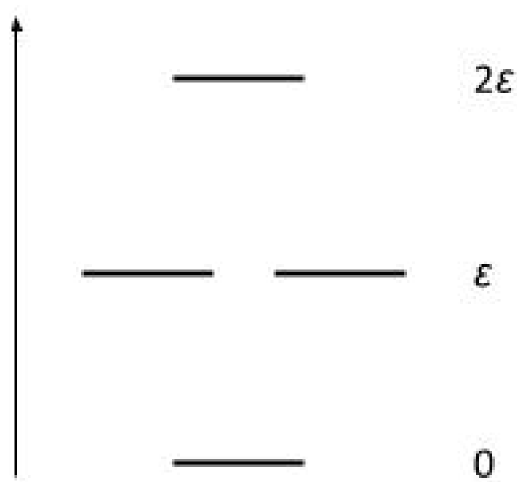
April 2, 2025

1 Chem 30324, Spring 2025, Homework 9

2 Due April 11, 2025

2.1 The canonical ensemble.

2.1.1 The energy spectrum of some molecule is described by the diagram below. A large number N of these distinguishable molecules is in thermal equilibrium with a much larger reservoir of temperature T.



2.1.2 **1. Write the partition function q for one of the molecules in the system (a) in terms of T and ε, (b) in terms of $\beta = 1/k_BT$ and ε, and (c) in terms of a characteristic temperature $\theta = \varepsilon/k_B$.**

2.1.3 **2. Plot the relative fractions of molecules of energy 0, ε, and 2ε vs. temperature. Assume $\theta = 300$ K. Be sure to indicate the probabilities in the limits of $T \to 0$ and $T \to \infty$.**

2.1.4 **3. Derive an expression for the internal energy U per molecule by summing over the possible microstates weighted by their probabilities. Plot the average energy vs. temperature, assuming $\theta = 300$ K.**

2.1.5 **4. Derive an expression for the internal energy U per molecule by taking the appropriate derivative of the partition function from problem 5 (*Hint:* it is easier to work with the expressions in term of β than in T.) Does your result agree with that from Question 3?**

2.1.6 **5. Derive an expression for the Helmholtz energy A per molecule from the partition function. Plot A vs. temperature, assuming $\theta = 300$ K.**

2.1.7 **6. Derive an expression for the entropy S per molecules and plot vs. temperature, again assuming $\theta = 300$ K.**

2.1.8 **7. In class we took the First Law as a postulate and demonstrated the Second Law. Look at your results for Problems 2 and 6. Can you use them to rationalize the Third Law? Explain your answer.**

2.2 Thermodynamics from scratch.

2.2.1 **Let's calculate the thermodynamic properties of an ideal gas of CO molecules at 1 bar pressure. CO has a rotational constant $B = 1.931$cm^{-1} and vibrational frequency $\nu = 2156.6$cm^{-1}. Suppose you have a 20 dm^3 cubic bottle containing 1 mole of CO gas that you can consider to behave ideally.**

2.2.2 **8. The characteristic temperature Θ of a particular degree of freedom is the characteristic quantum of energy for the degree of freedom divided by k_B. Calculate the characteristic translational, rotational, and vibrational temperatures of CO.**

2.2.3 **9. Plot the *translational*, *rotational* and *vibrational* partition functions of a CO molecule in the bottle from T = 200 to 2000 K (assume the CO remains a gas over the whole range). *Hint:* Use your answer to Problem 8 to simplify calculating the rotational partition function.**

2.2.4 **10. Plot the *total translational, rotational, and vibrational energies* of CO in the bottle from T = 200 to 2000 K (assume the CO remains a gas over the whole range). Which (if any) of the three types of motions dominate the total energy?**

2.2.5 **11. Plot the *total translational, rotational, and vibrational constant volume molar heat capacities* of CO in the bottle from T = 200 to 2000 K. Which (if any) of the three types of motions dominate the heat capacity?**

2.2.6 **12. Plot the *total translational, rotational, and vibrational Helmholtz energies* of CO in the bottle from T = 200 to 2000 K. Which (if any) of the three types of motions dominate the Helmholtz energy?**

2.2.7 **13. Use your formulas to calculate ΔP, ΔU, ΔA, and ΔS associated with isothermally expanding the gas from 20 dm^3 to 40 dm^3.**