

HW10

April 18, 2024

1 Chem 30324, Spring 2024, Homework 10

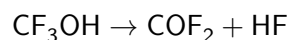
2 Due April 26, 2024

2.1 Thermodynamics from scratch.

- 2.1.1 Let's calculate the thermodynamic properties of an ideal gas of CO molecules at 1 bar pressure. CO has a rotational constant $B = 1.931\text{cm}^{-1}$ and vibrational frequency $\nu = 2156.6\text{cm}^{-1}$. Suppose you have a 20 dm^3 cubic bottle containing 1 mole of CO gas that you can consider to behave ideally.
- 2.1.2 1. 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.
- 2.1.3 2. 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 1 to simplify calculating the rotational partition function.
- 2.1.4 3. 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?
- 2.1.5 4. 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?
- 2.1.6 5. 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?
- 2.1.7 6. Use your formulas to calculate ΔP , ΔU , ΔA , and ΔS associated with isothermally expanding the gas from 20 dm^3 to 40 dm^3 .

2.2 Reactions from scratch

- 2.2.1 In 1996, Schneider and co-workers used quantum chemistry to compute the reaction pathway for unimolecular decomposition of trifluoromethanol, a reaction of relevance to the atmospheric degradation of hydrofluorocarbon refrigerants (*J. Phys. Chem.* 1996, 100, 6097- 6103, [doi:10.1021/jp952703m](https://doi.org/10.1021/jp952703m)):



- 2.2.2 Following are some of the reported results, computed at 298 K :

	CF ₃ OH	C(O)F ₂	HF	
E^{elec}	-412.90047	-312.57028	-	(Hartree)
			100.31885	
ZPE	0.02889	0.01422	0.00925	(Hartree)

	CF ₃ OH	C(O)F ₂	HF	
U^{trans}	3.7	3.7	3.7	(kJ mol ⁻¹)
U^{rot}	3.7	3.7	2.5	(kJ mol ⁻¹)
U^{vib}	4.3	1.2	0	(kJ mol ⁻¹)
q^{trans}/V	7.72×10^{32}	1.59×10^{32}	8.65×10^{31}	(m ⁻³)
q^{rot}	61830	679	9.59	
q^{vib}	2.33	1.16	1	

- 2.2.3 8.** Using the data provided, determine $\Delta U^\circ(298 \text{ K})$, in kJ mol⁻¹, assuming ideal behavior and 1 M standard state. Recall that $U(T)$ is the sum of the contributions of all degrees of freedom.
- 2.2.4 9.** Using the data provided, determine $\Delta A^\circ(298 \text{ K})$ in kJ mol⁻¹, assuming ideal behavior and 1 M standard state. Recall that $A^\circ = E^{\text{elec}} + \text{ZPE} - RT \ln(q^\circ) - RT$, where $q^\circ = ((q^{\text{trans}}/V)q^{\text{rot}}q^{\text{vib}})/c^\circ$ and $c^\circ = 6.022 \times 10^{26} \text{ m}^{-3}$ for a 1 M standard state.
- 2.2.5 10.** Determine $\Delta G^\circ(298 \text{ K})$. Recall that $G = A + PV = A + RT$ for an ideal gas.
- 2.2.6 11.** Determine $\Delta S^\circ(298 \text{ K})$, in J mol⁻¹ K⁻¹, assuming a 1 M standard state. Recall that $S = (U - A)/T$.
- 2.2.7 12.** Using the data provided, determine $K_c(298 \text{ K})$, assuming a 1 M standard state. You may either determine from partition functions or from the relationship between K_c and ΔG° .
- 2.2.8 13.** 1 mole of CF₃OH is generated in a 20 L vessel at 298 K and left long enough to come to equilibrium with respect to its decomposition reaction. What is the composition of the gas (concentrations of all the components) at equilibrium (in mol/L)?
- 2.2.9 14.** How, directionally, would your answer to Question 13 change if the vessel was at a higher temperature? Use the van'T Hoff relationship to determine the equilibrium constant and equilibrium concentrations at 273 and 323 K. How good was your guess?
- 2.2.10 15.** How, directionally, would your answer to Question 13 change if the vessel had a volume of 5 L? Redo the calculation at this volume to verify your guess.
- 2.2.11 16.** (Extra credit) Consult a thermodynamics source (e.g. <https://webbook.nist.gov/chemistry/>) to determine $\Delta H^\circ(298 \text{ K})$, $\Delta S^\circ(298 \text{ K})$, and $\Delta G^\circ(298 \text{ K})$ for the homologous reaction CH₃OH (g) → H₂ (g) + H₂CO (g). Does the substitution of F by H make the reaction more or less favorable?

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