Chem 30324, Spring 2018, Homework 11

Due May 5 2018

Thermodynamics from scratch.

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 ν = 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.

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. Calculate the *translational partition function* of a CO molecule in the bottle at 298 K. What are the units of the partition function?

3. Plot the *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.

4. 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?

5. 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?

6. 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?

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

Equilibrium constants from first principles.

In 1996, Schneider and co-workers reported calculations on the energetics of decomposition of trifluoromethanol, a reaction of relevance to the atmospheric degradation of hydrofluorocarbon refrigerants (*J. Phys. Chem.* 1996, *100*, 6097- 6103):

$$CF_3OH \rightarrow COF_2 + HF$$

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

	CF_3OH	$[CF_3OH]^\ddagger$	COF_2	HF	
E^{elec}	-412.90047	-412.82771	-312.57028	-100.31885	(Hartree)
ZPE	0.02889	0.02313	0.01422	0.00925	(Hartree)
U^{trans}	3.7	3.7	3.7	3.7	(kJ mol^{-1})
U^{rot}	3.7	3.7	3.7	2.5	(kJ mol^{-1})
U^{vib}	4.3	4.1	1.2	0	(kJ mol^{-1})
q^{trans}/V	7.72×10^{32}	7.72×10^{32}	1.59×10^{32}	8.65×10^{31}	(1/m^3)
q^{rot}	61830	68420	679	9.59	
q^{vib}	2.33	2.28	1.16	1	

8. Make a rough estimate of ΔS°(298 K), in J mol^{-1} K^{-1}, assuming a 1 bar standard state. (*Hint:* What degrees of freedom will dominate the entropy?)

9. Using the data provided, determine ΔU°(298 K) and ΔH°(298 K), in kJ mol^{-1}.

10. Using the data provided, determine K_c (298 K), assuming a 1 mole/liter standard state.

11. 1 mole of CF_3OH 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)?

12. How, directionally, would your answer to Question 11 change if the vessel was at a higher temperature? Why, in statistical mechanical terms?

13. How, directionally, would your answer to Question 11 change if the vessel had a volume of 5 L? Why, in statistical mechanical terms?