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):

$$\mathrm{CF_3OH} \rightarrow \mathrm{COF_2} + \mathrm{HF}$$

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

	CF_3OH	$C(O)F_2$	HF	
E^{elec}	-412.90047	-312.57028	-100.31885	(Hartree)
ZPE	0.02889	0.01422	0.00925	(Hartree)

	CF_3OH	$C(O)F_2$	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 ΔU°(298 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 ΔA°(298 K) in kJ mol^{-1}, assuming ideal behavior and 1 M standard state. Recall that $A^{\circ} = E^{\mathsf{elec}} + \mathsf{ZPE} - RT\ln(q^{\circ}) - RT$, where $q^{\circ} = ((q^{\mathsf{trans}}/V)q^{\mathsf{rot}}q^{\mathsf{vib}})/c^{\circ}$ and $c^{\circ} = 6.022 \times 10^{26}\ \mathsf{m}^{-3}$ for a 1 M standard state.

2.2.5 10. Determine ΔG°(298 K). Recall that $G = A + PV = A + RT$ for an ideal ga.

2.2.6 11. Determine ΔS°(298 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 K), assuming a 1 M standard state. You may either determine from partition functions of from the relationship between K_c and ΔG°.

2.2.8 13. 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)?

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 ΔH°(298 K), ΔS°(298 K), and ΔG°(298 K) for the homologous reaction CH_3OH (g)$\rightarrow$ H_2 (g) + H_2CO (g). Does the substitution of F by H make the reaction more or less favorable?

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