HW10

April 18, 2025

1 Chem 30324, Spring 2025, Homework 10

2 Due April 26, 2025

2.1 Reactions from scratch

2.1.1 In 1996, Schneider and co-workers used DFT 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):

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

2.1.2 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)
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	unitless
q^{vib}	2.33	1.16	1	unitless

2.1.3 1. Compute $\Delta\bar{U}^{\text{trans}}$(298 K) in kJ/mol.

2.1.4 2. Compute $\Delta\bar{U}^{\text{rot}}$(298 K) in kJ/mol. *Don't forget that HF is linear!*

2.1.5 3. Combine your answers with the table to determine $\Delta\bar{U}^{\circ}$(298 K), in kJ mol^{-1}.

2.1.6 4. Determine $\Delta\bar{H}^{\circ}$(298 K), in kJ mol^{-1}, assuming all species are ideal gases.

2.1.7 5. Determine $\Delta\bar{G}^{\circ}$(298 K) in kJ mol^{-1}, assuming ideal behavior and 1 bar standard state. Recall that $\bar{G}^{\circ} = E^{\mathsf{elec}} + \mathsf{ZPE} - RT\ln(q^{\circ})$, where $q^{\circ} = ((q^{\mathsf{trans}}/V)q^{\mathsf{rot}}q^{\mathsf{vib}})/c^{\circ}$ and $c^{\circ} = P^{\circ}/RT$.

2.1.8 6. Determine $\Delta\bar{S}^{\circ}$(298 K), in J mol^{-1} K^{-1} , assuming a 1 bar standard state. Recall that $S = (H - G)/T$.

2.1.9 7. Using the data provided, determine K_p (298 K), assuming a 1 bar standard state.

2.1.10 8. 1 bar of CF_3OH is introduced into 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 mixture (mole fractions of all the components) at equilibrium?

2.1.11 9. How, directionally, would your answer to Question 8 change if the vessel was at a higher temperature? Provide a sketch incorporating the Boltzmann distribution to rationalize your answer.

2.1.12 10. Use the van'T Hoff relationship to determine the equilibrium constant and equilibrium mole fractions at 273 and 323 K.

2.1.13 11. How, directionally, would your answer to Question 8 change if the vessel was compressed to a smaller volume? Rationalize your answer in terms of partition functions.

2.1.14 12. Check your answer to Question 11 by computing the equilibrium composition after compressing the vessel to 5 L.

2.1.15 13. 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 lean more or less towards products?