

# HW10

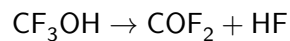
April 18, 2025

## 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](https://doi.org/10.1021/jp952703m)):



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

	CF <sub>3</sub> OH	C(O)F <sub>2</sub>	HF	
$E^{\text{elec}}$	-412.90047	-312.57028	-	(Hartree)
			100.31885	
ZPE	0.02889	0.01422	0.00925	(Hartree)
$U^{\text{vib}}$	4.3	1.2	0	(kJ mol <sup>-1</sup> )
$q^{\text{trans}}/V$	$7.72 \times 10^{32}$	$1.59 \times 10^{32}$	$8.65 \times 10^{31}$	(m <sup>-3</sup> )
$q^{\text{rot}}$	61830	679	9.59	unitless
$q^{\text{vib}}$	2.33	1.16	1	unitless

- 2.1.3 1. Compute  $\Delta\bar{U}^{\text{trans}}(298\text{ K})$  in kJ/mol.
- 2.1.4 2. Compute  $\Delta\bar{U}^{\text{rot}}(298\text{ K})$  in kJ/mol. *Don't forget that HF is linear!*
- 2.1.5 3. Combine your answers with the table to determine  $\Delta\bar{U}^{\circ}(298\text{ K})$ , in kJ mol<sup>-1</sup>.
- 2.1.6 4. Determine  $\Delta\bar{H}^{\circ}(298\text{ K})$ , in kJ mol<sup>-1</sup>, assuming all species are ideal gases.
- 2.1.7 5. Determine  $\Delta\bar{G}^{\circ}(298\text{ K})$  in kJ mol<sup>-1</sup>, assuming ideal behavior and 1 bar standard state. Recall that  $\bar{G}^{\circ} = E^{\text{elec}} + \text{ZPE} - RT \ln(q^{\circ})$ , where  $q^{\circ} = ((q^{\text{trans}}/V)q^{\text{rot}}q^{\text{vib}})/c^{\circ}$  and  $c^{\circ} = P^{\circ}/RT$ .
- 2.1.8 6. Determine  $\Delta\bar{S}^{\circ}(298\text{ K})$ , in J mol<sup>-1</sup> K<sup>-1</sup>, 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<sub>3</sub>OH 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  $\Delta H^{\circ}(298\text{ K})$ ,  $\Delta S^{\circ}(298\text{ K})$ , and  $\Delta G^{\circ}(298\text{ K})$  for the homologous reaction  $\text{CH}_3\text{OH (g)} \rightarrow \text{H}_2\text{ (g)} + \text{H}_2\text{CO (g)}$ . Does the substitution of F by H make the reaction lean more or less towards products?