

Chem 30324, Spring 2018, Homework 11

Due May 4 2018

Equilibrium constants from first principles.

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://pubs.acs.org/doi/abs/10.1021/jp952703m>)):



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

	CF ₃ OH	[CF ₃ OH] [‡]	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	

1. Estimate $\Delta S^\circ(298 \text{ K})$, in J mol⁻¹ K⁻¹, assuming a 1 bar standard state. (*Hint: What degrees of freedom will dominate the entropy?*)

2. Using the data provided, determine $\Delta U^\circ(298 \text{ K})$ and $\Delta H^\circ(298 \text{ K})$, in kJ mol⁻¹.

3. Using the data provided, determine K_c (298 K), assuming a 1 mole/liter standard state.
4. 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)?
5. How, directionally, would your answer to Question 4 change if the vessel was at a higher temperature? Why, in statistical mechanical terms?
6. How, directionally, would your answer to Question 4 change if the vessel had a volume of 5 L? Why, in statistical mechanical terms?

Chemical kinetics from first principles.

While chemical equilibrium describes what can happen, chemical kinetics determines what *will* happen. The same paper reports results for the transition state for the unimolecular decomposition reaction, also shown in the table above.

7. Provide a rough sketch of what you expect the transition state to look like.
8. Based on the data in the table, sketch out an approximate potential energy surface for the unimolecular decomposition reaction. Indicate on the PES the location of the reactants, the products, and the transition state. Also indicate relevant zero point energies, the 0 K reaction energy, and the activation energy.
9. Using data from the table and harmonic transition state theory, compute the first-order rate constant for CF_3OH decomposition at 298 K, in s^{-1} .

10. Which factor in your rate constant dominates the temperature dependence? Estimate the change in temperature necessary to double the rate constant.

11. Based on your computed rate constant, what is the half-life of the CF_3OH in the vessel of Question 4?

12. Experiments reveal that the CF_3OH comes to equilibrium far faster than the unimolecular rate would suggest. Provide a possible explanation for this observation (other than that Schneider calculations are incorrect!).