

# HW11

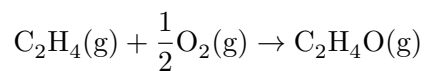
April 26, 2024

## 1 Chem 30324, Spring 2024, Homework 11

## 2 Due May 3, 2024

### 2.1 What to do with ethylene?

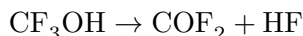
2.1.1 Ethylene ( $\text{C}_2\text{H}_4$ ) is an important commodity chemical. Partial oxidation to ethylene oxide (oxirane) is a useful way to introduce additional functionalization:



- 2.1.2 At 500 K over an appropriate catalyst, the reaction is first-order in ethylene, half-order in  $O_2$ , zero order in products, and has a rate constant of  $0.8 \text{ bar}^{-1/2} \text{ s}^{-1}$ . You plan to study the reaction in an isothermal, constant pressure reactor, starting with a 20 mole % excess of ethylene ( $n_{C_2H_4}/n_{O_2} = 1.2$ ) at 2 bar total pressure.
- 2.1.3 1. Draw the structure of ethylene oxide.
- 2.1.4 2. Is the reaction as written an elementary step? Why or why not?
- 2.1.5 3. Write down the rate law for the formation of ethylene oxide.
- 2.1.6 4. Create an ICE table for this reaction. My advice is to create the table in terms of *moles* of species and an advancement  $\xi$ . What is the maximum possible value of  $\xi$ ?
- 2.1.7 5. Define a conversion  $X$  as  $\xi/\xi_{\max}$ , so  $0 \leq X \leq 1$  Plot the partial pressures of all species vs  $X$ . *Hint*: Recall the partial pressure is  $Py_i$ , and  $y_i = N_i/N_{\text{tot}}$  from the ICE table.
- 2.1.8 6. Plot the forward reaction rate vs  $X$ . Be sure to include appropriate units.
- 2.1.9 7. The apparent activation energy of the reaction is  $60 \text{ kJ mol}^{-1}$ . What is the reaction prefactor? Include appropriate units.
- 2.1.10 8. The apparent activation energy of the reaction is  $60 \text{ kJ mol}^{-1}$ . Estimate the rate constant at 550 K.
- 2.1.11 9. From the information given, can you predict the rate law for the reverse reaction?

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



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

	$CF_3OH$	$[CF_3OH]^\ddagger$	$C(O)F_2$	HF
$E^{\text{elec}}$ (Hartree)	-412.90047	-412.82771	-312.57028	-
				100.31885
ZPE (Hartree)	0.02889	0.02313	0.01422	0.00925
$U^{\text{trans}}$ ( $\text{kJ mol}^{-1}$ )	3.7	3.7	3.7	3.7
$U^{\text{rot}}$ ( $\text{kJ mol}^{-1}$ )	3.7	3.7	3.7	2.5
$U^{\text{vib}}$ ( $\text{kJ mol}^{-1}$ )	4.3	4.1	1.2	0
$q^{\text{trans}}/V$ ( $\text{m}^{-3}$ )	$7.72 \times 10^{32}$	$7.72 \times 10^{32}$	$1.59 \times 10^{32}$	$8.65 \times 10^{31}$
$q^{\text{rot}}$	61830	68420	679	9.59
$q^{\text{vib}}$	2.33	2.28	1.16	1

- 2.2.2 10. Provide a rough sketch of what you expect the transition state to look like.
- 2.2.3 11. 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.
- 2.2.4 12. Using data from the table and harmonic transition state theory, compute the first-order rate constant for  $\text{CF}_3\text{OH}$  decomposition at 298 K, in  $\text{s}^{-1}$ .
- 2.2.5 13. In Homework 10, you computed the equilibrium constant for this reaction at 298 K. Use that result and your rate constant for the decomposition to determine the rate constant for the reverse,  $\text{CF}_3\text{OH}$  formation reaction.
- 2.2.6 14. Use the data in the table to compute the overall reaction enthalpy, and the forward and reverse reaction enthalpies.
- 2.2.7 15. Based on your computed rate constant, what is the half-life of  $\text{CF}_3\text{OH}$  at 298 K?
- 2.2.8 16. Experiments reveal that the  $\text{CF}_3\text{OH}$  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!).