HW11
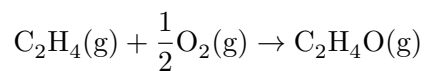
April 27, 2025

1 Chem 30324, Spring 2025, Homework 11

2 Due May 3, 2025

2.1 What to do with ethylene?

2.1.1 Ethylene (C_2H_4) is an important commodity chemical. Partial oxidation to ethylene oxide (oxirane) is a useful way to introduce additional functionalization:

$$C_2H_4(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_4O(g)$$

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 bar$^{-1/2}$ s^{-1}**. You plan to study the reaction in an isothermal, contant pressure reactor, starting with a **20 mole % excess of ethylene ($n_{\mathbf{C2H4}}/n_{\mathbf{O2}} = 1.2$) 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 ξ. What is the maximum possible value of ξ?

2.1.7 5. Define a conversion X as ξ/ξ_{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 $y_i = N_i/N_{\mathrm{tot}}$ 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 kJ mol^{-1}**. What is the reaction prefactor? Include appropriate units.

2.1.10 8. The apparent activation energy of the reaction is **60 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):
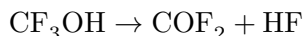
$$CF_3OH \rightarrow COF_2 + HF$$

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

	CF_3OH	$[CF_3OH]^{\ddagger}$	$C(O)F_2$	HF
E^{elec} (Hartree)	-412.90047	-412.82771	-312.57028	- 100.31885
ZPE (Hartree)	0.02889	0.02313	0.01422	0.00925
U^{trans} (kJ mol^{-1})	3.7	3.7	3.7	3.7
U^{rot} (kJ mol^{-1})	3.7	3.7	3.7	2.5
U^{vib} (kJ mol^{-1})	4.3	4.1	1.2	0
q^{trans}/V (m^{-3})	7.72×10^{32}	7.72×10^{32}	1.59×10^{32}	8.65×10^{31}
q^{rot}	61830	68420	679	9.59
q^{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, create a 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 CF_3OH decomposition at 298 K, in s^{-1}.

2.2.5   **13.** Based on your computed rate constant, what is the half-life of CF_3OH at 298 K?

2.2.6   **14.** 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!).