

Dynamics and Kinetics. Exercise 10

Problem 1

Ozone undergoes unimolecular decomposition $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$. Suppose that the vibrational degrees of freedom are excited by 40 quanta of energy. Estimate the probability that at least a) 10, b) 20, c) 30 quanta are present in a particular vibration. Use the fact that ozone has a nonlinear molecule and assume for simplicity that all vibrations have the same frequency.

Problem 2

Consider the isomerization of cis-but-2-ene into trans-but-2-ene. The experiment yielded the following values for the apparent first-order rate coefficient at 469 °C:

Pressure [mTorr]	$k_{\text{app}}^1 [10^{-6} \text{ s}^{-1}]$
3.08	6.67
4.69	7.14
10	8.06
38.4	10
111.1	12.5
250	16.1

- Analyze these results using the Lindemann-Christiansen theory. How well do the data correspond to the theory?
- Compare the rate constant for the energization step with the value obtained by collision theory. The diameter of collisions is $d = 500 \text{ pm}$ and the threshold energy for isomerization is $262.5 \text{ kJ mol}^{-1}$.
- Using the same parameters, estimate the rate constant of the energization step using the Hinshelwood theory.