

This is a closed-book exam, with one 3"x5" card of notes allowed. Write your name on any sheets of graph paper used, and hand in with exam. Please state any assumptions explicitly to ensure adequate credit. Read the entire exam before beginning.

Problem 1 (30 points)

The gas-phase reaction $A + B \rightarrow C + D + E$ is conducted in a vessel at constant temperature and volume. The following data for total reactor pressure with time is obtained for an initial reaction mixture is $A : B : \text{Inert} = 1 : 1 : 2$.

time (min)	Ptotal (Torr)
0	600
1	643
2	668
5	699
7	711
10	720

- For these initial conditions, when the rate is modeled with a power law, do you obtain reaction order in A, order in B, or total order? Suggest different experimental conditions to determine each of the reaction orders not chosen above.
- Determine the reaction order as possible from this data.
- What rate constant do you obtain? (include units)

Problem 2 (40 points)

A. Define the following terms and explain their import regarding mechanisms and rates.

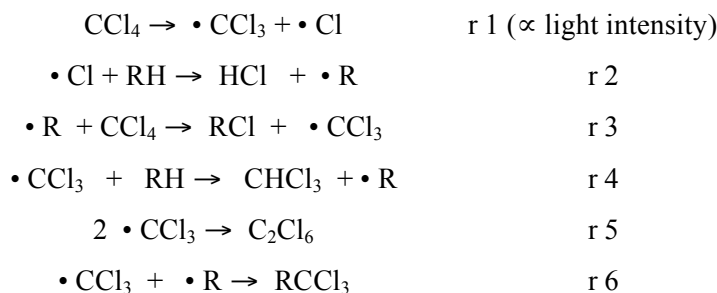
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|------------------------------|------------------------------|
| a) Elementary Reaction Step | c) Thermodynamic Consistency |
| b) Microscopic Reversibility | d) Rate-Limiting Step |

B. You can often tell the overall order of a reaction just from the units on the rate constant. Show how this can be done.

C. Kinetics problems are variously solved using reactant concentration directly, molar extent of reaction, or fractional conversion (c_A , ξ , or f_A). When is each of these approaches useful or appropriate?

Problem 3 (30 points)

The gas-phase photolysis reaction $\text{CCl}_4 + \text{RH} \rightarrow \text{CHCl}_3 + \text{RCl}$, where RH is cyclohexane, is thought to proceed by the following mechanism:



- Classify the steps as Initiation, Propagation, Chain Transfer, and Termination types.
- Show that your propagation steps produce the advertised products. Identify likely trace products.
- Determine the overall rate expression if termination proceeds via step 5.
- Under what conditions will step 6 be more important than step 5?

Optional (10 bonus points): Determine the rate expression if step 6 is faster than step 5. Experimentally, the reaction order in cyclohexane is observed to be one. Which step controls termination?