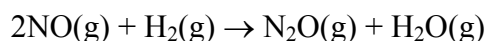


Kinetics Problem Set

1) Nitric oxide (NO) reacts with H₂ to give nitrous oxide (N₂O) and water as follows:

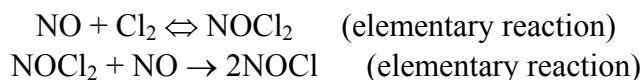


In a series of experiments, the following rates of disappearance of NO were obtained:

	Initial		
	Molar Concentrations		M/s
	NO	H ₂	NO rxn rate
Exp. 1	6.4*10 ⁻³	2.2*10 ⁻³	2.6*10 ⁻⁵
Exp. 2	12.8*10 ⁻³	2.2*10 ⁻³	1.0*10 ⁻⁴
Exp. 3	6.4*10 ⁻³	4.5*10 ⁻³	5.1*10 ⁻⁵

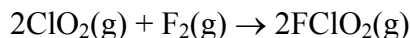
Find the rate law and the value of the rate constant for the reaction of NO.

2) NO is believed to react with Cl₂ according to the following mechanism:



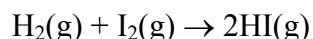
Identify any reaction intermediate. What is the overall equation?

3) The following reaction is first order in ClO₂ and first order in F₂:

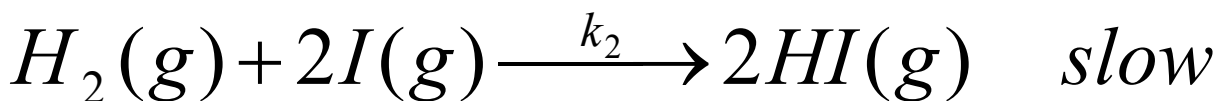
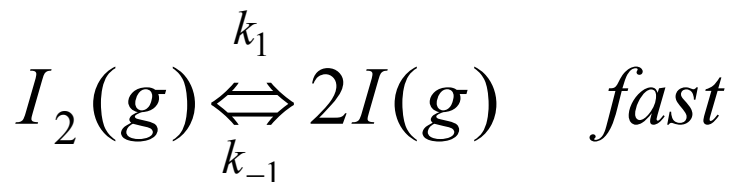


Write the rate law and devise a two-step mechanism consistent with the rate law.

4) HI forms from its elements as follows:

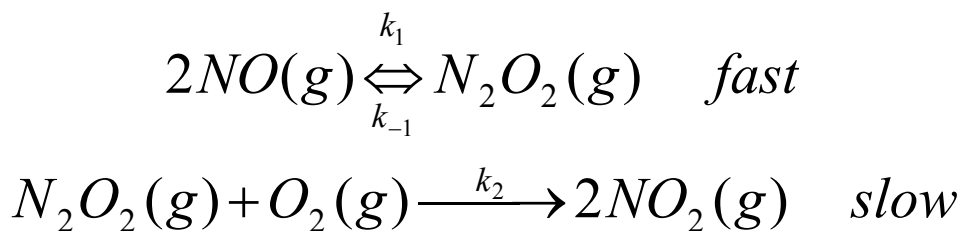


The principle mechanism at moderate temperatures is believed to consist of the following steps:



Using the steady state approximation, derive the rate law for this reaction.

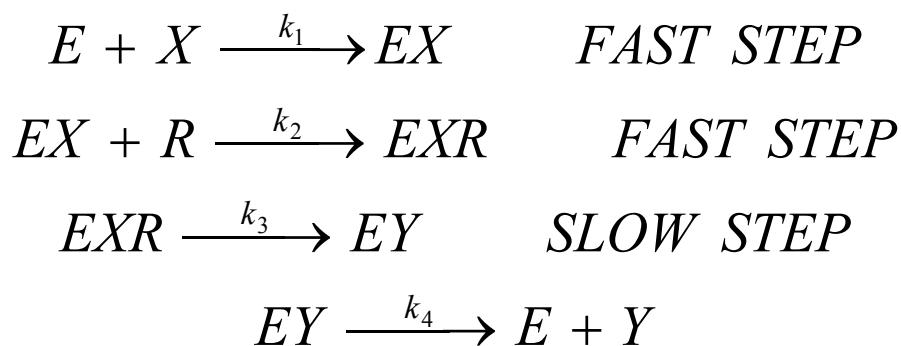
5) The following mechanism has been proposed for the reaction between NO and O₂ gases:



a) write the overall equation and identify any intermediates that are present.

b) use the steady state approximation to derive the rate law for the reaction.

6) The following reaction information has been provided to you by a researcher who needs you to prove that this reaction is an Ordered Bi Uni reaction and that EX forms first:



A) What is the steady state approximation expression?

B) What is the slow step?

C) What are the intermediates in this example?

D) What is the rate equation for the loss of EXR with respect to time?

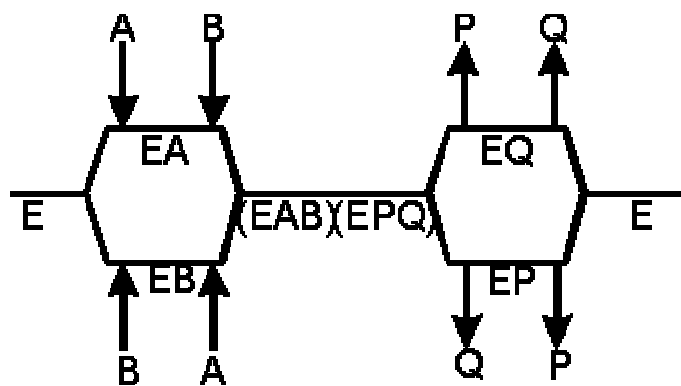
E) What is the rate equation for the formation of EY with respect to time?

F) What is the rate equation for the rate limiting step?

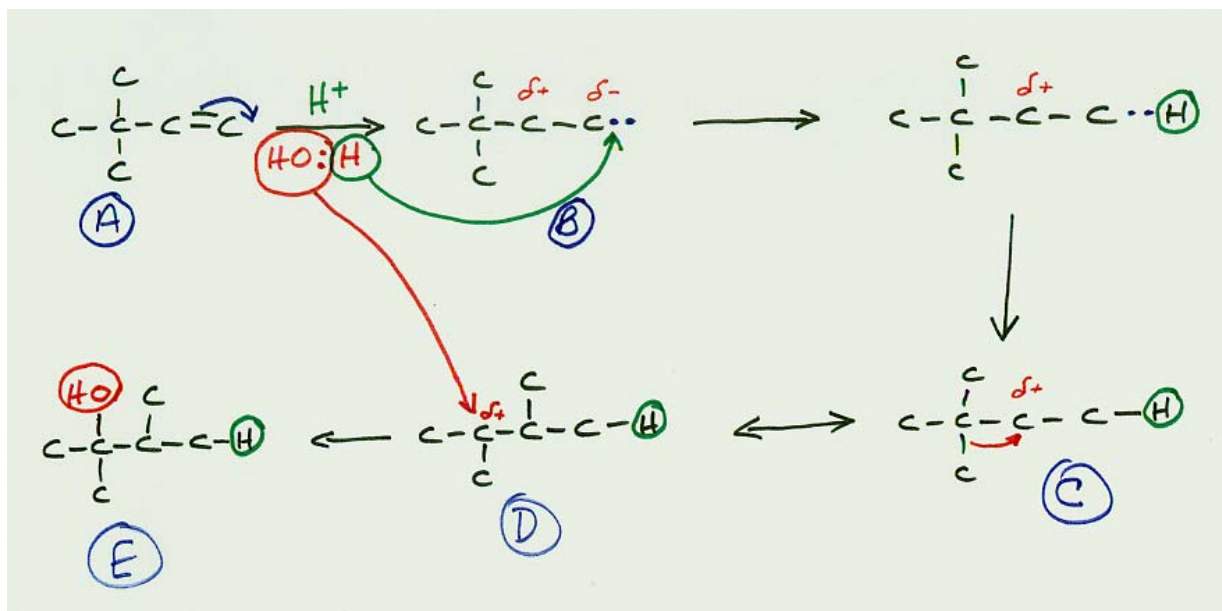
G) What is the rate equation for this reaction sequence?

H) Write the overall reaction in standard form.

I) Write the overall reaction using a Cleland Plot {a diagrammatic summary of the reaction sequence in which the enzyme (in this case) is represented as a horizontal line and arrows are used to represent the arrival and departure of substrates (in this case) and products (in this case).} to demonstrate that this is, indeed, an Ordered Bi Uni Reaction. A sample Cleland Plot (Random Sequential Bi Bi) follows:



7) There are various types of acid-catalyzed hydration reactions in organic chemistry. One of the more fascinating reactions involves Markovnikov addition with carbocations that can rearrange as follows:



Based upon the above reaction mechanism, predict the following:

- the intermediate[s] necessary for the steady state approach for rate equation/law determination
- the rate equations/laws to meet this equilibration of intermediate[s]
- Using your information, determine the correctness, or lack thereof, of the reaction mechanism and write out the mechanism in the usual line and arrows (Cleland Plot) method.