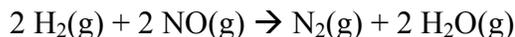


CH353 – Physical Chemistry I  
Spring 2013, Unique 52575

Homework, Week 14

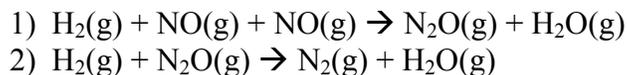
1. The following reaction:



has an experimentally observed rate law of:

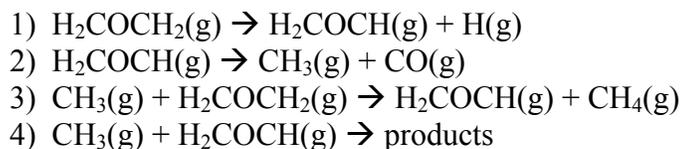
$$d[\text{N}_2]/dt = k_{\text{obs}}[\text{H}_2][\text{NO}]^2$$

A proposed mechanism is:



Determine the conditions under which this mechanism gives the experimentally observed rate law, and express  $k_{\text{obs}}$  in terms of the rate constants or equilibrium constants of the individual elementary reactions.

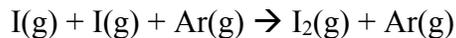
2. The thermal decomposition of ethylene oxide occurs,  $\text{H}_2\text{COCH}_2$ , through the following chain reaction:



a) Determine which steps are the initiation, propagation, and termination steps.

b) Determine that if the intermediates  $\text{CH}_3$  and  $\text{H}_2\text{COCH}$  are treated by the steady-state approximation, then the rate law expressed as the appearance of products is first order in ethylene oxide.

3. The reaction of atomic I to form molecular iodine is catalyzed by the presence of any inert gas, Ar:

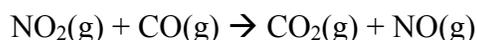


The observed rate law of the reaction is:

$$v(t) = k_{obs}[Ar][I]$$

Propose a series of elementary steps that explain this rate law. State all of your assumptions.

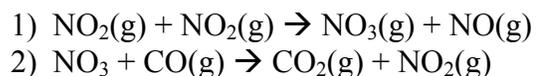
4. The reaction



has the experimentally determined rate law

$$v(t) = k_{obs}[NO_2]^2$$

The following mechanism has been proposed for this reaction:



where the first elementary step is rate determining. Show that this mechanism is consistent with the experimentally determined rate law and express  $k_{obs}$  in terms of the rates of each individual steps. State all your assumptions clearly.

5. The rate law for the reaction of carbon monoxide and chlorine gas to form phosgene ( $Cl_2CO$ ) has the experimentally determined rate law

$$v(t) = k_{obs}[Cl_2]^{3/2}[CO]$$

Show that the following mechanism is consistent with this rate law and express  $k_{obs}$  in terms of rate or equilibrium constants for individual steps of the mechanism.

