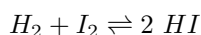


CHEM 3410: Physical Chemistry I — Fall 2008

## Kinetics practice problems

November 21, 2008

1. The formation of HI from H<sub>2</sub> and I<sub>2</sub> can be described by reversible second order kinetics.



However, direct bimolecular reaction between H<sub>2</sub> and I<sub>2</sub> is not observed to occur. A proposed mechanism for the forward reaction is:



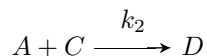
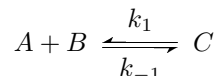
- (a) Derive a rate law assuming that step (1) is reversible, step (2) is irreversible and step (2) is the slowest process.
- (b) Derive a rate law assuming that step (1) is reversible, step (2) is irreversible and step (2) is the fastest process. You can use the steady-state approximation for the concentration of the intermediate [I].

Hint: For both parts, be sure to pay careful attention to the stoichiometry of the proposed elementary reactions.

2. Consider the reaction:



Suppose that the mechanism of this reaction is found to consist of the following elementary reactions:



- (a) Show that this mechanism is consistent with the overall reaction.
- (b) Write expressions for  $\frac{d[C]}{dt}$  and  $\frac{d[D]}{dt}$  in terms of [A], [B], [C], [D],  $k_1$ ,  $k_{-1}$ , and  $k_2$ .
- (c) Impose the steady-state approximation and solve for  $[C]_{ss}$ .
- (d) Use the steady-state approximation to derive the rate law for  $\frac{d[D]}{dt}$  in terms of [A], [B],  $k_1$ ,  $k_{-1}$ , and  $k_2$ .
- (e) If  $k_2[A] \gg k_{-1}$  what are the apparent orders of the reaction with respect to [A] and [B]?
- (f) If  $k_2[A] \ll k_{-1}$  what are the apparent orders of the reaction with respect to [A] and [B]?