The Richard Stockton College of New Jersey
Chemistry Program, School of Natural Sciences and Mathematics
PO Box 195, Pomoma, NJ

CHEM 3410: Physical Chemistry I — Fall 2008

Kinetics practice problems — Solutions

1. (a) The rate law for the formation of HI for the given mechanism is:

$$\frac{d[HI]}{dt} = 2k_2[H_2][I]^2$$

We need to use approximations to eliminate the intermediate, I, from the above expression. Assuming the the second step is the slowest, we can employ the pre-equilibrium approximation. This assumes that the first reaction will reach equilibrium much faster than the second reaction proceeds ($k_2 \ll k_{-1}$ and k_1). At equilibrium the rate of reaction 1 in the forward and reverse directions is equal:

$$k_1[I_2] = k_{-1}[I]^2 \quad \longrightarrow \quad [I]^2 = \frac{k_1}{k_{-1}}[I_2]$$

$$\frac{d[HI]}{dt} = 2k_2[H_2][I]^2 = 2\frac{k_1k_2}{k_{-1}}[H_2][I_2]$$

$$\boxed{\frac{d[HI]}{dt} = 2\frac{k_1k_2}{k_{-1}}[H_2][I_2]}$$

(b) Assuming the second step is fastest means that the intermediate species I forms much slower than it is removed ($k_1 \ll k_2$). This allows us to employ the steady state approximation for the concentration of the intermediate.

$$\frac{1}{2}\frac{d[I]}{dt} = k_1[I_2] - k_{-1}[I]^2 - k_2[H_2][I]^2 = 0$$

$$[I]^2_{ss} = \frac{k_1[I_2]}{k_{-1} + k_2[H_2]}$$

Now can substitute this into our rate expression for the product from above:

$$\frac{d[HI]}{dt} = 2k_2[H_2][I]^2 = 2k_2[H_2]\frac{k_1[I_2]}{k_{-1} + k_2[H_2]} = 2\frac{k_1k_2[H_2][I_2]}{k_{-1} + k_2[H_2]}$$

$$\boxed{\frac{d[HI]}{dt} = 2\frac{k_1k_2[H_2][I_2]}{k_{-1}+k_2[H_2]}}$$

2. (a) The sum of the two elementary does indeed equal the overall reaction.

(b) The expressions can be written for the formations of C and D as follows:

$$\frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] - k_2[A][C]$$

$$\frac{d[D]}{dt} = k_2[A][C]$$

(c) Using the steady state approximation to assume $\frac{d[C]}{dt} = 0$ we can write:

$$[C]_{ss} = \frac{k_1[A][B]}{k_{-1} + k_2[A]}$$

(d) For the evolution of D with time:

$$\frac{d[D]}{dt} = k_2[A][C] = k_2[A]\frac{k_1[A][B]}{k_{-1} + k_2[A]} = \frac{k_1k_2[A]^2[B]}{k_{-1} + k_2[A]}$$

(e) If $k_2[A] \gg k_{-1}$ then we can rewrite the expression in (d) as:

$$\frac{d[D]}{dt} = k_1[A][B]$$

which would look first order in both A and B.

(f) If $k_2[A] \ll k_{-1}$ then we can rewrite the expression in (d) as:

$$\frac{d[D]}{dt} = \frac{k_1 k_2}{k_{-1}}[A]^2[B]$$

which would look second order in A and first order in B.