

Chemistry 2710 Spring 2004 Test 2 Solutions

1.

$$\begin{aligned}\frac{d[B]}{dt} &= k_1[A] - k_2[B]. \\ [A] &= a[A]_0; \\ [B] &= k_1[A]_0 b / k_2; \\ t &= \tau / k_1. \\ \therefore \frac{d(k_1[A]_0 b / k_2)}{d(\tau / k_1)} &= k_1(a[A]_0) - k_2(k_1[A]_0 b / k_2). \\ \therefore \frac{k_1^2[A]_0}{k_2} \frac{db}{d\tau} &= k_1[A]_0(a - b). \\ \therefore \frac{k_1}{k_2} \frac{db}{d\tau} &= a - b.\end{aligned}$$

The steady-state approximation can be used if the factor multiplying the derivative is small, i.e. if $k_1 \ll k_2$, which is just what we would have expected in this very simple case.

2. (a) $R + CO_2 \rightarrow 2P$

(b) For the overall reaction,

$$K = \frac{[P]^2}{[R][CO_2]}.$$

For the four reactions which make up the mechanism, we have

$$\begin{aligned}\frac{k_1}{k_{-1}} &= \frac{[C_1]}{[E][R]}, \\ \frac{k_2}{k_{-2}} &= \frac{[C_2]}{[C_1][CO_2]}, \\ \frac{k_3}{k_{-3}} &= \frac{[C_3][P]}{[C_2]}, \\ \frac{k_4}{k_{-4}} &= \frac{[E][P]}{[C_3]}.\end{aligned}$$

Multiplying these four equations together, we get

$$\frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} \frac{k_3}{k_{-3}} \frac{k_4}{k_{-4}} = \frac{\cancel{[C_1]} \cancel{[C_2]} \cancel{[C_3]} [P] \cancel{[E]} [P]}{\cancel{[E]} [R] \cancel{[C_1]} [CO_2] \cancel{[C_2]} \cancel{[C_3]}} = \frac{[P]^2}{[R][CO_2]} = K.$$

(c) From the kinetic data, we have

$$K = \frac{(1 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1})(5 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1})(7.5 \text{ s}^{-1})(7.5 \text{ s}^{-1})}{(0.5 \text{ s}^{-1})(0.15 \text{ s}^{-1})(5 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1})(5 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1})} = 1.5 \times 10^6.$$

This is larger than the separately measured equilibrium constant, so there's something wrong with the rate constants.

3. Equilibrium approximation for step 1:

$$k_1[\text{NO}_{2(\text{g})}]^2 \approx k_{-1}[\text{N}_2\text{O}_{4(\text{g})}]. \quad (1)$$

Equilibrium approximation for step 2:

$$k_2[\text{N}_2\text{O}_{4(\text{g})}] \approx k_{-2}[\text{N}_2\text{O}_{4(\text{surface})}]. \quad (2)$$

SSA for ONONO_2 :

$$\begin{aligned} \frac{d[\text{ONONO}_{2(\text{surface})}]}{dt} &= k_3[\text{N}_2\text{O}_{4(\text{surface})}] - k_4[\text{ONONO}_{2(\text{surface})}][\text{NO}_{2(\text{g})}] \\ &\quad - k_5[\text{ONONO}_{2(\text{surface})}][\text{H}_2\text{O}_{(\text{surface})}] \approx 0. \end{aligned} \quad (3)$$

We're going to use these three equations to eliminate the concentrations of the intermediates N_2O_4 (both gas-phase and on the surface) and ONONO_2 . From equation 1, we have

$$[\text{N}_2\text{O}_{4(\text{g})}] \approx k_1[\text{NO}_{2(\text{g})}]^2/k_{-1}.$$

Equation 2 gives

$$[\text{N}_2\text{O}_{4(\text{surface})}] \approx k_2[\text{N}_2\text{O}_{4(\text{g})}]/k_{-2}.$$

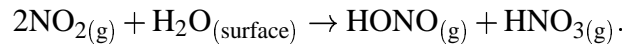
Combining the two, we get

$$[\text{N}_2\text{O}_{4(\text{surface})}] \approx \frac{k_1 k_2 [\text{NO}_{2(\text{g})}]^2}{k_{-1} k_{-2}}.$$

We can substitute this last relation into equation 3, and then solve for the ONONO_2 concentration:

$$\begin{aligned} k_3 \frac{k_1 k_2 [\text{NO}_{2(\text{g})}]^2}{k_{-1} k_{-2}} - k_4 [\text{ONONO}_{2(\text{surface})}] [\text{NO}_{2(\text{g})}] - k_5 [\text{ONONO}_{2(\text{surface})}] [\text{H}_2\text{O}_{(\text{surface})}] &\approx 0. \\ \therefore [\text{ONONO}_{2(\text{surface})}] &\approx \frac{k_1 k_2 k_3 [\text{NO}_{2(\text{g})}]^2}{k_{-1} k_{-2} (k_4 [\text{NO}_{2(\text{g})}] + k_5 [\text{H}_2\text{O}_{(\text{surface})}])}. \end{aligned}$$

Note that the fourth reaction doesn't contribute to the overall reaction. All it does is turn the intermediate ONONO_2 back into N_2O_4 . The overall reaction is therefore



The rate of reaction is thus

$$\begin{aligned} v &= \frac{d[\text{HNO}_{3(\text{g})}]}{dt} = k_5 [\text{ONONO}_{2(\text{surface})}] [\text{H}_2\text{O}_{(\text{surface})}] \\ &= \frac{k_1 k_2 k_3 k_5 [\text{H}_2\text{O}_{(\text{surface})}] [\text{NO}_{2(\text{g})}]^2}{k_{-1} k_{-2} (k_4 [\text{NO}_{2(\text{g})}] + k_5 [\text{H}_2\text{O}_{(\text{surface})}])}. \end{aligned} \quad (4)$$

Since k_2 and k_4 are both proportional to the area, these rate “constants” will increase in containers with larger surface areas. The exact dependence will however depend on the concentrations. If $k_4[\text{NO}_{2(\text{g})}] \gg k_5[\text{H}_2\text{O}_{(\text{surface})}]$, the rate reduces to

$$v = \frac{k_1 k_2 k_3 k_5 [\text{H}_2\text{O}_{(\text{surface})}] [\text{NO}_{2(\text{g})}]}{k_{-1} k_{-2} k_4},$$

which should be roughly independent of area since both k_2 and k_4 increase with area. On the other hand, if $k_4[\text{NO}_{2(\text{g})}] \ll k_5[\text{H}_2\text{O}_{(\text{surface})}]$,

$$v = \frac{k_1 k_2 k_3 [\text{NO}_{2(\text{g})}]^2}{k_{-1} k_{-2}}$$

which will be proportional to the area since k_2 is proportional to the area. If the two terms in the denominator of the rate expression 4 are of similar sizes, then the best we can say is that the rate will depend on the area in a complicated way.