

Practice Chem 6 Exam 1

1. (a) If the reaction was first order, $[A]/[A]_0$ would fall from 0.5 to 0.25 in the same time as it took to fall from 1.0 to 0.5, since the first-order half-life is constant. The graph shows, however, that the time to fall from 0.5 to 0.25 is *twice* the initial half-life, and this is characteristic of a second-order reaction.

Thus, the rate must be $-(1/2)d[A]/dt = k[A]^2$. Since $t_{1/2} = 1/(2[A]_0k)$ for a second-order rate law, and for $[A]_0 = 2.5 \times 10^{-3} \text{ M}$ and $t_{1/2} = 4 \text{ s}$ (read from the graph), $k = 50 \text{ M}^{-1} \text{ s}^{-1}$.

(b) Since $-(1/2)d[A]/dt = d[B]/dt$, the rate of production of B, $d[B]/dt$, equals $k[A]^2$. At $t = 10 \text{ s}$, we read from the graph $[A]/[A]_0 = 0.3$, or $[A] = (0.3)(2.5 \times 10^{-3} \text{ M}) = 7.5 \times 10^{-4} \text{ M}$ so that $d[B]/dt = (50 \text{ M}^{-1} \text{ s}^{-1})(7.5 \times 10^{-4} \text{ M})^2 = 2.81 \times 10^{-5} \text{ M s}^{-1}$.

2. The two rate constants and their associated temperatures lead to an activation energy (using $\ln(k_2/k_1) = -E_a/R(1/T_2 - 1/T_1)$ to find E_a) of 88.4 kJ mol^{-1} . This value along with either rate constant and its associated temperature can be used in the same equation along with the new temperature, 320 K , to find the rate constant at 320 K . It is $1.85 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Since the rate law is $\text{Rate} = k[\text{C}_2\text{H}_5\text{I}][\text{OH}^-]$ but $[\text{C}_2\text{H}_5\text{I}]_0 \gg [\text{OH}^-]$, we can assume that $[\text{C}_2\text{H}_5\text{I}]$ stays nearly constant during the reaction and define an effective first-order rate constant $k_{\text{eff}} = (1.85 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})([\text{C}_2\text{H}_5\text{I}]_0) = 0.462 \times 10^{-3} \text{ s}^{-1}$, and from this easily find the half-life from $t_{1/2} = \ln(2)/k = 1498 \text{ s}$.

3. Solve $k_{\text{col}} = (\text{relative speed})(\text{reaction cross-section})(\text{steric factor})(N_0)(1000 \text{ L m}^{-3})$ for the reaction cross-section, πd^2 , and solve for d , the reaction distance. The cross-section is $6.0 \times 10^{-19} \text{ m}^2$, and $d = 4.38 \times 10^{-10} \text{ m} = 4.38 \text{ \AA}$.

4. The steady-state assumption applied to intermediate AM: $d[\text{AM}]/dt = 0 = k_1[\text{A}][\text{M}] - k_{-1}[\text{AM}] - k_2[\text{A}][\text{AM}]$. Rate of production of A_2 product: $d[\text{A}_2]/dt = k_2[\text{A}][\text{AM}]$. Solve steady-state expression for $[\text{AM}]$ and find $[\text{AM}] = k_1[\text{A}][\text{M}]/(k_{-1} + k_2[\text{A}])$. Substitute into rate law: $d[\text{A}_2]/dt = k_2[\text{A}]\{k_1[\text{A}][\text{M}]/(k_{-1} + k_2[\text{A}])\} = k_1k_2[\text{A}]^2[\text{M}]/(k_{-1} + k_2[\text{A}])$. If $k_{-1} \gg k_2[\text{A}]$, this simplifies to $d[\text{A}_2]/dt = (k_1k_2/k_{-1})[\text{A}]^2[\text{M}]$.

5. (a) Using $T_1 = 698.6 \text{ K}$, $k_1 = 67.0 \text{ M}^{-1} \text{ s}^{-1}$ and $T_2 = 666.8 \text{ K}$, $k_2 = 15.6 \text{ M}^{-1} \text{ s}^{-1}$, the Arrhenius equation in the form

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

with $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ yields $E_a = 177 \text{ kJ mol}^{-1}$.

(b) $K_{\text{eq}} = (\text{forward rate constant})/(\text{reverse rate constant}) = (15.6 \text{ M}^{-1} \text{ s}^{-1})/(0.259 \text{ M}^{-1} \text{ s}^{-1}) = 60.2$.

(c) If the forward activation energy is 177 kJ mol^{-1} from part (a), and the reverse activation energy is 191 kJ mol^{-1} , the the reaction itself must be *exothermic* by $(191 - 177) \text{ kJ mol}^{-1} = 14 \text{ kJ mol}^{-1}$. The graph would have the $\text{H}_2 + \text{I}_2$ reactants at an initial energy, rising to the transition state activated complex 177 kJ mol^{-1} higher, then falling 191 kJ mol^{-1} to products 2 HI some 14 kJ mol^{-1} lower than the reactants.

6. (a) $\text{Rate} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = -\frac{d[\text{F}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NO}_2\text{F}]}{dt}$

(b) Atomic F is the intermediate: $\frac{d[\text{F}]}{dt} = k_1[\text{NO}_2][\text{F}_2] - k_{-1}[\text{NO}_2\text{F}][\text{F}] - k_2[\text{NO}_2][\text{F}]$

(c) If k_2 is smallest, then (2) is the slow, rate-limiting step and step (1) is in equilibrium:

$$\text{Rate of step (2)} = \frac{d[\text{NO}_2\text{F}]}{dt} = k_2[\text{NO}_2][\text{F}]$$

$$\text{Step (1) in equilibrium: } K_{\text{eq}} = \frac{k_1}{k_{-1}} = \frac{[\text{NO}_2\text{F}][\text{F}]}{[\text{NO}_2][\text{F}_2]} \quad \text{so that} \quad [\text{F}] = \frac{K_{\text{eq}}[\text{NO}_2][\text{F}_2]}{[\text{NO}_2\text{F}]}$$

$$\text{Net reaction rate} = \frac{1}{2} \frac{d[\text{NO}_2\text{F}]}{dt} = \frac{k_2 K_{\text{eq}} [\text{NO}_2]^2 [\text{F}_2]}{2[\text{NO}_2\text{F}]}$$

Note that you can arrive at this same expression using the steady-state approximation for the F atom intermediate:

$$\frac{d[\text{F}]}{dt} = k_1[\text{NO}_2][\text{F}_2] - k_{-1}[\text{NO}_2\text{F}][\text{F}] - k_2[\text{NO}_2][\text{F}] = 0 \quad \text{so that} \quad [\text{F}] = \frac{k_1[\text{NO}_2][\text{F}_2]}{k_{-1}[\text{NO}_2\text{F}] + k_2[\text{NO}_2]}$$

but if k_2 is smallest, then

$$[\text{F}] = \frac{k_1[\text{NO}_2][\text{F}_2]}{k_{-1}[\text{NO}_2\text{F}] + k_2[\text{NO}_2]} \approx \frac{k_1[\text{NO}_2][\text{F}_2]}{k_{-1}[\text{NO}_2\text{F}]} = \frac{K_{\text{eq}}[\text{NO}_2][\text{F}_2]}{[\text{NO}_2\text{F}]}$$

which is the same expression for [F] that the prior equilibrium approach derived.