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 \(t_{1/2} = 4\) 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 \(t = 10\) 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 \(d[B]/dt = (50 \text{ M}^{-1} \text{ s}^{-1})(7.5 \times 10^{-4} \text{ M})^2 = 2.81 \times 10^{-5} \text{ M} \text{ s}^{-1}\).

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[C_2H_5I] \text{[OH}^-\] but \([C_2H_5I]_0 >> \text{[OH}^-\]\), we can assume that \([C_2H_5I]\) stays nearly constant during the reaction and define an effective first-order rate constant \(k_{\text{eff}} = (1.85 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})([C_2H_5I]_0) = 0.462 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}\) and from this easily find the half-life from \(t_{1/2} = \ln(2)/k = 1498\) 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, \(\pi d^2\), and solve for \(d\), the reaction distance. The cross-section is \(6.0 \times 10^{-19} \text{ m}^2\), and \(d = 4.38 \times 10^{-10} \text{ m} = 4.38 \text{ Å}\).

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

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 \(\ln(k_1/k_2) = -E_a/R (1/T_1 - 1/T_2)\) 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 \(H_2 + I_2\) 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) Rate = \(-1/2 d[NO_2]/dt = -d[F_2]/dt = +1/2 d[NO_2F]/dt\)

(b) Atomic F is the intermediate: \(d[F]/dt = k_1[NO_2][F_2] - k_{-1}[NO_2F][F] - k_2[NO_2][F]\)

(c) If \(k_2\) is smallest, then (2) is the slow, rate-limiting step and step (1) is in equilibrium:
Rate of step (2) = $\frac{d[NO_2F]}{dt} = k_2[NO_2][F]$

Step (1) in equilibrium: $K_{eq} = \frac{k_1}{k_1} = \frac{[NO_2F][F]}{[NO_2][F_2]}$ so that $[F] = \frac{K_{eq}[NO_2][F_2]}{[NO_2F]}$

Net reaction rate = $\frac{1}{2} \frac{d[NO_2F]}{dt} = \frac{k_2K_{eq}[NO_2]^2[F_2]}{2[NO_2F]}$

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

$\frac{d[F]}{dt} = k_1[NO_2][F_2] - k_{-1}[NO_2F][F] - k_2[NO_2][F] = 0$ so that $[F] = \frac{k_1[NO_2][F_2]}{k_{-1}[NO_2F] + k_2[NO_2]}$

but if $k_2$ is smallest, then

$[F] = \frac{k_1[NO_2][F_2]}{k_{-1}[NO_2F] + k_2[NO_2]} \approx \frac{k_1[NO_2][F_2]}{k_{-1}[NO_2F]} = \frac{K_{eq}[NO_2][F_2]}{[NO_2F]}$

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