

2.

The rate constant for the reaction $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ is $k = 0.522 \text{ L mol}^{-1} \text{ s}^{-1}$ at 592 K and $k = 5.030 \text{ L mol}^{-1} \text{ s}^{-1}$ at 656 K. What is the activation energy, E_a , for the reaction? (Assume a one-step reaction.)

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln \frac{k(656\text{K})}{k(592\text{K})} = \frac{E_a}{R} \left(\frac{1}{592\text{K}} - \frac{1}{656\text{K}} \right)$$

$$E_a = R \left(\frac{1}{592\text{K}} - \frac{1}{656\text{K}} \right)^{-1} \ln \frac{k(656\text{K})}{k(592\text{K})} = 114 \text{ kJ/mol}$$

$\downarrow 0.00831477 \text{ kJ K}^{-1} \text{ mol}^{-1}$ $\leftarrow 5.030 \text{ L mol}^{-1} \text{ s}^{-1}$
 $\leftarrow 0.522 \text{ L mol}^{-1} \text{ s}^{-1}$

3. A reaction $2A \rightarrow B$ is second order in A and goes to completion in a reaction vessel of constant volume and temperature. The half-life of A is $t_{1/2} = 1$ hr. Initially, only A is present and the pressure is 1 bar. Determine the total pressure after 2 hr and at equilibrium.

Pressure is proportional to concentration, so we can work in terms of P .

$$r = -\frac{1}{2} \frac{dP_A}{dt} = k P_A^2 \Rightarrow \frac{dP_A}{P_A^2} = -2k dt \Rightarrow \int_{P_{A0}}^{P_A} \frac{dP_A}{P_A^2} = -2k \int_0^t dt$$

$$(1) \quad \frac{1}{P_{A0}} - \frac{1}{P_A} = -2kt$$

Obtain k from half-life:

$$\frac{1}{P_{A0}} - \frac{1}{\frac{1}{2} P_{A0}} = -2k t_{1/2} \Rightarrow k = \frac{1}{2} \text{ hr}^{-1} \text{ bar}^{-1}$$

$$\text{From (1), } \frac{1}{P_A} = \frac{1}{P_{A0}} + 2kt \Rightarrow P_A = \frac{P_{A0}}{1 + 2kt P_{A0}}$$

$$P_B = P_{B0} + \frac{1}{2} (P_{A0} - P_A) = \frac{1}{2} (P_{A0} - P_A)$$

$$\text{After 2 hr: } P_A = 0.33 \text{ bar, } P_B = 0.33 \text{ bar} \Rightarrow \boxed{P_{\text{tot}} = 0.66 \text{ bar}}$$

At equilibrium, all of A is converted to B:

$$P_A = 0 \quad P_B = \frac{1}{2} (P_{A0} - P_A) = 0.5 \text{ bar} \quad \boxed{P_{\text{tot}} = 0.5 \text{ bar}}$$

4.

Consider the following overall reaction in basic aqueous solution:



- a. The following tables gives initial rate data. Determine the rate law for formation of $[\text{OI}^-]$ from these data. [NOTE: $[\text{OH}^-]$ will appear in the rate law even though it does not appear in the overall reaction. This is because the reaction occurs in basic solution and OH^- is involved in the mechanism.]

$[\text{I}^-]_0$ (M)	$[\text{OCl}^-]_0$ (M)	$[\text{OH}^-]_0$ (M)	r_0 (M s^{-1})
2.0×10^{-3}	1.5×10^{-3}	1.00	1.8×10^{-4}
4.0×10^{-3}	1.5×10^{-3}	1.00	3.6×10^{-4}
2.0×10^{-3}	3.0×10^{-3}	2.00	1.8×10^{-4}
4.0×10^{-3}	3.0×10^{-3}	1.00	7.2×10^{-4}

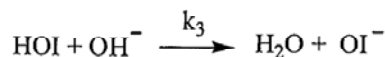
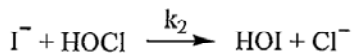
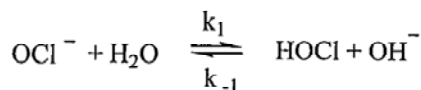
$$r = \frac{d[\text{OI}^-]}{dt} = k [\text{I}^-]^\alpha [\text{OCl}^-]^\beta [\text{OH}^-]^\delta$$

Doubling $[\text{I}^-]$ alone doubles rate $\Rightarrow \alpha = 1$

Doubling $[\text{I}^-]$ and $[\text{OCl}^-]$ quadruples rate $\Rightarrow \beta = 1$

Doubling $[\text{OCl}^-]$ and $[\text{OH}^-]$ leave rate unchanged $\Rightarrow \delta = -1$

- b. The following mechanism has been proposed. Derive the rate law for the formation of OI^- based on this mechanism, applying the steady state approximation where needed. [NOTE: $[\text{H}_2\text{O}]$ and $[\text{OH}^-]$ may appear in your final rate law because both are present at substantial concentrations in basic, aqueous solution. Do not apply the steady state approximation to these species.]



$$v = \frac{d[\text{O}_2]}{dt} = k_3 [\text{HOI}] [\text{OH}^-]$$

intermediate

$$s-s: \frac{d[\text{HOI}]}{dt} = 0 = k_2 [\text{I}^-] [\text{HOCl}] - k_3 [\text{HOI}] [\text{OH}^-]$$

intermediate

$$\frac{d[\text{HOCl}]}{dt} = 0 = k_1 [\text{OCl}^-] [\text{H}_2\text{O}] - k_{-1} [\text{HOCl}] [\text{OH}^-] - k_2 [\text{I}^-] [\text{HOCl}]$$

$$[\text{HOCl}] = \frac{k_1 [\text{OCl}^-] [\text{H}_2\text{O}]}{k_{-1} [\text{OH}^-] + k_2 [\text{I}^-]}$$

$$[\text{HOI}] = \frac{k_2 [\text{I}^-] [\text{HOCl}]}{k_3 [\text{OH}^-]} = \frac{k_1 k_2 [\text{OCl}^-] [\text{I}^-] [\text{H}_2\text{O}]}{k_3 [\text{OH}^-] (k_{-1} [\text{OH}^-] + k_2 [\text{I}^-])}$$

$$v = \frac{k_1 k_2 k_3 [\text{OCl}^-] [\text{I}^-] [\text{H}_2\text{O}] [\text{OH}^-]}{k_3 [\text{OH}^-] (k_{-1} [\text{OH}^-] + k_2 [\text{I}^-])} = \frac{k_1 k_2 [\text{OCl}^-] [\text{I}^-] [\text{H}_2\text{O}]}{k_{-1} [\text{OH}^-] + k_2 [\text{I}^-]}$$

- c. State whether the rate law determined from the mechanism is consistent with the empirical rate law determined from the data in part (a). Discuss any restrictions necessary for the two rate laws to be consistent.

If $k_2 [\text{I}^-] \ll k_{-1} [\text{OH}^-]$, or will be the case under sufficiently basic conditions, the rate law simplifies to:

$$v = \frac{k_1 k_2}{k_{-1}} [\text{H}_2\text{O}] [\text{I}^-] [\text{OCl}^-] [\text{OH}^-]^{-1}$$

k_{eff}

In aqueous solution, $[\text{H}_2\text{O}]$ is essentially constant, so it may be included in the effective rate constant, k_{eff} . Clearly, the mechanism is consistent with the data.

5. Suppose that an enzyme has a turnover number of 10^4 min^{-1} and a molar mass of 60,000 g/mol. How many moles of substrate can be turned over per hour per gram of enzyme if the substrate concentration is twice the Michaelis constant? (Assume that the substrate concentration is maintained constant, for example by a preceding enzymatic reaction.)

$$v = \frac{v_{\max} [S]}{[S] + K_M} = \frac{2}{3} v_{\max} = \frac{2}{3} k_{\text{cat}} [E]_0$$

$\nwarrow \frac{1}{2}[S]$
 $\uparrow k_{\text{cat}}[E]_0$

If $[S]$ is constant, $v = \frac{d[P]}{dt} = \frac{\Delta n_s L^{-1}}{\Delta t} = \frac{2}{3} k_{\text{cat}} [E]_0$

$\uparrow n_{E_0} L^{-1}$

$$\Delta n_s = \frac{2}{3} k_{\text{cat}} n_{E_0} \Delta t = 6.67 \text{ mol}$$

$\uparrow 10^4 \text{ min}^{-1}$
 \uparrow
 $\nwarrow 60 \text{ min}$

$$n_{E_0} = 1 \text{ g} \cdot \frac{1}{6 \times 10^4} \text{ mol g}^{-1} = (6 \times 10^4)^{-1} \text{ mol}$$

6.67 mol substrate turned over per hour per gram enzyme