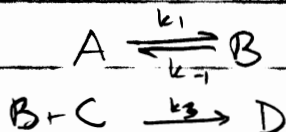


S212
(graded)



$$\frac{d[B]}{dt} = k_3[B][C]$$

$$\frac{d[B]}{dt} = k_1[A] - k_3[B][C] - k_{-1}[B] = 0$$

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

$$k_1[A] = [B](k_3[C] + k_{-1})$$

$$\frac{d[C]}{dt} = -k_3[C]$$

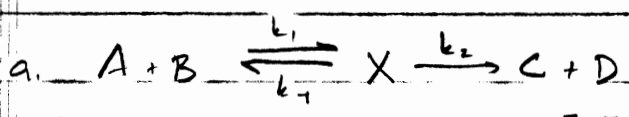
$$[B] = \frac{k_1[A]}{k_3[C] + k_{-1}}$$

$$\frac{d[D]}{dt} = k_3[C] \left(\frac{k_1[A]}{k_3[C] + k_{-1}} \right)$$

At high P, B will tend to react to form D as soon as it forms
(to consume C of which there is a lot thus lower the pressure). This will make k_{-1} small relative to $[C]$,
giving: rate = $\frac{k_3[C]k_1[A]}{k_3[C] + k_{-1} \rightarrow 0} = k_1[A] \rightarrow 1^{\text{st}} \text{ order}$

At low P, the amount of C will be small (low P = low conc.) so
 $(k_3[C] + k_{-1}) \approx k_{-1}$, giving: rate = $\frac{k_3[C]k_1[A]}{k_{-1}} = k[A][C] \rightarrow 2^{\text{nd}} \text{ order}$

S2.5
graded



$[A]_0 = 2 \quad [B]_0 = 1 \quad [X]_0 = [C]_0 = [D]_0 = 0$

Ultimately X will be converted to C+D (irreversibly) so at the rxn. endpoint $[X] = 0$. The reaction goes to completion.

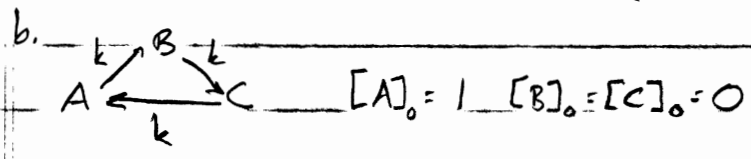
- Can then calc. $[C] + [D]$ by stoichiometry:

B is the limiting reagent, so $[C] = [D] = 1$

$[B] = 0$

$[A] = 2 - 1 = 1$ (limited by amt. of B so only 1 mol A used)

graded



$\frac{d[A]}{dt} = -k[A] + k[C]$

$\frac{d[B]}{dt} = k[A] - k[B]$

$\frac{d[C]}{dt} = -k[C] + k[B]$

All three species are essentially intermediates so $\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = 0$

$-kA + kC = kA - kB$	} k's cancel \rightarrow	$-[A] + [C] = [A] - [B]$
$-kA + kC = -kC + kB$		$-A + C = -C + B$
$kA - kB = -kC + kB$		$A - B = -C + B$

$-2A = -C - B \rightarrow 2A = (C+B)$

$-2C = -A - B \rightarrow 2C = \frac{1}{2}(C+B) + B$

$-2B = -A - C \rightarrow \frac{2}{2}C = \frac{3}{2}B \rightarrow [C] = [B]$

$2A = C + B = 2B \rightarrow [A] = [B]$

so, $[A] = [B] = [C] \rightarrow \therefore$ all must be $\frac{1}{3}[A]_0 = \boxed{\frac{1}{3}}$

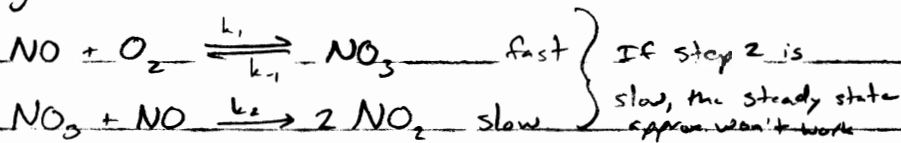
S2.8



told overall third order, but without proposed mech, cannot know

exact rate law (i.e., it could be $k[\text{NO}]^2[\text{O}_2]$ or $k[\text{NO}][\text{O}_2]^2$, etc...)

Problem gives mechanism in words:



can derive rate law from proposed elementary steps:

$$\begin{aligned} \frac{1}{2} \frac{d[\text{NO}_2]}{dt} &= k_2 [\text{NO}_3] [\text{NO}] \\ \frac{d[\text{NO}_2]}{dt} &= 2 k_2 [\text{NO}_3] [\text{NO}] \end{aligned}$$

↑ NO_3 is an intermediate - must eliminate
from expression

use equilibrium expression:

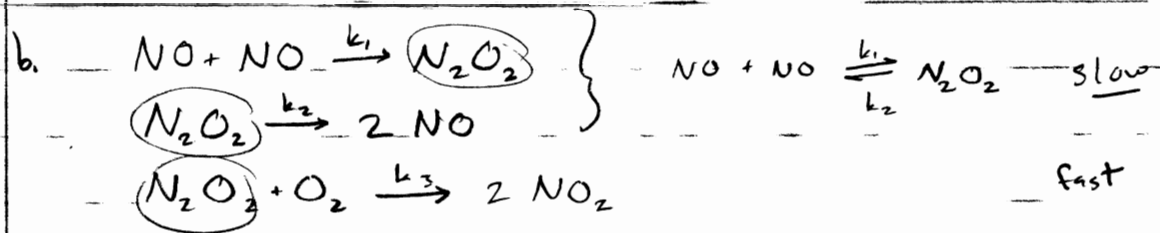
$$k_1 [\text{NO}] [\text{O}_2] = k_{-1} [\text{NO}_3]$$

$$[\text{NO}_3] = \frac{k_1 [\text{NO}] [\text{O}_2]}{k_{-1}}$$

substitute: $\frac{d[\text{NO}_2]}{dt} = 2 k_2 \left(\frac{k_1}{k_{-1}} \right) [\text{NO}] [\text{O}_2] [\text{NO}]$

$$\boxed{\frac{d[\text{NO}_2]}{dt} = k [\text{NO}]^2 [\text{O}_2]} \quad (\text{third order})$$

S2.8
graded



$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_3 [\text{N}_2\text{O}_2] [\text{O}_2]$$

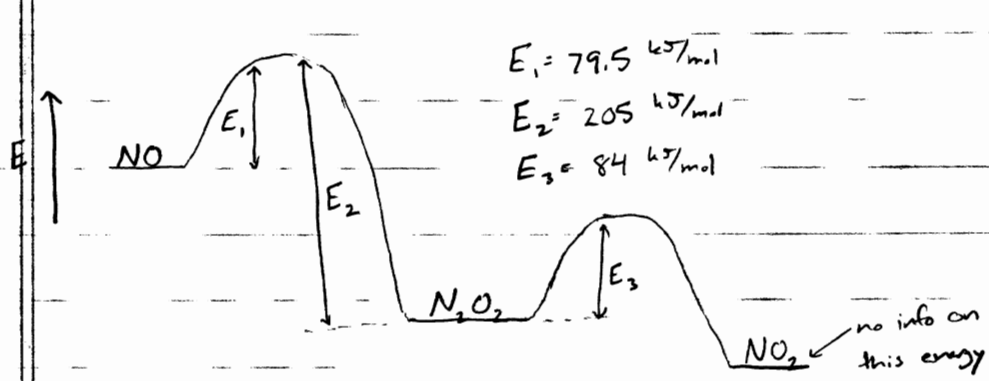
$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1 [\text{NO}]^2 - k_2 [\text{N}_2\text{O}_2] - k_3 [\text{N}_2\text{O}_2] [\text{O}_2] \approx 0$$

$$k_1 [\text{NO}]^2 = k_2 [\text{N}_2\text{O}_2] + k_3 [\text{N}_2\text{O}_2] [\text{O}_2]$$

$$[\text{N}_2\text{O}_2] = \frac{k_1 [\text{NO}]^2}{k_2 + k_3 [\text{O}_2]}$$

$$\frac{d[\text{NO}_2]}{dt} = 2k_3 \left(\frac{k_1 [\text{NO}]^2}{k_2 + k_3 [\text{O}_2]} \right) [\text{O}_2] = \boxed{2k_1 k_3 \left(\frac{[\text{O}_2] [\text{NO}]^2}{k_2 + k_3 [\text{O}_2]} \right)}$$

so N_2O_2 must be a weakly bound intermediate



$$E_a = E_1 + E_3 - E_2 = (79.5 + 84 - 205) \text{ kJ/mol} = -41.5 \text{ kJ/mol}$$

If very little rxn. 3 compared to rxn. 2 then $k_2 \gg k_3$, so

$$\frac{d[\text{NO}_2]}{dt} \approx 2k_1 k_3 \left(\frac{[\text{O}_2] [\text{NO}]^2}{k_2} \right) = k [\text{O}_2] [\text{NO}]^2$$

$$k = \frac{2k_1 k_3}{k_2}$$

$$k = A e^{-E_a/RT} \quad \frac{2k_1 k_3}{k_2} = \frac{2(A_1 e^{-E_1/RT})(A_3 e^{-E_3/RT})}{(A_2 e^{-E_2/RT})}$$

$$= (\text{constant}) e^{-(E_1 + E_3 - E_2)/RT}$$

So $E_a = E_1 + E_3 - E_2$

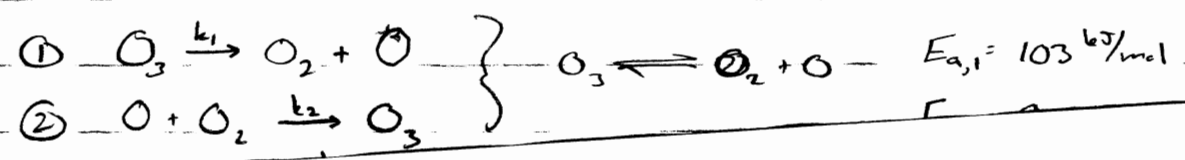
S2.8
graded

c. - If the mechanism in a applies and the second step is much slower than the first, then it should be possible to detect an accumulation of the NO_2 intermediate.

- If a large concentration of O_2 is used, the first mechanism will follow pseudo-first order kinetics and the second will follow pseudo-second order kinetics.

- Because of the negative E_a , mech. B should lead to increased rate at lower T.

S2.9



11/15

H1.11

graded

$$F(v) dv = 4\pi v^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

fraction greater than speed of light:

$$\int_{3 \times 10^8}^{\infty} F(v) dv$$

$$= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{3 \times 10^8}^{\infty} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

OR

The answer in Houston indicates that he integrated the energy distribution fn., $G(\mathcal{E})$

$$\text{If } v > 3 \times 10^8 \text{ m/s, } \mathcal{E} > \frac{1}{2}(m)(3 \times 10^8 \text{ m/s})^2$$

$$m = 28.9 \text{ g/mol} \left(\frac{1 \text{ mol}}{6.02 \times 10^{23}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 4.7 \times 10^{-26} \text{ kg}$$

$$\mathcal{E} > \frac{1}{2}(4.7 \times 10^{-26} \text{ kg})(3 \times 10^8 \text{ m/s})^2 = 2 \times 10^{-9} \text{ J}$$

$$G(\mathcal{E}) d\mathcal{E} = 2\pi \left(\frac{1}{\pi k_B T} \right)^{3/2} \sqrt{\mathcal{E}} \exp\left(-\frac{\mathcal{E}}{k_B T}\right) d\mathcal{E}$$

fraction greater than speed of light:

$$\int_{2 \times 10^{-9} \text{ J}}^{\infty} 2\pi \left(\frac{1}{\pi k_B T} \right)^{3/2} \sqrt{\mathcal{E}} \exp\left(-\frac{\mathcal{E}}{k_B T}\right) d\mathcal{E}$$

$$= 2\pi \left(\frac{1}{\pi k_B T} \right)^{3/2} \int_{2 \times 10^{-9}}^{\infty} \mathcal{E}^{1/2} \exp\left(-\frac{\mathcal{E}}{k_B T}\right) d\mathcal{E}$$

$$\text{eqn. 1.41} \quad = \frac{2}{\sqrt{\pi}} a e^{-a^2} + \text{erfc}(a) \quad a = \left(\frac{\mathcal{E}^*}{k_B T} \right)^{1/2} \quad \mathcal{E}^* = 2 \times 10^{-9} \text{ J}$$

$$a = \left(\frac{2 \times 10^{-9} \text{ J}}{1.38 \times 10^{-23} \text{ J/K} \cdot 300 \text{ K}} \right)^{1/2} = 7 \times 10^5$$

$$\text{erfc}(a) = 1 - \text{erf}(a) \quad \leftarrow \text{from Fig 1.16 erf}(a) \rightarrow 1 \text{ if } a \geq 2.5$$

$$\text{fraction } > c = \frac{2}{\sqrt{\pi}} (7 \times 10^5) e^{-(7 \times 10^5)^2} = 8 \times 10^5 e^{-5 \times 10^{11}} \quad \leftarrow \text{tiny but non-zero}$$