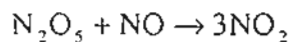


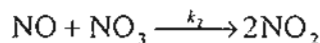
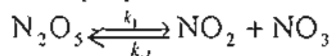
~ key ~

# Reaction Mechanisms/Kinetics In-Class Practice Problems

1. Nitrogen pentoxide reacts with nitric oxide in the gas phase according to the stoichiometric equation



The following mechanism has been proposed.



- (a) Assume that the steady-state approximation can be applied to  $\text{NO}_3$  and derive an equation for the rate of production of  $\text{NO}_2$ .

$$v(t) = \frac{d[\text{NO}_2]}{dt} = 2k_2[\text{NO}][\text{NO}_3] + k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3]$$

defined

$$\frac{d[\text{NO}_3]}{dt} = 0 = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}][\text{NO}_3]$$

$$[\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]}$$

$$v(t) = \frac{d[\text{NO}_2]}{dt} = 2k_2[\text{NO}] \left( \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]} \right) + k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2] \left( \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]} \right)$$

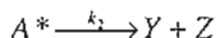
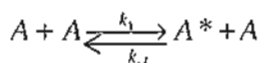
$$= \frac{2k_2k_1[\text{NO}][\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]} + \frac{k_1[\text{N}_2\text{O}_5](k_{-1}[\text{NO}_2] + k_2[\text{NO}])}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]} - \frac{k_{-1}k_1[\text{NO}_2][\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]}$$

$$= \frac{3k_1k_2[\text{NO}][\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}]}$$

- (b) How does the rate of production of  $\text{NO}_2$  relate to the rate of consumption of  $\text{N}_2\text{O}_5$ ?

$$\frac{1}{3} \frac{d[\text{NO}_2]}{dt} = - \frac{d[\text{N}_2\text{O}_5]}{dt} \quad \text{so} \quad \frac{d[\text{NO}_2]}{dt} = -3 \frac{d[\text{N}_2\text{O}_5]}{dt}$$

2. A. Lindemann (Trans Faraday Soc., 17, 598(1922)) proposed the following mechanism for a unimolecular gas reaction



The species  $A^*$  is an energized molecule that is present in low concentrations.

- (a) Apply the steady-state approximation to  $A^*$  and obtain an expression for the rate (i.e.,  $d[Y]/dt$  or  $d[Z]/dt$ ) in terms of  $[A]$ ,  $k_1$ ,  $k_{-1}$ , and  $k_2$ .

$$V(t) = k_2 [A^*]$$

$$\frac{d[A^*]}{dt} = 0 = k_1 [A]^2 - k_{-1} [A^*][A] - k_2 [A^*]$$

$$[A^*] = \frac{k_1 [A]^2}{k_{-1} [A] + k_2}$$

$$V(t) = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2}$$

- (b) Identify the conditions under which the rate is first order and those under which it is second order, and give expressions for the observed first and second order rate constants in terms of  $k_1$ ,  $k_{-1}$  and  $k_2$ .

1st order  
 $k_{-1} [A] \gg k_2$

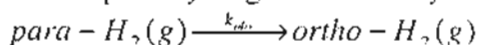
$$V(t) = \frac{k_1 k_2 [A]}{k_{-1}}$$

2nd order  
 $k_2 \gg k_{-1} [A]$

$$V(t) = k_1 [A]^2$$

$\uparrow$   
 $k_{obs}$

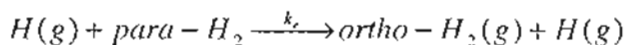
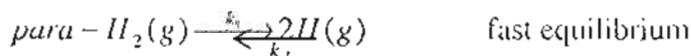
3. The rate law for the reaction of para-hydrogen to ortho-hydrogen



is

$$\frac{d[ortho-H_2]}{dt} = k_{obs} [para-H_2]^{3/2}$$

Show that the following mechanism is consistent with this rate law and express  $k_{obs}$  in terms of the rate constants for the individual steps of the reaction mechanism.



$$V(t) = \frac{d[ortho-H_2]}{dt} = k_2 [H][para-H_2]$$

$$k_c = k_1/k_{-1} = \frac{[H]^2}{[para-H_2]}$$

$$[H] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} [para-H_2]^{1/2}$$

$$V(t) = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [para-H_2]^{3/2}$$

$\uparrow$   
 $k_{obs}$