

1. If the reaction is not elementary, one cannot know the order. If the reaction is elementary, the order is 2<sup>nd</sup> in either direction.

$$\frac{-[A]}{dt} = k_1[A][B]$$

$$\frac{d[A]}{dt} = k_{-1}[R]^2$$

2.  $\frac{1}{2} \frac{-d[\text{NO}_2]}{dt} = -2 \frac{d[\text{O}_2]}{dt} = \frac{d[\text{N}_2\text{O}_5]}{dt}$

3. The same. ( $r_A = \frac{d[A]}{dt}$ , regardless of how the stoichiometric equation is written.)

4.  $1760 \text{ (s}^{-1}\text{)}$   
 $6 \text{ (mol/m}^3\text{)}$

5. No, they are not.  $-r_A = -\frac{1}{3}r_B = \frac{1}{2}r_R = -\frac{[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{1}{2} \frac{d[R]}{dt}$

6.  $3.0 \times 10^{-4} \frac{\text{L}}{\text{mol} \cdot \text{hr}}$

7. a)  $\text{atm}^{-1} \text{ hr}^{-1}$

b) One mole of an ideal gas at 400°K occupies 32.82 L·atm .

$$\frac{PV}{n} = RT = 0.082053 \left( \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) \times 400(\text{K}) = 32.82 \left( \frac{\text{L} \cdot \text{atm}}{\text{mol}} \right)$$

$$3.66 \left( \frac{1}{\text{atm} \cdot \text{hr}} \right) \times 32.82 \left( \frac{\text{L} \cdot \text{atm}}{\text{mol}} \right) = 1.20 \times 10^2 \left( \frac{\text{L}}{\text{mol} \cdot \text{hr}} \right)$$

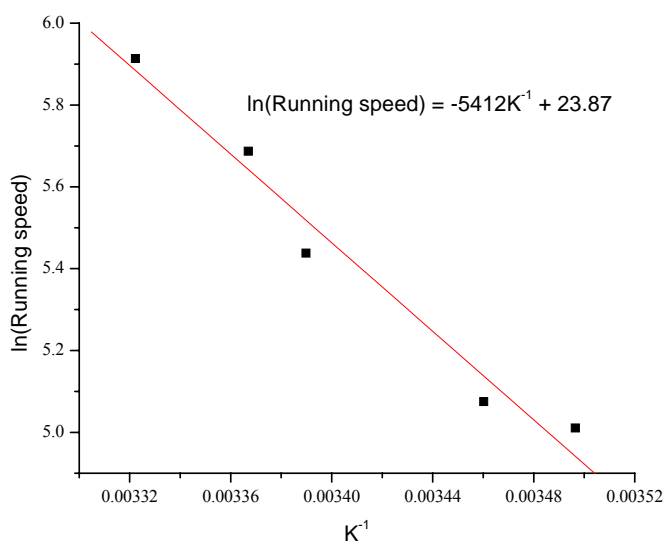
8. If  $1 \gg k_2[\text{N}_2\text{O}]$ , then the reaction is second order in  $\text{N}_2\text{O}$ , and second order overall.  
 If  $1 \ll k_2[\text{N}_2\text{O}]$ , then the reaction is first order in  $\text{N}_2\text{O}$ , and first order overall.  
 If  $1 \approx k_2[\text{N}_2\text{O}]$ , then the order cannot be specified.

$$9. \quad \ln \frac{k_1}{k_2} = -\frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = -\frac{300 \text{ kJ mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{923} - \frac{1}{773} \right) \text{ K}^{-1} = 7.586$$

$$\frac{k_1}{k_2} = 1.97 \times 10^3 \text{ times faster}$$

$$10. \quad 2.74 \times 10^2 \text{ kJ mol}^{-1}$$

$$11. \quad E = 45.0 \text{ kJ mol}^{-1}$$



$$12. \quad 1.5 \text{ times}$$

$$13. \quad \text{Growth rate} = 1/\text{Growing days.}$$

$$28.2 \text{ kJ mol}^{-1}$$

$$14. \quad \text{At } 60^\circ\text{F (288.6 K)}, k = 1.333 \text{ chirps s}^{-1}$$

$$\text{At } 80^\circ\text{F (299.7 K)}, k = 2.667 \text{ chirps s}^{-1}$$

$$E = 44.9 \text{ kJ mol}^{-1}$$

$$15. \quad \text{Reaction order} = \ln 3 / \ln 2 = 1.585$$

$$16. \quad \text{Order in A} = 1/2. \quad \text{Order in B} = 2/3.$$

$$17. \quad \text{Order in A} = 1. \quad \text{Order in B} = 2/3.$$

18. First, assume second step is rate limiting.

$$\frac{d[\text{O}_2]}{dt} = k_3[\text{NO}_3^*]$$

Apply steady-state approximation to  $\text{NO}_3^*$  and  $\text{NO}^*$ :

$$\frac{d[\text{NO}_3^*]}{dt} = 0 = k_1[\text{N}_2\text{O}_5] - k_2[\text{NO}_2][\text{NO}_3^*] - k_3[\text{NO}_3^*] - k_4[\text{NO}^*][\text{NO}_3^*]$$

$$[\text{NO}_3^*] = \frac{k_1[\text{N}_2\text{O}_5]}{k_2[\text{NO}_2] + k_3 + k_4[\text{NO}^*]}$$

$$\frac{d[\text{NO}^*]}{dt} = 0 = k_3[\text{NO}_3^*] - k_4[\text{NO}^*][\text{NO}_3^*]$$

$$[\text{NO}^*] = \frac{k_3}{k_4}$$

$$\text{Therefore, } [\text{NO}_3^*] = \frac{k_1[\text{N}_2\text{O}_5]}{k_2[\text{NO}_2] + 2k_3}$$

Inserting this into the rate equation yields:

$$\frac{d[\text{O}_2]}{dt} = \frac{k_1 k_3 [\text{N}_2\text{O}_5]}{k_2 [\text{NO}_2] + 2k_3}$$

But, this yields first-order kinetics only if  $k_2[\text{NO}_2] \ll k_3$ , which contradicts the assumption that step 2 is rate-limiting.

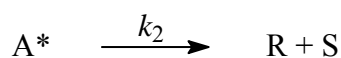
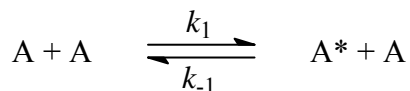
Therefore, assume step 3 is rate-limiting:

$$\frac{d[\text{O}_2]}{dt} = k_4[\text{NO}^*][\text{NO}_3^*] = \frac{k_1 k_3 [\text{N}_2\text{O}_5]}{k_2 [\text{NO}_2] + 2k_3}$$

If  $k_2 \ll k_3$ , then this analysis is consistent with first-order kinetics:

$$\frac{d[\text{O}_2]}{dt} = \frac{k_1 [\text{N}_2\text{O}_5]}{2}$$

19. a)



$$\frac{d[\text{R}]}{dt} = k_2[\text{A}^*]$$

$$\text{But, } K_{eq} = \frac{k_1}{k_{-1}} = \frac{[A^*]}{[A]}; \text{ therefore } \frac{d[R]}{dt} = k_2 K_{eq} [A]$$

- b) One could attempt to prove the existence of  $A^*$ , and better yet, measure its steady-state concentration.

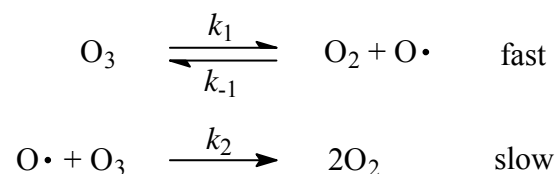
$$\frac{d[A^*]}{dt} = 0 = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$$

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

Or, one could see the effect on rate of a scavenger or trapping agent for the proposed intermediate,  $A^*$ .

20. a) Overall first order.

b)



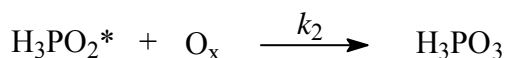
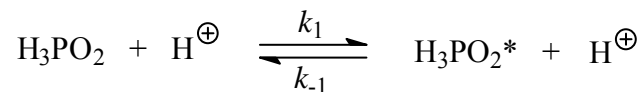
$$\text{Rate} = -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \frac{d[\text{O}_2]}{dt} = k_2[\text{O}\cdot][\text{O}_3]$$

$$[\text{O}\cdot] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} = K_{eq} \frac{[\text{O}_3]}{[\text{O}_2]}$$

$$\frac{1}{3} \frac{d[\text{O}_2]}{dt} = k_2 K_{eq} [\text{O}_3]^2 [\text{O}_2]^{-1}$$

To test the mechanism, one would wish to prove the participation of  $\text{O}\cdot$  and demonstrate inhibition using common free radical scavengers.

21.



$$\frac{d[\text{H}_3\text{PO}_3]}{dt} = k_2[\text{H}_3\text{PO}_2^*][\text{O}_x]$$

Application of the steady-state approximation to the active intermediate yields,

$$[\text{H}_3\text{PO}_2^*] = \frac{k_1[\text{H}_3\text{PO}_2][\text{H}^\oplus]}{k_{-1}[\text{H}^\oplus] + k_2[\text{O}_x]}$$

and therefore,

$$\frac{d[\text{H}_3\text{PO}_3]}{dt} = \frac{k_1 k_2 [\text{H}^\oplus][\text{O}_x][\text{H}_3\text{PO}_2]}{k_{-1}[\text{H}^\oplus] + k_2[\text{O}_x]}$$

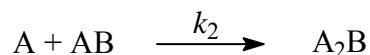
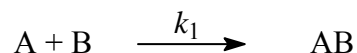
At low  $[\text{O}_x]$ , the right term of the denominator is negligible, and,

$$\frac{d[\text{H}_3\text{PO}_3]}{dt} = \frac{k_1 k_2 [\text{O}_x][\text{H}_3\text{PO}_2]}{k_{-1}}$$

At high  $[\text{O}_x]$ , the left term is negligible, and,

$$\frac{d[\text{H}_3\text{PO}_3]}{dt} = k_1[\text{H}^\oplus][\text{H}_3\text{PO}_2]$$

22. With the first step rate limiting, the following mechanism is consistent with the experimental rate law:



23.  $K = \frac{k_1}{k_2} = \frac{[\text{X}]}{[\text{A}][\text{E}]}$  and  $[\text{E}_0] = [\text{E}] + [\text{X}]$

- a) Combining the two equations above yields,  $[\text{X}] = \frac{k_1[\text{A}][\text{E}_0]}{k_2 + k_1[\text{A}]}$

The rate expression is then given by,

$$-r_A = k_3[\text{X}] = \frac{k_1 k_3 [\text{A}][\text{E}_0]}{k_2 + k_1[\text{A}]} = \frac{k_3 [\text{A}][\text{E}_0]}{\frac{k_2}{k_1} + [\text{A}]}$$

- b) In this case, apply steady-state approximation.

$$\frac{d[X]}{dt} = k_1[A][E] - k_2[X] - k_3[X] = 0$$

Substituting  $[E]_o = [E] + [X]$  and solving for  $[X]$  yields,

$$[X] = \frac{k_1[A][E_o]}{(k_2 + k_3) + k_1[A]}$$

The rate expression is then given by,

$$-r_A = k_3[X] = \frac{k_1 k_3 [A][E_o]}{(k_2 + k_3) + k_1[A]} = \frac{k_3 [A][E_o]}{\left(\frac{k_2 + k_3}{k_1}\right) + [A]}$$

Note that the only difference is that the fast equilibrium approach imposes the restriction that  $k_2 \gg k_3$ ; whereas the steady-state approach does not.