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1. Consider a reaction obeying the overall stoichiometry: $2 A(g) + B(g) \rightarrow D(g)$
   Proposed mechanism is:

   Step1: $A(g) + B(g) \leftrightarrows C(g)$ (reached equilibrium quickly) K_{eq}

   Step2: $C(g) + A(g) \longrightarrow D(g)$ (super slow) k_2 **RDS**
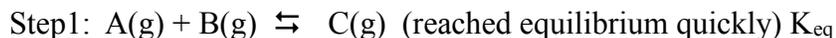
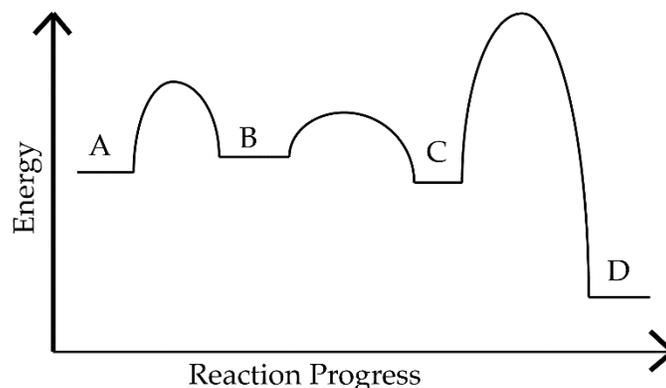   Write the rate law for this reaction: **rate = $k_2 \cdot K \cdot [A]^2 [B]$**

2. Consider the reaction progress diagram below for **A $\leftrightarrows$ D**. Circle the reaction step below that corresponds to the rate limiting step (i.e. rate determining step).
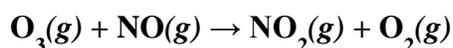
   a.
      A $\leftrightarrows$ B

      B $\leftrightarrows$ C

      C $\leftrightarrows$ D exothermic

   b. Is the A $\leftrightarrows$ D reaction endothermic or **exothermic**?

   c. Which step is an endothermic reaction? A $\leftrightarrows$ B

3. The net reaction of atmospheric ozone with nitric oxide and its rate law are:

   $$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$

   reaction rate= $k[O_3(g)][NO(g)]$ (from an experiment)

   Two pathways proposed for this reaction are:

   Mechanism I: $O_3(g) \leftrightarrows O(g) + O_2(g)$ fast equilibrium, $K_{(ii)}$
   ** $NO(g) + O(g) \rightarrow NO_2(g)$ slow, $k_{(ii)}$**

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   Net RXN: **$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$**
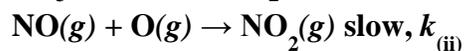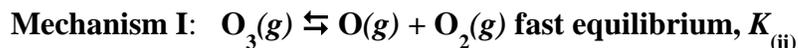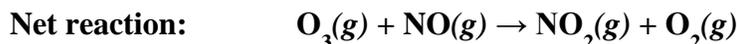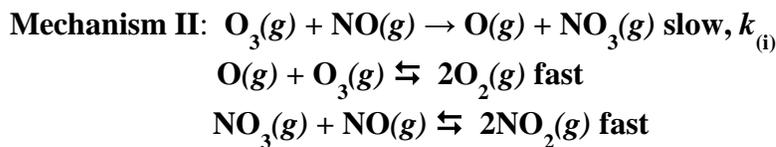
   Which step is the rate-determining step (RDS)? Why? **Step 2, because it is the slowest**

   Write the rate law for the RDS: **Rate = k_1 (NO)(O)**

What is the rate law for the overall reaction that is predicted by this mechanism (remove intermediates)?   **Rate** $= k_1\ K_1 \dfrac{(NO)(O_3)}{(O_2)}$

Sketch the reaction progress diagram for **Mechanism 1** (assuming that reaction is exothermic):

Mechanism II: $O_3(g) + NO(g) \rightarrow O(g) + NO_3(g)$ **slow,** $k_{(i)}$
$\qquad\qquad\quad O(g) + O_3(g) \leftrightarrows 2O_2(g)$ **fast**
$\qquad\qquad\quad NO_3(g) + NO(g) \leftrightarrows 2NO_2(g)$ **fast**

Net reaction: $O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$

Which step is the rate determining step (RDS)? **first step because slow**

Write the rate law for the RDS: **rate = k₂(O₃)(NO)**

What is the rate law for the overall reaction predicted by this mechanism? How does this compare to the rate law determined with RDS? Is it different, why/why not?

rate = k₂(O₃)(NO)

Sketch the reaction progress diagram for **Mechanism 2** (assuming that reaction is exothermic):

Which mechanism 1 or 2 is best supported by an experiment? **Mechanism 2 matches the experimental rate law.**

4. The following reaction (elementary step) has a favored frequency factor $A_F = 5 \times 10^6$/m.sec. Forward and reverse activation energies are 80 kJ/mol and 60. kJ/mol, respectively. Assume T=300K.
$$A + B \rightarrow C$$

   a. What is $\Delta H°$ of the reaction?

   $\Delta H°_{rxn} = E_{a(forward)} - E_{a(reverse)} =$ **80 kJ/mol - 60 kJ/mol = 20kJ/mol   Endothermic**
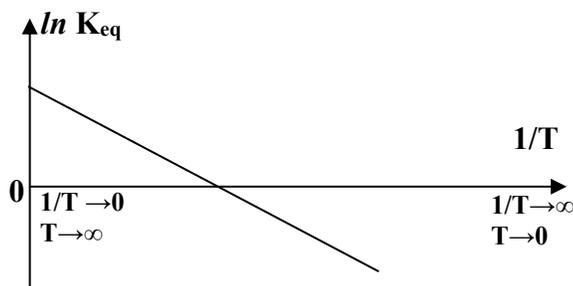
   b. If the reverse frequency factor is 5 times smaller than the forward frequency factor, what is $\Delta S°$ of the reaction?

   $\Delta S°_{rxn} = R\ \ln \dfrac{A_f}{A_r} = R2.3\log \dfrac{A_f}{A_r} =$ **8.314(J/molK)*2.3*log5=13.38J/molK=13.4**

c. Draw the line on the graph of lnK_{eq} verses 1/T for this reaction? And answer the following questions using two expressions below(Hint: y=mx+b):

$$\ln K_{eq} = \frac{-\Delta H^{\circ}_{rxn}}{R} \cdot \frac{1}{T} + \frac{\Delta S^{\circ}_{rxn}}{R}$$

$$\ln \frac{k_f}{k_r} = \frac{-(E_a(f)-E_a(r))}{R} \cdot \frac{1}{T} + \ln \frac{A_f}{A_r}$$

d. Discuss which one of the following is true for this reaction and at what temperatures:

- $k_f < k_r$ at low T
- $k_f = k_r$ at $T = T_{eq}$
- **$k_f > k_r$ at high T**

e. Decide which one of the following is true for this reaction you drew and at what temperatures:

- $A_f < A_r$
- **$A_f > A_r$ independent of temperature**
- $A_f = A_r$

f. Are E_a and the Arrhenius factor temperature-dependent?   No

5. Consider the following exothermic reaction:
$$3A\ (g) \leftrightarrows B\ (g) + C\ (l)$$
If the temperature is increased, what will happen to each of the quantities below?

E_a(forward)	increase	decrease	**stay the same**
K	increase	**decrease**	stay the same
k_f	**increase**	decrease	stay the same
k_r	**increase**	decrease	stay the same
A(reverse)	increase	decrease	**stay the same**
Order of the reaction:	increase	decrease	**stay the same**
Rate of the revers reaction:	**increase**	decrease	stay the same
Rate of the forward reaction:	**increase**	decrease	stay the same

Which rate constant will increase more with temperature for this reaction? k_f or **k_r**

3

6. A first order reaction is 75% complete after 100 seconds. Calculate the rate constant k and $t_{1/2}$ for this reaction.

Means 25% remains 2 half lifes $t_{1/2} = t/2 = 50s$

$2.3\log(25/100) = -kt$

$k = 13.8 \times 10^{-3}$ 1/s   Or $t_{1/2} = 0.693/k = 0.693/13.8 \times 10^{-3} = 50$ s

7. The half-life of a radioactive isotope is 11 days. How long does it take for the isotope to decay **by** 10%? (1.7 days)

$$\frac{N_n}{N_0} = \frac{90}{100} = \left(\frac{1}{2}\right)^n ; \quad \log(N_{fin}N_{in}) = n \log(1/2); \quad n=0.15; \quad t=t_{1/2} \cdot n = 1.7 \text{days}$$

8. Bromophenol blue decomposes by a first-order process with a half-life of 33 minutes. What fraction remains after 75 minutes?

$n = 75/33 = 25/11 = 2.2727$

$$\frac{A_t}{A_0} = \left(\frac{1}{2}\right)^{2.27} ; \quad \log(A_t/A_0) = 2.2727 \log(1/2); \quad A_t/A_0 = 0.2069 \text{ or } 21\%$$

9. A certain flu virus can be thermally decomposed in humans in 6.0 days at normal body temperature, 37 °C. If a person has a fever, with temperature of 41 °C, the same virus can be decomposed in 2.0 days. What is the activation energy of the virus decomposition reaction? Express your answer in kJ/mol, to one significant figure.

$$k=1/\text{time}$$

$$\ln\left(\frac{k_{310}}{k_{314}}\right) = \ln\left[\frac{Ae^{-E_a/R \cdot 310}}{Ae^{-E_a/R \cdot 314}}\right] = -\frac{E_a}{R}\left(\frac{1}{310} - \frac{1}{314}\right)$$

$$\ln(1/3) = -\frac{E_a}{R}\left(\frac{1}{310} - \frac{1}{314}\right) \quad E_a = 222kJ$$

10. The following reaction $k_1(\text{at } T_1=350K)=9.4 \times 10^{-6}$(1/s) and $k_2(\text{at } T_2=400K)=6.9 \times 10^{-4}$ (1/s)

   a. What is the overall rate order of the reaction? **1st order** (Hint :look at the units of k)

   b. Write an expression to solve for activation energy of the forward reaction that does not include Arrhenius factor. **What is E_a of the forward reaction?**
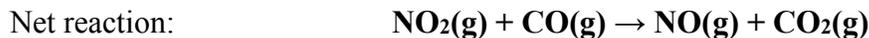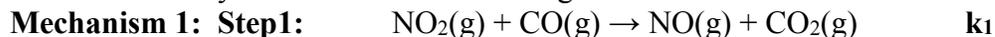
$$\frac{k_1}{k_2} = \frac{Ae^{-\frac{E_A}{RT_1}}}{Ae^{-\frac{E_A}{RT_2}}} ; \quad \ln\frac{k_1}{k_2} = \frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{E_A}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

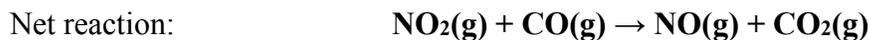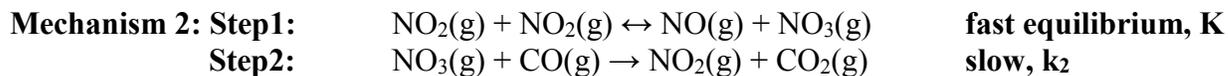$$E_A = \ln\frac{k_1}{k_2} RT_1 T_2 / (T_1 - T_2) = 100kJ/mol$$

   c. Write an expression to calculate Arrhenius factor of the forward reaction. **What is A_f of the forward reaction?**

$$A = \frac{k_1}{e^{-\frac{E_A}{RT_1}}} = 7.9 \times 10^9 \text{ }^1/s$$
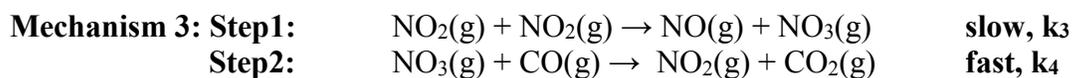
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11. Possible Pathways for the reaction of Nitrogen Dioxide with Carbon Monoxide:

Mechanism 1: Step1: $\qquad$ $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ $\qquad$ **k₁**

Net reaction: $\qquad$ **$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$**

What is the rate law predicted by this mechanism? **Rate = k₁[NO₂][CO**

Mechanism 2: Step1: $\qquad$ $NO_2(g) + NO_2(g) \leftrightarrow NO(g) + NO_3(g)$ $\qquad$ **fast equilibrium, K**
$\qquad$ **Step2:** $\qquad$ $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ $\qquad$ **slow, k₂**

Net reaction: $\qquad$ **$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$**

What is the rate law predicted by this mechanism? **Rate $= \dfrac{k_2\ K\ [NO2]^2[\ CO]}{[NO]}$**

Mechanism 3: Step1: $\qquad$ $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ $\qquad$ **slow, k₃**
$\qquad$ **Step2:** $\qquad$ $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ $\qquad$ **fast, k₄**
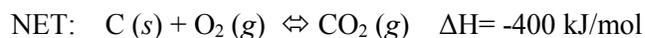
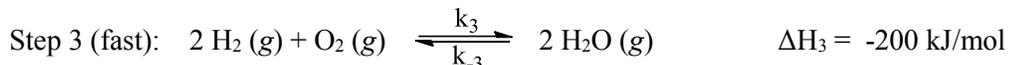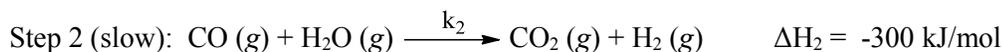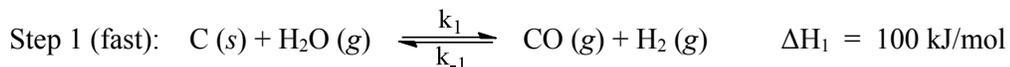Net reaction: $\qquad$ **$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$**

What is the rate law predicted by this mechanism? **Rate = k₃[NO₂]²**

Propose how you could experimentally distinguish between mechanism 1, 2 and 3.

<u>Double concentration of NO_2; Double concentration of NO; Double concentration of CO</u>

12. Below are the proposed elementary steps and enthalpies for the mechanism of burning coal, C (s).

Step 1 (fast): $C(s) + H_2O(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO(g) + H_2(g)$ $\qquad$ $\Delta H_1 = 100$ kJ/mol

Step 2 (slow): $CO(g) + H_2O(g) \xrightarrow{k_2} CO_2(g) + H_2(g)$ $\qquad$ $\Delta H_2 = -300$ kJ/mol

Step 3 (fast): $2 H_2(g) + O_2(g) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2 H_2O(g)$ $\qquad$ $\Delta H_3 = -200$ kJ/mol

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NET: $C(s) + O_2(g) \Leftrightarrow CO_2(g)$ $\Delta H = -400$ kJ/mol

a. Identify each of the following molecules as either a reactant, product, intermediate, or catalyst for the net reaction.

$\quad$ C (s): reactant $\qquad$ H_2O (g): _ catalyst $\qquad$ CO (g): intermediate

$\quad$ H_2 (g): intermediate $\qquad$ O_2 (g): reactant $\qquad$ CO_2 (g): product

b. Write the rate law for the reaction corresponding to the mechanism above.

$$\text{Rate}=k_2 \cdot \frac{k_1}{k_{-1}} \sqrt{\frac{k_3}{k_{-3}}} \cdot [H_2O] \cdot [O_2]^{1/2}$$

c. Sketch the reaction progress profile with appropriate relative energies.

13. The first order reaction is 20% complete after 100 seconds. What is rate constant k and $t_{1/2}$ for this reaction?

$$\frac{N_n}{N_0} = \frac{80}{100} = \left(\frac{1}{2}\right)^n; \quad n=0.3219=0.3 \quad ; t_{1/2} = t/n= 310.6 \text{ s}=300\text{s}; \quad k = \frac{0.693}{t_{1/2}} = 2.2 \cdot 10^{-3} \text{ 1/s}$$

14. Metastable thallium-201 decays with a half-life of 48 hr by γ emission to stable thallium-201. The detected γ radiation is used to diagnose heart function. What fraction of metastable thallium-201 *remains* after 24 hr?

$$t_{1/2} = \frac{t_{passed}}{n} = 48; \quad n=0.5$$

$$\frac{N_n}{N_0} = \left(\frac{1}{2}\right)^{1/2} \quad \log(N_{in}/N_{final})=1/2 \log(1/2)=-0.15; \quad \frac{N_n}{N_0} =10^{-0.15}=0.71$$

15. A first order reaction is 75% complete after 100. seconds. Calculate the rate constant k and $t_{1/2}$ for this reaction.
Means 25% remains 2 half lifes $t_{1/2}$ =t/2=50s

$$\ln \frac{25}{100} = -kt$$

$$k=13.9 \cdot 10^{-3} \text{ 1/s} \qquad \text{Or} \quad t_{1/2} = \frac{ln2}{k} = 0.693/13.8 \cdot 10^{-3} = 50 \text{ s}$$

16. The half-life of a radioactive isotope is 11 days. How long does it take for the isotope to decay **by** 10%? (1.5 days)

$$\frac{N_n}{N_0} = \frac{90}{100} = \left(\frac{1}{2}\right)^n$$

17. A sample decays 25% in 15 minutes. What is the half-life of this first-order process?

$$\frac{N_n}{N_0} = \frac{75}{100} = \left(\frac{1}{2}\right)^n \quad n=0.415 \quad \text{half-life}=15\text{min}/0.415 =36 \text{ min}$$

18. A first order reaction is 40% complete in 120s. What are the values of k and $t_{1/2}$?

$$\frac{A_t}{A_0} = \frac{60}{100} = \left(\frac{1}{2}\right)^n \quad n=0.74 \quad t_{1/2}=120/n =163\text{s} \quad k=\ln2/ t_{1/2}=4.26*10^{-3} \text{ 1/s}$$