CH102 Spring 2019
Discussion #14
Chapter 18

Student name________________________ TA name_______________________ Section_____________________

Things you should know when you leave Discussion today:

1. $aA_{(aq)} + bB_{(aq)} \rightarrow cC_{(aq)}$ $\quad Rate\left(\frac{M}{sec}\right) = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} = k[A]^x[B]^y$
2. Pathways or reaction mechanisms
    - Individual steps
    - Elementary reactions
    - Rate determining step (RDS)
    - Derivation of the rate law from reaction mechanisms
3. Reaction rate temperature dependence: $k = Ae^{\frac{-E_a}{RT}}$ *and* $\ln k = -\frac{E_a}{R}\cdot\frac{1}{T} + \ln A$

    where: • k is rate constant • E_a is activation energy • A is Arrhenius frequency factor
4. Kinetic and thermodynamic connections
    a. Connection between enthalpy and activation energy: $\Delta H^\circ_{sys} = E_a(\text{forward}) - E_a(\text{reverse})$
        - If E_a(forward) > E_a(reverse) then $\Delta H^\circ_{sys} > 0$; Endothermic process
        - If E_a(forward) < E_a(reverse) then $\Delta H^\circ_{sys} < 0$; Exothermic process
        - If E_a(forward) = E_a(reverse) then $\Delta H^\circ_{sys} = 0$; no heat transferred

    b. Connection between Reaction Rate and Equilibrium: $Rate_{(forward)} = Rate_{(reverse)}$ at equilibrium (NOTE: $k_{reverse} \neq k_{forward}$)

    c. Connection between rate constant (k) and equilibrium constant (K): $K = \frac{k_{forward}}{k_{reverse}}$; Where $k_{forward}$ and $k_{reverse}$ are the rate constants of the forward and reverse reaction respectively and K is the equilibrium constant.

    At standard conditions:
    - If $k_f < k_r$ then $K < 1$, $\ln K < 0$, $\Delta G^\circ_{rxn} = -R\cdot T\cdot \ln K > 0$, not spontaneous
    - If $k_f = k_r$ then $K = 1$, $\ln K = 0$, $\Delta G^\circ_{rxn} = -R\cdot T\cdot \ln K = 0$, equilibrium
    - If $k_f > k_r$ then $K > 1$, $\ln K > 0$, $\Delta G^\circ_{rxn} = -R\cdot T\cdot \ln K < 0$, spontaneous

    Since Rate constant: $k = Ae^{\frac{-E_a}{RT}}$ and $\ln k = -\frac{E_a}{R}\cdot\frac{1}{T} + \ln A$

$$K = \frac{k_{forward}}{k_{reverse}} = \frac{A_{forward}}{A_{reverse}} e^{-\left(\frac{E_{a(forward)} - E_{a(reverse)}}{RT}\right)} = \frac{A_{forward}}{A_{reverse}} \cdot e^{\left(\frac{-\Delta H^\circ_{sys}}{RT}\right)}$$

$$ln\frac{k_{forward}}{k_{reverse}} = \frac{-\left(E_{a(forward)} - E_{a(reverse)}\right)}{R}\cdot\frac{1}{T} + \ln\frac{A_{forward}}{A_{reverse}}$$

$$\ln K = \frac{-\Delta H^\circ_{sys}}{R}\cdot\frac{1}{T} + \frac{\Delta S^\circ_{sys}}{R}$$

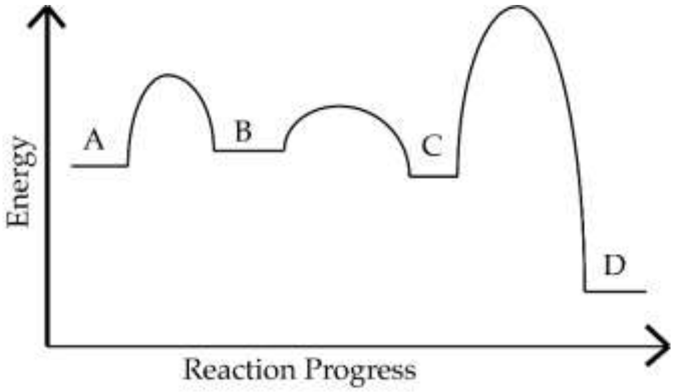
    d. Connection between entropy and Arrhenius frequency factor: $\frac{\Delta S^\circ_{sys}}{R} = \ln\frac{A_{forward}}{A_{reverse}}$

$$\ln\frac{A_{forward}}{A_{reverse}} = \ln\frac{k_{forward}}{k_{reverse}} \; at\; T \rightarrow \infty$$

- If $A_f < A_r$ then $\frac{A_{forward}}{A_{reverse}} < 1$ and $\ln\frac{A_{forward}}{A_{reverse}} < 0$ hence $\Delta S^\circ_{sys} < 0$

- If $A_f > A_r$ then $\frac{A_{forward}}{A_{reverse}} > 1$ and $\ln\frac{A_{forward}}{A_{reverse}} > 0$ hence $\Delta S°_{sys} > 0$
- If $A_f = A_r$ then $\frac{A_{forward}}{A_{reverse}} = 1$ and $\ln\frac{A_{forward}}{A_{reverse}} = 0$ hence $\Delta S°_{sys} = 0$

1. Consider the reaction progress diagram for $A \leftrightarrows D$.



   a. Circle the reaction step below that corresponds to the rate limiting step (i.e. rate determining step)

      $A \rightarrow B$

      $B \rightarrow C$

      $C \rightarrow D$

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

   c. Which step is an endothermic reaction?

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

Step 1 (fast): $C(s) + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (g) \quad CO(g) + H_2(g)$ $\qquad \Delta H_1 = 100$ 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): $2\,H_2(g) + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (g)\ 2\,H_2O(g)$ $\qquad \Delta H_3 = -200$ kJ/mol

---

Net Reaction: $\qquad \Delta H_{net} =$

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

$C_{(s)}$: ______________ $\quad H_2O_{(g)}$: ______________ $\quad CO_{(g)}$: ______________

$H_{2(g)}$: ______________ $\quad O_{2(g)}$: ______________ $\quad CO_{2(g)}$: ______________

b. Write the rate law for the reaction corresponding to the mechanism above. *Hint: Remove intermediates.*

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

3. The following reaction (elementary step) has a favored frequency factor $A_F = 5.0\cdot10^6$/M·sec. Forward and reverse activation energies are 80. kJ/mol and 60. kJ/mol, respectively. Assume T=25°C

$$A + B \rightarrow C$$

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

   b. If the reverse frequency factor is 5 times smaller than the forward frequency factor, what is $\Delta S°$ of the reaction?

   c. Draw the line on the graph of *lnK* verses 1/T for this reaction? And answer the following questions using two expressions below. *Hint: $y = mx + b$*

   d. Discuss which one of the following is true for this reaction and at what temperatures:
      - $k_f < k_r$
      - $k_f = k_r$
      - $k_f > k_r$

   e. Decide which one of the following is true for this reaction you drew and at what temperatures:
      - $A_f < A_r$
      - $A_f > A_r$
      - $A_f = A_r$

   f. Are $\mathbf{E_a}$ and the Arrhenius factors (A) temperature-dependent?

4. 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 reverse 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? $\mathbf{k_f}$ or k

5. A first order reaction is 75% complete after 100. seconds. Calculate the rate constant k and $t_{1/2}$ for this reaction. *Half Life*: $\frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n$ $t_{pass} = n \cdot t_{1/2}$ $t_{1/2} = \frac{\ln 2}{k}$

6. The half-life of a radioactive isotope is 11 days. How long does it take the isotope to decay by 10%?

7. Dinitrogen pentoxide (N_2O_5) decomposes in the gas phase to form nitrogen dioxide and oxygen gas. The reaction is first order in dinitrogen pentoxide and has a half-life of 2.80 h at 25°C. If initially the pressure of dinitrogen pentoxide in the 1.50L container is 0.967bars at 25°C, what will be the partial pressure of O_2 and N_2O_5 in the container after 240.minutes?

$t_{1/2}$=2.80 h
t_{passed}=240.min=n· $t_{1/2}$
$n=\frac{t_{passed}}{t_{1/2}} = \frac{240min}{60min} \times \frac{1hour}{2.80h} = 1.429$

	$2N_2O_5$ (g) ⇆	$4NO_2$ (g) +	O_2 (g)
Initial:	0.967bars	0	0
Change:	−0.614	+1.228	+0.307
Final:	0.353bar	1.23bar	0.307bar

$$\frac{remainig\ pressure}{inital\ pressure} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^{1.429} = 0.365$$

Remaining pressure of N_2O_5= 0.365· 0.967bars =0.353bar

8. Consider a reaction obeying the overall stoichiometry: $2\ A_{(g)} + B_{(g)} \rightarrow D_{(g)}$
The proposed mechanism is:

Step 1: $A_{(g)} + B_{(g)} \leftrightarrows C_{(g)}$ (reaches equilibrium quickly) K_{eq}
Step 2: $C_{(g)} + A_{(g)} \rightarrow D_{(g)}$ (very slow) k_2

Net RXN:

Which step is a rate determining step (RDS)? Why?

Write the rate law using RDS:

What is the rate law for the overall reaction predicted by this mechanism? *Hint: Remove intermediates.*

9. 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 = $k[O_{3(g)}][NO_{(g)}]$ (Predicted by an experiment)

Two pathways were proposed for this reaction:

Mechanism I: $O_3(g) \leftrightarrows O(g) + O_2(g)$ fast equilibrium, K_I
$NO(g) + O(g) \rightarrow NO_2(g)$ slow, k_I

Net RXN:

Which step is the RDS? Why?

Write the rate law using RDS:

What is the rate law for the overall reaction that is predicted by this **Mechanism I** (remove intermediates)?

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

Mechanism II: $O_3(g) + NO(g) \rightarrow O(g) + NO_3(g)$ slow, k_{II}
$O(g) + O_3(g) \leftrightarrows 2O_2(g)$ fast K_2
$NO_3(g) + NO(g) \leftrightarrows 2NO_2(g)$ fast K_3

Net RXN:

Which step is the RDS? Why?

Write the rate law using RDS:

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?

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

Which mechanism I or II best supported by an experiment?

10. 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

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

11. A certain flu virus can thermally decompose in humans in 6.00 days at normal body temperature, 37 °C. If a person has a fever, with temperature of 41°C, the same virus can decompose in 2.00 days. What is the activation energy of the virus decomposition reaction? Express your answer in kJ/mol, to one significant figure. *Hint k=1/time.*

k=1/time

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

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

12. The following reaction k_1*(at* $T_1 = 350.\text{K}) = 9.4\cdot10^{-6}(1/\text{s})$ and k_2 *(at* $T_2 = 400.\text{K}) = 6.90\cdot10^{-4}\,(1/\text{s})$

$$2\text{NOCl(g)} \rightarrow 2\text{NO(g)} + \text{Cl}_2\text{ (g)}$$

a. What is the overall rate order of the reaction? Hint :look at the units of k

b. Write and calculate an expression to solve for activation energy of the forward reaction that does not include Arrhenius factor.

$$\frac{k_1}{k_2} = \frac{Ae^{-\frac{E_A}{RT_1}}}{Ae^{-\frac{E_A}{RT_2}}} \quad ; \quad \ln\frac{k_1}{k_2} = \frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{E_A}{R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$$

$E_A = \ln\frac{k_1}{k_2} RT_1T_2/(T_1-T_2) = 100$kJ/mol

c. What is E_a of the forward reaction?

d. Write an expression to calculate Arrhenius factor of the forward reaction. What is A of the forward reaction?

$$A = \frac{k_1}{e^{-\frac{E_A}{RT_1}}} = 7.9*10^9 \ ^1/\text{s}$$

13. Three different mechanisms proposed for the following reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Mechanism I: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ k_1

Net RXN:

What is the rate law predicted by this mechanism?

Mechanism II: $NO_2(g) + NO_2(g) \leftrightarrows NO(g) + NO_3(g)$ K_{eq}(fast equilibrium)

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ k_2(slow)

Net RXN:

What is the rate law predicted by this mechanism:

Mechanism III: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ k_3(slow)

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast)

Net RXN:

What is the rate law predicted by this mechanism?

How you could experimentally distinguish between the different mechanisms?

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?

$t_{½} = \frac{t_{passed}}{n} = 48$; 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. The first order reaction is 20.% complete after 100. seconds. What is rate constant *k* and $t_{½}$ for this reaction? *Hint: what percent is remaining?*

$$\frac{N_n}{N_0} = \frac{80}{100} = \left(\frac{1}{2}\right)^n; \quad n=0.3219=0.3 \quad ; t_{½} = t/n = 310.6\ s = 300s; \quad k = \frac{0.693}{t_{1/2}} = 2.2 \cdot 10^{-3}\ 1/s$$

16. A sample decays 25% in 15 minutes. What is the half-life of this first-order process?
    $\ln\frac{25}{100}$=-kt ; k=$13.9\cdot10^{-3}$ 1/s Or $t_{1/2}=\frac{ln2}{k}$=$0.693/13.8\cdot10^{-3}$ =50 s

17. A first order reaction is 40.% complete in 120.s. What are the values of *k* and $t_{½}$?

Numerical Answers

1.
    a. C→D
    b. Exo
    c. A→B
2. $C_{(s)}$: reactant; $H_2O_{(g)}$: catalyst; $CO_{(g)}$: intermediate; $H_{2(g)}$: intermediate; $O_{2(g)}$: reactant; $CO_{2(g)}$: product
    a. $Rate = k_2 \cdot \frac{k_1}{k_{-1}} \sqrt{\frac{k_3}{k_{-3}}} \cdot [H_2O] \cdot [O_2]^{1/2}$
3.
    a. 20 kJ/mol
    b. 13.4
    c.
    d. $k_f > k_r$ at high T
    e. $A_f > A_r$ independent of temperature
    f. No
4. Stay the same, Decrease, Increase, Increase, Stay the same, Stay the same, Increase, Increase; k_r
5. k = 13.9×10^{-3}; t = 50s
6. 1.7 days
7. 0.307bar, 0.353bar
8. rate = $k_2 \cdot K \cdot [A]^2[B]$
9.
    a. $O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$
    b. Step 2, because it is the slowest
    c. Rate = k_i (NO)(O)
    d. Rate = k_i K (NO)(O_3)/(O_2)
    e.
    f. $O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$
    g. Step 1, because it is the slowest
    h. Rate = $k_2(O_3)(NO)$
    i. rate = $k_2(O_3)(NO)$
    j.
    k. Mechanism 2
10. 20%
11. 222kJ
12.

a. 1st order
b. 100 kJ/mol
c. 7.9×10^9

13.

14. 0.2069 or 21%

15. $t_{½} = 300$s; $k = 2.2\cdot 10^{-3}$ 1/s

16. 36min

17. $t_{½} = 163$s; $k = 4.26\cdot 10^{-3}$ 1/s

Useful information: N_A = 6.022140857 × 10^{23}/mol, R = 8.314 J/(mol K) = 0.08206 L atm/(mol K), 1 J = 1 kg m^2/s^2, 1 L = (0.1 m)^3, 1 atm = 1.01325 bar, 1 bar = 10^5 Pa, 1 Pa = 1 kg/(m s^2), $u_{rms} = \sqrt{3RT/M} = u_{\mathrm{mp}}\sqrt{3/2}$, $[p + a(n/V)^2](V - nb) = nRT$, $\Pi = icRT$, $\Delta T_{\mathrm{fp}} = -imK_{\mathrm{fp}}$, $\Delta T_{\mathrm{bp}} = +imK_{\mathrm{bp}}$, $p_{solvent} = x_{\mathrm{solvent}} p°_{\mathrm{solvent}}$, 1 V = 1 J/C, F = 96,485 C/mol, $\ln(x) = \ln(10)\log(x) = 2.303\log(x)$, $\Delta G = -n_{\mathrm{e}}FE = RT\ln(Q/K) = \Delta H - T\Delta S$, $\ln(K) = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$, at 25 °C $E = -(0.05912/n_{\mathrm{e}})$ V $\log(Q/K)$, $S = (R/N_{\mathrm{A}})\ln(W) = k_{\mathrm{B}}\ln(W)$,
$\left(\frac{1}{2}\right)^n = \frac{[A]_n}{[A]_0}$, $\ln\left(\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0}\right) = -kt$, $nt_{\mathrm{half}} = t$, $k = A\,e^{-E_a/(RT)}$