ChemE 2200 - Physical Chemistry II for Engineers
Solutions to Exercises for Calculation Session 11

1. It is useful to begin by recalling the criteria for the steady-state approximation (on B), the pre-equilibrium approximation (on A and B), and the post-equilibrium approximation (on B and C).

For the steady-state approximation, B must be consumed much faster than B is created. Stated mathematically,

$$k_{-1} + k_2 \gg k_1 + k_{-2} \qquad \text{steady-state approximation}$$

Either k_{-1} or k_2 must be much larger than *both* k_1 and k_{-2}.

For the pre-equilibrium approximation, the coupling between A and B must be much stronger than the coupling between B and C. Stated mathematically,

$$k_1 + k_{-1} \gg k_2 + k_{-2} \qquad \text{pre-equilibrium approximation}$$

Either k_1 or k_{-1} must be much larger than *both* k_2 and k_{-2}.

For the post-equilibrium approximation, the coupling between B and C must be much stronger than the coupling between A and B. Stated mathematically,

$$k_2 + k_{-2} \gg k_1 + k_{-1} \qquad \text{post-equilibrium approximation}$$

Either k_2 or k_{-2} must be much larger than *both* k_1 and k_{-1}.

(A) Apply the steady-state approximation to the intermediate B because the reaction B → C is much faster than all other reactions; $k_2 \gg k_{-2}, k_1, k_{-1}$ thus $k_{-1} + k_2 \gg k_1 + k_{-2}$. It is also valid to apply the post-equilibrium approximation because $k_2 \gg k_1, k_{-1}$ thus $k_2 + k_{-2} \gg k_1 + k_{-1}$. B and C will come to equilibrium relative to the rate that A converts to B. However, the ratio [B]/[C] will be very small at equilibrium, about $e^{-50} = 10^{-22}$.

(B) Apply the pre-equilibrium approximation to A and B. The barrier between A and B is small, so A and B will rapidly equilibrate relative to the slower reaction of B → C; $k_1 \approx k_{-1}$ and $k_1 \gg k_2$, $k_{-1} \gg k_2$, thus $k_1 + k_{-1} \gg k_2 + k_{-2}$.

(C) All rates are comparable; $k_1 \approx k_{-1} \approx k_2 \approx k_{-2}$. There are no valid approximations.

(D) Apply a post-equilibrium approximation to B and C. The barrier between B and C is small, so B and C will rapidly equilibrate relative to the slower reaction of A → B; $k_2 \approx k_{-2}$ and $k_2 \gg k_1$, $k_{-2} \gg k_1$ thus $k_2 + k_{-2} \gg k_1 + k_{-1}$. However, the ratio [B]/[C] will be very small at equilibrium, about $e^{-10} = 5 \times 10^{-5}$.

2.(A) The first-order dependence on $[F_2]$ suggests unimolecular decomposition of F_2 is the rate-limiting step. Consider this mechanism:

$$F_2 \xrightarrow{k_1} F\cdot + F\cdot \qquad \text{rate-limiting step}$$

$$NO_2 + F\cdot \xrightarrow{k_2} NO_2F \qquad \text{fast}$$

Write the rate equation for the rate of formation of NO_2F.

$$\frac{d[NO_2F]}{dt} = k_2[NO_2][F\cdot] \qquad (1)$$

Apply the steady-state approximation to the reactive free radical, F·.

$$\frac{d[F\cdot]}{dt} = 0 = 2k_1[F_2] - k_2[NO_2][F\cdot]$$

$$2k_1[F_2] = k_2[NO_2][F\cdot] \qquad (2)$$

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Substitute eqn (2) into eqn (1) to obtain the observed result.

$$\frac{d[\mathrm{NO_2F}]}{dt} = 2k_1[\mathrm{F_2}]$$

(B) The dependence on the product of $[F_2]$ and $[NO_2]$ suggests a bimolecular reaction. Try this mechanism:

$$\mathrm{NO_2} + \mathrm{F_2} \xrightarrow{k_1} \mathrm{NO_2F} + \mathrm{F\cdot} \qquad \text{rate-limiting step}$$

$$\mathrm{NO_2} + \mathrm{F\cdot} \xrightarrow{k_2} \mathrm{NO_2F} \qquad \text{fast}$$

The rate equation for this mechanism is:

$$\frac{d[\mathrm{NO_2F}]}{dt} = k_1[\mathrm{NO_2}][\mathrm{F_2}] + k_2[\mathrm{NO_2}][\mathrm{F\cdot}] \qquad (3)$$

Again apply the steady-state approximation to the reactive free radical, $F\cdot$.

$$\frac{d[\mathrm{F\cdot}]}{dt} = 0 = k_1[\mathrm{NO_2}][\mathrm{F_2}] - k_2[\mathrm{NO_2}][\mathrm{F\cdot}]$$

$$k_1[\mathrm{NO_2}][\mathrm{F_2}] = k_2[\mathrm{NO_2}][\mathrm{F\cdot}] \qquad (4)$$

Substitute eqn (4) into eqn (3) to obtain the observed result.

$$\frac{d[\mathrm{NO_2F}]}{dt} = k_1[\mathrm{NO_2}][\mathrm{F_2}] + k_1[\mathrm{NO_2}][\mathrm{F_2}]$$

$$\frac{d[\mathrm{NO_2F}]}{dt} = 2k_1[\mathrm{NO_2}][\mathrm{F_2}]$$

3. Because the rate equation is proportional to the concentration of NO_2Cl to the 1st power, the rate-limiting step probably involves a single NO_2Cl molecule. Begin with the unimolecular decomposition of NO_2Cl.

$$\mathrm{NO_2Cl} \xrightarrow{k_1} \mathrm{NO_2} + \mathrm{Cl\cdot}$$

Assume the chlorine atom collides with a NO_2Cl molecule and extracts another chlorine atom.

$$\mathrm{NO_2Cl} + \mathrm{Cl\cdot} \xrightarrow{k_2} \mathrm{NO_2} + \mathrm{Cl_2}$$

Use the second reaction to write a rate equation for $d[\mathrm{Cl_2}]/dt$.

$$\frac{d[\mathrm{Cl_2}]}{dt} = k_2[\mathrm{NO_2Cl}][\mathrm{Cl\cdot}] \qquad (1)$$

The chlorine atom is a highly reactive intermediate. Apply the steady-state approximation to the chlorine atom.

$$\frac{d[\mathrm{Cl\cdot}]}{dt} = 0 = k_1[\mathrm{NO_2Cl}] - k_2[\mathrm{NO_2Cl}][\mathrm{Cl\cdot}]$$

$$k_1[\mathrm{NO_2Cl}] = k_2[\mathrm{NO_2Cl}][\mathrm{Cl\cdot}] \qquad (2)$$

Substitute eqn (2) into eqn (1),

$$\frac{d[\mathrm{Cl_2}]}{dt} = k_1[\mathrm{NO_2Cl}]$$

Our mechanism is consistent with the observed rate equation. We could have obtained the rate equation by noting that the overall reaction rate equals the rate of the rate-limiting step.

$$r_{\mathrm{rxn}} = -\frac{1}{2}\frac{d[\mathrm{NO_2Cl}]}{dt} = -\frac{1}{2}\frac{d[\mathrm{NO_2}]}{dt} = \frac{d[\mathrm{Cl_2}]}{dt} = r_{\mathrm{RLS}}$$

We assume the unimolecular decomposition of NO_2Cl is slow and rate limiting. Therefore,

$$r_{\text{rxn}} = \frac{d[\text{Cl}_2]}{dt} = k_1[\text{NO}_2\text{Cl}]$$

An alternative for the second reaction is the collision of two chlorine atoms to form Cl_2.

$$\text{Cl}\cdot + \text{Cl}\cdot \xrightarrow{k_2} \text{Cl}_2$$

The reaction is less plausible for two reasons. First, because [Cl·] is small, the rate of this reaction, $k_2[\text{Cl}\cdot]^2$, will be slow, perhaps as slow as the first step which will yield a different rate equation. Second, a third body is required for two atoms to combine, as explained in exercise 4. The correct mechanism for combining two chlorine atoms is

$$\text{Cl}\cdot + \text{Cl}\cdot + \text{M} \xrightarrow{k_2} \text{Cl}_2 + \text{M}$$

where M is any molecule. This reaction, too, is less plausible - it requires a ternary collision in which two of the substances are in low concentration. Also, this elementary reaction would cause a factor [M] to appear in the rate equation. Assuming $[\text{M}] \approx [\text{NO}_2\text{Cl}]$, the rate equation would be second order in NO_2Cl, which is inconsistent with the observed rate equation.

4. The energy of two stationary H atoms at a large H-H distance is the asymptotic limit of the H-H potential. Two H atoms on a collision course have kinetic energy, and therefore the total energy is above the potential energy curve. When the H-H atoms collide, they rebound at the H-H distance that the potential energy curve equals the total energy. Note - this is a classical description. Of course, H-H collisions must be described by quantum mechanics. There is a finite probability the H-H distance will tunnel to negative kinetic energy. In either description, the rebounding H-H atoms will dissociate because the total energy of the H_2 molecule is greater than the energy of the dissociation limit.

   An H-H collision could create a bound H_2 if a photon is emitted during the collision. This is possible, but highly improbable. The H-H collision complex will persist for a time comparable to the inverse of a typical vibration frequency, about 10^{-15} sec. The lifetime of a vibrational excited state is roughly 10^{-8} sec. A crude estimate of the probability is therefore about 10^{-7}. It is improbable that an elementary step in a reaction mechanism is the collision of two atoms to form a diatomic molecule.

5. The rate of an elementary unimolecular reaction is the product of the concentration and the rate constant. The rate constant increases exponentially with temperature. For the overall rate to decrease with temperature, the concentration must decrease with temperature. Furthermore, the concentration must decrease exponentially with temperature, at a rate faster than the rate constant increases with temperature.

   We can show this with the reaction-coordinate energy-level diagram given in the hint. The reaction A ↔ B comes to pre-equilibrium. The ratio [B]/[A] is determined by the equilibrium constant, which is proportional to the Gibbs energy difference between A and B. Note that $\Delta\overline{G}_{\text{A}\to\text{B}} < 0$.

$$\frac{[\text{B}]}{[\text{A}]} = e^{-\Delta\overline{G}_{\text{A}\to\text{B}}/RT}$$

   The rate constant for the reaction B → C is given by Arrhenius theory,

$$k_2 = Ae^{-E_{\text{a},2}/RT}$$

   The overall reaction rate is given the by rate of the RLS, B → C

$$r_{\text{rxn}} = k_2[\text{B}] \propto e^{-E_{\text{a},2}/RT} e^{-\Delta\overline{G}_{\text{A}\to\text{B}}/RT}[\text{A}] = \exp(-(\Delta\overline{G}_{\text{A}\to\text{B}} + E_{\text{A},2})/RT)[\text{A}]$$

   Because $\Delta\overline{G}_{\text{A}\to\text{B}} + E_{\text{A},2} < 0$, the exponent in the above equation is positive. As temperature increases, the exponent gets smaller, and the reaction rate decreases.

6. Use the plotted data to determine the form of the rate equation. The data form a straight line when plotted as [A]/(d[P]/dt) vs. 1/[A].

$$\frac{[\mathrm{A}]}{\frac{d[\mathrm{P}]}{dt}} = m\frac{1}{[\mathrm{A}]} + b$$

$$\frac{[\mathrm{A}]}{\frac{d[\mathrm{P}]}{dt}} = \frac{m + b[\mathrm{A}]}{[\mathrm{A}]}$$

$$\frac{\frac{d[\mathrm{P}]}{dt}}{[\mathrm{A}]} = \frac{[\mathrm{A}]}{m + b[\mathrm{A}]}$$

$$\frac{d[\mathrm{P}]}{dt} = \frac{[\mathrm{A}]^2}{m + b[\mathrm{A}]}$$

The form of the rate equation – a sum in the denominator – suggests the steady-state approximation is applied to an intermediate.

Mechanism I. We first verify that the mechanism is consistent with the overall reaction. It is. From the second reaction, we have

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{A}][\mathrm{X}]$$

We need an expression for [X]. Apply the steady-state approximation to intermediate X.

$$\frac{d[\mathrm{X}]}{dt} = 0 = k_1[\mathrm{A}] - k_{-1}[\mathrm{X}] - k_2[\mathrm{A}][\mathrm{X}]$$

$$[\mathrm{X}] = \frac{k_1[\mathrm{A}]}{k_{-1} + k_2[\mathrm{A}]}$$

Substitute the expression for [X] into the rate equation.

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{A}][\mathrm{X}] = k_2[\mathrm{A}]\frac{k_1[\mathrm{A}]}{k_{-1} + k_2[\mathrm{A}]} = \frac{k_1 k_2[\mathrm{A}]^2}{k_{-1} + k_2[\mathrm{A}]}$$

Mechanism I is consistent with the kinetic rate data.

Mechanism II. We first verify that the mechanism is consistent with the overall reaction. It is. From the second reaction, we have

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{A}][\mathrm{Y}]$$

We need an expression for [Y]. Apply the steady-state approximation to intermediate Y.

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

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

Substitute the expression for [Y] into the rate equation.

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{A}][\mathrm{Y}] = k_2[\mathrm{A}]\frac{k_1[\mathrm{A}]^2}{k_{-1} + k_2[\mathrm{A}]} = \frac{k_1 k_2[\mathrm{A}]^3}{k_{-1} + k_2[\mathrm{A}]}$$

Mechanism II is *not* consistent with the kinetic rate data.

Mechanism III. First we verify that the mechanism is consistent with the overall reaction. It is not. The overall reaction for mechanism III is A → P, not 2A → P. Although a consistent rate equation obtains with a steady-state approximation on Z,

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2 [\mathrm{A}]^2}{k_2 + k_{-1}[\mathrm{A}]}$$

mechanism III is not consistent.

$$\boxed{\text{Only mechanism I is consistent with the kinetic rate data.}}$$

The most common error was to assume that a second-order rate equation,

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{A}]^2$$

was consistent with the kinetic rate data. But this rate equation predicts the y intercept is zero, which is not consistent.

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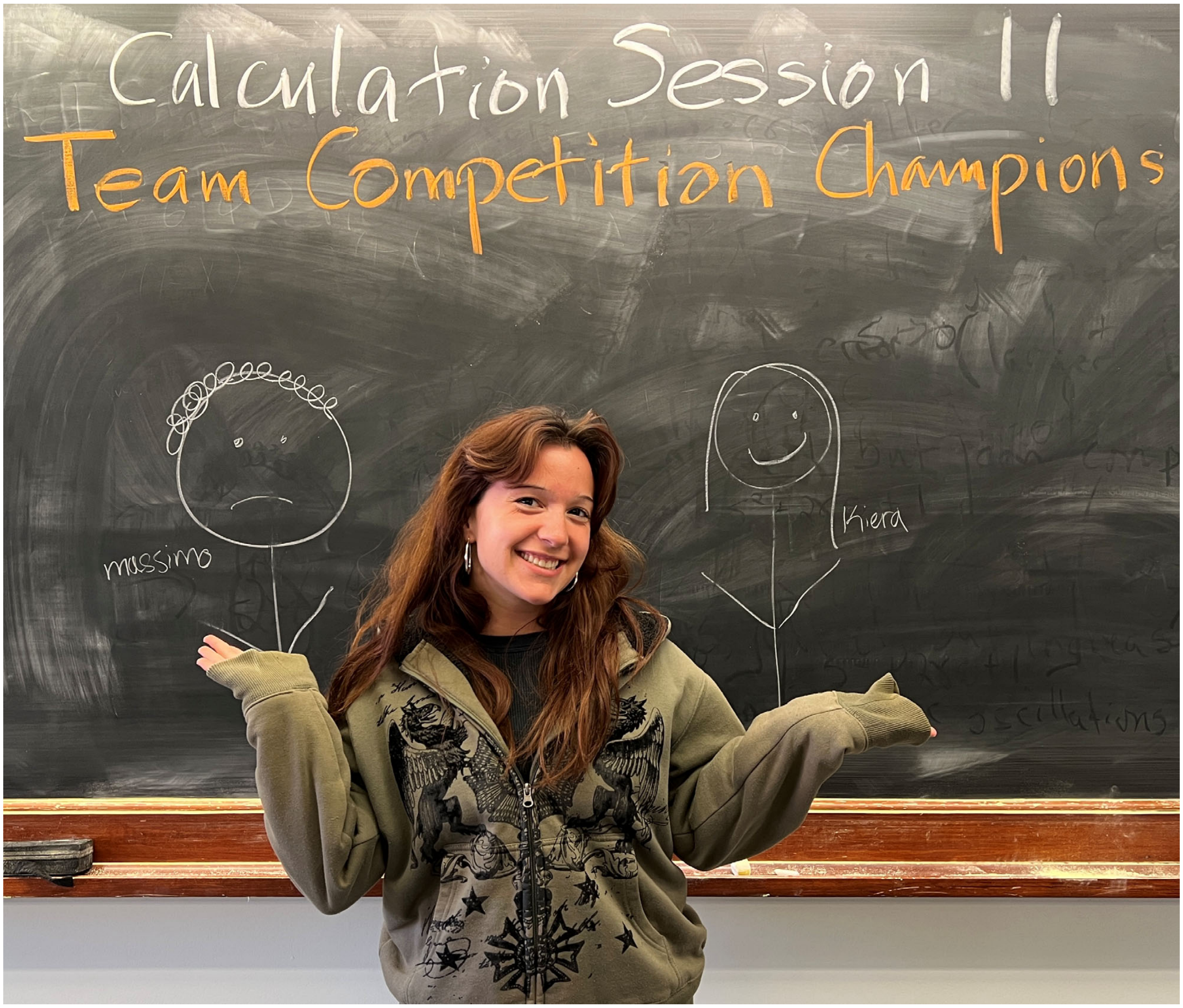
Team Competition Champions for Calculation Session 11

Team JV

Massimo Terrizzi, Julia Vizza, and Kiera Joyce



Team JV was the only team with 5 correct out of 6.

Team Competition Solution:

1. The principles for analyzing the various plots are as follows.

   $\log(-d[\mathrm{A}]/dt)$ vs. $\log[\mathrm{A}]$. A straight line has a slope n, where n is the reaction order with respect to A.

   log(half life) vs. $\log[\mathrm{A}]$. A straight line has a slope $1-n$, where n is the reaction order with respect to A.

   [A] vs. time. This plot will yield a straight line for a zero order reaction.

   $\log([\mathrm{A}]/[\mathrm{A}]_0)$ vs. time. This plot will yield a straight line for a first order reaction.

   $1/[\mathrm{A}]$ vs. time. This plot will yield a straight line for a second order reaction.

Graph 1. This is a straight line on a plot of 1/[A] vs. time, which indicates a second order reaction. This is reaction 3.

Graph 2. This is a straight line on a plot of [A] vs. time, thus $-d[\mathrm{A}]/dt$ is a constant, which indicates a zero order reaction. This is reaction 1.

Graph 3. This is a straight line on a plot of $\log([\mathrm{A}]/[\mathrm{A}]_0)$ vs. time, which indicates a first order reaction. This is reaction 2.

Graph 4. At high [A] the graph is a straight line on a plot of log(half life) vs. log[A] with a slope of 0, which indicates a first order reaction. At low [A] the graph is a straight line with a slope of −1, which indicates a second order reaction. The Lindemann reaction is first order at high [A] and second order at low [A]. Graph 4 is reaction 5.

Graph 5. At low [A] the graph is a straight line on a plot of $\log(-d[\mathrm{A}]/dt)$ vs. log[A] with a slope of one. This indicates a first order reaction with respect to A at low [A]. At high [A], the graph is a straight line with a slope of zero. This indicates a zero order reaction with respect to A at high [A].

Derive the rate equation for reaction 6. The rate of the reaction is given by the second step.

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{A}][\mathrm{C}]$$

Apply the steady state approximation to intermediate C to obtain an expression for [C].

$$\frac{d[\mathrm{C}]}{dt} = 0 = k_1[\mathrm{B}] - k_{-1}[\mathrm{C}] - k_2[\mathrm{A}][\mathrm{C}]$$

$$(k_{-1} + k_2[\mathrm{A}])[\mathrm{C}] = k_1[\mathrm{B}]$$

$$[\mathrm{C}] = \frac{k_1[\mathrm{B}]}{k_{-1} + k_2[\mathrm{A}]}$$

Substitute the expression for [C] into the rate equation.

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{A}][\mathrm{B}]}{k_{-1} + k_2[\mathrm{A}]}$$

With B in excess, the reaction is zero order at high [A] and first order at low [A]. Graph 5 is reaction 6.

Graph 6. The graph is a straight line on a plot of log(half life) vs. log[A] with a slope of −½, which indicates a 3/2 order reaction. Derive the rate equation for reaction 4. Use the rate-limiting step (RLS) to write a rate equation

$$\frac{d[\mathrm{A}]}{dt} = -k_2[\mathrm{A}][\mathrm{B}]$$

Apply pre-equilibrium to obtain an expression for [B].

$$k_1[\mathrm{A}] = k_{-1}[\mathrm{B}]^2$$

$$[\mathrm{B}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{A}]^{1/2}$$

Substitute into the rate equation.

$$\frac{d[\mathrm{A}]}{dt} = -k_2[\mathrm{A}]\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{A}]^{1/2} = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{A}]^{3/2}$$

Graph 6 is reaction 4.

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