ChemE 2200 - Physical Chemistry II for Engineers - Spring 2025
Solution to Homework Assignment 10

1. Devise a progression of steps that includes all the species needed for each reaction. Let M be CO_2.

$$CH_4 + CO_2 \rightarrow \cdot CH_3 + \cdot H + CO_2 \rightarrow \cdot CH_3 + \cdot OH + CO \rightarrow CH_3OH + CO$$

Use the thermodynamic data to calculate the energies of the various stages of the reaction.

$CH_4 + CO_2$: $\Delta G = -51 + -394 = -445$ kJ/mol

$\cdot CH_3 + \cdot H + CO_2$: $\Delta G = 148 + 203 + -394 = -43$ kJ/mol

$\cdot CH_3 + \cdot OH + CO$: $\Delta G = 148 + 35 + -137 = +46$ kJ/mol

$CH_3OH + CO$: $\Delta G = -162 + -137 = -299$ kJ/mol

The activation energy for the first elementary step is obtained from the rate constant.

$$k = A e^{-E_a/RT} = 3\times10^{-7}\, e^{-54{,}500/T}$$

$$\frac{E_a}{R} = 54{,}500 \text{ K}$$

$$E_a = 54{,}500 \text{ K} \times R = 54{,}500 \text{ K} \times 8.314 \frac{\text{J}}{(\text{K})(\text{mol})} = 453 \text{ kJ/mol}$$

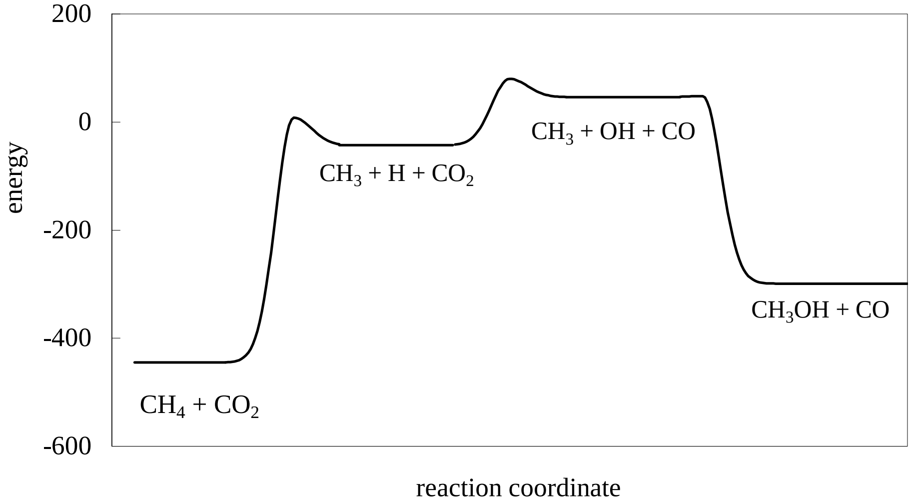
The first activation barrier peak is 453 kJ/mol above the first level; the first peak is at –445 + 453 = +8 kJ/mol.

For the second elementary step the activation energy for the *reverse* reaction is

$$E_a = 4{,}030 \text{ K} \times R = 4{,}030 \text{ K} \times 8.314 \frac{\text{J}}{(\text{K})(\text{mol})} = 34 \text{ kJ/mol}$$

The second activation barrier peak is 34 kJ/mol above the *third* level; the second peak is at +46 + 34 = +80 kJ/mol. In the forward direction, the second activation barrier peak is 80 – (–43) = 123 kJ/mol.

The activation energy for the third reaction is assumed to be zero.



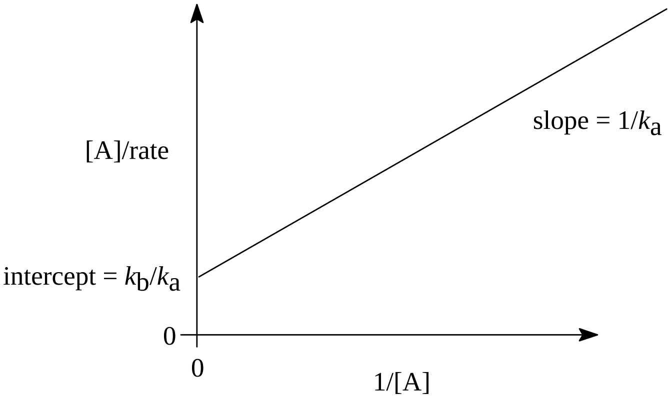
2. To test the theory, we should plot the data so the rate equation is a straight line. If the actual system deviates from the proposed mechanism and assumptions, deviations from the straight line will be obvious. To obtain an equation of the form "$y = mx + b$" invert the rate equation and multiply both sides by [A].

$$-\frac{d[\mathrm{A}]}{dt} = \frac{k_a[\mathrm{A}]^2}{1+k_b[\mathrm{A}]}$$

$$\frac{1}{\left(-\dfrac{d[\mathrm{A}]}{dt}\right)} = \frac{1+k_b[\mathrm{A}]}{k_a[\mathrm{A}]^2} = \frac{1}{k_a[\mathrm{A}]^2} + \frac{k_b}{k_a[\mathrm{A}]}$$

$$\frac{[\mathrm{A}]}{\left(-\dfrac{d[\mathrm{A}]}{dt}\right)} = \frac{1}{k_a}\left(\frac{1}{[\mathrm{A}]}\right) + \frac{k_b}{k_a}$$

We should plot 1/[A] on the x axis and $[\mathrm{A}]/(-d[\mathrm{A}]/dt)$ on the y axis. The slope is $1/k_\mathrm{a}$ and the intercept is $k_\mathrm{b}/k_\mathrm{a}$.

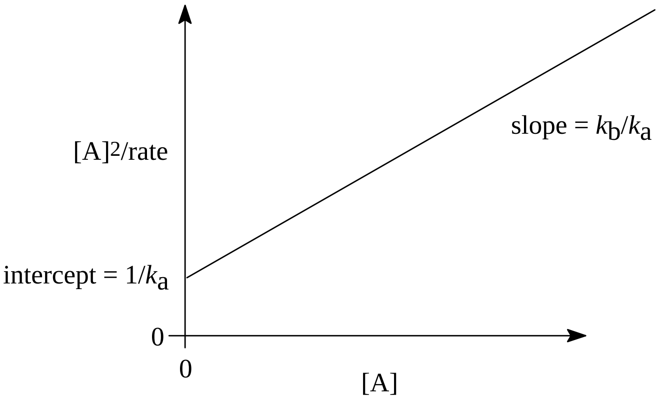


Another expression yields a straight line. Multiply the previous expression by [A].

$$\frac{[\mathrm{A}]}{\left(-\dfrac{d[\mathrm{A}]}{dt}\right)} = \frac{1}{k_a}\left(\frac{1}{[\mathrm{A}]}\right) + \frac{k_b}{k_a}$$

$$\frac{[\mathrm{A}]^2}{\left(-\dfrac{d[\mathrm{A}]}{dt}\right)} = \frac{1}{k_a} + \frac{k_b}{k_a}[\mathrm{A}]$$

In this case, we would plot [A] on the x axis and $[\mathrm{A}]^2/(-d[\mathrm{A}]/dt)$ on the y axis. The slope is $k_\mathrm{b}/k_\mathrm{a}$ and the intercept is $1/k_\mathrm{a}$.



3. Start with the Arrhenius formula for rate constants and take the logarithm of each side.

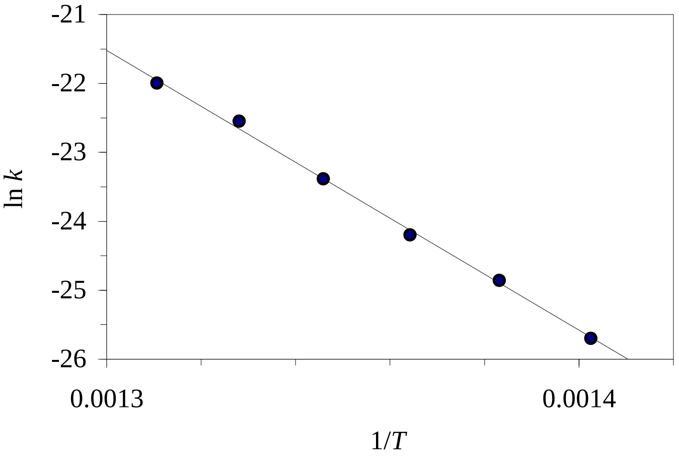
$$k = A\exp\left[-\frac{E_a}{RT}\right]$$

$$\ln k = \ln A + -\frac{E_a}{R}\left(\frac{1}{T}\right)$$

Thus the activation energy can be calculated from the slope of a plot of ln k versus $1/T$. Rather than use semi-log graph paper, we will prepare a table of $1/T$ and ln k and then use standard graph paper.

T (°C)	$1/T$ (K^{-1})	k (sec^{-1})	ln k
440	1.403×10^{-3}	6.9×10^{-12}	–25.7
450	1.383×10^{-3}	1.6×10^{-11}	–24.9
460	1.364×10^{-3}	3.1×10^{-11}	–24.2
470	1.346×10^{-3}	7.0×10^{-11}	–23.4
480	1.328×10^{-3}	1.61×10^{-10}	–22.6
490	1.311×10^{-3}	2.81×10^{-10}	–22.0

The data are plotted below.



The slope of the fitted line can be calculated from the two points where the line intersects the border: (0.0013, –21.5) and (0.00141, –26).

$$-\frac{E_a}{R} = \text{slope} = \frac{\text{rise}}{\text{run}} = \frac{-26-(-21.5)}{0.00141-0.0013} = -4.09\times10^4\ \text{K}$$

$$E_a = R\times4.09\times10^4\ \text{K} = \frac{8.31\,\text{J}}{\text{K}\cdot\text{mol}}4.09\times10^4\ \text{K} = 340\,\text{kJ/mol}$$

To calculate the preexponential, we calculate the preexponential at each temperature and calculate the average.

T (K)	k (sec^{-1})	$A = k\exp[E_a/RT]$
713	6.9×10^{-12}	5.6×10^{13}
723	1.6×10^{-11}	5.9×10^{13}
733	3.1×10^{-11}	5.3×10^{13}
743	7.0×10^{-11}	5.6×10^{13}
753	1.61×10^{-10}	6.3×10^{13}
763	2.81×10^{-10}	5.4×10^{13}

The average value is $A \approx 6 \times 10^{13}$ sec^{-1}. Because A is extremely sensitive to the activation energy and the activation energy is somewhat uncertain, there will be considerable variation in this value.

4. The generic reaction is

$$\text{protein} \xrightarrow{k} \text{denatured protein}$$

Assume an Arrhenius behavior for the rate constant: $k = A \exp(-E_a/RT)$. To reach the same point in the reaction, the ratio of reaction time is inversely proportional to the ratio of rate constants.

$$\frac{\text{x minutes at 92°C}}{\text{3 minutes at 100°C}} = \frac{k_{100\text{C}}}{k_{92\text{C}}} = \frac{A_{100\text{C}} \exp(-E_a / R(373\text{ K}))}{A_{92\text{C}} \exp(-E_a / R(365\text{ K}))}$$

Further assume that the preexponential A is independent of temperature.

$$\begin{aligned}\frac{\text{x minutes at 92°C}}{\text{3 minutes at 100°C}} &= \frac{\exp(-E_a / R(373\text{ K}))}{\exp(-E_a / R(365\text{ K}))} \\ &= \exp\left[-\frac{E_a}{R}\left(\frac{1}{373\text{ K}} - \frac{1}{365\text{ K}}\right)\right] \\ &= \exp\left[-\frac{40{,}000\text{ J / mol}}{8.314\text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}}\left(\frac{1}{373\text{ K}} - \frac{1}{365\text{ K}}\right)\right] \\ &= 1.33 \\ x &= 1.33\times 3 = 4\text{ minutes}\end{aligned}$$

Note that the Gibbs energy of the reaction is not needed.

5. Begin with a mass balance on ${}^{24}_{11}\text{Na}$,

$$\frac{d[{}^{24}_{11}\text{Na}]}{dt} = (\text{rate of creation by neutron absorption}) - (\text{rate of decay})$$

The rate of creation is determined by the neutron flux. In this case the rate is constant;

$$r_n = \frac{10^7\ {}^{24}_{11}\text{Na atoms}}{\text{sec}}\left(\frac{1\text{ mol } {}^{24}_{11}\text{Na}}{6.02\times10^{23}\ {}^{24}_{11}\text{Na atoms}}\right)\left(\frac{3600\text{ sec}}{1\text{ hr}}\right) = \frac{6.0\times10^{-14}\text{ mol } {}^{24}_{11}\text{Na}}{\text{hr}}$$

The decay of ${}^{24}_{11}\text{Na}$ is first order,

$$\text{rate of decay} = k_2[{}^{24}_{11}\text{Na}]$$

For a first-order reaction the half life is (ln 2)/k. Calculate k_2.

$$k_2 = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{15\text{ hr}} = \frac{4.6\times10^{-2}}{\text{hr}}$$

Derive an integrated rate equation for [${}^{24}_{11}\text{Na}$].

$$\frac{d[{}^{24}_{11}\text{Na}]}{dt} = r_n - k_2[{}^{24}_{11}\text{Na}]$$

$$\frac{d[{}^{24}_{11}\text{Na}]}{r_n - k_2[{}^{24}_{11}\text{Na}]} = dt$$

$$\int_0^{[{}^{24}_{11}\text{Na}]} \frac{d[{}^{24}_{11}\text{Na}]}{r_n - k_2[{}^{24}_{11}\text{Na}]} = \int_0^t dt$$

$$-\frac{1}{k_2}\left[\ln\left[r_n - k_2[{}^{24}_{11}\text{Na}]\right]\Big|_0^{[{}^{24}_{11}\text{Na}]}\right] = t$$

$$\ln\left[\frac{r_n - k_2[{}^{24}_{11}\mathrm{Na}]}{r_n}\right] = -k_2 t$$

$$r_n - k_2[{}^{24}_{11}\mathrm{Na}] = r_n \mathrm{e}^{-k_2 t}$$

$$k_2[{}^{24}_{11}\mathrm{Na}] = r_n - r_n \mathrm{e}^{-k_2 t}$$

$$[{}^{24}_{11}\mathrm{Na}] = \frac{r_n}{k_2}(1 - \mathrm{e}^{-k_2 t})$$

Calculate [${}^{24}_{11}\mathrm{Na}$] at t = 30 hrs.

$$[{}^{24}_{11}\mathrm{Na}] = \frac{6.0\times10^{-14}\ \mathrm{mol}\ {}^{24}_{11}\mathrm{Na\,/\,hr}}{4.6\times10^{-2}\ /\ \mathrm{hr}}(1 - \mathrm{e}^{-(4.6\times10^{-2}\,/\,\mathrm{hr})(30\ \mathrm{hr})}) = 9.7\times10^{-13}\ \mathrm{mol}\ {}^{24}_{11}\mathrm{Na}$$

Check the result. At t = 0,

$$[{}^{24}_{11}\mathrm{Na}] = \frac{r_n}{k_2}(1 - \mathrm{e}^{-k_2 0}) = 0\,.$$

This is correct. There is no radioactive Na when the neutron bombardment starts. At $t = \infty$,

$$[{}^{24}_{11}\mathrm{Na}] = \frac{v_n}{k_2}(1 - \mathrm{e}^{-k_2 \infty}) = \frac{r_n}{k_2} = \text{a constant}$$

After a long time ($k_2 t > 10$) the system reaches steady state. The rate of formation equals the rate of decay.

6.(A) Rewrite the first reaction as two forward reactions and add the reactions.

$$\mathrm{O_2} + \mathrm{M} \xrightarrow{k_1} 2\mathrm{O} + \mathrm{M}$$

$$2\mathrm{O} + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{O_2} + \mathrm{M}$$

$$\mathrm{NO} + \mathrm{O} \xrightarrow{k_2} \mathrm{O_2} + \mathrm{N}$$

$$\mathrm{NO} + \mathrm{N} \xrightarrow{k_3} \mathrm{N_2} + \mathrm{O}$$

$$\text{sum}: \quad 2\mathrm{NO} \rightarrow \mathrm{N_2} + \mathrm{O_2}$$

(B) Use the second and third reactions to write a rate equation for NO.

$$\frac{d[\mathrm{NO}]}{dt} = -k_2[\mathrm{NO}][\mathrm{O}] - k_3[\mathrm{NO}][\mathrm{N}] \qquad (1)$$

We need expressions for the concentrations of the intermediates O and N. Apply the steady-state approximation to N.

$$\frac{d[\mathrm{N}]}{dt} = 0 = k_2[\mathrm{NO}][\mathrm{O}] - k_3[\mathrm{NO}][\mathrm{N}]$$

$$k_2[\mathrm{NO}][\mathrm{O}] = k_3[\mathrm{NO}][\mathrm{N}] \qquad (2)$$

Apply the steady-state approximation to O.

$$\frac{d[\mathrm{O}]}{dt} = 0 = 2k_1[\mathrm{O_2}][\mathrm{M}] - 2k_{-1}[\mathrm{O}]^2[\mathrm{M}] - k_2[\mathrm{NO}][\mathrm{O}] + k_3[\mathrm{NO}][\mathrm{N}] \qquad (3)$$

Eqn (2) shows that the third and fourth terms in eqn (3) cancel. Solve eqn (3) for [O].

$$0 = 2k_1[\mathrm{O}_2][\mathrm{M}] - 2k_{-1}[\mathrm{O}]^2[\mathrm{M}]$$

$$[\mathrm{O}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{O}_2]^{1/2} \qquad (4)$$

Substitute eqn (2) into (1).

$$\frac{d[\mathrm{NO}]}{dt} = -k_2[\mathrm{NO}][\mathrm{O}] - k_2[\mathrm{NO}][\mathrm{O}] = -2k_2[\mathrm{NO}][\mathrm{O}] \qquad (5)$$

Substitute eqn (4) into eqn (5).

$$\frac{d[\mathrm{NO}]}{dt} = -2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{NO}][\mathrm{O}_2]^{1/2}$$

After you work exercise 8 and reflect on exercise 6, you may question if the result of the steady-state approximation on N - eqn (2) - is a sufficiently good approximation to justify canceling these terms in eqn (3). That is, what if k_2[NO][O] = 1,000,000 and k_3[NO][N] = 1,000,001? Although it is a good approximation that k_2[NO][O] = k_3[NO][N], the difference between these two terms might be comparable to the difference between the first two terms in eqn (3).

The answer is provided by a topic we will cover next week - chain reactions. Reactions 2 and 3 form a cycle. For every occurrence of reaction 2 there is exactly one occurrence of reaction 3, to maintain the total number of radicals, O and N atoms, in the cycle. So the approximation in eqn (2) is very good; better than the approximation of pre-equilibrium for reaction 1.

But the result in eqn (4) leads to another question - is it valid to assume a steady-state approximation for O? The approximation is $d[\mathrm{O}]/dt = 0$, but this leads to eqn (4), which shows [O] is proportional to [O_2]. O_2 is a product; it increases as the reaction proceeds; $d[\mathrm{O}_2]/dt = -\tfrac{1}{2}d[\mathrm{NO}]/dt \neq 0$. Use eqn (4) to calculate an expression for $d[\mathrm{O}]/dt$.

$$\frac{d[\mathrm{O}]}{dt} = \frac{d}{dt}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{O}_2]^{1/2} = \left(\frac{k_1}{k_{-1}}\right)^{1/2}\frac{1}{2}\frac{d[\mathrm{O}_2]}{dt}$$

The key is the ratio k_1/k_{-1} is small. The molar Gibbs energy of reaction for $\mathrm{O}_2 \rightarrow 2\mathrm{O}$ is 464 kJ/mol. At a reaction temperature of 600 K, $(k_1/k_{-1})^{1/2}$ is about 10^{-20}. It is a good approximation that $d[\mathrm{O}]/dt = 0$.

7.(A) Write a rate equation from the second reaction.

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{C}] \qquad (1)$$

Apply the pre-equilibrium approximation to the first reaction.

$$k_1[\mathrm{A}][\mathrm{B}] = k_{-1}[\mathrm{C}][\mathrm{Q}]$$

$$[\mathrm{C}] = \frac{k_1[\mathrm{A}][\mathrm{B}]}{k_{-1}[\mathrm{Q}]} \qquad (2)$$

Substitute the expression for [C] into eqn (1).

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

(B) Again, begin with the rate equation from the second reaction.

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{C}] \qquad (1)$$

Apply the steady-state approximation to C.

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

$$[\mathrm{C}] = \frac{k_1[\mathrm{A}][\mathrm{B}]}{k_{-1}[\mathrm{Q}] + k_2} \qquad (4)$$

Again, substitute the expression for [C] into eqn (1).

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

8.(A) Start with the differential rate equation for *A*,

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

and then separate and integrate.

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k_1 \int_0^t dt$$

$$\ln \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -k_1 t$$

$$[\mathrm{A}] = [\mathrm{A}]_0\, \mathrm{e}^{-k_1 t}$$

(B) Write a mass balance on the closed vessel.

$$\text{mass in the vessel initially} = \text{mass in the vessel later}$$

$$m_{\mathrm{A},0} + m_{\mathrm{B},0} + m_{\mathrm{C},0} = m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}}$$

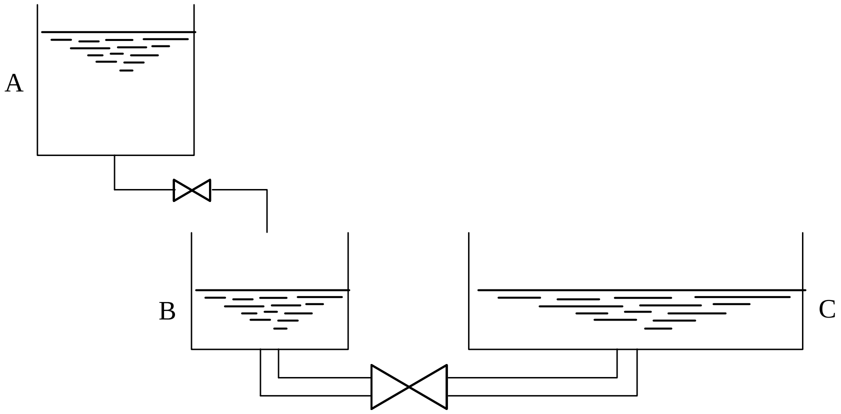
Because initially the reactor contains only A, $m_{\mathrm{B},0} = m_{\mathrm{C},0} = 0$.

$$m_{\mathrm{A},0} = m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}}$$

Convert from units of mass to units of molar concentration by dividing each term by the vessel volume and each molecular weight. Note that A, B and C each have the same molecular weight. We thus arrive at

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]$$

The rate of consumption of A is slow compared to the rate of interconversion between B and C. Using the draining tank analogy, tank A drains slowly into tank B. Tanks B and C are connected by a large pipe, so they quickly reach equilibrium. The diagram below assumes that C is thermodynamically lower than B, so there is more C than B at equilibrium. That is, we assumed $k_2 > k_{-2}$.



We thus assume “post” equilibrium. The rate that B converts to C equals the rate that C converts to B.

$$k_2[\mathrm{B}] = k_{-2}[\mathrm{C}]$$

$$[\mathrm{C}] = \frac{k_2}{k_{-2}}[\mathrm{B}] = K_2[\mathrm{B}]$$

Substitute the expression for [C] above and the expression for [A] derived in part (A) into the mass balance.

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]$$

$$[\mathrm{A}]_0 = [\mathrm{A}]_0\,\mathrm{e}^{-k_1 t} + [\mathrm{B}] + K_2[\mathrm{B}]$$

$$[\mathrm{B}] = [\mathrm{A}]_0\,\frac{1-\mathrm{e}^{-k_1 t}}{1+K_2}$$

Some students neglected to assume post-equilibrium and instead solved the full differential equation:

$$\begin{aligned}\frac{d[\mathrm{B}]}{dt} &= k_1[\mathrm{A}] - k_2[\mathrm{B}] + k_{-2}[\mathrm{C}] \\ &= k_1[\mathrm{A}] - k_2[\mathrm{B}] + k_{-2}([\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}]) \\ &= (k_1 - k_{-2})[\mathrm{A}] + k_{-2}[\mathrm{A}]_0 - (k_2 + k_{-2})[\mathrm{B}] \\ &= (k_1 - k_{-2})[\mathrm{A}]_0 e^{-k_1 t} + k_{-2}[\mathrm{A}]_0 - (k_2 + k_{-2})[\mathrm{B}]\end{aligned}$$

The full solution is

$$[\mathrm{B}] = \left[\frac{(k_1 - k_{-2})}{k_2 + k_{-2} - k_1}\left(e^{-k_1 t} - e^{-(k_2+k_{-2})t}\right) + \frac{k_{-2}}{k_2 + k_{-2}}\left(1 - e^{-(k_2+k_{-2})t}\right)\right][\mathrm{A}]_0$$

Consider an alternate approximation: If we can assume post-equilibrium, such that $k_2[\mathrm{B}] = k_{-2}[\mathrm{C}]$, then we should be able to cancel these terms from the rate equation for [B], as such

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] + k_{-2}[\mathrm{C}] \approx k_1[\mathrm{A}]$$

$$[\mathrm{B}] = [\mathrm{A}]_0(1 - \mathrm{e}^{-k_1 t})$$

This expression for [B] is different from the expression for [B] derived above, yet both used a post-equilibrium assumption. Which estimate is better? And in general, when can equilibrium assumptions be used to cancel opposing terms in a differential rate equation?

To explore which estimate is better, we start with the expression for [B] obtained with no assumptions and apply the facts that $k_1 \ll k_2$ and $k_1 \ll k_{-2}$, as given in the exercise statement. The exponentials $\exp(-(k_2 + k_{-2})t)$ will decrease to zero much faster than the exponentials $\exp(-k_1 t)$.

$$k_1 - k_{-2} \approx -k_{-2}$$

$$k_2 + k_{-2} - k_1 \approx k_2 + k_{-2}$$

With these assumptions, the exact expression for [B] simplifies as follows.

$$\begin{aligned}[\mathrm{B}] &= \left[\frac{(k_1 - k_{-2})}{k_2 + k_{-2} - k_1}\left(e^{-k_1 t} - e^{-(k_2+k_{-2})t}\right) + \frac{k_{-2}}{k_2 + k_{-2}}\left(1 - e^{-(k_2+k_{-2})t}\right)\right][\mathrm{A}]_0 \\ &\approx \left[\frac{-k_{-2}}{k_2 + k_{-2}}\left(e^{-k_1 t} - 0\right) + \frac{k_{-2}}{k_2 + k_{-2}}(1 - 0)\right][\mathrm{A}]_0 \\ &\approx \left[\frac{-k_{-2}e^{-k_1 t} + k_{-2}}{k_2 + k_{-2}}\right][\mathrm{A}]_0 \approx \frac{1 - \mathrm{e}^{-k_1 t}}{1 + K_2}[\mathrm{A}]_0\end{aligned}$$

We obtain the expression derived by substituting an integrated rate equation for [A] into the mass balance. This is the better estimate.

So why is it less accurate to use the post-equilibrium approximation to cancel terms in the rate equation for [B]? The key is that $k_2[\mathrm{B}] \approx k_{-2}[\mathrm{C}]$, or $k_2[\mathrm{B}] - k_{-2}[\mathrm{C}] \approx 0$. How small is the difference between $k_2[\mathrm{B}]$ and $k_{-2}[\mathrm{C}]$? The difference is approximately equal to the remaining term, $k_1[\mathrm{A}]$. For example, consider $k_2[\mathrm{B}] = 1{,}000{,}000$, $k_{-2}[\mathrm{C}] = 1{,}000{,}001$, and $k_1[\mathrm{A}] = 1$. It is a good approximation that $k_2[\mathrm{B}] \approx k_{-2}[\mathrm{C}]$, but it is not a good approximation that $k_1[\mathrm{A}] + k_2[\mathrm{B}] - k_{-2}[\mathrm{C}] = k_1[\mathrm{A}]$. In this case, the error is a factor of 2.

Or consider another explanation. As above, if we assume post-equilibrium, such that $k_2[\mathrm{B}] = k_{-2}[\mathrm{C}]$, then these terms cancel from the rate equation for [B], as such

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] + k_{-2}[\mathrm{C}] \approx k_1[\mathrm{A}]$$

Recall the differential rate equation for *A*,

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

With the post-equilibrium approximation $k_2[\mathrm{B}] = k_{-2}[\mathrm{C}]$ applied to the rate equation for B, we have the result

$$\frac{d[\mathrm{B}]}{dt} \approx \frac{d[\mathrm{A}]}{dt}$$

This approximation yields the (incorrect) result that all the A reacts to form B; no C.

In a chemical sense, the slight difference in the dynamic balance of the equilibrium between B and C is approximately equal to the rate that A converts to B.

So what of the pre-equilibrium approximation, for example, in the series reaction,

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

such that $k_2 \ll k_1$ and $k_2 \ll k_{-1}$? The pre-equilibrium approximation gives us $k_1[\mathrm{A}] \approx k_{-1}[\mathrm{B}]$. Is it valid to cancel these terms in the rate equation for [B], such as

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] - k_2[\mathrm{B}] \approx -k_2[\mathrm{B}]\,?$$

This a reasonable approximation, but not as accurate as first integrating the rate equation for [A], similar to part (A),

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}] = k_{-1}[\mathrm{A}]_0 - (k_1 + k_{-1})[\mathrm{A}]$$

$$[\mathrm{A}] = [\mathrm{A}]_0 \frac{k_1}{k_1 + k_{-1}} \mathrm{e}^{-(k_1 + k_{-1})t}$$

Substitute this expression for [A] into the differential rate equation for [B] and then integrate. So, canceling the terms $k_1[\mathrm{A}]$ and $k_{-1}[\mathrm{B}]$ would be a reasonable approximation (perhaps within a factor of 10), depending on the relative sizes of k_1, k_{-1} and k_2.