ChemE 2200 – Physical Chemistry II for Engineers

Solutions to Calculation Session 9 Exercises

1. First reaction path: $CH_4 + 2O_2 \rightarrow CO + 2H_2O + ½O_2 \rightarrow CO_2 + 2H_2O$

   Second reaction path: $CH_4 + 2O_2 \rightarrow H_2CO + H_2O + O_2 \rightarrow CO_2 + 2H_2O$

   Calculate the Gibbs energies of the various stages of the reaction.

   $CH_4 + 2O_2$:

$$\Delta G = \left(\frac{-51\text{ kJ}}{\text{mol CH}_4}\right)\left(\frac{1\text{ mol CH}_4}{1\text{ mol rxn}}\right) + \left(\frac{0\text{ kJ}}{\text{mol O}_2}\right)\left(\frac{2\text{ mol O}_2}{1\text{ mol rxn}}\right) = -51\text{ kJ/mol rxn}$$

   $CO + 2H_2O + ½O_2$:

$$\Delta G = \left(\frac{-137\text{ kJ}}{\text{mol CO}}\right)\left(\frac{1\text{ mol CO}}{1\text{ mol rxn}}\right) + \left(\frac{-229\text{ kJ}}{\text{mol H}_2\text{O}}\right)\left(\frac{2\text{ mol H}_2\text{O}}{1\text{ mol rxn}}\right) + \left(\frac{0\text{ kJ}}{\text{mol O}_2}\right)\left(\frac{½\text{ mol O}_2}{1\text{ mol rxn}}\right) = -595\text{ kJ/mol rxn}$$

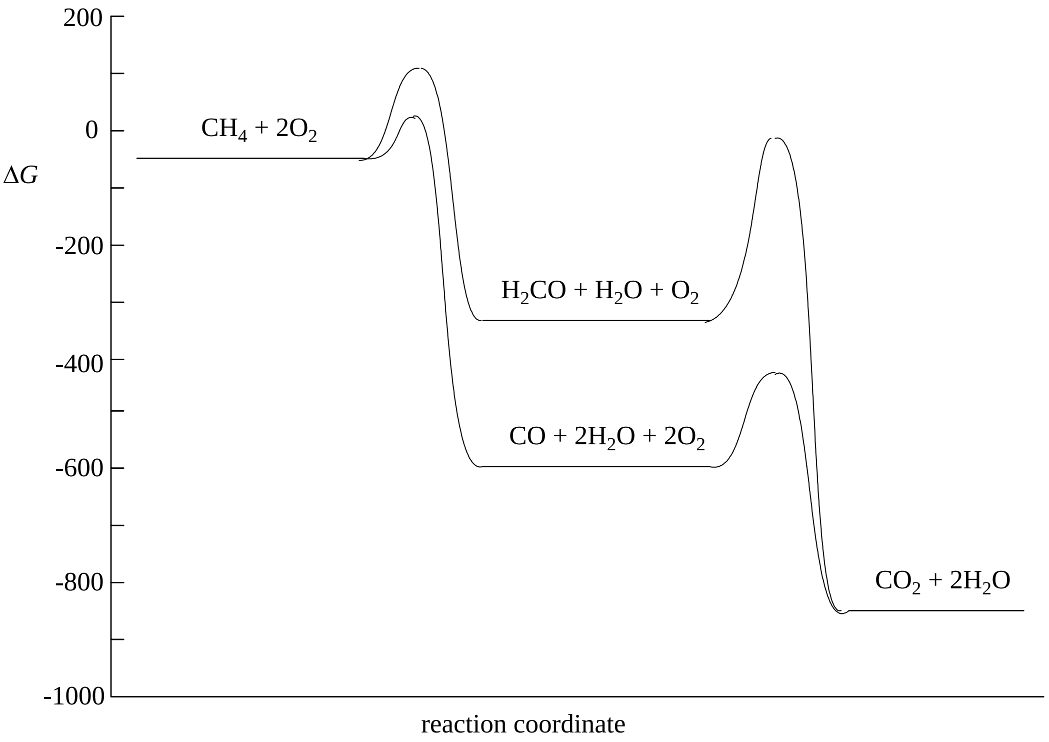
   $CO_2 + 2H_2O$:

$$\Delta G = \left(\frac{-394\text{ kJ}}{\text{mol CO}_2}\right)\left(\frac{1\text{ mol CO}_2}{1\text{ mol rxn}}\right) + \left(\frac{-229\text{ kJ}}{\text{mol H}_2\text{O}}\right)\left(\frac{2\text{ mol H}_2\text{O}}{1\text{ mol rxn}}\right) = -852\text{ kJ/mol rxn}$$

   $H_2CO + H_2O + O_2$:

$$\Delta G = \left(\frac{-103\text{ kJ}}{\text{mol H}_2\text{CO}}\right)\left(\frac{1\text{ mol H}_2\text{CO}}{1\text{ mol rxn}}\right) + \left(\frac{-229\text{ kJ}}{\text{mol H}_2\text{O}}\right)\left(\frac{1\text{ mol H}_2\text{O}}{1\text{ mol rxn}}\right) + \left(\frac{0\text{ kJ}}{\text{mol O}_2}\right)\left(\frac{1\text{ mol O}_2}{1\text{ mol rxn}}\right) = -332\text{ kJ/mol rxn}$$

   The reaction-coordinate energy-level diagram is sketched below. Note that the heights of the barriers are unknown. Only the four levels of the reactants, stable intermediates, and products are known.



2. We begin by assuming a power law for the reaction rate. That is, the rate equation is assumed to have the following form: rate = $k[A]^a[B]^b[C]^c$. We must determine a, b, and c. Compare the 1st and 2nd data sets. When [A] decreases by a factor of 1.03/0.52 = 2, the rate decreases by a factor of 0.059/0.015 = 4. Thus the exponent on [A] is 2, because $2^2 = 4$. Stated mathematically,

$$\frac{r_{\text{rxn},1}}{r_{\text{rxn},2}} = \frac{k[A]_1^a[B]_1^b[C]_1^c}{k[A]_2^a[B]_2^b[C]_2^c} = \left(\frac{[A]_1}{[A]_2}\right)^a\left(\frac{[B]_1}{[B]_2}\right)^b\left(\frac{[C]_1}{[C]_2}\right)^c$$

$$\frac{0.059}{0.015} = \left(\frac{1.03}{0.52}\right)^a\left(\frac{0.914}{0.914}\right)^b\left(\frac{10.27}{10.27}\right)^c$$

$$3.93 = (1.98)^a(1)^b(1)^c$$

$$\ln(3.93) = a\ln(1.98)$$

$$a = \frac{\ln(3.93)}{\ln(1.98)} = 2$$

Compare the 2nd and 3rd data sets. When [B] increases by a factor of 1.37/0.914 = 1.5, the rate increases by a factor of 0.023/0.015 = 1.5. Thus the exponent on [B] is 1.

Compare the 1st and 4th data sets. When [C] decreases by a factor of 10.27/3.43 = 3, the rate decreases by a factor of 0.059/0.0070 = 8.4. Since $8.4 = 3^{1.9}$, we will assume the exponent is an integer and $1.9 \approx 2.0$. The exponent on [C] is thus 2.0.

Use all four data sets to evaluate the rate constant, k.

$$k = \frac{\text{rate}}{[A]^2[B][C]^2}$$

data set	k
1.	5.77×10^{-4}
2.	5.75×10^{-4}
3.	5.89×10^{-4}
4.	6.10×10^{-4}

The average is $k = 5.9 \times 10^{-4}$ $(\text{mol/L})^{-4}\text{sec}^{-1}$.

3. Apply the method of initial rates. We assume a rate equation of the form

$$-\frac{1}{2}\frac{d[C_4H_6]}{dt} = k[C_4H_6]^n\,.$$

Take the log of both sides to convert the equation into the form of a straight line with slope n.

$$\log\left[-\frac{1}{2}\frac{d[C_4H_6]}{dt}\right] = \log k + n\log[C_4H_6]$$

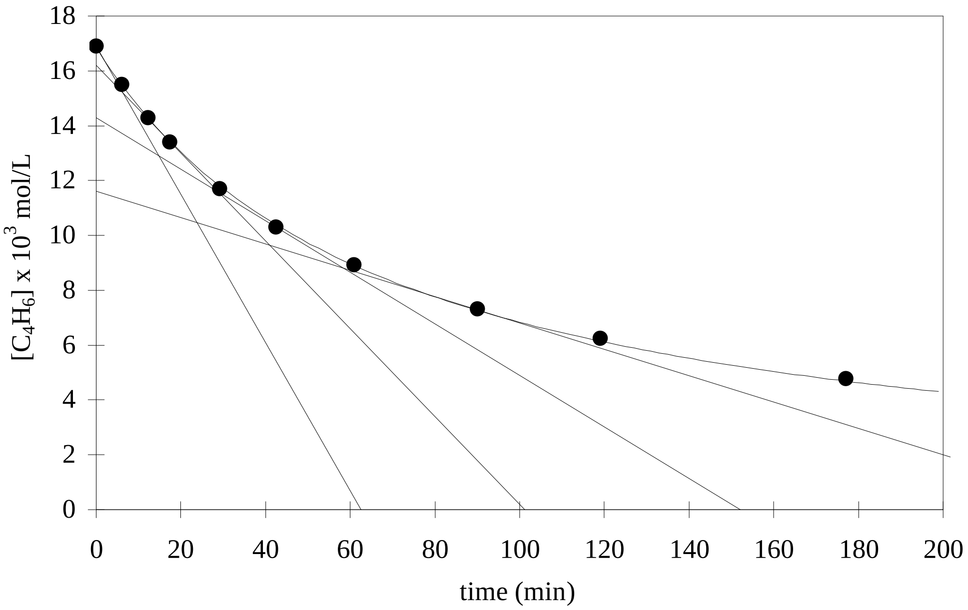
A log-log plot of $-½d[C_4H_6]/dt$ versus $[C_4H_6]$ will yield a straight line with slope n. We use the data provided - $[C_4H_6]$ as a function of time - to estimate the rate at various concentrations as follows.

i. Plot the concentration as a function of time and sketch a line through the points.

ii. Draw a line tangent to the curve at an arbitrary point. To draw a tangent line at a point, hold a straightedge next to the curve. When the angle between the straightedge and the curve is the same on both sides of the point, the line is tangent.

iii. Determine the tangent line's slope by measuring the rise/run. Draw other tangent lines and tabulate the slope vs. [C_4H_6].

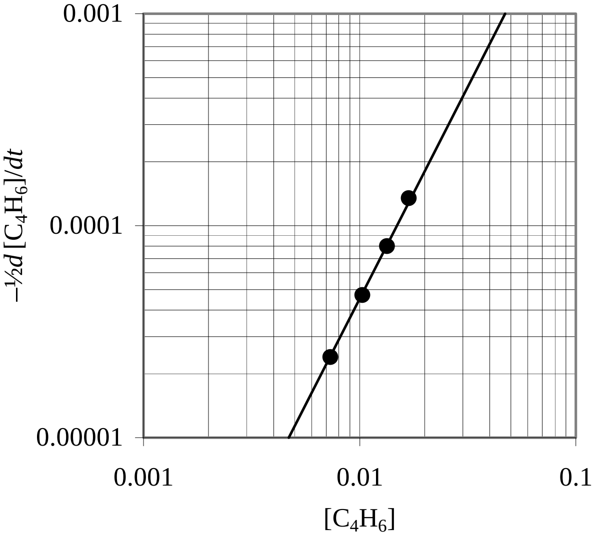
Tangent lines are drawn at the 1st, 4th, 6th, and 8th data points, as shown below.



We measure the slopes of the tangent lines above (note that the rise/run is easier to calculate if you extend each line to both axes) and prepare the following table:

$[C_4H_6] \times 10^3$ mol/L	$-\frac{1}{2}d[C_4H_6]/dt$ mol/L/min
16.9	0.000135
13.4	0.000080
10.3	0.000047
7.32	0.000024

Plot the rates on a log-log grid and fit a straight line through the data. The slope of the line is the reaction order.



Use the points at $y = 0.00001$ and $y = 0.001$ to calculate the slope.

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\log(0.001) - \log(0.00001)}{\log(0.047) - \log(0.0047)} = \frac{-3 - (-5)}{-1.3 - (-2.3)} = 2$$

Thus the reaction order is 2.

4. error 1. To extract a half life from the graph, one must subtract the initial time from the final time. For example, [A] = 2 mol/L at 2.75 min and [A] = 1 mol/L at 5.5 min. So $t_{1/2}$ = 5.5 – 2.75 = 2.75 min. Similarly, at [A] = 0.5 mol/L, $t_{1/2}$ = 8.25 – 5.5 = 2.75 m

error 2. The slope is calculated incorrectly. For a log-log plot, one must calculate the rise and run of the logarithms of the points. The correct slope is

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\log(3) - \log(9)}{\log(4) - \log(1)} = \frac{-0.48}{0.6} = -0.8$$

error 3. If the slope on the plot of $t_{1/2}$ vs. [A] is a, the reaction order is $1 - a$ not $-a$. Using the slope calculated by the coop student, $1 - a = -2$, so $a = 3$. The coop student should have reported a reaction order of 3.

The Team Competition Champions for Calculation Session 9:

Carmen Dai, Lynden Cellini, and Synthia Shohel

Competition topic “*How Well Do You Know Cornell*?”

Team CSC answered 21 out of 34 questions correctly!