Reactor Engineering Week 2 Problem Set

Question 1a

The first order irreversible reaction

$$A \to B \tag{1}$$

has a rate constant, k, which varies with temperature according to the Arrhenius Equation:

$$k = k_0 e^{-E/RT}. \tag{2}$$

At $300\,\mathrm{K}$, the reaction rate constant, k, is $1\,\mathrm{s}^{-1}$, while at $310\,\mathrm{K}$ the reaction rate constant has increased to $2\,\mathrm{s}^{-1}$. Calculate the activation energy of the reaction.

Question 1b

A catalyst is now added to the mixture, which increase the reaction rate at $300\,\mathrm{K}$ to $3\,\mathrm{s}^{-1}$, and increases the reaction rate at $310\,\mathrm{K}$ to $4\,\mathrm{s}^{-1}$. What is the new activation energy?

Question 1c

The *half-life* of reactant A is defined as the time for exactly half of A to be consumed by the reaction and converted to B. Assume the reaction occurs at constant volume, and the temperature is held constant at $320\,\mathrm{K}$. Calculate the ratio of the half-life of A under these conditions with the catalyst present, to the half-life of A under these conditions but with no catalyst in the system. **Hint:** To begin, you will need to use the Arrhenius equation to calculate values of k at $320\,\mathrm{K}$.

Question 2

Alice has discovered a new catalyst for the creation of ethylene dichloride (EDC.) EDC is the main reactant in the production of polyvinyl chloride (PVC), one of the most widely used polymers in the construction industry (think of all those white plastic pipes.) Alice dreams of becoming rich! (Or, at least, getting a small bonus while her company makes millions...)

EDC is produced by reacting ethylene with liquid chlorine:

$$C_2H_2 + 2\,Cl \longrightarrow C_2H_2Cl_2. \tag{3}$$
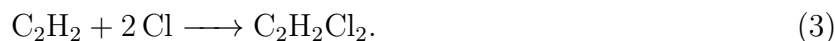
In the table below, Alice has listed the values for the reaction rate constant using her new catalyst at various temperatures. She has also measured the reaction rate constant with the old, traditional catalyst, ferric chloride. She is very excited, as the reaction rate constants with her catalyst are a lot larger! However, her boss is a bit concerned. To assist in product separation, the reaction needs to be operated at a temperature of $100\,°C$. Assuming the reaction rate constants change with temperature according to Arrhenius Law, help Alice find out whether her catalyst is still better than the traditional catalyst at the practical operating temperature!

T (K)	313	319	323	328	333
k for Alice's Catalyst ($\mathrm{m}^6\,\mathrm{mol}^{-2}\,\mathrm{s}^{-1}$)	0.00043	0.00103	0.00180	0.00355	0.00717
k for traditional catalyst ($\mathrm{m}^6\,\mathrm{mol}^{-2}\,\mathrm{s}^{-1}$)	1.431×10^{-5}	6.237×10^{-5}	0.000161	0.000513	0.00157

Question 3a

Jeremy is doing an experiment, in which the following irreversible reaction occurs in the liquid phase in a batch reactor at constant temperature and volume:

$$A \to B. \tag{4}$$

He finds that, whatever initial concentration of A he chooses, 50% of A has converted to B after 1 hour. What is the order of the reaction?

Question 3b

Jeremy is doing another experiment, again with an irreversible liquid phase reaction in an isothermal, isochoric batch reactor:

$$C \to D. \tag{5}$$

He finds that, whatever the intitial concentration of C, the reaction rate is the same at the start of the reaction, and stays the same until all C has been consumed. What is the order of the reaction?

Question 3c

Jeremy is still doing experiments on liquid-phase reactions in his isothermal, isochoric batch reactor. This time, he is interested in the irreversible reaction:

$$E \to F, \tag{6}$$

and he starts with pure E in his reactor. As the reaction proceeds, the concentration of F increases, while the concentration of E decreases. However, Jeremy notices that for this particular reaction, the ratio of the concentration of F to the concentration of E increases at a constant rate over time. In other words, the ratio of the concentration of F to the concentration of E is always proportional to the time since the reaction began. Find the order of the reaction.

Super-Duper-Extra-Hard-Fredo-Frog Challenge Question.
Note: This is a very difficult challenge problem. Students who submit a correct solution to this problem by next week's session can claim a Fredo Frog as a reward.
The exothermic, irreversible, first-order reaction,

$$A \to B \tag{7}$$

takes place in an adiabatically insulated batch reactor of constant volume V. The first-order reaction rate constant, k, varies with temperature according to the Arrhenius Equation:

$$k = k_0 e^{-E/RT} \tag{8}$$

where E is the activation energy and R the universal gas constant. The heat of reaction per mole of A consumed is given by $\Delta_{rxn}\underline{U}$ (note that this will be negative for our exothermic reaction), and the constant-volume specific heat capacity of the contents of the reactor is c_v (whose units are J/K.mol, and which is independent of reaction conversion.)

If the initial temperature of the reactor is T_0, and initially the reactor contains n moles of A and 0 moles of B, find an expression relating reaction conversion to time.

*   **Hint:** The first step is to derive two differential equations: one describing the rate of change of reaction conversion with time, and the other the rate of change of temperature with time. The second step is to solve these equations - they can be solved numerically, but full marks will only be given for an analytical solution (Wolfram Alpha may be helpful here.)*

Solutions.

Question 1a

For the first temperature,

$$k_1 = k_0 e^{-E/RT_1} \tag{9}$$

while for the second temperature

$$k_2 = k_0 e^{-E/RT_2}. \tag{10}$$

Dividing these by each other gives

$$\frac{k_2}{k_1} = \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \tag{11}$$

Rearranging,

$$E = R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln\frac{k_2}{k_1} \tag{12}$$

Substituting in $k_1 = 1\,\mathrm{s}^{-1}$, $T_1 = 300\,\mathrm{K}$, $k_2 = 2\,\mathrm{s}^{-1}$, $T_2 = 310\,\mathrm{K}$, gives $E = 53.6\,\mathrm{kJ\,mol}^{-1}$.

Question 1b

Using (12) with $k_1 = 3\,\mathrm{s}^{-1}$, $T_1 = 300\,\mathrm{K}$, $k_2 = 4\,\mathrm{s}^{-1}$, $T_2 = 310\,\mathrm{K}$, gives $E = 22.2\,\mathrm{kJ\,mol}^{-1}$, so the catalyst causes a substantial reduction in the activation energy.

Question 1c

We begin by calculating the values of k_0 in the Arrhenius equation. Without a catalyst, $E = 53.6\,\mathrm{kJ\,mol}^{-1}$ while $k_1 = 1\,\mathrm{s}^{-1}$, $T_1 = 300\,\mathrm{K}$. Rearranging the Arrhenius equation,

$$k_0 = k e^{E/RT} \tag{13}$$

and substituting in these values gives $k_0 = 2.15 \times 10^9\,\mathrm{s}^{-1}$ when no catalyst is present. A similar procedure when the catalyst is present gives $k_0 = 2.23 \times 10^4\,\mathrm{s}^{-1}$.

We can now use these k_0 values to calculate k values at $320\,\mathrm{K}$. Without a catalyst present, the Arrhenius equation becomes:

$$k = (2.15 \times 10^9\,\mathrm{s}^{-1}) e^{-53\,600\,\mathrm{J\,mol}^{-1}/RT} \tag{14}$$

and substituting $T = 320$ K gives $k = 3.83\,\mathrm{s}^{-1}$.

When a catalyst is present,

$$k = (2.23 \times 10^4\,\mathrm{s}^{-1}) e^{-22\,200\,\mathrm{J\,mol}^{-1}/RT} \tag{15}$$

and substituting $T = 320$ K gives $k = 5.3\,\mathrm{s}^{-1}$.

We now solve the differential equation describing reaction in a batch reactor:

$$\frac{dC_A}{dt} = -kC_A \tag{16}$$

to get:

$$-\ln(1 - X_A) = kt. \tag{17}$$

At 50% converstion,

$$t = \frac{\ln 2}{k} \tag{18}$$

and so the ratio of the half-lives will be the inverse of the ratio of the reaction rate constants:

$$\frac{t_{cat}}{t_{nocat}} = \frac{k_{nocat}}{k_{cat}} = \frac{3.83}{5.3} = 0.72. \tag{19}$$

3

Question 2. To begin we need to find k_0 and E for each case. We do this by noting that the Arrhenius equation is

$$k = k_0 e^{-E/RT} \tag{20}$$

and if we take the logarithm of both sides,

$$\ln k = \ln k_0 - \frac{E}{RT} \tag{21}$$

so if we plot $\ln k$ vs $1/T$, the slope will be $-E/R$ and the intercept will be $\ln k$. We do this in Excel for each material to get:

- **Alice's Catalyst:** $E = 120\,\text{kJ}\,\text{K}^{-1}\,\text{mol}$; $k_0 = 8.0 \times 10^{16}\,\text{s}^{-1}$

- **Traditional Catalyst:** $E = 204\,\text{kJ}\,\text{K}^{-1}\,\text{mol}$; $k_0 = 1.4 \times 10^{29}\,\text{s}^{-1}$

We then substitute $T = 373$ K into each Arrhenius equation. For Alice:

$$k = 8.0 \times 10^{16} e^{-120000/(8.314 \times 373)} = 1.25\ \text{s}^{-1}. \tag{22}$$

For the traditional catalyst:

$$k = 1.4 \times 10^{29} e^{-204000/(8.314 \times 373)} = 3.77\ \text{s}^{-1}. \tag{23}$$

So, at practical operating conditions, it appears the traditional catalyst is slightly outperforming Alice's :(.

Question 3a
We are told that the conversion is independent of the starting concentration. However, this only occurs for first-order reactions - to see this, consider the general n^{th} order case for reaction at constant volume:

$$\frac{dC_A}{dt} = -kC_A^n \tag{24}$$

If we substitute $C_A = C_{A0}(1 - X_A)$ we get:

$$C_{A0}\frac{dX_A}{dt} = k(C_{A0})^n(1 - X_A)^n \tag{25}$$

With initial conditions $X_A = 0$ at $t = 0$. The only time when C_{A0} doesn't appear in the mathematical description is when $n = 1$, in which case the C_{A0} values cancel from both sides. Other than that, the value of C_{A0} will influence the rate of change of conversion with time. Thus, the reaction is first order.

Question 3b
We are told that the reaction rate, dC_A/dt is independent of the concentration of A. Once again considering the general case for a reaction at constant volume,

$$\frac{dC_A}{dt} = -kC_A^n \tag{26}$$

the only way the reaction rate can be independent of concentration is when $n = 0$ (or $k = 0$, but then there's no reaction!) In that case,

$$\frac{dC_A}{dt} = -k \tag{27}$$

and the reaction is zeroth order.

Question 3c

We are told that the ratio of F to E grows linearly with time:

$$\frac{C_F}{C_E} = \alpha t \tag{28}$$

where α is a constant of proportionality, and we are asked for the reaction order. The standard way to solve this question would be to assume a reaction order, find expressions for how C_E and C_F change with time, and see if they can be expressed in the form of the equation above. However, that trial and error could be time-consuming. Instead, we note that $C_F = C_{E0} - C_E$, and so the equation above can be expressed as:

$$\frac{C_{E0} - C_E}{C_E} = \alpha t. \tag{29}$$

Now we take the time derivative of both sides. Applying the quotient rule gives:

$$\frac{d}{dt}\left(\frac{C_{E0} - C_E}{C_E}\right) = -\frac{dC_E}{dt}C_E^{-1} - \frac{dC_E}{dt}C_E^{-2}(C_{E0} - C_E) = \alpha \tag{30}$$

Rearranging this, and noting a few terms cancel,

$$\frac{dC_E}{dt} = -\alpha\frac{C_E^2}{C_{E0}} = -kC_E^2 \tag{31}$$

and the reaction is second order. Note that the appearance of C_{E0} in this last equation is not a concern, as when we defined α, it was unclear whether or not α itself depended on C_{E0}. As it turns out, $\alpha = kC_{E0}$.

Challenge Question

As the reaction is first order, the rate of reaction of A is given by:

$$r_A = \frac{dC_A}{dt} = -kC_A = -k_0 e^{-E/RT} C_A \tag{32}$$

where the Arrhenius equation has been substituted in for k. Re-writing this in terms of reaction conversion, $X_A \equiv 1 - C_A/C_A^0$,

$$\frac{dX_A}{dt} = k_0 e^{-E/RT}(1 - X_A). \tag{33}$$

Meanwhile, the temperature of the reactor also changes as the reaction proceeds. The reactor is adiabatically insulated, and so any heat released by the reaction will lead to a direct temperature increase according to:

$$\frac{dT}{dt} = \frac{\dot{Q}}{nc_v} \tag{34}$$

where $\dot{Q}$ is the rate of heat released by the reaction occuring inside the reactor, with units J/s. This is, in turn, is given by:

$$\dot{Q} = \Delta_{rxn}\underline{U}\frac{dC_A}{dt}V = -\Delta_{rxn}\underline{U}\frac{dX_A}{dt}n \tag{35}$$

and so the rate of change of temperature over time is:

$$\frac{dT}{dt} = -\frac{\Delta_{rxn}\underline{U}}{c_v}\frac{dX_A}{dt} \tag{36}$$

or, substituting (33),

$$\frac{dT}{dt} = -\frac{\Delta_{rxn}\underline{U}}{c_v}k_0e^{-E/RT}(1 - X_A) \tag{37}$$

Overall, we have the following coupled system of differential equations:

$$\begin{cases} \dfrac{dX_A}{dt} = k_0e^{-E/RT}(1 - X_A) \\[2mm] \dfrac{dT}{dt} = -\dfrac{\Delta_{rxn}\underline{U}}{c_v}k_0e^{-E/RT}(1 - X_A) \\[2mm] X_A = 0 & \text{when t} = 0 \\[1mm] T = T_0 & \text{when t} = 0. \end{cases} \tag{38}$$

In a sense, that's the engineer's problem solved, and so well done! Now all we need to do is solve these differential equations to find X_A and T as functions of time, and a computer can be used to do just that very easily. MATLAB or Octave's ode toolkits would work, as would DifferentialEquations.jl in Julia, or various numerical Python libraries. It's worth becoming familiar with at least one of these pieces of software, as much of classical chemical engineering follows the pattern of this problem: first we derive some differential equations (the engineer's job), second we solve these equations (the computer's job.)

However, in this case, it turns out these equations can be solved analytically. Integrating (36) from $t = 0$, we have:

$$T = T_0 - \frac{\Delta_{rxn}\underline{U}}{c_v}X_A \tag{39}$$

Substituting this into (33) we have:

$$\frac{dX_A}{dt} = k_0 \exp\left(\frac{-E}{R(T_0 - \Delta_{rxn}\underline{U}X_A/c_v)}\right)(1 - X_A). \tag{40}$$

Integrating from $t = 0$ to t, we have

$$\int_0^{X_A} \exp\left(\frac{E/RT_0}{1 - (\Delta_{rxn}\underline{U}/c_vT_0)X_A}\right)\frac{dX_A}{1 - X_A} = k_0t \tag{41}$$

To make things neater, lets define $a \equiv E/RT_0$ and $b \equiv \Delta_{rxn}\underline{U}/c_vT_0$. Then our equation is:

$$\int_0^{X_A} \exp\left(\frac{a}{1 - bX_A}\right)\frac{dX_A}{1 - X_A} = k_0t \tag{42}$$

At this point, Wolfram Alpha comes in handy. The solution is:

$$\text{Ei}\left(\frac{a}{1 - bX_A}\right) - \text{Ei}(a) - \exp\left(\frac{a}{1 - b}\right)\left[\text{Ei}\left(\frac{ab(1 - X_A)}{(b - 1)(1 - bX_A)}\right) - \text{Ei}\left(\frac{ab}{b - 1}\right)\right] = k_0t \tag{43}$$

where $\text{Ei}(\cdot)$ is the exponential integral function. This is the relationship between conversion and time we set out to find; once we've calculated a conversion, we can substitute it into (39) to find the temperature.

It's interesting making some plots of our solution. As the activation energy drops ($a \to 0$) or as the reaction becomes more exothermic ($b \to -\infty$) the conversion approaches the ideal first-order irreversible reaction with reaction constant k_0. Under no circumstances can the reaction be made to go faster than the irreversible isothermal first-order system with $k = k_0$, because the Arrhenius equation forbids k exceeding k_0 at any temperature.

You can also play with making the reaction endothermic, and so $b > 0$. Then, you have two cases: $b < 1$, when there is enough energy in the reactor to (eventually) bring the conversion to 1, or $b > 1$, when there isn't enough energy, and the temperature asymptotes to zero Kelvin with only partial reaction conversion.

Conversion of A vs time

a goes to 0 or b goes to negative infinity

Legend:
Adiabatic Exothermic Reaction, a=1,b=-1
Isothermal First Order Kinetics

x-axis: time
y-axis: Conversion of A