

Reactor Engineering Week 3 Problem Set

Question 1a

Jeremy is very excited about his brand new, home made variable volume, isothermal, isobaric batch reactor (constant-volume reactors are *so* last week...) He is now investigating the following gas-phase, irreversible, first-order chemical reaction:



where ξ is some unknown stoichiometric constant: Jeremy can see that A is decaying, but he doesn't know what it's decaying into! If the reactor initially contained pure A at concentration C_A^0 and had volume V^0 , find expressions for the conversion of A and the volume of the reactor as a function of time. Do you notice anything strange about the expression for the conversion of A ? Why do you think this is case?

Question 1b

Jeremy has noticed that the volume of his reactor changes quickly initially, and slows down later. In particular, he notices that if the volume had continued changing at its *initial* rate, it would have reached its *final* value in τ seconds. What is the value of k ? Does it depend on the value of ξ ?

Question 1c

Jeremy now faces the exact same situation as in question (1a), except he's switched to a reaction that is second order in A . Find a relationship between X_A and time. Do you notice the same interesting coincidence in the conversion expression that we saw in question (1a)? Why or why not?

Question 2

Consider the irreversible reaction



with second-order forward reaction constant k (the reaction is first order in both A and B .) The initial concentration of A , C_A^0 , is ξ times larger than the initial concentration of B , C_B^0 . Without consulting your notes, derive the following relationship for conversion of A as a function of time, assuming $\xi \neq 1$:

$$\ln \frac{\xi - X_A}{\xi(1 - X_A)} = ktC_A^0(\xi - 1). \quad (3)$$

Question 3 - Thermodynamics and Kinetics

We have seen that reaction kinetics are intrinsically related to chemical equilibrium. For instance, consider the chemical reaction



with first-order forward reaction constant k_1 and first-order backwards reaction constant k_2 . At equilibrium, the forward and reverse reaction rates must be equal, and so

$$k_1 C_A^{eq} = k_2 C_B^{eq}. \quad (5)$$

But this may be rearranged to:

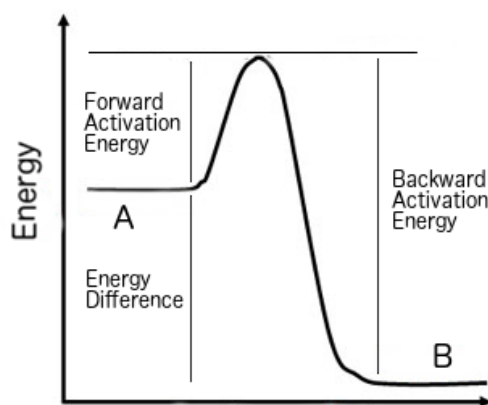
$$\frac{k_1}{k_2} = \frac{C_B^{eq}}{C_A^{eq}} \equiv K^{eq} \quad (6)$$

where K^{eq} is the *equilibrium constant* from thermodynamics.

However, thermodynamics has its own laws, which in many ways are much more reliable and rigorous than chemical kinetic expressions such as the Arrhenius equation. The following questions will investigate whether kinetic expressions are consistent with the rigorous theory of thermodynamics.

Question 3a - Le Chatelier's Principle

Consider the simple reaction shown in (4) above. Each reaction rate constant obeys its own Arrhenius expression, however while the frequency factors, k_0 , are identical, the activation energies for the forward and reverse reactions differ by the difference in energy between the product and the reactant (see the figure). Using the Arrhenius equation, demonstrate that, for an exothermic reaction, an increase in temperature will decrease equilibrium conversion of A , while a decrease in temperature will increase the conversion of A . This is an example of *Le Chatelier's Principle* in thermodynamics.



Question 3b - A More General Relationship.

A slightly more rigorous version of the Arrhenius equation, which appears in some statistical models of chemical reactions, is the *Eyring equation*:

$$k = \frac{\kappa k_B T}{h} \exp \frac{-\Delta G^{++}}{RT} \quad (7)$$

where ΔG^{++} is the difference between Gibb's free energy of the activated state (i.e. the state at the peak of the curve in the figure) and of the pure reactant, and any other symbols you may not recognise are just constants.

Meanwhile, in thermodynamics, the equilibrium constant, K^{eq} , may be related to the temperature of reaction via the following equation:

$$K^{eq} = \exp \frac{-\Delta G^0}{RT} \quad (8)$$

where ΔG^0 is the standard Gibb's Free Energy of reaction (i.e. the difference in Gibb's free energy between pure products and pure reactants). For the simple reaction (4) above, derive equation (8) from (7).

Bonus: *Warning: This is a very difficult problem.* Can we go the other direction, and derive (7) from (8)? The answer is: almost. Show that for the simple reaction (4), the only kinetic expressions consistent with the thermodynamic equation (8) are equations of the form:

$$k = f(T) \exp \left(-\frac{\Delta G^{++}}{RT} \right). \quad (9)$$

Super-Tricky-Fredo-Frog-Challenge-Question

Note: This is a difficult question. Any student who can answer this question by next week's tutorial will be eligible for a Fredo Frog.

Erico's housemate Kevin has a birthday party coming up, and as a good chemical engineering student, Erico has decided that filling balloons with helium is simply boring. Instead, Erico has invented a new kind of balloon! Erico's balloon contains an ideal gas, A, that spontaneously breaks down into two other ideal gases according to the following irreversible reaction:



The reaction is first order in A, with reaction rate constant k_1 .

Erico expects his balloons to expand over time as the reaction progresses. He believes he can model this as a variable-volume batch reactor. However, he's realised that the pressure inside his balloon is going to increase as the balloon expands, and he's not sure how that will affect the results.

Using the pressure gauge on his bike pump, Erico has found that the balloon is initially very easy to inflate, but as soon as the rubber begins to stretch, the pressure inside increases. He finds that, above a volume of V_0 , the pressure increases in proportion with the added gas:

$$p = \begin{cases} p_{atm} & \text{if } V < V_0 \\ \xi(V - V_0) + p_{atm} & \text{if } V \geq V_0 \end{cases} \quad (11)$$

where p is the absolute pressure in the balloon, p_{atm} is the pressure of the atmosphere, and ξ is a constant of proportionality.

If Erico initially fills his balloon with N_A^0 mols of pure A and to a volume V_0 and a pressure of p_{atm} , and if the temperature of the balloon is held constant, find an expression for how the volume of the balloon will change over time! Show that the dimensionless volume, V/V_0 , depends only on the dimensionless time of reaction, kt , and the dimensionless elasticity of the balloon, $\xi V_0/p_{atm}$.

Solutions.

Question 1a.

The local reaction rate constant for this reaction is:

$$r_A = -kC_A \quad (12)$$

And the rate of change of A inside the reactor is

$$\frac{dN_A}{dt} = V \times r_A = -V \times kC_A = -kN_A. \quad (13)$$

So, for this first order case, the volume doesn't even appear in this expression! This is because, if we double the volume, we are halving the reaction rate but doubling the space in which the reaction can occur, which has no net effect. Physically, first-order decay reactions are usually reactions in which individual molecules break down on their own, independent of what's surrounding them. Thus, changing the volume changes the spacing of the molecules, but doesn't affect their decay rate in any way.

Using $N_A = N_A^0(1 - X_A)$, we can rewrite this equation as:

$$\frac{dX_A}{dt} = k(1 - X_A) \quad (14)$$

with solution (for $X_A = 0$ initially) of

$$X_A = 1 - e^{-kt}. \quad (15)$$

This is exactly the same expression as for a constant volume, isothermal reactor! The reason is exactly what we described above.

The volume, V , grows linearly as more product is produced according to

$$V = V^0(1 + \varepsilon_A X_A). \quad (16)$$

We can find ε_A by noting that, when all A is consumed ($X_A = 1$) the new volume will be the original multiplied by ξ times. Thus

$$V^0\xi = V^0(1 + \varepsilon_A \times 1) \quad (17)$$

so

$$\varepsilon_A = \xi - 1 \quad (18)$$

and

$$V = V^0(1 + (\xi - 1)X_A) \quad (19)$$

and so

$$V = V^0(1 + (\xi - 1)(1 - e^{-kt})) = V^0(\xi - (\xi - 1)e^{-kt}). \quad (20)$$

Question 1b.

The initial rate of volume change is:

$$\frac{dV}{dt} = kV^0(\xi - 1). \quad (21)$$

At this rate, the volume will have increased to $V^0\xi$ (it's final value) in $\tau = 1/k$ seconds (remember that we start at a volume of V^0 , so we only need to increase by $V^0(\xi - 1)$.) Thus the reaction rate constant $k = 1/\tau$, and is independent of ξ .

Question 1c

The local reaction rate constant for this reaction is:

$$r_A = -kC_A^2 \quad (22)$$

And the rate of change of A inside the reactor is

$$\frac{dN_A}{dt} = V \times r_A = -V \times kC_A^2 = -k\frac{N_A^2}{V}. \quad (23)$$

So, in this case, it appears that the volume will have an influence on the reaction rate. We can rewrite this as

$$\frac{dX_A}{dt} = k\frac{N_A^0(1 - X_A)^2}{V}. \quad (24)$$

We also know that

$$V = V^0(1 + \varepsilon_A X_A). \quad (25)$$

For this case, as for 1(a) above, $\varepsilon_A = \xi - 1$. Thus

$$V = V^0(1 + (\xi - 1)X_A). \quad (26)$$

and substituting this into (24)

$$\frac{dX_A}{dt} = k \frac{N_A^0(1 - X_A)^2}{V^0(1 + (\xi - 1)X_A)}. \quad (27)$$

Integrating,

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)^2} + (\xi - 1) \int_0^{X_A} \frac{X_A}{(1 - X_A)^2} = kC_A^0 \int_0^t dt. \quad (28)$$

$$\frac{X_A}{(1 - X_A)} + \frac{1}{1 - X_A} + \ln(1 - X_A) - 1 = kC_A^0 t. \quad (29)$$

This is a much more complex relationship between X_A and t than the constant-volume, isothermal, 2nd order irreversible reaction. Unlike first-order reactions, second order reactions typically require *interactions* between multiple molecules. Thus, unlike the first-order case, the changing volume affects the rate of conversion of gas.

To find the volume at a given time, you would need to plug the time into (29) and solve for X_A , then substitute this into (26).

Question 2

This was worked out on p.16-17 of your lectures notes.

Question 3a

The forward reaction has Arrhenius expression

$$k_1 = k_0 \exp\left(-\frac{E_1}{RT}\right) \quad (30)$$

while the backward reaction has expression

$$k_2 = k_0 \exp\left(-\frac{E_2}{RT}\right) \quad (31)$$

The reaction rate constant, K^{eq} , is

$$K^{eq} = \frac{k_1}{k_2} = \exp\left(-\frac{E_1 - E_2}{RT}\right) \quad (32)$$

From the figure in the question, it is clear that

$$\Delta E = E_B - E_A = E_1 - E_2. \quad (33)$$

If the reaction is exothermic, $\Delta E < 0$, in which case $E_1 - E_2 < 0$ and the exponent in (32) is of the form:

$$K^{eq} = k_0 \exp\left(\frac{\alpha}{T}\right) \quad (34)$$

where α is positive. Thus an increase in T will cause K^{eq} to decrease, pushing the reaction backwards, while an decrease in T will increase K^{eq} , pushing the reaction forward. The opposite will occur for an endothermic reaction. All of this is exactly as would be predicted by Le Chatelier's Principle.

Question 3b

Once again, we have

$$K^{eq} = \frac{k_1}{k_2} \quad (35)$$

but now, for the forward reaction,

$$k_1 = \frac{\kappa k_B T}{h} \exp\left(-\frac{(G^{++} - G_A)}{RT}\right) \quad (36)$$

and

$$k_2 = \frac{\kappa k_B T}{h} \exp\left(-\frac{(G^{++} - G_B)}{RT}\right). \quad (37)$$

Here G^{++} is the Gibbs Free Energy of the activated state, while G_B and G_A are the Gibbs Free Energies of pure B and A respectively. Substituting these into (35), and noting that κ, k_B and h all cancel, we get

$$K^{eq} = \frac{k_1}{k_2} = \exp\left(-\frac{G^{++} - G_A}{RT} + \frac{G^{++} - G_B}{RT}\right) = \exp\left(-\frac{G_B - G_A}{RT}\right) = \exp\left(-\frac{\Delta G^0}{RT}\right). \quad (38)$$

Bonus Question.

Now let's think about the bonus question. This is a very tricky problem - I'm sure there's some literature on this, but I haven't been able to find much. Let's consider a simple, binary reaction,



with a single activated state with Gibbs Free energy G^{++} , that must be overcome in order to pass from A (with Gibbs Free Energy G_A) to B (with Gibbs Free Energy G_B .) Then it seems reasonable to assume that the forward reaction rate, k_1 , depends upon the temperature T and the height of the energy barrier that must be overcome, so $k_1 = k(T, G^{++} - G_A)$. Similarly, $k_2 = k(T, G^{++} - G_B)$. Meanwhile, we know from thermodynamics how $K_{eq} = k_1/k_2$ depends upon G and T :

$$K_{eq} = \frac{k(T, G^{++} - G_A)}{k(T, G^{++} - G_B)} = \exp\left(\frac{G_A - G_B}{RT}\right) \quad (40)$$

Note that the left hand side depends upon G^{++} but the right hand side doesn't. This means that all the G^{++} terms must cancel from denominator and numerator. In general these cancelling terms will be of the form $f(T, G^{++})$ and so we can write this equation as:

$$K_{eq} = \frac{f(T, G^{++})g(T, G_A)}{f(T, G^{++})g(T, G_B)} = \exp\left(\frac{G_A - G_B}{RT}\right) \quad (41)$$

and just considering the numerator

$$k(T, G^{++} - G_A) = f(T, G^{++})g(T, G_A). \quad (42)$$

If we keep T constant, this is of the form:

$$k(G^{++} + (-G_A)) = f(G^{++})g(-G_A). \quad (43)$$

Now, If we take the logarithm of both sides, this gives us an equation of the form:

$$h(x + y) = j(x) + m(y) \quad (44)$$

(here h, j, m, x and y are just generic functions/constants. We're only demonstrating the *form* of the equation.) It's not hard to show that this is a modified Cauchy's Functional Equation in disguise, and the only solutions are linear functions of the form $j = ax + b$. Under this assumption,

$$\ln k(G^{++} + (-G_A)) = mG^{++} + nG_A + p \quad (45)$$

where m, n and p are arbitrary constants (as long as T is constant - in general they are functions of T). Continuing:

$$k(G^{++} - G_A) = \exp(mG^{++} + nG_A + p) \quad (46)$$

and, by observation, (and adding back T) this must be of the form

$$k(G^{++} - G_A, T) = c(T) \exp(m(T) \cdot (G^{++} - G_A)) \quad (47)$$

where $c(T), m(T)$ are arbitrary functions of temperature.

This is pretty close to the Eyring-Polng Equation or the Arrhenius equation :) We can conclude that the rate must exponentially change as the activation energy increases or decreases and the temperature remains fixed. Now let's substitute this expression into (41):

$$\frac{c(T) \exp(m(T) \cdot (G^{++} - G_A))}{c(T) \exp(m(T) \cdot (G^{++} - G_B))} = \exp\left(\frac{G_A - G_B}{RT}\right) \quad (48)$$

Rearranging this a little,

$$\exp(m(T)(G_B - G_A)) = \exp\left(\frac{G_A - G_B}{RT}\right). \quad (49)$$

and so $m(T) = -1/RT$. Thus, the only rate equations consistent with thermodynamic theory are those of the form:

$$k = f(T) \exp\left(-\frac{\Delta G^{++}}{RT}\right) \quad (50)$$

where ΔG^{++} is the 'activation energy' that must be overcome (i.e. it is $G^{++} - G_A$ or $G^{++} - G_B$). It seems that pure thermodynamics can tell us a whole lot about reaction kinetics!

Challenge Question

The rate of change of total moles of A inside the balloon is given by:

$$\frac{dN_A}{dt} = r_A \times V = -kC_A \times V = -kN_A \quad (51)$$

So, for this first order case, the volume doesn't even appear in this expression! This is because, if we double the volume, we are halving the reaction rate but doubling the space in which the reaction can occur, which has no net effect. We can rewrite this equation as:

$$\frac{dX_A}{dt} = k(1 - X_A) \quad (52)$$

with solution (for $X_A = 0$ initially) of

$$X_A = 1 - e^{-kt} \quad (53)$$

This gives us the conversion of A - now we need to relate this to a balloon volume. We can do this via the ideal gas law. Because the temperature is constant, at any time:

$$\frac{pV}{N_{tot}} = \frac{p_{atm}V_0}{N_A^0} \quad (54)$$

where N_{tot} is the total number of moles in the balloon at the given time. The pressure will be increasing over time as the balloon grows bigger, so we will have $p = \xi(V - V_0) + p_{atm}$. Further, we can relate the total number of mols in the balloon at any time, N_{tot} , to the conversion of A via $N_{tot} = N_A^0(1 + X_A)$. Substituting these in, we have

$$\frac{(\xi(V - V_0) + p_{atm})V}{N_A^0(1 + X_A)} = \frac{p_{atm}V_0}{N_A^0} \quad (55)$$

Rearranging this and substituting in the expression for X_A found in (53) above,

$$V^2 + (p_{atm}/\xi - V_0)V - \frac{p_{atm}V_0}{\xi}(2 - e^{-kt}). \quad (56)$$

Solving this quadratic equation gives:

$$V(t) = \frac{V_0 - p_{atm}/\xi + \sqrt{(V_0 - p_{atm}/\xi)^2 + 4\frac{p_{atm}V_0}{\xi}(2 - e^{-kt})}}{2} \quad (57)$$

or, slightly neater,

$$\frac{V}{V_0} = \frac{(1 - \alpha) + \sqrt{(1 - \alpha)^2 + 4\alpha(2 - e^{-kt})}}{2} \quad (58)$$

where $\alpha = p_{atm}/\xi V_0$. This is plotted below for various values of α . Large α corresponds to minimal elastic pressure (and, in the limit as $\alpha \rightarrow \infty$, reaction under constant pressure) while small α means the balloon is relatively hard to inflate. Several solutions can easily be plotted in MATLAB.

