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:

$$A \xrightarrow{k} \xi B \tag{1}$$

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

$$A + B \xrightarrow{k} C \tag{2}$$

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 $\xi \neq 1$:

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

Question 3 - Thermodynamics and Kinetics

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

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \tag{4}$$

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

$$k_1 C_A^{eq} = k_2 C_B^{eq}. \tag{5}$$

But this may be rearranged to:

$$\frac{k_1}{k_2} = \frac{C_B^{eq}}{C_A^{eq}} \equiv K^{eq} \tag{6}$$

where K^{eq} is the *equilbrium 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.
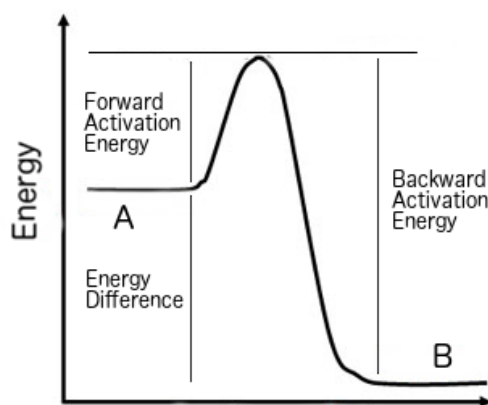
Question 3b - A More General Relationship.

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

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

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:

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

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:

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

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:

$$A \xrightarrow{k_1} B + C \tag{10}$$

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

Erico expects his balloons to expand over time as the reaction progressess. 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:

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

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, $\xi V_0/p_{atm}$.