

# Introduction to Reactor Design, 3K4

## Tutorial 4/Assignment 3A

Kevin Dunn, kevin.dunn@mcmaster.ca

Due at class, 11 February; no late hand-ins

### Assignment objectives:

- To demonstrate your understanding of chemical equilibrium in system with and without change in volume.
- To use the reactor design equations in terms of conversion.

### Question 1 [5]

Consider the reversible reaction of A going to 2B, with only pure A fed to the flow reactor at 340K and 202.6 kPa. The equilibrium constant at 340K is  $K_C = 100 \text{ mol.m}^{-3}$ .

Show that the equilibrium conversion,  $X_{\text{eq}}$ , leaving the reactor is  $X_{\text{eq}} = 0.51$ .

#### *Solution*

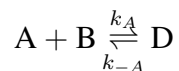
Using stoichiometric tables, and noting that  $\varepsilon = 1$

$$\begin{aligned}C_A &= \frac{F_A}{q} = \frac{F_{A0}(1 - X)}{q_0(1 + \varepsilon X)} = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)} \\C_B &= \frac{2C_{A0}X}{(1 + \varepsilon X)} \\K_C &= \frac{\{B\}^2}{\{A\}} \\K_C &= \frac{\left(\frac{2C_{A0}X_{\text{eq}}}{(1 + \varepsilon X_{\text{eq}})}\right)^2}{\frac{C_{A0}(1 - X_{\text{eq}})}{(1 + \varepsilon X_{\text{eq}})}} \\K_C &= \frac{4C_{A0}X_{\text{eq}}}{(1 + \varepsilon X_{\text{eq}})(1 - X_{\text{eq}})}\end{aligned}$$

then use the quadratic equation to solve for  $X_{\text{eq}} = 0.51$

### Question 2 [4]

Consider the system producing product, D, from raw materials A and B in the reversible reaction:



If the equilibrium constant,  $K_C$  has a value of 40 at room temperature, 25°C:

1. What are the units of  $K_C$ ?
2. What is the value of  $K_C$  at 50°C, if the heat of reaction is 150 kJ.mol<sup>-1</sup>?
3. Draw of a plot of the equilibrium constant against temperature.

*Solution*

1. The units are inverse concentration,  $\frac{[m^3]}{mol}$ .
2. Using formula in Appendix C (Fogler, 2006):

$$K_{p2} = K_{p1} e^{\frac{\Delta H_{rxn}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

where  $K_C = \frac{K_p}{RT}$  and  $\delta = 1 - 1 - 1 = -1$

$$K_p = \frac{K_C}{RT}$$

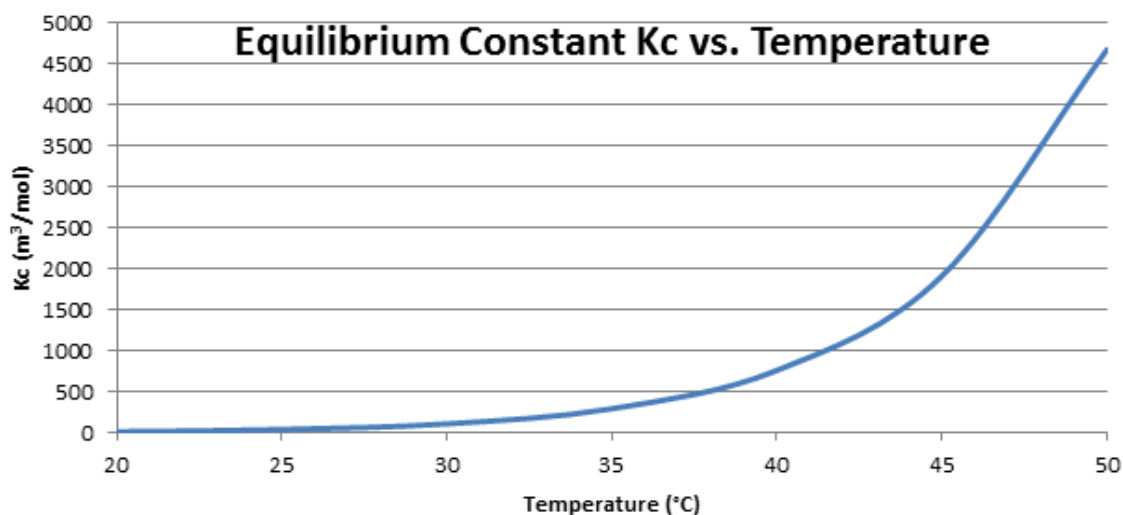
Substituting and rearranging:

$$\frac{K_{C2}}{RT_2} = \frac{K_{C1}}{RT_1} e^{\frac{\Delta H_{rxn}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$K_{C2} = (40 \text{ m}^3 \cdot \text{mol}^{-1}) \left( \frac{323.15 \text{ K}}{298.15 \text{ K}} \right) e^{\frac{150000 \text{ J} \cdot \text{mol}^{-1}}{8.314} \left( \frac{1}{298.15 \text{ K}} - \frac{1}{323.15 \text{ K}} \right)}$$

$$K_{C2} = 4679 \text{ m}^3 \cdot \text{mol}^{-1}$$

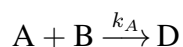
3. A plot of  $K_C$  against temperature is:



### Question 3 [20]

At your company there is an existing glass-lined, and well-mixed CSTR. With the inlet and outlet valves closed it becomes a batch reactor. The volume of this vessel is 1800 L. The temperature of the vessel is easily controlled.

You are working to produce a product, D, from raw materials A and B in the reaction:



which is a liquid-phase reaction system that operates with the following kinetics:  $-r_A = k_A C_A$ , where  $k_A = 0.18 \text{ hour}^{-1}$  helpfully determined by your company's laboratory, at room temperatures of 25°C.

Your boss is giving you, the engineering team lead, the task of determining how to maximize production of species D. Because there is such a high demand for it, you must figure out how to produce the most amount of D within a regular production shift in that vessel. Species A is available in pure form at 50 mol per litre, and species B is available at 70 mol per litre.

There is only one constraint: you must operate at room temperature, because the product is extremely temperature sensitive and starts to degrade rapidly at temperatures exceeding 30°C. Also consider that you want the stream leaving the reactor to have a high purity, so you can minimize the amount on downstream separation of D from A and B.

Describe *clearly and concisely to your operators* how to produce product D and how much of D will be produced in a 12 hour period. You must show all your calculation steps to obtain full grade.

#### *Solution*

This is an open-ended question and there are many answers that could be considered. Grading in this question is done based on *how* you express your answer and your technical accuracy. There are few key elements that must appear in the solution though:

- whether you did calculations for both batch and CSTR options
- that you compare, within a 12 hour period, which option would produce more product of D (not conversion)
- that you recognize for the batch option that there are trade-offs between batch duration and conversion and that you show those trade-offs
- that you recognize for the CSTR option that there are trade-offs between inlet flow and conversion and that you show those trade-offs
- for the batch option: you must specify to your operators how much A and how much B to add, and these must be added in their stoichiometric ratios
- for the CSTR option: you must specify to your operators what flow of A and B to use, and these must be added in their stoichiometric ratios
- you must discuss product purity in the stream leaving the reactor as a critical decision factor.

For either the CSTR or batch option you must tell your operators how to operate the reactor. This requires telling them how much of A and B to add in terms of litres, not in mols (operators do not understand mols). Since they must be added in their stoichiometric ratio, and not in an equi-volume ratio, consider as a basis 100L of feed to either the batch or CSTR.

Let  $\alpha$  L of A be added and  $\beta$  L of B be added, then  $\alpha + \beta = 100$  L. For the equi-molar requirement, then  $50\alpha = 70\beta$ , or in other words,  $\alpha = \frac{7}{5}\beta$ . Solving these equations gives  $\alpha = 58.33$  L and  $\beta = 41.67$  L. This makes sense: add less B, because it has a higher concentration.

Note that for a CSTR we will need to now the total inlet flow rate,  $q$ . This is the flow of A and B combined. The inlet concentration of A and B in the combined stream will be different to the inlet concentration of the pure streams. So continuing with our basis of 100L, the blended inlet concentration A in an equi-molar mixture of A and B is:

$$C_{A0} = \frac{50\alpha \text{ mol of A}}{100 \text{ L}} = 29.165 \frac{\text{mol}}{\text{L}}$$

Incidentally you can show that  $C_B = 29.165 \text{ mol.L}^{-1}$  as well. So up to this point, we've done no engineering, just revised basic first year chemistry concepts of mixtures and mass balances to calculate concentrations.

### Batch option

The performance equation for a batch system is (using the stoichiometric tables)

$$\begin{aligned} t &= N_{A0} \int_0^X \frac{dX}{-r_A V} \\ -r_A V &= k C_A V \\ -r_A V &= k C_{A0} (1 - X) V \\ -r_A V &= k N_{A0} (1 - X) \\ t &= \frac{1}{k_A} \int_0^X \frac{dX}{(1 - X)} \\ t &= -\frac{1}{k_A} \ln(1 - X) \end{aligned}$$

A plot of  $t$  against  $X$  shows that longer batch times are required for higher conversions, making intuitive sense.

Once we know the conversion,  $X$ , to find the number of moles of D produced, we use that  $N_D = N_{A0} - N_A = N_{A0} - N_{A0}(1 - X) = N_{A0}X$ , where  $N_{A0} = 0.5833 \times 1800 \text{ L} \times 50 \text{ mol.L}^{-1} = 52,500$  mol of A added to the reactor.

Let's investigate a few examples, where  $N_A$  are the mols of A leaving and  $N_D$  are the number of moles of D leaving after all batches are run in the 12 hour period.

Number of batches/12hrs	$X$	$N_A$	$N_D$
1	0.88	6055	46445
2	0.66	35658	69342
3	0.51	76663	80837
4	0.42	122377	87623
6	0.30	219768	95232

There is rounding in the table, but the values were calculated in a spreadsheet to higher precision. For example, if we run 2 batches, each will have 66% conversion, the total moles from both batches will be  $52500 \times (1 - 0.66) \times 2 = 35658$  mols of A leaving; which implies a total of  $52500 \times 0.66 \times 2 = 69342$  mols of D will be produced.

This table clearly shows the trade-off: we can produce more D with many, short batches, but the amount of A leaving the reactor also increases, making subsequent separation harder and less economical.

### Continuous CSTR operation

For a CSTR flow reactor we have the design equation:

$$V = \frac{F_{A0}X}{-r_A}$$

$$V = \frac{qC_{A0}X}{k_A C_{A0}(1 - X)}$$

$$q = (V k_A) \left( \frac{1 - X}{X} \right)$$

A quick plot shows a inverse hyperbolic relationship between conversion and flow. Please note that  $q$  in the above equation is the *total* inlet flowrate of A and B combined. As explained above,  $C_{A0} = 29.165 \text{ mol.L}^{-1}$  is the overall concentration of A entering the reactor.

Note that once we have the total volumetric flow, we can calculate the amount of D leaving the reactor as  $F_D = F_{A0}X = qC_{A0}X$  then multiply this by 12 to get total moles in a 12 hour period. Again a table of values showing the trade offs at different conversions:

$X$	$q$	$F_{A0}$	$F_A$	$F_D$	<b>In 12 hours</b>
0.5	324	9449.5	4725	1530813	18369750
0.7	138.9	4049.8	1215	393638	4723650
0.9	36	1049.9	105	34018	408217
0.95	17.1	497.3	25	8057	96683
0.98	6.6	192.8	3.9	1250	14996

All the flow rates for  $q$  are reasonable [ $\text{L.hour}^{-1}$ ]. At low flows we obtain high conversions, but corresponding low number of moles of D produced.

However, comparing the CSTR row with 95% conversion quickly makes one realize that in a 12 hour period we will produce approximately the same amount of product D that 6 batches of 2 hours would produce (note that 6 batches could not be realistically completed, because we have assumed it takes no time to drain, clean and refill the batch reactor).

These two tables quickly show the superiority of the CSTR option *for this system*. At 95% conversion we can produce 95,683 mols of D with very little contamination from unreacted A and B (only 25 mols of A and 25 mols of B). Compare that with the 30% conversion case in the batch reactor, where we produce about 95 232 mols of D, but it is contaminated with 219,768 moles of unreacted A and B.

So the operator instructions are:

- Open the inlet and exit valves and operate the vessel as a CSTR.
- Operate with a feed flow rate of 17.1 L/hour combined flow, made up of  $17.1 \times 0.5833 \approx 10 \text{ L}\cdot\text{hour}^{-1}$  of A at  $50 \text{ mol}\cdot\text{L}^{-1}$  and  $17.1 \times 0.4167 \approx 7.12 \text{ L}\cdot\text{hour}^{-1}$  of B at  $70 \text{ mol}\cdot\text{L}^{-1}$ . This is a feed that is in the 1:1 stoichiometric ratio of A:B.
- The amount of D produced will be  $\{8057, \text{mols}\cdot\text{hour}\}$ , or 96,683 mols in a 12 hour period.

#### Question 4 [12]

The following gas phase reaction is taking place:  $A \longrightarrow 3B$  at 350K and 900 kPa; the equilibrium constant is  $0.20 \text{ mol}^2\cdot\text{L}^{-6}$  at these conditions. Calculate (a) the equilibrium concentration of A, (b) the equilibrium concentration of B, and (c) the conversion of A, for the following 3 cases:

1. The material is reacting in a flow reactor.
2. The material is reacting in a constant volume batch reactor.
3. The material is reacting in a constant pressure batch reactor.

Then,

4. Compare the above answers for the 3 situations and explain why they make sense/do not make sense. In particular, explain any differences in the equilibrium concentration of A among the 3 reactors.

#### *Solution*

The general strategy is to express the concentrations in terms of conversion. Solve for the equilibrium conversion and calculate the equilibrium concentration. Similar to question 1 in this tutorial.

---

END