

# Fundamentals of Reaction Engineering - Examples

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# Fundamentals of Reaction Engineering

## Worked Examples

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# Contents

Chapter I:	Homogeneous reactions – Isothermal reactors	5
Chapter II:	Homogeneous reactions – Non-isothermal reactors	13
Chapter III:	Catalytic reactions – Isothermal reactors	22
Chapter IV:	Catalytic reactions – Non-isothermal reactors	31



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## Worked Examples - Chapter I

### Homogeneous reactions - Isothermal reactors

#### Problem 1.1

Problem 1.1a: For a reaction  $A \rightarrow B$  (rate expression:  $r_A = kC_A$ ), taking place in an isothermal tubular reactor, starting with the mass balance equation and assuming plug flow, derive an expression for calculating the reactor volume in terms of the molar flow rate of reactant 'A'.

Solution to Problem 1.1a: Assuming plug flow, the mass balance over a differential volume element of a tubular reactor is written as:

$$(M_A n_A)_V - (M_A n_A)_{V+\Delta V} - M_A r_A \Delta V_R = 0$$

Taking the limit as  $\Delta V_R \rightarrow 0$

$$-\frac{dn_A}{dV_R} - r_A = 0; \quad r_A = -\frac{dn_A}{dV_R}; \quad V_R = -\int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{r_A}$$

Problem 1.1b: If the reaction is carried out in a tubular reactor, where the total volumetric flow rate  $0.4 \text{ m}^3 \text{ s}^{-1}$ , calculate the reactor volume and the residence time required to achieve a fractional conversion of 0.95. The rate constant  $k=0.6 \text{ s}^{-1}$ .

Solution to Problem 1.1b: The molar flow rate of reactant "A" is given as,

$$n_A = n_{A0}(1 - x_A).$$

Also  $n_A = C_A v_T$ . The rate is then given as  $r_A = kC_A = \frac{kn_A}{v_T}$ . Substituting,

$$V_R = -\frac{v_T}{k} \int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{n_A} = \frac{v_T}{k} \int_0^{x_{Ae}} \frac{n_{A0} dx_A}{n_{A0}(1-x_A)} = \frac{v_T}{k} \int_0^{x_{Ae}} \frac{dx_A}{(1-x_A)}$$

$$V_R = -\frac{v_T}{k} \ln(1-x_{Ae}) \cong 2 \text{ m}^3$$

In plug flow the residence time is defined as

$$\tau \equiv \frac{V_R}{v_T} \quad \left[ \frac{\text{m}^3}{\text{m}^3 \text{ s}^{-1}} \right] = [s]; \quad \tau = 2 / 0.4 = 5 \text{ s}$$

#### Problem 1.2

The gas phase reaction  $A \rightarrow 2S$  is to be carried out in an isothermal tubular reactor, according to the rate expression  $r_A = k C_A$ . Pure A is fed to the reactor at a temperature of 500 K and a pressure of 2 bar, at a rate of 1000 moles  $\text{s}^{-1}$ . The rate constant  $k= 10 \text{ s}^{-1}$ . Assuming effects due to pressure drop through the reactor to be negligible, calculate the volume of reactor required for a fractional conversion of 0.85.

Data:

$R$ , the gas constant	: $8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ bar m}^3 \text{ kmol}^{-1} \text{ K}^{-1}$
$P$ the total pressure	: 2 bar
$n_{T0}$ total molar flow rate at the inlet	: $1000 \text{ moles s}^{-1} = 1 \text{ kmol s}^{-1}$
$k$ , reaction rate constant	: $10 \text{ s}^{-1}$

### Solution to Problem 1.2

In Chapter I we derived the equation for calculating the volume of an isothermal tubular reactor, where the first order reaction,  $A \rightarrow 2S$ , causes volume change upon reaction:

$$V_R = \frac{RT}{Pk} n_{T0} \left\{ (1 + y_{A0}) \ln \left[ \frac{1}{1 - x_{Ae}} \right] - y_{A0} x_{Ae} \right\} \quad (\text{Eq. 1.37})$$

In this equation, for pure feed "A",  $y_{A0} \equiv n_{A0}/n_{T0} = 1$ .

$$V_R = \frac{(0.08314)(500)}{(2)(10)} (1) \{ 2 \ln(6.67) - 0.85 \}$$

$$V_R = 6.1 \text{ m}^3$$

Let us see by how much the total volumetric flow rate changes between the inlet and exit of this reactor. First let us review how the total molar flow rate changes with conversion:

$n_I$	=	$n_{I0}$	for the inert component
$n_A$	=	$n_{A0} - n_{A0} x_A$	for the reactant
$n_S$	=	$n_{S0} + 2 n_{A0} x_A$	for the product
-----			
$n_T$	=	$n_{T0} + n_{A0} x_A$	$n_T$ is the <u>total</u> molar flow rate

$$v_{T0} = \frac{n_{T0} RT}{P} = (1)(0.08314)(500) / 2 = 20.8 \text{ m}^3 \text{ s}^{-1}$$

$$v_{T,exit} = n_{T,exit} RT / P; \quad \text{but} \quad n_{T,exit} = n_{T0} + n_{A0} x_{A,exit}$$

and  $n_{T0} = n_{A0}$ ; therefore

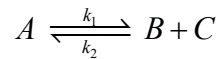
$$v_{T,exit} = (1 + 0.85)(0.08314)(500) / 2 = 38.5 \text{ m}^3 \text{ s}^{-1}$$

$$v_{T0} = 20.8 \text{ m}^3 \text{ s}^{-1}; \quad v_{T,exit} = 38.5 \text{ m}^3 \text{ s}^{-1}$$

The difference is far from negligible! In dealing with gas phase reactions, rates are often expressed in terms of partial pressures:  $r_A = kp_A$ , as we will see in the next example.

### Problem 1.3

The gas phase thermal decomposition of component A proceeds according to the chemical reaction



with the reaction rate  $r_A$  defined as the rate of disappearance of A:  $r_A = k_1 C_A - k_2 C_B C_C$ . The reaction will be carried out in an isothermal continuous stirred tank reactor (CSTR) at a total pressure of 1.5 bara and a temperature of 700 K. The required conversion is 70 %. Calculate the volume of the reactor necessary for a pure reactant feed rate of 4,000 kmol hr<sup>-1</sup>. Ideal gas behavior may be assumed.

Data

$$k_1 = 10^8 e^{-10,000/T}$$

$$s^{-1} \quad (T \text{ in K})$$

$$k_2 = 10^8 e^{-8,000/T}$$

$$m^3 \text{ kmol}^{-1} s^{-1} \quad (T \text{ in K})$$

$$\text{Gas constant, } R = 0.08314$$

$$\text{bar } m^3 \text{ kmol}^{-1} K^{-1}$$



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## Solution to Problem 1.3

Using the reaction rate expression given above, the “design equation” (i.e. isothermal mass balance) for the CSTR may be written as:

$$V_R = \frac{n_{A0} - n_A}{k_1 C_A - k_2 C_B C_C} = \frac{n_{A0} x_A v_T}{k_1 n_A - \left(\frac{k_2}{v_T}\right) n_B n_C}, \quad \text{where } \frac{n_i}{v_T} = C_i \quad (\text{Eq. 1.1.A})$$

We next write the mole balance for the reaction mixture:

$$\begin{aligned} n_A &= n_{A0} - n_{A0} x_A \\ n_B &= \quad + n_{A0} x_A \\ n_C &= \quad + n_{A0} x_A \end{aligned}$$

$$n_T = n_{A0} + n_{A0} x_A = n_{A0} (1 + x_A).$$

This result is used in the “ideal gas” equation of state:

$$v_T = \frac{n_T R T}{P_T} = \frac{n_{A0} R T}{P_T} (1 + x_A).$$

Substituting into Eq. 1.1.A derived above, we get:

$$V_R = \frac{n_{A0} x_A (n_{A0} R T) (1 + x_A)}{P_T \left\{ k_1 n_{A0} - k_1 n_{A0} x_A - \frac{k_2 P_T n_{A0}^2 x_A^2}{n_{A0} R T (1 + x_A)} \right\}}$$

Simplifying,

$$V_R = \left( \frac{n_{A0} R T}{P_T} \right) \frac{x_A (1 + x_A)}{\left\{ k_1 - k_1 x_A - \frac{k_2 P_T}{R T} \frac{x_A^2}{1 + x_A} \right\}}$$

To further simplify, we define  $a \triangleq \frac{k_2 P_T}{R T}$ .

$$V_R = \left( \frac{n_{A0} R T}{P_T} \right) \frac{x_A (1 + x_A)^2}{k_1 + k_1 x_A - k_1 x_A - a x_A^2 - k_1 x_A^2} \quad (\text{Eq. 1.1.B})$$

Next we calculate the values of the reaction rate constants

$$k_1 = 62.49 \text{ s}^{-1}; \quad x_{A,\text{exit}} = 0.70; \quad T = 700 \text{ K}$$

$$k_2 = 1088 \text{ m}^3 \text{ s}^{-1} \text{ kmol}^{-1}; \quad P_T = 1.5 \text{ bar}$$

Substituting the data into Eq. 1.1.B

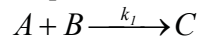
$$V_R = \frac{(4000)(0.08314)(700)}{(3600)(1.5)} \left[ \frac{0.7(1+0.7)^2}{62.49 - k_1 x_A^2 - a(0.7)^2} \right]; \quad a = \frac{(1088)(1.5)}{(0.08314)(700)} = 28$$

$$V_R = (43.11)(0.11) \cong 4.74 \text{ m}^3$$

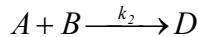


### Problem 1.4

The liquid phase reaction for the formation of compound C



with reaction rate  $r_{A_1} = k_1 C_A C_B$ , is accompanied by the undesirable side reaction



with reaction rate  $r_{A_2} = k_2 C_A C_B$ . The combined feed of 1000 kmol per hour is equimolar in A and B. The two components are preheated separately to the reactor temperature, before being fed in. The pressure drop across the reactor may be neglected. The volumetric flow rate may be assumed remain constant at  $22 \text{ m}^3 \text{ hr}^{-1}$ .

The desired conversion of A is 85 %. However, no more than 20 % of the amount of “A” reacted may be lost through the undesirable side reaction. Find the volume of the smallest isothermally operated tubular reactor, which can satisfy these conditions.

Data

$$\begin{aligned} k_1 &= 2.09 \times 10^{12} e^{-13,500/T} & \text{m}^3 \text{ s}^{-1} \text{ kmol}^{-1} & ; & (T \text{ in K}) \\ k_2 &= 10^{17} e^{-18,000/T} & \text{m}^3 \text{ s}^{-1} \text{ kmol}^{-1} & ; & (T \text{ in K}) \end{aligned}$$

#### Solution to Problem 1.4

For equal reaction orders:  $(n_1/n_2) = (k_1/k_2)$ , where  $n_1$  is moles reacted through Reaction 1, and  $n_2$  is moles reacted through Reaction 2. Not allowing more than 20 % loss through formation of by-product “D” implies:  $(n_1/n_2) = (k_1/k_2) \geq 4$ .

Since  $\Delta E_2 > \Delta E_1$ , the rate of Reaction 2 increases faster with temperature than the rate of Reaction 1. So the maximum temperature for the condition  $\{n_1/n_2 \geq 4\}$  will be at  $(n_1/n_2) = (k_1/k_2) = 4$ . This criterion provides the equation for the maximum temperature:

$$\frac{2.09 \times 10^{12}}{10^{17}} e^{4500/T} = 4 ; \quad \frac{4500}{T} = \ln \left\{ \frac{4 \times 10^{17}}{2.09 \times 10^{12}} \right\}. \text{ Solving, } T = \frac{4500}{12.16} = 370 \text{ K}.$$

The temperature provides the last piece of information to write the integral for calculating the volume.

$$\begin{aligned} V_R &= \int_0^{0.85} \frac{n_{A0} dx_A}{(k_1 + k_2) C_A C_B}; \quad \text{define } k \triangleq k_1 + k_2 \\ V_R &= \int_0^{0.85} \frac{v_T^2 n_{A0} dx_A}{k n_{A0}^2 (1 - x_A)^2} = \frac{v_T^2}{k n_{A0}} \int_0^{0.85} \frac{dx_A}{(1 - x_A)^2} \\ V_R &= \frac{(22)^2}{k (3600)(1000)(0.5)} \left\{ \frac{1}{(1 - 0.85)} - 1 \right\} \\ V_R &= \frac{2.69 \times 10^{-4} (5.67)}{k}; \quad (k_1 + k_2) = 2.98 \times 10^{-4} + 0.74 \times 10^{-4} = 3.72 \times 10^{-4} \end{aligned}$$

$$\boxed{V_R = 4.1 \text{ m}^3}$$

### Problem 1.5

A first order, liquid phase, irreversible chemical reaction is carried out in an isothermal continuous stirred tank reactor  $A \rightarrow \text{products}$ . The reaction takes place according to the rate expression  $r_A = k C_A$ . In this expression,  $r_A$  is defined as the rate of reaction of  $A$  ( $\text{kmol m}^{-3} \text{s}^{-1}$ ),  $k$  as the reaction rate constant (with units of  $\text{s}^{-1}$ ) and  $C_A$  as the concentration of  $A$  ( $\text{kmol m}^{-3}$ ). Initially, the reactor may be considered at steady state. At  $t = 0$ , a step increase takes place in the inlet molar flow rate, from  $n_{A0,ss}$  to  $n_{A0}$ . Assuming  $V_R$  (the reactor volume) and  $v_T$  (total volumetric flow rate) to remain constant with time,

a. Show that the unsteady state mass balance equation for this CSTR may be expressed as:

$$\frac{dn_A}{dt} + \left[ \frac{1}{\tau} + k \right] n_A = \frac{n_{A0}}{\tau},$$

Also write the appropriate initial condition for this problem. The definitions of the symbols are given below.

b. Solve the differential equation above [Part a], to derive an expression showing how the *outlet* molar flow rate of the reactant changes with time.

c. How long would it take for the exit flow rate of the reactant A to achieve 80 % of the change between the original and new steady state values (i.e. from  $n_{A,ss}$  to  $n_A$ ) ?

#### DEFINITIONS and DATA:

$n_{A0,ss}$	steady state inlet molar flow rate of reactant A before the change :	$0.1 \text{ kmol s}^{-1}$
$n_{A0}$	new value of the inlet molar flow rate of reactant A	$: 0.15 \text{ kmol s}^{-1}$
$V_R$	reactor volume	$: 2 \text{ m}^3$
$k$	reaction rate constant	$: 0.2 \text{ s}^{-1}$
$v_T$	total volumetric flow rate	$: 0.1 \text{ m}^3 \text{ s}^{-1}$
$n_{A,ss}$	steady state molar flow rate of reactant A exiting from the reactor, before the change,	$\text{kmol s}^{-1}$
$n_A$	the molar flow rate of reactant A exiting from the reactor at time t,	$\text{kmol s}^{-1}$
$t$	time, s	
$\tau$	average residence time, $V_R/v_T$ ,	s
$r_A$	rate of reaction of A,	$\text{kmol m}^{-3} \text{ s}^{-1}$
$C_A$	concentration of A,	$\text{kmol m}^{-3}$

## Solution to Problem 1.5

a. CSTR mass balance with accumulation term: material balance on component A, over the volume  $V_R$  for period  $\Delta t$ :

$$\left\{ \bar{n}_{A0}(t) - \bar{n}_A(t) - \bar{r}_A(t)V_R \right\} \Delta t = N_A|_{t+\Delta t} - N_A|_t$$

Bars indicate averages over the time interval  $\Delta t$ , and  $N_A(t)$  is the total number of moles of component A in the reactor at time  $t$ . Also  $C_A = n_A/v_T = N_A/V_R$ , and the average residence time,  $\tau = V_R/v_T$ . Taking the limit as  $\Delta t \rightarrow dt$  in the above equation, we get:

$$n_{A0} - n_A - r_A V_R = \frac{dN_A}{dt}$$

Combining this with  $N_A \equiv V_R C_A = V_R (n_A/v_T)$  leads to the equation:

$$n_{A0} - n_A - k C_A V_R = \frac{V_R}{v_T} \frac{dn_A}{dt}$$

Rearranging,

$$n_{A0} - n_A - \frac{k n_A V_R}{v_T} = \tau \frac{dn_A}{dt}, \text{ and,}$$

$$\boxed{\frac{dn_A}{dt} + \left[ \frac{1}{\tau} + k \right] n_A = \frac{n_{A0}}{\tau}}$$

$$\boxed{\text{with initial condition: at } t=0, \quad n_A = n_{A,ss}}$$

b. We define  $\beta \equiv \left[ \frac{1}{\tau} + k \right]$  and write the complementary and particular solutions for the first order ordinary differential equation derived above.

$$n_{A,\text{complementary}} = C_1 e^{-\beta t} \quad ; \quad n_{A,\text{particular}} = C_2 (\text{const})$$

where the solution is the sum of the two solutions:  $n_A(t) = n_{A,c}(t) + n_{A,p}(t)$ . We substitute the particular solution into differential equation to evaluate the constants:

$$\left[ \frac{1}{\tau} + k \right] C_2 = \frac{n_{A0}}{\tau} \quad ; \quad C_2 = \frac{n_{A0}}{\beta \tau}$$

The most general solution can then be written as  $n_A = C_1 e^{-\beta t} + \frac{n_{A0}}{\beta \tau}$ . To derive  $C_1$ , we substitute the initial condition:  $n_A = n_{A,ss}$  at  $t=0$ , into the general solution:

$$n_{A,ss} = C_1 + \frac{n_{A0}}{\beta \tau} \quad ; \quad \Rightarrow \quad C_1 = n_{A,ss} - \frac{n_{A0}}{\beta \tau}$$

The solution of the differential equation can then be written as:

$$\boxed{n_A = \left\{ n_{A,ss} - \frac{n_{A0}}{\beta \tau} \right\} e^{-\beta t} + \frac{n_{A0}}{\beta \tau}}$$

$$\text{where } \beta \tau = 1 + k \tau.$$

c.  $\lim_{t \rightarrow \infty} n_A = \frac{n_{A0}}{\beta \tau} = \frac{n_{A0}}{1 + k \tau} \Rightarrow$  The new steady state exit molar flow rate of A

The relationship linking  $t$ ,  $n_{A,ss}$  and  $n_A$  is derived from the solution of the differential equation

$$t = \frac{\tau}{1+k\tau} \left\{ \ln \left( \frac{n_{A,ss} - \frac{n_{A0}}{\beta\tau}}{n_A - \frac{n_{A0}}{\beta\tau}} \right) \right\} = \frac{\tau}{1+k\tau} \left\{ \ln \left( \frac{\frac{n_{A0}}{\beta\tau} - n_{A,ss}}{\frac{n_{A0}}{\beta\tau} - n_A} \right) \right\}$$

$$\tau = \frac{2}{0.1} = 20 \text{ s} \quad ; \quad n_{A,ss} = \frac{n_{A0,ss}}{1+k\tau} = \frac{0.1}{1+(20)(0.2)} = 0.02 \text{ kmol s}^{-1}$$

$$\frac{\tau}{1+k\tau} = \frac{20}{1+(0.2)(20)} = 4 \text{ s}$$

$$n_{A,final} = \frac{n_{A0}}{\beta\tau} = \frac{n_{A0}}{1+k\tau} = \frac{0.15}{1+(20)(0.2)} = 0.03 \text{ kmol s}^{-1}$$

For 80 % of the change to be accomplished:  $n_A = n_{A,ss} + 0.8 (n_{A,final} - n_{A,ss})$


$$n_A = 0.8 n_{A,final} + 0.2 n_{A,ss} = 0.8(0.03) + 0.2 (0.02) = 0.028 \text{ kmol s}^{-1}$$

$$t = \frac{\tau}{1+k\tau} \left\{ \ln \left[ \frac{n_{A0}}{\beta\tau} - n_{A,ss} \right] - \ln \left[ \frac{n_{A0}}{\beta\tau} - n_A \right] \right\}$$


$$t = 4 \left\{ \ln [0.03 - 0.02] - \ln [0.03 - 0.028] \right\} = 6.44 \text{ s}$$

$$t = 6.44 \text{ s}$$

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## Worked Examples - Chapter II

### Homogeneous reactions – Non-isothermal reactors

#### Problem 2.1

Problem 2.1a: Identify the terms in the energy balance equation for a continuous stirred tank reactor:

$$-\sum n_{i0} \int_{T_0}^T C_{pi} dT + V_R \sum H_{fi}(T) r_i + Q = 0$$

Solution to Problem 2.1a:

- 1<sup>st</sup> term: heat transfer by flow
- 2<sup>nd</sup> term: heat generation/absorption by the reaction(s)
- 3<sup>rd</sup> term: sensible heat exchange
- Steady state: no accumulation

Problem 2.1b: What form does the equation take for the single reaction:  $A \rightarrow B + C$

Solution to Problem 2.1b:

$$\sum H_{fi} r_i = H_{fA} r_A + H_{fB} r_B + H_{fC} r_C$$

and  $r_A = -r_B = -r_C$ .

$$= r_A \{H_{fA} - H_{fB} - H_{fC}\}$$

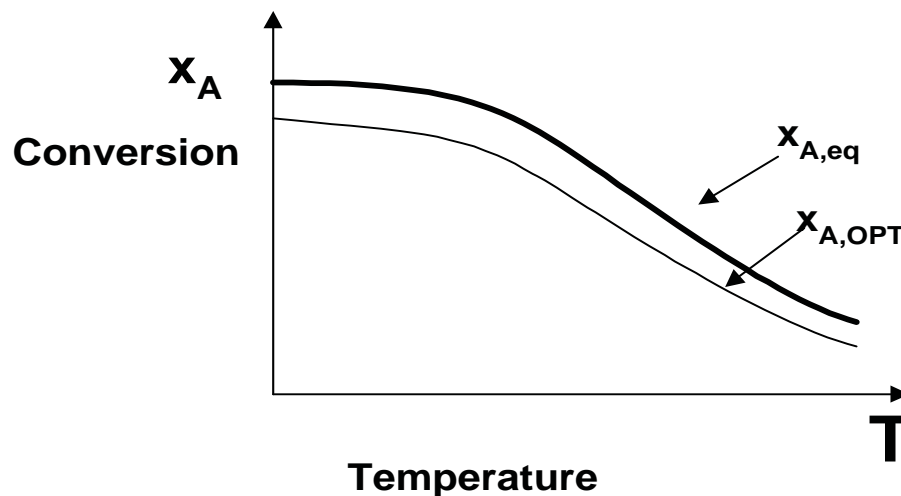
$$= -r_A \Delta H_r$$

Then the energy balance equation takes the form:

$$-\sum n_{i0} \int_{T_0}^T C_{pi} dT - V_R \Delta H_r r_A + Q = 0$$

Problem 2.1c: For a simple reversible-*exothermic* reaction  $A \rightleftharpoons B$ , qualitatively sketch the locus of maximum reaction rates on an  $x_A$  vs.  $T$  diagram (together with the  $x_{A,eq}$  line).

Solution to Problem 2.1c:



Problem 2.1d: The chemical reaction  $A \rightarrow B$  is carried out in a continuous stirred tank reactor. Calculate the adiabatic temperature rise for 100 % conversion.

The mole fraction of A in the input stream  $y_{A0} = (n_{A0}/n_{T0}) = 1$ .

The total heat capacity,  $\bar{C}_p = 80 \text{ J mol}^{-1} \text{ K}^{-1}$

The heat of reaction,  $\Delta H_r = -72 \text{ kJ mol}^{-1}$

Solution to Problem 2.1d: From notes, the simplified energy balance for an adiabatic CSTR

$$x_A = - \left\{ \frac{\bar{C}_p}{y_{A0} \Delta H_r} \right\} (T - T_0).$$

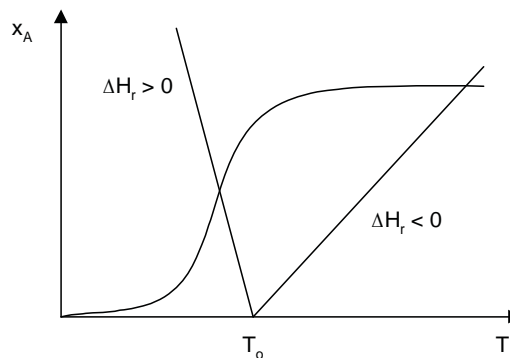
Solving for  $(T - T_0)$

$$(T - T_0) = \frac{\Delta H_r}{\bar{C}_p} = \frac{72,000}{80} = 900 \text{ K}$$

## Problem 2.2

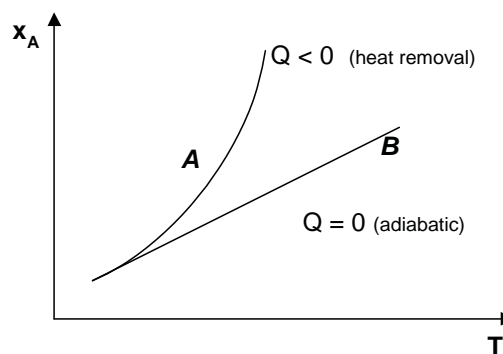
Problem 2.2a: Sketch the operating line on an  $x_A$  vs.  $T$  diagram (i) for an *endothermic* reaction carried out in an adiabatic CSTR; (ii) for an *exothermic* reaction carried out in an *adiabatic* CSTR.

Solution to Problem 2.2a:



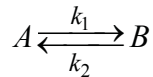
Problem 2.2b: Sketch the operating line on an  $x_A$  vs.  $T$  diagram for an *exothermic* reaction carried out in a CSTR, with cooling ( $Q < 0$ ):

Solution to Problem 2.2b:



## Problem 2.3

The gas phase reaction



with reaction rate expression  $r_A = k_1 p_A - k_2 p_B$  will be carried out in a continuous stirred tank reactor. The feed is pure A. The required conversion of  $x_A$  is 0.62. Calculate

- the minimum reactor size in which the required conversion can be achieved, and,
- the amount of heat to be supplied or removed for steady state operation.

Ideal gas behaviour may be assumed.

DATA:

Volumetric flow rate of feed $v_{T0}$	: 10 m <sup>3</sup> sec <sup>-1</sup>
Average heat capacities of A and B	: 42 kJ kmol <sup>-1</sup> K <sup>-1</sup>
Feed temperature, $T_0$	: 573 K
Pressure of feed line and reactor	: 10 bar
Gas constant, $R$	: 0.08314 (bar m <sup>3</sup> K <sup>-1</sup> kmol <sup>-1</sup> ) = 8.314 kJ K <sup>-1</sup> kmol <sup>-1</sup>
Heat of reaction, $\Delta H_r$	: - 41570 kJ kmol <sup>-1</sup>

$$k_1 = 10^3 \exp\{-41570 / RT\} \quad \text{kmol m}^{-3} \text{ s}^{-1} \text{ bar}^{-1}$$

$$k_2 = 10^6 \exp\{-83140 / RT\} \quad \text{kmol m}^{-3} \text{ s}^{-1} \text{ bar}^{-1}$$

Activation energies are given in kJ kmol<sup>-1</sup>

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## Solution to Problem 2.3

The minimum reactor size for achieving a given conversion implies operating at the temperature where the reaction rate is a maximum. The reaction rate expression is written as:

$$r_A = k_1 p_A - k_2 p_B, \text{ where } p_A = P_T (1 - x_A) \text{ and } p_B = P_T x_A.$$

$$r_A = k_1 P_T (1 - x_A) - k_2 P_T x_A = P_T \{k_1 - (k_1 + k_2) x_A\}$$

The temperature for the maximum reaction rate can be found from  $\left(\frac{dr_A}{dT}\right)_{x_A} = 0$

$$\left(\frac{dr_A}{dT}\right)_{x_A} = P_T \frac{dk_1}{dT} - \left\{\frac{dk_1}{dT} + \frac{dk_2}{dT}\right\} P_T x_A = 0$$

$$x_A = \frac{1}{1 + \frac{(dk_2/dT)}{(dk_1/dT)}}$$

where

$$\frac{dk_2}{dT} = k_{20} \frac{\Delta E_2}{RT^2} e^{-\Delta E_2/RT} ; \frac{dk_1}{dT} = k_{10} \frac{\Delta E_1}{RT^2} e^{-\Delta E_1/RT}$$

and

$$\frac{dk_2/dT}{dk_1/dT} = \frac{k_{20} \Delta E_2}{k_{10} \Delta E_1} \exp\left\{-\frac{(\Delta E_2 - \Delta E_1)}{RT}\right\}$$

$$\frac{dk_2/dT}{dk_1/dT} = \frac{10^6}{10^3} \left(\frac{83200}{41600}\right) \exp\left\{-\frac{(83140 - 41570)}{8.314 T}\right\} = 2000 \exp\left(\frac{-5000}{T}\right)$$

$$x_A = \frac{1}{1 + 2000 e^{-5000/T}}$$

Solving for the temperature:

$$T = \frac{-5000}{\ln\left\{\left(\frac{1}{x_A} - 1\right) \frac{1}{2000}\right\}} = 618 \text{ K}$$

The reactor volume is obtained from the mass balance equation

$$V_R = \frac{n_{A0} x_A}{P_T \{k_1 - (k_1 + k_2) x_A\}}$$

$$n_{A0} = \frac{P_T v_{T0}}{RT} = \frac{(10)(10)}{(0.08314)(573)} = 2.099 \text{ kmol / sec}$$

At 618 K,  $k_1 = 0.306$  ;  $k_2 = 0.094$ . Combining, we find:

$$V_R = 2.24 \text{ m}^3$$

b) The heat balance:

$$Q = \Delta H_r n_{A0} x_A + n_{T0} \bar{C}_p (T - T_0)$$

$$Q = -54098 + 3967 = -50131 \cong -50000 \text{ kJ / sec}$$

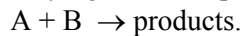
The amount of heat to be removed is

$$Q \cong -50000 \text{ kJ / sec}$$



## Problem 2.4

A continuous stirred tank reactor is used for carrying out the liquid phase reaction:



The reaction rate expression is  $r_A = k(T) C_A C_B \text{ kmol h}^{-1} \text{ m}^{-3}$ . The total molar flow rate at the inlet is  $3 \text{ kmol h}^{-1}$ . The inlet flow is equimolar in A and B. The total volumetric flow rate ( $v_T$ ) is:  $1 \text{ m}^3 \text{ h}^{-1}$ . Calculate the operating temperature required for a fractional conversion of 0.7. Also calculate how much heat must be added to the reactor to maintain the system at steady state, if the feed is introduced at the reactor operating temperature.

The vessel is designed to withstand the vapour pressure of the reaction mixture. No reaction takes place in the vapour phase. Density changes due to (i) the chemical reaction and (ii) changes in temperature may be ignored.

Data:

Reactor volume, $V_R$	: $3 \text{ m}^3$
Heat of reaction, $\Delta H_r$	: $35,000 \text{ kJ (kmol A reacted)}^{-1}$
Reaction rate constant, $k(T)$ ,	: $10^{15} e^{-13000/T} \text{ m}^3 \text{ kmol}^{-1} \text{ h}^{-1}$ (T in K)

### Solution to Problem 2.4

The material balance equation for a CSTR may be written as:

$$V_R = \frac{n_{A0} - n_A}{r_A} = \frac{n_{A0} x_A v_T^2}{k(T) n_{A0}^2 (1 - x_A)^2}$$

where

$n_i$	= molar flow rate of component i
$n_{i0}$	= initial molar flow rate of component i
$v_T$	= total volumetric flow rate
$x_A$	= fractional conversion of A
$n_A$	= $C_A v_T$

Solving for  $k(T)$ , we get:

$$k(T) = \frac{x_A v_T^2}{V_R n_{A0} (1 - x_A)^2} = \frac{(0.7)(1)^2}{(3)(1.5)(0.3)^2} = 1.73 \text{ m}^3 \text{ kmol}^{-1} \text{ h}^{-1}$$

$$10^{15} \exp\{-13000/T\} = 1.73 ; -\frac{13000}{T} = \ln\left\{\frac{1.73}{10^{15}}\right\} = -34.0$$

$$\boxed{T = 382.3 \text{ K}}$$

Heat balance

$$n_{T0} \bar{C}_p (T_0 - T) - \Delta H_R x_A n_{A0} + Q = 0$$

for  $\Delta T = 0$ , heat must be added

$$Q = \Delta H_R x_A n_{A0} = 35000(0.7)(1.5) = 36750 \text{ kJ h}^{-1}$$

$$\boxed{Q = 36750 \text{ kJ h}^{-1}}$$

## Problem 2.5

The gas phase reaction  $A \rightarrow B + C$  is carried out in an adiabatic continuous stirred tank reactor. The reaction rate expression is given by the equation:  $r_A = k(T) p_A$ , where  $k(T)$  is the reaction rate constant and  $p_A$  the partial pressure of the reactant A. The feed stream is pre-heated to 600 K; it contains an equimolar amount of reactant A and inert component D and. The total pressure is 1 bar; it may be assumed constant throughout the system. Calculate the steady state reactor operating temperature and the conversion of the reactant. (Note: There are *two* equally valid solutions to this problem. *One* of the two solutions will suffice as an adequate answer.) Ideal gas behaviour may be assumed. You may also assume total heat capacities of the feed and product streams to be equal.

Data:

Reactor volume, $V_R$	: $10 \text{ m}^3$	
Inlet total molar flow rate, $n_{T0}$	: $10 \text{ kmol s}^{-1}$	
Reaction rate constant, $k(T)$	: $1.0 \times 10^{20} e^{-30,000/T} \text{ kmol bar}^{-1} \text{ m}^{-3} \text{ s}^{-1}$	( $T$ in K)
Heat of reaction, $\Delta H_r$	: $-48\,000 \text{ kJ (kmol A reacted)}^{-1}$	
Heat capacity of the feed stream, $\bar{C}_p$	: $200 \text{ kJ kmol}^{-1} \text{ K}^{-1}$	

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## Solution to Problem 2.5

The mass and energy balances must be solved simultaneously. The energy balance equation:

$$n_{T0} \bar{C}_P (T_0 - T) - n_{A0} x_A \Delta H_R = 0 \quad ; \quad n_{T0} = 2n_{A0}$$

where

- $x_A$ : fractional conversion  
 $v_T$ : total volumetric flow rate  
 $V_R$ : Reactor volume  
 $n_i$ : molar flow rate of component i  
 $n_{T0}$ : total inlet molar flow rate

From the energy balance equation

$$x_A = \frac{n_{T0} \bar{C}_P}{n_{A0} \Delta H_r} (T_0 - T) = \frac{(2)(200)}{48000} (T - 600); \quad x_A = \frac{T}{120} - 5$$

The mass balance equation:  $V_R = \frac{n_{A0} x_A}{k p_A}$ . Next we need to calculate  $n_T$  as a function of  $x_A$ .

$$\begin{aligned}
 n_A &= n_{A0} - n_{A0} x_A \\
 n_I &= n_{I0} && \leftarrow \text{inert component} \\
 n_B &= n_{A0} x_A \\
 n_C &= n_{A0} x_A \\
 \hline
 n_T &= n_{T0} + n_{A0} x_A
 \end{aligned}$$

$$\begin{aligned}
 p_A &= \frac{n_A}{n_T} p_{total} = \frac{n_{A0}(1-x_A)}{n_{T0} + n_{A0} x_A} p_{total}; \quad \text{then} \quad V_R = \frac{n_{A0} x_A}{k(T)} \frac{n_{T0} + n_{A0} x_A}{n_{A0}(1-x_A) p_{total}}; \\
 1 &= \left\{ \frac{x_A}{V_R k(T) p_{total}} \right\} \left\{ \frac{n_{T0} + n_{A0} x_A}{1-x_A} \right\} \rightarrow 1 = \left\{ \frac{x_A}{10(1)(1)(10^{20})(e^{-30000/T})} \right\} \left\{ \frac{10+5x_A}{1-x_A} \right\}
 \end{aligned}$$

$$\text{Solve } 1 = \left\{ \frac{x_A}{10^{21}(e^{-30000/T})} \right\} \left\{ \frac{10+5x_A}{1-x_A} \right\} \quad \text{with} \quad x_A = \frac{T}{120} - 5 \quad \text{with}$$

### Two possible solutions

T	635	640	645	650	655
$x_A$	0.292	0.333	0.375	0.417	0.458
numerator	3.346	3.884	4.453	5.039	5.629
$\exp(-30000/T)$	$3.035 \times 10^{-21}$	$4.390 \times 10^{-21}$	$6.313 \times 10^{-21}$	$9.029 \times 10^{-21}$	$1.284 \times 10^{-20}$
RHS	1.557	1.326	1.129	0.957	0.809

**ANS: T = ~ 647 K ;  $x_A$  = ~0.39**

**Alternative solution:**

T	601	602	603	604	605
$x_A$	0.00833	0.0167	0.025	0.0333	0.0417
numerator	0.0836	0.168	0.281	0.339	0.426
$\exp(-30000/T)$	$2.096 \times 10^{-22}$	$2.277 \times 10^{-22}$	$2.437 \times 10^{-22}$	$2.686 \times 10^{-22}$	$2.916 \times 10^{-22}$
RHS	0.402	0.750	1.183	1.306	1.524

**ANS: T ~ 602.5 ;  $x_A = \sim 0.021$**

### Problem 2.6

The rate of the first order irreversible gas-phase reaction,  $A \rightarrow B$  is given by  $r_A = k p_A$ . The reaction will be carried out in a tubular *adiabatic* reactor. The reaction is *exothermic*. Calculate the reactor volume,  $V_R$  ( $m^3$ ), required for a fractional conversion of “A”:  $x_A = 0.9$ . Plug flow and ideal gas behaviour may be assumed.

#### Definitions & data:

Inlet mole fractions:  $y_{A0} = 0.20$ ;  $y_{I0}$  (inerts) = 0.8

$T_0$	Feed temperature	:400 K
$n_{T0}$	inlet total molar flow rate	:1 kmol s <sup>-1</sup>
$P_T$	total pressure	:1 bar
$k$	reaction rate constant	: $1.8 \times 10^4 \exp\{-5000/T\}$ kmol s <sup>-1</sup> m <sup>-3</sup> bar <sup>-1</sup> (T in K)
$\Delta H_r$	Heat of Reaction	:- 50,000 kJ (kmol A reacted) <sup>-1</sup>
$\overline{C}_p$	Heat capacity of the reaction mixture	: 40 kJ kmol <sup>-1</sup> K <sup>-1</sup>

$Q$	Heat exchange with surroundings
$r_A$	Reaction rate of component A, kmol m <sup>-3</sup> s <sup>-1</sup>
$p_A$	partial pressure of A, bar
$n_{A0}$	molar flow rate of A, kmol s <sup>-1</sup>

Note 1. The operating line for a tubular reactor assumed to operate in plug flow is given by:

$$\frac{dT}{dx_A} = \frac{n_{A0}}{n_{T0}} \left\{ \frac{Q}{r_A \overline{C}_p} + \frac{(-\Delta H_r)}{\overline{C}_p} \right\}$$

Note 2. The Trapezoidal Rule for integration is given by

$$\int_0^x f(x) dx \approx (\Delta x) \left\{ \frac{f_0}{2} + f_1 + f_2 + \dots + f_{n-1} + \frac{f_n}{2} \right\}$$

where, the interval of integration is divided into n equal segments and  $\Delta x = x/n$ . For the purposes of this exercise, use  $n = 3$ .

### Solution to Problem 2.6

The mass balance equation for a plug flow reactor is given by:

$$V_R = - \int_{n_{A0}}^{n_{A,exit}} \frac{dn_A}{r_A}$$

where  $r_A = kp_A = k(1-x_A) p_{A0}$ ,  $V_R$  is the reactor volume ( $m^3$ ),  $n_A$  the molar flow rate of “A” ( $kmol m^{-3} s^{-1}$ ) and  $p_{A0}$  the inlet partial pressure of “A” (bar).

$$V_R = \int_0^{x_{A,exit}} \frac{n_{A0} dx_A}{k(1-x_A) p_{A0}} = \int_0^{x_{A,exit}} \frac{n_{A0} dx_A}{[k_0 \exp(-5000/T)](1-x_A) p_{A0}}$$

$$V_R = \frac{n_{A0}}{p_{A0} k_0} \int_0^{x_{A,exit}} \frac{dx_A}{(1-x_A) \exp(-5000/T)} ; \quad x_{A,exit} = 0.9$$

$$V_R = (5.55 \times 10^{-5}) \int_0^{0.9} \frac{dx_A}{(1-x_A) \exp(-5000/T)} \quad \text{(Eq. 2.6.A)}$$

To express  $T$  in terms of  $x_A$ , we use the operating line for an *adiabatic* tubular reactor, assumed to operate in plug flow [i.e  $Q=0$ ]:

$$\frac{dT}{dx_A} = \frac{n_{A0} (-\Delta H_r)}{n_{T0} C_p} = \frac{(0.2)(50000)}{(1)(40)} = 250 \text{ K}$$

Integrating:  $T = T_0 + 250 x_A$ . This equation can then be substituted for  $T$  in Equation Eq. 2.6.A.

$$V_R = (5.55 \times 10^{-5}) \int_0^{0.9} \frac{dx_A}{(1-x_A) \exp[-5000/(T_0 + 250x_A)]}$$

We use the Trapezoidal Rule for the integration, with

$$f(x_A) = \frac{1}{(1-x_A) \exp[-5000/(400 + 250x_A)]} ; \quad \Delta x_A = x_A/3 = (0.9/3) = 0.3$$

$x_A$	$[f(x_A)]^{-1}$	$f(x_A)/2$	$f(x_A)$
0	$3.73 \times 10^{-6}$	$13.4 \times 10^4$	
0.3	$1.88 \times 10^{-5}$		$5.33 \times 10^4$
0.6	$4.51 \times 10^{-5}$		$2.22 \times 10^4$
0.9	$3.35 \times 10^{-5}$	$1.49 \times 10^4$	

$$\left\{ \frac{f_0}{2} + f_1 + f_2 + \frac{f_3}{2} \right\} = 2.24 \times 10^5$$

$$V_R = (5.55 \times 10^{-5}) \int_0^{0.9} f(x) dx \approx (5.55 \times 10^{-5}) (\Delta x) \left\{ \frac{f_0}{2} + f_1 + f_2 + \frac{f_3}{2} \right\}$$

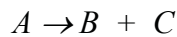
$$V_R = (5.55 \times 10^{-5})(0.3) (2.24 \times 10^5) \cong 3.73 \text{ m}^3$$

## Worked Examples - Chapter III

### Catalytic reactions – Isothermal reactors

#### Problem 3.1

The first order irreversible gas phase reaction



is to be carried out in an *isothermal* tubular fixed bed catalytic reactor operating at atmospheric pressure. The intrinsic reaction rate expression is  $r_A = k C_A$ . Pure “A” will be fed to the reactor at a rate of  $0.13 \text{ kmol s}^{-1}$ .

- a. Compare the relative magnitudes of the rates of external mass transport and chemical reaction.
- b. Calculate the mass of catalyst required for a conversion of 80 %.

For purposes of calculating  $k_m$ , an average Reynolds number of 500 may be assumed over the length of the reactor. Plug flow and ideal gas behaviour may be assumed. The pressure drop along the length of the reactor may be neglected.

Data:

Reaction rate constant, $k$ :	0.042	$\text{m}^3 (\text{kg-cat s})^{-1}$
Average gas density, $\rho_g$ :	1.0	$\text{kg m}^{-3}$
Average gas viscosity, $\mu_g$ :	$5.0 \times 10^{-5}$	$\text{kg m}^{-1} \text{s}^{-1}$
Average diffusivity of “A”, $D_A$ :	$5.0 \times 10^{-5}$	$\text{m}^2 \text{s}^{-1}$
External surface area of catalyst pellets, $a_m$ :	0.667	$\text{m}^2 \text{kg}^{-1}$
Bed void fraction, $\varepsilon_B$ :	0.5	
Mass flow rate, $G$ :	8.3	$\text{kg m}^{-2} \text{s}^{-1}$
Effectiveness factor, $\eta$ :	0.12	
Reactor temperature, T:	423	K

$$j_D = \frac{0.46}{\varepsilon_B} Re^{-0.4} \text{ where } Re = d_p G / \mu_B \text{ and } j_D = \frac{k_m \rho_B}{G} \left\{ \frac{\mu_B}{\rho_b D_{AB}} \right\}^{2/3}$$

where  $k_m$  is defined by the equation:  $r_{A,p} = k_m a_m (C_b - C_s)$ .

$$R (\text{gas constant}) = 8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1} = 0.08314 \text{ bar m}^3 \text{ K}^{-1} \text{ kmol}^{-1}$$

#### Solution to Problem 3.1

From the course notes  $r_p = k_m a_m (C_b - C_s) = \eta k C_s$ .

$$\text{Solving for } C_s, C_s = \frac{k_m a_m}{\eta k + k_m a_m} C_b \text{ and } r_p = \left\{ \frac{1}{k_m a_m} + \frac{1}{\eta k} \right\}^{-1} C_b.$$

(a) Compare  $\frac{l}{k_m a_m}$  and  $\frac{l}{\eta k}$ , given Re constant at a value of 500.

$$j_D = \left\{ \frac{0.458}{0.5} \right\} \times (500)^{-0.4} = 0.077$$

$$Sc = \frac{\mu}{\rho D_A} = \frac{5 \times 10^{-5}}{1 \times 5 \times 10^{-5}} = 1.$$

$$k_m = \frac{j_D G}{\rho} (Sc)^{-2/3} = \frac{(0.077) \times (8.3)(1)}{1} = 0.64 \text{ m s}^{-1}$$

$$\frac{l}{k_m a_m} = \frac{l}{(0.64) \times (0.667)} = 2.34; \quad \frac{l}{\eta k} = \frac{l}{(0.12) \times (0.042)} = 198.4$$

Comparing magnitudes, chemical reaction turns out to be the controlling (slower) step.

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(b) Let us define the overall rate constant as  $K \equiv \left\{ \frac{1}{k_m a_m} + \frac{1}{\eta k} \right\}^{-1}$ . Then,

$r_p = KC_b$ , and since  $n_A = C_A v_T$ , we can write

$$r_p = K (n_A / v_T). \quad (\text{Eq. A})$$

Also

$$K = (2.34 + 198.4)^{-1} = 4.98 \times 10^{-1} \quad (\text{Eq. B})$$

Since the reaction “ $A \rightarrow B + C$ ” in the gas phase leads to a molar change upon reaction, we next need to express  $v_T$  in terms of the conversion. We start with the change in molar flow rate.

$$\begin{aligned} n_A &= n_{A0} - n_{A0}x_A \\ n_B &= \quad + n_{A0}x_A \\ n_C &= \quad + n_{A0}x_A \\ &\text{-----} \\ n_T &= n_{A0} (1 + x_A) \end{aligned}$$

Here,  $n_T$  is the total volumetric flow rate expressed as a function of the fractional conversion of “ $A$ ”. Using the ideal gas law:

$$v_T = \frac{n_T RT}{P_T} = \frac{n_{A0} RT}{P_T} (1 + x_A).$$

Substituting in Eq. (A), we get

$$r_p = \frac{K n_{A0} (1 - x_A)}{\frac{n_{A0} RT}{P_T} (1 + x_A)} = \frac{K P_T}{RT} \frac{(1 - x_A)}{(1 + x_A)} \quad (\text{Eq. C})$$

To calculate the mass of catalyst required:

$$W = - \int_{n_{A0}}^{n_{A,exit}} \frac{dn_A}{r_A} = \frac{n_{A0} RT}{K P_T} \int_0^{x_{A,exit}} \frac{(1 + x_A)}{(1 - x_A)} dx_A$$

$$\int_0^{x_{A,exit}} \frac{(1 + x_A)}{(1 - x_A)} dx_A = \int_0^{x_{A,exit}} \left\{ \frac{1}{(1 - x_A)} - 1 + \frac{1}{(1 - x_A)} \right\} dx_A = -2 \ln(1 - x_{A,exit}) - x_{A,exit}$$

$$W = - \frac{n_{A0} RT}{K P_T} \{ 2 \ln(1 - x_{A,exit}) + x_{A,exit} \}$$

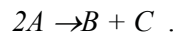
$$W = - \frac{(0.13)(0.08314)(423) \{ 2 \ln(0.2) + 0.8 \}}{[4.98 \times 10^{-3}](1)} \cong 2220 \text{ kg}$$

Weight of catalyst: 2220 kg



### Problem 3.2

A tubular reactor packed with spherical pellets will be used for carrying out the catalytic reaction:



Reactant “A” is available as 20 (mole) % A in an inert gas and will be fed to the reactor at the rate of 0.02 kmol s<sup>-1</sup>. The intrinsic reaction rate given by

$$r_{A,V} = k_V C_A^2 \text{ kmol m}^{-3} \text{ s}^{-1},$$

where  $C_A$  denotes the concentration of A. The intended conversion is 75 %.

(a) The reactor is to be operated isothermally at 600 K and 1 bar pressure. Estimate whether intraparticle diffusion resistances affect the overall reaction rate. For the purposes of this part of the calculation

$$C_{A,s} \cong C_{A,b}$$

may be assumed.

(b) Estimate whether bulk to catalyst surface mass transport resistances affect the overall reaction rate.

Due to dilution by the inert gas, bulk properties of the gas mixture may be considered as approximately constant. The pressure drop over the length of the reactor and deviations from the ideal gas law may be neglected.

#### Data

Catalyst pellet density, $\rho_p$ :	2200	kg m <sup>-3</sup>
Catalyst pellet diameter, $d_p$	$5 \times 10^{-3}$	m
Effective diffusivity of A within the pellet, $D_{A,eff}$ :	$1 \times 10^{-6}$	m <sup>2</sup> s <sup>-1</sup>
Molecular diffusivity of A in the gas mixture, $D_A$ :	$1 \times 10^{-4}$	m <sup>2</sup> s <sup>-1</sup>
Reaction rate constant, $k_V$ :	$3.46 \times 10^4$	m <sup>3</sup> kmol <sup>-1</sup> s <sup>-1</sup>
Mass flow rate, $G$ :	10	kg m <sup>-2</sup> s <sup>-1</sup>
Density of the gas mixture, $\rho_g$ :	1	kg m <sup>-3</sup>
Viscosity of the gas mixture, $\mu$ :	$1.5 \times 10^{-5}$	kg m <sup>-1</sup> s <sup>-1</sup>
Void fraction of the bed, $\varepsilon_b$ :	0.42	

For integral reaction rate orders the effectiveness factor may be expressed as

$$\eta = \frac{S_x}{V_p} \frac{\sqrt{2}}{k[C_{A,s}]^n} \left\{ \int_0^{C_{A,s}} D_{A,eff} k[C]^n dC \right\}^{1/2}.$$

The dimensionless mass flux  $j_D$  is given by the correlation

$$j_D = (0.46 / \varepsilon) (Re)^{-0.4}, \text{ where } Re = d_p G / \mu$$

where  $j_D$  is related to  $k_m$ , the bulk stream to particle surface mass transfer coefficient, by

$$j_D = (k_m \rho_g / G) \left\{ \frac{\mu}{\rho_g D_A} \right\}^{2/3}$$

$$R \text{ (gas constant)} = 8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1} = 0.08314 \text{ bar m}^3 \text{ K}^{-1} \text{ kmol}^{-1}$$

### Solution to Problem 3.2

If intraparticle diffusion resistances are significant,  $\eta \cong 1/\Phi$  where  $\Phi$  is usually  $>5$ . Now let us calculate  $\Phi$  by assuming that  $\eta \cong 1/\Phi$ . From the main text (Chapter 6), we have:

$$\Phi = \frac{V_p}{S_x} \frac{k [C_{A,s}]^n}{\sqrt{2}} \left\{ \int_0^{C_{A,s}} D_{A,eff} k [C]^n dC \right\}^{-1/2} \quad \text{(Eq. 6.74)}$$

$$\Phi = \frac{V_p}{S_x} \frac{k_V [C_{A,s}]^n}{\sqrt{2}} \left\{ D_{A,eff} \frac{k [C_{A,s}]^{n+1}}{n+1} \right\}^{-1/2} = \frac{V_p}{S_x} \left\{ \frac{2D_{eff}}{n+1} \frac{1}{k_V C_{A,s}^{n-1}} \right\}^{-1/2}$$

For  $n = 2$ , we get

$$\Phi = \frac{d_p}{6} \left\{ \frac{3}{2D_{eff}} k_V C_{A,s} \right\}^{1/2} = 1.9 \times 10^2 C_{A,s}^{1/2} \quad \text{(Eq. A)}$$

Neglecting external transport resistances, at the reactor inlet:

$$C_A = \frac{n_A}{v_T} = \frac{P_{A,partial}}{RT} = \frac{0.2(1)}{(0.08314)(600)} = 4 \times 10^{-3} \text{ kmol m}^{-3}$$

At the reactor exit:

$$C_A = \frac{(0.05)(1)}{(0.08314)(600)} = 1 \times 10^{-3} \text{ kmol m}^{-3}$$

Substituting these values into Eq. A above, we get

$\Phi \approx 12$  at the reactor inlet and  $\Phi \approx 6$  at the reactor exit. So we must conclude that diffusion resistances are not negligible within this reactor.

Part (b):

At steady state, the rate of reaction within a particle must be equal to the net rate of diffusion of the reactant.

$$\text{net flux} = k_m a_m (C_b - C_s)$$

Let us calculate  $k_m a_m$ .

$$Re = \frac{d_p G}{\mu} = \frac{5 \times 10^{-3} (10)}{1.5 \times 10^{-5}} = 3333$$

From  $j_D = (0.46 / \varepsilon) (Re)^{-0.4}$  we can calculate  $j_D = 0.043$ . Meanwhile

$$k_m = \frac{j_D G}{\rho_g} \frac{1}{\left\{ \frac{\mu}{\rho_g D_A} \right\}^{2/3}}$$

$$\left\{ \frac{\mu}{\rho_g D_A} \right\}^{2/3} = \left\{ \frac{1.5 \times 10^{-5}}{1 \times 1 \times 10^{-4}} \right\}^{2/3} = 0.28$$

$$k_m = \frac{(0.043)(10)}{1} \frac{1}{0.28} = 1.54 \text{ and}$$

$$a_m = \frac{4\pi r_p^2}{\frac{4}{3}\pi r_p^3 \rho_p} = \frac{3}{r_p \rho_p} = \frac{6}{5 \times 10^{-3} \times 2200} = 0.545 \text{ m}^2 \text{ kg}^{-1}$$

$$k_m a_m = 0.84 \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$$

The catalyst bed density is calculated from  $\rho_B = (1 - \varepsilon) \rho_p = (0.58) \times (2200) = 1276 \text{ kg m}^{-3}$

Then we use the concept that, at steady state, net diffusion of reactant to the catalyst pellet equals the amount of reactant that has been converted.

$$\rho_B k_m a_m (C_{Ab} - C_{As}) = \eta k C_{As}^2 \quad \text{kmol}/(\text{m}^2 \text{ s})$$

Define a constant  $\alpha$ . At the inlet  $\alpha = \frac{\rho_B k_m a_m}{\eta k} = \frac{(1276) \times (0.84)}{\left(\frac{1}{12}\right) (3.46 \times 10^4)} = 0.372 \text{ kmol m}^{-3}$

The equation to solve now takes the form:

$$\alpha (C_{Ab} - C_{As}) = C_{As}^2 \quad \text{(Eq. B)}$$

and at the inlet  $C_{Ab} = 4 \times 10^{-3} \text{ kmol m}^{-3}$ .

Eq. B can be solved as a quadratic equation or by trial and error.

$$C_{As} \cong 3.95 \times 10^{-3} \text{ kmol m}^{-3}$$

Comparing  $C_{Ab}$  and  $C_{As}$ , we can see the difference is small. Therefore, in this case, the bulk-stream to pellet surface mass transport resistance appears negligible *at the reactor inlet*.

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### Problem 3.3

*Differential reactors* are used to simulate an infinitesimally thin (“slice”) section of, say, a tubular reactor. In the laboratory, this is done to measure reaction rates and other parameters of catalytic reactions, in the context of a small amount of conversion.

The first order irreversible reaction  $A \rightarrow B + C$  will be carried out over 0.002 kg packed catalyst in a differential test reactor. The intrinsic rate expression for the reaction is

$$r_A = 7 \times 10^{15} \exp\{-18,000/T\} C_A \quad \text{kmol (kg-cat} \times \text{s)}^{-1}$$

where the temperature  $T$  is given in  $K$  and  $C_A$ , the concentration of the reactant “ $A$ ”, is expressed in  $\text{kmol m}^{-3}$ . Assuming isothermal operation at 500 K and given the data listed below,

- Estimate whether intraparticle diffusion resistances would be expected to affect the overall rate.
- Estimate whether bulk to surface diffusion resistances would be expected to affect the overall rate.
- Calculate the conversion through the reactor.

Data:

Catalyst pellet diameter, $d_p$ :	0.001	m
Catalyst pellet density $\rho_p$ :	1500	$\text{kg m}^{-3}$
Effective diffusivity of $A$ within the pellet, $D_{A,eff}$ :	$1 \times 10^{-6}$	$\text{m}^2 \text{s}^{-1}$
Molecular diffusivity of $A$ in the bulk stream, $D_A$ :	$1 \times 10^{-4}$	$\text{m}^2 \text{s}^{-1}$
Mass flow rate, $G$ :	0.1	$\text{kg m}^{-2} \text{s}^{-1}$
Viscosity of the gas mixture, $\mu$ :	$1 \times 10^{-6}$	$\text{kg m}^{-1} \text{s}^{-1}$
Density of the gas mixture, $\rho_g$ :	$1 \text{ kg m}^{-3}$	
Void fraction of the bed, $\varepsilon$ :	0.42	
Total volumetric flow rate, $v_T$ :	0.005	$\text{m}^3 \text{s}^{-1}$

The dimensionless mass flux  $j_D$  is given by the correlation

$$j_D = (0.46 / \varepsilon) (Re)^{-0.4}, \text{ where } Re = d_p G / \mu$$

where  $j_D$  is related to  $k_m$ , the bulk stream to particle surface mass transfer coefficient, by

$$j_D = (k_m \rho_g / G) \left\{ \frac{\mu}{\rho_g D_A} \right\}^{2/3}.$$

The Thiele modulus for spherical catalyst pellets is given by:

$$\Phi_s = \left( \frac{R_s}{3} \right) \left\{ \frac{k \rho_p}{D_{A,eff}} \right\}^{1/2} \quad \text{(Eq. A)}$$

where  $R_s$  is the pellet radius,  $k$  the reaction rate constant;  $\rho_p$  and  $D_{eff}$  have been defined above.

## Solution to Problem 3.2

Part (a)

$$R_s = 0.0005 \text{ m}.$$

At 500 K, the reaction rate constant  $k = 1.62$ . Substituting into Eq. A, we can calculate  $\Phi_s$ .

$$\Phi_s = \frac{0.0005}{3} \sqrt{\frac{(1.62)(1500)}{1 \times 10^{-6}}} = 8.225$$

$\Phi_s$  is large. We conclude that intraparticle diffusion resistances are significant and would be expected to affect the overall rate.

Part (b):

$$a_m = \frac{4\pi r_p^2}{\frac{4}{3}\pi r_p^3 \rho_p} = \frac{3}{r_p \rho_p} = \frac{3}{5 \times 10^{-4} \times 1500} = 4.0 \text{ m}^2 \text{ kg}^{-1}$$

To calculate  $k_m$ , we first need the Reynolds number.  $Re = \frac{(0.001)(0.1)}{1 \times 10^{-6}} = 100$ . Using this value we can get

$$j_D = 0.174. \text{ Then}$$

$$k_m = \frac{j_D G}{\rho_g} \left\{ \frac{\mu}{\rho_g D_A} \right\}^{-2/3} = 0.375 \text{ m s}^{-1}$$

The basic equation to use for comparing external and intraparticle diffusion effects is:

$$r_p = \frac{1}{\frac{1}{\eta k} + \frac{1}{k_m a_m}} C_{Ab}. \text{ We now compare } \frac{1}{\eta k} \text{ and } \frac{1}{k_m a_m}.$$

$$k_m a_m = (4)(0.375) = 1.5 \text{ m}^3 \text{ s}^{-1}; \quad \frac{1}{k_m a_m} = 0.66$$

$$\eta k \cong k / \Phi_s = 1.62 / 8.225 = 0.197; \quad \frac{1}{\eta k} = 5.1$$

External diffusion resistance less significant!

Part (c):

For a “differential reactor” the mass balance equation  $dW = -\frac{dn_A}{r_p}$  can be written as:

$$\Delta W \cong -\frac{\Delta n_A}{r_p}, \text{ where } \Delta n_A = -n_{A0} \Delta x_A. \text{ We also have } r_p = \frac{1}{\frac{1}{\eta k} + \frac{1}{k_m a_m}} C_{Ab} \text{ and}$$

$$C_A = n_A / v_T. \text{ Thus we can write } C_{Ab} = \frac{n_{A0}(1-x_A)}{v_T} \text{ and } r_p = \frac{I}{\frac{I}{\eta k} + \frac{I}{k_m a_m}} \times \frac{n_{A0}(1-x_A)}{v_T}.$$

In the case of the differential reactor,  $x_A \cong \Delta x_A$ . Thus

$$\frac{1-x_A}{x_A} \cong \frac{v_T}{\Delta W} \left\{ \frac{I}{\eta k} + \frac{I}{k_m a_m} \right\}$$

$$\Delta W = \frac{n_{A0} \Delta x_A}{n_{A0}(1-x_A)} \times \left\{ \frac{I}{\eta k} + \frac{I}{k_m a_m} \right\} v_T; \text{ then } \frac{1-x_A}{x_A} = \frac{0.005}{0.002} \{5.1 + 0.667\} = 14.42$$

$$x_A = \frac{1}{15.41} = 0.066$$

$$x_A = 0.066$$

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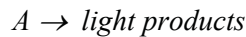


## Worked Examples - Chapter IV

### Catalytic reactions – Non-isothermal reactors

#### Problem 4.1

The exothermic catalytic gas phase cracking reaction



is carried out with a feed of 10 % “A” in an inert diluent, “B”. The intrinsic rate for the reaction is given by:

$$r_A = 125 \exp\{-5000/T\} p_A \quad \text{kmol s}^{-1} (\text{kg-cat})^{-1}$$

where  $p_A$  denotes the partial pressure (bar) of “A” and  $T$  denotes the local temperature in  $K$ . The catalyst pellets (dia. 0.004 m) may be considered isothermal and the value of the effectiveness factor is estimated as 0.08 throughout the reactor. We select a point within the reactor where,  $G$ , the superficial mass velocity of the gas stream is  $0.8 \text{ kg m}^{-2} \text{ s}^{-1}$ , the bulk temperature,  $T_b$ , is 500 K, and the partial pressure of “A” in the bulk,  $p_{A,b}$ , is 0.05 bar. Calculate:

- (i) the global rate of reaction,
- (ii) the external concentration gradient (expressed in terms of the partial pressures), and,
- (iii) the temperature gradient between the bulk gas stream and external catalyst pellet surfaces,

at the selected point in the reactor. Bulk gas properties may be taken as those of the diluent. The pressure drop along the reactor axis may be neglected.

Data:

Effectiveness factor, $\eta$ :	0.08	(see statement of problem)
Total reactor pressure, $p_T$ :	1 bar	
Void fraction of the packed bed, $\varepsilon_B$ :	0.5	
Surface area of catalyst pellets, $a_m$ :	$0.4 \text{ m}^2 \text{ kg}^{-1}$	
Heat of reaction, $\Delta H_r$ :	$-20\,000 \text{ kJ (kmol A reacted)}^{-1}$	
Molecular diffusivity of A in B, $D_{AB}$ :	$2 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$	
Density of “B”, $\rho_B$ :	$0.1 \text{ kg m}^{-3}$	
Viscosity of “B”, $\mu_B$ :	$1.0 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$	
Heat capacity of “B”, $C_{p,B}$ :	$1.0 \text{ kJ kg}^{-1} \text{ K}^{-1}$	
Thermal conductivity of “B”, $\lambda_B$ :	$1.5 \times 10^{-5} \text{ kJ m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$	

$$j_D = (0.7) j_H = \frac{0.46}{\varepsilon_B} Re^{-0.4} ; \quad Re = d_p G / \mu_B$$

$$j_D = \frac{k_m \rho_B}{G} \left\{ \frac{\mu_B}{\rho_b D_{AB}} \right\}^{2/3} ; \quad j_H = \frac{h}{C_p G} \left\{ \frac{C_p \mu_B}{\lambda_B} \right\}^{2/3}$$

In these equations,  $k_m$ , the bulk to surface mass transfer coefficient is defined in terms of the equation:

$$r_{A,p} = (k_m a_m / RT_b) (p_b - p_s),$$

and,  $h$  is the surface to bulk heat transfer coefficient, defined by

$$h a_m (T_s - T_b) = (-\Delta H_r) r_{A,p}.$$

Finally,  $R$  (gas constant) =  $8.314 \text{ kJ kmol}^{-1} \text{K}^{-1} = 0.08314 \text{ bar m}^3 \text{K}^{-1} \text{ kmol}^{-1}$

#### Solution to Problem 4.1

$$Re = d_p G / \mu_B = \frac{(0.004) \times (0.8)}{1 \times 10^{-5}} = 320; \text{ substituting this value into the correlations, we get}$$

$$j_D = 9.16 \times 10^{-2} \text{ and } j_H = 0.131.$$

Next, we calculate the Prandtl and Schmidt numbers

$$Pr = \frac{C_{pB} \mu_B}{\lambda_B} = \frac{1 \times 1 \times 10^{-5}}{1.5 \times 10^{-5}} = 0.67 \text{ and } Sc = \frac{\mu_B}{\rho_B D_{AB}} = \frac{1 \times 10^{-5}}{0.1 \times 2 \times 10^{-4}} = 0.5.$$

On the other hand

$$h a_m (T_s - T_b) = r_{A,p} \times \Delta H_r, \text{ leads to}$$

$$h = \frac{j_H C_p G}{(Pr)^{2/3}}$$

$$(T_s - T_b) = \frac{r_{A,p} (-\Delta H_r) (Pr)^{2/3}}{j_H C_p G a_m} = \frac{(r_{A,p}) (20,000) (0.67)^{2/3}}{(0.131)(1)(0.8)(0.4)} = 3.65 \times 10^5 r_{A,p}$$

recalling that  $T_b = 500 \text{ K}$ ,

$$T_s = 500 + 3.65 \times 10^5 r_{A,p}. \quad \text{(Eq. A)}$$

Similarly

$$\frac{k_m a_m}{RT_b} (p_b - p_s)_A = r_{A,p} \text{ and } k_m = \frac{j_D G}{\rho_B Sc^{2/3}}$$

Then

$$(p_b - p_s)_A = \frac{r_{A,p} \rho_B (Sc^{2/3}) R T_b}{a_m j_D G} = \frac{r_{A,p} (0.1) (0.5)^{2/3} (0.08314) (500)}{(0.4) (9.16 \times 10^{-2}) (0.8)}$$

leads to

$$(p_b - p_s)_A = 89.1 \times r_{A,p}, \text{ where } p_{A,b} = 0.05 \text{ leads to}$$

$$p_{A,s} = 0.05 - 89.1 \times r_{A,p} \quad \text{(Eq. B)}$$

The intrinsic reaction rate was given as  $r_A = 125 \exp\{-5000/T\} p_A$



Since  $r_{A,p} = \eta r_{A,s} = \eta r_A$  (at surface conditions), and the intrinsic reaction rate expression was given in the problem statement as  $r_A = (125) \exp\{-5000/T\} p_A$ , the global reaction rate expression can be written as

$$r_{A,p} = \eta r_{A,s} = (0.08) \times (125) \exp\{-5000/T_s\} p_{A,s}$$

Substituting expressions for  $T_s$  from **Eq. (A)** and  $p_{A,s}$  from **Eq. (B)**, we get

$$r_{A,p} = \eta r_{A,s} = (0.08) \times (125) \times \left[ 0.05 - 89.1 \times r_{A,p} \right] \times \exp\left\{-5000 / (500 + 3.65 \times 10^5 r_{A,p})\right\}$$

$\downarrow$   $T_s$   $\downarrow$   
 $p_{A,s}$

This equation can be solved by a simple trial and error procedure.

$$r_{A,p} = 2.6 \times 10^{-5} \text{ kmol (kg-cat} \times \text{s)}^{-1}$$

Then

$$T_s = 500 + 3.65 \times 10^5 [2.6 \times 10^{-5}] \cong 509.5$$

$$\Delta T = 9.5 \text{ K} \quad \text{Not negligible!}$$

$$p_s = 0.05 - 89.1 r_{A,p} = 4.77 \times 10^{-2}$$

$$\Delta p = 0.05 - 0.0477 = 0.0023 \text{ bar} \rightarrow \sim 5 \% \text{ of total pressure.}$$

Probably negligible...just.

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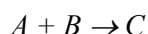
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## Problem 4.2

The exothermic gas phase reaction



is carried out over a porous catalyst, in a non-isothermal/non-adiabatic fixed bed catalytic reactor. The feed stream is equimolar in A and B.

(a) Using a one-dimensional, pseudo-homogeneous model framework, derive steady-state mass and energy balance equations and state boundary conditions to describe the behaviour of the reactor. Define your terms carefully.

(b) Calculate the maximum temperature that the exit gas stream would attain if the reactor were to be operated adiabatically. Judging by this result, what change would you recommend in reactor operating conditions.

(c) Discuss briefly for the present case, advantages and disadvantages of using a one-dimensional reactor model over a two-dimensional model.

Data:

Heat of reaction, $\Delta H_r$ :	–300 000	kJ (kmol A reacted) <sup>-1</sup>
Average heat capacities		
$C_{pA} \cong C_{pB}$ :	30	kJ kmol <sup>-1</sup> K <sup>-1</sup>
$C_{pC}$ :	60	kJ kmol <sup>-1</sup> K <sup>-1</sup>

### Solution to Problem 4.1

Part A:

Mass balance:

The mass balance over an infinitesimally thin (“slice”) element of the catalyst packed reactor ( $dW$ ) gives:

$dn_A = -r_A dW$ , where  $n_A$  is defined by the equation  $n_A = n_{A0}(1 - x_A)$  and  $dn_A = n_{A0} dx_A$ . In these equations  $W$  denotes the mass of catalyst and  $n_A$  the molar flow rate of “A”.  $n_{T0} \bar{C}_p$  is the total heat capacity of the inlet stream. It is assumed not to change with conversion; so we shall use it as the total heat capacity of the reaction mixture.

From  $dn_A = -r_A dW$  we can then write the full mass balance equation as:  $\frac{dx_A}{dW} = \frac{r_A}{n_{A0}}$ . **(Eq. A)**

Energy balance:

$$\left[ \sum n_i C_{pi} \right] dT = dW (Q - r_A \Delta H_r)$$

where  $Q$  is the external heat transfer term and  $\sum n_i C_{pi} \cong n_{T0} \bar{C}_p$  as explained in Chapter 3 of the main text. The energy balance equation may then be written as:

$$\frac{dT}{dW} = \frac{Q - r_A \Delta H_r}{n_{T0} \bar{C}_p} \quad \text{(Eq. B)}$$

The *initial* condition is given as:

$$\text{At } W = 0, T = T_0 = T_{wall}.$$

There are many ways of formulating  $Q$ , the heat loss term. One common way would be:

$$Q = A h (T - T_{wall}),$$

where  $A$  denotes the contact surface area and  $h$  the heat transfer coefficient.

Part B:

Combining Eqs. A and B, we can write

$$\frac{dT}{dx_A} = \frac{n_{A0}}{r_A} \left\{ \frac{Q - r_A \Delta H_r}{n_{T0} C_p} \right\}.$$

For adiabatic operation,  $Q = 0$ .

$$\frac{dT}{dx_A} = - \frac{\Delta H_r}{[n_{T0} C_p]} n_{A0}$$

Integrating

$$\Delta T = - \frac{\Delta H_r}{C_p} \frac{n_{A0}}{n_{T0}} = \frac{(0.5)(3 \times 10^5)}{30} = 5000 \text{ K}$$

Unacceptably high! Improve cooling and/or reduce reactant concentrations and/or dilute the catalyst.

Part C:

The main difficulty arises from ignoring the radial temperature distribution. In dealing with highly exothermic reactions, when the maximum temperature along the central axis turns out to be much larger than the radially averaged temperature, runaway may occur under conditions where the 1-dimensional model would predict “safe” operation. The disadvantage of 2-dimensional operation is the requirement for *accurate* additional data for radial heat (and mass) transport:  $\lambda_{rad, effective}$ ,  $D_{rad, effective}$ .

### Problem 4.3

The exothermic reaction



was carried out using two different catalyst particle sizes: 8 mm diameter catalyst pellets and 50  $\mu$  (average) diameter catalyst particles. Both sets of experiments were carried out under conditions where external temperature and concentration gradients were negligible. Global rates of reaction, measured as a function of temperature, using approximately similar external surface concentrations of A and B for all experiments, are given in the table below. Assuming the 50  $\mu$  particles to be isothermal under all operating conditions,

- Calculate from this data, the energy of activation most likely to approximate the true value for the chemical reaction step at the catalytic sites.
- For the 8 mm catalyst pellets, calculate the effectiveness factor at each temperature. State your assumptions clearly.
- Briefly explain observed changes in the values of effectiveness factors as a function of the experimental temperature. What do values above unity imply?

**Table A.** Experimental global reaction rates as a function of catalyst particle size and temperature.

Temp (K)	Catalyst Particles	
	Rate, $r_{A,p}$ (kg mol s <sup>-1</sup> )	8 mm pellets
425.5	$9.2 \times 10^{-8}$	$5.12 \times 10^{-7}$
458.7	$2.5 \times 10^{-7}$	$5.95 \times 10^{-7}$
495.1	$6.95 \times 10^{-7}$	$7.18 \times 10^{-7}$
549.5	$1.85 \times 10^{-6}$	$8.58 \times 10^{-7}$
637.0	$4.12 \times 10^{-6}$	$9.39 \times 10^{-7}$

## Solution to Problem 4.3

Part (a):

“Series 2” Arrhenius plot for 50  $\mu\text{m}$  particles (Figure A) shows the line bending above 495 K. The slope of the straight component of the line gives the correct ( $\Delta E_a/R$ ) value for chemical control, i.e. for  $\eta=1$ . Using values of the rate between 425 and 495 K, we can calculate the slope of the straight part of the line.

$$\text{Slope} = - \frac{\ln r_1 - \ln r_2}{\frac{1}{T_2} - \frac{1}{T_1}} = - \left\{ \frac{-1.42 + 1.62}{(2.02 - 2.35) \times 10^{-3}} \right\}$$

$$\frac{\Delta E_a}{R} = 6060 \text{ K}; \text{ the gas constant } R = 8.314 \text{ kJ}/(\text{kmol} \times \text{K})$$

$$\Delta E_a = 5.04 \text{ kJ kmol}^{-1}$$



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Sources: Keuzegids Master ranking 2013; Elsevier 'Beste Studies' ranking 2012; Financial Times Global Masters in Management ranking 2012

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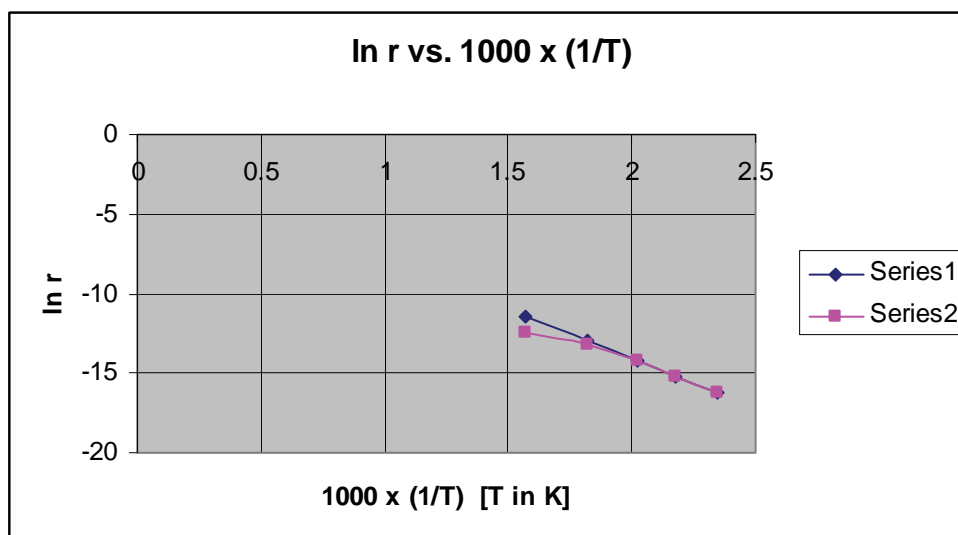


Figure A. Arrhenius plot based on data for 50  $\mu\text{m}$  particles in Table A

Part (b):

The first three rates in rows 1-3 of column-2 in Table A and Table B are the same. The data corresponds to the part of the Series 2 curve in Figure A *before it begins to bend*. Since the line is straight up to and including 495 K, we can safely conclude we have chemical control and  $\eta = 1$ .

Above that temperature, the line bends. If there had been no diffusive limitations the line would have continued as a straight line. That is why the extrapolated line still corresponds to  $\eta = 1$ . We can read off (in an enlarged diagram) that the extrapolated rate for 549.5 K is  $2.26 \times 10^{-6}$  and for 637 K, the rate corresponding to  $\eta = 1$  is  $1.07 \times 10^{-5}$ .

We then use Eq. 6.76 (Chapter 6) from the main text.

$$\frac{(r_{obs})_1}{(r_{obs})_2} = \eta_1/\eta_2 \quad (\text{Eq. 6.76})$$

where  $(r_{obs})_1$  is the second column in Table B and  $(r_{obs})_2$  third column in Table B. With  $\eta_1$  taken as unity, we can calculate the effectiveness factors for the 8 mm pellets at different temperatures.

Table B. Experimental global reaction rates as a function of catalyst particle size and temperature.

Temp (K)	Rate, $r_{A,p}$ (kmol s <sup>-1</sup> (kg cat) <sup>-1</sup> )		$\eta$ Effectiveness factor for 8 mm pellets
	50 $\mu\text{m}$ catalyst particles ( $\eta_1=1$ )	8 mm pellets (data from Table A)	
425.5	$9.2 \times 10^{-8}$	$5.12 \times 10^{-7}$	5.56
458.7	$2.5 \times 10^{-7}$	$5.95 \times 10^{-7}$	2.38
495.1	$6.95 \times 10^{-7}$	$7.18 \times 10^{-7}$	1.03
549.5	$2.26 \times 10^{-6}$	$8.58 \times 10^{-7}$	0.38
637.0	$1.07 \times 10^{-6}$	$9.39 \times 10^{-7}$	0.228

Part (c):

For exothermic reactions  $\eta=1$  means that the temperature at the centre of the pellet is greater than the surface temperature  $T_s$ . That in turn implies that the rate at the centre of the pellet is greater than the rate at the surface. In this example, the effect was more visible at relatively low surface temperatures. This explains the change in the nature of the value of effectiveness factor with increasing temperature.

### Problem 4.4

*Differential reactors* are used to simulate an infinitesimally thin (“slice”) section of, say, a tubular reactor. In the laboratory, this is done to measure reaction rates and other parameters of catalytic reactions, in the context of a small amount of conversion.

The intrinsic rate for the *endothermic* catalytic gas phase cracking reaction “A → products”, is given by the first order reaction rate expression

$$r_A = 4,000 \{ \exp(-10,000/T) \} p_A \quad \text{kmol}/(\text{kg-cat} \times \text{s})^{-1},$$

where  $p_A$  is the partial pressure (bar) of A, and  $T$  denotes the local temperature in K. The reaction is carried out in a differential reactor, where reactant “A” is supplied, mixed 1:1 with an inert diluent. The superficial mass velocity of the gas stream flowing over the catalyst particles,  $G$ , is  $1 \text{ kg m}^{-2} \text{ s}^{-1}$ , and the temperature of the bulk stream is 750 K. The overall conversion in the reactor has been determined experimentally as 3.6 %.

The catalyst pellets have a diameter of 0.004 m and may be considered isothermal. Calculate the global rate of reaction, the magnitude of the effectiveness factor, and the external concentration and external temperature gradients.

The bulk gas properties can be taken as those of the diluent, B. The pressure drop through the reactor may be neglected.

Data:

Molecular diffusivity of A in B, $D_{AB}$ :	$3 \times 10^{-4}$	$\text{m}^2 \text{ s}^{-1}$
Density of diluent B, $\rho_B$ :	0.1	$\text{kg m}^{-3}$
Viscosity of B, $\mu_B$ :	$1.5 \times 10^{-5}$	$\text{kg m}^{-1} \text{ s}^{-1}$
Heat capacity of B, $C_{p,B}$ :	1.0	$\text{kJ kg}^{-1} \text{ K}^{-1}$
Thermal conductivity of B, $\lambda_B$ :	$2.5 \times 10^{-5}$	$\text{kJ m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$
Reactor pressure, $p_T$ :	1	bar
Void fraction of the packed bed, $\varepsilon$ :	0.48	
Surface area of the catalyst pellets, $a_m$ :	0.4	$\text{m}^2 \text{ kg}^{-1}$
Heat of reaction, $\Delta H_R$ :	25,000	$\text{kJ (kmol A)}^{-1}$
Pellet effective diffusivity, $D_{eff}$ :	$1 \times 10^{-6}$	$\text{m}^2 \text{ s}^{-1}$
Pellet density, $\rho_c$ :	2,000	$\text{kg m}^{-3}$

$$j_D = (0.7) j_H = \frac{0.46}{\varepsilon_B} Re^{-0.4}; \quad Re = d_p G / \mu_B$$

$$j_D = \frac{k_m \rho_B}{G} \left\{ \frac{\mu_B}{\rho_b D_{AB}} \right\}^{2/3}; \quad j_H = \frac{h}{C_p G} \left\{ \frac{C_p \mu_B}{\lambda_B} \right\}^{2/3}.$$

In these equations,  $k_m$ , the bulk to surface mass transfer coefficient is defined in terms of the equation:

$$r_{A,p} = (k_m a_m / RT_b) (p_{A,b} - p_{A,s}),$$

and,  $h$  is the surface to bulk heat transfer coefficient, defined by

$$h a_m (T_s - T_b) = (-\Delta H_r) r_{A,p}$$

Finally,  $R$  (gas constant) =  $8.314 \text{ kJ kmol}^{-1} \text{K}^{-1} = 0.08314 \text{ bar m}^3 \text{K}^{-1} \text{ kmol}^{-1}$

#### Solution to Problem 4.4

$$h a_m (T_s - T_b) = r_{A,p} (-\Delta H_r), \text{ where } h = \frac{j_H C_p G}{(Pr)^{2/3}}$$

$$(T_s - T_b) = \frac{r_{A,p} (-\Delta H_r) (Pr)^{2/3}}{j_H C_{pB} G a_m} \quad \text{(Eq. A)}$$

$$Pr = \frac{C_{pB} \mu_B}{\lambda_B} = \frac{1 \times 1.5 \times 10^{-5}}{2.5 \times 10^{-5}} = 0.6; \quad (Pr)^{2/3} = 0.71$$

$$Re = \frac{d_p G}{\mu_B} = \frac{(0.004)(1)}{1.5 \times 10^{-5}} = 267; \text{ from equations in the data section } j_D = 0.103 \text{ and } j_H = 0.147.$$

Substituting in Eq. A, we get

$$(T_s - T_b) = \frac{(r_{A,p}) \times (-25000) \times (0.71)}{(0.147)(1)(1)(0.4)} = -3.02 \times 10^5 r_{A,p}$$

$$T_s = 750 - 3.02 \times 10^5 r_{A,p} \quad \text{(Eq. B)}$$



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Using the mass transfer equation:  $r_{A,p} = \frac{k_m a_m}{RT_b} (p_{A,b} - p_{A,s})$ ; we can write (Eq. C)

$$k_m = \frac{j_D G}{\rho_B} \left\{ \frac{\mu_B}{\rho_b D_{AB}} \right\}^{-2/3} = \frac{j_D G}{\rho_B} (Sc)^{-2/3}$$

$$k_m = \frac{(0.103)(1)}{0.1} \left[ \frac{1.5 \times 10^{-5}}{(0.1) \times (3 \times 10^{-4})} \right] = 1.59$$

Substituting this result in Eq. C, we get:

$$p_{A,b} - p_{A,s} = \frac{r_{A,p} RT_b}{k_m a_m} = \frac{(0.08314)(750)r_{A,p}}{(1.59)(0.4)} = 98.04 r_{A,p}$$

Reactor pressure: 1 bar. Conversion is 3.6%. Exit stream composition assumed equal to reactor composition. This basically means that we treat the “differential reactor” as a mini-CSTR. The feed is 50 % “A”. Therefore:  $p_b = (0.5)(1 - 0.036) = 0.482 \text{ bar}$ . Thus:

$$p_s = 0.482 - 98.04 r_{A,p}$$

$$r_{A,p} = \eta r_{A,s} \text{ and } \eta = \frac{1}{\Phi_s} \left\{ \frac{1}{\tanh 3\Phi_s} - \frac{1}{3\Phi_s} \right\}; \text{ rearranging}$$

$$\Phi_s = \frac{R_s}{3} \left\{ \frac{k RT_s \rho_c}{D_{eff}} \right\}^{1/2}$$

$\Phi_s$  in the above equation is form of the Thiele modulus appropriate for the given reaction rate expression.

$$\Phi_s = \frac{0.002}{3} \left\{ 4,000 \exp \left[ \frac{-10000}{T_s} \right] \times T_s \times \frac{(0.08314)(2000)}{1 \times 10^{-6}} \right\}^{1/2}$$

$$\Phi_s = 544 \{ T_s \exp(-10000/T_s) \}^{1/2} \quad \text{(Eq. D)}$$

At  $T_s = 750 \text{ K}$ ,  $\Phi_s \cong 14$ ; therefore we can safely consider  $\eta \cong 1/\Phi_s$ . Going back to the global reaction rate expression:

$$r_{A,p} = 4000 \eta \times \exp \{ -10,000/T_s \} \times p_{A,s} \quad \text{(Eq. E)}$$

$$r_{A,p} = 4000 \eta \times \exp \left\{ -10,000 / (750 - 3.02 \times 10^5 r_{A,p}) \right\} \times (0.482 - 98.04 r_{A,p}) \quad \text{(Eq. F)}$$

We need to substitute for  $\eta$  in Eq. E. As already mentioned,  $\eta \cong 1/\Phi_s$ ;  $\Phi_s$  is given by Eq. C, and  $T_s$  by Eq. B. Then:

$$\Phi_s = 544 \left\{ (750 - 3.02 \times 10^5 r_{A,p}) \times \exp \left[ \frac{-10,000}{(750 - 3.02 \times 10^5 r_{A,p})} \right] \right\}^{1/2} \quad \text{(Eq. G)}$$

The easier way to solve for  $r_{A,p}$  is by trial-and-error between  $\eta \cong 1/\Phi_s$ , Eq. G and Eq. F.



Close enough answers:

$$r_{A,p} \cong 1.15 \times 10^{-4}$$

$$\eta = 0.075$$

$$T_s = 715.3 \text{ K}$$

$$\Delta T = 34.7 \text{ K}$$

$$p_{A,s} = 0.47 \text{ bar}$$

$$p_{A,b} - p_{A,s} = 0.011 \text{ bar}$$

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