A First Course on Kinetics and Reaction Engineering
## Example 22.2

Problem Purpose

This problem illustrates the quantitative analysis of a steady state CSTR where two reactions are taking place.

Problem Statement

Reactants A and B can react irreversibly to produce either a desired product, D, or an undesired product, U, as shown in equations (1) and (2). The corresponding rate expressions are given in equations (3) and (4). A liquid feed mixture containing 10 mol A per gal and 12 mol B per gal at 350 K is fed to a 25 gal adiabatic reactor at a rate of 12.5 gal min^{-1}. If the standard heats at 298 K of reactions (1) and (2) are -12.0 and -21.3 kJ mol^{-1}, respectively, and if the temperature-independent heat capacities of A, B, D and U are 85, 125, 200 and 170 J mol^{-1} K^{-1}, what are the conversion of the limiting reagent, the outlet selectivity (in mol D per mol U) and the outlet temperature? What might be done to increase the outlet selectivity?

$$A + B \rightarrow D \tag{1}$$

$$A + B \rightarrow U \tag{2}$$
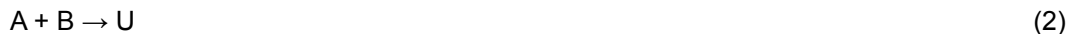
$$r_1 = \left(1.12 \times 10^2 \text{ min}^{-1}\right)\exp\left\{\frac{-15300 \text{ J mol}^{-1}}{RT}\right\}C_A \tag{3}$$

$$r_2 = \left(1.87 \times 10^2 \text{ min}^{-1}\right)\exp\left\{\frac{-23700 \text{ J mol}^{-1}}{RT}\right\}C_B \tag{4}$$

Problem Analysis

In this problem, two reactions are taking place in a CSTR and the kinetics of the reactions are known. Therefore it is a CSTR reaction engineering problem. The problem specifies that the reactor is operating at steady state. To model the system, a mole balance will be written for each reactant and product and an energy balance will be written for the reaction volume. Since the reactor is adiabatic, there is no heat transfer fluid, and consequently an energy balance on the heat transfer fluid is not needed. Thus the complete set of design equations for modeling the system comprise the mole balances and the energy balance on the reaction volume. Solving these equations will allow the calculation of the conversion, selectivity and outlet temperature.

Problem Solution

Figure 1 shows a schematic representation of the reactor. The quantities provided in the problem statement are given in a consistent set of units, and they have been entered in the diagram. The reacting fluid is stated to be a liquid, and it will be assumed that the liquid density is constant. With this

assumption, the outlet volumetric flow rate will equal the inlet volumetric flow rate as indicated in the schematic diagram.
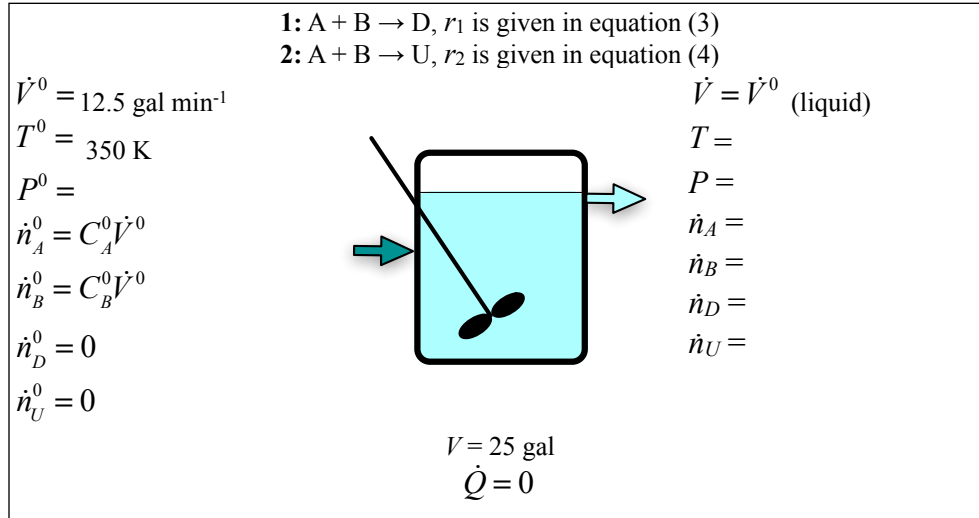

1: $A + B \rightarrow D$, r_1 is given in equation (3)
2: $A + B \rightarrow U$, r_2 is given in equation (4)

$\dot{V}^0 = 12.5$ gal min^{-1}

$T^0 = 350$ K

$P^0 =$

$\dot{n}_A^0 = C_A^0 \dot{V}^0$

$\dot{n}_B^0 = C_B^0 \dot{V}^0$

$\dot{n}_D^0 = 0$

$\dot{n}_U^0 = 0$

$\dot{V} = \dot{V}^0$ (liquid)

$T =$

$P =$

$\dot{n}_A =$

$\dot{n}_B =$

$\dot{n}_D =$

$\dot{n}_U =$

$V = 25$ gal

$\dot{Q} = 0$

Figure 1. Schematic representation of the CSTR.

Mole balances can be written for each species present in the system. The generalized, steady state mole balance equation is given by equation (5). Writing equation (5) once for each reactant and product in the system leads to equations (6) through (9).

$$0 = \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j = \dot{n}_i^0 - \dot{n}_i + V \left(\nu_{i,1} r_1 + \nu_{i,2} r_2 \right) \tag{5}$$

$$0 = \dot{n}_A^0 - \dot{n}_A + V \left(-r_1 - r_2 \right) \tag{6}$$

$$0 = \dot{n}_B^0 - \dot{n}_B + V \left(-r_1 - r_2 \right) \tag{7}$$

$$0 = -\dot{n}_D + V \left(r_1 \right) \tag{8}$$

$$0 = -\dot{n}_U + V \left(r_2 \right) \tag{9}$$

The general, steady state energy balance is given by equation (10). The heat term equals zero because the reactor is adiabatic and the work term can be assumed to be negligible because there are no shafts or moving boundaries other than, possible, an agitator. The heat capacities are stated to be constant allowing evaluation of the integrals. Applying these simplifications results in the energy balance given in equation (11).

$$0 = \sum_{\substack{i=all \\ species}} \left(\dot{n}_i^0 \int_{T^0}^{T} \hat{C}_{pi} dT \right) + V \sum_{\substack{j=all \\ reactions}} r_j \Delta H_j (T) - \dot{Q} + \dot{W} \tag{10}$$

$$0 = \left(\dot{n}_A^0 \hat{C}_{p,A} + \dot{n}_B^0 \hat{C}_{p,B} \right)\left(T - T^0 \right) + V\left(r_1 \Delta H_1\left(T \right) + r_2 \Delta H_2\left(T \right) \right) \tag{11}$$

In order for the design equations (equations (5) through (7) and equation (9)) to be solved, the number of unknowns must equal the number of design equations, in this case five. Figure 1 indicates that the four outlet molar flow rates and the outlet temperature are unknown, so they will be chosen as the unknown variables. In that case the three mole balances and the energy balance can be written as shown in equations (12) through (16).

$$0 = f_1\left(\dot{n}_A, \dot{n}_B, \dot{n}_D, \dot{n}_U, T \right) = \dot{n}_A^0 - \dot{n}_A + V\left(-r_1 - r_2 \right) \tag{12}$$

$$0 = f_2\left(\dot{n}_A, \dot{n}_B, \dot{n}_D, \dot{n}_U, T \right) = \dot{n}_B^0 - \dot{n}_B + V\left(-r_1 - r_2 \right) \tag{13}$$

$$0 = f_3\left(\dot{n}_A, \dot{n}_B, \dot{n}_D, \dot{n}_U, T \right) = -\dot{n}_D + V\left(r_1 \right) \tag{14}$$

$$0 = f_4\left(\dot{n}_A, \dot{n}_B, \dot{n}_D, \dot{n}_U, T \right) = -\dot{n}_U + V\left(r_2 \right) \tag{15}$$

$$0 = f_5\left(\dot{n}_A, \dot{n}_B, \dot{n}_D, \dot{n}_U, T \right) = \left(\dot{n}_A^0 \hat{C}_{p,A} + \dot{n}_B^0 \hat{C}_{p,B} \right)\left(T - T^0 \right) + V\left(r_1 \Delta H_1 + r_2 \Delta H_2 \right) \tag{16}$$

Equations (12) through (16) do not contain integrals or derivatives. As such, one could attempt to solve them manually, using symbolic algebra software or using numerical methods software. A variety of software packages are available for doing so, and you should use the one you feel most comfortable with. Supplemental Unit S2 presents a brief introduction to the numerical solution of sets of non-differential equations like these using numerical methods software. No matter what software package you use, you typically will need to provide two things as input in order to solve the equations:

- Code that evaluates the functions, f_1 through f_5 in equations (12) through (16), given values of the unknown variables, $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_D$, $\dot{n}_U$ and T
- A guess for the solution, that is, a guess for the values of $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_D$, $\dot{n}_U$ and T that cause all of the functions, f_1 through f_5, to equal zero

The functions to be evaluated contain quantities other than the four unknown variables. In order to evaluate the functions, values will be needed for each of those other quantities. Here the inlet molar flow rates ($\dot{n}_A^0$, $\dot{n}_B^0$), the reaction volume (V), the heat capacities ($\hat{C}_{p,A}$, $\hat{C}_{p,B}$ and $\hat{C}_{p,Z}$) and the inlet temperature (T^0) are all known constants whose values are given in the problem statement. (The inlet molar flow rates of D and U are equal to zero, so they do not appear in any of the design equations.) The rates of the reactions (r_1 and r_2) and the heats of the reactions ($\Delta H_1(T)$ and $\Delta H_2(T)$) are variable quantities whose values will need to be computed in order to evaluate the functions, f_1 through f_5.

The rates can be computed using equations (2) and (3), which introduces the concentrations of A and B. Those concentrations can be calculated by expressing them in terms of the molar flow rates and

the volumetric flow rate as in equations (17) and (18). The code that evaluates the functions, f_1 through f_5, will be given $\dot{n}_A$ and $\dot{n}_B$, and the volumetric flow rate is a known constant.

$$C_A = \frac{\dot{n}_A}{\dot{V}} \tag{17}$$

$$C_B = \frac{\dot{n}_B}{\dot{V}} \tag{18}$$

The heat of reaction depends upon the temperature according to equation (19); see Unit 2. Noting that the heat capacities are constant allows evaluation of the integrals, leading to equations (20) and (21) for the heats of reactions (1) and (2) at the outlet temperature, T. These quantities can be evaluated since T will be given and the heat capacities and the standard heats of reaction at 298 K are known constants.

$$\Delta H^0_j(T) = \Delta H^0_j(298\ \text{K}) + \sum_{\substack{i=\text{all} \\ \text{species}}} \left(v_{i,j} \int_{298K}^{T} \hat{C}_{p,i}\, dT \right) \tag{19}$$

$$\Delta H^0_1(T) = \Delta H^0_1(298\ \text{K}) + \left(\hat{C}_{p,D} - \hat{C}_{p,A} - \hat{C}_{p,B} \right)\left(T - 298\ \text{K} \right) \tag{20}$$

$$\Delta H^0_2(T) = \Delta H^0_2(298\ \text{K}) + \left(\hat{C}_{p,U} - \hat{C}_{p,A} - \hat{C}_{p,B} \right)\left(T - 298\ \text{K} \right) \tag{21}$$

That is everything that is needed in order to evaluate the functions, f_1 through f_5. The only other thing that will be needed in order to solve the equations numerically is a guess for the values of the unknowns. Since all that is needed is a guess, one possibility is to use the inlet molar flow rates and temperature as the guess. With that, equations (12) through (16) can be solved numerically to find $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_D$, $\dot{n}_U$ and T. The problem asked for the conversion of the limiting reagent, the outlet selectivity (in mol D per mol U) and the outlet temperature. The latter is found directly by solving the design equations. Noting that A is the limiting reagent, its fractional conversion can be computed using equation (22) once the design equations have been solved to obtain $\dot{n}_A$ ($\dot{n}_A^0$ is a known constant). Similarly, the overall selectivity, $S_{D/U}$, can be calculated using equation (23) once the design equations have been solved to obtain $\dot{n}_D$ and $\dot{n}_U$.

$$f_A = \frac{\dot{n}_A^0 - \dot{n}_A}{\dot{n}_A^0} \tag{22}$$

$$S_{D/U} = \frac{\dot{n}_D}{\dot{n}_U} \tag{23}$$

Performing these calculations one finds the outlet temperature is 397 K, the conversion of A is 72.8 % and the selectivity is 4.39 mol D per mol U. We are also asked what might be done to improve the selectivity. As pointed out in Unit 18, the selectivity parameter, here denoted as $s_{D/U}$, can be useful in

assessing how possible changes will affect the selectivity. The selectivity parameter is just the ratio of the rate expressions for the desired and undesired reactions. In this case, that gives the expression in equation (26).

$$s_{D/U} = \frac{r_D}{r_U} = \frac{r_1}{r_2} \tag{24}$$

$$s_{D/U} = \frac{\left(1.12 \times 10^2 \ \text{min}^{-1}\right) \exp\left\{\dfrac{-15300 \ \text{J mol}^{-1}}{RT}\right\} C_A}{\left(1.87 \times 10^2 \ \text{min}^{-1}\right) \exp\left\{\dfrac{-23700 \ \text{J mol}^{-1}}{RT}\right\} C_B} \tag{25}$$

$$s_{D/U} = 0.599 \exp\left\{\frac{8400 \ \text{J mol}^{-1}}{RT}\right\} \frac{C_A}{C_B} \tag{26}$$

Looking at equation (26), it is apparent that three things would be expected to increase the selectivity: decreasing the temperature, increasing the concentration of A or decreasing the concentration of B. Decreasing the temperature would be expected to additionally decrease the rate, and hence the conversion. If the inlet concentration of A is increased from 10 mol gal^{-1} to 14 mol gal^{-1}, then the conversion of A (which is no longer the limiting reagent) decreases slightly to 70.9 %, but the selectivity increases to 14.6 mol D per mol U. Similarly, decreasing the concentration of B from 12 mol gal^{-1} to 8 mol gal^{-1} decreases the conversion of A (again not the limiting reagent any more) to 70.5 %, but it increases the selectivity to 23.1 mol D per mol U.

Calculation Details Using MATLAB

Supplemental Unit S2 describes how to solve sets of non-differential equations numerically using MATLAB, and it provides a template file named SolvNonDif.m for doing so. Before it can be used to solve a problem, that template file must be modified in four places, each indicated by a comment that begins "% EDIT HERE". In addition to those required modifications I made a few additional modifications that will be described here along with the required modifications.

I recommend that you work with a copy of the file that has been given a more meaningful name; I used Example_22_2.m. Since the function name must match the filename, I changed the name of the function to Example_22_2. At the same time, knowing that I won't need to use the results from these calculations in subsequent calculations, I changed the function so that it does not return any values. The template file begins with a long set of comments describing what it does and how to use it; I replaced these comments with a brief comment stating the purpose of the modified version. None of these modifications were required. The first _required_ modification is to enter the values of all universal and problem specific constants at the point indicated. At the same time these are entered, they should be converted to a consistent set of units. At this point I also calculated $\dot{n}_A{}^0$ and $\dot{n}_B{}^0$, since they, too, are constants. Listing 1 shows the section of Example_22_2.m where these modifications were made.

```
% Modified version of the MATLAB template file SolvNonDif.m used in the
% solution of Example 22.2 of "A First Course on Kinetics and Reaction
% Engineering."
%
function Example_22_2
    % Known quantities and constants (in consistent units)
    CA0 = 10; % mol/gal
    CB0 = 12; % mol/gal
    T0 = 350; % K
    V = 25; % gal
    VFR = 12.5; % gal/min
    dH1_298 = -12; % kJ/mol
    dH2_298 = -21.3; % kJ/mol
    cPA = 85/1000; % kJ/mol/K
    cPB = 125/1000; % kJ/mol/K
    cPD = 200/1000; % kJ/mol/K
    cPU = 170/1000; % kJ/mol/K
    k01 = 1.12e2; % /min
    k02 = 1.87e2; % /min
    E1 = 15.3; % kJ/mol
    E2 = 23.7; % kJ/mol
    R = 8.31446/1000; % kJ/mol/K
    nA0 = CA0*VFR; % mol/min
    nB0 = CB0*VFR; % mol/min
```

Listing 1. Portion of the modified template file SolvNonDif.m where problem-specific and universal constants were entered in consistent units.

The second *required* modification involves entering the code to evaluate functions f_1 through f_5, equations (12) through (16). In the code, this occurs within an internal function named evalEqns; within evalEqns, both the unknowns and the equations are provided as vector quantities named z and f, respectively. Thus, it is necessary to map the variables used in the problem solution to represent the unknowns ($\dot{n}_A$, $\dot{n}_B$, $\dot{n}_D$, $\dot{n}_U$ and T) to a vector z, and to return the values of the functions in the vector f. I find it useful at the start of the internal function that will evaluate the functions, to define local variables with the names used in the problem statement. This modification is not required, but in my opinion, it makes the code more readable and easier to debug. In addition, the list of variables here serves as a reminder of the mapping of the problem statement variables to the vector z.

Recall from the solution that the functions contained variable quantities (r_1, r_2, C_A, C_B, ΔH_1 and ΔH_2) that depend upon the unknowns. In the code being written here to evaluate the functions, we are given values of the unknowns as just described. Therefore, these variable quantities can be evaluated here using the equations given in the problem statement; specifically equations (3), (4), (17), (18), (20) and (21). The constants from the problem statement have already been entered and are available at this point in the MATLAB file, so the functions f_1 through f_5 can now be evaluated. The code containing all these modifications is shown in Listing 2.

```
% Function that evaluates the equations
  function f = evalEqns(z)
    % mapping of unknowns into vector z
    nA = z(1);
    nB = z(2);
    nD = z(3);
    nU = z(4);
    T = z(5);
    % calculate variables quantities
    CA = nA/VFR;
    CB = nB/VFR;
    r1 = k01*exp(-E1/R/T)*CA;
    r2 = k02*exp(-E2/R/T)*CB;
    dH1 = dH1_298 + (cPD - cPA - cPB)*(T-298);
    dH2 = dH2_298 + (cPU - cPA - cPB)*(T-298);
    % evaluate the functions being solved
    f = [
        nA0 - nA + V*(-r1 - r2)
        nB0 - nB + V*(-r1 - r2)
        -nD + V*r1
        -nU + V*r2
        (nA0*cPA + nB0*cPB)*(T - T0) + V*(r1*dH1 + r2*dH2)
    ];
  end % of internal function evalEqns
```

Listing 2. Portion of the modified template file SolvNonDif.m showing the entry of the code to evaluate the functions being solved.

The third _required_ modification is where guesses for the unknowns are provided. The guesses are entered in the array named z_guess. They must be entered using the same mapping of the unknowns to the vector z as was used above. The previous modification, where variables with more meaningful names were defined, serves as a key to remind you which variable is z_1, which is z_2, and so on. As noted in the problem solution, one possibility for a guess is to simply use the inlet values of $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_D$, $\dot{n}_U$ and T, and that is what is done in Listing 3.

```
% guesses for the solution
z_guess = [
    nA0
    nB0
    0
    0
    T0
];
```

Listing 3. Portion of the modified template file SolvNonDif.m where guesses are provided for the unknowns.

The final _required_ modification only applies if you need to use the results from solving the set of equations to calculate other quantities. In this case, the problem asked for the conversion of the limiting reagent, equation (22), the outlet selectivity in mol D per mol U, equation (23) and the outlet temperature. Listing 4 shows the code that was used to do this.

```
            % Report the results
            T = z(5)
            pct_conv_A = 100*(nA0-z(1))/nA0
            sel_D_per_U = z(3)/z(4)
```

Listing 4. Portion of the modified template file SolvNonDif.m where the results of solving the set of non-differential equations are used to calculate additional quantities.

At this point, the modified template file can be used to solve the equations. To do so, the function name is typed at the MATLAB command prompt. Numerical methods for solving non-differential equations don't always converge to an acceptably accurate final answer (see Supplemental Unit S2 for more reasons why and what to do if this happens). Therefore, you should always examine the output from MATLAB closely; it should indicate that the equations were solved. If it doesn't, then you need to determine why a solution was not obtained. In addition, you should check the values of the functions that are calculated using the final solution and printed. These should all be close to zero if the solution is accurate. In the present problem, an accurate solution was found as can be seen in Listing 5.

```
>> Example_22_2

Equation solved.

fsolve completed because the vector of function values is near zero
as measured by the default value of the function tolerance, and
the problem appears regular as measured by the gradient.

<stopping criteria details>

The solver found the following values for the unknowns:

z =
    33.9714
    58.9714
    74.1296
    16.8991
   397.3287

The corresponding values of the functions being solved are as follows:

f =
    1.0e-08 *

     0.0295
     0.0292
    -0.0252
    -0.0041
     0.4436

T =
   397.3287

pct_conv_A =
    72.8229

sel_D_per_U =
     4.3866
```

Listing 5. Output from the execution of Example_22_2.m.