

# A First Course on Kinetics and Reaction Engineering

## Example 2.3

### Problem Purpose

This problem illustrates the calculation of the adiabatic temperature change as a function of the conversion for a reaction when the initial composition is known. It also illustrates a situation where it is necessary to choose a basis of calculation.

### Problem Statement

Suppose that a mixture of 3% ethane in air at an initial temperature of 150 °C reacted adiabatically at constant pressure (1 atm) according to reaction (1). Using the data and results from Examples 2.1 and 2.2, derive a relationship between the fractional conversion of ethane and the corresponding final temperature. Ideal gas behavior may be assumed.



### Problem Analysis

In most cases, the only way to relate the temperature of a reacting system to the progress of the reaction(s) is by solving the reactor design equations for the system. The two exceptions are an isothermal system, where the temperature is constant, and an adiabatic system, where the temperature can be computed using thermodynamics. The problem statement here never mentions any type of reactor, but it does state that the reaction occurs adiabatically. Hence, this is a problem where thermodynamics will be used to relate the temperature to the reaction progress.

### Problem Solution

In this problem we have a chemical reaction taking place adiabatically with the initial composition temperature and pressure given. We are asked to calculate the final temperature as a function of the conversion. Recall that during adiabatic reaction the net heat released must be equal to the change in the latent and specific heat of the system. Furthermore, since enthalpy is a state function, the temperature change can be calculated using any pathway that leads from the initial condition to the final condition. The standard heat of reaction (1) at 150 °C was calculated in Example 2.1. As such, a convenient pathway for the present calculations would be one where the reaction takes place isothermally at 150 °C in the first step and the resulting mixture is heated to the final temperature in the second step. If reaction (1) takes place at 150 °C, all of the resulting products will be gases. Consequently, no phase changes will occur during the heating step. In such cases, equation (2.6) from the informational reading, reproduced as equation (2) below, sets the net heat released equal to the change in the sensible heat of the system. Expanding the summations, substituting the initial temperature (150 °C = 423 K) and dropping the subscript for the reaction (since there is only one reaction involved) leads to equation (3).

$$\sum_{j=1}^{N_{ind}} \xi_j (-\Delta H_j(T_1)) = \sum_{\substack{i=all \\ species}} \int_{T_1}^{T_2} \hat{C}_{p,i} (n_i^0 + \nu_{i,j} \xi_j) dT \quad (2)$$

$$\begin{aligned} \xi(-\Delta H(423 \text{ K})) = & (n_{C_2H_6}^0 - 2\xi) \int_{423 \text{ K}}^{T_2} \hat{C}_{p,C_2H_6} dT + (n_{O_2}^0 - \xi) \int_{423 \text{ K}}^{T_2} \hat{C}_{p,O_2} dT \\ & + (n_{C_2H_4}^0 + 2\xi) \int_{423 \text{ K}}^{T_2} \hat{C}_{p,C_2H_4} dT + (n_{H_2O}^0 + 2\xi) \int_{423 \text{ K}}^{T_2} \hat{C}_{p,H_2O} dT \\ & + (n_{N_2}^0) \int_{423 \text{ K}}^{T_2} \hat{C}_{p,N_2} dT \end{aligned} \quad (3)$$

The quantities provided in the problem statement are all intensive variables. Consequently, we can choose the value of one extensive variable and use that as the basis for our calculations. Here it is convenient to choose a value for the total starting moles; 100 moles will be used here as the basis for the calculations. The problem states that 3% of that is ethane, meaning that 97% is air. Here we will neglect the minor components of air and assume it contains 21% O<sub>2</sub> and 79% N<sub>2</sub>. With this information, the initial moles of each species can be calculated.

$$n_{C_2H_6}^0 = 0.03n_{total}^0 = 0.03(100 \text{ mol}) = 3 \text{ mol}$$

$$n_{O_2}^0 = 0.21n_{air}^0 = 0.21(0.97n_{total}^0) = 0.21(0.97)(100 \text{ mol}) = 20.4 \text{ mol}$$

$$n_{N_2}^0 = 0.79n_{air}^0 = 0.79(0.97n_{total}^0) = 0.79(0.97)(100 \text{ mol}) = 76.6 \text{ mol}$$

$$n_{C_2H_4}^0 = n_{H_2O}^0 = 0$$

The heat of reaction at 423 K was calculated to equal -49,650 cal mol<sup>-1</sup> in Example 2.2, which also provided expressions for the heat capacities of all of the reagents, but not for N<sub>2</sub>. The original source for the heat capacity data (Smith and Van Ness [1]) lists the following parameters for the heat capacity of N<sub>2</sub> (see the table in Example 2.2):  $\alpha = 6.524$ ,  $\beta = 1.25 \times 10^{-3}$ , and  $\gamma = -0.001 \times 10^{-6}$ . Substitution of all the known values into equation (3) and integration leads to an implicit expression for the temperature as a function of the extent of reaction, equation (4).

$$\begin{aligned}
 \xi(-49,650 \text{ cal mol}^{-1}) &= (3 \text{ mol} - \xi) \int_{298}^T (2.247 + 38.201 \times 10^{-3}T - 11.049 \times 10^{-6}T^2) dT \\
 &\quad + (20.4 \text{ mol} - \xi) \int_{298}^T (6.148 + 3.102 \times 10^{-3}T - 0.923 \times 10^{-6}T^2) dT \\
 &\quad + (2\xi) \int_{298}^T (2.830 + 28.601 \times 10^{-3}T - 8.726 \times 10^{-6}T^2) dT \\
 &\quad + (2\xi) \int_{298}^T (7.256 + 2.298 \times 10^{-3}T + 0.283 \times 10^{-6}T^2) dT \\
 &\quad + (76.6 \text{ mol}) \int_{298}^T (6.524 + 1.25 \times 10^{-3}T - 0.001 \times 10^{-6}T^2) dT \\
 -49,648\xi &= -2108\xi + 631.9T + 0.1368T^2 - 1.735 \times 10^{-5}T^3 \\
 &\quad + 9.53\xi T - 8.853 \times 10^{-3}\xi T^2 + 2.045 \times 10^{-6}\xi T^3 - 2.0 \times 10^5
 \end{aligned} \tag{4}$$

The problem asks for an equation relating the fractional conversion of ethane, not the extent of reaction, to the final temperature. Indeed, since we assumed a basis when solving this problem, equation (4) would only apply for our chosen basis. The fractional conversion of ethane can be related to the extent of reaction by writing the defining equation for fractional conversion and then substituting for the moles of ethane in terms of the extent of reaction, leading to equation (5).

$$\begin{aligned}
 f_{C_2H_6} &= \frac{n_{C_2H_6}^0 - n_{C_2H_6}}{n_{C_2H_6}^0} \\
 f_{C_2H_6} &= \frac{n_{C_2H_6}^0 - (n_{C_2H_6}^0 - \xi)}{n_{C_2H_6}^0} \\
 n_{C_2H_6}^0 f_{C_2H_6} &= \xi
 \end{aligned} \tag{5}$$

Substitution of equation (5) into equation (4), along with the initial moles of ethane, leads to the desired result, equation (6), that provides the relationship between the fractional conversion and the final temperature.

$$\begin{aligned}
 -1.489 \times 10^5 f_{C_2H_6} &= -6324 f_{C_2H_6} + 631.9T + 0.1368T^2 - 1.735 \times 10^{-5}T^3 \\
 &\quad + 28.59 f_{C_2H_6} T - 0.02656 f_{C_2H_6} T^2 + 6.135 \times 10^{-6} f_{C_2H_6} T^3 \\
 &\quad - 2.0 \times 10^5
 \end{aligned} \tag{6}$$

#### Reference Cited

1. Smith, J.M. and H.C.V. Ness, *Introduction to Chemical Engineering Thermodynamics*. 2nd Ed. ed. 1959, New York: McGraw-Hill.