

# Kinetics and Reactor Design HW10

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Assigned: April 11, 2023

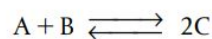
Due: April 24, 2023

## 1 Problem Statement

### 1.1 P11-8<sub>B</sub> (a-f)

#### P11-8<sub>B</sub> Algorithm for reaction in a PBR with heat effects

The elementary gas-phase reaction



is carried out in a packed-bed reactor. The entering molar flow rates are  $F_{A0} = 5 \text{ mol/s}$ ,  $F_{B0} = 2F_{A0}$ , and  $F_I = 2F_{A0}$  with  $C_{T0} = 0.3 \text{ mol/dm}^3$ . The entering temperature is 330 K.

Additional information:

$$C_{p_A} = C_{p_B} = C_{p_C} = 20 \text{ cal/mol}\cdot\text{K}, \quad C_{p_I} = 40 \text{ cal/mol}\cdot\text{K}, \quad E = 25 \frac{\text{kcal}}{\text{mol}},$$

$$\Delta H_{R_x} = -20 \frac{\text{kcal}}{\text{mol}} @ 298 \text{ K}$$

$$\alpha = 0.0002 \text{ kg}^{-1}, \quad k = 0.004 \frac{\text{dm}^6}{\text{kg}\cdot\text{mol}\cdot\text{s}} @ 310 \text{ K},$$

$$K_C = 1000 @ 303 \text{ K}$$

Note: This problem is continued in P12-1<sub>B</sub> with some of the entering conditions (e.g.,  $F_{B0}$ ) modified.

- (a) Write the mole balance, the rate law,  $K_C$  as a function of  $T$ ,  $k$  as a function of  $T$ , and  $C_A$ ,  $C_B$ ,  $C_C$  as a function of  $X$ ,  $p$ , and  $T$ .
- (b) Write the rate law as a function of  $X$ ,  $p$ , and  $T$ .
- (c) Show the equilibrium conversion is

$$X_e = \frac{\frac{3K_C}{4} - \sqrt{\left(\frac{3K_C}{4}\right)^2 - 2K_C\left(\frac{K_C}{4} - 1\right)}}{2\left(\frac{K_C}{4} - 1\right)}$$

and then plot  $X_e$  vs.  $T$ .

- (d) What are  $\sum \Theta_i C_{p_i}$ ,  $\Delta C_p$ ,  $T_0$ , entering temperature  $T_1$  (rate law), and  $T_2$  (equilibrium constant)?
- (e) Write the energy balance for adiabatic operation.
- (f) **Case 1 Adiabatic Operation.** Plot and then analyze  $X_e$ ,  $X$ ,  $p$ , and  $T$  versus  $W$  when the reaction is carried out adiabatically. Describe why the profiles look the way they do. Identify those terms that will be affected by inerts. Sketch what you think the profiles  $X_e$ ,  $X$ ,  $p$ , and  $T$  will look like before you run the Polymath program to plot the profiles. (**Ans.:** At  $W = 800 \text{ kg}$  then  $X = 0.3583$ )

Figure 1

## 1.2 P12-8<sub>A</sub> (a-c)

**P12-8<sub>A</sub>** The gas-phase reversible reaction as discussed in P11-7<sub>B</sub>



is now carried out under high pressure in a packed-bed reactor with pressure drop. The feed consists of both inerts I and species A with the ratio of inerts to the species A being 2 to 1. The entering molar flow rate of A is 5 mol/min at a temperature of 300 K and a concentration of 2 mol/dm<sup>3</sup>. Work this problem in terms of volume. *Hint:*  $V = W/\rho_B$ ,  $r_A = \rho_B r'_A$

*Additional information:*

$F_{A0} = 5.0 \text{ mol/min}$	$T_0 = 300 \text{ K}$	$\Delta H_{Rxx} = -20,000 \text{ cal/mol}$	$\alpha \rho_b = 0.02 \text{ dm}^{-3}$
$C_{A0} = 2 \text{ mol/dm}^3$	$T_1 = 300 \text{ K}$	$K_C = 1,000 \text{ at } 300 \text{ K}$	<u>Coolant</u>
$C_I = 2 C_{A0}$	$k_1 = 0.1 \text{ min}^{-2} \text{ at } 300 \text{ K}$	$C_{p_B} = 160 \text{ cal/mol/K}$	$\dot{m}_C = 50 \text{ mol/min}$
$C_{p_I} = 18 \text{ cal/mol/K}$	$Ua = 150 \text{ cal/dm}^3/\text{min/K}$	$p_B = 1.2 \text{ kg/dm}^3$	$C_{p_{\text{Cool}}} = 20 \text{ cal/mol/K}$
$C_{p_A} = 160 \text{ cal/mol/K}$	$T_{a0} = 300 \text{ K}$		
$E = 10,000 \text{ cal/mol}$	$V = 40 \text{ dm}^3$		

Plot and then analyze  $X$ ,  $X_e$ ,  $T$ ,  $T_a$ , and the rate ( $-r_A$ ) profiles in a PFR for the following cases. In each case, explain why the curves look the way they do.

- (a) Co-current heat exchange
- (b) Countercurrent heat exchange (**Ans.:** When  $V = 20 \text{ dm}^3$  then  $X = 0.86$  and  $X_e = 0.94$ )
- (c) Constant heat-exchanger temperature  $T_a$

Figure 2

## 2 Problem Solution

### 2.1 P11-8<sub>B</sub> (a-f)

a)

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}} \quad (1)$$

$$-r_A = k \left[ C_A C_B - \frac{C_C^2}{K_C} \right] \quad (2)$$

$$k = k_1 \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (3)$$

$$K_C = K_2 \exp \left[ \frac{\Delta H_{Rx}}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) \right] \quad (4)$$

$$\varepsilon = y_{A0} \delta = 2 - 1 - 1 = 0 \quad (5)$$

$$\Theta_B = 2 \quad (6)$$

$$C_A = C_{A0}(1 - X)p \frac{T_0}{T} \quad (7)$$

$$C_B = C_{A0}(2 - X)p \frac{T_0}{T} \quad (8)$$

$$C_C = C_{A0}Xp \frac{T_0}{T} \quad (9)$$

$$\frac{dp}{dW} = \frac{-\alpha}{2p} \frac{T}{T_0} \quad (10)$$

b)

$$-r_A = k \left[ C_A C_B - \frac{C_C^2}{K_C} \right] \quad (11)$$

$$-r_A = k \left[ \left( C_{A0}(1 - X)p \frac{T_0}{T} \right) \left( C_{A0}(2 - X)p \frac{T_0}{T} \right) - \frac{(C_{A0}Xp \frac{T_0}{T})^2}{K_C} \right] \quad (12)$$

c) We need to isolate  $K_C$  from the rate equation for this. All X's become  $X_e$ .

$$K_C = \frac{4C_{A0}^2 X_e^2}{C_{A0}^2(1 - X_e)(2 - X_e)} \quad (13)$$

$$X_e^2 = \frac{2K_C}{4} - \frac{3K_C}{4}X_e + \frac{K_C}{4}X_e^2 \quad (14)$$

$$0 = \frac{2K_C}{4} - \frac{3K_C}{4}X_e + \left( \frac{K_C}{4} - 1 \right) X_e^2 \quad (15)$$

$$X_e = \frac{\frac{3K_C}{4} - \sqrt{\left( \frac{3K_C}{4} \right)^2 - 2K_C \left( \frac{K_C}{4} - 1 \right)}}{2 \left( \frac{K_C}{4} - 1 \right)} \quad (16)$$

d)

$$T = T_0 + \frac{-\Delta H_{Rx}X}{\Sigma \Theta_i C_{p_i}} \quad (17)$$

$$\Delta H_{Rx} = \Delta H_R^\circ + \Delta C_p(T - T_R) \quad (18)$$

$$\Delta C_p = 2 \times 20 - 20 - 20 = 0 \quad (19)$$

$$\Sigma \Theta_i C_{p_i} = C_{p_A} + \Theta_B C_{p_B} + \Theta_C C_{p_C} + \Theta_I C_{p_I} = 100 \text{ cal}/(\text{mol K}) \quad (20)$$

e)

$$T = T_0 + \frac{-\Delta H_{Rx}X}{\Sigma \Theta_i C_{p_i}} \quad (21)$$

$$330 + \frac{20000X}{100} = 330 + 200X \quad (22)$$

f)

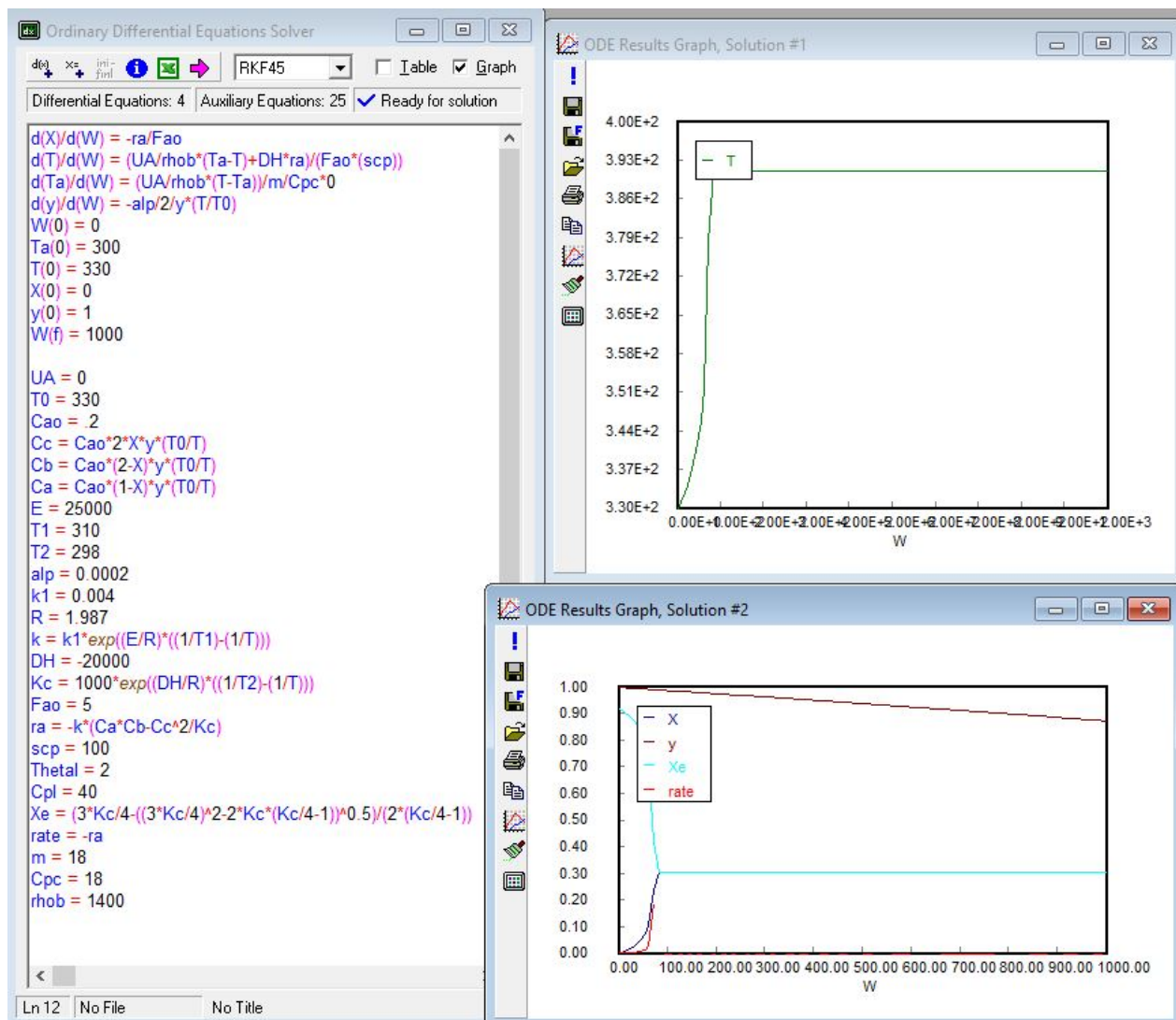


Figure 3: My Plots for Adiabatic (see  $UA = 0$ )

$X_e$  and  $X$  converge (as is expected for equilibrium reactions), there is pressure drop with more catalyst (also expected), and temperature quickly rises and then stabilizes upon the reaction reaching equilibrium. Before plotting this in Polymath, I would expect the graphs to look quite similar to the adiabatic ones we covered in lecture.

## 2.2 P12-8<sub>A</sub> (a-c)

In this problem, A and B have identical heat capacities, and identical stoichiometry, so  $\Delta C_p = 0$

$$\frac{dT}{dV} = \frac{(-r_A)(-\Delta H_{Rx}) - Ua(T - T_a)}{\Sigma F_i C_{p_i}} \quad (23)$$

$$\Sigma F_i C_{p_i} = F_{A0} [\Sigma \Theta_i C_{p_i} + \Delta C_p X] \quad (24)$$

$$\frac{dT}{dV} = \frac{(-r_A)(-\Delta H_{Rx}) - Ua(T - T_a)}{F_{A0} \Sigma \Theta_i C_{p_i}} \quad (25)$$

$$(26)$$

Co-current:

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}C_{pc}} \quad (27)$$

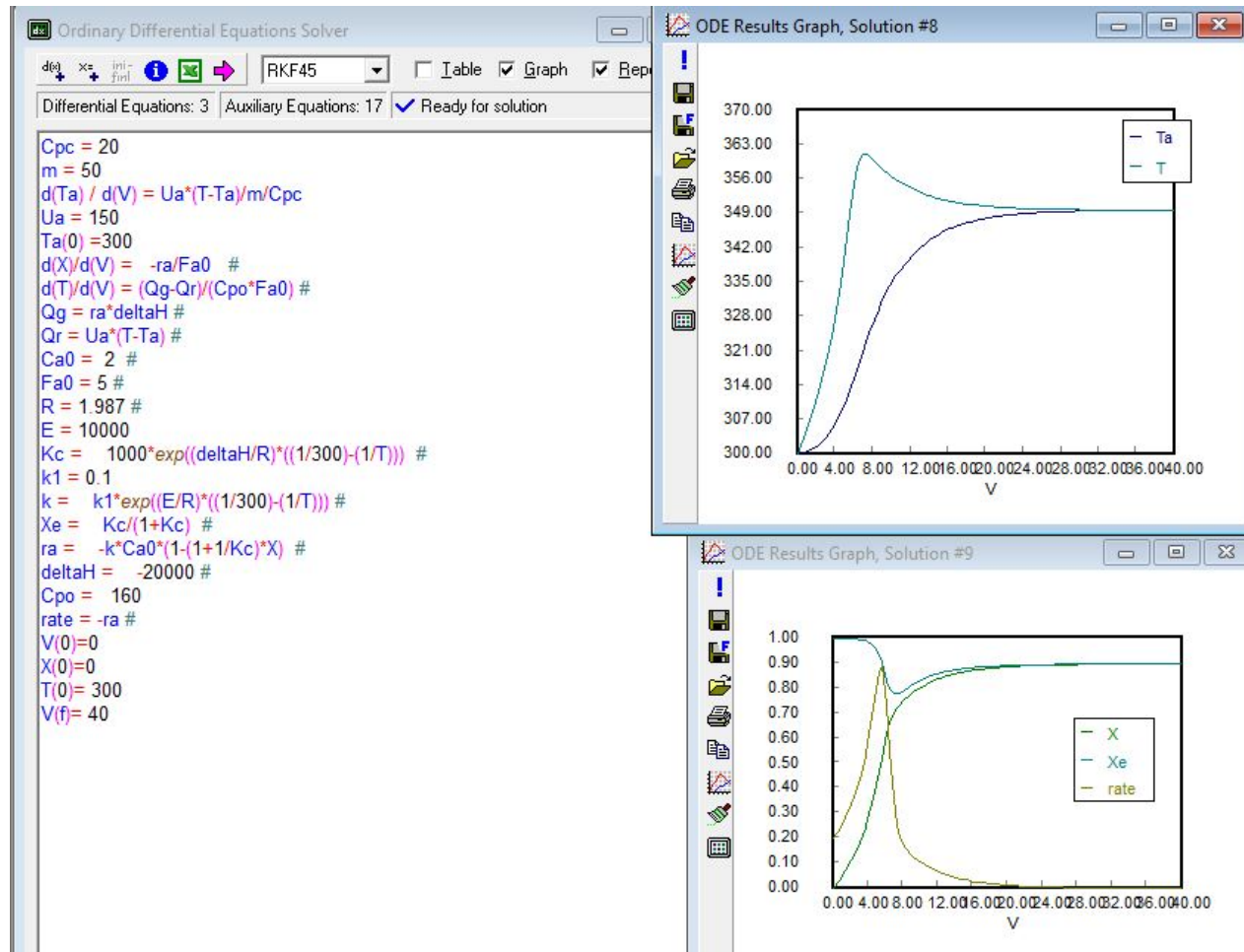


Figure 4: Co-Current Coupled ODEs Solved in Polymath



Explainer: as expected, for co-current, T rises up until equilibrium is reached and stabilizes. Ta also catches up to T. For the conversion, X and Xe converge on a value, which is consistent with what we learned. The rate spikes up initially but quickly drops to 0 as X becomes roughly equal to Xe.

Counter-Current:

$$\frac{dT_a}{dV} = \frac{-Ua(T - T_a)}{\dot{m}C_{pc}} \quad (28)$$

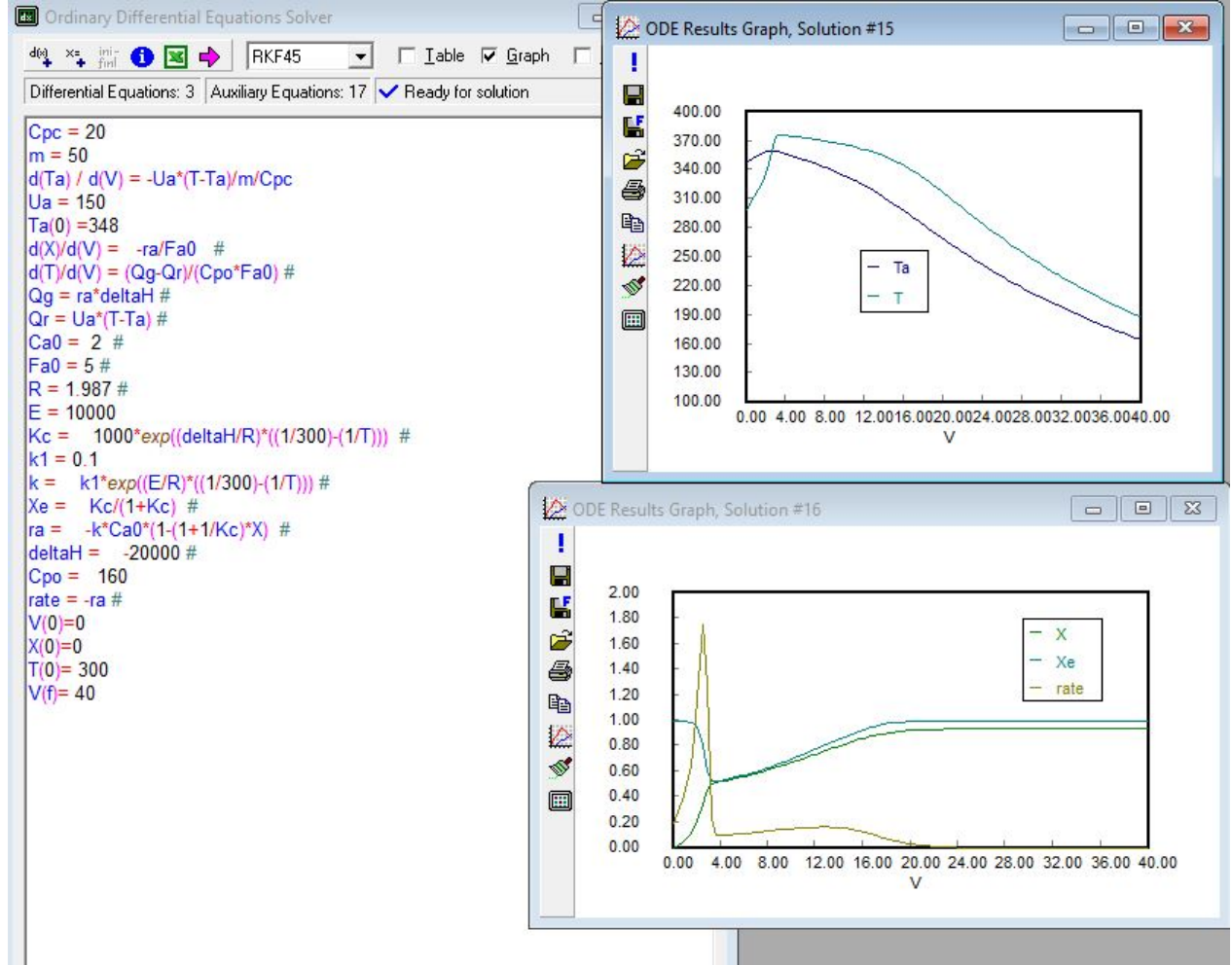


Figure 5: Counter-Current Coupled ODEs Solved in Polymath

Explainer: as expected, for counter-current, T rises up due to a large amount of reactions taking place, then starts being cooled due to difference with Ta. Ta, which comes in at V = 40 (hence it should be looked at from right to left) is heated by the exothermic reaction and exits the reactor at V = 0 at a higher temperature. For the conversion, X and Xe converge on a value (though I'm not exactly sure why they separate later, it might be a mistake in equation set up), which is consistent with what we learned. The rate spikes up initially but quickly drops to a small value as X becomes roughly equal to Xe.

Constant  $T_a$

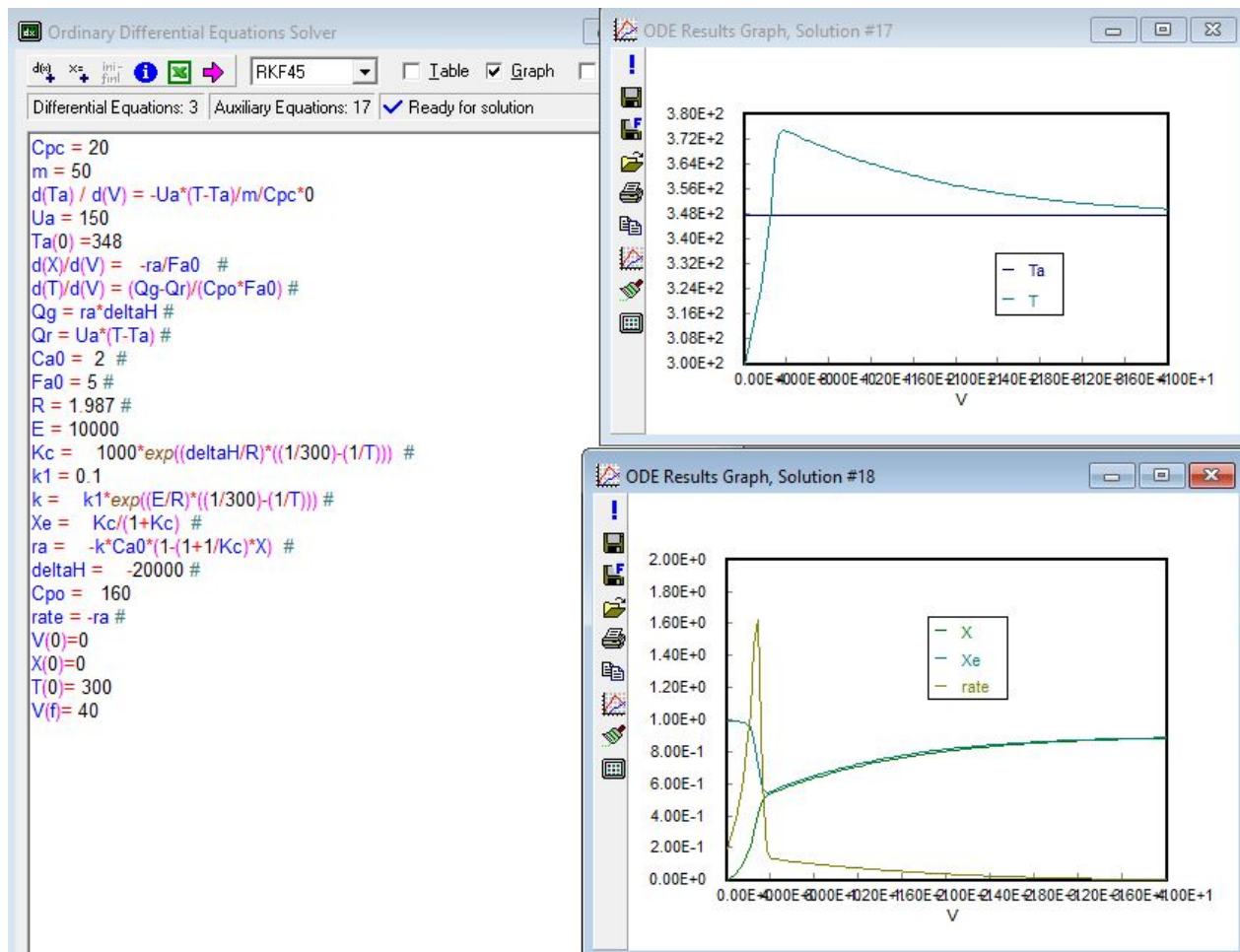


Figure 6: High Volumetric Flow Rate (Const  $T_a$ ) Coupled ODEs Solved in Polymath

Explainer: as expected, for constant  $T_a$  current,  $T$  rises up until equilibrium is reached and is then cooled down over time by  $T_a$ .  $T_a$  is constant (due to a situation like very high flow rate of coolant fluid). For the conversion,  $X$  and  $X_e$  converge on a value, which is consistent with what we learned. The rate spikes up initially but quickly drops to 0 as  $X$  becomes roughly equal to  $X_e$ .