Lecture: Multiple Steady States in a Reactor – Simplest Case

David J. Keffer
Department of Chemical and Biomolecular Engineering
The University of Tennessee, Knoxville
dkeffer@utk.edu
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Multiple steady states occur in non-isothermal reactors. The simplest case in which one can observe multiple steady states is a first order reaction of A → B in an adiabatic CSTR. These notes are modeled off the discussion in section 5-5 (pp. 246-250) of Chemical Engineering Kinetics by J.M. Smith, McGraw-Hill, Third Edition, 1981. They are modified to use notation consistent with the rest of this course.

We have previously derived the material balance for the isothermal CSTR.

$$\frac{dC_A}{dt} = \frac{F_{in}}{V} C_{A.in} - \frac{F_{out}}{V} C_A + \nu_A r \tag{1}$$

For a constant volume system at steady state, this equation becomes,

$$0 = \frac{F}{V}\left(C_{A.in} - C_A\right) + \nu_A r \tag{2}$$

The steady state conversion of A for a first order reaction (obtained from the material balance (MB)) is

$$X_A^{MB} = \frac{C_{A.in} - C_A}{C_{A.in}} = \frac{k\tau_R}{1 + k\tau_R} \tag{3}$$

where

$$\tau_R = \frac{V}{F} \tag{4}$$

$$\nu_A = -1 \tag{5}$$

$$r = kC_A \tag{6}$$

and

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

We have also previously derived the energy balance for the adiabatic CSTR.

$$C_T C_{p,mix}\left(\frac{dT}{dt}\right) = \frac{F_{in}}{V} C_{T,in} C_{p,mix,in}\left(T_{in} - T\right) - \Delta H_R r \tag{8}$$

For a constant volume system at steady state, this equation becomes,

$$0 = \frac{F}{V} C_{T,in} C_{p,mix,in}\left(T_{in} - T\right) - \Delta H_R r \tag{9}$$

We eliminate the rate by substituting in the material balance, equation (2) for the rate,

$$0 = \frac{F}{V} C_{T,in} C_{p,mix,in}\left(T_{in} - T\right) + \Delta H_R \frac{F}{\nu_A V}\left(C_{A.in} - C_A\right) \tag{10}$$

Rearranging (assuming first order, i.e. ν_A = -1) yields

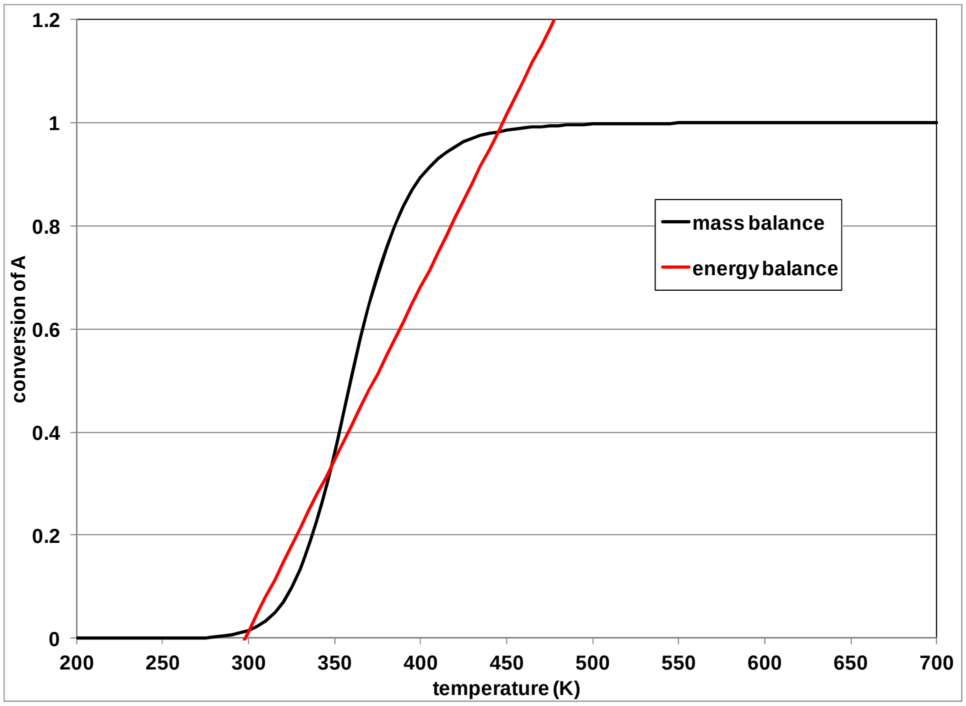
$$C_{A.in} - C_A = \frac{C_{T,in} C_{p,mix,in}\left(T_{in} - T\right)}{\Delta H_R} \tag{11}$$

The steady state conversion of A obtained from this energy balance (EB) is

$$X_A^{EB} = \frac{C_{A.in} - C_A}{C_{A.in}} = \frac{C_{T,in} C_{p,mix,in}\left(T_{in} - T\right)}{C_{A.in}\Delta H_R} \tag{12}$$

Thus we have two expressions for conversion as a function of temperature from the material balance, equation (3), and the energy balance, equation (12).

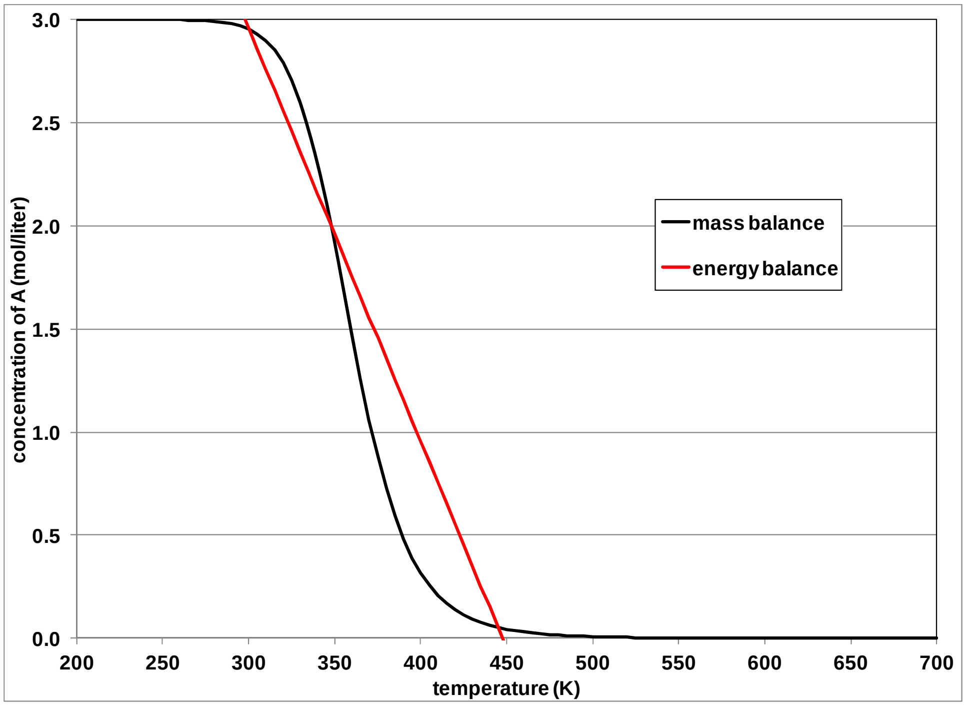
In a plot of steady state conversion vs steady state reaction temperature, we have a plot of the general form shown below. In this example there are three steady states. There is a low-temperature, low-conversion steady state, a high-temperature, high-conversion steady state and an intermediate steady state.



where the following parameters were used:

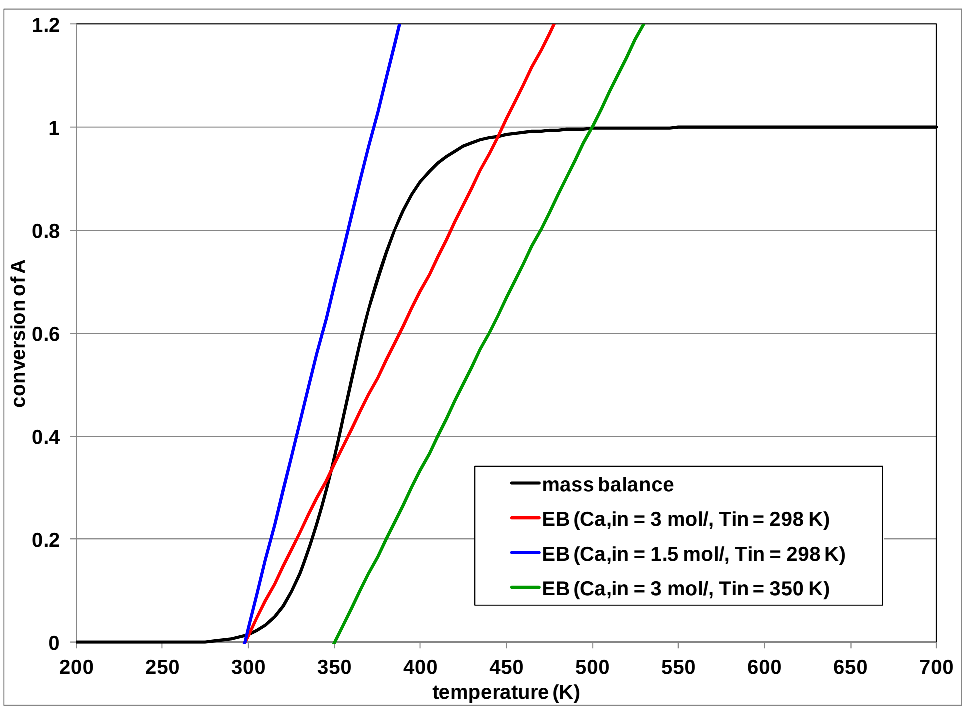
inlet conditions		
F	0.06	liters/sec
Cain	3	moles/liter
Ctin	55.5556	moles/liter
Tin	298	K
V	18	liters
tau_r	300	s
reaction conditions		
	-	
dHR	2.09E+05	J/mole
Ea	62800	J/mole
ko	4.48E+06	1/sec
R	8.314	J/mol/K
physical properties		
Cp_spec	4.19	J/g/K
MW	1.80E+01	g/mol
Cp	7.54E+01	J/mol/K

The same data can be plotted as a function of concentration vs temperature rather than conversion vs temperature, if so desired, as shown below.



The low conversion, low temperature steady state corresponds to the high concentration of reactant and low temperature steady state. The high conversion, high temperature steady state corresponds to the low concentration of reactant and high temperature steady state.

Changes in the inlet conditions results in changes in the energy balance but not the energy balance, resulting in curves like those shown below.



In the second energy balance, the inlet concentration was changed to 1.5 mol/liter from 3.0 mol/liter. In the third energy balance, the inlet temperature was changed to 350 K from 298 K. The first energy balance has three steady states. The other two energy balances only have one steady state. The reactor with the higher inlet temperature and higher inlet concentration of reactant tend to result in the high temperature, high conversion steady state. Similarly, the reactor with the lower inlet temperature and lower inlet concentration of reactant tend to result in the low temperature, low conversion steady state.