10.37 Chemical and Biological Reaction Engineering, Spring 2007
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Lecture 11: Non-isothermal Reactors, equilibrium limitations, and stability

This lecture covers: Derivation of energy balances for ideal reactors; equilibrium conversion, adiabatic and non-adiabatic reactor operation.

Non-isothermal Reactors

$$\frac{dN_i}{dt} = \sum_{m=1}^{N\ streams} F_{i,m} + V_{cv} \sum_{l=1}^{N\ rxns} \underbrace{\upsilon_{i,l}}_{\text{stoichiometric coefficient}} r_l$$

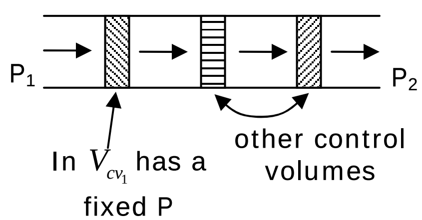
r_l - depends on concentration
- T
- catalyst

$$\frac{dU_{cv}^{total}}{dx} + P\frac{dV_{cv}}{dt} = \sum_{m=1}^{N\ streams} H_m^{conc}(T_m)F_m^{total} + \dot{Q} + \dot{W}_s + (\text{other energy terms})$$

extensive work
expansion work
intensive
flow work
heat
shaft work

do work → $\dot{W}_s$ negative

If small control volume, pressure constant.



$P_1 \neq P_2$

Figure 1. Schematic of a PFR with small control volumes, each with a fixed P.

PFR has many small control volumes, each with its own constant P.

For isothermal – $\dot{Q}$ adjusted to keep T constant
– Practical – have big cooling bath
– or just operate at a particular temperature found after reactor built
  ⇒ not a good strategy, for design we want to know ahead of time
– before assumed uniform T, actually have hot spots

Where is T? In U_{cv}^{total} and $r_l(T)$.

$$\frac{dU_{cv}^{total}}{dt} = \frac{dU_{cv}^{total}}{dT}\frac{dT}{dt} + \sum_{i=1}^{N\ streams}\left(\frac{dU_{cv}^{total}}{dN_i}\right)\frac{dN_i}{dt}$$

heat capacity of system

intensive contribution of each species

substitute for $\frac{dN_i}{dt}$

Want $\frac{dY}{dt} = F(Y)$

Assume ideal mixtures

$$U_{cv}^{total} \approx \sum N_i U_i(T_{cv})$$

extensive intensive

$$\frac{dU_{cv}^{total}}{dN_i} = U_i(T_{cv})$$

If P=Constant (Isobaric)

$$\frac{dH^{total}}{dt} = \frac{d(U+PV)}{dt} = \frac{dU}{dt} + \underbrace{\frac{dP}{dt}}_{0}V + P\frac{dV}{dt}$$

$$\underbrace{\frac{dU_{cv}^{total}}{dt} + P\frac{dV_{cv}}{dt}}_{\downarrow}$$

$$\frac{dH^{total}}{dt}$$

Assume isobaric, all ideal mixtures, neglecting K.E., P.E., other energies

$$\left(\sum_{i}^{N\ species} N_i C_{p,i}\right)\frac{dT_{cv}}{dt} = \sum_{m}^{N\ streams}\sum_{i}^{N\ species} F_{i,m}\left(H_i(T_m) - H_i(T_{cv})\right)$$
$$- \sum_{i}^{N\ streams}\sum_{l}^{N\ rxns} H_i(T_{cv})V_{cv}\upsilon_{i,l}r_l(T_{cv}) + \dot{Q} + \dot{W}_s$$

stoichiometric coefficient

$$\sum_i \upsilon_{i,l}H_i(T_{cv}) \equiv \underset{l}{\Delta H_{rxn}}(T_{cv})$$

$$-\sum_{i}^{N\ streams}\sum_{l}^{N\ rxns} H_i(T_{cv})V_{cv}\upsilon_{i,l}r_l(T_{cv}) = -\sum_{l} V_{cv}r_l(T_{cv})\Delta \underset{l}{H}_{rxn}(T_{cv})$$

Assume

$$\dot{Q} \cong UA(T_a - T_{cv}) \qquad \text{(conduction)}$$

heat transfer coefficient

area of contact

coolant

reactor

$\dot{W}_s \approx 0$ (As a stirrer, heat negligible)

If designing engines $\dot{W}_s \neq 0$.

Now just put into MATLAB and solve

Chapter 8 in Fogler – lots of special case equations
– be careful of assumptions

Special case: Start up CSTR to a steady state
want to know ultimate T

$$\frac{dT_{cv}}{dt} = 0 \cong \sum_{m}^{N\ streams}\sum_{i}^{N\ species} F_{i,m}\left(H_i(T_m) - H_i(T_{cv})\right) - \sum V_{cv}r_l\Delta \underset{l}{H}_{rxn} + UA(T_a - T_{cv})$$

All depend on T_{CV}

When we reach steady state, no more accumulation

$F_{A,\,in} - F_{A,\,out} + r_A V = 0$ at steady-state

See Fogler: 8.2.3

If just one reaction, one input stream, one output stream, and the system is at steady-state:

$$X_A = \frac{UA(T - T_a) + \sum F_{i,\,input}C_{p,\,i}(T - T_{in})}{F_{Ao}(-\Delta H_{rxn})}$$

In this special case, conversion and T linear
1 reaction making heat as product is made.
When $\Delta H_{rxn} =$ (-) Exothermic, reactor is hotter than cooling reactor (heat transfer important)
(+) Endothermic, reactor must be heated so that reaction will run

$$G(T) \equiv (-\Delta H_{rxn})(-r_A V/F_{Ao})$$ Generation

$$R(T) = \left(\sum \frac{F_{i,\,in}}{F_{Ao}} C_{p,\,i}\right)\left(1 + \underbrace{\frac{UA}{\sum F_{i,\,in} C_{p,\,i}}}_{K}\right)(T - T_c)$$

Heat removal

$K = 0$ Adiabatic
$K =$ Big Cooling

$$T_c = \frac{KT_a + T_{in}}{1+K}$$

$R(T)$ linear with T

$G(T) \rightarrow$ constant at high T
- not linear with T

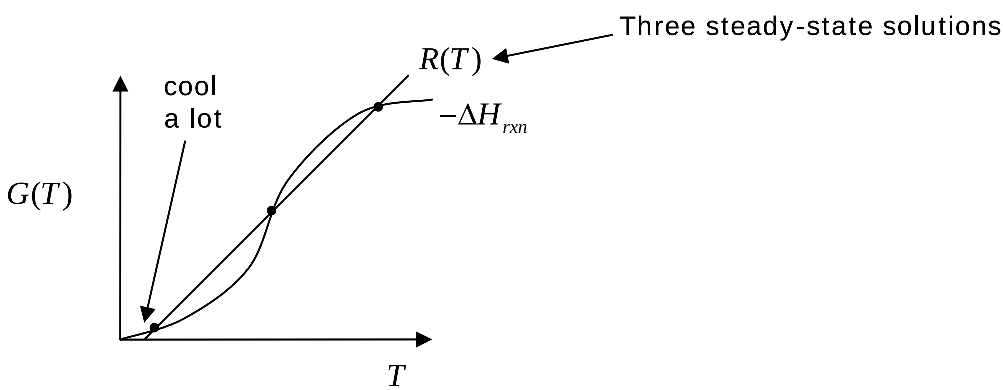


Figure 2. Graph of G(T) versus T. Three steady-state points are shown where R(T) intersects with the heat of reaction.

With multiple steady states must consider stability.