

Non-isothermal Unsteady State Operation of Reactors

Advanced Reactor Design, Spring 2024 Week 1

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Unsteady State Nonisothermal

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Change in System Energy with Time

$$\frac{d\mathsf{E}_{sys}}{dt} = \dot{\mathsf{Q}} - \dot{\mathsf{W}} + \sum_{i=1}^{n} \mathsf{F}_i\mathsf{E}_i \Big|_{in} - \sum_{i=1}^{n} \mathsf{F}_i\mathsf{E}_i \Big|_{out}$$
Energy of system is the sum of products of each species specific energy E_i & the moles of each species: $\mathsf{E}_{sys} = \sum_{i=1}^{n} \mathsf{N}_i\mathsf{E}_i$
 $\mathsf{E}_i \approx \mathsf{U}_i \ \& \ \mathsf{U}_i = (\mathsf{H}_i - \mathsf{PV}_i) \ \text{so:} \rightarrow \mathsf{E}_{sys} = \sum_{i=1}^{n} \mathsf{N}_i (\mathsf{H}_i - \mathsf{PV}_i) \ \text{Differentiate wrt time}$

$$\Rightarrow \frac{d\mathsf{E}_{sys}}{dt} = \frac{d}{dt} \left[\sum_{i=1}^{n} \mathsf{N}_i (\mathsf{H}_i - \mathsf{PV}_i) \right] \Rightarrow \frac{d\mathsf{E}_{sys}}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \frac{d\mathsf{H}_i}{dt} + \sum_{i=1}^{n} \mathsf{H}_i \frac{d\mathsf{N}_i}{dt} - \frac{d}{dt} \left[\mathsf{P}\sum_{i=1}^{n} \mathsf{N}_i \mathsf{V}_i \right] \right]$$

$$\Rightarrow \frac{d\mathsf{E}_{sys}}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \left(\mathsf{H}_i - \mathsf{PV}_i \right) \right] \Rightarrow \frac{d\mathsf{E}_{sys}}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \frac{d\mathsf{H}_i}{dt} + \sum_{i=1}^{n} \mathsf{H}_i \frac{d\mathsf{N}_i}{dt} - \frac{d}{dt} \left[\mathsf{P}\sum_{i=1}^{n} \mathsf{N}_i \mathsf{V}_i \right] \right]$$

$$\Rightarrow \frac{d\mathsf{E}_{sys}}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \frac{d\mathsf{H}_i}{dt} + \sum_{i=1}^{n} \mathsf{H}_i \frac{d\mathsf{N}_i}{dt} - \frac{\mathsf{d}}{\mathsf{dt}} \mathsf{N}_i \right]$$

$$\Rightarrow \frac{d\mathsf{E}_{sys}}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \frac{d\mathsf{H}_i}{dt} + \sum_{i=1}^{n} \mathsf{H}_i \frac{d\mathsf{N}_i}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \frac{d\mathsf{H}_i}{dt} + \sum_{i=1}^{n} \mathsf{H}_i \frac{d\mathsf{N}_i}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \frac{\mathsf{d}}{\mathsf{H}_i} + \sum_{i=1}^{n} \mathsf{H}_i \frac{\mathsf{d}}{\mathsf{H}_i} \right]$$

$$\Rightarrow \frac{d\mathsf{E}_{sys}}{dt} = \sum_{i=1}^{n} \mathsf{N}_i \frac{d\mathsf{H}_i}{dt} + \sum_{i=1}^{n} \mathsf{H}_i \frac{\mathsf{d}}{\mathsf{H}_i} = \sum_{i=1}^{n} \mathsf{N}_i \frac{\mathsf{d}}{\mathsf{H}_i} + \sum_{i=1}^{n} \mathsf{H}_i \frac{\mathsf{d}}{\mathsf{H}_i} \right]$$

$$\Rightarrow \frac{\mathsf{d}\mathsf{E}_{sys}}{\mathsf{d}\mathsf{d}\mathsf{d}\mathsf{d}} = \sum_{i=1}^{n} \mathsf{N}_i \frac{\mathsf{d}}{\mathsf{d}}\mathsf{d} + \sum_{i=1}^{n} \mathsf{H}_i \frac{\mathsf{d}}{\mathsf{d}}\mathsf{d} + \sum_{i=1}^{n} \mathsf{H}_i \frac{\mathsf{d}}{\mathsf{d}} + \sum_{i=1}^{n} \mathsf{H}_i \frac{\mathsf{$$

Well-Mixed Reactors, Constant PV

EB for Well-Mixed Reactors, $\Delta PV=0^{-1}$



Simplified EB for Well-Mixed Reactors

olve for dT/dt:
$$\dot{Q} - \dot{W}_{S} + \sum_{i=1}^{n} F_{i0}H_{i0} = \sum_{i=1}^{n} N_{i}C_{pi} \frac{dT}{dt} + \sum_{i=1}^{n} H_{i}F_{i0} + \Delta H^{\circ}_{RX}(T)(\frac{dT}{dt} + \frac{dT}{dt})$$

Bring $\Sigma F_{i0}H_i$ and $\Delta H^{\circ}_{RX}(T)$ terms to other side of equation:

$$\rightarrow \dot{Q} - \dot{W}_{S} + \sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} H_{i}F_{i0} - \Delta H^{\circ}_{RX}(T)(-r_{A}V) = \sum_{i=1}^{n} N_{i}C_{pi}\frac{dT}{dt}$$

Factor $\Sigma F_{i0}H_{i0}$ and $\Sigma F_{i0}H_i$ terms and divide by ΣN_iC_{Di} :

Energy balance for unsteady state reactor with phase change:

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$$\frac{\dot{Q} - \dot{W}_{S} - \sum\limits_{i=1}^{n} F_{i0} \left(H_{i} - H_{i0}\right) + \Delta H^{\circ}_{RX} \left(T\right) \left(r_{A}V\right)}{\sum\limits_{i=1}^{n} N_{i}C_{pi}} = \frac{dT}{dt}$$

Energy balance for unsteady state reactor without phase change:

 $\frac{\dot{Q} - \dot{W}_{S} - \sum_{i=1}^{\prime\prime} F_{i0}C_{pi} \left(T - T_{i0}\right) + \Delta H^{\circ}_{RX} \left(T\right) \left(r_{A}V\right)}{L^{2}}$ $\sum_{i=1}^{n} N_i C_{pi}$ كلية الهندسة - COLLEGE OF ENGINEERING

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dt

Unsteady State EB, Liquid-Phase Rxns

$$\frac{\dot{Q} - \dot{W}_{S} - \sum_{i=1}^{n} F_{i0}C_{pi}(T - T_{i0}) + \Delta H^{\circ}_{RX}(T)(r_{A}V)}{\sum_{i=1}^{n} N_{i}C_{pi}} = \frac{d^{T}}{d^{T}}$$

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For liquid-phase reactions, often $\Delta C_p = \Sigma v_i C_{pi}$ is so small it can be neglected

When ΔC_p can be neglected, then: $\sum_{i=1}^{n} N_i C_{pi} = N_{A0} C_{ps} \text{ where } C_{ps} = \Sigma \Theta_i C_{pi} \text{ is the heat capacity of the solution}$ If the feed is well-mixed, it is convenient to use:

 $\Sigma F_{i0}C_{pi} = F_{A0}C_{ps}$

Plug these equations and $T_{i0} = T_0$ into the EB gives:

 $\frac{\dot{Q} - \dot{W}_{S} - F_{A0}C_{ps}(T - T_{i0}) + \Delta H^{\circ}_{RX}(T)(r_{A}V)}{N_{A0}C_{ps}} = \frac{dT}{dt}$ This equation for the EB is simultaneously solved with the mass balance (design eq) for unsteady state, nonisothermal reactor design **COLLEGE OF ENGINEERING** - كلبة المنحسة تكريت - Tikrit University - جامعة تكريت - Particular -

Nonisothermal Batch Reactor Design

$$\frac{\dot{Q} - \dot{W}_{S} - \sum_{i=1}^{n} F_{i0}C_{pi}(T - T_{i0}) + \Delta H^{\circ}_{RX}(T)(r_{A}V)}{\sum_{i=1}^{n} N_{i}C_{pi}} = \frac{dT}{dt}$$
No flow, so: $\rightarrow \frac{\dot{Q} - \dot{W}_{S} + \Delta H^{\circ}_{RX}(T)(r_{A}V)}{\sum_{i=1}^{n} N_{i}C_{pi}} = \frac{dT}{dt}$
Put the energy balance in terms of X_A: $N_{i} = N_{A0}(\Theta_{i} + \nu_{i}X_{A})$ where $\Theta_{i} = \frac{N_{i0}}{N_{A0}} \& \nu_{i}C_{pi} = \Delta C_{p}$
 $\rightarrow \frac{\dot{Q} - \dot{W}_{S} + \Delta H^{\circ}_{RX}(T)(r_{A}V)}{N_{A0}\left[\sum_{i=1}^{n} \Theta_{i}C_{pi} + \Delta C_{p}X_{A}\right]} = \frac{dT}{dt}$

Solve with the batch reactor design equation using an ODE solver (Polymath)

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$$N_{A0} \frac{dX_A}{dt} = -r_A V$$

Adiabatic Nonisothermal Batch **Reactor Design**

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Solve for how X_A
changes with T =
$$\left[\Delta H^{\circ}_{RX}(T_R) + \Delta C_p(T - T_R)\right] \frac{dX_A}{dt} = \left[C_{pS} + \Delta C_p X_A\right] \frac{dT}{dt}$$

 $\rightarrow - \left[\Delta H^{\circ}_{RX}(T_R) + \Delta C_p(T - T_R)\right] dX_A = \left[C_{pS} + \Delta C_p X_A\right] dT$



Get like terms together:

$$\rightarrow \int_{X_{A0}=0}^{X_{A}} \frac{dX_{A}}{C_{pS} + \Delta C_{p}X_{A}} = \int_{T_{0}}^{T} \frac{-dT}{\Delta H^{\circ}_{RX}(T_{R}) + \Delta C_{p}(T - T_{R})}$$

Integrate & solve for X_A :

$$\rightarrow X_{A} = \frac{C_{p_{S}}(T - T_{0})}{-\left(\Delta H^{\circ}_{RX}(T_{R}) + \Delta C_{p}(T - T_{R})\right)} \rightarrow X_{A} = \frac{C_{p_{S}}(T - T_{0})}{-\Delta H_{RX}(T)}$$

Solving for T:

$$T = T_0 + \frac{\left[-\Delta H^{\circ}_{RX}(T_0)\right]X_A}{C_{p_s} + X_A \Delta C_p} \rightarrow T = T_0 + \frac{\left[-\Delta H^{\circ}_{RX}(T_0)\right]X_A}{\sum_{i=1}^n \Theta_i C_{p_i} + X_A \Delta C_p}$$

city of soln (calculate C_{ps} if not given)

Heat capacity of soln (calculate C_{ps} if not given)

Solve with the batch reactor design equation using an ODE solver (Polymath)

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$$t = N_{A0} \int_{0}^{X_{A}} \frac{dX_{A}}{-r_{A}V}$$

A 1st order, liquid-phase, exothermic reaction $A \rightarrow B$ is run in a batch reactor. The reactor is well-insulated, so no heat is lost to the surroundings. To control the temperature, an inert liquid C is added to the reaction. The flow rate of C is adjusted to keep T constant at 100 °F. What is the flow rate of C after 2h?



 $T_{C0} = 80 \text{ °F} \qquad V_0 = 50 \text{ ft}^3 \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1} \qquad (100 \text{ s}^{-1}) = 1.2 \times 10^{-4} \text{$

 ΔH°_{RX} =-25000 Btu/lb mol C_{p,} (all components)= 0.5 Btu/lb mol °F

- 1. Solve design eq for comp as function of t
- 2. Solve EB for F_{C0} using that info & T=100 °F

This is essentially a semi-batch reactor since only C is fed into the reactor

reactor is well-insulated, so no heat is lost to the surroundings. To control the temperature, an inert liquid C is added to the reaction. The flow rate of C is adjusted to keep T constant at 100 °F. What is the flow rate of C after 2h? Use EB to find how the flow rate of C depends on the rxn (solve EB for F_{co}) $\frac{dT}{dt} = \frac{\int_{i=1}^{n} F_{i0}C_{pi} \left(T - T_{i0}\right) + \Delta H^{\circ}_{RX} \left(T\right) \left(r_{A}V\right)}{\sum_{i=1}^{n} N_{i}C_{pi}}$ $\rightarrow 0 = -\sum_{i=1}^{n} F_{i0}C_{pi}(T - T_{i0}) + \Delta H^{\circ}_{RX}(T)(r_{A}V) \rightarrow \sum_{i=1}^{n} F_{i0}C_{pi}(T - T_{i0}) = \Delta H^{\circ}_{RX}(T)(r_{A}V)$ C is the only species that flows, so: $\rightarrow F_{C0}C_{pC}(T - T_{i0}) = \Delta H^{\circ}_{RX}(T)(r_A V)$ $r_A V = -kC_A V = -kN_A$ where $N_A = N_{A0} \exp[-kt]$ $\rightarrow F_{C0}C_{pC}\left(T-T_{i0}\right) = \Delta H^{\circ}_{RX}\left(T\right) \left(-kN_{A0} e^{-kt}\right)$ Isolate F_{C0} : COLLEGE OF ENGINEERING - كلبة الهندسة $ightarrow F_{C0} = rac{\Delta H^{\circ}_{RX} (T) (-kN_{A0} e^{-kt})}{C_{pC} (T - T_{i0})}$ جامعة تكريت - Tikrit University

A 1st order, liquid-phase, exothermic reaction $A \rightarrow B$ is run in a batch reactor. The

A 1st order, liquid-phase, exothermic reaction $A \rightarrow B$ is run in a oatch reactor. The reactor is well-insulated, so no heat is lost to the surroundings. To control the temperature, an inert liquid C is added to the reaction. The flow rate of C is adjusted to keep T constant at 100 °F. What is the flow rate of C after 2h?

 $T_{C0} = 80 \text{ °F} \qquad V_0 = 50 \text{ ft}^3$ k(100 °F)= 1.2 x 10⁻⁴ s⁻¹ $C_{A0} = 0.5 \text{ lb mol/ft}^3$

$$\Delta H^{\circ}_{RX}$$
=-25000 Btu/lb mol
C_{p,} (all components)= 0.5 Btu/lb mol °F

$$F_{C0} = \frac{\Delta H^{\circ}_{RX} \left(T\right) \left(-k N_{A0} e^{-kt}\right)}{C_{pC} \left(T - T_{i0}\right)} \quad N_{A0} = C_{A0} V_0 = 0.5 \frac{lb \ mol}{ft^3} \left(50 ft^3\right) = 25 \ lb \ mol$$

At 2h (7200s):

$$\frac{-25,000 \frac{Btu}{lb mol}}{-1.2 \times 10^{-4} s^{-1} (25 lb mol) e^{-(1.2 \times 10^{-4} s^{-1}) 7200s}}{0.5 \frac{Btu}{lb mol \cdot {}^{\circ}F} (100^{\circ}F - 80^{\circ}F)} \rightarrow F_{C0} = 3.16 \frac{lb mol}{s}$$
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Instead of feeding coolant to the reactor, a solvent with a low boiling point is added (component D). The solvent has a heat of vaporization of 1000 Btu/lb mol, and initially 25 lb mol of A are placed in the tank. The reactor is well-insulated. What is the rate of solvent evaporation after 2 h if T is constant at 100 °F?



Additional info: $k(100 \text{ °F}) = 1.2 \times 10^{-4} \text{ s}^{-1}$ $\Delta H^{\circ}_{RX} = -25000 \text{ Btu/lb mol}^{-1}$

Still a semibatch reactor, where D is removed from the reactor

Use EB that accounts for a phase change:

Clicker Question: Does
$$dT/dt = 0$$
?

a) Yes

b) No

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Instead of feeding coolant to the reactor, a solvent with a low boning point is added (component D). The solvent has a heat of vaporization of 1000 Btu/lb mol, and initially 25 lb mol of A are placed in the tank. What is the rate of solvent evaporation after 2 h? Additional info: $k(100 \text{ }^{\circ}\text{F}) = 1.2 \times 10^{-4} \text{ s}^{-1}$ $\Delta H^{\circ}_{RX} = -25000 \text{ Btu/lb mol}$

Still a semibatch reactor, where D is removed from the reactor

Use EB that accounts for a phase change:

$$\begin{split} & \underset{i=1}{\overset{n}{\overset{}}} F_{i0} \begin{pmatrix} H_{i0} - H_{i} \end{pmatrix} + \Delta H^{\circ}_{RX} (T) (r_{A} V) & \underset{i=1}{\overset{}}{\overset{}} e^{=0} \\ & \underset{i=1}{\overset{n}{\overset{}}} N_{i}C_{pi} & \text{d}T/dt = 0 \\ & \rightarrow \sum_{i=1}^{n} F_{i0} (H_{i0} - H_{i}) = \Delta H^{\circ}_{RX} (T) (r_{A} V) & \text{D is the only species that 'flows', and} \\ & \rightarrow F_{D0} (H_{i0} - H_{i}) = \Delta H^{\circ}_{RX} (T) (-kN_{A0} e^{-kt}) & \stackrel{r_{A}V = -kN_{A0}(exp[-kt]), so;}{\rightarrow F_{D0}} = \frac{\Delta H^{\circ}_{RX} (T) (-kN_{A0} e^{-kt})}{(H_{i0} - H_{i})} \\ & \qquad F_{D0} = \frac{-25,000 \frac{Btu}{lbmol} (-\frac{0.00012}{s} (25 \text{ lb mol}) e^{-(0.00012/s)7200s})}{1000Btu/lb \text{ mol}} & \qquad F_{D0} = 0.0316 \frac{lb \text{ mon}}{s} \\ & \qquad$$

طريقك إلى انداح

A liquid phase exothermic reaction $A \rightarrow B$ is carried out at 358K in a 0.2 m³ CSTR. The coolant temperature is 273K and the heat transfer coefficient (U) is 7200 J/min·m²·K. What is the heat exchange area required for steady state operation? Using this heat exchange area, plot T vs t for reactor start-up.

SS operation means that T is constant, so:

$$\begin{array}{l} \text{heans} \\ \text{ht, so:} \quad \frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_{S} - \sum\limits_{i=1}^{\tilde{L}} F_{i0}C_{pi}\left(T - T_{i0}\right) + \Delta H^{\circ}_{RX}(T)(r_{A}V)}{\sum\limits_{i=1}^{n} N_{i}C_{pi}} \\ \rightarrow \dot{Q} - \dot{W}_{S} - \sum\limits_{i=1}^{n} F_{i0}C_{pi}\left(T - T_{i0}\right) = -\Delta H^{\circ}_{RX}(T)(r_{A}V) \end{array}$$

 \dot{Q} =UA(T_a-T), \dot{W}_{S} =0, and A is only species that flows

$$\rightarrow \mathsf{UA}(\mathsf{T}_{\mathsf{a}}-\mathsf{T})-\mathsf{F}_{\mathsf{A0}}\mathsf{C}_{\mathsf{pA}}(\mathsf{T}-\mathsf{T}_{\mathsf{A0}})=-\Delta\mathsf{H}^{\circ}_{\mathsf{RX}}(\mathsf{T})(\mathsf{r}_{\mathsf{A}}\mathsf{V})$$

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Plug in $r_A = -kC_A$ and solve for A

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= 0

J/min·m²·K. What is the heat exchange area required for steady state operation? Using this heat exchange area, plot T vs t for reactor start-up. $C_{PA} = C_{PS} = 20 \text{ J/g} \cdot \text{K}$ $\dot{W}_{S} = 0$ $C_{A0} = 180 \text{ g/dm}^{3}$ $\upsilon_{0} = 500 \text{ dm}^{3}/\text{min}$ $T_{0} = 313 \text{ K}$ $\rho = 900 \text{ g/dm}^3$ $\Delta H^{\circ}_{RX}(T) = -2500 \text{ J/g}$ E=94852 J/mol·K k(313K)= 1. Use material balance to determine steady state value of C_A $F_{A0} - F_A + r_A V = 0 \rightarrow C_{A0} \upsilon_0 - C_A \upsilon_0 - kC_A V = 0 \rightarrow C_{A0} \upsilon_0 = C_A \upsilon_0 + kC_A V$ $\rightarrow \frac{C_{A0}\nu_{0}}{\nu_{0} + kV} = C_{A} \quad k(358K) = \frac{1.1}{\min} \exp\left|\frac{94852 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{313} - \frac{1}{358}\right)\right| \rightarrow k(358K) = \frac{107.4}{\min}$ $C_{A} = \frac{180 \,\text{g/dm}^{3} \left(500 \,\text{dm}^{3}/\text{min}\right)}{500 \,\text{dm}^{3}/\text{min} + \left(107.4 \,\text{min}^{-1}\right) 200 \,\text{dm}^{3}} \rightarrow C_{A} = 4.1 \,\text{g/dm}^{3}$ Solve EB for A: $A = \frac{-\Delta H^{\circ}_{RX}(T)(-kC_{A}V) + F_{A0}C_{pA}(T - T_{A0})}{U(T_{a} - T)}$ $F_{A0} = \left(180\frac{g}{dm^{3}}\right)\left(500\frac{dm^{3}}{min}\right) = 90000 \text{ g/min}$ $V=0.2m^{3}\left(\frac{1000dm^{3}}{m^{3}}\right) = 200dm^{3}$ كلبة الهندسة - COLLEGE OF ENGINEERING جامعة تكريت - Tikrit University

A liquid phase exothermic reaction $A \rightarrow B$ is carried out at 258K in -0.2 m^3 CSTR.

The coolant temperature is 273K and the heat transfer coefficient (U) is 7200

A liquid phase exothermic reaction $A \rightarrow B$ is carried out at 358K in a 0.2 m³ CSTR. The coolant temperature is 273K and the heat transfer coefficient (U) is 7200 J/min·m²·K. What is the heat exchange area required for steady state operation? Using this heat exchange area, plot T vs t for reactor start-up. $C_{PA} = C_{PS} = 20 \text{ J/g} \cdot \text{K}$ $\dot{W}_{S} = 0 \quad C_{A0} = 180 \text{ g/dm}^{3} \quad \upsilon_{0} = 500 \text{ dm}^{3}/\text{min}$ $T_{0} = 313 \text{ K}$ $\rho = 900 \text{ g/dm}^{3} \quad \Delta H^{\circ}_{RX}(T) = -2500 \text{ J/g}$ $E = 94852 \text{ J/mol} \cdot \text{K}$ $k(313K) = 1.1 \text{ min}^{-1}$ Solve for heat exchange area at SS:

$$A = \frac{-\Delta H^{\circ}_{RX} (T) (-kC_{A}V) + F_{A0}C_{pA} (T - T_{A0})}{U(T_{a} - T)}$$

$$F_{A0} = 90,000 \text{ g/min V} = 200 \text{ dm}^{3}$$

$$\Delta H^{\circ}_{RX} (T) = -2500 \text{ J/g} \qquad k = 107.4 \text{ min}^{-1} \quad C_{A} = 4.1 \text{ g/dm}^{3} \quad C_{PA} = 20 \text{ J/g} \cdot \text{K}$$

$$U = 7200 \text{ J/min} \cdot \text{m}^{2} \cdot \text{K} \qquad T_{A0} = 313 \text{ K} \qquad T = 358 \text{K} \text{ T}_{a} = 273 \text{K}$$

$$\Rightarrow A = \frac{-\left(-2500 \frac{\text{J}}{\text{g}}\right) \left(-\frac{107.4}{\text{min}} \left(4.1 \frac{\text{g}}{\text{dm}^{3}}\right) 200 \text{dm}^{3}\right) + \left(90000 \frac{\text{g}}{\text{min}}\right) \left(20 \frac{\text{J}}{\text{g} \cdot \text{K}}\right) (358 \text{K} - 313 \text{K})}{\left(7200 \frac{\text{J}}{\text{min} \cdot \text{m}^{2} \cdot \text{K}}\right) (273 \text{K} - 358 \text{K})}$$

$$A = 227.4 \text{ m}^{2}$$
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Will use Polymath to plot T vs t for CSTR start-up (unsteady state). Need equations for dC_A/dt , dT/dt, and k.

 C_{Ps} is in terms of mass (J/g-K), so $F_{A0} \& N_{i0}$ must also be in terms of mass

F_{A0}=90,000 g/min

Substitute \dot{m}_{i0} for N_{i0} , & use ρ for the solution to calculate:

$$\dot{m}_{i0} = V\rho \rightarrow \dot{m}_{i0} = 200 \text{dm}^3 \left(900 \frac{\text{g}}{\text{dm}^3}\right) \rightarrow \dot{m}_{i0} = 180,000\text{g} \qquad r_A = -kC_A$$
Amount of gas leaving reactor (L7)
$$k = \frac{1.1}{\text{min}} \exp\left[\frac{94852 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{313} - \frac{1}{\text{T}}\right)\right] \rightarrow k = \frac{1.1}{\text{min}} \exp\left[\frac{11408.7}{\text{K}} \left(\frac{1}{313} - \frac{1}{\text{T}}\right)\right] \qquad \forall k = \frac{1.1}{\text{min}} \exp\left[\frac{11408.7}{\text{K}} \left(\frac{1}{313} - \frac{1}{\text{T}}\right)\right] \qquad U = 7200 \text{ J/min} \cdot \text{m}^2 \cdot \text{K} \qquad A = 227.4 \text{m}^2} \\ U = 7200 \text{ J/min} \cdot \text{m}^2 \cdot \text{K} \qquad A = 227.4 \text{m}^2} \\ C_{A0} = 180\text{g/dm}^3 \qquad \tau = V/\upsilon_0 \quad T_a = 273\text{K} \\ \Delta H_{RX} = -2500 \text{ J/g} \qquad N_{i0} = m_{i0} \quad V = 200 \text{ dm}^3} \\ C_{P_S} = 20 \text{ J/g}^{-1} \text{K} \qquad \upsilon_0 = 500 \text{ dm}^3 \quad T_0 = 313$$

Will use Polymath to plot T vs t for CSTR start-up (unsteady state). Need equations for dC_A/dt , dT/dt, and k.

$$k = \frac{1.1}{\min} \exp\left[\frac{11408.7}{K}\left(\frac{1}{313} - \frac{1}{T}\right)\right]$$







 $\rightarrow \frac{dC_A}{dt} = \frac{C_{A0}}{\tau} - \frac{C_A}{\tau} + r_A$

$$\dot{m}_{i0} = 180,000g$$

 $F_{A0} = 90,000 g/min$

U= 7200 J/min·m²·K A=227.4m² C_{A0}=180g/dm³ τ =V/ υ_0 T_a=273K ΔH_{RX} =-2500 J/g N_{i0}=m_{i0} V=200 dm³ C_{Ps}=20 J/g K v₀=500 dm³ T₀=313

	Ordinary Differential Equations Solver	- • •
	de ×= ini- 1 ≤ → RKF45 ▼ □ Iable ⊽ Graph ⊽ Beport	
	Differential Equations: 2 Auxiliary Equations: 11 🗸 Ready for solution	
	d(Ca) / d(t) = (Cao/tau)-(Ca/tau)-k*Ca tau=V/vo	^
	Ca(0) = 180	
	k=1.1*exp(11408.7*(1/313-1/T))	
	Cao=180 d(T) / d(t) = (U*A*(273-T)-90000*20*(T-313)+dHrx*ra*V)/(mio*Cps)	
	T(0) = 313 U=7200	
	A=227.4 dHrx=-2500	
	V=200	
	Cps=20	
	$ \begin{aligned} ra=-k^{*}Ca \\ t(0) &= 0 \end{aligned} $	
	t(f) = 15	
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Reaches steady state at ~12 minutes کلبه الهندسه - COLLEGE OF ENGINEERING

The elementary, liquid phase, exothermic reaction $A \rightarrow B$ is carried $a \sim 2 \text{ m}^3$ **CSTR** that is equipped with a heat jacket. Pure A enters the reactor at 60 mol/min and a temperature of 310K. The coolant in the heat jacket is kept at 280 K. Provide all equations, all constants, the initial time, and the final time that must be entered into Polymath in order to plot temperature vs time for the first 20 min of reactor start-up. $\Delta H_{RX}(T_R) = -10,000$ cal/mol $C_{PS} = 15$ cal/mol·K $C_{pB} = 15$ cal/mol·K $\dot{W}_S = 0$ E = 20,000 cal/mol $k = 1 \text{ min}^{-1}$ at 400 K UA= 3200 cal/min•K $v_0 = 300$ L/min

Need equations for how T changes with time, C_A changes with time, & k changes with T.

$$\begin{split} \frac{dT}{dt} &= \frac{\dot{Q} - \dot{W}_{S} - \sum\limits_{i=1}^{n} F_{i0}C_{pi}\left(T - T_{i0}\right) + \Delta H^{\circ}_{RX}\left(T\right)(r_{A}V\right)}{\sum\limits_{i=1}^{n} N_{i}C_{pi}} \qquad \dot{W}_{S} = 0 \quad \dot{Q} = UA\left(T_{a} - T\right) \\ \Delta H_{RX}\left(T\right) &= \Delta H^{\circ}_{RX}\left(T_{R}\right) + \Delta C_{P}\left(T - T_{R}\right) \quad \Delta C_{P} = \frac{b}{a}C_{PB} - C_{PA} \quad \rightarrow \Delta C_{P} = [15 - 15]\frac{cal}{mol \cdot K} = 0 \\ &\rightarrow \Delta H^{\circ}_{RX}\left(T\right) = \Delta H^{\circ}_{RX}\left(T_{R}\right) + 0 \rightarrow \Delta H^{\circ}_{RX}\left(T\right) = -10,000\frac{cal}{mol} \\ \sum_{i=1}^{n} F_{i0}C_{pi} &= F_{A0}C_{p,A} + F_{B0}C_{p,B} \quad F_{B0} = 0 \rightarrow \sum\limits_{i=1}^{n} F_{i0}C_{pi} = F_{A0}C_{p,A} \quad \sum\limits_{i=1}^{n} N_{i}C_{pi} = N_{A0}C_{ps} \\ Combine with EB: \\ COLLEGE OF ENGINEERING - to serve the s$$

The elementary, liquid phase, exothermic reaction $A \rightarrow B$ is carried out in a 2 m³ CSTR that is equipped with a heat jacket. Pure A enters the reactor at 60 mol/min and a temperature of 310K. The coolant in the heat jacket is kept at 280 K. Provide all equations, all constants, the initial time, and the final time that must be entered into طريقك المي ابتداح Polymath in order to plot temperature vs time for the first 20 min of reactor start-up. $\Delta H_{RX}(T_R) = -10,000 \text{ cal/mol} \quad C_{PA} = C_{PS} = 15 \text{ cal/mol} \cdot K \quad C_{DB} = 15 \text{ cal/mol} \cdot K \quad \dot{W}_S = 0$ E = 20,000 cal/mol $k = 1 \text{ min}^{-1} \text{ at } 400 \text{ K}$ UA= 3200 cal/min•K $v_0 = 300 \text{ L/min}$ Need equations for how T changes with time, C_A changes with time, & k changes with T. $\underline{dT} = \frac{UA(T_{a} - T) - F_{A0}C_{p,A}(T - T_{i0}) + \Delta H^{\circ}_{RX}(T_{R})r_{A}V}{L}$ $\Delta H^{\circ}_{RX}(T) = -10,000 \frac{cal}{...}$ N_{A0}C_{ps} dt $T_{a} = 280$ UA = 3200 $\begin{bmatrix} C_{PA} = 15 \\ T_{i0} = 310 \end{bmatrix} \begin{bmatrix} r_{A} = kC_{A} \\ T_{A} = kC_{A} \end{bmatrix} = \begin{bmatrix} 1 \\ 1.987 \end{bmatrix} \begin{bmatrix} 20,000 \\ 1.987 \end{bmatrix} \begin{bmatrix} 1 \\ 400 \end{bmatrix} = \begin{bmatrix} 1 \\ T \end{bmatrix}$ $|F_{A0} = 60|$ $F_{A0} = \frac{N_{A0}}{V} \upsilon_0 \rightarrow \begin{bmatrix} N_{A0} = \frac{F_{A0}V}{\upsilon_0} \end{bmatrix} \qquad \begin{bmatrix} \upsilon_0 = 300 \\ \hline C_{PS} = 15 \end{bmatrix} \qquad V = 2m^3 (1000L/1m^3) \rightarrow V = 2000$ t(f) = 20) = 0Use the mass balance to get eq for $C_A(t)$ $\frac{dN_{A}}{dt} = F_{A0} - F_{A} - r_{A}V \rightarrow \frac{dN_{A}}{dt} = C_{A0}\upsilon_{0} - C_{A}\upsilon_{0} - kC_{A}V \rightarrow \left|\frac{dC_{A}}{dt} = \frac{C_{A0}}{\tau} - \frac{C_{A}}{\tau} - kC_{A}V\right|$ COLLEGE OF ENGINEERING - خلية الهندسة $\tau = V/\upsilon_0 ||C_{A0} = F_{A0}/\upsilon_0|$ جامعة تكريت - Tikrit University

Case Studies



- Ammonium Nitrate Explosion
- Monsanto Explosion
- T2 Laboratories Explosion

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Case 1 – Ammonium Nitrate Explosion



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Massive blast at Terra plant kills four.

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Example 1: Safety in Chemical Reactors





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Example 1: Safety in Chemical Reactors

Only liquid A in the vat as the product gases N_2O and H_2O escape immediately after being formed.

$$\frac{\mathrm{dT}}{\mathrm{dt}} = \frac{\mathrm{Q}_{\mathrm{g}} - \mathrm{Q}_{\mathrm{r}}}{\mathrm{N}_{\mathrm{A}}\mathrm{C}_{\mathrm{PA}}}$$

$$Q_g = (r_A V)(\Delta H_{Rx})$$

$$Q_{r} = F_{A0} \left[C_{PA} (T - T_{0}) + \theta_{B} (H_{B} - H_{B0}) \right] + UA(T - T_{a})$$

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Unsteady State Energy Balance





Case 2 – Monsanto Chemical Company



- Keeping MBAs away from Chemical Reactors
- The process worked for 19 years before "they" showed up!
- Why did they come?
- What did they want?

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Nitroanline Synthesis Reaction





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Nitroanline Synthesis Reaction





Nitroanline Synthesis Reactor





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Same Nitroanline Synthesis Reaction





Batch Reactor, 24 hour reaction time

Management said: TRIPLE PRODUCTION

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Batch Reactor Energy Balance



$$NC_{P} = N_{A0}C_{pA} + N_{B0}C_{pB} + N_{W}C_{pW}$$
$$\frac{dT}{dt} = \frac{Q_{g} - Q_{r}}{NC_{p}}$$

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Batch Reactor Energy Balance $\frac{dT}{dt} = \frac{Q_g - Q_r}{NC_p}$

The rate of "heat removed" is

$$Q_{r} = \dot{m}_{c}C_{P_{c}}\left\{ \left(T_{a1} - T\right)\left[1 - exp\left(\frac{-UA}{\dot{m}_{c}C_{P_{c}}}\right)\right] \right\} \quad \text{Equation (12-13) p547}$$

For high coolant flow rates, \dot{m}_{c} , the maximum rate of heat removal is

$$Q_r = UA(T - T_a)$$

The rate of "heat generated" is $Q_g = (r_A V)\Delta H_{Rx} = (-r_A V)(-\Delta H_{Rx})$

$$-r_{A} = k_{1}C_{A}C_{B}$$
$$Q_{g} = k_{1}C_{A}C_{B}(-\Delta H_{Rx})$$

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Batch Reactor Energy Balance Recall $\frac{dT}{dT} = \frac{Q_r - Q_g}{NC_{P_s}}$

For isothermal operation at Qr = Qg, T = 448 K

$$Q_{g} = k(448 \text{ K})C_{A0}^{2}(1-X)(\Theta_{B} - X)(-\Delta H_{Rx})$$
$$Q_{r} = Q_{g}$$
$$\dot{m}_{c}C_{P_{c}}\left\{ (T_{a1} - T)\left[1 - \exp\left(\frac{-UA}{\dot{m}_{c}C_{P_{c}}}\right)\right] \right\} = (0.0001167)C_{A0}^{2}(1-X)$$

Vary $\, m_c^{}$ to keep "heat removed" equal to "heat generation"

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Isothermal Operation for 45 minutes



At the time the heat exchanger fails X = 0.033, T = 448 K $Q_{g} = r_{A}V\Delta H_{Rx} = 3850kcal/min$

The maximum rate of removal at T = 448 K is $Q_r = UA(T - T_a) = 35.85(448 - 298) = 5378 k cal / min$

 $Q_r > Q_g$ Everything is OK

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Adiabatic Operation for 10 minutes







Temperature-Time trajectory

 $\frac{dT}{dt} = \frac{Q_q - Q_r}{NC_r} = 0.2 \,^{\circ}C \,/ \min$



Disk Rupture

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Ti



The pressure relief disk should have ruptured when the temperature reached 265°C (ca. 700 psi) but it did not.

If the disk had ruptured, the maximum mass flow rate out of the reactor would have been 830 kg/min (2-in orifice to 1 atm).

$$\begin{aligned} Q_r &= \dot{m}_{vap} \Delta H_{vap} + UA(T - T_a) \\ Q_r &= 449,000 \frac{kcal}{min} \\ Q_g &= 27,460 \frac{kcal}{min} \\ Q_r &>>> Q_g \quad \text{No explosion} \end{aligned}$$
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Disk Rupture





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All the following three things must have occurred for the explosion to happen



2. Heat Exchange Failure

3.Relief Valve Failure

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methylcyclopentadiene manganese tricarbonyl (MCMT)

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Production of methylcyclopentadienyl manganese tricarbonyl (MCMT). Step 1a. Reaction between methylcyclopentadiene (MCP) and sodium in a solvent of diethylene glycol dimethyl ether (diglyme, $C_6H_{14}O_3$) to produce sodium methylcyclopentadiene and hydrogen gas:





Step 1b. At the end of Step 1a, MnCl₂ is added to the reactor. It reacts with sodium methylcyclopentadiene to produce manganese dimethylcyclopentadiene and sodium chloride:



Step 1c. At the end of Step 1b, CO is added. The reaction between manganese dimethylcyclopentadiene and carbon monoxide produces the final product, methylcyclopentadienyl manganese tricarbonyl (MCMT), a fuel additive.



Only consider Step 1



Desired Reaction



Undesired Reaction of Dygline

$$CH_3 - O - CH_2 - CH_2 - O - CH_2 - CH_2O - CH_3 \xrightarrow{Na} 3H_2 + misc(l) \& (s)$$

Simplified Model

Let A = methycylcopentadiene, B = sodium, S = Solvent (diglyme), and D = H_2 . These reactions are:

(1) $A + B \rightarrow C + 1/2 D$ (gas) (2) $S \rightarrow 3 D$ (gas) + miscellaneous liquid and solid products $-r_{2S} = k_{2s}C_S$ $\Delta H_{Rx1A} = -45,400 J/mol$ COLLEGE OF ENGINEERING - خلبة المنحسة $\Delta H_{Rx2S} = -3.2 \times 10^5 J/mol$



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Solution

(1) Reactor Mole Balances

Reactor (Assume Constant Volume Batch)

Liquid

$$\frac{dC_{\rm A}}{dt} = r_{\rm 1A}$$
(E13-6.1)
$$\frac{dC_{\rm B}}{dt} = r_{\rm 1A}$$
(E13-6.2)
$$\frac{dC_{\rm S}}{dt} = r_{\rm 2S}$$
(E13-6.3)
$$\frac{dP}{dt} = \left(F_{\rm D} - F_{vent}\right) \frac{RT_{\rm H}}{V_{\rm H}}$$

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$$r_{\rm D} = -\frac{1}{2}r_{\rm 1A} + -3r_{\rm 2S}$$
 (gas generated) (E13-6.19)

(3) Stoichiometry – Liquid Phase

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(4) Energy Balance:

Applying Equation (E13-18) to a batch system ($F_{i0} = 0$)

$$\frac{dT}{dt} = \frac{V_0 [r_{1A} \Delta H_{Rx1A} + r_{2S} \Delta H_{Rx2S}] - UA (T - T_a)}{\sum N_j C_{P_j}}$$
(E13-6.24)

Substituting for the rate laws and $\sum N_j C_{P_j} = 1.26 \times 10^7 \text{ J/K}$

$$\frac{dT}{dt} = \frac{V_0 \left[-k_{1A} C_A C_B \Delta H_{Rx1A} - k_{2S} C_S \Delta H_{Rx2S} \right] - UA \left(T - T_a \right)}{1.26 \times 10^7 \left(J/K \right)}$$
(E13-6.25)

 $\Delta H_{\rm Rx1A} = -45,400 \text{ J/mol}$ $\Delta H_{\rm Rx2S} = -3.2 \times 10^5 \text{ J/mol}$

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Figure E13-6.3(a) Temperature (K) versus time (h) trajectory.



Figure E13-6.3(b) Pressure (atm) versus time (h) trajectory.

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