UNIT-V NON ISOTHERMAL REACTOR DESIGN

The reaction temperature and pressure also influence the progress of reactions. A three-step procedure is followed: First, we must find how equilibrium composition, rate of reaction, and product distribution are affected by changes in operating temperatures and pressures. This will allow us to determine the optimum temperature progression, and it is this that we strive to approximate with a real design. Second, chemical reactions are usually accompanied by heat effects, and we must know how these will change the temperature of the reacting mixture. With this information we are able to propose a number of favorable reactor and heat exchange systems-those which closely approach the optimum. Finally, economic considerations will select one of these favorable systems as the best. So, with the emphasis on finding the optimum conditions and then seeing how best to approach them in actual design for single reactions and follow this with the special considerations of multiple reactions.

Single Reactions

With single reactions conversion level and reactor stability are the important criteria. Questions of product distribution do not occur. Thermodynamics gives two important pieces of information, the first being the heat liberated or absorbed for a given extent of reaction, the second being the maximum possible conversion.

Heats of Reaction from Thermodynamics

The heat liberated or absorbed during reaction at temperature *T*, depends on the nature of the reacting system, the amount of material reacting, and the temperature and pressure of the reacting system, and is calculated from the heat of reaction ΔH , for the reaction in question. When this is not known, it can in most cases be calculated from known and tabulated

thermochemical data on heats of formation ΔH , or heats of combustion ΔH , of the reacting materials. These are tabulated at some standard temperature, *T1*, usually 25°C. As a brief reminder, consider the reaction

aA + rR + sS

By convention we define the heat of reaction at temperature T as the heat transferred to the reacting system from the surroundings when a moles of A disappear to produce r moles of R and s moles of S with the system measured at the same temperature and pressure before and after the change. Thus

aA + rR + sS, *AHrT* { positive, endothermic

negative, exothermic

$$aA \rightarrow rR + sS$$
, $\Delta H_{rT} \begin{cases} \text{positive, endothermic} \\ \text{negative, exothermic} \end{cases}$

$$\begin{pmatrix} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_2 \end{pmatrix} = \begin{pmatrix} \text{heat added to} \\ \text{reactants to} \\ \text{change their} \\ \text{temperature} \\ \text{from } T_2 \text{ to } T_1 \end{pmatrix} + \begin{pmatrix} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_1 \end{pmatrix} + \begin{pmatrix} \text{heat added to} \\ \text{products to} \\ \text{bring them} \\ \text{back to } T_2 \\ \text{from } T_1 \end{pmatrix}$$

Heats of Reaction and Temperature.

The first problem is to evaluate the heat of reaction at temperature T2 knowing the heat of reaction at temperature T1. This is found by the law of conservation of energy .

 $aA + bB \Leftrightarrow rR + sS$



 $\begin{array}{ll} - & a_i \mbox{ activity of component I} \\ Gas \mbox{ Phase, } a_i = \phi_i y_i P, \\ - & \phi_i = \mbox{ fugacity coefficient of i} \\ Liquid \mbox{ Phase, } a_i = \gamma_i \ x_i \ \exp[V_i \ (P-P_i^{\ s})/RT] \\ - & \gamma_i = \mbox{ activity coefficient of i} \end{array}$

Energy Balance with "dissected" enthalpies:

$$\dot{Q} - \dot{W}_{s} - F_{A0} \int_{T_{R}}^{T} \sum \Theta_{i} C_{ri} dT - F_{A0} X \left[\Delta H_{R}^{\circ} (T_{R}) + \int_{T_{R}}^{T} \Delta C_{r} dT \right] = 0$$

For constant or mean heat capacities:

$$\dot{Q} - \dot{W}_{s} - F_{A0} X \left[\Delta H_{R}^{\circ} \left(T_{R} \right) + \Delta \hat{C}_{P} \left(T - T_{R} \right) \right] = F_{A0} \sum \Theta_{i} \widetilde{C}_{Pi} \left(T - T_{i0} \right)$$

V_i =Partial Molar Volume of i

$$\Delta H_{r2} = -(H_2 - H_1)_{\text{reactants}} + \Delta H_{r1} + (H_2 - H_1)_{\text{products}}$$

$$\Delta H_{r2} = \Delta H_{r1} + \int_{T_1}^{T_2} \nabla C_p \, dT$$

$$\begin{split} C_{p\mathrm{A}} &= \alpha_{\mathrm{A}} + \beta_{\mathrm{A}}T + \gamma_{\mathrm{A}}T^{2} \\ C_{p\mathrm{R}} &= \alpha_{\mathrm{R}} + \beta_{\mathrm{R}}T + \gamma_{\mathrm{R}}T^{2} \\ C_{p\mathrm{S}} &= \alpha_{\mathrm{S}} + \beta_{\mathrm{S}}T + \gamma_{\mathrm{S}}T^{2} \end{split}$$

Knowing the heat of reaction at any one temperature as well as the specific heats of reactants and products in the temperature range concerned allows us to calculate the heat of reaction at any other temperature. From this the heat effects of the reaction can be found.

Equilibrium Constants from Thermodynamics

From the second law of thermodynamics ,equilibrium constants, hence equilibrium compositions of reacting systems, may be calculated. We must remember, however, that real systems do not necessarily achieve this conversion; therefore, the conversions calculated from thermodynamics are only suggested attainable values.

Equilibrium Conversion

The equilibrium composition, as governed by the equilibrium constant, changes with temperature, and from thermodynamics the rate of change is given by

$$\frac{d ln K_{P}}{dT} = \frac{\Delta H_{R}(T)}{RT^{2}} = \frac{\Delta H_{R}^{o}(T_{R}) + \Delta \hat{C}_{P}(T - T_{R})}{RT^{2}}$$

On integrating , we see how the equilibrium constant changes with temperature. When the heat of reaction ΔH , can be considered to be constant in the temperature interval, integration yields

$$K_{P}(T_{2}) = K_{P}(T_{1}) \exp\left[\frac{\Delta H_{R}^{0}(T_{R})}{R}\left(\frac{1}{T_{1}} - \frac{1}{T_{2}}\right)\right]$$

These expressions allow us to find the variation of the equilibrium constant, hence, equilibrium conversion, with temperature.



1. The thermodynamic equilibrium constant is unaffected by the pressure of the system, by the presence or absence of inerts, or by the kinetics of the reaction, but is affected by the temperature of the system.

2. Though the thermodynamic equilibrium constant is unaffected by pressure or inerts, the equilibrium concentration of materials and equilibrium conversion of reactants can be influenced by these variables.

3. K > 1 indicates that practically complete conversion may be possible and that the reaction can be considered to be irreversible. K < 1 indicates that reaction will not proceed to any appreciable extent.

4. For an increase in temperature, equilibrium conversion rises for endothermic reactions and drops for exothermic reactions.

5. For an increase in pressure in gas reactions, conversion rises when the number of moles decreases with reaction; conversion drops when the number of moles increases with reaction.

6. A decrease in inerts for all reactions acts in the way that an increase in pressure acts for gas reactions.

For an increase in pressure in gas reactions, conversion rises when the number of moles decreases with reaction; conversion drops when the number of moles increases with reaction. *Le Chatelier's Principle*



General Graphical Design Procedure

Temperature, composition, and reaction rate are uniquely related for any single homogeneous reaction, and this may be represented graphically in one of three ways, as shown in figure. The first of these, the composition-temperature plot, is the most convenient so we will use it throughout to represent data, to calculate reactor sizes, and to compare design alternatives.

For a given feed and using conversion of key component as a measure of the composition and extent of reaction, the XA versus T plot has the general shape shown in figure. This plot can be prepared either from a thermodynamically consistent rate expression for the reaction (the rate must be zero at equilibrium) or by interpolating from a given set of kinetic data in conjunction with thermodynamic information on the equilibrium. Naturally, the reliability of all the calculations and predictions that follow are directly dependent on the accuracy of this chart. Hence, it is imperative to obtain good kinetic data to construct this chart. The size of reactor required for a given duty and for a given temperature progression is found as follows:

1. Draw the reaction path on the XA versus T plot. This is the *operating line* for the operation.

- 2. Find the rates at various *XA* along this path.
- 3. Plot the l/(-rA) versus XA curve for this path.
- 4. Find the area under this curve. This gives V/FAo.

For exothermic reactions the procedure is illustrated for three paths: path AB for plug flow with an arbitrary temperature profile, path CD for nonisothermal plug flow with 50% recycle, and point E for mixed flow. Note that for mixed flow the operating line reduces to a single point. This procedure is quite general, applicable for any kinetics, any temperature progression, and any reactor type or any series of reactors. So, once the operating line is known, the reactor size can be found.



Optimum Temperature Progression

The optimum temperature progression is defined to be that progression which minimizes *VIFAO*, for a given conversion of reactant. This optimum may be an isothermal or it may be a changing temperature: in time for a batch reactor, along the length of a plug flow reactor, or from

stage to stage for a series of mixed flow reactors. It is important to know this progression because it is the ideal which we try to approach with a real system. It also allows us to estimate how far any real system departs from this ideal. The optimum temperature progression in any type of reactor is as follows: At any composition, it will always be at the temperature where the rate is a maximum. The locus of maximum rates is found by examining the r(T, C) curves .Figure shows this progression. For irreversible reactions, the rate always increases with temperature at any composition, so the highest rate occurs at the highest allowable temperature. This temperature is set by the materials of construction or by the possible increasing importance of side reactions.For endothermic reactions a rise in temperature increases both the equilibrium conversion and the rate of reaction. Thus, as with irreversible reactions, the highest allowable temperature should be used. For exothermic reversible reactions the situation is different, for here two opposing factors are at work when the temperature is raised-the rate of forward reaction speeds up but the maximum attainable conversion decreases. Thus, in general, a reversible exothermic reaction starts at a high temperature which decreases as conversion rises. Figure shows this progression, and its precise values are found by connecting the maxima of the different rate curves. This line is known as the *locus of maximum rates*.



Heat Effects

When the heat absorbed or released by reaction can markedly change the temperature of the reacting fluid, this factor must be accounted for in design. Thus we need to use both the material and energy balance expressions, First of all, if the reaction is exothermic and if heat transfer is unable to remove all of the liberated heat, then the temperature of the reacting fluid will rise as conversion rises. By similar arguments, for endothermic reactions the fluid cools as conversion rises. Let us relate this temperature change with extent of conversion. We start with adiabatic operations, later extending the treatment to account for heat interchange with the surroundings.

Adiabatic Operations

Consider either a mixed flow reactor, a plug flow reactor, or a section of plug flow reactor, in which the conversion is *XA* as shown in figure. Usually the limiting reactant, is selected as the basis for all material balance calculations. The same procedure is used here, with limiting reactant A taken as the basis.

 ΔH = heat of reaction per mole of entering reacting A, and at temperature Ti.

With TI as the reference temperature on which enthalpies and heats of reaction are based . The relation between temperature and conversion, as given by the energy balances is shown in figure. The resulting lines are straight for all practical purposes . This figure illustrates the shape of the energy balance curve for both endothermic and exothermic reactions for both mixed flow and plug flow reactors. This representation shows that whatever is the conversion at any point in the reactor, the temperature is at its corresponding value on the curve. For plug flow the fluid in the reactor moves progressively along the curve, for mixed flow the fluid immediately jumps to its final value on the curve. These are the adiabatic operating lines for the reactor. With increased

inerts Cp rises, and these curves become more closely vertical. A vertical line indicates that temperature is unchanged as reaction proceeds.

The size of reactor needed for a given duty is found as follows. For plug flow tabulate the rate for various XA along this adiabatic operating line, prepare the l/(-r,) versus XA plot and integrate. For mixed flow simply use the rate at the conditions within the reactor. Figure illustrates this procedure. The best adiabatic operations of a single plug flow reactor are found by shifting the operating line (changing the inlet temperature) to where the rates have the highest mean value. For endothermic operations this means starting at the highest allowable temperature. For exothermic reactions this means straddling the locus of maximum rates as shown in figure. A few trials will locate the best inlet temperature, that which minimizes VIFAO. For mixed flow the reactor should operate on the locus of maximum rates.

The best reactor type, that which minimizes VIF,,, is found directly from this X, versus T graph. If the rate progressively decreases with conversion, then use plug flow. This is the case for endothermic reactions and close to isothermal exothermic reactions. For exothermic reactions that have a large temperature rise during reaction, the rate rises from a very low value to a maximum at some intermediate XA, then falls. This behavior is characteristic of autocatalytic reactions, thus recycle operations are best.





For MFR

$$\frac{F_{ko}X_k}{-r_k}$$

V

Nonadiabatic Operations

For the adiabatic operating line of above figure to more closely approach the ideals of below figure ,we may want deliberately to introduce or remove heat from the reactor. In addition, there are heat losses to the surroundings to account for. Let us see how these forms of heat interchange modify the shape of the adiabatic operating line. Let Q be the total heat added to a reactor per mole of entering reactant A, and let this heat also include the losses to the surroundings.

The energy balance line rotates about TI. This change is shown in figure. Other modes of heat addition or removal yield corresponding shifts in the energy balance line. Using this modified operating line, the procedure for finding the reactor size and optimum operations follows directly from the discussion on adiabatic operations.











$$X_{\rm A} = \frac{{\bf C}_{\rm p}' \,\Delta T - {\bf Q}}{-\Delta {\bf H}_{r2}} = \begin{pmatrix} \text{net heat still needed after heat} \\ \frac{\text{transfer to raise feed to } T_2}{\text{heat released by reaction at } T_2} \end{pmatrix}$$

$$Q = UA \Delta T$$

Exothermic Reactions in Mixed Flow Reactors-A Special Problem

For exothermic reactions in mixed flow (or close to mixed flow) an interesting situation may develop in that more than one reactor composition may satisfy the governing material and energy balance equations. This means that we may not know which conversion level to expect. Van Heerden (1953, 1958) was the first to treat this problem. First, consider reactant fluid fed at a given rate (fixed r or V/FAO) to a mixed flow reactor. At each reactor temperature there will be some particular conversion which satisfies the material balance equation. At low temperature the rate is low so this conversion is low. At higher temperature the conversion rises and approaches the equilibrium. At a still higher temperature we enter the region of falling equilibrium so the conversion for given T will likewise fall.