

Reattori

①

o) Reattori isotermini: T uniforme

⇒ L'equazione di bilancio materiale è sufficiente

$$\left(\begin{array}{c} \text{Accumulo} \\ \text{specie } i \end{array} \right) = \left(\begin{array}{c} \text{flusso netto} \\ \text{entrante} \end{array} \right) + \left(\begin{array}{c} \text{Produz.} \end{array} \right)$$

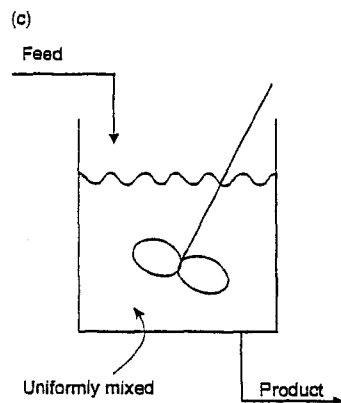
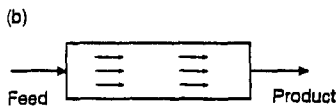
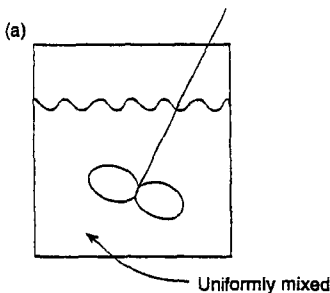


Fig. 2.1 Schematic representation of: (a) a batch reactor; (b) a plug flow reactor; (c) a continuous stirred tank reactor.

a) reattore discontinuo

reatt. perfettamente miscela
e intrinsec. non starz.

Piccole produzioni
⇒ campagne

b) reattore continuo a flusso a pistone (PFR)

reattore perfettamente
segregato, elevate produzioni
(fascio tubiero); buon controllo
termico. Ipotesi valida se
 $Re > 10^4$; $L/D > 50$

c) reattore continuo agitato (CSTR)

reattore perfettamente miscelato

($t_{mix} \ll t_{permanenza}$)

Buon controllo termico

Comfronto PFR & CST

②

CSTR ($Q = \text{cost}$)

$$Q(C_A^0 - C_A) = -r_A V$$

$$X_{AF} = \frac{C_A^0 - C_A}{C_A^0}$$

$$V = \frac{Q C_A^0 X_{AF}}{-r_A}$$

PFR ($Q_0 = \text{cost}$)

$$Q \frac{dC_A}{dz} = -r_A A_0$$

$$C_A = -C_A^0 X_A + C_A^0$$

$$C_A^0 Q \frac{dX_A}{dz} = -r_A A_0$$

$$V = \left[\int_0^{X_{AF}} \frac{dX_A}{-r_A} \right] C_A^0 Q$$

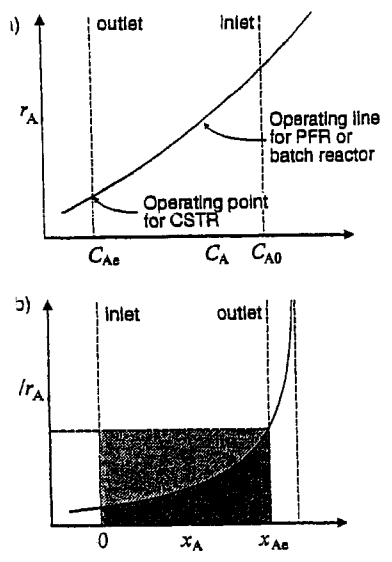


Fig. 3.2 (a) Rate versus concentration for a positive-order reaction. The PFR is represented by an operating line while the CSTR is represented by an operating point. (b) Inverse of reaction rate versus conversion for a positive-order reaction. The shaded area under the curve is proportional to the volume of a PFR while the total shaded area is proportional to the volume of a CSTR.

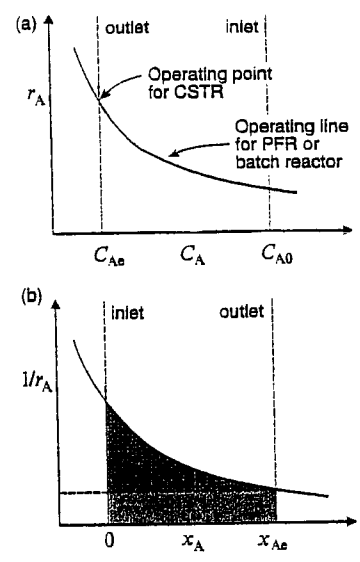


Fig. 3.3 (a) Rate versus concentration for a negative-order reaction. (b) Inverse of reaction rate versus conversion for a negative-order reaction. The total shaded area under the curve is proportional to the volume of a PFR while the lightly shaded area is proportional to the volume of a CSTR.

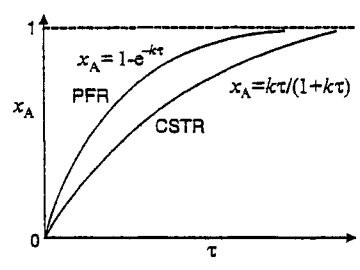


Fig. 3.1 Conversion versus residence time for a PFR and for a CSTR (first-order reaction kinetics).

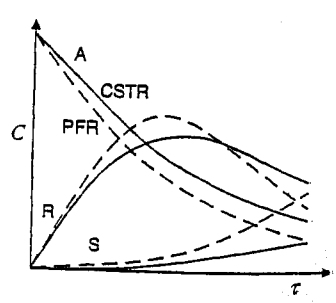


Fig. 4.6 Concentrations (not to scale) of species involved in a series reaction, $A \rightarrow R \rightarrow S$, in a PFR and a CSTR.

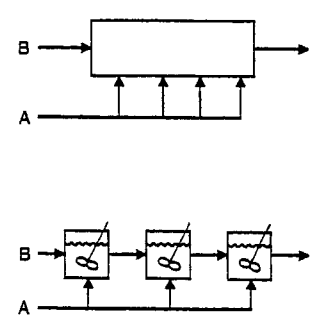
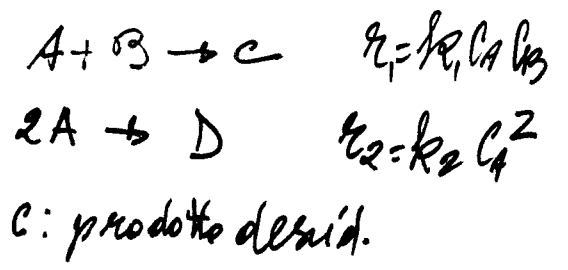


Fig. 4.4 Schematic representation of advantageous reactor systems for increasing selectivity when the desired reaction is bimolecular.



Reattori CSTR in serie

4

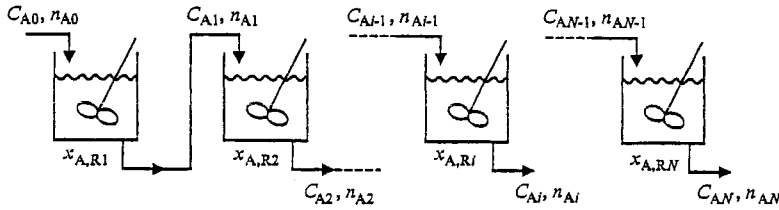


Fig. 3.7 Schematic showing N CSTRs in series.

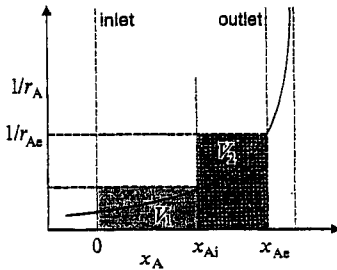


Fig. 3.5 Plot of inverse of reaction rate versus conversion showing that the volume of two CSTRs in series is less than that required of one CSTR alone but more than that of a PFR.

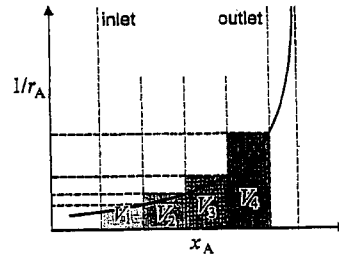


Fig. 3.6 Plot of inverse of reaction rate versus conversion for four CSTRs in series (all with approximately equal conversions).

Per una reaz. del I ordine e $Q = \text{cost}$:

$$C_{AN} = \frac{C_{A0}}{(1 + k_1 \tau / N)^N}$$

$$\tau = \frac{V_{\text{TOT}}}{Q} = \sum_{i=1}^N V_i / Q$$

per $N \rightarrow \infty$:

$$\lim_{N \rightarrow \infty} C_{AN} = \lim_{N \rightarrow \infty} \frac{C_{A0}}{(1 + k_1 \tau / N)^N} = C_{A0} \exp[-k_1 \tau]$$

Reattori in serie: volume ottimale

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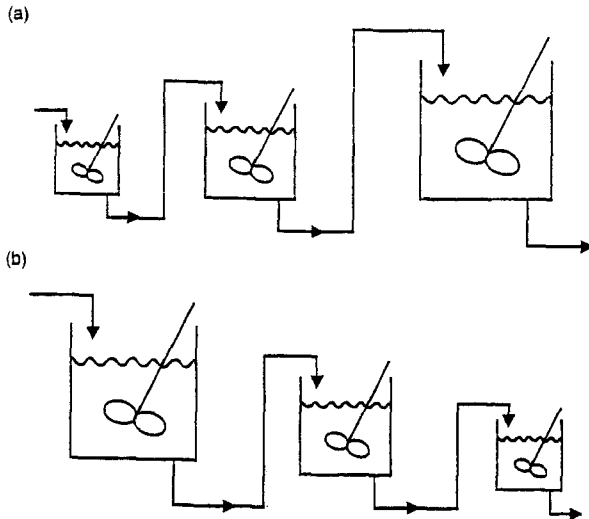
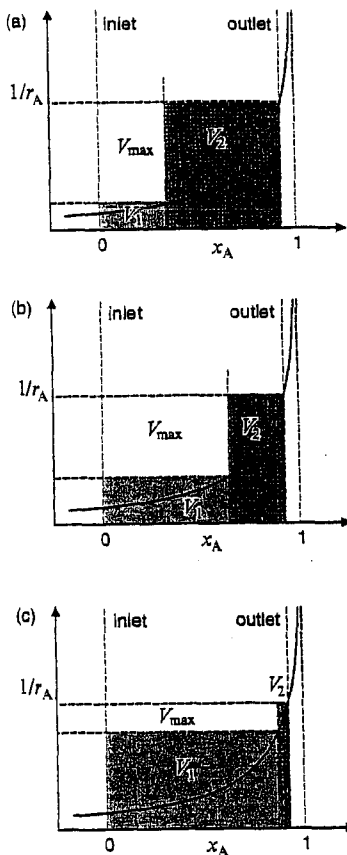


Fig. 3.8 (a) For reactions with positive-order kinetics small CSTRs should be used early to maximize conversion, (b) For reactions with negative-order kinetics large CSTRs should be used early to maximize conversion.



a) cinetica di ordine 1

$$V_1 = V_2$$

b) cinetica di ordine ≤ 1

$$V_1 > V_2$$

c) cinetica di ordine > 1

$$V_1 < V_2$$

Fig. 3.9 Plot of inverse of reaction rate versus conversion showing the volume of two CSTRs in series; (a) the first reactor is much smaller than the second; (b) the reactors are of similar size; (c) the second reactor is much smaller than the first.

Reattore PFR con Riciclo

(5.1)

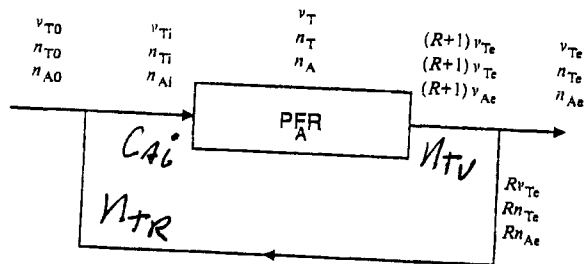


Fig. 3.10 Schematic of a recycle reactor.

v : portate volumetriche

n : portate molarie

$$\left(\text{Rapporto di Riciclo} \right) = \frac{(\text{moli riciclate})}{(\text{moli uscenti})} = \frac{N_{TR}}{N_{Te}} \quad (1)$$

$$\Rightarrow N_{TR} = R \cdot N_{Te}; \quad N_{TV} = (R+1) N_{Te}$$

$$\left(\text{Conversione per-passaggio} \right) = \frac{N_{Ai} - N_{Au}}{N_{Ai}} = X_{A} \quad (2)$$

$$\left(\text{Conversione globale} \right) = \frac{N_{A0} - N_{Ae}}{N_{A0}} = X_A \quad (3)$$

Dal bilancio materiale (in condizioni stazionarie) su A:

$$N_{Ai} = N_{A0} + R N_{Ae}; \quad N_{Ae} = N_{A0} (1 - X_A)$$

$$\Rightarrow N_{Ai} = N_{A0} (1 + R - R X_A) \quad (4)$$

$$Y_{0A} = \frac{N_{A0}(1+R - R X_A) - N_{A0}(1+R)(1-X_A)}{N_{A0}(1+R - R X_A)}$$

$$\Rightarrow Y_{0A} = \frac{X_A}{1+R - R X_A} \quad (5)$$

Segue allora:

i) per $R = 0 \Rightarrow Y_{0A} = X_A !!$

ii) per $R \rightarrow \infty \Rightarrow Y_{0A} = 0$

Cosa sta ad indicare la condizione ii)??

\Rightarrow il reattore PFR con un rapporto di riciclo grandissimo ($\gg 1$) si comporta come un reattore CSTR:

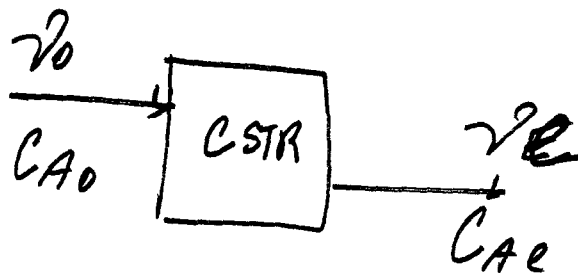


Fig. 1

Verifi chiomolo per un sistema semplice: (5.3)

a) reaz. di ordine 1;

b) la reazione non porta ad una variazione del numero di moli totali;

c) la densità della miscela rimane costante

Con queste ipotesi è facile verificare che:

$$v_{T0} = v_{Te} \quad ; \quad v_0 = v_e \quad (6)$$
$$v_i = (R+1)v_0$$

Il bilancio materiale indefinito per il PFR è:

$$\left\{ \begin{array}{l} \frac{(R+1)v_0}{A_0} \frac{dC_A}{dz} = -R_1 C_A \\ C_A = C_{Ai} \quad \text{per } z=0 \end{array} \right. \quad (7)$$

A_0 : sezione del reattore

$$C_{Ae} = C_{Ai} \exp \left[- \frac{V_R k_1}{(R+1) \gamma_0} \right] \quad (8)$$

(5.4)

$$(V_R = A_0 L)$$

Da cui segue:

$$V_R = \frac{(R+1) \gamma_0}{k_1} \ln \left(\frac{C_{Ai}}{C_{Ae}} \right) \quad (9)$$

Dal bilancio al nodo di miscelazione a monte del PFR si ha:

$$(R+1) \gamma_0 C_{Ai} = \gamma_0 C_{A0} + R \gamma_0 C_{Ae}$$

$$\Rightarrow C_{Ai} = \frac{C_{A0} + R C_{Ae}}{(R+1)} \quad (10)$$

Quindi:

$$(11) \quad \frac{C_{Ai}}{C_{Ae}} = \frac{C_{A0} + R C_{Ae}}{(R+1) C_{Ae}} = \frac{C_{A0} - C_{Ae}}{(R+1) C_{Ae}} + 1$$

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Per $R \gg 1$ ① è molto piccolo

$$\Rightarrow \ln \frac{C_{Ai}}{C_{Ae}} = \ln \left[1 + \frac{C_{A0} - C_{Ae}}{(R+1) C_{Ae}} \right] \approx \frac{C_{A0} - C_{Ae}}{(R+1) C_{A0}} \quad (12)$$

Quindi, sostituendo l'eq. (12) nella (9) si ottiene: (5.5)

$$V_R = \frac{V_0}{k_1} \frac{C_{AO} - C_{AE}}{C_{AE}} \quad (13)$$

ovvero:

$$C_{AE} = \frac{C_{AO}}{1 + Da} \quad (14)$$

$$Da = \frac{V_R}{V_0} k_1 = \tau k_1 ; \tau = V_R / V_0$$

Da = Damköhler number

L'eqn. (14) coincide con l'espressione di C_{AE} che si ottiene per il reattore di Fig. 1 (pg. 5.2).

Infatti dal bilancio materiale si ricava:

$$V_0 C_{AO} = V_0 C_{AE} + V_R \cdot k_1 C_{AE}$$

$$\Rightarrow C_{AE} = \frac{C_{AO}}{1 + Da} \quad (14.1)$$

Dimensionless Numbers

'A'	momentum transfer / momentum cond., (analog to Sh and Nu numbers)	$= k_m l / \eta$
'B'	momentum production/momentum cond., (analog to St and $f' / 2$ numbers)	$= F / \rho \eta u l$
Bi	Biot (heat transfer/thermal cond. of solid)	$= Nu(k_s/k_{s,i})$
Bo	Bodenstein (Pe number for mass)	$= u l / D$
β	adiabatic temperature rise potential	$= C(-\Delta H)/\rho c T$
Ca	Carberry	$= r l / C k_m$
Da _I	Damköhler number - I	$= r l / C u$
Da _{II}	Damköhler number - II	$= r l^2 / C D$
Da _{III}	Damköhler number - III	$= r (-\Delta H) l / \rho c T u$
Da _{IV}	Damköhler number - IV	$= r (-\Delta H) l^2 / k_t$
Da _V	Damköhler number - V	$= r (-\Delta H) l / h T$
$f' / 2$	Fanning friction factor	$= k_m / u$
'E'	momentum production/ conduction	$= F / \rho k_m u l^2$
Fr	Froud = $1/Fa = 1/\text{Fanning}$	$= u^2 / g l$
Ha	Hatta number	$= \sqrt{(kD)/k_g}$
j_D	Colburn factor for mass ($Sh Sc^{2/3}$)	$= (k_m l / D)(\eta/D)^{0.66}$
j_H	Colburn factor for heat ($St Pr^{2/3}$)	$= (h / \rho c u)(\eta/a)^{0.66}$
Le	Lewis number	$= a / D$
Nu	Nusselt number	$= h l / k_t$
Pe	Peclet number	$= u l / a$
Pr	Prandtl number	$= \eta / a = c\mu/k_t$

Re	Reynolds number	$= u l / \eta$
Sc	Schmidt number	$= \eta / D$
Sh	Sherwood number	$= k_m l / D$
St	Stanton number	$= h / \rho c u$
St'	Stanton number for mass	$= k_g / u$
We	Weber number	$= \rho u^2 l^2 / F$

A, B, E are unnamed numbers results of the systematization by László (1964).

The unnamed number C is now called the Carberry number, and D is identical with $Da_{IV} = Da_V$.

Exemplo

(5.7)



$$r = k_1 C_A ; \quad k_1 \tau = Da = 2$$

a) PFR

$$C_{Ae} = C_{A0} e^{-Da}$$

$$X_A = \frac{C_{A0} - C_{Ae}}{C_{A0}} = 1 - e^{-Da}$$

b) CSTR

$$X_A = \frac{Da}{1 + Da}$$

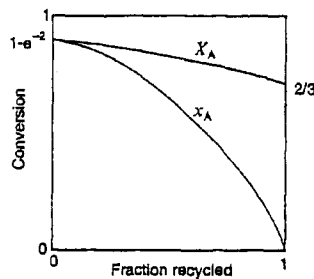


Fig. 3.11 Plot of conversion versus fraction recycled for a PFR with recycle. Both per-pass conversion, x_A and overall conversion, X_A , are shown.

Osservazioni sui reattori PFR e

(5.8)

Batch

-) Equaz. di progetto per un PFR ($Q = \text{cost}$)
 $\Rightarrow u_0 = \text{cost}; u_0 = Q/A_0$

$$u_0 \frac{dC_A}{dz} = -r_A r$$

Se facciamo $t = z/u_0$

$$\Rightarrow \frac{dC_A}{dt} = -r_A r \quad (15)$$

-) Equaz. di progetto per un reattore batch:
($V_R = \text{cost}$):

$$V_R \frac{dC_A}{dt} = +r_A r V_R$$

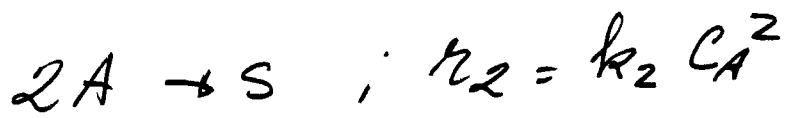
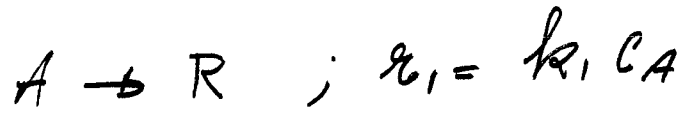
$$\Rightarrow \frac{dC_A}{dt} = r_A r \quad (16)$$

\Rightarrow nota che l'eqn. (15) è simile alla (16) !!!

Reazioni in Parallelo

(5.9)

1) Due reazioni di ordine differente



Supponiamo che il prodotto desiderato sia R, possiamo, allora, definire due selettività:

$$\left(\begin{array}{l} \text{selettività} \\ \text{locale o} \\ \text{istantanea} \end{array} \right)_{R/A} = \frac{r_1}{r_1 + r_2} = \phi_{R/A} \quad (17.1)$$

$$\left(\begin{array}{l} \text{Selettività} \\ \text{globale} \end{array} \right)_{R/A} = \frac{(\text{moli di R prodotte})}{(\text{moli di A consumate})} = (17.2)$$
$$= S_{R/A}$$

$$\phi_{R/A} = \frac{k_1 C_A}{k_1 C_A + k_2 C_A^2 \times 2}$$

$$\phi_{S/A} = \frac{k_2 C_A^2}{k_1 C_A + k_2 C_A^2 \times 2} \quad (18)$$

a) reattore PFR o batch

(5.1c)

$$\frac{dC_A}{dt} = - (k_1 C_A + k_2 C_A^2)$$

$$\frac{dC_R}{dt} = k_1 C_A ; \quad \frac{dC_S}{dt} = k_2 C_A^2 \quad (19)$$

$$\tau = \begin{cases} t: \text{ per reatt. batch.} \\ \frac{L}{u_0} = \frac{V}{Q} \text{ per PFR} \end{cases}$$

$$S_{R/A} = \frac{C_{R2} C_{R0}}{C_{A0} - C_{A2}} \quad \text{e} \quad S_{S/A} = \frac{C_{S2} C_{S0}}{C_{A0} - C_{A2}}$$

Dall'eqn. (19) si ottiene:

$$\frac{dC_R}{dC_A} = - \frac{k_1 C_A}{k_1 C_A + k_2 C_A^2} = - \Phi_{R/A}$$

$$\frac{dC_S}{dC_A} = - \frac{k_2 C_A^2}{k_1 C_A + k_2 C_A^2} = - \Phi_{S/A} \quad (20)$$

Case:

(5.11)

$$C_{Re} - C_{Ro} = \int_{C_{Ae}}^{C_{Ao}} \phi_{R/A} dC_A$$

$$C_{Se} - C_{So} = \int_{C_{Ae}}^{C_{Ao}} \phi_{S/A} dC_A \quad (21)$$

$$\int \{R/A, S/A\} = \int_{C_{Ae}}^{C_{Ao}} \phi_{\{R/A, S/A\}} dC_A \int \frac{1}{C_{Ao} - C_{Ae}} \quad (22)$$

b) reactore CSTR

$$\frac{Q}{V} (C_{Ao} - C_{Ae}) = k_1 C_{Ae} + k_2 C_{Ae}^2$$

$$\frac{Q}{V} (C_{Re} - C_{Ro}) = k_1 C_{Ae}$$

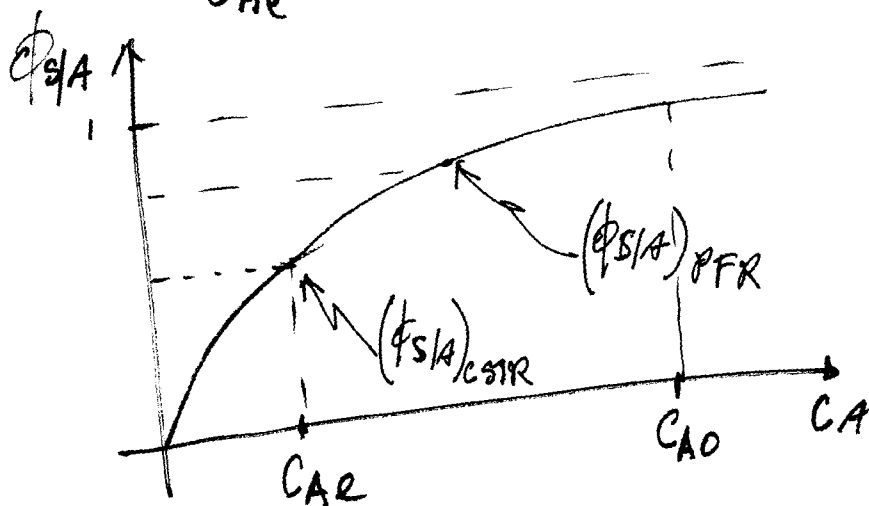
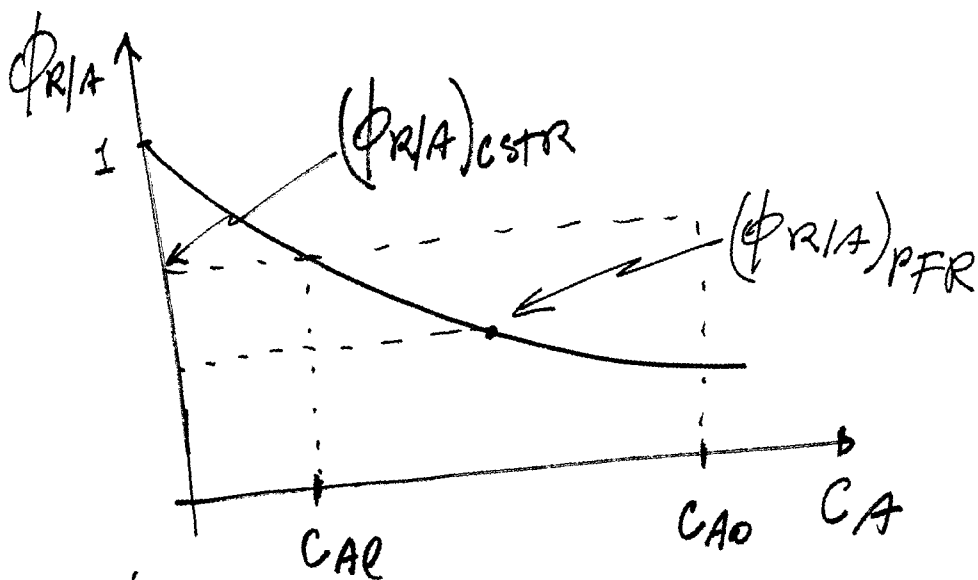
(23)

$$\frac{Q}{V} (C_{Se} - C_{So}) = k_2 C_{Ae}^2$$

$$S_{R/A} = \frac{C_{Re} - C_{Ro}}{C_{Ao} - C_{Ae}} ; S_{S/A} = \frac{C_{Se} - C_{So}}{C_{Ao} - C_{Ae}} \quad (24)$$

Nota che $S_{\{R/A; S/A\}} \equiv \Phi_{\{R/A; S/A\}} !!$

$$\Rightarrow S_{\{R/A; S/A\}} = \Phi_{\{R/A; S/A\}} \Big|_{C_{Ae}}$$

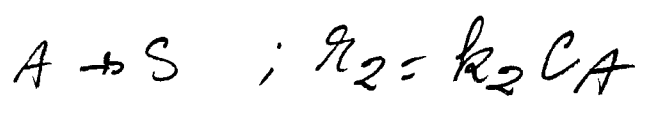
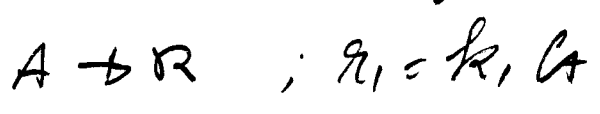


Dall'analisi segue :

i) se il prodotto desiderato è R
⇒ è meglio utilizzare un CSTR

ii) se il prodotto desiderato è S
⇒ è meglio utilizzare un PFR

•) Due reazioni di ugual ordine



$$\phi_{R/A} = \frac{k_1}{k_1 + k_2} ; \phi_{S/A} = \frac{k_2}{k_1 + k_2}$$

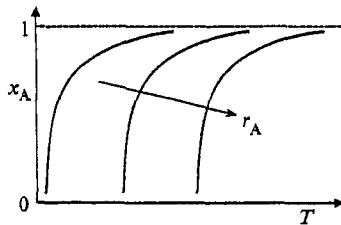
⇒ in questo caso la tipologia di reattore prescelto non influenza la ~~selettività~~ !!

Reazioni non isoterme

(6)

1) Reaz. irreversibili

$$r = k_0 \exp\left(-\frac{E_A}{RT}\right) C_{A0}(1-X_A)$$



linee a $r_A = \text{cost}$

Fig. 5.1 Lines of constant rate of reaction shown in conversion-temperature space for a first-order irreversible reaction.

2) Reaz. reversibili

$$r_A = k_0 \exp\left(-\frac{E_A}{RT}\right) C_{A0} \left[(1-X_A) - \frac{X_A}{K_{eq}} \right]$$

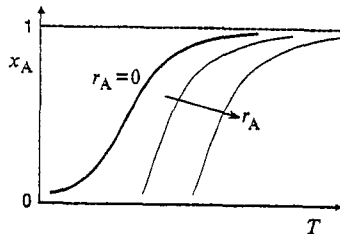


Fig. 5.3 Lines of constant rate of reaction shown in conversion-temperature space for a reversible endothermic reaction.

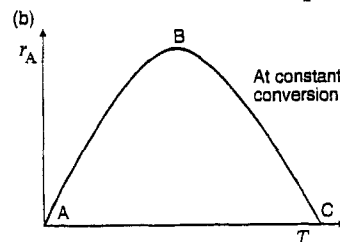
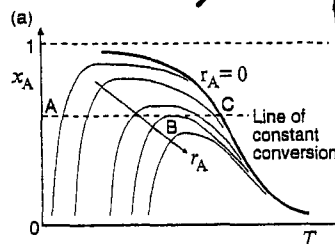


Fig. 5.4 (a) Lines of constant rate of reaction shown in conversion-temperature space for a reversible exothermic reaction. Also shown is a line at constant conversion. On this line the rate will be zero at point A, will reach a maximum at point B, and will be zero at point C. (b) Plot of rate versus temperature on line of constant conversion.