

Fig. 1
Batch reactor

If the volume of mixture does not change with the progress of the reaction, Equation (11) can be written as

$$(-r_i) = -\frac{1}{V} \frac{dn_i}{dt} = -\frac{dc_i}{dt} \quad (15)$$

where $(-r_i)$ is the rate of disappearance of the reactant i . For first order irreversible reaction, $(-r_i) = kc_i$, we get the so-called Wilhelmy equation:

$$-\frac{dc_i}{dt} = k c_i \quad (16)$$

The evolution of the concentration of the species i with time is then

$$c_i = c_{i0} e^{-kt} \quad (17)$$

CONTINUOUS STIRRED TANK REACTORS (CSTR)

This open system is sketched in fig. 2; the perfect mixing implies that the concentration is the same everywhere within the reactor and obviously the outlet concentration is equal to the concentration inside the tank. The residence time for a given molecule in the reactor may be comprised between 0 and ∞ .

The general unsteady state mass balance is

$$F_{iE} + v_i r V = F_i + \frac{dn_i}{dt} \quad (18)$$

flow in flow out
 “appearance” by accumulation
 chemical reaction

where $F_{iE} = Q_0 c_{iE}$ is the molar flow at the inlet, $F_i = Q c_i$ is the molar flow at the outlet, V the volume

of the reactant mixture within the reactor and the flowrate Q is generally a function of X , $Q = \beta Q_0(1 + \alpha X)$. If the feed has no converted reactants we can use the feed conditions as a reference state; Equation (6) can be written as

$$F_i = F_{iE} + v_i F_0 X^0 \quad (6')$$

which, combined with Equation (18), leads to

$$rV = F_o X^o + n_o \frac{dX^o}{dt} \quad (19)$$

where X^o is the extent of reaction measured at the outlet (or within the reactor) at time t .

Obviously if no inlet and outlet streams exist Equation (19) becomes Equation (12) (batch reactor).

In steady state operation ($\frac{dn_i}{dt} = 0$ or $\frac{dX^o}{dt} = 0$) we get the so-called design equation for a CSTR which relates the *volume* occupied by the mixture and the *extent of reaction*.

$$V = -\frac{F_o X^o}{r(X^o)} \quad (20)$$

or, in terms of the space time, $\tau(\tau = V/Q_0)$

$$\tau = \frac{c_0 X^0}{r(X^0)} \quad (21)$$

Equation (21) shows that a measure of the extent X° is sufficient to get the rate of reaction $r(X^\circ)$ in a given reactor, without any integration. For this reason this type of reactor is called a *differential reactor*.

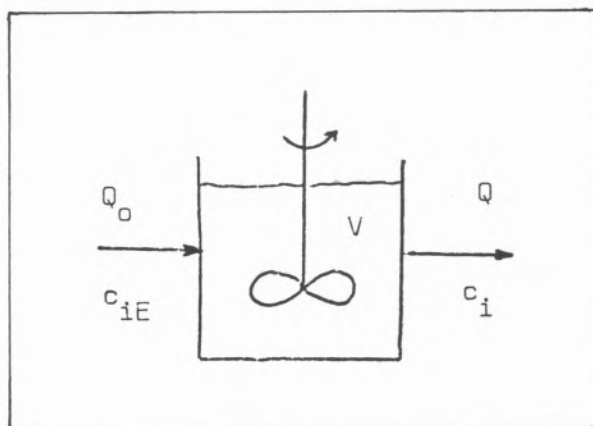


Fig. 2
CSTR

PLUG FLOW REACTOR

In this reactor there is no mixing between fluid elements, all the molecules staying in the reactor the same time (this can be viewed as a flat velocity profile in the reactor). The concentration of any species depends both on the position in the reactor, z (or \tilde{V} , where \tilde{V} is the volume correspondent to abscissa z , $\tilde{V} = \Omega z$ and Ω is the cross section area of the reactor) and time, t .

So we have to choose a differential element of volume (fig. 3) where the mass balance is applied; for the chemical species i we get

$$F_i \Big|_{\tilde{V}} + v_i r d\tilde{V} = F_i \Big|_{\tilde{V} + d\tilde{V}} + \frac{\partial c_i}{\partial t} d\tilde{V} \quad (22)$$

For steady state operation we get, combining Equations (6) and (22) and taking into account that

$$F_i \Big|_{\tilde{V} + d\tilde{V}} = F_i \Big|_{\tilde{V}} + \frac{\partial F_i}{\partial \tilde{V}} d\tilde{V}, \quad \frac{d\tilde{V}}{dX} = \frac{F_0}{r(X)} \quad (23)$$

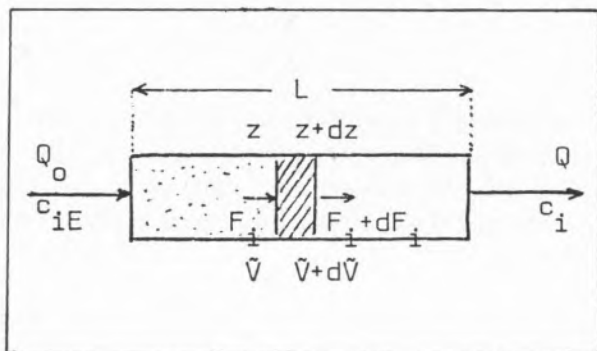


Fig. 3
Plug flow reactor

If we compare Equations (20) and (23) we can notice that the rate of reaction is changing from the inlet to the outlet; the design equation for this *integral reactor* is then

$$V = F_0 \int_0^{X^0} \frac{dX}{r(X)} \quad (24)$$

where $V = \Omega L$ and X^0 the extent of reaction at the outlet.

In terms of the space time $\tau = V/Q_0$ we get

$$\tau = C_0 \int_0^{X^0} \frac{dX}{r(X)} \quad (25)$$

We should also notice the analogy between the batch reactor and the plug flow reactor, displayed by Equations (12) and (23). i.e., the correspondence between the variable time, t (for batch reactors) and the space variable, \tilde{V} (for plug flow reactors) for reactions without volume change.

For unsteady-state operation and reactions without volume change, i.e., $Q = \text{constant}$, we get

$$Q \frac{\partial c_i}{\partial \tilde{V}} + \frac{\partial c_i}{\partial t} + (-r_i) = 0 \quad (26)$$

SOME REMARKS ON RATE OF REACTION AND MATERIAL BALANCES

The *mass balance equation for a component in a batch reactor*, Equation (15)

$$(-r_i) = -\frac{1}{V} \frac{dn_i}{dt} \quad (15)$$

is sometimes presented as a definition of rate of reaction [5, 6, 7, 8] which is erroneous and leads to a great number of misinterpretations.

I would like to recall that the validity of an equation (definition of rate) does not depend only on the correctness of the dimensions.

In fact, if we take the mass balance for a species i in a CSTR, we get, for steady state operation, from Equation (18)

$$(-r_i) = \frac{F_{iE} - F_i}{V} \quad (27)$$

or, if the reaction has no volume change,

$$(-r_i) = \frac{Q_0 (c_{iE} - c_i)}{V} \quad (27')$$

No book presents this equation as a definition of the rate of reaction, and it is not. It is simply a mass balance for a CSTR in steady state operation (reaction with no volume change). However it gives also the amount of substance of species i transformed per unit of time and unit of volume; the dimensions are correct but it is not a definition of rate.

In fact when the CSTR is in steady state operation $\frac{dn_i}{dt} = 0$, i.e., the amount of substance of i within the reactor is constant. However the reaction is taking place — the outlet concentration of a reactant is lower than the inlet concentration.

If Equation (15) were a definition of rate then we would get $(-r_i)=0$: Equation (15) is not a definition of rate and this confusion has led to a very funny derivation of the design equation for a CSTR operating in steady state [9]. This is a nice example which shows how, *starting with a wrong mass conservation equation*, some authors apparently arrive at the "good" result.

Those authors began with the wrong equation for CSTR, assuming no volume changes.

$$Qc_{iE} = Qc_i + V \frac{dc_i}{dt} \quad (28)$$

which is a *nonsteady state mass balance when no reaction exists* (compare with the correct formulation, Equation (18)).

Then the authors used this wrong equation (28) together with their definition of rate (which is, as we said before, the mass balance in another type of reactor), Equation (15)

$$(-r_i) = -\frac{dc_i}{dt} \quad (15)$$

and they got

$$Qc_{iE} = Qc_i + r_i V \quad (29)$$

which they assumed to be the correct equation for the CSTR in steady state operation, but it is not, since the sign of r_i is changed.

For first order irreversible reactions, $(-r_i) = kc_i$ and finally they obtain

$$Qc_{iE} = Qc_i + kc_i V \quad (30)$$

I believe that the point is that when those authors write

$$(-r_i) = -\frac{dc_i}{dt} = kc_i \quad (31)$$

they are mixing up a definition of rate, $(-r_i) = kc_i$, with a completely different thing, which is a mass balance in a batch reactor, $(-r_i) = -\frac{dc_i}{dt}$.

Also they mixed up unsteady state mass balance without reaction and steady state mass balance with reaction.

We hope this note can contribute to a fruitful discussion on these concepts, which have been so mis-treated (as well as some others, for instance, the concept of rate controlling step, etc.) and cause a lot of obscurity for students from the very beginning.

NOMENCLATURE

A_i	— chemical species
c_i	— concentration of species i (mole \times m ⁻³)
c_o	— total concentration of active species in the feed of an open reactor (mole \times m ⁻³)
F_i	— molar flow of species i (mole \times sec ⁻¹)
F_{io}	— molar flow of species i in a reference state
F_{iE}	— molar flow of species i at the inlet of an open reactor
F_o	— total molar flow of active species
k	— constant rate for first order reaction (sec ⁻¹)
M_i	— molar mass of species i (mass \times amount of substance ⁻¹)
n_i	— amount of substance of species i in a time t (mole)
n_{io}	— amount of substance of species i in a time $t=0$ (mole)
n_i	— amount of substance of inerts (mole)
n_o	— total amount of substance of active species at $t=0$ (mole)
Q	— flowrate (m ³ \times sec ⁻¹)
r	— rate of reaction (mole \times sec ⁻¹ \times m ⁻³)
r_i	— rate of reaction referred to the species i
t	— time variable (sec)
V	— volume of mixture in a reactor (m ³)
V_o	— initial volume of the mixture in a batch reactor
\bar{V}	— space variable in a plug flow reactor
X	— extent of reaction, dimensionless
X_i	— conversion, dimensionless
X^o	— extent of reaction at the outlet of an open reactor

GREEK SYMBOLS

α	— chemical expansion factor
β	— physical expansion factor
ξ	— thermodynamic extent of reaction (mole)
ξ_{\max}	— maximum thermodynamic extent of reaction (mole)
ν	— stoichiometric coefficients, dimensionless
τ	— space time (sec)
Ω	— cross section area (m ²)

The notation used in this paper was suggested by the Working Party of Chemical Reaction Engineering of the EFChE.

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