Chemical Reaction Engineering

Definitions and Rate of Reaction

A homogeneous reaction such as

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D} \tag{1}$$

can also be written as

$$v_1\mathrm{A}_1 + v_2\mathrm{A}_2 + v_3\mathrm{A}_3 + v_4\mathrm{A}_4 = 0 \tag{2}$$

where $v_1 = -|a|$, $v_2 = -|b|$, $v_3 = |c|$, and $v_4 = |d|$.

In summation form

$$\sum_{i=1}^{N} v_i\mathrm{A}_i = 0 \tag{3}$$

where the v_i's are the stoichiometric coefficients for the reactants and products, A_i.

The v_i's are positive for products and negative for reactants. The rate of reaction in a

given volume, V, is defined by

$$r = \frac{1}{-|a|}\frac{1}{V}\frac{dn_\mathrm{A}}{dt} = \frac{1}{-|b|}\frac{1}{V}\frac{dn_\mathrm{B}}{dt} = \frac{1}{|c|}\frac{1}{V}\frac{dn_\mathrm{C}}{dt} = \frac{1}{|d|}\frac{1}{V}\frac{dn_\mathrm{D}}{dt} = \frac{1}{v_i}\frac{1}{V}\frac{dn_{\mathrm{A}_i}}{dt} \tag{4}$$

where n_{A_i} refers to the number of moles of chemical species A_i. If the reaction vol-

ume is constant then concentrations can be used ($C_{\mathrm{A}_i} = \dfrac{n_{\mathrm{A}_i}}{V}$) and the rate can be

expressed as

$$r = \frac{1}{v_i}\frac{dC_{\mathrm{A}_i}}{dt} \tag{5}$$

Another important concept (which holds only for reactants, and not for products) is

that of fractional conversion. For reactant A, the fractional conversion, f_A, is defined

as

$$f_A = \frac{n_{A_0} - n_A}{n_{A_0}} \tag{6}$$

where n_{A_0} is the initial number of moles of reactant A. The fractional conversion runs from 0 for no reaction to 1 for complete reaction.

A related quantity (used for both reactants and products) is extent of reaction, ξ. The extent of reaction is defined as

$$\xi = \frac{n_i - n_{i_0}}{\nu_i}. \tag{7}$$

The extent of reaction does not depend on the chemical species chosen. The relationship between rate of reaction and extent of reaction is

$$\frac{d\xi}{dt} = \int_V r dV, \tag{8}$$

which for a steady-state reactor can be written

$$\dot{\xi} = \int_V r dV. \tag{9}$$

Rate Laws

Experimentally and from theoretical considerations, a reaction such as (1) follows a rate law such as

$$r = k_f (C_A)^n (C_B)^m - k_r (C_C)^q (C_D)^s \tag{10}$$

where k_f and k_r are the forward and reverse rate coefficients respectively. The exponents n, m, q, and s are known as the order of reaction with respect to the reactants A, B, C, and D. They are not necessarily the same as the stoichiometric coefficients a, b, c, and d. For an irreversible reaction the overall order of reaction is the sum of the exponents *e.g.*, if $n=1$, and $m=2$ then the forward reaction is first order in A, second order in B and overall third order. A reaction does not have to have an integral order (*i.e.*, $n,m, etc.$ do not have to be integers) but non-integral orders imply a complex

mechanism for the reaction.

As defined the rate laws are differential equations. For simple reaction orders and reactors the equations can be integrated.

Determination of kinetic parameters

The rate expressions given above can be used to determine the kinetic parameters from experimental data. Given an irreversible reaction ($k_r = 0$) such as:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}, \tag{11}$$

there are several possible approaches for determining the parameters n, m, and k_f (or k for short). If it is possible to maintain the concentrations uniform in space (with a stir-bar for example), one can begin with a large excess of reactant B (so that the concentration of B does not change appreciably during the reaction) and measure C_A versus time. The resultant simplified rate law will be

$$r = -\frac{1}{|a|}\frac{dC_\text{A}}{dt} = k'(C_\text{A})^n \text{ where } k' = (C_{\text{B}_0})^m \tag{12}$$

or

$$\ln r = \ln k' + n \ln C_\text{A}. \tag{13}$$

A log-log plot of r versus C_A will be a line of slope n and intercept $\ln k'$. The only difficulty with this procedure is that of taking numerical derivatives from experimental data. The experiment can be repeated with an excess of A and the values of m and k determined. This method is known as a differential method.

An integral method consists again of operating with an excess of all but one reactant and measuring C_A versus t (again the concentrations must be uniform throughout the reactor volume). The data are then plotted according to the form of the assumed rate law and the best fit is chosen as the correct form. For example, one would plot C_A vs. t to check for 0th order, $\ln C_\text{A}$ vs. t for 1st order, $1/C_\text{A}$ vs. t for 2nd order *etc.*

However, if the reaction has not proceeded very far, the data will typically plot as straight lines for all cases and engineering judgement must be used to distinguish which is the true reaction order.

Temperature Dependence

There is a slight dependence of concentration on temperature especially in gases, but the major temperature dependence of the reaction rate is contained in the rate coefficient k. It has been found empirically that the rate coefficient can be expressed as

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{14}$$

where k_0 is known as the pre-exponential or frequency factor, E_a is the activation energy, R is the universal gas constant, and T the absolute temperature. Equation (14) is known as the Arrhenius equation. For certain situations slightly more accurate expressions which have a stronger theoretical basis can be used, but the accuracy of experimental data rarely warrants more accurate models. The activation energy and pre-exponential can be determined by measurement of k at several temperatures (preferably by one of the above integral methods). Usually, the log of k is plotted versus $1/T$. The result is a line of slope $(-E_a)/R$ and an intercept of $\ln k_0$. A change in slope of the line usually indicates a change in mechanism (reaction pathway) for the reaction.

Chemical Reactors

We will concern ourselves only with isothermal (constant temperature) reactors. In a generalized reactor, fluid can be flowing into and out of the reactor, and the concentrations of the reactants can be changing with both position and time. A molecular balance on a differential element of fluid yields the following

$$\frac{\partial C_i}{\partial t} + \nabla \bullet (C_i \mathbf{u}) + \nabla \bullet \mathbf{J}_i \ = \ v_i r \tag{15}$$

where $\mathbf{u}$ is the velocity vector of the fluid and $\mathbf{J}_i$ is the flux vector of species i due to diffusion and related transport phenomena. For the three idealized chemical reactors, simplifying assumptions are made which makes the partial differential equation much easier to solve.

The batch reactor

A batch reactor is a reactor where all of the feeds are introduced at the beginning, the reactor is sealed, the reaction proceeds under spatially uniform conditions and the products are removed at the end of the reaction. There is no net fluid motion or flux throughout the reactor so Equation (15) reduces to

$$\frac{\partial C_i}{\partial t} \ = \ v_i r \tag{16}$$

which for species A and $|a| \ = \ 1$ can be rearranged and integrated as

$$t \ = \ n_{A_0} \int_0^{f_0} \frac{df_A}{Vr} \tag{17}$$

which is the general equation for the time required to reach a given conversion in a batch reactor. To integrate Equation (16) one must have an expression for the reaction rate as a function of conversion. For constant density Equation (17) simplifies to

$$t \ = \ C_{A_0} \int_0^{f_0} \frac{df_A}{r} \ = \ - \int_{C_{A_0}}^{C_A} \frac{dC_A}{r} \tag{18}$$

Integration of Equation (18) requires that one has an expression for the reaction rate as a function of the concentration. For example, for 0th order kinetics, r is equal to k, and Equation (18) integrates to

$$t = \frac{1}{k}(C_{A_0} - C_A) \tag{19}$$

or

$$C_{A_0} - C_A = kt. \tag{20}$$

Note that for a batch reactor, the composition is spatially uniform at any given time but it varies as a function of time.

Well-Mixed Reactor

A steady-state reactor in which the contents are well mixed (*i.e.* uniform in composition) is known as a well-mixed reactor, a perfectly-mixed reactor, a continuous stirred-tank reactor (CSTR), or a constant-flow stirred-tank reactor (CFSTR). In a CSTR the exit stream has the same composition and temperature as the interior of the reactor, and the feed is considered to be instantly mixed into the bulk of the reactor. Equation (15) simplifies to

$$\dot{n}_{i_{\text{exit}}} - \dot{n}_{i_0} = v_i r V \tag{21}$$

where $\dot{n}_{i_0}$ is the molar feed rate of species i and $\dot{n}_{i_{\text{exit}}}$ is the molar flow rate of species i at the exit. Make special note the derivation assumes that $\dot{n}_{i_0}$ and $\dot{n}_{i_{\text{exit}}}$ do not change with time.

The molar feed rate is related to the volumetric flow rate by $\dot{n}_{i_0} = C_{i_0} \dot{V}_0$ where $\dot{V}_0$ is the volumetric feed rate (*e.g.* [m^3/sec]).

For species A and $|a| = 1$, Equation (21) expressed in terms of fractional conversion is

$$f_A = \frac{V}{\dot{n}_{A_0}} r. \tag{22}$$

If the fluid density is constant Equation (22) simplifies to

$$\tau \equiv \frac{V}{\dot{V}_0} = \frac{C_{A_0} - C_A}{r} \qquad (23)$$

The 0 subscripts refer to the feed conditions and the non-0 subscripts refer to the exit (identical to the reactor) conditions. The residence time, τ, is the time required to flow one reactor volume of reactant through the reactor at the feed conditions. It corresponds roughly to the reaction time in the batch reactor.

As an example, let us plug in r for 0th order kinetics. Equation. (23) becomes

$$\tau = \frac{1}{k}(C_{A_0} - C_A) \qquad (24)$$

or

$$C_{A_0} - C_A = k\tau \qquad (25)$$

which shows the similarity between t for batch reactors and τ for CSTR's. However, you can't measure τ with a stopwatch. Do the expressions look the same for 1st order kinetics?

The Plug-Flow Reactor

The plug-flow reactor (PFR) is an idealized pipe in which there is perfect radial mixing and no axial mixing. The PFR can be considered either as a conveyor belt of batch reactors or as an infinite series of CSTR's connected in series. If one considers z as the direction along the length of the reactor, Equation (15) simplifies to

$$u_0 \frac{df_A}{dz} = \left(-\frac{1}{C_{A_0}}\right) v_A r. \qquad (26)$$

For the usual assumptions of species A and $|a| = 1$, Equation (26) simplifies to

$$\tau \equiv \frac{V}{\dot{V}_0} = C_{A_0} \int_0^{f_{A_{exit}}} \frac{df_A}{r} \qquad (27)$$

where the *exit* subscript refers to the conditions at the end of the reactor.

For constant density systems Equation (27) can be written as

$$\tau = -\int_{C_{A_0}}^{C_{A_{exit}}} \frac{dC_A}{r} \qquad (28)$$

Again, for 0th order kinetics, Equation (28) integrates to

$$C_{A_0} - C_{A_{exit}} = k\tau. \qquad (29)$$

As before, τ cannot be measured with a stopwatch.

Comparison among the various reactors.

It may at first glance appear that there is no difference among the various reactors in terms of performance. The batch reactor is obviously not suitable for continuous processing as the reactor must be filled at the beginning of a cycle and emptied at the end of a cycle. For 0th order reactions, identical feed conditions result in identically sized reactors. But for other than 0th order reactions, the CSTR and the PFR behave quite differently. For elementary reactions with orders larger than 0, the CSTR will always have to have a larger volume (larger τ) than a PFR for the same conversion. The reason for this is that the reaction in a CSTR proceeds at a constant rate because the concentration in the reactor is constant, whereas the rate in a PFR varies continuously from the inlet to the outlet. For any reaction system in which the reaction rate decreases monotonically with conversion, the PFR is superior. As an example consider a constant-density system where a first-order reaction is being carried out to 99% conversion. The residence time for the CSTR is (from Equation (23))

$$\tau = \frac{C_{A_0} - 0.01C_{A_0}}{0.01kC_{A_0}} = \frac{99}{k} \qquad (30)$$

which compares to the PFR case (from Eqation (28))

$$\tau = -\int_{C_{A_0}}^{C_{A_{exit}}} \frac{dC_A}{kC_A} = -\frac{1}{k}\ln(0.01) = \frac{4.6}{k} \qquad (31)$$

which is more than 20 times smaller than the CSTR.

In cases where the reaction rate does not monotonically decrease with conversion (e.g., autocatalytic reactions or multi-step or competing reactions) the best reactor can only be determined by examining the process in detail.