Important Concepts in Undergraduate
KINETICS AND REACTOR DESIGN COURSES

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Most chemical engineers will never *design* a reactor; they will, however, often be in a position to *specify* a reactor type, size, material, and design. Or, they will be asked to analyze an existing reactor to 1) fit a new reaction at a required production rate into the reactor, or 2) improve product quality, or 3) determine how to squeeze more production from the reactor without spending much money, adversely affecting the product, or blowing anything up.

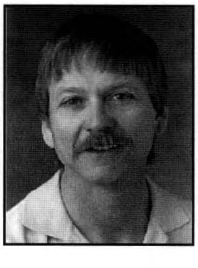
Most industrial chemical reactions are scaled up and put into production without detailed knowledge of the chemical kinetics and physical chemistries that affect the reactions. Quite often, reaction engineers must design using instinct, an understanding of how other, similar systems behave, and a proper application of the important concepts related to reactor design. We present a concise list of important kinetics, thermodynamics, reactor design concepts, rules-of-thumb, and applications that chemical engineering undergraduates need for entry-level industrial positions or to start graduate studies. Most are from texts widely used in undergraduate courses.[1-5] Although many other aspects of kinetics and reactor design are arguably as important for particular problems, our list should serve as a solid foundation for attacking the types of problems typically encountered by recent graduates.

Successfully teaching undergraduates to remember the points below is only half the battle. We want them to be able to *do* things with the information—analyze, design, specify, simulate, estimate, explain, etc. Felder and Brent[6] discussed the use of instructional objectives as a route to incorporating higher-level thinking skills into undergraduate courses. They differentiate between simply listing course topics in a syllabus and writing proactive objectives that teach students to apply the factual information to problems. In a forthcoming paper, we will use the list as a starting point for a set of instructional objectives for an undergraduate kinetics and reaction engineering course.

THERMODYNAMICS

1. Thermodynamics does not predict kinetics. A more negative, free-energy change (*i.e.,* a larger equilibrium constant) does *not* imply a faster reaction rate.
2. Catalysts can only increase the rate of processes that are thermodynamically favored; they cannot initiate reactions that are not thermodynamically feasible. A catalyst does not change ΔG, ΔH, or the equilibrium constant.
3. Three of the most important calculations for a reactor are

- *Adiabatic temperature:* if the heat released for an exothermic reaction is not removed, this temperature will be attained at complete conversion
- *Equilibrium* composition: no reactor can produce



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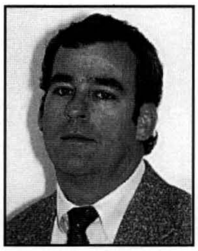

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yields of products beyond those predicted by equilibrium, but we can often choose which reactions to consider in the equilibrium calculations (see below).

- *Isothermal heat load:* heat must be removed (added) at the same rate at which it is generated (consumed) by reaction to keep a reactor isothermal.

4. As temperature increases for an exothermic reaction, equilibrium conversion decreases. For an endothermic reaction, equilibrium conversion increases.

KINETICS: RATE LAWS AND MECHANISMS

1. As long as a reaction is not limited by equilibrium or mass transfer, then longer reaction times, higher temperature, and more catalyst all increase conversion. A reaction that takes place in one hour at 200°C could take place in less than one second at 400°C. There are exceptions for certain ionic polymerization reactions (negative apparent activation energies).

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2. The rate of reaction is often the product of a rate constant, which *usually* increases exponentially with temperature (relatively few reaction rates decrease with temperature) and reactant concentrations raised to some power. The activation energy is the term in the exponential that determines how fast the rate increases with temperature.
3. Most chemical processes involve multiple reactions. Higher temperatures increase selectivity for reactions with higher activation energies. Higher reactant concentrations increase selectivity for reactions with higher reaction orders.
4. Local concentrations determine reaction rates (*e.g.,* if an insoluble solid product forms from a *pure* liquid reactant, the *concentration* of reactant does not change).
5. The steady-state approximation can be applied to a series of reaction steps by assuming that all reaction steps proceed at the same rate.
6. The rate-determining step in a series of reaction steps is the step furthest from equilibrium, and all the other steps are assumed to be in quasi-equilibrium.
7. For homogeneous reactions, rates are proportional to volume. In contrast, for heterogeneous reactions, rates are proportional to *surface area* (interphase area or catalyst surface area before deactivation).

DETERMINATION OF RATE PARAMETERS

1. A kinetic rate expression cannot reliably be extrapolated outside the concentration, conversion, or temperature regime where the data were obtained.
2. For an uncatalyzed reaction, the rate law (rate constant, activation energy, order of reaction) is an intrinsic property of the reaction and *not* the reactor. For a catalyzed reaction, the rate law changes when the catalyst is changed.
3. For a first-order, isothermal reaction, fractional conversion (X) depends on time but *not* the initial concentration: $X=1-e^{-kt}$. Thus, half life ($t_{1/2}$: the time for X=0.5) contains the same information as the rate constant (k). $t_{1/2}=(\ln 2)/k$
4. A reaction mechanism can be suggested, but *not* proven, by fitting data to a rate expression derived from a reaction sequence.
5. Rate parameters can be determined from experimental kinetic data (conversion versus time) in batch or plug flow reactors by the methods of integration and differentiation. The method of integration, which makes use of data in integrated form, is preferred over the method of differentiation (which exacerbates the impact of experimental error). If rates are determined, regression can be used to determine the rate parameters.

MATERIAL AND ENERGY BALANCES

1. Material balances on *individual* components are most useful for reactor design:

   Accumulation(±) = In(+) - Out(+) + Generation by reaction(±)

2. For systems with multiple reactions, at least as many material balances should be solved as the number of independent reactions, but a material balance can be solved for every component in the system.
3. The first law of thermodynamics applies to reactors, both closed and open systems, and is used to determine reactor temperature:

$$dU/dt = \sum_i (F_iH_i)_{in} - \sum_i (F_iH_i)_{out} + Q - W$$

where U is the total internal energy of the system, F_i is the molar flow rate into or out of the reactor of a given component, H_i is the enthalpy per mole of a given component at inlet or outlet conditions (the heat of reaction is contained in these terms), Q is the heat added per time, and W is the work done by the system per time.

4. For reactions where the heat of reaction is independent of temperature, the temperature change in an adiabatic reactor is proportional to the conversion.
5. In viscous reaction systems, heat developed by agitator work is often an important term in the energy balance.

IDEAL AND REAL REACTORS

1. Except for an ideal plug flow reactor (PFR), not all molecules spend the same amount of time in a flow reactor, and the residence time distribution can affect both rate and selectivity.
2. The material balances for batch reactors (BR) and ideal PFRs are mathematically equivalent; time in a BR is equivalent to residence time in an ideal PFR.
3. Material entering an ideal continuous stirred tank reactor (CSTR) undergoes a step change in concentration and temperature. An ideal CSTR operates at the exit temperature and concentrations.
4. Although all reaction occurs in an ideal CSTR at constant concentration and temperature, molecules flowing through both ideal and real CSTRs have a broad distribution of residence times. The residence time distribution of an ideal CSTR is exactly known.
5. CSTRs are often used in series to decrease the average residence time required for a given conversion (relative to a single, large CSTR) or to narrow the residence time distribution to one closer to that of a PFR.
6. Reactor temperature and concentrations can be sensitive to feed conditions. Reactor behavior is nonlinear because of the exponential Arrhenius rate constant, and reactors are the most likely equipment in a plant to explode.
7. For an exothermic reaction in a nonisothermal CSTR ($t_{feed} \neq t_{reactor}$), multiple steady states can exist (*i.e.,* the material and energy balances have multiple solutions). Multiple steady states are the result of energy feedback and the nonlinear behavior of the rate constant. This can result in an unstable operating condition leading to a quench (the reaction stops) or a runaway (the reactor overheats). Either situation can be dangerous and is to be avoided.
8. Reactor tank volume, and thus heat generated for a homogeneous exothermic reaction, increases as the cube of the reactor dimension, but heat transfer through the external surface increases only as the square, so temperature control is much more difficult for larger reactors without internal cooling coils. For exothermic reactions in jacketed reactors, an upper limit on reactor volume exists. If the reaction is carried out in a reactor larger than this, the heat cannot be removed as fast as it is generated without other means for cooling.
9. For gas-phase reactions, when the number of moles changes due to reaction, the concentration of reactants changes as a result, and flow rates and reaction rates also change.
10. For series reaction, the more important variable is space time or reaction time, and for positive-order kinetics, higher selectivity to an intermediate is obtained in a PFR than in a CSTR.

CATALYSIS

1. A catalyst usually lowers the activation energy for reaction.
2. The three most important attributes of a catalyst are selectivity, activity, and stability. Often, selectivity is the most important attribute.
3. All catalysts eventually deactivate, usually due to a loss of catalytic sites.
4. A catalyst does more than allow a system to achieve its most thermodynamically stable state; it can selectively accelerate a desired reaction. In the majority of industrial processes, the products are not those expected from equilibrium conversion for all reactions.
5. Many industrial reactions are limited by diffusion (mass- transfer limited). Concentration gradients external to a catalyst particle are determined from mass-transfer coefficient correlations. Concentration gradients within a porous catalyst particle are accounted for by an effectiveness factor.
6. If a catalyst increases the rate constant of a forward reaction, it also increases the rate constant of the reverse reaction (microscopic reversibility).

MIXING

1. Whenever reaction rates are of the same magnitude as, or faster than, the mixing rate in a stirred reactor, mixing will have a serious impact on results. Poor mixing is a primary source of variability in products made in batch reactors. The results for a reaction run in a poorly mixed CSTR may deviate strongly from those expected.
2. There is no single "correct" agitator type. Different agitator designs may perform equally well (or equally poorly) for a given application. Although some

detailed design calculations can be carried out, workable designs are often developed by trial and error.

3. Many reactions involve shear-sensitive materials, which severely limit the maximum mixing rate and make impeller and reactor design important. Mixing becomes the limiting factor (see item #1).

THE REAL WORLD

1. Real processes involve multiple reactions with multiple heat effects.
2. Most industrial chemical reactions are exothermic and heat transfer is often the most important design criteria.
3. Most bioreactions can only be carried out within a narrow temperature range. Generally, these reactions are relatively non-energetic and temperature control is easily achieved. Like other heterogeneous reactions, mass transfer is usually the most important design criteria.
4. The largest number of different chemical reactions (but not the largest quantity of material) are run in batch reactors, which are especially common in the pharmaceutical, biotech, polymer, and cosmetics industries. Sizes vary from a few liters to over 200,000 liters.
5. CSTRs are the next most common reactors, followed by PFRs and then by hybrid reactor types (fluidized beds, transport beds, trickle beds).
6. Continuous catalytic reactors are common in the petrochemical industries and, by far, the largest quantities of materials are produced in these types of reactors.

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ChE *letter to the editor*

Dear Editor:

In the recent paper titled "Permeation fo Gases in Asymmetric Ceramic Membranes" [*CEE*, **33**(1), p. 58 (1999)], by C. Finol and J. Coronas, there was an error in the equation used to calculate the Knudsen number. The correct equation for this clculation is:

$$\mathrm{Kn} = \frac{\lambda}{r}, \quad \lambda = \frac{16\,\mu}{5\,\pi P}\sqrt{\frac{\pi R T}{2\,M}}$$

where all the parameters employed in the equation were already defined in the mentioned article. We apologize for any trouble that this mistake may have caused.

Thank you for your consideration.

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