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Stoichiometry, Thermodynamics, Kinetics, Equilibrium, and Reaction Engineering

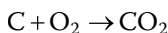
We will now cover several topics that affect some of the practical aspects of scaling up a chemical reaction and the integration of chemistry and chemical engineering.

Stoichiometry and Thermodynamics

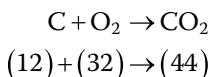
First, there is the general topic of *stoichiometry*. This is a word, derived from Greek, which describes the ratio and amounts of chemicals that react with each other in a chemical reaction. Here we must introduce some basic chemistry concepts. Every chemical has a different molecular structure, size, and weight as determined by its molecular content. In the early 1900s, a brilliant Russian chemist, Mendeleev, was able to organize the known chemical elements according to their atomic number, atomic weight, as well as by the nature of their chemical activity. By adding the number of protons in a molecule and the corresponding number of electrons that balance the charge, its atomic number is determined. For example, carbon, C in the table, has an atomic number of 6 and an atomic weight of 12. The table is grouped into types of elements with similar chemical behavior. For example, the “active” metals, such as lithium (Li), sodium (Na), and potassium (K), are in the same column. We see that the halogens fluorine (F), chlorine (Cl), and bromine (Br) are also grouped together. We see the “inert” gases such as helium (He), neon (Ne), argon (Ar), and krypton (Kr) also grouped together. Some gaseous molecules such as nitrogen, oxygen, chlorine, and bromine exist, at normal conditions, as *diatomic* molecules (N_2 , O_2 , Cl_2 , and Br_2 , respectively). In these cases the *molecular* weight will be twice the atomic weight. For example, the atomic weight of nitrogen is 2×14 (its atomic weight) or 28. Chlorine’s would be 71 or 2×35.5 . These distinctions are important as chemicals react according to their molecular weight, not their atomic weight. In some cases these are the same, but in these cases, they are not. A *mole* is the amount of a given chemical equal to its molecular weight,

expressed in any units that are consistent. For example, one gram mole of diatomic chlorine (Cl_2) is 71 g, one gram mole of diatomic hydrogen (H_2) is 2 g, and one gram mole of diatomic nitrogen (N_2) is 28 g. We could also express these as pound moles if we were working in the English system. A mole is a critical concept to understand as chemicals react as moles, not as weights. Weight is a secondary function, not the primary one. It is possible to produce diatomic molecules monoatomically but only under extreme and unusual conditions (Table 4.1).

Another very basic concept is that, when writing a chemical reaction equation, the molecular weights on both sides of the equation must “balance.” Consider the example of burning carbon in air as described by this equation:

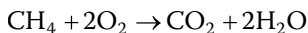


We have one carbon on each side of the equation and two oxygen molecules on both sides, so the equation “balances.” If we take into account the atomic or molecular weights of the molecules, this also balances:



A balanced equation does not mean that the chemical reaction we have described will happen. For example, if you expose a piece of charcoal (virtually all carbon, C) to air (21% oxygen, O_2), does it burn and produce carbon dioxide? No—it needs a “spark” or initiation of some sort.

As another example, many homes are heated by natural gas (primarily methane or CH_4) via a combustion process. We can show a simplified version of this reaction as



This reaction is exothermic, or “heat generating,” heating the air going through the furnace that then flows through the ductwork and heats the house. This chemical equation is balanced in the sense that it has the same number of carbon, hydrogen, and oxygen atoms on both sides, and so it will also balance from a weight standpoint. But does natural gas burn itself? No, your furnace or your gas-fired hot water heater, using natural gas as fuel, has a pilot light to initiate this reaction, and once done, the reaction continues. We will discuss the concept of initiating a reaction in the next section.

Another important point is that just because someone has written a balanced equation does not mean that it will *ever* occur. It just says that if it occurs, this is a possible outcome. For example, we know it is possible to burn natural gas and also produce carbon monoxide (an odorless, poisonous gas) by also burning natural gas:

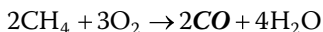


Table 4.1 Periodic table of elements.

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be															9 F	10 Ne
3	11 Na	12 Mg															17 Cl	18 Ar
4	19 K	20 Ca															35 Br	36 Kr
5	37 Rb	38 Sr															53 I	54 Xe
6	55 Cs	56 Ba															85 At	86 Rn
7	87 Fr	88 Ra															117 Uus	118 Uuo
			21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
			39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
			71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
			103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W
	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg

Source: Sandbh, https://en.wikipedia.org/wiki/Periodic_table. Used under CC BY-SA 4.0. © Wikipedia.

Note that in the second equation, the ratio of oxygen to methane is less (3/2) versus (2/1) in the first equation. It makes sense that less oxygen present is more likely to produce more carbon monoxide. That is why any home natural gas heater is always set to use more oxygen (air) than it needs. This wastes some energy but provides a safety factor for the homeowner. Any balanced chemical equation, by itself, does not tell us what *other* chemistry may be possible.

There are many exothermic reactions that require an initiating source of energy, after which they will sustain themselves. The technical term for energy content is enthalpy, usually with the letter H or ΔH , and this will be seen in many of these types of diagrams. We can picture this as shown in Figure 4.1. The difference between the reactants and products line is the overall energy released in the reaction (when the enthalpy or energy of the system drops, this indicates energy has been released, indicating an exothermic reaction).

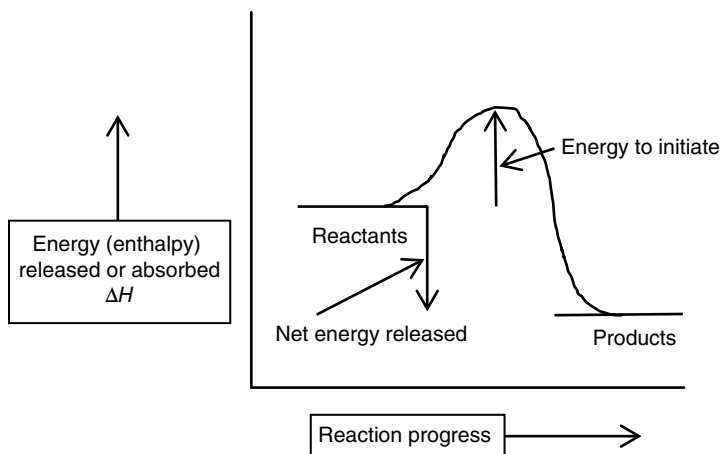


Figure 4.1 Activation energy and energy release for an exothermic reaction.

“Enthalpy” is the thermodynamic word we use to describe the energy content of a material. When enthalpy is reduced, the energy reduction is compensated for by a release of energy (what comes in must come out). The amount of this released energy is shown as the “net energy released” in Figure 4.1. The activation energy needed to initiate the reaction is also shown in the graph. This is the equivalent to the amount of energy required to be supplied by a spark plug or match in a combustion process.

If a reaction is highly exothermic and requires no initiation energy, there is a high probability that it is inherently unstable. An example would be peroxides or explosives, which are typically stored under refrigerated conditions to prevent decomposition. There would be little or no initiation required.

Let's look at the basic concepts of thermodynamics as applied to chemical reactions. As stated earlier, thermodynamics relates to the energy states and energy consumption or input of a chemical reaction system. Each element in the periodic table is assigned a net energy value of zero, reflecting its natural state. If we wish to change the form of an element, or have it react with some other element, this requires an energy change to move away from equilibrium (the natural state of an element). For example, coal (mostly carbon or "C") in the periodic table has a net energy of zero. If we burn it with air (oxygen), we produce carbon dioxide, or CO_2 , what is the net energy of this reaction? Instinctively, we know that energy is released in this reaction, but how much? The "heats of formation" (ΔH_f) of most chemical compounds have been previously measured and can be found in numerous literature references or on the web. The net energy release from a reaction is the net energy contained in the molecules on the right-hand side of the chemical reaction minus that of the molecules on the left. In this simple case, since carbon and oxygen are natural elements, their thermodynamic heat value (in their natural state as gases) is zero. We can look up the heat of formation of CO_2 and find that it is a *minus* 394 kJ/mole (-394 kJ/mole). The convention in thermodynamics is that minus indicates heat release, while a plus or positive sign indicates the need for energy input. So the burning of carbon is a large net generator of energy. The fact that this number is negative is also an indication that CO_2 is a more stable state than carbon and oxygen by themselves, so if there is a way to make this reaction happen, it is preferred. However, in many cases where there is a net energy release to a more preferred state, this doesn't happen automatically. It frequently takes an input of energy to *initiate* the reaction. That's what is done with a pilot light, a spark plug, or a match. Once the reaction is initiated, there is a sustained release of energy, which will sustain the reaction as long as the supply of materials is maintained. If there is a net release of energy during a chemical reaction, we refer to it as an *exothermic* reaction. On the other hand, if the calculation of the net energy between raw materials and products is positive (meaning we need a constant input of energy to sustain the reaction), it is referred to as *endothermic*. The energy consumed in an endothermic reaction must be taken into account when calculating cost and economics. The energy output of an exothermic reaction has the potential to be reused elsewhere in a process or chemical complex. However, exothermic reactions are also inherently less safe than endothermic reactions in the sense that they produce enough energy to sustain themselves. If this energy is less than a reaction system's ability to remove heat, a runaway chemical reaction can occur. We will discuss this further in Chapter 9 when we review the concept of reactive chemicals.

An important reminder, when calculating heats of reactions, is to make sure that the heats of formation (ΔH_f) are for the compounds as they are actually going to be used in the process. For example, if water (H_2O) is a reactant or

product of a reaction, it is important to specify whether the water is in solid, liquid, or vapor form as the heats of formation of water and steam (water vapor) are significantly different due to the energy required (44 kJ/mole) to boil liquid water and turn it into a gas. The freezing or melting of water also has an energy change associated with it.

A general comment about units at this point in time is necessary. We stated the energy release of the carbon dioxide reaction as a -394 kJ/mole. We could have stated this in terms of BTUs, calories, kcals, or any other number of unit forms. In today's global world with competing unit systems (British, metric, SI), it is *imperative* that any technical value be consistent, in terms of units used, with other technical values in the same system. There is no right or wrong about any choice, but it must be consistent or serious consequences in terms of chemical reactivity and process control can result. This is especially important within multinational corporations whose calculations, drawings, and memos may be generated in many different countries. This warning and caution applies to all future subjects to be discussed, as every chemical engineering unit operation will have activities expressed in terms of scientific units that can be expressed in multiple ways. Serious safety and design consequences can result if one part of a team within a multinational organization is thinking and working in English units and the other working and communicating in metric or SI units.

Kinetics, Equilibrium, and Reaction Engineering

Let's first review the concept of equilibrium. Any chemical reaction, even with a large negative energy output, does not necessarily go to completion, meaning that all of the reactants convert to all the desired products. When a chemical reaction system reaches equilibrium, it may look like the system is stagnant, but in actuality the forward and backward reactions are going on at the same rate. The point at which this happens for any chemical reaction system will be affected by temperature as well as the ratios of reactants, and for gases, the pressure as well. For an endothermic (heat consuming) reaction, the equilibrium will almost always move further to the right (i.e., more conversion) as the temperature of the reaction is increased. There also may be a point, if the temperature is increased, that the products may begin to decompose into other products, usually undesirable. For exothermic (heat releasing) reactions, there will be a temperature reached at which the equilibrium shifts back in favor of the reactants. The effects of pressure, when gases are involved in the reaction, will be discussed later.

Another pair of terms used in describing chemical reactions is *reversible* and *irreversible*. A reversible reaction would be one that is at equilibrium but can be reversed through a change in process conditions such as temperature or

pressure. A gas–gas reaction might be of this type. An irreversible reaction describes a reaction that cannot be reversed. This would normally be the case, where a liquid–liquid reaction produces a gas, which escapes and cannot be recaptured or recycled, or when such a reaction produces a solid, which precipitates out of solution and cannot be redissolved without significant change in process conditions.

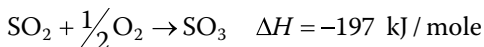
A French chemist Le Chatelier, in the 18th century, made a key observation about chemical reactions and that was that they reacted and changed to relieve “stress.” For example, if we raised the amount of one of the reactants on the left-hand side of a chemical reaction equation, and all else being equal, the system would react by trying to minimize the effect of this change by moving the reaction further to the right (product) side. The same would be true if we added additional product to the right-hand side of the reaction equation; the reaction would shift back to the left in an attempt to maintain equilibrium. This concept is very useful in a practical chemical engineering sense in that it provides options to push a reaction further to completion to improve conversions and yields as well as giving us a fundamental understanding of how a reaction system will qualitatively respond to changes in stoichiometry, pressure, and temperature.

An industrial example illustrating all of these points is the manufacture of sulfuric acid (H_2SO_4). The first step in the currently used contact process is the combustion of sulfur (usually produced from mining an underground deposit or possibly recovered from another process). The equation for this exothermic reaction (generating 297 kJ/mole—note the minus sign in front of the amount of energy meaning energy is released; an exothermic reaction) is



As we discussed earlier, this is a highly exothermic reaction but still needs a “spark” to ignite the sulfur. Sulfur does not start burning by itself. However, once ignited, the sulfur will burn continuously (producing SO_2 and releasing energy) until either the air or sulfur is withdrawn or consumed.

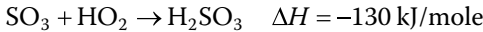
The second step in this process is to convert the SO_2 into SO_3 (sulfur trioxide) via the following reaction, also exothermic (but less so than the first reaction):



This reaction requires a catalyst, typically based on vanadium pentoxide (V_2O_5), and the reaction is a *heterogeneous* (two different phases) catalytic reaction in that the sulfur dioxide gas is passed over pellets of catalyst, similar to what happens in your car exhaust catalytic converter. In this reaction, as in many other exothermic reactions, the yield to SO_3 *decreases* as the temperature increases. In order to achieve complete conversion of SO_2 to SO_3 , the temperature must be reduced. In the actual process this is done in stages with

cooling water to eventually achieve nearly 100% conversion. This, unfortunately, reduces the amount of possible reuse of the heat generated during this reaction. This is a classic contradiction in many exothermic chemical reactions.

Finally, the sulfur trioxide is reacted and absorbed into water, producing sulfuric acid (H_2SO_4), in another exothermic reaction:



In practice, the SO_3 is absorbed (more about the unit operation of absorption later) into already produced concentrated sulfuric acid, producing what is known in this industry as “oleum,” or fuming 100% sulfuric acid, which is then later diluted to the concentration desired. Any unabsorbed/reacted SO_3 must be recycled into the previous reaction step.

A simple block flow sheet of how all of these reactions are linked together is shown in Figure 4.2.

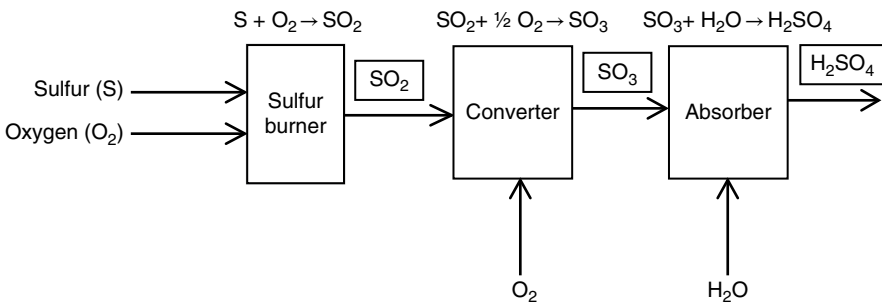


Figure 4.2 Manufacture of sulfuric acid via contact process.

The converter unit operation is far more complex than the other steps due to the equilibrium limitations discussed earlier. In order to achieve conversions above 97%, the reaction gases are cooled in a series of stages to push the equilibrium to the right. This wastes some of the exothermic reaction energy but is the only way to achieve a 100% conversion of SO_2 to SO_3 . A detailed diagram of this last process stage is shown in Figure 4.3. At the entrance to the converter step, the incoming SO_2 is preheated with the outlet gas from the final exit gas from the converter step to raise the inlet gas temperature to the final step to 730 K (or about 460°C). As the final reaction begins to occur, further heat is released, but now the equilibrium begins to limit the conversion. To overcome this, the reaction gases are cooled to shift the reaction equilibrium to the right. This is done in a series of stages, and the process design attempts to recover as much of the reaction-generated heat as possible. This is a traditional chemical engineering design compromise between kinetics and thermodynamics.

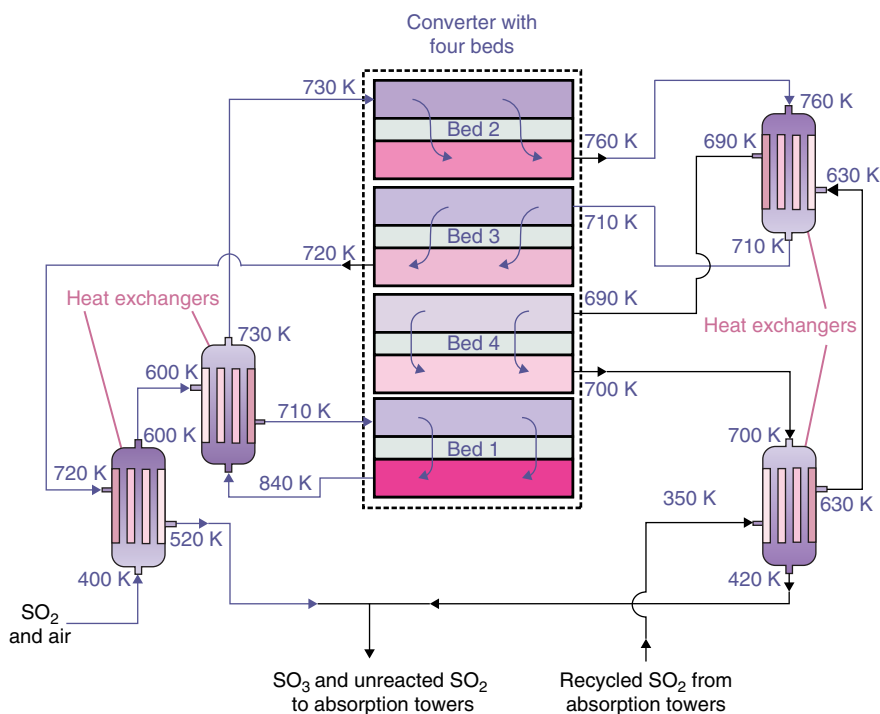


Figure 4.3 Contact sulfuric acid process converter step. Source: Reproduced with permission of Centre for Industry Education Collaboration.

All of these topics we have discussed can be grouped under the general heading of chemical and reaction thermodynamics. They help us understand how much energy is released or consumed during a reaction, which reactions are favored, and how to enhance a reaction system to produce the most desired products and minimize raw materials and energy consumption. Most of these properties are measured in laboratory experiments or obtained from reliable literature resources and are indispensable to chemical engineers in optimizing a full-scale chemical process.

Physical Properties Affecting Energy Aspects of a Reaction System

Since energy is absorbed or released in a reaction (as well as in other chemical process operations such as pumping and agitation), we must be able to calculate the effects of these energy changes on the system. Temperature change in

a system is determined primarily by its inherent ability to absorb heat. The physical property that determines a material's ability to absorb and contain heat is its *heat capacity*. This physical property has the units of energy/unit mass/unit time, frequently designated as C_p and expressed as BTU/#/°F or cal/g/°C. Water is used as a standard and has a heat capacity of 1 BTU/#/°F at room temperature. This property does change slightly with temperature but not to a significant degree. A material with a higher heat capacity will be able to absorb more heat without raising temperature, and conversely, one with a lower heat capacity will see a greater rise in temperature for the same thermal input. This is important when we are thinking about exothermic reactions and how to contain the heat that is generated.

Here are some examples of heat capacities of some common substances at 25°C.

Table 4.2 Heat capacities of common materials.

Water	1.0
Ethyl alcohol	0.6
Graphite	2.1
Oxygen	7.0
Nitrogen	7.0
Methane	8.4
Salt (NaCl)	12.2

Source: Average of publicly available information.

In general, the heat capacities of solids are greater than liquids, which in turn are greater, in general, than gases. In comparing ethanol and water in the previous list, we can say that water can absorb about 2/3 more energy per unit mass than ethanol. If we used water versus ethanol, say, in a heat exchanger, it would take roughly 1.5 times as much ethanol to contain the same amount of heat rise. The heat capacity will have a direct impact on how much energy a storage or reaction system can absorb or could release.

Two equally important properties in the sense of a material's ability to absorb heat are its heat of fusion/melting (ΔH_f), which is a measure of how much energy change is seen when a solid melts or freezes, and its heat of vaporization (ΔH_v), the amount of energy it takes to boil a material or, conversely, how much energy it releases when it condenses. In a chemical process design, this property can have a major impact on the ability of a system to maintain temperature at a constant point, especially if the boiling of a liquid is being used as a temperature control mechanism.

Another material property is its *thermal conductivity*, k . This property is usually expressed in units of energy/unit time/ ΔT , or BTU/h/°F (cal/s/°C). As opposed to heat capacity, which measures a material's ability to absorb heat, thermal conductivity measures how rapidly heat moves *through* a material at constant temperature. The most common place we think about this property is when we are evaluating how much insulation to install in a house to prevent heat loss, or in the chemical industry, how much insulation is installed around hot pipelines, reactor vessels, or buildings. In a chemical process, k will affect the rate at which heating or cooling can be supplied to a reaction vessel, as well as the capital cost of insulating equipment or piping and the resulting savings. Examples of thermal conductivity values are shown in Table 4.3.

Table 4.3 Thermal conductivities of materials.

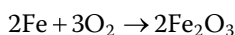
Hexane	0.08 BTU/h/°F
Water	0.34–0.38 BTU/h/°F
Sodium metal	45–50 BTU/h/°F
Hydrogen	0.10–0.12 BTU/h/°F
Methane	0.18–0.22 BTU/h/°F
Air	0.014–0.018 BTU/h/°F
Argon	0.01 BTU/h/°F
Carbon dioxide	0.025 BTU/h/°F

Source: Average of Public Source Information.

The extraordinarily high thermal conductivity of sodium metal is the primary reason it is used as a heat sink in commercial nuclear power plant reactors in the event of an emergency situation. The 40%+ lower thermal conductivity of argon versus air is the reason that argon-filled window panes are used in extreme northern climates to minimize heat loss in the winter.

Kinetics and Rates of Reaction

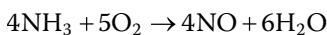
We have discussed aspects of a chemical reaction in terms of its net energy release and its ultimate equilibrium. But how fast does a reaction reach its endpoint or equilibrium? That is determined by a reaction's *kinetic rate constant*, usually designated by k . Its units are typically moles/s or moles/h for slow reactions. An example of a fast reaction rate would be the combustion of carbon (in the form of wood) in a forest fire versus a slow reaction rate as exhibited by the oxidation of iron to produce rust:



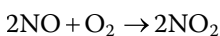
Both are harmful and are oxidations, but one occurs at a much faster rate than the other.

Very slow reaction rates, involving very slow degradation or decomposition of materials in storage, may not be readily obvious. It is always important to be alert to signs of such reactions, which may take the physical form, for example, of bulging drums or corrosion deposits external to a pipeline. It is also possible to ignore expiration dates on raw materials in storage or products in inventory for shipping.

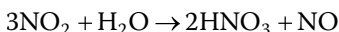
If there are multiple reactions occurring, each will have its own kinetic rate constant, and if the chemistries occurring in the reaction system have overlap in their raw materials and products, then the rate of each reaction will affect that of others. For example, consider the chemistry of nitrogen oxides. The first step in the manufacture of nitric acid is the oxidation of ammonia:



The NO produced is further oxidized to nitrogen dioxide (NO_2):



The nitrogen dioxide (NO_2) is then reacted and absorbed into water to produce nitric acid (HNO_3) via this reaction:



Since this last reaction produces NO in addition to the desired product, we need to find a way to recycle it back into the second reaction, which uses NO as a feedstock.

Kinetic rate constants tend to be *logarithmic* with temperature, that is, they increase exponentially with temperature. If we were to plot a kinetic rate constant as a function of temperature for almost any reaction, we would see a curve that looks similar to Figure 4.4.

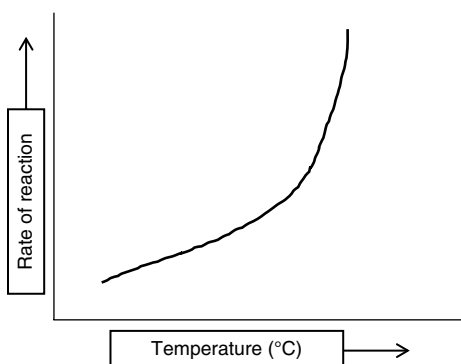


Figure 4.4 Rates of reactions accelerating as temperature increases.

If we were to plot this as a semilogarithmic plot, with the log of the kinetic rate constant plotted against the inverse of the absolute temperature, we would see a graph similar to that in Figure 4.5.

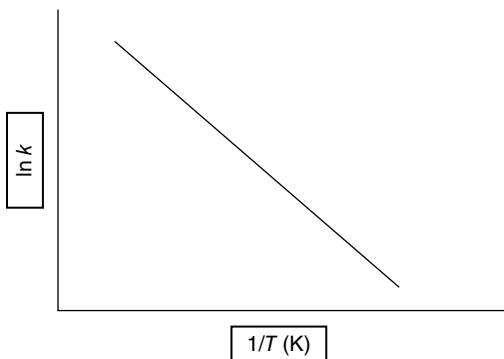


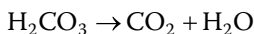
Figure 4.5 Rates of reaction versus temperature (semilog plot).

The slope of this line represents the activation energy (how much energy does it take to initiate the reaction?) for the reaction. The greater the slope, the higher the activation energy, meaning that it will take a greater amount of energy to initiate the reaction. Remember though, for an exothermic reaction, once it has been initiated, the reaction will continue without further energy input. For many systems, the slope of this line represents a doubling of reaction rates every 10°C. The greater the slope, the more sensitive the reaction rate is to temperature. The lower the slope, the less sensitivity and the less activation energy required to initiate the reaction.

When the chemistry is simple, the relationship between the stoichiometry and rate of reaction clear, we may see descriptions of reactions as being “zero,” “first,” or “second” order, referring to the response of reaction rate to the concentration of reactants, as opposed to temperature, which is still the dominant factor.

For example, if a reaction had involved $A + B$ to produce a single product C and the reaction rate, k , was proportional to the concentrations of both A and B , respectively, we would say the reaction was first order with respect to A , first order with respect to B , and second order overall. If the reaction was proportional to the concentration of A but proportional to the concentration of B to the second power (B^2), we would say that the reaction rate was first order with respect to A , second order with respect to B , and third order overall. There are some reactions that are zero order, meaning their rates respond only to temperature and not the concentrations of reactants. An example of this is the decomposition of carbonic acid (H_2CO_3) to carbon dioxide and

water (this is the loss of carbon dioxide in a soda pop, which loses its “fizz” when left out of the refrigerator too long):



For these basic reaction types, here is a list of plots, which would be a straight line:

Zero order: concentration versus time (t)

First order: concentration versus $1/t$

Second order: $1/\text{concentration}$ versus t

In qualitative graphical format, the approximate change in concentration of component A, decomposing according to these various rate laws, would look as shown in Figure 4.6.

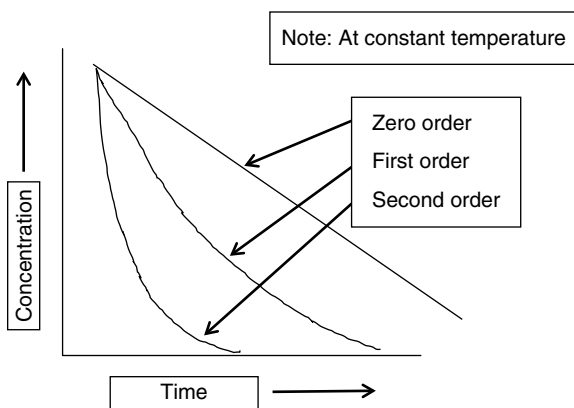


Figure 4.6 Concentration of reactants versus time as a function of reaction order.

The sharper the drop-off in initial reactant concentration, the higher order is the reaction and the higher is the reaction rate constant. These two factors combine into a reaction rate expression equivalent to

$$r = kA^aB^b$$

The sum of a and b is the order of the reaction. Remember that these exponents could be any kind of mathematical figure including square roots. None of these general descriptions describe in any way the detailed molecular interactions that are going on, only an empirical representation of the end result.

There is some standard terminology used in the chemical industry to describe some of the concepts we have discussed. Unfortunately, some of these terms are confused with each other and often used interchangeably. Here is the list suggested for your use:

Reaction Conversion. How much of the primary raw material fed into the reactor reacted to something (not necessarily the product of desire)

Reaction Yield. How much of the reacted raw material was converted to the product desired

Selectivity. Ratio of the desired product produced divided by all the products produced

High conversion, yield, and selectivity are always what we are striving for in a chemical reaction system unless we desire to produce a distribution of products.

Other terms seen in the description of reaction systems include “reversible” and “irreversible.” In the case of gas-to-gas reactions, a simple change of temperature or pressure can reverse a reaction since nothing is condensed or removed. An irreversible reaction would be one in which one of the products changes phase (vaporizes, precipitates, condenses).

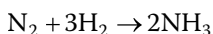
In summary, thermodynamics determines the *possibility of a reaction* and under what conditions, and kinetics determine the *rate at which it occurs*.

Catalysts

Catalysts are materials that do one of several things:

- 1) Allow a chemical reaction to occur under less severe conditions than normal or promote a reaction that does not occur at all at reasonable conditions. For example, the unburned hydrocarbons in your car’s gasoline engine need to be reduced to meet current EPA emission guidelines. These unburned hydrocarbons could have been eliminated through the use of some kind of an afterburner, but that would have added a great deal of cost and complexity to the car’s engine and exhaust systems. The catalytic converter currently installed in your car provides an “activating” catalytic surface, containing platinum, upon which the hydrocarbons and oxygen can react at the temperatures present in the exhaust stream. This unique catalytic surface provides a pathway for the unburned hydrocarbon to react with oxygen in the air to produce carbon dioxide and water. The net result is the same as any other hydrocarbon oxidation process to carbon dioxide and water but at a lower temperature.

Another example is the reaction of nitrogen (N_2) and hydrogen (H_2) to produce ammonia:



This reaction does not proceed to any measurable degree under room temperature and atmospheric pressure, but with an iron-based catalyst and

high pressure (>1000 psig), the reaction yields a 15–20% conversion to ammonia. The discovery of this catalyst, which indirectly feeds a large share of the world's population, was awarded the Nobel Prize in 1919. In these situations, what the catalyst is doing is lowering the “energy of activation” (or, more accurately, providing a lower energy pathway) to allow the chemistry to proceed (refer back to Figure 4.1).

- 2) Change the rate of a reaction. A catalyst can change the rate of a reaction significantly without necessarily changing the outcome of the reaction. If we mix hydrogen (H_2) and bromine (Br_2) together at room temperature, virtually nothing happens. If, however, we pass these gases over a platinum metal catalyst at 300K, the rate is enhanced many orders of magnitude. Note that the final product of the reaction does not change, only the rate.
- 3) Change the selectivity reactor conditions to produce one product in favor of another. An example here might be the reaction of ethylene oxide with ammonia to produce a class of materials we call ethanolamines. These compounds are extremely effective in absorbing carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from sour natural gas to produce “sweet” gas, which can then be put into the natural gas pipeline distribution system. The chemistry used to manufacture these amines is shown in Figure 4.7.

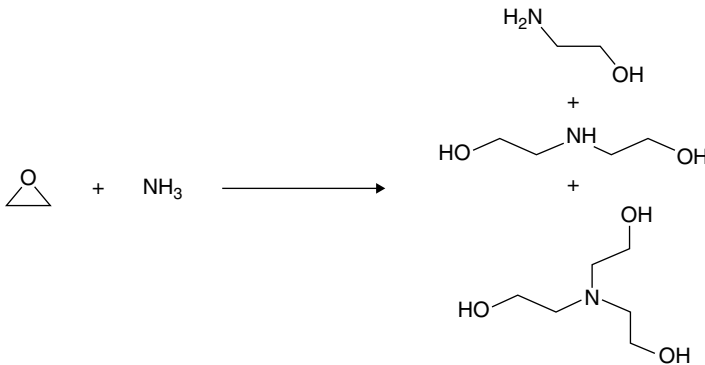


Figure 4.7 Reactions of ammonia with ethylene oxide to produce ethanol amines.

Each of these reactions has a different reaction rate constant and using a catalyst, which enhances one reaction over another, can allow a change in the product distribution according to customer and business needs.

Catalysts, in general, do not change the outcome of the reaction; they merely change the conditions under which the process operates by providing a different pathway for the chemistry to occur. They *can* change the favorability of one reaction over another when multiple reactions are possible.

There are two general classes of catalysts, homogeneous and heterogeneous. *Homogeneous* refers to a catalyst that is dissolved in the reaction solution. The most common of these are organometallic compounds. They are used in the manufacture of materials such as acetic acid and acetic anhydride and in some polymerization processes. They are typically very sensitive, and are deactivated, by water.

A *heterogeneous* catalyst is one that is in a separate phase from the primary reactants. The catalytic converter in our cars is such a catalyst since exhaust gases flow over a platinum metal coated on a ceramic substrate. Many gas phase polymerization processes use such a catalyst. Such a catalyst could also be a solid in suspension in a liquid–liquid or gas–liquid reaction.

Catalysts do not sustain their performance forever and can be poisoned by certain contaminants. Poisoning refers to a chemical reaction that renders the catalyst nonactive or coats its surface in a way that makes the catalytic surface not accessible to the reactants. There can also be physical degradation of solid catalysts at grain boundaries within their structures. The platinum catalyst in the automobile that converts unburned hydrocarbons into carbon dioxide and water is poisoned by lead (Pb), which is one of the reasons we now use unleaded gasoline in our cars. One of the first major operations in a gasoline refinery is the catalytic cracking of its primary feedstock into lighter, more valuable components. This catalyst is poisoned, though not irreversibly, by carbon and needs to be shut down and regenerated, by burning off the carbon, on a regular basis. Sulfur is also a well-known poison for many hydrocarbon reactions so the sulfur in high-sulfur oil or the hydrogen sulfide in natural gas must be removed prior to downstream processing.

Physical aspects of a chemical reaction can significantly affect the equilibrium of a reaction. These types of reactions are normally *irreversible*:

- 1) Two (or more) liquids or a gas–liquid reaction that produces a solid precipitating out of solution
- 2) Oxidation reactions, that is, combustion, such as the burning of a fuel

When there is no change in phase, it is probable that the reversibility concepts we have reviewed need to be considered.

Summary

The fundamentals of chemistry, kinetics, and physical properties are key aspects that determine many of the design parameters of a chemical reaction system. It is easy to overlook the impact of changes in properties, especially with respect to how they change with temperature. This especially applies to reaction rates and gas volumes.

Coffee Brewing: Is Kinetics Relevant?

Let's now look at the coffee brewing process from a materials, reaction, and chemical kinetics point of view. As we have discussed, reaction rates are, in general, a strong function of temperature. We all recognize that "fresh" coffee tastes better than "old" or "stale" coffee, possibly sitting on a hot plate for a long time. Why is that? Coffee, as well as any other food product, is a composite of chemicals. We drink coffee both because of its taste and its ability to keep us awake. How does it do this? It contains caffeine, a chemical, which for most people, is a stimulant. But how does the coffee taste after sitting on a hot plate for a few hours? Is it the same? Unless someone is very desperate for caffeine, the answer is "no" and new pot will be brewed. What is going on is a chemical degradation of some of the ingredients of the coffee into a class of chemical compounds known as aldehydes and ketones. The longer the coffee sits on the hot plate, the greater the extent of this chemical degradation. Since most people have no interest in cold coffee, the temperature of the hot plate is not reduced and the chemical degradation continues, and the degradation (a chemical reaction!) increases rapidly with temperature. As the coffee sitting on the hot plate evaporates, the concentrations of the materials that are degrading increases, raising the chemical degradation rate due to concentration increase.

What are some approaches that you have seen used to minimize this issue? There are coffee carafes that are basically heavily insulated vacuum containers that do not sit on a hot plate. Is degradation still occurring? Yes, but the concentration of the degrading solution is minimized due to the lack of evaporation and degradations (chemical reactions) are proportional to concentration. We now have individual coffee brewing systems that only brew one cup at a time with nothing left to degrade in taste or quality. Since these machines brew coffee so rapidly, the inconvenience of having to wait less than a minute for a fresh cup of coffee is tolerable versus the alternative of being able to pour a new cup instantaneously, but that cup tasting far worse.

When you buy coffee, what kind (not brand) of coffee do you buy? Instant? Freeze dried? Ground? Beans? Ground in the store? Stored at home and then ground? Where stored? Freezer? Refrigerator? Normal cabinet? What is the difference, from a chemical kinetics standpoint, between them? Why do they taste differently?

Do we envision coffee brewing in our homes as a reversible or irreversible process? Though the primary step of brewing is not a chemical reaction (it is a leaching process, to be discussed later), do we think of this process as reversible? In other words, do we think that if the coffee does not taste the way we prefer it, we can easily reverse the process and start all over again? We would have to evaporate the coffee, dry the grounds, etc. essentially producing a recycled version of instant coffee!

(Continued)

(Continued)

When we decide to brew a cup of coffee, we have a “recipe” in mind (i.e., “stoichiometry”). We may like weak- or strong-tasting coffee. Unsuspected impurities in any of the raw materials (coffee, water, additives) can cause health problems. We may care about an added flavor or caffeine levels. In any of our home brewing systems, we have a choice of coffee serving size, and given a fixed amount of coffee dumped into a filter or in a “pod,” this is decided by how much water is used and at what temperature it is delivered. All of these individual choices will affect the outcome of the “process” we are running (brewing coffee), just as in a real chemical process. The water that is used in the brewing process can come from any number of sources, including tap water (whose quality and impurities vary all over the world), “spring” water purchased in a store (what spring?), distilled water, or water that has been run through an attachment to a faucet to remove “impurities.” The variation in these raw materials will affect the final product no differently than changing raw materials entering a chemical process. Just as a chemical plant’s customers desire a consistent product, according to the specifications agreed upon in a contract, produced from whatever raw materials the supplier uses, the coffee drinker desires the same taste in their final cup they drink.

So we have a compromise, not uncommon in reaction systems, between our desire to have product at a high temperature (hot coffee) and parallel reactions that may degrade the product if left at a high temperature for an extended time. More as we go along.

Discussion Questions

- 1 Is the detailed stoichiometry of your process known? Are there intermediate steps in the reactions, the study and understanding of which could improve process efficiency or product quality? Does everyone involved in the operation of a process plant have a basic understanding of the process chemistry?
- 2 Are the consequences of poor stoichiometry control well understood? From a quality standpoint? From a reactive chemical standpoint? From a process control standpoint?
- 3 Are the kinetics and rate constants of the reactions being run understood? If not, what is the basis for deciding on a reaction “recipe” or sequence? Have deviations from this “recipe” ever given signs of a problem (quality, safety)?
- 4 Thinking about your current commercial processes—which ones experienced start up problem due to a lack of understanding of process chemistry? Is improving this understanding part of your organization’s R&D program? If not, why not?

- 5 Are the thermodynamics of all your process steps understood? Which reactions are exothermic? Endothermic? If exothermic, is the crossover point, where the reaction rate generates more heat than is possible to remove, known? What prevention steps have been taken? How many layers of protection are needed? How was this decided?
- 6 Are all the basic physical properties of the materials you are using and generating (heat capacity, density, thermal conductivity, viscosity) known? Is their sensitivity to temperature and pressure known and applied in how the process is run? How could changes in raw materials fed into a reaction change these values during a reaction or for the products produced?
- 7 Are the equilibrium constants for the reactions known? Is it well understood how temperature and pressure changes can affect these values? Are these effects important? If so, how is the information used? If not, why not? How are the processes run and controlled without this information? How are decisions made with regard to changing operational conditions without this information?
- 8 When chemists, chemical engineers, analytical chemists, and process managers discuss chemical reactions, do they all use the same “dictionary”? What are the consequences if terms such as conversion, yield, and selectivity are misinterpreted in defining process control and process measurements?
- 9 Are catalysts used in your process? How well is their exact role in the chemistry understood? If it were better understood, what be some advantages in terms of quality? Productivity? Are mechanisms for poisoning or reducing effectiveness of catalysts understood? How are decisions made regarding when and how to either regenerate or replace a catalyst? Science or history?
- 10 Are gases used as raw materials or produced as intermediates or products? If so, are their effects on physical properties within a reactor understood? Do these effects change with process conditions or within a process cycle? Is it known whether gases used or formed are ideal? If not, are the relationships between pressure, temperature, and the number of moles of gas understood? What are the consequences if this information is not known?

Review Questions (Answers in Appendix with Explanations)

- 1 Stoichiometry determines ratios and kinetics determine:
 - A Kinetic energy
 - B Rate
 - C Energy release
 - D Ratio of rate to energy
- 2 Competitive reactions refer to:
 - A Reactions that are also practiced by a competitor
 - B Multiple reactions that may occur from the same starting raw materials
 - C One or more reactions that compete for raw materials based on price
 - D One reaction that runs right after another
- 3 The same raw materials, combined in the same ratio, can produce differing products:
 - A Yes
 - B No
 - C Sometimes, depending upon value of the products produced
 - D Yes, depending upon reaction conditions
- 4 Thermodynamics of a chemical reaction determine:
 - A The amount of energy released or consumed (needed) if the reaction occurs
 - B Under what circumstances a reaction will occur
 - C Time delay in a reaction starting
 - D How dynamic the reaction is
- 5 A kinetic rate constant:
 - A Is affected by temperature
 - B Is not affected by stoichiometry
 - C Is not affected by altitude
 - D Is affected by size of reaction equipment
- 6 The rate of a chemical reaction:
 - A Can be changed by changing pressure and/or temperature
 - B Will be affected by stoichiometry and ratios of reactants
 - C Will be affected by how fast products are removed
 - D All of the above

- 7 The rate of a chemical reaction is typically _____ with temperature:
A __ Linear
B __ Quadratic
C __ Logarithmic
D __ Semilogarithmic
- 8 Conversion of a chemical reaction will always be:
A __ The same or greater than yield of the same reaction
B __ Less than the selectivity to multiple reaction products
C __ Unaffected by the kinetic rate constant
D __ Different from the selectivity of a reaction
- 9 If a calculated heat of a particular reaction is negative (exothermic), it means:
A __ We don't want the reaction to occur
B __ The heat calculation is incorrect as it should be a positive number
C __ Energy is released if the reaction occurs
D __ Energy is required to sustain the reaction
- 10 If a calculated heat of a particular reaction is positive (endothermic), it means:
A __ It is good for the reaction to occur
B __ Constant energy input is required to sustain the reaction
C __ The reaction will never stop once started
D __ All of the above
- 11 Equilibrium in a chemical reaction system can be affected by:
A __ Ratio of reactants
B __ Temperature
C __ Number of possible reactions
D __ All of the above
- 12 The equilibrium constant K_e refers to:
A __ The ratios of reactants to products
B __ The ratio of reactants to products under certain conditions
C __ The ratio of products to reactants
D __ The ratio of products to reactants under specific conditions
- 13 A change in pressure will most likely affect reaction equilibrium for:
A __ Liquid–liquid reactions
B __ Liquid–solid reactions
C __ Gas–gas, gas–liquid, or gas–solid reactions
D __ Reactions using a gas whose price is increasing

- 14 The total time for a reaction to go to completion is affected by all of these except:
- A __ Kinetic rate constants
 - B __ Rate of heat removal in an exothermic reaction
 - C __ Stoichiometry of reactants
 - D __ Size of the reactor
- 15 Catalysts can do these things:
- A __ Lower the temperature or severity of conditions of a reaction
 - B __ Initiate an exothermic reaction
 - C __ Favor one product over another in a reaction system
 - D __ All of the above
- 16 The loss of catalyst effectiveness over time is most likely due to:
- A __ Change in stoichiometry in the feed
 - B __ Poisoning or contamination
 - C __ Change in catalyst vendors
 - D __ The introduction of arsenic into the feed

Additional Resources

- Fontes, E. (2015) "Modeling Chemical Reactors" *Chemical Engineering Progress*, 2, pp. 46–49.
- Loffler, D. (2001) "Avoiding Pitfalls in Evaluating Catalyst Performance" *Chemical Engineering Progress*, 7, pp. 74–77.
- Milne, D.; Glasser, D.; Hildebrandt, D. and Hausberger, B. (2006) "Graphically Assess a Reactor's Characteristics" *Chemical Engineering Progress*, 3, pp. 46–51.
- Worstell, J. (2001) "Don't Act Like a Novice about Reaction Engineering" *Chemical Engineering Progress*, 3, pp. 68–72.

5

Flow Sheets, Diagrams, and Materials of Construction

The conceptualization of a full-scale process is usually done in stages. The exception to this might be the design and construction of a well-established process for producing a commodity chemical whose design has remained relatively unchanged over the years and may be in the hands of an engineering and construction contractor as an “off-the-shelf” plant.

Assuming this is a new process for scale-up, chemical engineers will work with a chemist to understand the product being made and the laboratory process by which it is made. The chemical engineer will watch the lab process being run to ensure an understanding of the reaction conditions and their limitations. Since it is unlikely that the full-scale process will look exactly like the lab process (and may become continuous vs. the batch process used in the lab), a simple qualitative flow sheet, frequently called a “block” flow diagram, will be developed showing the types of equipment that might be used and their relationship to one another. An example of such a flow sheet for a waste treatment process is shown in Figure 5.1.

This type of flow diagram is only qualitative and shows only the basic concept of how the process is envisioned to work. It shows the feeds (air and screened effluent), a clarifier/settler (without saying exactly how it operates or under what conditions), and the fact that some of the activated sludge is recycled in the process (but not how much). It also shows the end product and the treated effluent but says nothing about the composition or temperature. It also does not indicate how the air is actually introduced into the tank or under what conditions (pressure, temperature). This type of flow sheet is just a starting point for discussion and an initial thinking about how the chemistry will be practiced on an industrial scale. For example, the handling of raw materials will certainly be different. They will not come out of reagent grade bottles, but more likely from pipelines, rail cars, trucks, or drums. There will need to be storage facilities and safety systems in place to handle large quantities of raw materials. If there is a reaction vessel or system, the reactor may or may not be a stirred vessel, but the raw materials still need to

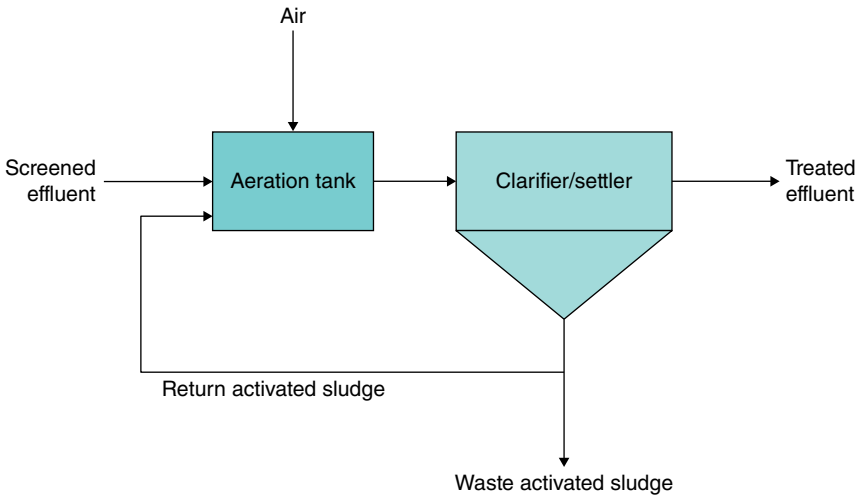


Figure 5.1 Simple block flow diagram. Source: *Chemical Engineering Progress*, 3/12, pp. 29–34. Reproduced with permission of American Institute of Chemical Engineers.

go in and the products and by-products still need to be separated and recovered (the carbon dioxide removal box in this diagram is an example of this). There may be separation processes needed, assuming that what comes out of a reactor is not the final product and needs to be separated and purified in some way.

As we obtain more knowledge of the chemistry and the process, we can then begin to add detailed information to the flow sheet such as flow rates, compositions, and temperatures. This will take the form of process flow diagrams and are known as a piping and instrumentation diagram, showing the details of the process and how each unit operation will be controlled, as shown in Figures 5.2 and 5.3.

Figure 5.2 shows additional details of the internal designs of the vessels, how the sludge will be recycled, preliminary indications of what will be measured and controlled, and an indication of the need for “backup” equipment (as in the pumps and blowers).

Figure 5.3 shows the detail of just one section of the process flow diagram and the manner in which it will be controlled.

As a subset to this level of diagramming and flow sheets, we now see 3D diagrams of much of the equipment, generated by CAD/CAM programs, as shown in Figure 5.4.

This level of detail, which was not possible without the 3D software tools now available, allows the chemical engineer, along with mechanical, piping, and instrumentation engineers, to view access points to equipment and

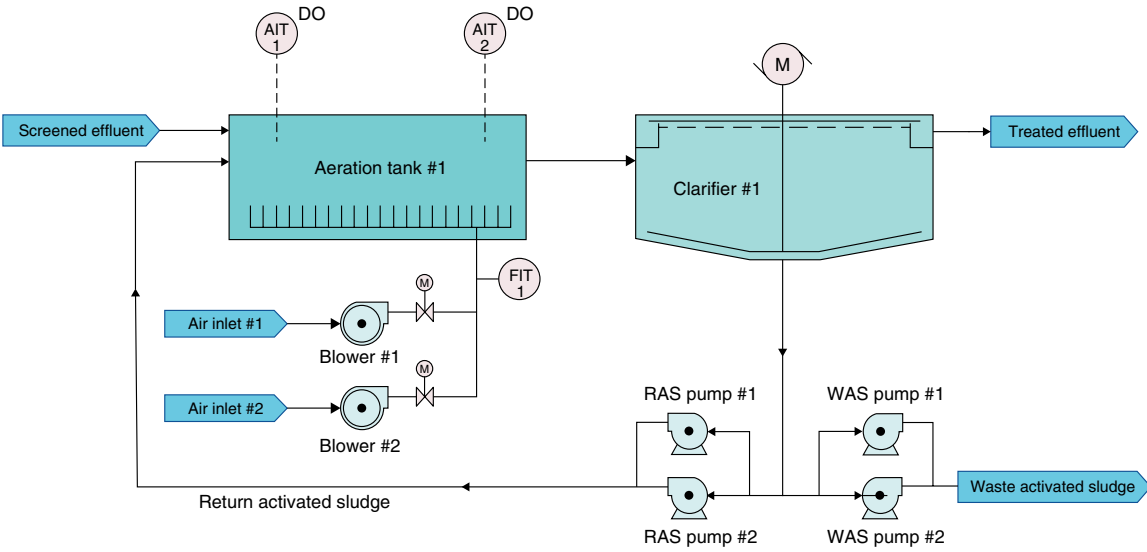


Figure 5.2 Process flow diagram. Source: Chemical Engineering Progress, 3/12, pp. 29–34. Reproduced with permission of American Institute of Chemical Engineers.

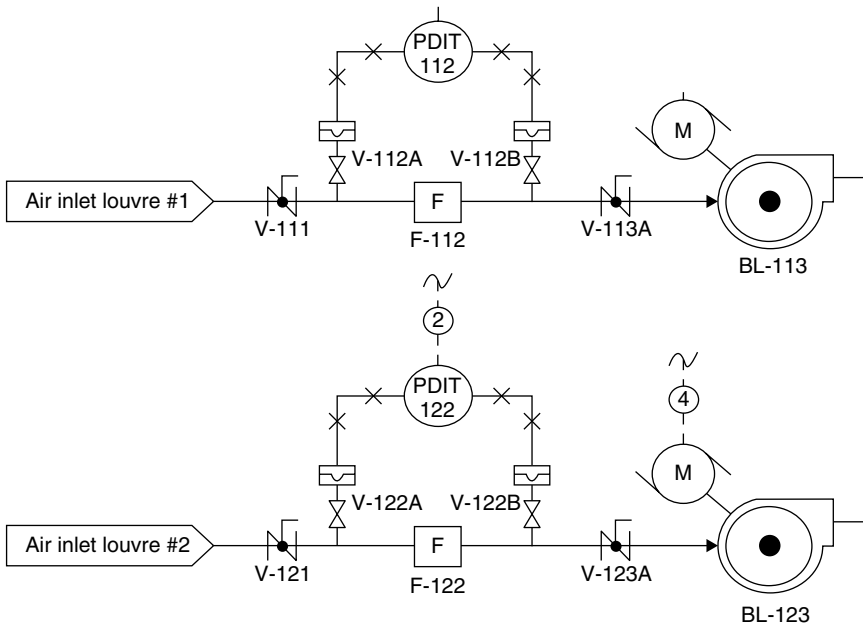


Figure 5.3 Detailed process flow diagram including instrumentation. Source: Chemical Engineering Progress, 3/12, pp. 29–34. Reproduced with permission of American Institute of Chemical Engineers.

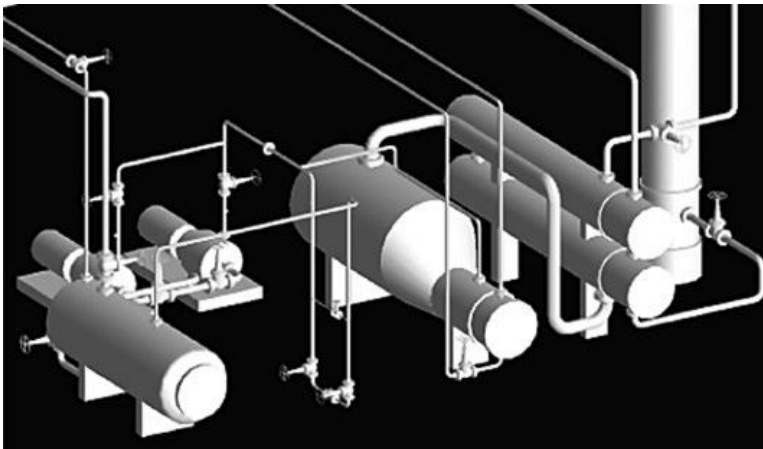


Figure 5.4 3D process view for public release from slide share.

instrumentation. This is important not only from a practical operational and maintenance standpoint but also from a safety standpoint. We need to understand how easy it is to access emergency valves and to access escape routes in emergency situations.

One of the challenges with any kind of flow sheet, whether it be on paper or in electronic format, is keeping it up to date. There must be a disciplined process for keeping these important records accurate and up to date in the face of minor process improvements, as well as maintenance and instrumentation changes. If an outdated flow sheet is used in a safety, HAZOP, or reactive chemicals review, the consequences can be serious.

Materials of Construction

When we build a large chemical facility, we will not be using the glass material that may have been used in the laboratory. Glass, though corroded by some materials such as fluorides and strong alkalis, is a very corrosion-resistant material. However, it is not pressure resistant, unless used as glass lined metal, and has very low shock resistance. If used on a large scale in a non-glass lined form, it presents the possibility of large-scale chemical releases.

Large plants will replace glass with the least costly metal or glass-lined metal material that will provide sufficient corrosion resistance. Experienced corrosion engineers are heavily involved in these decisions as there are many corrosion situations where the proper choice of materials goes against common sense. For example, chlorine (Cl_2) is known to be a corrosive compound, but if it is kept very dry, it can be handled in steel for an extended period of time. However, if the chlorine is wet or saturated with water, it will corrode normal steel extremely rapidly. Wet chlorine is typically handled in titanium piping. If dry chlorine is used in titanium, it will ignite and actually burn within the pipe ($2\text{Cl}_2 + \text{Ti} \rightarrow \text{TiCl}_4$). It is never a good idea to make the assumption that a more expensive metal is more corrosion resistant. Copper is also an unusual material in terms of its ability to resist corrosion to different classes of materials.

Another aspect of corrosion is the phenomenon of stress corrosion cracking. Materials such as stainless steel, having grain boundaries between their various phases, are subject to “short circuiting” along grain boundary paths, especially by chloride ions. This can appear as a catastrophic failure if a pipe “breaks” along its grain boundaries. This phenomenon can lead to catastrophic failure while a normal corrosion study may show very low corrosion rates. The grain boundaries in stress crack-prone materials can be seen in Figure 5.5, where the “short-circuit” paths are plainly visible.

A similar unusual behavior is “pitting” where holes develop in a material though its overall corrosion rate may be very low.

Corrosion testing and evaluation is typically done under closely controlled laboratory conditions, attempting to simulate actual process conditions. Basically, the sample of material of concern is inserted into the solution to which it will be exposed for a set amount of time, at a given temperature, and the weight of the sample compared with its original weight converted into loss of thickness of material and expressed typically in “mils/year,” or



Figure 5.5 Stress corrosion versus general corrosion. Source: Reproduced with permission of NASA.

thousandths of an inch per year. A material with a corrosion rate of less than 5 mils/year would ordinarily be considered noncorrosive. Numbers greater than this will be classified as moderate or severe. The exact classifications are determined by industry standards set by organizations such as ASTM.

In many cases, it is not possible to provide a corrosion test that directly simulates a 30-year exposure to a given environment. We simply don't have that much time! In these cases, accelerated corrosion tests are frequently used, taking advantage of our knowledge of the basic chemistry of the corrosion chemistry, its rate constant, and the effects of temperature. For example, if we wanted to know the corrosion rate for water in steel at room temperature, we could raise the temperature of the water, and knowing how the corrosion reaction rate is affected by temperature, we take the data at a higher temperature and extrapolate it back to room temperature, obtaining the information in a shorter time.

Summary

Flow sheets are the visual way that chemical engineers show how a process is intended to run, the connections between the various unit operations, and the connections with raw material and utility supplies. In their advanced stages, they also show material and energy balances, recycle loops, and how a process is controlled. The visualization of the process, especially including a 3D perspective, can be an effective training and safety tool.

Coffee Brewing: Materials of Construction and Flow Sheets

Have you ever drawn a flow sheet or diagram of how you make a cup of coffee? Try it! What are the raw materials? What comes in? Goes out (spent grounds, waste pod, coffee not consumed)? In which order? Does it make a difference? What if you were asking someone else to make a cup of coffee, with a complicated recipe, for you? Of course it would! That's why we use flow sheets and the information on them to communicate how a process is run, connected, and controlled. What materials are used in the process? Most coffee carafes are glass, enabling us to see how much coffee is contained. We often see coffee residue (coffee "degradation" products) on these containers, despite having been through a washing machine. Carafes that insulate (as opposed to sitting on a hot plate) typically use a sealed vacuum layer. The metal is necessary to enable the construction of a vacuum layer. All three of these (clean glass, glass with residue, metal vacuum container) have different potential for product contamination, no different than the concerns we have in a chemical process for corrosion, cleaning, and impurities. More are discussed as we continue!

The materials used to construct a process must be chosen carefully and take into account not only normal operating conditions (temperature, pressure, quality/impurities in process streams) but also reasonable consideration for possible unexpected process conditions and impurities in raw materials. The materials that we use to construct the equipment and piping determine, to a great extent, how long the equipment and piping will last, the potential for corrosion products to cause product quality problems, and the original cost of the plant.

Discussion Questions

- 1 How up to date are your process flow sheets? What is the process for updating them? How would you know whether a flow sheet is up to date? Who would you ask?
- 2 When changes to a process are made, what is the mechanism for ensuring that these changes are transferred to the process and the plant records? How is it assured that the changes are accurate?
- 3 How are flow sheets used in safety and reactive chemicals reviews? How could they be used better?

- 4 How are the various levels of process flow sheets used in new employee training? How could they be used better?
- 5 Are the corrosion rates of the materials used in your process known? By whom? Where are the records kept? When tests are made, where are they recorded? How is the information communicated?
- 6 What actions are taken when a corrosion leak occurs in a process?
- 7 What possible contamination possibilities exist that might affect the corrosion resistance of currently used materials? How are these possible contaminants monitored?
- 8 What procedures are in place to prevent the use or installation of a “substitute/readily available” material or process component with less corrosion resistance?

Review Questions (Answers in Appendix with Explanations)

- 1 The level of detail contained in a flow sheet, in order of increasing complexity, is:
 - A P&ID, mass and energy balance, 3D
 - B Mass and energy balance, P&ID, 3D
 - C Block flow, process flow, P&ID, 3D
 - D 3D, P&ID, mass and energy balance, block flow
- 2 Process flow diagrams are important because they:
 - A Ensure disk space is used on a process control computer
 - B Provide a sense of process stream and equipment interactions
 - C Provide a training exercise for new engineers and operators
 - D Make effective use of flow sheet software
- 3 3D process diagrams are most important because they:
 - A Enable personnel to envision the interaction between people and equipment
 - B Allow the use of 3D glasses from the movies that otherwise would be thrown away
 - C Enable the use of 3D software
 - D Show the best location for a security camera

- 4 It is important to ensure flow sheets are up to date because:
- A __ They are used by maintenance personnel to identify connections and equipment
 - B __ They show safety valves and relief systems
 - C __ They are a means of common communication between engineers, operators, and maintenance personnel
 - D __ All of the above
- 5 Accurate measurement and knowledge of corrosion rates, as well as what affects them, within process equipment is important because:
- A __ Pipe vendors need to know when to schedule the next sales call
 - B __ Corrosion meters need to be tested once in a while
 - C __ It is important to understand the estimated life of process equipment and the potential for corrosion products to contaminate process streams
 - D __ We need to keep evacuation plans up to date for equipment failures
- 6 A process fluid with higher water content than one with a lower water content:
- A __ Will be more corrosive
 - B __ Will be less corrosive
 - C __ Depends on the temperature
 - D __ Can't tell without laboratory data

Additional Resources

- Crook, P. (2007) "Selecting Nickel Alloys for Corrosive Applications" *Chemical Engineering Progress*, 5, pp. 45–54.
- Gambale, D. (2010) "Choosing Specialty Metals for Corrosion-Sensitive Equipment" *Chemical Engineering Progress*, 7, pp. 62–66.
- Geiger, G. and Esmacher, M. (2011) "Inhibiting and Monitoring Corrosion (I)" *Chemical Engineering Progress*, 4, pp. 36–41.
- Geiger, G. and Esmacher, M. (2012) "Inhibiting and Monitoring Corrosion (II)" *Chemical Engineering Progress*, 3, pp. 29–34.
- Hunt, M. (2014) "Develop a Strategy for Material Selection" *Chemical Engineering Progress*, 5, pp. 42–50.
- Nasby, G. (2012) "Using Process Flowsheets as Communication Tools" *Chemical Engineering Progress*, 2, pp. 36–44.
- Picciotti, M. and Picciotti, F. (2006) "Selecting Corrosion-Resistant Materials" *Chemical Engineering Progress*, 12, pp. 45–50.

Prugh, R. (2012) "Handling Corrosive Acids and Caustics Safely" *Chemical Engineering Progress*, 9, pp. 27–32.

Richardson, K. (2013) "Recognizing Corrosion" *Chemical Engineering Progress*, 10, p. 26.

Walker, V. (2009) "Designing a Process Flowsheet" *Chemical Engineering Progress*, 5, pp. 15–21.

6

Economics and Chemical Engineering

As we have discussed, there must be an incentive to commercially produce a product or service. This means that the price of the product must exceed all the costs of making the product, including a return on the capital invested to build the facility. In principle, this is no different than the expectations someone has for a return from a bank deposit or stock market investment. This margin may vary to some degree with the cost of borrowing money over time, but it still must be greater than zero. For example, if we want to commercialize a reaction of the type $A + B \rightarrow C$, what should be considered and estimated?

What is the cost of A? B? At what volumes? At what purity? The value of C? What might affect these values? What is the cost of the arrow? Capital? Energy? Labor? Waste disposal? Ultimate equipment disposal? Ultimate site cleanup? Does the reaction go to 100% to the product desired? It is unlikely that "C" is the only product produced. What are the other materials produced? How are they separated from the desired product? Can they be recycled and reused? Separated and used as raw materials for other useful reactions? Are there waste disposal costs and issues? How hazardous are A, B, and C? What is the cost of ensuring that they are all handled and stored safely? What are the safety aspects of the arrow of conversion?

In addition to evaluating overall costs, there are two basic categories to be considered, fixed and variable. What is the difference? Fixed costs describe funds that are spent ahead of actually producing any product and, in addition, are independent, or nearly independent, of the rate of product produced (a plant may be designed to produce 1000 #/h, but actually may run and produce only 800 #/h so this would be 80% of capacity). Examples of such costs are the purchase and installation of the equipment in the plant, utility and waste handling facilities related solely to this process, purchase of land to site the facility (if it is not already owned), and insurance and taxes. In addition, there are costs in operating a plant that are nearly independent of its operating rate. Labor cost, in many situations, is relatively fixed as it is unlikely that a large personnel

reduction will occur in a continuous plant whose rate may vary. However, in a batch chemical manufacturing facility which reduces the number of shifts it operates, labor costs may be somewhat variable. Liability insurance and workman's compensation fees will also normally be considered a fixed cost. Basic supplies for plant facilities such as personnel facilities are also fixed. There are many situations where a state or county may provide tax incentives to a company to locate a facility and create jobs. This normally takes the form of eliminating or reducing local property tax costs for an extended period of time. It could also take the form of providing access streets and roads that would have an effect of reducing the total capital cost of building the facility. These incentives may also be impacted by the continuing number of jobs versus those created initially.

An important factor in evaluating fixed costs is the concept of depreciation. The US (and most other countries') tax code provides an indirect incentive for companies to build plants via this concept. Let's assume that a plant costs \$100 M to be built. This is the capital cost referred to earlier. In general, the tax code allows a company to "depreciate" approximately 10% of this fixed cost every year and deduct this amount from its tax bill. This is a part of the federal tax code system and could be changed by the US Congress, either permanently or on a short-term basis for economic stimulation. We can look at this as a type of "forced" savings account that generates funds to rebuild the plant at a future date. The amount of this depreciation can be (and has been on occasion) changed by national and state legislatures to provide an incentive to build plants that provide jobs. This is shown as a "cost" on the company's accounting books when profits are being reviewed, but when a company is showing its "cash flow," the depreciation is added back in. Cash flow includes both profit and depreciation.

The cost of buying equipment is only one part of the fixed cost. The equipment must be installed. The cost of this will vary greatly with a number of factors including buildings needed to enclose the process, piping connections between equipment and process vessels, electrical supply to the equipment, foundation preparation, cost of supplying utilities (Are they already available? Are they coming from a city or public utility?), fireproofing required, cost of instrumentation, emergency backups, and contractor fees and margins. The last item will be greatly affected by conventional supply and demand economics and how busy the contractor is or wants to be!

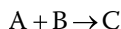
Variable costs are those directly related to the rate at which the process operates. This would include raw materials and energy costs directly related to the process (e.g., as opposed to heating and lighting for the building in which the plant operates). Note that energy costs could be offset to some degree if a reaction generates heat that can be used elsewhere in a facility. Also included here would be environmental control or waste disposal/destruction costs. Typically these are proportional to the level of production.

In all cost estimates, a contingency is included. This can vary from a small percentage to account for minor unanticipated events during a plant start-up to a large percentage if the plant is the first of its kind using new chemistry that a company has no previous experience with.

The sum total of all these factors can vary from 3 to 7 times the cost of the purchased equipment. Unless this process is “first of its kind” on a bare plot of land, a number frequently used is 3.5–4 times the purchased equipment cost.

Distribution and shipping costs also come into consideration. Most chemical materials are sold on a cost plus freight basis, meaning that the customer pays the transportation costs (rail car rates, truck rates for drums, etc.). However, in many cases of large-volume commodity products such as chlorine, sulfuric acid, ammonia, and so on, we will frequently hear the term “freight equalized,” meaning that the producer has partially compensated for the freight cost if there is another supplier physically closer to the customer.

Let’s take a look at a hypothetical example using the following general chemical reaction:



We will assume the following:

- 1) The reaction is endothermic (i.e., it requires constant supply of energy to proceed; without energy input, it stops), requiring 2000 BTU/mole of “C” produced.
- 2) The cost of “A” is \$1/mole and “B” is \$2/mole.
- 3) The value (selling price) of “C” is \$5/mole.
- 4) The cost of the solvent, in which the reaction is run, is \$0.50/mole, and we need 10 moles of solvent per mole of product. Most of the solvent can be recycled.
- 5) The cost of building a plant (installed cost) is \$50 M (million).
- 6) The capacity of the plant is 5 M moles/year.
- 7) The depreciation rate is 10%.
- 8) The combined federal, state, and local taxes are 40% of net profit.
- 9) This is a new process and product for the company.
- 10) The process is a one-step process, using a catalyst under high pressure and a reaction solvent.
- 11) The product is a solid which precipitates from the reaction as it is formed. The reactants are soluble in the solvent; but the product is not. The product must be filtered and dried prior to storage and sale.
- 12) The conversion in the reaction is 100%, but the yield is only 90%, meaning that there is some unreacted raw material that must be recycled for reuse. This is done by recovering the solvent and unreacted raw material and recycling them.
- 13) One of the raw materials, as well as the reaction solvent, is flammable and hazardous.

An overall early-stage process flow diagram might look like that shown in Figure 6.1.

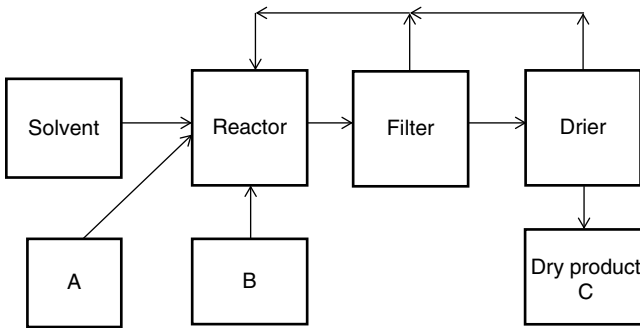


Figure 6.1 Simple block flow diagram for early-stage economic analysis.

The general points about this diagram are as follows:

- 1) Possible slow degradation of either the solvent or either of the reactants.
- 2) The storage and inventory requirements of any of the reactants, the solvent, or the product.
- 3) Materials of construction requirements.
- 4) The type of instrumentation required.
- 5) The effect of any physical property changes.
- 6) The nature of the pumps, the drier, and solids transport equipment.
- 7) This flow sheet also assumes that the unreacted raw material and the solvent can be recycled together.
- 8) The flow diagram shows no detail on the storage and handling of the final product.

Depending upon the volume of products made, the kinetics and batch reaction size, and the limitations of building and equipment, this type of process might actually be installed and run in two or more parallel reaction systems.

What would the variable costs look like? The raw material costs are \$1 and \$2/mole for A and B, respectively, and both are eventually converted to product, though “B” must be recycled. Since we need one mole of each, the total raw material cost is \$3/mole of product. The other raw material that needs to be considered is the process solvent. It is not logical to assume that there will be no solvent loss, and environmental regulations may have a role to play in the decision as to the degree of recovery required.

The energy cost is at least the cost of energy addition for the endothermic reaction, stated at 2000 BTU/mole of product. But it is also stated that this is

a high-pressure reaction, implying the need for moderate pressure steam. The thermal value of steam condensing is about 1000 BTU/pound, so if we assume that this energy is supplied by steam to the jacket of the reaction vessel and that the steam costs are \$4/M BTU at a higher than normal pressure, this amounts to $\$4/1\,000\,000 = 0.00004/\text{BTU} \times 2000 \text{ BTU/mole of product}$ or \$0.008/mole of product. To this we might add utility costs related to hot and cold water for restrooms, safety showers, and process equipment wash-downs, estimating the total at around \$0.01/mole of product. There will also be some very minor cost associated with office space, external maintenance, and other miscellaneous items, but, compared with the three costs we have considered, are most likely insignificant. So here is the summary of the approximate variable costs:

Variable costs for product "C"	
Raw materials (\$1 + \$2)/mole	\$3.00/mole of product
Solvent (1% loss) 10 moles/mole of product at 0.50/mole \times .01	0.05/mole of product
Energy	0.01/mole of product
Total variable costs	\$3.06/mole of product

Let's now take a look at the fixed cost side. The cost of building this plant is \$50M to produce 5M moles/year, so the capital cost, on a ratioed basis, is \$10.00/mole. Assuming that we are allowed to depreciate this in the normal 10%/year fashion, this amounts to \$10.00/10 or \$1.00/mole.

Maintenance is figured as a percentage of capital costs, and we are told this is a high-pressure reaction system, so it is likely to be on the higher side, possibly 8% of capital, or $0.08 \times \$50 \text{ M}/5$ or \$.80/mole.

Labor, unless the plant is temporarily shut down, will normally use the same number of employees, even if the product rate is reduced slightly. Let's assume there are two operators per shift in a 24h operation. This is the equivalent of eight full-time employees. Assuming that this is a normal Fortune 500 company with the usual benefits, this would probably cost the company about \$80 000/employee or \$640 000/year or \$640 000/5 000 000 or \$0.13/mole.

There will be other fixed costs such as local taxes, liability, and workmen's compensation insurance which tend to be rather minor (per pound or mole). On the fixed capital side, we are assuming the availability of utilities such as moderate pressure steam, water, and electricity for lights and pumps. If this were a "grassroots" facility, additional capital would be required.

The following is the summary of the capital costs:

Fixed costs for product "C"	
Depreciation	\$1.00/mole of product
Solvent (1% loss) 10 moles/mole of product at 0.50/mole \times 0.01	0.05/mole of product
Energy	0.01/mole of product
Total variable costs	\$1.06/mole of product
Adding back in the variable costs, we see the total picture:	
Variable costs	
Raw materials (\$1 + \$2)/mole	\$3.00/mole of product
Solvent (1% loss) 10 moles/mole of product at 0.50/mole \times 0.01	0.05/mole of product
Energy	0.01/mole of product
Total variable costs	\$3.06/mole of product
Total costs	\$4.12/mole of product

At a selling price of \$5.00/mole, that leaves a gross profit of \$5.00 minus \$4.12 or \$0.88/mole.

What is the return on investment (ROI) before taxes? It's the profit divided by the capital invested – no different than how we make decisions about where to invest our money. Our profit is \$0.88/mole \times 5 000 000 moles/year or \$4 400 000/year. Dividing this by the investment made gives the ROI before taxes of \$4 400 000/\$50 000 000 or 8.8%. For a moment, think about this in the context of your own personal investment decisions, before taxes. Would you make this investment? For most chemical companies, unless this is a carbon copy of a plant built and run many times before, 8.8% would be below the minimal acceptable return, given the risk of running a chemical plant versus investing in a long-term bond, for example. Now we have to pay taxes at 40%, equal to $0.4 \times \$0.88$ or \$0.352/mole. At a production rate of 5 M moles/year, this amounts to $5\,000\,000 \times \$0.352$ or \$1 760 000/year.

The after-tax profit is the after-tax income divided by the investment or \$1 760 000/50 000 000 or 3.5%. Is this worth doing? In general, the answer would be no. Again, it's possible to get this level of return on a long-term bond of some sort.

So what would chemical engineers consider if they were reviewing this project and its economics and were charged with making some positive input to the R&D program associated with it?

- 1) Seventy-five percent of the total cost is in raw materials. What is the basis for the numbers used? Were they just taken from a trade magazine or from a substantive conversation with a purchasing agent? What is the purity of the raw materials assumed? If the prices in this review were at 99.9% purity, what is the change in price if 99% were acceptable? What would have

to be changed about the process to accommodate this lower-quality raw material? How would this impact the capital costs?

- 2) The reaction, as currently described, does not use a catalyst. Has this been considered? If the reaction rate could be enhanced (e.g., lower temperature, lower pressure), how much less capital would be required? If this were possible, how does the raw material cost change?
- 3) It is stated that this is an endothermic reaction requiring heat input. Is there another process nearby, using exothermic chemistry, which could be coupled in some way to provide the energy?
- 4) What could be changed about the composition, purity, or form of the product which would allow a higher price?

These are just a few of many questions that should be asked at an early stage of such a project.

Summary

The four primary issues in determining the profitability of a chemical process are costs of raw materials, cost of building and maintaining the plant, cost of utilities (energy, water, and electricity), taxes and depreciation, and selling price of the product being manufactured. The impact of changes and variability in the variable cost side of the total is critical. These numbers and what underlies them can also serve as a foundation for long-term process R&D activities to reduce the most significant costs and to look at less expensive raw material sources tied to new chemistry. Fixed costs, once incurred, are spent and cannot be retrieved without a “write-off” of the facility.

Coffee Brewing: Cost

Does all coffee cost the same? Of course not! But why? What is the cost of the raw material (the beans)? How rare are they? From what country? How easy is it to harvest, inventory, and ship? From where? The various processes to produce and package beans, evaporation to produce instant coffee, vacuum to produce freeze-dried coffee, grinding coffee, ground coffee in a vacuum container (vacuum is not free), and shipping/distribution/storage all have different costs associated with them. This must be weighed against what we think the consumers are willing to pay for all these different options. There are indirect costs associated with specialized coffee brewing at home. It is in the form of time which indirectly has a cost associated with it. After a pot of coffee is made, a significant portion of it may be thrown away. How much does this cost? The new “K-Cups” avoid this, but the cost of the coffee in them is significantly higher than that in cans or bags. What is this convenience worth versus the cost of making these very small packages? More later! No rights or wrongs... just choices based on criteria set ahead of time.

Discussion Questions

- 1 Is the split between fixed and variable costs for all of your processes well understood? How is this ratio affected by % capacity the plant is running?
- 2 Does the process R&D prioritization reflect that difference?
- 3 What operating plans are in place for a significant decrease or increase in product demand?
- 4 What possible major shifts in raw material costs and supply might be anticipated? What resources are dedicated to scouting for possible paradigm shifts in this area?
- 5 What possible changes to tax and depreciation laws may be on the horizon? In what areas? Who has the responsibility to monitor these and make recommendations?
- 6 What variables determine your organization's "acceptable" return on investment (ROI) criteria? How were they determined? Are these criteria reviewed? How often? By whom? What are the criteria?
- 7 To the extent that utilities such as power and water are critical parts of the economics and reliability of the process, what kinds of communication are in place with the utility supplier? What are their long-term plans? Do they know about yours, or do you just assume that whatever you need will be there when you need it? If a utility merger or acquisition involving your utility supplier is considered a possibility, how might it affect you?
- 8 How would a severe drought affect you? Your utility supplier? What backup and alternatives have you considered and planned for?

Review Questions (Answers in Appendix with Explanations)

- 1 The cost of manufacturing a chemical includes:
 - A __Capital cost (cost of building the plant)
 - B __Cost of raw materials
 - C __Taxes, labor, supplies
 - D __All of the above

- 2 The most important factors in determining the variable cost of manufacture are typically:
- A __Shipping costs
 - B __Labor contract changes
 - C __Raw material and energy costs
 - D __Security
- 3 If capital costs are 50% of the total cost of manufacture, and the production rate is reduced by 50%, the impact on the product's cost of manufacture will be:
- A __10%
 - B __25%
 - C __50%
 - D __75%
- 4 If the cost of one raw material, representing 20% of a product's total cost, is raised by 25%, the impact on total cost will be:
- A __24%
 - B __4.4%
 - C __5.4%
 - D __6.4%

Additional Resources

- Bohlmann, G. (2005) "Biorefinery Process Economics" *Chemical Engineering Progress*, 10, pp. 37–44.
- Burns, D.; McLinn, J. and Porter, M. (2016) "Navigating Oil Price Volatility" *Chemical Engineering Progress*, 1, pp. 26–31.
- Moore, W. (2011) "'Lowest-Cost' Can Cost You" *Chemical Engineering Progress*, 1, p. 6.
- Nolen, S. (2016) "Leveraging Energy Management for Water Conservation" *Chemical Engineering Progress*, 4, pp. 41–47.
- Swift, T. (2012) "New Chemical Activity Barometer Signals Future Economic Trends" *Chemical Engineering Progress*, 8, p. 15.
- Swift, T. (2012) "Energy Savings through Chemistry" *Chemical Engineering Progress*, 3, p. 17.