

# 1

## Introduction

Chemical process technology has had a long, branched road of development. Processes such as distillation, dyeing, and the manufacture of soap, wine, and glass have long been practiced in small-scale units. The development of these processes was based on chance discoveries and empiricism rather than thorough guidelines, theory, and chemical engineering principles. Therefore, it is not surprising that improvements were very slow. This situation persisted until the seventeenth and eighteenth centuries.<sup>1</sup> Only then were mystical interpretations replaced by scientific theories.

It was not until the 1910s and 1920s, when continuous processes became more common, that disciplines such as thermodynamics, material and energy balances, heat transfer, and fluid dynamics, as well as chemical kinetics and catalysis became (and still are) the foundations on which process technology rests. Allied with these are the unit operations including distillation, extraction, and so on. In chemical process technology various disciplines are integrated. These can be divided according to their scale (Table 1.1).

Of course, this scheme is not complete. Other disciplines, such as applied materials science, information science, process control, and cost engineering, also play a role. In addition, safety is such an important aspect that it may evolve as a separate discipline.

In the development stage of a process or product all necessary disciplines are integrated. The role and position of the various disciplines perhaps can be better understood from Figure 1.1, in which they are arranged according to their level of integration. In process development, in principle the *x*-axis also roughly represents the time progress in the development of a process. The initial phase depends on thermodynamics and other scale-independent principles. As time passes, other disciplines become important, for example, kinetics and catalysis on a micro/nanolevel, reactor technology, unit operations and scale-up on the mesolevel, and process technology, process control, and so on on the macrolevel.

Of course, there should be intense interaction between the various disciplines. To be able to quickly implement new insights and results, these disciplines are preferably applied more or less in parallel rather than in series, as can also be seen from Figure 1.1. Figure 1.2 represents the relationship between the different levels of development in another way. The plant is the macrolevel. When focusing on the chemical

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<sup>1</sup> This remark is not completely fair. Already in the sixteenth century Agricola published his book “De Re Metallica” containing impressive descriptions of theory and practice of mining and metallurgy, with relevance to chemical engineering.

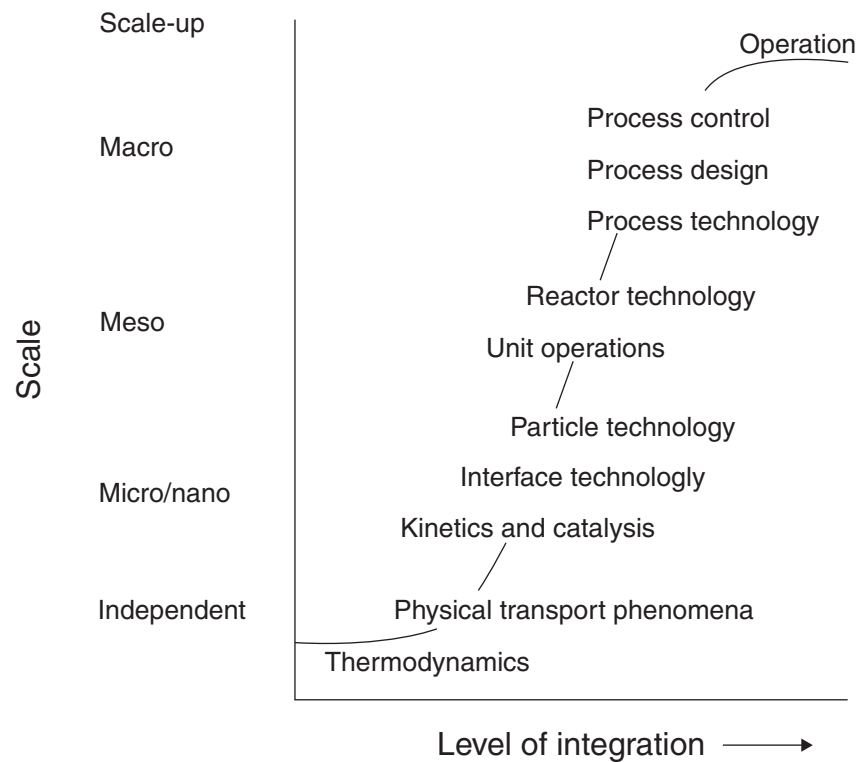
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**Table 1.1** Chemical process technology disciplines

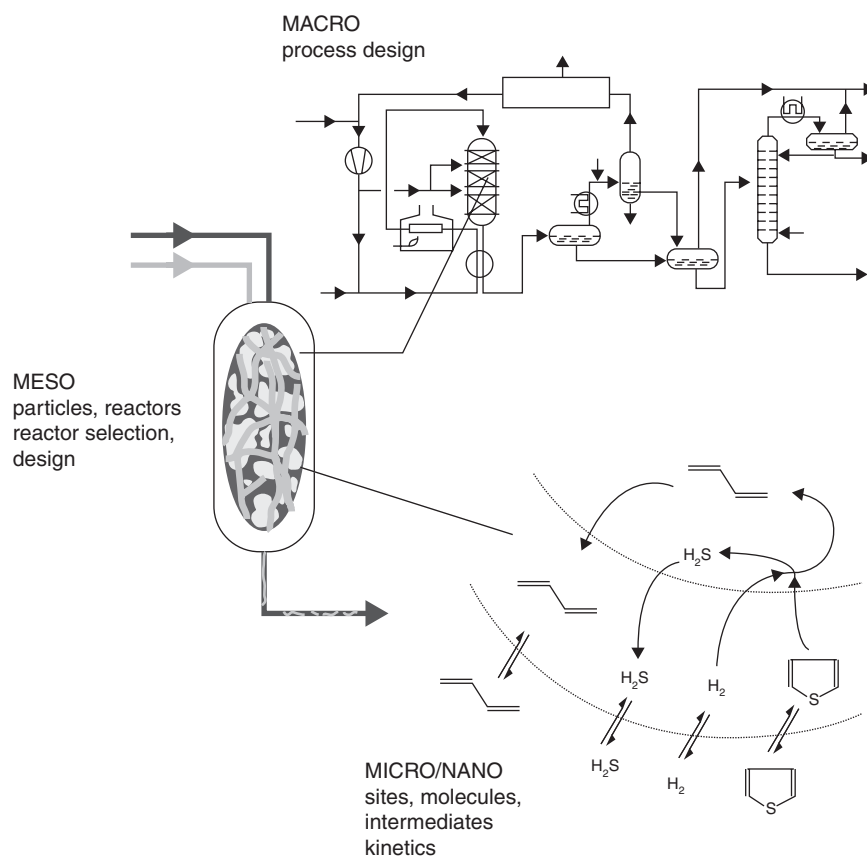
| Scale             | Discipline                                                                                                    |
|-------------------|---------------------------------------------------------------------------------------------------------------|
| Scale independent | Chemistry, biology, physics, mathematics<br>Thermodynamics<br>Physical transport phenomena                    |
| Micro/nanolevel   | Kinetics<br>Catalysis on a molecular level<br>Interface chemistry<br>Microbiology                             |
| Mesolevel         | Particle technology<br>Reactor technology<br>Unit operations                                                  |
| Macrolevel        | Process technology and process development<br>Process integration and design<br>Process control and operation |

conversion, the reactor would be the level of interest. When the interest goes down to the molecules converted, the micro- and nanolevels are reached.

An enlightening way of placing the discipline Chemical Engineering in a broader framework has been put forward by Villermeaux [personal communication], who made a plot of length and time scales



**Figure 1.1** Disciplines in process development organized according to level of integration.



**Figure 1.2** Relationship between different levels of development.

(Figure 1.3). From this figure it can be appreciated that chemical engineering is a broad integrating discipline. On the one hand, molecules, having dimensions in the nanometer range and a vibration time on the nanosecond scale, are considered. On the other hand, chemical plants may have a size of half a kilometer, while the life expectancy of a new plant is 10–20 years. Every division runs the danger of oversimplification. For instance, the atmosphere of our planet could be envisaged as a chemical reactor and chemical engineers can contribute to predictions about temperature changes and so on by modeling studies analogous to those concerning “normal” chemical reactors. The dimensions and the life expectancy of our planet are fortunately orders of magnitude larger than those of industrial plants.

Rates of chemical reactions vary over several orders of magnitude. Processes in oil reservoirs might take place on a time scale of a million years, processes in nature are often slow (but not always), and reactions in the Chemical Process Industry usually proceed at a rate that reactor sizes are reasonable, say smaller than  $100 \text{ m}^3$ . Figure 1.4 indicates the very different productivity of three important classes of processes.

It might seem surprising that despite the very large number of commercially attractive catalytic reactions, the commonly encountered reactivity is within a rather narrow range; reaction rates that are relevant in practice are rarely less than one and seldom more than  $10 \text{ mol m}_R^{-3} \text{ s}^{-1}$  for oil refinery processes and processes in the chemical industry. The lower limit is set by economic expectations: the reaction should take place in a reasonable amount of (space) time and in a reasonably sized reactor. What is reasonable is determined by

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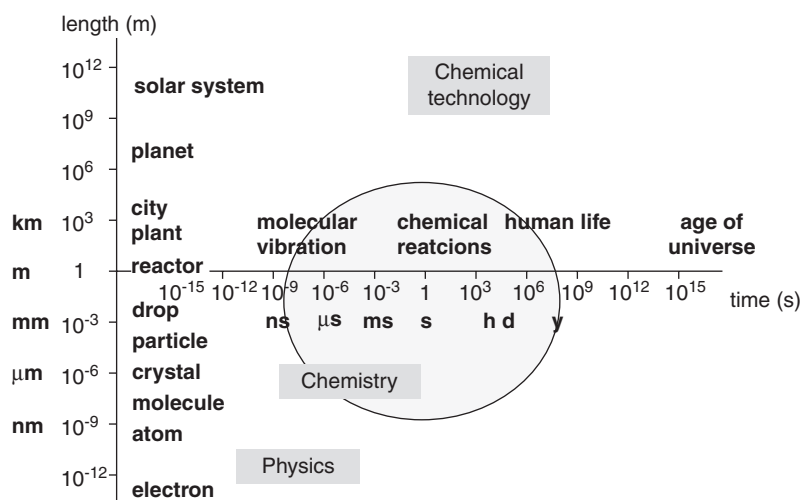


Figure 1.3 Space and time scales [J. Villermaux, personal communication].

physical (space) and economic constraints. At first sight it might be thought that rates exceeding the upper limit are something to be happy about. The rates of heat and mass transport become limiting, however, when the intrinsic reaction rate far exceeds the upper limit.

A relatively recent concept is that of Process Intensification, which aims at a drastic decrease of the sizes of chemical plants [2, 3]. Not surprisingly, the first step often is the development of better catalysts, that is, catalysts exhibiting higher activity (reactor volume is reduced) and higher selectivity (separation section reduced in size). As a result, mass and heat transfer might become rate determining and equipment allowing higher heat and mass transfer rates is needed. For instance, a lot of attention is given to the development of compact heat exchangers that allow high heat transfer rates on a volume basis. Novel reactors are also promising in this respect, for instance monolithic reactors and microreactors. A good example of the former is the multiphase monolithic reactor, which allows unusually high rates and selectivities [4].

In the laboratory, transport limitations may lead to under- or overestimation of the local conditions (temperature, concentrations) in the catalyst particle, and hence to an incorrect estimation of the intrinsic reaction rate. When neglected, the practical consequence is an oversized, or worse, undersized reactor. Transport limitations also may interfere with the selectivity and, as a consequence, upstream and downstream processing units, such as the separation train, may be poorly designed.

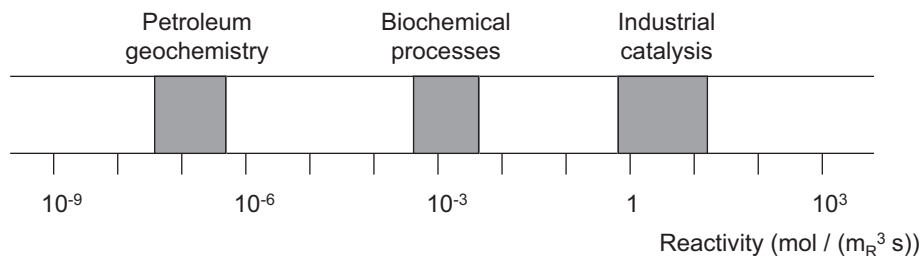


Figure 1.4 Windows on reality for useful chemical reactivity [1].

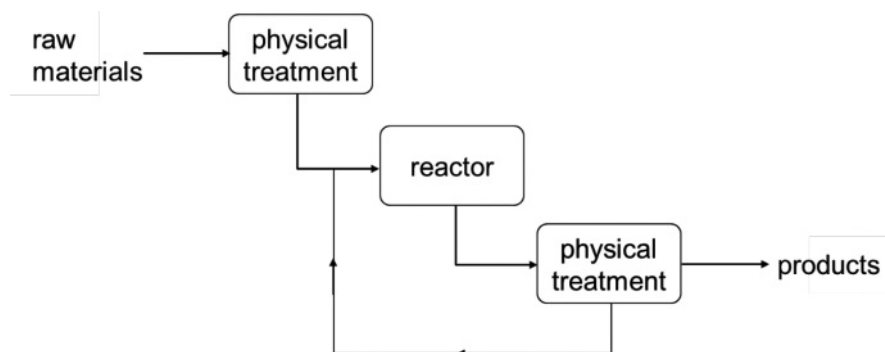


Figure 1.5 Typical chemical process structure.

## QUESTIONS

*What would have been the consequence of much lower and of much higher reactivity of petroleum geochemistry for humanity?*

*Which factors determine the lower and upper limits of the window for biochemical processes? Given a production rate of between  $10^4$  and  $10^6$  t/a of large volume chemicals (bulk chemicals), estimate required reactor volumes. Do the same for the production of petroleum products ( $10^6$ – $10^8$  t/a).*

*$A \rightarrow B \rightarrow C$  kinetics in which  $B$  is the desired product is often encountered. Explain why the particle size of the catalyst influences the observed selectivity to  $B$ .*

*How would you define the “intrinsic” reaction rate?*

Every industrial chemical process is designed to produce economically a desired product or range of products from a variety of raw materials (or feeds, feedstocks). Figure 1.5 shows a typical structure of a chemical process.

The feed usually has to be pretreated. It may undergo a number of physical treatment steps, for example, coal has to be pulverized, liquid feedstocks may have to be vaporized, water is removed from benzene by distillation prior to its conversion to ethylbenzene, and so on. Often, impurities in the feed have to be removed by chemical reaction, for example, desulfurization of the naphtha feed to a catalytic reformer, making raw synthesis gas suitable for use in the ammonia converter, and so on. Following the actual chemical conversion, the reaction products need to be separated and purified. Distillation is still the most common separation method, but extraction, crystallization, membrane separation, and so on can also be used.

In this book, emphasis is placed on the reaction section, since the reactor is the heart of any process, but feed pretreatment and product separation will also be given attention. In the discussion of each process, typically the following questions will be answered:

- Which reactions are involved?
- What are the thermodynamics of the reactions, and what operating temperature and pressure should be applied?
- What are the kinetics, and what are the optimal conditions in that sense?
- Is a catalyst used and, if so, is it heterogeneous or homogeneous? Is the catalyst stable? If not, what is the deactivation time scale? What are the consequences for process design? Are conditions feasible where deactivation is minimized? Is regeneration required?

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- Apart from the catalyst, what are the phases involved? Are mass and heat transfer limitations important?
- Is a gas or liquid recycle necessary?
- Is feed purification necessary?
- How are the products separated?
- What are the environmental issues?

The answers to these questions determine the type of reactor and the process flow sheet. Of course, the list is not complete and specific questions may be raised for individual processes, for example, how to solve possible corrosion problems in the production of acetic acid. Other matters are also addressed, either for a specific process or in general terms:

- What are the safety issues?
- Can different functions be integrated in one piece of equipment?
- What are the economics (comparison between processes)?
- Can the sustainability of the technology be improved?

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