GRAPHIC EXERGY ANALYSIS

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Summary

The synthesis of chemical or energy systems is very creative work. It is thought that only a designer with special skill can accomplish it. In this section, I stress the importance of thermodynamics in creating new systems. Especially, I show that graphic methods can present the essence of thermodynamics very clearly. Several applications are also illustrated.

1. Introduction

Chemical process systems or energy systems are much more complicated than other systems. The number of the constituent parts in a system is generally large. The substances that are treated in them may often be composed of multiple components, and the mixture of those components show very peculiar properties that may not be predicted easily. Sometimes there are multiple phases.

We can find in a system many kinds of processes such as chemical reactions, separation, heat exchange, and power-related processes taking place in a compressor or a turbine. Chemical reactions are investigated by chemists, and power-related processes by mechanical engineers, but the designer of process systems should cover all fields. Fortunately, by using the laws of thermodynamics, we can discuss all fields in a unified manner.

2. A New Approach to Thermodynamics

2.1. The Hierarchical Nature of Thermodynamics

Figure 1 shows that there are three kinds of scale to which thermodynamics is applied. In (a), a phenomenon, for example a chemical reaction, takes place in a test tube or a reactor column. In (b), several to a few tens of phenomena proceed in a reactor with auxiliary mechanisms such as external cooling. In (c), scales of a few tens to a few hundred phenomena take place in cooperation with other phenomena in an entire chemical plant including reactors, separators, heat exchangers, and so on.



Figure 1. Various scales of objects for application of thermodynamics

The approach that has generally been taken in thermodynamics is to consider simple objects first. Hence, first a small-scale object, say a test tube or a flask, is considered. Then we extend the applications to complicated objects of medium or large scale, such as a reactor with auxiliary mechanisms or an entire system. Although it seems reasonable to start from a simple case, we do not have a good method for extending the approach for simple objects to the level that it can be applied to complicated ones. Then we may be confused, because it is not possible to judge to what extent the results obtained for the simple objects can be applied to large-scale objects.

Here we take the approach of considering all three scales in Figure 1 simultaneously from the beginning, and of developing thermodynamics that can be applied to not only

small-scale phenomena in a test tube or in a flask, but also medium, leading eventually to large-scale, phenomena. We do not need to change the method depending on the complexity of the application object.

2.2. Three Kinds of Thermodynamics

Let us try to extract the common elements from all of those three scales. In each scale of (a), (b), and (c), we find substances such as the reactant, the product, and the cooling medium. Hence, "substance" is common to the three scales. We also find a change in substances. The reaction in the test tube in (a) is a typical example. Hence, "change of substances" is the second common element. Furthermore, we find plural changes in substances. Even at the smallest scale, (a) in Figure 1, we can observe a rise in the temperature of the test tube. Hence we can find the change by the reaction, and the rise in the temperature of the test tube by the exothermic reaction taking place in the test tube. In other words, "assembly of changes of substances" is the third common element. Consequently, it may be a good idea to discuss thermodynamics based on these three common elements. This means that we can construct three kinds of thermodynamics. By dividing thermodynamics into these three kinds, we shall cover the full width of its applications.

2.3. Thermodynamics of a Substance

When the number of phases, the quantity of each component in each phase, and the temperature and pressure, are specified, the energy H and entropy S of a substance can be determined independently from its production path. This is the "thermodynamics of a substance." The energy of a substance is called "internal energy" or "enthalpy" depending on whether or not the process proceeds under constant volume.

2.4. Thermodynamics of a Process

The circle in Figure 2 represents a change in a substance. The solid arrows going into and out of the circle show the input and output substances respectively. Since their energy *H* and entropy *S* can be determined, we can calculate the energy change ΔH and the entropy change ΔS for this change:

$$\Delta H = H_{\rm out} - H_{\rm in} \tag{1}$$

$$\Delta S = S_{\rm out} - S_{\rm in} \tag{2}$$

When there are plural streams for input, say 1 and 2, H_{in} and S_{in} in the above equations can be replaced by $(H_{1,in} + H_{2,in})$ and $(S_{1,in} + S_{2,in})$, respectively. This is the "thermodynamics of a process." This view can be applied to all changes in substances, such as chemical reactions or processes of heating, cooling, compression, expansion, and so on. We may call this change in substances a process.



Figure 2. Description of a process

It should be noted that some energy, such as heat or work, is accepted or released by this change. The thick outlined arrows in Figure 2 represent this kind of energy. It is called intermediary energy, because the energy released by a process is generally accepted by another process, and the combination of acceptance and release of this energy comprises an energy transformation.

2.5. Thermodynamics of a System

Figure 3 shows an assembly of processes. Figure 3(a) is called a system or a thermodynamic system, where the flow of substances (solid line arrows) may intersect the system boundary, but the flow of intermediary energy (thick outlined arrows) does not. Hence, Figure 3(b) is not a thermodynamic system, because intermediary energy released by process 4 intersects the system boundary.

For a thermodynamic system, the following equations hold:

$$\sum_{i} \Delta H_{i} = 0 \quad \text{(The first law of thermodynamics)} \tag{3}$$

 $\sum_{j} \Delta S_{j} \ge 0$ (The second law of thermodynamics) (4)



Figure 3. Assembly of processes

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Biographical Sketch

Masaru Ishida is Director and Professor at the Chemical Resources Laboratory, Tokyo Institute of Technology, Japan. He received a Diploma in Chemical Engineering from Tokyo Institute of Technology in 1964, then performed graduate studies in chemical engineering with a major in fluidization technology at Tokyo Institute of Technology, leading to the M.Sc. degree (1966) and Dr.Eng. degree (1969). He joined the Research Laboratory of Resources Utilization as a faculty member in 1969, and lectured on environmental process system design in undergraduate and graduate courses.

His research activity is related to process system analysis and synthesis, evaluation of energy systems, design and operation of energy systems such as power plants and cogeneration systems, analysis of chemical plants, development of new separation systems such as sandwiched recycle chromatography,

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