

**Textbook:** J. M. Smith, H. C. Van Ness, M.M. Abbott, **Introduction to Chemical Engineering Thermodynamics**, Seventh Edition, McGraw-Hill International Editions, 2005.

### **Supplementary References**

Stanley I. Sandler, **Chemical and Engineering Thermodynamics**, Third edition John Wiley & Sons Inc, 1998.

J. Richard Elliott, Carl T. Lira, **Introductory Chemical Engineering Thermodynamics**, 2nd edition Prentice Hall International Series in the Physical and Chemical Engineering Sciences, 1999.

# Thermodynamic Analysis of Processes

The object of this chapter is the evaluation of processes from the thermodynamic point of view.

**No new fundamental ideas** are needed; a combination of **the first and second laws** provides the basis. Hence, the chapter affords a review of thermodynamic principles.

**Real irreversible processes** are amenable to thermodynamic analysis. The goal of such an analysis is to determine how efficiently energy is used or produced and to show quantitatively the effect of inefficiencies in each step of a process.

**The cost of energy** is of concern in any manufacturing operation, and **the first step** in any attempt to reduce energy requirements is to determine where and to what extent energy is wasted through process irreversibilities.

The treatment here is limited to **steady-state flow processes**, because of their predominance in industrial practice.

## Calculation of Ideal Work

**In any steady-state flow process** requiring work, there is an absolute minimum amount which must be expended to accomplish the desired change of state of the fluid flowing through the control volume.

**In a process producing work**, there is an absolute maximum amount which may be accomplished as the result of a given change of state of the fluid flowing through the control volume. In either case the limiting value obtains when the change of state associated with the process is accomplished *completely reversibly*. The implications of this requirement, listed in Chap. 7 in connection with Eq. (7.19), are repeated here:

- 1. The process is internally reversible within the control volume.**
- 2. Heat transfer external to the control volume is reversible.**

The second item means that heat transfer between the control volume and its surroundings must occur at the temperature of the surroundings.

We presume that the control volume exists in surroundings that constitute a heat reservoir at a constant and **uniform temperature denoted by  $T_\sigma$** . In many cases **Carnot engines** or **heat pumps** must be presumed present so as to provide for the reversible transfer of heat between temperatures at the control surface and the temperature  **$T_\sigma$  of the surroundings**. Since **Carnot engines** and **heat pumps** are cyclic, they undergo no **net change of state**.

For any completely reversible process, **the entropy generation is zero**, and Eq. (7.20), written for the uniform surroundings temperature  $T_\sigma$ , becomes

$$\Delta(S\dot{m})_{fs} = \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} + \dot{S}_{G,\text{total}}$$

$$\dot{Q} = T_\sigma \Delta(S\dot{m})_{fs}$$

**Substituting for  $\dot{Q}$**  in the energy balance given by Eq. we

$$\Delta \left[ \left( \mathbf{H} + \frac{1}{2} \mathbf{u}^2 + \mathbf{g}z \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s$$

and

$$\Delta \left[ \left( H + \frac{1}{2} u^2 + gz \right) \dot{m} \right]_{\text{fs}} = T_{\sigma} \Delta(S \dot{m})_{\text{fs}} + \dot{W}_s(\text{rev})$$

where  $\dot{W}_s(\text{rev})$  **indicates that the shaft work** is for a completely reversible process. We call this work **the ideal work**,  $\dot{W}_{\text{ideal}}$ . Thus

$$\Delta \left[ \left( H + \frac{1}{2} u^2 + gz \right) \dot{m} \right]_{\text{fs}} - T_{\sigma} \Delta(S \dot{m})_{\text{fs}} = \dot{W}_{\text{ideal}}$$

In most applications to chemical processes, **the kinetic- and potential- energy terms** are negligible compared with the others;

$$\boxed{\Delta(H \dot{m})_{\text{fs}} - T_{\sigma} \Delta(S \dot{m})_{\text{fs}} = \dot{W}_{\text{ideal}}}$$

For the special case of a single stream flowing through **the control volume**, Eq. becomes

$$\dot{m}(\Delta H - T_{\sigma} \Delta S) = \dot{W}_{\text{ideal}}$$

**Division by  $\dot{m}$  puts** this equation on a unit-mass basis

$$\Delta H - T_{\sigma} \Delta S = W_{\text{ideal}}$$

A completely reversible process is **hypothetical**, devised solely for determination of the ideal work associated with a given change of state.

$$\dot{W}_{\text{ideal}} < \dot{W}_s \text{ or } (W_{\text{ideal}} < W_s)$$

$$\eta_t (\text{work required}) = \frac{\dot{W}_{\text{ideal}}}{\dot{W}_s}$$

**When  $\dot{W}_{\text{ideal}}$  (or  $W_{\text{ideal}}$ ) is negative,  $|\dot{W}_{\text{ideal}}|$  is the *maximum work obtainable* from a given change in the properties of the flowing streams, and is larger than  $|\dot{W}_s|$ . In this case, the thermodynamic efficiency is defined as the ratio of the actual work to the ideal work:**

$$\dot{W}_{\text{ideal}} > |\dot{W}_s| \text{ or } (W_{\text{ideal}} > |W_s|)$$

$$\eta_t (\text{work produced}) = \frac{\dot{W}_{\text{sl}}}{\dot{W}_{\text{ideal}}}$$

## Lost work

Work that is wasted as the result of irreversibilities in a process is called *lost work*,  $W_{\text{lost}}$ , and is defined as the difference between the actual work of a process and the ideal work for the process. Thus by definition,

$$W_{\text{lost}} \equiv W_s - W_{\text{ideal}}$$

**In terms of rates this is written**

$$\dot{W}_{\text{lost}} \equiv \dot{W}_s - \dot{W}_{\text{ideal}}$$

### The actual work

$$\dot{W}_s = \Delta \left[ \left( H + \frac{1}{2} u^2 + gz \right) \dot{m} \right]_{\text{fs}} - \dot{Q}$$

### The ideal work rate

$$\Delta \left[ \left( H + \frac{1}{2} u^2 + gz \right) \dot{m} \right]_{\text{fs}} - T_\sigma \Delta(S\dot{m})_{\text{fs}} = \dot{W}_{\text{ideal}}$$

### The difference between these two equations gives

$$\dot{W}_{\text{lost}} = \Delta \left[ \left( H + \frac{1}{2} u^2 + gz \right) \dot{m} \right]_{\text{fs}} - \dot{Q} - \Delta \left[ \left( H + \frac{1}{2} u^2 + gz \right) \dot{m} \right]_{\text{fs}} + T_\sigma \Delta(S\dot{m})_{\text{fs}}$$

$$\boxed{\dot{W}_{\text{lost}} = T_\sigma \Delta(S\dot{m})_{\text{fs}} - \dot{Q}}$$

$$\dot{W}_{\text{lost}} = T_{\sigma} \dot{S}_{G,\text{total}}$$

Since **the second law of thermodynamics** requires that  $\dot{S}_{G,\text{total}} \geq 0$ , it follows that  $\dot{W}_{\text{lost}} \geq 0$ . When a process is completely reversible, the equality holds, and the lost work is zero. **For irreversible processes** the inequality holds, and the lost work, i.e., the energy that becomes unavailable for work, is positive.

The engineering significance of this result is clear: **The greater the irreversibility** of a process, **the greater the rate of entropy** production and **the greater the amount of energy** that becomes unavailable for work. Thus every irreversibility carries with it a price.



# Thermodynamic Analysis of Steady-State Flow Processes

Many processes consist of a number of steps, and lost-work calculations are then made for each step separately. ]

$$\dot{W}_{\text{lost}} = T_{\sigma} \dot{S}_{G,\text{total}}$$

Summing over the steps of a process gives

$$\sum \dot{W}_{\text{lost}} = T_{\sigma} \sum \dot{S}_{G,\text{total}}$$

Dividing the former equation by the latter yields

$$\frac{\dot{W}_{\text{lost}}}{\sum \dot{W}_{\text{lost}}} = \frac{\dot{S}_{G,\text{total}}}{\sum \dot{S}_{G,\text{total}}}$$

Thus an analysis of **the lost work**, made by calculation of the fraction that each individual **lost-work term represents of the total lost work**, is the same as an analysis of the rate of entropy generation, made by expressing each individual entropy-generation term as a fraction of the sum of all entropy-generation terms.

**An alternative to the lost-work or entropy-generation analysis is a **work analysis**.**

$$\sum \dot{W}_{\text{lost}} = \dot{W}_s - \dot{W}_{\text{ideal}}$$

**For a work-requiring process**, all of these work quantities are **positive** and  $\dot{W}_s > \dot{W}_{\text{ideal}}$ . We therefore write the preceding equation as

$$\dot{W}_s = \dot{W}_{\text{ideal}} + \sum \dot{W}_{\text{lost}}$$

A work analysis then expresses each of the individual work terms in the summation on the right as a fraction of  $\dot{W}_s$ .

**For a work producing process**,  $\dot{W}_e$  and  $\dot{W}_{\text{ideal}}$  are negative, and  $|\dot{W}_{\text{ideal}}| > |\dot{W}_s|$ .

$$|\dot{W}_{\text{ideal}}| = |\dot{W}_s| + \sum \dot{W}_{\text{lost}}$$

**A work analysis** here expresses each of **the individual work terms** on the right as a fraction of  $|\dot{W}_{\text{ideal}}|$ . A work analysis cannot be carried out in the case where a process is so inefficient that  $\dot{W}_{\text{ideal}}$  is **negative**, indicating that the process should produce work, but  $\dot{W}_s$  is **positive**, indicating that the process in fact requires work. **A lost-work or entropy-generation analysis** is always possible.