

CEN 202 THERMODYNAMICS

CHAPTER 5: THE SECOND LAW OF THERMODYNAMICS

TEXT BOOK: : J. M. SMITH, H. C. VAN NESS, M. M. ABBOTT, M. T. SWIHART. "INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS", EIGHTH EDITION. 2018

ENTROPY BALANCE FOR OPEN SYSTEMS

Just as an energy balance is written for processes in which fluid enters, exits, or flows through a control volume, therefore an entropy balance may be written. There is, however, an important difference: **Entropy is not conserved.**

Entropy:

- one for the difference in entropy between exit and entrance streams,
- one for entropy change within the control volume,
- and one for entropy change in the surroundings.

If the process is **reversible**, these three terms sum to zero, making $\Delta S_{\text{total}} = 0$.

If the process is **irreversible**, they sum to a positive quantity, the entropy-generation term.

The statement of balance, expressed as rates, is therefore:

ENTROPY BALANCE FOR OPEN SYSTEMS

$$\left\{ \begin{array}{l} \text{Time rate of} \\ \text{change of} \\ \text{entropy} \\ \text{in control} \\ \text{volume} \end{array} \right\} + \left\{ \begin{array}{l} \text{Net rate of} \\ \text{change in} \\ \text{entropy of} \\ \text{flowing streams} \end{array} \right\} + \left\{ \begin{array}{l} \text{Time rate of} \\ \text{change of} \\ \text{entropy in} \\ \text{surroundings} \end{array} \right\} = \left\{ \begin{array}{l} \text{Total rate} \\ \text{of entropy} \\ \text{generation} \end{array} \right\}$$

The equivalent **equation of entropy balance** is

$$\frac{d(mS)_{cv}}{dt} + \Delta(S\dot{m})_{fs} + \frac{dS_{surr}^t}{dt} = \dot{S}_G \geq 0$$

(15)

where \dot{S}_G is the rate of entropy generation. This equation is the general rate form of the entropy balance, applicable at any instant.

ENTROPY BALANCE FOR OPEN SYSTEMS

Let rate of heat transfer \dot{Q}_j with respect to a particular part of the control surface be associated with $T_{\sigma,j}$ where subscript σ,j denotes a temperature in the surroundings. The rate of entropy change in the surroundings as a result of this transfer is then $-\frac{\dot{Q}_j}{T_{\sigma,j}}$. The minus sign converts \dot{Q}_j , defined with respect to the system, to a heat transfer rate with respect to the surroundings. The third term in Eq. (15) is therefore the sum of all such quantities:

$$\frac{dS_{surr}^t}{dt} = - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}}$$

Equation given above is now written:

$$\frac{d(mS)_{cv}}{dt} + \Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0$$

(16)

The final term, representing the rate of entropy generation \dot{S}_G , reflects the second-law requirement that it be positive for irreversible processes.

ENTROPY BALANCE FOR OPEN SYSTEMS

There are two sources of irreversibility:

(a) those within the control volume, i.e., **internal irreversibilities**, and (b) those resulting from heat transfer across finite temperature differences between system and surroundings, i.e., **external thermal irreversibilities**.

For a steady-state flow process the mass and entropy of the fluid in the control volume are constant, and $d(mS)_{cv}/dt$ is zero. Equation (16) then becomes:

$$\Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \quad (17)$$

If in addition there is but one entrance and one exit, \dot{m} is the same for both streams, and dividing through by \dot{m} yields:

$$\Delta S - \sum_j \frac{Q_j}{T_{\sigma,j}} = S_G \geq 0 \quad (18)$$

CALCULATION OF IDEAL WORK

In any steady-state flow process requiring work, an absolute minimum amount of work is required to produce the desired change of state in the fluid flowing through the control volume.

In a process producing work, an absolute maximum amount of work can be realized from a given change of state of the fluid flowing through the control volume. **In either case, the limiting value results when the change of state associated with the process is accomplished completely reversibly.** For such a process, **the entropy generation is zero**, written for a uniform surroundings temperature T_σ , becomes:

$$\Delta(S\dot{m})_{fs} - \frac{\dot{Q}}{T_\sigma} = 0 \quad \text{or} \quad \dot{Q} = T_\sigma \Delta(S\dot{m})_{fs}$$

Substituting this expression for \dot{Q} in the energy balance :

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

The shaft work, $\dot{W}_s (rev)$, is here the **work of a completely reversible process**. If $\dot{W}_s (rev)$ is given the name **ideal work**, \dot{W}_{ideal} , the preceding equation may be rewritten:

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

CALCULATION OF IDEAL WORK

In most applications to chemical processes, the kinetic- and potential-energy terms are negligible compared with the others; in this event Eq. (19) reduces to:

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

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

The sole connection between an actual process and an imagined hypothetical reversible process employed for determining **ideal work** is that they both apply to the same changes of state.

Our objective is to compare the actual work of a process \dot{W}_s (or W_s) and the ideal work \dot{W}_{ideal} (or W_{ideal}).

CALCULATION OF IDEAL WORK

When \dot{W}_{ideal} (or W_{ideal}) is **positive**, it is the minimum work required to bring about a given change in the properties of the flowing streams, and is **smaller than** \dot{W}_s . In this case a thermodynamic efficiency η_t is defined as the ratio of the ideal work to the actual work:

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

When \dot{W}_{ideal} (or W_{ideal}) is **negative**, $|\dot{W}_{ideal}|$ 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:

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

LOST WORK

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

$$W_{lost} \equiv W_s - W_{ideal} \quad (25)$$

In terms of rates,

$$\dot{W}_{lost} \equiv \dot{W}_s - \dot{W}_{ideal} \quad (26)$$

The **actual work** rate comes from the energy balance and the **ideal work** rate is obtained using Eq. (19):

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

LOST WORK

By difference, as given by Eq. (5.26),

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

For the case of a single surroundings temperature T_{σ} , the steady-state entropy balance, Eq. (17), becomes:

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

Multiplication by T_{σ} gives:

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

The right sides of this equation and Eq. (27) are identical; therefore,

$$\dot{W}_{lost} = T_{\sigma} \dot{S}_G$$