Lecture 1

Separation processes. Thermodynamics of separation operations

Most industrial separation operations utilize large quantities of energy in the form of heat and/or shaft work. A study by Mix et al. reports that two quads (1 quad = 10^{15} Btu) of energy were consumed by distillation separations in petroleum, chemical, and natural-gas processing plants in the United States in 1976. This amount of energy was 2.7% of the total U.S. energy consumption of 74.5 quads and is equivalent to the energy obtained from approximately .1 million bbl of crude oil per day over a one-year period. This amount of oil can be compared to 13 million bbllday, the average amount of crude oil processed by petroleum refineries in the United States in early 1991. At a crude oil price of approximately \$40/bbl, the energy consumption by distillation in the United States is approximately \$20 trillion per year. Thus, it is of considerable interest to know the extent of energy consumption in a separation process, and to what degree energy requirements might be reduced. Such energy estimates can be made by applying the first and second laws of thermodynamics.

Consider the continuous, steady-state, flow system for a general separation process in Figure 1.
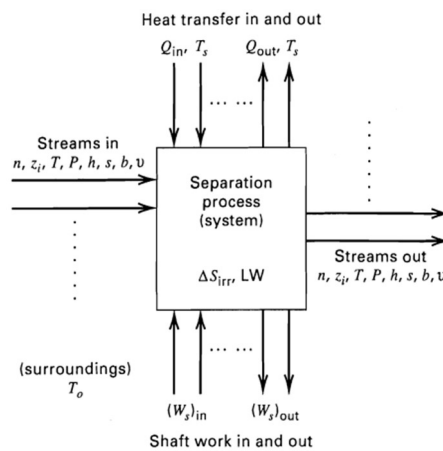

Figure 1 - General separation system

One or more feed streams flowing into the system are separated into two or more product streams that flow out of the system. For all these streams, we denote the molar flow rates by n, the component mole fractions by z_i, the temperature by T, the pressure by P, the molar enthalpies by h, the molar entropies by s, and the molar availabilities by b. If chemical reactions occur in the process, enthalpies and entropies are referred to the elements, as discussed by Felder and Rousseau; otherwise they can be referred to the compounds. Heat flows in or out of the system are denoted by Q, and shaft work crossing the boundary of the system is denoted by Ws. At steady state, if lunetic, potential, and surface energy changes are neglected, the first law of thermodynamics (also referred to as the conservation of energy or the

energy balance), states that the sum of all forms of energy flowing into the system equals the sum of the energy flows leaving the system:

(stream enthalpy flows + heat transfer + shaft work)$_{\text{leaving system}}$ - (stream enthalpy flows + heat transfer + shaft work)$_{\text{entering system}} = 0$

In terms of symbols, the energy balance is given by Eq. (1) in Table 1, where all flow rate, heat transfer, and shaft work terms are positive. Molar enthalpies may be positive or negative depending on the reference state.

Table 1 - Universal Thermodynamic Laws for a Continuous, Steady-State, Flow System

Energy balance:

$$(1) \sum_{\substack{\text{out of} \\ \text{system}}} (nh + Q + W_s) - \sum_{\substack{\text{in to} \\ \text{system}}} (nh + Q + W_s) = 0$$

Entropy balance:

$$(2) \sum_{\substack{\text{out of} \\ \text{system}}} \left(ns + \frac{Q}{T_s}\right) - \sum_{\substack{\text{in to} \\ \text{system}}} \left(ns + \frac{Q}{T_s}\right) = \Delta S_{\text{irr}}$$

Availability balance:

$$(3) \sum_{\substack{\text{in to} \\ \text{system}}} \left[nb + Q\left(1 - \frac{T_0}{T_s}\right) + W_s\right]$$
$$- \sum_{\substack{\text{out of} \\ \text{system}}} \left[nb + Q\left(1 - \frac{T_0}{T_s}\right) + W_s\right] = LW$$

Minimum work of separation:

$$(4) W_{\min} = \sum_{\substack{\text{out of} \\ \text{system}}} nb - \sum_{\substack{\text{in to} \\ \text{system}}} nb$$

Second-law efficiency:

$$(5) \eta = \frac{W_{\min}}{LW + W_{\min}}$$

where $b = h - T_0 s$ = availability function
$LW = T_0 \Delta S_{\text{irr}}$ = lost work

All separation processes must satisfy the energy balance. Inefficient separation processes require large transfers of heat andlor shaft work both into and out of the process; efficient processes require smaller levels of heat transfer and/or shaft work. The first law of thermodynamics provides no information on energy efficiency, but the second law of thermodynamics (also referred to as the entropy balance), given by Eq. (2) in Table 2.1, does. In words, the steady-state entropy balance is

(Stream entropy flows 1 + entropy flows by heat transfer)$_{\text{leaving system}}$ - (stream entropy flows + entropy flows by heat transfer)$_{\text{entering system}}$ = production of entropy by the process

In the entropy balance equation, the heat sources and sinks in Figure 1 are at absolute temperatures T_s. For example, if condensing steam at 150°C supplies heat, Q, to the reboiler of a distillation column, $T_s = 150 + 273 = 423$ K. If cooling water

at an average temperature of 30°C removes heat, Q, in a condenser, $T_s = 30 + 273 = 303$ K. Unlike the energy balance, which states that energy is conserved, the entropy balance predicts the production of entropy, ΔS_{irr} which is the irreversible increase in the entropy of the universe. This term, which must be a positive quantity, is a quantitative measure of the thermodynamic inefficiency of a process. In the limit, as a reversible process is approached, ΔS_{irr} tends to zero. Note that the entropy balance contains no terms related to shaft work.

Although ΔS_{irr} is a measure of energy inefficiency, it is difficult to relate to this measure because it does not have the units of energy/time (power). A more useful measure or process inefficiency can be derived by combining (1) and (2) in Table 1 to obtain a combined statement of the first and second laws of thermodynamics, which is given as (3) in Table 1. To perform this derivation, it is first necessary to define an infinite source of or sink for heat transfer at the absolute temperature, $T_s = T_0$ of the surroundings. This temperature is typically about 300 K and represents the largest source of coolant associated with the processing plant being analyzed. This might be the average temperature of cooling water, air, or a nearby river, lake, or ocean. Heat transfer associated with this surrounding coolant and transferred from (or to) the process is termed Q_0. Thus, in both (1) and (2) in Table 1, the Q and Q/Ts terms include contributions from Q_0 and Q_0/T_0, respectively.

The derivation of (3) in Table 1 can be made, as shown by de Nevers and Seader, by combining (1) and (2) to eliminate Q_0. The resulting equation is referred to as an availability (or exergy) balance, where the term availability means "available for complete conversion to shaft work."

First law:

$$Q_{in} = W_s + Q_{out}$$

Second law:

$$\frac{Q_{in}}{T_s} = \frac{Q_{out}}{T_0}$$

Combined first and second laws (to eliminate Q_{out}):

$$W_s = [1 - (T_0/T_s)]\, Q_{in}$$

$T = T_s$
$Q = Q_{in}$

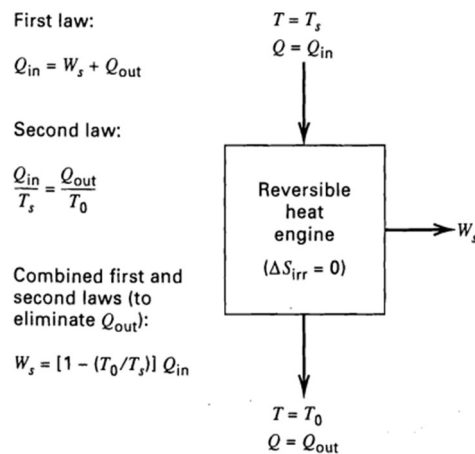Reversible heat engine ($\Delta S_{irr} = 0$)

W_s

$T = T_0$
$Q = Q_{out}$

Figure 2 - Carnot heat engine cycle for converting heat to shaft work