The ChemSep Book

Harry A. Kooijman
Consultant

Ross Taylor
Clarkson University, Potsdam, New York
University of Twente, Enschede, The Netherlands

13.1.7 Enthalpy

The mixture enthalpy can be calculated from the component enthalpies with:

$$H = \sum_{i=1}^{c} z_i H_i \tag{13.1}$$

where z_i is the mole fraction of species i in the phase in question. The component enthalpy may be expressed as the sum of the ideal contribution and an excess enthalpy:

$$H_i = H_i^{id} + H_i^{ex} \tag{13.2}$$

where H_i^{ex} is the excess enthalpy and H_i^{id} is the ideal contribution. The ideal gas enthalpy of component i is given by:

$$H_i^{g,id} = \int_{T_0}^{T} C_{p,i}^{g,id} dT + H_{form,i}^{298K} \tag{13.3}$$

where $C_{p,i}^{id}$ is the ideal gas heat capacity of component i, T_0 is a reference temperature, $H_{form,i}^{298K}$ the enthalpy of formation at 298 K, and T is the actual temperature at which the enthalpy is to be calculated Note that there is no composition dependence in the ideal gas enthalpy! The enthalpy of formation are only included when reactions are present. This is done because the enthalpies of formation are large compared to the other contributions and this makes the enthalpy balance less accurate. Also note that enthalpies are computed relative to a reference point, 0, and are not absolute! Normally, this reference point for the enthalpy in **ChemSep** is chosen as an ideal gas at 298 K. However, the reference state and temperature as well as the inclusion of heat of formations can be changed in the "References" menu under the properties selection.

For liquids, the latent heat of vaporization is subtracted from the ideal gas enthalpy:

$$H_i^{l,id} = H_i^{g,id} - \Delta H_i^{vap} \tag{13.4}$$

where ΔH_i^{vap} is computed with a temperature correlation (see the section on physical properties below) or, if no correlation parameters are known, using the method of Pitzer *et al.*:

$$\Delta H_i^{vap} = RT_{c,i}(7.08(1 - T_{r,i})^{0.354} + 10.95(1 - T_{r,i})^{0.456}\omega_i) \tag{13.5}$$

If an equation of state model is used for the K-values in **ChemSep**, the excess enthalpy of both phases is calculated from an equation of state as follows:

$$H_i^{ex} = -RT^2 \left(\frac{\partial \ln \phi_i}{\partial T} \right) \tag{13.6}$$

If an activity coefficient model is used for the liquid phase, then the component excess enthalpy is computed from:

$$H_i^{ex} = -RT^2 \left(\frac{\partial \ln \gamma_i}{\partial T} \right) \tag{13.7}$$

ChemSep incorporates the following methods for estimating the enthalpy:

None No enthalpy balance is used in the calculations. WARNING: the use of this model with subcooled and superheated feeds or for columns with heat addition or removal on some of the stages will give incorrect results. The heat duties of the condenser and reboiler will be reported as zero since there is no basis for calculating them.

Ideal (B152) In this model the enthalpy is computed from the ideal gas contribution and the excess enthalpy is assumed to be zero.

Excess (B518) This model includes the ideal enthalpy as above. The excess enthalpy is calculated from the activity coefficient model or the temperature derivative of the fugacity coefficients dependent on the choice of the model for the K-values, and is added to the ideal part.

Polynomial vapor as well as liquid enthalpy are calculated as functions of the absolute temperature (K). Both the enthalpies use the following function:

$$H_i = A_i + B_i T + C_i T^2 + D_i T^3 \tag{13.8}$$

You must enter the coefficients A through D in the 'Load Data' option of the Properties menu for vapor and liquid enthalpy for each component.

13.1.8 Entropy

The mixture entropy can be calculated from the component entropies in a similar manner as the enthalpy:

$$S = \sum_{i=1}^{c} z_i S_i \tag{13.9}$$

where z_i is the mole fraction of species i in the phase in question. The component entropy may be expressed as the sum of the component entropy plus the contributions of ideal and excess mixing entropy:

$$S_i = S_i^{id} + S_i^{ex} \tag{13.10}$$

where S_i^{ex} is the excess entropy and S_i^{id} is the ideal contribution for component i. The ideal gas entropy of component i is given by:

$$S_i^{id,g} = S_{0,i} + \int_{T_0}^{T} \frac{C_{p,i}^{g,id}}{T} dT - R \ln \left(\frac{p}{p_0} \right) - R \ln z_i \qquad (13.11)$$

where $C_{p,i}^{id}$ is the ideal gas heat capacity of component i, T_0 is the reference temperature, p_0 the reference pressure, $S_{0,i}$ the absolute entropy of component i at T_0 and p_0, z_i the mole fraction of i, and T and p are the actual temperature and pressure at which the entropy is to be calculated. The reference point for entropy is fixed at 298 K and 1 atm because the absolute component entropies are defined at this temperature and pressure. These component absolute entropies are stored in the pure component database. For the ideal liquid entropy we subtract the entropy of vaporization:

$$S_i^{id,l} = S_i^{id,g} - \frac{\Delta H_{vap,i}}{T_{boil}} \qquad (13.12)$$

where $\Delta H_{vap,i}$ is the vaporizations enthalpy of component i at T_{boil}, the component normal boiling temperature. Excess mixture entropies are computed with

$$S_i^{ex} = -R \left(T \frac{\partial \ln \gamma_i}{\partial T} + \ln \gamma_i \right) \qquad (13.13)$$

when an activity coefficient model is used. If an equation of state is used γ_i is replaced by ϕ_i, the fugacity coefficient of i.

13.1.9 Exergy

The exergy (Ex) of a mixture or stream can be calculated from the enthalpy and entropy with

$$\mathsf{Ex} = H - T_{surr} S \qquad (13.14)$$

where T_{surr} is the surroundings temperature of the process (this temperature is normally set to 298 K but can be changed under the "References" menu in the properties selection). Note that with the inclusion of the enthalpy, the exergy in **ChemSep** is also a relative quantity with respect to the enthalpy reference point.

Exergy is sometimes also referred to as "availability", it indicates the work that can be extracted from a stream that is brought to equilibrium with its surrounding state. Therefore, exergies provide useful insights in the thermodynamic efficiency of processes. The second law of thermodynamics states that for any real, irreversal process there is a nett entropy production (ΔS_{irr}), for which work (either direct or indirect in the form of exergy) is lost. The lost work equals $T_o \Delta S_{irr}$ and the higher this amount relative to the work/exergy input, the lower is the thermodynamic efficiency.