

Enthalpy balance

It is a generalized concept of the First theorem of thermodynamics applied to flow systems.

Total energy balance:

$$\dot{E}_1 + \dot{Q} + \dot{W} = \dot{E}_2 + \frac{dE_S}{d\tau}$$

where

$$\dot{E} = \dot{U} + \dot{E}_{kin} + \dot{E}_{pot}$$

$$\dot{W} = P + (p_1\dot{V}_1 - p_2\dot{V}_2)$$

U ... internal energy

E_{kin} ... kinetic energy

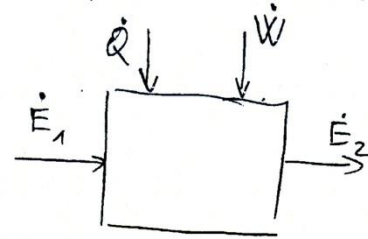
E_{pot} ... potential energy

W ... work

P ... power input

pV ... flow work done by the pressure force as it pushes the volume of the fluid through the input and output

Q ... heat



Remark: in a closed system where kinetic and potential energy is neglected we recover 1st theorem of thermodynamics $\dot{Q} + \dot{W} = \frac{dU}{d\tau}$ or $Q + W = \Delta U$

We are interested here mainly with heat and then **kinetic** and **potential** energies and power **can be neglected**, $E_{kin} = E_{pot} = P = 0$

Also we assume steady state $\rightarrow \frac{dE_S}{d\tau} = 0$

Therefore the energy balance becomes:

$$\dot{U}_1 + p_1\dot{V}_1 + \dot{Q} = \dot{U}_2 + p_2\dot{V}_2$$

$$\dot{H}_1 + \dot{Q} = \dot{H}_2$$

This equation seems to calculate heat flow Q and from that we can calculate heat-exchange area (see later)

Evaluation of \dot{H} :

$$\dot{H} = \dot{m}h = \dot{n}h$$

h ... specific enthalpy (per unit of mass) [J/kg]

\underline{h} ... molar enthalpy [J/mol]

h (or \underline{h}) is calculated as follows:

$$h = \sum x_i h_i + \Delta h_{mix} \quad , x_i \dots \text{molar fraction of component } i$$

$$\underline{h} = \sum w_i \underline{h}_i + \Delta \underline{h}_{mix} \quad , w_i \dots \text{mass fraction of component } i$$

where enthalpies of pure components are:

$$h_i = \int_{t_{ref}}^t c_{p,i} dt + \sum_{\substack{\text{phase} \\ \text{changes}}} \Delta h_{i, \text{phase change}} \doteq \langle c_{p,i} \rangle (t - t_{ref}) + \sum_{\substack{\text{phase} \\ \text{changes}}} \Delta h_{i, \text{phase change}}$$

$$\langle c_{p,i} \rangle \dots \text{average thermal capacity evaluated at } t = \frac{t + t_{ref}}{2}$$

Typical reference temperature is $t_{ref} = 0 \text{ } ^\circ\text{C}$

relation between \underline{h}_i and h_i :

$$h_i = M_i \underline{h}_i \quad , M_i \dots \text{molar mass of component } i$$

Remarks:

- 1) If chemical reactions take place, then enthalpy of formation Δh_i must be added to h_i (useful only for chemical reactors)
- 2) $c_{p,i}$ can be found in Tables, as well as the mixing enthalpy Δh_{mix} and the enthalpy of phase change

More detailed description of enthalpy balance with and without chemical reaction

General enthalpy balance in a system with more **inputs/outputs** with **heat input** and with **accumulation** is

$$\sum_j^{\substack{\text{inputs} \\ \text{+initial}}} H_j + Q = \sum_j^{\substack{\text{outputs} \\ \text{+final}}} H_j$$

Heat Q represents a **non-material input**, H_j refers to enthalpy carried in and out by mass/moles plus enthalpy in the system at the beginning and at the end.

H_j can be expressed as $H_j = n_j h_j$ or $H_j = m_j \underline{h}_j$

Let us take the moles as basis:

$$\text{- the molar enthalpy: } h_j = \sum_i^{\text{species}} x_{i,j} h_{i,j} + \Delta h_{j,mix} = \sum_i^{\text{species}} x_{i,j} (\Delta h_{i,j} + h_{i,j}^{ref}) + \Delta h_{j,mix}$$

For simplicity, we will assume now **ideal mixtures**, that is $\Delta h_{j,mix} = 0$

Crucial point is the definition of the reference (molar) enthalpy $h_{i,j}^{ref}$:

- (i) For systems **without** any **chemical reaction** we can choose $h_{i,j}^{ref} = 0$
- (ii) For system **with chemical reactions** (molar) **enthalpy of formation** at standard conditions (denoted by upper script = 0)

$$h_{i,j}^{ref} = h_{i,j}^{f,0}$$

This **standard enthalpy of formation** can be found in tables (usually at $t_0 = 25\text{ }^\circ\text{C}$). It is the enthalpy of formation of a component out of elements in their most stable form at standard pressure and temperature

For $\Delta h_{i,j}$ we can write

$\Delta h_{i,j}$ = contribution due to temperature change + contribution to phase change

$$\Delta h_{i,j} = \underbrace{\int_{t_{ref}}^t c_p dt}_{\langle c_p \rangle (t - t_{ref})} + (\Delta h_{vap} \text{ or } \Delta h_{cond} \text{ or } \Delta h_{melt} \text{ etc.})$$

Remark: a possible pressure contribution can be neglected

In practice the choice of the reference temperature is as follows

- (i) $t_{ref} = 0\text{ }^\circ\text{C}$... particularly if no chemical reaction takes place
- (ii) $t_{ref} = 25\text{ }^\circ\text{C}$... when chemical reactions take place because tabular values of are often at
- (iii) t_{ref} = temperature of the input stream if there is only one. Then $h_{input} = 0$

The enthalpy balance now reads:

$$\sum_j^{inputs + init} \sum_j n_j x_{i,j} (\Delta h_{i,j} - \Delta h_{i,j}^{f,0}) + Q = \sum_j^{outputs + final} \sum_j n_j x_{i,j} (\Delta h_{i,j} - \Delta h_{i,j}^{f,0})$$

It is convenient to use molar balances and thus simplify the enthalpy balance. The balance on moles of component are:

(i) **with the use of reaction extent**

$$\sum_j^{inputs + init} n_j x_{i,j} + \sum_j^{react.} v_{i,j} \xi_j = \sum_j^{outputs + final} n_j x_{i,j}$$

(ii) **with the use of fictitious streams**

$$\sum_j^{inputs + init} n_j x_{i,j} + \underbrace{\sum_j^{react.} n_j x_{i,j}}_{\substack{\text{generation of } i \\ = \text{product } i}} = \sum_j^{outputs + final} n_j x_{i,j} + \underbrace{\sum_j^{react.} n_j x_{i,j}}_{\substack{\text{consumption of } i \\ = \text{reactant } i}}$$

Now multiply molar balance of i by $h_{i,j}^{ref} = h_{i,j}^{f,0}$ and take sum over all components:

$$\sum_i \sum_j n_j x_{i,j} \Delta h_{i,j}^{f,0} + \sum_i \sum_j \Delta h_{i,j}^{f,0} v_{i,j} \xi_j = \sum_i \sum_j n_j x_{i,j} \Delta h_{i,j}^{f,0}$$

$$\sum_i \sum_j n_j x_{i,j} \Delta h_{i,j}^{f,0} + \underbrace{\sum_i \sum_j \Delta h_{i,j}^{f,0} n_j x_{i,j}}_{\substack{\text{fictitious streams} \\ \text{for all product}}} = \sum_i \sum_j n_j x_{i,j} \Delta h_{i,j}^{f,0} + \underbrace{\sum_i \sum_j \Delta h_{i,j}^{f,0} n_j x_{i,j}}_{\substack{\text{fictitious streams} \\ \text{for all reactants}}}$$

Subtracting each of the two equations from the enthalpy balance **cancels out terms with $\Delta h_{i,j}^{f,0}$** in input/initial and output/final streams and the net result is

(i) **the reaction extent version:**

$$\sum_j^{input+init} n_j \underbrace{\sum_i x_{i,j} \Delta h_{i,j}}_{\Delta h_j} + Q + \sum_j \xi_j \left(\underbrace{-\sum_i v_{i,j} \Delta h_{i,j}^{f,0}}_{-\Delta h_r} \right) = \sum_j^{output+final} n_j \underbrace{\sum_i x_{i,j} \Delta h_{i,j}}_{\Delta h_j}$$

Δh_j ... enthalpy carried by streams, which does not include (the mixing enthalpy can be now added)

Δh_r ... **reaction enthalpy** (molar)

$\Delta h_r > 0$... reaction consumes heat

$\Delta h_r < 0$... reaction produces heat

Notice that $(-\Delta h_r)$ is positive for heat producing (**exothermic**) reaction and negative for heat consuming (**endothermic**) reaction.

(ii) **the version with fictitious stream:**

$$\begin{aligned} \sum_j^{input+init} n_j \underbrace{\sum_i x_{i,j} \Delta h_{i,j}}_{\Delta h_j} + Q + \sum_j n_j \underbrace{\left(\sum_i (-\Delta h_{i,j}^{f,0}) x_{i,j} \right)}_{-\Delta h_j} \\ = \sum_j^{output+final} n_j \underbrace{\sum_i x_{i,j} \Delta h_{i,j}}_{\Delta h_j} + \sum_j n_j \underbrace{\left(\sum_i (-\Delta h_{i,j}^{f,0}) x_{i,j} \right)}_{-\Delta h_j} \end{aligned}$$

In practical calculations the work with e. balance using fictitious stream is very simple. First, the molar balances must be solved and then to each stream a molar enthalpy is assigned (including the fictitious pair of stream for each reaction) and the enthalpy balance is written and solved. Mostly the unknown is Q (easy to solve), sometimes the unknown is temperature of output streams (more difficult to solve).

Remark: For flow systems replace simply $H \rightarrow \dot{H}$ and $n \rightarrow \dot{n}$ (this works usually at **steady state**)