Equations for mass, energy, entropy and exergy

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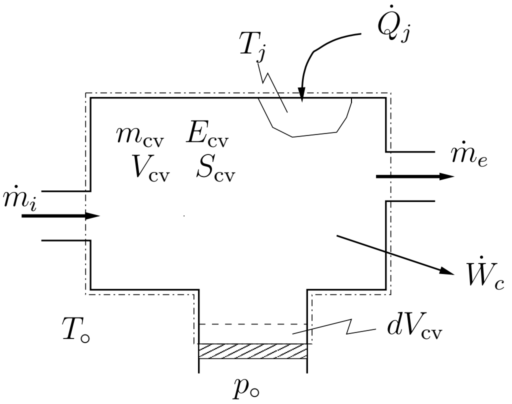
This note can be found at
http://folk.ntnu.no/ivarse/energi/balances_e.pdf

These equations are part of the syllabus because they can also be found in the textbook. The explanations can also be found there, e.g. Moran and Shapiro (2006).

1 Summary: Balances on rate form



The sketch shows a system with inflow and outflow (can be more), heat transfer into a region with temperature T_j ($j = 1, 2, \ldots$), volume change, and work done on an shaft or similar.
Some explanation of the equations and symbols will follow in later sections.

Mass balance:

$$\frac{dm_{\mathrm{cv}}}{dt} = \sum_{\text{inflow}} \dot{m}_i - \sum_{\text{outflow}} \dot{m}_e \tag{1}$$

Energy balance:

$$\frac{dE_{\mathrm{cv}}}{dt} = \sum_{\text{inflow}} \dot{m}_i(h_i + \tfrac{1}{2}\vec{V}_i^2 + gz_i) - \sum_{\text{outflow}} \dot{m}_e(h_e + \tfrac{1}{2}\vec{V}_e^2 + gz_e) + \dot{Q}_{\mathrm{cv}} - \dot{W}_{\mathrm{cv}} \tag{2}$$

$E_{\mathrm{cv}} = U_{\mathrm{cv}} + E_{\mathrm{kin,cv}} + E_{\mathrm{pot,cv}}$

Entropy balance:

$$\frac{dS_{\mathrm{cv}}}{dt} = \sum_{\text{inflow}} \dot{m}_i s_i - \sum_{\text{outflow}} \dot{m}_e s_e + \sum_j \int_{T_j} \frac{\delta \dot{Q}_j}{T_j} + \dot{\sigma}_{\mathrm{cv}} \tag{3}$$

Exergy balance:

$$\frac{d\mathcal{E}_{\mathrm{cv}}}{dt} = \sum_{\text{inflow}} \dot{m}_i \varepsilon_{f,i} - \sum_{\text{outflow}} \dot{m}_e \varepsilon_{f,e} + \sum_j \int_{T_j} \left(1 - \frac{T_\circ}{T_j}\right) \delta \dot{Q}_j - \left(\dot{W}_{\mathrm{cv}} - p_\circ \frac{dV_{\mathrm{cv}}}{dt}\right) - T_\circ \dot{\sigma}_{\mathrm{cv}} \tag{4}$$

$\mathcal{E}_{\mathrm{cv}} = (E - U_\circ)_{\mathrm{cv}} + p_\circ(V - V_\circ)_{\mathrm{cv}} - T_\circ(S - S_\circ)_{\mathrm{cv}} + \mathcal{E}^{\mathrm{ch}}_{\mathrm{cv}}$,
$\varepsilon_{f,i} = (h - h_\circ)_i - T_\circ(s - s_\circ)_i + \frac{1}{2}\vec{V}_i^2 + g(z - z_\circ)_i + \varepsilon^{\mathrm{ch}}_i$

List of symbols

Latin letters

E	energy (internal, kinetic, potential) [J]
e	$= E/m$, specific energy [J/kg]
$\mathcal{E}$	exergy [J]
$\mathcal{E}^{\mathrm{ch}}$	chemical exergy [J]
g	axeleration of gravity [m/s^2]
h	$= u + pv$, specific enthalpy [J/kg]
$h_\circ$	$= h(T_\circ, p_\circ)$
m	mass [kg]
$\dot{m}$	mass flow (rate) [kg/s]
p	pressure [Pa]
$p_\circ$	pressure of the environment [Pa]
Q_j	heat transferred to temperature T_j $(j = 1, 2, ...)$ [J]
$\dot{Q}_j$	rate of heat transferred to temperature T_j $(j = 1, 2, ...)$ [J/s]
S	entropy [J/K]
s	$= S/m$, specific entropy [J/(kgK)]
$s_\circ$	$= s(T_\circ, p_\circ)$
T	temperature [K]
$T_\circ$	temperature of the environment [K]
t	time [s]
U	internal energy [J]
u	$= U/m$, specific internal energy [J/kg]
$u_\circ$	$= u(T_\circ, p_\circ)$
$\vec{V}$	velocity (vector) [m/s]
V	volume [m^3]
v	$= V/m$, specific volume [m^3/kg]
$v_\circ$	$= v(T_\circ, p_\circ)$
W	work [J]
$\dot{W}$	rate of work (work rate) [J/s]
W_c, $\dot{W}_c$	work, rate of work conducted through an axle, shaft, rod, etc.
z	hight above reference level [m]

Greek letters

Δ	change
δ	small change, small quantity
ε	$= \mathcal{E}/m$, specific exergy [J/kg]
$\varepsilon^{\mathrm{ch}}$	$= \mathcal{E}^{\mathrm{ch}}/m$, specific chemical exergy [J/kg]

ε_f	specific exergy in flow of matter [J/kg]
$\dot{\sigma}$	rate of entropy production [J/(sK)]

Subscripts

cv	that pertains to the system (control volume)
e	pertains to otflow(s)
i	pertains to inflow(s)
$\circ$	pertains to state of the environment
kin	kinetic (of energy)
pot	potential (of energy)

2 Reformulation of the equations for state changes

The equations above are written on rate form. That is, the changes inside the CV and exchanges over its boundary are accounted per unit of time.

A change of state has a start and an end. A finite change from state (1) to state (2) takes place in the CV, and finite amounts of mass, energy, entropy and exergy are exchanged.

The math of the reformulation is more complex, but the following can be used as a rule of memory:

A derivative becomes a change: $\frac{d(\,)_{\text{cv}}}{dt} \quad \rightarrow \quad \Delta(\,)_{\text{cv}} = (\,)_{\text{cv},2} - (\,)_{\text{cv},1}$.

That is, what is there after the change minus what was there before the change.

For instance $\frac{dm_{\text{cv}}}{dt}$[kg/s] $\rightarrow \Delta m_{\text{cv}} = m_{\text{cv},2} - m_{\text{cv},1}$ [kg].

Flows/rates (exchange per unit of time) become finite quantities: $(\dot{\,}) \quad \rightarrow \quad (\,)$,
for instance $\dot{m}_i$[kg/s] $\rightarrow m_i$[kg], $\dot{Q}_j$[J/s] $\rightarrow Q_j$[J]

3 Terminology

Rate form: "Rate" is used for something that is taken or accounted per unit of time. "Mass rate" or "rate of mass" is mass per unit of time, "rate of heat" is heat (energy) per unit of time, etc.
Within the thermodynamics syllabus we usually keep the flows of mass and energy steady. When these flows varies with time, we have to deal carefully with the equations – although it can indeed be handled.

Change of state: We have a system that goes through a process such that at least one property is changed, for instance pressure, temperature, volume or mass. The process has a starting point (state, time) and an end point. This occurs over a finite time interval and finite amounts of mass and energy are exchanged.

System an **control volume**: The usage of these two terms shows some variation in textbooks and other literature, and among scientists – an no-one has a monopoly of the "right". (Moran and Shapiro give their version in Sec. 1.2).
A simple approach is to say that we define a **system boundary** (control-volume boundary, control surface). What is inside, is the system (control volume, "CV"). This is a certain amount of matter, which has mass, energy and other properties. Mass and energy can be exchanged accross the boundary.

Types of systems:
The simplest classification is into open and closed systems. The latter do not exchange matter across the system boundary. A special case is the isolated system; where neither energy nor mass are exchanged over the boundary.

Like the forms of the equations above, we can distinguish between
– systems with stady change, where we account changes and exchanges per unit of time
– systems with change of state, that is, from start to end.
Both these types of systems can be open or closed.

Examples:
1) A heat exchanger, a combustion chamber and a turbine in steady operation are three examples of open systems with steady (often zero) changes and steady flows.
2) When air is compressed from the atmosphere into a container, we have a finite process with start and end, and the container will be an open system.
3) A closed container with gas that is heated from the outside will be a system with a finite process, that is, a change of state from start to end. This is a closed system.
4) For a steam cycle in steady operation, we can put the system boundary such that heat and work are exchanged over the boundary (heating surfaces in boiler and condenser), however, with no mass exchange. We then have closed system with steady changes and steady internal flows.

"Steady operation" can be an important specification. A turbine or heat exchanger in a start-up operation are not in steady operation but a process with a finite change. A car engine is rarely in steady operation, whereas a ship engine or a power plant (with some exeptions) usually are.

4 Mass balance

$$\underbrace{\frac{dm_{\text{cv}}}{dt}}_{(1)} = \underbrace{\sum_{\text{inflow}} \dot{m}_i}_{(2)} - \underbrace{\sum_{\text{outflow}} \dot{m}_e}_{(3)} \tag{5}$$

(1): temporal change (increase, storage) of mass in the control volume
(2): mass flow rate into the CV, sum of all inflows
(3): mass flow rate out of the CV, sum of all outflows

5 Energy balance

$$\underbrace{\frac{dE_{\text{cv}}}{dt}}_{(1)} = \underbrace{\sum_{\text{inflow}} \dot{m}_i(h_i + \tfrac{1}{2}\vec{V}_i^2 + gz_i)}_{(2)} - \underbrace{\sum_{\text{outflow}} \dot{m}_e(h_e + \tfrac{1}{2}\vec{V}_e^2 + gz_e)}_{(3)} + \underbrace{\dot{Q}_{\text{cv}}}_{(4)} - \underbrace{\dot{W}_{\text{cv}}}_{(5)} \tag{6}$$

(1): temporal change (increase, storage) of energy in the CV, cf. Eq. (7)
(2): rate of energy with the mass flow into the CV; enthalpy, kinetic and potential energy of the mass that crosses the system boundary, sum of all inflows
(3): rate of energy with mass flow out of the CV
(4): rate of heat transferred to the CV, cf. Eq. (9)
(5): rate of work conducted by the CV, cf. Eq. (8)

The energy inside the control volume can be written as internal energy, kinetic and potensial energy of the mass inside the CV:

$$E_{\text{cv}} = U_{\text{cv}} + E_{\text{kin,cv}} + E_{\text{pot,cv}} = m_{\text{cv}}(u + e_{\text{kin}} + e_{\text{pot}})_{\text{cv}} \tag{7}$$

The work is the sum of work through a shaft, rod or similar, $\dot{W}_c$, and the work against the environment (in order to "displace" the atmosphere at pressure $p_\circ$)

$$\dot{W}_{\text{cv}} = \dot{W}_c + p_\circ \frac{dV_{\text{cv}}}{dt} \tag{8}$$

The heat transferred is the sum of all heat transfers into the CV. When there is a temperature variation over a heat transfer surface, the heat transfer has to be integrated over this variation.

$$\dot{Q}_{\text{cv}} = \sum_j \dot{Q}_j = \sum_j \int_{T_j} \delta\dot{Q}_j \tag{9}$$

For the energy balance, we rarely have to think of the integration. It is included here since we need the corresponding term in the entropy balance (see below).

6 Entropy balance

$$\underbrace{\frac{dS_{\text{cv}}}{dt}}_{(1)} = \underbrace{\sum_{\text{inflow}} \dot{m}_i s_i}_{(2)} - \underbrace{\sum_{\text{outflow}} \dot{m}_e s_e}_{(3)} + \underbrace{\sum_j \int_{T_j} \frac{\delta\dot{Q}_j}{T_j}}_{(4)} + \underbrace{\dot{\sigma}_{\text{cv}}}_{(5)} \tag{10}$$

(1): temporal change (increase, storage) of entropy in the CV; $S_{\text{cv}} = m_{\text{cv}} s_{\text{cv}}$
(2): rate of entropy with the mass flow into the CV, sum of all inflows
(3): rate of entropy with the mass flow out of the CV, sum of all outflows
(4): rate entropy with all heat transfer (rate of heat) into the CV ($j = 1, 2, \ldots$)
(5): rate of entropy production inside the CV

If the temperature T_j varies and the heat exchange $\delta \dot{Q}_j$ varies with the temperature, we have to integrate the ratio $\delta \dot{Q}_j / T_j$ over this change. If there are more heat flows ($j = 1, 2, \ldots$), we have to sum their contributions.

7 Exergy balance

The exergy balance can be developed from the balances of energy, entropy and mass. This means that it does not provide anything new, and that it can replace one of the three others. In practice, we will choose between entropy and exergy.

$$\underbrace{\frac{d\mathcal{E}_{\text{cv}}}{dt}}_{(1)} = \underbrace{\sum_{\text{inflow}} \dot{m}_i \varepsilon_{f,i}}_{(2)} - \underbrace{\sum_{\text{outflow}} \dot{m}_e \varepsilon_{f,e}}_{(3)} + \underbrace{\sum_j \int_{T_j} \left(1 - \frac{T_\circ}{T_j}\right) \delta \dot{Q}_j}_{(4)} - \underbrace{\left(\dot{W}_{\text{cv}} - p_\circ \frac{dV_{\text{cv}}}{dt}\right)}_{(5)} - \underbrace{T_\circ \dot{\sigma}_{\text{cv}}}_{(6)} \tag{11}$$

(1): temporal change (increase, storage) of exergy in the CV, cf. Eq. (12)
(2): rate of exergy with the mass flow into the CV, i.e. that crosses the system boundary; sum of all inflow, cf. Eq. (14)
(3): rate of exergy with mass flows out of the CV
(4): rate of exergy with heat transferred into the CV, cf. Eq. (9)
(5): rate of work conducted by the CV through a shaft, rod, etc., cf. Eq. (8)
(6): irreversibility rate (rate of exergy destruction) inside the CV

The exergy of the mass inside the CV is expressed as

$$\mathcal{E}_{\text{cv}} = (U - U_\circ)_{\text{cv}} + p_\circ (V - V_\circ)_{\text{cv}} - T_\circ (S - S_\circ)_{\text{cv}} + E_{\text{kin,cv}} + E_{\text{pot,cv}} + \mathcal{E}^{\text{ch}}_{\text{cv}} \tag{12}$$

or on the basis of mass,

$$\varepsilon_{\text{cv}} = \frac{\mathcal{E}_{\text{cv}}}{m_{\text{cv}}} = (u - u_\circ)_{\text{cv}} + p_\circ (v - v_\circ)_{\text{cv}} - T_\circ (s - s_\circ)_{\text{cv}} + e_{\text{kin,cv}} + e_{\text{pot,cv}} + \varepsilon^{\text{ch}}_{\text{cv}}. \tag{13}$$

The specific exergy of mass crossing the system boundary into the CV:

$$\varepsilon_{f,i} = (h - h_\circ)_i - T_\circ (s - s_\circ)_i + \tfrac{1}{2} \vec{V}_i^2 + g(z - z_\circ)_i + \varepsilon^{\text{ch}}_i \tag{14}$$

and correspondingly $\varepsilon_{f,e}$ for out-flows.

Enthalpy and internal energy: Notice that in the energy balance, the change term contains the internal energy, whereas the entalpy represents the energy of matter that crosses the system boundary. This is also seen in the exergy balance: The change term contains the internal energy, whereas the exergy of a mass inflow is expressed using the enthalpy.

8 Developing the exergy balance

The short version: We can see the relation between the exergy balance and the three other balances when writing

$$\left(\frac{dE_{\text{cv}}}{dt} + p_\circ \frac{dV_{\text{cv}}}{dt}\right) - T_\circ \frac{dS_{\text{cv}}}{dt} - (u_\circ + p_\circ v_\circ - T_\circ s_\circ)\frac{dm_{\text{cv}}}{dt} = \frac{d\mathcal{E}_{\text{cv}}}{dt}. \tag{15}$$

Here, we recall that when $T_\circ$ and $p_\circ$ are constant, also $u_\circ$, $v_\circ$ and $s_\circ$ are constant. In this turn, we also assume no chemical reactions. Then the sum of the left-hand side of Eq. (15) must be equal to the exergy change. If we use the energy balance in the first term, the entropy balance in the second and the mass balance in the third, we obtain Eq. (11). If there are chemical reactions in the system, the development is, in principle, the same although somewhat more complex.