

REVIEW OF MACROSCOPIC BALANCES

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1 Introduction

In the study of chemical engineering systems, we find it necessary to write conservation laws for “macroscopic systems” that include large pieces of equipment or parts thereof, like chemical reactors, pumps, compressors, flash drums, distillation columns, pipes and other. The conservation laws allow us to monitor the behavior of these systems and take corrective action if necessary. They also allow us to size the equipment and to optimize the process behavior in order to minimize costs of production or maximize revenues. In this monograph we will present the generic form of these macroscopic balances for a general system depicted in Figure 1. below. The conservation laws for mass, momentum, energy and mechanical energy will be written and some examples will be presented to illustrate their use for practical situations.

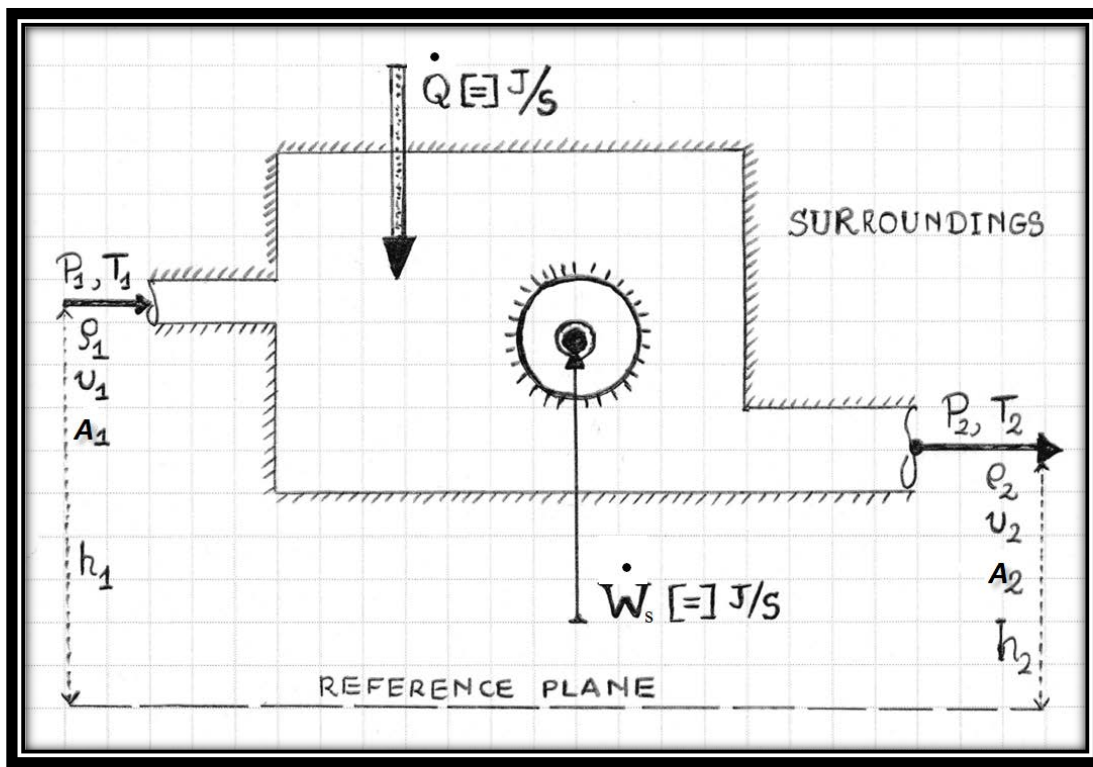


Figure 1. A stationary open system and its surroundings

The general form of the conservations laws for mass, momentum and energy can be written in qualitative terms as follows:

$$\mathbf{(ACCUMULATION)=(INPUT)-(OUTPUT)+(GENERATION)}$$

Although this universal equation describes the conservation of a physical quantity, very often we find it necessary to include various constraints that arise from numerical considerations, as well as from thermodynamic principles. The most common constraints include:

1. Thermodynamic equilibrium constraints if multiple phases are present in the mixture.
2. The second law of thermodynamics or equivalently $\delta Q = TdS$ for systems undergoing a reversible process.
3. Entropy and lost work macroscopic balances for irreversible processes.
4. Summation constraints if the state variables are the molar or mass fractions.
5. Numerical constraints that impose physical bounds on certain unknown variables, such as non-negative flows, mole[mass] fractions in the range [0,1] and other similar constraints.

We are now going to describe in some detail the macroscopic balances for mass, momentum, mechanical energy and total energy. In all balances we assume that the property profiles in the direction perpendicular to the flow are flat so that $\langle p \rangle = p$ where $\langle p \rangle$ indicates the average value of a property p , like fluid density, velocity, enthalpy etc.

2 Macroscopic Mass Balance

The macroscopic mass balance equation for a component i can be written as follows:

$$\frac{dM_{\text{tot}}^i}{dt} = (\rho_1^i v_1 A_1) - (\rho_2^i v_2 A_2) + (\mathfrak{R}^i V_{\text{tot}}) = w_1^i - w_2^i + \mathfrak{R}^i V_{\text{tot}}$$

whereas the macroscopic total mass balance is given by the equation:

$$\frac{dM_{\text{tot}}}{dt} = (\rho_1 v_1 A_1) - (\rho_2 v_2 A_2) = w_1 - w_2$$

The following definitions and units apply to the symbols used in the above equation:

Symbol	Meaning	Units
M_{tot}^i	Total Mass of component i in the System	kg
ρ_1^i, ρ_2^i	Component i density at planes 1 and 2	$\frac{kg}{m^3}$
w_1^i, w_2^i	Component i mass rate at planes 1 and 2	
M_{tot}	Total Mass of the System	kg
t	Time	s
ρ_1, ρ_2	Fluid density at planes 1 and 2	$\frac{kg}{m^3}$
v_1, v_2	Fluid velocity at planes 1 and 2	$\frac{m}{s}$
A_1, A_2	Flow cross section area at planes 1 and 2	m^2
\mathfrak{R}^i	Component i generation term (for Reactive systems)	$\frac{kg}{m^3 \cdot s}$
V_{tot}	Total Volume of the System	m^3
w_1, w_2	Fluid mass rate at planes 1 and 2	$\frac{kg}{s}$

Under steady-state conditions and if no reactions are present the macroscopic component and total mass balance reduce to the following simple equations:

$$\rho_1 v_1 A_1 - \rho_2 v_2 A_2 = w_1 - w_2 = 0 \Rightarrow w_1 = w_2 = w$$

$$\rho_1^i v_1 A_1 - \rho_2^i v_2 A_2 = w_1^i - w_2^i = 0 \Rightarrow w_1^i = w_2^i = w^i$$

3 Macroscopic Momentum Balance

Recognizing the v represents momentum per unit mass the steady-state macroscopic momentum balance is given by the following equation:

$$(v_1 \rho_1 v_1 A_1 + P_1 A_1) - (v_2 \rho_2 v_2 A_2 + P_2 A_2) + (M_{\text{tot}} g + F) = 0$$

where the symbol definitions presented above apply also here and in addition we have the following

Symbol	Meaning	Units
g	Gravity acceleration	m / s^2
P_1, P_2	Fluid pressure at planes 1 and 2	$Pa [=] kg / (m \cdot s^2)$
F	External force acting on the fluid	$N [=] kg \cdot m / s^2$

4 Macroscopic Energy Balance

The total energy of the systems consists of the sum of its internal energy plus kinetic energy plus potential energy. The unsteady-state macroscopic energy balance is described by the following equation:

$$\frac{d}{dt}(U_{\text{tot}} + K_{\text{tot}} + \Phi_{\text{tot}}) = \left(\left[U_1 + \frac{1}{2}v_1^2 + gh_1 + \frac{P_1}{\rho_1} \right] \rho_1 v_1 A_1 \right) - \left(\left[U_2 + \frac{1}{2}v_2^2 + gh_2 + \frac{P_2}{\rho_2} \right] \rho_2 v_2 A_2 \right) + \dot{Q} + \dot{W}_s$$

For stationary systems the kinetic and potential terms are not present and therefore the macroscopic energy balance reduces to the following equation:

$$\frac{dU_{\text{tot}}}{dt} = \left(\left[U_1 + \frac{1}{2}v_1^2 + gh_1 + \frac{P_1}{\rho_1} \right] \rho_1 v_1 A_1 \right) - \left(\left[U_2 + \frac{1}{2}v_2^2 S_2 + gh_2 + \frac{P_2}{\rho_2} \right] \rho_2 v_2 A_2 \right) + \dot{Q} + \dot{W}_s$$

This equation for a closed system with no input and output reduces to

$$\frac{dU_{\text{tot}}}{dt} = \dot{Q} + \dot{W} \Rightarrow dU = \dot{Q}dt + \dot{W}dt \Rightarrow \boxed{dU = \delta Q + \delta W} \Leftrightarrow \boxed{\Delta U = Q + W}$$

The last equation of course is the mathematical rendition of the first law of thermodynamics.

Recognizing now that $U + \frac{P}{\rho} = H$ the macroscopic energy balance can be written as:

$$\frac{dU_{\text{tot}}}{dt} = \left(\left[H_1 + \frac{1}{2}v_1^2 + gh_1 \right] \rho_1 v_1 A_1 \right) - \left(\left[H_2 + \frac{1}{2}v_2^2 + gh_2 \right] \rho_2 v_2 A_2 \right) + \dot{Q} + \dot{W}_s$$

Usually the kinetic and potential terms are small compared to the enthalpy and internal energy terms, so the above equation can further be simplified to:

$$\frac{dU_{\text{tot}}}{dt} = ([H_1] \rho_1 v_1 A_1) - ([H_2] \rho_2 v_2 A_2) + \dot{Q} + \dot{W}_s$$

Under steady-state conditions there is a further simplification that leads to:

$$\Delta H = H_2 - H_1 \Rightarrow \Delta H = Q + W_s$$

which is similar to the first law of thermodynamics but for open systems.

In the above equations we have made use of the mathematical relation: $\delta Q = \dot{Q}dt$. The Greek symbol δ is used for the heat and work differentials, instead of the standard differential symbol d , since δQ is not a true differential. As an example, and to clarify the two differential symbols consider a stationary system that undergoes a change from a state 1 to a state 2. Then the following mathematical relations hold for the internal energy and the heat input or output to or from the system:

$$\int_1^2 dU = \Delta U \quad \text{and} \quad \int_1^2 \delta Q = Q$$

The symbol definitions presented in the mass, momentum and mechanical energy balances apply also here and in addition we have the following:

Symbol	Meaning	Units
U_{tot}	Fluid total Internal Energy	J
K_{tot}	Fluid total Kinetic Energy	J
Φ_{tot}	Fluid total Potential Energy	J
H_1, H_2	Fluid specific Enthalpy at planes 1 and 2	$\frac{J}{kg}$
\dot{Q}	Heat input into the system	$\frac{J}{s}$
\dot{W}_s	Shaft work done on the fluid	$\frac{J}{s}$
\dot{W}	Compression work on the fluid	$\frac{J}{s}$
Q	Heat input into the system per unit mass	$\frac{J}{kg}$
W_s	Shaft work done on the fluid per unit mass	$\frac{J}{kg}$
W	Compression work on the fluid per unit mass	$\frac{J}{kg}$

5 Macroscopic Mechanical Energy Balance

The mechanical energy of a system is the sum of its kinetic and potential energy. The mechanical energy balance is not a fundamental principle.. It is rather a corollary of the equation of motion.

Recognizing the $\frac{1}{2}v^2$ represents kinetic energy per unit mass and gh represents potential energy per unit mass the macroscopic mechanical energy balance for constant fluid density is given by the equation:

$$\frac{d}{dt}(K_{\text{tot}} + \Phi_{\text{tot}}) = \left(\frac{1}{2}v_1^2 + gh_1 + \frac{P_1}{\rho_1} \right) \rho_1 v_1 A_1 - \left(\frac{1}{2}v_2^2 + gh_2 + \frac{P_2}{\rho_2} \right) \rho_2 v_2 A_2 - \dot{E}_v + \dot{W}_s = 0$$

Applying the steady-state macroscopic mass balance to the above momentum equation we obtain under steady-state conditions:

$$\left(\frac{1}{2}v_1^2 + gh_1 \right) - \left(\frac{1}{2}v_2^2 + gh_2 \right) - \int_1^2 \frac{dP}{\rho} - E_v + W_s = 0$$

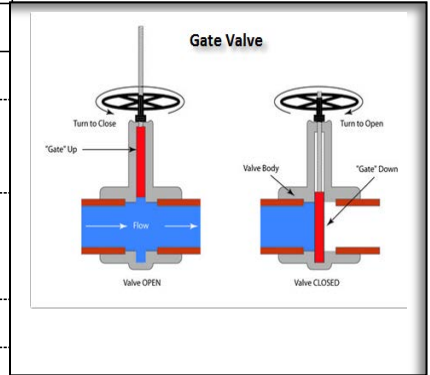
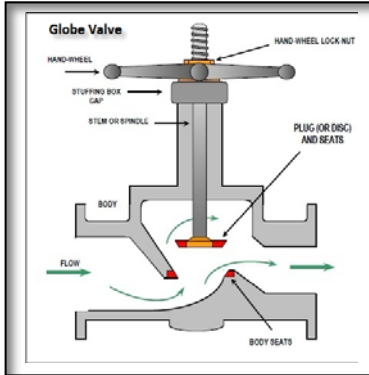
where the symbol definitions presented above apply also here and in addition we have the following:

Symbol	Meaning	Units
h_1, h_2	Fluid inlet and outlet heights from a reference plane	m
\dot{E}_v	Friction loss	$\frac{J}{s}$
\dot{W}_s	Shaft work done on the fluid	$\frac{J}{s}$
E_v	Friction loss per unit mass of fluid	$\frac{J}{kg}$
W_s	Shaft work done on the fluid per unit mass	$\frac{J}{kg}$

The friction loss E_v consists of two parts: (a) the loss in all sections of straight conduits and (b) the loss due to fittings(round and square elbows), valves, entrance, contraction and expansion effects. The following formula gives the friction loss in a piping system:

$$E_v = \frac{1}{2} v^2 \frac{L}{R_h} f + \frac{1}{2} v^2 e_v \quad \text{where} \quad R_h = \frac{A}{Z}$$

R_h	hydraulic radius
A	cross section area of conduit
Z	wetted perimeter
L	pipe length
f	Fanning friction factor
Disturbance	e_v
Entance to pipe	0.05
Sudden contraction	$0.45(1 - \beta) \quad \beta = \frac{\text{Small area}}{\text{Large area}}$
Sudden expansion	$\left(\frac{1}{\beta} - 1\right)^2 \quad \text{If } \beta \approx 0 \text{ then } e_v = 1$
90° rounded elbow	0.4 – 0.9
90° square elbow	1.3 – 1.9
45° elbow	0.3 – 0.4
Globe valve (open)	6 – 10
Gate valve (open)	0.2



The friction factor can be calculated from the Colebrook equation which is given by the formula:

$$\frac{1}{\sqrt{f}} + 1.737 \ln \left\{ \frac{1.256}{\text{Re} \sqrt{f}} + \frac{k}{3.707D} \right\} = 0 \quad \left| \quad \text{Re} = \frac{\rho v D}{\mu} > 2100 \right.$$

An explicit formula for the friction factor is given by the Blasius equation:

$$f = 0.0791 \text{Re}^{-0.25} \quad \left| \quad \text{Re} = \frac{\rho v D}{\mu} > 2100 \right.$$

An approximation to Colebrook's equation is given by the Haaland explicit equation:

$$\frac{1}{\sqrt{f}} = -3.6 \log_{10} \left\{ \frac{6.9}{\text{Re}} + \frac{k}{3.707D} \right\} \quad \left| \quad \text{Re} = \frac{\rho v D}{\mu} > 4000 \right.$$

where in the above equations k is the tube roughness, D is the tube diameter and Re is the Reynolds number. For laminar flow ($\text{Re} < 2100$) the friction factor is given by the equation:

$$f = \frac{16}{\text{Re}}$$

For packed tubes the friction factor is given by the Ergun equation:

$$f = \frac{1-\varepsilon}{\varepsilon^3} \left(75.0 \frac{1-\varepsilon}{\text{Re}} + 0.875 \right) \left| \text{Re} = \frac{\rho v d_p}{\mu} \right| v [=] \text{ superficial velocity}$$

where in the above equation ε is the porosity of the tube packing, and d_p is the particle diameter. Remember that the **Darcy** friction factor is four times the **Fanning** friction factor.

6 Macroscopic Entropy Balance

The derivation of the macroscopic entropy balance is similar to the one for the energy balance, however one needs to consider the entropy of the system and that of the surroundings. Recognizing that there is a generation term, the macroscopic entropy balance can be written as follows:

$$\frac{dS_{\text{tot}}}{dt} = ([S_1] \rho_1 v_1 A_1) - ([S_2] \rho_2 v_2 A_2) + \frac{\dot{Q}}{T_o} + \dot{S}_{\text{gen}}$$

Under steady-state conditions the above equation reduces to:

$$\Delta S = S_2 - S_1 \Rightarrow w \Delta S = \frac{\dot{Q}}{T_o} + \dot{S}_{\text{gen}} \quad \text{where } w = \rho_1 v_1 A_1 = \rho_2 v_2 A_2$$

Dividing the left and right hand side of the above equation by the mass flow rate we obtain an expression for the entropy generation for irreversible processes:

$$\Delta S = \frac{Q}{T_o} + S_{\text{gen}} \Rightarrow S_{\text{gen}} = \Delta S - \frac{Q}{T_o}$$

And the lost work due to the irreversibility of the process can be calculated from the formula:

$$W_{\text{lost}} = T_o \cdot S_{\text{gen}}$$

For reversible process, since the entropy generation is equal to zero, we obtain the second law of thermodynamics:

$$\Delta S = S_2 - S_1 \Rightarrow \Delta S = \frac{Q}{T_o} \text{ and in differential form } dS = \frac{\delta Q}{T_o}$$

Furthermore for reversible adiabatic processes the change in entropy is equal to zero $dS = 0$.

The symbol definitions presented in the mass, momentum, mechanical and total energy balances apply also here and in addition we have the following:

Symbol	Meaning	Units
S_{tot}	Fluid total Entropy	$\frac{J}{K}$
S_1, S_2	Fluid specific Entropy at planes 1 and 2	$\frac{J}{K \cdot kg}$
T_0	Bath Temperature	K
\dot{S}_{gen}	Rate of Fluid Entropy Generation	$\frac{J}{K \cdot s}$
S_{gen}	Fluid Specific Entropy Generation	$\frac{J}{K \cdot kg}$

Note: Specific thermodynamic properties, such as specific enthalpy, entropy, internal energy and volume are often given per mole (mol) of substance instead of per mass (kg) of substance.

Note: SI Fundamental Units



7 Differential Forms of Macroscopic Balances

When the properties of a system change continuously differential forms of the macroscopic balances must be used. Consider the flow of a compressible fluid in a horizontal pipe. The pressure, temperature and specific volume of the fluid change continuously along the length of the pipe. In this particular case the macroscopic balances must be written in a differential form as indicated below. In the equations below we make use of the formulas $\rho = \frac{1}{V}$ and

$\rho v = G \Rightarrow v = GV$ where ρ is the compressible fluid mass density, G is the mass velocity, which is constant under steady-conditions and constant cross section area for flow, V is the mass specific volume of the fluid, and v is the linear velocity of the fluid.

Macroscopic Mass Balance:

$$v = GV \Rightarrow \boxed{\frac{dv}{dz} = G \frac{dV}{dz}} \text{ or } dv = GdV$$

Macroscopic Energy Balance:

$$dH + vdv = qdz \Rightarrow C_p \frac{dT}{dz} + v \frac{dv}{dz} = q \Rightarrow \boxed{C_p \frac{dT}{dz} + G^2 V \frac{dV}{dz} = q}$$

where q is the linear heat flux per unit length of pipe, per unit mass of fluid flowing through the pipe and C_p is the heat mass capacity of the fluid.

Mechanical Energy Balance

$$v dv + \frac{dP}{\rho} + \frac{1}{2} v^2 \frac{4f}{D} dz = 0 \Rightarrow \boxed{G^2 V \frac{dV}{dz} + V \frac{dP}{dz} + G^2 V^2 \frac{2f}{D} = 0}$$

The above equations must be combined with an equation of state in order to create a well-defined system of coupled differential equations. If we assume ideal gas behavior then we have

$PVM_w = RT$, where M_w is the molecular weight of the fluid, and therefore we can replace the temperature derivative with:

$$\frac{dT}{dz} = \frac{PM_w}{R} \frac{dV}{dz} + \frac{VM_w}{R} \frac{dP}{dz}$$

Combining the ideal gas law with the differential forms of the macroscopic energy and mechanical energy balances, the equations that describe flow of a compressible ideal gas fluid in linear pipe can be written as:

$$G^2 \frac{dV}{dz} + \frac{dP}{dz} + G^2 V \frac{2f}{D} = 0$$

$$\left(G^2 V + C_p \frac{PM_w}{R} \right) \frac{dV}{dz} + C_p \frac{VM_w}{R} \frac{dP}{dz} = q$$

These two coupled differential equations can then be solved simultaneously using available commercial software, like Athena Visual Studio.

An alternative method is to start with the macroscopic mechanical energy balance and replace the specific volume with a value calculated at the average temperature $T_a = \frac{T_1 + T_2}{2}$. Then we have:

$$G^2 \frac{dV}{V} + \frac{dP}{V_a} + G^2 \frac{2f}{D} dz = 0 \Rightarrow G^2 \frac{dV}{V} + \frac{PM_w}{RT_a} dP + G^2 \frac{2f}{D} dz = 0$$

Integrating the last equation between the inlet and the outlet of the pipe and assuming that the Reynolds number remains constant (i.e. the viscosity of the fluid does not change appreciably over the length of the pipe) we obtain:

$$G^2 \ln \frac{V_2}{V_1} + \frac{M_w}{2RT_a} (P_2^2 - P_1^2) + G^2 \frac{2Lf}{D} = 0$$

Applying the ideal gas law the above equation becomes:

$$G^2 \ln \frac{P_1 T_2}{P_2 T_1} + \frac{M_w}{2RT_a} (P_2^2 - P_1^2) + G^2 \frac{2Lf}{D} = 0$$

This last equation can be solved for the outlet pressure using a numerical method, like secant, or Newton or Goalseek in Microsoft Excel. Once the outlet pressure is calculated, one can also calculate the specific mass volume as well as the outlet velocity of the fluid. An easier equation to solve, can be derived by introducing a new variable $x = P_2 / P_1$. Then the equation for the pressure drop becomes:

$$-G^2 \ln \left(x \frac{T_1}{T_2} \right) + \frac{M_w P_1^2}{2RT_a} (x^2 - 1) + G^2 \frac{2Lf}{D} = 0$$

We also know that the unknown variable lies in the open interval (0,1) because the pressure always drops and therefore we can easily come up with an initial guess like ($x_0 = 0.5$) for the solution of the above equation.