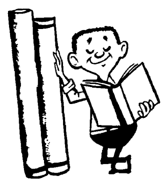
Review of First and Second Law of Thermodynamics



Reading	Problems
4-1 → 4-4	4-32, 4-36, 4-87, 4-246
5-2 → 5-4, 5.7	
6-1 → 6-13, 6-13	6-122, 6-127, 6-130

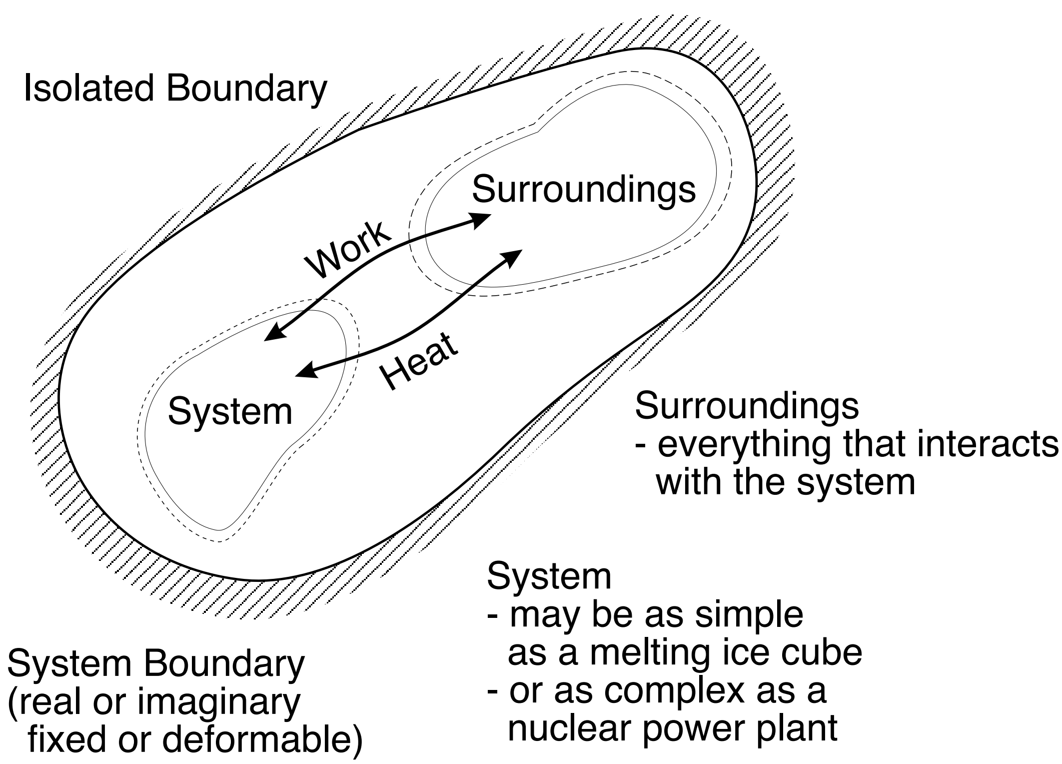
Definitions

SYSTEM:

- any specified collection of matter under study.
- all systems possess properties like mass, energy, entropy, volume, pressure, temperature, etc.

WORK & HEAT TRANSFER:

- thermodynamics deals with these properties of matter as a system interacts with its surroundings through work and heat transfer
- work and heat transfer are <u>NOT</u> properties → they are the forms that energy takes to cross the system boundary



First Law of Thermodynamics

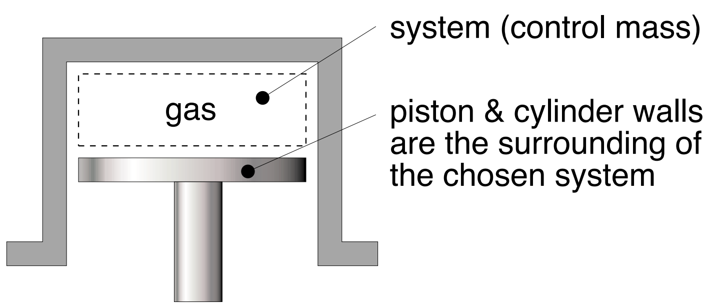
Control Mass (Closed System)

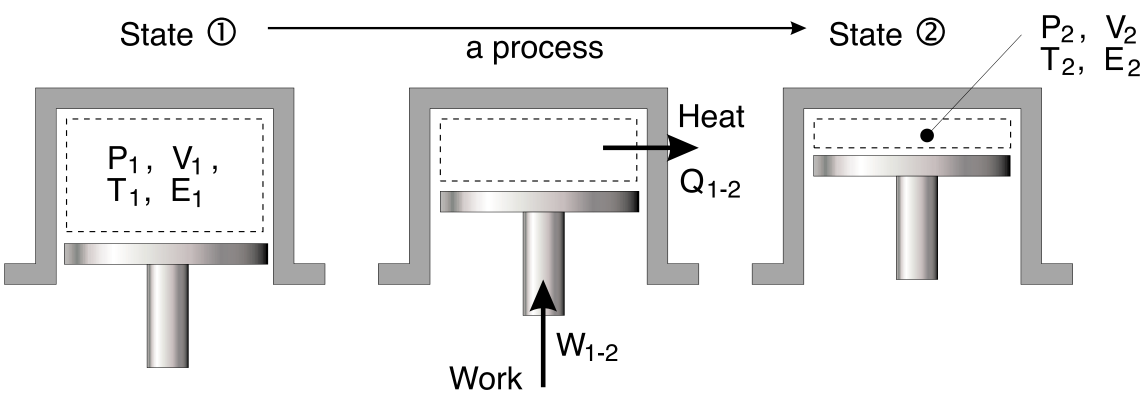
CONSERVATION OF ENERGY:

- the energy content of an isolated system is constant

$$\boldsymbol{energy\ entering - energy\ leaving = change\ of\ energy\ within\ the\ system}$$

Example: A Gas Compressor





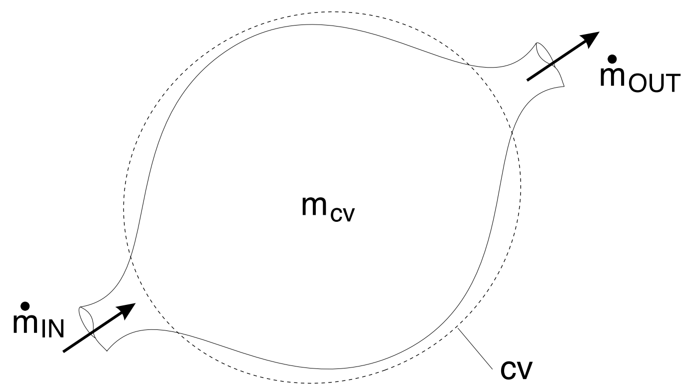
Performing a 1st law energy balance:

$$\left\{ \begin{array}{c} \boldsymbol{Initial} \\ \boldsymbol{Energy} \\ \boldsymbol{E_1} \end{array} \right\} \begin{array}{c} + \\ - \end{array} \left\{ \begin{array}{c} \boldsymbol{Energy\ gain\ W_{1-2}} \\ \boldsymbol{Energy\ loss\ Q_{1-2}} \end{array} \right\} = \left\{ \begin{array}{c} \boldsymbol{Final} \\ \boldsymbol{Energy} \\ \boldsymbol{E_2} \end{array} \right\}$$

$$\boxed{\boldsymbol{E_1 + W_{1-2} - Q_{1-2} = E_2}}$$

Control Volume Analysis (Open System)

CONSERVATION OF MASS:



$$\left\{ \begin{array}{c} \textit{rate of increase} \\ \textit{of mass within} \\ \textit{the CV} \end{array} \right\} = \left\{ \begin{array}{c} \textit{net rate of} \\ \textit{mass flow} \\ \textit{IN} \end{array} \right\} - \left\{ \begin{array}{c} \textit{net rate of} \\ \textit{mass flow} \\ \textit{OUT} \end{array} \right\}$$

$$\frac{d}{dt}(m_{CV}) = \dot{m}_{IN} - \dot{m}_{OUT}$$

where:

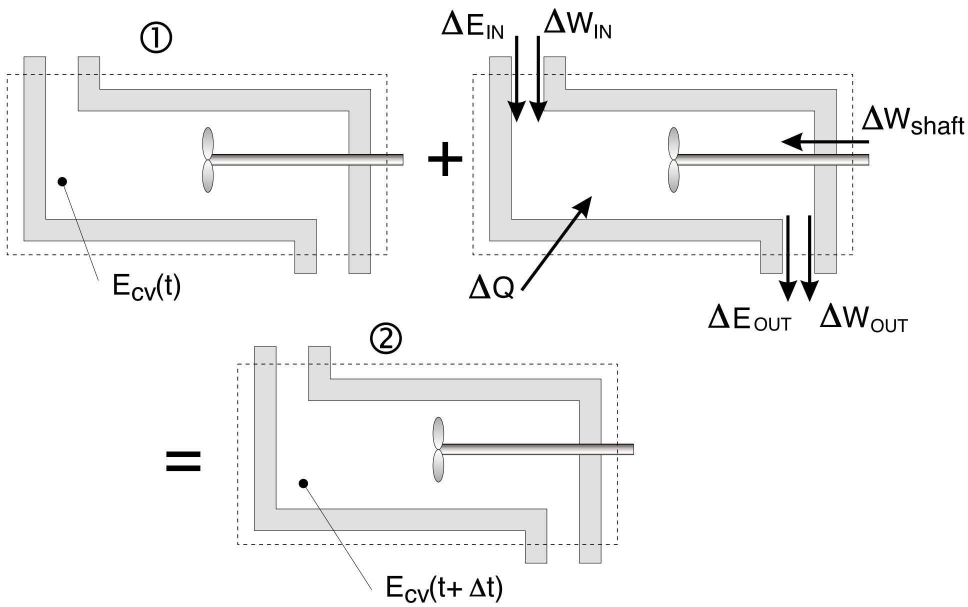
$$\begin{aligned} m_{CV} &= \int_V \rho \, dV \\ \dot{m}_{IN} &= (\rho \, v^* \, A)_{IN} \\ \dot{m}_{OUT} &= (\rho \, v^* \, A)_{OUT} \end{aligned}$$

with v^* = average velocity

CONSERVATION OF ENERGY:

The 1st law states:

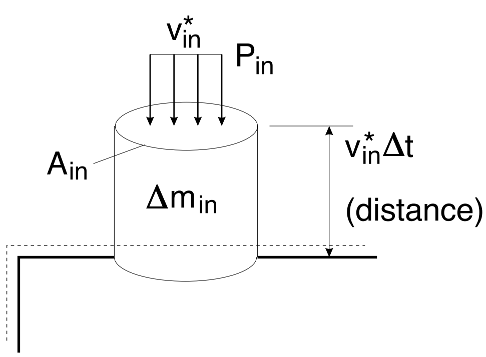
$$\begin{aligned} E_{CV}(t) + \Delta Q + \Delta W_{shaft} + (\Delta E_{IN} - \Delta E_{OUT}) + & \\ (\Delta W_{IN} - \Delta W_{OUT}) &= E_{CV}(t + \Delta t) \qquad (1) \end{aligned}$$



where:

$$\begin{aligned}
\boldsymbol{\Delta E_{IN}} &= \boldsymbol{e_{IN} \Delta m_{IN}} \\
\boldsymbol{\Delta E_{OUT}} &= \boldsymbol{e_{OUT} \Delta m_{OUT}} \\
\boldsymbol{\Delta W} &= \textbf{flow work} \\
\boldsymbol{e} &= \frac{\boldsymbol{E}}{\boldsymbol{m}} = \underbrace{\boldsymbol{u}}_{internal} + \underbrace{\frac{\boldsymbol{(v^*)^2}}{\boldsymbol{2}}}_{kinetic} + \underbrace{\boldsymbol{gz}}_{potential}
\end{aligned}$$

What is flow work?



$$\boldsymbol{\Delta m_{IN}} = \boldsymbol{\rho_{IN}} \overbrace{\boldsymbol{A_{IN}\ v^*_{IN}\ \Delta t}}^{volume}$$

$$
\begin{aligned}
\Delta W_{IN} &= F \cdot distance \\
&= \underbrace{P_{IN}\ A_{IN}}_{F} \cdot \underbrace{v^*_{IN}\ \Delta t}_{\Delta s} \\
&= \frac{P_{IN}\ \Delta m_{IN}}{\rho_{IN}}
\end{aligned}
$$

with

$$v = \frac{1}{\rho}$$

$$\Delta W_{IN} = (P\ v\ \Delta m)_{IN} \quad \longrightarrow \text{flow work} \tag{2}$$

Similarly

$$\Delta W_{OUT} = (P\ v\ \Delta m)_{OUT} \tag{3}$$

Substituting Eqs. 2 and 3 into Eq. 1 gives the 1st law for a control volume

$$
\begin{aligned}
E_{CV}(t+\Delta t) - E_{CV}(t) &= \Delta Q + \Delta W_{shaft} + \Delta m_{IN}(e+Pv)_{IN} \\
&\quad - \Delta m_{OUT}(e+Pv)_{OUT}
\end{aligned} \tag{4}
$$

Equation 4 can also be written as a rate equation $\longrightarrow$ divide through by Δt and take the limit as $\Delta t \longrightarrow 0$

$$\frac{d}{dt}E_{CV} = \dot{Q} + \dot{W}_{shaft} + [\dot{m}(e+Pv)]_{IN} - [\dot{m}(e+Pv)]_{OUT}$$

where:

$$\dot{m} = \rho\ v^*\ A$$

Note that:

$$
\begin{aligned}
e + Pv &= \underbrace{u + Pv} + \frac{(v^*)^2}{2} + gz \\
&= h(enthalpy) + KE + PE
\end{aligned}
$$

Second Law of Thermodynamics

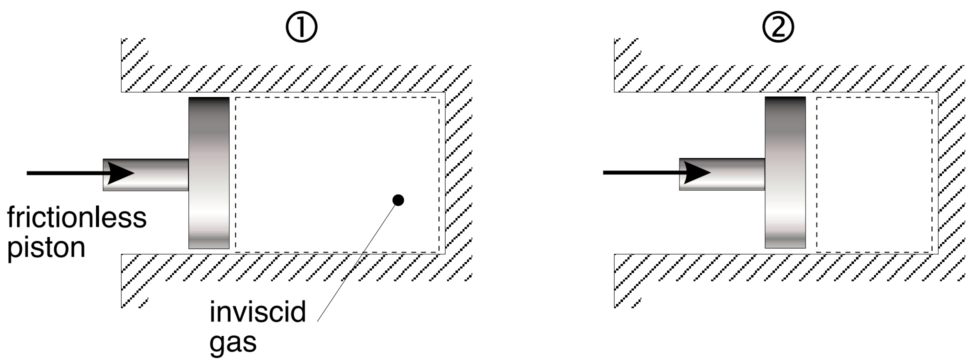
1. *Entropy is a measure of the degree of* <u>*microscopic disorder*</u> *and represents our* <u>*uncertainty*</u> *about the microscopic state.*

2. The entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

   The second law states:

   $$(\Delta S)_{system} + (\Delta S)_{surr.} \geq 0 \qquad \text{where} \;\; \Delta \equiv final - initial$$

   <u>Example: Slow adiabatic compression of a gas</u>

   A process $\mathbf{1} \longrightarrow \mathbf{2}$ is said to be reversible if the reverse process $\mathbf{2} \longrightarrow \mathbf{1}$ restores the system to its original state without leaving any change in either the system or its surroundings.

   $\longrightarrow$ idealization where $S_2 = S_1 \;\; \Rightarrow \mathcal{P}_S = 0$

   $T_2 > T_1 \quad \Rightarrow$ increased microscopic disorder

   $V_2 < V_1 \quad \Rightarrow$ reduced uncertainty about the whereabouts of molecules

   $$Reversible \; + \; Adiabatic\ Process \Rightarrow Isentropic\ Process$$

   The 2nd law states:

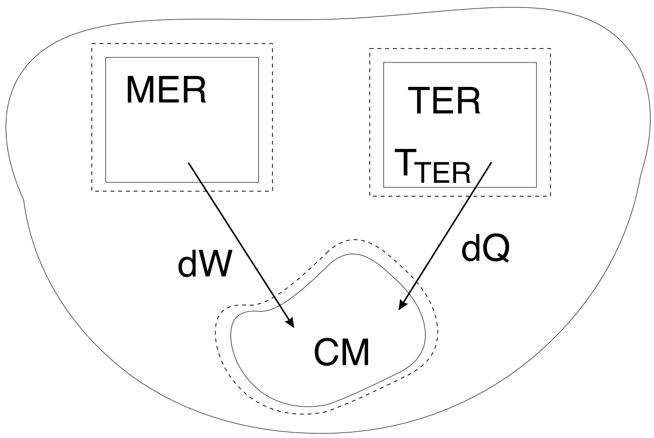
   $$\mathcal{P}_S = (\Delta S)_{system} \; + \; (\Delta S)_{surr} \geq 0$$

   where:

   $> 0 \qquad irreversible\ (real\ world)$

   $= 0 \qquad reversible\ (frictionless,\ perfectly\ elastic,\ inviscid\ fluid)$

How do we determine entropy in a system?



For an isolated system $\boldsymbol{\mathcal{P} \geq 0}$.

$$\boldsymbol{(dS)_{CM} + \underbrace{(dS)_{TER}}_{-\frac{dQ}{T_{TER}}} + (d\cancel{S}^{\,0})_{MER} = d\mathcal{P}_S}$$

Therefore

$$\boldsymbol{(dS)_{CM} = \frac{dQ}{T_{TER}} + d\mathcal{P}_S}$$

Integrating gives

$$\boldsymbol{(S_2 - S_1)_{CM} = \frac{Q_{1-2}}{T_{TER}} + \underbrace{\mathcal{P}_{S_{1-2}}}_{\geq 0}}$$

where

$\boldsymbol{\frac{Q_{1-2}}{T_{TER}}}$ - the entropy associated with heat transfer across a finite temperature difference

Gibb's Equation for a Simple Compressible Substance

simple $\longrightarrow$ has only one work mode

compressible $\longrightarrow$ the work mode is $\boldsymbol{Pdv}$ work

$$
\begin{aligned}
\boldsymbol{S} &= \boldsymbol{S(U,V)} \\
\boldsymbol{dS} &= \underbrace{\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{U}}\right)_{\boldsymbol{V}}}_{=\frac{\boldsymbol{1}}{\boldsymbol{T}}} \boldsymbol{dU} + \underbrace{\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{V}}\right)_{\boldsymbol{U}}}_{=\frac{\boldsymbol{P}}{\boldsymbol{T}}} \boldsymbol{dV}
\end{aligned}
$$

$$\boxed{\boldsymbol{T\ dS = dU\ +\ PdV}}$$

This form of Gibb's equation is very general and very useful.

The general derivation of Gibb's equation:

from the 1st law $\Rightarrow$ $\boldsymbol{dq = du + Pdv}$ **(1)**

from the 2nd law $\Rightarrow$ $\boldsymbol{ds = \frac{dq}{T}}$ **(2)**

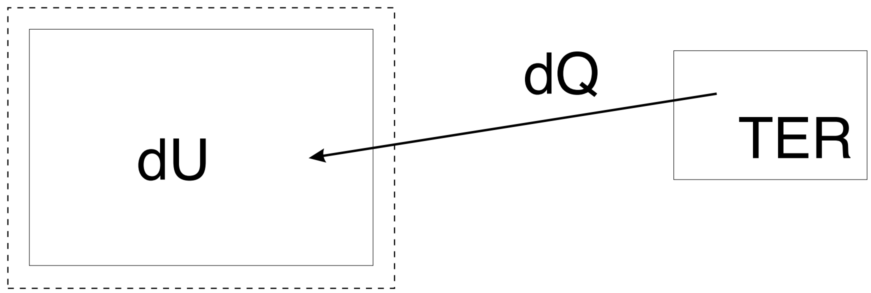
Combining (1) and (2) gives

$$\boldsymbol{ds = \frac{du}{T} + P\frac{dv}{T}}$$

or

$$
\begin{aligned}
\boldsymbol{T\ ds} &= \boldsymbol{du\ +\ P\ dv} \\
\boldsymbol{T\ dS} &= \boldsymbol{dU\ +\ P\ dV}
\end{aligned}
$$

Second Law Analysis for a Control Mass



- control mass is uniformly at $\boldsymbol{T_{TER}}$ at all times
- control mass has a fixed size ($\boldsymbol{V = constant}$)

From Gibb's equation

$$\boldsymbol{T_{TER}\, dS = dU + P\, d\cancelto{0}{V}}$$

From the 1st law

$$\boldsymbol{dU = dQ}$$

Therefore for a reversible process

$$\boldsymbol{dS = \frac{dQ}{T_{TER}}}$$

We integrate to give

$$\boldsymbol{S_2 - S_1 = \frac{Q_{1-2}}{T_{TER}}}$$

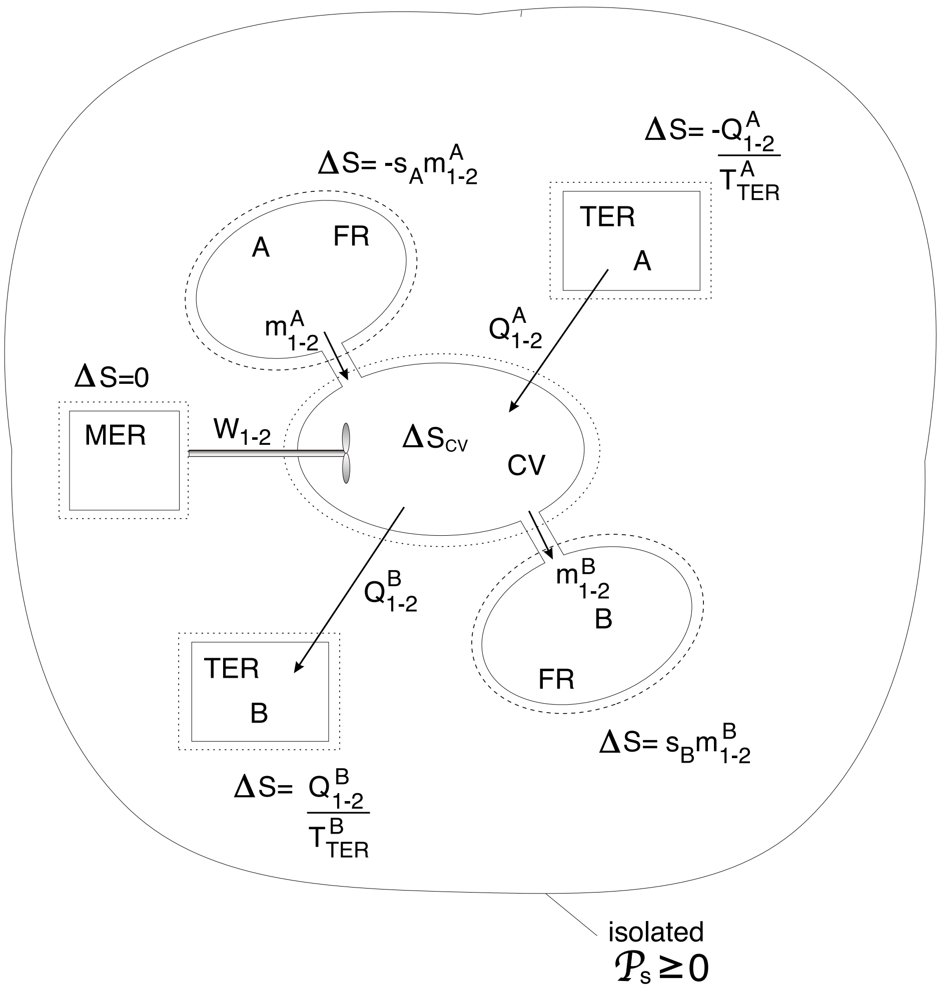
and for a non-reversible process

$$\boldsymbol{dS = \frac{dQ}{T_{TER}} + d\mathcal{P}_S}$$

We integrate to give

$$\boldsymbol{S_2 - S_1 = \frac{Q_{1-2}}{T_{TER}} + \mathcal{P}_{S_{1-2}}}$$

Second Law Analysis for a Control Volume



For the isolated system

$$(\boldsymbol{\Delta S})_{sys} + (\boldsymbol{\Delta S})_{sur} = \mathcal{P}_{S_{1-2}} \geq \mathbf{0}$$

$$\Delta S_{CV} - s_A m^A_{1-2} + s_B m^B_{1-2} - \frac{Q^A_{1-2}}{T^A_{TER}} + \frac{Q^B_{1-2}}{T^B_{TER}} = \mathcal{P}_{S_{1-2}}$$

or as a rate equation

$$\left(\frac{dS}{dt}\right)_{CV} = \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{IN} - \left(s\dot{m} + \frac{\dot{Q}}{T_{TER}}\right)_{OUT} + \dot{\mathcal{P}}_S$$

This can be thought of as $\boldsymbol{accumulation = IN - OUT + generation}$