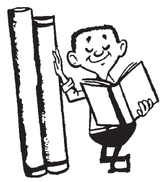
Review of First and Second Law of Thermodynamics



Reading	Problems
2-6, 4-1, 4-2	4-27, 4-40, 4-41
5-1 → 5-3	
6-1, 6-2, 7-13	

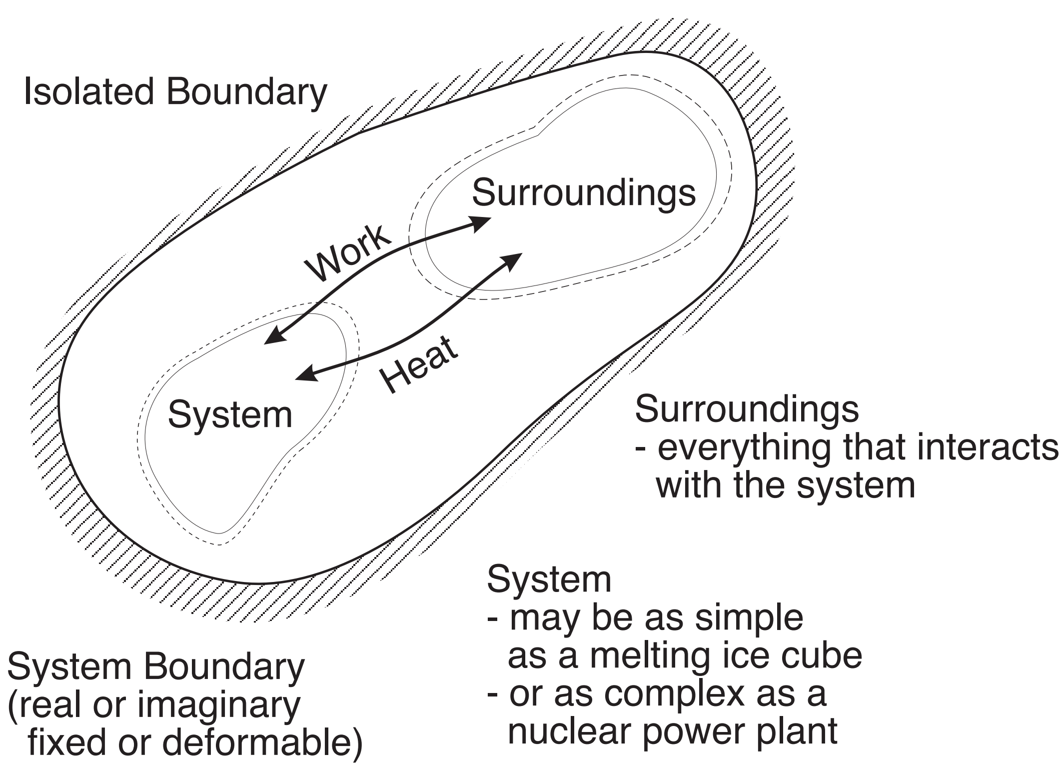
Definitions

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

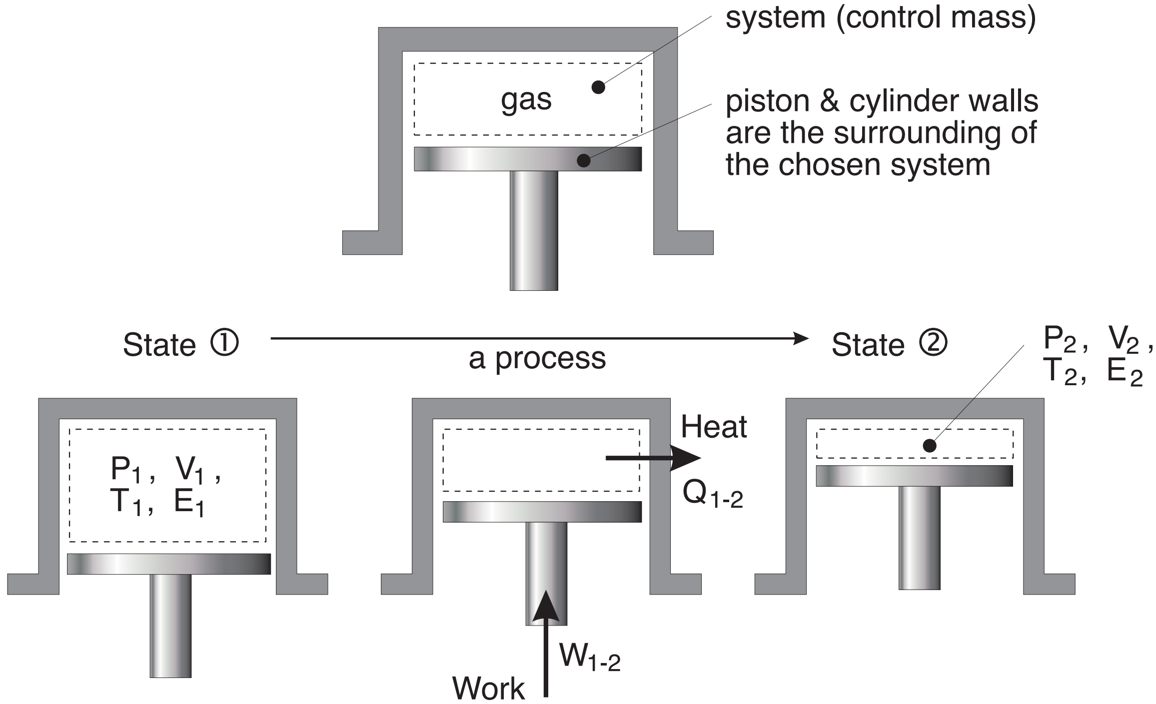
Control Mass (Closed System)

CONSERVATION OF ENERGY:

- the energy content of an isolated system is constant

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

Example: A Gas Compressor



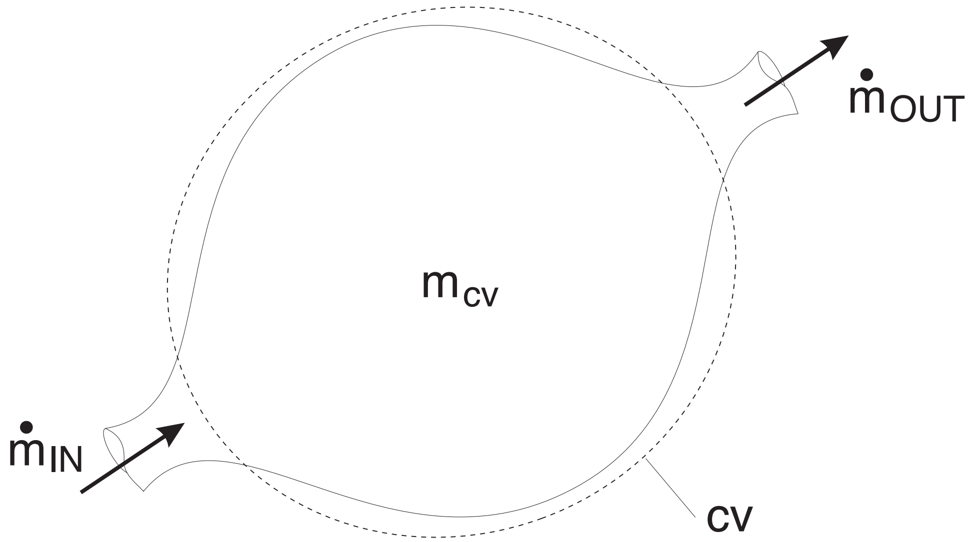
Performing a 1st law energy balance:

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

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

Control Volume Analysis (Open System)

CONSERVATION OF MASS:



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

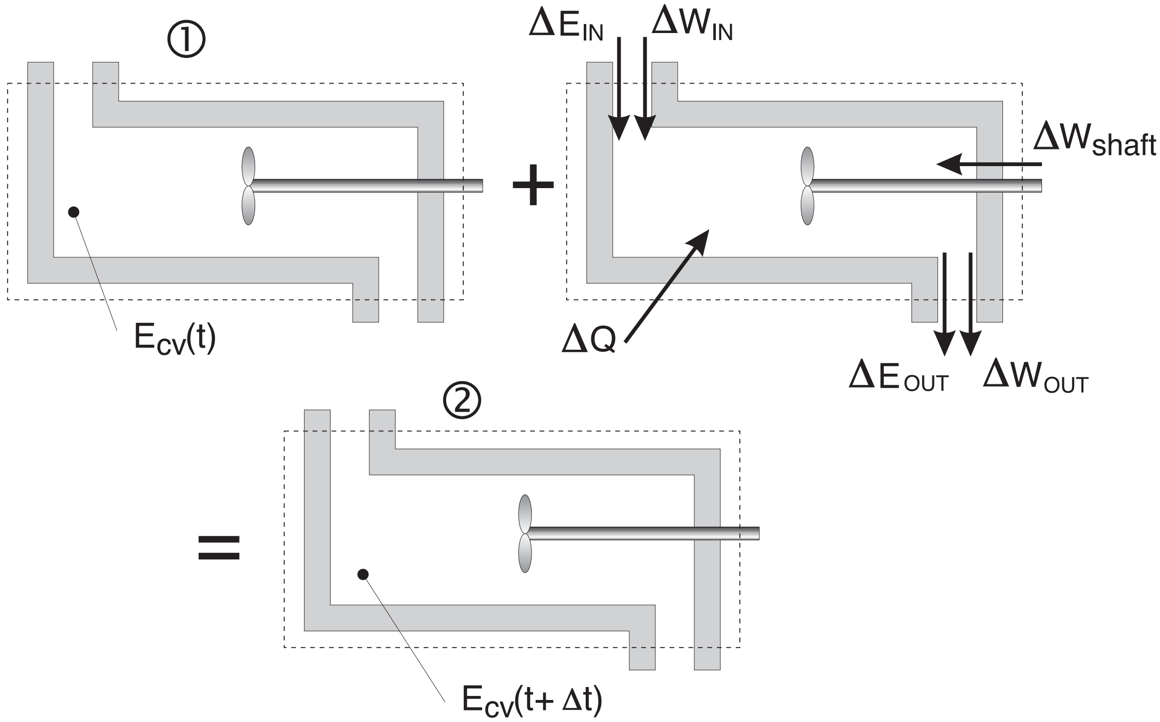
$$\frac{d}{dt}(m_{CV}) = \dot{m}_{IN} - \dot{m}_{OUT}$$

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:

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

Second Law of Thermodynamics

Fundamentals

1. Like mass and energy, every system has entropy.

   Entropy is a measure of the degree of microscopic disorder and represents our uncertainty about the microscopic state.

2. Unlike mass and energy, entropy can be produced but it can never be destroyed. That is, the entropy of a system plus its surroundings (i.e. an isolated system) can never decrease (2nd law).

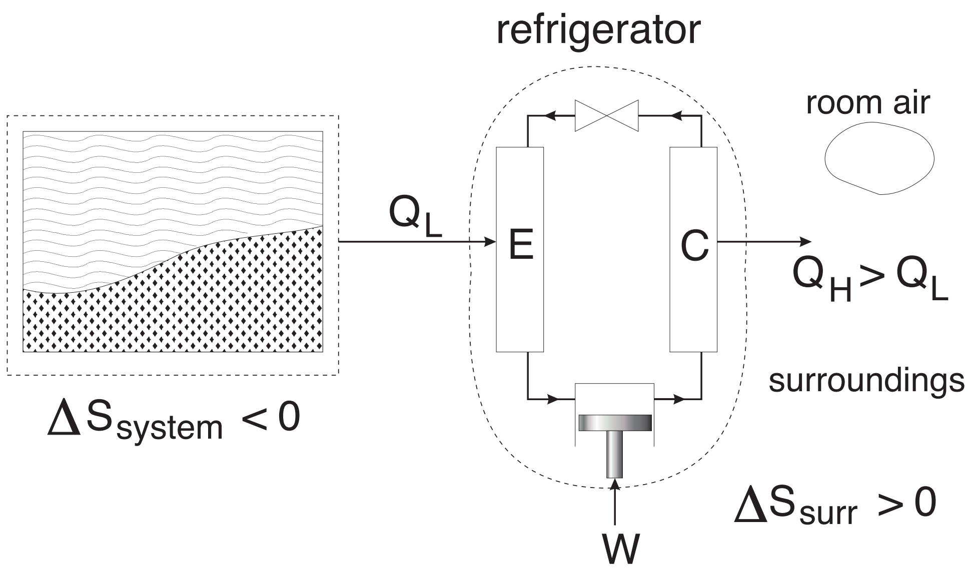
$$\begin{aligned}
\mathcal{P}_m &= m_2 - m_1 = 0 \ \text{(conservation of mass)} \\
\mathcal{P}_E &= E_2 - E_1 = 0 \ \text{(conservation of energy)} \rightarrow \text{1st law} \\
\mathcal{P}_S &= S_2 - S_1 \geq 0 \ \rightarrow \text{2nd law}
\end{aligned}$$

The second law states:

$$(\Delta S)_{system} + (\Delta S)_{surr.} \geq 0$$

where $\Delta \equiv final - initial$

Example: A freezing process



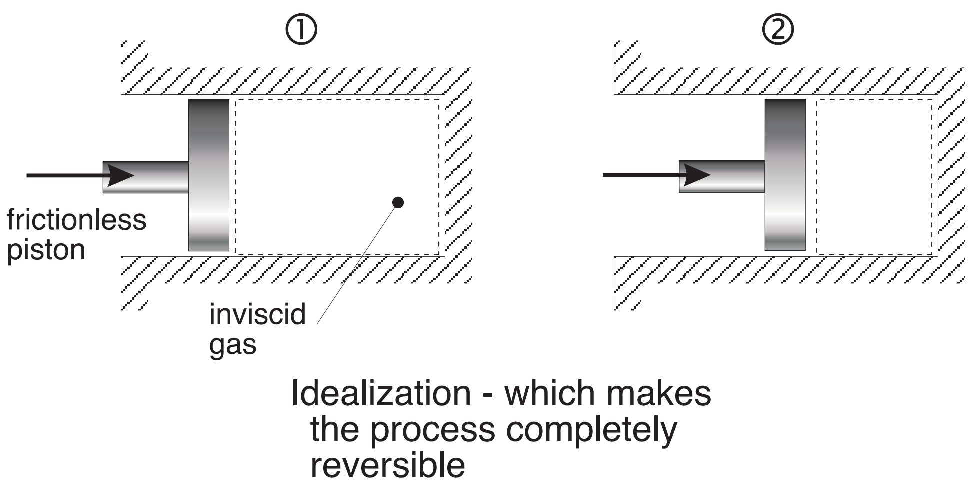
3. ***Reference:*** In a prefect crystal of a pure substance at $T = 0\ K$, the molecules are completely motionless and are stacked precisely in accordance with the crystal structure. Since entropy is a measure of microscopic disorder, then in this case $S = 0$. That is, there is no uncertainty about the microscopic state.

4. ***Relationship to Work:*** For a given system, an increase in the microscopic disorder (that is an increase in entropy) results in a loss of ability to do useful work.

5. ***Heat:*** Energy transfer as heat takes place as work at the microscopic level but in a random, disorganized way. This type of energy transfer carries with it some chaos and thus results in entropy flow in or out of the system.

6. ***Work:*** Energy transfer by work is microscopically organized and therefore entropy-free.

Example: Slow adiabatic compression of a gas



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

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

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

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

$$\underbrace{Reversible}_{\mathcal{P}_S=0} + \underbrace{Adiabatic\ Process}_{Q=0} \Rightarrow \underbrace{Isentropic\ Process}_{S_1=S_2}$$

The 2nd law states:

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

where:

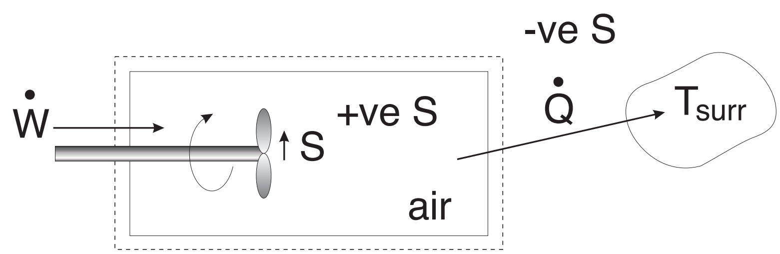
> 0 irreversible (real world)

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

But does:

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

NOT ALWAYS - the entropy increase of a substance during a process as a result of irreversibilities may be offset by a decrease in entropy as a result of heat losses.



General Derivation of Gibb's Equation

From a 1st law energy balance when KE and PE are neglected

$$Energy\ Input = Energy\ Output\ +\ Increase\ in\ Energy\ Storage$$

$$\underbrace{dQ}_{amount} = dW + \underbrace{dU}_{differential} \qquad (1)$$

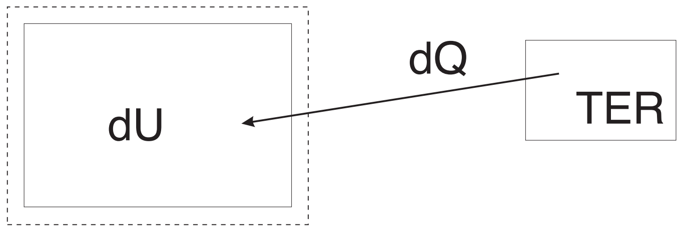
We know that the differential form of entropy is

$$dS = \frac{dQ}{T} \qquad (2) \qquad\qquad dW = PdV \qquad (3)$$

Combining Eqs. 1, 2 and 3

$$dS = \frac{dU}{T} + \frac{PdV}{T} \quad \Rightarrow \quad \underbrace{ds = \frac{du}{T} + \frac{Pdv}{T}}_{\text{per unit mass}}$$

Second Law Analysis for a Control Mass



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

From Gibb's equation

$$T_{TER}\, dS = dU + P\, d\cancel{V}^{0}$$

From the 1st law

$$dU = dQ$$

Therefore for a reversible process

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

We integrate to give

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

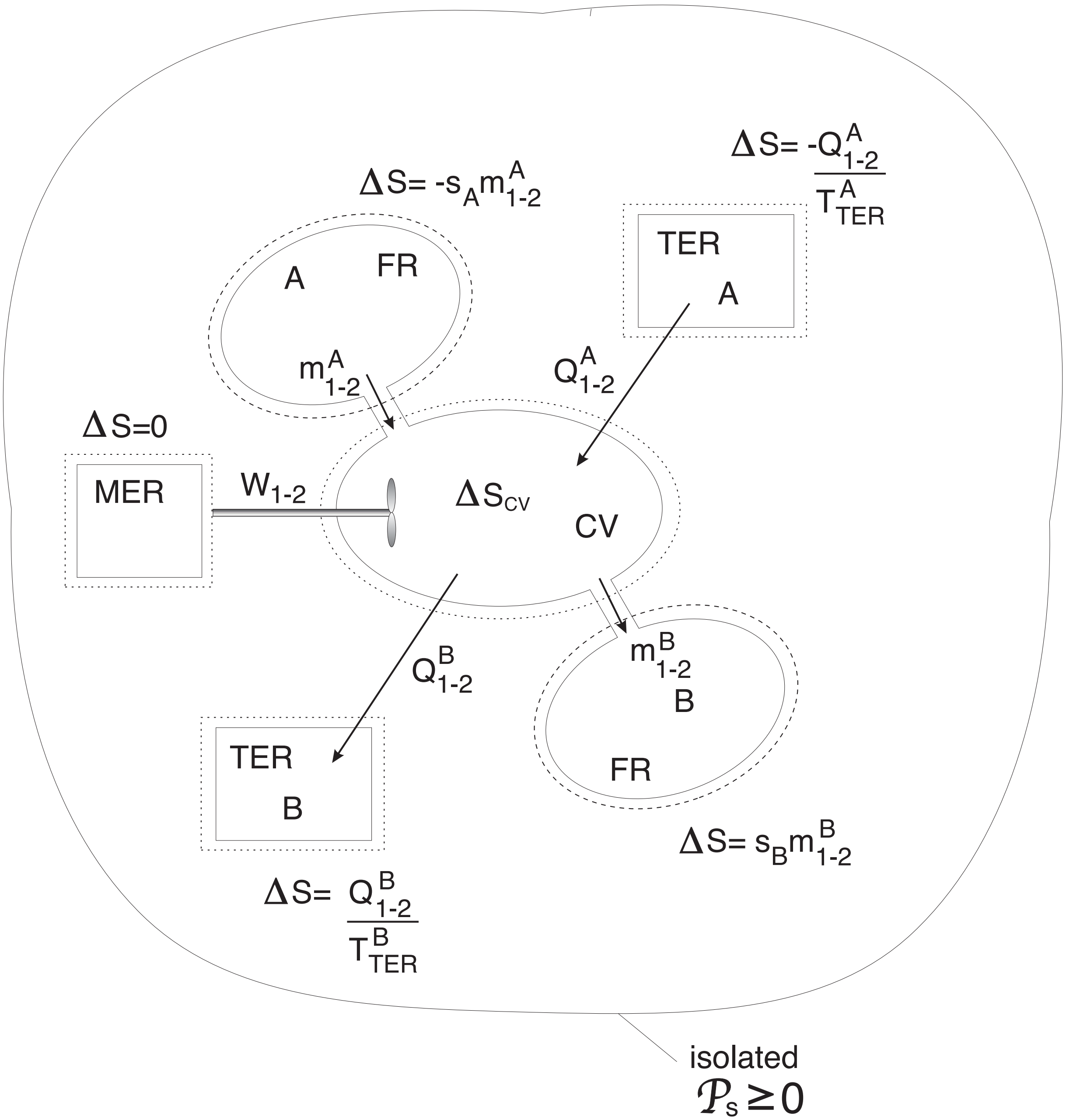
and for a non-reversible process

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

We integrate to give

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

Second Law Analysis for a Control Volume



where:

FR	-	fluid reservoir
TER	-	thermal energy reservoir
MER	-	mechanical energy reservoir

For the isolated system

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

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

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

$$accumulation = IN - OUT + generation$$