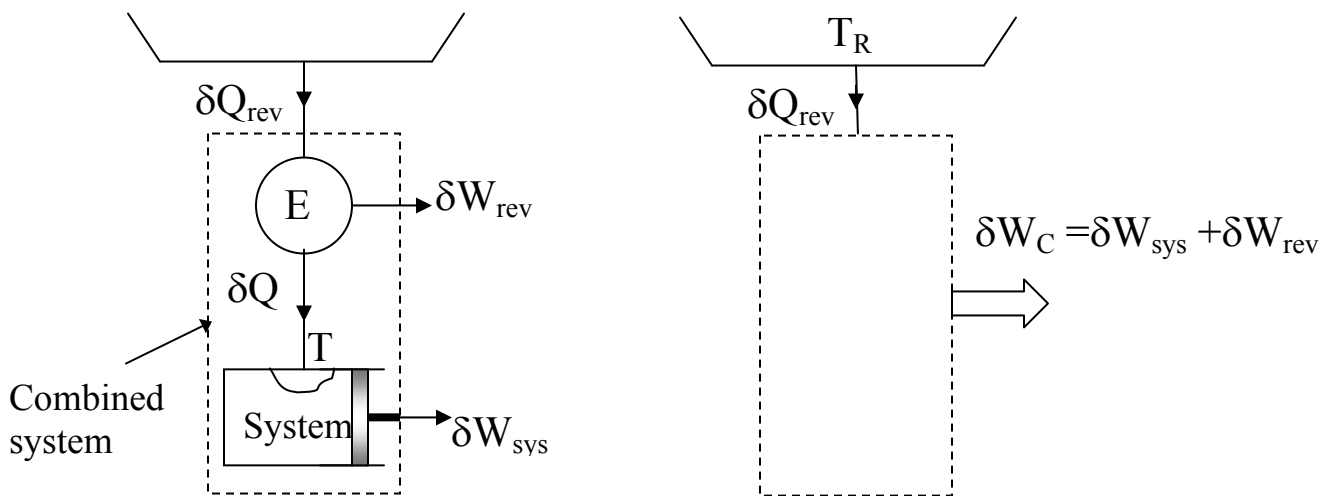


Derivation of Entropy from Second Law

Consider the following combined system consisting of a Carnot heat engine and a piston cylinder system



First Law applied to the combined system

$$dE_C = \delta Q_{rev} - \delta W_C$$

$$\delta W_C = \delta Q_{rev} - dE_C$$

For a Carnot Engine (reversible cycle)

$$\frac{\delta Q_{rev}}{\delta Q} = \frac{T_R}{T} \quad \rightarrow \quad \delta Q_{rev} = \delta Q \cdot \frac{T_R}{T}$$

substituting $\delta W_C = \frac{\delta Q}{T} \cdot T_R - dE_C$

Let the system undergo a cycle while the Carnot cycle undergoes one or more cycles. Integrate over entire cycle (recall system energy is a state property)

$$\oint \delta W_C = \oint \frac{\delta Q}{T} \cdot T_R - \oint dE_C$$

The net work for one cycle is

$$W_C = T_R \oint \left(\frac{\delta Q}{T} \right)_{boundary}$$

The integral must be evaluated at the system boundary

The combined system (cycle) draws heat from a single reservoir while involving work W_C

Based on K-P statement the combined system cannot produce net work output $\rightarrow W_C \leq 0$

$$\boxed{\oint \left(\frac{\delta Q}{T} \right)_{boundary} \leq 0}$$

This is the **Clausius Inequality** which is valid for all thermodynamic cycles, reversible or irreversible.

For a *reversible* cycle (no irreversibilities in the system)

$$\oint \left(\frac{\delta Q}{T} \right)_{\text{int rev}} = 0$$

Since the cycle integral of $(\delta Q/T)$ is 0, the quantity $\delta Q/T$ is a *state property*, it does not depend on the path (similar $\oint dE = 0$).

We call this new property **entropy**, S ,

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{int rev}} \quad \text{units : kJ/K}$$

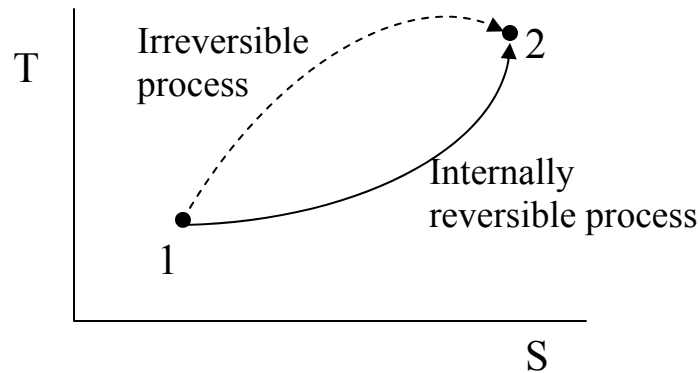
For a process where the system goes from state 1 to 2

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{int rev}}$$

Specific entropy $s = S/M$

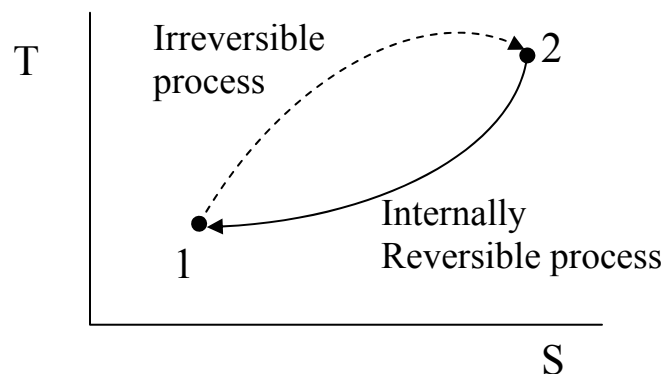
$$s_2 - s_1 = \int_1^2 \left(\frac{\delta Q / M}{T} \right)_{\text{int rev}} = \int_1^2 \left(\frac{\delta q}{T} \right)_{\text{int rev}}$$

The entropy change between two specified states is the same whether the process is reversible or irreversible



To calculate $S_2 - S_1$ evaluate $\int \delta Q / T$ for the reversible path

Consider a cycle made up of an irreversible process followed by a reversible process



Applying Clausius Inequality to the cycle

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_b + \int_2^1 \left(\frac{\delta Q}{T} \right)_{\text{int rev}} \leq 0$$

$$\int_1^2 \left(\frac{\delta Q}{T} \right)_b + (S_1 - S_2) \leq 0$$

$$S_2 - S_1 \geq \int_1^2 \left(\frac{\delta Q}{T} \right)_b$$

Remove inequality sign to get the entropy balance equation for a closed system

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_b + S_{gen}$$

Change in entropy
of the system

Entropy transfer
to the system by
heat transfer

Entropy generated in
the system due to
irreversibilities

$$S_{gen} \begin{cases} > 0 & \text{irreversible process} \\ = 0 & \text{reversible process} \\ < 0 & \text{impossible process} \end{cases}$$

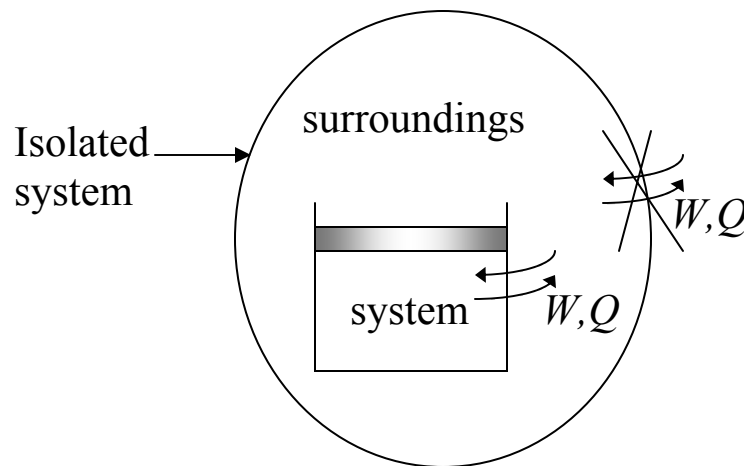
Note: Moran and Shapiro uses symbol σ instead of S_{gen}

For an **isolated system** (adiabatic closed system)

$$\Delta S_{\text{isol}} = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}}$$

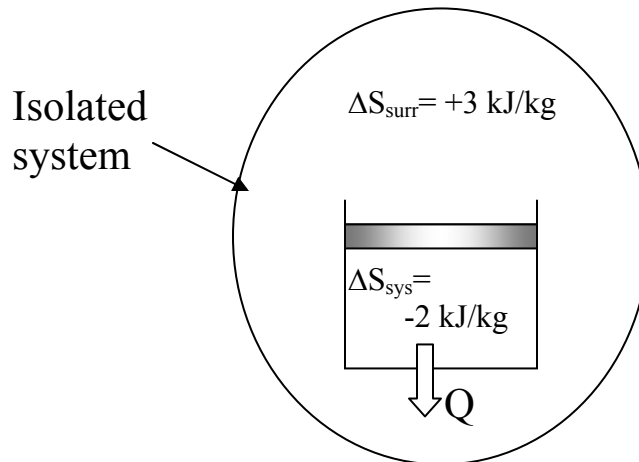
Since $S_{\text{gen}} \geq 0 \rightarrow$ $\Delta S_{\text{isol}} \geq 0$

This is the **Increase in Entropy Principle** which simply stated says that for an isolated system the entropy always increases or remains the same



$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} \geq 0$$

The increase of entropy principle does not say that the entropy of a system cannot decrease



A process that is both adiabatic and reversible is referred to as **isentropic**, and for a closed system

$$\Delta S_{\text{isentropic}} = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}} = 0$$

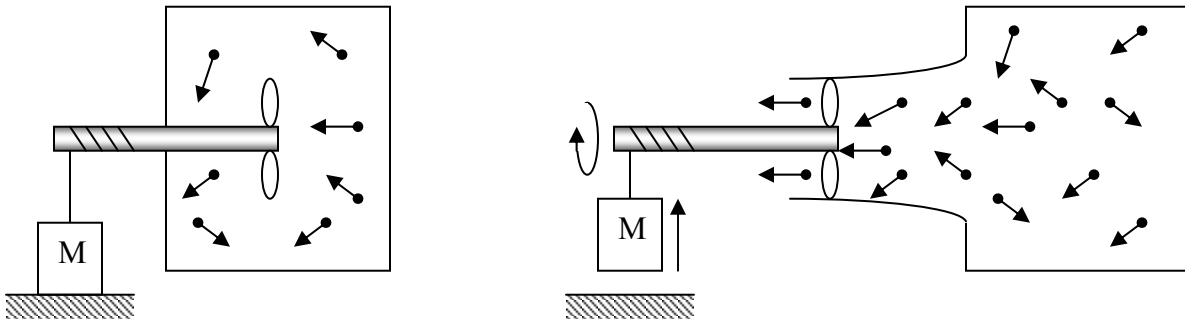
entropy is constant, $S_1 = S_2$.

Microscopic Point of View:

Entropy is the measure of molecular disorder or randomness. As a system becomes more disordered, the position of the molecules becomes less predictable and the entropy increases. Entropy is the lowest in a solid because molecules are held in place and simply vibrate and highest in a gas where the molecules are free to move

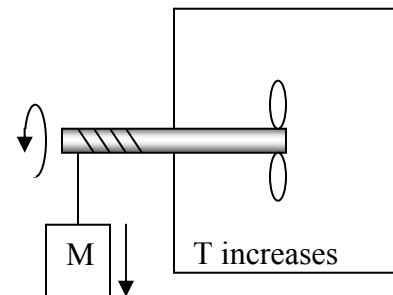
in any direction. Entropy of a pure crystalline substance at absolute zero temperature is zero since the state of each molecule is known \rightarrow Third Law of Thermodynamics

Disorganized energy does not have potential to do useful work,

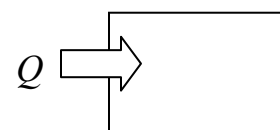


Organize the KE of the molecules (on average moving in one direction) by expanding through a nozzle increases the ability to do useful work. Some of the IE of the molecules is converted into KE resulting in a temperature drop and corresponding drop in entropy.

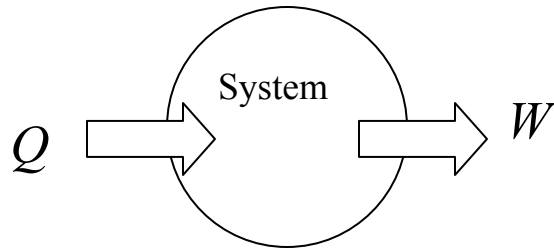
The paddle-wheel work done on a gas increases the level of disorder (entropy) of the gas and thus the energy is degraded during this process



Heat is a form of “disorganized energy” and some entropy will flow with it



Evaluation of Entropy Change in a Closed System



Apply First Law neglecting KE and PE effects, no shaft work

In differential form $du = \delta q - \delta w = \delta q - Pdv$

$$\delta q = du + Pdv$$

For an internally reversible process $ds = \frac{\delta q}{T}$ so

$$Tds = du + Pdv$$

recall $h = u + Pv \rightarrow du = d(h - Pv) = dh - Pdv - vdP$

substitute du into the above equation

$$Tds = (dh - Pdv - vdP) + Pdv$$

$$Tds = dh - vdP$$

These are the Gibb's equations (or simply Tds equations)

For a system undergoing a process from state 1 to state 2

$$s_2 - s_1 = \int_1^2 ds = \int_1^2 \frac{du}{T} + \int_1^2 \frac{P}{T} dv$$

$$s_2 - s_1 = \int_1^2 ds = \int_1^2 \frac{dh}{T} - \int_1^2 \frac{v}{T} dP$$

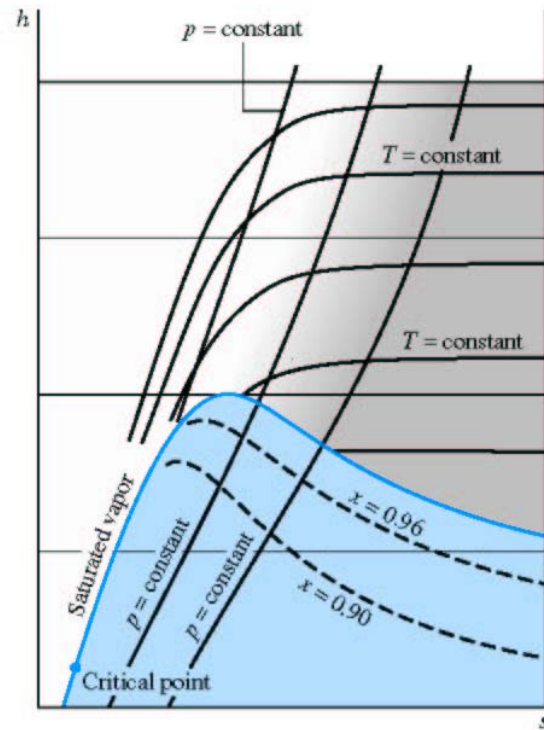
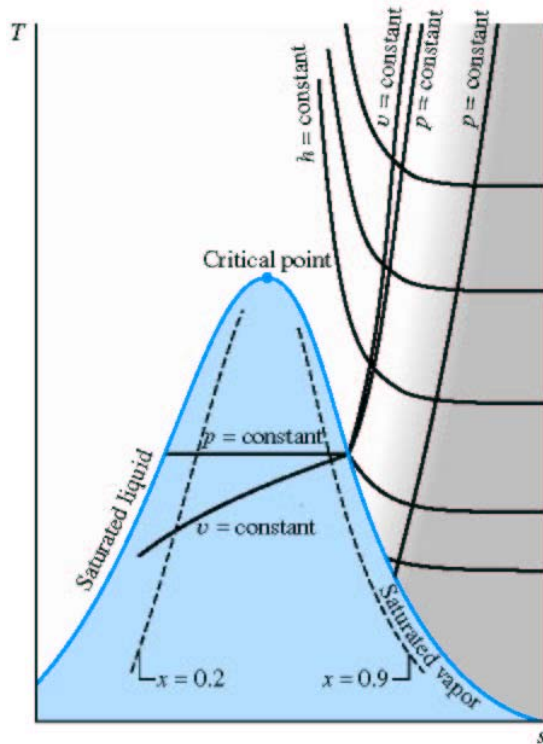
Note the terms on the RHS are state properties, so the terms on the LHS, i.e., entropy, must also be a state property

Although we derived the Tds equations for a reversible process since entropy is a state property we can integrate these equations to get the change in entropy between any two states for any process

$$s_2 - s_1 = \int_1^2 \frac{c_V(P, T)dT}{T} + \int_1^2 \frac{P}{T} dv$$

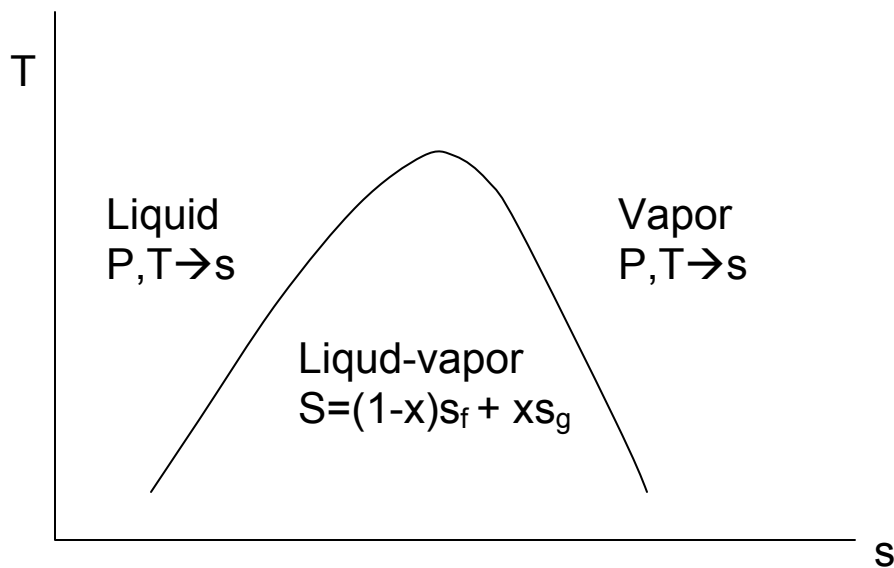
$$s_2 - s_1 = \int_1^2 \frac{c_P(P, T)dT}{T} - \int_1^2 \frac{v}{T} dP$$

The above integration is not straight forward, so entropy is tabulated along with u and h in the steam tables and plotted on T-s and h-s (Mollier) diagrams.



Entropy tabulated in steam tables is relative to an arbitrary reference state

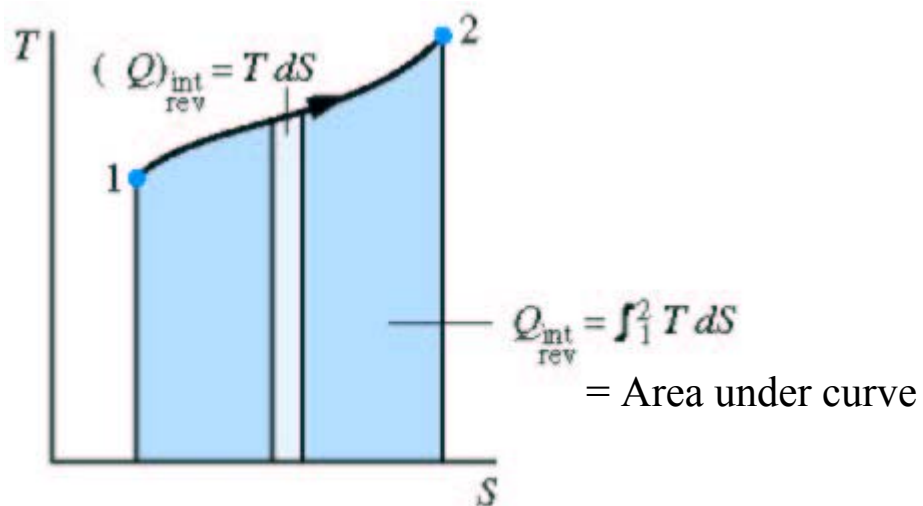
The value of entropy at a given state is determined just like for the other state properties u and h



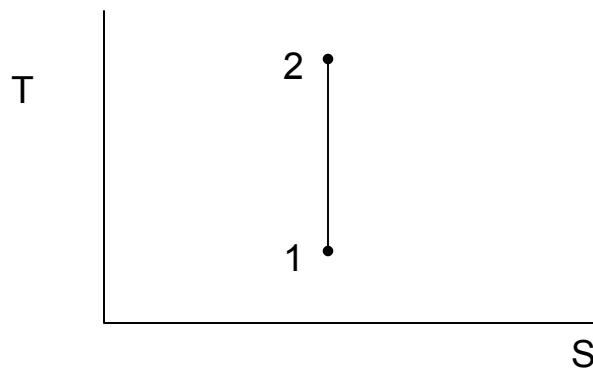
Recall for an internally reversible process $dS = \frac{\delta Q}{T}$

Therefore, $\delta Q_{\text{int}, \text{rev}} = T dS$

Heat added in process from 1 \rightarrow 2 is $Q_{\text{int}, \text{rev}} = \int_1^2 T dS$



For an isentropic process S is constant



No heat transfer \rightarrow area under the curve is zero

Entropy Change for an Ideal Gas

For an ideal gas $du = c_V(T)dT$, $dh = c_P(T)dT$, $Pv = RT$

$$s_2 - s_1 = \int_1^2 \frac{du}{T} + \int_1^2 \frac{P}{T} dv = \int_1^2 \frac{c_V(T)dT}{T} + R \int_1^2 \frac{dv}{v}$$

$$s_2(T_2, v_2) - s_1(T_1, v_1) = \int_1^2 \frac{c_V(T)dT}{T} + R \ln\left(\frac{v_2}{v_1}\right)$$

and

$$s_2 - s_1 = \int_1^2 \frac{dh}{T} - \int_1^2 \frac{v}{T} dP = \int_1^2 \frac{c_P(T)dT}{T} - R \int_1^2 \frac{dP}{P}$$

$$s_2(T_2, P_2) - s_1(T_1, P_1) = \int_1^2 \frac{c_P(T)dT}{T} - R \ln\left(\frac{P_2}{P_1}\right)$$

The value of the specific entropy is set to zero at 0K and 1 atm, e.g., $s(0K, 1 \text{ atm}) = 0$

The specific entropy at temperature T and 1 atm is

$$s(T, 1 \text{ atm}) - s(0K, 1 \text{ atm}) = \int_0^T \frac{c_P(T)dT}{T} - R \ln\left(\frac{1 \text{ atm}}{1 \text{ atm}}\right)$$

$$s^\circ = s(T, 1 \text{ atm}) = \int_0^T c_p(T) \frac{dT}{T}$$

Values of s° are tabulated as a function of T for air in Table A-22

$$\text{so } \int_1^2 c_p(T) \frac{dT}{T} = \int_0^2 c_p(T) \frac{dT}{T} - \int_0^1 c_p(T) \frac{dT}{T} = s_2^\circ - s_1^\circ$$

Therefore,
$$s_2 - s_1 = (s_2^\circ - s_1^\circ) - R \ln\left(\frac{P_2}{P_1}\right)$$

If the specific heats c_p and c_v are taken as *constant*

$$s_2 - s_1 = c_v \int_1^2 \frac{dT}{T} + R \ln\left(\frac{v_2}{v_1}\right)$$

$$s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)$$

$$s_2 - s_1 = c_p \int_1^2 \frac{dT}{T} - R \ln\left(\frac{P_2}{P_1}\right)$$

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$$

