

Specific entropy changes of liquids and solids :

If the values of specific entropy are not tabulated for specific liquid or a specific solid, we can estimate the entropy changes using following method. Recall that liquids and solids are generally considered as incompressible, i.e., the specific volume does not change significantly with pressure at constant temperature. We can then simplify the following relation for entropy change

$$s_2 - s_1 = \int_1^2 \frac{1}{T} du + \int_1^2 \frac{P}{T} dv$$

Substituting $dv \approx 0$ (incompressible substance), $C_p \approx C_v = C$, and $dU = C dT$ we get

$$s_2 - s_1 = \int_1^2 \frac{C(T)}{T} dT$$

Considering $C(T) \approx C_{avg}$ (constant), we get

$$s_2 - s_1 = C_{avg} \ln \left(\frac{T_2}{T_1} \right)$$

Derivation of ideal gas equation based on Carnot cycle :

If we consider an 'isotherm' of an ideal gas in P-v plot, the equation of the isotherm is $Pv = \text{constant}$ or we can write

$$Pv = k\theta \quad (1)$$

where k

is a constant and θ is the 'temperature' defined by the above equation.

Additionally, from Joule's experiment we know that internal energy of a given quantity of ideal gas depends only on its temperature which is defined by θ in this case. Thus :

$$U = U(\theta) \quad (2)$$

Using Carnot cycle for an ideal gas and equations (1) and (2) above, It can be shown (derivation done in class) :

$$\theta = k'T \quad (3)$$

where k' is a constant and T is the absolute temperature. Combining Equation (1) and (3), and using Carnot heat engine with ideal gas as one of the reservoirs, we get $Pv = RT$

Entropy change for adiabatic process :

Note that system together with surroundings (with which energy exchange in the form of heat transfer occurs) undergo an adiabatic process and hence the Second law takes the form (recall fifth statement of Second law for adiabatic process) :

$$(dS_{\text{system}} + dS_{\text{surr.}}) \geq 0$$

Assuming that surrounding undergo quasi-static processes such that surroundings are in internal equilibrium throughout the process and temperature is uniform throughout the process, we can Apply Clausius equation to surroundings. If dQ_{in} is the amount of heat transferred to the system from the surroundings, then

$$dS_{\text{surr.}} = - \left(\frac{dQ_{\text{in}}}{T} \right)$$

Temperature of the surrounding (considered to be at a uniform temperature) .

This is NOT necessarily equal to the system temperature.

Entropy change for adiabatic process :

Substituting entropy change of surroundings in the expression for total entropy change (see last slide), we get

$$dS_{\text{system}} - \left(\frac{dQ_{\text{in}}}{T} \right) \geq 0$$

$$\text{(OR)} \quad dS_{\text{system}} \geq \left(\frac{dQ_{\text{in}}}{T} \right)$$

Here the equality applies to a reversible process. For the entire adiabatically isolated system which consists of system + surroundings (see last slide) the total entropy change is positive (irreversible process) or zero (reversible process). The total entropy change is also known as entropy generated which is positive or zero. Thus,

$$dS_{\text{gen}} = (dS_{\text{system}} + dS_{\text{surr.}}) \geq 0$$

Entropy change for adiabatic process :

In case the surrounding consists of multiple thermal energy reservoirs, then

$$dS_{\text{surr.}} = - \sum_k \left(\frac{dQ_k}{T_k} \right)$$

Here dQ_k is the heat transferred to the system from the thermal energy reservoir at a uniform temperature T_k . It is assumed that process is sufficiently slow so that all of the thermal energy reservoirs are in a state of internal equilibrium throughout the process.

Substituting above in the last equation of previous slide, we get

$$dS_{\text{gen}} = \left[dS_{\text{system}} - \sum_k \left(\frac{dQ_k}{T_k} \right) \right] \geq 0$$

Entropy changes in rate processes :

If we are considering changes with respect to time, we can differentiate the last equation of the previous slide to obtain

$$\dot{S}_{\text{gen}} = \left[\dot{S}_{\text{system}} - \sum_k \left(\frac{\dot{Q}_k}{T_k} \right) \right] \geq 0$$

In the above equation,

$\dot{S}_{\text{system}} = \frac{d}{dt} (S_{\text{system}})$ = Rate of increase of entropy of the (control mass) system

\dot{Q}_k = Rate at which heat is transferred to the system from the thermal energy reservoir at a uniform temperature T_k

\dot{S}_{gen} = Rate at which entropy of the (system+surroundings) increases. Note that surroundings include all of the thermal energy reservoirs with which the system exchanges heat.

Entropy changes in rate processes :

Rearranging the equation on the last slide, we get

$$\dot{S}_{\text{system}} = \sum_k \left(\frac{\dot{Q}_k}{T_k} \right) + \dot{S}_{\text{gen}}$$

The entropy of the system at a given time can be expressed as:

$$S_{\text{system}}(t) = \int_{\text{CM}} s \rho \, dV$$

In the above equation, s and ρ are the specific entropy and mass density at a given point within the control mass (CM).

Rates of change of entropy of the control mass and control volume:

The entropy of a control volume (this could be an equipment through which fluid flows) is defined as the entropy of the mass of the fluid within the CV at any given instant of time t .

$$S_{CV}(t) = \int_{CV} s \rho \, dV$$

According to Reynolds transport theorem (see Lecture 8), the rates of change entropy of the control mass and the control volume satisfy the following equation:

$$\frac{d}{dt}(S_{\text{system}}) = \frac{d}{dt}(S_{CV}) + \int_{CS} s \rho (\vec{V} \cdot \vec{n}) \, dA$$

Here the integral on the right hand side is over the control surface (CS) that bounds the control volume (see also Lecture 8)

Rates of change of entropy of the control volume:

Substituting the right hand side of the last equation (see previous slide) in the expression of the rate of change of entropy of the (control mass) system, we get

$$\frac{d}{dt}(S_{cv}) + \int_{cs} s \rho (\vec{V} \cdot \vec{n}) dA = \sum_k \left(\frac{\dot{Q}_k}{T_k} \right) + \dot{S}_{gen}$$

The control volume is so chosen that the direction of the flow at the inlet or outlet is perpendicular to the control surface. If we assume the properties s and ρ to be constant over the area of an inlet or outlet, the product $(s \rho)$ in the integral on the left hand side can be taken outside of the integral sign. In that case, we get the following simplified form.

$$\frac{d}{dt}(S_{cv}) + \sum_{out} \dot{m} s - \sum_{in} \dot{m} s = \sum_k \left(\frac{\dot{Q}_k}{T_k} \right) + \dot{S}_{gen}$$

Rates of change of entropy of the control volume:

Rearranging the last equation in the previous slide, we get

$$\frac{d}{dt}(S_{cv}) = \sum_{in} \dot{m} s - \sum_{out} \dot{m} s + \sum_k \left(\frac{\dot{Q}_k}{T_k} \right) + \dot{S}_{gen}$$

Here the first and second sums on the right hand side are over inlets and outlets respectively. The third sum on the right hand side is over all the thermal energy reservoirs with which there is a exchange of heat of the fluid in the control volume. The last term is the rate of change of entropy of (fluid in the control volume + surroundings). This is also called rate of generation of entropy. It is positive for irreversible processes and zero for a reversible process.

For a steady-flow equipment,

$$\frac{d}{dt}(S_{cv}) = 0$$