TdS Equation

Consider a reversible process for a simple, compressible substance:

$$(\delta Q)_{rev} = dU + (\delta W)_{rev},$$

$$TdS = dU + pdV, \quad \text{where dS=}\left(\frac{\delta Q}{T}\right)_{rev}, \ (\delta W)_{rev} = pdV$$

Since $H = U + pV, \quad dH = dU + pdV + Vdp = TdS + Vdp$

$$TdS = dH - Vdp$$

The equations can be written on a unit mass basis as

$$Tds = du + pdv, \quad \text{or} \quad Tds = dh - vdp$$

- Derived using reversible process, but the relations can be used for any process, reversible or irreversible, since entropy, internal energy, enthalpy, etc are all properties and are independent of the processes links the states.

Entropy Change of an Ideal Gas

Tds equations: $ds = \frac{du}{T} + \frac{p}{T}dv, \qquad ds = \frac{dh}{T} - \frac{v}{T}dp$

For an ideal gas: $u = u(T) = c_v(T)dT,\ h = h(T) = c_p(T)dT,\ pv = RT$

$$ds = c_v(T)\frac{dT}{T} + R\frac{dv}{v}, \qquad ds = c_p(T)\frac{dT}{T} - R\frac{dp}{p}$$

Entropy at any state can be determined by integrating these relations (from state 1 to 2) :

Functions of temperature only

$$s(T_2, v_2) - s(T_1, v_1) = \boxed{\int_{T_1}^{T_2} c_v(T)\frac{dT}{T}} + R\ln\left(\frac{v_2}{v_1}\right) \quad \text{or}$$

$$s(T_2, p_2) - s(T_1, p_1) = \boxed{\int_{T_1}^{T_2} c_p(T)\frac{dT}{T}} - R\ln\left(\frac{p_2}{p_1}\right)$$

$c_p(T)$ & $c_v(T)$ are not necessary constants

Specific Entropy

Define specific entropy s°(T):

$s^\circ(T)=\int_0^T \frac{c_p(T)}{T}dT$ as the specific entropy at temperature T and a pressure of 1 atm.

$$\int_{T_1}^{T_2} c_p(T)\frac{dT}{T} = \int_0^{T_2} c_p(T)\frac{dT}{T} - \int_0^{T_2} c_p(T)\frac{dT}{T} = s^\circ(T_2) - s^\circ(T_1)$$

$$s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} c_p(T)\frac{dT}{T} - R\ln\left(\frac{p_2}{p_1}\right) = s^\circ(T_2) - s^\circ(T_1) - R\ln\left(\frac{p_2}{p_1}\right)$$

The use of specific entropy allows one to determine the entropy changes between states when c_p might not be a constant. s° can be looked up from standard thermodynamic tables (see Appendix in the FGT book).

Isentropic Process

For two states between isentropic process:

$$0 = s(T_2, p_2) - s(T_1, p_1) = s^\circ(T_2) - s^\circ(T_1) - R\ln\left(\frac{p_2}{p_1}\right)$$

$$p_2 = p_1 \exp\left[\frac{s^\circ(T_2) - s^\circ(T_1)}{R}\right], \text{ or } \frac{p_2}{p_1} = \frac{\exp\left[s^\circ(T_2)/R\right]}{\exp\left[s^\circ(T_1)/R\right]}$$

Now, define a new term called relative pressure $p_r(T)$

such that: $p_r(T) = \exp\left[\dfrac{s^\circ(T)}{R}\right]$; it should be a function of temperature only.

Therefore, for an isentropic process: $\dfrac{p_2}{p_1} = \dfrac{p_{r2}}{p_{r1}} = \dfrac{p_r(T_2)}{p_r(T_1)}$.

Note: P_r is not truly a pressure.

Example

Air undergoes an isentropic compression process from p_1=1 atm, T_1=300k, to a final state of T_2=1000 K. Assume ideal gas, determine the final pressure p_2 using (a) specific entropy, (b) relative pressure from table.

(a) Isentropic process: $s°(T_2) - s°(T_1) - R\ln\left(\frac{p_2}{p_1}\right) = 0$

$$p_2 = p_1 \exp\left[\frac{s°(T_2) - s°(T_1)}{R}\right] = (1\,atm)\exp\left[\frac{7.9716 - 6.7052}{0.287}\right] = 82.5\,atm$$

(b) $\frac{p_2}{p_1} = \frac{p_{r2}}{p_{r1}} = \frac{p_r(T_2)}{p_r(T_1)}$, $P_2 = p_1\left(\frac{p_{r2}}{p_{r1}}\right) = (1\,atm)\left(\frac{114.41}{1.3894}\right) = 82.3\,atm.$

All values in this problem are read from table B.1

Example (cont.)

Use the previous example as air undergoes an isentropic process from p_1=1 atm, T_1=300k, to a final state of T_2=1000 K. Assume ideal gas and constant c_p and γ=1.4, determine the final pressure $p_{2.}$

Ideal gas relation for a constant c_p :

$$\frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{\gamma/\gamma-1}, \quad \frac{p_2}{1atm} = \left(\frac{1000}{300}\right)^{3.5} = 67.6(atm)$$

Much smaller since c_p increases with an increasing temperature.

The air can absorb more thermal energy for given temperature increase, therefore, assuming a constant c_p value underestimates the pressure required to compress the air to the specific temperature.