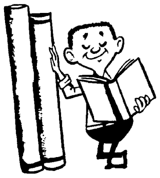
State Equations



Reading	Problems
6-4 ⟶ 6-12	

An Isentropic Process for an Ideal Gas

Given:

- constant specific heats over a wide range of temperature
- $ds = 0$
- $du = c_v dT \equiv c_v = \left(\frac{\partial u}{\partial T}\right)_V$
- $dh = c_p dT \equiv c_p = \left(\frac{\partial h}{\partial T}\right)_P$

Gibb's equation can be written as

$$Tds = du + Pdv = c_v dT + Pdv = 0 \qquad (1)$$

where $ds = 0$ because we have assumed an isentropic process.

The definition of enthalpy is

$$h = u + Pv$$

Taking the derivative yields

$$dh = \underbrace{du + Pdv}_{\equiv Tds} + vdP$$

$$dh = Tds + vdP \quad \Rightarrow \quad Tds = 0 = dh - vdP$$

$$\boxed{c_p dT - vdP = 0} \qquad (2)$$

Equating Eqs. (1) and (2) through the $\boldsymbol{dT}$ term gives

$$\boldsymbol{\frac{dP}{P} = -\frac{c_p}{c_v}\,\frac{dv}{v}} \qquad \textbf{(3)}$$

Integrating (3) from its initial state to a final state

$$\boldsymbol{P_1 v_1^k = P_2 v_2^k = constant = P v^k}$$

where

$$\boldsymbol{k = \frac{c_p}{c_v}}$$

The product of $\boldsymbol{P \cdot v^k}$ remains constant for an ideal gas when:

- specific heats are constant
- the gas undergoes an isentropic process ⟶ reversible + adiabatic

Combining this result with the ideal gas equation of state

$$\boxed{\boldsymbol{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}}}$$

The isentropic process is a special case of a more general process known as a polytropic process

where ⟶ $\boldsymbol{Pv^n = constant}$ and $\boldsymbol{n}$ is any number.

Special Cases

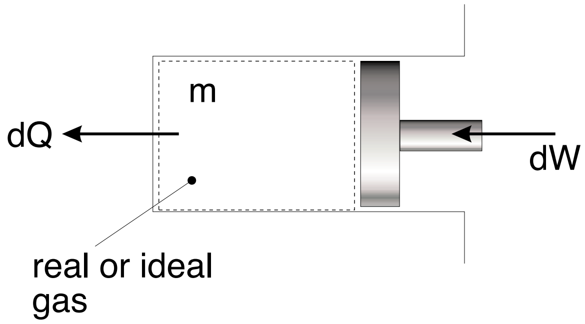
$\boldsymbol{n = 1}$ $\quad \boldsymbol{Pv = RT = constant}$ $\Rightarrow$ isothermal process

$\boldsymbol{n = 0}$ $\quad \boldsymbol{Pv^0 = constant = P}$ $\Rightarrow$ isobaric process (constant pressure)

$\boldsymbol{n = k}$ $\quad \boldsymbol{Pv^k = constant}$ $\Rightarrow$ isentropic process ($\boldsymbol{k = c_p/c_v}$)

$\boldsymbol{n = \infty}$ $\quad \boldsymbol{Pv^\infty = constant}$ $\Rightarrow$ isochoric process (constant volume)

Reversible Compression/Expansion for a Fixed Mass



$$\begin{aligned} dU &= dW - dQ \\ mdu &= dW - dQ \qquad (1) \end{aligned}$$

$$dS = -\frac{dQ}{T} + \mathcal{P}_S$$

where $\mathcal{P}_S = 0$ for a reversible process.

$$mds = -\frac{dQ}{T} \qquad (2)$$

Combining (1) and (2) through the $-dQ$ term gives

$$mdu = dW + mTds \qquad (3)$$

From Gibb's Eq., $Tds = du + Pdv$

$$mdu = mTds - mPdv \qquad (4)$$

Combining Eqs. (3) and (4)

$$\begin{aligned} mTds - mPdv &= dW + mTds \\ dW &= -mPdv \end{aligned}$$

$$W_{1-2} = -m\int_1^2 Pdv \qquad \Rightarrow \qquad w_{1-2} = \frac{W_{1-2}}{m} = -\int_1^2 Pdv$$

Reversible Isothermal Process for an Ideal Gas

We know for an ideal gas

$$\boldsymbol{Pv = constant = RT}$$

or

$$\boldsymbol{P = \frac{constant}{v}} \qquad \textbf{(1)}$$

$$\boldsymbol{Pv = constant = P_1v_1 = P_2v_2} \qquad \textbf{(2)}$$

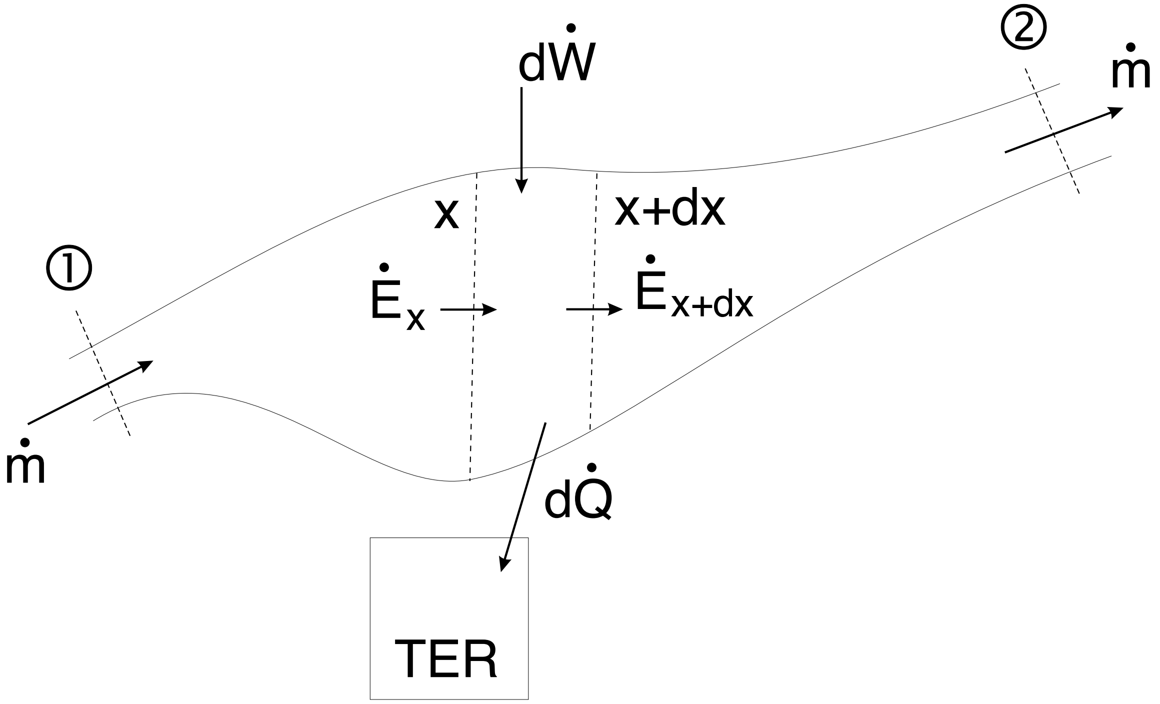
The work done at the boundary of a simple, compressible substance (S.C.S.) during a reversible process

$$\begin{aligned} \boldsymbol{w_{1-2} = -\int_1^2 Pdv} &= \boldsymbol{-constant \int_1^2 \frac{dv}{v}} \\ &= \boldsymbol{-P_1v_1 \ln\frac{v_2}{v_1}} \\ &= \boldsymbol{P_1v_1 \ln\frac{v_1}{v_2}} \end{aligned}$$

$$\begin{aligned} \boldsymbol{W_{1-2} = mRT \ln\frac{v_1}{v_2}} &= \boldsymbol{mRT \ln\frac{V_1}{V_2}} \\ &= \boldsymbol{mRT \ln\frac{P_2}{P_1}} \end{aligned}$$

A General Formulation

Steady State, Steady Flow in a Flow Channel of Arbitrary Cross-section with Work and Heat Transfer



$$
\begin{aligned}
d\dot{E} &= \dot{E}_{final} - \dot{E}_{initial} \\
&= \dot{E}_{x+dx} - \dot{E}_x
\end{aligned}
$$

where

$$
\begin{aligned}
\dot{E} &= \dot{m}(e + Pv) \\
&= \dot{m}(u + \frac{(v^*)^2}{2} + gz + Pv)
\end{aligned}
$$

From the 1st law

$$
\begin{matrix} rate\ of\ energy \\ storage \end{matrix} = \begin{matrix} rate\ of \\ work \end{matrix} + \begin{matrix} rate\ of \\ heat\ transfer \end{matrix} + \begin{matrix} net\ rate\ of\ energy \\ leaving\ the\ system \end{matrix}
$$

$$\frac{dE_{CV}}{dt} = d\dot{W} - d\dot{Q} - d\dot{E} \qquad (1)$$

where $\frac{dE_{CV}}{dt} = 0$ for steady state.

Equation (1) becomes

$$0 = d\dot{W} - d\dot{Q} - \dot{m}\; d\left[u + Pv + \frac{(v^*)^2}{2} + gz\right] \qquad (2)$$

From the 2nd law

$$\begin{matrix} rate\ of \\ entropy \\ storage \end{matrix} = \left\{ \begin{matrix} rate\ of \\ entropy \\ inflow \end{matrix} - \begin{matrix} rate\ of \\ entropy \\ outflow \end{matrix} \right\} + \begin{matrix} rate\ of \\ entropy \\ production \end{matrix}$$

$$\frac{dS_{CV}}{dt} = [\dot{m}s]_x - [\dot{m}s]_{x+dx} - \frac{d\dot{Q}}{T_{TER}} + \dot{\mathcal{P}}_S$$

where $\frac{dS_{CV}}{dt} = 0$ for steady state.

$$0 = -\dot{m}ds - \frac{d\dot{Q}}{T_{TER}} + \dot{\mathcal{P}}_S$$

or

$$d\dot{Q} = T_{TER}\dot{\mathcal{P}}_S - T_{TER}\dot{m}ds \qquad (3)$$

Combining (2) and (3) through $d\dot{Q}$

$$\boxed{T_{TER}\;\dot{\mathcal{P}}_S - T_{TER}\;\dot{m}ds = d\dot{W} - \dot{m}\; d\left(u + Pv + \frac{(v^*)^2}{2} + gz\right)} \qquad (4)$$

Equation (4) can be used for any SS-SF process.

Special Cases

1. Reversible, SS-SF Process

$$\frac{\dot{W}}{\dot{m}} = \int_{in}^{out} v dP$$

2. Incompressible Substance

$$\frac{\dot{W}}{\dot{m}} = v_{in}(P_{out} - P_{in})$$

3. Incompressible Substance and $d\dot{W} = 0$

$$\frac{P}{\rho} + \frac{(v^*)^2}{2} + gz = constant$$

4. Isothermal Ideal Gas, Compression/Expansion

$$\frac{\dot{W}}{\dot{m}} = P_{in} v_{in} \ln\left(\frac{P_{out}}{P_{in}}\right)$$

5. Isentropic Ideal Gas, Compression/Expansion

$$\frac{\dot{W}}{\dot{m}} = \left(\frac{k}{k-1}\right)(Pv)_{in}\left[\left(\frac{P_{out}}{P_{in}}\right)^{(k-1)/k} - 1\right] = c_p(T_{out} - T_{in})$$

Incompressible Liquids

- a substance whose volume cannot be changed
- no substance is truly incompressible, but this model is good for most liquids and solids

State Postulate

- the number of independent intensive thermodynamic properties is equal to the number of relevant <u>reversible</u> work modes <u>plus one</u>.
- the "plus one" is for the independent control on energy through heat transfer
- we know that for a *simple* (has only one work mode), *compressible* (the work model is Pdv work) substance
  - 2 thermodynamic properties will fix the rest
    - ∗ list of intensive properties includes, T, u, P, v, s
    - ∗ state postulate says two will fix the rest, i.e. if u and v are known, the equations of state are

$$\begin{aligned} T &= T(u, v) \\ P &= P(u, v) \\ s &= s(u, v) \end{aligned}$$

Hence, if the substance is assumed to be incompressible, then its internal energy, for example, cannot be varied independently by work transfer $\longrightarrow$ but it can be varied by heat transfer at constant volume, i.e. $Pdv = 0$ since $dv = constant$. There are no reversible work modes.

i.e.

$$u = u(T) \;\; only$$

$$dh = du + P\cancelto{0}{dv} + vdP$$

where $Pdv = 0$ for an incompressible substance.

For an incompressible substance

$$c_p = c_v = \overline{c}$$

Gibb's Equation. states

$$T ds = du + P \cancelto{0}{dv}$$

therefore

$$ds = \frac{du}{T} = \overline{c}\, \frac{dT}{T}$$

Integrating from the initial state to the final state

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

as $T_2 \longrightarrow T_1$, i.e. isothermal condition $\Rightarrow s_2 \longrightarrow s_1$, i.e. isentropic.

In summary

$$\begin{aligned}
u_2 - u_1 &= \overline{c}\, (T_2 - T_1) \\
h_2 - h_1 &= (u_2 - u_1) + v(P_2 - P_1) \\
s_2 - s_1 &= \overline{c}\ \ln(T_2/T_1)
\end{aligned}$$