Entropy balance and isentropic processes

Entropy changes in solids and liquids (i.e. incompressible)

For incompressible substances $dV = 0$, and $c_V = c_P = c(T)$.

The first law (or equivalently Gibbs equation) gives:

$$du = c(T) \, dT = \delta q = T \, ds$$

The infinitesimal variation of specific entropy is thus:

$$ds = c(T)\frac{dT}{T}$$

For a finite process:

$$s(2) - s(1) = \int_1^2 ds = \int_{T_1}^{T_2} c(T)\frac{dT}{T}$$

For constant (temperature independent) specific heat:

$$s(2) - s(1) = c\int_{T_1}^{T_2} \frac{dT}{T} = c\ln\frac{T_2}{T_1}$$

Entropy changes in ideal gases - volume integral

Ideal gases are compressible: *dV ≠ 0*
For ideal gases, the internal energy only depends on *T*: $du = c_v(T)\, dT$
However, energy is exchanged as heat *and* work:

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

We replace the expession for du, and we use the ideal gas law to eliminate the pressure. (Ideal gas law: $Pv = RT$ with $R = R_u/M = R_u m/N$)
The infinitesimal variation of specific entropy is thus:

$$ds = \frac{1}{T} c_v(T)\, dT + \frac{R}{v} dv$$

For a finite process:

$$s(2) - s(1) = \int_1^2 ds = \int_{T_1}^{T_2} \frac{c_v(T)}{T} dT + \int_{v_1}^{v_2} \frac{R}{v} dv$$

The temperature integral is the same as before. The volume integral gives:

$$\int_{v_1}^{v_2} \frac{R}{v} dv = R \ln \frac{v_2}{v_1}$$

Entropy changes in ideal gases - pressure integral

Alternatively, we can use the specific enthalpy $h = u + Pv$
For ideal gases, the enthalpy only depends on T: $dh = c_p(T)dT$
Once again, we start from Gibbs equation, but we use $dh = du + Pdv + vDP$

$$ds = \frac{1}{T}du + \frac{P}{T}dv = \frac{1}{T}dh - vdP$$

We replace the expession for dh, and we use the ideal gas law to eliminate the volume. (Ideal gas law: $Pv = RT$ with $R = R_u/M = R_u m/N$)
The infinitesimal variation of specific entropy is thus:

$$ds = \frac{1}{T}c_p(T)\ dT - \frac{R}{P}dP$$

For a finite process:

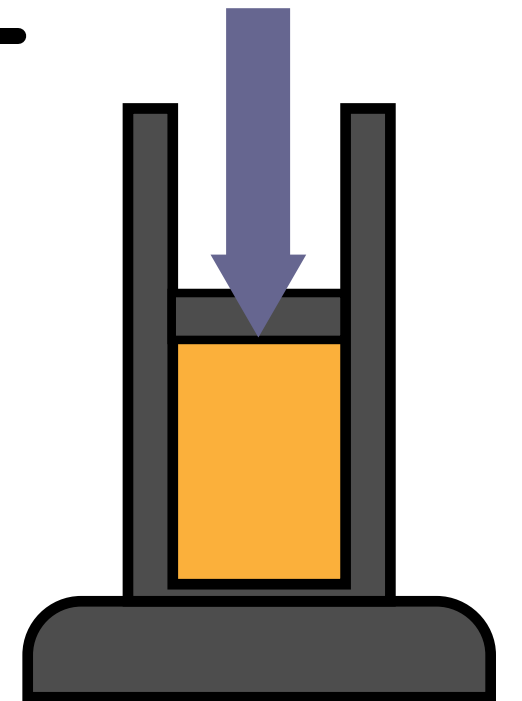$$s(2) - s(1) = \int_1^2 ds = \int_{T_1}^{T_2} \frac{c_p(T)}{T}dT - \int_{P_1}^{P_2} \frac{R}{P}dP$$

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$$\int_{P_1}^{P_2} \frac{R}{P}dP = R\ln\frac{P_2}{P_1}$$

Example 6.2

A cylinder contains $m = 0.2\ kg$ of hydrogen gas with specific volume $v_1 = 1.0\ m^3/kg$ and temperature $T_1 = 350\ K$. The gas is compressed by a piston to a final state of $v_2 = 0.2\ m^3/kg$ and $T_2 = 650\ K$. Find the entropy change ΔS of the gas during this process.

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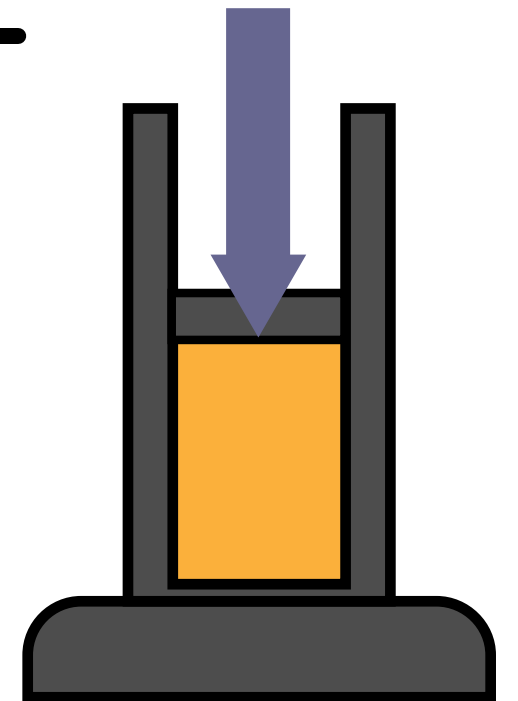
Gas constant of hydrogen (Appendix 1)

$R = 4.124 \text{ kJ/kgK}$

Average temperature

$T_{\text{avg}} = (T_1 + T_2)/2 = (650\,\text{K} + 350\,\text{K})/2 = 500\,\text{K}$

Specific heat capacity at constant volume (Appendix 4)

$c_{v,\text{avg}} = 10.389 \text{ kJ/kgK}$

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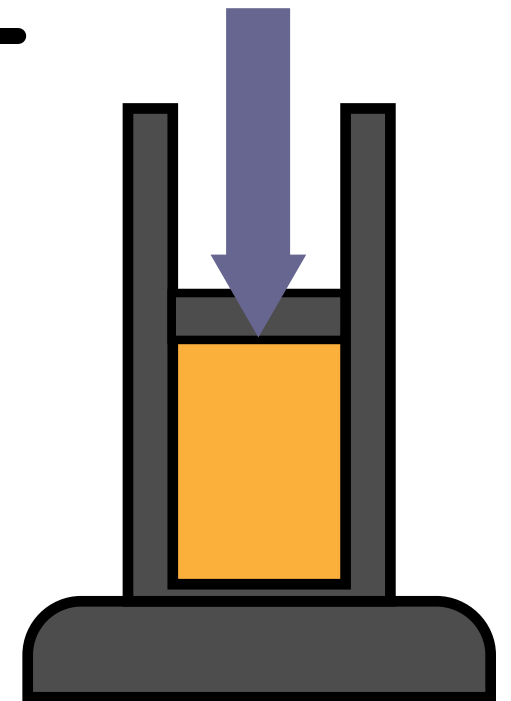
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$$\Delta s = s_2 - s_1 = c_v \ln\frac{T_2}{T_1} + R \ln\frac{v_2}{v_1}$$

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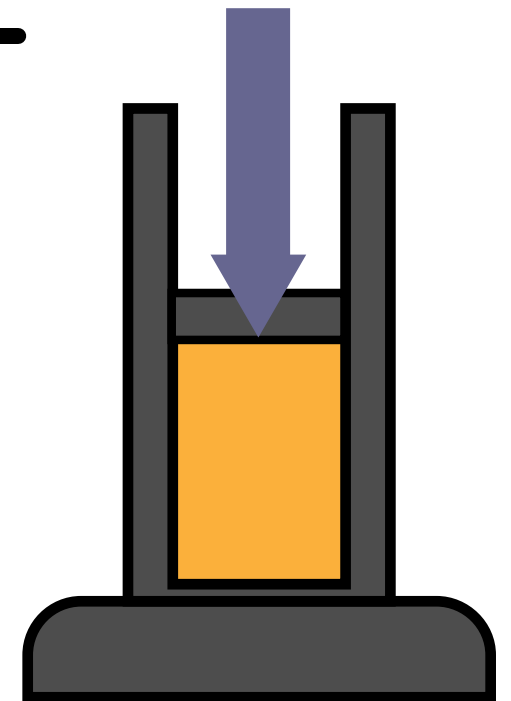
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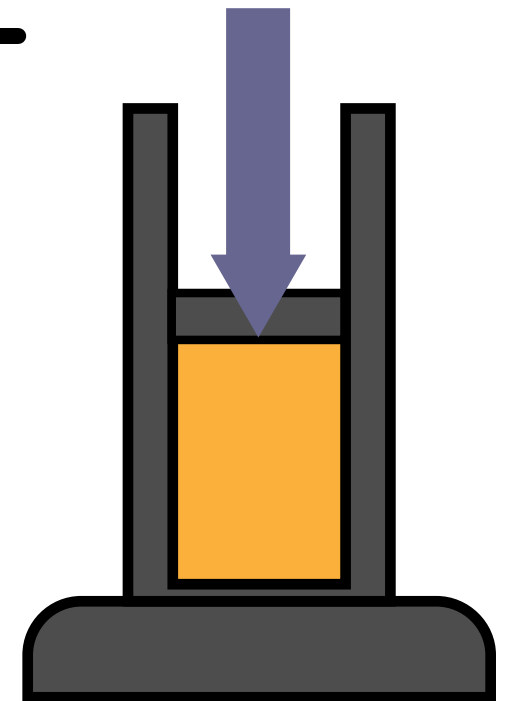Specific heat capacity at constant volume (Appendix 4)

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Change of entropy

$$\Delta S = m\Delta s = 0.2 \text{ kg} \times (-0.20645 \text{ kJ/kgK}) = \boxed{-0.041289 \text{ kJ/K}}$$

Ideal gas tables

When the heat capacity is not constant, we can use the ideal gas tables. The entropy variation from a reference temperature (usually $T_{ref} = 0$ K) is tabulated for some gases:

$$s^0(T) = \int_{T_{ref}}^{T} \frac{c_p(T')}{T'} dT'$$

Then we split the integral in two terms:

$$\int_{T_1}^{T_2} \frac{c_p(T)}{T} dT = \int_{T_{ref}}^{T_2} \frac{c_p(T)}{T} dT - \int_{T_{ref}}^{T_1} \frac{c_p(T)}{T} dT = s^0(T_2) - s^0(T_1)$$

Alternatively, we can use linear interpolation, or use numerical methods.

Isentropic processes in ideal gases

An adiabatic (i.e $\delta Q = 0$) reversible process is isentropic: $\Delta S = 0$

For ideal gases, and with the further assumption that the specific heats are constant (temperature independent) we can compute different relations between the initial and final values of temperature, pressure and volume.

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The starting point is:

$$\Delta s = c_v \ln\frac{T_2}{T_1} + R \ln\frac{v_2}{v_1} = 0 \implies c_v \ln\frac{T_2}{T_1} = -R \ln\frac{v_2}{v_1}$$

and the analogous relation for pressure:

$$\Delta s = c_v \ln\frac{T_2}{T_1} - R \ln\frac{P_2}{P_1} = 0 \implies c_v \ln\frac{T_2}{T_1} = R \ln\frac{P_2}{P_1}$$

Using $c_p - c_v = R$ and $\gamma = \dfrac{c_p}{c_v}$

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With some manipulations (see sec. 6.7.1 in the book) we obtain:

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{(\gamma-1)}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^{\gamma}$$

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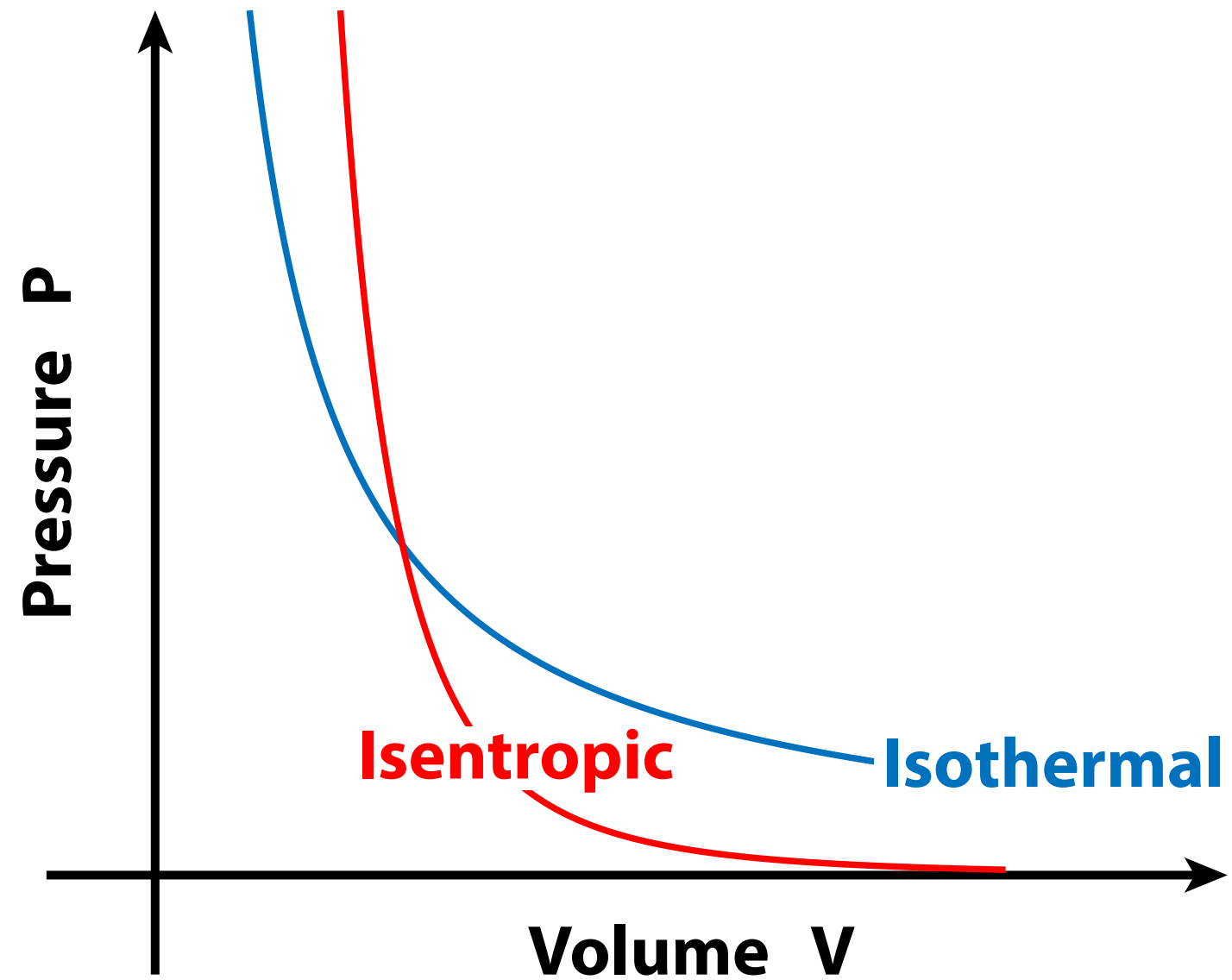
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$$\implies Pv^{\gamma} = \text{constant}$$

Isentropic processes in ideal gases

Isothermal: $Pv = \text{constant}$

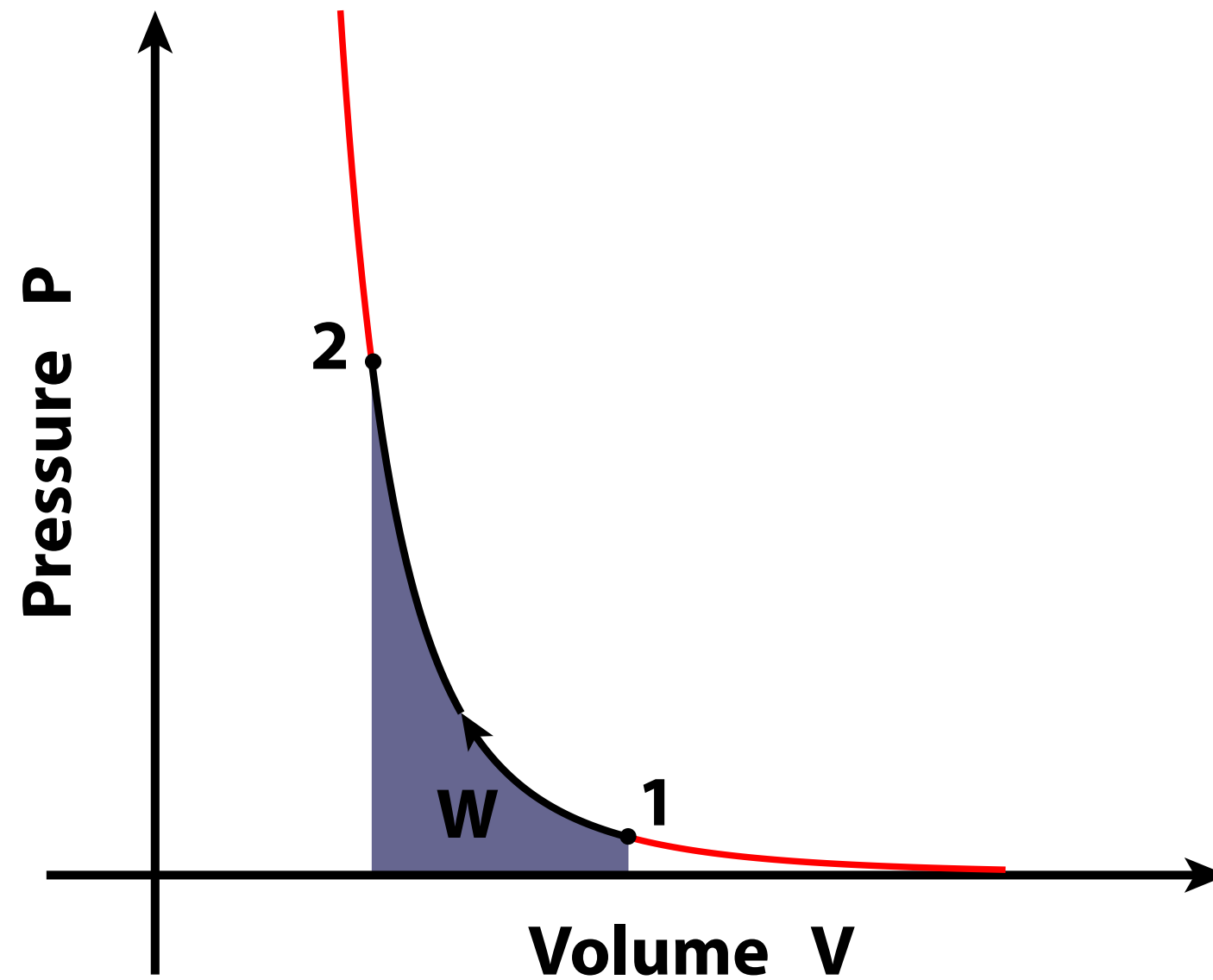Isentropic: $Pv^{\gamma} = \text{constant}$

Isentropic processes in ideal gases - work calculation

The energy transferred *to* the system in the form of work is: $\delta W = -P \, dV$

For an isentropic process: $P = P_1 \left(\dfrac{V_1}{V} \right)^{\gamma}$

For a finite process:

$$W = \int_1^2 \delta W = - \int_{V_1}^{V_2} P_1 \left(\frac{V_1}{V} \right)^{\gamma} dV$$

Pressure P

Volume V

2

1

W

$$P_2 v_2^{\gamma} = P_1 v_1^{\gamma}$$

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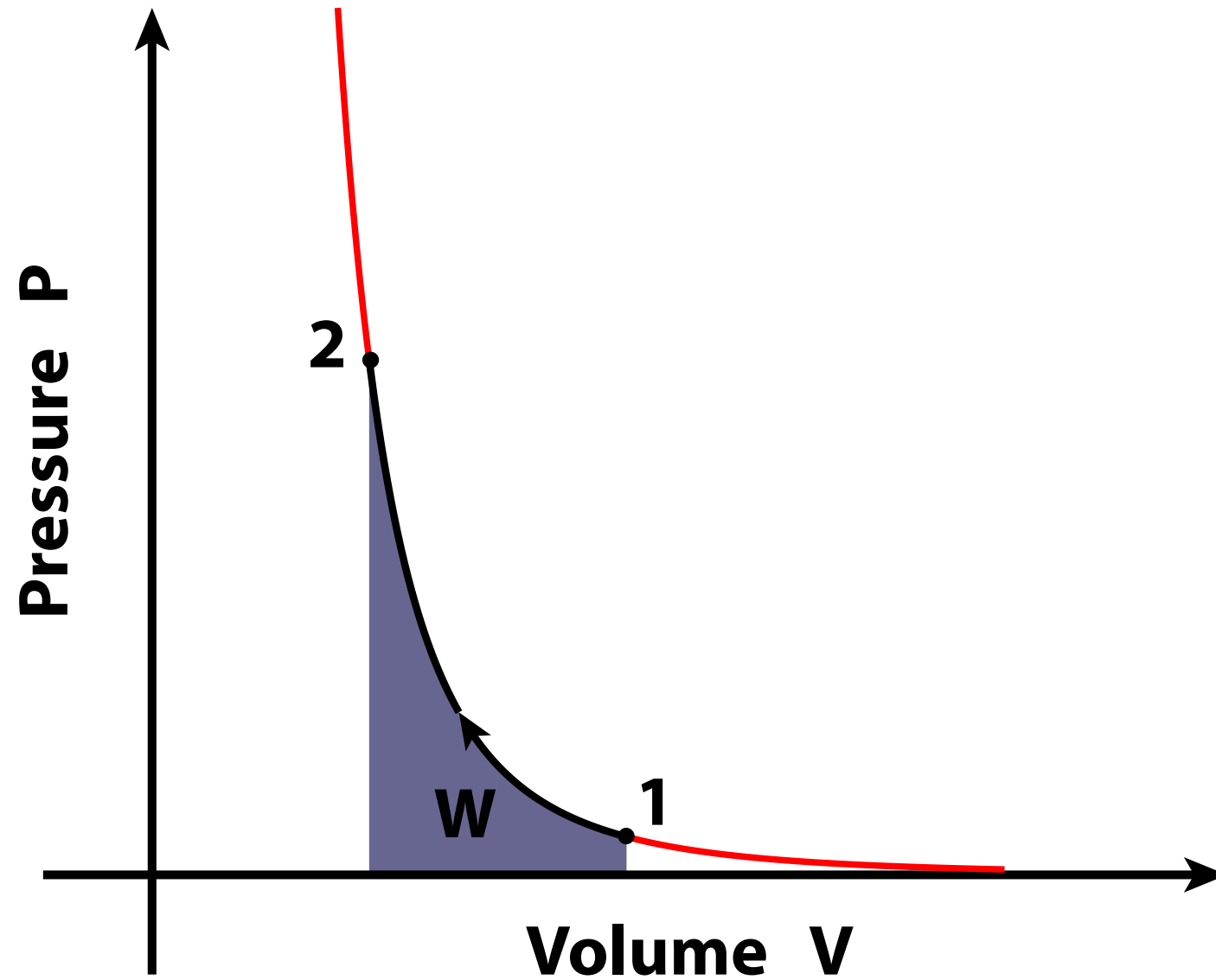$$W = \int_1^2 \delta W = - \int_{V_1}^{V_2} P_1 \left(\frac{V_1}{V} \right)^{\gamma} dV$$

$$= -P_1 V_1^{\gamma} \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2} = -P_1 V_1^{\gamma} \frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma}$$

$$W = \frac{P_1 V_1 - P_2 V_2}{1-\gamma}$$

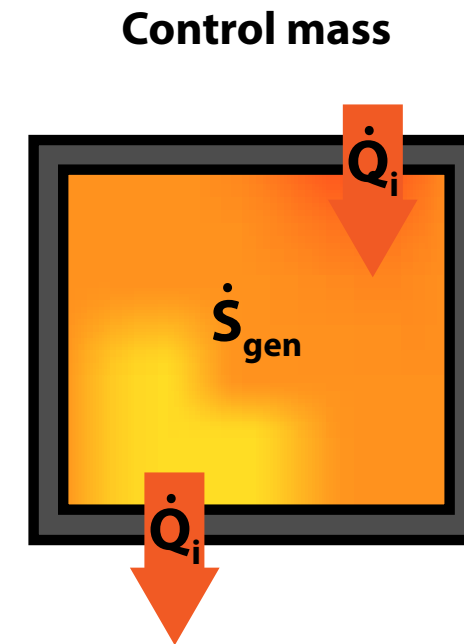$$P_2 v_2^{\gamma} = P_1 v_1^{\gamma}$$

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Entropy balance

		Heat transfer	Mass transfer
Control mass	Closed system	yes	no

$\dot{Q}_i$

$\dot{S}_{gen}$

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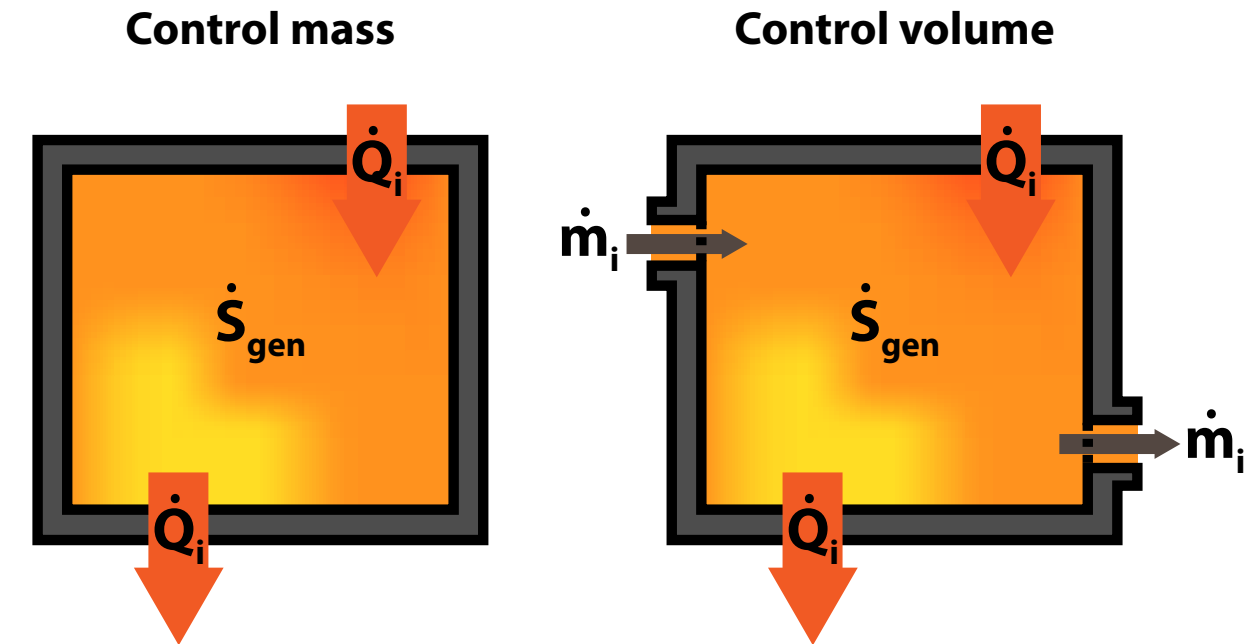
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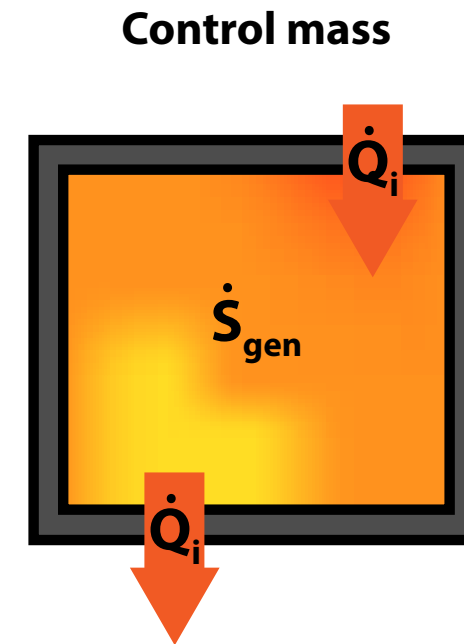
Total entropy variation of the system: $$\dot{S} = \dot{S}_{\text{gen}} + \sum_j \frac{\dot{Q}_j}{T_j}$$

$\dot{S}_{\text{gen}}$ Entropy generation within the system: irreversible processes
- Associated to dissipation (e.g. viscosity, friction, Joule heating)
- Associated to gradients (e.g. temperature, pressure, concentration)

Entropy transfer to/from outside the system

$\sum_j \dfrac{\dot{Q}_j}{T_j}$ • Associated to heat transfer (in absence of T-gradients: $T_j = T$)

Entropy balance

		Heat transfer	Mass transfer
Control mass	Closed system	yes	no
Control volume	Open System	yes	yes

Control mass   Control volume

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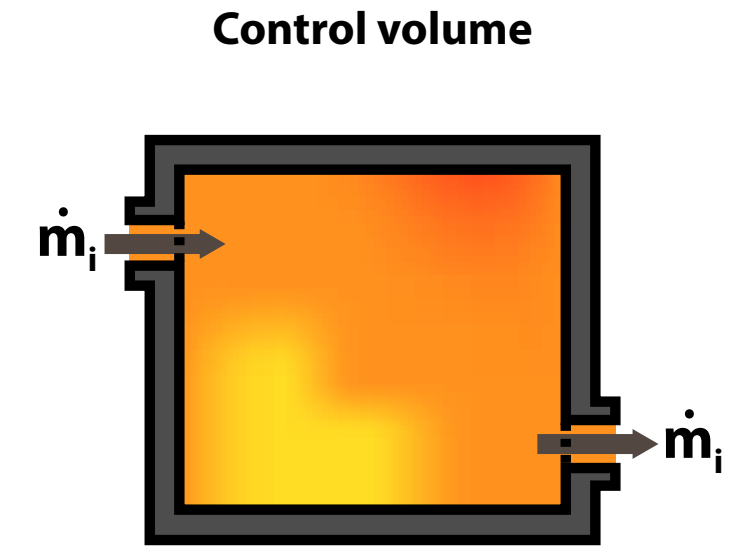
Entropy balance at steady flow

Examples: turbines, nozzles, etc
Steady flow, adiabatic, reversible, isentropic:

$$\sum_i \dot{m}_i = \dot{S}_{\text{gen}} = \dot{Q}_j = \dot{S} = 0$$

$$\dot{m}_{\text{In}} = \dot{m}_{\text{Out}} \quad \text{and} \quad s_{\text{In}} = s_{\text{Out}}$$

Total entropy variation of the system: $\dot{S} = \dot{S}_{\text{gen}} + \sum_j \dfrac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i$

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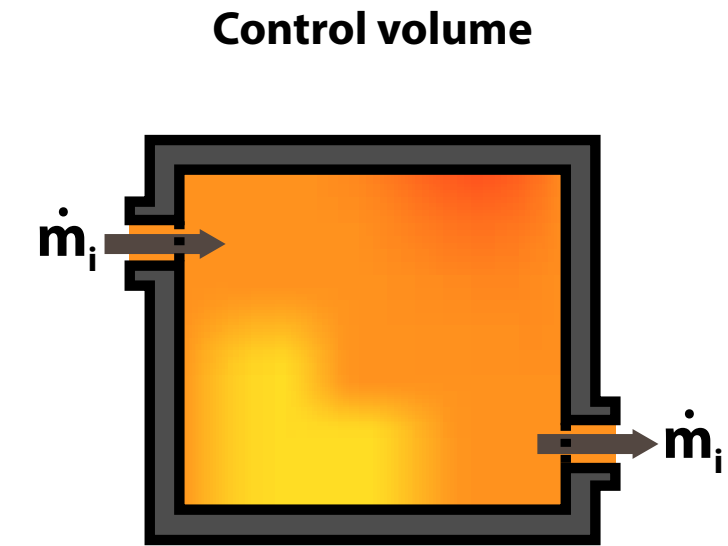Entropy transfer to/from outside the system

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Example 6.12

Air enters an adiabatic turbine at $P_1 = 6$ MPa
and $T_1 = 500$ °C = 773.15 K and leaves at
$P_2 = 100$ kPa with a flow rate of $\dot{m}=2$ kg / s.
Determine the maximum possible power output $\dot{W}$.

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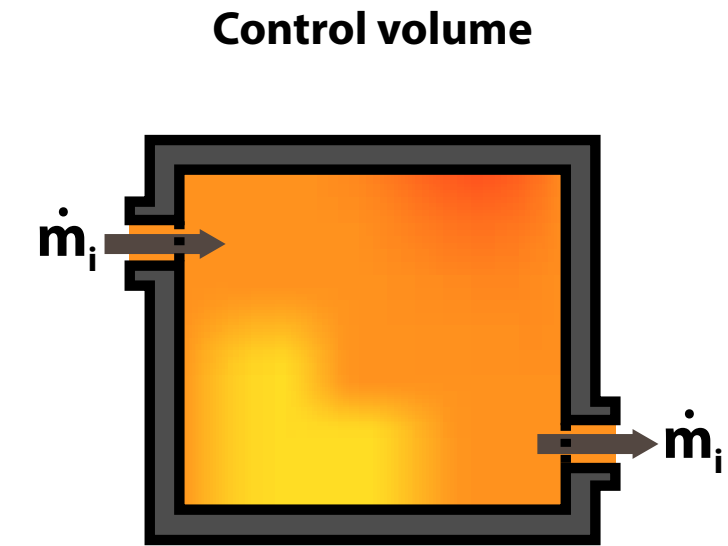Determine the maximum possible power output $\dot{W}$.

Isentropic process (ideal gas, constant specific heats):

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$

Maximum power <u>input</u>:

$$\dot{W} = \dot{m}\times(h_2 - h_1) = \dot{m}\times c_p\times(T_2 - T_1)$$

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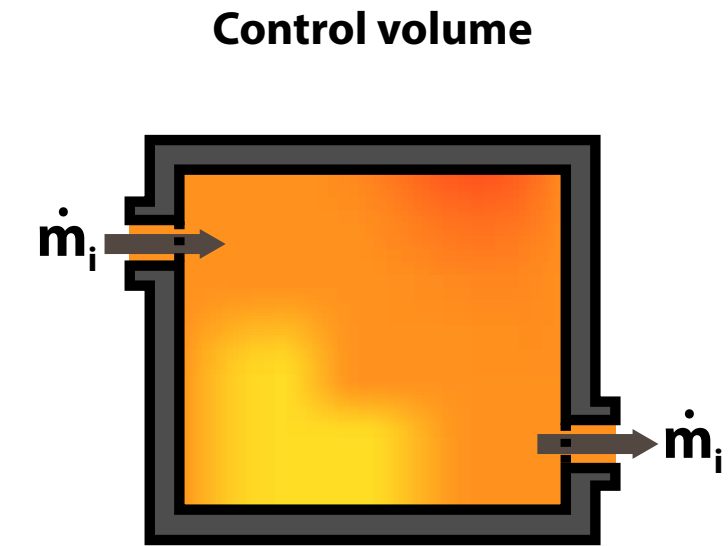$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$

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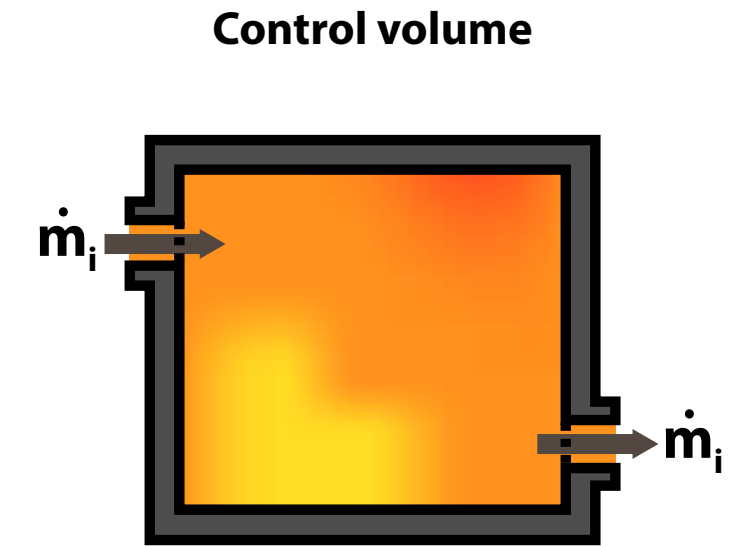
Appendix 4 (Air)

Temp. (K)	c_p (kJ/ kgK)	c_v (kJ/ kgK)	$\gamma = c_p/c_v$
750	1.087	0.800	1.359
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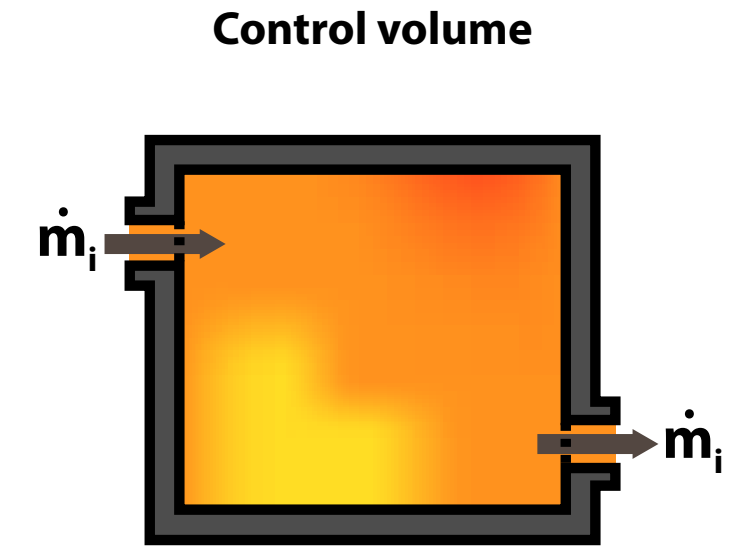
Maximum power <u>input</u>: $\dot{W} = \dot{m} \times (h_2 - h_1) = \dot{m} \times c_p \times (T_2 - T_1)$

$$\dot{W} = (2\ \mathrm{kg/s}) \times (1.093\ \mathrm{kJ/kgK}) \times (263.3\ \mathrm{K} - 773.15\ \mathrm{K}) = -1115\ \mathrm{kW}$$

Maximum power <u>output</u>:   1115 kW

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Exergy: maximum amount of useful work

Exergy is the maximum amount of useful work a system can do before it reaches equilibrium with its surroundings.

When the system reaches equilibrium with the surrounding (i.e. "dead state") it can no longer do any useful work.

Therefore the exergy depends on the properties of the system, but also on the properties of the surrounding.

Denoting with the subscript "o" the properties of the surrounding (i.e. the properties of the system at equilibrium) the exergy is given by:

$$\Phi = (U - U_O) + P_O(V - V_O) - T_O(S - S_O)$$

This is the amount of work extracted from the system when going from the <u>initial state</u> (U,T,P,V,S) to the <u>final state</u> (U_o,T_o,P_o,V_o,S_o) during a reversible process, i.e. no entropy generation.

Exergy: maximum amount of useful work

The equation below expresses energy conservation: $dU = -\delta W_b - \delta Q - \delta W_u$

$dU = -(U - U_O)$ variation of internal energy of the system

$\delta W_b = -P_O(V - V_O)$ work done by the system against the external pressure

$\delta Q = +T_O(S - S_O)$ heat lost by the system to the surrounding

$\delta W_u = \Phi$ useful work done by the system (e.g. lifting a weight)

(mind the signs - direction of energy transfer)

Denoting with the subscript "o" the properties of the surrounding (i.e. the properties of the system at equilibrium) the exergy is given by:

$$\Phi = (U - U_O) + P_O(V - V_O) - T_O(S - S_O)$$

This is the amount of work extracted from the system when going from the <u>initial state</u> (U,T,P,V,S) to the <u>final state</u> (U_O,T_O,P_O,V_O,S_O) during a reversible process, i.e. no entropy generation.

Exergy: maximum amount of useful work

The equation below expresses energy conservation: $dU = -\delta W_b - \delta Q - \delta W_u$

$dU = -(U - U_O)$ variation of internal energy of the system

$\delta W_b = -P_O(V - V_O)$ work done by the system against the external pressure

$\delta Q = +T_O(S - S_O)$ heat lost by the system to the surrounding

$\delta W_u = \Phi$ useful work done by the system (e.g. lifting a weight)

If kinetic / potential energy is available it can be converted into useful work.

Denoting with the subscript "o" the properties of the surrounding (i.e. the properties of the system at equilibrium) the exergy is given by:

$$\Phi = (U - U_O) + P_O(V - V_O) - T_O(S - S_O) + K_E + P_E$$

This is the amount of work extracted from the system when going from the initial state (U,T,P,V,S) to the final state (U_o,T_o,P_o,V_o,S_o) during a reversible process, i.e. no entropy generation.

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Generating entropy is equivalent to destroying exergy: $\boxed{\Phi_{\text{destroyed}} = T_O S_{\text{gen}}}$

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