

Entropy for a Control Mass (2)

(Lecture 9)

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(*) Some texts and figures are borrowed from Sonntag & Borgnakke unless noted otherwise.

6.5 The Thermodynamic Property Relation

- For a simple compressible substance without PE and KE, the first law and the second law are combined to give **Gibbs equations**.

$$\delta Q_{rev} = dU + \delta W_{rev} \quad \text{and} \quad \delta Q_{rev} = TdS$$

$$\rightarrow TdS = dU + PdV$$

$$\rightarrow TdS = d(H - PV) + PdV = dH - VdP$$

For a unit mass,

$$Tds = du + Pdv$$

$$Tds = dh - vdP$$

Gibbs equations

- The Gibbs equations can be applied to both rev. and irrev. processes in a given set of states. **Integration of the equation** can be performed **along a known path (typically, reversible path)** between the states.

6.6 Entropy Change of a Solid or Liquid

- For a solid or liquid, **small specific volume** and **small change in specific volume** as states change.

$$ds = \frac{du}{T} + \frac{P}{T} dv \approx \frac{du}{T} \approx \frac{c}{T} dT$$

$$s_2 - s_1 \approx c \ln\left(\frac{T_2}{T_1}\right) \quad \text{when } c \text{ is constant.}$$

$$s_2 - s_1 \approx \int_1^2 \frac{c}{T} dT \quad \text{in general}$$

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6.7 Entropy Change of An Ideal Gas

→ From the Gibbs equations,

$$Tds = du + Pdv \rightarrow ds = \frac{du}{T} + \frac{P}{T} dv$$

For **an ideal gas**, $du = C_{v0}dT$, $\frac{P}{T} = \frac{R}{v}$

$$\text{Then, } ds = \frac{C_{v0}}{T} dT + \frac{R}{v} dv \rightarrow s_2 - s_1 = \int_1^2 \frac{C_{v0}}{T} dT + R \ln \frac{v_2}{v_1}$$

Similarly,

$$Tds = dh - vdP \rightarrow ds = \frac{dh}{T} - \frac{v}{T} dP = \frac{C_{p0}}{T} dT - \frac{R}{P} dP$$

$$\text{Then, } s_2 - s_1 = \int_1^2 \frac{C_{p0}}{T} dT - R \ln \frac{P_2}{P_1}$$

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To evaluate the entropy change,

1. **Constant** specific heats:

$$s_2 - s_1 = \int_1^2 \frac{C_{v0}}{T} dT + R \ln \frac{v_2}{v_1} \rightarrow s_2 - s_1 = C_{v0} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

$$s_2 - s_1 = \int_1^2 \frac{C_{p0}}{T} dT - R \ln \frac{P_2}{P_1} \rightarrow s_2 - s_1 = C_{p0} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

2. Use the analytical equation for specific heats (Table A.6 in Sonntag)

3. Use **the standard entropy** (Table A.7, A.8 in Sonntag) :

$$s_T^0 = \int_{T_0}^T \frac{C_{p0}}{T} dT \rightarrow s_2 - s_1 = (s_{T_2}^0 - s_{T_1}^0) - R \ln \frac{P_2}{P_1}$$

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For an **isentropic process** ($s_2 = s_1$), assuming the **constant specific heats**,

$$s_2 - s_1 = 0 = C_{p0} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\ln \left(\frac{T_2}{T_1} \right) = \frac{R}{C_{p0}} \ln \left(\frac{P_2}{P_1} \right) \rightarrow \left(\frac{T_2}{T_1} \right) = \left(\frac{P_2}{P_1} \right)^{\frac{R}{C_{p0}}}$$

Here, $\frac{R}{C_{p0}} = \frac{C_{p0} - C_{v0}}{C_{p0}} = \frac{k-1}{k}$ (where k : the ratio of the specific heats = $\frac{C_{p0}}{C_{v0}}$)

Then,

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

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

$$\left(\frac{P_2}{P_1} \right) = \left(\frac{v_1}{v_2} \right)^k \rightarrow P v^k = \text{const}$$

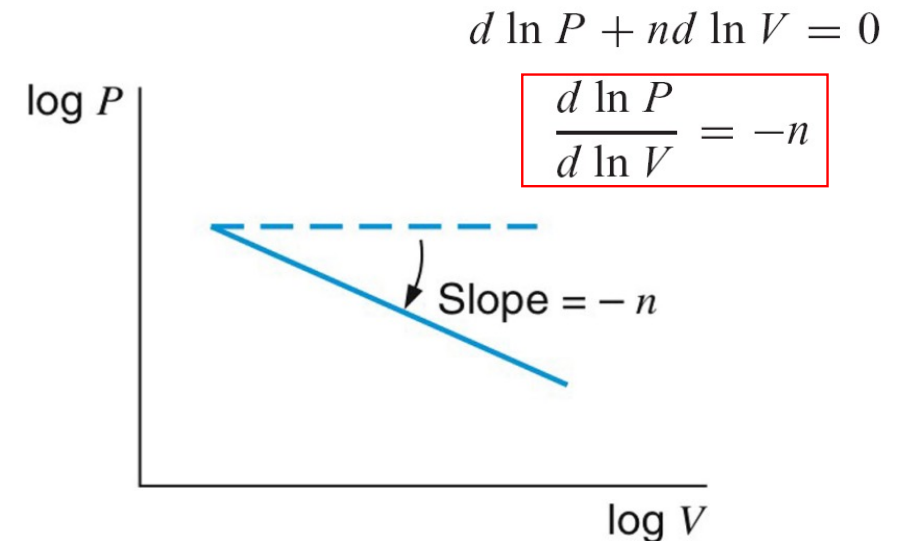
6.8 The Reversible Polytropic Process for an Ideal Gas

→ **Polytropic process:**

$$PV^n = \text{constant} = P_1 V_1^n = P_2 V_2^n$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^n$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(n-1)/n} = \left(\frac{V_1}{V_2} \right)^{n-1}$$



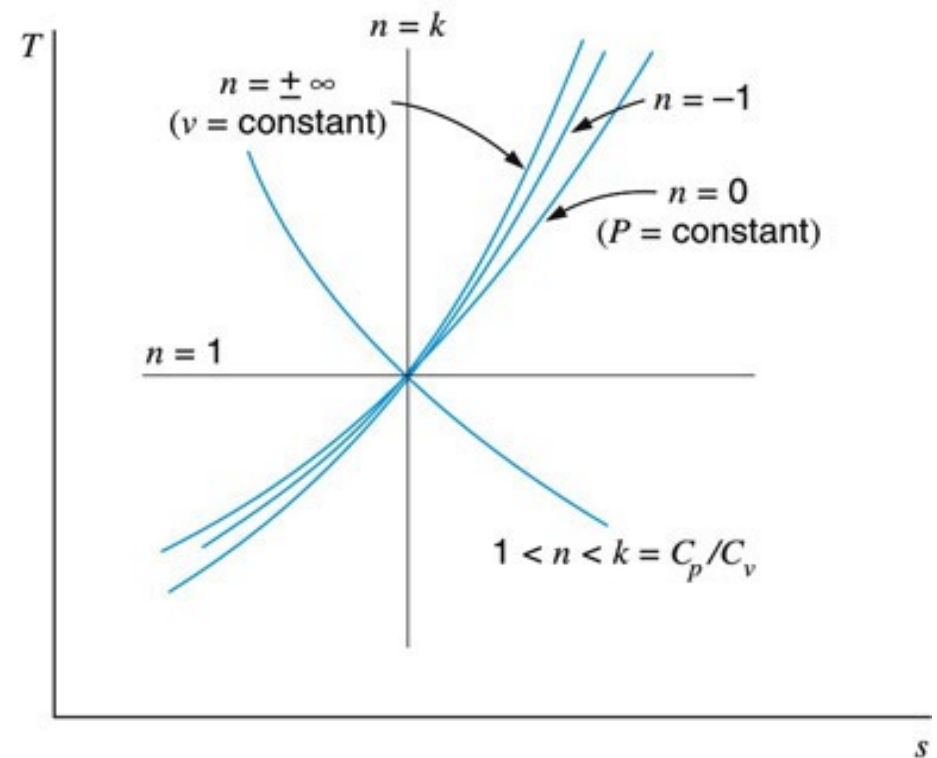
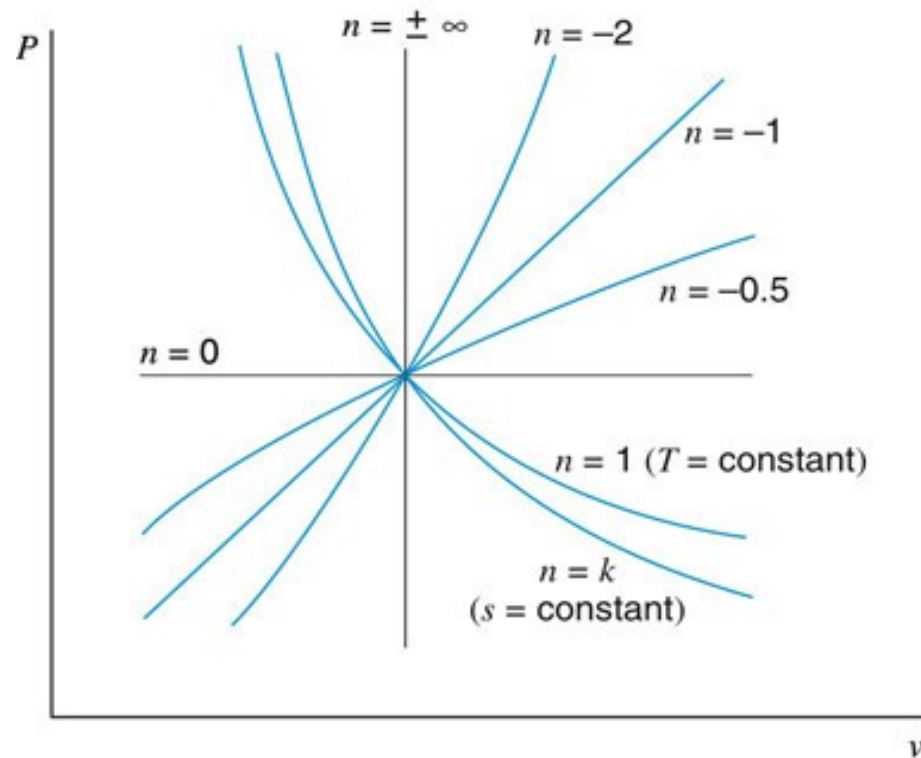
→ Work during polytropic process
($n \neq 1$)

$$\begin{aligned} {}_1W_2 &= \int_1^2 P dV \quad \text{and} \quad PV^n = \text{constant} \\ {}_1W_2 &= \int_1^2 P dV = \text{constant} \int_1^2 \frac{dV}{V^n} \\ &= \frac{P_2 V_2 - P_1 V_1}{1 - n} = \frac{mR(T_2 - T_1)}{1 - n} \end{aligned}$$

($n=1$)

$$\begin{aligned} {}_1W_2 &= \int_1^2 P dV = \text{constant} \int_1^2 \frac{dV}{V} \\ &= P_1 V_1 \ln \frac{V_2}{V_1} = P_1 V_1 \ln \frac{P_1}{P_2} \end{aligned}$$

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$$P V^n = \text{constant}$$

Isobaric process:	$n = 0,$	$P = \text{constant}$
Isothermal process:	$n = 1,$	$T = \text{constant}$
Isentropic process:	$n = k,$	$s = \text{constant}$
Isochoric process:	$n = \infty,$	$v = \text{constant}$

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6.9 Entropy Change of a Control Mass During an Irreversible Process

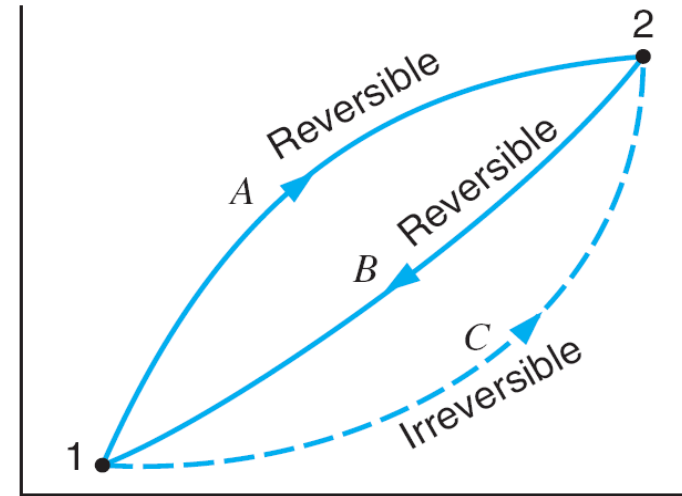
→ Consider **reversible** processes **A & B** and **irreversible** process **C**. From the inequality of Clausius,

$$1 \xrightarrow{A} 2 \xrightarrow{B} 1$$

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_B = 0$$

$$1 \xrightarrow{C} 2 \xrightarrow{B} 1$$

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_C + \int_2^1 \left(\frac{\delta Q}{T} \right)_B < 0$$



$$\int_1^2 \left(\frac{\delta Q}{T} \right)_A > \int_1^2 \left(\frac{\delta Q}{T} \right)_C$$

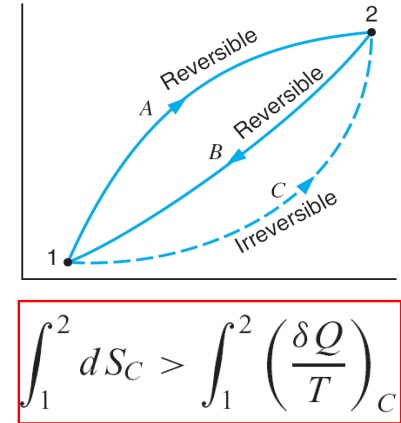
→ Because entropy is a point function,

$$\int_1^2 \left(\frac{\delta Q}{T} \right)_A = \int_1^2 dS_A = \int_1^2 dS_C \longrightarrow \int_1^2 dS_C > \int_1^2 \left(\frac{\delta Q}{T} \right)_C$$

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As path C was an arbitrary irreversible process, in general,

$$dS \geq \frac{\delta Q}{T}$$
$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$



For a reversible process,

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

For an irreversible process,

$$dS > \left(\frac{\delta Q}{T} \right)_{\text{irr}}$$

If any irreversible effects occur while the amount of heat(δQ) is transferred, the change of entropy will be greater than for the reversible process.

6.10 Entropy Generation and the Entropy Equation

- The entropy change in an irreversible process is larger than in a reversible process for the same δQ and T .

$$dS = \frac{\delta Q}{T} + \delta S_{\text{gen}}$$

where S_{gen} : **entropy generation** due to irreversibilities inside the system
and $\delta S_{\text{gen}} \geq 0$

For a reversible process,

$$\delta Q = T dS \quad \text{and} \quad \delta W = P dV$$

For an irreversible process,

$$\delta Q_{\text{irr}} = T dS - T \delta S_{\text{gen}} \longrightarrow$$

For the same change of entropy,
smaller heat transfer is needed.

(or)

For the same amount of heat transfer,
the change of entropy is larger.

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For an irreversible process, the work transfer is **smaller** than for the reversible process during the same state change.

$$(1^{\text{st}} \text{ law}) \quad \delta Q_{\text{irr}} = dU + \delta W_{\text{irr}}$$

$$(2^{\text{nd}} \text{ law}) \quad \delta Q_{\text{irr}} = T dS - T \delta S_{\text{gen}}$$

$$(\text{Gibbs eqn.}) \quad T dS = dU + P dV$$

Then,

$$\delta W_{\text{irr}} = P dV - T \delta S_{\text{gen}}$$

lost work

For an irreversible process,

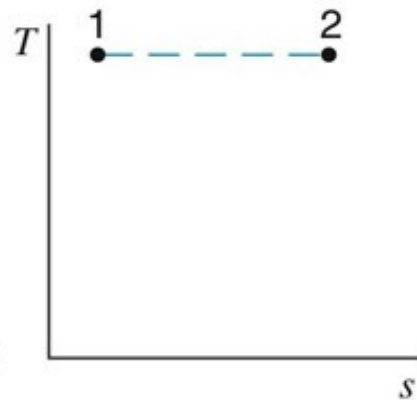
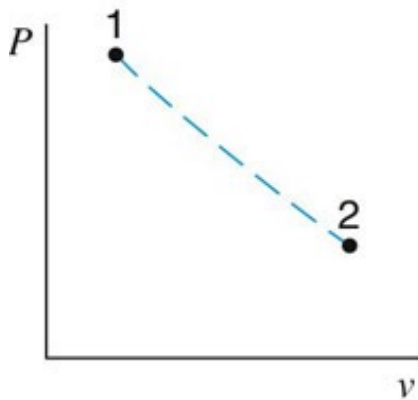
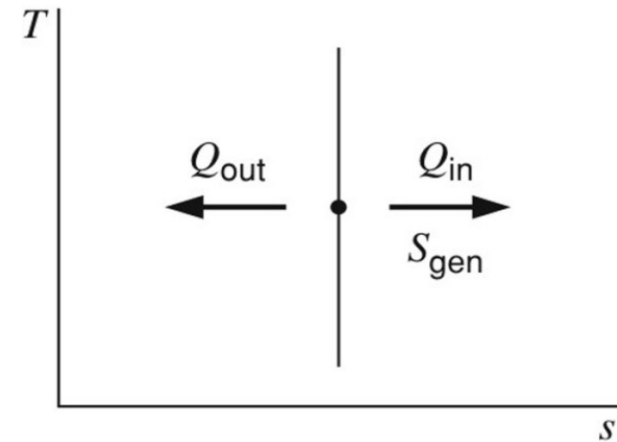
$$dS = \frac{\delta Q}{T} + \delta S_{\text{gen}} \longrightarrow S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} + S_2 - S_1_{\text{gen}}$$

$$\Delta \text{Entropy} = +\text{in} - \text{out} + \text{gen}$$

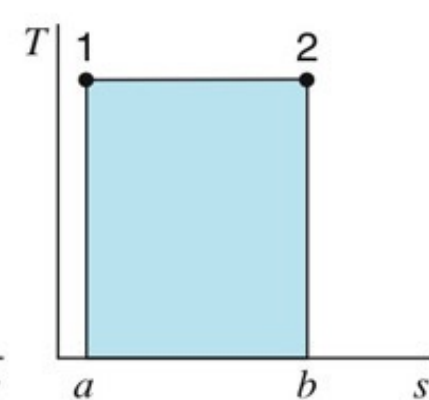
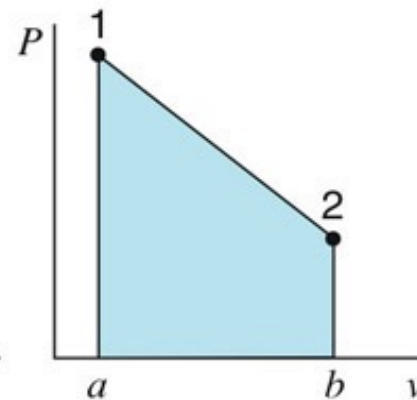
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$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} + {}_1S_2 \text{ gen}$$

$$\delta W_{\text{irr}} = P dV - T \delta S_{\text{gen}}$$



Non-equilibrium process
→ Intrinsically irreversible



Quasi-equilibrium process
→ Either reversible or
irreversible (but possibly internally reversible)

area under P-v = Work transfer
area under T-S = Heat transfer

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6.11 Principle of the Increase of Entropy

Consider a heat transfer process between a finite temperature difference.
For the boundary B with no change of state in time,

$$\text{Energy Eq.:} \quad dE = 0 = \delta Q_1 - \delta Q_2 \Rightarrow \delta Q_1 = \delta Q_2 = \delta Q$$

$$\text{Entropy Eq.:} \quad dS = 0 = \frac{\delta Q}{T_0} - \frac{\delta Q}{T} + \delta S_{\text{gen } B}$$

$$\delta S_{\text{gen } B} = \frac{\delta Q}{T} - \frac{\delta Q}{T_0} = \delta Q \left(\frac{1}{T} - \frac{1}{T_0} \right) \geq 0$$

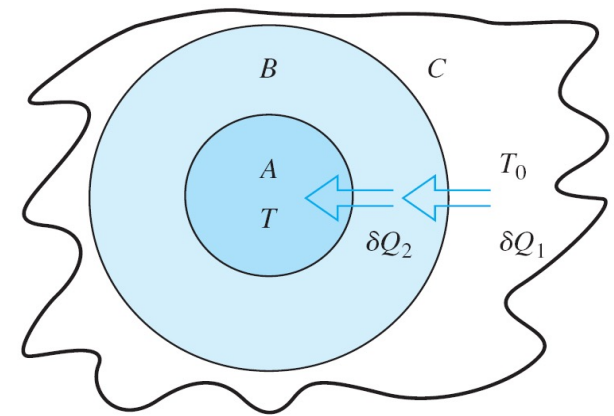
The second law tells $\delta S_{\text{gen}} > 0$ for an **irreversible** process:

If $T_0 > T$, $\delta Q > 0$.

If $T_0 < T$, $\delta Q < 0$.

The second law tells $\delta S_{\text{gen}} = 0$ for a **reversible** process:

If $\delta Q \neq 0$, $T_0 = T$.

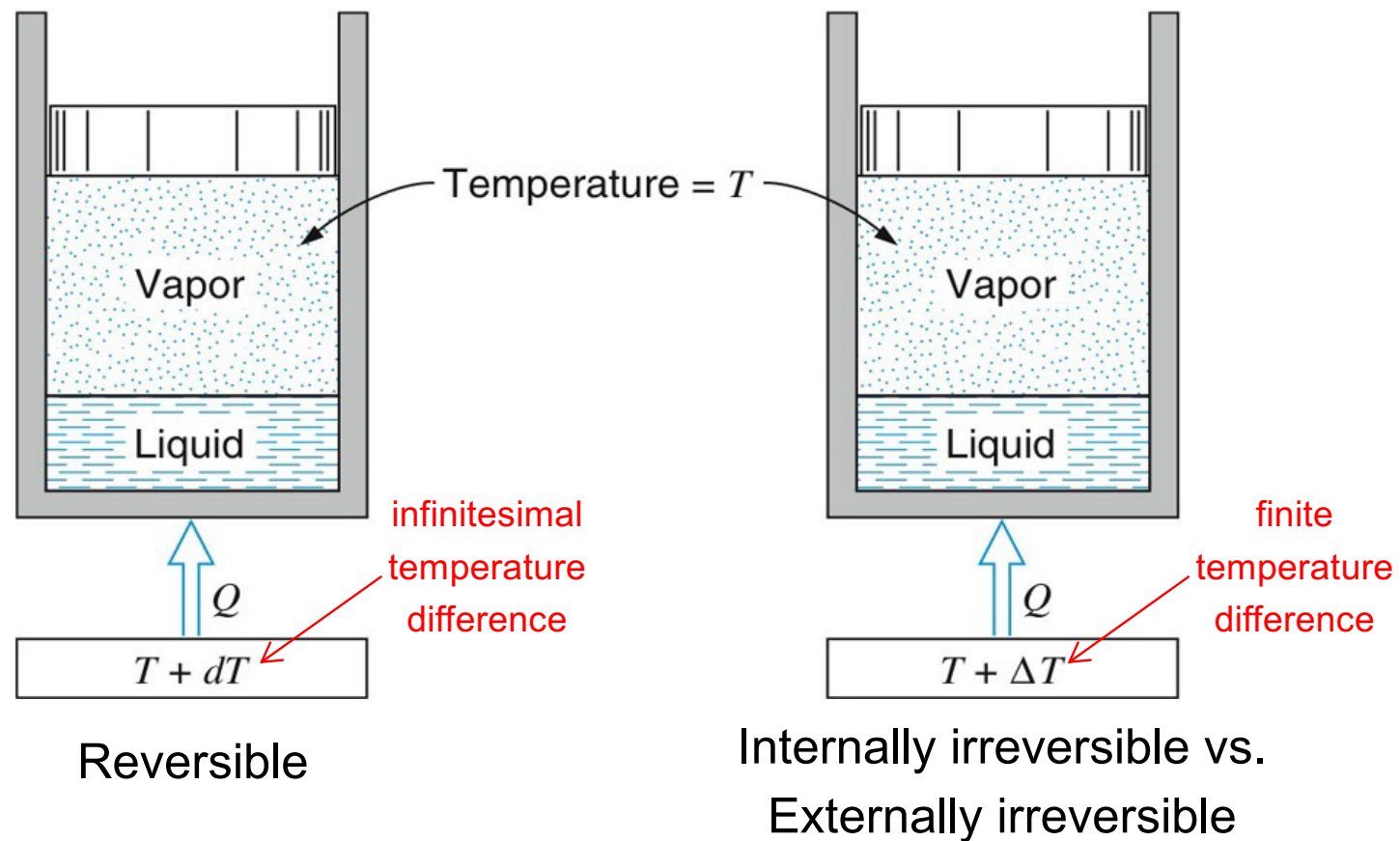


A: system at T
B: boundary at steady state
C: surrounding at T_0

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Internal irreversibility: irreversibility occurs inside the system, or inside the control volume.

external irreversibility: irreversibility occurs outside the system, or in the surroundings.



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6.12 Entropy as a Rate Equation

→ The second law can be written:

$$dS = \frac{\delta Q}{T} + \delta S_{\text{gen}}$$

Differential

$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} + {}_1S_2 \text{ gen}$$

Finite change

$$\frac{dS}{\delta t} = \frac{1}{T} \frac{\delta Q}{\delta t} + \frac{\delta S_{\text{gen}}}{\delta t}$$
$$\frac{dS_{c.m.}}{dt} = \sum \frac{1}{T} \dot{Q} + \dot{S}_{\text{gen}}$$

Rate basis

Temperature at the boundary where heat transfer occurs