Chapter 5. Entropy and the Second Law of Thermodynamics

Summary

- the **First Law of Thermodynamics** describes energy changes for physical and chemical processes
- no exceptions to the First Law and the conservation of energy have been discovered

But many processes obeying the First Law ***never occur***.

Why?

- the **Second Law of Thermodynamics** and the entropy are introduced to predict spontaneous processes
- combining the First and Second Laws unleashes the full power of thermodynamics

First Law of Thermodynamics

The change in internal energy of a system (ΔU) equals the heat absorbed from the surroundings (q) plus the work done on the system (w) by the surroundings.

$$\Delta U = q + w$$

The energy of an isolated system (no contact with the surroundings, $q = w = 0$) is constant.

$$\Delta U = 0 \text{ (isolated system)}$$

(conservation of energy)

Section 5.1 Spontaneous Processes

First Law calculations:

$$\Delta U \qquad q \qquad w \qquad \Delta H$$

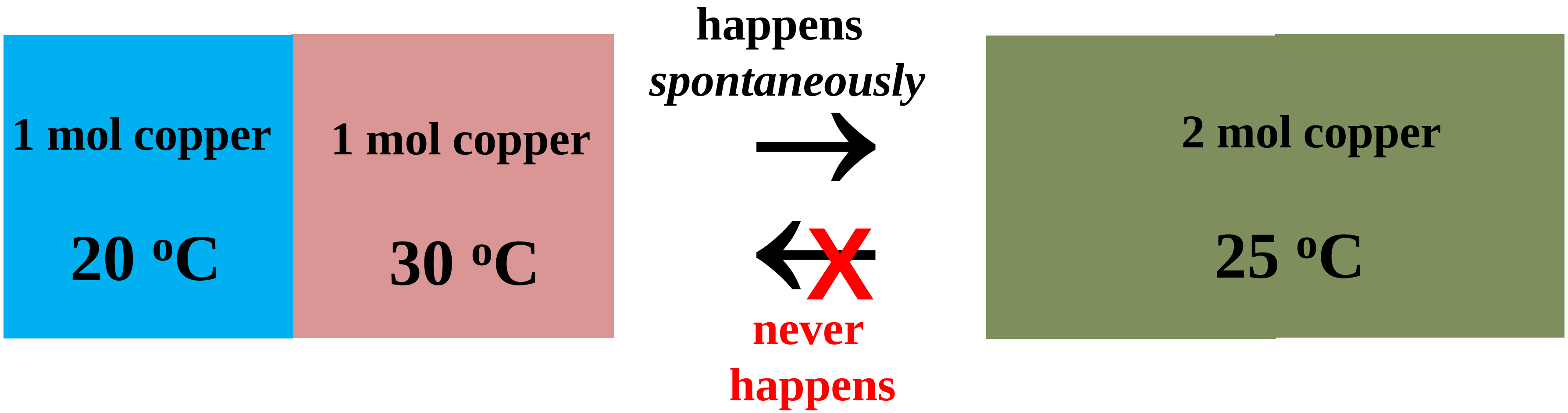
for physical and chemical processes.

But from everyday experience, many processes consistent with the First Law never occur. Others occur “spontaneously”.

Why ?

Mystery: Some <u>heat flow</u> processes obeying the First Law never occur, others occur spontaneously

isolated system ($\Delta U = 0$):



1 mol copper

$20\ ^oC$

1 mol copper

$30\ ^oC$

happens *spontaneously*

$\rightarrow$

$\leftarrow$

never happens

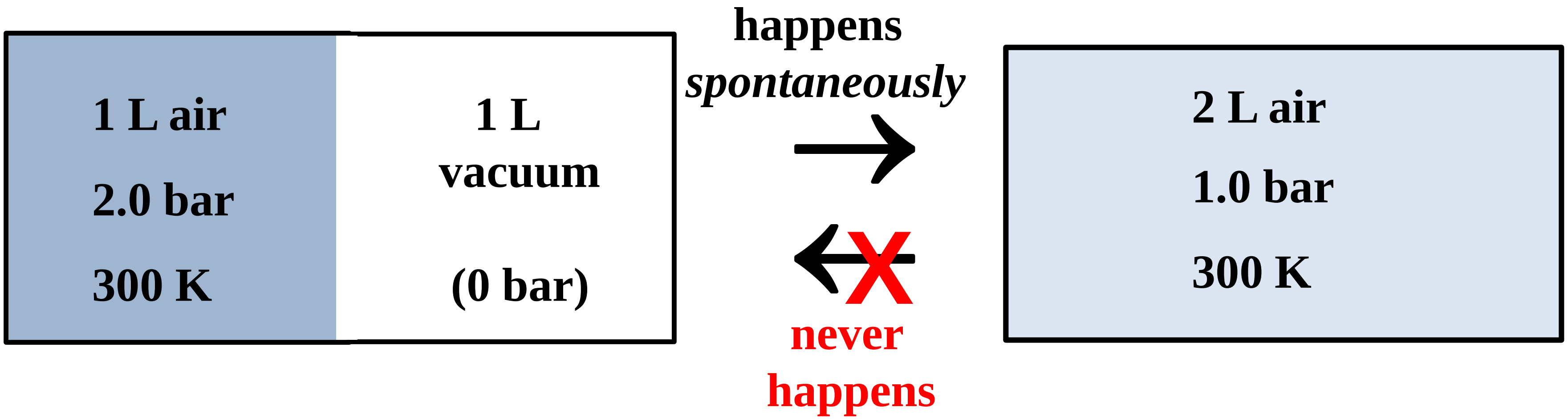
2 mol copper

$25\ ^oC$

- the forward and reverse processes both obey the First Law
- the forward process **<u>occurs spontaneously</u>** (“by itself”)
- the reverse process **<u>is never observed</u>** (for an isolated system)

Mystery: Some mechanical processes obeying the First Law never occur, others occur spontaneously

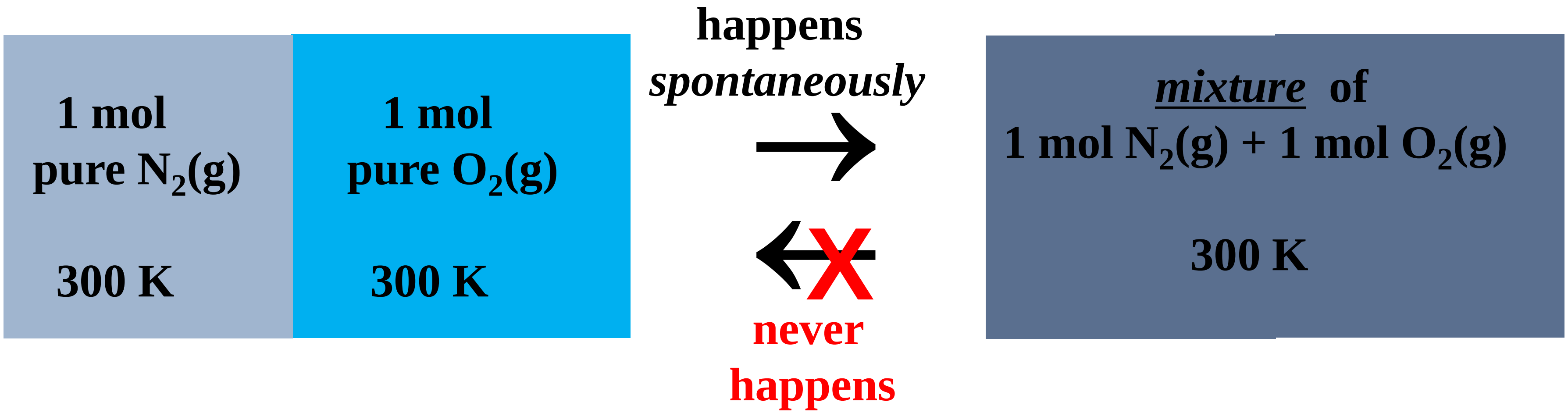
isolated system ($\Delta U = 0$):



- the forward and reverse processes both obey the First Law
- the forward expansion process **occurs spontaneously**
- the reverse process **is never observed** for an isolated system

***Mystery*: Some mixing processes obeying the First Law never occur, others occur spontaneously**

isolated system ($\Delta U = 0$):



1 mol
pure N_2(g)

300 K

1 mol
pure O_2(g)

300 K

happens
spontaneously

$\rightarrow$

$\leftarrow$ X

never
happens

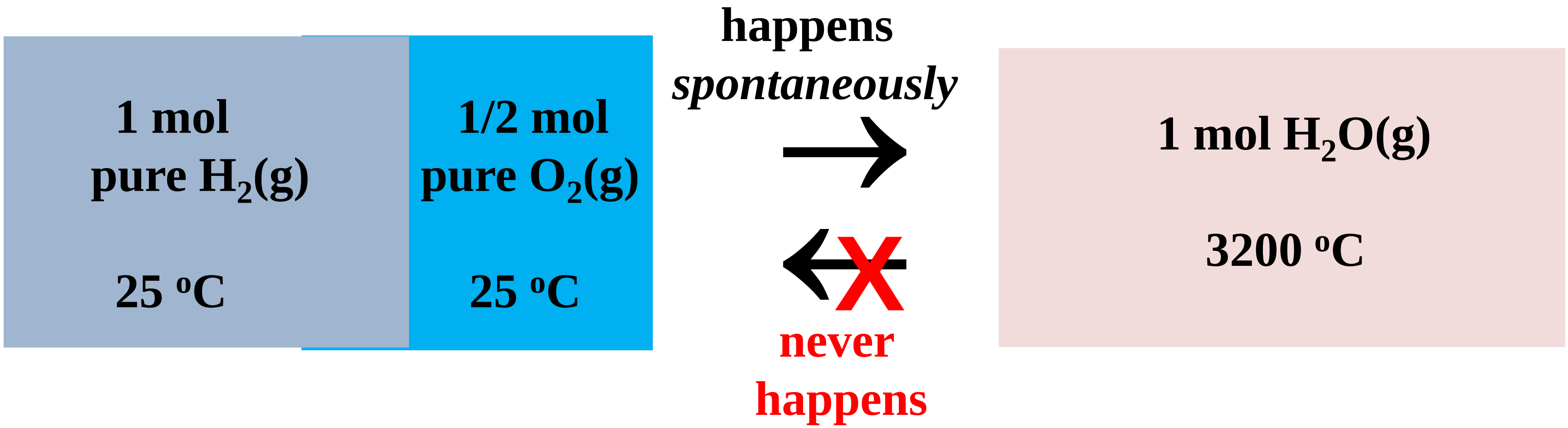
***mixture* of**
1 mol N_2(g) + 1 mol O_2(g)

300 K

- the forward and reverse processes both obey the First Law
- the forward mixing process **occurs spontaneously**
- the de-mixing process **is never observed** for an isolated system

Mystery: Some chemical reactions obeying the First Law never occur, others occur spontaneously

isolated system ($\Delta U = 0$):



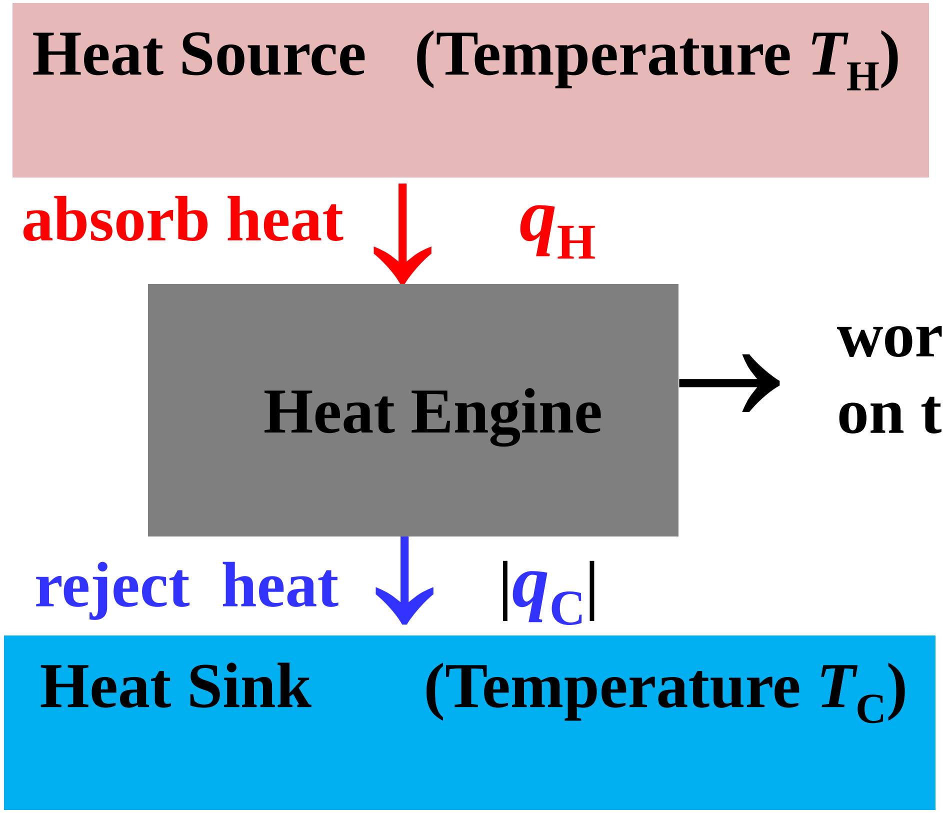
- the forward and reverse processes both obey the First Law
- the forward reaction process **occurs spontaneously**
- the reverse reaction **is never observed** for an isolated system

Sections 5.2 Heat Engines and the Second Law

Analysis of the **efficiency of heat engines** (*e.g.*, how much work can be done per ton of coal burned?) led to the **discovery of the Second Law of Thermodynamics** for predicting spontaneous processes.

"The steam engine has done more for science than science has ever done for the steam engine."

Heat Engines



Heat Source (Temperature T_H)

absorb heat q_H

Heat Engine

work $|w|$ done on the surroundings

reject heat $|q_C|$

Heat Sink (Temperature T_C)

$$q_H > 0$$
$$q_C < 0$$
$$w < 0$$

First Law :

$$q_H + q_C + w = 0$$

(conservation of energy)

Heat Engines

It’s impossible to overestimate the importance of heat engines!

cars and trucks
trains
ships
electricity generating stations
small engines: motorcycles, lawn mowers, chain saws, ….

No heat engines? Then:

walk or use a horse to travel
take a ship with sails to visit overseas
cut your lawn with a scythe
light your home with candles

Reversible Carnot Engine Cycle

Step I Isothermal Expansion at T_H

$V_1 \rightarrow V_2$ absorb heat q_H

Step II Adiabatic Expansion

$V_2 \rightarrow V_3$ $q = 0$

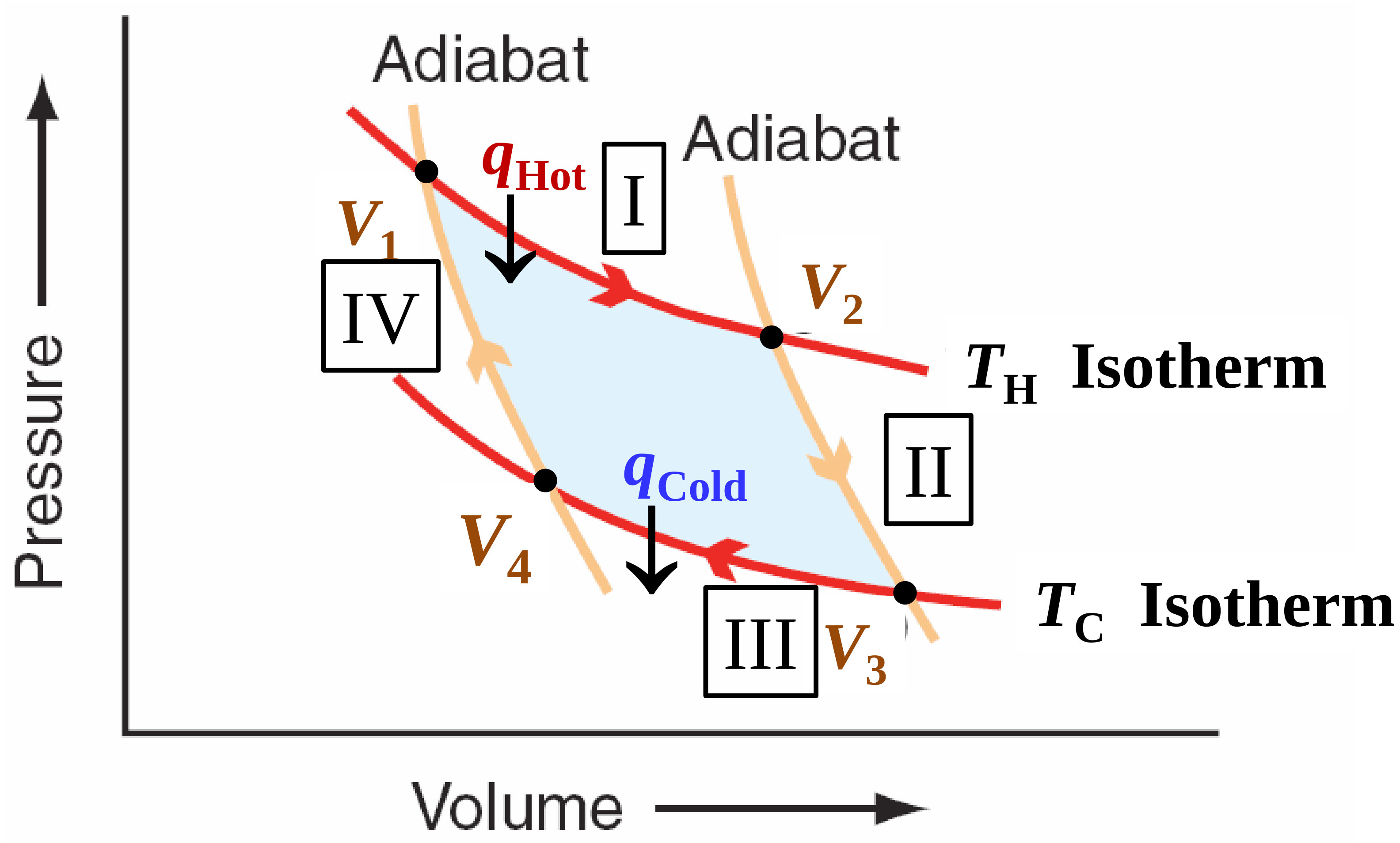
Step III Isothermal Compression at T_C

$V_3 \rightarrow V_4$ reject heat $|q_C|$

Step IV Adiabatic Compression

$V_4 \rightarrow V_1$ $q = 0$

Reversible Carnot Cycle
Steps I, II, III, IV



Reversible Carnot Engine Cycle – *the details*

system: n moles of ideal gas (the “working fluid” in the engine)

Step I Isothermal Expansion at $\boldsymbol{T_{\mathrm{H}}}$ $V_1 \rightarrow V_2$

$w_{\mathrm{I}} = -nRT_{\mathrm{H}}\ln(V_2/V_1)$ $\Delta U_{\mathrm{I}} = 0$ $q_{\mathrm{I}} = -w_{\mathrm{I}}$

Step II Adiabatic Expansion $\boldsymbol{T_{\mathrm{H}}} \rightarrow \boldsymbol{T_{\mathrm{C}}}$ $V_2 \rightarrow V_3$

$w_{\mathrm{II}} = C_V(T_{\mathrm{C}} - T_{\mathrm{H}}) = \Delta U_{\mathrm{II}}$ $q_{\mathrm{II}} = 0$

Step III Isothermal Compression at $\boldsymbol{T_{\mathrm{C}}}$ $V_3 \rightarrow V_4$

$w_{\mathrm{III}} = -nRT_{\mathrm{H}}\ln(V_4/V_3)$ $\Delta U_{\mathrm{III}} = 0$ $q_{\mathrm{III}} = -w_{\mathrm{III}}$

Step IV Adiabatic Compression $\boldsymbol{T_{\mathrm{C}}} \rightarrow \boldsymbol{T_{\mathrm{H}}}$ $V_4 \rightarrow V_1$

$w_{\mathrm{IV}} = C_V(T_{\mathrm{H}} - T_{\mathrm{C}}) = \Delta U_{\mathrm{IV}}$ $q_{\mathrm{IV}} = 0$

Relation between volumes V_1, V_2, V_3, V_4 (*will be useful later*):

Steps II and IV [reversible ($p = p_{\mathrm{external}}$) and adiabatic ($q = 0$)]

$$\mathrm{d}U = \mathrm{d}w + \cancelto{0}{\mathrm{d}q}$$

$$C_V \mathrm{d}T = -p\mathrm{d}V$$

$$C_V \mathrm{d}T = -\frac{nRT}{V}\mathrm{d}V$$

$$C_V \frac{dT}{T} = -nR\frac{dV}{V}$$

$$\int_{T_\mathrm{C}}^{T_\mathrm{H}} C_V \frac{\mathrm{d}T}{T} = -nR\int_{V_4}^{V_1} \frac{\mathrm{d}V}{V} = -\int_{T_\mathrm{H}}^{T_\mathrm{C}} C_V \frac{\mathrm{d}T}{T} = nR\int_{V_2}^{V_3} \frac{\mathrm{d}V}{V}$$

$$-\ln\frac{V_1}{V_4} = \ln\frac{V_3}{V_2}$$

$$\boxed{\begin{aligned} \boldsymbol{V_1 / V_4} &= \boldsymbol{V_2 / V_3} \\[1em] \boldsymbol{V_2 / V_1} &= \boldsymbol{V_3 / V_4} \end{aligned}}$$

Reversible Carnot Engine Cycle – First Law Analysis

Internal Energy Change for One Cycle (I → II → III → IV → I)

$$
\begin{aligned}
\oint_{1}^{1} \mathrm{d}U &= \Delta U_{\mathrm{I}} + \Delta U_{\mathrm{II}} + \Delta U_{\mathrm{III}} + \Delta U_{\mathrm{IV}} \\
&= 0 + C_V(T_{\mathrm{C}} - T_{\mathrm{H}}) + 0 + C_V(T_{\mathrm{H}} - T_{\mathrm{C}}) \\
&= U_{\mathrm{I}} - U_{\mathrm{I}} \\
\Delta U_{\mathrm{cycle}} &= 0
\end{aligned}
$$

Reversible Carnot Engine Cycle – First Law Analysis

Work Done for One Cycle (I → II → III → IV → I)

$$\oint_{1}^{1} \mathrm{d}w = w_{\mathrm{I}} + w_{\mathrm{II}} + w_{\mathrm{III}} + w_{\mathrm{IV}}$$

$$= -nRT_{\mathrm{H}} \ln\frac{V_2}{V_1} + \cancel{C_V(T_{\mathrm{C}} - T_{\mathrm{H}})} - nRT_{\mathrm{C}} \ln\frac{V_4}{V_3} + \cancel{C_V(T_{\mathrm{H}} - T_{\mathrm{C}})}$$

use $V_4 / V_3 = V_1 / V_2$

$$= -nRT_{\mathrm{H}} \ln\frac{V_2}{V_1} + 0 + nRT_{\mathrm{C}} \ln\frac{V_2}{V_1} + 0$$

$$w_{\mathrm{cycle}} = -nR(T_{\mathrm{H}} - T_{\mathrm{C}}) \ln\frac{V_2}{V_1}$$

*****notice the work done by the engine (-w_{cycle}) is proportional to **T_{H}** – **T_{C}**. No temperature difference, then no work is done.

Reversible Carnot Engine Cycle – First Law Analysis

Heat Absorbed for One Cycle (I → II → III → IV → I)

$$\oint_{1}^{1} \mathrm{d}q \;=\; q_{\mathrm{I}} + q_{\mathrm{II}} + q_{\mathrm{III}} + q_{\mathrm{IV}}$$

$$= nRT_{\mathrm{H}} \ln\frac{V_2}{V_1} + 0 - nRT_{\mathrm{C}} \ln\frac{V_3}{V_4} + 0$$

$$q_{\mathrm{cycle}} \;=\; nR(T_{\mathrm{H}} - T_{\mathrm{C}}) \ln\frac{V_2}{V_1}$$

use
$V_3 / V_4 = V_2 / V_1$

Check: Can you verify that $q_{\mathrm{cycle}} + w_{\mathrm{cycle}} = 0 \;\; (= \Delta U_{\mathrm{cycle}})$?

Efficiency ε of a Reversible* Carnot Engine

$$\varepsilon = \frac{\text{work done on the surroundings}}{\text{heat absorbed from the hot reservoir}}$$

$$= \frac{-w_{\text{cycle}}}{q_{\text{H}}}$$

$$= \frac{nR(T_{\text{H}} - T_{\text{C}})\ln(V_2/V_1)}{nRT_{\text{H}}\ln(V_2/V_1)}$$

$$\boxed{\varepsilon = \frac{T_{\text{H}} - T_{\text{C}}}{T_{\text{H}}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}}}$$

So What?

This result is a big deal!

It places a fundamental limit on heat engine efficiency.

*reversible heat engine: infinitesimal temperature and pressure differences between the gas and the surroundings

Efficiency ε of a Reversible* Carnot Engine

Example: Calculate the efficiency of a reversible steam engine operating between $T_H = 373\ \mathrm{K}$ (the boiling point of water at 1 bar) and $T_C = 293\ \mathrm{K}$. How much work is done if 10.0 MJ of heat is absorbed at 373 K?

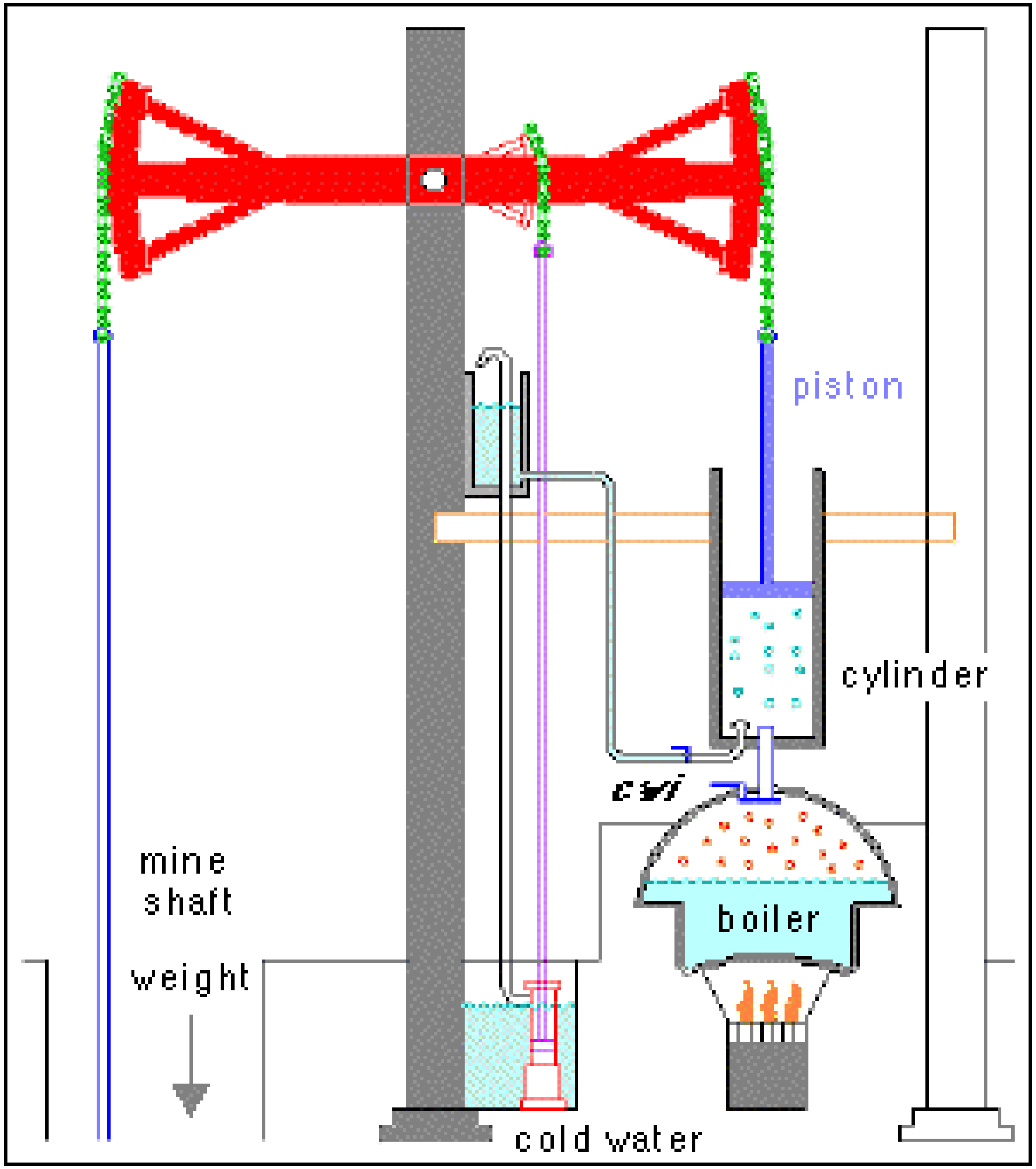
$$\varepsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{293\ \mathrm{K}}{373\ \mathrm{K}} = 0.214 = 21.4\,\%$$

$$\varepsilon = \frac{-w}{q_H} = 0.214 = \frac{-w}{10.0\ \mathrm{MJ}}$$

$-w = 0.214 \times 10.0\ \mathrm{MJ} = 2.14\ \mathrm{MJ}$ work done on the surroundings*

*this is the maximum amount of work that can be done – real engines are less efficient than reversible engines

Newcomen Atmospheric Steam Engine



- first practical steam engine (1712)
- hot steam slightly above 1 atm flows into a cylinder fitted with a piston
- cold water is injected into the cylinder, condensing the steam
- atmospheric pressure pushes the piston back into the cylinder
- important advance, but low efficiency

Other Heat Engines

see:

Engine Animations

http://www.animatedengines.com/

Section 5.3 Important Consequences of the Carnot Cycle

For one complete cycle, all steps reversible, it was noticed that:

$$\oint \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \int_1^2 \frac{\mathrm{d}q}{T} + \int_2^3 \frac{\mathrm{d}q}{T} + \int_3^4 \frac{\mathrm{d}q}{T} + \int_4^1 \frac{\mathrm{d}q}{T}$$

$$= \frac{q_{\mathrm{H}}}{T_{\mathrm{H}}} + 0 + \frac{q_{\mathrm{C}}}{T_{\mathrm{C}}} + 0$$

$$= \frac{nRT_{\mathrm{H}} \ln(V_2/V_1)}{T_{\mathrm{H}}} + \frac{nRT_{\mathrm{C}} \ln(V_4/V_3)}{T_{\mathrm{C}}}$$

$$= nR\ln(V_2/V_1) + nR\ln(V_4/V_3) = nR\ln(V_2/V_1) - nR\ln(V_2/V_1)$$

$$= 0$$

So what?

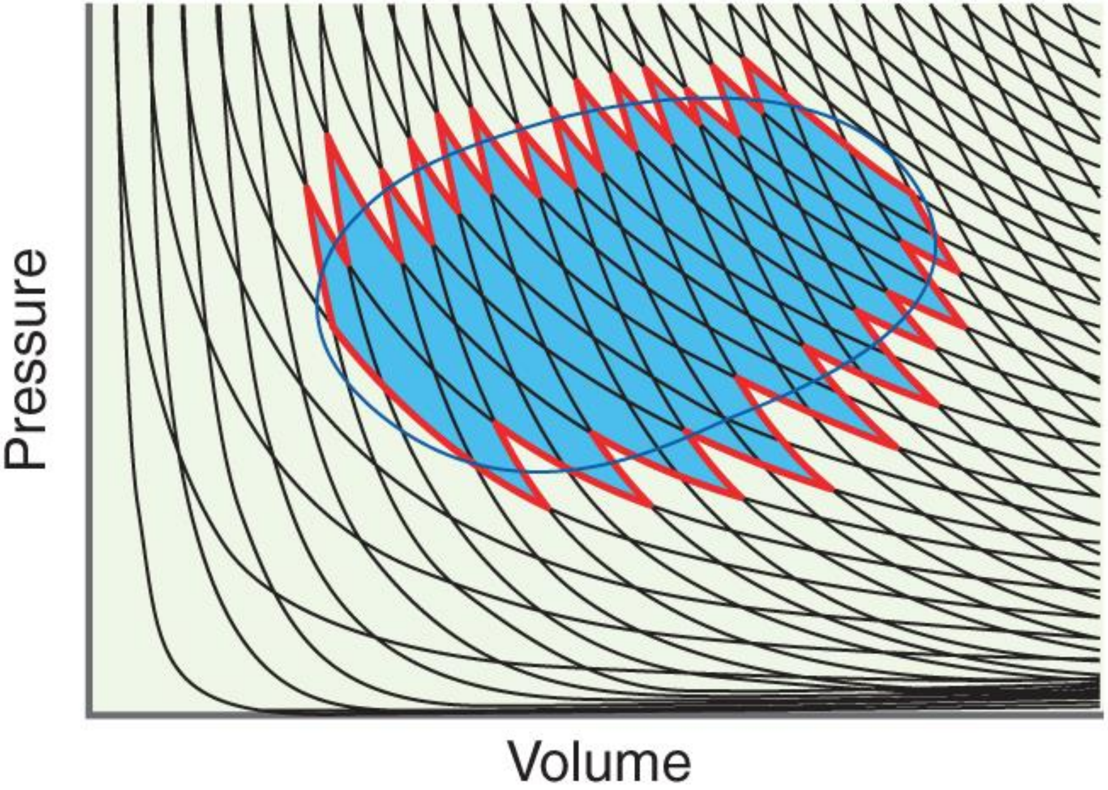
Important Consequences from the Carnot Cycle

A. The Entropy *S* (a New State Function)

The result

$$\boxed{\oint \frac{dq_{\text{rev}}}{T} = 0}$$

can be generalized
to **any reversible cycle**
for **any system**.



Important Consequences from the Carnot Cycle

A. <u>The Entropy *S*</u> (a New <u>State Function</u>)

Conclusion:

The entropy *S* defined by

$$\boxed{dS = \frac{dq_{\mathrm{rev}}}{T}}$$

is a function of the state of the system (like the internal energy *U* and the enthalpy *H* state functions).

Important Consequences from the Carnot Cycle

B. Clausius Inequality – *the breakthrough !*

For a **reversible** Carnot cycle, from the First Law

$$\Delta U_{\text{cycle}} = q_{\text{H}} + q_{\text{C}} + w = 0$$

so $$-w = q_{\text{H}} + q_{\text{C}}$$

$$\varepsilon = \frac{-w}{q_{\text{H}}} = \frac{q_{\text{H}} + q_{\text{C}}}{q_{\text{H}}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}}$$

multiply by $T_{\text{H}}q_{\text{H}}$

$$T_{\text{H}}q_{\text{H}} + T_{\text{H}}q_{\text{C}} = T_{\text{H}}q_{\text{H}} - T_{\text{C}}q_{\text{H}}$$

divide by $T_{\text{H}}T_{\text{C}}$

$$\left(\frac{q_{\text{H}}}{T_{\text{H}}} + \frac{q_{\text{C}}}{T_{\text{C}}}\right)_{\text{reversible}} = 0$$

generalizes to

$$\boxed{\oint \frac{\mathrm{d}q_{\text{rev}}}{T} = 0}$$

Important Consequences from the Carnot Cycle

B. Clausius Inequality

For a **less-efficient** and therefore **irreversible** Carnot cycle:

$$\varepsilon = \frac{-w}{q_\mathrm{H}} = \frac{q_\mathrm{H} + q_\mathrm{C}}{q_\mathrm{H}} < 1 - \frac{T_\mathrm{C}}{T_\mathrm{H}}$$

multiply by $T_\mathrm{H} q_\mathrm{H}$

$$T_\mathrm{H} q_\mathrm{H} + T_\mathrm{H} q_\mathrm{C} < T_\mathrm{H} q_\mathrm{H} - T_\mathrm{C} q_\mathrm{H}$$

divide by $T_\mathrm{H} T_\mathrm{C}$

$$\left(\frac{q_\mathrm{H}}{T_\mathrm{H}} + \frac{q_\mathrm{C}}{T_\mathrm{C}} \right)_\mathrm{irreversible} < 0$$

generalizes to

$$\boxed{\oint \frac{\mathrm{d}q_\mathrm{irrev}}{T} < 0}$$

Important Consequences from the Carnot Cycle

B. Clausius Inequality

For any cyclic process:

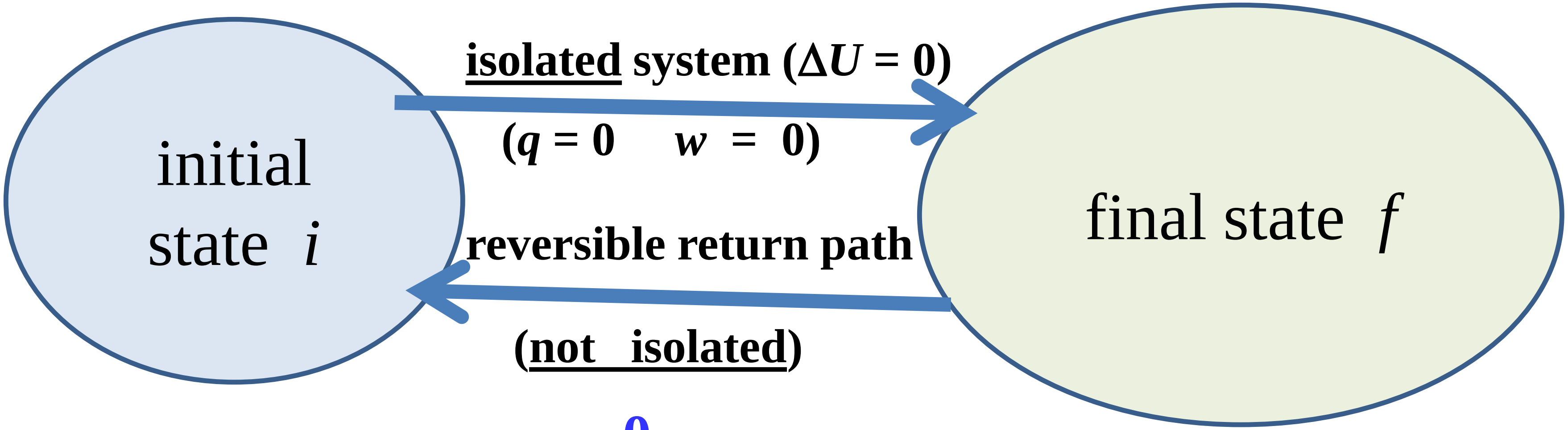
$$\boxed{\oint \frac{\mathrm{d}q}{T} \leq 0}$$

= 0 for reversible processes

< 0 for irreversible (spontaneous) processes

Important Consequences from the Carnot Cycle

C. *At Last !* A Rule for Predicting Spontaneous Processes !



initial state i

isolated system ($\Delta U = 0$)

($q = 0$ $w = 0$)

final state f

reversible return path

(not isolated)

$$\int_i^i \frac{\mathrm{d}q}{T} = \oint \frac{\mathrm{d}q}{T} = \cancelto{0}{\int_i^f \frac{\mathrm{d}q}{T}} + \int_f^i \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = 0 + S_i - S_f \le 0$$

$$\boxed{(S_f - S_i = \Delta S \ge 0)_{\text{isolated system}}}$$

Important Consequences from the Carnot Cycle

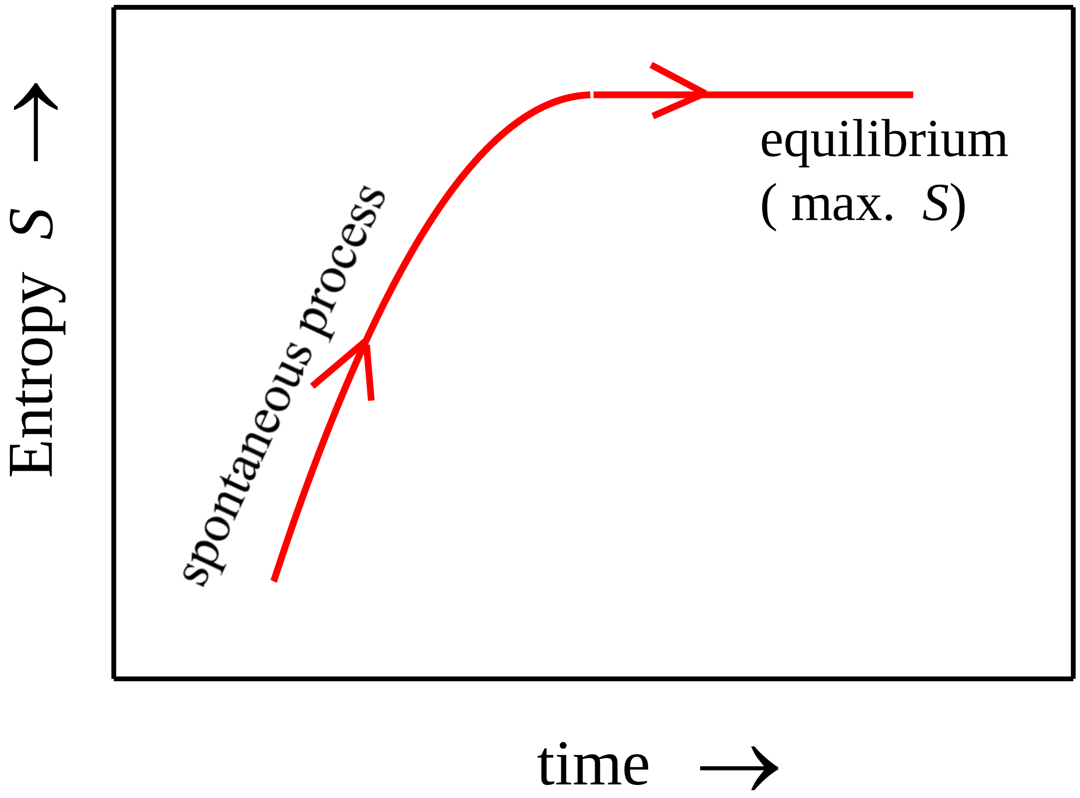
C. A Rule for Predicting Spontaneous Processes

Clausius Principle for isolated systems (constant U, V):

$$\boxed{(\Delta S)_{U,V} \geq 0}$$

- the entropy of an isolated system can never decrease
- the entropy of an isolated system remains constant during a reversible process: $\Delta S = 0$
- the entropy of an isolated system increases during a spontaneous (irreversible) process: $\Delta S > 0$
- **fundamental rules of nature!**
- **apply to any isolated system (gases, liquids or solids)**

Entropy of an <u>Isolated</u> System



Note that entropy is <u>not conserved</u>.

Important Consequences from the Carnot Cycle

D. Carnot’s Theorem

No heat engine operating between heat reservoirs at temperatures T_H and T_C can be more efficient than a reversible Carnot engine operating between the same two temperatures.

Proof:

Suppose a “super-engine” exists that is more efficient than a reversible Carnot engine.

It would then be possible to use the “super-engine” to run a **Carnot engine in reverse**.

Important Consequences from the Carnot Cycle

D. Carnot's Theorem. An Example:

Reversible Carnot Engine

$T_\mathrm{H} = 400\ \mathrm{K}$

$T_\mathrm{C} = 300\ \mathrm{K}$

$q_\mathrm{H} = 100\ \mathrm{J}$

$q_\mathrm{C} = -75\ \mathrm{J}$

$w = -25\ \mathrm{J}$

Efficiency:

$$\begin{aligned} \varepsilon &= 1 - (T_\mathrm{C}/T_\mathrm{H}) \\ &= -w/q_\mathrm{H} \\ &= (25\ \mathrm{J}) / (100\ \mathrm{J}) \\ &= 25\ \% \end{aligned}$$

"Super-Engine" ???

$T_\mathrm{H} = 400\ \mathrm{K}$

$T_\mathrm{C} = 300\ \mathrm{K}$

$q_\mathrm{H} = 100\ \mathrm{J}$

$q_\mathrm{C} = -25\ J$???

$w = -75\ J$???

Super-Efficiency:

$$\begin{aligned} \varepsilon &= -w/q_\mathrm{H} \\ &= (50\ J) / (100\ \mathrm{J}) \text{ ???} \\ &= 75\ \% \text{ ???} \end{aligned}$$

Important Consequences from the Carnot Cycle

D. Carnot's Theorem. An Example:

Reversible Carnot Engine

$T_H = 400\ \mathrm{K}$
$T_C = 300\ \mathrm{K}$
$q_H = 100\ \mathrm{J}$
$q_C = -75\ \mathrm{J}$
$w = -25\ \mathrm{J}$

One Cycle *Reversed*:

$q_H = 100\ \mathrm{J} \times (-1)$
$q_C = -75\ \mathrm{J} \times (-1)$
$w = -25\ \mathrm{J} \times (-1)$

"Super-Engine ???

$T_H = 400\ \mathrm{K}$
$T_C = 300\ \mathrm{K}$
$q_H = 100\ \mathrm{J}$
$q_C = -25\ J$???
$w = -75\ J$???

Three Cycles *Forward*:

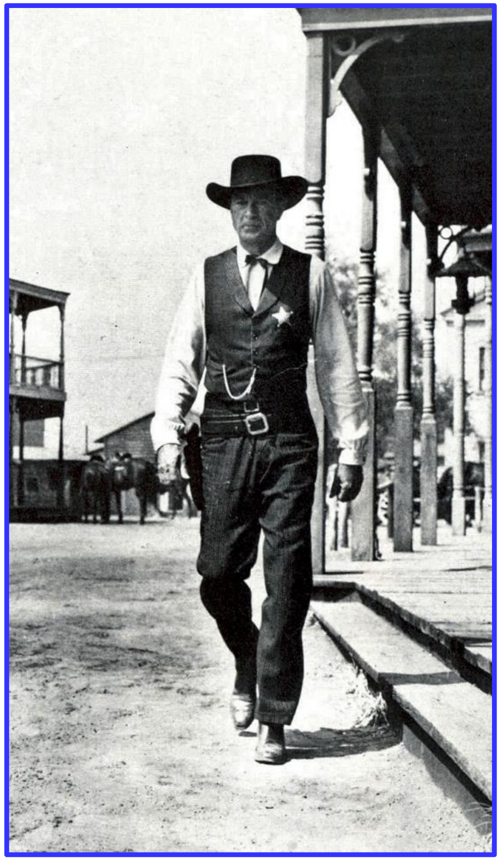
$q_H = 100\ \mathrm{J} \times (3)$
$q_C = -25\ J \times (3)$???
$w = -75\ J \times (3)$???

Net Result: $q_H = -100\ \mathrm{J} + 300\ \mathrm{J} = 200\ \mathrm{J}$
$q_C = +75\ \mathrm{J} - 75\ J = 0\ \mathrm{J}$
$w = 25\ \mathrm{J} - 225\ J = -200\ \mathrm{J}$

Impossible! Can't convert 200 J heat from a **single reservoir** to 200 J work done on the surroundings.

Important Consequences from the Carnot Cycle

E. The Second Law of Thermodynamics



It is impossible for a system to undergo a cyclic process in which the only effects are the absorption of heat from a single reservoir and the performance of an equal amount of work done on the surroundings.

Too Bad! Rules out **“perpetual motion machines of the second kind”**. “**Perpetual motion machines of the first kind**” violating conservation of energy (the First Law) also are impossible.

Clausius Statements of the First and Second Laws

1. **The energy of the universe is constant.**

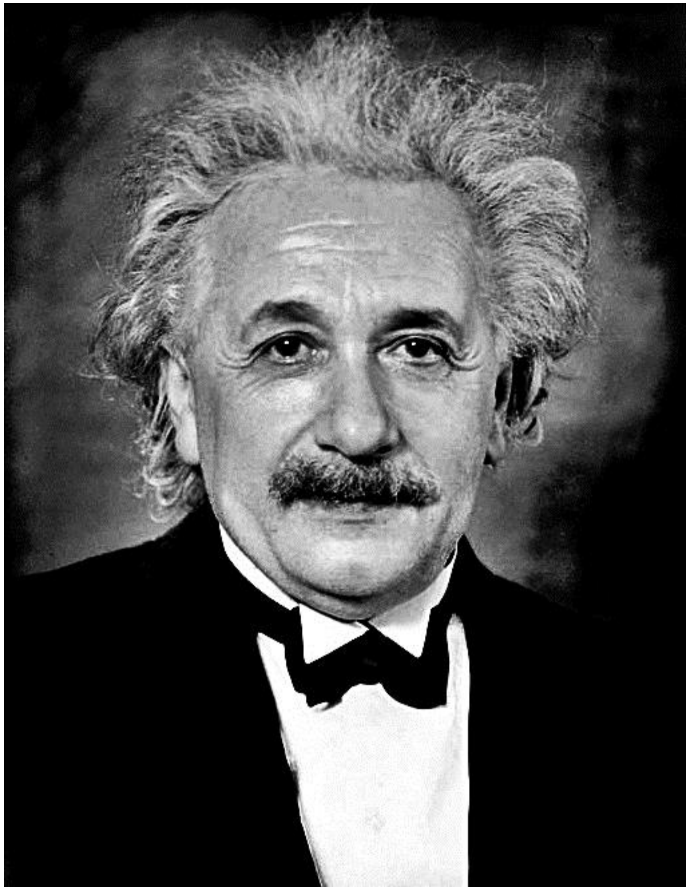
   $\Delta U = 0$ **(isolated systems)**

2. **The entropy of the universe tends toward a maximum.**

   $\Delta S \geq 0$ **(isolated systems)**

These are the only postulates on which all of thermodynamics is based!

Albert Einstein on Thermodynamics:



“A theory is more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its areas of applicability. Therefore, the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced, within the framework of applicability of its concepts, will never be overthrown.”

Section 5.4 Entropy Calculations

Useful Entropy Equations for Ideal Gases

First Law: $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$

for an ideal gas: $\mathrm{d}U = C_V\mathrm{d}T$

for a reversible process: $\mathrm{d}q_{\mathrm{rev}} = T\mathrm{d}S$ and $\mathrm{d}w = -p\mathrm{d}V$

combine to get $C_V\mathrm{d}T = T\mathrm{d}S - p\mathrm{d}V$

rearranges to

$$\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{p}{T}\mathrm{d}V = \frac{C_V}{T}\mathrm{d}T + \frac{nRT/V}{T}\mathrm{d}V$$

gives $\boxed{\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V}$ in terms of T, V

Exercise: derive $\boxed{\mathrm{d}S = \frac{C_p}{T}\mathrm{d}T - \frac{nR}{p}\mathrm{d}p}$ in terms of T, p

Entropy Calculations

Example. 5.00 mol of helium gas (assumed to be ideal) is heated from 298 K to 500 K in a 75.0 L container. Calculate Δ*S*.

constant volume

He(g): $C_{V\mathrm{m}} = 3(R/2)$

(3 translational modes)

To calculate Δ*S*, take a reversible path.

$$\mathrm{d}U = \mathrm{d}q_{\mathrm{rev}} - \cancelto{0}{p\mathrm{d}V} = C_V\mathrm{d}T$$

$$\mathrm{d}q_{\mathrm{rev}} = C_V\mathrm{d}T$$

$$\Delta S = \int \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \int_{T_i}^{T_f} \frac{C_V}{T}\mathrm{d}T = nC_{V\mathrm{m}}\int_{T_i}^{T_f}\frac{\mathrm{d}T}{T} = nC_{V\mathrm{m}}\ln\frac{T_f}{T_i}$$

$$\Delta S = (5.00\ \mathrm{mol})(1.5 \times 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln\frac{500\ \mathrm{K}}{298\ \mathrm{K}}$$

$$\boxed{\Delta S = 32.3\ \mathrm{J\ K^{-1}}}$$

Entropy Calculations

Example. 5.00 mol of helium gas (assumed to be ideal) is heated from 298 K to 500 K at 2.00 bar. Calculate ΔS.

constant pressure

To calculate ΔS, take a reversible path.

He(g): $C_{pm} = C_{V\mathrm{m}} + R$
$= 3(R/2) + R = 2.5\,R$

$$\mathrm{d}U = C_V\mathrm{d}T = \mathrm{d}q_{\mathrm{rev}} - p\mathrm{d}V$$

$$\mathrm{d}q_{\mathrm{rev}} = C_V\mathrm{d}T + p\mathrm{d}V = C_V\mathrm{d}T + p\mathrm{d}(nRT/p)$$

$$\mathrm{d}q_{\mathrm{rev}} = C_V\mathrm{d}T + nR\mathrm{d}T = (C_V + nR)\mathrm{d}T = Cp\mathrm{d}T = \mathrm{d}H$$

$$\Delta S = (5.00\,\mathrm{mol})(2.5 \times 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\ln\frac{500\ \mathrm{K}}{298\ \mathrm{K}}$$

$$\boxed{\Delta S = 53.8\ \mathrm{J\,K^{-1}}}$$

Why does heating at constant pressure cause a larger entropy increase than heating at constant volume?

Entropy Calculations

Example. Calculate ΔS for the <u>isothermal</u> expansion of 2.00 moles of ideal gas from 15.0 L to 45.0 L at 300 K.

The internal energy of an isothermal ideal gas is constant, $\Delta U = 0$.
To calculate ΔS, take a reversible path ($p_{\text{external}} = p$).

$$\mathrm{d}U = 0 = \mathrm{d}q_{\text{rev}} - p\,\mathrm{d}V$$

$$\mathrm{d}q_{\text{rev}} = p\,\mathrm{d}V$$

$$\Delta S = \int \frac{\mathrm{d}q_{\text{rev}}}{T} = \int_{V_i}^{V_f} \frac{p}{T}\,\mathrm{d}V = \int_{V_i}^{V_f} \frac{nRT}{VT}\,\mathrm{d}V = nR\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = nR\ln\frac{V_f}{V_i}$$

$$\Delta S = nR\ln\frac{V_f}{V_i} = (2.00\ \text{mol})(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ln\frac{45.0\ \text{L}}{15.0\ \text{L}}$$

$$\boxed{\Delta S = 18.3\ \text{J K}^{-1}}$$

Entropy Calculations

Example. 2.00 moles of helium ($C_{V\text{m}}$ = 3R/2) initially at 300 K expands <u>reversibly and adiabatically</u> from 15.0 L to 45.0 L. Calculate ΔS.

Trick question! $\Delta S = 0.$ ***Why*?**

$$\Delta S = \int \frac{\cancelto{0}{dq_{\text{rev}}}}{T} = 0$$

But how can ΔS be zero for an expansion? Shouldn't S increase?

During an **adiabatic expansion**, the entropy increase due to the volume increase is cancelled by the entropy decrease due to the cooling of the gas.

$$dS = 0 = \frac{C_V}{T}\overset{\text{negative}}{dT} + \frac{nR}{V}\overset{\text{positive}}{dV}$$

Exercise: show T_f = 144 K.

Entropy Changes for Reversible Phase Changes

Example: **Calculate ΔS for the melting of 2.00 moles of ice (solid H_2O) at 0 ^{o}C and 1 bar.**

Data $\Delta H_{\text{fusion}}(H_2O) = 6.010 \text{ kJ mol}^{-1}$

Melting ice at 0 ^{o}C is reversible: $dq = dq_{\text{rev}}$ ***(Why?)***

At constant pressure: $dq = dH$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{1}{T}\int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T}$$

$$\Delta S = \frac{2\Delta H_{\text{fusion,m}}}{T} = \frac{(2 \text{ mol})(6010 \text{ J mol}^{-1})}{273.15 \text{ K}}$$

$$\boxed{\Delta S = 44.10 \text{ J K}^{-1}}$$

Section 5.5 to 5.7 Using Entropy to Predict Spontaneous Processes

for an __isolated system__ ($\Delta U = 0$, $w = 0$, $q = 0$):

Nothin's happening?
No !!!

1 L $H_2(g)$
1.00 bar
300 K

1 L
0 bar
(vacuum)

Spontaneous mechanical process?

→

Yes!

2 L $H_2(g)$
0.500 bar
300 K

$$dS = \frac{C_V}{T} dT + \frac{nR}{V} dV$$

isothermal ($dT = 0$) →

$$\Delta S = nR \int_{V_i}^{V_f} \frac{dV}{V}$$

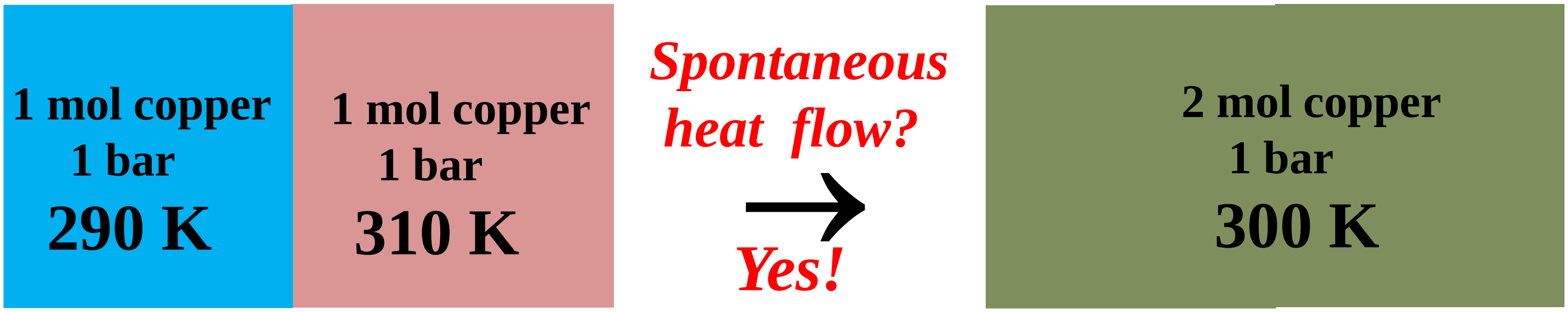
$$\Delta S = nR \ln \frac{V_f}{V_i} = nR \ln \frac{2\ \text{L}}{1\ \text{L}} = nR \ln 2 > 0$$

$\Delta S > 0$ for an isolated system: the process is spontaneous.

Using Entropy to Predict Spontaneous Processes

for an isolated system ($\Delta U = 0, q = 0, w = 0$):

Nothin's happening?
No !!!



1 mol copper
1 bar
290 K

1 mol copper
1 bar
310 K

Spontaneous heat flow?

$\rightarrow$

Yes!

2 mol copper
1 bar
300 K

$$q = 0 = q_{\text{left block}} + q_{\text{right block}}$$

$$\Delta S = \Delta S_{\text{left block}} + \Delta S_{\text{right block}} = \int_{290\text{K}}^{300\text{K}} \frac{C_{pm}\,\mathrm{d}T}{T} + \int_{310\text{K}}^{300\text{K}} \frac{C_{pm}\,\mathrm{d}T}{T}$$

$$\Delta S = C_{pm} \ln \frac{300\text{ K}}{290\text{ K}} + C_{pm} \ln \frac{300\text{ K}}{310\text{ K}} = C_{pm}(0.03390) + C_{pm}(-0.03279) > 0$$

$\Delta S > 0$ for an isolated system: the process is spontaneous.

Section 5.8 Absolute Entropies and the “Third Law”

Energy, heat, and work are intuitively understandable from everyday experience.

The entropy is just as important.

But *what is entropy*?

Is there a molecular interpretation of entropy?

Yes! Take Chem 332 …

Molecular Interpretation of the Entropy

The greater the number of microscopic arrangements of atoms, ions, or molecules over positions or energy levels in a system, the greater the entropy of the system.

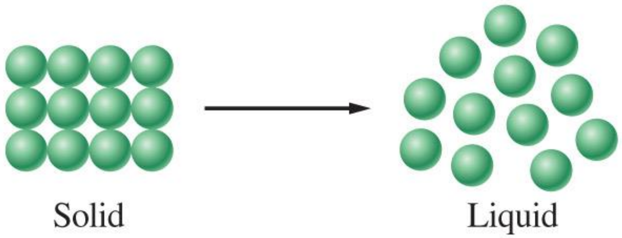
Boltzmann equation $\boldsymbol{S = k \ln W}$

$\boldsymbol{W}$ is the number of microscopic arrangements (microstates) of a system (calculated using **statistical thermodynamics**)

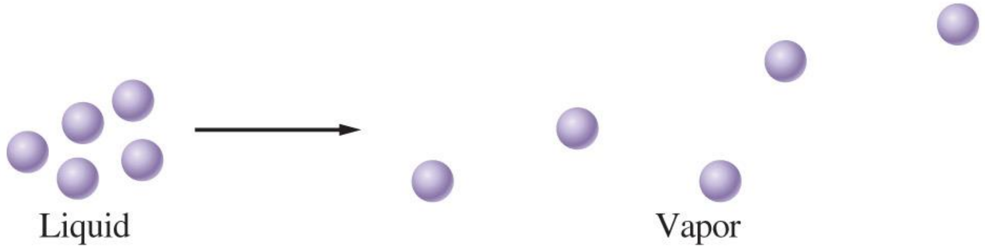
$\boldsymbol{k}$ is the Boltzmann constant

$\boldsymbol{k = R / N_A}$ (gas constant R divided by Avogadro’s number N_A)

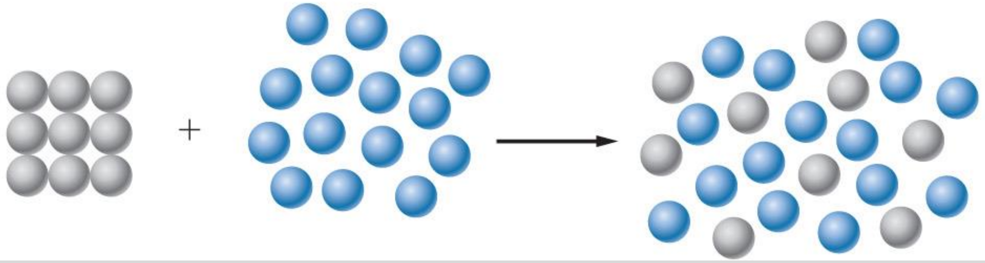
Processes that Increase the Entropy



Melting (fusion)
$S_\mathrm{m}(l) > S_\mathrm{m}(\mathrm{s})$



Vaporization $S_\mathrm{m}(\mathrm{g}) > S_\mathrm{m}(l)$



Dissolution
$S(\text{solution}) > S(\text{pure solute}) + S(\text{pure solvent})$

$N_2O_4(g) \rightarrow NO_2(g) + NO_2(g)$

$S_\mathrm{m}(\text{products}) > S_\mathrm{m}(\text{reactants})$

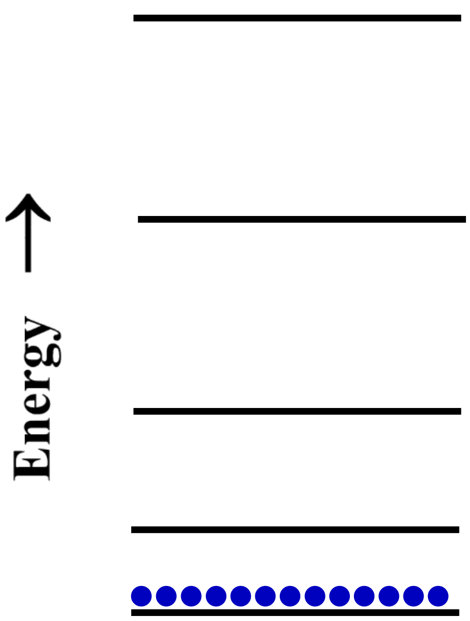
Entropy Changes Caused by **Heating**

$T_{\text{initial}} = 0\ \text{K}$

$W_{\text{initial}} = 1$

$T_{\text{final}} > 0$

$W_{\text{final}} >> 1$



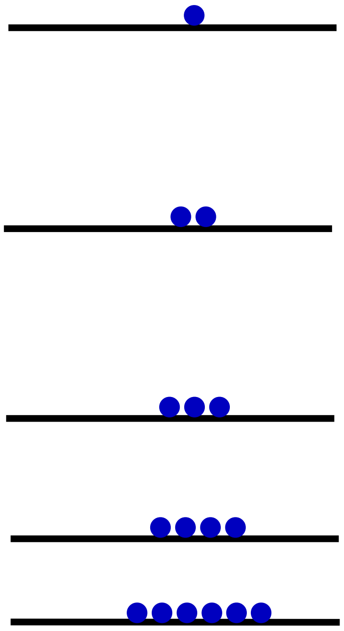
(only one arrangement)

heat →

$$\Delta S = \int \frac{dq_{\text{rev}}}{T}$$

$$= k \ln W_{\text{final}} - \cancelto{0}{k \ln W_{\text{initial}}}$$

$$= k \ln W_{\text{final}} >> 0$$



(many arrangements)

Heating promotes molecules to higher energy levels, increasing the number of microstates and the entropy.

Important processes that increase the entropy:

- heating a substance
- vaporizing a liquid
- subliming a solid
- melting a solid
- dissolving a solute in a solvent
- mixing pure liquids or pure gases
- chemical reactions increasing the number of gas molecules
- heat flow from higher to lower temperature
- expansions from higher to lower pressure

Absolute Entropies: Third Law of Thermodynamics

The entropy of a perfect crystal at $T = 0$ K is zero.

Why ?

Only the lowest energy level is populated at $T = 0$ K.

$$W(T = 0) = 1$$

$$S(T = 0) = k \ln W = k \ln(1) = 0$$

Absolute Entropies: Third Law of Thermodynamics

Chemical Applications Use molar heat capacities ($C = \mathrm{d}q/\mathrm{d}T$) and phase transition enthalpies (ΔH_{tr}) to calculate molar entropies of substances as a function of temperature.

$$S^{\mathrm{o}}_{\mathrm{m}}(T, 1\,\mathrm{bar}) \;=\; \cancelto{0}{S^{\mathrm{o}}_{\mathrm{m}}(0\,\mathrm{K}, 1\,\mathrm{bar})} \;+\; \int_{T=0}^{T} \frac{C^{\mathrm{o}}_{p\mathrm{m}}\,\mathrm{d}T}{T} \;+\; \sum_i \frac{\Delta H^{\mathrm{o}}_{\mathrm{tr,m}}(i)}{T_i}$$

Why is this important?

The entropies of reactants and products can be used to calculate ΔS to decide if a reaction is spontaneous

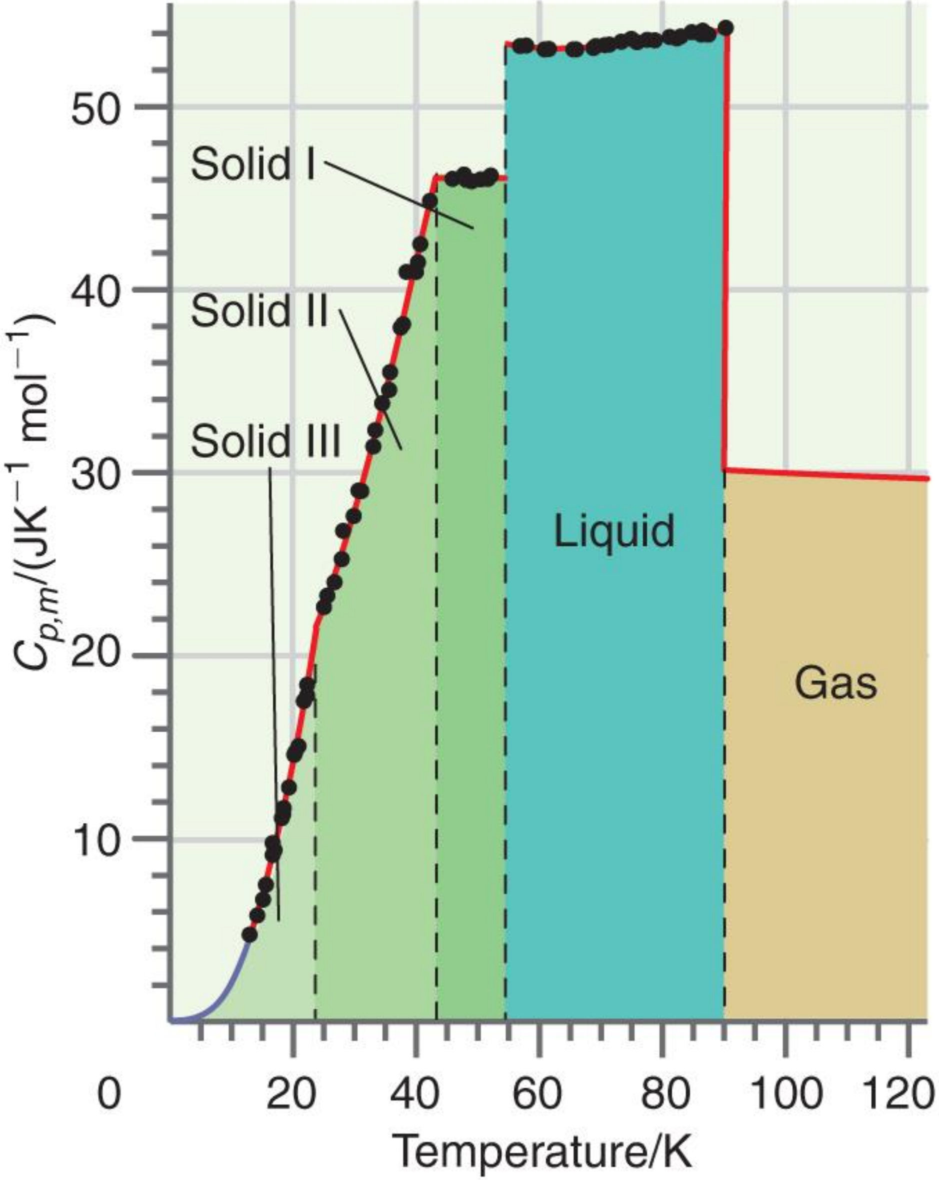
without carrying out the reaction !

Standard molar entropies at 25 ^{o}C (p^{o} = 1 bar)

Substance	S_m^{o} / J K^{-1} mol^{-1}
He (gas)	126.2
Hg (gas)	175.0
H_2 (gas)	130.7
O_2 (gas)	205.1
N_2 (gas)	191.6
I_2 (gas)	260.7
H_2O (gas)	188.8
H_2O (liquid)	69.9
C (graphite)	5.74
C (diamond)	2.38

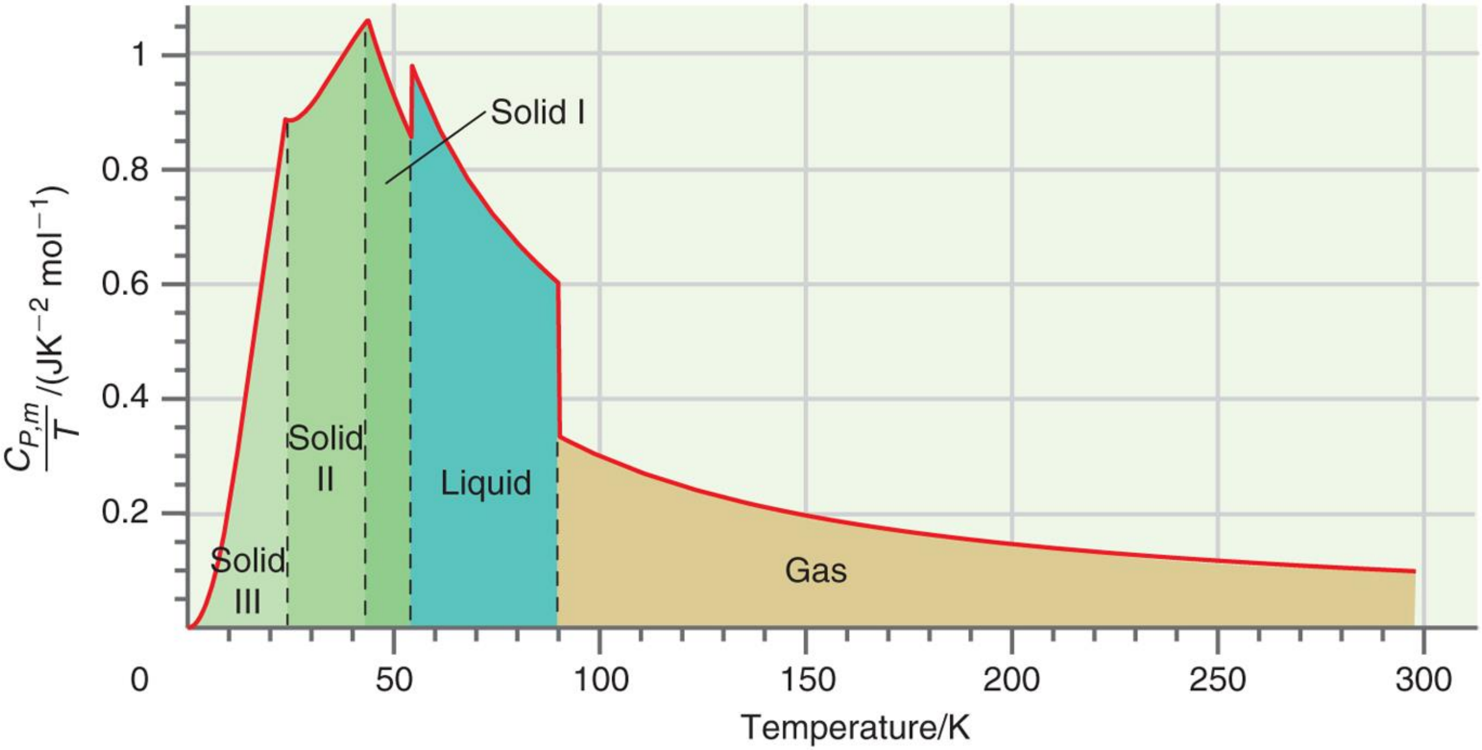
Example: Molar Heat Capacity Data

Molar heat capacity of oxygen at 1 bar



Example: C_{pm} / T Data

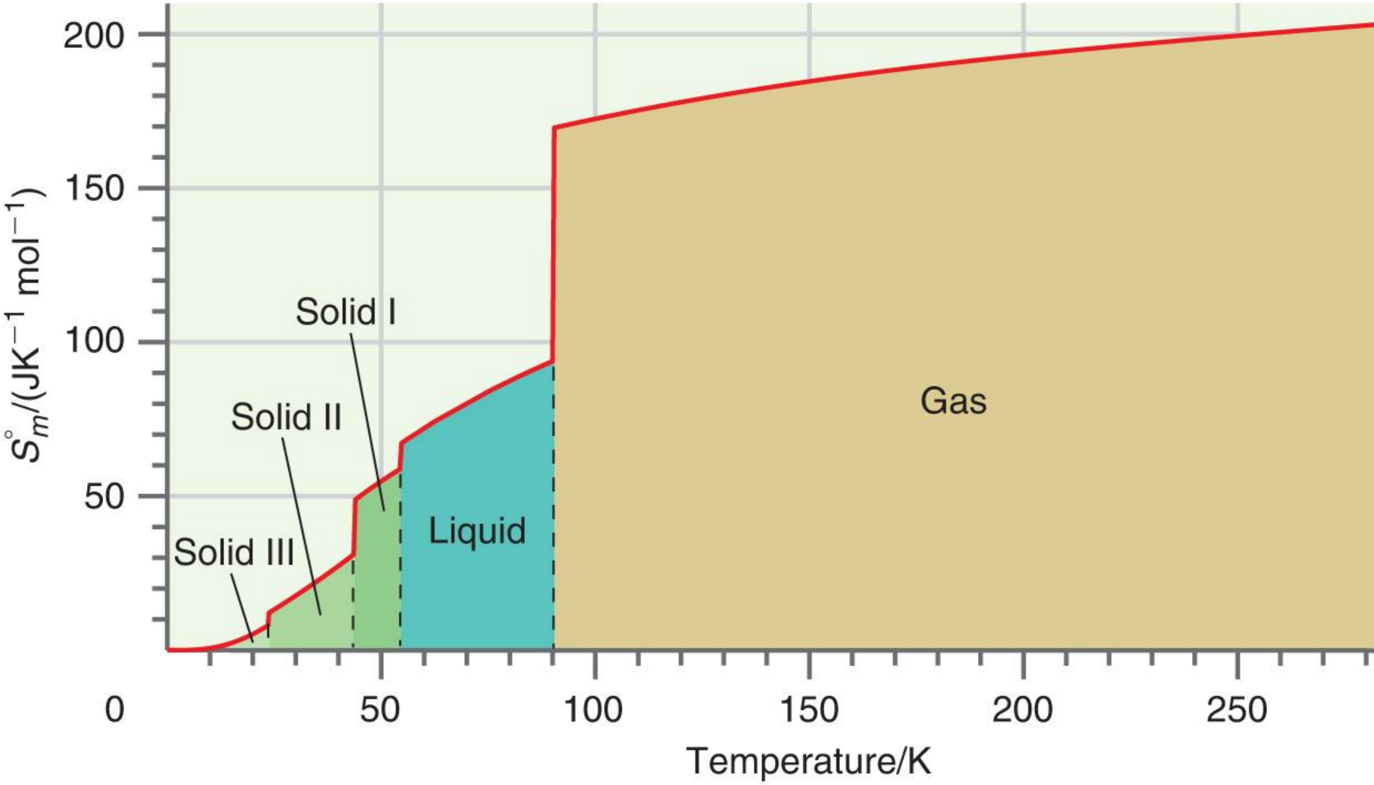
C_{pm}/T for oxygen at 1 bar



Example: Absolute Entropy of Oxygen

$$S^{\mathrm{o}}_{\mathrm{m}}(T, 1\,\mathrm{bar}) = \int_{T=0}^{T} \frac{C^{\mathrm{o}}_{p\mathrm{m}}\,\mathrm{d}T}{T} + \sum_i \frac{\Delta H^{\mathrm{o}}_{\mathrm{tr,m}}(i)}{T_i}$$

Molar entropy of oxygen at 1 bar as a function of temperature



Sections 5.9 and 5.10 Applications of the Entropy

Chemical Reactions

- Energy is often considered to be the most important consideration for whether or not chemical reactions occur.

- The entropy change for chemical reactions can be important too, sometimes more important than energy changes.

- Fortunately, entropy changes for chemical reactions can be calculated from absolute entropies of the reactants and products.

- Even better, this means ΔS for chemical reactions can be calculated <u>without carrying out the reactions</u>.

Entropy Changes for Chemical Reactions

Example: Calculate the entropy change Δ*S* for the reaction

$$\mathrm{C(graphite)} \xrightarrow[\textbf{1 bar}]{\textbf{25 °C}} \mathrm{C(diamond)}$$

Easy! Look up (Table 4.2, at 25 °C and 1 bar):

$$S_m^o(\text{graphite}) = 5.74 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_m^o(\text{diamond}) = 2.38 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S = (1 \text{ mol})S_m^o(\text{diamond}) - (1 \text{ mol})S_m^o(\text{graphite})$$

$$= 2.38 \text{ J K}^{-1} - 5.74 \text{ J K}^{-1}$$

$$\boxed{\Delta S = -3.36 \text{ J K}^{-1}}$$

- Can you suggest why diamond has a lower molar entropy than graphite?

Entropy Changes for Chemical Reactions

Example: Calculate the entropy change ΔS for the reaction

$$\mathbf{Fe_3O_4(s) + 4\,H_2(g) \xrightarrow[1\ \text{bar}]{25\ ^{o}\text{C}} 3\,Fe(s) + 4\,H_2O\,(\mathit{l})}$$

$$\Delta S = 3S_m{}^o(\text{Fe, s}) + 4S_m{}^o(\text{H}_2\text{O}, l) - S_m{}^o(\text{Fe}_3\text{O}_4\text{, s}) - 4S_m{}^o(\text{H}_2\text{, g})$$

From (Table 4.2, at 25 °C and 1 bar):

$$\Delta S = (3)(27.28) + (4)(69.61) - (1)(146.4) - (4\ \text{mol})(130.684\ \text{J K}^{-1}\ \text{mol}^{-1})$$

$$\boxed{\Delta S = -308.9\ \text{J K}^{-1}}$$

- Can you suggest why ΔS is large and **negative** for this reaction?

Section 5.11 Efficiency of Heat Engines, Refrigerators and Heat Pumps

Heat Engine Efficiency ε

$$\varepsilon \equiv \frac{\text{work done on surroundings}}{\text{heat absorbed at } T_\mathrm{H}} = \frac{-w}{q_\mathrm{H}}$$

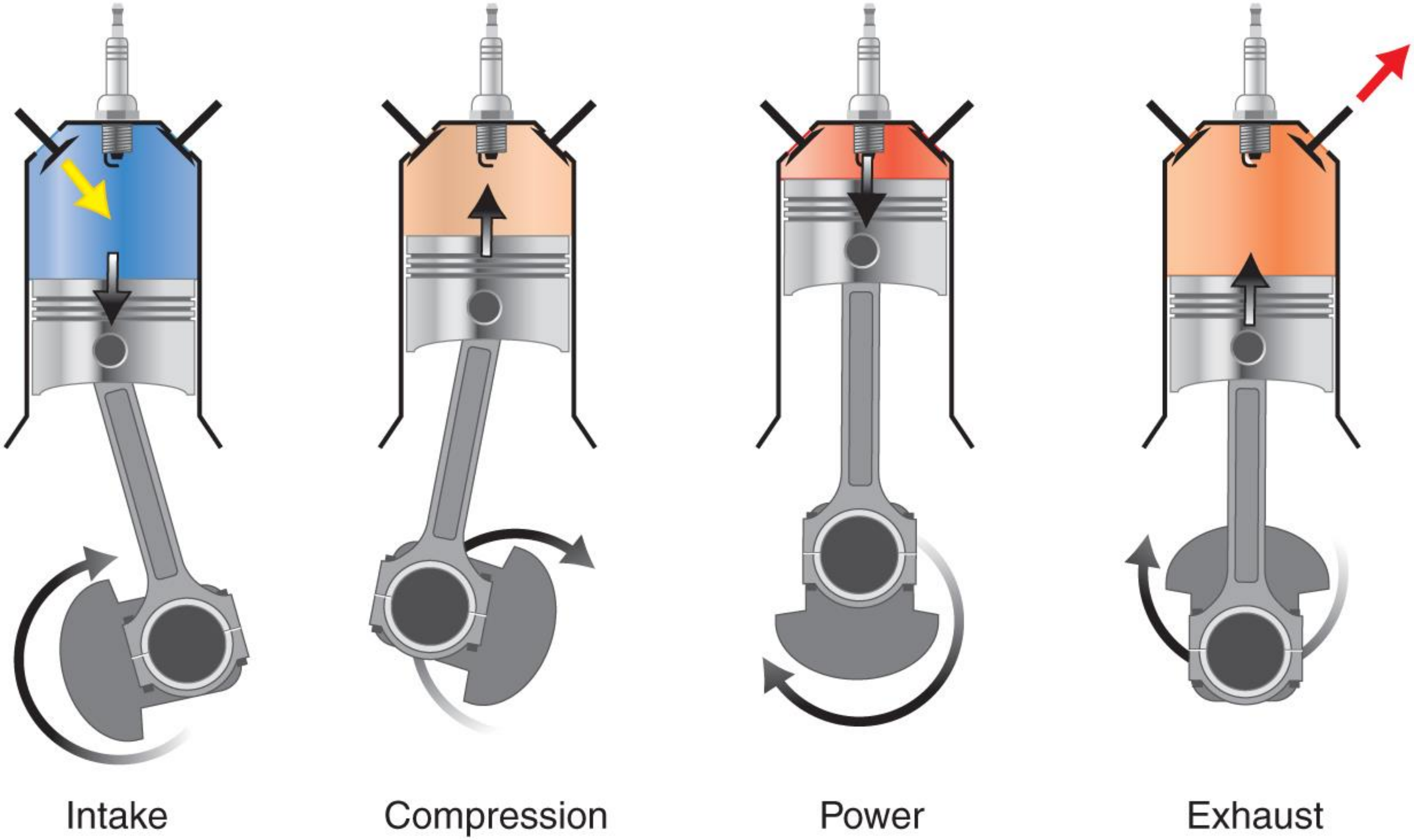
From the Second Law:

$$\boxed{\varepsilon_\text{maximum} = 1 - \frac{T_\mathrm{C}}{T_\mathrm{H}}}$$

Internal Combustion Engines

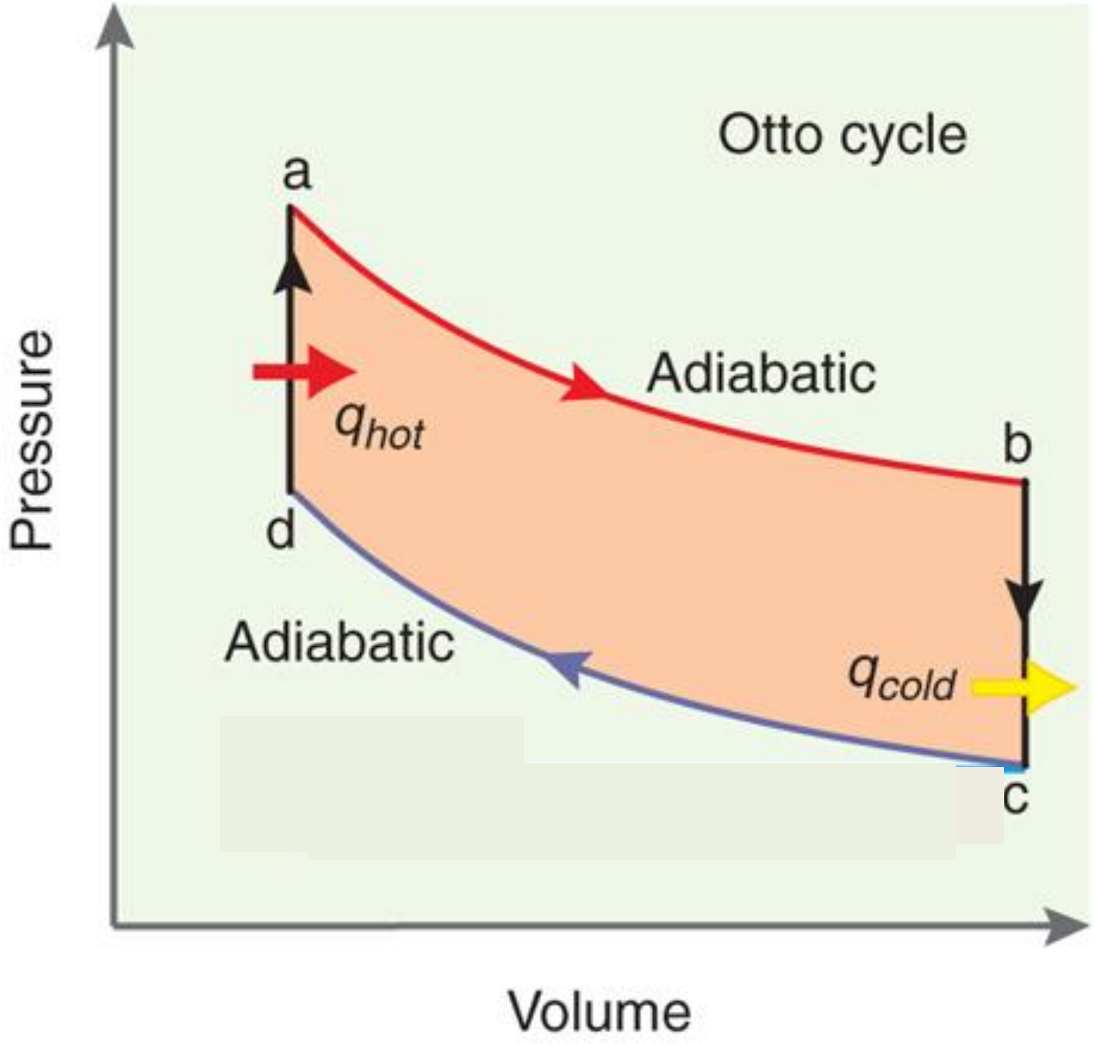
15 % to 25 % efficiency

Four-Stroke Otto* Cycle

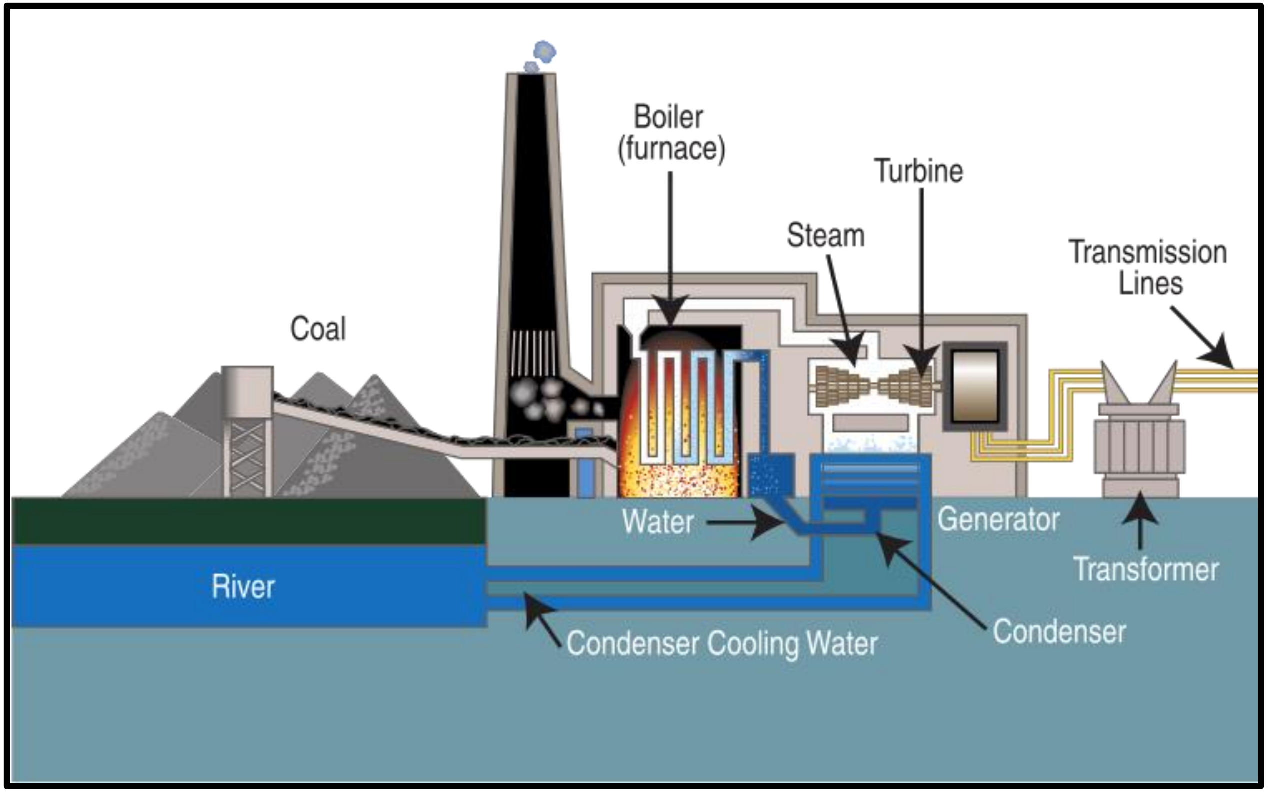


*no pun intended

Otto Cycle Indicator Diagram



High-Pressure Steam Turbines

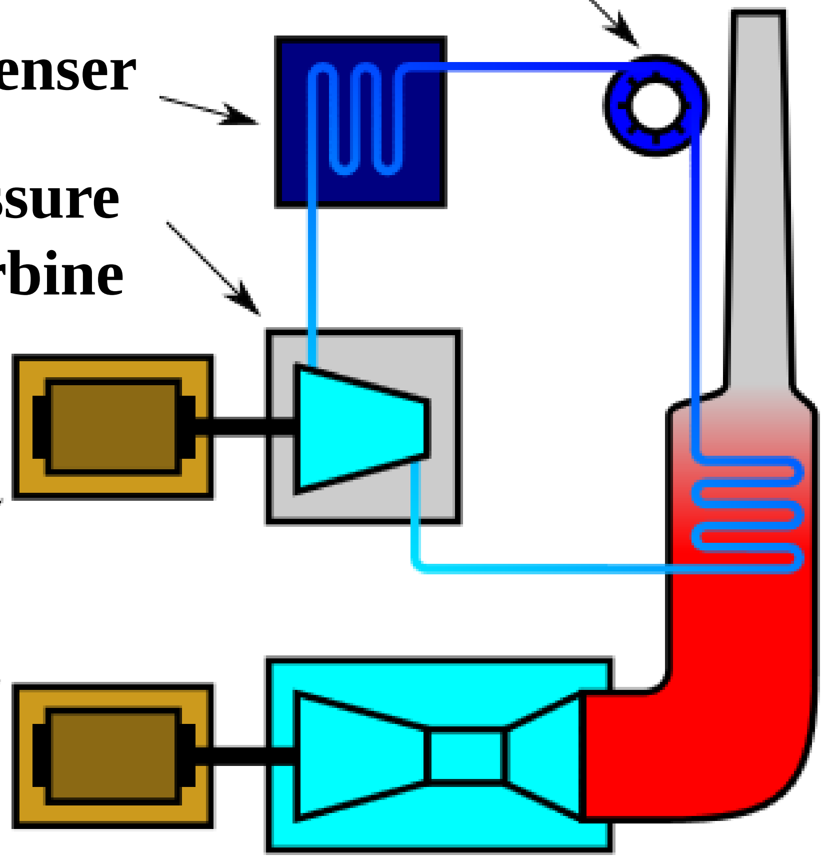


Why ***high*** *pressure?*

- coal, natural gas, wood, or nuclear heat sources
- T_H from 500 to 700 K, T_C about 300 K

35 % to 50 % efficiency

Combined Cycle Generation (CCG)



liquid-water return pump

condenser

high-pressure
steam turbine

electrical
generators

two engines
operated
in tandem

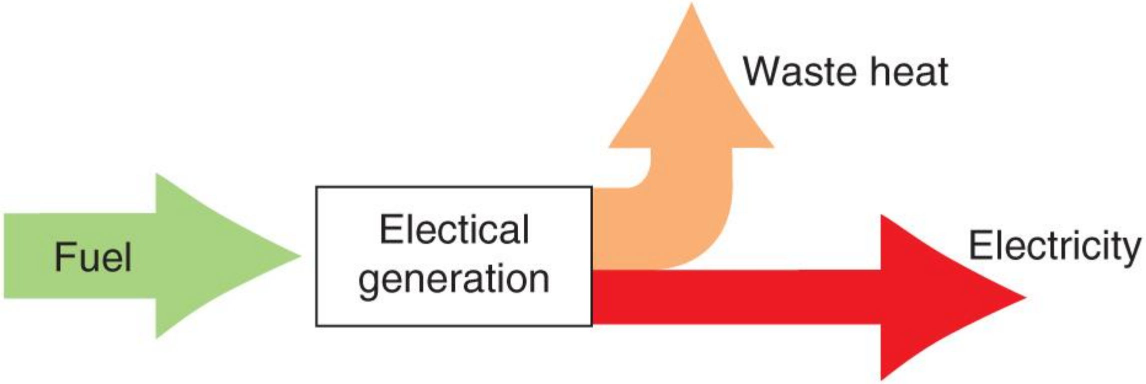
2. Boiler heated
by gas-turbine
exhaust at
450 to 650 ^{o}C

1. High-temperature
gas turbine operating
at 900 to 1400 ^{o}C

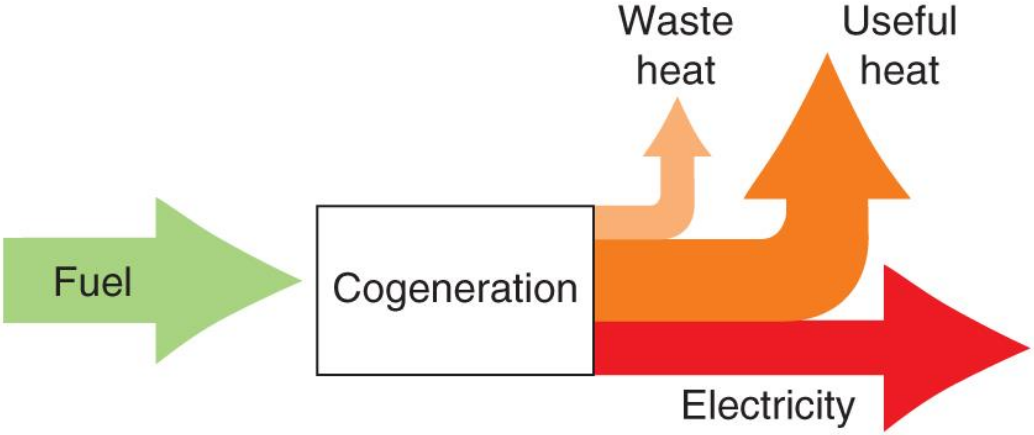
up to 60 % overall efficiency

Cogeneration

Waste heat from a generating station **rejected at T_C** is usually **lost** into cooling water from a lake or river.



<u>Cogeneration</u>: Heat rejected at T_C <u>is used</u> to heat buildings, greenhouses, chemical process streams, …



Heat Pumps and Refrigerators

Consider a **heat engine** operating between:

$$\boldsymbol{T_H = 300\ \mathrm{K}\quad (27\ ^{o}\mathrm{C})}$$

$$\boldsymbol{T_C = 270\ \mathrm{K}\quad (-\ 3\ ^{o}\mathrm{C})}$$

Max. efficiency $= 1 - (T_C/T_H)$

$= 1 - (270/300)$

$= 0.100$

Small ΔT $= T_H - T_C$ means **poor efficiency (10 % *at best*)**

***But wait*! What if this engine runs *<u>in reverse</u>* ...**

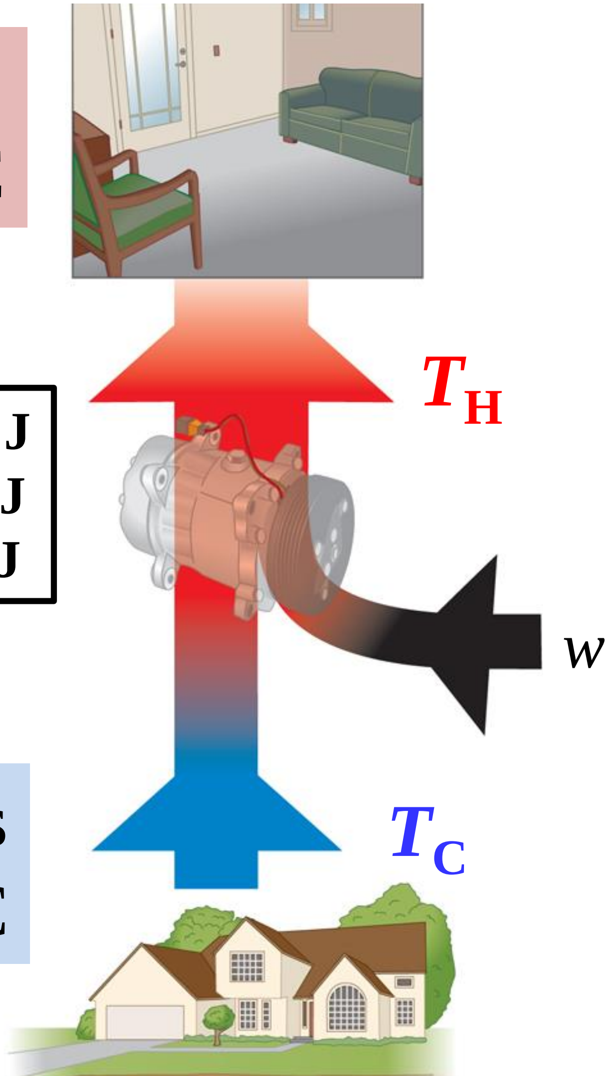
Heat Pumps and Refrigerators ($w > 0$)

- heat flow from lower to higher temperatures is not spontaneous
- work must be done **on** heat pumps ($w > 0$) to drive heat **up** temperature gradients
- heat pumps (and refrigerators) are heat engines run **in reverse**

indoors
at 27 °C

$$w = 1{,}000\ \mathrm{J}$$
$$q_H = -10{,}000\ \mathrm{J}$$
$$q_C = 9{,}000\ \mathrm{J}$$

outdoors
at −3 °C



For every 1,000 J work done **on** a reversible heat pump, notice:

$$\varepsilon = 0.100 = -w / q_H$$
$$= -1000\ \mathrm{J} / q_H$$

$$q_H = -10{,}000\ \mathrm{J}$$

Important: 1000 J of work delivers 10,000 J heat to keep the indoors warm, yielding **a ten-fold magnification**.

It's magic!

No. It's thermodynamics.

Depressed by the Carnot rule on the efficiency of heat engines?

Stay tuned.

Chem 232 Chapter 11:

Electrochemical reactions
for generating electricity in

batteries

fuel cells

exempt from Carnot limitations

Section 5.12 Dependence of the Entropy on Temperature and Volume

Entropy is important, by any definition.

From Section 5.4, for an **ideal gas**:

$$\boxed{\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V \qquad (\text{if} \quad pV = nRT)}$$

A useful result.

But what about real gases, liquids, solids, … ?

How does the entropy of **any system** change if the system is heated, cooled, compressed, or expanded?

Section 5.12 Dependence of the Entropy on Temperature and Volume

For the entropy as a function of *T* and *V*, **mathematics gives:**

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

But to be convenient, how are $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$ calculated?

In the next Chapter, **in terms of measurable quantities**, we'll find:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad\qquad \left(\frac{\partial S}{\partial V}\right)_T = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\beta}{\kappa}$$

$$\boxed{\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{\beta}{\kappa}\,\mathrm{d}V}$$

Section 5.12 Dependence of the Entropy on Temperature and Pressure

From Section 5.4, for an **ideal gas**:

$$\boxed{\mathrm{d}S = \frac{C_p}{T}\mathrm{d}T - \frac{nR}{p}\mathrm{d}p \qquad (\text{if} \quad pV = nRT)}$$

Another useful result.

But what about real gases, liquids, solids, … ?

How does the entropy of **any system** change if the system is heated, cooled, or the pressure is changed?

Standard entropy data at p^{o} = 1 bar are available for many Systems. **What if the system pressure isn't 1 bar?**

Section 5.12 Dependence of the Entropy on Temperature and Pressure

For the entropy as a function of T and p, **mathematics gives:**

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

But to be convenient, how are $(\partial S/\partial T)_p$ and $(\partial S/\partial p)_T$ calculated?

In the next Chapter, **in terms of measurable quantities**, we'll find:

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad\qquad \left(\frac{\partial S}{\partial p}\right)_T = -V\beta$$

$$\boxed{\mathrm{d}S = \frac{C_p}{T}\mathrm{d}T - V\beta\,\mathrm{d}p}$$

Chapter 6. Chemical Equilibrium

Summary

- the **First and Second Laws** are combined to predict conditions for spontaneous processes, including chemical reactions
- the **Helmholtz energy** $\boldsymbol{A = U - TS}$ provides $\boldsymbol{\Delta A_{T,V} < 0}$ for spontaneous processes at constant temperature and volume
- the **Gibbs energy** $\boldsymbol{G = U + pV - TS}$ provides $\boldsymbol{\Delta G_{T,p} < 0}$ for spontaneous processes at constant temperature and pressure
- the Gibbs energy is used to derive expressions for the equilibrium constant of chemical reactions

Motivation for Chapter 6

Could do most of thermodynamics with *p*, *V*, *T*, *q*, *w*, *U*, *S* .

Ok. But sometimes the calculations are ***very inconvenient*!**

Example: Prove that freezing liquid water is spontaneous at –10 ^{o}C.

Take the **3-step reversible path** (Why? So Δ*S* can be calculated.):

$$\begin{tikzcd}
\mathbf{H_2O(\mathit{l})} \arrow[r, "\textbf{II}", "\textbf{freeze}"'] & \mathbf{H_2O(s)} \arrow[d, "\textbf{III}", "\textbf{cool}"'] & 0\ ^{o}\mathrm{C} \\
\mathbf{H_2O(\mathit{l})} \arrow[u, "\textbf{I}", "\textbf{heat}"'] & \mathbf{H_2O(s)} & -10\ ^{o}\mathrm{C}
\end{tikzcd}$$

$$H_2O(l) \xrightarrow[\Delta H_{\mathrm{m,freeze}} \;=\; -\Delta H_{\mathrm{m,fusion}}]{\textbf{Spontaneous ?}} H_2O(s) \qquad -10\ ^{\mathrm{o}}\mathrm{C}$$

$$\Delta H(-10\ ^{\mathrm{o}}\mathrm{C}) = \Delta H_{\mathrm{I}} + \Delta H_{\mathrm{II}} + \Delta H_{\mathrm{III}}$$

$$= C_{pm}(l)(273-263)\mathrm{K} - \Delta H_{\mathrm{fus,m}}(273\mathrm{K}) + C_{pm}(\mathrm{s})(263-273)\mathrm{K}$$

$$= -\,5618\ \mathrm{J\ mol^{-1}}$$

$$\Delta S(-10\ ^{\mathrm{o}}\mathrm{C}) = \Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} + \Delta S_{\mathrm{III}} \quad \text{(all steps reversible)}$$

$$= \int_{263\,\mathrm{K}}^{273\,\mathrm{K}} \frac{C_{pm}(l)}{T}\,\mathrm{d}T + \frac{-\Delta H_{\mathrm{fus,m}}}{273\ \mathrm{K}} + \int_{273\,\mathrm{K}}^{263\,\mathrm{K}} \frac{C_{pm}(\mathrm{s})}{T}\,\mathrm{d}T$$

$$= -\ 19.20\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\boxed{q/T = 21.36\ \mathrm{J\ K^{-1}} \neq \Delta S\ \ !}$$

$$\Delta S_{\mathrm{system}} + \Delta S_{\mathrm{surroundings}} = -19.20\ \mathrm{J} + \frac{5618\ \mathrm{J}}{263\ \mathrm{K}} = +2.15\ \mathrm{J\ K^{-1}}$$

$$\boxed{\Delta S > 0 \text{ [isolated (system + surroundings)]} \quad \therefore \textbf{ Spontaneous}}$$

This is inconvenient. What to do?

Legendre Transformations ***to the rescue.***

Given the exact differential dY_I

$$dY_\mathrm{I} = C_1 dX_1 + C_2 dX_2$$

the function $Y_\mathrm{I}(X_1,X_2)$ can be "transformed" into the new functions (*maybe more convenient?*):

$$Y_\mathrm{II} = Y_\mathrm{I} - C_1X_1$$

$$Y_\mathrm{III} = Y_\mathrm{I} - C_2X_2$$

$$Y_\mathrm{IV} = Y_\mathrm{I} - C_1X_1 - C_2X_2$$

Legendre Transformations for Thermodynamics

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \qquad \text{(First Law)}$$

For a reversible path ($\mathrm{d}q = T\mathrm{d}S$ and $\mathrm{d}w = -p\mathrm{d}V$):

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

Legendre transforms of $U(S,V)$ are:

$U - TS$ (A = Helmholtz function)

$U + pV$ (H = enthalpy)

$U - TS + pV$ (G = Gibbs function)

Section 6.1 Predicting Spontaneous Processes

a) Using the Internal Energy ($\mathrm{d}U_{S,V} \leq 0$)

$\Delta U_{S,V} < 0$	spontaneous process	
$\Delta U_{S,V} = 0$	reversible process	

Where do these rules come from?

First Law: $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$

For a reversible path: $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ (I)

($\mathrm{d}q = T\mathrm{d}S$ and $\mathrm{d}w = -p\mathrm{d}V$)

For a spontaneous path: $\mathrm{d}U = \mathrm{d}q - p_{\mathrm{ext}}\mathrm{d}V$ (II)

Eq. I minus Eq. II: $0 = T\mathrm{d}S - \mathrm{d}q - (p_{\mathrm{ext}} - p)\mathrm{d}V$

same as: $\mathrm{d}q = T\mathrm{d}S - (p_{\mathrm{ext}} - p)\mathrm{d}V$

Irreversible Expansions $p - p_{\text{ext}} > 0 \quad \mathrm{d}V > 0$

Irreversible Compressions $p - p_{\text{ext}} < 0 \quad \mathrm{d}V < 0$

notice: $\boldsymbol{(p - p_{\text{ext}})\mathrm{d}V \geq 0}$

always ≥ 0

from previous slide: $\mathrm{d}q = T\mathrm{d}S - \boxed{(p_{\text{ext}} - p)\mathrm{d}V}$

Important Result: $\boxed{\boldsymbol{\mathrm{d}q \leq T\mathrm{d}S}}$

Why important? First Law: $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w = \mathrm{d}q - p_{\text{ext}}\mathrm{d}V$

(assuming only p-V work)

using $\mathrm{d}q \leq T\mathrm{d}S$ gives $\mathrm{d}U \leq T\mathrm{d}S - p_{\text{ext}}\mathrm{d}V$

at constant S, V this means $\mathrm{d}U_{S,V} \leq 0$

($\mathrm{d}S = 0$, $\mathrm{d}V = 0$)

$\mathrm{d}U_{S,V} < 0$	**spontaneous**
$\mathrm{d}U_{S,V} = 0$	**reversible**

$\Delta U_{S,V} \le 0$ is a useful result, but **experimentally inconvenient**.
How do you keep the entropy constant? Try the enthalpy?

b) Predicting Spontaneous Processes using the Enthalpy

$$H \equiv U + pV$$

$$\boxed{\begin{array}{lll} \Delta H_{S,p} < 0 & & \textbf{spontaneous process} \\ \Delta H_{S,p} = 0 & & \textbf{reversible process} \end{array}}$$

$$\begin{aligned} \mathrm{d}H &= \mathrm{d}(U + pV) \\ &= \mathrm{d}U + \mathrm{d}(pV) \\ &= \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p \\ &= \mathrm{d}q - p_{\mathrm{ext}}\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p \end{aligned}$$

At constant pressure ($p_{\mathrm{ext}} = p$):

$$\mathrm{d}H_p = \mathrm{d}q - \cancel{p_{\mathrm{ext}}\mathrm{d}V} + \cancel{p\mathrm{d}V} + \cancel{V\mathrm{d}p} = \mathrm{d}q \le T\mathrm{d}S$$

At constant S,p: $\boxed{\mathbf{d}H_{S,p} \le 0}$

Still inconvenient.
How is S held constant?

c) Predicting Spontaneity using the Helmholtz Energy *A*

$$A \equiv U - TS$$

$$\boxed{\begin{array}{ll} \Delta A_{T,V} < 0 & \textbf{spontaneous process} \\ \Delta A_{T,V} = 0 & \textbf{reversible process} \end{array}}$$

The Helmholtz energy, like the enthalpy, is an "auxiliary" thermodynamic state function. Useful property:

$$\begin{aligned} \mathrm{d}A &= \mathrm{d}(U - TS) \\ &= \mathrm{d}U - \mathrm{d}(TS) \\ &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \\ &= \mathrm{d}q + \mathrm{d}w - T\mathrm{d}S - S\mathrm{d}T \\ &= \mathrm{d}q - p_{\mathrm{ext}}\mathrm{d}V - T\mathrm{d}S - S\mathrm{d}T \\ \mathrm{d}A &\le -p_{\mathrm{ext}}\mathrm{d}V - S\mathrm{d}T \qquad (\text{using } \mathrm{d}q - T\mathrm{d}S \le 0) \end{aligned}$$

At constant temperature and volume (can be arranged):

$$\boxed{\mathbf{d}A_{T,V} \le 0}$$

constant T,V conditions are <u>experimentally convenient</u>