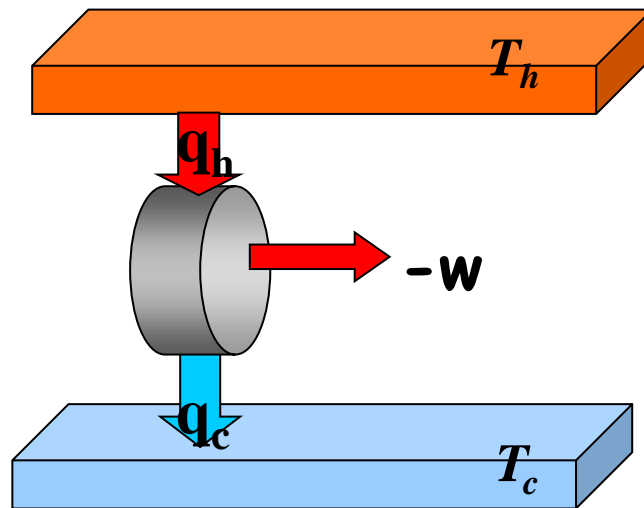
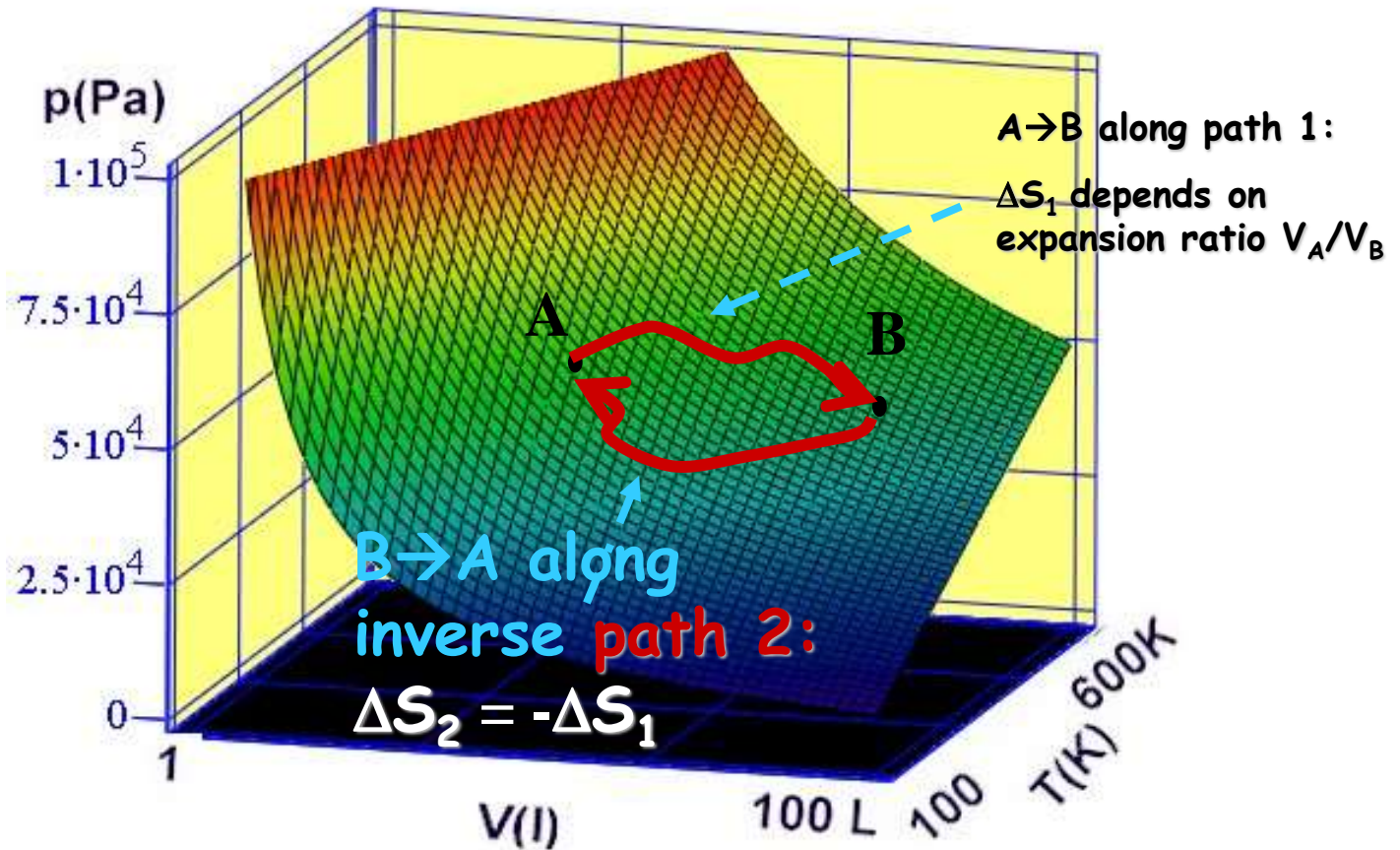


Entropy & and the 2nd Law



Entropy as a State Function

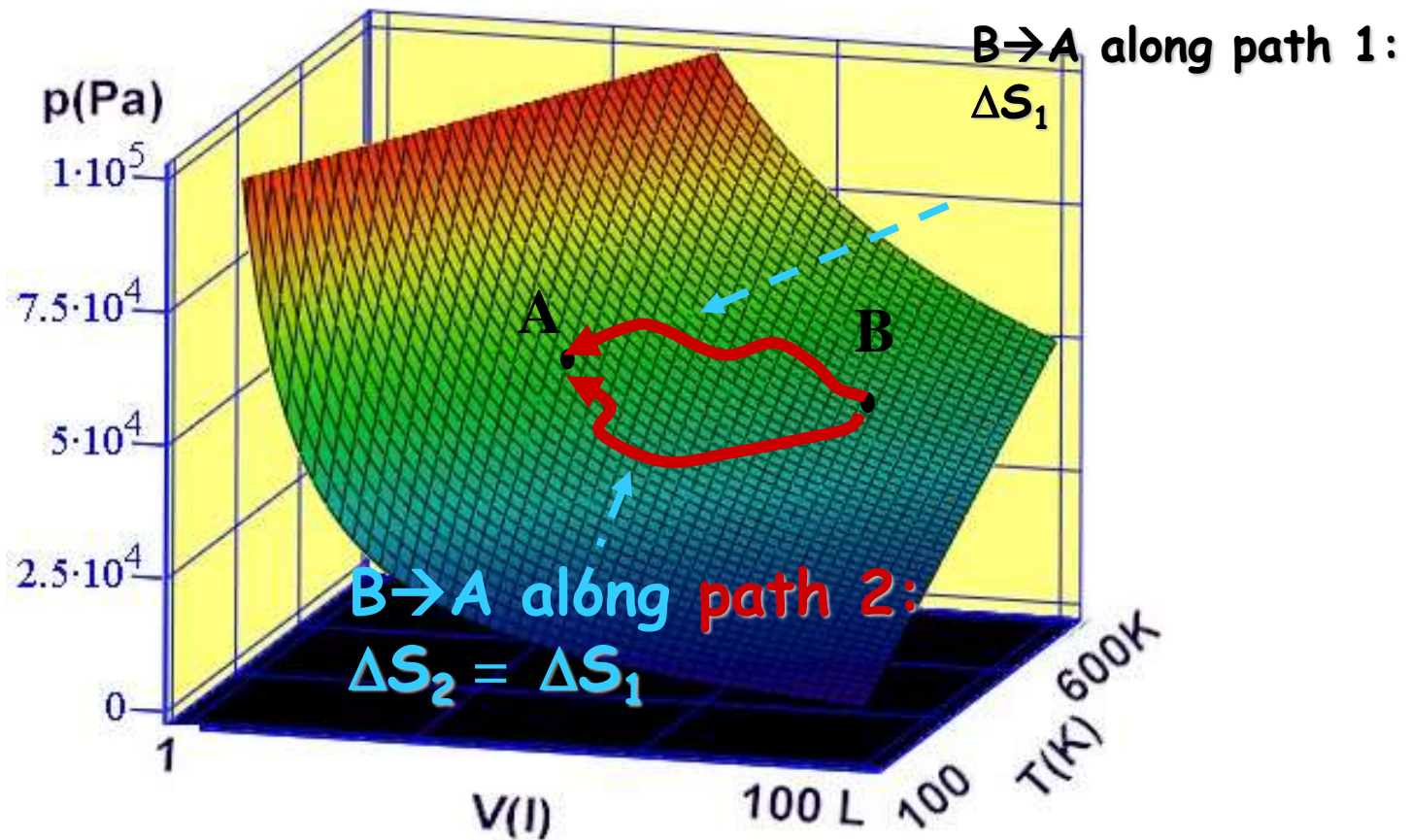
Ideal Gas EOS



A completely reversible process $A \rightarrow B \rightarrow A$ returns the system to its initial state after a combination of different processes. In reversible processes, the system retains its entropy, $\Delta S = 0$, even if $\Delta q_1 \neq \Delta q_2$. \square **S = State Function**

Entropy as a State Function

Ideal Gas EOS



Two different processes $B \rightarrow A$ produce the same system entropy gain or loss, $\Delta S_2 = \Delta S_1$. Even though different amounts of heat are generated along different pathways $B \rightarrow A$, the entropy change $\Delta S = q_{\text{rev}}/T$ is the same. ΔS does not depend on the way on which a state is reached, even if it is an irreversible process. S is a function alone of the state of the system.

Entropy in Thermodynamic Processes

Heat absorption by a system is maximum in reversible processes $A \rightarrow B$:

System: $dS \cdot T = q_{rev} > q_{irrev} > 0$

$$dS \geq dq/T > 0$$

$$\Delta S_{A \rightarrow B} \geq \int_A^B \frac{dq}{T}$$

Always true (sign incl.) for thermodynamic states.

= for reversible (isothermal), adiabatic ($q=0$)

Rev. entropy gains by system are made up by surroundings

Entropy in Thermodynamic Processes

Heat emission by a system is minimum in reversible processes $A \rightarrow B$:

System: $q_{\text{irrev}} < q_{\text{rev}} = dS \cdot T < 0$

$$dq/T \leq dS < 0$$

$$\Delta S_{A \rightarrow B} \geq \int_A^B \frac{dq}{T}$$

Always true (sign incl.) for thermodynamic states.

= for reversible (isothermal), adiabatic ($q=0$)

Rev. entropy losses by system are made up by surroundings

Examples: Entropy Gains and Losses

Expansion/compression $V_{\text{initial}} \rightarrow V_{\text{final}}$

Isothermal compression ($q = q_{\text{rev}} < 0$),

System: $q_{\text{rev}} > q_{\text{irrev}}$ (irrev: more negative)

Surr.: $q_{\text{irrev}} > q_{\text{rev}}$ (rev: more negative)

System $\frac{\Delta q}{T_{\text{sys}}} \leq R \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right) = \Delta S_{\text{sys}} \leq 0$ **Loss**

Isothermal expansion ($q = q_{\text{rev}} > 0$),

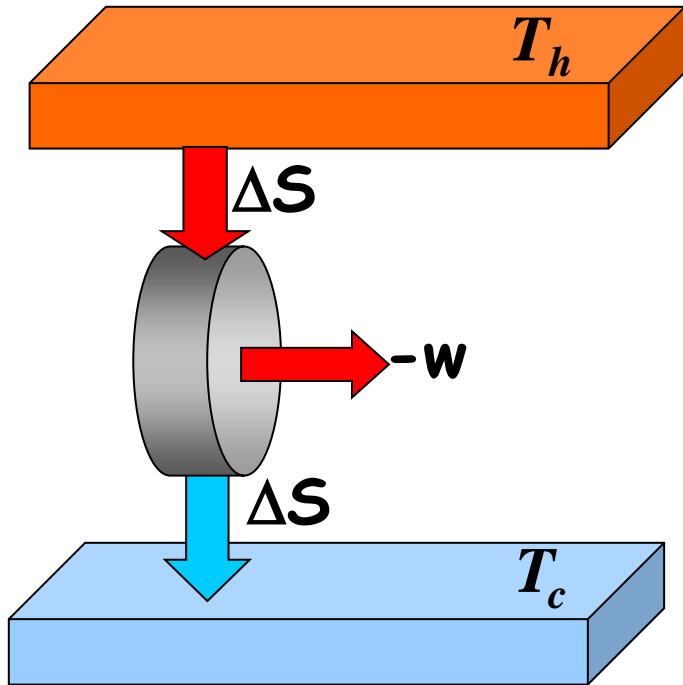
System: $q_{\text{rev}} > q_{\text{irrev}}$ (irrev: less positive)

Surr.: $q_{\text{irrev}} > q_{\text{rev}}$ (rev: less positive)

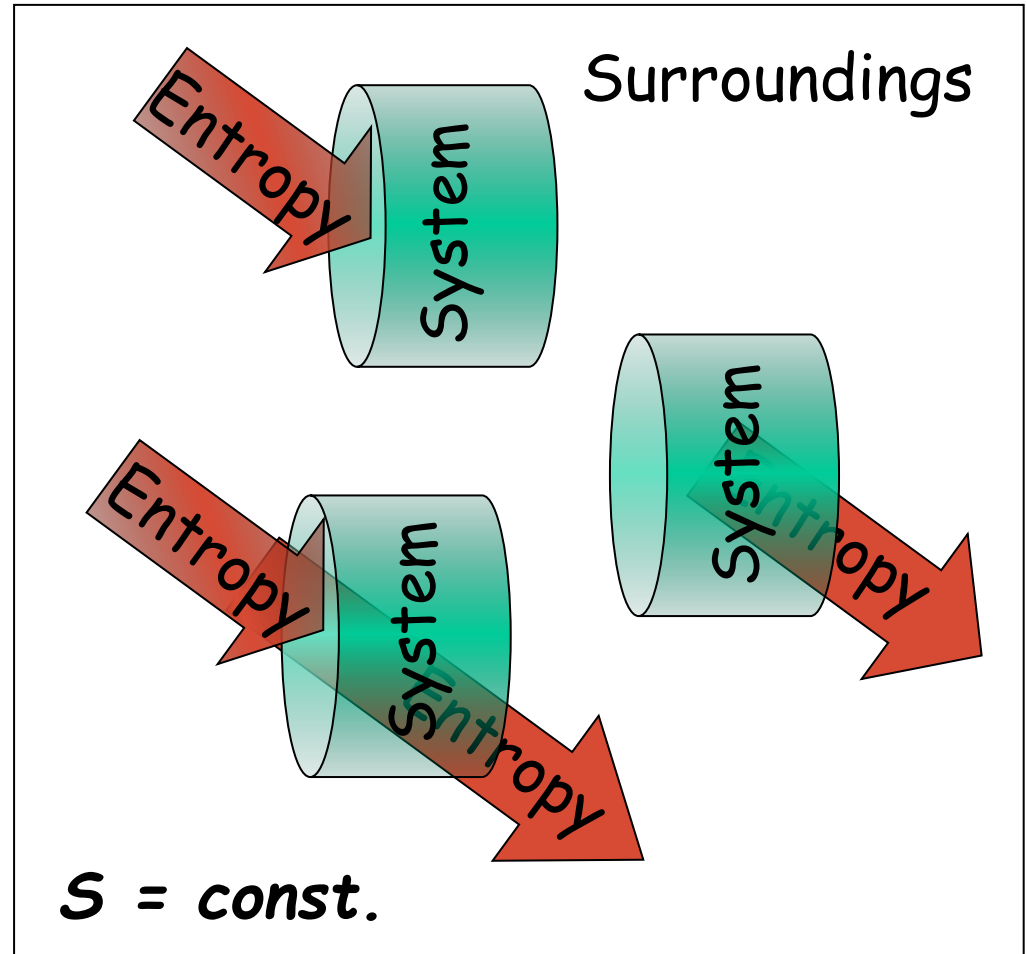
System $0 < \frac{\Delta q}{T_{\text{sys}}} \leq R \ln \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right) = \Delta S_{\text{sys}}$ **Gain**

$$\Delta S_{A \rightarrow B} \geq \int_A^B \frac{dq}{T}$$

Entropy Balance in Reversible Processes

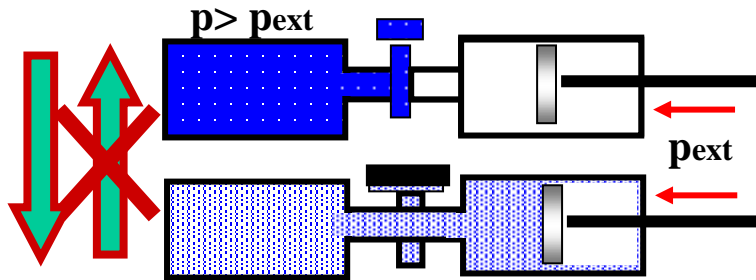


Equilibrium between system and surroundings: $T_{sys} = T_{surr}$



Entropy is exchanged between system and surroundings. In a cyclic process, entropy flows through the system.

Irreversible Processes



Spontaneous,
irreversible

8 **Corollary:**

If the total entropy is not conserved in a process $A \rightarrow B$,

$$\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \neq 0$$

$A \rightarrow B$ must be irreversible !

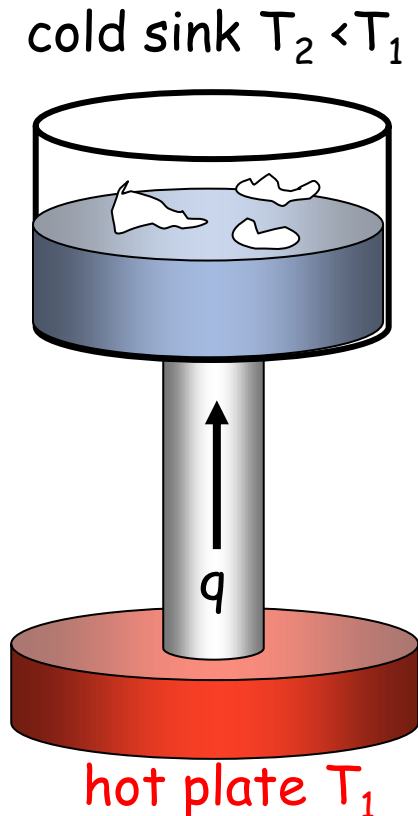
Do all irreversible processes have $\Delta S \neq 0$, $\Delta S < 0$, $\Delta S > 0$?

Entropy in Irreversible Processes

System is not in equilibrium with surroundings.
Or System 1 and System 2 in contact are not in equilibrium with each other.

Example: Heat Convection/Conduction

9



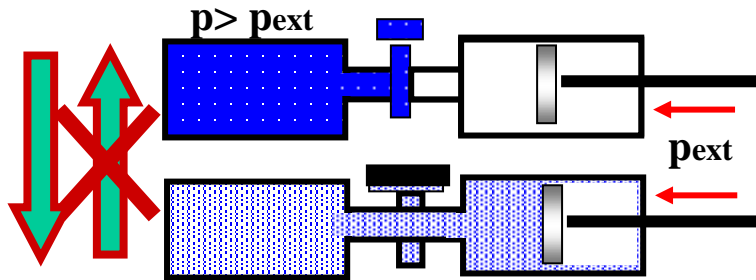
$$\Delta S_{A \rightarrow B} = \frac{q}{T_2} - \frac{q}{T_1} > 0$$

$$\frac{d}{dt} J_S > 0 \quad \text{Entropy created}$$

$$T_1 \xrightarrow{q} T_2 < T_1$$

Asymmetry of Nature "Arrow of Time"

Irreversible Processes



Spontaneous,
irreversible

Corollary:

If the total entropy is not conserved in a process $A \rightarrow B$,

$$\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

All irreversible $A \rightarrow B$ increase entropy of system plus surroundings.

The 2nd Law of Thermodynamics

**The entropy of a system
and its surroundings
never decreases!**

$$\Delta S_{A \rightarrow B} \geq \int_A^B \frac{dq}{T}$$

Predicted here for non-interactive systems.

Large Magellanic Cloud SN 1987A



Limits to the 2nd Law?

Every empirical law has a range of applicability. How universal is the 2nd LTD? Universe is 14 Ba old. Started with Big Bang (thermal equil.?) but is now far from equilibrium.

→ Theory of Chaos, Synergetics, adaptive complex systems.

Calculating the Entropy Change

Calculating the entropy in a (reversible) **isothermal** (**T=const.**) expansion/compression $V_1 \rightarrow V_2$ is simple:

Since $q_{rev} = \Delta U - w_{rev} = -w_{rev} = -RT \ln\left(\frac{V_1}{V_2}\right)$

$$\Delta S = \frac{q_{rev}}{T} = -R \ln\left(\frac{V_1}{V_2}\right) = -R \ln\left(\frac{p_2}{p_1}\right) = -R \ln\left(\frac{c_2}{c_1}\right) \text{ concentration } c=1/V$$

The entropy of a system increases, when it absorbs heat ($q_{rev} > 0$), expands ($V_1 < V_2$), gets decompressed ($p_1 > p_2$), or diluted ($c_1 > c_2$). Spontaneous processes: $\Delta S > 0$.

Entropy Calculations

Entropy change $\Delta S = \Delta S(q_{rev}, T)$ depends on the heat q_{rev} and the ambient T at transfer.

If $T \square$ const, isochoric pressurization if $T_1 \rightarrow T_2 > T_1$:
integrate over $dq_{rev} = C_V dT$ for $V = \text{const}$.

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

$$\Delta S_{1 \rightarrow 2} = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

$$\Delta S_{1 \rightarrow 2} = C_V \ln \left(\frac{T_2}{T_1} \right) \text{ for } C_V = \text{const.}$$

The entropy of a system increases, when it is heated ($\Delta T > 0$) at $V = \text{const}$.

Entropy Calculations

Entropy change $\Delta S = \Delta S(q_{rev}, T)$ depends on the heat q_{rev} and the ambient T at transfer.

If $T \square$ const, isobaric decompression if $T_1 \rightarrow T_2 > T_1$
integrate over $dq_{rev} = C_p dT$

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

$$\Delta S_{1 \rightarrow 2} = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT$$

$$\Delta S_{1 \rightarrow 2} = C_p \ln \left(\frac{T_2}{T_1} \right) \text{ for } C_p = \text{const.}$$

The entropy of a system increases, when it is heated ($\Delta T > 0$) at $p = \text{const}$. Spontaneous processes: $\Delta S > 0$.

Example

Q: By how much does the entropy of 2 moles of water vapor at normal pressure (1 atm) change, when it is heated from $T_1 = 100^\circ\text{C}$ to $T_2 = 150^\circ\text{C}$.

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Hint: For water, $C_p = 36.4 \text{ J/Kmol}$.

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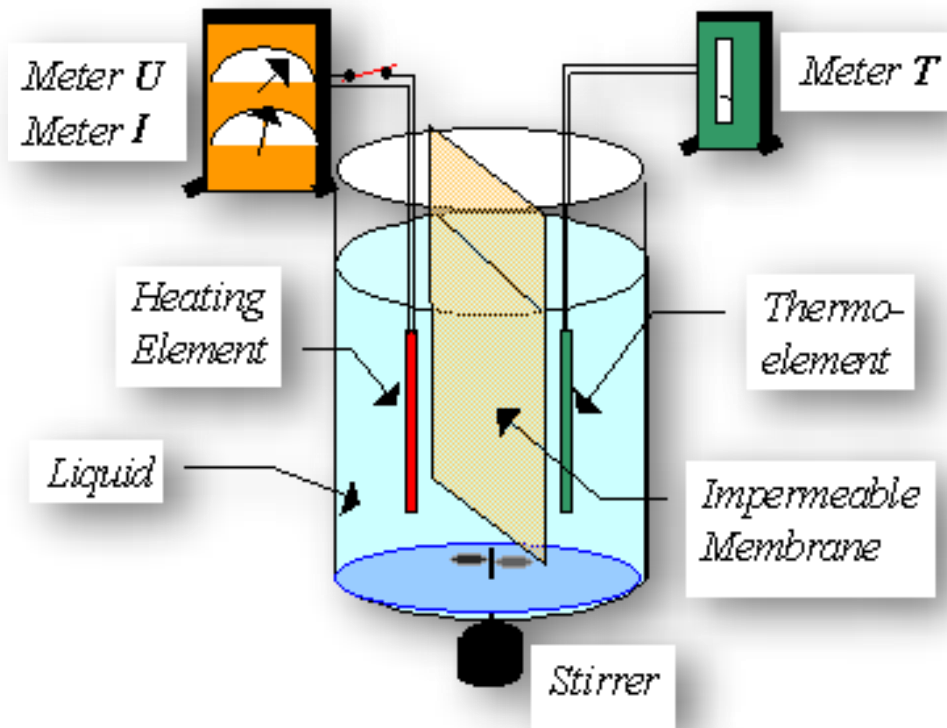
Hint: For water, $C_p = 36.4 \text{ J/Kmol}$.

A:

$$\Delta S_{1 \rightarrow 2} = n \cdot C_p \int_{T_1}^{T_2} \frac{dT}{T} = n \cdot C_p \ln \left(\frac{T_2}{T_1} \right) =$$
$$= 2 \text{ moles} \cdot 36.4 \frac{\text{J}}{\text{Kmol}} \cdot \ln \frac{423}{373} = 9.16 \frac{\text{J}}{\text{K}} > 0$$

How to Measure Entropy

Experiment to Measure the Entropy of a Liquid

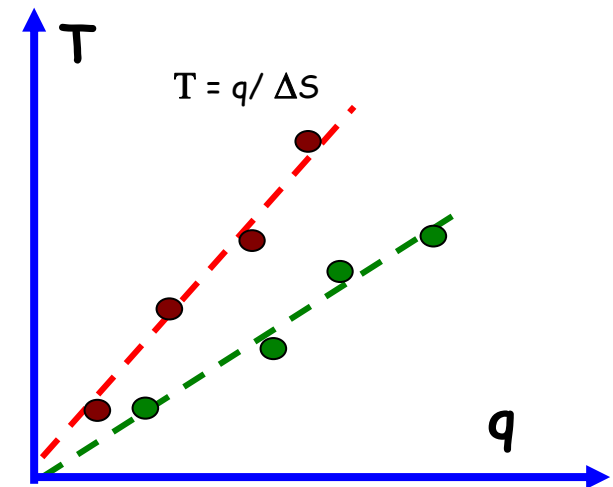


Measure electric energy

$$\Delta E_{el} = I \cdot U \cdot \Delta t \rightarrow q$$

Measure T,

record $\Delta S = q/T$



Experimental Entropies: 3rd Law TD

Substance	Entropy (298 K, 1at)
Diamond	2.4 J K ⁻¹ mol ⁻¹
Carbon	5.74 J K ⁻¹ mol ⁻¹
Water	69.9 J K ⁻¹ mol ⁻¹
Alcohol	160.7 J K ⁻¹ mol ⁻¹
Oxygen (gas)	205.0 J K ⁻¹ mol ⁻¹
CO ₂	213.6 J K ⁻¹ mol ⁻¹

Experimental entropies are different for different states. Crystals with perfect lattice order have lowest entropy S , gases have highest.

Crystals with perfect lattice order close to $T = 0\text{K}$ have lowest entropy. All substances at $T = 0\text{K}$:

3rd Law of Thermodynamics

$$S = 0 \quad (T = 0\text{K}).$$

~~Kelvin-Clausius Controversy~~

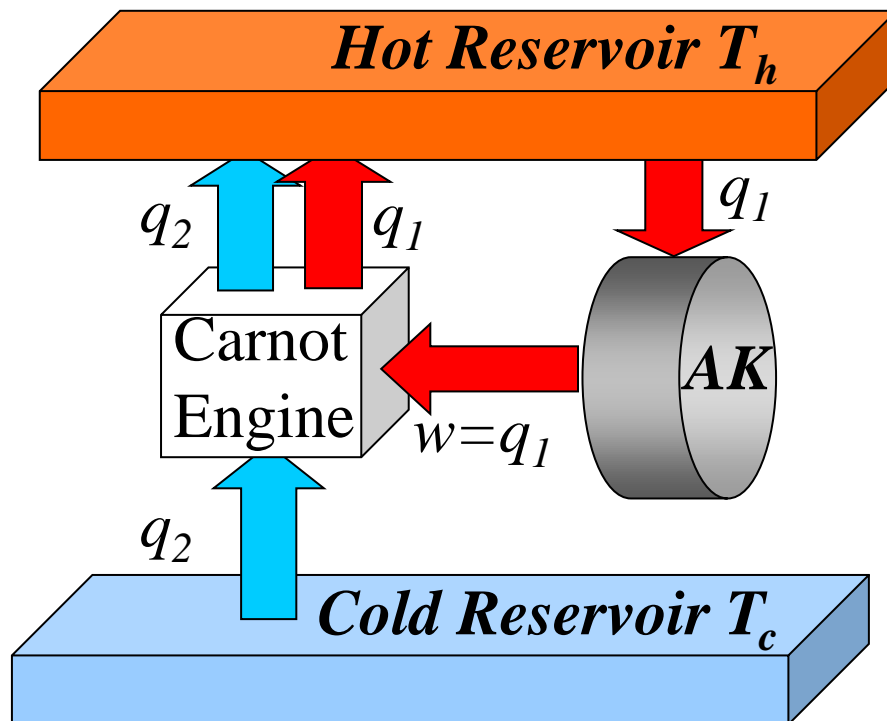
***A (Kelvin):** No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.*

***B (Clausius):** No process is possible in which the sole result is the transfer of heat from a cooler to a hotter reservoir.*

Kelvin

A: *No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.*

Construct an anti-Kelvin engine violating A



Absorbs heat q_1 and converts it completely into work w .

Carnot E. transforms $w \rightarrow q_1$

also transfers q_2 from cold to hot reservoir, violating

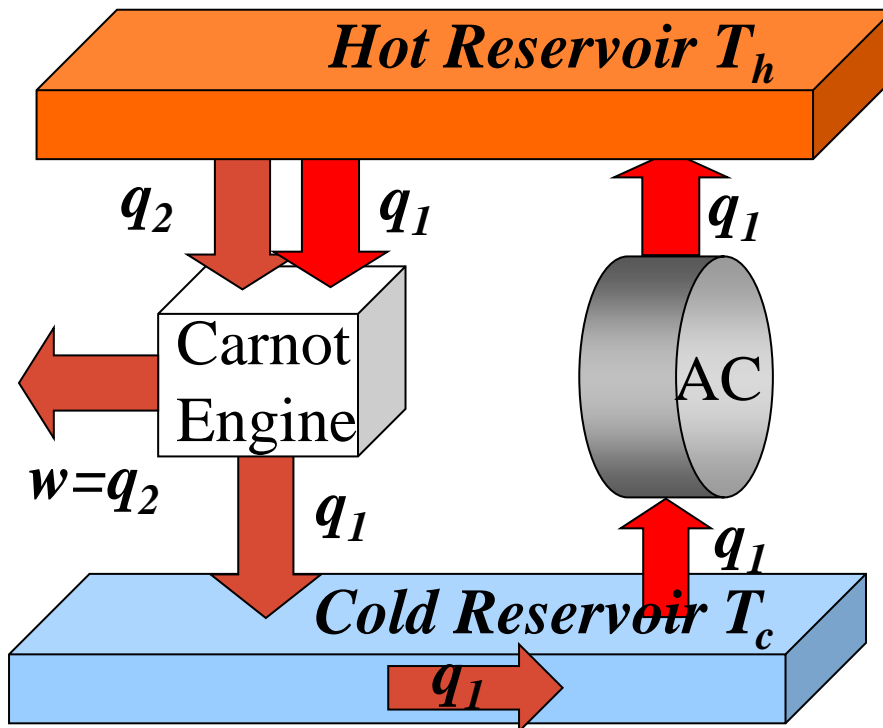
Clausius **B**.

$\neg A \quad \square \quad \neg B$

Clausius

B: No process is possible in which the sole result is the transfer of heat from a cooler to a hotter reservoir.

Construct an anti-Clausius engine violating **B**



Absorbs heat q_1 from colder and transfers it completely to warmer reservoir.

Carnot E. transforms $q_2 \rightarrow w$

Dumped q_1 is recycled to hot reservoir, violating Kelvin A.

$\neg B \quad ? \quad \neg A \quad ? \quad A \Leftrightarrow B$

The End

