

PHYS 10352

PART I: CLASSICAL THERMODYNAMICS

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WEEK 4: ENTROPY

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RECAP

- ▶ Heat engines produce work from heat using a cycle where $\Delta E = \oint dE = 0$.
- ▶ The efficiency of an engine is defined as $\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} < 1$.
- ▶ The “efficiency” of a refrigerator is $\eta = \frac{Q_C}{W}$.
- ▶ The second law of thermodynamics can be expressed in multiple ways:
- ▶ the Kelvin-Planck formulation of the 2nd law says that it’s impossible to convert heat to work perfectly;
- ▶ the Clausius formulation of the 2nd law says that it’s impossible to construct a process which transfers heat from a colder to a hotter body without doing any work.
- ▶ Carnot’s theorem: a reversible engine is the most efficient, and that all reversible engines operating between two heat baths have the same efficiency.
- ▶ The Carnot efficiency is given by:

$$\eta_C = 1 - \frac{T_C}{T_H}.$$

ENTROPY

CLAUSIUS' INEQUALITY

The **Clausius inequality** states that if a system is taken over a cycle then:

$$\oint \frac{\delta Q}{T} \leq 0$$

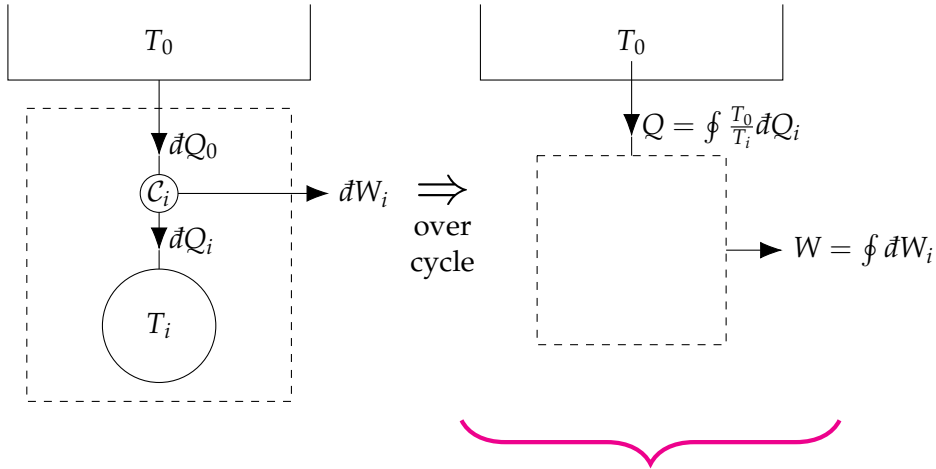
where the system has absorbed infinitesimal amounts of heat, δQ , from various reservoirs at varying temperatures, T , throughout the cycle.

Original German: https://archive.org/details/sim_annalen-der-physik_1865_125_7/mode/2up

Translation: <https://web.lemoyne.edu/~giunta/Clausius1865.pdf>

ENTROPY

CLAUSIUS' INEQUALITY



Appears to violate Kelvin-Planck statement...
unless:

$$\oint dW_i \leq 0 \text{ and } \therefore T_0 \oint \frac{dQ_i}{T_i} \leq 0$$

ENTROPY

CLAUSIUS' INEQUALITY

$$dS = \frac{\delta Q}{T}$$

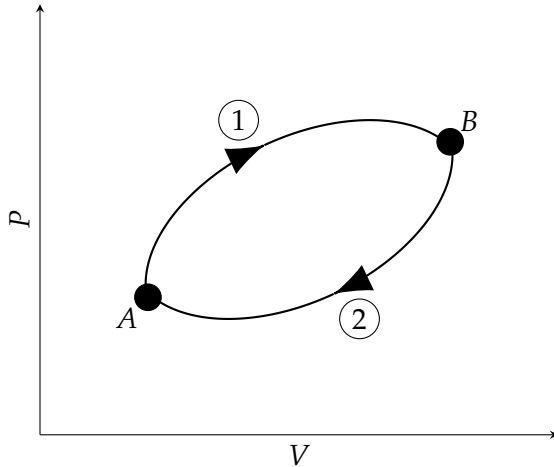
Clausius named the quantity, S , ἡ τροπή (entropy), or "transformation".

His 1865 paper had two conclusions:

1. The energy of the Universe is constant.
2. The entropy of the Universe strives towards a maximum.

ENTROPY

THE DEFINITION OF ENTROPY



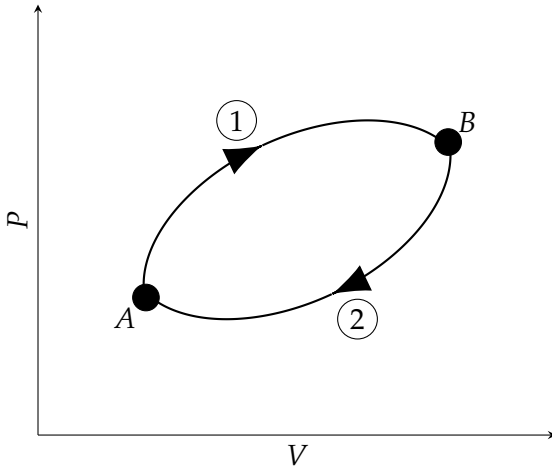
From the **Clausius inequality** we know that $\oint \frac{dQ}{T}$ over the full cycle will be zero:

$$\begin{aligned}\oint \frac{1}{T} dQ &= \underbrace{\int_A^B \frac{1}{T} dQ}_1 + \underbrace{\int_B^A \frac{1}{T} dQ}_2, \\ &= \underbrace{\int_A^B \frac{1}{T} dQ}_1 - \underbrace{\int_A^B \frac{1}{T} dQ}_2 = 0.\end{aligned}$$

$\Rightarrow dQ/T$ is *path independent*, i.e. it is a function of state.

ENTROPY

THE DEFINITION OF ENTROPY



From the **Clausius inequality** we know that $\oint \frac{dQ}{T}$ over the full cycle will be zero:

$$\begin{aligned}\int_A^B \frac{dQ}{T} &= \int_A^O \frac{dQ}{T} + \int_O^B \frac{dQ}{T}, \\ &= \int_O^B \frac{dQ}{T} - \int_O^A \frac{dQ}{T}, \\ &= S(B) - S(A).\end{aligned}$$

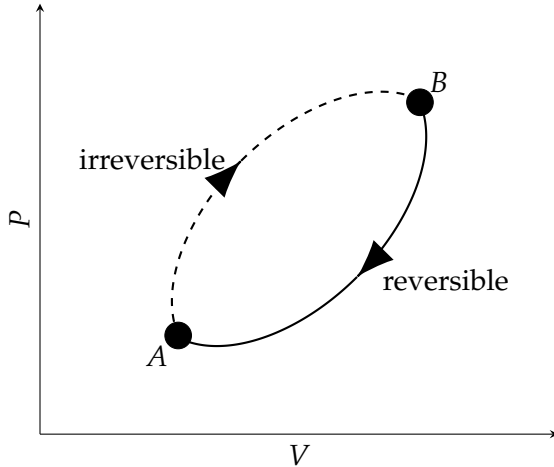
⇒ the entropy is a function of the equilibrium state, i.e.

$$S(A) = \int_O^A \frac{dQ_{\text{rev.}}}{T}.$$

note: the definition of entropy requires a **reversible process**

ENTROPY

THE DEFINITION OF ENTROPY



Applying the **Clausius inequality** we can write:

$$\int_A^B \frac{dQ_{\text{irrev.}}}{T} + \int_B^A \frac{dQ_{\text{rev.}}}{T} \leq 0.$$

which means:

$$\int_A^B \frac{dQ_{\text{rev.}}}{T} \geq \int_A^B \frac{dQ_{\text{irrev.}}}{T}$$

and therefore:

$$S(B) - S(A) \geq \underbrace{\int_A^B \frac{dQ_{\text{irrev.}}}{T}}$$

note: this is **not** entropy

REVERSIBLE VS. IRREVERSIBLE²

Consider a free expansion¹ vs. a reversible isothermal expansion with the same initial and final equilibrium states.

We can write:

$$dQ_{\text{irrev.}} + dW_{\text{irrev.}} = dQ_{\text{rev.}} + dW_{\text{rev.}}$$

In the free expansion the work done is zero, whilst it is negative in the isothermal expansion:

$$dW_{\text{irrev.}} > dW_{\text{rev.}}$$

There is no heat exchange in the free expansion, whilst heat is supplied from the reservoir in the isothermal expansion:

$$dQ_{\text{irrev.}} < dQ_{\text{rev.}}$$

This is consistent with the relation found on the previous slide.

¹ which is irreversible because it is not quasistatic

²Section 2.1.3 in the notes

ENTROPY

WORKED EXAMPLE - 2018/19 EXAM

1(b) An impermeable barrier confines n moles of an ideal gas to one third of the volume of an insulated container. The barrier is removed without doing any work. By considering a reversible process with the same initial and final states, calculate the change in entropy of the gas.

ENTROPY

WORKED EXAMPLE - 2018/19 EXAM

1(b) An impermeable barrier confines n moles of an ideal gas to one third of the volume of an insulated container. The barrier is removed without doing any work. By considering a reversible process with the same initial and final states, calculate the change in entropy of the gas.

This is a free expansion, which is an *irreversible* process.

Entropy changes are defined only for reversible processes. However, entropy is a function of state and therefore we can calculate the entropy change for an equivalent reversible process.

In this free expansion no work is done, i.e. $dW = 0$, and no heat is exchanged, i.e. $dQ = 0$ (we are told that the container is thermally insulated). Therefore:

$$dE = dQ + dW = 0 \Rightarrow dT = 0 \text{ because } E \equiv E(T)$$

So to reach the same final state, we can consider an equivalent reversible *isothermal* expansion. In this case:

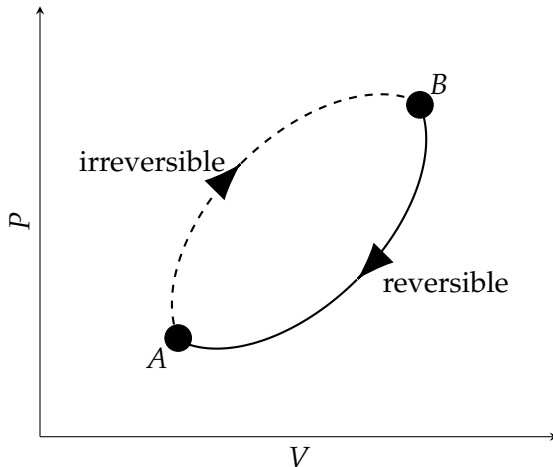
$$dE = dQ + dW = 0 \Rightarrow dQ = -dW = \frac{nRT}{V} dV$$

and therefore

$$dS = \frac{dQ}{T} \Rightarrow \Delta S = \int_{V_0}^{3V_0} \frac{nR}{V} dV = nR \ln 3$$

ENTROPY

ENTROPY & THE 2ND LAW



What happens if $A \rightarrow B$ is thermally isolated?

In that case, $dQ_{\text{irrev.}} = 0$ and:

$$S(B) - S(A) \geq \int_A^B \frac{dQ_{\text{irrev.}}}{T} \geq 0$$

The entropy of an isolated system can only (i) increase or (ii) stay the same.

- (i) if an isolated system is not at equilibrium, its entropy must increase further;
- (ii) at equilibrium functions of state do not change, i.e. $dS = 0$, \therefore equilibrium = maximum entropy.

An isolated system at equilibrium must be in the state of maximum entropy.

ENTROPY

WORKED EXAMPLE - 2018/19 EXAM

2(d) The second law of thermodynamics can be stated in the form: *The entropy of a thermally isolated system cannot decrease.* Use the second law to show that the efficiency of an engine that operates between temperatures T_H and T_C must be less than or equal to the Carnot efficiency:

$$\eta_C = 1 - \frac{T_C}{T_H}.$$

ENTROPY

WORKED EXAMPLE - 2018/19 EXAM

2(d) The second law of thermodynamics can be stated in the form: *The entropy of a thermally isolated system cannot decrease.* Use the second law to show that the efficiency of an engine that operates between temperatures T_H and T_C must be less than or equal to the Carnot efficiency:

$$\eta_C = 1 - \frac{T_C}{T_H}.$$

For an engine operating between two temperatures, the entropy of the heat baths defining those temperatures must change over the course of the cycle. The entropy of the hot bath decreases and the entropy of the cold bath increases: $Q_H = T_H \Delta S_H$ and $Q_C = T_C \Delta S_C$.

The efficiency of the engine is defined as:

$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C \Delta S_C}{T_H \Delta S_H}$$

The second law of thermodynamics requires $\Delta S_{\text{tot}} \geq 0$ then $\Delta S_C \geq \Delta S_H$ and consequently:

$$\eta \leq 1 - \frac{T_C}{T_H}.$$

ENTROPY

ENTROPY AND HEAT CAPACITY

For an infinitesimal change, we have

$$dS = \frac{dQ_{\text{rev.}}}{T}.$$

If this change is at constant X (e.g. $X = P$ or V)

$$dQ_{\text{rev.}} = C_X dT \Rightarrow C_X dT = T dS.$$

Therefore,

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

ENTROPY

WORKED EXAMPLE - 2021/22 EXAM

3(e) A rigid vessel contains 5 moles of ideal diatomic gas at a temperature of 270 K. The vessel is placed in thermal contact with a large heat bath at 330 K and is left to reach equilibrium. By how much does the entropy of the Universe change in this process?

ENTROPY

WORKED EXAMPLE - 2021/22 EXAM

3(e) A rigid vessel contains 5 moles of ideal diatomic gas at a temperature of 270 K. The vessel is placed in thermal contact with a large heat bath at 330 K and is left to reach equilibrium. By how much does the entropy of the Universe change in this process?

The change in entropy of the Universe is given by:

$$\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{bath}}$$

Gas:

$$\Delta S_{\text{gas}} = C_V \int_{T_i}^{T_f} \frac{dT}{T} = \frac{5}{2}nR \cdot \ln\left(\frac{T_f}{T_i}\right)$$

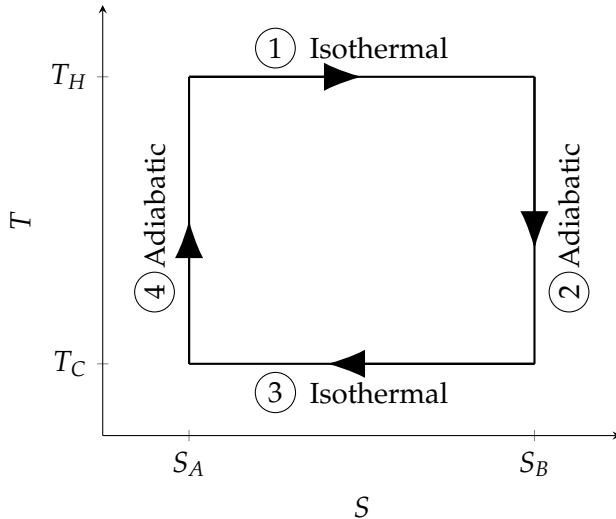
Heat bath:

$$Q = T_f \Delta S_{\text{bath}} = -C_V \Delta T = -C_V(T_f - T_i)$$
$$\therefore \Delta S_{\text{bath}} = -C_V \frac{(T_f - T_i)}{T_f} = -\frac{5}{2}nR \frac{(T_f - T_i)}{T_f}$$

$$\Rightarrow \Delta S_{\text{universe}} = \frac{5}{2}nR \left[\ln\left(\frac{T_f}{T_i}\right) - \frac{(T_f - T_i)}{T_f} \right] = 1.96 \text{ J/K} > 0$$

ENTROPY

THE CARNOT CYCLE REVISITED



Adiabatic changes have $dQ = 0$.

Since

$$dS = \frac{dQ}{T}$$

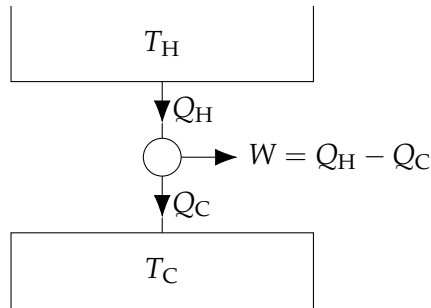
then adiabatic changes are also *isentropic*, i.e. $dS = 0$.

Therefore the only entropy changes are in the isothermal steps.

Challenge: starting from the ideal gas law, can you demonstrate that adiabatic changes are isentropic? Hint: embrace the natural logarithm!

ENTROPY

THE CARNOT CYCLE REVISITED



For a Carnot cycle operating between a heat source with constant temperature T_H and a heat sink with constant temperature T_C , we know that the efficiency will be

$$\eta_C = 1 - \frac{T_C}{T_H}.$$

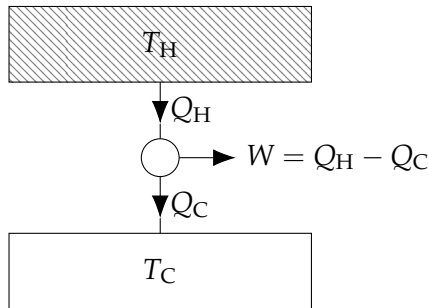
So, for example, if we have a Carnot cycle operating between two infinite temperature reservoirs with $T_H = 100^\circ\text{C}$ and $T_C = 10^\circ\text{C}$, then the efficiency will be

$$\eta_C = 1 - \frac{283}{373} = 0.24,$$

i.e. for every 1 J of heat, Q_H , that is input from the heat source, 0.24 J of work will be produced.

ENTROPY

THE CARNOT CYCLE REVISITED



What happens in the case where one of the temperature reservoirs is *finite*?

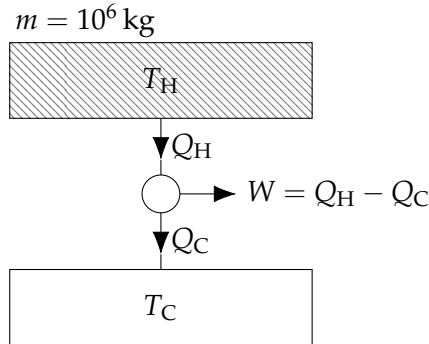
For example, a Carnot cycle where the heat source is a finite volume of water at an initial temperature of 100°C , and the heat sink is a lake with constant temperature of 10°C .

In this case the temperature of the hot reservoir will gradually *decrease* until it reaches a final temperature of $T_f = T_C$.

What is the maximum amount of work that can be extracted from such a cycle?

ENTROPY

THE CARNOT CYCLE REVISITED



The maximum work that can be extracted is

$$W = Q_H - Q_C$$

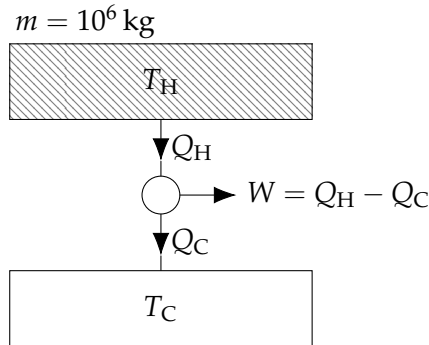
and we know that enough heat is extracted from the hot reservoir to cause a change in temperature of $\Delta T = 373 - 283 = 90 \text{ K}$

$$\therefore Q_H = m \cdot c \cdot \Delta T = 37.8 \times 10^{10} \text{ J.}$$

But what is Q_C ? The heat capacity of a fixed temperature reservoir is $\infty \dots$

ENTROPY

THE CARNOT CYCLE REVISITED



To find Q_C , we use the 2nd law of thermodynamics:

$$\Delta S = \Delta S_H + \Delta S_C \geq 0.$$

Since T_C is constant, $\Delta S_C = Q_C/T_C$, and

$$\Delta S_H = \int \frac{dQ}{T} = \int_{T_H}^{T_f} \frac{m \cdot c \cdot dT}{T} = m \cdot c \cdot \ln \left(\frac{T_f}{T_H} \right)$$

Taking the limiting case where $\Delta S = 0$, and replacing $T_f = T_C$, we find

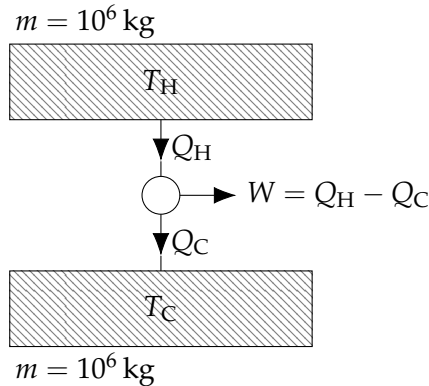
$$Q_C = m \cdot c \cdot T_C \ln \left(\frac{T_C}{T_H} \right) = -32.8 \times 10^{10} \text{ J}$$

Therefore, the maximum work extracted is

$$W = Q_H - Q_C = (37.8 - 32.8) \times 10^{10} = 5 \times 10^{10} \text{ J}$$

ENTROPY

THE CARNOT CYCLE REVISITED



What happens in the case where both of the temperature reservoirs are *finite*?

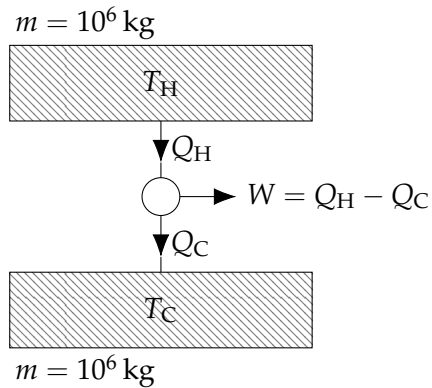
For example, a Carnot cycle where the heat source is a **finite** volume of water at an initial temperature of 100°C , and the heat sink is a **finite** volume of water at an initial temperature of 10°C .

In this case the temperature of the hot reservoir will gradually *decrease* and the temperature of the cold reservoir will *increase* until they reach some intermediate final temperature, T_f .

What is the maximum amount of work that can be extracted from such a cycle?

ENTROPY

THE CARNOT CYCLE REVISITED



Just as in the previous case, the maximum work that can be extracted is

$$W = Q_H - Q_C$$

and here we can write

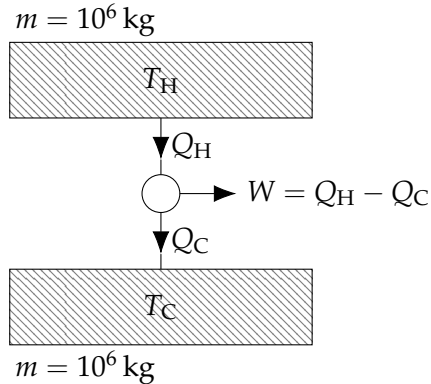
$$Q_H = m \cdot c \cdot (T_H - T_f)$$

$$Q_C = m \cdot c \cdot (T_f - T_C)$$

So the question becomes: What is T_f ?

ENTROPY

THE CARNOT CYCLE REVISITED



Using the 2nd law of thermodynamics:

$$\Delta S = \Delta S_H + \Delta S_C \geq 0$$

In this case,

$$\begin{aligned} \Delta S &= \int_H \frac{dQ}{T} + \int_C \frac{dQ}{T} \\ &= m \cdot c \cdot \ln\left(\frac{T_f}{T_H}\right) + m \cdot c \cdot \ln\left(\frac{T_f}{T_C}\right) \end{aligned}$$

Taking the limiting case where $\Delta S = 0$, we find that

$$T_f = \sqrt{T_C T_H} = 325 \text{ K}$$

and consequently

$$W = Q_H - Q_C = 2.5 \times 10^{10} \text{ J}$$

ENTROPY

ENTROPY AND THE ARROW OF TIME (NON-EXAMINABLE)

The entropy of an isolated system can only increase or stay the same.

"Let us draw an arrow arbitrarily. If as we follow the arrow we find more and more of the random element in the state of the world, then the arrow is pointing towards the future; if the random element decreases the arrow points towards the past. That is the only distinction known to physics.

*This follows at once if our fundamental contention is admitted that the introduction of randomness is the only thing which cannot be undone. I shall use the phrase **time's arrow** to express this one-way property of time which has no analogue in space".*

- Arthur Eddington, 1928

<https://calteches.library.caltech.edu/4326/1/Time.pdf>

<https://academic.oup.com/astrogeo/article/46/1/1.26/253257>

THE FUNDAMENTAL THERMODYNAMIC RELATION

From the 1st law:

$$dE = \delta Q_{\text{rev.}} + \delta W_{\text{rev.}},$$

$$dE = T dS + \delta W_{\text{rev}}$$

the fundamental thermodynamic relation

For a fluid, we can update this to:

$$dE = TdS - PdV$$

Therefore, we can think of $E \equiv E(S, V)$ and write

$$dE = \left(\frac{\partial E}{\partial S} \right)_V dS + \left(\frac{\partial E}{\partial V} \right)_S dV$$

$$\text{where : } T = \left(\frac{\partial E}{\partial S} \right)_V \quad \text{and} \quad P = - \left(\frac{\partial E}{\partial V} \right)_S$$

THE FUNDAMENTAL THERMODYNAMIC RELATION

WORKED EXAMPLE - ENTROPY CHANGE

Starting from the fundamental thermodynamic relation, show that a general expression for the entropy change of one mole of an ideal gas can be written as

$$\Delta S = C_V \left[\ln \left(\frac{T_f}{T_i} \right) + (\gamma - 1) \ln \left(\frac{V_f}{V_i} \right) \right]$$

THE FUNDAMENTAL THERMODYNAMIC RELATION

WORKED EXAMPLE - ENTROPY CHANGE

Starting from the fundamental thermodynamic relation, show that a general expression for the entropy change of one mole of an ideal gas can be written as

$$\Delta S = C_V \left[\ln \left(\frac{T_f}{T_i} \right) + (\gamma - 1) \ln \left(\frac{V_f}{V_i} \right) \right]$$

$dE = TdS - PdV \Rightarrow TdS = C_V dT + PdV$ where $dE = C_V dT$ for an ideal gas

$$\therefore dS = \frac{C_V}{T} dT + \frac{P}{T} dV = \frac{C_V}{T} dT + \frac{R}{V} dV \quad \text{using the ideal gas law}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{R}{V} dV = C_V \ln \left(\frac{T_f}{T_i} \right) + R \ln \left(\frac{V_f}{V_i} \right)$$

Using $C_P = C_V + nR$ and $C_P/C_V = \gamma$ to find $nR = C_V(\gamma - 1)$:

$$\Delta S = C_V \left[\ln \left(\frac{T_f}{T_i} \right) + (\gamma - 1) \ln \left(\frac{V_f}{V_i} \right) \right]$$

as required.

SUMMARY

- ▶ The Clausius inequality states that **over a cycle**: $\oint \frac{dQ}{T} \leq 0$
- ▶ The quantity $\frac{dQ}{T}$ is path independent, i.e. it is a **function of state**.
- ▶ We define this function of state as the *entropy*, S , where

$$\Delta S = S(B) - S(A) = \int_A^B \frac{dQ_{rev}}{T} \geq 0$$

- ▶ Entropy is defined in terms of **reversible processes**.
- ▶ The entropy of an isolated system can only increase or stay the same.
- ▶ An isolated system at equilibrium must be in a state of maximum entropy.
- ▶ We can define heat capacity in terms of entropy.
- ▶ From the first law, we can use entropy to define **the fundamental thermodynamic relation**:

$$dE = T dS + dW_{rev}$$