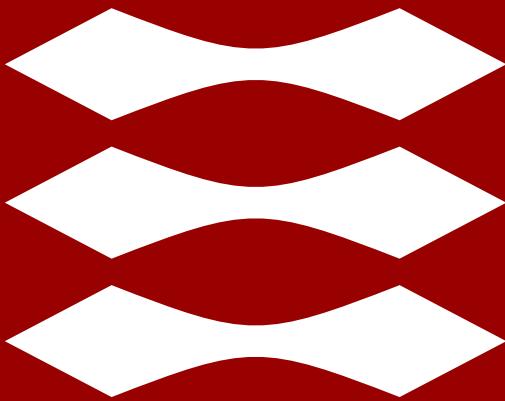


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# DTU



47201 Engineering thermodynamics

# Module 1a

# Teachers and Teaching Assistants



Andrea  
Teacher



Apurv  
Teacher



Cenk  
Teaching  
Assistant



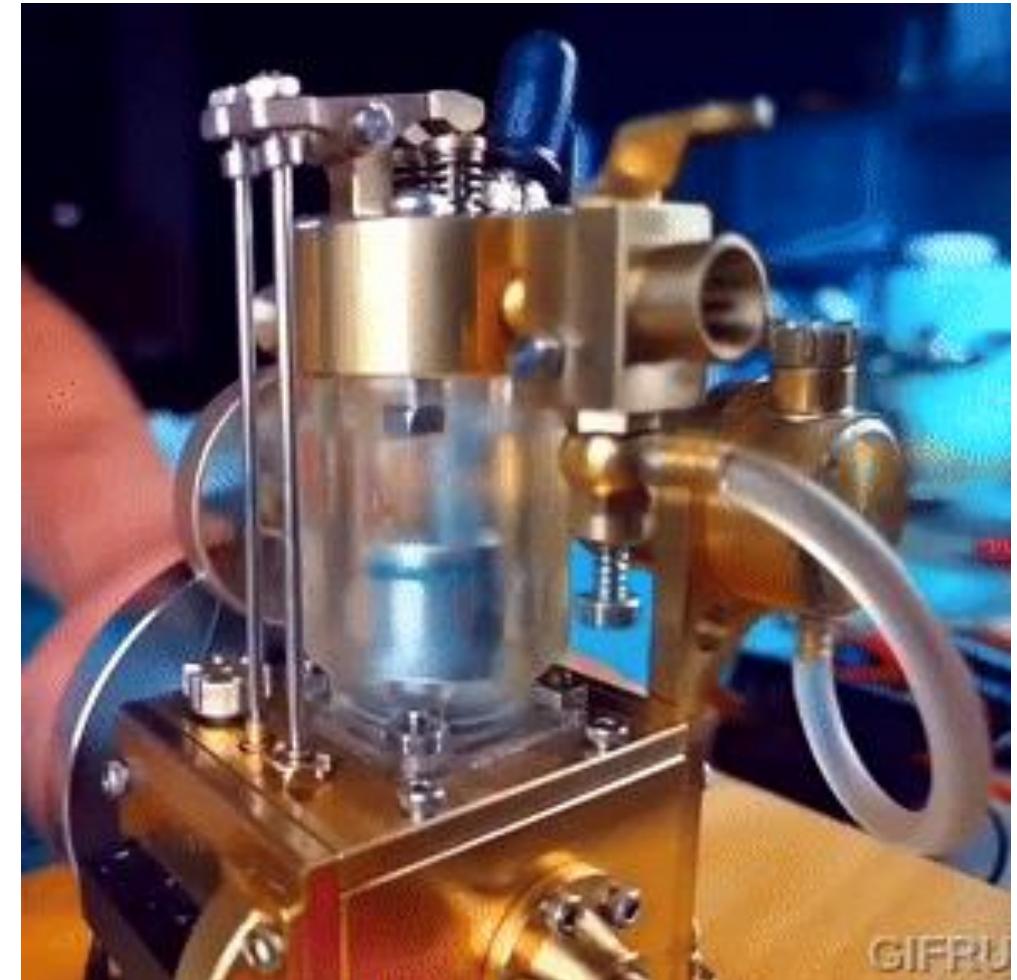
Hendrik  
Teaching  
Assistant



Javid  
Teaching  
Assistant

# What is thermodynamics?

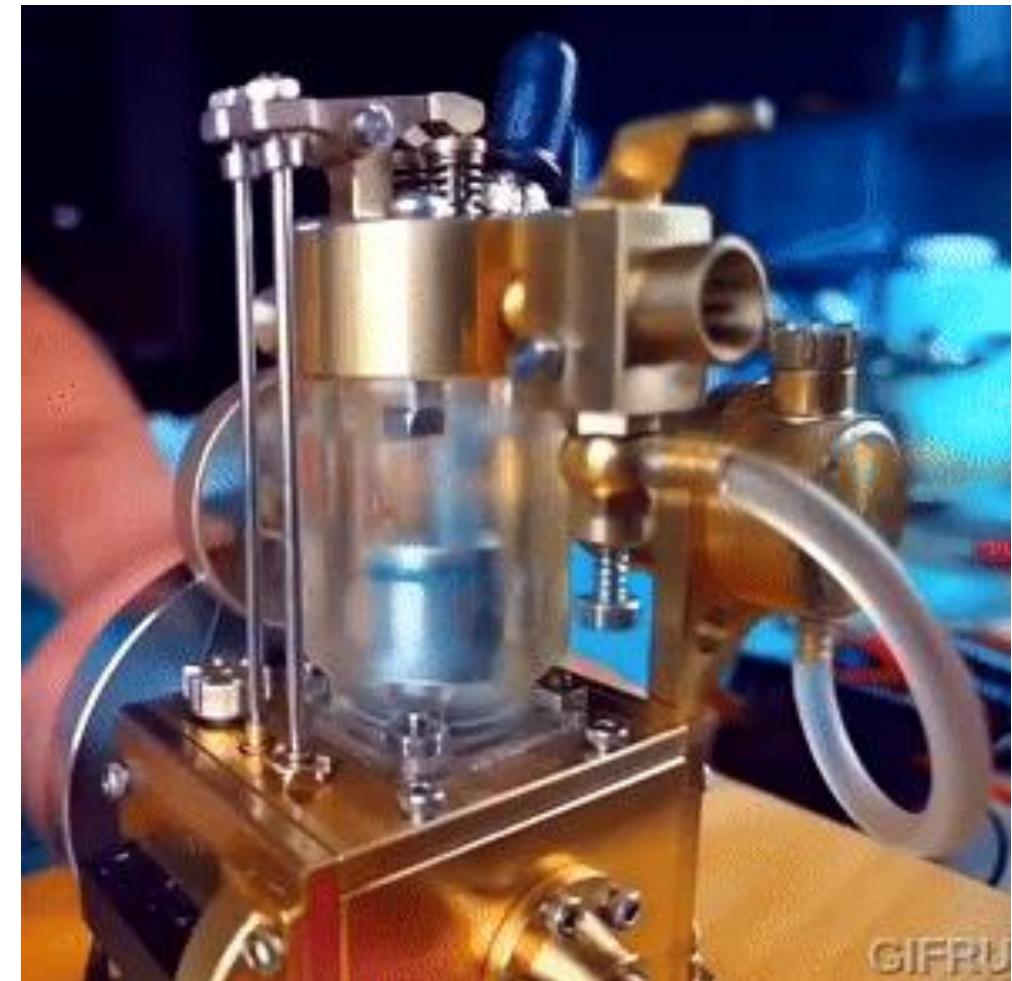
- Thermodynamics studies the conversion between heat and work - and the relation of these concepts with energy, temperature and entropy. [The usual definition]



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# What is thermodynamics?

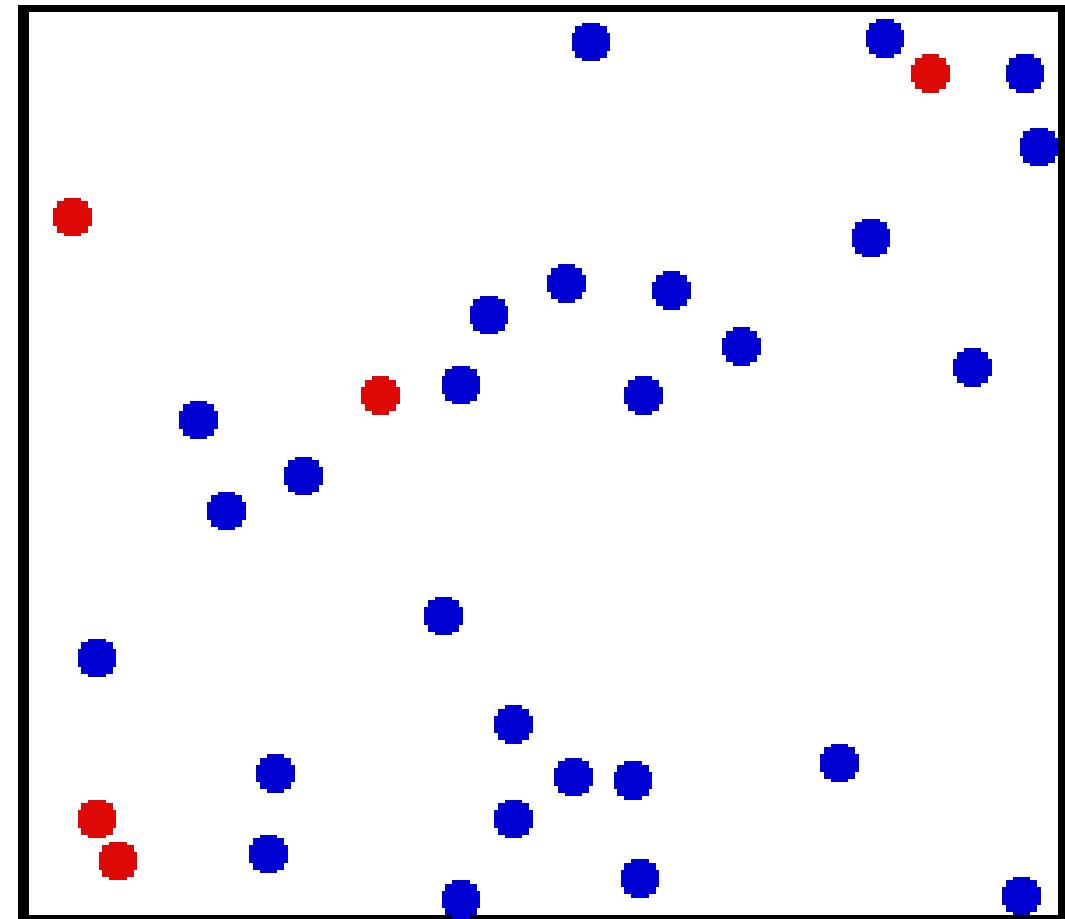
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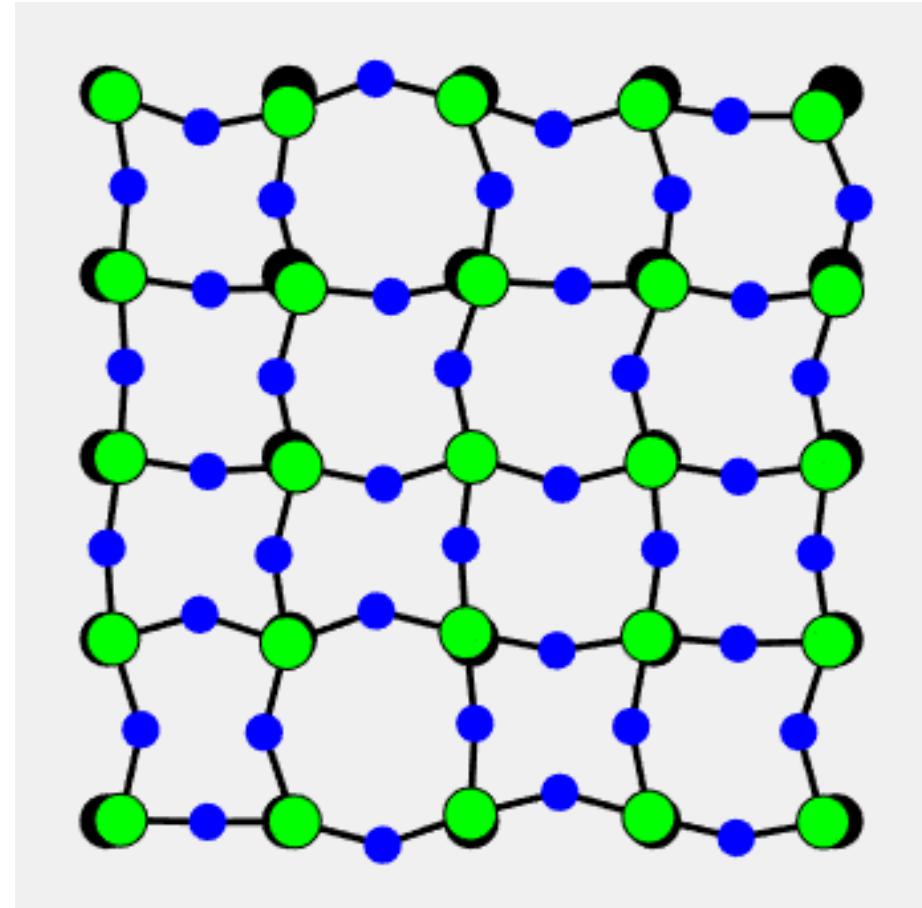
# Molecules in a gas

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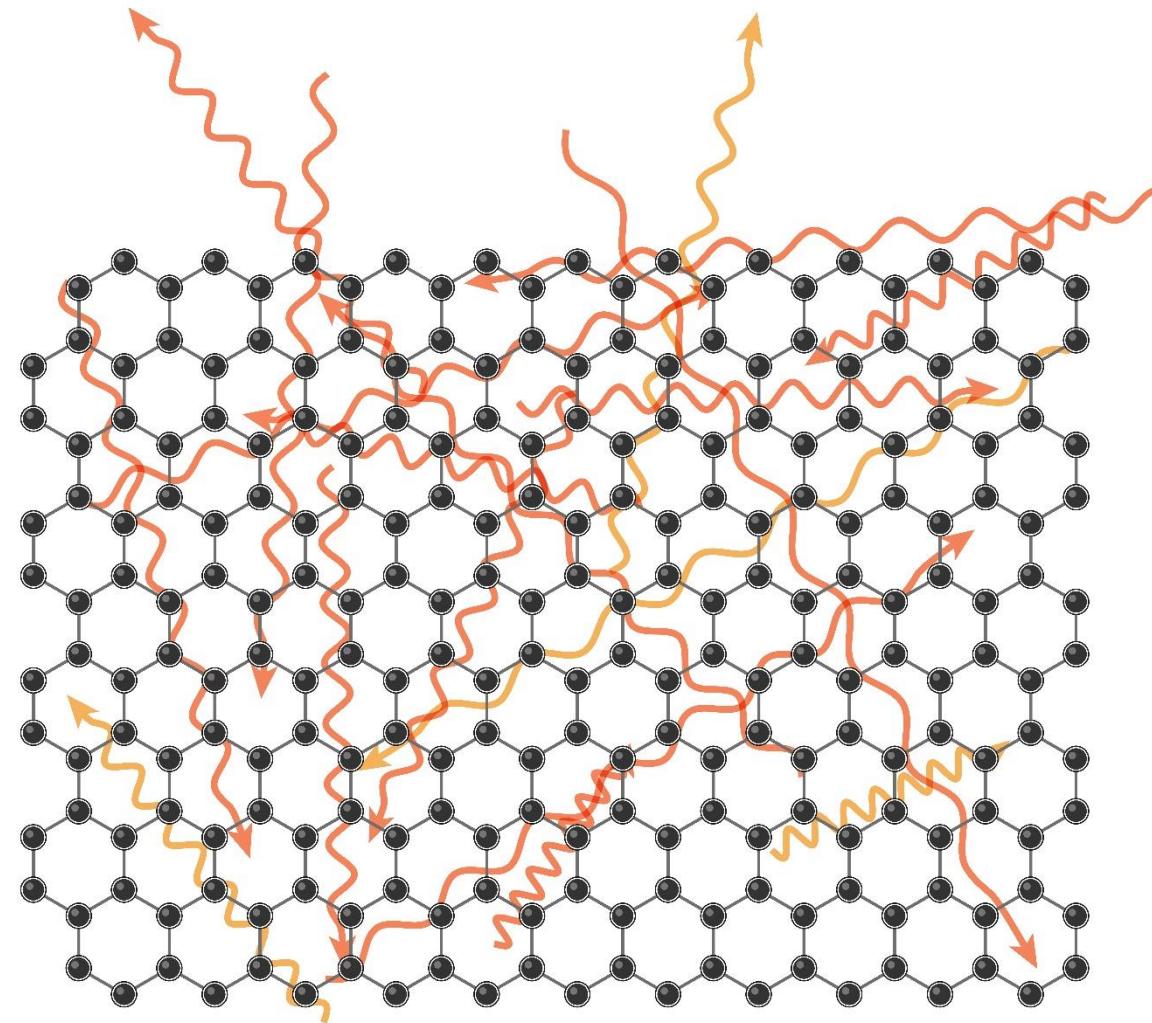
# Atoms in a solid

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# Thermal photons

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Other examples:

- conduction electrons in a metal
- molecules undergoing a chemical reaction in a solution
- spins in a magnetic material
- ...

# What is thermodynamics?

- Thermodynamics studies the conversion between heat and work - and the relation of these concepts with energy, temperature and entropy.
- Thermodynamics is the study of large systems where, due to the large number of identical composing sub-systems, statistical methods and probability theory can be applied to reliably predict some macroscopic properties of the whole system.

Thermodynamics doesn't describe any specific kind of interaction, fundamental force, or physical phenomenon.

It is transversal: it's relevant and linked to many areas of physics. Probably all?

It describes the consequences of the fundamental *randomness* that is intrinsic in many situations.

# What is thermodynamics?

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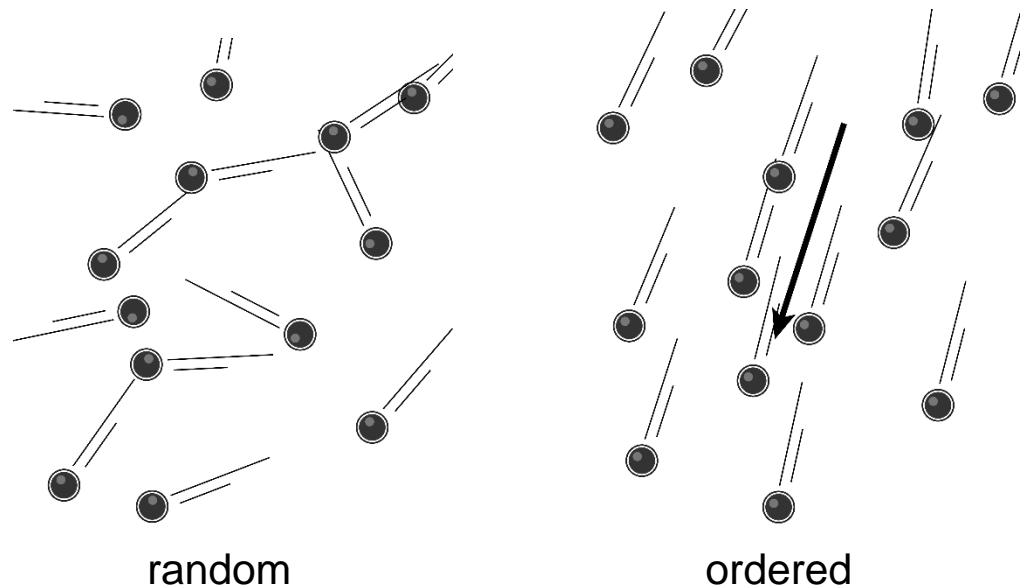
In all the examples we have seen:

- The specifics of the interaction between subsystems are not the main interest.  
E.g.: in a gas, it's enough to say that molecules bounce on each other.
- The whole system has some energy, but its randomly subdivided into the energy of the composing subsystems.

It describes the consequences of the fundamental *randomness* that is intrinsic in many situations.

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- The whole system has some energy, but its randomly subdivided into the energy of the composing subsystems.

$$K = \sum_i m_i v_i^2$$

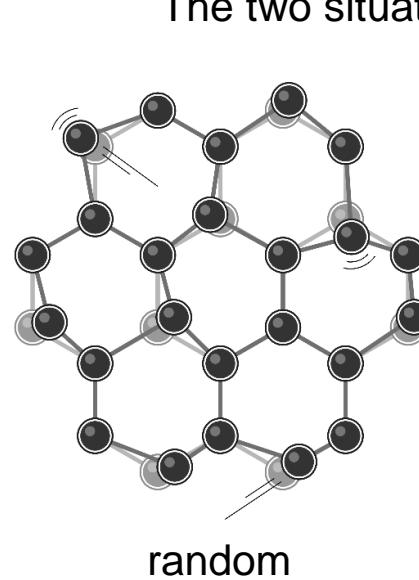
Total kinetic energy

# What is thermodynamics?

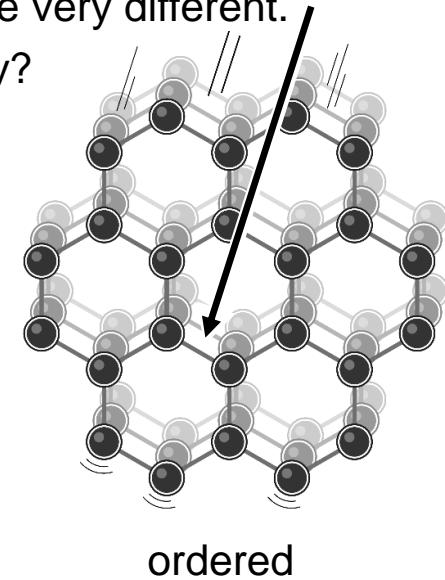
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The two situations are very different.

But why?



random



ordered

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$$K = \sum_i m_i v_i^2$$

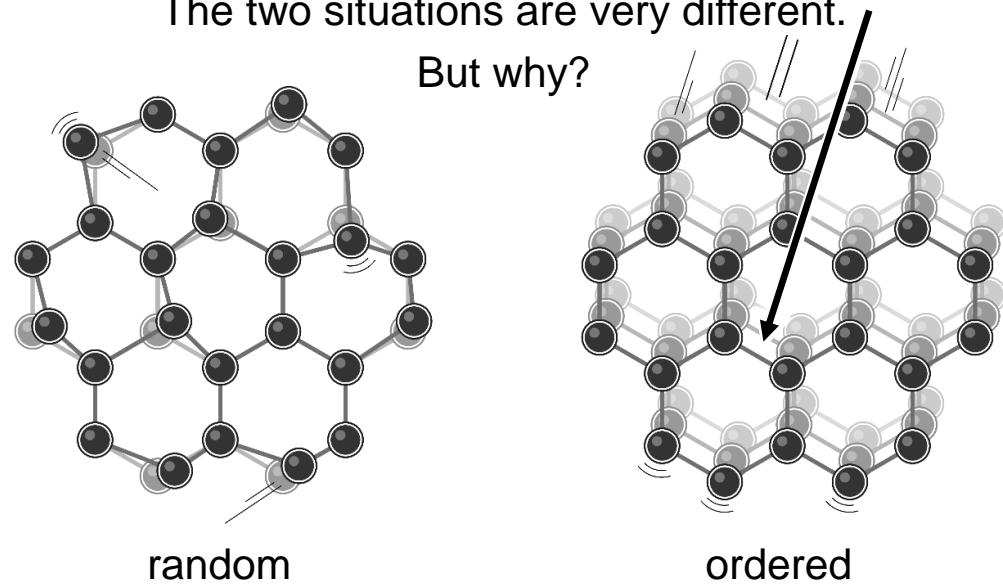
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In the random case, it is more difficult to harvest and utilize the energy.

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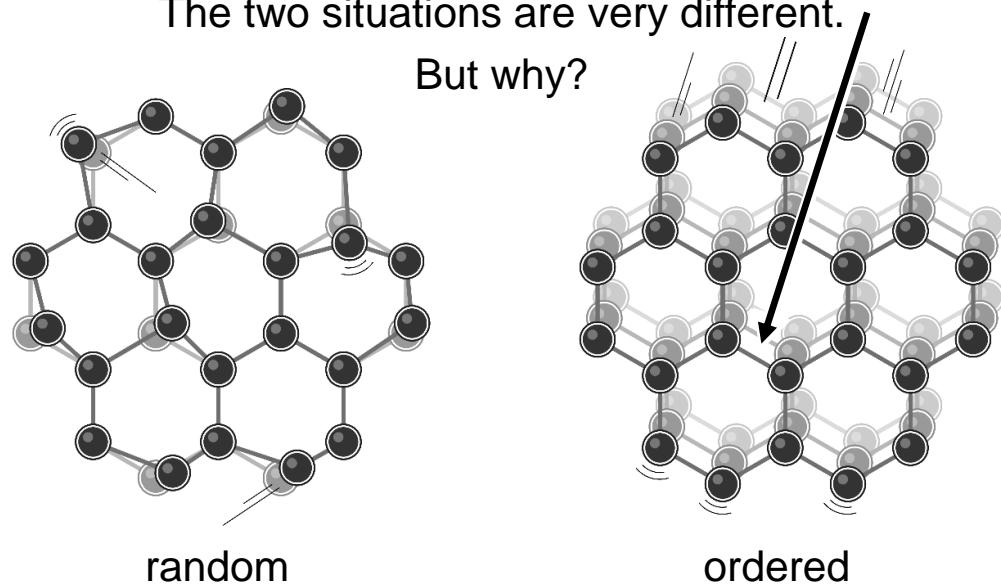
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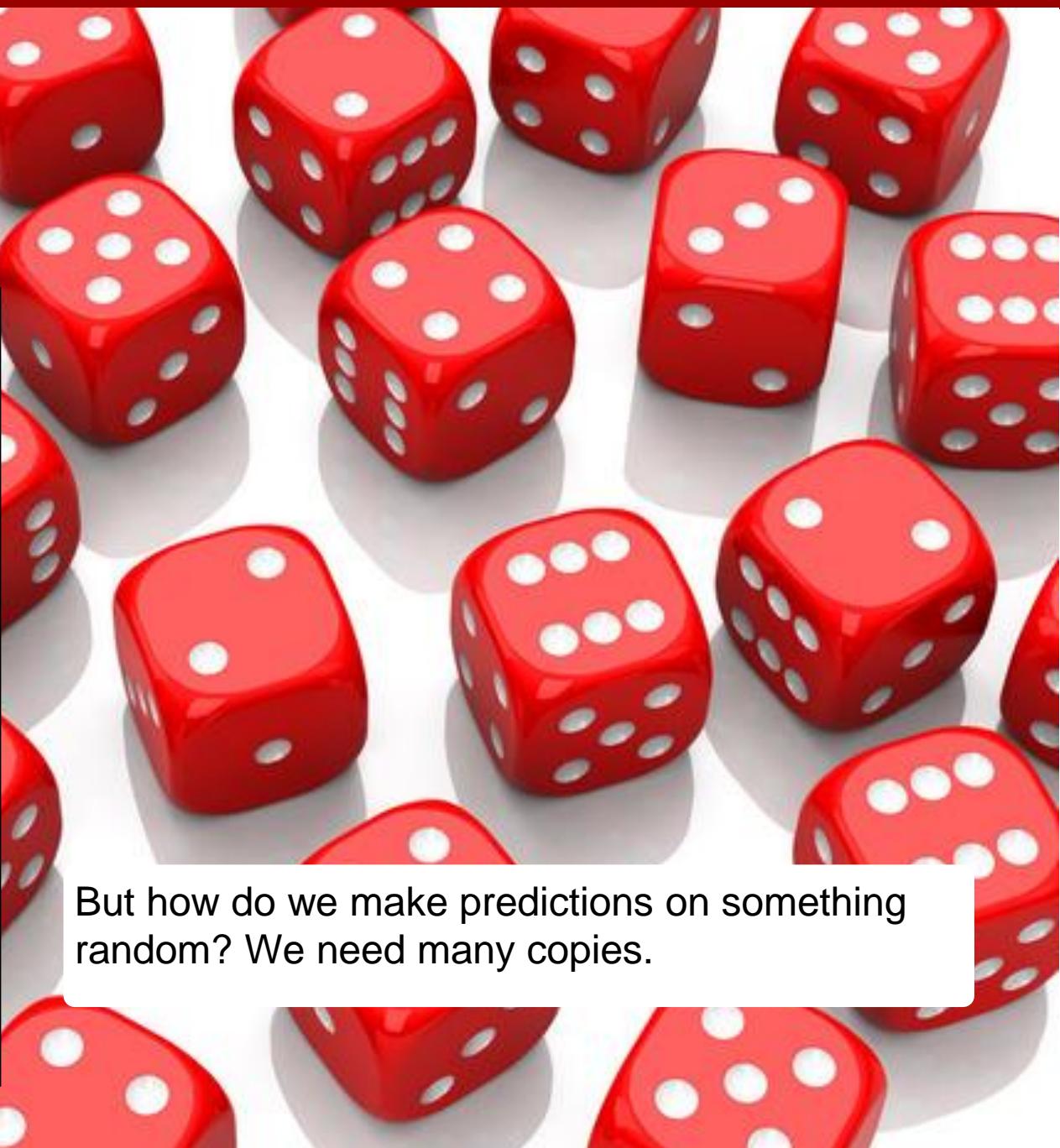
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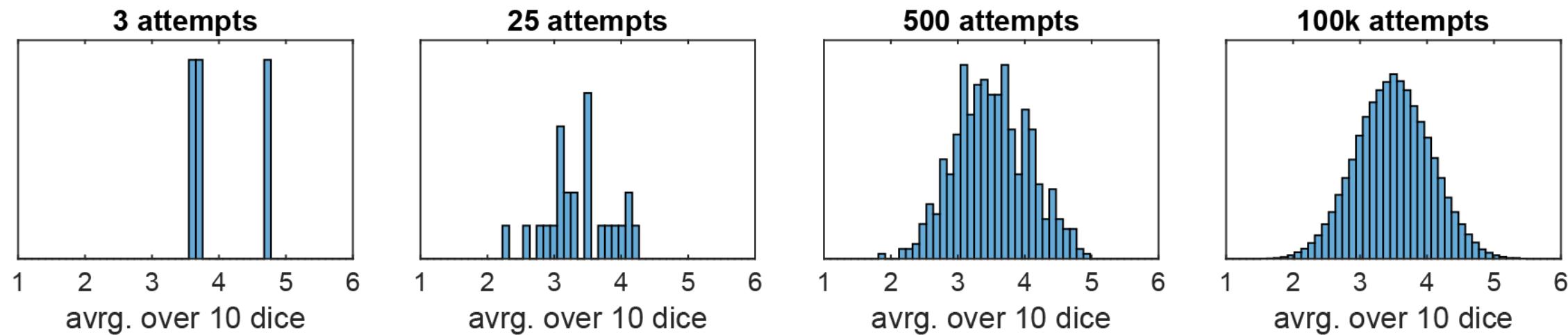
This is the main subject of thermodynamics.

*But how do we make predictions on something random?*

# Large numbers

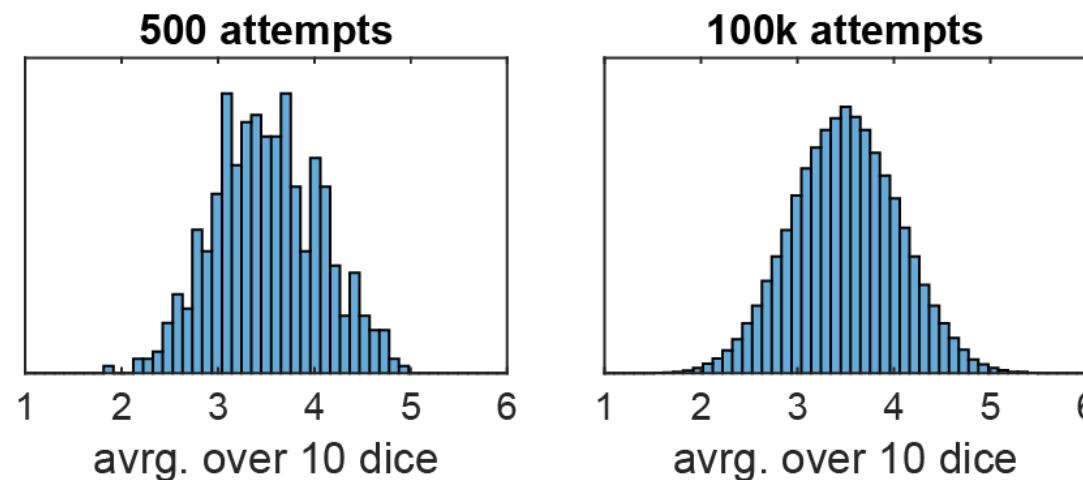
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This is why the second law of thermodynamics seems to be so hostile from our perspective.

It expresses the ungenerous laws of randomness and probability: things are very likely to go in the most likely way

This limits the efficiency of our attempts of converting energy from one form to another.

# Engineering applications of thermodynamics



Engines



Refrigeration



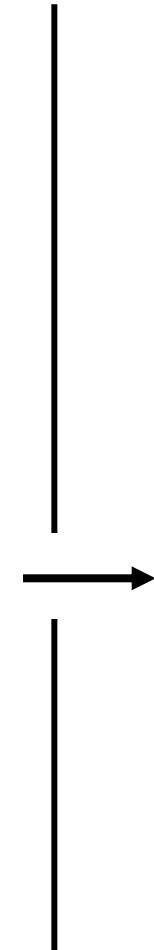
Chemical reactions



Power plants

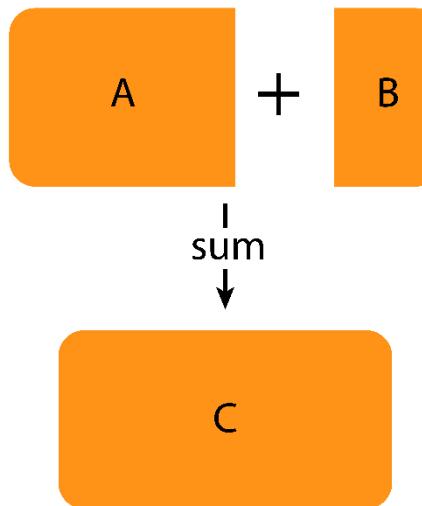
# Which properties are we interested about?

- Thermodynamics is the study of large systems where, due to the large number of identical composing sub-systems, statistical methods and probability theory can be applied to reliably predict some *macroscopic properties* of the whole system.

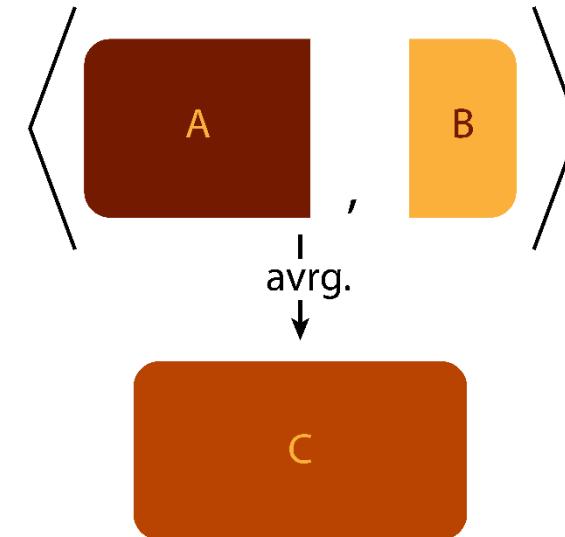


- Microscopic properties (not known):  
Examples:
  - velocity of each particle in a gas
  - frequency of each photon emitted by a body
- Macroscopic properties (predictable):  
Examples:
  - Total energy
  - Average temperature
  - Total amount of substance
  - ...

# Systems and properties: extensive and intensive

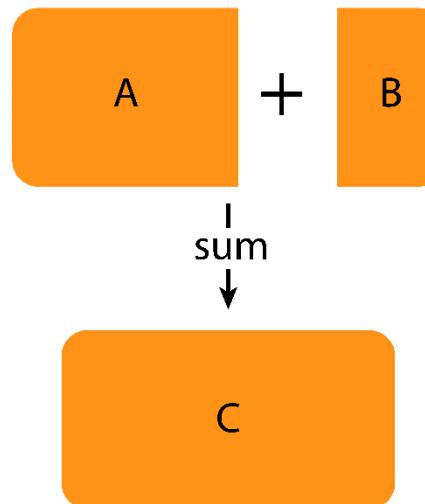


When I compose two systems A and B  
The *extensive* properties are *summed*



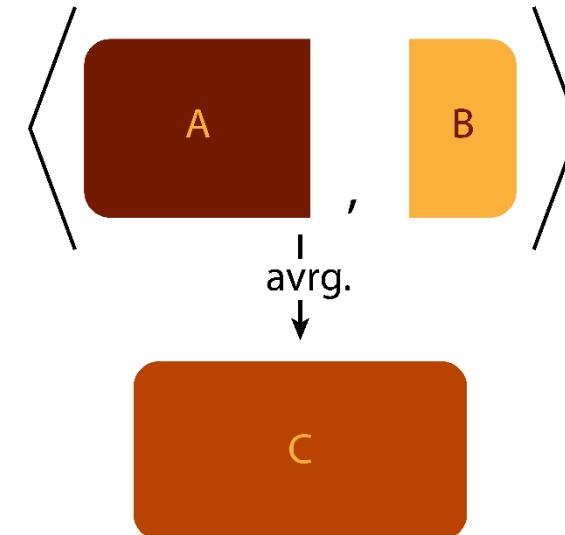
When I compose two systems A and B  
The *intensive* properties are *averaged*

# Systems and properties: extensive and intensive



When I compose two systems A and B  
The *extensive* properties are *summed*

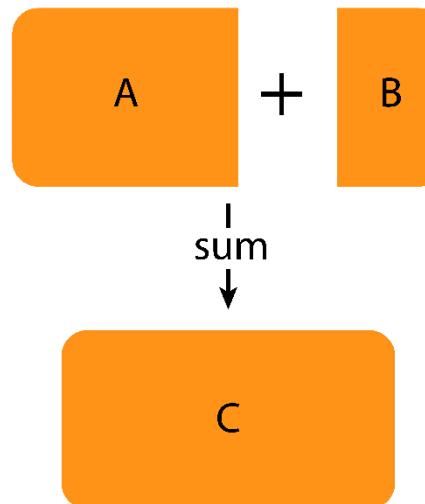
Example: (total) mass



When I compose two systems A and B  
The *intensive* properties are *averaged*

Example: (average) mass density

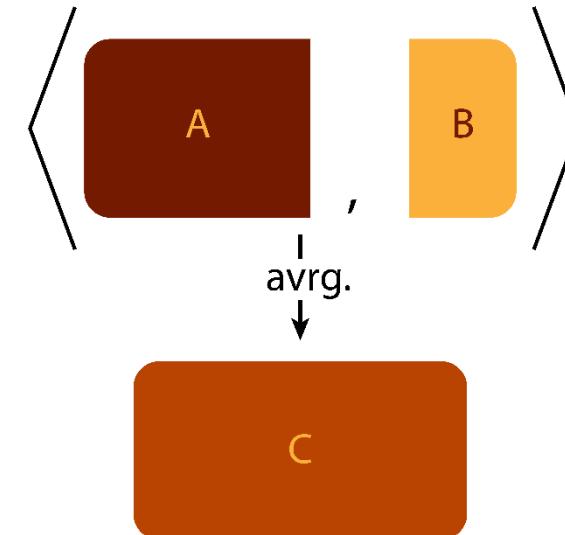
# Systems and properties: extensive and intensive



When I compose two systems A and B  
The *extensive* properties are *summed*

Example: (total) mass

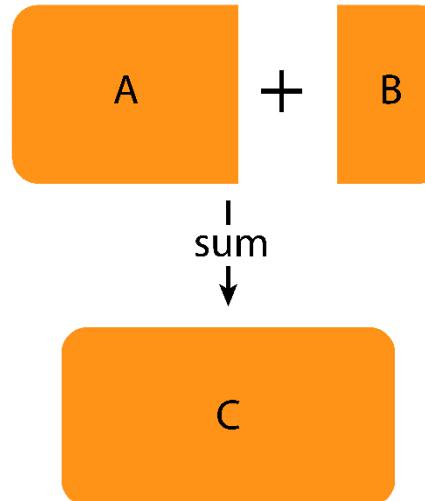
density →



When I compose two systems A and B  
The *intensive* properties are *averaged*

Example: (average) mass *density*

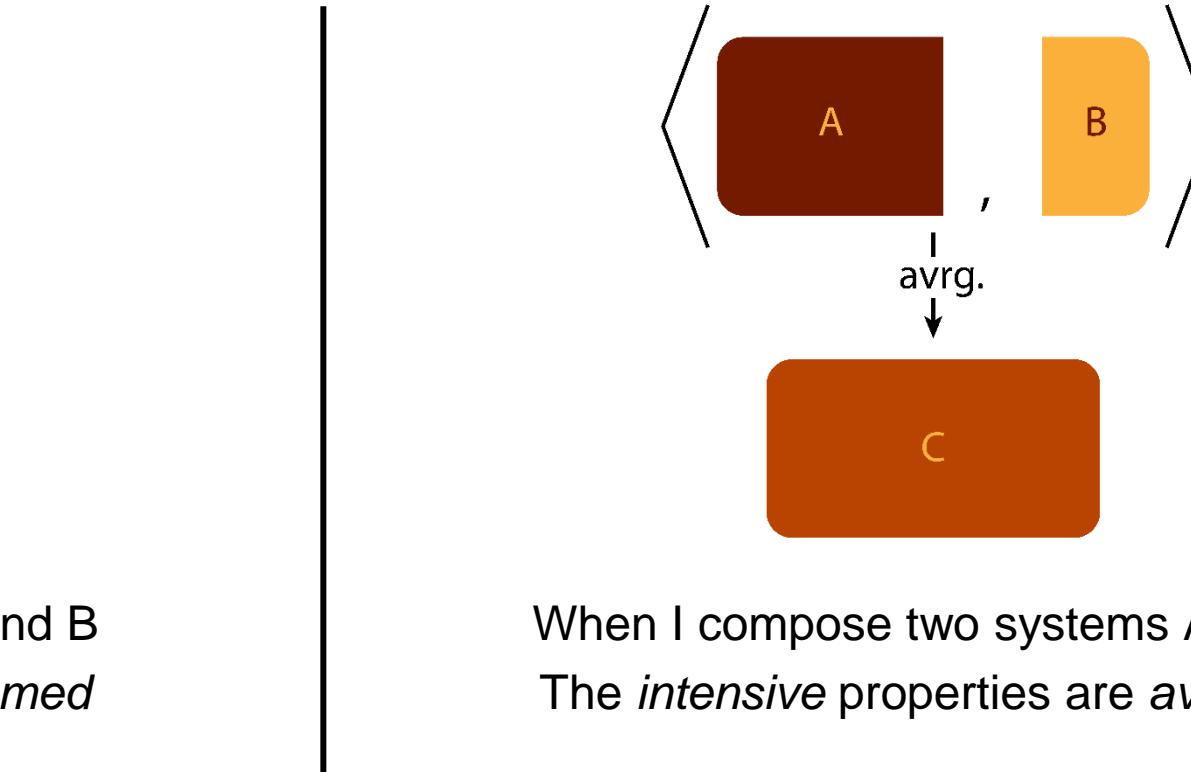
# Systems and properties: extensive and intensive



When I compose two systems A and B  
The *extensive* properties are *summed*

Example: (total) mass

Example: (total) charge



When I compose two systems A and B  
The *intensive* properties are *averaged*

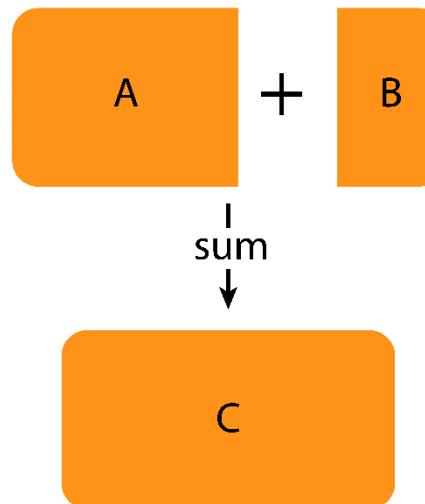
density →

density →

Example: (average) mass *density*

Example: (average) charge *density*

# Systems and properties: extensive and intensive

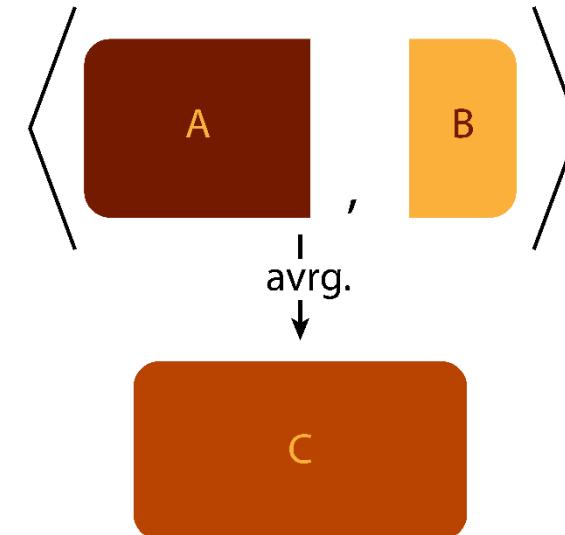


When I compose two systems A and B  
The *extensive* properties are *summed*

Example: (total) charge

— density —→

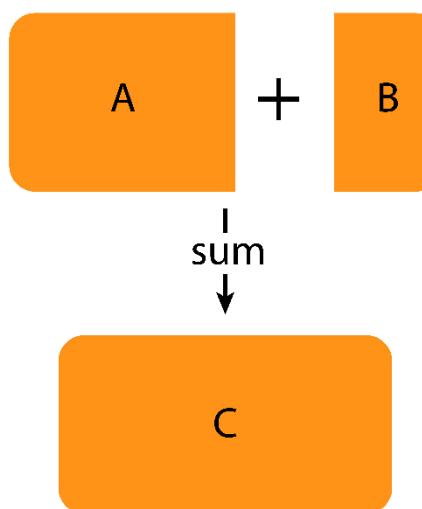
Example: charge density *at point x*



When I compose two systems A and B  
The *intensive* properties are *averaged*

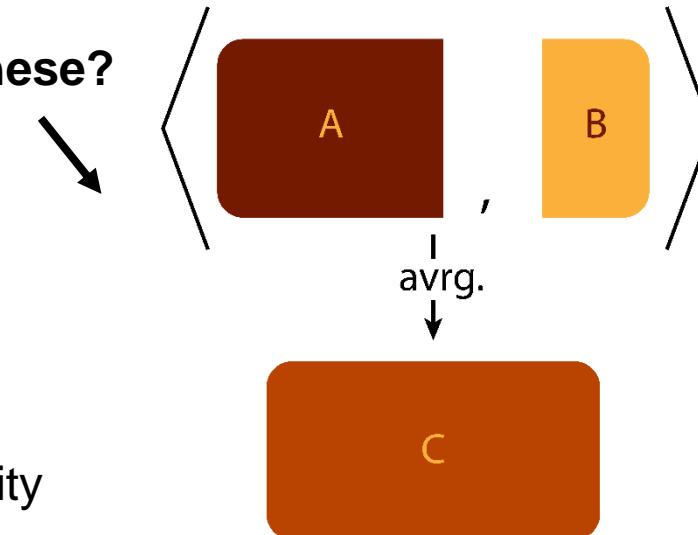
For intensive properties, it is also relevant to  
consider the value in each point.

# Systems and properties: extensive and intensive



How do we classify these?

- Energy
- Temperature
- Volume
- Pressure
- Entropy
- Heat capacity
- Specific heat capacity
- Energy density



When I compose two systems A and B  
The *extensive* properties are *summed*

When I compose two systems A and B  
The *intensive* properties are *averaged*

Example: (total) charge

— density —

Example: (average) charge *density*

# What is thermodynamics?

- Thermodynamics studies the conversion between *heat* and *work* - and the relation of these concepts with energy, temperature and entropy



<https://youtu.be/cBRo1uH5H6Y?feature=shared>

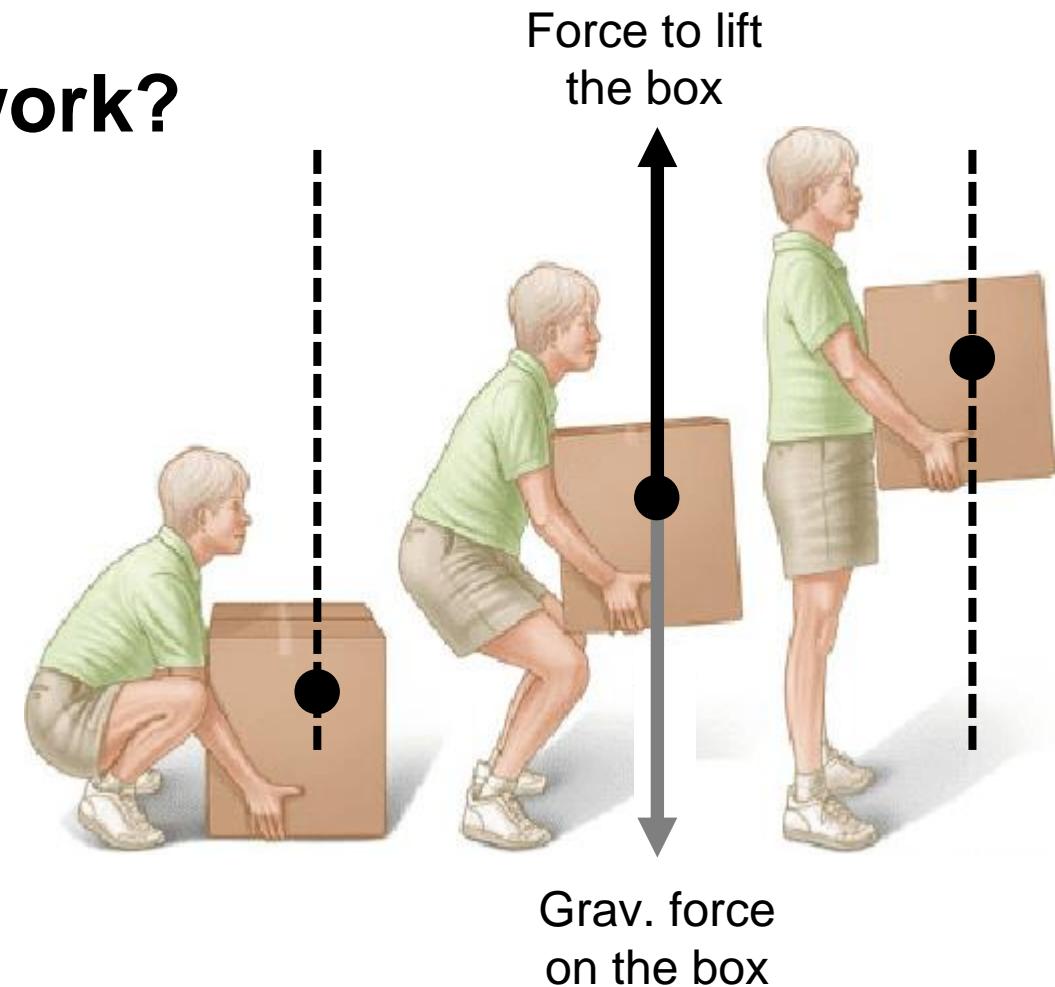
# Heat and work – what is work?

- Work is the product of a force and a displacement.

$$W = F\Delta x$$

- It has dimensions of energy, so it is measured in joules [  $J = N \cdot m$  ].
- For a variable force, we have to use an integral:

$$W = \int_{x_1}^{x_2} F \, dx$$



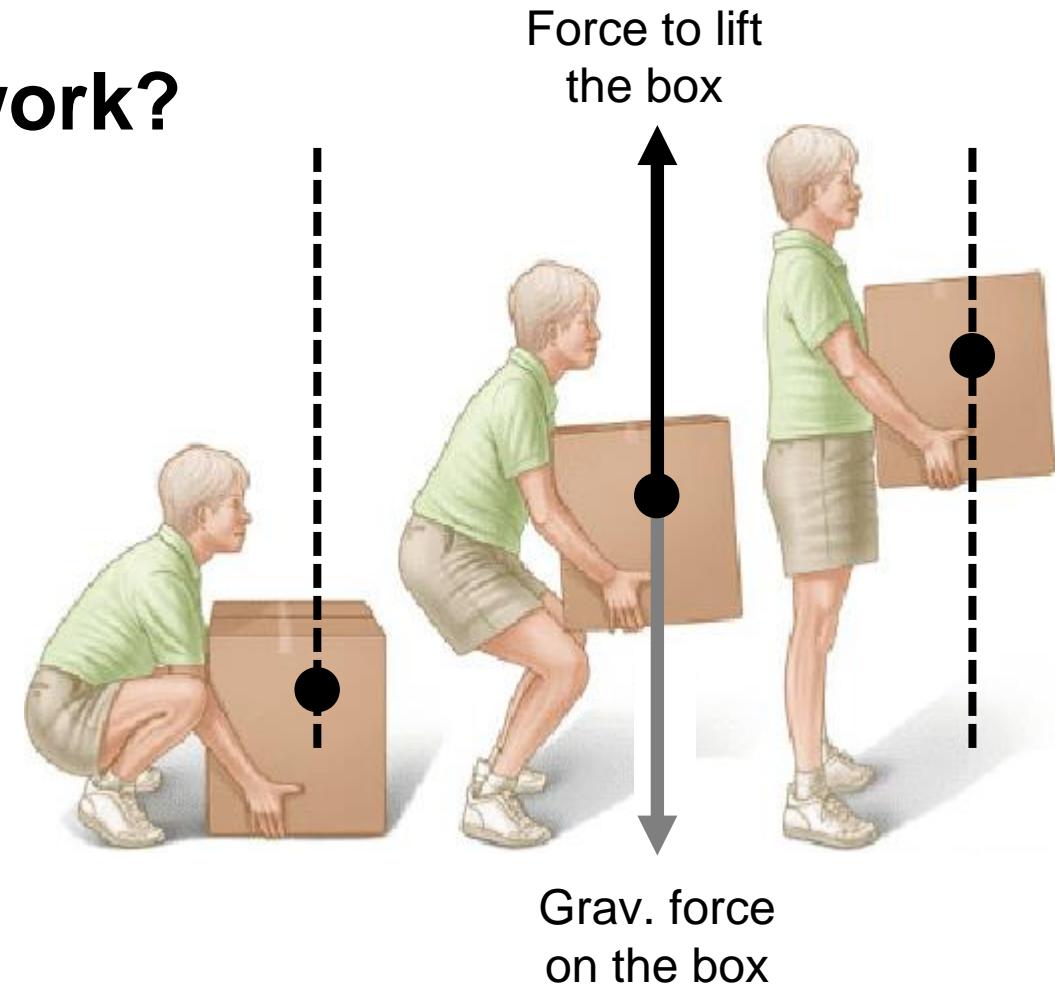
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- $$W = \int_{x_1}^{x_2} F \, dx$$
- For 3D situations, we have to take into account the direction:

$$W = \int_{\gamma} F \cdot dx$$

# Work and kinetic energy

- Work is the product of a force and a displacement.

$$W = F\Delta x$$

- It has dimensions of energy, so it is measured in joules [  $J = N \text{ m}$  ].
- For a variable force, we have to use an integral:

$$W = \int_{x_1}^{x_2} F \, dx$$

The total force acting on a body is proportional to the acceleration

$$F = ma$$

$$a = \frac{dv}{dt} = \frac{dv}{dx} \frac{dx}{dt} = \frac{dv}{dx} v$$

$$\begin{aligned} W &= m \int_{x_1}^{x_2} a \, dx = m \int_{x_1}^{x_2} \frac{dv}{dx} v \, dx \\ &= m \int_{v_1}^{v_2} v \, dv = \frac{1}{2} m [v^2]_{v_1}^{v_2} = \Delta K \\ \Rightarrow W &= \Delta K \quad \text{Kinetic energy } K = \frac{1}{2} mv^2 \end{aligned}$$

# Conservative forces and potential energy

Some forces are conservative, some are not.

It depends on the way the force depends on the position.

(Velocity-dependent forces are never conservative).



Position dependent forces are conservative when the work between two positions does not depend on the path

For conservative forces, we have can define a potential energy difference  $\Delta PE$

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For conservative forces, we have can define a potential energy difference  $\Delta PE$

In 1D all forces are conservative. The work is:

$$W = \int_{x_1}^{x_2} f(x) dx$$

Let's consider two examples

- Gravitational force<sup>§</sup>  $f = -mg$

$$W = \int_{x_1}^{x_2} -mg dx = -mg \Delta x = -\Delta PE$$

- Spring force  $f = -kx$

$$W = \int_{x_1}^{x_2} -kx dx = -\frac{1}{2}k\Delta x^2 = -\Delta PE$$

<sup>§</sup> Note that most commonly, the symbol used for the vertical direction (i.e. the variable appearing in the expression of the gravitational potential energy) is "z", and not "x".

# Conservative forces and potential energy

Some forces are conservative, some are not.

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Position dependent forces are conservative when the work between two positions does not depend on the path

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Energy conservation

Let's consider two examples

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kinetic energy  
potential energy

In 1D all forces are conservative. The work is:

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Energy conservation

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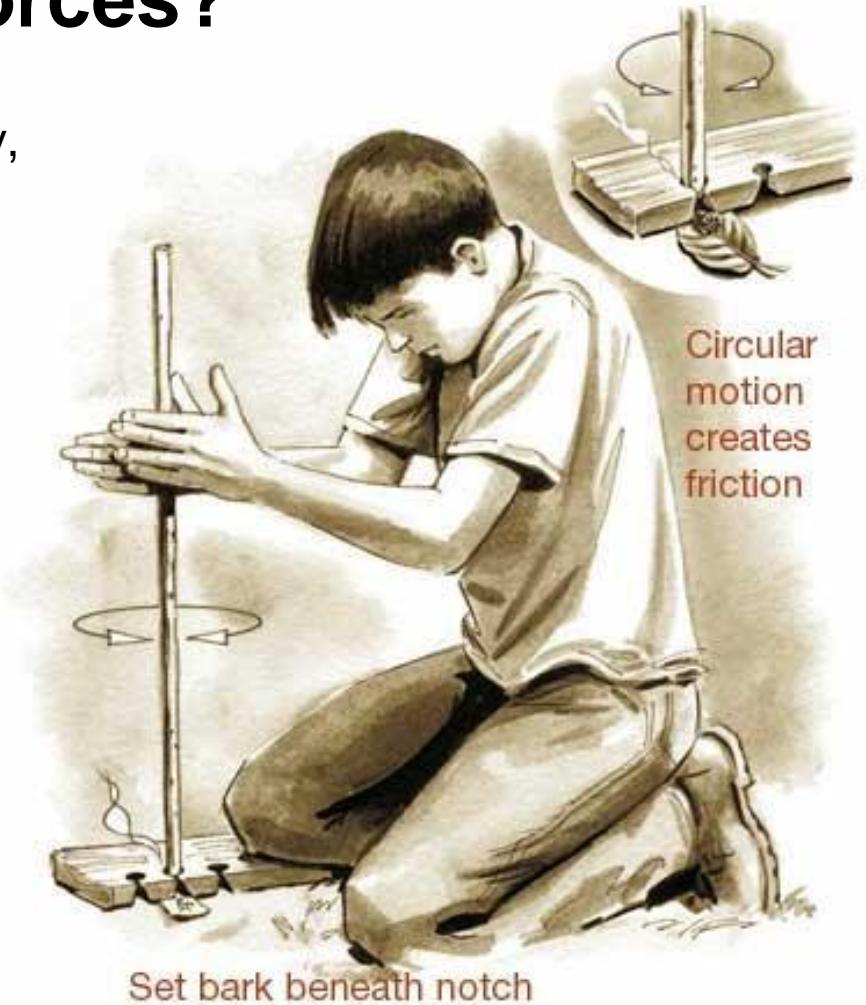
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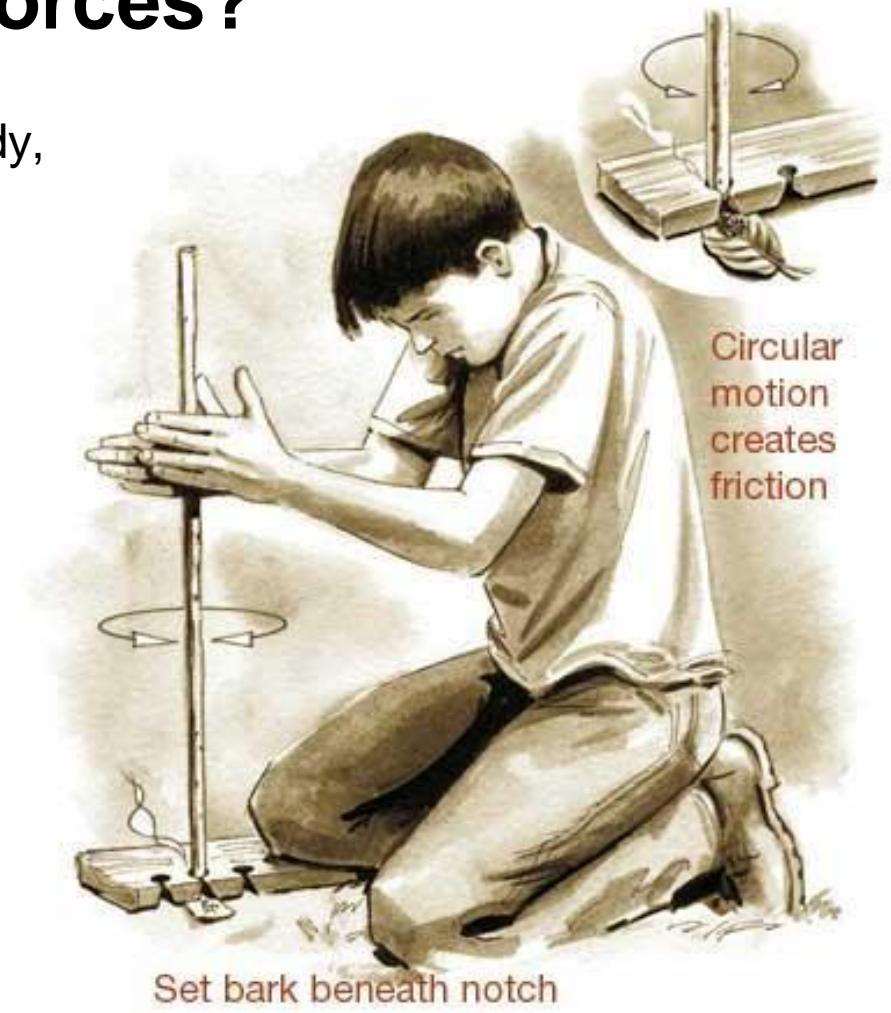
# What about non conservative forces?

When a non conservative force is doing work on an body, it may seem that the energy is disappearing.



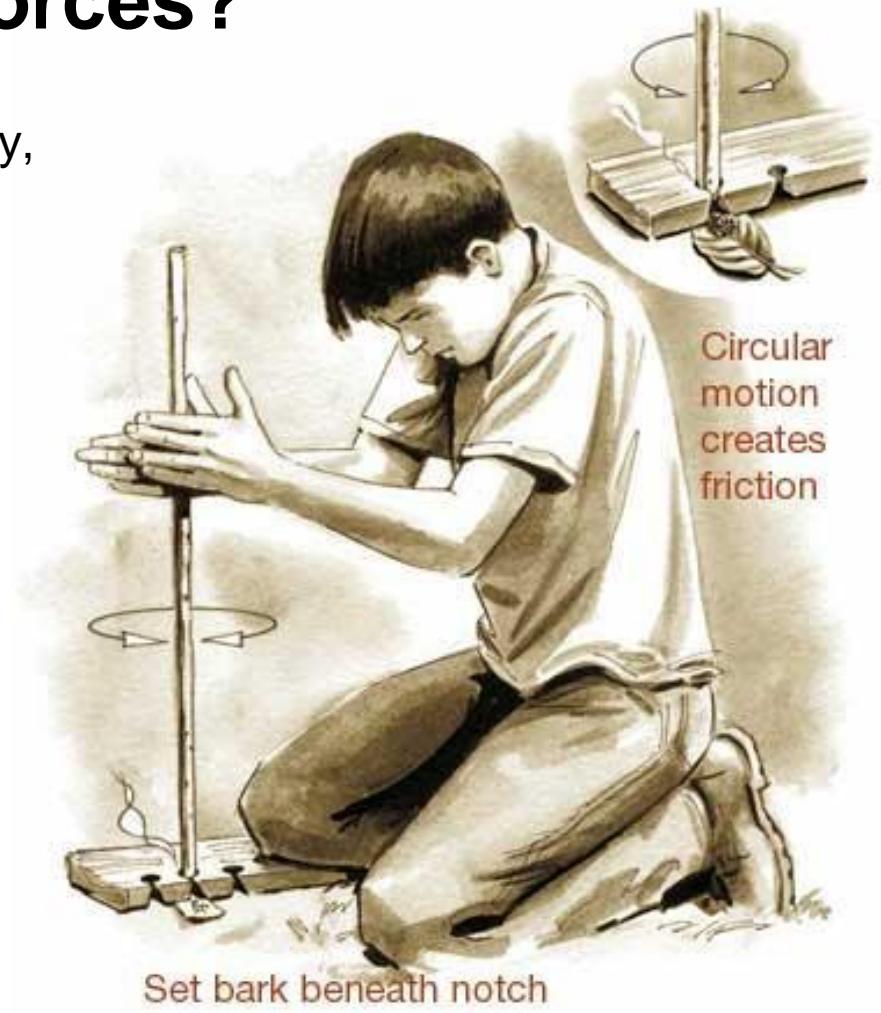
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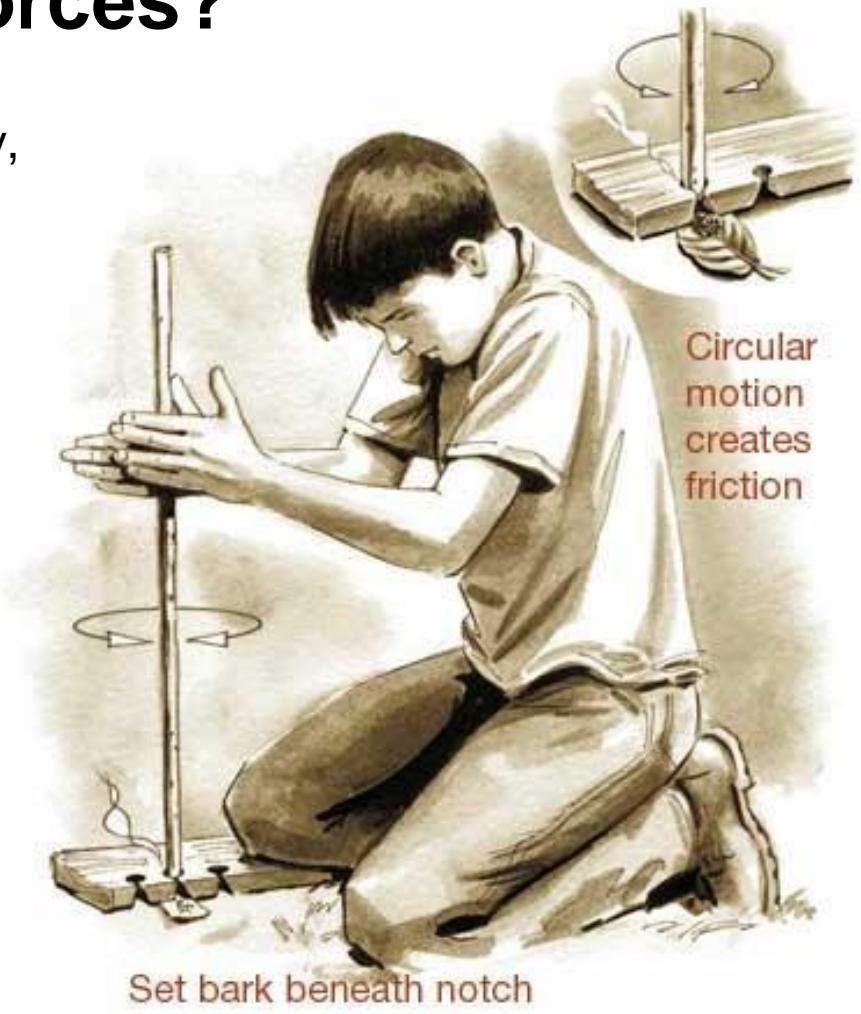
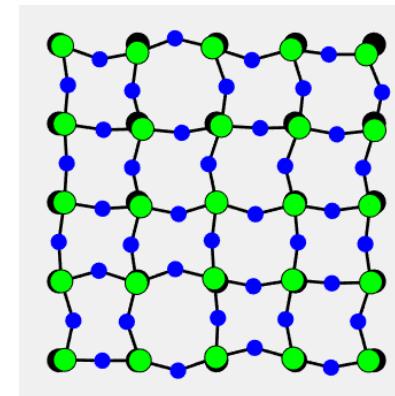
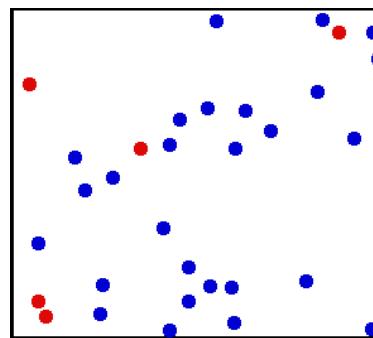


# What about non conservative forces?

When a non conservative force is doing work on a body, it may seem that the energy is disappearing.

$\Delta U$   
It increased the  
*internal* energy  
of something

Where did the  
energy go?



# Thermodynamic systems

- It can be anything. Whatever is relevant to our analysis.
- However, very often we concern ourselves with relatively simple cases:
  - A given amount of gas
  - A mixture of a liquid and the vapor of the same substance
  - A solid that can be considered homogeneous
- We define the system by delimiting from the rest of the universe. The boundary between the system and the universe can be
  - a real boundary (the walls of a container) or → matter cannot be exchanged (closed system)
  - an imaginary boundary (a region of space) → matter can be exchanged (open system)



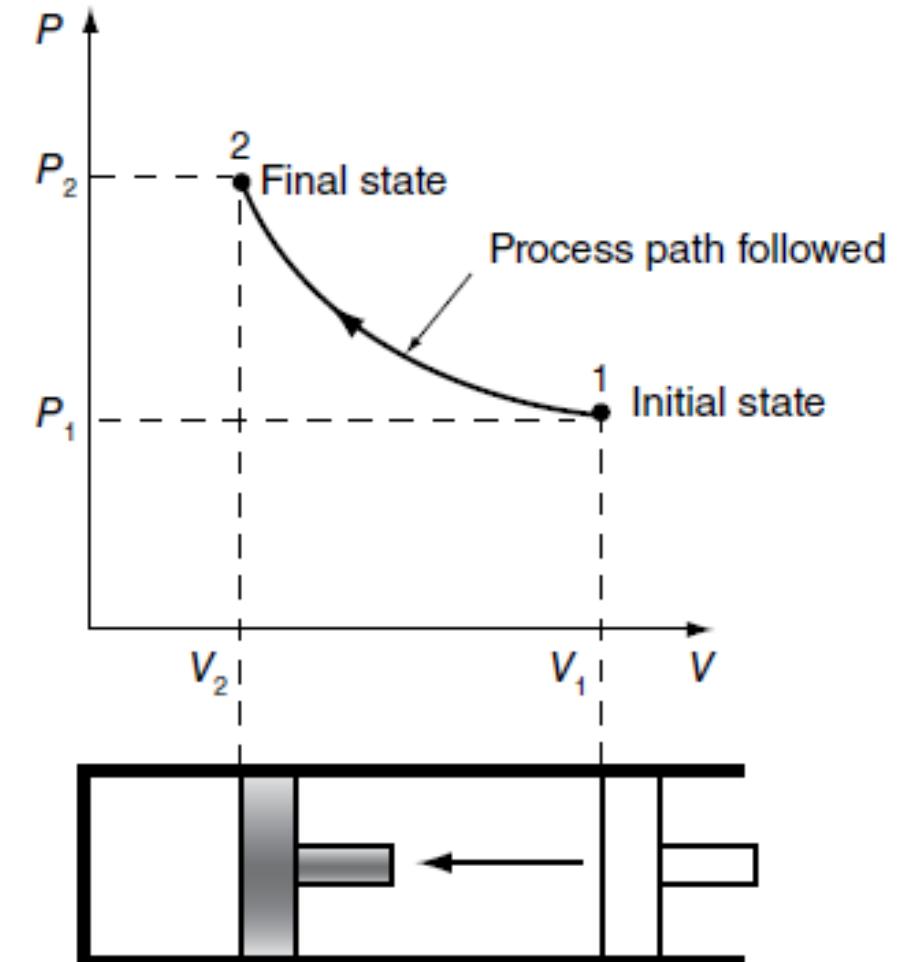
# Thermodynamic states

A state is the record of properties for a system.  
It can be described by a range of thermodynamic coordinates (properties)

Changing the properties of a system brings it to another state.

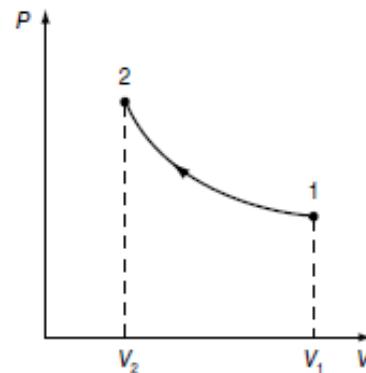
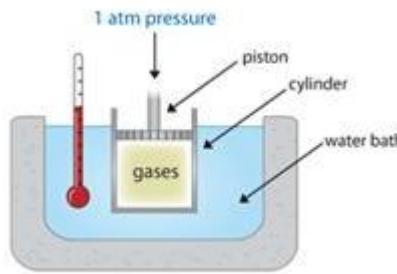
The journey from one state to another is called a process.

We will mostly concern ourselves with 4 types of processes: isothermal, isochoric, isobaric, adiabatic



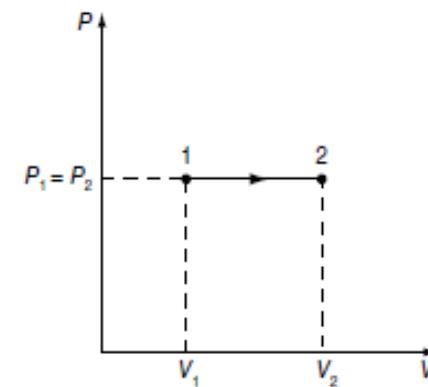
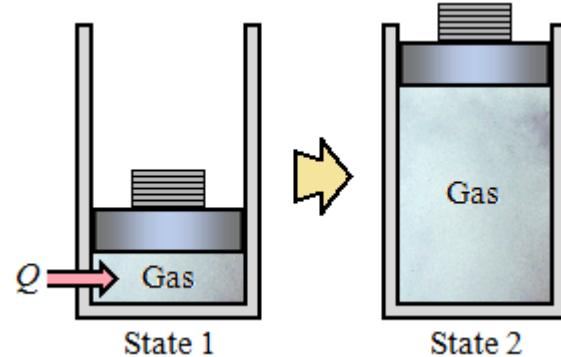
## Isothermal process

- Constant temperature



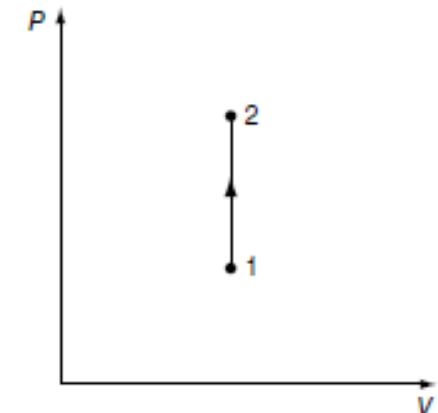
## Isobaric process

- Constant pressure



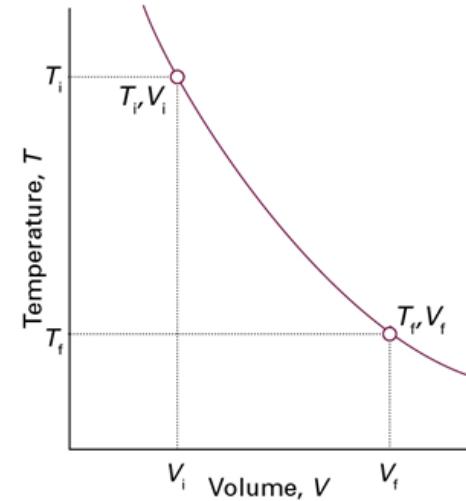
## Isochoric process

- Constant volume



## Adiabatic process

- No heat exchange



# State functions and Path functions

## State Function

- Independent of path  $\gamma$  taken to establish property or value
- Can integrate using final and initial values
- Based on established state of system
  - Temperature
  - Pressure
  - Amount of substance

## Path Function

- Dependent of path  $\gamma$  taken to establish property or value
- Needs information on function and limits to integrate
- Based on *how* the state of the system was established
  - Heat
  - Work



# Cyclic processes

A cycle is a process or series of processes that restore a system to its initial state

This means that integrating a property over a cycle will always give zero, e.g.

It is true for any state functions!

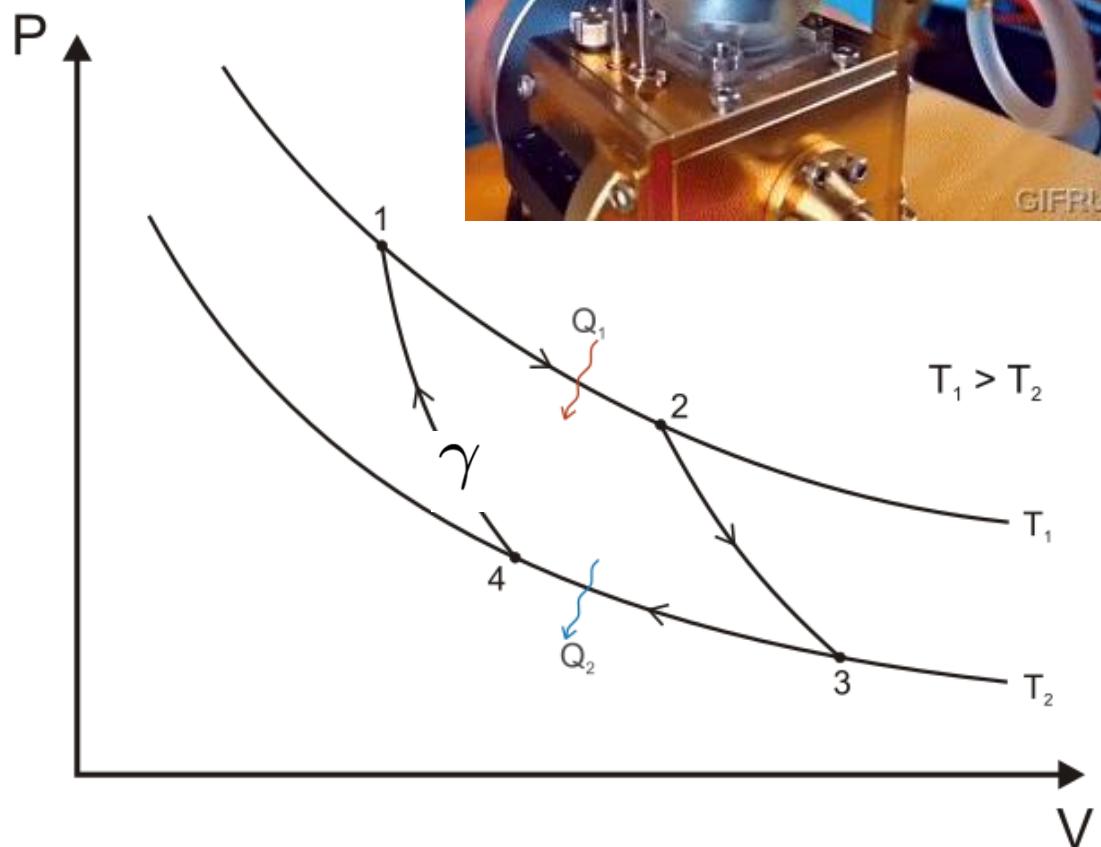
$$\oint_{\gamma} dV = 0$$

However, the transfer of energy in the form of heat or work will not be zero.

These are path functions!

$$\oint_{\gamma} dW = ?$$

All processes that do work *continuously* must be cycles. This makes the analysis of cycles immensely important!



## Example problem 2.7

A cylindrical water tank, 3 m high and 3 m in diameter is filled with water. If the density of water is  $1000 \text{ kg/m}^3$ , what is the mass of the contained water? If the acceleration due to gravity is  $9.81 \text{ m/s}^2$ , what is the weight of the water?

## Problem 2.7 - Solution

A cylindrical water tank, 3 m high and 3 m in diameter is filled with water. If the density of water is 1000 kg/m<sup>3</sup>, what is the mass of the contained water? If the acceleration due to gravity is 9.81 m/s<sup>2</sup>, what is the weight of the water?

- The volume of a cylinder is:

$$V_{cyl} = \frac{\pi}{4} D^2 H = \frac{\pi}{4} (3 \text{ m})^2 3 \text{ m} = 21.21 \text{ m}^3$$

- Then the mass is:

$$m = \rho V = 1000 \frac{\text{kg}}{\text{m}^3} 21.21 \text{ m}^3 = 21210 \text{ kg}$$

- And the weight is

$$F_w = m a = 21210 \text{ kg} 9.81 \frac{\text{m}}{\text{s}^2} = 208,030 \text{ N}$$

# Exercises chapter 2

- 2.5
- 2.8
- 2.12
- 2.27
- 2.28

47201 – Engineering Thermodynamics

# Lecture 1b: Thermodynamic system properties (Ch 3)

# Describing a thermodynamic system

Once the system is defined, it is important to inspect it and determine what the state of the system is.

- Is it a solid, liquid or gas?
- Is it a single substance or a mixture? Are there multiple phases (gas/liquid/solid)?
- How much mass is in the system? Is there a mass flow into and out of the system?
- What are properties such as temperature, pressure and volume? Is the system at steady state or will the temperature, volume, etc. Change?



# Mass

In this course mass will be given in both kg and mol

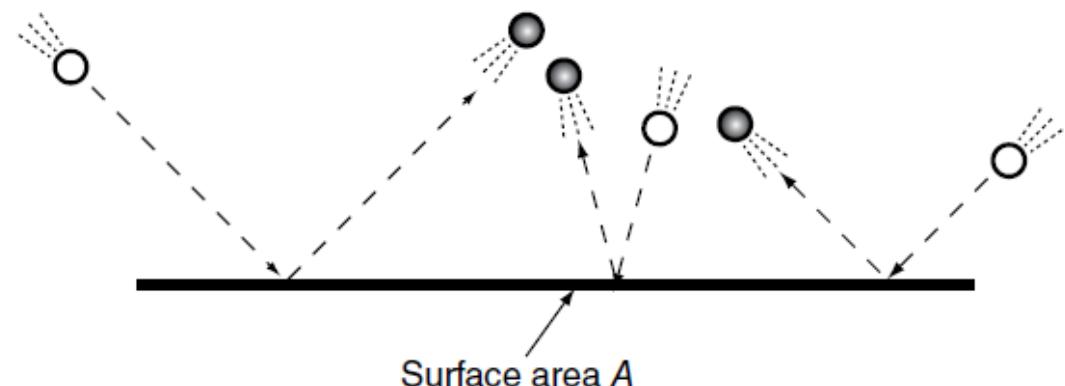
- Remember that 1 mol contains Avogadro's number ( $N_A$ ) molecules,  $6.022 \cdot 10^{23}$ , and molar mass is given in grams
- A kmol has molecular mass in kg
- The mass corresponding a number of moles is
$$m [\text{kg}] = N [\text{kmol}] M [\text{kg} / \text{kmol}]$$
- Molecular masses of common gases are given in Appendix 1 of the book. Otherwise, the molecular mass can be calculated from the chemical composition and a periodic table



# Pressure

Pressure is the force exerted by molecules on a wall

$$P = \frac{F}{A}$$



- Units N/m<sup>2</sup> is Pa. 1 bar is 10<sup>5</sup> Pa and atmospheric pressure is 1.01325 bar
- When there is an atmosphere, the entire system is under some background pressure ( $P_{atm}$ ). So on Earth we have an absolute pressure of 1.01325 bar. Since we don't "feel" this pressure, we can also call ambient pressure a gage pressure of 0 bar.

$$P_{abs} = P + P_{atm}$$

- The pressure is a function of the height of a fluid column,  $h$ , and the relation is

$$P_{abs} - P_{atm} = \rho g h$$

# Temperature

We will deal only with SI units in this course. However we will need to take care when dealing with temperature scales for some calculations.

- The Celsius scale defines 0 °C as the freezing point of water
- However, it is also important to consider that there is a lowest possible temperature, absolute zero. This occurs when there is no kinetic energy in the molecules. For this reason an absolute temperature scale has been introduced, called the Kelvin scale. Absolute zero has been estimated for gases and is defined as 0 K. To convert between temperature scales

$$T \text{ [K]} = T \text{ [°C]} + 273.15$$

- It is important to use absolute temperature when using the ideal gas equation or, in the future, calculating the Carnot efficiency

# Ideal gas law background

Equations that give relations between intensive properties are known as *equations of state*. The ideal gas law is an equation of state for a specific set of materials, in this case gases that are not close in temperature to being liquids and not at very high pressure.

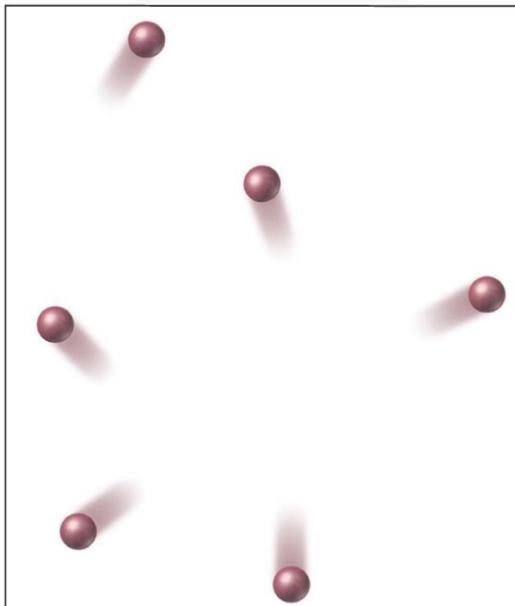
The assumptions used to derive the ideal gas law are:

1. The gas is made of a very large number of elementary particles called molecules that are in constant, random motion. All molecules have the same mass ( $m_e$ ).
2. The total number of molecules ( $n$ ) is very large.
3. Molecules collide perfectly elastically with each other and with the walls of the container. They obey Newton's laws during collisions.
4. There is no force acting on molecules except during collisions.
5. The volume of molecules is negligible – they are considered to be point masses.



# Deviation from ideality

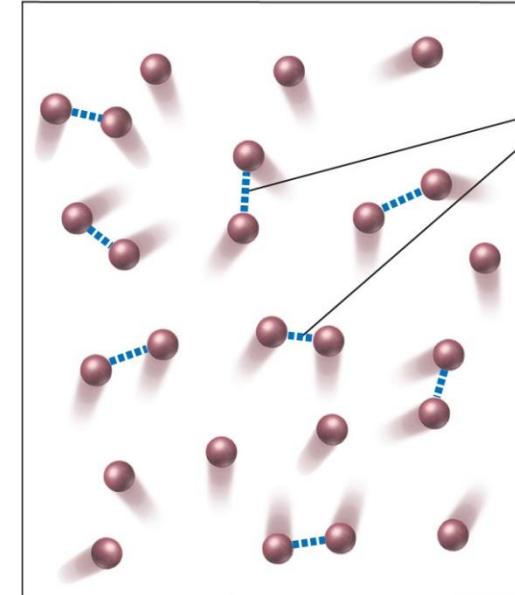
**Ideal gas conditions**  
• High temperature  
• Low pressure



- Particle size small compared to space between particles.
- Interactions between particles are insignificant.

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**Non-ideal gas conditions**  
• Low temperature  
• High pressure



- Particle size significant compared to space between particles.
- Interactions between particles are significant.

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# Ideal gas law

The **ideal gas law** describes the relation between properties of a gas.

These properties are connected by a constant, the (universal) **ideal gas constant  $R_u$**  (often just R):

$$PV = nR_u T$$

P: Pressure

n: number of moles

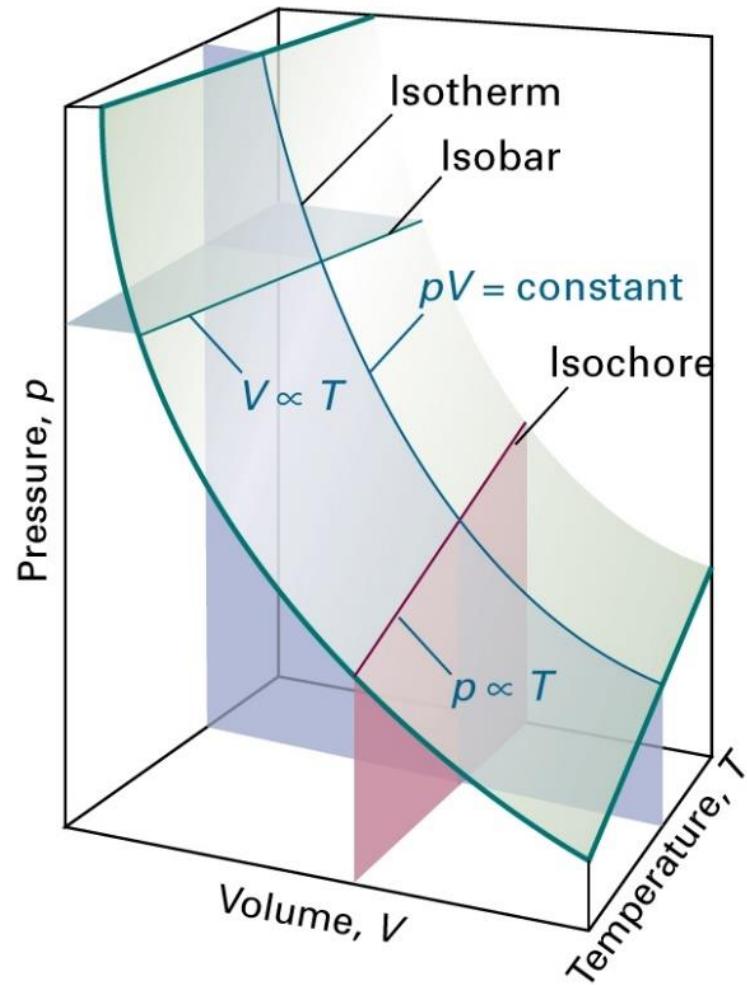
$R_u$ : Universal gas constant = 8.314(47) J/(mol · K)

V: Volume

T: Temperature

The ideal gas law is also often given in terms of a specific ideal gas constant defined as  $R = R_u/M$  and then the ideal gas law can be stated as

$$P V = m R T$$



# Energy implications of the ideal gas law

Section 3.8 and 3.9 give a derivation of the internal energy of an ideal gas based on the kinetic energy of all molecules. The conclusion is:

$$u_2 - u_1 = \frac{3}{2}R(T_2 - T_1)$$

Where  $u$  is the internal energy of an ideal gas. Note that is only for a “perfect” monatomic gas and many gases, such as air have a different relation.

- One important conclusion from this analysis is that the internal energy of an ideal gas is only dependent on its temperature and not pressure



# A brief summary of energy

## Gravitational potential energy

Energy stored in a body raised in a gravitational field

$$PE = E_p = mgz$$

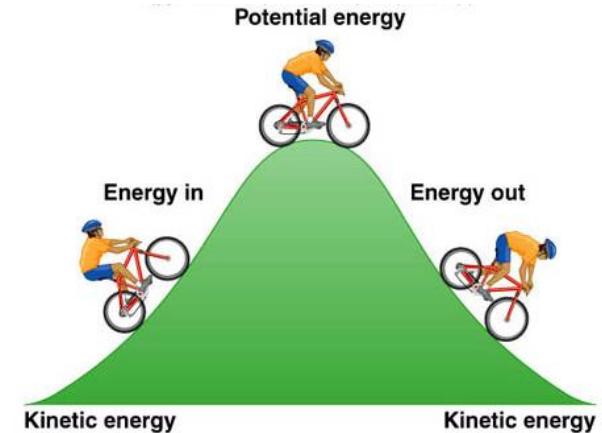
## Kinetic energy

The energy stored in or possessed by an object due to motion

$$KE = E_k = \frac{1}{2} mV^2$$

## Internal energy

The total microscopic energy of all atoms and molecules in a system



# Specific Heats – Constant volume

We define the specific heat for **constant volume** systems as the change in internal energy with changing temperature:

$$c_v(T) \equiv \left( \frac{\partial u}{\partial T} \right)_v$$

For **ideal gasses** the **internal energy  $U$  depends only on  $T$**  (not  $P$ ). Meaning we can integrate:

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} c_v(T) dT = c_v(T_2 - T_1)$$

# Specific Heats of Liquids and Solids

We can assume liquids and solids to be practically incompressible, no volume change  
*(it takes roughly 200 x atmospheric pressure to compress water 1%)*

Under this assumption one can show that:

$$c_v(T) = c_p(T) = c(T)$$

Incompressible substances have only one heat capacity. We call it  $c$

It further follows that under these circumstances:

$$\Delta u = u_2 - u_1 = c(T_2 - T_1)$$

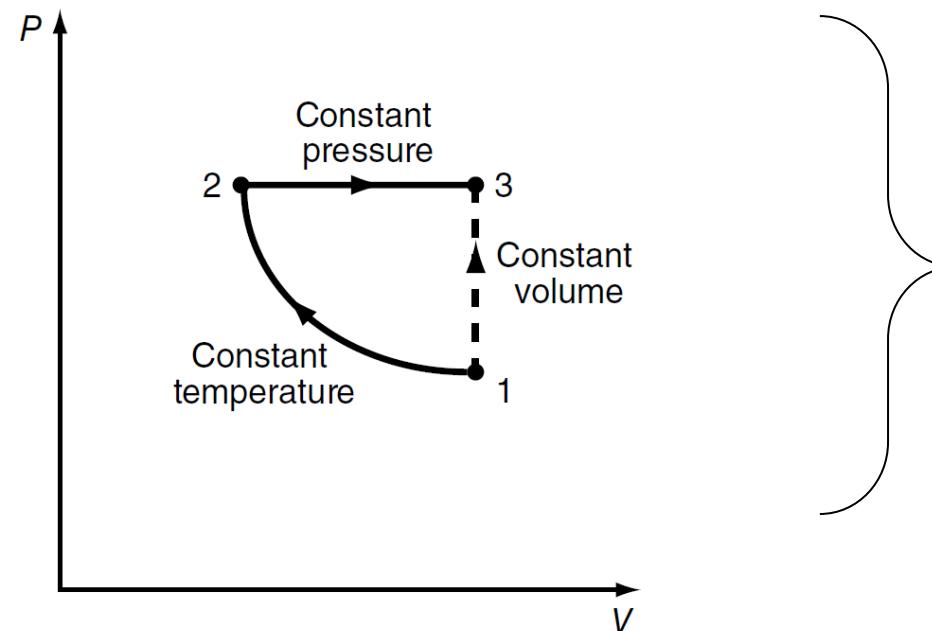
And

$$\Delta h = h_2 - h_1 = c(T_2 - T_1) + v(P_2 - P_1)$$



# C<sub>v</sub> or C<sub>p</sub> – The path from initial to final state...

We can use internal energy (U) and enthalpy (H) for processes that are not at constant pressure, nor constant volume by noting that they are both state functions, and thus independent on path



*Always hold for ideal gasses in thermodynamic processes*

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} c_v(T) dT$$

$$\Delta h = h_2 - h_1 = \int_{T_1}^{T_2} c_p(T) dT$$

**We can use Cv and Cp to calculate the changes in internal energy and enthalpy, respectively, for an ideal gas no matter the route getting there.**

## Example 3.8

How much energy does it take to raise the temperature of 1 kmol of argon by 1 K?

- Argon is a monatomic gas, so it follows Eq. (3.28)
- Then energy required to raise the temperature of the Argon is just the change in internal energy. So:

$$U_2 - U_1 = \frac{3}{2} N R_u (T_2 - T_1) = \frac{3}{2} 1 \text{ kmol} 8.314 \frac{\text{KJ}}{\text{kmol} - \text{K}} 1 \text{ K} = 12.471 \text{ KJ}$$

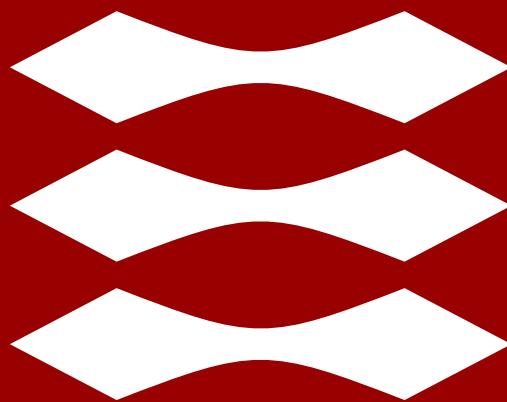
# Exercises – chapter 3

- 3.3
- 3.7
- 3.9
- 3.15
- 3.20
- 3.27 use 26 g of the gas, not 2.6 g. There is an error in the book.
- 3.39

# Exercises – chapter 3 with solutions

- 3.3 (  $m_{O_2} = 19.9 \text{ g}$ ,  $m_{CO_2} = 13.7 \text{ g}$  and  $m_{H_2O} = 11.2 \text{ g}$  )
- 3.7 (3500 N)
- 3.9 (8632.8 Pa)
- 3.15 (22.4 L)
- 3.20 (0.728 mm)
- 3.27 (4.03 g/mol, helium)
- 3.39 ( $c = 0.720 \text{ kJ/kg}$ )

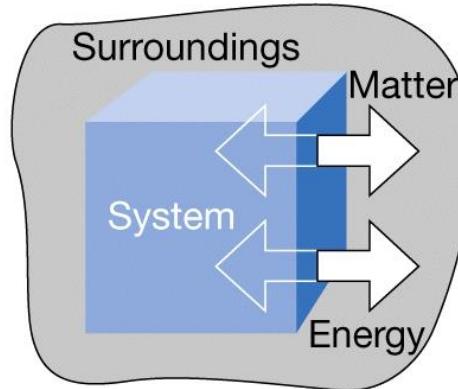
# DTU



47201 Engineering thermodynamics

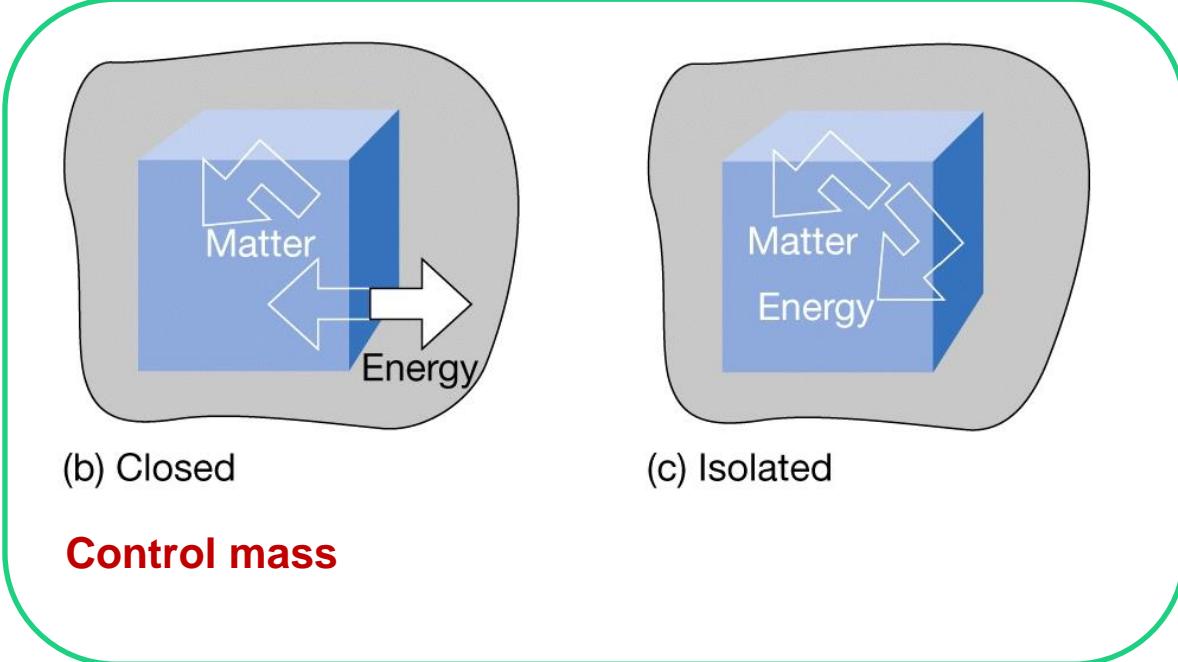
# Lecture 2a: First law for closed systems (Ch 4.1-4.12)

# Closed systems



(a) Open

**Control volume**



(b) Closed

(c) Isolated

**Control mass**

- No transfer of mass to and from the system
- There can be heat and work interaction with the surroundings

# Forms of energy

## Gravitational potential energy

Energy stored in a body raised in a gravitational field

$$\text{PE} = mgz$$
$$\Delta\text{PE} = \Delta mgz$$

## Kinetic energy

The energy stored in or possessed by an object due to motion

$$\text{KE} = E_k = \frac{1}{2}m\mathbf{V}^2$$

## Internal energy

The total microscopic energy of all atoms and molecules in a system

$$U = U(T, P, \dots)$$

# Specific energy of a system

## Specific energies

For each of the total energies above, there is a corresponding specific energy (energy per amount of substance)

$$pe = g z \quad ke = \frac{1}{2} v^2 \quad u = \frac{U}{m}$$

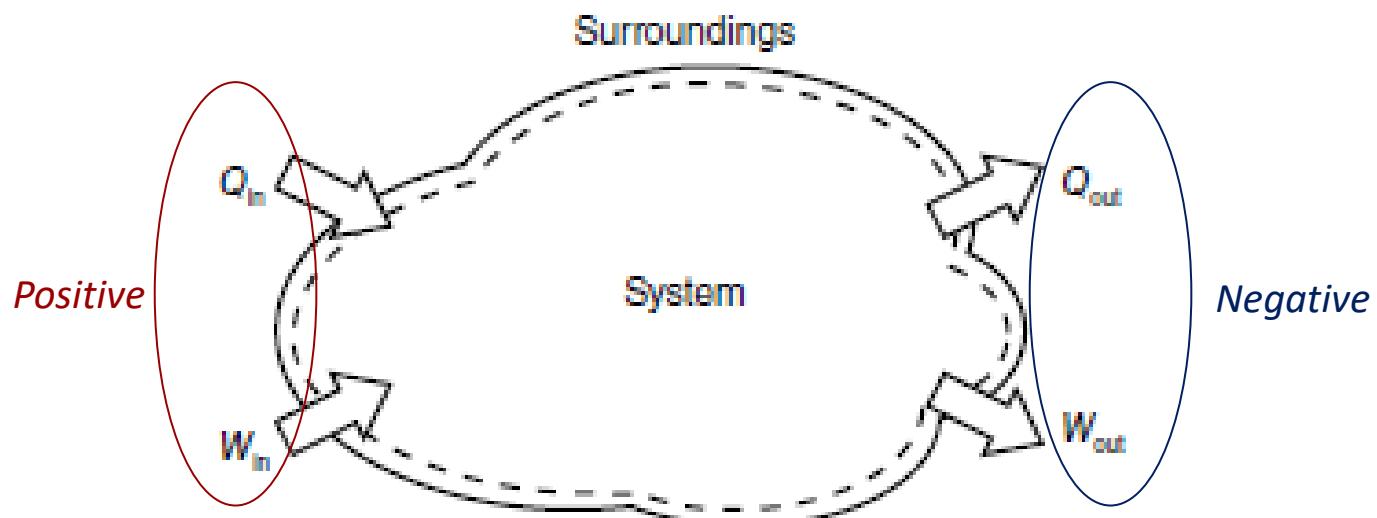
**The total specific energy of a system is the sum of all energy forms**

$$e = gz + \frac{1}{2} v^2 + u$$

# Transfer of Energy to/from a system

Transfer of energy – either via work (W) or heat (Q)

By definition: Energy from a system to surroundings = negative



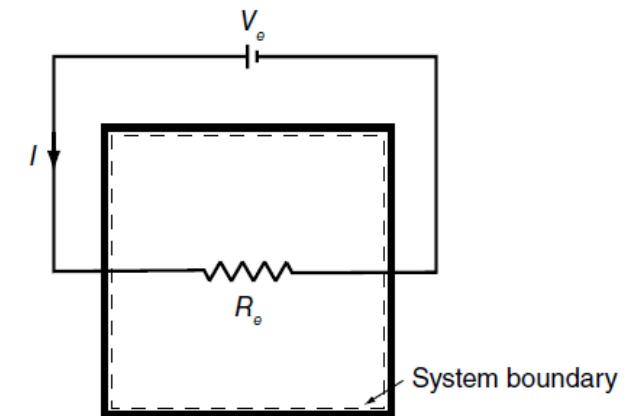
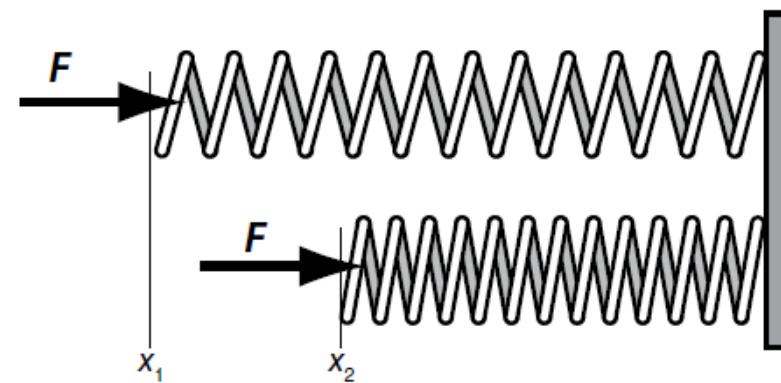
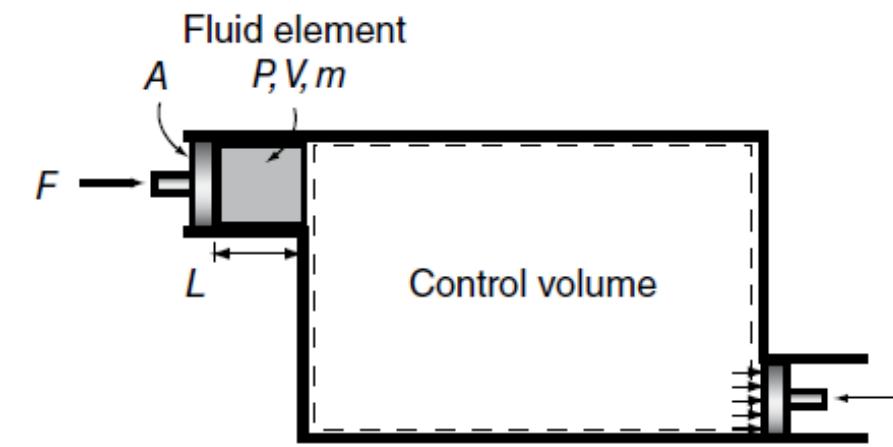
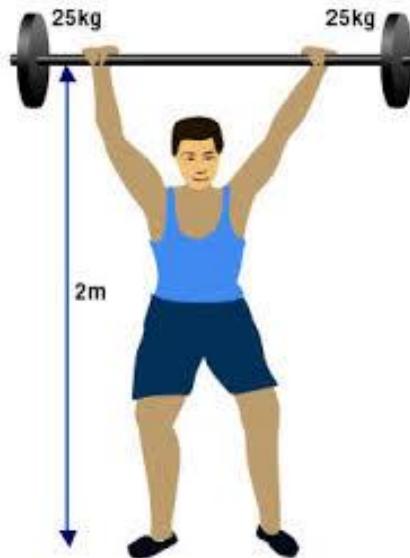
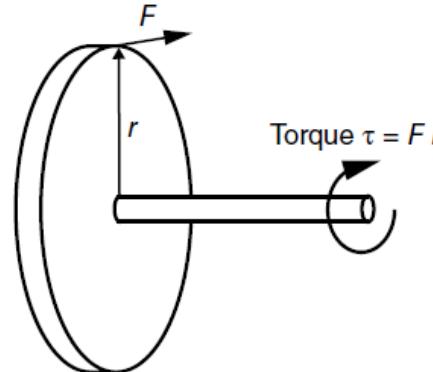
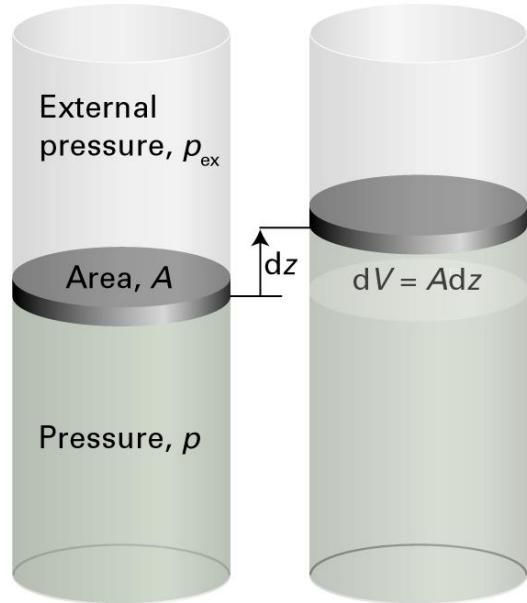
The sign is (just) an indication of the direction of energy transfer.

**Heat is transferred to a system by a temperature difference and typically through some medium, such as the system walls**

- The heat can change the conditions in the system and/or the internal energy depending on the system
- Q is the heat in Joules and the heat transfer rate is

$$\dot{Q} = \frac{\delta Q}{dt}$$

# Types of work



# Calculating work interactions

**Open or closed systems can have a work interaction with the environment in the following ways**

- Boundary work from a changing volume  $W_{vol} = \int_{V_1}^{V_2} PdV$  (Eq. 4.21)

- Flow work  $W_{flow} = PV$  (Eq. 4.34)

- Shaft work  $\dot{W}_{shaft} = 2 \pi \omega \tau$  (Eq. 4.38) in rev/s

- Spring work  $W_{spring} = \int_{x_1}^{x_2} k x dx$  (Eq. 4.40)

- Mechanical work  $W_{mech} = \int_{x_1}^{x_2} F dx$

- Electrical work  $\dot{W}_{elec} = VI$  (Eq. 4.41)

# Boundary, or expansion, work

Movement of the system boundary against an outside force (external pressure  $P_{ex}$ )

*Volume increases  $\Rightarrow$  Expansion*

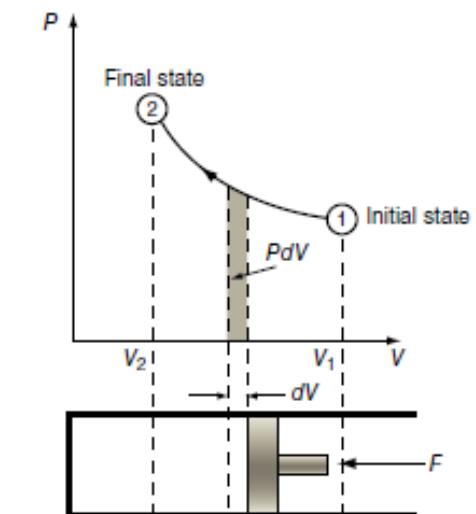
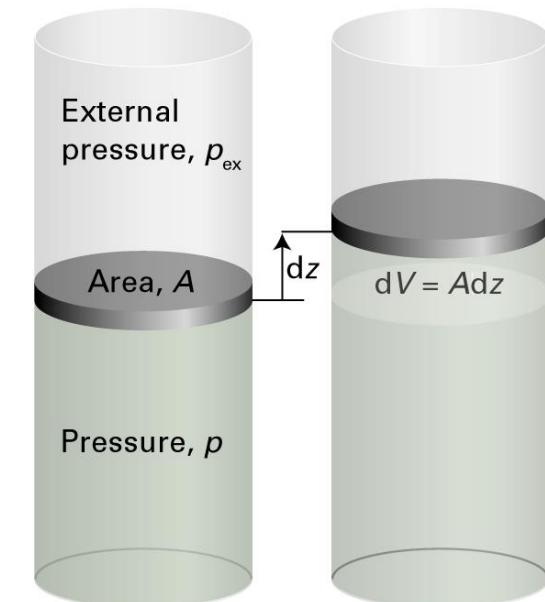
The system does work on the surroundings and the internal energy  $U$  of the system is reduced ( $\Delta U < 0$  if  $q=0$ )

*Volume decreases  $\Rightarrow$  Compression*

The surroundings does work on the system and the internal energy  $U$  of the system increases ( $\Delta U > 0$  if  $q=0$ )

The system is often assumed in mechanical equilibrium with the surroundings, making the process reversible ( $P_{ex} =$  pressure  $P$  in system at all points during the process)

Be sure the process is assumed reversible before using  $P = P_{ex}$



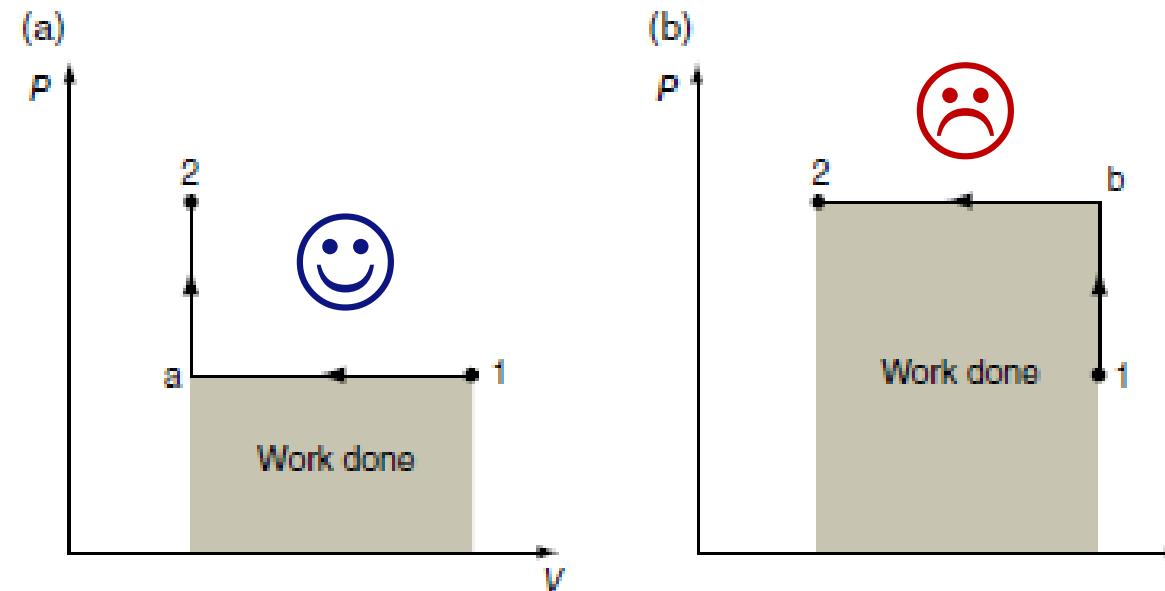
# Boundary work: Path

$$W_{boundary} = - \int_{V_1}^{V_2} P_{ex} dV$$

General expression of boundary work

Here we see the consequence of **work** being a **path function** (= dependent on the path from state 1 to state 2).

What is the “lesson-learned” in an industrial perspective?

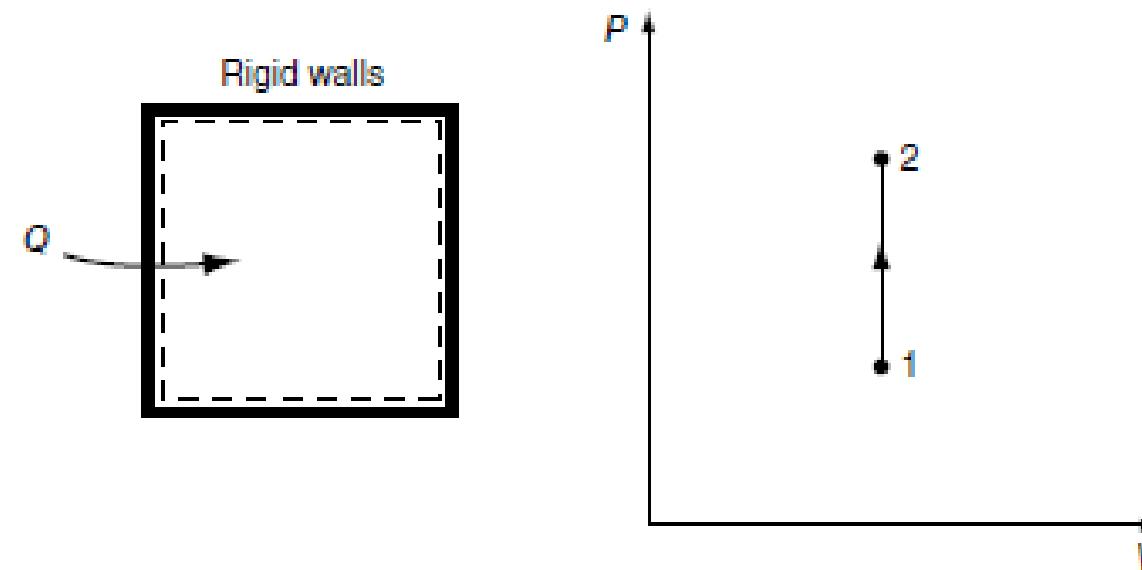


# Boundary work: Isochoric

At **constant volume (isochoric)** work is calculated as:

$$W = - \int_{V_1}^{V_2} P_{ex} dV = -P_{ex} \cdot 0 = 0$$

Therefore – No boundary work done for a system where volume remains constant!

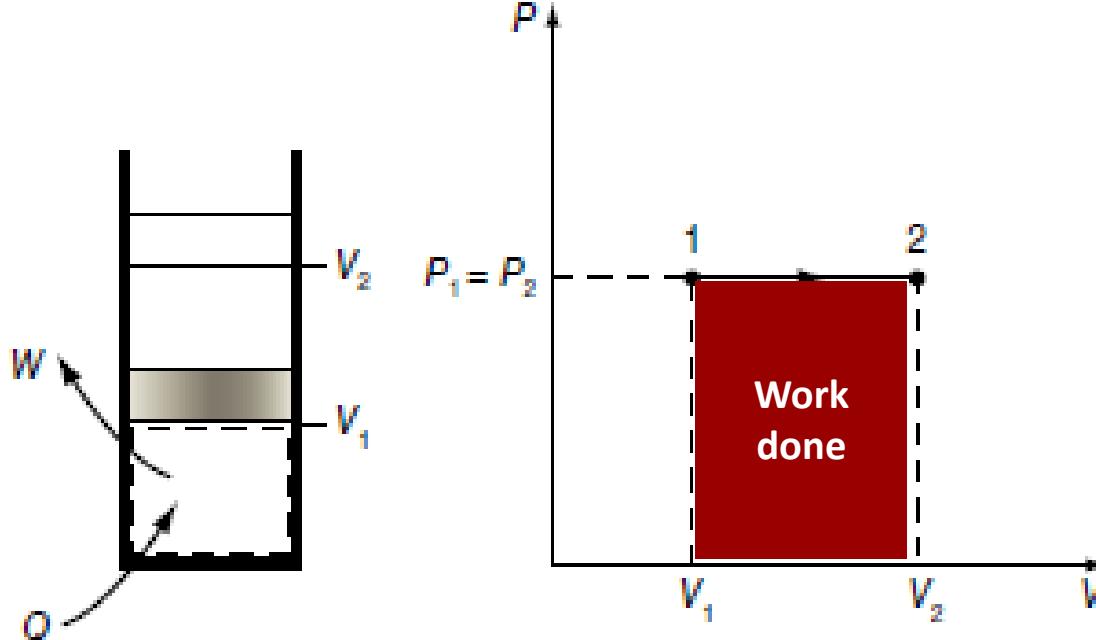


# Boundary work: Isobaric

At **constant (external) pressure (isobaric)** work is calculated as:

$$W = - \int_{V_1}^{V_2} P dV = -P_1 \int_{V_1}^{V_2} dV = P_1(V_1 - V_2) = P_1 \Delta V$$

The system is in mechanical equilibrium with the surroundings so  $P_{\text{ex}} = P$

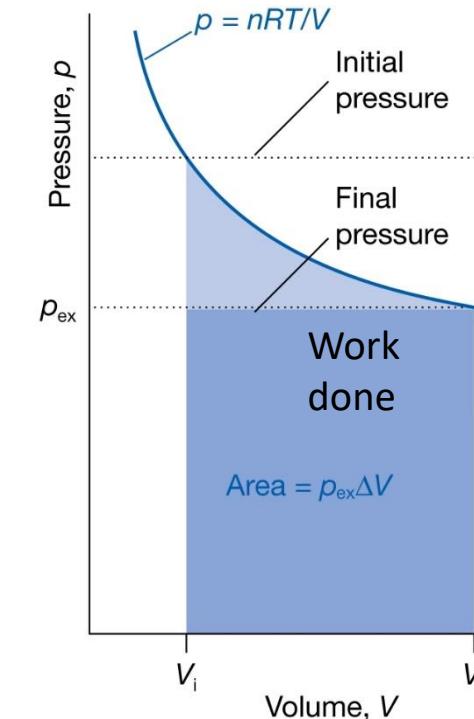
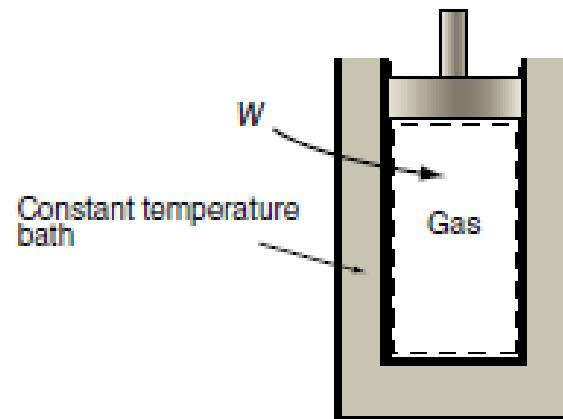


# Boundary work, isothermal (reversible)

At **constant temperature (isothermal)** for ideal gas work is found as:

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \left( \frac{mRT}{V} \right) dV = (mRT) \ln \left( \frac{V_1}{V_2} \right) (= (nR_u T) \ln \left( \frac{V_1}{V_2} \right))$$

If ideal gas then:  $P = mR_u T/V$



# The 1<sup>st</sup> Law of Thermodynamics

***The change in energy of a closed system equals the net energy transferred to it in the form of work and heat. Stated mathematically,***

$$Q + W = \Delta E$$

$$\Delta E = \Delta PE + \Delta KE + \Delta U$$

- This is one of the most important concepts of this course. It simply states that energy cannot be created or destroyed. Therefore we will do an energy balance in almost all exercises
- This also shows that work and heat can be converted to internal energy in a material

# Systems with multiple heat and work inputs

*For systems with multiple work and heat inputs, we can simply add up each energy interaction, keeping in mind the sign of each input*

$$Q_{net} = \sum Q_i$$

$$W_{net} = \sum W_i$$



# Methodology for solving thermodynamics problems

1. Carefully review the problem statement and what is known.
2. Choose the system.
3. Apply a mass balance on the chosen system (for a closed system the mass is always balanced).
4. Apply an energy balance on the chosen system

# Example energy conversion

An egg is thrown downward from a window 20 m high at a velocity of 20 m/s. What is the change in specific internal energy when it hits the ground (height of 0 m)?

$$Q + W = \Delta E$$

## Assume

- air resistance is negligible
- The egg doesn't bounce and all kinetic energy is converted

$$\Delta E = \Delta PE + \Delta KE + \Delta U = 0$$

Divide by mass and substitute energy equations

$$g \Delta z + \frac{1}{2} \Delta v^2 + \Delta u = 0$$



# Example energy conversion contd

$$\Delta E = \Delta PE + \Delta KE + \Delta U = 0$$

Divide by mass and substitute energy equations

$$g z + \frac{1}{2} \Delta v^2 + \Delta u = 0$$

Plug in the given values and solve for  $\Delta u$

$$9.8 \frac{m}{s^2} (0 - 20 m) + \frac{1}{2} \left[ 0 - \left( 20 \frac{m}{s} \right)^2 \right] + \Delta u = 0$$

$$\Delta u = 396 \frac{\text{J}}{\text{kg}}$$

# Different energy types

***Kinetic and potential energy can be converted back and forth, and they can both be converted directly to heat, but it doesn't go back the other way as effectively.***

- Heat has a lower thermodynamic value than other types of energy
- Electricity, kinetic energy, potential energy, and mechanical energy (such as a shaft providing a torque) are all pure work, but heat is lower grade.
- Heat can be converted to kinetic energy - <https://www.youtube.com/watch?v=9EA3wa7w5CQ>
- It can also be converted into mechanical work or electricity
- However, the efficiency is less than 100%



# Specific Heats – Constant volume

What if we have a material in rigid contain (= constant volume)?

Then  $W = 0$  and  $\delta q = du$

We define the specific heat for **constant volume** systems as the change in internal energy with changing temperature:

$$c_v(T) \equiv \left( \frac{\partial u}{\partial T} \right)_v$$

For **ideal** (mono atomic) **gasses** the **internal energy  $U$  depends only on  $T$**  (not  $P$ )

$$c_v(T) \equiv \left( \frac{\partial u}{\partial T} \right)_v \Rightarrow c_v(T) = \frac{du}{dT} \Rightarrow du = c_v(T)dT$$

Meaning we can integrate:

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} c_v(T) dT$$

# Internal energy as a function of temperature: $C_V$

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

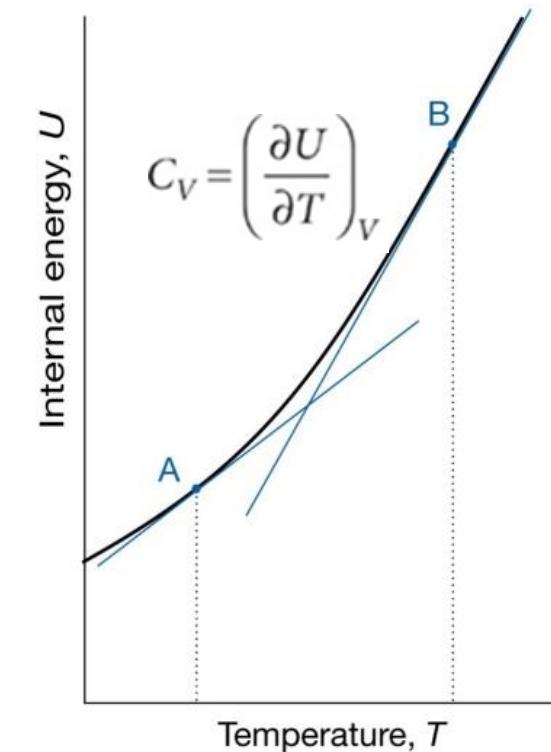
Definition of heat capacity  
at constant volume

$$dU = C_V dT \quad (\text{at constant volume})$$

$C_V$  can often be assumed constant over small temperature ranges  $\Delta T$ :

$$\Delta U = C_V \Delta T = m \cdot c_v \Delta T = q_V$$

Large (constant volume) heat capacity,  $C_V$ , = small change in temperature with heat addition.



# Lifting a weight with heat

We want to try converting internal energy to potential energy. To do this, we will heat up air (which we assume acts as an ideal gas) to lift a heavy piston. The piston is 100 mm in diameter and has a mass of 10 kg with an initial height of 100 mm. The atmosphere in the room has a pressure of 101.3 kPa. The initial temperature of the air is 20 C.

- 1) Find the pressure and mass of air inside the cylinder
- 2) Calculate how much the potential energy of the piston increases when 0.5 kJ of energy is added to the air in the cylinder

## Assume

- air is an ideal gas
- Cylinder does not lose heat to the surroundings
- There is no friction around the piston

$$Q + W = \Delta PE + \Delta KE + \Delta U$$

And remember that the air in the cylinder has to follow the ideal gas law

$$P V = m R T$$



# Lifting a weight with heat 1)

- Let's draw the system
- The absolute pressure inside the cylinder must counteract the atmospheric pressure and the force of the piston mass

$$P_{cyl} = \frac{F_{pist}}{A_{pist}} + P_{atm} = \frac{10 \text{ kg} \cdot 9.8 \frac{\text{m}}{\text{s}^2}}{\frac{\pi}{4}(0.1 \text{ m})^2} + 101.3 \text{ kPa} \frac{1000 \text{ Pa}}{1 \text{ kPa}}$$
$$= 113787 \text{ Pa}$$

$$m_{air} = \frac{P_1 V_1}{R T} = \frac{113787 \text{ Pa} \frac{\pi}{4}(0.1 \text{ m})^2 0.1 \text{ m}}{0.287 \frac{\text{kJ}}{\text{kg} - \text{K}} \frac{1000 \text{ J}}{1 \text{ kJ}} (20 + 273.15) \text{ K}}$$
$$= 0.00106 \text{ kg}$$

# Lifting a weight with heat 2)

Now let's look at the energy side. First define the system

Since there is no friction on the piston and the piston weight and atmospheric pressure are constant, the pressure in the cylinder will also be constant so  $P_1 = P_2$

$$Q + W = \Delta PE + \Delta KE + \Delta U$$

Plugging in values

$$Q_{in} + P_1(V_1 - V_2) = m_{pist} g \left( \frac{T_2}{T_1} h_1 - h_1 \right) + m_{air} c_v (T_2 - T_1) \text{ since the pressure is constant, } V_2 = \frac{T_2}{T_1} V_1$$

$$\text{Then } Q_{in} + P_1 \left( V_1 - \frac{T_2}{T_1} V_1 \right) = m_{pist} g \left( \frac{T_2}{T_1} h_1 - h_1 \right) + m_{air} c_v (T_2 - T_1)$$



# Lifting a weight with heat 2) contd

Now we can solve for  $T_2$

$$\begin{aligned} T_2 &= \frac{Q_{in} + P_1 V_1 + m_{air} c_v T_1}{m_{pist} g \frac{h_1}{T_1} + m_{air} c_v + P_1 \frac{V_1}{T_1}} \\ &= \frac{0.5 \text{ kJ} + 10 \text{ kg } 9.8 \frac{\text{m}}{\text{s}^2} 0.1 \text{ m } \frac{1 \text{ kJ}}{1000 \text{ J}} + 113787 \text{ Pa } * 7.854 \text{ e}^{-4} \text{ m}^3 \frac{1 \text{ kJ}}{1000 \text{ J}} + 0.00106 \text{ kg } 0.742 \frac{\text{kJ}}{\text{kg} - \text{K}} 293.15 \text{ K}}{10 \text{ kg } 9.8 \frac{\text{m}}{\text{s}^2} \frac{0.1 \text{ m}}{293.15 \text{ K}} \frac{1 \text{ kJ}}{1000 \text{ J}} + 0.00106 \text{ kg } 0.742 \frac{\text{kJ}}{\text{kg} - \text{K}} + 113787 \text{ Pa } \frac{7.854 \text{ e}^{-4} \text{ m}^3}{293.15 \text{ K}} \frac{1 \text{ kJ}}{1000 \text{ J}}} = 737.7 \text{ K} \end{aligned}$$

And finally find the change in potential energy

$$\Delta PE = m_{pist} g \left( \frac{T_2}{T_1} h_1 - h_1 \right) = 10 \text{ kg } 9.8 \frac{\text{m}}{\text{s}^2} \left( \frac{737.7 \text{ K}}{293.2 \text{ K}} 0.1 \text{ m} - 0.1 \text{ m} \right) = 14.9 \text{ J} = 0.0149 \text{ kJ}$$

Let's do the problem also in EES

# What I want you to learn from the previous example

- Converting heat to work is less efficient than work to heat
  - Much of the heat goes to increasing the air's internal energy rather than raising the mass
  - But heat can still be useful for such applications
- The conversion process will depend on the conditions but also the properties of the materials that are being used
- Choosing the system can have a significant effect on how you solve the problem
- Be careful with units. Pressure in kPa will give energy in kJ and pressure in bar will give energy in  $10^2$  kJ. Kinetic energy and potential energy will be in J if you use kg, m, and m/s

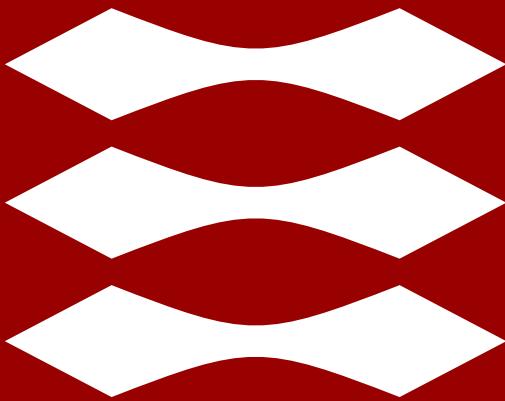
# Exercises part 1

- 4.4
- 4.5
- 4.7
- 4.8
- 4.10

# Exercises part 1 with answers

- 4.4 15.7 kW
- 4.5 160 J
- 4.7 981 J
- 4.8  $T = 450 \text{ K}$ ,  $V = 0.075 \text{ m}^3$
- 4.10 184.9 kJ

# DTU



47201 Engineering thermodynamics

# Lecture 2b: First law for closed systems (Ch 4.1-4.12)

# Energy Units

- Energy has units of [Force x Distance  $\frac{kg\ m^2}{s^2}$ ], and the SI unit is Joules – J
  - kJ, GJ etc.
- Because energy changes measured in J usually become very large and for convenience, the term kWh (kWhr, kW-h) is often used as a unit of energy
  - $1\ kWh \equiv 1000\ W\ 3600\ s = 3,600,000\ J$
  - Energy can also be expressed in MWh GWh etc.
- kWh units are often convenient for calculating electrical consumption. For example, if a building consumes 2.65 kW on average over a day, then the electrical energy usage is

$$E_{el} = 2.65\ kW\ 24\ h = 63.6\ kWh$$



# Power vs Energy

- Power is the rate of change in energy – equivalent to velocity and position in kinetics. For this reason, it is often represented as a rate of work,  $\dot{W}$ , or a rate of heat,  $\dot{Q}$
- Power has units of Watts  $\left[\frac{\text{kg m}^2}{\text{s}^3}\right]$  – W, kW and also horsepower – hp
  - $1 \text{ W} \equiv \frac{1 \text{ J}}{\text{s}}$
- The change in energy of a system can be calculated by integrating the power from both heat over time

$$\Delta E = \int (\dot{W} + \dot{Q}) dt$$



# Power vs Energy examples

- Electric water boiler with a power of 2400 W
  - Power tells how fast it will boil the water
  - The change in energy depends on the properties of the water
- Electricity bills are calculated in kWh
  - Depends on how much energy was used, not how fast it was used (power)
- An electric car has a battery capacity 33 kWh and a motor power of 135 kW
  - Battery capacity indicates the driving range of the car
  - Motor power indicates how fast the car can accelerate



# Power vs Energy common mistakes

- It's very common to mix up power and energy, but for those of you studying energy systems it's important to be careful with the terms
- Some common mistakes to avoid
  - “The building uses 10 kW of energy per day”
  - Stating energy in kW or power in J
  - Forgetting that most systems have independent power and energy ratings that both need to be specified.



# Polytropic processes

***Remember that work done by, for example, a piston during expansion is path dependent, meaning that we need to know the pressure and volume during the entire process to calculate the work correctly***

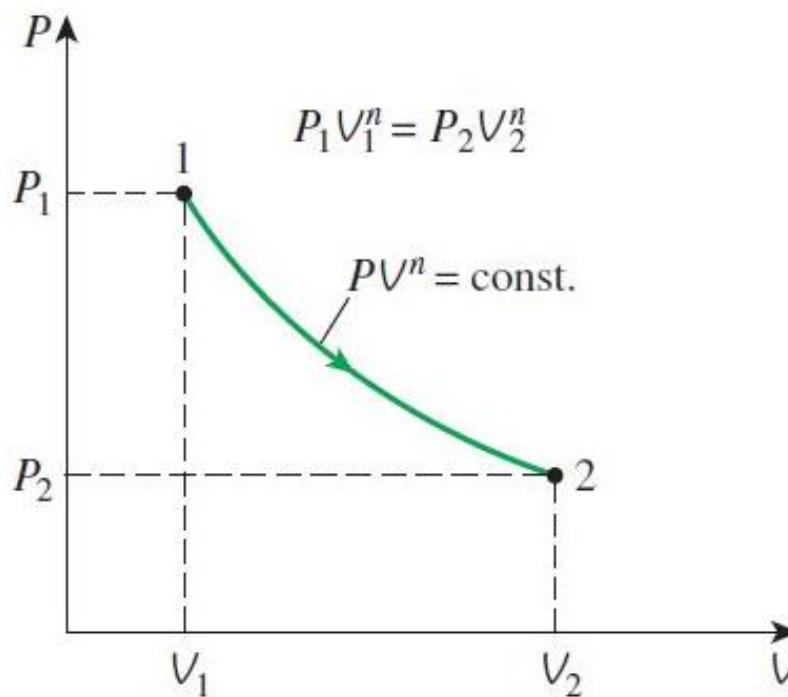
- During the expansion of a gas, the pressure and temperature often decrease simultaneously
- To solve problems with changing pressure and temperature, we introduce relations for the pressure and volume during these processes, which are called polytropic processes

$$C = P_1 V_1^n = P_2 V_2^n$$



# Boundary work, polytropic processes

- The work for a polytropic process can be calculated as for any boundary work as:
- $$W_{12} = - \int_{V_1}^{V_2} P \, dV$$
- Since  $P = C \frac{1}{V^n}$  we can substitute  $P$  into the work equation and get  $W_{12} = -C \int_{V_1}^{V_2} \frac{dV}{V^n}$



- Evaluating the integral
- $$W_{12} = \frac{1}{n-1} \left[ \frac{C}{V_2^{n-1}} - \frac{C}{V_1^{n-1}} \right] n \neq 1$$
- Plugging in  $C = P_1V_1^n$  and  $C = P_2V_2^n$  gives
- $$W_{12} = \frac{P_2V_2 - P_1V_1}{n-1} n \neq 1 \text{ and}$$
- $$W_{12} = P_2V_2 \ln \left( \frac{V_1}{V_2} \right) n = 1$$

## Example 4.7

Gas in a cylinder is expanded by a piston in a process for which  $PV^n = C$ , where  $C$  and  $n$  are constants. The initial pressure and volume are 3 bar and  $0.2 \text{ m}^3$  respectively and the final volume is  $0.6 \text{ m}^3$ . Determine the work done by the gas if (a)  $n = 1.4$  and (b)  $n = 1.0$ .

**Find:** Work  $W$  done by the gas.

- Part a) We will use the work equation (Eq. 4.30) for a polytropic process. For part a)  $n$  is not equal to 1, so we use:

$$W_{12} = \frac{P_2 V_2 - P_1 V_1}{n - 1}$$

- First we need  $P_2$ , so  $P_2 = P_1 \left( \frac{V_2}{V_1} \right)^{1.4} = 3 \text{ bar} \left( \frac{0.2 \text{ m}^3}{0.6 \text{ m}^3} \right)^{1.4} = 0.644 \text{ bar}$

- Then we can calculate the work

$$W_{12} = \frac{P_2 V_2 - P_1 V_1}{n - 1} = \frac{0.644 \text{ bar } 0.6 \text{ m}^3 - 3 \text{ bar } 0.2 \text{ m}^3}{1.4 - 1} \frac{100 \text{ kPa}}{1 \text{ bar}} = -53.4 \text{ kJ}$$

## Example 4.7 part b)

- Part b)  $n = 1$  so we use Eq. 4.32:

$$W_{12} = P_1 V_1 \ln\left(\frac{V_1}{V_2}\right)$$

- Here we don't need  $P_2$  so we can calculate the work directly

$$W_{12} = P_1 V_1 \ln\left(\frac{V_1}{V_2}\right) = 3 \text{ bar} \frac{100 \text{ kPa}}{1 \text{ bar}} 0.2 \text{ m}^3 \ln\left(\frac{0.2 \text{ m}^3}{0.6 \text{ m}^3}\right) = -65.917 \text{ kJ}$$

## Exercise 4.16

The pressure in a balloon increases linearly with its diameter. When it is filled with air at 200 kPa its volume is 1 m<sup>3</sup>. Find the work done when the balloon is inflated to a volume of 1.5 m<sup>3</sup>.

- Assume the system undergoes a polytropic process
- First draw the system



# Exercise 4.16 solution

First, we need to determine the exponent,  $n$ , for the polytropic process. We know: Pressure increases linearly with diameter of balloon, initial air pressure  $P_1 = 200 \text{ kPa}$ , initial volume of air  $V_1 = 1 \text{ m}^3$ , final volume  $V_2 = 1.5 \text{ m}^3$  and  $P V^n$  are constant for the process. And remember that the volume of a sphere is  $\frac{4}{3}\pi r^3$

- From the expression for pressure in the balloon

$$P = \gamma D = C V^{\frac{1}{3}}$$

- Solving for  $C$  gives

$$C = P V^{-\frac{1}{3}}$$

- Then we need to find  $P_2$  corresponding to the given volumes



# Exercise 4.16 solution contd

We can first solve for  $C$

- Since we know  $P_1$  and  $V_1$  we can calculate  $C$

$$C = P_1 V_1^{-\frac{1}{3}} = 200 \text{ kPa} (1 \text{ m}^3)^{-\frac{1}{3}} = 200 \frac{\text{kPa}}{\text{m}}$$

- Then the final pressure is

$$P_2 = C V_1^{\frac{1}{3}} = 200 \frac{\text{kPa}}{\text{m}} (1.5 \text{ m}^3)^{-\frac{1}{3}} = 228.9 \text{ kPa}$$

- The work done is then

$$\bullet \quad W = \frac{P_2 V_2 - P_1 V_1}{n-1} = \frac{228.9 \text{ kPa} 1.5 \text{ m}^3 - 200 \text{ kPa} 1 \text{ m}^3}{-\frac{1}{3}-1} = -107.561 \text{ kJ}$$

# Exercise 4.16 work on surroundings

On the outside of the balloon, the atmospheric pressure is constant at 101.3 kPa. In that case the work for an isobaric process is  $W_{12} = P(V_1 - V_2)$

$$W = 101.3 \text{ kPa} (1 \text{ m}^3 - 1.5 \text{ m}^3) = -50.65 \text{ kJ}$$

- This is less than the -107.56 kJ done on the inside of the balloon.
- The difference is due to the fact that the balloon acts as a spring. Once the balloon is blown up, there is some energy stored in it (for example if you let go of one end without tying it). So the extra work that went on the inside of the balloon is stored energy or if the balloon suddenly popped, it would be dissipated as heat.



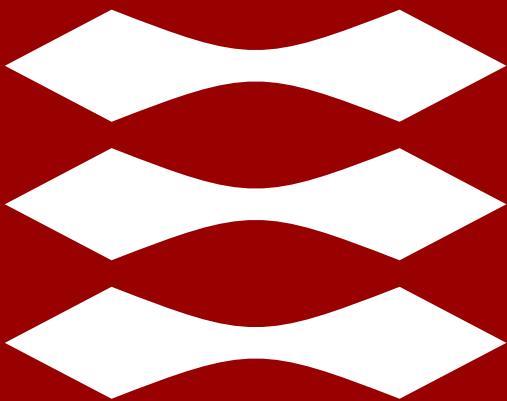
# Exercises part 2

- 4.13
- 4.14
- 4.15

# Exercises part 2 with answers

- 4.13 3.37 kJ
- 4.14  $T = 337 \text{ K}$ ,  $w = 221.3 \text{ kJ/kg}$
- 4.15 -3.99 kJ

# DTU



47201 Engineering thermodynamics

# Lecture 3a: First law for open systems (Ch 4.13-4.16)



# Review: Real world thermodynamics example

<https://www.youtube.com/watch?v=gOMibx876A4>

# Did Lisa violate the laws of thermodynamics?

Given:

- Perpetual motion machine – started with some initial kinetic energy
- There was a light bulb – some work output

$$@ t = 0 \quad E_0 = KE_0 - \dot{W}_{light} dt$$

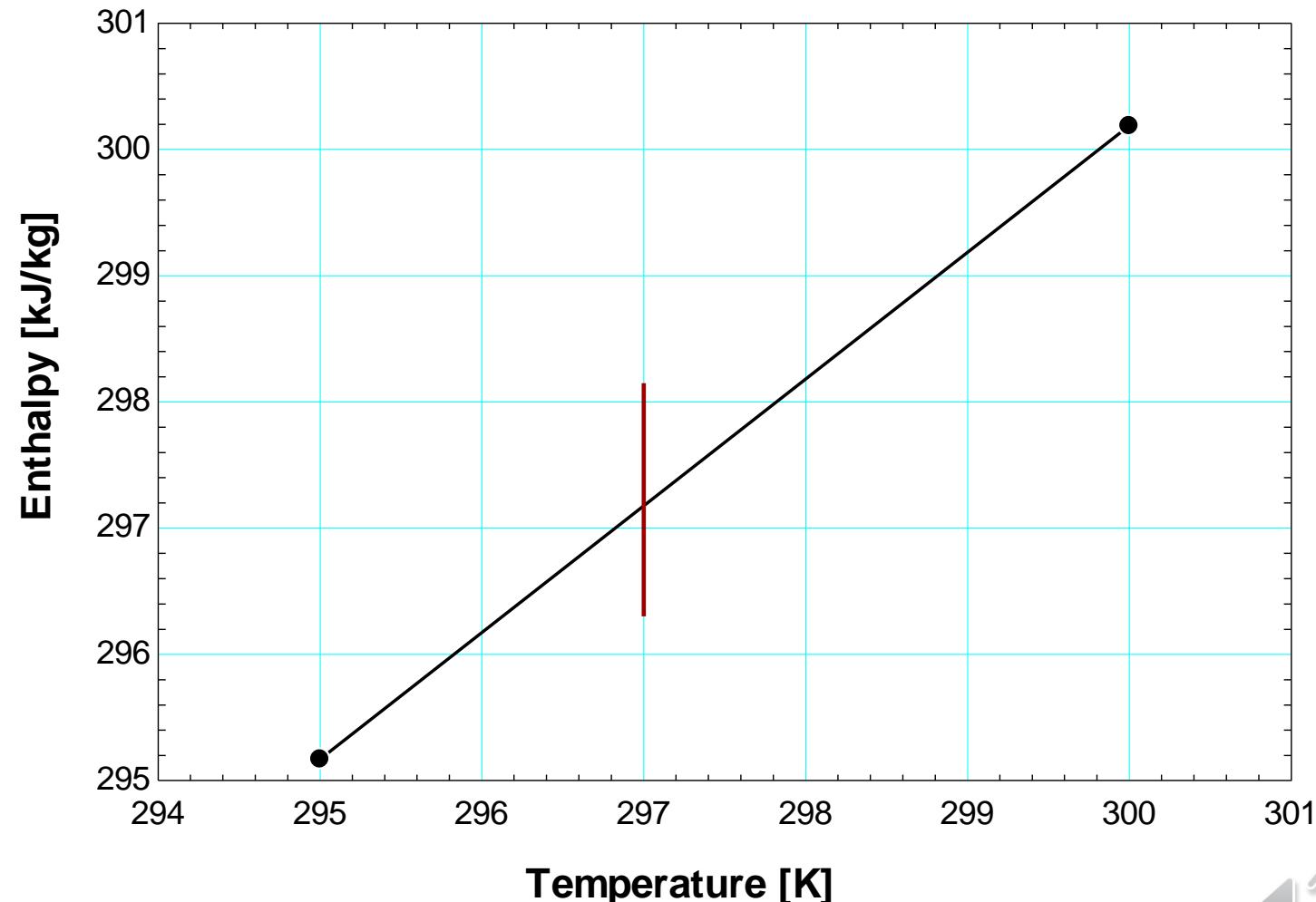
So the kinetic energy should reduce with time due to the work to power the light



However, Homer says that it keeps going faster – so the kinetic energy keeps increasing. Therefore, Lisa has violated the first law of thermodynamics

# Interpolating properties from tables

- You will often need properties at conditions (temperature, pressure, etc.) that are not given in the tables. When that happens, you need to interpolate values
  - Tables are set up to give properties at small enough intervals that linear interpolation gives an excellent estimate of the real values
- The technique is to fit a line between two points and find the intermediate value



# Interpolation example

Find the enthalpy,  $h$ , of air at 297 K

- From Appendix 7: Ideal Gas Properties for Air we get:

$T, \text{K}$	$h, \text{kJ/kg}$	$P_r$	$u, \text{kJ/kg}$	$v_r$	$s^o, \text{kJ/kgK}$
200	199.97	0.3363	142.56	1707.0	1.29559
210	209.97	0.3987	149.69	1512.0	1.34444
220	219.97	0.4690	156.82	1346.0	1.39105
230	230.02	0.5477	164.00	1205.0	1.43557
240	240.02	0.6355	171.13	1084.0	1.47824
250	250.05	0.7329	178.28	979.0	1.51917
260	260.09	0.8405	185.45	887.8	1.55848
270	270.11	0.9590	192.60	808.0	1.59634
280	280.13	1.0889	199.75	738.0	1.63279
285	285.14	1.1584	203.33	706.1	1.65055
290	290.16	1.2311	206.91	676.1	1.66802
295	295.17	1.3068	210.49	647.9	1.68515
300	300.19	1.3860	214.07	621.2	1.70203

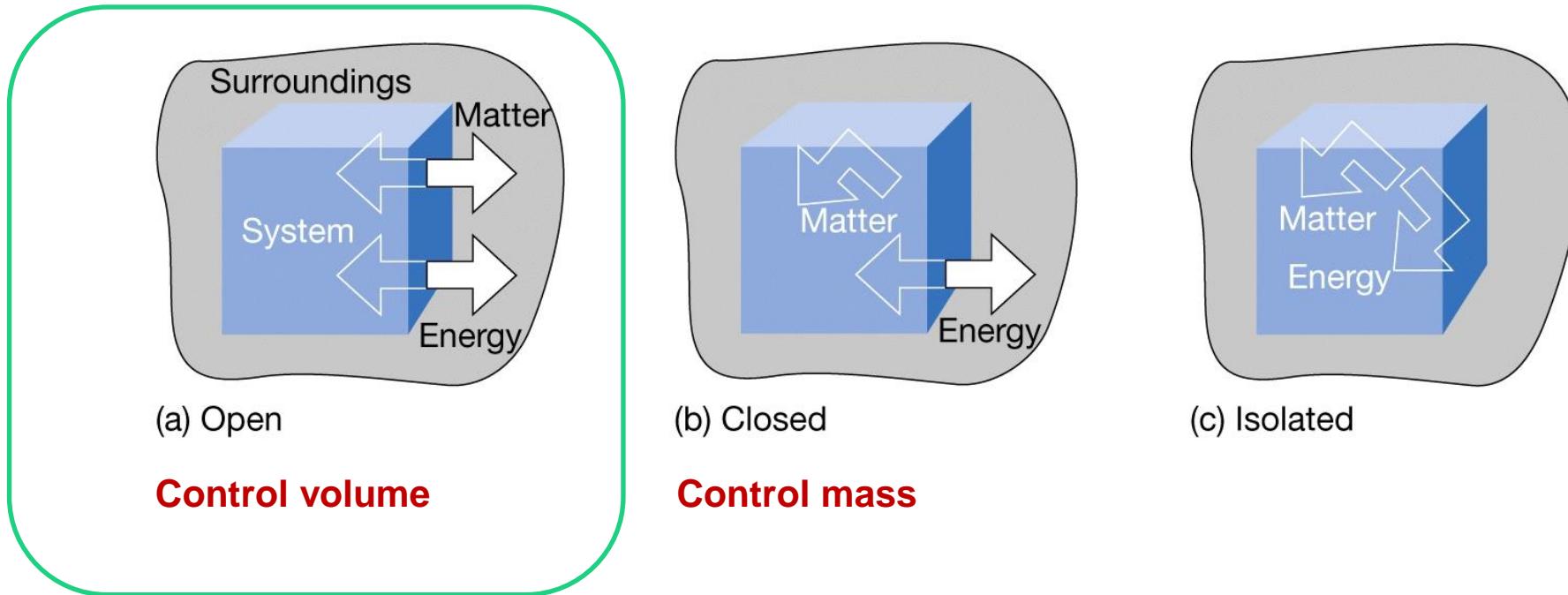
- Let's call point 1 295 K and point 2 300 K. Then the equation of the line will be:

$$h(T) = \frac{h_2 - h_1}{T_2 - T_1} (T - T_1) + h_1$$

- Then for a temperature of 297 K we can calculate the enthalpy

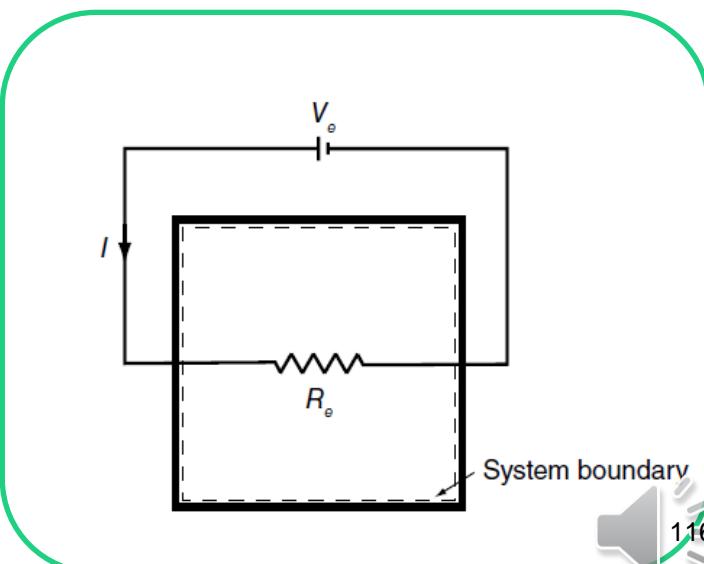
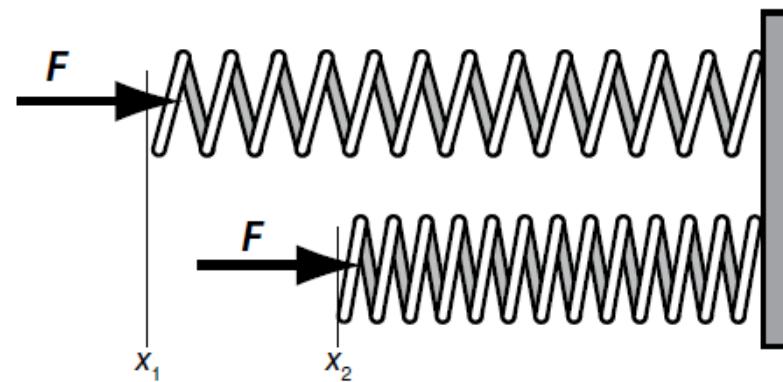
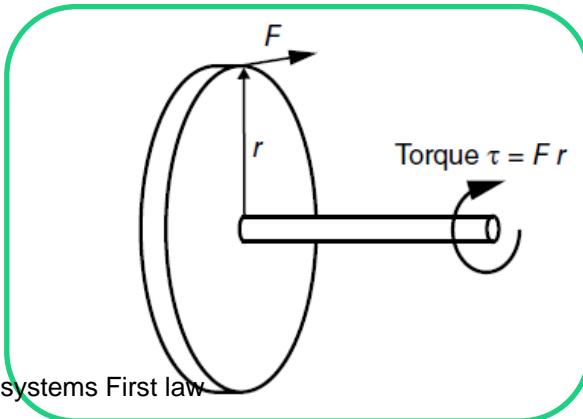
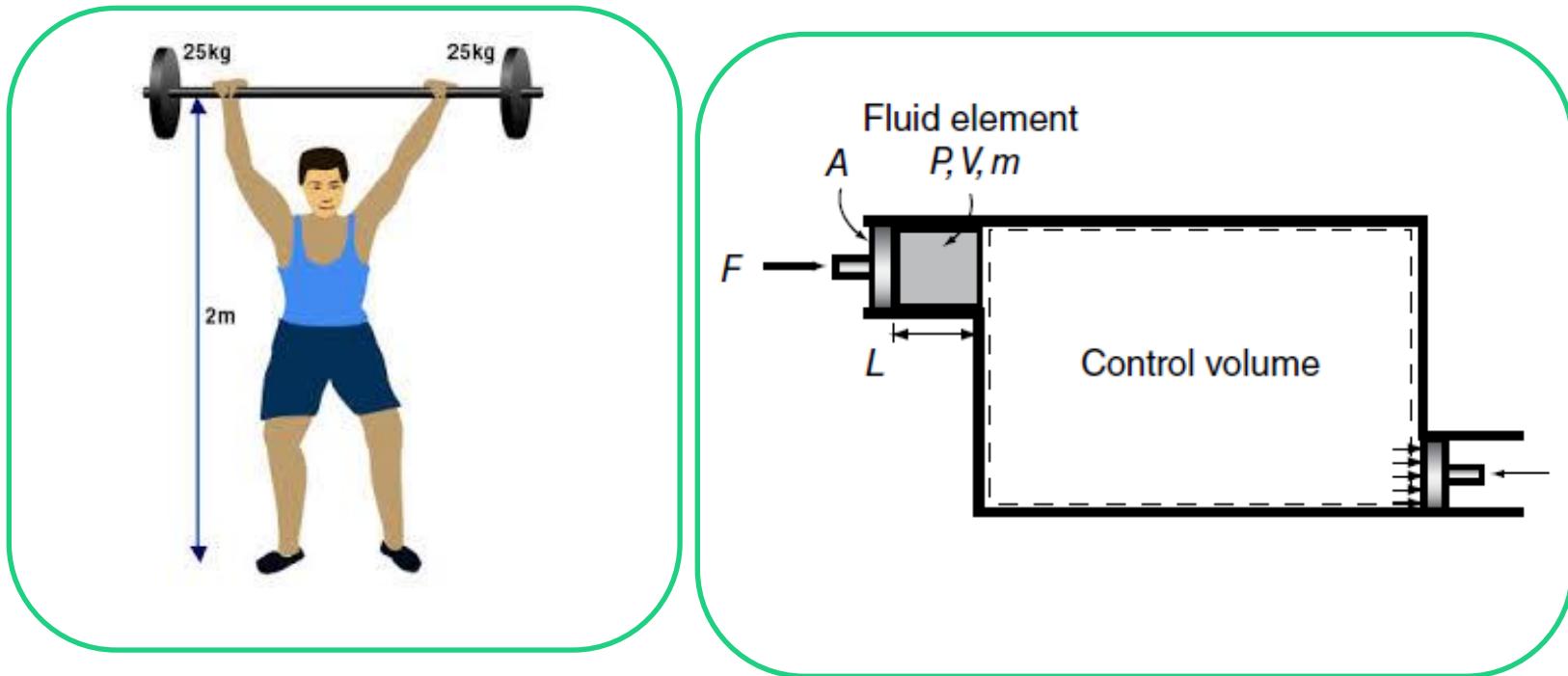
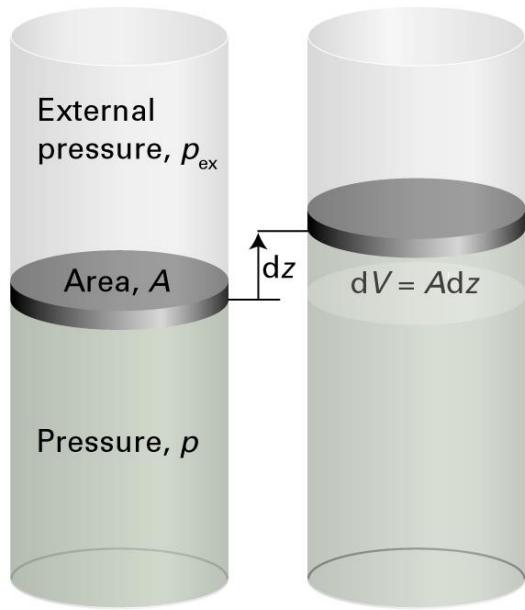
$$h(297 \text{ K}) = \frac{300.19 \frac{\text{kJ}}{\text{kg}} - 295.17 \frac{\text{kJ}}{\text{kg}}}{300 \text{ K} - 295 \text{ K}} (297 \text{ K} - 295 \text{ K}) + 295.17 \frac{\text{kJ}}{\text{kg}} = 297.18 \frac{\text{kJ}}{\text{kg}}$$

# Open systems



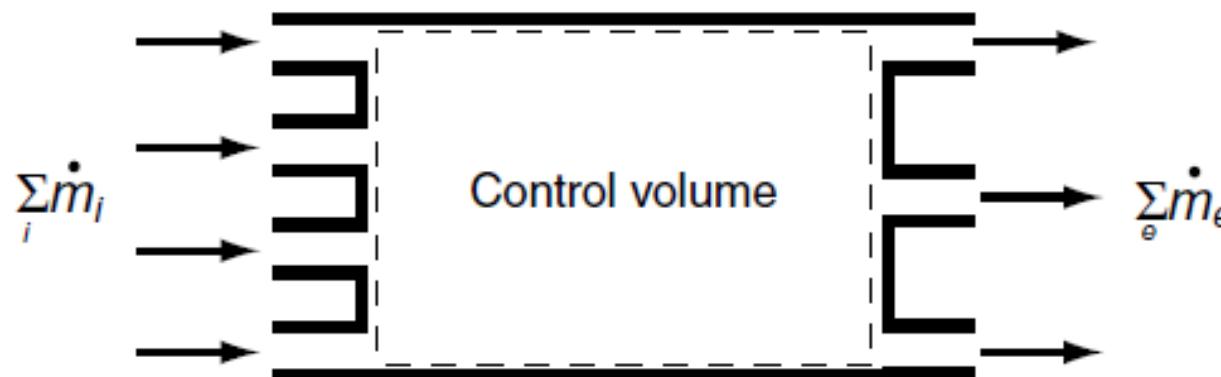
- Rather than a control mass, we have a control volume where mass enters and exits
- There can be heat and work interaction with the surroundings

# Types of work



# Open systems – mass balance

- The difference between an open and closed system is that there is a mass flow into and out of the control volume
  - There will be flow work and a mass balance is also required
- We will focus on steady state operation where the flow and work interactions have gone on long enough that the control volume remains constant with time



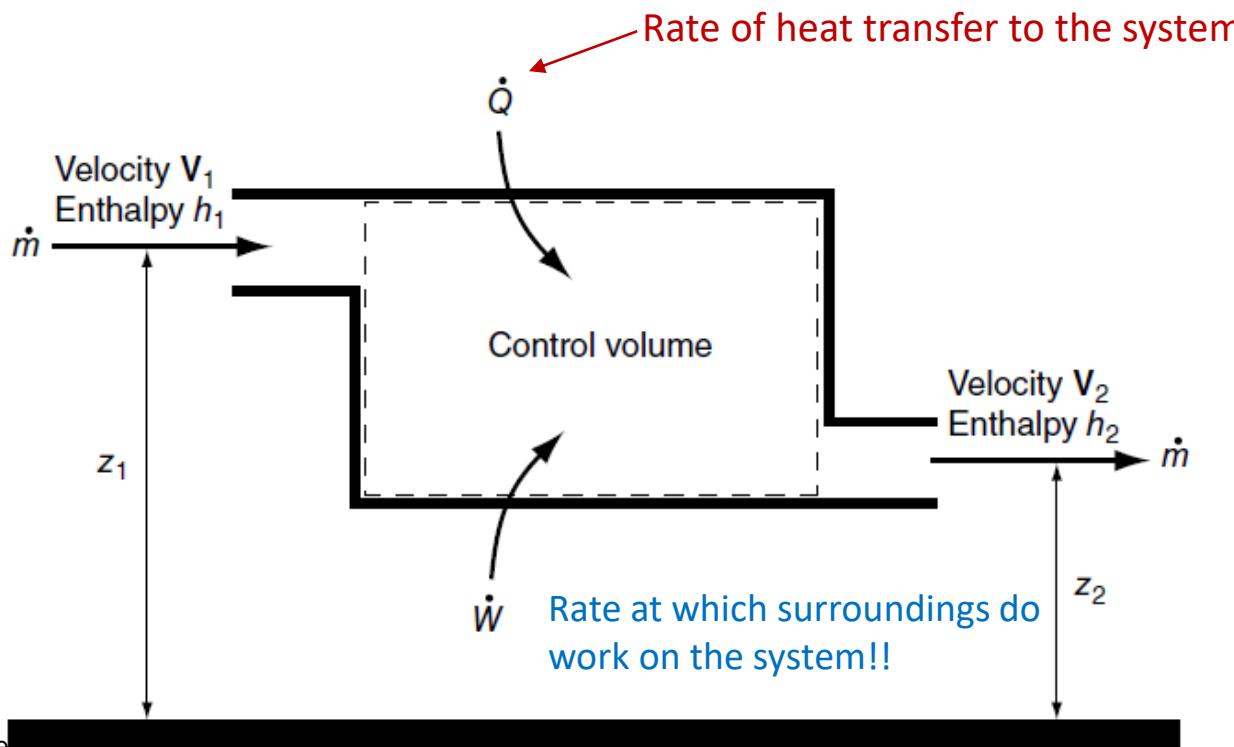
$$\dot{m} = \rho V A_c$$

Where  $\dot{m}$  is mass flow rate,  $\rho$  is the fluid density,  $V$  is the average velocity and  $A_c$  is the cross sectional area.

$$\sum \dot{m}_i = \sum \dot{m}_e$$

# Applying the 1<sup>st</sup> Law to a single inlet/single outlet control volume

- The energy balance concept for an open system is exactly the same as for a closed system – we just need to account for mass flow
- At steady state, mass flowing into the system equal the mass flowing out and the energy entering the control volume is the same as the energy leaving the control volume

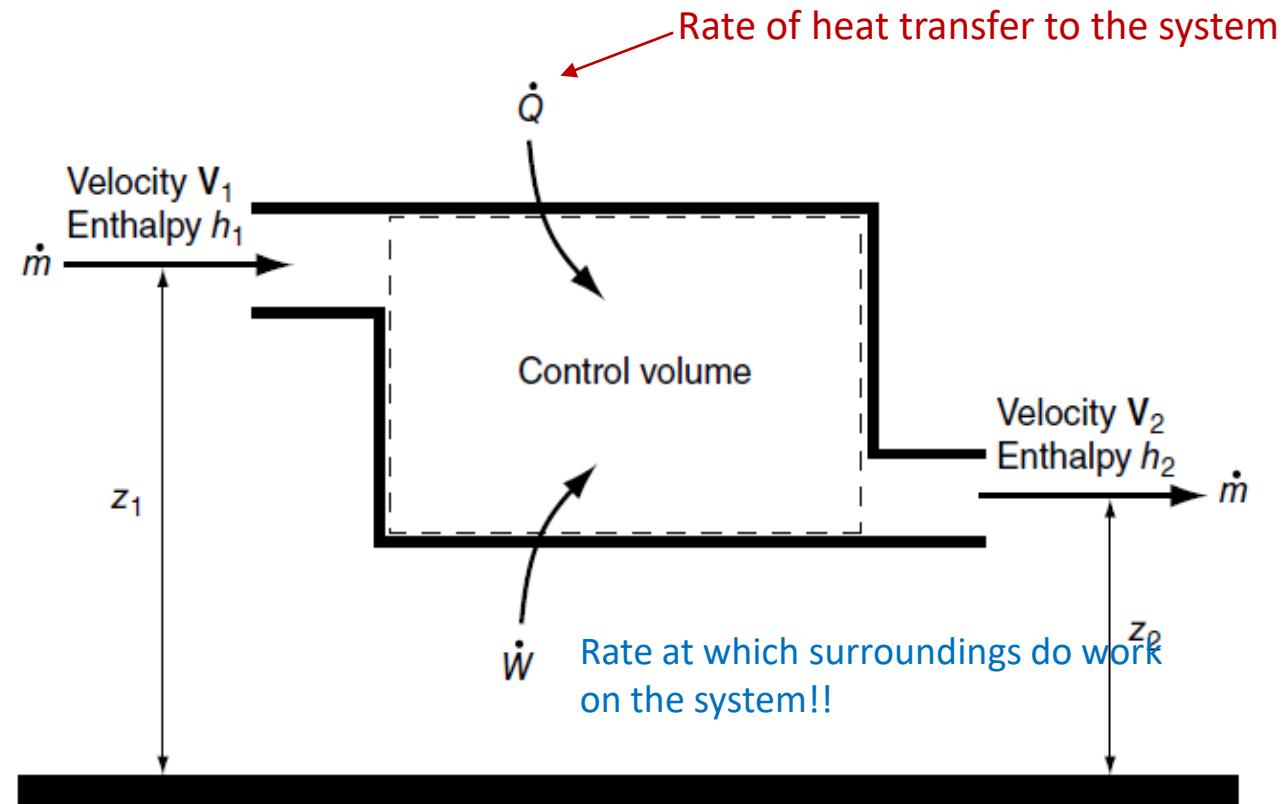


$$\frac{dE_{in}}{dt} = \frac{dE_{out}}{dt}$$

# 1<sup>st</sup> Law energy balance: single inlet/single outlet control volume

- At steady state, the energy in is the same as the energy out. Accounting for all forms over energy entering and exiting the system gives the energy balance for an open system
- For a single inlet, single outlet  $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left( u + P v + \frac{v^2}{2} + gz \right)_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left( u + P v + \frac{v^2}{2} + gz \right)_{out}$$



- Enthalpy a property that is convenient to use when analyzing open systems. It is referred to as  $h$  for specific enthalpy and  $H$  for total enthalpy. The definition of specific enthalpy is given by Eq. 4.48

$$h = u + P v$$

- There is a separate specific heat that corresponds to enthalpy and that is the specific heat at constant pressure,  $c_p$ . It is defined in Eq. 4.58 as

$$c_p \equiv \left( \frac{\partial h}{\partial T} \right)_p$$

- When you want to calculate the change in internal energy, use  $c_v$  and when you want to calculate the change in enthalpy, use  $c_p$

# 1<sup>st</sup> Law energy balance using enthalpy

- The first law for an open system is usually stated in terms of enthalpy, where we substitute  $u + P v = h$
- Then for a single inlet and a single outlet, the energy balance becomes:

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left( h + \frac{v^2}{2} + gz \right)_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left( h + \frac{v^2}{2} + gz \right)_{out}$$

# Problems 3a

4.60

4.66

4.68

4.82

# Problems 3a - solutions

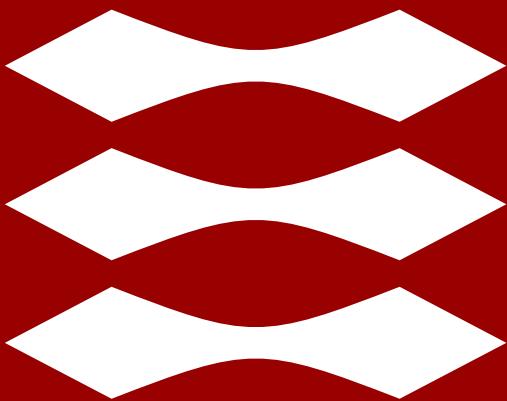
4.60 Heater power is 80.9 kW

4.66 0.646 kg/s

4.68 311 K

4.82 Heat loss is 9.83 kW

# DTU



47201 Engineering thermodynamics

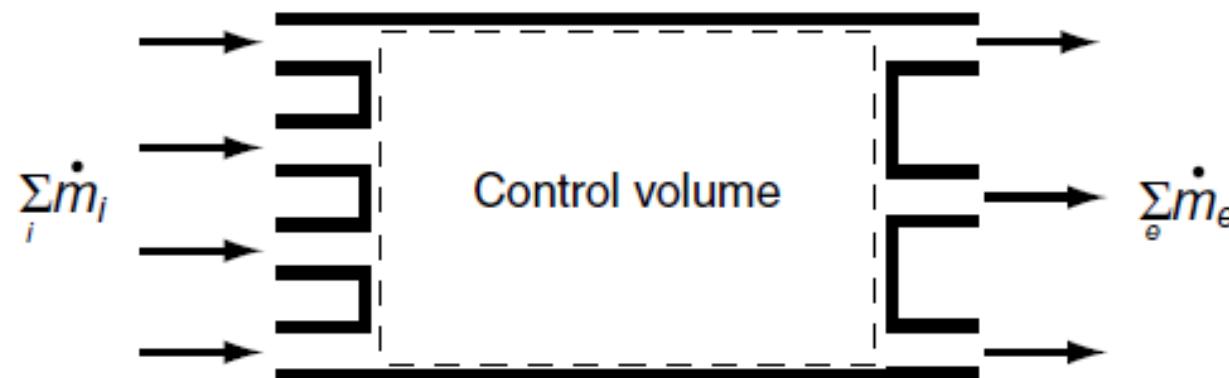
# Lecture 3b: First law for open systems (Ch 4.13-4.16)



# Open systems – multiple inlets and outlets

For systems with multiple inlets and outlets, it is just a matter of performing the same analysis on each stream. For steady state:

$$\sum_{i=1}^{\# \text{inlets}} \dot{m}_{in,i} \left( h_{in,i} + \frac{1}{2} v_{in,i}^2 + gz_{in,i} \right) + \sum_{i=1}^{\# \text{heat terms}} \dot{Q}_i + \sum_{i=1}^{\# \text{work terms}} \dot{W}_i = \sum_{i=1}^{\# \text{outlets}} \dot{m}_{out,i} \left( h_{out,i} + \frac{1}{2} v_{out,i}^2 + gz_{out,i} \right) + \sum_{i=1}^{\# \text{heat terms}} \dot{Q}_{out} + \sum_{i=1}^{\# \text{work terms}} \dot{W}_{out}$$



# When to use $c_v$ or $c_p$ (section 4.10)

- When we deal with state variables, often we only care about the internal energy or enthalpy at the end of some process. In this case, we can use  $c_v$  if we are looking at the internal energy and  $c_p$  when looking at the enthalpy. For an ideal gas,  $c_v$  is a function only of temperature.
  - Using the definition of enthalpy  $h = u + Pv$  and substituting the ideal gas law for the pressure and specific volume gives
$$h = u + R T$$
  - Then using the definition of  $c_p$
- So for an ideal gas,  $c_p$  is also a function only of temperature. However, for most other fluids,  $c_p$  and  $c_v$  are a function of both temperature and pressure and possibly other fields.
- For example, for an incompressible liquid  $c_p(T) = c_v(T) = c(T)$  (Eq. 4.86)

$$\Delta u = \int_{T_1}^{T_2} c \, dT$$
$$\Delta h = \int_{T_1}^{T_2} c \, dT + \int_{v_1}^{v_2} v \, dP \quad Eq \ (4.88)$$

# Methodology for solving thermodynamics problems

1. Carefully review the problem statement and what is known.
2. Choose the system.
3. Apply a mass balance on the chosen system
4. Apply an energy balance on the chosen system

# Steady Flow Devices – Turbines and Compressors

**Turbine :**

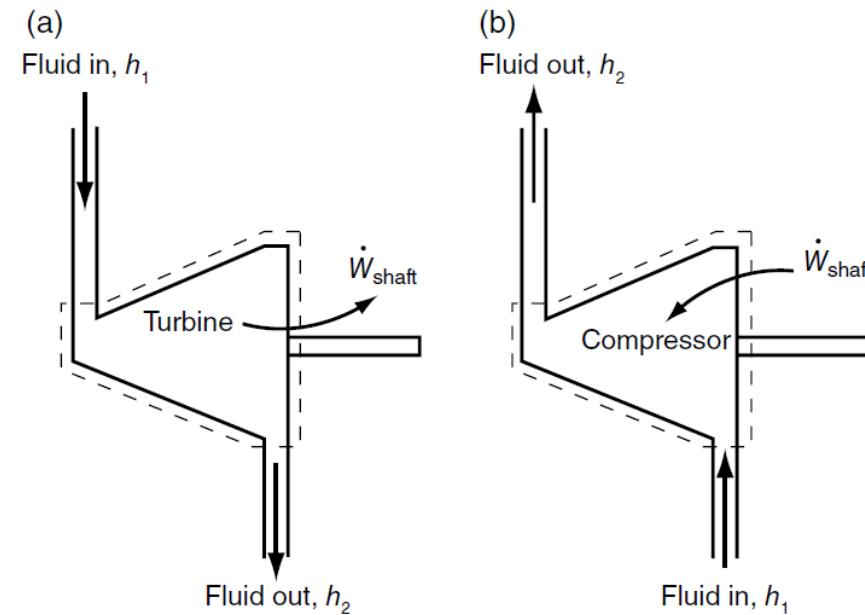
device that uses a high energy fluid flow to turn a shaft (output work)

**Compressor :**

A device that increases the pressure (and temperature) of a gas (requires work input)

The first law energy balance for a turbine

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{out}$$



If  $Q=0$  (Thermal insulated)  
 $z_2 = z_1$  and  $V_2 = V_1$ ;

$$\dot{W}_{shaft} = \dot{m} (h_{out} - h_{in})$$



Calculated from  $C_p$

# Steady Flow Devices – Pumps

A pump refers to a device that increase the elevation or pressure of a liquid, while a compressor increases the pressure or elevation of a gas.

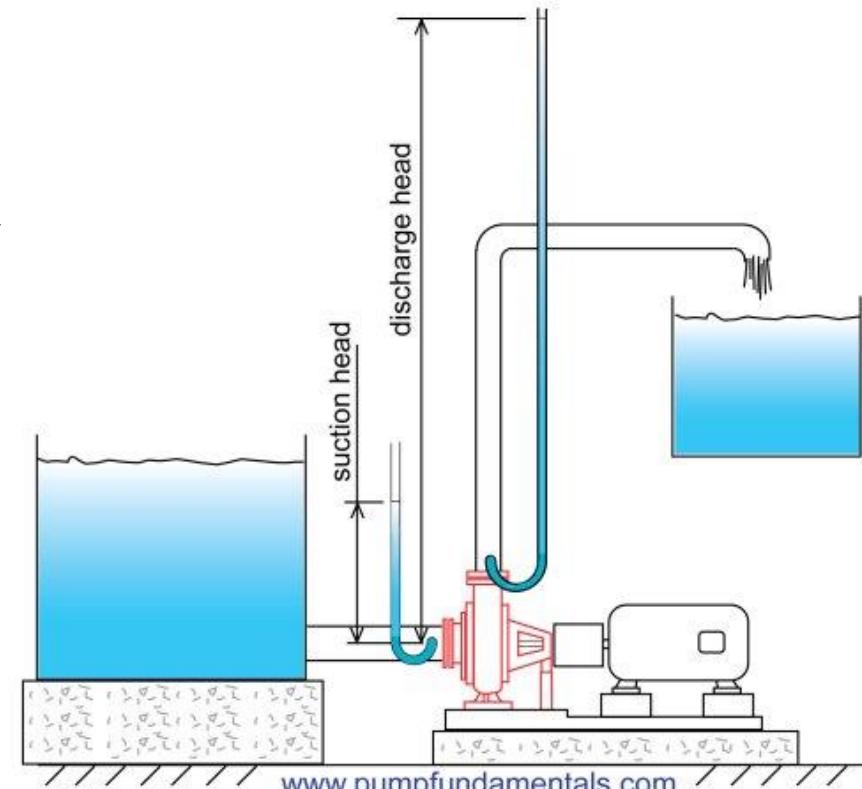
So for a pump, we assume an incompressible liquid

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{out}$$

$$\dot{W}_{shaft} = \dot{m} \left[ (h_2 - h_1) + g(z_2 - z_1) \right].$$

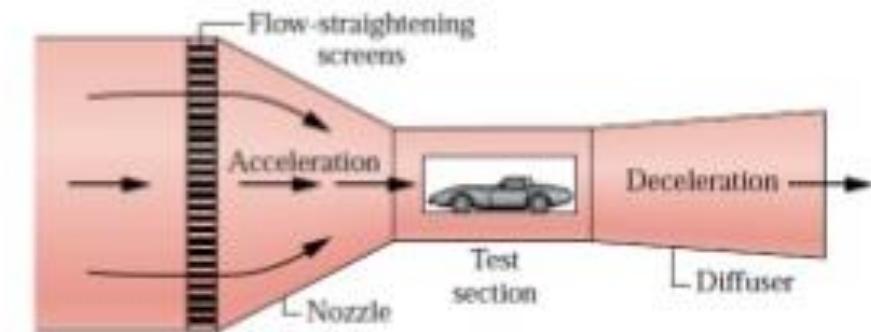
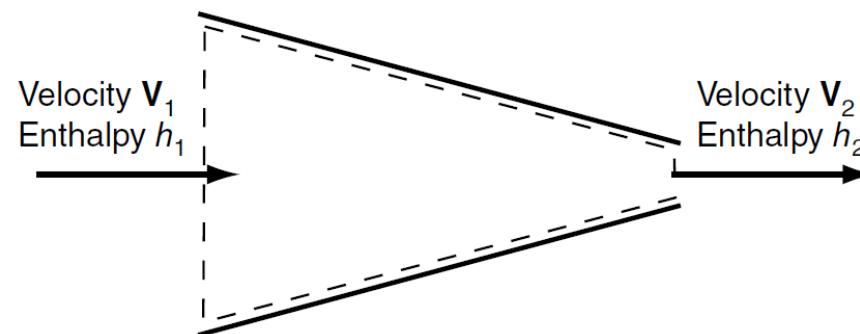
$$h_2 - h_1 = c(T_2 - T_1) + v(P_2 - P_1)$$

$$\dot{W}_{shaft} = \dot{m} \left[ v(P_2 - P_1) + g(z_2 - z_1) \right].$$



# Steady Flow Devices – Nozzles and Diffusers

**Nozzle:** device to accelerate gases before expelled



**Diffuser** = “reverse operation” of nozzle

The first law energy balance for a nozzle:

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{out}$$

$$V_2 = \sqrt{2(h_1 - h_2)}.$$

No potential energy changes, no heat transfer, no work, and  $V_2 >> V_1$

# Problems 3b

4.76

4.77

4.80

4.81

# Problems 3b with solutions

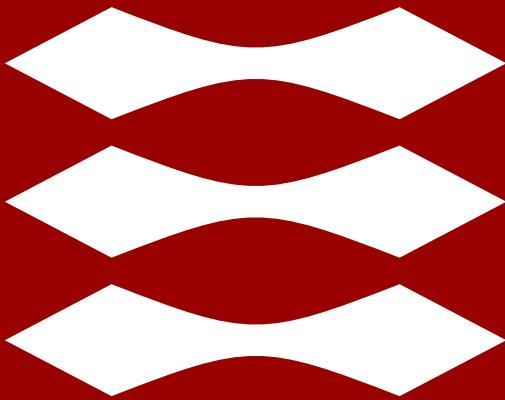
4.76 Power to compressor is 140 kW

4.77 502.2

4.80 369 C

4.81 644.6 kW

**DTU**



47201 Engineering thermodynamics

# Module 4

# Heat transfer

# What is heat?

Heat is a mechanism of energy *transfer* between bodies or different regions within a body.

It has the unit of energy, but it's not to be confused with the internal energy  $U$  of a body.

It does *not* make sense to ask how much heat is within a body, but only how much heat has been transferred between two bodies.

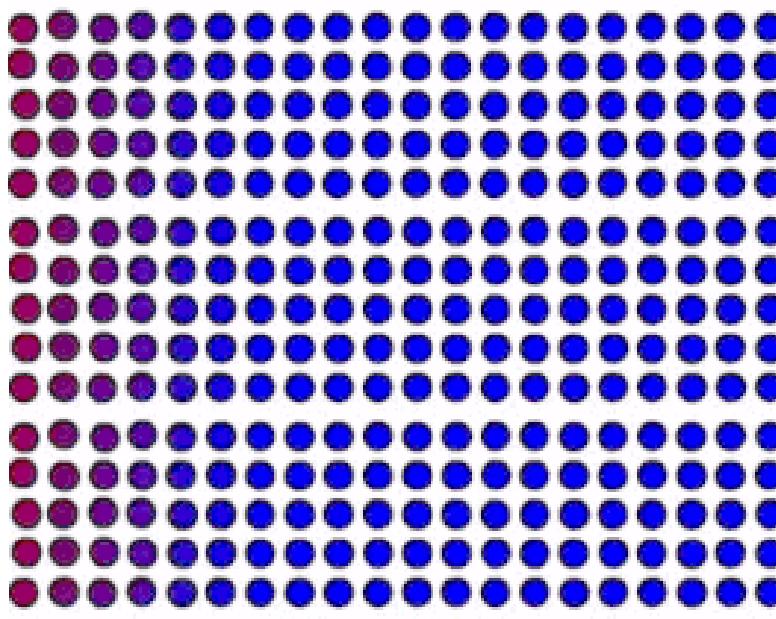
This process happens spontaneously: it cannot be controlled

It happens at the microscopic level: it cannot be directly observed

It happens because of the randomness of microscopic interactions. When there is a lot of these interaction, the overall effect becomes predictable.

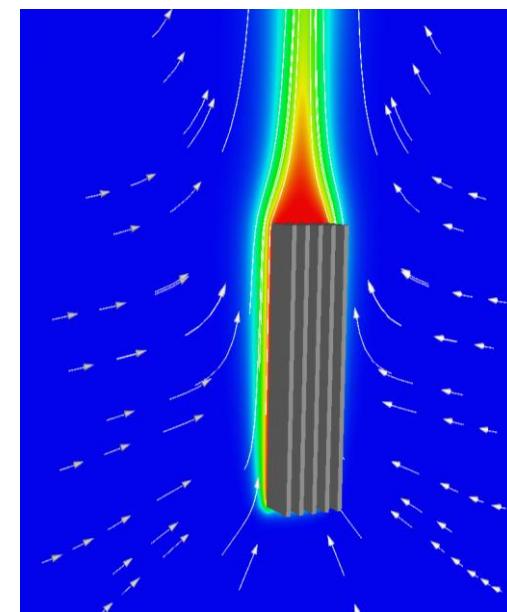


# The three mechanisms of heat transfer



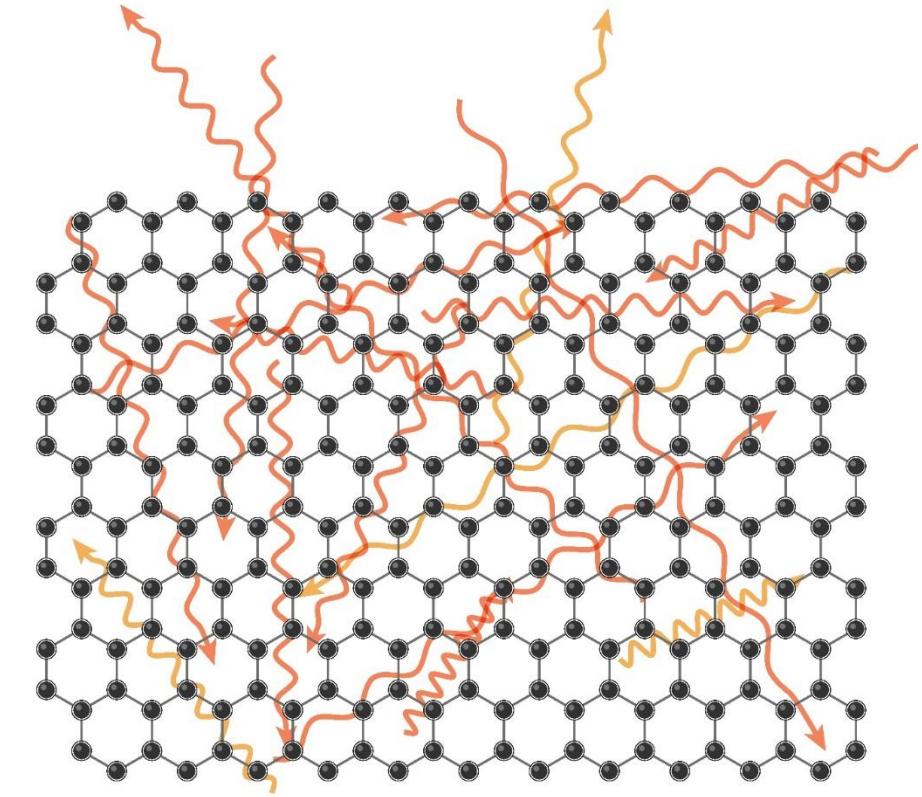
## Conduction

Vibration and collisions of molecules and  $e^-$  in solids or fluids



## Convection

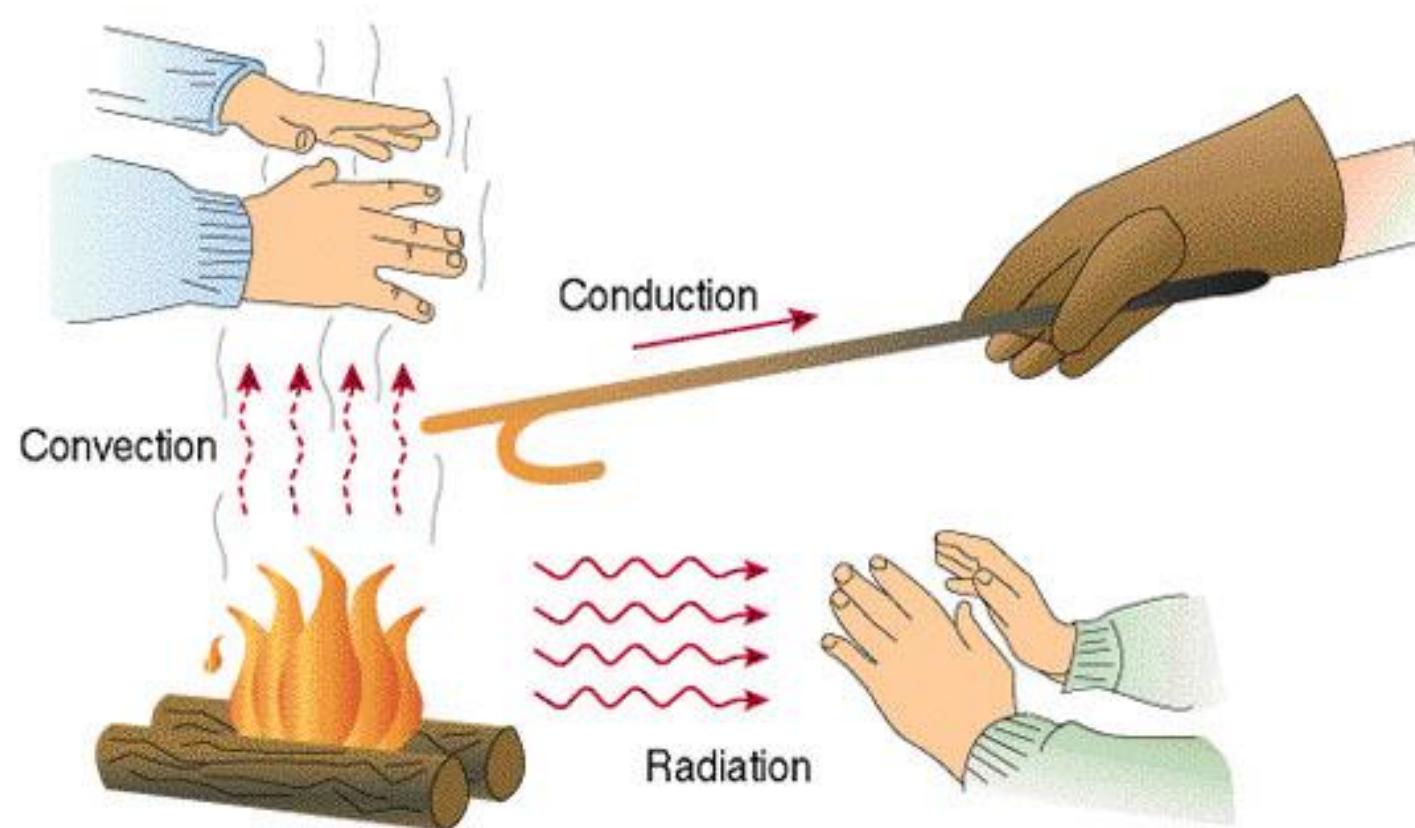
Associated to the flow in fluids  
(forced or natural flow)



## Radiation

Mediated by (thermal) photons emitted and absorbed by solids

# The three mechanisms of heat transfer



# How does it work? It follows the second law

- Heat flows spontaneously from warmer bodies (higher temperature) to colder ones (lower T).
- Within a body, if temperature gradients are present, it flows from warmer regions to colder ones.
- The higher the temperature difference, the higher is the rate of heat transfer.
- When two bodies are in thermal equilibrium, i.e. same T, or when within a body there are no temperature gradients, there is no heat flow.



# Physical quantities

$Q$  Heat [J]

$\dot{Q}$  Heat flux (or heat transfer rate) [W = J/s]

$q$  Heat flux (surface) density [W/m<sup>2</sup> = J/(s m<sup>2</sup>)]

$T$  Temperature [K]

$\nabla T$  Temperature gradient [K/m]

$\dot{Q}_{\text{vol}}$  Volumetric heat source [W/m<sup>3</sup>]

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How do we compute each of these two quantities from the other one?

# Physical quantities

$Q$  Heat [J]

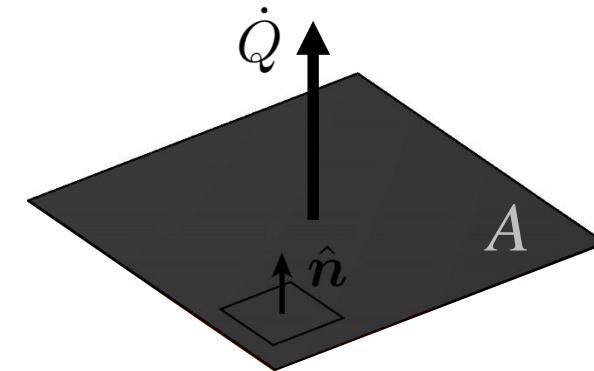
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$\dot{Q}_{\text{vol}}$  Volumetric heat source [ $W/m^3$ ]



$$\mathbf{q} = \frac{\dot{Q}}{A} \hat{n}$$

$$\dot{Q} = \iint \hat{n} \cdot \mathbf{q} dS$$

# Physical quantities

$Q$	Heat [J]
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$\nabla T$	Temperature gradient [K/m]
$\dot{Q}_{\text{vol}}$	Volumetric heat source [W/m <sup>3</sup> ]

## Properties of materials / bodies

\*extensive – #intensive

$C$	Heat capacity * [J/K]
$c$	Specific heat capacity # [J/(kg K)]
$R_{\text{heat}}$	Thermal (or heat) resistance * [K/W]
$1/R_{\text{heat}}$	Thermal conductance * [W/K]
$k$	Thermal (or heat) conductivity # [W/(m K)]
$1/k$	Thermal (or heat) resistivity # [m K/ W]
$\alpha = \frac{k}{\rho c}$	Thermal diffusivity # [m <sup>2</sup> /s]

# Heat conduction

# Microscopic view of heat conduction

It is a diffusion phenomenon: caused by probabilistic effects.

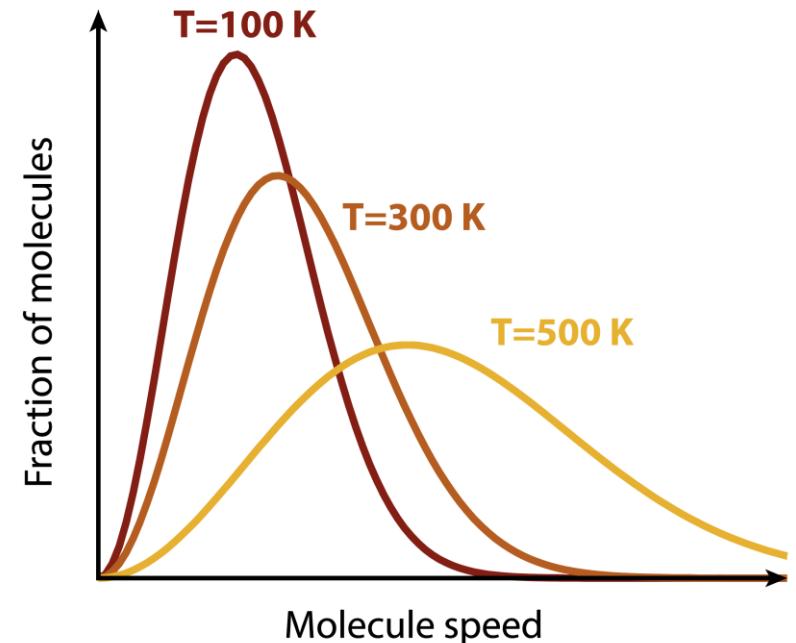
- In a *fluid*: random thermal motion of free molecules
- In a *solid*: random thermal vibration of ions in the lattice

The warmer the material (i.e. higher the temperature),  
the faster are the molecules moving.

If initially they are faster in a certain region than elsewhere,  
(i.e. if temperature gradients are present), then random collisions  
and other interactions will eventually equilibrate things  
(i.e. the temperature will become uniform).

In solids, the quantum mechanical description of vibration is given  
in terms of phonons: collective modes of vibrations of the ions in the lattice.

Example: ideal gas  
Maxwell-Boltzmann distribution



# Newton's law of cooling

Heat flows from warmer bodies (higher temperature) to colder ones (lower temperature).

The normal component of the heat flux density is proportional to the temperature difference.

$$\mathbf{q} \cdot \hat{\mathbf{n}} = -h\Delta T$$

$h$  is the heat transfer coefficient. *What are its units?*



# Newton's law of cooling

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$$\mathbf{q} \cdot \hat{\mathbf{n}} = -h\Delta T$$

$h$  is the heat transfer coefficient. What are its units?

Heat transfer coefficient *between two bodies*.

Clearly, it depends on a lot of things:

- roughness
- materials involved
- ...



# Newton's law of cooling

Heat flows from warmer bodies (higher temperature) to colder ones (lower temperature).

The normal component of the heat flux density is proportional to the temperature difference.

$$\mathbf{q} \cdot \hat{\mathbf{n}} = -h\Delta T$$

$h$  is the heat transfer coefficient.

As the colder body absorbs heat, and the warmer body releases heat, the temperature difference decreases until thermal equilibrium is reached.

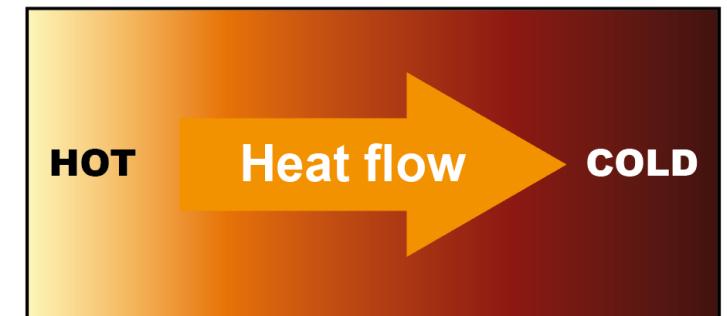
**Thermal equilibrium:**  
same temperature  
no heat transfer

# Fourier's law of heat conduction

The heat flux density,  $q$ , is directed opposite to the temperature gradient  $\nabla T$ .

The proportionality factor is the thermal conductivity,  $k$ , of the material. *What are its units?*

$$q = -k \nabla T \xrightarrow{\text{in 1D}} q_x = -k \frac{\partial T}{\partial x}$$

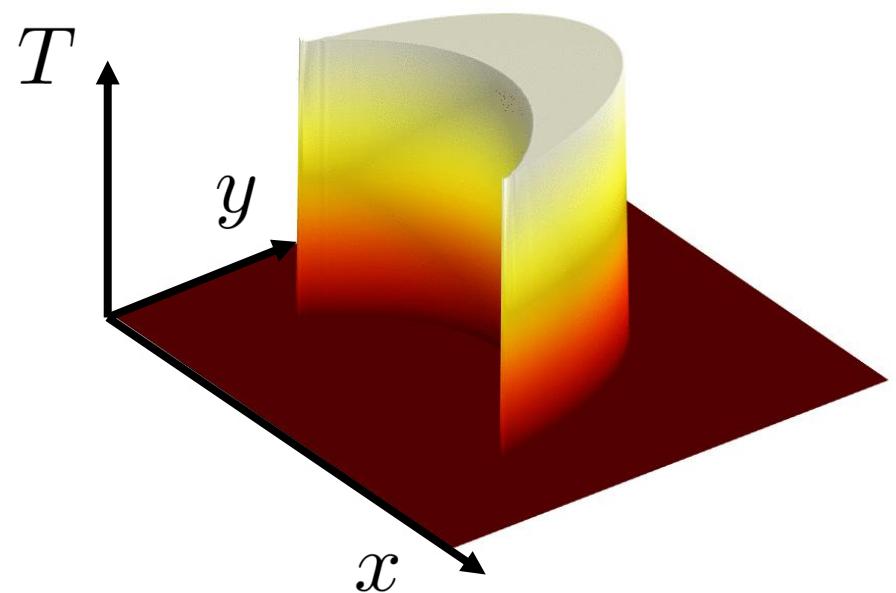


# Heat equation and thermal circuits

# The heat equation

How does the temperature,  $T$ , evolve inside a solid material?

$T = T(x, y, z, t)$  is a **continuous** function.



$$T = T(x, y, t)$$

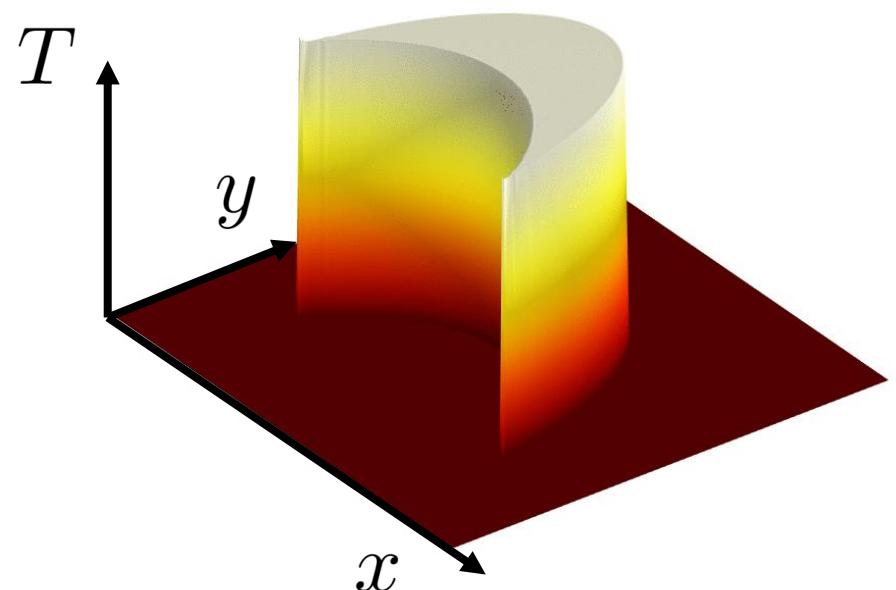
# The heat equation

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$T = T(x, y, z, t)$  is a **continuous** function.

The time-evolution is governed by:

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T; \quad \alpha : \text{diffusivity}$$



$$T = T(x, y, t)$$

# The heat equation

How does the temperature,  $T$ , evolve inside a solid material?

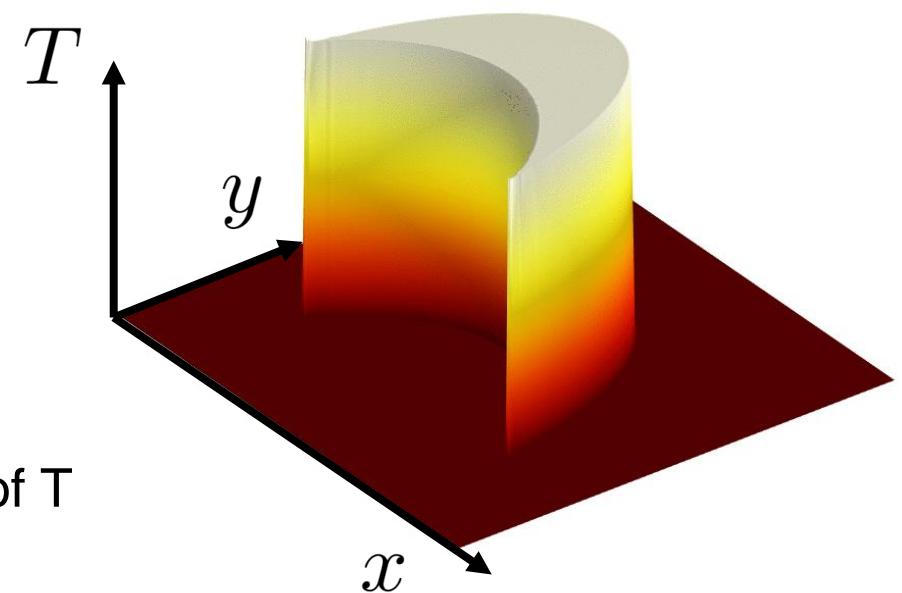
$T = T(x, y, z, t)$  is a **continuous** function.

The time-evolution is governed by:

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T; \quad \alpha : \text{diffusivity}$$

This equation relates the first-order time-derivative of  $T$  with its second-order space-derivative.

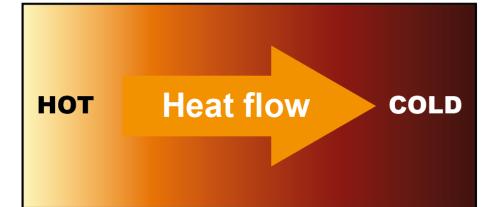
**Laplace operator**  $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$



$$T = T(x, y, t)$$

# Deconstructing the heat equation

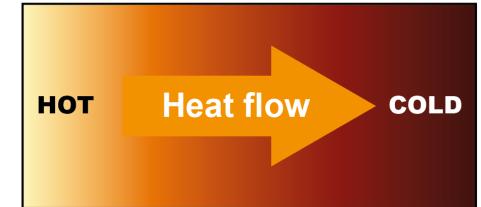
- Fourier's law of heat conduction  $q = -k \nabla T$



The heat flux density,  $q$ , is directed opposite to the temperature gradients.  
The proportionality factor is the thermal conductivity,  $k$ , of the material.

# Deconstructing the heat equation

- Fourier's law of heat conduction  $q = -k \nabla T$

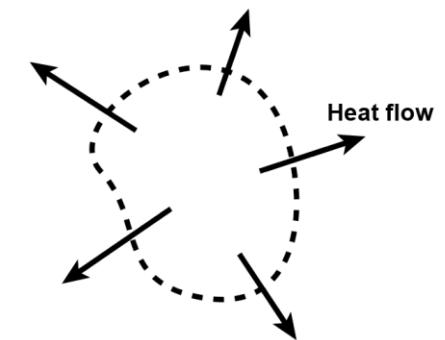


The heat flux density,  $q$ , is directed opposite to the temperature gradients.

The proportionality factor is the thermal conductivity,  $k$ , of the material.

- Energy conservation

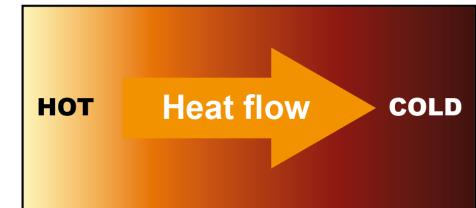
$$\frac{\partial U_{\text{vol}}}{\partial t} = -\nabla \cdot q$$



The time derivative of the internal energy density,  $U_{\text{vol}}$  in a point is the amount of heat flowing “into that point”, i.e. the opposite of the divergence of the heat flux density.

# Deconstructing the heat equation

- Fourier's law of heat conduction  $q = -k \nabla T$



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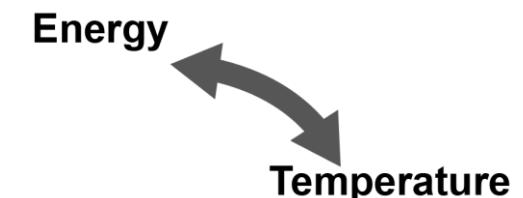
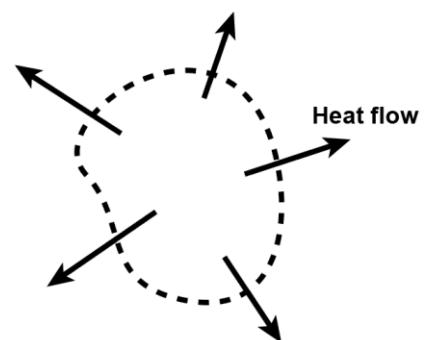
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The time derivative of the internal energy density,  $U_{\text{vol}}$  in a point is the amount of heat flowing “into that point”, i.e. the opposite of the divergence of the heat flux density.

- Heat capacity

$$\frac{\partial T}{\partial t} = \frac{1}{c\rho} \frac{\partial U_{\text{vol}}}{\partial t}$$

The temperature variation is related to the variation of the internal energy via the specific heat capacity,  $c$ , and the mass density,  $\rho$ .



$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T, \quad \alpha = \frac{k}{c\rho}$$

# Deconstructing the heat equation

- Fourier's law of heat conduction  $q = -k \nabla T$

- Energy conservation

$$\frac{\partial U_{\text{vol}}}{\partial t} = -\nabla \cdot q \rightarrow \frac{\partial T}{\partial t} = -\frac{1}{c\rho} \nabla \cdot q$$

- Heat capacity

$$\frac{\partial T}{\partial t} = \frac{1}{c\rho} \frac{\partial U_{\text{vol}}}{\partial t}$$

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T, \quad \alpha = \frac{k}{c\rho}$$

## Deconstructing the heat equation

- Fourier's law of heat conduction

$$q = -k \nabla T$$



$$\frac{\partial T}{\partial t} = \frac{1}{c\rho} \nabla \cdot (k \nabla T)$$

- Energy conservation

$$\frac{\partial U_{\text{vol}}}{\partial t} = -\nabla \cdot q$$



$$\frac{\partial T}{\partial t} = -\frac{1}{c\rho} \nabla \cdot q$$

- Heat capacity

$$\frac{\partial T}{\partial t} = \frac{1}{c\rho} \frac{\partial U_{\text{vol}}}{\partial t}$$

# Deconstructing the heat equation

- Fourier's law of heat conduction

$$\mathbf{q} = -k \nabla T$$

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T, \quad \alpha = \frac{k}{c\rho}$$

↑  
Uniform  $k$   
↓

$$\frac{\partial T}{\partial t} = \frac{1}{c\rho} \nabla \cdot (k \nabla T)$$

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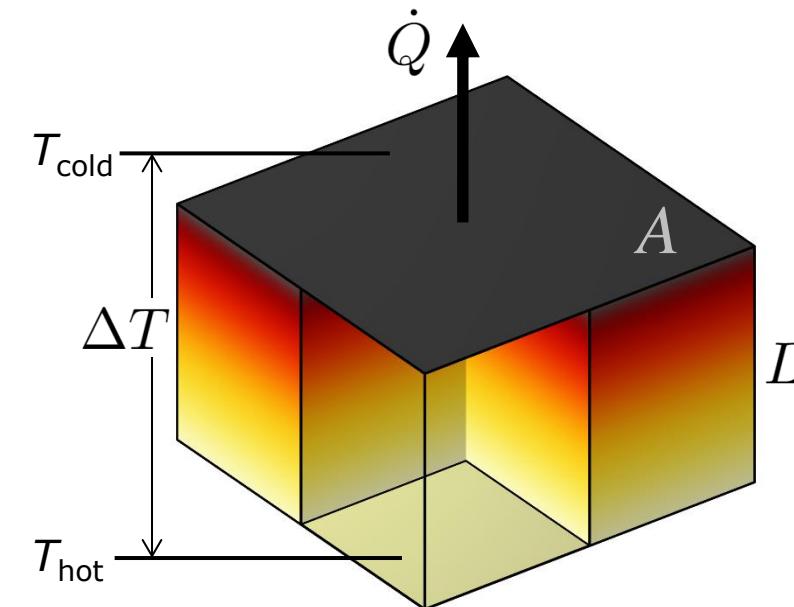
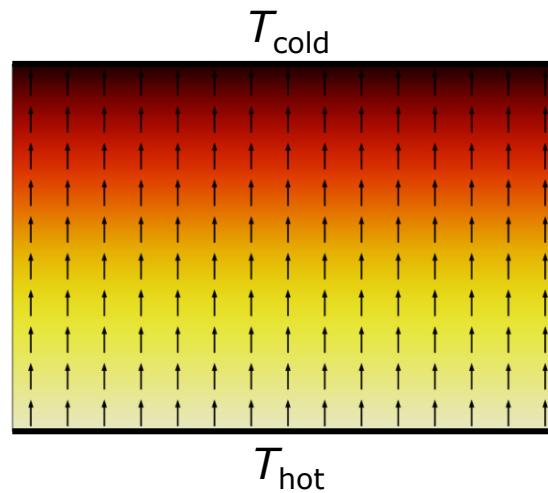
- Heat capacity

$$\frac{\partial T}{\partial t} = \frac{1}{c\rho} \frac{\partial U_{\text{vol}}}{\partial t}$$

# From continuous to discrete

Let's consider a block of conductive material surrounded by an insulating medium. The bottom and top faces are *kept at fixed temperatures*  $T_{\text{hot}}$  and  $T_{\text{cold}}$ , respectively.

A temperature gradient will thus be established along the vertical direction, accompanied by a corresponding heat flow.

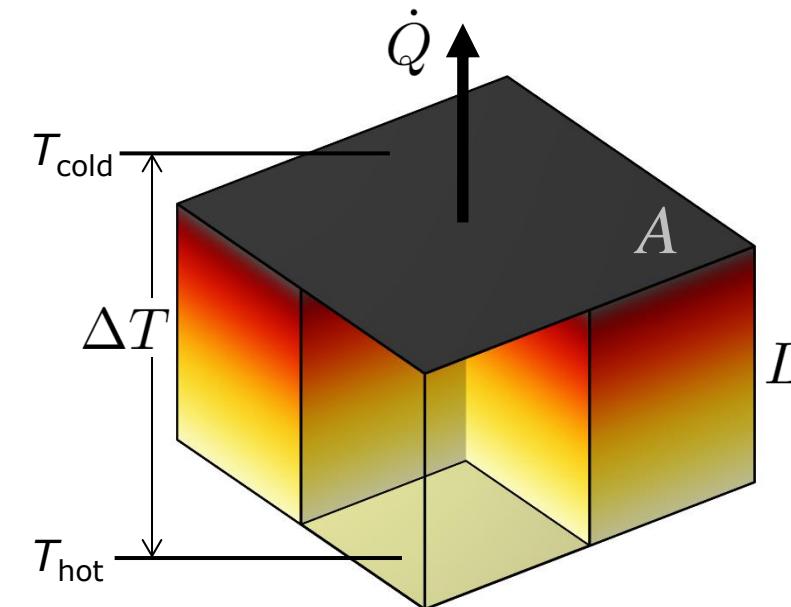
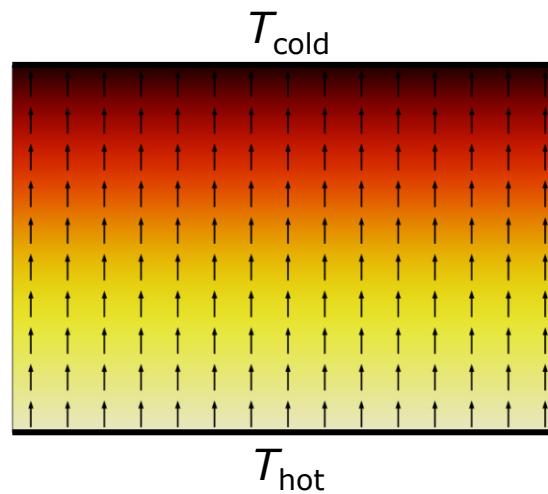


# The lumped-element model: Circuits

This situation is the most essential. We can express it in terms of the net amounts:

$$\|q\| = \dot{Q}/A, \text{ total heat transfer rate } \dot{Q} \leftrightarrow \text{heat flux density } q, \text{ with cross section area } A$$

$$\|\nabla T\| = \Delta T/L, \text{ temperature difference } \Delta T \leftrightarrow \text{temperature gradient } \nabla T, \text{ with length } L$$

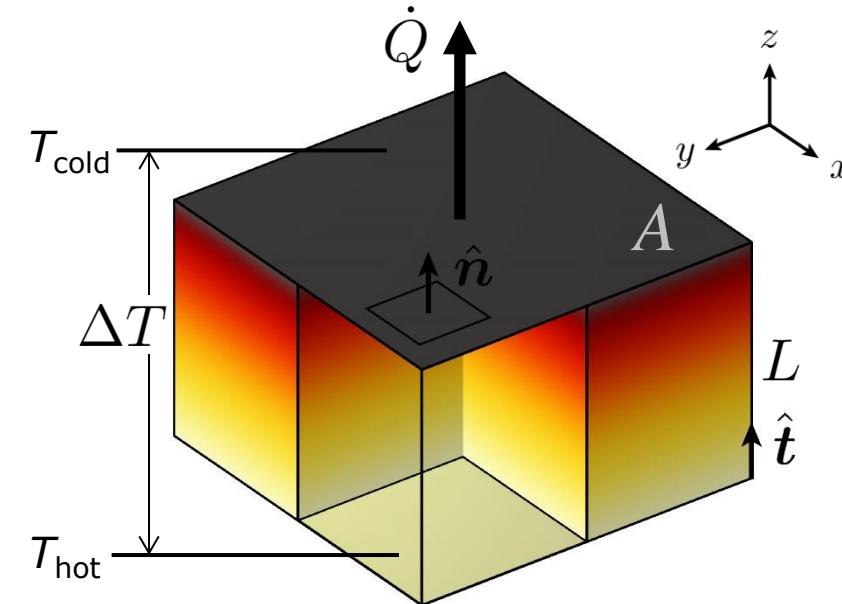
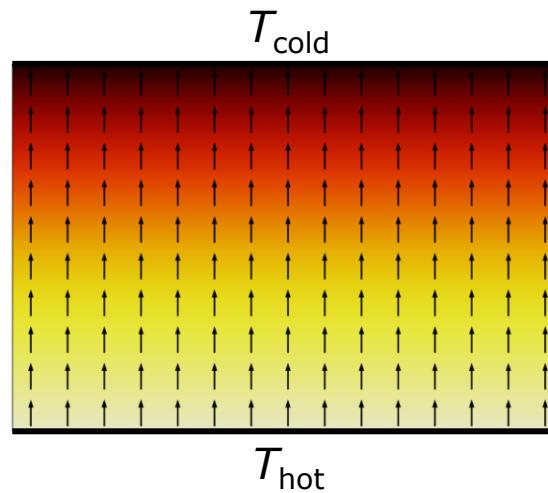


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$$\dot{Q} = \iint \hat{n} \cdot q \, dS$$

$$\dot{Q} = \iint \sum_k n_k q_k \, dS$$

z dir.  
↓

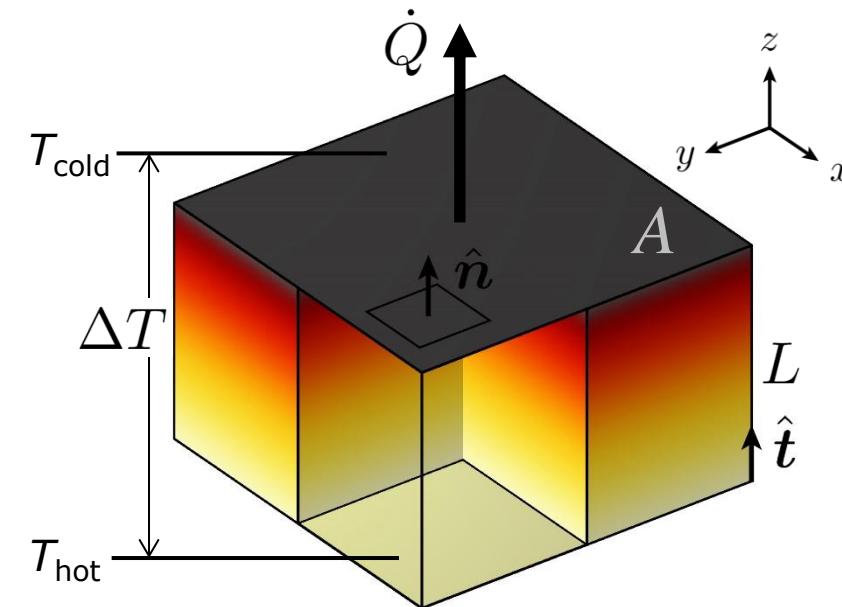
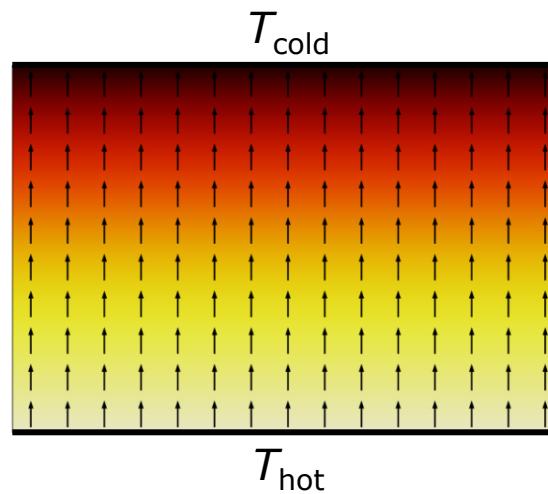
$$\dot{Q} = \iint n_z q_z \, dx dy$$

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$$\Delta T = \int \hat{t} \cdot (\nabla T) d\ell$$

$$\Delta T = \int \sum_k t_k \frac{\partial T}{\partial x_k} d\ell$$

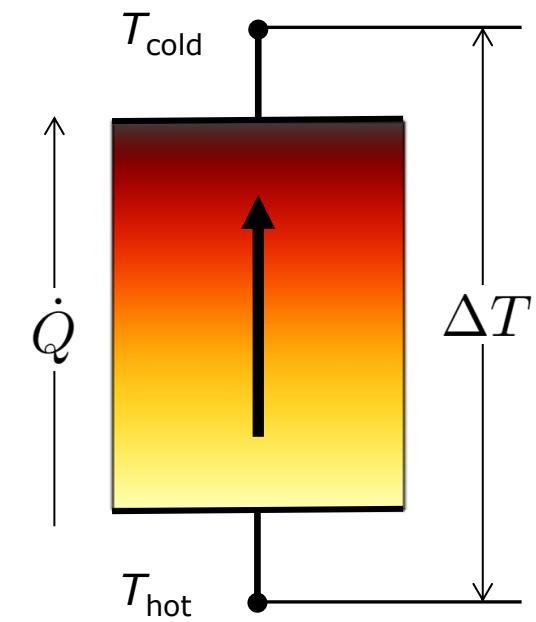
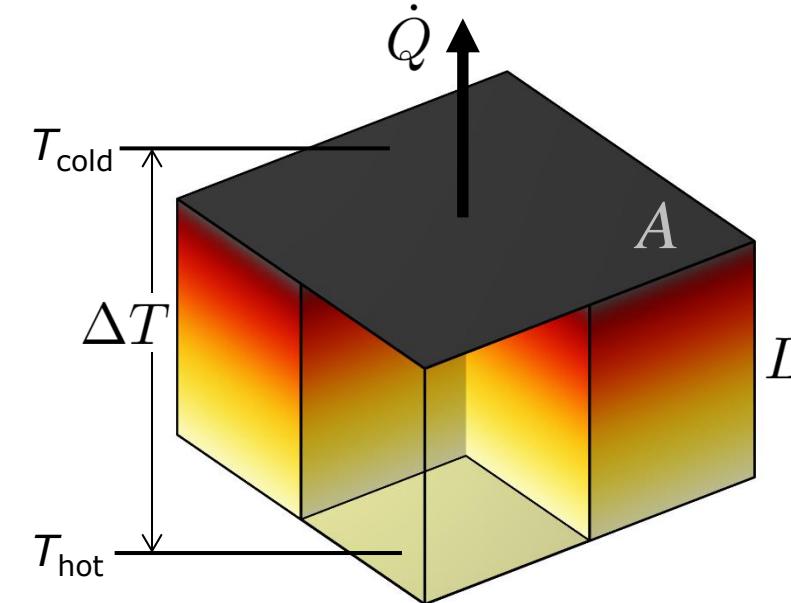
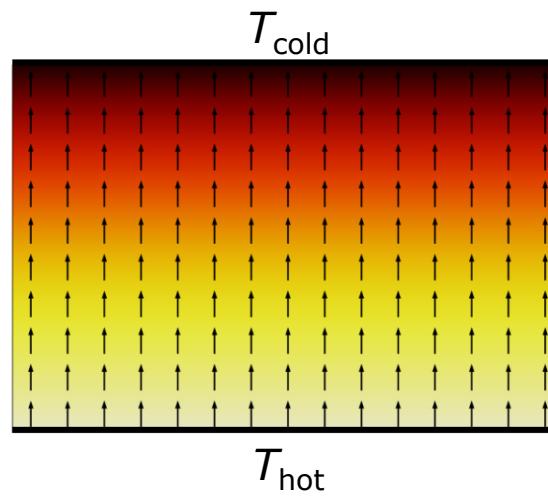
z dir.  
↓

$$\Delta T = \int t_z \frac{\partial T}{\partial z} dz$$

$$R = \frac{L}{kA}$$

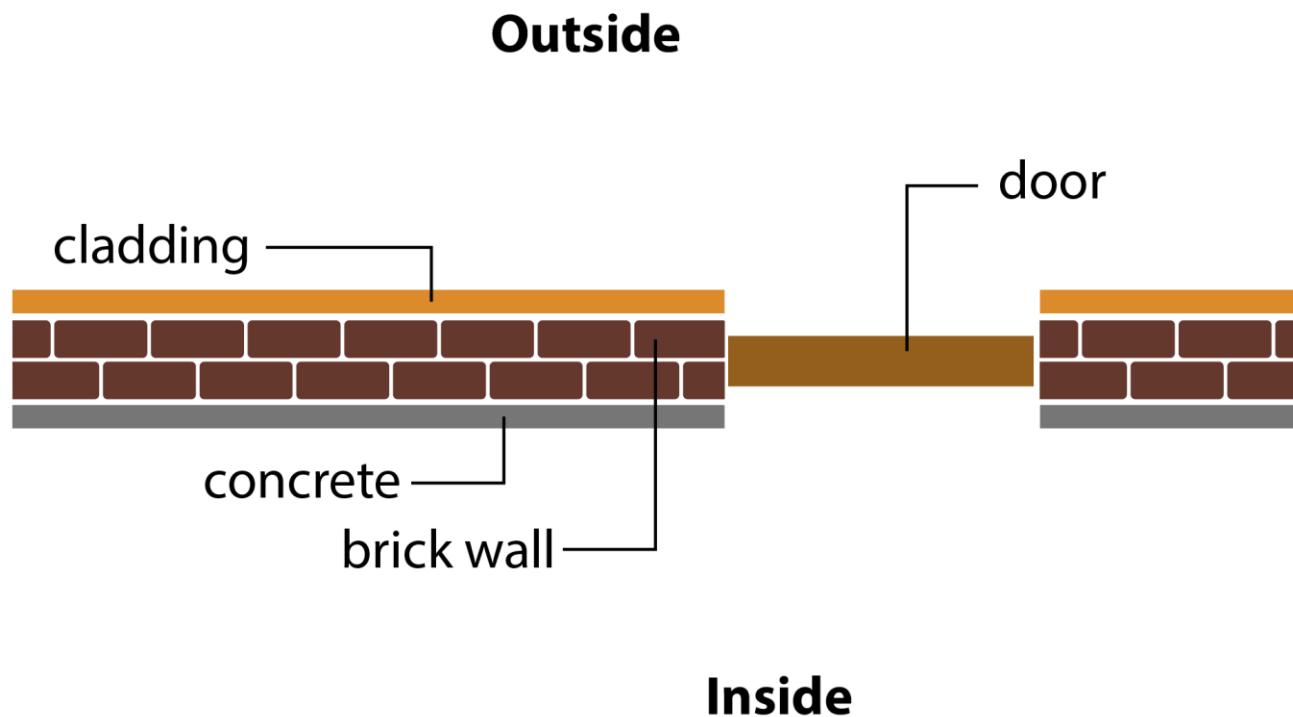
# The lumped-element model: Circuits

$$q = -k\nabla T$$
$$R\dot{Q} = \Delta T$$



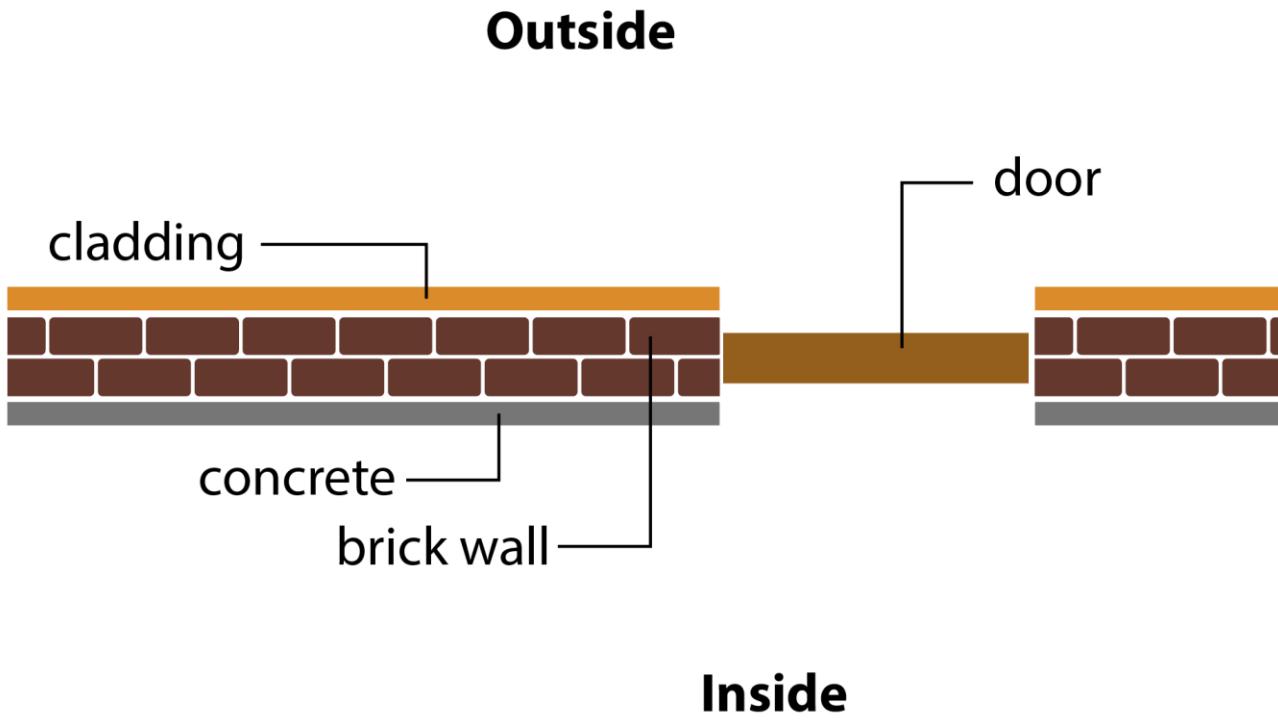
$$R = \frac{L}{kA}$$

# Thermal circuits



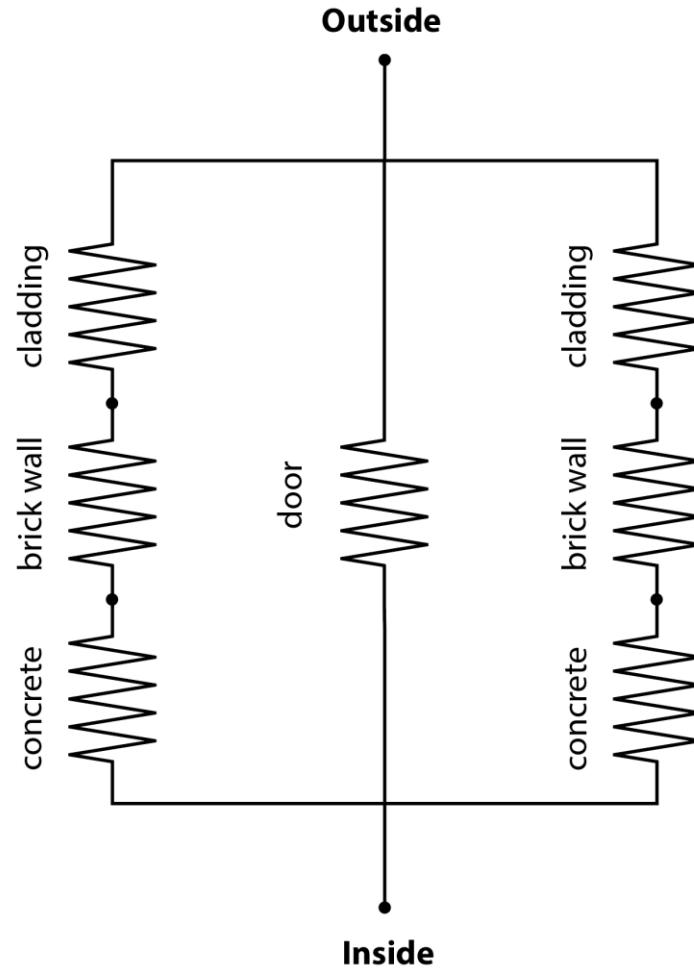
Example: how do we calculate the thermal resistance between the inside and the outside of a house?

# Thermal circuits



**Thermal resistance**

$$R = \frac{L}{kA}$$



# Example

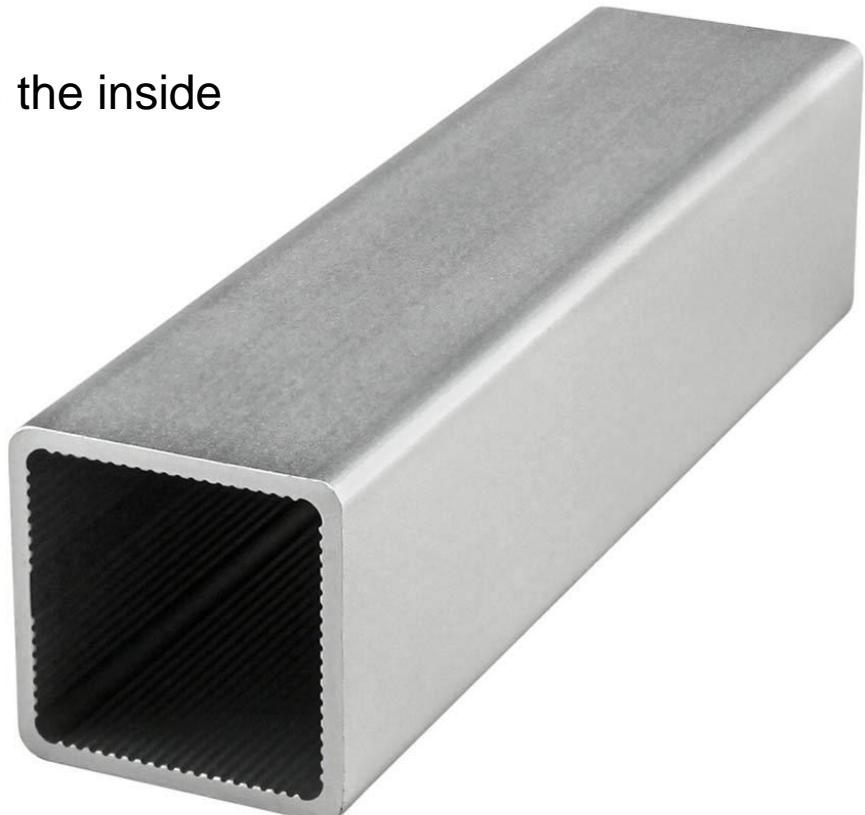
Look up the thermal conductivity of aluminum.

- 1) What is the thermal resistance per unit length between the inside and the outside of this profile?

Assume that the side is 5 cm and the thickness is 5 mm.

- 2) What is the thermal resistance for 20 cm length?

- 3) If the temperature difference between inside and outside is kept at 30 K, how much heat will be transferred during 1 min?



# Convection

# Convection vs conduction

- **Conduction** – it is a diffusion phenomenon: caused by probabilistic effects.
  - In a solid: random thermal vibration of ions in the lattice (phonons)
  - In a fluid: random thermal motion of free molecules
- **Convection** – it is a transport phenomenon: caused by deterministic effects
  - In a fluid: organized motion (flow) of the molecules
  - There can't be convection in a solid.

# Heat diffusion vs heat transport

Mathematically, we just need to include an extra contribution term to the flux density.

**Diffusion only:**  $\mathbf{J} = -k \nabla c$        $q^{\text{heat}} = -k \nabla T$

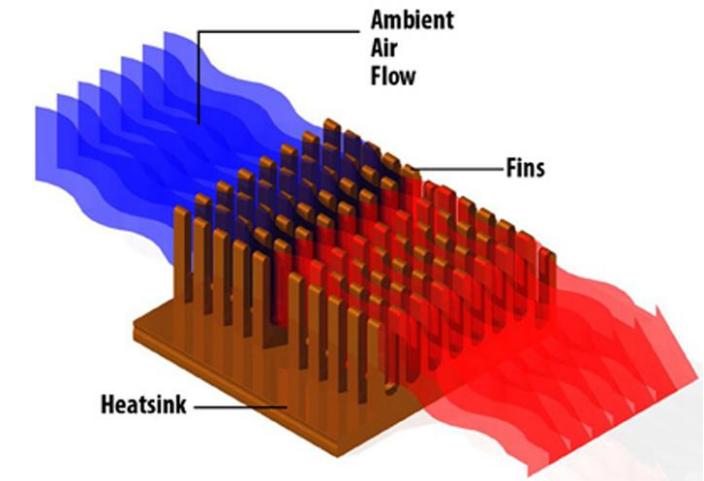
- Driven by concentration gradients
- It counteracts the gradients over time
- Eventually leads to equilibrium, i.e. uniform concentration, i.e. no gradients

**Diffusion + transport**     $\mathbf{J} = \mathbf{u} - k \nabla c$        $q^{\text{heat}} = \mathbf{u} - k \nabla T$

- In a reference frame that moves together with the fluid, the perceived flow velocity  $\mathbf{u}$  is zero, and there is no transport.
- It is just expressing the fact that when the fluid moves, its properties move with it.
- These properties can be: local concentration of a species mixed with the fluid, or the local temperature of the fluid.

# Coupling with fluid dynamics

- Clearly, unless we know the flow velocity field  $\mathbf{u}(x)$  we need to calculate it in order to then solve the heat equation.
- The flow is governed by the equation of fluid dynamics, i.e. the Navier Stokes equations, which are again similar to the other equations mentioned so far, except that:
  - The rank is greater (rank-1 tensors  $\rightarrow$  rank-2, and rank-2  $\rightarrow$  rank-4)
  - The phenomenon is inertial (the time dependent equation involves second order time derivative), instead of relaxation (first order time derivative)
  - The equation also involves an advective derivative term that is non-linear, specifically quadratic, with respect to  $\mathbf{u}(x)$

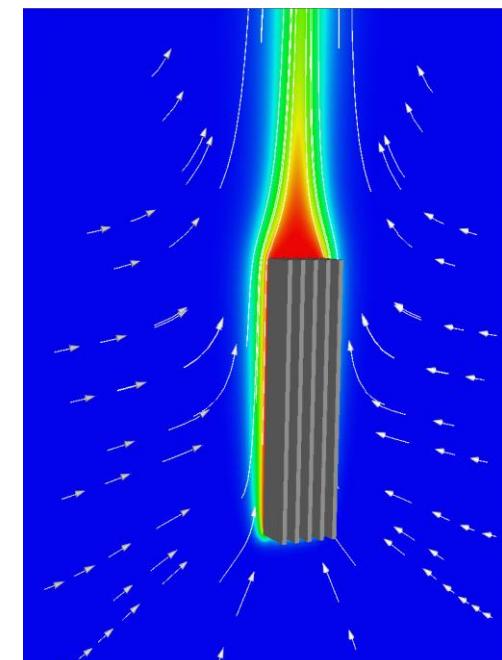
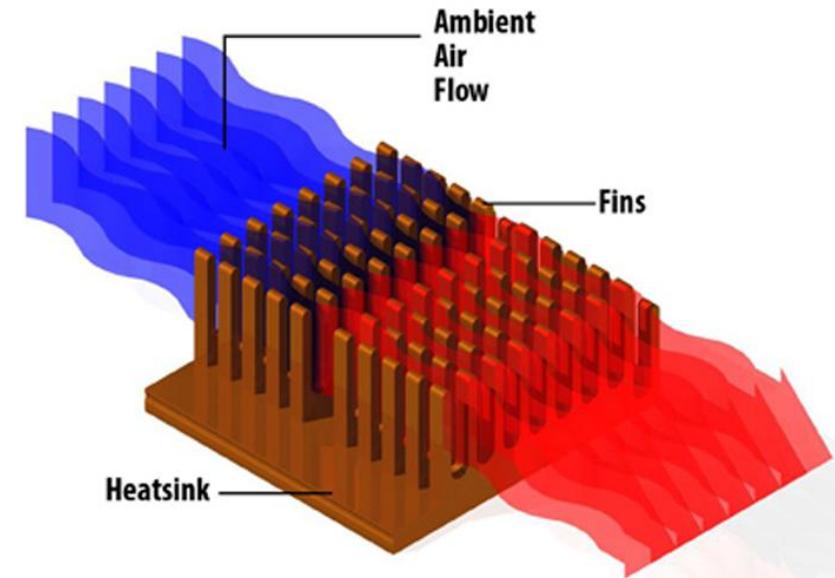


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  - The phenomenon is inertial (the time dependent equation involves second order time derivative), instead of relaxation (first order time derivative)
  - The equation also involves an advective derivative term that is non-linear, specifically quadratic, with respect to  $\mathbf{u}(\mathbf{x})$
- The inverse coupling can also be of interest, i.e.: temperature dependence of flow property, e.g. viscosity, density (thermal expansion), etc.

# Forced vs Natural convection

- **Forced convection:** the fluid flow is deliberately created by human intervention with the purpose of enhancing heat transfer, generally between the fluid and a solid that the fluid is flowing past. Examples: water inside radiators, air in heat exchangers, heat sinks, dissipators, fans.
- **Natural convection,** the fluid flow is occurring spontaneously due to the combined effect of thermal expansion (temperature dependent pressure) and buoyancy (pressure mediated gravitational forces in fluids). Example: air *outside* radiators.



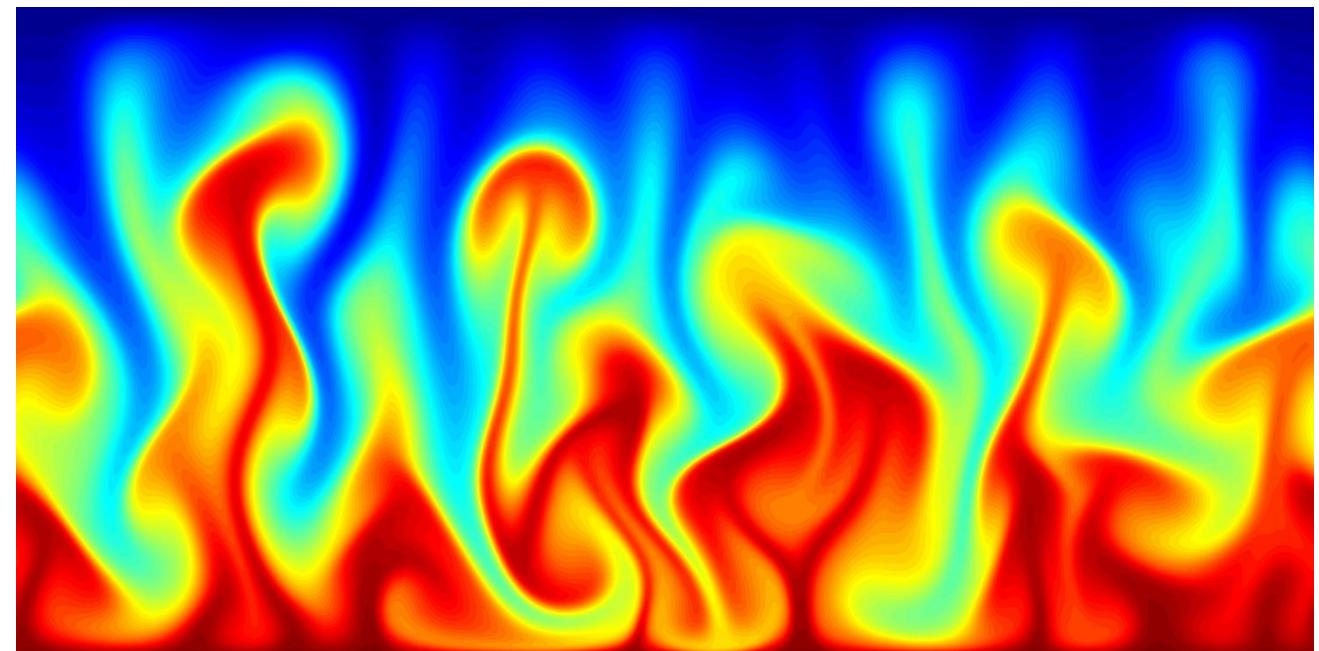
# Convection coefficient

The exact calculation of the convection between an object and the surrounding fluid requires to solve the coupled equations of heat transfer and fluid dynamics (by numerical simulation).

However, we can approximate with a simple formula analogous to Newton's law of cooling:

$$\mathbf{q} \cdot \hat{\mathbf{n}} = -h\Delta T$$

$h$  is the convection coefficient.



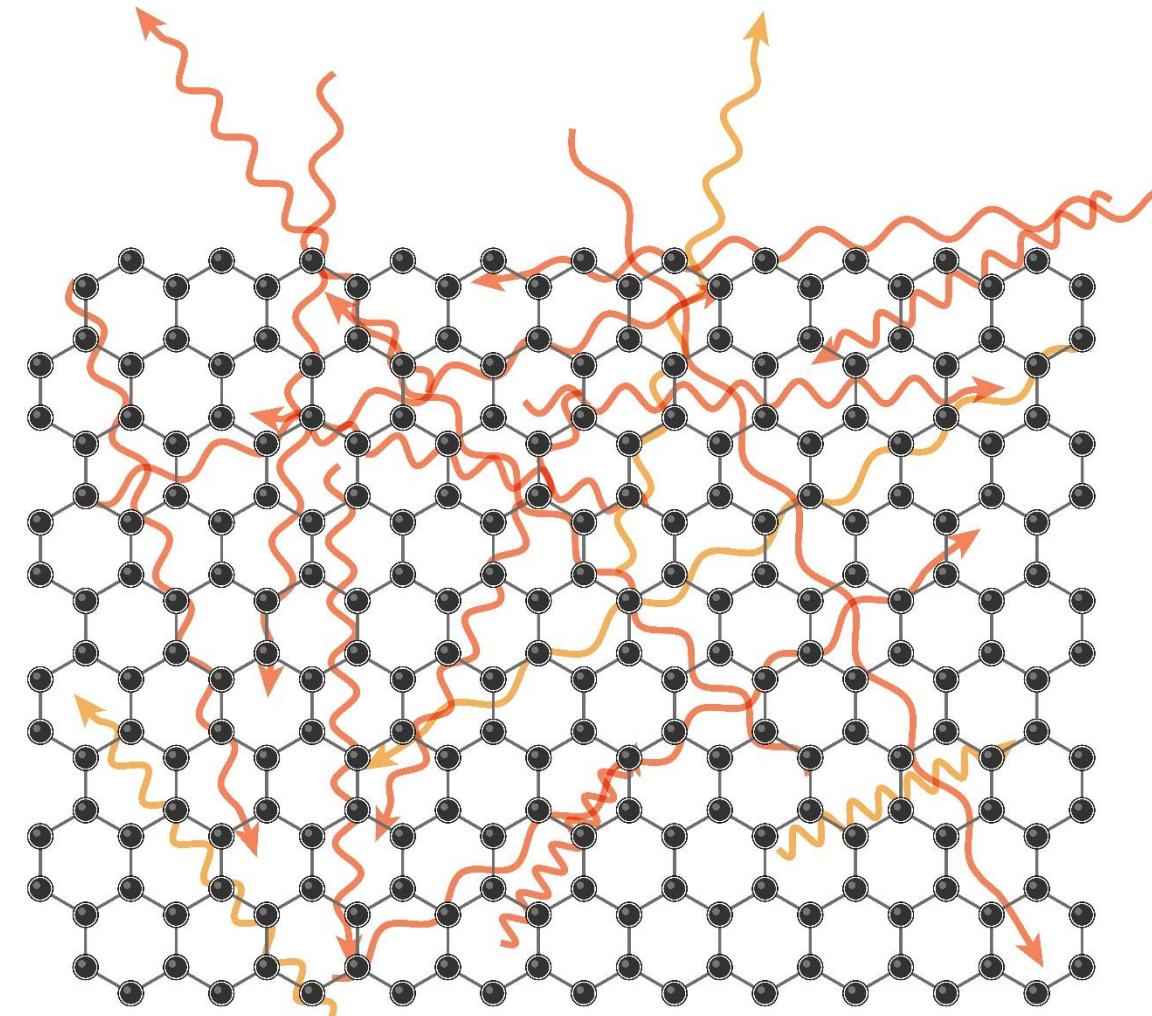
# Radiation

# Black-body radiation

Within a body, photons are continuously being emitted and absorbed.

We can visualize photons just as the molecules in a gas:

- they travel in a straight line until they interact with the body.
- on average, there are an equal number of photons traveling in any direction
- two photons may have different energies  $E$
- the probability  $P$  depends on the energy:  $P = P(E)$
- the probability distribution  $P(E)$  can be calculated from thermodynamics

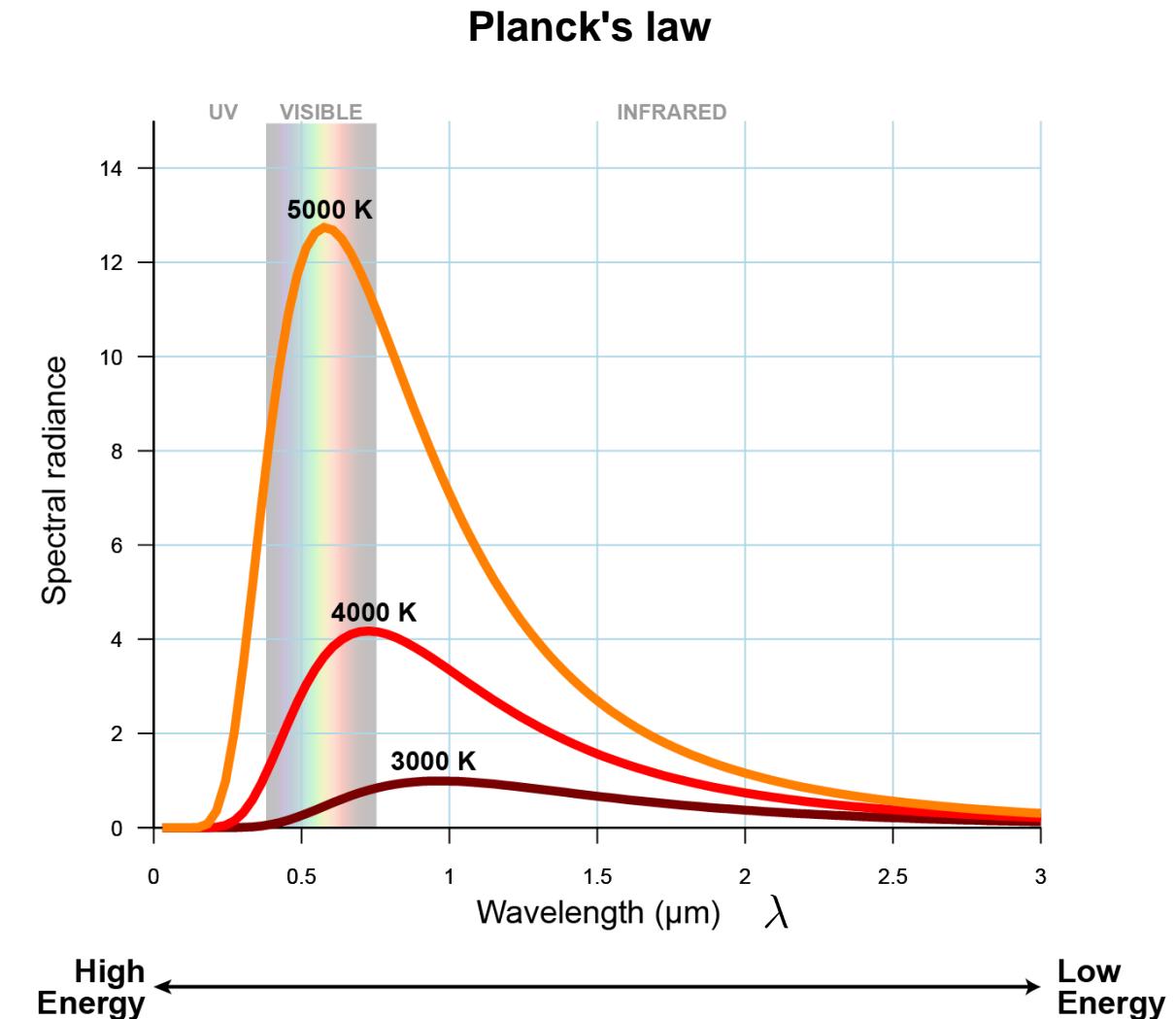


# Black-body radiation

Within a body, photons are continuously being emitted and absorbed.

We can visualize photons just as the molecules in a gas:

- they travel in a straight line until they interact with the body.
- on average, there are an equal number of photons traveling in any direction
- two photons may have different energies  $E$
- the probability  $P$  depends on the energy:  $P = P(E)$
- the probability distribution  $P(E)$  can be calculated from thermodynamics



# Black-body radiation

Within a body, photons are continuously being emitted and absorbed.

Plank's law – energy spectrum  $P(E)$  – is obtained from these considerations:

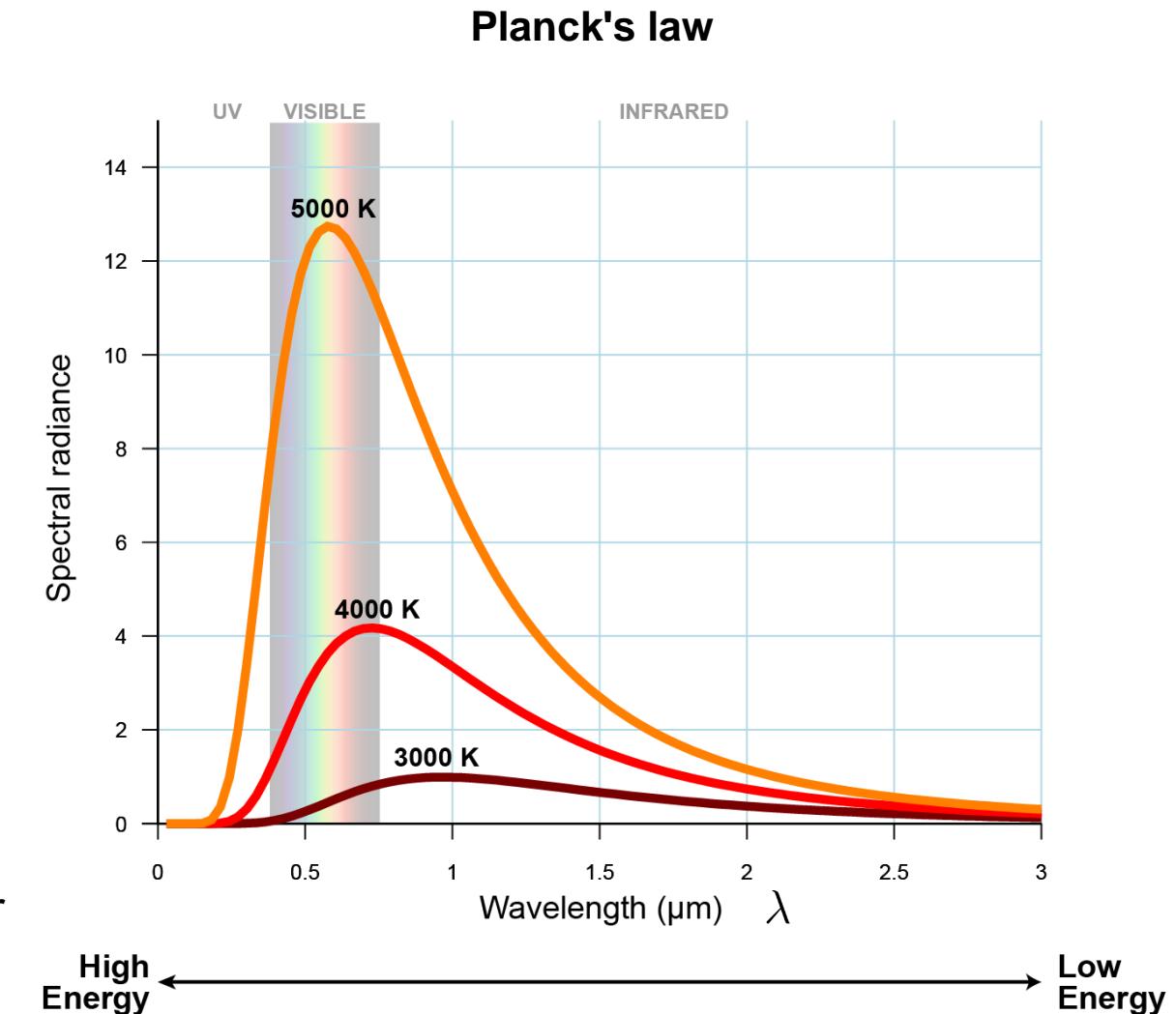
- Boltzmann factor (probability)

$$P \propto e^{-\frac{E}{k_B T}}$$

- Energy of a photon

$$E = h\nu = \frac{hc}{\lambda}$$

- Density of states,  $\frac{dE}{dk}$ , where  $k$  is the wavenumber

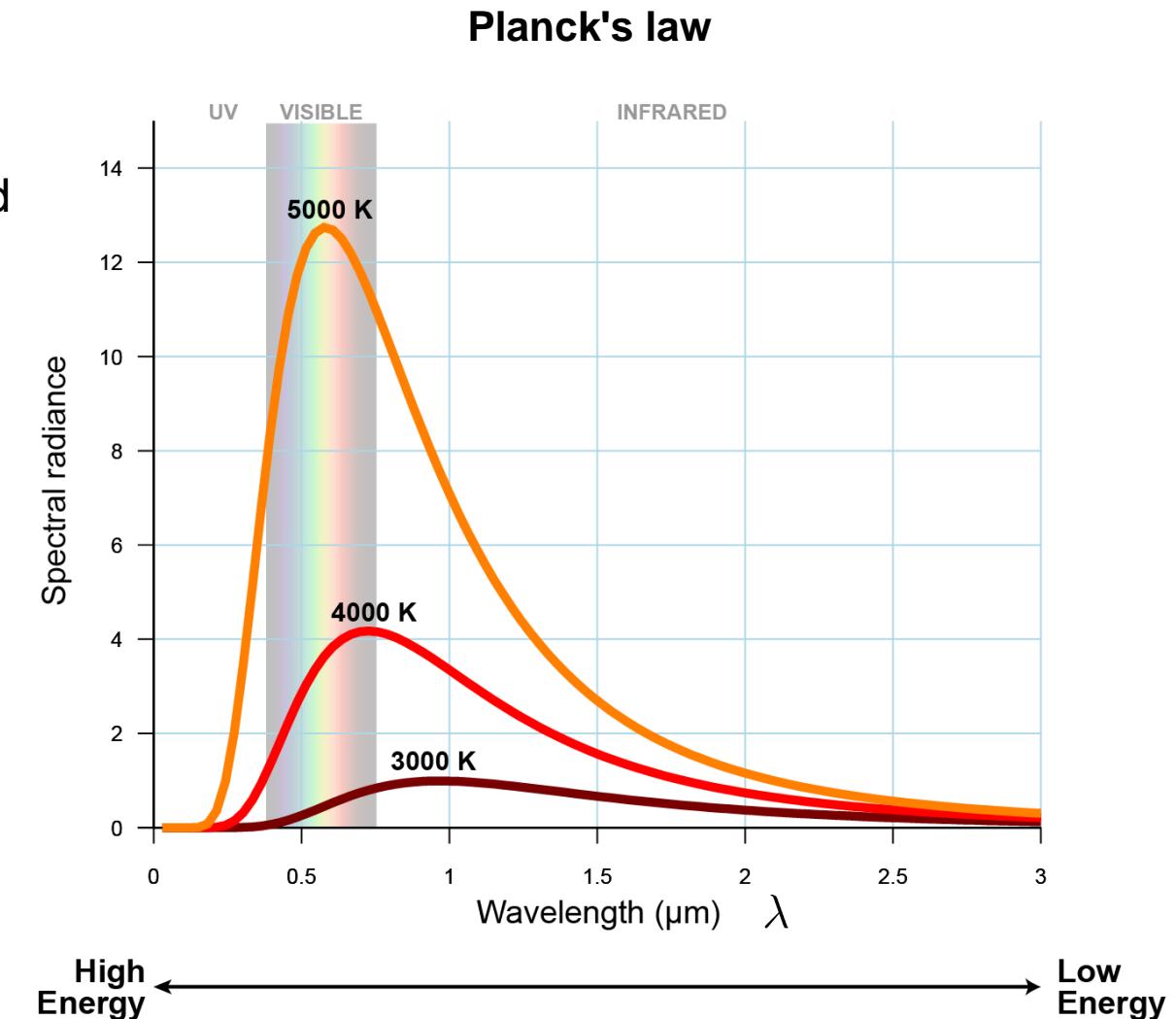


# Black-body radiation

Within a body, photons are continuously being emitted and absorbed.

Stefan–Boltzmann law: energy radiated per unit-area [ $\text{W/m}^2$ ], over the whole spectrum

$$\mathbf{q} \cdot \hat{\mathbf{n}} = \varepsilon \sigma T_{\text{body}}^4$$



# Black-body radiation

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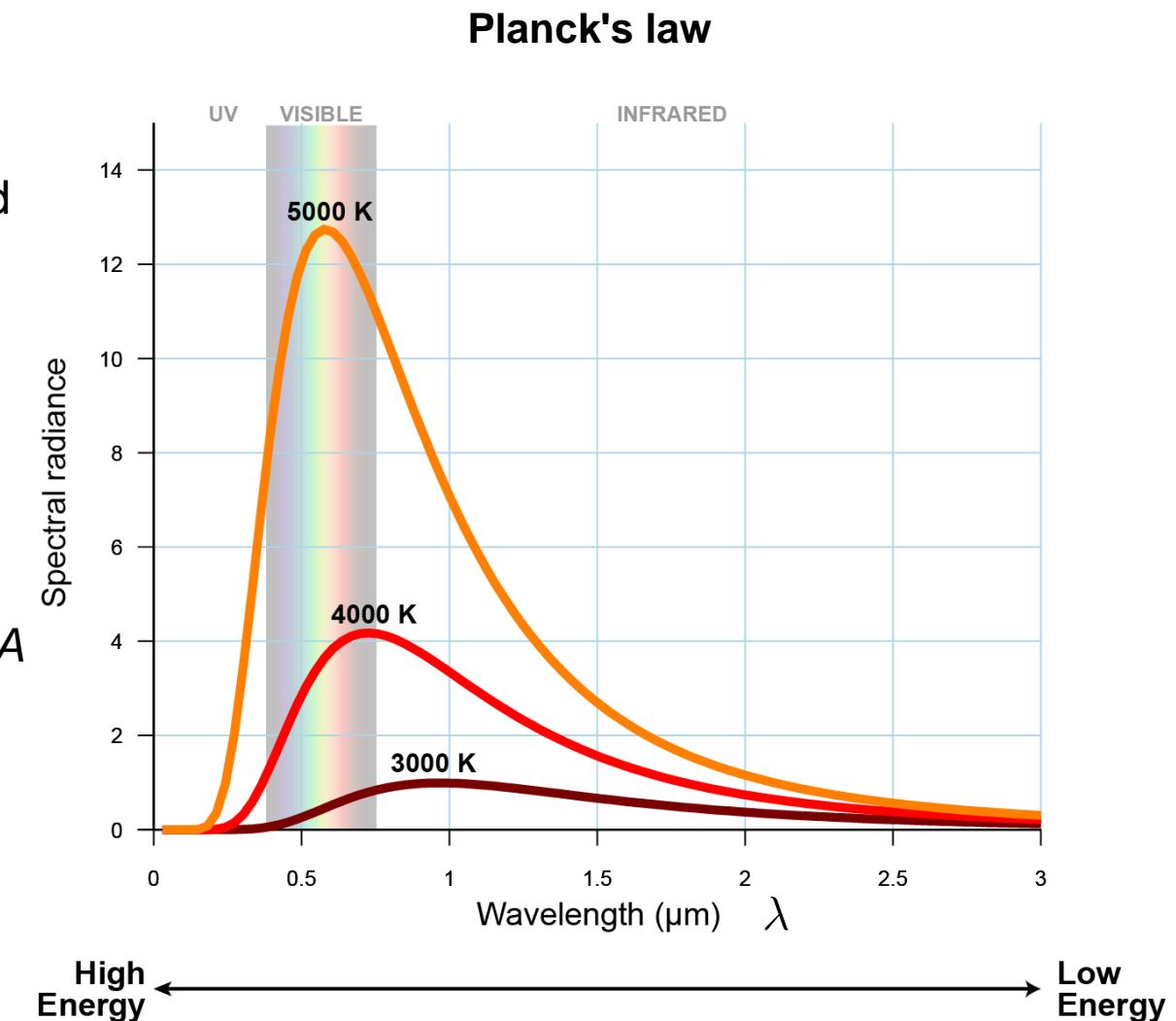
$$\mathbf{q} \cdot \hat{\mathbf{n}} = \varepsilon \sigma T_{\text{body}}^4$$

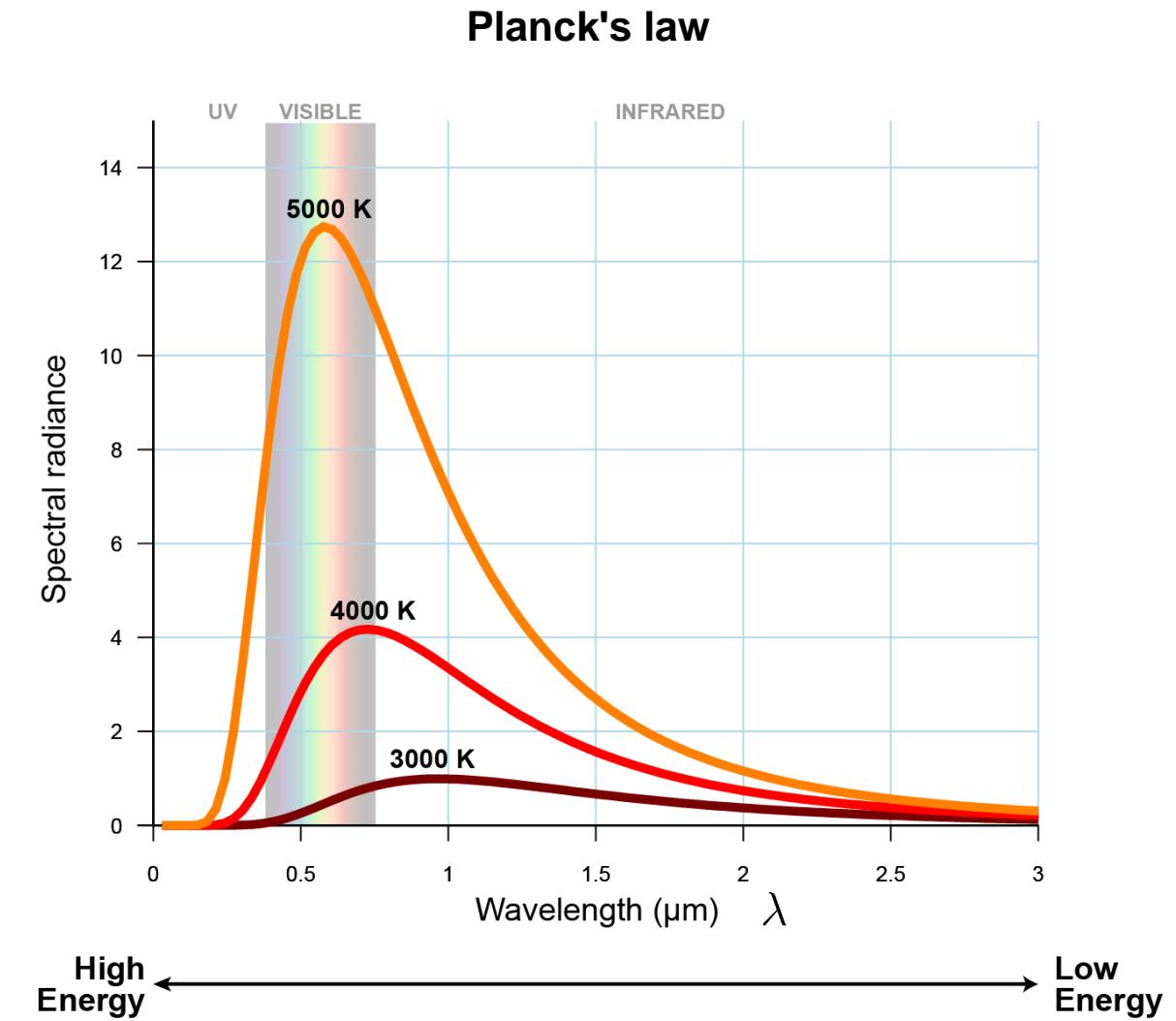
Total energy radiated, [W], by a body of surface area  $A$

$$\dot{Q}_{\text{emitted}} = A \varepsilon \sigma T_{\text{body}}^4$$

Where  $\varepsilon \in [0, 1]$  is the emissivity of the material.

It is a dimensionless quantity that goes to 1 for an ideal blackbody. Less than 1 for “gray bodies”.

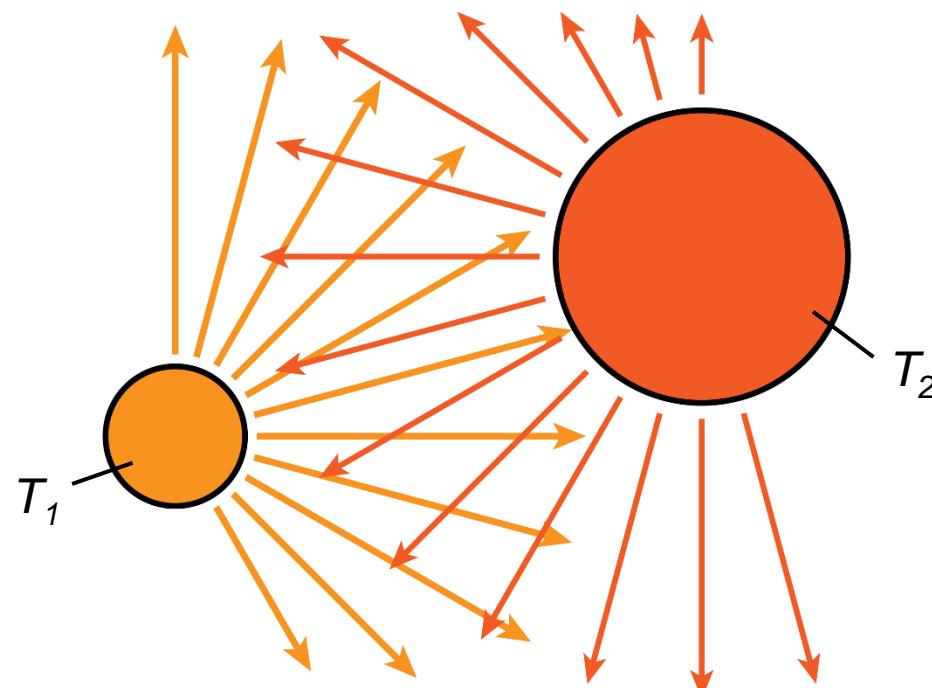




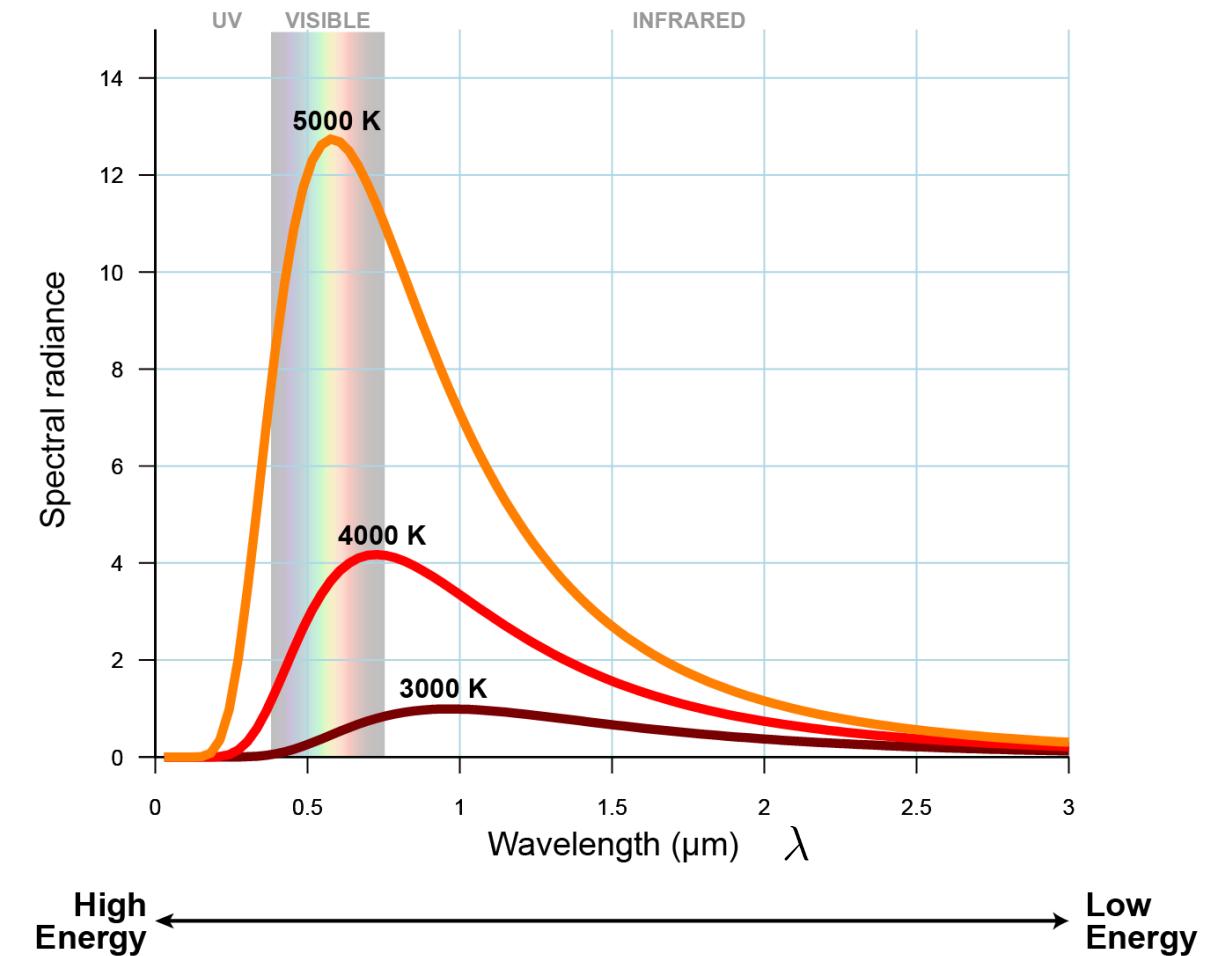
# Black-body radiation

Total energy radiated by a body:

$$\dot{Q}_{\text{emitted}} = A \varepsilon \sigma T_{\text{body}}^4$$



Planck's law



# Black-body radiation

Total energy radiated by a body:

$$\dot{Q}_{\text{emitted}} = A\varepsilon\sigma T_{\text{body}}^4$$

In many cases, it is realistic to assume that a body is also receiving radiation from all directions:

$$\dot{Q}_{\text{absorbed}} = A\varepsilon\sigma T_{\text{ambient}}^4$$

The net absorbed energy is thus given by:

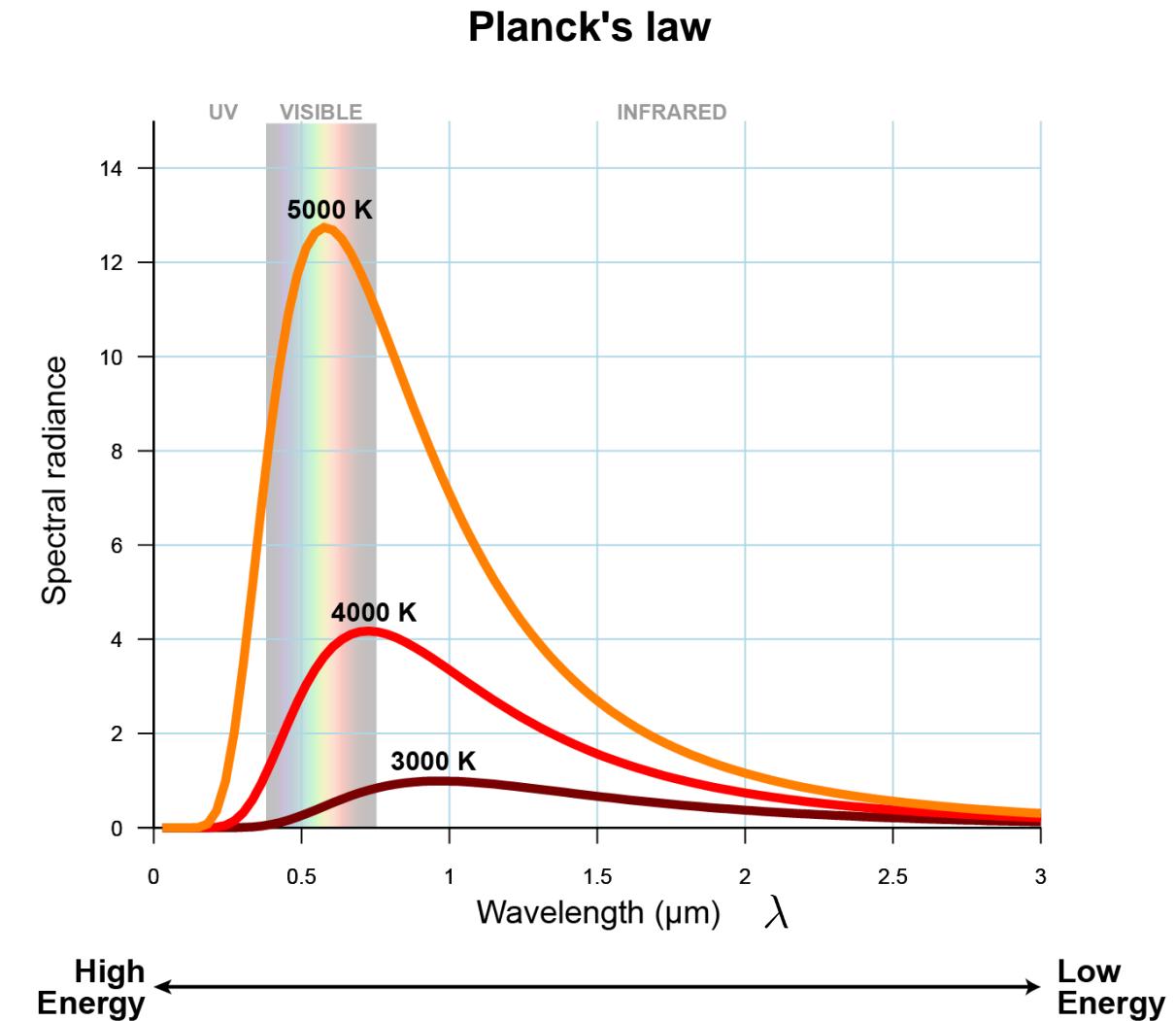
$$\dot{Q}_{\text{absorbed, net}} = \dot{Q}_{\text{absorbed}} - \dot{Q}_{\text{emitted}}$$

At equilibrium:

$$\dot{Q}_{\text{absorbed}} = \dot{Q}_{\text{emitted}}$$

$\Updownarrow$

$$T_{\text{body}} = T_{\text{ambient}}$$



# Summary of heat transfer mechanisms

Fourier's law of heat conduction

$$\mathbf{q} = -k \nabla T$$

Convection at the boundary of a solid

$$\mathbf{q} \cdot \hat{\mathbf{n}} = h(T - T_{\text{fluid}})$$

Radiation

$$\mathbf{q} \cdot \hat{\mathbf{n}} = \varepsilon \sigma (T^4 - T_{\text{ambient}}^4)$$

$\mathbf{q}$  Heat flux density [W/m<sup>2</sup> = J/(s m<sup>2</sup>)]

$\mathbf{q} \cdot \hat{\mathbf{n}}$  Rate of heat loss of a body per unit area [W/m<sup>2</sup> = J/(s m<sup>2</sup>)]

$T$  Temperature of the body

$k$  Thermal conductivity [W/(mK)]

$h$  Convection coefficient [W/(m<sup>2</sup>K)]

# Earth's equilibrium temperature



- Sunlight arrives to earth with a solar irradiance (power per unit area) of  $1366 \text{ W/m}^2$
- The average albedo of earth (fraction of incident light that is absorbed) is 0.3.
- The average emissivity of the earth's surface is  $\varepsilon = 0.95$ .
- What is the equilibrium temperature of earth?

# Session 5

## The second law: Spontaneity and reversibility. Entropy generation.

# Entropy and the second law in classical thermodynamics

# Introduction - Second law of thermodynamics

## First law

- Expresses the conservation of energy for thermodynamical systems
- Comes from first principles
- It is obeyed separately by any individual interaction (and therefore also globally)

## Second law

- Describes spontaneous processes and establishes a limit to the ability of extracting useful work from a system
- Comes from probabilistic considerations: it does not make sense for individual interactions
- It might be locally (or temporarily) violated due to fluctuations
- It is strictly obeyed only in the thermodynamic limit (i.e. large systems)

# Reminder: heat reservoirs

A *heat reservoir* (or *thermal reservoir*) is a system whose temperature remains constant in spite of heat transfer to or from it.

They are called *heat sources* or *heat sinks* depending on the direction of heat transfer.

Examples:

- very large masses such as the atmosphere, an ocean or a lake, where local temperature gradients are quickly counteracted.
- a combustor that is continuously supplied fuel and generates heat maintaining a constant temperature

# Reminder: P-V diagrams

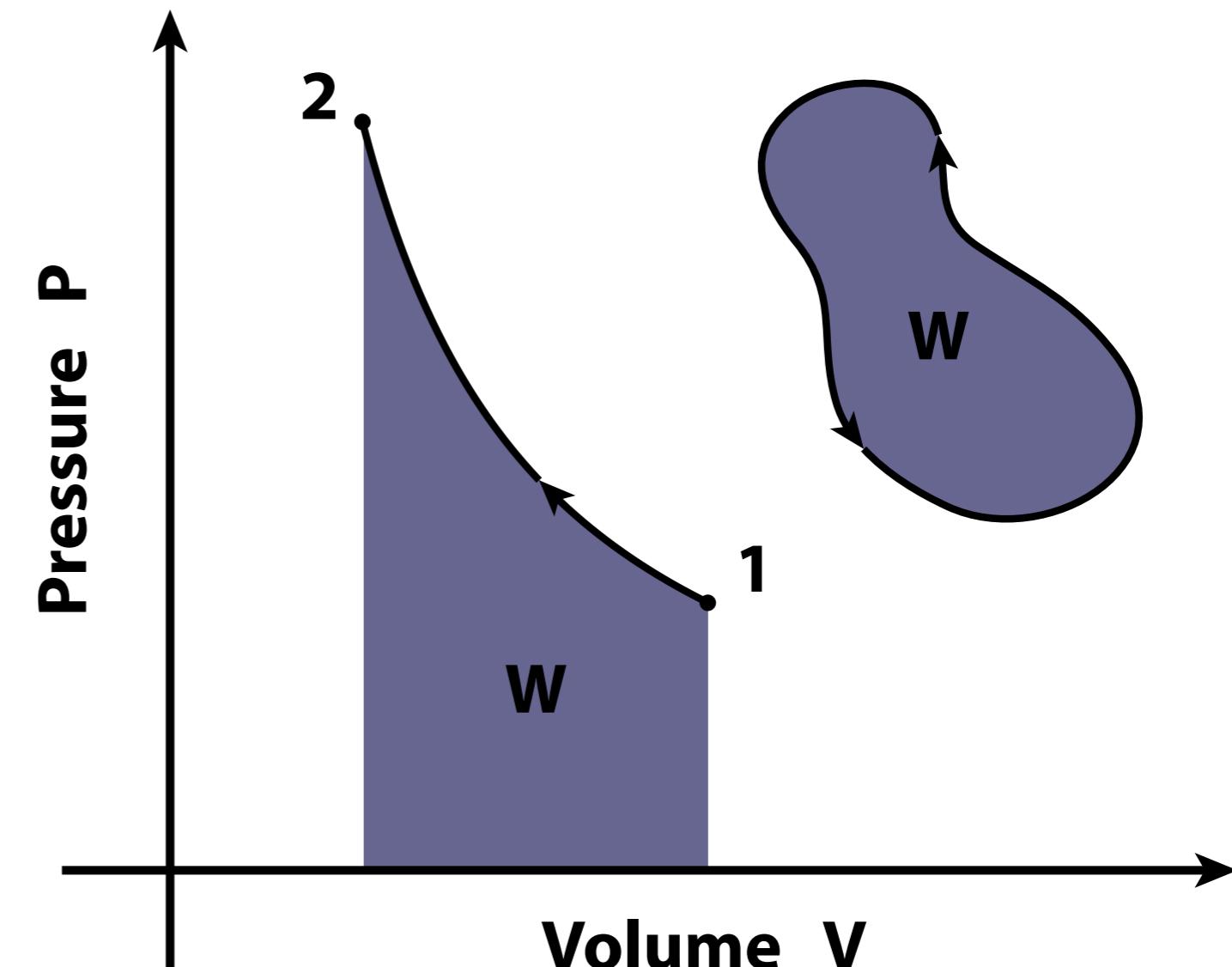
- They describe simple, pure compressible substances
- The temperature is determined by the equation of state.
- E.g. for ideal gases:

$$PV = N R_u T$$

- The energy transferred to the system in form of work is associated to its volume changes:

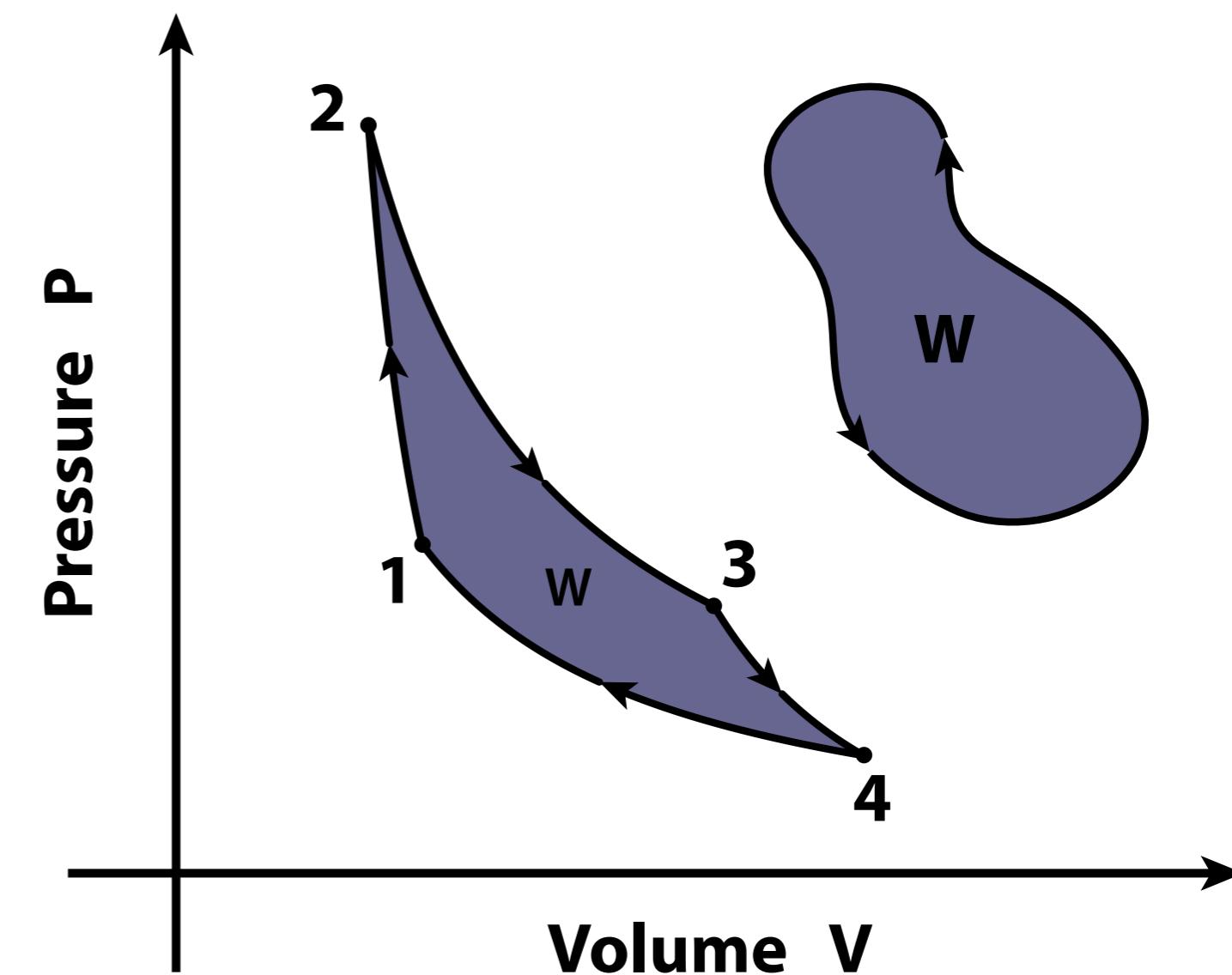
$$\delta W = -P dV$$

(mind the sign)

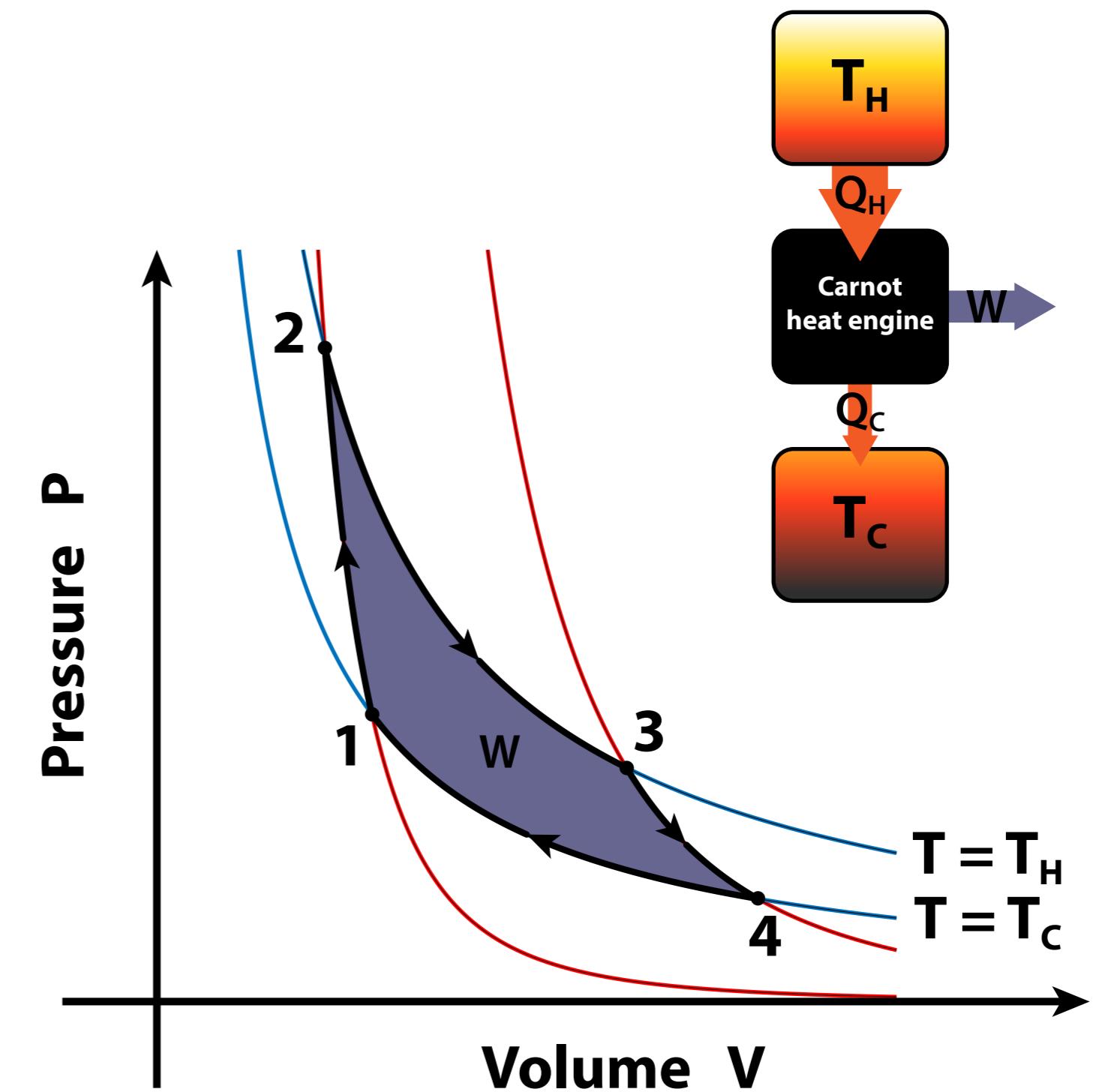
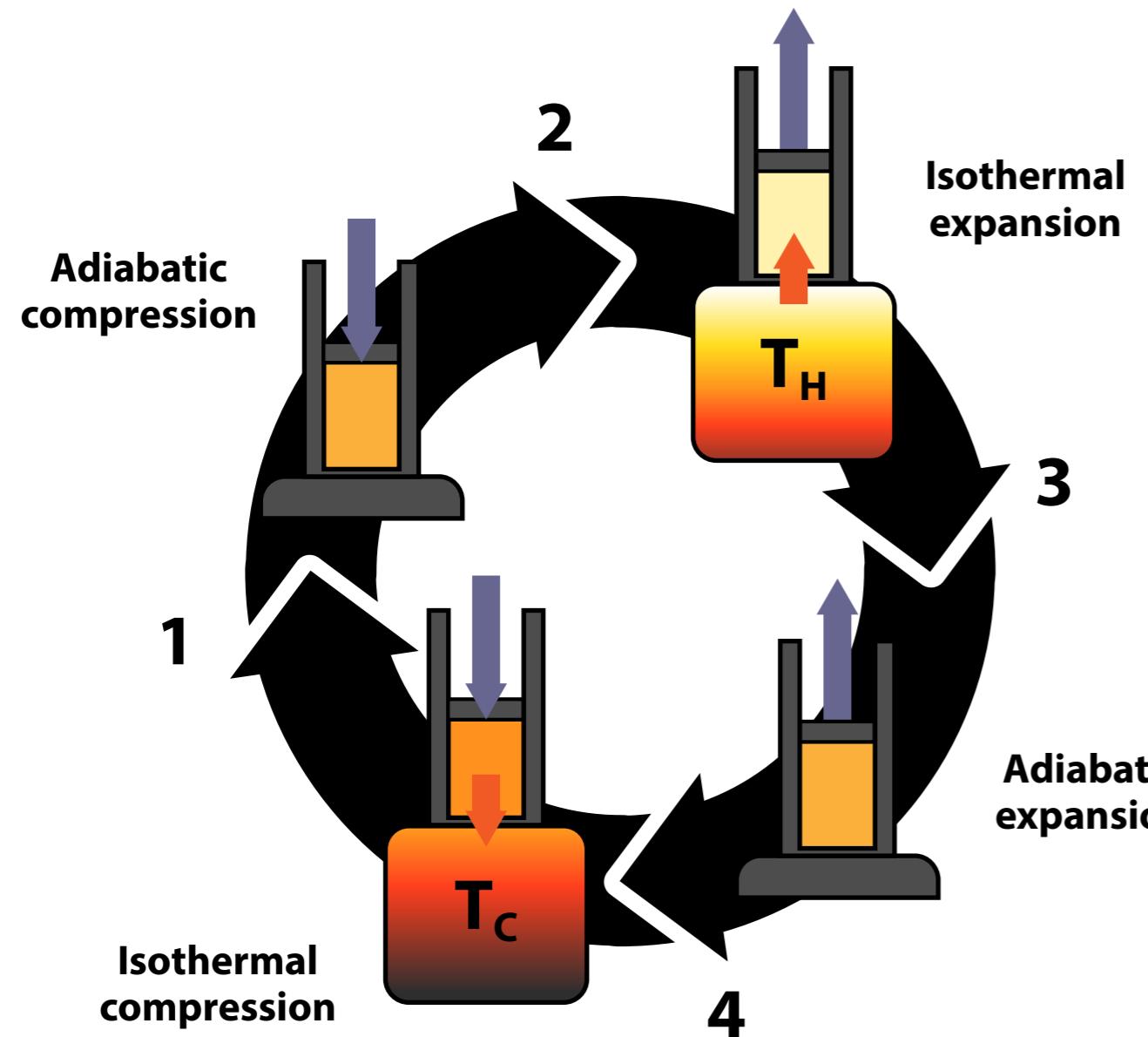


# Reminder: cyclic processes

- Any process for which the initial state of the system and the final state are the same.
- Therefore, after completing the process, the same transformation can be applied again with the same result. Hence the name “cycle”.
- Can be composed of a sequence of processes. After the sequence is completed it can be applied again.



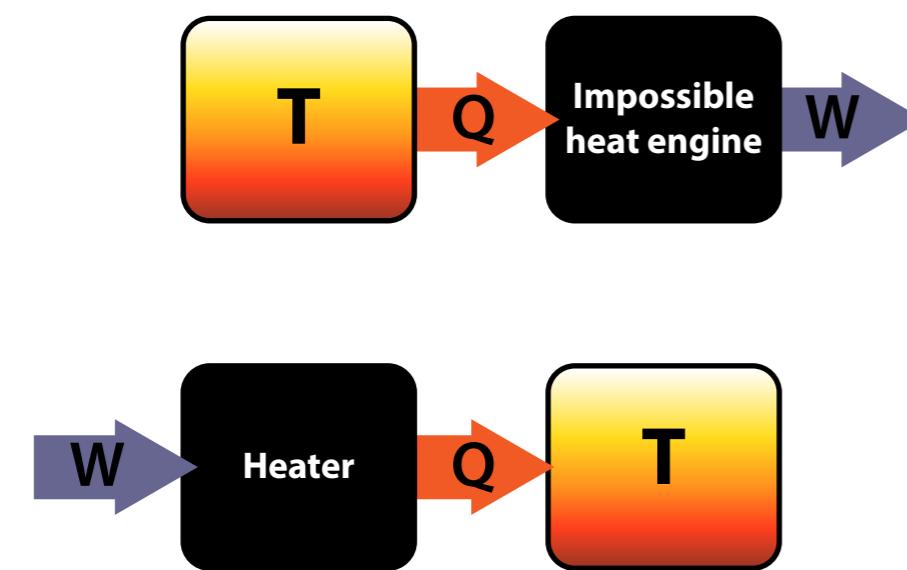
# The Carnot cycle: ideal heat engine



# Second law - classical statements

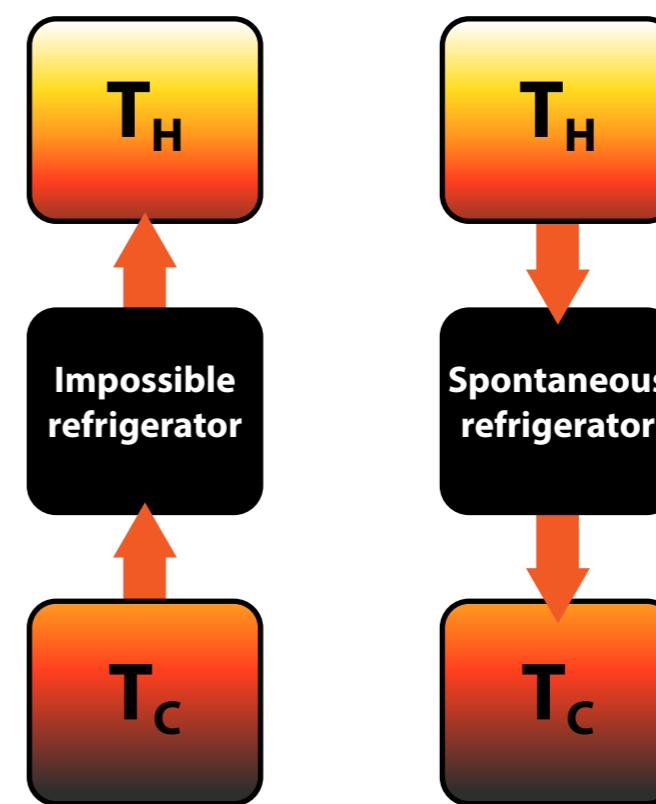
## Kelvin's statement

*A transformation whose only final result is to transform into work heat extracted from a thermal reservoir is impossible.*



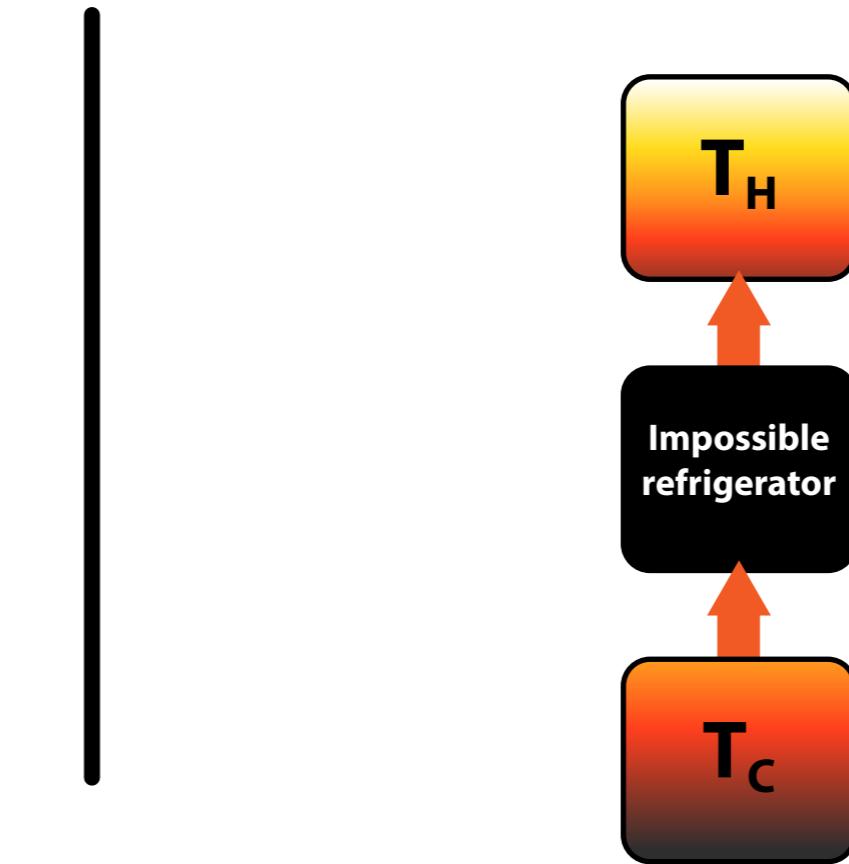
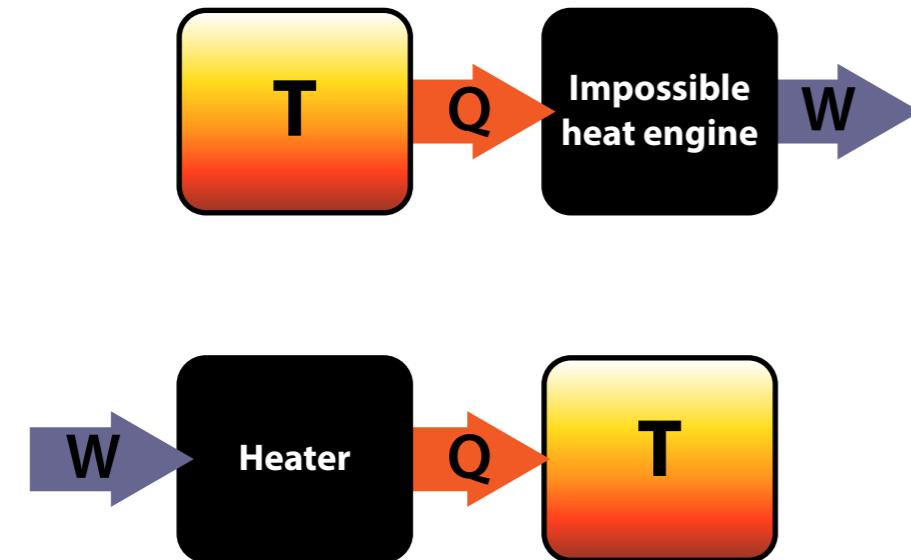
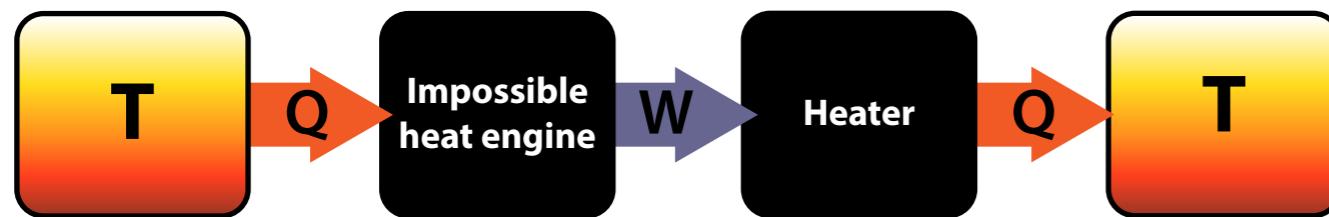
## Clausius' statement

*A transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible.*



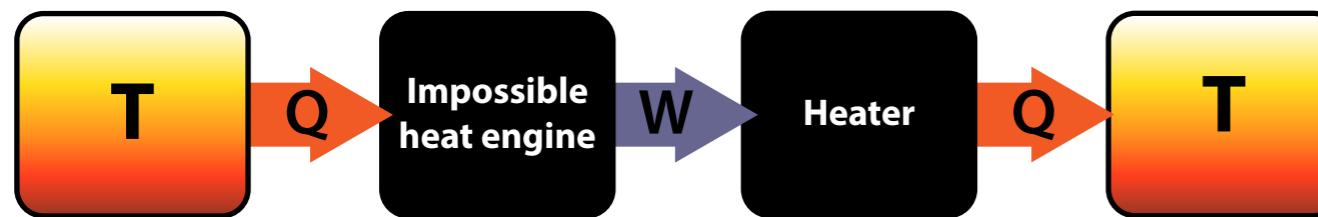
# Second law - classical statements

Combined machine:

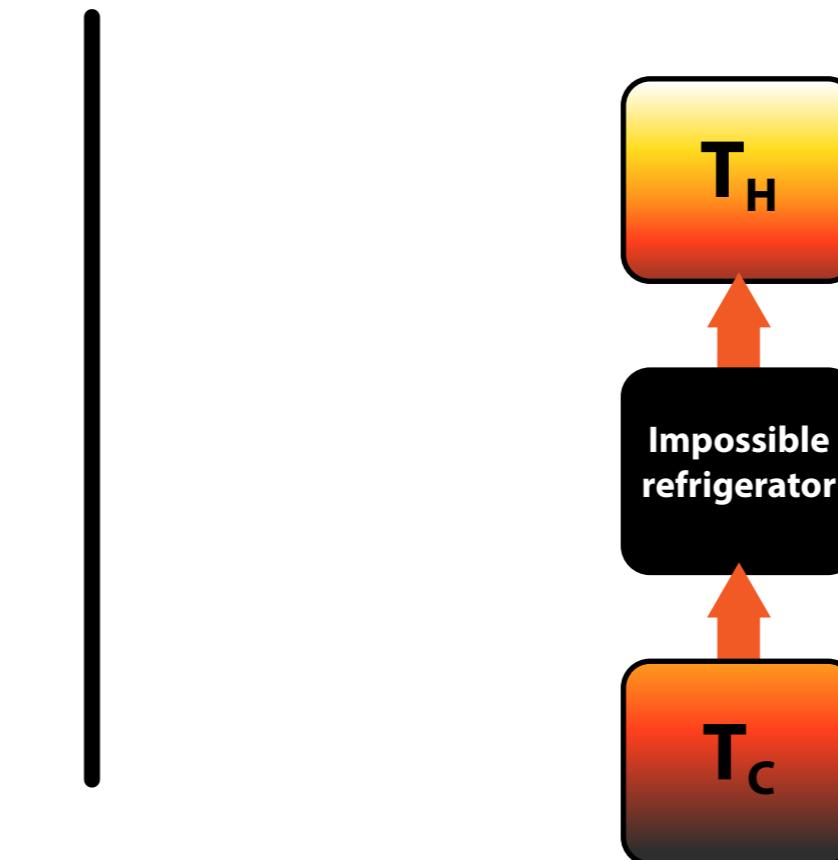
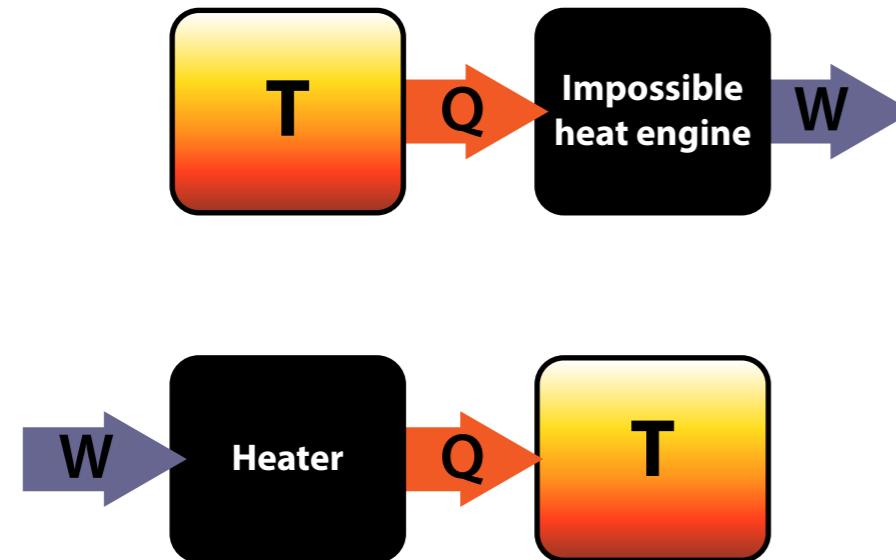


# Second law - classical statements

Combined machine:

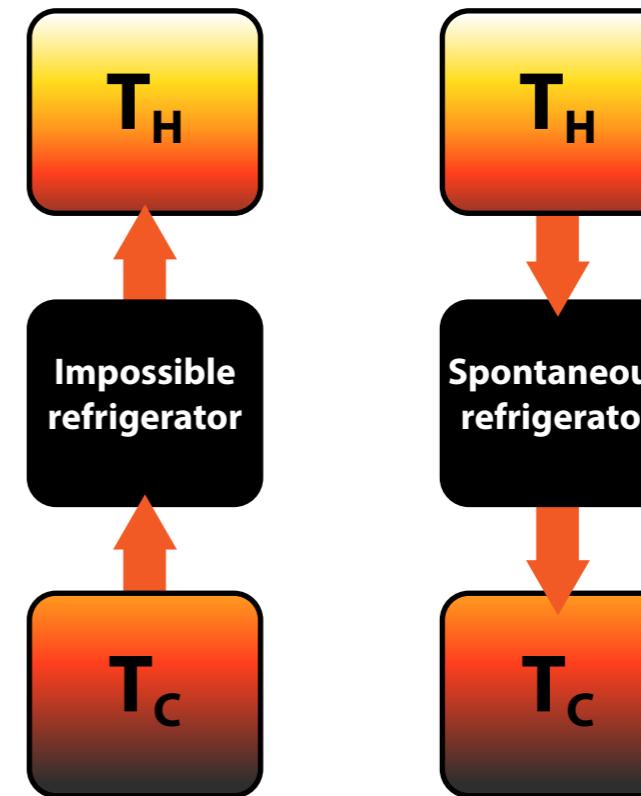
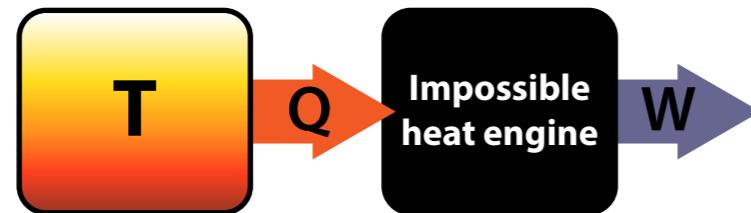
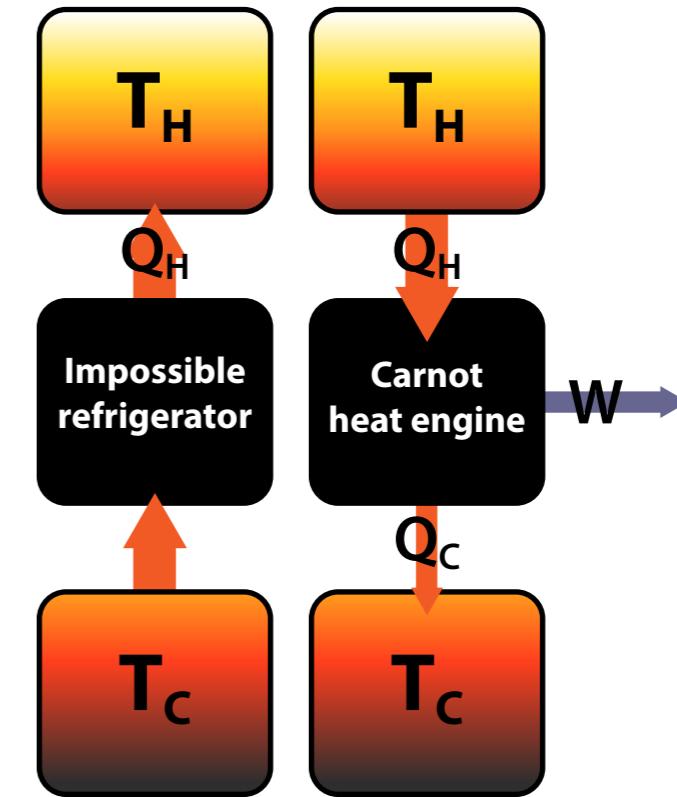


is  
equal  
to

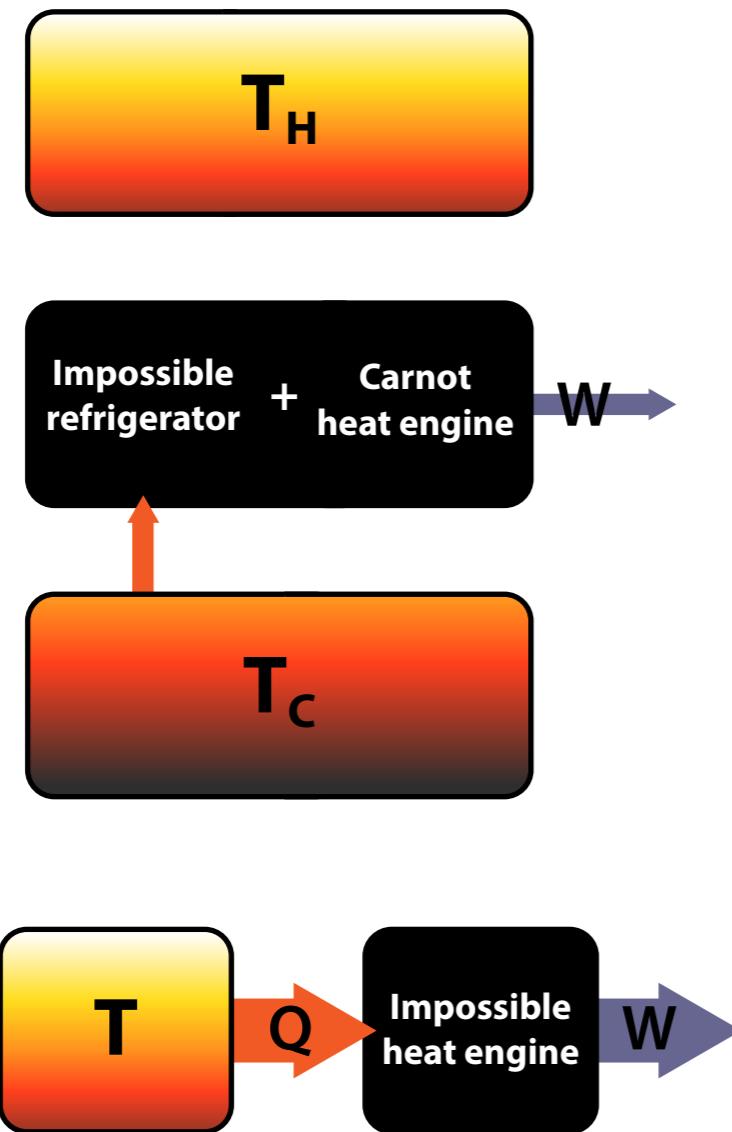


# Second law - classical statements

Combined machine:

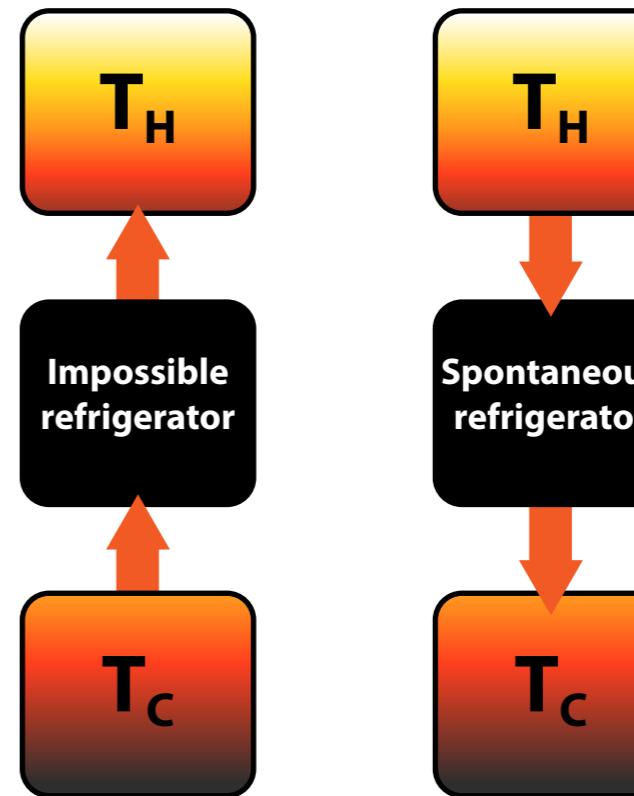
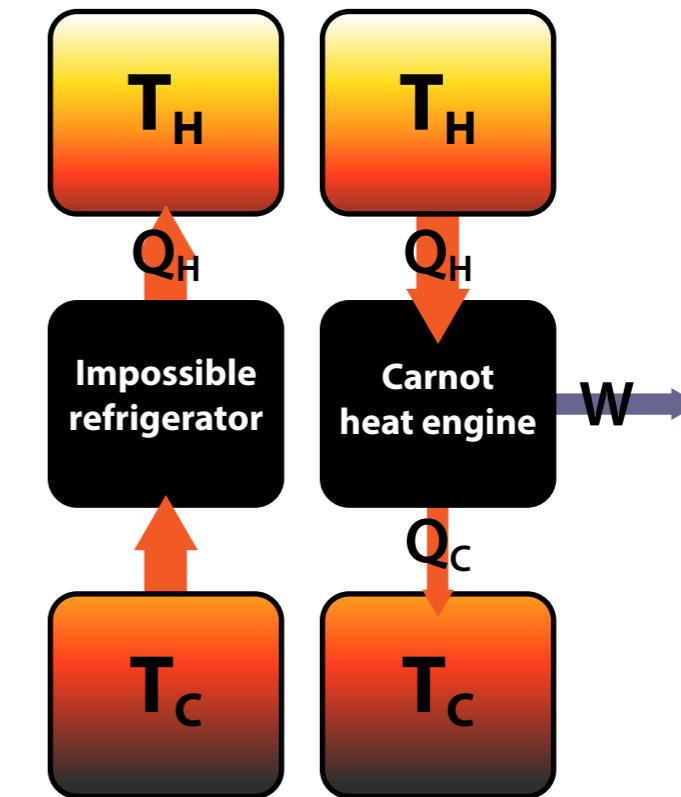


# Second law - classical statements



is  
equal  
to

Combined machine:



# Entropy - classical thermodynamics

## For reversible processes

Infinitesimal entropy variation:

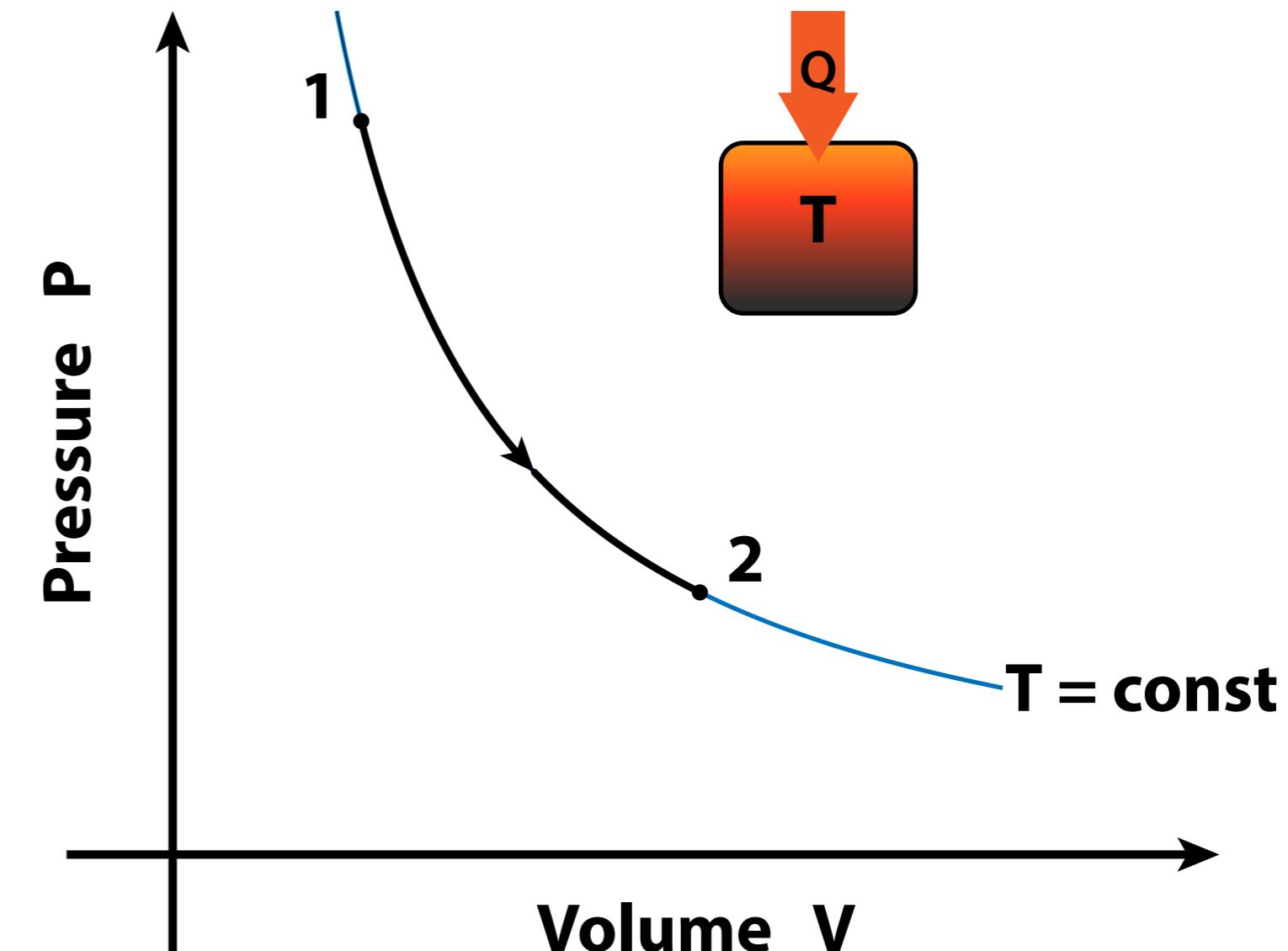
$$dS = \frac{\delta Q}{T}$$

Variation during finite process:

$$\Delta S = \int_1^2 \frac{\delta Q}{T}$$

At constant temperature  
(for isothermal processes or  
for thermal reservoirs)

$$\Delta S = \frac{1}{T} \int_1^2 \delta Q = \frac{Q}{T}$$



# Exact and inexact differentials

## For reversible processes

Entropy variation is path independent

$$\left( \int_1^2 dS \right)_I = \left( \int_1^2 dS \right)_{II}$$

(e.g.) Heat exchange is path dependent

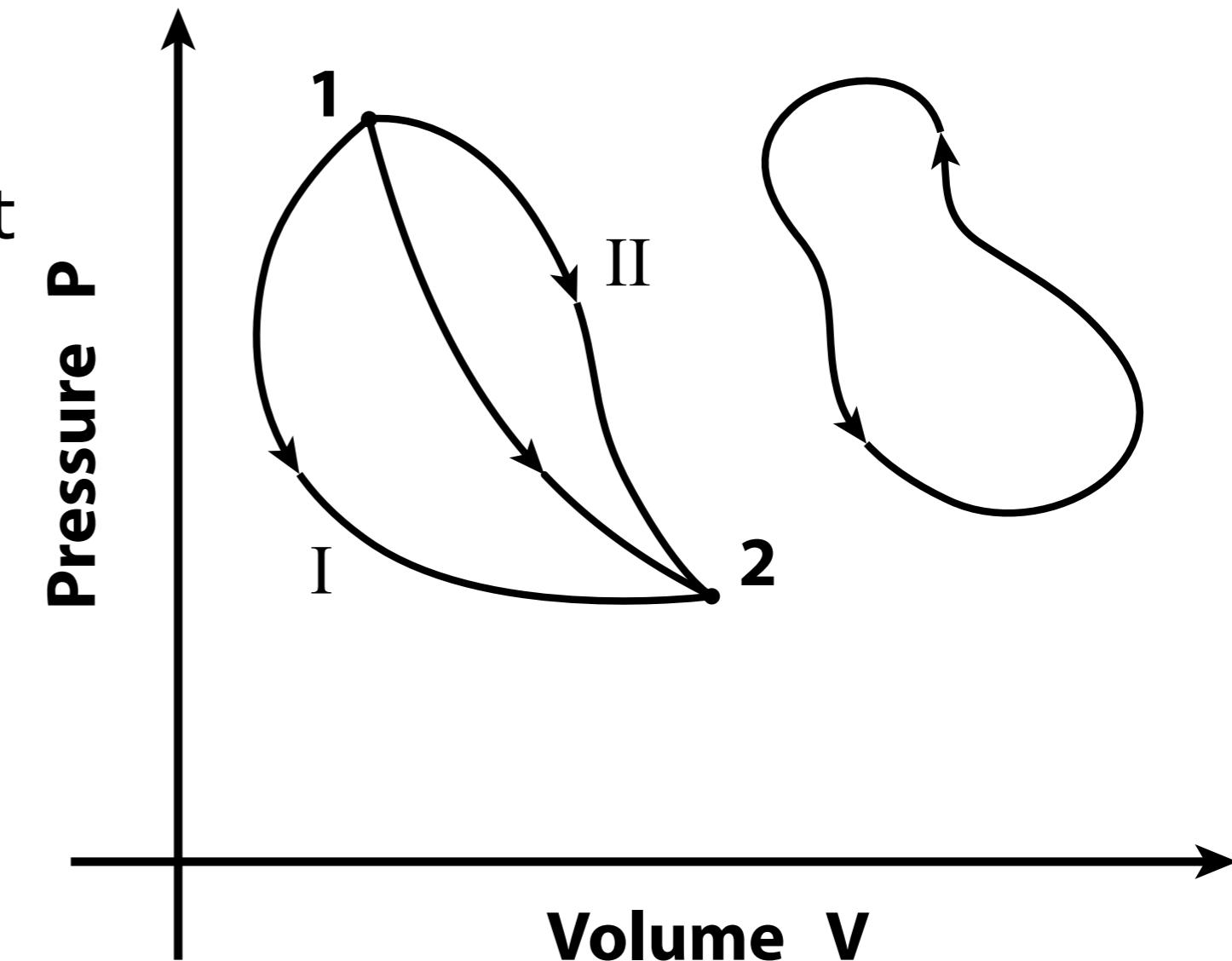
$$\left( \int_1^2 \delta Q \right)_I \neq \left( \int_1^2 \delta Q \right)_{II}$$

Entropy variation for cyclic process

$$\oint dS = 0$$

Entropy is a state function:

$$\int_1^2 dS = S(2) - S(1)$$



# Entropy generation

**Heat exchange between two thermal reservoirs**

Entropy decrease of the hotter system

$$\Delta S_A = \frac{Q}{T + \Delta T}$$

Entropy increase of the colder system

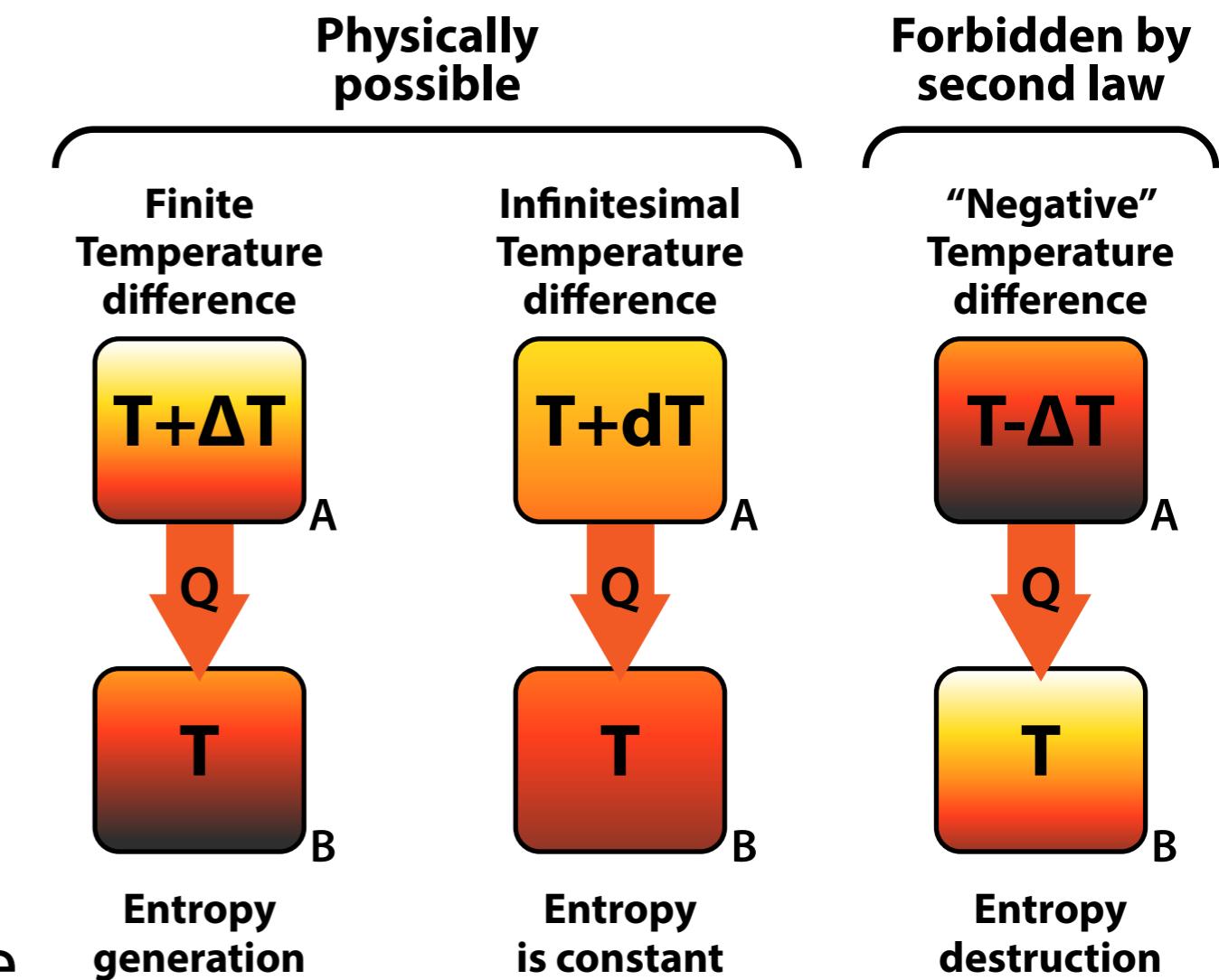
$$\Delta S_B = \frac{Q}{T} > \Delta S_A$$

Entropy *generation*: finite T difference

$$S_{\text{gen}} = \Delta S_B - \Delta S_A$$

Entropy is *constant*: infinitesimal T difference

Entropy *destruction*: violates second law  
(hotter system would have to receive heat)



# Entropy and the second law of thermodynamics

For a reversible process:

$$\int_1^2 \frac{\delta Q}{T} = S(2) - S(1)$$

In general:

$$\int_1^2 \frac{\delta Q}{T} \leq S(2) - S(1)$$

For an isolated system  $\delta Q = 0$

$$S(2) \geq S(1)$$

For an isolated system

$dS > 0$  evolving towards equilibrium

$dS = 0$  at equilibrium

$dS < 0$  forbidden by second law

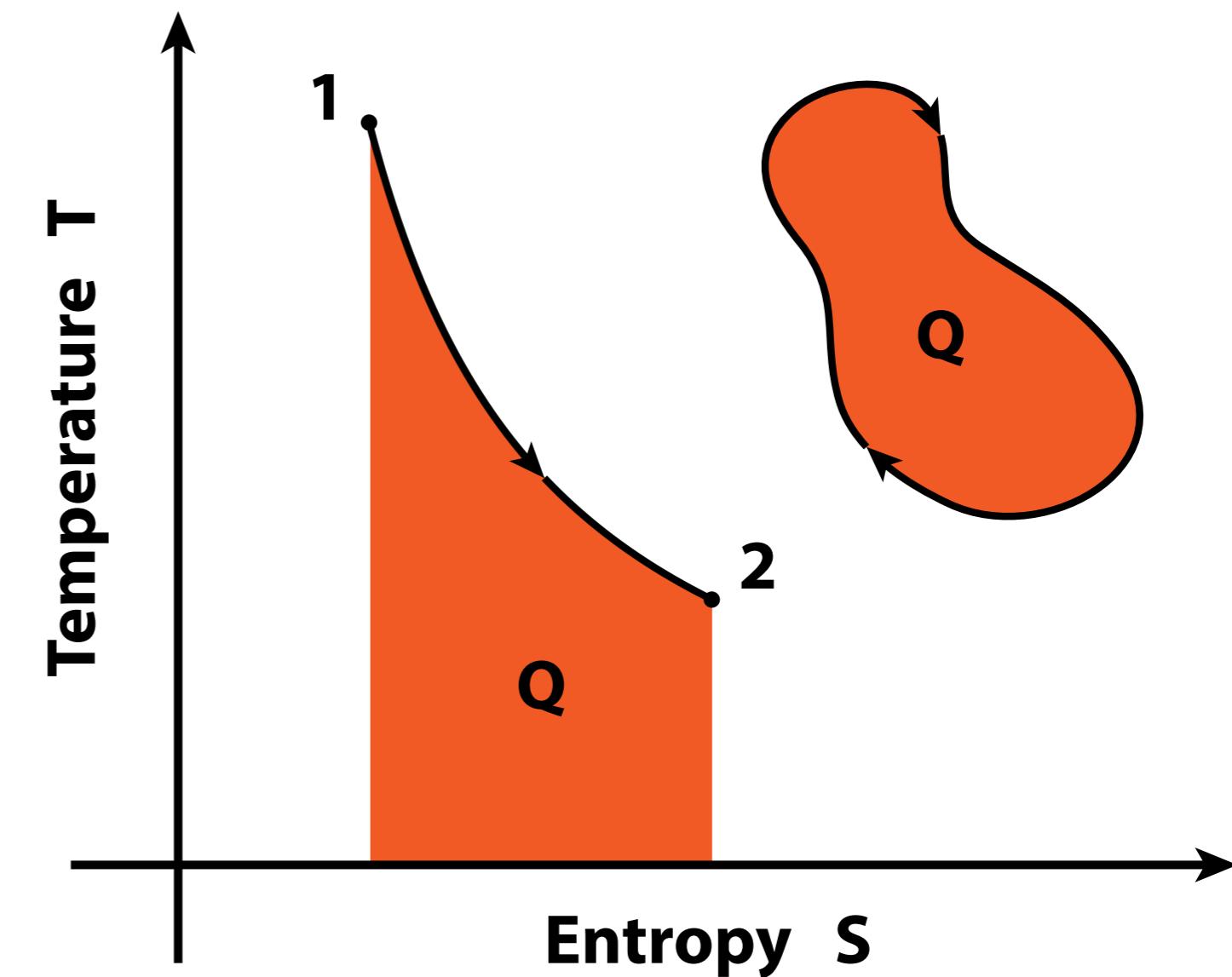
*For any transformation occurring in an isolated system, the entropy of the final state can never be less than that of the initial state.*

*The state of maximum entropy is the most stable state for an isolated system.*

# T-S Diagrams

- As we will see, for a simple, pure compressible substance, two independent variables (such as T and S) completely determine the state of the system at equilibrium.
- The other state variables are determined by the equation of state.
- For reversible processes, the energy transferred to the system in form of heat is associated to its entropy changes:

$$\delta Q = +T dS$$



# Specific entropy

Entropy variation is the ratio:

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

The heat exchange is additive (energy is an extensive property)

The temperature is an intensive property.

Therefore entropy is additive: it is an *extensive property*.

For a composite system, as long as:

- the energy of the system is the sum of the energies of its parts
- the work performed by the system during a transformation  
    is the sum of the work performed by all the parts

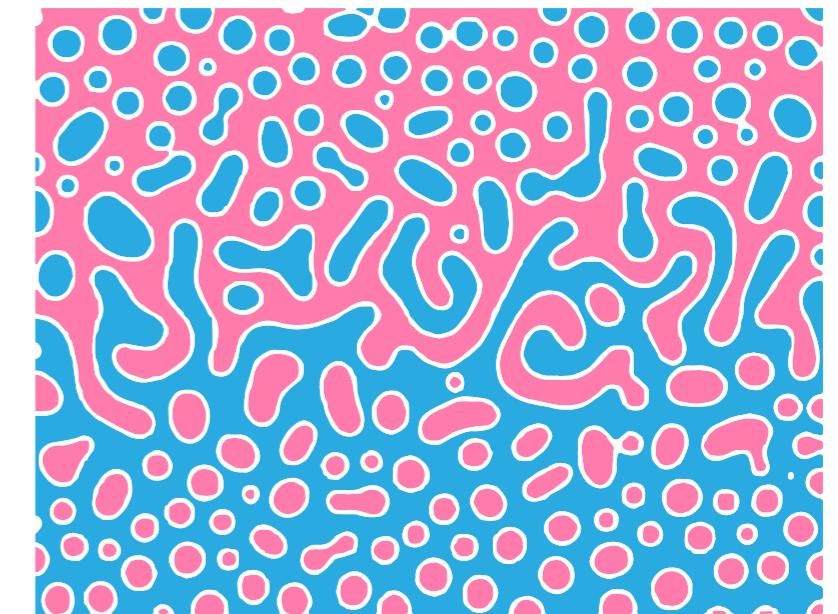
then *the entropy of the composite system is the sum of the entropies of all its parts*.

The *specific entropy* is an intensive property defined as:  $s = \frac{S}{m}$

# Specific entropy

Counterexample:

the energy of a system composed of two substances  
is the sum of the energies of the two substances  
only if we can neglect the surface energy  
at the interface between them (e.g. surface tension)



For a composite system, as long as:

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- the work performed by the system during a transformation  
    is the sum of the work performed by all the parts

then *the entropy of the composite system is the sum of the entropies of all its parts.*

The *specific entropy* is an intensive property defined as:  $s = \frac{S}{m}$

# The state postulate

Entropy is a state function.

The state of a given amount (i.e. given mass  $m$  or number of moles) of a pure, simple compressible substance is completely described by two state variables (e.g. internal energy  $U$  and volume  $V$ ):

$$S = S(U, V, m)$$

The *specific entropy*  $s = S/m$  can be written as function of the specific internal energy  $u = U/m$  and the specific volume  $v = V/m$

$$s = s(u, v)$$

# Entropy, temperature and pressure

We consider a fixed amount of pure, simple compressible substance. The first law of thermodynamics for an infinitesimal process is:

$$dU = \delta Q + \delta W$$

Where:

$dU$  is the variation of internal energy of the system

$\delta Q = +T dS$  is the energy transferred to the system in the form of heat

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

Since the amount is fixed, the mass  $m$  is constant.

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Since the amount is fixed, the mass  $m$  is constant.

If the process is isochoric ( $\text{const } V$ ):  $\delta W = 0$

$$dU = \delta Q = T dS$$

therefore:

$$T = \left( \frac{\partial U}{\partial S} \right)_{m,V}$$

or:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{m,V} = \left( \frac{\partial s}{\partial u} \right)_v$$

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or:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{m,V} = \left( \frac{\partial s}{\partial u} \right)_v$$

If the internal energy is constant:  $dU = 0$

$$\delta Q = -\delta W \implies T dS = P dV$$

therefore:

$$P = T \left( \frac{\partial S}{\partial V} \right)_{m,U}$$

or:

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{m,U} = \left( \frac{\partial s}{\partial v} \right)_u$$

# Gibbs Equation - the fundamental thermodynamic relation

We consider a fixed amount of pure, simple compressible substance.  
The first law of thermodynamics for an infinitesimal process is:

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Where:

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The first law can thus be written as:

$$dU = T dS - P dV$$

Or in term of specific quantities:

$$du = T ds - P dv$$

# Gibbs Equation - the fundamental thermodynamic relation

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The first law can thus be written as:

$$dU = T dS - P dV$$

or:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

Or in term of specific quantities:

$$du = T ds - P dv$$

or:

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

**Gibbs  
equation**

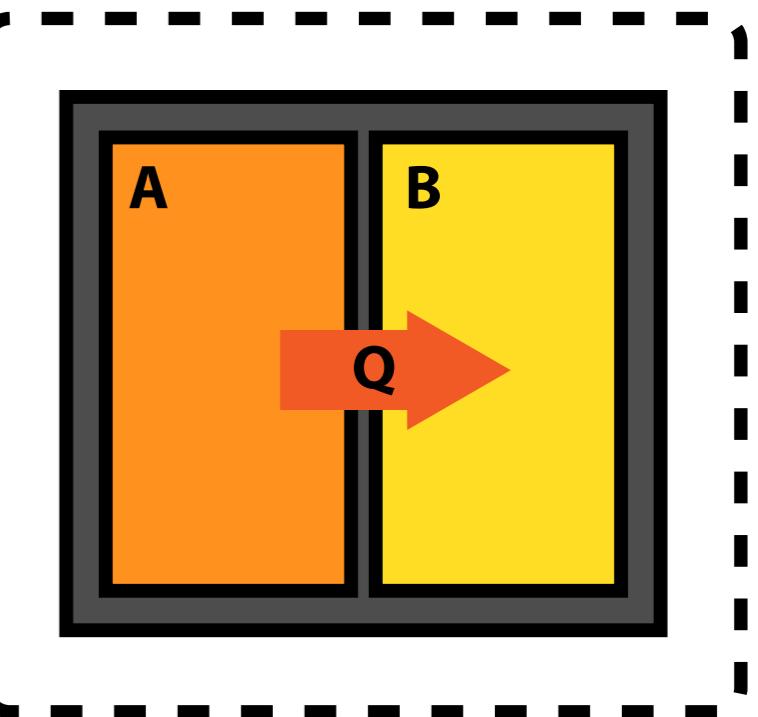
# Thermal equilibrium and temperature

Two chambers A and B of pure substances are connected so that:

- they cannot exchange mass (masses fixed).
- they can exchange energy in form of heat.
- they cannot exchange work (volumes fixed)

Initially, they are not in thermal equilibrium:  $T_A \neq T_B$ .

Composite system C



The composite system C is isolated:  $dU_C = dU_A + dU_B = 0$   
Its entropy is:

$$S_C = S_A(U_A, V_A, m_A) + S_B(U_B, V_B, m_B)$$

$$dS_C = \left( \frac{\partial S_A}{\partial U_A} \right)_{m_A, V_A} dU_A + \left( \frac{\partial S_B}{\partial U_B} \right)_{m_B, V_B} dU_B \quad \text{using} \quad \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{m, V}$$

$$dS_C = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A = \left( \frac{1}{T_B} - \frac{1}{T_A} \right) dU_B$$

If  $T_A \neq T_B$ , then  $dS_c > 0$   
If  $T_A = T_B$ , then  $dS_c = 0$

# Mechanical equilibrium and pressure

Two chambers A and B of pure substances are connected so that:

- they cannot exchange mass (masses fixed).
- they can exchange energy in form of heat.
- they can exchange energy in form of work.

Initially, they are not in thermal equilibrium:  $T_A \neq T_B$ .  
they are not in mechanical equilibrium:  $P_A \neq P_B$ .

Following a similar procedure, and using  $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{m,U}$  and  $dV_A + dV_B = 0$

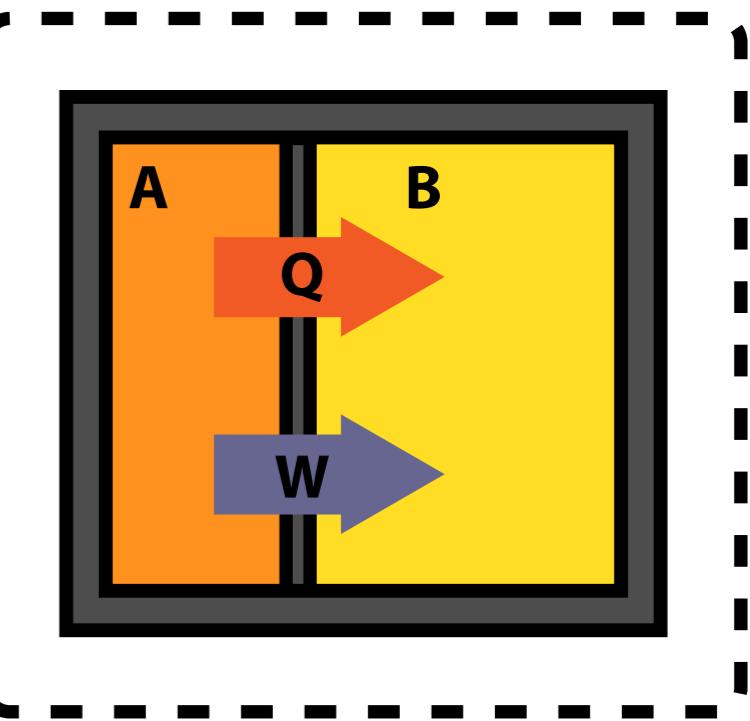
$$dS_C = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV_A$$

Assuming thermal equilibrium ( $T_A = T_B = T$ ):

$$dS_C = \frac{1}{T} (P_A - P_B) dV_A = \frac{1}{T} (P_B - P_A) dV_B$$

If  $P_A \neq P_B$ , then  $dS_c > 0$   
If  $P_A = P_B$ , then  $dS_c = 0$

Composite system C

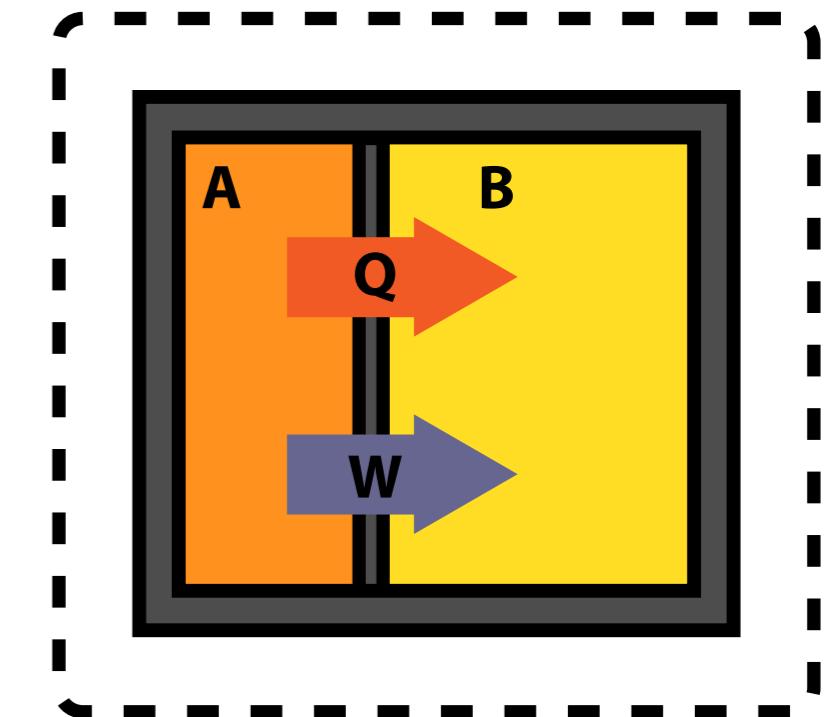


# Entropy variation

The previous results can be generalized:

*Whenever pressure gradients or temperature gradients are present within an isolated system, it will evolve towards the equilibrium thus reducing the gradients until pressure and temperature are uniform.*

Composite system C



*During this spontaneous process, the entropy increases until it reaches its maximum value corresponding to the equilibrium state.*

---

Now we will see how to calculate entropy variation in some cases.

# 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:  $dV \neq 0$

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 expression for  $du$ , and we use the ideal gas law to eliminate the pressure. (Ideal gas law:  $Pv = RT$  with  $R = R_u/M = R_um/N$ )

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 expression for  $dh$ , and we use the ideal gas law to eliminate the volume. (Ideal gas law:  $Pv = RT$  with  $R = R_u/M = R_um/N$ )

The infinitesimal variation of specific entropy is thus:

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

For a finite process:

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

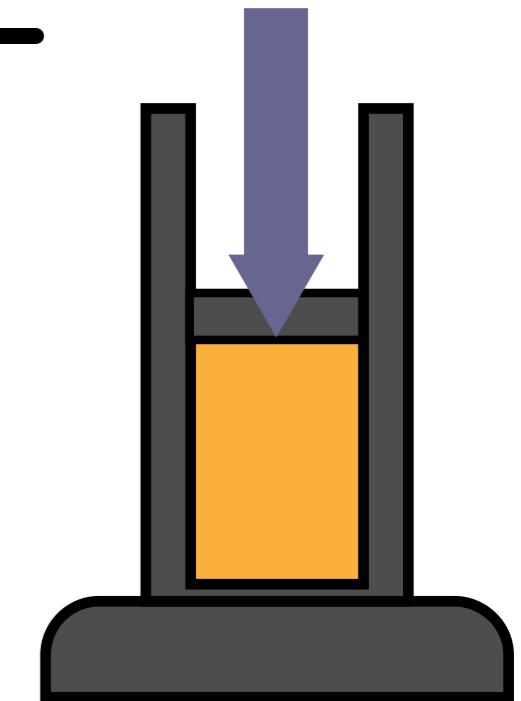
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## Example 6.2

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

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Gas constant of hydrogen (Appendix 1)

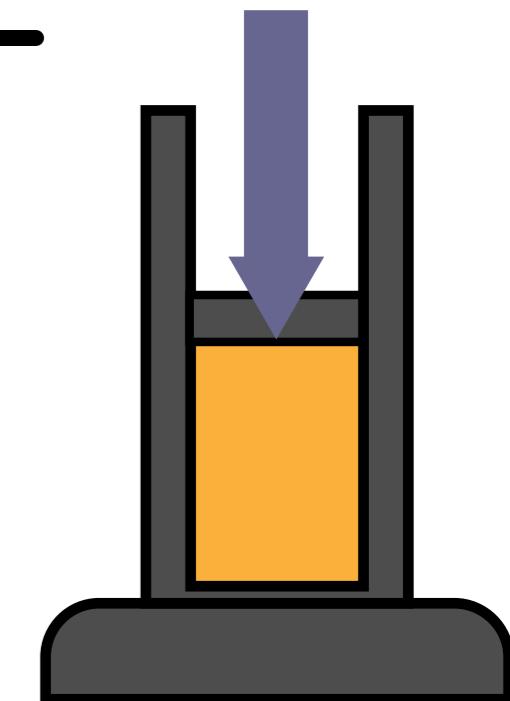
$$R = 4.124 \text{ kJ/kgK}$$

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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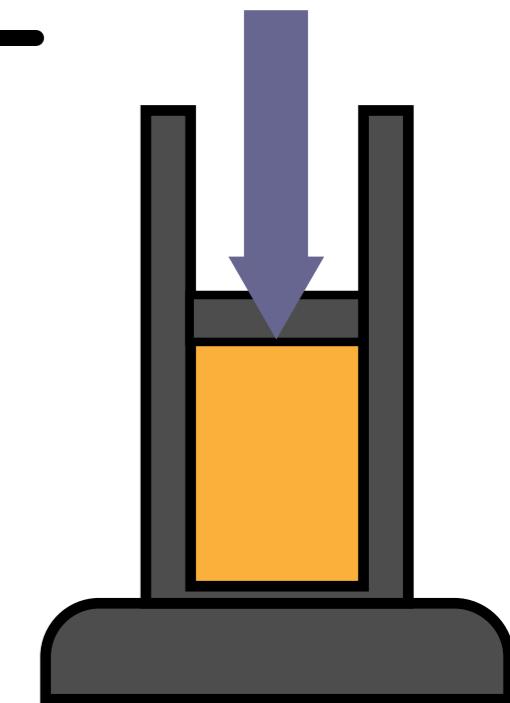
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Change of specific entropy

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



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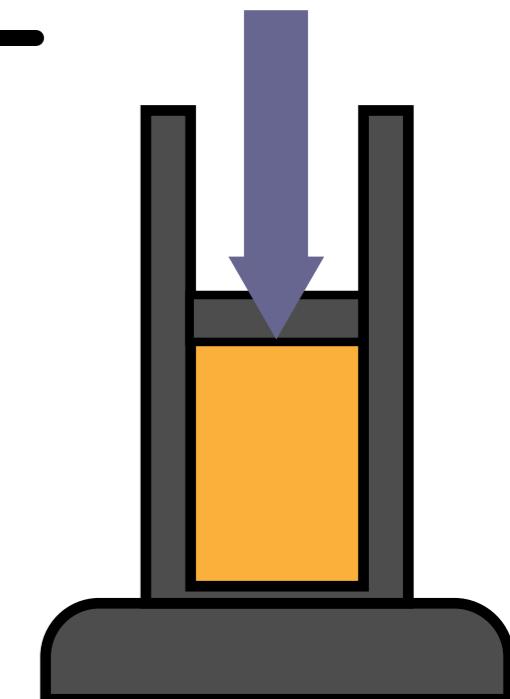
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$$\Delta s = 10.389 \text{ kJ/kgK} \times \log \left( \frac{650 \text{ K}}{350 \text{ K}} \right) + 4.124 \text{ kJ/kgK} \times \log \left( \frac{0.2 \text{ m}^3/\text{kg}}{1.0 \text{ m}^3/\text{kg}} \right) = -0.20645 \text{ kJ/kgK}$$



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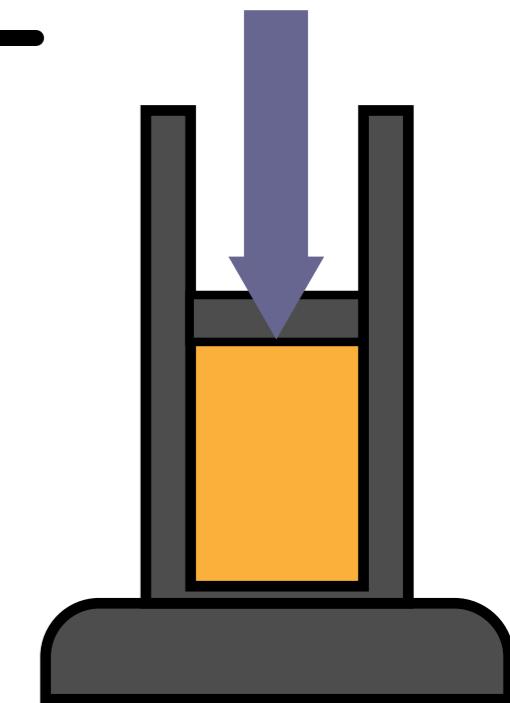
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Change of entropy

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



# 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  $T_{\text{ref}} = 0 \text{ K}$ ) is tabulated for some gases:

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

Then we split the integral in two terms:

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

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:

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

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

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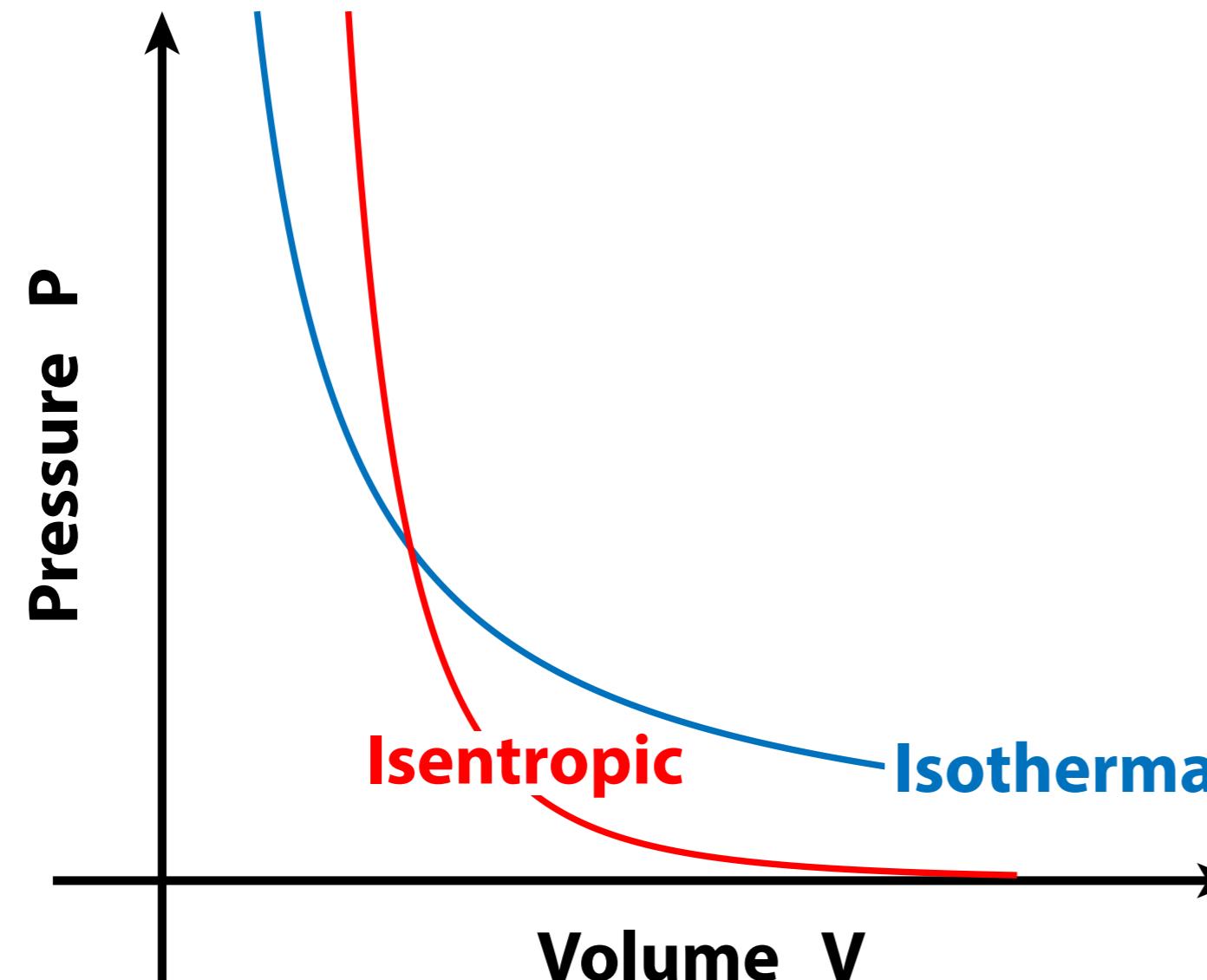
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$$\frac{P_2}{P_1} = \left( \frac{v_1}{v_2} \right)^\gamma \implies P_2 v_2^\gamma = P_1 v_1^\gamma$$

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

# Isentropic processes in ideal gases

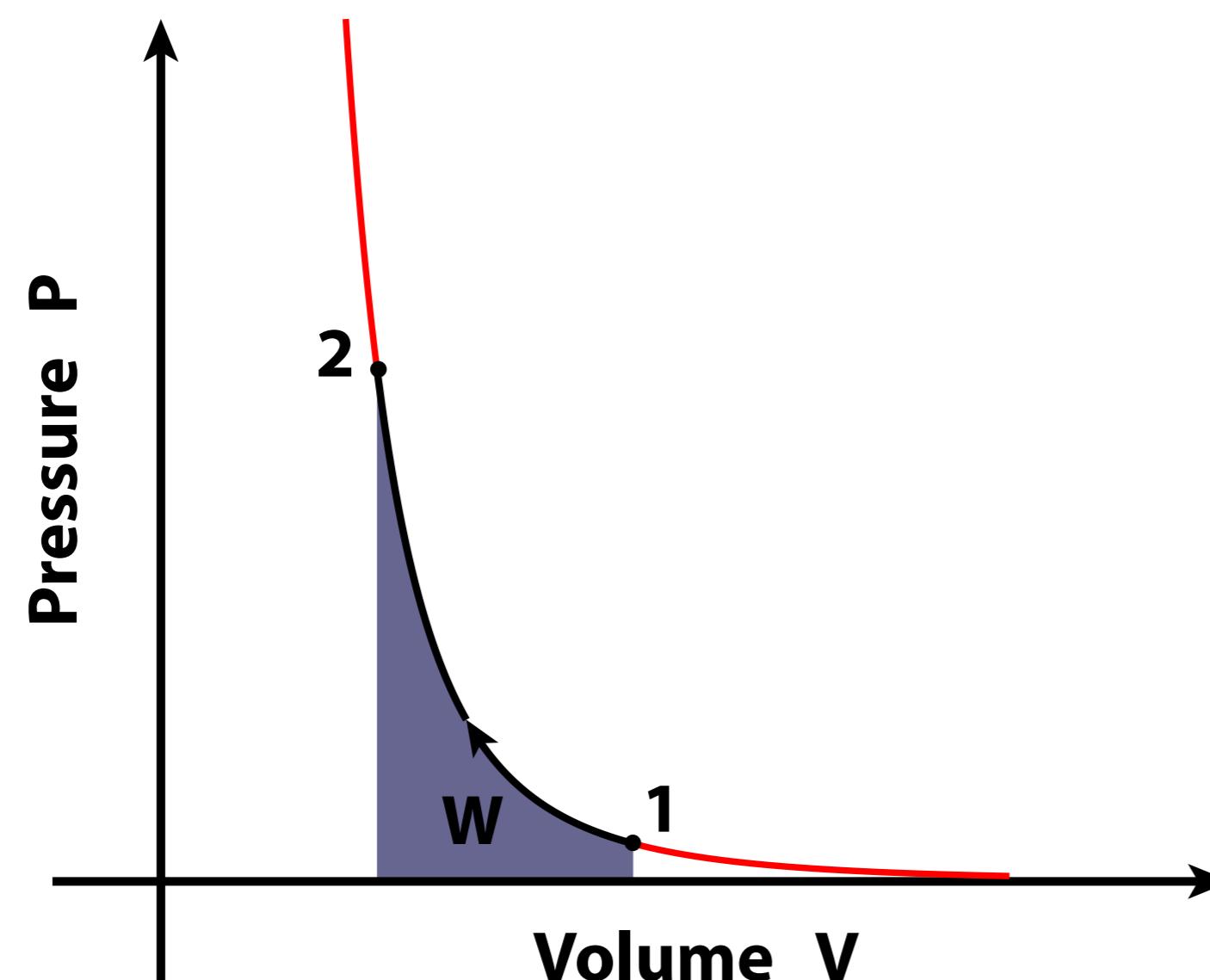


Isothermal:  
Isentropic:

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

# 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:  $P = P_1 \left( \frac{V_1}{V} \right)^\gamma$

For a finite process:

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

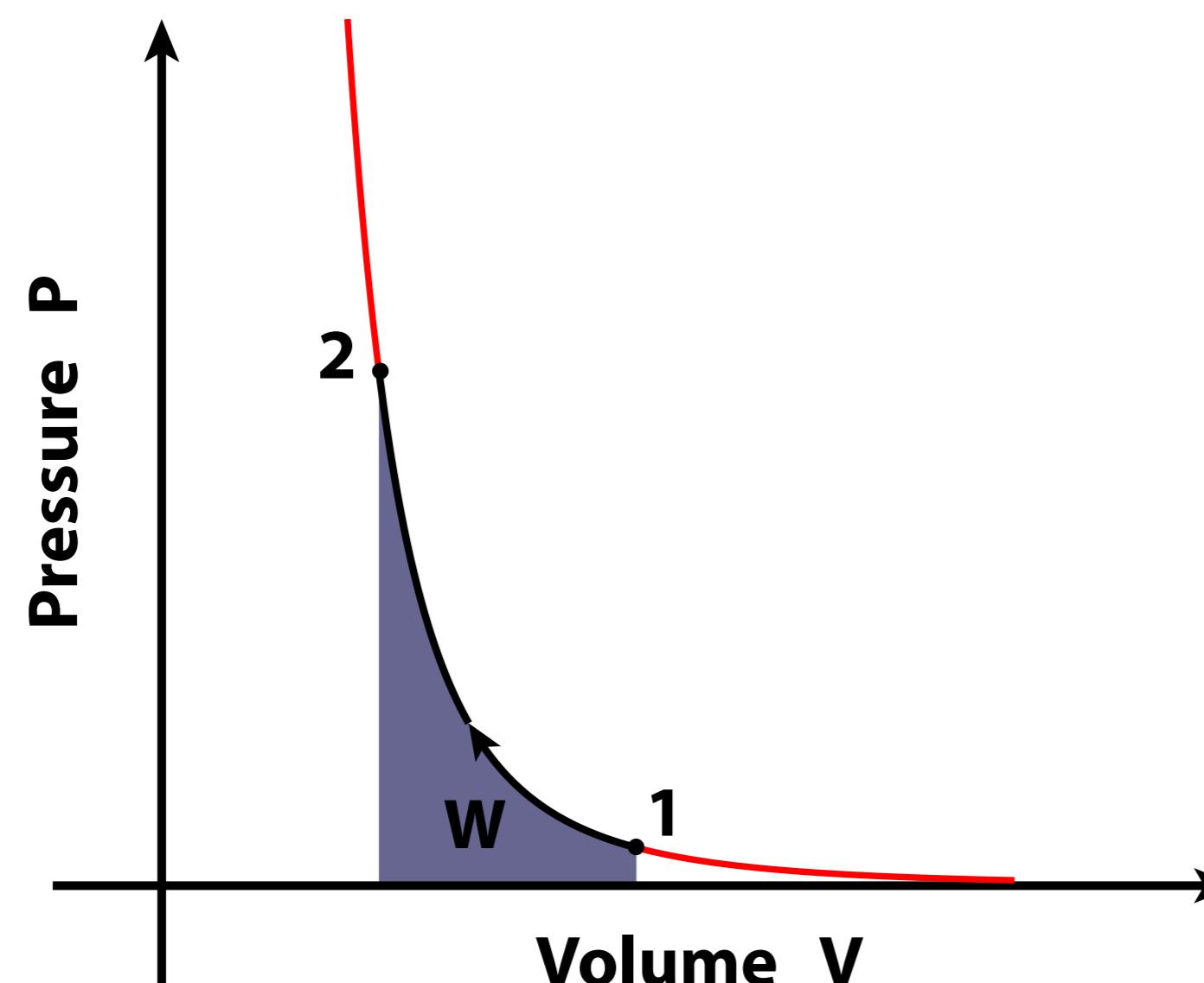
$$P_2 v_2^\gamma = P_1 v_1^\gamma$$

Isentropic:

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

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For a finite process:

$$\begin{aligned} W &= \int_1^2 \delta W = - \int_{V_1}^{V_2} P_1 \left( \frac{V_1}{V} \right)^\gamma dV \\ &= -P_1 V_1^\gamma \left[ \frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2} = -P_1 V_1^\gamma \frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma} \end{aligned}$$

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

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

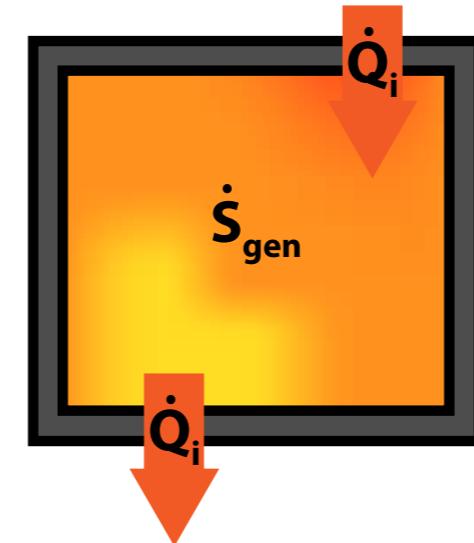
Isentropic:

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# Entropy balance

Control mass	Closed system	Heat transfer	Mass transfer
		yes	no

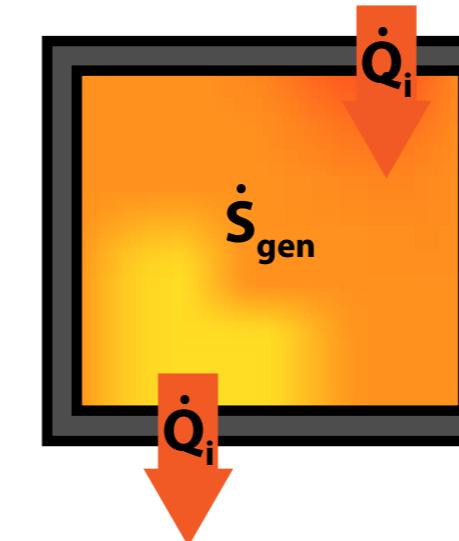
Control mass



# Entropy balance

	Heat transfer	Mass transfer
Control mass	yes	no
Closed system		

Control mass



**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

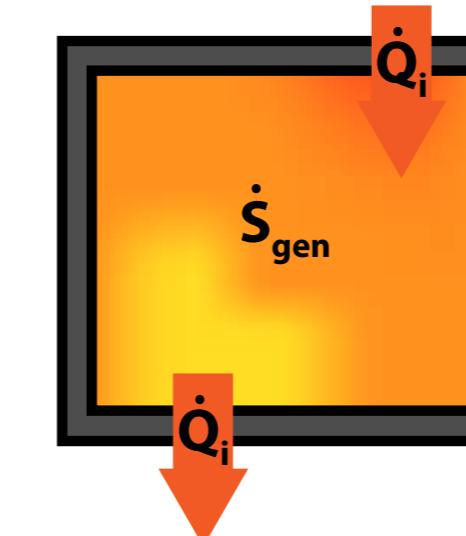
$$\sum_j \frac{\dot{Q}_j}{T_j}$$

- Associated to heat transfer (in absence of T-gradients:  $T_j = T$ )

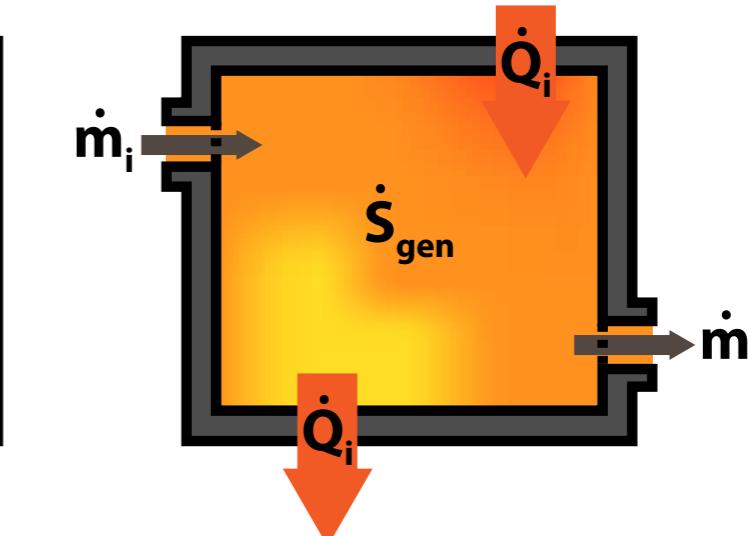
# Entropy balance

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

Control mass



Control volume



**Total entropy variation of the system:**

$$\dot{S} = \dot{S}_{\text{gen}} + \sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i$$

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Entropy transfer to/from outside the system

$$\sum_j \frac{\dot{Q}_j}{T_j}$$

- Associated to heat transfer (in absence of T-gradients:  $T_j = T$ )

$$\sum_i \dot{m}_i s_i$$

- Associated to mass transfer ( $\dot{m}_i$  mass flow-rate,  $s_i$  specific entropy)

# Entropy balance at steady flow

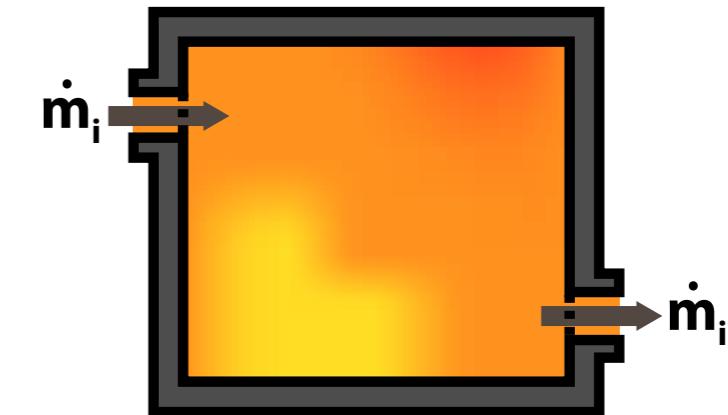
Control volume

Examples: turbines, nozzles, etc

Steady flow, adiabatic, reversible, isentropic:

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

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



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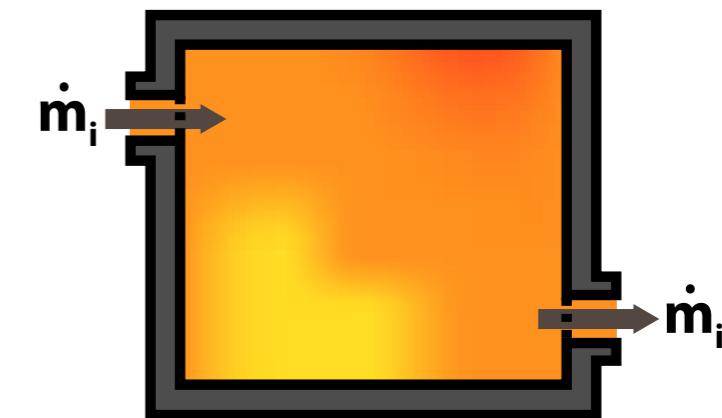
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## Example 6.12

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

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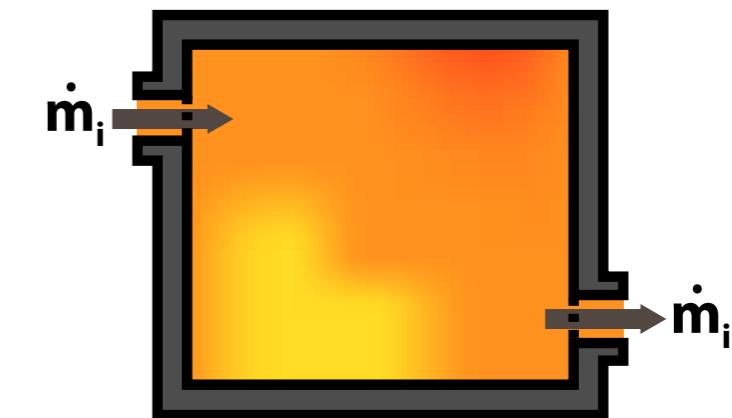
Control volume



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Control volume



ISENTROPIC process (ideal gas, constant specific heats):

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

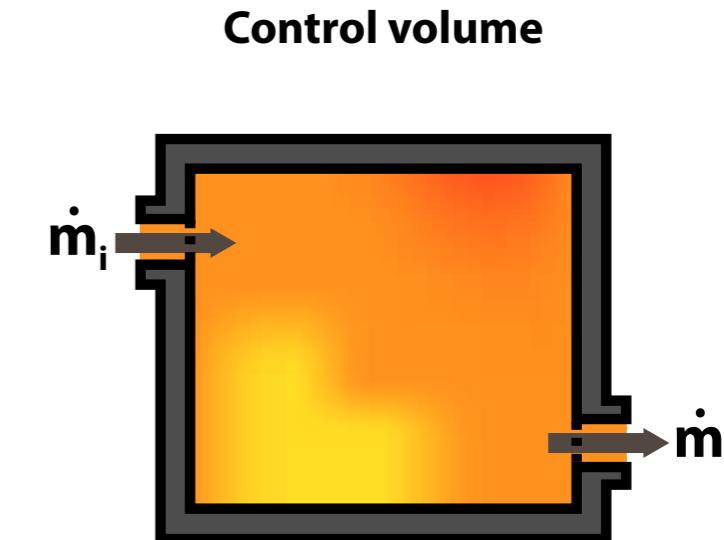
Maximum power input:

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

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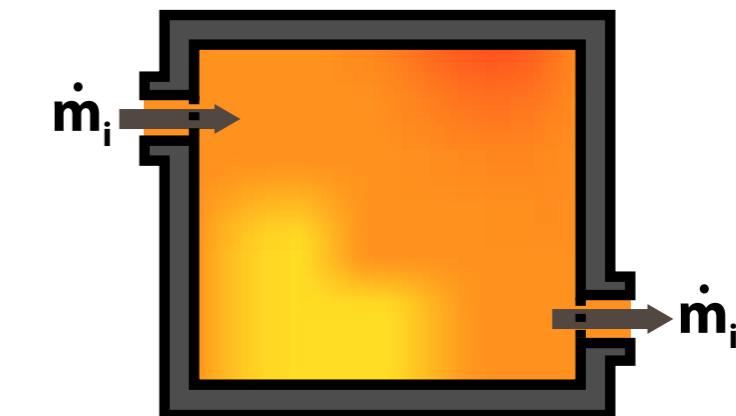
### Appendix 4 (Air)

Temp. (K)	$c_p$ (kJ/ kgK)	$c_v$ (kJ/ kgK)	$\gamma = c_p/c_v$
750	1.087	0.800	1.359
800	1.099	0.812	1.354
773.15	1.093		1.357

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$$\Rightarrow T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} = 773.15 \text{ K} \left( \frac{100 \times 10^3 \text{ Pa}}{6 \times 10^6 \text{ Pa}} \right)^{\frac{1.357-1}{1.357}} = 263.3 \text{ K}$$

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

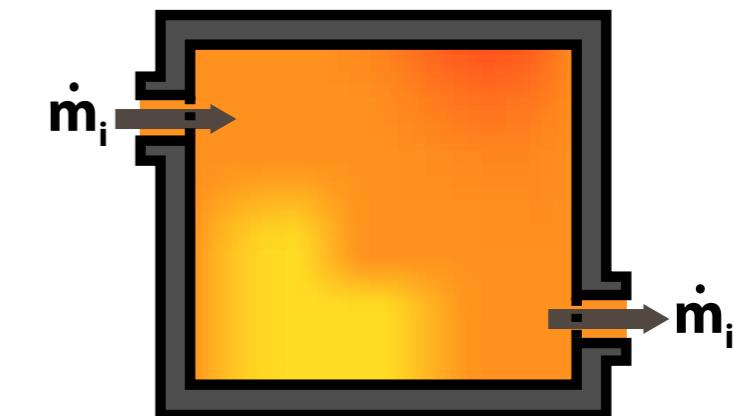
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Control volume



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

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

Maximum power output: 1115 kW

### Appendix 4 (Air)

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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 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.

# 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)

---

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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:

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

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

---

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

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

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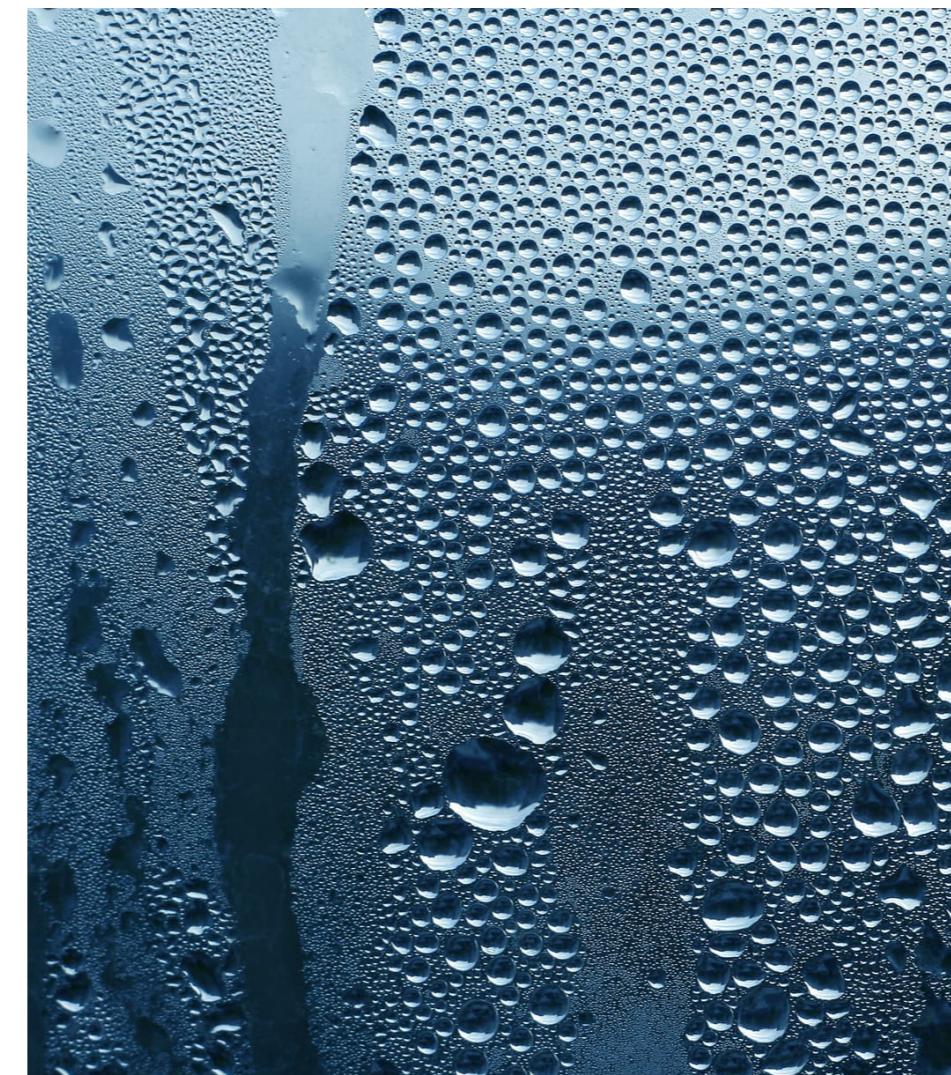
# Session 6

# Phase diagrams and phase transitions

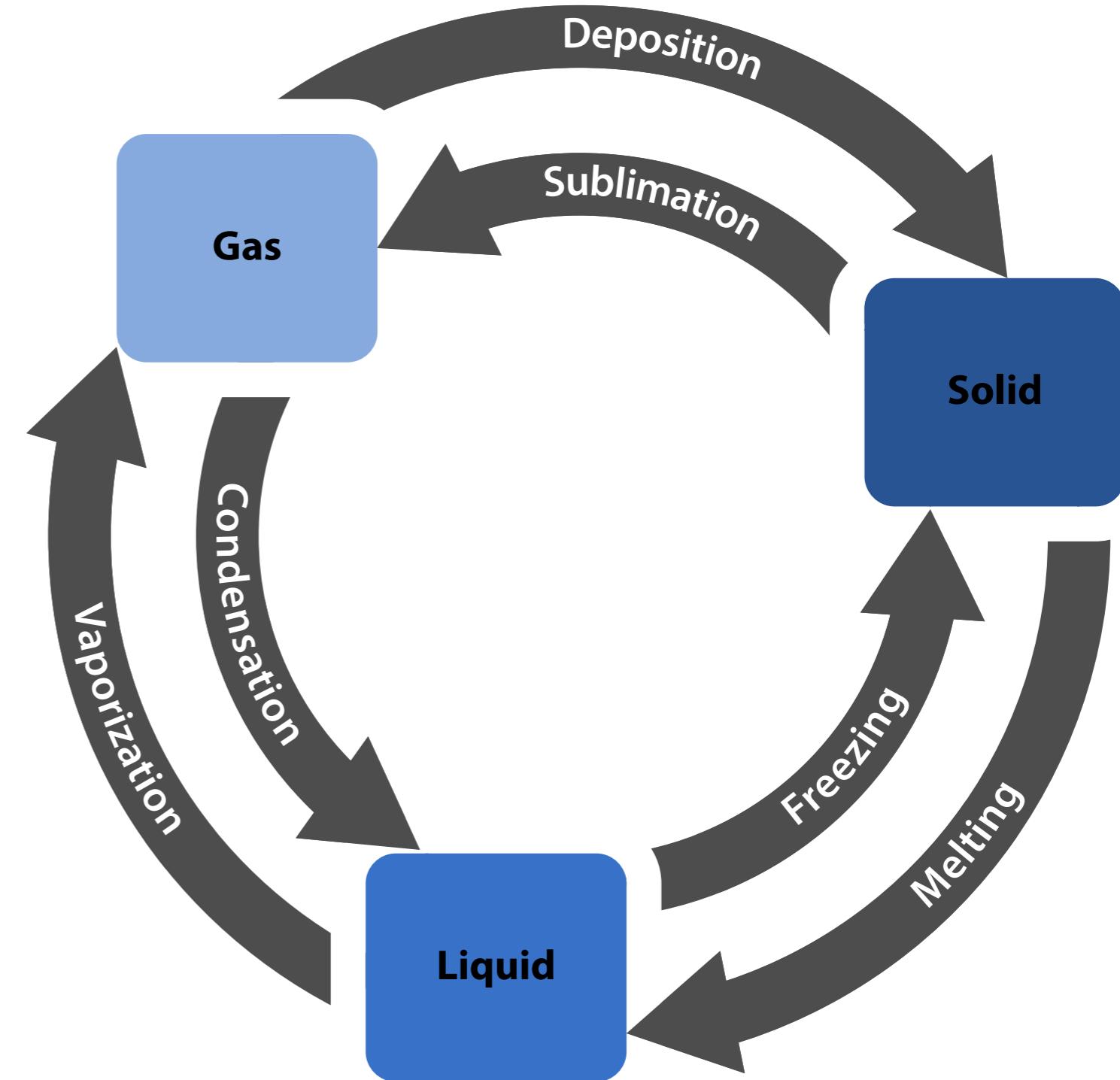
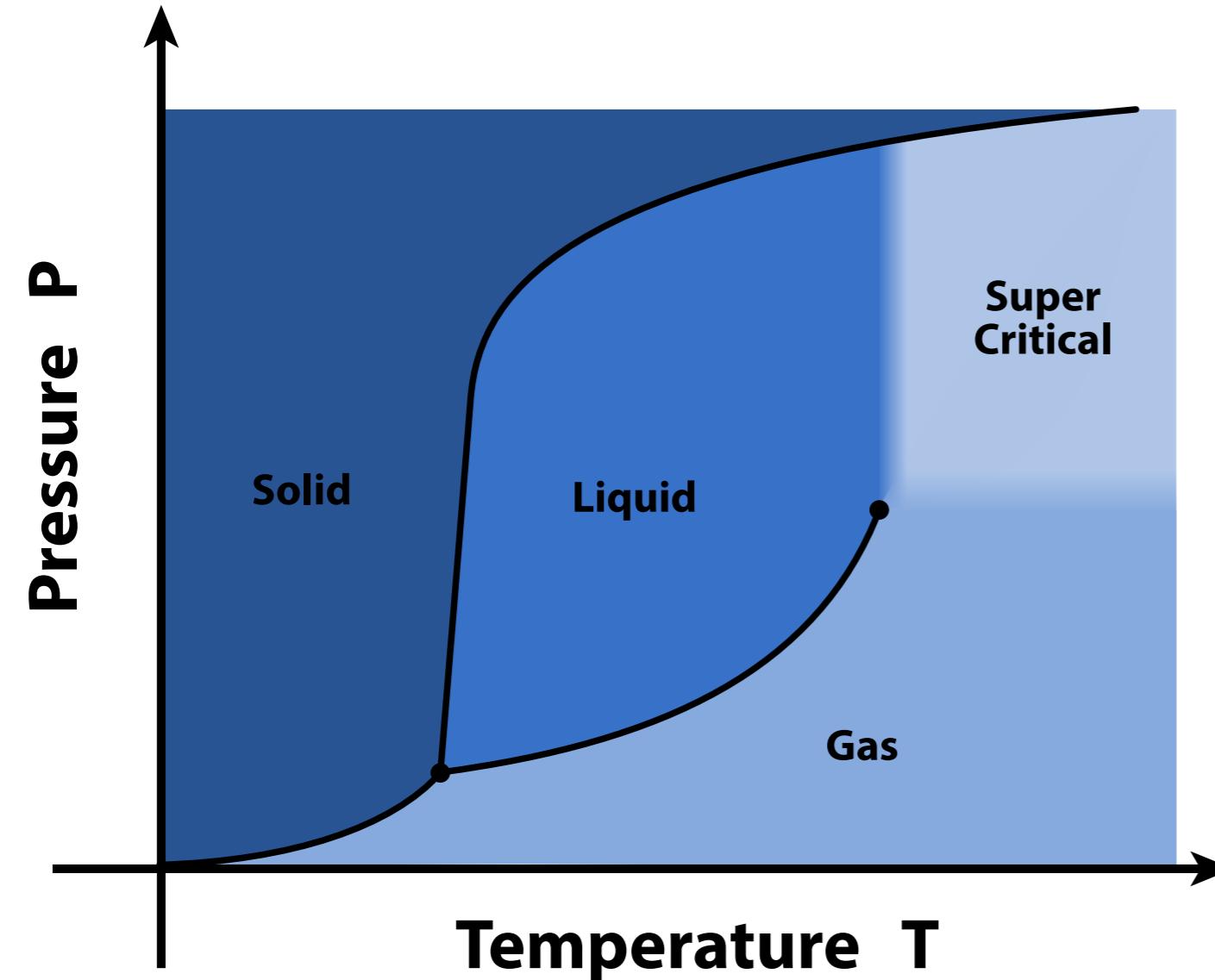
# Introduction

# Phase transitions

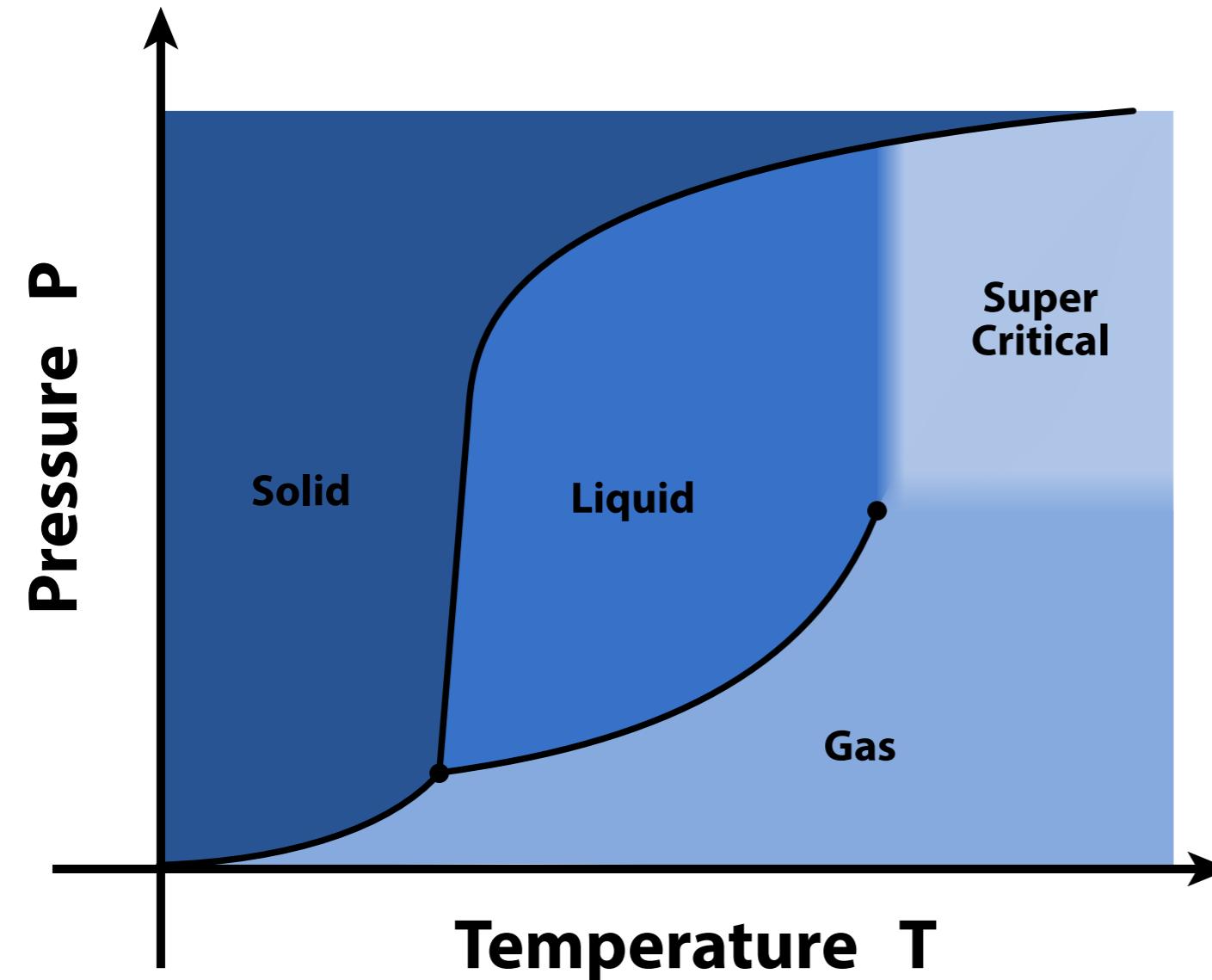
Phase transitions are changes in the state of the matter. They are qualitative transformations in the appearance and behavior of a substance that are triggered by a change in the external conditions (such as temperature or pressure).



# Solid - Liquid - Gas phase transitions

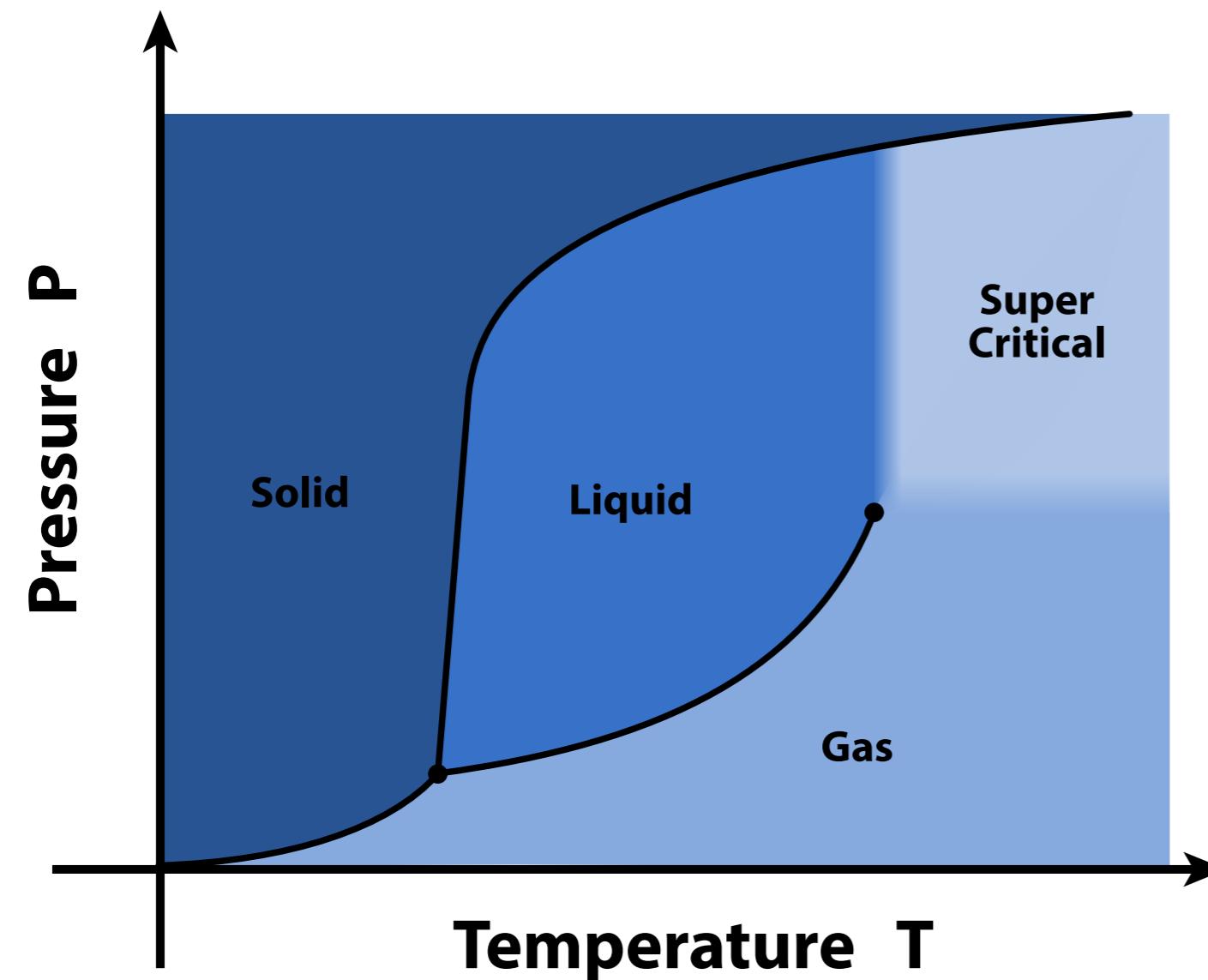


# Phase diagrams



Phase diagrams are charts that indicate the conditions (i.e. pressure, temperature, volume, ...) at which the different phases occur.

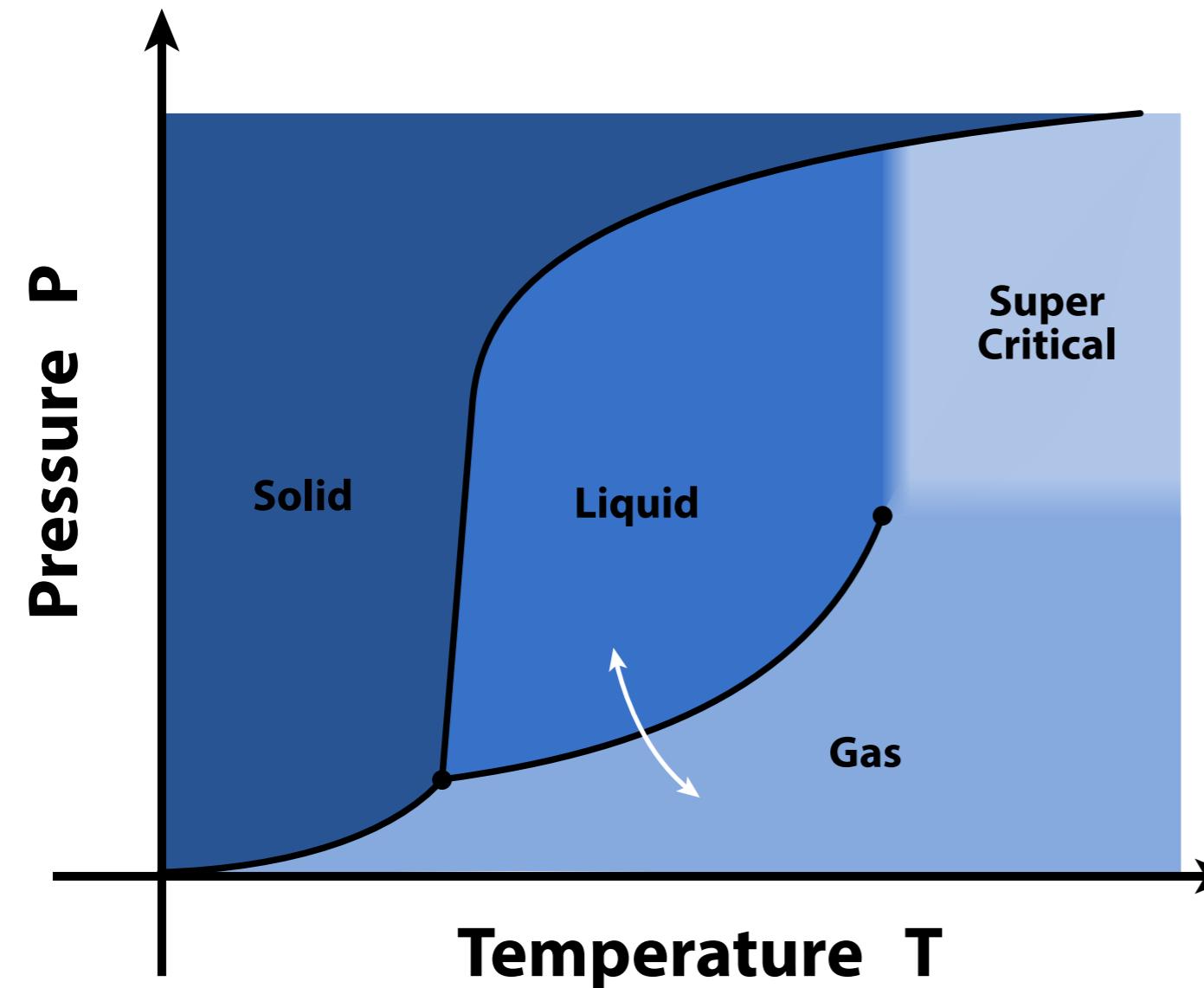
# Phase diagrams



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At the boundary between two regions, i.e. along a phase equilibrium curve, two phases can coexist at equilibrium.

# Phase diagrams

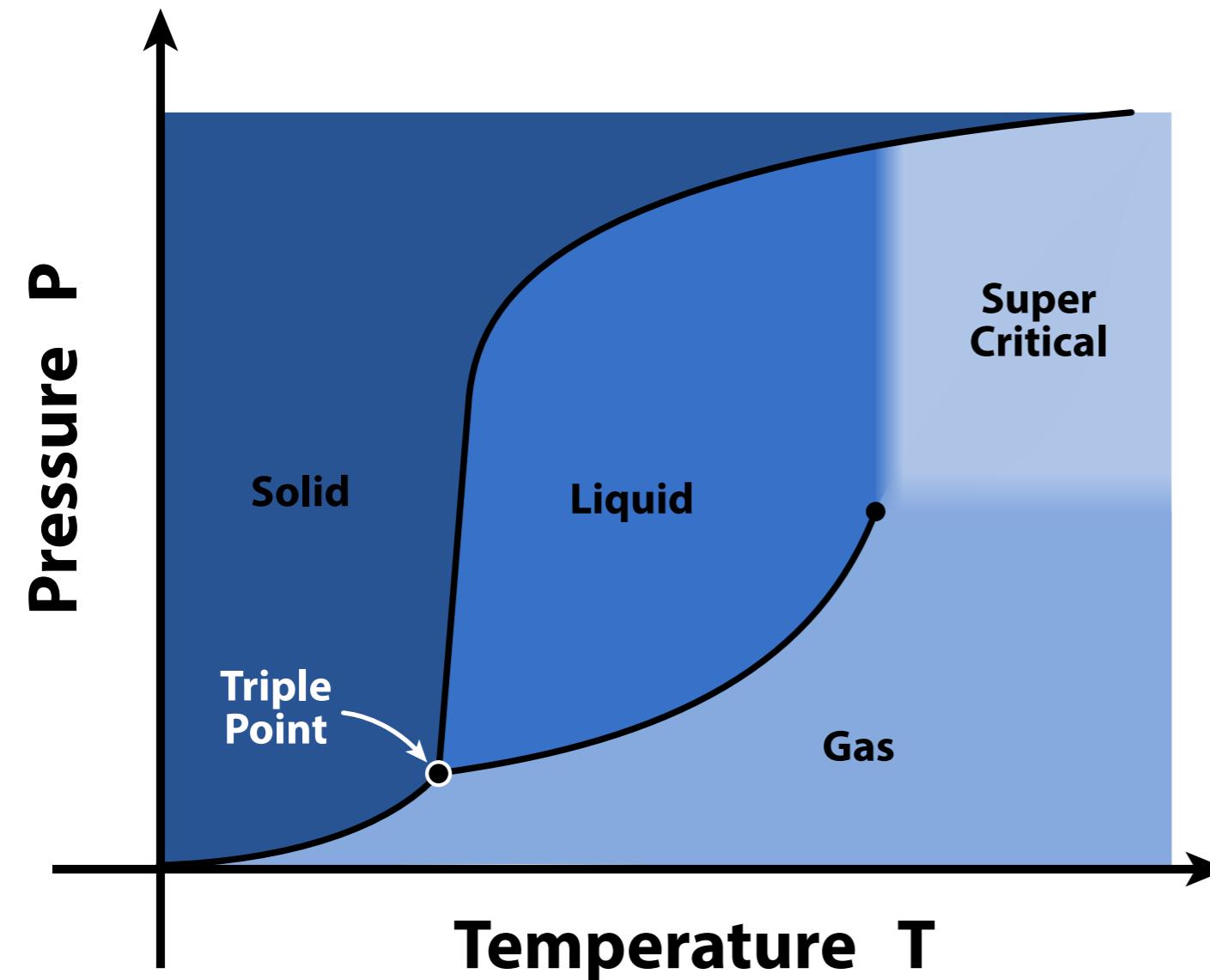


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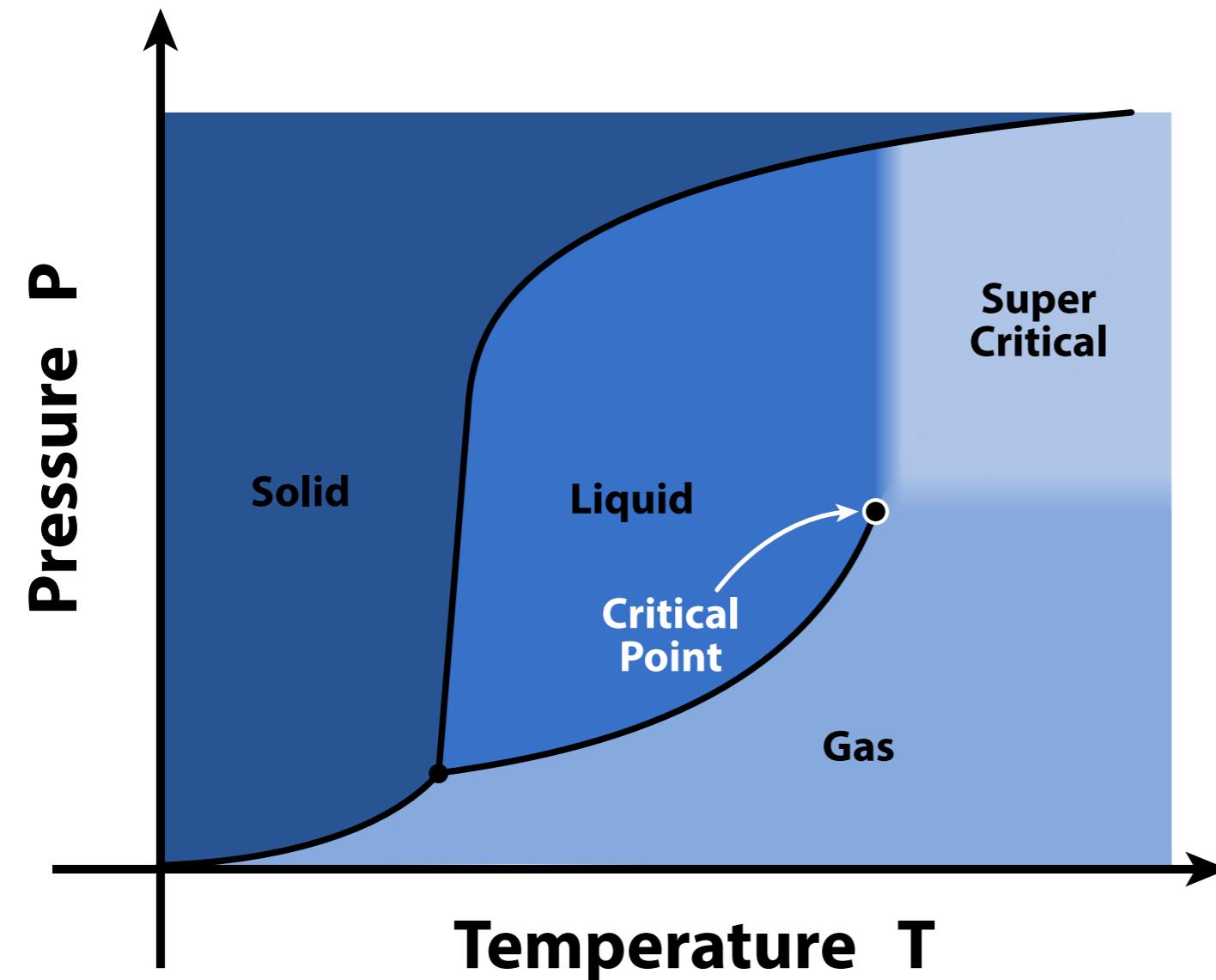
When the conditions change such that a phase equilibrium curve is crossed, the transition is triggered.

# The concept of triple point



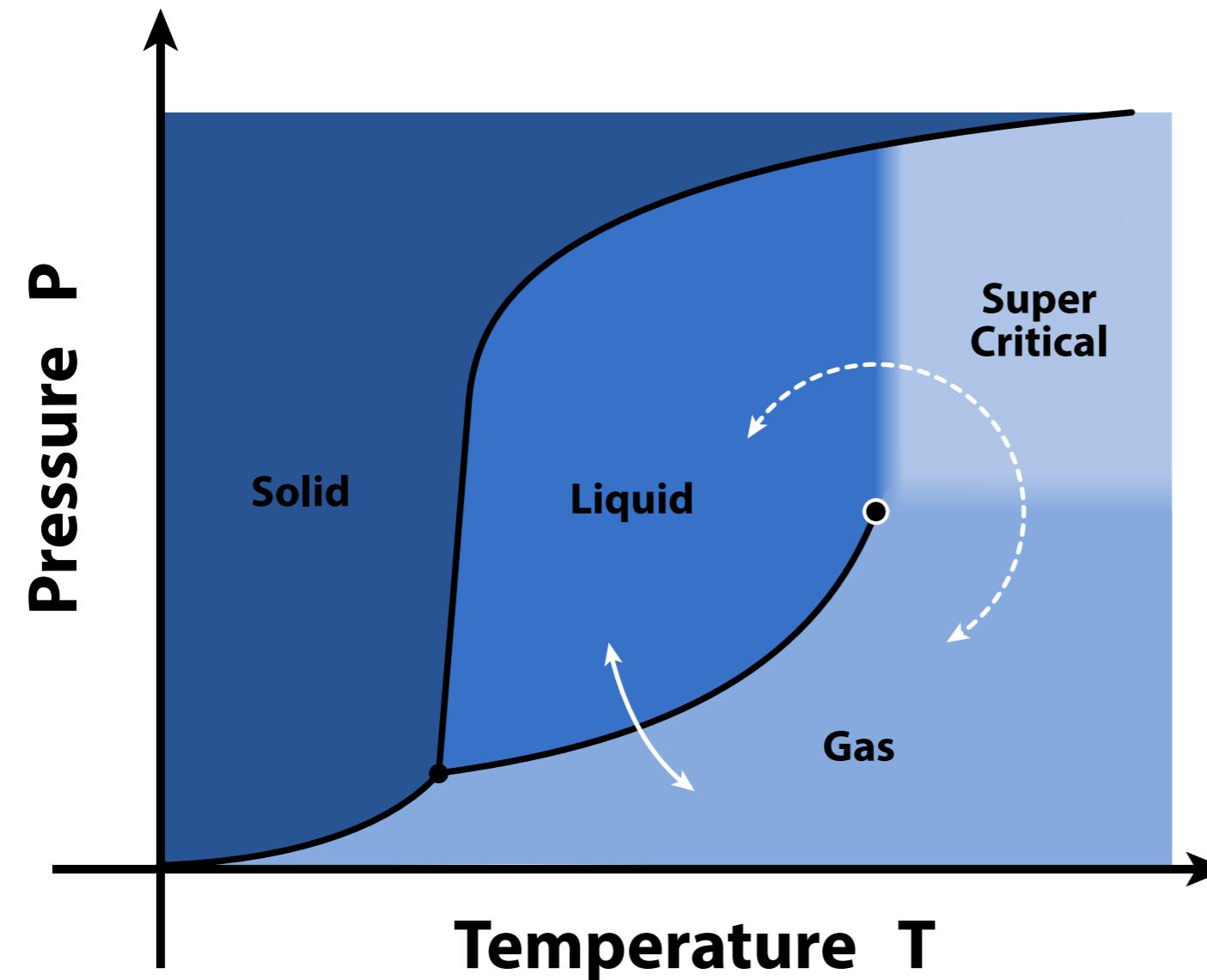
*For a given substance, the triple point corresponds to the temperature and pressure at which the three phases (gas, liquid, and solid) coexist in thermodynamic equilibrium.*

# The concept of critical point



*For a given substance, the critical point corresponds to the temperature and pressure of the end point of a phase equilibrium curve.*

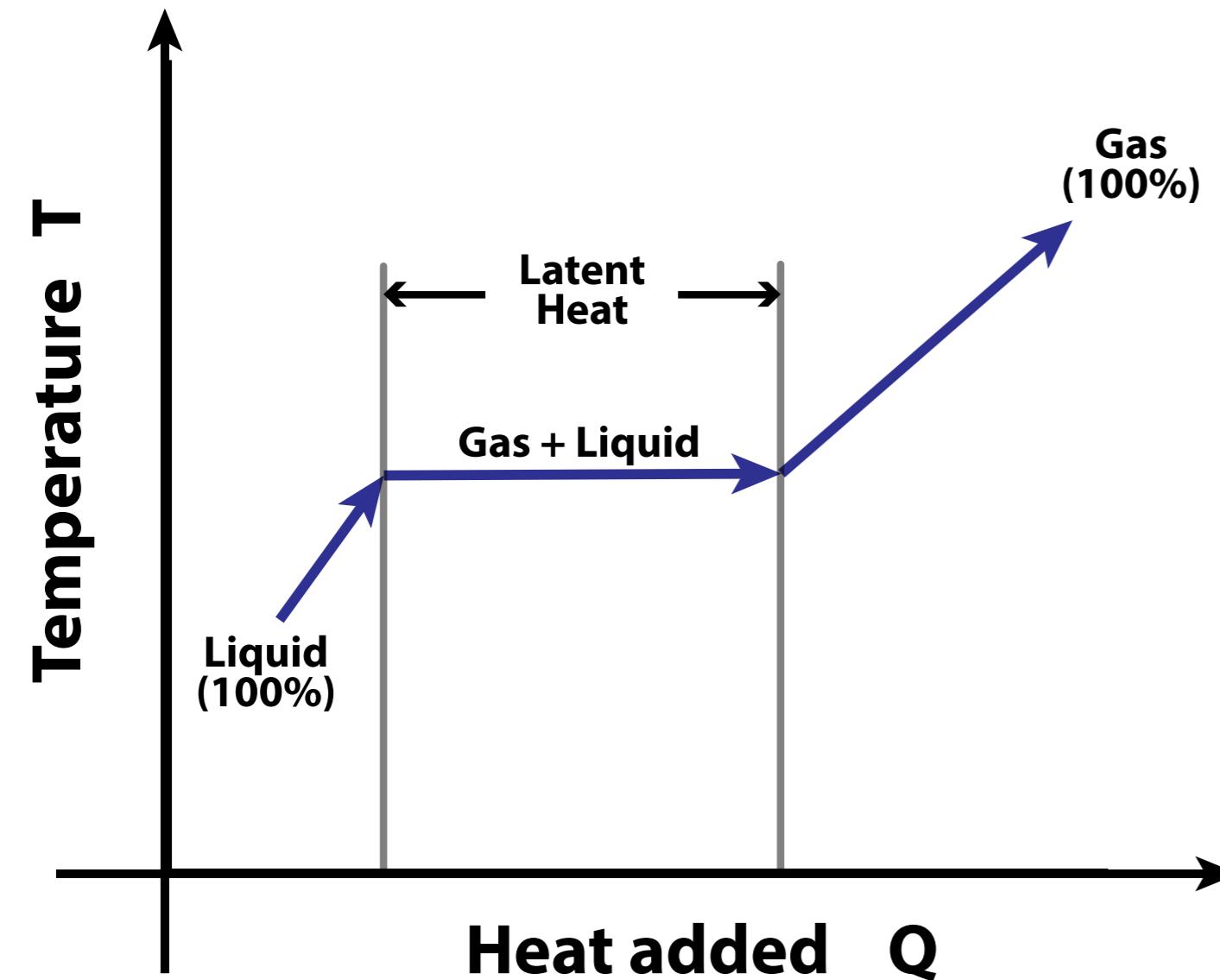
# The concept of critical point



*For a given substance, the critical point corresponds to the temperature and pressure of the end point of a phase equilibrium curve.*

Beyond the critical point phase boundaries vanish: the transition between the two phases happens smoothly.

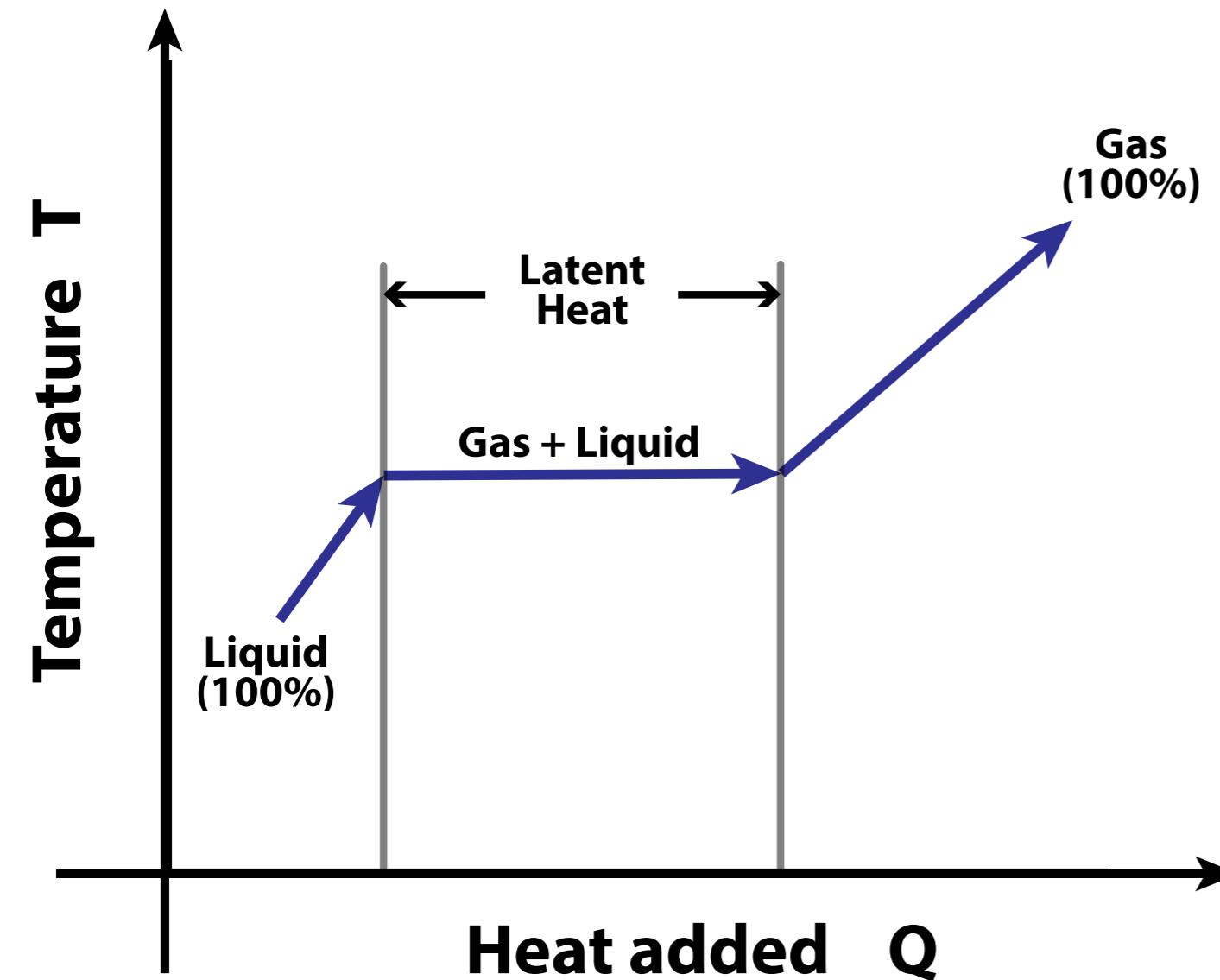
# The concept of latent heat



*Latent heat is energy that is supplied to or released by a substance during a phase transition while its temperature remains constant.*

In other words is the energy difference between the two phases when both their temperatures are equal to the transition temperature.

# The concept of latent heat



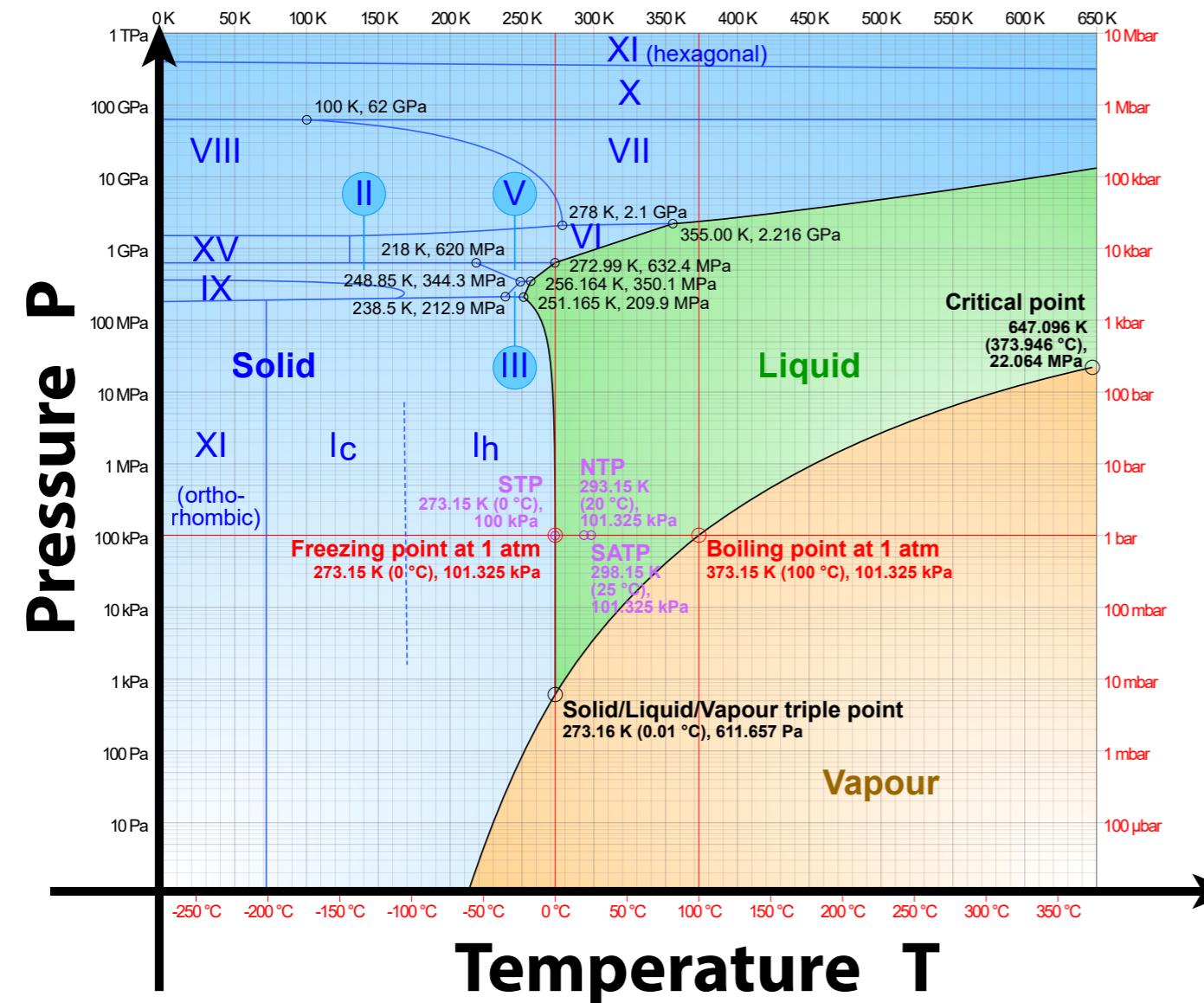
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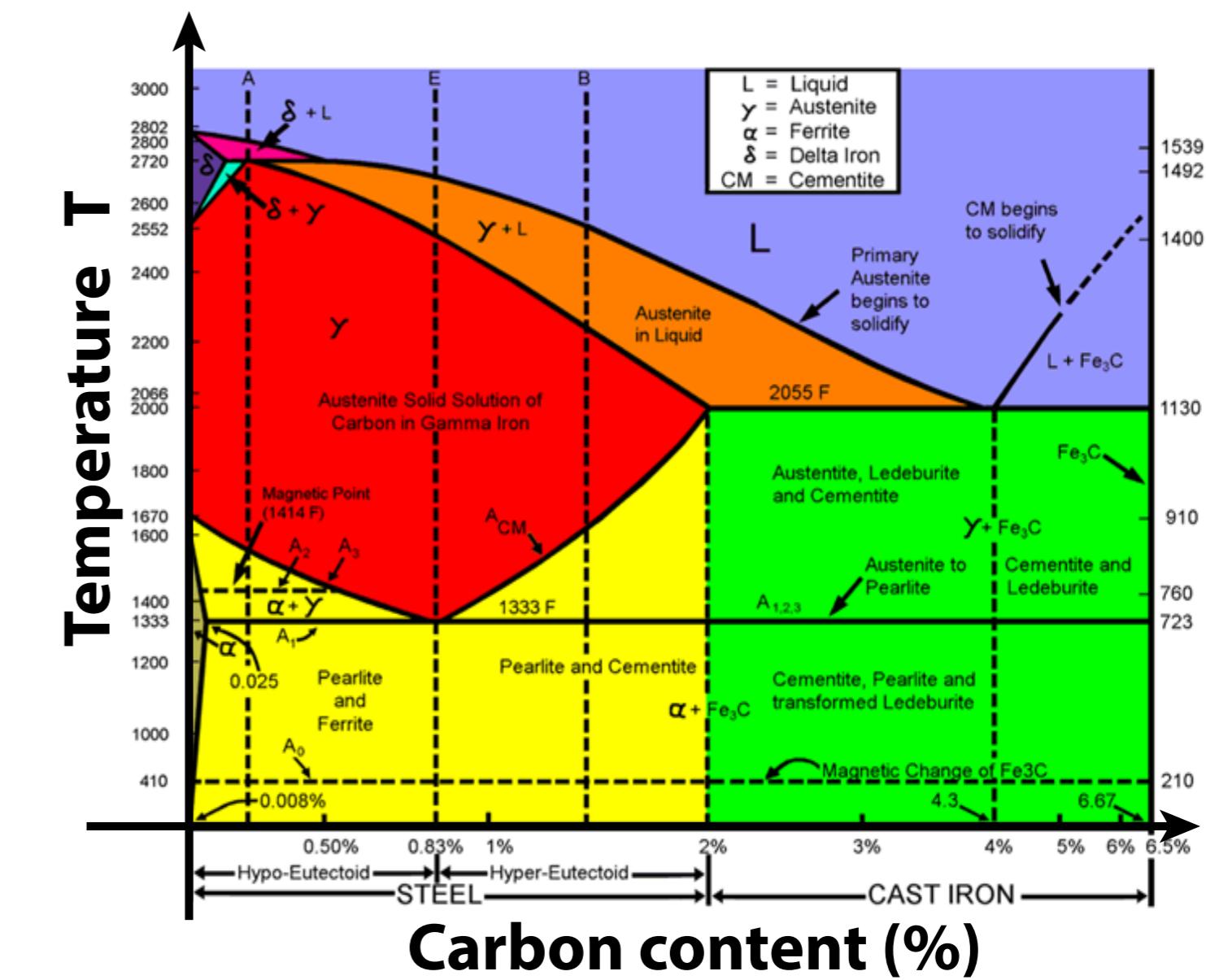
Specific latent heat: latent heat per unit of mass.

# Other examples of phase transitions and phase diagrams

Phase diagram of water

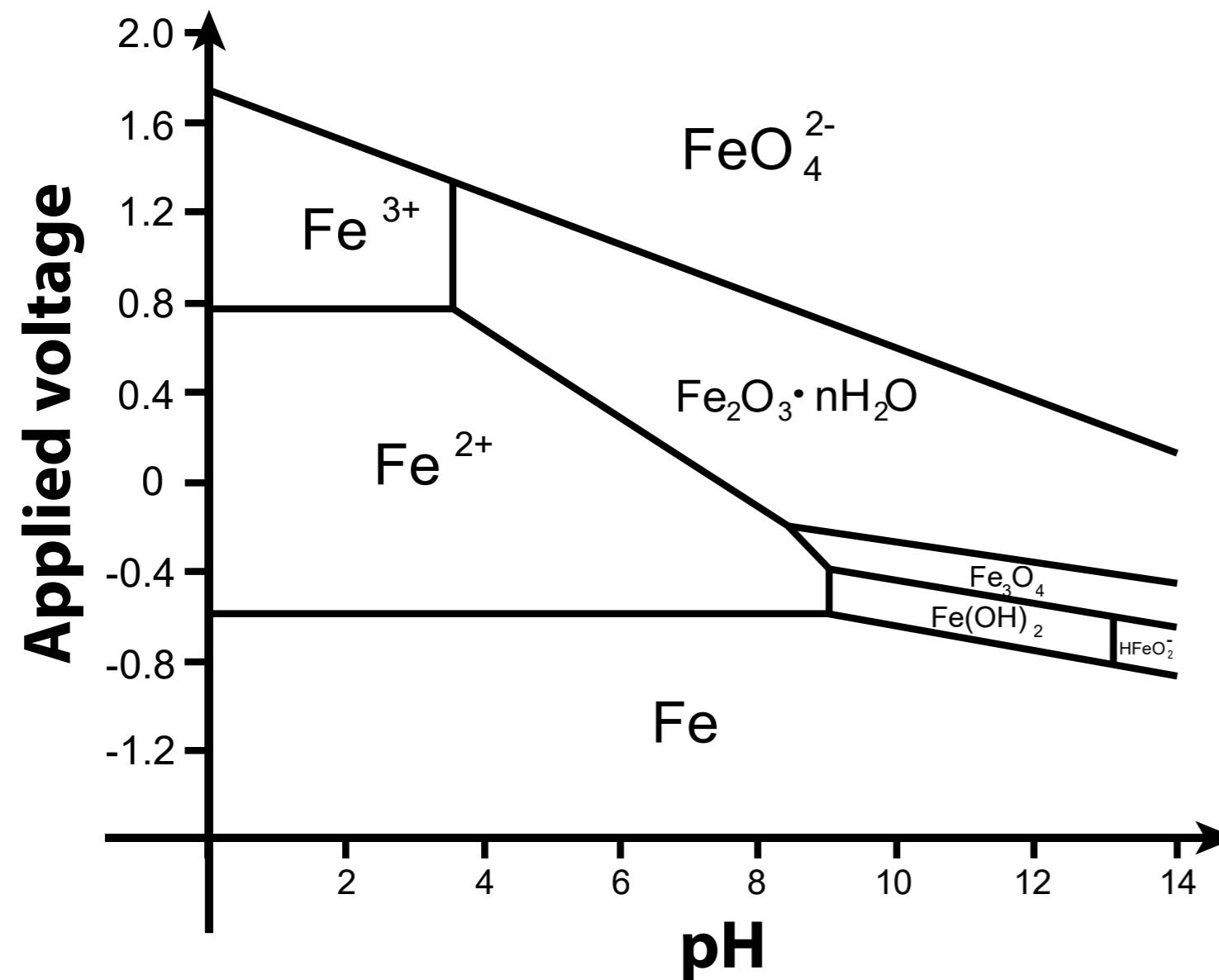


Phase diagram of iron/carbon

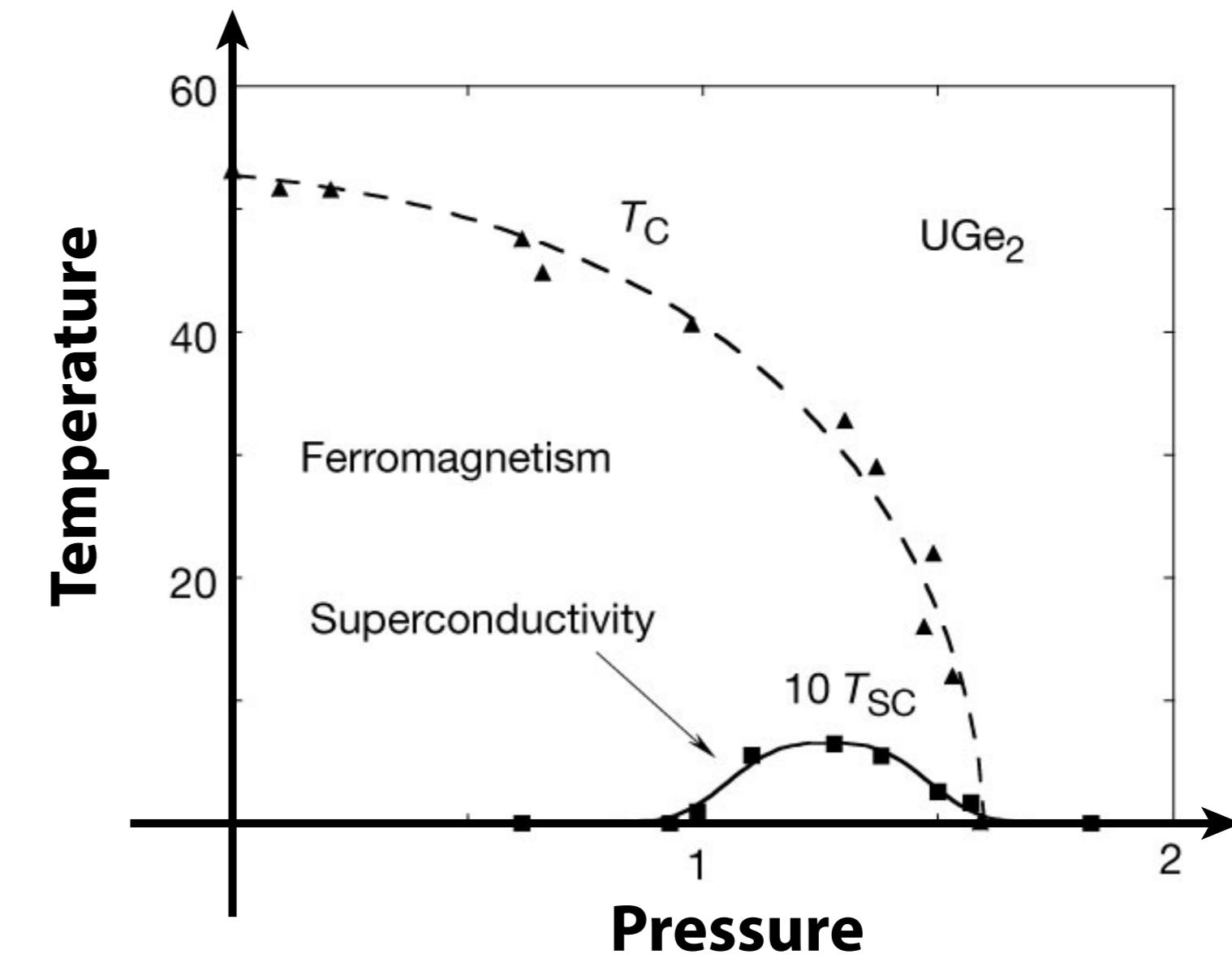


# Other examples of phase transitions and phase diagrams

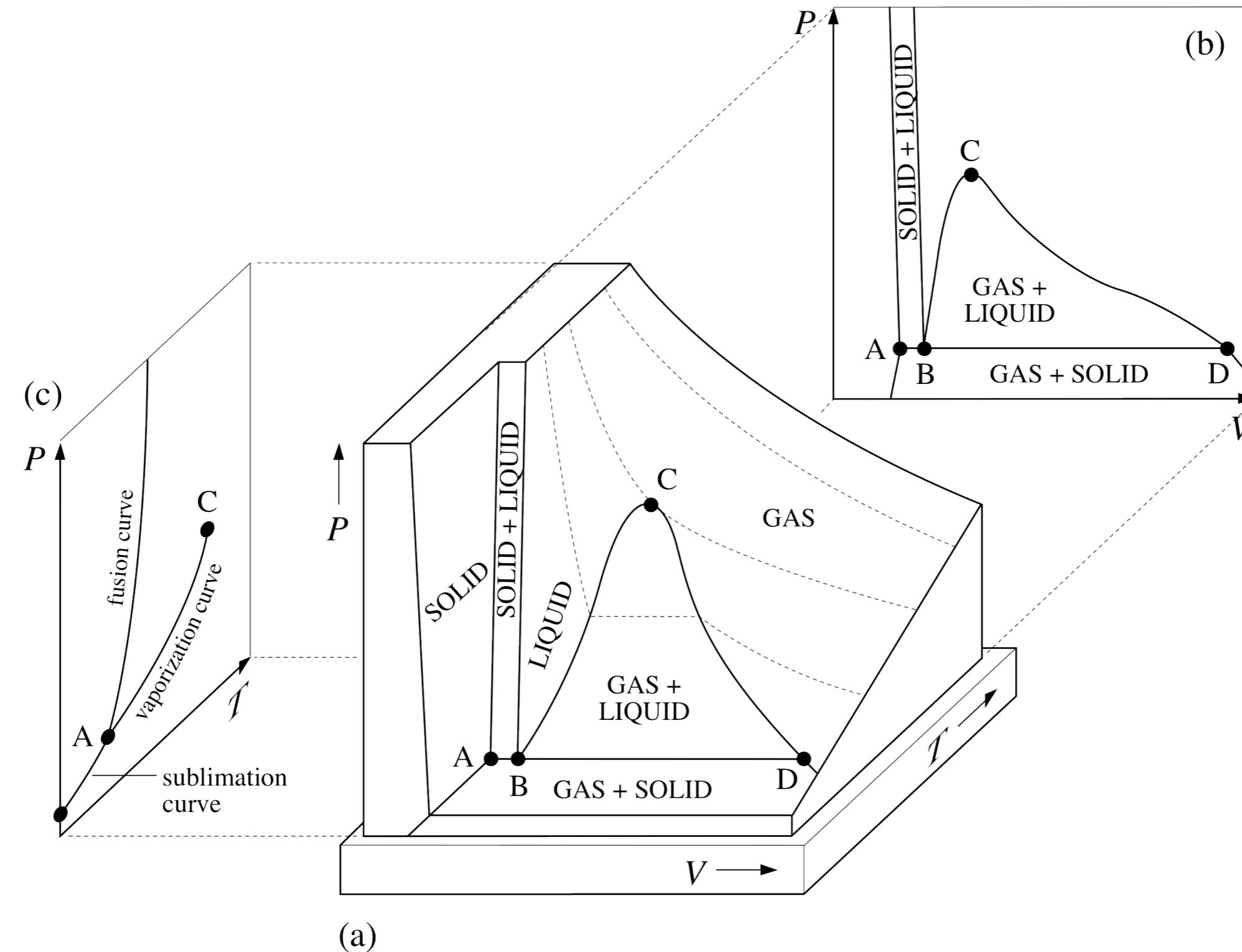
Pourbaix diagram of iron



Phase diagram of UGe<sub>2</sub>

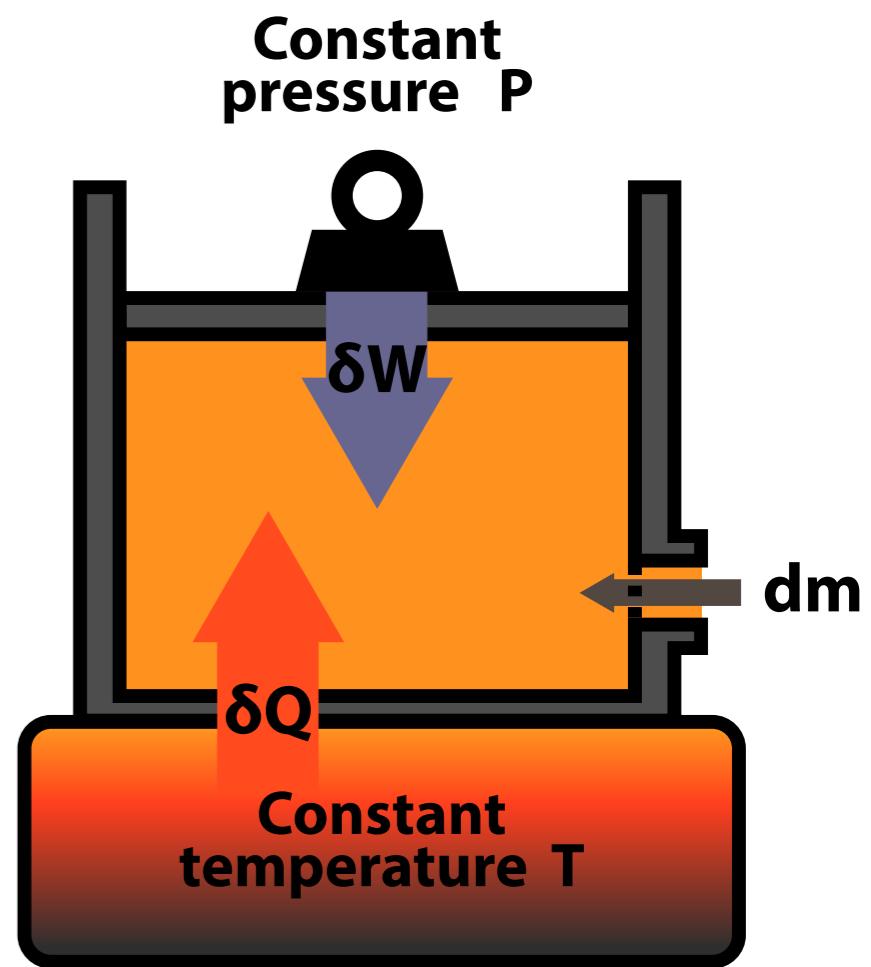


# P-V-T phase diagram



# Gibbs Energy and Chemical Potential

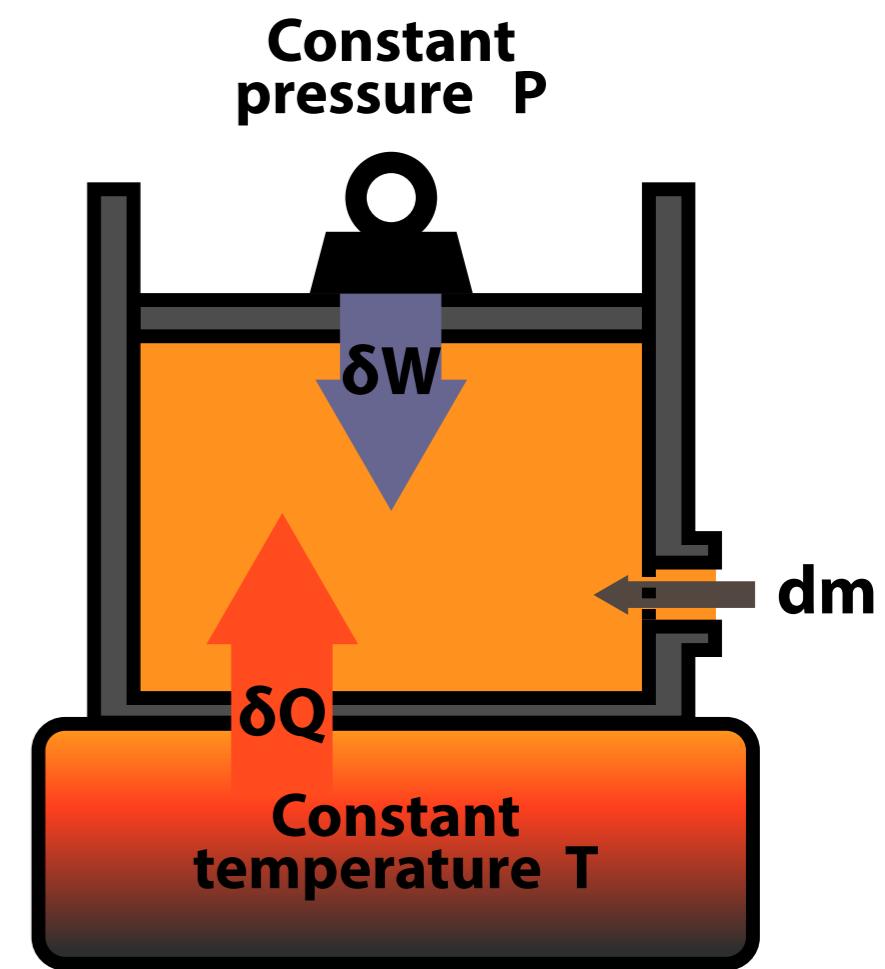
Open system at constant  $T$  and  $P$ , with mass transfer  $dm$ .  
The mass enters with specific enthalpy  $h$ , and specific entropy  $s$ .



# Gibbs Energy and Chemical Potential

Open system at constant  $T$  and  $P$ , with mass transfer  $dm$ . The mass enters with specific enthalpy  $h$ , and specific entropy  $s$ . Taking into account the work done to force the mass in, the energy balance equation is:

$$dU = \delta Q + \delta W + h dm$$



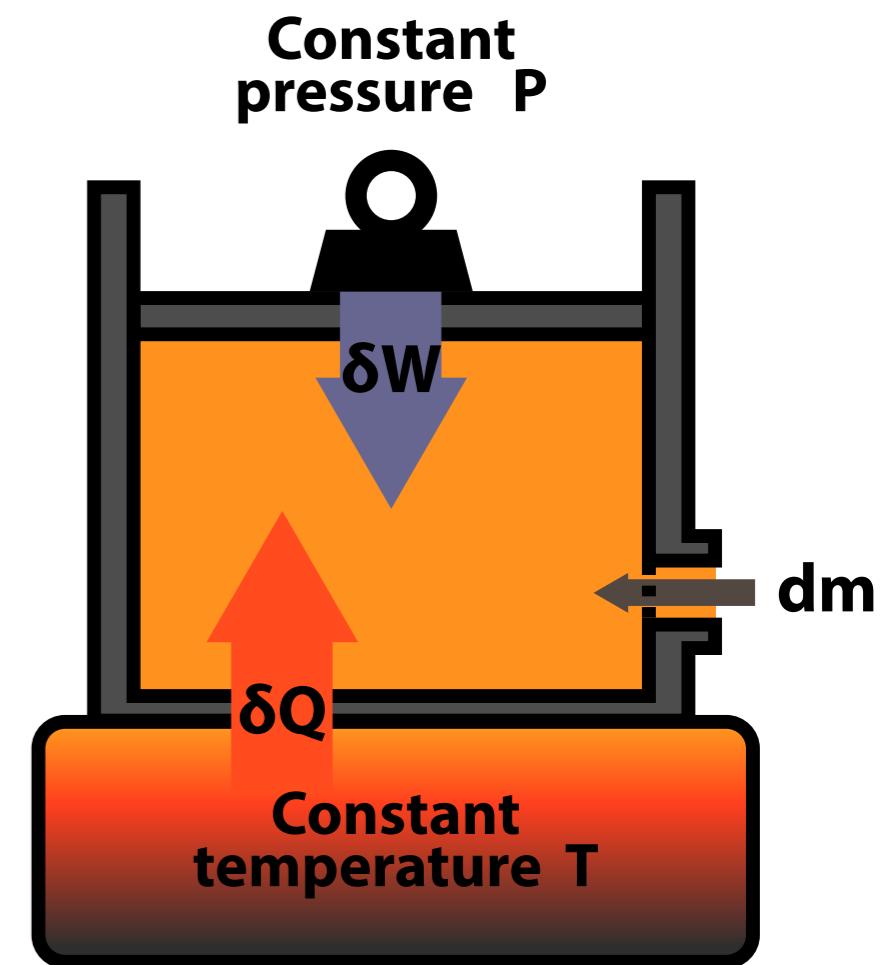
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The entropy balance equation is:

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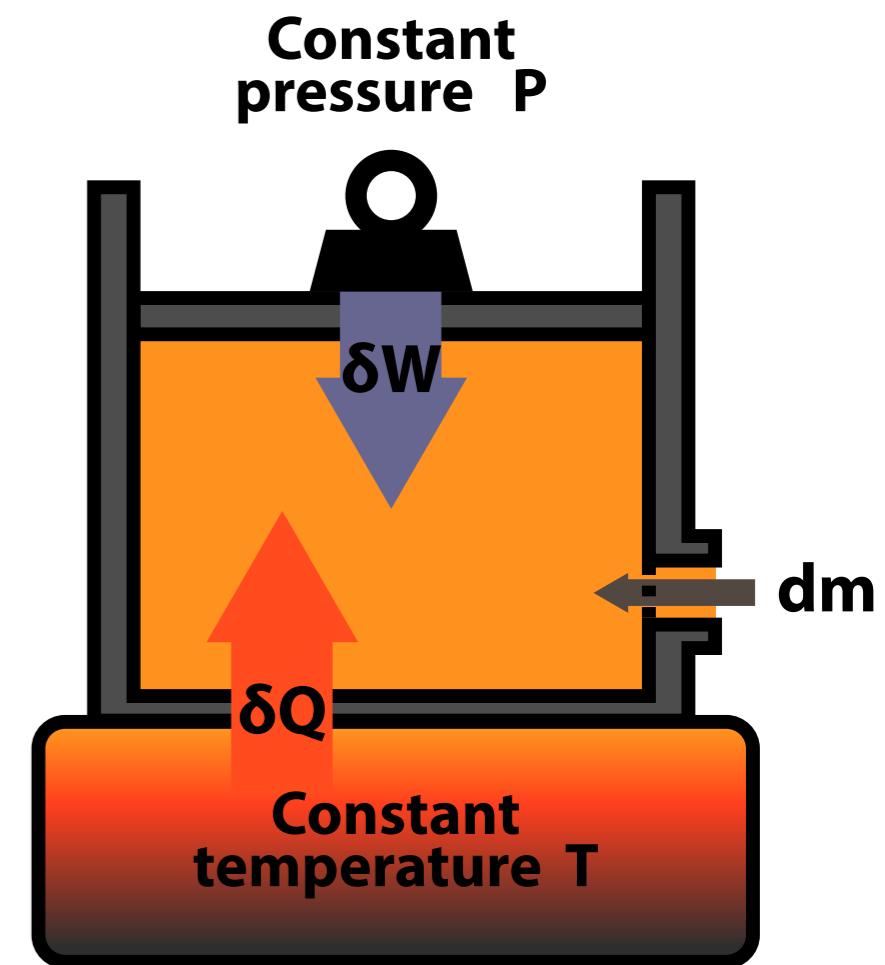
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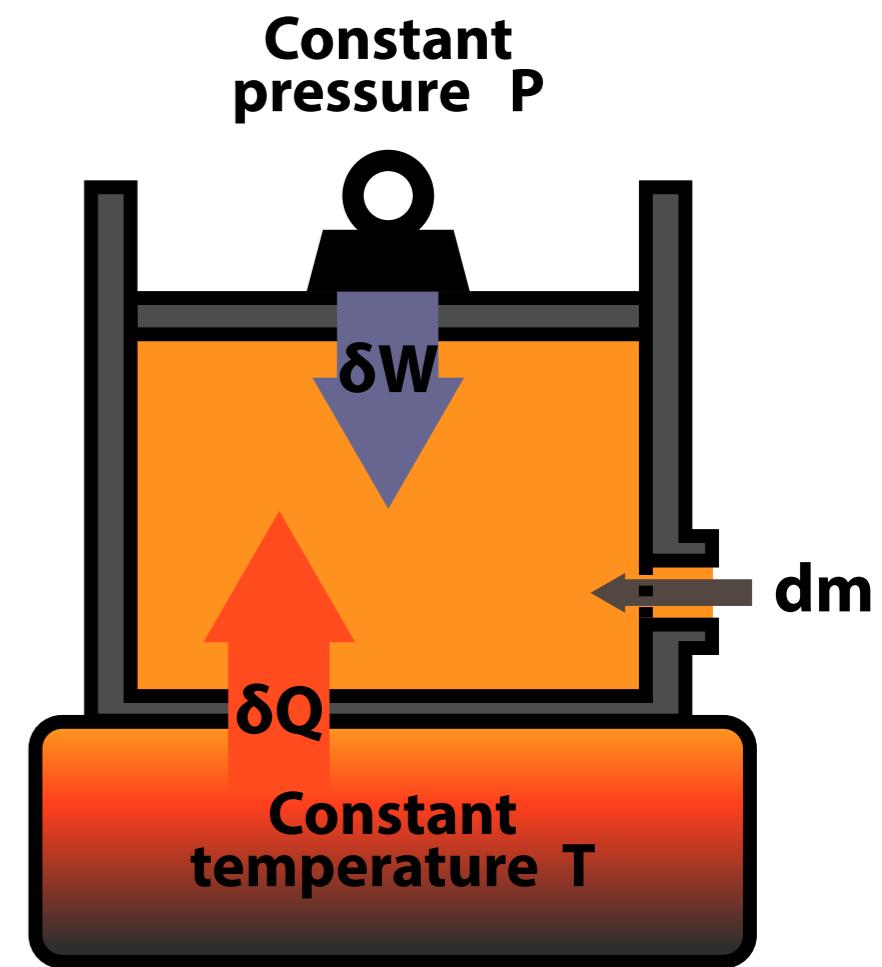
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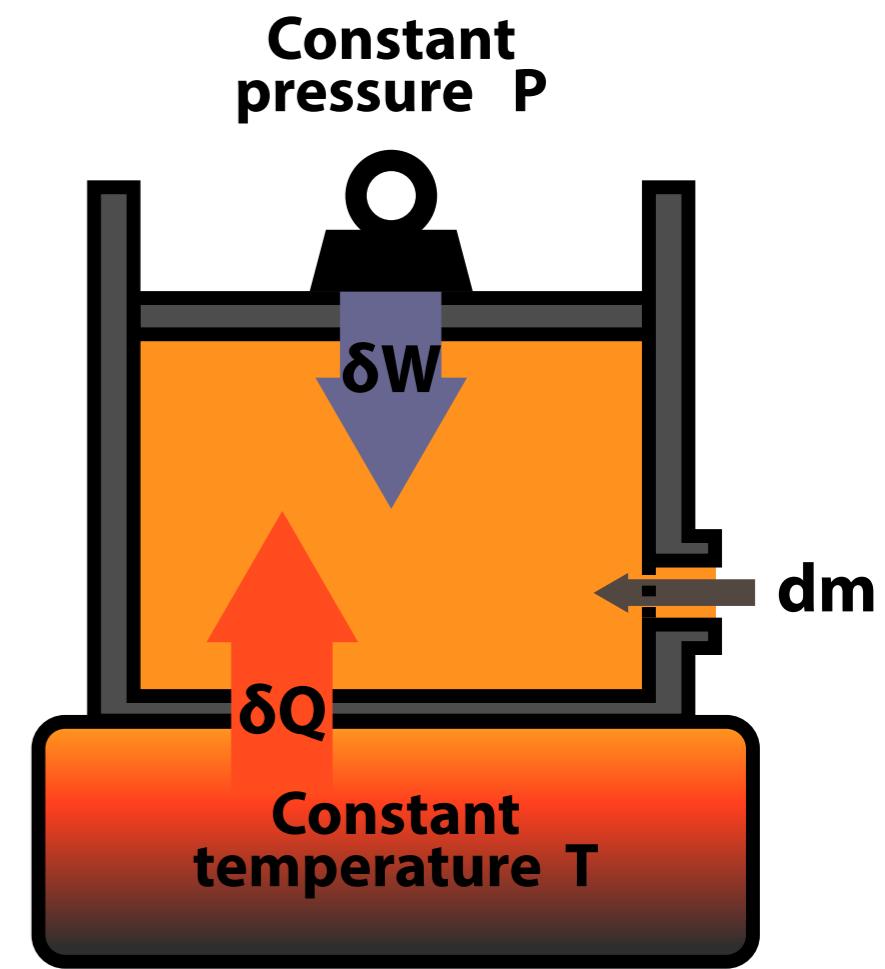
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We introduce the Gibbs energy  $G$ , and the specific Gibbs energy  $g = G/m$ , (also known as chemical potential):

$$G = H - TS \Rightarrow g = \frac{G}{m} = h - Ts$$



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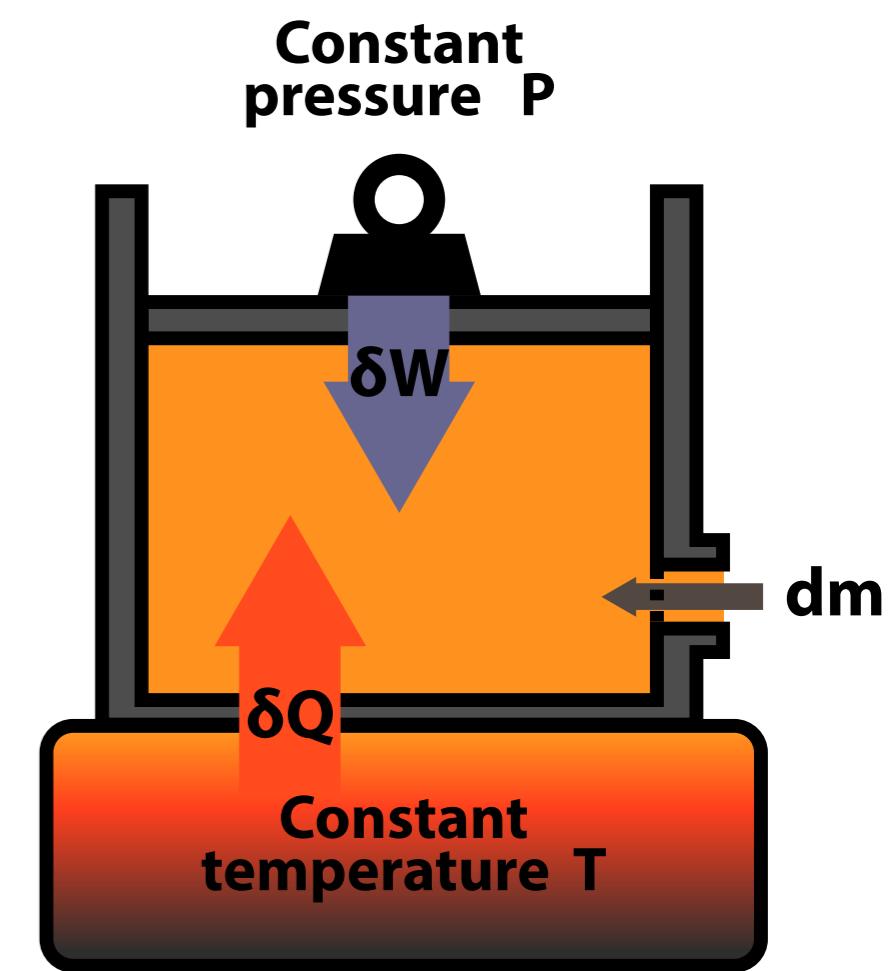
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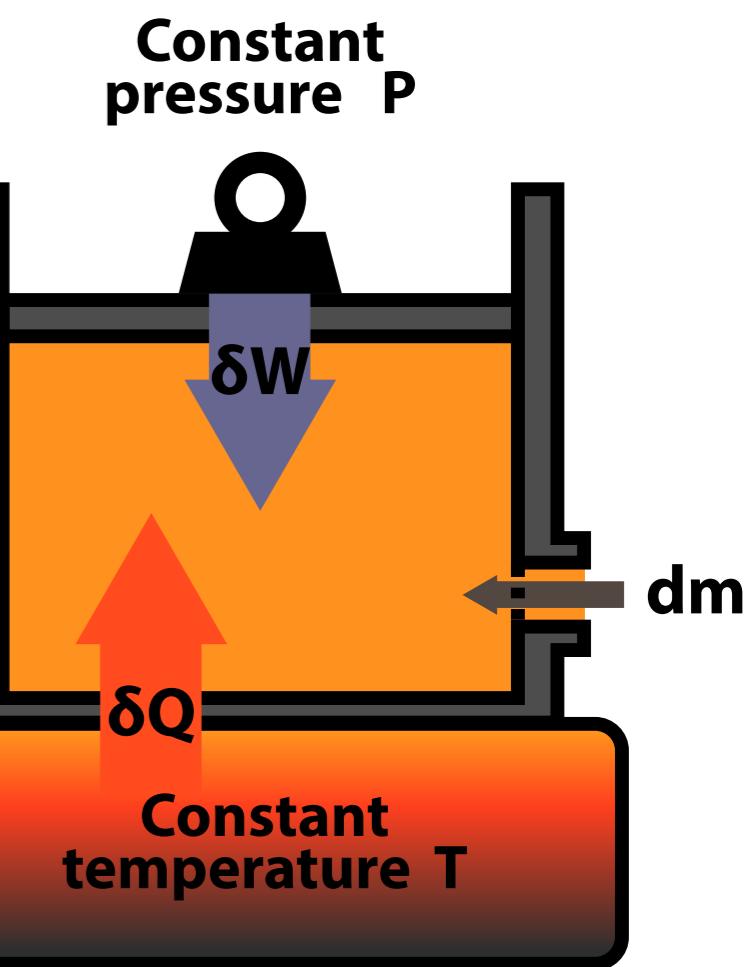
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rearranging:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{g}{T}dm$$



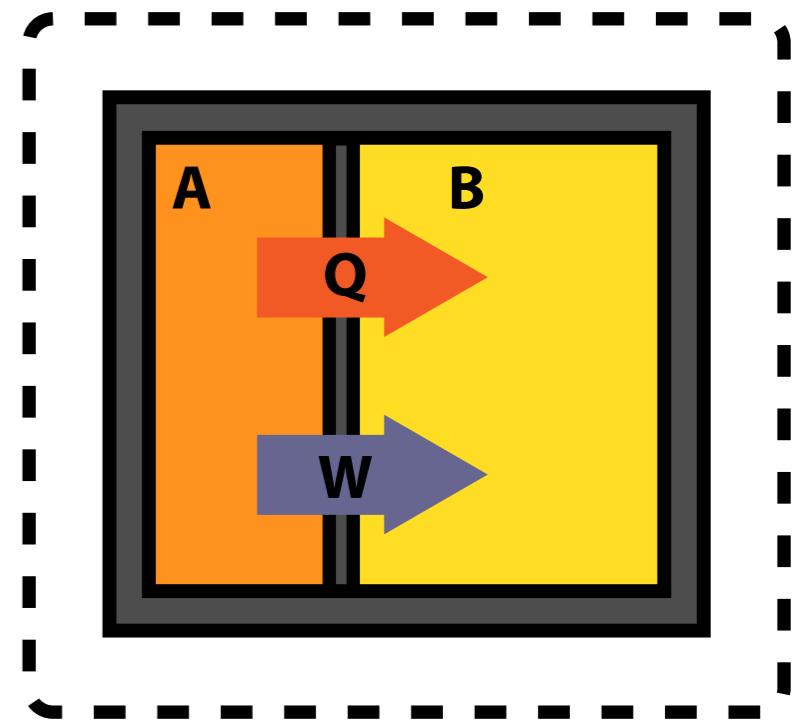
**Gibbs  
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# Equilibrium with mass transfer

As we have seen in the previous lecture, for two systems A and B that can exchange work and heat, the entropy variation of the composite system C is given by:

$$dS_C = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV_A$$

Composite system C



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**Gibbs  
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# Equilibrium with mass transfer

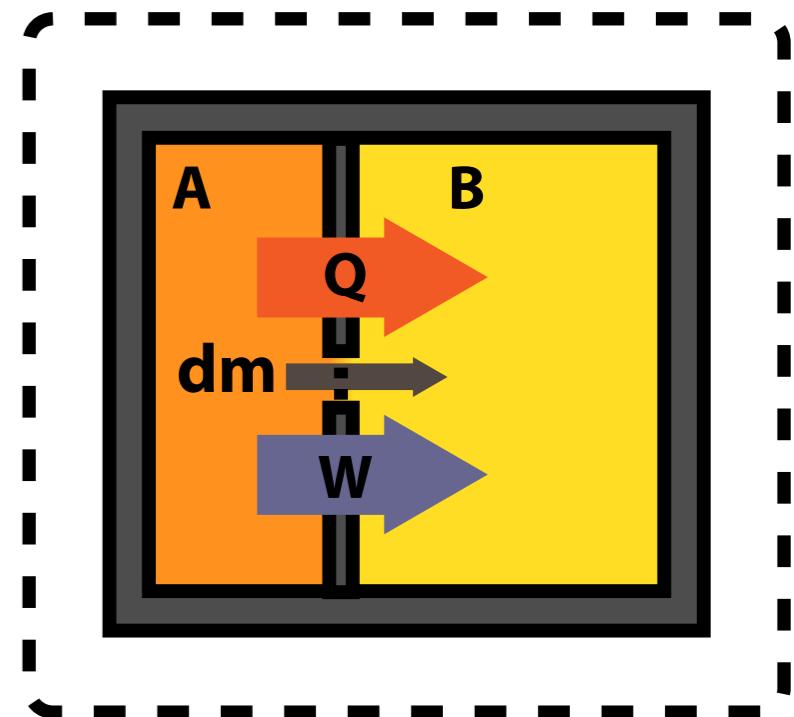
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Composite system C



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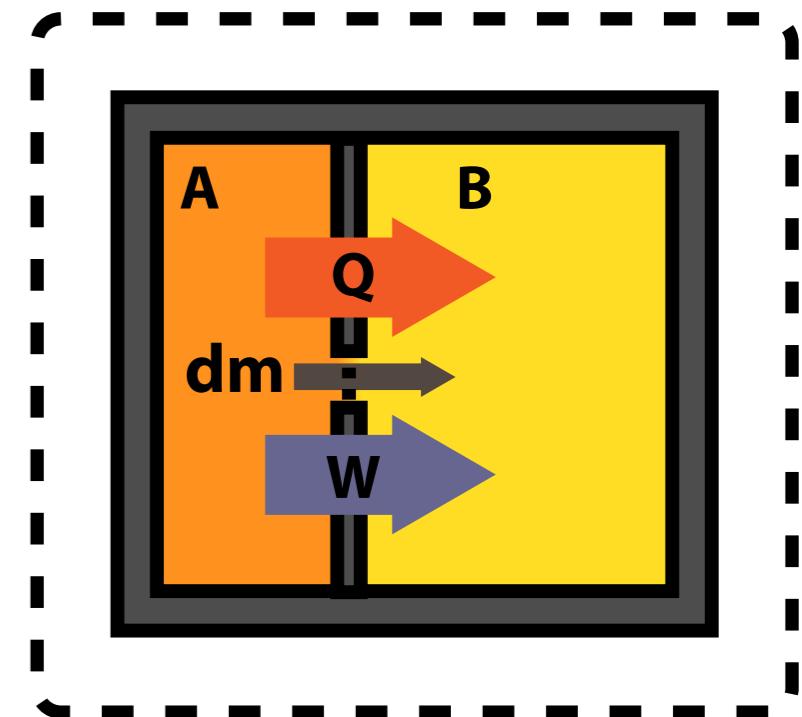
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Composite system C



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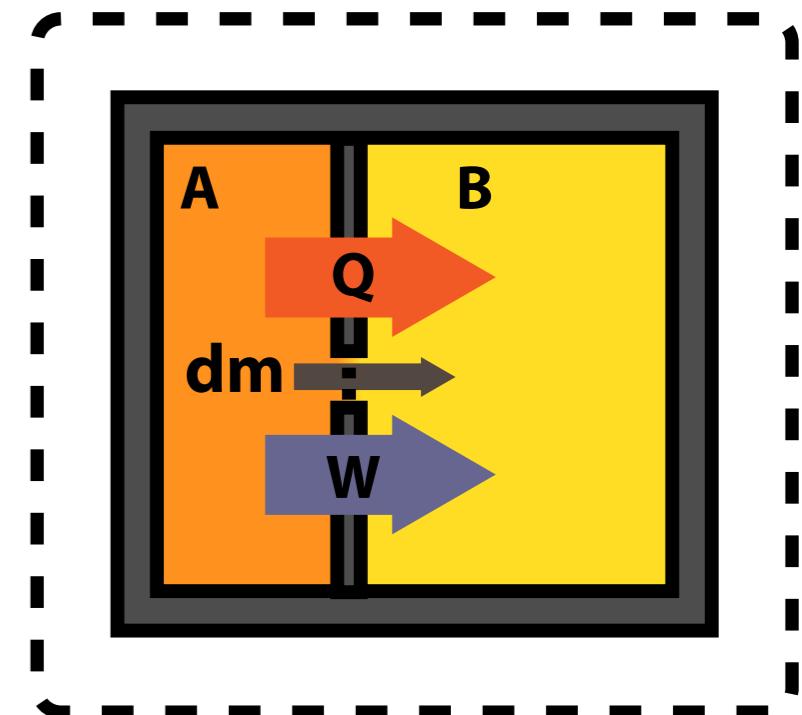
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$$dS_C = -\frac{1}{T} (g_A - g_B) dm_A$$

Composite system C



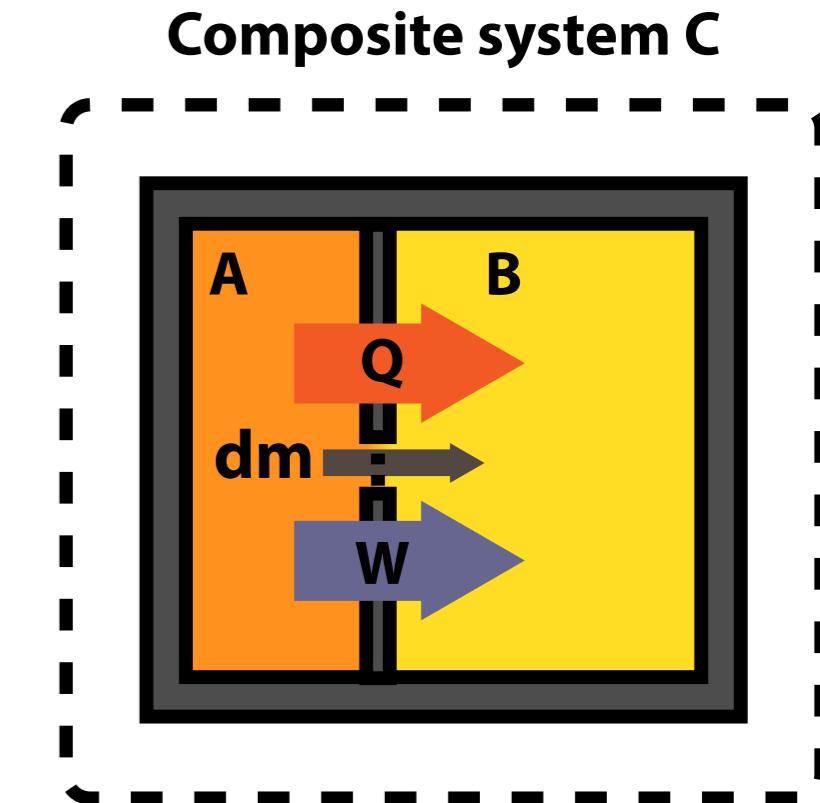
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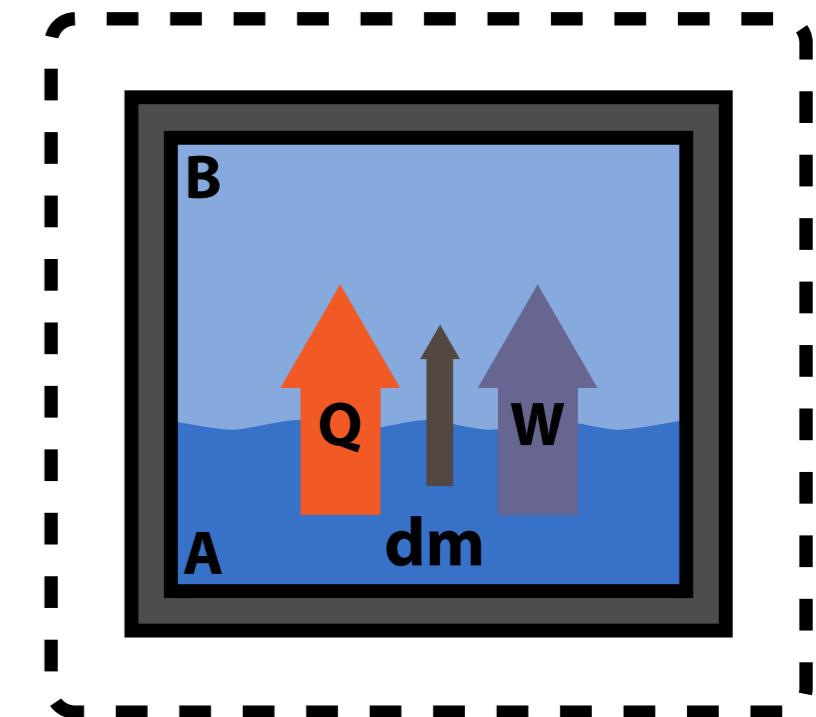
$$dS_C = -\frac{1}{T} (g_A - g_B) dm_A > 0$$

In the same way that  $T$  determines the direction of heat transfer and  $P$  of work transfer, the chemical potential  $g$  determines the direction of mass transfer, i.e. from higher chemical potential to lower chemical potential.

# Phase Equilibrium

We can apply the same argument to two phases that are in contact such that they can exchange heat, work, and mass.

Composite system C



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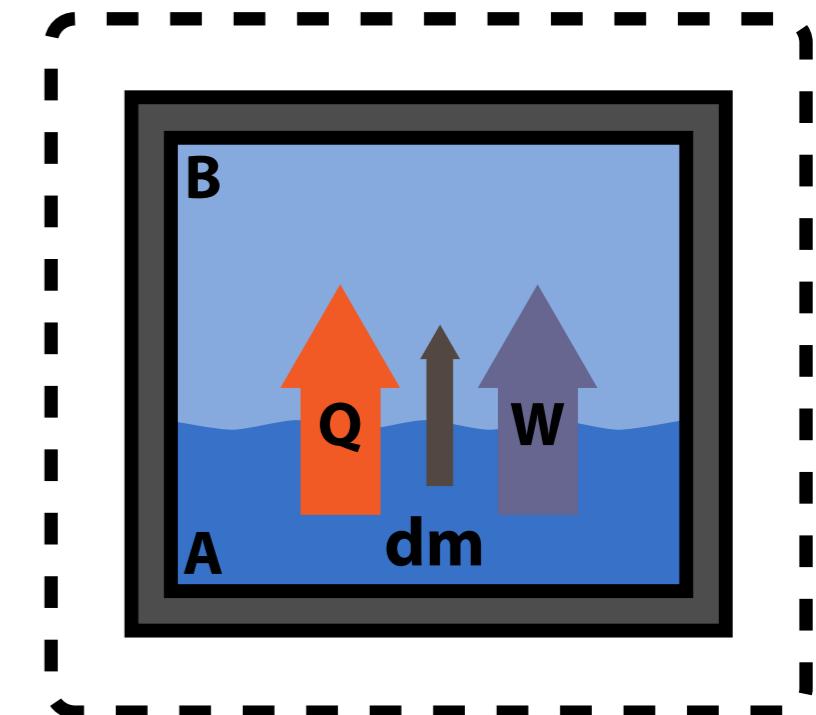
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# Phase Equilibrium

We can apply the same argument to two phases that are in contact such that they can exchange heat, work, and mass. The mass exchange between the two phases corresponds to a *phase transition*. The equilibrium between the two phases is called *phase equilibrium*.

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Composite system C



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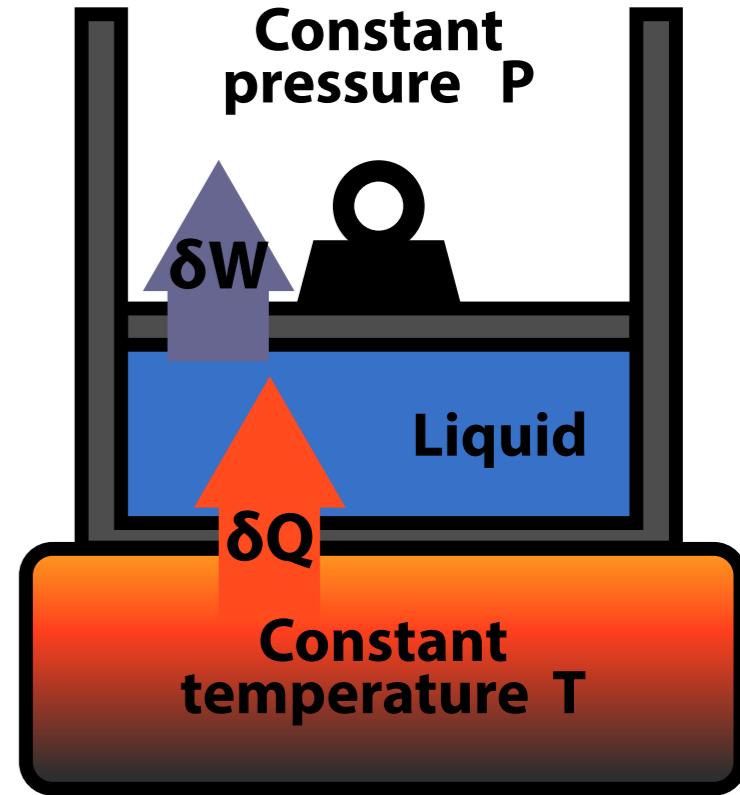
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# Phase transitions and phase equilibrium

# Enthalpy of vaporization

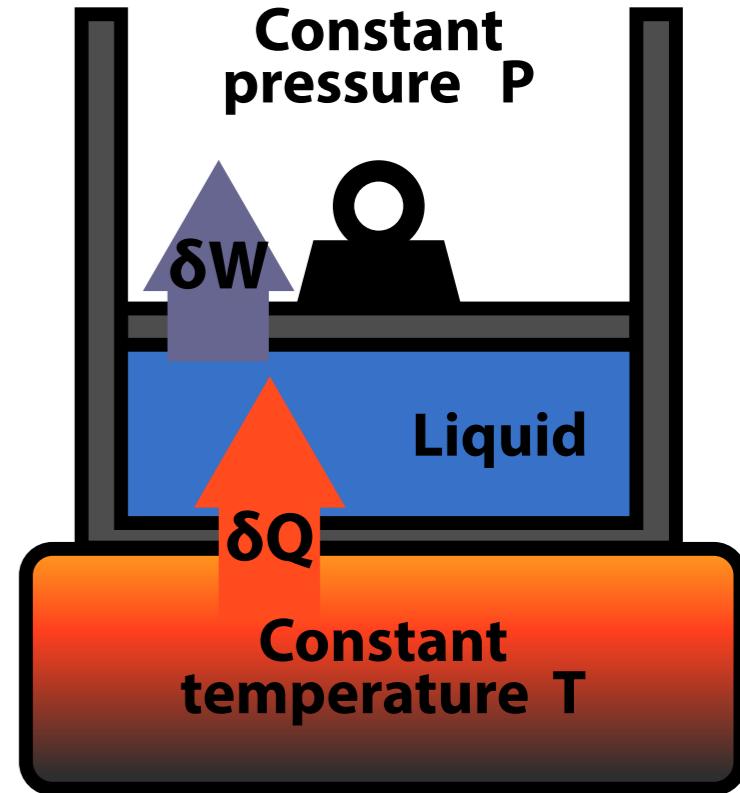
The enthalpy of vaporization, (or latent heat of vaporization), is the amount of energy that must be added to a liquid substance to transform it into a gas while keeping the pressure constant.



# Enthalpy of vaporization

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It is equal to the difference of internal energy between vapor and liquid, plus the work done against the external pressure.

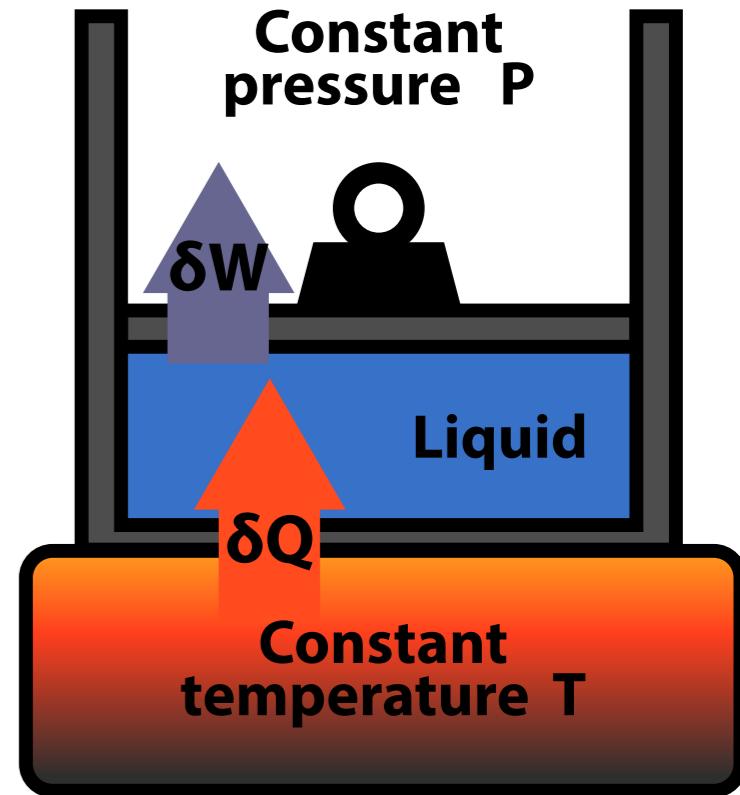


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It is a function of the pressure at which that transformation takes place.



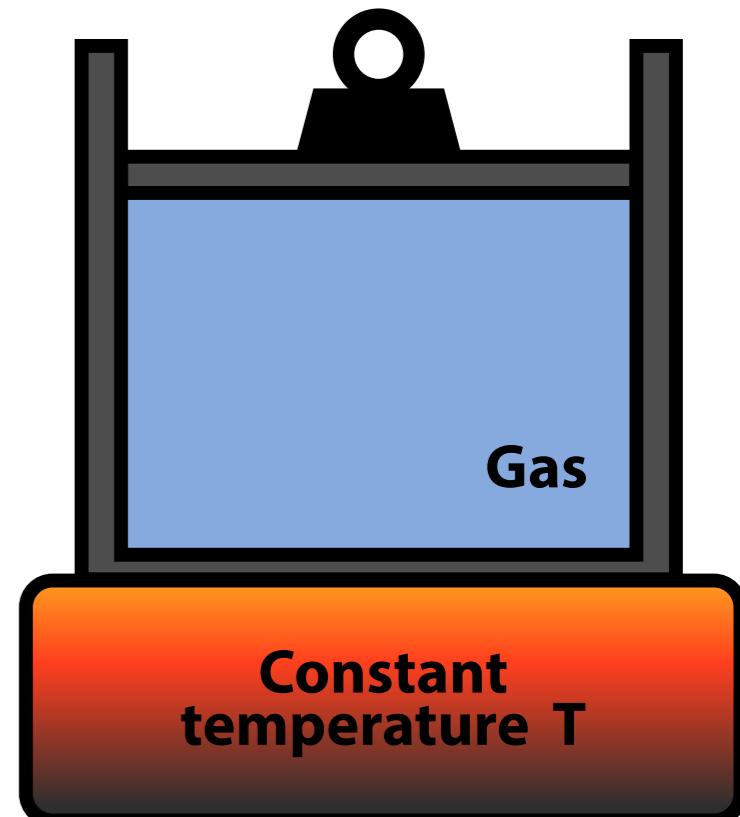
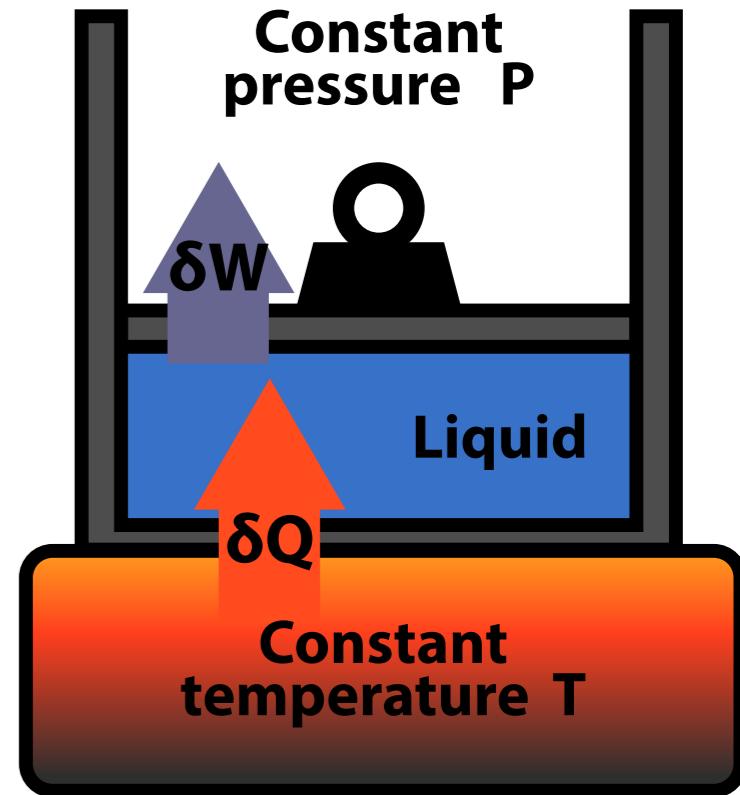
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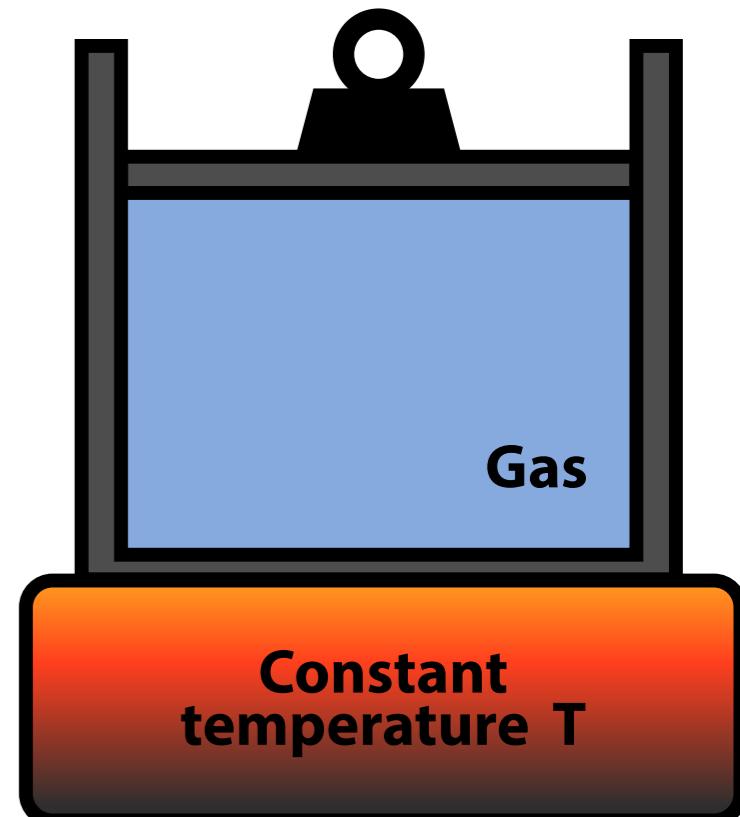
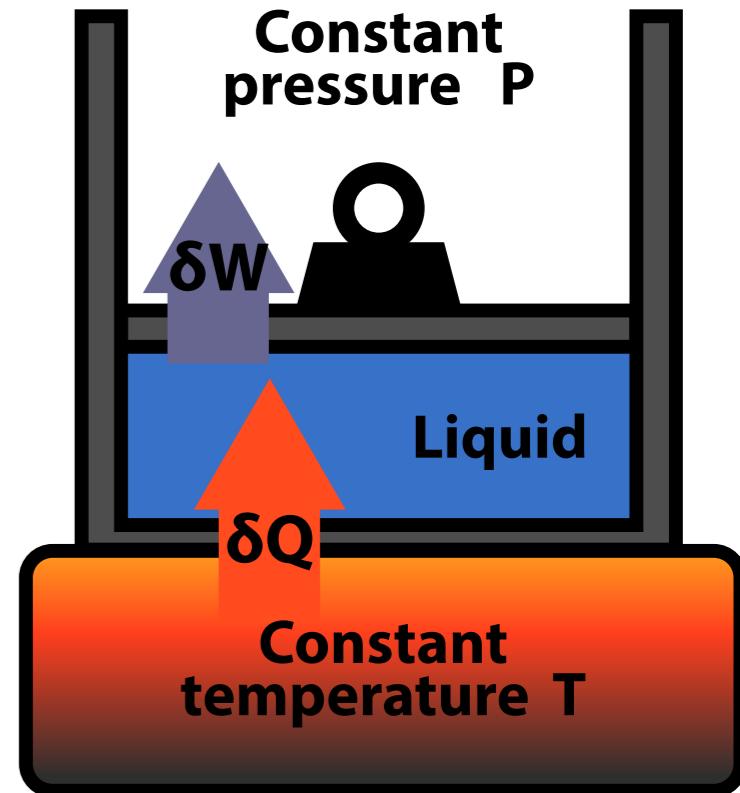
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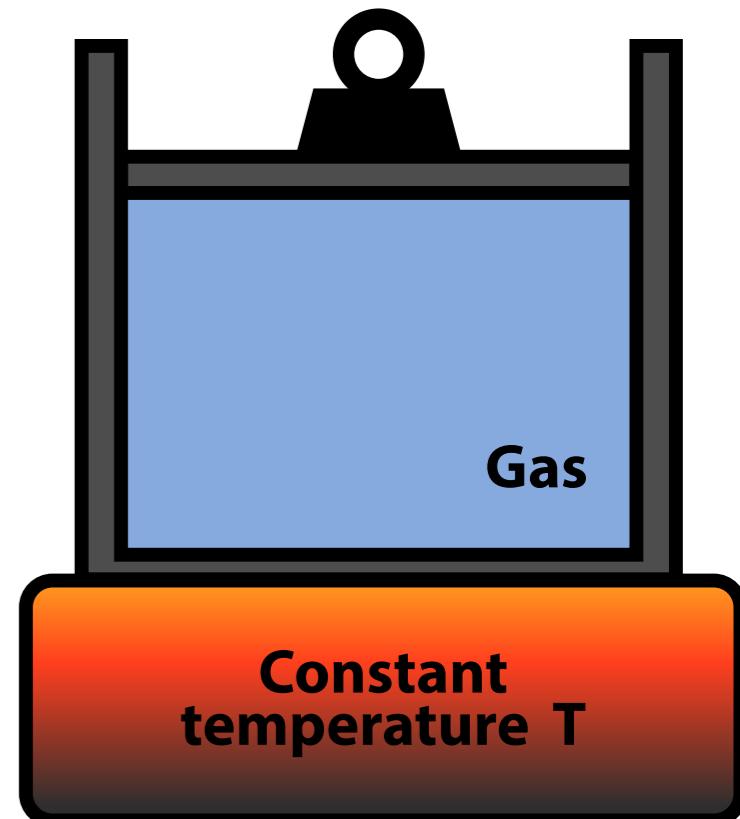
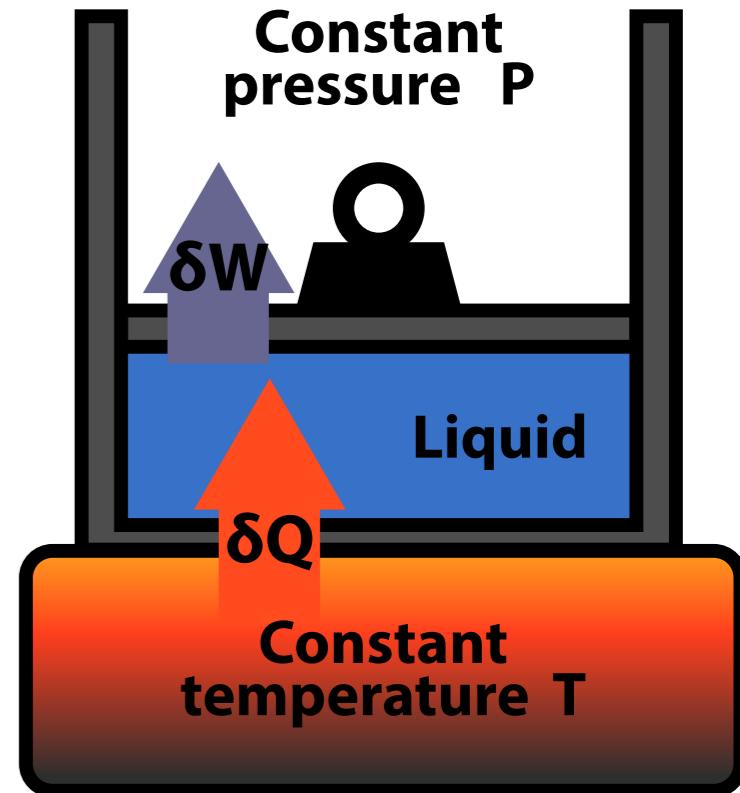
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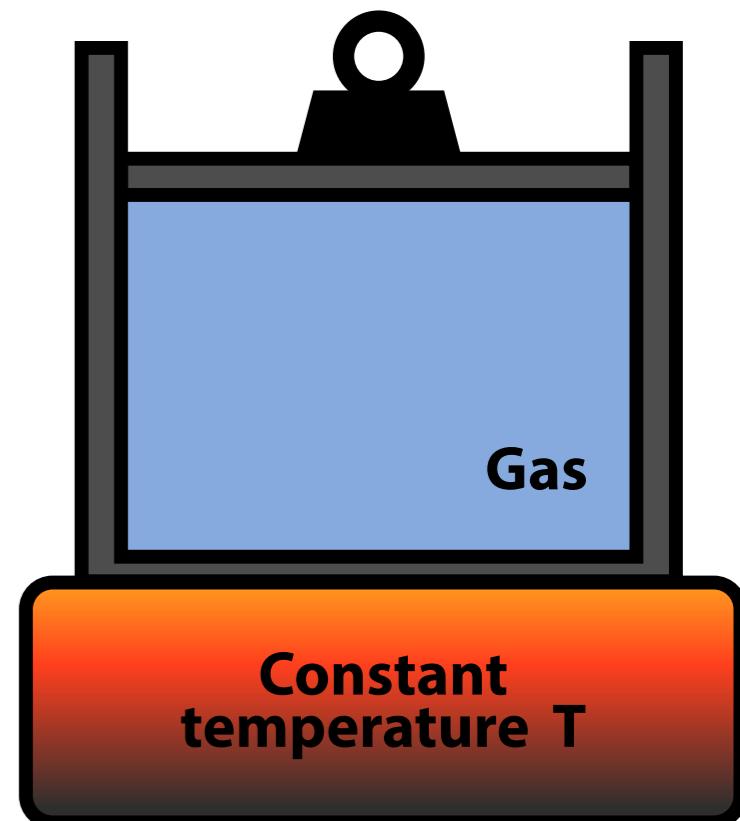
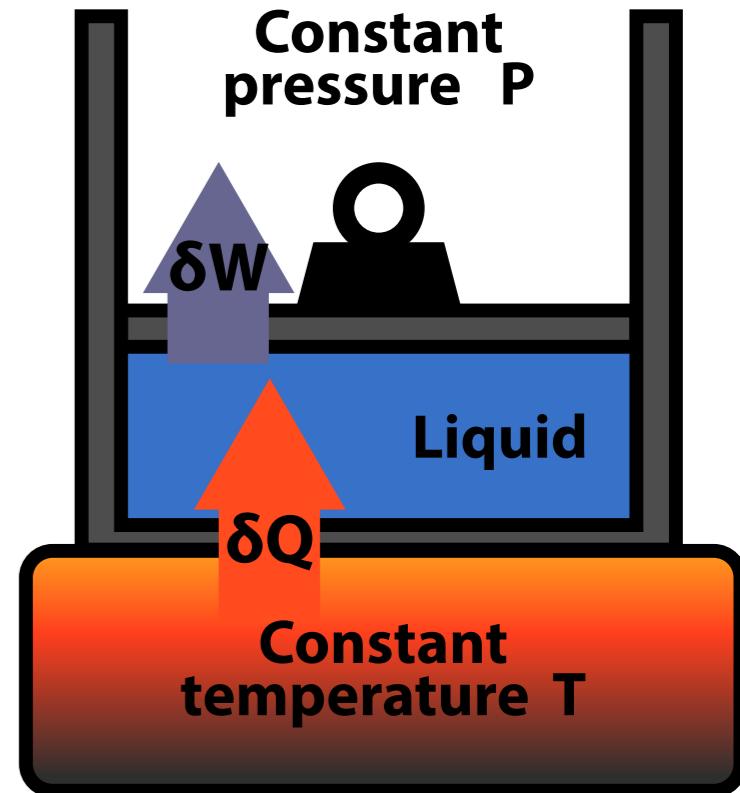
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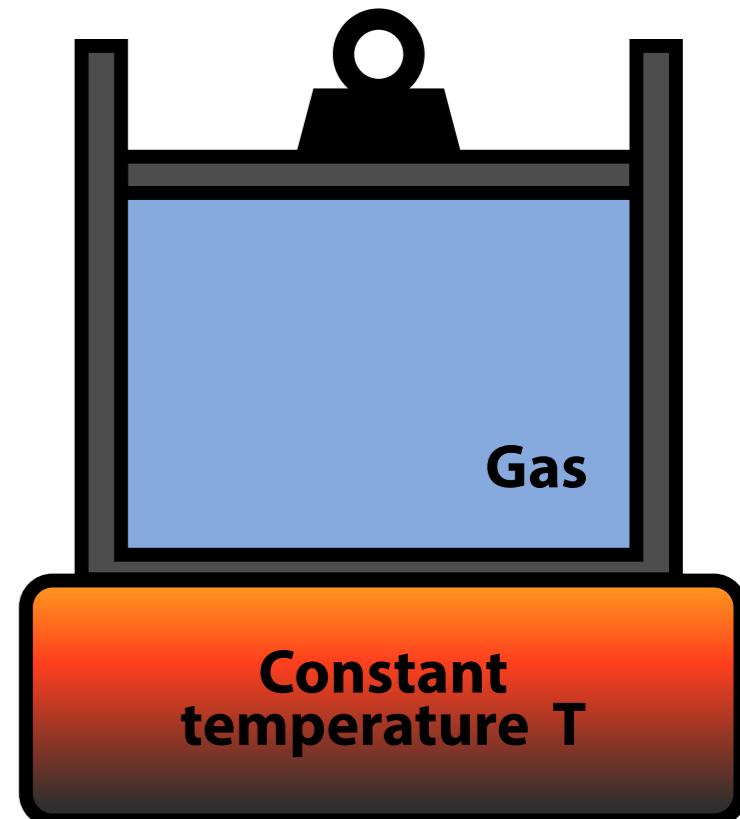
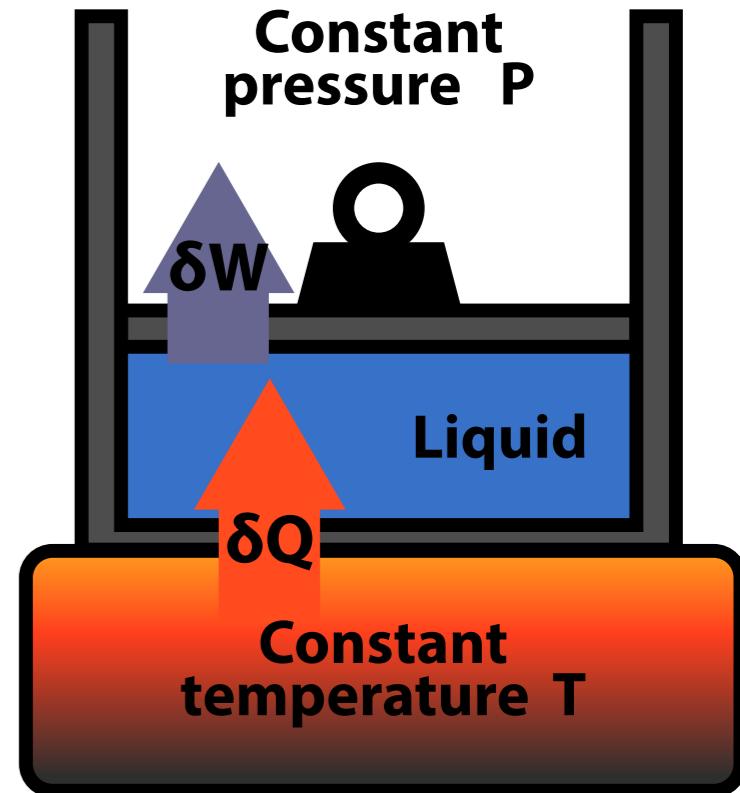
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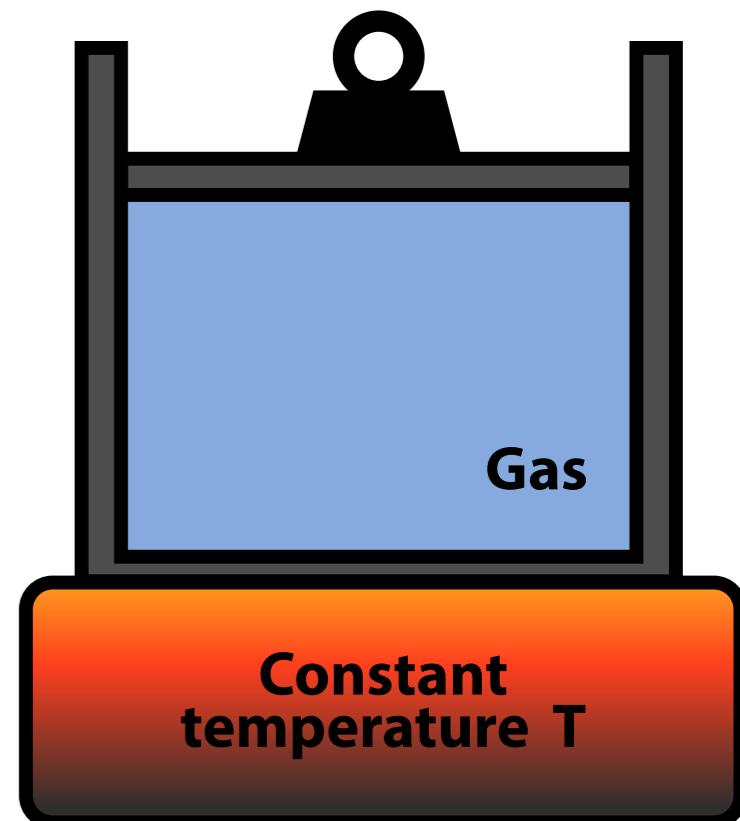
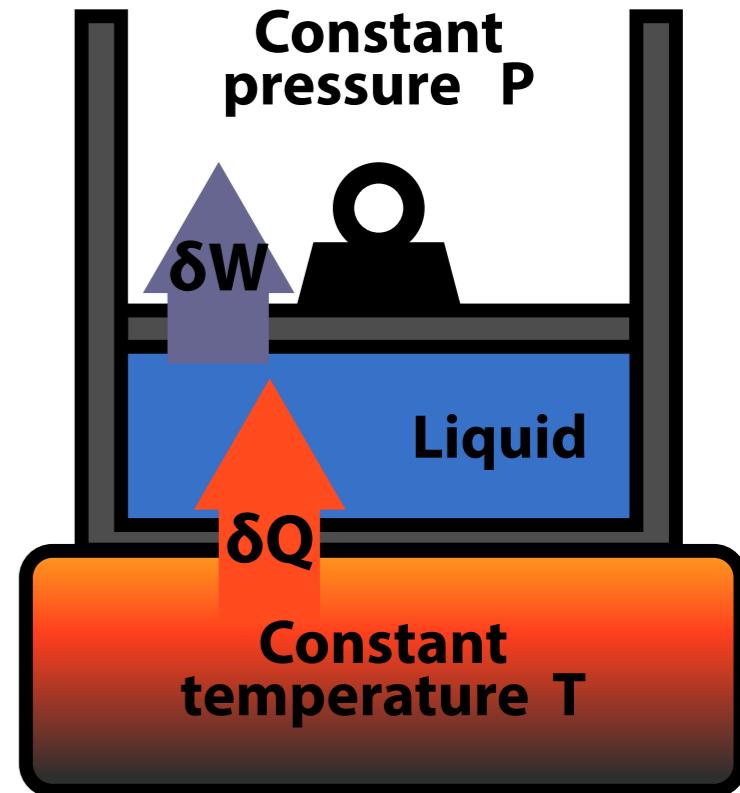
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# Gibbs-Duhem equation - variation of chemical potential

It can be shown that the variation of Gibbs energy is given by:

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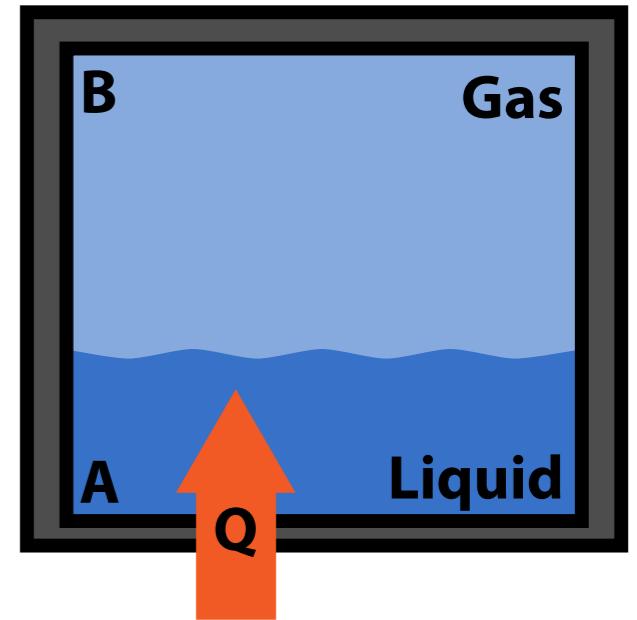
The variation of specific Gibbs energy is thus given by:

$$dg = vdP - SdT$$

known as the Gibbs–Duhem equation, used to calculate how the chemical potential  $g$  changes with pressure and temperature.

# Clausius-Clapyeron equation

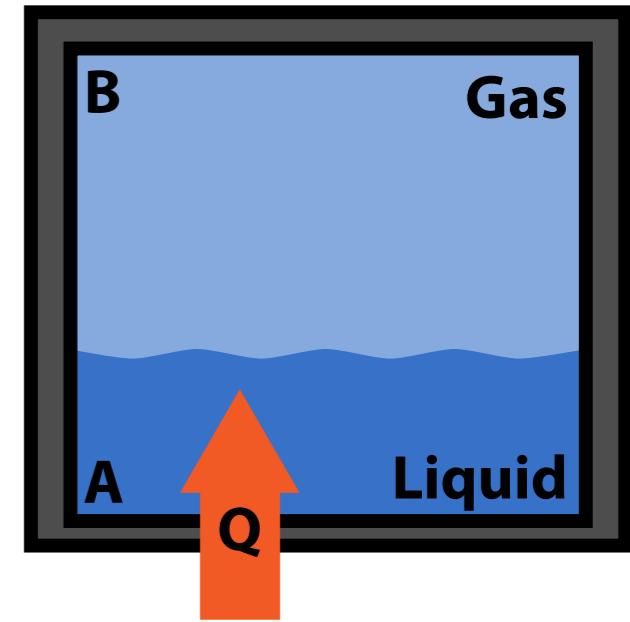
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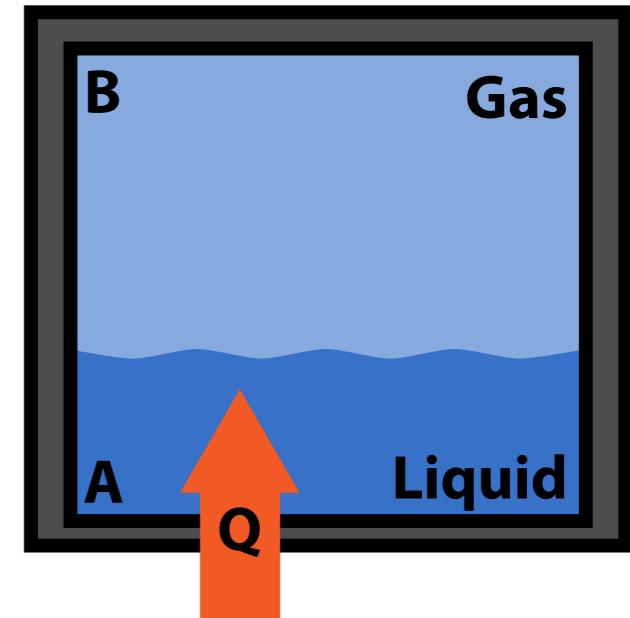


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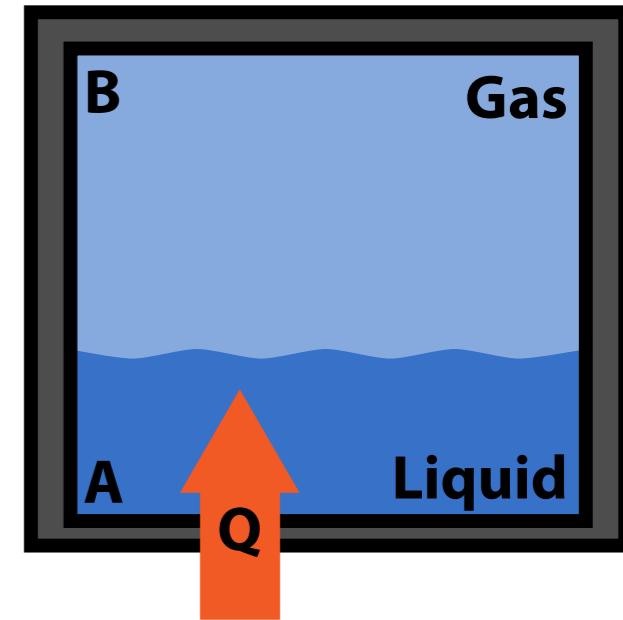
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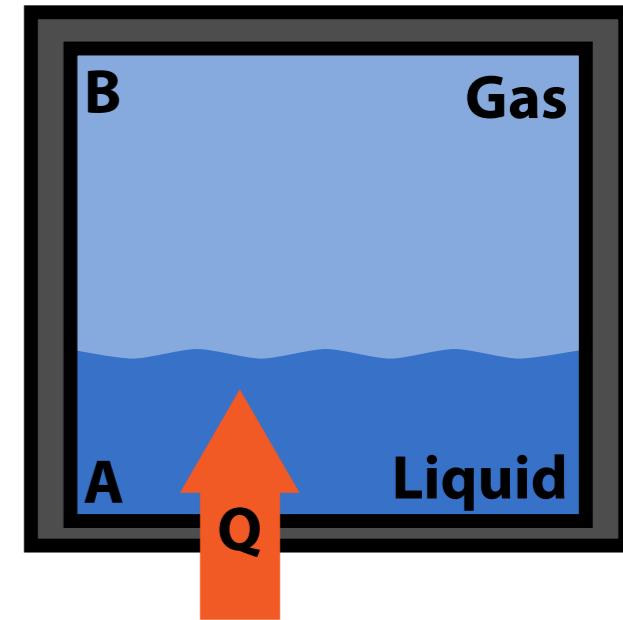
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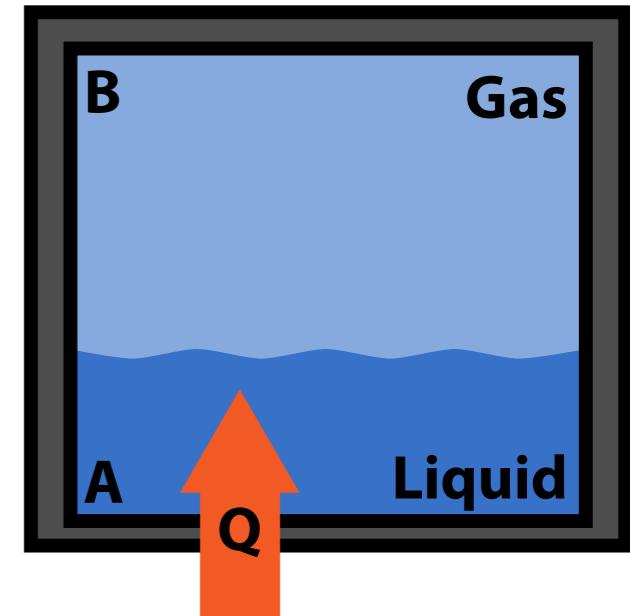
Rearranging:

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Rearranging, then using  $T\Delta s = \Delta h_{\text{vap}}$ :

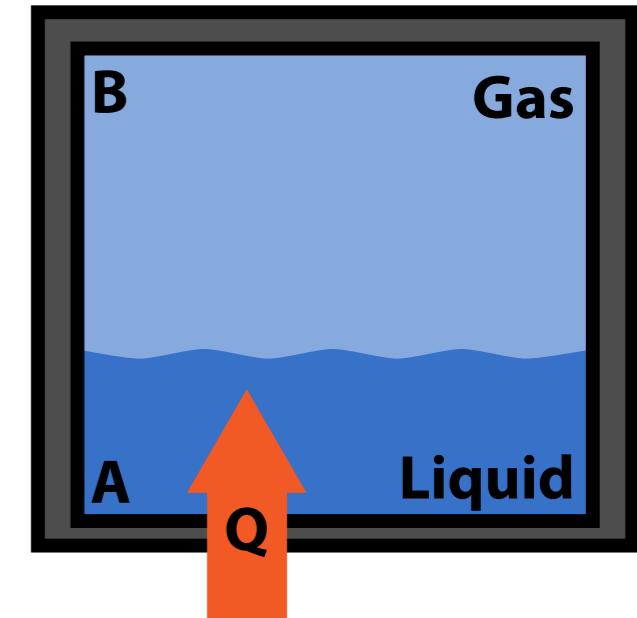
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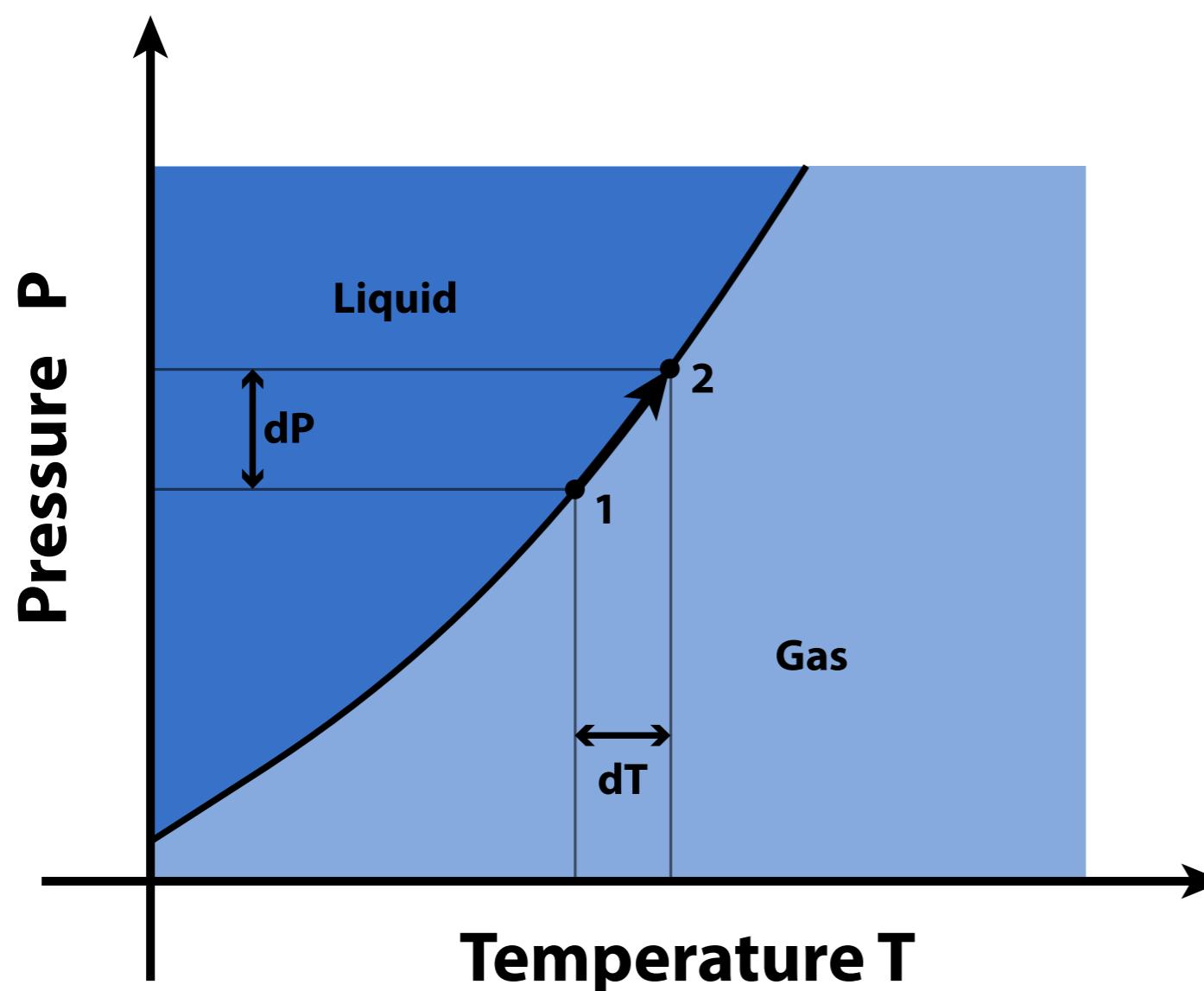
With  $v_A \approx 0$  and  $v_B = RT/P$

$$\frac{dP}{dT} = \frac{\Delta h_{\text{vap}} P}{RT^2}$$

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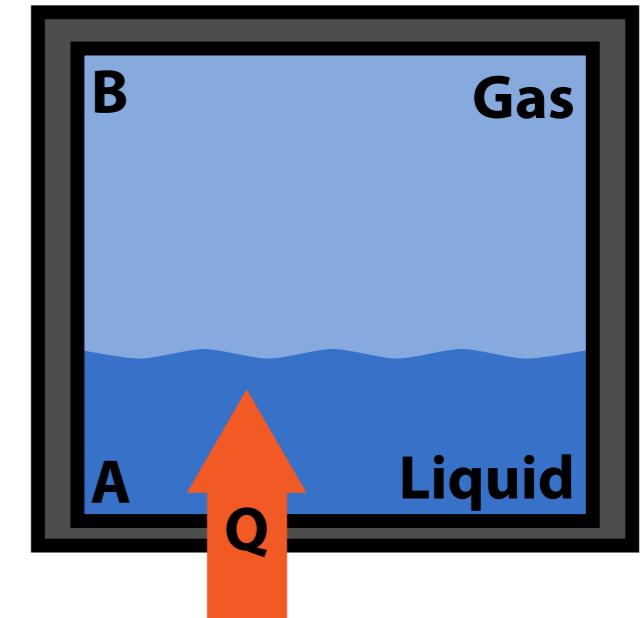
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We can visualize the process on the  $P-T$  phase diagram.



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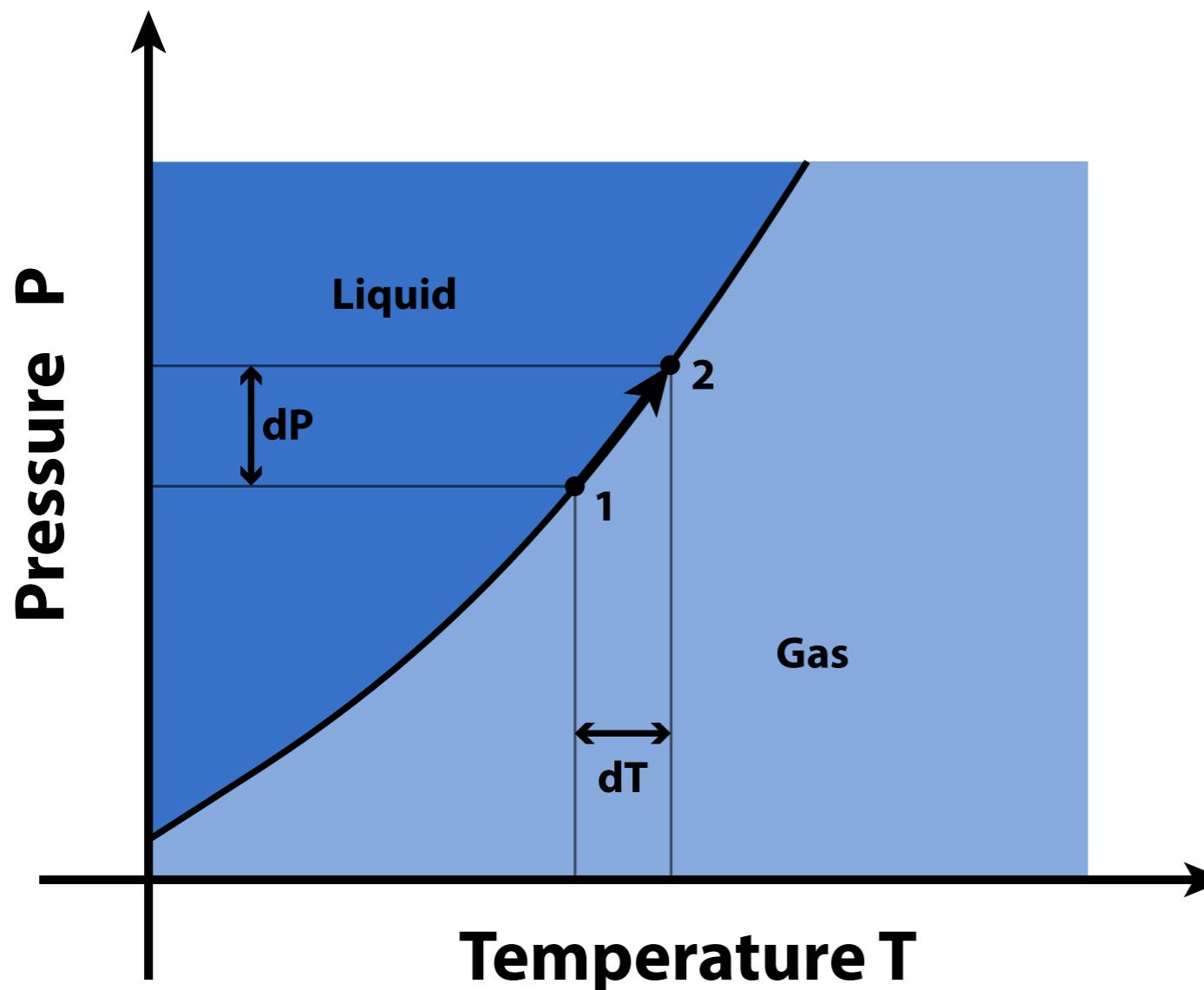
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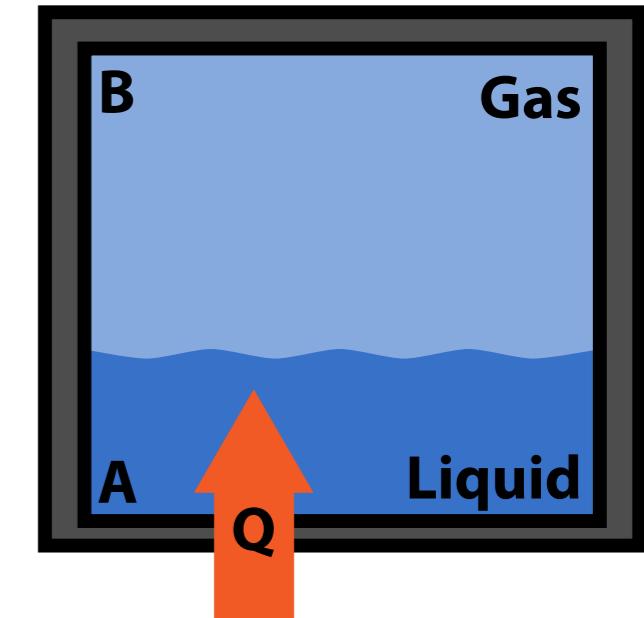
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$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{\Delta h_{\text{vap}}}{RT^2} dT$$



$$\frac{dP}{dT} = \frac{\Delta h_{\text{vap}} P}{RT^2}$$

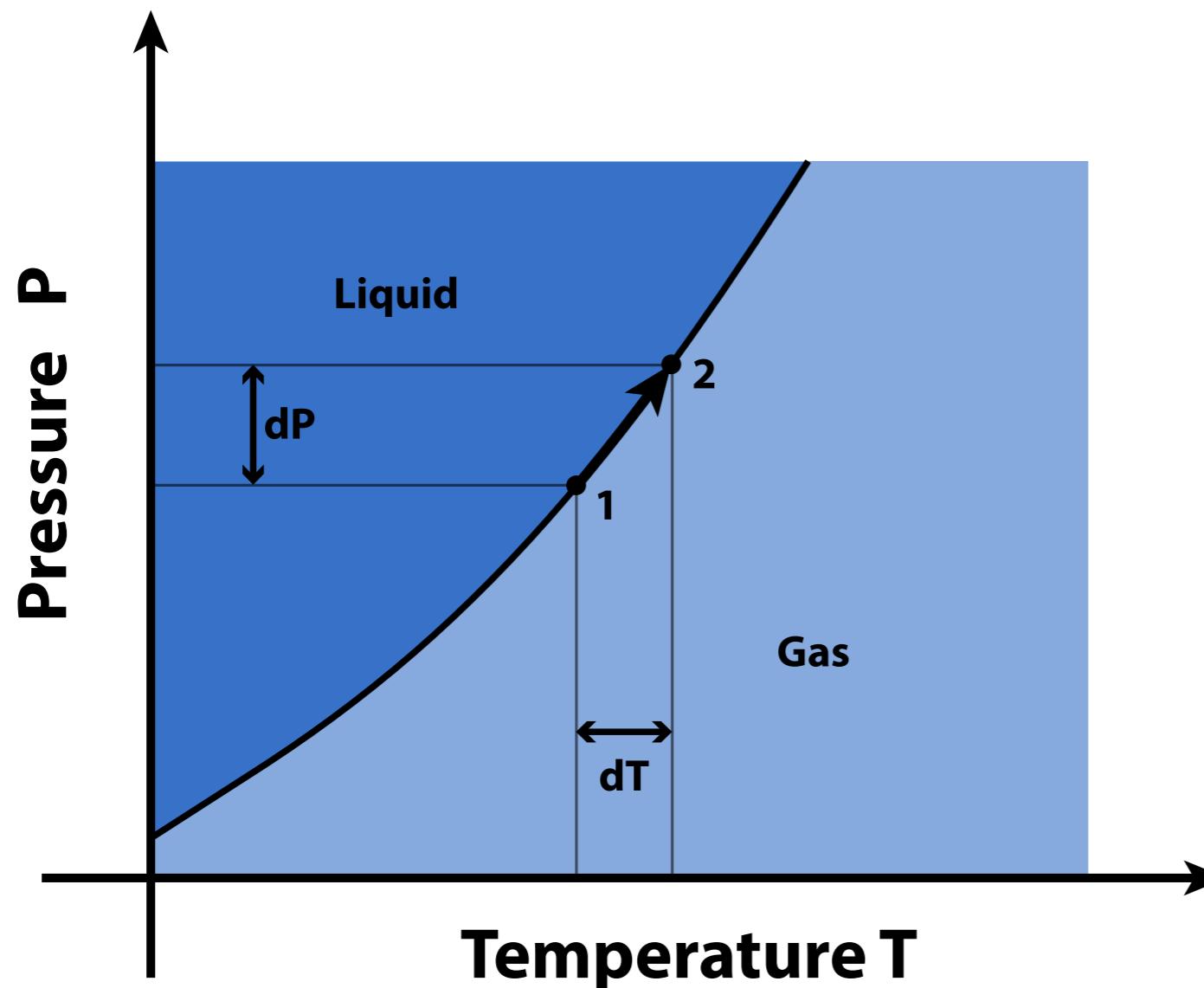
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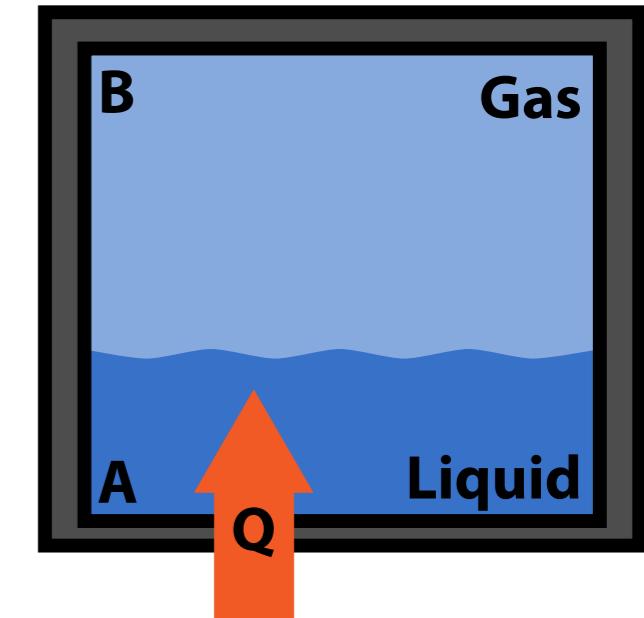
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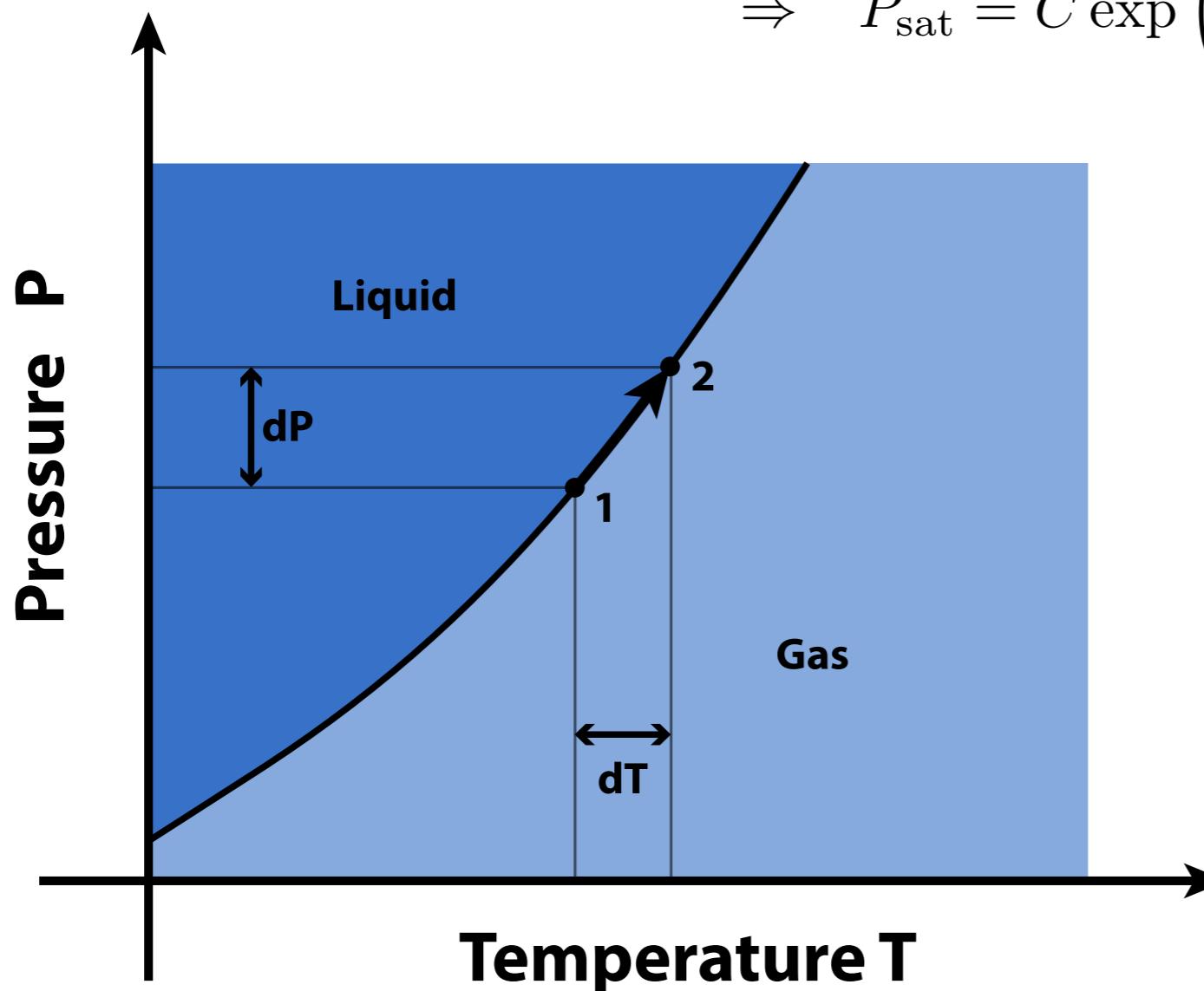


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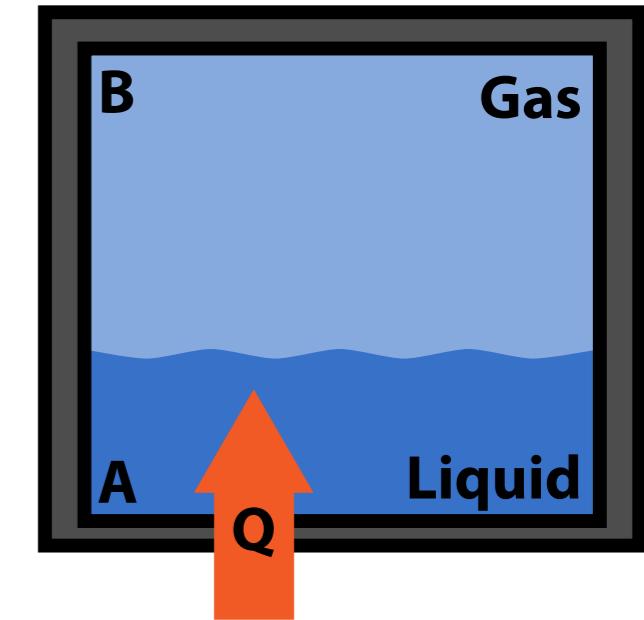
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$$\Rightarrow P_{\text{sat}} = C \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_{\text{sat}}}\right)$$



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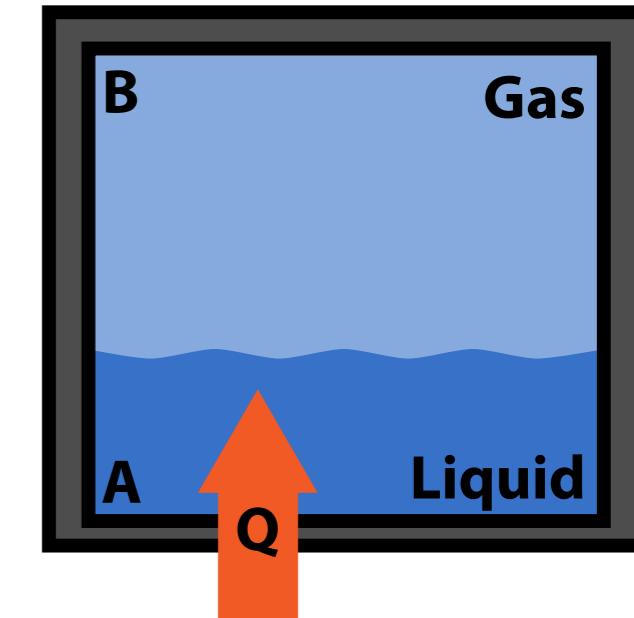
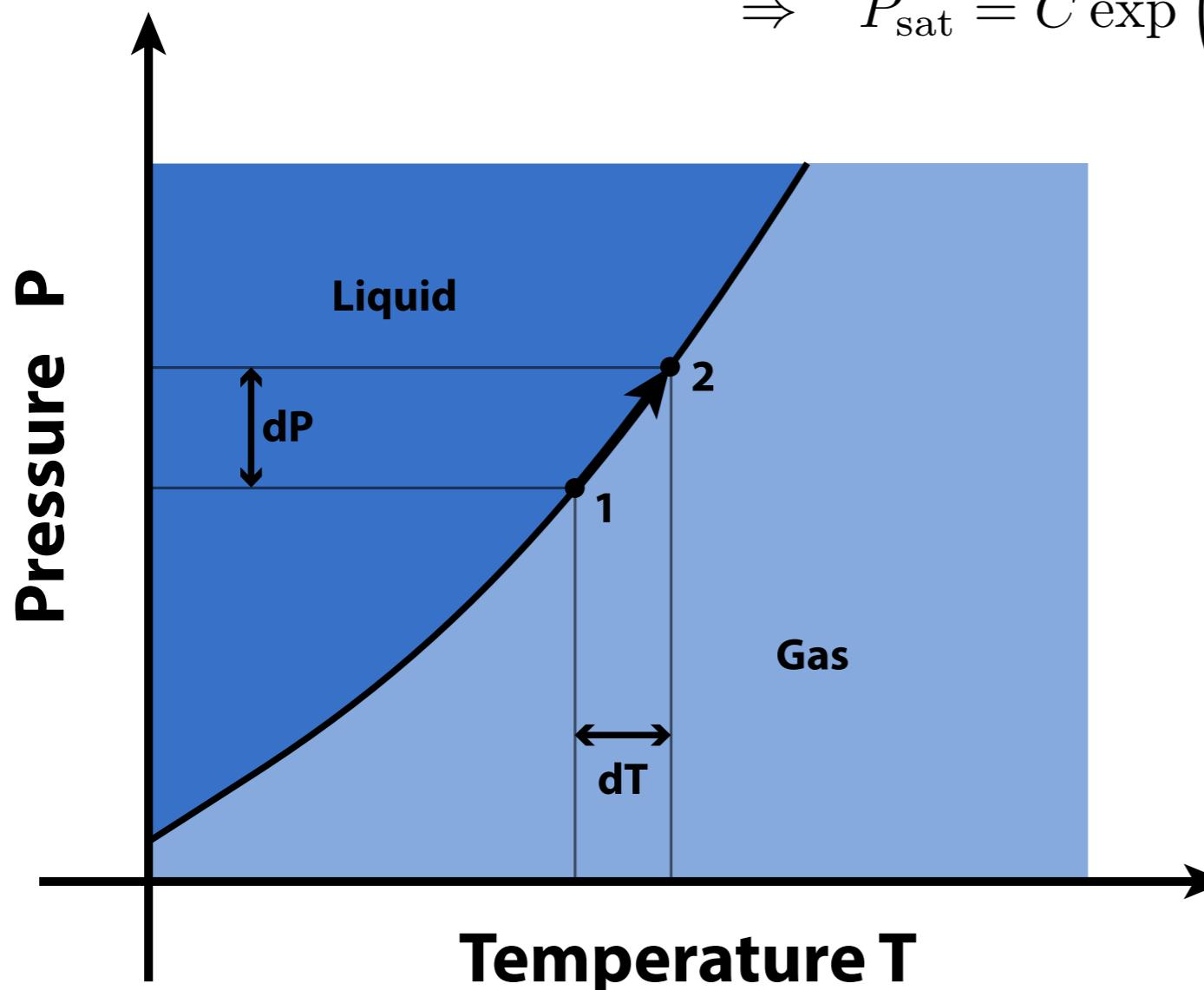


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Where the properties ( $P$  and  $T$ ) at the phase equilibrium are known as

- Saturation pressure  $P_{\text{sat}}$
- Saturation temperature  $T_{\text{sat}}$

$$\frac{dP}{dT} = \frac{\Delta h_{\text{vap}} P}{RT^2}$$

**Clausius-Clapyeron  
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## Example 7.1

The saturation pressure of water at  $T_1 = 100 \text{ } ^\circ\text{C}$  is  $P_1 = 101.35 \text{ kPa}$ . What is the saturation pressure at  $T_2 = 105 \text{ } ^\circ\text{C}$ ? Assume the latent heat of vaporisation  $\Delta h_{vap} = 2257.06 \text{ kJ / kgK}$ .

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We use the relation

$$P_{\text{sat}} = C \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_{\text{sat}}}\right)$$

to calculate C from  $T_1$  and  $P_1$ .

$$C = P_1 / \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_1}\right) = 4.98510 \times 10^7 \text{ kPa}$$

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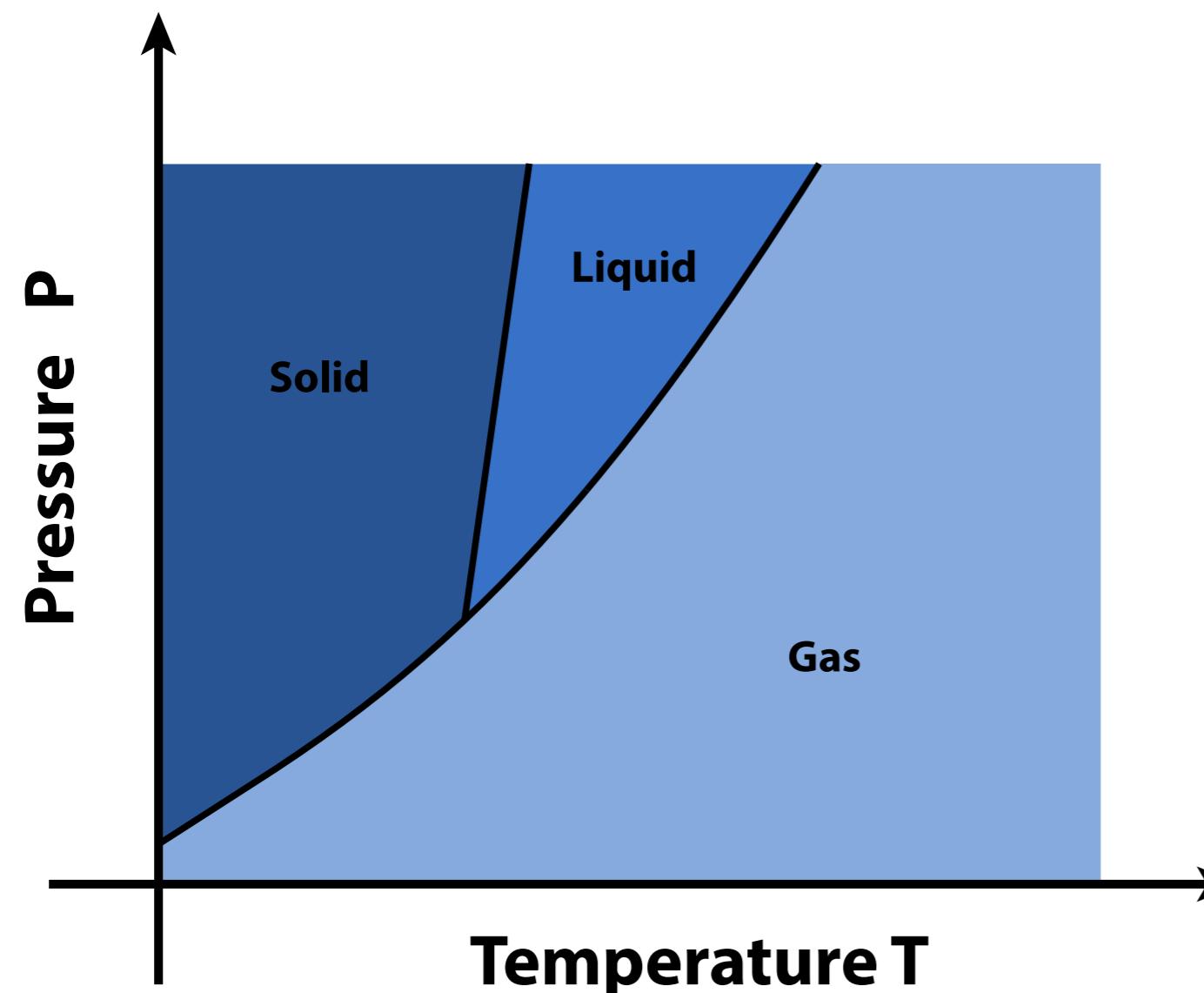
$$C = P_1 / \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_1}\right) = 4.98510 \times 10^7 \text{ kPa}$$

Then we plug  $T_2$  the same relation to obtain  $P_2$ .

$$P_2 = C \exp\left(-\frac{\Delta h_{\text{vap}}}{RT_2}\right) = 120.527 \text{ kPa}$$

# Liquid-Solid and Gas-Solid Equilibria

The previous derivation remains valid for gas-solid phase transitions. For liquid-solid transitions, we must use Claperyon equation. Below, the specific enthalpy for the generic transition is denoted by  $\Delta h_{\text{tr}}$



$$\frac{dP}{dT} = \frac{\Delta h_{\text{tr}}}{T(v_B - v_A)}$$

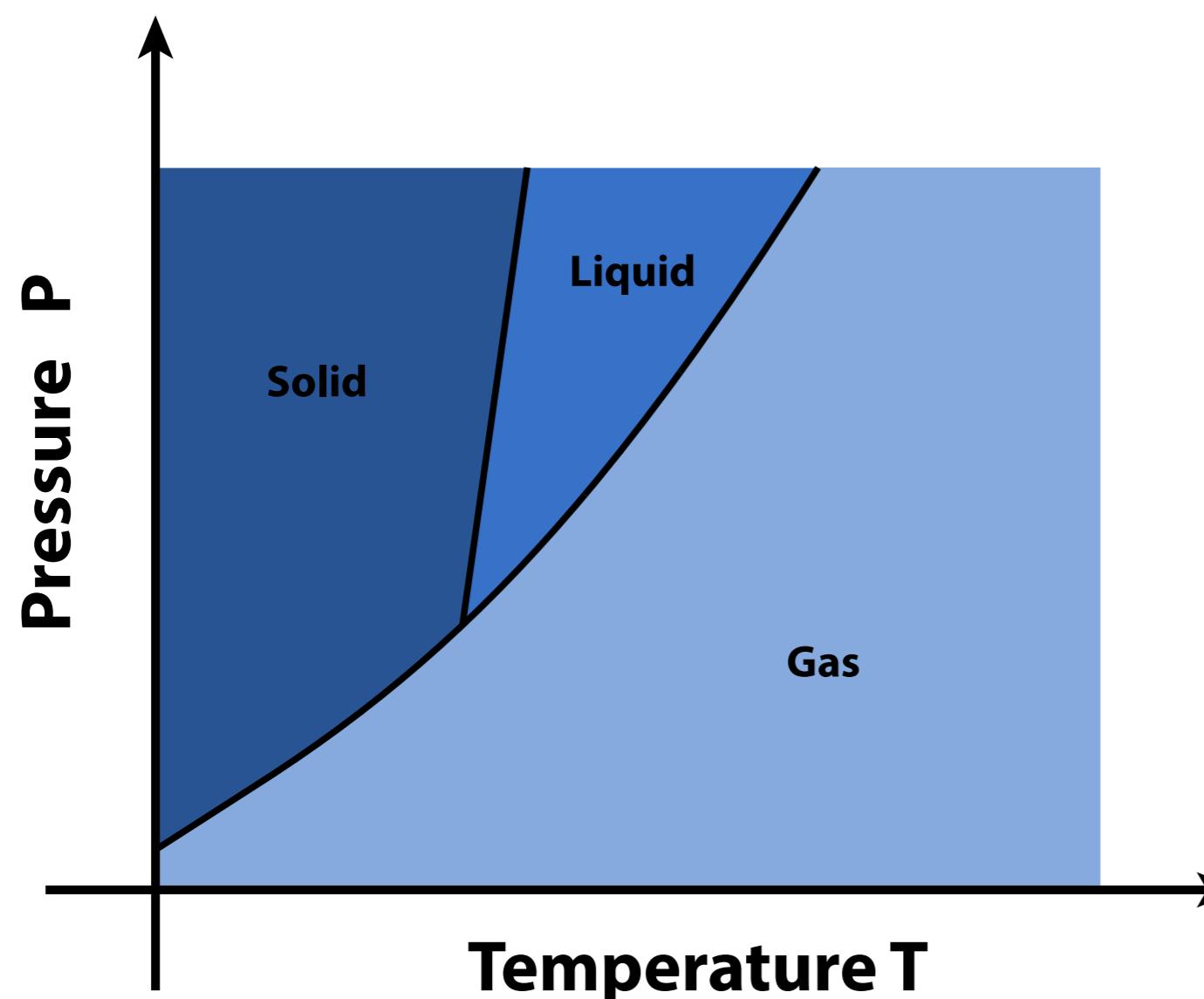
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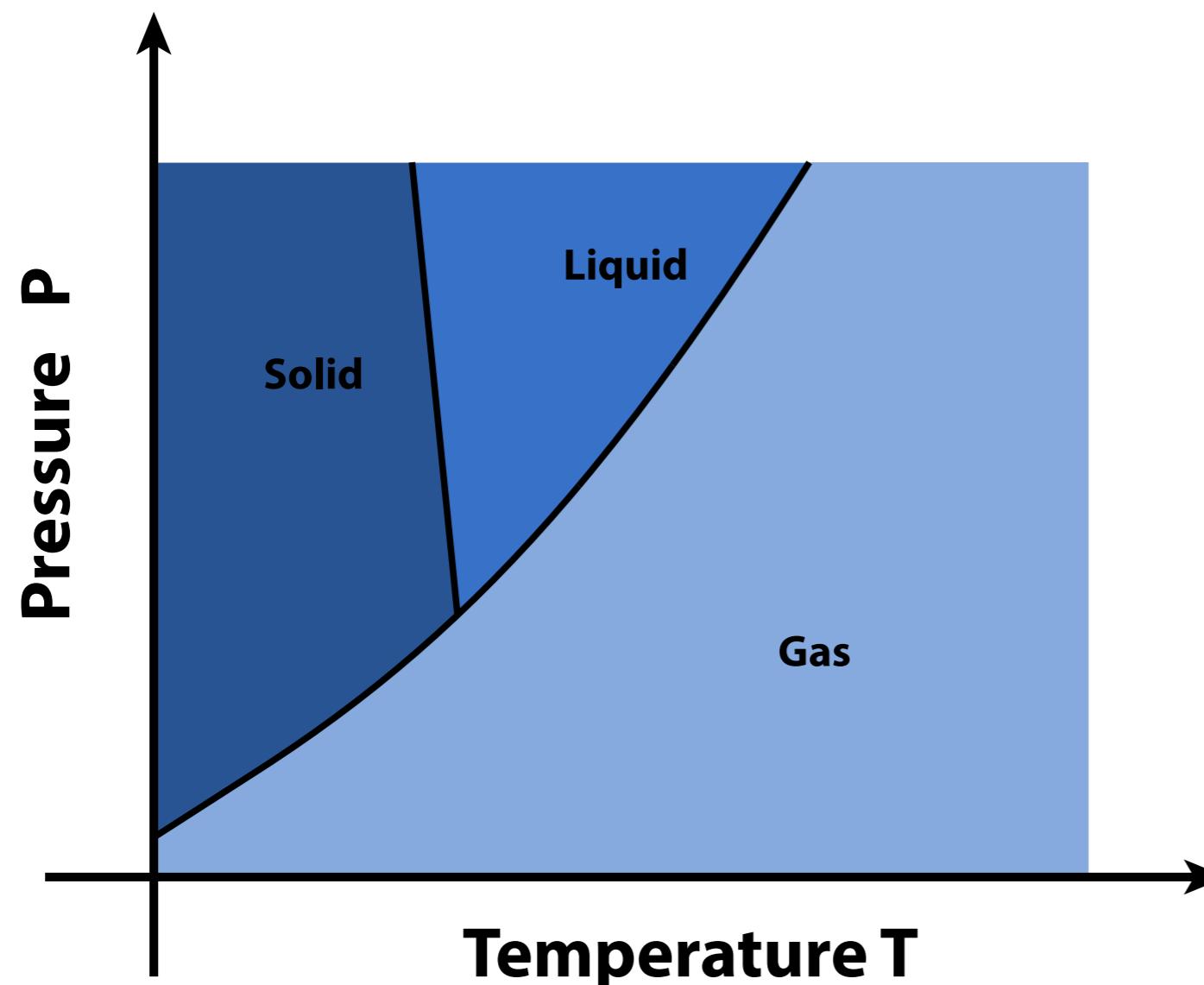
In most cases the solid has a lower specific volume than that of the liquid. The slope  $\frac{dP}{dT}$  of the phase equilibrium curve is thus  $> 0$

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Otherwise the slope is  $< 0$  (e.g. water)

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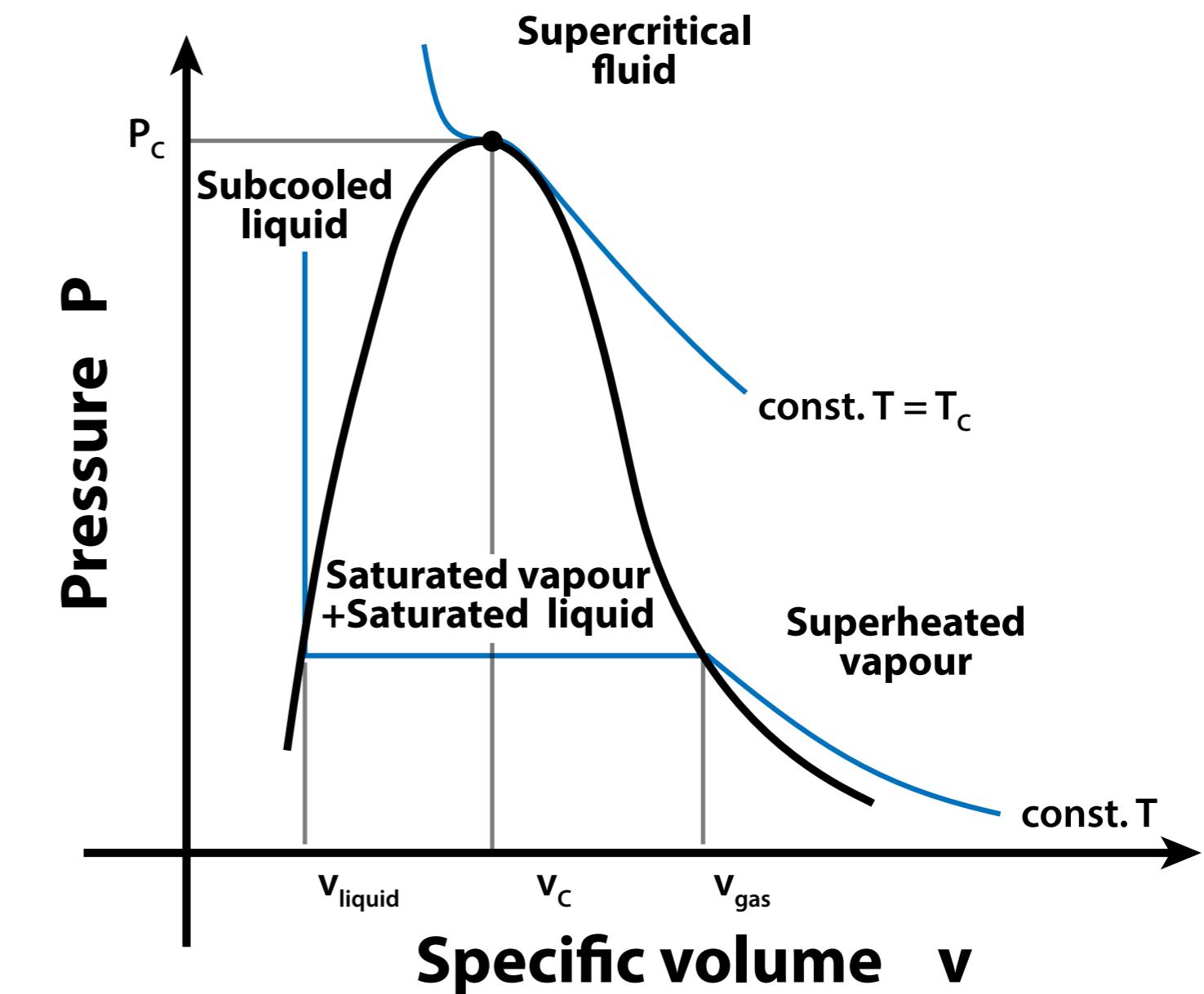
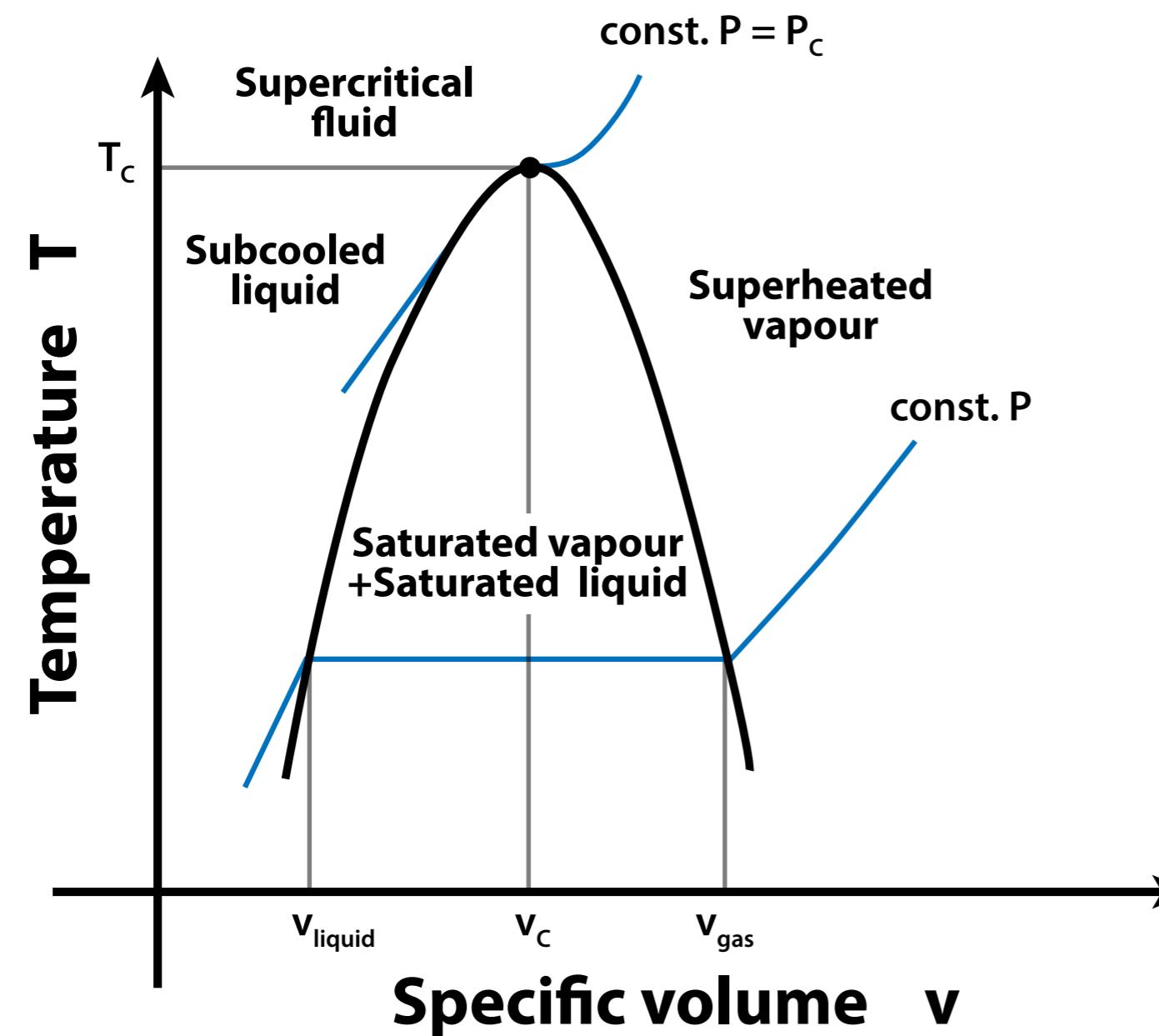
**Clapyeron  
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**Clausius-Clapyeron  
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# Phase Change on P-v and T-v Diagrams

The region of coexistence of vapour and liquid is known as *vapour dome*.



# Quality of a mixture

The quality of a mixture of vapour and liquid is defined as:

$$x = \frac{m_{\text{vapour}}}{m_{\text{mixture}}}$$

Since  $m_{\text{mixture}} = m_{\text{vapour}} + m_{\text{liquid}}$ , we have:

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The properties of the mixture are the weighted average of the properties of the individual phases. For example, for the specific volume we have:

$$v_{\text{mixture}} = x v_{\text{vapour}} + (1 - x) v_{\text{liquid}}$$

For the specific internal energy:

$$u_{\text{mixture}} = x u_{\text{vapour}} + (1 - x) u_{\text{liquid}}$$

For the specific entropy:

$$s_{\text{mixture}} = x s_{\text{vapour}} + (1 - x) s_{\text{liquid}}$$

# Van der Waals equation

The Van der Waals equation of state generalizes the ideal gas law, and predicts more realistically the behavior of fluids over a wider range of parameters  $T$  and  $V$ .

The equation is written as:

$$\left(P + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_u T$$

where  $\bar{v} = V/N$  is the specific molar volume, and  $a$  and  $b$  are known as Van der Waals constants and are tabulated for different substances.

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$$\left( P + \frac{a}{\bar{v}^2} \right) (\bar{v} - b) = R_u T$$

where  $\bar{v} = V/N$  is the specific molar volume, and  $a$  and  $b$  are known as Van der Waals constants and are tabulated for different substances.

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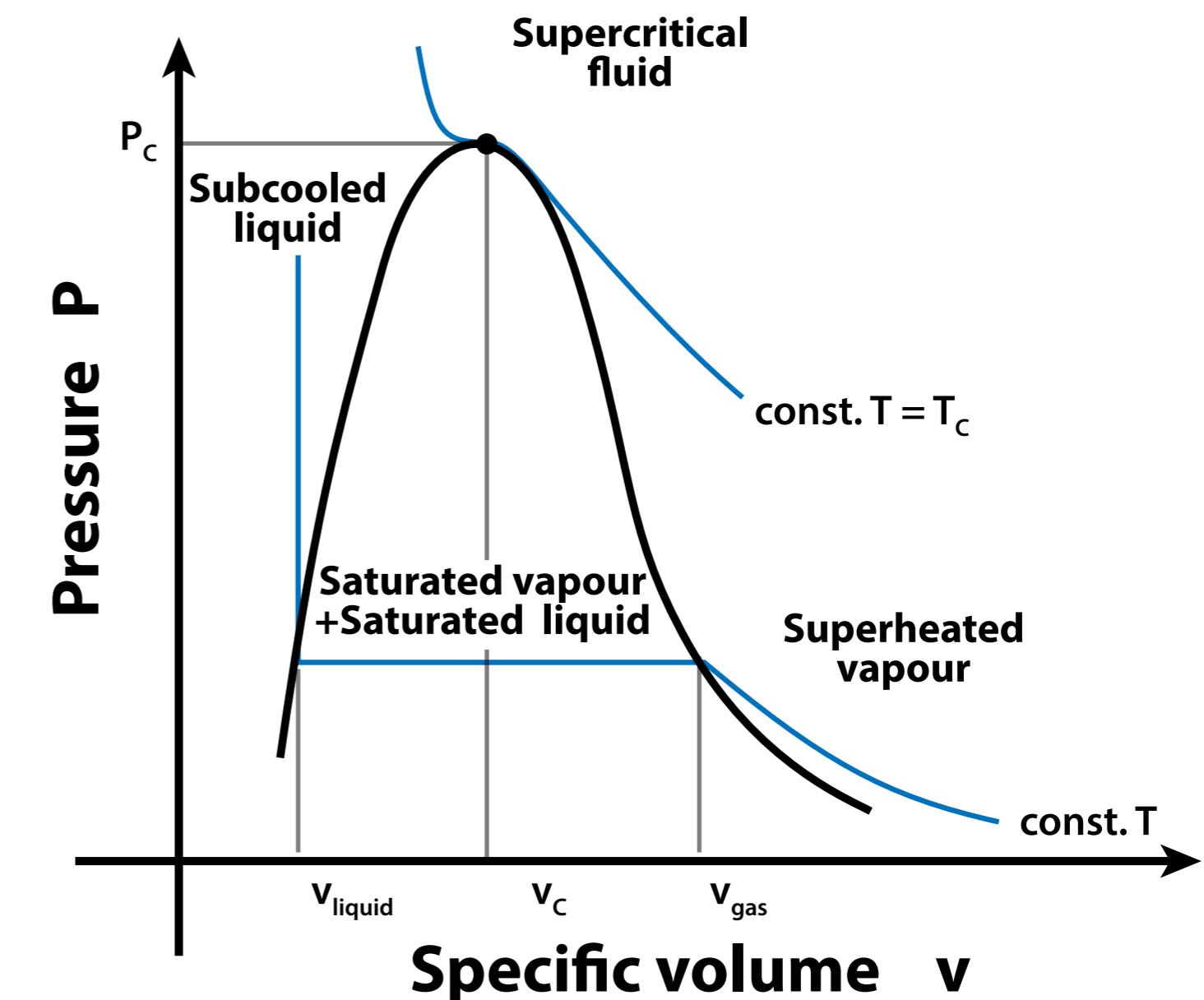
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The equation gives the behavior of incompressible fluids at high pressure, as well as the ideal gas behavior at low pressure, and the critical point.

However, in the region of the vapour dome, the equation does not predict correctly the experimental observation that during an isothermal process the pressure is constant with respect to the volume.

# Van der Waals equation and the critical point

We notice from the P-v diagram that the critical isotherm at the critical point has zero first and second derivative. It is a stationary point that is also an inflection point.



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Starting from the equation and applying the two additional conditions

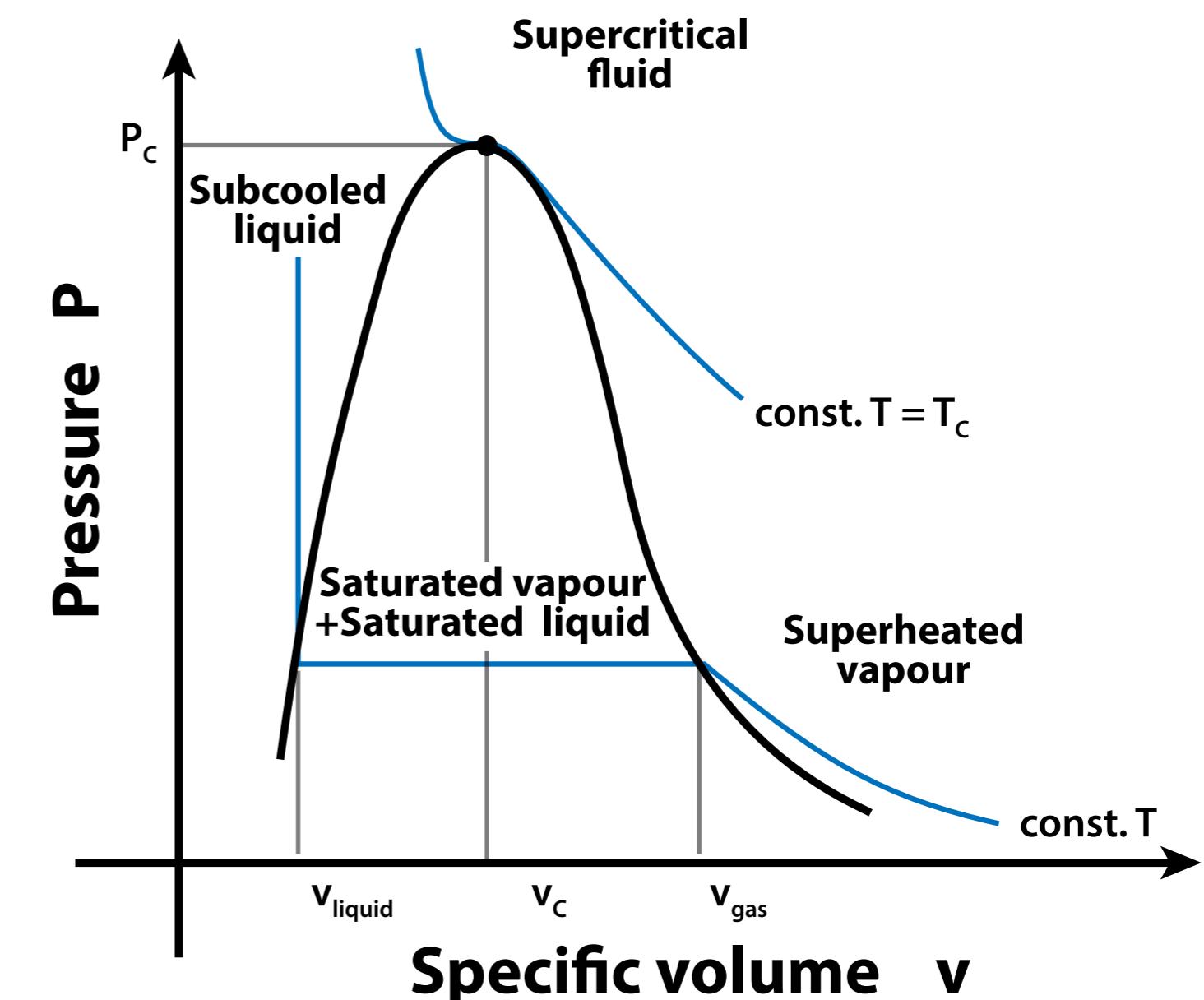
$$\left(\frac{\partial P}{\partial \bar{v}}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \bar{v}^2}\right)_T = 0$$

at  $T = T_c$ ,  $P = P_c$  and  $\bar{v} = \bar{v}_c$ , we get:

$$a = \frac{27}{64} \frac{R_u T_c^2}{P_c}$$

$$b = \frac{1}{8} \frac{R_u T_c}{P_c}$$

$$\bar{v}_c = \frac{3}{8} \frac{R_u T_c}{P_c}$$



# Van der Waals equation and the compressibility factor

We define the reduced pressure  $P_r = P/P_c$ , the reduced temperature  $T_r = T/T_c$ , and reduced specific molar volume  $\bar{v}_r = \bar{v}/\bar{v}_c$ .

Using these definitions and the relations below, we can express the Van der Waals equation as:

$$P_r = \frac{8T_r}{3\bar{v}_r - 1} - \frac{3}{\bar{v}_r^2}$$

This equation is a *universal equation of state*: it is applicable to all gasses. In fact, the compressibility factor, defined as  $Z = Pv/(RT)$ , has for all gasses the same dependence on  $P_r$  and  $T_r$ .

---

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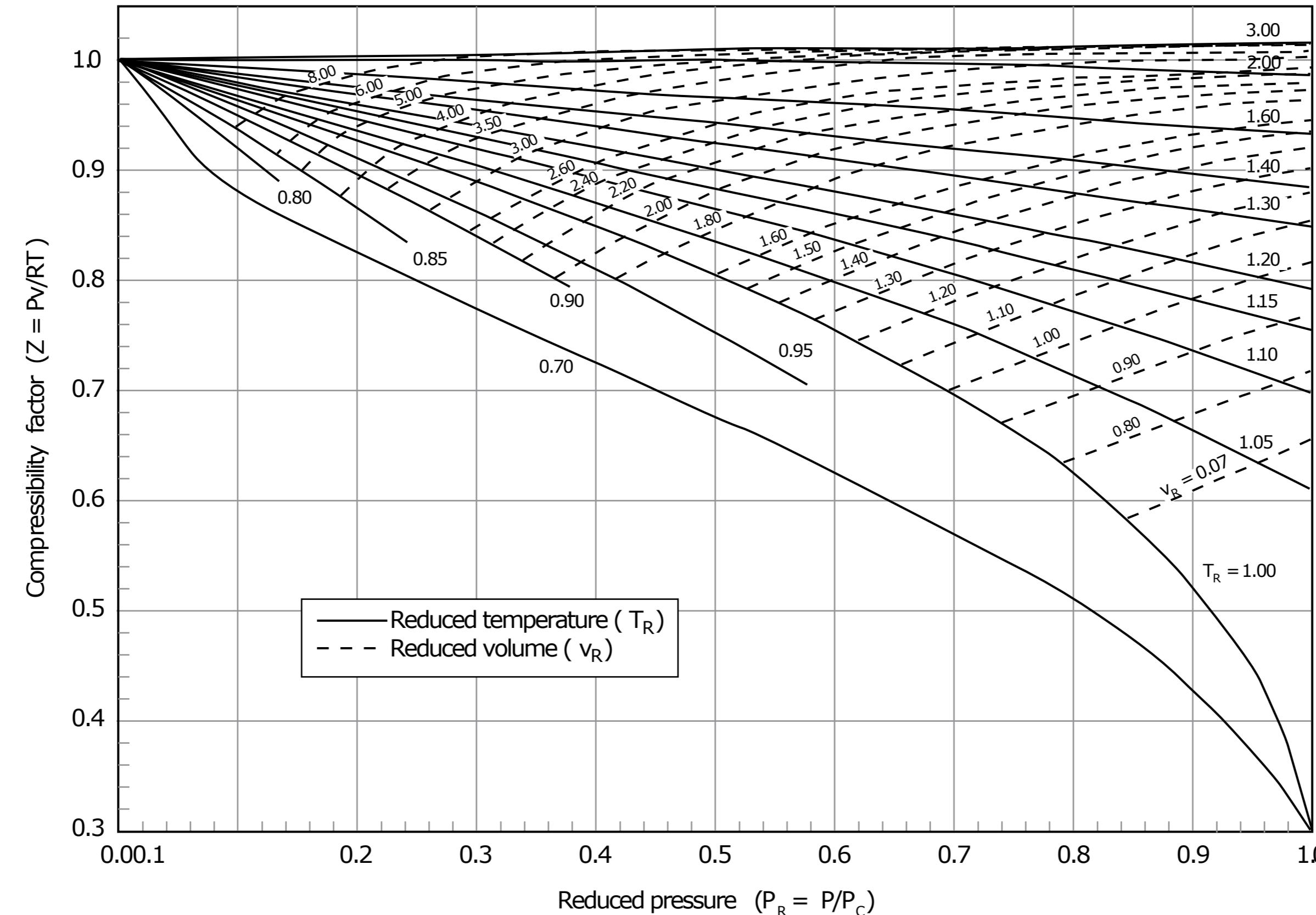
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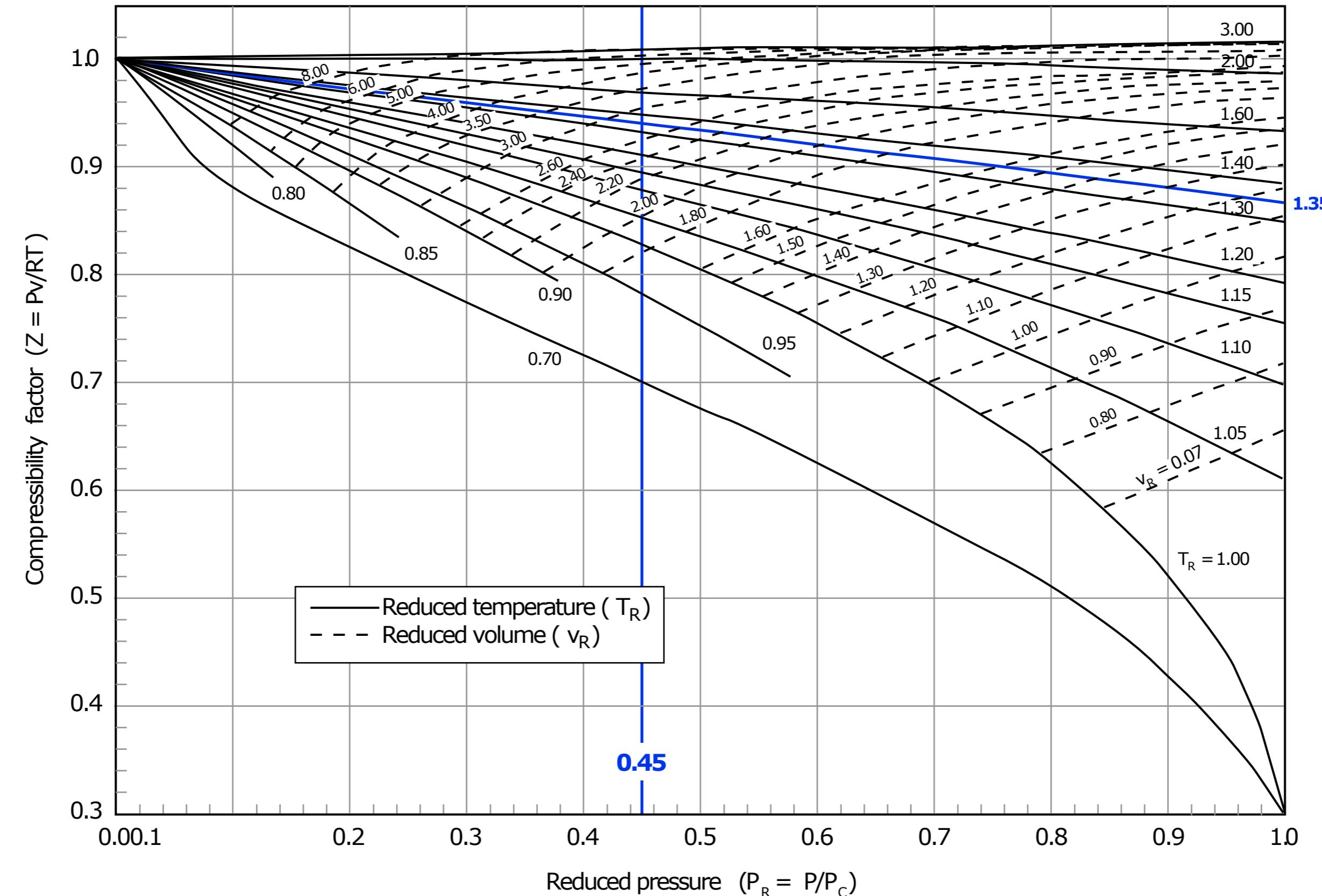
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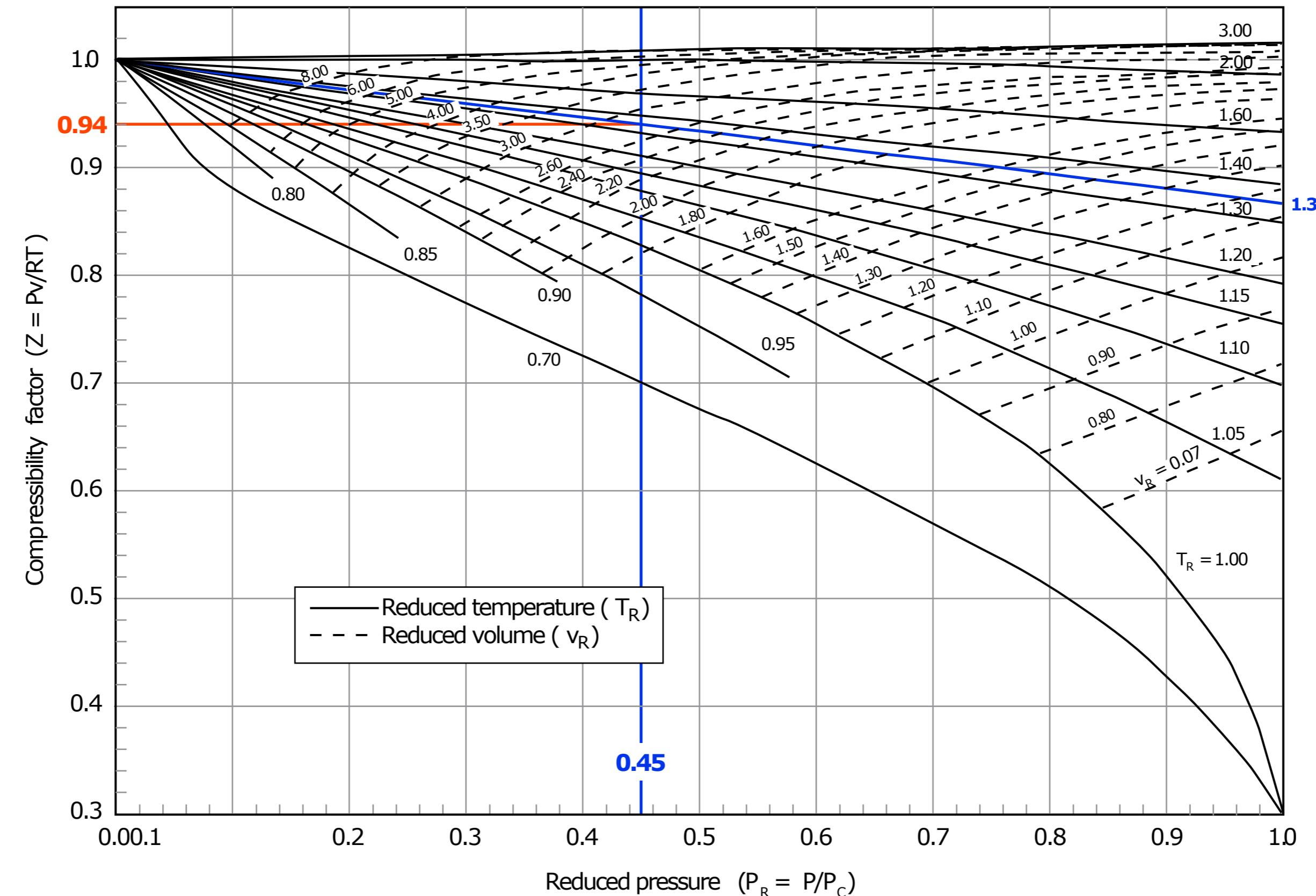
# Example 7.14 - generalised compressibility charts



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Then we extract the required information from the generalised compressibility charts (Appendix 10). We obtain  $Z = 0.94$ .

Using  $Z = 0.94$ , we get  $v = ZRT/P = 0.0378 \text{ m}^3/\text{kg}$ .

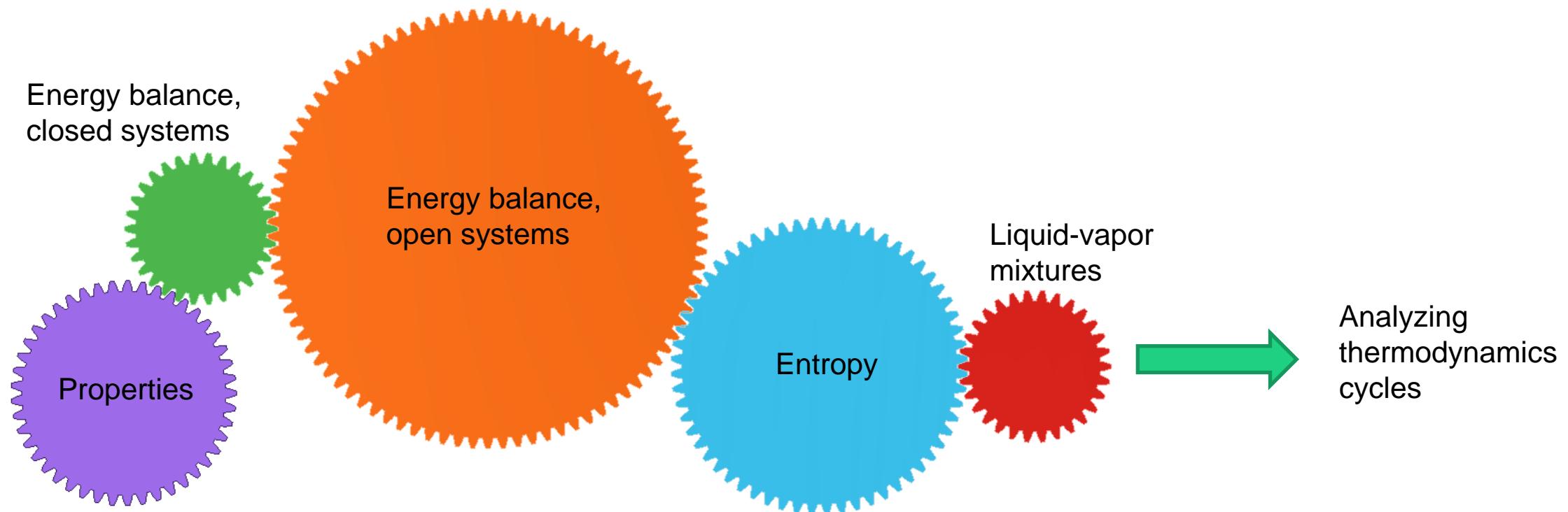
47201 Engineering thermodynamics

# Lecture 7a: Ideal heat engines (Ch. 8.1-3)



# Thermodynamic cycles

- What we have done in this course up to now has prepared us to look at how a thermodynamic cycle can be applied, in the first case, to produce work/electricity from heat



# Cycles

## Definition

A **cycle** is a process or **series of processes** that **restore** a system to its **initial state** and does something useful

## Implications:

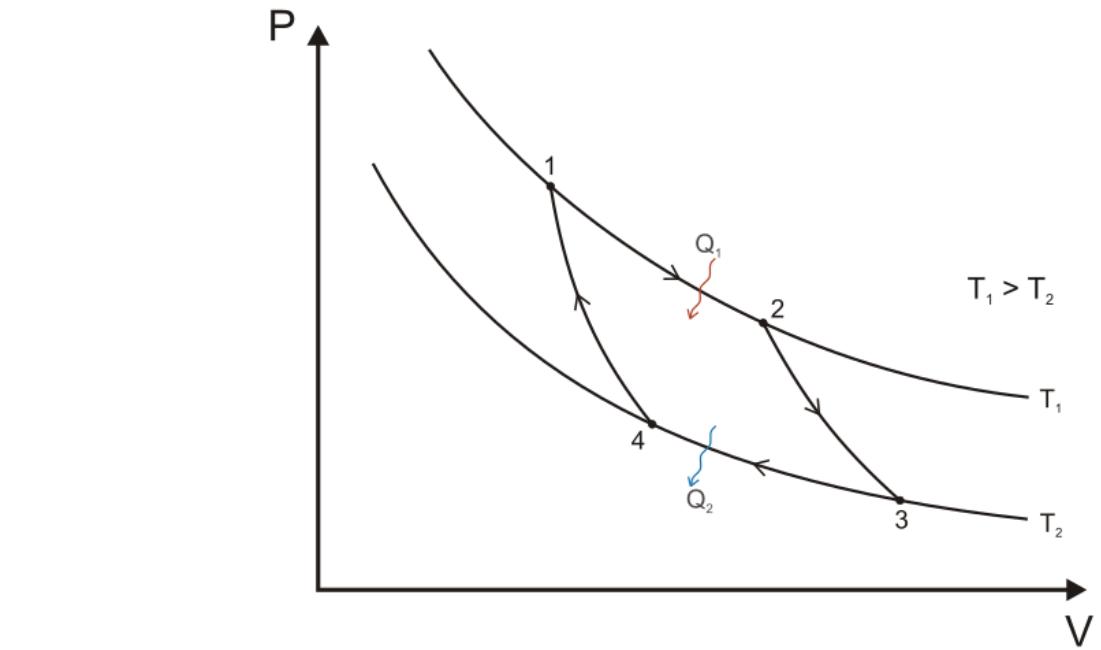
Integrating a **property over a cycle will always give 0**

However, the **transfer of energy in the form if heat or work will not be 0!**

All **processes** that do **work repeatedly** must be cycles.  
This makes the analysis of cycles immensely important!



7a - Ideal heat engines or carnot cycle



# Heat engine

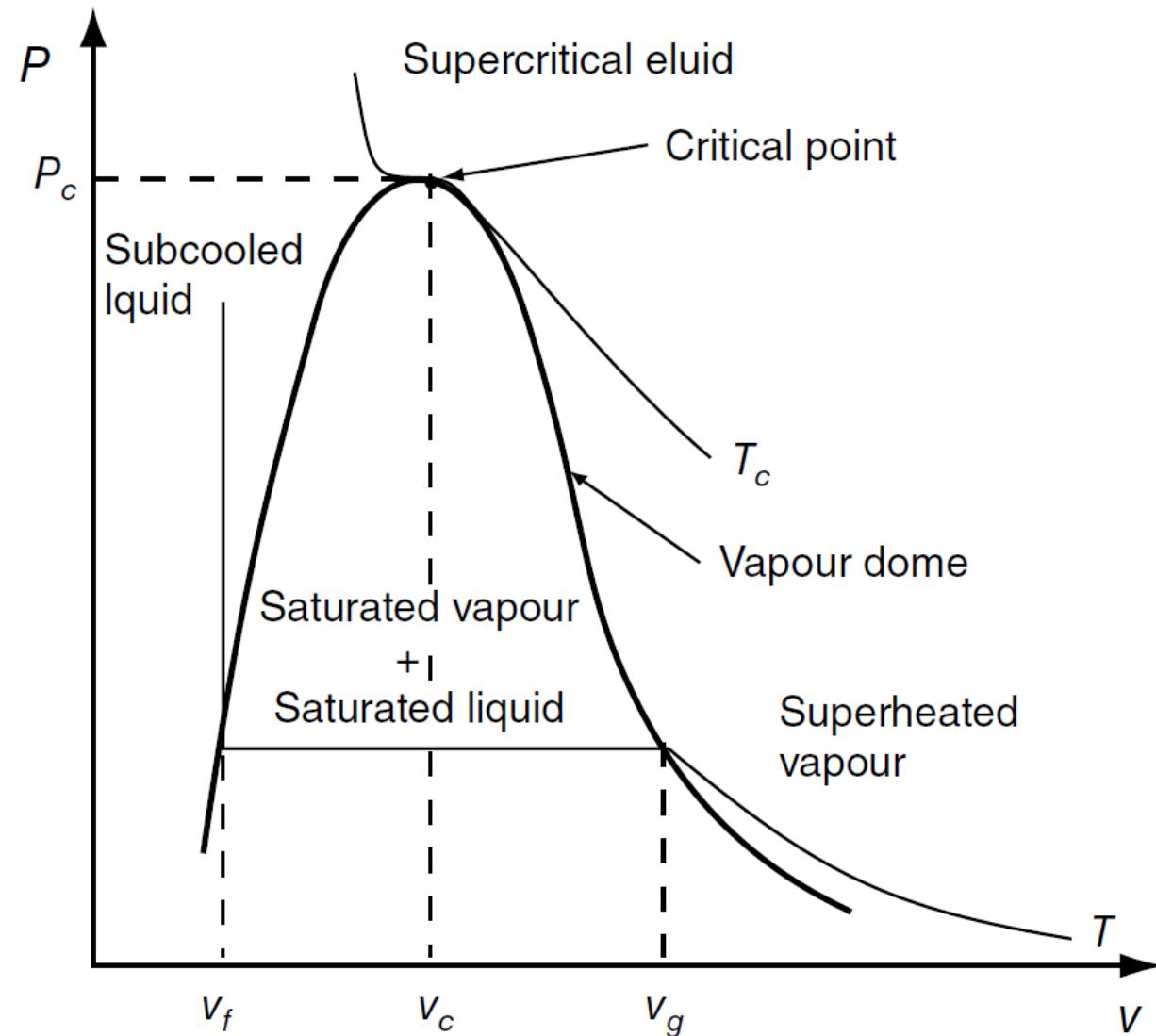
A heat engine is any device that operates in a cycle and does work on the surroundings when heat is input.

- By operating in a cycle, the device do work repeatedly
- Examples of heat engines include internal combustion engines, locomotives, gas turbines, and power plants
- Batteries and fuel cells produce electricity from chemical reactions and are not heat engines, although there are still heat transfer interactions

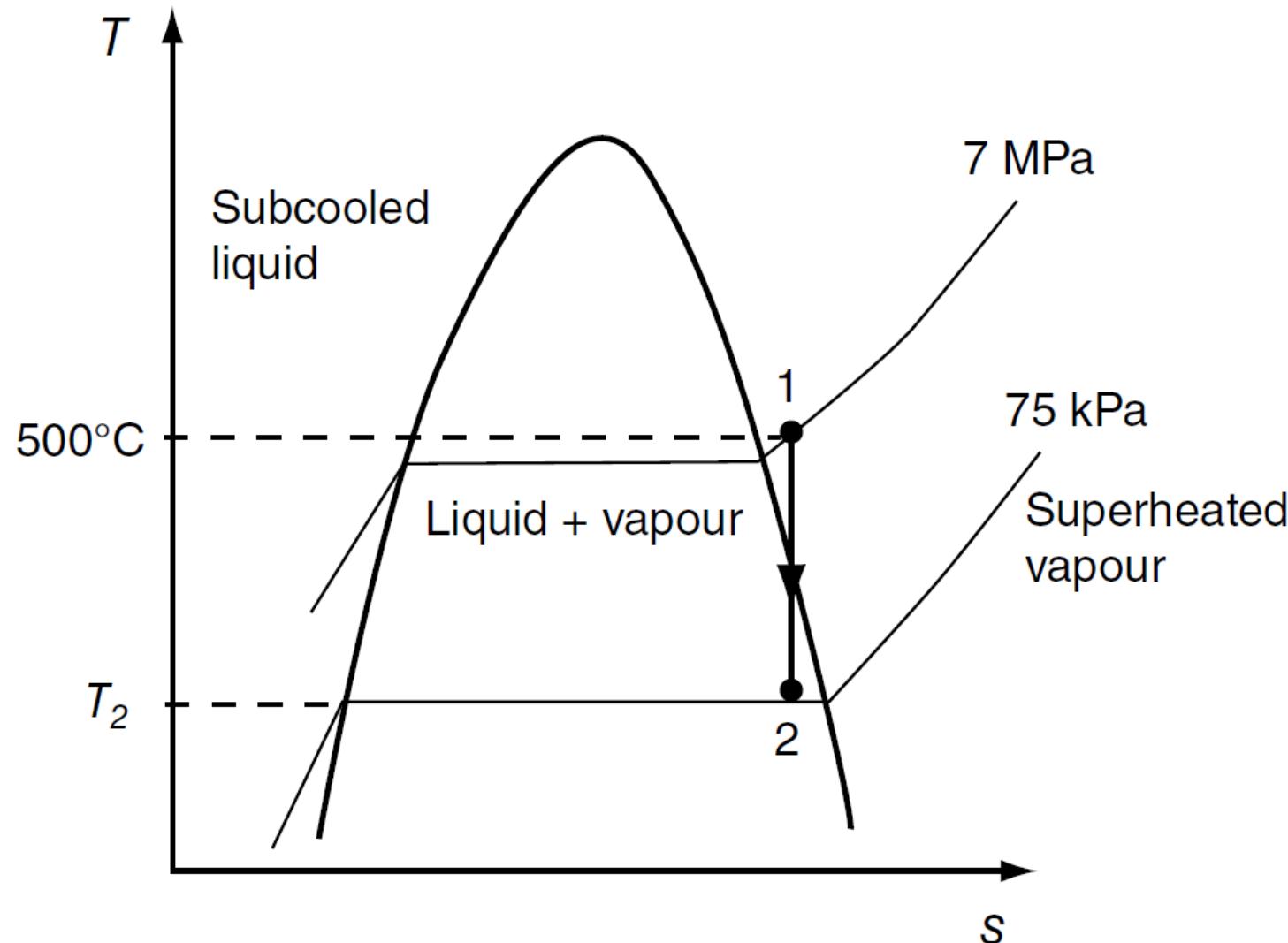
# Phase diagrams and cycles

- We use phase diagrams when analyzing cycles because they help visualize the operating points
- Plotting state points on a phase diagram can also be a way to double check calculations and property values
- For power production and refrigeration/heat pump cycles we will visualize the cycles using both T-s and p-v diagrams
  - The book focuses more on T-s diagrams and therefore the lectures will as well

# Property charts from the book



# Property charts from the book



# Heat engine - efficiency

One of the most important figures of merit for any thermodynamic device is the efficiency,  $\eta$ .

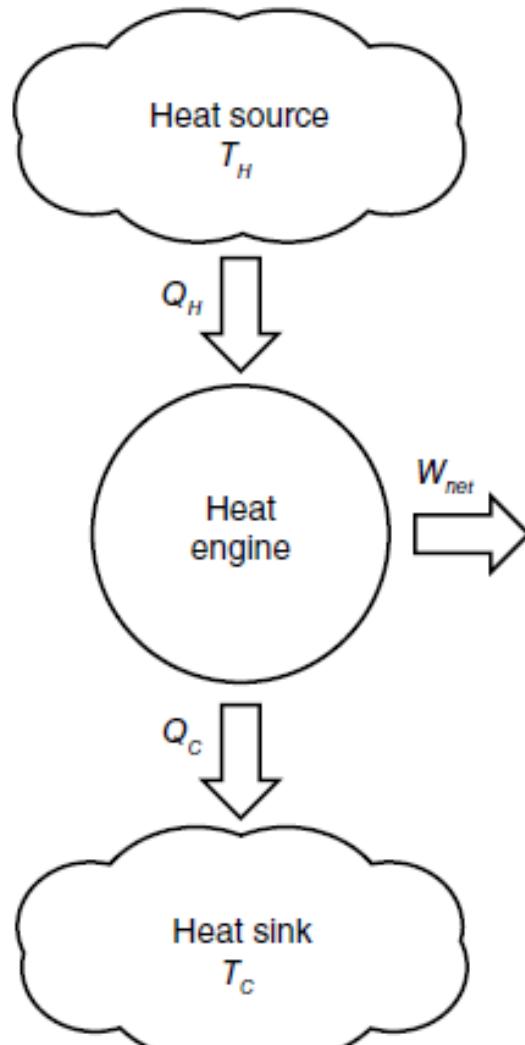
$$\eta = \frac{\text{net work output}}{\text{heat input}} = \frac{W_{net}}{Q_{in}}$$

- We can also define the efficiency on a rate basis

$$\eta = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$$

- This is also called a 1st law efficiency because it is based purely on energy

# Power cycles – overall analysis



The overall energy balance for any similar heat engine is:

- $\dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{out}$

$$\dot{Q}_H = \dot{W}_{out} + \dot{Q}_C$$

- And on an energy basis

$$Q_H = W_{out} + Q_C$$

# What is the maximum efficiency of a heat engine?

According to the 1st law of thermodynamics, it is possible to put in some energy in the form of heat and get that same energy out in the form of work. This would correspond to an efficiency of 100%.

- However, we are constrained by the physics of the working fluids. The heat added has a lower thermodynamic value (higher entropy) and it cannot be converted completely to work in a heat engine.
- From the Kelvin-Planck statement: it is impossible for any device operating in a cycle to receive heat from a high temperature source and produce a net amount of work without rejecting heat to a low temperature sink.
  - Since some heat also leaves the system, the efficiency must be below 100%.

# Carnot engine – historical perspective

- Sadi Carnot – French physicist – 1796-1832
- Carnot's book (the only one he published) "*Reflections on the motive power of fire*" – 1824
- Based on his desire to understand and optimize steam engines
- Work was the basis of the 2<sup>nd</sup> law of thermodynamics (before 1<sup>st</sup> law)
- Some false theory (caloric etc.) but correct conclusions:
  - 1) A heat engine must lose heat to surroundings to operate ( $\neq 100\%$  efficiency) – 2<sup>nd</sup> law.
  - 2) Efficiency only depends on the temp. of heat source and sink (not on the type of working fluid)
- Carnot's book not read by many scientists at the time of publication.
- Later (and translated) became part of the foundation for modern thermodynamics



# The Carnot cycle [Carnot engine]

The Carnot cycle uses four processes where each step is as efficient as possible. Carnot found that the most efficient process is independent of working fluid so the Carnot cycle is specified only in terms of the operating temperatures.

- The cycle is built between a hot reservoir and a cold reservoir.
- The compressor (work input) and expander (work generation) operate isentropically (reversibly) which is the most efficient way for them to operate
- Heat is added isothermally at the hot reservoir and removed isothermally at the cold reservoir

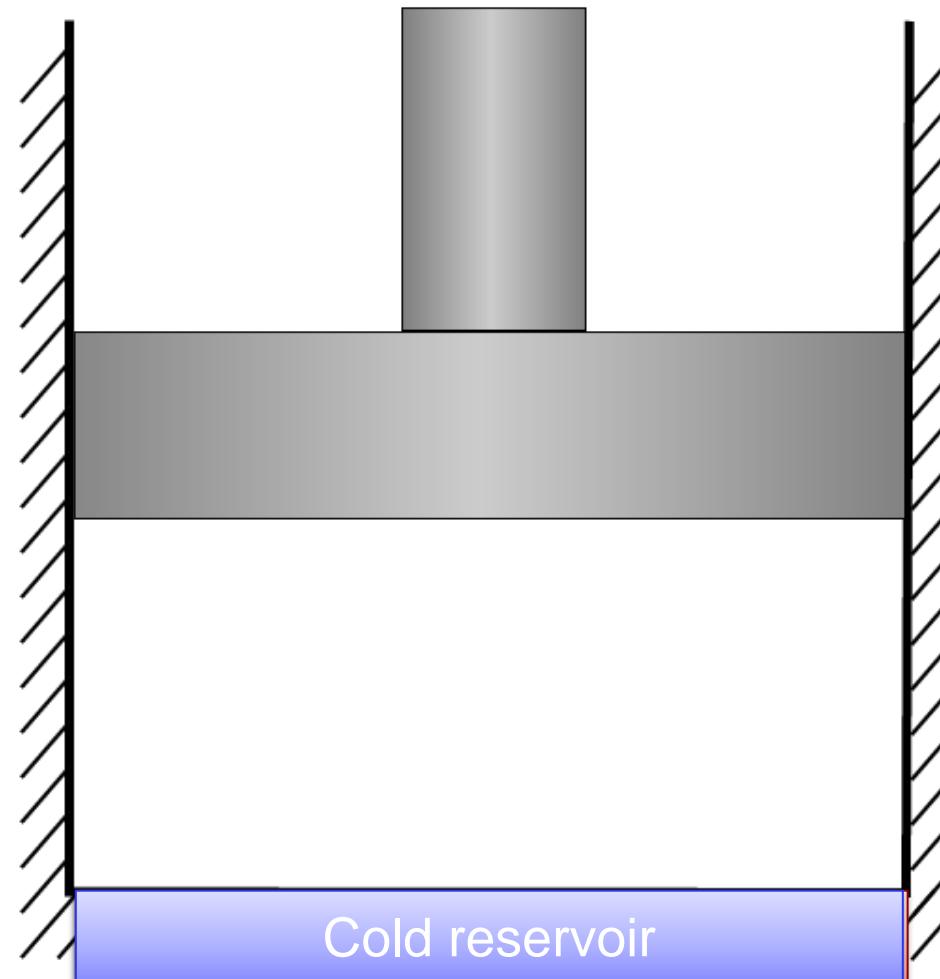
# The single-phase (closed system) Carnot cycle

State 1

State 2

State 3

State 4



Adiabatic compression  
Isothermal expansion  
Adiabatic expansion  
Isothermal compression

# Entropy addition for the Carnot cycle

- If the heat is added reversibly and the expansion and compression are isentropic, then the change in entropy of the system is 0

$$\Delta S_{cycle} = \oint \frac{\delta Q_{int,rev}}{T} = 0$$

- At the hot reservoir, the entropy addition is

$$\Delta S_{addition} = \frac{Q_H}{T_H}$$

- Similarly at the cold reservoir

$$\Delta S_{rejection} = \frac{Q_C}{T_C}$$

# Carnot cycle analysis

- Since the overall cycle is reversible and there is no entropy associated with work, the entropy associated with the heat addition is equal to the entropy associated with the heat rejection

$$\Delta S_{addition} = \Delta S_{rejection} \Rightarrow \frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

- The ratio of the heat additions is then

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

- Remembering that  $Q_H = W_{out} + Q_C$  for a heat engine, we can express the work as

$$W_{out,Carnot} = Q_H - Q_H \frac{T_C}{T_H} = Q_H \left( 1 - \frac{T_C}{T_H} \right)$$

- Then the efficiency of the Carnot cycle is

$$\eta_{th,Carnot} = \frac{W_{out}}{Q_H} = \frac{Q_H \left( 1 - \frac{T_C}{T_H} \right)}{Q_H} = \left( 1 - \frac{T_C}{T_H} \right)$$

# Two-phase Carnot cycle

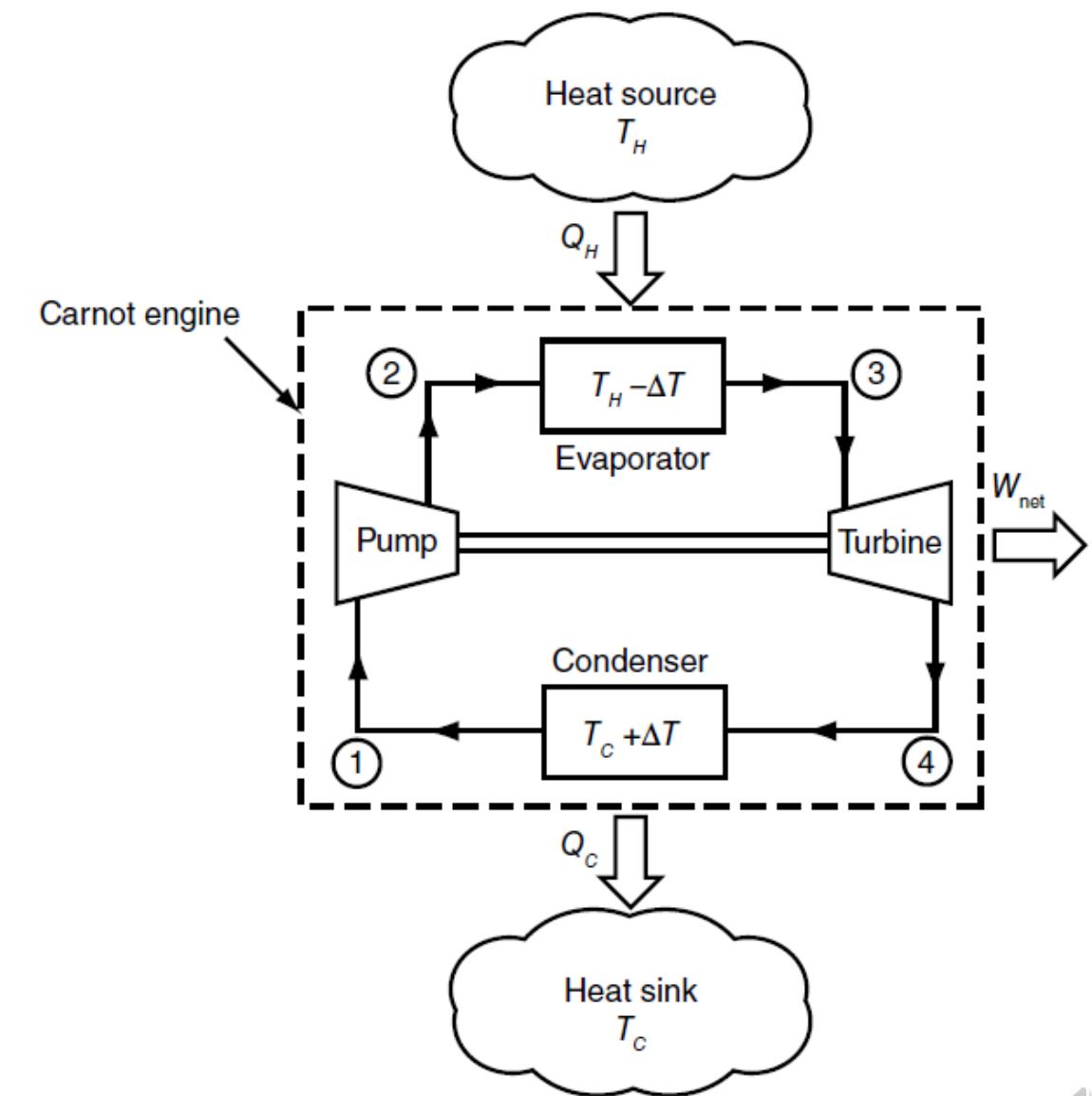
The two-phase Carnot cycle is built on the same principles as the single phase cycle, but now four separate devices are used, which allows the cycle to produce work constantly

1-2 a two-phase fluid is compressed adiabatically to a higher temperature and pressure

2-3 heat is added at a high pressure and constant temperature while the fluid is always within the vapor dome

3-4 the working fluid is expanded isentropically to produce work

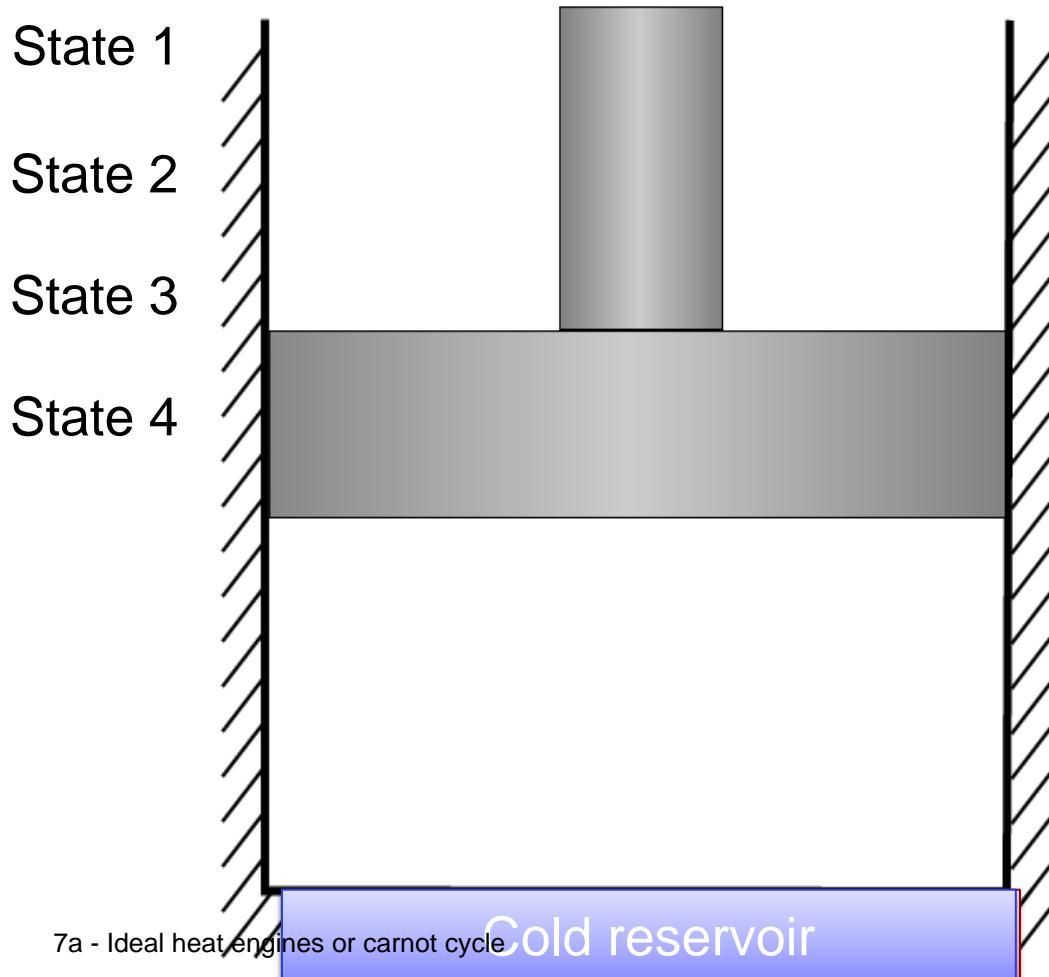
4-1 the working fluid is condensed isothermally and at low pressure to return it to its original state



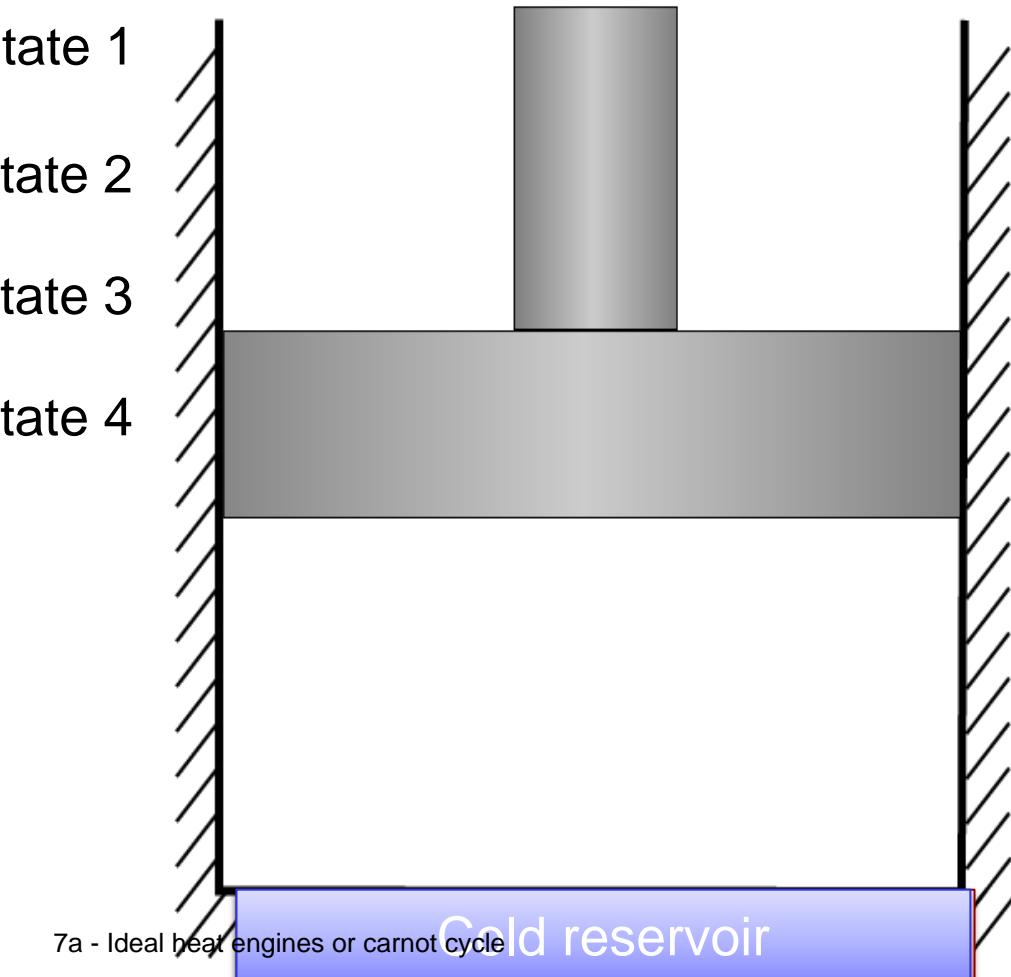
# Two-phase vs single phase Carnot cycles

- The single phase cycle uses a gas in a control mass that completes the four steps of the cycle sequentially
  - The cycle produces work approximately half of the time and consumes work approximately half the time
- The two phase cycle uses four separate control volumes, with each one operating continuously.
  - The two phase cycle makes use of the fact that a fluid can increase in energy while remaining at a constant temperature as it is converted from a saturated liquid to a saturated vapor
  - Since all four devices operate continuously, the cycle outputs and consumes work continuously

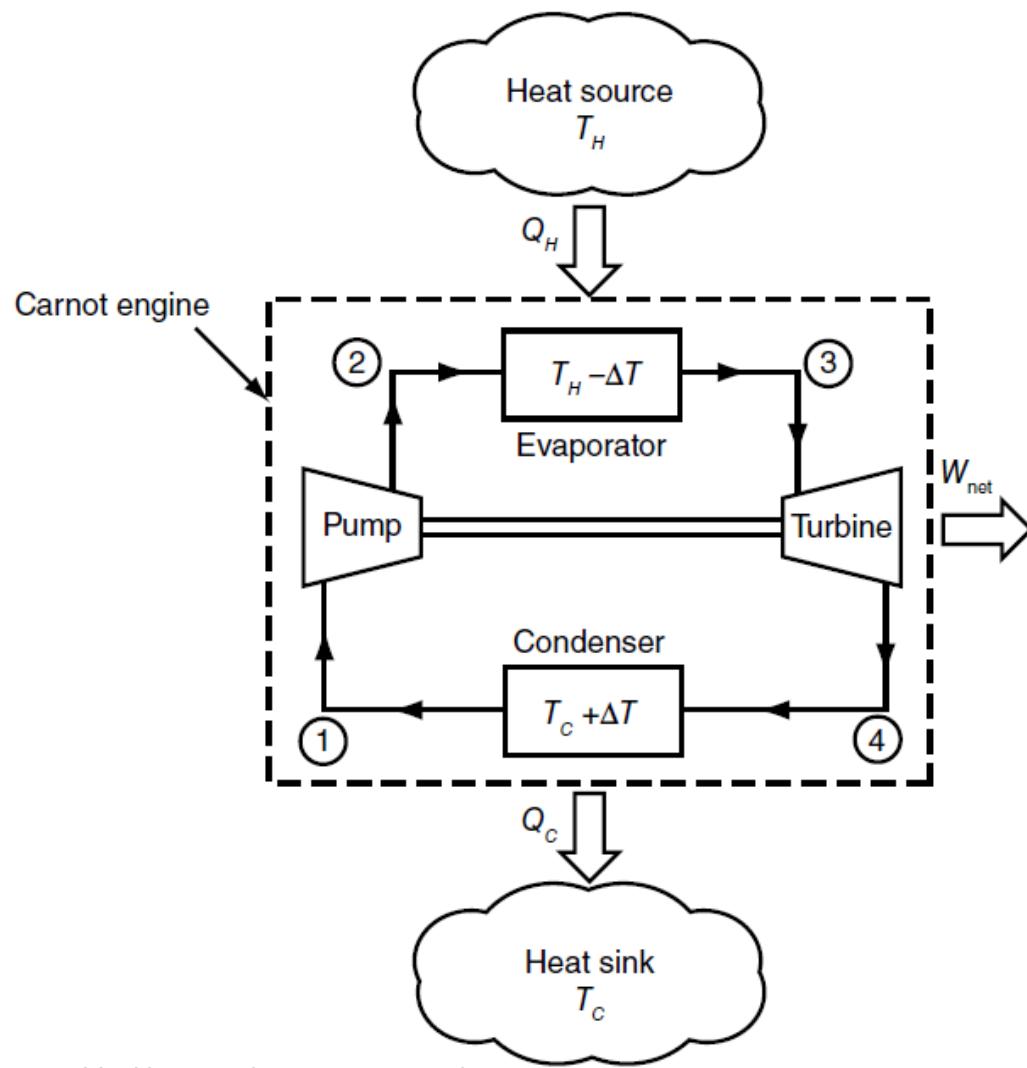
# The single-phase Carnot cycle P-V diagram



# The single-phase Carnot cycle T-s diagram



# Two-phase Carnot cycle T-s diagram



# Review: quality

Many heat engines use the fact that fluids can absorb a large amount of heat at a constant temperature during the phase change from liquid to gas. Inside the vapor dome, an additional term can be used to specify the state: the quality, which is denoted as  $x$ . The book uses a subscript  $g$  for vapor and  $f$  for liquid.

- A quality of 0 corresponds to saturated liquid and a quality of 1 corresponds to saturated vapor.

$$x = \frac{m_g}{m}$$

- Within the vapor dome, the properties can be calculated based on the the quality

$$x = \frac{u - u_f}{u_g - u_f}$$

## Example 8.2

A Carnot engine using 10 kg / s of water as the working fluid operates between an evaporator temperature of 300 C and a condenser temperature of 80 C. Find the rate of heat addition in the boiler and the steam quality at the turbine exhaust.

**Find:** Rate of heat addition  $Q_H$  and steam quality  $x_4$  at the turbine exhaust.

**Assume:**

1. Carnot cycle with isentropic expansion and compression
2. Quality entering the turbine is 1
3. Quality leaving the compressor is 0

# Example 8.2 solution: heating

1<sup>st</sup> law analysis of the evaporator (boiler)

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left( h + \frac{V^2}{2} + gz \right)_{out}$$

The change in enthalpy is from saturated liquid to saturated gas (state 2-3)

$$\dot{Q}_H = \dot{m}(h_3 - h_2) = \dot{m} (h_g - h_f)$$

Looking up the values in Appendix 8a gives

$$\dot{Q}_H = 10 \frac{kg}{s} \left( 2749.0 \frac{kJ}{kg} - 1344.0 \frac{kJ}{kg} \right) \frac{1 MW}{1000 kW} = 14.05 MW$$

# Example 8.2 solution: quality exiting the turbine

Since the expansion is isentropic, the entropy at the inlet and exit are equal.

- The entropy entering the turbine (state 3) is the entropy of saturated vapor from Table 8a

$$s_3 = s_g(T = 300\text{ }C) = 5.7045 \frac{\text{kJ}}{\text{kg K}}$$

The entropy at the turbine exit can be calculated based on the quality

$$x = \frac{s_4 - s_f}{s_g - s_f} = \frac{5.7045 \frac{\text{kJ}}{\text{kg K}} - 1.0753 \frac{\text{kJ}}{\text{kg K}}}{7.6122 \frac{\text{kJ}}{\text{kg K}} - 1.0753 \frac{\text{kJ}}{\text{kg K}}} = 0.7078$$

## Example 8.3

**Problem:** A Carnot engine using air as the working fluid works between temperatures of 573 K and 293 K. The pressure at the start of isothermal expansion is 100 kPa and at the end is 50 kPa. Find the work output and heat added per kilogram of air.

**Find:** Work output  $W$  and heat added  $Q$  both per kilogram of air in the Carnot engine.

**Assume:**

1. Air is an ideal gas

# Example 8.3 solution: Input heat

The isothermal expansion is where heat is added. We can use Eq. 6.40 to find the change in entropy during the process

$$\Delta s_{23} = c_p \ln\left(\frac{T_3}{T_2}\right) - R \ln\left(\frac{P_3}{P_2}\right) = -0.287 \frac{kJ}{kg K} \ln \frac{50 kPa}{100 kPa} = 0.1989 \frac{kJ}{kg K}$$

Then the heat addition can be calculated using Eq. 6.63

$$Q_{23} = T_H \Delta s_{23} = 573 K \cdot 0.1989 \frac{kJ}{kg K} = 113.99 \frac{kJ}{kg}$$

# Example 8.3 solution: Work output

Work is done during the adiabatic expansion. We can calculate the work from the two heat flows Eq. 8.10

$$W_{net} = Q_H - Q_C$$

Knowing that the entropy entering via  $Q_H$  is the same as exiting via  $Q_C$  because it is a Carnot cycle, we can use the mass specific version of Eq. 8.16 to calculate the work

$$W_{net} = (T_H - T_C) (s_3 - s_2) = (573 \text{ K} - 293 \text{ K}) 0.1989 \frac{\text{J}}{\text{kg K}} = 55.70 \frac{\text{kJ}}{\text{kg}}$$

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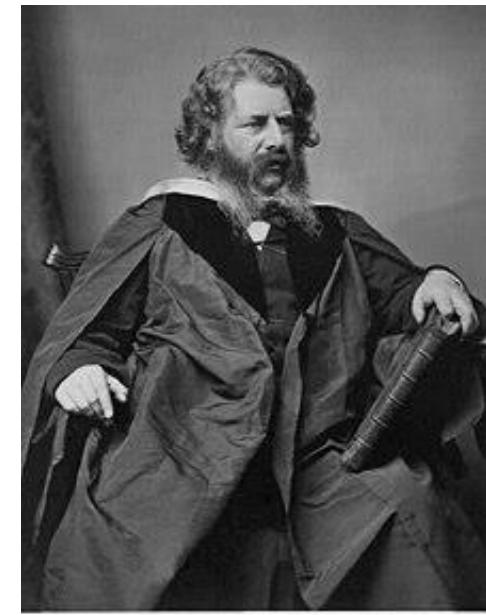
# Lecture 7b: Vapour power cycles (Ch. 9.1-3)

# Practical issues with the Carnot cycle

- Compressors, especially, do not like two phase fluids. Water droplets can damage blades on turbomachinery and can cause difficulties in designing an efficient compressor
- Isothermal heat exchange is efficient but not so fast
- A more realistic but still idealized power cycle is the ideal Rankine cycle

# William John Macquorn Rankine

- July 1820 – December 1876
- Professor at Glasgow University
- One of the founding fathers of modern thermodynamics
- Proposed the absolute temperature scale now called the Rankine scale.
- Developed a model of a thermal power cycle that has been named the Rankine cycle



W.J. Macquorn Rankine

# Basic principles of the Rankine cycle (Chapter 9)

The main purpose of the Rankine cycle is to avoid two phase fluids in the compressor. The main modification to the Carnot cycle is that the working fluid is cooled to a saturated liquid before entering a pump. It is then pumped to the higher pressure, where it is a subcooled liquid.

- Whereas the Carnot cycle refers to specific operating conditions, the Rankine cycle exists in several configurations.

# Ideal Rankine cycle overview

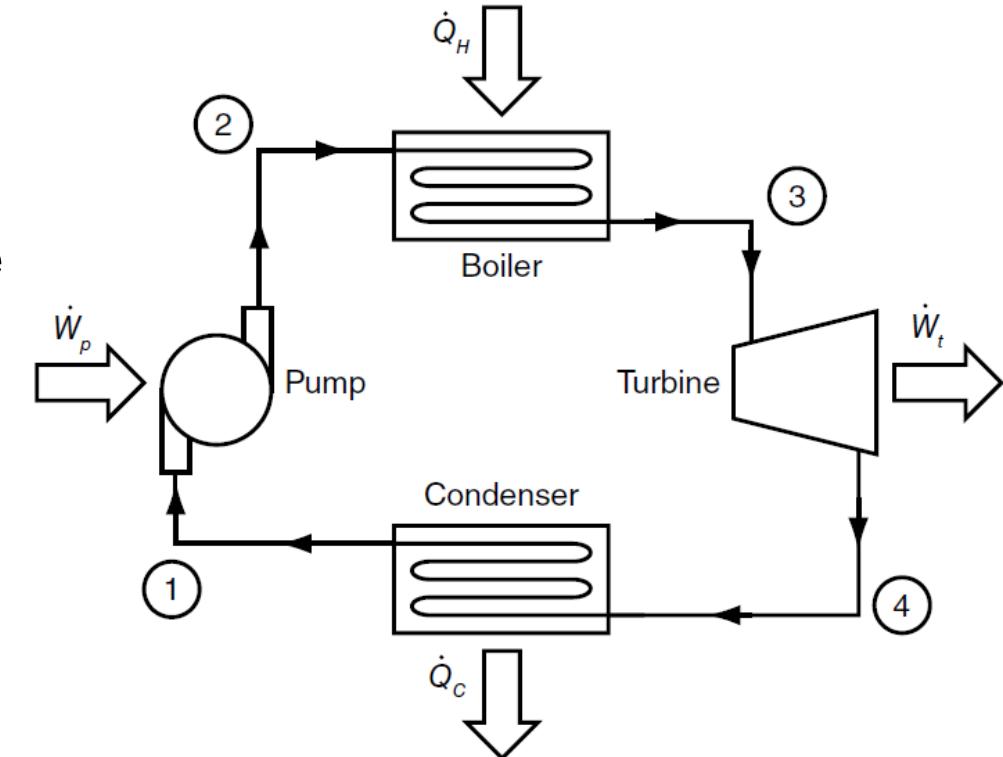
The most basic form is the ideal Rankine cycle, which operates using a two-phase fluid. The cycle consists of the following processes:

1-2 Saturated liquid enters a pump at the lower pressure and is pumped to the high pressure.

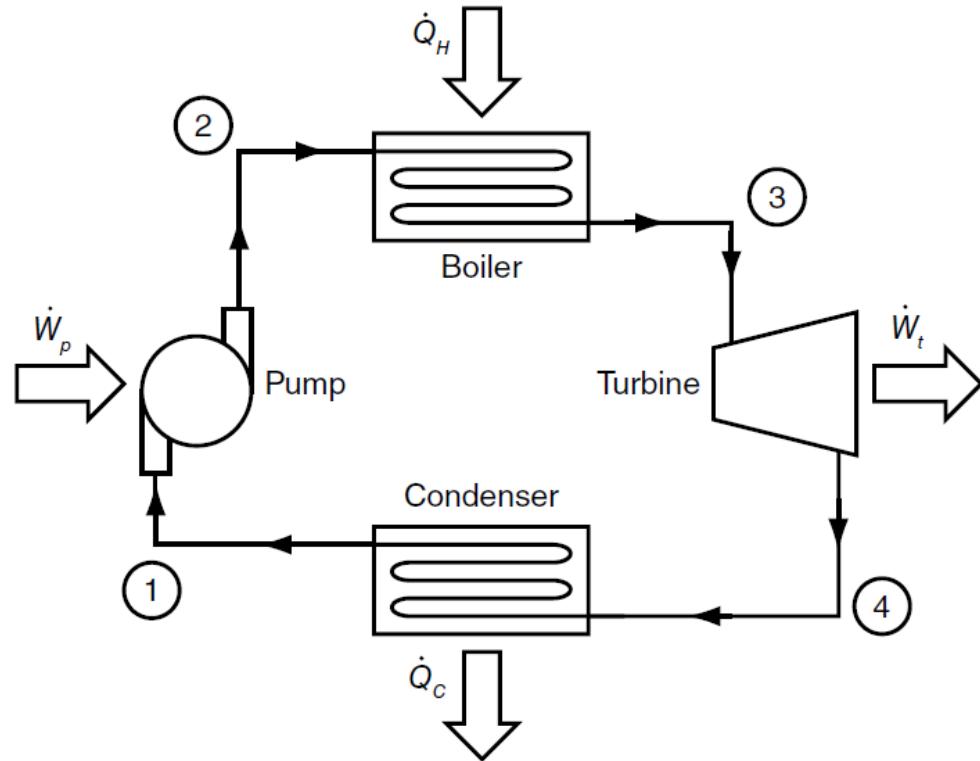
2-3 Heat is added from the hot reservoir until the fluid becomes a saturated vapor.

3-4 The fluid is expanded isentropically to the lower pressure (condenser pressure)

4-1 Heat is rejected to the cold reservoir until it reaches the state of a saturated liquid.



# Ideal Rankine cycle T-s diagram



# Analyzing the Rankine cycle

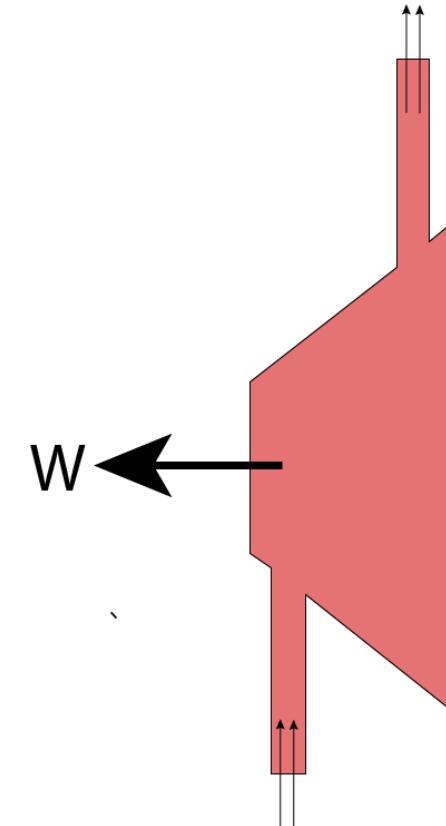
The basic concept is to start from a few known states and move around the cycle component-by-component using techniques that have already been covered.

1. Turbine (Ch 6.13.1)
2. Boiler (Ch 8.3)
3. Pump or compressor (Ch 6.13.3)

# Modelling the turbine

Assuming steady state, no changes in kinetic or potential energy and no heat losses, the work output becomes:

$$\dot{W}_{turb} = \dot{m}(h_i - h_o) \quad \text{Eq. 6.81}$$



# Modelling compressors and pumps

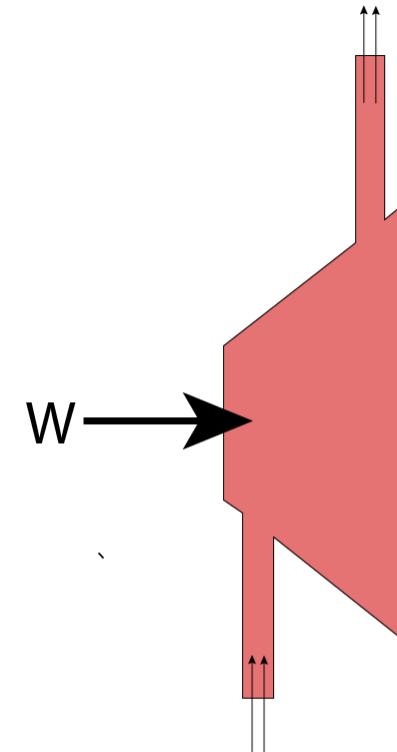
Again, we often Assume steady state, no changes in kinetic or potential energy and no heat losses.  
For a compressor, the work input is:

$$\dot{W}_{comp} = \dot{m}(h_o - h_i) \quad \text{Eq. 6.85}$$

And for a pump with an incompressible fluid the work is:

$$\dot{W}_{pump} = \dot{m}v(P_o - P_i) \quad \text{Eq. 9.2}$$

$$\dot{W}_{pump} = \dot{m}(h_o - h_i)$$



# Modelling the heat exchangers (boiler and condenser)

Assuming steady state, no changes in kinetic or potential energy and no heat losses, the heat transfer in the heat exchangers is:

$$\dot{Q}_{HX} = \dot{m} (h_o - h_i) \quad \text{Eq. 9.5}$$

# Efficiency of the Rankine cycle

The efficiency in thermodynamics is generally defined as the desired output over the required input.

- In the case of the Rankine cycle, the desired output is power and the required input is heat to the hot reservoir.

$$\eta_{Rankine} = \frac{\dot{W}_{Turb} - \dot{W}_{pump}}{\dot{Q}_H} \quad \text{Eq. 9.7}$$

A measure of the work required to power the pump compared to that produced by the turbine is the back work ratio (*bwr*)

$$bwr = \frac{\dot{W}_{pump}}{\dot{W}_{Turb}} \quad \text{Eq. 9.6}$$

# Basic steps to analyzing cycles

1. Read the problem carefully to determine as many known states as possible
2. Draw a schematic of the system and label each state with a number (starting point does not matter)
3. Start from known states and perform analysis on the different components in order to determine the state of the working fluid at the other side of that component.
4. Step all the way around the cycle until all the states are known.
5. Calculate the inputs, outputs and overall efficiency

## Example 9.1

**Problem:** Saturated steam at a pressure of 6 MPa enters the turbine of a Rankine cycle and leaves at a condenser pressure of 30 kPa. What is the back work ratio? Find the thermal efficiency of the cycle and compare it to that of a Carnot cycle operating between the same temperatures.

**Find:** Back work ratio  $bwr$  of the Rankine cycle, thermal efficiency of the Rankine cycle  $\eta_{th, \text{Rankine}}$ , thermal efficiency of a Carnot cycle  $\eta_{th, \text{Carnot}}$  operating between the same temperatures.

**Assume:**

1. All components are adiabatic with no significant changes in KE or PE
2. Expansion in the turbine is isentropic

# Example 9.1 Solution

**Draw the T-s diagram**

Let's start at state 3 because it is fully defined and we can use it to find state 4.

- State 3 is saturated vapor, so we can look up the value of enthalpy and entropy directly from Appendix 8b. The enthalpy entering the turbine is  $h_3 = h_g = 2784.3 \frac{kJ}{kg}$  and the entropy is  $s_3 = s_g = 5.8892 \frac{kJ}{kg K}$

## Example 9.1 Solution continued

The expansion is isentropic so  $s_4 = s_3$ . We also know that state 4 is within the vapor dome, so

$$x_4 = \frac{s_4 - s_{4,f}}{s_{4,g} - s_{4,f}} = \frac{5.8892 \frac{\text{kJ}}{\text{kg K}} - 0.9439 \frac{\text{kJ}}{\text{kg K}}}{7.7686 \frac{\text{kJ}}{\text{kg K}} - 0.9439 \frac{\text{kJ}}{\text{kg K}}} = 0.7246$$

Now that we know the quality and pressure, we can find the enthalpy

$$h_4 = h_{4,f} + x_4 (h_{4,g} - h_{4,f}) = 289.23 \frac{\text{kJ}}{\text{kg}} + 0.7246 \left( 2625.3 \frac{\text{kJ}}{\text{kg}} - 289.23 \frac{\text{kJ}}{\text{kg}} \right) = 1982.0 \frac{\text{kJ}}{\text{kg}}$$

State 1 is fully defined because it is saturated liquid at the condenser pressure

$$h_1 = h_{1,f} = 289.23 \frac{\text{kJ}}{\text{kg}}$$

## Example 9.1 Solution continued II

Then we can find the state after the pump by applying Eq 9.2

$$h_2 = h_1 + v_1(P_2 - P_1) = 289.23 \frac{kJ}{kg} + 0.001022 \frac{m^3}{kg} (6000 \text{ kPa} - 30 \text{ kPa}) = 295.3 \frac{kJ}{kg}$$

Where  $v_1$  is the specific volume entering the pump.

Now all states are defined and we can evaluate the entire cycle. No mass flow rate is given, but it is equal in each component. We will calculate each energy interaction on a mass specific basis. Let's look at the heat input, work output and pump work input separately.

$$\dot{q}_H = h_3 - h_2 = 2784.3 \frac{kJ}{kg} - 295.33 \frac{kJ}{kg} = 2489.0 \frac{kJ}{kg}$$

## Example 9.1 Solution continued III

The work out of the turbine can be calculated as:

$$\dot{w}_{out} = h_3 - h_4 = 2784.3 \frac{kJ}{kg} - 1982.0 \frac{kJ}{kg} = 802.3 \frac{kJ}{kg}$$

And the pump work is

$$\dot{w}_{pump} = h_2 - h_1 = 295.33 \frac{kJ}{kg} - 289.23 \frac{kJ}{kg} = 6.1 \frac{kJ}{kg}$$

The back work ratio is

$$bwr = \frac{\dot{w}_{pump}}{\dot{w}_{out}} = \frac{6.1 \frac{kJ}{kg}}{802.3 \frac{kJ}{kg}} = 0.00761$$

And the system efficiency is

$$\eta = \frac{\dot{w}_{out}}{\dot{q}_{in}} = \frac{802.3 \frac{kJ}{kg} - 6.1 \frac{kJ}{kg}}{2489.0 \frac{kJ}{kg}} = 0.320$$

## Example 9.1 Solution continued IV

For a Carnot cycle operating at the same conditions, we need the temperatures at the hot and cold sides of the cycle. To find those, we look up the saturation temperature as a function of pressure in Appendix 8b.

Using those values, the efficiency would be:

$$\eta_{Carnot} = 1 - \frac{T_c}{T_h} = 1 - \frac{342.25\text{ K}}{548.79\text{ K}} = 0.374$$

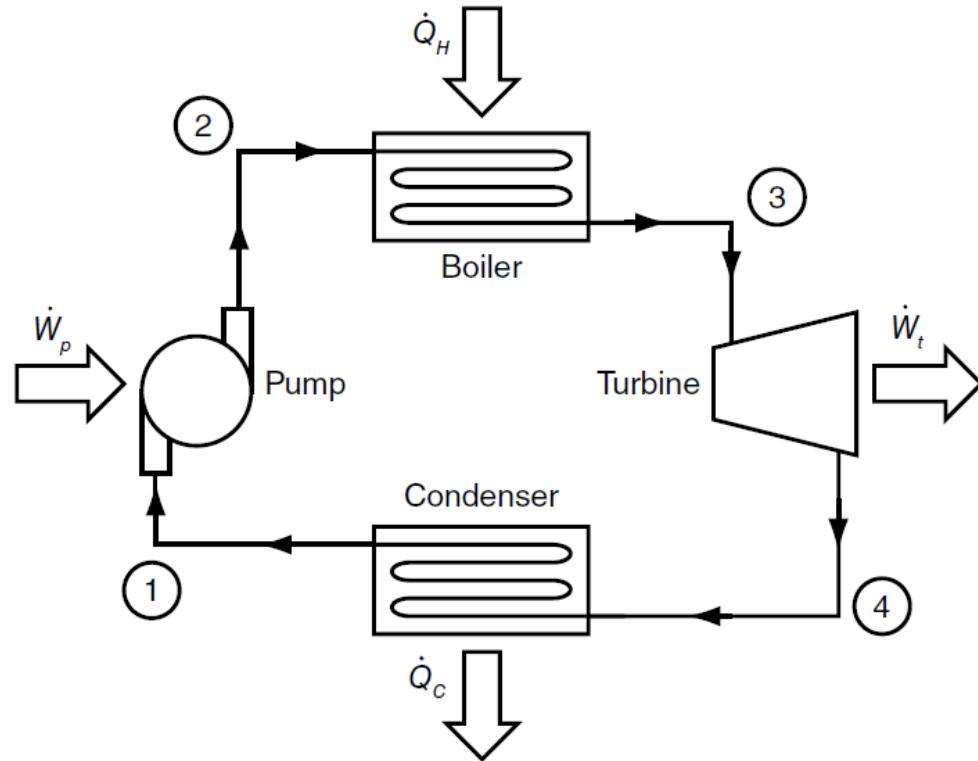
So the efficiency of the ideal Rankine cycle is fairly close to the Carnot cycle

# Rankine cycle with superheat

The ideal Rankine cycle can be modified by superheating the fluid in the boiler, which can increase the efficiency and power output. Isentropic efficiencies of the components may be included to model more realistic conditions. The cycle consists of the following processes:

- 1-2 Saturated liquid enters a pump at the lower pressure and is pumped to the high pressure.
- 2-3 Heat is added from the hot reservoir until it reaches a desired temperature.
- 3-4 The fluid is expanded to the lower pressure (condenser pressure)
- 4-1 Heat is rejected to the cold reservoir until it reaches the state of a saturated liquid.

# Rankine cycle with superheat T-s diagram



# Isentropic efficiency of components

- Entropy can be used to find the most efficient way that many processes can occur. One method that will be used quite often is the concept of isentropic efficiency. For a turbine the form is:

$$\eta_t = \frac{h_i - h_o}{h_i - h_{o,s}} \quad \text{Eq (9.10)}$$

- One interpretation of the 2nd law of thermodynamics is that entropy always increases with any process so entropy is always generated in turbines, compressors, heat exchangers, etc.

## Example 9.2

**Problem:** Superheated steam at a pressure of 6 MPa and temperature of 400 ° C enters the turbine of a Rankine cycle and leaves at a condenser pressure of 30 kPa. Find the thermal efficiency of the cycle if (a) the turbine is isentropic and (b) the turbine isentropic efficiency is 92%.

**Find:** Thermal efficiency of the Rankine cycle for (a) an isentropic turbine  $\eta_{R,s}$  (b) a non-isentropic turbine  $\eta_{R,a}$ .

**Assume:**

1. All components are adiabatic with no significant changes in KE or PE
2. Expansion in the turbine is isentropic for part (a)

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# Lecture 8a: Ideal refrigeration and heat pump cycles (Ch. 8.4-5)

# Clarification on the Rankine cycle

A pump operating with an incompressible fluid (as we assume in our Rankine cycle analysis) does not operate isentropically. So  $s_o \neq s_i$  for a pump.

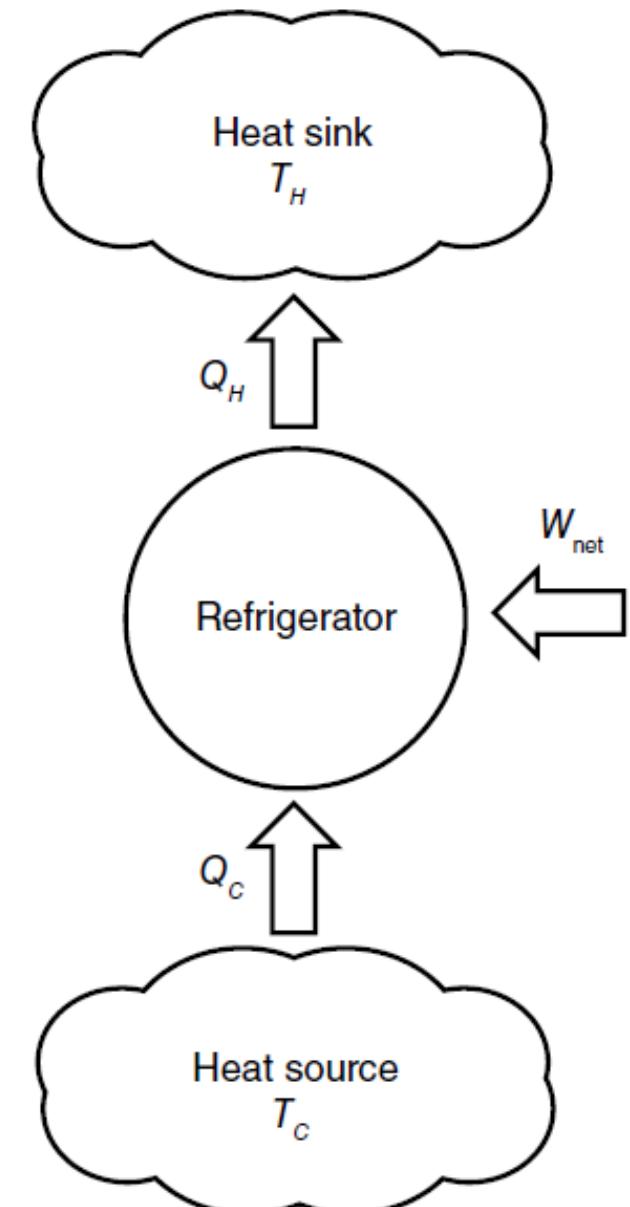
- The enthalpy at the pump outlet will be higher than at the inlet, according to  $h_o = h_i + v(P_o - P_i)$
- Since the pump operates with a subcooled liquid, the increase in enthalpy through the pump will correspond to an increase in temperature, and a corresponding increase in entropy. So the entropy will increase across the pump.

# Refrigerators

We can also run the heat engine "backwards" by adding work rather than generating it. The system then becomes a refrigerator

- The energy balance for the system is exactly the same as for a heat engine, but the signs of all the terms are flipped. We typically rearrange to give the energy balance in terms of cooling power

$$\dot{Q}_C = \dot{Q}_H - \dot{W}_{net}$$



# Efficiency of a cooling cycle

For a cooling cycle, the desired output is heat absorption at the cold end and the input is electricity. The ratio of the two is the coefficient of performance, *COP*

$$COP = \frac{\text{heat absorbed at the cold end}}{\text{work input}} = \frac{Q_C}{W_{net}}$$

- We can also define the *COP* on a rate basis

$$COP = \frac{\dot{Q}_C}{\dot{W}_{net}}$$

# A note on mass balance in power and refrigeration cycles

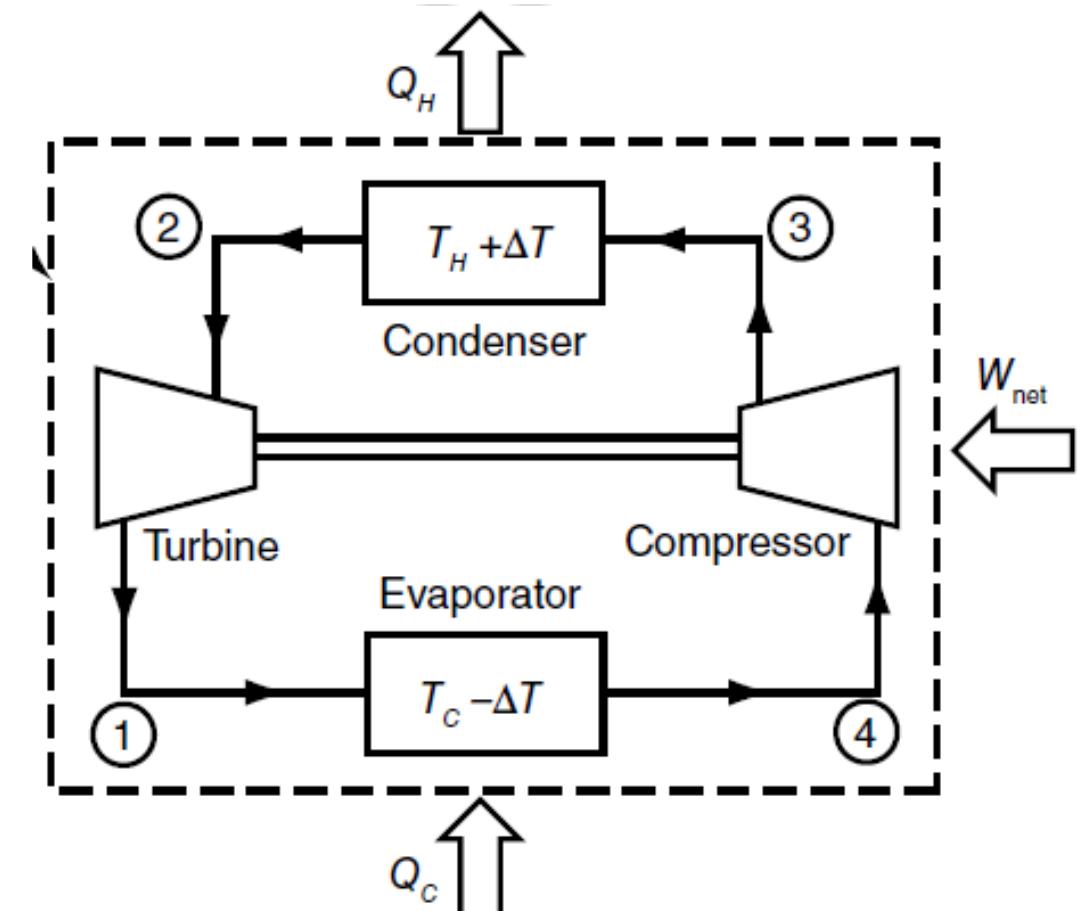
For the cycles that we will study in this course, each component has a single inlet and outlet and operates at steady state. Therefore, the mass balance is straightforward, with the same mass flow rate in and out of each component.

# Carnot refrigeration cycle

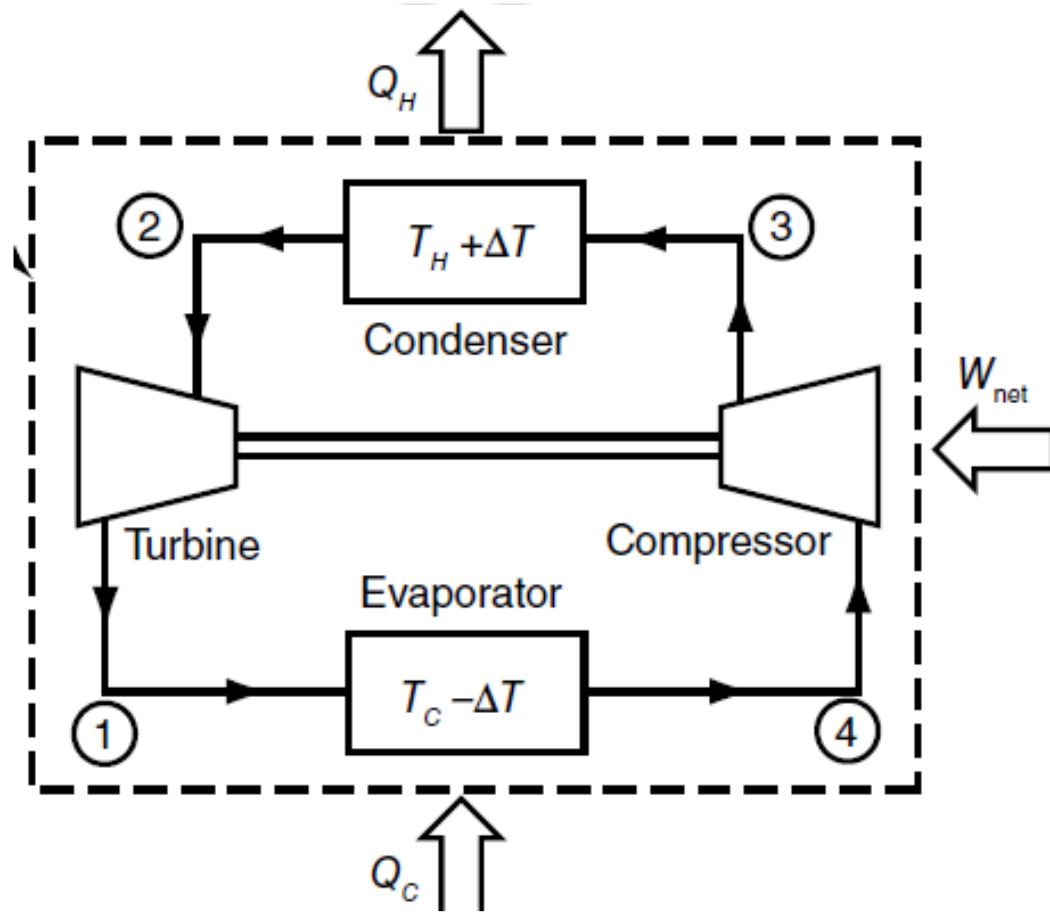
The two-phase Carnot cycle can operate in cooling mode where electricity is input to the system and the goal is to cool a load at the evaporator.

The cycle consists of:

1. Isentropic compression of a two phase fluid
2. Isothermal heat transfer to a hot reservoir
3. Expansion of the two-phase fluid to extract work
4. Isothermal heat transfer from the cold reservoir



# Carnot refrigeration cycle T-s diagram



# Efficiency of the Carnot refrigeration cycle

The Carnot cycle represents the most efficient cooling cycle between two thermal reservoirs. The efficiency is defined as the amount of heat accepted from the cold reservoir over the work input. This efficiency can be greater than 1 and is called the coefficient of performance (COP)

$$COP_{Carnot} = \frac{Q_C}{W_{comp} - W_{ex}} = \frac{T_C}{T_H - T_C} \text{ or } \frac{1}{\frac{T_H}{T_C} - 1}$$

## Example 8.5

- **Problem:** A Carnot refrigerator using 0.005 kg / s of refrigerant 134a has a condenser pressure of 700 kPa and requires 500 W to operate. What is the rate at which it cools the low temperature region?.
- **Assumptions:**
  1. Carnot cycle (isentropic expansion and compression)
  2. Steady state

## Example 8.5 solution

- We know the properties at states 2 and 3 because they are defined by the Carnot cycle. State 2 is a saturated liquid and state 3 is a saturated vapor and both are at the condenser pressure (high pressure). So, using values from Appendix 9b, the heat rejected at the condenser can be calculated as

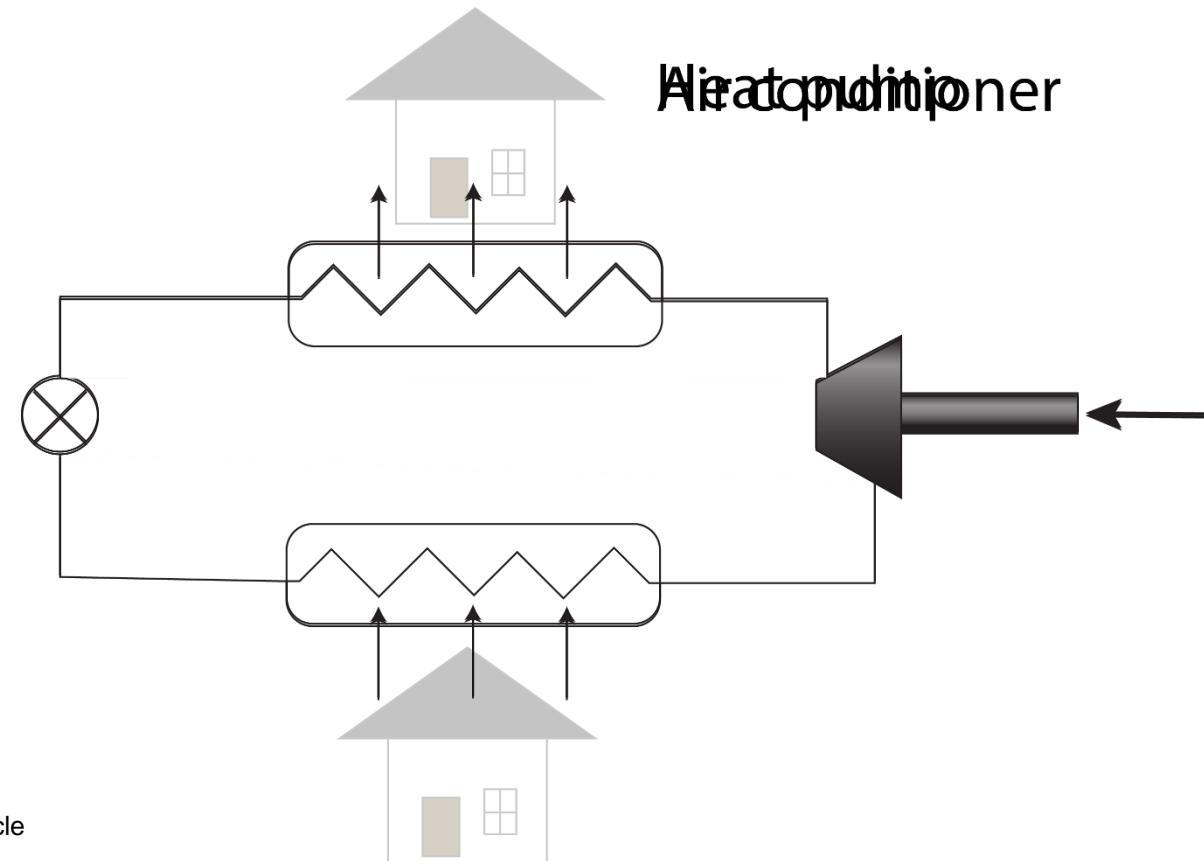
$$\dot{Q}_H = \dot{m}(h_2 - h_3) = 0.005 \frac{kg}{s} \left( 261.85 \frac{kJ}{kg} - 86.78 \frac{kJ}{kg} \right) = 0.875 \text{ kW}$$

- Then the heat absorbed at the cold end can be calculated from the energy balance of the cycle

$$\dot{Q}_C = \dot{Q}_H - \dot{W}_{net} = 0.875 \text{ kW} - 0.5 \text{ kW} = 0.375 \text{ kW}$$

# Heat pumps

- A heat pump is a type of refrigeration cycle. The difference between a refrigeration cycle and a heat pump is that the goal of a heat pump is to provide heat from the condenser.



# Why a heat pump

Electric heaters are cheap, compact and can approach 100% efficiency. Why would anyone build a heat pump?

Electric heaters can achieve near 100% efficiency, but the heat we get from an electric heater would be the same power that we provide to the compressor in a heat pump.

Going the energy balance of a refrigeration cycle, the heat that we would get from a heat pump is the work to the compressor plus the heat absorbed in the evaporator

$$\dot{Q}_H = \dot{Q}_C + \dot{W}_{comp}$$

# Heat pump COP

For a refrigeration cycle, the COP is

$$COP_{cool} = \frac{\dot{Q}_c}{\dot{W}_{comp}}$$

For a heat pump, the COP is based on the heat it provides

$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{comp}}$$

Substituting the fact that  $\dot{Q}_H = \dot{Q}_c + \dot{W}_{comp}$

$$COP_{HP} = \frac{\dot{Q}_c + \dot{W}_{comp}}{\dot{W}_{comp}} = COP_{COOL} + 1$$

# Heat pump Carnot cycle COP

The maximum COP of a heat pump operating between two temperature reservoirs is

$$COP_{HP,Carnot} = \frac{T_H}{T_H - T_C}$$

# Heat pump analysis

- Analyzing a heat pump is the same as a cooling cycle. The COP definition is different but calculating all the states is the same.
- Although the cycle is the same, the operating conditions and output levels can be quite different. That means that different refrigerants and operating pressures are often used.
  - Operating temperatures will depend on local climate and the application.

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# Lecture 8b: Vapor refrigeration cycles (Ch. 9.4)

# Carnot limitations

As with the Carnot power cycle, there are practical limitations of the Carnot cycle. The main practical limitations of the Carnot cooling cycle are:

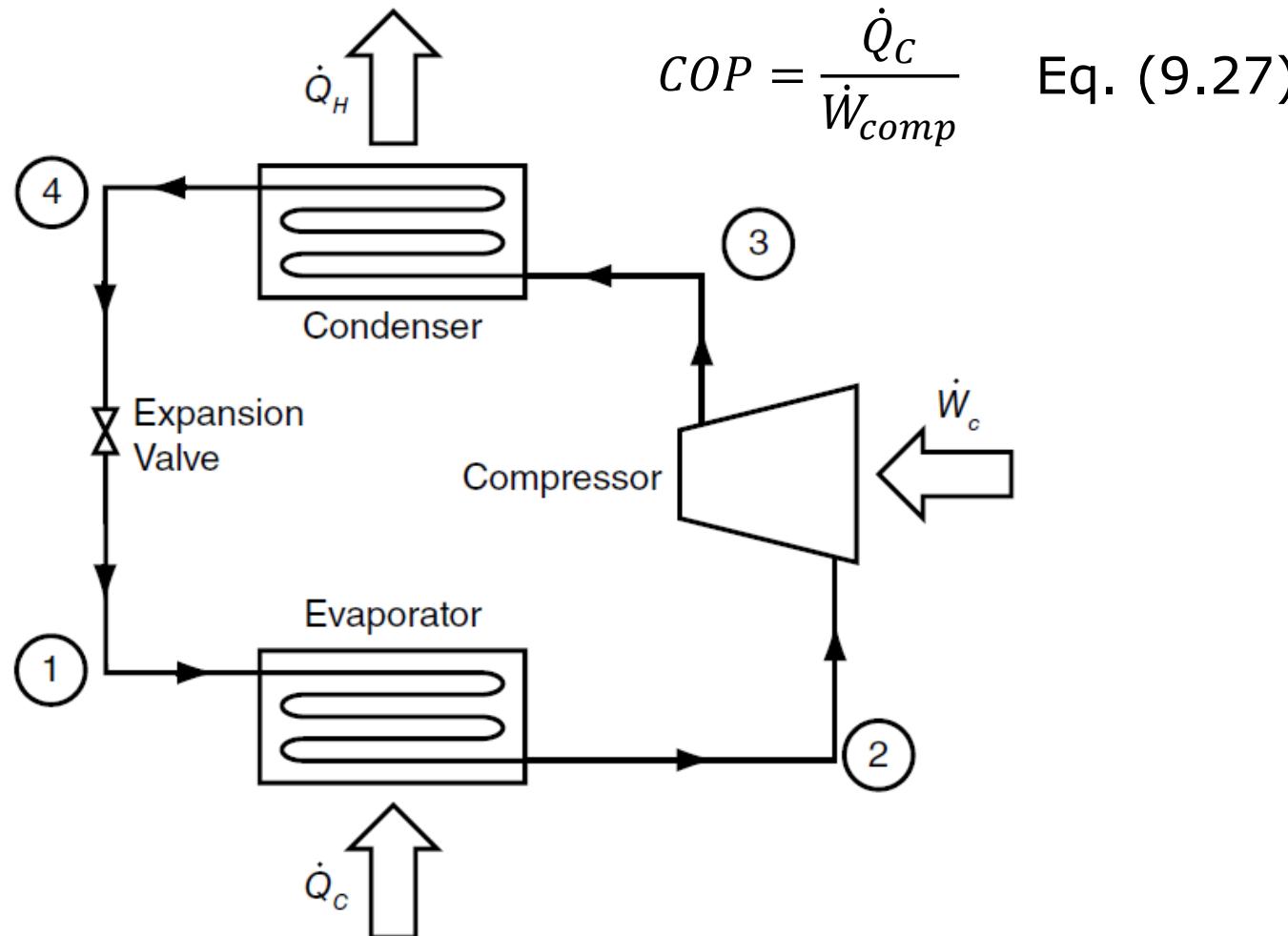
1. The compressor failure rate goes up dramatically when it has to compress a mixture of gas and liquid droplets.
2. The expander is expensive and does not produce very much work

# The (ideal) vapor compression (reverse Rankine) cycle

Similar to the Rankine cycle, the vapor compression cycle modifies the Carnot cycle to make components more practical. The cycle consists of

1. Two phase fluid enters the evaporator and absorbs heat until it reaches a saturated vapor.
2. The vapor is then compressed isentropically to the high pressure (condenser pressure) where it is a superheated vapor
3. Heat is rejected from the high pressure fluid in the condenser until it reaches a saturated liquid.
4. The liquid goes through an expansion valve where no work is extracted. This is modelled as a constant enthalpy process.

# The vapor compression (reverse Rankine) cycle



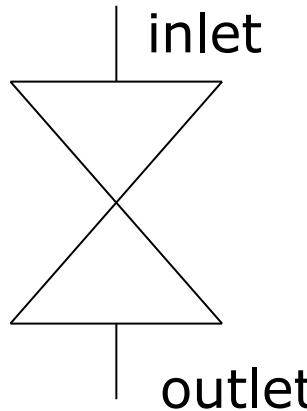
$$COP = \frac{\dot{Q}_c}{\dot{W}_{comp}} \quad \text{Eq. (9.27)}$$

# Analyzing the vapor compression cycle

The approach is similar to analyzing power cycles. Start from a known state and analyze individual components to determine subsequent states. A suggested approach is:

1. Typically, the inlet to the compressor or the inlet to the expansion valve is known.
  - Inlet to the compressor is saturated vapor at the evaporator pressure, inlet to the expansion valve is saturated liquid at the condenser pressure.
2. Model compression as isentropic unless a compressor efficiency is given.
3. Expansion across the valve is isenthalpic (see next slide).
4. Main outputs are cooling at the evaporator and work input to the compressor

# Expansion valve



The expansion valve is generally modelled as isenthalpic

$$h_i = h_o$$

**Example:** Calculate the difference in quality of fluid exiting the isenthalpic valve compared to an isentropic expansion. The valve operates between pressures of 800 kPa and 200 kPa using R134a as a refrigerant. Saturated liquid enters the valve at 800 kPa.

**Solution:** Quality exiting the isenthalpic valve is 0.277 while it is 0.255 from the isentropic valve. The increased quality from the isenthalpic valve reduces the possible cooling of the cycle.

## Example 9.5

**Problem:** A freezer working on a reverse Rankine cycle uses refrigerant 134a with a mass flow rate of 0.10 kg / s. The refrigerant leaves the evaporator as saturated vapour at a temperature of  $-8^{\circ}\text{C}$ . It leaves the condenser as saturated liquid at a pressure of 0.8 MPa.

**Find:** Power required to drive the compressor, coefficient of performance of refrigeration  $\text{COP}$  of the Rankine cycle, the coefficient of performance of refrigeration  $\text{COP}$  of a Carnot cycle operating between the same temperatures.

**Note:** the book calculates the COP of the vapor compression cycle incorrectly.  $h_2$  and  $h_3$  get mixed up.

### Assumptions:

1. Steady state
2. Isentropic compression
3. Isenthalpic expansion

# Example 9.5 solution strategy

Draw the T-s diagram

- Start from state 2 where the properties are fully defined (saturated vapor at the lower pressure)
- Find state 3 using the fact that compression is isentropic ( $s_3 = s_2$ )
- State 4 is fully defined (saturated liquid at the high pressure)
- Find state 1 by know that expansion through the valve is isenthalpic ( $h_1 = h_4$ )
- Calculate cooling power and work input once all states are known.
- We can use values in Appendix 9 or EES

## Example 9.5 finding the compressor outlet

We can look up the state of the compressor inlet (state 2) from Appendix 9a:  $h_2 = 242.54 \frac{kJ}{kg}$  and  $s_2 = 0.9239 \frac{kJ}{kg K}$

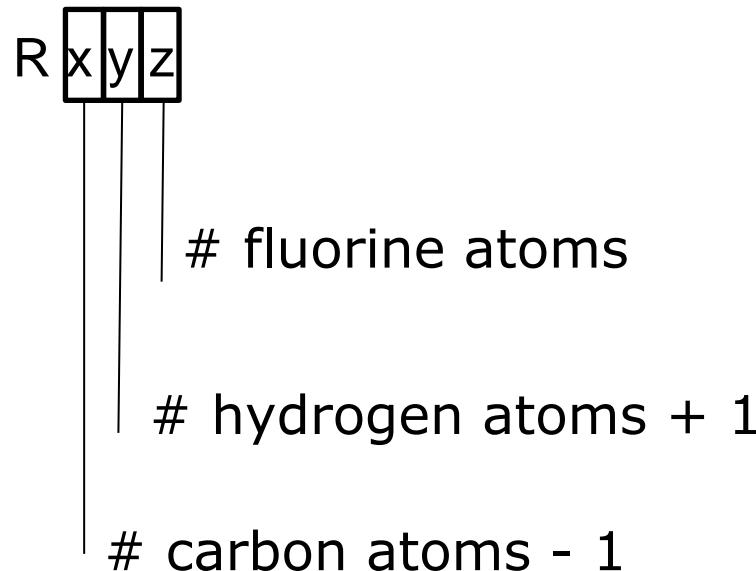
- We calculate state 3 by knowing that  $s_3 = s_2 = 0.9239 \frac{kJ}{kg K}$ . However, state 3 is a superheated vapor so we need to use Appendix 9c.
- We can interpolate the enthalpy directly using the entropy. So from Appendix 9c, at 0.8 MPa and T=31.33 C,  $s = 0.9066 \frac{kJ}{kg K}$ ,  $h = 264.15 \frac{kJ}{kg}$  and at 0.8 MPa and T = 40 C,  $s = 0.9374 \frac{kJ}{kg K}$ ,  $h = 273.66 \frac{kJ}{kg}$
- We then interpolate to find that  $h_3 = 269.49 \frac{kJ}{kg}$

# Refrigerants

In contrast to power production equipment, refrigerants used in cooling cycles are constantly changing for practical and regulatory reasons

- Many refrigerants have ozone depleting potential or a high global warming potential when they leak out of the system.
  - Ozone depleting refrigerants (primarily CFCs) have been phased out. This is the Montreal protocol.
  - Refrigerants with high global warming potential are being phased out (HFCs). This is the Paris Agreement.
- Refrigerents also have a number of practical requirements, such as having a positive gage pressure in the evaporator, critical temperature, chemical compatibility etc.
- There are a large number of available refrigerants and many are available in EES

# Refrigerant naming



All remaining atoms are chlorine

For example R12 (Freon) has one carbon atom, no hydrogen atoms, 2 fluorine and then two chlorine atoms (technically R012). R12 is a chlorofluorocarbon, CFC

Designations such as "a" refer to different molecular structures of the same elements

# Some videos about refrigeration cycles/systems

<https://www.youtube.com/watch?v=L5jQqmaFKOE>

<https://www.youtube.com/watch?v=1Hva1PLCYUA>

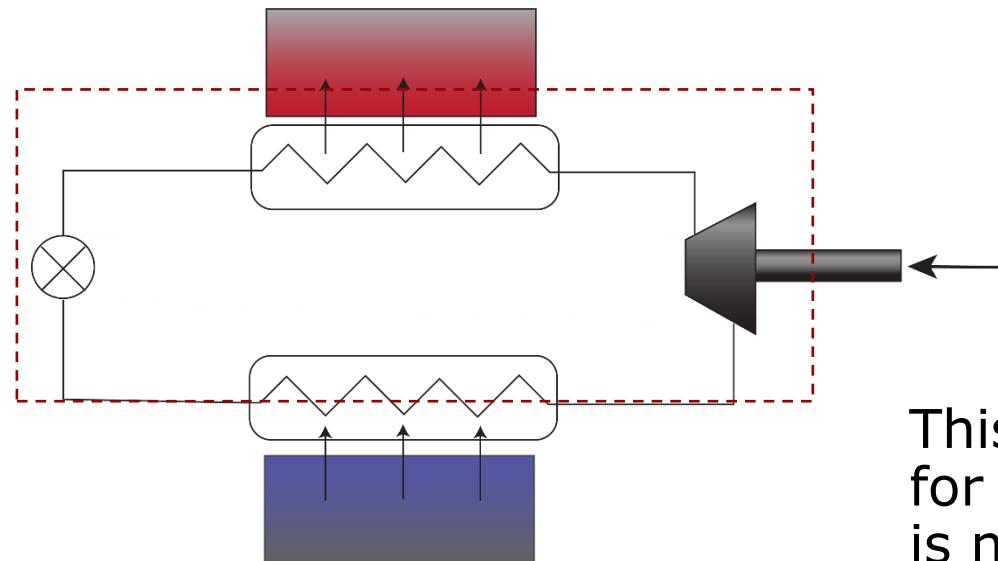
# Analyzing vapor compression with isentropic efficiencies

- Just as we analyzed turbines with isentropic efficiencies, the compressor in a vapor compression cycle can also have an isentropic efficiency

$$\eta_{comp} = \frac{h_{o,s} - h_i}{h_o - h_i} \quad \text{Eq. (6.86)}$$

# 1st law analysis of vapor compression cycles

System has two inputs (heat at the cold end and work into the compressor) and one output (heat rejected from the cold end)



$$\dot{Q}_C + \dot{W}_{comp} = \dot{Q}_H$$

$$\dot{W}_{comp} = \dot{Q}_H - \dot{Q}_C$$

This energy balance is the same for power cycles, but the power is negative

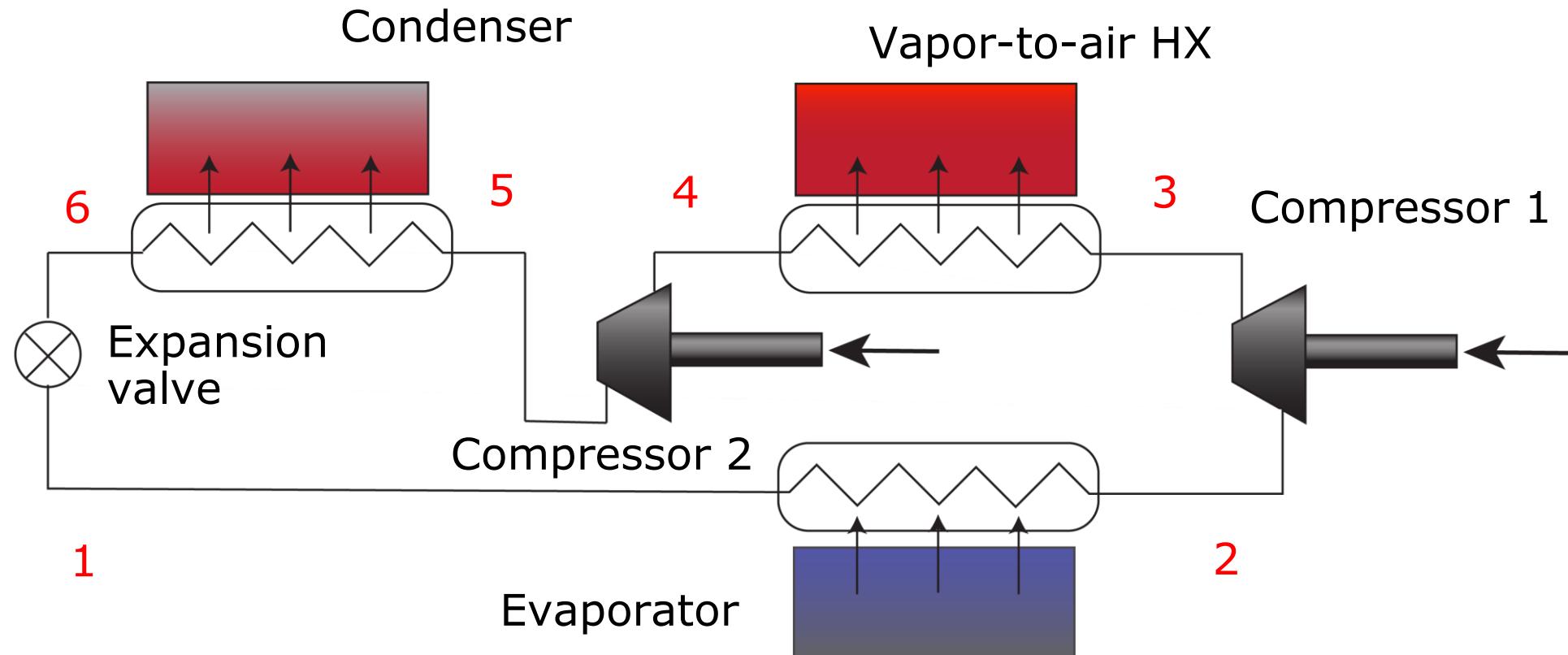
# Advanced vapor compression configurations

Just as the Rankine cycle has been modified to improve efficiency, reliability and power density, the vapor compression cycle also has several modifications. We will look at:

- The intercooled cycle. This concept is analogous to the superheat and reheat concept
- Cascaded cycle. Using cascaded vapor compression cycles can increase the overall temperature span

# Intercooled cycle

- The intercooled cycle uses a two-stage compression to reduce superheat



# Intercooled cycle efficiency

- The only modification to the COP is that the work from both compressors must be included.

For an intercooled cycle

$$COP = \frac{\dot{Q}_c}{\dot{W}_{comp1} + \dot{W}_{comp2}}$$

# Intercooled cycle example

**Start from example 9.5:** A freezer working on a reverse Rankine cycle uses refrigerant 134a with a mass flow rate of 0.10 kg / s. The refrigerant leaves the evaporator as saturated vapour at a temperature of  $-8^{\circ}\text{C}$ . It leaves the condenser as saturated liquid at a pressure of 0.8 MPa.

**Add:** a second stage compressor with an inlet pressure of 0.45 MPa (the condenser pressure remains at 0.8 MPa). The intercooler cools the vapor back to saturated vapor before it enters the high pressure compressor.

**Find:** Power required to drive the two compressors and coefficient of performance of refrigeration COP of the Rankine cycle.

From example 9.5, the COP is 5.548

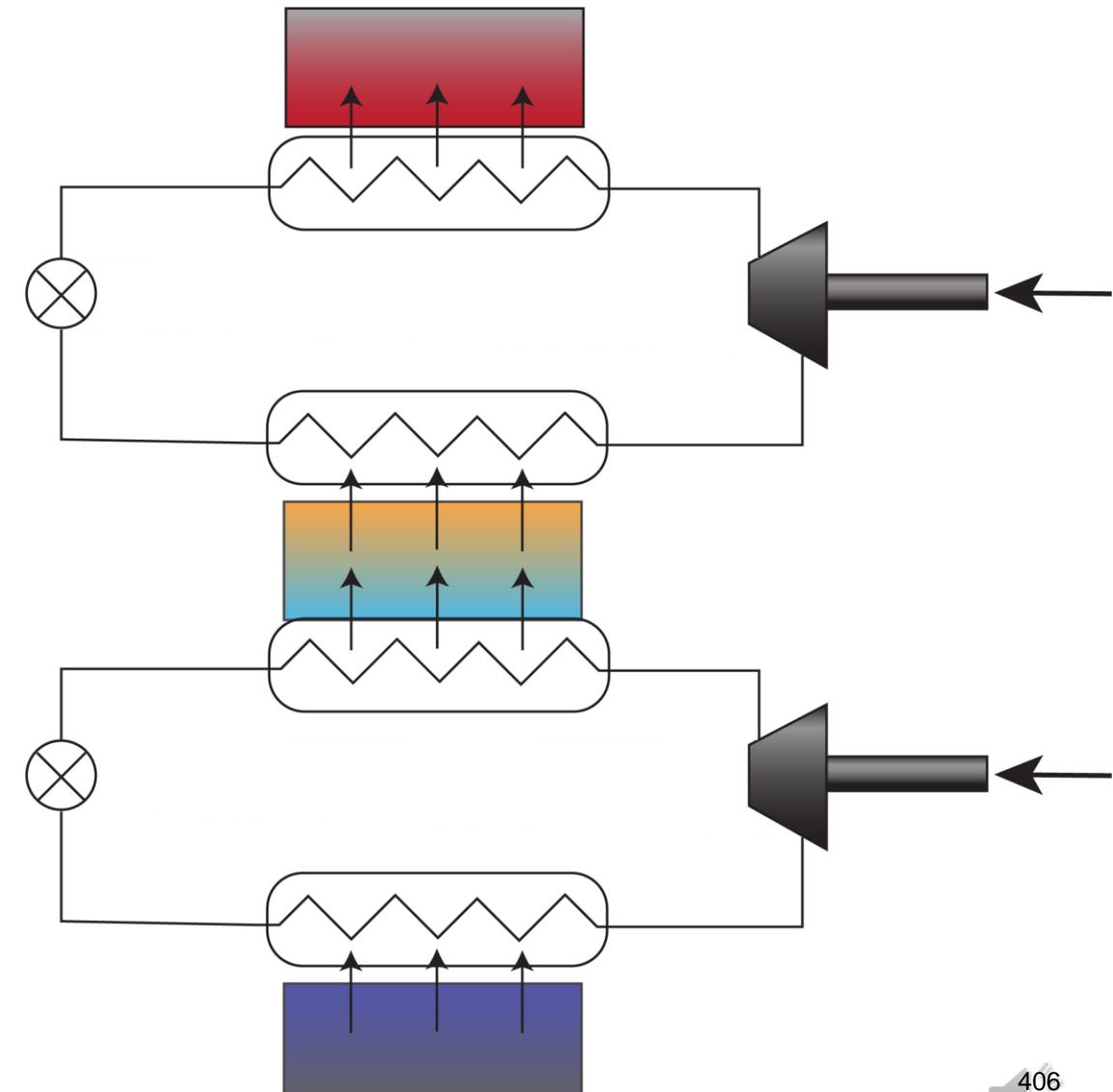
# Example 9.5 intercooled solution strategy

Draw the T-s diagram

- Start from state 2 where the properties are fully defined (saturated vapor at the lower pressure)
- Find state 3 using the fact that compression is isentropic ( $s_3 = s_2$ )
- State 4 is saturated vapor at the intermediate pressure
- Find state 5 and 6 the same way as 3 and 4.
- Find state 1 by know that expansion through the valve is isenthalpic ( $h_1 = h_4$ )
- Calculate cooling power and work input once all states are known.

# Cascaded cycle

- The cascaded cycle consists of two independent vapor compression systems coupled at the evaporator of the high temperature cycle to the condenser of the low temperature cycle.
- The two cycles are completely independent, meaning they can operate at different pressures, using different refrigerants and can have different configurations.
- The one constraint is that the heat rejected from the low temperature cycle must match the cooling power of the high temperature cycle.



# Cascaded cycle analysis

- We can call the cooling power absorbed by the low temperature cycle  $\dot{Q}_{c,Lo}$ , the compressor work for the low temperature cycle is  $\dot{W}_{comp,Lo}$  and the compressor work for the high temperature cycle is  $\dot{W}_{comp,Hi}$
- The desired output is the cooling at the low temperature reservoir so the cycle COP is:

$$COP = \frac{\dot{Q}_{c,Lo}}{\dot{W}_{comp,Lo} + \dot{W}_{comp,Hi}}$$

- With the constraint that

$$\dot{Q}_{H,Lo} = \dot{Q}_{c,Hi}$$

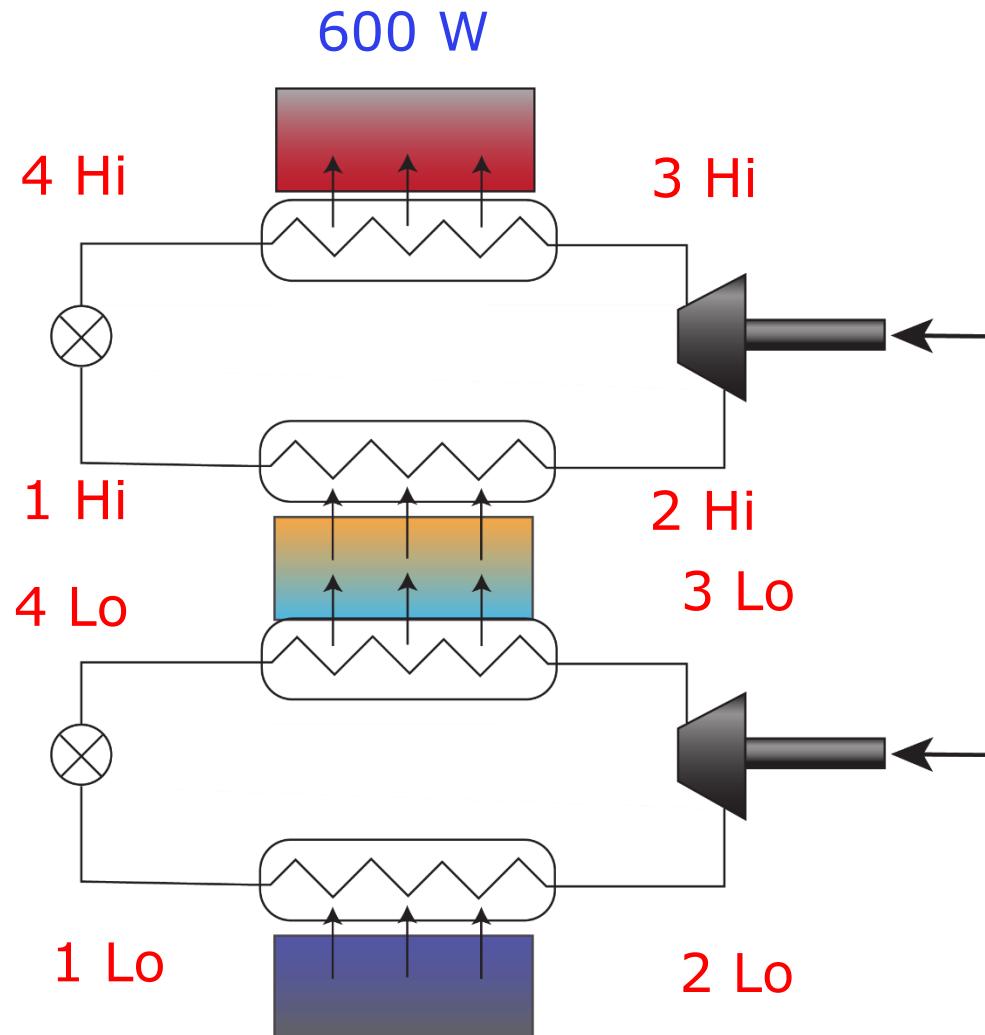
# Example: heat pump for domestic hot water

**Given:** domestic hot water must be heated to 60 C in an area where temperatures can be expected to go as low as -20 C. A two stage cascaded heat pump is used, where the cold cycle evaporator operates at -20 C and the hot side condenser operates at 60 C. Both cycles use R134a as the working fluid. The hot side of the cold cycle and the cold side of the hot cycle both operate at 20 C. The heating power to the water is 600 W.

**Find:** (a) the refrigerant flow rate in each cycle and (b) the COP of the hot water heater.

# Example: heat pump for domestic hot water

1. Define the states
2. Start from the high temp cycle (because heating power there is defined)
3. Work all the way around the cycle to define all states
4. Find total work input and efficiency



47201 Engineering thermodynamics

# Lecture 9a: Otto cycle (Ch. 10.1-2)

# Internal combustion engines

Internal combustion engines are most relevant for transportation, where low weight and compact design are major constraints. Some design aspects that minimize size are:

1. Instead of having a closed circuit with a working fluid, air from the atmosphere is brought into the combustion chamber and exhausted back out to the atmosphere
2. There is no separate combustor or boiler. Instead fuel is burned (generating heat) in the same components used for power production
3. Much of the heat is rejected when the exhaust is vented to atmosphere, which reduces heat exchanger sizes

# Otto cycle

The Otto cycle is a four cycle internal combustion engine that is by far the most common cycle used for gasoline engines

- Named after Nicolaus August Otto (Germany 1832-1891)
- Spark ignition engine, which means that a spark plug is used to ignite the mixture of fuel and air in the cylinder
- Output is mechanical work delivered by the crankshaft

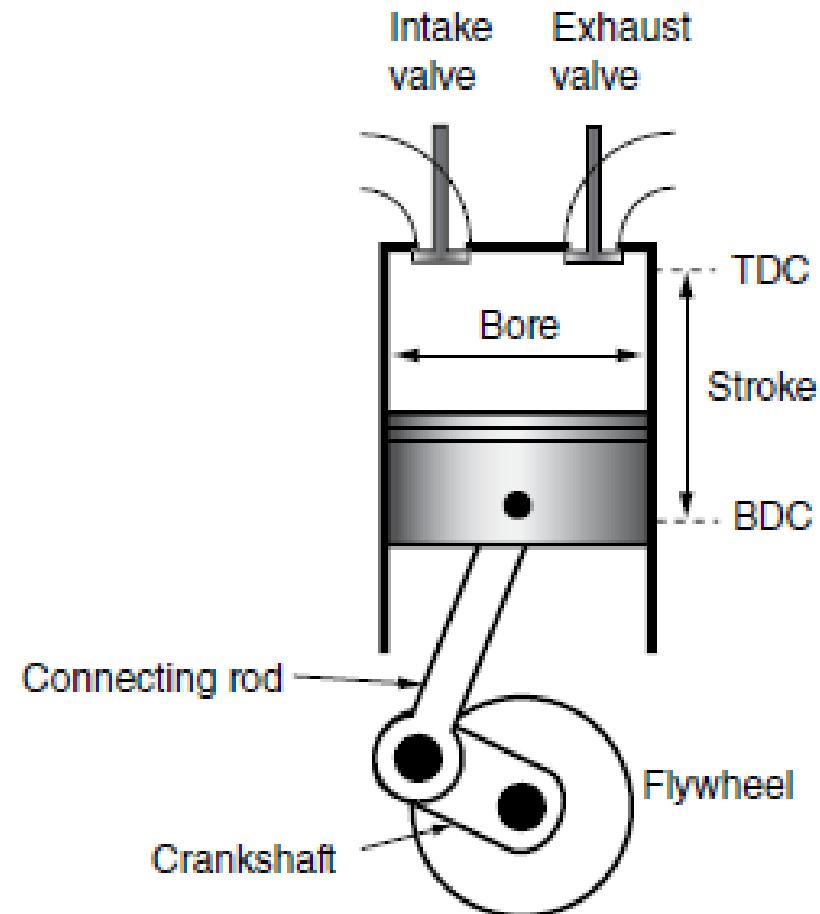
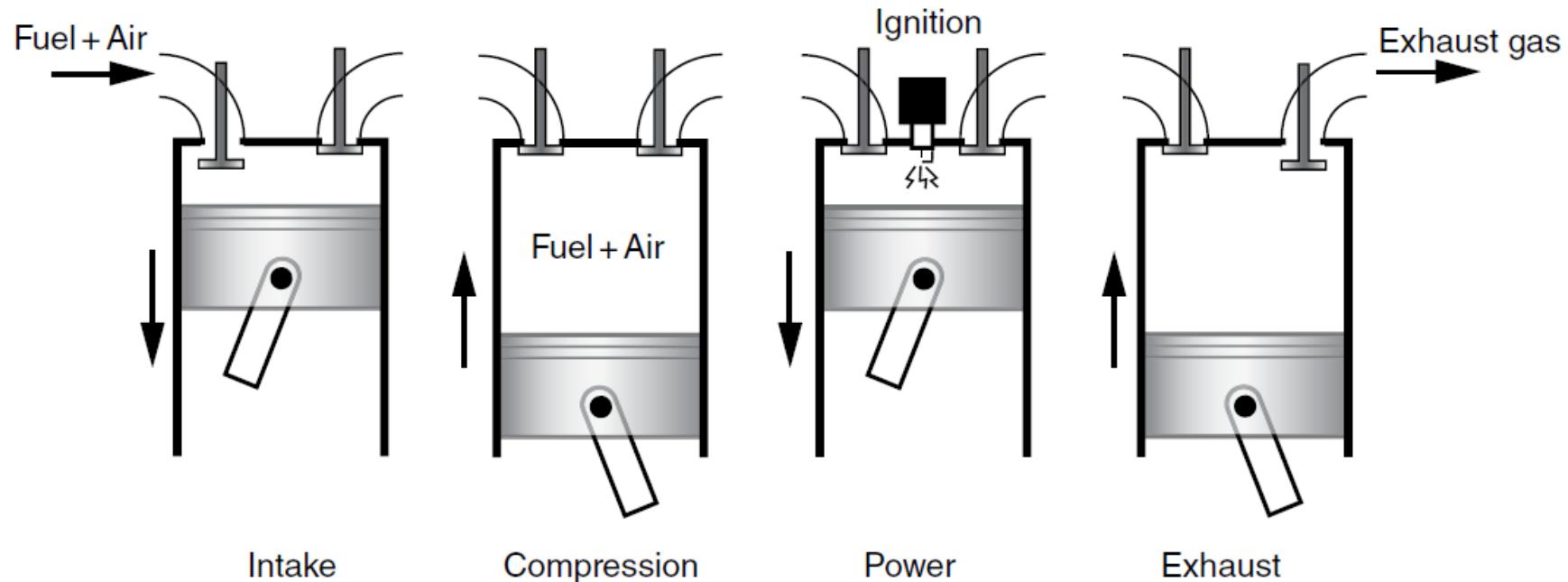


Figure 10.1 Reciprocating engine nomenclature.

# Otto cycle steps



**Figure 10.2** Four-stroke cycle for a spark-ignition engine.

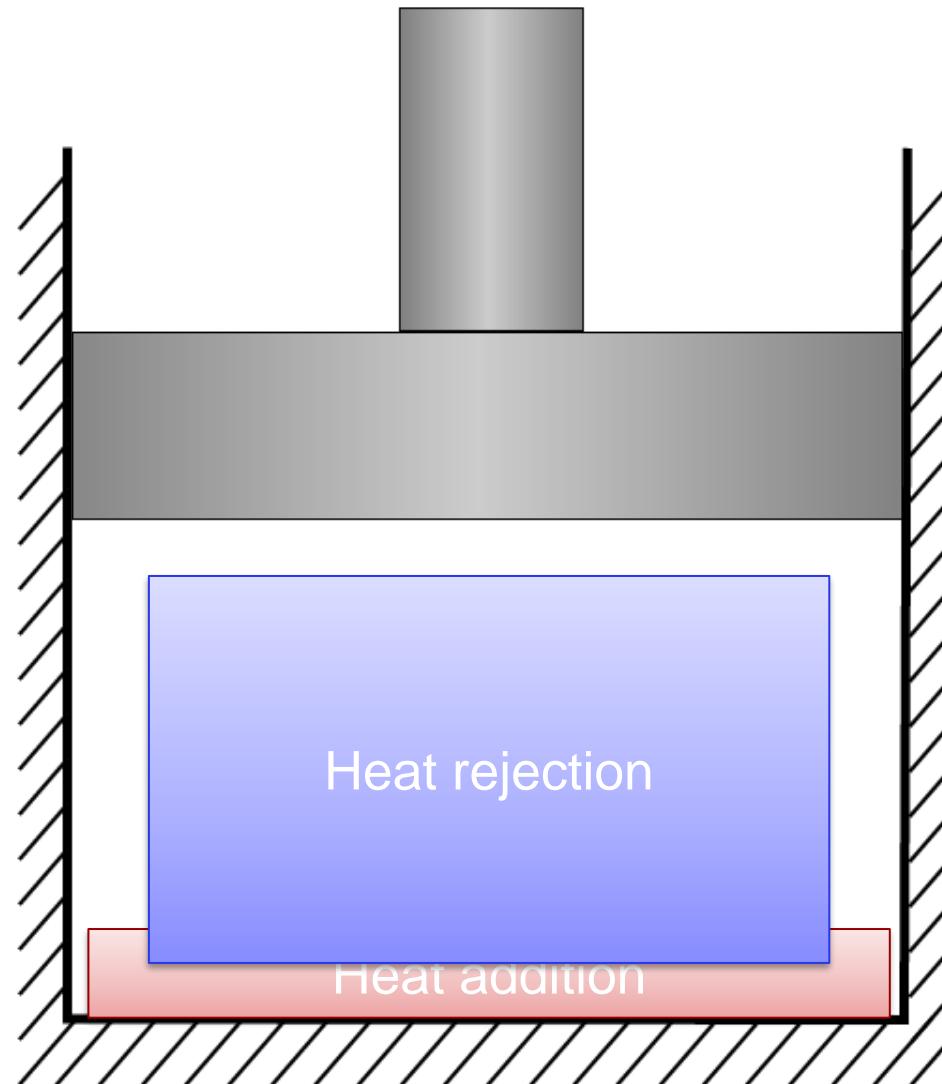
# Thermodynamic model of the Otto cycle

We will use the air standard model to look at Otto cycle engines. The simplifying assumptions are:

1. The working fluid is air, which behaves as an ideal gas
  2. All processes are reversible
  3. Fuel addition is approximated as a heat addition from an external source
  4. Exhausting combustion products and taking in fresh air is equivalent to heat loss to the surroundings
- 
- Also assume that the work associated with intake and exhaust of the air/fuel mixture is negligible.

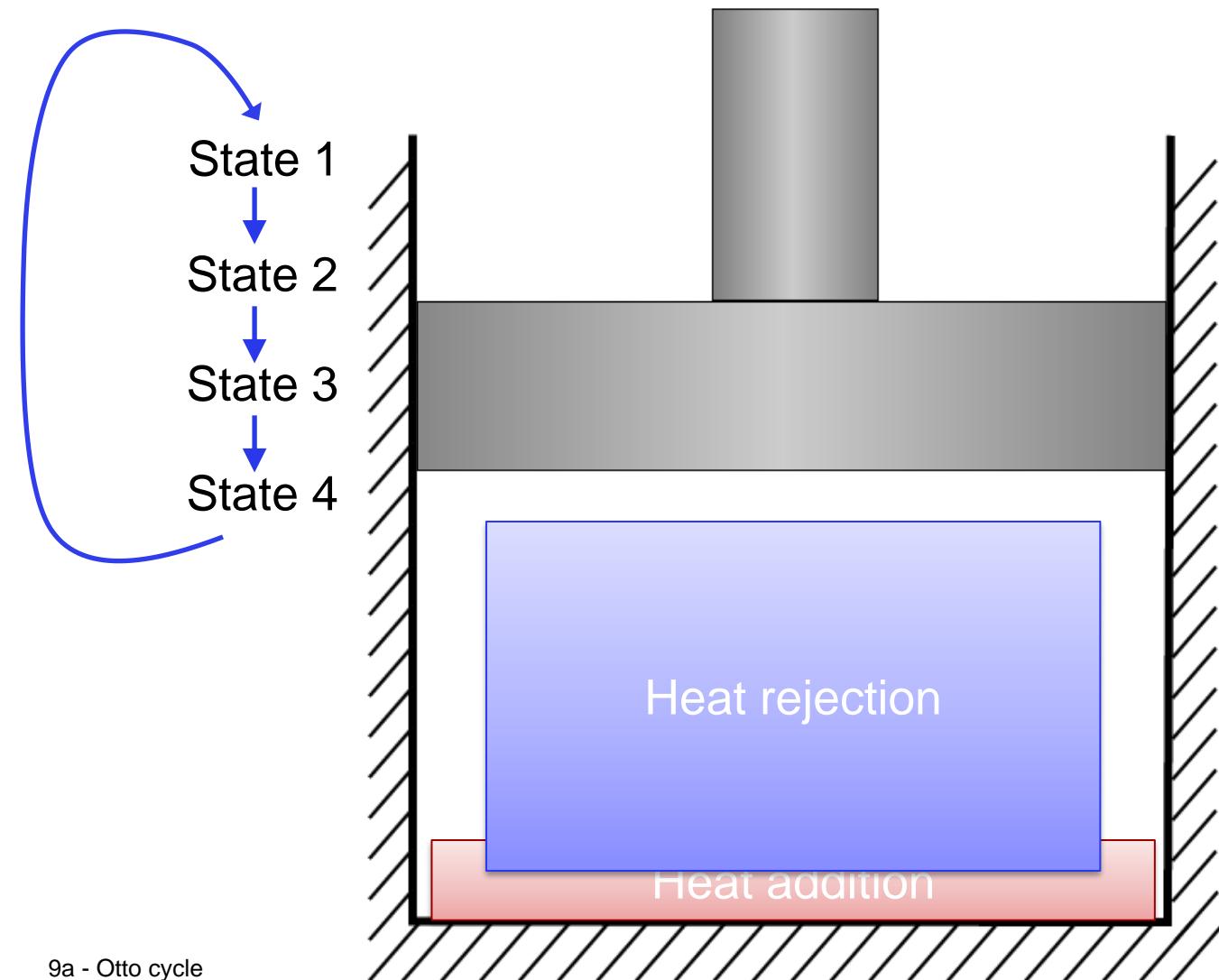
# The air cycle Otto analysis

State 1  
↓  
State 2  
↓  
State 3  
↓  
State 4

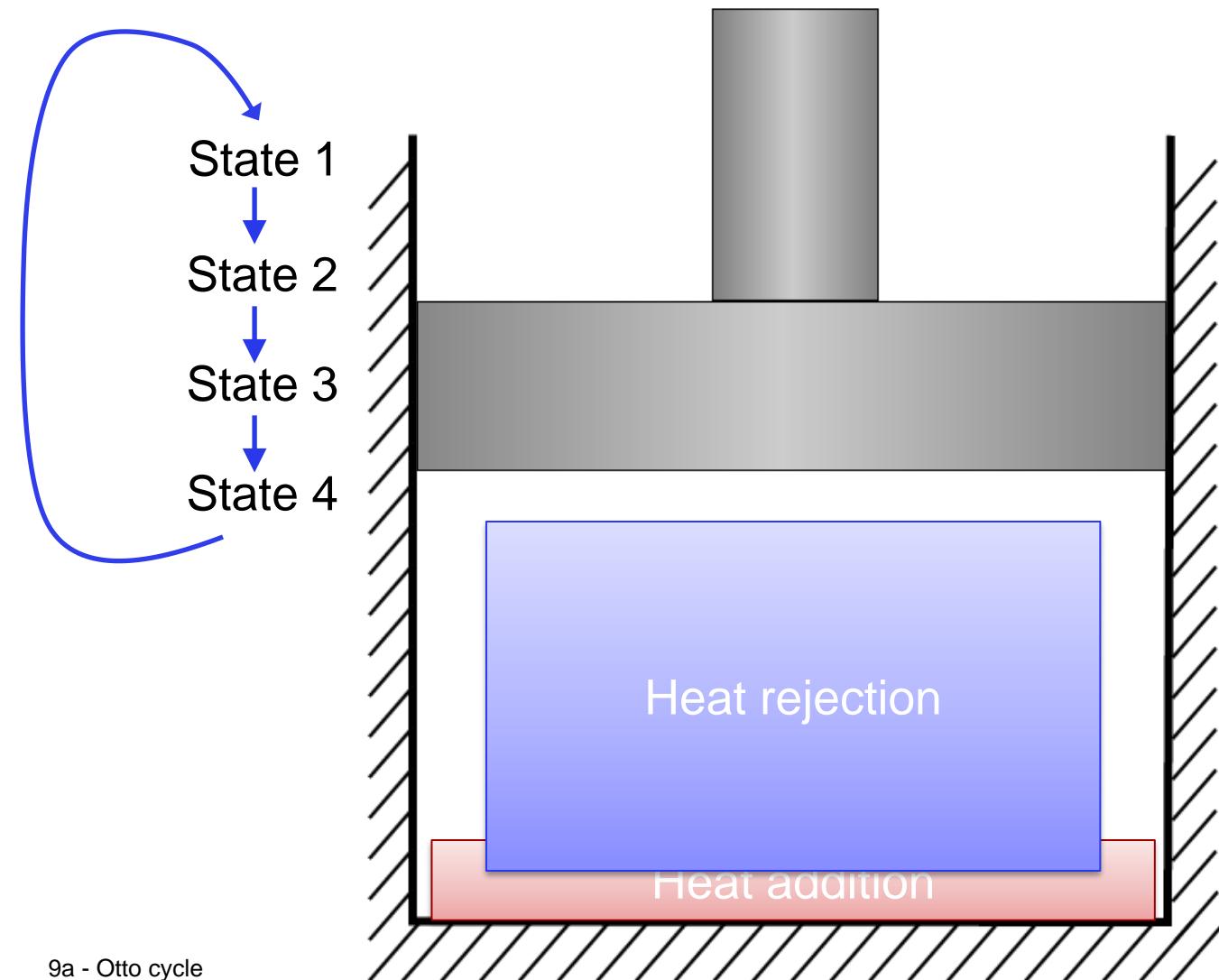


Isentropic compression  
Constant volume heat addition  
Isentropic expansion  
Constant volume heat rejection

# The air cycle Otto analysis p-v diagram



# The air cycle Otto analysis T-s diagram



# Compression ratio

- The compression ratio is a widely used term to describe an ICE, and it is defined as:

$$r = \frac{V_{max}}{V_{min}}$$
Eq. (10.1)

# Cycle efficiency

- The efficiency is calculated based on the net work output over the thermal energy provided:

$$\eta_{th,Otto} = \frac{W_{ex} - W_{comp}}{Q_H} \quad \text{Eq. (10.4)}$$

# Cycle efficiency

- The efficiency is calculated based on the net work output over the thermal energy provided:

$$\eta_{th,Otto} = \frac{W_{ex} - W_{comp}}{Q_H} \quad \text{Eq. (10.4)}$$

# Example 10.1

**Problem:** An engine operating on a cold air standard Otto cycle takes air at 100 kPa and 25 C and compresses it isentropically to 2.2 MPa. The work output from the cycle is 200 kJ / kg of air. Find the efficiency of the cycle, and the maximum temperature reached in the cycle.

**Find:** Efficiency  $\eta_{th,Otto}$  of the Otto cycle, maximum temperature  $T_3$  reached.

**Known:** Cold air standard Otto cycle, intake air pressure  $P_1 = 100$  kPa, intake temperature  $T_1 = 25$  C, pressure after compression  $P_2 = 2.2$  MPa, work output  $w_{net} = 200$  kJ / kg.

**Assume:**

1. Cyclical steady state
2. Isentropic compression and expansion
3. Air behaves as an ideal gas

# Example 10.1 Solution

The uses a solution for a constant specific heat, but let's look at a more general solution. To solve, we will

1. The temperature and pressure at state 1 (before compression) are given. So we can look up the enthalpy and entropy from some table
2. Compression is isentropic, so we know  $s_2$  and  $P_2$  so we can find the temperature at state 2
3. State 3 will depend on the heat input, but that is unknown.
4. State 4 has the same entropy as state 3 and the same pressure as state 1
5. Since we know the net work from the system, we can solve for the heat addition that completes the cycle.

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# Lecture 9b: Diesel cycle (Ch. 10.3)

# Diesel cycle

The Diesel cycle is a four stroke internal combustion engine that uses compression ignition rather than spark ignition

- Named after Rudolf Diesel (Germany 1858-1913)
- The cycle intakes pure air and compresses it to a high pressure and temperature. Then fuel in the form of small droplets is injected, which spontaneously combusts due to the high temperature
- Diesel engines typically have higher compression ratios and are built more robustly to withstand the resulting higher pressures.

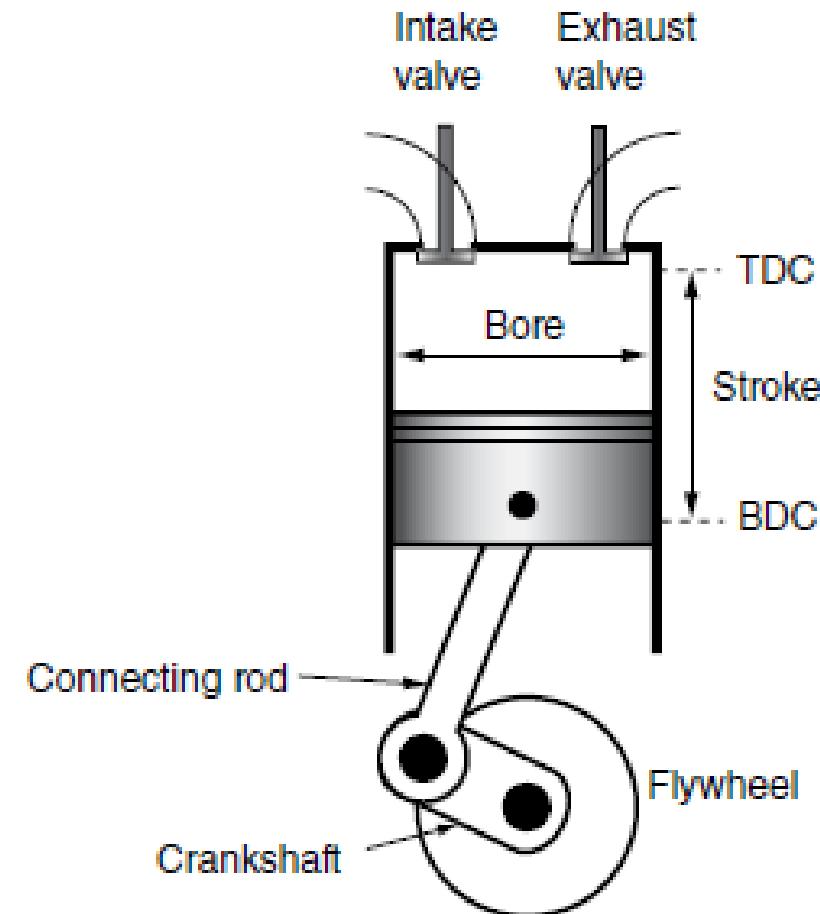


Figure 10.1 Reciprocating engine nomenclature.

# Diesel cycle steps

The Diesel cycle is similar to the Otto cycle, with a main difference that combustion occurs concurrently with part of the power stroke. The steps are:

1. Intake of air only
2. Compression of air (higher compression ratio than Otto cycle)
3. Injection of fuel (small droplets) that spontaneously combusts due to the high air temperature and starts the power stroke. Combustion occurs over a longer period (during a portion of the power stroke) than for an Otto cycle
4. Exhaust stroke

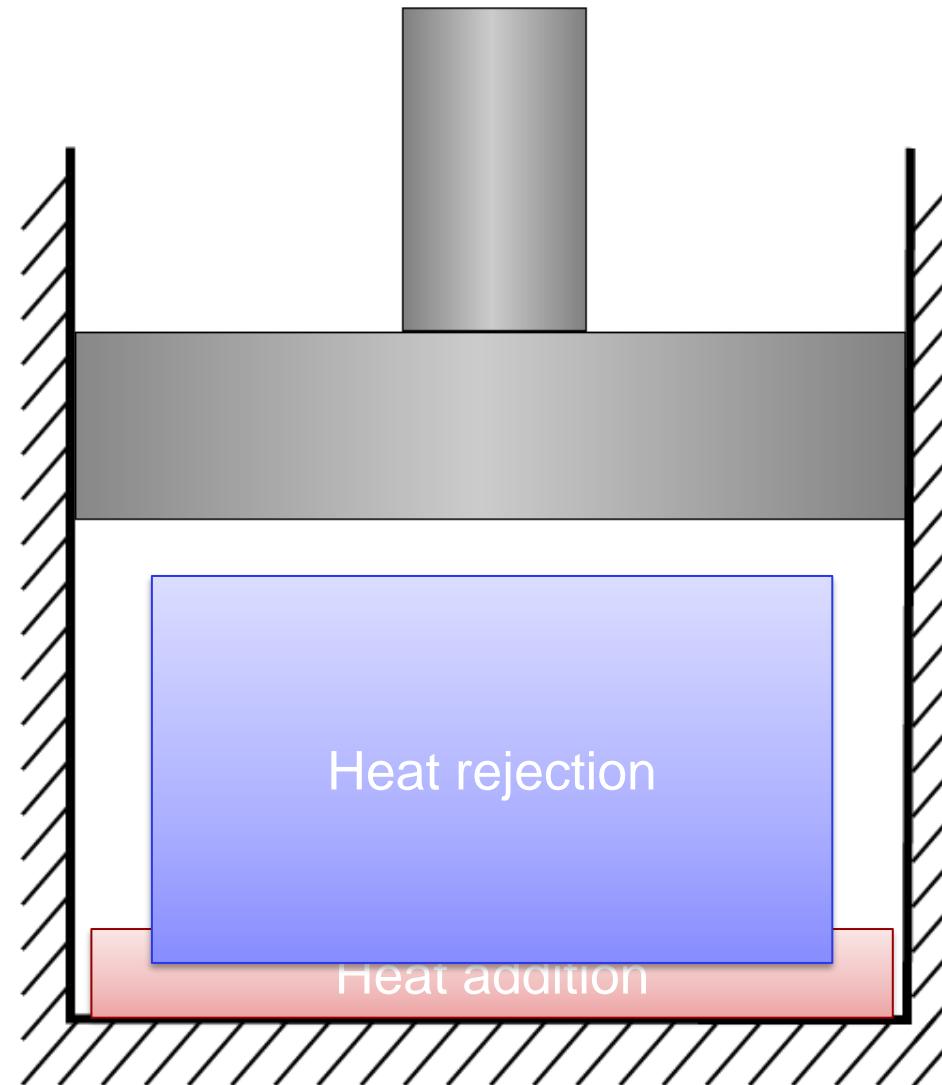
# Cold air standard Diesel cycle

The difference between a Diesel and Otto cold air standard cycle is the combustion process. For the Diesel cycle, the steps are:

1. Isentropic compression
2. Constant pressure heat addition until the cycle hits the cut-off ratio
3. Isentropic expansion
4. Constant volume heat rejection

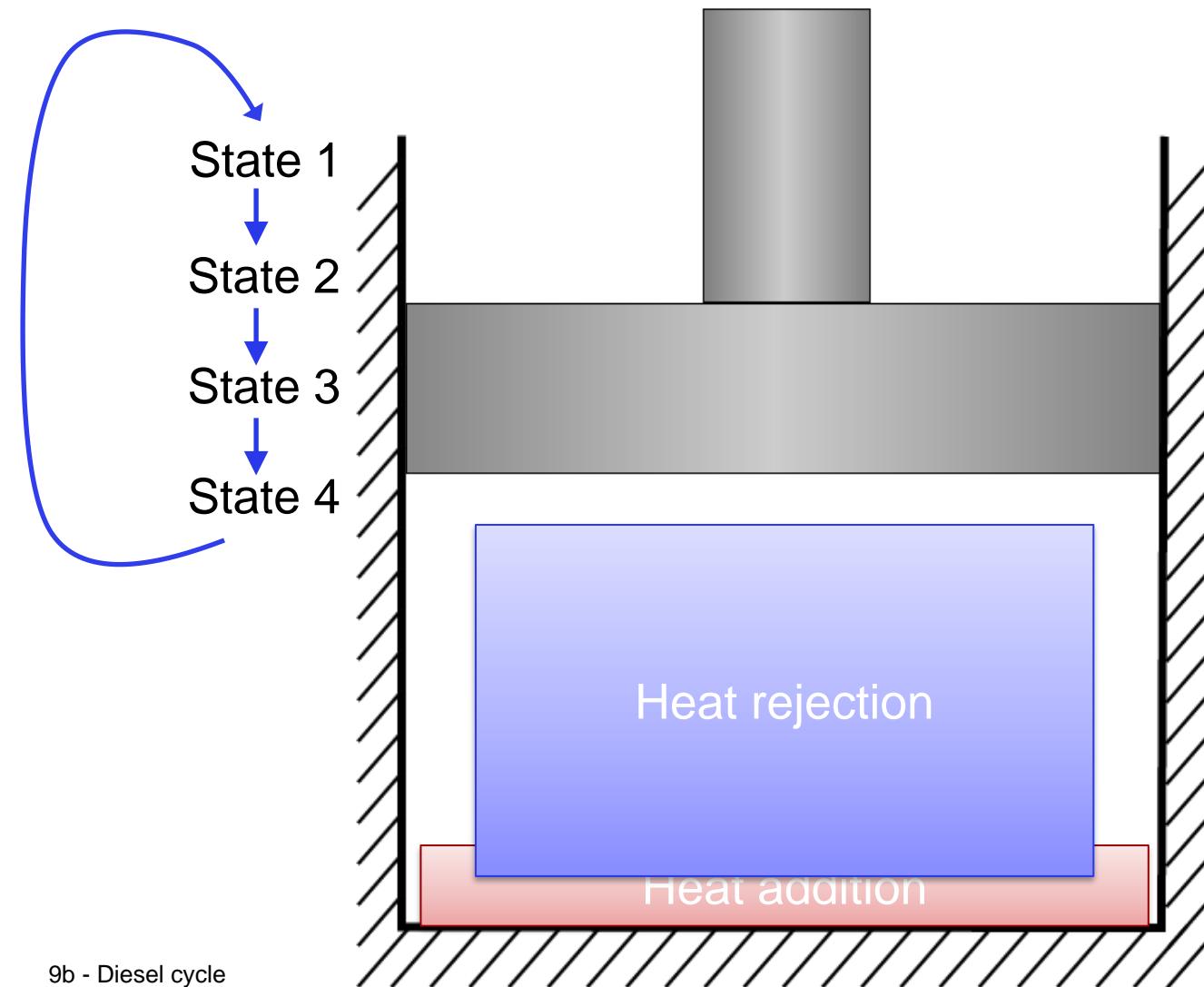
# The cold air cycle Diesel cycle

State 1  
↓  
State 2  
↓  
State 3  
↓  
State 4

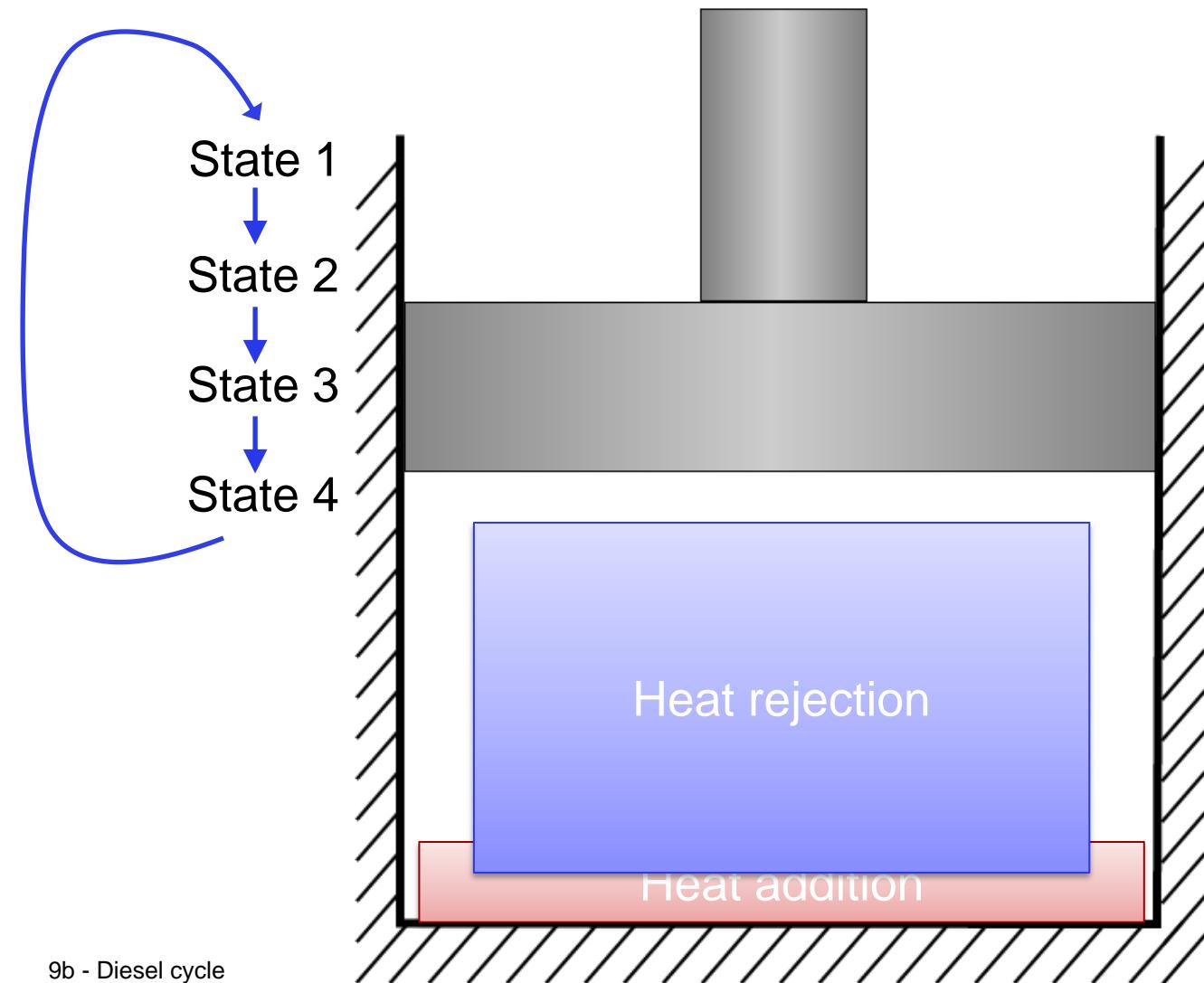


Isentropic compression  
Constant pressure heat addition  
Isentropic expansion  
Constant volume heat rejection

# The cold air cycle Diesel analysis P-v diagram



# The cold air cycle Diesel analysis T-s diagram



# Cut-off ratio

- The cut-off ratio is the ratio of the volumes at the beginning and end of the fuel combustion process:

$$r_c = \frac{V_3}{V_2} \quad \text{Eq. (10.14)}$$

- And remember that the compression ratio for this cycle is

$$r = \frac{V_1}{V_2} = \frac{V_4}{V_2}$$

# Cycle efficiency

- The efficiency is the same as for an Otto cycle:

$$\eta_{th,Diesel} = \frac{W_{ex} - W_{comp}}{Q_H}$$

- Remember that there is work during the combustion phase of the Diesel cycle so:

$$W_{ex} = P_2(v_3 - v_2) + (u_3 - u_4)$$

# Calculating the heat input for Diesel cycle

- Remember that the heat addition (fuel combustion) occurs at constant pressure. Since there is a  $Pv$  term, it is important to use the enthalpy and not internal energy when calculating the heat input:

$$Q_{H,Diesel} = h_3 - h_2$$

## Example 10.2

**Problem:** An engine operating on a cold air standard Diesel cycle with a compression ratio of 20 and a cut-off ratio of 2 compresses air that is at 100 kPa and 25 °C at the start of the cycle. Find the maximum temperature reached in the cycle and the heat added per kilogram of air.

**Find:** Maximum temperature  $T_3$  reached during the cycle, heat added  $q$  per kilogram of air.

**Assume:**

1. Cyclical steady state
2. Constant pressure combustion to the cut-off ratio
3. Isentropic compression and expansion after the cut-off ratio
4. Cold air standard cycle

# Note on the book solution for Ex 10.2

In the solution,  $T_3$  is calculated incorrectly. Eq. 10.12 should have been used. Using Eq. 10.12 gives

$$\frac{T_1}{T_2} = \frac{1}{r^{\gamma-1}}$$

$$T_2 = T_1 r^{\gamma-1} = 298.15 \text{ K } 20^{1.4-1} = 988.2 \text{ K}$$

While the book gets 701.1 K. This is clearly too low because in Example 10.1, a compression ratio of 9.9 gives a  $T_2$  of 721.1 K.

## Example 10.2 solution

The solution procedure is mostly the same as for an Otto cycle, but the combustion step is different. To solve, we will use the following steps:

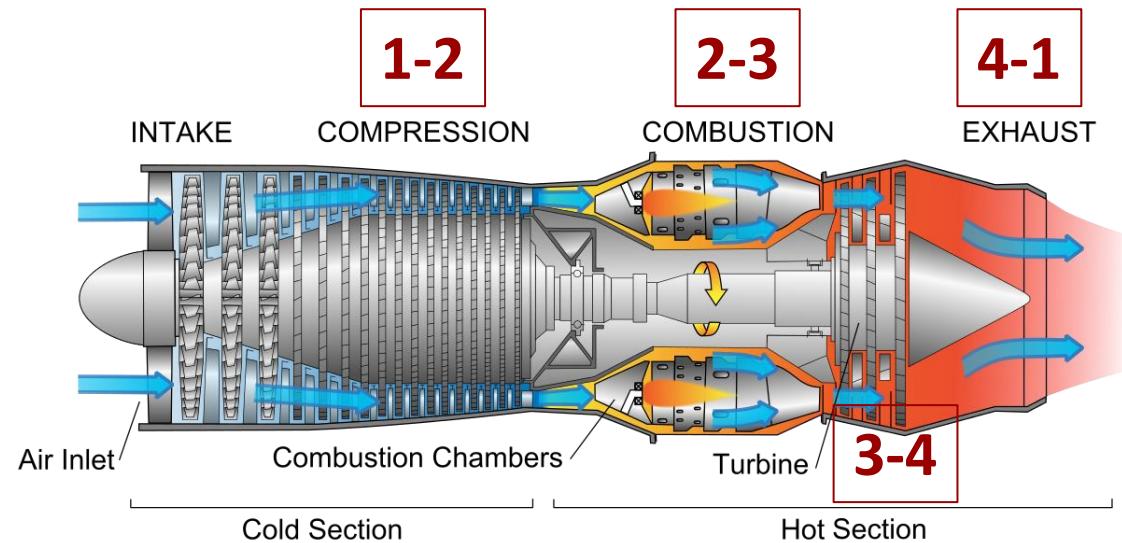
1. State 1 is fully defined, so we can look up internal energy, entropy etc. directly.
2. We can find state 2 because we know the entropy ( $s_1$ ) and the compression ratio
3. For state 3, we know the pressure and the volume (based on the cut-off ratio), which will fully define the state. We can look up entropy, enthalpy etc.
4. For state 4, the entropy is known (same as  $s_3$ ) and we know the volume from the compression ratio and cut-off ratio.
5. The cycle is fully defined, and we can calculate the specific work and efficiency

47201 Engineering thermodynamics

# Lecture 9c: Gas turbines and the Brayton cycle (Ch. 10.4-5)

# Gas turbine

- Gas turbines use rotary compressors to increase the pressure of air as it enters the combustion chamber
- Fuel is then injected into the combustion chamber, and it ignites, which causes a large increase in temperature and pressure
- The high pressure gas then is exhausted through a turbine where the enthalpy of the exhaust gas is converted to mechanical work
- The cycle can be optimized to produce work (often as electricity) or for propulsion
  - For work, the turbine should remove as much energy from the exhaust as possible.
  - For propulsion, the turbine only recovers enough work to power the compressor



# Gas turbine components

- We can simplify a gas turbine engine as having three components: the compressor, combustor and turbine
- The compressor and turbine are mounted on a common shaft, which allows the turbine to power the compressor
- Air is taken in from the atmosphere and exhaust gas is rejected back to the atmosphere
- No heat exchanger for heat rejection is necessary because the heat is carried out with the exhaust gases

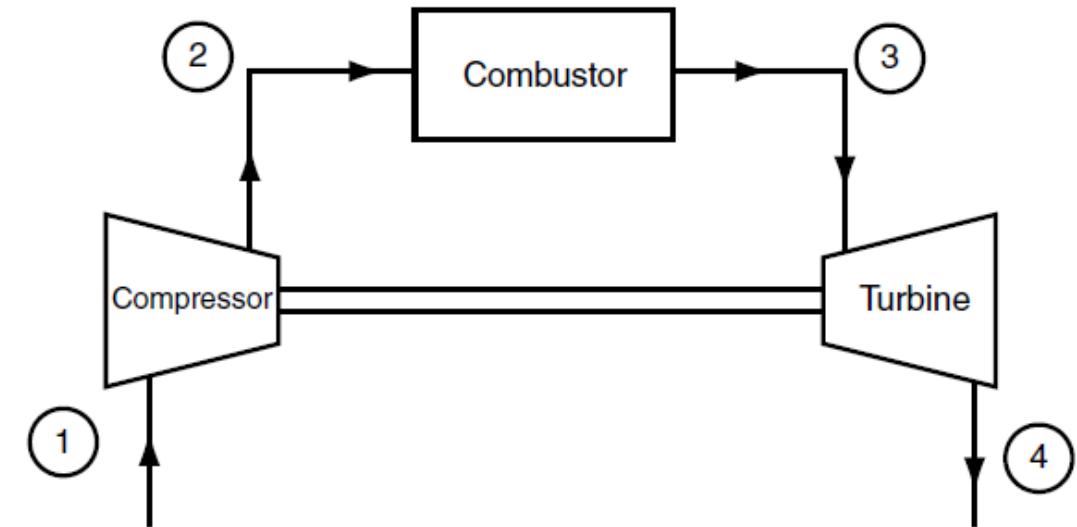


Figure 10.8 Schematic diagram of a gas turbine.

# Gas turbine thermodynamic model – the Brayton cycle

An air standard model of a gas turbine engine is the Brayton cycle: It is modelled as having two heat exchangers, a compressor and a combustor. The cycle steps are:

1. Isentropic compression
2. Constant pressure heat addition
3. Isentropic expansion
4. Constant pressure heat rejection

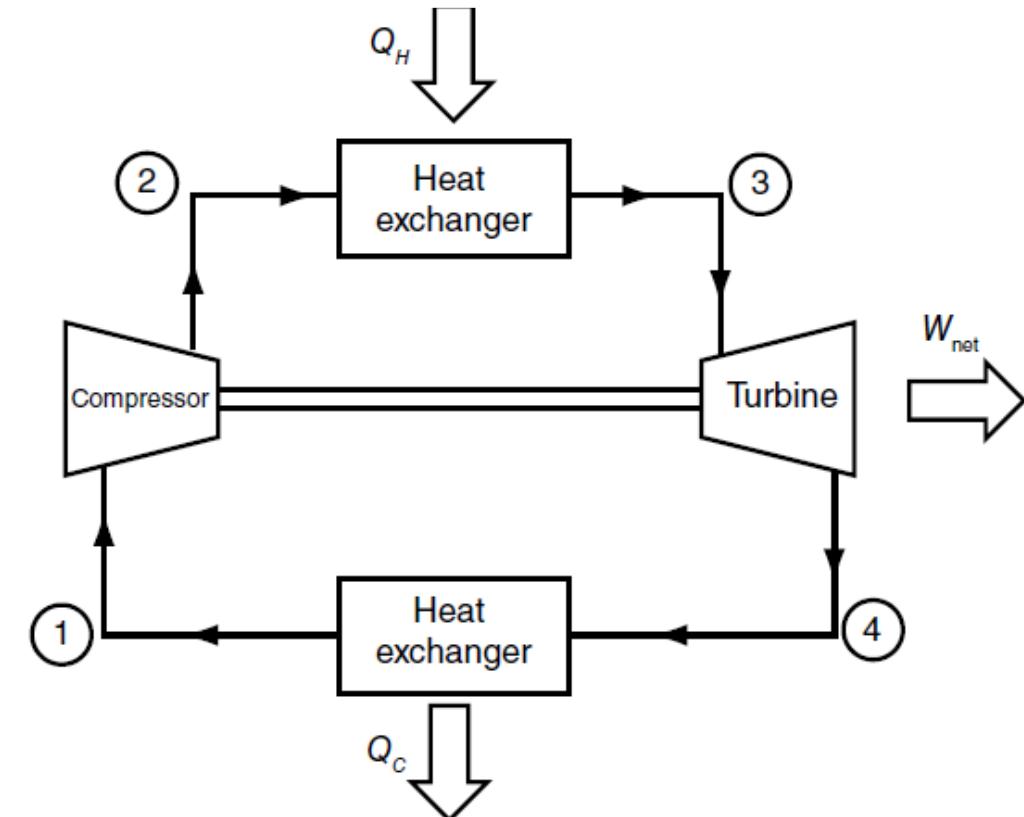
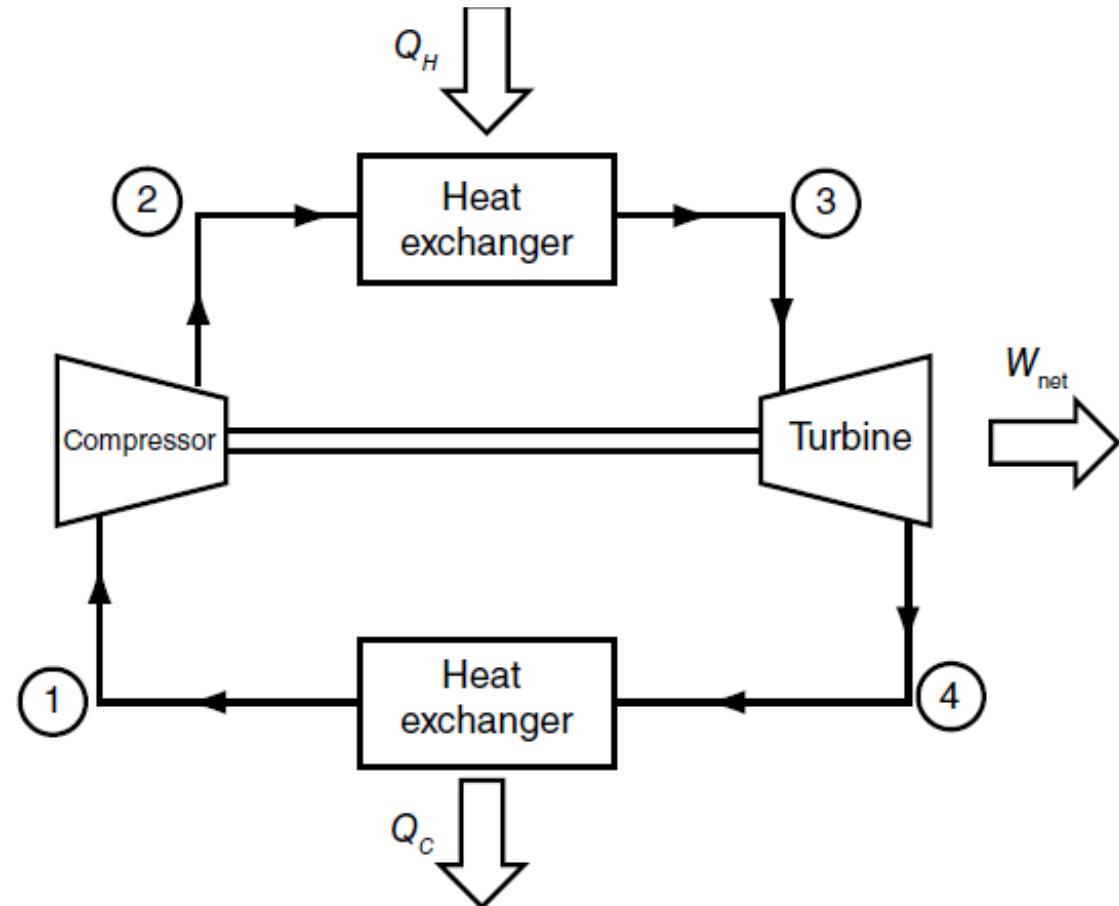
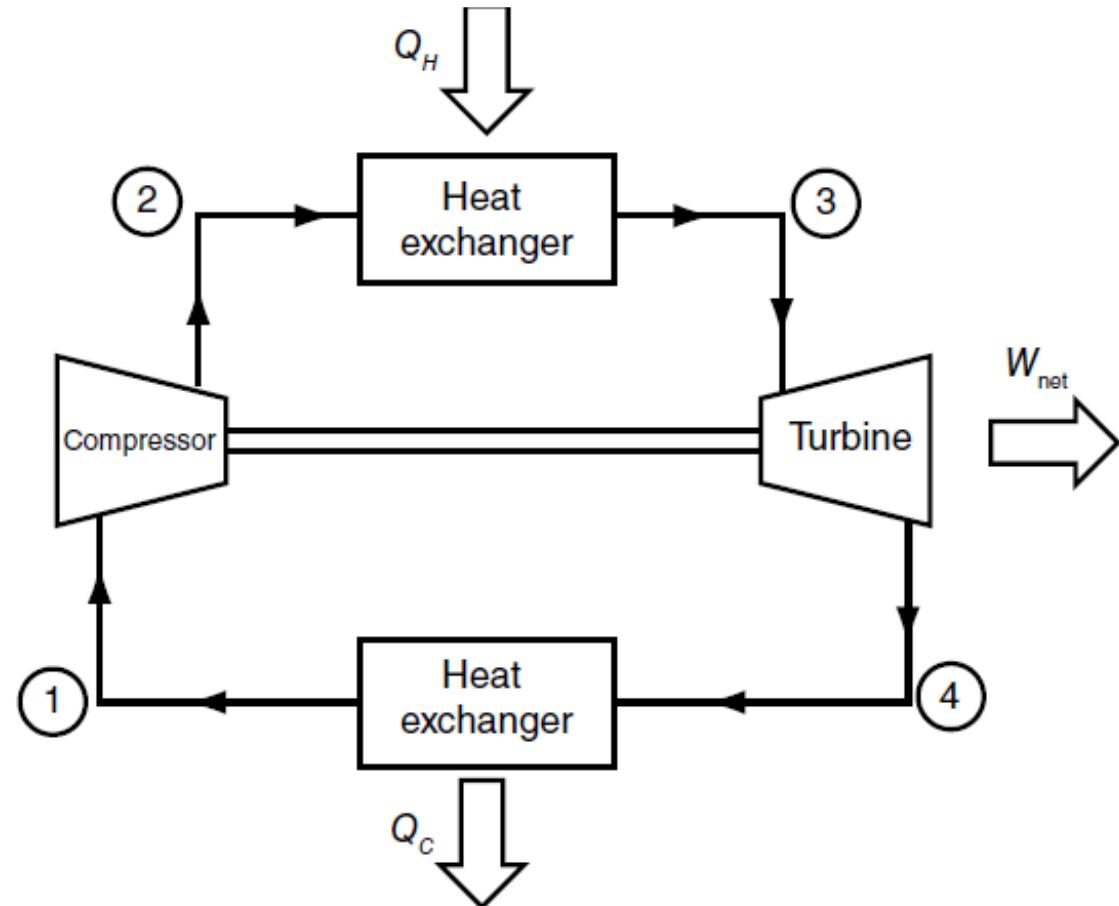


Figure 10.9 Gas turbine modelled as a closed cycle.

# Brayton cycle P-v diagram



# Brayton cycle T-s diagram



# Brayton cycle analysis

Looking at the work done at constant entropy:

$1 \rightarrow 2$  Isentropic compression

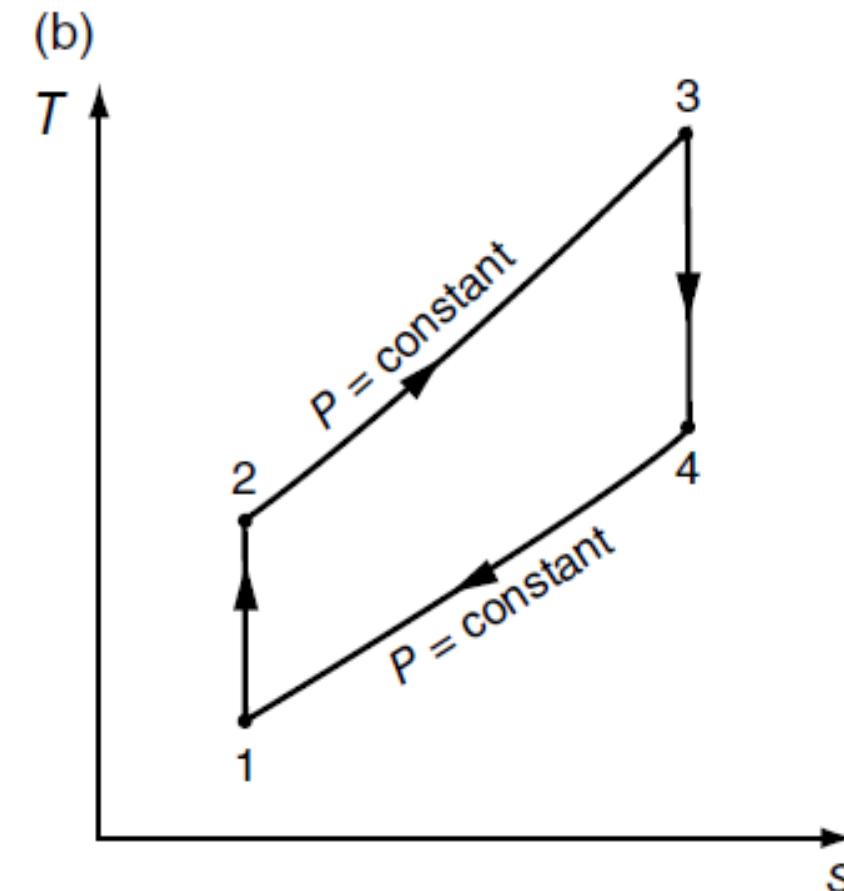
$$w_{comp} = h_2 - h_1 = c_p(T_2 - T_1)$$

$3 \rightarrow 4$  Isentropic expansion

$$w_{turb} = h_3 - h_4 = c_p(T_3 - T_4)$$

We can then express how much of the turbines work is taken by the compressor:

$$bwr = \frac{w_{comp}}{w_{turb}} = \frac{h_2 - h_1}{h_3 - h_4}$$



# Brayton cycle efficiency

- The efficiency for the Brayton cycle is:

$$\eta_{th,Brayton} = \frac{W_{net}}{Q_H} = \frac{W_{turb} - W_{comp}}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

## Example 10.3

**Problem:** An air standard Brayton cycle with a compressor pressure ratio of 10 takes in air at 100 kPa and 300 K and a mass flow rate of 5 kg / s. The air leaves the combustor at 1260 K. Find the efficiency of the cycle and the net power output. Use air tables to find the properties of air.

**Find:** Efficiency  $\eta_{th,Brayton}$  of the cycle, net power output  $W_{net}$  of the cycle.

**Assume:**

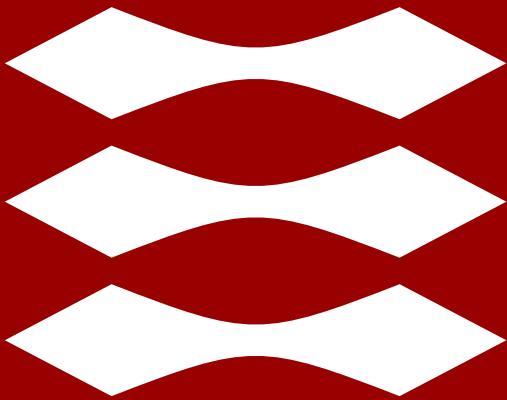
1. Steady state
2. Isentropic compression and expansion
3. Constant pressure heat addition and extraction

## Example 10.3 solution

The solution procedure is mostly the same as for the other air standard cycles. To solve, we will use the following steps:

1. State 1 is fully defined, so we can look up enthalpy, entropy etc. directly.
2. We can find state 2 because we know the entropy ( $s_1$ ) and the pressure ratio.
3. For state 3, we know the pressure and the temperature, which will fully define the state. We can look up entropy, enthalpy etc.
4. For state 4, the entropy is known (same as  $s_3$ ) and we know pressure is the same as the inlet.
5. The cycle is fully defined, and we can calculate the specific work and efficiency.

**DTU**



47201 Engineering thermodynamics

# Module 10

# Recap: Enthalpy, $C_v$ , and $C_p$

Variation of internal energy:

$$dU = \delta Q + \delta W$$

Boundary work

$$\delta W = -PdV$$

Enthalpy:  $H = U + PV$

$$dH = dU + d(PV) = dU + PdV + VdP$$

At constant volume

$$\text{Heat capacity } C = \frac{\delta Q}{\delta T}$$

$$dU = \delta Q \longrightarrow C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

At constant pressure:

$$dH = \delta Q \longrightarrow C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

At a given temperature, which one  
has more internal energy?

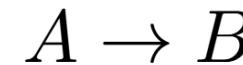


or



# Reaction heat (const. volume)

$$\Delta u = q_V + \cancel{w}$$

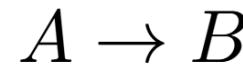


The heat of reaction,  $q_V$ , is the quantity of heat associated with a chemical reaction occurring within the system.

If the reaction occurs at *constant temperature*, the heat of reaction is exchanged between the system and its surroundings.

# Reaction heat (const. volume)

$$\Delta u = q_V + \cancel{w}$$



exothermic reaction

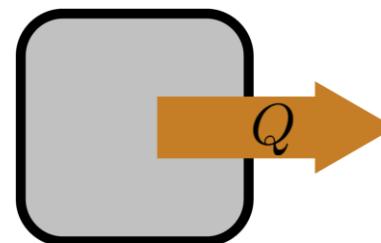
$$q_V < 0$$

endothermic reaction

$$q_V > 0$$

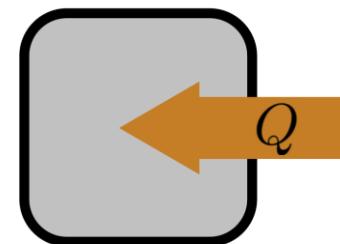
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If the reaction occurs at *constant temperature*, the heat of reaction is exchanged between the system and its surroundings.



releases heat  
to the  
surroundings

produces a  
temperature increase

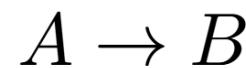


absorbs heat  
from the  
surroundings

produces a  
temperature decrease

# Reaction heat (const. volume)

$$\Delta u = q_V + \cancel{w}$$



exothermic reaction

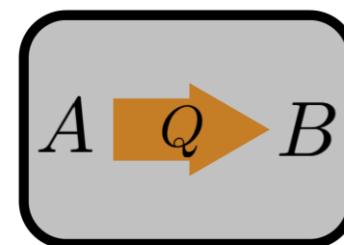
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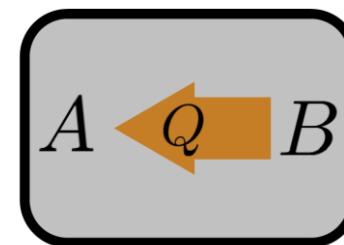
The heat of reaction,  $q_V$ , is the quantity of heat associated with a chemical reaction occurring within the system.

If the reaction occurs in an *isolated system*, it produces a change in the temperature of the system.



reaction  
releases heat

produces a  
temperature increase

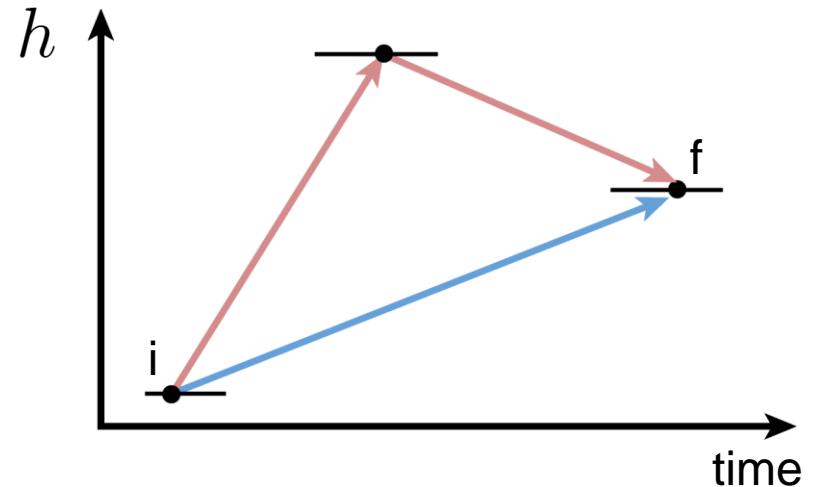


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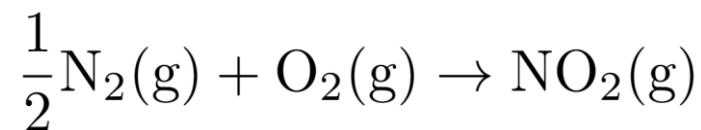
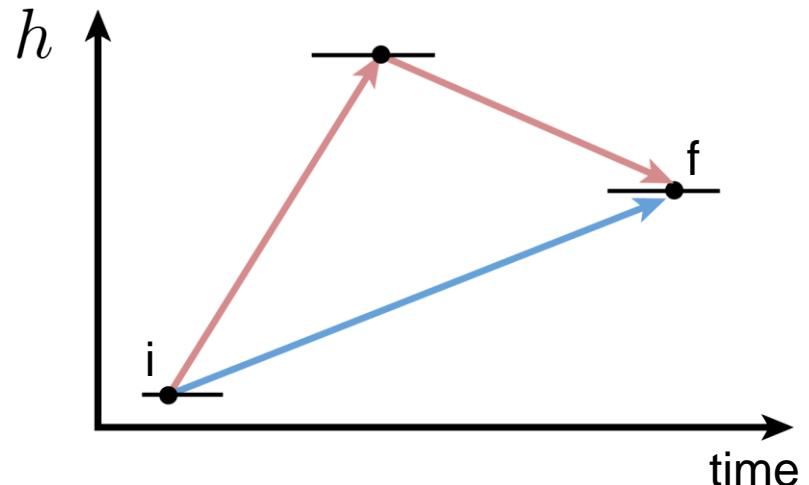
# Hess's law

*The enthalpy of a chemical process is independent of the path taken from the initial to the final state*



# Hess's law

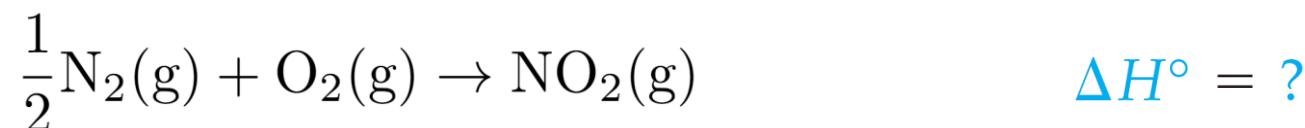
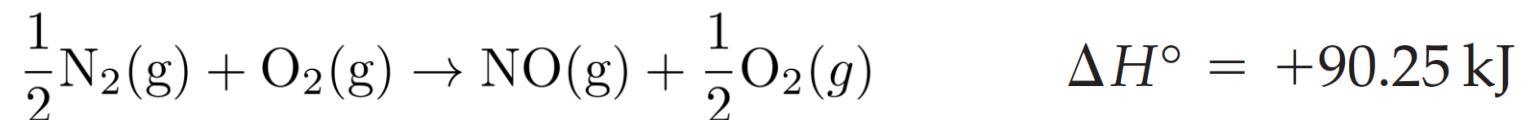
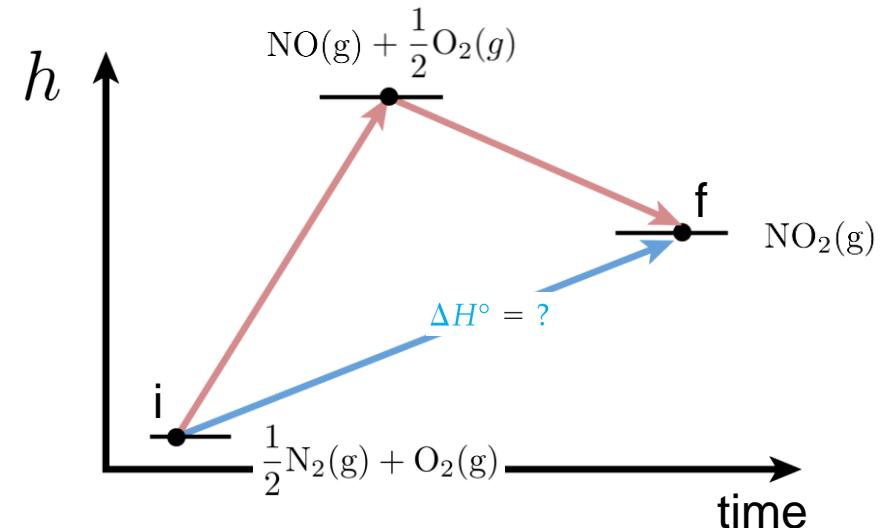
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$$\Delta H^\circ = ?$$

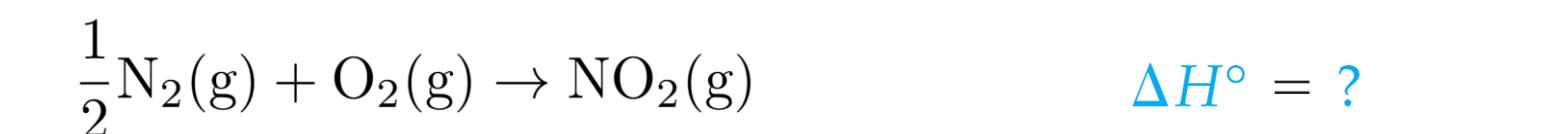
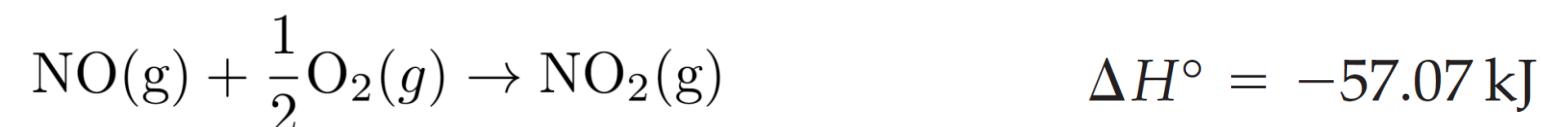
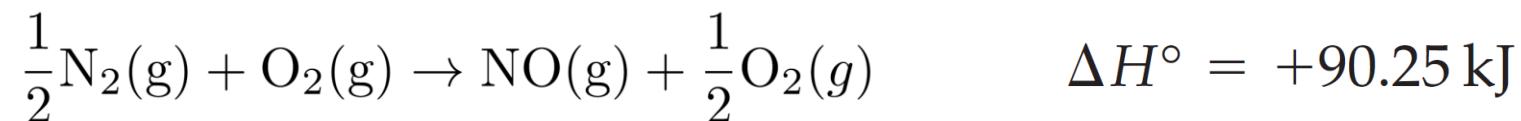
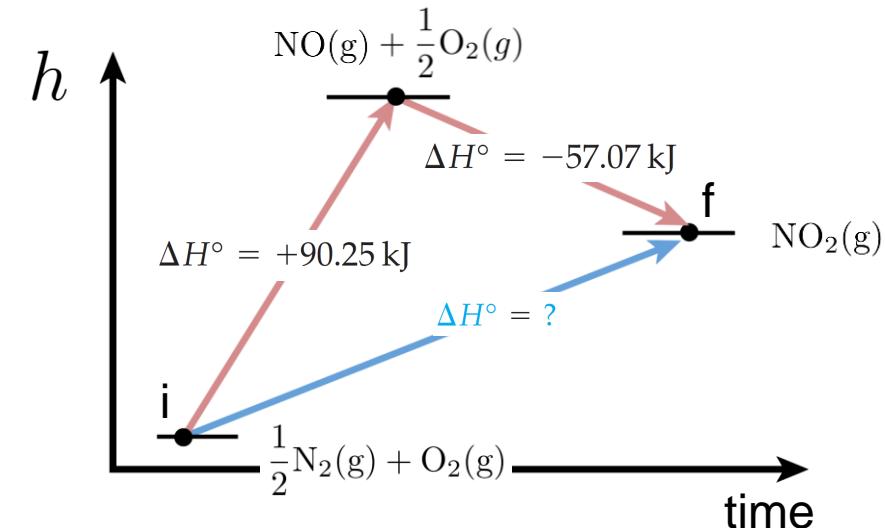
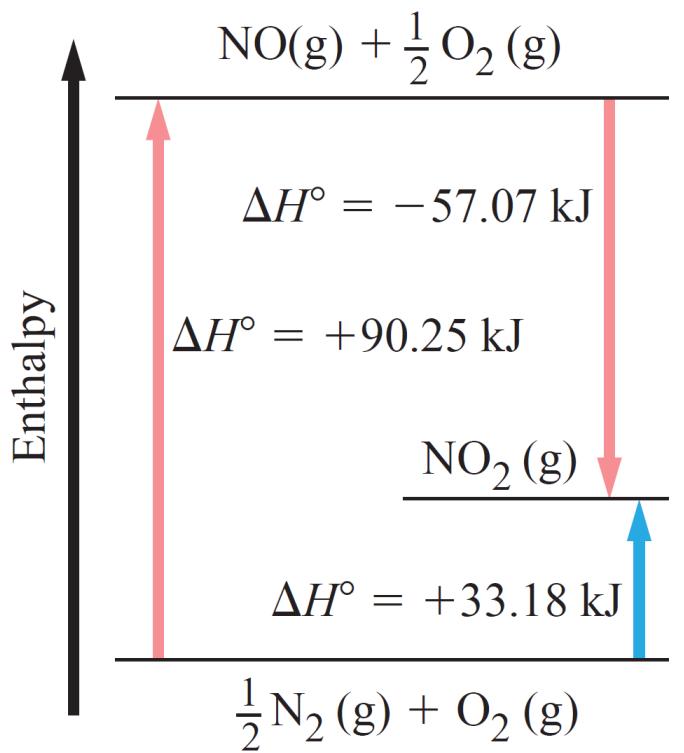
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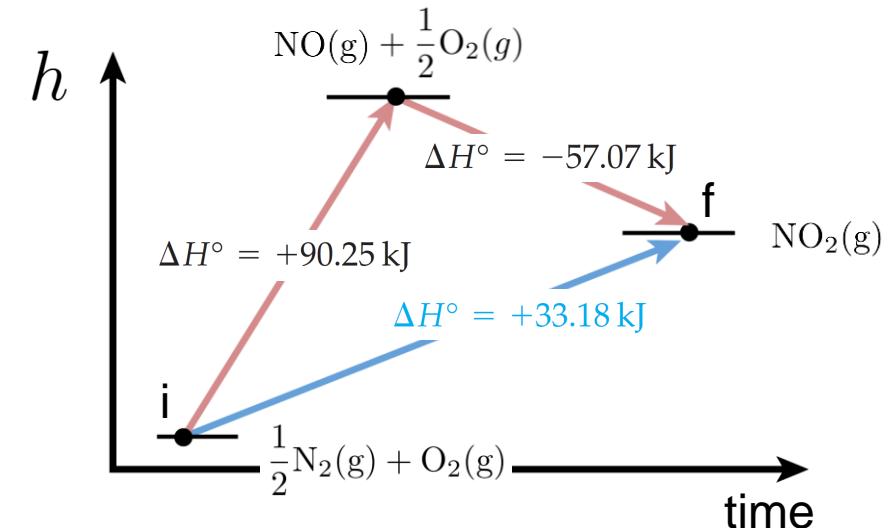
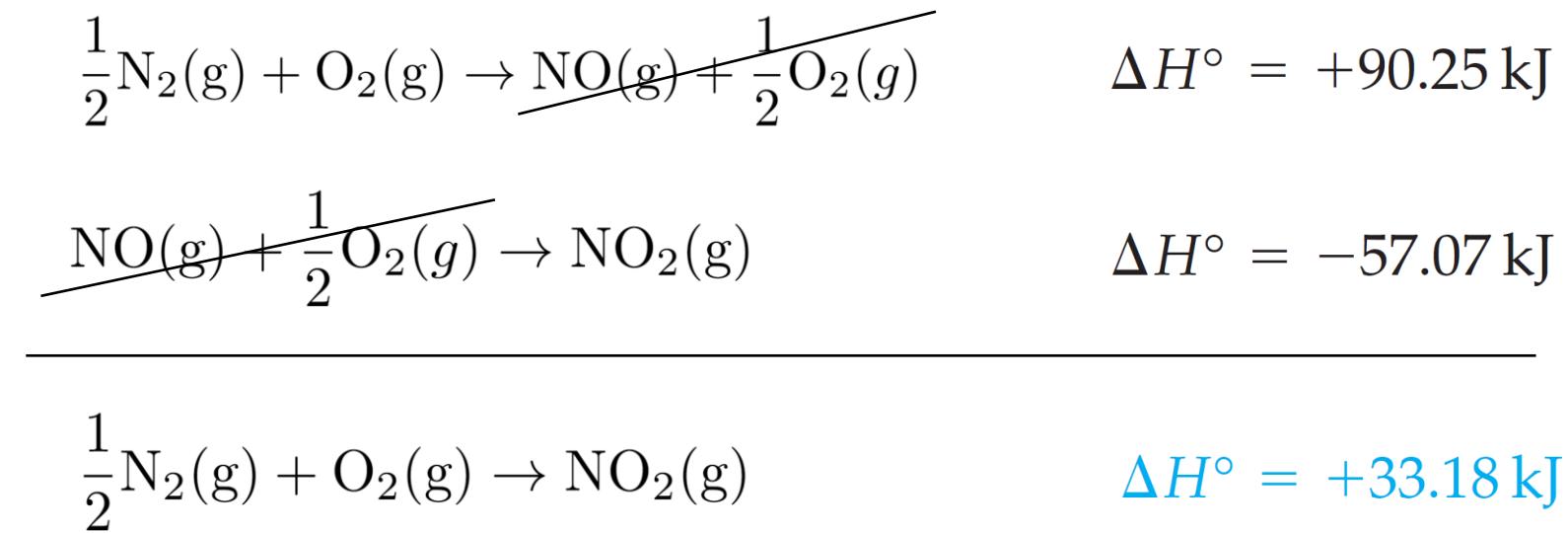
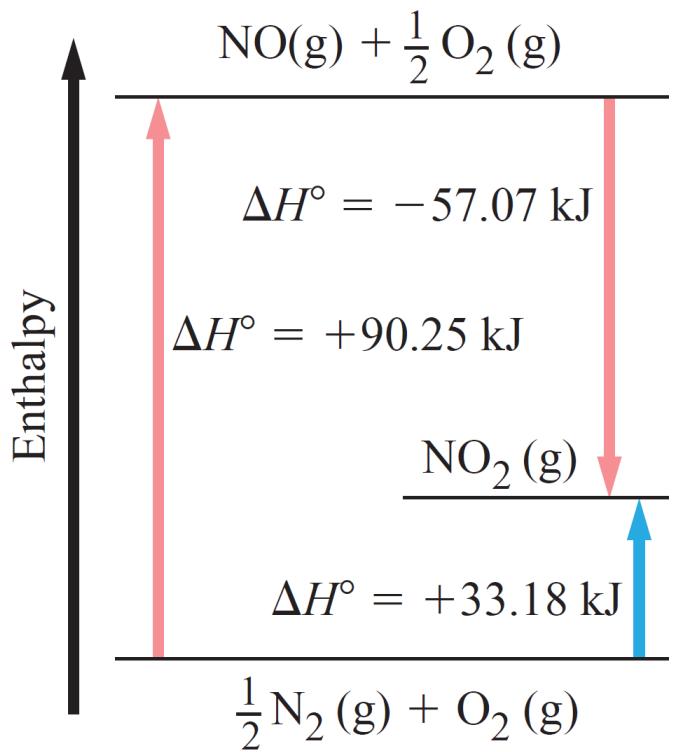
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# Enthalpy of formation

*Change of enthalpy during the formation of 1 mole of the substance from its constituent elements in their reference form.*

The standard enthalpy of formation of a pure element in its reference form is 0.

*Reference form* means the molecules spontaneously formed by elements, e.g. H<sub>2</sub>

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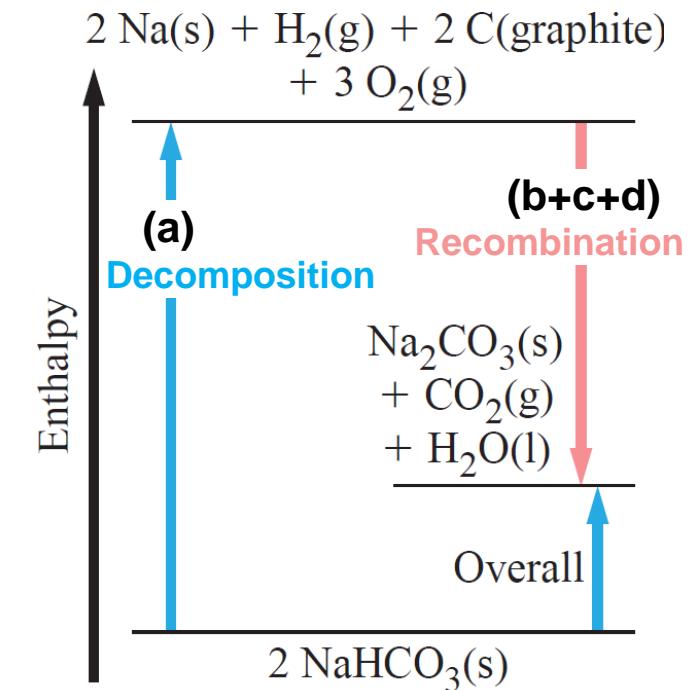
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Why is this useful?

# Enthalpy of formation

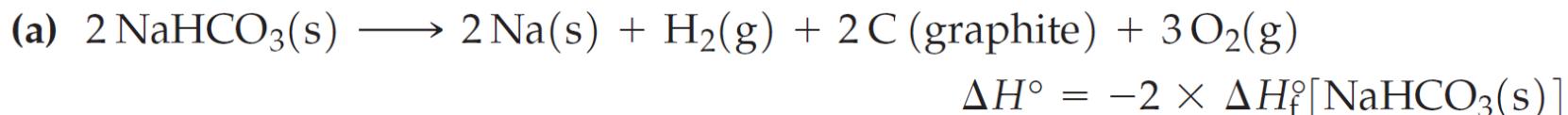
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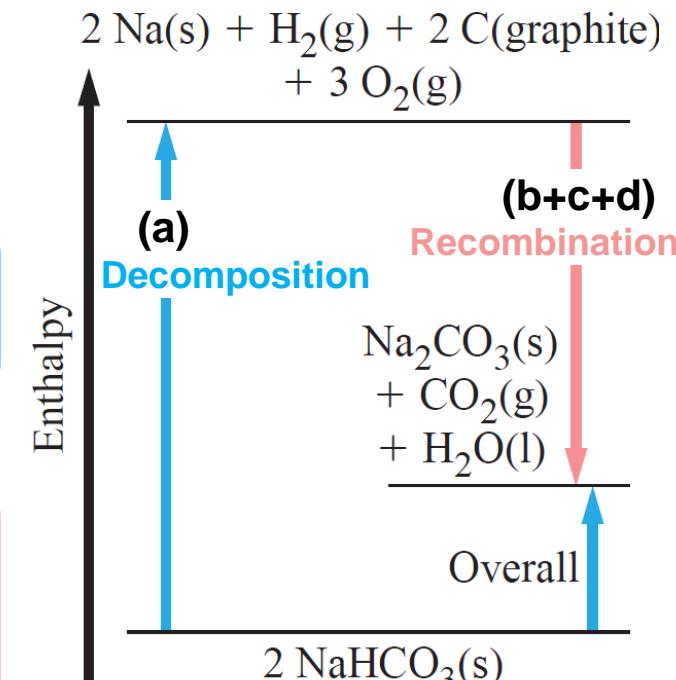
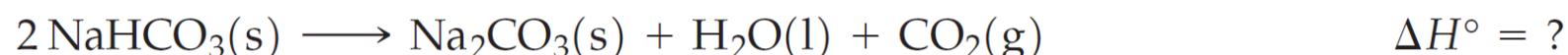
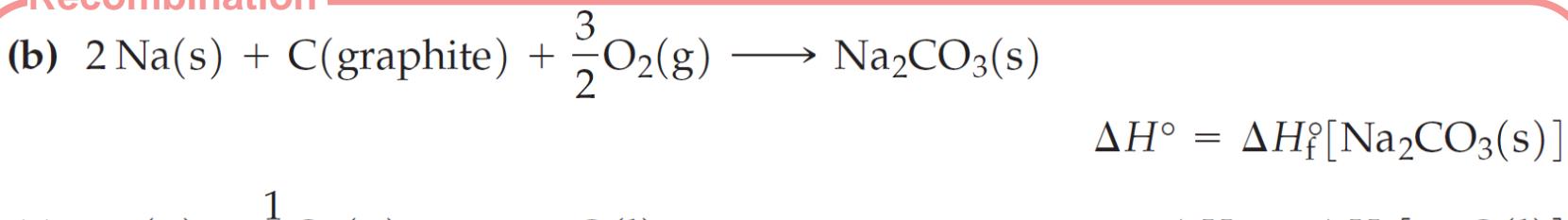
$$\Delta H^\circ = ?$$

# Enthalpy of formation

## Decomposition



## Recombination



**Inorganic substances** [ edit ]

# Enthalpy of formation

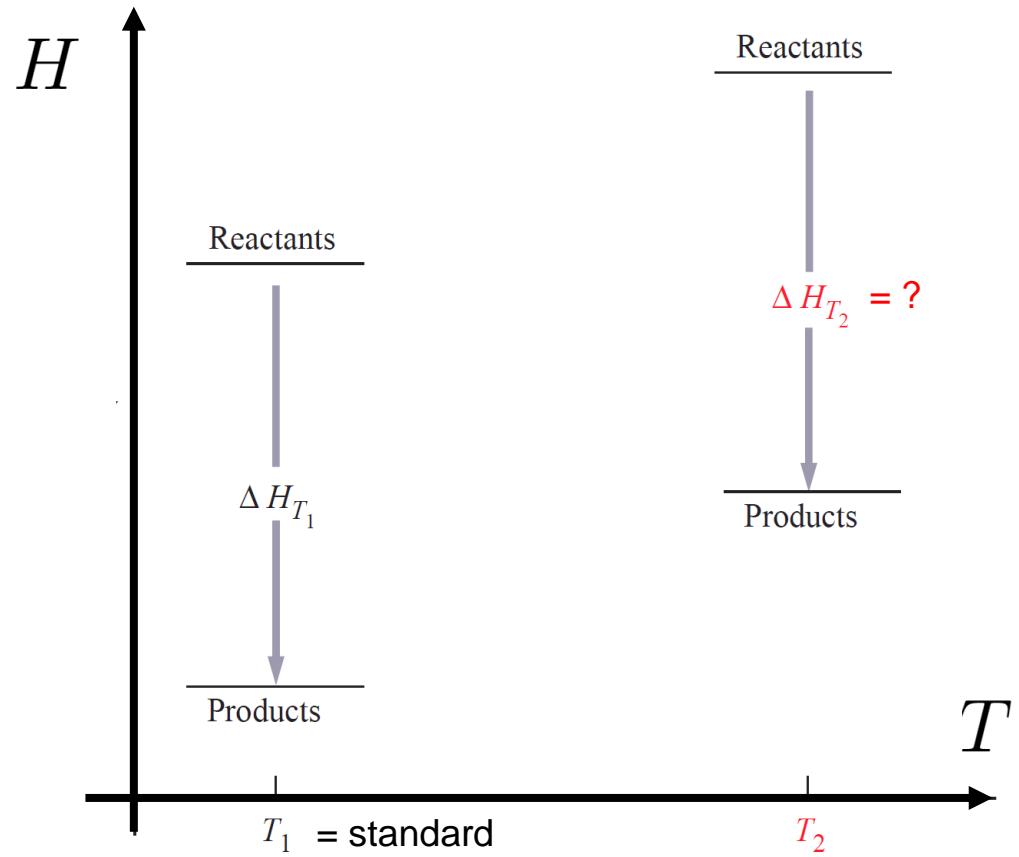
[See wikipedia page](#)

Species	Phase	Chemical formula	$\Delta_f H^\ominus /(\text{kJ/mol})$
Aluminium	Solid	Al	0
Aluminium chloride	Solid	AlCl <sub>3</sub>	-705.63
Aluminium oxide	Solid	Al <sub>2</sub> O <sub>3</sub>	-1675.5
Aluminium hydroxide	Solid	Al(OH) <sub>3</sub>	-1277
Aluminium sulphate	Solid	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-3440
Barium chloride	Solid	BaCl <sub>2</sub>	-858.6
Barium carbonate	Solid	BaCO <sub>3</sub>	-1216
Barium hydroxide	Solid	Ba(OH) <sub>2</sub>	-944.7
Barium oxide	Solid	BaO	-548.1
Barium sulfate	Solid	BaSO <sub>4</sub>	-1473.3
Beryllium	Solid	Be	0
Beryllium hydroxide	Solid	Be(OH) <sub>2</sub>	-903
Beryllium oxide	Solid	BeO	-609.4
Boron trichloride	Solid	BCl <sub>3</sub>	-402.96
Bromine	Liquid	Br <sub>2</sub>	0
Bromide ion	Aqueous	Br <sup>-</sup>	-121

# Temperature dependence

Standard enthalpies of formation refer to standard pressure ( $10^5$  Pa) and specified temperature  $T_1$  (which may vary, but often is  $25^\circ\text{C} = 298.15\text{ K}$ ).

How do we calculate the reaction enthalpy if the reaction happens at a different temperature  $T_2$ ?



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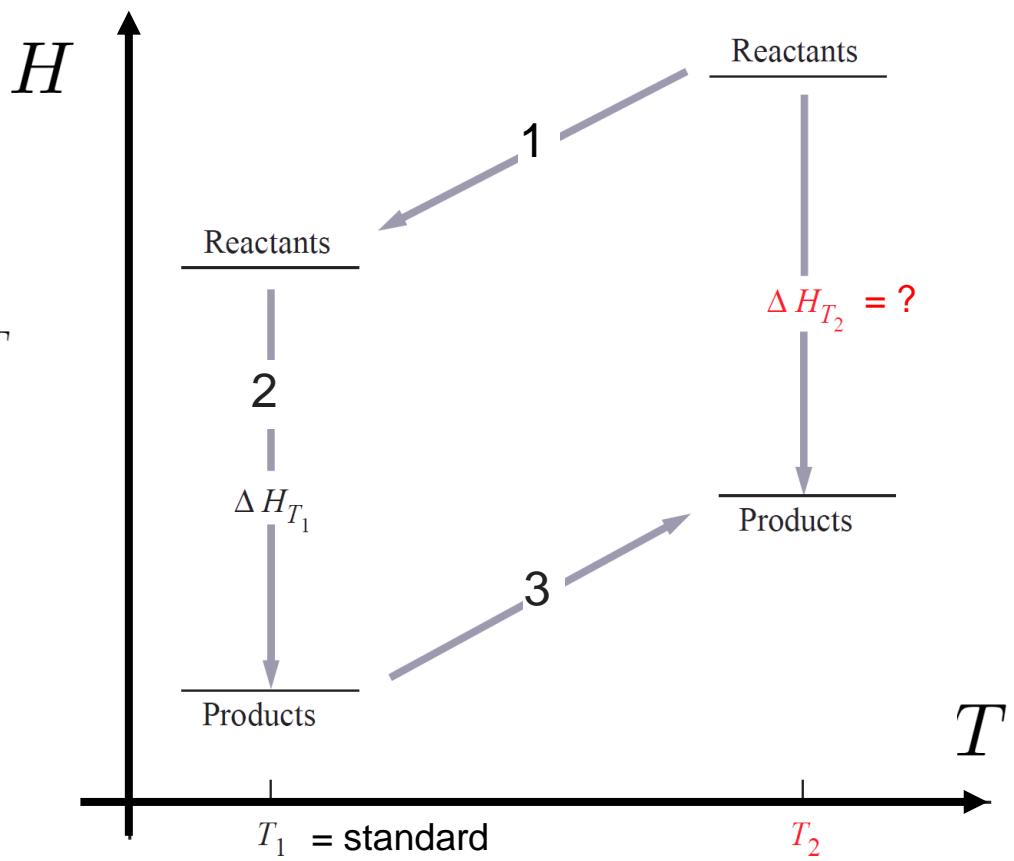
We split it in steps and apply conservation of energy:

1. We bring the reactants from  $T_2$  to  $T_1$ :  $\Delta H = \sum_{\text{Reactants}} \int_{T_2}^{T_1} C_p(T) dT$

2. We perform the reaction at standard temperature  $T_1$

3. We bring the products back to  $T_2$ :  $\Delta H = \sum_{\text{Products}} \int_{T_1}^{T_2} C_p(T) dT$

We add the enthalpy variations for the three steps.



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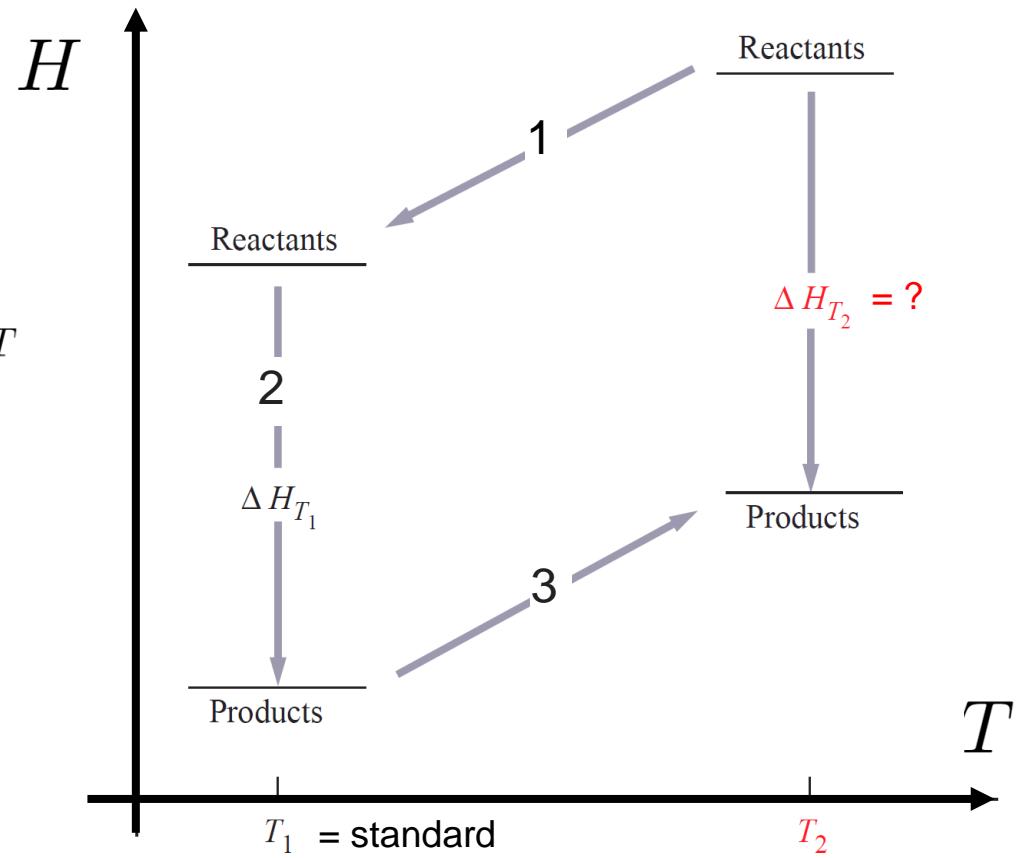
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We add the enthalpy variations for the three steps.

The result might be different due to the different heat capacities between reactants and products.



# Constant volume reactions

How do we calculate the heat of reaction at constant volume from the reaction enthalpy?

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For a constant pressure reaction, the enthalpy is equal to the heat of reaction.

For obtaining the heat of reaction at constant pressure, we need to consider the work done against the external pressure.

$$q_V = q_P + w \quad \textit{Is it clear why do we have a plus sign?}$$

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While at constant pressure some energy is used for boundary work, at constant volume all the energy is entirely converted into heat.

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$$w = -P\Delta v \quad \text{work that would be done in const. P}$$

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Sometimes, we just need to consider the gases (using the ideal gas law) since the volumes of solids and liquids are very small in comparison.

# Reactions happening at a different pressure

*Standard* enthalpies of formation refer to standard pressure ( $P_1 = 10^5 \text{ Pa}$ ) and specified temperature  $T$ .

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To calculate the work, we need to know the pressure and specific volumes of all the reactants and products (at the right pressure!).

$$w_1 = -P_1 \Delta v_1$$

$$w_2 = -P_2 \Delta v_2$$

# Conclusions

There is some book-keeping to be done, but ultimately it always boils down to conservation of energy.

One always has to remember that specific enthalpy and specific internal energy are state functions: for each substance they only depend on the temperature.

Since they are extensive properties, they are proportional to the amount of each substance, and we have to sum the contributions for each chemical compound.