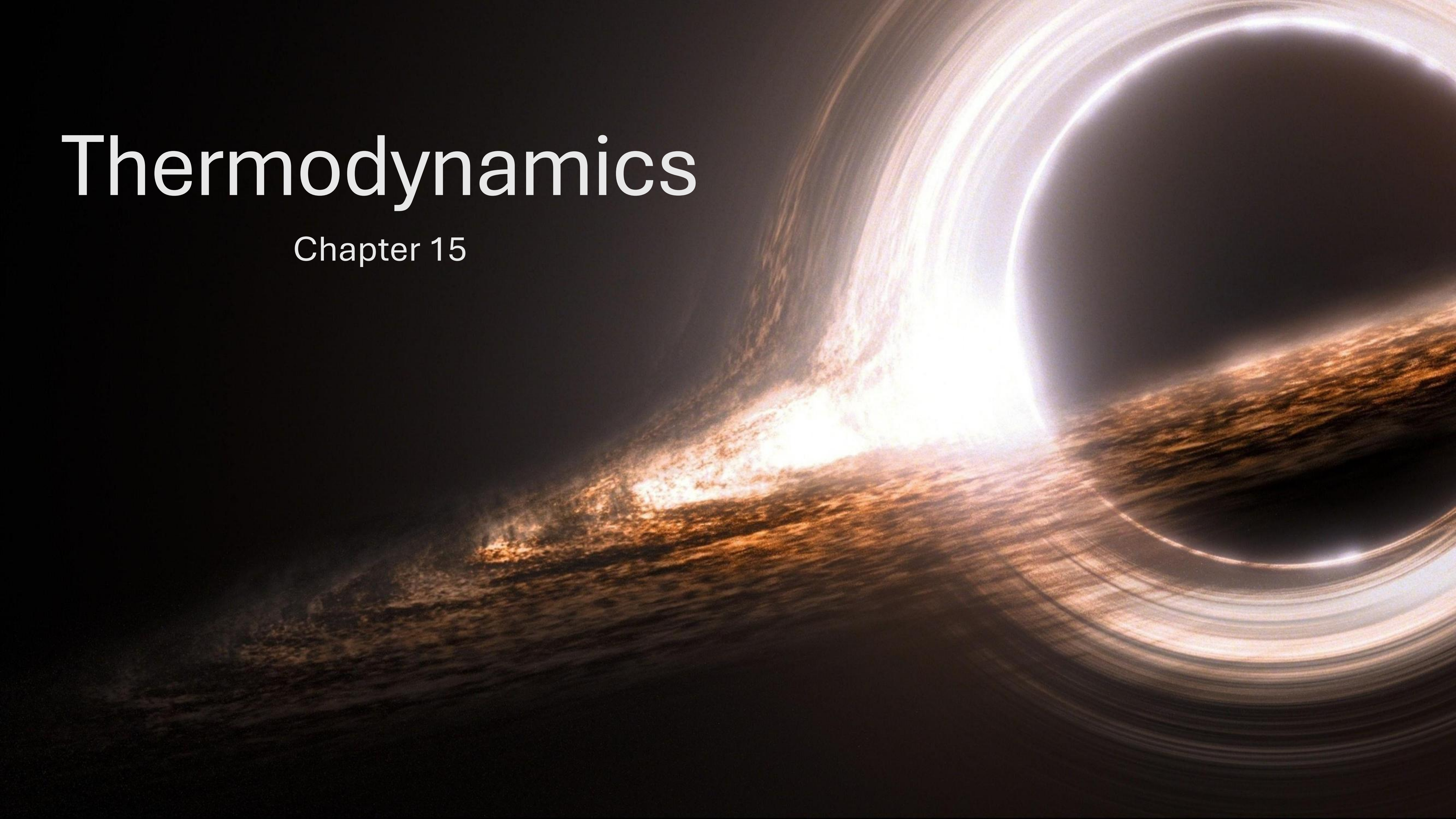
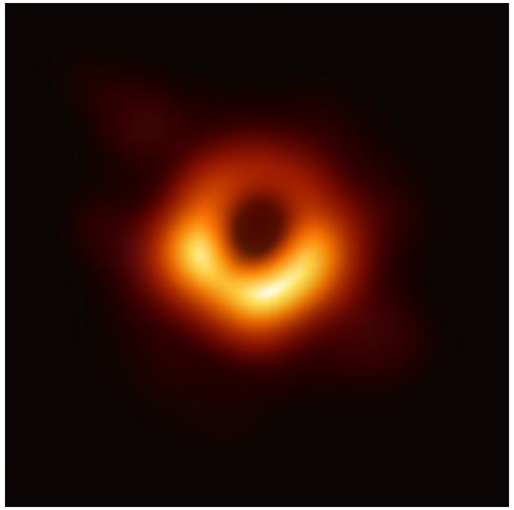


Thermodynamics

Chapter 15

Why a Blackhole?

A black hole is a region of space where gravity is so strong that nothing, not even light, can escape once it crosses a boundary called the event horizon. Black holes form when very massive stars collapse under their own gravity, compressing an enormous amount of mass into an extremely small volume. From the outside, a black hole can be completely described by just a few properties: its mass, spin, and electric charge. The bright ring is glowing gas heated to extreme temperatures as it spirals around the black hole, while the dark center is the "shadow" cast by the event horizon itself. This image confirms predictions made by Einstein's theory of general relativity and shows that black holes are real physical objects, not just theoretical ideas.



So why introduce blackholes in a thermodynamics lecture? Black holes obey laws that closely resemble the laws of thermodynamics: A black hole has a well-defined **temperature** and **entropy**, the area of a black hole's event horizon is related to its entropy, much like entropy measures the number of microscopic arrangements in ordinary systems, black holes even emit a tiny amount of thermal radiation, known as Hawking radiation.

These ideas show that thermodynamics is not limited to gas filled cylinders, but the most extreme edges of the universe. By studying black holes, we see that energy, heat, entropy, and temperature are fundamental concepts that connect everyday physics to the deepest questions about space, time, and the nature of the universe itself. In fact, the thermodynamics of black holes, particularly entropy, are one of the most active areas of study in astrophysics today!

What is Thermodynamics?

Thermodynamics: The study of the fundamental laws of heat, work, and temperature.

- Heat and work often occur simultaneously. For example, a kitchen refrigerator.

System: The part of the universe we wish to study. For example, the air and contents inside a kitchen refrigerator.

Surroundings: Everything external to the system that can interact with it. For the refrigerator system, the kitchen air, the refrigerator walls, the compressor and coils, and the rest of the room.

Walls:

- **Diathermal:** Allow heat transfer between the system and surroundings. For example, warm food and air inside the refrigerator.
- **Adiabatic:** Prevent heat transfer. For example, the insulated refrigerator walls and doors approximate this.

State of as system: Defined by *pressure, volume, temperature*, and mass. For example, for the interior of the refrigerator, temperature and pressure or the air and the mass of the contents.

The Laws of Thermodynamics

The Zeroth Law of Thermodynamics

- If two systems are each in thermal equilibrium with a third system, they are in thermal equilibrium with each other.

The First Law of Thermodynamics

- Energy cannot be created or destroyed, only transferred or transformed.

The Second Law of Thermodynamics

- Natural process have a preferred direction; heat flows spontaneously from hot to cold.

The Third Law of Thermodynamics

- It is not possible to lower the temperature of any system to absolute zero ($T = 0\ K$) in a finite number of steps.

The Zeroth Law of Thermodynamics

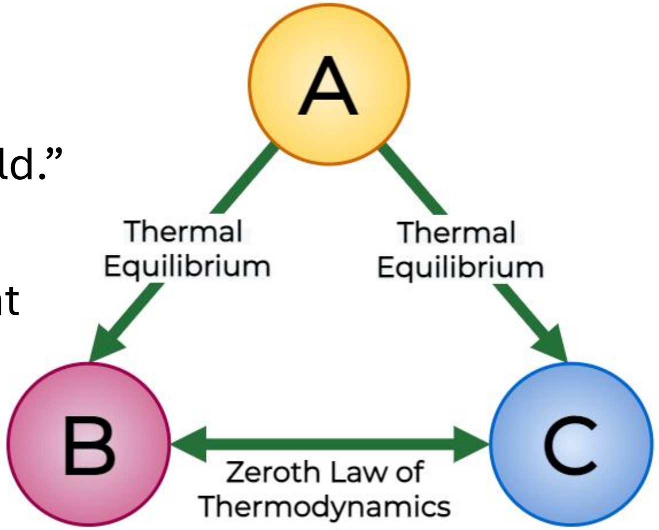
If two systems, A and B, are each in thermal equilibrium with a third system C, then A and B are also in thermal equilibrium with each other.

- **Before:** Heat was understood as a form of energy transfer, but there was no clear way to define "temperature" beyond intuitive concepts like "hot" and "cold."

- **After:** The Zeroth Law introduces the idea that temperature is a property that determines whether two systems will exchange heat. Systems in **thermal equilibrium** have the **same** temperature, and this property is intrinsic to the system itself.

- Enables Thermometry: Allows the use of a thermometer (System C) to compare temperatures of different objects (Systems A & B).

- Foundation of Thermodynamics: This law is the basis for the definition of temperature scales (Kelvin, Celsius, Fahrenheit).



The First Law of Thermodynamics 1/5

In the previous chapter we student the internal energy of a monatomic ideal gas

$$U = \frac{3}{2}nRT$$

Internal energy is the total microscopic kinetic energy of the gas particles due to their random motion. When T changes, v_{rms} changes, and the microscopic kinetic energy, $\overline{KE}$, changes.

There are only two physically distinct ways to change $\overline{KE}$ of gas particles:

a. Energy transferred by heat, Q (e.g., change particle speed)
b. Energy transferred by work, W (e.g., Compression or expansion of the gas)

The First Law of Thermodynamics 2/5

In the previous chapter we student the internal energy of a monatomic ideal gas

$$U = \frac{3}{2}nRT$$

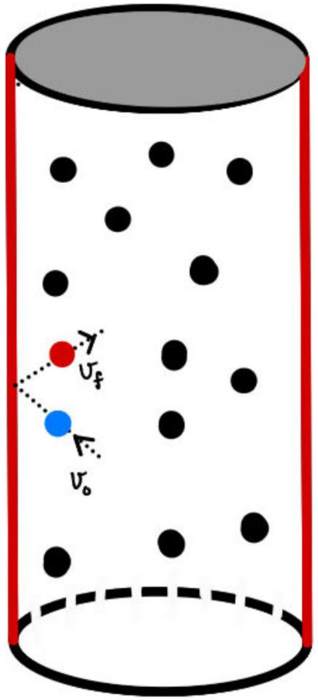
If $\overline{KE}$ increases, $\Delta U > 0$ and if it decreases $\Delta U < 0$. So, the net change in internal energy must equal,

$$\Delta U = (energy\ added\ by\ heat) - (energy\ lost\ to\ work)$$

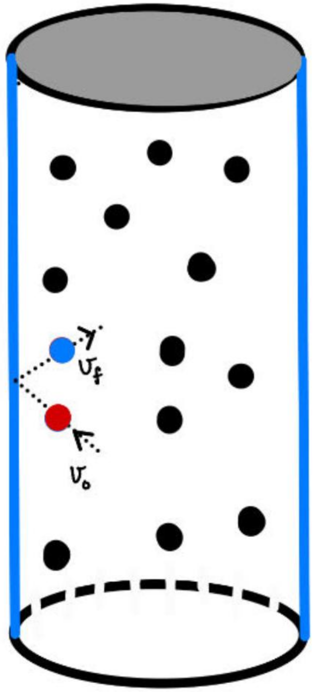
$$\boxed{\Delta U = U_f - U_i = Q - W}$$

1st Law

The First Law of Thermodynamics 3/5



$$\Delta U = Q - W$$



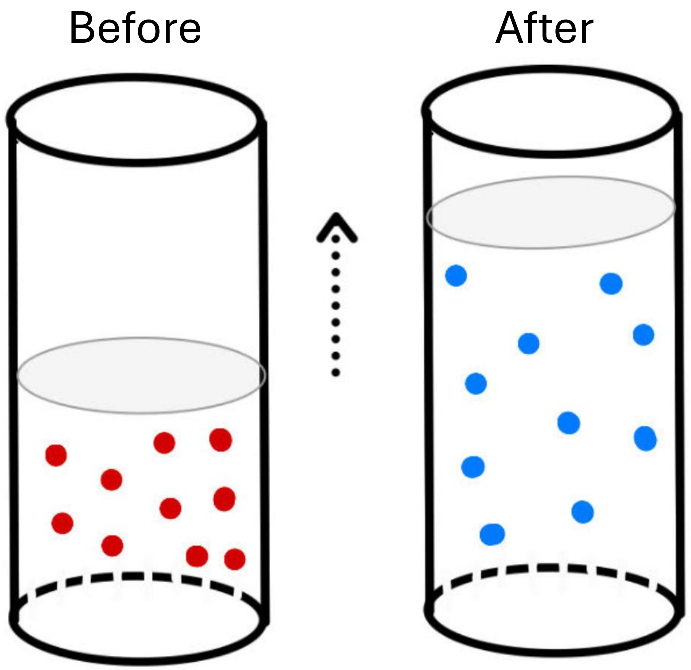
$Q > 0 \rightarrow U \uparrow$: the system gains heat

- particles gain KE from collisions with walls that are warmer than the gas

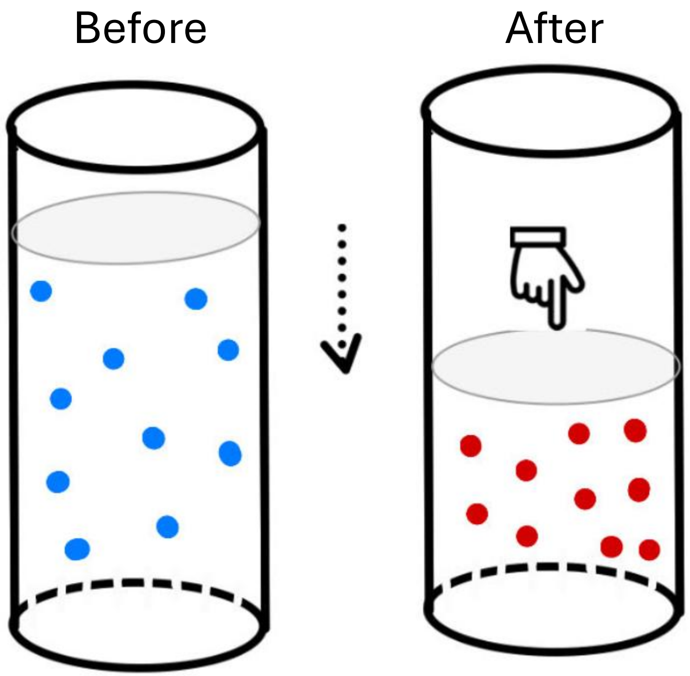
$Q < 0 \rightarrow U \downarrow$: the system loses heat

- particles lose KE from collisions with walls that are cooler than the gas

The First Law of Thermodynamics 4/5



$$\Delta U = Q - W$$



$W > 0 \rightarrow U \downarrow$: work is done by the system

- Particles in the gas push a piston, expanding the gas.

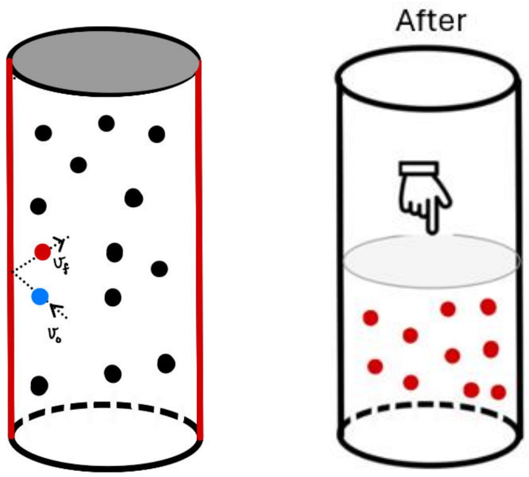
$W < 0 \rightarrow U \uparrow$: work is done on the system

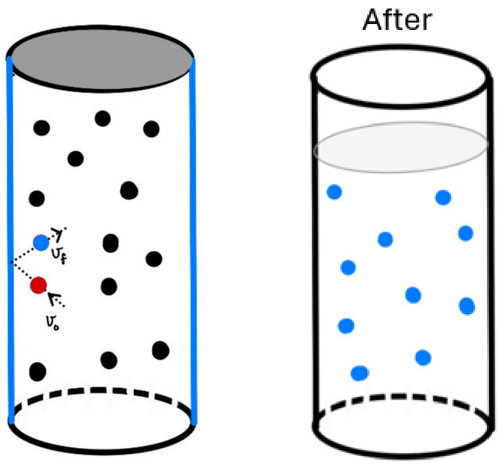
- Push the piston to compress the gas.

The First Law of Thermodynamics 5/5

In both cases, internal energy changes because particle kinetic energy changes.

Heat and work differ not in what happens to the particles, but in **how energy is transferred to or from the system**.

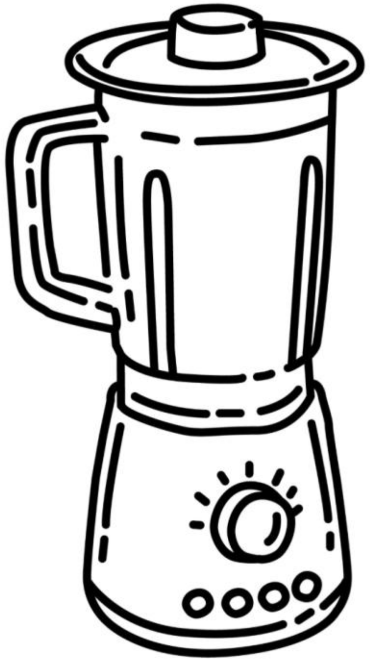




Example: Why does food heat up in a blender?

If you mix food in a blender, the electric motor does work on the system, which consists of food inside the container. This work can noticeably warm up the food. Suppose the blender motor runs at a power of $250\ W$ for $40\ s$. During this time, $2000\ J$ of heat flow from the now-warmer food to its cooler surroundings. By how much does the internal energy of the food increase?

Solution: During the same 40s interval, energy is being added by work and removed by heat transfer,



Work is done on the system: $W < 0$: $W = -\mathrm{P}\Delta T = -(250\ W)(40\ s) = -10000\ J$

Heat is leaving the system: $Q < 0$: $Q = -2000\ J$

The first law: $\Delta U = Q - W = -2000\ J\ - (-10000\ J) = 8000\ J$

The food warms up because more energy is added than removed.

Example: And Ideal Gas

The temperature of three moles of monatomic ideal gas is reduced from $T_i = 540\ K$ to $T_f = 350\ K$ by two different methods with the same initial and final states. In the first method $5500\ J$ of heat flows into the gas, whereas in the second, the gas is cooled while $8000\ J$ of heat flows out. In each case find (a) the change in the internal energy and (b) the work done by the gas.

Solution:

(a) For a monatomic ideal gas, the internal energy depends only on temperature,

$$\Delta U = \frac{3}{2}nR\Delta T = \frac{3}{2}(3.0\ mol)[8.32\ J \cdot (mol \cdot K)^{-1}](350\ K - 540\ K) = -7100 J$$

(same for both processes)

(b) The first law: $\Delta U = Q - W \rightarrow W = Q - \Delta U$.

In the first method, heat flows *into* the gas, so we know that $Q > 0$,

First Method: $W = Q - \Delta U = 5500\ J - (-7100\ J) = 12600\ J$

In the second, heat flows out of the gas so we know $Q < 0$: $Q = -8000\ J$

Second Method: $W = Q - \Delta U = -8000 J - (-7100\ J) = -900\ J$

Sanity Check ✓

$W > 0 \rightarrow U \downarrow$: work is done by the system

$W < 0 \rightarrow U \uparrow$: work is done on the system

State Functions vs. Path Functions

Why did ΔU stay the same in both processes in the previous example problem?

A state function is a property that depends only on the current state of the system, not on how the system got there.

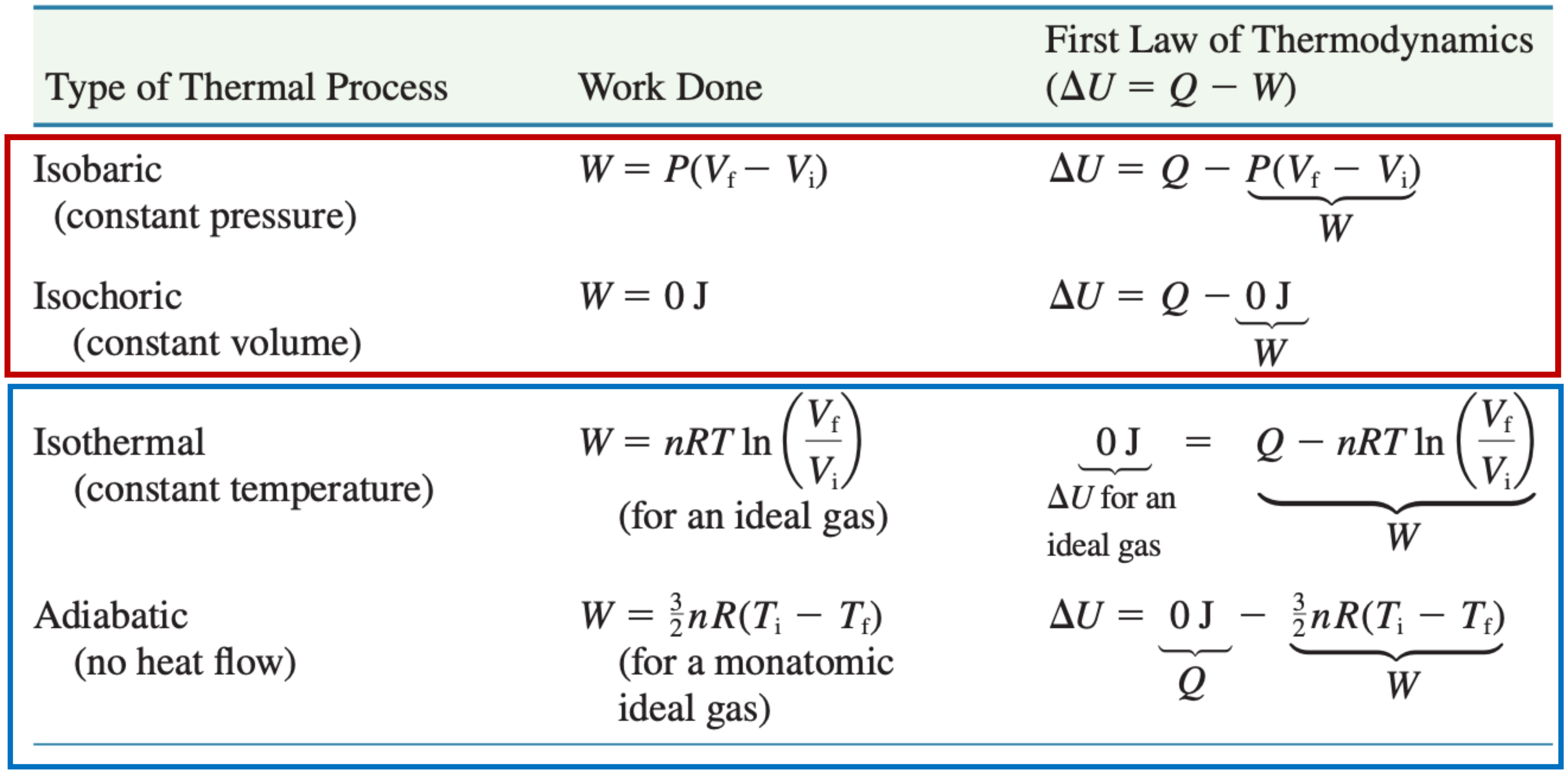
A path function is a quantity that depends on the specific process or path taken between states.

Property	State Function	Path Function
Definition	Depends only on the current state of the system.	Depends on the process used to change the state.
Dependence on path	No	Yes.
Examples	Temperature (T), Pressure (p), Volume (V), Internal Energy (U)	Work (W), Heat (Q)
Calculation	Can be found using only final and initial states, regardless of the process.	Requires knowing the entire process.

Because ΔU is a state function, while Q and W are path functions

"ΔU is about where you are; Q and W are about how you got there." – *Somebody smart*

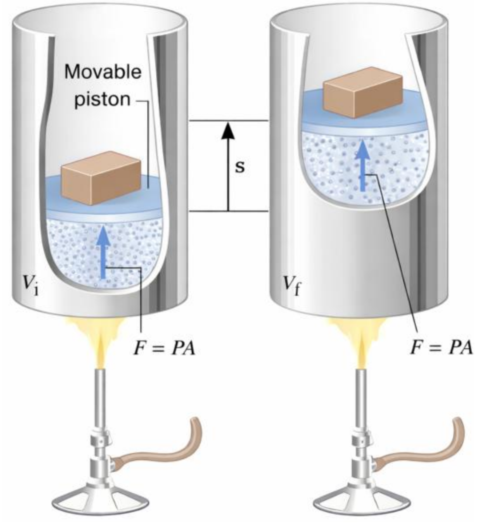
Thermal Processes



Type of Thermal Process	Work Done	First Law of Thermodynamics ($\Delta U = Q - W$)
Isobaric (constant pressure)	$W = P(V_\text{f} - V_\text{i})$	$\Delta U = Q - \underbrace{P(V_\text{f} - V_\text{i})}_{W}$
Isochoric (constant volume)	$W = 0\text{ J}$	$\Delta U = Q - \underbrace{0\text{ J}}_{W}$
Isothermal (constant temperature)	$W = nRT\ln\left(\frac{V_\text{f}}{V_\text{i}}\right)$ (for an ideal gas)	$\underbrace{0\text{ J}}_{\Delta U \text{ for an ideal gas}} = \underbrace{Q - nRT\ln\left(\frac{V_\text{f}}{V_\text{i}}\right)}_{W}$
Adiabatic (no heat flow)	$W = \frac{3}{2}nR(T_\text{i} - T_\text{f})$ (for a monatomic ideal gas)	$\Delta U = \underbrace{0\text{ J}}_{Q} - \underbrace{\frac{3}{2}nR(T_\text{i} - T_\text{f})}_{W}$

Some thermal processes can be analyzed without knowing the equation of state (like the ideal gas law) because one of the variables in the PV diagram is held constant; others cannot, because both P and V change, so we must know how they are related.

Isobaric (Constant Pressure)



The figure shows a substance in a chamber with a frictionless piston. Pressure is constant because it's created by the external atmosphere + the weight of the piston and the block resting on it. Heating the substance makes it expand and do work in lifting the piston and block:

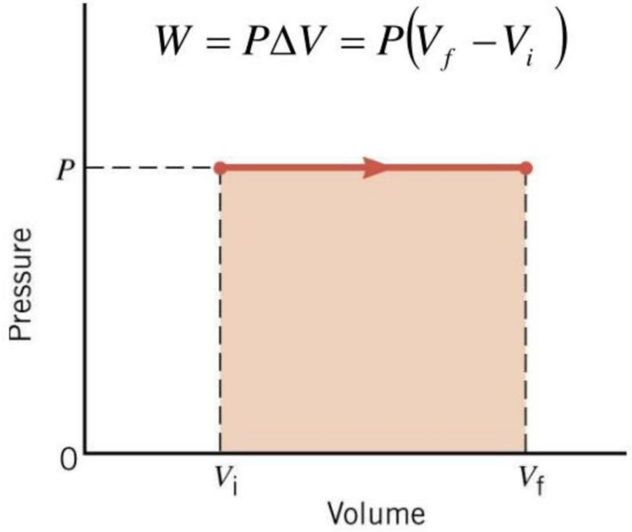
$$W = Fs = (PA)s = P\Delta V = P(V_f - V_i)$$

Work is the area of the shaded region. For an isobaric process, it is a rectangle because the pressure does not change along each volume,

$$W = lh = P\left(V_f - V_i\right) = P\Delta V$$

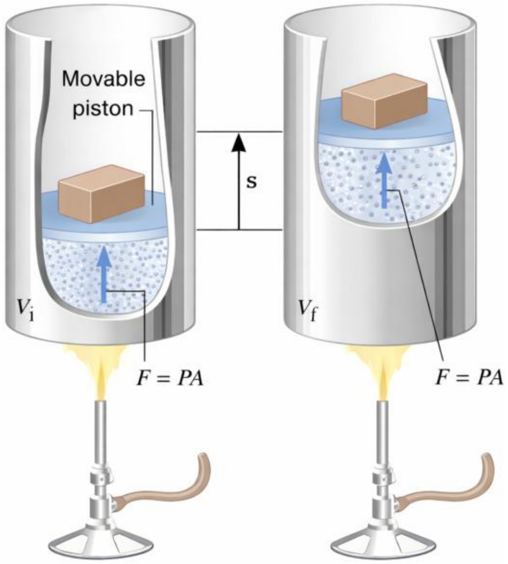
If $V_f < V_i \rightarrow W < 0$: *Work is done on the system (compression),* $U \uparrow$

If $V_f > V_i \rightarrow W > 0$: *Work is done by the system (expansion),* $U \downarrow$



Example: Isobaric Expansion of Water

One gram of water is placed in the cylinder. The pressure is maintained at $2.0 \times 10^5\ Pa$. The temperature of the water is raised by $31^o C$. In one case, the water is in the liquid phase, expands by the small amount of $1.0 \times 10^{-8}\ m^3$, and has a specific heat capacity of $4186\ J \cdot (kg \cdot C^o)^{-1}$. In another case, the water is in the gas phase, expands by the much greater amount of $7.1 \times 10^{-5}\ m^3$, and has a specific heat capacity of $2020\ J \cdot (kg \cdot C^o)^{-1}$. Determine the change in the internal energy of the water in each case.



Solution: Using the 1st law, heat and specific heat capacity, and work done at a constant pressure,

$$\Delta \mathrm{U} = \mathrm{Q} - \mathrm{W} = \mathrm{cm}\Delta T - W = cm\Delta T - p\Delta V$$

$$\Delta U_{liquid} = (4186\ J \cdot (kg \cdot C^o)^{-1})(0.0010\ kg)(31^o C) - (2.0 \times 10^5\ Pa)(1.0 \times 10^{-8}\ m^3) = 130\ J - 0.002\ J = 130\ J$$

$$\Delta U_{gas} = (2020\ J \cdot (kg \cdot C^o)^{-1})(0.0010\ kg)(31\ C^o) - (2.0 \times 10^5 Pa)(7.1 \times 10^{-5}\ m^3) = 63\ J - 14\ J = 49\ J$$

Liquid: Volume change is negligible, so almost all added heat increases internal energy, $W \ll Q \rightarrow \Delta U \approx Q$

Gas: Large volume change means much of the added heat goes into expansion work, $W \sim Q \rightarrow \Delta U < Q$

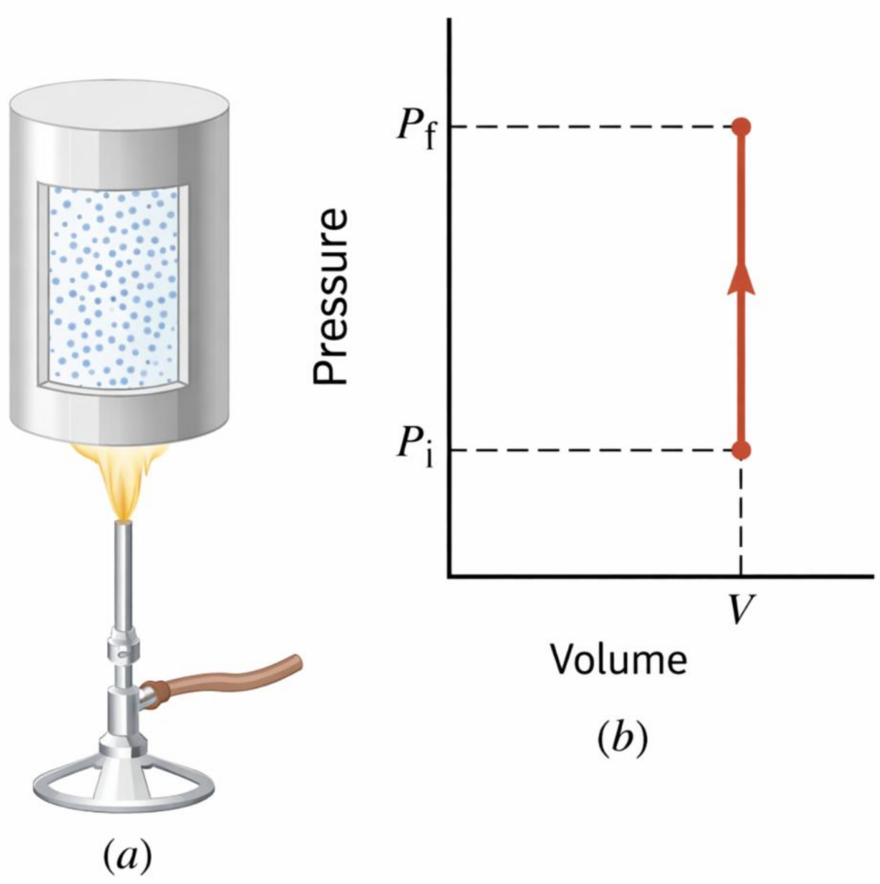
For the liquid, $\Delta V \approx 0 \rightarrow W \approx 0$, approximates an ***isochoric process***.

Isochoric (Constant Volume)

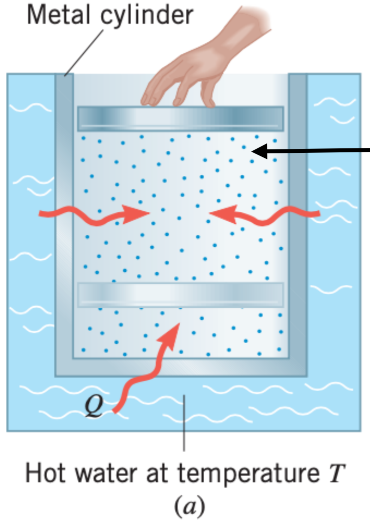
Consider a substance in the chamber shown here. The chamber is rigid and doesn't allow for volume change. So, what gives?

If we analyze with a PV-diagram we see that the pressure dramatically increases but without a volume change, there is no area under it, and therefore there is no work. Recall that $W = F \cdot s$, despite enormous forces that can be generated like this, nothing is moving because the volume isn't changing. So, for an isochoric process,

$$\Delta U = Q - W = Q$$



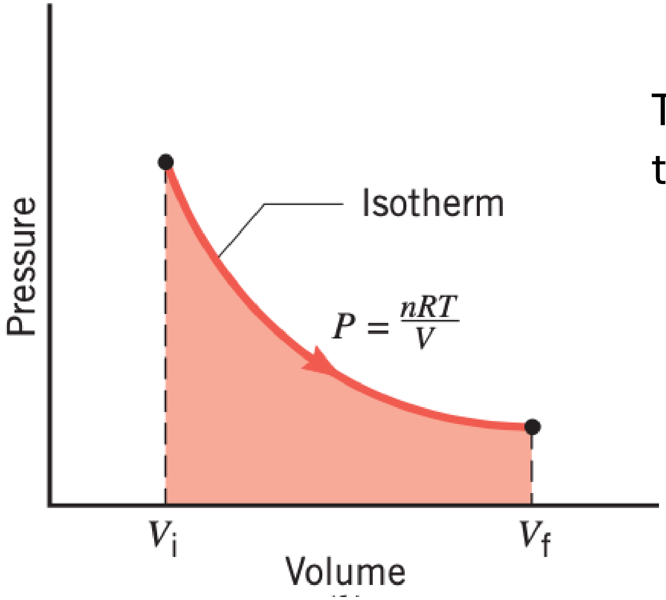
Isothermal (Ideal Gas, Constant Temperature)



n moles of an ideal gas

constant

$$V_i \rightarrow V_f$$
$$P_i \rightarrow P_f$$



The piston is held in place at V_i and then released until it reaches V_f.

$$W \neq P\Delta V \rightarrow P \neq Constant$$

Evident in the area under the curve, no longer a simple rectangle.

Where does the energy to do work come from? Recall $\Delta U = \frac{3}{2}nR\Delta T$ but $\Delta T = 0$

$$\Delta U = Q - W = 0 \rightarrow Q = W$$

It comes from heat transfer!

During expansion, heat flows into the gas from the hot water.

During compression, heat flows out of the gas into the water.

The heat exchange maintains the constant temperature of the gas.

The result comes from calculus by integrating $p = nRT/V$ from $V_i \rightarrow V_f$:

$$\boxed{W = nRTln\left(\frac{V_f}{V_i}\right)}$$

Isothermal expansion or compression of an ideal gas

Example: Isothermal Expansion of and Ideal Gas

Two moles of the monatomic gas argon expand isothermally at 298 K, from an initial volume of $V_i = 0.025\ m^3$ to a final volume of $V_f = 0.050\ m^3$. If argon behaves as an ideal gas, find (a) the work done by the gas, (b) the change in internal energy of the gas, and (c) the heat supplied to the gas.

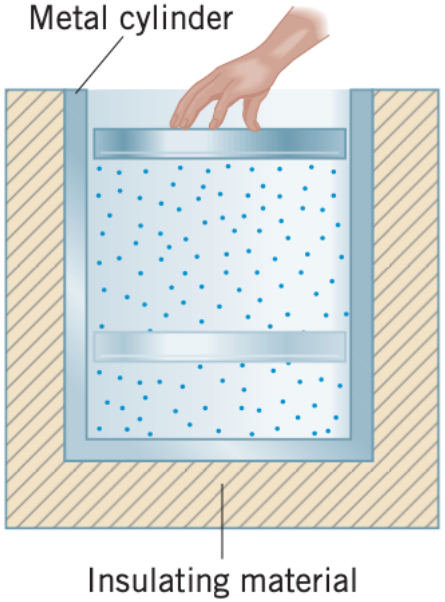
Solution: (a) The work done by the gas is,

$$W = nRTln\left(\frac{V_f}{V_i}\right) = (2.0\ mol)(8.31\ J \cdot (mol \cdot K)^{-1})(298\ K)\left(\frac{0.050m^3}{0.025m^3}\right) = 3400\ J$$

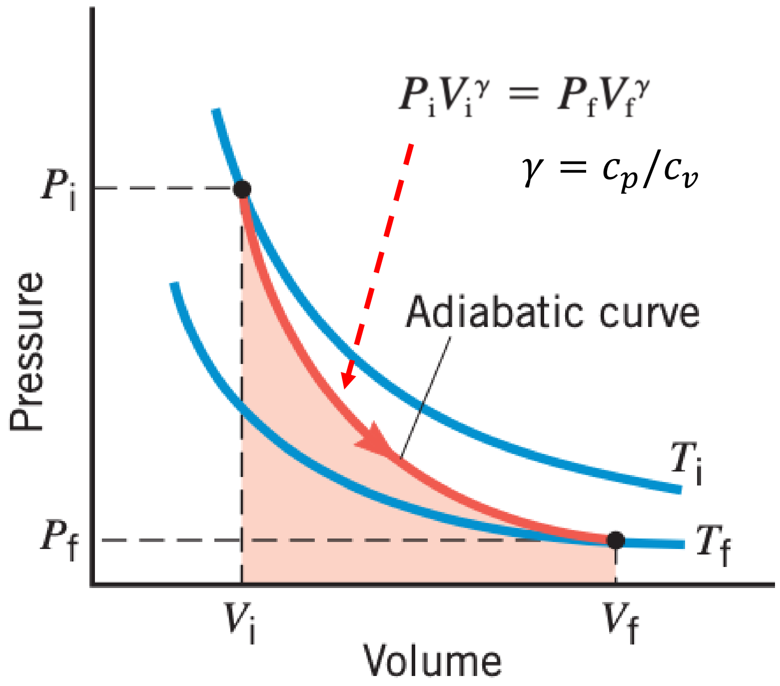
(b) The internal energy of a monoatomic ideal gas is $U = \frac{3}{2}nRT \rightarrow \Delta U = \frac{3}{2}nR\Delta T = 0\ J$ because $\Delta T = 0$

(c) Use the first law: $\Delta U = Q - W \rightarrow Q = \Delta U + W = 0\ J + 3400\ J = 3400\ J$

Adiabatic (no heat flow)



(a)



(b)

Now we insulate the vessel to prevent heat flow $Q = 0$.

The red curve: $P_iV_i^\gamma = P_fV_f^\gamma$, where $\gamma = c_p/c_v$

Each point on the curve satisfies $PV = nRT$

$$\Delta U = Q - W = 0 - W = -W$$

Recall that for a monatomic ideal gas,

$$\Delta U = \frac{3}{2}nR\Delta T = -W$$

$$W = -\frac{3}{2}nR(T_f - T_i)$$

or

Adiabatic expansion or compression of a monatomic ideal gas

$$\boxed{W = \frac{3}{2}nR(T_i - T_f)}$$

1st Law and Specific Heat Capacities for Ideal Gasses

Molar Heat Capacity J/(mol K)

$$Q = cm\Delta T \xrightarrow[\substack{n\ =\ m\,/M_{mol} \\ C\ =\ cM_{mol}}]{\textit{Molar Equivalent}} Q = \overset{\downarrow}{C}n\Delta T$$

Heat needed $T_i \rightarrow T_f$: $\Delta U = Q - W \rightarrow Q = \Delta U + W = \frac{3}{2}nR\left(T_f - T_i\right) + \mathrm{W}$

Isobaric: $Q_p = \frac{3}{2}nR\left(T_f - T_i\right) + P\left(V_f - V_i\right) = \frac{3}{2}nR\left(T_f - T_i\right) + nR\left(T_f - T_i\right) = \frac{5}{2}nR\left(T_f - T_i\right)$

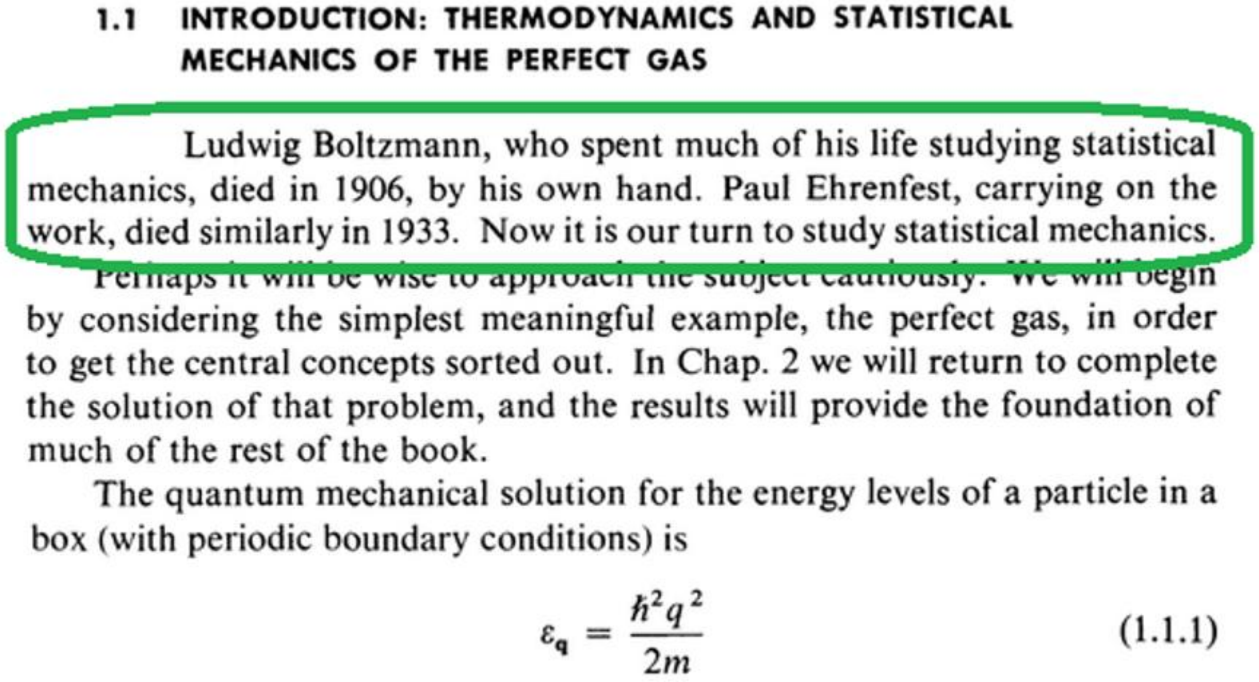
$$= C_p n\left(T_f - T_i\right) \rightarrow C_p = \frac{5}{2}R$$

Isochoric: $Q_V = \frac{3}{2}nR\left(T_f - T_i\right) = C_V n\left(T_f - T_i\right) \rightarrow C_V = \frac{3}{2}R$

$$\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = \frac{5}{3}$$

Thermodynamics and Statistical Mechanics

- There's a long-standing joke among physicists that statistical mechanics is the subject where thermodynamics finally admits it needs probability. Boltzmann spent his life trying to convince people that irreversible macroscopic laws could arise from reversible microscopic ones.
- He was right—but it took decades for the community to fully accept it.



1.1 INTRODUCTION: THERMODYNAMICS AND STATISTICAL MECHANICS OF THE PERFECT GAS

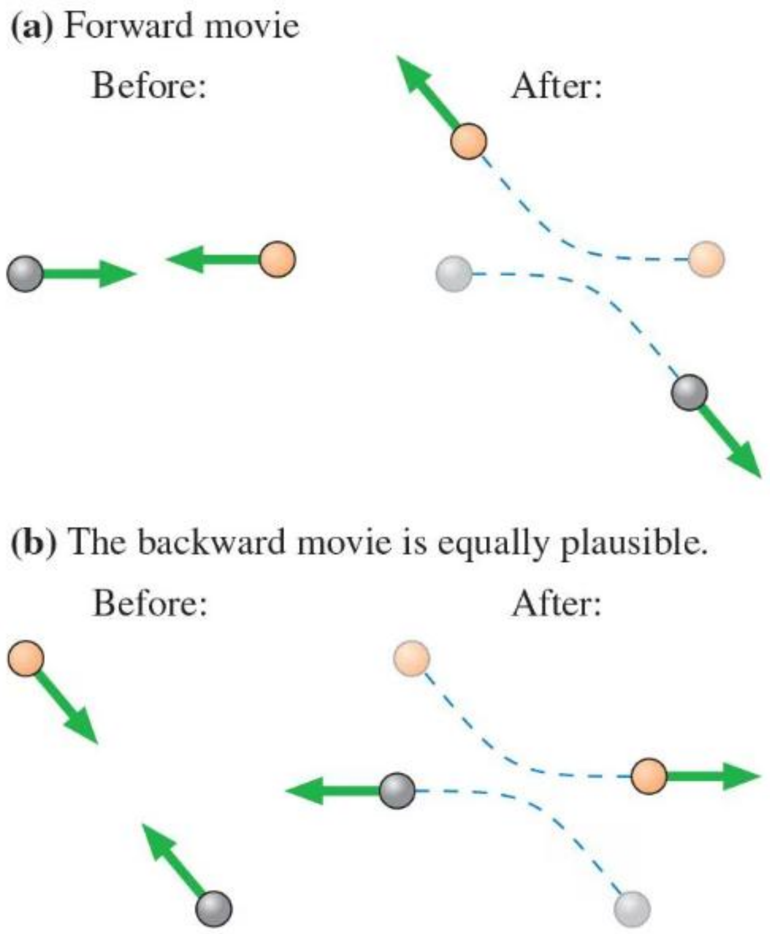
Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously. We will begin by considering the simplest meaningful example, the perfect gas, in order to get the central concepts sorted out. In Chap. 2 we will return to complete the solution of that problem, and the results will provide the foundation of much of the rest of the book.

The quantum mechanical solution for the energy levels of a particle in a box (with periodic boundary conditions) is

$$\varepsilon_{\mathbf{q}} = \frac{\hbar^2 q^2}{2m} \tag{1.1.1}$$

Reversible Processes



At a microscopic level, collisions between molecules are completely reversible. Let's consider two possible “movies” of a collision between two gas molecules.

The first one is forward, two molecules move toward each other along a horizontal path, collide slightly off center, and move off into antiparallel diagonal paths.

Let’s play this movie backwards. Now we have two molecules moving toward each other, along our diagonal path, they collide slightly off center, sending them along a horizontal path, away from each other.

Nothing in either collision looks wrong, and no measurements you might make on either would reveal any violations of Newton’s laws, or any other law we have learned thus far.

Interactions at a molecular level are ***reversible***.

Irreversible Processes

At a macroscopic level, it’s a different story. Here we see two possible “movies” of the collision of a car with a barrier.

The first one, the car is moving toward the wall and collides with it.

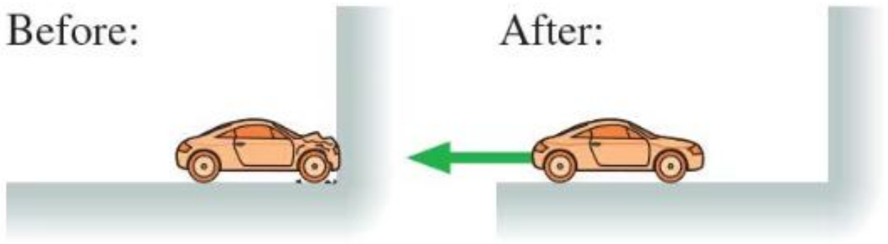
In the second one, the car starts in a “crashed state” , returns to its original shape, and springs away from the wall.

This is clearly ***irreversible***. For this to happen would be absurd but what law does this violate that we have encountered so far?

If microscopic motions are all reversible, how can macroscopic phenomena like the car crash be irreversible?

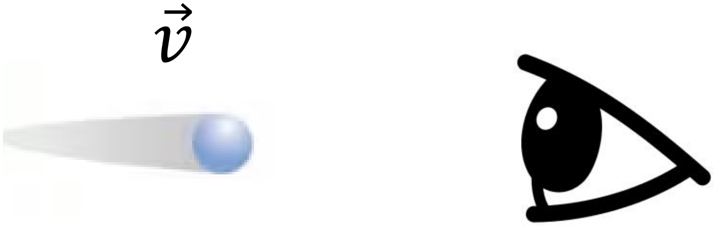
(a) Forward movie

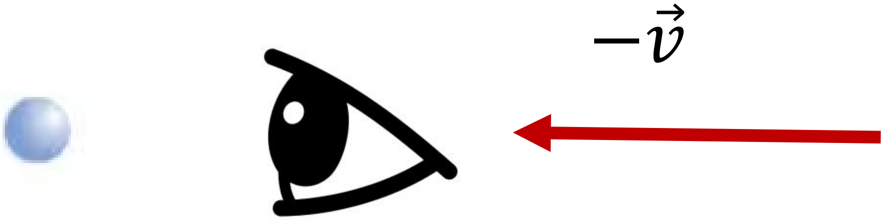
(b) The backward movie is physically impossible.



Does a single particle have internal energy?

Imagine that you are in a void in space, no stars, nothing. A particle seems to move past you.





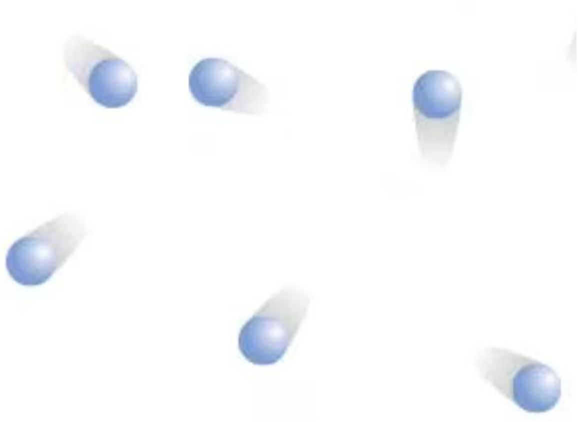
You measure the kinetic energy: $\frac{1}{2}mv^2$

This measurement was made in your stationary frame. That is, you consider yourself motionless, and the particle is in motion.

But how would you know that you are the one that is moving and the particle is stationary. If we consider that scenario, in the particle's stationary frame, it is us that has some velocity, moving with some kinetic energy $\frac{1}{2}mv^2$

Kinetic energy of a single particle is not internal energy, because it depends on the reference frame and can be eliminated by choosing a different frame.

What changes when you have many particles?



For a gas with $N \gg 1$ particles,

$$K_i = \frac{1}{2} m v_i^2$$

But now two crucial things happen:

1. There is no single velocity that represents the system, but we can consider a center of mass velocity, the total mass for $N = 5$ identical particles with mass m is $M = 5m$ and its center of mass velocity,

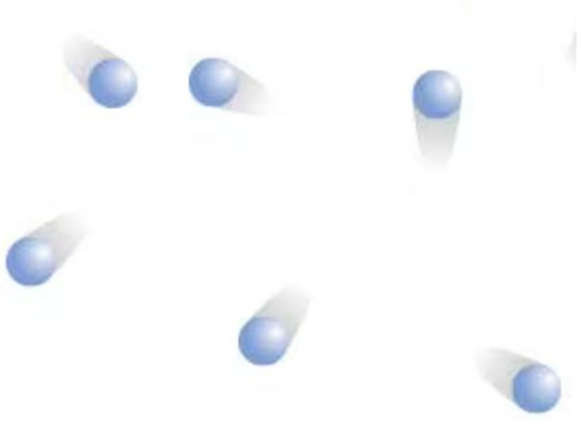
$$\vec{V}_{cm} = \frac{\vec{v}_1 + \vec{v}_2 + \cdots + \vec{v}_5}{5} = \frac{1}{5} \sum_{i=1}^{5} \vec{v}_i$$

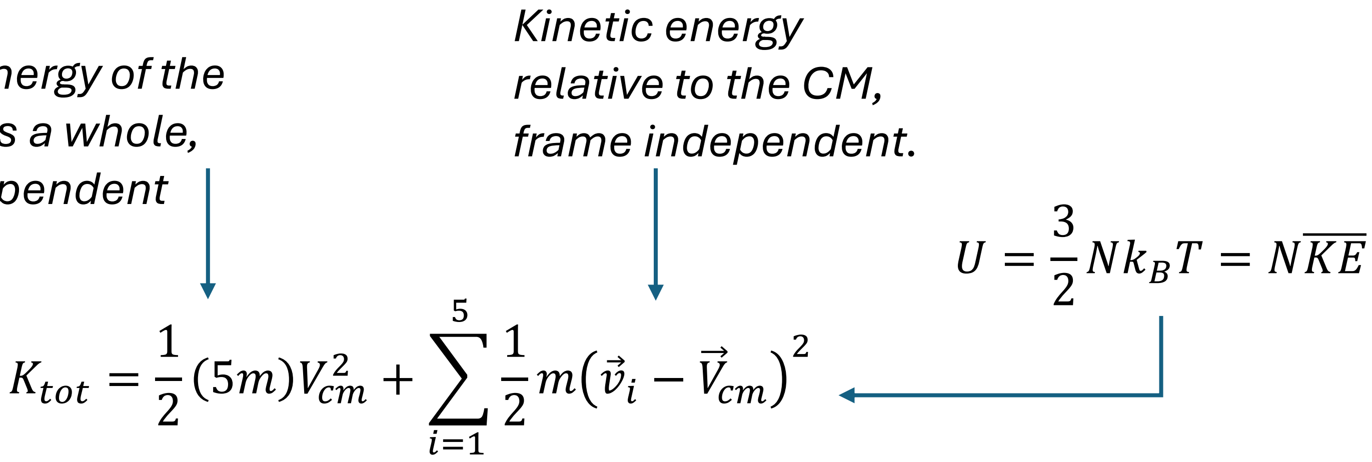
We can define each particle's velocity relative to the center of mass, $\vec{u}_i = \vec{v}_i - \vec{V}_{cm}$. The total kinetic energy:

$$K_{tot} = \sum_{i=1}^{5} \frac{1}{2} m v_i^2 = \sum_{i=1}^{5} \frac{1}{2} m \left(\vec{u}_i + \vec{V}_{cm}\right)^2 = \sum_{i=1}^{5} \frac{1}{2} m \left(u_i^2 + 2\vec{u}_i \cdot \vec{V}_{cm} + V_{cm}^2\right)$$

$$= \sum_{i=1}^{5} \frac{1}{2} m u_i^2 + \sum_{i=1}^{5} \frac{1}{2} m \left(2\vec{u}_i \cdot \vec{V}_{cm}\right) + \sum_{i=1}^{5} \frac{1}{2} m V_{cm}^2 = \sum_{i=1}^{5} \frac{1}{2} m u_i^2 + \frac{1}{2}(5m) V_{cm}^2 = \frac{1}{2}(5m) V_{cm}^2 + \sum_{i=1}^{5} \frac{1}{2} m \left(\vec{v}_i - \vec{V}_{cm}\right)^2$$

Internal energy comes from relative motion!





Kinetic energy of the system as a whole, frame dependent

Kinetic energy relative to the CM, frame independent.

$$U = \frac{3}{2}Nk_BT = N\overline{KE}$$

$$K_{tot} = \frac{1}{2}(5m)V_{cm}^2 + \sum_{i=1}^{5}\frac{1}{2}m\left(\vec{v}_i - \vec{V}_{cm}\right)^2$$

In kinetic theory when you say $U = \frac{3}{2}Nk_BT = N\overline{KE}$, what this really means is that the internal energy of the gas equals the sum of the kinetic energies of particles measured relative to the center-of-mass motion.

Internal energy is not the kinetic energy of a particle—it is the kinetic energy **spread across many particles in many directions**.

Energy is accessible for organized work if it can be reliably converted into a controlled, macroscopic motion without coordinating microscopic details.

Back to the car crash

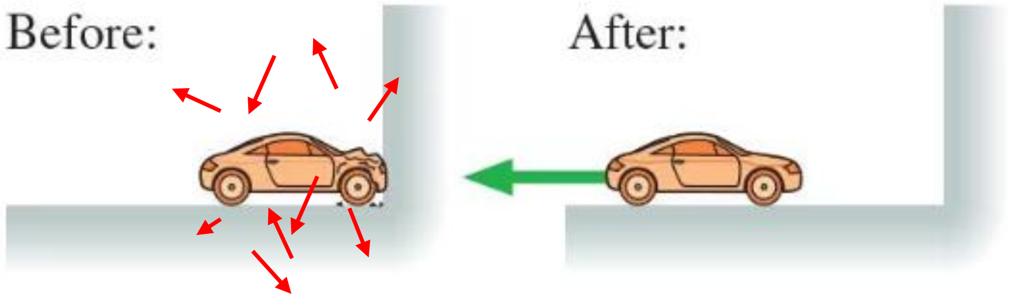
$$K_{tot} = \frac{1}{2}(5m)V_{cm}^2 + \sum_{i=1}^{5}\frac{1}{2}m\left(\vec{v}_i - \vec{V}_{cm}\right)^2$$

Before the crash, the car's energy is stored almost entirely in the motion of its center of mass. All of the particles in the car are moving in nearly the same direction at nearly the same speed. Their associated forces aggregated $\vec{F}_{\text{net}}$ are oriented in whole or part toward the same direction $\vec{s}$

$$W = \vec{F}_{net} \cdot \vec{s}$$

(a) Forward movie

(b) The backward movie is physically impossible.



During the crash, that energy is redistributed into many internal motions: vibrations, bending, heating, sound, and microscopic motion of particles in many different directions.

Enormous forces still exist internally, but because they act in many directions and over very short distances, they do not produce a sustained force on the car as a whole. Even though the total energy is still there, it can no longer make the car move forward, lift a weight, or turn a wheel. To reverse the crash, the internal motions of trillions of particles would have to spontaneously coordinate in just the right way.

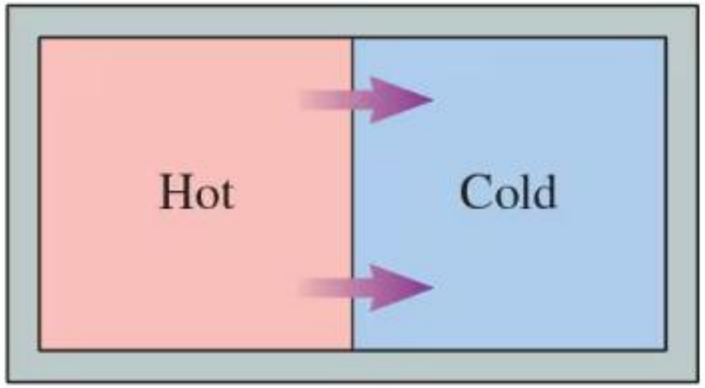
Recap on Reversible/Irreversible Processes

- Microscopic laws are reversible
- Macroscopic systems contains enormous internal degrees of freedom (the independent ways a system's particles can move or store energy).
- Energy naturally spreads into relative motion
- Once spread, energy no longer produces coordinated motion

If energy spreads this way inside objects, what happens when two objects at different temperatures are placed in contact?

So why HOT → COLD?

Internal energy is already stored in many microscopic motions, but with ***larger*** average relative speeds



Internal energy is already stored in many microscopic motions, but with ***smaller*** average relative speeds

larger $\overline{KE}$ of relative motion

Smaller $\overline{KE}$ of relative motion

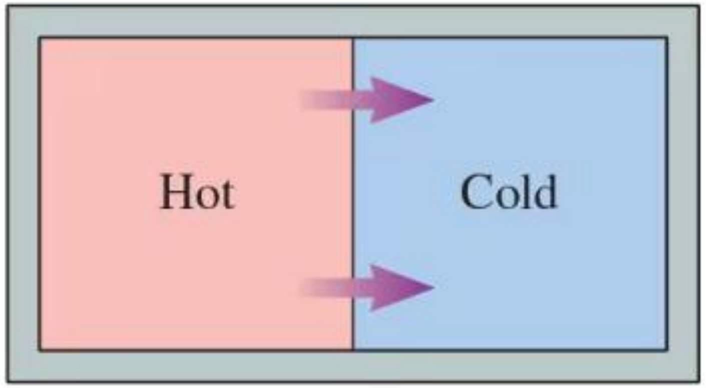
Imagine tracking just one fast particle from the hot side as it enters the cold side. It will collide with many slower particles. Each collision slightly reduces its speed and slightly increases the speeds of several others.

For the fast particle to regain its original speed, all those surrounding particles would have to collide with it in just the right sequence. That is mechanically allowed – but extremely unlikely.

As a result, while individual collisions can move energy in either direction, most collisions produced outcomes that reduce large speed differences.

HOT → COLD?

Zooming out from individual collisions to the behavior of the system as a whole:



When all possible microscopic arrangements are considered, there are vastly more ways for energy to be shared between both objects than for it to remain concentrated in the faster motions of the hot object.

This is the same as the car crash logic:

Few coordinated state → vastly many uncoordinated states

When the energy spreads from hot to cold, it becomes shared among even more particles and directions, making it even less able to produce coordinated motion.

Hot → Cold is *further spreading of internal energy,* and *further spreading makes energy less recoverable for organized work!*

Entropy

We need a way to quantify how spread-out internal energy is.

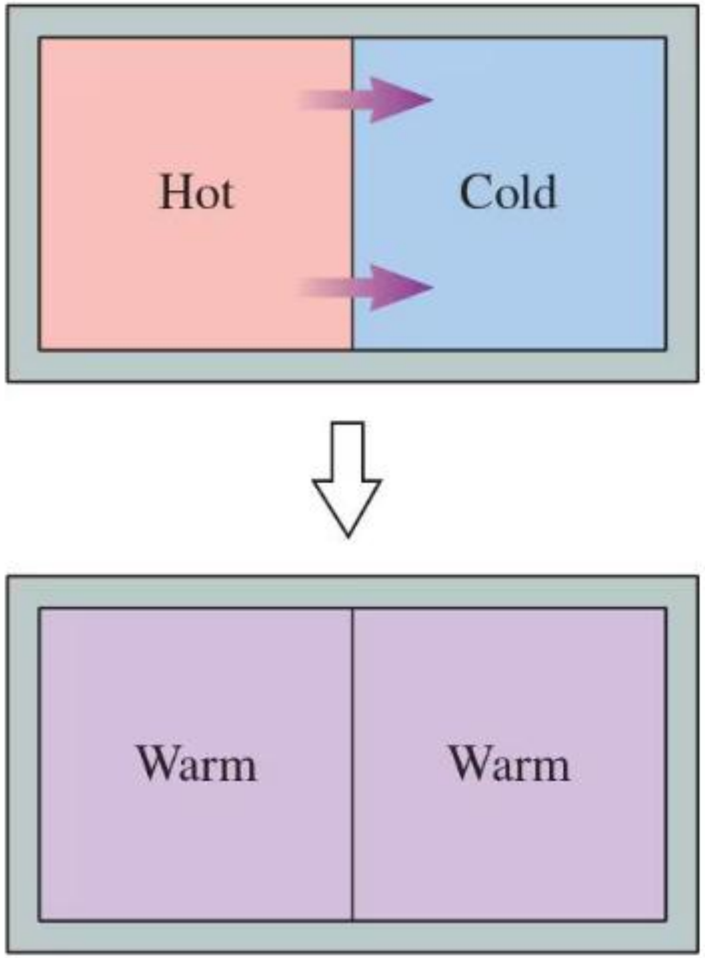
Entropy is defined for a specified system and depends on how energy is distributed within that system.

A system in which energy is concentrated in fewer internal degrees of freedom has ***low entropy***. In the hot–cold state, energy is unevenly distributed and constrained: a subset of particles in one object have access to larger speeds, while the other subset does not.

A system in which energy is more spread out across more particles and relative motions has ***high entropy***. At equilibrium, the same total energy is free to be distributed across *all* particles and motions in both objects without constraint.

The initial state, right when the hot object touches the cold object, represents a lower entropy state of the two-object system. The internal energy becomes more spread out, increasing entropy, until thermal equilibrium, where the entropy of the system is maximum and the system is most likely to be found at.

low entropy



thermal equilibrium → maximum entropy

The Second Law of Thermodynamics

The observation that internal energy spreads and that macroscopic systems evolve irreversibly toward equilibrium is captured by a fundamental law of physics: the Second Law of Thermodynamics.

Second Law of Thermodynamics:
The entropy of an isolated system never decreases. It either increases as the system evolves toward equilibrium or, if the system is already in equilibrium, remains constant. Entropy is maximum when the system is in equilibrium.

What do we mean by an Isolated System?

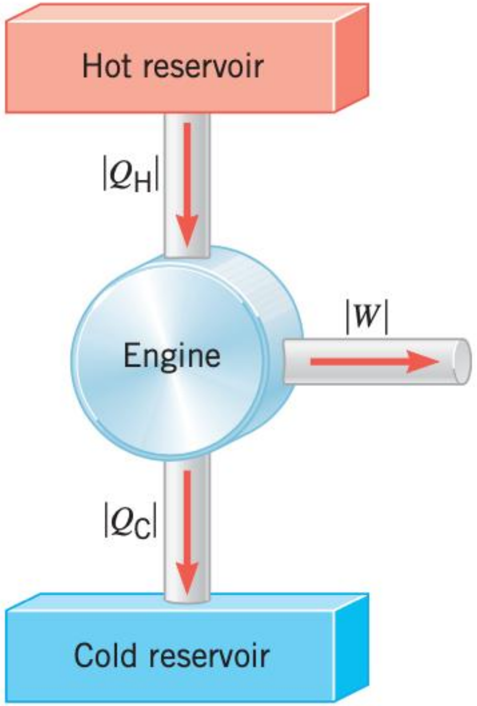
- In thermodynamics, a system is called *isolated* if no energy or matter enters or leaves the system.
- This does not mean the system is perfectly sealed or completely unaffected by its surroundings.
- It means that, for the process we are analyzing, all energy transfers are contained within the system.
- When a system is isolated, energy can still be redistributed internally among its particles and degrees of freedom – but the total energy remains fixed.
- In non-isolated systems, the entropy of a subsystem can decrease – but only if the entropy of the surroundings increases by a greater amount.
    - Ice cubes in your freezer – ice is lower entropy than water, but entropy is increased at the power plant supplying electricity to your refrigerator.

Heat Engines

A **heat engine** is an idealized energy-flow device that converts heat extracted from a hot reservoir into work while rejecting heat to a cold reservoir. It is not an actual machine – it has no pistons, cylinders, or fuel. It is defined only by:

1. **Hot Reservoir** – Supplies heat (Q_H) at a high temperature.
2. **Working Substance** – Uses part of the heat to perform work, W
3. **Cold Reservoir** – Releases the remaining heat, Q_C, at a lower temperature.

A heat engine is a bookkeeping framework for energy and entropy.



The first law tells us,

$$|Q_H| = |W| + |Q_C|$$

This is just energy conservation. In the real world, there are limitations.

The **efficiency** (e) of a heat engine is the ratio of the work output (W) to the input heat (Q_H), or how much of the energy transferred from the hot reservoir yields accessible work:

$$e = \frac{|W|}{|Q_H|}$$

$$e = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

But what constrains the ratio $\frac{|Q_C|}{|Q_H|}$?

Carnot's Principle

$$e = 1 - \frac{|Q_C|}{|Q_H|}$$

Reversible Engine: *An ideal engine that operates with no energy loss and can run forward or backward without increasing entropy. It is the most efficient engine possible representing a benchmark.*

$$\frac{|Q_C|}{|Q_H|} = 0$$

Irreversible Engine: *A real-world engine where energy is lost due to friction, heat loss, and inefficiencies. It cannot be perfectly reversed and is less efficient than a reversible engine.*

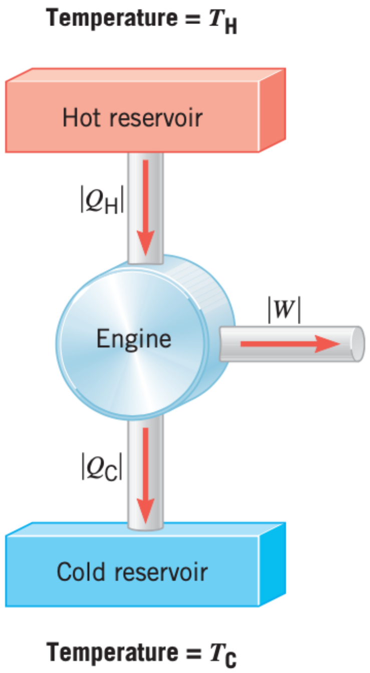
$$\frac{|Q_C|}{|Q_H|} > 0$$

Carnot's Principle: An Alternative Statement of the Second Law of Thermodynamics

No irreversible engine operating between two reservoirs at a constant temperature can have a greater efficiency that a reversible engine operating between the same temperatures. Furthermore, all reversible engines operating between the same temperatures have the same efficiency.

Carnot Engine

No real engine is truly reversible, but a reversible engine serves as a useful benchmark for evaluating real engine performance. The most efficient heat engine cycle is the Carnot cycle, consisting of two isothermal processes and two adiabatic processes. Use ideal gas to analyze! Temperatures must be in KELVIN



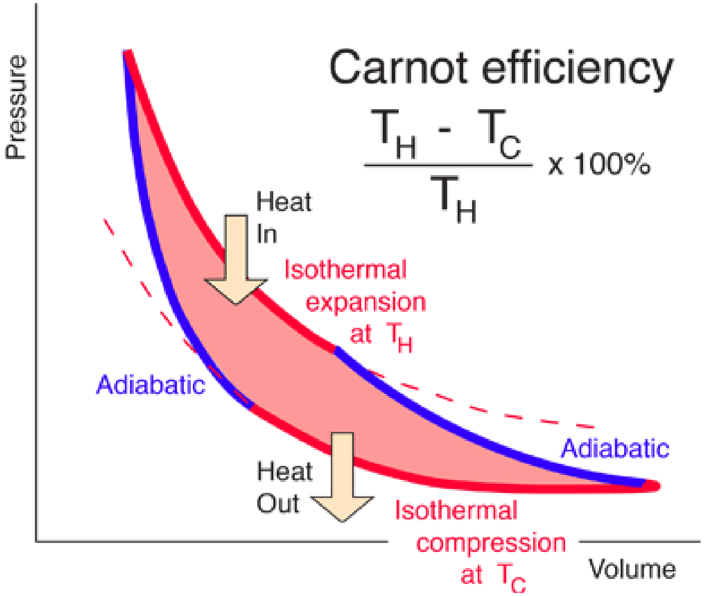
The Carnot cycle:

1. Isothermal expansion at T_H (absorb Q_H)
2. Adiabatic expansion (drop from $T_H \rightarrow T_C, Q = 0$)
3. Isothermal compression at T_C (reject Q_C)
4. Adiabatic compression ($T_C \rightarrow T_H, Q = 0$)

First Law: $\Delta U = Q - W \rightarrow Q = \Delta U + W$

For and ideal gas: $U = \frac{3}{2}nRT \rightarrow \Delta U = 0 \; if \; T = constant$

Equation of State: $PV = nRT$



So, for an isothermal step: $Q = 0 + W = W$, for and adiabatic step $\Delta U = -W = \frac{3}{2}nR\Delta T$

Using these relationships and calculus, it can be shown that

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \rightarrow e_{carnot} = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$

No engine, not even a theoretical one, can reach $e = 1$ because that would require $T_C = 0\;K$ which is unattainable (3rd Law of Thermodynamics). But why?

We already know why! Entropy!

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \rightarrow \frac{|Q_C|}{T_C} = \frac{|Q_H|}{T_H} \rightarrow \Delta S \equiv \left(\frac{Q}{T}\right)_{rev}$$

When heat leaves the hot reservoir, energy spreads internally in a way that work alone cannot undo (like a car crash).

For the process to be reversible, that “spread” must be exported somewhere else. The cold reservoir is the only place it can go. A reversible heat engine MUST dump entropy in the cold reservoir! So,

$$\Delta S_{dumped} = \frac{Q_H}{T_H} > 0$$

But $Q = T\Delta S$, and for $T = 0 \rightarrow Q = 0$ for any finite ΔS which means that a system at 0 K cannot absorb entropy at all! So, we can restate the third law we stated at the beginning of the lecture:

The Third Law of Thermodynamics: As temperature approaches zero, systems lose the ability to absorb entropy.

The Entropy of the Universe

Using the Carnot engine as a benchmark and rearranging,

$$\frac{|Q_C|}{T_C} = \frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H} = 0 \rightarrow \Delta S_C - \Delta S_H = 0$$

A reversible process produces no net entropy change in the universe. But reversible processes do not occur in nature as we've seen $(e < 1)$. If even the best possible process produces zero entropy change, then any real process must produce more, and so every real process increases the entropy of the universe,

$$\Delta S_{universe} \geq 0$$

Example: Heat Transfer from Hot to Cold

Suppose $100\ J$ of heat flows from a hot reservoir at $500\ K$ to a cold reservoir at $300\ K$. Determine the amount by which this irreversible process changes the entropy of the universe, assuming that no other changes occur.

Solution: The hot-to-cold heat flow is irreversible, so the relationship $\Delta S = (Q/T)_R$ is a hypothetical process whereby the $1200\ J$ heat is taken reversibly from the hot reservoir and added reversibly to the cold reservoir.

$$\Delta S_{universe} = \Delta S_{hot} + \Delta S_{cold} = -\frac{100J}{500K} + \frac{100J}{300K} = -0.2\ J \cdot K^{-1} + 0.333\ J \cdot K^{-1} = 0.133\ J \cdot K^{-1} > 0$$

The actual heat flow is irreversible, but entropy change is a state property. That means we can replace the real process with any convenient reversible path that produces the same initial and final states, and the entropy change will be the same. ΔS → state function that only depends on the initial and final states, whereas reversibility and irreversibility describe the path taken between those states. This is why an irreversible process can be analyzed using a hypothetical reversible path.

State Functions vs. Path Functions Updated

A state function is a property that depends only on the current state of the system, not on how the system got there.

A path function is a quantity that depends on the specific process or path taken between states.

Property	State Function	Path Function
Definition	Depends only on the current state of the system.	Depends on the process used to change the state.
Dependence on path	No	Yes.
Examples	Temperature (T), Pressure (p), Volume (V), Internal Energy (U), Entropy (S)	Work (W), Heat (Q)
Calculation	Can be found using only final and initial states, regardless of the process.	Requires knowing the entire process.

This is why entropy change can be calculated using a reversible path even when the actual process is irreversible.

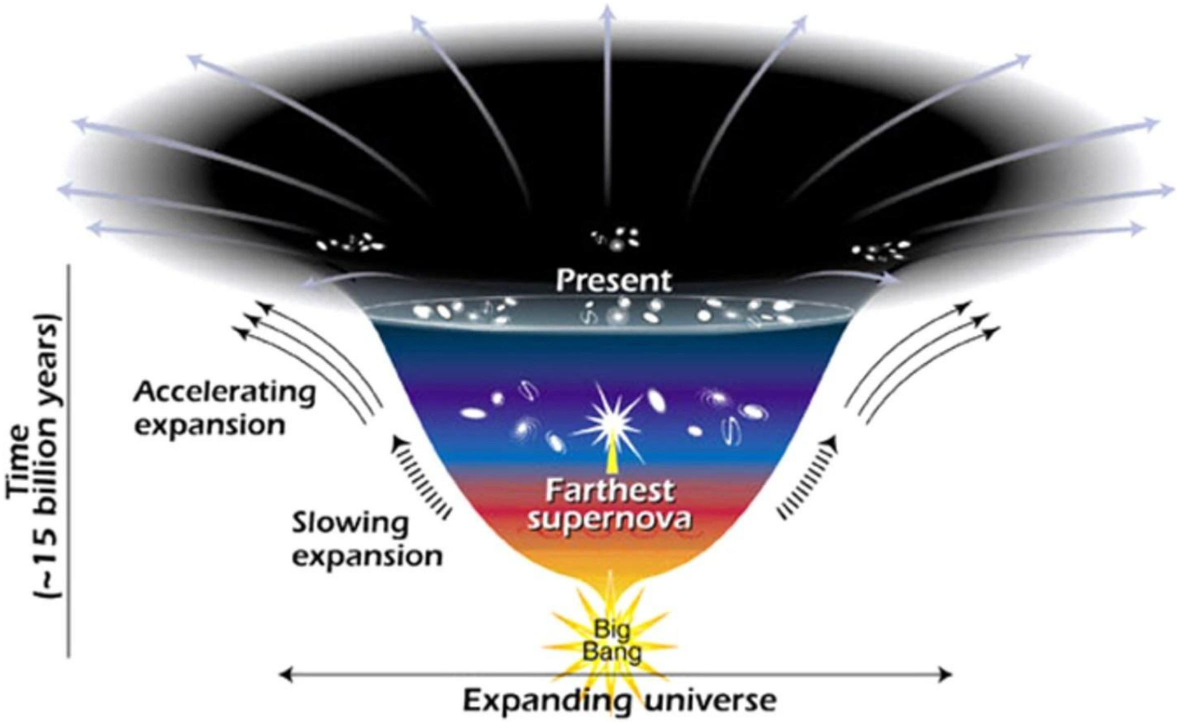
Entropy is about the state; reversibility is about the path. This is why entropy change can be calculated using a reversible path even when the actual process is irreversible.

The Heat Death of the Universe

The universe is one big heat engine with

- Stars, planets, chemistry, life → all rely on energy flowing from hot to cold.
- All that flow produces entropy
- All of it reduces temperature gradients.

Heat death is the state where the universe, if isolated, has reached maximum entropy, so there are no temperature differences left to drive any processes requiring work.



Entropy and the Arrow of Time

- In the past, the universe had more energy arranged in ways that could do work.
- As real processes occur, entropy increases and that energy becomes more spread out.
- As a result, less energy can be coordinated to do work, causing physical processes to run in one direction — the arrow of time.
- Up to now, we have used time operationally:
  - Time orders processes
  - Time is what clocks measure
  - Time distinguishes before from after
- Time is usually treated as a dimension with only one direction. But in a universe of maximum entropy, no physical process would exist to distinguish one moment from the next.
- This raises a deep question: is time fundamentally a dimension, or is it simply our observation of entropy increasing?
- ***The answer is: we don’t know.***