

Introduction to Thermodynamics

- Laws
- First Law of Thermodynamics (closed system)
- Differentials and State Functions
- Paths of PV Work

Definitions

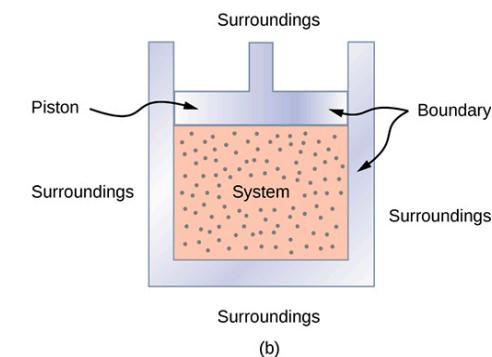
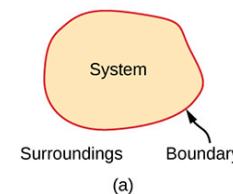
System:

Part of the universe we are interested in. (**SYSTEM MUST BE LARGE relative to molecular dimension**)

Surrounding: Everything else

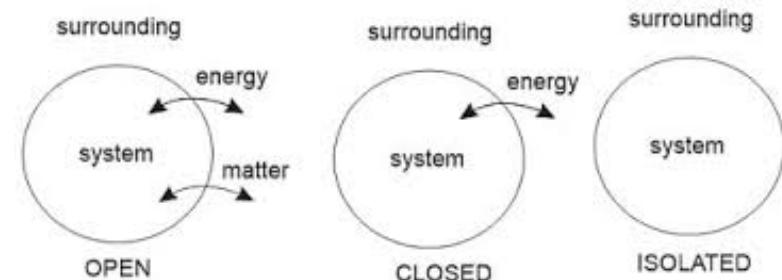
Boundary: Separate System and Surrounding

Universe: System + Surrounding



Types of Systems

1. Open
2. Closed
3. Isolated



Properties of the System:

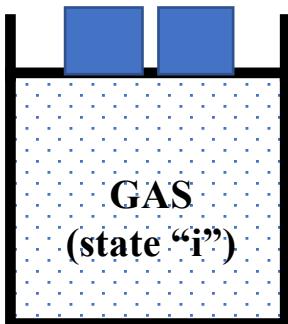
Measurable macroscopic quantities characteristic of the system. (at EQUAILIBRIUM)

Types of Properties :

1. Intensive (*Mass independent*) : Temperature, Pressure, density etc
2. Extensive (*Mass dependent*): Mass, Volume, number of particles etc

EQUILIBRIUM:

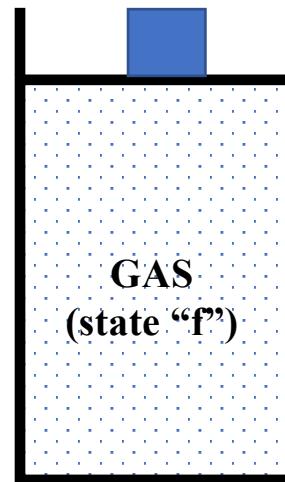
Macroscopic property not changing



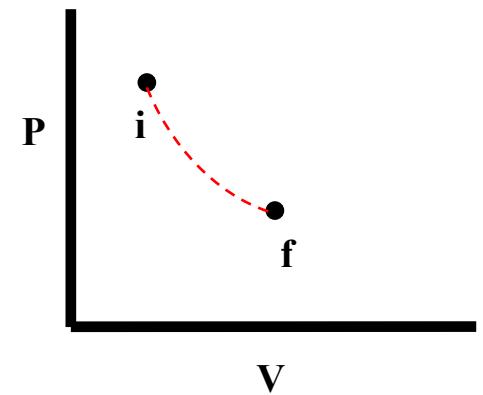
Temperature NOT DEFINED

You are no longer in
the PV plot

- Fixed Temp (T) and Pressure (P)



- New Temp (T') and pressure (P')



THE STATE OF THERMODYNAMIC EQUILIBRIUM:

When properties of the system remain fixed over time, the system is said to be at “Thermodynamic equilibrium”.

Thermodynamic equilibrium involves three kinds of equilibrium:

1. Mechanical equilibrium:

Pressure of the system (P) is uniform and is equal to the surrounding. Pressure of the system determine “P” determines the equilibrium.

2. Thermal equilibrium:

Temperature of the system (T) is uniform and is equal to the surrounding. Temperature of the system determine “T” determines the equilibrium.

3. Chemical equilibrium:

Composition of the system is uniform and does not change over time. *Thus, for pure system the equation of chemical equilibrium does not arise.*

Laws of Thermodynamics

1. Zeroth Law: $T_a = T_b$, $T_b = T_c$ then $T_a = T_c$.

Define Thermal equilibrium and provide means of measuring temperature.

2. First Law: Energy can have different forms but the total energy is conserved.

Energy conservation and define internal energy.

3. Second Law: **Introduce entropy** and explain directional of a process.

4. Third Law: *The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0K). Define absolute zero of “entropy”.*

What First Law can address:

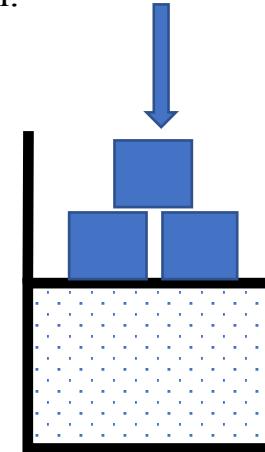
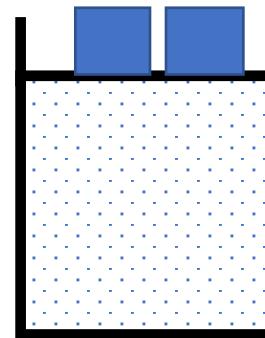
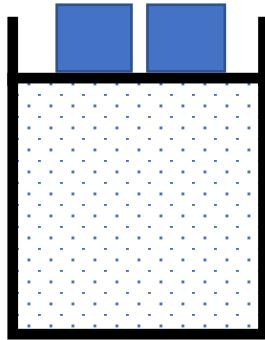
Whether a gas will cool upon expansion ?

Calculate the energy changes for chemical reactions.

How much heat will be released from a chemical reaction.

First Law of Thermodynamics

Conservation of energy: Energy can not be created or destroyed, but can change its form.



Internal Energy
 $U = KE + PE$



Work (w)

$$\Delta U = q + w$$

State Function

Path Function

Energy change can produce heat and work

STATE FUNCTIONS

A *state function* is a property that depends only upon the state of the system. That is, it is independent of how the system was brought to that state (*independent of the path*).

A key property of a state function is that its *differential* can be integrated in a normal, path independent way.

- Energy is a state function:

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

Energy is independent of the path from 1 to 2; it depends only on the initial (1) and final (2) states.

- Work and heat are *not* state functions.

DIFFERENT DIFFERENTIALS

Since work depends upon how a process is carried out, work is not a state function, work is a *path function*, so we write,

$$\int_1^2 \delta w = w \quad (\text{not } \Delta w \text{ or } w_2 - w_1)$$

An *inexact differential* Cannot be integrated in the normal way

Energy is a state function, and dU is an *exact differential*.

State functions:

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

Path functions:

$$\int_1^2 \delta q = q \quad (\text{not } \Delta q \text{ or } q_2 - q_1)$$

$$\int_1^2 \delta w = w \quad (\text{not } \Delta w \text{ or } w_2 - w_1)$$

THE FIRST LAW OF THERMODYNAMICS

Energy is conserved

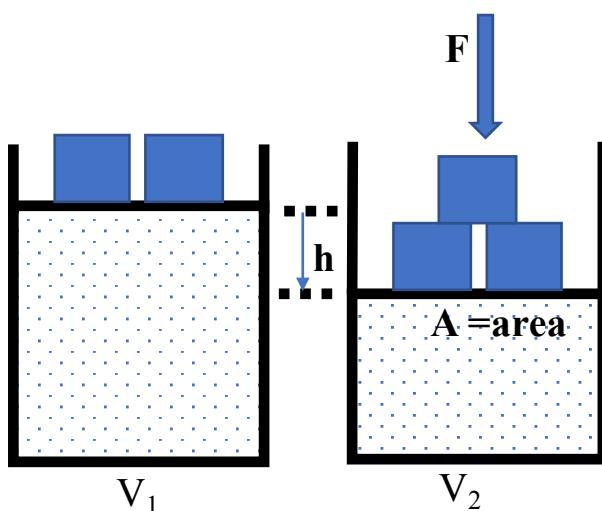
$$dU = \delta q + \delta w \quad (\text{differential form})$$

$$\Delta U = q + w \quad (\text{integral form})$$

Even though δq and δw are path functions (inexact differentials)
their sum is a state function (an exact differential).



CLOSE SYSTEM



**Mechanical Work
(w_{Mech})**

$$\Delta U = q + w \quad (\text{First Law})$$

$$\Delta U = q + (w_{\text{Mech}} + w_{\text{non-Mech}})$$

LETS NOT WORRY ABOUT $w_{\text{non-Mech}}$

$$\begin{aligned} w_{\text{Mech}} &= \text{Force} \times \text{displacement} \\ &= F \times h \\ &= (F/A) \times (A \times h) \\ &= P \times \Delta V \end{aligned}$$

Change in volume

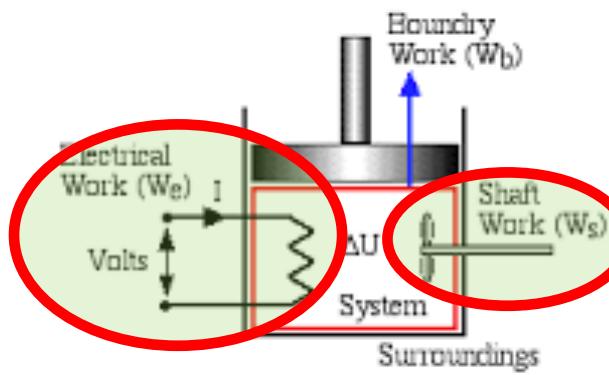
$$\Delta U = U_2 - U_1 = q - P \Delta V$$

Sign Convention:

- $q = +$, heat added to the system
- $q = -$, Heat released by the system
- $w = +$, Workdone on the system
- $w = -$, Workdone by the system

ALWAYS THINK ABOUT SIGN OF ΔU

Mechanical (PV) Work: $W = - \int_{V_1}^{V_2} P dV$



Other type of works

Three forms of Work considered:

- Boundary Work $W_b \Rightarrow$ Piston - Cylinder
- Shaft Work $W_s \Rightarrow$ Paddle Wheel
- Electrical Work $W_e = \text{Volts} \cdot I(\text{Amps}) \cdot \text{time}$

Mechanical Forms of Work

Shaft Work

➤ A force F acting through a moment arm r generates a torque T of:

$$T = F \times r \quad \rightarrow \quad F = \frac{T}{r}$$

➤ This force acts through a distance s , which is related to the radius r by:

$$s = (2\pi r)n$$

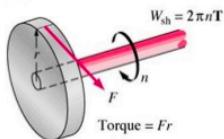
where n is the number of revolutions

➤ The shaft work will be:

$$W_{sh} = Fs = \left(\frac{T}{r}\right)(2\pi r)n = 2\pi n T$$

➤ The power transmitted through the shaft is the shaft work done per unit time:

$$\dot{W}_{sh} = 2\pi n T$$



Energy Transfer by Work

Electrical Work

The rate of electrical work done by electrons crossing a system boundary is called electrical power and is given by the product of the voltage drop in volts and the current in amps.

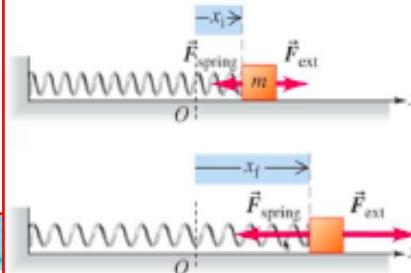
$$\dot{W}_e = VI \quad (\text{W})$$

The amount of electrical work done in a time period is found by integrating the rate of electrical work over the time period.

$$W_e = \int_1^2 V I dt \quad (\text{kJ})$$

Work Done by a Spring

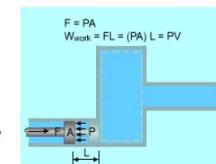
Work done by a spring

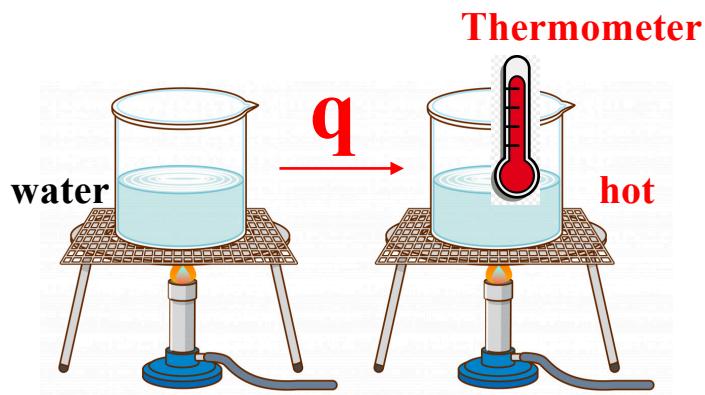


$$\begin{aligned} W_i &= \int_{x_i}^{x_f} F_n dx = - \int_{x_i}^{x_f} kx dx \\ &= -\frac{1}{2}k(x_f^2 - x_i^2) \\ x_i &= \text{initial displacement from equilibrium} \\ x_f &= \text{final displacement from equilibrium} \end{aligned}$$

OTHER TYPES OF WORK TRANSFER

- 3) Flow work
- Significant in open system
- It represents the energy imparted to the fluid by a pump, blower or compressor to make the fluid flow across the control volume.





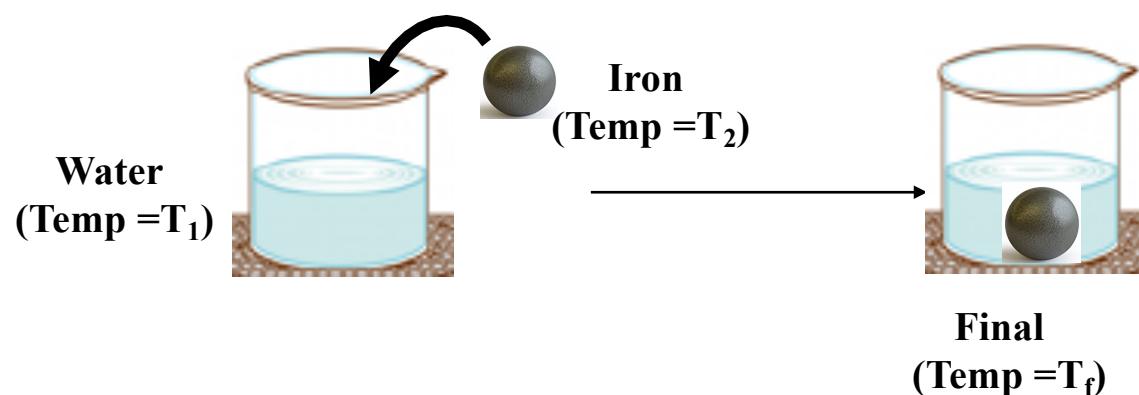
Heat ?

$$\begin{aligned} Q &\propto \Delta T \\ &\propto m_w \Delta T \\ &= C m_w \Delta T \end{aligned}$$

ΔT = temperature change
 m_w = Mass of water (gms)
 C = Specific heat (property of material)

For water, $C = 1 \text{ cal}/(\text{gm } {}^{\circ}\text{C})$

Now one can find “C” for other material (say Iron)



Apply 1st Law,
Energy conservation

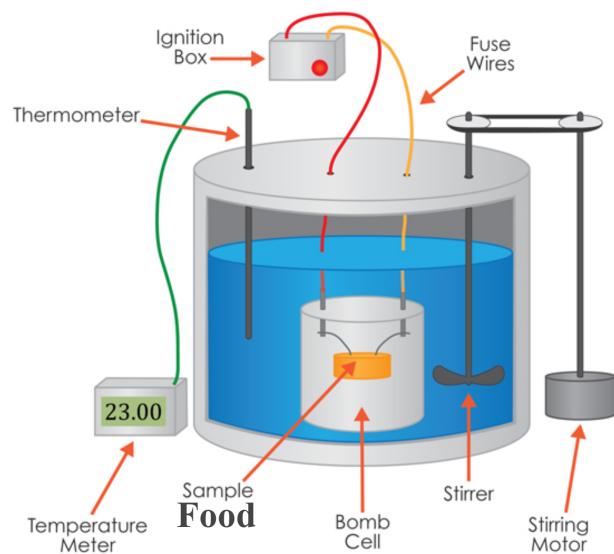
$$\begin{aligned} \sum Q &= 0 \\ \Rightarrow 1 \cdot m_w \cdot (T_f - T_1) + C_{Fe} \cdot m_{Fe} \cdot (T_f - T_2) &= 0 \end{aligned}$$

I know m_w, T_f, T_1, T_2

Application

How to determine energy content (kcal) of food?

Bomb Calorimeter



$$Q \propto \Delta T$$

$$Q = C M \Delta T$$

Q = Heat [Cal]

C = Specific heat of water [1 cal/(gm °C)]

M = Mass of liquid [gm]

ΔT = Change in temperature [°C]

<https://www.youtube.com/watch?v=cw7q433ynYg>



History: Heat

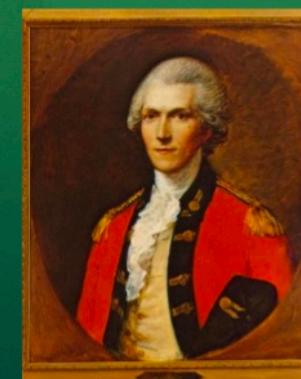
Caloric versus Kinetic

Caloric Theory of Heat: Heat is an invisible fluid called the “caloric” that flows between objects with different temperatures. The caloric naturally flowed from a hot object with a lot of it, to a cold object with only a little of it. The cold object expanded as it warmed because it had absorbed the invisible fluid.



*The caloric was first proposed by Antoine Lavoisier in the 1770s.
(Lavoisier also proposed the conservation of mass and discovered that water was made from oxygen and hydrogen).*

Benjamin Thompson (aka Count Rumford)

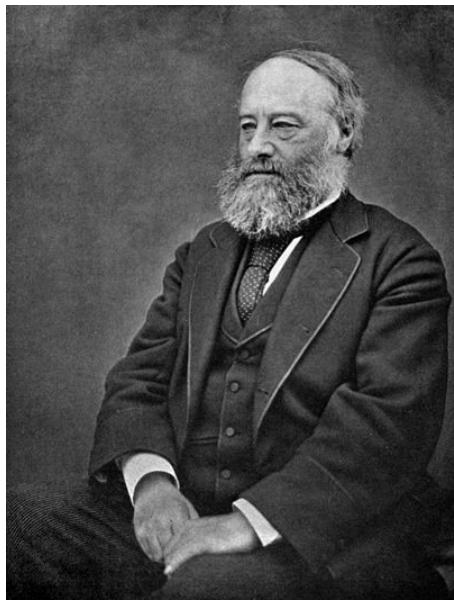


Count Rumford lived in Bavaria, Germany and was in charge of looking after the military cannons.

He noticed that after boring a hole into the metal cannon, the tools and metal became very hot – but weren’t hot previously.

How would the Caloric Theory explain this?

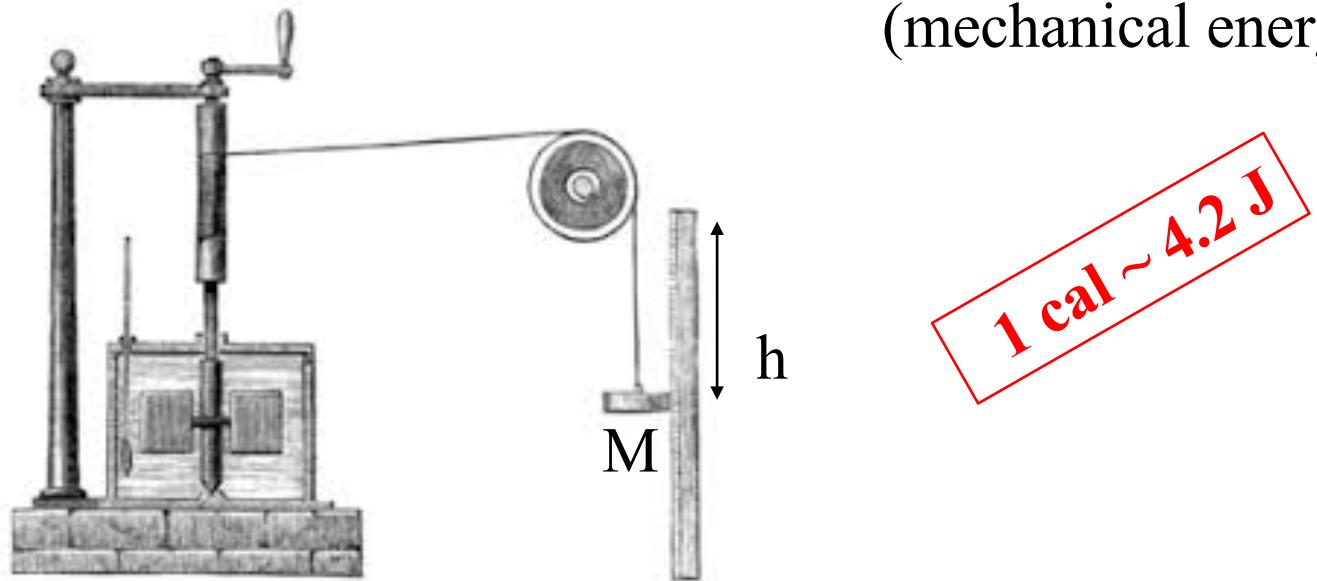
"An Experimental Enquiry Concerning the Source of the Heat which is Excited by Friction",
(1798), Philosophical Transactions of the Royal Society p. 102.



James Prescott Joule

History: Heat

$$\begin{aligned} Q &= 1. m_w \Delta T \\ &= Mgh - KE \\ &\quad (\text{mechanical energy}) \end{aligned}$$



Mechanical equivalent of heat (1841)

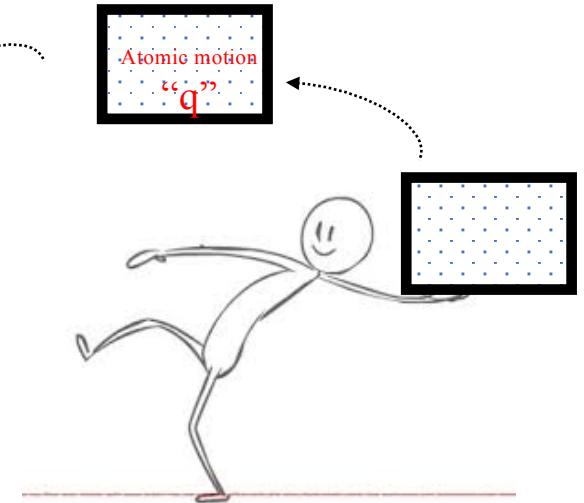
Understanding “Heat” require the knowledge: Everything is made up of atoms

Colliding car



K.E goes into
atoms = Heat

Kinetic Energy
of the box \neq heat (q)





Next: Paths of PV work