Thermodynamics

Jan 2025

Laws of thermodynamics

They state empirical facts found in the history of physics and chemistry.

The zeroth law of thermodynamics

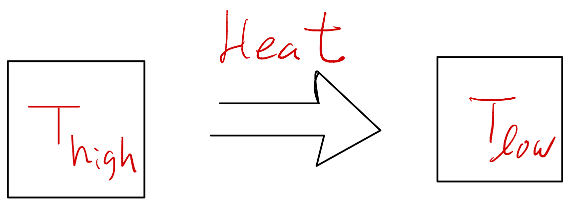
- Defines thermal equilibrium:

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

- Forms a basis for the definition of Temperature.

① Temperature reflects the degree of hotness or coldness of an object or a system.

② Temperature (T) determines the direction of heat transfer.



Heat is a transfer of energy, always flows spontaneously from an object with higher T to an object with a lower T until the two objects reach the same T, which is called the thermal equilibrium is reached.

③ Temperature is transitive:

$$\left.\begin{array}{l} \text{If } T_A = T_C \text{ and } T_B = T_C, \\ \text{then } T_A = T_B. \end{array}\right\} \text{The zeroth law}$$

Temperature

- In the International system of Units (SI), the unit of temperature is the kelvin (T_K)
Other commonly used ones are
Celsius (T_c) and
Fahrenheit (T_F)

- Fahrenheight to Celsius

$$T_C = \frac{5}{9}(T_F - 32°F)$$

- Celsius to Fahrenheight

$$T_F = \frac{9}{5}T_C + 32\ °F$$

- Celsius to Kelvin

$$T_K = T_C + 273.15\ °C$$

- Kelvin to Celsius

$$T_C = T_K - 273.15\ °C$$

- Absolute Zero is defined as $T_K = 0$.

① In classical physics, it results in zero kinetic energy.

② In Quantum physics, particles will have non-vanishing zero-point energy, due to the Heisenberg uncertainty principle.

$$\left(\Delta x \Delta p \geq \frac{h}{4\pi}\right)$$

h is the Planck constant

→ Temperature can be measured by a thermometer, such as

thermometer.

Siede Preis/Getty Images

Thermal Expansion

— It's not always linear, but in the case of linear expansion :

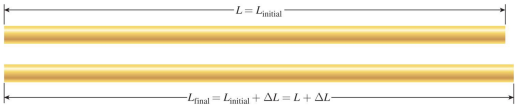
① Define α as the coefficient of linear expansion for a solid object

$$\frac{\Delta L}{L_0} \equiv \alpha \Delta T$$ for one-dimension (1-d), ΔT is small.

where $\Delta T \equiv T_f - T_i$

$\Delta L \equiv L_f - L_i$

- Let's consider a rod of length L.



The unit of $[\alpha] = \frac{1}{\text{temperature}}$ ← (either $\frac{1}{°C}$ or $\frac{1}{°F}$ or $\frac{1}{°K}$)

$\Rightarrow$ Assuming the isotropic property of the object,

For 2-d, $$\frac{\Delta A}{A} = 2\alpha \Delta T$$ (for area $A = L^2$)

For 3-d, $$\frac{\Delta V}{V} = 3\alpha \Delta T$$ (for volume $V = L^3$)

② For liquid object, we define β as the volume expansion coefficient, such that for small ΔT,

$$\frac{\Delta V}{V} \equiv \beta \Delta T$$

— Note: Water is special!

③ For ideal gas, the thermal expansion coefficient is defined as

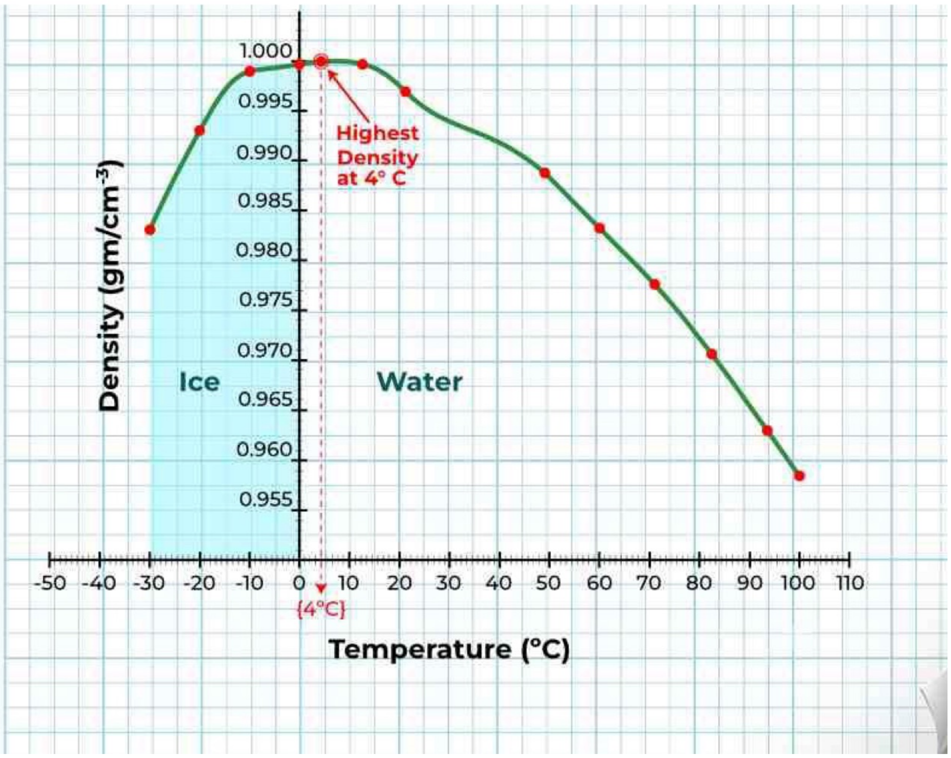
$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$ ← for a fixed pressure p

$$= \frac{1}{T}$$ ← in the unit of Kelvin (K)

($PV = nRT$ for ideal gas)

Density of Water & Volume expansion of Water

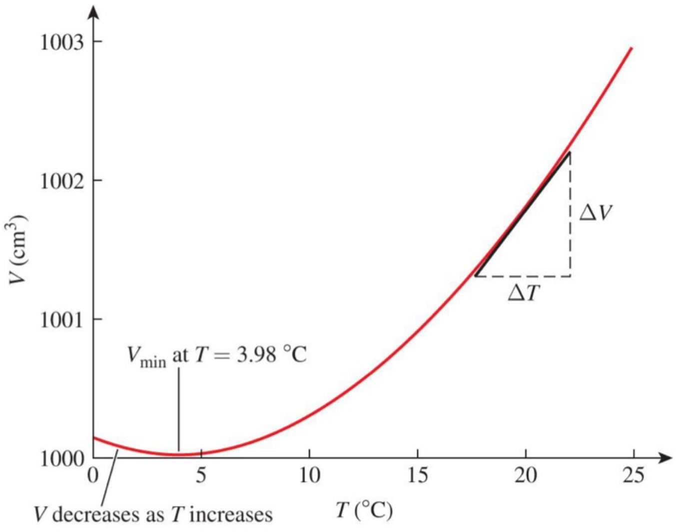
— Water is special !



(density) $\rho \equiv \frac{M}{V}$ (mass) (volume)

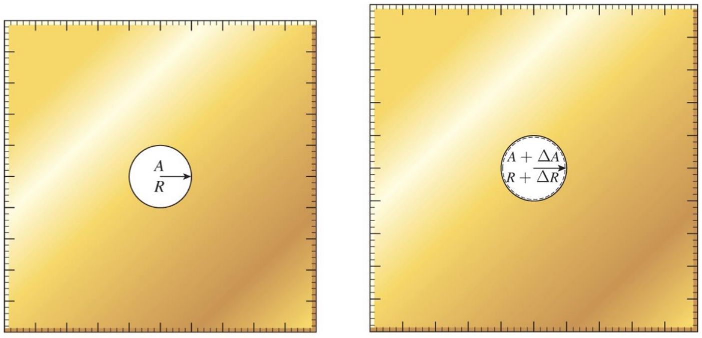
Volume Expansion of Water

- The change in volume with temperature is never linear for water.



Hint to think about solving this problem

Expansion of a Plate with a Hole in It[3]



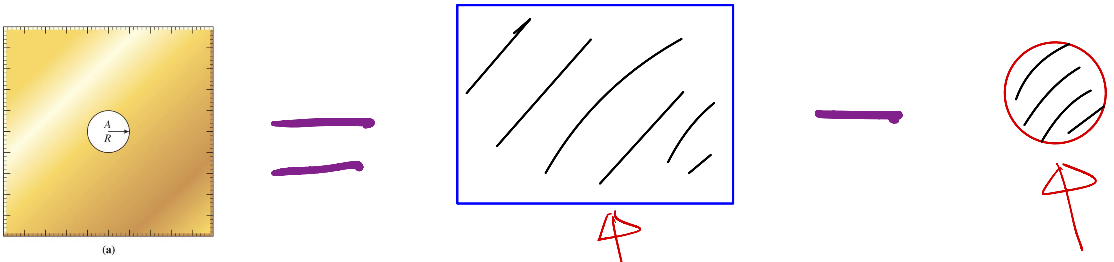
(a) (b)

The change in the area of the hole is

$$\frac{\Delta A}{A} = 2\alpha\ \Delta T$$

Research

- The area of the plate increases as the temperature increases and the area of the hole increases proportionally.



When T increases, $\Delta T > 0 \Rightarrow$ expand expand

The First law of Thermodynamics

— The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic processes. In general, the conservation law states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed.

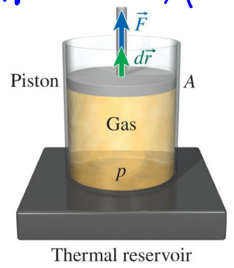
> In a closed system (i.e. there is no transfer of matter into or out of the system), the first law states that the change in internal energy of the system (ΔU_{system}) is equal to the difference between the heat supplied to the system (Q) and the work (W) done *by* the system on its surroundings. (Note, an alternate sign convention, not used in this article, is to define W as the work done *on* the system by its surroundings):
>
> $$\Delta U_{\text{system}} = Q - W.$$
>
> $(dU = dQ - pdV)$

(ΔU_{sys} is denoted as the internal energy ΔE_{int}.)

For processes that include the transfer of matter, a further statement is needed.

> When two initially isolated systems are combined into a new system, then the total internal energy of the new system, U_{system}, will be equal to the sum of the internal energies of the two initial systems, U_1 and U_2:
>
> $$U_{\text{system}} = U_1 + U_2.$$

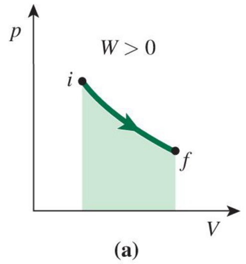
(Pressure $p = \frac{F}{A}$)



— The work done by the system is

$$W = \int dW = \int \vec{F} \cdot d\vec{r} = \int_{V_i}^{V_f} p\,dV$$

It's a path-dependent process.



(a)

p-V diagram

— Heat is a form of energy tranfer.

① Joule's experiments quantified the relation between mechanical work and heat.

② In the above equation, we define the heat to be supplied into the system.

— When matter is transferred into a system, the internal energy increases by

$$\Delta U_{sys} = (u\,\Delta M)_{int}$$

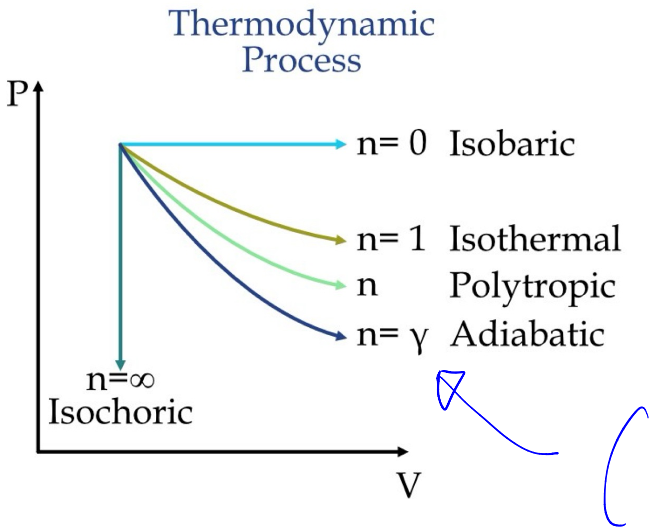
(where u denotes the internal energy per unit mass of the transferred matter, and ΔM denotes the amount of transferred mass.)

Types of thermodynamic processes

- **Adiabatic:** No heat transfer into or out of the system
- **Isobaric:** Pressure remains constant
- **Isochoric:** Volume remains constant
- **Isothermal:** Temperature remains constant
- **Isenthalpic:** Enthalpy remains constant
- **Isentropic:** A reversible adiabatic process where entropy remains constant
- **Steady state:** Internal energy remains constant

The first law:

$$\Delta U = Q - W$$



$$\boxed{PV^n = \text{Constant}}$$

($\gamma = \frac{C_p}{C_v}$ is the heat capicity ratio.)

— Heat transfer during various processes (for an ideal gas),

① Isobaric: $\Delta P = 0$, $Q = n C_p (T_f - T_i) = n C_p (\Delta T)$

heat capacity at constant pressure

② Isothermal: $\Delta T = 0$, $\Delta U = 0$,

$$\boxed{\Delta U = Q - W} \Rightarrow Q = W$$

For idea gas: $pv = nRT$

heat capacity at constant volume

③ Isochoric: $\Delta V = 0$, $\Rightarrow \Delta W = 0 \Rightarrow Q = \Delta U = n C_v (\Delta T)$

④ Adiabatic: $Q = 0 \Rightarrow PV^{\gamma} = \text{Constant}$, with $\gamma = \frac{C_p}{C_v}$

Heat transfer during various processes (for an ideal gas)

① Isobaric: $\Delta P = 0$, $Q = nC_p(T_f - T_i) = nC_p(\Delta T)$

heat capacity at constant pressure

$PV = nRT$

$W = \int p\,dV = p(V_f - V_i) \Rightarrow \Delta U = Q - W$

(Using $PV = nRT$)

change of Entropy: $\Delta S = \int \frac{dQ}{T} = \int_{T_i}^{T_f} nC_p \frac{dT}{T} = nC_p \ln\left(\frac{T_f}{T_i}\right)$

$= nC_p \ln\left(\frac{V_f}{V_i}\right)$

② Isothermal: $\Delta T = 0$, $\Delta U = 0$,

$$\boxed{\Delta U = Q - W} \Rightarrow Q = W$$

$$W = \int p\,dV = \int \frac{nRT}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = \frac{Q}{T} = nR \ln\left(\frac{V_f}{V_i}\right)$$

③ Isochoric: $\Delta V = 0$, $\Rightarrow W = 0$

heat capacity at constant volume

$$\Rightarrow Q = \Delta U = nC_v(\Delta T)$$

$$\Delta S = \int \frac{dQ}{T} = \int_{T_i}^{T_f} nC_v \frac{dT}{T} = nC_v \ln\left(\frac{T_f}{T_i}\right)$$

(a constant)

④ Adiabatic: $Q = 0 \Rightarrow PV^\gamma = C$, with $\gamma = \frac{C_p}{C_v}$

($C_p = C_v + R$ for ideal gas)

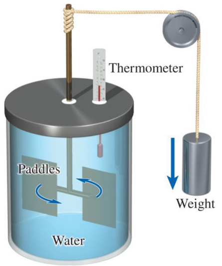
$$W = \int p\,dV = \int \frac{C}{V^\gamma} dV = \frac{P_f V_f - P_i V_i}{1 - \gamma}$$

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

$$\Delta S = \int \frac{dQ}{T} = 0$$

Mechanical Equivalent of Heat

— In 1843, Joule's experiment



① Found $W = C_J Q$

(mechanical work done)

Joule's constant

(heat produced)

$$C_J = 4.186 \ \frac{\text{Joule}}{\text{Calorie}}$$

⇒

Work:

$1\ J = 1\ (kg)\frac{m^2}{s^2}$ = (1 newton of force times one meter of distance)

$$W = Fd = \underset{(kg)}{m}\,\underset{(m/s^2)}{g}\,\underset{(m)}{d}$$

Heat:

1 Cal = the amount of heat needed to raise the temperature of 1 g water by 1°C.

= 4.186 J

② Unified Different forms of energies.

(mechanical energy versus heat)

③ Established the concept of Energy Conservation

⇒

$$\Delta E_{int} \equiv \Delta E_{int,f} - \Delta E_{int,i} = Q - W$$

Calorimeter and Specific heat capacity

- To measure the amount of heat involved in a chemical or physical process.
- To measure the specific heat capacity (C) of substances.

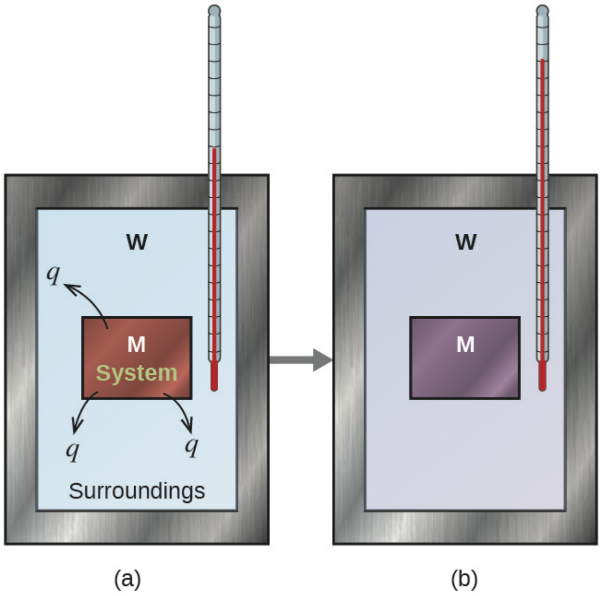
$$Q = m\,C\,\Delta T$$

heat

the tempeture change.

the mass of the sample

In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.



Energy Conservation

$$Q_{metal} + Q_{water} = 0$$

$\Rightarrow$

$$C_M m_M (\Delta T)_M + C_W m_W (\Delta T)_W = 0$$

where

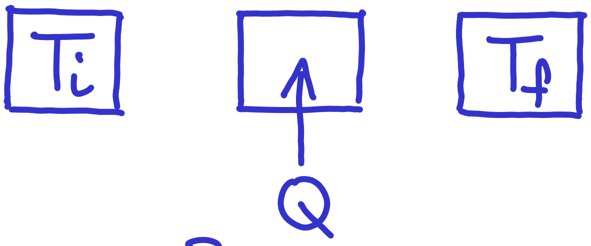
$$(\Delta T)_M \equiv T - T_{iM}$$

$$(\Delta T)_W \equiv T - T_{iW}$$

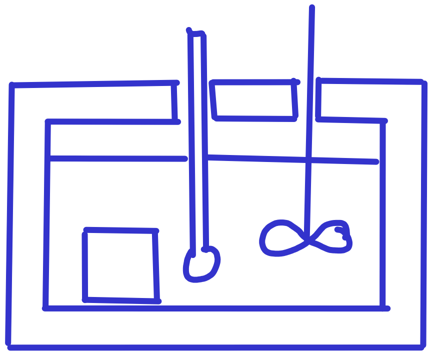
initial temperature

temperature of thermal equilibrium

Heat and mechanical work



$$Q \xleftrightarrow{?} \Delta T = (T_f - T_i)$$



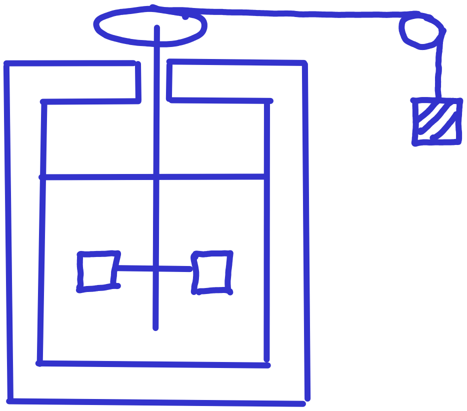
calorimeter

Definition: 1 calorie is the amount of heat which raises the temperature of 1 g water by 1°C.
(Warning: 1 Cal = 1000 cal = 1 kcal.
Reminder: 1 g is the mass of 1 cm^3 water at 4°C temperature.)

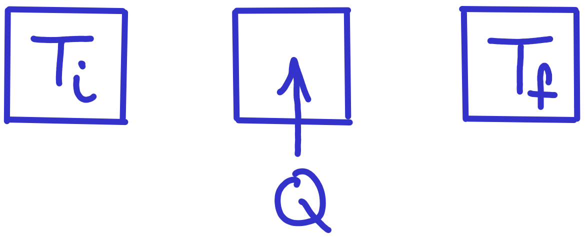
Question: what is the relation between heat Q and mechanical work W = Fd?

James Prescott Joule (1818-1899):

1843 : 1 cal = 4.186 J



Heat capacity, specific heat



$$Q = C \cdot \Delta T = C \cdot (T_f - T_i)$$

$$C = \frac{Q}{\Delta T} \qquad [C] = J/K$$

C : heat capacity: amount of heat needed to raise the temperature of the object by 1K. (The object can be complex or composite.)

Homogeneous objects : $Q = cm\Delta T$

$$c = \frac{Q}{m\Delta T} = \frac{C}{m} \qquad [c] = \frac{J}{kg\,K}$$

<u>c : Specific heat</u>: amount of heat needed to raise the temperature of a unit mass of material.

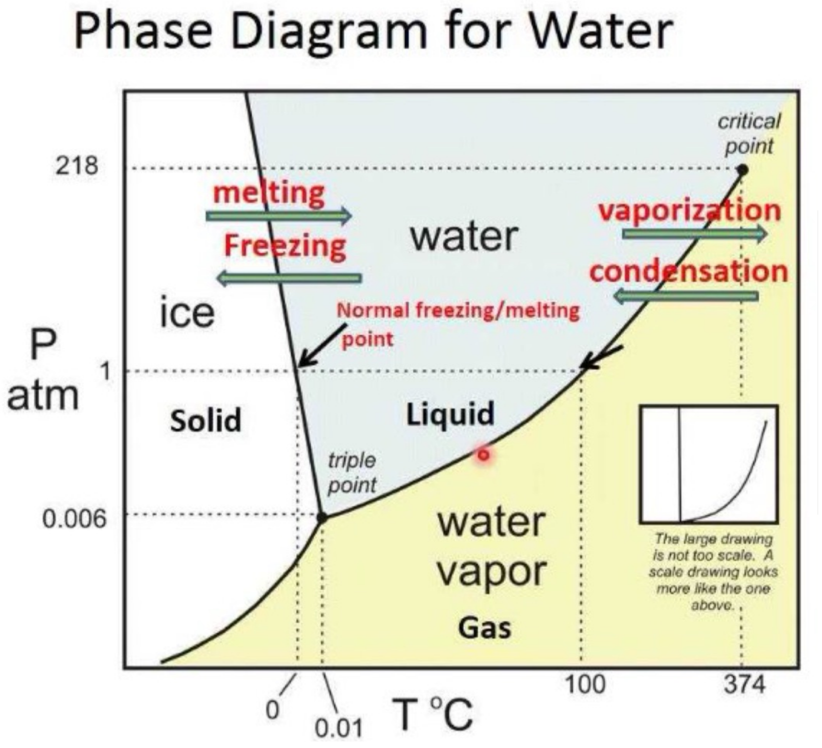
water : $1 \frac{cal}{g°C} = 4186.8 \frac{J}{kg\,K}$

Al : $0.215 \frac{cal}{g°C} = 900 \frac{J}{kg\,K}$

Cu : $0.0923 \frac{cal}{g°C} = 386 \frac{J}{kg\,K}$

Molar heat $= C_m = \frac{C}{n}$

Phase Diagram of Water



Phase Diagram for Water

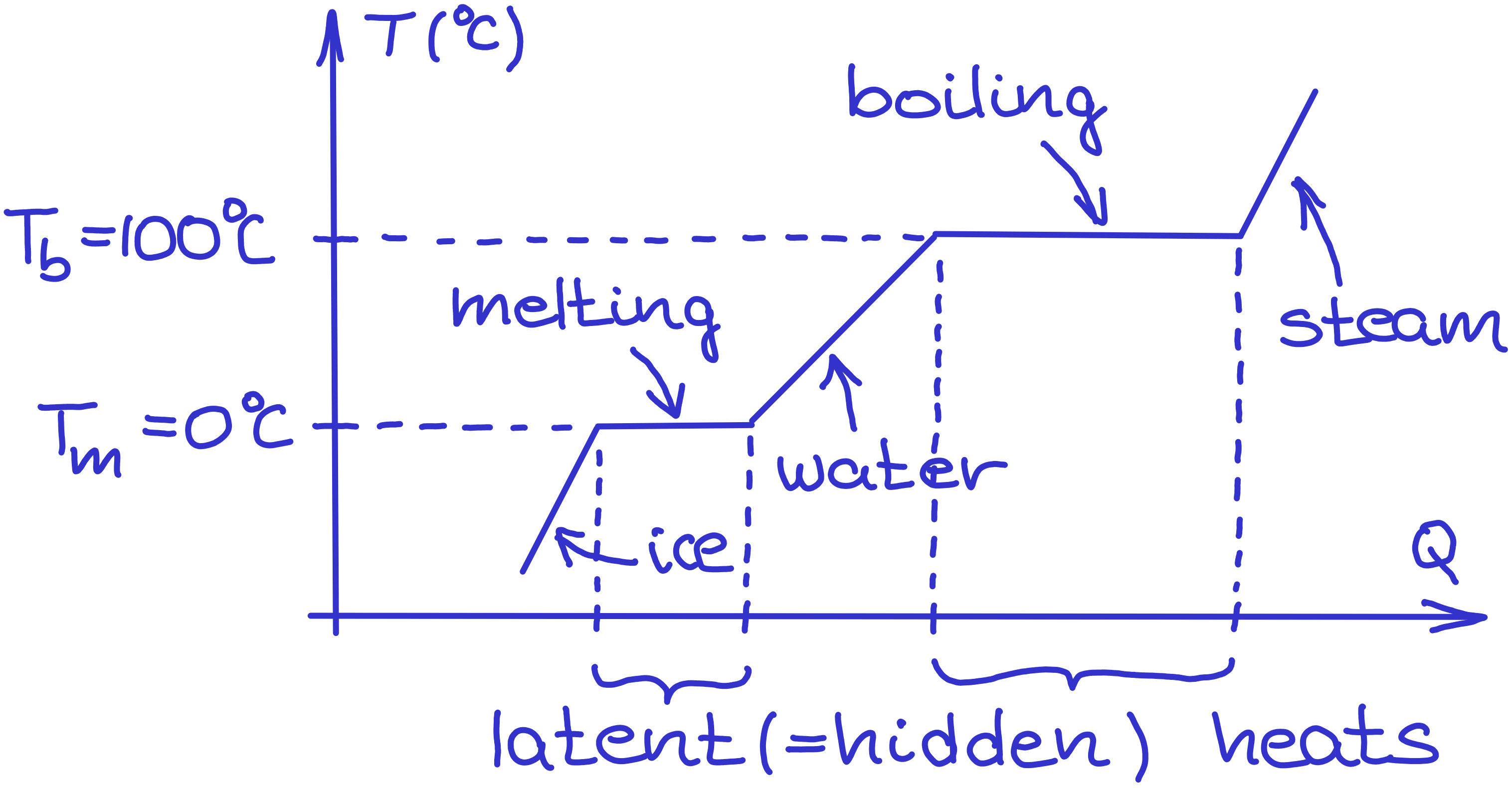
- Melting: When ice turns into water
- Boiling: When water turns into steam
- Condensation: When steam turns back into water
- Freezing: When water turns back into ice

The lines on the phase diagram are the lines of equilibrium. Along these lines, any two phases coexist in thermal equilibrium. However, a change in pressure or temperature will cause the phase to change abruptly. The AB line is the ice-vapor line, the BC line is the ice-water line, and the BD line is the water-vapor line. We can use the phase diagram to identify the state where water exists under specific temperature and pressure conditions. For example, water is ice at 50 kPa and – 10 °C.

Water has a triple point corresponding to the temperature and pressure at which ice, water, and vapor coexist in a stable equilibrium. It also has a critical point – the temperature at which water vapor cannot be forced back into water, no matter how much pressure is applied. The triple point and the critical point are listed in the table below.

Property	**Temperature in Celsius (°C)**	**Temperature in Kelvin (K)**	**Pressure in atmosphere (atm)**	**Pressure in kilo Pascal (kPa)**
Triple Point	0.01	273.16	0.006	0.608
Critical Point	373.99	647.14	217.7	22058.453

Heat(s) of transformation(s)



melting
solidification } solid-liquid phase transition

$$Q = L_F \cdot m \; ; \; L_F = \frac{Q}{m} \quad [L_F] = \frac{J}{kg}$$

↑ heat of fusion

boiling
condensation } liquid-gas phase transition

$$Q = L_v \cdot m \; ; \; L_v = \frac{Q}{m} \; ; \; [L_v] = \frac{J}{kg}$$

↑ heat of vaporization

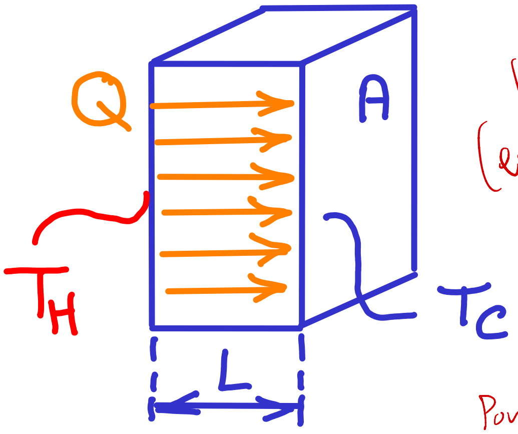
H_2O : $L_F = 333 \frac{kJ}{kg}$; $L_v = 2256 \frac{kJ}{kg}$

(79.7 cal/g) (540 cal/g)

The three heat transfer mechanisms

conduction, convection, radiation

Conduction:



$Q \propto t$, time

$Q \propto \Delta T = (T_H - T_C)$

$Q \propto A$

$Q \propto \frac{1}{L}$

heat (energy)

Power

$$\boxed{\begin{aligned} Q &= k \cdot \frac{A}{L} \cdot \Delta T \cdot t \\ P &= \frac{Q}{t} = k \, \frac{A}{L} \cdot \Delta T \end{aligned}}$$

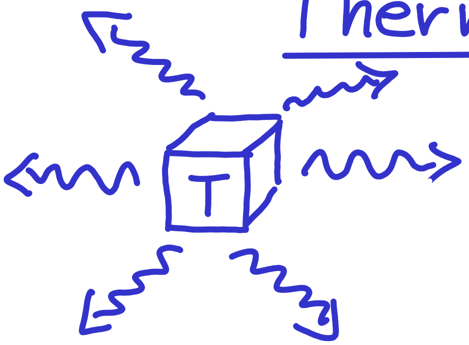
k : thermal conductivity

Examples for k in $\frac{W}{m \cdot K} = \frac{W \cdot m}{m^2 \cdot K}$

Silver : 428
Copper : 401
Steel : 14
Glass : 1-2
Air : 0.026

Convection: fluid dynamics plus thermodynamics (way too complex)
"Hot air rises."

Thermal radiation



radio- and microwave, mostly infrared, can be visible or ultraviolet

Stefan-Boltzmann law : $\boxed{P = \sigma \varepsilon A T^4}$

T : absolute temperature in kelvin

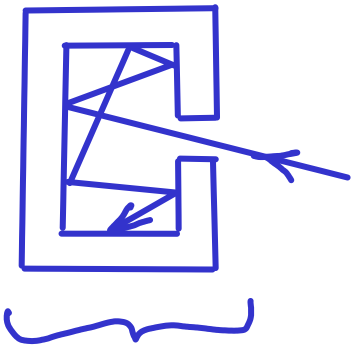
A : surface area of the object

ε or e : emissivity $0 \leq \varepsilon \leq 1$

σ : Stefan-Boltzmann constant:

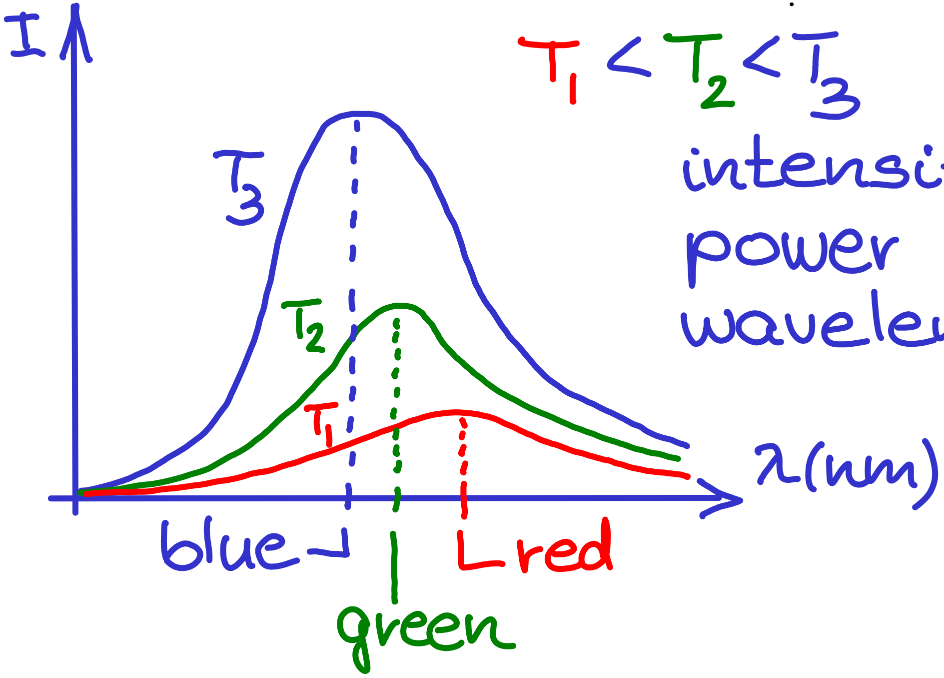
$$5.6703 \cdot 10^{-8} \frac{W}{m^2 K^4}$$

Black-body : $a=1$ absorbs everything
$e=1$ emits the most



The hole on the cavity behaves like a black-body: it absorbs all the radiation landing on it.

Blackbody radiation



$I = I(\lambda, T)$: intensity distribution: power per area per wavelength

$$[I] = \frac{W}{m^2} \cdot \frac{1}{m}$$

Wien's displacement law (1911 Nobel)

$$\boxed{\lambda_{max} \cdot T = b \; ; \quad b = 2.898 \cdot 10^{-3} \; m \cdot K}$$

Sun: $\lambda_{max} = 550 nm \Rightarrow T = 5800 K$

Stefan-Boltzmann law:

$$\boxed{P = \sigma \varepsilon A T^4 \; ; \quad \sigma = 5.6705 \cdot 10^{-8} \frac{W}{m^2 K^4}}$$

P: total area under the intensity distribution curve.

Max Planck (1918 Nobel): the exact shape of the intensity distribution curve. (You will learn about it in Quantum Mechanics.)