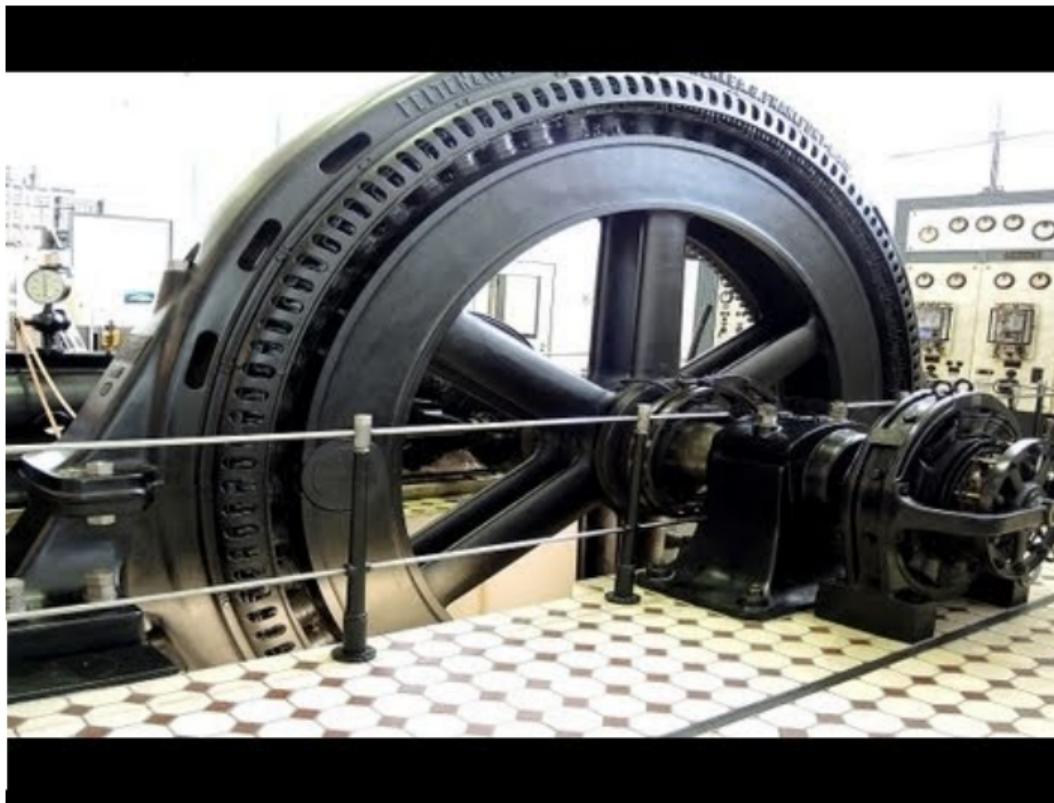


The steam engine is the root of the industrial revolution

The industrial revolution is the transforming of thermal energy into mechanical work allowing for the people and animals to do other things.



Thermodynamics is a timeless branch of physics

- ▶ Thermodynamics studies *thermal* interactions and the transformation of heat into mechanical work.
- ▶ *Thermal* interaction is an interaction between two systems when their macroscopic parameters stay the same. Volume, density.
- ▶ Heat is a conventional name for the *energy* transferred between two objects via thermal interaction.
- ▶ In terms of statistical mechanics, the interaction is *thermal* when the possible internal *states* of the system are the same.
- ▶ The interaction is *not thermal*, for example *mechanical*, when the internal *states* of the system change. Example: a change of volume changes the internal energy states.
- ▶ Intensive state variables do not depend on the system size: temperature, pressure, density.
- ▶ Extensive state variables depend on the system size: internal energy, entropy, total number of molecules

Thermodynamics deals with systems having MANY degrees of freedom

- ▶ The number of molecules in a mole of gas is $N_A = 6.022 \cdot 10^{23}$
- ▶ Average number of stars in the universe is $\approx 10^{11}$
- ▶ If each star were a new universe in itself with it's own 100 billion stars, the number of stars in these 100 billion universes, would still be less than the number of molecules in a mole.
- ▶ In other words, the numbers were're dealing with in thermodynamics and statistical mechanics are numbers we can hardly imagine.

Temperature

- ▶ The material is from University Physics Volume 2 ch. 1. Read all the chapter.
- ▶ Book URL: [Book URL: https://openstax.org/books/university-physics-volume-2/pages/1-introduction](https://openstax.org/books/university-physics-volume-2/pages/1-introduction)

Two objects are in **thermal equilibrium** if they are in close contact , but nevertheless, no net energy is transferred between them.

The zeroth law of thermodynamics: if object A is in equilibrium with object B, and object B is in equilibrium with object C, then object A is in equilibrium with object C.

If A is a thermometer it will have the same "reading" when moved from object B to object C. Any physical property that depends consistently and reproducibly on temperature can be used as the basis of a thermometer.

Volume change (usual alcohol thermometers), **density change** (Galileo thermometer), **voltage change** (K-thermocouple thermometer), and so on.

The Kelvin scale

- ▶ To make a temperature scale we must identify two defined temperatures and define the gradations between them.
- ▶ In the Celsius scale, 0 degrees are the freezing temperature of water at normal pressure and 100 degrees is the boiling temperature of water.
- ▶ The ideal gases law, or Boyle-Charles-Gay-Lussac law, found experimentally, says that $pV = nR(t + 273, 15^\circ C)$, where V is the volume, n the number of moles, R a universal constant and t the temperature in Celsius degrees.
- ▶ The absolute temperature in Kelvin (K) is defined as $T(K) = t^\circ C + 273, 15^\circ C$
- ▶ The ideal gases law becomes $pV = nRT$
- ▶ There is no temperature below the absolute zero, that is, *0 Kelvin*.
- ▶ Observe that $\Delta T(K) = \Delta T(^\circ C)$

Entropy: a function that must be maximized

Two systems are in thermal contact.

The total energy is constant, $E = E_1 + E_2$

The entropy S must be at maximum. $S = S(E_1) + S(E_2)$. The only variable is E_1 , because E is constant.

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} = 0$$

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2} = \frac{1}{T}$$

Definition: $\left(\frac{\partial E}{\partial S}\right)_V = T$ The temperature is:

- ▶ Intensive
- ▶ All parts of a system in equilibrium have the same temperature
- ▶ The energy flows from high temperature to low one

This is the Second Law of Thermodynamics. It probably is the only conceptually new law of thermodynamics. We also discussed the "zeroth law of thermodynamics".

If $T_a = T_b$ and $T_c = T_b$, then $T_a = T_c$.

The "first" law of thermodynamics

Pressure: In a **thermally insulated** system

$dE = dW = -PdV$, where W is the mechanical work done by the system.

More rigorously, $P = -\left(\frac{\partial E}{\partial V}\right)_S$

The first law of thermodynamics is the simple realization that "Heat" is a form of energy.

$$dE = dQ + dW = dQ - PdV = TdS - PdV$$

E : internal energy of the system, T temperature, S is entropy, P pressure and V volume.

Specific heats

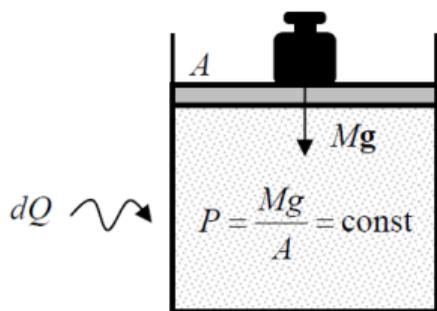


Figure: The simplest implementation of an isobaric process. Isobaric=constant pressure, that is, $dP = 0$

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

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

Because at constant volume the work is zero, $C_V = \left(\frac{\partial E}{\partial T}\right)_V$ ¹

¹The image is from Konstantin Likharev, Essential Graduate Physics Lecture

Specific heats, applications

- ▶ The equation on previous slide, $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$, becomes for simple applications $\Delta Q = mC_V\Delta T$, where C_V is the specific heat at constant volume.
- ▶ C_V is what we encounter in most applications where two objects are put in thermal contact with each other.
- ▶ The specific heat is numerically equal to the amount of heat necessary to change the temperature of 1.00 kg of mass by 1.00 °C
- ▶ The SI unit for specific heat is $\frac{J}{kg \cdot K}$

Question: You put in thermal contact two objects, one of mass m_1 , specific heat c_1 and temperature T_1 and one with mass m_2 , specific heat c_2 and temperature T_2 . Assuming no heat exchange with the exterior, what is the final temperature of the two objects? Calculate for 250g of water at 100°C poured in a 200g glass cup at 20°C. Water has a specific heat of $4186 \frac{J}{kg \cdot K}$ and glass has a specific heat of $840 \frac{J}{kg \cdot K}$.

Thermodynamic potentials

$$d(XY) = YdX + XdY$$

Because Q is not a state function, we want to define the C_P in a different way, we want it to be defined as a function of a state function, as we just did with C_V .

$dQ = dE + PdV$, at constant P we can add VdP to this equation and we get

$$(dQ)_P = d(E + PV)_P$$

If $H = E + PV$ then

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

$$dH = dE + PdV + VdP = TdS - PdV + PdV + VdP = TdS + VdP$$

$H(S, P)$ is called enthalpy.

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \quad V = \left(\frac{\partial H}{\partial P}\right)_S,$$

Free energy and the Gibbs potential

How much work can you extract from a system at constant temperature?

$$(dW)_T = dE - TdS = d(E - TS) = dF$$

$F(T, V) = E - TS$ is the free energy

$$dF = -SdT - PdV$$

$$S = \left(\frac{\partial F}{\partial T}\right)_V, P = -\left(\frac{\partial F}{\partial V}\right)_T$$

The last thermodynamic potential we define is the Gibbs potential: $G(T, P) = E + PV - TS$

$$dG = -SdT + VdP$$

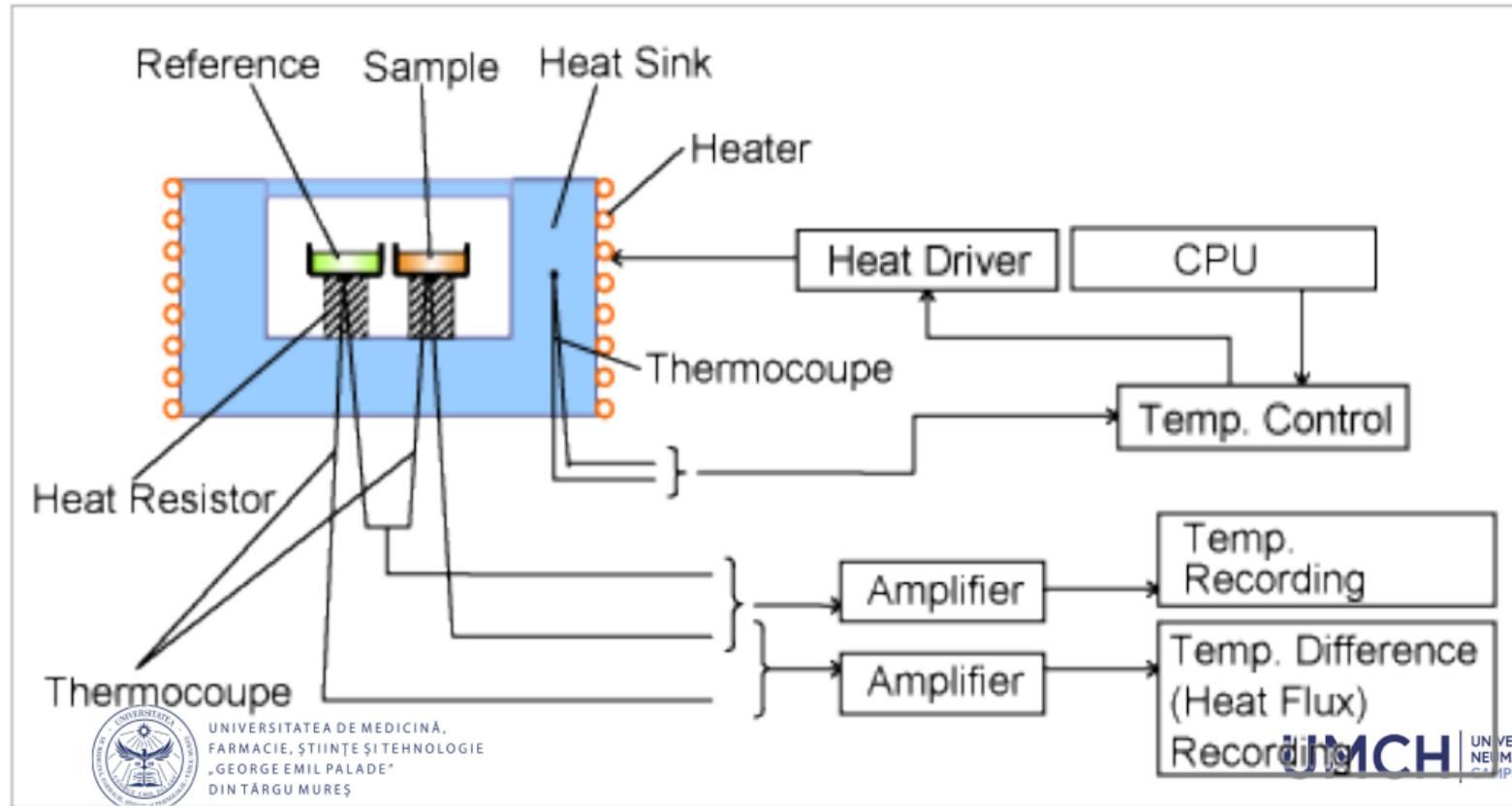
$$S = -\left(\frac{\partial G}{\partial T}\right)_P, V = \left(\frac{\partial G}{\partial P}\right)_T$$

$G(T, P)$ is the only thermodynamic potential that has to be extensive, because T, P are intensive. $G(T, P) = Nf(T, P)$

In a system with variable number of particles, $dG = -SdT + VdP + \mu dN$, where μ is the "chemical potential". $\mu = \left(\frac{G}{N}\right)$, that is, the chemical potential per molecule.

This is why at Biochemistry the reaction activation energy is given by the Gibbs potential. Compare with the reaction kinetics equation from Lehninger's Principles of Biochemistry.

Differential Scanning Calorimetry: what do you measure? 1



Will you measure $E(S, V)$, $H(S, P)$, $F(T, V)$ or $G(T, P)$?

Differential Scanning Calorimetry: what do you measure? 2

You have in the cell a protein solution to look at protein denaturation, or phospholipids solution to look at phase transitions in vesicles (we will discuss vesicles).

The pressure stays constant. You measure the specific heat at constant pressure.

$$dE = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$

The entropy change during the transition will be $\delta S = \frac{\delta H}{T}$

The phase transition is given by a very sharp peak, Heat vs. Temperature, and one has to measure the area below the peak. ²

²<https://www.hitachi-hightech.com/global/products/science/tech/ana/thermal/descriptions/dsc.html> ▶

Temperature, entropy, Boltzmann's constant

Recall the definition: $(\frac{\partial E}{\partial S})_V = T$ The entropy has no units. The temperature T has units of *energy*. The absolute temperature is measured in Kelvin (K), and to convert it to an energy we multiply it with a "scaling constant" called Boltzmann's constant, k_B .

One consequence of doing this scaling is that the definition of entropy is:

$$S = k_B \ln(\Omega)$$

where Ω is the total number of possible states that are compatible with the macroscopic state of the system.

In the **canonical** distribution the probability for a **system** in thermal contact with a temperature bath at temperature T to be in an energy state E_i above the ground energy (lowest energy) E_0 is

$$P_i \propto e^{-\frac{E_i - E_0}{k_B T}}$$

This distribution is called the Gibbs distribution a result of the canonical ensemble.

$k_B T$ at room temperature or at body temperature

- ▶ The relative strength of a bond, interaction with respect to $k_B T$ gives an indication of it's stability.
- ▶ At room temperature $k_B T$ is $4.11 \cdot 10^{-21} J$ or $25.7 meV$ or $2479 \frac{J}{mol}$.
- ▶ The ground state of a hydrogen atom is $-13.6 eV$.
- ▶ The hydrogen bond in water is $3.6 \cdot 10^{-20} J$ or $21 \frac{kJ}{mol}$, that is, $8,4 k_B T$.

Bond breaking

The probability to break a bond is proportional to:

$$\propto t \cdot e^{-\frac{E_i - E_0}{k_B T}}$$

or $n_{jumps} = \nu_{atom} t e^{-\frac{E_i - E_0}{k_B T}}$ where t is the time the system is subjected to temperature T .³ This behaviour is used in

- ▶ Pasteurization.
- ▶ Sterilization of medical instrumentary.

Schrödinger: $t = \tau_{atom} e^{\frac{E_i - E_0}{k_B T}}$ Where τ is a characteristic time of the bond.

Homework: problem 4.3 p. 68, Rodney Cotterill.

³Rodney Cotterill

Solving problem 4.3 p 68 Rodney Cotterill.

$$P_i = C \frac{t}{\tau_{\text{atom}}} e^{-\frac{E_i - E_0}{kT}} = C \nu_{\text{atom}} t e^{-\frac{E_i - E_0}{kT}}$$

$$t = \frac{P_i \tau_{\text{atom}}}{e^{-\frac{E_i - E_0}{kT}}} = P_i \tau_{\text{atom}} e^{\frac{E_i - E_0}{kT}}$$

t : warming

τ : time

$$\tau \cdot \nu = 1$$

time
heating

ν : frequency (Hz)

Solving problem 4.3 p 68 Rodney Cotterill.

$$T_B = 20^\circ\text{C}, t_B, m_B = 10000$$

$$T_A, t_A, m_A = 56$$

$$m_A = c t_A e^{-\frac{\Delta E}{kT_A}}; m_B = c t_B e^{-\frac{\Delta E}{kT_B}}$$

$$\frac{m_A}{m_B} = \frac{t_A}{t_B} \frac{e^{-\frac{\Delta E}{kT_A}}}{e^{-\frac{\Delta E}{kT_B}}} = \frac{t_A}{t_B} e^{-\frac{\Delta E}{k} \left(\frac{1}{T_A} - \frac{1}{T_B} \right)}$$

Phase changes

- ▶ At the phase transition the temperature and pressure stay at constant values.
- ▶ Heat transfer at phase transition does not change the temperature of a material, only the phase of the material.
- ▶ For example, heat transferred to boiling water, transforms liquid water into water vapors.
- ▶ The equation describing the heat transfer during phase transitions is $Q = m \cdot \lambda$, where lambda is called the latent heat of evaporation/melting.
- ▶ Notice there is no ΔT when writing up the equation for the heat transferred during a phase transition.
- ▶ The SI units for the latent heat are $\frac{J}{kg}$

Further Reading

- ▶ Chapter 1 from University Physics Volume 2:
<https://openstax.org/details/books/university-physics-volume-2>
- ▶ The documents in our intranet called "Cooling coffee" and "Killing a virus"
- ▶ Rodney Cotterill, Biophysics an Introduction, chapter 4.