

Thermodynamics

Physics Olympiad
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*"When did you become an expert in thermonuclear astrophysics?"
"Last night."*

--- Tony Stark

Relevant Constants

Avogadro's number $N_A = 6.022 \times 10^{23}$

Mathematical Treatment

Suppose you were asked: What is the percentage of molecules travelling at a speed of 3 ms^{-1} exactly? The answer is probably 0 or close to 0, because there is a really low chance that any particle is travelling at *exactly* 3 ms^{-1} .

The right question to ask will then be: What is the percentage of molecules travelling between speed v and $v + dv$? Now, it makes sense to introduce the *probability density function*:

$$P(v \leq V \leq v + dv) = f(v) dv$$

The probability density function is just the derivative of P with respect to the continuous variable:

$$f(v) = \frac{dP}{dv}$$

To find the percentage of particles with speed between 0 and v , we just have to integrate the probability density function

$$P(0 \leq V \leq v) = \int_0^v f(v) dv$$

The *expected value* of a random variable v is the weighted average of v with the weights being the probabilities:

$$\langle v \rangle = \sum P_i v_i = \int v f(v) dv$$

Boltzmann Distribution

For a system with a total energy of E , we define $\Omega(E)$ to be the number of microstates for that macrostate. For example, let us imagine the scenario where the Grandmaster has 100 coins. If I told you that 42 coins were heads and the rest were tails, that would be a *macrostate*. A *microstate* of the macrostate will be the configuration of each individual coin, which means I need to tell you whether coin 1 is heads or tails, coin 2 is heads or tails and so on...

Each macrostate comprises a lot of possible microstates. However, a system will always appear to choose a macroscopic configuration that maximises the number of microstates.

Now, instead of describing a macrostate by the number of heads, we describe it by its total energy E . Given two systems in thermal contact, the first with energy of E_1 and the second with energy of E_2 , the number of microstates is $\Omega_1(E_1)\Omega_2(E_2)$.

To maximise the number of microstates, $\frac{d(\Omega_1(E_1)\Omega_2(E_2))}{dE_1} = 0$.

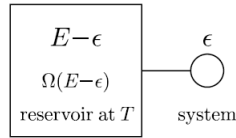
$$\frac{d}{dE_1}(\Omega_1(E_1)\Omega_2(E_2)) = \Omega_2(E_2) \frac{d\Omega_1(E_1)}{dE_1} + \Omega_1(E_1) \frac{d\Omega_2(E_2)}{dE_2} \frac{dE_2}{dE_1} = 0$$

$$\frac{1}{\Omega_1} \frac{d\Omega_1}{dE_1} = \frac{1}{\Omega_2} \frac{d\Omega_2}{dE_2} \Leftrightarrow \frac{d \ln \Omega_1}{dE_1} = \frac{d \ln \Omega_2}{dE_2}$$

Hence, we can define *temperature* as:

$$\frac{1}{k_B T} = \frac{d \ln \Omega}{dE} \Leftrightarrow T = k_B \frac{dE}{d \ln \Omega}$$

This is the statistical definition of temperature.



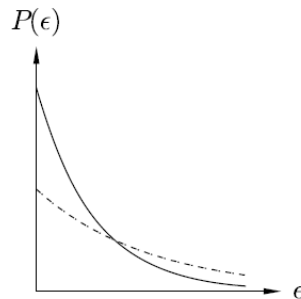
Consider two systems with total energy E , we make one enormous, like a reservoir or the entire universe. Assume that for each allowed energy of the small system, there is only one microstate, the probability density function of the system having an energy of ϵ is proportional to the number of microstates:

$$P(\epsilon) \propto \Omega(E - \epsilon)$$

$$\ln \Omega(E - \epsilon) = \ln \Omega(E) - \frac{d \ln \Omega(E)}{dE} \epsilon + \dots = \ln \Omega(E) - \frac{\epsilon}{k_B T} + \dots$$

Hence, we get the Boltzmann distribution

$$P(\epsilon) \propto e^{-\frac{\epsilon}{k_B T}}$$

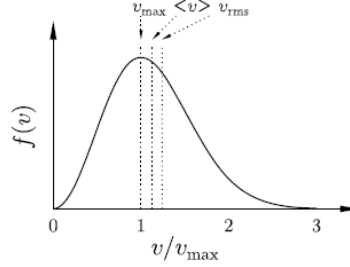


Kinetic Theory of Gases

If each particle of a room is inspected, each component of its velocity will follow the Boltzmann distribution. However, we are more interested in the total velocity, i.e. the probability of finding a particle in the region of v to $v + dv$.

Converting the integral over space to an integration over the shells of a sphere, we obtain the Maxwell Boltzmann distribution.

$$f(v) \propto v^2 e^{-\frac{mv^2}{2k_B T}}$$



The average velocity is $\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$ and the root-mean-squared velocity is

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}$$

$$\langle E_{KE} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

Now, we can use the above equation to calculate the pressure by considering the number of molecules hitting a wall. The number of molecules hitting a wall with speed v to $v + dv$ and hitting at an angle of θ to $\theta + d\theta$ is:

$$v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta$$

Hence, the total pressure P can be found by integrating over all angles and all speeds.

$$P = \int_0^\infty \int_0^{\pi/2} (2mv \cos \theta) \left(v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta \right) = \frac{1}{3} nm \langle v^2 \rangle$$

Substituting $\langle v^2 \rangle$ with $\frac{3k_B T}{m}$, we have the ideal gas equation:

$$PV = Nk_B T$$

Laws of Thermodynamics

Heat is thermal energy in transition. *Heat capacity* is the amount of heat dQ to be supplied to an object to raise its temperature by dT . If it is considered as per unit mass, then it is called *specific heat capacity*.

$$C = \frac{dQ}{dT}$$

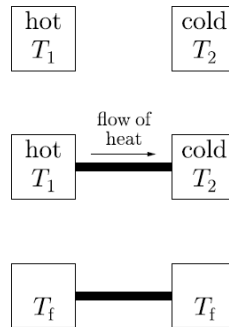
A system can be described by P , V and T . These are the parameters of state, because they are macroscopic quantities which are path independent for any change in thermal equilibrium.

$$PV = nRT$$

$$PV = Nk_B T$$

Zeroth Law of Thermodynamics

If two systems are both in thermal equilibrium (no net flow of heat) with a third system, then they are in thermal equilibrium with each other.



First Law of Thermodynamics

In a closed system (no transfer of matter in or out of the system), the change in internal energy (ΔU) is equal to the difference between the heat supplied to the system (ΔQ) and the work done (ΔW) by the system on the surroundings. Note that Q and W are not parameters of state.

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

The first law encompasses the principle of conservation of energy and the concept of internal energy and its relation to temperature.

A change is *reversible* if the time-reversal process is possible. A change is *quasi-static* if it is done so slowly that the system remains in equilibrium throughout the change. A reversible change must be a quasi-static one.

For an isometric process (constant pressure), $\Delta P = 0$:

$$W = \int P \, dV = P \, \Delta V$$

For an isometric process (constant volume), $\Delta V = 0$:

$$W = \int P \, dV = 0$$

For an isothermal process (constant temperature), $\Delta T = 0$:

$$W = \int_{V_1}^{V_2} P \, dV = \int_{V_1}^{V_2} \frac{nRT}{V} \, dV = nRT \int_{V_1}^{V_2} \frac{1}{V} \, dV = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\boxed{W = nRT \ln\left(\frac{V_2}{V_1}\right)}$$

For an adiabatic process (no heat entering or leaving the system), $PV^\gamma = \text{constant}$:

$$W = \int_{V_1}^{V_2} P \, dV = \int_{V_1}^{V_2} \frac{c}{V^\gamma} \, dV = c \int_{V_1}^{V_2} \frac{1}{V^\gamma} \, dV = -\frac{c}{\gamma-1} \left[\frac{1}{V^{\gamma-1}} \right]_{V_1}^{V_2} = \frac{c}{\gamma-1} \left(\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}} \right)$$

Recall that $c = P_1 V_1^\gamma = P_2 V_2^\gamma$

$$W = \frac{1}{\gamma - 1} (P_1 V_1 - P_2 V_2) = \frac{nR}{\gamma - 1} (T_1 - T_2)$$

The adiabatic index γ is defined to be the ratio of C_p to C_v . It must necessarily be a number greater than 1, because at constant pressure, work is done by the gas. To achieve the same ΔU , the heat supplied must be more.

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dQ &= dU - p dV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV - P dV \\ \frac{dQ}{dT} &= \left(\frac{\partial U}{\partial T}\right)_V + \left(\left(\frac{\partial U}{\partial V}\right)_T - P\right) \frac{dV}{dT} \end{aligned}$$

The last equation is valid for any change in T or V . Under constant volume, $dV = 0$

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

For an ideal mono-atomic gases, $U = \frac{3}{2}RT$. Hence $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R$.

Under constant pressure

$$C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\left(\frac{\partial U}{\partial V}\right)_T - P\right) \left(\frac{dV}{dT}\right)_P$$

For an ideal mono-atomic gases, $U = \frac{3}{2}RT$, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$C_P = \frac{3}{2}R - P \left(\frac{dV}{dT}\right)_P = \frac{3}{2}R + R = \frac{5}{2}R$$

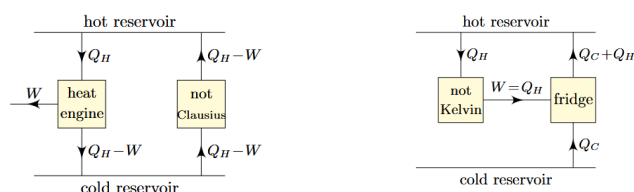
For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$, hence, $C_P = C_V + R$. $C_V = \frac{R}{\gamma - 1}$

Second Law of Thermodynamics

[Clausius' statement] There is no process whose sole effect is to transfer heat from a colder body to a hotter body.

[Kelvin's statement] There exists no process whose sole effect is to extract heat from a heat reservoir and convert it into work.

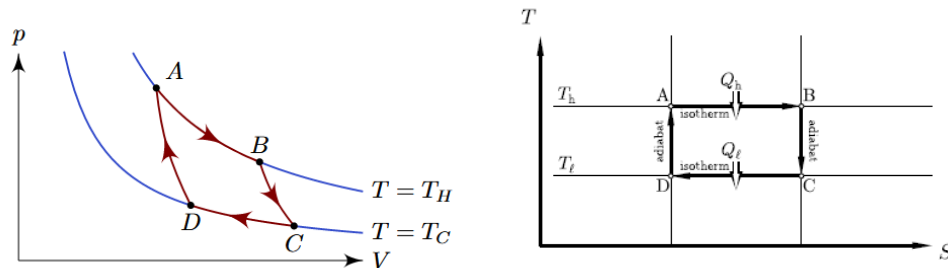
These two statements are equivalent. The violation of any of the two statements will imply a violation in the conservation of energy.



Carnot Engine

Kelvin's statement forbids the complete conversion of heat into work. This raises the question of *efficiency*. What is the maximum possible conversion of heat into work?

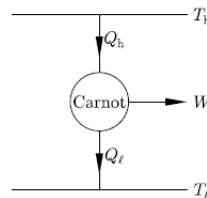
An engine is a system that converts heat into work and operates in a cyclic process, so that it can be continuously operated and produce a steady power.



The system consists of a box of gas that can be expanded or compressed. The Carnot cycle involve compressing and expanding this box of gas about two temperatures T_c and T_h . For a Carnot engine shown above, the process DA and BC are adiabatic. Only at AB and CD does heat enter/leave the system.

$$W = Q_H - Q_C$$

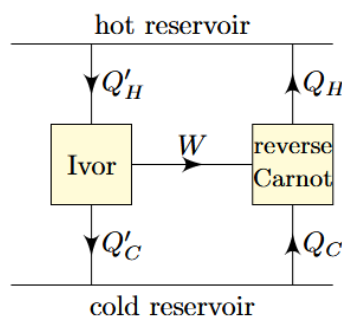
$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$



The important feature of this heat engine is that it is reversible, so we can run it backwards and turn it into a fridge.

Carnot's Theorem

Of all engines operating between heat reservoirs, reversible engines are the most efficient. In particular, all reversible engines have the same efficiency, and is a function of the temperature of the two reservoirs.



Clausius' Theorem

For any closed cycle, $\oint \frac{dQ}{T} \leq 0$, where equality necessarily holds for a reversible cycle.

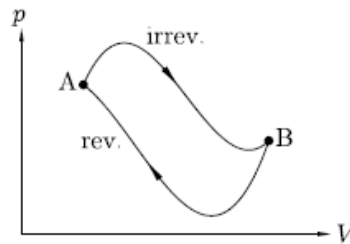
By Clausius' Theorem, $\oint \frac{dQ_{rev}}{T} = 0$. This means that the value $\frac{dQ_{rev}}{T}$ is path independent. It makes sense to introduce a new concept to illustrate this state function.

Entropy

$$dS = \frac{dQ_{rev}}{T}$$

The entropy of a system can be thought of as the number of arrangements of molecules at given volume V and temperature T . Increasing entropy therefore implies increasing chaos, i.e. heat flowing from hotter region to colder region.

$$S(B) - S(A) = \int_A^B \frac{dQ_{rev}}{T}$$



Consider a scenario where we have an irreversible process from A to B and a reversible process back from B to A . Clausius' theorem implies:

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{rev}}{T} \leq 0$$

This is true however close B gets to A . Therefore:

$$dS = \frac{dQ_{rev}}{T} \geq \frac{dQ}{T}$$

For a thermally isolated system, $dQ = 0$ for any process,

$$dS \geq 0$$

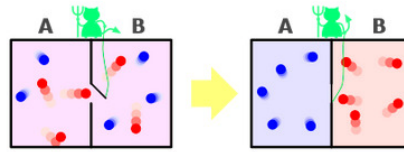
Assuming the Universe is an isolated system, $U_{\text{Universe}} = \text{constant}$ and S_{Universe} can only increase. This shows how the entropy of a particular system (or the Universe in that regard) changes in an irreversible way.

Entropy can also be inspired by the statistical definition of temperature, where is depends on the number of microstates of the system (an indication of chaos).

$$\frac{1}{T} = \frac{dS}{dE}$$

$$S = k_B \ln \Omega$$

Maxwell's Demon



Maxwell's demon is a thought experiment in which Maxwell suggested how the second law of thermodynamics might hypothetically be violated. A demon controls a small door between two compartment of gases. As individual gas molecules approach the door, the demon quickly opens and shuts the door so that only fast molecules are passed into the other chamber, while slow molecules are kept in the other. The demon's behaviour causes one chamber to warm up and the other to cool down, thereby decreasing entropy and violating the second law of thermodynamics.

A possible resolution to Maxwell's Demon is that for the demon to decide which gas molecules to let in, it itself must incur an increase in entropy. This possibly relates thermodynamics to information theory and is currently a topic in nanotechnology.

Third Law of Thermodynamics

The entropy of a system approaches a constant value as its temperature approaches absolute zero.

Thermal Conductivity

Newton's Law of Cooling

The rate of heat loss of a body is proportional to the difference in temperatures between the body and its surroundings. For a temperature independent heat transfer coefficient h and a heat transfer surface area of A ,

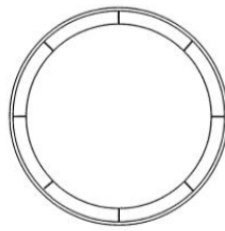
$$Q = hA\Delta T$$

A. Sample Problems

1. A horizontal frictionless piston of negligible mass and heat capacity, divides a vertical insulated cylinder into two halves. Each half of the cylinder contains 1 mole of air at standard temperature and pressure p_0 . A load of weight W is now suspended from the piston, as shown in the figure. It pulls the piston down and comes to rest after a few oscillations. How large a volume does the compressed air in the lower part of the cylinder ultimately occupy if W is very large?



2. The sealed lower half of a straight glass tube, of height 152 cm is filled with air. The top half contains mercury and the top of the tube is left open. The air is slowly heated. How much heat has been transferred to the air by the time all the mercury has been pushed out of the tube?
3. A totally black spherical space probe is very far from the solar system. As a result of heating by a nuclear energy source of strength I inside the probe, its surface temperature is T . The probe is now enclosed within a thin thermal protection shield, which is black on both sides and attached to the probe's surface by a few insulating rods. Find the new surface temperature of the probe and determine the surface temperature which would result from using N such shields.



4. Two thermally insulated containers hold identical masses of water. The water is at temperature T_1 in one of them, but at temperature T_2 ($T_2 > T_1$) in the other. What is the maximum work that this system can do if it is used as a heat engine? Take the specific heat of water as constant over the working range.
5. What is the change of entropy that occurs when two moles of helium and three moles of oxygen, both at $T \approx 273K$ and $P \approx 1.01 \times 10^5$ Pa) and in adjacent volumes, are allowed to mix by removing the partition between them?
6. By slowly pumping air into a 10-litre container, its pressure is increased to ten times atmospheric pressure. How much work is done during this process if the displacement of the piston in the pump is 1 liter? The walls of the container and the pump are all good heat conductors and so the temperature can be taken as a constant.
7. An enclosed, upright cylinder as shown in the figure below has a movable, frictionless massive piston of the same area as its base. The piston divides the cylinder into 2 compartments, one containing hydrogen gas and the other containing oxygen gas. The piston is also a good conductor of heat and does not leak. The compartment above the piston contains 1.5 moles of hydrogen gas and the compartment below contains 1 mole of oxygen gas. The two gases have the same temperature throughout. It is known that at 320K the volume of the hydrogen gas is 4 times that of the oxygen gas. At what temperature would the volume of the hydrogen gas be 3 times that of the oxygen gas?
8. 1 mole of ideal gas with internal energy $U = \frac{3}{2}RT$ expands from initial volume $V_i = \frac{1}{10}V_0$ following the equation

$$p = -\frac{p_0}{V_0}V + p_0$$

Find the highest temperature reached by the gas during the expansion and the maximum amount of heat taken in by the gas.

9. The surface temperature and radius of the Sun are approximately 5800 K and 6.96×10^8 m respectively. You may assume the Sun behaves as a blackbody radiator
 - a. Calculate the total energy radiated by the Sun in each second, given that the Stefan-Boltzmann constant $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$.
 - b. What is the intensity of the solar radiation reaching the top of the Earth's atmosphere? (Distance from the Earth to the Sun = 1.50×10^{11} m)
 - c. If the Earth has no atmosphere, what would be the Earth's equilibrium temperature be so that at steady state, it radiates as much as it absorbs? (Radius of the Earth = 6.38×10^6 m)
 - d. From the measurements of the temperature at different parts of the Earth, the Earth's average temperature is estimated to be about 15°C. Give possible reasons for the difference between this temperature and that you have calculated in (c).
 - e. Estimate the temperature on Mars' surface, given that the distance from Mars to the Sun = 2.28×10^{11} m and the radius of Mars = 3.40×10^6 m.
10. Consider an isolated system consisting of equal masses m of water at temperature $T_0 = 273.15$ K and ice. The ice is at a slightly lower temperature $T_0 - t$, where t is of the order of few Kelvins. This isolated system also includes ideal reversible heat engines of negligible heat capacity. One heat engine is used to produce mechanical energy which is consumed by another heat engine which is operated as a refrigerator. What is the lowest temperature T which can be given to a n th part of the ice of mass $\frac{m}{n}$ if $n \gg 1$?
11. In a two state system, there are only two states, one with energy 0 and one with energy $\epsilon > 0$. What is the average energy of the system?
12. Estimate the number of molecules in an isothermal atmosphere as a function of height.

B. Recommended Resources

- Concepts in Thermal Physics by Stephen Blundell
- Physics By Example: 200 Problems and Solutions by W.G. Rees.
- 200 Puzzling Physics Problems by P. Gnädig et al.