

PHYSICS PHYS1121 – HIGHER PHYSICS 1131

3. THERMODYNAMICS

3.3 Heat and The First Law of Thermodynamics

3.3.1 The Ideal Gas and Work

Internal Energy $E_{\text{int.}}$

The internal energy of a system is all the kinetic energy that is associated with its microscopic components – atoms or molecules – when viewed from a reference frame at rest with respect to the centre of mass of the system. It is the kinetic energy from its atoms or molecules which arises from the translational, rotational or vibrational degrees of freedom.

In the case of a monoatomic gas the internal energy is:

$$E_{\text{int.}} = n N_A \cdot E_{\text{kin.,avg.}} = n N_A \cdot \frac{3}{2} k_B T = \frac{3}{2} n R T$$

Note that the internal energy is a function of temperature only!

Heat Q

Heat Q is defined as the transfer of energy across the boundaries of a system due to the temperature difference between the system and its surrounding. Its unit is Joule [J].

Work W

When the gas expands (the pressure of a gas increases), a piston of a cylinder is pushed up. The work done by the gas is:

$$\begin{aligned} W &= -F \cdot s \\ dW &= -F \cdot ds \\ &= -P \cdot A ds \quad \text{since : } F = P \cdot A \\ &= -P dV \\ W &= - \int_{V_1}^{V_2} P dV \end{aligned}$$

First Law of Thermodynamics

$$\Delta E_{\text{int.}} = E_{\text{int.,f}} - E_{\text{int.,i}} = Q + W$$

The internal energy $E_{\text{int.}}$ of a system increases if energy is added as heat Q to a system and decreases if energy is lost as work W done by the gas $W = -F \cdot s = - \int P dV$.

Further considerations about the work done by a gas:

$$W = - \int_{V_1}^{V_2} P dV$$

The work corresponds to the negative area under the curve in the P–V phase diagram.

Note that the work depends on the path in the P–V phase diagram:

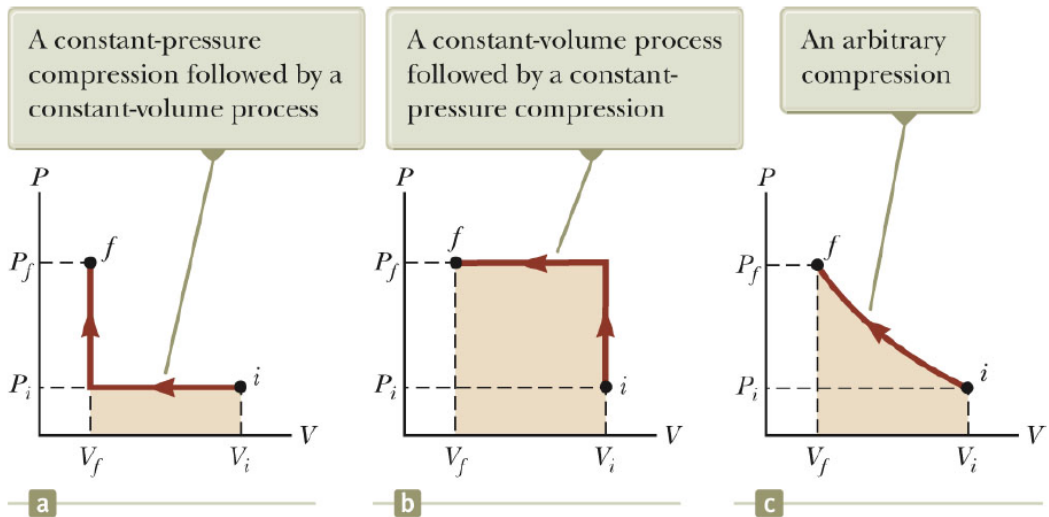


Figure 3.1: Work done by a gas for different paths in the P–V phase diagram (from the lecture notes of Liz Angstmann)

- a) isobaric: constant pressure \rightarrow isovolumetric: constant volume
- b) isovolumetric: constant volume \rightarrow isobaric: constant pressure
- c) arbitrary path in the P–V phase diagram.

Constant Volume Process: Isovolumic

$$W = -P \cdot \Delta V = 0 \quad \text{since : } \Delta V = 0$$

Constant Pressure Process: Isobaric

$$W = -P \cdot \Delta V = P(V_1 - V_2)$$

Constant Temperature Process: Isothermal

$$P \cdot V = nRT \implies P = nRT \cdot \frac{1}{V}$$

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT(\ln V_2 - \ln V_1) = nRT \ln \frac{V_1}{V_2}$$

3.3.2 Molar Specific Heat

Gases have a specific heat. This is the amount of heat (energy) required to raise the temperature of 1 mole of gas by 1 Kelvin:

$$\Delta E_{\text{int.}} = Q + W$$

$$E_{\text{int.}} = \frac{3}{2} N k_B T$$

$$\Delta E_{\text{int.}} = \frac{3}{2} N k_B \cdot \Delta T$$

If the temperature changes by a fixed amount, the internal energy changes by a fixed amount proportional to ΔT .

The transferred heat Q is:

$$Q = n \cdot c_{\text{molar}} \cdot \Delta T$$

where c_{molar} is the **molar specific heat**.

Isovolometric Specific Heat c_V and Isobaric Specific Heat c_P

One has to distinguish between the isovolometric process with $W = 0$ and the isobaric process, where $W = -P \cdot \Delta V$ and $Q = \Delta E_{\text{int.}} - W$.

$$\text{isovolometric} \quad Q = n c_V \Delta T$$

$$\text{isobaric} \quad Q = n c_P \Delta T$$

Constant Volume Process: Isovolometric

$$W = -P \cdot \Delta V = 0 \quad \text{since } \Delta V = 0$$

$$c_V = \frac{1}{n} \frac{\Delta E_{\text{int.}}}{\Delta T}$$

$$\text{Monoatomic gas: } \Delta E_{\text{int.}} = \frac{3}{2} N k_B \Delta T = \frac{3}{2} n R \Delta T$$

$$c_V = \frac{1}{n} \frac{\Delta E_{\text{int.}}}{\Delta T} = \frac{1}{n} \frac{3}{2} n R = \frac{3}{2} R = 12.47 \text{ J/mol} \cdot K$$

In general:

$$c_V = \frac{1}{n} \frac{\Delta E_{\text{int.}}}{\Delta T}$$

$$\Delta E_{\text{int.}} = \frac{1}{2} n f R \Delta T$$

$$c_V = \frac{1}{2} f R = f \cdot 4.157 \text{ J/mol} \cdot K$$

$$c_V = \frac{1}{2} f R$$

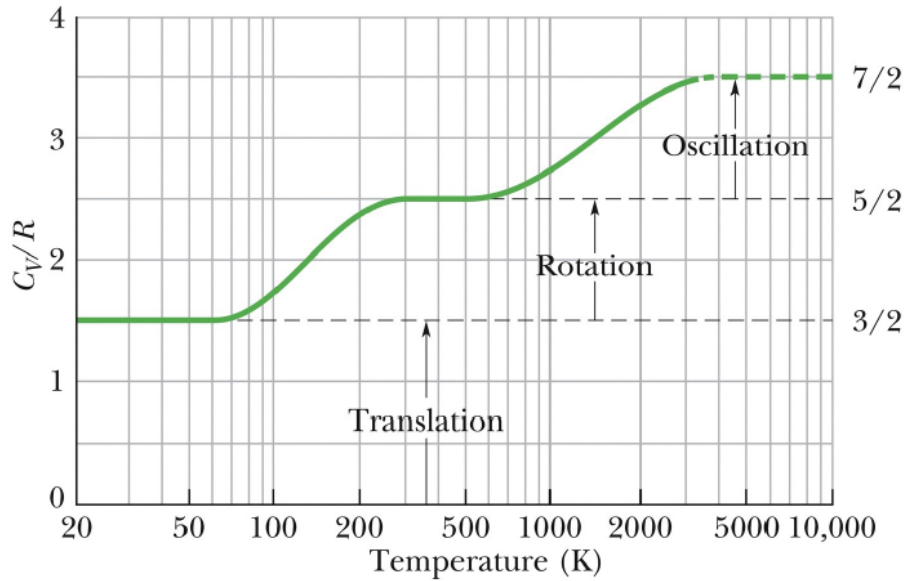


Figure 3.2: c_V/R versus temperature for a diatomic gas such as H_2 , N_2 , or O_2 .

Figure 3.2 shows the diagram of c_V/R versus temperature for a diatomic gas such as H_2 , N_2 , or O_2 . At lowest temperatures, i.e. below about 100 K, only the three translations in x , y , and z -direction are the possible degrees of freedom which contribute to the internal energy E_{int} . The specific heat at constant volume is: $c_V = \frac{3}{2}R$.

In the temperature range between about 100 K and 1000 K, rotations around the two distinguishable axes become possible and the total number of degrees of freedom is 5. The specific heat at constant volume is then: $c_V = \frac{5}{2}R$.

Above ≈ 1000 K the molecules also start to vibrate and the specific heat reaches its final value of $c_V = \frac{7}{2}R$.

At higher temperatures, e.g. 3200 K for H_2 , the bonds break due to the large thermal vibrations and the molecules dissociates into two atoms.

Table of the specific heat at constant volume c_V at room temperature (300 K):

Monoatomic Gas	$c_V = \frac{3}{2}R$	$12.47 \text{ J/mol} \cdot \text{K}$
Diatomic Gas	$c_V = \frac{5}{2}R$	$20.79 \text{ J/mol} \cdot \text{K}$
Polyatomic Gas	$c_V = \frac{6}{2}R = 3R$	$24.94 \text{ J/mol} \cdot \text{K}$
Crystals	$c_V = \frac{6}{2}R = 3R$	$24.94 \text{ J/mol} \cdot \text{K}$

Constant Pressure Process: Isobaric

For a monoatomic gas the following equation can be derived:

$$\begin{aligned}\Delta E_{\text{int.}} &= Q + W = n c_P \Delta T - P \Delta V \\ P \cdot V &= nRT \implies P \cdot \Delta V = nR \Delta T \\ \Delta E_{\text{int.}} &= n c_V \Delta T = n c_P \Delta T - n R \Delta T \\ c_V &= c_P - R \\ c_P &= c_V + R = \frac{5}{2} R = 20.785 \text{ J/mol} \cdot \text{K}\end{aligned}$$

$$c_P - c_V = R$$

In general, for a gas with f degrees of freedom the specific heat at constant pressure is:

$$c_P = \frac{1}{2} f R + R$$

Table of specific heats at constant volume c_V and constant pressure c_P at room temperature ($\approx 300 \text{ K}$):

Monoatomic Gas	$c_V = \frac{3}{2} R$	$c_P = \frac{5}{2} R$	20.79 J/mol · K
Diatomic Gas	$c_V = \frac{5}{2} R$	$c_P = \frac{7}{2} R$	29.10 J/mol · K
Polyatomic Gas	$c_V = \frac{6}{2} R = 3R$	$c_P = 4R$	33.26 J/mol · K

Ratio of Specific Heats:

$$\gamma = \frac{c_P}{c_V} = \frac{(5/2) R}{(3/2) R} = \frac{5}{3} = 1.667 \quad \text{for a monoatomic gas}$$

In general for a gas with f degrees of freedom:

$$\gamma = \frac{c_P}{c_V} = \frac{\frac{1}{2} f R + R}{\frac{1}{2} f R} = 1 + \frac{2}{f}$$

3.3.3 Adiabatic Process

During an adiabatic process no energy enters or leaves the system in the form of heat Q .

This is realized for example in the following cases:

- perfect thermal insulation of the walls of a container for an ideal gas, or
- fast processes, where the system does not have enough time to exchange energy.

$$Q = 0 \quad \Delta E_{\text{int.}} = Q + W = W$$

During an adiabatic process all the three, pressure P , volume V and temperature T change.

The relation between P , V and T will be calculated in the following:

$$\begin{aligned} \Delta E_{\text{int.}} &= -P \Delta V = n c_V \Delta T \\ -P \Delta V &= n c_V \Delta T \quad \text{therefore} \quad \Delta T = \frac{-P \Delta V}{n c_V} \end{aligned}$$

By taking the derivative of $P \cdot V = nRT$ by dT one obtains:

$$\begin{aligned} P \cdot \frac{dV}{dT} + V \cdot \frac{dP}{dT} &= nR \\ P dV + V dP &= nR dT \\ P dV + V dP &= nR \frac{(-P dV)}{n c_V} \\ P dV + V dP &= -\frac{R}{c_V} P dV \end{aligned}$$

Substitute $R = c_P - c_V$ and divide by $P \cdot V$:

$$\begin{aligned} \frac{dV}{V} + \frac{dP}{P} &= -\left(\frac{c_P - c_V}{c_V}\right) \frac{dV}{V} \\ \frac{dV}{V} + \frac{dP}{P} &= (1 - \gamma) \frac{dV}{V} \\ \frac{dP}{P} &= -\gamma \frac{dV}{V} \\ \int \frac{1}{P} dP &= -\int \gamma \frac{1}{V} dV \end{aligned}$$

$$\ln P + \gamma \ln V = \text{const.}$$

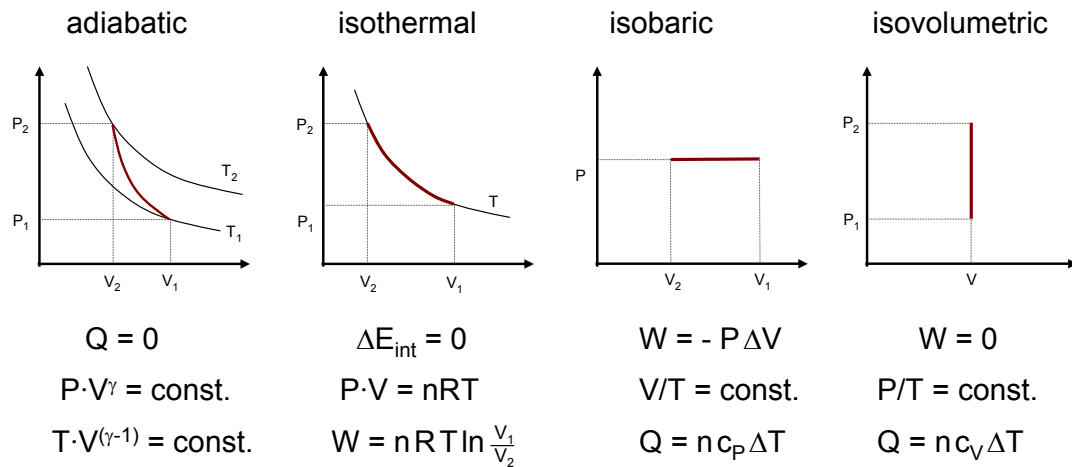
$$\ln P \cdot V^\gamma = \text{const.}$$

$P \cdot V^\gamma = \text{const.}$

$T \cdot V^{(\gamma-1)} = \text{const.}$
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The second equation can be derived in a similar way by substitution P with T in the equation of the ideal gas law: $P \cdot V = nRT$.

Summary: Thermodynamic Processes



The Stirling Engine

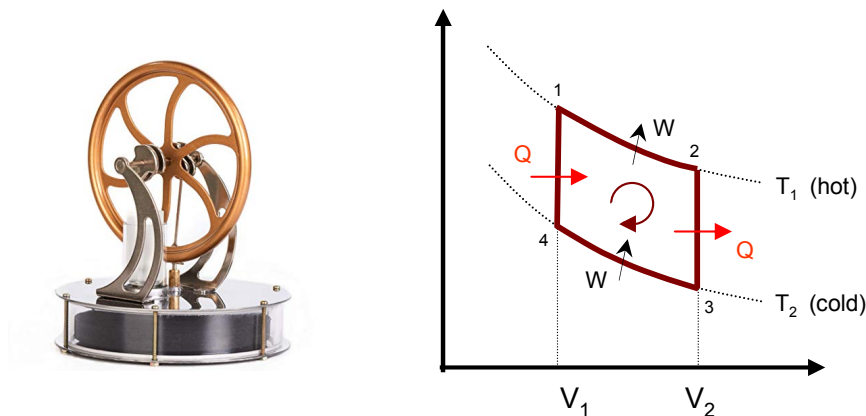


Figure 3.3: P-V diagram of a Stirling engine.

A Stirling engine is a heat engine which operates between the temperatures of two heat reservoirs, a hotter and a colder. Two pistons work with the cyclic expansion and compression of air. The thermal process is a closed cycle with the following individual steps:

- 1 → 2 **isothermal expansion**: constant temperature - absorbing heat from the reservoir with higher temperature.
- 2 → 3 **constant volume process**: temperature decrease.
- 3 → 4 **isothermal compression**: at constant temperature of the colder reservoir.
- 4 → 1 **constant volume process**: increase of the temperature.

Since this is a closed cycle process, the change in ΔE_{int} after one full cycle is zero.

The work done by the Stirling engine is the area inside the red lines of this closed cycle process.

3.3.4 Specific Heat of Solids and Liquids

The amount of heat (energy) that is needed to raise the temperature of 1 kg of a substance by $\Delta T = 1^\circ\text{C}$ is:

$$Q = mC\Delta T$$

where m is the mass in [kg] and C is the specific heat of the solid [$\text{J}/\text{kg}^\circ\text{C}$].

The heat capacity c is the specific heat per unit mass:

$$c = \frac{C}{m} \quad \text{with } Q = c \cdot \Delta T$$

For a solid under pressure the volume hardly changes. Therefore there is no major difference between C_P and C_V and the following approximation can be made: $C_P \approx C_V = C$.

The specific heat C is different for different substances. Examples are give in the table below.

The specific heat is typically constant for the temperature range around room temperature, but decreases for temperatures below 100 K and converges towards zero for $T \rightarrow 0\text{ K}$. Note that the specific heat becomes infinitely small close to zero temperature, but never reaches zero.

TABLE 20.1 Specific Heats of Some Substances at 25°C and Atmospheric Pressure

Substance	Specific Heat ($\text{J}/\text{kg} \cdot ^\circ\text{C}$)	Substance	Specific Heat ($\text{J}/\text{kg} \cdot ^\circ\text{C}$)
<i>Elemental solids</i>		<i>Other solids</i>	
Aluminum	900	Brass	380
Beryllium	1 830	Glass	837
Cadmium	230	Ice (-5°C)	2 090
Copper	387	Marble	860
Germanium	322	Wood	1 700
Gold	129	<i>Liquids</i>	
Iron	448	Alcohol (ethyl)	2 400
Lead	128	Mercury	140
Silicon	703	Water (15°C)	4 186
Silver	234	<i>Gas</i>	
		Steam (100°C)	2 010

Note: To convert values to units of $\text{cal}/\text{g} \cdot ^\circ\text{C}$, divide by 4 186.

3.3.5 Latent Heat

Energy is needed when a system undergoes a ‘phase change’, i.e. a ‘change of state’ from solid-to-liquid (melting), liquid-to-gas (boiling) or solid-to-gas (sublimation). The heat required for such a phase change is:

$$Q = \Delta m \cdot L$$

where $\Delta m = m_f - m_i$ is the change of mass of one state, i.e. the reduction of the amount of ice when it melts. L is the ‘Latent Heat’ in $[J/kg]$.

Table 19.3
Latent heats of fusion and vaporisation

Substance	Melting point (°C)	Latent heat of fusion	Boiling point (°C)	Latent heat of vaporisation (J/kg)
Helium	-269.65	5.23×10^3	-268.93	2.09×10^4
Oxygen	-218.79	1.38×10^4	-182.97	2.13×10^5
Nitrogen	-0.97	2.55×10^4	-195.81	2.01×10^5
Alcohol, ethyl	-114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1750	8.70×10^5
Aluminium	660	3.97×10^5	2450	1.14×10^7
Silver	960.80	8.82×10^4	2193	2.33×10^6
Gold	1063.00	6.44×10^4	2660	1.58×10^6
Copper	1083	1.34×10^5	1187	5.06×10^6

Example:

How much energy is required to heat 1 kg of water ice from 100 K to 1000 K?

$$100 \text{ K} \rightarrow 273 \text{ K} (0^\circ\text{C}) \quad E = 173 \text{ K} \cdot 1 \text{ kg} \cdot 2090 \text{ J/kg} \cdot \text{K} = 361.6 \text{ kJ}$$

$$\text{ice} \rightarrow \text{water} \quad E = 1 \text{ kg} \cdot 3.33 \cdot 10^5 \text{ J/kg} = 333.0 \text{ kJ}$$

$$273 \text{ K} (0^\circ\text{C}) \rightarrow 373 \text{ K} (100^\circ\text{C}) \quad E = 100 \text{ K} \cdot 1 \text{ kg} \cdot 4186 \text{ J/kg} \cdot \text{K} = 418.6 \text{ kJ}$$

$$\text{water} \rightarrow \text{gas (steam)} \quad E = 1 \text{ kg} \cdot 2.26 \cdot 10^6 \text{ J/kg} = 2260 \text{ kJ}$$

$$373 \text{ K} (100^\circ\text{C}) \rightarrow 1000 \text{ K} \quad E = 627 \text{ K} \cdot 1 \text{ kg} \cdot 2010 \text{ J/kg} \cdot \text{K} = 1260 \text{ kJ}$$

The total energy required to heat 1 kg of ice from 100 K to 1000 K is $E_{\text{total}} = 4633.5 \text{ kJ}$.

Note that water has the highest specific heat among common substances, i.e. the largest amount of energy is required to heat up water as compared to other substances.

3.3.6 Heat Transfer

The three methods of heat transfer are:

- **Conduction**
- **Convection**
- **Radiation**

Conduction

Thermal conduction takes place within a material. Metals are good thermal conductors whereas electrical insulators are typically poor thermal conductors.

The thermal conduction is defined as follows:

$$P = \frac{Q}{\Delta t} \propto A \cdot \frac{\Delta T}{\Delta x}$$

where P is the thermal conduction rate, Q is the heat, Δt is the time interval, and A is the area, e.g. diameter of the material.

$$P = \frac{Q}{t} = k \cdot A \cdot \frac{T_{\text{hot}} - T_{\text{cold}}}{L}$$

where L is the length of the thermal conductor and k is the thermal conductivity [Watt/m · K]. Alternatively one can use the following expression for the thermal conduction rate:

$$P = k \cdot A \cdot \frac{dT}{dx}$$

where dT/dx is the temperature gradient inside the thermal conductor.

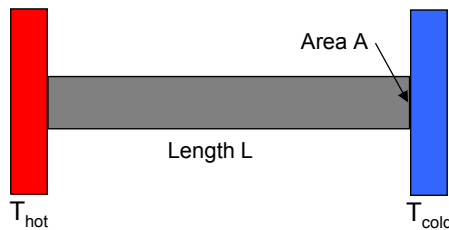


Figure 3.4: Thermal transport between a warmer and a cooler heat reservoir.

Thermal conductivities k for different materials [Watt/m · °C] at a temperature of 20°C:

Aluminum	238	Glass wool	0.04
Copper	397	Brick	0.7
Gold	314	Glass	1.05
Iron	79.5	Plastic	0.174
Silver	427	Water	0.6

In the left column metals are listed, which possess a higher thermal conductivity. The right column shows materials with a lower thermal conductivity.

An exceptional material is diamond. Diamond is a semiconductor, i.e. at normal conditions diamond is a perfect electrical insulator. However, diamond has the highest known thermal conductivity of $2300 \text{ W/m} \cdot ^\circ \text{C}$.

Note the glass wool is an excellent thermal insulator. Formerly asbestos with a thermal conductivity of $0.08 \text{ W/m} \cdot ^\circ \text{C}$ was used. However, there are severe health issues with asbestos. Therefore glass wool is currently the most commonly used material for the thermal insulation of houses.

***R*-value:**

The term L/k is referred to as the *R*-value. If various materials are connected to each other the total thermal conductivity rate through them is:

$$P = \frac{A(T_{\text{hot}} - T_{\text{cold}})}{\sum_i R_i}$$

Convection

Convection is the transport of heat through the transfer of gas (movement of a gas).

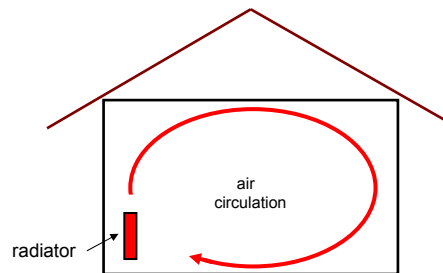


Figure 3.5: Convection. Circulation of air in a room due to the heating by a radiator.

In a room the air expands at the radiator. It becomes less dense and moves upwards. This causes a circulation of the air in the room. The hot air transports the heat.

Radiation

Objects radiate energy in the form of electromagnetic radiation (infrared radiation).

The radiation power is given by:

$$P = \sigma \cdot A \cdot e T^4$$

where A is the area. i.e. the surface of the object, T is the temperature of the object and e is a constant which describes the emission strength of a certain surface.

$$\sigma = 5.6696 \cdot 10^8 \text{ W/m}^2 \text{ K}^4 \quad \text{Stefan's Constant}$$