Contents

18   Temperature, Heat , and the First law of thermodynamics

In this chapter we will explore the following topics:

Temperature and the Zeroth law of thermodynamics. Thermometers and temperature scales. Thermal expansion. Temperature and Heat Specific heat Heat of transformation. Heat, Work, and the First law of thermodynamics. Heat transfer mechanisms.

18.1   Temperature

Temperature is a fundamental physical parameter. In what follows we will describe it and also study the methods used to measure it. It is an experimental fact that many properties of an object depend on temperature. For example the resistance R of a conductor . In the lower figure we plot the resistivity ρ of Copper as function of T. We can use R or any other parameter that depends on T to pin down the concept of temperature.
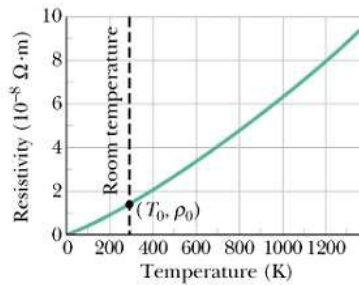
The upper picture shows an instrument that measures the resistance R of a wire inside. Such an uncalibrated instrument is known as a thermoscope. A calibrated thermoscope is called a thermometer.

18.1.1   The Zeroth law of thermodynamics

Consider picture (a) in the following figure.
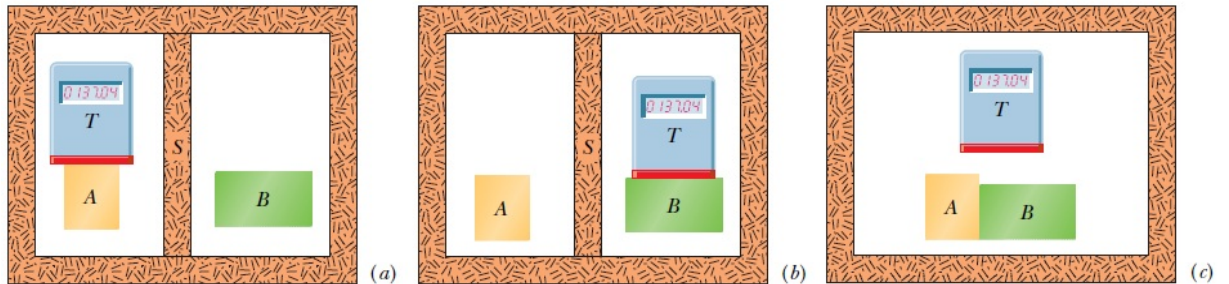

We place a thermoscope (body T) in close contact with body A and the two objects are put inside a thick - walled insulated box. The reading of body T will eventually reach a constant value (137.04 in this example). We say that the two bodies are in thermal equilibrium. Every measurable parameter of

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body A and T is stable. In addition, the two bodies have the same temperature. Assume now that bodies T and B are placed in close contact as shown in the middle picture, and that the reading of T is still 137.04. If we now place bodies A and B in close contact we find experimentally that they are at thermal equilibrium with each other. If bodies A and B are each in thermal equilibrium with body T, then A and B are in thermal equilibrium with each other. The statement above is known as the zeroth law of thermodynamics.

18.1.2   The triple point of water

In this section we will define the temperature on the Kelvin scale. Then we calibrate a thermoscope and thus convert it into a thermometer. Although the temperature of a body does not have an upper limit, it does have a lower limit which we define it to be the zero of the Kelvin scale. To set up a temperature scale we pick a reproducible thermal phenomenon and arbitrarily assign a Kelvin temperature to its environment. Examples are the freezing point and the boiling point of water at atmospheric pressure.

Gas thermometer bulb

Vapor

Ice
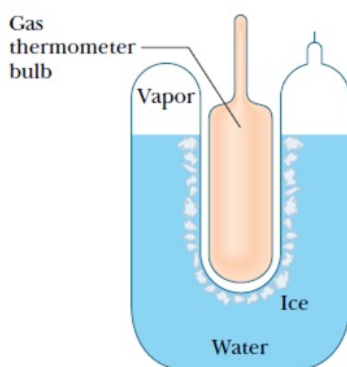
Water

It turns out that the triple point of water is easier to reproduce and is thus chosen to define the Kelvin scale. The triple point of water is defined as the coexistence of solid, liquid and gaseous forms of water at a certain temperature and pressure. The temperature at this point is taken to be $T_3 = 273.16K$.

18.1.3   The constant volume gas thermometer

In the figure below, is shown a constant volume gas thermometer.
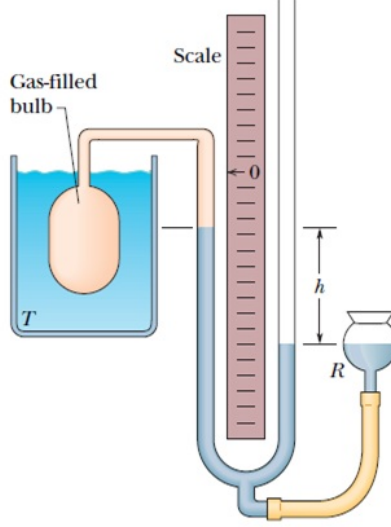
It consists of a glass bulb containing a gas. The bulb is connected to a mercury manometer. The temperature T of the bath surrounding the bulb is measured as follows: The mercury reservoir is raised or lowered so that the mercury level is at mark A. This insures that the volume of the gas is constant. The gas pressure is given by the equation:

$$p = p_0 - \rho g h.$$

Here ρ is the density of mercury and h is the height difference between point A and the mercury surface in the open end of the manometer.

The temperature T of the bath and the gas pressure pare connected by the equation:

$$T = Cp \tag{1}$$

Here C is a constant. The glass bulb is net placed inside a triple point cell at temperature $T_3 = 273.16K$, and the gas pressure $p_3$is measured. In this case:

$$T_3 = Cp_3 \tag{2}$$

If we divide equation (2) with equation (1) we get:

$$\frac{T}{T_3} = \frac{p}{p_3} \rightarrow T = (273.16K)\frac{p}{p_3}$$

In order to get consistent results, we must make sure that the gas quantity inside the bulb is small. This is expressed as:

$$T = (273.16K) \lim_{gas \to 0} \frac{p}{p_3}$$

Under these conditions the thermometer reading does not depend what type of gas is used inside the bulb.

18.1.4   The Celsius and Fahrenheit Scales

The Kelvin temperature scale is used in basic scientific work. For more practical every day applications, the Celsius scale is widely used. The Celsius degree has the same size as the Kelvin. The zero of the Celsius scale is shifted so that:

$$T_C = T - 273.15°$$

The Fahrenheit scale used in the US employes a smaller degree than the Celsius scale and a different zero:

$$0°C = 32°F$$

The relation ship between the two temperature scales is given by the equation:

$$T_F = \frac{9}{5}T_C + 32°F$$

18.2   Thermal Expansion

(a)

Circle Circular
hole

(b)
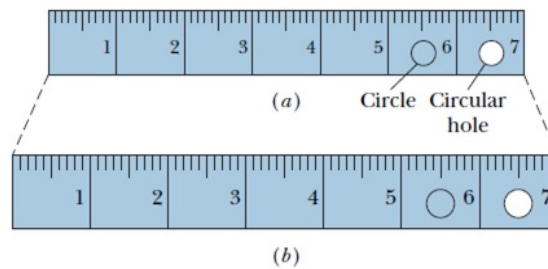
18.2.1   Linear expansion

If the temperature of a metal rod of length L, is increased by an amount ΔT, its length also increases by an amount

$$\Delta L = \alpha L \Delta T$$

The term α is known as the coefficient of linear expansion and it depends on the material of the rod. The constant α does not change very much with temperature. Thus for most practical purposes it can be taken as a constant.

18.2.2   Volume Expansion.

All three dimensions of a solid expand with temperature, and thus the volume also expands. For liquids this is the only meaningful expansion parameter. For a liquid of volume V, an increase ΔT in temperature results in an increase in volume
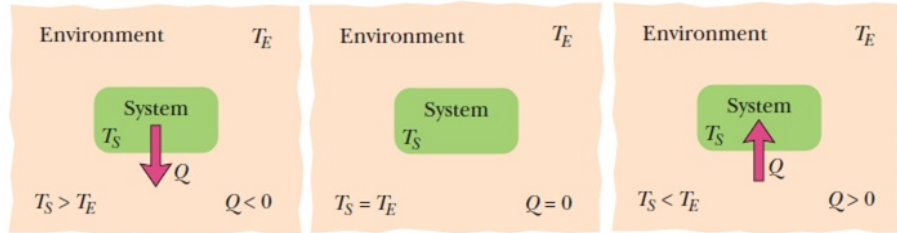
$$\Delta V = \beta V \Delta T$$

The term β is known as the coefficient of volume expansion. For a solid,

$$\beta \Delta T = \frac{\Delta V}{V} = \frac{(L + \Delta L)^3 - L^3}{L^3} = \left(1 + \frac{\Delta L}{L}\right)^3 - 1$$

$$\simeq 3\frac{\Delta L}{L} = 3\alpha \Delta T$$

$$\beta = 3\alpha$$

18.3   Temperature and Heat

Consider the two objects shown in the figure.

One is called the system and the other the environment. In the example of the text, the system is a can of cola and the environment is the kitchen table. If the system temperature T_S is bigger than the environment temperature T_E (see fig. a), then energy is transferred from the system to the environment. This energy is known as heat (symbol Q). In this case, the heat is taken as negative. If $T_S = T_E$ (see fig. b) we have no heat transfer. If $T_S < T_E$ (see fig. c) heat is transferred from the environment to the system. In this

case, $Q > 0$. Thus heat is the energy transferred between a system and its environment because a temperature difference exists between the two. SI unit for Q: The *Joule*. Another non - SI unit is the calorie (cal) defined as the amount of heat to raise the temperature of 1g of water from $14.5°C$ to $15.5°C$. In British system, the unit of heat is the British thermal unit (Btu) defined as the amount of heat that would raise the temperature of 1lb of water from $63°F$ to $64°F$. The relations among the various units are

$$1cal = 4.1868 J = 3.968 \times 10^{-3} Btu$$

18.4   The Absorption of Heat by Solids and Liquids

18.4.1   Heat Capacity.

If an object whose initial temperature is T_i absorbs an amount Q of heat, its temperature increases to a value T_f according to the equation:

$$Q = C\Delta T = C \left(T_f - T_i\right).$$

The proportionality constant C is known as the object's heat capacity.

18.4.2   Specific Heat.

The heat capacity C of an object is proportional to its mass m. Thus the equation above can be written as:

$$Q = mc \left(T_f - T_i\right).$$

The constant c is known as the specific heat and it depends on the material out of which the object is made.

18.4.3   Molar Specific Heat.

If we measure the heat capacity that corresponds to one mole of a substance, this is known as molar specific heat. It is a convenient parameter because 1 mole of any substance contains the same number (6.02×10^{23}) of atoms or molecules.

18.4.4 Heats of Transformation

An object can exist in one of three states or phases. These are the solid, the liquid, and the gas states. In the solid phase, the atoms are locked in a rigid structure. In the liquid phase, the object does not have a rigid structure but takes the shape of the container. In the gas state, the atoms are free of one another and fill completely the volume of the container. When the state of an object of mass m changes, the object can absorb or release an amount of heat Q without any change in temperature T.

The heat Q is given by the equation:

$$Q = Lm.$$

The constant L is known as the heat of transformation. If the object changes from the liquid to the gas phase, the heat of transformation L_V is known as heat of vaporization. For water at its normal boiling or condensation temperature,

$$L_V = 539 cal/g = 40.7 kJ/mol = 2256 kJ/kg$$

If the object changes from solid to liquid the heat of transformation, L_F is known as heat of fusion. For water at its normal freezing or melting temperature
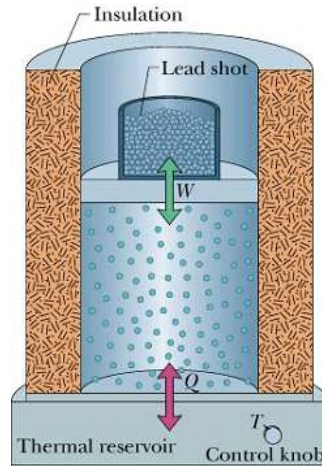
$$L_F = 79.5 cal/g = 6.01 kJ/mol = 333 kJ/kg$$

An object absorbs heat to go from the solid to the liquid or from the liquid to the gas phase. Conversely, an object releases heat to go from the liquid to the solid or from the gas to the liquid phase.

18.5 A closer look at heat and work

Consider an amount of gas contained in the cylinder shown in the figure.

The gas can absorb or release heat to or from the thermal reservoir at the bottom of the cylinder. The pressure of the gas is determined by the amount of mass placed on top of the piston of area A. Work W is done by or on the gas by removing or adding mass on top of the piston. For example if mass is removed and the piston moves upward by a distance ds, the gas does work

$$dW = \vec{F} \cdot d\vec{s} = (pA)\,ds = p\,(Ads) = pdV$$

Here p is the gas pressure and dV is the volume change. The gas starts from an initial state described by the pressure p_i, volume V_i and temperature T_i and its is slowly changed to a final state described by the pressure p_f, volume V_f and temperature T_f. The work W done by the gas during the change (known as thermodynamic process) is given by:

$$W = \int dW = \int_{V_i}^{V_f} pdV$$

There are many ways to get from the initial to the final state of the gas.

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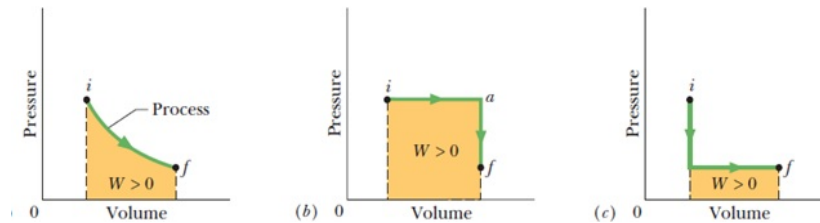
One such process is shown in the P versus V plot of fig. a. The work

$$W = \int_{V_i}^{V_f} pdV = \text{Area colored under the plot}$$

In fig. b, we first keep the pressure constant at p_i and change the volume from V_i to V_f by absorbing heat from the reservoir. Then we decrease the pressure to its final value p_f by removing some of mass sitting on top of the piston. In fig. c, we reverse the process. First we change the pressure from p_i to p_f and then we change the volume. Thus the gas can be taken from an initial to a final state by an infinite number of processes. The heat absorbed and the work done depends on the path taken on the p versus V diagram.

18.6   The First Law of Thermodynamics

Consider a gas changes from an initial to a final state by absorbing heat Q and by doing work W. Both Q and W depend on the nature of the process. The quantity $Q - W$ on the other hand is independent of the process and depends only on the initial and final states of the system. The quantity $Q - W$ represents the change in the internal energy E_{int} of the system.

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

The equation above is known as the first law of thermodynamics. In differential form:
$$dE_{int} = dQ - dW$$

The internal energy E_{int} of a system tends to increase if energy is added as heat Q and tends to decrease if energy is lost as work W done by the system The first law is a restatement of the principle of the conservation of energy.

18.6.1   Some special cases of the first law of thermodynamics

1. Adiabatic process   In this process, the system is so well insulated and the process occurs so fast that no heat is exchanged with the environment ($\Delta Q = 0$)Thus the first law takes the form:

$$\Delta E_{int} = -\Delta W$$

If work is done by the system ($\Delta W > 0$), the internal energy decreases by the same amount.

2. Constant volume process   The volume of the gas is kept constant. Thus $\Delta W = 0$ and the first law takes the form:

$$\Delta E_{int} = \Delta Q$$

If heat is absorbed by the gas $(\Delta Q > 0)$ the internal energy increases by the same amount.

3. Cyclical process   This is a process in which a system undergoes interchanges of heat and energy but returns to its initial state.
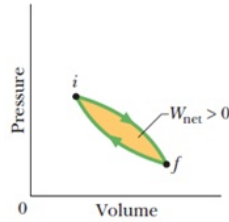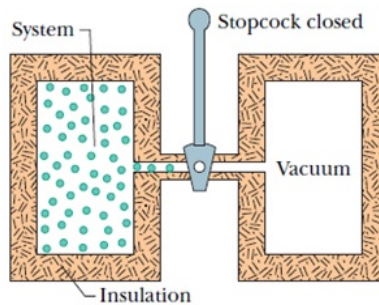

In this case

$$\Delta E_{int} = 0$$

and the first law predicts that:

$$\Delta Q = \Delta W$$

The net work during a cyclical process is equal to the the amount of heat transferred.

4. Free expansion   In this type of process, no transfer of heat occurs to the system and no work is done by it. i.e. $\Delta Q = 0$ and $\Delta W = 0$. The first law predicts that $\Delta E_{int} = 0$. The following picture shows such a process.


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An amount of gas is initially confined to the left chamber while the right chamber is empty. Both chambers are thermally insulated so that no heat can be exchanged with the environment. The valve is opened and the gas occupies both chambers. No work is done in the process.

18.7 Heat transfer mechanisms

There are three mechanisms via which heat is transferred from one to another object. These are: conduction, convection, and radiation.

18.7.1 Conduction

Consider the slab of area A and thickness L shown in the figure, sandwiched between a hot and a cold reservoir of temperature T_H and T_C, respectively.
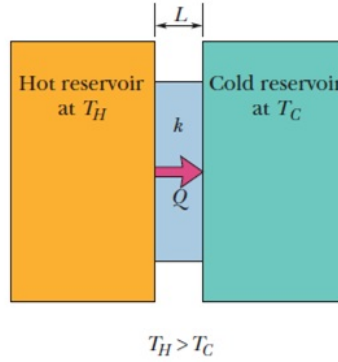
$$T_H > T_C$$

Experiment shows that heat will flow from the hot to the cold reservoir through the slab at the rate:

$$P_{cond} = \frac{\Delta Q}{\Delta t} = kA\frac{T_H - T_C}{L}$$

The constant k is known as thermal conductivity and it depends on the material out of which the slab is made of. Rewrite the above as

$$T_H - T_C = \frac{L}{Ak}P_{cond} = P_{cond}R_T$$

where $R_T = \frac{L}{Ak}$ plays the same role as the resistance in the Ohm's law $V = IR$ of the electric circuit theory if we identify $T_H - T_C$ as the potential difference and P_{cond} as the electric current.
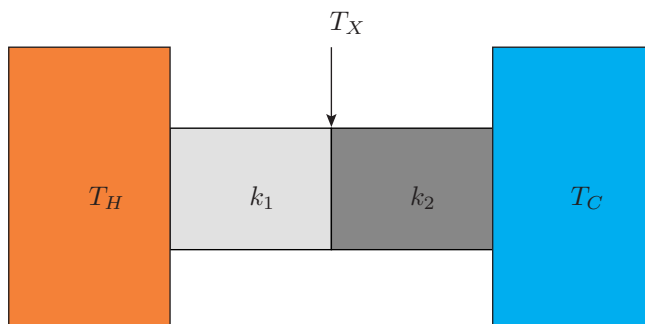
Thermal conductors in parallel
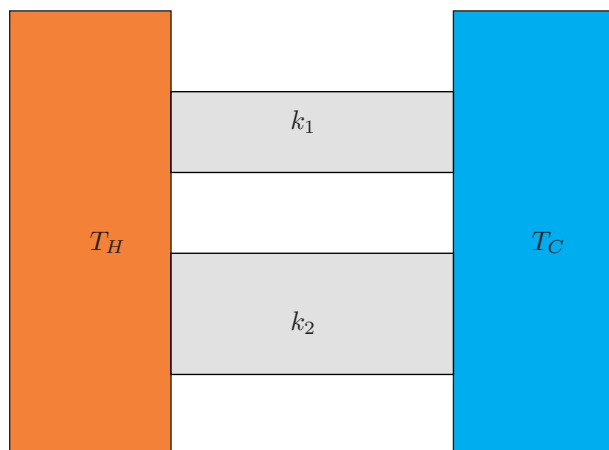
$$P_{cond} = \frac{\Delta Q_1 + \Delta Q_2}{\Delta t} = (k_1 A_1 + k_2 A_2)\frac{T_H - T_C}{L}$$

Use thermal Ohm's law:

$$\frac{1}{R_T} = \frac{1}{R_{T1}} + \frac{1}{R_{T2}} = \left(\frac{L}{A_1 k_1}\right)^{-1} + \left(\frac{L}{A_1 k_2}\right)^{-1}$$

$$P_{cond} = \frac{T_H - T_C}{R_T} = \left(\frac{k_1 A_1}{L} + \frac{k_2 A_2}{L}\right)(T_H - T_C)$$

18.7.2   Thermal conductors in serial

$$P_{cond} = \frac{\Delta Q}{\Delta t} = k_1 A \frac{T_H - T_X}{L_1} = k_2 A \frac{T_X - T_C}{L_2}$$

$$\frac{k_1}{L_1} T_H + \frac{k_2}{L_2} T_C = \left(\frac{k_1}{L_1} + \frac{k_2}{L_2} \right) T_X$$

So

$$T_X = \frac{\frac{k_1}{L_1} T_H + \frac{k_2}{L_2} T_C}{\frac{k_1}{L_1} + \frac{k_2}{L_2}}$$

and then

$$P_{cond} = \frac{\Delta Q}{\Delta t} = k_1 A \frac{T_H - T_X}{L_1}$$

$$= A \frac{k_1}{L_1} \left(T_H - \frac{\frac{k_1}{L_1} T_H + \frac{k_2}{L_2} T_C}{\frac{k_1}{L_1} + \frac{k_2}{L_2}} \right)$$

$$= A \frac{k_1}{L_1} \frac{k_2}{L_2} \frac{T_H - T_C}{\frac{k_1}{L_1} + \frac{k_2}{L_2}} = A \frac{T_H - T_C}{\frac{L_1}{k_1} + \frac{L_2}{k_2}}$$

Use thermal Ohm's law:

$$R_T = R_{T1} + R_{T2} = \frac{L_1}{A k_1} + \frac{L_2}{A k_2}$$

$$P_{cond} = \frac{T_H - T_C}{R_T} = \frac{1}{\frac{L_1}{A k_1} + \frac{L_2}{A k_2}} (T_H - T_C)$$

$$= \frac{A}{\frac{L_1}{k_1} + \frac{L_2}{k_2}} (T_H - T_C)$$

18.7.3 Convection

When a fluid comes in contact with an object whose temperature is higher than that of the fluid, the temperature of the fluid increases and the fluid expands and its becomes less dense. The lighter warmer fluid rises while some of the surrounding cooler fluid takes its place. In the process heat is transferred by convection.

18.7.4 Radiation

This exchange of heat occurs via the emission or absorption of electromagnetic radiation. Thus this process can occur in vacuum. The rate P_{rad} at which an object of area A and temperature T emits radiation is given by:

$$P_{rad} = \sigma \varepsilon A T^4$$

The constant $\sigma = 5.6703 \times 10^{-8} W/m^2 \cdot K^4$ is known as the Stefan-Boltzman constant. The constant ε is the emissivity of the object surface. For a totally absorbing surface $\varepsilon = 1$. Such an object is known as a **blackbody radiator**. The rate at which an object absorbs thermal radiation from its environment at temperature T_{enc} is given by the equation:

$$P_{abs} = \sigma \varepsilon A T_{env}^4$$

The net energy gain is:

$$P_{net} = P_{abs} - P_{rad} = \sigma \varepsilon A T_{env}^4 - \sigma \varepsilon A T^4 = \sigma \varepsilon A \left(T_{env}^4 - T^4 \right)$$

Note: $P_{net} > 0$ if $T_{env} > T$