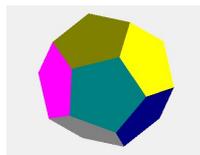


Elementary

Thermodynamics and Calorimetry

Chapter 7 and 9 of the textbook Elementary Physics 1

This is an article from my home-page: www.olewithhansen.dk



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1. What is heat

At an early stage in the history of physics one has realized that certain rules of conservation apply for amounts of heat.

If you bring a hot body in contact with a cold body, then the hot body will get cooler and the colder body will get warmer, but never the other way round.

Making such calorimetric experiments they always show that heating of one body is accompanied by the cooling of another.

Based on such observations the Alchemists postulated the existence of a "heat substance" called Flogiston that was present everywhere in unchangeable amounts that could be transferred from one body to another without loss, and could only be created as a result of chemical processes as burning, but not as a result of mechanical processes.

(Somewhat in contradiction to the methods of making fire in several thousand years before)

Lord Rumford (1753 – 1844) observed, however, that when drilling cannons large amount of heat was created, so large that it "was able to boil water", while there was no detectable cooling of other substances. And that marked the end of the calorimetric theory of heat. What Rumford discovered was

that mechanic energy through a frictional work was converted to heat.

When the concept of conservation of energy became established, it became natural to perceive heat as a form of energy.

This point of view can, however, only be substantiated, if a certain amount of mechanical energy always result in the same amount of heat.

All experiments dealing with conversion of mechanical energy to heat has proved to be in accordance with the conservation of energy.

In thermodynamics we are not so much occupied with the nature of heat is as long as we are able to do calculations with amounts of heat.

With the discoveries of the molecule structure of materials, it is however, natural to link the concept of heat the properties of the atoms and molecules in the materials.

Notably Ludvig Boltzmann (1844 – 1906) occupied himself with this issue and he expressed his results in his *kinetic theory of molecules*. (Statistical mechanics).

The cornerstone in the kinetic theory of molecules is:

<i>Heat = The kinetic energy of the molecules.</i>
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This perception explains in a simple manner some elementary observations of the behaviour of materials when they are heated. But more decisive, the concept of heat is thereby directly coupled to elementary concepts in classical mechanics, based on the laws of Newton.

2. Melting and evaporation

In a solid material the molecules are located in fixed positions and hold together by electrical forces. However, the molecules are able to vibrate (oscillate) around these positions.

In a crude model for a solid material, one may conceive the molecules as small bullets held together by springs. The molecules can acquire energy by hitting or rubbing the material. The molecules will

then be brought away from their equilibrium positions and start to vibrate. The stronger the vibrations are the warmer the body gets, we say.

In the kinetic theory of molecules it is shown that the temperature measured on the Kelvin scale is directly proportional to average kinetic energy of the molecules.

The Kelvin temperature (or the absolute temperature) has its zero point at -273°C , but otherwise it has the same graduation as the Celsius scale.

If a solid material is heated, the vibration of the molecules may become so violent that the electrical forces no longer can hold them together. The solid material disintegrate.

We say that the material is melting

At the same time this qualitative model explains the fact that during the melting the temperature is fixed at the melting point in spite of a steady supply of heat.

The supplied heat does not contribute to the raise of temperature, but it delivers the work necessary to tore the molecules apart from each other.

In the melted material the molecules are no longer bound to fixed positions, but they are still hold together in a gravy of torn springs.

The heat that must be supplied per unit of mass to melt a solid material, when it in advance is heated to the melting point, is called the melt-heat..

The different states of a material (solid, liquid, gas) are called the phases of the material, and the transitions from one phase to another is called a phase transition. Above we have figuratively described the transition from the solid phase to the liquid phase.

If additional heat is supplied after the material has melted, then the temperature reach a critical level, where the kinetic energy of the molecules (and thereby their velocities) has reached a level, where a molecule is able to free itself from the forces from which it has been held by the other molecules, and thereby leave the liquid. The liquid is boiling. It has become a gas.

As it is the case with melting, the transition from the liquid phase to the gaseous phase happens at a constant temperature until all the liquid has evaporated. The supplied energy does not cause the temperature to raise, but goes to free the molecules from the liquid.

When the liquid is evaporated, then the molecules move independently of each other under frequent collisions. The liquid has turned into a gas.

The heat that must be supplied to convert one unit of mass from the liquid phase to the gas phase is called the evaporating heat.

The behaviour of gasses, that is the relation between pressure, volume and (Kelvin) temperature, can be derived from the kinetic theory of gasses.

We shall, however, first study gasses experimentally, and thus derive the *gas laws* before we return to the molecule theoretically explanation.

The description we have given above is obviously vastly simplified. For example it should be mentioned that the molecules have substantial different velocities, and therefore evaporation takes place from the surface of a liquid even if the temperature is far below the boiling point. That you must supply heat to evaporate a liquid, and that there is released heat, when a gas condense is, however, a common experience from daily life.

The existence of a absolute zero point for temperature comes as a consequence of the gas laws as well as the kinetic theory of gasses, since it is the temperature where the molecules are at rest. This leads to the Kelvin scale of temperature, which has its zero point at -273°C .

3. Internal and external energy

In daily language one often uses the word heat in the meaning that a body is hot that it has thermal energy. Her we shall give a more precise content to the concept of heat, as it is used i physics and place this concept in the most general formulation of *the conservation of energy theorem*. We have earlier defined the mechanical energy of a system as the sum of the kinetic and potential energy. Since the mechanical energy is related to external surroundings we shall call it *external energy*.

If you perform a frictional work on a body you add energy to the body, resulting in a rise of the temperature. The body acquires energy corresponding to a increase of the kinetic energies of the molecules. Since thermal energy is bound to the body independently of the external surroundings, we shall call this kind of energy for *internal energy*.

Since an increase in temperature means that the body gets warmer it would could seem sensibly to call this kind of energy for *heat*. However, this is not what we do in that part of physics called thermodynamics. Instead, we shall from now on call this kind of energy for internal energy or *thermal energy*. Internal energy also include any other type of energy that is attached to the body exclusively e.g. the energy that is contained in an explosive, or other forms of chemical or nuclear energy.

The reason for this distinction is that the meaning of *heat* in physics is a quantity, which similar to work can be transferred from one body to another making a change of the energies of the two bodies.

So in the same manner as we distinguish between work and mechanical energy, we distinguish heat from thermal energy

Supplying heat to a body does not always mean a corresponding increase of thermal energy.

If the body is a machine, then a part of the heat (but not all) can be converted to mechanical energy to make a machine do useful work.

For example gasoline contains (a lot of) chemical energy. When it burns (explosively), making a compound with oxygen, heat is freed to the surrounding gas. The increase of the thermal energy of the gas and the following expansion are used in the internal combusting engine to do piston work.

4. The first law of thermodynamics

In mechanics we have defined the mechanical energy by the work necessary to bring a system in a certain mechanical state.

You may think of lifting a weight in a uniform motion. The work done equals the increase of the potential energy of the body. If the body is dropped the work done by gravity is converted to kinetic energy

In mechanics, one may (for systems without friction) formulate a *mechanical energy conservation theorem*.

For a frictionless mechanical system applies that the work done on a system is equal to the change of mechanical energy of the system.

$$(4.1) \quad W = \Delta E_{mek} \quad \text{where} \quad \Delta E_{mek} = \Delta E_{kin} + \Delta E_{pot}$$

The equation (4.1) cannot, however, be maintained in general for the following two reasons.

Firstly: If the system is not frictionless, the work done does not need to go into mechanical energy, it may also be converted into internal (thermal) energy

If you pull a block a distance s with a constant velocity to compensate for a frictional force F_{fric} , then you perform a work $W = F_{fric} s$. Since the block neither gains height nor velocity, the mechanical energy is unchanged. On the other hand it is possible to measure a (small) increase in the temperature of the block. The work has been converted into thermal energy.

To maintain the energy conservation theorem, we must modify it to include internal energy.

$$\Delta E = \Delta E_{kin} + \Delta E_{pot} + \Delta E_{internal}$$

Secondly: It is possible to change the energy of a system, without doing a mechanical work. Alternatively you may supply heat Q to the system. However, it is not possible to give a definition of heat which correspond to the definition of work. We can only state that energy which is not supplied from performing a work is called *heat*.

A supply of heat can both cause a change in the mechanical energy as well as the thermal energy. For a machine one usually is interested in converting as much mechanical energy as possible to mechanical energy.

The second law of thermodynamics states, however, that it is theoretically impossible to convert an amount Q of heat entirely to mechanical work.

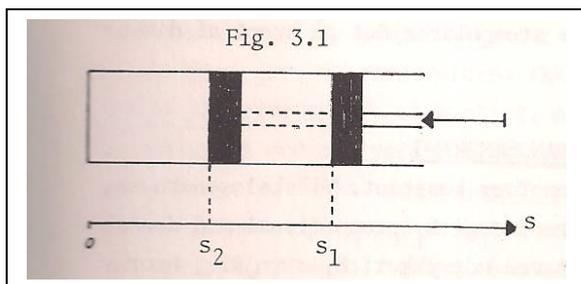
Therefore we must in general add heat Q to the left side of the energy conservation theorem.

For an arbitrary physical system, which is able to exchange energy with the surroundings it applies without restriction that the sum of the work done W on the system plus the heat Q supplied to the system are equal to the change of the energy of the system.

$$(4.3) \quad W + Q = \Delta E \quad \text{where} \quad \Delta E = \Delta E_{kin} + \Delta E_{pot} + \Delta E_{internal}$$

Using the equation, however, it should be noticed that all the quantities W , Q and ΔE are signed. If W is negative it means that the system is doing work on the surroundings. If Q is negative it means the system leaks heat into the surroundings, and if ΔE is negative it means a loss of energy of the system.

5. Piston work



The figure (5.1) shows a cylinder containing an ideal gas and equipped with a sliding piston.

We shall then derive an expression for the work done by a shift of the piston.

First we shall assume that the gas is compressed and it is done under constant pressure. (This will be the case when the gas is expanding against an outer pressure, caused by heating of the gas).

Let the area of the piston be A , and let Δs be the shift in the position. The pressure of the gas is P . With the chosen orientation $\Delta s = s_2 - s_1$ is negative, since the gas is compressed.

When the piston is pressed inwards it requires a force $F = PA$. If the piston moves a distance Δs in a uniform movement, then a (positive) work: $W = F(-\Delta s) = -PA\Delta s = -P\Delta V$ has been performed, where the change in volume is $\Delta V = V_2 - V_1 = A\Delta s$.

The piston work, which is performed by reducing the volume an amount ΔV against an external pressure P , is the given by:

$$(5.2) \quad W = -P\Delta V \quad (\Delta V = V_2 - V_1)$$

If the piston moves outward a piece Δs and hence $\Delta V = A\Delta s$ is positive, then the work done by gas is given by the expression: $W_{gas} = P\Delta V$.

But when the gas performs work on the surroundings this should be counted negative in the first law of thermodynamics.

For the performed work it therefore applies: $W = -W_{gas} = -P\Delta V$. Since this is the same expression as we used in (5.2), this equation remain unaltered irrespectively of whether the piston goes in or out.

So if the work done is piston work, which means a change in volume against a constant outer pressure the first law of thermodynamic becomes.

$$(5.3) \quad W + Q = \Delta E \quad \text{and} \quad W = -P\Delta V \quad \text{gives} \quad Q = \Delta E + P\Delta V$$

If the pressure is not constant during the volume change ΔV , we must divide the change of volume into minor pieces, so small that P can be assumed to be constant in each of the pieces, and afterwards sum it up. Later we shall see, how the summation can be done by integration.

6. Isothermal and adiabatic changes of state for a gas

A **isothermal change** means that the temperature is constant. In the kinetic theory of gasses it is shown that for an ideal gas the energy of the gas is proportional to the absolute temperature T .

$$E_i = \gamma n_M R T$$

n_M is the number of moles in the gas, and $R = 0.0821 \frac{l \cdot atm}{mol \cdot K}$ is the gas constant. γ is a constant,

which is dependent on the gas. The significance of γ will be revealed later.

For an ideal gas the internal energy depends only on the absolute temperature, so by an isothermal change of state, the change of energy is zero, and hence $\Delta E_i = 0$. From the first law of thermodynamics, we then get with $\Delta E = \Delta E_i = 0$.

$$(6.1) \quad Q + W = 0 \Rightarrow Q = -W = \sum_{(1)}^{(2)} P \Delta V \quad (\text{Isothermal change})$$

In (6.1) we have used the summation symbol indicating that the pressure is not constant in an isothermal process, as the volume is changed from V_1 to V_2 for the reason that (according to Boyle-Mariottes law) the pressure changes in inverse proportion to the volume.

From (6.1) it is further seen that a piston work on an ideal gas is always accompanied by absorption or loss of heat.

An isothermal change of state thus means an exchange of heat with the surroundings, which emphasize the conceptual difference between heat and thermal energy (in physics).

An adiabatic change of state means that the system is heat isolated, so that $Q = 0$. There is no gain or loss of heat. According to the first law of thermodynamics $W + Q = \Delta E$, we then find:

$$(6.2) \quad W = \Delta E \quad \text{and} \quad W = -P \Delta V \quad \text{then} \quad \Delta E + P \Delta V = 0 \quad (\text{Adiabatic change})$$

An adiabatic change of state always causes a change in the internal energy, that is, a change in temperature. This follows from $\Delta E_i = \gamma n_M R \Delta T$ and $\Delta E_i \neq 0$ according to (6.2).

Boyle-Mariottes law is valid for isothermal changes, but not for adiabatic changes of an ideal gas, since in the latter case the temperature is not constant.

By compressing the air in a container so quickly, that there is no time for temperature equalization with the surroundings, one may achieve a large increase in temperature.

In a minor measure that is what you may experience when you pump a bike tire with a pump with a metal cylinder. On industrial scale, it is what happens in the diesel engine, since it has no electrical ignition, but where the mixture of air and fuel ignites, when the gas is compressed adiabatically by the piston.

Applying integral calculus it is fairly easy to derive the relations between pressure, volume and temperature for an adiabatic change of state. The result is:

$$(6.3) \quad PV^\beta = \text{constant} \quad \text{and} \quad TV^{\gamma-1} = \text{konstant} \quad (\text{Adiabatic change of state})$$

In (6.3) $\beta = \frac{\gamma + 1}{\gamma}$ and γ is the same constant, which goes into the expression for the internal energy.

Examples and exercises

6.4 Example

0.1 mole of an ideal gas is confined in a cylinder, which is equipped with a piston, and where the pressure is held constant at 2.0 atm. The constant $\gamma = 5/2$ for the gas in question, and the internal energy can be written $E_i = 5/2 n_M RT$. The gas is heated from 20° C to 250° C.

- Find the initial and the final volume.
- Calculate the work done by the piston, and the supplied heat during the heating.

Solution:

- The initial volume V_1 is calculated from the equation of state for ideal gasses.

$$PV_1 = n_M RT \Rightarrow V_1 = \frac{n_M RT}{P} = \frac{0.1 \text{ mol} \cdot 0.0821 \frac{\text{l} \cdot \text{atm}}{\text{mol} \cdot \text{K}} 293 \text{ K}}{2.0 \text{ atm}} \Rightarrow V_1 = 1.20 \text{ l}$$

The final volume is calculated from the second law of Gay-Lussacs.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow V_2 = \frac{T_2}{T_1} V_1 = \frac{523 \text{ K}}{293 \text{ K}} \cdot 1.20 \text{ l} = 2.14 \text{ l}$$

- $W = -P\Delta V \Rightarrow W = 2.0 \text{ atm} (2.14 - 1.20) \text{ l} = 1.88 \text{ l atm}.$

$$W = -1.88 \cdot 10^{-3} \text{ m}^3 \cdot 1.013 \cdot 10^5 \text{ N/m}^2 = -190 \text{ J}.$$

The heat supplied is calculated from the first law using (5.3).

$$Q = \Delta E + P\Delta V \quad \text{og} \quad \Delta E = 5/2 n_M R\Delta T \Rightarrow Q = 5/2 n_M R\Delta T + P\Delta V$$

$$Q = 5/2 \cdot 0.1 \text{ mol} \cdot 8.31 \text{ J/(mol K)} \cdot 230 \text{ K} + 190 \text{ J} = 4.97 \cdot 10^3 \text{ J}.$$

8. C_p og C_v for ideal gasses

For gasses it is necessary to define two specific heat capacities, one for constant pressure C_p and one for constant volume C_v . This is because of the heat that must be supplied to give a rise in temperature of 1 Kelvin differ in the two cases.

C_v is defined as the heat Q that must be supplied one mole of the gas to give rise of a temperature of 1 Kelvin, when the volume is held constant.

C_p is defined as the heat Q that must be supplied one mole of the gas to give a rise of temperature of 1 Kelvin, when the pressure is held constant:.

It then follows immediately:

$$(8.1) \quad Q = C_v n_M \Delta T \quad \text{and} \quad Q = C_p n_M \Delta T$$

The proportionality with the number of moles is evident, since if you double the number of moles it requires twice as much heat.

In the definition it is assumed that C_P and C_V are independent of where on the temperature scale the heat is supplied, something which is reasonably fulfilled within moderate temperature changes.

To find an expression for C_P and C_V , we shall apply the formula for the change of internal energy: $\Delta E_i = \gamma n_M R \Delta T$, where γ is the previously mentioned constant, which has the value $3/2$ for an one-atomic gas.

We shall first look at C_V . Constant volume means that $\Delta V = 0$, such that no piston work is done. From The first law of thermodynamics it then follows:

$$Q = \Delta E + P\Delta V \quad \wedge \quad \Delta V = 0 \quad \wedge \quad \Delta E = \gamma n_M \Delta T \quad \Rightarrow \quad Q = \gamma n_M \Delta T$$

If we insert $n_M = 1 \text{ mole}$ and $\Delta T = 1 \text{ K}$, then Q is equal to C_V by definition.

$$(8.2) \quad C_V = \gamma R \quad (C_V = 3/2 R \text{ for an one-atomic gas})$$

Then we shall calculate C_P . From the equation of state for ideal gasses: $PV = n_M RT$, it follows that $P\Delta V = n_M R \Delta T$, when the pressure is held constant. Using this relation, we can find C_P from the first law.

$$\begin{aligned} Q &= \Delta E + P\Delta V \quad \wedge \quad P\Delta V = n_M R \Delta T \quad \wedge \quad \Delta E = \gamma n_M R \Delta T \quad \Rightarrow \\ Q &= \gamma n_M R \Delta T + n_M R \Delta T \quad \Rightarrow \quad Q = (\gamma + 1) n_M R \Delta T \end{aligned}$$

If we insert $n_M = 1 \text{ mole}$ and $\Delta T = 1 \text{ K}$, Q becomes (according to the definition) equal to C_P .

$$(8.2) \quad C_P = (\gamma + 1) R \quad (C_P = 5/2 R \text{ for an one-atomic gas})$$

9. The specific heat capacity for solids and liquids

For solid materials and liquids we have that the heat that must be supplied at constant pressure to obtain a certain raise in temperature is almost independent of where on the temperature scale the heat is supplied (as long as there are no phase changes), but it must evidently be proportional with mass of the material and the temperature rise. This is expressed in the general formula:

(9.1) $Q = c \cdot m \cdot \Delta T$

The constant c depends only on the material, and it is called the specific heat capacity for the material.

m is the mass of the material and ΔT is the temperature change i.e. it may be negative if the material is cooled.

From the defining equation it follows that the SI-unit for specific heat capacity is $J/(kg \text{ K})$.

According to the first law, the supplied heat goes to thermal energy and to do piston work against an external pressure $P_{external}$. Doing experiments in a laboratory the external pressure is the atmospheric pressure. If we hold (9.1) together with the first law, we find.

$$(9.2) \quad Q = \Delta E + P_{external} \Delta V_{material} \quad \wedge \quad Q = c \cdot m \cdot \Delta T \quad \Rightarrow \quad c \cdot m \cdot \Delta T = \Delta E + P_{external} \Delta V_{material}$$

However the increase in volume for solid material and liquids are in general so small that we (within the accuracy of measurement) can neglect the term $P_{\text{external}}\Delta V_{\text{material}}$, and we may then rewrite (9.1) in the form that is most often used.

$$(9.3) \quad \Delta E = c \cdot m \cdot \Delta T$$

Equation (9.3) is the most general relation between temperature changes and the change in thermal energy for solids and liquids. It is therefore often refers to as

The calorimetric equation

Calorimetry means measurement of heat.

Often c and m are put together in one quantity $C = c \cdot m$, called the *heat capacity* of the material. The thermodynamic quantities temperature T , energy ΔE , pressure P and volume V are called state variables, because they are only function of the state of the gas, and not how that state is reached. In thermodynamics another state variable is defined, which does not have the same familiar significance as the other variables of state. It is called the enthalpy. It is defined as:

$$(9.4) \quad H = E + PV \quad \text{In the external pressure is fixed: } \Delta H = \Delta E + P\Delta V$$

The enthalpy ΔH applies, (instead of ΔE) in chemistry when very accurate calorimetric calculations are required. The reason for this is that in laboratory work the expansion of volume against the outer pressure is inevitable, and for very accurate measurements it is necessary to take this work into the energy accounting.

For solid materials and liquids one does *not* normally distinguish between the specific heat capacities c_p for maintained pressure and c_v for maintained volume. Firstly they normally differ only very little from each other, and secondly one always measures c_p .

With the introduction of the state function enthalpy, it is possible to give a precise definition of c_v and c_p .

$$(9.5) \quad Q = \Delta H = \Delta E + P_{\text{ext}} \Delta V \quad \text{and} \quad Q = c_p \cdot m \cdot \Delta T \quad \Rightarrow \quad \Delta H = c_p \cdot m \cdot \Delta T$$

$$\Delta V = 0 \Rightarrow Q = \Delta E = c_v \cdot m \cdot \Delta T \quad \Rightarrow \quad \Delta E = c_v \cdot m \cdot \Delta T$$

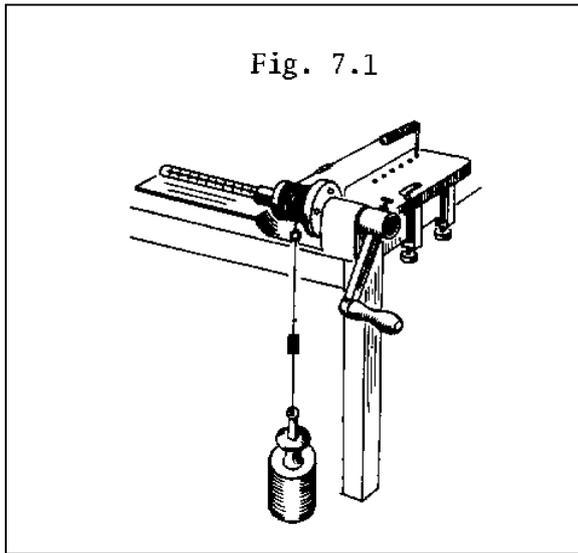
From (9.5) we see that c_p is equal to the change in enthalpy per unit mass and degree temperature, while c_v is equal to the change of thermal energy per unit mass and degree temperature.

10. Eksperimental determination of the specific heat capacity

We shall in the following assume, that the calorimetric equation (9.3) applies, that is, $\Delta E = c \cdot m \cdot \Delta T$.

From the first law of thermodynamics $Q + A = \Delta E$, we can read that we may increase the thermal energy of a body either by adding heat to the body or to perform a frictional work on the body. In the latter case, however, the process must be an adiabatic one.

10.1: Experimental measurement of the specific heat capacity with Schürholtz apparatus



We shall now demonstrate how one (earlier) in high school determined the specific heat capacity with a setup called Schürholtz apparatus. The solid brass cylinder is designed either as a massive or hollow cylinder with a hole along the axis, in which one can insert a very delicate thermometer (1/10 degree) where the temperature of the cylinder can be read. Around the cylinder is wrapped a metal tape, made of the same material as the cylinder. The one end of the tape is fixed to a spring, and in the other end is hung a mass M . The apparatus is so cleverly designed that when the handle is turned clockwise, the frictional force between the tape and the cylinder F_{fric} balances the gravitational force on the mass: $F_T = Mg$.

If m is the mass of the cylinder plus the metal tape, c is their common specific heat, and d is the diameter of the cylinder, we can calculate the work done if the handle has been turned n rounds:

$$W = W_{fric} = F_{fric}s = Mg \cdot n \cdot \pi \cdot d \quad (\pi \cdot d \text{ is the perimeter of the cylinder})$$

When doing this work, the cylinder and the metal tape get an increase in thermal energy $\Delta E = c \cdot m \cdot \Delta T$, where the increase in temperature is read on the thermometer.

If we can ignore the exchange of heat with the surroundings, what is reasonable if the increase in temperature is less than 5°C , then we have according to the first law:

$$(10.2) \quad W = \Delta E \quad \Rightarrow \quad Mgn\pi d = cm\Delta T \quad \Rightarrow \quad c = \frac{Mgn\pi d}{m\Delta T}$$

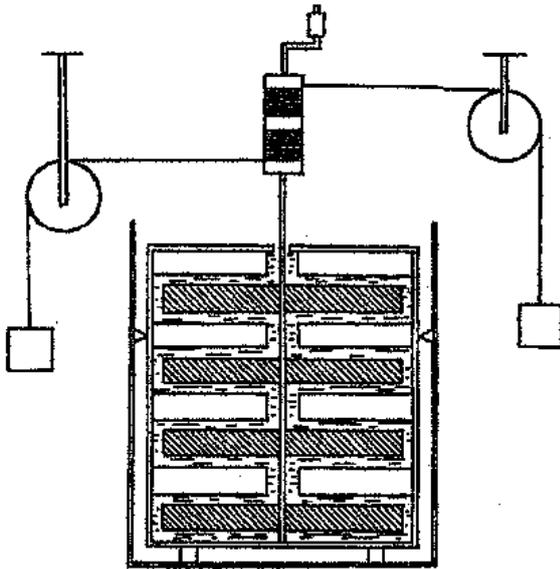
When the values measured in the experiment are inserted, we find the specific heat capacity in mechanical units $J/(kg \cdot K)$, and if the experiment is performed using a brass cylinder, we will obtain the specific heat capacity for brass, which has the scientific value $c_{brass} = 380 \text{ J/kg K}$.

The experiment is however often performed using a hollow cylinder filled with water. In this way it is possible to determine the very important specific heat capacity for water. Earlier heat and thermal energy has been measured in calories. One reason is that this unit is much easier to comprehend than the unit Joule. (Which is the work performed when the force 1 N moves a body 1 m).

One calorie (1 cal) is defined as the heat required to raise the temperature of 1 g of water 1°C .

The unit calorie is still used, also because it gives a notion of e.g. how much heat is necessary to make a cup of tea. To heat one liter of water from 20° to the boiling point requires $(1000 \text{ g})(80^\circ\text{C}) 1 \text{ cal}/(\text{g}^\circ\text{C}) = 80.000 \text{ cal} = 80 \text{ kcal}$.

Fig. 7.3



10.4 Joules experiment

To do calculations where energies are exchanged, it is necessary to know the conversion factor between the mechanical energy unit *Joule* and the calorimetric unit *cal*. The Englishman J. P. Joule, and the Danish Colding, using different methods, and independently of each other, were the first to determine this conversion factor.

The figure (10.3) shows a schematic setup of Joules apparatus.

Joule performed several accurate experiments letting water be heated by the friction of shovel wheels. The simple principle is that the wheels are mounted on an axis driven by two heavy weights. Joule could calculate the potential energy lost by the weights (measured in Joule), and the increase of the thermal energy of the water, measured in calories.

Doing the experiments over and over again Joule found that it requires 4.186 Joule to heat 1 g of water 1 °C.

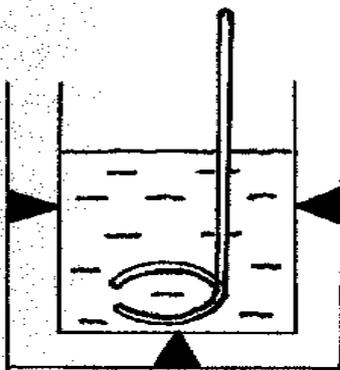
$$(10.4) \quad 1 \text{ cal} = 4.186 \text{ J}$$

From this follows the specific heat capacity of water

$$(10.5) \quad c_{\text{water}} = 1 \text{ cal}/(\text{g } ^\circ\text{C}) = 4.186 \text{ J}/(\text{g K}) = 4186 \text{ J}/\text{kg K}$$

11. Calorimetry

Fig. 8.1



When the heat capacity for water and brass are determined it is straightforward to determine the heat capacity for almost all other solid materials and liquids.

The method is called calorimetry. A calorimeter may have many different designs, and the one shown to the left, which possibly does not exist anywhere any longer, (although it has been used in class for about 100 years), but the reason for exposing it, is that it is apt to illustrate calculation when exchanging thermal energies.

The apparatus consists of two cylindrical brass bowls, which are isolated from each other at a few points by a highly non conducting material as cork.

The idea is that the inner bowl can then be considered as an adiabatic system. To the calorimeter also belongs a stirrer made of the same material as the inner bowl. We may ignore the frictional work, when stirring in the inner bowl.

Since neither heat is supplied or work is done on the inner bowl, it consists of an adiabatic system, and according the first law of thermodynamics: $W + Q = \Delta E$, with $W = 0$ and $Q = 0$, it gives:

$$(11.2) \quad \Delta E = 0$$

We shall then proceed to establish a calorimeter equation, which makes it possible to determine the specific heat capacities for solid materials and liquids.

We shall assume that we know the heat capacity for water $c_{water} = 4186 \text{ J/kg K}$, as determined by Joules experiment and since the calorimeter is usually made of brass, we first determine this heat capacity.

Apart from the calorimeter it is only necessary to have a weight and an accurate thermometer. The experiment is then performed as follows.

The mass of the inner bowl of the calorimeter plus stirrer (m_{cal}) is determined. The calorimeter is filled half full of water, and the mass of water (m_{water}) is determined by another weighing. Also the mass of a brass weight (200 g) is determined.

The brass weight is heated to 100°C in boiling water, and just before it is put into the calorimeter the temperature of the calorimeter and water is determined (t_0). The brass weight is put into the calorimeter, and it is stirred until the temperature does not raise any more (t_f)

We shall then setup the equation $\Delta E = 0$, where ΔE is the sum of the changes in energy of the brass weight, the calorimeter and the water.

$$(11.3) \quad \Delta E = \Delta E_{cal} + \Delta E_{water} + \Delta E_{weight} = 0$$

For each of the changes we apply the calorimetric equation: $\Delta E = c \cdot m \cdot \Delta T$.

For the calorimeter: $\Delta E_{cal} = c_{brass} \cdot m_{cal} (t_f - t_0)$ ($\Delta E_{cal} > 0$ Heat is supplied to the calorimeter)

For the water: $\Delta E_{water} = c_{water} \cdot m_{water} (t_f - t_0)$ ($\Delta E_{water} > 0$ Heat is supplied to the water)

For the weight: $\Delta E_{weight} = c_{brass} \cdot m_{weight} (t_f - 100^\circ\text{C})$ ($\Delta E_{weight} < 0$. The weight gives away heat)

When these expressions are inserted in (11.3), we have:

$$(11.4) \quad c_{brass} \cdot m_{weight} (t_f - 100^\circ\text{C}) + c_{water} \cdot m_{water} (t_f - t_0) + c_{brass} \cdot m_{cal} (t_f - t_0) = 0$$

The equation is solved for c_{brass} .

$$(11.5) \quad c_{brass} = - \frac{c_{water} m_{water} (t_f - t_0)}{m_{cal} (t_f - t_0) + m_{weight} (t_f - 100^\circ\text{C})}$$

When the heat capacity for brass is known, the heat capacity for almost any other solid materials can be determined by the calorimeter equation above, with the only difference that c_{brass} is replaced with e.g. c_{pb}

$$(11.6) \quad c_{pb} \cdot m_{weight} \cdot (t_f - 100 \text{ } ^\circ\text{C}) + c_{water} \cdot m_{water} \cdot (t_f - t_0) + c_{brass} \cdot m_{cal} \cdot (t_f - t_0) = 0$$

Which is solved for c_{pb} .

$$(11.7) \quad c_{pb} = - \frac{c_{brass} m_{cal} (t_f - t_0) + c_{water} m_{water} (t_f - t_0)}{m_{weight} (t_f - 100 \text{ } ^\circ\text{C})}$$

12. Melt-heat

If heat is supplied to ice having a temperature below $0 \text{ } ^\circ\text{C}$, then the temperature rises, until the melting point is reached. The specific heat capacity of ice is $2.0 \cdot 10^3 \text{ J/(kg K)}$, roughly half of that for water.

When the melting point $0 \text{ } ^\circ\text{C}$ is reached, the ice does not melt instantaneous, however, although heat is still supplied. Instead the temperature remains at the melting point until all the ice is melted.

It is a basic experience that you must add heat to melt a substance, even if the temperature is at the melting point.

Qualitatively this can be explained by the molecular description of the nature of heat. In a solid the molecules are bound in fixed positions, and it requires energy to tear them apart. During the melting process the supplied heat goes solely to disintegrate the solid structure of the molecules, and only afterwards the heat is applied to raise the temperature further. This leads us to the following definition (9.1).

The heat that per unit of mass must be supplied to melt a material, when the temperature is already at the melting point, is called the melt heat. It is usually designated L and is has the SI-unit J/kg . If the heat Q is supplied to melt the mass m , then:

$$Q = m \cdot L$$

It is a consequence of the energy conservation theorem, that the same amount of energy must be released when a liquid solidifies. Otherwise one could gain or loose energy by the process melting/solidify. The solidify-heat is therefore also given by the equation: $Q = m \cdot L$.

Ice has a very high melt-heat (thick layers of ice and snow on the ground remain a substantial period after the temperature is raised above the melting point). $L_{ice} = 334 \text{ kJ/kg}$. For a comparison $L_{lead} = 25 \text{ kJ/kg}$ at the melting point $327 \text{ } ^\circ\text{C}$.

Some materials can be cooled below their melting point without the solidification starts. One example is hypo-fixing salt. But if only a small crystal is added to the under cooled salt, then the temperature is immediately raised to the melting point and stays there until everything is solidified.

13. Evaporation-heat

What applies for melting applies as well for evaporation (boiling).

All liquids evaporate from the surface at all temperatures, but when the evaporation also takes place from the bottom and inside the liquid, we say that the liquid boils. The temperature at which boiling begins is called the boiling point.

When water is heated the temperature rises until the boiling point $100\text{ }^{\circ}\text{C}$ is reached, but from this point the temperature is fixed, until all the water is evaporated (provided that heat is still supplied).

Qualitatively this can be explained by the molecular description of the nature of heat. Although the molecules move more or less freely in the liquid, it requires energy to give the molecules enough kinetic energy, (and thereby enough velocity) to leave the liquid entirely and form a gas.

This leads to the definition (9.2)

The heat necessary to transform a unit mass of liquid to gas at the same temperature, when the liquid is already at the boiling point, is called the evaporation-heat, and is usually designated L . The SI-unit for evaporation-heat is J/kg. The heat Q required to evaporate the mass m is therefore.

$$Q = m \cdot L$$

Notice that the evaporation-heat is also defined at other temperatures than the boiling point. The evaporation-heat is temperature dependent.

14. Determination of the melt-heat

The melt-heat of ice can be determined by calorimetric experiments in much the same manner as we determined the specific heat capacities for alloys and metals.

A lump of ice, with the temperature $0\text{ }^{\circ}\text{C}$, is put into the calorimeter, where the mass of the jar plus stirrer and water has been determined, and the temperature of the water has been measured.

Using the stirrer, one waits until the ice has melted and the lowest temperature is measured.

The calorimeter and water is weighed again to determine the mass of the ice.

Since the calorimeter is considered to be an adiabatic system, the change of energy must be zero.

$$(13.1) \quad \Delta E = 0 \quad \text{where} \quad \Delta E = \Delta E_{cal} + \Delta E_{water} + \Delta E_{ice} + \Delta E_{melted\ ice}$$

Using the same notation as previously we have:

$$\Delta E_{cal} = c_{brass} \cdot m_{cal} \cdot (t_f - t_0) \quad (\Delta E_{cal} < 0 : \text{The calorimeter delivers heat to melt the ice})$$

$$\Delta E_{water} = c_{water} \cdot m_{water} \cdot (t_f - t_0) \quad (\Delta E_{water} < 0 : \text{The water delivers heat to melt the ice})$$

$$\Delta E_{isvand} = c_{vand} \cdot m_{is} \cdot (t_s - 0\text{ }^{\circ}\text{C}) \quad (\Delta E_{melted\ ice} > 0 : \text{The melted ice is supplied with heat to warm it from } 0\text{ }^{\circ}\text{C} \text{ to the final temperature } t_f)$$

$$\Delta E_{melt} = m_{ice} L_{ice} \quad (\Delta E_{melt} > 0 : \text{The ice receives melt-heat})$$

The calorimeter equation then becomes:

$$(13.2) \quad c_{brass} \cdot m_{cal} \cdot (t_f - t_0) + c_{water} \cdot m_{water} \cdot (t_s - t_0) + c_{melted\ ice} \cdot m_{ice} \cdot (t_f - 0\text{ }^{\circ}\text{C}) + m_{ice} L_{ice} = 0$$

14.1 Determination of condensing-heat = the evaporating-heat

Fifty years ago this experiment was performed with a calorimeter, and a flask with boiling water, where the steam was led down into the calorimeter, where it condensed into water.

Like numerous other class experiments that previously was part of the curriculum, it has been banned many years ago for security reasons.

So in the last 15 years I have done the determination of the condensing heat of water with a Cappuccino machine, where the stem is lead down into a flamingo coffee cup. Otherwise the experiments go as described above. The mass of water and its temperature is measured, before you let the stem in. When the temperature has risen about 15°C , the experiment is stopped and the highest temperature of the water in the cup is read on the thermometer. The flamingo cup is assumed to have zero heat capacity.

In this case the heat is supplied to the system, so $Q = \Delta E$, where:

$$(13.3) \quad Q = \Delta E_{\text{water}} + \Delta E_{\text{condensed}}$$

Using the same notation as earlier:

$$Q = m_{\text{steam}}L_{\text{steam}} \quad (Q > 0: \text{Condensing heat is lead into the water})$$

$$\Delta E_{\text{water}} = c_{\text{water}} \cdot m_{\text{water}} \cdot (t_f - t_0) \quad (\Delta E_{\text{vand}} > 0: \text{The water receives condensing heat})$$

$$\Delta E_{\text{condensed}} = c_{\text{water}} \cdot m_{\text{steam}}(t_f - 100^{\circ}\text{C}) \quad (\Delta E_{\text{condensed}} < 0: \text{Condensed stem at } 100^{\circ}\text{C} \text{ is cooled to } t_f)$$

Then we may write the calorimeter equation:

$$(13.4) \quad m_{\text{steam}}L_{\text{steam}} = c_{\text{water}} \cdot m_{\text{water}} \cdot (t_f - t_0) + c_{\text{water}} \cdot m_{\text{steam}}(t_f - 100^{\circ}\text{C})$$

From which L_{steam} can be determined.