

### Related topics

Mixture temperature, boiling point, Dulong Petit's law, lattice vibration, internal energy, Debye temperature.

### Principle and task

Heated specimens are placed in a calorimeter filled with water at low temperature. The heat capacity of the specimen is determined from the rise in the temperature of the water.

### Equipment

|                                    |          |   |
|------------------------------------|----------|---|
| Calorimeter, 500 ml                | 04401.00 | 1 |
| Metal bodies, set of 3             | 04406.00 | 4 |
| Aluminium pot, 3000 ml             | 05934.00 | 1 |
| Butane burner, Labogaz 206 type    | 32178.00 | 1 |
| Butane cartridge                   | 47535.00 | 1 |
| Aneroid barometer                  | 03097.00 | 1 |
| Stopwatch, digital, 1/100 sec.     | 03071.01 | 1 |
| Thermometer, -10...+ 50 C          | 38033.00 | 1 |
| Portable balance Mod. LS200        | 46001.93 | 1 |
| Fish line, l 100 m                 | 02090.00 | 1 |
| Triangle w. pipeclay, l 60 mm      | 33278.00 | 1 |
| Tripod, ring dia. 140 mm, h 240 mm | 33302.00 | 1 |

|                               |          |   |
|-------------------------------|----------|---|
| Glass beaker, short, 250 ml   | 36013.00 | 1 |
| Glass beaker, short, 600 ml   | 36015.00 | 1 |
| Glass beads, d 6 mm, 850 pcs. | 36756.25 | 1 |

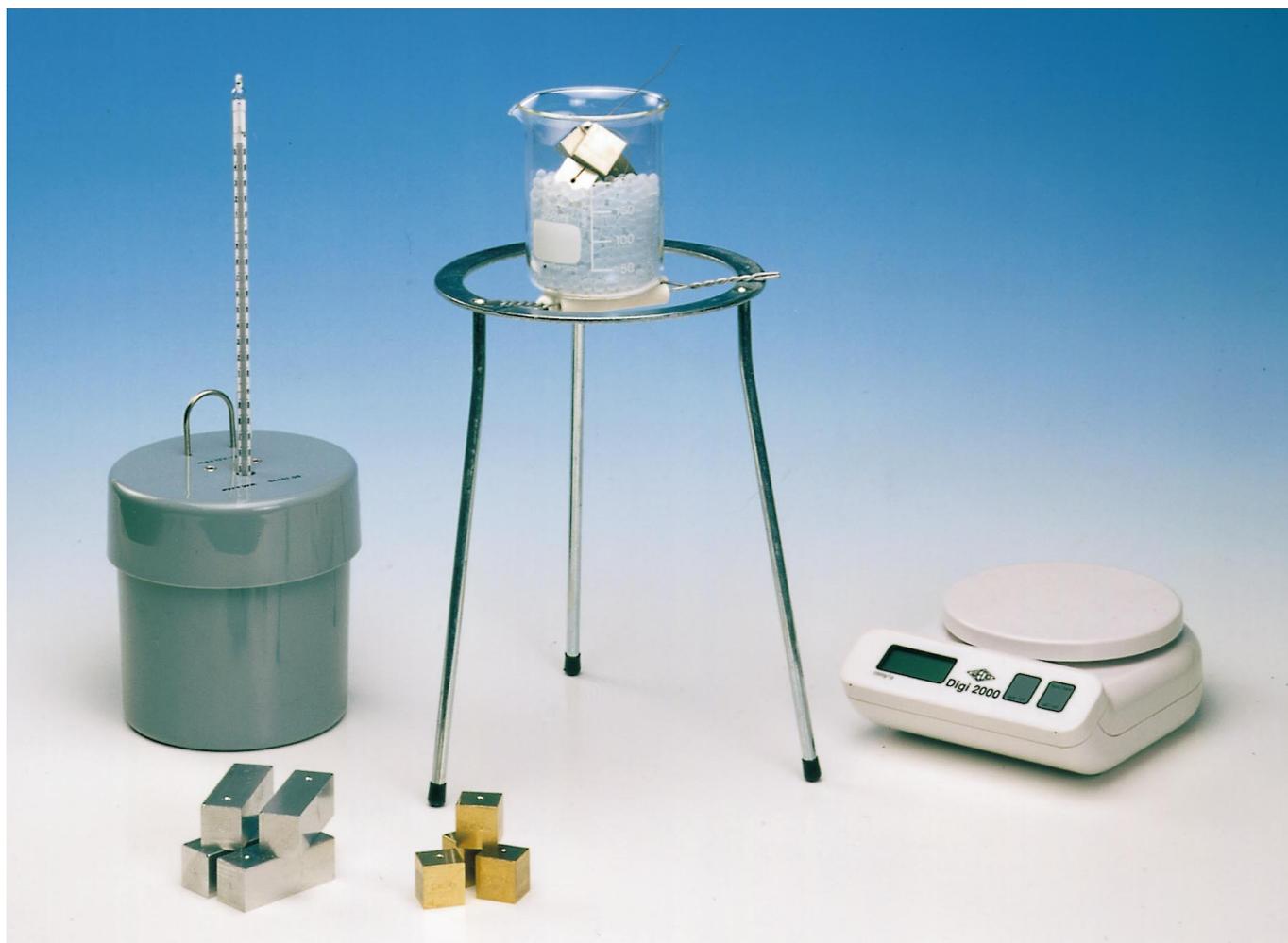
### Problems

1. To determine the heat capacity of the calorimeter by filling it with hot water and determining the rise in temperature.
2. To determine the specific heat capacity of aluminium, iron and brass.
3. To verify Dulong Petit's law with the results of these experiments.

### Set-up and procedure

1. Fill the calorimeter with hot water (approx. 50°C) of known mass.  
Read off the temperature in the calorimeter several times after the water has been put in, stirring continuously, and plot the results over time on a graph. The mixture temperature can be determined by extrapolation from the graph (Fig. 3).

Fig. 1: Experimental set-up for determining the heat capacity of metals.



Repeat the experiment to increase the accuracy of the measurement. Keep ready a vessel containing water at room temperature, so that the calorimeter can quickly be returned to room temperature after the measurement. Leave this water in the calorimeter for approx. 5 minutes and then empty and dry it. Start the next measurement after another five minutes.

2. Tie the four brass test pieces together with fishing line and weigh them to obtain their mass  $m_p$ . Do the same with the four steel test pieces and with three aluminium test pieces.

Put a layer of glass beads about 3 cm deep in the bottom of the beaker so that the metal specimens do not touch it when they are being heated.

Fill the calorimeter with cold water of known mass.

Leave the specimens in the boiling water for about 10 minutes, then drain them quickly and put them into the calorimeter.

Read off the temperature in the calorimeter for a little while before and after putting the specimens in, stirring continuously, and plot the readings over time in a graph. Compare the temperature of the specimens with the boiling point of the water at the prevailing atmospheric pressure  $p$  (read this off on the barometer).

### Theory and evaluation

The heat capacity  $C$  of a substance is defined as the quotient of the quantity of heat absorbed  $\delta Q$  and the change in temperature  $dT$ .

$$C = \frac{\delta Q}{dT} \quad (1)$$

and is proportional to the mass of the heated substance.

$$c = \frac{C}{m} \quad (2)$$

is the specific heat capacity.

The quantity of heat absorbed  $\delta Q$  depends on the conditions prevailing as the temperature rises, and a differentiation is made in particular between heat capacity  $C_V$  at constant volume  $V$  and heat capacity  $C_p$  at constant pressure  $p$ .

In accordance with the First Law of Thermodynamics ( $U$  = internal energy),

$$\delta Q = dU + p dV \quad (3)$$

$C_p$  is always greater than  $C_V$ . In the case of solids, the change in volume is so small that we can write

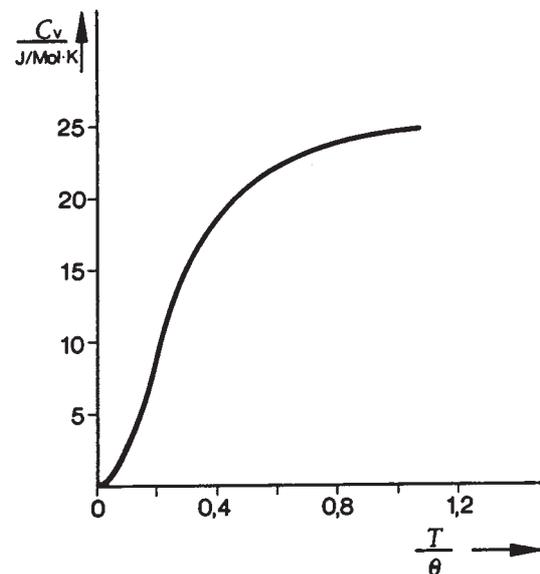
$$C_p \approx C_V$$

$C_V$  can be calculated from the change in internal energy with temperature in accordance with (1) and (3):

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (4)$$

The internal energy  $U$  in a solid is essentially the result of lattice vibrations caused by heat.

Fig. 2: Molar heat capacity of a solid in accordance with Debye's approximation.



According to Debye's theory, which considers lattice vibrations up to a limiting frequency  $\nu_D$ , the heat capacity is given by

$$C_V(T) = 3 Nk \left( \frac{T}{\Theta} \right)^3 \cdot 3 \int_0^{\Theta/T} \frac{z^4 e^z dz}{(e^z - 1)^2} \quad (5)$$

$$= 3 Nk \cdot D(T/\Theta)$$

where  $z = h\nu/kT$ ,

$\Theta = h\nu_D/k$ , called the Debye temperature

$h$  = Planck's constant,

$k$  = Boltzmann constant,

$N$  = number of atoms in the volume considered.

$D(T/\Theta)$  is called the Debye function.

For large values of  $T/\Theta$  the upper integration limit is small, the integrand can be expanded and we obtain the law of Dulong and Petit:

$$C_V = 3 Nk$$

We thus obtain the molar heat capacity

$$C_m = 3 N_L \cdot k = 3R = 24.94 \text{ J/K} \quad (6)$$

where  $N_L$  is the Loschmidt number and  $R$  the gas constant.

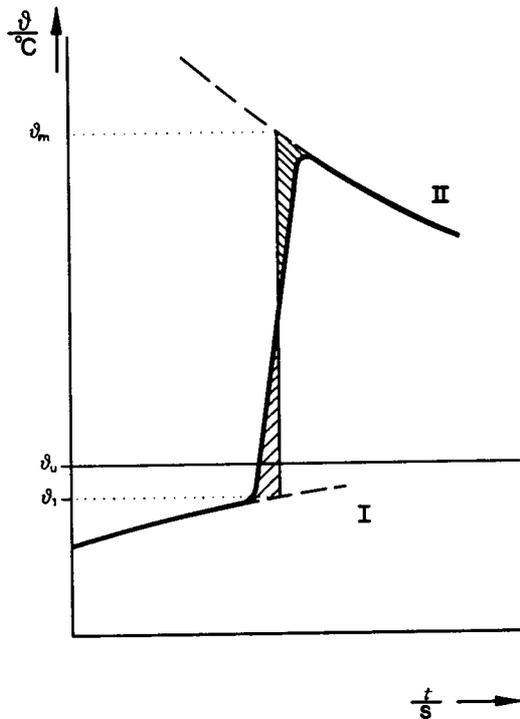
Debye temperature:

Aluminium: 419 K                      Copper: 335 K

Iron: 462 K                              Zinc: 100 K

For the evaluation, the heat capacity is assumed to be constant in the temperature range considered.

Fig. 3: Determination of the initial temperature  $\vartheta_1$  and the mixture temperature  $\vartheta_m$  in the method of mixtures experiment when heat loss takes place.  $\vartheta_u$  = temperature of the surrounding atmosphere.



The mixture (heat sharing) temperature  $\vartheta_m$  is determined by extrapolating the curves plotted, as the sketch in Fig. 3 shows.

The temperatures before and after heat sharing are not constant because of the exchange of heat with the surroundings; they approach the ambient temperature exponentially.

For the evaluation we draw a straight line parallel to the temperature axis in the graph of temperature rise, so that the shaded parts in Fig. 3 are equal in area.

$\vartheta_m$  and  $\vartheta_1$  are read off at the points where the straight line intersects the extended partial curves I and II.

1. First of all, the heat capacity of the calorimeter is determined:

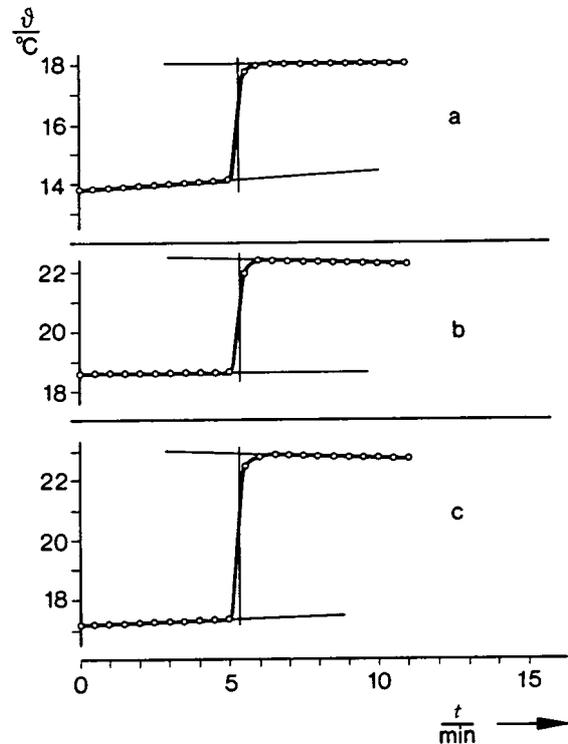
$$C_k = c_w \cdot m_w \frac{\vartheta_w - \vartheta_m}{\vartheta_m - \vartheta_k}$$

where  $\vartheta_k$  is the temperature of the calorimeter before the experiment,  $\vartheta_m$  is the temperature of the mixture,  $\vartheta_w$  is the temperature of the hot water,  $m_w$  is the mass of the water and  $c_w = 4.187 \text{ J/gK}$ , the specific heat capacity of water.

The average value from several measurements (with the vessel half full) is

$$C_k = (66 \pm 1) \text{ J/K}$$

Fig. 4: Temperature as a function of time in the method of mixtures experiment a) steel, b) brass, c) aluminium.



2. The test pieces of mass  $m_p$  are heated in the boiling water. The boiling point  $\vartheta_2$  is determined as a function of the atmospheric pressure  $p$ :

$$\vartheta_2 = 100 + 0.0276 (p - 1013 \text{ hPa}) - 0.000017 (p - 1013 \text{ hPa}^2), \quad (8)$$

where  $p$  is in hPa and  $\vartheta_2$  in  $^\circ\text{C}$ .

The specific heat capacity of the material from which the test pieces are made is obtained from the energy balance as:

$$c = \frac{(c_w \cdot m_w + C_k) (\vartheta_m - \vartheta_1)}{m_p (\vartheta_2 - \vartheta_1)} \quad (9)$$

The values of molar heat capacity of brass and aluminium as measured in the experiment agree well with the values from Dulong and Petit's law.

The specific heat capacity of steel depends very much on the composition of the steel.

|           | $\frac{\vartheta_2}{^\circ\text{C}}$ | $\frac{m_p}{\text{g}}$ | $\frac{m_w}{\text{g}}$ | $\frac{c}{\text{J/g}\cdot\text{K}}$ | $\frac{C_m}{\text{J/Mol}\cdot\text{K}}$ |
|-----------|--------------------------------------|------------------------|------------------------|-------------------------------------|---|
| Brass     | 99.8                                 | 120.8                  | 214.6                  | 0.387                               | 24.9                                    |
| Aluminium | 99.3                                 | 90.6                   | 251.1                  | 0.897                               | 24.2                                    |
| Steel     | 99.3                                 | 117.2                  | 257.4                  | 0.469                               |   |