King Saud University
Science College
Physics and Astronomy Department

Thermodynamics Laboratory
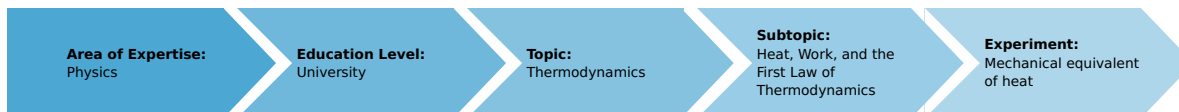# - 391 Phys -

Contents

Mechanical equivalent of heat (Item No.: P2330200)

Curricular Relevance

| Area of Expertise: Physics | Education Level: University | Topic: Thermodynamics | Subtopic: Heat, Work, and the First Law of Thermodynamics | Experiment: Mechanical equivalent of heat |

Difficulty	**Preparation Time**	**Execution Time**	**Recommended Group Size**
Easy	10 Minutes	10 Minutes	1 Student

Additional Requirements:	**Experiment Variations:**

Keywords:

Mechanical equivalent of heat, Mechanical work, Thermal energy, Thermal capacity, First law of thermodynamics, Specific thermal capacity, Newton`s law of cooling

Overview

Short description

Principle

In this experiment, a metal test body is rotated and heated by the friction due to a tensed band of synthetic material. The mechanical equivalent of heat for problem 1 is determined from the defined mechanical work and from the thermal energy increase deduced from the increase of temperature. Assuming the equivalence of mechanical work and heat, the specific thermal capacity of aluminium and brass is determined.

Fig. 1: Experimental set-up: Mechanical equivalent of heat.

Equipment

Position No.	Material	Order No.	Quantity
1	Mechanical equiv.of heat app.	04440-00	1
2	Friction cylinder CuZn, m 1.28 kg	04441-02	1
3	Friction cylinder Al, m 0.39 kg	04441-03	1
4	Support rod, stainless steel, l = 250 mm, d = 10 mm	02031-00	1
5	Right angle clamp expert	02054-00	1
6	Spring balance 10 N	03060-03	1
7	Spring balance 100 N	03060-04	1
8	Stopwatch, digital, 1/100 s	03071-01	1
9	Bench clamp PHYWE	02010-00	1
10	Universal clamp with joint	37716-00	1
11	Commercial weight, 1000 g	44096-70	1
12	Commercial weight, 2000 g	44096-78	1
13	Universal balance, 5.300 g / 1 g	46007-00	1

Tasks

1. Determination of the mechanical equivalent of heat.
2. Determination of the specific thermal capacity of aluminium and brass.

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Set-up and procedure

The experimental set-up is shown in Fig. 1. To start with, the friction cylinder and the crank handle are fixed to the rotating bearing and the base plate is clamped very firmly to the table with the screw clamps. Failure to do so may cause tilting of the base plate during cranking, which in turn may cause the thermometer introduced into the bore hole to break. The friction band fastened to the dynamometer is laid 2.5 times around the friction cylinder (so that the dynamometer is relieved when the crank is turned clockwise). The 2 kg weight is attached to the lower end of the friction band. To measure temperature, the thermometer is held with a universal clamp and carefully introduced into the bore hole of the friction cylinder. The thermometer and the bore hole of the cylinder must be carefully aligned, so the thermometer will not be damaged while the cylinder is rotating. To improve thermal contact, the bore hole is filled with heat conducting paste. Weigh the friction cylinders at the beginning of the experiment.

At the beginning of the measurement, temperature is recorded every thirty seconds during four minutes. After this, the crank handle is turned a certain number of times (e. g. 200 times) as fast and regularly as possible. Simultaneously, the force F_D acting on the suspension is determined with the dynamometer. Subsequently, the continuous temperature decrease is noted at intervals of thirty seconds.

The second part of the experiment is carried out similarly, in order to measure the thermal capacity of an aluminium cylinder and that of a brass cylinder whose mass is double the mass of the aluminium cylinder. Before starting the experiment, the friction cylinder and the friction band should be wiped with a dry cloth to rid them from metallic abrasion dust. When using the aluminium cylinder, friction should not exceed 10 N, (for this, the 1 kg weight is used), in order to avoid severe abrasion and soiling of the friction band. The specific thermal capacity of the cylinder is calculated from the number of crank rotations n, the mean force at the dynamometer F_D and the increase of temperature ΔT .

Theory and evaluation

For a long time it was debated as to whether the heat of a system, which used to be defined in terms of its temperature, was a form of energy or an independent magnitude which is conserved. During the first half of the nineteenth century, it was proven that mechanical energy due to friction is completely converted to heat, independently of the course of the transformation process and of the physical and chemical characteristics of the material used. Heat was accordingly defined as the energy of disorganized, macroscopically invisible molecular movements.

The quotient between realized mechanical work ΔW and the quantity of heat ΔQ generated through friction is called the mechanical equivalent of heat. In this experiment, mechanical work is performed by rotating the friction cylinder against the sliding frictional force F_R of the synthetic friction band. As weight M (cf. Fig. 2) is not accelerated when the crank is rotated, weight $F_G = Mg = 49 \text{ N}$ (*M*: mass of the weight, *g*: terrestrial gravitational acceleration) on one side and the sliding frictional force F_R acting together with force F_D on the suspension of the dynamometer on the other side, must cancel each other:
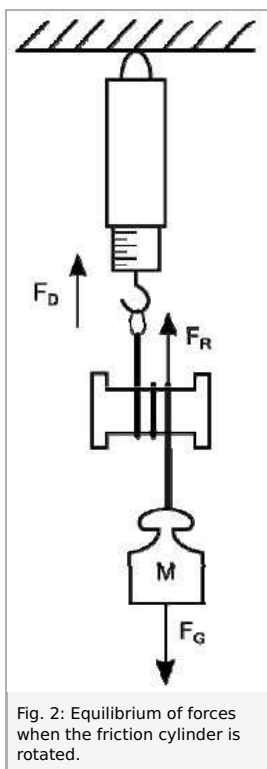
$$F_R = F_G - F_D \text{ (1)}$$

Fig. 2: Equilibrium of forces when the friction cylinder is rotated.

Friction work *W* is thus determined from the friction path of $2\pi r \, n$ (*r*: radius of the cylinder, *n*: number of turns) and is found to be:

$$W = 2\pi r \, n \, F_{\mathrm{R}} = 2\pi r \, n \, (F_{\mathrm{G}} - F_{\mathrm{D}}) \text{ (2)}$$

Whilst the synthetic band slides over the cylinder, a large portion of mechanical work is converted to thermal energy ΔQ through inelastic deformations of the friction material. Accordingly, the temperature T of the friction cylinder increases by a temperature difference ΔT :

$$\Delta Q = C_{\mathrm{tot}} \cdot \Delta T \text{ (3)}$$

C_{tot} is the total thermal capacity of the heated parts. It is the sum of the thermal capacity C_{cyl} of the friction cylinder (*m*: mass, specific thermal capacity (CuZn: *c* = 0.385 J / gK)):

$$C_{\mathrm{cyl}} = c \cdot m \text{ (4)}$$

Of the thermal capacity of the friction band ($C_{\mathrm{band}} = 4 \text{ J/K}$) and of the thermal capacity of the thermometer ($C_{\mathrm{th}} = 4 \text{ J/K}$). If the mass of the friction cylinder is *m* = 640 g, total thermal capacity amounts to:

$$C_{\mathrm{tot}} = C_{\mathrm{cyl}} + C_{\mathrm{band}} + C_{\mathrm{th}} = 254 \text{ J/K} \text{ (5)}$$

The thermal capacities of the insulated bearing and of the heat conducting paste were neglected. Fig. 3 displays a temperature-time diagram for an example of measurement. The shape of the graph makes it clear, that thermal energy is continuously given off to the environment while the crank is being turned. Hence, temperature difference ΔT is determined as is generally done for the determination of specific heat: momentary temperature compensation is extrapolated through prolongation of both straight graph branches. If a parallel line to the temperature axis is drawn in such a way that two equal surfaces A_1 and A_2 are formed, the difference of the ordinates of the points of intersection of the two straight lines is the temperature difference ΔT sought after.
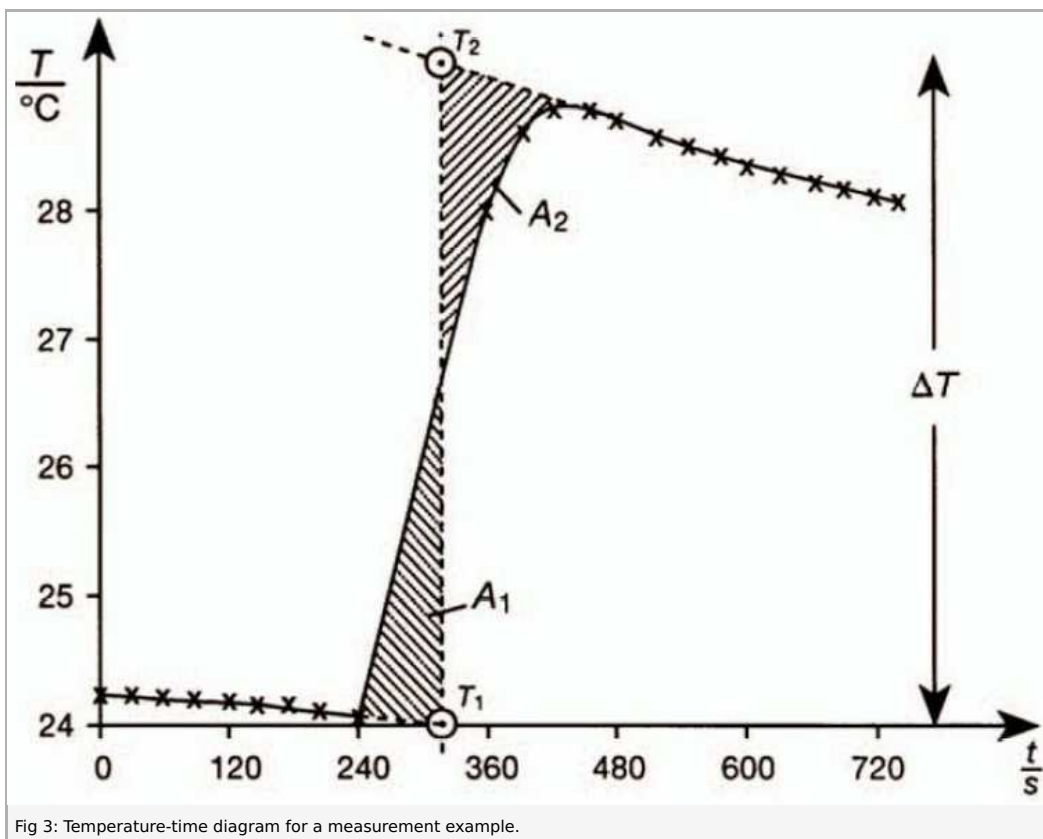
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Fig 3: Temperature-time diagram for a measurement example.

The cylinder is cooled mainly due to convection. In this case we can use the Newton`s law of cooling as a good approximation: "The rate of heat loss of a body is proportional to the difference in temperatures between the body and its surroundings".

In this approximation the temperature difference in Fig. 3 corresponds to the heat loss rate (first derivative of total heat amount). The integral of temperature difference thus equals to the total amount of lost heat, which graphically corresponds to the area confined under the temperature curve in Fig. 3.

There are two curves in Fig. 3. The first one (real experiment) corresponds to the mechanical work slowly transferred into heat. The second curve (imaginary experiment) shows instantaneous transfer. In both experiments the cylinder has the same amount of heat in the beginning of the experiment and after heating due to friction. Mechanical work is the same for both curves. Thus the amount of lost heat (area under curves) due to convection must be the same for both curves. This is possible only if $A_1 = A_2$, which uniquely defines the position of the vertical line (instantaneous process) in Fig. 3.

Exponential cooling process can be approximated with straight lines for short time intervals.

In the case of a measurement example where the residual load on the dynamometer is $F_D = 3\,\text{N}$, work after 200 rotations of the friction cylinder amounts to:

$$\Delta W = 1301\,\text{J}$$

According to equation (3), the resulting temperature increase of the friction cylinder, $\Delta T = 5.1\,\text{K}$, produces the following amount of thermal energy:

$$\Delta Q = 1296\,\text{J}$$

If the mechanical heat equivalent is calculated, the quotient (1.003) amounts to 1 within the limits of measurement error. As heat is a form of energy, the total amount of mechanical energy must be transformed into an equal amount of heat energy according to the law of conservation of energy. In fact, the mechanical equivalent of heat must thus amount to:

$$\frac{\Delta W}{\Delta Q} = 1 \ (6)$$

Similar experiments, in which electric energy is converted to thermal energy, show that the corresponding electric equivalent of heat $\Delta W_{\text{el}}/Q$ also amounts to 1. These results are comprehensively summarized in the first law of thermodynamics.

The change of internal energy ΔU of a system is equal to the amount of heat energy ΔQ and to the amount of work ΔW supplied from outside, independently of the supply procedure:

$$\Delta U = \Delta Q + \Delta W \ (7)$$

If, inversely, equation 6 is assumed ($\Delta W = \Delta Q$), the specific thermal capacity can be determined with this equipment. If equations 3 and 5 are transformed according to the thermal capacity of the friction cylinder, the following result is obtained:

$$C = \frac{\Delta W}{\Delta T} - 8\frac{J}{\mathrm{gK}} \quad (8)$$

The specific thermal capacity, defined as the quotient between the thermal capacity of a body *C* and its mass:

$$c = C/m \text{ (9)}$$

Is a material constant, which at normal ambient room temperatures and atmospheric pressure depends very little on absolute temperature. It is to be noted from equation 9 that the thermal capacity of a homogeneous material is strictly proportional to its mass.

An example measurement with a rest load *F* = 4 N on the dynamometer, 200 turns of the crank, and a temperature increase of $\Delta T = 2.5 \text{ K}$ yielded a thermal capacity of

$$C = 501 \text{ J/gK}$$

for a brass cylinder of 1280 g. (that is actually about twice the thermal capacity of a cylinder of half the weight (247 J / gK)). The specific thermal capacity calculated with equation 9 is:

$$C_{\mathrm{brass}} = 0.392 \text{ J/gK}$$

The measurement of the aluminium cylinder yielded the following value:

$$c_{\mathrm{al}} = 0.870 \text{ J/gK} \text{ ,}$$

as compared to the theoretical value $c_{\mathrm{al}} = 0.902 \text{ J/gK}$ for the specific thermal capacity of aluminium at room temperature.

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Related topics

Liquid, Newtonian liquid, Stokes law, fluidity, dynamic and kinematic viscosity, viscosity measurements.

Principle and task

Due to internal friction among their particles, liquids and gases have different viscosities. The viscosity, a function of the substance's structure and its temperature, can be experimentally determined, for example, by measuring the rate of fall of a ball in a tube filled with the liquid to be investigated.

Equipment

Falling ball viscometer	18220.00	1
Thermometer, 24..+51C, f. 18220.00	18220.02	1
Immersion thermostat A100	46994.93	1
Accessory set for A100	46994.02	1
Bath for thermostat, Makrolon	08487.01	1
Retort stand, h 750 mm	37694.00	1
Right angle clamp	37697.00	1
Universal clamp with joint	37716.00	1
Pyknometer, calibrated, 25 ml	03023.00	1
Volumetric flask 100 ml, IGJ12/21	36548.00	9
Glass beaker, tall, 150 ml	36003.00	11
Glass beaker, short, 250 ml	36013.00	1
Pasteur pipettes, 250 pcs	36590.00	1
Rubber caps, 10 pcs	39275.03	1

Hose clip, diam. 8-12 mm	40996.01	6
Rubber tubing, i.d. 7 mm	39282.00	6
Stopwatch, digital, 1/100 sec.	03071.01	1
Laboratory balance, data outp. 620 g	45023.93	1
Wash bottle, plastic, 500 ml	33931.00	2
Methanol 500 ml	30142.50	2
Water, distilled 5 l	31246.81	1

Problems

Measure the viscosity

1. of methanol-water mixtures of various composition at a constant temperature,

2. of water as a function of the temperature and

3. of methanol as a function of temperature.

From the temperature dependence of the viscosity, calculate the energy barriers for the displaceability of water and methanol.

Set-up and procedure

Perform the experimental set-up according to Fig. 1. Connect the falling ball viscometer to the pump connection unit of the thermostat with rubber tubing (secure the tubing connections with hose clips!). Fill the bath of the circulating thermostat with

Fig. 1: Experimental set up: Viscosity measurements with the falling ball viscometer.
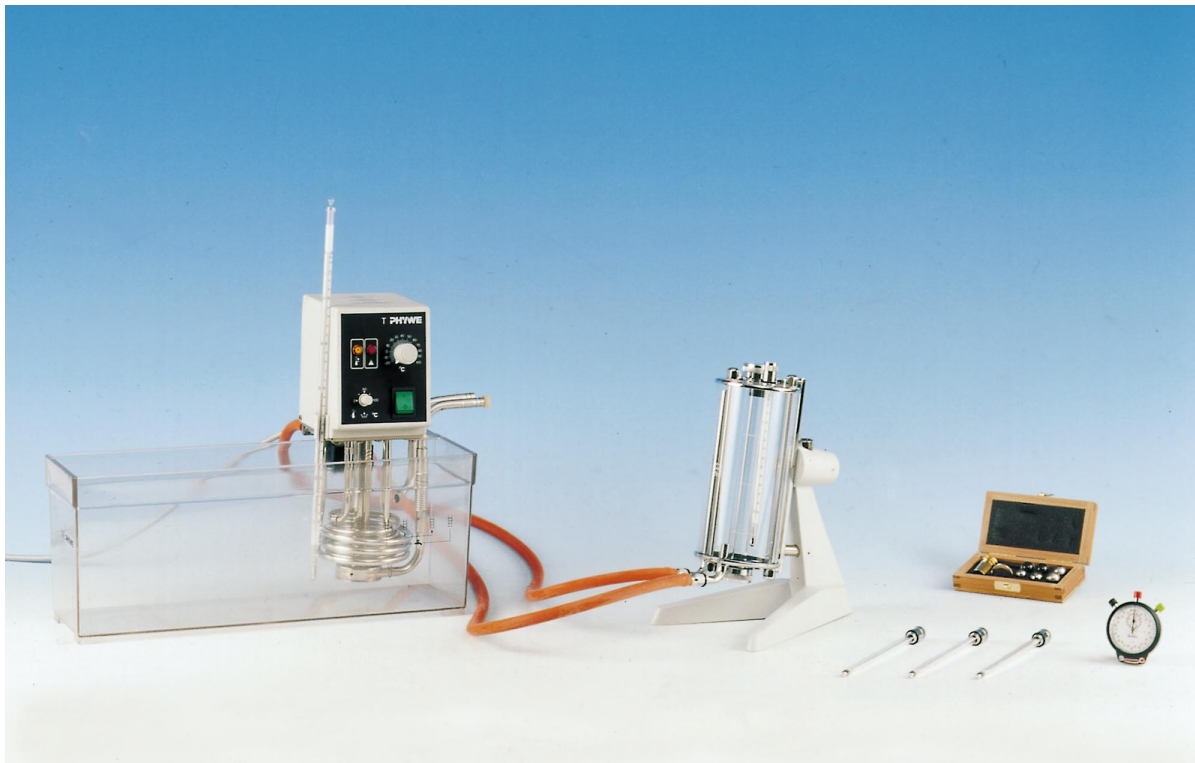
distilled or demineralised water to avoid furring. Connect the cooling coil of the thermostat to the water supply line with tubing (secure the tubing connections with hose clips!).

In addition, prepare the falling ball viscometer according to its operating instructions; calibrate it; and for each experiment fill it with the liquid to be investigated (water, methanol or methanol-water mixtures according to Tab. 1) in such a manner that it is bubble-free.

Ball number 1, which is made of borosilicate glass, is appropriate for investigations in the given viscosity range. Its characteristic data can be obtained from the enclosed test certificate. After the ball has been placed in the gravity tube, first allow the viscometer to equilibrate to the selected working temperature T for approximately 10 minutes before determining 3 to 5 falling times t. Calculate the arithmetic mean of the measured values in each case.

A constant working temperature of 298 K is recommended for the viscosity measurements in methanol- water mixtures (Problem a).
Conduct the investigations on the temperature dependence of the viscosity of pure liquids (Problems b and c) in steps of 5 K in the temperature range between 293 K and 323 K. Parallel to this, determine the density of the respective liquids, which is required for the calculations. To do this, weigh the clean and dry pycnometer; fill it with the liquid to be investigated; fix it to the retort stand, and equilibrate it in the thermostatic water bath for approximately 15 minutes. Subsequent to bubble-free closure with the accompanying stopper and a quick external drying, reweigh the filled pycnometer. From the mass difference of the two weighings and the volume of the pycnometer, determine the density of the liquid. Rinse the gravity tube and the pycnometer thoroughly with the next liquid to be investigated each time before it is refilled.

Tab. 1: Literature values for the density ρ and the dynamic viscosity η of methanol-water mixtures of different compositions at constant temperature $(T = 298.15$ K)

$m(CH_3OH)$ /g	$m(H_2O)$ /g	ρ /g·cm^{-3}	η /mPa·s
0	100	0.9970	0.897
10	90	0.9804	1.178
20	80	0.9649	1.419
30	70	0.9492	1.581
40	60	09316	1.671
50	50	0.9122	1.577
60	40	0.8910	1.427
70	30	0.8675	1.234
80	20	0.8424	1.025
90	10	0.8158	0.788
100	0	0.7867	0.557

Tab. 2: Literature values for the density ρ and the dynamic viscosity η of water and methanol at different temperatures

T / K	Water		Methanol	
	ρ /g·cm^{-3}	η /mPa·s	ρ /g·cm^{-3}	η /mPa·s
293.15	0.9982	1.002	0.7915	0.608
398.15	0.9970	0.897	0.7868	0.557
303.15	0.9956	0.797	0.7819	0.529
308.15	0.9940	0.726	0.7774	0487
313.15	0.9922	0.653	0.7729	0.458
218.15	0.9902	0.597	0.7690	0.425
323.15	0.9880	0.548	0.7650	0.396

Note
The measurements are time consuming and take approximately 10 hours when painstakingly performed. It is therefore appropriate to divide the experiment according to the three given problems or to have them performed optionally. Another possibility is to have the complete experiment carried out on two laboratory days.

Theory and evaluation
The dynamic viscosity η of a liquid (1) is defined by the force F which is required to move two parallel layers of liquid both having the area A and separated by dx with the velocity $d\omega$ with respect to each other.

$$\eta = \frac{F}{A \frac{d\omega}{d\omega}} \tag{1}$$

By relating the dynamic viscosity to the density ρ of the liquid, one obtains the kinematic viscosity v (2); the reciprocal of the dynamic viscosity is designated as fluidity φ (3).

$$v = \frac{\eta}{\rho} \tag{2}$$

$$\varphi = \frac{1}{\eta} \tag{3}$$

A spherical particle with a radius r moves in a liquid under the influence of a force F and the viscosity φ with a constant velocity ω.

$$\omega = \frac{F}{6 \pi \eta r} \tag{4}$$

(Stokes Law)

For the fall of a sphere in the gravitational field of the earth the motive force Fis equal to the product of the acceleration of gravity g and the effective mass $m,$ which can be expressed as the density difference between the sphere (ρ_1) and the liquid (ρ_2).

Fig. 2: Dependence of the viscosity η of the methanol-water system on the composition described by the mass traction *w* at constant temperature *(T*= 298 K).
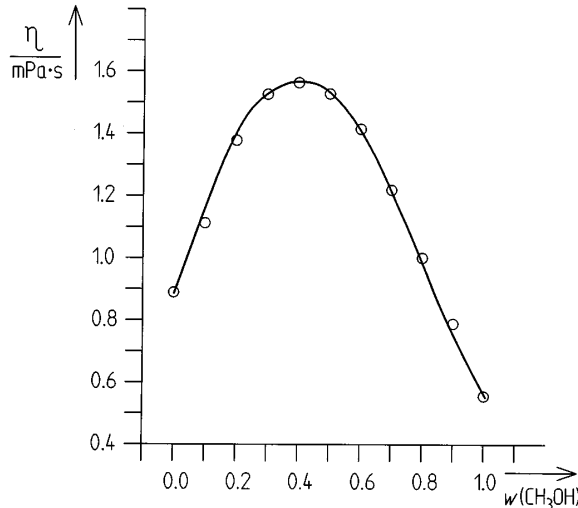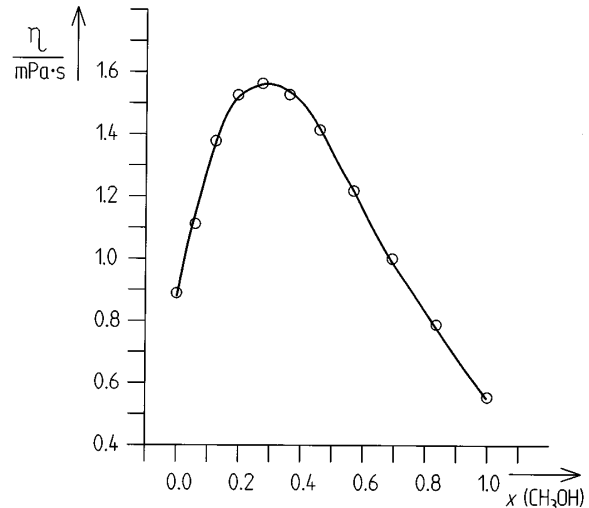

Fig. 3: Dependence of the viscosity η of the methanol water system on the composition described by the mole fraction x at constant temperature *(T*= 298K).

$$F = m'g = \frac{4}{3}\pi r^3 g(\rho_1 - \rho_2) \qquad (5)$$

The correlation (6) for the calculation of the viscosity, which is derived from (4) and (5), is only considered as the limit law for expanded media (the radius can be neglected with respect to that of the gravity tube); otherwise, the relationship can be approximated by corrections (Ladenburg Correction).

$$\eta = \frac{2\,g\,r^2\,(\rho_1 - \rho_2)}{g\,\omega} \qquad (6)$$

For commercial falling ball viscometers with sets of calibrated spheres, the constants in equation (6) are combined with the apparative factors to form the spherical constant *K;* this makes the calculations much simpler:

$$\eta = K\,t\,(\rho_1 - \rho_2) \qquad (7)$$

(*t* = rate of fall of the sphere for a measuring distance of *s* = 100 mm)

The density ρ_2 of the liquid at temperature *T* which is contained in eqn. (7), can be calculated using the relationship

$$\rho_2 = \frac{m}{V} \qquad (8)$$

(*m* = mass of the liquid; *V* = volume of the pycnometer)

using the experimentally determined pycnometer data or alternatively that obtained from Tables 1 and 2.

The viscosity is a function of the structure of the system and the temperature. The alteration in the measured viscosity in

which the composition of methanol-water mixtures are expressed as the mass fraction *w* (9.1) or the mole fraction x (9.2) is an expression of the non-ideal behaviour of the liquids. It correlates to additional mixing phenomena such as mixing volume (volume contraction) and mixing enthalpy.

$$w_1 = \frac{m_1}{m_1 + m_2} \qquad (9.1)$$

(w_i= mass fraction, rn_i = mass of the substance i)

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{\dfrac{m_1}{M_1}}{\dfrac{m_1}{M_1} + \dfrac{m_2}{M_2}} \qquad (9.2)$$

(w_i = mole fraction, n_i quantity of substance, m_i = mass of the substance i, M_i = molar mass of substance i)

For many liquids the reduction of the viscosity with temperature is described by an empirically determined exponential function (10).

$$\frac{1}{\eta} = \varphi = C\,e^{-\frac{E}{RT}} \qquad (10)$$

(R = 8.31441 J·K^{-1}·mol^{-1}, universal gas constant)

In this relationship which is analogous to the Arrhenius equation, *C* represents a system-dependent constant; *E* is an expression of the molar energy which is required to overcome the internal friction. This activation energy can be determined from the slope obtained by the linear relation (10.1) between ln η and 1/*T* (Fig. 4).

$$\ln \eta = \frac{E}{R} \cdot \frac{1}{T} - \ln C. \qquad (10.1)$$

Data and results

The experimentally determined viscosities are presented graphically in the Figures 2 to 4 as a function of the composition of the methanol-water mixtures or of the temperature.

The following values are determined for the slopes of the linear relationships between ln η and $1/T$, which are obtained by linear regression analysis:

$\Delta (\ln \eta)/\Delta (1/T) = 1.799 \cdot 10^3$ K (H_2O) and

$\Delta (\ln \eta)/\Delta (1/T) = 1.134 \cdot 10^3$ K (CH_3OH).

Substituting these values in Eq. (10.1), the corresponding energy barriers are obtained

$E = 14.8$ kJ$\cdot$mol^{-1} (H_2O) and $E = 9.4$ kJ$\cdot$mol^{-1} (CH_3OH).

The energy barriers, which are obtained by using the literature values for η (given in Table 2), are $E = 15.9$ kJ$\cdot$mol^{-1} and $E = 11.1$ kJ$\cdot$mol^{-1}.

Fig. 4: Temperature dependence of the dynamic viscosity η of water (o) and methanol (+), respectively.
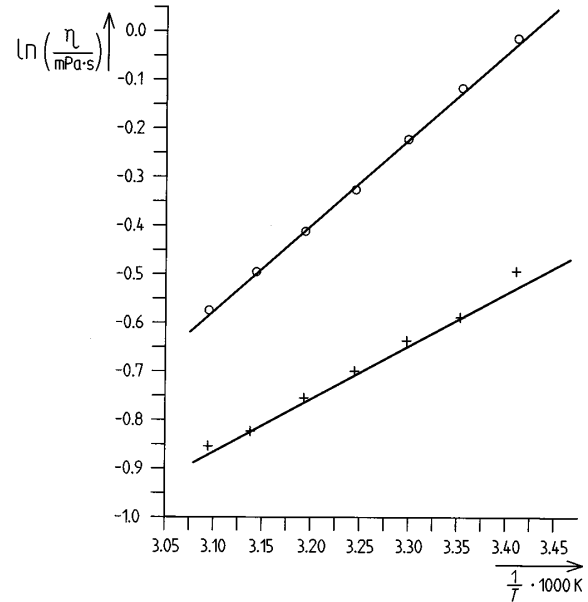
Related topics
Electrical conductivity, Wiedmann-Franz law, Lorenz number, diffusion, temperature gradient, heat transport, specific heat, four-point measurement.

Principle
The thermal conductivity of copper and aluminium is determined in a constant temperature gradient from the calorimetrically measured heat flow. The electrical conductivity of copper and aluminium is determined, and the Wiedmann-Franz law is tested.

Equipment

1	Calorimeter vessel, 500 ml	04401-10
1	Calor. vessel w. heat conduct. conn.	04518-10
1	Heat conductivity rod, Cu	04518-11
1	Heat conductivity rod, Al	04518-12
1	Magn. stirrer, mini, controlable	47334-93
1	Heat conductive paste, 50 g	03747-00
1	Gauze bag	04408-00
1	Rheostat, 10 Ω, 5.7 A	06110-02
1	Immers.heater, 300 W, 220-250 V DC/AC	05947-93
1	Temperature meter digital, 4-2	13617-93
1	Temperature probe, immers. type	11759-01
2	Surface temperature probe PT100	11759-02
1	Stopwatch, digital, 1/100 sec.	03071-01
1	Tripod base PHYWE	02002-55
1	Bench clamp PHYWE	02010-00
1	Support rod PHYWE, square, l = 630 mm	02027-55
1	Support rod PHYWE, square, l = 1000 mm	02028-55
4	Universal clamp	37715-00
6	Right angle clamp PASS	02040-55
1	Supporting block 105×105×57 mm	02073-00
1	Glass beaker, short, 400 ml	36014-00
1	Multitap transf., 14 VAC/12 VDC, 5 A	13533-93
2	Digital multimeter	07129-00
1	Universal measuring amplifier	13626-93
4	Connecting cord, l = 500 mm, red	07361-01
4	Connecting cord, l = 500 mm, blue	07361-04

Fig. 1: Set-up

Caution: Keep the water level such, that the immersion heater is always sufficiently immersed, keep refilling evaporated water during the experiment – the heater will be destoyed by overheating, if the water level is too low.

**Thermal and electrical conductivity
of metals**

Tasks

1. Determine the heat capacity of the calorimeter in a mixture experiment as a preliminary test. Measure the calefaction of water at a temperature of 0°C in a calorimeter due to the action of the ambient temperature as a function of time.

2. To begin with, establish a constant temperature gradient in a metal rod with the use of two heat reservoirs (boiling water and ice water) After removing the pieces of ice, measure the calefaction of the cold water as a function of time and determine the thermal conductivity of the metal rod.

3. Determine the electrical conductivity of copper and aluminium by recording a current-voltage characteristic line.

4. Test of the Wiedemann-Franz law.

Set-up and procedure

1. Measurement of the heat capacity of the lower calorimeter

- Weigh the calorimeter at room temperature.
- Measure and record the room temperature and the temperature of the preheated water provided.
- After filling the calorimeter with hot water, determine the mixing temperature in the calorimeter.
- Reweigh the calorimeter to determine the mass of the water that it contains.
- Calculate the heat capacity of the calorimeter.
- Determine the influence of the heat of the surroundings on the calefaction of the water (0 °C without pieces of ice) by measuring the temperature change in a 30-minute period.

2. Determination of the thermal conductivity

- Perform the experimental set-up according to Fig. 1.
- Weigh the empty, lower calorimeter.
- Insert the insulated end of the metal rod into the upper calorimeter vessel. To improve the heat transfer, cover the end of the metal rod with heat-conduction paste.
- Attach the metal rod to the support stand in such a manner that the lower calorimeter can be withdrawn from beneath it.

- The height of the lower calorimeter can be changed with the aid of the supporting block. When doing so, care must be taken to ensure that the non-insulated end of the rod remains completely immersed in the cold water during the experiment.
- The surface temperature probe must be positioned as close to the rod as possible.
- The outermost indentations on the rod (separation: 31.5 cm) are used to measure the temperature difference in the rod. To improve the heat transfer between the rod and the surface probe, use heat-conduction paste.
- Using an immersion heater, bring the water in the upper calorimeter to a boil, and keep it at this temperature.

Caution: Keep the water level such, that the immersion heater is always sufficiently immersed, keep refilling evaporated water during the experiment – the heater will be destroyed by overheating, if the water level is too low.

- Ensure that the upper calorimeter is well filled to avoid a drop in temperature due to contingent refilling with water.
- Keep the water in the lower calorimeter at 0°C with the help of ice (in a gauze pouch).

- The measurement can be begun when a constant temperature gradient has become established between the upper and lower surface probes, i.e. when no changes occur during the differential measurement.
- At the onset of measurement, remove the ice from the lower calorimeter.
- Measure and record the change in the differential temperature and the temperature of the water in the lower calorimeter for a period of 5 minutes.
- Weigh the water-filled calorimeter and determine the mass of the water. Settings of the temperature measuring device 4-2:
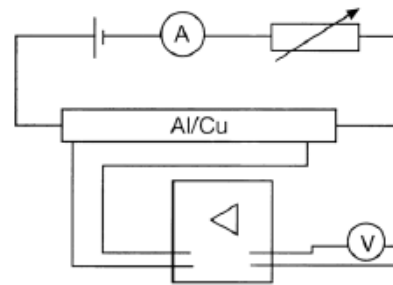
Fig. 2: Circuit diagram.

  - o In the first display on the measuring device, the temperature of the lower calorimeter is displayed.
  - o In the second display, the differential measurement between the upper and the lower surface probe is shown.
- The thermal conductivity of different metals can be determined from the measuring results.

3. Measurement of the electrical conductivity.

- Perform the experimental set-up according to the circuit diagram in Fig. 2 (set-up in accordance with a 4-conductor measuring method).
- Set the voltage on the variable transformer to 6 V.
- The amplifier must calibrated to 0 in a voltage-free state to avoid a collapse of the output voltage.
- Select the amplifier settings as follows:

  Input: Low Drift

  Amplification: 10^4

  Time Constant: 0
- Set the rheostat to its maximum value and slowly decrease the value during the experiment.
- Read and note the values for current and voltage
- The resistance, and thus the electrical conductivity, can be determined from the measured values.

Theory and evaluation

If a temperature difference exists between different locations of a body, heat conduction occurs. In this experiment there is a one-dimensional temperature gradient along a rod. The quantity of heat dQ transported with time dt is a function of the cross-sectional area A and the temperature gradient $\delta T/\delta x$ perpendicular to the surface.

$$\frac{dQ}{dt} = -\lambda A \cdot \frac{\partial T}{\partial x} \qquad (1)$$

**Thermal and electrical conductivity
of metals**

The temperature distribution in a body is generally a function of location and time and is in accordance with the Boltzmann transport equation

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho \cdot c} \cdot \frac{\partial^2 T}{\partial x^2} \qquad (2)$$

Where ρ is the density and c is the specific heat capacity of the substance.
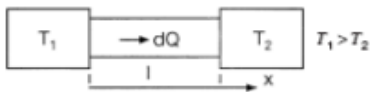
After a time, a steady state

$$\frac{\partial T}{\partial x} = 0 \qquad (3)$$

is achieved if the two ends of the metal rod having a length l are maintained at constant temperatures T_1 and T_2, respectively, by two heat reservoirs.

Substituting equation (3) in equation (2), the following equation is obtained:

$$T(x) = \frac{T_2 - T_1}{l} \cdot x + T_1 \qquad (4)$$

1. The heat capacity of the calorimeter is obtained from results of the mixing experiment and the following formula:

$$C = c_W \cdot m_W \cdot \frac{\vartheta_W - \vartheta_M}{\vartheta_M - \vartheta_R} \qquad (5)$$

c_W = Specific heat capacity of water
m_W = Mass of the water
ϑ_W = Temperature of the hot water
ϑ_M = Mixing temperature
ϑ_R = Room temperature
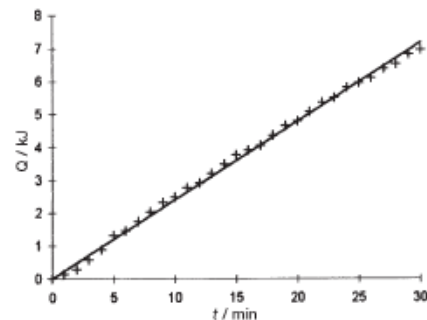
Fig. 3. Diagram: Heat of surroundings over time.

The measurement supplies a value of approximately 78 J/K ±25%. The large variations in the results are a result of the manner in which the experiment is performed and of the experimental set-up.

The addition of heat from the surroundings is calculated from the temperature increase (T of the cold water in the calorimeter.

$$\Delta Q = (c_W \cdot m_W + C) \cdot \Delta T \qquad (6)$$
$$\text{where } \Delta T = T - T_0$$

T_0 = Temperature at time $t = 0$

2. The heat energy supplied to the lower calorimeter can be calculated using Equation (6). The values and the change in the temperature difference on the metal rod are plotted as a function of time.

In the diagram illustrating the temperature difference, one can see that the temperature essentially remains constant. Consequently, equation 3 can be considered as having been satisfied. In order to calculate the heat energy transported by the metal rod according to Equation 1, the ambient heat fraction must be subtracted.

$$\frac{dQ_{rod}}{dt} = \frac{dQ_{tot}}{dt} - \frac{dQ_{surr}}{dt} \qquad (7)$$

dQ/dt for the ambient heat can be calculated from the slope of the graph in Fig. 3. *dQ/dt* for the entire set-up can be calculated from the slope of the graph of *Q* over *t* in Figs. 4 and 5. With the values for the length of the rod (Δx = 31.5 cm), the area (A = 4.91 $\cdot$ 10^{-4} m^2) and the averaged temperature on the metal rod, the heat conduction number can be calculated using Equation (1). The following result as the average values:

λ_{Al} = 254 W/Km
λ_{Cu} = 447 W/Km

The literature values are:
λ_{Al} = 220 W/Km
λ_{Cu} = 384 W/Km

3. At room temperature the conduction electrons in metal have a much greater mean free path than the phonons. For this reason heat conduction in metal is primarily due to the electrons. The resulting correlation between the thermal conductivity λ and the electrical conductivity σ is established by the Wiedemann-Franz law:

$$\frac{\lambda}{\sigma} = L\,T \qquad (8)$$
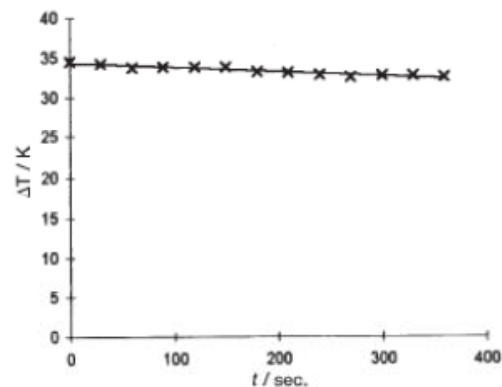
Fig. 4a: ΔT as function of time for aluminium.

The Lorenz number L, which can be experimentally determined
using Equation (8), is established by the theory of electron vapour (for temperatures above the Debye temperature) to be:

$$L = \frac{\pi^2}{3} \cdot \frac{k^2}{e^2} = 2.4 \cdot 10^{-8} \frac{W\Omega}{K^2} \qquad (9)$$

k = Universal gas constant = $1.38 \cdot 10^{-23}$ J/K
e = Elementary unit charge = $1.602 \cdot 10^{-19}$ AS

The electrical conductivity is determined by the resistance R of the rod and its geometric dimensions (l = 0.315 m, A = $4.91 \cdot 10^{-4}$ m^2).

$$\sigma = \frac{l}{A \cdot R} \qquad (10)$$

From Equation (8) the following values result for T = 300 K and the λ from the second part of the experiment.
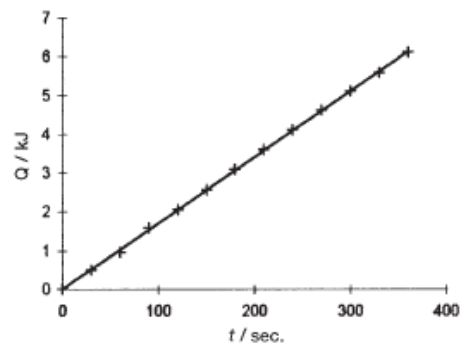
Fig. 4b: Q as a function of time for aluminium.

	R/10^{-6} Ω	σ/10^7 (Ωm)$^{-1}$	L/10^{-8} WΩK^{-2}
Al	19.6	3.27	2.5
Cu	12.04	5.33	2.35

The Debye temperatures of copper and aluminium are 335 K and 419 K, respectively. Below the Debye temperature the ratio of the conductivity is smaller than given by Equation (8).
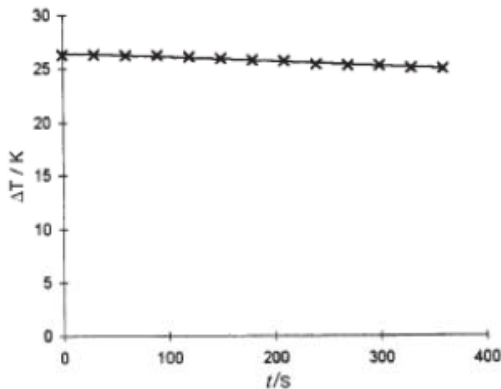
Fig. 5a: ΔT as function of time for copper.
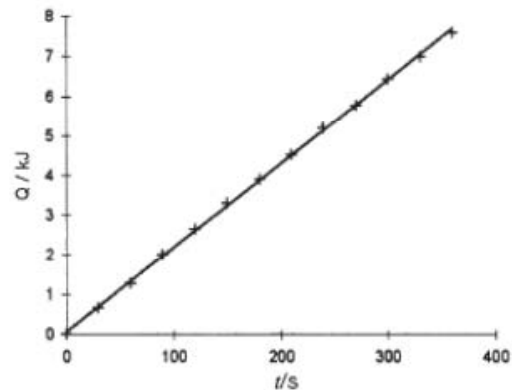
Fig. 5b: Q as function of time for copper.

Heat

Heat quantity
Heat capacities

Determining the specific heat of solids

Objects of the experiments

■ Mixing cold water with heated copper, lead or glass shot and measuring the mixture temperature.

■ Determining the specific heat of copper, lead and glass.

Principles

The heat quantity ΔQ that is absorbed or evolved when a body is heated or cooled is proportional to the change of temperature $\Delta \vartheta$ and to the mass m:

$$\Delta Q = c \cdot m \cdot \Delta \vartheta \qquad (I).$$

The factor of proportionality c, the specific heat capacity of the body, is a quantity that depends on the material.

In this experiment, the specific heat capacities of different substances, which are available as shot, are determined. In each case the shot is weighed, heated with steam to the temperature ϑ_1 and then poured into a quantity of water that has been weighed out and that has the temperature ϑ_2. After the mixture has been carefully stirred, the pellets and the water reach the common temperature ϑ_M through heat exchange. The heat quantity evolved by the shot

$$\Delta Q_1 = c_1 \cdot m_1 \cdot (\vartheta_1 - \vartheta_M) \qquad (II)$$

m_1: mass of the shot
c_1: specific heat capacity of the shot

is equal to the heat quantity absorbed by the water

$$\Delta Q_2 = c_2 \cdot m_2 \cdot (\vartheta_M - \vartheta_2) \qquad (III)$$

m_2: mass of the water

The specific heat capacity of water c_2 is assumed to be known. The temperature ϑ_1 is equal to the temperature of steam. The unknown quantity c_1 can therefore be calculated from the measured quantities ϑ_2, ϑ_M, m_1 and m_2:

$$c_1 = c_2 \cdot \frac{m_2 \cdot (\vartheta_M - \vartheta_2)}{m_1 \cdot (\vartheta_1 - \vartheta_M)} \qquad (IV).$$

The calorimeter vessel too absorbs part of the heat evolved by the shot. Therefore, the heat capacity

$$C_K = c_2 \cdot m_K \qquad (V)$$

or the water equivalent m_K of the calorimeter vessel has to be taken into account. The absorbed heat quantity calculated in Eq. (III) is thus more precisely

$$\Delta Q_2 = c_2 \cdot (m_2 + m_K) \cdot (\vartheta_M - \vartheta_2) \qquad (VI),$$

and Eq. (IV) is extended to

$$c_1 = c_2 \cdot \frac{(m_2 + m_K) \cdot (\vartheta_M - \vartheta_2)}{m_1 \cdot (\vartheta_1 - \vartheta_M)} \qquad (VII).$$

1
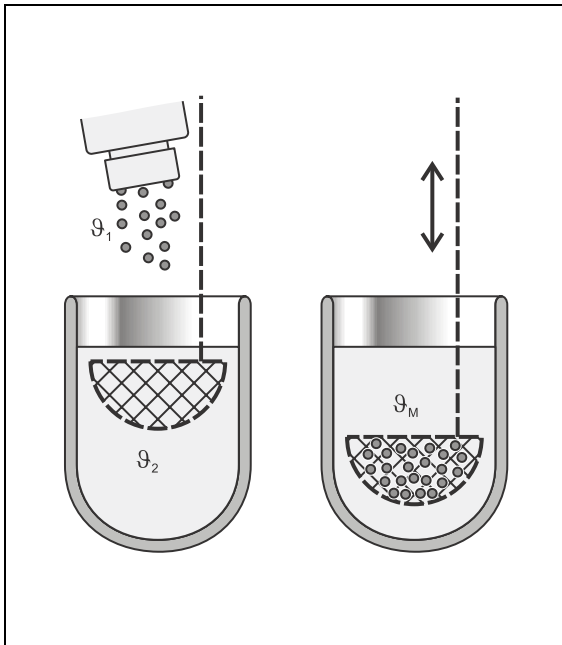
Apparatus

1 Dewar vessel	386 48
1 cover for Dewar vessel	384 161
1 copper shot, 200 g	384 35
1 glass shot, 100 g	348 36
1 lead shot, 200 g	315 76
1 school and lab. balance 610 Tare, 610 g .	315 23
1 thermometer –10 °C to +110 °C	382 34
or	
1 temperature sensor NiCr-Ni	666 193
1 digital thermometer	666 190
1 steam generator, 550 W / 220 V	303 281
1 heating apparatus	384 34
1 beaker, 400 ml	664 104
1 stand base, V-shape, 20 cm	300 02
1 stand rod, 47 cm	300 42
1 Leybold multiclamp	301 01
1 universal clamp, 0 … 80 mm dia.	666 555
1 silicone tubing int. dia. 7 × 1.5 mm, 1 m .	667 194
1 pair of heat protective gloves	667 614

Setup and carrying out the experiment

The experimental setup is illustrated in Fig. 1.

– Mount the heating apparatus in the stand material.
– Fill water into the steam generator, close the device cautiously, and connect it to the top hose connection of the heating apparatus (steam inlet) with silicone tubing.
– Attach silicone tubing to the bottom hose connection of the heating apparatus (steam outlet), and hang the other end in the beaker. See to it that the silicone tubings are securely seated at all connections.
– Fill the sample chamber of the heating apparatus as completely as possible with lead shot, and seal it with the stopper.
– Connect the steam generator to the mains, and heat the shot for about 20–25 minutes in the heating apparatus flowed through by steam.

In the meantime:

– Determine the mass of the empty Dewar vessel, and fill in about 180 g of water.
– Mount the cover for the Dewar vessel and insert the thermometer or the temperature sensor respectively.
– Measure the temperature ϑ_2 of the water.
– Open the cover of the Dewar vessel and shift it aside; leave the mesh for samples of the cover in the Dewar vessel.

– Drop the shot with the temperature of 100 °C into the mesh for samples, close the cover, and thoroughly mix the water with the shot.
– Read the mixture temperature when the temperature of the water stops rising.
– Determine the additional mass m of the shot.

– Repeat the experiment with copper and glass shot.

Fig. 1   Experimental setup for determining the specific heat of solids.
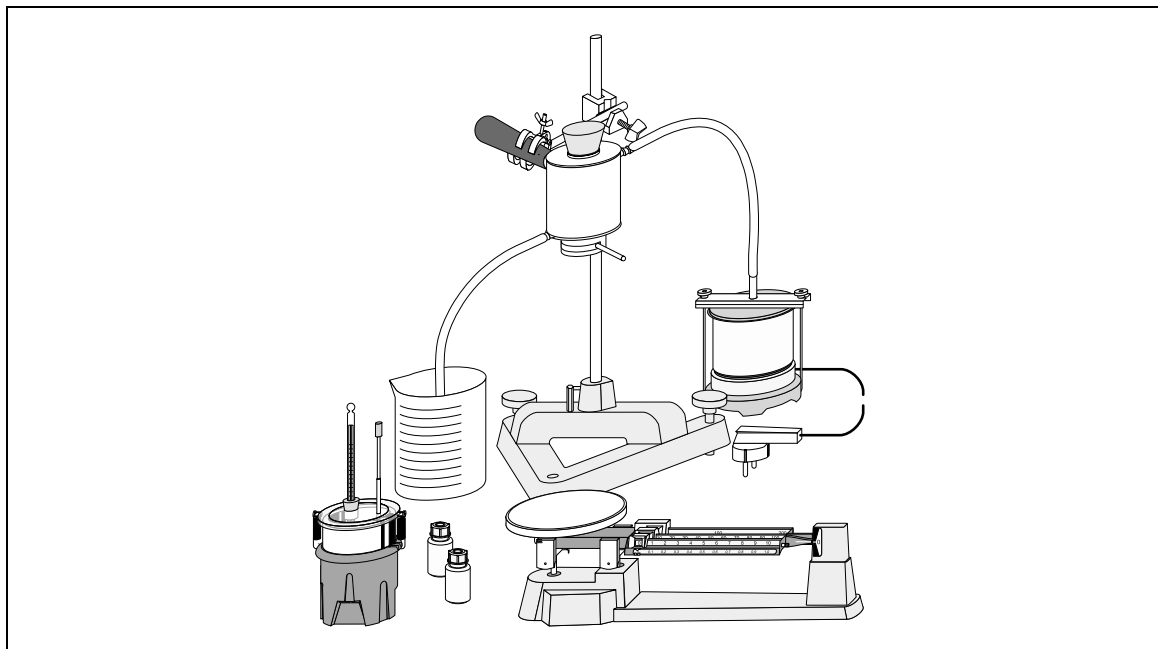
Measuring example

Mass of the water: m_1 = 180 g

Temperature of the shot: ϑ_2 = 100 °C

Table 1: Measured values for determining the specific heat capacities

substance	$\dfrac{m_2}{\text{kg}}$	ϑ_1	ϑ_M
lead	77	24.5 °C	25.4 °C
copper	69	24.0 °C	26.2 °C
glass	19	23.8 °C	24.9 °C

Evaluation

Water equivalent of the calorimeter: m_K = 23 g

specific heat capacity of water: $c_2 = 4.19 \dfrac{\text{kJ}}{\text{K} \cdot \text{kg}}$:

Table 2: Specific heat capacities determined experimentally and the corresponding values quoted in the literature

substance	$\dfrac{c}{\frac{\text{kJ}}{\text{K} \cdot \text{kg}}}$	$\dfrac{c}{\frac{\text{kJ}}{\text{K} \cdot \text{kg}}}$
	experiment	literature
lead	0.133	0.1295
copper	0.367	0.385
glass	0.656	0.746

In Table 2, the specific heat capacities calculated according to Eq. (VII) are given. The agreement with the values quoted in the literature is satisfactory.

Results

The specific heat capacities of the solids studied depend on the material and are considerably smaller than the specific heat capacity of water.

Heat

Thermal expansion
Thermal expansion of solids

*LD
Physics
Leaflets*

P2.1.1.3

Measuring the linear expansion of solids as a function of temperature

Objects of the experiment

■ Measuring the linear thermal expansion of brass, steel and glass tubes as a function of temperature.

■ Determining the linear expansion coefficients of brass, steel and glass.

Principles

The length *s* of a solid body is linearly dependent on its temperature ϑ :

$$s = s_0 \cdot (1 + \alpha \cdot \vartheta) \tag{I}$$

s_0: length at room temperature

ϑ: temperature in °C

The linear expansion coefficient α is determined by the material of the solid body.

In this experiment a circulation thermostat is used to heat the water which flows through the various tube samples. A dial gauge with 0.01 mm scale graduations is used to measure the change of length $\Delta s = s - s_0$ as a function of temperature ϑ.

Fig. 1: Schematic representation of the experimental setup to measure the linear thermal expansion of tubes with the expansion apparatus as a function of temperature.
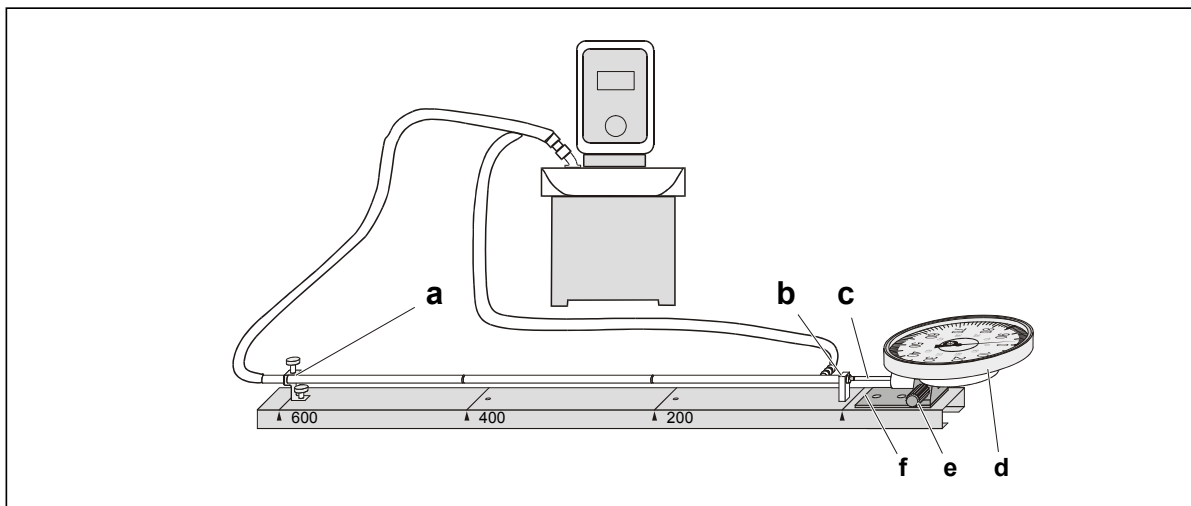
LD Didactic GmbH · Leyboldstrasse 1 · D-50354 Huerth / Germany · Phone: (02233) 604-0 · Fax: (02233) 604-222 · e-mail: info@ld-didactic.de

Apparatus

1 Longitudinal expansion apparatus D.................	381 341
1 Dial gauge, 10 mm...	361 15
1 Holder for dial gauge	381 36
1 Thermometer -10 ... +110°C	382 34
1 Circulation thermostat +25 ... +100 °C..............	666 768
1 Pump set	666 7703
2 Silicone tubing, 7 mm Ø....................................	667 194
2 Water, pure, 5 l	675 3410

Setup

The set up of the experiment is shown in Fig. 1 schematically.

- Screw on the holder for dial gauge 381 36 **(e)** (for details refer to instruction sheet 381 341 of expansion apparatus) and clamp the dial gauge in place 361 15 **(d)**.

- Attach the fixed bearing **(a)** of the expansion apparatus at the 600 mark and slide the open end of the brass tube into the fixed bearing.

- Slide the closed end of the brass tube into the guide fitting **(b)** so that the hose nipple **(f)** is pointing laterally downwards.

- Tighten the screw to fix the brass tube in the fixed bearing (the screw must engage the ring groove of the tube).

- Insert the extension piece **(c)** (see instruction sheet for dial gauge 361 15).

- Prepare the circulation thermostat and the pump set. For a detailed description refer to instruction sheet 666 768.

Note: Be sure to read the instruction sheet of the circulation thermostat 666 768 before using this device.

- Fill the water bath of the circulation thermostat with distilled water.
- Connect the expansion apparatus to the circulation thermostat using the silicone tubing, i.e. connect the open end of the brass tube and the hose nipple **(f)** to the hose nipples of the pump set of circulation thermostat.
- Use the thermometer 382 34 to measure the temperature ϑ of the water bath.

Safety notes

- ■ Check the seating of the silicone tubing every time before putting the apparatus into operation, to ensure that no hot water can escape in an uncontrolled manner and cause damage or injury.
- ■ Follow the safety hints of the circulation thermostat.
- ■ When using the glass tube follow the instructions printed on the thermal expansion apparatus.

Carrying out the experiment

- Turn the housing of the dial gauge to set the zero position.

- Measure the initial temperature, i.e. room temperature ϑ_0.

- Switch on the circulation thermostat and set the temperature about 5 °C above ϑ_0.

- Wait until a thermal equilibrium has been established.

- Measure the temperature ϑ.

- Read off and write down the pointer deflection of the dial gauge.

- Increase the temperature ϑ in steps of approx. 5° C until approx. 100° C.

- Allow the brass tube to cool down to room temperature.

- Replace the brass tube with the steel tube, i.e. attach the fixed bearing **(a)** of the expansion apparatus at the 600 mark and slide the open end of the steel tube into the fixed bearing.

- Conduct such a measurement on the glass tube. For this measurement increase the temperature ϑ in steps of approx. 10° C

Measuring example

Table 1: Measured change of length Δs as a function of the temperature ϑ.

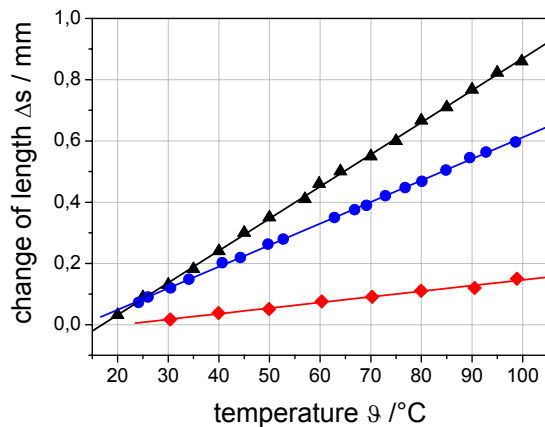| brass		steel		glass	
$\dfrac{\vartheta}{°C}$	$\dfrac{\Delta s}{mm}$	$\dfrac{\vartheta}{°C}$	$\dfrac{\Delta s}{mm}$	$\dfrac{\vartheta}{°C}$	$\dfrac{\Delta s}{mm}$
20.0	0.03	24.1	0.07	30.4	0.02
25.0	0.09	26.0	0.09	39.9	0.04
30.0	0.13	30.5	0.12	49.9	0.05
35.0	0.18	34.1	0.15	60.3	0.08
40.0	0.24	40.7	0.20	70.3	0.09
45.0	0.30	44.3	0.22	79.9	0.11
50.0	0.35	49.7	0.26	90.5	0.12
57.0	0.41	52.7	0.28	98.9	0.15
59.8	0.46	62.8	0.35	–	–
64.0	0.50	66.8	0.38	–	–
70.0	0.55	69.1	0.39	–	–
75.0	0.60	72.9	0.42	–	–
80.0	0.67	76.8	0.45	–	–
85.0	0.71	80.1	0.47	–	–
90.0	0.77	84.9	0.51	–	–
95.0	0.82	89.6	0.55	–	–
99.8	0.86	92.8	0.56	–	–
–	–	98.6	0.60	–	–

Fig. 2: Change of length Δs as a function of temperature ϑ : brass (▲), steel (●), glass (♦). The solid lines correspond to a fit according equation (II).

Evaluation and results

The various measurements are summarized in Table 1. To determine the linear expansion coefficient α the change of length Δs is plotted as a function of temperature ϑ (Fig. 2).

Subtracting the initial length s_0 at room temperature at both sides of equation (I) gives the change of length Δs:

$$s - s_0 = s_0 \cdot \alpha \cdot \vartheta$$

$$\Delta s = k \cdot \vartheta \tag{II}$$

with

$$k = s_0 \cdot \alpha$$

The linear fit of equation (II) to the measured data gives the linear expansion coefficients α (Fig. 2). The results are summarized in Table 2.

Table 2: Linear expansion coefficients α determined from Fig. 2 according equation (II).

Material	$\dfrac{\Delta s}{mm}$	Measurement $\dfrac{\alpha}{K^{-1}}$	Literature $\dfrac{\alpha}{K^{-1}}$
brass	600	$17.8 \cdot 10^{-6}$	$18 \cdot 10^{-6}$
steel	600	$11.7 \cdot 10^{-6}$	$11 \cdot 10^{-6}$
glass	600	$3.1 \cdot 10^{-6}$	$3 \cdot 10^{-6}$

Supplementary information

Additionally, the linear thermal expansion can be measured as function of the overall tube length s_0. The experimental procedure to determine the linear thermal expansion from a temperature difference $\Delta\vartheta = \vartheta_1 - \vartheta_0$ is described in the leaflet P2.1.1.2.

Instead of using the steam generator of P2.1.1.2 the circulation thermostat can be used to determine the change in length Δs. Thus the linear expansion coefficient e.g. of brass tubes of different lengths (200 mm, 400 mm, 600 mm) can be determined as shown in Fig. 2 in leaflet P2.1.1.2 by measuring the initial temperature ϑ_0 and the final temperature ϑ_1 by setting the temperature with the circulation thermostat (see also instruction sheet 381 341 of expansion apparatus).

Heat

Kinetic theory of gases
Gas laws

Pressure-dependency of the volume of a gas at a constant temperature (Boyle-Mariotte's law)

Objects of the experiments

- Measuring the volume V of an air column as a function of the pressure p at a constant temperature T.
- Confirming Boyle-Mariotte's law.

Principles

The state of a quantity of ν moles of an ideal gas is completely described by the measurable quantities p (pressure), V (volume) and T (temperature). The relation between these three quantities is given by the perfect gas laws:

$$p \cdot V = \nu \cdot R \cdot T \tag{I}$$
$R = 8.31$ J K^{-1} mol^{-1}: gas constant

If p, V or T remains constant, then the other two quantities cannot be varied independently of each other. At a constant temperature, for example, Boyle-Mariotte's law states

$$p \cdot V = \text{const.} \tag{II}$$

This law is confirmed in the experiment by means of a gas thermometer. The gas thermometer consists of a glass capillary open at one end. A certain quantity of air is enclosed by means of a mercury seal. At an outside pressure p_0, the enclosed air has a volume V_0.

By pumping off air at room temperature with a hand pump, an underpressure Δp with respect to the outside pressure p_0 is generated at the open end of the capillary so that the pressure there is $p_0 + \Delta p$. The mercury seal itself exerts a pressure

$$p_{Hg} = \rho_{Hg} \cdot g \cdot h_{Hg} \tag{III}$$
$\rho_{Hg} = 13.6$ g cm^{-3}: density of mercury
$g = 9.81$ m s^{-2}: acceleration of free fall
h_{Hg}: height of the mercury seal

on the enclosed air so that the pressure of the enclosed air is

$$p = p_0 + p_{Hg} + \Delta p \tag{IV}$$

The volume V of the enclosed air column is determined by the pressure p. V can be calculated from the height h of the air column and the cross-section of the capillary.

$$V = \pi \cdot \frac{d^2}{4} \cdot h \tag{V}$$
$d = 2.7$ mm: inside diameter of the capillary

pV diagram of an ideal gas at a constant temperature T
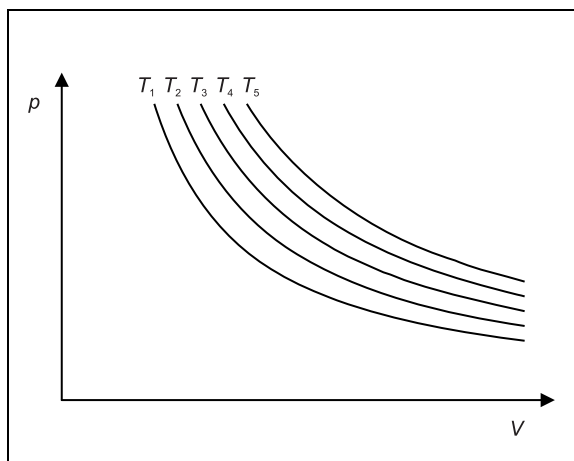
0110-Sel

Setup

Collecting the mercury globules:

– Connect the hand pump to the gas thermometer, and hold the thermometer so that its opening is directed downward (see Fig. 1).

– Generate maximum underpressure Δp with the hand pump, and collect the mercury in the bulge **(a)** so that it forms a drop.

   The manometer of the pump displays the underpressure Δp as a negative value.

– If there are mercury globules left, move them into the bulge **(a)** by slightly tapping the capillary.

   A small mercury globule which might have remained at the sealed end of the capillary will not affect the experiment.

Adjusting the gas volume V_0:

– Slowly turn the gas thermometer into its position for use (open end upward) so that the mercury moves to the inlet of the capillary.

– Open the ventilation valve **(b)** of the hand pump carefully and slowly to reduce the underpressure Δp to 0 so that the mercury slides down slowly as one connected seal.

– Mount the gas thermometer in the stand material.

If the mercury seal bursts due to strong ventilation or vibration:

– Recollect the mercury.
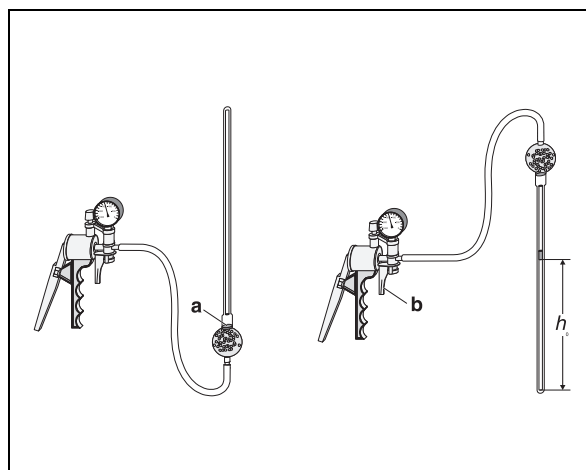
Fig. 1   Collecting the mercury globules and adjusting the initial volume V_0:

Fig. 2   Experimental setup for investigating the pressure-dependency of the gas volume at a constant temperature
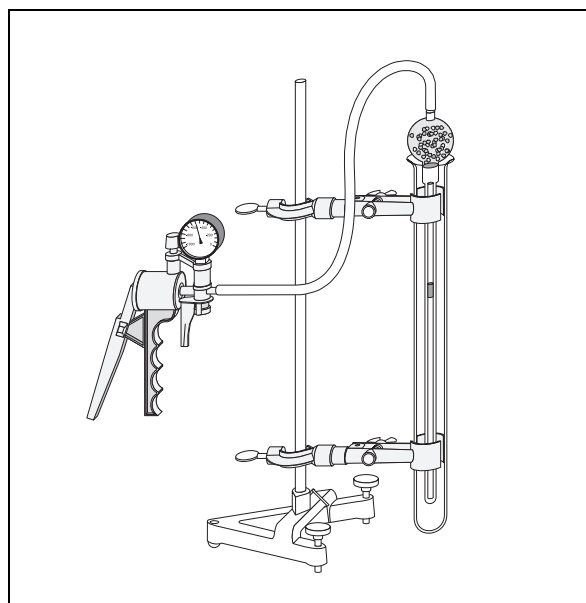
Carrying out the experiment

– Determine the outside pressure p_0.

– Read the height h_{Hg} of the mercury seal from the scale of the gas thermometer.

– Generate an underpressure Δp with the hand pump and increase it step by step.

– Each time read the height h of the air column, and record it together with Δp.

Measuring example

Outside pressure: p_0 = 1011 hPa

Height of the mercury seal: h_{Hg} = 11 mm

Table 1: The height *h* of the enclosed quantity of air as a function of the underpressure Δp.

$\dfrac{\Delta_P}{hPa}$	$\dfrac{h}{cm}$
0	7.0
− 60	7.7
−100	8.0
−150	8.45
−200	8.9
−250	9.5
−300	10.5
−340	10.95
−410	12.1
−450	12.95
−500	14.1
−550	15.4
−600	17.15
−650	20.05
−690	22.5
−740	26.75
−780	31.35
−800	34.75

Evaluation

According to Eq (III) the pressure p_{Hg} exerted by the mercury seal is:

$$p_{Hg} = 13.6 \frac{g}{cm^3} \cdot 9.81 \frac{m}{s^2} \cdot 11 \text{ mm} = 15 \text{ hPa}$$

Table 2: The pressure *p* (calculated from the measuring values Δp of Table 1) of the enclosed quantity of air as a function of the volume *V* (calculated from the measuring values *h* of Table 1).

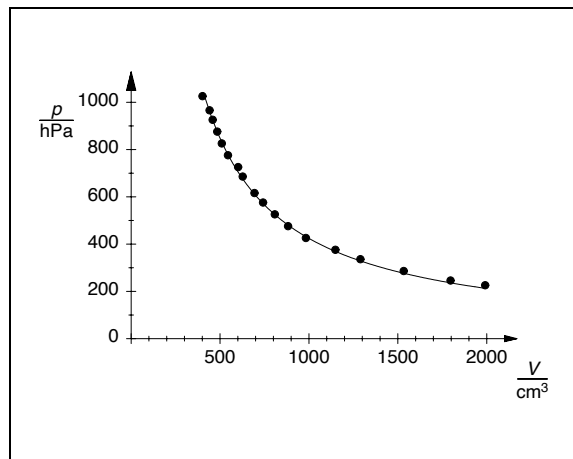| $\dfrac{V}{mm^3}$	$\dfrac{p}{hPa}$
401.1	1026
441.2	966
458.4	926
484.2	876
510	826
544.4	776
601.7	726
627.4	686
693.3	616
742	576
807.9	526
882.4	476
982.7	426
1148.9	376
1289.3	336
1532.8	286
1796.4	246
1991.2	226

Fig. 3   The pressure *p* of the enclosed air column as a function of the volume *V* at a constant temperature T

Fig. 3 shows a plot of the measuring values of Table 2. The smooth curve drawn in is the hyperbola

$$p = \frac{C}{V}$$

with C = 424 000 hPa mm³.

Within the accuracy of measurement, this curve agrees with the measuring values. Eq. (II) is thus fulfilled for the enclosed air column, that is, the air column behaves as an ideal gas.

Results

At a constant temperature, the pressure and the volume of an ideal gas are inversely proportional to each other.

or:

The product of the pressure and the volume of an ideal gas is constant if the temperature is constant (Boyle-Mariotte's law).

Heat

Thermal expansion
Thermal expansion of liquids

P2.1.2.1

Determining the
volumetric expansion coefficient
of liquids

Objects of the experiments

■ Determining the volume V_0 of the dilatometer.

■ Measuring the volume expansion of water and ethanol as a function of the temperature and determining the volumetric expansion coefficient γ.

■ Comparing the volumetric expansion coefficients of water and ethanol.

Principles

If the temperature ϑ of a liquid of volume V_0 is changed by $\Delta\vartheta$, then the volume will – as in the case of a solid – change by

$$\Delta V_0 = \gamma \cdot V_0 \cdot \Delta\vartheta \tag{I}.$$

The volumetric expansion coefficient γ is practically independent of the temperature ϑ, but it does depend on the material. In general, liquids expand more than solids.

The volumetric expansion coefficient can be determined by means of a dilatometer. A dilatometer consists of a glass flask with a capillary of known radius r at the opening as a riser tube. The level h of the liquid in the riser tube is read from a mm-scale. It increases when the glass flask is uniformly warmed in a water bath and the volume of the liquid expands.

The change in the liquid level Δh corresponds to a change in volume

$$\Delta V = \pi \cdot r^2 \cdot \Delta h \tag{II}$$

with $r = (1.5 \pm 0.08)$ mm.

However It has to be taken into account that the dilatometer itself also expands because of the warming. This expansion counteracts the change in the liquid level. The change in volume of the liquid thus is

$$\Delta V_0 = \Delta V + \Delta V_D \tag{III},$$
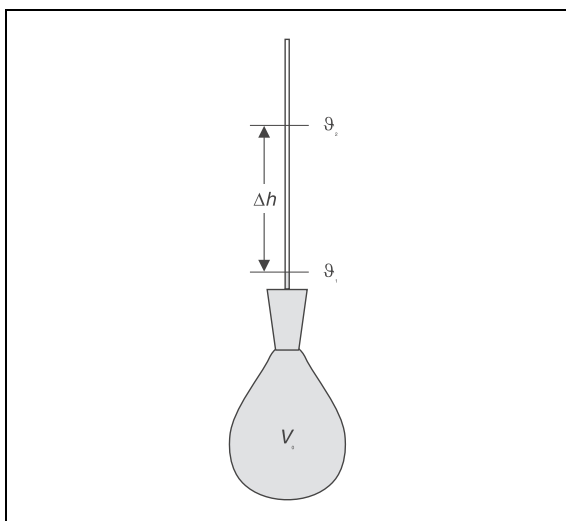
where the volume change ΔV_D of the dilatometer is

$$\Delta V_D = \gamma_D \cdot V_0 \cdot \Delta\vartheta \tag{IV}$$

with $\gamma_D = 0.84 \cdot 10^{-4}$ K^{-1}.

From (I), (III), and (IV) the volumetric expansion coefficient of the liquid is found to be

$$\gamma = \frac{1}{V_0} \cdot \frac{\Delta V}{\Delta\vartheta} + \gamma_D \tag{V}.$$

Determining the volumetric expansion coefficient of liquids

1

Setup and carrying out the experiment

Notes:

Measurement of the liquid level h may be considerably distorted by capillary forces of different strengths.

Keep the capillary clean, and, if necessary, clean it with an appropriate purifying solution, then rinse it with distilled water.

a) Calibration of the dilatometer:

– Determine the mass m_1 of the empty dilatometer.
– Fill the flask with pure water up to the bottom third of the ground opening.
– To eliminate air bubbles, heat the dilatometer in the water bath almost to boiling without the riser tube attached.
– Allow the water bath to cool off to room temperature; top off the liquid level as necessary. Take down the temperature ϑ.
– Attach the riser tube, press your finger on the opening, then remove the riser tube and allow it to drain.
– Replace the riser tube on the flask, dry the dilatometer and measure the mass m_2 of the water-filled dilatometer.

So there is still the volume V_0 of the dilatometer to be determined. This is done by determining the masses m_1 of the empty, dry dilatometer and m_2 of the dilatometer filled with pure water up to the lower end of the riser tube. Since the density ρ of water at a known temperature ϑ is known to a high accuracy (see Table 1), the volume is obtained from

$$V_0 = \frac{m_2 - m_1}{\rho} \qquad (VI).$$

Tab. 1: Values quoted in the literature for the density ρ of pure water as a function of the temperature ϑ:

ϑ	$\dfrac{\rho}{g \cdot cm^{-3}}$	ϑ	$\dfrac{\rho}{g \cdot cm^{-3}}$
15 °C	0.999099	23 °C	0.997540
16 °C	0.998943	24 °C	0.997299
17 °C	0.998775	25 °C	0.997047
18 °C	0.998596	26 °C	0.996785
19 °C	0.998406	27 °C	0.996515
20 °C	0.998205	28 °C	0.996235
21 °C	0.997994	29 °C	0.995946
22 °C	0.997772	30 °C	0.995649

b) Measuring the volume expansion of water and ethanol:

Note: After the hot plate has been switched off, the heating of the liquid continues for some time so that the dilatometer may run over.

Especially when filling in ethanol, switch the hot plate early enough.

The experimental setup is illustrated in Fig. 1.

– Dip the dilatometer into the heating bath so that the riser tube sticks out.
– Switch the hot plate on at the lowest step, and switch it off when the liquid level in the dilatometer is just below the highest mark of the scale.
– Wait until the liquid level has reached its maximum, then allow the water bath to cool down by about 1–2 K.
– Let the water bath continue cooling down, and determine the level h of the water in the riser tube as a function of the temperature (see Table 2).
– Then fill in ethanol into the thoroughly dried dilatometer, warm it up in the water bath, and repeat the measurement of the liquid level h as a fnction of the temperature (see Table 3).

Measuring example

a) Calibration of the dilatometer:

m_1 = 31.29 g
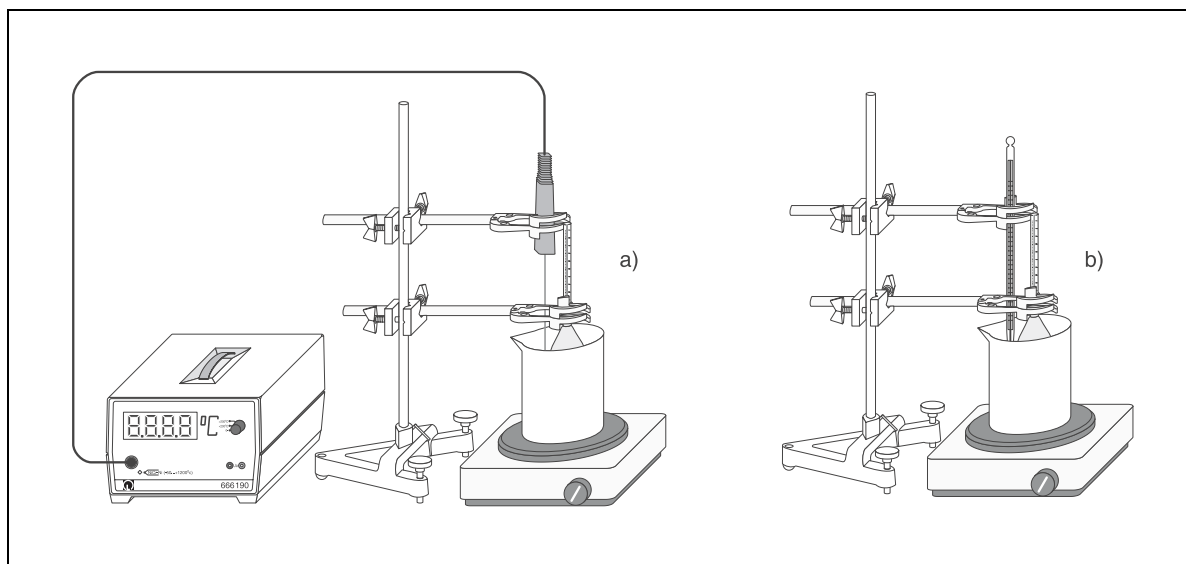
m_2 = 88.01 g

ϑ = 22 °C

2

Fig. 1   Experimental setup for the determination of the volumetric expansion coefficient of liquids.
a) Use of the temperature sensor   b) Use of the thermometer

b) Measuring the volume expansion of water and ethanol:

Table 2: The level h of pure water as a function of the temperature ϑ.

ϑ	$\dfrac{h}{\text{cm}}$	ϑ	$\dfrac{h}{\text{cm}}$
60 °C	9.5	45 °C	4.25
59 °C	9.3	44 °C	3.9
58 °C	8.9	43 °C	3.55
57 °C	8.6	42 °C	3.2
56 °C	8.2	41 °C	2.9
55 °C	7.85	40 °C	2.6
54 °C	7.5	39 °C	2.3
53 °C	7.1	38 °C	2.0
52 °C	6.75	37 °C	1.7
51 °C	6.4	36 °C	1.4
50 °C	6.0	35 °C	1.1
49 °C	5.7	34 °C	0.8
48 °C	5.3	33 °C	0.55
47 °C	4.95	32 °C	0.3
46 °C	4.6		

Tab. 3: The level h of ethanol as a function of the temperature ϑ.

ϑ	$\dfrac{h}{\text{cm}}$	ϑ	$\dfrac{h}{\text{cm}}$
38 °C	9.9	32 °C	4.6
37 °C	9.1	31 °C	3.7
36 °C	8.25	30 °C	2.7
35 °C	7.4	29 °C	1.8
34 °C	6.5	28 °C	0.9
33 °C	5.55		

Evaluation and results

a) Calibration of the dilatometer:

mass difference: $m_2 - m_1$ = 56.72 g

density ρ at ϑ = 22 °C: ρ = 0.9978 g cm^{-3} (cf. Table 1)

From (VI) you obtain: V_0 = 56.85 cm^3

b) Measuring the volume expansion of water and ethanol:

Fig. 2 shows a graph of the volume change ΔV as a function of the temperature difference $\Delta \vartheta = \vartheta - \vartheta_0$ (ϑ_0 = 32 °C for water and 28 °C for ethanol respectively, cf. Tables 2 and 3) calcu-

Fig. 2   Thermal volume expansion ΔV of water (circles) and ethanol (boxes) as functions of the temperature difference $\Delta \vartheta$.

3
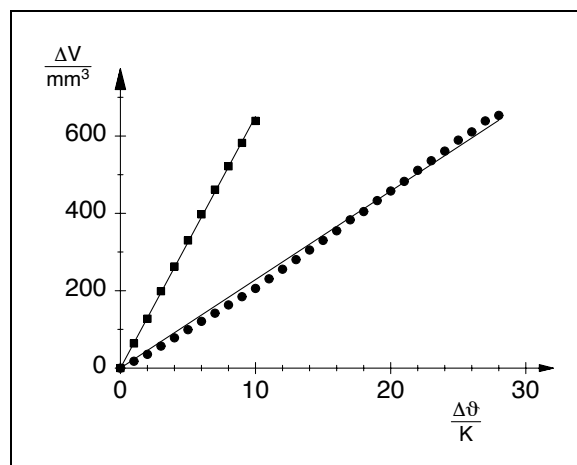
lated according to Eq. (II) from the change $\Delta h = h - h_0$ in the level. The slope of the straight line drawn through the origin is

$$\frac{\Delta V}{\Delta \vartheta} = 22.9 \, \frac{mm^3}{K}$$

for water and

$$\frac{\Delta V}{\Delta \vartheta} = 65.0 \, \frac{mm^3}{K}$$

for ethanol. With Eq. (V) the volumetric extension coefficient is obtained:

$\gamma = 4.9 \cdot 10^{-4} \, K^{-1}$ (water), $\gamma = 12.3 \cdot 10^{-4} \, K^{-1}$ (ethanol).

In the case of water, there is a systematic deviation of the measuring values from the straight line through the origin. The volumetric expansion coefficient of water is not constant, but increases with temperature in the range between 30 °C and 60 °C which has been considered here.

The volumetric expansion coefficient of ethanol is considerably larger than that of water. Since it does not change even in wider temperature ranges, it is a suitable thermometer liquid.

Supplementary note:

The thermal anomaly of water, that is, the decrease of the volume of water in the temperature range between 0 °C and 4 °C, will be studied in the experiment P2.1.3.1.

Related topics

Boiling point, heat of vaporisation, Clausius-Clapeyron equation, Van't Hoff law, Carnot cycle.

Principle and task

Water is heated in a closed pressure chamber; as much water vaporises as to make the pressure in the chamber correspond to the vapour pressure at the temperature at any time. The heat of vaporisation is determined at various temperatures from the measurement of vapour pressure as a function of temperature.

Equipment

High pressure vapour unit	02622.12	1
Heat conductive paste, 50 g	03747.00	1
Heating apparatus	32246.93	1
Pipette, with rubber bulb, long	64821.00	1
Tripod base -PASS-	02002.55	1
Bosshead	02043.00	1
Support rod, stainl. steel, 250 mm	02031.00	1

Fig. 1: Experimental set-up for measuring vapour pressure as a function of temperature.

Problems

1. To measure the vapour pressure of water as a function of temperature.

2. To calculate the heat of vaporisation at various temperatures from the values measured.

3. To determine boiling point at normal pressure by extrapolation.

Set-up and procedure

Set up the experiment as shown in Fig. 1. Fill the high pressure steam unit with distilled water, with the aid of a pipette, ensuring that there are no air bubbles in the line leading to the pressure gauge.

Now screw the vessel together carefully (the lead seals may need replacing).

The unit is fastend with a bosshead and lays on the electric heater. Put the thermometer in the hole provided, which should be filled with heat conductive paste.

Heat the pressure vessel until the gauge reads 4 MPa 40 bar. Now switch off the heater and record the pressure and temperature as the equipment cools down.

Check the locking screws from time to time while the equipment is being heated and cooling down and tighten them if necessary.

Theory and evaluation

The thermal energy which must be taken up by one mole of liquid, to vaporise at constant temperature is called the molar heat of vaporisation Λ.

At a given temperature T resp. ϑ in degrees Celsius there is a vapour pressure p at which liquid and gaseous phase are in equilibrium (Fig. 2). When a liquid boils the vapour pressure is equal to the external (atmospheric) pressure.

The Clausius-Clapeyron differential equation

$$\frac{dp}{dT} = \frac{\Lambda}{T\,(V_{\text{vap.}} - V_{\text{liq.}})} \qquad (1)$$

where $V_{\text{vap.}}$ and $V_{\text{liq.}}$ are the molar volumes of vapour and liquid respectively and Λ is the heat of phase transition, applies here to the binodal curve bounding two phases.

The phase equilibrium when T and p are constant is governed by the function

$$G = U + pV - TS \qquad (2)$$

where G = free enthalphy, U = internal energy, S = entropy.
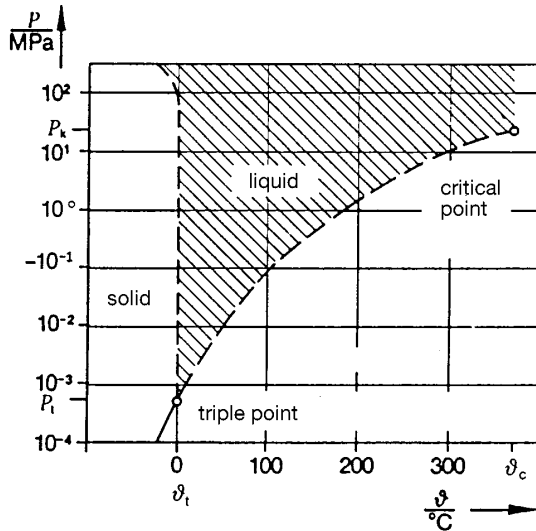
Along the binodal curve

$$G_1\,(T,p) = G_2(T,p) \qquad (3)$$

or, in differential form

$$\left(\frac{\partial G_1}{\partial p} - \frac{\partial G_2}{\partial p}\right) dp + \left(\frac{\partial G_1}{\partial T} - \frac{\partial G_2}{\partial T}\right) dT = 0. \qquad (4)$$

Fig. 2: Vapour pressure curve: water
p_t = 6.1 hPa, ϑ_t = 0.01°C,
pc = 22.12 MPa, ϑ_c = 374.2°C.

The semi-logarithmic plot of the measured values (Fig. 3) shows an almost linear relationship between ln p and 1/T. The heat of vaporisation changes with the temperature.

By fitting to a regression line in the ranges 190°– 250°C and 150°– 190°C, for example, we obtain the heat of vaporisation at 220°C and 170°C:

Heat of vaporisation (water)		
ϑ/°C	Molar Λ/10^3 J mol^{-1}	Specific λ/J g^{-1}
220	36.2	2012
170	38.3	2126

By extrapolating the straight line in the low temperature range we can read off the boiling point of water at normal pressure, T_b. The measurements we have taken give:

$$\vartheta_b = 97°C$$

The boiling point determined by extrapolation is too low because the curve for ln p = f(T) (Fig. 3) is slightly convex owing to differences in the heat of vaporisation.

With

$$\frac{\partial G}{\partial T} = -S \text{ and } \frac{\partial G}{\partial p} = V \qquad (1)$$

it follows from (3) that

$$(V_2 - V_1) \, dp = (S_2 - S_1) \, dT \qquad (6)$$

The difference in entropy between the two phases can be expressed by the reversible latent heat of transformation

$$S_2 - S_1 = \frac{\Lambda}{T} \qquad (7)$$

(6) and (7) together give (1) for the binodal curve between the liquid and the vapour phase.

At low vapour pressures $p << p_c$, $V_{liq.} << V_{vap.}$ can be disregarded. In this range the vapour behaves very like an ideal gas and

$$V_{vap.} = \frac{R \cdot T}{p} \qquad (8)$$

where R = 8.3141 J/K·mol, the universal gas constant.

From (1), therefore:

$$\frac{dp}{p} = \frac{\Lambda}{R} \cdot \frac{dT}{T^2} \qquad (9)$$

Assuming Λ to be constant, by integrating we obtain the Van't Hoff equation

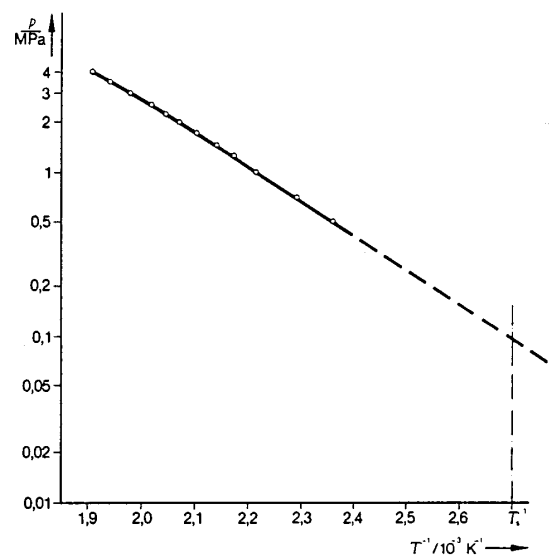$$\ln p = -\frac{\Lambda}{R} \cdot \frac{1}{T} + \text{const.} \qquad (10)$$

Fig. 3: Natural logarithm of vapour pressure p as a function of the reciprocal of the temperature $(1/T)$: T_b = boiling point at normal pressure.

Experiment Title

Student Name　　　　　　　　　　　　　　　　Group #

dd/mm/yyyy

1　Objective(s):

Give a brief summary of the purpose of the experiment.

2　Principle(s):

Write briefly the principle of the experiment.

3　Apparatus:

List all the tools and apparatus you used to perform the experiment

4　Data:

In this section you need to show your experimental results (data tables).

x (m)	V (V)
0.0031	0.015
0.0024	0.020
0.0056	0.045
0.0080	0.066

Table 1: Caption is important

5　Graphs:

Here you should include all the graphs you plotted from your data and write a caption for each one.

6　Data Analysis:

In this section, you need to explain the results you obtained in the data section, comment on the behavior of the data, and if there is any anomalies results, try to explain them. Also explain any calculations you performed in the tables.

7   Calculations:

In this section, you should illustrate your calculations and explain them briefly, Also you may need to include the calculation of the error percentage if required.

8   Conclusion:

Summarize your results and comment on them.