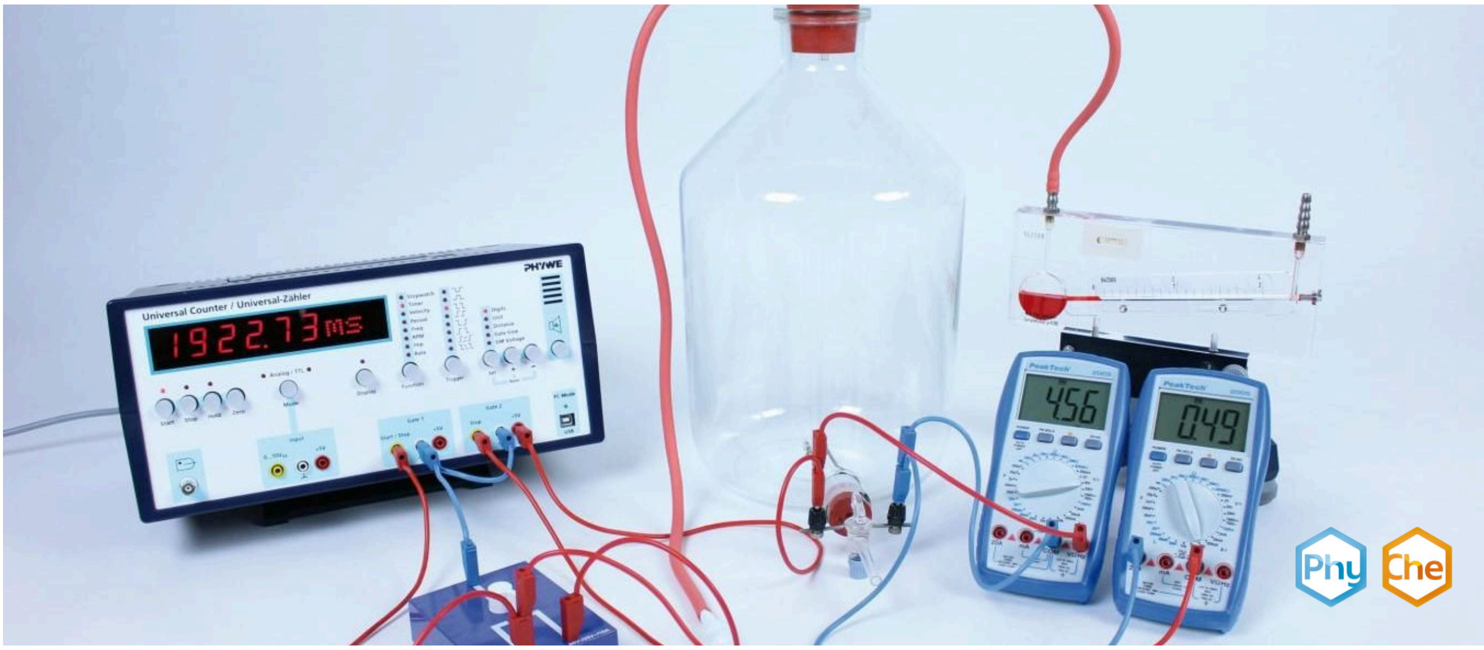
Heat capacity of gases



Physics	Thermodynamics	Heat energy, thermal capacity	
Chemistry	Physical chemistry	Thermochemistry, calorimetry	
Applied Science	Engineering	Renewable Energy	Basic Principles
Applied Science	Engineering	Photonics	Basic Principles

Difficulty level	Group size	Preparation time	Execution time
medium	2	45+ minutes	45+ minutes

This content can also be found online at:

http://localhost:1337/c/6011399e8b903a00038a5737

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General information

Application

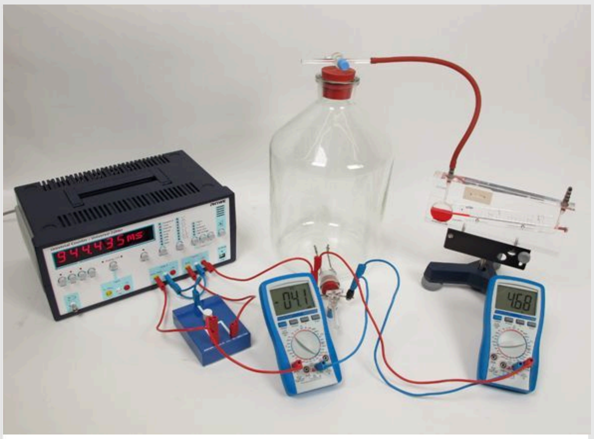

Fig.1: Experimental set-up for the determination of C_V

An understanding about the heat capacity of gases is fundamentally important for the energy industry, as the heating of gases is used to produce electricity. This experiment can be used to gain a first understanding of the heating behaviour of gases.

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Other information (1/2)

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Prior knowledge

The prior knowlege required for this experiment is found in the theory section.

Main principle

Heat is added to a gas in a glass vessel by an electric heater which is switched on briefly. The temperature increase results in a pressure increase, which is measured with a manometer. Under isobaric conditions a temperature increase results in a volume dilatation, which can be read from a syringe. The molar heat capacities C_V and C_P are calculated from the pressure and volume change respectively.

Other information (2/2)

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Learning objective

The goal of this experiment is to investigate the heat capacity of air.

Tasks

1. Determine the molar heat capacities of air at constant volume C_V
2. Determine the molar heat capacities of air at constant pressure C_P

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Theory (1/4)

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The first law of thermodynamics can be illustrated particularly well with an ideal gas. This law describes the relationship between the change in internal energy dU, the heat exchanged with the surroundings dQ and the work performed by the system generally speaking. In our case the work being performed is the pressure-volume work results into a volume increase dV keeping constant the pressure p.

$\mathrm{d}Q = \mathrm{d}U_\mathrm{i} + p\mathrm{d}V$ (1)

The molar heat capacity C of a substance results from the amount of absorbed heat dQ and the temperature change dT per mole where n is the number of moles:

$C = \frac{1}{n} \cdot \left(\frac{\mathrm{d}Q}{\mathrm{d}T} \right)$ (2)

One distinguishes between the molar heat capacity at constant volume C_V and the molar heat capacity at constant pressure C_P. According to equations (1) and (2) and under isochoric conditions (v = const, dV = 0), the following holds true:

Theory (2/4)

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$C_V = \frac{1}{n} \cdot \left(\frac{\mathrm{d}U_\mathrm{i}}{\mathrm{d}T} \right)$ (3)

Under isobaric conditions (p = const; dp = 0):

$C_p = \frac{1}{n} \cdot \left(\frac{\mathrm{d}U_\mathrm{i}}{\mathrm{d}T} + p\frac{\mathrm{d}V}{\mathrm{d}T} \right)$ (4)

It is obvious form equation (3) that the molar heat capacity C_V is a function of the internal energy of the gas. The internal energy can be calculated with the aid of the kinetic gas theory with the number of degrees of freedom f and the universal gas constant R:

$U_\mathrm{i} = \frac{1}{2} f \cdot R \cdot T \cdot n$ (5)

Taking equation (3) into consideration it follows that:

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Theory (3/4)

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$C_V = \left(\frac{f}{2}\right) R$ (6)

Differentiating the equation of state for ideal gases

$pV = nRT$ (7)

gives the following for constant pressure:

$p \frac{\mathrm{d}V}{\mathrm{d}T} = n \cdot R$ (8)

From relation (4) we obtain

$C_p = \left(\frac{f+2}{2}\right) R$ (9)

With relations (6) and (9) follows that the difference between C_V and C_P for ideal gases is equal to the universal gas constant R.

$C_p - C_V = R$ (10)

The number of degrees of freedom of a molecule is a function of its structure. All particles have three degrees of translational freedom. Diatomic molecules have an additional two degrees of rotational freedom around the principal axes of inertia.

Theory (4/4)

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Triatomic molecules have three degrees of rotational freedom. Air consist primarily of oxygen (approximately 20 %) and nitrogen (circa 80 %), As a first approximation, the following can be assumed to be true for air:

f = 5

$C_V = 2.5\ R$

$C_V = 20.8\ \mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}$

and

$C_p = 3.5\ R$

$C_p = 29.1\ \mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}$

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Equipment

Position	Material	Item No.	Quantity
1	Precision manometer	03091-00	1
2	PHYWE Universal Counter	13601-99	1
3	Digital multimeter, 600V AC/DC, 10A AC/DC, 20 MΩ, 200 µF, 20 kHz, −20°C… 760°C	07122-00	2
4	Mariotte flask, 10 l	02629-00	1
5	Stopcock,1-way,straight, glass	36705-00	1
6	Stopcock,3-way,t-sh.,capil.,glass	36732-00	1
7	Rubber stopper 26/32, 3 holes, 1 x 7 mm + 2 x 1,5 mm	39258-14	1
8	Rub.stop.d=59.5/50.5mm, 1 hole	39268-01	1
9	Rubber tubing, i.d. 6 mm	39282-00	2
10	Silicone tubing, inner diameter 3 mm	39292-00	1
11	Nickel electrode,d 3mm,w.socket	45231-00	2
12	Chrome-nickel wire, d.0,1mm,100m	06109-00	1
13	Scissors,straight,blunt,l 140mm	64625-00	1
14	Two-way switch, single pole	06005-00	1
15	Connecting cord, 32 A, 500 mm, red	07361-01	4
16	Connecting cord, 32 A, 250 mm, red	07360-01	1
17	Connecting cord, 32 A, 500 mm, blue	07361-04	1
18	Connecting cord, 32 A, 250 mm, blue	07360-04	1
19	Connecting cord, 32 A, 100 mm, blue	07359-04	2
20	Syringe 10ml, Luer, 100 pcs	02590-10	1
21	Tubing adaptor, ID 3-5/6-10 mm	47517-01	1
22	Weather monitor, 6 lines LCD	87997-10	1
23	Tripod base PHYWE	02002-55	1

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Setup and Procedure

Setup (1/3)

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- Perform the experimental set-up according to Figs. 1 and 2 respectively.
- Insert the two nickel electrodes into two holes of the three hole rubber stopper and fix the terminal screws to the lower ends of the electrodes.
- Screw two pieces of chrome nickel wire, which are each about 15 cm long, into the clamps between these two electrodes so that they are electrically connected in parallel. The wires must not touch each other.
- Insert the one-way stopcock into the third hole of the stopper and insert the thus prepared stopper in the lower opening of the bottle. Give special attention to the wires which have to protrude into the middle of the bottle.

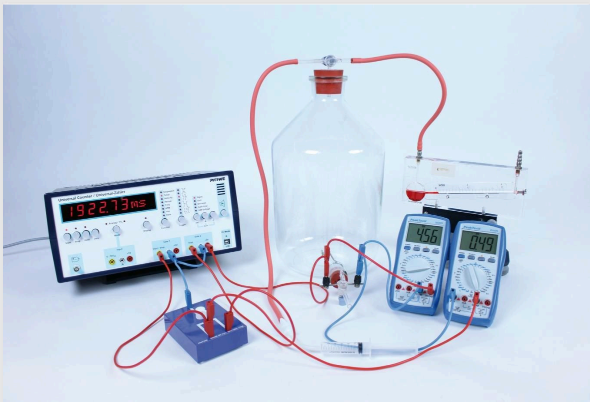

Fig. 2: Experimental set-up for the determination of C_P

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Setup (2/3)

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- Insert the second stopper, which has been equipped with the three-way stopcock, into the upper opening of the bottle (Fig. 1) and connect the precision manometer to the bottle with a piece of tubing.
- The manometer must be positioned exactly horizontally.
- It is equipped with a spirit level to facilitate the correct adjustment. Use the adjusting screws of the tripod base to align the manometer completely horizontally.
- The manometer must be filled with the oil which is supplied with the device.

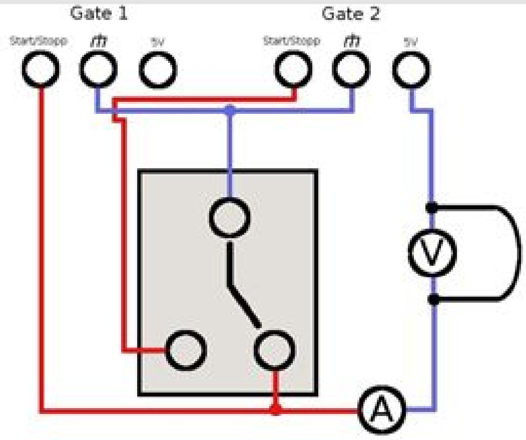

Fig. 3: Schematic circuit for measuring the heating time.

Setup (3/3)

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- The scale is now calibrated in hPa.
- You can choose the scale of either 2 hPa or 4 hPa by altering the inclination angle of the manometer. For these measurements 2 hPa are sufficient so just leave it horizontal.
- One of the 5 V outputs of the universal counter serves as the power source. The electrical circuit is illus-trated in Fig. 3 and Fig. 4.
- To determine C_P connect the syringe to the bottle via the three-way stopcock (compare Fig. 2).

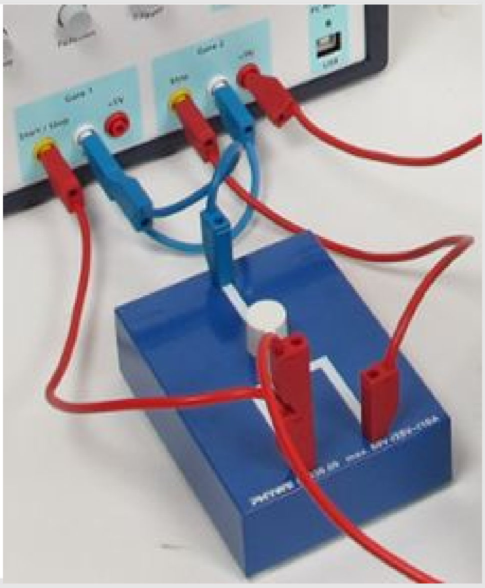

Fig. 4: Connecting two-way switch and counter.

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Procedure (1/5)

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- For each task perform at least ten measurements.
- The rise tube of the manometer must be well wetted before each measurement.
- As the counter has to measure the heating time choose the following settings:
  Function: Timer
  Trigger: 
- Determine the current which flows through the heating wire and the voltage separately at the end of the measuring series.
  To achieve this, connect one of the digital multimeters in series as an ammeter and the other in parallel as a voltmeter (compare Fig. 3). Determine the air pressure, which is required for the calculations, with the aid of the weather station.

Procedure (2/5)

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Task 1:

- Start and stop the measuring procedure by operating the two-way switch.
- The measuring procedure should be as short as possible (less than two seconds).
- The three-way cock must be positioned in such a manner, that it connects the bottle with the precision manometer.
- Upon heating the pressure in the bottle will start to rise.
- Read the maximum pressure increase immediately after cessation of the heating process.
- After each measurement wait a sufficient time until the gas in the volume cooled down again to room temperature thereby regaining ambient pressure.

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Procedure (3/5)

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- The electrical current which flows during the measurements must not be too strong, i.e. it must be sufficiently weak to limit the pressure increase due to the heating of the gas to a maximum of 1 hPa.
- For this reason it may be necessary to use only one heating wire or to reduce the electrical current at the power supply.

Task 2:

- Start and stop the measuring procedure by operating the two-way switch.
- The measuring procedure should be as short as possible (less than two seconds).
- While measuring, the three-way cock must be positioned in such a manner that it connects the syringe and the manometer with the bottle.

Procedure (4/5)

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- Upon heating the pressure in the bottle will start to rise.
- As you want to determine the heat capacity at constant pressure you have to compensate the pressure rise by increasing the volume via the syringe.
- You can hold the syringe in your hand and use your thumb to gently push the plunger.
- When the heating stopped, the volume of the gas in the bottle will still increase for a moment.
- Be careful to notice the turning point when the volume starts decreasing again because the gas starts cooling down. In this moment the pressure should have its initial value and start falling while you have already stopped increasing the volume.
- You can read the volume increase directly from the syringe’s scale. You may need some practice until you are able to keep the pressure fairly constant during the whole measurement and recognize the turning point correctly.

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Procedure (5/5)

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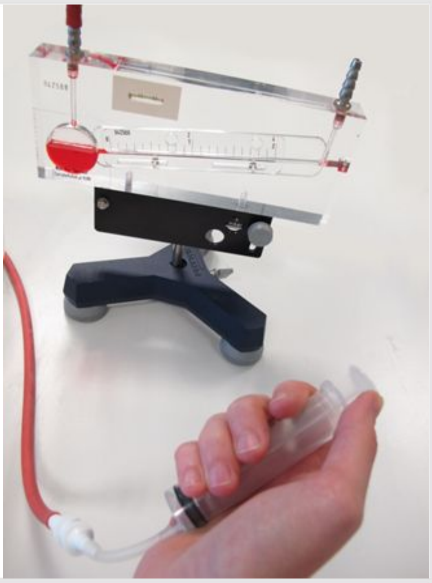
- After each measurement reset the initial volume and wait until the gas cooled down again to room temperature.
- Before starting a new measurement both the volume in the syringe and the pressure should have regained their initial values.

Fig. 5: For the second task operate the syringe with one hand while operating the switch with the other hand.



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Evaluation

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Task 1 (1/5)

Under isochoric conditions, the temperature increase dT produces a pressure increase dp. The pressure measurement results in a minute alteration of the volume which must be taken into consideration in the calculation:

$$\mathrm{d}T = \frac{p}{nR}\mathrm{d}V + \frac{V}{nR}\mathrm{d}p = \frac{T}{pV}(p\mathrm{d}V + V\mathrm{d}p) \quad (11)$$

It follows from equations (3) and (1) that:

$$C_V = \frac{1}{n} \cdot \frac{\mathrm{d}Q - p\mathrm{d}V}{\mathrm{d}t} \quad (12)$$

The energy dQ is supplied to the gas by the electrical heater:

$$\mathrm{d}Q = U \cdot I \cdot \mathrm{d}t \quad (13)$$

Task 1 (2/5)

There U is the voltage which is applied to the heater wires, I s the current which flows through the heater wires and dt is the period of time of the measurement.

With equations (11) and (13) one obtains:

$$C = \frac{p \cdot V}{n \cdot T} \cdot \frac{U \cdot I \cdot \mathrm{d}t - p \cdot \mathrm{d}V}{p \cdot \mathrm{d}V + V \cdot \mathrm{d}p} \quad (14)$$

where dV is the volume change due to the rising oil in the manometer.

The indicator tube in the manometer has a radius of r = 2 mm and a length of l = 140 mm. The pressure change per length is accordingly $1/70\,\mathrm{hPa} \cdot \mathrm{mm}^{-1}$ and the corresponding change in volume is therefore:

$$\mathrm{d}V = a \cdot \mathrm{d}p \quad (15)$$

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Task 1 (3/5)

where $a = \pi r^2 \cdot 70\,\frac{\text{mm}}{\text{hPa}} = 880\,\frac{\text{mm}^3}{\text{hPa}} = 8.8 \cdot 10^{-4}\,\frac{\text{l}}{\text{hPa}}$ (16)

thus $C_V = \frac{\text{p}V\cdot(\text{d}Q - a\cdot p\cdot \text{dp})}{n\cdot T\cdot(a\cdot p + V)\cdot \text{dp}}$ (17)

The molar volume of a gas at standard pressure $p_0 = 1013\,\text{hPa}$ and $T_0 = 273.2\,\text{K}$ is $V_0 = 22.414\,\text{l/mol}^{-1}$.

The molar volume is:

$V_{\text{mol}} = \frac{p_0 \cdot V_0 \cdot T}{T_0 \cdot p}$ (18)

In accordance with the following, the number of moles in volume V is: $n = \frac{V}{V_{\text{mol}}}$ (19)

Task 1 (4/5)

Taking equations (18) and (19) into consideration, it follows that:

$C_V = \frac{p_0 \cdot V_0}{T_0} \cdot \left(\frac{U\cdot I\cdot \text{dt}}{(ap+V)\cdot \text{dp}} - \frac{ap}{ap+V} \right)$ (20)

The slope of the linear regression in Fig. 6 is equal to:

$\frac{\text{dp}}{\text{dt}} = 0.518\,\frac{\text{hPa}}{\text{s}}$

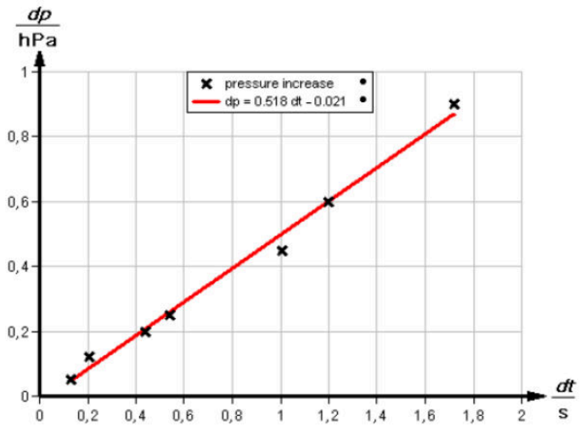

Fig. 6: Pressure change dp as a function of the heat-up time dt with U = 4.59 V, I = 0.43 A.

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Task 1 (5/5)

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C_V can be calculated using equation (20) if equation (16) is taken into consideration.

With p = 1011 hPa, V = 101, U = 4.59 V and I = 0.43 A the following value for C_V is obtained:

$C_V = 21.67\,\mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1} \pm 5\,\%$ (21)

Task 2 (1/3)

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At constant pressure the temperature increase dT induces a volume increase dV. From the equation of state for ideal gases follows that:

$\mathrm{d}V = \frac{nR}{p}\mathrm{d}t = \frac{V}{T}\mathrm{d}T$ (22)

Taking equation (2) into consideration, the following results from equations (13) and (22):

$C_p = \frac{1}{n} \cdot \frac{U \cdot I \cdot \mathrm{d}t \cdot V}{\mathrm{d}V \cdot T}$ (23)

C_P can be calculated using equation (23) under consideration of (18) and (19):

$C_p = \frac{p_0 \cdot V_0}{T_0} \cdot \left(\frac{UI}{p}\right) \cdot \left(\frac{\mathrm{d}t}{\mathrm{d}V}\right)$ (24)

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Task 2 (2/3)

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The slope of the linear regression in Fig. 7 is equal to

$\frac{\mathrm{d}V}{\mathrm{d}T} = 4.53\,\frac{\mathrm{ml}}{\mathrm{s}}$

with U = 4.49 V and I = 0.38 A.

From which follows $C_p = 30.98\,\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1} \pm 7\,\%$ (25)

As a consequence of heat losses to the surroundings the experimental values for C_V and C_P are somewhat larger than the theoretical values. The difference between the molar heat capacities provides the value for R. The experimental results give

$R = C_p - C_V = 9.31\,\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1} \pm 9\,\%$

Which is congruent to the value given in the literature of $R = 8.3\,\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$.

Task 2 (3/3)

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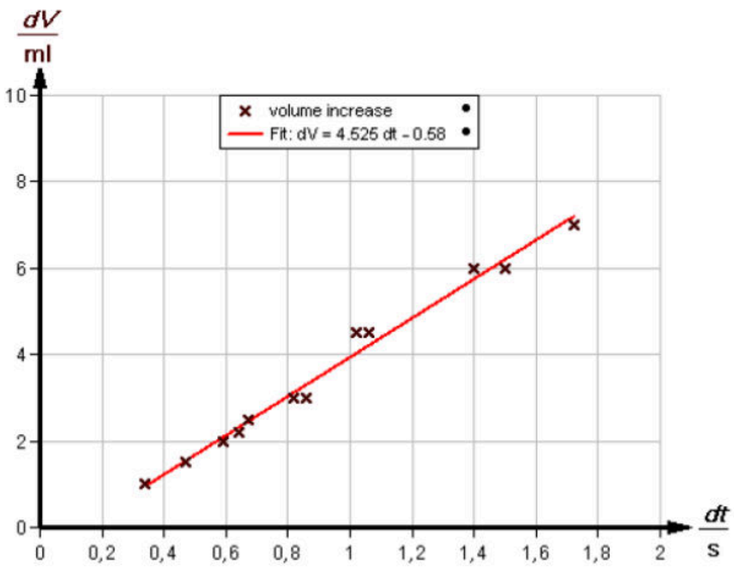

Fig. 7: Volume change dV as a function of the heating time dt with U = 4.49 V and I = 0.38 A.

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Conclusion

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Literature values:

$C_{p(\text{Oxygen})} = 29.4\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$C_{V(\text{Oxygen})} = 21.1\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$C_{p(\text{Nitrogen})} = 29.1\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$C_{V(\text{Nitrogen})} = 20.8\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$R = 8.314\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Experimental results:

$C_{p(\text{air})} = 31\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$C_{V(\text{air})} = 22\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Note

Using this apparatus, other gases (e.g. carbon dioxide or argon) can also be measured. These gases are then introduced through the stopcock on the bottom ot the vessel.

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