Heat capacity of gases with Cobra4 (Item No.: P2320261)

Curricular Relevance

Area of Expertise: Chemistry | **Education Level:** University | **Topic:** Physical Chemistry | **Subtopic:** Thermochemistry, Calorimetry | **Experiment:** Heat capacity of gases with Cobra4

Difficulty
Intermediate

Preparation Time
10 Minutes

Execution Time
10 Minutes

Recommended Group Size
2 Students

Additional Requirements:

- PC, Windows® XP or higher

Experiment Variations:

Keywords:

Equation of state for ideal gases, 1st law of thermodynamics, Universal gas constant, Degree of freedom, Mole volumes, Isobars, Isotherms, Isochors, Adiabatic changes of state

Overview

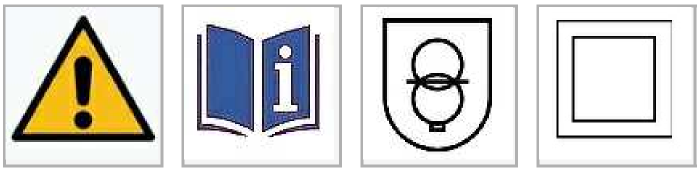
Short description

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.

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

Safety instructions



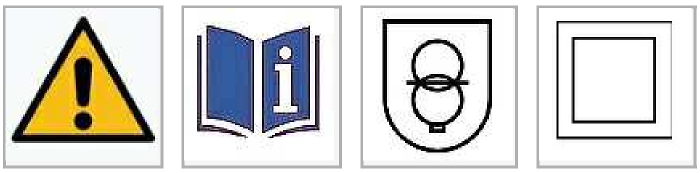
Equipment

Position No.	Material	Order No.	Quantity
1	Cobra4 USB-Link	12610-00	1
2	Cobra4 Sensor-Unit Energy: Current, voltage, work, power	12656-00	1
3	Software Cobra4 - multi-user licence	14550-61	1
4	Precision manometer	03091-00	1
5	PHYWE Power supply DC: 0...12 V, 2 A / AC: 6 V, 12 V, 5 A	13505-93	1
6	Mariotte flask, 10 l	02629-00	1
7	Weather monitor, 6 lines LCD	87997-10	1
8	Tripod base PHYWE	02002-55	1
9	On/off switch	06034-01	1
10	Stopcock,3-way,t-sh.,capil.,glass	36732-00	1
11	Nickel electrode,d 3mm,w.socket	45231-00	2
12	Chrome-nickel wire, d.0,1mm,100m	06109-00	1
13	Stopcock,1-way,straight, glass	36705-00	1
14	Scissors,straight,blunt,l 140mm	64625-00	1
15	Rub.stop.d=59.5/50.5mm, 1 hole	39268-01	1
16	Connecting cord, 32 A, 500 mm, red	07361-01	2
17	Connecting cord, 32 A, 250 mm, blue	07360-04	1
18	Connecting cord, 32 A, 500 mm, blue	07361-04	2
19	Syringe 10ml, Luer, 10 pcs	02590-03	1
20	Rubber stopper 26/32, 3 holes 7 mm + 2 x 1,5 mm	39258-14	1
21	Silicone tubing, inner diameter 3 mm	39292-00	1
22	Rubber tubing, i.d. 6 mm	39282-00	2
23	Tubing adaptor, ID 3-5/6-10 mm	47517-01	1
Additional material			
	PC, Windows® XP or higher		

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 .

Setup and procedure



- Perform the experimental set-up according to Figs. 1 and 3 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.
- 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.
- 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.
- Combine the Cobra4 Sensor Unit Energy with the Cobra4 USB Link.
- Connect the power supply and the nickel electrodes with the Cobra4 Sensor Unit Energy as shown in Fig. 2.

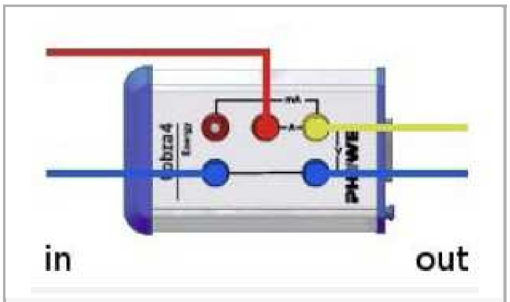


Fig. 2: Connection between the Cobra4 Sensor Unit Energyand the power supply (“in”) and the heating coil (“out”).

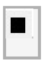
- Start the PC and connect the Cobra4 USB Link with the computer via a USB cable.
- Call up the “Measure” programme and boot the experiment “Heat capacity with Cobra4” (experiment > open experiment). The measurement parameters for this experiment are loaded now.
- Now the sensor is automatically recognized and an ID number (01) is allocated to the sensor, which is indicated in the display of the Cobra4 USB Link.
- To determine C_p connect the syringe to the bottle via the tree-way stopcock (compare Fig. 3).

Fig. 3: Experimental set-up for the determination of Cp.

- For each task perform at least ten measurements.
- The rise tube of the manometer must be well wetted before each measurement.
- Determine the air pressure, which is required for the calculations, with the aid of the weather station.
- Start the measurement with

Task 1:

- Start and stop the measuring procedure by operating the on/off 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.
- 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.
- Stop the measurement by pressing



- Send all data to „measure“ and save the measurement (File > Save meausrement as...).

Task 2:

- Start and stop the measuring procedure by operating the on/off 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.
- 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.
- 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.

Theory and evaluation

Theory

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_i 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 .

$$dQ = dU_i + pdV \quad (1)$$

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:

$$C = \frac{1}{n} \cdot \left(\frac{dQ}{dT}\right) \quad (2)$$

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:

$$C_V = \frac{1}{n} \cdot \left(\frac{dU_i}{dT}\right) \quad (3)$$

Under isobaric conditions (p = const., dp = 0):

$$C_p = \frac{1}{n} \cdot \left(\frac{dU_i}{dT} + p\frac{dV}{dT}\right) \quad (4)$$

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 :

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

Taking equation (3) into consideration it follows that:

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

Differentiating the equation of state for ideal gases

$pV = nRT$ (7)

gives the following for constant pressure:

$p \frac{dV}{dT} = n \cdot R$ (8)

From relation (4) we obtain

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

With relations (6) and (9) follows that the difference between C_p and C_V 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. 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:

$f = 5$

$C_V = 2.5R$

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

and

$C_p = 3.5R$

Evaluation

In the following the evaluation of the obtained values is described with the help of example values. Your results may vary from those presented here.

Task 1: Determine the molar heat capacities of air at constant volume C_V *.*

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:

$$dT = \frac{p}{nR} dV + \frac{V}{nR} dp = \frac{T}{pV}(pdV + Vdp) \quad (11)$$

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

$$C_V = \frac{1}{n} \cdot \frac{dQ - pdv}{dt} \quad (12)$$

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

$$dQ = U \cdot I \cdot dt \quad (13)$$

There U is the voltage which is applied to the heater wires, I is the current which flows through the heater wires and dt is the period of time of the measurement. Therefore dQ is the integral of the power-overtime-spectrum you recorded with the calculated channel. In order to obtain the integral load the spectrum into “Measure” and use the option show integral in the menu *measurement analysis*.

With equations (11) and (12) one obtains:

$$C = \frac{p \cdot V}{n \cdot T} \cdot \frac{dq - p \cdot dV}{p \cdot dV + V \cdot dp} \quad (14)$$

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 $1/70\ hPa \cdot mm^{-1}$ and the corresponding change in volume is therefore:

$$dV = a \cdot dp \quad (15)$$

where

$a = \pi r^2 \cdot 70 \cdot (\frac{mm}{hPa}) = 881 \cdot 10^{-4} \frac{1}{hPa}$ (16)

thus

$C_V = \frac{pV \cdot (dQ - a \cdot p \cdot dp)}{n \cdot T \cdot (a \cdot p + V) \cdot dp}$ (17)

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

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

In accordance with the following, the number of moles in volume V is:

$n = \frac{V}{V_{mol}}$ (19)

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

$C_V = \frac{p_0 \cdot V_0}{T_0} \cdot (\frac{dQ}{(ap+V) \cdot dp} - \frac{ap}{ap+V})$ (20)

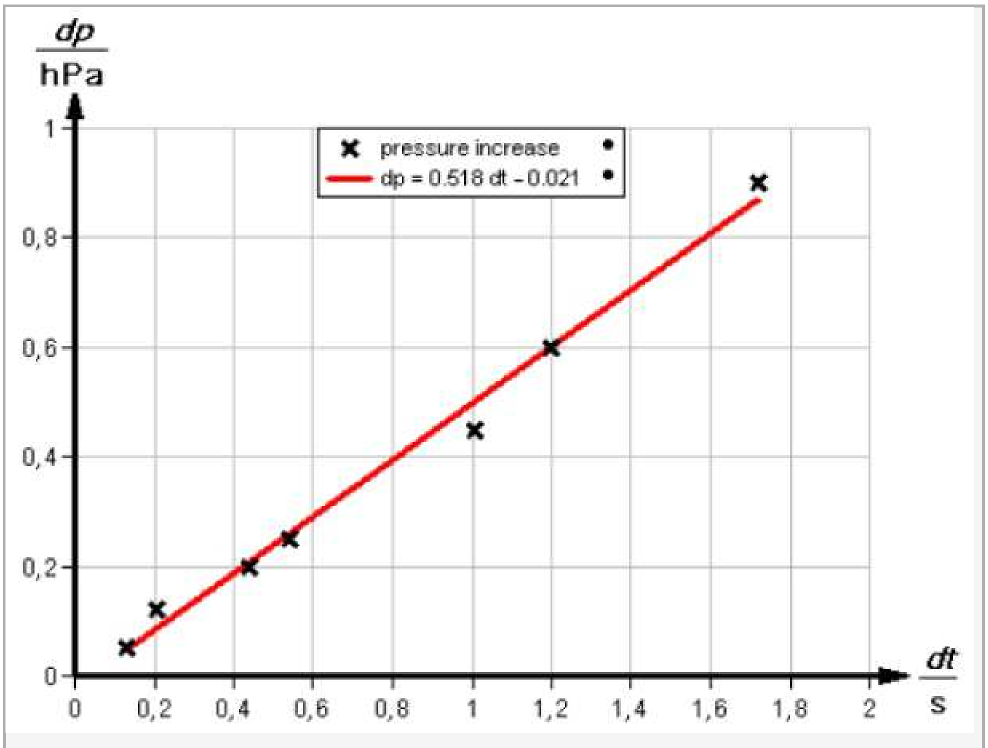


Fig. 4: Pressure change dp as a function of the heat supply dQ.

The slope of the linear regression in Fig. 4 is equal to:

$$\frac{dp}{dQ} = 0.253 \frac{hPa}{VAs}$$

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

With

$$P = 1011 hPa$$
$$V = 10l$$

The following value for C_V is obtained:

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

Task 2: Determine the molar heat capacities of air at constant pressure C_p *.*

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

$$dV = \frac{nR}{p} dt = \frac{V}{T} dT \quad (22)$$

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

$$C_p = \frac{1}{n} \cdot \frac{dQ \cdot V}{dV \cdot T} \quad (23)$$

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

$$C_p = \frac{p_0 \cdot V_0}{T_0} \cdot \left(\frac{1}{p}\right) \cdot \left(\frac{dQ}{dV}\right) \quad (24)$$

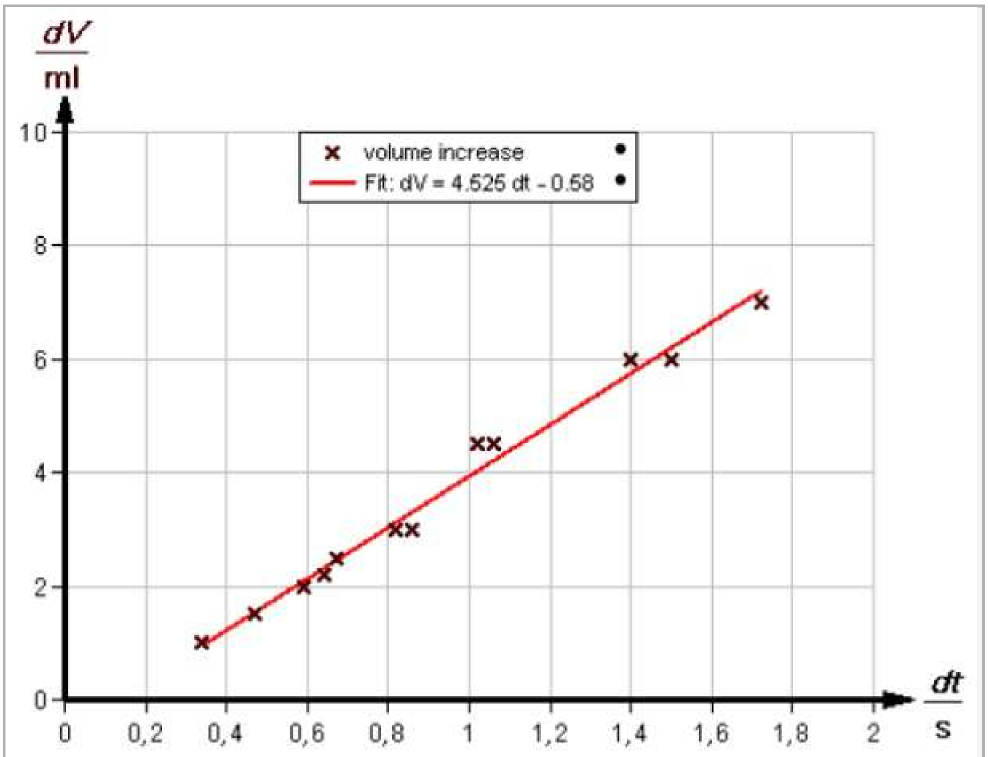


Fig. 5: Volume change dV as a function of the heat supply dQ.

The slope of the linear regression in Fig. 5 is equal to

$$\frac{dV}{dT} = 2.65 \cdot \frac{ml}{VAs}$$

From which follows

$$C_p = 30.98 J \cdot K^{-1} \cdot mol^{-1} \pm 7\% \quad (25)$$

As a consequence of heat losses to the surroundings the experimental values for C_p and C_V are somewhat larger than the theoretical values.

The difference between the molar heat capacities provides the value for R . The experimental results give

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

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

Literature values:

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

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

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

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

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

Experimental results:

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

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

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.