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Related concepts

Thermal tension coefficient, General equation of state for ideal gases, Universal gas constant, Pressure, temperature, volume, coefficient of thermal expansion, coefficient of thermal tension, ideal gas law, universal gas constant, Gay-Lussac's law, Charles' (Amontons') law, coefficient of cubic compressibility, Boyle and Mariotte's law.

Principle

The state of a gas is determined by temperature, pressure, volume and amount of substance. For the limiting case of ideal gases, these state variables are linked via the general equation of state. For a change of state under isochoric conditions this equation becomes Amontons' law.

In the case of isothermal process control this equation converts to Boyle and Mariotte's law.

In the case of isobaric conditions the ideal gas law converts to Gay-Lussac's law.

Tasks

For a constant amount of gas (air) investigate the correlation of

- Volume and pressure at constant temperature (Boyle and Mariotte's law)
- Volume and temperature at constant pressure (Gay-Lussac's law)
- 3. Pressure and temperature at constant volume (Charles' (Amonton's law))

From the relationships obtained calculate the universal gas constant as well as the coefficient of thermal expansion, the coefficient of thermal tension, and the coefficient of cubic compressibilty.

Equipment

Equipment		
Cobra3 Basic-Unit	12150.00	1
Power supply 12 V/2 A	12151.99	1
Data cable, RS232	14602.00	2
Measuring module, pressure	12103.00	1
Temperature measuring module, NiCr-Ni	12104.00	1
Thermocouple, NiCr-Ni, sheated	13615.01	1
Software Cobra 3 Gas laws	14516.61	1
Module converter	12150.04	1
Cobra3 sensor, -10120°C	12120.00	1
Glass jacket	02615.00	1
Glass syringe, 100 ml	02614.00	1
Heating apparatus	32246.93	1
Power regulator	32247.93	1
H-base -PASS-	02009.55	1
Support rod, $l = 250 \text{ mm}$	02031.00	2
Right angle clamp	37697.00	3
Universal clamp	37715.00	_
Universal clamp with joint	37716.00	1
Magnet, $l = 200 \text{ mm}, d = 10 \text{ mm}$	06311.00	1
Magnetic stirrer bar, $l = 30 \text{ mm}$	46299.02	1
Glass beaker, 250 ml, tall	36004.00	1
Funnel, $d_0 = 55 \text{ mm}$	34457.00	1
Rubber caps	02615.03	1
Silicone tubing, $d_i = 7 \text{ mm}$	39296.00	1
Tubing adaptor 3-5 / 6-10 mm	47517.01	1
Silicone tubing, $d_i = 2 \text{ mm}$	39298.00	1
Hose clips, $d = 812 \text{ mm}$	40996.01	2
Motor oil		
Water, distilled	31246.81	1
PC, Windows® 95 or higher		

Fig. 1. Experimental set-up for Gay-Lussac's law





I. Gay-Lussac's law Set-up and procedure

Set up the experiment as shown in Fig. 1.

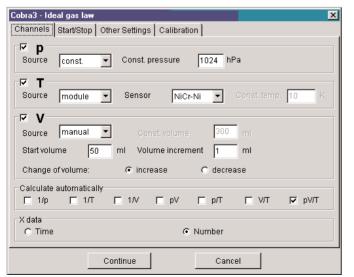
Install the gas syringe in the glass jacket as described in the operating instructions supplied with the glass jacket. Pay particular attention to the air-tightness and ease of movement of the gas syringe. Fill the glass jacket with water via the funnel and insert a magnetic stirrer bar. Punch a hole in a rubber cap with a straight pin. After adjusting the initial volume of the gas syringe to exactly 50 ml, close its nozzle with the rubber cap. Insert the thermocouple into the internal chamber through the hole in the rubber cap. Make sure that it does not touch the wall of the syringe, but is located in the centre of the gas volume. Connect a silicone tube to the hose nipple of the jacket's upper tubular sleeve so that the bath fluid which expands on heating can flow through the tube into a beaker.

Connect the temperature probe to T1 of the measuring module. Call up the "Measure" programme in Windows and enter <Ideal gas law> as gauge. Set the measuring parameters as shown in Fig. 2. Under <Start / Stop> choose <Get value on key press>. Under <Other Settings> select Digital Display 1 for <Temperature T1> and Diagram 1 with Channel <Temperature T>, X bounds <from 1 to 15> and Mode <no auto range>. Now calibrate your sensor under <Calibration> by entering a temperature value measured with a thermometer and pressing <Calibrate>. After having made these settings, press <Continue> to reach the field for the recording of measured values. Arrange the displays as you want them.

Record the first value at the initial temperature by pressing <Save value>, then switch on the heating apparatus and adjust the power regulator so that the glass jacket is slowly heated. Mix the water in the glass jacket by moving the magnetic stirrer bar with the aid of a bar magnet and facilitate pressure equilibration in the gas syringe by turning the plunger. After each 1 ml increase in volume, take the next value. After the gas volume has reached 60 ml, switch off the heating apparatus and terminate measurement by pressing <Close>. Save the measurement with <File> <Save the measurement as...>.

To have the plot of Temperature versus Volume carried out, make the following alterations. Under the menu prompt <Measurement> <Channel manager>, choose Temperature for the x-axis and Volume for the y-axis. Fig. 3 shows the graph as it is then presented by the programme. If you choose pV/T as y-axis, you obtain a graph as shown in Fig. 4.

Fig. 2: Measurement parameters



Theory and evaluation

The state of a gas is a function of the state variables temperature T, pressure p, volume V and the amount of substance n, which mutually determine each other. Thus, the dependence of volume on the temperature, pressure and amount of substance variables is described by the total differential

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,n} dT + \left(\frac{\partial V}{\partial p}\right)_{T,n} dp + \left(\frac{\partial V}{\partial n}\right)_{T,p} dn \tag{1}$$

For a given amount of substance (n = const., dn = 0; enclosed quantity of gas in the gas syringe) and isobaric change of state (p = const., dp = 0) this relationship simplifies to

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,n} dT \tag{1.1}$$

The partial differential quotient $(\partial V/\partial T)_{p,n}$ corresponds geometrically to the slope of a tangent to the function V=f(T) and thus characterises the mutual dependence of volume and temperature. The degree of this dependence is determined by the initial volume. The thermal coefficient of expansion γ_0 is therefore defined as a measure of the temperature dependence of the volume by referring it to V or V_0 at $T_0=273.15$ K.

$$\gamma_0 = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_{p,n} \tag{2}$$

Fig. 3: Dependence of the volume V on the temperature T at constant pressure (p = 1020 hPa) and constant amount of substance (n = 2.23 mmol)

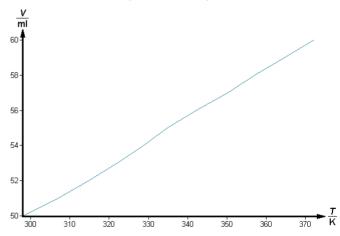
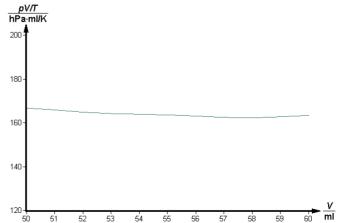


Fig. 4: The quantity pV/T depending on the volume





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For the limiting case of an ideal gas (sufficiently low pressure, sufficiently high temperature), the integration of a differential equation resulting from (1) and (2), where γ_0 = constant, yields

$$\frac{V_0}{T_0} = \frac{V}{T} \tag{3.1}$$

and

$$V = \text{const.} \cdot T$$
 (3.2)

According to this correlation, which was discovered by Gay-Lussac, the graphic presentation of the volume as a function of the temperature provides ascending straight lines (Fig. 3) where V = 0 for T = 0.

From (2) and the ideal gas law

$$pV = nRT (4)$$

R Universal gas constant

the following is true for the slope of these linear relationships

$$\left(\frac{\partial V}{\partial T}\right) = V_0 \, \gamma_0 = \frac{nR}{p} \tag{5}$$

From this, the thermal coefficient of expansion γ_0 and the universal gas constant R are experimentally accessible for a known initial volume V_0 and a known amount of substance n. The confined constant amount of substance n is equal to the quotient of the volume V and the molar volume $V_{\rm m}$

$$n = \frac{V}{V_{\rm m}} \tag{6}$$

which is V_0 = 22.414 l·mol⁻¹ at T_0 = 273.15 K and p_0 = 1013.25 hPa at standard conditions. A volume measured at pand T is therefore first reduced to these conditions using the relationship obtained from (4):

$$\frac{p_0 V_0}{T_0} = \frac{p_1 V_1}{T_1} = \frac{p V}{T} = \text{const.}$$
 (7)

Fig. 4 shows the quantity pV/T appearing to be constant.

Data and results

The investigation of the correlation between volume and temperature with a constant quantity of gas of n = 2.23 mmol, calculated according to the relations (6) and (7), confirms the validity of the Gay-Lussac's first law, with the linear relationship demonstrated in Fig. 3.

From the corresponding slope $(\partial V/\partial T)_{p,n}$ = 0.18 ml/K and for the initial volume V_0 = 50 ml, the following values are obtained for the universal gas constant R and the coefficient of thermal expansion γ_0 . R (exp.) = 8.07174 Nm \cdot K⁻¹ \cdot mol⁻¹ γ_0 (exp.) = 3.04 \cdot 10⁻³ K⁻¹

The theoretical values for an ideal gas are

= $8.31441 \text{ Nm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ R (lit.)

 $= 3.661 \cdot 10^{-3} \text{ K}^{-1}$ γ_0 (lit.)

II. Amonton's law Set-up and procedure

Set up the experiment as shown in Fig. 5.

Install the gas syringe in the glass jacket as described in the operating instructions supplied with the glass jacket. Pay particular attention to the air-tightness of the gas syringe. As an exception here, because no air is to be allowed to leak out even at higher pressures, lubricate the plunger with a few drops of multigrade motor oil, so that the glass plunger is covered with an uninterrupted clear film of oil throughout the entire experiment; but avoid excess oil. Fill the glass jacket with water via the funnel and place a magnetic stirrer bar in it. Attach a piece of silicone tubing to the hose nipple of the tubular sleeve through which the water that expands during heating can drain into a beaker. Insert the thermocouple and place it as close to the syringe as possible. After adjusting the initial volume of the gas syringe to exactly 50 ml, connect the nozzle of the gas syringe to a reducing adaptor via a short piece of silicone tubing, whereby the reducing adaptor should directly abut on the glass tubular sleeve after the tubing has been slipped over it. Secure the tubing on both the gas syringe's nozzle and on the reducing adaptor with hose clips. Connect the reducing adaptor to the measuring module by means of a short piece of silicone tubing $(d_i = 2 \text{ mm})$. Keep the tubing connections as short as possible.

Connect the measuring module to the Cobra3 Basic-Unit using a module converter and a data cable. Call up the "Measure" programme in Windows and enter <ldeal gas law> as gauge. Set the measuring parameters as shown in Fig. 6. Under <Start / Stop> choose <Get value on key press>. Under <Other Settings> select Digital Display 1 for <Pressure p>, Digital Display 2 for <Temperature> and Diagram 1 with Channel <Pre><Pre>ressure p>, X bounds <from 1 to 15> and Mode <no auto</pre> range>. Now calibrate your sensors under <Calibration> by entering temperature and pressure values measured with a thermometer respectively manometer and pressing <Calibrate>. After having made these settings, press < Continue > to reach the field for the recording of measured values. Arrange the displays as you want them.

Record the pressure corresponding to the initial temperature by pressing <Save value>. Subsequently, adjust the heating apparatus to slow heating with the power regulator. Mix the water in the glass jacket by moving the magnetic stirrer bar with the aid of a bar magnet. After each temperature increase of 5 K, push the plunger rapidly into the gas syringe until the gas volume is compressed to the initial volume of V = 50 ml and take the next value. After the temperature has reached approximately 370 K or if there is an evident loss of air during compression, switch off the heating apparatus and terminate measurement by pressing <Close>. Save the measurement with <File> <Save the measurement as...>.

To have the plot of Pressure versus Temperature carried out, make the following alterations. Under the menu prompt <Measurement> <Channel manager>, choose Temperature for the x-axis and Pressure for the y-axis. Fig. 7 shows the graph as it is then presented by the programme. If you choose pV/T as y-axis, you obtain the graph as it is shown in Fig. 8.

Theory and evaluation

The state of a gas is a function of the state variables temperature T, pressure p, volume V and the amount of substance n, which interactively determine each other. Thus, the dependence

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of pressure on the temperature, volume and amount of substance variables is described by the total differential

$$dp = \left(\frac{\partial p}{\partial T}\right)_{V,n} dT + \left(\frac{\partial p}{\partial V}\right)_{T,n} dV + \left(\frac{\partial p}{\partial n}\right)_{T,V} dn \tag{8}$$

For a given amount of substance (n = const., dn = 0; enclosed quantity of gas in the gas syringe) and isochoric change of state (V = const., dV = 0) this relationship simplifies to

$$dp = \left(\frac{\partial p}{\partial T}\right)_{V,p} dT \tag{8.1}$$

The partial differential quotient $(\partial p/\partial T)_{V,n}$ corresponds geometrically to the slope of a tangent to the function $p=\mathrm{f}(T)$ and thus characterises the dependence of the pressure on the temperature. The degree of this dependence is determined by the initial pressure. Therefore, one defines the thermal coefficient of tension β_0 as a measure of the temperature dependence by referring it to p or p_0 at $T_0=273.15$ K.

$$\beta_0 = \frac{1}{p_0} \left(\frac{\partial p}{\partial T} \right)_{V,n} \tag{9}$$

For the limiting case of an ideal gas (sufficiently low pressure, sufficiently high temperature), the integration of a differential equation resulting from (8) and (9), where $\beta_0 = \text{const.}$, yields

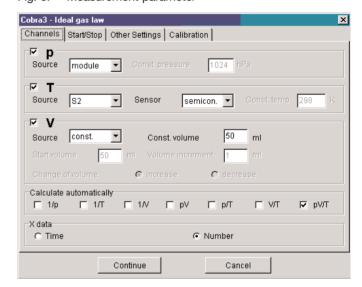
$$\frac{p_0}{T_0} = \frac{p}{T} \tag{10.1}$$

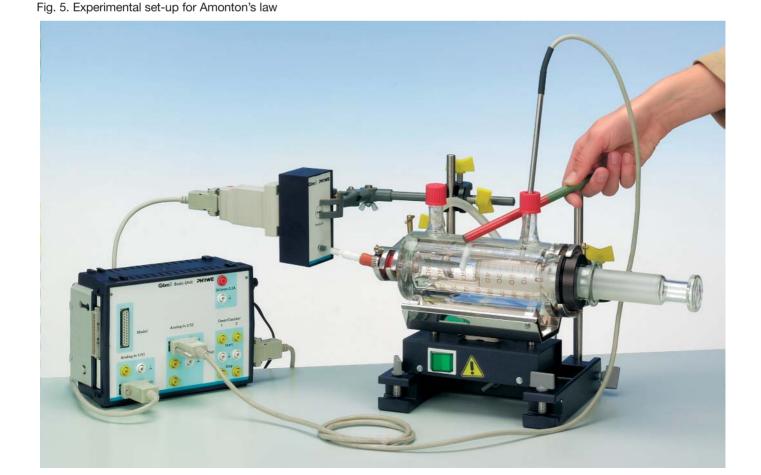
and

$$p = \text{const.} \cdot T$$
 (10.2)

According to this correlation, which was discovered by Charles and Amontons, the graphic presentation of the pressure as a function of the temperature results in an ascending straight line (Fig. 7) where p = 0 at T = 0.

Fig. 6: Measurement parameter







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From (9) and the ideal gas law

$$pV = nRT (11)$$

R Universal gas constant

the following is true for the slope of these linear relationships

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = p_0 \,\beta_0 = \frac{nR}{V} \tag{12}$$

From this, the thermal coefficient of tension β_0 and the universal gas constant R can be determined for a known initial pressure p_0 and a known quantity of substance n. The enclosed constant amount of substance n is equal to the quotient of the volume V and the molar volume V_m

$$n = \frac{V}{V_{\rm m}} \tag{13}$$

which is $V_0 = 22.414 \text{ I} \cdot \text{mol}^{-1}$ at $T_0 = 273.15 \text{ K}$ and $p_0 = 1013.25 \text{ hPa}$ at standard conditions. A volume V measured at p and T is therefore first reduced to these conditions using the relationship obtained from (11):

$$\frac{p_0 V_0}{T_0} = \frac{p_1 V_1}{T_1} = \frac{p V}{T} = \text{const.}$$
 (14)

Fig. 8 shows the quantity pV/T appearing to be constant.

Data and results

The investigation of the correlation between pressure and temperature with a constant quantity of gas of n=2.23 mmol, calculated according to the relations (6) and (7), confirms the validity of the Charles' (Amontons') law with the linear relationship demonstrated in Fig. 7. From the corresponding slope $(\partial p/\partial T)_{V,n}=3.72$ hPa/K and for the initial pressure $p_0=1002.2$ hPa, the following values are obtained for the universal gas constant R and the coefficient of thermal tension β_0 .

 $R \text{ (exp.)} = 8.34 \text{ Nm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

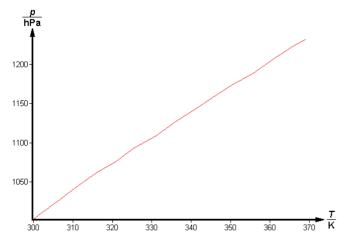
 $\beta_0 \text{ (exp.)} = 3.71 \cdot 10^{-3} \text{ K}^{-1}$

The theoretical values for an ideal gas are

R (lit.) = 8.31441 Nm · K⁻¹ · mol⁻¹ = J · K⁻¹ · mol⁻¹

 β_0 (lit.) = 3.661 · 10⁻³ K⁻¹

Fig. 7: Dependence of the pressure p on the temperature T at constant colume ($V=50\,$ ml) and constant amount of substance ($n=2.23\,$ mmol)



Boyle and Mariotte's law Set-up and procedure

Set up the experiment as shown in Fig. 9.

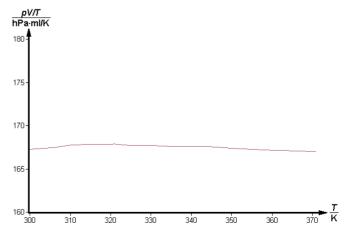
Install the gas syringe in the glass jacket as described in the operating instructions supplied with the glass jacket. Pay particular attention to the air-tightness of the gas syringe. As an exception here, because no air is to be allowed to leak out even at higher pressures, lubricate the plunger with a few drops of multigrade motor oil, so that the glass plunger is covered with an uninterrupted clear film of oil throughout the entire experiment; but avoid excess oil. Fill the glass jacket with water via the funnel. The water avoids fluctuations of the temperature connected with compression and expansion because of its high heat capacity. Insert the thermocouple and place it as close to the syringe as possible. After adjusting the initial volume of the gas syringe to exactly 50 ml, connect the nozzle of the gas syringe to a reducing adaptor via a short piece of silicone tubing, whereby the reducing adaptor should directly abut on the glass tubular sleeve after the tubing has been slipped over it. Secure the tubing on both the gas syringe's nozzle and on the reducing adaptor with hose clips. Connect the reducing adaptor to the measuring module with a short piece of silicone tubing $(d_i =$ 2 mm). Keep the tubing connections as short as possible.

Connect the measuring module to the Cobra3 Basic-Unit using a module converter and a data cable. Call up the "Measure" programme in Windows and enter <Ideal gas law> as gauge. Set the measuring parameters as shown in Fig. 10. Under <Start / Stop> choose <Get value on key press>. Under <Other Settings> select Digital Display 1 for <Pressure p>, Digital Display 2 for <Temperature> and Diagram 1 with Channel <Pressure p>, X bounds <from 1 to 20> and Mode <no auto range>. Now calibrate your sensors under <Calibration> by entering temperature and pressure values measured with a thermometer respectively manometer and pressing <Calibrate>. After having made these settings, press <Continue> to reach the field for the recording of measured values. Arrange the displays as you want them.

Subsequently expand the enclosed quantity of air in 1 ml steps to a volume of approximately 70 ml. Record the volume for each step by pressing <Save value>. Terminate measurement by pressing <Close>. Save the measurement with <File> <Save the measurement as...>.

To have the plot of Pressure versus Volume carried out, make the following alterations. Under the menu prompt <Measurement> <Channel manager>, choose Volume for the x-axis

Fig. 8: The quantity pV/T depending on the temperature



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and Pressure for the y-axis. Fig. 11 shows the graph as it is then presented by the programme. If you choose 1/V as x-axis, you get the graph as it is shown in Fig. 12. Under menu prompt Analysis you can let the programme show the slope.

Theory and evaluation

The state of a gas is a function of the state variables temperature T, pressure p, volume V and the amount of substance n, which reciprocally determine one another. Thus, the dependence of pressure on the temperature, volume and amount of substance variables is described by the total differential

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,n} dT + \left(\frac{\partial V}{\partial p}\right)_{T,n} dp + \left(\frac{\partial V}{\partial n}\right)_{T,p} dn (15.1)$$

Analogously, the following is true for the change of pressure with $T,\,V$ and n:

$$\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_{V,n} \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_{T,n} \mathrm{d}V + \left(\frac{\partial p}{\partial n}\right)_{T,V} \mathrm{d}n \, \text{(15.2)}$$

This relationship simplifies for a given amount of substance (n = const., dn = 0; enclosed quantity of gas in the gas syringe) and isothermal change of state (T = const., dT = 0) to

$$dV = \left(\frac{\partial V}{\partial T}\right)_{T,n} dp \tag{16.1}$$

and

$$dp = \left(\frac{\partial p}{\partial T}\right)_{V,n} dT \tag{16.2}$$

The partial differential quotient $(\partial V/\partial p)_{T,n}$ resp. $(\partial p/\partial V)_{T,n}$ corresponds geometrically to the slope of a tangent to the function $V=\mathsf{f}(p)$ or $p=\mathsf{f}(V)$ and therefore characterises the mutual dependence of pressure and volume. The degree of this dependence is determined by the initial volume or the initial pressure. One thus defines the cubic compressibility coefficient χ_0 by referring it to V or V_0 at $T_0=273.15$ K.

$$\chi_0 = \frac{1}{V_0} \left(\frac{\partial V}{\partial p} \right)_{T,n} \tag{17}$$

For the limiting case of an ideal gas (sufficiently low pressures, sufficiently high temperatures), the correspondence between the state variables p, V, T and n is described by the ideal gas law:

$$pV = nRT (18)$$

R Universal gas constant

For cases of constant quantity of substances and isothermal process control this equation changes into the following equations:

$$p V = \text{const.} \tag{18.1}$$







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and

$$p = \text{const.} \cdot \frac{1}{V} \tag{18.2}$$

According to this correlation, which was determined empirically by Boyle and Mariotte, a pressure increase is accompanied by a volume decrease and vice versa. The graphic representation of the functions V = f(p) or p = f(V) results in hyperbolas (Fig. 11). In contrast, plotting the pressure p against the reciprocal volume 1/V results in straight lines where p = 0 at 1/V = 0 (Fig. 12). From the slope of these linear relationships,

$$\left(\frac{\partial p}{\partial V^{-1}}\right)_{T\,n} = n\,R\,T\tag{19}$$

it is possible to determine the gas constant R experimentally when the enclosed constant quantity of air n is known. This is equal to the quotient of the volume V and the molar volume V_{m}

$$n = \frac{V}{V_{m}} \tag{20}$$

which is V_0 = 22.414 l·mol⁻¹ at T_0 = 273.15 K and p_0 = 1013.25 hPa at standard conditions. A volume measured at pand T is therefore first reduced to these conditions using the relationship obtained from (18):

$$\frac{p_0 V_0}{T_0} = \frac{p_1 V_1}{T_1} = \frac{p V}{T}$$
 (21)

Data and results

Figs. 11 and 12 confirm the validity of Boyle and Mariotte's law. From the slope obtained for n = 2.086 mmol and T = 295.15 K. $(\partial p/\partial V^{-1})_{T,n}=4.6464$ kPa/m⁻³ = 4.6464 Nm of the linearised correlation between p and 1/V (Fig. 4), the universal gas constant can be calculated to be $R = 7.547 \text{ Nm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

The deviation from the literature value

 $(R = 8.31441 \text{ Nm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 8.31441 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$ is due to the unavoidable lack of gas-tightness with increasing deviation from atmospheric pressure through compression or expansion, whereby the condition dn = 0 is violated and the observed slope $(\partial p/\partial V^{-1})_T$ is diminished in comparison with the value measurable with a constant quantity of substance.

Fig. 11: Correlation between the volume V and the pressure p at constant temperatures (T = 295.15 K) and constant quantity of substance (n = 2.086 mmol)

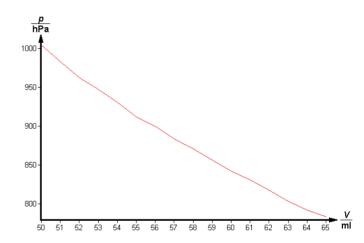


Fig. 10: Measurement parameters

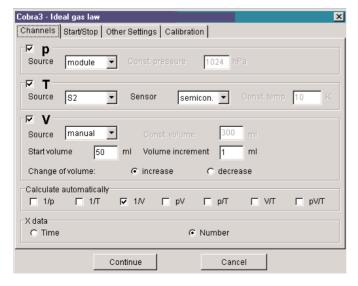
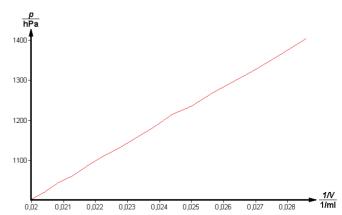


Fig. 12: Pressure p as a function of the reciprocal volume 1/V at constant temperature (T = 295.15 K) and constant quantity of substance (n = 2.086 mmol)



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