Equation of state of ideal gases

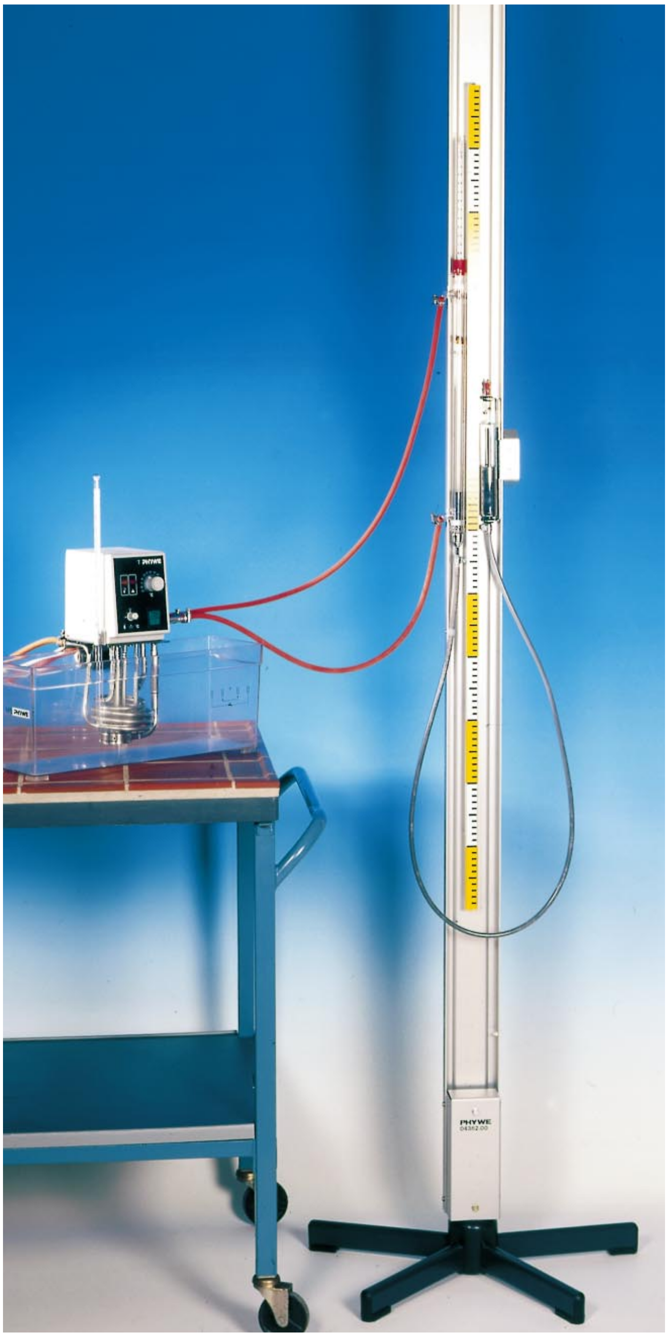
Related topics

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

Principle and task

The state of a gas is determined by its temperature, its pressure and the amount of substance. For the limiting case of an ideal gas these state variables are linked by the general equation of state, from which special correlations can be derived for specific changes of state.

Fig. 1: Experimental set-up: Equation of state of ideal gases.



Equipment

Gas laws apparatus		04362.00	1
Immersion thermostat A100		46994.93	1
Bath for thermostat, Makrolon		08487.02	1
Accessory set for A100		46994.02	1
Digital barometer		03099.00	1
Lab thermometer, -10…+100C		38056.00	1
Mercury tray		02085.00	1
Support base -PASS-		02005.55	1
Support rod, stainl. steel, 1000 mm		02034.00	1
Right angle clamp		37697.00	2
Universal clamp		37715.00	2
Pinchcock, width 15 mm		43631.15	1
Hose clip, diam. 8-12 mm		40996.01	6
Rubber tubing, i.d. 7 mm		39282.00	1
Mercury, filtered	1000 g	31776.70	1
Water, distilled	5 l	31246.81	1

Problems

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

1. Volume and pressure at constant temperature (Boyle and Mariotte's law)
2. Volume and temperature at constant pressure (Gay-Lussac's law)
3. Pressue and temperature at constant volume Charles' (Amontons') 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 compressibility.

Set-up and procedure

The experiment is set-up according to Fig. 1 and connected with the pump branch unit of the thermostat (Secure the tubing connections with hose clips!).
Fill the reservoir on the demonstration device carefully with mercury according to the operating instructions until the measuring tube is filled up to about one-quarter of the graduated measuring range with mercury (equal levels of mercury in the measuring tube and the levelling container).
Fill the bath of the circulating thermostat with distilled or demineralised water to avoid furring. Connect the cooling coil of the thermostat to the water supply line using rubber tubing (Secure the tubing connections with hose clips!).

Problem 1:
During the experiment, the temperature in the measuring tube must be kept constant. Consequently, water having the desired temperature is pumped through the jacket pipe with the aid of a circulating thermostat; wait until the temperature has become constant before beginning the measurements.
To investigate the correlation between the pressure *p* and the volume *V,* the pressure in the measuring tube is varied by raising or sinking the mercury reservoir. The length of the column of air in the measuring tube *l* and the height difference *h* between the mercury level in the reservoir and the level in the measuring tube is read off the scale of the device. If the external air pressure p_a (determine it with the digital barometer) is known, the two variables volume *V* and pressure p are determined to be:

$$V = V_l + V_R = \pi \left(\frac{d}{2}\right)^2 \cdot l + V_2 \qquad (1)$$

$$= \pi \left(\frac{11.4\ mm}{2}\right)^2 \cdot l + 1.01\ \text{ml}$$

$$p = p_a + \Delta p \qquad (2)$$

$$= p_a + \Delta h \cdot 0.1333\ \text{kPa} \cdot \text{mm}^{-1}$$

The volume of the measuring tube segment marked in brown (closure of tubing) can be assumed to be $V = 1.01$ ml as first approximation. This value must always be added to the volume calculated from the length of the column of air. Table 1 presents the results of a sample measurement by $T = 298.15$ K (see Table 1).

Problems 2 and 3:
For the further performance of the experiment it is advisable to determine the temperature dependence of pressure and volume in parallel. Consequently, in each case, set the desired temperature on the thermostat and wait for temperature constancy in the measuring tube.
At an initial temperature of $T_1 \approx 290$ K, the volume corresponding to the pressure $p = p_a$ is determined by lowering the mercury reservoir until the mercury in the measuring tube and the reservoir are at the same height. Mark this level with a marker on the measuring tube. Subsequently, raise the temperature in 5 K steps up to a temperature of $T \approx 360$ K.
To determine the volume V corresponding to the respective temperature T at constant pressure ($p = p_a$) (Problem 2), conduct the pressure equilibration in the measuring tube with atmospheric pressure (level equilibration of the mercury level in the measuring tube and in the reservoir) and then measures the length l of the column of air in the measuring tube. From this length the volume V is determined according to equation (1).

Determined Length l/mm	Height Difference Hg Δh/mm	V / ml	p / kPa
221	0	23.57	100.3
215	25	22.96	103.63
203	64	21.73	108.83
193	103	20.71	114.03
185	145	19.89	119.63
175	185	18.87	124.96
167	227	18.06	130.56
160	270	17.34	136.29
153	313	16.63	142.02
147	357	16.01	147.89
141	400	15.40	153.62
135	445	14.79	159.62
129	499	14.18	166.82
125	535	13.77	171.62

Table 1: Temperature and pressure of a constant amount of air (n = 0.9536 mmol) at a constant temperature ($T = T_1$); external pressure p_a = 100.3 kPa (atmospheric pressure)

Table 2: Results of an exemplary measurement.

Temperature T / K	Determined length l / mm	Difference in Hg Height Δh / mm	V / ml	p / kPa
293.15	218	0	23.26	100.6
298.15	221	10	23.57	101.93
303.15	225	24	23.98	103.80
308.15	229	37	24.38	105.53
313.15	233	50	24.79	107.27
318.15	237	64	25.20	109.13
323.15	240	74	25.51	110.46
328.15	245	89	26.01	112.46
333.15	248	99	26.32	113.80
338.15	252	113	26.73	115.66
343.15	256	127	27.14	117.53
348.15	260	141	27.55	119.40
353.15	264	152	27.96	120.86
358.15	267	163	28.26	122.33

The pressure p corresponding to the respective temperature at a constant volume V_1 (marking) is determined from the effective height difference h of the mercury column (Problem 3) according to equation (2). The height difference is read from the scale, after the level of mercury in the measuring tube has again been brought to the marked initial volume (V_1).

Theory and Evaluation

The state of a gas is given by the state variables temperature T, pressure p, volume V and the amount of substance n, which interactively determine one another. Thus, the dependence of the volume on the variables temperature and pressure at a constant amount of substance (n = const; dn = 0; enclosed amount of gas in the measuring tube) is given by the total differential (3.1).

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,n} dT + \left(\frac{\partial V}{\partial p}\right)_{T,n} dp \qquad (3.1)$$

Analogously, the following is valid for the change of pressure with T and V

$$dp = \left(\frac{\partial p}{\partial T}\right)_{V,n} dT + \left(\frac{\partial p}{\partial V}\right)_{T,n} dV \qquad (3.2)$$

The partial differential quotients $(\partial V/\partial T)_{p,n}$, $(\partial p/\partial T)_{V,n}$ and $(\partial V/\partial p)_{T,n}$ correspond geometrical to the slope of a tangent to the function $V = f(T)$, $p = f(T)$ or $V = f(p)$ and thus characterise the dependence of the selected state function (V,P) on the respective state variables (T,p). Their values are dependent on the initial volume V or the initial pressure p. Therefore, one defines the following intensive variables by referring them to V or p or V_0 or p_0 at T_0 = 273.15 K:

$$\gamma_0 = \frac{1}{V_0} \left(\frac{\partial p}{\partial T}\right)_{p,n} \qquad (4.1)$$

(coefficient of thermal expansion)

$$\beta_0 = \frac{1}{p_0}\left(\frac{\partial p}{\partial T}\right)_{V,n} \qquad (4.2)$$

(coefficient of thermal tension)

$$\chi_0 = -\frac{1}{V_0}\left(\frac{\partial V}{\partial p}\right)_{T,n} \qquad (4.3)$$

(coefficient of cubic compressibility).

For the limiting case of an ideal gas (pressure which is sufficiently small, temperature which is sufficiently high), these relationships can be derived from empirically determined laws, which each describe the correlation between two state variables.
For isobaric process control (p = const., dp = 0) eqn. (3.1) becomes

$$dV = V_0\, \gamma_0\, dT \qquad (5)$$

For γ_0 = const., the integration of this differential equation results in

$$V = V_0\left(1 + \gamma_0\,(T - T_0)\right) = V_0\left(1 + \gamma_0\,\vartheta\right) \qquad (5.1)$$

(ϑ = temperature on the Celsius scale)
or

$$\frac{V_0}{T_0} = \frac{V}{T} \qquad (5.2)$$

or

$$V = \text{const.} \cdot T \qquad (5.3)$$

In accordance with this correlation, which was discovered by Gay-Lussac, the graphic presentation of the volume as a function of the temperature supplies rising straight lines (Fig. 2) with V = 0 for T = 0.

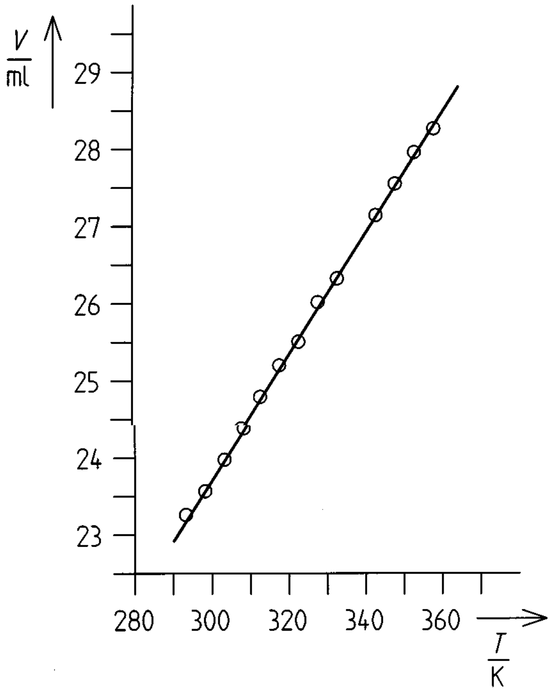


Fig. 2: Dependence ot the volume V on the temperature T at constant pressure (p = 100.6 kPa) and a constant substance quantity (n = 0.9536 mmol).

At isochoric conditions (V = const., dV = 0), the following results analogously from (3.2)

$$dp = p_0\, \beta_0\, dT \qquad (6)$$

and from integration with β_0 = const.

$$p = p_0\left(1 + \beta_0\,(T - T_0)\right) = p_0\left(1 + \beta_0\,\vartheta\right) \qquad (6.1)$$

or

$$\frac{p_0}{T_0} = \frac{p}{T} \qquad (6.2)$$

and

$$p = \text{const.} \cdot T \qquad (6.3)$$

These equations are the expression of Charles' (Amontons') law and describe the linear increase in the pressure with increasing temperature (Fig. 3).

For the isothermal expansion and compression (T = const., dT = 0) of a constant quantity of gas, the following is valid:

$$dV = -\,V_0\, \chi_0\, dp \qquad (7)$$

or

$$V_0\, p_0 = V p \qquad (7.1)$$

and

$$V = \text{const.} \cdot \frac{1}{p} \qquad (7.2)$$

The graphic presentation of this correlation, which was investigated by Boyle and Mariotte, results in hyperbolas for V = f(p) (Fig. 4); in contrast, for V = f(1/p) straight lines are obtained (Fig. 5).

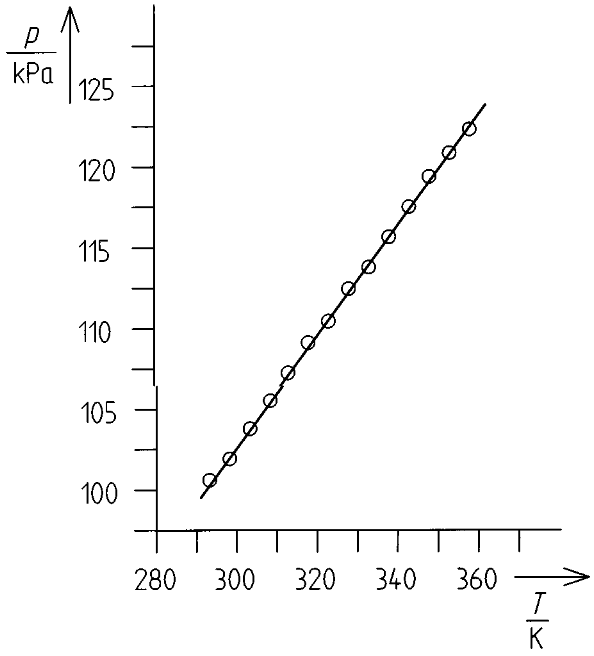


Fig. 3: Pressure p as a function of the temperature T at constant volume (V = 2.326 · 10^{-5} m^3) and a constant substance quantity (n = 0.9536 mmol).

Fig. 4: Correlation between pressure p and volume V for a constant quantity of air (n = 0.9536 mmol) during an isothermic change of state (T= 298.15 K).

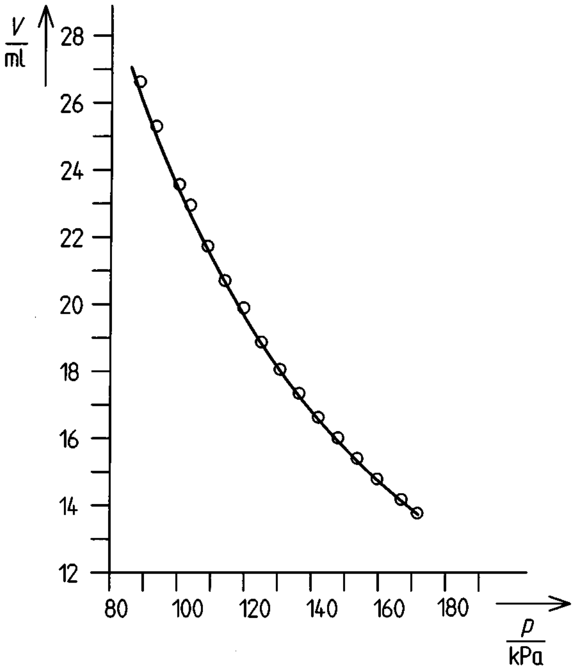
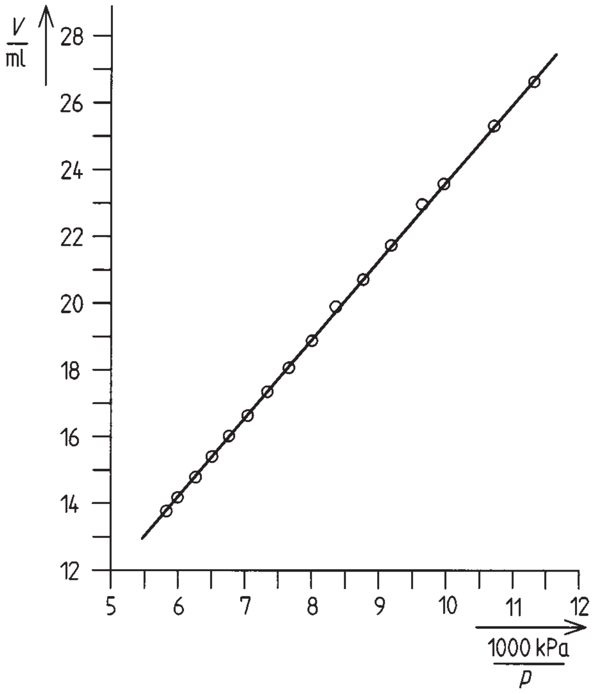


Fig. 5: Volume V as a function of the reciprocal pressure $1/p$ at constant temperature (T= 298.15 K) and a constant substance quantity (n = 0.9536 mmol).



By combining the equations (5.2) or (6.2) with (7.1) one directly obtains via

$$\frac{p_0 V_0}{T_0} = \frac{p_1 V_1}{T_1} = \frac{p V}{T} \tag{8}$$

the general or thermal equation of state for ideal gases (9) with the universal gas constant R.

$$p V = n R T \tag{9}$$

This equation allows retroactive comprehension of the correlations obtained for p = const. (5.3), V = const. (6.3), or p = const. (7.2).

Thus from the slopes of these linear relationships:

$$\left(\frac{\partial V}{\partial T}\right)_{p,n} = V_0 \gamma_0 = \frac{nR}{p} \tag{10.1}$$

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = p_0 \beta_0 = \frac{nR}{V} \tag{10.2}$$

$$\left(\frac{\partial V}{\partial p^{-1}}\right)_{T,n} = n R T \tag{10.3}$$

which can be obtained experimentally, the gas constant R can be calculated if the enclosed quantity of gas n is known. This is equal to the quotient (11) of the volume V and the molar volume V_m.

$$n = \frac{V}{V_m} \tag{11}$$

At T_0 = 273.15 K and p_0 = 101.325 kPa (standard conditions) this amounts to $V_0 = 0.022414\ \mathrm{m^3 \cdot mol^{-1}}$. A volume V measured at p and T must first be reduced to these conditions using Eq. (8).

Moreover, from the equations (10.1) and (10.2) the coefficients γ_0 and β_0 can be determined. The required values for the volume V_0 and the pressure p_0 can be obtained by extrapolation to T_0 = 273.15 K on the corresponding graphs or from the corresponding regression equations or calculated using the relationships (5.2) and (6.2).

Therefore, it is possible to calculate the compressibility coefficient χ_0 from the total differential (3.1) using

$$\chi_0 = \frac{1}{p_0} \cdot \frac{\gamma_0}{\beta_0} = \frac{1}{101.325\ \mathrm{kPA}} \cdot \frac{\gamma_0}{\beta_0} \tag{12}$$

the values for γ_0 and β_0 which are now known.

Data and results

Experiments with a constant quantity of gas (n = 0.9536 mmol) calculated according to the relations (8) and (11) confirm the validity of the investigated gas laws with their resulting linear correlations – which are in accordance with the equations (5.3), (6.3), and (7.2).

From the respective slopes

$(\partial V/\partial T)_{p,n} = 7.838 \cdot 10^{-8}\ \mathrm{m^3 \cdot K^{-1}}$ (Fig. 2),

$(\partial p/\partial T)_{V,n} = 0.340\ \mathrm{kPa \cdot K^{-1}}$ (Fig. 3) and

$(\partial V/\partial p^{-1})_{T,n} = 2.362\ \mathrm{Pa \cdot m^3} = 2.362\ \mathrm{Nm}$ (Fig. 5), the following values have been calculated for the universal gas constant R according to equations (10.1), (10.2), or (10.3):

$R = 8.269$ Nm $\cdot$ K^{-1} $\cdot$ mol^{-1},

$R = 8.289$ Nm $\cdot$ K^{-1} $\cdot$ mol^{-1}, and

$R = 8.308$ Nm $\cdot$ K^{-1} $\cdot$ mol^{-1}.

The value obtained from the literature is

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

In addition, from the determined slopes $(\partial p/\partial T)_{p,n}$ and $(\partial p/\partial T)_{V,n}$ and by using the values for V_0 and p_0 determined with reference to the regression equations for $T_0 = 273.15$ K, the coefficients γ_0 and β_0 can be calculated in a manner analogous to (10.1) and (10.2):

$\gamma_0 = 3.62110^{-3}$ K^{-1} and $\beta_0 = 3{,}62810^{-3}$ K^{-1}.

From them, the following value for the compressibility coefficient χ_0 is obtained from equation (12):

$\chi_0 =9.84910^{-3}$ kPa^{-1}.

The theoretical values for an ideal gas at T_0 and p_0 are

$\gamma_0 = \beta_0 = 3.66110^{-3}$ K^{-1} = 1/273.15 K^{-1} and
$\chi_0 = 9.872$ kPa^{-1} = 1/101.325 kPa^{-1}.