

Real Gases and Critical Point

QUANTITATIVE ANALYSIS OF A REAL GAS AND DETERMINING ITS CRITICAL POINT

- Observing sulphur hexafluoride in both the liquid and gaseous states.
- Plotting isotherms in a p - V diagram.
- Observing how the behaviour of real gases deviates from that for the ideal gas state.
- Determining the critical point.
- Plotting pressure curves for a saturated vapour.

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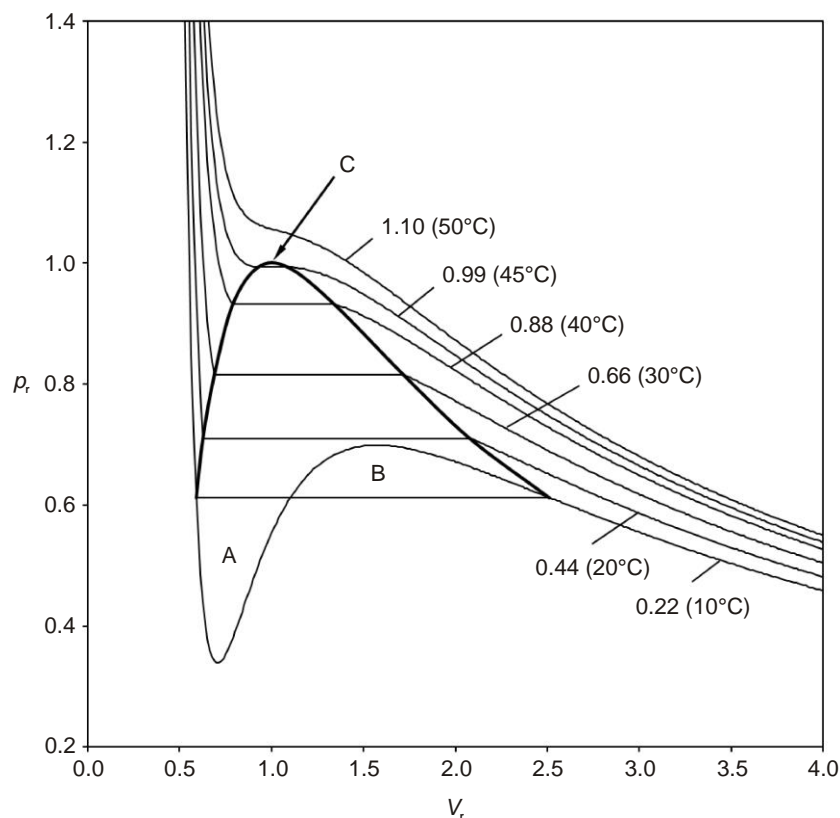


Fig. 1: Clapeyron phase diagram, isotherms calculated from simplified form of Van der Waals' equation (values in brackets are material-specific temperatures for sulphur hexafluoride).

BASIC PRINCIPLES

The critical point of a real gas is characterised by the critical temperature T_c , the critical pressure p_c , and the critical density ρ_c . Below the critical temperature, the substance is gaseous at large volumes and liquid at small volumes. At intermediate volumes it can exist as a liquid/gas mix-

ture, in which changing the volume under isothermal conditions causes a change of state: the gaseous fraction increases as the volume is increased, while the pressure of the mixture remains constant. As the liquid and the vapour have different densities, they are separated by the gravita-

tional field. As the temperature rises, the density of the liquid decreases and that of the gas increases until the two densities converge at the value of the critical density. Above the critical temperature, the gas can no longer be liquefied. However, under isothermal conditions the gas does not obey Boyle's Law until the temperature is raised considerably above the critical temperature.

The ideal gas equation applies for any ideal gas:

$$(1) \quad p \cdot V = n \cdot R \cdot T.$$

p : Pressure]

V : Volume

n : Moles

$R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$: Universal gas constant

T : Absolute temperature

The behaviour of real gases is given to a good approximation by the Van-der-Waals equation:

$$(2) \quad \left(p + \frac{n^2 \cdot a}{V^2} \right) \cdot (V - n \cdot b) = n \cdot R \cdot T.$$

a : Cohesion pressure (internal pressure)

b : Covolume.

Cohesion pressure specifically takes into account Van der Waals forces between gas molecules, while the covolume takes account of finite expansion of gas molecules.

For the isotherms in the p-V diagram, the following equation therefore suffices:

$$(3) \quad p(V) = \frac{R \cdot T}{(V/n) - b} - \frac{a}{(V/n)^2}.$$

Since there is a point of inflection at the critical temperature (Fig. 1), the following is true:

$$(4) \quad \left. \frac{dp}{dV} \right|_{\text{crit}} = 0 \quad \text{and} \quad \left. \frac{d^2p}{dV^2} \right|_{\text{crit}} = 0.$$

From this the cohesion pressure and covolume are found to be as follows:

$$(5) \quad a = \frac{3 \cdot V_{\text{crit}} \cdot p_{\text{crit}}}{n^2} \quad \text{and} \quad b = \frac{V_{\text{crit}}}{3 \cdot n}.$$

By substituting into equation (3) and introducing the simplified values.

$$(6) \quad p_r = \frac{p}{p_{\text{crit}}}, \quad V_r = \frac{V}{V_{\text{crit}}} \quad \text{and} \quad T_r = \frac{T}{T_{\text{crit}}}$$

This results in the simplified form of the Van der Waals-equation

$$(7) \quad \left(p_r + \frac{3}{V_r^2} \right) \cdot (3 \cdot V_r - 1) = 8 \cdot T_r,$$

This is independent of material. In the simplified representation, the following equation suffices for the isotherms:

$$(8) \quad p_r(V_r) = \frac{8 \cdot T_r}{3 \cdot V_r - 1} - \frac{3}{V_r^2}.$$

In the Clapeyron diagram graph (Fig. 1) they exhibit a maximum and minimum below the critical pressure. In fact, though, in the case of isothermal compression the pressure remains

constant after a specific value, even when the volume continues to be reduced. The isotherms thus follow an even, isobaric path (horizontal lines in Fig. 1). It is along these horizontal lines where the condensation of the gas takes place. The condition for the position of the lines is that the areas A and B are required to be equal. The envelope for the horizontal lines is called a binodal curve and indicates the region where gas and liquid phases coexist.

Sulphur hexafluoride is especially suitable for investigating the properties of real gases, as its critical temperature ($T_c = 319 \text{ K}$) and its critical pressure ($p_c = 37.6 \text{ bar}$) are both relatively low. It is also non-toxic and is quite safe for use in teaching and in practical classes.

The apparatus for investigating the critical point consists of a transparent measurement cell, which has very thick walls and can withstand high pressures. The internal volume of the cell can be changed by turning a hand-wheel, which allows one to make fine adjustments and can be read with a precision down to 1/1000 of the maximum volume. Pressure is applied by a hydraulic system using castor oil of pharmaceutical quality. The hydraulic system is separated from the cell by a conical rubber seal, which rolls up when the volume is changed. This form of construction ensures that the pressure difference between the measurement cell and the oil space is practically negligible. Therefore, instead of measuring the gas pressure directly, a manometer measures the oil pressure, which avoids having a dead volume in the gas space. The measurement cell is enclosed within a transparent water jacket. During the experiment a thermostatic water bath maintains a precisely controlled and adjustable constant temperature, which is measured by a digital thermometer.

During observations of the transition from the gaseous to the liquid phase and the reverse process, the fact that there is very little dead volume makes it possible to observe the formation of the first drop of liquid or the disappearance of the last bubble of gas.

LIST OF EQUIPMENT

1	Critical Point Apparatus	1002670 (U104001)
1	Immersion/Circulation Thermostat @230V	1008654 (U144002-230)
or		
1	Immersion/Circulation Thermostat @115V	1008653 (U144002-115)
1	Digital Quick Response Pocket Thermometer	1002803 (U11853)
1	K-Type NiCr-Ni Immersion Sensor -65–550°C	1002804 (U11854)
2	Silicone Tubing, 6 mm	1002622 (U10146)

Additionally required:

Sulphur hexafluoride (SF_6)

Anti-freeze protection (e.g. Glystantin® G 30 from BASF) to establish calibrated temperature medium

Compressor or bicycle pump and valve for volume calibration

SAFETY INSTRUCTIONS

Before set-up and operation of the critical point apparatus, it is essential for the safety instructions in section 2 of the instruction manual for the apparatus to be read through carefully and complied with.

GENERAL INSTRUCTIONS

On delivery, the critical point apparatus is filled with hydraulic fluid. The test gas is not included.

Before filling with the test gas, carry out a volume calibration using air as an approximation of an ideal gas. Volume calibration and filling with test gas are described under "Procedure" in these experiment instructions.

Instructions for storage after long periods out of use are to be found in section 9 of the manual for the critical point apparatus.

Owing to the inevitable diffusion of the test gas through the conical seal, it is necessary to degas the hydraulic fluid in the equipment, as described in chapter 10. This must be done before the equipment is put away for storage (after removing the test gas) or if it has been in use for a long time.

The threaded bush in the frame must be lubricated regularly and also inspected at lengthier intervals. Refer to section 11 for instructions.

Maintenance work as described in chapter 12 is only required if the rubber components get worn out and their functionality is adversely affected.

SET-UP

- Set up the apparatus at a height suitable for a good view of the measurement cell and align it in such a way that the safety valve is pointing away from any people or property which might sustain damage.
- Use silicone tubing to connect the outlet of the circulation thermostat to the inlet of the calibrated temperature jacket and the outlet of the jacket to the inlet of the circulation thermostat.
- Make the calibrating medium from 2 parts of water and 1 part of anti-freeze by volume.
- Fill the circulation thermostat.

EXPERIMENT PROCEDURE

Zero point calibration

The zero point for the volume scale must be determined by conducting a calibration.

For this, we take advantage of the fact that in a pressure range of 1-50 bar and in a temperature range of 270-340 K, air acts as a near-ideal gas (the real gas factor has a deviation of less than 1% from 1). Therefore, at a constant temperature (e.g. room temperature) for two piston displacements s_0 and s_1 and for the corresponding pressures p_0 and p_1 of the trapped air, we get:

$$(9) \quad p_0 \cdot s_0 = p_1 \cdot s_1$$

Substituting $s_0 = s_1 + \Delta s$ and rearranging gives:

$$(10) \quad s_1 = \frac{p_0}{p_1 - p_0} \cdot \Delta s$$

Rough calibration of scales:

- Open the regulating valve wide.
- Loosen the grub screw for the vernier scale by half a turn (it is now possible to turn the scale easily on the threaded axle without moving the handwheel, although a counter-pressure acts against this independent movement).
- Wind the handwheel out till you detect a noticeable resistance.
- Without turning the handwheel, turn the vernier scale on the threaded axle till the 0.0 mark is on the top and the fixed scale shows approx. 48 mm.
- Loosen the knurled screws of the fixed scale and shift the scale to the side till the 48-mm bar is exactly above the centre line of the vernier scale (see Fig. 2).
- Tighten the knurled screws again. In doing so, make sure that the fixed scale does not press against the vernier scale.

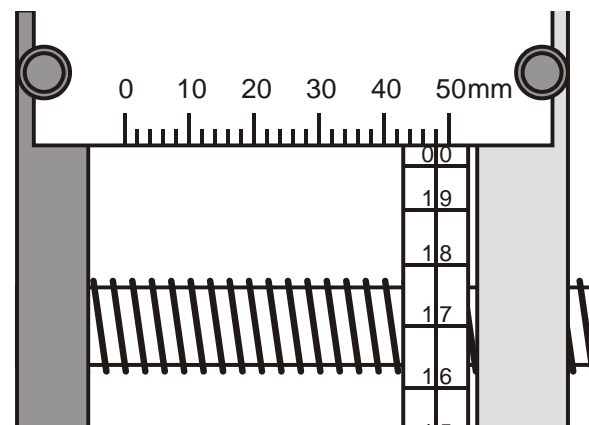


Fig. 2: Piston position reading at 48.0 mm

Zero correction:

- Shut the regulating valve (the pressure in the measuring cell now corresponds to the ambient pressure $p_0 = 1$ bar. To within the accuracy of the measurement, the manometer should display an excess pressure of 0 bar).

- Wind the handwheel in till an excess pressure of 15 bar has been reached (absolute pressure $p_1 = 16$ bar).
- Read the piston position s_1 and calculate the displacement $\Delta s = s_0 - s_1$.
- Calculate the zero corrected piston position $s_{1, \text{corr}}$ using equation 10.
- Adjust the vernier scale to the corrected value.
- If required, wind the handwheel out a little and secure the vernier scale with the grub screw.

Measurement example:

$p_0 = 1$ bar, $p_1 = 16$ bar, $p_1 - p_0 = 15$ bar
 $s_0 = 48.0$ mm, $s_1 = 3.5$ mm, $\Delta s = 44.5$ mm
 Therefore, $s_{1, \text{corr}} = 2.97$ mm.

The vernier scale must therefore be adjusted so that now only 2.97 mm are shown instead of 3.50 mm.

Note:

After calibrating the zero point, it is possible to obtain qualitatively accurate measured values. With regard to temperature T and pressure p , it is also possible to obtain quantitatively accurate measurements of the isotherms in range around to the critical point where the two phases exist simultaneously. However, especially in the liquid phase, the measured isotherms are rather too widely separated.

Volume calibration using air as an ideal gas

The exact relation between the volume V_G in the measuring cell and the scale reading s is dependent on the volume of oil in the oil chamber. The oil chamber also expands marginally in proportion to the pressure as a result of the spring in the manometer tube. Additionally, when the temperature is increased, the castor oil expands to a greater extent than the rest of the equipment. This means that the pressure rises at a slightly greater rate at higher temperatures. All of these phenomena can be calculated if appropriate calibration has been effected using air as an ideal gas.

The following applies according to the ideal gas equation (1):

$$(11) \frac{p \cdot V}{T} = n \cdot R.$$

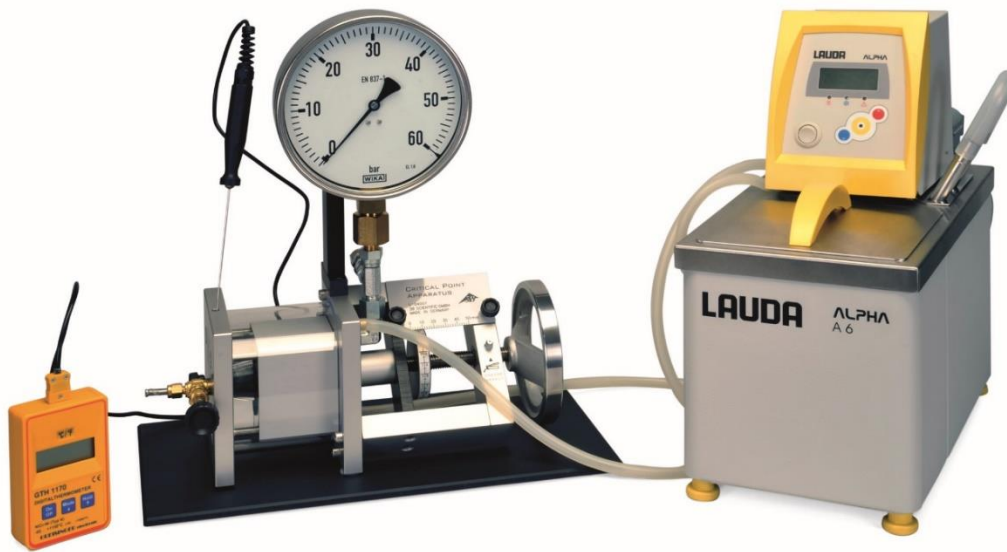


Fig. 3: Experiment set-up

After taking the overpressure reading p_e , the absolute pressure can be calculated from:

$$(12) p = p_e + 1 \text{ bar}$$

The absolute temperature is given by:

$$(13) T = \vartheta + \vartheta_0 \text{ where } \vartheta_0 = 273.15^\circ\text{C}$$

The volume is given by:

$$(14) V = A \cdot s$$

where $A = 3.14 \text{ cm}^2$ and at the effective piston position

$$(15) s = s_e + s_0 + \beta_p \cdot p - \beta_\vartheta \cdot \vartheta$$

s_e : Piston position reading

p : Absolute pressure

ϑ : Temperature in $^\circ\text{C}$

$s_0, \beta_p, \beta_\vartheta$: Free parameters

Substituting equations (13), (14) and (15) into equation (11) results in the following:

$$(16) \frac{p \cdot (s_e + s_0 + \beta_p \cdot p - \beta_\vartheta \cdot \vartheta) \cdot A}{\vartheta + \vartheta_0} - n \cdot R = 0.$$

If we take several readings N at various temperatures and pressures, we can calculate the term:

$$(17) Q = \sum_{i=1}^N \left(\frac{p_i \cdot (s_{ei} + s_0 + \beta_p \cdot p_i - \beta_\vartheta \cdot \vartheta_i) \cdot A}{\vartheta_i + \vartheta_0} - n \cdot R \right)^2$$

The free parameters s_0 , β_P , β_θ and n should be appropriately selected so that the value of Q is reduced to a minimum.

- Connect the plastic tube (3-mm internal diameter) to the 1/8" gas connection fittings.
- Open the regulating valve.
- Wind the handwheel outwards, making the piston move till it reaches say the 46.0 mm position.
- Use a compressor or a bicycle pump to create an excess air pressure of approx. 3-8 bar in the measuring cell.
- Shut the regulating valve.
- To record measurements, vary the volume in the measuring cell or the temperature of the thermostat and wait till a stationary equilibrium has been attained. Then take a pressure reading.
- Use appropriate adjustment software to set the s_0 , β_P , β_θ and n parameters so that the quadratic equation for the errors Q is reduced to a minimum (see equation 17).
- If you like, you can adjust the vernier scale around s_0 so that this correction is not necessary.

With the set parameters, it is possible to calculate the “effective” piston displacement s from the measured displacement s_e using Equation 15 and then to calculate the calibrated measuring cell volume using Equation 14.

Filling with test gas

Sulphur hexafluoride (SF_6) is a non-toxic gas and is absolutely safe for humans. The MAC value for danger of suffocation on account of oxygen deprivation is 1000 ppm. That is equivalent to 6 filled measuring cells per 1 m³ of air.

However, SF_6 is extremely harmful to the environment and can give rise to a greenhouse effect 24,000 times stronger than CO_2 . Therefore, do not allow large quantities to be released into the environment.

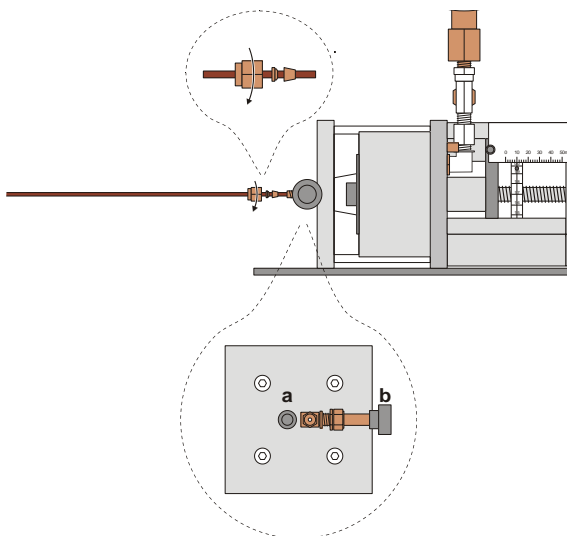


Fig. 4: Connecting a fixed pipe (a) flush valve, (b) regulating valve

According to the principles of “good laboratory practice”, it is recommended to utilise a gas supply (e.g. SH ILB gas cylinder and Y11 L215DLB180 regulating valve from Airgas (www.air-gas.com)) via fixed pipes (outer diameter of 1/8" and, if necessary, adapters, e.g. from Swagelok (www.swagelok.com)), especially if the equipment is regularly in operation.

Filling begins with several flush cycles in which the air is flushed out of the pipe. The number of cycles required to flush out the air depends on the length of the pipe (more precisely, on the ratio of the pipe length to the volume of the measuring cell). In the process, care should be taken that the quantity of the greenhouse gas SF_6 released in the environment is reduced to a minimum.

- If necessary, pull out the protection for the gas connection and loosen the valve nut (11 mm) to remove the 1/8" gas connection fittings.
- Connect the pipe (if necessary with adapters) to the gas fitting.
- Beginning with the valve nut, slide the supplied screw joints onto the tubing. (See Fig. 4: follow the sequence and alignment specified along with the cable binder)
- Insert the pipe into the regulating valve and tighten the valve nut till the point is reached where it is no longer possible to move the pipe any further using only your fingers.
- Hold the regulating valve still with an open-end spanner (13 mm) and tighten the valve nut by a further 270°.

Now, the connection is gas-tight. When loosening the valve nut afterwards, the regulating valve also needs to be held still with a spanner.

- Use the handwheel to set the piston position to 10 mm.
- Slowly open the regulating valve and let in the SF_6 till a pressure of approx. 10 bar has been attained.
- Shut the regulating valve.
- Open the flush valve slightly till the pressure has dropped to almost 0 bar.
- Shut the flush valve.
- After at least four flush cycles, open the regulating valve till the pressure attained is once again 10 bar.
- Shut the regulating valve.
- Turn the handwheel in the reverse direction till the piston reaches a position of say 46 mm.
- Slowly open the regulating valve and shut it again when a pressure of 10 bar has been attained.

If the equipment is used only occasionally, it is more practical to draw the test gas from a MINICAN® gas container (e.g. from the company Westfalen (www.westfalen-ag.de)). The gas connection of a MINICAN® container is similar in design to a commercial spray can, i.e. it opens when the MINICAN® container is pressed directly onto the gas connection fittings.

Here too, filling begins with several rinsing cycles for flushing out the air.

- If necessary, pull off the protection for the gas connection.
- Use the handwheel to set the piston position to 10 mm.
- After removing the protective cap, position the MINICAN® container with SF_6 onto the gas connection fittings (Fig. 5).
- Press the MINICAN® container onto the gas connection fittings, slowly open regulating valve (b) and let in SF_6 till a pressure of approx. 10 bar has been attained.
- Shut the regulating valve.
- Open the flush valve slightly till the pressure has dropped to almost 0 bar.
- Shut the flush valve.

- After at least four flush cycles, press the MINICAN® gas container against the gas connection fittings. Slowly open the regulating valve and let in SF₆ till a pressure of approx. 10 bar has been attained.
- Shut the regulating valve.
- Wind the handwheel in the opposite direction till the piston reaches a position of say 46 mm.
- Press the Minican® gas container against the gas connection fittings, slowly open the regulating valve and shut it again when a pressure of 10 bar has been attained.

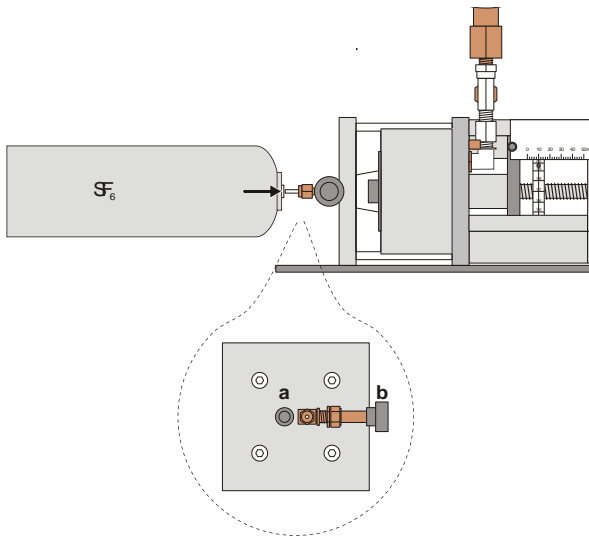


Fig. 5: Filling with test gas from a MINICAN® gas container (a) flush valve, (b) regulating valve

One gas filling can remain in the measuring cell for several days.

If no experiments are being conducted, wind the handwheel back till the piston is in a position where it is subjected to the lowest possible pressure – say, for instance, 46 mm.

If possible the apparatus should always be kept filled with the thermal medium.

Recording of isotherms

Due to the bubbles of vapour which develop throughout the liquid, the interphase boundary surface in the case of the phase transition from liquid to gas is much greater than that for the transition from gas to liquid where the interphase boundary area is limited to the surface of the liquid itself. In order for equilibrium to settle down as quickly as possible during each recording, the following procedure is recommended (Fig. 6):

When the pressure of SF₆ at maximum volume, i.e. when the handwheel is wound all the way out, is 8 – 10 bars, the piston position is set up till there is 10 mm between the lowest and highest pressure settings, the highest being when the wheel is wound all the way in.

For small volumes where s_e < 10 mm, the piston position is set for 10 mm between the highest pressure and the lowest pressure, i.e. when the handwheel is wound all the way out.

The setting for equilibrium takes about 1 - 5 min using this method, whereby recording the measurements at the edge of the region where both phases are present takes up the greatest amount of the time.

- With the volume at its maximum, set up temperatures θ = 10°C, 20°C, 30°C, 40°C, 45°C and 50°C on the circulation thermostat.
- For each of these temperatures, decrease the volume in the measurement cell step by step until the piston is at the 10 mm position. For each piston position wait until stable equilibrium is reached then read off the piston position s_e and the pressure p_e over atmospheric, making a note of both these.
- Next, starting with the lowest volume possible, start increasing the volume step by step until the piston position is 10 mm. For each piston position wait until stable equilibrium is reached then read off the piston position s_e and the pressure p_e over atmospheric, making a note of both these.

During the experiment keep observing the liquid and gas states, the dynamic state at the phase transition and the development of transition points at various temperatures.

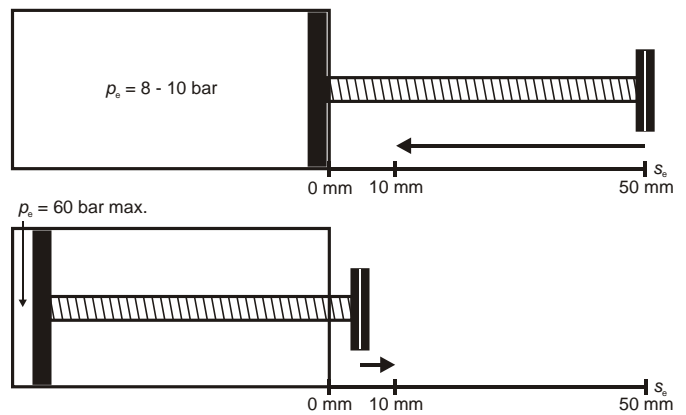


Fig. 6: Setting volume as a function of pressure

Determining the mass of gas

- If necessary, remove the gas supply pipe and attach gas connection fittings.
- Wind out the handwheel, say to 46 mm.
- Open the regulating valve a little and release the gas through the gas connection fittings into a gas-tight plastic bag.
- Shut the regulating valve.
- Determine the mass of the released gas. In doing this, take into consideration the empty weight of the bag and the buoyancy of air.
- Reduce the volume of the measuring cell till the pressure in the measuring cell has reached its original value.
- Calculate the original mass of gas from the volume difference before and after emptying the measuring cell and the volume which is still present in the measuring cell.

Alternatively the mass of gas can be determined by comparison with values quoted in literature (e.g. Clegg et al. in: Landolt-Börnstein – Coefficient values and functions, volume II, part 1, Springer-Verlag, Berlin, 1971).

SAMPLE MEASUREMENT AND EVALUATION

Volume calibration using air as an ideal gas

Minimising the value of Q in equation (17) gives the following values of the parameters with the measurements in Table 1:

$$(18) \begin{aligned} s_0 &= 0.19 \text{ mm} \\ \beta_p &= 0.023 \text{ mm/bar} \\ \beta_\vartheta &= 0.034 \text{ mm/}^\circ\text{C} \\ n &= 0.00288 \text{ mol} \end{aligned}$$

Note:

These parameters apply to the apparatus used for this example. Volume calibration needs to be carried out specifically for every apparatus and may also need to be checked.

Determining the mass of gas

Mass of gas m : 1.05 g

Tab. 1: Measurements for volume calibration

i	s_e / mm	ϑ	p / bar
1	40.0	20.0°C	6.6
2	20.0	20.0°C	12.4
3	10.0	20.0°C	23.3
4	5.0	20.0°C	41.8
5	3.5	20.0°C	53.9
6	5.0	20.0°C	41.8
7	5.0	10.0°C	38.9
8	5.0	30.0°C	45.3
9	5.0	40.0°C	49.0
10	5.0	50.0°C	53.5

Recording of isotherms

- For each of the configured temperatures, convert the readings for pressure over atmospheric p into absolute pressures p using equation (12) with atmospheric pressure $p_0 = 1 \text{ bar}$ and enter these into Table 2 using the unit MPa (1 MPa = 10 bars).
- Calculate the volumes V using equation (14) with the parameters (18) and use them to obtain the specific volumes $v = V/m$, entering them into Table 2 for each of the temperatures using the unit ml/g (1 cm³ = 1 ml).

Plot of isotherms as a p-V diagram (Clapeyron diagram)

- Plot the absolute pressures p against the specific volumes v for each temperature ϑ (Table 2, Fig. 7).
- Read off the parameters for the critical temperature from the p-v diagram in Fig. 7:

$$\vartheta_{\text{crit}} = 45^\circ\text{C}$$

$$p_{\text{crit}} = 3.74 \text{ MPa}$$

$$\rho_{\text{crit}} = 1 / v_{\text{crit}} = 0.74 \text{ g/ml}$$

The values agree very well with those quoted in literature for sulphur hexafluoride $\vartheta_{\text{crit}} = 45.5^\circ\text{C}$, $p_{\text{crit}} = 3.76 \text{ MPa}$ and $\rho_{\text{crit}} = 1/v_{\text{crit}} = 0.74 \text{ g/ml}$.

Below the critical temperature the isotherms in Fig. 7 differ markedly from the hyperbolic curve for ideal gases but approximate to the hyperbola above that temperature. Sulphur hexafluoride acts like a real gas, which even above the critical temperature does not completely reach the state of an ideal gas.

The deviation from the state for an ideal gas is also evident in the Amegat diagram, i.e. a plot of isotherms in a graph of pV against p .

Tab. 2: Recording of isotherms: Specific volumes calculated from effective piston position and determined mass of gas as well as the absolute pressure converted from readings of pressure over atmospheric

$\vartheta = 10^{\circ}\text{C}$		$\vartheta = 20^{\circ}\text{C}$		$\vartheta = 30^{\circ}\text{C}$		$\vartheta = 40^{\circ}\text{C}$		$\vartheta = 45^{\circ}\text{C}$		$\vartheta = 50^{\circ}\text{C}$	
v ml / g	p MPa	v ml / g	p MPa	v ml / g	p MPa	v ml / g	p MPa	v ml / g	p MPa	v ml / g	p MPa
0.651	5.24	0.678	5.37	0.724	5.28	0.792	5.14	0.841	5.23	0.913	5.28
0.652	4.75	0.680	4.91	0.729	4.40	0.811	4.48	0.853	4.93	0.947	4.90
0.657	3.88	0.683	4.00	0.741	3.60	0.839	3.92	0.883	4.44	1.017	4.53
0.659	2.96	0.690	3.15	0.757	2.92	0.874	3.54	0.922	4.09	1.069	4.38
0.666	2.07	0.716	2.13	0.801	2.68	0.923	3.37	0.969	3.89	1.203	4.24
0.668	1.65	0.775	2.12	0.860	2.67	0.983	3.35	1.022	3.77	1.350	4.16
0.696	1.64	0.925	2.13	1.009	2.66	1.101	3.35	1.078	3.74	1.498	4.09
0.995	1.63	1.221	2.11	1.158	2.65	1.396	3.33	1.139	3.72	1.642	4.06
1.293	1.62	1.816	2.10	1.754	2.63	1.696	3.31	1.196	3.71	1.789	4.01
1.889	1.61	2.411	2.09	2.349	2.63	1.993	3.30	1.254	3.71	1.937	3.97
2.485	1.60	3.007	2.09	2.348	2.63	2.290	3.32	1.315	3.70	2.079	3.93
3.079	1.60	3.603	2.09	2.944	2.63	2.290	3.30	1.373	3.71	2.229	3.87
3.674	1.61	4.199	2.09	3.541	2.62	2.587	3.27	1.434	3.70	2.371	3.80
4.271	1.61	4.795	2.09	3.838	2.60	2.880	3.20	1.492	3.70	2.517	3.73
4.867	1.60	5.092	2.06	4.130	2.52	3.463	2.98	1.553	3.70	2.662	3.66
5.461	1.59	5.388	2.03	4.716	2.36	4.045	2.77	1.611	3.70	2.804	3.60
5.463	1.60	5.976	1.91	5.889	2.06	4.627	2.57	1.670	3.68	3.095	3.44
6.057	1.60	7.155	1.70	7.066	1.82	5.797	2.23	1.671	3.69	3.386	3.30
6.059	1.61	8.336	1.52	8.247	1.62	6.972	1.95	1.730	3.67	3.386	3.30
6.654	1.59	9.519	1.38	9.429	1.46	6.974	1.95	1.789	3.67	4.544	2.80
7.248	1.56	10.703	1.26	10.613	1.33	8.152	1.73	1.849	3.67	5.710	2.41
7.250	1.58	11.890	1.15	11.797	1.21	9.332	1.55	1.909	3.66	6.884	2.09
8.431	1.42	-	-	-	-	10.515	1.41	1.966	3.66	8.063	1.85
8.432	1.42	-	-	-	-	11.697	1.28	2.114	3.64	9.239	1.65
9.615	1.30	-	-	-	-	-	-	2.262	3.60	10.420	1.49
10.803	1.18	-	-	-	-	-	-	2.555	3.50	11.604	1.35
11.985	1.09	-	-	-	-	-	-	2.844	3.38	11.609	1.35
11.988	1.09	-	-	-	-	-	-	3.425	3.14	-	-
-	-	-	-	-	-	-	-	4.008	2.90	-	-
-	-	-	-	-	-	-	-	4.588	2.68	-	-
-	-	-	-	-	-	-	-	5.756	2.31	-	-
-	-	-	-	-	-	-	-	6.930	2.02	-	-
-	-	-	-	-	-	-	-	8.107	1.79	-	-
-	-	-	-	-	-	-	-	9.287	1.60	-	-
-	-	-	-	-	-	-	-	10.467	1.45	-	-
-	-	-	-	-	-	-	-	11.651	1.32	-	-
-	-	-	-	-	-	-	-	11.660	1.32	-	-

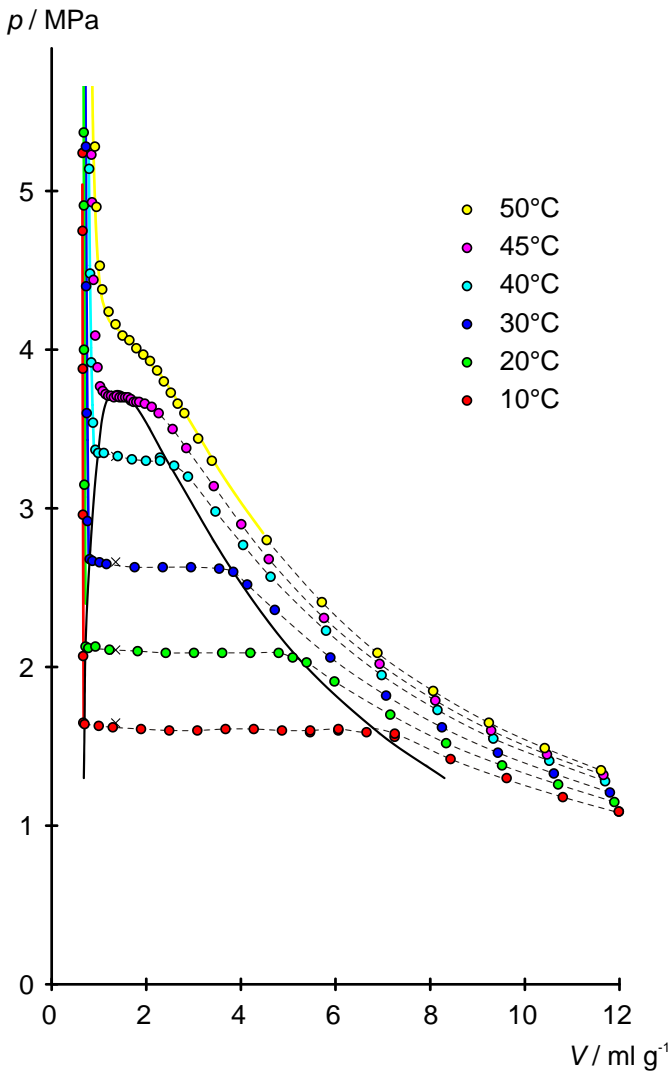


Fig. 7: p - V diagram of sulphur hexafluoride

Pressure curve for saturated vapour

- Calculate absolute temperatures T in Kelvin from the temperatures ϑ in degrees Celsius using equation (3). Read off the constant absolute pressures p inside the binodal curves drawn in Fig. 7 and plot them against absolute temperature T (Fig. 8).

The measurements can be very well described using the integrated form of the Clausius-Clapeyron equation (solid line in Fig. 8):

$$(19) \quad p = p_0 \cdot e^{\frac{\Delta H}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)} = p_0 \cdot e^{a \left(\frac{1}{T_0} - \frac{1}{T} \right)}$$

ΔH : Molar heat of vaporisation
 T_0 : Temperature at pressure p_0

The molar heat of vaporisation can be determined by plotting $\ln(p/p_0)$ against $1/T_0 - 1/T$ and fitting a straight line to the points (Fig. 9). Usually the fixed point (T_0, p_0) is quoted as the standard boiling point, i.e. the temperature at which the substance boils under standard pressure $p_0 = 1013.25$ hPa. Since for SF_6 standard pressure is lower than the pressure at the triple point, there is no standard boiling point but a standard sublimation point instead.

The standard sublimation temperature for SF_6 is $T_0 = 209.25$ K ($\vartheta_0 = -63.9^\circ\text{C}$). The molar heat of vaporisation at the standard sublimation point is derived from the gradient a :

$$(20) \quad \Delta H = a \cdot R = 2136 \text{ K} \cdot 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} = 18 \frac{\text{kJ}}{\text{mol}}$$

The value is about 20% different from the value quoted in literature $\Delta H = 22$ kJ/mol (Messer AG's data sheet: $153.20 \text{ kJ/kg} \cdot 146.05 \text{ g/mol} = 22.37 \text{ kJ/mol}$ bei -63.9°C). This is because the selected fixed point lies on the sublimation curve. Also, the molar heat of vaporisation is temperature-dependent and not constant as was assumed for the fitting of the curve.

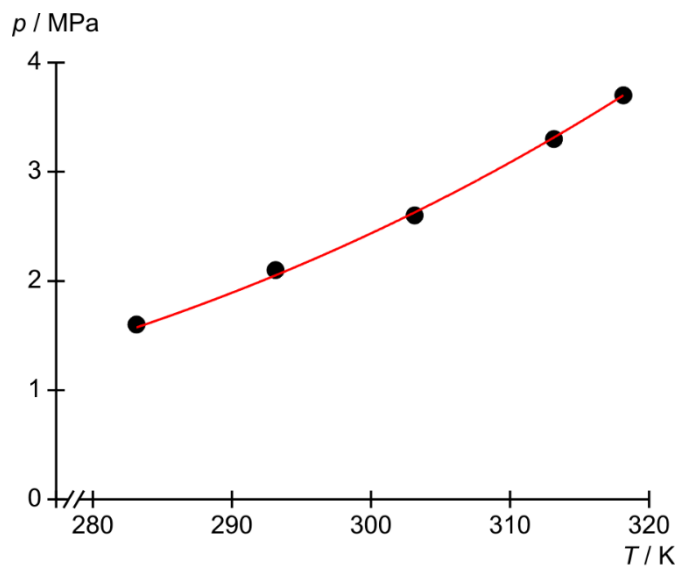


Fig. 8: Pressure curve for saturated vapour of sulphur hexafluoride

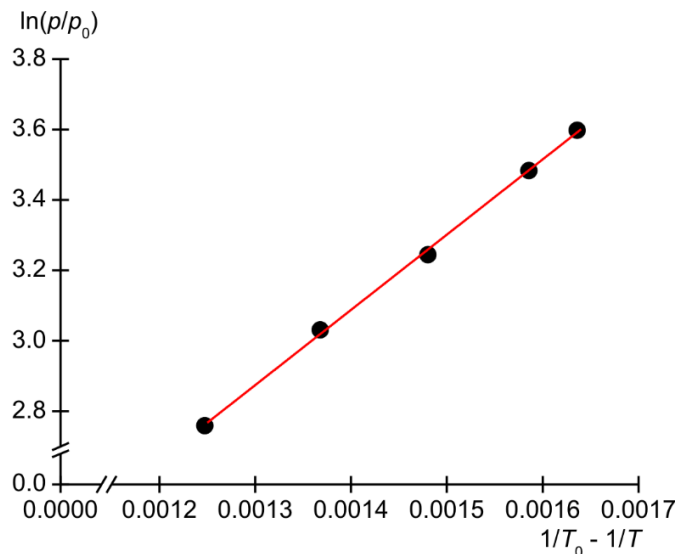


Fig. 9: Simple logarithmic plot of measurements to determine molar heat of vaporisation from a straight line fitted to the points