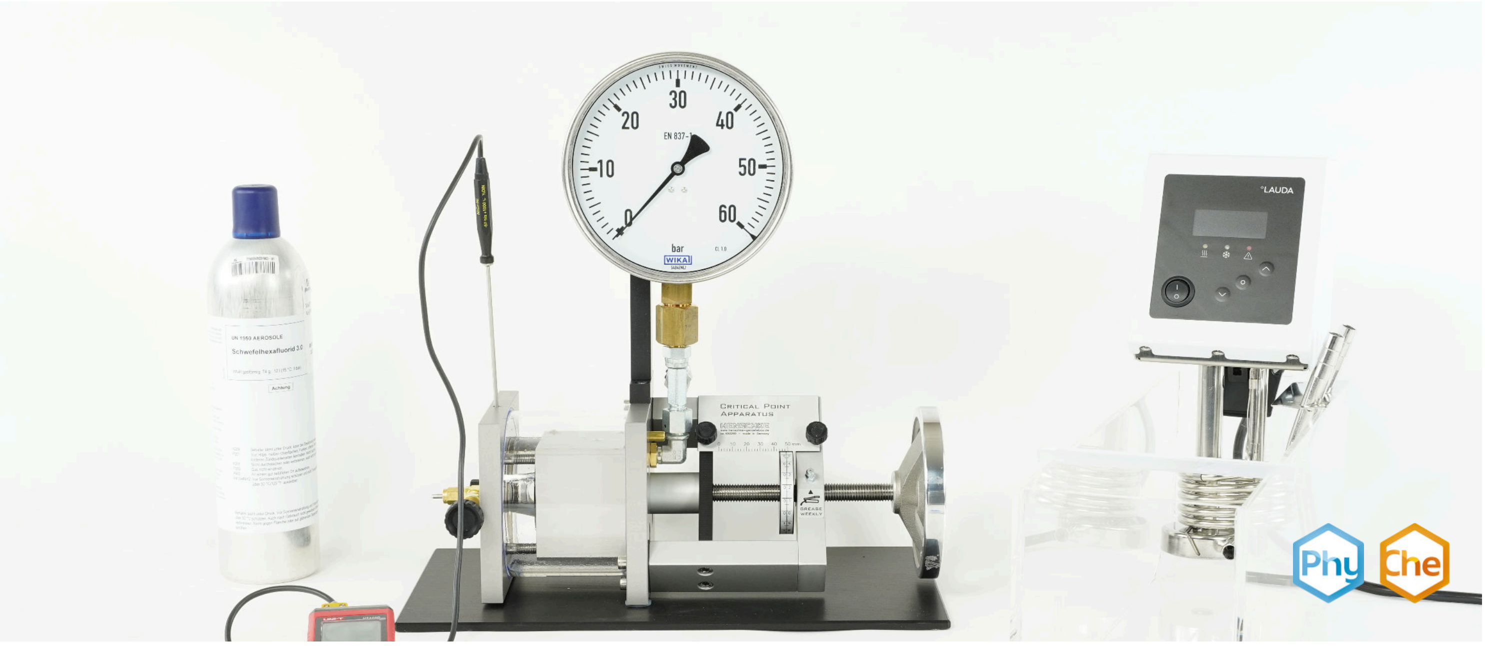
Thermal equation of state and critical point



P2320410

Physics | Thermodynamics | States of matter, dissolution (kinetic particle theory)

Difficulty level	Group size	Preparation time	Execution time
medium	-	10 minutes	10 minutes

This content can also be found online at:

http://localhost:1337/c/64d48450e1d33a00022a51ab

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General information

Application

Fig.1: supercritical fluid

The critical point of a substance is the point at which the phase boundaries between gas and liquid disappear, and there is no longer any distinction between the two states. Experiments that investigate the critical point have both practical applications and significant scientific implications.

Near the critical point, many substances exhibit universal behavioral tendencies, regardless of their chemical composition. This allows for the development of general theories and models for critical phenomena.

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Other information (1/2)

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Prior knowledge

Experiments on the critical point and the thermal equation of state play a crucial role in the exploration of phase transitions and thermodynamic properties of substances.

Scientific principle

These experiments are crucial for understanding and describing the thermal equation of state of substances near their critical point. The thermal equation of state depicts the relationship between pressure, temperature, and volume of a substance, enabling the prediction of its behavior in various phases and states. Experiments on the critical point contribute to refining the thermal equation of state and deepening our understanding

Other information (2/2)

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Learning objective

Qualitative observations: Liquid and gaseous states, dynamic state during phase transition, critical opalescence, formation of transition points at different temperatures.

Tasks

Quantitative measurements: p(V) at constant T (isotherms) and p(T) at constant V (isochors).

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Safety instructions

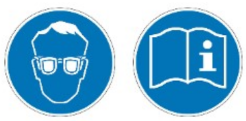
For this experiment the general instructions for safe experimentation in science lessons apply.

For H- and P-phrases please consult the safety data sheet of the respective chemical.

Carbon dioxide
H280: Contains gas under pressure; may explode if heated.
P403: Store in a well ventilated place.

Nitrogen
H280: Contains gas under pressure; may explode if heated.
P403: Store in a well ventilated place.

Safety instructions



Wear protective goggles. Operate the device only under supervision. Maximum allowable pressure: 6 MPa Maximum allowable temperature range: 10 - 60 °C An increase in temperature should only be carried out at low pressure and with pure gas phase in the measurement cell. The bracket (17) contains a threaded socket, which is classified as a safety-relevant component. Therefore, regular lubrication as per Section 4 and inspection as per Section 4.5 must be observed particularly. SF6 is completely harmless to humans and can therefore be used safely in teaching and practical work. The maximum workplace concentration (MAK value) at which there is a risk of suffocation due to oxygen displacement is 1000 ppm. This corresponds to approximately 6 measurement cell fillings per m3 of air. However, SF6 is highly environmentally damaging. Therefore, larger quantities should not be released into the environment.

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Theory (1/5)

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Isotherms in the Clapeyron diagram

While under "normal" environmental conditions, the ideal gas equation (Eq. 4) is approximately satisfied for air, significant deviations from ideal behavior must be taken into account for states in the two-phase region and near the critical point. The simplest equation of state that quite intuitively represents the fundamental fluid behavior was proposed by van der Waals:

$$(12)\quad \left(p+\frac{n^2 a}{V^2}\right)(V-nb)=nRT$$

In this equation, in addition to the already known quantities, the two parameters a and b appear. Following experimental observations, if it is required that at the critical point (denoted by index c),

$$(13)\quad \left.\frac{\delta p}{\delta V}\right|_c=0 \quad \text{and} \quad \left.\frac{\delta^2 p}{\delta V^2}\right|_c=0$$

Theory (2/5)

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holds true, then parameters a and b can be determined:

$$(14)\quad a=\frac{3V_c^2 p_c}{n^2} \quad \text{and} \quad b=\frac{V_c}{3n}$$

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Theory (3/5)

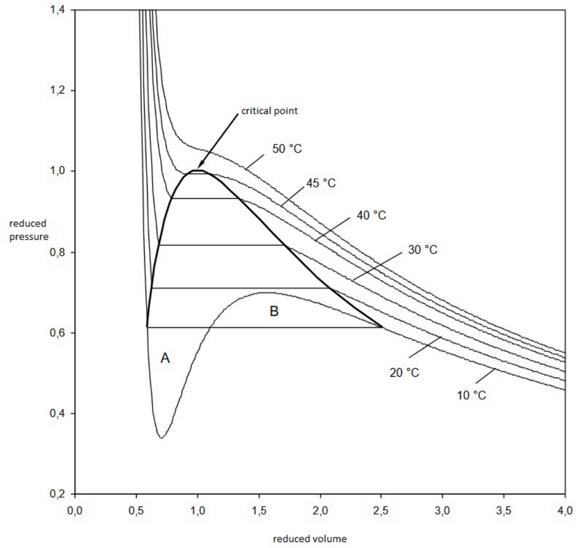

Figure 2: Isotherms calculated according to van der Waals. Although the diagram is applicable in principle to all gases, in this case, the specific temperatures for SF6 were used as parameters along the curves instead of reduced temperatures, in order to facilitate a better comparison with the measured values.

Theory (4/5)

Now, if the reduced quantities are considered,

(15) $p_r = \frac{p}{p_c}, V_r = \frac{V}{V_c}, T_r = \frac{T}{T_c}$

If the reduced variables are now introduced, then substituting them into Eq. 12 and performing some rearrangements yields the general, substance-independent form of the van der Waals equation.

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

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Theory (5/5)

This equation is cubic in terms of Vr. The graphical representation of multiple curves pr(Vr) at constant temperature is called a Clapeyron diagram. These curves can have two extreme points - a minimum and a maximum (see Figure 2). However, since experiments in the two-phase region usually exhibit a constant pressure profile rather than extreme points, a horizontal line is drawn between the minimum and the maximum, with the boundary condition of equal area between the curve and the line.

The line connecting the intersections of the curves and the lines at different temperatures is called the binodal. It delineates the two-phase region between the liquid and vapor. The connection line between the maximum and minimum values also holds significance. It's called the spinodal and defines the region where phase decomposition is certain. Between the spinodal and the binodal, there can exist superheated liquid or subcooled vapor.

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Equipment

Position	Material	Item No.	Quantity
1	Critical point apparatus	04365-00	1
2	Immersion thermostat Alpha A, 230 V	08493-93	1
3	Bath for thermostat, makrolon	08487-02	1
4	External circulation set for thermostat Alpha A	08493-02	1
5	Compressed gas, sulphur hexafluoride	41772-21	1
6	Digital thermometer, -50...+1300°C, for type K and J sensor	07022-00	1
7	Immersion probe NiCr-Ni, steel, -50...400 °C	13615-03	1
8	Tubing connector, ID 6-10mm	47516-01	4
9	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	4
10	Hose clamp for 8-12 mm diameter	41000-00	4
11	Silicone tubing, ID 10 mm	47532-00	2
12	Silicone tubing i.d. 7mm, 1 m	39296-00	1

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Setup and procedure

Setup

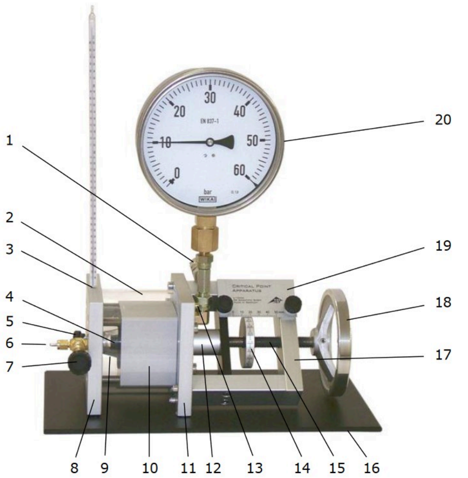

Fig. 3: Critical Point Apparatus

Device Description:

1 Safety Valve
2 Temperature Jacket (Acrylic Glass)
3 Hole for Temperature Sensor
4 Cap Seal
5 Purge Valve
6 Gas Connection 3.2 mm (1/8 inch)
7 Control Valve
8 Valve Plate
9 Measurement Cell (Acrylic Glass)
10 Cylinder
11 Base Plate
12 Piston Guard
13 Connection for Temperature Medium

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Setup

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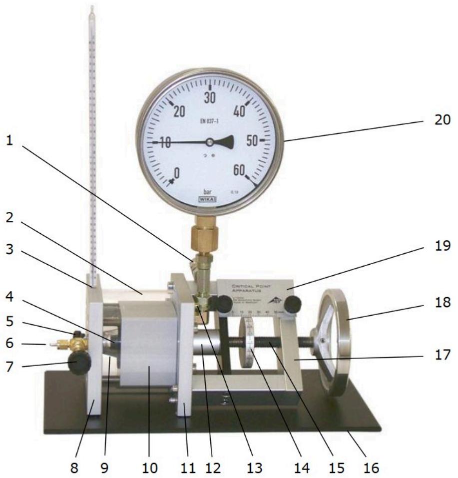

Fig. 3: Critical Point Apparatus

Device Description:

14 Rotating Scale (0.05 mm Division)
15 Threaded Rod with Piston (in 10,12)
16 Base Plate
17 Bracket
18 Handwheel
19 Fixed Scale
20 Manometer not shown:
21 Grease Gun
22 Oil Filling Device
23 Valve Protection
24 Hose, Inner Diameter 3 mm
25 Pipe Fitting for 1/8"
26 Hex Key Wrench 1.3 mm

Setup

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The device for investigating the critical point enables the study of gas compressibility and liquefaction, the determination of the critical point, and the recording of isotherms on the p-V diagram (Clapeyron diagram). Sulfur hexafluoride (SF_6) is used as the test gas, which, with a critical temperature of 318.6 K (45.5°C) and a critical pressure of 3.76 MPa (37.6 bar), allows for a simple experimental setup that quickly and effortlessly yields qualitatively accurate results. With a pressure- and temperature-dependent volume correction (calibration, see setup), quantitatively accurate results can even be obtained, comparable to literature values. The following points are particularly noteworthy:

- Mercury-free! (Classical experimental devices for the critical point are filled with nerve- and kidney-damaging mercury).
- Pressure is generated by a hydraulic system with castor oil (DAB quality).

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Setup

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- A conical rubber seal that rolls up during volume changes separates the gas chamber (measurement cell) from the hydraulic system. Due to this design, the pressure difference between the gas chamber and the oil chamber is practically negligible, and the pressure gauge can measure the oil pressure (= gas pressure) without requiring any dead volume in the gas chamber.
- Minimal dead volume in the measurement cell. Both the formation of the first liquid droplet and the disappearance of the last gas bubble can be observed.

Setup

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Technical specifications:

- Using two scales (fixed and rotating), a volume change can be read with an accuracy of 1/1000 of the maximum volume (15.7 ml).
- Class 1.0 pressure gauge (maximum deviation of 1% from the scale end value) with a diameter of 160 mm and a display up to 60 bar.
- Bore with a diameter of 6 mm for standard thermometers or temperature sensors.
- The theoretical endurance strength of the measurement cell is 70 bar; the theoretical burst pressure is above 200 bar.
- A safety valve (set to approximately 63 bar) protects experimenters and the apparatus.
- Dimensions: Base plate 38 cm x 20 cm, height 40 cm. Weight: approximately 7 kg.

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Setup

Operating Instructions and Maintenance:

The device for the critical point, upon delivery, is filled with hydraulic oil, but not with test gas. Prior to filling with test gas, a volume calibration should be performed as described in the setup. The filling with test gas is explained in also here in the section. Due to the unavoidable diffusion of the test gas through the sealing cap (4), it is necessary to degas the hydraulic oil according after extended periods of inactivity. The maintenance tasks are only required when the rubber components are compromised in their function due to aging.

There is a grease nipple located at the lever (17) which allows for the injection of grease into the threaded bushing to reduce wear. This should be done approximately every 100 cycles (a cycle consists of a pressure increase from 12 to 60 bar and the subsequent relaxation back to 12 bar) or once weekly, using a full piston stroke of the supplied grease gun into the bushing. Any excess grease extruding from the bushing should be wiped away. It also contains some plastic debris, which is thus removed. Greasing takes about 1 minute and significantly extends the bushing's lifespan!

Setup

Operating Instructions and Maintenance:

Since the threaded bushing wears over time, its condition should be checked annually, and if necessary, a new bushing should be installed. The relevant procedures are described in here in this section

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Setup

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Calibrate the device:

The numbers provided for part identification in the following description can be found in Figures 1 and 2.

By turning the handwheel (18), the piston with an exact diameter of 20 mm is threaded into or out of the cylinder (10) through the threaded rod (15), thereby altering the volume in the oil chamber (35). Since oil is nearly incompressible and, except for the sealing cap (4), all other parts are nearly rigid, the volume change in the oil chamber causes deformation of the sealing cap, resulting in an almost equal volume change in the gas chamber. For the volume change ΔV in the gas chamber, the following approximation holds:

$$(1) \quad \Delta V_g = A_k \Delta s$$

Ak = 2cm² is the cross-sectional area of the piston, and Δs is the displacement. The displacement is indicated in steps of 2 mm on the fixed scale (19). Intermediate values can be read on the rotating scale (14) in steps of 0.05 mm. Before precise calibration, the scales should be roughly adjusted as follows:"

Setup

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Calibrate the device:

1. Open regulating valve (7) widely. **Caution: With the regulating valve or flushing valve open, meaning no gas counter pressure in the measuring cell, pressures exceeding 5 bar must never be set. Otherwise, the sealing cap could be damaged. Additionally, when the valves are closed, vacuum must not be created by turning the handwheel in reverse.**
2. Loosen the set screw located on the rotating scale (14) between the 0.9 and 1.0 marks using the Allen wrench (26) by turning it 1/2 revolution. The scale can now be slightly rotated on the threaded rod (15) without moving the handwheel. However, there is still a resilient pressure piece opposing independent rotation.
3. Unscrew the handwheel (18) until you feel noticeable resistance.
4. Close the regulating valve (7).
5. The pressure in the measuring cell is now quite precisely pu = 1 bar (ambient pressure). The pressure gauge indicates the overpressure, which should now be 0±0.6 bar.

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Setup

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Calibrate the device:

6. Rotate the rotating scale on the threaded rod without moving the handwheel until the 0.0 mark is at the top and approximately 48 mm is shown on the fixed scale (19).
7. Loosen the knurled screws of the fixed scale and laterally shift the scale until the mark at 48 mm is precisely aligned with the centerline of the rotating scale. Tighten the knurled screws again, making sure that the fixed scale does not press onto the rotating scale.
8. Screw the handwheel in until an overpressure of 15 bar (p1 = 16 bar absolute pressure) is displayed. Read the scales (e.g., 3.5 mm) and note the piston's displacement (in this example: Δs = 48.0 mm - 3.5 mm = 44.5 mm).
9. As air behaves like an ideal gas in the pressure range of 1 - 50 bar and in the temperature range of 270 - 340 K (real gas factor deviates by less than 1% from 1, see [5, 6]), the following applies:

(2) $p_0 s_0 = p_1 s_1$ with $s_0 = s_1 + \Delta s$ and $p_0 = p_u$ is obtained after rearrangement

Setup

PHYWE

Calibrate the device:

With Δs = 10 and p0 = pu, the rearranged equation gives:

(3) $s_1 = \frac{p_u \Delta s}{p_1 - p_u}$

In the example, s1 is 2.97 mm. The rotating scale is now adjusted to this value (if necessary, adjust the fixed scale again).

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Setup

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If necessary, unscrew the handwheel slightly and secure the rotating scale with the set screw.

With this simple adjustment, qualitatively correct measurement values are already obtained. Regarding T and p, the isotherms in the two-phase region up to the critical point are also captured quantitatively correctly. However, particularly in the liquid region, the measured isotherms are slightly spread out.

The precise relationship between the gas chamber volume and the scale reading depends, firstly, on the amount of oil filled in the oil chamber. Secondly, the oil chamber expands proportionally with pressure, which is mainly attributed to the tube springs in the pressure gauge. And thirdly, castor oil expands more significantly with temperature increase than the rest of the apparatus, causing the pressure to increase slightly excessively with increasing temperature. All these effects can be relatively easily corrected. The procedure is as follows:

Setup

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1. Open regulating valve (7).
2. Unscrew the piston using the handwheel (18) until 46.0 mm are indicated.
3. Attach the hose (24) to connection (6) and generate an air overpressure of about 3 - 8 bar in the measuring cell using an air compressor (or a bicycle pump), then close the regulating valve.
4.Connect the temperature control (see also section 4.2) to the nozzles (13), set the desired temperature, and wait for at least 10 minutes for equilibrium to be established in the measuring cell.
5. Record several V-p and p-T measurement values. Example:

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Setup

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p_e/bar	s_e/mm	$t/^\circ C$
5,6	40,0	20,0
11,4	20,0	20,0
22,3	10,0	20,0
40,8	5,0	20,0
52,9	3,5	20,0
40,8	5,0	20,0
48,0	5,0	40,0
44,3	5,0	30,0
52,5	5,0	50,0
37,9	5,0	10,0

Table 1: since, as already explained, air behaves in the measurement range like an ideal gas, the ideal gas equation applies.

Setup

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As already explained, since air behaves like an ideal gas in the measurement range, the ideal gas equation applies:

(4) $\frac{pV}{T} = nR$

p is the absolute pressure, which is higher than the gauge pressure pe read on the pressure gauge by the ambient pressure pu (approximately 1 bar)

(5) $p = p_e + p_u$

for the absolute temperature:

(6) $T = t + 273^\circ C$

The volume is calculated according to

(7) $V = A_k s$

Setup

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from the piston cross-sectional area A = 2cm² and the 'effective' piston displacement s. The effective piston displacement is obtained by correcting the read piston displacement s_e as follows:

$$(8) \quad s = s_e + s_0 + C_p p + C_t (t_0 - t)$$

The reference temperature t0 is arbitrarily chosen. If t0 is set to 273.15 K (=0°C), then Equation 8 simplifies to:

$$(9) \quad s = s_e + s_0 + C_p p + C_t t$$

Setup

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Substituting Equation 9 into Equation 7 and further substituting Equations 5-7 into Equation 4 yields:

$$(10) \quad \frac{(p_e+p_u)[s_e+s_0+C_p(p_e+p_u)-C_t t]A_k}{t+t_0} - nR = 0$$

"If the part on the left-hand side of the equation is squared and summed for all measurement values i, the following error squared minimization is obtained:

$$(11) \quad \sum_{i=1}^{n} \left(\frac{(p_e+p_u)[s_e+s_0+C_p(p_e+p_u)-C_t t]A_k}{t+t_0} - nR \right)^2 = min$$

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With the free parameters n, Cp, Cs, and t0. Programs for error squared minimization are typically provided by university computing centers. For instance, the Nelder-Mead simplex algorithm [7] is highly efficient. But parameter estimation can also be carried out through trial and error in a spreadsheet software (e.g., included in 'OpenOffice'). For the example in the table above, the following values are obtained:

s0 = 0.19 mm, Cp = 0.23 mm/MPa, Ct = 0.034 mm/°C, and n = 0.00288 mol.

This way, the previously unknown amount of gas (0.00288 mol) in the measuring cell is determined, and the calibration is completed. If desired, the rotating scale can be rotated by the value of s0, eliminating this correction in the experiments.

Setup

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Gas filling, preparing the experiment

Sulfur hexafluoride (SF6) is used as the test gas, which is supplied in steel cylinders. A suitable pressure regulator is required for the cylinder, usually having a G1/4" thread at the outlet. The easiest way to connect the pressure regulator to the device is by using pneumatic components from the South Korean company SANG-A. In Europe, these components are distributed by LANDEFELD (landefeld.com), whose article numbers are provided below. A quick-connect fitting for 4 mm hoses (article number: IQSF 144) is attached to the pressure regulator using thread sealant (e.g., Loxeal, article number: 53-14/10). A polyurethane hose with an outer diameter of 4 mm and an inner diameter of 2.5 mm (article number: PUN 4X2.5 BLACK) is inserted into the quick-connect fitting. The maximum allowable operating pressure is 13 bar. The other end of the hose can be directly connected to the device's 3.2 mm gas connection, creating a secure connection for occasional filling.

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Setup

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Both threads are tightened hand-tight with thread sealant. Important:

Gas filling, preparing the experiment

A more professional connection can be made at the device using another IQSF 144 connector. However, a reducing nipple with G1/4" external thread and M8 internal thread is required, and the connecting piece (6) is removed by loosening the union nut (size 11 wrench required). The reducing nipple can be fabricated in a mechanical workshop, for example, from the nipple G1/4 to M5 (article number: RN 145 MS). Both threads are tightened hand-tight with thread sealant.

Important:

The regulating valve (7) is screwed into the valve plate (8) with thread sealant and must not be twisted, as this would cause the connection to become leaky. When screwing the union nut of the valve, the valve needs to be held in place with a wrench (size 13) and the device should be placed on a soft surface, such as foam, to accommodate slight movements of the wrench.

Setup

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Gas filling, preparing the experiment

The gas connection can also be made using a pipe with an outer diameter of 3.17 mm (1/8"). Pipes and, if necessary, reducers are manufactured by companies like Swagelok (www.swagelok.com). To connect the pipe to the apparatus, first remove the connecting piece (6) by loosening the union nut (size 11 wrench required). Then, slide the provided pipe fitting (25) onto the pipe, starting with the union nut (follow the sequence and orientation as indicated by the cable tie!). After that, insert the pipe into the regulating valve and tighten the union nut until the pipe can no longer be moved by hand. Give the nut an additional 270° turn to make the connection gas-tight. Secure it as described above!

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Setup

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Gas filling, preparing the experiment

After these preparations, the measuring cell can be filled as follows:

1. Set the piston using the handwheel (18) to the 10 mm position.
2. Slowly open the regulating valve (7) and allow SF6 to flow in until approximately 12 bar are indicated.
3. Close the regulating valve.
4. Slightly open the flushing valve (5) until the pressure reading drops to nearly 0 bar.
5. Close the flushing valve.

Setup

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Gas filling, preparing the experiment

After these preparations, the measuring cell can be filled as follows:

6. Repeat steps 2-5 at least 3 times. Depending on the length of the pipeline, additional flushing cycles might be required (estimate based on pipeline volume / measuring cell volume). When dealing with SF6 as a greenhouse gas, minimize its release into the environment.

7.Open the regulating valve until 12 bar are indicated again.

8.Close the regulating valve.

9.Turn the piston back to 46 mm using the handwheel.

10.Slowly open the regulating valve and close it when reaching 12 bar.

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The gas fill can remain in the measuring cell for several weeks. When no experiments are being conducted, the piston should be turned back to a low-pressure position, around 46 mm, using the handwheel.

If experiments are not planned for an extended period (such as holidays), the gas should be mostly released, and the sealing cap (4) should be relieved. For this purpose, the piston is turned to the 'resting position' at around 6 mm. The sealing cap will then be minimally indented in the conical part and will not press against the measuring cell (9). The gas is released through the regulating valve until the pressure is reduced to about 1 bar overpressure.

Setup

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To conduct experiments at different temperatures, a circulating thermostat is connected to the nozzles (13) through hoses with an inner diameter of 6 mm. The inlet should be positioned at the bottom and the outlet at the top. It is recommended to use a mixture of 2 parts water to 1 part antifreeze coolant as the temperature-controlling medium to avoid corrosion and deposits caused by electrochemical interactions between different materials. Any antifreeze coolant with additives suitable for protecting aluminum engines can be used. BASF's Glysantin® G30 has been tested so far. Ideally, the apparatus should always be filled with the temperature-controlling medium. Now, experiments can be conducted as outlined in Section 5.

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Setup

Degassing and Refilling of Hydraulic Oil

Due to the inevitable diffusion of the test gas through the sealing cap (4), the pressure in the measuring cell gradually decreases over an extended period. The gas diffusing through the sealing cap first dissolves in the hydraulic oil and doesn't have a significant impact on the measurements. However, if the test gas is released for the storage of the apparatus and, consequently, the pressure in the hydraulic oil drops to ambient pressure, the test gas according to Henry's law escapes from the hydraulic oil, resulting in a slow pressure increase in the oil chamber. This pressure increase, without gas counterpressure in the measuring cell, must be avoided at all costs (see also section 4.1). The following image should serve as a 'reminder' during maintenance work, placed near the apparatus:

Setup

Degassing and Refilling of Hydraulic Oil

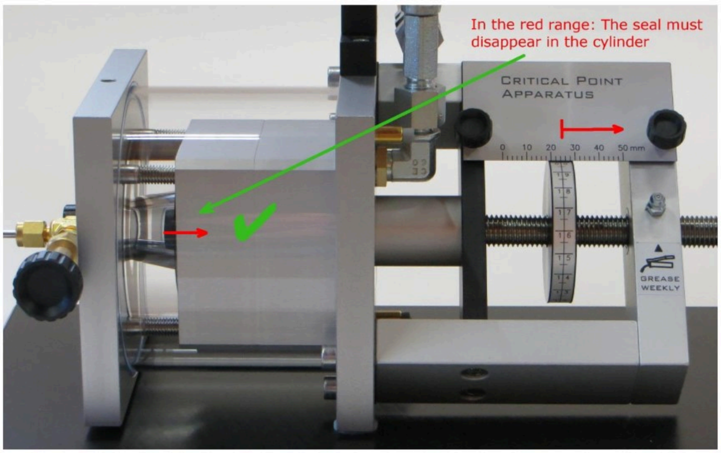

Fig. 4: setup with handwheel

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Setup

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Degassing and Refilling of Hydraulic Oil

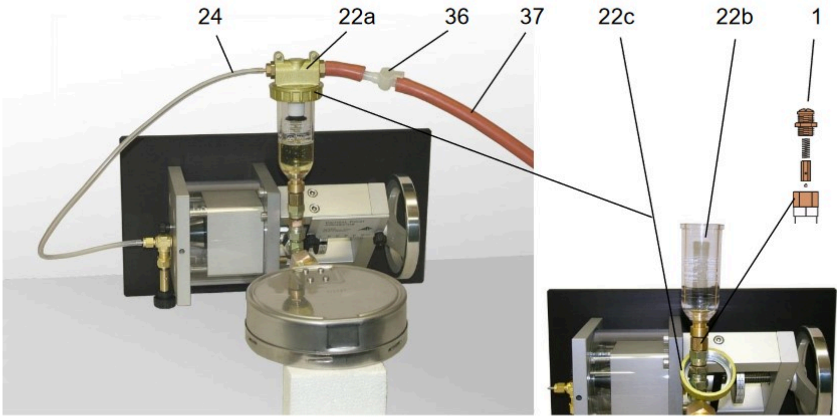

Fig. 5: Degassing of hydraulic oil using the oil filling device (items 36, 37 not included)

1 Safety valve

22a Attachment

22b Container

22c Union nut

24 Hose, inner diameter 3 mm

36 Shut-off valve

37 Vacuum hose"

Setup

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Before storage, the hydraulic oil should be degassed. The procedure is as follows (see also Fig. 3):

1. Release test gas through the flushing valve (5), then close the flushing valve.
2. If necessary, dismantle the gas pipeline and mount the gas connection (6).
3. Open the control valve (7).
4. Turn the piston using the handwheel (18) until an excess pressure of 1 bar is reached (if necessary, release the scale rotating along).
5. Close the control valve.
6. Turn the handwheel back 2 turns. Under no circumstances turn it out more than 25 mm, as otherwise, during the following work, the guide tube (31) can slip out of the piston.

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7. Place the apparatus with the pressure gauge scale facing downward on the work area, with the pressure gauge supported by an approximately 6 cm thick base (Figure 3).
8. Loosen the lock nut (size 14) of the safety valve (1) and unscrew the valve cap using a screwdriver. Successively, remove the pressure spring, the hexagonal plunger, and the steel ball (using tweezers) and place them, for example, in a box.
9. Loosen the union nut (22c) of the oil filling device (22) and remove the attachment (22a). Place the union nut over the safety valve (Figure 3, right) and screw the container (22b) onto it without overtightening: the O-ring must not be squeezed out.
10. Open the control valve and turn the handwheel all the way in until it touches the bracket (17) (if necessary, release the rotating scale). Afterward, turn the handwheel back 6 mm (3 rotations).

Setup

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11. Fill container (22b) with castor oil (pharmacy-grade) up to a maximum of half capacity.
12. Screw on the attachment (22a) using the union nut (22c).
13. Attach a hose with a 3 mm inner diameter (24) to the gas connector (6) and the smaller nozzle of the attachment (22a). **Verify that the control valve is open and the purging valve is closed.**
14. Connect a vacuum hose with a 6 mm inner diameter (37) to the larger nozzle of the attachment using a shut-off valve (36).
15. Slightly open the shut-off valve while observing the castor oil. If the foam formation becomes so intense that it reaches the filter attached to the attachment, close the shut-off valve and only reopen it after the foam subsides.

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16. After some time (approximately 15 minutes, depending on the connected vacuum pump), the vapor pressure of the castor oil is reached, and it begins to boil. This is indicated by the emergence of vapor bubbles "out of nowhere" that rapidly expand as they travel through the oil. At this point, the oil is sufficiently degassed.
17. Close the control valve (7) and shut-off valve (36). Disconnect the vacuum hose (37) from the shut-off valve (the hose section with the valve remains attached to the oil filling device).
18. To prevent pressure surges, slowly open the shut-off valve and wait for pressure equalization.
19. Disconnect the hose (24) from both nozzles.
20. Unscrew the container (22b) from the safety valve. As castor oil is relatively viscous, it flows out of the container very slowly, allowing this operation to be carried out without issues. Placing a cleaning cloth (paper towel) right under the container immediately after unscrewing it prevents any dripping.

Setup

21. Use a cleaning cloth to remove excess oil from the safety valve, and then slightly turn the handwheel inward until the oil level in the valve aligns precisely with the resting edge of the steel ball.
22. Insert the steel ball, place the hexagonal punch with the short hole over the ball (using tweezers), and insert the compression spring into the longer hole. Carefully screw the valve cap onto the valve (not too tightly) until it reaches the stop, and then loosen it by 2 turns.
23. Adjust the safety valve: Open the control valve and fully unscrew the handwheel. Close the control valve again.
24. Turn the handwheel inward until an excess pressure of approximately 65 bar is reached.

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25. Slowly unscrew the valve cap of the safety valve. **During this procedure, the safety valve must not be aimed in the direction of individuals or objects that could be harmed or damaged by the cap shooting out. The person working on the valve should be positioned in front of the apparatus and reach around the apparatus with their arms to access the valve.** Once the pressure drops to approximately 63 bar, the set point is reached, and the lock nut (14 mm wrench) is tightened.
26. Rotate the handwheel back until the pressure falls to around 10 bar. Open the control valve and turn the handwheel to the "resting position" at around 6 mm. Close the control valve. After these tasks, the apparatus can be stored or refilled with test gas as needed.

Setup

Disassemble and assemble the apparatus

After a certain period of time (especially if the apparatus is exposed to direct sunlight), it may be necessary to replace the cap seal (4) and/or other seals. To do so, follow these steps:

A. Disassemble the apparatus:

1. Release the test gas through the purging valve (5) and close the purging valve.
2. If necessary, disassemble the gas pipeline, and open the control valve (7).
3. Turn the handwheel (18) to the 25 mm extended position.
4. Tilt the apparatus to the right and place it on the handwheel (use a suitable support) and the edge of the base plate (16).

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Disassemble and assemble the apparatus

5. Use a hexagonal angle screwdriver (6 mm) to evenly loosen the 4 screws on the valve plate (8) in a cross pattern, turning each 1/8 turn until the preload is released. Completely unscrew and remove the screws. Also remove the copper gaskets.

6. Rotate the valve plate with increasing force in both directions until the seals come loose (Caution: do not turn the control valve while doing this).

7. Remove the valve plate (8). The measurement cell (9) might still be stuck to the plate.

8. Once again, use twisting motion to release the remaining seal between the measurement cell and the cylinder (10) or between the measurement cell and the valve plate.

9. Remove the guide tube (31) from the cap seal by twisting.

Setup

PHYWE

Disassemble and assemble the apparatus

10. Clean all parts that are to be reinstalled. Castor oil can be relatively easily removed with rubbing alcohol, but acrylic glass (measurement cell, casing) is susceptible to alcohol. Fingerprints and other contaminants can be removed with a (mild) solution of dish soap. The new seals should also be cleaned with rubbing alcohol and a dish soap solution.

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Setup

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Disassemble and assemble the apparatus

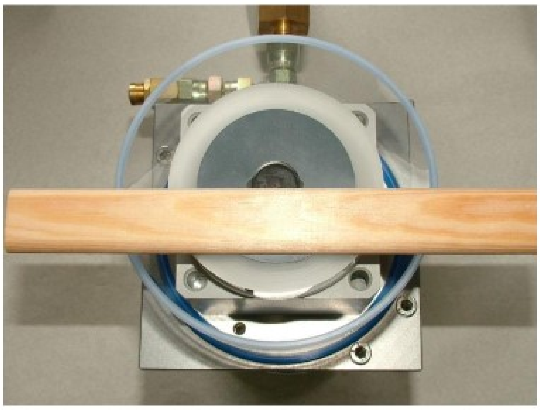

Fig. 6: Aligning the circular rubber seal (27)

Setup

PHYWE

Assembling the apparatus

11. If castor oil has been removed from the oil chamber, fill new castor oil up to about 5 mm below the top edge of the cylinder (start of depression).

12. Place the two silicone gaskets (29).

13. Turn the cap seal inside out and moisten the pin with some castor oil before inserting it into the guide tube.

14. Turn the cap seal back, place the spring (30) onto the piston, and insert the guide tube into the piston.

15. Place the measuring cell and align it evenly along the edges of the cylinder.

16 .Place and center the temperature jacket (2) on the lower silicone gasket.

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Setup

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Assembling the apparatus

17. Place the round rubber gasket (27) and using a ruler placed on the temperature jacket, align it parrallel to the cylind (see Fig. 4). The half-moons shuld later be positioned under the valve openings.

18. Place the valve plate, center it, and align it parallel to the base plate (11)

19. Attach M8x40 screws with new copper wahsers and screw them in loosely.

20. Tighten the screws diagonally. While doing so, check for even compression of the round rubber gasket (inareas with high pressure, the rubber gasket appears gray on the acrylic glass of the measuring cell, while areas with low pressure appear cloudy).

21. Degas the oil chamber and castor oil according to Section 4.3.

Setup

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Check threaded bushing and replace if necessary

The threaded bushing in the bracket (17) undergoes slow but continuous wear and should therefore be checked annually for axial play: Release pressure from the measuring cell. Hold a M12 nut (or another approximately 10mm wide planar parallel part) between the handwheel flange and the bracket. Now press firmly in the axial direction against the handwheel while simultaneously turning it until the nut is just not firmly clamped. Read and note the position on the scales. Then pull firmly on the handwheel, once again not firmly clamping the nut, and read the position. If the difference between the two positions is greater than 0.3 mm, then the bushing needs to be replaced.

If the bushing does not reach the wear limit within 10 years (in test stand experiments, no measurable wear [< 0.05 mm] was observed after 1000 cycles), it should still be replaced, as reliable long-term stability data for the used plastic material (POM-C) are not yet available.

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Replacement of the bushing:

1. Release pressure from the measuring cell.

2. Unscrew the fixed scale (19).

3. Loosen the threaded pin in the handwheel flange and remove the handwheel (18).

4. Loosen the 4 screws on the crossbar (with the threaded bushing) (17) and turn the crossbar down from the threaded rod.

5. Unscrew the grease nipple (SW 7) and use a 3mm Allen wrench to loosen the threaded pin threaded into the threaded bushing by 4 turns.

6. Unscrew the M6 lock nut opposite the grease nipple and remove the threaded pin."

Setup

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Replacement of the bushing:

7. Drive out the bushing from the handwheel side using a suitable drift. Alternatively, a loose M14 screw can be threaded into the bushing, and the bushing can be driven out by striking the screw head.

8. Place the new bushing so that the crosshole aligns with the grease nipple.

9. Press the bushing into place using a vice (with smooth jaws or suitable padding).

10. Screw in the threaded pin on the grease nipple side (at least 6.0 mm recessed).

11. On the opposite side of the grease nipple, use a 5mm drill to penetrate the existing M6 hole and partially drill through the new bushing. Then tap an M6 thread.

12. Thread the crossbar onto the M14 threaded rod and screw in the M6x16 threaded pin until it contacts the threaded rod, then loosen it by half a turn. In this position, install the lock nut.

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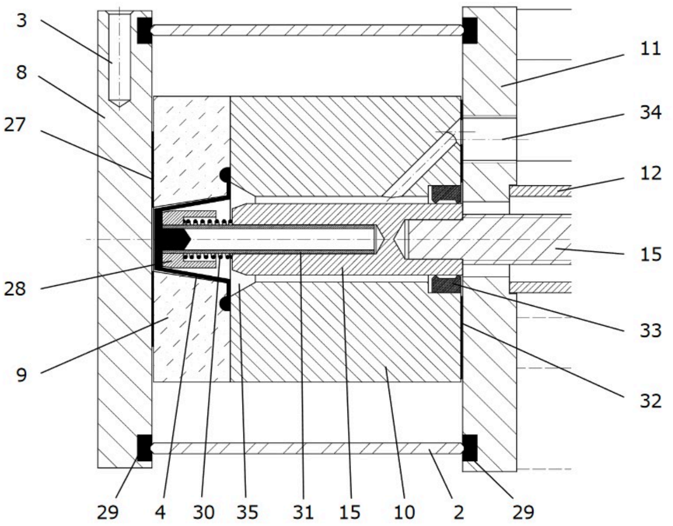

Fig. 6: Detailed drawing of the apparatus

2 Temperature jacket (Acrylic glass)
3 Hole for temperature sensor
4 Sealing cap
8 Valve plate
9 Measuring cell (Acrylic glass)
10 Cylinder
11 Base plate
12 Piston guard
15 Threaded rod with piston
27 Round rubber seal
28 Sleeve

Setup

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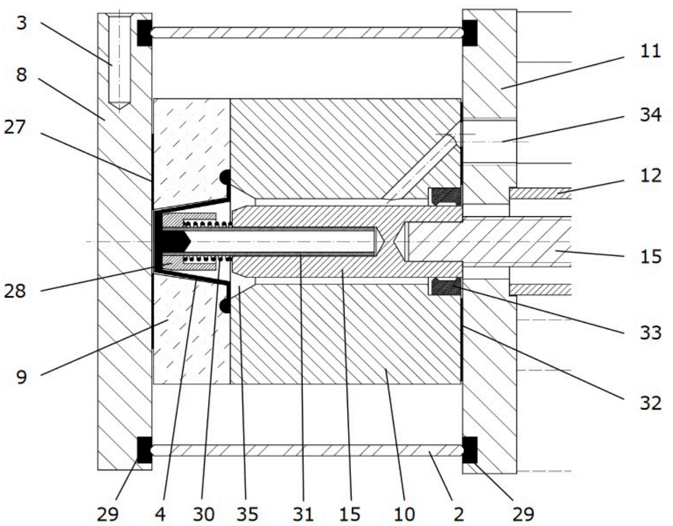

Fig. 6: Detailed drawing of the apparatus

29 Silicone seal
30 Spring
31 Guide tube
32 Square rubber seal
33 Seal ring
34 Pressure connection (to pressure gauge)
35 Oil chamber

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Procedure

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Qualitative observations: Liquid and gaseous states, dynamic state during phase transition, critical opalescence, formation of transition points at different temperatures.

Quantitative measurements: p(V) at constant T (isotherms) and p(T) at constant V (isochors).

After the preparations, systematic series of experiments can now be conducted at constant temperature with varying volume to determine isotherms. If the test gas pressure at maximum volume (handwheel fully turned out) is at 12 bar, it is advisable to approach the measurement points 'from below' up to a piston position of about 10 mm. This means that the handwheel is turned to a certain position, the position is noted, and the corresponding pressure is read after equilibrium is reached. The attainment of equilibrium can be recognized by the pressure remaining unchanged for an extended period of time."

Procedure

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In the range of small volumes below the 10 mm position, for the sake of rapid equilibrium establishment, it is sensible to approach the measurement points 'from above,' meaning from higher pressures (up to a maximum of 60 bar) to lower pressures. This is due to the fact that during the phase transition from liquid to gas, the phase boundary surface, formed by vapor bubbles that emerge throughout the liquid, is significantly larger than in the case of the phase transition from gas to liquid, where the phase boundary surface is limited to the liquid surface. The order of measurements naturally has no influence on the equilibrium state.

If the experiments are conducted in the described manner, it takes approximately 1 to 5 minutes to reach equilibrium, with the measurement points at the edge of the two-phase region taking the longest time.

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Procedure

Alternatively, with constant volume, the temperature can be varied. This method results in obtaining the vapor pressure curve when the measurement points fall within the two-phase region. However, equilibrium establishment takes significantly longer during a temperature change compared to a volume change, as both the water bath and the measuring cell need to reach the desired temperature initially. Depending on the quality of the circulation thermostat, this process can take up to 20 minutes.

During the experiments, near the critical point, the **critical opalescence** can also be observed: Continuous transitions between liquid and gaseous states in small regions of the measuring cell create a kind of 'mist,' causing sulfur hexafluoride to appear cloudy.

Evaluation

During the experiment procedure according to Section 5, temperatures, overpressures, and piston positions are measured. Initially, the overpressures should be converted to absolute pressures and the piston positions to volumes according to Eq. 7 and Eq. 9.

The determination of the SF6 mole quantity in the measuring cell according to Eq. 11 is not feasible due to SF6 not behaving as an ideal gas. One way to ascertain the gas mass is by blowing the gas from the measuring cell into a plastic bag and subsequently weighing it (taking buoyancy into account). To avoid errors caused by dead volumes, the following approach can be taken:

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Evaluation

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The handwheel is turned out considerably (for instance, to 46 mm and 8 bar overpressure). Then, the gas is released into the plastic bag through the control valve with the attached connector. After closing the control valve, the pressure in the measuring cell is raised back to the original value (in this example, 8 bar). By calculating the difference in volume before and after the emptying process (this quantity is in the plastic bag) and considering the remaining volume in the measuring cell, the original gas quantity can be easily calculated.

A simpler way to determine the gas quantity is by comparing it with literature values.

Evaluation

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In Table 2, several measurements from Clegg et al. [4] are compiled. For instance, if a measurement was taken at t = 49.86 °C, p = 28.44 bar, and V = 4.7 ml, then according to the table, the specific volume is calculated as 4.469 ml/g, and the gas mass in the measuring cell amounted to 1.05 g during the experiments.

n / V mol / dm³	$Z = pV / nRT$ -	t °C	V / m ml / g	p bar
1,532	0,6911	49,86	4,469	28,44
1,934	0,6242	49,86	3,540	32,42
2,522	0,5391	49,86	2,715	36,52
3,962	0,3797	49,86	1,728	40,40
6,989	0,2420	49,86	0,980	45,42
7,848	0,2562	49,86	0,872	54,00
1,371	0,6832	34,19	4,994	23,94
1,582	0,6409	34,19	4,328	25,91
1,777	0,6032	34,19	3,853	27,39
2,027	0,5573	34,19	3,378	28,87

Table 2: The first 3 columns contain several measurements from Clegg et al. [4]. From these measurements, the specific volume and pressure were calculated.

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Evaluation

This gas mass determination was performed during the measurements depicted in Figure 6, obtained using the experimental setup described here, up to the critical point. It can be observed that despite the relatively simple apparatus, the obtained data points, which are also plotted on the graph, stand up well in comparison to the literature values.

A comparison with the van der Waals equation (Figure 5) reveals that the simple theory does not yield satisfactory results here. While the vapor pressure decreases by only around 40% according to van der Waals when lowering the temperature from 45°C to 10°C, the measured values show a decrease of nearly 60%. In reality, there is still no model that accurately describes all substances across the entire range from liquid to two-phase, gaseous, and supercritical phases. Depending on the substance and application, different equations are employed. As pointers for further research, the 'Peng-Robinson equation of state' and 'GE models' can be mentioned.

Evaluation

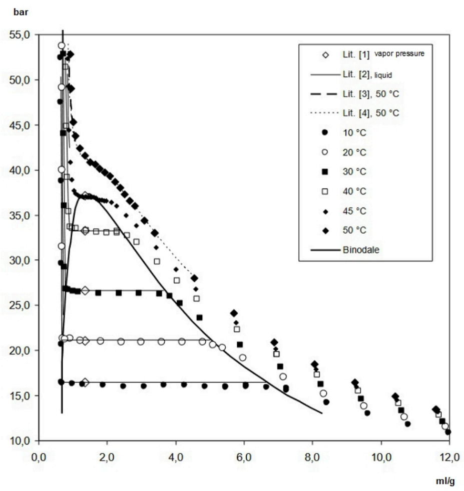

Figure 7: Comparison of literature data [1-4] and measured values. To prevent overcrowding the diagram, the literature values are depicted as lines.

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