PHYWE

Critical point apparatus

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Operating instruction

The unit complies with the applicable EC-guidelines

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1 Scope of delivery, designation of components

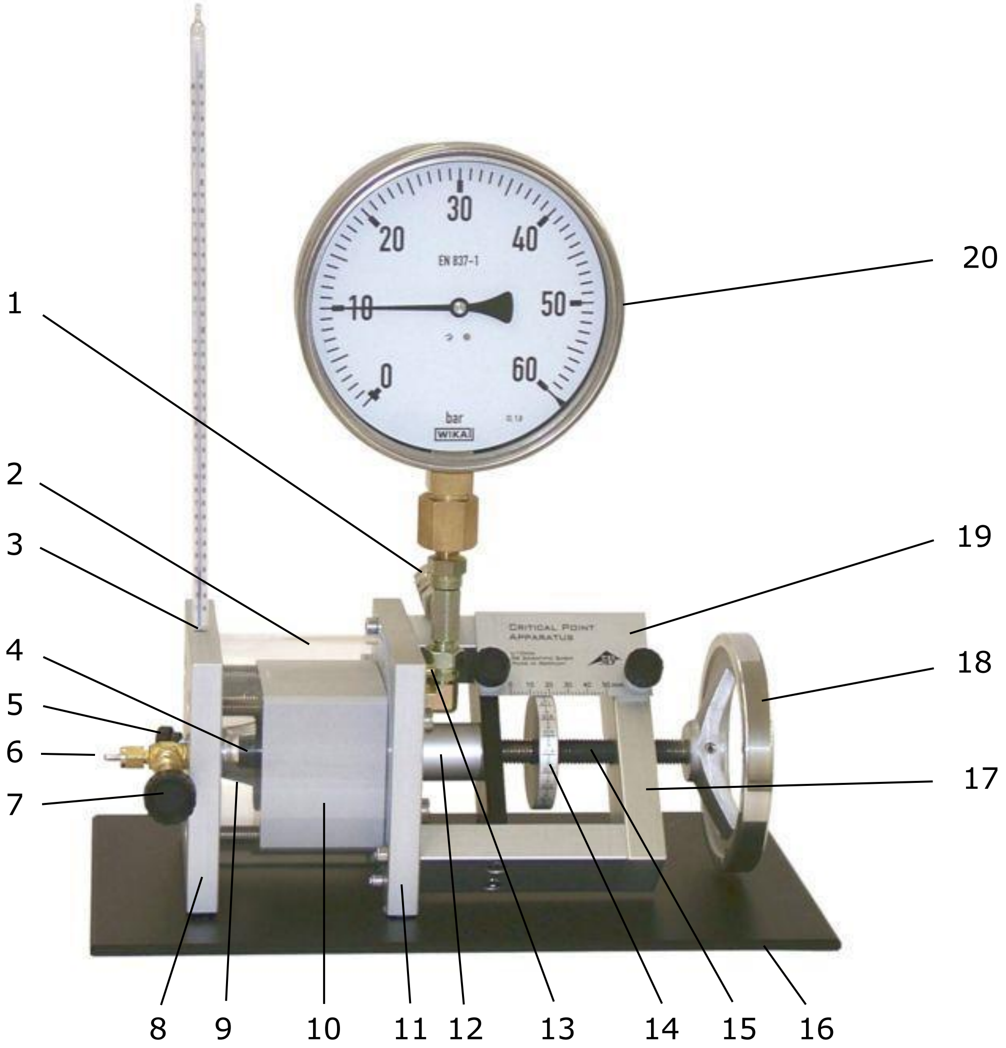
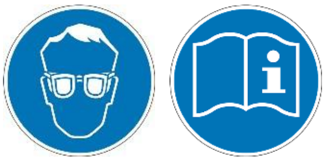


Fig. 1: Scope of delivery

1 Safety valve
2 Tempering jacket (acrylic glass)
3 Hole for temperature sensor
4 Hat gasket
5 Flush valve
6 Gas connection 3.2 mm (1/8 inch)
7 Regulating valve
8 Valve plate
9 Measuring cell (acrylic glass)
10 Cylinder
11 Base plate
12 Piston protection
13 Connection f. temp. control medium
14 Rotating scale (0.05 mm pitch)
15 Threaded rod with piston (in 10,12)
16 Base plate
17 Hanger
18 Handwheel
19 Fixed scale
20 pressure gauger

Not pictured
21 Grease gun
22 Oil filling device
23 Valve protection
24 Hose, inner diameter 3 mm
25 Pipe fitting for 1/8
26 Hexagon socket screwdriver 1.3 mm

2 Safety precautions



Read the operating instructions completely before commissioning.
Wear protective goggles. Only operate the appliance under supervision.
Maximum permissible pressure: 6 MPa
Maximum permissible temperature range: 10 - 60 °C

A temperature increase may only be carried out at low pressure and pure gas phase in the measuring cell.

In the bracket (17) there is a threaded bush which is to be classified as a safety-relevant component. Therefore, the regular lubrication according to section 4 and the inspection according to section 4.5 must be particularly observed.

Ethane is a highly flammable gas. Open flames, sparks, and hot surfaces must be avoided. Operations should be carried out in well-ventilated areas. At high concentrations, ethane acts as an asphyxiant by displacing oxygen, but it has no significant intrinsic toxicity. Only release small amounts of the gas and avoid unnecessary emissions into the environment whenever possible.

Additional safety point (recommended):

- Avoid ignition sources
- Ensure good ventilation of the room

3 Introduction, technical data

The critical point device enables the investigation of compressibility and liquefaction of a gas, the determination of the critical point and the recording of the iso- therms of the p-V diagram (Clapeyron diagram). The test gas used is ethane, which, with a critical temperature of 318.6 K (45.5°C) and a critical pressure of 3.76 MPa (37.6 bar), enables a simple test set-up with which qualitatively correct test results can be obtained quickly and without great effort. With a pressure- and temperature-dependent volume correction (calibration, see 4.1), even quantitatively correct results are obtained that stand up to comparison with literature values. The following points should be emphasised in particular:

- Without mercury! (classical critical point test devices are filled with mercury, which damages nerves and kidneys).
- Pressure build-up through a hydraulic system with castor oil (DAB quality).
- A conical rubber seal, which rolls in when the volume changes, separates the gas chamber (measuring 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 claiming a dead volume in the gas chamber.
- Minimum dead volume in the measuring cell. Both the formation of the first liquid drop and the disappearance of the last gas bubble can be observed.

Technical data:

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

4 Operating instructions and maintenance

The critical point unit is delivered filled with hydraulic oil but not with test gas. Before filling with test gas, a volume calibration should be carried out according to section 4.1. Filling with test gas is described in section 4.2. Due to the unavoidable diffusion of the test gas through the cap seal (4), the hydraulic oil must be degassed after longer standing times according to section 4.3. The maintenance work described in section 4.4 is only necessary if the rubber parts are impaired in their function due to ageing.

There is a grease nipple on the bracket (17) through which grease can be pressed into the threaded bush to reduce wear. This should be done approximately every 100 cycles (one cycle consists of a pressure increase from 12 to 60 bar and the subsequent release to 12 bar again) or once a week, whereby a full piston stroke of the supplied grease gun is pressed into the bushing. The excess grease coming out of the bushing is wiped off. It also contains some plastic abrasion, which is removed in this way. Lubrication takes approx. 1 min. and considerably extends the life of the bushing!

As the threaded bushing wears out over time, its condition must be checked once a year and a new bushing inserted if necessary. The corresponding work is described in section 4.5.

4.1 Calibrate unit

The numbers given in the following description to identify the parts can be found again in Figs. 1 and 2.

By turning the handwheel (18), the piston with a diameter of exactly 20 mm is turned into or out of the cylinder (10) via the threaded rod (15), which changes the volume in the oil chamber (35). Since oil is almost incompressible and all other parts except the cap seal (4) are almost rigid, the change in volume in the oil chamber causes a deformation of the cap seal and thus an almost equally large change in volume in the gas chamber space.
For the volume ΔV_G in the gas space therefore applies as a first approximation:

$$\Delta V_G = A_K \, \Delta s \qquad (1)$$

Thereby $A_K = 3{,}14$ cm² is the cross-sectional area of the piston Δs and the displacement.
The adjustment travel is displayed 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 exact calibration, the scales should first be roughly adjusted as follows:

1. Open the regulating valve (7) wide.

!

Caution: Pressures above 5 bar must never be set when the regulating valve or flush valve is open, i.e. without gas back pressure in the measuring cell. Otherwise, the cap seal may be destroyed. Furthermore, no vacuum may be created by turning back the handwheel when the valves are closed.

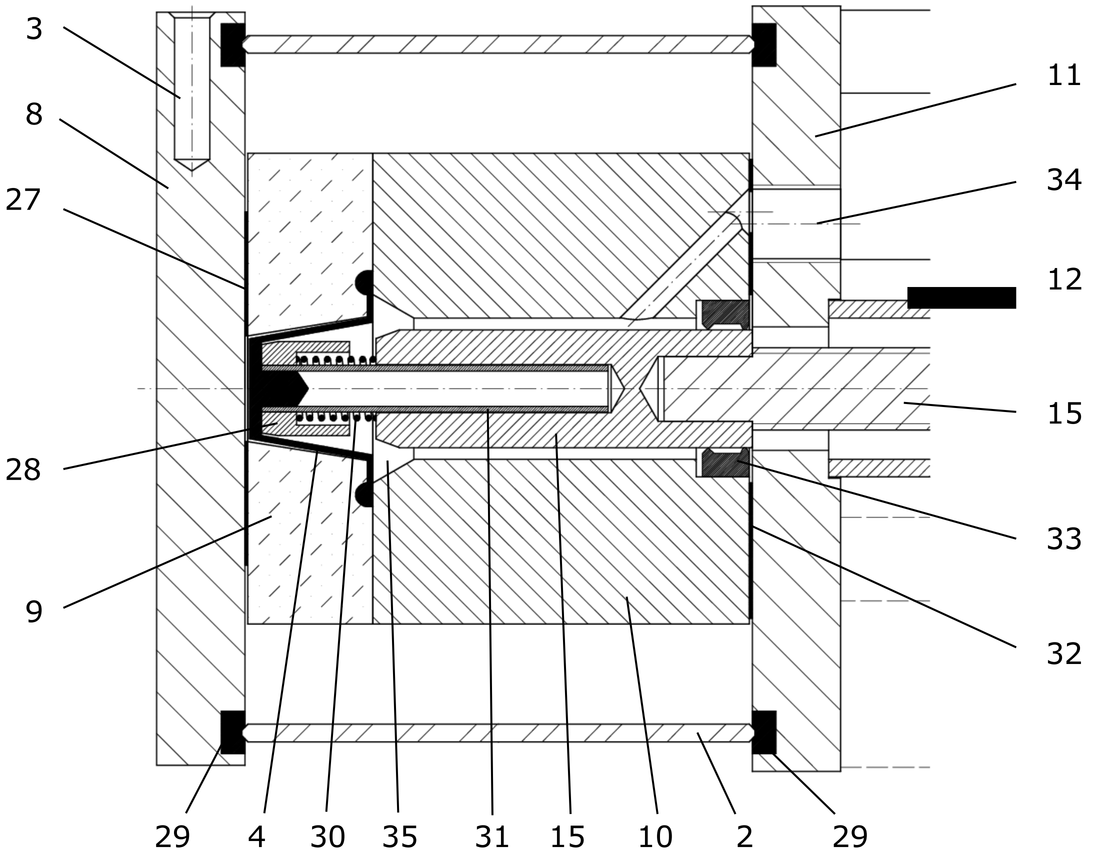


Fig. 2: Detail drawing of the apparatus

2 Temperature control jacket (acrylic glass)
3 Hole for temperature sensor
4 Cap seal
8 Valve plate
9 Measuring cell (acrylic glass)
10 Cylinder
11 Base plate
12 Piston protection
15 Threaded rod with piston
27 Round rubber seal
28 Sleeve
29 Silicon seal
30 Spring
31 Guide tube
32 Square rubber seal
33 Sealing ring
34 Pressure connections)
35 Oil chamber

2. Loosen the grub screw located in the rotating scale (14) between the 0.9 and the 1.0 mark by 1/2 turn with the Allen key (26). The scale can now be easily turned on the threaded rod (15) without moving the handwheel. However, a spring-loaded pressure piece still counteracts independent turning.
3. Turn out the handwheel (18) until noticeable resistance is felt.
4. Close the regulating valve.
5. The pressure in the measuring cell is now quite accurately pu = 1 bar (ambient pressure). The pressure gauge shows the overpressure, which should now be 0±0.6 bar
6. Without moving the handwheel, turn the scale on the threaded rod until the 0.0 mark is at the top and approx. 48 mm is displayed on the fixed scale (19).
7. Loosen the knurled screws of the fixed scale and move the scale sideways until the line at 48 mm is exactly above the centre line of the rotating scale. Tighten the knurled screws again. Make sure that the fixed scale does not press on the rotating scale.

8. Turn the handwheel until 15 bar overpressure (p1 = 16 bar absolute pressure) is displayed. Read off the scales (e.g. 3.5 mm) and note the piston stroke travelled (in the example: Δs = 48,0 mm - 3,5 mm = 44,5 mm).
9. Since 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 from 1 by less than 1%, cf. [5, 6]), the following applies:

$$p_0 s_0 = p_1 s_1 \tag{2}$$

with $s_0 = s_1 + \Delta s$ and $p_0 = p_u$ results after conversion:

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

In the example, s1 = 2.97 mm. The rotating scale is now set to this value (if necessary, move the fixed scale again).
10. If necessary, unscrew the handwheel a little and fix the rotating scale with the grub screw.

With this simple adjustment, qualitatively correct measured values are already obtained. With regard to T and p, the isotherms in the two-phase range up to the critical point are also recorded quantitatively correctly. However, especially in the liquid range, the measured isotherms are spread a little too wide.

The exact correlation between the gas chamber volume and the scale display depends on the one hand on the amount of oil filled into the oil chamber. Secondly, the oil chamber expands slightly in proportion to the pressure, which is probably mainly due to the tube threads in the pressure gauge. And thirdly, castor oil expands more than the rest of the apparatus when the temperature increases, which causes the pressure to rise slightly excessively with increasing temperature. All these effects can be calculated out relatively easily. The procedure is as follows:

1. Open the regulating valve (7).
2. Turn out the piston with the handwheel (18) until 46.0 mm is displayed.
3. Connect the hose (24) to the connection (6) and create an air overpressure of approx. 3 - 8 bar in the measuring cell using a compressor (or a bicycle air pump) and close the regulating valve.
4. Connect the temperature control (see also section 4.2) to the connection pieces (13), set the desired temperature and wait at least 10 minutes until equilibrium has been reached in the measuring cell.
5. Take some V-p and p-T readings. Example:

p_e / bar	s_e / mm	t / °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

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

$$\frac{pV}{T} = nR\,. \tag{4}$$

Here p is the absolute pressure, which is higher by the ambient pressure p_u (approx. 1 bar) than the overpressure p_e read off the pressure gauge:

$$p = p_e + p_u\,. \tag{5}$$

For the absolute temperature applies:

$$T = t + 273{,}15°\text{C}. \tag{6}$$

The volume is calculated according to

$$V = A_K s \tag{7}$$

from the piston cross-sectional area $A_K = 3{,}14\ \text{cm}^2$ and the 'effective' piston path *s.*

The effective piston travel is obtained by correcting the measured piston travel s_e as follows:

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

The reference temperature t_0 is freely selectable. If $t_0 = 273{,}15\ \text{K}$ (=0°C) is used, then Equation 8 simplifies to:

$$s = s_e + s_0 + C_p p - C_t t \tag{9}$$

Substituting Eq. 9 into Eq. 7 and further substituting Eqs. 5-7 into eq. 4 results in:

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

If the term on the left-hand side of the equation is squared and summed over all measured values i, the following least-squares (error square minimization) is obtained.

$$\sum_{i=1}^{n}\left(\frac{(p_{e,i} + p_u)[s_{e,i} + s_0 + C_p(p_{e,i} + p_u) - C_t t_i]A_K}{t_i + t_0} - nR\right)^2 = \min \tag{11}$$

with the free parameters s_0, C_p, C_t und n.

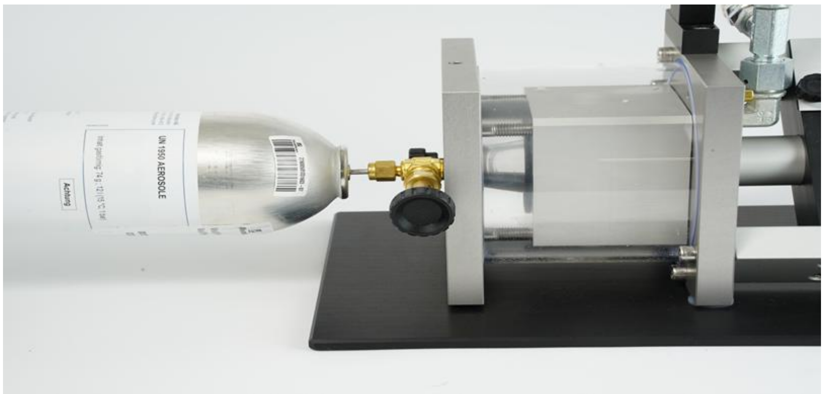
Error square minimisation programmes are usually university computer centres are usually available. The simplex algorithm according to Nelder and Mead [7], for example, is very efficient. But the parameters can also be determined by "trying it out" in a spreadsheet (e.g. included in "Open Office"). For the example in the table above, the following values resulet.

s_0 = 0,19 mm, C_p = 0,23 mm/MPa, C_t = 0,034 mm/°C und n = 0,00288 mol.

In this way, the previously unknown amount of gas (0.00288 mol) is also obtained in the measuring cell and the calibration is completed. If desired, the rotating scale can be rotated by the value s_0, which eliminates this correction during the experiments.

4.2 Gas filling, prepare experiment

Ethane is used as the test gas, which is supplied in pressurized canisters.



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

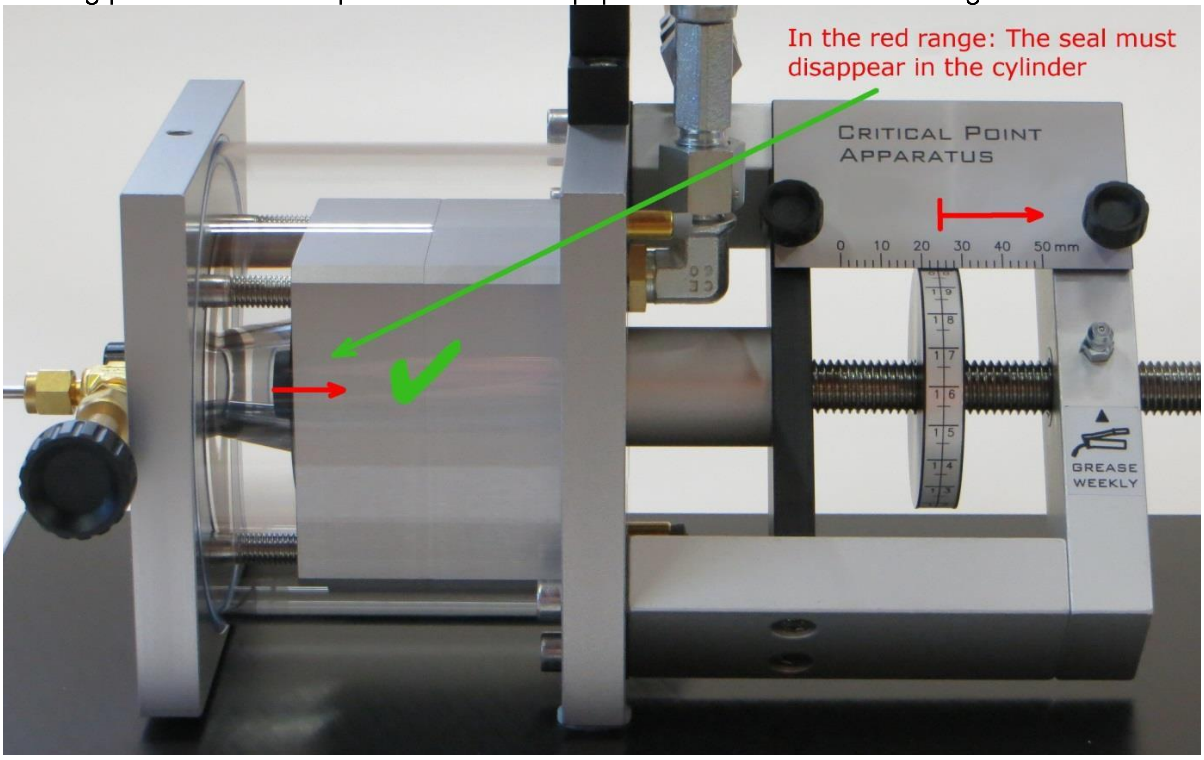
1. Set the piston with the handwheel (18) to position 10 mm.
2. Open the regulating valve (7) slowly and let ethane flow in.
   Slowly open the regulating valve (7) and allow ethane to flow in until approx. 12 bar is indicated.
3. Close the regulating valve.
4. Open the flush valve (5) slightly until the pressure display has dropped to almost 0 bar.
5. Close the flush valve.
6. Repeat steps 2-5 at least 3 times. Depending on the length of the pipe, further flushing processes may be necessary (estimate via pipe volume / measuring cell volume).
   As little as possible of the gas should be released into the environment.
7. Open the regulating valve until 12 bar is displayed again.
8. Close the regulating valve.
9. Turn the piston back to 46 mm with the handwheel.
10. Open the regulating valve slowly and close it again when 12 bar has been reached. The gas filling can remain in the measuring cell for a few weeks. If no tests are carried out, the piston should be turned back with the handwheel to a position with as little pressure as possible - i.e. to about 46 mm.

If no experiments are planned over a longer period of time (holidays), the gas should be largely drained and the cap seal (4) relieved. To do this, turn the piston to the "rest position" at about 6 mm. The hat seal is then minimally dented in the conical part and does not press against the measuring cell (9). Via the regulating valve the gas is to approx. 1 bar overpressure.

To carry out experiments at different temperatures, a circulation thermostat is connected to the connection pieces (13) via hoses with an inner diameter of 6 mm. The inlet should be at the bottom and the outlet at the top. As a temperature control medium, the use of a mixture of 2/1 volume parts water/cooler protection agent is recommended in order to avoid corrosion and efflorescence caused by electrochemical tensions between the different materials. Any radiator protection agent with additives for the protection of aluminium engines should be usable. Glysantin® G30 from BASF has been tested so far. If possible, the apparatus should always remain filled with the tempering medium. Now the tests can be carried out according to section 5.

4.3 Degassing and refilling the hydraulic oil

Due to the unavoidable diffusion of the test gas through the cap seal (4), the pressure in the measuring cell slowly decreases over a longer period of time. The gas diffusing through the hat seal is initially dissolved in the hydraulic oil and has no appreciable influence on the measurements. However, if the test gas is drained off to store the equipment and the pressure in the hydraulic oil falls to the ambient pressure, test gas escapes from the hydraulic oil in accordance with Henry's law and leads to a slow increase in pressure in the oil chamber, which must be avoided at all costs without gas back pressure in the measuring cell (see also 4.1). The following picture should be placed near the equipment as a "memorial" during maintenance work:


In the red range: The seal must disappear in the cylinder

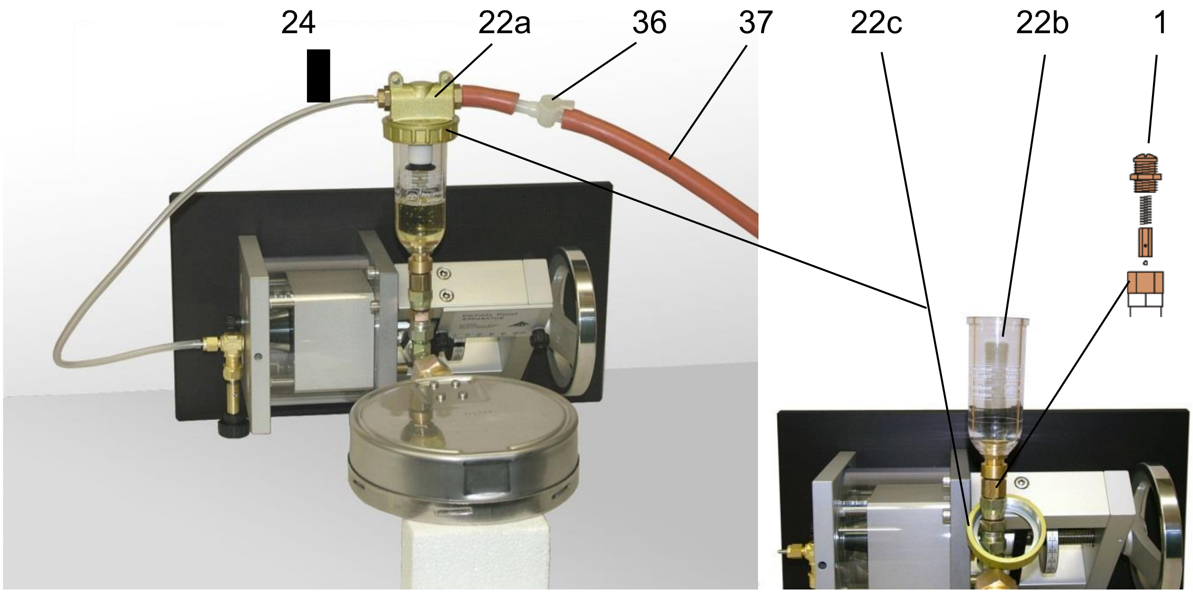


Fig. 3: Degassing the hydraulic oil using the oil filling device (items 36, 37 not included)   1 Safety valve

22a Attachment
22b Reservoir
22c Union nut
24 Hose, Inner diameter 3 mm
36 Stop cock
37 Vacuum hose

The hydraulic oil should therefore be degassed before storage. The procedure is as follows (see also Fig. 3):

1. Drain the test gas via the flush valve (5), close the flush valve.
2. If necessary, dismantle the gas pipe and fit the gas connection (6).
3. Open the regulating valve (7).
4. Turn the piston in with the handwheel (18) until 1 bar overpressure is reached (if necessary, loosen the rotating scale).
5. Close the regulating valve.
6. Turn the handwheel back by 2 revolutions. Do not turn out further than 25 mm, otherwise the guide tube (31) may slip out of the piston during the following work!
Place the apparatus on the workstation with the manometer scale facing downwards, supporting the manometer with an approx. 6 cm thick base (Fig. 3).
8. Loosen the lock nut (SW 14) of the safety valve (1) and unscrew the valve cap with a screwdriver. Remove the pressure spring, the hexagonal stem and the steel ball one after the other (tweezers) and place them in a box, for example.
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 (Fig. 3 right) and screw in the container (22b) not too tightly: the O-ring must not squeeze out.
10. Open the regulating valve and turn the handwheel all the way in on the bracket (17) (loosen the scale if necessary). Then unscrew the handwheel 6 mm (3 turns).
11. Fill the container (22b) up to halfway with castor oil (pharmacy).
12. Screw the attachment (22a) to the union nut (22c).
13. Fit the hose with an internal diameter of 3 mm (24) onto the gas connection (6) and the smaller connection piece of the attachment (22a). Check that the regulating valve is open and the flushing valve is closed (see fig. 3).
14. Connect the vacuum hose with an inner diameter of 6 mm (37) to the larger nozzle of the attachment via a stopcock (36).

15. Open the stopcock slightly and observe the castor oil. When the foaming is so strong that it reaches the filter attached to the attachment, close the stopcock and only open it again after the foam has dissipated.

16. After some time (approx. 15 min., depending on the vacuum pump connected) the vapour pressure of the castor oil is the vapour pressure of the castor oil is reached and it begins to boil. This can be bubbles appear "out of nowhere" and rapidly increase in size as they pass through the oil. rapidly as they move through the oil. Now the oil is sufficiently degassed. Close the regulating valve (7) and the stopcock (36). Pull the vacuum hose (37) off the stopcock (the piece of hose with the stopcock still remains on the oil filling device).

18. To avoid a pressure surge, open the stopcock slowly and wait for the pressure to equalise.

19. Remove the hose (24) from both nozzles.

20. Unscrew the container (22b) from the safety valve. As the castor oil is relatively viscous, it runs out of the container very slowly and this operation can be carried out without any problems. Can be carried out without any problems. A cleaning cloth (kitchen paper) held under the container immediately after unscrewing prevents any drips from forming.

21. Use a cleaning cloth to remove the excess oil from the safety valve and then turn the handwheel in slightly until the oil level in the valve is exactly at the level of the support edge of the steel plate.
22. Insert the steel ball, place the hexagonal punch with the short hole on the ball (tweezers) and insert the pressure spring into the longer hole. Tighten the valve cap (not too tight) as far as it will go and loosen by 2 turns.
23. Adjust the safety valve: To do this, open the regulating valve and turn the handwheel all the way out. Close the regulating valve again.
24. Turn the handwheel in until approx. 65 bar overpressure is reached.
25. Slowly unscrew the valve cap of the safety valve.

!

During this operation the safety valve must not point in the direction of persons or property that could be injured or destroyed if the valve cap were to shoot out. The person screwing the valve must be in front of the apparatus and reach backwards with their arms around the apparatus to reach the valve.

When the pressure drops to approx. 63 bar, the adjustment point is found and the lock nut (SW 14) is tightened.

26. Turn the handwheel back until the pressure has dropped to approx. 10 bar. Open the regulating valve and turn the handwheel to the "rest position" at approx. 6 mm. Close the regulating valve.

After this work, the apparatus can be stored or refilled with test gas.

4.4 Disassembling and reassembling the apparatus

After some 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 this, carry out the following steps.

A. Disassemble the apparatus.
1. Drain the test gas via the flush valve (5), close the flush valve.
2. If necessary, dismantle the gas pipe and open the regulating valve (7).
3. Turn out the handwheel (18) to position 25 mm.
4. Tilt the appliance to the right and place it on the handwheel (use a suitable base) and the edge of the base plate (16).
5. Use a hexagonal Allen key (SW 6) to loosen the 4 screws in the valve plate (8) evenly crosswise by 1/8 turn each until the pre-tension is relieved. Unscrew the screws completely and remove them. Also remove the copper sealing washers.

6. Turn the valve plate to the left and right with increasing force until the seals loosen (caution: do not turn the regulating valve).
7. Remove the valve plate (8). The measuring cell (9) may still be stuck to the plate.
8. Loosen the remaining seal between the measuring cell and the cylinder (10) or between the measuring cell and the valve plate by turning it again.
9. Pull off the guide tube (31) from the cap seal by twisting.
10. Clean all parts that are to be refitted. Castor oil can be removed relatively well with methylated spirit, but the acrylic glass (measuring cell, jacket) is attacked by methylated spirit. Fingerprints and other dirt can be removed in a (mild) washing-up liquid solution. The new seals should also be cleaned with spirit and a washing-up liquid solution.


Fig. 4: Aligning the round rubber seal (27)

B Assemble the equipment.

11. If castor oil has been removed from the oil chamber, pour in new castor oil up to about 5 mm below the upper edge of the cylinder (start of lowering).
12. Insert the two silicone seals (29).
13. Turn the cap seal upside down and screw the spigot into the guide tube moistened with a little castor oil.
14. Turn back the cap seal, place the spring (30) on the piston and insert the guide tube into the piston.
15. Place the measuring cell and align it evenly with the edges of the cylinder.
16. Place the temperature control jacket (2) on the lower silicone seal and centre it.
17. Place the round rubber seal (27) and align it parallel to the cylinder using a ruler placed on the temperature control jacket (see Fig. 4). The half-moons must later be located under the valve openings.
18. Place the valve plate, centre it and align it parallel to the base plate (11).
19. Fit new copper sealing washers to the M8x40 screws and screw them in loosely.
20. Tighten the screws crosswise. Check the even pressure of the round rubber seal (in areas of high pressure, the rubber seal appears grey on the acrylic glass of the measuring cell, while areas of low pressure appear milky).
21. Degas the oil chamber and castor oil according to section 4.3.

4.5 Check threaded bush and replace if necessary

The threaded bush in the bracket (17) is subject to slow but constant wear and must therefore be checked once a year for axial play: Release the pressure from the measuring cell. Hold a nut M12 (or another approximately 10 mm wide, plane-parallel part) between the handwheel flange and the bracket. Now press firmly in axial direction against the handwheel and at the same time screw it in until the nut is just not clamped. Read off the position on the scales and note it down. Then pull firmly on the handwheel, again just not tightening the nut, and read off the position. If the difference between the two positions is greater than 0.3 mm, the bushing must be replaced. If the bushing does not reach the wear limit within 10 years (no measurable wear [< 0.05 mm] could be detected after 1000 cycles in test stand trials), it must still be replaced, as no reliable data on the long-term stability of the plastic used (POM-C) is yet available.

Replacing the bushing:

1. Release the pressure from the measuring cell.
2. Unscrew the fixed scale (19).
3. Loosen the grub screw in the handwheel flange and pull off the handwheel (18).
4. Loosen the 4 screws in the cross strut (with the threaded bush) (17) and unscrew the cross strut from the threaded rod.
5. Unscrew the grease nipple (SW 7) and loosen the threaded pin screwed transversely into the threaded bush by 4 turns using a 3 mm Allen key.
6. Unscrew the M6 lock nut opposite the grease nipple and remove the threaded pin.
7. Knock out the bushing from the handwheel side with a suitable mandrel. Alternatively, an M14 screw can be loosely screwed into the bushing and the bushing driven out by hitting the screw head.
8. Position the new bushing so that the cross hole is aligned with the grease nipple.
9. Press the bushing into the vice (with flat jaws or suitable shim).
10. Screw in the set screw on the grease nipple side (recessed by at least 6.0 mm).
11. Opposite the grease nipple, plunge a 5 mm drill into the existing M6 hole and drill through the new threaded bush on one side. Then cut an M6 thread.
12. Screw the cross strut onto the M14 threaded rod and screw the M6x16 threaded pin down to the threaded rod and then loosen it again by ½ turn. Attach the lock nut in this position.

If bushings are manufactured in-house: Material POM-C = polyoxymethylene copolymer. The interference (press fit) of the bushing is 0.05 to a maximum of 0.1 mm.

5 Experimental studies

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

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

After the preparations according to section 4.2, series of experiments can now be systematically carried out at constant temperature and varying volume to determine isotherms. If the test gas pressure at maximum volume (handwheel fully turned out) is 12 bar, it is advisable to approach the measuring points "from below" up to a piston position of approx. 10 mm, i.e. the handwheel is turned in to a certain position, the position is noted and the corresponding pressure is read off after the equilibrium setting. Reaching equilibrium can be recognized by the fact that the pressure no longer changes over a longer period of time.

In the range of small volumes below the 10 mm position, it makes sense to approach the measuring points "from above", i.e. from high (max. 60 bar) to lower pressures, in order to achieve a quick equilibrium setting. This is due to the fact that during the phase transition from liquid to gaseous, the phase boundary surface is significantly larger due to vapour bubbles that occur everywhere in the liquid than in the case of the phase transition from gaseous to liquid, where the phase boundary surface is limited to the liquid surface. Of course, the order of the measurements has no influence on the state of equilibrium. If the experiments are carried out in the manner described, then about 1 - 5 min. pass until equilibrium is reached, whereby the measuring points at the edge of the two-phase area require the longest time.

Alternatively, the temperature can also be varied at constant volume. If the measuring points are in the two-phase range, the vapour pressure curve is obtained in this way. However, with a temperature change, the equilibrium setting takes considerably longer than with a volume change, since the water bath and the measuring cell must first reach the desired temperature. Depending on the quality of the circulator, up to 20 min. can be expected.

During the experiments, the **critical opalescence** can also be observed near the critical point: Due to a constant change between the liquid and gaseous state in small areas of the measuring cell, a kind of "fog" is created and the sulphur hexafluoride appears cloudy.

6 Test evaluation

6.1 Theoretical basics - Isotherms in the Clapeyron diagram

While the ideal gas equation (Eq. 4) is fulfilled in a good approximation for air under "normal" ambient conditions, considerable deviations from the ideal behaviour must be taken into account for states in the two-phase range and in the vicinity of the critical point. Van der Walls proposed the simplest equation of state, which illustrates the principle fluid behaviour quite clearly:

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

In this equation, the two parameters a and b occur in addition to the already known variables. If - according to experimental observations - it is required that at the critical point (index c)

$$\left.\frac{\partial p}{\partial V}\right|_c = 0 \text{ und } \left.\frac{\partial^2 p}{\partial V^2}\right|_c = 0 \tag{13}$$

holds, then a and b can be determined:

$$a = \frac{3V_c^2 p_c}{n^2} \text{ und } b = \frac{V_c}{3n}. \tag{14}$$

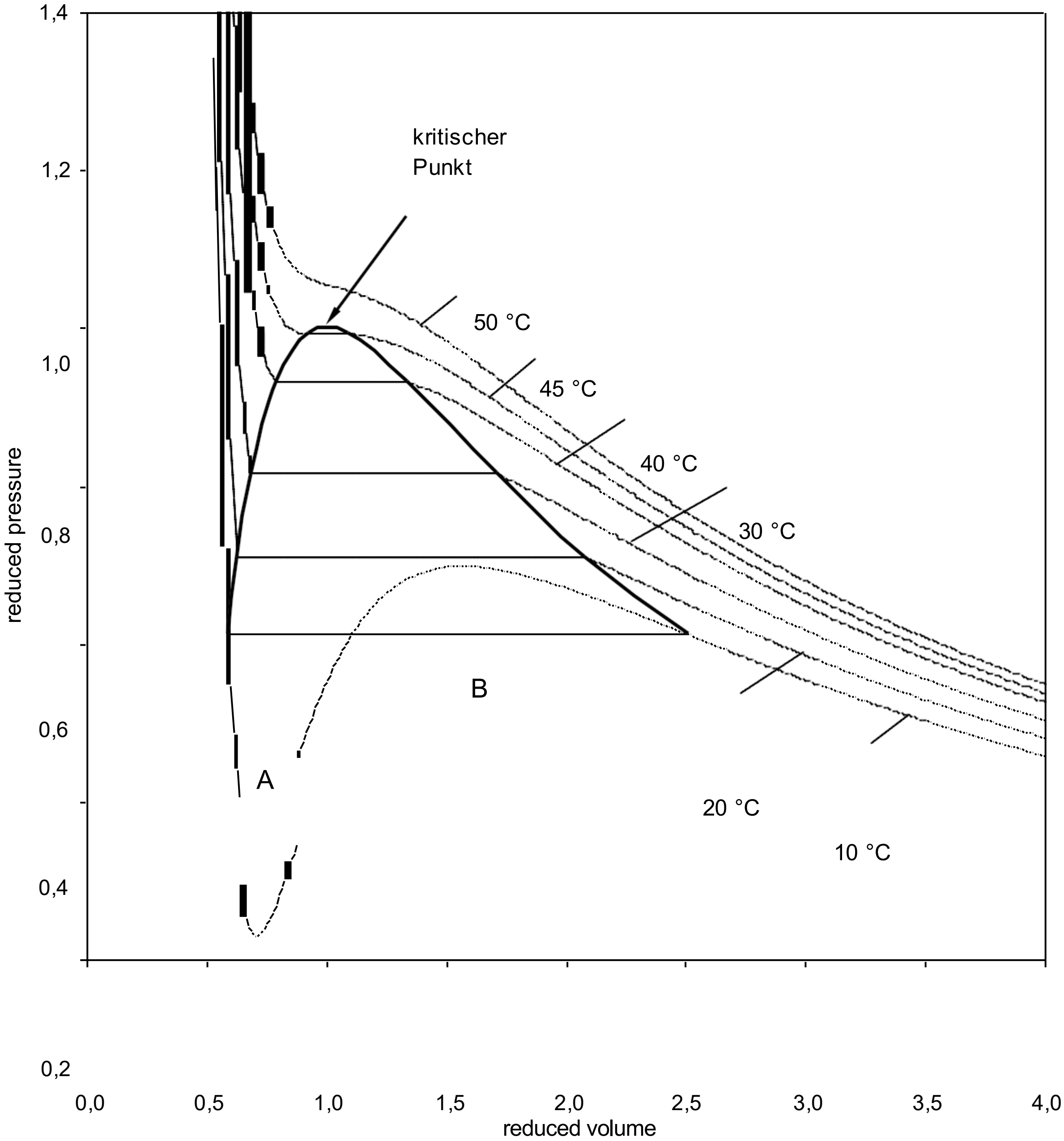


Fig. 5: Isotherms calculated according to van der Wall. Although the diagram is valid in principle for all gases, the parameters on the curves are not the reduced temperatures, but the substance-specific temperatures for ethane, in order to enable a better comparison with the measured values.

Will the reduced sizes now still be

$$p_r = \frac{p}{p_c}, \; V_r = \frac{V}{V_c} \text{ und } T_r = \frac{T}{T_c} \tag{15}$$

is introduced, then substituting in eq. 12 after some transformations yields the general, shock-dependent form of the van der Waals equation of state

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

This equation is cubic with respect to Vr. The graphical representation of several curves pr(Vr) at constant temperature is called a Clapeyron diagram. The curves can have two extreme values - a minimum and a maximum (cf. Fig. 5). However, since experiments in the two-phase range usually do not show extreme values but a constant pressure curve, a horizontal straight line is placed between the minimum and the maximum, whereby equality of the two surfaces A and B between the curve and the straight line is required as a boundary condition.

The line connecting the intersections of the curves and the straight lines at different temperatures is called a binodal. It separates the two-phase region from the liquid or steam. The line connecting the maximum and minimum values also has a physical meaning. It is called spinodal and delimits the area in which phase decay occurs in any case. Between the spinodal and the binodal, superheated liquid or supercooled vapour can be present.

6.2 Comparison of measured values, literature data and theory

During the experimental procedure according to section 5, temperatures, overpressures, and piston positions are measured. First, the overpressures should be converted into absolute pressures and the piston positions into volumes according to Eq. 7 and Eq. 9.

It is not possible to determine the ethane molar quantity in the measuring cell according to Eq. 11 because ethane is not an ideal gas. One possibility to determine the gas mass is to blow the gas out of the measuring cell into a plastic bag and to weigh it afterwards (consider air buoyancy!). To avoid errors due to dead volumes, proceed as follows: The handwheel is turned out far (e.g. to 46 mm and 8 bar overpressure) then the gas is released into the plastic bag via the regulating valve with mounted connection piece. After closing the regulating valve, the pressure in the measuring cell is increased again to the original value (8 bar in the example). From the difference in volume before and after emptying (this quantity is in the plastic bag) and the volume still present in the measuring cell, it is easy to calculate the quantity of gas originally present.

A simpler way to determine the gas quantity is to compare it with literature values. Table 1 shows some measured values from Clegg et al [4]. If, for example, a measured value was recorded at t = 49.86 °C, p = 28.44 bar and V = 4.7 ml, the specific volume is 4.469 ml/g and the gas mass in the measuring cell was 1.05 g during the experiments.

n / V mol / dm^3	$Z = pV / nRT$ -	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 1: In the first 3 columns some measured values from Clegg et al [4] are entered. From these measured values, the specific volume and the pressure were calculated.

This gas mass determination was made in the measurements shown in Fig. 6, which were obtained with the experimental apparatus described here at the critical point. It can be seen that despite the relatively simple apparatus, measured values are obtained that need not fear comparison with the literature values also plotted in the diagram.

A comparison with the equation of state according to van der Walls (Fig. 5) shows that the simple theory does not lead to satisfactory results here. While according to van der Walls the vapour pressure decreases by only about 40 % when the temperature is lowered from 45°C to 10°C, the measured values show a decrease of almost 60 %. In fact, there is still no model that correctly describes all substances in the entire range from liquid to two-phase and gaseous to supercritical. Depending on the substance and the application, different equations are used. As keywords for further research, only the "Peng- Robinson equation of state" and "GE models" are mentioned here.

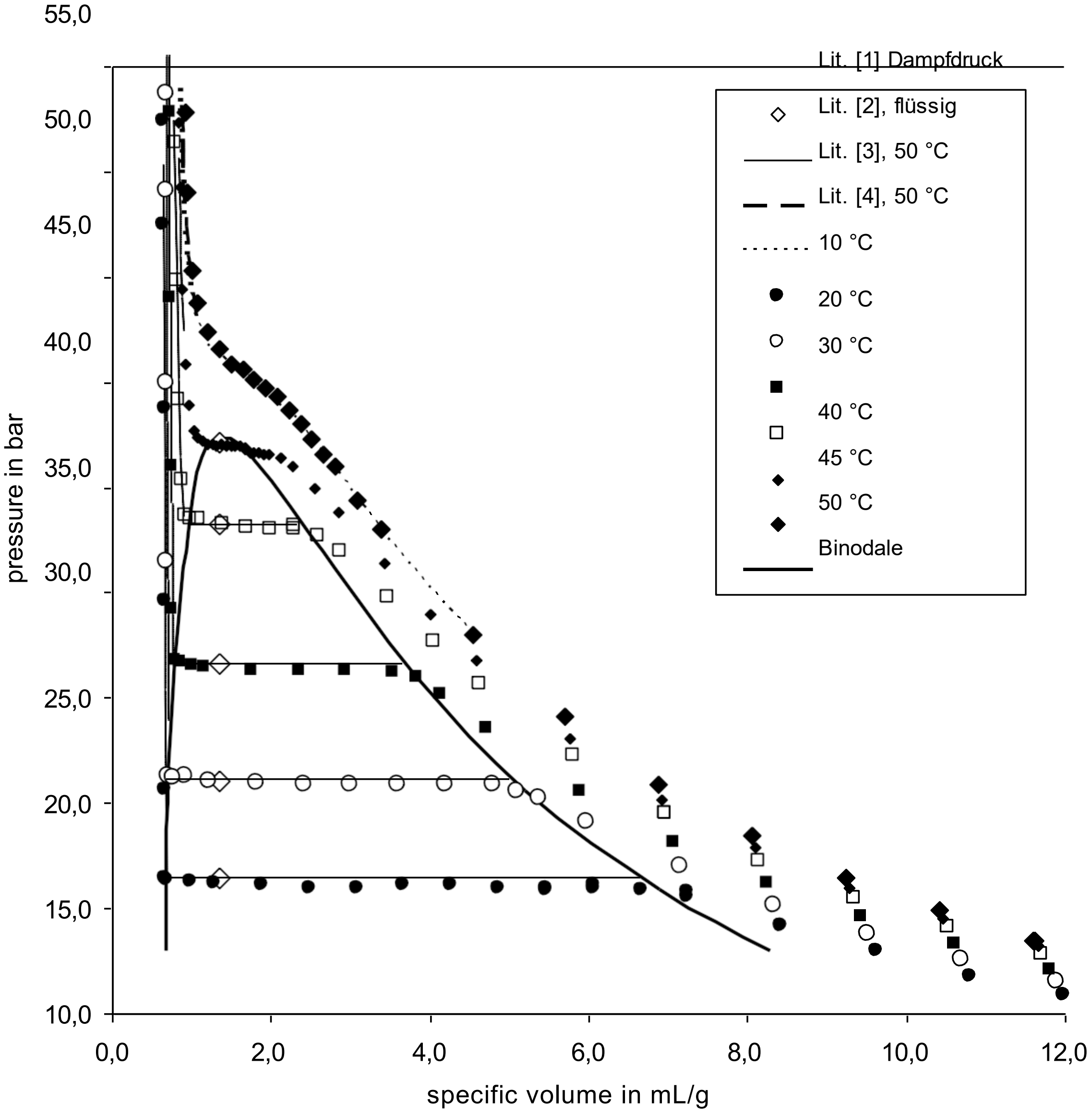


Fig. 6: Comparison of literature data [1-4] and measured values. In order not to overload the diagram, the literature values are shown as lines.