TRANSPARENT CELL FOR THE MEASUREMENT OF THE HIGH-PRESSURE VAPOUR–LIQUID EQUILIBRIUM*

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An equilibrium still with a transparent cell and recirculation of the vapour phase was constructed. The cell makes it possible to observe visually phase equilibria at temperatures and pressures up to critical. Correct performance of component parts was tested by measurement of saturated vapour pressures of ethane and propane from 20°C to the critical temperature.

The experimental apparatus and technique of the measurement of the high-pressure vapour–liquid equilibria have been verified and tested by Vejrosta[1,2]. A disadvantage of this apparatus consisted in the fact that the equilibrium cell had been fabricated as a steel autoclave so that for its correct filling — namely in the critical region — a considerable experimental skill was required and, moreover, a visual observation of the system was impossible. In this work a high-pressure glass cell is described, which not only enables such direct observations in the vicinity of the critical point but it also facilitates them considerably.

EXPERIMENTAL

The basic part of the apparatus imbedded in a two-stage thermostat is the equilibrium still consisting of the equilibrium cell, recirculation pump and pressure transducer. Further parts are the charging system, sampling and analytical parts, pressure compensating system and measurement of the temperature.

The main part of the *equilibrium cell* (Fig. 1) is a 150 mm-long thick-walled tube 1 made of 18 mm I.D. and 65 mm O.D. tempered Simax glass. Parallelly ground and polished faces of the tube are clasped with two stainless steel flanges 3 provided with teflon packings 6 and 7. The flanges are connected with four bolts 2 which, due to different thermal expansion coefficients of steel and glass, are manufactured from kovar protected against corrosion by nickel electroplating. The upper flange contains a teflon-packed bushing 4 with two soldered capillaries 5 serving for sampling the equilibrium phases. Both flanges are provided with holes for inlet 8 and outlet 9

of the recirculated vapour phase. The hole in the bottom flange is also employed for introducing the prepared substance (mixture) from the charging system. The assembled equilibrium cell (with a non-tempered tube) was subjected to a pressure test with water and it yielded to a pressure of 200 atm.

The magnetic recirculation pump (constructed according to[3]) takes away the vapour phase from the upper part of the equilibrium cell and pushes it back from below. Thus, the liquid is mixed thoroughly with bubbles of the vapour phase, reaching effectively the equilibrium state. The basic part of the pump is a stainless (internally ground) seamless tube, in which a stainless magnetic piston provided with a teflon check valve is moving. The bottom of the pump contains the check valve, too. A permanent external magnet, composed of ferrite rings is moving along the tube. It is driven by a motor whose revolutions are reduced by a worm gear box and the rotational movement is transmitted by a crosshead and rods so that a frequency of 12 min^{-1} at lift of about 20 ml is reached.

The most important part of the *pressure transducer* is a phosphor bronze membrane of the diameter of 50 mm and thickness 0·1 mm. The whole transducer is constructed so that a permanent deformation of the membrane by overpressure from its both sides may be excluded. For this purpose, the spaces both above and below the membrane are minimal — the resulting space is less than 1 mm. Through the centre of the upper part of the transducer passes an adjustable electrically insulated steel needle which, being in contact with the membrane, closes the electric circuit of the pressure compensating system. A zero position of the needle with respect to the membrane must be adjusted before the measurements. After connecting the equilibrium apparatus with the compensating system and atmosphere, the needle is adjusted so that the electric circuit may be just disconnected. The overpressure in the equilibrium apparatus, which closes consequently the contacts in the transducer, determines sensitivity and accuracy in the pressure adjustment which amounts to 0·01 atm.

In view of large heat capacities, the assembled equilibrium apparatus is determined rather for measuring isothermal data. For maintaining the constant temperature, a two-stage thermostat
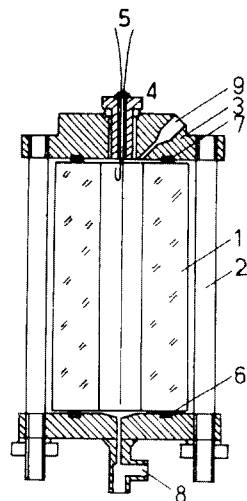

Fig. 1

Equilibrium Cell
1 Glass tube, 2 bolt, 3 flange, 4 bushing, 5 sampling capillaries, 6, 7 teflon ring, 8 inlet, 9 outlet.

of the volume of 120 l was constructed. In the centre of the double-walled bath vessel is located a glass tube (with a bottom) of the diameter of 300 mm and height 350 mm, which constitutes the inner thermostat serving as a termal capacity for eliminating temperature fluctuations. It has no own heating and its content is mixed intensely with a screw stirrer. The temperature of the external thermostat is controlled by a contact thermometer so that the long-term stability of $\pm 0.01°C/24$ h and local time accuracy $\pm 0.005°C$ in the inner thermostat might be achieved. All parts of the apparatus which come into contact with the measured system are manufactured from stainless steel. Connecting lines are made uniformly of 4×1 mm tubes and removable joints.

The charging system contains glass fingers serving for the degassing and approximate sampling of materials condensed into the steel finger connected with the equilibrium apparatus through a closing valve. The pressure resulting from an external heating of this finger may displace its contents into the system.

The sampling is performed by the copper-capillary technique[1] with 0.15 mm O.D. and 0.05 mm I.D. capillaries. One of the capillaries reaches to the bottom of the equilibrium cell so that the sampling of the liquid phase may be possible even at low amounts of the liquid in the cell. The second capillary ends approximately 10 mm below the upper flange and its end is directed upwards. This removes the possibility of entraining a drop condensed on the capillary into the sample of the vapour phase. Both capillaries pass loosely through the thermostat lid, where they may be easily opened, closed or injected directly into the inlet of the gas chromatograph (if it is used for the analysis).

The primary side of the *pressure compensating system* consisting of a 2000 ml nitrogen container is separated from the secondary (measuring) side by two solenoid valves with different nozzle diameters. The measuring side is formed by the same buffering vessel (2000 ml) connected to a precise manometer and the pressure transducer which controls the valves. The pressure in the system is measured by a Heise bourdon gauge with the range of 50 atm. The manometer has two pointer revolutions (660°) with the diameter of 280 mm. It was calibrated by the manufacturer against a pressure standard certified by the National Bureau of Standards and its relative error is 0.1% of full scale. The local reproducibility amounts, however, to 0.01 atm.

TABLE I

Comparison of the Experimental and Literature Saturated Vapour Pressures of Ethane

T K	P_{exp} atm	$P_{calc} - P_{exp}$, atm		
		this work	ref.[7]	ref.[6]
283.36	29.92	0.00	0.01	0.18
288.17	33.32	−0.01	0.00	0.21
293.37	37.31	0.01	0.02	0.24
298.17	41.37	0.00	0.00	0.18
303.19	45.99	−0.01	−0.02	0.07
305.13	47.87	0.01	0.00	0.04

The temperature of the inner thermostat is measured by a Heraeus three-lead platinum resistance thermometer ($R_0 = 100$ ohm). This thermometer was calibrated against a Leeds and Northrup standard platinum resistance thermometer provided with the National Bureau of Standards certificate and connected to a Mueller bridge. The accuracy of the temperature measurements was better than $0.01°C$.

Construction details of the whole apparatus are described elsewhere[4].

Materials used. Ethane, research grade (*puriss.*) was manufactured by Fluka, Switzerland with a 99.97% certified purity and containing acetylene as the main admixture. Propane (*puriss.*) was also manufactured by Fluka with a 99.9% certified purity and containing mainly isobutane. Both substances were not purified further.

RESULTS AND DISCUSSION

To verify different functions of the apparatus, saturated vapour pressures of ethane (in the range $20-32°C$) and propane ($20-96°C$) were measured. The results were correlated by the reduced Waring equation[5]

$$\log P_r = A + B/T_r + C \log T_r + DT_r^6 , \qquad (1)$$

TABLE II

Comparison of the Experimental and Literature Saturated Vapour Pressures of Propane

T K	P_{exp} atm	$P_{calc} - P_{exp}$, atm		
		this work	ref.[6]	ref.[8]
283·36	6·32	0·00	0·01	0·00
283·48	6·34	0·01	0·02	0·00
293·34	8·33	−0·02	0·00	−0·03
303·07	10·66	0·00	0·02	−0·03
303·15	10·68	0·00	0·02	−0·03
303·20	10·71	−0·01	0·00	−0·05
312·88	13·46	0·02	0·05	−0·03
313·10	13·55	−0·01	0·03	−0·05
323·15	16·95	0·02	0·07	−0·05
323·16	16·96	0·01	0·07	−0·05
333·09	20·91	0·02	0·10	−0·05
343·17	25·66	−0·05	0·06	−0·11
363·17	37·25	−0·04	0·03	−0·02
367·66	40·31	0·00	0·02	0·05
369·18	41·36	0·04	0·05	0·11

where P_r is the reduced pressure and T_r reduced temperature. The constants are $A = 1\cdot00317, B = -1\cdot03039, C = 3\cdot58447, D = 0\cdot02717$ for ethane and $A = 3\cdot53169$, $B = -3\cdot61951, C = -3\cdot05116, D = 0\cdot08710$ for propane.

The following procedure was used so that a comparison between the measured and literature data might be possible. Saturated vapour pressures (P_{calc}) were calculated from correlated literature data at our experimental temperatures (T) and these were compared with our data (P_{exp}). As one of the consistent sources, published constants of the six-parameter Thodos equation[6] were employed. The most recent data for ethane by Douslin and Harrison[7] and critically evaluated data by Das and Eubank[8] were also used; both of them were correlated by the Waring equation. Results of our measurements and comparisons are shown in Tables I and II.

The measured saturated vapour pressures of ethane practically coincide with the excellent data[7], the pressures of propane lie between both sets of the literature data. The relative scatter of single points from the correlation curve is even lower than the accuracy of the pressure measurements.

These results show that the described apparatus for measuring the phase equilibria at high pressures is reliable and that it can also be used for measuring two- and multicomponent systems.

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Translated by K. Hlavatý.