

SEMIMICROSTILL FOR THE DETERMINATION OF HIGH PRESSURE VAPOUR-LIQUID EQUILIBRIUM*

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The equilibrium still consisting of a small volume cell, a simple capillary sampling system (which requires no valves and eliminates dead volumes), and a specially designed mixer was constructed and tested on the propane-pentane system at pressures up to 45 atm.

Despite of considerable progress of prediction methods the experimental determination of phase equilibrium still remains the only reliable source of the data needed for the design of the industrial separation units. A lot of papers has been devoted to experimental techniques suitable for the measurements of temperature, pressure, and composition of equilibrium phases. Most of these papers deal with normal or slightly elevated pressures at which the measurement is easy. The determination of phase equilibrium is much more difficult at high pressures, especially in the critical region. For the petrochemical industry, natural gas processing, and low temperature rectification the description of critical region is extremely important. The high pressure region also offers more space for a further development of experimental techniques comparing it with low pressure region which has been investigated very thoroughly.

In the present work a new static semimicromethod for the determination of vapour-liquid equilibrium in the high pressure region is described. The static still was chosen for the following reasons: *a*) it is suitable for the measurement almost in the whole two-phase region; *b*) the volume of the equilibrium cell can be reduced substantially finding a proper sampling system; *c*) its construction is the simplest comparing it with other stills. Particularly, the special attention was paid: to small volume of equilibrium cell; to the elimination of dead volumes; to simple sampling with direct connection to the gas chromatograph; to intensive stirring of the equilibrium phases.

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EXPERIMENTAL

The flow diagram of the complete apparatus is schematically shown in Fig. 1. The *equilibrium cell* (Fig. 2) is made of stainless steel with inner volume of 22 ml. It is immersed in the tempering bath enabling the temperature control within the range of 0.01°C. The effective mixing in the cell is not only time-saving but also guarantees the reaching of equilibrium at given conditions. Therefore, the ferromagnetic mixing body underlaid with the coil spring is placed into the cell. The jet-shaped hole drilled through the body, being periodically pulled into the liquid phase by means of the electromagnet, causes the intensive dispersing of liquid drops in the vapour phase.

The *pressure* is measured indirectly in the compensating nitrogen system by using the membrane type pressure transducer. The main parts of the pressure transducer are an elastic bronze membrane and an adjustable contact. The contact connected with the relay controls the pressure in the compensating system. Before the measurement the contact must be adjusted to the zero position (at atmospheric pressure on both sides of a membrane). The adjustment must be done in such a way that the difference between "on" and "off" contact positions is as small as possible. This pressure difference (never greater than 0.02 atm) corresponds to the sensitivity of the transducer. The compensating pressure is equilibrated automatically (by means of the electromagnetic valves) according to the system pressure. At the equilibrium (or at constant) pressure the continuous control of zero position is reached by slight discharge of the compensating gas (nitrogen). Then the pressure of the system is equal to the reference pressure with an accuracy corresponding to the sensitivity of the transducer. The pressure of nitrogen is measured by means of Heise pressure gauge rated up to 100 atm with the accuracy 0.1% of the full scale value.

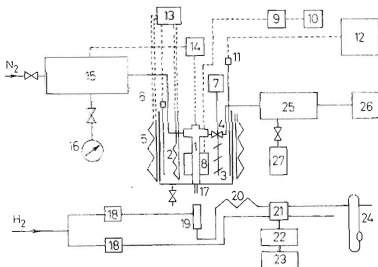


FIG. 1

Flow Diagram of the Apparatus

1 Equilibrium cell, 2 inner heater, 3 paddle-wheel stirrer, 4 needle valve, 5 outer heater, 6 contact thermometer, 7 motor drive, 8 electromagnetic coil of mixing system, 9 contactor and transformer, 10 timer for mixing system, 11 Pt-resistance thermometer, 12 resistance bridge, 13 temperature control system, 14 pressure control, 15 compensating pressure system, 16 pressure gauge, 17 sampling capillaries, 18 carrier gas flow rate control, 19 injector, 20 chromatographic column, 21 thermal conductivity detector, 22 measuring bridge, 23 recorder, 24 differential flow meter, 25 charging system, 26 vacuum pump, 27 propane cylinder.

The withdrawal of the *phase samples* without considerable affection of the equilibrium is the problem which is usually solved as the case may be. In this work the sampling is realized using thin copper capillaries with 0.5 mm O. D. and 0.1 mm I. D. approximately which can be also used for the injection into the gas chromatograph. These capillaries were simply made of 2 mm O. D. soft copper tubing by cold drawing through the draw plate. The main advantage is above all the easy handling because the capillary can be closed squeezing its end by pliers and opened after scoring and breaking off. For sampling the capillary is opened and after a few seconds of flushing its end can be directly injected into the gas chromatograph inlet likewise a needle of a syringe. This kind of sampling is very simple and due to the small amount withdrawn, the equilibrium in the cell is disturbed only slightly and does not affect the results at all. The inner volume of capillary (2.5 mm^3) represents about 0.01% of the cell volume.

RESULTS AND DISCUSSION

The vapour pressure of propane was measured to check the pressures transducer operation. The comparison of experimental vapour pressures with those calculated by

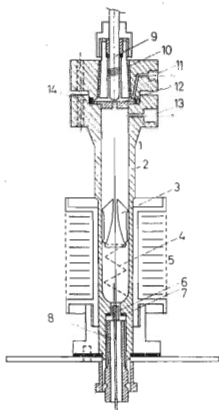


FIG. 2

Equilibrium Cell and Pressure Transducer

1. Equilibrium cell body, 2 vapour sample line, 3 ferromagnetic jet-shaped mixer, 4 coil spring, 5 coil of electromagnet, 6 bushing for sampling line, 7 teflon packing, 8 liquid sample line, 9 adjustable contact, 10 insulation, 11 nitrogen inlet, 12 membrane, 13 cell inlet, 14 teflon packings.

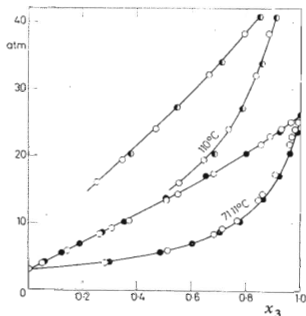


FIG. 3

Comparison of Experimental Data of the Propane-Pentane System

x_3 Mole fraction of propane. Data: \circ this work, \bullet Sage and Lacey², \bullet Kay³.

TABLE I
Comparison of Experimental and Calculated Vapour Pressures of Propane

Temperature, K	P_{exp} , atm	P_{calc} , atm	ΔP^a , atm
313.76	13.81	13.78	-0.03
324.59	17.52	17.56	0.04
336.56	22.48	22.55	0.07
344.26	26.25	26.27	0.02
350.95	29.76	29.85	0.09
360.92	35.81	35.82	0.01
365.70	39.06	38.98	-0.08
367.67	40.46	40.34	-0.12
		<i>Mean</i>	± 0.06

$$^a \Delta P = P_{\text{calc}} - P_{\text{exp}}$$

means of the Thodos equation (constants taken from¹) is presented in the Table I. The agreement with experimental vapour pressures ranging from 13 to 41 atm (critical pressure is 42 atm) is within the accuracy of pressure measurement.

The vapour-liquid equilibrium measurement of the propane-pentane system was used to test the complete still operation. It was carried out isothermally and compared with Sage and Lacey² data (for isotherm lower than critical temperature of propane) and with data published by Kay³ (for higher temperature). Even though there are small deviations along the vapour curve the agreement is within the accuracy limits and generally very good. As for these deviations, the recent investigations⁴ showed the course of data presented here seems more probable in comparison with literature data. The pressure *versus* composition diagram is presented in Fig. 3.

The results show that the new still is suitable for the high pressure vapour-liquid equilibrium measurements. The procedure is very simple and it requires only small amount (5-10 ml) of liquid phase for the determination of one experimental point. The method is applicable to any system which can be analyzed by means of gas chromatograph, especially to hydrocarbon mixtures.

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