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Vapor-Liquid Equilibria Up to 40 000 KPa and 400°C: A New Static Method

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The present work was undertaken in order to obtain data for hydrogen-hydrocarbon systems at high pressures and temperatures. The cell materials and the measurement method were chosen with this objective. The method is especially suitable to study mixtures composed of at least one permanent gas and one high boiling liquid between 150° and 400°C and 5 000 and 40 000 KPa.

Both dynamic and static methods can be used at high temperatures and pressures. A static method seemed more appropriate for a not too expensive laboratory apparatus.

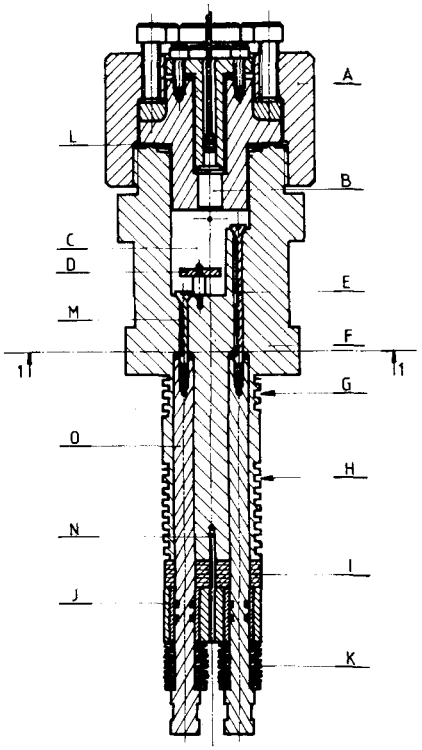

Figure 1*a*. Equilibrium cell: A cell cap, B pressure transducer, C equilibrium compartment, D magnetic stirrer, E valve, F cell body, G heating resistance place, H coaling coil place, I teflon thermal shield, J viton O-ring, K spring washers, L copper gasket, M channel, N thermocouple well, O valve pusher.

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The existing sampling methods are not entirely satisfactory, and that is the reason which led us to devise a new sampling method.

The sampling procedure uses a microexpansion which is obtained through the rapid opening of a small aperture valve. The amount of withdrawn sample is small enough (about 1μl) not to modify equilibrium conditions in a 50 cm^3 cell. Such small samples can then be analyzed by means of gas-liquid chromatography.

EQUILIBRIUM CELL

The cell (Figure 1) is made of a special stainless steel which is amagnetic and hydrogen resistant.

The sampling system is located at the bottom of the cell body. Two holes were drilled through the cell bottom. The lower opening is used to sample the liquid phase, and the higher one samples the gas phase. These holes contain the stems of two valves, the seats of which are machined in the cell body material. The main difficulty is to achieve a reliable leakproof seal; we found that the best way is to deposit a smooth metal into the conical part of the valve. The samples flow through slits machined along the valve stems (Figure 1*b*) and encounter the chromatographic carrier gas at level 1.1 (Figure 1). Sampling is achieved thanks to rapid vertical percussions generated by a hammer activated by an electromagnet and transmitted to the valves by pushers, O (Figure 1). The valves are brought back on their seatings by very strong spring washers K (force $\simeq$ 200 daN). Tightness around the pushers is achieved by means of viton O rings, J (Figure 1) which must be cooled not to be heat damaged. Heat transfer from top to bottom of the

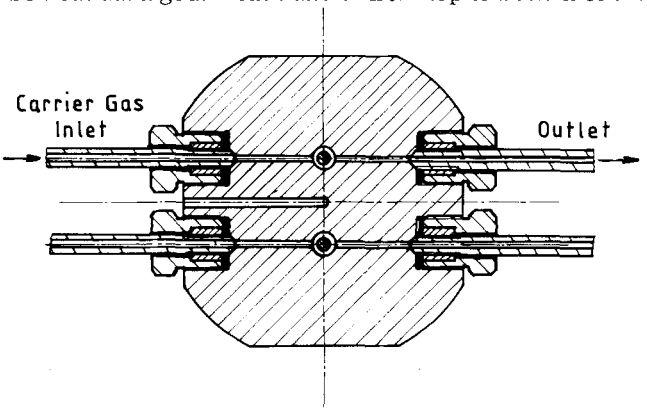

Figure 1*b*. Carrier gas circulation through the cell to sweep samples (cross section 1-1).

cell is minimized by means of Teflon thermal shield I. Water cooling tubing H is wounded around the low part of the cell just above the Teflon shield to preserve it from overheating. In order to check that the whole studied mixture remains at the same temperature, four thermocouples are located within the cell body at different levels. A heating resistance G is used to compensate for the cooling effect of water cooling H. The cell cap A contains the pressure transducer B. Leak proof connection to the cell body is achieved by means of a copper gasket (width: 0.2 mm).

In order to rapidly reach equilibrium inside the cell, efficient stirring is achieved by means of a magnetic stirrer rotating in an orientable magnetic field induced by four coils located outside the cell.

An air thermostat has been chosen to control temperature; after each experiment, the cell is still clean and can be easily handled. Furthermore, when we work with hydrogen containing mixtures, the thermostat chamber can be filled with nitrogen instead of air to prevent explosion hazard.

Temperature is measured in different points of the cell through calibrated thermocouples with an accuracy of 0.5°K; the gas thermostat temperature is controlled to better than 0.5°K.

The pressure transducer is calibrated for each experimental temperature. A dead weight gauge tester is used, and the pressure accuracy has been found to be 40 KPa.

OVERALL EXPERIMENTAL SETUP

Figure 2 shows the whole experimental system which is composed of a degassing cell D which is used to degas liquids and then to feed them to the pressure cell under a vacuum, a compressor C which feeds gases under pressure to the cell, a Bourdon gauge manometer B to check the pressure during the latter operation, cooling (CW) and heating (TC) systems, a gas liquid chromatograph GLC with its inert gas supplier protected against the risk of sampling valve rupture by two rupture disks (upper resistance 1 000 KPa) and the electromagnet EM and its power supply EPS.

When we work with hydrogen, the gas thermostat and chromatograph are placed inside a ventilated box (2 000 m³/h air flow).

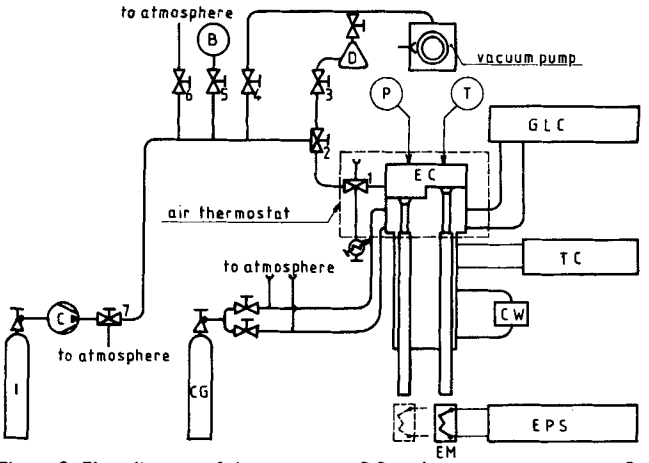

Figure 2. Flow diagram of the apparatus: B Bourdon gauge manometer, C compressor, CG carrier gas for GLC, CW cooling regulator, D degassing cell, EC equilibrium cell, EM electromagnet, EPS electromagnet power supply, GLC chromatograph, I gas cylinder, P pressure transducer, T temperature measurement from 5 thermocouples, TC temperature controller for the bottom of the equilibrium cell, Y rupture disc, ▷|◁ valve.

TEMPERATURE AND PRESSURE RANGE OF OPERATION

Such a sampling and analytical method requires the liquid sample to be in a vapor phase. This requirement

Table 1. Total Pressure as a Function of Mole Fraction of Nitrogen in Liquid and Vapor Phases for Nitrogen (1)-*n*-heptane System

P (100 K Pa)	x_1	y_1	P (100 K Pa)	x_1	y_1
T = 180.0°C			T = 224.0°C (first experiment)		
294.5	0.67	0.69	130.5	0.33	0.69
276.5	0.56	0.79_5	111	0.25	0.70
250.5	0.49*	0.84	97.5	0.23	0.69
223	0.43	0.86*	80.5	0.18	0.68*
201	0.39	0.87	78	0.17	0.67_5
161	0.305	0.88	60.5	0.12	0.61_5
116	0.215	0.87	43.5	0.08	0.56
91.5	0.16_8*	0.86_5	31	0.04*	0.43_5
72	0.12	0.85			
56	0.09_8*	0.83_5			
37	0.06_2*	0.77			
26.5	0.04*	0.67			
25.5	0.04*	0.66			
21	0.03*	0.61			
17.5	0.02_3*	0.54_5			
15.5	0.01_8*	0.47_5			
T = 190.0°C			T = 224.0°C (second experiment)		
238.5	0.63	0.68_5	28	0.03	0.38
205.5	0.46	0.80_5	37.5	0.06_3*	0.48
186.5	0.40	0.80_5	49.5	0.09_4*	0.57
165.5	0.35	0.80	67.5	0.14_2*	0.63_5
139	0.30	0.80_5	86	0.19_2*	0.69_5
125	0.26_2*	0.80_5	140.5	0.36_5	0.66_5
94.5	0.19	0.80_5	146.5	0.41	0.65
60	0.11	0.75_5	150.5	0.44	0.62_5
43	0.07	0.69	154.8	0.49	0.59
35.5	0.06*	0.65			
31.5	0.05_5	0.61_5			
21	0.02_7*	0.48_5			
12	0.008	0.170			

*Smoothed values from experimental curve $P = f(x_1)$ or $P = f(y_1)$.

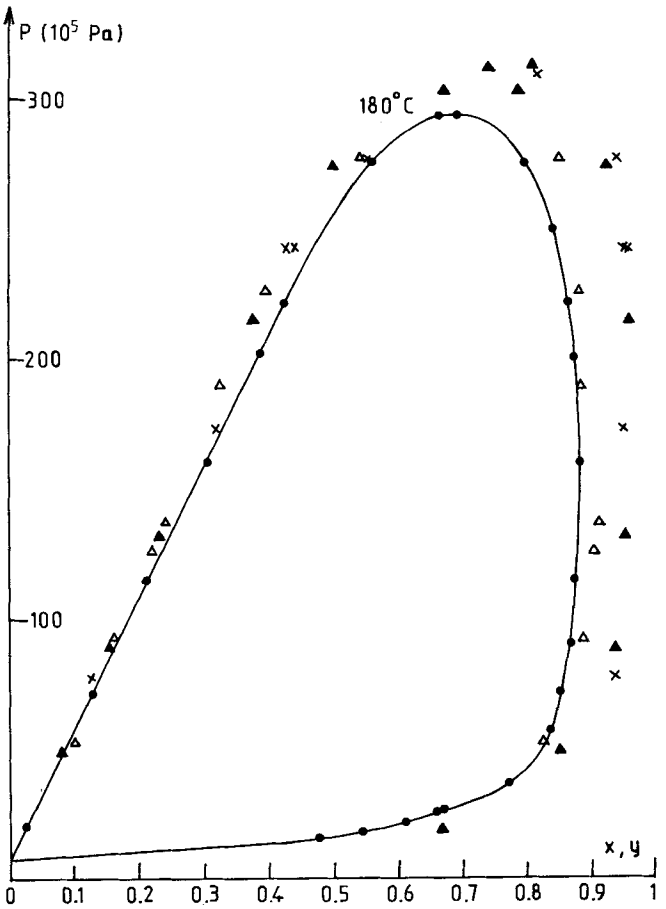

Figure 3. Pressure as a function of nitrogen mole fraction in nitrogen (1) -n-heptane (2) system at 180.0°C. ● our results, △ Peter's results (1974), ▲ Peter's results (1970), X Aker's results (1954).

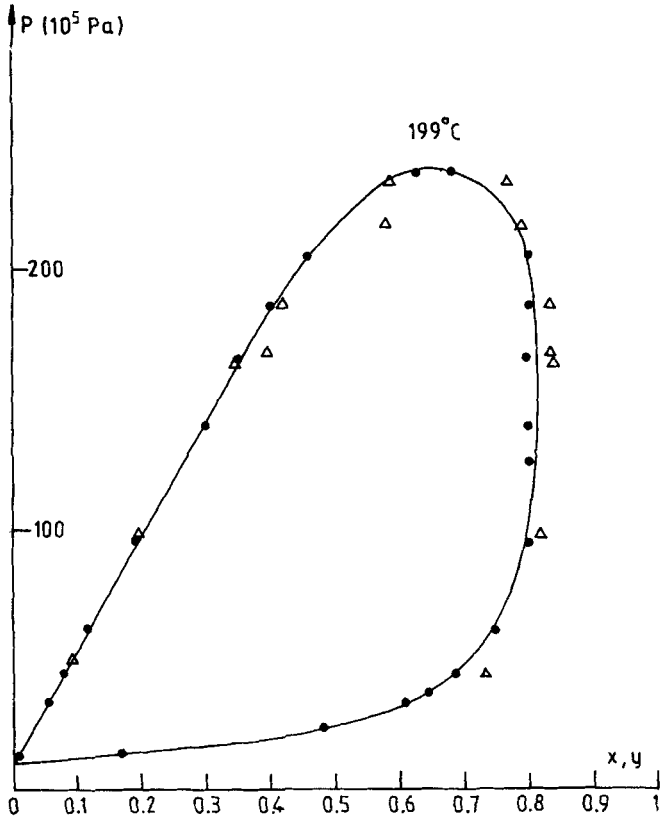

Figure 4. Pressure as a function of nitrogen mole fraction in nitrogen (1)-n-heptane (2) system at 199.0°C. ● our results, △ Peter's results (1974).

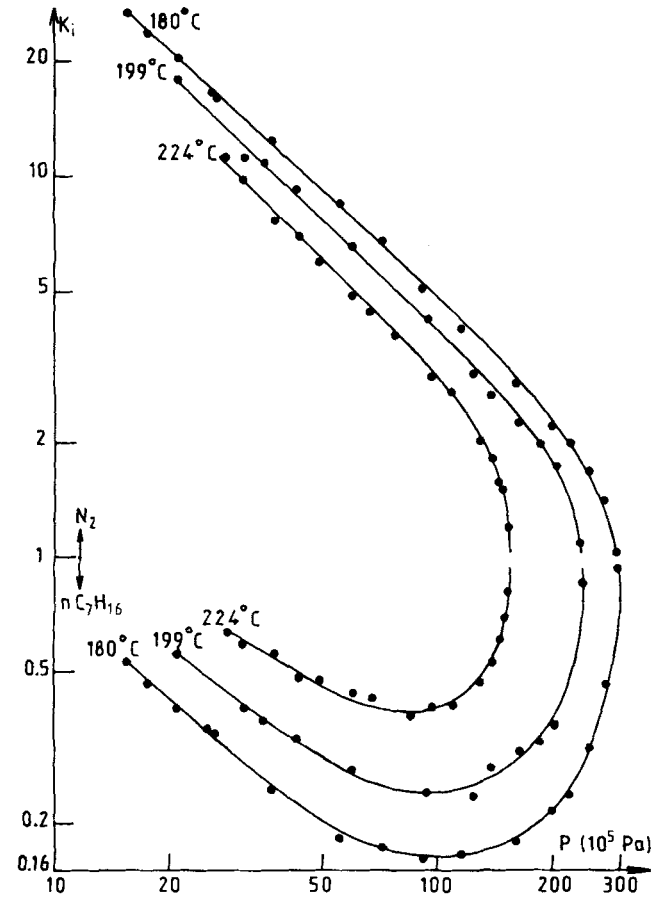

Figure 6. Partition coefficients K_i a function of pressure for nitrogen-n-heptane system at three temperatures.

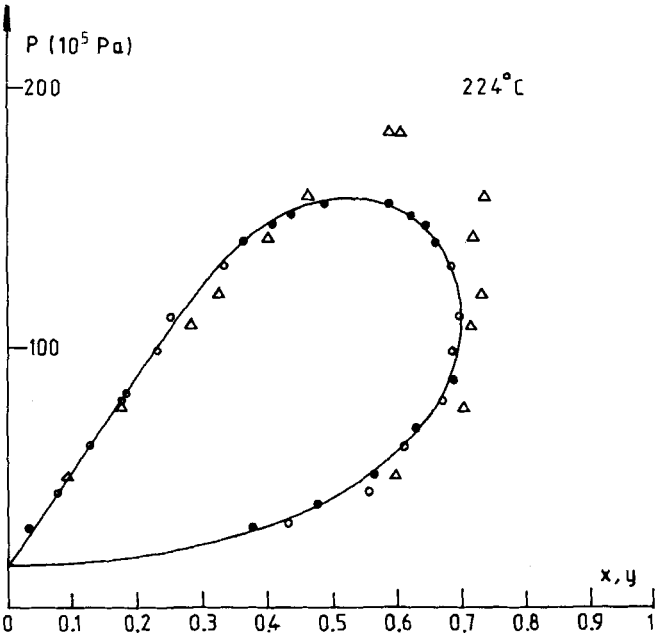

Figure 5. Pressure as a function of nitrogen mole fraction in nitrogen (1) -n-heptane (2) system at 224.0°C. ● our results (from decreasing pressure method), ○ our results (from increasing pressure method), △ Peter's results (1974).

defines the lowest possible experimental temperature. Upper pressure (40 000 KPa) and temperature (400°C) are imposed by the pressure tranducer. Pressure must be kept above 2 000 KPa for sufficient accuracy.

EXPERIMENTAL PROCEDURE

After pressure transducer and chromatographic detectors have been calibrated, the components are introduced into the cell. Liquid components are degassed in the degassing cell D accoring to the method of Battino (1971). The degassed liquid flows into the cell under a vacuum, and valve 3 is closed. The gaseous component is introduced from cylinder I at a pressure up to 1 000 KPa. Valve 1 is closed, and temperature in the thermostat is raised to the required value. When the desired temperature is reached at the top of the cell, the temperature of the bottom is adjusted to the same value by means of the heating resistance G. Compressor C is used to raise pressure through valve 1 at the desired value; then valve 1 is closed. Magnetic stirring is activated to reach equilibrium which is indicated by pressure stabilization. Then three samples of each phase are gathered through the two valves in order to obtain the phase compositions and to test reproducibility. The amount of a sample depends on the opening time of the corresponding valve (a few hundredths of a second). The valve opening is calibrated by supplying different powers to the electromagnet. For this purpose, charged condensators are used. Temperature is kept constant and pressure is changed either by adding more gaseous component or by substracting part of gaseous phase. Lowering pressure is performed by expanding the gas phase into the volume lying between valves 1 and 2; each expansion allows a pressure decrease of about 5%. New samples are then analyzed in the same way at each intermediate pressure to give a complete P, T, x, y isothermal diagram.

RESULTS AND DISCUSSION

The nitrogen n-heptane system has been previously studied by several authors (Akers, 1954; Peter, 1970, 1974). We have chosen this very system to check the reliability of our system and especially that of our sampling method.

We have used 99.9% certified purity nitrogen and 99% GLC certified purity n-heptane without further purification.

TABLE 2. COMPARISON BETWEEN EXTRAPOLATED VAPOR PRESSURE OF *n*-HEPTANE AND PUBLISHED DATA

T(°C)	P^S extrapolated	P^S (API table)
180.0	700	680
199.0	950	950
224.0	1400	1420

P, T, x, y measurements were carried out at three temperatures: 180.0°, 199.0° and 224.0°C. Our results are compared with those obtained by Akers (1954) and Peter (1970, 1974). Experimental values are reported in Table 1. P as a function of x, and y is plotted in Figures 3 to 5. Partition coefficients $K_i = y_i/x_i$ calculated from experimental values are plotted on Figure 6.

Figures 3 to 5 shows that our experimental results seem less scattered than those determined by others and lie closer to the critical point. Far from the initial pressure, our results are in good agreement with Peter's (1974), the maximum deviation in vapor phase mole fraction being around 4%. The dew curves, extrapolated to $x_1 = 0$, give a vapor pressure for *n*-heptane in good agreement with previous data (Table 2).

Chromatograph calibration has been performed by introducing pure components with a syringe; the introduced quantities were of the same order of magnitude as those of the samples withdrawn from the cell. the overall reproducibility depends on chromatographic conditions (carrier gas, column and detector temperature, sample size, ...) and on the sampling reproducibility. The chromatographic reproducibility is estimated by standard methods, and the sampling reproducibility has been tested by gathering several samples and studying the resulting scatter. For our system, the overall scatter has been observed to be 0.015 in mole fraction.

Furthermore, reproducibility has been tested for the 224°C isotherm which has been done two ways. In the first experiment, pressure was changed by adding nitrogen, and in the second one, pressure was changed by removing part of the vapor phase. Figure 5 shows the agreement between the two experiments.

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NOTATION

K = partition coefficient = y/x
P = total pressure
P^s = vapor pressure of pure component
T = temperature
x = liquid phase, mole fraction
y = vapor phase, mole fraction

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