Flow Apparatus for Phase Equilibrium Measurement at Elevated Temperatures

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A flow apparatus was developed to determine phase equilibria at elevated temperatures and pressures. The key component of the apparatus is a high-pressure view cell equipped with transparent sapphire windows for visual observation of the liquid level. The flow apparatus is used to the best advantage when the residence time of chemicals (or bio-materials) in the high-temperature zone has to be minimized to eliminate the possibility of thermal decomposition or polymerization reactions. Because the technique has the advantages of rapid attainment of equilibrium conditions and straightforward sampling procedures, it produces a fairly large quantity of data with a minimum amount of time. The sample system also offers the option of taking a desired size of sample by controlling the length of sampling time. This is important particularly for the asymmetric mixtures of a light gas in a very heavy compound of low volatility at some extreme conditions, for which a sufficiently large amount of samples are needed to determine the phase compositions with reasonable accuracy. The flow apparatus of different designs have been used for measurements of vapor-liquid and liquid-liquid equilibria for years. However, it is difficult for multiphase mixtures, and the liquid feed pump cannot handle solids of high-melting points.

In operation of a flow apparatus, the liquid level in the equilibrium cell must be sensed and controlled at a certain range of elevation. Simnick et al. (1977) designed a blind cell in which an electric capacitor was installed to detect the liquid level. A similar cell was later fabricated by Inomata and coworkers (1986). However, the capacitor fails to function properly for the mixtures which are electrically conductive (Lin et al., 1985, 1986). Lin and coworkers (1985) developed a visual cell in which a transparent sapphire window was equipped at each end of the cell body to permit observation of liquid level. A modification of this cell with a new design to improve its sealing of the sapphire windows for operation at higher pressures is detailed here. The apparatus was tested with mixtures of known equilibrium behavior on carbon dioxide/toluene and on hydrogen/1-methylnaphthalene. Equilibrium conditions of hydrogen/tetralin mixtures are reported at 621.5 K for which previous results from different sources are inconsistent.

Experimental methods for determination of high-pressure phase equilibria at temperatures up to about 500 K have been reviewed by Deiters and Schneider (1986). Among a few notable studies, Connolly (1962) measured vapro-liquid equilibria (VLE) for hydrogen/benzene mixtures with a static apparatus over the temperatures of 430–530 K and the pressures of 2–18 MPa, while Grayson and Streed (1963) used a flow apparatus to determine VLE of hydrogen/gas oils at temperatures up to 750 K and pressures to 20 MPa. Renon and coworkers at Ecole des Mines de Paris (Richon and Renon, 1983; Laugier et al., 1983, 1986; Cohen and Richon, 1986) have developed various apparatus for high-pressure VLE measurements at elevated temperatures. Other apparatus, which have been constructed in recent years essentially for mixtures of interest in coal conversion processes, include those of Prather et al. (1977), Simnick et al. (1977), Nasir et al. (1980), Wilson et al. (1981), Sung (1981), Harrison et al. (1982, 1985), Lin et al. (1985), Ramanujan et al. (1985), Ding et al. (1985), Inomata et al. (1986), and Thies and coworkers (Theis and Paulaities, 1984, 1986; Thies et al., 1988).

Experimental Method

The apparatus consists of three major sections: feed, equilibration, and sampling. The feed and the sampling systems are similar to those described by Simnick et al. (1977) and by Lin et al. (1985). All parts exposed to high pressures are made of stainless steel type 316. The heart of the apparatus is an equilibrium cell, which is housed in a thermostated bath. The cell serves as an equilibrator where the final equilibration between gas and liquid takes place and is a separator where the equilibrated vapor and liquid phases are separated. Figure 1 details the design of the new visual cell. Transparent sapphire

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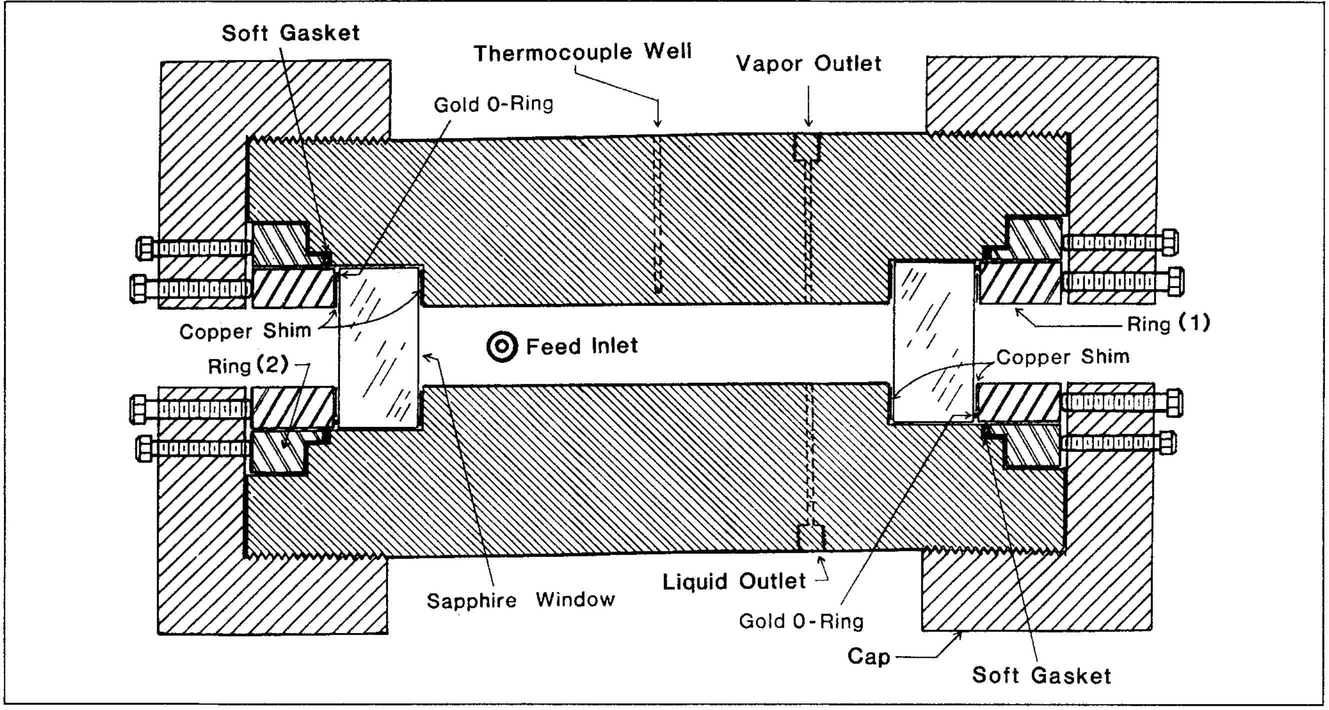

Figure 1. Equilibrium cell.

windows enclose the open space at both ends. Sealing the sapphire windows are extremely difficult, because no organic elastomer can sustain the experimental conditions of interest. Soft metal gaskets are applied in this work. The concept for enclosure of the cell was briefed by Lin and Chao (1986).

Two rings are used at each end of the cell body to seal off leakage of cell fluid. The first ring presses a gold O-ring that is backed up by a copper shim to seal the sapphire window, while the second ring seals the lip of the first ring with a brass (or graphite) gasket. Fluid pressure in the cell tends to facilitate sealing against leakage.

Visual cells of similar design have been used extensively in our Biotechnology Laboratory to investigate food processings with supercritical and subcritical fluids under high pressures. In those applications where the process temperatures are usually well below 550 K, deirin and teflon are two of the most useful packing materials. Graphite gaskets have also been used with success even at elevated temperatures.

A thermostated nitrogen bath was constructed to maintain the equilibrium cell at experimental temperature. The design of bath was detailed by Huang et al. (1988), while Lin and coworkers (1985) described the experimental procedure.

Carbon dioxide was purchased from Matheson Gas Products with a minimum purity of 99.9% and hydrogen from Airco with 99.95%. Tetralin and 1-methylnaphthalene were supplied by Aldrich Chemical Co., and toluene by T. J. Baker Chemical Co. All these chemicals were claimed to be 99% or higher in purity.

Experimental Results

Operation of the apparatus was tested with mixtures of CO_2/toluene at 477 K over the pressures of 1 to 5 MPa. The results were compared with the data of Ng and Robinson (1978) from a static apparatus and with Sebastian et al. (1980) from a flow apparatus. Good agreement was obtained which verified the attainment of equilibrium in the apparatus. The comparison is much the same as shown previously by Lin and coworkers (1985) and, therefore, need not be elaborated. Equilibrium conditions were further verified periodically by collecting samples at a fixed condition of temperature and pressure with different feed flow rates. The phase compositions from the repeated samples were found to have no consistent bias with variation of flow rates.

Measurements were extended to mixtures of hydrogen/1-methylnaphthalene and hydrogen/tetralin at higher temperatures and pressures. Figure 2 shows the results of hydrogen/1-methylnaphthalene at 730.1 K over the pressure range of 5–27.5 MPa, which are compared with previous work of Lin et al. (1980). The expeirmental conditions of Figure 2 are among the severest that have been ever reported for VLE in hydrocarbon-containing mixtures. The agreement is well within experimental uncertainties, concluding that this apparatus is capable of operating at high temperatures under elevated pressures.

The mixtures of hydrogen/tetralin were investigated in this work, because data from different sources do not show consistency, Simnick et al. (1977) measured the hydrogen solubilities in tetralin with a flow apparatus which appeared to discriminate from the studies of Harrison et al. (1985) and Nasir et al. (1980) with static techniques. Figure 3 compares the solubilities of hydrogen at 621.5 K where the discrepancies among various sources are relatively apparent. This temperature is also the highest that was measured by Nasir and coworkers. This work agrees well with the data of Harrison et al. and Nasir et al., but is systematically higher than the data of Simnick et al. over the pressures of 10–20 MPa with a maximum deviation of about 7% at 15 MPa. Nevertheless, the disparity is not particularly serious in view of the degree of experimental difficulties. In fact, the

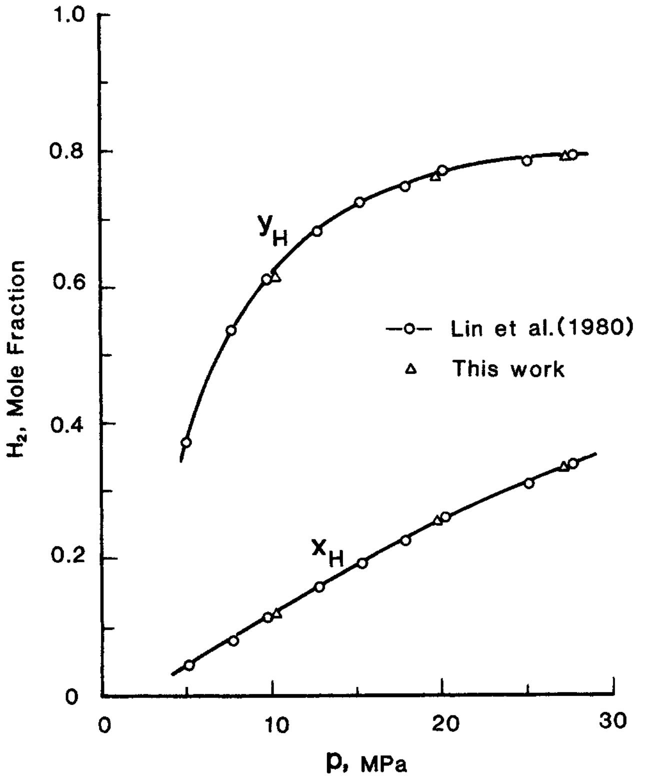

Figure 2. Vapor-liquid equilibria of hydrogen/1-methylnaphthalene mixtures at 730.1 K.

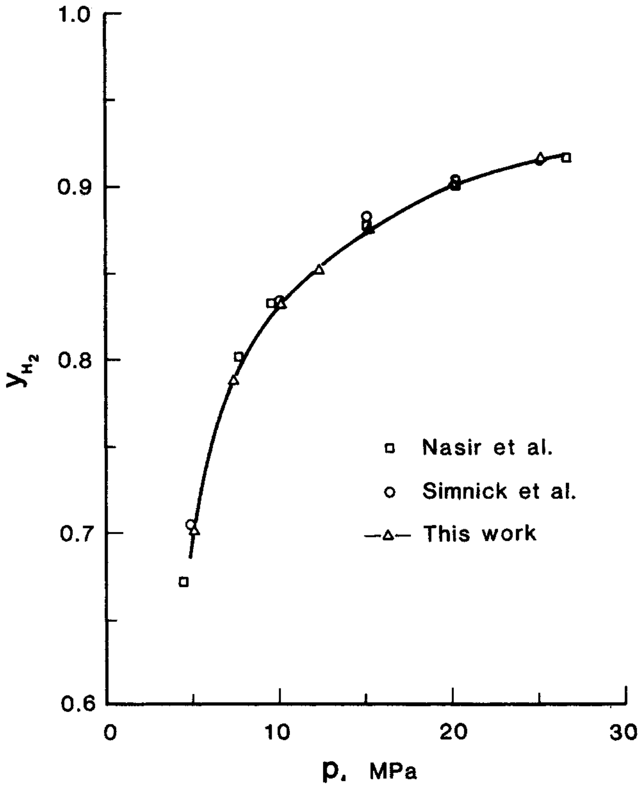

Figure 4. Mole fraction of hydrogen in saturated vapor of hydrogen/tetralin mixtures at 621.5 K.

work of Simnick and coworkers has been used as a reference by Harrison et al. and Nasir et al. to compare with the test data of their apparatus and to verify operation of the apparatus and experimental procedures. Sung (1981) has also determined the VLE on hydrogen/tetralin from an apparatus, in which hydrogen probes were installed to measure partial pressures of hydrogen (and thus its phase compositions). Good agreement was claimed of his data with those of Simnick and coworkers that served as a test for the experimental method. However, the reported phase compositions by Sung are seen considerably scattering and, for this reason, are not included in the figure for comparison.

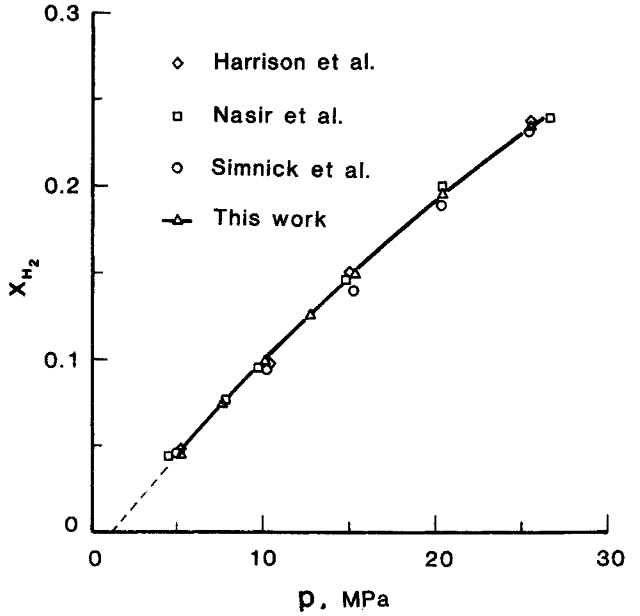

Figure 3. Solubility of hydrogen in liquid tetralin at 621.5 K.

Figure 4 shows mole fractions of hydrogen in saturated gas mixtures of hydrogen/tetralin as a function of pressure at 621.5 K. Again, Sung's data are not shown in the figure because of scattering. Harrison and coworkers did not determine the vapor-phase compositions. This work compares well with the data of Nasir et al. and coincides with the data of Simnick and coworkers except for a single datum at 15 MPa.

Experimental results on hydrogen/tetralin of this work are reported in Table 1. At least two replicate samples were taken for each phase at an experimental condition of temperature and pressure. All the results presented in this work are the average

Table 1. Vapor-Liquid Equilibrium Data for Hydrogen (H)/Tetralin (T) at 621.5 K

p, MPa	x_H	y_H	K_H	K_T
5.099	0.0463_2	0.7024	15.16	0.312
7.649	0.0747_4	0.7876	10.54	0.230
10.08	0.0996	0.8315	8.35	0.187
12.65	0.1256	0.8535	6.80	0.167
15.15	0.1500	0.8742	5.83	0.148
20.27	0.1956	0.8992	4.60	0.125
25.33	0.2342	0.9160	3.91	0.110

values of multiple samples, which are in general reproducible to within 1.5% in mole fractions of the gas component. Samples of condense from cell effluents on both gas and liquid streams of all the runs were collected and analyzed by gas chromatography to check for any thermal decomposition. No significant amount of impurities was detected at any of experimental conditions, although the samples from the cell effluents at higher temperatures did show a slight coloration.

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K. C. Chao provided valuable suggestions on design of the apparatus. Financial support of this work was provided by CSE Company, Inc.

Notation

K = vaporization equilibrium ratio
p = pressure
x = mole fraction of liquid phase
y = mole fraction of vapor phase

Subscripts

H = hydrogen
T = tetralin

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