APPARATUS FOR DETERMINATION OF LIQUID-LIQUID-GAS EQUILIBRIA AT ADVANCED PRESSURES

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A novel apparatus has been designed and built for studying liquid-liquid-gas equilibria. The experimental equipment features a new magnetic pump to recirculate all three phases, sampling from the recirculating streams, minimization of dead space, and analysis of all phases by gas chromatography. Typical operating pressures are up to about 1000 p.s.i.a. Special methods for sampling gases and liquids under pressure were developed.

IN CONNECTION with some initial experimental research on high-pressure vapor extraction, it was necessary to design and construct an apparatus for the determination of liquid-liquid-gas equilibria at higher pressures (50 to 1000 p.s.i.a.). Elgin and Weinstock (1959) had previously studied equilibria of this type. In the present work a new experimental approach was taken with a view toward using more recent techniques and instrumentation. Design criteria for the new apparatus included the following:

Small liquid volumes
High corrosion resistance
Good temperature control
Operation at pressures up to 1000 p.s.i.a.
Magnetic pumping of all three phases
Minimal dead space
Sampling from flowing streams
Analysis of all phases by gas chromatography

We describe here briefly the apparatus which we have designed and operated. A more complete description is available (Fleck, 1967).

Layout of Apparatus

Figure 1 shows a scale elevation view of the location of major components of the equilibrium apparatus.

All of the major vessels, valves, and lines were mounted on a rack made of 1-inch angle stock (stainless steel). The rack was submerged in the liquid-filled, constant-temperature bath as shown in Figure 1.

Gas Sampling

A linear valve consists of a bore fitted with ports and a loosely fitting shaft which mounts several O-rings to provide a series of seals between the shaft and the bore. To alter the flow of gas from one port to another through the annular space between the shaft and the bore, the shaft is pushed or pulled coaxially within the bore to alter the relative location of the seals with respect to the ports. Gas sampling in a gas chromatograph uses a six-port, two-position, linear valve where a loop between two ports is connected integrally between two other outer ports when the plunger is pulled out, and between the two innermost ports when the plunger is pushed in. By this means a sample of gas flowing to and from the outer ports can be injected into a carrier-gas stream flowing to and from the inner ports by simply pushing in the plunger.

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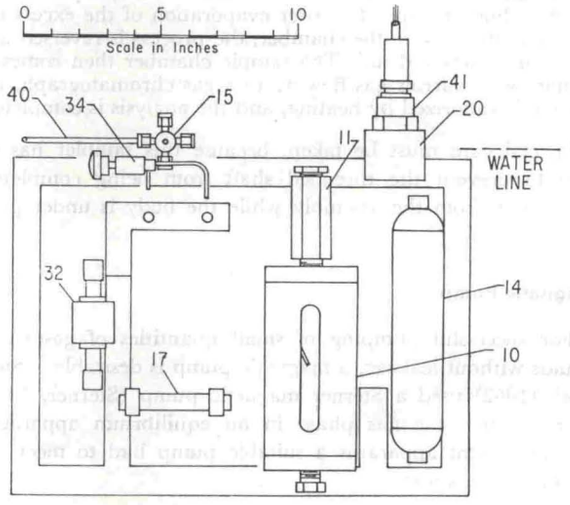

Figure 1. Elevation view of major components

10.	Equilibrium cell	20.	Transducer receiver
11.	Safety head	32.	Magnetic pump
14.	Gas-surge vessel, 300 cc.	34.	Liquid sampler
15.	Linear valve	40.	Gas-sample loop
17.	Small gas-surge vessel	41.	Pressure transducer

When this valve was used to sample a stream at higher pressures, the O-rings pushed out into the annulus provided for the gas flow, and leaks developed. A new shaft was machined which had a lip on either side of each O-ring, with backup rings on the two outermost O-ring seals. With this shaft O-ring failure did not occur at pressures of 1000 p.s.i.a. and an annular space was still available for the gas flow between ports.

After the pressure limitation of the linear valve had been solved, it became apparent that the gas-sample loop had to be heated somewhat above the equilibrium temperature of the system in order to obtain a representative gas sample. In the final design the linear valve was positioned above the constant-temperature bath and the gas-sample loop was wrapped with an insulated electric heating tape to provide the necessary heating.

Liquid Sampling

The liquid-sampling device is shown in an exploded view in Figure 2.

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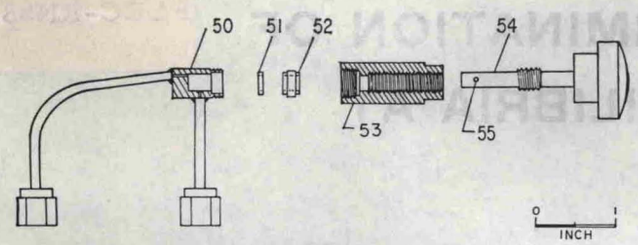

Figure 2. Liquid sampler

50. Body
51. Retaining washer
52. Plastic seal
53. Cap
54. Threaded shaft
55. Sample chamber (small hole drilled diametrically through cylindrical end of threaded shaft, 54)

The liquid flows upward into the body, 50, and out the top. A threaded shaft, 54, has a hole in the end which functions as a sample chamber, 55. When the threaded shaft is screwed in, the sample chamber comes in contact with the flowing fluid to be sampled. When the shaft is screwed out, a part of the flowing fluid is trapped. After evaporation of the excess untrapped sample from the chamber, the process is reversed and the shaft is screwed in. The sample chamber then comes in contact with carrier gas flowing to a gas chromatograph, the sample is vaporized by heating, and the analysis is completed.

Special care must be taken, because this sampler has no stop to prevent the threaded shaft from being completely withdrawn from the assembly while the body is under pressure.

Magnetic Pump

For successful pumping of small quantities of gases and liquids without leakage, a magnetic pump is desirable. Stein *et al.* (1962) used a Sterner magnetic pump (Sterner, 1960) to recirculate the gas phase in an equilibrium apparatus. In the present apparatus a suitable pump had to meet the following demands:

One pump design for either gas or liquid service
Self-priming
Low holdup and minimal dead space
Pressures up to 1000 p.s.i.a.
Stainless steel construction with O-ring seals
Small size
Intermittent pulsing for low heat generation
Submersible in a constant-temperature bath liquid
Solid-state pulse generator for low maintenance

A modification of the Sterner pump (1960) was built and tested but proved to be too large and did not pump liquids easily.

Figure 3 shows the pump design which was developed to fill the present needs.

The basic components of the pump include two check valves, a piston, 101, and a pump bore, 104. The lower check valve is formed by check ball 102, which seals onto a seat in piston 101 when the piston is thrust upward. A second check valve is built into upper closure 106 (not shown in Figure 3). Lower closure 105 is similar to upper closure 106, but contains no check valve. During the operation of the pump an electrical pulse to solenoid coil 100 causes ferromagnetic piston 101 to be lifted upward in bore 104; this motion seats check ball 102 and carries fluid upward through the pump. At the end of the electrical pulse the magnetic field collapses, allowing piston 101 to fall by gravity down through bore 104. During this period the upper check valve seats to prevent backflow; fluid then enters the upper part of the pump through the coaxial hole in piston 101, which has been uncovered by the unseating of check ball 102.

The pump is self-priming and pumps either gases or liquids. However, it fails to pump a gas if the piston becomes so wet with liquid that the gravity fall of the piston is impeded.

The solid-state pulse generator for driving the pumps was designed so that the voltage, pulse width, and frequency of the pulse train could be varied independently.

Minimization of Dead Space

Minimization of dead space is important in order to attain equilibrium more rapidly and to facilitate meaningful sampling. The major sources of dead space relative to a recirculating stream exist where a tee connects the line to a sampling valve, to a control valve, to a rupture disk, or to a pressure-measuring device.

A special three-port valve (made to order by the Whitey Valve Co., Emeryville, Calif.) acts both as a tee and as a valve to control one of the three ports. Thus dead space in the usual connecting line between the tee and the valve is eliminated. The symbol used to represent the three-port valve is a circle with three entering lines and a cross within the circle on the controlled port (Figure 4).

A flush-diaphragm pressure transducer was used to minimize the dead space in the connecting line and in the pressure-measuring apparatus. The safety head was rebuilt in such a way that the recirculating gas stream flowed up through the head and out a port near the top just under the rupture disk.

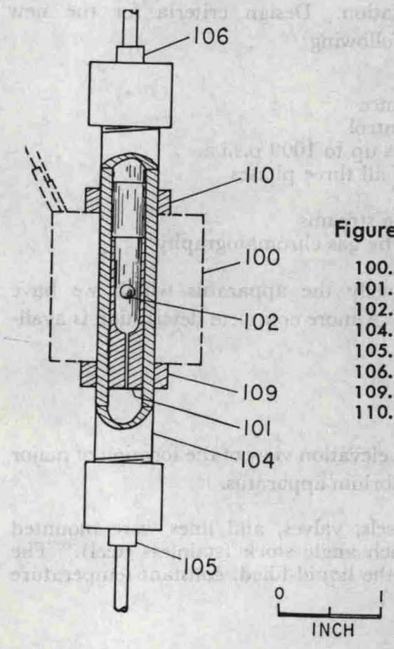

Figure 3. Magnetic pump

100. Solenoid coil
101. Piston (ferromagnetic)
102. Floating check ball
104. Pump bore
105. Lower cap
106. Upper cap
109. Lower collar
110. Upper collar

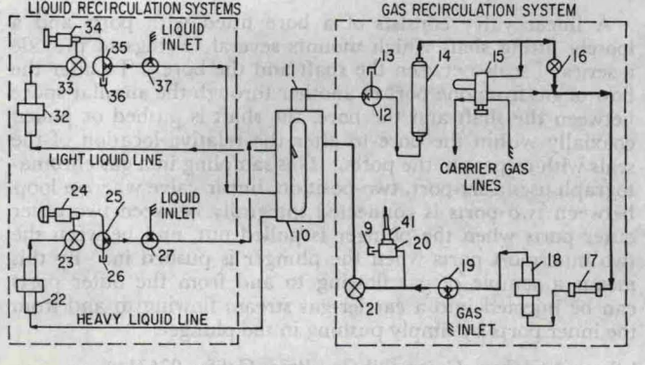

Figure 4. Gas and liquid recirculation systems

Recirculation Systems

Figure 4 shows schematically the gas and liquid recirculation systems.

All connecting lines are $^1/_8$-inch stainless steel tubing, except that two sections carrying the gas phase are $^1/_4$ inch; the latter are represented by a heavier line.

The mixing and equilibration of the phase take place in the equilibrium cell, 10. The gas phase flows from the top of the cell through the modified safety head, 11, and through the three-port valve, 12, which is capped with cap 13. From valve 12 the gas flows through a 300-cc. gas-surge vessel, 14, and then to either linear valve 15 or block valve 16. When the plunger of linear valve 15 is pulled out, the recirculating gas passes through the sample loop and then to the small gas-surge vessel, 17. When the plunger is pushed in, the sample loop is connected to the carrier gas lines of the gas chromatograph and the sample is thus injected for analysis. When the plunger is in, block valve 16 is opened to allow the recirculating gas to bypass linear valve 15. Gas in the small gas-surge vessel, 17, is pumped by magnetic pump 18 through three-port valve 19, which is used to admit gas to the system. Gas from valve 19 passes through a tee connection which is connected to capped (cap 9) transducer receiver 20, into which is screwed the flush-diaphragm pressure transducer, 41. From the tee connection the gas flows through valve 21 and back to the equilibrium cell, 10, where it enters just below the upper liquid level.

In the original design of the apparatus the recirculating gas flowed through the transducer receiver and across the face of the pressure transducer diaphragm, so that all dead space was eliminated—i.e., no tee connection was used. A change of the gas flow to go through transducer receiver 20—i.e., by placing transducer receiver 20 in the $^1/_4$-inch line between valve 19 and valve 21—is still desirable for the further elimination of dead space.

After the plunger of linear valve 15 has been pushed in, the gas sample loop will normally be filled with carrier gas. The compressed gas being studied is used to purge the loop. The same gas is then used to pressure the loop to a pressure somewhat above that in the equilibrium apparatus and the plunger is pulled out to begin sampling.

The heavy liquid is withdrawn from the bottom of equilibrium cell 10 by magnetic pump 22, from which it flows through valve 23, liquid sampler 24, three-port valve 25, and three-port valve 27. From valve 27 the liquid returns to equilibrium cell 10 and is directed away from the wall of the cell by a welded ramp.

The recirculation system for the less dense liquid is identical to that for the denser liquid, except that the less dense liquid is withdrawn from the equilibrium cell through a port underneath the heavy-liquid inlet ramp and is later returned below the level of the heavy liquid. Parts 32 to 37 of the light-liquid recirculation system correspond in function to components 22 to 27 of the heavy-liquid system.

During equilibration, the recirculating heavy liquid flows through liquid sampler 24 and bathes the hole in the end of the threaded shaft. When the sample is to be trapped, the threaded shaft is screwed out the proper number of turns to trap the sample. Valves 23 and 25 are closed and the sampler is removed and purged with carrier gas. On injection the threaded shaft is screwed in to release the trapped sample into the carrier gas for analysis.

After analysis, sampler 24 is fitted to valves 23 and 25, cap 26 is loosened, and valve 23 is opened slowly to allow a small amount of liquid to flash into the sampler to purge out the air. Cap 26 is then tightened, valve 23 is opened, and then valve 25 is opened.

A large number of operating details are necessary for the successful startup, maintenance, and shutdown of the apparatus. These and other details of the apparatus are reported elsewhere (Fleck, 1967).

Experimental Data

Figure 5 shows gas-phase data obtained for the binary system ethylene–*n*-propyl alcohol at 15° C. With this binary system both liquid-gas and liquid-liquid-gas equilibria were encountered. A minimum solubility of *n*-propyl alcohol in the gas phase was found at about 410 p.s.i.a. Figure 5 shows the relatively good reproducibility of the data at very low concentrations of *n*-propyl alcohol.

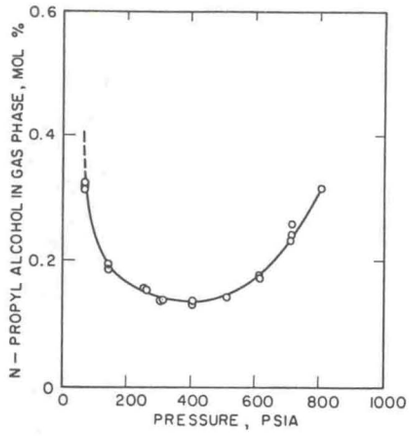

Figure 5. Gas-phase data

System. Ethylene–*n*-propyl alcohol at 15°C.

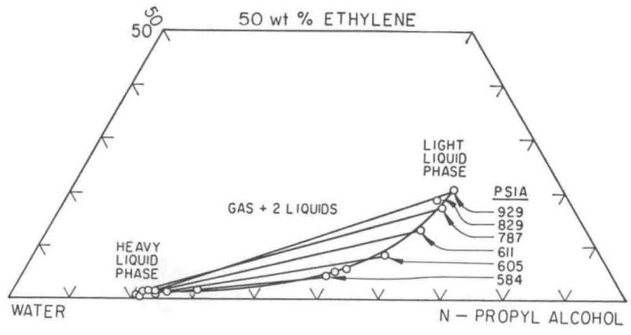

Figure 6. Liquid-liquid tie lines

System. Water–*n*-propyl alcohol–ethylene at 15° C.

Figure 6 shows the liquid-liquid tie lines for several pressures at 15° C. in the liquid-liquid-gas region of the ternary system water–*n*-propyl alcohol–ethylene. Interpolated data for 715 p.s.i.a. agree reasonably well with those obtained by Elgin and Weinstock (1959).

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