A Vapor-Liquid Equilibrium Still Suitable for Small Amounts of Samples*

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Details are described for the apparatus and procedures for the accurate measurement of vapor–liquid equilibria by use of small amounts of samples. The new recirculation still described is a modification of the Brown's still (*Aust. J. Sci. Res., A*, **5**, 530 (1952)) and its total amount of operating charge is *ca.* 53 cm^3, of which each 7 cm^3 is in the vapor- and liquid-sample traps and *ca.* 23 cm^3 is in the boiler. A method of determining an optimum value of the heating current of the boiler is described. Partial condensation of the vapor and entrainment of the liquid phase into the vapor were eliminated. Some results obtained for the system hexane+chlorobenzene at 338.15 K agreed with the thermodynamically consistent values of Brown, showing the reliability of this still operating with the samples having relative volatilities up to 13. The construction of a thermostatted sample vessel without vapor space for a Pulfrich refractometer is also illustrated which is suitable for small quantity of volatile or hygroscopic solution.

Vapor pressures of binary solutions may be measured[1,2] by the static method, the boiling-point method, the gas-saturation method, the isopiestic method, the dew-point method, the method used with the so-called vapor phase osmometer or vapor pressure osmometer, and others. Of those the first two methods are most widely used. The boiling-point method is preferred when both components of a binary solution are volatile, because the sufficient amounts of representative samples of vapor and liquid phases can easily be obtained if the apparatus is properly handled, and hence the thermodynamic consistency among the values obtained for the temperature, pressure, and compositions of vapor and liquid phases can be checked by means of the Gibbs-Duhem relation. In this paper the author will describe a recirculation still which was constructed to obtain sufficient amounts of representative samples of both vapor and liquid phases with use of relatively small amounts of solution.

After a survey of literatures of existing stills, including some actual trials, the equilibrium still of Brown (the still No. 2)[3] was selected as a basis for modification. The Brown's still incorporates many refinements designed to ensure that the samples of condensate and liquid accurately reflect the equilibrium compositions at a well-defined temperature and pressure. Using his still, Brown obtained the thermodynamically consistent results for miscible systems having a relative volatility in the range 1.0 to 14.[3] The amount of operating charge of his still is, however, approximately 200 cm^3.

Apparatus

Description of the Vapor–Liquid Equilibrium Still. The design of the new still is shown in Fig. 1. This still was made of borosilicate glass. Its total amounts of operating charge are approximately 53 cm^3, of which 7 cm^3 is in each trap and about 23 cm^3 is in a boiler. On the inner surface of boiler B finely powdered borosilicate glass was sintered to promote even bubbling which ensures effective stirring of the content. The outer heater O is a nichrome ribbon heater wound on the outer wall. The internal heater P is a closely coiled platinum wire[4] whose diameter is *ca.* 0.1 mm. It was spot-welded with tungsten wires which had been sealed with a glass ground joint S. For being insulated thermally and increasing the heat capacity, the boiler was pasted thick with asbestos leaving each peep slit in front and behind, through which condition of the platinum coil and mode of bubbling were observed. The Cottrell pump C is *ca.* 39 cm long and its inside diameter is *ca.* 3.5 mm. The equilibrium chamber A has a thermometer well Q whose depth is *ca.* 9.0 cm and inside diameter is 10 mm. A spiral guide made of glass cane was welded on the outside wall of the thermometer well to ensure sufficient thermal contact of the liquid and vapor with the well. Three concentric tubes in the equilibrium chamber form two annular spaces, of which the outer space is *ca.* 6 to 7 mm wide and it serves as a vapor jacket to prevent fractional condensation of the vapor phase in the inner space. The inner annular space of *ca.* 5 mm width may contribute to eliminate entrainment of liquid phase into the vapor. The upper end of the middle tube was slightly bent toward the center to prevent entering of sprays. The narrowest width of this annular space is 3 mm. Special care was taken to eliminate spattering of sprays as follows. The middle and lower portions of the middle tube were gently tapered. The bottom of the innermost tube was slightly made narrower so as to drain for the liquid gently along the wall of the middle tube. The equilibrium chamber was completely enclosed in a vacuum jacket R whose wall was silvered except vertical peep slits. The inside diameter of condenser D is *ca.* 12 mm. A vertical condenser E (shown as B in Fig. 2) is a total condenser whose vacuum jacket has been silvered leaving peep slits. Inside diameters of the tubes designated U and L are *ca.* 4 mm and *ca.* 5 mm, respectively. The extended portion I, *ca.* 20 mm i.d., and the constriction J in a return path were inserted so as to reduce fluctuations of the liquid level. About 8.5 cm long U-shaped tube K was required to avoid flowing upstream. Inside diameters of this portion are 2 to 3 mm. The vertical extension of a capillary,

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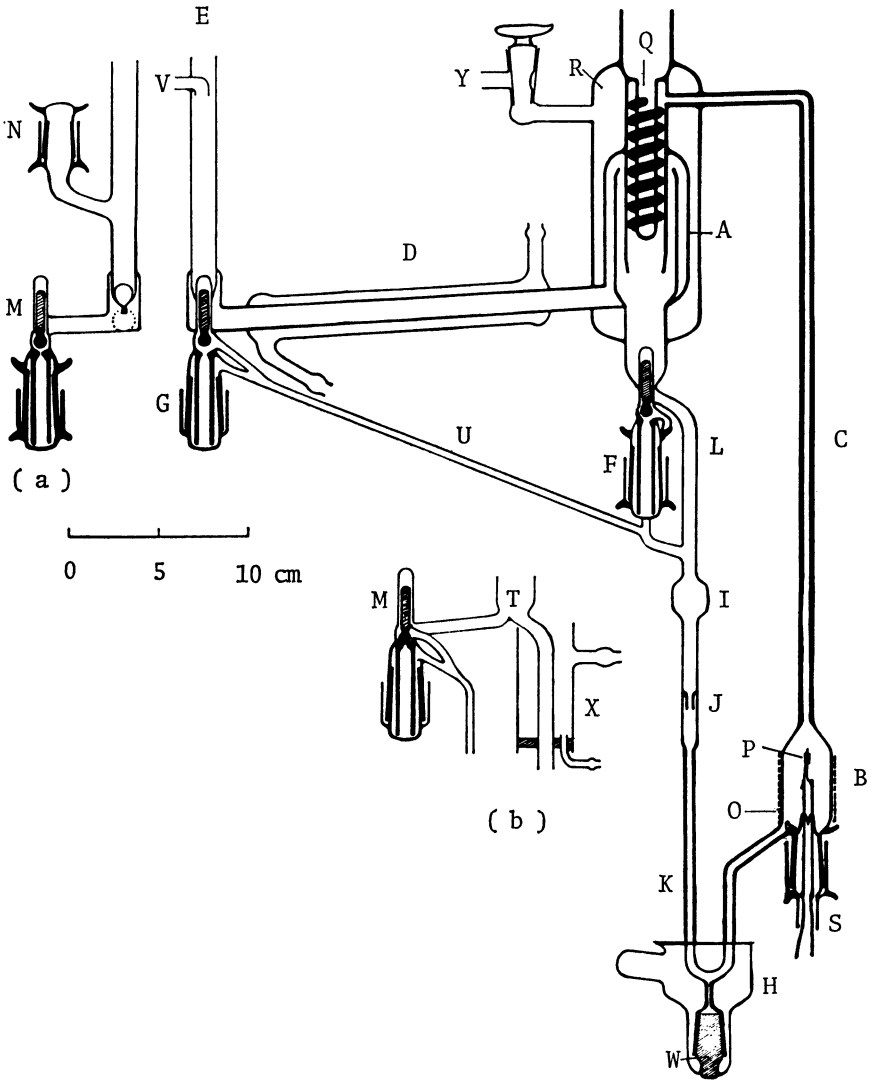

Fig. 1. Equilibrium still. (a) and (b) are side views of the sample traps G and F and their neighbors.
A: Equilibrium chamber, B: boiler, C: Cottrell pump, D: condenser, E: to a total condenser (shown in Fig. 2, B), F: liquid sample trap, G: vapor sample trap, H: cup for collecting the contents, I and J: devices for reducing fluctuations of the liquid level, K: U-shaped tube, L: path of a main flow of the liquid, M: magnetically operated ball valve, N: opening for filling, O: outer heater, P: internal heater, Q: thermometer well, R: vacuum jacket, S: tapered ground stopper, T: ridge for dividing liquid into two 2 : 1 portions, U: path of the returning condensate, V: vent for filling by distillation, W: ground stopper, X: cooler, Y: to a diffusion pump through a liquid nitrogen trap.

ca. 3.5 cm long and *ca.* 0.1 mm i.d., was connected with a ground tapered joint. A cup H with the core of ground joint W for collecting the contents of the still was copied from that originally introduced by Smit and Ruyter.[5] Both the vapor trap G and the liquid trap F are essentially similar to those introduced by Brown:[3] each trap has a small vapor hold-up, a small area of free surface of liquid, and a magnetically operated ball valve M. The both surfaces of the ball and the top of the trap were well ground. In the design of this still a spiral heat-exchanger B of the Brown's still was omitted for simplification of the design and reduction of the volume of dead space. However, a small cooler of *ca.* 6 cm long was mounted on L as shown in Fig. 1, (b) after the construction was completed. A vent V was provided for filling hygroscopic liquids by distillation through a mercury cut-off (shown in Fig. 2). All tapered joints of F, G, and N and the ground stoppers S and W were supported with springs and hooks and sealed with mercury in use.

Measurement of Pressure. The apparatus for the control and measurement of pressure was essentially the same as that used by Scatchard *et al.*[6] It is illustrated schematically in Fig. 2. The maintenance of constant pressure was ensured by connecting the still with a manostat through a liquid nitrogen trap D. The manostat F filled with dry nitrogen is a

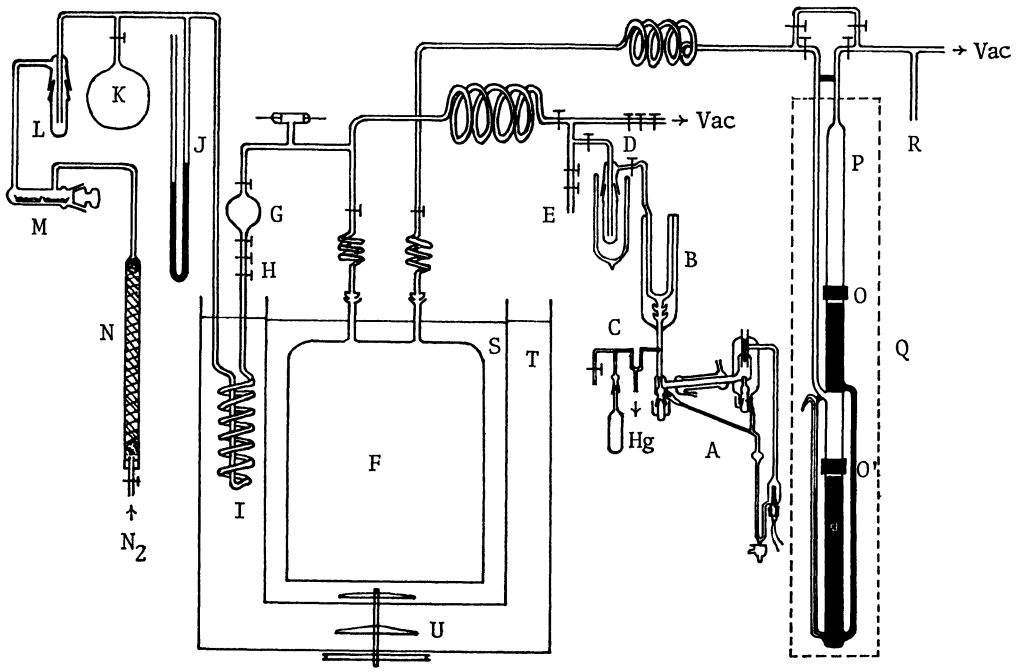

Fig. 2. Arrangement of pressure measuring apparatus.
A: Main part of the still, B: total condenser, C: distillation device for hygroscopic liquid, D: liquid nitrogen trap, E: openning for atmosphere or a dry nitrogen reservoir, F: manostat, G and H: bulb and stopcocks for fine adjustment of nitrogen pressure, Hg: to a mercury reservoir, I: heat-exchanger for nitrogen, J: rough manometer, K: dry nitrogen reservoir, L: liquid nitrogen trap for drying nitrogen gas, M: P_2O_5, N: silica-gel column, N_2: nitrogen from a cylinder, O and O': tubular brass screens, P: precision manometer, Q: thermostat, R: to a rotatable McLeod gauge, S and T: inner and outer baths of a double water thermostat, U: stirrer, Vac: to a high vacuum system.

painted 100-dm^3 iron tank submerged in a double thermostat S and T made of tinplate whose temperature was regulated to within ±0.001 K. The pressure of dry nitrogen in the manostat F was measured with a precision manometer P immersed in a thermostat Q in which the thermostatted water in the outer thermostat T was circulated. The circulating water was ejected through three nozzles as jet streams into the thermostat Q and the water was gently stirred with a stirrer driven with a synchronous motor so as to prevent any temperature difference along the manometer P. A high quality plate glass for mirror was used for the front window of the thermostat. A good quality tubing with constant bore size, 20 mm i.d., and uniform thickness was used for making the precision manometer. Two brass collars O and O′ painted black were fitted around the tubes and connected to an adjustment device. The readings of mercury menisci were made with a 1-m Shimazu cathetometer readable to 0.05 mm under illumination of a diffuse pale yellow, vertically parallel light from behind; an angular displacement of *ca.* 30° from the diametrical position. The pressure in the vacuum side of manometer was checked with a rotatable McLeod gauge. The temperature of the scale was read with a thermometer immersed in a mercury pool attached to the cathetometer.

Measurement of Temperature. Temperatures were measured with a specially constructed platinum resistance thermometer of the four-lead type,[7,8] a Yokogawa P-7 vernier potentiometer, and a calibrated 100-ohm standard resistance of four-lead type. A lead storage battery was lagged with foamed polystyrene boards. The thermometer was calibrated at the triple point of water[9] and compared with a Leeds and Northrup No. 8163 platinum resistance thermometer calibrated by the National Bureau of Standards, U.S.A. The values obtained of the coefficients of the Callendar equation:[7]

$$t/°\mathrm{C} = \frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t/°\mathrm{C}}{100} - 1\right)\frac{t/°\mathrm{C}}{100} \qquad (1)$$

were

$$\frac{R_{100}}{R_0} = 1.39145, \quad \alpha = 0.0039145_1, \text{ and } \delta = 1.49225, \qquad (2)$$

which indicated the platinum to be of the requisite purity. A clearance of *ca.* 0.7 mm wide between the outer wall of thermometer and the inside wall of thermometer well was filled with silicone oil. A space between the thermometer and a wide tube welded on the top of thermometer well was plugged with cotton wool.

Operation of the Still

After the solution was charged, the still was evacuated and kept to boil below the room temperature for a few minutes. Then, it was isolated from the vacuum line and connected to the manostat whose pressure had been adjusted to an approximately predicted value.

Heating was commenced adjusting the pressure to the value corresponding to the required temperature by using a calibrated mercury-in-glass thermometer at first and finally the platinum resistance thermometer. After the still was allowed to make steady boiling, the valves on the traps were closed, and the samples were withdrawn for analysis.[3]

The measured height h_T between the menisci was converted to the pressure P given in the standard mm of mercury† by Eqs. 3 and 4.[10] The corrections due to the capillary depressions of the mercury were found to be negligible.

$$\frac{h^{\circ}_{273.15}}{\text{mm}} = \frac{h_T}{\text{mm}} \times \frac{1+1.84\times10^{-5}\{(T_S/\text{K})-293.15\}}{1+1.818\times10^{-4}\{(T/\text{K})-273.15\}} \quad (3)$$

$$\frac{P}{\text{mmHg}^{\dagger}} = \frac{h^{\circ}_{273.15}}{\text{mm}} - 0.0974_8\left(\frac{h^{\circ}_{273.15}/\text{mm}}{100}\right) \quad (4)$$

Here T_S and T are the temperatures of the cathetometer scale and the manometer, respectively.

Performance Tests

Optimum Value of Heating Current. Electric currents were supplied to the outer and internal heaters under observation on each ammeter. A fine adjustment was made with each autotransformer whose input voltage was adjusted to ten volts. The heating current of the internal heater was fixed so as to ensure smooth bubbling of the liquid. The current through the outer heater was changed and the plots of equilibrium temperature *vs.* heating current were made. A range of the optimum heating currents was determined from a horizontal portion of the curve where the equilibrium temperature was independent of the value of current supplied. As the range of optimum values of heating current was dependent on the concentration of solution, boiling temperature, or systems to be measured, this test was carried out before the measurement. Portions of the Cottrell pump were wrapped with asbestos ropes, if necessary.

Entrainment of the Liquid Phase into the Vapor. A saturated ethanolic solution of fluorescein at a room temperature (296 K) was charged into the boiler and a lower portion of the return line by means of a syringe fitted with a bent needle. The liquid trap was filled with this solution and the vapor trap was filled with pure ethanol. After 5-h recirculation at atmospheric, 542-mmHg, and 330-mmHg pressures, no color could be detected in the vapor trap.

Comparison with the Reported Values of Hexane+Chlorobenzene at 338 K. *Materials*: Reagent grade hexane was passed through a column filled with silica gel six times to remove aromatics. The hexane obtained was rectified and the portion of distillates boiling at 341 to 342 K was collected. This material was shaken with chlorosulphonic acid to remove methylcyclopentane by means of the method described by Brown,[3,11] and finally rectified over phosphorus pentaoxide through a 1-m column packed with Dixon packing. The boiling temperature of the purified material was 341.83 K. Gas-chromatography analysis showed that the impurities having shorter retention times than hexane were completely removed and methylcyclopentane was almost completely removed. Reagent grade chlorobenzene showed only very small peaks of a gas-chromatography curve in the shorter side of retention time apart from the main peak. It was rectified, shaken with 10% aqueous solution of sodium hydroxide, washed with water, dried over anhydrous calcium chloride and then phosphorus pentaoxide, and finally rectified over phosphorus pentaoxide through the column described above. The boiling temperature was 404.85 K.

† Throughout this paper 1 mmHg=133.3224 Pa.

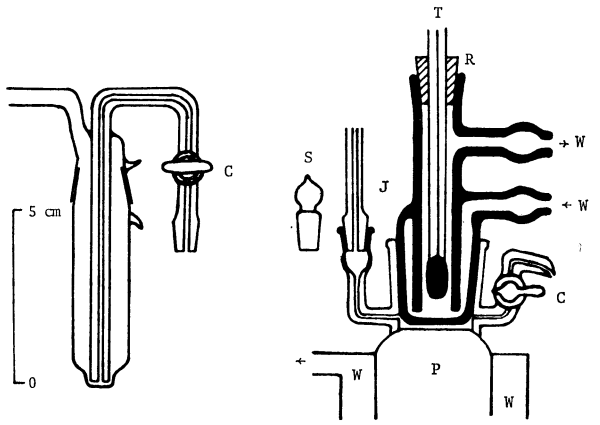

Fig. 3. Thermostatted sample vessel without vapor space suitable for small amounts of volatile or hygroscopic solutions for a Pulfrich refractometer and a device for the transfer of samples.
The both equipments were made of borosilicate glass.
C: stopcocks, J: tapered ground joint, P: prism, R: rubber stopper, S: ground stopper, T: thermometer, W: thermostatted water.

TABLE 1. MOLE FRACTIONS x_1 AND y_1 OF HEXANE IN LIQUID AND VAPOR PHASES, EQUILIBRIUM VAPOR PRESSURES P, AND RELATIVE VOLATILITIES $\alpha=y_1x_2/y_2x_1$ FOR THE SYSTEM HEXANE(1)+CHLOROBENZENE(2) AT 338.15 K
(1 mmHg=133.3224 Pa)

x_1	y_1	P/mmHg	α
0.089	0.564	174.2_1	13.2
0.321	0.822	344.7_0	9.8
0.442	0.870	410.1_6	8.4

Procedures and Results: Since the refractive indices of both components agreed with those reported by Brown,[3] the equilibrium compositions were determined by the refractive index *vs.* mole fraction curve which had been drawn from his data. The refractive indices of small quantities of samples were accurately measured on a Pulfrich refractometer by use of the thermostatted liquid vessel without gas phase designed by the author as shown in Fig. 3. The results of vapor–liquid equilibria obtained are given in Table 1. These values agreed well with the Brown's data[3] within the experimental error. Since the Brown's data for this system satisfied the Gibbs-Duhem relation well,[3] the vapor–liquid equilibrium still for small sample size, *ca.* 52 cm^3, here described is also reliable to operate

with the samples having relative volatilities up to $\alpha=$ 13.

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