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Note

AN APPARATUS FOR THE DETERMINATION OF VAPOR—LIQUID EQUILIBRIUM

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The experimental determination of vapor—liquid equilibrium, in the pressure range normal to low, can be conveniently carried out by the dynamic method [1]. The apparatus usually used for this purpose is a circulating still. In the design and construction of such an apparatus it is necessary to exercise good care in order to avoid undesirable phenomena such as superheating, false state of equilibrium, concentration gradients, etc., which may cause inaccurate results.

A number of circulating stills have been described in the literature [1—3]. However, most of these have a complicated design and their construction and maintenance are difficult or even impossible for laboratories having limited resources. The aim of the present work was the development of a simple apparatus which enables prompt acquisition of precise measurements.

EXPERIMENTAL

Apparatus

The apparatus evolved from our work is shown in Fig. 1. It is a still with circulation of both vapor and liquid phases. Its operation involves the following steps: boiling the liquid mixture and measuring its equilibrium temperature; condensing the vapors; sampling the condensate and the boiling liquid separately; mixing the condensate and the boiling liquid, and bringing them back to the boiler.

The boiling flask K (capacity 160 ml) is heated by an external heating mantle M, which is in contact with a glass surface activated inside in order to lower superheating. The activated surface L was prepared by sintering a thin layer of 20—60 mesh particles of ground glass, using the lowest possible temperature to minimize fusing the sharp edges of the particles. The amount of heat supplied by the heating mantle varies with the nature of the chemical mixture being studied and is chosen by inspecting the flow of condensate and boiling liquid in the samples F and G. The boiling flask embodies a Cottrell pump I (7 mm inner diameter) and has a small opening J (4 mm inner diame-

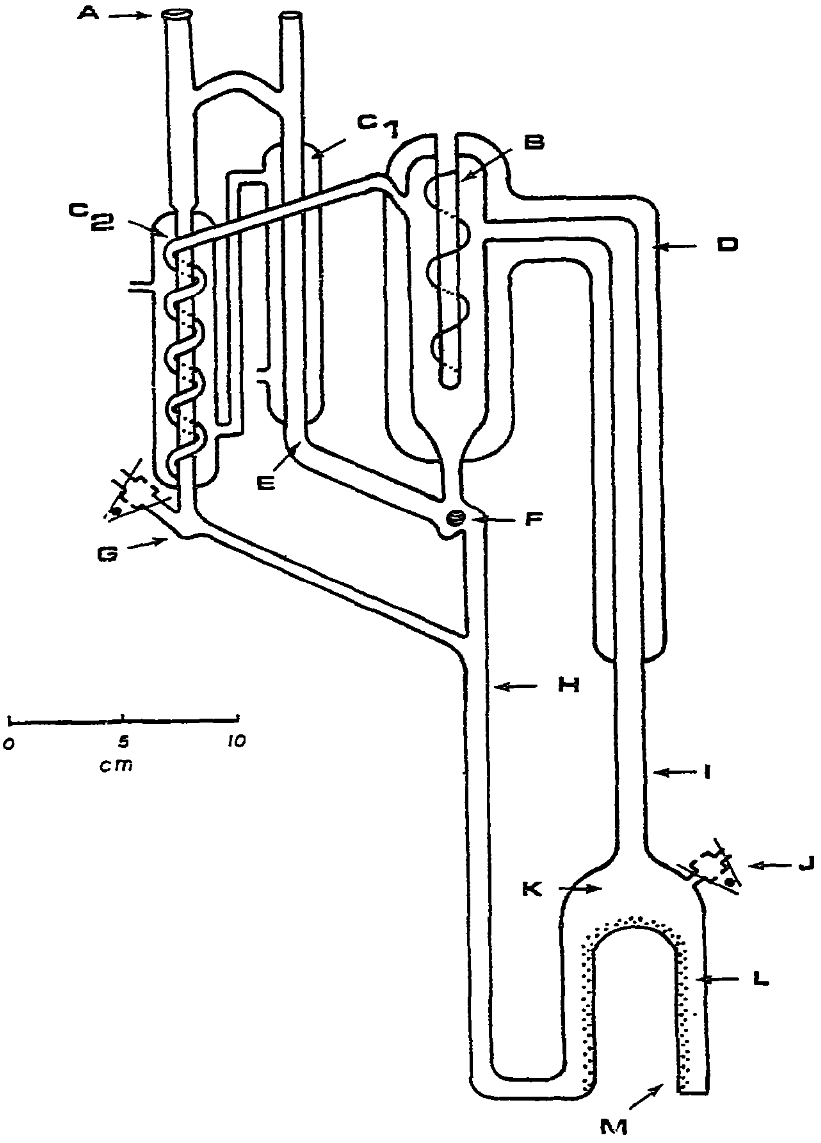

Fig. 1. Vapor—liquid equilibrium still.

ter) which is useful in charging and cleaning operations. This opening is stopped with a silicon rubber cap, covered with Teflon tapes and clamped on top.

Measurement of the equilibrium temperature is done when the boiling liquid streams down the glass spiral on the surface of the thermometer well B. The upper part of the Cottrell tube and the thermometer well are protected against heat losses by means of a vacuum jacket D. Careful insulation of the apparatus has proved to be very important and was accomplished by wrapping the boiling flask, the Cottrell pump and the vacuum jacket, first with layers of asbestos cord and glass wool, and then lagging heavily with polyurethane foam.

The vapor—liquid mixture pours over the thermometer well and separates into vapor and descending liquid. The vapor flows into a water-cooled condenser C2, where it is completely condensed. Any vapors coming from the boiling liquid are condensed in C1. Pressure equilibrium in the boiling-liquid sampler is provided by tube E, which also helps in charging and cleaning the apparatus.

Samples from the condensate and the boiling liquid are taken by piercing the silicon rubber caps with a syringe. Analyses of the equilibrium samples have been carried out using chromatography and the determination of refractive index. The volume of both samplers (F and G) is quite small (about 0.7 ml) and the liquids soon overflow. The mixture of condensate and boiling liquid returns to the boiling flask through tube H (5 mm inner diameter). When working with mixtures of compounds having very large differences (>170°C) in boiling points, it was found necessary to place a one-way valve inside tube H to prevent contamination of the samplers due to occasional bumps, apparently caused by mixing a cool condensate with a very hot boiling liquid.

The still is attached (at A) to a vacuum line which has a 200 l pressure vessel working as ballast. The value of the pressure is measured with U-tube monometers checked with standards. The equilibrium boiling temperatures are determined with certified mercury thermometers with a precision of ±0.05°C.

Reagents

Reagent grade toluene and cyclohexane were distilled and the 40—90% middle cut was used for the measurements. The values of the refractive index (n_D) at 20.0°C for the purified compounds were 1.4969 and 1.4262, respectively, for toluene and cyclohexane.

RESULTS AND DISCUSSION

In the present design the circulation volume of both condensate and boiling liquid is very small, permitting equilibrium to be attained rapidly. The time required for establishing equilibrium after changing the composition of the boiling liquid is around 10 min. A small circulation volume also leads to smaller changes in the concentration of the boiling liquid, resulting in more precise temperature measurements.

Several designs of boiling flasks and heating mantles were built and tested, and the arrangement shown in Fig. 1 gave the best results. In this type of flask the rising vapor bubbles agitate the liquid more efficiently, avoiding concentration gradients. This design also diminishes bumping which is troublesome when working, under low pressure, with liquids of high boiling points.

The vapor—liquid equilibrium of the system cyclohexane—toluene was determined in order to test the performance of the apparatus. Isobaric measurements at a pressure of 713.0 mm Hg were performed and the data used to calculate activity coefficients, γ_i, using the relation

$$RT \ln \gamma_i = RT \ln(y_i p / x_i p_i^0) + (B_{ii} - v_i^0)(p - p_i^0) + (1 - y_i)^2 p\, \delta$$

where R is the gas constant, T is the absolute temperature, p is the pressure of the system, and x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively. The vapor pressure and molar volume of pure component i are denoted by p_i^0 and v_i^0, respectively. The quantity δ is related to the virial coefficients (B_{11} and B_{22}) of the pure species and to the cross-coefficient (B_{12}) between the species by the equation

$$\delta = 2B_{12} - B_{11} - B_{22}$$

Vapor pressures of the pure liquids were taken from Boublik et al. [4] and the molar volumes were based on densities [5]. The virial coefficients were calculated from critical data, following the procedure given by Prausnitz et al. [6].

Figure 2 shows the activity coefficients determined with the present apparatus compared with values found in the literature [7]. The uncertainty in the literature values is not stated but it is probably greater than 1%. Therefore, it seems possible to conclude that the agreement is very good over the entire concentration range.

The apparatus reported here has been used successfully in the determination of the vapor—liquid equilibria of several systems, in the pressure range

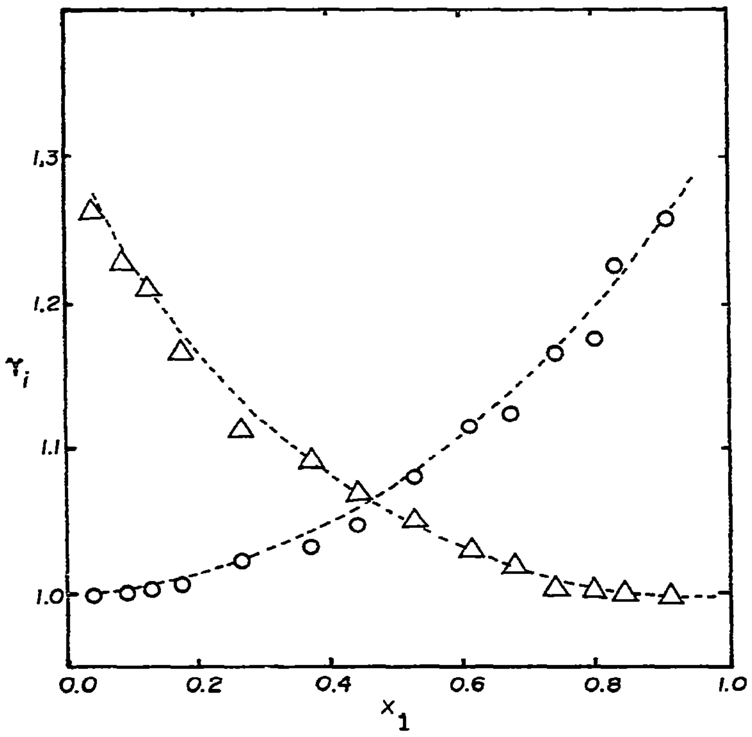

Fig. 2. Activity coefficients (γ_i) of cyclohexane (Δ) and toluene (O) as a function of the mole fraction of cyclohexane in the liquid (x_1). The dotted lines represent literature values [7].

normal to about 10 mm Hg, and with mixtures of compounds having differences in boiling points as large as 260° C.

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