

## EXPERIMENTAL DETERMINATION OF VAPOUR-LIQUID EQUILIBRIUM; NORMAL AND LOW-PRESSURE REGION

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Received May 12, 1988

Accepted June 12, 1988

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### 1. INTRODUCTION

For the design of industrial distillation columns and for the determination of their optimal operating conditions, quantitative characterization is necessary of the vapour-liquid equilibrium in systems whose components are to be separated. Direct experimental data are the primary informations and the purpose of this survey is to review different experimental methods used for measurement of vapour-liquid equilibria in two- and multicomponent systems in the normal and low pressure region.

The development of the vapour-liquid equilibrium experimental techniques was reviewed by Fowler<sup>22,23</sup>, Ridgway<sup>47</sup> and Ridgway and Butler<sup>48</sup>, description of the widely used stills was published by Hála et al.<sup>26</sup> and Williamson<sup>67</sup>. Malanowski<sup>36</sup> presented a survey of circulation methods and "bubble-dew-point" methods<sup>37</sup>. Abbott<sup>1</sup> surveyed techniques for measurement of low-pressure VLE with emphasis on development of the past decade.

The present review is concerned mainly with advances being made during the past twenty five years, both in the improvement of the design of existing forms of stills, and the evolution of new types.

The methods for direct determination of equilibrium data are divided into the following groups: 1. Static methods. 2. Circulation methods. 3. Flow methods. 4. Dew and bubble point methods. 5. Saturation methods.

## 2. STATIC METHODS

The principle of static methods is very simple: The solution is charged into a closed vessel which is placed in a thermostat. The content is stirred or shaken until equilibrium is established between the liquid and its vapours. Then, the total pressure of the system is measured, eventually samples are removed from both phases for analysis.

In practice, the static methods are not as simple as they seem to be. The measurements are often time consuming, the degassing and sampling cause difficulties. In recent years many well known authors developed static methods suitable for the range of normal and low pressures; see for example: McGlashan and Williamson<sup>39</sup>, Scatchard et al.<sup>57</sup>, Orey and Prausnitz<sup>44</sup>, March<sup>38</sup>, Harris and Prausnitz<sup>27</sup>, Vera and Prausnitz<sup>63</sup>. Critical survey of static methods till 1972 was published by Aim<sup>4</sup>.

A precise and relatively rapid procedure was proposed by Gibbs and Van Ness<sup>24</sup>. Liquid solutions of known composition are prepared in a test cell by volumetric metering of degassed liquids from accurate piston-injectors. Once the injectors are charged, vapour pressures for a binary system at constant temperature over the entire composition range are measured in a day. Solution of the coexistence equation provides the isothermal vapour-liquid equilibrium relationship.

A schematic diagram of the major components of the apparatus appears in Fig. 1. Operation of the apparatus starts with the introduction of pure liquids into the degassing unit, where dissolved gases are removed over a period of time. After evacuation of the system the degassed liquids are transferred to the piston injectors, where they are stored under positive pressure. With the test cell submerged in the constant-temperature bath, the cell is half-filled by metering in one of the pure liquids. After equilibration, the vapour pressure is recorded, and a small amount of the second liquid is metered into the cell. The vapour pressure of this dilute solution is recorded, and the process is repeated for increasingly concentrated solutions until the cell is nearly full. The cell is then emptied, evacuated, and a second run is made with the components added in the reverse order. The compositions in the cell are calculated from the accurately measured volumes injected. Vacuum is produced

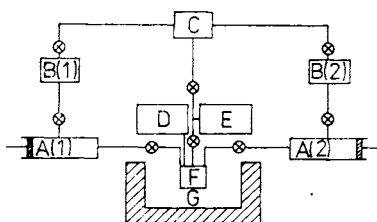


FIG. 1

Schematic diagram of equipment of Gibbs and Van Ness<sup>24</sup>. A Piston injector; B de-gas compartment; C vacuum system; D vapour pressure gauge; E vacuum gauge; F test cell; G constant-temperature bath

by combination of a mechanical pump and an oil diffusion pump, and the system is evacuated to a pressure below 0.1 Pa.

The degassing apparatus is shown in Fig. 2. Compartment C holds up to 300 cm<sup>3</sup> of sample; compartment A has an external diameter of about 15 cm, and the cold finger B has a diameter of about 6 cm. The sample to be degassed is charged to C through the opening made by removal of the stem of needle valve E. This valve is then closed, and A evacuated through stopcock D. The cold finger B is filled with an ice-water mixture, E is opened, and heat is applied to C. Gentle refluxing follows. After 1 h the heater is removed, E is closed, and A is evacuated. This sequence is repeated a number of times until the liquid is judged to be sufficiently degassed. This process may be followed by a vacuum sublimation. In this event B is filled with liquid nitrogen, and D is opened to the vacuum system. The rate of sublimation on to the cold finger is regulated by the setting of needle valve E. Following degassing, the liquid is brought up into compartment A (by sublimation) and valve E is then closed; once thawed, the liquid is drawn through port F into the piston injectors (Fig. 3).

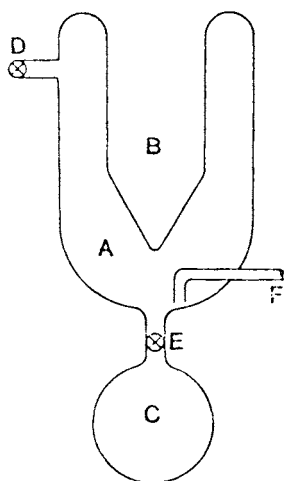


FIG. 2

Degassing apparatus<sup>24</sup>. A Reflux chamber; B cold finger; C liquid-storage bulb; D vacuum stopcock; E teflon needle valve; F port to piston-injector

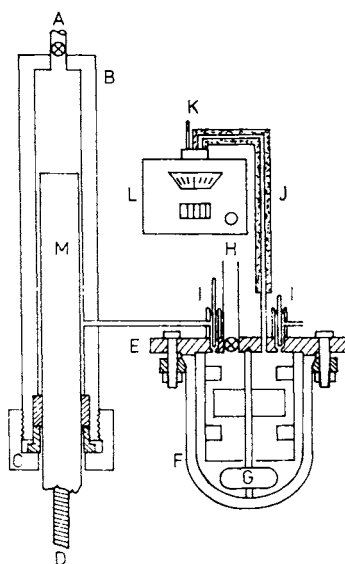


FIG. 3

Piston-injector and test cell<sup>24</sup>. A Line to degassing vessel; B piston-injector body; C packing nut; D lead screw; E cell cover; F glass cup; G teflon-coated magnet; H port to vacuum system; I needle valves; J heated line; K line to reference vacuum; L Texas Instruments pressure gauge; M piston

Gibbs and Van Ness<sup>24</sup> recommend the piston-injectors of Ruska Instrument Corp. Model 2 200, stainless steel, 100 cm<sup>3</sup> capacity. Displaced volume is indicated by a travelling marker on a hub graduated to 0.01 cm<sup>3</sup>.

The test cell F (made from glass) has a capacity of about 100 cm<sup>3</sup>. The cell, injection lines, and piston-injectors are evacuated through a 1 cm port H. The cell is connected through line J to the Texas Instruments fused quartz pressure gauge L. Line J is insulated and heated to a temperature above the cell temperature so as to prevent condensation in the line. The authors recommended to interpose a Ruska Instrument Corp. differential pressure null indicator between the cell and the pressure gauge.

Gibbs and Van Ness<sup>24</sup> tested their apparatus by measuring vapour pressures for the ethanol–heptane system at 30°C. The average deviation between two (independent) sets of data is less than 0.3 rel. %.

Aim<sup>3</sup> has developed a precise static apparatus for accurate measurement of total vapour pressures of solutions. Mixtures of known compositions are prepared synthetically in a thermostatted equilibrium cell (40 cm<sup>3</sup>, see Fig. 4) by weight from pure degassed components. Total pressure is measured by quartz Bourdon Gauge (Texas precision model 144) with accuracy  $\pm 0.3$  Pa. The applicability of the method may be expanded to temperatures higher than 35°C by introducing a sensitive pressure null indicator between the equilibrium cell and pressure gauge.

The apparatus described by Aim<sup>3</sup> provides the means by which highly accurate isothermal data may be obtained within two experimental runs. The apparatus is suitable for studying systems with very different volatilities of components where other methods fail, especially at low temperatures. Sufficient degassing of the liquids is a crucial problem of static vapour pressure measurement, as the presence of residual gases dissolved in the investigated solution may lead to large errors in pressure determination.

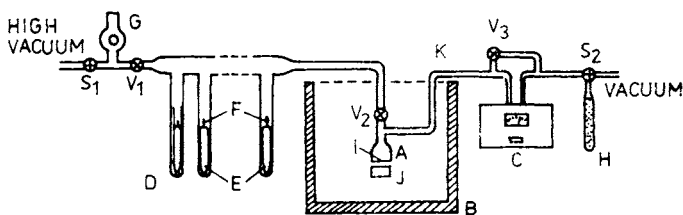


FIG. 4

Static apparatus for vapour pressure measurements<sup>3</sup>. A Equilibrium cell; B thermostat; C Texas Instruments pressure gauge; D ampoule holders; E ampoules; F nickel cylinders; G Penning gauge head; H finger with active carbon; I magnetic stirrer; J magnetic drive; K interconnecting line; S<sub>1</sub>, S<sub>2</sub> vacuum glass stopcocks; V<sub>1</sub> to V<sub>3</sub> vacuum bellows valves

Numerous procedures of degassing pure liquids were carried out, namely of the repeated freezing–pumping–thawing technique of Bell et al.<sup>6</sup> and Battino et al.<sup>5</sup>. Aim<sup>3</sup> did not succeed in reproducing any of these methods in such a way that the liquid was degassed within a reasonable time. For these reasons, he proposed the degassing apparatus (see Figs 5 and 6) where, by heating, the liquid is forced to circulate vigorously (by using the Cottrell pump). At 10 to 20 min intervals the vapour phase is exhausted by opening a valve to vacuum for 5 seconds. After thirteen such exhausting cycles have been performed, the liquid in the apparatus is degassed sufficiently.

Van Ness and Abbott<sup>62</sup> published a similar degassing procedure. Maher and Smith<sup>35</sup> published a total pressure vapour–liquid equilibrium apparatus whose scheme is seen in Fig. 7.

Fifteen cells (approximately 25 cm<sup>3</sup> each) provide thirteen mixtures and two pure component points on the  $P$  vs  $x$  isotherm. The cells are loaded by adding the desired amounts of liquids to each cell and weighing after each addition. After loading, the 15 cells are attached via Cajon Ultra-Torr fittings to 15 valves mounted in a ring and connected to a common low-volume manifold. Multiple freezing–evacuation–thawing cycles are used to degas the loaded cells. The uncertainty in the cell mole fractions is within  $\pm 0.00005$ . The temperature is measured by using suitable thermometer (i.e. platinum resistance thermometer); the desired accuracy is within  $\pm 0.003$  K. A Datametrics Model 531 transducer is used for the nulling device. The pressure of the equilibrium vapour is balanced with nitrogen gas and the pressure of the nitrogen

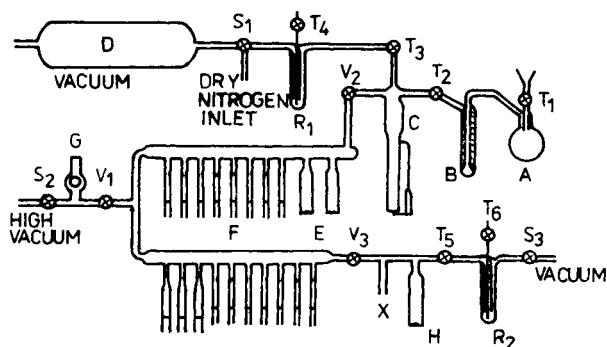


FIG. 5

Assembly for the degassing of liquids and preparation of ampoules<sup>3</sup>. A Storage flask; B molecular sieve; C degassing apparatus; D vacuum container; E fingers with stirrers; F ampoules; G Penning gauge head; H degassing finger; X point to seal on the NMP storage ampoule; R<sub>1</sub>, R<sub>2</sub> cold traps; S<sub>1</sub> to S<sub>3</sub> vacuum glass stopcocks; T<sub>1</sub> to T<sub>6</sub> vacuum teflon/glass valves; V<sub>1</sub> to V<sub>3</sub> vacuum bellows valves

is measured with Datametrics Model 572 transducer mounted outside the apparatus. The accuracy of the described pressure measurements, including possible error in the null, is  $\pm 0.035\%$  of the reading.

The described techniques provide some advantages, especially in speed, over the titration devices which have been so effectively used for total pressure measurements. Usually three isotherms are measured in a typical 5-day run (including loading, degassing, and isotherm measurements).

Tomlins and March<sup>61</sup> described a static apparatus for measuring the vapour pressures of liquid mixtures (see Fig. 8). A capacitance manometer (in conjunction with an automatic pressure controller) is used as a null device to isolate the liquid and

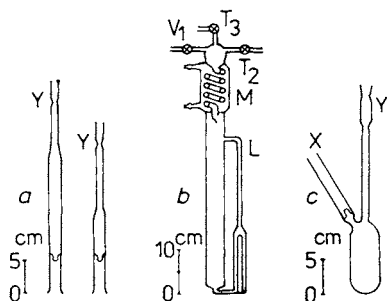


FIG. 6

Accessories for the transfer and degassing of pure liquids<sup>3</sup>. *a* Ampoules with spherical break seals used for degassed pure liquids (at constriction Y sealed off from the main line); *b* apparatus for the degassing of volatile liquids (K heater; L Cottrell pump; M condenser; the valves are designated in accordance with Fig. 5); *c* NMP storage ampoules (at constriction Y sealed off the vacuum distillation apparatus, at X sealed to the degassing assembly)

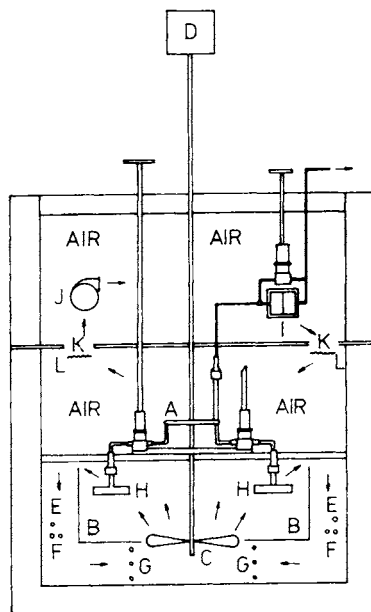


FIG. 7

Schematic sketch of the Maher and Smith<sup>35</sup> apparatus showing the liquid and air baths. A Manifold assembly; B baffle tank; C impeller; D impeller motor; E auxiliary heater; F auxiliary cooling coils; G control heater; H cells; I nulling transducer, J air bath blower; K openings for air flow; L air bath heaters

vapour. The vapour pressure is measured with a precision mercury manometer. The continuous-dilution technique for sample introduction has been incorporated in the apparatus so that the composition range of a mixture can be covered in two

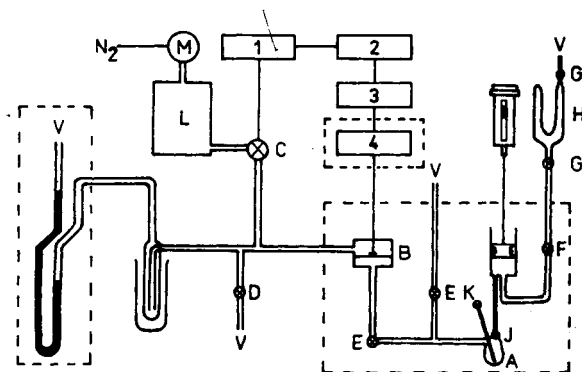


FIG. 8

Tomlins and March<sup>61</sup> static apparatus. A Servosystem (which comprises the capacitance manometer); B sensing head of a capacitance manometer; C, D, E, F valves; G teflon tap; H sublimation vessel; J microvalve; L nitrogen reservoir; M vacuum regulator; V connection to vacuum pump, 1 pressure controller, 2 phase-advance amplifier, 3 capacitance manometer, 4 balance unit

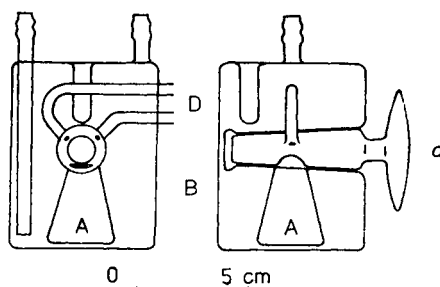
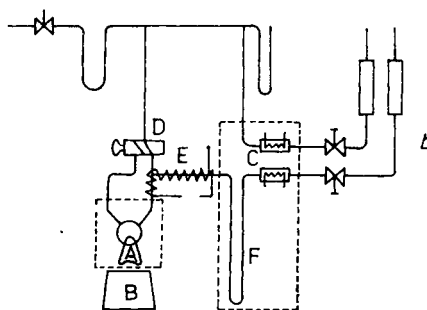


FIG. 9

Wichterle and Hála still<sup>66</sup>. a Equilibrium chamber: A equilibrium chamber; B thermostated jacket; C sampling cock; D carrier gas inlet and out put. b Scheme of the apparatus: A equilibrium vessel (thermostated); B manetic stirrer; C carrier gas; D two-way column cock; F electric heater; E chromatographic column; G chromatographic detector (catharometer)



runs. For degassing of liquids, the sublimation method described by Bell and co-workers<sup>6</sup> is used. The accuracy of measured quantities is as follows: pressure, 3 Pa; temperature, 0.002 K; volume, 0.002 cm<sup>3</sup>. Sample introduction is described in detail in the original paper.

Wichterle and Hála<sup>66</sup> developed a rapid static semimicro method based on sampling of very small volumes of the vapour phase which is analyzed by gas chromatography (see Fig. 9). Only about 2 ml of liquid sample is needed for the determination of one experimental point. The solution of known composition is poured into the equilibrium chamber. The stopcock plug has in the middle a cavity (volume of about 0.5 ml). During saturation this cavity is connected with the vessel. The sample of the vapour phase is taken by turning the plug by 180° so that the vapour phase is swept from the cavity by the carrier gas into the chromatograph for analysis. The sampling cock is carefully polished and is not lubricated. Electric heating of the connecting tubing is used to prevent condensation of vapour between the equilibrium vessel and gas chromatograph.

It is useful to analyse both phases chromatographically about four times. The small amount of vapour phase sample makes it possible to repeat the analysis while leaving the concentration in the liquid practically unchanged.

The accuracy of the semimicro method described is about  $\pm 1$  rel. % which is sufficient for many chemical engineering purposes. The accuracy can be increased with the aid of a more accurate analyser, for instance mass spectrometer. The static semimicro method is advantageous especially for systematical study of extraction agents for extractive distillation.

Many modifications of this method have been published: Boublíková<sup>65</sup>; Benson, Anand, Kiohara<sup>7</sup>; Monfort, Guzman et al.<sup>40</sup>; Schmidt<sup>59</sup>.

### 3. CIRCULATION METHODS

These methods are the most widely used. They are convenient to use both in the region of medium and low pressures.

Even though the various equilibrium stills with simple circulation differ significantly from one another in their construction details, they are all based on a common principle which is shown schematically in Fig. 10. The vapours evolved from the boiling mixture in the distilling flask A pass through the vapour conduit ( $\rightarrow$ ) and after complete condensation collect in the receiver B. After filling the receiver the condensate returns to the distilling flask through the liquid conduit ( $\leftarrow$ ), in which there is usually inserted a weir (trap) or cock to prevent the flow of liquid from the distilling flask back into the receiver (not shown on the diagram). If we start the still with the receiver B empty, at the instant when it fills for the first time, its contents are richer in the more volatile constituent than is the vapour phase over the boiling mixture in the distilling flask. With further operation of the still, the contents of the



distillation flask become richer in the volatile component and the receiver becomes poorer. This process continues until the steady state is attained, in which the compositions in both vessels no longer change with time. Then both compositions are determined analytically. It can be shown that the steady state corresponds to the equilibrium.

### 3.1. Stills with Circulation of the Vapour Phase

The first still with circulation of the vapour phase was proposed by Jamaguchi and Sameshima<sup>55</sup>, but the first equilibrium still which functioned satisfactorily was constructed by Othmer<sup>43</sup> (Fig. 11).

The results obtained with this instrument may contain certain errors: The vapour jacket around the tube carrying vapour to the cooler does not completely prevent partial condensation. This is especially evident with systems having high boiling points. For this reason it is recommended to insulate the upper part of this instrument or to heat it with a resistance coil. On the other hand it is necessary to avoid super-

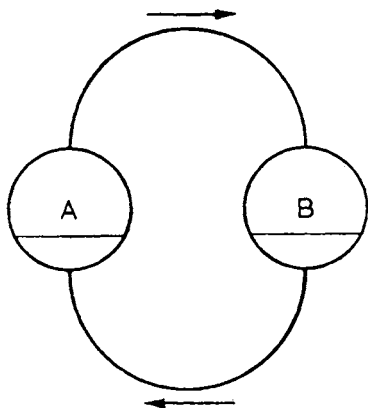


FIG. 10  
Schematic diagram of circulation stills

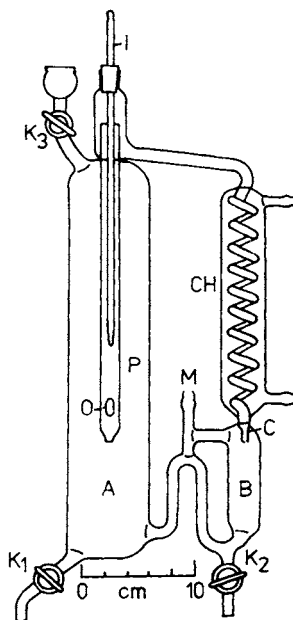


FIG. 11  
Othmer still<sup>43</sup>. A Boiling vessel; B receiver; K<sub>1</sub>, K<sub>2</sub> sampling cocks; K<sub>3</sub> vent cock; T thermometer; CH cooler; P vapour tube; O inlet; C drop counter; M to manostat

heating the walls of the still, as this could lead to non-equilibrium total evaporation of droplets sprayed on the walls. Because the boiling itself is not sufficient to ensure thorough mixing of the boiling liquid with the returning cold condensate, concentration gradients can arise in the distilling flask. The liquid in equilibrium with vapour mixes with part of the returning condensate during the withdrawal of the sample. This error is important only with systems having comparatively high relative volatilities and can be diminished by the use of a large amount of solution. The temperature measured in the vapour phase does not always correspond to the true boiling point.

Othmer<sup>41,42</sup>, in an effort to remove some of these weaknesses, proposed further modifications. The equilibrium stills have to fulfil the following requirements:

- 1) Concentration gradients must not occur in the boiling liquid.
- 2) The equilibrium vapour must not partially condense.
- 3) The walls of the boiling flask must not be superheated in order to avoid non-equilibrium total evaporation of adhering droplets of liquid.
- 4) The cold condensate returned to the distillation flask must be perfectly mixed with the main portion of liquid, in order to avoid its non-equilibrium vaporization as a result of its lower boiling point.
- 5) The vapour leaving the boiling liquid must not entrain droplets of liquid and carry them into the vapour receiver.
- 6) The instrument must make possible the accurate measurement of the boiling point.
- 7) Mixing of the equilibrium liquid with part of the returning condensate should not occur on stopping the instrument.
- 8) The equilibrium should be established as quickly as possible.
- 9) The consumption of substances should be as small as possible.
- 10) The instrument should be as simple as possible.

### 3.2. Stills with Circulation of the Vapour and Liquid Phases

The imprecise measurement of boiling point is a drawback to the stills having a circulating vapour phase. This error is eliminated with instruments containing the Cottrell pump. The first instrument of this type giving precise results was proposed by Gillespie<sup>25</sup>. Its functioning is clear from Fig. 12.

Gillespie himself pointed out the one serious error in this apparatus, namely that the samples withdrawn from the boiling flask do not correspond to the liquid which is in true equilibrium with the vapour leaving the separator.

Brown's modification<sup>13</sup> completely eliminates the possibility of non-equilibrium vaporization in the distilling flask (Fig. 13).

Dvořák stated in a systematical study that intense stirring is necessary both in the liquid as well as in the condensate receivers. He proposed in collaboration with Boublík<sup>18</sup> a precise apparatus (shown in Fig. 14) suitable even for systems having very high relative volatility.

The modification published by Hlavatý<sup>28</sup> (Fig. 15) consisted in the diminution of the still, which was achieved by the use of a small Pt-thermometer in the head H, and in mounting two magnetically operated valves  $V_1$  and  $V_2$ . These valves prevented

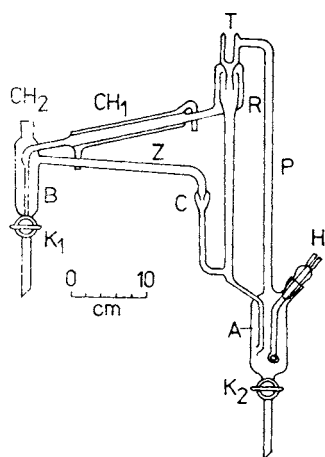


FIG. 12

Gillespie<sup>25</sup> still. A Boiling flask; P Cottrell pump; T thermometer well; R droplet separator; K<sub>1</sub>, K<sub>2</sub> sampling cocks; B receiver; CH<sub>1</sub>, CH<sub>2</sub> coolers; Z return line for condensate; C drop counter; H internal heater

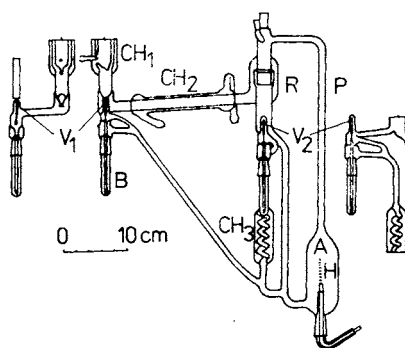


FIG. 13

Brown<sup>13</sup> still. A Boiling flask; H internal heater; R droplet separator; P Cottrell pump; B receiver; CH<sub>1</sub> to CH<sub>3</sub> coolers; V<sub>1</sub>, V<sub>2</sub> electromagnetic valves

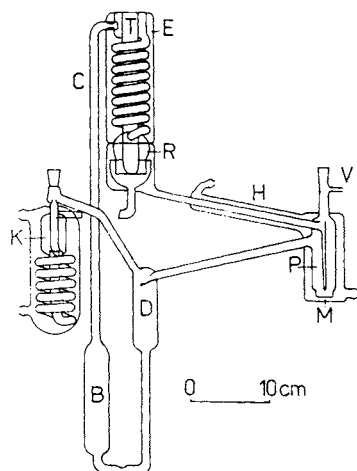


FIG. 14

Dvořák and Boublík<sup>18</sup> still: B Boiling flask; P reservoir of condensate; K reservoir of liquid; D drop counter; E evacuated mantle; C Cottrell tube; R equilibrium cell; T flask for thermometer; V connexion to outer atmosphere; M magnetic stirrer

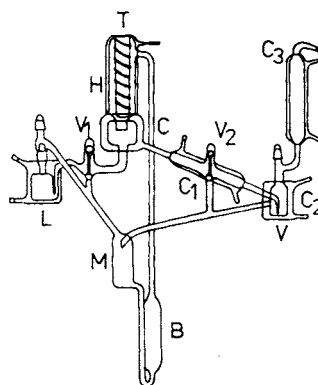


FIG. 15

Hlavatý<sup>28</sup> still. H Head; T thermometer; V<sub>1</sub>, V<sub>2</sub> magnetically operated valves; L vessel with liquid; V vessel with condensate; C Cottrell tube; C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> coolers; B boiler

the liquid and condensed vapour from flowing through vessels V and L after the equilibrium had been reached and the pressure let in. The liquid in all three vessels L, M and V was agitated by magnetic stirrers. The equilibrium is reached reliably during 30–40 min.

Yerazunis, Flowright and Smola<sup>68</sup> improved the contact between the liquid and vapour phase of the circulation still (see Fig. (16).

In Kay modification<sup>31</sup> the samples of equilibrium phases are withdrawn by means of microsyringe (precision sampling by Baton Rouge Louisiana) from the reservoirs (the regime in the still is not disturbed).

Scatchard and Ticknor<sup>56</sup> made many very precise measurements by means of the still, which is shown in Fig. 17.

Röck and Sieg<sup>54</sup> fitted their apparatus with a thermostated jacket (see Fig. 18)

Packer, Ellis and Soares<sup>45</sup> (Figs 19 and 20) proposed a 40 cm<sup>3</sup> recycling vapour–liquid equilibrium still with direct injection of the vapour sample into carrier stream of a chromatographic analytical unit. They found good accuracy of isobaric vapour–liquid results both for miscible and for partially miscible vapour condensate systems.

Berro, Deyrieux, Péneloux and Rogalski<sup>8,9</sup> (Figs 21 and 22) proposed an apparatus in which the steady state can be reached very quickly. The still uses the well

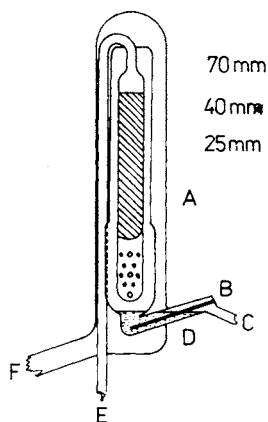


FIG. 16

Head of the apparatus Yerazunis, Flowright and Smola<sup>16</sup>. The diameters of the tubes are given in millimeters; A packing of glass helices (6 mm); B thermowell; C liquid outlet; D liquid trap; E outlet to Cottrell pump; F vapour outlet

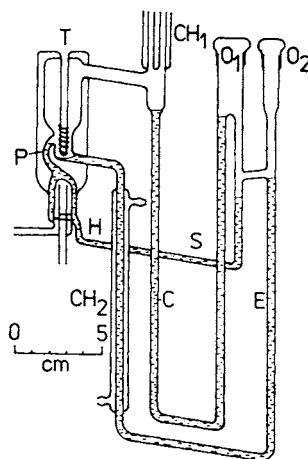


FIG. 17

Scatchard and Ticknor<sup>56</sup> still. T' Thermometer well; P Cottrell pump; H internal heater; CH<sub>1</sub>, CH<sub>2</sub> coolers; E tube withdrawing liquid from equilibrium chamber; C tube withdrawing condensate; S common return line; O<sub>1</sub>, O<sub>2</sub> sampling openings

known parts of Brown-Ewald and Röck-Sieg stills. The claimed accuracy is 0.01 K and 5 Pa.

FIG. 18

Röck and Sieg<sup>54</sup> still: A Boiling flask; B Cottrell pump; C cooler; D droplet separator; E receiver for collecting liquid; F receiver for collecting condensate; H heater; T thermometer wells

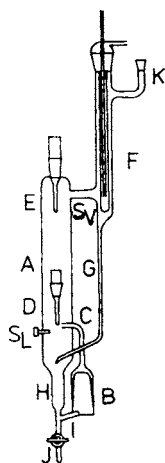
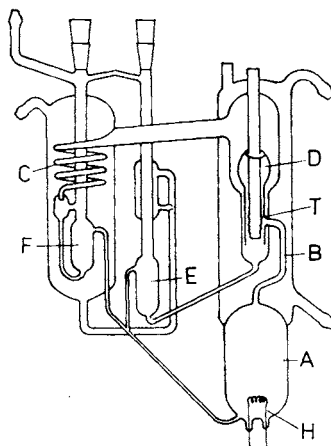


FIG. 19

Packer, Ellis and Soares<sup>45</sup> miniature equilibrium still. A Still; B bayonet heater; C Cottrell tube; D thermistor well (for determining the boiling point of the mixture); E thermistor well (for determining the temperature of the vapour leaving the still); F condenser; G capillary tube; H section packed with Fenske helices (to ensure good mixing); S<sub>L</sub> sampling of liquid; S<sub>V</sub> sampling of vapour

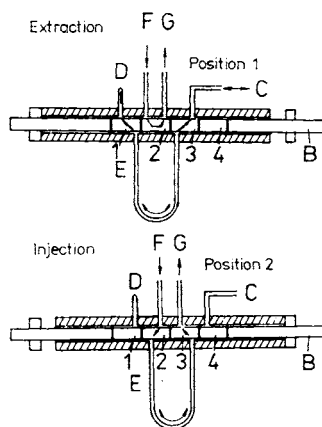


FIG. 20

Operation of the vapour injection (see Fig. 19)

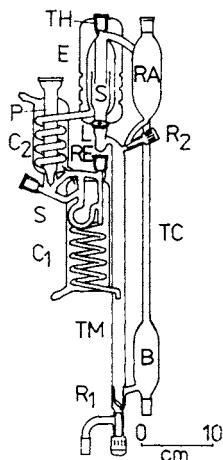


FIG. 21

Berro, Deyrieux, Pénéloux and Rogalski<sup>8,9</sup> apparatus. Schematic diagram of the ebullimeter: B boiler, TC Cottrell pump; TH temperature well; S separator;  $C_1$  and  $C_2$  condensers; P to manostat; V condensed-vapour sample; L liquid sample; RE liquid and vapour return; R resistance wire;  $R_1$ ,  $R_2$  stopcocks

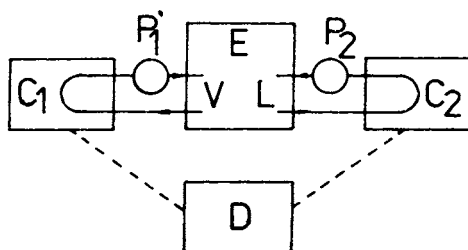


FIG. 22

Scheme of the still of Berro, Rogalski, Pénéloux<sup>8,9</sup>. E ebullimeter;  $C_1$ ,  $C_2$  densitometric cells; V, L vapour and liquid samples;  $P_1$ ,  $P_2$  peristaltic pumps

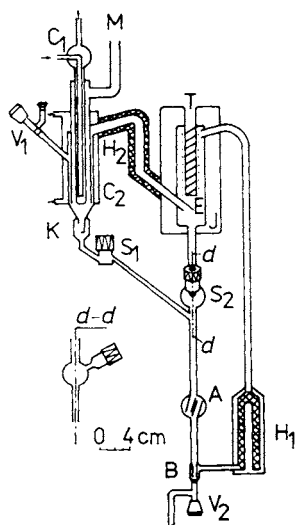


FIG. 23

Ebullimeter of Rogalski and Malanowski<sup>51,52</sup>. A, B Mixers for uniform mixing;  $C_1$ ,  $C_2$  coolers; E equilibrium chamber;  $H_1$  heater providing thermal lift to Cottrell pump;  $H_2$  heater for overheating vapour stream; J vacuum jacket; K flow meter (drop counter); M to pressure control system;  $S_1$  vapour condensate container;  $S_2$  liquid phase container; T thermometer;  $V_1$  valve for introducing samples to still;  $V_2$  valve for drainage of still

To the same type belong the ebulliometer of Swętoslawski type modified by Rogalski, Rybakiewicz and Malanowski<sup>52,53</sup> (Fig. 23). Berro, Rogalski and Pénélox<sup>8</sup> developed a circulation still with continuous densitometric analysis (Paar Densitometer DM A 60).

#### 4. FLOW METHODS

The effort to attain the steady state as quickly as possible have led to the development of dynamic flow methods. In the flow method, we feed to the equilibrium chamber a steady stream of constant composition which can be either in the liquid or in the vapour phase or combination of both of them.

The flowstills have the advantage that the data may be determined rapidly. The Cathala still and its modifications have the further advantage that they were designed for use with reacting systems, for which the circulation or the total pressure methods are not suitable. Cathala flow still<sup>14,15</sup> is shown in Fig. 24.

Constant head supply vessels containing the pure components supply two feeds whose compositions are about the expected equilibrium values; one, the liquid feed, to a pre-heater raising its temperature just below its boiling point, the other to a total evaporator and superheater, producing a slightly superheated vapour feed. The vapour enters from below the mixing chamber which is fitted with two sintered glass disks to ensure perfect contact between the phases. The preheated liquids is introduced into the mixing chamber from the side and mixed with the vapour. After passage through the second porous disk, the mixture of phases rises into the Cottrell pump, from which it spurts on the thermometer well. Vapour and liquid phases are separated and then condensed, or cooled, and collected for subsequent analysis.

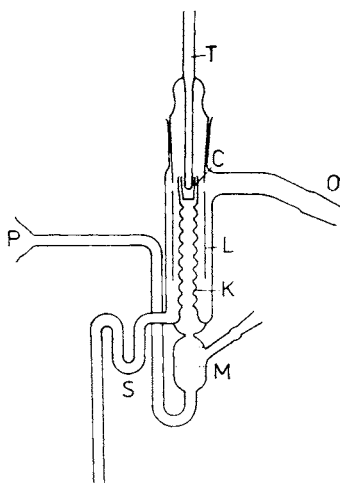


FIG. 24

Dynamic Cathala ebulliometer<sup>14,15</sup>. M Mixing chamber; K column; C Cottrell pump; T thermometer well; L jacket; P vapour inlet; K liquid inlet; O vapour outlet; S liquid outlet

The Cathala flow still and its modifications have the advantages that the data may be determined rapidly (within 20 min) – also in systems with limited miscibility or, if there is a danger of chemical reaction occurring on long heating, when circulation and static methods cannot be used. Disadvantages are the relatively difficult feeding and large consumption of pure components.

Jenkins and Gibson-Robinson<sup>29</sup> tested thoroughly several sets of data, all obtained on Cathala still for binary systems different in type. They found that the flow still produces results comparable fully to those obtained from other (i.e. circulation) stills.

Vilím, Hála, Pick and Fried<sup>64</sup> proposed the flow still which is shown in Fig. 25. The apparatus consists of three units: feed vessel, boiler, and equilibrium chamber. The liquid mixture is contained in the feed vessel which maintains a constant level of liquid in the boiler.

The boiler is connected to the equilibrium chamber of the still by a Cottrell pump. Vapour and liquid phases are separated in the equilibrium chamber and then condensed, or cooled, and collected for subsequent analysis. During operation, the power supplied to the internal heater of the boiler is adjusted to give a liquid–vapour ratio about 1 : 10. After running the still for 10 min the temperature in the equilibrium chamber is usually steady. A further 10 min is sufficient for the temperature and pressure to be measured and for the liquid- and vapour-phase samples to be collected so that the single determination takes about 20 min (while the liquid is heated to the boiling point only for several seconds).

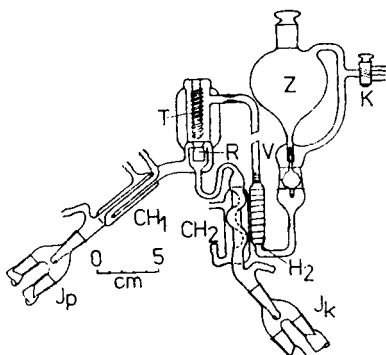


FIG. 25

Vilím, Hála, Pick and Fried<sup>64</sup> still. V Vapourizing tube; H<sub>1</sub>, H<sub>2</sub> heaters; Z supply vessel; K three-way cock; T thermometer well; R droplet separator; CH<sub>1</sub>, CH<sub>2</sub> coolers; J<sub>p</sub>, J<sub>k</sub> vapour and liquid samplers

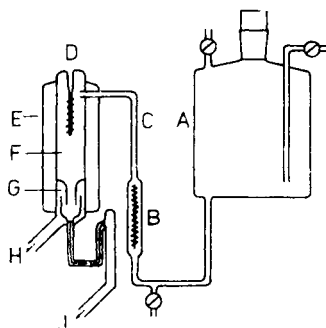


FIG. 26

El-Yafi, Martiner, Newsham and Vahdat<sup>19</sup> flow still. A Supply vessel; B heater; C Cottrell tube; D thermometer well; E vacuum kacket; F equilibrium chamber; H vapour samples; J liquid samples



Boublík<sup>11</sup> proposed a modification of the feed vessel which enables to determine equilibria in systems with limited miscibility.

Dawe, Newsham and Ng<sup>16</sup> modified the just mentioned flow still in that the thermometer well was designed to accommodate the platinum resistance thermometer; further, the vacuum jacket that insulated the equilibrium chamber was extended to include the droplet separator in order to minimize thermal losses. Similar modifications have been proposed by El-Yafi, Martinez, Newsham and Vahdat<sup>19</sup> (Fig. 26) and Acosta, Rodriguez and Guardia<sup>2</sup>.

The thermodynamically consistent data measured under various operating conditions show the usefulness of this flow still especially for determining equilibria in systems with thermally unstable components.

## 5. BUBBLE-DEW POINT METHODS

The static and circulation methods (described in previous parts) are suitable for the determination of points which lie on the horizontal lines of  $P$ - $x$ - $y$  diagrams. It is

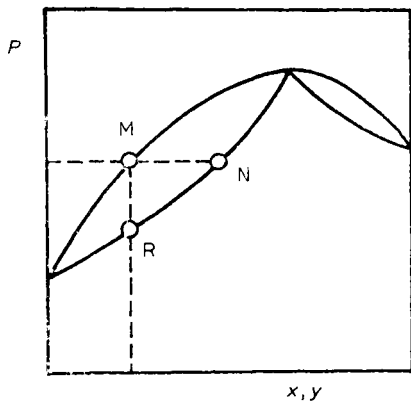


FIG. 27

Principle of the dew and bubble point method  $P$ - $x$ - $y$  diagram

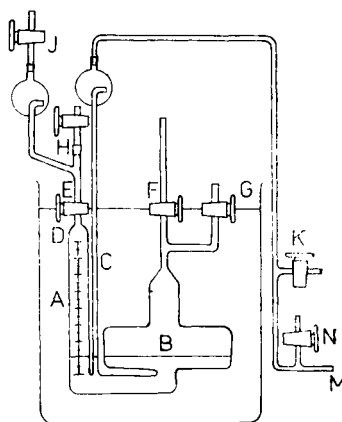


FIG. 28

Instrument for determining the dew and bubble point by Feller and McDonald<sup>21</sup>. A Graduated cylinder; B mercury reservoir; D contraction of the graduated cylinder; H neck for adding sample; J, F, N cocks joining the equipment to the pumping unit; G, K cocks joining the equipment with the external atmosphere; E cock for adding sample; M to manostat

evident (see Fig. 27) that the diagram VLE can be taken as the set of points which lie on vertical lines (i.e. "bubble-dew" points).

Feller and McDonald<sup>21</sup> method (Fig. 28): The graduated cylinder is situated in a thermostat. The liquid sample of known composition is introduced into the cylinder through the inlet. The sample is degased (which is not a simple procedure), then gasified, slowly compressed and after setting level of mercury in the parallel tube to the same height as in the cylinder, the volume and pressure are read off simultaneously. The measured values are plotted on the  $P$ - $V$  diagrams and from the break on the extended curve we determine the dew point; by extrapolation of the curves to the volume ( $l$ ) of the sample, we find the bubble-point. The advantage of the just mentioned method is that for the determination of the diagram it is not necessary to analyse liquid and vapour phases.

Brewster and McGlashan<sup>12</sup>, Kato et al.<sup>30</sup>, McGlashan and Williamson<sup>39</sup> have published methods of the BDP type. It must be mentioned at the end, that BDP are used mainly for VLE determination in systems at high pressures.

## 6. SATURATION METHODS

The partial vapour pressures of the constituents in mixture can be measured with saturation methods which consist in passing a measured amount of inert gas through the solution, removing the absorbed vapours, and determining their weight and composition.

The principle of saturation methods is known for a long time (see Linebarger<sup>33</sup>). The methods are used chiefly at low and moderate pressures for systems whose components differ widely in volatility. The advantage of the saturation procedures is that the composition of the liquid phase can be readily deduced from a knowledge of the amount of the components in the solution (which can be prepared by weighing). It is necessary, indeed, that the measured solution does not dissolve appreciable quantities of carrier gas.

The most important part of the method is the saturator. It must ensure that the inert gas (nitrogen, argon, helium) is bubbled through the solution under conditions such that equilibrium is reached.

Many different types of saturators have been published. Bichowsky and Storch<sup>10</sup> proposed the horizontal saturation tube.

Horizontal saturators are often used. For example, Shaw and Butler<sup>59</sup> used them for the determination of the partial pressures of water and alcohol in mixed solutions containing lithium chloride. Dowles and Perman<sup>17</sup> proposed the vertical type. Randall and Weber<sup>46</sup> measured by means of vertical saturators the vapour-liquid equilibria in the system 1-butanol and water.

Linek and Hála<sup>34</sup> proposed the saturator vessel shown in Fig. 29b. The saturator is designed so as to provide intimate contact between the carrier gas and the solution

and to prevent the entrainment of the droplets. The length of the helical path along which the inert gas bubbles rise exceeds one meter. The saturator contains about 20 cm<sup>3</sup> of solution when at least a quarter of the spiral length is in vapour phase. Schematic layout of the saturation battery and auxiliary equipment is shown in Fig. 29a.

The carrier gas is taken from a pressure vessel via reduction valve, and its flow rate is finely controlled by a needle valve A; the pressure of carrier gas is maintained constant by a suitable simple manostat M. Impurities (i.e. water) are removed from the inert gas in two washing bottles C, D. In the battery of six saturators F, which are placed in the thermostat E the inert gas is saturated with vapours. The pressure at the exit from the last saturator is measured by manometer G. The carrier gas with vapours passes then through the heated tube (to prevent condensation) into the absorber (I, J). Here, the vapours are removed and their weight and composition determined. The amount of inert gas passed through the apparatus is then measured. The eudiometer K, with constant hydrodynamic resistance proposed by Erdős

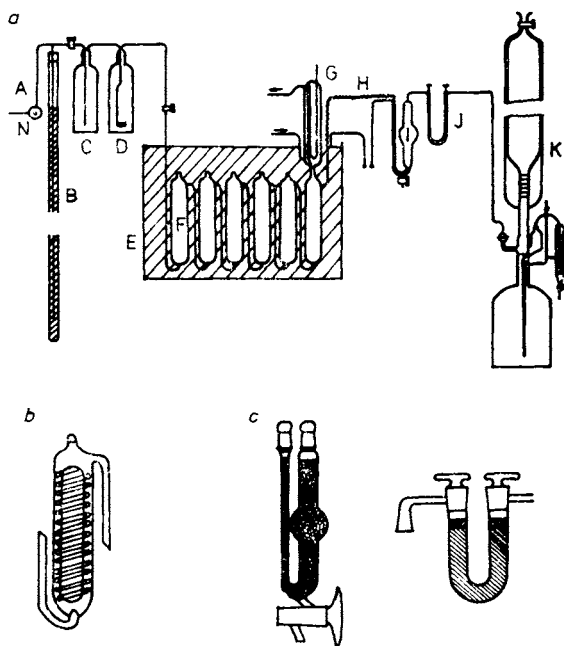


FIG. 29

Linck and Hála<sup>34</sup> saturation apparatus. *a* A Needle valve; B manostat; C, D washing bottles; F battery of saturators; E thermostat; G manometer; H heated tube; I, J adsorber, K eudiometer. *b* Saturator. *c* Absorbers

and Bareš<sup>20</sup> is very suitable for this purpose. The accuracy of the method is of the order 0.5 rel. %. (according to the analytical method).

Several interesting modifications have been published which combine the saturation procedure with gas chromatographic analysis. Teruya, Hosako, Nakano and Nakamori<sup>60</sup> proposed a simple and rapid method for estimating water activities of aqueous solutions containing electrolytes. The carrier gas passes with constant flow alternatively into two saturators of the same type; one of them contains pure water and the other the solution of known composition. Signals of gas chromatographic detectors are recorded which correspond to the amount of water in the gas phases. The authors claim that the results agree within 0.5% with the literature values. Details see in original paper.

Leroi, Masson, Renon, Fabries and Sannier<sup>32</sup> described the inert gas stripping method for fast determination of limiting activity coefficient of a solute in a liquid mixture. Their method is based on the study of the solute elution with time. The solute is stripped from the solution by a constant flow of inert gas, the gas leaving the saturator is periodically sampled and analyzed by gas chromatography.

The limiting activity coefficient,  $\gamma_i^\infty$ , can be calculated (as it was shown) from the equation

$$\gamma_i^\infty = - \frac{NRT}{DP_i^0} \frac{1}{t} \ln \frac{S_i}{(S_i)_{t=0}}$$

where  $N$  denotes total amount of solvent in the cell,  $D$  carrier gas flow rate,  $R$  gas constant,  $T$  absolute temperature,  $P_i^0$  vapour pressure of pure component  $i$ ,  $t$  time,  $S_i$  peak area of  $i$ .

The advantages of the method are as follows: a) The determination of limiting activity coefficient of a solute does not need any calibration of the chromatographic detector nor any preparation of the experimental device. b) It is possible to study activity coefficient of any solute dissolved in any multicomponent mixture. c) With detector calibration it is possible to study the variation of the solute activity coefficient with concentration in the liquid mixture.

The reproducibility of the measurement is of the order 1 or 2 rel. %. Richon, Antoine and Renon<sup>49</sup> modified the saturator to improve mass transfer and to prevent liquid entrainment. Richon and Renon<sup>50</sup> and Richon, Sorentino and Voiley<sup>51</sup> extended the described method to measurements of Henry's constant.

## 7. DISCUSSION

A number of general features follow from what has hitherto been said about the stills for determining vapour-liquid equilibria. Advantages and disadvantages of different experimental methods are summarized in Table I.

TABLE I

Advantages and disadvantages of different experimental methods used for the determination of vapour-liquid equilibrium at normal and low pressures

*Static methods*

- Advantages:
1. simple principle
  2. small consumption of pure substances
  3. analysis of equilibrium phases is unnecessary
- Disadvantages:
1. degassing is time-consuming
  2. preparation of samples for measurement is complicated
  3. long period to establish equilibrium

*Circulation methods*

- Advantages:
1. degassing of substances is not necessary
  2. establishing equilibrium is comparatively rapid
  3. boiling point measurement is accurate (by using Cottrell pump)
- Disadvantages:
1. precise circulation stills are demanding on glass glowing
  2. analysis of composition of both phases is unavoidably necessary
  3. consumption of pure substances is considerable

*Flow methods*

- Advantages:
1. especially rapid establishment of equilibrium
  2. precise measurement of boiling points
  3. degassing need not be carried out
- Disadvantages:
1. complicated feeding
  2. both phases must be analyzed
  3. rather large consumption of pure substances

*Dew and bubble point methods*

- Advantages:
1. analysis of both phases is unnecessary
  2. smaller consumption of pure substances
  3. simple temperature control (thermostat)
- Disadvantages:
1. accuracy of measurements is comparatively low
  2. measurements are tedious
  3. method is suitable only for binary systems

*Saturation methods*

- Advantages:
1. partial pressures of components are measured
  2. analysis of liquid phase is unnecessary
  3. method is suitable for systems with especially different volatilities of components
- Disadvantages:
1. determination of passed-through amount of inert gas is necessary
  2. vapour phase must be analyzed
  3. relatively time-consuming measurement

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Translated by the author.