

Determination of Liquid-Vapor Equilibria

New Dew Point-Bubble Point Apparatus

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A new form of dew point-bubble point apparatus is suitable for determining the liquid-vapor equilibria of binary systems which are liquid at room temperature and atmospheric pressure. The technique of operation and the theory and method of deriving both the individual dew points and bubble points and the total dew point curve and bubble point curve are given. Suitability of the dew point-bubble point apparatus for obtaining liquid-vapor equilibria was established by reproducing closely the results obtained by Scatchard on the methanol-

benzene system. The method is advantageous because only small amounts of reagents are needed for the complete determination of a system; no analyses are required; identical solutions are run at each temperature; and the independent determination of the dew point curve allows the selection of evenly spaced points at desired concentrations. Possible application of apparatus is in determination of molecular weights of liquids, analysis of binary liquid systems, and study of liquid-vapor equilibria of ternary and higher order systems.

APPARATUS designed to determine bubble points and dew points has been used for many years to study the phase behavior of hydrocarbons in petroleum. In nearly all instances, this work has been done on substances of low molecular weight, such as methane, ethane, etc., which are ordinarily gases or low boiling liquids. The apparatus generally used was constructed of metal which could be employed at very high pressures, inasmuch as data up to the critical point were commonly desired. The work done by Sage and Lacey (2) is typical. In some instances, glass capillary apparatus was used (1).

Systems which are liquid at room temperature have not been studied with apparatus such as those mentioned. The dew point-bubble point apparatus constitutes a new form which utilizes essentially the same basic principles as the types referred to above, but is specifically adapted to examine systems which are liquid at room temperature and atmospheric pressure.

THEORY OF THE METHOD

A generalized liquid-vapor diagram of a binary system which forms a minimum boiling mixture is given in Figure 1. The data are plotted at constant temperature; if they were plotted at constant pressure a somewhat similar, inverted curve would be obtained.

The horizontal line, MN , is a tie line connecting phases M and N , which are in equilibrium with each other. The usual forms of apparatus used for obtaining liquid-vapor equilibrium data are designed to determine points M and N simultaneously. After a series of such tie lines has been determined along the entire range of concentration, a line is drawn through all the points analogous to M to give the "liquid curve," and a line is drawn through the points analogous to N to give the "vapor curve."

Examination of Figure 1 shows that the diagram could also be produced by joining the end points of a series of vertical lines such as RM . This is not a tie line; it is merely a constant composition line which describes what happens to a mixture of a given composition as the pressure on it is changed at constant temperature. For a sample having the composition N_A and a pressure greater than P_1 , the system will consist of a liquid phase only. As the pressure is lowered, the vapor pressure becomes equal to the external pressure at P_1 , and an infinitesimal amount of vapor which is in equilibrium with the liquid is formed. This is known as the bubble point, M . Further lowering of the pressure results in two phases which constantly change in relative amounts; the liquid phase decreases while the vapor phase increases until pressure P_2 is reached. At this point, an infinitesimal amount of liquid in equilibrium with the vapor remains, and now the vapor has the same composition as the original liquid. This point is known as the dew point, R , because when it is approached from the opposite

direction, it represents the point at which initial condensation takes place. By joining all the points analogous to M , the "bubble point (liquid) curve" is produced. Connection of all the points corresponding to R gives the "dew point (vapor) curve."

APPARATUS AND OPERATION

Figure 2 shows the apparatus, which was designed according to the principles discussed above. It is of all-glass construction and has three major parts.

A is the body of a 500-ml. graduated cylinder, which ends in a gradual taper at the top, culminating in a capillary. This arm serves as the vaporizing chamber.

B is a large mercury reservoir.

C is used for balancing the mercury height in A . It is made of 10-mm. tubing to minimize meniscus errors. When the levels of the mercury in A and C are equal, the pressure in the vapor space of A is equal to that of the manometer, which is connected in series with C . Correction for the pressure due to the weight of the sample is -0.1 mm. of mercury per milliliter. In constructing

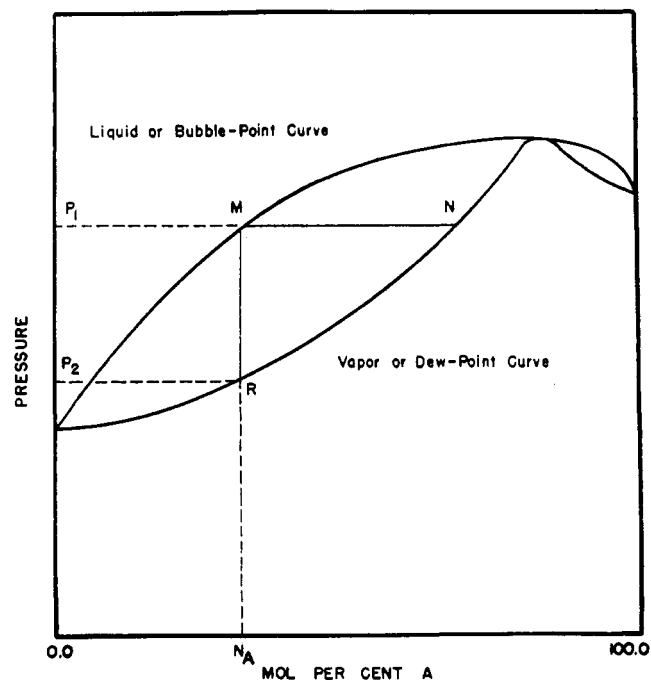


Figure 1. Dew Point-Bubble Point Curves for Generalized System with Minimum Boiling Azeotrope

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the apparatus, *C* is placed as close to *A* as possible in order to increase the accuracy of matching the mercury levels of *A* and *C*.

The entire apparatus is immersed in a constant temperature bath, *L*, in which water is maintained at the level indicated by the dotted line passing through stopcocks *E*, *F*, and *G*. The apparatus is supported in the bath by a ringstand and clamp combination which is also located within the bath. A split rubber tube is fitted on the bottom arm, which rests on cork stoppers to cushion the weight of 20 pounds (9 kg.) of mercury. The introduction of samples, vaporization, balancing of mercury, etc., are all accomplished by balancing vacuum and atmospheric pressure through the suitable adjustment of the various stopcocks.

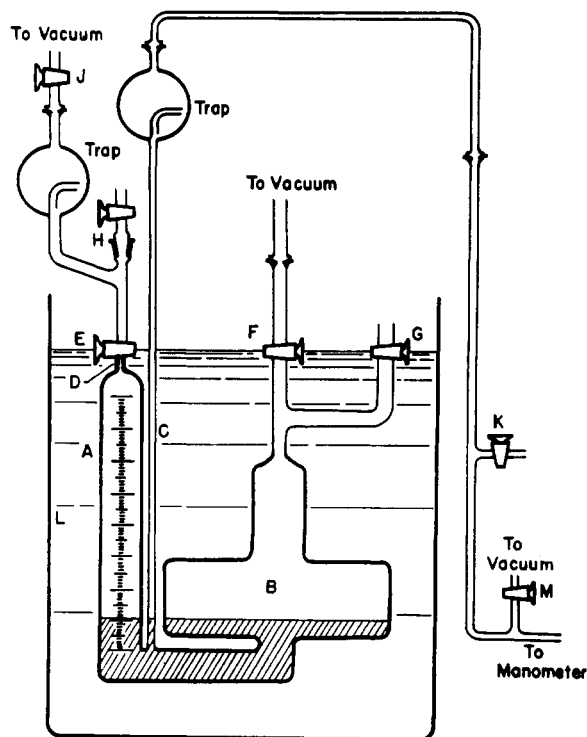


Figure 2. Dew Point-Bubble Point Apparatus

The 7-gallon (26.5-liter) thermostat is held to within $\pm 0.02^\circ \text{C}$. of the operating temperature, which is a smaller variation than the average error in reading pressure. An absolute manometer with attached graduated scale capable of $\pm 0.2\text{-mm.}$ accuracy is used for pressure readings. The vacuum source for the system consists of a mechanical pump which is connected to a 5-gallon bottle and a 3-gallon bottle, which act as vacuum reservoirs. These are used as the operating source of vacuum and allow good control over pressure changes in the system. The vaporization chamber and the mercury reservoir are connected with the 5-gallon bottle, while the manometer arm is connected with the 3-gallon bottle. A complete system of stopcocks and T-tube connections within the pump-reservoir system allows separate control over each part of the apparatus.

The procedure for making a run is as follows:

After the bath has come to temperature, the mercury in *A* is forced up to a point just above stopcock *E*, which is then closed. The apparatus is opened to the atmosphere at *H*, *G*, and *K*. Plug *H* is removed, a sample somewhat larger than will be used is introduced by means of a hypodermic syringe, and *H* is replaced. By carefully opening *E*, the mercury which is above it and also the proper amount of sample varying from 1 to 5 ml. are drawn into *D* and into the tapered part of *A*, and the stopcock is closed. With *E* closed, *J*, *F*, and *M* are opened to vacuum in such a way that the liquid in *A* forms about 300 ml. of vapor. *C* and *B* are then brought to atmospheric pressure. This causes condensation in *A* and brings the liquid line to a point just below *D*. The bubble above the liquid represents air which has been dissolved at atmospheric pressure. By carefully opening *E* to vacuum, this bubble, plus a small amount of liquid, is forced up above *E*, which

is then quickly shut off. Thus, the trapped liquid is left fairly free of dissolved gases. This degassing procedure is followed only when obtaining bubble points; dissolved air in the very small dew point samples has no effect on the dew points.

With the sample at temperature, the mercury in *C* is held at a level approximately the same as the top of *A* while the pressure in *B* is gradually lowered until a volume of 20 to 30 ml. of vapor forms in *A*. The mixture in *A* is brought to equilibrium by swirling the liquid with a rocking motion of *A*. Then the mercury levels in *A* and *C* are equalized by matching the reflection of the mercury in *C* on tube *A* with the mercury in *A*, and a reading on the manometer is taken. The pressure in *B* is again lowered a little to allow 25 ml. more of vapor to form, and the above procedure is repeated. In dew point determinations a 0.01- to 0.1-ml. sample is used and no swirling is employed to attain equilibrium. In both bubble point and dew point determinations equilibrium is usually reached in 1 or 2 minutes, as indicated by a constant pressure reading.

A series of volume and pressure readings is obtained, which can be plotted against each other. From the curves obtained in this way, the bubble points and dew points are determined. Some typical individual bubble and dew point determination curves are shown in Figure 3. In curves *a* and *b*, extrapolation of the volume vs. pressure curve back to the pressure axis gives the bubble point (*B.P.*) of the initial mixture. In curves *c*, *d*, and *e*, the dew point is located where the change of slope indicates that all the liquid has vaporized, and the vapor is expanding as a gas. These points are indicated by *D.P.*

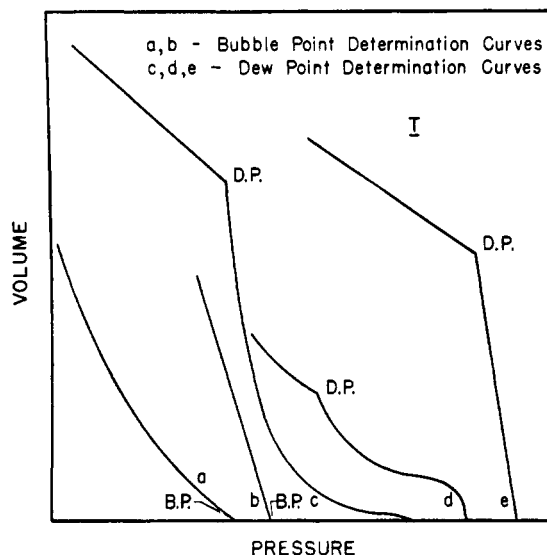


Figure 3. Generalized Volume vs. Pressure Curves for Determination of Dew Points and Bubble Points

The present form of the apparatus is suitable for the pressure range 0 to 1 atmosphere and for temperatures up to about 50°C . By replacing the vacuum pump with a pressure pump the range of pressure may be increased to several atmospheres with a probable revision of the equipment employed for sample introduction. The temperature range could probably be increased to well over 100°C . if the bath liquid were properly changed and extensions placed on the stopcocks, which are immersed in the liquid surface, to avoid burning the operator's hands. Corrections for the vapor pressure of mercury should be made for any temperature above 80°C .

ACCURACY OF APPARATUS

The suitability of the apparatus for obtaining liquid-vapor equilibria was established by repeating the work of Scatchard and co-workers (3) on the methanol-benzene system. The reasons for choosing this system were twofold: It is similar to the methanol-toluene system for whose determination the apparatus was

Table I. Composition of Methanol-Benzene Solutions Made Up at 25° C.

Vol. of CH ₃ OH Ml.	Vol. of Benzene Ml.	CH ₃ OH Mole %	CH ₃ OH (Scatchard) Mole %
0.63	9.43	12.8	13.02
1.71	8.29	30.7	31.07
3.14	6.93	49.8	49.89
3.30	6.70	51.9	51.91
4.41	5.60	63.2	63.05
6.45	3.54	80.0	79.65
8.40	1.60	91.8	91.97

Table II. Dew Points and Bubble Points of Methanol-Benzene System at 35.0° C.

CH ₃ OH in Liquid Mole %	Dew Point ° C.	Bubble Point ° C.
0.0	...	149.4
12.8	164.5	276.2
30.7	206.5	288.4
49.8	280.0	292.7
63.2	289.0	292.8
80.0	244.0	283.1
91.8	222.0	255.8
100.0	...	209.9

originally developed; and the accurate results of Scatchard *et al.* provided a good standard for comparison.

The reagents were distilled through a fractionating column and their vapor pressure was checked at $34.97^\circ \pm 0.02^\circ \text{C}$. The values obtained were almost exactly the same as given by Scatchard. Seven solutions were made up corresponding as closely as possible to the compositions used by Scatchard. Pertinent data are given in Table I. The solutions were run in the apparatus, and the data obtained are given in Table II. A diagram of the methanol-benzene system at 35.0°C . as drawn from the data of Scatchard is shown in Figure 4. The data obtained by the apparatus were superimposed on the diagram as indicated by the legend.

Examination of the bubble point data shows very good agreement. The dew point data do not appear to be in as good agreement, a condition which may be due to the relatively few points used to delineate the curve. In any case, the results justified going on to determine the liquid-vapor equilibrium data for the methanol-toluene system, which will be reported in a forthcoming paper.

APPLICATIONS

There are three applications of the dew point-bubble point method and apparatus.

Molecular Weights. The accurate determination of molecular weights should be possible. For this purpose, it would be necessary to incorporate a microvolumetric bulb into the apparatus for measuring a very small liquid sample to be completely vaporized. The density of the liquid is determined at the same temperature with a pycnometer using a separate, larger sample. Thus the weight of samples used can be found. The sample is completely vaporized, and a series of values of V and P in the vapor state is obtained. From these, an accurate value of molecular weight can be obtained by the method of limiting densities according to the formula:

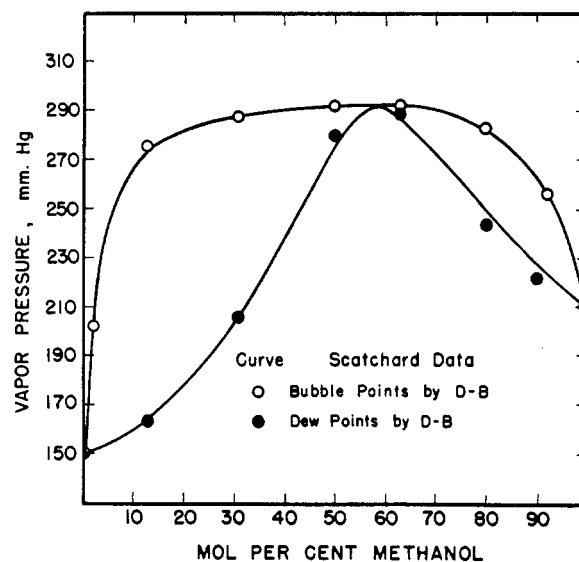
$$M = RT \left(\frac{d}{P} \right)_{P=0}$$

where $\left(\frac{d}{P} \right)_{P=0}$ is the limiting value obtained when $\frac{d}{P}$ is plotted

against P and extrapolated to $P = 0$. R is the gas constant, and T is the absolute temperature.

Analysis. Often binary mixtures are encountered which are difficult to analyze by refractive index or density. If the liquid-vapor diagrams of such mixtures were accurately known, they

could be analyzed by determining the bubble point and dew point of a given sample. Because each pair of points corresponds to a particular composition, the correct value can be picked out on the diagram. In many instances, the same small sample will be satisfactory for determining both bubble and dew points, thus allowing economy in size of sample and time for determination.

**Figure 4. Methanol-Benzene System at 35.0° C.**

Ternary Systems. The determination of liquid-vapor composition data for higher order systems has been heretofore avoided because of the difficulties of analysis. A method such as that suggested, where use of synthetic samples of known composition eliminates the need for analysis, should make the determination of these systems much less difficult.

CONCLUSIONS

Some of the important advantages of the dew point-bubble point method are: Small amounts of reagents may be used for the complete determination of a system. No analyses are required, because all samples are made up to accurately known compositions.

Identical solutions of a given composition can be used for each temperature at which a system is determined.

The independent determination of the dew point curve allows the selection of evenly spaced points at desired concentrations rather than leaving them to chance. Points close to the origin on each curve may readily be determined, so that the manner in which the bubble point and dew point curves come together in this region may be accurately delineated.

The apparatus should be applicable to the determination of molecular weights of liquids, to the analysis of binary liquid systems difficult to analyze by refractive index, density, etc., and to the study of liquid-vapor equilibrium data for ternary and higher order systems.

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