A Static Vapor Pressure Apparatus for Mixtures

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A static vapor pressure apparatus is described which is especially suitable for mixtures. A vapor pressure flask with a built-in condenser allows the mixture to be degassed without change in composition. The entire apparatus is assembled from simple parts. Equilibrium is rapidly attained with either an external pressure or a liquid of known vapor pressure used as a reference.

The vapor pressures of mixtures are usually determined in conjunction with vapor-liquid equilibrium measurements with the use of equilibrium stills. With binary mixtures, only total pressure and liquid composition data are needed for equilibrium determinations, so that ebulliometric or static devices may be employed without provision for vapor phase analysis. In spite of the apparent simplicity of static measurements, ebulliometers such as those developed by Swietoslawski (*1*) are usually easier to operate.

The basic problem with static equipment is degassing the liquid. To remove dissolved gases from the liquid, a considerable portion must be distilled. With pure components this is no problem, but with mixtures the composition is changed. A number of solutions to this problem have been worked out (*2, 3*). One simple device requires that the liquid be degassed prior to its entering the apparatus (*4, 5*). Modifications of the Smith and Menzies isoteniscope have been reported (*6, 7*) in which the boiled out portion of the liquid is caught in a cold trap, then melted and returned to the equilibrium flask.

In spite of their difficulties, static methods offer several advantages. Ebulliometers must be specially designed to handle heterogeneous mixtures; at high relative volatility when the volatile component is dilute, it is difficult to get accurate results because of the holdup of the more volatile component in the condenser. Ebulliometric measurements are sensitive to boiling rates, and the proper rate must be determined. Static determinations are free from all these complications.

EQUIPMENT DESCRIPTION AND ASSEMBLY

The novel feature of the static equilibrium flask shown in Figure 1 is the built-in condenser that enables the mixture to be thoroughly degassed without appreciably changing the composition. A number of flasks have been built with bulbs varying in capacity from 25 to 50 ml. The inside tubes in the condensers are about 8 mm. and the outside tubes about 16 mm. The stopcocks are 2- or 3-mm. straight bore with about an 8-mm. O.D. arm. On some flasks the condenser was made by plugging the ends of the outside tube with rubber stoppers prior to connecting the stopcock. With this modification the glass work is quite simple.

The apparatus shown in Figure 2 and schematically in Figure 3 is constructed from the parts shown in Figure 2 plus the manometers. All joints are 18/9 ground ball joints. The manometer joints, J-5, J-6, J-8, and J-9, are Scientific Glass Apparatus O-ring type. The necessity of seating two joints at once with restricted motion when connecting the manometers leads to occasional joint failure unless grease is used freely. This is undesirable from the standpoint of contamination, so the O-ring joints are used, which allow a minimum use of grease.

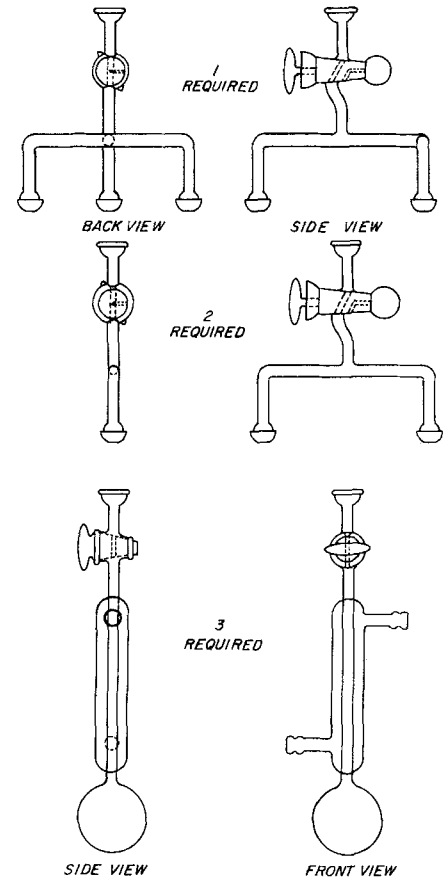

Fig. 1. The vapor pressure flask and other parts used in assembling the apparatus.

The manometers are filled with clean mercury before being connected to the apparatus. If necessary, the mercury may be degassed within the manometers before or after assembly. An infrared lamp playing on the manometer while under vacuum is usually sufficient.

The apparatus is assembled on the metal frame shown in Figure 4. The frame is suspended from a metal rod so that the entire setup may be suspended in a constant-temperature bath with valves V-1, V-2, and V-3 just at the surface. The frame oscillates about this rod, enabling the flasks to be agitated. When at rest, the manometers are kept vertical by a stop. Connection is made to the vacuum manifold by flexible tubing at ball joints J-1, J-2, and J-3.

An aquarium makes an ideal constant-temperature bath. Not only is the rectangular shape convenient, but the plate glass sides are almost necessary for accurate reading of the

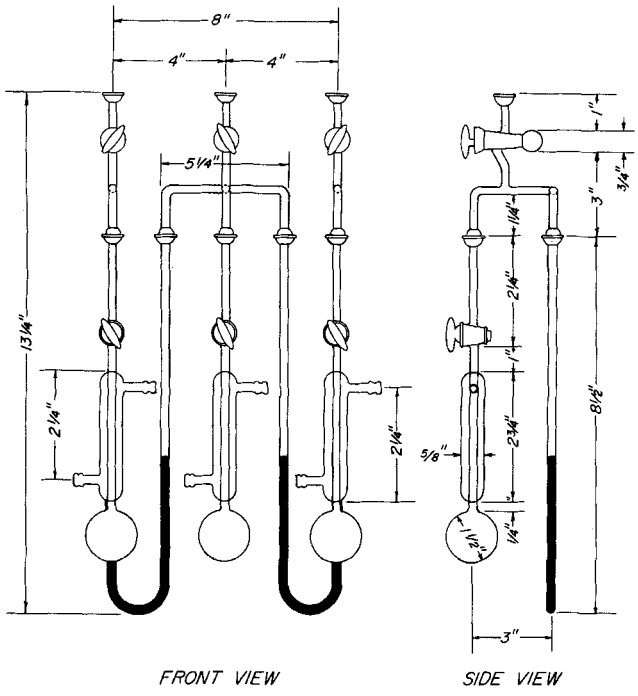

Fig. 2. Assembled vapor pressure apparatus.

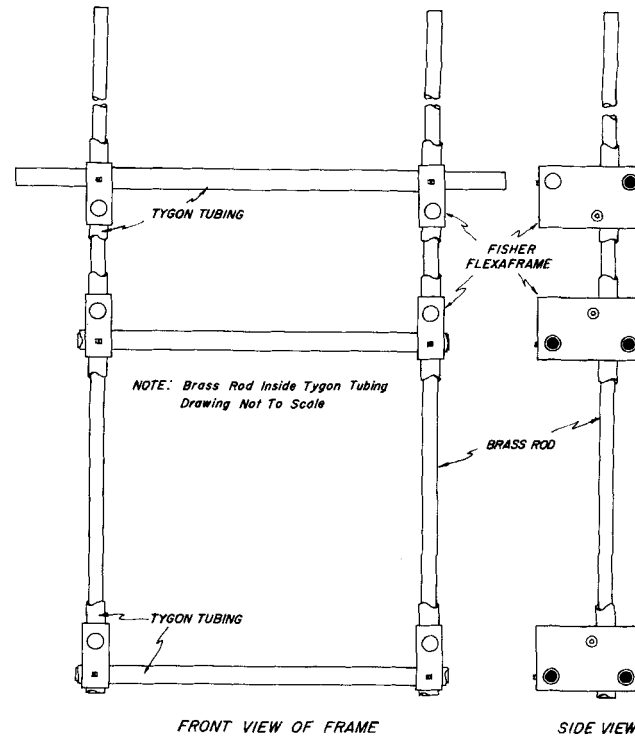

Fig. 4. Supporting frame for the vapor pressure device.

manometers. The manometers must be submerged, at least for temperatures above ambient, because they are in direct contact with the vapors.

The temperature in this apparatus is controlled by a Sargent thermistor actuated temperature controller and measured by a calibrated thermometer with 0.1°C. graduations. Temperature gradients within the bath do not exceed 0.01°C.

DEGASSING

Degassing is accomplished with the flask disconnected from the vapor pressure setup. Measured quantities of each component are added to the flask through the bore of the stopcock from a hypodermic syringe equipped with a long needle. The flask condenser is connected to the coolant and heat is applied to the flask with the stopcock open. Refrigerated coolant is employed with low boiling materials. Although the degassing may be accomplished at atmospheric pressure, it is best to use as high a vacuum as is consistent with smooth boiling. To accomplish this, a flexible hose from the vacuum manifold is connected to the ball joint of the flask. An absolute pressure of about 200 mm. is usually maintained during degassing.

Maintenance of smooth ebullition, imperative during this operation, has been most successfully accomplished with a magnetic stirrer. Small pieces of wire about ½ in. long are sealed in 1½- to 2-mm. melting point tubing of slightly greater length. These may be dropped down the neck of the flask when the stopcock plug is out. A 50-cc. heating mantle is used in which the fabric has been parted in the bottom to allow the flask to rest directly on the magnetic stirrer. The pieces of wire are easily removed with a bar magnet when the flask is empty.

The liquid in the flask is usually boiled for about 10 min. with all the vapors condensing and returning to the flask. The coolant flow is turned off, and the upper limit of condensation is allowed to rise until it reaches the stopcock which is then closed. After the stopcock is closed the flask is immersed in dry ice-acetone for several minutes while a high vacuum is pulled on the vacuum manifold. When the flask is very cold, the stopcock is opened for a few seconds to expel completely any inert gases that may remain. The flask is connected to the apparatus at ground glass joints J-4, J-7, or J-10.

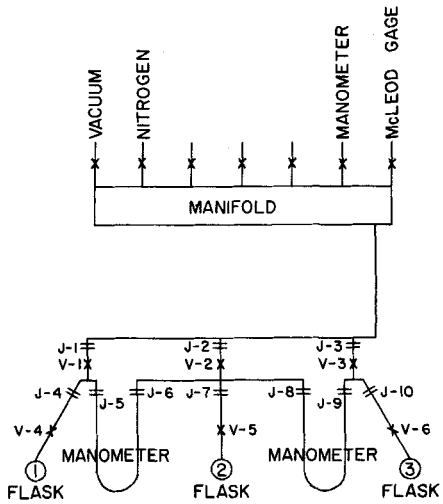

Fig. 3. Schematic of the vapor pressure equipment.

OPERATION

When low vapor pressure mixtures are in flasks 1 and 2 (Figure 3) the pressures may be determined directly from the manometer readings. This is accomplished with V-1 and V-3 closed and V-2 open with a high vacuum on the manifold. When the pressure exceeds the range of the manometers (about 130 mm.) a back pressure must be provided. This may be done by controlling a pressure on the manifold, but a more convenient method may be employed in this apparatus. Flask 2 is filled with a pure liquid of known vapor pressure; then with V-1, V-2, and V-3 closed and V-4, V-5, and V-6 open, the manometers record the difference between the known vapor pressure and that of the unknowns in flasks 1 and 2. With a liquid in flask 2 of approximately the same vapor pressure as the mixtures, the determination becomes relatively insensitive to temperature errors, as small variations in the temperature will result in similar pressure changes in each flask.

The complete operating procedure is as follows. The two unknown mixtures and the reference liquid are degassed as

previously described. The apparatus is evacuated after the installation of each flask to minimize leaks through the flask stopcocks while the others are being degassed. After the flasks are installed, and with V-1, V-2, and V-3 open to vacuum, stopcocks V-4, V-5, and V-6 may be opened momentarily to expel any traces of air that may have leaked into the flasks as they were being connected to the apparatus. This precaution is only possible at low vapor pressures or the mercury will be blown from the manometers; but chilling of the samples during degassing will ensure low pressure if reasonable speed is exercised during this operation.

Finally, V-1 and V-2 are closed and V-3 also, unless an external back pressure is used. Then the flask stopcocks are opened and the apparatus is agitated in the constant-temperature bath to hasten the approach to equilibrium. The manometers are read periodically to 0.05 mm. with a cathetometer until constant readings are obtained. The time required for equilibrium varies with the liquid and the temperature. At 5° to 10°C. from 30 to 45 min. may be required but above 20°C. 15 to 20 min. are usually adequate.

At the completion of each measurement, the temperature may be increased and the vapor pressure measured at a higher temperature on the same mixture. When the last measurement is completed, nitrogen is admitted into the manifold to a pressure slightly in excess of that in the vapor pressure apparatus. Stopcocks V-1, V-2, and V-3 can then be opened and the apparatus brought to atmospheric pressure. If the final vapor pressures are above atmospheric pressure, the stopcocks on the flasks should be closed before bringing the system to atmospheric pressure. Otherwise they may be closed after atmospheric pressure is reached. At the completion of the run, flasks 1 and 2 may be removed for analysis of the mixtures.

The extensive use of greased joints and stopcocks greatly facilitates operation of this equipment, but it is also the main course of trouble. The grease may be attacked, causing joint failure or contamination. With careful greasing this is not usually a problem at low temperatures, but above 40° to 50°C. difficulty is often encountered, particularly at the manometer joints. Both silicone and fluorosilicone greases were used.

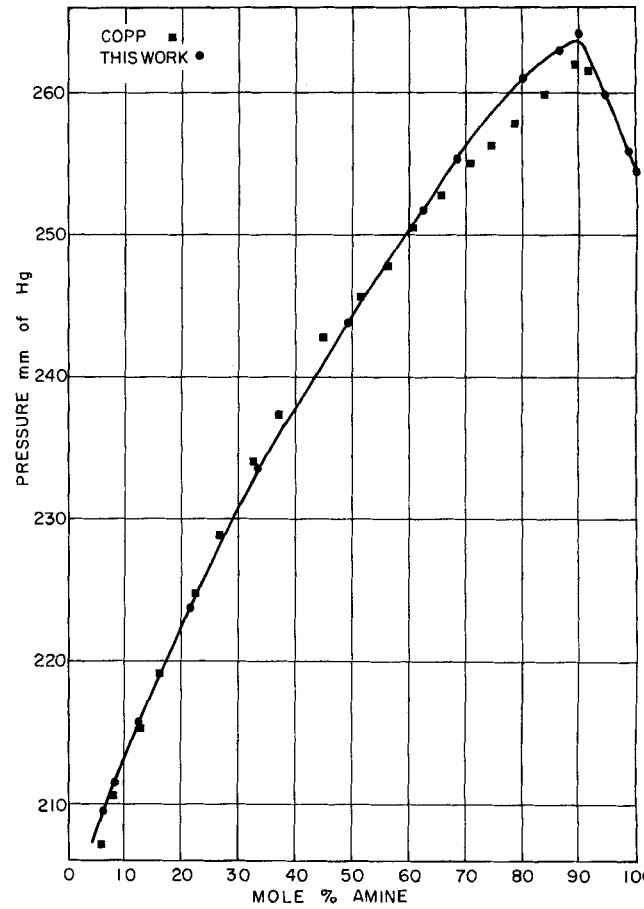

Fig. 5. The vapor pressure of the water-methyldiethylamine system at 35°C.

EXPERIMENTAL RESULTS

The apparatus was calibrated with the vapor pressures for water given by Lange (*8*). The agreement was within 0.1 mm. Hg from 10° to 30°C., except on occasion when droplets of water in the stopcock bore lowered the measured pressure by several tenths of a millimeter. The droplets may collect in the bore during boilout and are particularly likely to remain with a liquid of high surface tension such as water.

An interesting and inexplicable phenomenon occurred with triethylamine. Copp and Everett (*9*) have previously reported that triethylamine vapor pressures obtained by static methods are higher than those measured by dynamic methods. The values obtained with the static apparatus described in this paper agree with their reported dynamic values within 0.1 mm. up to 18°C., but at 20°C. the static value is 0.5 mm. higher and at 35°C. the difference is 1.4 mm. The triethylamine was purified by repeated distillation, and a fraction having a boiling range of 0.1°C. was used. A chromatograph showed a single peak, so it seems unlikely that impurities were responsible. Copp and Everett postulated that volatile decomposition products were formed which would be continuously removed in the dynamic device. But we found that upon cooling the bath, previous values were obtained, so that if a reaction occurs it is reversible at these temperatures. It is difficult to conceive of such a reaction and, furthermore, the very similar methyldiethylamine does not exhibit this phenomenon.

In Figure 5 the vapor pressures of water–methyldiethylamine mixtures at 35°C. are compared with those obtained by Copp (*10*) with an equilibrium still used. Chloroform was used as the reference liquid in the static measurements, since its vapor pressure is close to that of methyldiethylamine. It was found, however, that various literature values of chloroform vapor pressures differed considerably, and it was necessary to determine first the vapor pressure of chloroform. In these measurements, back pressure was maintained in the manifold and stopcock V-2 was open. Both the manifold manometer and the one in the bath were read with the cathetometer, and the results were combined with the appropriate temperature corrections to obtain the vapor pressures.

The results for the methyldiethylamine–water mixtures never differ by more than 2.0 mm. from Copp's values, but the deviation is definitely not random. For analysis Copp used amine titration with HCl, while in this work, concentrations below 60 mole % amine were titrated, and a gas chromatograph was used at higher concentrations. The chromatograph gave better reproducibility at low water content. The titration reproducibility ranged from 1 part in 250 to 500 parts of amine. The chromatograph generally gave water concentrations within 0.2 wt. %. However, analytical errors cannot account for a difference in azeotropic vapor pressures. The vapor pressures of the pure amine obtained by the two methods at 35° differ by only 0.1 mm.

Copp also reported the vapor pressure of methyldiethylamine–water solutions at 47°C. The results differ from static data in much the same way as the 35°C. data. The methods give identical results for the pure amine, but the static pressure is higher at the azeotrope. Each set forms a very smooth curve in each instance.

Data were obtained by the static method at 30° and 40°C. To test the consistency of the data, log P was plotted vs. $1/T$ at 30°, 35°, and 40°C. for various concentra-

tions. In each instance the static value at 35° fell a little above a straight line drawn between 30° and 40°. This is consistent with a decrease in the latent heat with increasing temperature. Some of Copp's 35° points fell above the line and some below. This does not prove Copp's values wrong, only that the static values are self consistent while not consistent with Copp's values. Both of the 35°C. total pressure curves were numerically integrated to obtain vapor compositions. The maximum difference in vapor composition occurs at 75 mole % amine in the liquid. At this point Copp's data yield an amine fraction of 0.865 in the vapor while the static data give 0.874.

ACKNOWLEDGMENT

The support of this work by the Office of Saline Water, Department of the Interior, Washington, D. C., is gratefully acknowledged.

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Manuscript received March 4, 1966; revision received September 23, 1966; paper accepted September 26, 1966.

Liquid-Vapor Equilibrium in the System Helium-Methane

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Liquid and gas phase compositions for the system helium-methane have been measured at 15° intervals from 95° to 185°K. up to 200 atm. pressure. Data for these seven isotherms were taken in a gas phase recirculation apparatus with chromatographic analysis. In most regions the phase compositions obtained are thought to be within ± 3% of the mole fraction of the minor component. The maximum deviation from the enhancement factor curve at the lowest concentration levels was 16%. These data are in excellent agreement with most of the very recent data but are in poor agreement with the older data for this system.

Until recently, data for the helium-methane system were very limited in the liquid-vapor region and nonexistent in the solid-vapor region. Prior to the present investigation measurements were made to determine the gas phase compositions in equilibrium with the solid phase in the helium-methane system from the triple-point temperature to as low a temperature as possible consistent with quantitative analysis limitations of the sensitive hydrogen flame-ionization technique (*1*). In that investigation, gas phase compositions were measured in the liquid-vapor region along the 91.00°K. isotherm for direct comparison with the existing data. Those measurements indicated that the data of Kharakhorin (*2*) at 91.1° were incorrect and suggested that data from the latter source in the higher temperature region might also be questionable.

The purpose of the present investigation was to measure the phase equilibria properties of the helium-methane system over the entire liquid-vapor region from a temperature just above the methane triple point to a temperature near the methane critical point. Compositions of both phases were determined chromatographically, with thermal conductivity detection, at 15° intervals from 95° up to 185°K. at total pressures up to 200 atm. The region studied in the present investigation essentially completes the coverage of this system within practical limits and provides a good comparison with all other equilibria data available for this system.

EXPERIMENTAL METHODS

The experimental apparatus used in this investigation, described in detail elsewhere (*3*) is a closed-loop flow system in which the gas phase is recirculated through the equilibrium cell by a magnetically operated pump at ambient temperature. The recirculated gas phase also passes through a ballast volume (in an ambient temperature water bath) which allows the removal of small samples of either phase from the system with no detectable change in system pressure. The equilibrium cell within the cryostat was refrigerated with cold gas from boiling liquid nitrogen in the bottom of the cryostat. This cold gas supplied an excess of refrigeration which was counteracted by an automatically controlled heater wrapped around the cell.

System pressure was measured with two Bourdon types of gauges with ranges of 0 to 100 and 0 to 300 atm. These gauges had a maximum error rating of ± 0.1% full scale. The temperature at the top of the cell was measured by a platinum resistance thermometer calibrated on the 1955 NBS tempera-