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Vapor–Liquid Equilibrium. I. Apparatus for the Study of Systems with Volatile Components[1]

BY GEORGE SCATCHARD, C. L. RAYMOND AND H. H. GILMANN

The study of vapor–liquid equilibria with volatile components consists of the determination of the compositions of the two phases in equilibrium, the pressure and the temperature. The chief difficulty is the attainment of equilibrium with enough of the vapor phase for analysis. It seemed to us highly desirable to combine the principle of the Cottrell pump[2] with continuous circulation of the distillate through a "hold-up trap" as devised by Sameshima.[3] An attempt to modify the apparatus of Swietoslawski[4] led to failure because the insertion of a trap necessitates pumping too high a column of liquid. Our final apparatus is also closely related in principle to those of Carveth[5] and of Rosanoff, Lamb and Breithut.[6] It was copied, with some modifications, from that described by Chilton.[7]

The Equilibrium Still

The still is shown in Fig. 1. As the liquid in the outer boiler E boils the vapor passes through the tube G into the inner boiler F. Part passes through the pump H carrying liquid from F to the thermometer well I from which the liquid drains slowly back to F, and the rest of the vapor bubbles around the edge of the pump and stirs the liquid in F. The vapor then passes through the connecting tube to the condenser D. The liquid from the condenser passes through the trap C and the tube L to the outer boiler E.

To maintain a steady state it is necessary that there be no change in the quantity of liquid in F due to evaporation or condensation, and therefore that the net gain of heat by other processes be zero. There is a slight loss of heat by conduction up the thermometer well, probably a small net loss due to radiation, and there is a gain from the outer vessel where the equilibrium temperature is somewhat higher because of the difference in hydrostatic pressure through the tube G. The liquid level in F should adjust itself so that these effects just compensate. In practice the level does change appreciably when the still is first put in operation but no longer changes measurably after the steady state is reached.[8]

If the composition of the liquid in trap C is to be the same as that of the vapor about I, there must be no reflux condensation and no entrainment. The height of wide-bored tube through which the vapor must rise makes entrainment unimportant. The flanged lip at the top of F has its lowest point at the tube leading to the condenser so that any liquid condensing on the top of F is led to C. The outer walls of F are kept very slightly superheated by the vapor from the outer boiler E, and the small area between the outer boiler and the lip is covered with asbestos to reduce condensation. There is presumably some slight condensation, however, on the thermometer well.

The vapor space in the outer boiler E has no direct connection with the outside. It is therefore important that

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[1] Most of the apparatus except the still itself was set up by Dr. H. H. Gilmann (present address, City Chemical Corp., New York City). The final touches, most of the calibrations and the design of the still were carried out by C. L. Raymond (present address, Shell Petroleum Company, St. Louis), in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) F. G. Cottrell, THIS JOURNAL, **41**, 734 (1919).

(3) J. Sameshima, *ibid.*, **40**, 1483 (1918).

(4) W. Swietoslawski, *Bull. Acad. Sci. Polonaise*, 434 (1929).

(5) H. R. Carveth, *J. Phys. Chem.*, **3**, 193 (1899).

(6) M. A. Rosanoff, A. B. Lamb and F. E. Breithut, THIS JOURNAL, **31**, 448 (1909).

(7) T. H. Chilton, *Proc. Fourth Symp. Chem. Eng. Education*, 64 (1935).

(8) Statements as to the behavior of the still in practice are based on the study of chloroform–ethanol mixtures described in paper II.

the top of G be as near as possible to the top of E so that the vapors may sweep out other gases rapidly. In order that the vapor pass through G and not back through L it is important that the distance between the liquid level in E to the bottom of L be much larger than that from the liquid level in F to the bottom of G. When the distillation is stopped by introducing gas at atmospheric pressure, on the other hand, the gas must enter through L and not through G or the liquid will be carried from F to E. So the total height of G must be considerably greater than that from the liquid level in E to the bottom of L. Our first boiler was critical in this respect and required very careful handling. The dimensions of the second boiler, shown in the figure, have been found satisfactory.

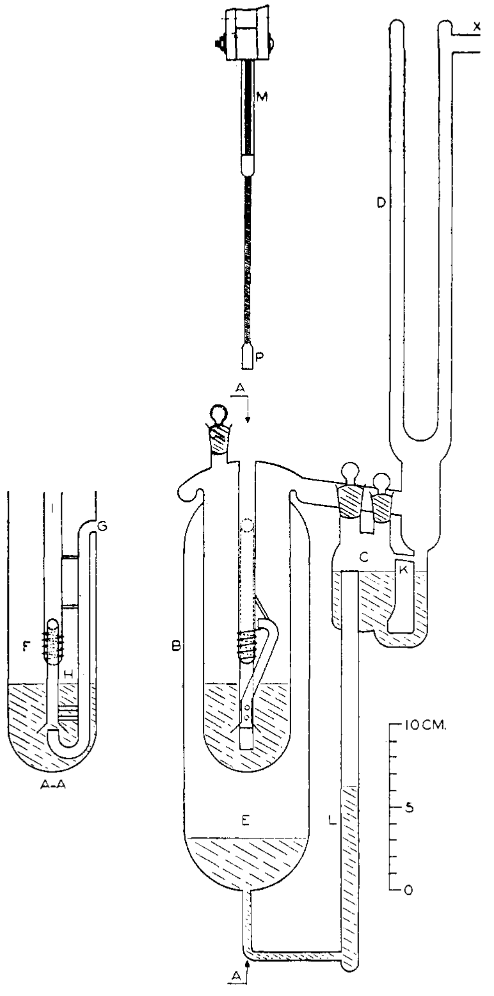

Fig. 1.—Equilibrium still.

The gas space in C is connected with the condenser by the tube K which is of small bore to lessen diffusion, and slants down from C to prevent liquid coming from the condenser to the top of the trap. A fixed, sharp line of condensation is necessary for constant pressure distillation in a closed system. This is attained by the use of a vertical annular condenser with cooling liquid on both inside and outside surfaces and a confining gas lighter than the vapor. A thermostated iron tank of ninety-liter capacity served as a manostat. The relative volumes are such that a change of 2 mm. in the condensation level produces a change of 1 part in 100,000 in the pressure in the system.

The tubular openings in the top of C, one exactly above the tube L, and one in the top of F, permit pipetting the liquids from C, E, and F. The tube between E and L slants down from E to L so that the liquid may be completely removed from E. These three openings are sealed with very carefully polished ground glass stoppers which are used without lubricant. With an internal pressure of less than 1 mm. the total leak was 0.007 mm. per minute. It is probably less during the measurement since the pressure gradient is smaller and the vapors probably condense in the joints to give some sealing.

The Measurement of Pressures

Figure 2, which is not drawn even approximately to scale, shows the apparatus for the regulation and measurement of the pressure. Tube X leads to the still through X of Fig. 1. A is the precision manometer, B a crude but easily read manometer in parallel with A, C is a McLeod gage for measuring the pressure in the vacuum arm of the manometers, D is the manostat. J is a liquid air trap to protect the rest of the apparatus from the vapors from the still. Condensed liquid may be removed from the trap through the tubular opening at the top (not shown in the figure). This and the stopcocks are lubricated since they are separated from the still by the liquid–air trap. The stopcocks U and T serve to isolate either the still or the manostat while the pressure is being changed in the other. Tube H is connected to a Hyvac pump and stopcocks R and S to the source of confining gas. The gas may be let in so slowly through Q, with the pressure reading of the manometer I as a guide, that the pressure in the apparatus may be easily controlled to 0.01 mm., or rapidly through R.

The tubes L indicate copper tubing with coils to take up strain due to any motion of the manostat relative to the still or to the manometer. All tubes between the still and the manostat are of large bore, that leading to the manometer is small. The manostat D is made of a piece of iron pipe with ends of boiler plate welded on. It is kept in a large oil thermostat.

The precision barometer is made of two pieces of 19 mm. i. d. glass tubing selected carefully for uniformity of thickness and of internal diameter. They are mounted coaxially. The adjacent ends are made as flat as possible and the side tubes brought in as near the ends as possible so that readings of low pressures may be made. The manometer is placed in a vigorously stirred air thermostat with plate glass front. The heights of the mercury levels are determined by comparison with a calibrated invar scale by means of a cathetometer.

The pressure at the lower end of the thermometer well in the still is determined from these mercury heights by correcting for the temperature and calibration of the scale, the mean temperature of the manometer mercury and the gravitational constant at the manometer, the capillary depressions in the two mercury menisci, the weight of the column of confining gas from the mercury in the lower arm of the manometer to the line of condensation, and the weight of the column of vapor from the line of condensation to the lower end of the thermometer well. The cathetometer, scale, methods of illuminating the scale and the menisci, and the methods of making the various corrections are nearly the same as those described by Beattie, Benedict and Blaisdell.[9] The lighting of the menisci is diffuse. No correction is made for the pressure gradient necessary to give the gas its velocity from the thermometer head to the condenser. Approximate calculations indicate that this gradient is less than 0.01 mm. at one atmosphere pressure and not more than 0.05 mm. at the lowest pressures. Aside from this correction pressures above 160 mm. are believed to be accurate to 0.01 mm. For smaller pressures both mercury levels had to be read with the same telescope and the pressures may be in error by 0.05 mm.

The pressure in the vacuum side of the manometers may be checked by the McLeod gage C. This side may be evacuated by connecting G to a mercury diffusion pump and lowering the mercury level below the U between C and G. When the mercury is raised to its normal level this side is only glass and mercury with no stopcocks.

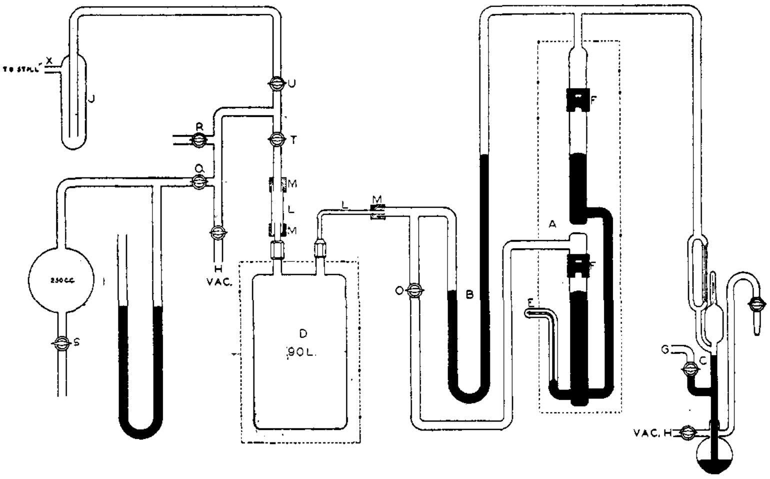

Fig. 2.—Pressure measuring apparatus. Schematic.

The Temperature Measurements

The temperature is measured with a twenty-junction copper–constantan thermocouple and a Leeds and Northrup type K potentiometer. Each junction head and each lead wire is individually insulated with four coats of bakelite enamel. The hot and cold ends each project $6^1/_2$ inches (16.5 cm.) from a rigid, horizontal bakelite support. The cold junction is surrounded by a glass tube filled to a depth of $4^1/_2$ inches (11.4 cm.) with mineral oil as a medium of heat transfer. The construction of the hot junction is shown in Fig. 1. The top 2 inches (5.1 cm.) are surrounded by a glass tube. The $4^1/_2$ inches (11.4 cm.) which project from the tube are tightly wound with silk thread impregnated after winding with bakelite enamel. The heads are given the additional protection of two turns of silk tape similarly impregnated. The lower end of the glass tube is sealed with glyptal. When inserted into the thermometer well, the hot junction reaches to the bottom with about $^1/_{16}$ inch (2.1 mm.) clearance between the heads and the side walls. The well is filled with mineral oil to a depth of $3^3/_4$ inches (9.5 cm.). The ratio of heat conductance vertically through the wires to the conductance horizontally through the glass and oil to the heads is small enough so that the thermocouple is not sensitive to small changes in the depth of immersion of either junction.

The thermocouple was calibrated from 25 to 100° by comparison with a carefully calibrated platinum resistance thermometer[9] in a well-stirred oil-bath, and also from 60 to 100° by comparison of the vapor pressure of water measured in our apparatus with the equation of Smith, Keyes and Gerry.[10] The two calibrations were in agreement to 0.01°.

The thermocouple is sensitive to 0.001°, which at 100° requires that the standard cell voltage remain constant to 10 microvolts. The unsaturated Weston cell used as working standard was therefore kept in the manostat thermostat and was regularly compared with five saturated cells kept in the same thermostat whose average was the primary standard. This average had changed only 10 microvolts over a period of several years. If there was no greater change during the course of our measurements and no greater error due to the change in the relative resistances of potentiometer coils, temperatures could be reproduced to 0.001°. We believe that they correspond to the international temperature scale to 0.01°.

Procedure

About 157 cc. of that mixture which will give the desired liquid and vapor compositions is added to the still. The condensate trap holds 27 cc. and after the steady state is reached 85 cc. should be in the inner boiler and 45 cc. in the outer boiler. After a little practice it is possible to adjust the initial distribution so that it will lead to this steady state. The still is evacuated until boiling begins at room temperature; then it is connected slowly to the manometer system which previously has been adjusted to the approximate pressure. The liquid is boiled vigorously for a few minutes at first so that the vapors may flush other gases from the still, then the heat is adjusted to give steady boiling. The potentiometer is set at the desired temperature and the pressure is regulated to give this temperature as closely as possible all during the attainment of the steady state. This is approximately reached in about twenty minutes but the final adjustment requires from forty-five minutes to two hours and a half. The steady state is assumed to be reached when the temperature changes very slowly and steadily in the closed system for at least five minutes. The temperature does not remain quite constant but rises slowly. For the pure liquids and the azeotropic mixture this rise is less than 0.001° per minute, which corresponds to the increase of pressure due to the leakage of air. In the most unfavorable cases the rise was 0.003° per minute, and was doubtless caused by changing composition due to the escape of chloroform through the condenser making the mixture in the still progressively

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[9] J. A. Beattie, M. Benedict and B. E. Blaisdell, *Proc. Am. Acad. Arts Sci.*, **71**, 327 (1937).

[10] L. B. Smith, F. G. Keyes and H. J. Gerry, *ibid.*, **69**, 137 (1934).

less rich in chloroform. The loss through the condenser was, however, not more than 0.5 cc. per hour, and the deviations from the steady state compositions should be less than the experimental error.

When the steady state is reached, the manometer system is shut off from the still, the heater is extinguished and nitrogen is admitted to the still as rapidly as possible to a pressure of slightly more than one atmosphere. This gives a very rapid change from steady state boiling to none at all. The pressure is measured on the main manometer. Then samples of the liquids in the inner boiler and in the condensate trap are removed for analysis by means of ice-jacketed pipets.

As previously noted the temperature may be reproduced to 0.001° and the pressure may be measured to 0.01 mm. In favorable cases the compositions of the liquids in the inner boiler and in the condensate trap may be determined to less than 0.1%. However, the equilibrium compositions, temperature and pressure can certainly not be determined to this order of accuracy. Only a careful study of several systems can show how accurately the equilibrium properties may be determined by this method.

Summary

An equilibrium still is described with a Cottrell pump which is heated only by the equilibrium vapor.

Auxiliary apparatus for the precise measurement of temperature and pressure is also described, and the procedure for making measurements is given.

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Vapor-Liquid Equilibrium. II. Chloroform-Ethanol Mixtures at 35, 45 and 55°

BY GEORGE SCATCHARD AND C. L. RAYMOND[1]

Many mixtures containing chloroform show interesting behavior. Mixtures with substances containing oxygen but no hydroxyl have large negative changes of heat content on mixing and negative non-ideal free energy changes, smaller in magnitude than the corresponding heat content changes. A plausible explanation is that two different dipoles can align themselves in the co-linear parallel position much more closely than can two like dipoles of either species. Mixtures with the lower aliphatic alcohols have negative changes of heat content when the alcohol is in excess but positive changes when the chloroform is in excess.[2] These measurements of the vapor-liquid equilibrium for chloroform-ethanol systems were undertaken in the hope of throwing light upon this very interesting phenomenon.

Equilibrium Measurements

The equilibrium measurements were carried out as described in Part I of this series except that the still was left connected to the barometer during the pressure measurements on the pure components. Fluctuations in the pressure due to the boiling were not greater than 0.02 mm. The compositions of the mixtures were determined from the densities.

Ethanol was purified as described by Harris[3] and kept in 100-cc. glass-stoppered bottles. Density measurements indicated the presence of 0.12-0.18% of water. The vapor pressures at 55° of the products of three purifications were 279.82, 279.90 and 279.81$_5$ mm. Chloroform was purified by the method of Timmermans and Martin.[4] The density and vapor pressures of the pure chloroform were determined immediately. The material used for mixtures was stored in ground-glass stoppered bottles in the dark after the addition of 1% ethanol as a stabilizer. The vapor pressures at 55° of the products of three different purifications were 617.77, 617.90 and 617.84 mm.

The vapor pressures of the pure components, measured at 5° intervals, are given in Table I. The measurements with alcohol agree excellently with most of those of Louder, Briggs and Browne, and below 60° are from 0.2 to 0.4% lower than those of Merriman. They are from 0.5 to 1.0% lower than the values of the "International Critical Tables.[5] The measurements with chloroform are in agreement with those of Beckmann and Leische and of Rex, and are about 5% lower than those of Herz and Rathmann. They are 1-2% lower than the values of the "International

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[1] Taken from the thesis submitted to the Massachusetts Institute of Technology by C. L. Raymond in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. Hirobe, *J. Fac. Sci. Tokyo*, [1] **1**, 155 (1925).

[3] L. Harris, THIS JOURNAL, **55**, 1940 (1933).

[4] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 763 (1926).

[5] "International Critical Tables," Vol. III, p. 215. The other literature references will be found there.