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Vapor–Liquid Equilibrium. X. An Apparatus for Static Equilibrium Measurements

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An apparatus is described for the study of vapor–liquid equilibrium by measuring the vapor pressure as a function of the temperature and the over-all composition of a system with about one-tenth of its volume liquid and nine-tenths vapor. This apparatus can be used from −10 to 120° at pressures not greater than 1 atmosphere with precisions of about 0.01 mm. and 0.01°.

In the course of developing "equilibrium stills" for the measurement of vapor–liquid equilibrium,[2-5] we have become more and more impressed by the intrinsic disadvantages and the uncertainties of this method.

The static method has the advantages that it measures true equilibrium, it is more precise, and it can be used to much smaller pressures. It has the disadvantage that it cannot be used with components which decompose, and that the vapor composition cannot be measured but must be calculated. There is a distinct advantage in calculating the liquid composition also by successive approximations from the temperature, the pressure, the total volume, and the total quantity of each component in the liquid plus the vapor. So used, the method is more rapid than the "equilibrium still" method because measurements can be made at a series of temperatures with a single analysis of the over-all composition. The apparatus and method described in this paper were developed to utilize these advantages.

Experimental

The apparatus consists of a cell in which equilibrium is maintained, a thermostat to contain it, a thermometer, a manometer, and vacuum manifolds to introduce approximately known quantities of the degassed components and to remove the mixture completely after the pressure–temperature relation has been studied. Since it is not practicable to place a sufficiently precise manometer in the thermostat, it is necessary to have a null manometer separating the vapor from an inert gas. Since the zero point of our null manometer is not constant, it is necessary to determine it before each measurement. This requires an auxiliary cell and an equalizing system to avoid admission of inert gas into the cell or loss of components from it.

Thermostat.—The thermostat is illustrated in Fig. 1. It is a box 2.5 × 2.5 × 4 ft. The outer wall is 0.5-in. plywood; next is 2 in. of Fiberglass insulation and the inner wall is ⅛-in. Masonite. One side wall is removable and on a second side there is a 11 × 17 in. Thermopane window which can also be removed or can be covered to cut down heat exchange.

Two inches from the inside wall is a baffle of ⅛-in. Masonite with a removable window and a removable side opposite the cor-

responding parts of the outer wall. The baffle ends 5 in. from the top and bottom of the thermostat. A 12-in. fan rotating in a 12.25-in. hole in the bottom of the baffle box circulates the air downward inside the baffle and upward outside it. Below the fan is a 40-ohm nichrome heater regulated by a Variac and a 50-ohm heater controlled by a Thyratron circuit. Above the fan is a 25-ohm heater used only to change from one temperature to another. Above this heater is a 35-ft. long square spiral of ⅜-in. copper tubing through which a glycol–water mixture is circulated from a cooling bath by an automobile fuel pump modified to pump at every cycle regardless of head. The flow rate is controlled by varying the displacement of the pump and varying the speed of the motor.

The baffle box is divided into two parts above the coil by a Masonite partition. One side, which contains everything but the two cells, is maintained about ⅓° higher than the cells by an electric heater at the top in order to prevent condensation on metallic parts of the apparatus. Another auxiliary heater keeps the temperature of the null manometer a little above that of its surroundings during heating and cooling.

The temperature is controlled by the apparatus described by Scatchard, Hamer, and Wood[6] with the platinum resistance thermometer replaced by a coil of piano wire with 20-ohm resistance and a temperature coefficient of 0.0032 at 0°. The short time regulation was ±0.001°, but there is a drift of about 0.02° in 24 hr. owing largely to a zero shift in the galvanometer.

Equilibrium Cell.—The equilibrium cell is shown in Fig. 2. It is a nearly flat-bottomed tube of 35-mm. glass tubing, 70 mm. long with a 10-mm. thermocouple well extending to within 20 mm. of the bottom. The stirrer is a loose-fitting glass ring about 30 mm. deep containing a soft iron core. At the top is an ungreased mercury-sealed ground-glass cap for removing material, which was never used. There is also a tube connecting the cell to the null manometer through a U-tube which can be closed with mercury. Between this seal and the null manometer is a tube which leads to the filling system through mercury float seal 2 and another which leads to the equalizing and collecting systems through metal valve 3.

The stirrer is raised and lowered by two powerful magnets beside the cell which are attached through a yoke to a Bakelite shaft extending through the top of the thermostat to an eccentric. The length of stroke is sufficient to raise the stirrer from the bottom of the cell entirely out of the liquid. The rate of stirring is about 10 cycles per minute. Thus the surface is broken twenty times a minute and most of the liquid is forced turbulently past the stirrer at the same frequency.

The metal values are Hoke packless bellow valves No. A432. The mercury float seals are glass U's which can be closed by mercury, with a ground-glass mercury-float seal in each arm. An expanded section of the tube contains a short glass float with a soft iron rod inside and with the male part of a cone joint ground at the top. The corresponding female part is in the tube itself. Dimples in the tube below the float limit its drop when the mercury is lowered. Such valves are mercury tight to rather high pressures. A sticking valve is easily opened with a magnet.

(1) Condensed from the Ph.D. Theses of Grant M. Wilson and Frank G. Satkiewicz, M.I.T. 1958. The preparation for publication of this and the three following papers was assisted by the Atomic Energy Commission under Contract AT(30-1)-905.

(2) G. Scatchard, C. L. Raymond, and H. H. Gilman, J. Am. Chem. Soc., **60**, 1275 (1938).

(3) G. Scatchard, S. E. Wood, and J. M. Mochel, ibid., **61**, 3206 (1939).

(4) G. Scatchard, G. M. Kavanagh, and L. B. Ticknor, ibid., **74**, 3715 (1952).

(5) G. Scatchard and L. B. Ticknor, ibid., **74**, 3724 (1952).

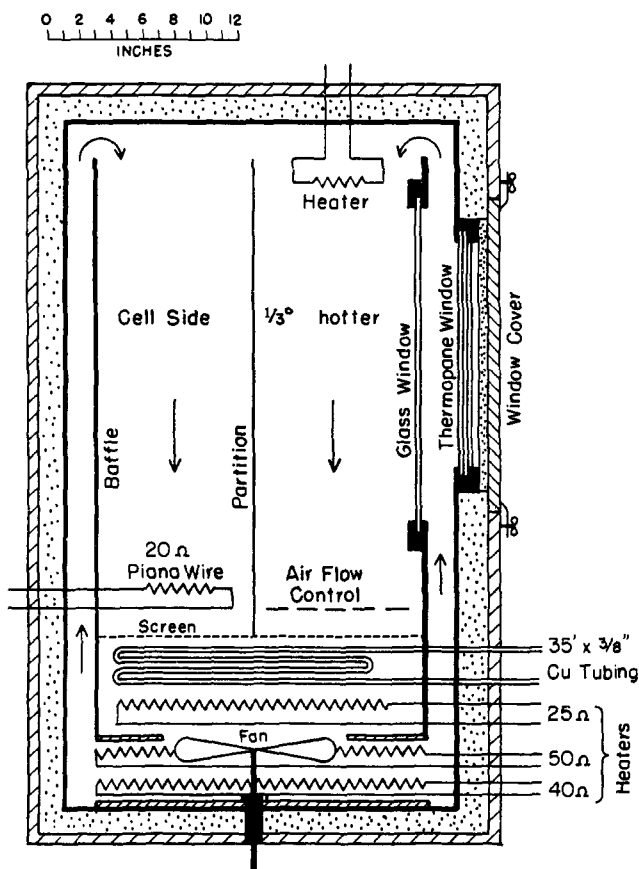(6) G. Scatchard, W. J. Hamer, and S. E. Wood, ibid., **60**, 3061 (1938).
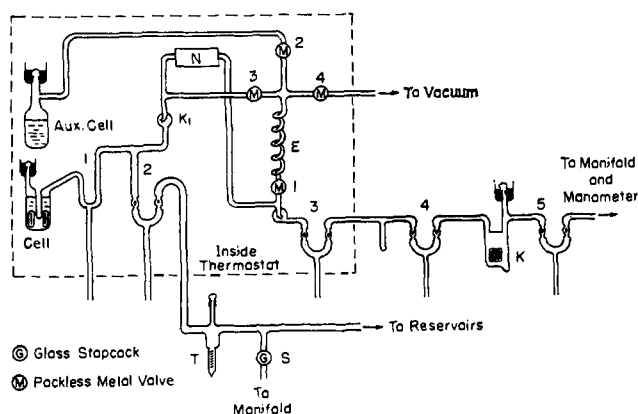
Fig. 1.—Air thermostat.

Fig. 2.—Equilibrium cell and connections.

Measurement of Pressure.—The null manometer is a 2-in. diameter phosphor bronze bellows about 2 in. long with flexibility such that its length changes 1 mm. for 14 mm. difference in pressure. It is shown in Fig. 3. The inside of the bellows is connected to the equilibrium cell. In order to reduce the vapor volume the bellows is nearly filled with a brass block with holes bored to the side and to the end. The box outside the bellows is filled with the containing gas, argon, and connected to the manometer. The mount for the bellows is 0.5 × 0.5 in. brass in the shape of a tuning fork. The cylinder s' and the circular plate fastened to the support above the bellows limit the flexing of the bellows to a few tenths of a millimeter even when large pressure differences are applied. The flexing of the bellows is transmitted to a cylindrical drum through the rod h and a piece of 0.004-in. stainless steel wire wrapped around the drum, which has a diameter of 2 mm. The drum is suspended between the points g and g' by a 0.006-in. stainless steel piano wire. A mirror is mounted on the drum parallel to its axis. Both the drum and the mirror are labeled d. The mirror serves to magnify the motion by a light beam of 4 m. equivalent length by use of a lens system similar to that in the Leeds and Northrup Type E self-contained galvanometer; 1 mm. deflection on the scale corresponds to 0.00385 mm. of Hg.

Even though the mirror has a counterweight so adjusted that there is no angular acceleration when the instrument is linearly
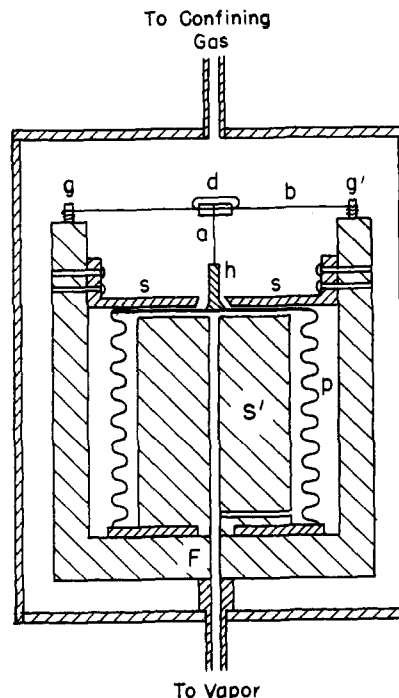

Fig. 3.—Null manometer.

accelerated, there is an oscillation, due to the building vibrations, which is sometimes as great as 7 mm. on the scale. The average can be determined as in weighing by the method of swings, but the inconvenience is one of the worst difficulties of the null instrument.

Another drawback is the shift in zero point, which has to be determined for each pressure measurement. The prevention of passage of argon into the equilibrium system or of vapors out of it requires rather complicated apparatus, illustrated in Fig. 2. The argon side of the null manometer is connected to the main manometer through a mercury float seal 3. The null manometer is by-passed before reaching the float valve by a line through metal valve 3, a meter long coil of 0.25-in. copper tubing with horizontal axis, and metal valve 1. Between valve 3 and the coil is a line to the vacuum system through metal valve 4 and a line to the auxiliary cell through metal valve 2. The auxiliary cell contains degassed solution of approximately the same composition as that in the equilibrium cell.

The main manometer and the thermostated 90-l. reservoir are essentially the same as those described by Scatchard, Kavanagh, and Ticknor[4] except that this part of the system is filled with argon and the temperature control of the manometer has been improved. The room is thermostated at 28.4 ± 0.1°, and the manometer case contains a mercury regulator half-way up the case regulated about half a degree below room temperature. This keeps the top and bottom at the same temperature, about 0.1° below that at the midpoint. The manometer lights are kept on throughout the measurements.

It was found that the pressures below 135 mm., for which both menisci must be read with the same telescope, can be read as accurately as the high ones if the telescope is rotated in the same direction for every reading.

With a static system the pressure reservoir is necessary only to stabilize the pressure for the final readings. It is often isolated during the preliminary adjustments. Sometimes it is convenient to isolate the whole manometer system beyond seal 3 by closing this seal partially and changing the pressure by raising or lowering the mercury in the seal and thus changing the volume between the seal and the null manometer.

Measurement of Temperature.—The temperature of the equilibrium cell is measured with the 20-junction copper–constantan thermocouple used previously,[4] with the cold junctions in an ice-water mixture. It was calibrated *in situ* by measuring the vapor pressures of benzene and of water, using for benzene the vapor pressure equation of Willingham, Taylor, Pignocco, and Rossini[7]

$$\log p = 6.89324 - 1203.835/(219.924 + t)$$

from measurements in the range 14.5–80.9°; and for water the equation of Keyes[8]

(7) C. B. Willingham, W. J. Taylor, J. M. Pignocco, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(8) F. G. Keyes, *J. Chem. Phys.*, **15**, 602 (1947).

$\log p = -2892.3693/T - 2.892736 \log T -$
$\qquad 4.9369728 \times 10^{-3}T + 5.606905 \times 10^{-6}T^2 -$
$\qquad 4.645869 \times 10^{-9}T^3 + 3.7874 \times 10^{-12}T^4 + 19.3011421$

converted from the thermodynamic to the International scale by the relation[9]

$T - t = 273.16 + (t/100)(t/100 - 1)(0.04217 - 0.00007481t)$

The average difference between the two temperatures in the two series was less than 0.01°, and the maximum difference less than 0.02°. The relation between temperature and e.m.f. was smoothed to the temperatures for the mixtures by plotting against the temperature the deviations of e.m.f. from a quadratic in the temperature. This plot gave an intercept of about −0.07° in· stead of zero at 0°, perhaps because the ice bath was rather shallow.

Three runs were made with water at the temperatures 5, 25, 45, 65, and 85°, two of them before the degassing technique had been developed so that the residual pressures were 0.200 and 0.340 mm. instead of the 0.023 and 0.044 in the third run and in the calibration. The average deviation of the values interpolated from the calibration, giving equal weights to the water and ben· zene series, was 0.015° from the first run and 0.006° from each of the others.

The potentiometer was set at exactly the same value for the measurements of the pressures of benzene and of water at about 7°, 19°, 35°, 50°, 65°, and 79°, and the vapor pressure of water was also measured at about 99°.

The water was conductivity water from the still in this Labora· tory. The benzene was Mallinckrodt thiophene·free benzene fractionated in the 2.5·m. fractionating column in this Laboratory. Three top fractions of about 40 cc. each and two bottom fractions of 100 cc. each were discarded. The boiling points of the last bottom and the last top fractions differed by 0.01°.

Material Transport.—Since days of degassing at 85° are neces· sary after even a few minutes exposure to argon or air, the appara· tus was opened only when necessary for repairs. The components are introduced into the cell and the mixture is removed after the measurements by distillation. The containers for the degassed components are a permanent part of the apparatus. The re· ceiving flask for the solutions is in the argon side of the apparatus. The receivers are cooled in ice water except as noted, and the evaporating liquid is sometimes warmed with warm water.

The loading arm is connected to the equilibrium cell through seal 2 and to the vacuum-argon manifold through a metal valve. It consisted of the two component containers and a calibrated 10-cc. centrifuge tube into which the desired quantity of a com· ponent is condensed and then distilled into the equilibrium cell. The measuring tube is never exposed to permanent gas and is kept evacuated except when in use.

The collecting train is connected to the argon side of the null manometer through seal 3. There is a finger which can be cooled in liquid air to collect the last traces of vapor; seal 4; a cell of about 20-cc. capacity with a magnetic stirrer, a vertical tube at the top with a mercury-sealed ground·glass cap, and a small dim· ple in the bottom below the tube to permit nearly complete re· moval of the contents with a hypodermic syringe; and seal 5 leading to the main manometer and pressure reservoir.

Procedure.—After the apparatus was built foreign vapors and gases were excluded from the equilibrium cell and the loading

(9) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

arm, thus decreasing considerably the amount of degassing necessary with each solution. Initially the apparatus was de· gassed by first pumping overnight with a mercury diffusion pump. Then one of the components was introduced, the system was heated to the highest temperature of measurement and vapor was expanded off periodically. This method degasses about ten times as fast as heating while pumping with a diffusion pump.

For each solution the equilibrium cell is filled as described above, seal 1 is closed, and the rest of the system evacuated. The seal is opened with the cell still at 0°, closed again, and the evacuation repeated. The first two measurements with each system are made at room temperature and at 5°; the others are made with ascending temperatures with a final reading after re· turn to room temperature. The difference between the two room temperature readings gives the permanent gas buildup, nearly all of which is attributed to the highest temperature.

During the temperature changes, care is taken to keep the equi· librium cell cooler than the rest of the apparatus, from which it is isolated by seal 1. The final adjustments of temperature and pressure are attained simultaneously.

After the null manometer reading has been taken, the equaliz· ing coil is filled with vapor from the auxiliary cell to the proper pressure. After seal 3 has been closed, the coil is connected to the argon side through valve 5 and then to the vapor side for the few seconds necessary for the zero reading. Then the valves are closed and the coil is evacuated. The change in reading is usually 0.05 mm. or less, so the gain or loss of material is negligible. The length and shape of the equalization coil prevents contamina· tion with argon by convection or diffusion.

The total volume of the equilibrium side of the apparatus is 113.5 ml., of which about 10 ml. is occupied by the liquid.[10] So at 5° the composition of the liquid is very close to the over-all composition. At only one point in our studies was the difference (0.0011) greater than 0.1%. Even at the highest temperature there was only one point at which the difference (0.0112) was greater than 1%. Calculating the free energy at the lowest temperature first and proceeding step by step to the highest eliminates any inconvenience of knowing the over-all composition rather than the liquid composition. The practical advantages are great. The two men required to operate the apparatus without undue tension can measure six equilibria at five different tem· peratures on a single sample every second day. The alternate days are used to analyze the sample, refill the apparatus, and other auxiliary tasks.

The apparatus can be used from −10 to 120° for pressures not greater than 1 atmosphere. The precision is about 0.01 mm. and about 0.01°. For pressures greater than about 20 mm., the precision of the pressure is better than that of the temperature. One common criterion for the choice of the two systems discussed in the following papers was that there should be very large dif· ferences between the vapor and liquid compositions since this condition leads to serious difficulties with "equilibrium stills."

NOTE ADDED IN PROOF.—Hermsen and Prausnitz[11] describe an apparatus embodying some of these characteristics. They compare it with our earlier apparatus,[2,3] but do not refer to the thesis of Wilson although they borrowed a copy of it in 1958.

(10) The volume of the equalizing coil is 23.6 ml., that of the argon side to seal 3 is 445 ml., and that between seals 3 and 5 is 80 ml.

(11) R. W. Hermsen and J. M. Prausnitz, *Chem. Eng. Sci.*, **18**, 485 (1963).

Vapor–Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing

BY GRANT M. WILSON[1]

An equation has been found which represents the excess free energy of mixing nonelectrolytes with two, or sometimes three, parameters for a binary mixture and no additional parameters for polycomponent systems. It is compared with the experimental values for several mixtures. The corresponding equations for the excess enthalpy and entropy of mixing are also derived. A semitheoretical interpretation is given. This equation should be particularly useful for large deviations from normality and for polycomponent mixtures.

A new expression has been found to represent the excess free energy of mixing which has the advantages that a system of any number, n, of components can probably be fitted with $n(n - 1)$ parameters obtained from the binaries. This equation which leads to Raoult's law and Henry's law at the limits $x_i = 1$ and $x_i = 0$ is

$$\bar{G}^{E}/RT = -\sum_i x_i \ln\left(1 - \sum_j x_j A_{j/i}\right) \qquad (1)$$

where x_i = mole fraction of component i and $A_{j/i}$ = adjustable parameters ($A_{i/i} = 0$, $A_{j/i} \neq A_{i/j}$).

The following equation results for a binary mixture.

$$\bar{G}^{E}/RT = -x_1 \ln(1 - A_{2/1}x_2) - x_2 \ln(1 - A_{1/2}x_1) \qquad (2)$$

The two parameters $A_{2/1}$ and $A_{1/2}$ of eq. 2 are positive if the deviation from ideality is positive, and the param-