VAPOR-LIQUID EQUILIBRIA FROM MEASUREMENTS OF PRESSURE TEMPERATURE AND OVER-ALL COMPOSITION

THE SYSTEM WATER-2BUTOXY ETHANOL

by

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ABSTRACT

Vapor-Liquid Equilibria from Measurements
of Pressure, Temperature and Over-all Composition
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Grant M. Wilson

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Measurements of total pressure and overall composition have been made on mixtures of water and 2-butoxy ethanol over the composition range at five temperatures from 5 °C. to 85 °C.

An air thermostat and the experimental apparatus is described for the static measurements of total pressure. The design of a null instrument used for the purpose of obtaining the same pressure on two sides of a metal bellows is given.

The determination of composition has been by liquid density measurements.

The excess free energy has been determined at each temperature from the total pressure. The expression obtained for the excess free energy is:

$$\overline{G}^E/RT = -x\ln \Big\{ x+(1-x) \Big[1.4786-\frac{0.0673\text{x}10^6}{T}(5.9701\text{x}10^{-3}-\frac{1}{T})\Big]\Big\}$$
$$-(1-x)\ln \Big\{ (1-x)+x \Big[0.3438-\frac{0.04401\text{x}10^6}{T}(5.5841\text{x}10^{-3}-\frac{1}{T}\Big]\Big\}$$
$$+x(1-x)(1-2x) \Big[0.4047-\frac{0.0642\text{x}10^6}{T}(5.747\text{x}10^{-3}-\frac{1}{T})\Big]$$

where x is the mole fraction of water.

The heat of mixing is calculated using the expression:

$$\frac{\overline{H}^M}{R} = \frac{\partial\, \overline{G}^E/RT}{\partial\, {}^1/T}$$

and the entropy of mixing is given by:

$$\frac{\overline{S}^E}{R} = \frac{\overline{H}^M}{RT} - \frac{\overline{G}^E}{RT}$$

$\overline{H}^M/RT$ goes from a significant negative value at 5 °C. to a small positive value at 85 °C. $\overline{G}^E/RT$ changes very little from 5 °C. to 85°, since the change in $\overline{S}^E$ is nearly equivalent to the change in $\overline{H}^M/RT$.

A semi-theoretical basis is given for the expression $\overline{G}^E/RT = -x\ln\left[x + a(1-x)\right] - (1-x)\ln\left[(1-x)+bx\right]$ which will usually give a better fit to vapor-liquid equilibrium measurements than the conventional expression:

$$\overline{G}^E = x(1-x)\sum_i A_i(1-2x)^i$$

Thesis Supervisor: George Scatchard
Title: Professor of Physical Chemistry, Emeritus; Lecturer.

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The apparatus was built through the joint effort of Frank G. Satkiewicz and the author. The experimental measurements were made by reciprocal aid. The help afforded by this type of arrangement is greatly appreciated.

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I. INTRODUCTION

The object of this research was to build an experimental apparatus for studying the vapor liquid equilibrium of mixtures and to make measurements on the system water-2 butoxy ethanol (butyl cellosolve).

In a great majority of the vapor-liquid equilibrium measurements reported in the literature the pressure, temperature, vapor composition , and liquid composition have been measured. In order to measure these vapor compositions it was necessary to use a still. Many of the problems connected with a still have been solved; such as the introduction of the principle of recirculation in order that equilibrium may be attained between the vapor and the liquid, and the introduction of the Cottrell pump to come closer to temperature equilibrium between the vapor and liquid at the point where the temperature is measured. Many of the developments made on the still were made in this laboratory and precise measurements have been obtained by this method.[1-9]

There are several cases in the literature where only the total pressure, the temperature, and the liquid composition were measured, and the vapor composition was calculated. Among them is a series of papers, the last of which is a report by Neckel and Kohler[10] on the thermodynamics of binary mixtures with components of approximately equal molar volumes. They use a numerical method to integrate the Gibbs-Duhem relation. Schulze[11] has studied binary mixtures containing ethanol. He used the expression:

$$\xi = \frac{x_1x_2}{\log p - x_1 \log p_1^0 - x_2 \log p_2^0}$$

to determine the limiting slope of the pressure curve where he found that a plot of ξ vs. x gives a straight line up to x = 0.2. Then the vapor composition was calculated by numerical integration. Huber[12] describes a way to calculate the vapor composition by graphical integration. Scatchard, Kavanagh and Ticknor[8] measured both the pressure and the vapor composition using a still for the system hydrogen peroxide-water. The reliability of the measured vapor composition was uncertain; therefore, the vapor compositions were calculated from the total pressure curve obtaining reasonable agreement between the calculated and measured vapor compositions. They assumed a simple form of expression for the excess free energy and determined the corresponding form for the total pressure. After the parameters of the expression had been fitted to the pressure curve the vapor composition and other desired quantities were then calculated.

If one measures only the total vapor pressure of a mixture a static method may be used. The advantages of a static method over an equilibrium still are:

1. If the liquid and vapor compositions are calculated from the overall composition, the vapor pressure of a sample can be measured at several temperatures without analyzing at each temperature.
2. Systems can be studied in which the composition of the liquid and vapor differ largely.

3. A larger temperature range may be studied because attainment of equilibrium is no problem.

The disadvantages of the static method are:

1. Only systems which do not produce gaseous products through chemical reaction may be studied.
2. The apparatus and materials have to be thoroughly degassed.

It was felt that the disadvantages of the static method could be overcome; this meant choosing a system, initially, which does not react to produce gas.

The system water-2 butoxy ethanol (more commonly known as butyl cellosolve) was chosen since this system exhibits the unusual behavior of not being completely miscible in the temperature range, 50 °C. to 128 °C., but being completely miscible both above and below this range.[13] Because of this behavior the thermodynamic properties of this mixture should prove quite interesting.

An apparatus based on the static method has been constructed. The total vapor pressure of this system has been determined over the composition range at five temperatures from 5 °C. to 85 °C.

II. EXPERIMENTAL

The Apparatus

To maintain the temperature of the sample constant an air thermostat was used. The temperature was measured with a 20 junction copper constantan thermocouple. The pressure was measured by a null method. In this method the vapors are separated from the confining gas by a bellows of a null instrument, and the pressure of the confining gas is adjusted until the instrument indicates zero pressure differential across the bellows. The pressure of the confining gas is then read on a mercury manometer.

The description of the apparatus will be broken down into three parts:

(a) The thermostat

(b) The cell system

(c) The manometer system, etc.

(a) The Thermostat

The air thermostat proved to be quite convenient. The advantages over a liquid bath are:

1. It doesn't have to be drained.
2. One can see clearly inside.
3. A side panel and a window can be removed, making it easy to make alterations or repairs.
4. No mess!

A disadvantage is that one has worse temperature gradients in an air bath because of the low specific heat of the air. For this thermostat gradients up to 0.1 °C. were measured between the top and the bottom of the inner part.

Figure 1 is a cut-away diagram of the $2\frac{1}{2}'$ x $2\frac{1}{2}'$ x 4' thermostat. The outer wall is $\frac{1}{2}''$ Plywood; next is two inches of Fiberglass insulation; and the inner wall is $\frac{1}{4}''$ Masonite. On one side of the thermostat is a 11" x 17" Thermopane window which may be covered to cut down heat loss when desirable, also one side wall is completely removable.

Two inches from the inside wall is a baffle which channels the air propelled by the fan so that it first goes up between the baffle and the wall and then down through the central part of the thermostat. Two heaters are located concentrically just below the fan, and a heavy duty heater which is used only to change the temperature is located above the fan. Just above this heavy duty heater is a coil of thirty-five feet of 3/8" copper tubing through which a refrigerated mixture of ehtylene glycol and water may be circulated.

A centrifugal type pump was found unsatisfactory in circulating this mixture because of the build up of bubbles in the line. This pump was replaced by a fuel pump from an automobile, altered in such a way that it would pump every cycle independent of the head. This has proved quite satisfactory.

The flow rate was varied by varying the speed of an a.c. motor with a Variac. Only limited variation was attainable this way and further variation was made possible by varying the displacement of the pump.

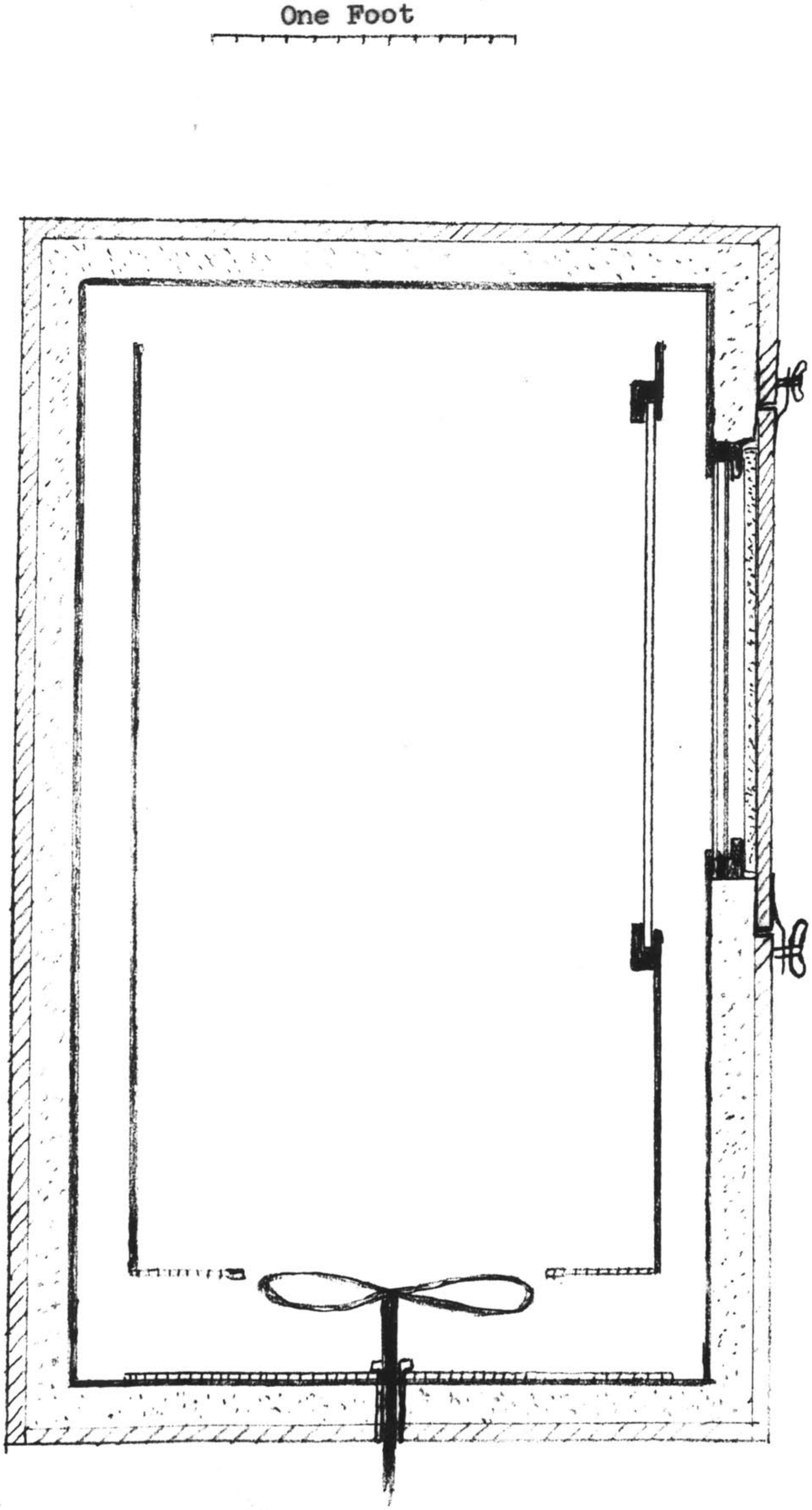


Figure 1 - Air Thermostat

The control unit used for temperature regulation of the air bath uses a phase shifting thyratron circuit, and is the same as the one used by Scatchard, Hamer and Wood[14] except that a coil of piano wire suspended in the air was used in place of a platinum resistance thermometer. With this arrangement it was necessary to keep the temperature of the vapor pressure cell under constant observation and adjust the temperature setting to compensate for drift; regulation in this manner was ±0.001 °C. If left alone the unit would regulate to within ±0.02 °C. in a 24 hour period; the main cause for drift is the shift in zero of the galvanometer.

(b) The Cell System

Figure 2 is a diagram of the vapor pressure cell. A 10 c.c. sample fills it about 2/3 of the way when the stirrer, s, is down. The 20 junction thermocouple used for measuring the cell temperature is inserted in the well, h. The sample was stirred constantly by means of stirrer, s, an iron sleeve sealed in glass. Externally two strong horseshoe magnets were moved up and down by means of an eccentric mounted on top of the thermostat. Stirring was such that the stirrer broke the surface of the liquid twice each cycle; the period being about nine seconds per cycle. The moving magnets affect e.m.f. readings taken of the 20 junction thermocouple only slightly. The galvanometer swings through a cycle corresponding to a temperature change of ±0.001 °C. An operator can average out this swing.

The cap, c, surrounded by mercury was provided to re-

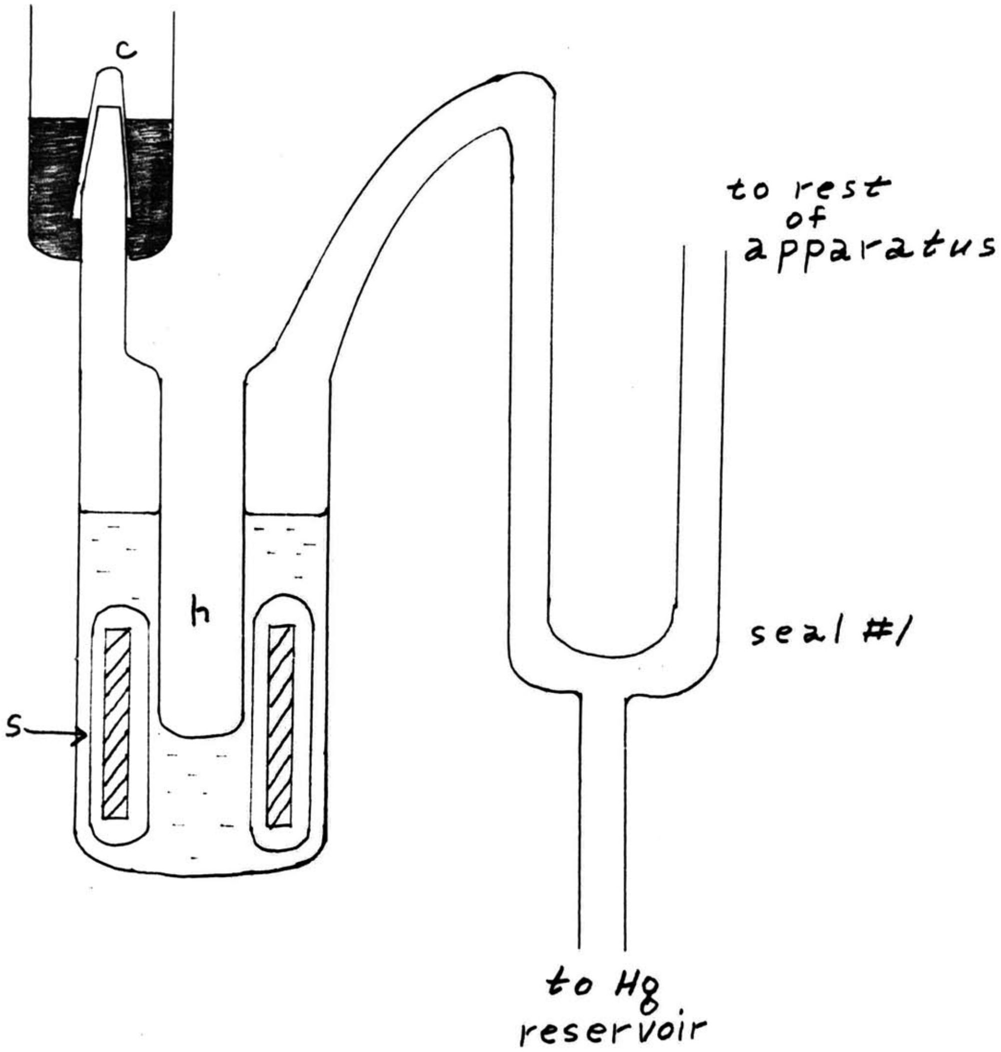


Figure 2 - Vapor Pressure Cell

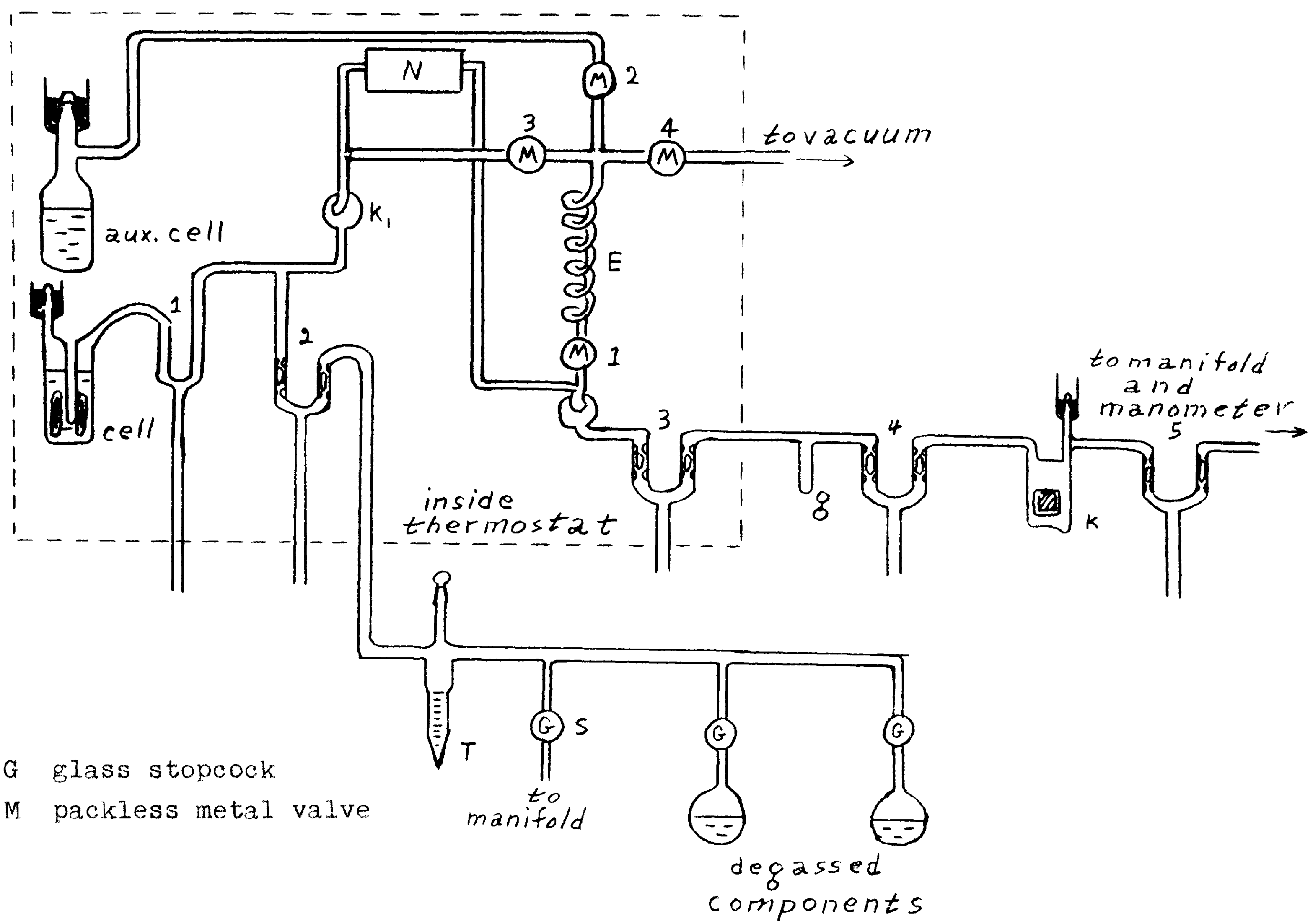
move samples from the cell, but it was never used. The samples were distilled from the cell as described in the experimental procedure. The cap is not greased; mercury provides the necessary seal.

Figure 3 is a diagram of the cell with those parts which are closely connected. It is very important that there be no leaks in the region which contains vapor from the cell. For this reason all connections were either soldered, glass to kovar, or glass to glass. All soldered connections were made with the particular part detached from the system; care being taken to have the joint look definitely leak tight. In addition each part was flushed with water to remove any solder flux which may have gotten inside. Final connection into the system was then made joining glass to glass.

The vapor region of the sample includes the cell, the lead to float valve #2, that to metal valve #3 and one side of the null instrument N. It is desirable to keep this volume as small as possible since correction must be applied for the amount of material in the vapor phase.

As mentioned earlier the null instrument is used to get the same pressure on each side. Mechanically this null instrument consists of a flexible phosphor bronze bellows, which displaces a mirror. The displacement of the mirror is observed by reflection of a light beam onto a scale. Further detail is given in Appendix A.

Obtaining the same pressure on the two sides of the null



G glass stopcock

M packless metal valve

Figure 3 - Experimental Apparatus

instrument involves a knowledge of the position of the beam when the pressures are equal. The zero is not a fixed value there being some hysteresis as with a galvanometer. It is therefore necessary to determine the zero with each pressure measurement.

In order to determine the zero it is necessary to connect the two sides so that any pressure difference may equilibrate. This must be done with the following restrictions:

1. The confining gas is not permitted to enter the vapor side.
2. The loss of vapor does not become large enough to affect the accuracy of the composition measurements.

A simple valve is not satisfactory since diffusion may become appreciable in the time that the valve is open. Therefore, the equalization is done through an auxiliary line as indicated by the coil E in Fig. 3. To equalize the coil is first filled with vapor of approximately the same composition as that in the cell by opening valve #2 to the auxiliary cell. Then after seal #3 has been closed valve #1 and then valve #3 are opened permitting equalization of pressure on the two sides of the null instrument. One can be certain of the zero after a period of from ten to twenty seconds; after this the valves are closed and seal #3 may be lowered.

Equilibration of the pressure is slower at low pressures (1 mm.Hg or less). In this range it is possible to evacuate the argon side; admit vapor from the auxiliary cell into the argon side and then open valves #1 and #3. In this way one can wait as long as is necessary without fear of contamination of the cell vapor with argon.

The metal valves #1, 2, 3, and 4 are Hoke packless bellows valves #A432. The valves are manipulated by means of extended handles projecting through the wall of the thermostat.

The confining gas, argon, was used instead of helium because of slower diffusion; thus lessening the chance for diffusion into the vapor side.

When equalizing in the usual manner one can adjust the differential from an approximate knowledge of the zero so that the usual change in pressure in equalizing is around 0.05 mm. With changes such as this the overall composition is affected to a negligible degree. As a precautionary measure the deflection of the beam upon opening valve #3 was always recorded so that a correction could be applied if necessary.

The rest of the apparatus is used to make up or remove a sample without admitting the atmosphere to the cell. The function of the various parts will become apparent in the description of the experimental procedure.

(c) The Manometer System, etc.

The manometer system is essentially the same as that described by Kavanagh.[15] A new vacuum system was built; its relation to the manometer system and the cell system is indicated in Fig. 4. The solenoid valves, A, B, and C were installed for the purpose of controlling the pressure automatically. With the null instrument ultimately used it was not necessary to do this; but with an earlier try with a strain gage transducer it was necessary to follow the pressure change on one side with a corresponding change on the other to prevent damage to the transducer. In the present scheme these valves make it convenient to adjust the pressure in the manifold of the vacuum system when the thermostated 90 liter tank is isolated at valve d.

Valve d is a Henry valve which when closed isolates the 90 liter tank and the main manometer from the rest of the system. Valves e and f are Hoke needle valves used either to admit or to remove argon. Through stopcocks h and j the vacuum arm of the manometer is pumped out periodically so as to maintain a pressure less than 0.0005 mm.Hg as indicated by readings taken with McLeod gage, M_2.

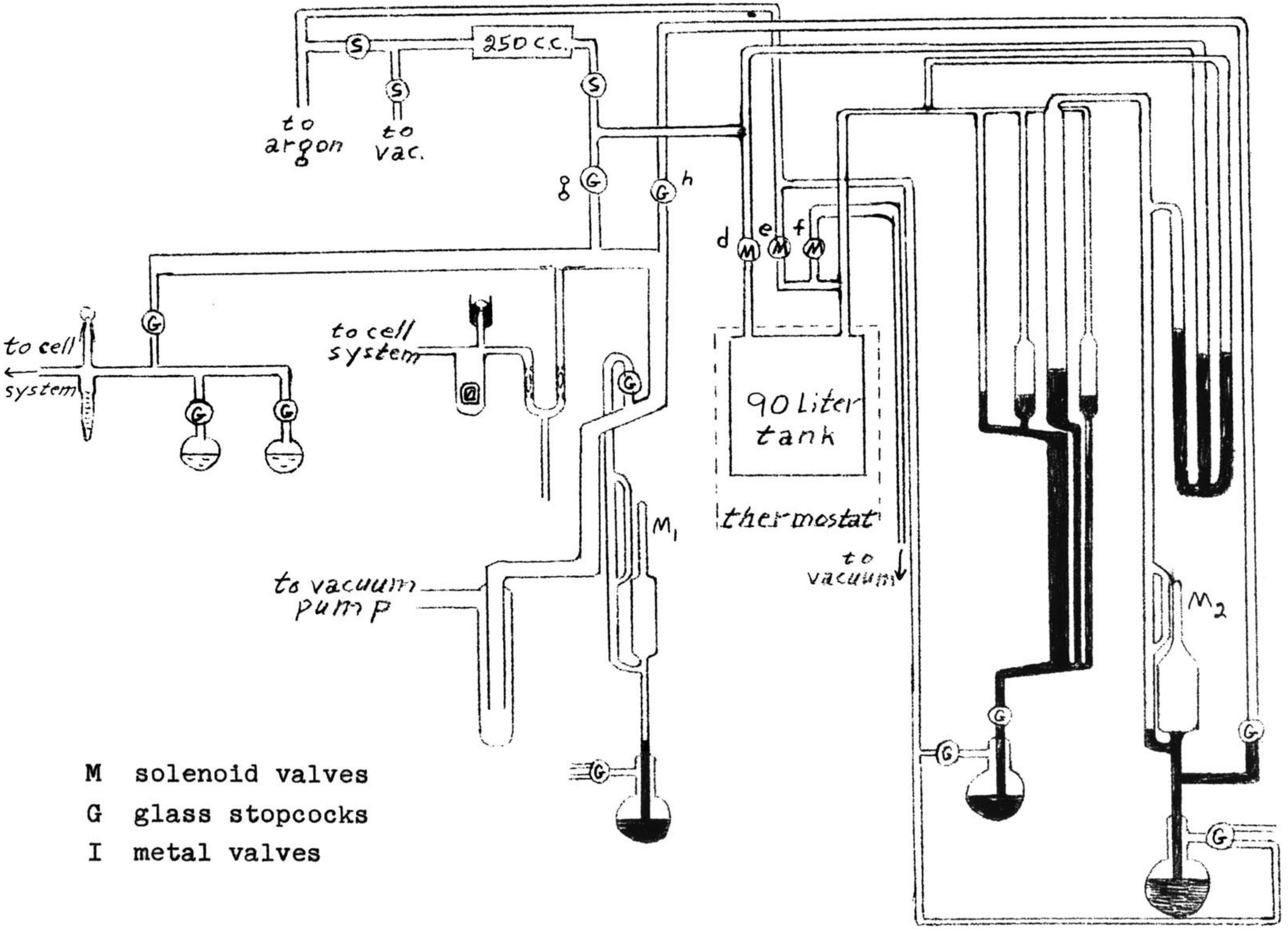


Figure 4 - Manometer System and Vacuum System

Pressure Measurement

The measurement of the pressure of the confining gas was done in the manner and with the same equipment described by Kavanagh;[15] except that some improvement was obtained in the temperature regulation of the manometer case. A mercury regulator was placed in the front of the case where the mercury columns are and about halfway up. In this way the temperature at this point is kept constant to within 0.01 °C. To avoid changes in temperature gradients inside the case the room was thermostated to ±0.1 °C.; in addition the gradient could be brought down to less than 0.1 °C. between any two points of the three points top, middle and bottom if the case temperature were maintained about ½ a degree below the temperature of the room. With this arrangement the case temperature was very constant; the middle region always being the warmest, with the top and bottom at about the same temperature. To avoid disturbing the heat balance in the case which might occur with turning on the manometer lights, they were left on permanently.

Pressures below 135 mm. were read with one telescope instead of two, since the height difference is too small to accomodate two telescopes. It was found that one could have the same precision in reading with one telescope as with two, if the cathetometer bar were rotated into position from the same direction each time. In these measurements the bar was always brought into position by first swinging it too far to the left and then bringing the line of sight to the right until the desired position was reached.

The static head correction was calculated for each measurement since the height of mercury in the lower arm of the manometer is variable. It was not necessary to correct for a static head of vapor since the junction at valve #1 is at the same level as the liquid in the cell. The height of the argon column was then from valve #1 to the level of the mercury in the pressure arm of the manometer. The vapor pressure of mercury was subtracted from the measured pressures.

The difference in pressure between that of the confining gas and the pressure in the cell is determined through the use of the null instrument described earlier. The sensitivity of this instrument is such that each millimeter scale deflection corresponds to a change in pressure differential of 0.00385 mm.Hg. The instrument was calibrated using the manometer.

The main problem related to the measurement of pressure is that of making sure that the pressure in the cell is the vapor pressure of the cell sample at that temperature. The main sources of error being:

1. Leakage of foreign gas into the cell.
2. Degassing of the cell system.
3. Introduction of samples which have not been degassed.
4. Condensation of vapor in regions other than the cell.

It is usually difficult to know whether the system either leaks or is simply degassing. In general, it can be stated that while pumping for a period of two or three days the build up rate will steady off to a constant value if there is a leak, but if the system is only degassing the build up rate, r , is roughly approximated by the relation $\frac{dr}{dt} \cong -kr$.

Further degassing of the cell system with the assumption that there are no leaks is discussed in the procedure for a run.

The samples were degassed by degassing enough of the pure components to last for all the measurements. The degassed materials were attached in bulbs with stopcocks to the cell system as shown in Fig. 3.

Water and benzene were degassed by simply placing the material in a bulb with a stopcock already attached and then blowing the combination into the system as shown. They were then degassed by repeated expansions of vapor from the bulb into the vacuum manifold over a period of about a month.

With butyl cellosolve the same procedure was attempted, but it became evident that a very long period of time would be required for complete degassing. For this reason the material was placed in a piece of glass apparatus intended to be used as a mercury diffusion pump. The intake end of the pump was closed off and the material was degassed by heating the boiler with a bath of water so as to get only surface evaporation. Operation of the apparatus was similar to the operation of a diffusion pump. In addition to the usual condenser the line leading to the forepump also had a condenser on it. The line to the forepump was small in diameter (4 mm.); this slowed down the loss of butyl cellosolve. It required about two days of continuous operation to degass the material in this way. During this period about eight c.c. of material condensed in the cold trap next to the fore pump.

Degassing was considered sufficient when a pressure of 0.0001 mm.Hg or less was measured on the McLeod gage after expanding out vapor from one of the compounds which had been standing for at least a day.

Degassing was followed with each compound with the McLeod gage. In doing this the vapor in the manifold is not condensed out and the mercury in the McLeod gage is raised in the usual manner. The mercury is raised above the usual line a height equal to the difference between the vapor pressure of the compound and the pressure in the manifold before a reading is taken. If the vapor pressure is too high for this, then a means of cooling may be provided. It is sufficient to simply cool the capillary at the top of the bulb. All measurements of gas in vapor were made by the above procedure.

To prevent condensation of vapor in regions other than the cell the inner part of the thermostat was partitioned off so that on one side there was simply the main cell and the auxiliary cell. The remaining part of the apparatus shown to be inside the thermostat in Fig. 3 was on the other side. The side opposite the cell was heated 1/3 °C. higher using a suspension of heating wire in the top of the thermostat but above just the one side. Air from the fan first blows over the heater and then over the apparatus. This was sufficient to prevent condensation when the thermostat and apparatus were in thermal equilibrium. When the temperature was being changed it was still necessary to have seal #1 Fig. 3 closed.

Measurement of Temperature

The twenty-junction thermocouple used by Kavanagh[15] was used to measure the temperature of the sample in the cell. The equipment and procedure are essentially the same as used previously[16] except that a Leeds and Northrup type E self-contained galvanometer No. 2430-a was used in place of the type R reflecting galvanometer No. 2500-a.

The thermocouple was calibrated by measuring the vapor pressures of water and of benzene vs. the observed e.m.f.'s from the thermocouple. The temperature was calculated from the pressure using for water the equation of Keyes:[17]

$$\log p = -2892.3693/T - 2.892736 \log T - 4.9369728\times10^{-3}T + 5.606905\times10^{-6}T^{2} - 4.645869\times10^{-9}T^{3} + 3.7874\times10^{-12}T^{4} + 19.3011421. \qquad (1)$$

For benzene the temperature was obtained from the equation of Willingham, Taylor, Pignocco and Rossini:[18]

$$\log p = 6.89324 - \frac{1203.835}{219.924+t} \qquad (2)$$

Equation (1) gives the thermodynamic temperature, but the temperature from equation (2) is on the International temperature scale. The thermodynamic temperatures were converted to the international scale using the following relationship:[15,19]

$$T - t = 273.16 + \left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)(0.04217-0.00007481t) \qquad (3)$$

Table 1 gives the observed e.m.f.'s with the corresponding pressures and calculated temperatures; in Table 2 are the e.m.f.'s calculated from the expression:

$$E_{mv} = 0.84963 - 8.2889\frac{t}{100}\left(1 - \frac{t}{100}\right) \qquad (4)$$

TABLE 1

Temperature Calibration

$E_{meas.}$ mv.	measured pressures mm. Hg		calculated temperatures t °C.		Difference
	H_2O	C_6H_6	H_2O	C_6H_6	$t_{H_2O}-t_{C_6H_6}$
5.712	7.738	39.713	7.442	7.459	-0.017
15.054	16.745	72.549	19.271	19.283	-0.012
27.992	42.593	149.332	35.185	35.174	+0.011
40.069	90.639	267.034	49.588	49.590	-0.002
53.298	186.927	464.518	64.923	64.924	-0.001
65.761	341.112	734.424	79.002	78.995	+0.007
83.660	723.990		98.646		
residual pressure	0.044	0.034			

TABLE 2

Deviations from Calculated e.m.f.

t °C.	E_{meas}.(m.v.)	E_{calc}.(m.v.)	E_{meas}-E_{calc}.(m.v.)
7.459	5.712	5.765	-0.053
7.442*	5.712	5.752	-0.040
19.283	15.054	15.093	-0.039
19.271*	15.054	15.084	-0.030
35.174	27.992	27.995	-0.003
35.185*	27.992	28.004	-0.012
49.590	40.069	40.061	+0.008
49.588*	40.069	40.059	+0.010
64.924	53.298	53.274	+0.024
64.923*	53.298	53.273	+0.025
78.995	65.761	65.741	+0.020
79.002*	65.761	65.748	+0.013
98.646*	83.660	83.702	-0.042

* From water measurements; the temperatures not starred are from the benzene measurements.

The differences between the observed and calculated values are plotted in Figure 5. The differences do not extrapolate to zero at 0 °C., but to about -0.05 mv.; this corresponds to an error of 0.03 mm. in the vapor pressure of water and 0.15 mm. in the vapor pressure of benzene or an error of .06 °C. in temperature. The author is unable to say what caused this.

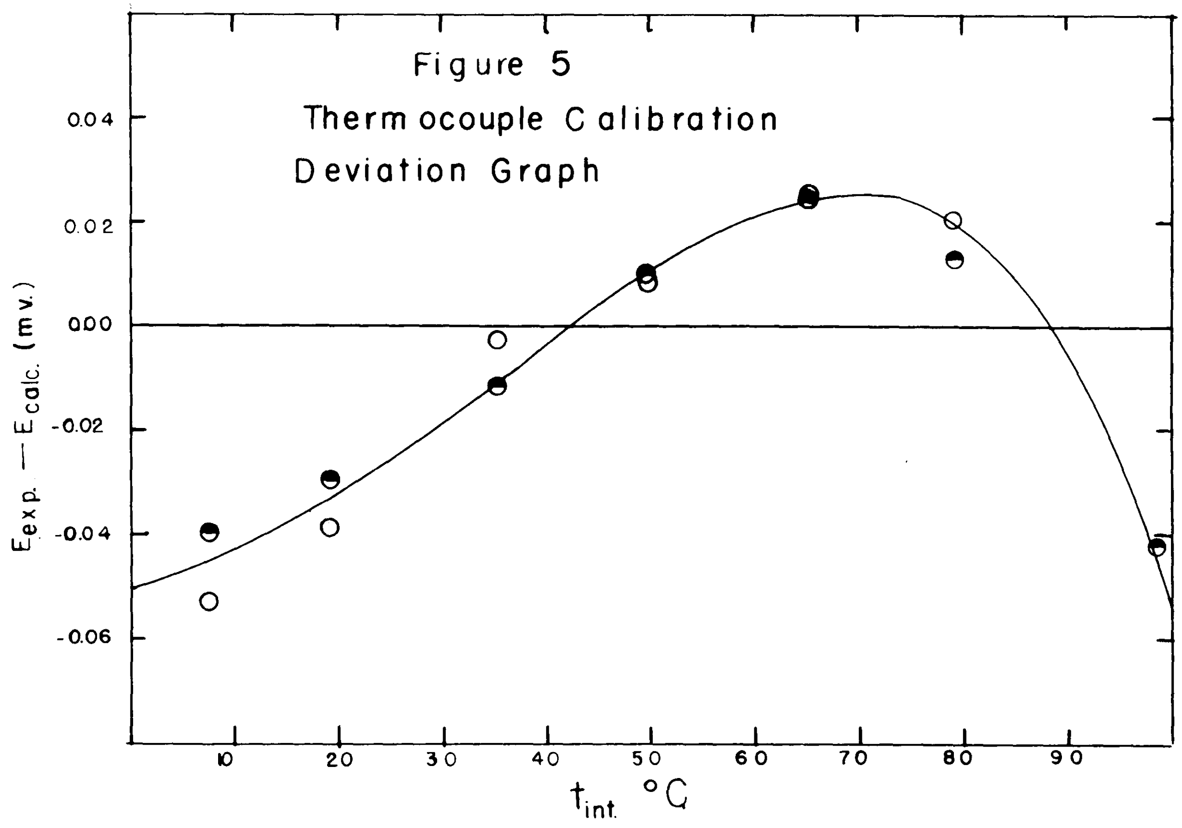


Figure 5

Thermocouple Calibration

Deviation Graph

Materials

The butyl cellosolve used in the measurements was obtained by removing top and bottom fractions repeatedly from Carbide and Carbon's commercial material in a still operated at a pressure of 45 mm.Hg. A bubbler was used to get smooth boiling, dry nitrogen gas being used for this purpose. The four foot fractionating column was packed with helices. The following table gives the results of the fourth and final distillation:

TABLE 3

Results of Final Distillation

Fraction	Approx.vol.	Δd	Δn
1st	15 c.c.	-0.00159	$+12\times10^{-5}$
2nd	15	-0.00134	$+11\times10^{-5}$
3rd	50	-0.00032	-0.6×10^{-5}
Bulk Material	300	0.00000	0.0×10^{-5}
Last Top	10	+0.00012	$+3.0\times10^{-5}$
Pot Material	60	-0.00022	-3.5×10^{-5}

Where Δd is the difference in density and Δn is the difference in refractive index. The first two fractions undoubtedly contain water as an impurity since the density is higher and the refractive index is lower. The differences in refractive indices were measured with an interferometer. The 50 c.c. in the third fraction was added to the bulk material.

The water used in these measurements was conductivity water collected hot in an atmosphere of nitrogen. The benzene used in calibrating was purified using the 2½ meter fractionating column in this laboratory. For details see the thesis of F. G. Satkiewicz.[20]

TABLE 4

Physical properties of butyl cellosolve

	Observed	Literature
Density d_4^{27}	0.89473 & 0.89460*	0.8945 ref.(21)**
Temp. of phase separation x_1=0.8955	50.36 °C.	50 °C. ref.(21)*** 52 °C. ref.(13)***

* After rigorous degassing.

** Using their values for d_{20}^{20} and $\frac{\Delta d_{20}^{t}}{\Delta t}$; $d_{20}^{20} = 0.9019$, $\frac{\Delta d_{20}^{t}}{\Delta t} = 0.00083$.

*** From their phase diagrams.

The change in the density of the butyl cellosolve during the degassing procedure was in the direction of removal of water. Therefore, the density after degassing is probably more nearly correct.

Determination of Composition

The composition of the unknown mixtures were determined from their densities. Accordingly, solutions of known composition were made up and their densities determined.

The density determinations were made at 27 °C. in a 7 c.c. pycnometer. One pycnometer was used for measurements on both the known and the unknown mixtures. The pycnometer used is the same as that described by Kavanagh.[15] The procedure in determining the density was to fill the pycnometer using a hypodermic syringe. A capillary guide was placed on the pycnometer when filling to avoid contacting the neck of the pycnometer above the capillary with the needle of the syringe. The pycnometer was not filled to a fixed mark but was filled to within ±3 mm. of the mark and the difference in height read in the field of a telescope using a vernier. It was found to be important that the capillary drain properly after having been in contact with liquid. To get uniform drainage the pycnometer and sample were warmed until the level was at the top of the capillary; the pycnometer was then placed in the thermostated bath constant to ±.005 °C. After the pycnometer equilibrated with the bath the level of the liquid was read as above described. The pycnometer was then removed and wiped with a fresh paper towel with care not to touch the pycnometer with fingers. The pycnometer was placed on the balance pan and the weight read when the balance arm deflection had steadied; it usually required about twenty minutes to settle down. With this procedure the zero of the balance was always the same after as initially. This was not found to be true when time was not allowed for steadying off. The change from the initial reading to the final ranged up to ±0.1 mg. The loss of sample through the cap was small, amounting to 0.1 mg. in a period of ten hours when the pycnometer was filled with water. No correction was therefore applied for leakage through the cap from the time the level is read to the point at which the pycnometer is weighed. A glass tare of size and shape comparable to the pycnometer was used on the weight pan of the balance. The weight of the liquid in air was reduced to weight in vacuum by correcting for the buoyancy effect as a result of the air displaced by the liquid and the brass weights. The density of brass was taken as 8.0 gr./cm^3.

The method of making up the known solutions is the same as previously used here^6 except that the mixtures were made up in a 25 c.c. erlenmeyer flask with a $\$$ 10/30 ground glass cap.

The density measurements at known compositions were fitted to the following analytical expression giving weight fraction as a function of specific volume, v, where v = 1/d.

$$\omega = \gamma - 0.5895 \left[\frac{\gamma}{\gamma + 1.22(1-\gamma)}\right]\left[\frac{1.22(1-\gamma)}{\gamma + 1.22(1-\gamma)}\right] \qquad (5)$$

γ is given by $\gamma = \frac{v_2 - v}{v_2 - v_1}$, $v_2 = 1.117649$ml/g and $v_1 = 1.003472$ml/g. The mole fraction $x_{calc.}$ was then calculated from the weight fraction. Table 5 gives the experimental and calculated values of mole fraction and Fig. 6 is a plot of $x_{exp.} - x_{calc.}$ vs.

TABLE 5

Density Measurements and Deviations from the Analytical Expression

$x_{exp.}$	d	$x_{calc.}$	$x_{exp.}-x_{calc.}$
0.0000	0.894735	0.0000	
0.0762	0.896915	0.0765	-0.0003
0.1300	0.898621	0.1309	-0.0009
0.2126	0.901528	0.2140	-0.0014
0.3232	0.906135	0.3257	-0.0024
0.3235	0.906109	0.3251	-0.0016
0.4126	0.910522	0.4141	-0.0015
0.5247	0.917273	0.5247	0.0000
0.6178	0.924311	0.6159	+0.0019
0.6190	0.924400	0.6169	+0.0021
0.7115	0.933353	0.7076	+0.0049
0.7119	0.933406	0.7081	+0.0038
0.8082	0.946085	0.8036	+0.0046
0.8121	0.946747	0.8078	+0.0043
0.8990	0.964336	0.8987	+0.0003
0.8991	0.964393	0.8989	+0.0002
0.9377	0.975652	0.9415	+0.0038
0.9785	0.991303	0.9873	+0.0088
0.9896	0.994433	0.9950	+0.0054
1.0000	0.996540	1.0000	

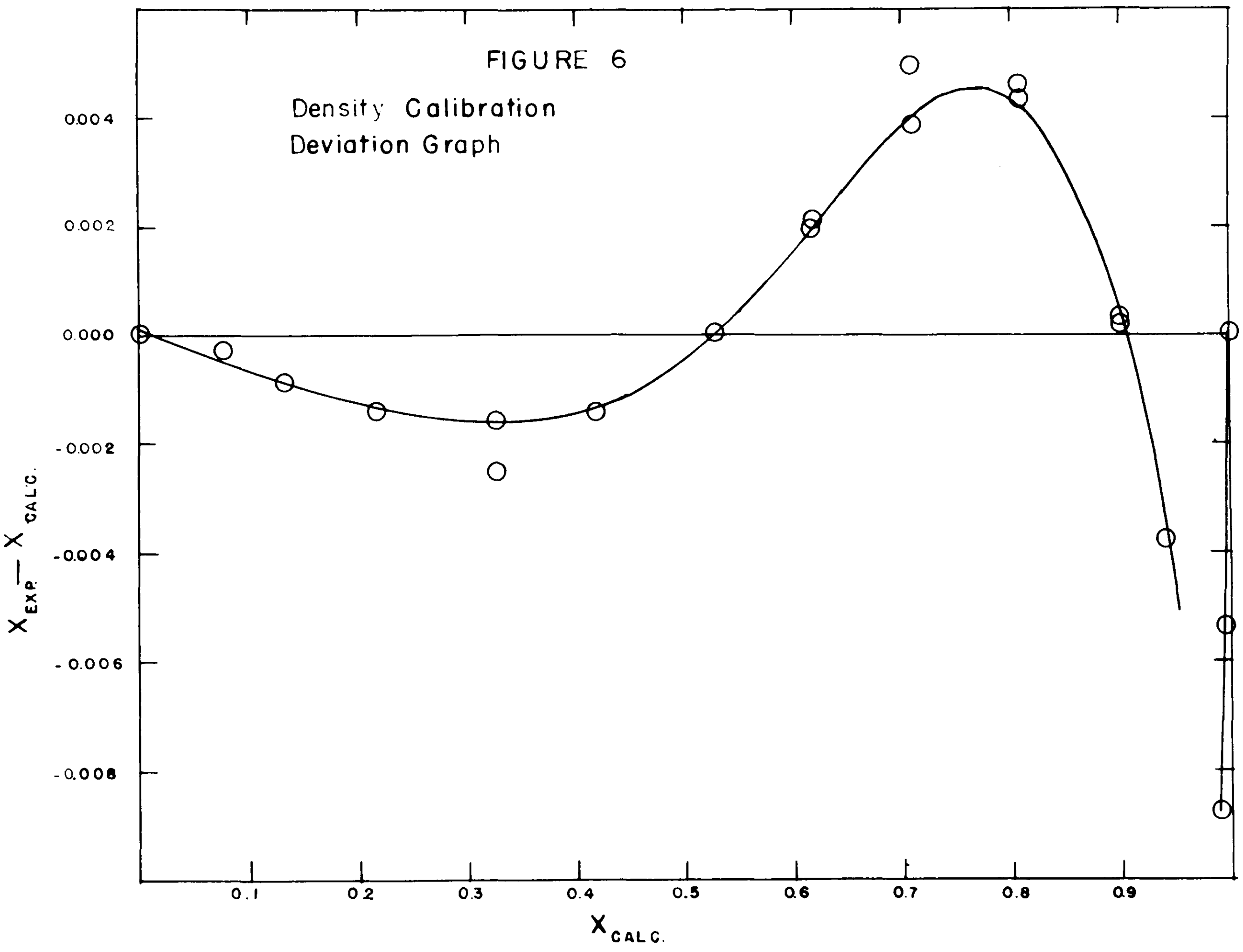


FIGURE 6

Density Calibration Deviation Graph

$x_{calc.}$. From this deviation plot and a value of $x_{calc.}$ determined from the analytical expression it is possible to get a value for $x_{exp.}$.

As mentioned earlier it was found that the butyl cellosolve had a lower density after degassing. The change is probably related to the removal of water. To correct the density of the unknown to correspond with the density of the butyl cellosolve used in making up the known mixtures it was assumed that the change was a linear one in the weight fraction, and a correction was applied accordingly to the densities of the unknown mixtures. The degassed water was found to have the same density after degassing as before. Therefore, the correction added to the observed densities of the unknowns was:

$$\Delta d = 0.000140(1-\omega)$$

where ω is the wt. frac. of H_2O

To correct for the amount of material in the vapor phase the volume of the cell was determined. A bulb of known volume was connected to the cell side. Then with argon in the cell region, the pressure was measured before displacing the volume in the bulb and then after. The volume was displaced using mercury. From the two measurements of pressure and the volume of the bulb the volume of the cell was calculated using Boyles law. The volume determined, along with the volumes of other parts determined in the same manner, are as follows:

TABLE 6

Volumes of Various Parts

Part	Volume
Cell vapor region*	113.5 c.c.
Equalizing coil	23.6 c.c.
Argon side to seal #3	445 c.c.
Between seal #3 and #5	79.6 c.c.

* Before subtracting the volume of the liquid.

Experimental Procedure

During a series of measurements it is possible to exclude completely extraneous gases from the cell system. For this reason it is not necessary to degass before each individual run. Initially the system was partially degassed by pumping over night with a mercury diffusion pump. Further degassing was then accomplished by introducing a sample of water or butyl cellosolve, heating the system to 85 °C. and expanding off vapor periodically. This was done because it has been found that the degassing rate increases by a factor of about 10 or more when there is a sample in the cell.

One can tell when the system is sufficiently degassed by expanding vapor plus gas build-up from the vapor region into the vacuum manifold and measuring the build-up with the McLeod gage. For these measurements the system was considered sufficiently degassed when the build-up in the cell was of the order of 0.5 μ/min. at 85 °C. This number seems fairly large but it has been found that almost all the degassing in a given run takes place at the highest temperature. This is indicated in Table 7.

It will be observed that although the gas build-up is fairly high in two of the runs compared to the other two, that the agreement in pressures is still reasonably good. Runs No. 1 and No. 2 were made without careful degassing of the apparatus.

In an individual run the first task is to synthesize a sample mixture since no degassing is necessary of the system or materials. To proceed the cell is isolated from calibrated tube, T, Fig. 3, by closing seal #2, and stopcock, S, is closed isolating the manifold and the diffusion pump. A point to mention is that it is not necessary in the course of a run to admit other gases to the calibrated tube volume, hence, when not in use it is kept evacuated.

A bath of ice slush is put around the calibrated tube and then vapor from one of the previously degassed compounds is admitted by opening the stopcock at the top of the bulb. When the required amount has distilled the stopcock is closed, the ice bath is placed around the cell and seal #2 is lowered. For butyl cellosolve it took on the average one hour to distill into the calibrated tube and about eight hours to go from there to the cell. For this reason mixture synthesis was begun in the evening so that transfer would be complete by morning. It was the practice to transfer the least volatile component first, so after the butyl cellosolve had transferred the water was added in the same manner.

After the water had transferred seal #1 was closed and the gas build-up was measured by expanding the vapor into the manifold and reading the McLeod gage as already described.

The vapor is then pumped out, the stopcock is closed and seal #1 is opened and then closed again and the residual pressure measured again. In no case did this pressure exceed 0.5 μ. After pumping out the vapor a second time, the seal isolating the cell and the calibrated tube is closed and the stopcock to the manifold is closed.

The first temperature at which the pressure was measured was at 25 °C. Since the room was thermostated at 28 °C. refrigerant is necessary and as a matter of fact, since one side of the thermostat was kept hotter than the other, it was necessary to use refrigerant up to a temperature of about 65 °C. In lowering the temperature there is not too much concern about condensation except that the cell seal has to be kept up until the new temperature is reached. After measuring the pressure at 25 °C. the cover was removed from the thermostat and crushed dry ice was scattered inside to speed up the cooling rate in going to 5 °C. It was found that it took about eight pounds of the crushed dry ice to cool the thermostat down. After measuring the pressure at 5 °C. the procedure for changing the temperature is the same.

Procedure for Changing Temperature

The cell seal is closed so that vapor will not distill into undesirable places. Then the heaters are turned on. After a short time there is a differential on the cell seal. When this differential becomes large enough to correspond to a temperature differential of a few degrees the cell seal is lowered enough to let vapor bubble past the mercury. After an amount has bubbled by which one considers to be sufficient to fill the volume with vapor at the next temperature the seal is raised back up again. It takes practice in order to know how much to let by. Even then one is not infallible. After raising the seal the heater to the null instrument is turned on with only a few watts of power. The optimum power being such that the pressure on the two sides is about the same when the desired temperature is reached. When this pressure is reached seal #1 is opened and the null instrument heater is turned off so as not to overheat the null instrument. Overheating causes undesirable drift of the zero.

After the desired temperature is reached which usually takes about thirty minutes, the thermostat is put into control. The temperature of the cell is observed constantly and manual adjustments are made in the bridge setting; this requires the constant attention of one operator.

Procedure for Measuring the Pressure

While the temperature is being raised the pressure in the 90 liter tank is adjusted to roughly the expected pressure. Then, when the temperature is pretty well adjusted, the pressure in the manifold is adjusted via the solenoid valves so that the null instrument indicates at a position close to the expected zero. Further adjustment is made in the 90 liter tank pressure by observing the three arm manometer. The Henry valve is opened and fine adjustments in pressure are made via the needle valves while the beam of the null instrument is observed.

A period of ten to fifteen minutes is then allowed for the pressure to settle down.

The pressure in the 90 liter tank is then read by one operator while the other maintains control of the temperature and follows the reading of the null instrument. After the pressure in the 90 liter tank has been read a final reading is taken of the null instrument and the zero is determined as described on page 19. This completes this particular phase and one then proceeds to the next temperature. After the measurement at 85 °C. the cover was removed from the thermostat and a cold bath placed around the cell while the box cooled to room temperature. Then the procedure was followed as in the beginning for a repeat measurement at 25 °C. The difference between the two pressures measured being an indication of the pressure build-up.

In addition to reading the pressure in the 90 liter tank, the following is a sample of the measurements taken at a given temperature and composition:

Sample of Measurements

Cell temperature	65 °C.
Thermocouple e.m.f.	53.375mv.

Null instrument readings:

Time	Beam position
2:32	-26 mm.
2:40	-27.5 mm. (2 μ v warm)
2:58	-27 mm.
2:58	zero determined
Before opening valve #3	-10 mm.
Null instrument zero	-8mm.

From these readings we find the pressure in the cell to be higher than that in the 90 liter tank by the quantity:

$$\Delta P = .00385 \left[-8-(-27)\right] = .073 \text{ mm.Hg}$$

Also the loss of material from the cell can be calculated from the volume of the argon side and the rise in pressure observed on the argon side upon opening the valve to the cell side. In this case that change in pressure was:

$$\Delta P = .00385 \left[-8-(-10)\right] = 0.008 \text{ mm.Hg.}$$

The usual change is about 0.05 mm.Hg, but even with a change of this size the overall composition is changed negligibly.

Removal of the Sample for Analysis

After the pressure measurements have been completed the sample is distilled from the cell through the equalizing coil to the bulb, K, surrounded by an ice bath outside the thermostat. In this case it is possible to elevate the thermostat temperature to speed up the process. Bulb, K, contains a stirrer for remixing the sample after distillation is complete.

The last trace of material is removed by freezing out with liquid nitrogen at tip, g, after closing seal #4. An indication of whether all the material has been removed or not can be obtained from the null instrument; which will indicate at its zero position when transfer is complete. Seal #3 is then closed and after the tip warms to room temperature seal #4 is opened permitting transfer between it and the bulk material.

At this point the sample is all in bulb, K. The sample is mixed by moving the stirrer with a magnet, then an atmosphere of argon is admitted by opening seal #5. Care must be taken so that argon flows into the sample when the seal is opened, otherwise, part of the sample is lost. After admitting the argon to a pressure of one atmosphere seal #5 is closed again and equilibration is permitted overnight. The following morning the contents of the bulb are restirred, the cap is removed and the sample is taken out with a hypodermic syringe and transferred to the pycnometer for the density determination.

III. RESULTS OF MEASUREMENTS

After the thermocouple was calibrated, pressure measurements were made on water$_1$, on butyl cellosolve$_2$ and mixtures of 1 and 2 covering the range of compositions. The measurements were made at twenty degree intervals from 5 °C. to 85 °C. on the pure components and each mixture. The thermocouple e.m.f.'s used are as follows:

t °C.	E mv.
5	3.799
25	19.657
45	36.189
65	53.364
85	71.170

Three temperature runs were made with pure water. Table 7 gives the results of these runs together with the pressures interpolated from the calibration. The differences in pressures measured at each temperature will give an idea of the precision of the measurements.

The results of the temperature runs on the mixtures are given in Table 8; the results with pure butyl cellosolve and the vapor pressures used for water are given also. In the table z represents the overall composition in terms of the ratio of the number of moles of water to the total number of moles. The sample at the composition $z = .8986$ separated into two liquid phases at 50.37 °C. and the composition of the two phases in equilibrium was not determined above this temperature.

A plot vs. composition of the vapor pressure divided

TABLE 7

Comparison of Vapor Pressure Measurements Made on Water

Temp. °C.	Measured Vapor Pressures of Water Run No.(mm.Hg)			Interpolated from Water Calibration Run**(mm.Hg)
	1	2	3	
5	6.518	6.543	6.535	6.537
25	23.740	23.745	23.748	23.743
45	71.890	71.891	71.862	71.858
65	187.542*	187.556	187.479	187.585
85	433.422	433.588	433.374	433.570
residual pressure	0.200	0.340	0.023	0.044

* 187.025 mm.Hg at 64.938 °C.

** See water calibration, page 29.

TABLE 8

Observed Pressures in mm.Hg.

z_{H_2O}	5 °C.	25 °C.	45 °C.	65 °C.	85 °C.	Residual Pressure
0.0000	0.161	0.852	3.455	11.511	32.535	0.064
0.0743	1.399	5.404	17.219	46.671	109.948	0.055
0.1478	2.432	9.225	28.880	76.757	177.651	0.055
0.2140	3.285	12.338	38.253	101.126	233.077	0.079
0.3074	4.243	15.909	49.324	130.204	300.473	0.136
0.5072	5.641	20.996	64.984	171.858	399.429	0.159
0.6836	6.173	23.092	70.211	188.218	439.037	0.020
0.7885	6.357	23.568	72.476	191.458	445.845	0.103
0.8986	6.436	23.965	72.887	(95.648 at 50.364 °C.)		0.085
Two phases (95.648 at 50.364 °C.)				191.706	446.139	
1.0000	6.537	23.743	71.858	187.585	433.570	

by the vapor pressure of water at that temperature is shown in Fig. 7 at 5 °C. and 85 °C.

The densities of the unknown mixtures are given in Table 9. The compositions calculated from these values, referred to as $x_{uncorr.}$, have to be corrected for the material in the argon saturated with vapor when the sample was removed. For this correction it was good enough to assume that the vapor was pure water. The value for the total number of moles present in the cell is included in order that correction can be applied for the amount of material in the vapor. The total number of moles was calculated from the volumes used in making up the mixtures; correction was applied for errors in the graduations of the tube, T, Fig. 3.

TABLE 9

Densities and Overall Compositions

density d	calc.comp. $x_{uncorr.}$	$N'-N''$	z
.896726	.0742	.0829	.0743
.899076	.1476	.0884	.1478
.901441	.2138	.0993	.2140
.905248	.3072	.1053	.3074
.915975	.5071	.1487	.5072
.930281	.6835	.186	.6836
.943061	.7885	.243	.7885
.964186	.8986	.347	.8986

The correction to be applied for the material in the vapor is calculated from the expression:

$$x-z = (z-y)\frac{N''}{N'} \qquad (6)$$

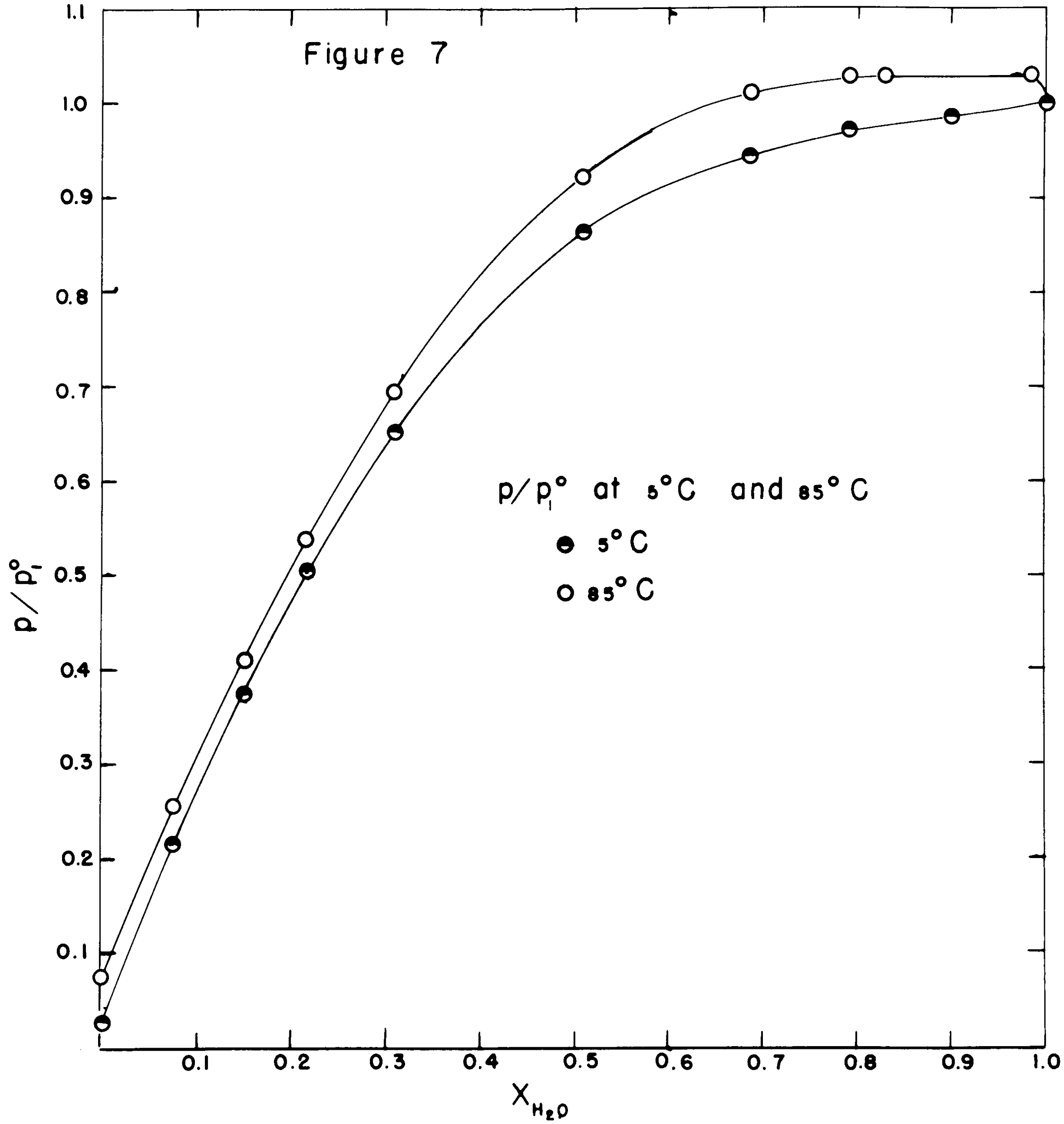


Figure 7
p/p_1° at 5°C and 85°C
● 5°C
○ 85°C
p/p_1°
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
X_{H_2O}

where
z = overall composition.
x = liquid composition.
y = vapor composition.
N''= number of moles (total) in vapor.
N'= number of moles (total) in liquid.

An expression of the type $\log p = B - \frac{A}{T}$ was fitted to the two points 5 °C. and 85 °C. for each run. In Table 10 is given the value for A and B for each run and the difference between the logarithm of the observed pressures and that calculated from the analytical expression. The deviations are all approximately parabolic when plotted versus temperature.

TABLE 10

A and B in $\log p = B - \frac{A}{T}$ and $\log p_{\text{meas.}} - \log p_{\text{calc.}}$

z	$A\times10^{-3}$	B	$\log p$ meas. $-\log p_{\text{calc.}}$				
			5 °C.	25 °C.	45 °C.	65 °C.	85 °C.
0.0000	2.8711	9.52869	-0.00003	+0.03143	+0.03415	+0.02302	0.00000
0.0743	2.3604	8.63167	-0.00003	+0.01784	+0.02350	+0.01769	-0.00006
0.1478	2.3208	8.72943	-0.00001	+0.01952	+0.02586	+0.01890	-0.00001
0.2140	2.3051	8.80352	+0.00003	+0.01904	+0.02449	+0.01812	0.00000
0.3074	2.3040	8.91076	-0.00003	+0.01851	+0.02419	+0.01739	-0.00001
0.5072	2.3055	9.03749	+0.00001	+0.01731	+0.02192	+0.01564	0.00000
0.6836	2.3064	9.08215	+0.00004	+0.01699	+0.01369	+0.01313	0.00000
0.7885	2.2988	9.06761	+0.00001	+0.01490	+0.01813	+0.01261	-0.00001
0.8986	2.2925	9.05031	+0.00003	+0.01468	+0.01808	+0.01184	0.00000
1.00000	2.2686	8.97117	+0.00003	+0.01326	+0.01593	+0.01084	0.00000

IV. CALCULATION OF THERMODYNAMIC PROPERTIES

From the measurements at each temperature it is possible to determine the excess free energy of mixing and the vapor composition. Then from a knowledge of the free energy as a function of temperature it is possible to determine the enthalpy of mixing and the excess entropy of mixing.

Treatment of Vapor Pressure Measurements

In order to relate the free energy to the vapor pressure, use is made of the excess chemical potential of each component. For a binary mixture the expressions are:

$$\overline{G}_1^E = RT\ln\frac{py}{p_1^o x} + (\beta_{11}-\overline{V}_1)(p-p_1^o)+(2\beta_{12}-\beta_{11}-\beta_{22})py^2 \qquad (7)$$

$$\overline{G}_2^E = RT\ln\frac{p(1-y)}{p_2^o(1-x)}+(\beta_{22}-\overline{V}_2)(p-p_2^o)+(2\beta_{12}-\beta_{11}-\beta_{22})p(1-y)^2 \qquad (8)$$

Here p is the vapor pressure of the solution, y the mole fraction of water in the vapor, and x the mole fraction of water in liquid. The β's come from the second virial coefficient of the vapor where $\beta = y^2\beta_{11}+2y(1-y)\beta_{12}+(1-y)^2\beta_{22}$, $\overline{V}_1$ and $\overline{V}_2$ are the molal volumes of water and butyl cellosolve. In the calculations the subscript 1 will refer to water, and 2 to butyl cellosolve.

To obtain a relation between the vapor pressure and the chemical potentials not containing the vapor composition except in small correcting terms the expressions are put in the exponential form and then added. The result is:

$$p = p_1^o x e^{\frac{\overline{G}_1^E}{RT} - \left[(\beta_{11}-\overline{V}_1)(p-p_1^o)+(2\beta_{12}-\beta_{11}-\beta_{22})py^2\right]/RT} + p_2^o(1-x)e^{\frac{\overline{G}_2^E}{RT} - \left[(\beta_{22}-\overline{V}_2)(p-p_2^o)+(2\beta_{12}-\beta_{11}-\beta_{22})p(1-y)^2\right]/RT} \tag{9}$$

The relationship between the excess chemical potentials and the excess free energy per mole is given in the following equations:

$$\overline{G}^E = x\overline{G}_1^E + (1-x)\overline{G}_2^E \tag{10}$$

$$\overline{G}_1^E = \overline{G}^E + (1-x)\frac{\partial \overline{G}^E}{\partial x} \tag{11}$$

$$\overline{G}_2^E = \overline{G}^E - x\frac{\partial \overline{G}^E}{\partial x} \tag{12}$$

Since the chemical potentials not only depend on the value of $\overline{G}^E$, but also on its slope, $\frac{\partial \overline{G}^E}{\partial x}$; it is not possible to calculate the chemical potentials or the free energy directly from individual measurements of p.

To obtain the free energy a procedure was followed similar to that described by Kavanagh.[15] An expression with adjustable parameters is assumed for $\overline{G}^E$ and then $\overline{G}_1^E$ and $\overline{G}_2^E$ are calculated from the expression. The expression for the pressure in terms of $\overline{G}_1^E$ and $\overline{G}_2^E$ is then fitted to the experimental measurements by adjusting the parameters. An indication of the agreement can be observed from the closeness of the fit.

Initially the correction for nonideality of the vapor was neglected. And at low temperature the correction for the material in the vapor was neglected.

Calculation was begun at 5 °C. To start it was assumed that $\overline{G}^E$ could be represented by the relation:

$$\overline{G}^E/RT = Ax(1-x) \tag{13}$$

From this expression it is found that:

$$\overline{G}_1^E/RT = A(1-x)^2 \tag{14}$$

$$\overline{G}_2^E/RT = Ax^2 \tag{15}$$

Since there is only one parameter a single pressure measurement is sufficient to calculate it. The half molar composition was chosen yielding the value $A \cong 2$. We assume now that this is approximately correct and the partial pressure of butyl cellosolve is calculated using the expression:

$$p_2 = p(1-y) = p_2^o(1-x)e^{\overline{G}_2^E/RT} = p_2^o(1-x)e^{Ax^2} \tag{16}$$

The partial pressure of water is then calculated by subtracting the partial pressure of butyl cellosolve from the vapor pressure of the mixture. Percentage wise the partial pressure of the water calculated in this manner is more precise than the partial pressure of the butyl cellosolve because of the higher vapor pressure of water.

The chemical potential of water was calculated from its partial pressure. In spite of the fact that some fairly crude approximations were made the value for $\overline{G}_1^E/RT$ calculated in this way differed at the most by only 0.007 from the final value.

From the plot of the calculated values of $\overline{G}_1^E/RT$ vs. x it was determined that an expression of the form:

$$\overline{G}^E/RT = -x\ln\left[x + a(1-x)\right] - (1-x)\ln\left[(1-x)+bx\right] \tag{17}$$

might fit the measurements. A discussion of this equation is given in Appendix B. The expressions for the excess chemical potentials calculated from this expression are:

$$\overline{G}_1^E/RT = -\ln\left[x+a(1-x)\right] + (1-x)\left[\frac{(1-x)(1-b)}{(1-x)+bx} - \frac{x(1-a)}{x+a(1-x)}\right] \qquad (18)$$

$$\overline{G}_2^E/RT = -\ln\left[(1-x)+bx\right] - x\left[\frac{(1-x)(1-b)}{(1-x)+bx} - \frac{x(1-a)}{x+a(1-x)}\right] \qquad (19)$$

A trial fit was obtained by a successive approximation method using the expression:

$$\Delta\overline{G}_1^E/RT = \frac{\partial\overline{G}_1^E/RT}{\partial a}\Delta a + \frac{\partial\overline{G}_1^E/RT}{\partial b}\Delta b \qquad (20)$$

The method is quite general and can be used to solve for the unknown quantities in any number of simultaneous transcendental equations. In this case $\Delta\overline{G}_1^E/RT$ represents the difference between the value found from the vapor pressure and the value calculated from the assumed expression using guessed parameters. Since there are two unknown quantities, one must use differences at two compositions. The approximation of new parameters can be repeated as many times as is necessary. In this case one approximation was sufficient.

After the trial fit it was observed that the expression:

$$\overline{G}^E/RT = dx(1-x)(1-2x) \qquad (21)$$

could improve the fit substantially if it were used in conjunction with the expression already used.

The expression for the excess free energy now becomes:

$$\overline{G}^E/RT = -x\ln\left[x+a(1-x)\right] - (1-x)\ln\left[(1-x)+bx\right] + dx(1-x)(1-2x) \qquad (22)$$

And the excess chemical potentials are:

$$\overline{G}_1^E/RT = -\ln\left[x+a(1-x)\right] + (1-x)\left[\frac{(1-x)(1-b)}{(1-x)+bx} - \frac{x(1-a)}{x+a(1-x)}\right] + d(1-x)^2(1-4x) \qquad (23)$$

$$\overline{G}_2^E/RT = -\ln\left[(1-x)+bx\right] - x\left[\frac{(1-x)(1-b)}{(1-x)+bx} - \frac{x(1-a)}{x+a(1-x)}\right] + dx^2(3-4x) \qquad (24)$$

After fitting the above expression for $\overline{G}_1^E$ to the values calculated from the pressures, new values for the partial pressure of butyl cellosolve were calculated, and from these new values for $\overline{G}_1^E/RT$ were obtained.

After obtaining a satisfactory fit at 5 °C. it was much easier to get a fit at the other temperatures, since the excess free energy changes only slightly with temperature.

To fit the next temperature the activity coefficient of butyl cellosolve was assumed to be the same and it was used to calculate the vapor composition which was then used to calculate the following:

1. The partial pressure of water.
2. The liquid composition from the overall composition.
3. The correction for vapor imperfection.

To calculate the liquid composition from equation (6) the ideal gas law was used to determine the total number of moles of material in the vapor phase.

Correction for Vapor Imperfections

In the absence of experimental measurements the values for β_{22} were estimated using the expression for the second virial coefficient of water given by Keyes, Smith, and Gerry[22] which is:

$$\beta_{11} = 18 \left[1.89 - \frac{2641.62}{T} . 10^{\frac{80870}{T^2}} \right] \qquad (25)$$

Temperatures are given in absolute degrees and the volumes in c.c. per mole. The values for water were calculated directly drom this equation.

Butyl cellosolve vapor probably behaves in about the same way as the equivalent straight chain alcohol does. This is indicated in Table 11 in a comparison of boiling points of compounds in the two series.

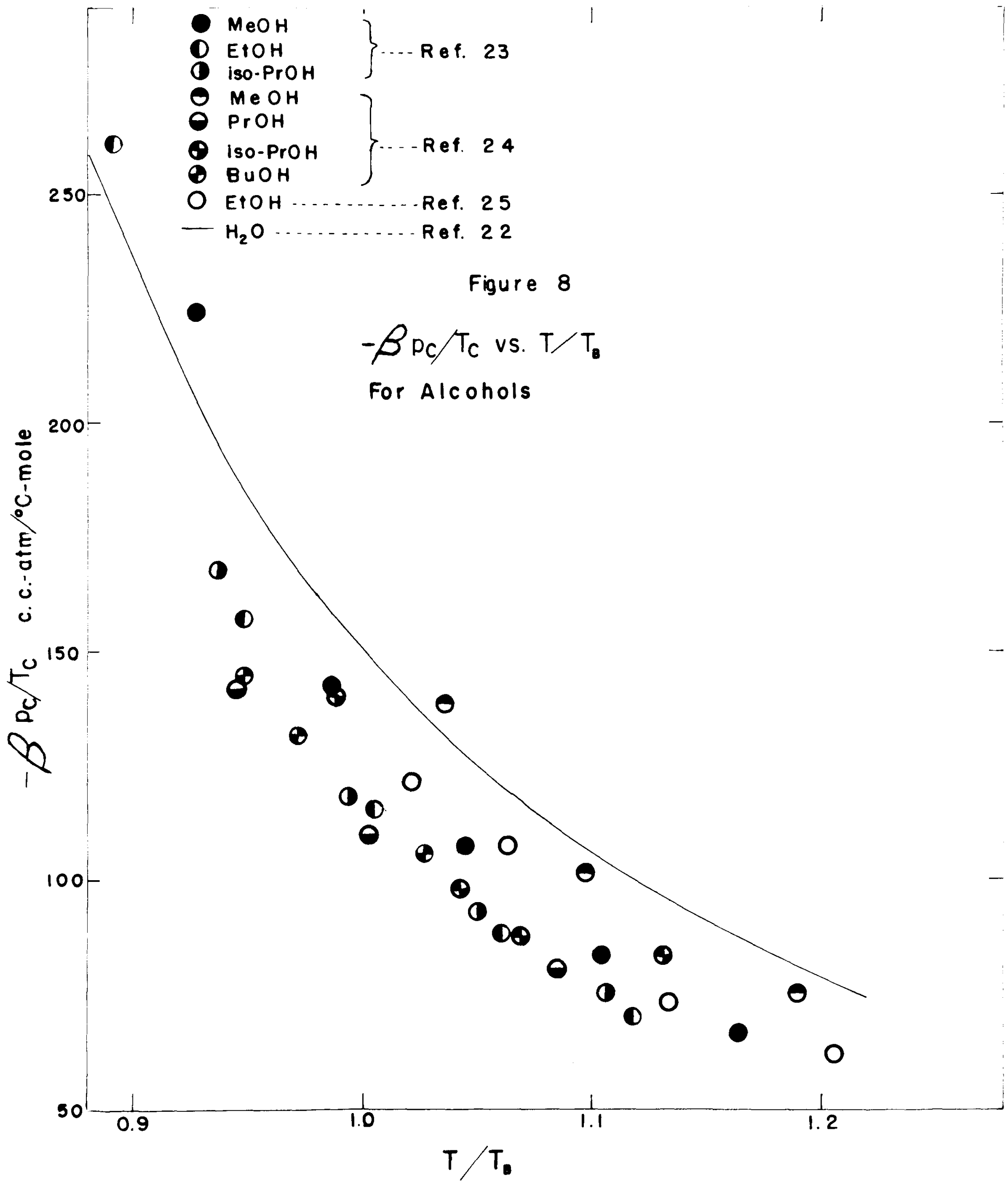
TABLE 11

Comparison of Boiling Point

Compound	B.p.	Equivalent Alcohol	B.p.
Butyl cellosolve	171 °C.	n-heptyl alc.	175 °C.
Ethyl cellosolve	135	n-pentyl alc.	138
Methyl cellosolve	124.5	n-butyl alc.	118

The problem thus reduces to approximating the virial coefficient as though the compound were a straight chain aliphatic alcohol even though there is an ether linkage.

Fig. 8 is a plot of $-\beta p_c/T_c$ vs. T/T_B for some of the alcohols where T_B is the boiling point. The literature references are given in the figure. The continuous line was calculated from β given for water. Since these points are in a T/T_B range much higher than the range in which the virial coefficients are desired and since the agreement between water and the alcohols is not too bad, and since the difference appears to decrease as T/T_B becomes smaller



● MeOH
◐ EtOH
◑ iso-PrOH
Ref. 23
MeOH
PrOH
iso-PrOH
BuOH
Ref. 24
○ EtOH ....Ref. 25
— H_2O ....Ref. 22
Figure 8
$-\beta P_C/T_C$ vs. T/T_B
For Alcohols
$-\beta P_C/T_C$ c.c.-atm/°C-mole
T/T_B
50
100
150
200
250
0.9
1.0
1.1
1.2

the expression for water was used in the following form:

$$\beta \frac{p_c}{T_c} = 11.5-\frac{42.70}{T/T_B} \cdot 10^{0.5813/(T/T_B)^2} \qquad (26)$$

where T_B is now given the value, 444 °K. instead of 373 °K. A value for T_c/p_c for butyl cellosolve was chosen after a study of the relation between the molar volume of the liquid and the ratio T_c/p_c for the alcohols. Table 12 gives a summary of the values of interest.

TABLE 12

The Molar Volume Compared to T_c/p_c

Compound	$\overline{V}$	T_c/p_c	$\overline{V}/(T_c/p_c)$
H_2O	18.0c.c.	2.98 °C/atm.	6.05 $\frac{\text{c.c-atm}}{\text{°C.}}$
MeOh	40.4	6.53	6.18
EtOh	58.3	8.19	7.13
isoPrOH	76.5	9.41	8.07
n-BuOH	91.3	11.5	7.93

From these values the ratio $\overline{V}/T_c/p_c = 8$ seemed reasonable and the expression for the virial coefficient of butyl cellosolve becomes:

$$\beta_{22} = 186-\frac{692}{(T/444)} \cdot 10^{.5813/(T/444)^2} \qquad (27)$$

To calculate β_{12}, values for β_{11} and β_{22} were calculated for each temperature. Then the polar and nonpolar parts were assumed to be in the same ratio as is found in the energy of vaporization using the method of Scatchard.[26] The quantity (E/V) non polar was calculated from the expression:

$$(E/V)_{\text{non polar}} = 614\, \rho^{5/3} \quad \text{cal./c.c.} \qquad (28)$$

The non polar fraction for water was found to be 0.078, and for butyl cellosolve 0.603.

The constant b_{12} was calculated from the relation:

$$b_{12} = \left(\frac{b_{11}^{1/3} + b_{22}^{1/3}}{2} \right)^3 \tag{29}$$

and the polar and non polar parts, β -b, divided by the molar volume of the liquid were combined quadratically.

$$\frac{(\beta - b)_{12}}{\overline{V}_{12}} = \sqrt{\frac{(\beta_{11} - b_{11})(\beta_{22} - b_{22})}{\overline{V}_1 \overline{V}_2}} \tag{30}$$

Table 13 lists the values of the virial coefficients used in the calculations.

TABLE 13

Values of Virial Coefficients Used in the Calculations

t °C.	β_{11}	β_{22}	β_{12}	$(2\beta_{12}-\beta_{11}-\beta_{22})$
5	-1860c.c./mole	-33400c.c./mole	-7650c.c./mole	+20000c.c./mole
25	-1260	-19900	-4780	+11600
45	-907	-12900	-3300	+7200
65	-683	-8950	-2380	+4870
85	-533	-6530	-1800	+3460

The molar volume of water was taken as 18 c.c./mole and for butyl cellosolve the value 130 c.c./mole was used.

The corrections made for imperfection of the vapor and for the molar volume of the liquid are given in Table 14, where $\Delta_1 = -[(\beta_{11} - \overline{V}_1)(p - p_1^o) + (2\beta_{12} - \beta_{11} - \beta_{22})py^2]/RT$ and

$$\Delta_2 = -[(\beta_{22} - \overline{V}_2)(p - p_2^o) + (2\beta_{12} - \beta_{11} - \beta_{22})p(1-y)^2]/RT.$$

TABLE 14

$\Delta_1 \times 10^4$

Corrections Made for Vapor Imperfections

z	5 °C.	25 °C.	45 °C.	65 °C.	85 °C.
.0743	-6.0	-13.6	-27.6	-52.5	-92.7
.1478	-4.5	-10.5	-21.1	-39.8	-70.1
.2140	-3.6	-8.1	-16.3	-30.7	-54.1
.3074	-2.5	-5.5	-10.9	-20.3	-35.8
.5072	-0.9	-2.0	- 3.4	-5.8	-9.9
.6836	-0.4	-0.5	-0.5	-0.2	+1.2
.7885	-0.2	-0.2	-0.1	+1.1	+2.1
.8986	-0.1	0.0	+0.3		

$\Delta_2 \times 10^4$

z	5 °C.	25 °C.	45 °C.	65 °C.	85 °C.
.0743	+11	+26	+50	+79	+143
.1478	18	43	83	148	241
.2140	25	55	110	195	319
.3074	30	72	143	251	410
.5072	42	95	186	328	543
.6836	45	103	202	358	593
.7885	46	104	205	362	601
.8986	47	104	206		

Final Fitting of Pressure Measurements

After an approximate fit was obtained at each temperature, the parameters obtained were each fitted to analytical expressions involving the temperature. Deviations in pressure were then calculated using the parameters obtained from the analytical expressions. From the appearance of the deviation plots it was possible to estimate how the analytical expressions for the parameters should be changed. In calculating the pressure deviations it was necessary to calculate the partial pressure of each component, therefore the vapor composition was easily calculated at the experimental points.

The final analytical expressions used for the parameters are as follows:

$$a = 1.4786 - \frac{.0673\text{x}10^6}{T}(5.9701\text{x}10^{-3} - \frac{1}{T}) \qquad (31)$$

$$b = 0.3438 - \frac{0.04401\text{x}10^6}{T}(5.5841\text{x}10^{-3} - \frac{1}{T}) \qquad (32)$$

$$d = 0.4047 - \frac{0.0642\text{x}10^6}{T}(5.747\text{x}10^{-3} - \frac{1}{T}) \qquad (33)$$

The values of the parameters at the experimental temperatures are given in Table 15.

TABLE 15

	Parameters Obtained		
t °C.	a	b	d
5	.9040	.02909	-.0920
25	.8881	.01461	-.1106
45	.8806	.00614	-.1207
65	.8790	.00191	-.1250
85	.8814	.00071	-.1250

A comparison of the measured and calculated pressures at each temperature together with the calculated vapor compositions are given in Tables 16, 17, 18, 19, and 20. In these tables z is the overall mole fraction of water, x is the mole fraction in the liquid and y is the calculated mole fraction in the vapor.

Fig. 9 is a plot of the pressure deviations at each temperature divided by the vapor pressure of water, and Fig. 10 is a plot of $\log_{10} \alpha$ at 5 °C. and 85 °C. where $\alpha = y(1-x)/x(1-y)$.

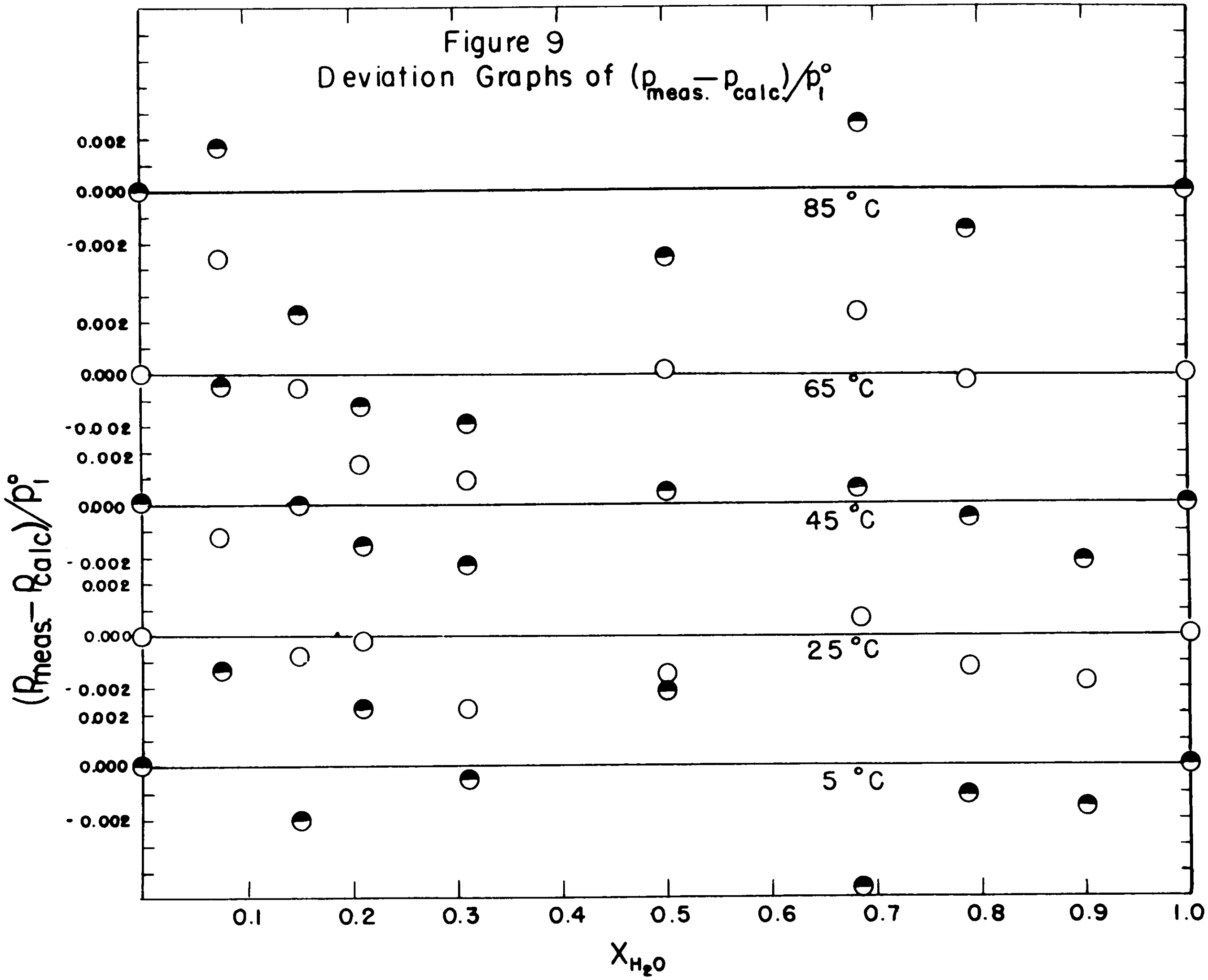


Figure 9

Deviation Graphs of $(p_{meas.} - p_{calc.})/p_1^\circ$

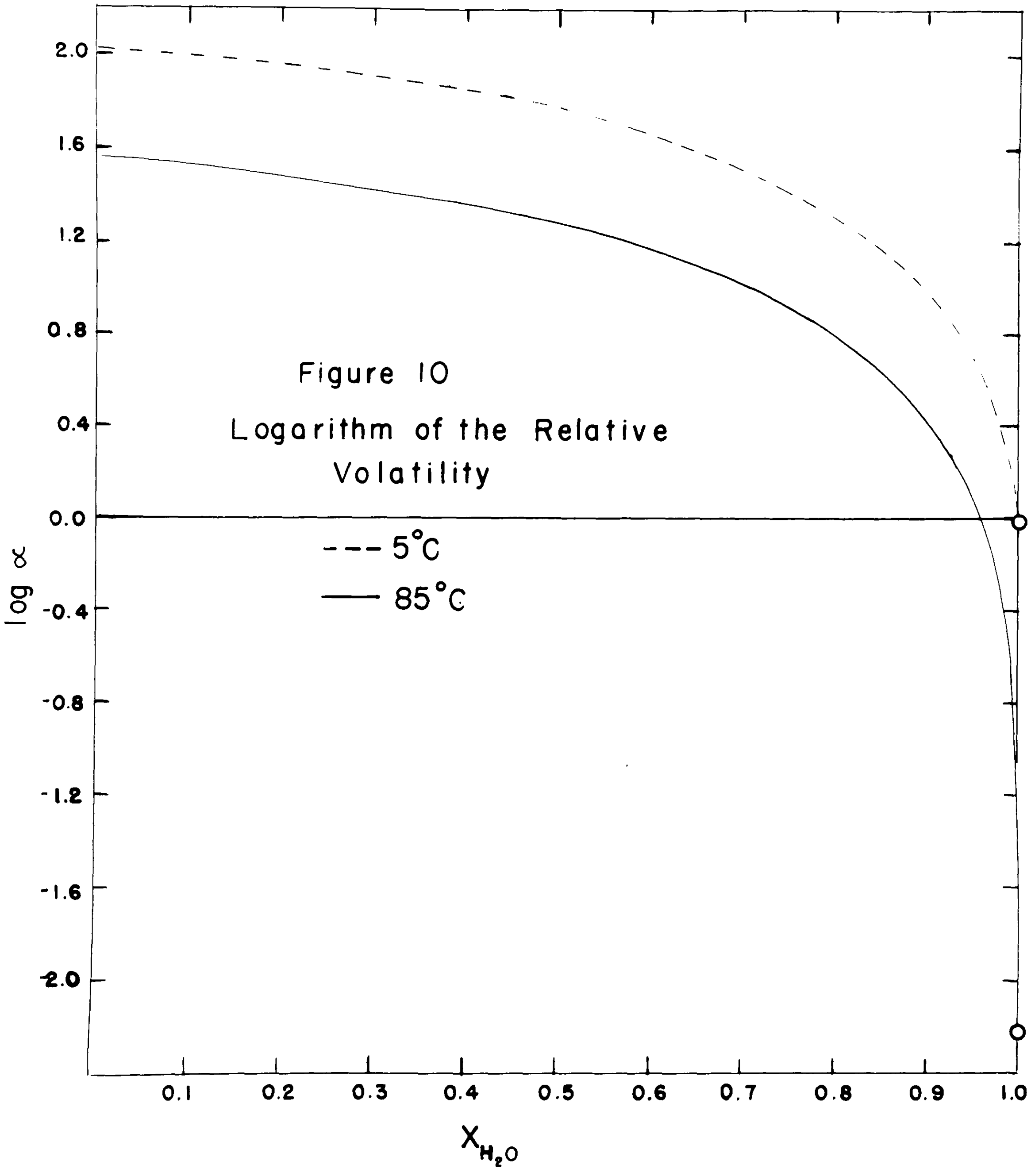


Figure 10

Logarithm of the Relative Volatility

TABLE 16

5 °C.

Calculated Vapor Composition and Comparison of Measured and Calculated Pressures

z	x	y	Calculated Pressure mm.Hg	Measured Minus Calculated mm.Hg
.0743	.0742	.8908	1.375	+.024
.1478	.1477	.9431	2.446	-.014
.2140	.2139	.9602	3.271	+.014
.3074	.3073	.9723	4.247	-.004
.5072	.5072	.9825	5.623	+.018
.6836	.6836	.9864	6.204	-.031
.7885	.7885	.9876	6.364	-.007
.8986	.8986	.9888	6.446	-.010

TABLE 17

25 °C.

Calculated Vapor Composition and Comparison of Measured and Calculated Pressures

z	x	y	Calculated Pressure mm.Hg	Measured Minus Calculated mm.Hg
.0743	.0741	.8510	5.315	+.089
.1478	.1473	.9203	9.243	-.018
.2140	.2135	.9442	12.345	-.007
.3074	.3069	.9608	15.977	-.068
.5072	.5068	.9753	21.032	-.036
.6836	.6834	.9804	23.079	+.013
.7885	.7884	.9820	23.593	-.025
.8986	.8986	.9831	23.806	-.041

TABLE 18

45 °C.

Calculated Vapor Composition and Comparison of Measured and Calculated Pressures

z	x	y	Calculated Pressure mm.Hg	Measured Minus Calculated mm.Hg
.0743	.0734	.8092	16.897	+.322
.1478	.1465	.8962	28.885	-.005
.2140	.2125	.9268	38.363	-.110
.3074	.3058	.9483	49.493	-.169
.5072	.5061	.9673	64.951	+.033
.6836	.6830	.9739	71.106	+.04
.7885	.7882	.9759	72.508	-.032
.8986	.8985	.9771	73.036	+.149

TABLE 19

65 °C.

Calculated Vapor Composition and Comparison of Measured and Calculated Pressures

z	x	y	Calculated Pressure mm.Hg	Measured Minus Calculated mm.Hg
.0743	.0724	.7647	45.847	+.824
.1478	.1446	.8688	76.845	-.088
.2140	.2105	.9071	101.785	-.659
.3074	.3036	.9340	130.982	-.778
.5072	.5046	.9581	171.837	+.021
.6836	.6822	.9665	187.801	+.417
.7885	.7878	.9690	191.489	-.031

TABLE 20

85 °C.

Calculated Vapor Composition and Comparison of Measured and Calculated Pressures

z	x	y	Calculated Pressure mm.Hg	Measured Minus Calculated mm.Hg
.0743	.0703	.7185	109.217	+.731
.1478	.1413	.8395	179.655	-2.004
.2140	.2067	.8853	236.717	-3.640
.3074	.2992	.9181	304.402	-3.929
.5072	.5016	.9480	400.459	-1.032
.6836	.6806	.9584	437.970	+1.067
.7885	.7870	.9616	446.536	-0.691

V. THE THERMODYNAMIC FUNCTIONS

The values found for the parameters may be substifuted directly into equation (22) to give the excess free energy of mixing:

$$\begin{aligned}\overline{G}^E/RT = & -x\ln\left\{x+(1-x)\left[1.4786-\frac{.0673\mathrm{x}10^6}{T}\left(5.9701\mathrm{x}10^{-3}-\frac{1}{T}\right)\right]\right\}\\ & -(1-x)\ln\left\{(1-x)+x\left[0.3438-\frac{.04401\mathrm{x}10^6}{T}\left(5.5841\mathrm{x}10^{-3}-\frac{1}{T}\right)\right]\right\}\\ & +x(1-x)(1-2x)\left[0.4047-\frac{.0642\mathrm{x}10^6}{T}\left(5.747\mathrm{x}10^{-3}-\frac{1}{T}\right)\right] \qquad (34)\end{aligned}$$

The heat of mixing is calculated using the expression:

$$\frac{\overline{H}^M}{R} = \frac{\partial\,\overline{G}^E/RT}{\partial\,1/T}$$

The resulting expression for the heat of mixing is:

$$\begin{aligned}\frac{\overline{H}^M}{RT} = & +x(1-x)\left\{\frac{+\frac{.0673\mathrm{x}10^6}{T}\left(5.9701\mathrm{x}10^{-3}-\frac{2}{T}\right)}{x+(1-x)\left[1.4786-\frac{.0673\mathrm{x}10^6}{T}\left(5.9701\mathrm{x}10^{-3}-\frac{1}{T}\right)\right]}\right.\\ & +\frac{\frac{.04401\mathrm{x}10^6}{T}\left(5.5841\mathrm{x}10^{-3}-\frac{2}{T}\right)}{(1-x)+x\left[0.3438-\frac{.04401\mathrm{x}10^6}{T}\left(5.5841\mathrm{x}10^{-3}-\frac{1}{T}\right)\right]}\\ & \left.-(1-2x)\left[\frac{0.0642\mathrm{x}10^6}{T}\left(5.747\mathrm{x}10^{-3}-\frac{2}{T}\right)\right]\right\} \qquad (35)\end{aligned}$$

The excess entropy of mixing is calculated as the difference between the heat of mixing and the excess free energy of mixing divided by the temperature:

$$\frac{\overline{S}^E}{R} = \frac{\overline{H}^M}{RT} - \frac{\overline{G}^E}{RT} \qquad (36)$$

Graphs of $\overline{G}^E/RT$, $\overline{H}^M/RT$ and $-\overline{S}^E/R$ are given in Fig. 11. The solid lines are the functions at 5 °C. and the dotted

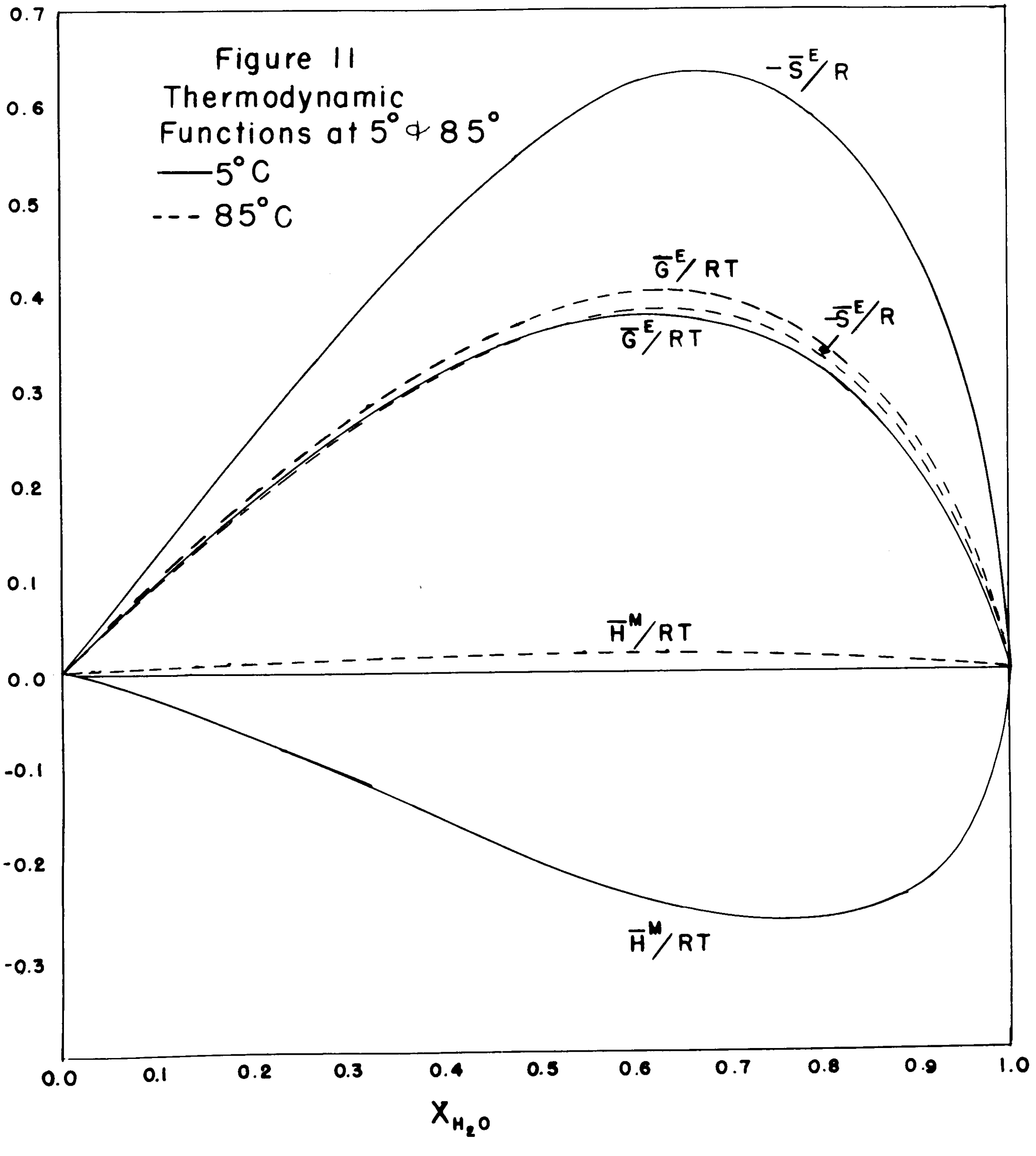


Figure 11
Thermodynamic
Functions at 5° & 85°
——5°C
--- 85°C
$-\bar{S}^E/R$
$\bar{G}^E/RT$
$-\bar{S}^E/R$
$\bar{G}^E/RT$
$\bar{H}^M/RT$
$\bar{H}^M/RT$
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
X_{H_2O}

lines are the functions at 85 °C.

It is first noted that the heat of mixing goes from a significant negative value at 5 °C. to a small positive value at 85 °C. This behavior was more or less expected since in the temperature range, 50 °C. to 128 °C. the mixture is not completely miscible at all compositions. Above and below this temperature range the liquids are miscible at all compositions.[13] Because of this behavior one would expect that $\bar{G}^E/RT$ would increase with temperature to a point roughly midway between 50 °C. and 128 °C. at which the direction of change would reverse and $\bar{G}^E/RT$ would decrease again. This is seen to be the case, as indicated by the change in sign of $\bar{H}^M/RT$.

Second, it is noted that although there is a large change in $\bar{H}^M/RT$, the change in $\bar{G}^E/RT$ is relatively small. The change in $\bar{G}^E/RT$ seems especially small when one considers the fact that the temperature goes from that at which there is no phase separation to that at which separation does occur.

The change in $\bar{H}^M/RT$ is compensated for by a change in $\bar{S}^E/R$. This also seems extraordinary since one generally assumes that the heat change and entropy change are nearly independent of temperature for a given thermodynamic system. Examples where use is made of this approximation are:

1. Use of the Clausius Clapeyron equation for vapor pressures.
2. The calculation of the heat change in a

> chemical reaction where log K is plotted vs. $1/T$ and the slope is taken to be $-\Delta H/2.3R$.

Graphs of the volume of mixing calculated from the density calibration and $-1.95\ \overline{G}^E/RT$ are given in Fig. 12. It is noted that the curve for the volume of mixing has about the same shape as the curve for $\overline{G}^E/RT$, with the extremum occurring at about the same composition for each. The only difference is that the volume of mixing is negative instead of positive as should be the case to agree with a simple theory given by Scatchard,[27] which predicts the following relation:

$$\overline{V}^M = \beta\,\overline{G}^E \qquad (37)$$

where β is the compressibility. The reason for this behavior is uncertain.

It is hard to say what the deviations in pressure from the analytical expression correspond to in terms of $\overline{G}^E/RT$, since the two are related by the expression:

$$\Delta p/p = \Delta\overline{G}^E/RT + (y-x)\frac{\partial\Delta\overline{G}^E/RT}{\partial x}$$

However the greatest error in $\overline{G}^E/RT$ is probably not much greater than the greatest value of $\Delta p/p_1^o$ and the error probably occurs in a range close to the large pressure deviation. On this basis there probably are no errors greater than ± 0.01 in $\overline{G}^E/RT$. However, the difference between the actual and the calculated is great enough so that even though phase separation does occur with this system the analytical expression does not predict it. In order to have this expression

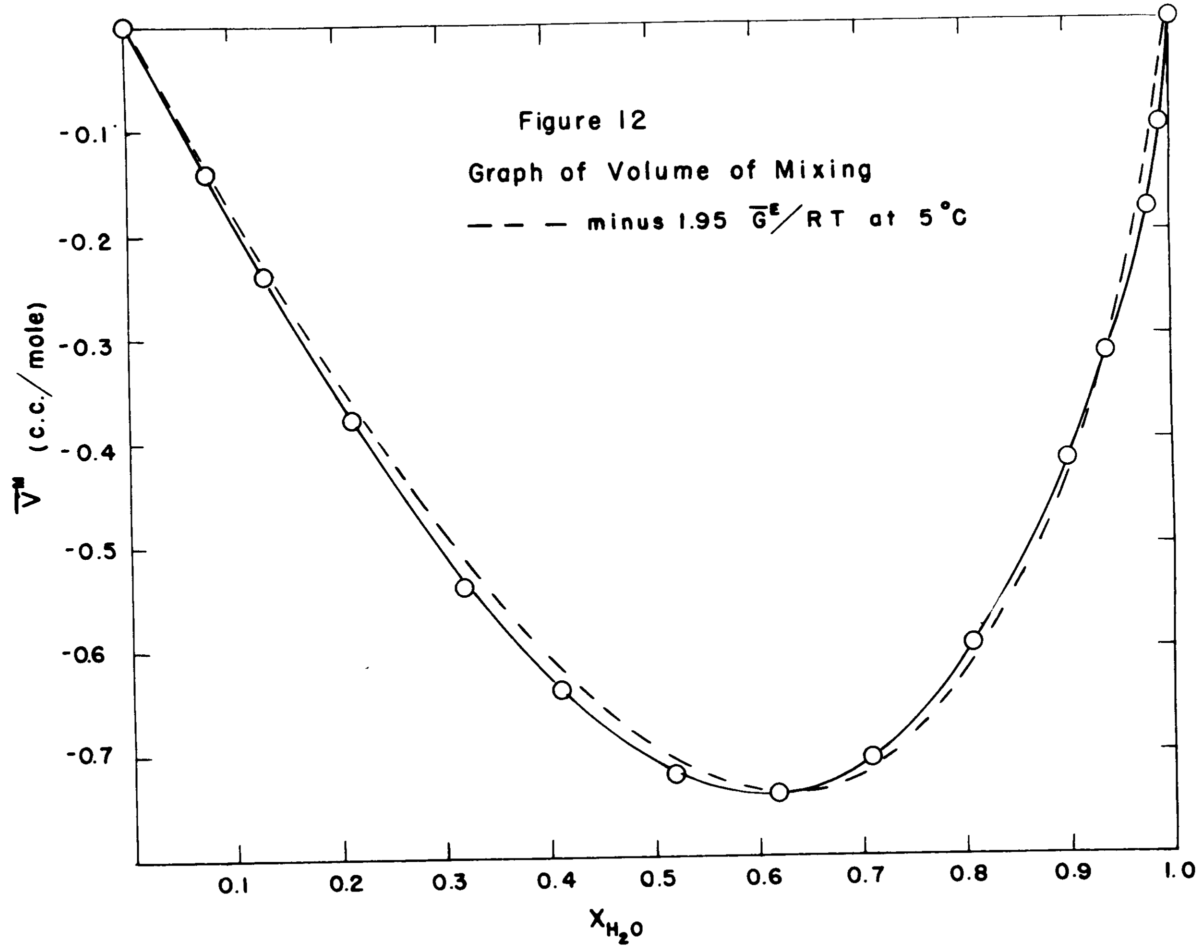


Figure 12

Graph of Volume of Mixing

predict phase separation when there is separation it would have been necessary to be satisfied with a poorer fit at other parts of the pressure curve. Alternatively one could use more parameters. The failure of this expression to indicate phase separation illustrates quite well the small change one would have to make in $\overline{G}^E/RT$ to go from no phase separation to the actual case.

APPENDIX A

The Null Instrument

The main qualities to consider in choosing a null instrument are:

1. sensitivity
2. stability
3. hysteresis
4. change of zero with pressure
5. change of zero with different gases
6. ruggedness
7. ease of getting leak tight
8. ease of repair
9. sensitivity to room vibration
10. cost.

A strain gage pressure transducer tried had high sensitivity and was not sensitive to room vibration, but the remaining qualities were against it. The null instrument used checks favorable except for items 3 and 9. If an instrument similar to this one could be found free of hysteresis it would not be necessary to determine the zero each time the differential is determined.

Fig. 13 is a diagram of the working parts of the null instrument used. A change in pressure differential flexes the bellows, p. The movement of the bellows turns the drum, d, suspended on a tight wire, b, by means of the connection to wire, a. Attached to drum, d, is a mirror and counter weight (not shown). Thus when the drum turns the rotation of the mirror deflects a light beam reflected onto a scale. The part, s, is a circular plate, with a hole through the center, bolted to the bellows mount, and part, s', is a circular cylinder with two holes drilled in it as shown. The

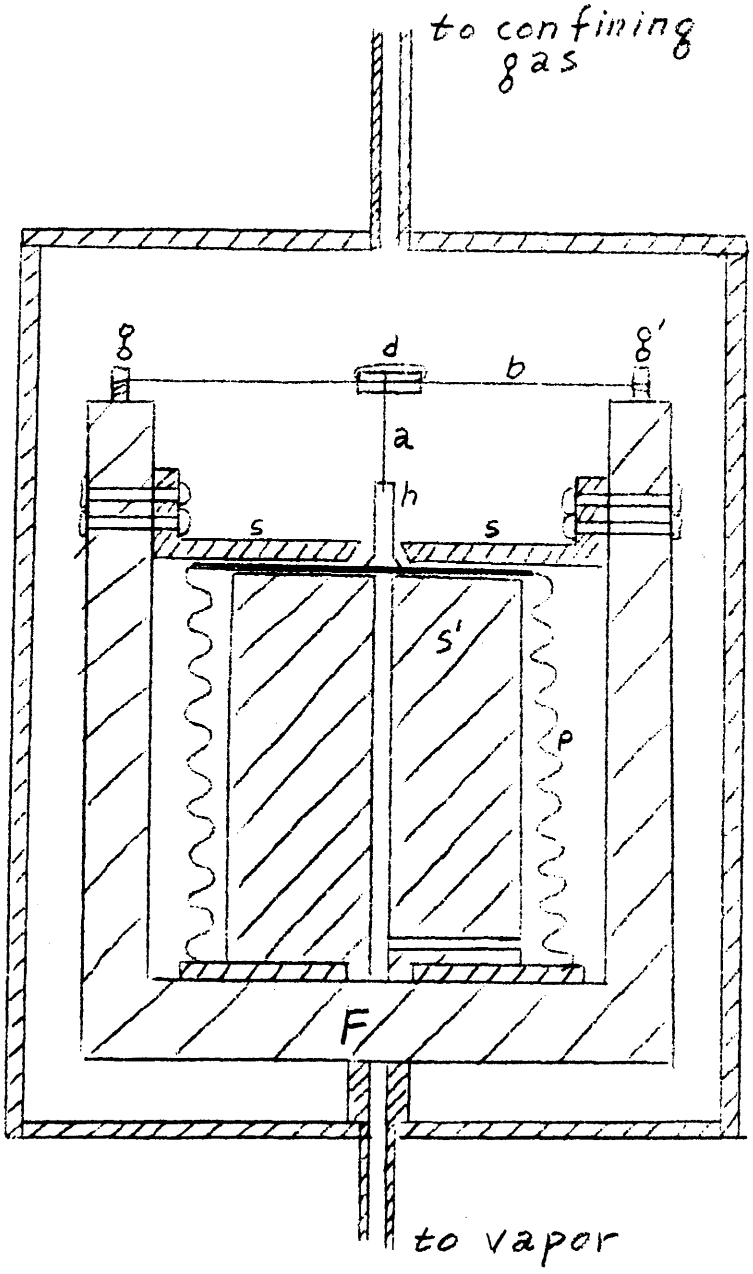


Figure 13 - Null Instrument

parts s and s' are stops which support the bellows when large differences in pressure are applied. The cylinder, s', occupies most of the volume inside the bellows; this cuts down the vapor volume of the cell sample.

The bellows is phosphor bronze and its outside diameter is two inches. It has a flexibility such that a differential of 14 mm.Hg will change its length 1 mm. The drum, d, is 2 mm. in diameter and is fixed to the 0.006" steel piano wire with soft solder. The wire is looped around the drum so that it passes through the center twice, this prevents slip between the wire and the drum.

The mount for the bellows and the tight wire is $\frac{1}{2}$" x $\frac{1}{2}$" brass in the shape of a tuning fork. The posts, g and g', are threaded screws with the heads cut off. The wire, b, is fixed in place with soft solder and to prevent slip the wire is wrapped around each post in such a way that the wire follows the threaded groove. The 0.004" stainless steel wire, a, is fixed with soft solder to the drum, d, after first hooking it under the loop of wire, b; the other end is slipped through a hole drilled in post, h, and soldered.

The main problem with this instrument is vibration. To reduce vibration to a minimum the mount which holds the mirror was made fairly heavy to lower the natural frequency of vibration. The reason for this is that the response of a linear oscillator drops off very quickly at frequencies above the natural frequency. The natural frequency of this unit is about 4 cycles/sec. Vibration was further reduced with a counter weight on the mirror mount. The weight was adjusted so that there is no angular acceleration of the mirror when the null instrument is accelerated linearly. This adjustment was made by observing the angular position of the mirror relative to the null instrument and adjusting the weight so that the position was the same for all orientations.

In this way the magnitude of the vibration varied from zero to a beam deflection on the scale of about seven millimeters from time to time. An observer can average out these swings in much the same way as is the rest position of a balance determined by the method of swings. It may be that the vibration could be further reduced, however, by means of magnetic damping.

It is desirable to keep the distance between the stops, s and s', as small as possible to prevent too much flexing of the wire connected between the bellows and the drum. In addition a large deflection changes the zero; therefore, shortening the movement of the bellows will lessen the change in zero occurring with the largest deflection possible.

An idea of the hysteresis was obtained by the following procedure:

1. read zero
2. apply differential Δp then relieve it
3. read zero
4. apply differential $-\Delta p$ then relieve it
5. read zero.

After repeating this procedure one or two times the change in zero between step 3 and step 5 is constant and indicates the size of the hysteresis loop for that given pressure differential. The following are the results at two different pressure differentials.

Δp	Change in Zero
±0.35 mm.Hg	not detectable(less than 0.0001 mm.Hg)
±0.75 mm.Hg	1.5 mm. = 0.006 mm.Hg

To get the sensitivity obtained the scale was placed a distance equivalent to four meters from the mirror of the null instrument. Actually the scale was mounted on the window of the air thermostat, since the beam deflection was amplified by means of a lens system similar to that in the Leeds and Northrup type E self-contained galvanometer. This made it convenient since one could manipulate valves while watching the scale.

The window in the housing of the instrument through which the light beam passes was put on with glyptal for lack of a better means, but it would be worth while to have a window which is fused to kovar in a future instrument.

APPENDIX B

An Expression for The Excess Free Energy of Mixing

The expression:

$$\overline{G}^E/RT = -x\ln\left[x+a(1-x)\right] -(1-x)\ln\left[(1-x)+bx\right]$$

is the form taken for a binary mixture of the more general expression:

$$\overline{G}^E/RT = -\sum_i x_i \left[\ln\sum_j x_j(\overline{V}_j+\beta_{ij})-\ln(\overline{V}_i+\beta_{ii})\right.$$

where $\overline{V}_j$ is the molar volume of component, j, and $\beta_{ij} = \frac{No}{2}\int(\rho_{ij}-1)d\tau$.

The theory by which this equation was derived does not seem very probable, but it will be presented for the benefit of the good which may be in it.

By analogy with the expression for Ω, where $S=-k\ln\Omega$, of independent localized systems where

$$\Omega = \frac{N!}{\prod_i n_i^*!}$$

with $n_i^* = n_{io}e^{-\epsilon_i/kT}$, a term of the same type should perhaps contribute to the configurational Ω. Thus, we take

$$n_i^* = n_{io}\rho.$$

In this definition, ρ might be considered to be the radial distribution function of molecules around a central molecule. Thus we are led to the partition function

$$Q_{\text{config.}} = \left[\int\rho\, d\tau\right]^N$$

or

$$Q = \left[\int d\tau + \int(\rho-1)d\tau\right]^N$$

This relation has to be corrected for the fact that the integration is carried out over the volume of the assembly, although there are N molecules in this assembly. Since the radial distribution function describes pairs, the correction is then made for the number of pairs, and we write

$$Q = \left[V + \frac{N}{2}\int(\rho - 1)\,d\tau\right]^{N}.$$

For a multicomponent system the expression is

$$Q = \prod_{i} Q_{i}$$

where

$$Q_i = \left[V + \sum_{j}\frac{N_j}{2}\int(\rho_{ij} - 1)\,d\tau\right]^{Ni}$$

If we define β_{ij} as $\beta_{ij} = \frac{No}{2}\int(\rho_{ij} - 1)\,d\tau$ we obtain the Helmholtz free energy defined by $A/RT = -\ln \Omega$. The free energy is an excess free energy, since no correction to Q was made for the ideal entropy. To a good approximation

$$\bar{A}_{v}^{M} = \bar{G}_{p}^{M}$$

therefore, we use

$$\bar{G}/RT = -\sum_{i} x_i \left[\ln \sum_{j} x_j(\bar{V}_j + \beta_{ij}) - \ln(\bar{V}_i + \beta_{ii})\right]$$

To obtain an expression for the excess free energy of mixing we set the chemical potentials equal to zero for the pure components. The result is

$$\bar{G}^{E}/RT = -\sum_{i} x_i \left[\ln \sum_{j} x_j(\bar{V}_j + \beta_{ij}) - \ln(\bar{V}_i + \beta_{ii})\right]$$

The reason for an account of this equation is that it seems one can usually obtain as good a fit using two parameters with this expression as one usually gets with three

TABLE 21

Deviations of Binaries from Analytical Expressions

MeOH-CCl_4			MeOH-C_6H_6		
x_1	$\overline{G}^E_{12\text{meas.}}$	Dev. in $\overline{G}^E_{12}$	x_1	$\overline{G}^E_{13\text{meas.}}$	Dev. in $\overline{G}^E_{13}$
.0169	38.31	+2.93	.0242	47.15	+4.85
.0189	43.10	+3.88	.0254	40.67	-3.54
.1349	194.17	+0.03	.1302	173.40	+0.06
.3500	316.03	+0.10	.3107	281.08	-3.79
.4776	326.64	+0.30	.4989	306.06	-2.43
.4939	325.61	+0.42	.5191	304.24	-2.15
.6557	284.25	+0.81	.6305	278.46	-1.30
.7912	206.67	0	.7965	192.65	+0.12
.9120	99.91	-0.86	.9197	89.15	+0.69

CCl_4-C_6H_6

x_2	$\overline{G}^E_{23\text{meas.}}$	Dev. in $\overline{G}^E_{23}$
1/4	14.5	-0.08
3/4	14	-0.11

or four parameters using the more conventional form

$$\bar{G}^E = x(1-x)\sum_i A_i(1-2x)^i.$$

For an example of what the equation will do, the expression was fitted to the excess free energy at 35° of each binary of the three compounds MeOH, CCl_4 and C_6H_6.[9] Then from the fit obtained to the binary mixtures the excess free energy for the ternary system was calculated and compared with the measured values. Table 21 gives the measured values with deviations of the calculated values from the measured values for the binary mixtures.

The parameters obtained are:

$$\frac{\bar{V}_2 + \beta_{12}}{\bar{V}_1 + \beta_{11}} = .04784 \qquad \frac{\bar{V}_1 + \beta_{12}}{\bar{V}_2 + \beta_{22}} = 0.3218$$

$$\frac{\bar{V}_3 + \beta_{13}}{\bar{V}_1 + \beta_{11}} = .08774 \qquad \frac{\bar{V}_1 + \beta_{13}}{\bar{V}_3 + \beta_{33}} = 0.3421$$

$$\frac{\bar{V}_3 + \beta_{23}}{\bar{V}_2 + \beta_{22}} = 0.875 \qquad \frac{\bar{V}_2 + \beta_{23}}{\bar{V} + \beta_{33}} = 1.000$$

The values calculated for the ternary mixture and a comparison with the measured values is given in Table 22 with good agreement.

TABLE 22

Comparison of Values Calculated from Binary Mixtures and Measured Values for the Ternary Mixture

x_1	x_2	$\bar{G}^E_{123\text{meas.}}$	$\bar{G}_{123\text{calc.}}$	Dev. in $\bar{G}^E$
.2075	.1900	248.3	248.8	-0.5
.2110	.3879	257.6	259.1	-1.5
.1987	.5876	253.6	252.2	+1.4
.3781	.3122	320.5	321.4	-0.9
.5543	.2078	314.3	313.8	+0.5
.7599	.1076	225.2	223.6	+1.6

This expression was fitted to the total pressure measurements[6] at 35 °C. on the system MeOH-C_6H_6 using the virial coefficients for the vapor given by ref. 9. Table 23 gives the deviations in pressure between that measured and the calculated values. A comparison is also made of the excess free energy and the vapor composition calculated with the values measured. The parameters obtained are:

$$\frac{\overline{V}_2 + \beta_{12}}{\overline{V}_1 + \beta_{11}} = 0.10744$$

$$\frac{\overline{V}_1 + \beta_{12}}{\overline{V}_2 + \beta_{22}} = 0.33413$$

The deviations of the excess free energy can be compared with those on page 85.

Although this expression gives good results one must be careful. The difficulty of this expression is that it alone will not predict phase separation. In addition the slope of the excess free energy curve becomes infinite at $x = 1$ if one of the parameters is zero or $x = o$ if the other is zero. Therefore, it is necessary to use parameters which are greater than zero; a negative parameter gives worse results than when the parameter is zero.

TABLE 23

Pressure Deviations and Comparison of Calculated and Observed Values for $\bar{G}^E$ and y

x_1	$p_{meas.}$	Dev. in p	$\bar{G}^E_{meas.}$	Dev. in $\bar{G}^E$	$y_{1(meas)}$	Dev. in y_1
.0242	203.29	-4.55	47.15	+7.20	0.2733	-.0251
.0254	211.10	+1.12	40.67	-1.21	.3128	+.0073
.1302	274.25	+0.43	173.40	+5.73	.4858	-.0042
.3107	288.47	0.00	281.08	+1.59	.5304	-.0016
.4989	292.50	+0.14	306.06	+1.68	.5546	-.0017
.5191	292.70	+0.16	304.24	+1.17	.5571	-.0022
.6305	292.49	+0.15	278.46	+0.85	.5790	-.0016
.7965	283.58	0.00	192.65	+0.76	.6421	-.0008
.9197	255.82	-0.70	89.15	+0.70	.7688	+.0020

APPENDIX C

Recommended Changes in the Apparatus

A review of the problems not completely solved are the following:

1. Temperature control of the air thermostat.
2. Condensation of vapor in the vapor region at places other than the cell.
3. Amalgamation of soft solder and copper parts by mercury.
4. Removal of a sample from the cell without distilling it and without admitting extraneous gas.
5. Gas buildup in the cell during a vapor pressure run.
6. The null instrument.

These problems are presented partly for contemplation, because suggestions can only be made on part of them.

1. The control of the thermostat was accomplished semimanually and required the full time attention of one operator. It is hard to see how a simple control unit could replace the operator since the operations include changing the temperature as well.

2. Although the side opposite the cell in the air thermostat was heated 1/3 °C. higher than the cell considerable care had to be taken when the temperature was changed so that condensation did not occur. This could be remedied by using a separate thermostat, instead of a simple baffle, where the temperature could be maintained at a significantly higher temperature. Regulation could perhaps be achieved

with a differential regulator; either a thermocouple type or a Wheatstone bridge where one junction or arm is in one thermostat and the other junction or arm is in the other thermostat. It may be that the regulation of the second bath could be coarse enough that no attention would be necessary even when the temperature is changed. If one is making measurements at a series of temperatures it is not recommended that the extra thermostat be maintained at a temperature higher than the ultimate temperature because of the fact that the gas buildup rate goes up very rapidly with temperature.

3. There are two alternatives which may be turned to in order to prevent amalgamation. One is to eliminate mercury and the other is to eliminate the parts which become amalgamated. The elimination of mercury could be accomplished by using a valve of the type used in the equalizing coil at every place where there is a mercury seal. If one used the seal to indicate pressure differentials it would also be necessary to include a pressure indicating device such as the null instrument.

On the other hand, the parts which become amalgamated could be replaced with either stainless steel in which all metal joints are welded, or glass. If glass is used one has to use either a mercury seal with or without float valves or a greaseless valve which is leak tight.

In view of these alternatives, it might be as easy to recognize the fact that amalgamation will occur and plan on replacing a part occasionally.

4. In these measurements the samples were distilled from the cell and then remixed before analysis. If one were to study a system in which one component is not volatile this would not be feasible.

To remove a mixture for analysis in this case or if for some other reason, it is desired to analyze without distilling one might use an apparatus as shown in Fig. 14. The sample is removed by first evacuating the receiving bulb through stopcock, c. The mercury is lowered in the float valve seal and if the valves stick they are opened with a magnet. The liquid in the cell runs into the receiving bulb from the force of gravity. The float valve seal is then closed and the sample may be removed at the point, d. Point, d, is a ground glass cap surrounded by mercury, it is not necessary to grease this joint if mercury is used.

5. The gas buildup is a difficult problem, aside from careful degassing, there is a possibility that the metal part of the system is the main source of gas. If this is the case, it is probable that the easiest way to cut the buildup rate is to eliminate the metal parts.

6. As mentioned earlier the null instrument used was satisfactory except for the fact that there is hysteresis and that it is sensitive to room vibration. Except for the suggestion

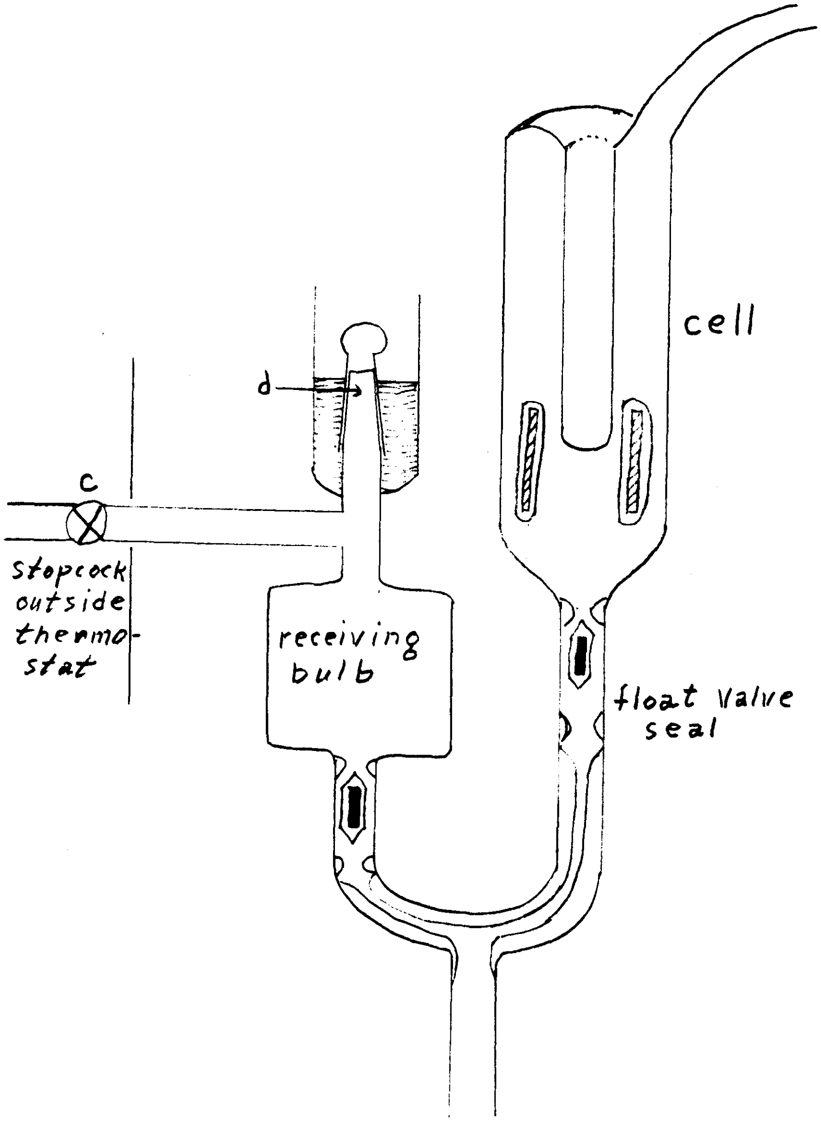


Figure 14 - **Apparatus** to Remove Samples from Cell

already given to out vibration there are no additional suggestions on these two qualities.

There is a possibility that in the future one will want an instrument with higher sensitivity. An instrument using a strain gage might be used if alterations were made to eliminate some of the bad qualities. It is felt that an instrument of this nature will not be available commercially, hence it will require building. Fig. 15 is a diagram of a proposed instrument. Parts a and b are each a flexible metal bellows, they are matched in such a way so that with a change in pressure in the chamber, B, there is no movement of a and b which are rigidly connected by the rod, d. The part, s, is a strain gage sensing element such as Statham's model G7A transducer. Its range of displacement is ±0.015 inch, therefore, it is possible that one might incorporate stops to protect the instrument from large pressure differentials.

Of the possible bad qualities of this instrument listed on page 78, items 3, 9 and 10 may be against it (hysteresis, sensitivity to room vibration and cost). The author feels that an instrument of this type would be quite satisfactory.

But in case one would like to try something along the line of the present instrument, the following design is given in Fig. 16. The connection, f, between the bellows and the mount is a metal ribbon which on one side of the middle is twisted in one sense of direction and on the other

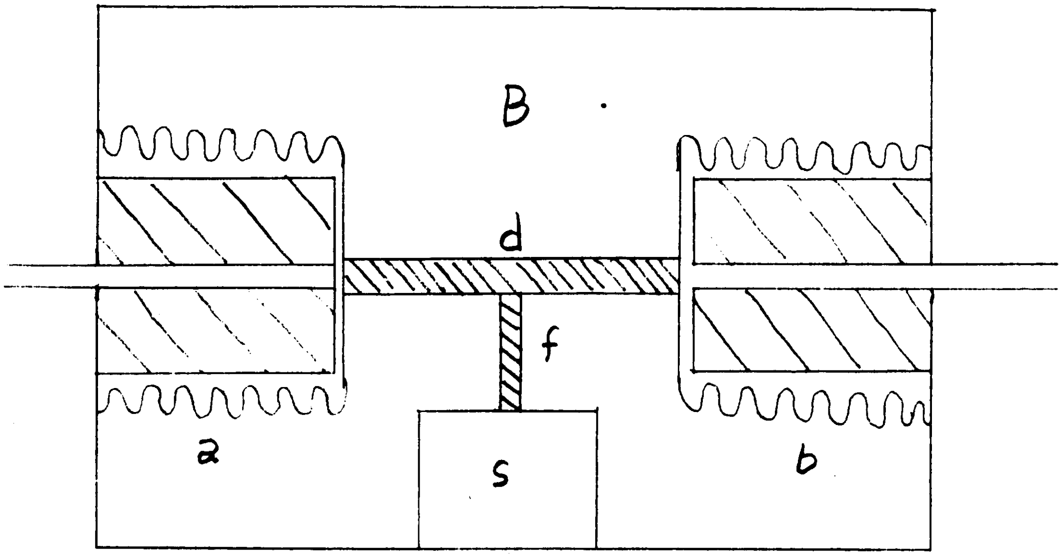


Figure 15 - Proposed Null Instrument

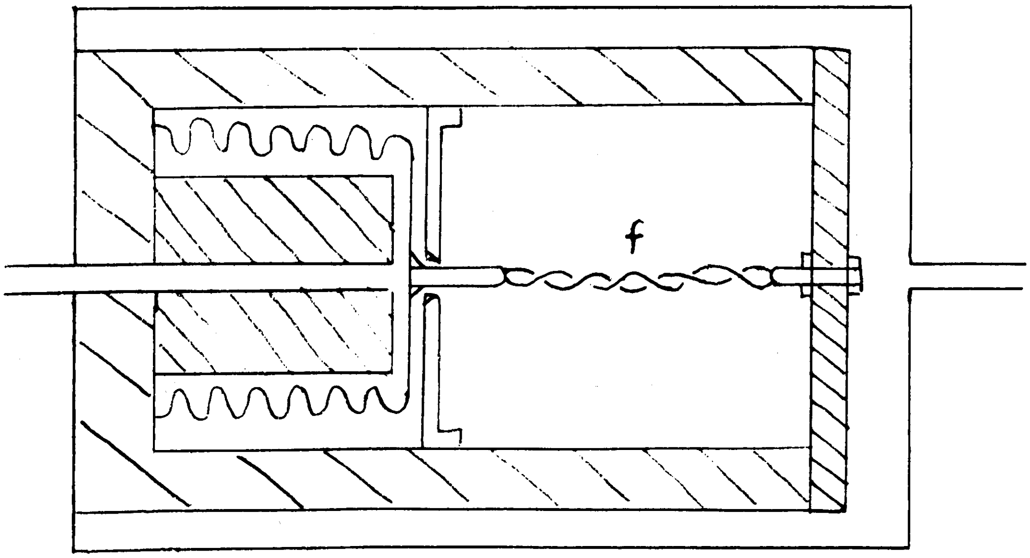


Figure 16 - Proposed Null Instrument

side in the opposite sense of direction. Thus when tension is applied the central portion rotates; therefore, the movement of the bellows can be detected by attaching a mirror at the central part of the ribbon. The main problem with this instrument is vibration.

Figure 17

Photograph showing the air thermostat with the front cover and front baffle removed. At the very bottom are the concentric heaters used in controlling the thermostat temperature. The vapor pressure cell and the auxiliary cell can be seen in the center. To the right and slightly above the cell is the null instrument.

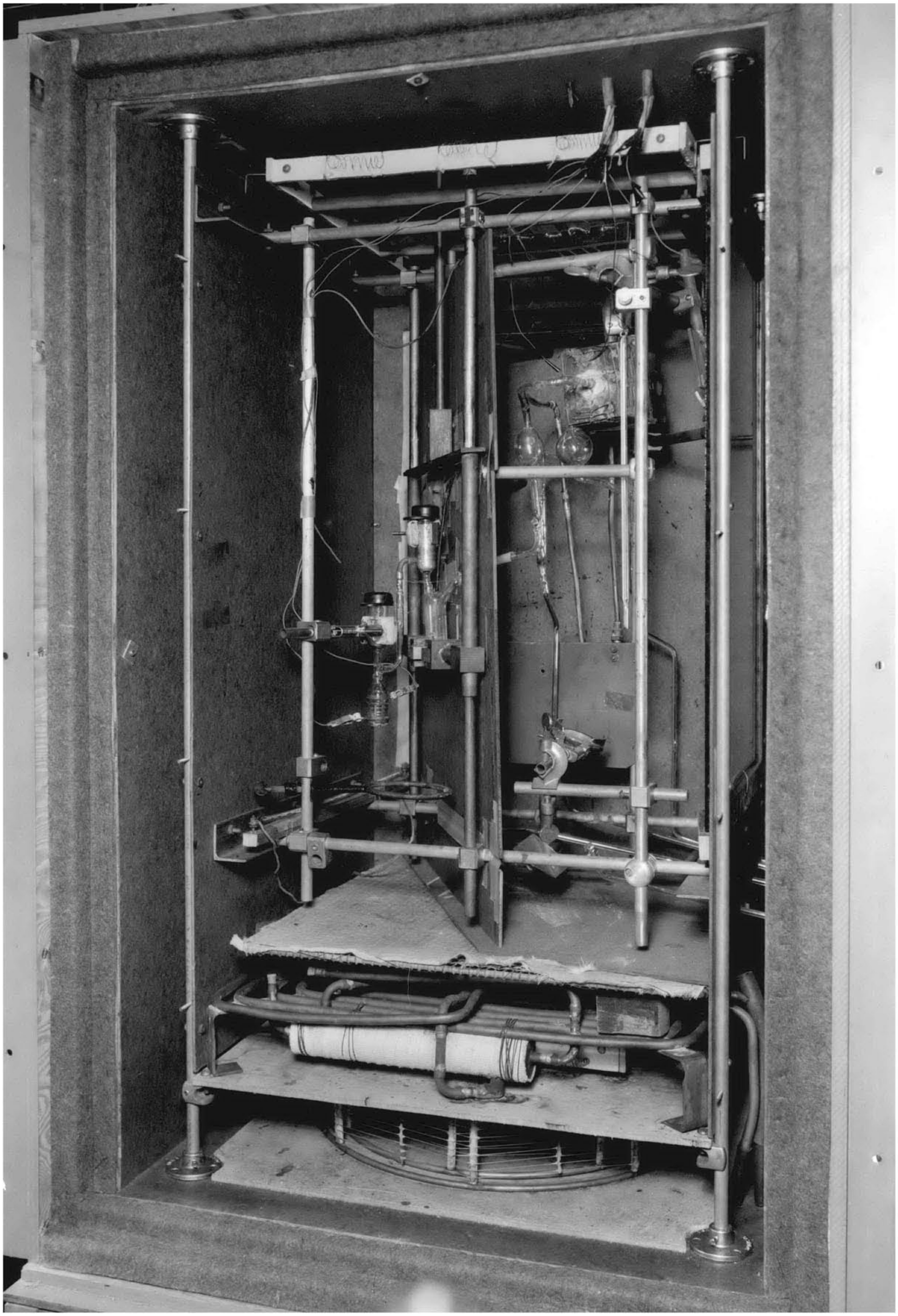
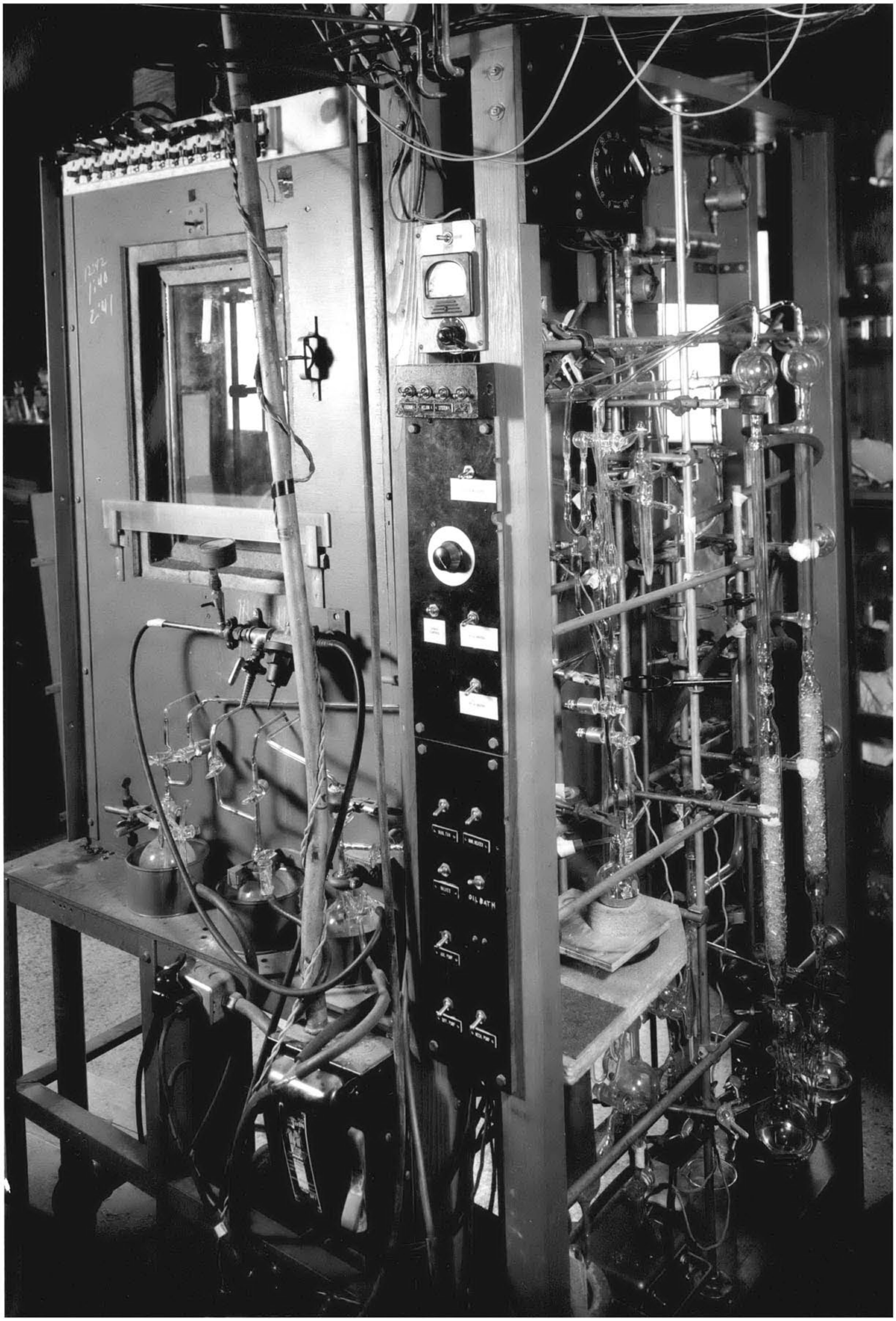


Figure 18

Photograph of the apparatus outside the thermostat. The control panel is in the center. The vacuum system is on the right and in the lower left are mercury reservoirs with connections to the mercury seals.


1242
1:40
2:41
OIL BATH

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BIOGRAPHICAL NOTE

Grant M. Wilson, a U. S. citizen through birth, was born in Colonia Pacheco, Chihuahua, Mexico, May 24, 1931. He attended a private two room grade school through the seventh grade; then he continued in the public schools of Rainier, Oregon and graduated from high school in 1949. He entered the Brigham Young University in 1949 and followed the undergraduate course in chemistry. During his second year he met and married Reta O'Neil Raphiel from Compti, Louisiana. He received the degree of Bachelor of Science in 1953. While going to school he worked full time as an attendant at a mental hospital during the years 1950-1953. After a year of graduate study and research at the Brigham Young University he entered Massachusetts Institute of Technology in 1954 as a candidate for the Ph.D. degree in Physical Chemistry.

He received the United States Rubber Company fellowship in Chemistry at M.I.T. for the year 1955-1956. He has been awarded either teaching or research assistantships while pursuing his Ph.D. degree for the remaining time.

The names and ages of his children are: Wesley, 6; Lauretta, 4; and Richard, 3.

He is a member of the Society of Sigma Xi.