Total Pressure Method for Vapor-liquid Equilibria at Low Absolute Pressures: Aniline-nitrobenzene Systems

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Binary vapor-liquid equilibrium data for use in the successful design and operation of mass transfer equipment at pressures down to approximately 5 mm. Hg may be advantageously obtained by the method of total pressures. In this method the desired equilibrium data are derived from pressure vs. temperature measurements on a convenient number of made-up solutions covering the entire composition range.

With a modified Smith and Menzies isoteniscope, it is possible to measure accurately the data required for making the equilibrium calculations down to 2 mm. abs. pressure without the "bumping," supercooling, and superheating encountered with equilibrium stills. The isoteniscope is simple to construct and operate from 1 atm. to 2 mm. abs.

The use of the total pressure method and the isoteniscope is illustrated by the determination of the vapor-liquid equilibrium in the aniline-nitrobenzene system at 5 and 10 mm. abs. In nineteen out of twenty instances the vapor compositions for a given liquid composition are precise to within ± 0.9% and the relative volatility, which varied between 2.54 and 1.85 over the composition and temperature ranges, is precise within ± 1.5%.

One of the basic types of data required for the successful design and operation of mass transfer equipment such as distillation columns, absorbers, strippers, and condensers is equilibrium vapor-liquid composition. Numerous methods of measuring and calculating vapor-liquid compositions as well as data on many specific systems have been reported in the literature, but comparatively few applications of the method of total pressure are reported for obtaining vapor-liquid data in the range of pressures from 5 mm. Hg to 1 atm. Only a few binary systems have been reported at pressures of 5 to 10 mm. which might be used for studying operating characteristics such as plate efficiencies of vacuum distillation columns.

This paper is concerned with the explanation and application of the total pressure method to a specific system as well as a description of apparatus which has been successfully used to measure the data required for this method. A large part of the discussion presupposes a knowledge of the theory of nonideal vapor-liquid phase behavior, as space will not permit a complete review of the development and reasoning behind many of the statements and equations. The reader desiring background information is referred to the papers published by Carlson and Colburn (*1*) and Wohl (*14*).

The total pressure method of obtaining vapor-liquid equilibrium data on binary systems was theoretically explored to some extent by Redlich, Kister, and Turnquist (*10*) and by Carlson and Colburn (*1*). Redlich and Kister (*9*) used a slightly modified form of the total pressure method to obtain values of α, the relative volatility, for the binary systems formed by the three isomers of xylene with ethylbenzene and for the system isopentane *n*-pentane. The values of the relative volatility obtained (*9*) were precise to ±0.10%.

Briefly stated, the total pressure method for measuring binary vapor-liquid equilibrium data consists of the following steps:

1. Measurement of the total pressure vs. temperature relationships for four to eight made-up solutions throughout the composition range of the binary system.
2. Use of curve-fitting techniques to obtain the constants in one of the integrated forms of the Gibbs-Duhem equation (a differential equation of thermodynamics which relates the composition of any phase to the activity of any given component).
3. Calculation of the vapor-liquid equilibrium from the constants and vapor-pressure data for any constant pressure within the range of data.

Since total pressure data may be measured in static equilibrium apparatus where no boiling takes place, the total pressure method eliminates the bumping and unsteady boiling frequently found in stills operating at low pressures. It is nearly always possible, therefore, to obtain low-pressure vapor-liquid data by this method which are much more precise than the data taken in equilibrium stills. Furthermore, in some systems where there are no convenient analytical methods for measuring the composition of the phases and where no contamination of the components occurs during experimental work, the total pressure method offers a means for obtaining vapor-liquid values, as data can be obtained from made-up solutions.

The apparatus best adapted for obtaining the total pressures at low absolute pressures is a slightly modified form of the isoteniscope reported by Smith and Menzies (*12*). This apparatus in combination with gauges, ballast tanks, and vacuum pumps has been used up to this time only to measure the vapor pressure of pure materials. For this work on the aniline-nitrobenzene system, the Smith and Menzies isoteniscope was modified, the vapor volume being decreased in relation to the liquid volume to minimize changes in liquid composition caused by vaporization of the more volatile component during operation. In addition, means for providing adequate agitation were included in the modifications, and a few other minor changes were made to aid in the operation of the device.

The total pressure method and isoteniscope were applied to the problem of obtaining precise vapor-liquid equilibrium data for the system aniline nitrobenzene at 5 and 10 mm. abs. pressure as an illustration of the techniques involved. This system was selected because it may be advantageously employed as a test system for determining operating characteristics of vacuum distillation columns. Its advantages for such use are (*a*) boiling temperatures are in the range of 50° to 100°C. at 5 to 10 mm.; (*b*) analytical determinations may be readily performed on the mixtures; (*c*) the components are completely miscible and there is no azeotrope in the system; (*d*) the relative volatility is of such value that a reasonable number of plates or transfer units may be included in any test column; and (*e*) the components have nearly equal molal latent heats. Data on the vapor-liquid behavior of this system, therefore, will prove valuable for the study of distillation column behavior as well as for the design of process equipment.

The following paragraphs describe the operation and construction of the apparatus used in obtaining the total pressure data and the techniques used in converting the information into the desired vapor-liquid compositions. The x-y data for the aniline-nitrobenzene system at 5 and 10 mm. abs. pressure are presented in tabular and graphical form.

APPARATUS AND EXPERIMENTAL PROCEDURE

The modified Smith and Menzies (*12*) isoteniscope used to measure the total pressures of the aniline-nitrobenzene solutions is shown in Figure 1. For this system the size of the liquid bulb was increased to 200 ml. to prevent appreciable change in the liquid composition when vaporization occurs. A stopcock was added to the outlet of the isoteniscope to give better control of the apparatus, and a magnetic stirrer was incorporated in the bulb to ensure intimate contacting of the vapor and liquid phases and also the rapid attainment of thermal equilibrium of the contents of the bulb with the surrounding bath liquid.

The following procedure was used during each run. The isoteniscope was connected to a vacuum pump and evacuation was allowed to proceed for several minutes. Stopcock *A* (Figure 1) was closed and the connection to the vacuum pump broken. A leveling bulb containing about 175 ml. of test liquid was connected by means of glass tubing and short lengths of gum-rubber hose to the isoteniscope. Stopcock *A* was then opened, the leveling bulb raised to a higher level than the isoteniscope, and the test fluid allowed to run into the isoteniscope, which then was placed in a bath of suitable heat transfer oil. The cold traps *C*, *F*, and *I* (Figure 2) were charged with dry ice–acetone mixture, and the magnetic stirrer and the vacuum pump were started. When the liquid in the bulb began to vaporize, the pressure in the system was fixed by setting the Cenco electronic manostat (*G*, Figure 2) to allow slow vaporization. Usually it was found necessary to keep the bath temperature between 60° and 80°C. while this step was performed. About 10% of the charge in the bulb was distilled over into the first dry-ice trap, where it was frozen and held for the remainder of the run. It was found necessary to do this with the aniline-nitrobenzene system in order to remove all traces of dissolved and adsorbed air from the bulb. When the desired amount of material had been distilled into the dry-ice trap, the condensate which had collected in the U leg was mixed thoroughly with the contents of the bulb by tilting the apparatus repeatedly, care being taken to continue boiling rapidly enough to exclude air from the bulb contents during the operation. An amount of this mixed liquid sufficient to act as manometer fluid was transferred to the U leg. The two legs of liquid in the U leg then were equalized by resetting the inert gas pressure on the system. With the aid of a small spirit level any setting in the range of 2 to 20 mm. Hg abs. could be maintained to within 0.5 mm. of the fluid in the manometer or 0.04 mm. Hg.

A series of pressure-temperature readings was taken on each charge to the apparatus over the pressure range of 2 to 20 mm. Hg abs. pressure, starting at the lower pressure and progressing upward. Less than 10 min. was required for the system to come substantially to equilibrium when a measurement was made. At the end of a run the isoteniscope was disconnected from the rest of the apparatus, taken from its bath, and connected to a nitrogen cylinder by a flexible hose. Stopcock *A* was opened and nitrogen allowed to bleed into the isoteniscope until a pressure of ½ to 1 lb./sq.in. gauge registered on the regulator of the nitrogen cylinder. Stopcock *A* was then closed and the flexible tubing disconnected from the end of the isoteniscope. The isoteniscope then was inverted over a suitable container and a sample taken by opening Stopcock *A*.

A mercury-filled Dubrovin gauge (*4* and *5*), calibrated against a McLeod gauge, was used to measure all pressures. These readings were reproducible to within ±0.05 mm. Hg. After each run the zero point of the gauge was checked by closing the stopcock on the isoteniscope, closing the air bleeds on the pressure regulator, and allowing the vacuum pump to exhaust the system. Use of a relatively large quantity of suitable heat transfer oil in the bath as thermal ballast maintained the temperature manually to within ±0.02°C. All temperatures were measured with a Leeds and Northrup semiprecision potentiometer in conjunction with a copper-constantan thermocouple which had been calibrated against a National Bureau of Standards certified platinum resistance thermometer.

The materials used in the experiments were C. P. grade aniline and nitrobenzene, which were redistilled at 10 mm. Hg abs. pressure at a reflux ratio of 20 to 1 in an 8-ft. frac-

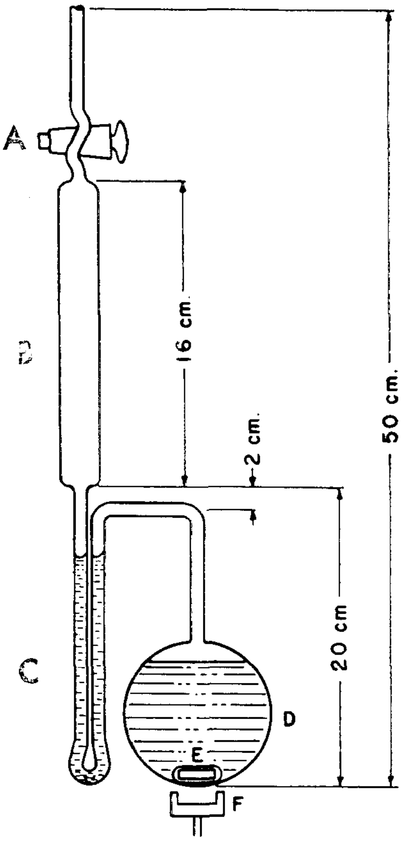

Fig. 1. Modified isoteniscope: *A*, 4-mm. oblique vacuum stopcock; *B*, entrainment trap and partial condenser (14-mm. tubing); *C*, U-tube manometer (10-mm. heavy-wall tubing); *D*, 200-ml. balloon flask; *E*, glass-covered magnetic stirrer bar; *F*, rotating bar magnet.

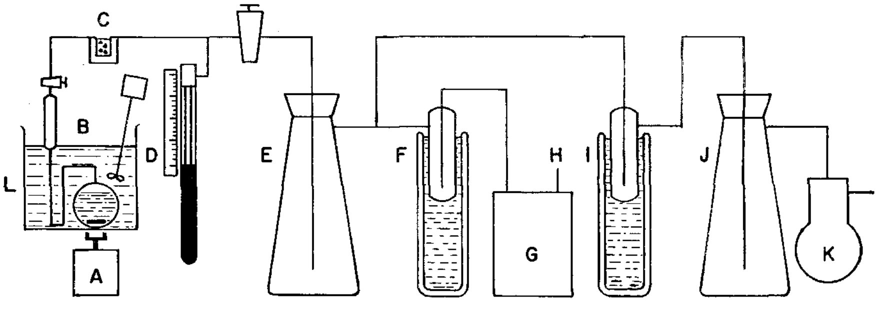

Fig. 2. Total pressure apparatus: *A*, magnetic stirrer; *B*, isoteniscope; *C*, cold trap; *D*, Dubrovin gauge; *E*, 4-liter ballast flask; *F*, cold trap; *G*, Cenco electronic manostat; *H*, air bleed; *I*, cold trap; *J*, 4-liter ballast flask; *K*, vacuum pump; *L*, oil bath.

TABLE 1.—EXPERIMENTAL DATA

Pressure, mm. Hg	Temperature, °C.	Pressure, mm. Hg	Temperature, °C.
100 mole % nitrobenzene		9.98 mole % aniline	
2.07	55.27	2.26	55.32
2.77	60.22	3.12	60.30
3.76	65.20	4.20	65.27
4.99	70.25	5.57	70.30
6.55	75.17	7.33	75.20
8.58	80.25	9.60	80.30
11.01	85.25	12.30	85.30
13.93	90.25	15.67	90.32
17.62	95.42	19.83	95.42
16.03 mole % aniline		25.45 mole % aniline	
1.83	50.55	2.08	50.40
2.52	55.45	2.74	55.32
3.42	60.35	3.73	60.32
4.60	65.25	5.02	65.30
6.04	70.35	6.64	70.32
7.90	75.30	8.72	75.22
10.33	80.35	11.30	80.20
13.23	85.27	14.48	85.29
16.66	90.32	18.29	90.25
39.01 mole % aniline		47.41 mole % aniline	
2.29	50.42	3.32	55.40
3.11	55.32	4.49	60.35
4.21	60.32	5.93	65.32
5.66	65.25	7.93	70.37
7.46	70.35	10.39	75.27
9.81	75.22	13.44	80.35
12.72	80.30	17.16	85.30
16.28	85.30		
59.52 mole % aniline		76.40 mole % aniline	
2.65	50.47	2.08	45.62
3.56	55.30	2.91	50.70
4.68	59.82	3.91	55.50
6.40	65.22	5.34	60.40
8.50	70.27	7.19	65.40
11.10	75.17	9.50	70.45
14.41	80.27	12.44	75.40
18.40	85.30	16.13	80.47
		19.19	83.72
100 mole % aniline			
3.25	50.57		
5.96	60.30		
8.01	65.25		
10.70	70.42		
13.90	75.45		
18.05	80.32		

tionating column, 1.5 in. in diam., packed with protruded stainless steel half rings. First cuts from the column were discarded. After a steady head temperature had been reached, the condensate product was collected in the distillate receivers. The contents of the receivers were stored under a nitrogen blanket in dark glass bottles until they were used in the experimental work. No tests for purity for either component were made other than the measurement of vapor pressure. These pressure-temperature relationships are tabulated in Table 1 and plotted in Figure 3. In addition to the pure components, seven mixtures of aniline and nitrobenzene covering the composition range were prepared and run in the apparatus as described in the preceding paragraphs. After each run with the mixtures the contents of the isoteniscope were removed and analyzed for aniline content by the method of Markunas and Riddick(7). A weighed portion of sample was titrated with $N/10$ perchloric acid in glacial acetic acid. Results of analyses were reproducible within 0.2 wt. % aniline.

EXPERIMENTAL DATA

The experimental data are presented in Table 1, in which readings of pressure and temperature are recorded for each mixture and for the pure components. These data are plotted in Figure 3 to enable the reader to visualize the pressure-temperature relationships. In order to facilitate mathematical treatment of the raw data, an Antoine vapor-pressure equation was fitted to each set of readings. This equation empirically expresses the relationship between pressure and temperature and has the following form:

$$\log_{10}(p^\circ \text{ or } P_t) = C + \frac{D}{E+t} \quad (1)$$

The constants C, D, and E were obtained by a least squares technique for the pressure range between 2 and 20 mm. Hg. The precision with which each curve represents the experimental data was determined by statistical analysis to be ±0.15 mm. in nineteen out of twenty observations. A tabulation of the constants is presented in Table 2.

Literature data for completely determining the absolute accuracy of the total pressure measurements by comparison are not available. A rough idea of the accuracy to be expected, however, may be obtained by comparing the experimental pressure-temperature relationships for pure aniline with measurements

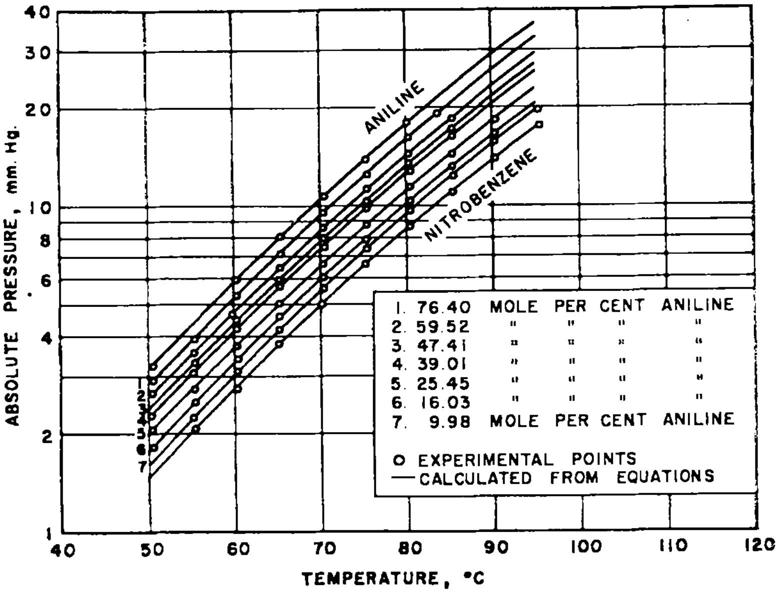

Fig. 3. Total pressures vs. temperature for the aniline-nitrobenzene system.

TABLE 2.—TABULATION OF CONSTANTS IN TOTAL PRESSURE EQUATION

Composition, mole %	C	D	E
100 Nitrobenzene	6.2576	−1279.117	159.90
9.98 Aniline	6.7021	−1449.532	173.09
16.03 Aniline	6.1114	−1184.762	152.04
25.45 Aniline	7.6387	−1950.693	215.84
39.01 Aniline	7.0323	−1586.584	187.33
47.41 Aniline	7.1491	−1639.674	191.98
59.52 Aniline	7.2130	−1665.063	194.71
76.40 Aniline	7.2520	−1635.551	190.23
100 Aniline	6.8102	−1400.285	171.76

already in the literature. That is, between 5 and 20 mm. Hg, the measured temperatures are from 0.21°C. higher to 0.08°C. lower than the data of Rechenberg(*8*), from 0.41°C. higher to 0.94°C. lower than the data of Stull(*13*), and 0.07°C. higher than the single data point of Gould, Holzman, and Niemann(*5*). Unfortunately the vapor pressures of nitrobenzene cannot be compared in a similar manner because literature data cannot be found which appear accurate enough for this purpose in the range of 1 to 20 mm. abs.

Comparison of vapor pressures does not give complete information on the accuracy of total pressure measurements. Additional obvious errors which might occur when the pressure of a mixture is measured are (*a*) the change in the liquid composition caused by vaporization of more volatile constituent into the vapor space above the solution and (*b*) errors in analysis of solutions. The maximum vaporization error may be estimated by assuming that the entire space is filled with vapors of the more volatile constituent at the maximum pressure and average temperature of the measurements. For the isoteniscope used in the experiments the error resulting from "vapor holdup" is —0.04 mole % in the liquid based on the assumptions previously described. From analysis of made-up solutions of aniline and nitrobenzene, the analytical error appeared to be a maximum of ±0.10 mole %. The maximum over-all error originating with composition changes, therefore, is estimated to be —0.14, +0.06 mole %.

CALCULATION OF VAPOR-LIQUID DATA FROM EXPERIMENTAL DATA

Two assumptions were used in computing vapor-liquid data from the total pressure data: (*a*) the vapor phase will behave as an ideal gas at 5 and 10 mm. and (*b*) activity coefficients can be expressed by some integrated form of the Gibbs-Duhem equation. It should be pointed out that any integrated form of the Gibbs-Duhem equation applies only at constant temperature and pressure. Guggenheim(*6*), however, shows that the external pressure has little effect upon the liquid-phase activity coefficient at total pressures up to several atmospheres. He integrates the differential form of the Planck function defined as

$$dY = \frac{H}{T^2}dT - \frac{V}{T}dP_t - R\ln P_1 dn_1 - R\ln P_2\, dn_2 \qquad (2)$$

at constant temperature and composition into the form

$$\ln\left(\frac{P_{1_{P_t=P_t}}}{P_{1_{P_t=0}}}\right) = \frac{(P_t-0)\;V_1'}{RT} \qquad (3)$$

The quantity $\gamma_1 x_1 p_1^{\circ}$ may be substituted for P_1 so that Equation (3) may be written

$$\ln\left(\frac{\gamma_{1_{P_t=P_t}}}{\gamma_{1_{P_t=0}}}\right) = \frac{(P_t-0)\;V_1'}{RT} \qquad (4)$$

which expresses the change in the activity coefficient with external pressure. Even at several atmospheres $P_t V_1' << RT$, and so the effect of pressure on the activity coefficient in the pressure region of 2 to 30 mm. Hg is negligible. The effect of temperature change on the activity coefficients, however, usually is quite large, and the calculations must include such effects. The following discussion will present the calculation procedures employed.

The calculation is started by drawing up several pressure-vs.-composition plots (each plot at constant temperature) from the total pressure equations or from the graph of total pressure vs. temperature. These plots cover the entire range of boiling temperatures of the mixtures at 5 and 10 mm. For each constant-temperature plot the constants in the integrated form of the Gibbs-Duhem equation are determined by curve-fitting techniques. These constants are then correlated as a function of temperature by a graph. Another cross plot of the total pressure data is made, this time at the pressure for which the vapor-liquid data are desired (actually a boiling point curve). For ten or twelve liquid compositions the boiling temperatures are read from the boiling point curve, and the constants for the integrated form of the Gibbs-Duhem equation are obtained from the plot of constants vs. temperature. The activity coefficients then are calculated for the proper liquid composition. The next step is to use activity coefficients, liquid compositions, and vapor pressures to calculate the vapor compositions. A few trial calculations may be necessary to obtain the exact boiling temperature which makes the summation of the vapor mole frac-

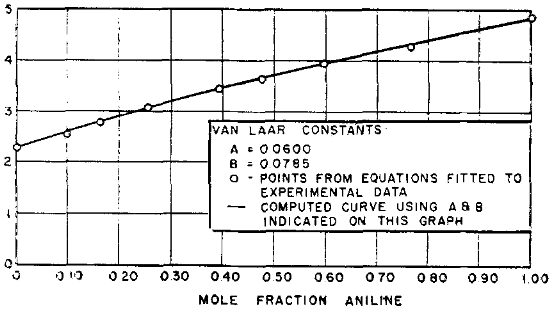

Fig. 4. Total pressure at 57°C.

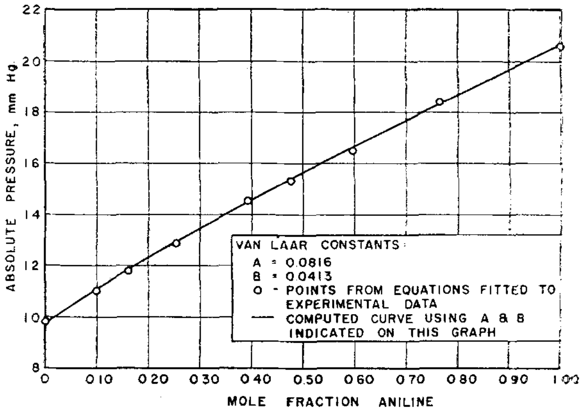

Fig. 5. Total pressure at 83°C.

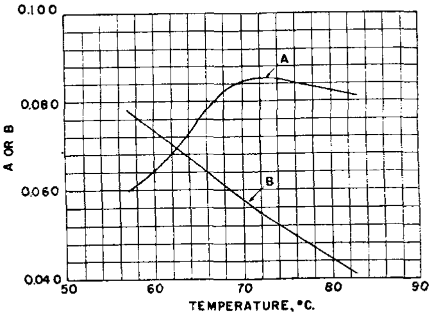

Fig. 6. Change in A and B with temperature.

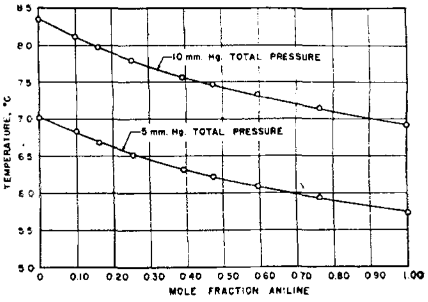

Fig. 7. Boiling-point curves for the aniline-nitrobenzene system.

TABLE 3.—TOTAL PRESSURES IN MM. HG ABS. OF THE EXPERIMENTAL SOLUTIONS AT THE INDICATED TEMPERATURES, AND THE VAN LAAR CONSTANTS GIVING THE BEST FIT TO THE TOTAL PRESSURES AT THE SAME TEMPERATURE

Temperature, °C.	Compositions, mole %								van Laar constants	
	100% Nitrobenzene	9.98 Aniline	16.03 Aniline	25.45 Aniline	39.01 Aniline	47.41 Aniline	59.52 Aniline	76.40 Aniline	100 Aniline	*A*	*B*
57°C.	2.29	2.53	2.77	3.08	3.46	3.66	3.96	4.33	4.89	0.0600	0.0785
62°C.	3.11	3.44	3.81	4.15	4.67	4.93	5.33	5.85	6.61	0.0680	0.0706
67°C.	4.17	4.62	5.04	5.52	6.22	6.57	7.09	7.83	8.82	0.0805	0.0640
72°C.	5.52	6.13	6.66	7.27	8.20	8.66	9.33	10.35	11.63	0.0857	0.0540
77°C.	7.21	8.06	8.68	9.49	10.72	11.30	12.16	13.54	13.13	0.0840	0.0495
83°C.	9.81	11.01	11.77	12.92	14.56	15.35	16.88	18.45	20.59	0.0816	0.0413

tions equal to unity. These adjustments are usually small and represent minute inaccuracies in the data and/or the empirical nature of the integrated form of the Gibbs-Duhem equation used. The following paragraphs will illustrate the application of the procedure to the calculation of the vapor-liquid equilibrium for aniline nitrobenzene at 5 and 10 mm. Hg abs.

Figures 4 and 5 are representative pressure-vs.-composition plots at constant temperatures of 57° and 83°C. These plots were obtained by substituting the respective temperatures into the total pressure equations derived from the experimental data. They might as easily be obtained directly from Figure 3, but with somewhat less accuracy than by using the equations. In addition to Figures 4 and 5 constant-temperature plots were also made at 62°, 67°, 72°, and 77°C. in the calculations. For the sake of brevity, these plots are not included. Table 3, however, tabulates the total pressure-vs.-composition data at the chosen temperatures of 57°, 62°, 67°, 72°, 77°, and 83°C.

Before the calculations were started, it was necessary to select the type of solutions to the Gibbs-Duhem equation which would express the activity coefficients for this system. As discussed by Carlson and Colburn(*1*), the choice of the type of solutions depends upon the value of AV_2/BV_1 as well as whether or not $V_2 = V_1$. At the start of the computations an estimation of AV_2/BV_1 for the aniline-nitrobenzene system indicated that the ratio might approximate 1.0 at the average temperature. In addition, at the midtemperature, V_1 is nearly equal to V_2. It appeared, therefore, that either the van Laar or Margules solutions might be applicable. Since, however, the van Laar equations gave good fits to the experimental data and are somewhat more easily handled in calculations than the Margules equations, they were selected for making the computations. The van Laar equations are

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \qquad (5)$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \qquad (6)$$

The constants in the van Laar equations were obtained by successive trial calculations for each of the constant-temperatures, 57° through 83°C. These calculations were carried out by use of the following equation, which relates the total pressure to the activity coefficients as well as vapor pressures and liquid compositions:

$$P_t = \gamma_1 x_1 p_1^\circ + \gamma_2 x_2 p_2^\circ \qquad (7)$$

The activity coefficients, of course, are functions of the A and B values as shown in Equations (5) and (6). The labor in fitting a set of A and B values to the constant-temperature plots was shortened by machine computation. In these computations a number of sets of A and B values were tried until the deviations from the experimental total pressures were minimized. The computed total-pressures-vs.-composition curve appears as a solid line on Figures 4 and 5, and the best values of the van Laar constants for each particular temperature are listed in Table 3. Temperature variation of A and B throughout the boiling-temperature range of the solutions was correlated by fitting the A and B values determined in the previous step on a graph (*see* Figure 6).

The boiling point curves for the system at 5 and 10 mm. Hg were obtained from the total pressure equations and are shown in Figure 7. They could also be cross-plotted from Figure 3 but with a decreased accuracy. These curves are used to get an approximate starting point for the final calculations and also for a comparison with computed boiling temperatures. In most situations, therefore, a simple cross plot of the total pressure data is all that is required.

The final calculations for obtaining the vapor composition in equilibrium with a given liquid composition were made by trial computations using the boiling point curve, vapor pressure curves, and the van Laar constants curves. For a given liquid composition a boiling temperature was obtained from the boiling point curve. This temperature was inserted in the vapor pressure equation for aniline and nitrobenzene, and the respective vapor pressures were computed. A and B were obtained at the same temperature from Figure 6. The activity coefficients, γ_1 and γ_2, were calculated from Equations (5) and (6). Vapor pressures, liquid composition, activity coefficients, and

TABLE 4.—VAPOR-LIQUID COMPOSITIONS AT 5 MM.

x_1, mole fraction aniline in liquid	γ_1, activty coefficient of aniline	γ_2, activity coefficient of nitrobenzene
0.050	1.1825	1.0006
0.100	1.1551	1.0024
0.200	1.1125	1.0080
0.300	1.0821	1.0160
0.400	1.0594	1.0264
0.500	1.0418	1.0398
0.600	1.0277	1.0569
0.700	1.0163	1.0792
0.800	1.0077	1.1079
0.900	1.0021	1.1456
0.950	1.0005	1.1691

y_1, mole fraction aniline in vapor	t, °C., boiling point	α, relative volatility
0.118	69.2	2.54
0.216	68.1	2.48
0.372	66.1	2.37
0.495	64.5	2.29
0.595	63.1	2.21
0.682	61.9	2.14
0.757	60.8	2.08
0.824	59.9	2.01
0.886	59.0	1.95
0.944	58.2	1.89
0.972	57.8	1.85

TABLE 5.—VAPOR-LIQUID COMPOSITIONS AT 10 MM.

x_1, mole fraction aniline in liquid	γ_1, activity coefficient of aniline	γ_2, activity coefficient of nitrobenzene
0.050	1.1674	1.0008
0.100	1.1381	1.0030
0.200	1.0958	1.0103
0.300	1.0665	1.0204
0.400	1.0452	1.0329
0.500	1.0294	1.0476
0.600	1.0179	1.0641
0.700	1.0096	1.0824
0.800	1.0042	1.1035
0.900	1.0010	1.1248
0.950	1.0003	1.1370

y_1, mole fraction aniline in vapor	t, °C., boiling point	α, relative volatility
0.116	82.3	2.49
0.212	81.1	2.42
0.366	79.0	2.31
0.488	77.2	2.23
0.590	75.7	2.16
0.678	74.3	2.10
0.755	73.1	2.05
0.824	72.0	2.00
0.887	71.1	1.96
0.945	70.1	1.91
0.973	69.7	1.89

total pressure were inserted in the following equations and the vapor compositions were calculated:

$$y_1 = \frac{\gamma_1 \, x_1 \, p_1^\circ}{P_t} \qquad (8)$$

$$y_2 = \frac{\gamma_2 \, x_2 \, p_2^\circ}{P_t} \qquad (9)$$

In all calculations use of the temperatures from the boiling point curve resulted in the summation of the vapor mole fractions being equal to 1 within the precision of the vapor pressure data.

For each pressure the vapor compositions for eleven liquid compositions were computed. Tables 4 and 5 present the x-y data activity coefficients, and boiling temperatures obtained and also values of α, the relative volatility, as a function of liquid composition. Since the computed boiling point curve is identical with the curve obtained by cross-plotting the data on Figure 3, no attempt was made to include it on Figure 7 in addition to the experimental curve. A statistical estimate of the precision of the data was made in which it was found that in nineteen out of twenty instances the vapor compositions will be expressed within ±0.9% and the relative-volatility values obtained will be precise within ±1.5%.

Just as in the case of the vapor pressure of nitrobenzene, paucity of data makes it difficult to compare these results with others to obtain an estimate of the absolute accuracy. Docksey and May(*2*), however, determined vapor-liquid data for aniline nitrobenzene at 10 mm. total pressure by the method of Rosanoff, Bacon, and White (*11*). Unfortunately, they presented only a graph of the equilibrium compositions and did not include a tabulation of the x-y values or of the boiling temperatures. It is impossible, therefore, to test the thermodynamic consistency of their data and to draw direct comparisons for estimating accuracies. Relative volatilities, however, may be estimated from the Docksey and May data. Such estimations indicate a value of α between 1.90 and 2.00 over the composition range. These values may be compared with the relative volatilities in Tables 4 and 5, which are from 1.85 to 2.54.

It will be noted from Figure 6 that the van Laar constant A goes through a maximum at about 72°C. and the value of B decreases steadily with increasing temperature. As pointed out by Carlson and Colburn(*1*), the variation of A and B with temperature may be related to the heat of mixing. The change in the trend of A with temperature, therefore, may indicate that the heat of mixing changes sign within the range of temperatures over which the data for this system were obtained. Since no data on heats of mixing for this system are available in the literature, calculations cannot be made which might indicate the validity of the A curve.

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NOTATION

A, B = constants in van Laar solutions to the Gibbs-Duhem equation
C, D, E = constants in the Antoine equation
p° = general vapor pressure, mm. Hg
$P_{1,2}$ = partial pressure of components (1) and (2), mm. Hg
P_t = total pressure, mm. Hg
t = temperature, °C.
V = molar volume, cc./g.mole
V_1' = partial molal volume, $(\partial V/\partial n_1)_{T,P,n_2}$
x = mole fraction in liquid
y = mole fraction in vapor
γ = Raoult's law activity coefficient
α = relative volatility, y_1x_2/x_1y_2
subscript 1 refers to aniline
subscript 2 refers to nitrobenzene

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