$\Delta \bar{V}$ for $C_4Cl_3F_7$ in system E gives 4.8 ml. The experimental value is about 9 ml. The compound $C_4Cl_3F_7$ occurs in the three systems B, D, and E. If it is assumed that the β's for the second component in each of these systems are approximately equal, the partial molal volumes of $C_4Cl_3F_7$ at infinite dilution in each of these systems should be in the ratio of the *B*-values for this compound in the respective solutions. The partial molal volume of $C_4Cl_3F_7$ in $C_8F_{16}O$ should be about three times as large as its value in $C_5Cl_2F_6$. Actually it is only about twice as large. A similar situation prevails for $C_5Cl_2F_6$ in mixtures with $C_8F_{16}O$ when compared with the pentene in mixture with $C_4Cl_3F_7$. The volume change on mixing of the two chlorofluorocarbons (system B) seems to be abnormally large. The ratio of the *B*-values (by Equation 1) for the $C_4Cl_3F_7$ in systems D and E is 1 to 5, and the ratio of the partial molal volumes for the butane in these systems at infinite dilution is 1 to 3. However, the ratio of the β's for $C_8F_{16}O$ and n-C_7H_{16} is probably approximately 1 to 2, so that the partial molal volume at infinite dilution for $C_4Cl_3F_7$ in these solutions should theoretically be about 1 to 10. As it was shown above that the limiting partial molal volume for $C_4Cl_3F_7$ in n-C_7H_{16} is about twice the theoretical, it may be concluded that the partial molal volume for $C_4Cl_3F_7$ with the hydrocarbon also shows abnormally large values.

ACTIVITY COEFFICIENTS

The empirical formulas of Scatchard, of Marguler, and of Van Laar relating activity coefficients to composition were fitted to the experimental values in the three systems (C, D, and E) which are not ideal. The Van Laar equations were the only ones which gave consistent relationships for all three systems. The constants in these equations when written as

$$\log_{10}\gamma_1 = bx_2^2/(ax_1 + x_2)^2$$
$$\log_{10}\gamma_2 = abx_1^2/(ax_1 + x_2)^2 \qquad (4)$$

are given in Table VII.

If these systems all obeyed the theory of Hildebrand (*5*), the values of A and B should be related to the theoretical V_1/V_2 values and the *B* values of Table V by

$$a = V_1/V_2 \qquad (5)$$

Table VII. Van Laar Constants in Equations 3 and 4

System	*a*	b
C. $C_5Cl_2F_6(1)$: $C_8F_{16}O(2)$	0.635	0.174
D. $C_4Cl_3F_7(1)$: $C_8F_{16}O(2)$	1.0	0.174
E. $C_4Cl_3F_7(1)$: n-$C_7H_{16}(2)$	0.945	0.246

$$b = B_1/686 \qquad (6)$$

Equations 5 and 6 hold only for system C. For system D, *a* is 1.0 instead of $V_1/V_2 = 0.703$, and 686*b* is 148 instead of the theoretical value $B_1 = 52$. For system E, *a* is 0.945 instead of $V_1/V_2 = 1.12$, and 686*b* is 207 as compared to the theoretical value of $B_1 = 278$. In system E the theoretical activity coefficients are greater than the experimental values, while in system D the theoretical values are too small. The theoretical values in system C are the same as the experimental values.

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Vapor-Liquid Equilibrium at High Pressures

The Systems Ethanol-Water and 2-Propanol—Water

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Vapor-liquid, phase-equilibrium data at elevated temperatures and pressures are necessary for the design of high pressure distillation processes, and in other fields of modern chemical engineering. At Yale University, research being conducted on the two-phase hydration of olefins has fostered interest in the vapor-liquid phase equilibria for the systems ethanol-water and 2-propanol-water; such data are necessary for the prediction of the equilibrium compositions in the hydration of ethylene and propylene, respectively. The determination of these data will also give experimental checks on various methods of calculation of relevant thermodynamic data, of great interest because of the departure of these systems from ideality. This experimental work, accordingly, adds to the supply of fundamental data, which, when sufficiently complete information is available, will allow accurate thermodynamic prediction of such reactions.

Previous studies of the vapor-liquid phase equilibrium for the systems ethanol-water and 2-propanol-water are reported in Table I and of the vapor pressure of 2-propanol in Table II.

The aim of this current experimental work was to enlarge the amount of data for the ethanol-water system obtained by Griswold, Haney, and Klein (*24*), and to extend the study of the isothermal vapor-liquid equilibrium for the systems ethanol-water and 2-propanol-water up to conditions approaching as closely as possible the critical point of pure water. The data of the investigators mentioned were to be used to check the operation of the equipment.

EXPERIMENTAL DETERMINATION OF VAPOR-LIQUID EQUILIBRIUM DATA

There are six main methods for determination of vapor-liquid equilibria: recirculation, static, dynamic flow, dew

Table I. Previous Studies of Vapor-Liquid Equilibrium for Systems Alcohol-Water

Temperature or Pressure	References	Remarks
	A. Ethanol-Water	
760 mm.	(*5*, *10*, *12*, *18*, *26*, *34*, *42*, *54*, *56*, *61*, *65*, *71*)	Isobaric
<760 mm.	(*5*)	Isobaric
760 mm.	(*1*)	Very low ethanol concentrations. Henry's law not obeyed
760 mm.-300 p.s.i.a.	(*56*)	Isobaric
Up to 150 p.s.i.a.	(*54*)	Isobaric
75 p.s.i.a.	(*53*)	Isobaric
Up to 15 atm.	(*25*)	Isobaric
50° and 60°C.	(*34*)	Isothermal
150°-275°C.	(*24*)	Isothermal
Up to 300 p.s.i.a.	(*56*)	Azeotropic composition and temperature
Subatmospheric	(*5*, *70*, *75*)	Azeotropic compositions
Up to 1450 mm.	(*75*)	Azeotropic compositions
	B. 2-Propanol-Water	
95 mm.-4 atm.	(*78*)	Isobaric
760 mm.	(*9*, *42*, *43*, *69*)	Isobaric
760 mm.	(*9*, *42*, *43*, *44*, *49*, *69*, *80*)	Azeotropic compositions and temperatures
	(*50*, *78*)	Effect of pressure on azeotropic composition and temperature

Table II. Reported Vapor Pressure for 2-Propanol

Temperature or Pressure	References
35°-90° C.	(*57*)
1-8 atm.	(*78*)

and bubble point, differential distillation, and continuous distillation methods.

Details of these methods, and the advantages and disadvantages of each, are discussed by Robinson and Gilliland (*66*) and Barr-David (*3*).

A study of the methods and apparatus used for the determination of vapor-liquid equilibrium shows that only a few are suitable for the determination of the high pressure vapor-liquid equilibrium for the systems ethanol-water and 2-propanol-water. Only two methods will be further considered—the dew and bubble point method, and the recirculation method.

The dew and bubble point method has the advantage of giving volume data as well as the $y-x$ data. There are two methods by which this technique may be used—namely, with a constant-mass, variable-volume cell, or with a variable-mass, constant-volume cell. Further detail is given by Barr-David (*3*). Because of the complexity of the equipment and other disadvantages, it was decided not to use this method.

The choice then lay in adopting an accurate method based on the use of a recirculation-type still. The operating conditions of high temperature and pressure, as well as operation with conditions approaching the critical point, greatly limited the choice. The theoretical advantages claimed for the vapor-recirculating still were considered outweighed by the increase in complexity of construction and operation for this type of still. It is doubtful that data determined for these systems would be appreciably affected by the theoretical shortcomings of the liquid-recirculation still. Vapor-recirculating stills have proved difficult to operate even at 1-atm. pressure in glass apparatus, in which the progress of operation may be watched; the difficulties would be enormously increased in an all-metal apparatus at conditions approaching the critical point, where the volumes of each phase are only approximately known. The large change in properties of each phase at elevated temperatures and pressures could well cause the still to cease operating in the desired manner.

The same can be said for many types of liquid-recirculating stills. Some of these are too complex in construction for simple adaptation to high pressures; others, such as the still of Gillespie (*20*), may cease operating. Stills designed for high pressure operation using the construction of a simple Othmer-type still have been very satisfactorily used by Scheeline and Gilliland (*68*) and Griswold, Andres, and Klein (*23*).

The equilibrium still used by the former investigators consisted of a glass cylinder sealed by neoprene packing. There are limitations to their apparatus imposed by the high-temperature strength of glass and the thermal and chemical stability of the sealing gasket. These difficulties were overcome in a simple still design by Griswold, Andres, and Klein (*23*), and used by Griswold, Haney, and Klein (*24*) for the study of the system ethanol-water up to 275°C. and pressures up to about 1500 p.s.i. This still was designed, bearing in mind the difficulties of high pressure operation. One of these was the greater tendency for condensate to flash as it returns to the still without mixing with all the liquid in the still. The vapor density is higher, and that of the liquid is lower, than at atmospheric pressure. Hence, there is a greater danger of entrainment and also of backflow surges of liquid from still to condensate chamber at higher pressures. The increased solubility of an inert gas at the high pressures would have an appreciable effect on the equilibrium, and the equipment was designed to operate without inert gas by maintaining conditions in the still by balancing heat input and output.

Their still accordingly has several important features,

A circulation pipe and collar in the heater section, to ensure adequate mixing of condensate and still liquid before the vapor is released from the boiling liquid.

Ample vapor space above the boiling liquid so that entrainment is negligible.

A condenser, the cooling duty of which can be easily varied to suit the conditions.

A ball-check valve in the condensate return line to prevent back-surges during momentary fluctuations of heat input or removal, or while samples are being withdrawn.

Because of the satisfactory results on the system ethanol-water obtained by Griswold, Haney, and Klein (*24*) using the apparatus just described, and other reasons, it was decided to use an apparatus similar in principle to that used by these investigators. However, the constructional detail of the present still is entirely different from the still of Griswold and others. The major changes were the fabrication of the vessel from commercially available high pressure components, wherever available; the use of accepted high pressure closures, such as the cone and the Bridgman-type closures, instead of welded joints; the addition of a siphon-breaker line; the design of the check valve; and the design of the equipment to operate at higher pressure and temperature—namely, 3200 p.s.i. and 370°C.

Details of Construction of Apparatus. Figure 1 shows a schematic equipment flowsheet.

Equilibrium Still. Figure 2 shows the equilibrium still used for this study. Omitted from Figure 2 for the sake of clarity are the insulation, electrical windings, and supports.

In the reboiler, 7, the liquid is heated by means of an external heater winding surrounding the leg. Thorough mixing of the returning liquid and liquid in the still is ensured by the circulation pipe and collar, 8. The vapor formed passes up through the main body, 9, in which any entrained liquid settles out. The vapors leave the top of the still and pass into a two-section condenser, which can be cooled by air or water. The main body of the still and the top fittings are maintained 2° to 3° above the vapor temperature to ensure nearly adiabatic operation of the still and prevent refluxing. The condensed vapor collects in the condensate chamber, 26, flows through a check valve, 19, and returns by the vapor-condensate return line 17, to the reboiler. A vent pipe from the check valve to the main vapor space has been added to prevent siphoning of the liquid from the condensate chamber to the still.

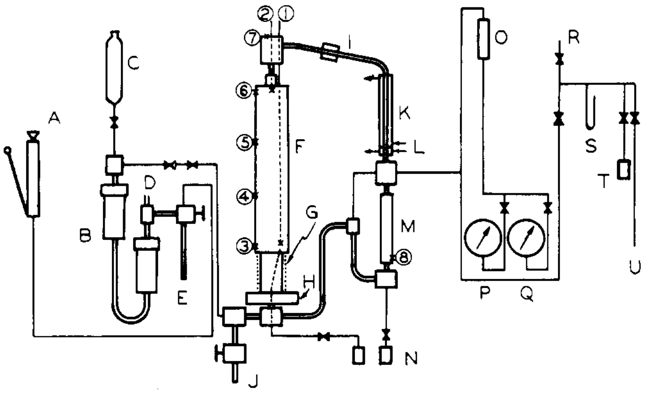

Figure 1. Schematic equipment flowsheet

A. Blackhawk pump
B. Mercury-piston pump
C. Glass charging funnel
D. Mercury level contact terminals
E. Oil drain
F. Main still
G. Main heater
H. Support
I. Support
J. Still drain
K. Condenser
L. Cooling fluid connections from air and water flowmeters
M. Condensate chamber
N. Phase sampling connections
O. Mercury reservoir
P. 0–500 p.s.i. Heise gage
Q. 0–3500 p.s.i. Heise gage
R. Vent
S. Manometer
T. Sample bomb evacuation connection
U. To vacuum pump

The reboiler, 7, main body, 9, and top plug, 15, were constructed from AISI 4130 steel. The rest of the equipment was fabricated from stainless steel.

The thermocouple wells, 12 and 13, are constructed from $\frac{1}{8}$-inch outside diameter tubing. Because of the small cross section of the metal of the thermowell, the length, and the fact that at the connection between the thermowell and the wall the temperature is only 2° to 3°C. above the temperature to be measured by the thermocouple, the error introduced in the temperature read by the thermocouple due to conduction along the thermowell is entirely negligible.

In the check valve, 19, the $\frac{5}{16}$-inch steel ball was replaced by a conical aluminum float, which required a pressure difference of about $\frac{1}{10}$ inch of water for opening. The steel ball required excessive pressure for operation. In the still design of Griswold and others (*23*), the check-valve design would have required large pressure differences for operation, which must have led to operation in a manner not desired as critical conditions were approached.

The location of the liquid sampling line is important, for the liquid phase sampled should be liquid in equilibrium with the vapor—that is, liquid from near the surface of the liquid in the reboiler, and not liquid contaminated with returning vapor condensate. The problem was solved by a $\frac{1}{8}$-inch outside diameter tube, 3, which terminated at about the circulation collar.

Thermocouples were inserted into the thermowells, 12 and 13, and wall thermocouples were attached to the outside wall of the main still body at four points, 16. Other thermocouples were attached at the top thermocouple tee, 14, and at the condensate chamber, 27.

The main heating element fits around the outside of the reboiler. The auxiliary winding consists of three sections, the winding on the main body, on the top fittings, and on about 3 inches of the vapor line, 22, from the tee to the support.

The insulated supports for the still were designed to obviate any complications in the adiabatic operation of the still caused by heat leaks through the supports. The main support is underneath the reboiler. The auxiliary support for stability is attached to the sloping vapor line, 22, at the top of the still. There are no connections to the main body of the still to cause refluxing.

The entire apparatus is insulated by means of 85% magnesia light-weight steam-pipe insulation.

After assembly, the equipment was tested repeatedly to 3500 p.s.i. hydraulically and to 2500 p.s.i. gas pressure.

The volume of the equilibrium still was measured by filling with water and found to be 2900 ml.

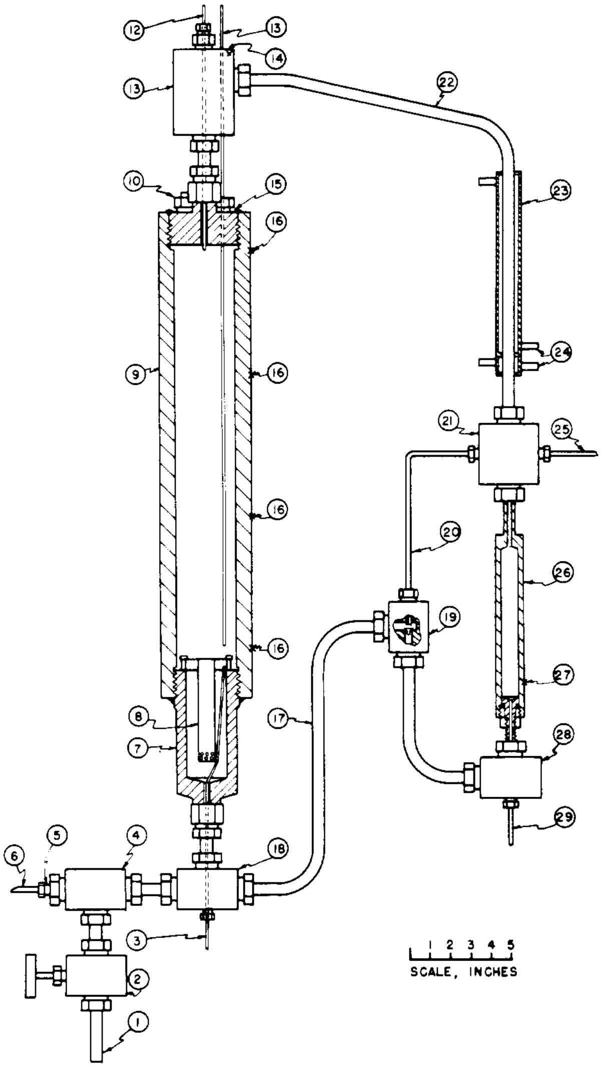

Figure 2. Charging assembly

1. Drain
2. $\frac{9}{16}$ inch valve
3. Liquid sample line
4. $\frac{9}{16}$ inch tee
5. $\frac{9}{16} \times \frac{1}{4}$ inch reducer
6. Liquid charging line
7. Reboiler
8. Circulation pipe and collar
9. Main body
10. Plug in place of Fenwal thermoswitch
11. Special thermocouple assembly
12,13. Thermocouple wells
14. Thermocouple
15. Top plug of still
16,27. Wall thermocouples
17. Vapor condensate return line
18. Special cross
19. Special check valve
20. Syphon break line
21. $\frac{9}{16} \times \frac{1}{4} \times \frac{9}{16} \times \frac{1}{4}$ inch cross
22. Vapor line
23. Condenser
24. Cooling fluid inlet connections
25. Line to pressure gages, vent, evacuation line
26. Condensate chamber
28. $\frac{9}{16} \times \frac{9}{16} \times \frac{1}{4}$ inch tee
29. Vapor sample line

Charging Assembly. The function of the charging assembly is to enable liquid of any desired composition to be injected into the equilibrium still when the latter is at the operating conditions of high temperature and pressure. Oil from a hand-operated Blackhawk pump is used to displace mercury in a liquid-piston pump, which in turn displaces the desired liquid through to the liquid charging line (6, Figure 2) of the main equilibrium still. The level of mercury in the lower of the liquid-piston pump vessels is kept between limits by means of electrical contacts which operate electrical warning lights. The amount of oil pumped, and thus the amount of liquid injected into the equilibrium still, is measured by means of a gage glass on the Blackhawk pump. The upper vessel of the liquid-piston pump may be refilled with liquid by means of a graduated glass funnel.

Accessory Equipment. The complete arrangement of still and accessories is shown in the schematic equipment flowsheet (Figure 1). The pressure is measured by two Heise gages, of pressure ranges 0 to 500 and 0 to 3500 p.s.i., respectively. Two gages were necessary to give the desired accuracy of pressure measurement. The accuracy claimed by the manufacturers of the Heise gages is 0.5% above 20% of full scale, and 0.2% of full scale below 20% of full scale, but may be much better. This accuracy was satisfactory for this experimental work. The pressure in the still is transmitted by line, 25 (Figure 2) to a mercury reservoir, then to the Heise gages.

The sample bombs were two small vessels of about 30-ml. capacity each, made of stainless steel. The seals in both these bombs are made of silicone rubber O-rings. The standard ½-inch cone connections used for connection of the sampling bombs proved easy to seal and withstood thousands of attachments and detachments without leaking.

Line 25 (Figure 2), connects to a valve, which isolates the high pressure of the equilibrium still. The other side of this valve is a vent and evacuation system.

Temperature Measurement. The temperatures at various parts of the equilibrium still are obtained by iron-constantan thermocouples which are numbered in Figure 1.

Thermocouple 1 is the most important junction, for this gives the temperature of the liquid-vapor equilibrium system. Thermocouple 2 gives the temperature of the vapor leaving the main body; in general this thermocouple shows a temperature 1° to 3° C. greater than that of thermocouple 1. Wall thermocouples 3, 4, 5, 6, and 7 should show a temperature 2° to 3° C. above the temperature of thermocouple 1, so that no refluxing can possibly occur within the main body of the still. It is important, however, that the wall of the still not be substantially hotter than the vapor within the still, or else vaporization of liquid splashes hitting the walls of the still will occur, leading to erroneous compositions. Thermocouple 8 was used to check that the condensate was cold enough to ensure complete condensation of the vapor, and not fractional condensation.

The electromotive forces developed by the thermocouples were read from a Leeds & Northrup K2 potentiometer. The K-2 triple range potentiometer gave more than sufficient accuracy and precision for this work. The accuracy of the e.m.f. measurement is far greater than the accuracy of the calibration of the thermocouples.

The thermocouples were calibrated up to 200° C. with a National Bureau of Standards calibrated mercury-in-glass thermometer and at the freezing point of lead using NBS certified lead. The accuracy of the temperature measurement was considered to be to about 0.5° C. The precision of the temperature measurements was probably at least 0.02° C. The operation of the equipment is described in detail by Barr-David (*3*).

Check on Operation of Equipment. The operation of the still was checked by a study of the 200° C. ethanol-water vapor-liquid isotherm and a comparison of the results with the work of Griswold, Haney, and Klein (*24*). The $y - x$ data showed excellent agreement, although the work of Griswold and others includes only five experimental points. Initially, because of insufficiently precise temperature control, the pressure data scattered, but with the K-2 potentiometer the desired temperature precision was obtained.

The data for this isotherm were obtained for a wide range of boil-up rates. No effect of boil-up rate could be detected. The amount of entrainment expected at a maximum boil-up rate (2200 watts) was calculated from the data given by Souders and Brown (*72*) and found to be negligible.

The operation of the still for a liquid volume from 400 to 1000 ml. was checked. No effect of liquid level was found.

Materials Used. A survey of ethanol available showed that very pure grades were available from many manufacturers, and that they were all equally suitable for this work. Two grades of U. S. Industrial Chemicals Co. ethanol were used. No difference between the grades could be detected in the results of the experimental determinations. Most work was performed using pure ethanol alcohol absolute, U. S. P. 200-proof. Experimental determinations gave the density at 20° C. to be 0.78979 gram per cc., which corresponds to 99.8 weight % of alcohol. Limited experimental work was done also with pure ethanol alcohol U. S. P. 190-proof. This had a density of 0.81083 gram per cc. at 20° C., which corresponds to 92.64 weight % of alcohol. No further purification of the ethanol was attempted.

Very pure 2-propanol was available from several manufacturers, "Isopropyl alcohol, Baker analyzed reagent." supplied by the J. T. Baker Chemical Co. was used for this study. Experimental determination of the specific gravity gave 0.78764, corresponding to 99.5 weight % of alcohol. No further purification was attempted with the 2-propanol used for the equilibrium determinations.

The 2-propanol used for the vapor-pressure determination was rendered as anhydrous as possible. Riddick and Toops (*64*) summarize the methods that have been used for this preparation. The 2-propanol for this study was prepared in a manner similar to that used by Maryott (*48*). This involved dehydration using magnesium, which is claimed to be superior to calcium oxide and many other materials. The 2-propanol was allowed to stand over magnesium turnings for 2 weeks, then refluxed for 10 hours with fresh magnesium turnings, followed by distillation at a reflux ratio of 10 to 1. A center cut boiling at 82.3 ° C. was collected. This material had a specific gravity 20°/20° C. of 0.78644, corresponding to 99.95 weight % of 2-propanol.

Analyses of Samples. Density is an accurate method of analysis of ethanol-water and 2-propanol-water mixtures. The density of ethanol-water mixtures at 20° C. is given by Perry (*58*), Hodgman and Holmes (*27*), and the National Bureau of Standards 19 (*73*). The density of 2-propanol-water mixtures at 20° C. is given by Lebo (*43*), which is cited by Perry (*60*) and International Critical Tables. For this work, the specific gravity of 2-propanol-water mixtures published by the Enjay Co., Inc. (*17*) was used.

Equipment Used for Density Determination. A multitude of devices has been used for defining a volume so that the filling and weighing of the vessel are reproducible and convenient. The accuracy, advantages, and disadvantages of various types of pycnometers are discussed by Weissberger (*76*). The pycnometers used for the present work have been described by Lipkin and others (*46*) and were obtained commercially (Catalog No. 5437, 10-ml. pycnometer type B, Ace Glass Co., Vineland, N.J.)

All weighings were performed on an Ainsworth Chain-Weight balance, capable of a precision to at least 0.1 mg. Tests were conducted to ensure proper operation of the balance and to calibrate the rider and chain. High quality lacquered brass weights were used for the weighings. The weights were calibrated against NBS calibrated Class M weights. These weights were also used for the calibration of the rider and chain of the balance.

All weighings were corrected for buoyancy of the air, as given by Drucker (*16*) and Diehl and Smith (*13*).

The densities were determined at 20° C. by thermostating the pycnometers in a water bath controlled to 20° ± 0.01 °C. by means of a mercury regulator. The density values recorded in this work are accurate to at least four figures. The equilibrium compositions of the phases in this study have been reported to three significant figures. Thus substantially no error in the final results may be attributed to the method of analysis.

SUMMARY OF RESULTS

The isotherms at 150°, 200°, 250°, 275°, 300°, 325°, and 350° C. were studied in the ethanol-water system. The pressure-temperature composition data are reported in Table III and graphically presented in Figures 3 and 4.

The vapor-liquid equilibria of 2-propanol-water were studied at the 150°, 200°, 250°, 275°, and 300° C. isotherms. The pressure-temperature-composition data are reported in Table IV and are shown graphically in Figures 5 and 6. Extensive decomposition of the 2-propanol into propene prevented the determination of any equilibrium data at higher temperatures.

The vapor pressure of pure 2-propanol is given in Table V and is graphically presented as a reference-substance plot in Figure 7.

For the ethanol-water system, critical data for the mixture have been given by Griswold and others (*24*) and White (*77*). White's data consist of limited critical temperature data, at variance with those of Griswold, and have not been used in this work. The method used by Griswold for the measurements of the critical properties could lead to small inaccuracies in these measurements. The method used for the measurement of the critical temperature—sealing glass tubes about one third full of liquid at room temperature and observing the meniscus as the tubes are heated—will give the critical temperature only if the tubes contain the critical volume of the mixture. Griswold reports that the tubes filled with liquid—that is, the bubble point line was reached and therefore the tubes contained too much material and the temperatures reported will be low. Similarly no attempt was made to introduce the critical volume into the bomb used for the critical pressure measurements. Because of the large density variations with small temperature changes near the critical point, the values reported are probably close to the true values. The critical locus from Griswold's data is plotted on Figure 3, and shows good agreement with the present data. The

Table III. Experimental Vapor-Liquid Equilibrium Data Ethanol-Water

Mole Fraction Ethanol in Liquid	Mole Fraction Ethanol in Vapor	Pressure, P.S.I.A.
	At 150° C.	
0.018	0.159	81
0.048	0.288	91
0.084	0.367	102
0.155	0.438	113
0.184	0.458	117
0.232	0.490	120
0.264	0.503	122
0.326	0.528	122
0.340	0.535	123
0.463	0.600	130
0.572	0.658	133
0.648	0.704	135
0.717	0.749	135
0.781	0.797	139
0.862	0.862	143
0.923	0.919	143
0.966	0.961	143
	At 200° C.[a]	
0.023	0.134	260
0.032	0.175	271
0.048	0.219	288
0.066	0.262	300
0.088	0.299	313
0.112	0.337	329
0.157	0.381	339
0.214	0.424	359
0.295	0.466	364
0.345	0.495	385
0.391	0.528	381
0.479	0.579	407
0.491	0.586	396
0.580	0.641	412
0.689	0.719	422
0.824	0.828	437
0.934	0.929	428
	At 250° C.	
0.009	0.044	592
0.034	0.135	665
0.063	0.206	718
0.098	0.264	764
0.135	0.306	795
0.172	0.340	827
0.223	0.376	858
0.285	0.417	892
0.339	0.446	910
0.402	0.487	940
0.463	0.530	965
0.565	0.605	1003
0.673	0.690	1032
0.702	0.715	1038
0.705	0.715	1037
	At 250° C.	
0.737	0.740	1040
0.756	0.756	1040[b]
0.79	0.79	1040[c]
	At 275° C.	
0.007	0.029	890
0.033	0.112	985
0.065	0.177	1060
0.105	0.233	1120
0.149	0.277	1173
0.201	0.322	1220
0.273	0.377	1282
0.348	0.429	1345
0.374	0.441	1363
0.414	0.465	1392
0.455	0.486	1421
0.490	0.490	1430[c]
0.512	0.512	1456[d]
	At 300° C.	
0.006	0.024	1283
0.030	0.087	1382
0.057	0.138	1470
0.091	0.186	1555
0.128	0.228	1634
0.178	0.276	1720
0.246	0.315	1785
0.330	0.330	1820[c]
0.350	0.350	1870[d]
	At 325° C.	
0.007	0.018	1798
0.035	0.075	1937
0.063	0.114	2032
0.084	0.134	2085
0.121	0.173	2185
0.161	0.191	2250
0.190	0.192	2278
	At 350° C.	
0.008	0.016	2475
0.033	0.057	2620
0.052	0.074	2691
0.085	0.085	2752[d]

[a] Pressure readings inaccurate because of inadequate temperature control.

[b] Compositions equal, either single phase or azeotrope.

[c] Critical point estimated from Figure 3.

[d] Point in single-phase region.

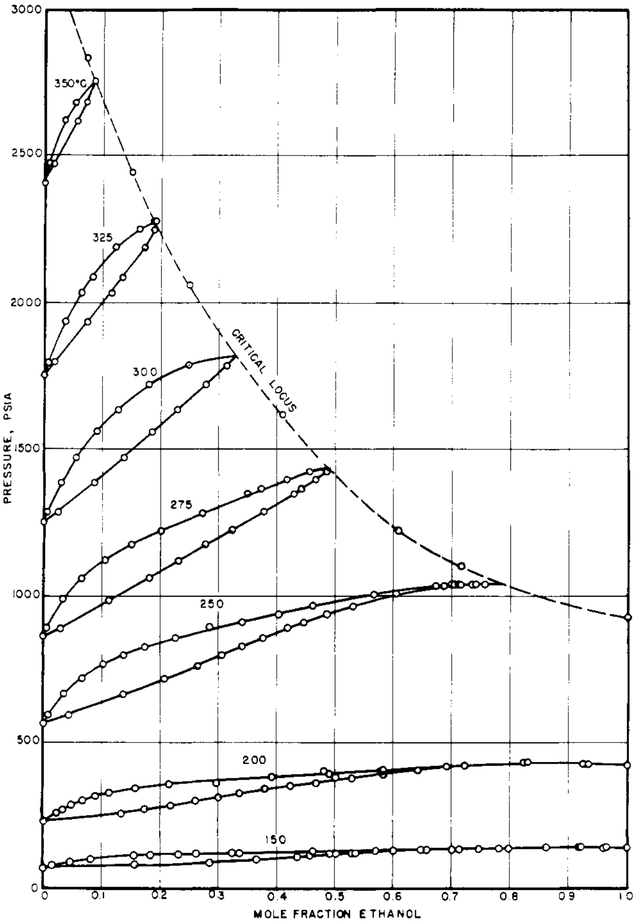

Figure 3. Pressure-composition isotherms of ethanol-water

locus has been used to estimate the critical composition of the mixture for the 275° and 300° isotherms, and thus to establish the limiting compositions on the $y-x$ curves (Figure 4).

Comparison of the ethanol-water equilibria of this work with those of Griswold and others (*24*), shows that the pressures reported in the latter experimental data are higher than those found in the present experimental work. The discrepancy can be explained by the error of the temperature measurements; because in each set of data the accuracy of the temperature is about 0.5°C., the combined error of 1°C. could explain the pressure discrepancy.

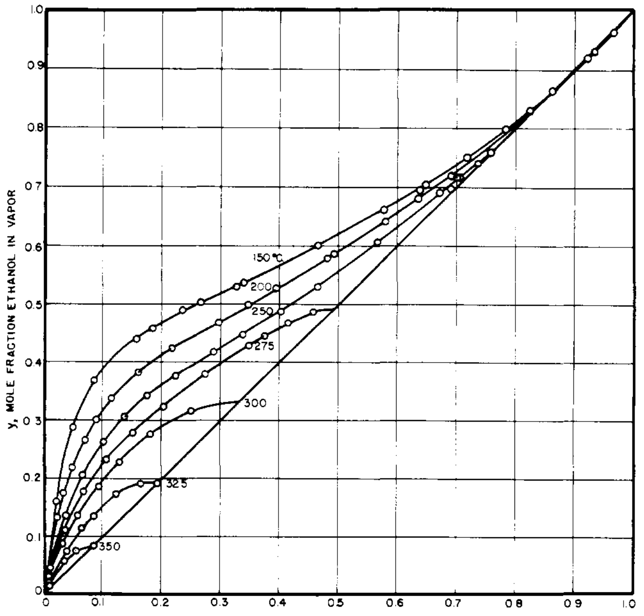

Figure 4. *y, x* isotherms of ethanol-water

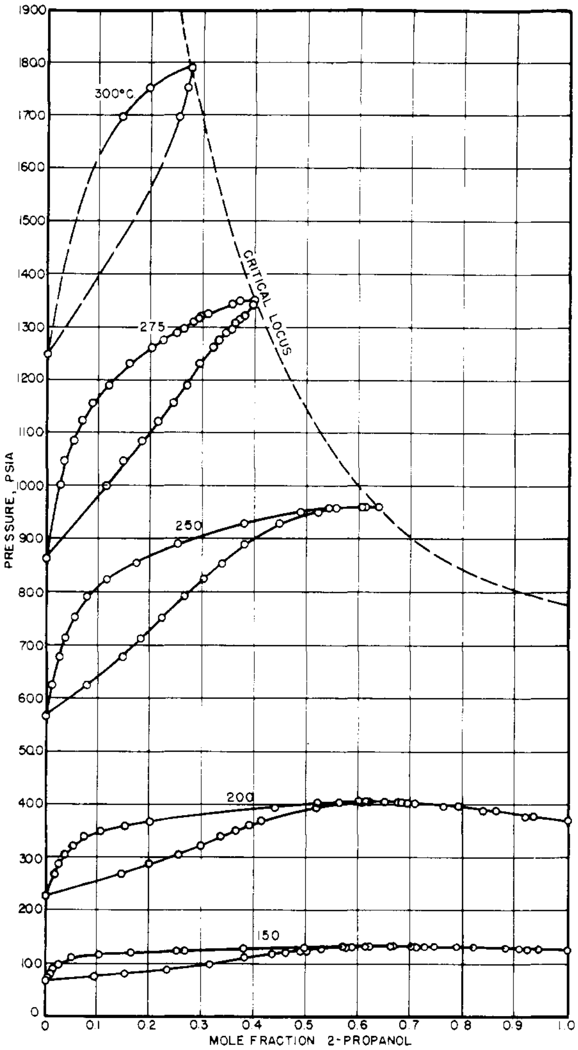

Figure 5. Pressure-composition isotherms of 2-propanol-water

The $y-x$ data, however, are relatively insensitive to small temperature changes, and good agreement should be expected. Comparison shows that the two sets agree well at 200°; at 150° and 250° the vapor compositions for the respective liquid compositions reported by Griswold lie a little below those of the present work, while at 275° Griswold's data are considerably less than those of this work. A possible explanation for Griswold's low values at the higher temperatures (275°) could lie in the fact that he charged insufficient material (600 ml.) to the vapor-liquid equilibrium still to maintain the level of the liquid in the still necessary so that the liquid sample should consist of liquid only and not one enriched in more volatile component because of contamination of the liquid sample by vapor.

A study of these results for the two systems 2-propanol-water and ethanol-water shows a great similarity in the data, as would be expected. As the degree of mutual solubility of comparable systems decreases—for example, in this case for the systems of water with alcohols of increasing number of carbon atoms—the $y-x$ curves at atmospheric pressure show: for methanol a concavity upward; for ethanol a homogeneous azeotrope; for 2-propanol a more pronounced homogeneous azeotrope; for butanol immiscibility over part of the composition range and a heterogeneous azeotrope; and for higher alcohols, an increasing range of immiscible section.

The effect of pressure on any one system is to decrease the differences between the components. Thus as the pressure is increased for the systems studied, the concavity

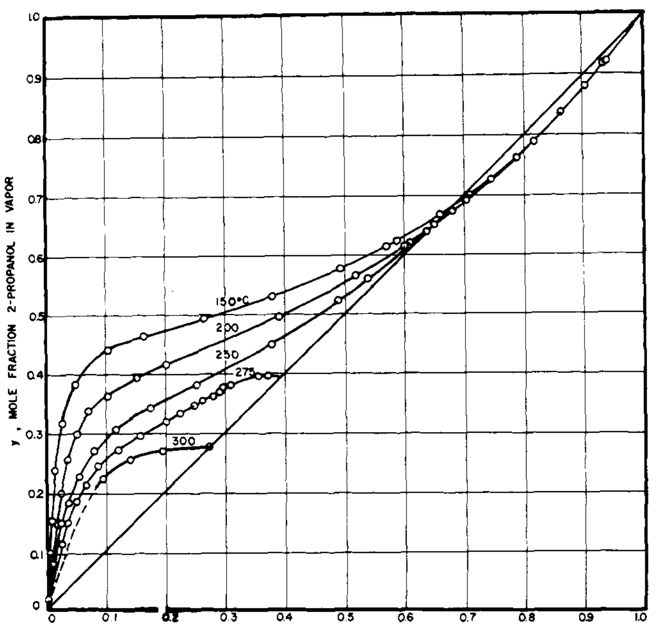

Figure 6. y, x isotherms of 2-propanol–water

upward decreases, and, at high pressures, the y – x curves are convex upward to the critical point of the mixture. The effect of pressure on the azeotrope will be discussed later.

A vapor-liquid equilibrium still is known to give inaccurate results at conditions approaching the critical point. Indeed, the whole operation of the still ceases; at the critical point the boil-up rate becomes infinite and the density difference between the phases becomes zero, and thus entrainment becomes infinite. Just how far below the critical point of the mixture entrainment becomes significant has not been demonstrated, but it probably is not appreciable at conditions reasonably removed from the critical point, because of the big changes in the densities of the phases and the heat of vaporization of the mixture, with a small temperature decrease from the critical temperature. For these reasons, it was not possible to establish accurately the shape of the pressure-composition curves and y – x curves, in the region of the critical point. The critical locus for the 2-propanol-water system in Figure 6 has been drawn through the single phase experimental points, and is only approximate; the amount of material in the still may not have been the quantity required to give the critical volume, although this amount was estimated approximately from the generalized charts and the pseudoreduced conditions computed using Kay's rule (*35*).

Hougen and Watson (*29*) state that, for all except pure compounds or mixtures of compounds differing little in

Table IV. Experimental Vapor-Liquid Equilibrium Data 2-Propanol-Water

Mole Fraction 2-Propanol in Liquid	Mole Fraction 2-Propanol in Vapor	Pressure, P.S.I.A.
	At 150°C.	
0.004	0.094	75
0.010	0.151	80
0.014	0.233	88
0.026	0.315	98
0.050	0.382	112
0.104	0.435	117
0.164	0.461	120
0.253	0.501	124
0.267	0.490	124
0.378	0.527	127
0.495	0.574	131
0.570	0.611	132
0.588	0.621	132
0.661	0.667	132
0.710	0.699	133
0.745	0.726	132
0.818	0.788	131
0.905	0.880	128
0.941	0.923	125
	At 200°C.	
0.017	0.145	268
0.024	0.198	286
0.036	0.253	305
0.052	0.297	321
0.072	0.336	339
0.105	0.363	349
0.151	0.390	361
0.201	0.413	369
0.389	0.495	394
0.521	0.564	402
0.599	0.613	407
0.610	0.618	404
0.650	0.648	406
0.682	0.673	403
0.706	0.691	404
0.788	0.762	397
0.862	0.837	389
0.934	0.917	379
	At 250°C.	
0.011	0.078	625
0.025	0.148	678
0.037	0.181	714
0.056	0.222	752
0.077	0.267	791
0.116	0.304	825
0.175	0.339	855
0.251	0.380	890
0.380	0.448	930
0.489	0.521	950
0.541	0.557	960
0.605	0.612	960
0.638	0.638	960^{a}
0.669	0.669	952^{a}
0.702	0.702	945^{a}
0.738	0.738	941^{a}
	At 275°C.	
0.026	0.114	1001^{b}
0.034	0.148	1047^{b}
0.050	0.184	1085^{b}
0.067	0.211	1122^{b}
0.087	0.243	1156^{b}
0.119	0.270	1190
0.158	0.293	1232
0.200	0.319	1261
0.223	0.330	1275
0.247	0.342	1289
0.262	0.353	1296
0.280	0.359	1310
0.291	0.366	1318
0.295	0.379	1323
0.310	0.379	1325
0.353	0.395	1345
0.369	0.394	1350
0.419	0.419	1348^{a}
	At 300°C.	
0.003	0.018	1290^{c}
0.015	0.210	1358^{d}
0.095	0.222	1690^{d}
0.142	0.253	1699
0.195	0.267	1753
0.273	0.273	1791^{a}

[a] Single phase.
[b] Slightly gassy vapor sample.
[c] Vapor sample gassy. Data in error.
[d] Both samples gassy. Data in error.

Table V. Vapor Pressure of 2-Propanol

Temp., °C.	Pressure, P.S.I.A.
144.3	108.9
150.0	126.7
175.0	233.2
200.0	389.5
216.3	542
225.0	650

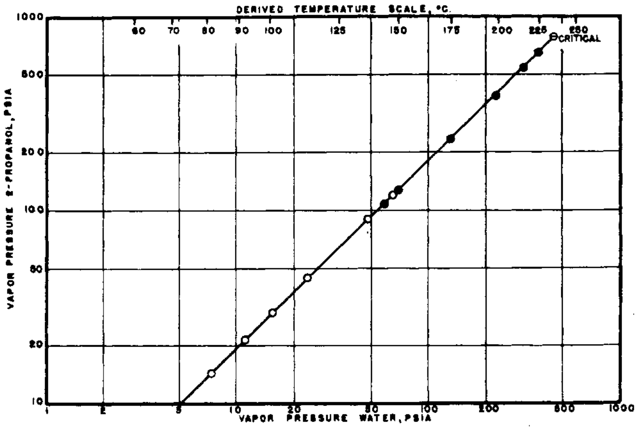

Figure 7. Vapor pressure of pure 2-propanol

Reference substance water
○ Wilson and Simons
⊖ Petrohol Data Book
● This work

physical properties, the pseudocritical temperature and pressure [using Kay's rule (*35*)] are less than the true critical temperature and pressure. This is not true for either of the systems studied here; the pseudocritical properties for mixtures rich in ethanol are considerably higher than the true critical properties.

The presence of a maximum pressure azeotrope is responsible for the flat maximum on the pressure-composition plots at 150° and 200° C. The liquid line (upper line) and the vapor line (lower line) lie so close together for the alcohol-rich end of the pressure-composition diagram that on Figure 5 they appear as a single line.

At 250° C. for both systems, the shape of the curves shows that the azeotropic composition is approximately the critical composition—that is, the curves reach a maximum with a zero slope on the pressure-composition diagram; and on the $y - x$ diagram, they become tangent to the 45° line. It is not possible to establish whether or not the azeotropes exist at this temperature. Isobaric $y - x$ plots for the systems have been prepared and presented in Figures 8 and 9. Also plotted on these figures are the 1-atm. vapor-liquid equilibrium data. From Figure 9, it can be seen that for liquid compositions below 0.05 mole fraction of 2-propanol, the vapor-liquid equilibria are substantially the same for this experimental work at 100 p.s.i.a. as for Wilson and Simon's work (*78*) at 1 atm. This result is unexpected, and

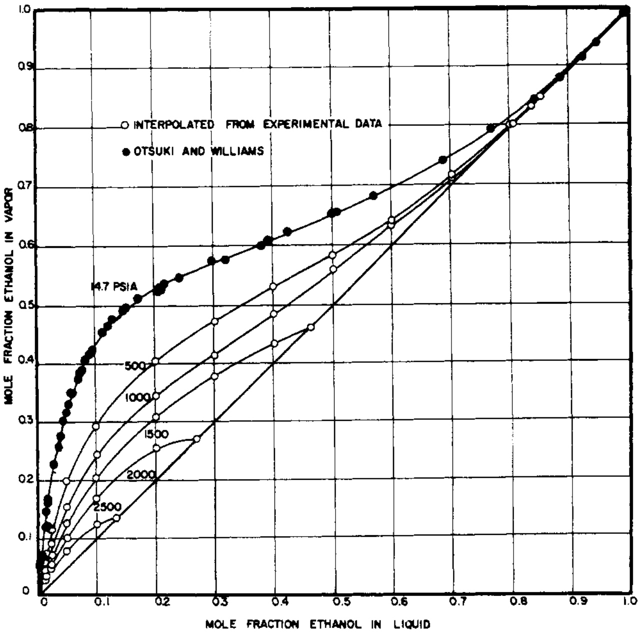

Figure 8. *y, x* isobars of ethanol-water

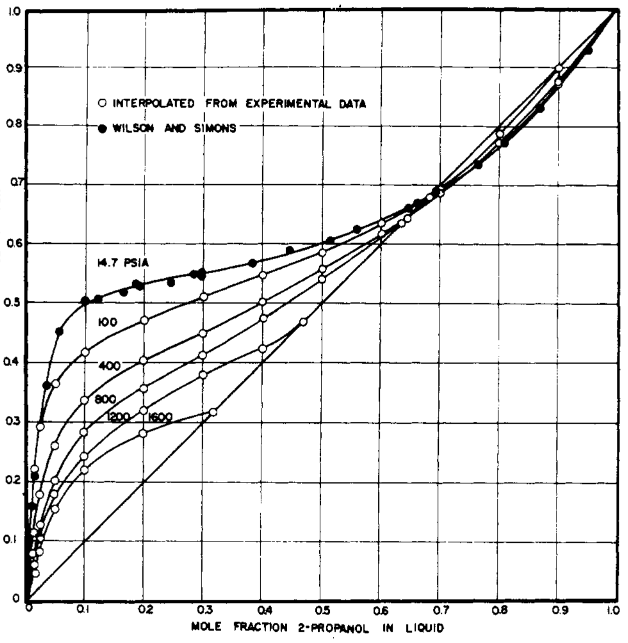

Figure 9. *y, x* isobars of 2-propanol-water

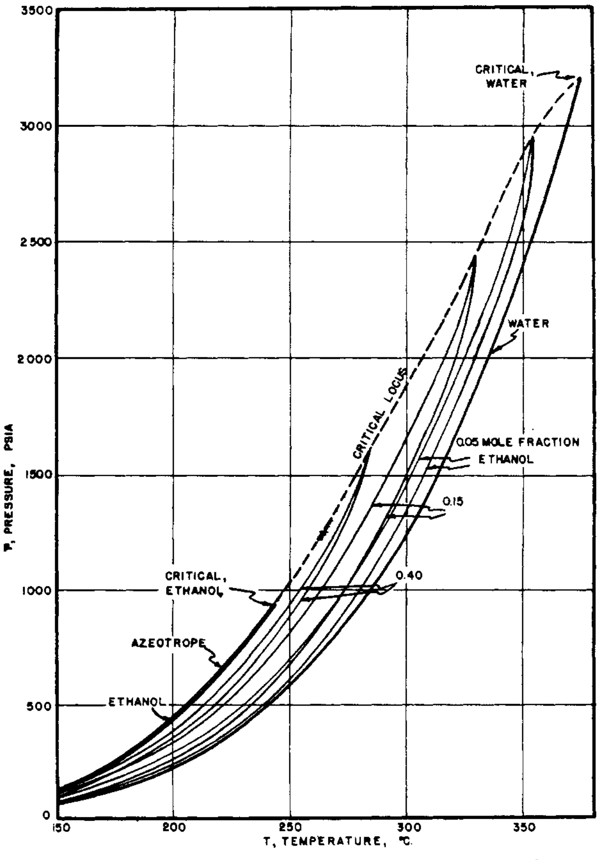

Figure 10. Pressure-temperature diagram of ethanol-water

indicates inaccuracy in one of these sets of data. There is no reason to believe that refluxing occurred in the still while the present data were being taken, a cause of rich vapor composition, as the external wall temperatures of the still were maintained 2° to 5°C. above the liquid temperature.

For comparison with other systems, pressure-temperature diagrams were constructed and are presented in Figures 10 and 11. Because of the crowding together of the border curves it is difficult to include many compositions on this type of plot. This *p, t, x, y* space figure so formed is typical of many systems exhibiting a maximum pressure homogeneous azeotrope. Similar remarks apply to the ethanol-water system.

Starting with the vapor-pressure curve of pure alcohol, the addition of water results in an extremely narrow border curve which lies completely above the vapor pressure curve for the alcohol (not shown in diagrams). As the water content is increased, the dew and bubble point curves merge into a single line for the azeotropic composition, which represents the maximum pressure possible at any temperature. As the water content is further increased, the space figure becomes curved and skewed, so that the upper part of the border curves lies below, and the lower part, above the vapor pressure curve for the alcohol. Eventually a composition is reached where the border curves lie completely between the vapor pressure curve of the alcohol and the curve for pure water. This skewing of the *p, t, x, y* space, as shown in the region rich in alcohol, is characteristic of systems whose components form a maximum-pressure azeotrope which persists up to the critical temperature, as has been pointed out by Kay and Rambosek (*36*). These relations can also be seen by studying the pressure-composition diagrams.

These systems do not exhibit any maximum or minimum critical temperature or pressure, as can be seen from the critical loci in Figures 10 and 11. The critical locus for the 2-propanol–water system (Figure 11) is only approximate because of the limited data available from this experimental work.

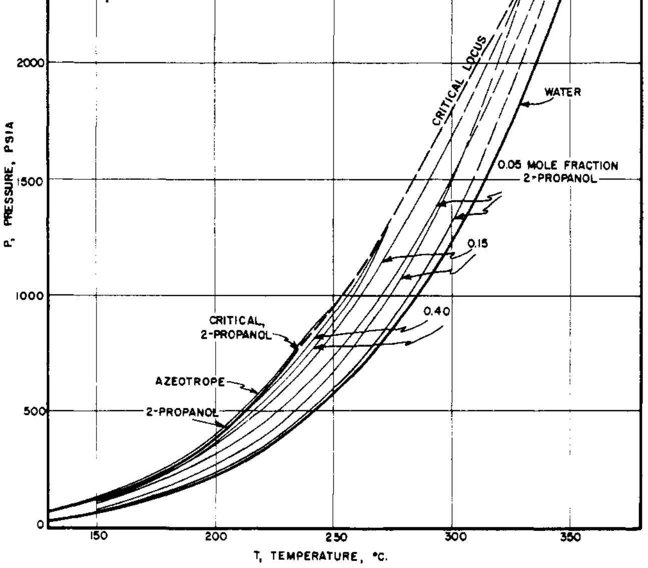

Figure 11. Pressure-temperature diagram of 2-propanol–water

The apparently sharp-pointed boundary curves on the pressure-temperature diagrams, or on the pressure-composition diagrams, indicate that the cricondentherm, the critical, and the point of maximum pressure coincide, and any zones of retrograde condensation are absent, or very small. Previous work by Griswold and others (*24*) for the ethanol-water system also led to this conclusion.

A more detailed discussion about the limiting shape of the various lines is given by Barr-David (*2*).

Alternative pressure-temperature plots were attempted to improve the clearness of these graphs. A plot of log pressure *vs.* reciprocal temperature gave a series of almost straight lines. As with the previous plots, the lines crowded together and became confusing. A better way of presenting the data was to use a reference-substance plot, and to plot the logarithm of the ratio of total pressure in the system to the vapor pressure of water, against the vapor pressure of water at the same temperature, as a reference substance. At conditions removed from the critical of either component, this should be a series of straight lines. As critical conditions are approached, the lines become curved. This method of plotting was found to be too sensitive and the data points were scattered.

Other methods of correlation of the vapor-liquid equilibrium data have been proposed. Othmer and Gilmont (*52*) claim that a logarithmic plot of the mole fraction in the vapor *vs.* the total pressure, with mole fraction in the liquid as parameter yields a series of straight lines for many binary mixtures including ethanol-water over limited ranges [Otsuki and Williams (*56*)]. Figures 12 and 13 show such plots. Over the extended range of the work, the lines are slightly curved, the curvature increasing as critical conditions are approached.

Azeotropic Behavior. The behavior of the azeotrope for the system 2-propanol–water is particularly interesting, be-

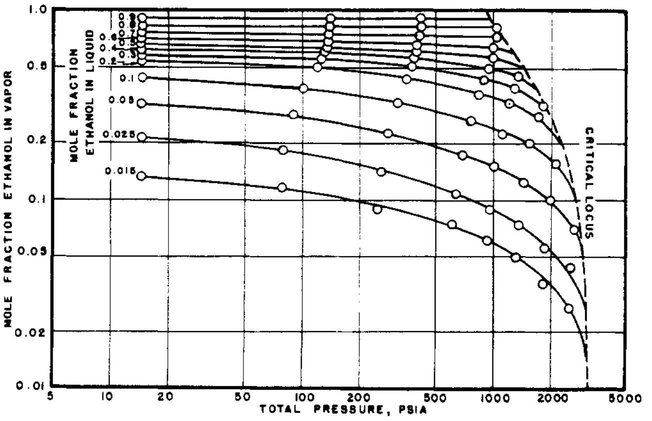

Figure 12. *y, p* diagram at constant *x* of ethanol-water

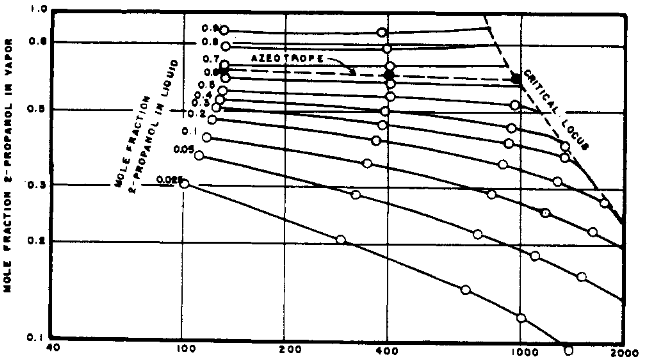

Figure 13. *y, p* diagram at constant *x* of 2-propanol–water

Table VI. Effect of Pressure on Azeotrope 2-Propanol-Water

Pressure, P.S.I.A.	Boiling Point, °C.	Composition M.F. 2-PrOH	Reference
59.7	120.45	0.6950	Wilson and Simons (*78*)
14.69	80.10	0.6870	Wilson and Simons (*78*)
7.35	63.90	0.6750	Wilson and Simons (*78*)
3.67	49.33	0.6705	Wilson and Simons (*78*)
1.83	36.00	0.6670	Wilson and Simons (*78*)
14.69	80.4	0.681	Lebo (*43*)
14.69	80.3	0.687	Lecat (*44*)
14.69	80.37	0.6854	Young and Fortley (*80*)
14.69	80.3	0.678	Schumaker and Hunt (*69*)
14.69	...	0.6835	Langdon and Keyes (*42*)
14.69	80.16	0.6813	Brunjes and Bogart (*9*)
	31.8	0.658	Miller and Graves (*50*)
	59.4	0.675	Miller and Graves (*50*)
	80.3	0.681	Miller and Graves (*50*)
	124.6	0.684	Miller and Graves (*50*)
	151.1	0.671	Miller and Graves (*50*)
	171.6	0.662	Miller and Graves (*50*)
	185.0	0.652	Miller and Graves (*50*)
	195.6	0.646	Miller and Graves (*50*)
	204.8	0.639	Miller and Graves (*50*)
132	150	0.6775	This work
405	200	0.6435	This work
960	250	0.64	This work

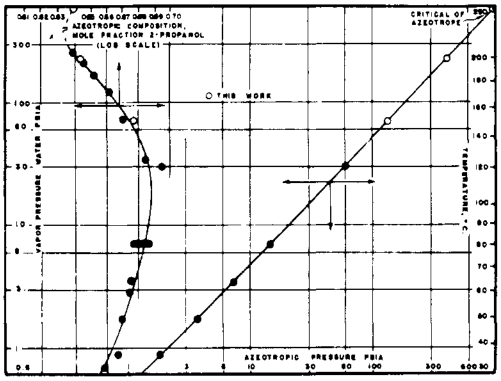

Figure 14. Correlation of azeotropic temperatures, pressures, and compositions of 2-propanol-water

cause it is the only system reported in which the azeotropic composition passes through a maximum with increasing pressure. The azeotropic compositions from this experimental work were determined by large scale $y-x$ plots and are reported in Table VI. From the experimental data it appears that the azeotropic composition is approximately the critical composition at 250° C. The present data show good agreement with those of other investigators.

Othmer and Ten Eyck (*55*) have indicated a method of correlating the azeotropic temperatures, pressures, and compositions for various binary systems. The azeotropic pressure when plotted against the vapor pressure of water as a reference substance, at the same temperature on a logarithmic plot yields a straight line. Figure 14 shows for these present data this line to be almost straight, the curvature probably being due to the extended range of these data. Othmer also claims that the azeotropic composition *vs.* the vapor pressure of water at the same temperature yields a straight line, as he illustrated for the system ethanol-water [Otsuki and Williams (*56*)]; but in this plot the composition scale is so compressed as to yield a horizontal, straight line. Figure 14 shows such a plot for the system 2-propanol-water, with an extended logarithmic composition scale. The plot is far from a straight line.

The azeotropic compositions for the ethanol-water system could not be determined with any degree of accuracy because of the shape of the plots. For this reason no attempt has been made to correlate the azeotropic data of this system with that reported in the literature.

Vapor Pressure of 2-Propanol. For determining limiting values of many of the previous graphs, and for thermodynamic calculations, the vapor pressure of pure 2-propanol was measured. The data are summarized in Table V and presented as a reference-substance plot in Figure 7. This plot shows the excellent agreement between the present work, the data given by Wilson and Simons (*78*) and the value of the critical pressure given in the Petrohol data book (*17*).

Decomposition Tests. During the study of the low alcohol-concentration end of the 250° and 275° isotherms of the 2-propanol-water system, traces of gas were found to be dissolved in the vapor sample. This gas formed small bubbles in the pycnometers, and care had to be taken to avoid errors from this cause in the density determinations. The gas formation was evident only for the dilute concentration range—namely, 0.15 mole fraction of 2-propanol in the reboiler, or less. At 300° large amounts of gas were formed for concentrations of 2-propanol in the reboiler of 0.15 mole fraction or less, the lowest concentration tested being 0.01 mole fraction of 2-propanol. The extent of gas formation was sufficient to prevent experimental vapor-liquid equilibrium data from being collected in this range. The higher concentration range of the 2-propanol-water isotherm at 300° up to the critical composition (0.273 mole fraction) did not show gas formation at all, and the data were collected satisfactorily. No attempts were made to measure the vapor-liquid equilibria for this system at any higher temperatures.

The gas was identified, by its infrared spectrum and by its power of decolorizing a solution of bromine in chloroform, to be propene. Because hydrogen and acetone can easily form from the dehydrogenation of 2-propanol in the presence of the correct catalysts, the absence of dehydrogenation was confirmed by the infrared spectrum and by 2,4-dinitrophenylhydrazine. The infrared spectrum also showed diisopropyl ether to be present.

Apparently the decomposition was a simple dehydration reaction. 2-Propanol is known to dehydrate and propene to hydrate with greater ease than ethanol and ethylene, respectively. Because only the more dilute propanol solutions decomposed, and the stronger solutions, the decomposition of which is more thermodynamically favorable, did not decompose, the reaction was considered to be catalyzed by the oxide on the A.I.S.I. 4130 steel walls of the still, or by the steel itself, rather than to be a homogeneous reaction. This was confirmed by a series of decomposition tests.

These decomposition tests were conducted as follows. A series of glass tubes containing aqueous solutions of 2-propanol ranging in concentration from 0.01 to 1.0 mole fraction of 2-propanol was sealed. Some tubes contained pieces of A.I.S.I. 4140 steel, previously cleaned and completely freed from oxide by boiling in a strong aqueous solution of hydrochloric acid. These tubes were placed in a high-pressure steel bomb, some dilute propanol was added to the bomb outside the tubes to maintain approximately equal pressures on both sides of the glass tubes, and the bomb was heated to 320° C. for 10 hours and then cooled.

The 2-propanol solution (0.1 mole fraction) which was placed in the steel bomb (Type 410 stainless steel) outside the glass tubes was extensively decomposed into propene, and much propene had polymerized to a yellow, oily polypropene. None of the samples of 2-propanol in the glass tubes was found to be decomposed. Apparently neither the glass (which was heavily etched by the aqueous solutions on both sides) nor the oxide-free steel is a catalyst for the dehydration of 2-propanol into propene.

Although no evidence of gas formation was found during the determination of the vapor-liquid equilibria of ethanol-water, similar tests were conducted using ethanol solutions in sealed glass tubes, some containing A.I.S.I. 4140 steel. Once again no decomposition of the solutions inside the glass tubes occurred. Very slight decomposition of the 0.1

mole fraction ethanol solution in the steel bomb did occur, a small amount of gas (presumed to be ethylene) collecting in the steel bomb.

From these tests it was concluded that the oxide formed on A.I.S.I. 4140 and similar steels is an active catalyst for the decomposition of dilute 2-propanol solutions. The catalyst is active only in solutions containing less than 0.15 mole fraction of 2-propanol in the liquid phase (at 250° this corresponds to about 0.33 mole fraction in the vapor phase). The decomposition is slow at 250° and 275°, but is fast and extensive at 300°C. No tests were made to determine in which phase the catalyst was active, nor were tests conducted to determine the catalytic properties of austenitic stainless steel in this dehydration reaction. Possibly a still made of 300-series stainless steel would have permitted the experimental work in the 2-propanol-water system to be continued to higher temperatures.

THERMODYNAMIC ANALYSIS OF DATA

Theoretical Considerations Based on Gibbs-Duhem Equation. Vapor-liquid equilibrium data may in principle be checked for thermodynamic consistency by means of the Gibbs-Duhem equation. For isothermal data a pressure-correction term is necessary, as the commonly presented simple form of this equation holds for constant pressure and constant temperature, which for binary solutions is not permitted by the phase rule. The error in omitting the pressure term becomes great as the critical state of one of the components is approached. A form of the Gibbs-Duhem equation, for the liquid phase of a binary solution, suitable for isothermal data, is given by Ibl and Dodge (*31*), and may be written:

$$\frac{x\, d\ln \bar{f}_a}{dx} + \frac{(1-x)\, d\ln \bar{f}_w}{dx} = \frac{v_m}{RT}\,\frac{dp}{dx} \tag{1}$$

If sufficient information is available, the necessary quantities in Equation 1 may be calculated, and the data may be checked by graphical differentiation at various compositions. It is convenient to use an integrated form of the Gibbs-Duhem equation to obviate the need for graphical differentiation. A suitable form is:

$$\int_0^1 \ln \frac{\bar{f}_a/x_a}{\bar{f}_w/x_w}\, dx = \ln f_a/f_w - \frac{1}{RT}\int_{p_w}^{p_a} v_m\, dp \tag{2}$$

Without the correction term for the variation in pressure, this equation can be put in the form:

$$\int_0^1 \ln \frac{\gamma_a}{\gamma_w}\, dx = 0 \tag{3}$$

This is the equation used by Redlich and others (*62*) for testing experimental data.

An integrated equation such as Equation 2 can be used only below the critical temperature of both components of the solution; above the critical temperature of one component the equation cannot be integrated over the composition range $x = 0$ to $x = 1$.

The most common method of correlating vapor-liquid equilibria by the Gibbs-Duhem equation is to make use of the solutions given by van Laar (*41*), Margules (*47*), or Scatchard and Hamer (*67*). A review of these relations is given by Wohl (*79*) and their application to specific cases is given by Carlson and Colburn (*11*). For a reliable thermodynamic check one must use equations such as 2 or 3, but when the experiments are made at elevated pressures this involves difficulties which make the results unreliable.

The problem of testing vapor-liquid equilibrium data resolves into calculation of the various terms in the Gibbs-Duhem equation. Difficulties arise in the calculation of the fugacities of the components in the solution for associating compounds at high pressure, because of insufficient information. Because at equilibrium the fugacity of a component in the vapor phase is equal to the fugacity of the component in the liquid phase, the fugacities of the components in the vapor solution are computed, and used in the equations involving liquid-phase fugacities.

Methods of Calculation of Fugacities. The fugacity of a component in a solution may be defined by the expression:

$$\ln \bar{f}_i = \frac{1}{RT}\int_0^p (\bar{V}_i - V_i)\, dp + \ln f_i\, y_i \tag{4}$$

If necessary *P-V-T* data are available, the fugacity of the components in the solution may be exactly evaluated by such an expression. Because of the very meagre amount of *P-V-T* data available for gas mixtures at various compositions, such methods are of little value, and for this reason many attempts have been made to use the data on the individual components to predict those for the mixture.

Two general methods of attack on the problem have been used. One involves the development of an equation of state for the mixture, which is then used to integrate the thermodynamic expression for the fugacity. The other approach is based on empirical rules such as the Lewis and Randall fugacity rule or the use of a pseudocritical pressure and temperature of the mixture combined with the use of generalized properties to obtain the fugacity of a mixture, and from this component fugacities are obtained by the relation for partial molal quantities.

Equations of State. In this method the equations of state for the pure components are used, the constants being combined in some manner, so that the resultant equation of state is valid for the mixture. Substitution of the equation of state for the mixture into an equation such as 4 gives the required fugacities.

Three commonly used equations of state are those of van der Waals, Beattie-Bridgeman (*4*) and Benedict, Webb, and Rubin (*6*, *7*). Methods of combination of the constants of equations of state are given by Dodge (*14*). However, the choice of method of combining constants is semiempirical, and no guiding rules can be given as to the best method in all cases.

This method of calculation of fugacities of components of a binary solution can never be strictly applied in the case of vapor-liquid equilibrium, because each component is necessarily stable in only one phase when pure at the temperature and pressure of the solution. It is still considered valid to combine the constants, even though one component does not exist as vapor under the conditions. Little work has been done to test the validity of this extrapolation.

Gilliland (*21*) proposed a method of treating the compressibility of gas mixtures that is based on the use of an equation of state of the linear-isometric form and on various schemes for combining the constants. The fugacity equation based on this method is given by Gilliland and Sullivan (*22*). Kritschewsky (*38*) states that this rule for fugacity gives better agreement with the true fugacities at high pressures than either Bartlett's rule or the Lewis and Randall rule. The linear isometric rule is complicated to use and does not hold as the saturation line is approached, which is the very region of interest in vapor-liquid equilibrium calculations.

More recently a simple equation of state has been proposed by Redlich and Kwong (*63*), whose constants can be determined from the critical pressure and temperature of the substance. Redlich, Kister, and Turnquist (*62*) show how the constants of this equation may be combined to give the fugacity of a component in a solution, and present graphs which greatly simplify the calculation of the fugacity.

Lewis and Randall Rule. Calculation of the fugacities by assuming ideal solution is probably the most widely used method. This method is commonly called the Lewis and

Randall (*45*) rule. Because of the extensive use of this rule, it will be considered in some detail.

Because volume is an extensive property,

$$v = \bar{v}_a x_a + \bar{v}_b x_b + \ldots + \bar{v}_n x_n \tag{5}$$

An ideal solution is one so defined that the partial molal volumes are independent of composition up to the pressures of the solution and in the range of temperatures which includes the temperature under consideration. If the various components of an ideal solution are stable in the pure state at the pressure and temperature of the solution, then

$$\bar{v}_i = v_i \tag{6}$$

the molal volume of pure i at p and t. Then Equation 5 becomes

$$v = v_a x_a + v_b x_b + \ldots v_n x_n \tag{7}$$

or the volumes are additive.

For the reasons previously stated in considering the equations of state for the components, Equation 7 can never be strictly applied in the case of vapor-liquid equilibrium because one component does not exist as a gas under the conditions. In practice the necessary information is extrapolated to give the information required.

Substitution of 6 in 4 gives

$$\bar{f}_i = y_i f_i \tag{8}$$

Equation 8 represents the Lewis and Randall fugacity rule. The fugacity of the pure component, f_i, at the temperature and pressure of the solution may be obtained from *P-V-T* data for pure *i*, or from generalized correlations.

It must be remembered that Equation 8 strictly applies only when the volumes are additive over the complete pressure range, from zero pressure up to the pressure of the experimental data, and the pure component is stable as a gas at the pressure and temperature of the solution. This can be readily seen from Equation 4.

The error in the Lewis and Randall rule is the value of the integral in this equation, and it can be seen that over the pressure range from zero pressure up to the pressure p of the solution, $\bar{v}_i$ must be equal to v_i.

To summarize the conditions for a solution to be ideal for all compositions, Equation 6, 7, or 8 must be valid for all pressures up to the pressure of the solution, and over the range of temperatures which includes the temperature of the solution. However, a solution can behave ideally at a certain composition if these equations hold over the composition range which includes the composition under question, the temperature range which includes the temperature of the solution, and for all pressures up to the pressure of the solution. Van Ness (*74*) gives a more complete discussion of the ideal solution and the conditions of its validity.

It is concluded by Gilliland and Sullivan (*22*) that the Lewis and Randall rule can give large errors at high pressure, and, as an approximate criterion for most mixtures, it is not likely to be satisfactory at pressures greater than 0.6 times the critical pressure of the component in question. Hougen and Watson (*30*) state that the rule is satisfactory for pseudoreduced pressures of less than 0.8. This is much less limiting than the restriction imposed by Gilliland and Sullivan, and would permit the use of this rule at pressures far in excess of the critical pressure for a component in solution with another component with a much higher critical pressure. The fugacities computed in the range permitted by Hougen and Watson's criterion must be in error under these circumstances.

Partial Molal Method. A method often employed for the calculation of fugacities is to calculate the fugacity of the mixture by means of correlations developed for pure gases, using the pseudoreduced temperature and pressure of the mixture, evaluated by combination of the critical constants of the pure components.

The fugacity of the mixture is defined by the equation:

$$\ln f_m = \frac{1}{RT} \int_0^p v_m \, dp \tag{9}$$

The concept of fugacity of a mixture differs from the concept of fugacity of a component—that is, an escaping tendency. A similar physical meaning cannot be applied to the concept. It is best regarded as a simple method of expressing the integral above.

The fugacity of any component in the gaseous mixture is then calculated by the relation

$$\ln \frac{\bar{f}_i}{y_i} = \frac{\partial [n_1 + n_2 + \ldots] \ln f_m}{\partial n_i} \tag{10}$$

The differentiation may be performed graphically on a plot of f_m vs. the number of moles of the component.

The need for carrying out the graphical differentiation has been removed by a modification of Gamson and Watson (*19*), while Joffe (*32*) showed that the generalized charts for gases may be used for calculation with a method similar to that of Gamson and Watson. The procedure developed by Joffe is the most convenient of the partial molal techniques and probably gives the most satisfactory method for calculation of the fugacities of components in a solution, except when partial molal volume data for the mixture are available.

Assuming (1) that f_m is a function of p, T, and the y's but that the fugacity coefficient $\frac{f_m}{p}$ is a function only of p_R and T_R; (2) that the generalized correlation for fugacity coefficient of a gas is valid; and (3) that Kay's rule may be used for the calculation of the pseudocritical pressure and temperature of the mixture, the following equation is obtained:

$$\ln \frac{\bar{f}_i}{y_i} = \ln f_m + \frac{Z_m - 1}{p_c}(p_c - p_{c_i}) + \frac{H^\circ_m - H_m}{RTT_c}(T_c - T_{c_i}) \tag{11}$$

In his development, Joffe assumed that f_m was a function only of p_R and T_R. Bretton (*8*) pointed out the error on this and gave a more logical derivation leading to the same final equation as obtained by Joffe.

Bartlett's Rule. Bartlett's rule of additive pressures states that

$$p = y_1 p_1 + y_2 p_2 \tag{12}$$

where p_1 and p_2 are taken at the molal concentration of the mixture.

Kritschewsky (*38*) has shown that combination of Equations 12 and 4 gives the fugacity equation, referred to by Gilliland and Sullivan (*22*) as Bartlett's rule.

$$\ln \bar{f}_1 = \ln y_1 f_1 + \frac{v_m (p - p_1)}{RT} \tag{13}$$

where

v_m = molal volume of mixture

Kritschewsky's Rule. Kritschewsky (*37, 39*) has proposed an improvement for Bartlett's rule of additive pressures by adding a correction term that is a function of the pressures and the compositions, but not the temperature. This rule, and the fugacity equation derived from it, are given by Gilliland and Sullivan (*22*). This method has the great disadvantage of requiring that *P-V-T* data for one mixture composition be known.

Thermodynamic Consistency of Experimental Data. The thermodynamic consistency of some of the experimental

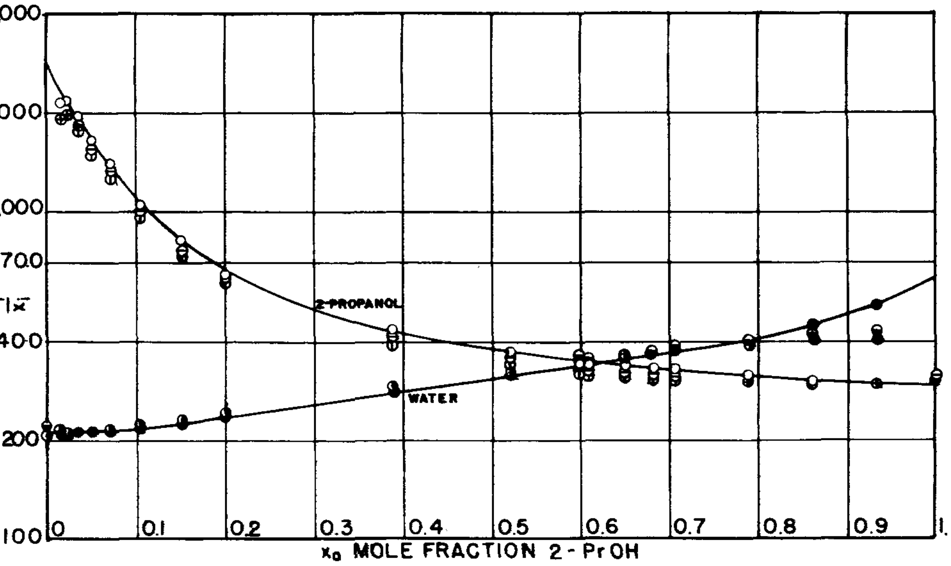

Figure 15. Fugacities of components in solution

2-propanol-water, 200 ° C.

Alcohol	Water	
⊙	○	Computed using method of Joffe
⊖	●	Computed using method of Redlich *et al.*
⦶	◑	Computed using ideal solutions

data of this research was tested by means of the Gibbs-Duhem equation, expressed in the form of Equation 2. Lack of *P-V-T* data for the ethanol-water and 2-propanol-water systems precludes the exact thermodynamic calculation of the fugacities of components in solution. It is therefore necessary to resort to other methods of calculation outlined in the previous section. Because of the inconclusive results due to questionable assumptions made, the consistency of the 200° isotherm for the 2-propanol-water system was the only one tested. The disadvantages and the assumptions involved in the various methods are discussed.

Calculation of Fugacities. The 200° isotherm for the 2-propanol-water system has been computed using the Lewis and Randall rule. The results are presented graphically in Figure 15. This graph was extrapolated to give limiting values of $(\bar{f}_i/x_i)$. The assumptions made in this computation are known to be not valid. Although the pressures involved are less than 0.6 times the critical pressure of the component in question, the limit imposed by Gilliland and Sullivan (*22*), the volumes of the components of the solution are not additive for the conditions previously stated because of the associated nature of each component, and interassociation of the two molecular species. Furthermore, some error is introduced by the use of the generalized fugacity coefficient plot of Hougen and Watson (*28*) for the evaluation of the fugacities of the pure components.

The fugacity data were calculated also by the method proposed by Joffe (*33*). This method probably is the most satisfactory approach, but the values obtained for the fugacities are still in question, because of the assumptions involved—namely, that the generalized correlations for gases are valid, and that Kay's rule may be used for calculation of the pseudocritical temperature and pressure. Both assumptions are known to be incorrect. The values obtained are also presented in Figure 15. These were computed using the generalized charts of Hougen and Watson (*28*).

Another method used for the calculation of the fugacities was that proposed by Redlich, Kister, and Turnquist (*62*) based on the Redlich and Kwong (*63*) equation of state. This method of calculation assumes that the Redlich and Kwong equation of state holds for both components and that the method of combination of the constants of the equations of state is valid. Again with the 2-propanol-water system the extent of deviation from these assumptions is unknown. The results for the 200° C. isotherm are summarized in Figure 15.

Examination of Figure 15 shows fair agreement between the three methods of calculation of fugacity. Because some of the assumptions which are open to doubt, such as the law of corresponding states, used for these calculations are common to all three methods, this result is not too surprising. The fugacity of 2-propanol in 2-propanol-rich mixtures is probably greatly in error, because, in the case of the fugacity computed by assuming ideal solutions, the integral term in Equation 4 is omitted. This integral is by no means negligible in the case of conditions approaching the critical of the component under consideration. Because the fugacities computed by the other methods agree well with the fugacities computed by ideal solutions in this range, these other methods are likewise probably in error.

Thermodynamic Consistency. The thermodynamic consistency of the 200° C. 2-propanol-water isotherm was checked by the use of Equation 2, based on the Gibbs-Duhem equation. The graphical integration

$$\int_0^1 \ln \frac{\bar{f}_a/x_a}{\bar{f}_w/x_w}\,dx$$

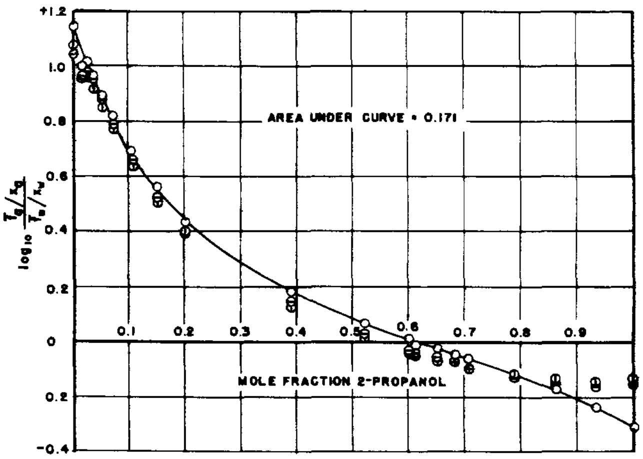

Figure 16. Evaluation of the integral $\int_0^1 \log \frac{\bar{f}_a/x_a}{\bar{f}_w/x_w}\,dx$

For legend see Figure 15.

is shown in Figure 16. For the fugacity data evaluated by Joffe's equation the value of this integral is 0.394.

From the generalized charts of Hougen and Watson (*28*) and the pseudoreduced temperature and pressure calculated by Kay's rule (*35*) the second term in Equation 2—, $\ln \frac{f_a}{f_w}$ — has the value of 0.375.

Obviously, no positive value of the pressure correction term $\frac{1}{RT}\int_{p_w}^{p_a} v_m \, dp$ in Equation 2 will satisfy this equation. Order of magnitude limits of the value of this correction can be calculated, and were found to lie between 0.01 and 0.06. Thus the data do not check by Equation 2. The fugacity calculations are known to be in error. Accordingly, no conclusions can be reached concerning the thermodynamic consistency of the data.

CONCLUSIONS

The thermodynamic consistency of binary liquid-vapor phase equilibrium data may, in principle, be checked by means of the Gibbs-Duhem equation which is a rigorous relation based on thermodynamics. In practice the use of the equation requires the calculation of the fugacities of the components in the vapor mixture. To do this rigorously requires *P-V-T* data on the gas mixture which are completely lacking for all mixtures of interest. Recourse must then be had to various empirical rules for this calculation, which give reasonably good approximations but not good enough for the purpose. Furthermore, these methods all give somewhat different results and it is obviously not possible to select any one as being the most reliable. These conclusions apply especially to the case of elevated—i.e., above atmospheric—pressures where the deviations from the ideal gas law become more and more marked as the pressure is increased. For equilibria determined at atmospheric pressure, the Gibbs-Duhem equation in the forms applying to an ideal gas can probably be relied upon for a consistency check.

NOMENCLATURE

f = fugacity of a pure component
$\hat{f}$ = fugacity of a component in a solution
H = enthalpy
n = number of moles of a component
p = total pressure
R = universal gas constant
T = absolute or thermodynamic temperature
v = molal volume of a pure liquid or vapor
$\bar{v}$ = partial molal volume of a component in a solution
x = mole fraction of a component in the liquid phase
y = mole fraction of a component in the vapor phase
Z = compressibility factor = $\frac{pv}{RT}$
γ = activity coefficient

SUBSCRIPTS AND SUPERSCRIPTS

a = alcohol or a component in general
b = a component
c = critical state (without another subscript it refers to a mixture)
i = any component
m = mixture
n = nth component of an n-component system
w = water
1,2 = components of a solution
o (super) = state of $p \to 0$

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Thermal Stability of Concentrated Nitric Acid

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Concentrated nitric acid containing more than 90 weight % of HNO_3, when confined in a closed container at room temperature and above, dissociates to form oxides of nitrogen, water, and oxygen. Because of the low solubility of the oxygen in the equilibrium mixture, considerable pressure may result if the ratio of the vapor volume to the liquid volume in the container is small. In view of the wide use of fuming nitric acid as a component of binary liquid rocket propellants and as a nitrating agent, a knowledge of the thermal stability, therefore, is of real practical importance in the handling and storage of the concentrated acid.

In the course of an investigation of the volumetric and phase behavior of concentrated nitric acid (*8–10*) *P-V-T* data were obtained at physicochemical equilibrium for mixtures of known initial composition. By the application of the principles of chemical thermodynamics to these data, information has been obtained on the chemical stability of the concentrated acid as a function of its initial composition.

ESTIMATION OF EQUILIBRIUM COMPOSITION

The dissociation of nitric acid in the heterogeneous vapor-liquid region is a kinetically complex reaction which is explained as proceeding according to the following steps (*6*):

$$\begin{aligned} 2\,HNO_3 &\rightleftarrows N_2O_5 + H_2O \\ N_2O_5 &\rightleftarrows N_2O_3 + O_2 \\ N_2O_3 &\rightleftarrows NO + NO_2 \\ NO + \tfrac{1}{2}O_2 &\rightleftarrows NO_2 \end{aligned}$$

The summation of these steps leads to the over-all stoichiometric relation

$$2\,HNO_3 = H_2O + N_2O_4 + \tfrac{1}{2}O_2 \qquad (1)$$

where N_2O_4 designates an equilibrium mixture of N_2O_4 and NO_2.

Because of the complexity of the solubility relations of oxygen and oxides of nitrogen and the paucity of data on the activity coefficients of the various species, calculation of the true thermodynamic equilibrium constants expressed in terms of the activities of the species is practically impossible. However, it is possible to calculate an apparent equilibrium "constant" in terms of the equilibrium mole fractions of nitric acid, nitrogen tetroxide, and water, defined as

$$K_x = \frac{(N_2O_4)\,(H_2O)}{(HNO_3)^2} \qquad (2)$$

For its calculation, the composition of the liquid phase at equilibrium conditions is needed. This was estimated on the basis of an oxygen material balance on the system and the stoichiometry of the dissociation reaction given by Equation 1. The oxygen balance on the system at equilibrium can be written (*9*) as

$$n_{O_2} = n^G_{O_2} + n^L_{O_2} \qquad (3)$$

$$= p_{O_2}\left[\frac{V^G}{z_{O_2}RT} + k_{O_2}V^L\right] \qquad (4)$$

where

n_{O_2} = total number of moles of oxygen in system at equilibrium formed from dissociation of nitric acid, at pressure p^∞ and temperature T
$n^G_{O_2}$ = number of moles of oxygen in gas phase
$n^L_{O_2}$ = number of moles of oxygen in liquid phase
p_{O_2} = partial pressure of oxygen in gas phase
V^G = volume of vapor phase at equilibrium
z_{O_2} = compressibility factor of oxygen at pressure p_{O_2} and temperature T
k_{O_2} = $C^L_{O_2}/p_{O_2}$ Henry's law constant for solubility of oxygen in liquid phase of equilibrium composition at temperature T
$C^L_{O_2}$ = concentration of oxygen in liquid phase
V^L = volume of liquid phase at equilibrium

The compressibility factor, z_{O_2}, obtained from a generalized compressibility chart, was found to be very nearly unity for the conditions investigated. The partial pressure of oxygen under equilibrium conditions, p_{O_2}, was obtained by correcting the total equilibrium pressure for the vapor pressures due to nitric acid, nitrogen dioxide, and water present in the liquid phase. For this purpose, the vapor pressure data for the ternary mixtures of nitric acid, nitro-