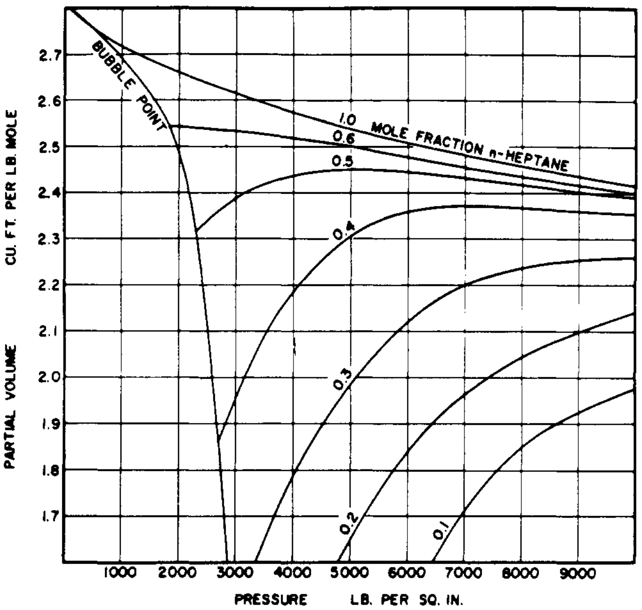

Figure 4. Effect of pressure upon partial volume of n-heptane at 280° F.

increased, at constant temperature. Such behavior is typical of that encountered for the partial volume of the less volatile component in binary hydrocarbon systems containing large mole fractions of methane. In a part of the single-phase region, negative partial volumes for the less volatile component may be encountered at the lower pressures for compositions rich in methane.

The influence of temperature, pressure, and composition upon the partial volumetric behavior appears to conform with that normally expected in such binary systems.

ACKNOWLEDGMENT

This work was carried out as part of the activities of the American Petroleum Institute Research Project 37 located at the Chemical Engineering Laboratory of the California Institute of Technology. Virginia Berry carried out most of the calculations reported here and B. Lawson Miller assisted in the preparation of the manuscript. W. N. Lacey reviewed the manuscript.

NOMENCLATURE

m_k = lb. moles of component k
n_k = mole fraction of component k
$\underline{V}$ = molal volume, cu.ft./lb. mole
$\bar{V}$ = partial molal volume, partial volume, cu.ft./lb. mole
$\underline{V}$ = total volume, cu. feet
∂ = partial differential operator

SUBSCRIPTS

j, k = components j and k
m_i = change in state during which quantity of all components other than k remains constant
m_j = change in state during which quantity of component j remains constant
P = pressure, p.s.i.
T = thermodynamic temperature, °R.

LITERATURE CITED

(1) Eduljee, H. E., Newitt, D. M., Weale, K. E., *J. Chem. Soc.* **1951**, p. 3086.
(2) Lewis, G. N., *Proc. Am. Acad. Arts Sci.* **43**, 259 (1907).
(3) Lewis, G. N., Randall, M., "Thermodynamics," McGraw-Hill, New York, 1923.
(4) Michels, A., Nederbragt, G. W., *Physica* **3**, 569 (1936).
(5) Nichols, W. B., Reamer, H. H., Sage, B. H., *Ind. Eng. Chem.* **47**, 2219 (1955).
(6) Olds, R. H., Reamer, H. H., Sage, B. H., Lacey, W. N., *Ibid.*, **35**, 922 (1943).
(7) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem., Chem. Eng. Data Ser.* **1**, 29 (1956).
(8) Roozeboom, H. W. B., "Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," vol. II, Part 1, p. 288, F. Vieweg und Sohn, Braunschweig, 1904.
(9) Sage, B. H., Lacey, W. N., *Calif. Oil World and Petrol. Ind.* **34**, 31 (1941).
(10) Smith, L. B., Beattie, J. A., Kay, W. C., *J. Am. Chem. Soc.* **59**, 1587 (1937).

Received for review July 11, 1958. Accepted August 26, 1958.

Vapor-Liquid Equilibria in Binary Systems Containing Fluorocarbons and Chlorofluorocarbons

LEWIS CHINSUN YEN and T. M. REED III
Department of Chemical Engineering, College of Engineering, University of Florida, Gainesville, Fla.

Binary solutions of the five-carbon-atom perfluorocarbons have been reported (*8*) to form ideal solutions. Solutions of perfluorocarbons with hydrocarbons form solutions which have large positive deviations from ideal behavior (*4*), to such a degree that they are usually only partially miscible at temperatures on the order of the boiling points of the compounds in the system. Molecules containing carbon, fluorine, and chlorine (called chlorofluorocarbons in this article) seem to be an intermediate class of compounds, in that they are completely miscible with hydrocarbons and with perfluorocarbons boiling in the same range. Data presented here show that chlorofluorocarbons do not form ideal solutions with either perfluorocarbons or with hydrocarbons, however. Vapor-liquid equilibria for five binary systems at 1-atm. pressure are given: perfluoroheptane (C_7F_{16}) with a perfluorocyclic oxide ($C_8F_{16}O$); 1,2-dichlorohexafluorocyclopentene ($C_5Cl_2F_6$) with 2,2,3-trichloroheptafluorobutane ($C_4Cl_3F_7$); $C_5Cl_2F_6$ with $C_8F_{16}O$; $C_4Cl_3F_7$ with $C_8F_{16}O$; and $C_4Cl_3F_7$ with normal heptane (n-C_7H_{16}).

In addition to their thermodynamic interest, some of these systems are useful as mixtures for testing the performance of distillation columns operating with the different classes of compounds (*16*). In terms of the height of packing equivalent to a theoretical plate the efficiency of a laboratory column distilling perfluorocarbons is about half that obtained when the same column is distilling hydrocarbons.

APPARATUS

Equilibrium Still. A vapor recirculating still designed by Hipkin and Myers (*7*) was adapted for the small quantities of pure compounds available. In the apparatus used by the authors the capacity of the vaporizer was only about 7 ml., while that of the contactor was 1.5 ml. The authors inserted a small collector of 0.5-ml. capacity in the vapor condensate return line, in place of the three-way valve of Hipkin and Myers. In this way a sample of the vapor may be removed without significantly disturbing the continuous recycle of condensed vapor to the vaporizer.

Such a modification was important when such small quantities were used in the still. The sampling lines were capillaries of 1-ml. internal diameter and Teflon valves were used throughout. In place of the vapor jacket described by Hipkin and Myers, a vacuum jacket was used and compensation was made for heat losses with an electrical winding on aluminum foil which was covered with asbestos insulation.

Adiabatic operation of this arrangement was accomplished by careful adjustments of the winding heater, so that the amount of liquid in the contactor remained constant during equilibration. A thermocouple well was provided in the annulus of the vacuum jacket for this purpose. The compensating windings were in two sections, one for the lower regions of the still around the contactor, and one for the upper part of the still above the contactor. The upper winding was kept at a temperature slightly above the equilibrium temperature to prevent any condensation before the condenser.

In operating the still it was supposed that equilibrium conditions had been reached after the contactor temperature remained constant over a period of 30 minutes. The vapor samples were then taken from the vapor condensate collector. Liquid samples were taken from the contactor immediately thereafter while the still was kept boiling. About 0.5 ml. of material was flushed before the samples were taken. Three samples of the vapor and three of the liquid were taken. The total sampling time was about 1 minute. The total amount of the samples was about 1.5 ml. These quantities were enough for analysis by refractive index or by gas chromatography.

The time required for this still to reach equilibrium varied with the relative volatility of the system. For a relative volatility less than 2, 40 minutes were required. For a relative volatility as high as 30 (encountered in the system of methanol with carbon tetrachloride) somewhat more than 2 hours were required. Generally, an average of 1.5 hours were required for each run.

Boiling Point Still. The vapor pressure-temperature relationships for the pure compounds were obtained in a Cottrell apparatus (*11*) by measuring the boiling temperature under various air pressures from 760 to 400 mm. of mercury. Temperatures were measured by copper-constantan thermocouples and a No. 8662 Leeds and Northrup potentiometer. The precision of the temperature measurements is ±0.02°C.

Chromatograph. A Perkin-Elmer Model 154 Vapor Fractometer was used for the gas chromatography. The separation of perfluorocarbon materials by gas chromatography has been described (*12*).

MATERIALS

The physical properties of the hydrocarbons, methanol, and carbon tetrachloride used in establishing the accurate performance of the equilibrium still are compared in Table I with published values.

Four fluorine-containing compounds, including the two chlorofluorocarbons, the perfluorocarbon oxide, and the perfluoroheptane, were obtained as follows:

1,2,-Dichlorohexafluorocyclopentene, $C_5Cl_2F_6$, from the Hooker Electrochemical Co., was distilled in a column 100 cm. long packed with 1/16-inch internal diameter single-turn helices. This column had 60 theoretical plates when distilling hydrocarbons. Center cuts showing only one component on gas chromatograms were blended. Two minor components originally in the crude material were completely absent in this blend.

2,2,3-Trichloroheptafluorobutane, $C_4Cl_3F_7$, from the Hooker Electrochemical Co. was purified in the same manner as the $C_5Cl_2F_6$. The gas chromatogram of the purified material had only one peak.

Perfluorocyclic oxide, $C_8F_{16}O$, was separated from Fluorochemical 0-75, a mixture of fluorocarbons marketed by Minnesota Mining and Manufacturing Co. The original mixture contained at least six compounds which appeared as peaks on the gas chromatogram. A partial separation of the desired compound was obtained by fractionation in the above column. The material was boiled for several days with potassium hydroxide pellets to remove hydrogen-containing materials, and was subjected to an azeotropic distillation using normal heptane as entrainer. The volume fraction of *n*-heptane in the charge to the distillation column was about 0.2. Minimum boiling azeotropes are formed between the hydrocarbon and the perfluorocarbons. These azeotropes are more easily separated from one another than are the pure compounds. The azeotrope with $C_8F_{16}O$ boils at about 84°C. The perfluorocyclic oxide was then separated from the normal heptane by cooling the azeotrope fractions to dry ice temperature where two liquid phases of very low mutual solubility are formed. The perfluorocarbon phase thus obtained was fractionally distilled to remove the last traces of the hydrocarbon. Chromatograms of the residue from this distillation showed only a single peak.

Perfluoroheptane, C_7F_{16}, was separated from Fluorochemical 101, a mixture marketed by the Minnesota Mining and Manufacturing Co. This mixture contains at least eight compounds, as shown by gas chromatography (*12*). The perfluoroheptane was purified by the same scheme as used for the perfluorocyclic oxide. The purified material had only one peak on the vapor chromatogram. The perfluoroheptane-*n*-heptane azeotrope boils at 74°C. The perfluorocarbon layer from the azeotrope fractions was a solid at dry ice temperature.

Table I. Hydrocarbon Materials and Carbon Tetrachloride

Compound	Refractive Index at 25°C.		Boiling Point, °C.		Density, Grams/Ml. at 25°C.	
	Exptl.	Lit. (*1*)	Exptl.	Lit. (*1*)	Exptl.	Lit. (*1*)
n-Heptane	1.3852	1.38511	98.53	98.427	0.6799	0.67951
Methylcyclohexane	1.4207	1.42058	100.98	100.934	0.76511	0.76506
Toluene	1.4941	1.49414	110.60	110.625	0.86232	0.86232
Methanol	1.3270	1.32657	64.50	64.51	0.7866	0.78654
CCl_4	1.4568	1.4573 (*15*)	76.90	76.8 (*15*)	1.5845	1.5845 (*15*)

Table II. Properties of Fluorocarbon Materials

Compound	Formula Weight	Refractive Index at 25°C.	Density at 25°C., Grams/Ml.	Boiling Point, °C.	Vapor Pressure Constants[a]		Av. Deviation in Calcd. Pressure
					A	*B*	
1,2-Dichlorohexafluorocyclopentene	$C_5Cl_2F_6$ 244.96	1.3658	1.6418	90.6	7.6201	1724.0	0.0021
2,2,3-Trichloroheptafluorobutane	$C_4Cl_3F_7$ 287.41	1.3505	1.7394	97.4	7.5691	1737.4	0.0010
Perfluorocyclic oxide	$C_8F_{16}O$ 416.09	1.2778	1.7678	102.6	7.6393	1788.5	0.0011
Perfluoroheptane	C_7F_{16} 388.07	1.2602	1.7278	81.9	7.7418	1727.4	0.0015

[a] $\log_{10} P(\text{mm. Hg}) = A - B/T$, T in °K.

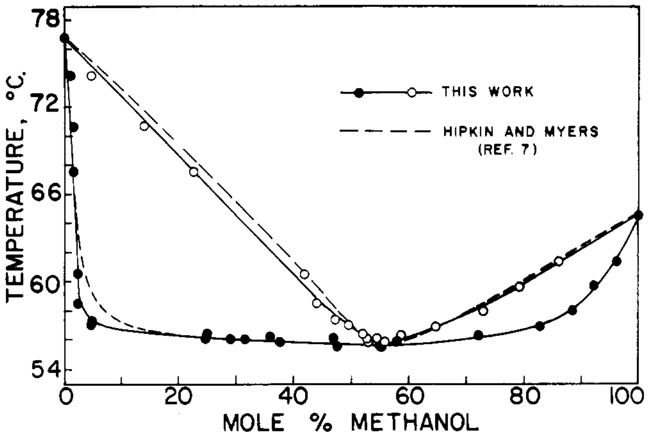

Figure 1. Performance of equilibrium still

Some of the physical properties of these compounds as measured in these laboratories are given in Table II. The structure of the perfluorocyclic oxide is not known in detail. The perfluoroheptane is not the normal perfluoroheptane studied by Oliver and others (*9, 10*). The density of C_7F_{16} is greater, the boiling point is lower, the refractive index is higher, and the heat of vaporization is lower than the values reported by Oliver. The molecular weights of the $C_8F_{16}O$ and of the C_7F_{16} were checked by the Dumas method to within one molecular weight unit of the formulas assigned.

EQUILIBRIUM STILL PERFORMANCE

Three binary systems for which accurate data have been published were run in the equilibrium still to establish the reliability of its operation. The apparatus reproduced the equilibrium curves of Hipkin and Myers (*7*) over the entire composition range for the system *n*-heptane with toluene at 1-atm. pressure. The data of Bromiley and Quiggle (*2*) for the system *n*-heptane with methylcyclohexane were also reproduced. In Figure 1 the data obtained for the system methanol with carbon tetrachloride are compared with those reported by Hipkin and Myers (*7*). A check on the thermodynamic consistency of these data by the method of Broughton and Breadsley (*3*) gave positive and negative areas which agreed in magnitude to within 5% of one another in each case.

ANALYSES OF SAMPLES

The refractive indices and the densities, all at 25 °C. *vs.* composition for the five new systems are given in Table III. Analysis by density would give compositions to within about ±0.1 percentage point in these mixtures. Except in a few cases where an effort was made to obtain sufficient sample size, the analyses could not be made by density. The refractive index will give compositions to within about ±0.5 percentage point for mixtures of C_7F_{16} with $C_8F_{16}O$ and for those of $C_5Cl_2F_6$ with $C_4Cl_3F_7$, and to within about ±0.1 percentage point for $C_5Cl_2F_6$ with $C_8F_{16}O$ and for $C_4Cl_3F_7$ with $C_8F_{16}O$. Refractive index will give compositions to within ±0.3 percentage point for mixtures of $C_4Cl_3F_7$ with n-C_7H_{16}, while the density in this system will give a precision of about ±0.1 percentage point. The compositions reported here were obtained by refractive index.

Quantitative analysis by gas chromatography was investigated for mixtures of C_7F_{16} with $C_8F_{16}O$ and for those of $C_4Cl_3F_7$ with n-C_7H_{16}. The results were satisfactory and gave a precision to about ±0.2 percentage point in each system with the apparatus available (*12*). The relationship found to be most useful was peak height fraction *vs.* weight per cent. Peak height, rather than peak area, requires only one measurement of each peak on the chromatogram, and thus introduces the least error from this source. Weight per cent, rather than some other composition variable, such as mole per cent, gave more linear relationships for systems where the molecular weights of the constituents differed greatly. In such systems peak area fraction gave greater deviations from a linear relationship than did peak height fraction.

Table III. Refractive Index and Density Calibrations for Fluorocarbon and Chlorofluorocarbon Binary Systems

Binary System[a]	Lower Boiling Material, Weight %	Lower Boiling Material, Mole %	Refractive Index at 25 °C.	Density at 25 °C., Grams/Ml.
Perfluoroheptane and perfluorocyclic oxide, $C_8F_{16}O$	0.00	0.00	1.2778	1.7678
	4.77	5.09	1.2770	1.7659
	11.29	12.01	1.2758	1.7634
	22.17	23.39	1.2740	1.7587
	30.77	32.27	1.2725	1.7555
	40.87	42.56	1.2708	1.7517
	50.25	51.99	1.2692	1.7486
	50.49	52.23	1.2692	1.7476
	59.69	61.35	1.2675	1.7447
	69.87	71.32	1.2658	1.7403
	79.74	80.84	1.2640	1.7363
	90.09	90.69	1.2622	1.7313
	95.31	95.61	1.2611	1.7296
	100.00	100.00	1.2602	1.7278
1,2-Dichlorohexafluorocyclopentene and 2,2,3-Trichloroheptafluorobutane	0.00	0.00	1.3505	1.7394
	4.80	5.59	1.3512	1.7333
	10.71	12.44	1.3521	1.7262
	19.66	22.33	1.3535	1.7166
	29.86	33.40	1.3550	1.7059
	39.99	43.80	1.3565	1.6999
	49.95	53.91	1.3580	1.6874
	50.21	54.09	1.3580	1.6856
	60.77	64.50	1.3596	1.6772
	68.52	71.01	1.3608	1.6700
	80.29	82.71	1.3622	1.6580
	86.52	91.30	1.3636	1.6525
	90.08	88.20	1.3640	1.6500
	95.15	95.79	1.3650	1.6457
	100.00	100.00	1.3658	1.6418
1,2-Dichlorohexafluorocyclopentene and perfluorocyclic oxide, $C_8F_{16}O$	0.00	0.00	1.2778	1.7678
	8.09	13.00	1.2846	1.7539
	19.15	28.68	1.2934	1.7367
	29.61	41.67	1.3031	1.7213
	39.25	52.32	1.3115	1.7082
	48.63	61.65	1.3197	1.6962
	50.86	63.74	1.3211	1.6947
	59.87	71.70	1.3294	1.6845
	70.60	80.31	1.3391	1.6733
	80.48	87.50	1.3479	1.6636
	90.76	94.35	1.3570	1.6525
	100.00	100.00	1.3658	1.6418
2,2,3-Trichloroheptafluorobutane and perfluorocyclic oxide, $C_8F_{16}O$	0.00	0.00	1.2778	1.7678
	5.48	7.74	1.2815	1.7643
	10.34	14.31	1.2845	1.7620
	19.22	25.62	1.2904	1.7570
	30.03	38.31	1.2979	1.7520
	39.13	48.20	1.3041	1.7494
	49.09	58.26	1.3111	1.7468
	49.77	58.91	1.3121	1.7460
	59.22	67.76	1.3188	1.7442
	68.85	76.19	1.3260	1.7421
	79.64	84.99	1.3342	1.7413
	89.59	92.57	1.3420	1.7400
	94.52	96.37	1.3463	1.7399
	100.00	100.00	1.3505	1.7394
2,2,3-Trichloroheptafluorobutane and *n*-heptane	0.00	0.00	1.3850	0.6799
	12.57	4.77	1.3823	0.7345
	22.61	9.24	1.3795	0.7845
	29.76	12.87	1.3786	0.8254
	40.09	18.92	1.3743	0.8918
	48.87	24.99	1.3715	0.9584
	59.67	34.03	1.3675	1.0556
	69.35	44.10	1.3638	1.1615
	80.03	58.29	1.3588	1.2999
	90.56	76.93	1.3544	1.5043
	100.00	100.00	1.3505	1.7394

[a] Material listed first in each binary system is lower boiling.

EQUILIBRIUM DATA

The pressure at which these measurements were made was the prevailing atmospheric pressure. This pressure was recorded each time the still was sampled. Over the period of 3 months in which these data were obtained the average pressure of 113 runs was 760 mm. of mercury (0°C.) with an average deviation of 1 mm. The maximum deviation was 5 mm. The observed equilibrium temperatures were corrected to 760 mm. using the values for the temperature coefficient of the vapor pressure for the pure compounds. The data for the five binary systems are given in Table IV.

C_7F_{16} with $C_8F_{16}O$. Both components obey Raoult's law over the whole composition range. The activity coefficients are unity to within the accuracy of these measurements. The average relative volatility calculated from the experimental compositions is 1.92. The Raoult's law relative volatility, calculated from the vapor pressures of the pure components varies from 1.84 at 102°C. to 1.88 at 82°C. These experimental and calculated values agree to within the maximum error of 0.1 relative volatility unit at 50 mole % vapor composition for this system.

$C_5Cl_2F_6$ with $C_4Cl_3F_7$. These compounds also form ideal solutions. The average relative volatility from the experimental compositions is 1.23. The Raoult's law values are 1.22 at 97°C. and 1.23 at 91°C. The experimental and calculated values are within the maximum error of 0.05 unit at 50 mole % vapor composition for this system.

$C_5Cl_2F_6$ with $C_8F_{16}O$. An azeotrope is formed at 87.2 mole % $C_5Cl_2F_6$ and 90.4°C. At this point the maximum error in the relative volatility in this system is 0.02 unit.

$C_4Cl_3F_7$ with $C_8F_{16}O$. An azeotrope is formed at 74.6 mole % $C_4Cl_3F_7$ and 96.35°C. At this point the maximum error in the relative volatility is 0.01 for this system.

$C_4Cl_3F_7$ with C_7H_{16}. An azeotrope is formed at 52.5 mole % $C_4Cl_3F_7$ and 92.3°C. At this point the maximum error in the relative volatility is 0.03 unit.

THEORETICAL CALCULATIONS

Except for mixtures of $C_4Cl_3F_7$ with C_7H_{16}, these systems seem to conform rather well to the theory of Hildebrand (*5*). In Table V are set forth heats of vaporization and the parameters δ calculated from them, at 25°. The heats of vaporization were calculated from vapor pressure-temperature data by means of the exact Clapeyron equation. The vapor volumes were calculated by the Berthelot equa-

Table IV. Vapor-Liquid Equilibrium Data for Fluorocarbon and Chlorofluorocarbon Binary Mixtures at 1-Atm. Pressure

Run No.	Mole % Lower Boiling Component		Equil. Temp. Corr. to 760 Mm. Hg, °C.	Relative Volatility	Activity Coefficients	
	Vapor	Liquid			1	2
A. C_7F_{16} with $C_8F_{16}O$						
1	0.0	0.0	102.6	...	...	1.000
2	5.1	2.8	101.7	1.865	1.006	1.002
3	13.5	7.6	100.3	1.905	1.020	1.005
4	21.0	12.3	99.0	1.895	1.030	1.004
5	28.5	17.2	97.7	1.920	1.030	1.002
6	34.6	21.5	96.6	1.932	1.039	1.067
7	51.0	34.6	93.6	1.969	1.040	1.076
8	61.2	44.4	91.7	1.975	1.028	0.998
9	71.8	57.3	89.4	1.900	1.002	0.986
10	75.7	62.1	88.4	1.900	0.997	0.997
11	80.9	68.8	87.3	1.920	0.993	0.978
12	88.2	79.5	85.5	1.920	0.993	0.990
13	94.8	90.6	83.6	1.890	0.994	1.010
14	97.2	95.1	82.8	1.790	0.997	1.073
15	100.0	100.0	82.0	...	1.000	...
B. $C_5Cl_2F_6$ with $C_4Cl_3F_7$						
1	0.0	0.0	97.4	...	...	1.000
2	11.9	10.3	96.6	1.177	1.046	1.008
3	27.1	23.4	95.7	1.217	0.993	1.002
4	36.8	32.0	95.1	1.235	1.003	1.001
5	45.1	39.6	94.6	1.250	1.008	0.991
6	52.3	46.5	94.3	1.263	1.004	0.985
7	57.2	51.1	94.0	1.278	1.011	0.992
8	65.9	59.8	93.5	1.300	1.006	0.994
9	71.8	66.5	93.1	1.294	1.002	0.993
10	80.4	76.9	92.4	1.230	0.991	0.984
11	86.3	84.5	91.9	1.155	0.992	1.042
12	92.6	91.6	91.3	1.148	0.991	1.054
13	100.0	100.0	90.6	...	1.000	...
C. $C_5Cl_2F_6$ with $C_8F_{16}O$						
1	0.0	0.0	102.57	...	...	1.00
2	14.9	7.8	100.03	2.070	1.44	1.00
3	23.1	12.7	98.26	2.065	1.44	1.00
4	32.6	19.25	96.50	2.028	1.42	1.01
5	39.2	26.1	95.36	1.825	1.30	1.03
6	48.7	36.3	93.75	1.697	1.23	1.07
7	56.7	45.1	92.63	1.595	1.18	1.07
8	62.0	51.8	91.95	1.517	1.15	1.10
9	65.3	56.1	91.48	1.474	1.13	1.11
10	69.2	61.9	91.23	1.383	1.10	1.15
11	72.7	68.0	90.92	1.252	1.05	1.22
12	77.4	74.0	90.63	1.203	1.04	1.26
13	79.7	77.5	90.60	1.140	1.03	1.31
14	82.9	81.5	90.60	1.101	1.02	1.34
15	85.6	85.15	90.49	1.037	1.01	1.41
16	87.2	87.2	90.40	1.000	1.10	1.46
17	88.5	88.7	90.43	1.036	1.00	1.49
18	89.5	89.9	90.49	1.044	1.00	1.51
19	90.6	91.15	90.52	1.068	1.00	1.54
20	92.8	93.5	90.55	1.116	1.00	1.61
21	96.6	97.1	90.55	1.178	1.00	1.70
22	98.0	98.3	90.58	1.180	1.00	1.71
23	100.0	100.0	90.60	...	1.00	...
D. $C_4Cl_3F_7$ with $C_8F_{16}O$						
1	0.0	0.0	102.60	...	...	1.000
2	3.0	1.5	102.00	2.031	1.750	1.003
3	8.1	4.8	101.40	1.750	1.510	1.003
4	15.3	9.7	100.56	1.679	1.439	1.000
5	24.3	17.0	99.50	1.569	1.350	1.002
6	30.15	22.7	98.92	1.481	1.259	1.006
7	35.2	27.1	98.36	1.460	1.260	1.010
8	39.2	31.6	97.99	1.424	1.220	1.024
9	46.4	39.9	97.44	1.304	1.161	1.045
10	53.0	47.1	97.00	1.267	1.140	1.050
11	60.3	56.3	96.70	1.179	1.100	1.091
12	67.2	65.5	96.45	1.079	1.055	1.145
13	69.7	68.75	96.40	1.045	1.041	1.158
14	71.2	70.5	96.40	1.033	1.040	1.218
15	74.6	74.7	96.35	1.004[a]	1.026	1.213
16	77.2	77.95	96.40	1.042[a]	1.016	1.249
17	79.6	80.9	96.48	1.085[a]	1.009	1.290
18	85.0	86.6	96.73	1.140[a]	1.010	1.340
19	88.7	90.2	96.85	1.172[a]	1.001	1.370
20	90.8	92.1	96.94	1.180[a]	1.000	1.380
21	93.8	94.8	97.10	1.204[a]	1.000	1.410
22	100.0	100.0	97.40	...	1.000	...
E. $C_4Cl_3F_7$ with n-C_7H_{16}						
1	0.00	0.00	98.4	...	...	1.00
2	0.6	0.2	98.3	3.0	2.93	1.00
3	4.1	2.1	97.7	1.99	1.94	1.00
4	5.0	2.9	97.35	1.76	1.64	1.01
5	10.2	6.5	96.55	1.63	1.61	1.01
6	13.5	8.5	96.0	1.68	1.66	1.02
7	22.2	16.4	94.65	1.45	1.46	1.04
8	22.2	16.5	94.55	1.45	1.46	1.04
9	23.2	17.8	94.2	1.39	1.44	1.06
10	24.5	18.1	94.2	1.47	1.49	1.04
11	28.4	21.3	93.7	1.46	1.49	1.05
12	34.2	28.4	93.45	1.31	1.35	1.06
13	40.3	38.2	92.6	1.09	1.22	1.15
14	45.7	43.1	92.5	1.11	1.23	1.14
15	67.1	70.2	92.95	1.16[a]	1.09	1.30
16	82.3	83.6	94.1	1.10[a]	1.09	1.23
17	100.00	100.00	97.43	...	1.00	...

[a] Component 2 relative to component 1.

Table V. Calculations of Azeotropes

System		Heat of Vapn. at 25 °C., Cal./Mole		(Cal./Cc.)$^{1/2}$ at 25 °C.[a]		°K. at 25 °C.		V_1/V_2 at 25 °C.	Azeotrope			
									Exptl.		Theor. (*14*)	
1	2	1	2	δ_1	δ_2	B_1[b]	B_2[b]		x_1	°C.	x_1	°C.
C_7F_{16}	$C_8F_{16}O$	8215	9440	5.83	6.13	1.0	1.1	0.960	None		None	
$C_5Cl_2F_6$	$C_4Cl_3F_7$	8730	8510	7.39	6.92	16.6	18.4	0.940	None		None	
$C_5Cl_2F_6$	$C_8F_{16}O$	8730	9440	7.39	6.13	119	188	0.635	0.872	90.4	0.90	90.2
$C_4Cl_3F_7$	$C_8F_{16}O$	8510	9440	6.92	6.13	52.0	74.0	0.703	0.746	96.35	0.91	97.4
$C_4Cl_3F_7$	C_7H_{16}	8510	8735 (*1*)	6.92	7.43	21.6 278[c]	19.3 248[c]	1.12	0.525	92.3	0.78 0.51	47.35 92.0

[a] δ^2 = energy of vaporization divided by molal liquid volume, V.

[b] $B_i = (V_i/R)(\delta_1 - \delta_2)^2$.

[c] B_i by Equation 1.

tion of state. In the system C_7F_{16} with $C_8F_{16}O$ the theoretical parameters give activity coefficients of unity. For $C_5Cl_2F_6$ with $C_4Cl_3F_7$ the theoretical activity coefficients are 1.05 in the infinitely dilute solutions. These solutions are essentially ideal both theoretically and experimentally.

The azeotropic conditions for the remaining three systems were calculated from the theory by the method of reference (*14*). These calculated conditions agree well with the experimental values of temperature and composition for one of the two systems containing a fluorocarbon and a chlorofluorocarbon, as shown in Table V. The simple theory in which only the δ parameters are required is inadequate for $C_4Cl_3F_7$ with n-C_7H_{16}. It has been shown (*13*) that an additional parameter, f, must be used to bring the calculated heats of mixing in fluorocarbon-hydrocarbon mixtures to the experimental values. f is a function of the ionization potential ratio and the molecular size ratio of the components. In fluorocarbon-hydrocarbon systems a value of about 0.97 was found for f. Using this value for f in the above chlorofluorocarbon-hydrocarbon system, and defining

$$B_i' = (V_i/R)\ [(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2\,(1 - f)] \qquad (1)$$

give a theoretical value of 92.0° and x_1 = 0.51 for the azeotrope. This compares almost exactly with the experimental azeotrope at 92.3° and x_1 = 0.525.

VOLUME CHANGES ON MIXING

The total volume changes on mixing per mole of mixture for the five binary systems are shown in Figure 2. Partial molal volumes are given in Table VI; approximate values for the partial molal volumes at infinite dilution are given in parentheses. The maximum experimental error in the total volume change is approximately 0.05 ml. The system C_7F_{16} with $C_8F_{16}O$ shows contractions of about this order of magnitude. The remaining systems show expansions which increase in magnitude in the order of increasing nonideal behavior. Even though the ratio of the molal volumes of the chlorofluorocarbons to those of the fluorocarbons are considerably less than 1, the maximum volume change in these systems occurs at a mole fraction near 0.5.

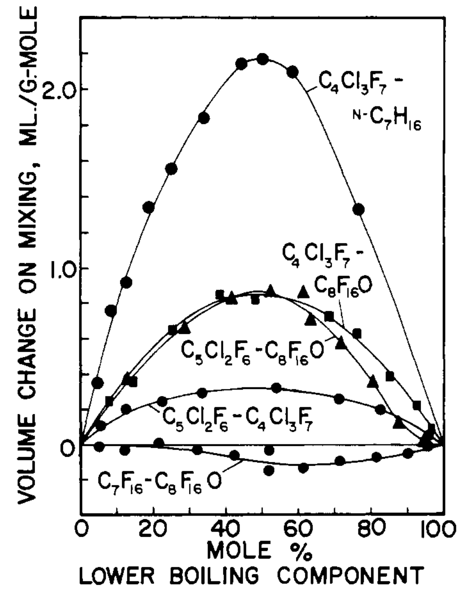

Figure 2. Volume changes on mixing

A theoretical equation for the partial molal volume change at infinite dilution is given by (*6*).

$$\Delta\bar{V}_1^\circ = \beta_2 RB_1 \qquad (2)$$

where β_2 is the isothermal compressibility of pure 2,2,3-trichloroheptafluorobutane. For C_7H_{16} between 90° and 100° β is 2.1×10^{-4} atm.$^{-1}$ Using this value for β_2 in Equation 2, with B_1 defined by Equation 1, to calculate

Table VI. Partial Molal Volume Changes on Mixing, Ml./Gram Mole

Mole % Lower Boiling Component in Liquid	$\Delta\bar{V}_1$	$\Delta\bar{V}_2$	Mole % Lower Boiling Component in Liquid	$\Delta\bar{V}_1$	$\Delta\bar{V}_2$
A. C_7F_{16} with $C_8F_{16}O$			D. $C_4Cl_3F_7$ with $C_8F_{16}O$		
0	...	0	0	(+3.0)	0
10	−0.07	0	10	+2.62	+0.04
20	−0.12	0	20	2.19	0.11
30	−0.19	+0.03	30	1.76	0.26
40	−0.26	+0.07	40	1.31	0.51
50	−0.31	+0.12	50	0.95	0.80
60	−0.11	−0.15	60	0.55	1.30
70	−0.04	−0.26	70	0.19	1.95
80	−0.01	−0.34	80	0.08	2.26
90	0	−0.39	90	0.03	2.51
100	0	...	100	0	(3.5)
B. $C_5Cl_2F_6$ with $C_4Cl_3F_7$			E. $C_4Cl_3F_7$ with $n - C_7H_{16}$		
0	(+1.5)	0	0	(+9.0)	0
10	+1.02	+0.06	10	+6.80	+0.11
20	0.72	0.11	20	5.45	0.36
30	0.52	0.18	30	4.15	0.79
40	0.44	0.22	40	3.22	1.29
50	0.35	0.30	50	2.37	1.98
60	0.19	0.50	60	0.95	3.73
70	0.11	0.63	70	0.32	4.85
80	0.06	0.79	80	0.04	5.69
90	0.02	1.04	90	0.02	5.76
100	0	(+1.5)	100	0	...
C. $C_5Cl_2F_6$ with $C_8F_{16}O$					
0	(+3.0)	0			
10	+2.49	+0.06			
20	2.02	0.14			
30	1.75	0.22			
40	1.40	0.42			
50	+0.98	+0.78			
60	0.31	1.61			
70	−0.06	2.25			
80	−0.24	2.80			
90	−0.10	1.68			
100	0	...			

$\Delta\bar{V}$ 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.

LITERATURE CITED

(1) American Petroleum Institute, Research Project 44, "Selected Values of Properties of Hydrocarbons," Carnegie Institute of Technology.
(2) Bromiley, E. P., Quiggle, D., *Ind. Eng. Chem.* **25**, 1136 (1933).
(3) Broughton, D. B., Breadsley, C. S., Ibid., **47**, 838 (1955).
(4) Hildebrand, J. H., Fisher, B. B., Benesi, H. A., *J. Am. Chem. Soc.* **72**, 4348 (1950).
(5) Hildebrand, J. H., Scott, R. L., "Solubility of Nonelectrolytes," Reinhold, New York, 1950.
(6) *Ibid.*, p. 143.
(7) Hipkin, H., Myers, H. S., *Ind. Eng. Chem.* **46**, 2524 (1954).
(8) Newcome, M. M., doctor of philosophy thesis, University of Washington, 1954.
(9) Oliver, G. D., Blumkin, S., Cunningham, C. W., *J. Am. Chem. Soc.* **73**, 5722 (1951).
(10) Oliver, G. D., Grisard, J. W., *Ibid.*, **73**, 1688 (1951).
(11) Quiggle, D., Tongberg, C. O., Fenske, M. R., *Ind. Eng. Chem., Anal. Ed.* **6**, 466 (1934).
(12) Reed, T. M. III, *Anal. Chem.* **30**, 221 (1958).
(13) Reed, T. M. III, *J. Phys. Chem.* **59**, 425 (1955).
(14) *Ibid.*, **61**, 1213 (1957).
(15) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
(16) Yen, L. C., master of science thesis, University of Florida, 1957.

Received for review February 6, 1958. Accepted May 23, 1958.

Vapor-Liquid Equilibrium at High Pressures

The Systems Ethanol-Water and 2-Propanol—Water

FRANK BARR-DAVID and BARNETT F. DODGE
Chemical Engineering Department, Yale University, New Haven, Conn.

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