Q = electrical heat input, cal.
S = salinity in weight per cent. Approximately per cent total solids (see Procedure section for discussion)
T = temperature, ° K.
t = temperature, ° C.
u = specific volume of saturated liquid, cm.^{3}/g.
u' = specific volume of saturated vapor, cm.^{3}/g.
V = internal volume of calorimeter, cm.^{3}
x = mass fraction of liquid in calorimeter
Z_i = charge on ion i
$\sigma I^{1/2}/3$ = $(1/I^{3/2})\,[1 + I^{1/2} - 1/(1 + I^{1/2}) - 2 \ln(1 + I^{1/2})]$
σ = standard deviation

LITERATURE CITED

(1) Am. Soc. Mechanical Engineers, United Engineering Center, New York, "ASME Steam Tables," 1967.
(2) Bromley, L.A., J. CHEM. ENG. DATA, **13**, 60 (1968).
(3) *Ibid.*, p. 399.
(4) Bromley, L.A., De Saussure, V.A., Clipp, J.C., Wright, J.A., *Ibid.*, **12**, 202 (1967).
(5) Cox, R.A., Smith, N.D., *Proc. Roy. Soc.* **A252**, 51 (1959).
(6) Jamieson, D.T., Tudhope, J.S., Morris, R., Cartwright, G., "Physical Properties of Sea Water Solutions. Heat Capacity," "Desalination" (to be published).
(7) Lewis, G.N., Randall, M., Pitzer, K.S., Brewer, L., "Thermodynamics," 2nd ed., p. 642, McGraw-Hill, New York, 1961.
(8) "National Engineering Laboratory Steam Tables," Her Majesty's Stationery Office, Edinburgh, 1964.
(9) Osborne, N.S., *J. Res. Natl. Bur. Std.* **4**, 609 (1930).
(10) Osborne, N.S., Stimson, H.F., Ginnings, D.C., *Ibid.*, **23**, 197 (1939).
(11) Oxner, M., Knudsen, M., "Determination of Chlorinity by the Knudsen Method," G.M. Mfg. Co., New York, 1962.
(12) Sverdrup, H.U., Johnson, M.W., Fleming, R.H., "The Oceans. Their Physics, Chemistry, and General Biology," 8th printing, Prentice-Hall, Englewood Cliffs, N. J., 1942.
(13) Wilkins, D.G., M.S. thesis, University of California, Berkeley, Calif., 1968.

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Vapor-Liquid Equilibria in the Ethane–*n*-Hexane System

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Vapor and liquid equilibrium phase compositions were determined in the ethane–*n*-hexane system at 150°, 250°, and 350° F. at pressures from approximately 60 p.s.i.a. to near the critical. Phase envelopes were extrapolated to yield critical composition and pressure at each temperature. Equilibrium ratios ($K = y/x$) from the experimental data are compared with those from the most recent revision of the NGPSA *K*-charts. As previous studies of the ethane–*n*-hexane binary are not found in the literature, no comparison with other experimental work is possible.

THE MIXTURES of ethane and *n*-hexane were confined over mercury in a 35-ml. windowed stainless steel cell. The equilibrium cell was immersed in a controlled-temperature oil bath. By means of a magnetic pump, vapor from the top of the cell was recirculated through the bottom of the cell for 2 to 4 hours, after which from 3 to 6 hours were allowed for complete phase separation. Sampling was carried out under constant pressure conditions by simultaneously injecting mercury into the bottom of the cell while the sample was being withdrawn. No single-phase samples were taken; however, in a number of instances, insufficient amount of one of the equilibrium phases precluded its being sampled.

The equilibrium temperature was determined from the average indication of four iron-constantan thermocouples at separate locations near the cell. The thermocouple-potentiometer combination was calibrated against mercury-in-glass thermometers which had been calibrated by the National Bureau of Standards. The accuracy of any indicated temperature is estimated to be 0.1° F., and deviations of the average cell temperature from the nominal temperature of each isotherm did not exceed 0.25° F.

Pressure measurements were made with 1000- and 5000-p.s.i.g. Bourdon tube pressure gages with sensitivities of 0.1% of full scale. These gages were calibrated against a dead-weight pressure gage with calibration traceable to NBS standards. Uncertainties in the reported experimental pressures are believed not to exceed 2 p.s.i. below 1000 p.s.i.g. but may be as great as 7.5 p.s.i. for pressures greater than 1000 p.s.i.g.

Further details of the apparatus and experimental procedures have been given by Roberts *et al.* (*3*) and Poston and McKetta (*2*). Recent modifications were described by Zais (*5*).

ANALYTICAL

The vapor and liquid phase samples were analyzed by means of a Beckman Model GC-2A gas chromatograph equipped with a 6-foot silicone column (Beckman No. 17449). Chromatograms were interpreted by the peak height

Table I. Experimental Equilibrium Data

Temp., °F.	Pressure, P.S.I.A.	Composition in Mole Fraction: Vapor Phase: Ethane	Vapor Phase: *n*-Hexane	Liquid Phase: Ethane	Liquid Phase: *n*-Hexane
150	59.4	0.807	0.193	. . .	. . .
	127.6	0.902	0.098	. . .	. . .
	224.0	0.941	0.059	0.297	0.703
	290.0	0.948	0.052	0.357	0.643
	394.0	0.965	0.035	0.427	0.573
	502.7	0.965	0.035	0.517	0.483
	594.7	0.970	0.030	. . .	. . .
	660.8	. . .	. . .	0.640	0.360
	754.3	0.974	0.026	. . .	. . .
	837.8	. . .	. . .	0.762	0.238
	917.8	0.959	0.041	0.853	0.147
	926.9	0.958	0.042	0.859	0.141
	932.2	0.964	0.036	0.907	0.093
250	97.3	0.396	0.604	. . .	. . .
	194.0	. . .	. . .	0.137	0.863
	203.0	0.700	0.300	0.140	0.860
250	405.5	0.799	0.201	0.275	0.725
	587.8	0.845	0.155	. . .	. . .
	807.3	0.865	0.135	. . .	. . .
	822.0	. . .	. . .	0.505	0.495
	936.4	0.875	0.125	. . .	. . .
	940.0	0.878	0.122	. . .	. . .
	1015.0	0.860	0.140	0.553	0.447
	1110.0	0.837	0.163	0.612	0.388
	1120.0	. . .	. . .	0.648	0.352
	1143.0	. . .	. . .	0.700	0.300
350	263.6	. . .	. . .	0.075	0.925
	447.2	0.515	0.485	0.150	0.850
	620.9	0.603	0.397	0.210	0.790
	722.6	. . .	. . .	0.252	0.748
	825.5	0.623	0.377	. . .	. . .
	930.8	0.601	0.399	0.397	0.603

Table II. Properties of the Coexisting Phases for the Ethane–*n*-Hexane System

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Temp., °F.	Pressure, P.S.I.A.	Composition in Mole Fraction: Vapor Phase: Ethane	Vapor Phase: *n*-Hexane	Liquid Phase: Ethane	Liquid Phase: *n*-Hexane	Equilibrium Ratio $K = y/x$: Ethane	Equilibrium Ratio: *n*-Hexane
150	13.6[a]	0.000	1.000	0.000	1.000	32.2	1.000
	25	0.486	0.514	0.026	0.974	18.9	0.528
	50	0.758	0.242	0.073	0.927	10.4	0.262
	75	0.842	0.158	0.113	0.887	7.45	0.178
	100	0.881	0.119	0.150	0.850	5.88	0.140
	150	0.918	0.082	0.215	0.785	4.28	0.104
	200	0.936	0.064	0.271	0.729	3.45	0.088
	300	0.953	0.047	0.365	0.635	2.61	0.073
	400	0.962	0.038	0.443	0.557	2.17	0.067
	500	0.968	0.032	0.515	0.485	1.88	0.066
	600	0.972	0.028	0.586	0.414	1.66	0.069
	700	0.974	0.026	0.658	0.342	1.48	0.076
	800	0.975	0.025	0.735	0.265	1.33	0.093
	900	0.970	0.030	0.829	0.171	1.17	0.175
	938[b]	0.920	0.080	0.920	0.080	1.00	1.000
250	59.7[a]	0.000	1.000	0.000	1.000	13.7	1.000
	100	0.406	0.594	0.046	0.954	8.75	0.623
	150	0.600	0.400	0.096	0.904	6.27	0.442
	200	0.690	0.310	0.138	0.862	4.98	0.361
	300	0.764	0.236	0.212	0.788	3.61	0.300
	400	0.802	0.198	0.276	0.724	2.90	0.272
	500	0.828	0.172	0.335	0.665	2.46	0.259
	600	0.847	0.153	0.392	0.608	2.16	0.252
	700	0.861	0.139	0.444	0.556	1.94	0.251
	800	0.870	0.130	0.489	0.511	1.78	0.254
	900	0.874	0.126	0.523	0.477	1.67	0.264
	1000	0.870	0.130	0.553	0.447	1.57	0.291
	1100	0.842	0.158	0.611	0.389	1.38	0.406
	1146[b]	0.735	0.265	0.735	0.265	1.00	1.000
350	179.5[a]	0.000	1.000	0.000	1.000	6.56	1.000
	200	0.090	0.910	0.015	0.985	6.01	0.924
	250	0.249	0.751	0.049	0.951	5.08	0.791
	300	0.351	0.649	0.079	0.921	4.44	0.704
	350	0.423	0.577	0.106	0.894	4.00	0.644
	400	0.477	0.523	0.130	0.870	3.68	0.600
	500	0.552	0.448	0.171	0.829	3.23	0.540
	600	0.597	0.403	0.204	0.796	2.93	0.506
	700	0.618	0.382	0.241	0.759	2.56	0.503
	800	0.624	0.376	0.292	0.708	2.14	0.531
	900	0.612	0.388	0.364	0.636	1.68	0.610
	950	0.587	0.413	0.423	0.578	1.39	0.715
	980[b]	0.525	0.475	0.525	0.475	1.00	1.000

[a] Vapor pressure of *n*-hexane (*4*). [b] Critical pressure.

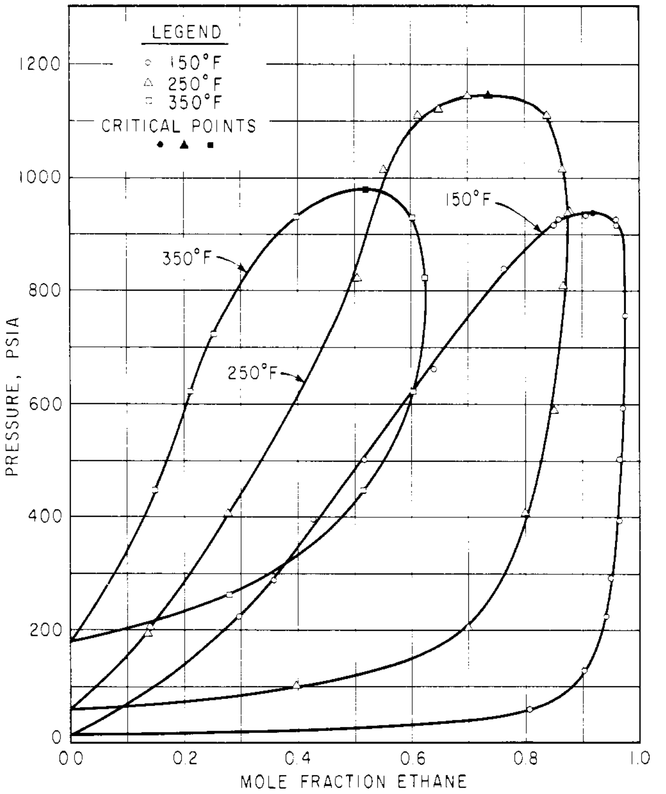

Figure 1. Vapor-liquid equilibria of ethane–*n*-hexane system

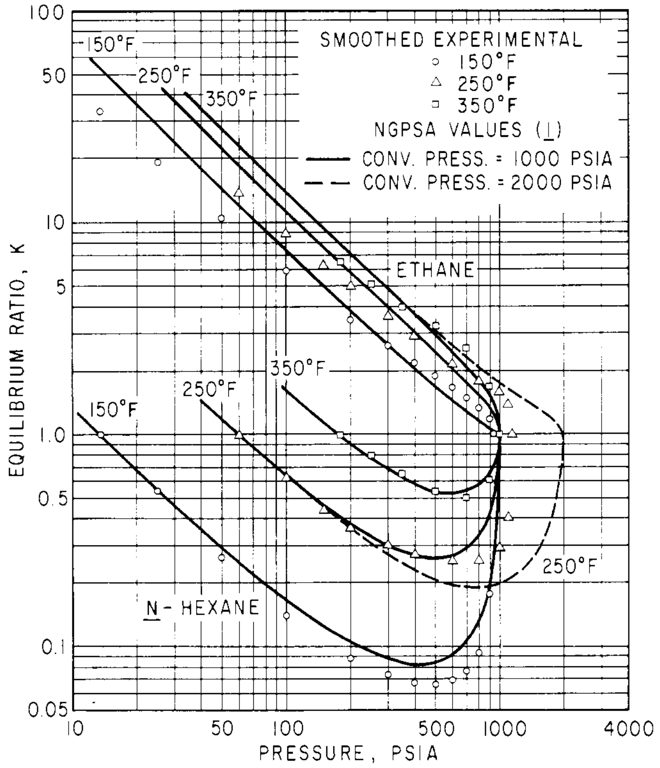

Figure 2. Equilibrium ratios for ethane–*n*-hexane system

method. At the beginning of the experimental work, the chromatograph was calibrated for ethane and *n*-hexane with mixtures of composition known to within ±0.003 mole fraction. Calibration was repeated toward the latter part of the work and found to agree with the original, well within the limits of experimental error. Twenty-five chromatograms were made from each phase sample. From these repetitive measurements, average probable errors in mole fraction are estimated to be 0.008 at 150° F., 0.015 at 250° F., and 0.010 at 350° F.

MATERIALS

The ethane and *n*-hexane used were provided by the Phillips Petroleum Co. The ethane was research grade with a stated minimum purity of 99.98 mole %. No further purification of the ethane was deemed necessary. The *n*-hexane was pure grade with a stated minimum purity of 99.0 mole %. It was purified by passage through a molecular sieve, followed by three successive solidifications under vacuum at dry ice temperature. Chromatographic analysis of the research grade ethane and the purified *n*-hexane indicated no detectable impurities.

RESULTS

The experimentally determined compositions of the equilibrium vapor and liquid phases are listed in Table I. The isothermal phase diagrams at 150°, 250°, and 350° F. are presented in Figure 1. No comparison is made with data from other sources, as no other investigation of this binary system has been reported in the literature.

Smoothed values of phase compositions read from the graphs in Figure 1 are listed in Table II, with estimated critical pressure and composition at each temperature. From the smoothed phase compositions, equilibrium ratios ($K = y/x$) were calculated and were in turn graphically smoothed as functions of pressure at each experimental temperature. These smoothed values of K are also presented in Table II. Internal consistency of the K, x, and y data is such that equilibrium phase compositions calculated from the smoothed values of the equilibrium ratios deviate by no more than 0.002 mole fraction from the smoothed phase compositions of Table II.

Selected values of the smoothed equilibrium ratios are compared in Figure 2 with values read from the charts in the Natural Gas Processors Suppliers Association Engineering Data Book (*1*). The NGPSA curves give good representation of the experimental results for *n*-hexane, particularly at 250° and 350° F. For ethane, however, the discrepancy is considerable.

ACCURACY

Accuracy of the smoothed phase compositions may be expected to be superior to that of any individual observation. Errors in the smoothed data of Table II are believed not to exceed the following limits.

Composition.	±0.005 mole fraction
Pressure.	±2 p.s.i.a. below 1000 p.s.i.a. ±5 p.s.i.a. above 1000 p.s.i.a.
Temperature.	±0.3° F.

Critical properties were estimated from the phase envelopes as drawn in Figure 1. Therefore, an additional uncertainty must be assigned to the critical pressure and composition. These uncertainties are summarized by the following:

At 150° ± 0.3° F.	Critical pressure = 938 ± 6 p.s.i.a. Critical composition = 0.920 ± 0.010 mole fraction
At 250° ± 0.3° F.	Critical pressure = 1146 ± 10 p.s.i.a. Critical composition = 0.735 ± 0.015 mole fraction
At 350° ± 0.3° F.	Critical pressure = 980 ± 7 p.s.i.a. Critical composition = 0.525 ± 0.010 mole fraction

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NOMENCLATURE

K = vapor-liquid equilibrium ratio, y/x
x = mole fraction of a component in liquid phase
y = mole fraction of a component in vapor phase

LITERATURE CITED

(1) Natural Gas Processors Suppliers Association, Tulsa, Okla., "Engineering Data Book," 8th ed., 1966.
(2) Poston, R.S., McKetta, J.J., J. Chem. Eng. Data **11**, 362 (1966).
(3) Roberts, L.R., Wang, A.Z., Azarnoosh, A., McKetta, J.J., *Ibid.*, **7**, 484 (1962).
(4) Rossini, F.D., Pitzer, K.S., *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
(5) Zais, E.J., "Phase Equilibria of the Ethane-*n*-Hexane System at 150°, 250°, and 350° F.," Texas Petroleum Research Committee, University of Texas at Austin, Austin, Tex., Rept. **UT69-1** (May 1, 1969).

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Extended Benedict-Webb-Rubin Equation of State

Application to Eight Fluorine Compounds

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The Benedict-Webb-Rubin equation of state (BWR) is extended by the introduction of three additional coefficients. The extended equation predicts the *P-V-T* behavior of pure fluids in a wide temperature and density range. It fits the critical point exactly and has the first two derivatives of pressure with respect to volume vanish at this point. The critical isometric and the vapor pressure curve have a common tangent at the critical point. Furthermore, the extended equation predicts the residual (excess) caloric properties more precisely than the original one. A program in FORTRAN IV has been developed to determine the coefficients for the equation. It allows the variation of the critical constants within an arbitrary given range to get closer results. The coefficients of the equation for CCl_2F_2, $CClF_3$, CF_4, CHF_3, $C_2Cl_2F_4$, C_2ClF_5, SF_6, and C_4F_8 are determined. The deviation between measured and calculated values of pressure and density is generally within the error limits of the experiments.

THE BENEDICT-WEBB-RUBIN equation of state (BWR equation) was originally developed in 1940 to correlate and predict the thermodynamic properties of light hydrocarbons and their mixtures (*3*). Since this time, many efforts have been extended towards investigation of the applicability of the BWR equation to other compounds. Successful results have been achieved by "normal" as well as polar [e.g., sulfur dioxide (*19*)] and quantum [e.g., helium-4 (*23*)] compounds. Cooper and Goldfrank (*10*) compiled the constants of the BWR equation of state for 38 compounds. As the BWR technique gained widespread use, more and more shortcomings were reported. Most of the difficulties have been observed in predicting pressure-volume-temperature (*P-V-T*) characteristics of fluids within the critical region and at a density more than 1.5 times the critical. Moreover, the representation of the caloric properties like enthalpy and heat capacity in many cases is not satisfactory (*32*).

To eliminate some of these difficulties, attempts (*4*) have been made to extend the BWR equation through additional coefficients. However, the literature does not give clear procedure for evaluating the new coefficients. This presentation discusses this aspect of the problem.

The present work involved the following steps. Extend the BWR equation by three additional coefficients. Establish the coefficients for eight fluorine compounds regarding the conditions at the critical point and by regression analysis of the available *P-V-T* data. Test the accuracy of pressure prediction. Test the effect of variation of the critical data on the prediction of the *P-V-T* data. Derive expressions for the thermodynamic properties: enthalpy, entropy, fugacity, isometric heat capacity, isobaric heat capacity, Joule-Thomson coefficients, and sound velocity. Demonstrate the superiority of the extended BWR equation to the original equation by predicting the thermodynamic properties of tetrafluoromethane.

EXTENSION OF THE BWR EQUATION OF STATE

The original BWR equation (*3*) expresses the pressure, *P*, as a function of the molal density, *d*, and the absolute temperature, *T*. It is commonly written as:

$$P = RTd + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)d^2 + (bRT - a)d^3 + \frac{c}{T^2}\,(1 + \gamma d^2)e^{-\gamma d^2}\,d^3 + a\alpha d^6 \qquad (1)$$

R is the universal gas constant. A_0, B_0, C_0, a, b, c, α, and γ are specific constants evaluated by a least-squares technique outlined by Brough, Schlinger, and Sage (*6*), minimizing the sum of squares of deviations in the calculated pressure values. Details of the method are outlined elsewhere (*6*). Although the least-squares technique was used,