Table III. Summary of Literature Values

Temp., °C.	Density of Carbon Tetrachloride, G./Ml.	Density of Nitromethane, G./Ml.	Density of Nitroethane, G./Ml.
30	1.57478 (*14*) 1.57480 (*13*)	1.12439 (*10*) 1.12453 (*13*)	1.03870 (*10*)
35	1.56480 (*2*) 1.56478 (*9*)	1.11700 (*2*)	
45	1.5442 (*2*)	1.1033 (*2*)	

Brown and Smith (*1*) have reported the maximum value of V^E for nitromethane–carbon tetrachloride solutions at 25° C. to be 0.17 ml. per mole. The present results are in agreement with this value as well as with the graphical results presented by Brown and Smith (*2*) and with their conclusion that the volume of mixing of solutions of which carbon tetrachloride is one component increases with an increase in temperature.

CONCLUSIONS

The density and volume data of binary solutions (in carbon tetrachloride) of nitroparaffins in the temperature range of 30° to 45° C. indicate that the solutions are nearly ideal. Nitroethane forms a more ideal solution than nitromethane. The conclusion follows that the nitroparaffin molecule in these solutions exists, predominantly, as a single specie. This conclusion applies whether one considers acid dissociation or dimer dissociation. In both instances, the more polar nature of nitromethane would predict a greater perchance for dissociation.

ACKNOWLEDGMENT

The authors gratefully acknowledge the use of the Data Processing and Computing Center of Southern Illinois University. They also wish to thank Commercial Solvents Corp. for complimentary samples, which were used in the initial phases of this research. The authors are greatly indebted to K. A. Van Lente for his assistance with experimental procedures.

LITERATURE CITED

(1) Brown, I., Smith, F., *Australian J. Chem.* **8**, 501 (1955).
(2) *Ibid.*, **15**, 9 (1962).
(3) Daniels, F., Williams, J.W., Bender, P., Alberty, R.A., Cornwell, C.D., "Experimental Physical Chemistry," 6th ed., McGraw-Hill, New York, 1962.
(4) Foley, R.L., Lee, W.-M., Musulin, B., *Anal. Chem.* **36**, 1100 (1964).
(5) Quayle, O.R., *Chem. Rev.* **53**, 439 (1953).
(6) Scatchard, G., *Ibid.*, **44**, 7 (1949).
(7) Skoog, D.A., West, D.M., "Fundamentals of Analytical Chemistry," Holt, Rinehart, and Winston, New York, 1963.
(8) Thacker, R., Rowlinson, J., *Trans. Faraday Soc.* **50**, 1036 (1954).
(9) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. **2**, Elsevier, New York, 1965.
(10) Toops, E.E., Jr., *J. Phys. Chem.* **60**, 304 (1956).
(11) Van Lente, K.A., "Density and Specific Gravity of Liquids," Duplicated Materials, Carbondale, Ill., 1957.
(12) Weissberger, A., Ed., "Technique of Organic Chemistry," Vol. **I**, Part I, "Physical Methods of Organic Chemistry," 3rd ed., Chap. IV, Interscience, New York, 1959.
(13) Weissberger, A., Proskauer, E.S., Riddick, J.A., Toops, E.E., Jr., "Technique of Organic Chemistry," Vol. **III**, "Organic Solvents," 2nd ed., Interscience, New York, 1965.
(14) Wood, S.E., Gray, J.A., III, *J. Am. Chem. Soc.* **74**, 3729 (1952).

RECEIVED for review July 13, 1966. Accepted May 17, 1967. Presented in part to the Division of Physical Chemistry, 152nd Meeting, ACS, New York, N. Y., September 1966. Work supported by a grant from the Petroleum Research Fund (602-B) Administered by the American Chemical Society.

Thermodynamic Properties of 1,1,1,2,2-Pentafluoropropane (Refrigerant 245)

R. L. SHANK
Research and Development Department, Union Carbide Corp., South Charleston, W. Va.

Experimental volumetric and spectral data have been used to calculate the thermodynamic properties of 1,1,1,2,2-pentafluoropropane. Properties are presented for the saturated liquid and vapor from −40° F. to the critical temperature, 224.52° F. The data for the superheated vapor range from the saturation temperature to 700° F. The properties listed are volume, enthalpy, entropy, heat capacity at constant pressure, and heat capacity ratio as functions of temperature and pressure.

IN DESIGNING refrigeration equipment using a particular refrigerant, tables of thermodynamic properties of the refrigerant and graphs representing the properties are a virtual necessity. This paper is part of a continuing program in progress at the UCON Refrigerant Laboratories, Union Carbide Corp., to compile tables and construct graphs presenting the thermodynamic properties of halogenated hydrocarbons.

The present study provided detailed information on the thermodynamic properties of Refrigerant 245. The properties listed are volume, enthalpy, and entropy as functions of temperature and pressure. The values of the thermodynamic properties were computed from analytical expressions representing the heat capacity of the ideal vapor and the pressure-volume-temperature (*P-V-T*) relations of the refrigerant.

The ideal vapor heat capacity was calculated by Angell (*1*) from the fundamental frequencies of vibration of the molecule and assumed molecular dimensions and conformation, using standard methods of statistical mechanics. The data were correlated as a polynomial function of temperature.

The *P-V-T* relations were determined by isothermal pressure-volume measurements. The pressure of the saturated vapor and densities of the saturated liquid and vapor were included in the volumetric measurements. The volumetric data were represented by three analytical expressions. The Benedict-Webb-Rubin (*2*) (BWR) equation of state was chosen to represent the experimental data in the superheated and saturated vapor region. Equations proposed by Martin (*3*) were used to correlate the vapor pressure and liquid density data.

All arithmetric operations invloved in the calculation and correlation of the experimental data were programmed for a digital computer using double precision arithmetic. The conventional method of least squares was followed to determine the coefficients of the various equations chosen to represent the experimental data.

Thermodynamic properties of the saturated liquid and vapor were computed from the four basic equations representing the volumetric data and the heat capacities of the ideal vapor. In addition, the Clausius-Clapeyron equation was used to determine the latent heat of vaporization, and enabled calculation of the entropy of vaporization. The properties of the superheated vapor were derived from the heat capacity function of the ideal vapor and the equation of state.

MATERIAL

The Refrigerant 245 used in the experimental observations was purified by scrubbing and distillation. The refrigerant was scrubbed with water and a 5% by weight solution of sodium hydroxide in water to remove acidic materials. The material as a vapor was passed through a tower of calcium chloride to remove moisture. The dry condensate was then distilled through a 0.5- by 48-inch glass column packed with protruded stainless steel packing (approximately 30 theoretical plates). A midfraction boiling between −1° and 0.5° F. at atmospheric pressure was taken at a 20 to 1 reflux ratio. A purity exceeding 99.9 mole % was indicated by gas chromatography.

APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental *P-V-T* data for Refrigerant 245 were compiled with a variable volume apparatus which has been described in detail (*4*). A known mass of material was confined with a liquid mercury piston in a closed-end glass tube. The effective volume of the system could be varied by changing the pressure on the mercury piston. Provisions were made for measuring volume, and controlling and measuring pressure and temperature. The experimental technique involved the measurement of the volume of a gas-free sample under increasing values of pressure at a constant temperature.

The volume was determined by measuring, with a cathetometer, the length of space occupied by the sample in the glass tube. The volume of the tube as a function of length was determined by calibration with mercury. Corrections were made for the thermal expansion of glass but not for the effect of pressure on the tube. The precision of the volume measurements was ±1 part in 5000 to ±1 part in 50,000, depending upon the volume.

Pressures were measured with a dead-weight piston gage calibrated in this laboratory. Corrections were made for the height and temperature of the mercury piston, mass of sample, vapor pressure of mercury, and atmospheric pressure. The precision of the pressure measurements was ±0.005 p.s.i.

The thermometric measuring system consisted of a 25-ohm sealed-in-glass platinum resistance thermometer, resistance bridge, and electronic galvanometer. The system could detect temperature differences of 0.0002° F. The temperature was controlled with a thermostat surrounding the sample tube. The precision of the controlled temperature was at all times ±0.01° F. or better.

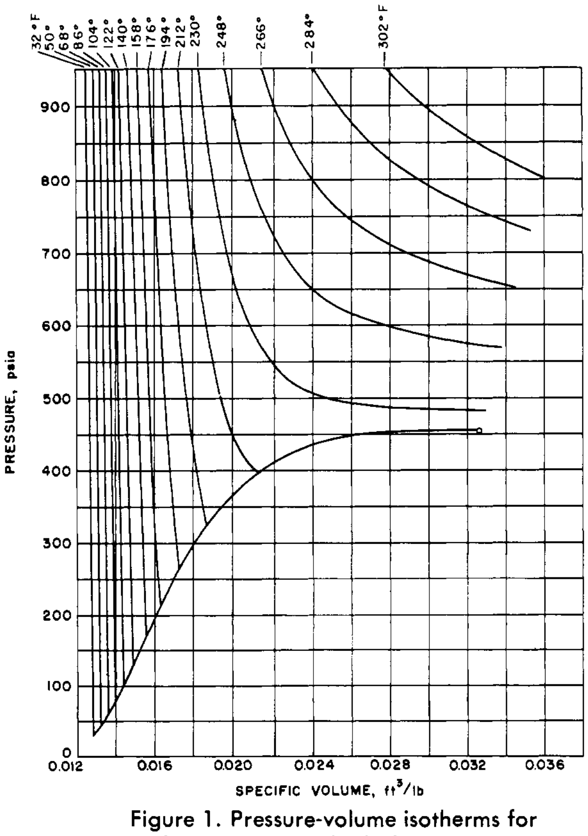

Figure 1. Pressure-volume isotherms for Refrigerant 245 in high-density region

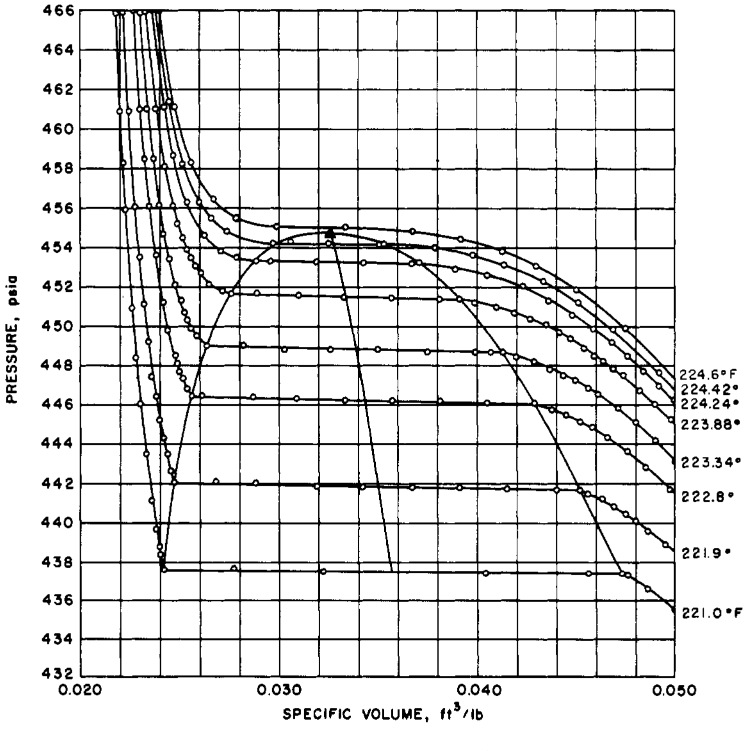

Figure 2. Pressure-volume isotherms for Refrigerant 245 in critical region

RESULTS AND DISCUSSION

The P-V-T relations for Refrigerant 245 were determined by pressure-volume measurements on 25 isotherms from 30 to 1025 p.s.i.a. at 18° F. intervals over the temperature range 32° to 464° F. The critical region was defined by 8 additional isotherms from 221° to 224.6° F. The pressure of the saturated vapor and densities of the saturated liquid and vapor were included in the volumetric measurements. The data for the density of the saturated liquid were extended to −40° F. using a standard volumnometer. The data for the pressure of the saturated vapor were extended to −41.6° F. using a Cottrell-type ebulliometer.

The experimental P-V-T data in the high-density region are presented graphically in Figure 1. These data represent the compressed liquid and were not used in the calculation of thermodynamic properties because of the limitations of the BWR equation of state. The P-V-T measurements of the pressure-volume isotherms in the critical region are plotted in Figure 2. The critical constants were determined graphically from large-scale plots of these isotherms. The critical constants are given in Table I.

The P-V-T measurements for 13 of the isotherms in the superheated and saturated vapor region are shown as compressibility factors in Figure 3. The BWR equation of state represented the experimental data in this region. The equation may be written as

$$P = \frac{RT}{V} + \frac{(B_0RT - A_0 - C_0/T^2)}{V^2} + \frac{(bRT - a)}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3T^2}\left(1 + \frac{\gamma}{V^2}\right)\exp.\,(-\gamma/V^2)$$

Numerical values for the coefficients of the BWR equation of state were determined with the restrictions that the critical isotherm would pass through the critical pressure at the critical volume with a slope of zero. As γ is a nonlinear coefficient, the remaining coefficients were determined with arbitrarily chosen values for this coefficient. The accepted set of coefficients was the set with the lowest value for the sum of the absolute percentage deviations that produced a maximum in the critical isotherm at the critical point. The values for the BWR coefficients accepted as a satisfactory representation of the experimental P-V-T data are given in Table I. The coefficients represented, where applicable, the experimental data with an average

Table I. Refrigerant 245 Critical Constants and Analytical Representation of Data

CRITICAL CONSTANTS

Critical temperature, ° F.	224.52
Critical pressure, p.s.i.a.	455.02
Critical volume, ft.^{3}/lb.	0.3265
Critical density, lb./ft.^{3}	30.628

BWR COEFFICIENTS

$A_0 = 3.9399734 \times 10^4$
$B_0 = 2.7476187$
$C_0 = 1.0380642 \times 10^{10}$
$a = -1.8097332 \times 10^3$
$b = 1.8437656$
$c = 3.1818746 \times 10^{10}$
$\alpha = 2.0300969 \times 10^2$
$\gamma = 1.8$

Units are p.s.i.a., ° R., and ft.^{3}/lb. mole.

VAPOR PRESSURE EQUATION

$$\ln P = A + B/T + C \ln T + DT + ET^2 + F \ln (G - T)$$

$A = 4.7047493$
$B = -6.3005946 \times 10^3$
$C = 3.3165496$
$D = -2.3991062 \times 10^{-2}$
$E = 1.1581305 \times 10^{-5}$
$F = -1.2646146 \times 10^{-2}$
$G = 6.986 \times 10^2$

Coefficients are for Naperian logarithms. Units are p.s.i.a. and ° R.

LIQUID DENSITY EQUATION

$$\rho_s = \rho_c + \sum_{i=1}^{6} A_i\left[(1 - T_r)^{1/3}\right]^i$$

$A_1 = 44.558561$
$A_2 = 2.117554 \times 10^2$
$A_3 = -9.7862135 \times 10^2$
$A_4 = 2.3263403 \times 10^3$
$A_5 = -2.5988686 \times 10^3$
$A_6 = 1.1138563 \times 10^3$
$T_r = T/684.19$
$\rho_c = 30.6288$

Units are lb./ft.^{3} and ° R.

HEAT CAPACITY OF IDEAL VAPOR

$$\text{Molal } C_p^\circ = a_0 + \sum_{i=1}^{6} a_iT^i$$

$a_0 = 2.349284$
$a_1 = 7.6410813 \times 10^{-2}$
$a_2 = -1.0952936 \times 10^{-4}$
$a_3 = 2.0013679 \times 10^{-7}$
$a_4 = -2.3444407 \times 10^{-10}$
$a_5 = 1.3931658 \times 10^{-13}$
$a_6 = -3.2818368 \times 10^{-17}$

Units are B.t.u./lb. mole (° R.) and ° R.

Table II. Refrigerant 245 Saturated Vapor Pressure

Temp., ° F.	Pressure, P.S.I.A.				
	Exptl.	Calcd.	Diff.	% Error	Slope, dP/dT
−41.62	4.834	4.826	−0.008	−0.167	0.1434
−20.74	8.702	8.670	−0.032	−0.367	0.2296
−12.82	10.635	10.646	0.011	0.108	0.2703
−5.98	12.569	12.626	0.057	0.455	0.3092
−0.22	14.406	14.509	0.103	0.713	0.3449
32	29.647	29.428	−0.219	−0.739	0.5964
50	41.908	41.755	−0.153	−0.365	0.7785
68	57.668	57.645	−0.023	−0.040	0.9926
86	77.600	77.692	0.092	0.119	1.2407
104	102.29	102.53	0.232	0.226	1.5249
122	132.65	132.82	0.169	0.127	1.8481
140	169.17	169.31	0.142	0.084	2.2143
158	212.85	212.83	−0.019	−0.009	2.6298
176	264.50	264.34	−0.162	−0.061	3.1043
194	325.46	325.05	−0.410	−0.126	3.6570
212	397.09	396.75	−0.343	−0.086	4.3403
221	437.42	437.75	0.332	0.076	4.7942
221.9	441.72	442.09	0.371	0.084	4.8487
222.8	446.09	446.48	0.391	0.088	4.9058
223.34	448.70	449.14	0.440	0.098	4.9415
223.88	451.40	451.82	0.418	0.093	4.9784
224.24	453.20	453.61	0.415	0.092	5.0038
224.42	454.20	454.52	0.317	0.070	5.0166
224.52	455.02	455.02	−0.001	0.000	5.0239

Table III. Refrigerant 245 Saturated Liquid Density

Temp., ° F.	Density, Lb./Cu. Ft.		
	Exptl.	Calcd.	% Error
−40	85.577	85.584	0.009
−4	82.124	82.121	−0.004
32	78.525	78.514	−0.014
50	76.639	76.608	−0.040
68	74.571	74.604	0.044
86	72.482	72.473	−0.012
104	70.152	70.183	0.044
122	67.717	67.692	−0.036
140	64.894	64.944	0.076
158	61.860	61.851	−0.015
176	58.312	58.264	−0.082
194	53.901	53.850	−0.094
212	47.312	47.456	0.303
221	41.256	41.294	0.093
221.9	40.339	40.202	−0.339
222.8	38.964	38.824	−0.360
223.34	37.748	37.750	0.004
223.88	36.178	36.287	0.302
224.24	34.552	34.769	0.628
224.42	33.612	33.437	−0.521

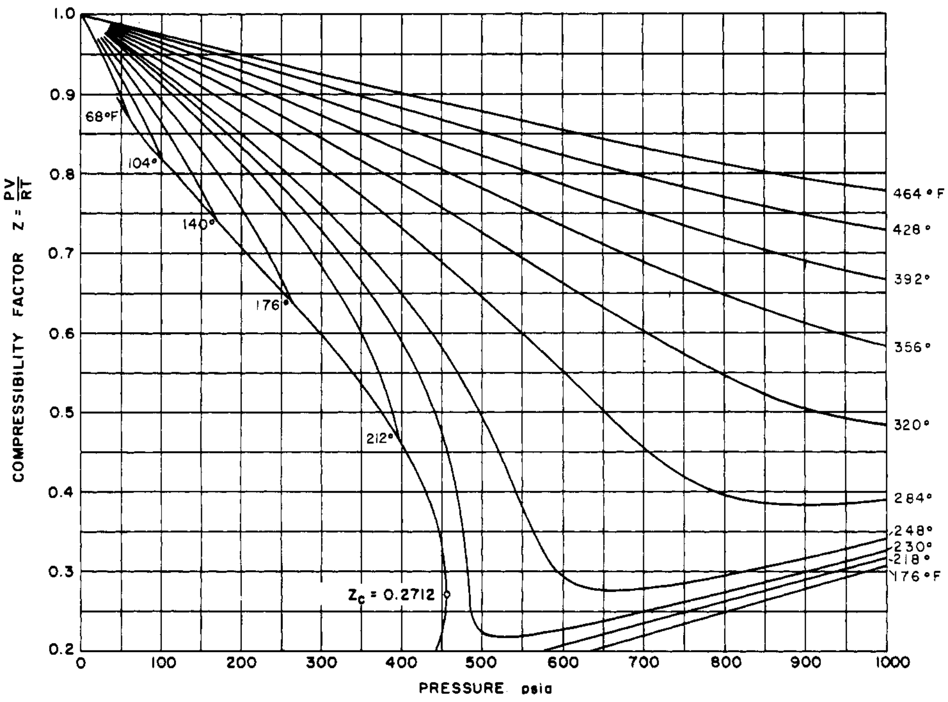

Figure 3. Compressibility factors for Refrigerant 245

Table IV. Refrigerant 245 Properties of Saturated Liquid and Vapor

Temp. °F.	Pressure		Volume, Cu. Ft./Lb.		Density, Lb./Cu. Ft.		Enthalpy, B.T.U./Lb.			Entropy, B.T.U./Lb. Deg.	
	P.S.I.A.	P.S.I.G.	Liquid	Vapor	Liquid	Vapor	Liquid	Latent	Vapor	Liquid	Vapor
−40	5.06286	19.6131[a]	0.011684	6.49157	85.5842	0.15405	0.00000	75.0580	75.0580	0.00000	0.17885
−30	6.74200	16.1943[a]	0.011816	4.96513	84.6285	0.20140	2.77547	73.9848	76.7603	0.00652	0.17871
−20	8.84126	11.9203[d]	0.011952	3.85118	83.6694	0.25966	5.59998	72.8699	78.4699	0.01301	0.17875
−10	11.4305	6.6485[a]	0.012091	3.02573	82.7041	0.33050	8.47241	71.7120	80.1844	0.01946	0.17893
0	14.5847	0.2266[a]	0.012235	2.40531	81.7298	0.41575	11.3914	70.5099	81.9013	0.02586	0.17925
10	18.3834	3.68740	0.012385	1.93278	80.7433	0.51739	14.3555	69.2627	83.6181	0.03222	0.17969
20	22.9104	8.21442	0.012541	1.56844	79.7414	0.63758	17.3629	67.9694	85.3323	0.03853	0.18023
30	28.2534	13.5574	0.012703	1.28426	78.7207	0.77866	20.4123	66.6290	87.0412	0.04479	0.18086
40	34.5035	19.8075	0.012874	1.06021	77.6776	0.94321	23.5020	65.2402	88.7422	0.05101	0.18158
50	41.7551	27.0591	0.013053	0.88179	76.6083	1.13406	26.6307	63.8015	90.4322	0.05717	0.18236
60	50.1057	35.4097	0.013244	0.73834	75.5085	1.35438	29.7976	62.3107	92.1083	0.06329	0.18319
70	59.6560	44.9600	0.013446	0.62199	74.3738	1.60774	33.0019	60.7649	93.7669	0.06935	0.18407
80	70.5096	55.8136	0.013661	0.52682	73.1992	1.89818	36.2438	59.1604	95.4041	0.07536	0.18498
90	82.7738	68.0778	0.013893	0.44834	71.9793	2.23043	39.5239	57.4919	97.1058	0.08132	0.18592
100	96.5596	81.8636	0.014143	0.38314	70.7078	2.61001	42.8439	55.7527	98.5965	0.08724	0.18686
110	111.982	97.2861	0.014414	0.32857	69.3777	3.04351	46.2065	53.9340	100.140	0.09313	0.18780
120	129.163	114.467	0.014710	0.28257	67.9806	3.53899	49.6159	52.0242	101.640	0.09898	0.18873
130	148.228	133.532	0.015036	0.24352	66.5067	4.10647	53.0779	50.0083	103.086	0.10481	0.18962
140	169.314	154.618	0.015398	0.21014	64.9435	4.75876	56.6010	47.8661	104.467	0.11063	0.19045
150	192.565	177.869	0.015804	0.18140	63.2753	5.51273	60.1965	45.5709	105.767	0.11647	0.19121
160	218.139	203.443	0.016265	0.15646	61.4805	6.39139	63.8798	43.0861	106.966	0.12234	0.19187
170	246.213	231.517	0.016799	0.13463	59.5288	7.42765	67.6733	40.3599	108.033	0.12827	0.19237
180	276.984	262.288	0.017430	0.11532	57.3732	8.67159	71.6095	37.3146	108.924	0.13432	0.19265
190	310.685	295.989	0.018203	0.09798	54.9346	10.2062	75.7399	33.8247	109.565	0.14055	0.19262
200	347.608	332.912	0.019209	0.08205	52.0593	12.1883	80.1588	29.6580	109.817	0.14711	0.19206
210	388.152	373.456	0.020673	0.06670	48.3712	14.9923	85.0859	24.2707	109.357	0.15429	0.19054
220	432.987	418.291	0.023636	0.04946	42.3079	20.2170	91.4534	15.3896	106.843	0.16346	0.18610
224.52[b]	455.019	440.323	0.032649	0.03265	30.6288	30.6288	99.5943	0.00000	99.5943	0.17523	0.17523

[a] Inches of vacuum. [b] Critical.

absolute deviation of 0.11%. The coefficients were not valid for the experimental data where the volume was less than the critical volume.

Simple models for vapor pressure-temperature relations were unable to represent the vapor pressure data adequately over the entire range. A seven-constant equation proposed by Martin (*3*) best represented the experimental data. The equation and values for the constants are presented in Table I. The vapor pressure equation described the experimental data with an average absolute deviation of 0.18%. The experimental and calculated values with their deviations and the first derivative are listed in Table II.

The analytical expression used to correlate the saturated liquid density with temperature was of the form proposed by Martin (*3*). The expression is a polynomial in the function $(1 - T_r)^{1/3}$, where T_r is the reduced temperature. The number of terms in the equation was determined by computing the coefficients with increasing number of terms and comparing the residuals. The experimental data were adequately reproduced with a six-degree polynomial. The equation and values for the constants are shown in Table I. The expression represented the experimental data with an average absolute deviation of 0.15%. The goodness of fit was 0.062% to within 2.5° F. of the critical temperature.

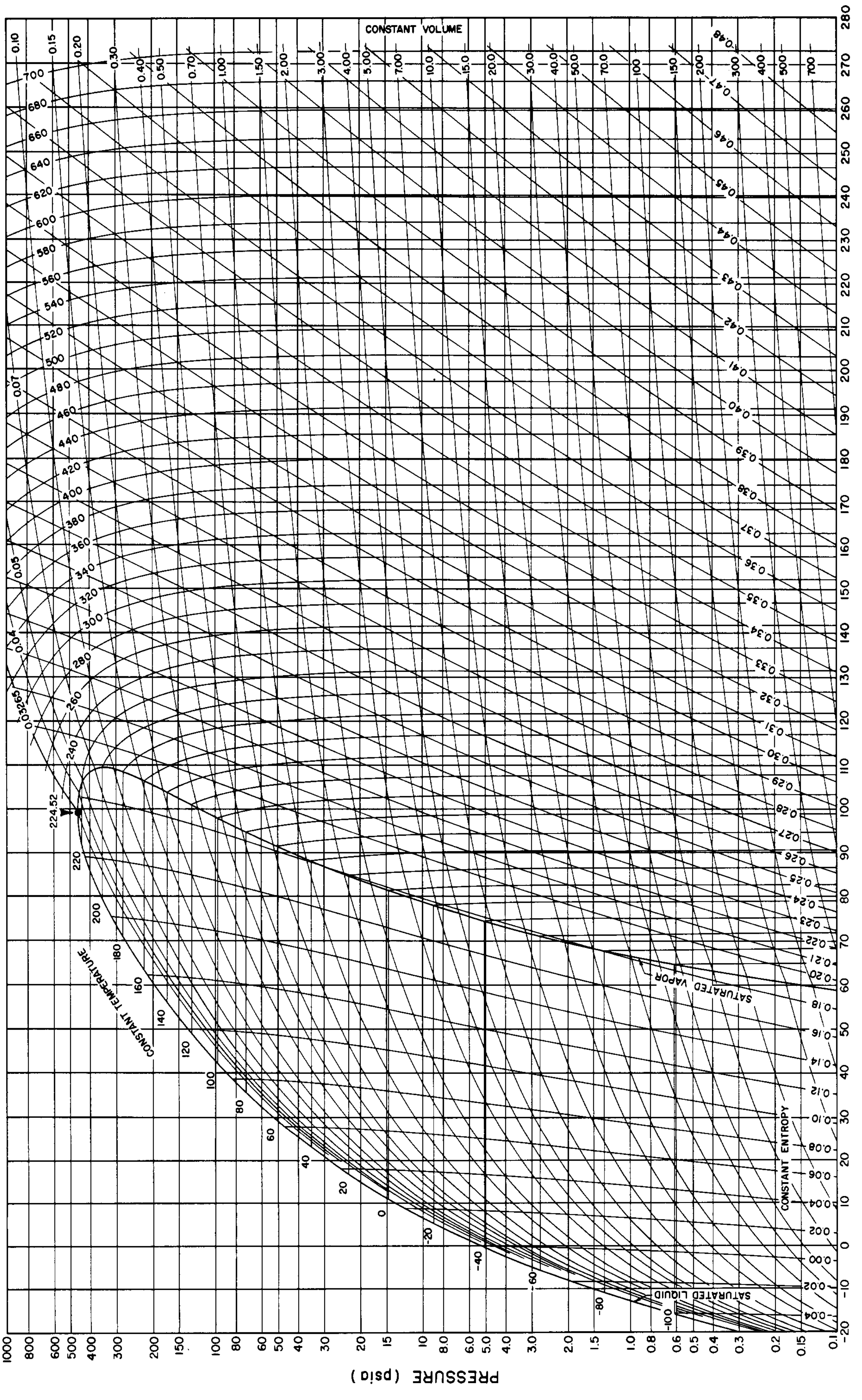

Figure 4. Pressure-enthalpy diagram for Refrigerant 245

Table V. Refrigerant 245 Properties of Superheated Vapor

Temp., ° F.	Volume, Cu. Ft./ Lb.	Enthalpy, B.T.U./ Lb.	Entropy, B.T.U./ Lb. Deg.	C_p, B.T.U./ Lb. Deg.	C_p/C_v
Pressure 1.000 P.S.I.A., 27.8851 Inches of Vacuum, Saturation Temp. –87.74° F.					
SAT	29.5840	67.106	0.18249	0.16680	1.1012
–50	32.6483	73.641	0.19920	0.17829	1.0930
0	36.6898	82.944	0.22060	0.19295	1.0846
50	40.7188	92.956	0.24126	0.20698	1.0780
100	44.7403	103.650	0.26126	0.22035	1.0727
150	48.7569	114.993	0.28066	0.23305	1.0683
200	52.7702	126.952	0.29951	0.24506	1.0647
250	56.7814	139.494	0.31783	0.25638	1.0616
300	60.7909	152.583	0.33565	0.26699	1.0589
350	64.7992	166.184	0.35298	0.27692	1.0567
400	68.8067	180.266	0.36985	0.28619	1.0547
450	72.8134	194.795	0.38628	0.29484	1.0530
500	76.8197	209.741	0.40227	0.30290	1.0515
550	80.8255	225.077	0.41785	0.31040	1.0502
600	84.8309	240.773	0.43302	0.31734	1.0490
650	88.8361	256.802	0.44780	0.32369	1.0480
700	92.8411	273.131	0.46219	0.32935	1.0472
Pressure 5.000 P.S.I.A., 19.7411 Inches of Vacuum, Saturation Temp. –40.42° F.					
SAT	6.56788	74.986	0.17886	0.18146	1.1002
0	7.24580	82.645	0.19629	0.19318	1.0904
50	8.07283	92.728	0.21709	0.20715	1.0817
100	8.89198	103.469	0.23718	0.22049	1.0751
150	9.70614	114.846	0.25664	0.23317	1.0700
200	10.5170	126.831	0.27552	0.24516	1.0659
250	11.3256	139.392	0.29387	0.25646	1.0625
300	12.1325	152.496	0.31171	0.26706	1.0596
350	12.9383	166.109	0.32906	0.27698	1.0572
400	13.7432	180.200	0.34594	0.28624	1.0552
450	14.5473	194.737	0.36238	0.29489	1.0534
500	15.3510	209.690	0.37838	0.30295	1.0518
550	16.1542	225.031	0.39396	0.31044	1.0504
600	16.9571	240.732	0.40914	0.31738	1.0493
650	17.7597	256.765	0.42392	0.32372	1.0482
700	18.5620	273.098	0.43831	0.32938	1.0473
Pressure 10.000 P.S.I.A., 9.5611 Inches of Vacuum, Saturation Temp. –15.27° F.					
SAT	3.43078	79.280	0.17882	0.18923	1.1033
0	3.56382	82.263	0.18541	0.19356	1.0984
50	3.99134	92.437	0.20641	0.20741	1.0865
100	4.41054	103.241	0.22661	0.22068	1.0783
150	4.82458	114.662	0.24615	0.23332	1.0722
200	5.23522	126.679	0.26509	0.24529	1.0674
250	5.64354	139.264	0.28347	0.25656	1.0636
300	6.05020	152.386	0.30133	0.26715	1.0605
350	6.45565	166.015	0.31870	0.27706	1.0579
400	6.86021	180.118	0.33560	0.28631	1.0557
450	7.26407	194.665	0.35205	0.29495	1.0538
500	7.66739	209.626	0.36805	0.30300	1.0522
550	8.07029	224.974	0.38364	0.31049	1.0508
600	8.47284	240.681	0.39882	0.31742	1.0495
650	8.87512	256.719	0.41361	0.32376	1.0484
700	9.27716	273.056	0.42801	0.32942	1.0475
Pressure 14.696 P.S.I.A., 0.000 P.S.I.G., Saturation Temp. 0.32° F.					
SAT	2.38812	81.956	0.17926	0.19410	1.1068
50	2.68658	92.159	0.20031	0.20769	1.0914
100	2.97825	103.023	0.22063	0.22088	1.0814
150	3.26456	114.487	0.24024	0.23347	1.0743
200	3.54738	126.534	0.25922	0.24541	1.0689
250	3.82783	139.143	0.27764	0.25667	1.0647
300	4.10660	152.283	0.29553	0.26724	1.0613
350	4.38416	165.926	0.31292	0.27713	1.0586
400	4.66080	180.040	0.32983	0.28638	1.0562
450	4.93675	194.597	0.34628	0.29501	1.0542
500	5.21216	209.566	0.36230	0.30305	1.0525
550	5.48714	224.920	0.37789	0.31054	1.0510
600	5.76177	240.633	0.39308	0.31747	1.0498
650	6.03613	256.675	0.40787	0.32380	1.0486
700	6.31025	273.017	0.42228	0.32946	1.0477
Pressure 50.000 P.S.I.A., 35.304 P.S.I.G., Saturation Temp. 59.88° F.					
SAT	0.739871	92.089	0.18318	0.21400	1.1362
100	0.821719	101.283	0.20022	0.22321	1.1113
150	0.917383	113.113	0.22046	0.23501	1.0930
200	1.00873	125.417	0.23985	0.24653	1.0816
250	1.09730	138.213	0.25854	0.25755	1.0738
300	1.18400	151.496	0.27662	0.26796	1.0681
350	1.26938	165.250	0.29415	0.27774	1.0637
400	1.35377	179.453	0.31117	0.28690	1.0603
450	1.43744	194.082	0.32771	0.29547	1.0575
500	1.52054	209.110	0.34379	0.30346	1.0552
550	1.60321	224.515	0.35943	0.31090	1.0533
600	1.68551	240.270	0.37466	0.31779	1.0516
650	1.76753	256.348	0.38949	0.32410	1.0503
700	1.84932	272.721	0.40392	0.32972	1.0491
Pressure 100.000 P.S.I.A., 85.304 P.S.I.G., Saturation Temp. 102.33° F.					
SAT	0.369568	98.960	0.18708	0.23174	1.1859
150	0.425944	110.954	0.20756	0.23902	1.1327
200	0.478863	123.720	0.22768	0.24895	1.1053
250	0.528202	136.831	0.24684	0.25920	1.0895
300	0.575296	150.343	0.26523	0.26920	1.0792
350	0.620875	164.269	0.28298	0.27873	1.0719
400	0.665382	178.607	0.30016	0.28772	1.0666
450	0.709099	193.343	0.31682	0.29616	1.0625
500	0.752218	208.460	0.33299	0.30406	1.0592
550	0.794875	223.938	0.34871	0.31143	1.0566
600	0.837166	239.754	0.36400	0.31826	1.0544
650	0.879163	255.885	0.37888	0.32452	1.0526
700	0.920920	272.303	0.39335	0.33011	1.0511

The experimental and calculated data with their deviations are listed in Table III.

Heat capacity data are conventionally represented analytically as a polynomial function of temperature. The ideal vapor heat capacity data calculated by Angell (*1*) were correlated as a sixth-degree polynomial function of temperature. The values for the coefficients are given in Table I. The equation represented the heat capacity data with an average absolute deviation of 0.00015%.

The four basic equations were inserted in thermodynamic relations which were differentiated and integrated analytically to obtain the derived thermal quantities. This procedure guaranteed perfect internal consistency and made it possible to interpolate and extrapolate the thermodynamic properties with a great degree of confidence. Details of the calculation have been presented (*4*).

The thermodynamic properties of the saturated liquid and vapor are listed in Table IV: temperature, pressure, volume, density, enthalpy, and entropy. The latent heat or enthalpy of vaporization is also included. The pressure was calculated at each tabulated temperature, directly from the vapor pressure equation. The volume of the saturated liquid was determined by taking the reciprocal of the density of the saturated liquid obtained from the liquid density equation. The volume of the saturated vapor was calculated from the BWR equation of state using the tabulated temperature and the calculated vapor pressure. The calculation required an iteration procedure and the Newton-Raphson method was used. The density of the saturated vapor was taken as the reciprocal of the volume.

The latent heat or enthalpy of vaporization was calculated from the Clausius-Clapeyron equation.

$$H_{\text{vap}} = \frac{T(V_g - V_l)\,(\mathrm{d}P/\mathrm{d}T)\,K}{M}$$

The enthalpy and entropy of the saturated vapor were derived by the exact integration of their thermodynamic relations utilizing the BWR equation of state and the equation representing the heat capacity of the ideal vapor. The thermodynamic relation used for enthalpy was

$$\mathrm{d}H = \mathrm{d}(PV) + C_v\mathrm{d}T + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]\mathrm{d}v$$

and for the entropy

$$\mathrm{d}S = \frac{C_v\mathrm{d}T}{T} + \left(\frac{\partial P}{\partial T}\right)_v \mathrm{d}v$$

where

$$C_v = C_p^0 - R + \int_\infty^v T\left(\frac{\partial^2 P}{\partial T^2}\right)_v \mathrm{d}v$$

The derivatives were obtained from the BWR equation of state. The thermodynamic relations for the enthalpy and entropy were integrated in a form that would give values at any desired temperature and pressure with a reference value of zero for the saturated liquid at −40° F.

The enthalpy of the saturated liquid was obtained by subtracting the enthalpy of vaporization from the enthalpy of the saturated vapor. The Clausius-Clapeyron equation was used without the temperature factor to give the entropy of vaporization which was subtracted from the entropy of the saturated vapor to obtain the entropy of the saturated liquid.

The thermodynamic properties of the superheated vapor are listed in Table V at constant absolute pressures with 50° F. intervals from the saturation temperature to 700° F. The properties listed are temperature, volume, enthalpy, entropy, C_p, and C_p/C_v.

The volume of the superheated vapor was calculated from the BWR equation of state using the Newton-Raphson method of iteration. The enthalpy and entropy were calculated from the integrated forms of their thermodynamic relations.

The heat capacity of the superheated vapor at constant pressure was calculated from the equation

$$C_p = C_v - T\left(\frac{(\partial P/\partial T)_v^2}{(\partial P/\partial V)_T}\right)$$

and the heat capacity ratio was determined by dividing C_p by C_v.

The thermodynamic properties of the superheated vapor have been calculated for 222 pressures representing ranges from 0.1 to 1000 p.s.i.a. at approximately equal log-pressure intervals. These tables are available upon request from Union Carbide Corp., Olefins Division, 270 Park Ave., New York, N. Y.

A large-scale pressure-enthalpy chart has been constructed presenting the data covered by the tables. The chart grid is 24 by 38 inches. This chart presents lines of constant temperature, volume, and entropy with log-pressure and enthalpy as ordinates. The chart was printed in four colors to facilitate its usage. This chart, shown in reduced form in Figure 4, is available upon request.

ACKNOWLEDGMENT

The author thanks R. I. Gray, Union Carbide Research Institute, for integrating the enthalpy and entropy relations in a form that could easily be programmed for a digital computer. Also, thanks are due to R. R. Paxton and B. L. Westfall, Union Carbide Technical Center, for assistance in compiling the P-V-T data.

NOMENCLATURE

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = constants of the BWR equation of state
A, B, C, D, E, F, G = constants of the vapor pressure equation
$A_1, A_2, A_3, A_4, A_5, A_6$ = constants of the saturated liquid density equation
$a_0, a_1, a_2, a_3, a_4, a_5, a_6$ = constants of the heat capacity equation for the ideal gas
C_p^0 = molar heat capacity of the ideal gas at constant pressure, B.t.u./lb. mole (° R.).
C_p = molar heat capacity of the real gas at constant pressure, B.t.u./lb. mole (° R.).
C_v = molar heat capacity of the real gas at constant volume, B.t.u./lb. mole (° R.).
$\mathrm{d}P/\mathrm{d}T$ = slope of the vapor pressure function, p.s.i./° R.
H = enthalpy, B.t.u./lb.
H_{vap} = latent heat or enthalpy of vaporization, B.t.u./lb.
K = conversion factor for work units
M = molecular weight
P = pressure, p.s.i.a.
R = gas constant
S = entropy, B.t.u./lb. (° R.).
T = absolute temperature, ° R.
T_r = reduced temperature
V = molar volume of superheated vapor, cu. ft./lb. mole
V_g = molar volume of saturated vapor, cu. ft./lb. mole
V_l = molar volume of saturated liquid, cu. ft./lb. mole
ρ_c = critical density, lb./cu. ft.
ρ_s = saturated liquid density, lb./cu. ft.

LITERATURE CITED

(1) Angell, C.L., J. Chem. Eng. Data **9**, 341-4 (1964).
(2) Benedict, M., Webb, G.B., Rubin, L.C., *J. Chem. Phys.* **8**, 334 (1940).
(3) Martin, J.J., "Thermodynamic and Transport Properties of Gases, Liquid, and Solids," p. 110, McGraw-Hill, New York, 1959.
(4) Shank, R.L., *ASHRAE J.* **7** (1), 94-101 (1965).

Received for review July 26, 1966. Accepted July 18, 1967.