times; the ether extracts were washed with water and dried over anhydrous magnesium sulfate.

The ether was removed and the residue taken up in benzene. The benzene solution was then run through a chromatography column containing Merck acid-washed alumina in benzene. The eluted benzene solution was collected and stripped of solvent. The oxime, 1,1′-spirocyclohexanehexahydroindan-3-oxime, was prepared from this material. The oxime (m.p. 138–40°) was recrystallized from water-ethanol.

Analysis. Calculated for $C_{14}H_{23}NO$: C, 75.96; H, 10.47; N, 6.33. Found: C, 76.09; H, 10.49; N, 6.31.

The same procedure was used for converting 1,1′-spirocyclohexane-$\Delta^{8(9)}$-tetrahydroindan-3-one to 1,1′-spirocyclohexanehexahydroindan-3-oxime. A mixed melting point of the oximes of the reduced products of the two isomeric ketones showed no depression.

The ultraviolet spectra were determined in 1-cm. quartz cells using a Cary Model II spectrophotometer.

Proton magnetic resonance spectra were determined in carbon tetrachloride solution using a Varian A-60 high resolution spectrometer. Spectra were obtained at 60 mc. using tetramethylsilane as an internal standard.

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Thermodynamic Properties of Perfluoropropane

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The thermodynamic properties of perfluoropropane (octafluoropropane) have been calculated over a temperature range of −1.00° to 71.9° C. for the saturated region and from −35° to 300° C. and over a pressure range from 1 to 40 atm. in the superheated region. The properties were determined from vapor pressure, heat capacity, and volumetric data using the Martin and Hou equation of state. The calculated results are internally consistent.

EXPERIMENTAL *P-V-T* data and physical properties for perfluoropropane have been published in the literature (*2*). However, the derived thermodynamic properties, enthalpy and entropy, have not been reported previously. This paper presents the calculated values of enthalpies, entropies, densities, and specific volumes for the saturated region from −100° C. to the critical point, and for the superheated region from 1 to 40 atm. and from −35° to 300° C.

The calculations were made based upon rigorous thermodynamic relations using the Martin and Hou equation of state (*5*).

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2e^{-kT/T_c}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT/T_c}}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{B_5T}{(V-b)^5} \qquad (1)$$

SOURCES OF DATA

Critical evaluation of the thermodynamic properties of a compound requires some knowledge of pressure-volume-temperature behavior as well as some measurements of vapor heat capacity over the range of temperatures involved. Limited data for perfluoropropane are available in the literature and were used in the preparation of this paper. A tabulation of these data with sources is presented in Table I.

Experimental gas heat capacities at low pressures and over a range of temperatures were obtained by Masi (*6*). Edgell (*4*) studied the Raman and infrared spectrum of perfluoropropane, and found 22 of the 27 fundamental frequencies of vibration. By using statistical methods, additional specific heat data were calculated (*1*). Data were then fitted to several generalized forms of heat capacity equations. The following equation was developed in the present study as the one most consistent with the data:

$$C_p^0 = 3.0911305 + 0.1485887T - 0.15309 \times 10^{-3}T^2 + 5.7292141 \times 10^{-8}T^3 \qquad (2)$$

Since there are no data available for temperatures below −30° C., extrapolation was necessary to cover the temperature range studied. Dobratz's (*7*) equation, a modification of the equation of Meghreblian, Crawford, and Parr (*7*), Crawford and Parr's (*3*) expression, and Equation 2 all yielded values agreeing with one another to within 10% when extrapolated to low temperatures. Equation 2 was chosen to be used throughout the entire temperature range in this study, since none of the other methods are considered reliable below 250° R.

Table I. Physical Properties of Perfluoropropane

Property		Source
Chemical formula	C_3F_8	(*1*)
Molecular weight	188.02	(*1*)
Normal boiling point	−36.7° C.	(2)
Normal freezing point	−160° C.	(*1*)
Critical temperature	71.9° C.	(2)
Critical pressure	26.45 atm.	(2)
Critical volume	0.299 liter/g.-mole	(2)

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Table II. Constants for the Martin and Hou Equation of State for Perfluoropropane

Units: atm.; liter; gram-mole; ° K.

Constant	Values
$A_2 \times 10^{-1}$	−1.5126979
$B_2 \times 10^{2}$	1.4656016
$C_2 \times 10^{-2}$	−3.8533552
A_3	1.7276043
$B_3 \times 10^{4}$	3.4736373
$C_3 \times 10^{-2}$	1.0435258
$A_4 \times 10^{1}$	−2.0515732
$B_5 \times 10^{5}$	1.8182426
$b \times 10^{2}$	5.332833
$R \times 10^{2}$	8.205

The vapor pressure equation was derived from Brown's (2) experimental data using the least squares method. Brown has also evaluated the Martin and Hou constants for perfluoropropane, and his numerical values were used in this investigation. Table II presents the calculated values of the constants.

The experimental vapor pressure data (2) were fitted to an equation by the least squares method using the following form:

$$\text{Log}_{10} P = a + b/T + cT + d\log_{10} T$$

where $a = 16.9953$, $b = -1435.89$, $c = 0.00282492$, $d = -4.8828$, and T in ° K., P in atm.

METHOD OF CALCULATION

The equations used to calculate the enthalpy and entropy of perfluoropropane in the superheated vapor region and for the saturated vapor were formulated by substituting the Martin and Hou equation of state into rigorous thermodynamic relations between the properties in the real gas state and in the ideal gas state at the same temperature. The integrated expressions which were used are:

$$H = H_0 + \int C_p^0 dT + \frac{1}{(V-b)}\left[2A_2 + (B_2 + bR)T + (k\frac{T}{T_c} + 2)\ C_2 e^{-[k(T/T_c)]}\right] + \frac{1}{(V-b)^2}\left[bA_2 + \frac{3}{2}A_3 + (B_3 + bB_2)T + \left(\frac{3C_3}{2} + \frac{C_3}{2}k\frac{T}{T_c} + bC_2\right) e^{-[k(T/T_c)]}\right] + \frac{1}{(V-b)^3}\left[bA_3 + \frac{4}{3}A_4 + bB_3T + bC_3 e^{-k(T/T_c)]}\right] + \frac{1}{(V-b)^4}\left[bA_4 + B_5T\right] + \frac{1}{(V-b)^5}\left[bB_5T\right] \tag{3}$$

In Equation 3, the boundary conditions are $V_f = V$, $V_i, = \infty$ $(P = O)$; and

$$S = S_0 + \int C_p^0 \frac{dT}{T} + R\ln\left[\frac{V-b}{\frac{RT}{P_i} - b}\right] - \left[B_2 - C_2\frac{k}{T_c}e^{-[k(T/T_c)]}\right]\left(\frac{1}{V-b} - \frac{1}{\frac{RT}{P_i} - b}\right) - \tfrac{1}{2}\left[B_3 - C_3\frac{k}{T_c}e^{-[k(T/T_c)]}\right]\left[\frac{1}{(V-b)^2} - \frac{1}{(\frac{RT}{P_i} - b)^2}\right] - \frac{B_5}{4}\left[\frac{1}{(V-b)^4} - \frac{1}{(\frac{RT}{P_i} - b)^4}\right] \tag{4}$$

Table III. Thermodynamic Properties of Saturated Perfluoropropane

(Datum: H and $S = 0$ for real gas at −100° C. and 0.0183 atm.)

Temp., ° C.	Pressure, Atm.	Volume, Liter/G.-Mole		Enthalpy, Calories/G.-Mole		Entropy, Calories/G.-Mole ° C.	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
−100	0.0183	0.09879	773.849	−5189.1	0.0	−29.9672	−0.0000
−95	0.0281	0.10047	517.877	−5013.8	122.0	−28.9807	−0.1539
−90	0.0421	0.10211	354.808	−4943.8	245.9	−28.6007	−0.2667
−85	0.0616	0.10369	248.630	−4835.4	371.6	−28.0133	−0.3403
−80	0.0882	0.10523	177.825	−4653.4	498.9	−27.0510	−0.3791
−75	0.1239	0.10673	129.492	−4461.5	627.6	−26.0699	−0.3881
−70	0.1709	0.10819	95.923	−4284.0	757.7	−25.1856	−0.3691
−65	0.2318	0.10962	72.174	−4122.1	889.0	−24.3979	−0.3251
−60	0.3095	0.11102	55.100	−3915.7	1021.2	−23.4188	−0.2584
−55	0.4074	0.11240	42.615	−3738.7	1154.3	−22.6078	−0.1793
−50	0.5291	0.11377	33.365	−3561.5	1288.1	−21.7992	−0.0675
−45	0.6787	0.11514	26.414	−3370.6	1422.5	−20.9547	0.0530
−40	0.8606	0.11652	21.124	−3173.5	1557.3	−20.1026	0.1872
−35	1.0795	0.11791	17.056	−2975.2	1692.3	−19.2641	0.3343
−30	1.3405	0.11934	13.893	−2777.3	1827.5	−18.4444	0.4928
−25	1.6489	0.12081	11.406	−2565.7	1962.6	−17.5868	0.6607
−20	2.0104	0.12234	9.434	−2353.4	2097.5	−16.7437	0.8375
−15	2.4311	0.12394	7.855	−2135.1	2232.0	−15.8952	1.0211
−10	2.9169	0.12564	6.581	−1914.5	2366.0	−15.0547	1.2111
−5	3.4743	0.12745	5.544	−1688.6	2499.1	−14.2105	1.4061
0	4.1099	0.12939	4.695	−1456.1	2631.3	−13.3585	1.6048
5	4.8303	0.13150	3.993	−1216.0	2762.2	−12.4961	1.8059
10	5.6425	0.13379	3.410	−973.4	2891.5	−11.6407	2.0084
15	6.5534	0.13630	2.922	−722.1	3018.9	−10.7715	2.2109
20	7.5701	0.13906	2.511	−465.4	3143.8	−9.8999	−2.4112
25	8.6996	0.14212	2.163	−201.3	3265.7	−9.0196	2.6084
30	9.9491	0.14553	1.866	71.3	3383.9	−8.1274	2.7994
35	11.326	0.14935	1.611	352.7	3497.4	−7.2231	2.9818
40	12.837	0.15365	1.390	642.4	3605.0	−6.3084	3.1522
45	14.490	0.15852	1.198	942.6	3705.0	−5.3771	3.3054
50	16.291	0.16406	1.029	1253.6	3795.8	−4.4289	3.4347
55	18.248	0.17042	0.8786	1578.6	3870.5	−3.4554	3.5288
60	20.367	0.17776	0.7426	1918.0	3925.3	−2.4561	3.5691
65	22.656	0.18631	0.6162	2274.1	3946.5	−1.4251	3.5405
70	25.122	0.19637	0.4930	2644.8	3905.1	−0.6727	3.3023
71.9	26.450	0.29900	0.2990	3374.0	3374.0	2.6489	2.6489

Table IV. Thermodynamic Properties of Superheated Perfluoropropane

(Datum: H and $S = 0$ for real gas at −100° C. and 0.0183 atm.)

(Units: H, cal./gram-mole; S, cal./gram-mole ° C.; V, liter/gram-mole)

P, Atm.	Property	Temperatures, ° C.						
		−30	−20	−10	0	20	40	60
1	H	1861.4	2187.2	2519.3	2857.9	3554.5	4277.1	5025.1
1	S	1.1817	2.4948	3.7814	5.0439	7.5047	9.8887	12.2036
	V	18.9746	19.9099	20.8258	21.7248	23.4923	25.2266	26.9385
	H		2098.5	2442.4	2790.5	3501.7	4234.6	4990.0
2	S		0.8519	2.1840	3.4825	5.9948	8.4125	10.7506
	V		9.4876	10.0023	10.4998	11.4546	12.3716	13.2658
	H					3325.9	4097.1	4878.7
5	S					3.7218	6.2664	8.6858
	V					4.1958	4.6394	5.0510
	H						3817.7	4666.3
10	S						4.2007	6.8280
	V						2.0120	2.2864
	H							4397.3
15	S							5.3853
	V							1.3291
	H							3974.3
20	S							3.7380
	V							0.7801

		Temperatures, ° C.							
		80	100	125	150	175	200	250	300
	H	5797.6	6593.6	7620.1	8679.3	9769.0	10887.0	13199.0	15599.1
1	S	14.4552	16.6475	19.3095	21.8893	24.3910	26.8182	31.4616	35.8419
	V	28.6348	30.3200	32.4156	34.5026	36.5834	38.6597	42.8029	46.9338
	H	5768.0	6568.3	7598.6	8660.7	9752.7	10872.4	13186.9	15588.9
2	S	13.0183	15.2221	17.8943	20.4812	22.9880	25.4190	30.0676	34.4514
	V	14.1434	15.0092	16.0801	17.1419	18.1975	19.2484	21.3406	23.4241
	H	5675.4	6489.5	7532.5	8603.9	9702.9	10828.0	13150.6	15558.2
5	S	11.0081	13.2500	15.9550	18.5645	21.0875	23.5304	28.1952	32.5893
	V	5.4417	5.8186	6.2761	6.7243	7.1656	7.6018	8.4641	9.3172
	H	5505.2	6348.1	7416.3	8505.4	9617.4	10752.6	13089.5	15507.0
10	S	9.2734	11.5948	14.3654	17.0182	19.5712	22.0357	26.7294	31.1417
	V	2.5264	2.7463	3.0046	3.2505	3.4883	3.7202	4.1735	4.6168
	H	5307.0	6190.8	7291.3	8401.8	9528.9	10675.3	13027.8	15455.8
15	S	8.0378	10.4721	13.3268	16.0316	18.6193	21.1084	25.8333	30.2649
	V	1.5379	1.7139	1.9103	2.0912	2.2626	2.4276	2.7448	3.0518
	H	5063.1	6012.0	7156.0	8292.6	9437.2	10596.2	12965.7	15404.8
20	S	6.9156	9.5301	12.4977	15.2663	17.8942	20.4106	25.1701	29.6218
	V	1.0242	1.1897	1.3603	1.5110	1.6501	1.7820	2.0321	2.2708
	H	4725.1	5803.0	7008.6	8177.5	9342.4	10515.4	12903.3	15354.1
25	S	5.6684	8.6399	11.7682	14.6157	17.2902	19.8373	24.6337	29.1068
	V	0.6859	0.8668	1.0282	1.1627	1.2833	1.3958	1.6056	1.8034
	H	4013.1	5548.9	6847.3	8056.4	9244.8	10433.4	12840.9	15303.8
30	S	3.4685	7.7162	11.0864	14.0321	16.7609	19.3416	24.1777	28.6729
	V	0.3777	0.6428	0.8054	0.9307	1.0398	1.1394	1.3226	1.4930
	H		5228.3	6670.8	7929.8	9144.9	10350.4	12778.7	15254.1
35	S		6.6770	10.4238	13.4916	16.2816	18.8992	23.7774	28.2954
	V		0.4750	0.6458	0.7660	0.8669	0.9575	1.1215	1.2724
	H		4842.6	6480.4	7798.5	9043.2	10267.1	12717.0	15205.1
40	S		5.5106	9.7682	12.9804	15.8388	18.4963	23.4180	27.9597
	V		0.3508	0.5273	0.6438	0.7387	0.8224	0.9719	1.1079

In Equation 4, V_i is replaced by $(RT)/(P_i)$, where P_i = 0.0001 p.s.i.a.

The enthalpy and entropy of vaporization were determined by differentiating the vapor pressure equation and substituting it into the Clausius-Clapeyron equation to give:

$$\Delta H_v = 2.303\ P\left(\frac{-b}{T^2} + c + \frac{d}{2.303T}\right) T(V_g - V_l) \tag{5}$$

$$\Delta S_v = 2.303\ P\left(\frac{-b}{T^2} + c + \frac{d}{2.303T}\right) \quad (V_g - V_l) \tag{6}$$

RESULTS

Fundamental thermodynamic relationships have been employed to check the internal consistency of the calculated enthalpy-entropy values.

Enthalpy-entropy relationships can be expressed as:

$$\left(\frac{\partial H}{\partial S}\right)_P = T,$$

integrating at constant pressure to give

$$\Delta H = H_2 - H_1 = \Delta(TS) - \int_{T_1}^{T_2} S\mathrm{d}T \tag{7}$$

Five values of enthalpy changes were calculated and compared by means of Equation 7. Agreement was within 0.1%.

This investigation is the basis for the compilation of thermodynamic tables for perfluoropropane as presented in Table III and IV. The calculations were made by digital computer. Since there were no experimental enthalpy and entropy data available for comparison, the accuracy of these calculated values can not be determined. However, based on the 29 experimental P-V-T data given by Brown (2), the average deviation of the calculated pressures using Equation 1 from the measured values was 0.22%, indicating the suitability of the equation for the calculation of thermodynamic properties of perfluoropropane.

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NOMENCLATURE

$A_2, A_3, A_4, B_2, B_3, B_5, C_2, C_3, b$ = constants in the Martin and Hou equation of state
a, b, c, d = constants in vapor pressure equation
C_p^0 = ideal heat capacity at constant pressure, cal./gram-mole ° K.
H = enthalpy, cal./gram-mole
H_0 = enthalpy evaluated at base temperature and pressure
ΔH_v = enthalpy of vaporization
k = a parameter in the Martin and Hou equation of state, 5.475
P = pressure, atm.
P_c = critical pressure
P_i = pressure at which gas is assumed to be ideal, 0.0001 p.s.i.a. or 0.6803×10^{-5} atm.
R = gas constant, 0.08205 liter-atm./gram-mole ° K.
S = entropy, cal./gram-mole ° C.
S_0 = entropy evaluated at base temperature and pressure
ΔS_v = entropy of vaporization
t = temperature, ° C.
T = absolute temperature, ° K. = t ° C. + 273.16°
T_c = critical temperature
V = specific volume, liter/gram-mole
V_g = vapor specific volume
V_l = liquid specific volume
V_i = initial specific volume
V_f = final specific volume

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Equilibria in the Hydration of Propylene and of Butylenes

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Precise thermochemical data which permit calculation of equilibrium states in the hydration of propylene and of the various isomers of butylene have recently become available. Comparisons are made between compositions thus calculated and reported values obtained by direct measurement. For the hydration of propylene with liquid and vapor phases simultaneously present, the thermochemical data, together with appropriate vapor-liquid equilibrium data, are used to estimate equilibrium compositions of both phases. The equilibrium constants for the hydration of the various C_2- through C_4- olefins show considerable similarities in behavior as functions of temperature, whereas those for the etherification of the corresponding alcohols differ more markedly. Etherification tendency decreases on progressing up the series, and is quite unfavorable for the formation of the sterically hindered *tert*-butyl ether.

A PREVIOUS ARTICLE (*6*) discussed equilibria in the hydration of ethylene with liquid and vapor phases simultaneously present. The importance of taking account of ethyl ether formation in this reaction system was pointed out. A comparison was made of equilibrium compositions calculated from available thermochemical and phase-equilibrium data and those measured experimentally. However, extension of the method of calculation to the propylene hydration system was severely restricted by the questionable reliability of various necessary thermochemical data. A more recent communication (*5*) indicated that thermochemical data of good precision have now become available for the propylene system.

One purpose of the present paper is to derive values of equilibrium constant, K_p, for the reactions

$$CH_3CH{=}CH_2 + H_2O = (CH_3)_2CHOH \qquad (1)$$

$$2(CH_3)_2CHOH = (CH_3)_2CHOCH(CH_3)_2 + H_2O \qquad (2)$$

from thermochemical data, and to compare these with reported values obtained by direct measurement of equilibrium composition. Later, an analogous treatment of reactions involved in the hydration of butylenes is presented. Another purpose is to utilize the low-pressure equilibrium data, together with appropriate phase-equilibrium data for the binary system isopropyl alcohol–water, to present an approximate calculation of equilibrium compositions for the hydration of propylene under two-phase conditions.

HYDRATION OF PROPYLENE

Calculation of Equilibrium Constants from Thermochemical Data; Results of Previous Direct Measurements of Equilibrium Constant. As indicated in the preceding equations, the hydration of propylene, when carried out in the presence of dilute mineral acid catalysts, follows the familiar