Part I

P-V-T Data and Thermodynamical Properties of Freon-12 (CCl_2F_2) and Freon-13 ($CClF_3$) Fluorocarbons at Temperatures between 0° and 150° C. and at Pressures up to 400 Atm.

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Compressibility isotherms of Freon-12 and Freon-13 are given in the temperature range 0° to 150° C. and for pressures up to 400 atm. From the results, internal thermodynamical properties are calculated.

WITH A METHOD described previously (*5*, *6*) compressibility isotherms of Freon-12 and Freon-13 have been determined in a density range up to about 130 and 230 Amagat units, respectively. Isotherms below the critical temperature were restricted in length by the two-phase boundary line. In the neighborhood of the critical point, some extra determinations were included to estimate the position of this point. The accuracy in the product PV does not exceed 1 in 4000, probably because of the presence of trace amounts of air or other impurities in the gas. The accuracy is based on previous evaluations (*5*, *6*).

The Freon-12 and Freon-13 used in this work were carefully fractionated materials supplied by E. I. du Pont de Nemours & Co., Inc. Each had a purity greater than 99.95%.

Results for Freon-12 Fluorocarbon. PV values at experimental densities are given in Table I. Pressures are expressed in atm., and densities and PV products in Amagat units. (One Amagat unit of density equals 4.5782×10^{-5} mole/cc., 1 Amagat unit of PV equals 528.783 cal./mole).

Polynomials of the form $PV = A + Bd + Cd^2 + Zd^3 + Dd^4$ were fitted to the experimental data. The coefficients of these polynomials are given in Table II, and the residues ($PV_{calcd.} - PV_{exptl.}$) in Table III (deposited with ADI). Separate equations for $PV = A + Bd + Cd^2$ were calculated from the data with density below 20 Amagat units; these coefficients are given in Table IV. The isotherms in the critical region could be used to estimate the critical point; this yielded the values $T_c = 111.80°$ C. $\pm$ 0.05, $P_c = 40.71$ atm. $\pm$ 0.05, $d_c = 102$ Amagat units $\pm$ 1.

Superheat pressures calculated as shown in the section on conversion factors, using the data of Table I, showed that a published equation (*2*) gave a fit having a standard deviation of only 0.21% and a maximum deviation of only 0.58%.

Vapor Pressure of Freon-12 Fluorocarbon. In some cases the isotherms were extended into the two-phase region to obtain vapor pressure data. The results are collected in Table V. A published vapor pressure equation (*2*) gave a fit having a standard deviation of only 0.27% and a maximum deviation of only 0.36%.

Thermodynamical Properties of Freon-12 Fluorocarbon. From the polynomials given in Table II, together with their residual curves, PV values at integral densities and at integral pressures were calculated—Tables VI (deposited with ADI) and VII. From these tables thermodynamical functions could be calculated by methods described previously (*3*, *4*). In Tables VIII to XIII, (all deposited with ADI)

Table I. Experimental PV Values for Freon-12 Fluorocarbon

	t, ° C.										
d	50	75	100	110.950	111.552	112.350	113.358	117.270	125	137	150
6.5668	1.07627	1.18251	1.28687		1.33447				1.38978		1.49174
8.4419	1.03758	1.14737	1.25473		1.30346				1.36024		1.46458
10.3074	0.99951	1.11301	1.22333		1.27329				1.33135		1.43814
12.2564		1.07759	1.19107		1.24235				1.30180		1.41096
14.5828		1.03596	1.15318		1.20604				1.26710		1.37913
16.8654		0.99571	1.11679		1.17109				1.23389		1.34849
19.0509			1.08244		1.13844				1.20257	1.25890	1.31961
19.7683		0.94559	1.07148		1.12775				1.19252		1.31028
23.8113			1.01019		1.06930				1.13688	1.19606	1.25952
28.6752			0.93989		1.00211				1.07304	1.13500	1.20118
33.4953			0.87365		0.93900				1.01313	1.07773	1.14653
38.5943			0.80732		0.87596				0.95331	1.02064	1.09210
43.6815					0.81690				0.89738	0.96721	1.04125
47.3303				0.77357	0.77728	0.78231		0.81287	0.85975	0.93102	1.00662
48.7200					0.76225				0.84551	0.91776	0.99418
52.1011				0.72434	0.72828	0.73343		0.76493	0.81327	0.88673	0.96436
53.9446					0.70959				0.79552	0.87010	0.94877
56.8387				0.67875	0.68278	0.68810		0.72052	0.77017	0.84551	0.92524
61.5257				0.63694	0.64099	0.64641		0.67960	0.73046	0.80758	0.88918
66.2828				0.59746	0.60171	0.60731		0.64123	0.69310	0.77180	0.85527
71.1215				0.56059	0.56503	0.57070		0.60525	0.65808	0.73823	0.82335
74.6576				0.53583	0.54024	0.54600	0.55321	0.58064	0.63418	0.71539	0.80149
75.9636				0.52684	0.53134	0.53708		0.57209	0.62574	0.70735	0.79414
80.4550				0.49785	0.50277	0.50849		0.54394	0.59817	0.68090	0.76895
82.1828				0.48759	0.49270	0.49861	0.50594	0.53381	0.58818	0.67134	0.76013
89.6558					0.45205	0.45792	0.46531	0.49337	0.54845	0.63347	0.72476
97.0490						0.42346	0.43071	0.45881	0.51453	0.60137	0.69541
104.552						0.39324	0.40045	0.42843	0.48502	0.57401	0.67114
112.185						0.36683	0.37391	0.40214	0.46003	0.55177	0.65242
119.822					(0.33838)	0.34410	0.35137	0.38023	0.43996	0.53516	0.64005
126.907					0.32050	0.32647	0.33406	0.36391	0.42622	0.52541	0.63502

Table II. Freon-12 Fluorocarbon Coefficients of Polynomials $PV = A + Bd + Cd^2 + Zd^3 + Dd^4$

t, ° C.	A	$B \times 10^2$	$C \times 10^5$	$Z \times 10^8$	$D \times 10^{10}$		
100	1.402186	−1.80888	6.90383	0	0	$A = RT$	d: 0–39 Am.
100.950	1.443333	(−1.7495)	7.051025	1.18677	0	$A = RT$	d: 0–82 Am.
111.552	1.445595	−1.733867	5.897258	26.69433	−16.3271	$A = RT$	d: 0–90 Am.
112.350	1.448595	(−1.742)	6.467117	18.61141	−12.8694	$A = RT$	d: 0–127 Am.
117.270	1.467082	(−1.715)	6.642205	13.61795	−10.6281	$A = RT$	d: 0–127 Am.
125	1.496129	−1.673102	6.718982	9.12624	−8.3527	$A = RT$	d: 0–127 Am.
137	1.541221	−1.625494	7.369097	−3.85962	−2.3878	$A = RT$	d: 0–127 Am.
150	1.590073	−1.552567	7.016695	−4.17308	−1.1887	$A = RT$	d: 0–127 Am.
113.358	1.421747	−1.705823	7.56943	0	−5.4783	$A = RT$	d: 74–127 Am.

Table IV. Freon-12 Fluorocarbon Coefficients of Polynomials $PV = RT + Bd + Cd^2$

t, ° C.	RT	$B \times 10^2$	$C \times 10^5$	
50	1.214301	−2.13426	4.88009	d: 0–10 Am.
75	1.308243	−1.95791	6.22871	d: 0–20 Am.
100	1.402186	−1.80163	6.49346	d: 0–20 Am.
111.552	1.445595	−1.73916	6.62639	d: 0–20 Am.
125	1.496129	−1.66513	6.52779	d: 0–20 Am.
150	1.590073	−1.53794	6.22573	d: 0–20 Am.

Table V. Vapor Pressure of Freon-12

P., Atm.	t, ° C.
6.474	25.338
7.326	29.951
9.447	39.959
11.875	49.549
15.975	62.894
20.498	74.923
25.686	86.522
32.701	99.654
40.089	110.925

the internal properties $S_i(d)$, U_i, H_i, ΔK, C_{V_i}, and C_{P_i} are given as functions of pressure. These functions result from deviations from Boyle's law. If A is an arbitrary thermodynamical function, the corresponding internal function A_i is, in mathematical terms, defined as

$$A_i = \int_0^P \left\{ \left(\frac{\partial A}{\partial P} \right)_T - \left(\frac{\partial A}{\partial P} \right)_{\text{ideal, } T} \right\} dP$$

Results for Freon-13 Fluorocarbon. PV values at experimental densities are given in Table XIV. Here 1 Amagat unit of density equals 4.5162×10^{-5} mole per cc., whereas 1 Amagat unit of PV equals 536.035 cal. per mole. Polynomials were again fitted to the experimental data. The coefficients are given in Tables XV and XVII, and the residues ($PV_{\text{calcd.}} - PV_{\text{exptl.}}$) in Table XVI (deposited with ADI). From the isotherms in the critical region the following values of the critical point could be calculated: $T_c = 29.15°$ C. ± 0.05, $P_c = 38.60$ atm. ± 0.05, $d_c = 121$ Amagat units ± 1. The data of Table XIV were not compared with other experimental and calculated values (*1*).

Thermodynamical Properties of Freon-13 Fluorocarbon. In the same way as described for Freon-12, Tables XVIII (deposited with ADI) and XIX were calculated giving PV values at respective integral densities and integral pressures. From these tables the internal thermodynamic properties $S_i(d)$, U_i, H_i, ΔK, C_{V_i}, and C_{P_i} were determined as functions of pressure, as described for Freon-12. The results are given in Tables XX to XXV (all deposited with ADI).

Table VII. Freon-12 Fluorocarbon *PV* Values for Integral Pressures

	t, ° C.									
p	50	75	100	110.950	111.552	112.350	117.270	125	137	150
0	1.21430	1.30824	1.40219	1.44333	1.44560	1.44860	1.46708	1.49613	1.54122	1.59007
1	1.19650	1.29314	1.38928	1.43120	1.43351	1.43658	1.45537	1.48495	1.53072	1.58029
5	1.11999	1.22966	1.33571	1.38116	1.38366	1.38692	1.40722	1.43909	1.48781	1.54074
10	1.00721	1.14150	1.26370	1.31468	1.31740	1.32108	1.34362	1.37880	1.43199	1.48954
15		1.03842	1.18438	1.24262	1.24575	1.24991	1.27534	1.31462	1.37333	1.43623
20			1.09460	1.16334	1.16698	1.17185	1.20109	1.24555	1.31124	1.38042
25			0.98841	1.07375	1.07818	1.08398	1.11872	1.17030	1.24505	1.32165
30			0.84959	0.96809	0.97377	0.98120	1.02455	1.08680	1.17373	1.25944
35				0.83149	0.83977	0.85103	0.91152	0.99147	1.09592	1.19369
40				0.53336	0.58951	0.62910	0.75935	0.87762	1.00958	1.12377
45							0.41026	0.72768	0.91197	1.04873
50								0.51158	0.80004	0.96853
55									0.67558	0.88419
60									0.57419	0.79935
65									0.53082	0.72447
70										0.67247
75										0.64491
80										0.63541

Table XIV. Freon-13 Fluorocarbon *PV* Values at Experimental Densities

	t, ° C.										
d	0	25	30	30.35	31.35	32.35	50	75	100	125	150
0	1.01253	1.10520	1.12374				1.19788	1.29055	1.38322	1.47589	1.56856
19.0777	0.78664	0.90351	0.92631				1.01642	1.12695	1.23599	1.34371	1.45061
23.8448		0.85736	0.88120				0.97520	1.09002	1.20288	1.31432	1.42473
28.7159		0.81177	0.83680				0.93464	1.05379	1.17050	1.28569	1.39955
33.5436		0.76834	0.79442				0.89608	1.01939	1.13997	1.25871	1.37607
38.6508		0.72441	0.75159				0.85718	0.98474	1.10930	1.23173	1.35264
43.7461		0.68252	0.71072				0.82020	0.95193	1.08029	1.20641	1.33092
45.3343		0.66984	0.69851				0.80904	0.94199	1.07152	1.19889	1.32490
48.7931		0.64301	0.67232				0.78537	0.92105	1.05317	1.18290	1.31064
49.9041		0.63469	0.66428				0.77805	0.91457	1.04741	1.17810	1.30715
54.0264		0.60417	0.63448				0.75115	0.89082	1.02674	1.16027	1.29153
54.4419		0.60116	0.63168				0.74860	0.88847	1.02463	1.15846	1.29061
58.9306		0.56969	0.60107				0.72086	0.86409	1.00327	1.14036	1.27561
63.4887		0.53942	0.57163				0.69422	0.84061	0.98313	1.12332	1.26169
65.2319			0.56108				0.68446	0.83200	0.97557	1.11677	1.25625
68.1238		0.51010	0.54326				0.66852	0.81811	0.96369	1.10717	1.24882
71.8073			0.52212				0.64930	0.80122	0.94933	1.09515	1.23933
72.7622		0.48248	0.51648				0.64432	0.79686	0.94553	1.09235	1.23732
77.0645			0.49309				0.62301	0.77835	0.93009	1.07984	1.22786
78.3373			0.48669				0.61710	0.77321	0.92567	1.07610	1.22499
84.7965			0.45472				0.58797	0.74805	0.90481	1.05987	1.21354
91.3550			0.42522				0.56100	0.72493	0.88622	1.04599	1.20472
96.4442			0.40426	0.40672	0.41380	0.42087	0.54160	0.70859	0.87351	1.03721	1.19980
98.0244			0.39817				0.53605	0.70401	0.86986	1.03463	1.19881
104.699			0.37384				0.51360	0.68549	0.85613	1.02631	1.19622
106.166			0.36883	0.37133	0.37848	0.38560	0.50894	0.68182	0.85379	1.02547	1.19582
110.890			0.35355				0.49466	0.67081	0.84606	1.02138	1.19719
115.821			0.33880	0.34134	0.34843	0.35555	0.48137	0.66046	0.84001	1.01963	1.19881
125.371			0.31351	0.31599	0.32312	0.33020	0.45886	0.64479	0.83253	1.02133	1.20937
131.166			0.29996				0.44728	0.63808	0.83107	1.02531	1.21966
135.069			0.29157	0.29405	0.30120	0.30847	0.44082	0.63479	0.83186	1.03017	1.22866
144.389			0.27382				0.42816	0.63127	0.83810	1.04702	1.25660
144.930			0.27265	0.27535	0.28273	0.29017	0.42762	0.63126	0.83878	1.04827	1.25808
154.800			0.25778	0.26049	0.26816	0.27602	0.42043	0.63516	0.85444	1.07694	1.29945
157.522			0.25449				0.41961	0.63792	0.86096	1.08672	1.31326
163.956			0.24796	0.25084	0.25902	0.26733	0.41998	0.64689	0.87855	1.11437	1.34974
170.513			0.24405				0.42392	0.66077	0.90272	1.14763	1.39346
183.708			0.24641				0.44546	0.70492	0.96947	1.23702	1.50503
197.129			0.26817				0.49079	0.77748	1.06864	1.36203	1.65590
210.566			0.31768				0.56781	0.88625	1.20799	1.53103	1.85398
223.037			0.39759				0.67678	1.02862	1.38252	1.73643	2.08952

Table XV. Freon-13 Fluorocarbon Coefficients of Polynomials $PV = A + Bd + Cd^2 + Zd^3 + Dd^4 + Ed^5 + Fd^6 + Gd^7$

	t, ° C.						
	25	30	50	75	100	125	150
$A = RT$	1.10520	1.12374	1.19788	1.29055	1.38322	1.47589	1.56856
$B \times 10^2$	−1.12601	−1.11914	−1.00886	−0.917560	−0.830716	−0.752346	−0.675207
$C \times 10^5$	3.56530	4.97747	2.88105	3.08387	3.05745	3.14967	3.01295
$Z \times 10^7$	0.205497	−4.48440	1.485614	0.743623	0.425042	−0.044730	0.049691
$D \times 10^9$	0	7.334543	−1.202476	−0.779226	−0.524262	−0.073935	−0.118628
$E \times 10^{11}$	0	−5.653134	0.1907077	0.1706838	0.1427885	0.0090547	0.0672223
$F \times 10^{13}$	0	1.916589	0.0463648	0.0334417	0.0299614	0.0450305	0.0321248
$G \times 10^{16}$	0	−2.284664	0	0	0	0	0
$d =$	0–72 Am	0–223 Am	0–223 Am	0–223 Am	0–223 Am	0–223 Am	0–223 Am

Table XVII. Freon-13 Fluorocarbon Polynomials

$PV = A + Bd + Cd^2 + Zd^3$

	t, ° C.		
	30.35	31.35	32.35
$A = RT$	1.04052	1.03465	1.03366
$B \times 10^2$	−0.965380	−0.930925	−0.908273
$C \times 10^5$	3.54286	3.23914	3.02729
$Z \times 10^8$	−3.61807	−2.72861	−2.06796
	96–164 Am	96–164 Am	96–164 Am

NOMENCLATURE

C_P = internal specific heat at constant pressure, cal./mole ° C.
C_V = internal specific heat at constant volume, cal./mole ° C.
d = vapor density, Amagat units
H_i = internal enthalpy = $\Delta(U_i + PV)$, cal./mole
ΔK = internal kinetic energy = $\Delta(3PV - U_i)$, cal./mole
P = pressure, international atmospheres
PV = energy per mole, Amagat units
S_i = internal entropy, cal./mole ° K.
t = temperature, ° C.
T = temperature, ° K.

Table XIX. PV Values Freon-13 Fluorocarbon for Integral Pressures

	t,° C.						
P	25	30	50	75	100	125	150
0	1.10520	1.12374	1.19788	1.29055	1.38822	1.47589	1.56858
1	1.09495	1.11385	1.18940	1.28340	1.37718	1.47078	1.56426
3	1.05255	1.07295	1.15462	1.25443	1.35289	1.45028	1.54708
10	0.99580	1.01371	1.10915	1.21721	1.32207	1.42460	1.52562
15	0.93365	0.96004	1.06116	1.17885	1.29079	1.39880	1.50426
20	0.86397	0.89528	1.01018	1.13921	1.25901	1.37297	1.48301
25	0.78253	0.82160	0.95569	1.09826	1.22681	1.34706	1.46195
30	0.67902	0.73318	0.89683	1.05595	1.19423	1.32118	1.44110
35	0.49182	0.61391	0.83232	1.01220	1.10136	1.29548	1.42054
40		0.25595	0.76023	0.96704	1.12831	1.26396	1.40032
45		0.24585	0.67810	0.92055	1.09513	1.24474	1.38053
50		0.25902	0.58505	0.87303	1.06226	1.21999	1.36125
60		0.29282	0.43760	0.77843	0.99804	1.17240	1.32459
70		0.32904	0.42092	0.69693	0.93905	1.12863	1.29111
80		0.36574	0.44059	0.64730	0.89009	1.09045	1.26167
90			0.46935	0.63146	0.85535	1.05952	1.23710
100			0.50144	0.63728	0.83631	1.03725	1.21801
120			0.56932	0.67878	0.83704	1.01927	1.19752
140			0.63872	0.73606	0.86983	1.03109	1.19950
160				0.79907	0.91856	1.06310	1.21985
180				0.86440	0.97501	1.10752	1.25365
200				0.93068	1.03547	1.15938	1.29680
220				0.99726	1.09808	1.21575	1.34631
240					1.18184	1.27491	1.40007
260					1.22620	1.33583	1.45675
280					1.29083	1.39782	1.51536
300					1.35551	1.46048	1.57533
320						1.52352	1.63622
340						1.58676	1.69772
360						1.65008	1.75060
380						1.71337	1.82173
400							1.88398
420							1.94826
440							2.00853

CONVERSION OF THERMODYNAMICAL DATA FOR FREON-12 FLUOROCARBON TO ENGLISH UNITS. EXAMPLE USING VALUES FOR FREON-12 FLUOROCARBON

Conversion Factors. 1 Amagat unit (d) = 4.5782×10^{-5} mole per cc. at P = 1 atm. t = 0° C.

× 120.925 = 0.00553619 gram per cc.
× 62.4280 = 0.345613 lb. per cu. ft.

1 Amagat unit (PV) = 528.783 cal. per mole

÷ 120.925 = 4.37282 cal. per gram
× 9.72061 = 42.5065 × cu. ft./lb. × p.s.i.a.

Example. From Table I we read the following set of values for Freon-12:

t = 100.00° C.
d = 6.5668 Amagat units
PV = 1.28687 Amagat units

Converting to English units:

Temperature = 1.8 (100.00 + 273.15) = 671.67° R.
Vapor density = 6.5668 × 0.345613 = 2.26957 lb. per cu. ft.
Pressure = 1.28687 × 42.5065 × 2.26957 = 124.15 p.s.i.a.

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