JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 74A, No. 5, September–October 1970

Specific Heats, C_v, of Compressed Liquid and Gaseous Fluorine*

Rolf Prydz and Robert D. Goodwin**

Institute for Basic Standards, National Bureau of Standards, Boulder, Colo. 80302

(May 11, 1970)

Experimental specific heats at constant volume for compressed gaseous and liquid fluorine are reported from 80 K to 300 K at pressures to about 23 MN/m^2.

Key words: Compressed gas; compressed liquid; fluorine; heat capacities; specific heats.

List of Symbols

$C_b(T)$	heat capacity of empty bomb
$C_v^\circ(T)$	ideal gas specific heat
$C_v(\rho, T)$	specific heat at constant volume
C_x	work done to expand calorimeter bomb
N	total g moles of fluid in closed system
N_c	g moles of fluid in capillary tube
P	pressure, 1 $MN/m^2 = 9.86923$ atm
Q	calorimeter heat input
ρ	density
T	temperature, K, on the IPTS (1968)
T_1, T_2	temperature at start and end of heating interval
T_a	average temperature in ΔT
$\Delta T \equiv$	$T_2 - T_1$, calorimetric temperature increment
$v \equiv$	$1/\rho$, molal volume
V_b	volume of calorimeter bomb.

1. Introduction

These specific heat measurements and the reported specific heat data along the vapor-liquid coexistence boundary [1] [1] are part of a program in this laboratory to determine the thermodynamic properties of compressed gaseous and liquid fluorine. Since no single-phase specific heat data of either liquid or gaseous fluorine have been published previously, it is the purpose of this paper to report new such measurements at constant volume, C_v, from just below the normal boiling point (85 K) to 300 K at pressures to 23 MN/m^2 (1 $MN/m^2 = 9.86923$ atm). These data supplement recent PVT measurements of fluorine in this laboratory for the computation of the thermodynamic properties of this fluid.

2. Experimental Apparatus

The calorimeter and the cryostat used for these experiments are the same as the ones used for oxygen [2, 3], though the valves in the system were modified for compatibility with high-pressure fluorine [4]. Briefly, the calorimeter is a thin, spherical stainless steel shell, 5 cm in diameter, surrounded by adiabatic shields automatically controlled at the temperature of the calorimeter. This temperature is measured using a platinum resistance thermometer calibrated by NBS on the IPTS 1968 temperature scale. Fluorine filling pressures are measured by referencing to oil pressure derived from an oil dead-weight gage through an intermediate nitrogen system (the nitrogen system is a safety precaution to reduce the possibility of direct contact between the fluorine and the dead-weight gage oil, a catastrophic situation).

A separate fluorine filling and recovery system was constructed consisting of a 10-liter stainless steel storage cylinder, a thermal pressure booster assembly, and a hydrogen fluoride (HF) absorber. The fluorine is kept in the storage cylinder at a pressure of about 1.5 MN/m^2. Calorimeter filling pressures are generated by the thermal booster, which is surrounded by a liquid nitrogen bath. Sodium fluoride pellets in the HF absorber serve to remove any traces of hydrogen fluoride in the fluorine before it is condensed in the booster.

A cabinet surrounding the cryostat and the supply system is maintained at a slightly reduced pressure, relative to ambient pressure, by an exhaust fan located outside the laboratory. This reduces the probability of venting the extremely toxic fluorine fumes into the laboratory if a leak should develop in the system. In

*This work was carried out at the National Bureau of Standards under the sponsorship of the United States Air Force (MIPR No. FO4611-70-X-0001).
**Cryogenics Division, National Bureau of Standards, Boulder, Colo. 80302.
[1] Figures in brackets indicate the literature references at the end of this paper.

the case of a system failure, however, provisions have been made for emergency venting of the fluorine through charcoal reactors outside the laboratory. Detailed description of materials that may be used for construction of fluorine handling systems and apparatuses is given by reference [5].

3. Procedures

The specific heat, C_v, of a substance is determined from the energy input, Q, to raise the temperature of a unit mass by ΔT. Experimental specific heats are obtained in the following way. The energy input to the calorimeter, Q, is obtained from simultaneous readings of potential and current as the heating time interval is measured by an electronic counter. The electric power input is obtained by averaging three pairs of potential and current readings. Five temperatures are measured immediately preceding a heating interval and are then extrapolated linearly to obtain the temperature, T_1, of the calorimeter at the mid-time of the heating period as if no heat had been added. At the end of the heating interval the temperature of the calorimeter may increase for about 20 min before a very slow cooling begins (imperfect adiabatic shielding). Five new temperatures are then measured and again linearly extrapolated to the mid-time of the heating interval to obtain T_2. Assigned to that particular specific heat observation is the average temperature $T_a=(T_1+T_2)/2$. The temperature increase of the calorimeter is $\Delta T=T_2-T_1$.

Calorimeter filling pressures are measured by the dead-weight gage and are corrected for the hydrostatic head of fluorine in the capillary tube leading down to the calorimeter bomb. From this pressure and the filling temperature, a one-phase density is calculated with an uncertainty of about 0.1 percent from an equation of state of the type previously applied to deuterium [6]. The fluorine mass in the calorimeter is then calculated from the known volume, V_b, of the calorimeter (uncertainty of about 0.1 percent) [2]. The number of moles of sample in the capillary volume ($0.0002 \cdot V_b$) is computed from an estimated temperature distribution [2] and the equation of state. Thus, the total mass of sample in the closed system is known to an uncertainty of about 0.2 percent.

To obtain the density, ρ, at each specific heat observation, corrections must be made for the expansion of the calorimeter bomb and the amount of fluorine in the capillary tube by calculating the pressures at T_1 and T_2. The application of a double iteration method to adjust for the relative change of the mass of sample in the capillary tube, N_c, and the combined effect of temperature and pressure expansion of the stainless steel calorimeter, has been discussed by Goodwin and Weber [3]. Thus, the expression for density is

$$\rho=[N-N_c(P,T)]/V_b(P,T) \tag{1}$$

where N is the total number of g moles in the closed system. The densities ρ_1, ρ_2 obtained in this manner at T_1, T_2 may be used to compute the adjustment in the heat capacity, C_x, due to the work done to expand the calorimeter bomb as

$$\Delta v=1/\rho_2-1/\rho_1$$

and

$$C_x=[T_2(\partial P/\partial T)_2-\Delta P/2]\cdot \Delta v/\Delta T. \tag{2}$$

Using this expression, the experimental specific heats are calculated from

$$C_v=[Q/\Delta T-C_b]/[N-N_c]-C_x \tag{3}$$

where Q is the total energy input and C_b is the heat capacity of the empty calorimeter bomb from [1]. The heat capacity adjustment, C_x, is largest for the highest densities, being of the order of 1.2 percent of the total heat capacity, $Q/\Delta T$, for run No. 8.

The purity of the fluorine sample used for these measurements was 99.99 percent as determined from residual gas analysis after reaction of the fluorine with mercury.

4. Experimental Results

The location of all experimental C_v data on the PVT surface is given in figure 1. Also indicated in this

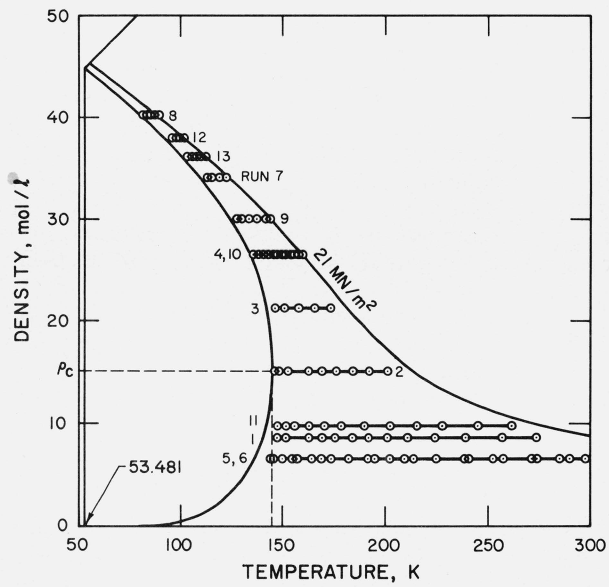

FIGURE 1. *Locus of* C_v *data on* $\rho-T$ *surface.*

figure is the critical point ($\rho_c=15.10$ mole/l; $T_c=144.31$ K), which helps to give the relative location of each experimental run. Upper limits of 300 K in temperature and 21 MN/m^2 in pressure bound the range of the data together with the vapor-liquid coexistence boundary. Table 1 gives the filling conditions of the calorimeter bomb for each run as determined by the temperature-pressure conditions of the first two columns of this table. Next is the calculated volume of the calorimeter and the density calculated from the equation of state. N is the total number of g moles

TABLE 1. *Loading conditions for the samples*

Run	T	P	V_b	D	N
	K	MN/m^2	cm^3	mol/l	mol
1	174.825	8.4244	73.014	8.709	0.6360
2	166.789	10.4272	73.008	15.184	1.1087
3	175.609	18.6026	73.114	21.245	1.5535
4	155.918	17.4279	73.040	26.238	1.9167
5	193.408	8.3099	73.071	6.551	0.4787
6	195.075	8.6601	73.079	6.770	0.4948
7	116.282	8.8620	72.850	34.098	2.4843
8	84.845	8.6315	72.774	40.123	2.9202
9	133.421	9.4309	72.901	29.905	2.1803
10	147.833	12.6624	72.972	26.611	1.9420
11	188.588	10.8379	73.080	9.807	0.7168
12	98.066	10.6331	72.819	37.922	2.7617
13	108.200	12.6513	72.860	36.220	2.6392

as obtained from the density and the calorimeter and capillary volumes.

The experimental results are given in table 2. Identification in the first column is the run number followed by two digits for the data point of that run. Next are the observed temperature, the estimated pressure, the calorimeter bomb volume, V_b, and the calculated density at these conditions. Further, the ΔT column is the temperature increment of the heating period. The following columns have the total heat capacity $Q/\Delta T$, the heat capacity of the empty calorimeter, and the adjusted specific heat of the fluorine sample as calculated from eq (3). These specific heat values also include curvature adjustments as discussed by Goodwin and Weber [2]. However, the adjustments changed only the two first points (points No. 215, 216) of run No. 2 which is closest to the critical density. The estimated maximum

TABLE 2. *Specific heats of fluorine*

ID	T_a	P	V_b	D	ΔT	$Q/\Delta T$	Tare	C_v	Error in C_v
	K	MN/m^2	cm^3	mol/l	K	J/K	J/K	$J/mol\ K$	%
115	147.552	5.380	72.905	8.723	3.394	85.994	65.724	31.77	1.37
116	152.783	5.985	72.926	8.720	7.150	85.764	66.936	29.50	1.11
117	162.897	7.122	72.966	8.715	7.083	86.406	69.066	27.16	1.21
118	169.884	7.888	72.994	8.712	7.023	87.170	70.396	26.26	1.26
119	176.795	8.636	73.022	8.708	6.951	88.028	71.613	25.69	1.30
120	184.349	9.443	73.053	8.704	8.321	89.004	72.845	25.28	1.27
121	192.537	10.314	73.088	8.700	8.225	90.032	74.078	24.96	1.30
122	201.228	11.230	73.125	8.696	9.643	91.099	75.285	24.73	1.28
123	211.965	12.355	73.171	8.690	12.101	92.340	76.653	24.52	1.24
124	225.285	13.739	73.230	8.683	14.820	93.804	78.188	24.40	1.22
125	240.581	15.316	73.298	8.675	16.052	95.418	79.769	24.44	1.22
126	257.055	16.999	73.373	8.666	17.250	96.938	81.293	24.42	1.23
127	275.383	18.851	73.457	8.656	19.832	98.526	82.811	24.52	1.22
215	145.586	5.509	72.901	15.207	1.592	116.052	65.248	44.63	1.17
216	148.230	6.116	72.914	15.204	3.738	106.091	65.886	35.76	0.86
217	153.049	7.229	72.938	15.199	5.966	102.260	66.995	31.65	.79
218	162.488	9.422	72.986	15.189	5.989	100.533	68.985	28.28	.86
219	169.101	10.969	73.021	15.181	7.341	100.628	70.252	27.21	.84
220	176.346	12.671	73.060	15.173	7.265	101.105	71.537	26.47	.86
221	184.279	14.535	73.103	15.164	8.736	101.761	72.834	25.88	.85
222	192.861	16.551	73.151	15.154	8.587	102.574	74.125	25.44	.87
223	201.351	18.538	73.199	15.144	8.576	103.543	75.301	25.24	.88
316	146.736	6.508	72.913	21.305	4.342	112.663	65.528	30.10	.75
317	151.590	8.466	72.945	21.295	5.439	111.336	66.667	28.49	.72
318	158.187	11.202	72.990	21.282	7.844	110.993	68.107	27.31	.67
319	165.967	14.489	73.044	21.265	7.819	111.295	69.664	26.48	.70
320	173.700	17.787	73.100	21.249	7.769	112.027	71.079	26.01	.71
401	138.316	5.515	72.880	26.298	4.171	117.573	63.374	27.84	.72
402	142.452	8.307	72.917	26.284	4.148	117.631	64.462	27.28	.73
403	146.560	11.092	72.954	26.270	4.130	118.010	65.485	26.93	.74
404	150.651	13.867	72.991	26.256	4.113	118.570	66.452	26.70	.76
405	154.652	16.575	73.028	26.243	4.098	118.889	67.349	26.38	.77
406	158.702	19.294	73.066	26.229	4.076	119.551	68.214	26.26	.78
407	162.321	21.709	73.100	26.216	3.241	120.014	68.952	26.11	.86
408	136.840	4.521	72.868	26.303	2.434	117.418	62.970	27.99	.90
409	140.138	6.741	72.896	26.292	4.197	117.547	63.860	27.56	.72
410	144.283	9.548	72.933	26.278	4.137	117.849	64.925	27.15	.74
411	148.395	12.338	72.971	26.264	4.129	118.233	65.925	26.81	.75
412	152.431	15.071	73.008	26.250	4.106	118.646	66.857	26.52	.76
413	156.495	17.813	73.046	26.236	4.088	119.232	67.748	26.35	.77
414	160.539	20.522	73.084	26.223	4.067	119.780	68.592	26.18	.78

ID	T_a	*P*	V_b	*D*	ΔT	$Q/\Delta T$	Tare	C_v	Error in C_v
	K	*MN/m²*	*cm³*	*mol/l*	*K*	*J/K*	*J/K*	*J/mol K*	*%*
501	143.968	4.531	72.887	6.568	6.264	78.966	64.846	29.41	1.39
502	150.160	5.035	72.909	6.566	6.193	79.565	66.338	27.54	1.50
503	157.025	5.576	72.934	6.563	7.630	80.543	67.861	26.40	1.48
504	164.958	6.186	72.963	6.561	8.344	81.731	69.470	25.52	1.51
505	173.561	6.837	72.995	6.558	9.010	83.033	71.055	24.92	1.54
506	182.850	7.530	73.030	6.554	9.728	84.443	72.608	24.62	1.55
507	192.588	8.249	73.068	6.551	10.269	85.684	74.085	24.12	1.58
508	203.140	9.021	73.109	6.547	11.047	87.039	75.538	23.91	1.59
509	214.436	9.841	73.154	6.543	11.777	88.433	76.950	23.86	1.60
510	226.887	10.738	73.204	6.539	13.401	89.815	78.362	23.79	1.58
511	241.823	11.806	73.265	6.533	16.807	91.380	79.890	23.86	1.55
512	258.287	12.975	73.333	6.527	16.518	92.961	81.400	24.00	1.57
513	274.496	14.114	73.401	6.521	16.373	94.356	82.741	24.10	1.59
514	290.482	15.228	73.469	6.515	16.164	95.605	83.946	24.18	1.60
612	146.154	4.772	72.896	6.788	11.929	79.850	65.387	29.14	1.17
613	157.907	5.751	72.938	6.784	11.696	81.181	68.048	26.45	1.30
614	169.905	6.709	72.983	6.779	12.437	82.937	70.400	25.24	1.37
615	182.617	7.701	73.031	6.775	13.158	84.761	72.571	24.53	1.42
616	196.025	8.731	73.083	6.770	13.861	86.567	74.574	24.12	1.46
617	210.026	9.795	73.139	6.765	14.402	88.329	76.415	23.96	1.48
618	224.468	10.883	73.197	6.759	15.194	89.981	78.098	23.88	1.50
619	239.344	11.994	73.258	6.754	14.932	91.523	79.647	23.86	1.53
620	253.945	13.075	73.319	6.748	14.696	92.969	81.017	24.00	1.55
621	271.674	14.377	73.394	6.741	15.897	94.492	82.517	24.04	1.55
622	285.815	15.406	73.455	6.735	12.963	95.630	83.605	24.13	1.62
623	298.381	16.315	73.509	6.730	12.775	96.617	84.503	24.30	1.63
708	113.159	4.271	72.804	34.121	2.987	128.246	55.210	28.37	0.73
709	116.127	8.617	72.848	34.100	2.960	128.856	56.333	28.18	.74
710	119.070	12.839	72.891	34.079	2.944	129.683	57.400	28.08	.75
711	121.991	16.927	72.934	34.058	2.916	130.538	58.415	28.04	.75
801	82.992	3.711	72.733	40.147	1.886	138.288	40.657	31.67	0.80
802	84.877	8.707	72.775	40.123	1.884	138.887	41.750	31.59	.81
803	86.751	13.555	72.815	40.100	1.866	139.729	42.811	31.51	.82
804	88.610	18.265	72.856	40.077	1.851	140.624	43.839	31.50	.82
805	90.459	22.835	72.895	40.055	1.847	141.300	44.836	31.41	.83
901	127.307	3.459	72.833	29.935	3.060	126.035	60.157	29.56	0.74
902	130.410	6.500	72.867	29.920	3.174	122.094	61.114	27.30	.77
903	133.766	9.761	72.905	29.904	3.573	122.720	62.103	27.12	.74
904	137.312	13.159	72.945	29.887	3.557	123.401	63.100	26.97	.75
905	141.435	17.057	72.992	29.867	2.324	123.929	64.200	26.70	.92
906	143.738	19.203	73.018	29.856	2.338	124.410	64.788	26.64	.92
1001	136.731	4.878	72.870	26.649	2.432	117.889	62.940	27.84	.90
1002	139.557	6.853	72.896	26.639	3.269	118.034	63.707	27.51	.79
1003	143.010	9.275	72.927	26.628	3.687	118.156	64.604	27.09	.77
1004	146.658	11.838	72.961	26.615	3.678	118.586	65.509	26.83	.78
1005	150.301	14.391	72.995	26.602	3.661	119.050	66.371	26.61	.79
1006	146.130	11.467	72.956	26.617	3.671	118.316	65.381	26.76	.78
1007	149.750	14.006	72.990	26.604	3.640	119.403	66.243	26.86	.78
1008	153.359	16.526	73.024	26.591	3.625	119.840	67.064	26.65	.79
1009	156.935	19.004	73.058	26.579	3.600	120.339	67.842	26.50	.80
1101	147.346	5.524	72.906	9.831	4.494	89.746	65.675	33.47	1.08
1102	151.817	6.133	72.924	9.829	4.528	88.710	66.718	30.56	1.16
1103	156.825	6.799	72.945	9.826	5.565	88.556	67.819	28.81	1.13
1104	163.000	7.603	72.971	9.822	6.890	88.838	69.087	27.43	1.11
1105	170.484	8.562	73.002	9.818	8.202	89.572	70.506	26.47	1.10
1106	179.341	9.681	73.040	9.813	9.833	90.590	72.039	25.75	1.09
1107	189.770	10.984	73.086	9.807	11.191	91.825	73.672	25.18	1.10
1108	201.740	12.466	73.139	9.799	12.942	93.192	75.353	24.74	1.10
1109	215.428	14.147	73.201	9.791	14.702	94.770	77.068	24.54	1.10
1110	230.571	15.991	73.271	9.781	15.862	96.420	78.754	24.47	1.11
1111	246.166	17.873	73.345	9.772	15.683	97.942	80.304	24.42	1.13
1112	262.176	19.784	73.421	9.761	16.772	99.494	81.734	24.58	1.13

TABLE 2. *Specific heats of fluorine*—Continued

ID	T_a	P	V_b	D	ΔT	$Q/\Delta T$	Tare	C_v	Error in C_v
	K	MN/m^2	cm^3	mol/l	K	J/K	J/K	J/mol K	%
1202	95.454	5.079	72.769	37.949	2.217	134.275	47.411	29.99	.78
1203	97.662	9.778	72.811	37.926	2.205	135.029	48.495	29.89	.79
1204	99.850	14.308	72.853	37.904	2.189	135.863	49.535	29.87	.79
1205	102.024	18.690	72.893	37.882	2.173	136.779	50.538	29.84	.80
1301	103.424	4.095	72.779	36.261	2.241	131.406	51.168	29.13	0.80
1302	105.653	8.130	72.817	36.242	2.233	131.819	52.144	28.95	.81
1303	107.863	12.051	72.855	36.222	2.206	132.602	53.082	28.89	.82
1304	110.062	15.860	72.892	36.204	2.211	133.243	53.986	28.83	.82
1305	112.247	19.560	72.928	36.185	2.185	133.987	54.856	28.78	.83

uncertainty in the C_v measurements is given in the last column. This uncertainty should rapidly increase with diminishing temperature intervals, ΔT, and with diminishing mass of sample, N. It is based on the following estimated uncertainties in the different variables:

N, 0.2%	Q, 0.05%	ΔT, 0.1%
C_b, 0.1%	ΔP, 0.1%	dP/dT, 1.0%.

The number of significant figures given in table 2 is not justified on the basis of the uncertainty of the data, but is presented to maintain internal consistency.

No single-phase specific heat data of fluorine are available for comparison with the new measurements. However, the general behavior of the data is illustrated in figure 2. For a wide range of densities about the critical isochore, the specific heat increases sharply as the temperature approaches the two-phase envelope, which is to be expected. At densities far removed from the critical, the temperature dependence is relatively weak. Data obtained earlier with this apparatus for oxygen [2, 3] indicated that the deviations from other published oxygen values were within the accuracy of the specific heat measurements as given in the last column of table 2.

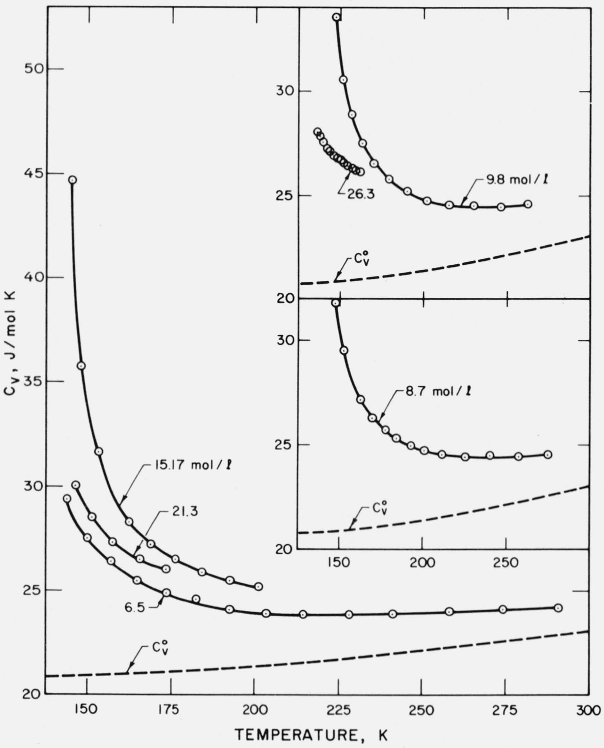

FIGURE 2. *Selected isochores of* C_v *data.*

The authors acknowledge the support of the Air Force Rocket Propulsion Laboratory, Edwards, California. Also, thanks are due to G. K. Johnson of Argonne National Laboratory for supplying the purified fluorine used for these experiments.

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