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Molar Heat Capacity at Constant Volume for Air from 67 to 300 K at Pressures to 35 MPa

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Measurements of the molar heat capacity at constant volume C_v for air were conducted with an adiabatic calorimeter. Temperatures ranged from 67 to 300 K, and pressures ranged up to 35 MPa. Measurements were conducted at 17 densities which ranged from gas to highly compressed liquid states. In total, 227 C_v values were obtained. The air sample was prepared gravimetrically from research purity gases resulting in a mole fraction composition of 0.78112 N_2 + 0.20966 O_2 + 0.00922 Ar. The primary sources of uncertainty are the estimated temperature rise and the estimated quantity of substance in the calorimeter. Overall, the uncertainty ($\pm 2\sigma$) of the C_v values is estimated to be less than $\pm 2\%$ for the gas and $\pm 0.5\%$ for the liquid.

KEY WORDS: air; calorimeter; heat capacity; high pressure; isochoric.

1. INTRODUCTION

A research program is being carried out at the National Institute of Standards and Technology to reduce substantially the existing state of uncertainty regarding the low-temperature properties of air. The research effort includes both measurements and models. The experimental phase of the study includes new measurements of pressure–density–temperature (p–ρ–T) properties [1], sound speed [2], phase equilibria [3], thermal conductivity [4], viscosity [5], and heat capacity. Concurrent with the experimental measurements is a modeling effort designed to produce accurate predicative models representing thermodynamic and transport properties.

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Heat-capacity measurements are valuable in process-design calculations and as test data for multiproperty regression analysis of equation-of-state coefficients. When combined with (p, ρ, T) data, vapor-pressure data, enthalpy values, and other thermodynamic properties, molar heat capacities are extremely useful in the formulation of a self-consistent thermodynamic network for the prediction of thermophysical properties at state conditions of interest to design engineers.

As pointed out by Sychev et al. [6], measurements of heat capacity for air are scarce, particularly those covering a broad range of state conditions. Published measurements of C_v for air include those of Eucken and Hauck [7] from 138 to 165 K at pressure from 6.7 to 19.6 MPa, those of Henry [8] from 288 to 623 K at 0.1 MPa, and those of Chashkin et al. [9] for air, with a 2% impurity content, from 128 to 138 K in the vicinity of the critical point. Holborn and Jakob [10] measured C_p at 332 K and at pressures from 0.1 to 29.4 MPa. Combined, Refs. 7, 8, and 10 present a total of 32 data points, with none at temperatures below 138 K. Thus, there is a clear need for measurements of heat capacity that cover the liquid phase from about 70 K up to temperatures overlapping the published results noted above. In view of this, it was the goal of this work to measure C_v over a sufficiently broad range of temperature and pressure conditions so that the data will be useful in the development of equations of state for air.

2. EXPERIMENTS

The heat-capacity measurements in this study were performed in the calorimeter described by Goodwin [11] and Magee [12]. Briefly, in this method, a sample of well-established mass (or number of moles N) is confined to a bomb of approximately 73-cm^3 volume; the exact volume varies with temperature and pressure. When a precisely measured electrical energy, Q, is applied, the resulting temperature rise, $\Delta T = T_2 - T_1$, is measured.

When the energy (Q_0) required to heat the empty bomb is subtracted from the total, the molar heat capacity is given by

$$C_v = (Q - Q_0)\, N^{-1}\, \Delta T^{-1} \tag{1}$$

For this study, a sample was charged to the bomb, then the charge valve was sealed. The bomb and its contents were then cooled to a temperature just above the saturation point. Then measurements begun and continued in the single-phase region until either the upper temperature (300 K) or the upper pressure (35 MPa) was obtained. At the completion of a run, some of the sample was discharged to obtain the next filling density. A series of such runs at different densities comprises the $C_v(\rho, T)$ surface for the substance under study.

3. SAMPLE

The air sample used in the experimental measurements of heat capacity was gravimetrically prepared from research grade gases in a thoroughly cleaned aluminum cylinder. The purity of the component gases has been verified by chemical analysis. A cylinder of air was prepared having a composition with the following mole fraction: $0.7812\,N_2 + 0.20966\,O_2 + 0.00922\,Ar$. The combined mole fraction uncertainty due to low levels of impurities and to weighting uncertainties is ± 0.000004.

4. RESULTS

Significant adjustments must be applied to the raw data to account for the energy required to heat the empty calorimeter from an initial temperature (T_1) to a final temperature (T_2). These adjustments are made by using the results of previous experiments done with an evacuated bomb. These results were fitted to a 12-parameter polynomial $Q_0(T)$ given by Magee [12]. Additionally, an adjustment for PV work done by the fluid on

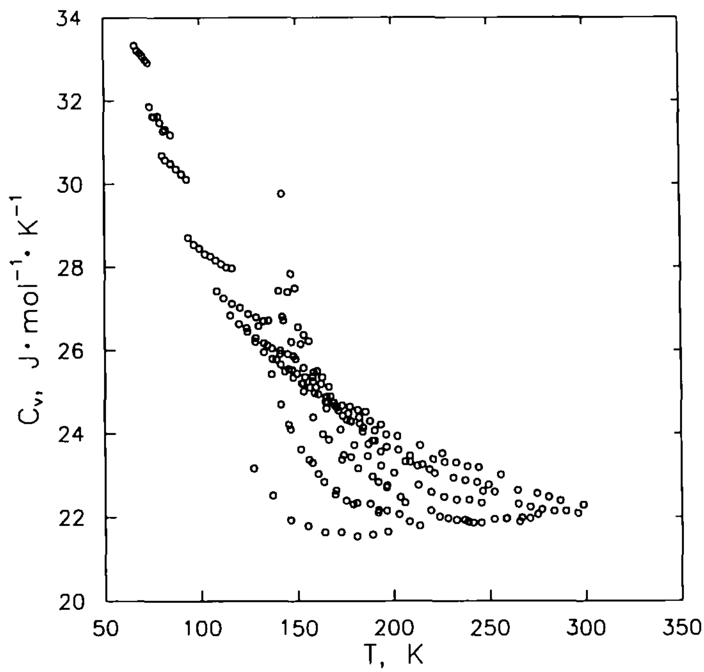

Fig. 1. Experimental C_v data for air.

Table I. Measurements of Molar Heat Capacity C_v for Gaseous and Liquid Air: T, Temperature (ITS-90); ρ, Density; p, Pressure

T (K)	ρ ($mol \cdot dm^{-3}$)	P (MPa)	Adj[a]	C_v ($J \cdot mol^{-1} \cdot K^{-1}$)	$C_{v,calc}$[b]	Dev[c] (%)
127.002	2.0395	1.7145	0.05	23.16	23.51	−1.51
136.694	2.0410	1.9126	0.05	22.51	22.83	−1.42
145.994	2.0425	2.0999	0.06	21.93	22.41	−2.18
154.975	2.0433	2.2783	0.06	21.79	22.13	−1.55
163.695	2.0436	2.4497	0.07	21.64	21.93	−1.34
172.196	2.0435	2.6153	0.07	21.64	21.78	−0.65
180.507	2.0434	2.7763	0.07	21.54	21.67	−0.59
188.653	2.0433	2.9334	0.08	21.58	21.58	0.02
196.656	2.0424	3.0862	0.08	21.65	21.50	0.68
136.250	4.0693	3.1005	0.07	25.42	25.30	0.49
141.258	4.0734	3.3329	0.07	24.69	24.66	0.11
146.184	4.0769	3.5587	0.07	24.10	24.17	−0.27
155.813	4.0730	3.9871	0.08	23.37	23.46	−0.37
160.522	4.0724	4.1947	0.08	23.03	23.20	−0.75
169.762	4.0713	4.5985	0.08	22.63	22.82	−0.84
178.783	4.0715	4.9901	0.09	22.30	22.55	−1.11
187.620	4.0704	5.3693	0.09	22.31	22.34	−0.14
191.968	4.0703	5.5554	0.10	22.16	22.26	−0.43
196.280	4.0687	5.7377	0.10	22.15	22.18	−0.13
145.413	4.0773	3.5241	0.07	24.21	24.24	−0.11
151.543	4.0808	3.8021	0.07	23.62	23.74	−0.50
157.556	4.0830	4.0716	0.08	23.30	23.36	−0.27
163.470	4.0834	4.3334	0.08	22.84	23.07	−1.02
169.288	4.0832	4.5885	0.08	22.54	22.84	−1.34
175.022	4.0836	4.8390	0.09	22.39	22.66	−1.19
180.676	4.0801	5.0807	0.09	22.33	22.50	−0.77
191.777	4.0751	5.5529	0.10	22.10	22.26	−0.73
202.643	4.0752	6.0173	0.10	22.06	22.08	−0.11
207.995	4.0739	6.2430	0.11	21.89	22.01	−0.55
213.293	4.0736	6.4673	0.11	21.79	21.95	−0.72
142.029	6.2034	4.2625	0.08	26.80	26.68	0.44
166.096	6.1985	6.0764	0.10	23.85	23.89	−0.19
173.793	6.1941	6.6402	0.10	23.48	23.48	0.01
181.356	6.2031	7.2017	0.11	23.16	23.17	−0.04
188.814	6.1978	7.7390	0.12	22.96	22.93	0.13
196.167	6.1966	8.2698	0.12	22.70	22.74	−0.17
203.424	6.1929	8.7877	0.13	22.47	22.58	−0.50
238.548	6.1829	11.2722	0.15	21.89	22.10	−0.96
245.377	6.1823	11.7528	0.16	21.87	22.04	−0.78
252.156	6.1773	12.2196	0.16	21.95	21.99	−0.17
258.877	6.1766	12.6894	0.17	21.97	21.94	0.13
265.559	6.1740	13.1514	0.17	21.89	21.90	−0.04

Table I. *(Continued)*

T (K)	ρ ($mol \cdot dm^{-3}$)	P (MPa)	Adj[a]	C_v ($J \cdot mol^{-1} \cdot K^{-1}$)	$C_{v,calc}$[b]	Dev[c] (%)
142.627	6.1965	4.3065	0.08	26.71	26.56	0.57
147.820	6.1979	4.7055	0.09	25.86	25.68	0.71
152.950	6.1990	5.0949	0.09	25.01	25.01	0.00
158.013	6.1996	5.4756	0.09	24.39	24.50	−0.45
163.017	6.1999	5.8489	0.10	23.98	24.10	−0.50
172.852	6.1982	6.5744	0.10	23.37	23.52	−0.66
177.686	6.1974	6.9282	0.11	23.43	23.31	0.52
191.906	6.1945	7.9595	0.12	22.83	22.84	−0.06
196.558	6.1935	8.2944	0.12	22.75	22.73	0.10
205.747	6.1911	8.9521	0.13	22.34	22.54	−0.88
219.266	6.1887	9.9148	0.14	22.15	22.32	−0.77
223.703	6.1849	10.2246	0.14	22.01	22.26	−1.15
228.117	6.1840	10.5363	0.14	21.97	22.21	−1.09
232.493	6.1840	10.8462	0.15	21.93	22.16	−1.06
236.846	6.1840	11.1540	0.15	21.93	22.12	−0.85
241.168	6.1823	11.4560	0.15	21.87	22.08	−0.95
258.258	6.1802	12.6536	0.17	21.96	21.95	0.07
266.686	6.1760	12.2344	0.17	21.98	21.89	0.39
270.878	6.1736	13.5218	0.17	21.97	21.87	0.45
275.049	6.1736	13.8127	0.18	22.06	21.85	0.95
150.272	8.2701	5.7249	0.11	26.56	26.48	0.30
157.704	8.2801	6.5430	0.11	25.36	25.37	−0.03
165.037	8.2808	7.3413	0.12	24.60	24.63	−0.11
172.268	8.2803	8.1232	0.12	24.09	24.11	−0.08
179.394	8.2790	8.8893	0.13	23.72	23.73	−0.03
186.400	8.2771	9.6382	0.14	23.45	23.44	0.05
193.347	8.2748	10.3770	0.14	23.22	23.21	0.05
200.213	8.2722	1.1038	0.15	23.05	23.02	0.12
212.730	8.2657	12.4184	0.16	22.76	22.76	0.01
219.426	8.2629	13.1188	0.17	22.59	22.65	−0.24
226.038	8.2592	13.8063	0.17	22.48	22.55	−0.31
232.610	8.2559	14.4876	0.18	22.41	22.47	−0.25
239.083	8.2532	15.1575	0.18	22.41	22.39	0.08
245.527	8.2507	15.8226	0.19	22.34	22.33	0.05
264.797	8.2400	17.7922	0.21	22.31	22.18	0.60
271.089	8.2368	18.4319	0.21	22.34	22.14	0.47
277.208	8.2348	19.0552	0.22	22.18	22.10	0.35
283.445	8.2340	19.6920	0.22	22.14	22.07	0.31
289.642	8.2291	20.3121	0.23	22.14	22.04	0.44
295.791	8.2262	20.9312	0.23	22.09	22.02	0.32

Table I. *(Continued)*

T (K)	ρ (mol · dm^{-3})	P (MPa)	Adj[a]	C_v (J · mol^{-1} · K^{-1})	$C_{v,\,calc}$[b] (J · mol^{-1} · K^{-1})	Dev[c] (%)
141.929	11.0831	5.3208	0.12	29.76	29.77	−0.03
148.875	11.0826	6.4609	0.13	27.49	27.38	0.41
155.799	11.0765	7.5960	0.14	26.22	26.04	0.69
162.666	11.0719	8.7207	0.15	25.35	25.20	0.59
169.447	11.0675	9.8291	0.16	24.66	24.63	0.12
175.734	11.0524	10.8444	0.17	24.32	24.24	0.33
182.449	11.0479	11.9348	0.17	24.23	23.92	1.29
189.075	11.0439	13.0084	0.18	23.83	23.67	0.69
208.542	11.0320	16.1433	0.21	23.31	23.16	0.64
214.915	11.0278	17.1627	0.21	23.25	23.04	0.89
221.221	11.0234	18.1677	0.22	23.05	22.94	0.47
246.374	10.9984	22.1240	0.25	22.62	22.64	−0.10
252.421	10.9947	23.0721	0.26	22.60	22.59	0.05
264.568	10.9860	24.9639	0.27	22.64	22.50	0.63
280.657	10.9759	27.4555	0.29	22.48	22.40	0.34
298.704	10.9613	30.2148	0.31	22.29	22.32	−0.15
274.718	10.9812	26.5430	0.28	22.56	22.44	0.55
280.725	10.9768	27.4694	0.29	22.47	22.40	0.30
286.713	10.9724	28.3892	0.30	22.39	22.37	0.07
146.349	12.2660	6.3787	0.14	27.83	27.87	−0.15
153.239	12.2624	7.6956	0.15	26.37	26.35	0.09
160.079	12.2556	9.0046	0.16	25.50	25.43	0.26
166.858	12.2510	10.3030	0.17	24.89	24.83	0.25
173.562	12.2484	11.5879	0.18	24.42	24.40	0.09
186.756	12.2431	14.1117	0.20	23.74	23.82	−0.35
193.245	12.2372	15.3446	0.21	23.56	23.62	−0.26
206.060	12.2269	17.7711	0.23	23.32	23.32	0.01
212.373	12.2223	18.9619	0.24	23.22	23.30	0.09
218.640	12.2157	20.1356	0.25	23.13	23.10	0.14
231.031	12.2056	22.4506	0.26	22.94	22.93	0.04
237.161	12.1999	23.5883	0.27	22.88	22.86	0.07
243.240	12.1949	24.7140	0.28	22.83	22.80	0.12
249.283	12.1896	25.8282	0.29	22.77	22.75	0.10
145.004	14.4172	6.8479	0.17	27.39	27.32	0.24
151.633	14.4305	8.5043	0.19	26.15	26.13	0.09
158.213	14.4274	10.1565	0.20	25.47	25.38	0.35
164.728	14.4274	11.8029	0.22	24.88	24.87	0.02
171.179	14.4237	13.4332	0.23	24.55	24.51	0.18
177.564	14.4191	15.0464	0.24	24.30	24.23	0.30
183.887	14.4122	16.6384	0.25	24.04	24.01	0.14
190.147	14.4060	18.2126	0.26	23.82	23.83	−0.04
196.343	14.3998	19.7667	0.27	23.67	23.68	−0.05

Table I. *(Continued)*

T (K)	ρ $(\mathrm{mol \cdot dm^{-3}})$	P (MPa)	Adj[a]	C_v $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$C_{v,\,calc}$[b]	Dev[c] (%)
202.492	14.3923	21.3017	0.29	23.60	23.56	0.18
208.585	14.3854	22.8183	0.30	23.46	23.45	0.04
220.622	14.3721	25.7993	0.32	23.38	23.28	0.44
226.571	14.3654	27.2635	0.33	23.31	23.21	0.45
232.483	14.3583	28.7116	0.34	23.30	23.14	0.68
238.350	14.3517	30.1439	0.35	23.21	23.08	0.54
244.183	14.3447	31.5614	0.36	23.19	23.03	0.67
255.736	14.3313	34.3526	0.37	23.01	22.95	0.28
140.189	16.3419	6.4319	0.21	27.42	27.25	0.63
146.643	16.3624	8.4584	0.22	26.20	26.19	0.05
153.049	16.3681	10.4940	0.24	25.58	25.51	0.27
159.399	16.3652	12.5212	0.26	25.11	25.04	0.27
165.677	16.3600	14.5310	0.27	24.73	24.70	0.11
178.050	16.3433	18.4833	0.30	24.28	24.24	0.17
184.139	16.3354	20.4240	0.32	24.14	24.07	0.27
190.179	16.3253	22.3377	0.33	24.07	23.94	0.55
196.156	16.3170	24.2289	0.34	23.97	23.82	0.62
202.092	16.3073	26.0955	0.36	23.93	23.72	0.86
213.803	16.2904	29.7603	0.38	23.71	23.56	0.63
225.337	16.2705	33.3240	0.41	23.52	23.43	0.37
134.845	18.8952	6.3833	0.28	26.71	26.64	0.26
140.928	18.8934	8.9881	0.30	25.99	25.96	0.13
147.006	18.8884	11.6144	0.32	25.53	25.48	0.18
152.753	18.8813	14.1059	0.34	25.21	25.16	0.21
158.751	18.8708	16.7032	0.36	24.97	24.90	0.28
164.682	18.8604	19.2679	0.38	24.76	24.70	0.24
170.552	18.8485	21.7945	0.40	24.62	24.54	0.32
176.367	18.8372	24.2882	0.42	24.48	24.41	0.28
182.100	18.8256	26.7339	0.43	24.38	24.30	0.32
187.805	18.8152	29.1583	0.45	24.29	24.21	0.34
193.466	18.8042	31.5479	0.46	24.21	24.13	0.35
129.757	20.4461	5.9066	0.33	26.58	26.53	0.18
134.275	20.4392	8.2490	0.35	26.11	26.09	0.07
138.755	20.4315	10.5832	0.37	25.77	25.76	0.03
143.192	20.4236	12.9002	0.39	25.48	25.51	−0.11
147.591	20.4153	15.1974	0.41	25.34	25.31	0.12
151.950	20.2041	17.4620	0.42	25.20	25.15	0.21
156.267	20.3952	19.7053	0.44	25.10	25.01	0.34
160.551	20.3846	21.9184	0.46	24.94	24.90	0.16
164.802	20.3751	24.1089	0.47	24.87	24.80	0.27
169.019	20.3658	26.2733	0.49	24.73	24.72	0.04

Table I. *(Continued)*

T (K)	ρ ($mol \cdot dm^{-3}$)	P (MPa)	Adj[a]	C_v ($J \cdot mol^{-1} \cdot K^{-1}$)	$C_{v,calc}$[b]	Dev[c] (%)
173.204	20.3572	28.4135	0.50	24.67	24.64	0.10
177.358	20.3453	30.5132	0.52	24.64	24.58	0.26
181.481	20.3380	32.6067	0.53	24.56	24.52	0.18
185.577	20.3287	34.6669	0.54	24.52	24.46	0.24
123.562	22.2820	5.7515	0.41	26.53	26.51	0.09
128.010	22.2698	8.6581	0.44	26.20	26.18	0.07
132.408	22.2580	11.5323	0.46	25.95	25.94	0.04
136.760	22.2459	14.3694	0.48	25.79	25.75	0.15
141.067	22.2342	17.1669	0.50	25.65	25.60	0.19
145.331	22.2226	19.9238	0.52	25.54	25.48	0.23
149.556	22.2108	22.6400	0.54	25.44	25.38	0.25
153.743	22.1993	25.3161	0.56	25.36	25.29	0.28
157.892	22.1882	27.9530	0.58	25.25	25.21	0.16
162.007	22.1771	30.5523	0.60	25.19	25.14	0.19
166.091	22.1662	33.1152	0.62	25.12	25.08	0.16
115.211	24.0892	4.8120	0.51	26.84	26.85	−0.06
119.598	24.0714	8.4067	0.54	26.63	26.59	0.16
123.930	24.0547	11.9383	0.57	26.44	26.39	0.19
128.210	24.0391	15.4064	0.59	26.29	26.24	0.19
132.441	24.0241	18.8103	0.62	26.17	26.12	0.20
136.626	24.0096	22.1516	0.64	26.04	26.02	0.08
140.764	23.9946	25.4234	0.66	25.91	25.93	−0.09
144.870	23.9811	28.6496	0.68	25.90	25.86	0.17
148.933	23.9677	31.8160	0.71	25.79	25.79	0.01
108.386	26.0330	7.2710	0.67	27.42	27.38	0.16
111.867	26.0162	10.8956	0.69	27.25	27.23	0.08
116.099	25.9953	15.2481	0.72	27.12	27.09	0.12
120.274	25.9762	19.4976	0.75	27.02	26.98	0.16
124.396	25.9583	23.6480	0.78	26.87	26.88	−0.05
128.472	25.9409	27.7050	0.81	26.79	26.80	−0.05
132.503	25.9241	31.6732	0.84	26.70	26.73	−0.11
93.412	28.1327	3.3325	0.84	28.71	28.72	−0.04
96.331	28.1120	7.2880	0.85	28.54	28.57	−0.09
99.214	28.0931	11.1520	0.87	28.45	28.45	0.01
102.067	28.0758	14.9348	0.90	28.31	28.35	−0.15
104.889	28.0594	18.6358	0.92	28.26	28.28	−0.05
107.683	28.0438	22.2605	0.94	28.16	28.21	−0.17
110.451	28.0287	25.8122	0.96	28.07	28.14	−0.26
113.192	28.0140	29.2934	0.98	27.99	28.09	−0.34
115.911	27.9993	32.7082	1.01	27.97	28.03	−0.21

Table I. *(Continued)*

T (K)	ρ $(\mathrm{mol \cdot dm^{-3}})$	P (MPa)	Adj[a]	C_v $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	$C_{v,\mathrm{calc}}$[b] $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	Dev[c] (%)
80.274	30.6770	8.8001	1.14	30.69	30.70	−0.03
84.700	30.6452	16.8364	1.13	30.50	30.52	−0.05
90.244	30.6072	26.6148	1.18	30.24	30.36	−0.40
81.869	30.6644	11.7077	1.14	30.58	30.62	−0.14
84.682	30.6445	16.7920	1.15	30.48	30.51	−0.11
87.459	30.6257	21.7365	1.16	30.36	30.43	−0.24
90.204	30.6074	26.5440	1.19	30.23	30.36	−0.43
92.919	30.5896	31.2324	1.21	30.11	30.29	−0.61
73.757	31.5750	8.4441	1.24	31.86	31.69	0.53
76.572	31.5516	14.1280	1.24	31.61	31.53	0.27
79.356	31.5309	19.6710	1.24	31.47	31.42	0.16
82.105	31.5115	25.0577	1.25	31.31	31.34	−0.09
84.823	31.4926	30.2982	1.27	31.18	31.27	−0.28
75.487	31.5583	11.9150	1.24	31.62	31.58	0.13
78.282	31.5072	17.0366	1.06	31.63	31.43	0.64
81.045	31.4852	22.4374	1.42	31.27	31.34	−0.21
67.397	32.9438	17.2527	1.39	33.20	33.21	−0.02
70.151	32.9228	23.6427	1.37	33.07	33.07	0.01
72.870	32.9031	29.8393	1.36	32.91	32.98	−0.22
66.134	32.9561	14.3221	1.42	33.32	33.30	0.05
68.900	32.9327	20.7645	1.38	33.14	33.12	0.06
71.634	32.9121	27.0393	1.36	32.97	33.02	−0.14

[a] Equation (2).
[b] From Ref. 17.
[c] $100\,(C_{v,\mathrm{exp}} - C_{v,\mathrm{calc}})/C_{v,\mathrm{exp}}$.

the thin-walled bomb as the pressure rises from P_1 to P_2 is applied for each point. Corrections for PV work on the bomb are given by

$$W_{PV} = k[T_2(\partial P/\partial T)_{\rho_2} - \Delta P/2]\,\Delta V_m/\Delta T \tag{2}$$

where $k = 1000\ \mathrm{J \cdot MPa^{-1} \cdot dm^{-3}}$, the pressure rise is $\Delta P = P_2 - P_1$, and the volume change per mole is $\Delta V_m = \rho_2^{-1} - \rho_1^{-1}$. The derivative has been calculated with an extended corresponding-states model [13].

Table I gives the raw data and final values of the single-phase gas or liquid heat capacity. Data for a total of 227 state conditions are given. All original temperature measurements were made with a platinum resistance thermometer calibrated on the IPTS-68. The temperatures in Table I were obtained by applying a table of corrections [14] to the original measurements to change them from the IPTS-68 to the ITS-90. A correction for the PV work on the bomb, given by Eq. (2), has been applied.

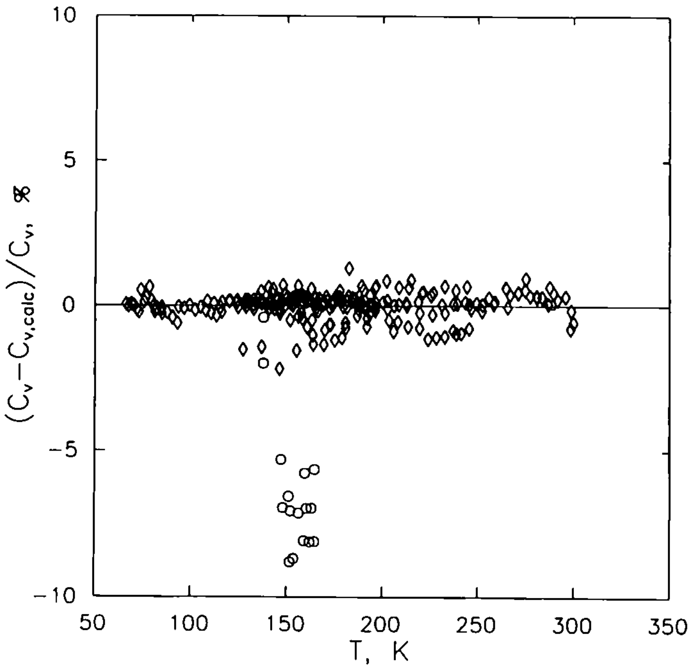

Fig. 2. Comparison of experimental C_v results with the values calculated with the model of Ref. 17: this study, ◇; Eucken and Hauck [7], ○; Henry [8], □.

Given under the column labeled Adj, the magnitude of the PV work adjustment ranges from 0.2 to 4% of the final heat capacity values. The final experimental C_v values are plotted in Fig. 1. This figure illustrates that the temperature dependence is practically the same as observed for N_2 [12, 15] and for O_2 [16] in previous studies with the same calorimeter. This finding is not surprising considering that 99% of the molecules in air are simple diatomic oscillators with similar modes of energy storage.

The calculated C_v values in Table I were derived from the equation of state of Jacobson et al. [17] as

$$C_v(T, \rho) = C_v^0(T) - T \int_0^\rho (\partial^2 P/\partial T^2)_\rho \, d\rho/\rho^2 \tag{3}$$

It is noted that the equation of state of Jacobsen et al. was developed in part with the C_v data from this study. The deviations of the experimental results from this study from the calculated values are plotted in Fig. 2.

This figure shows that the predicted values are generally within $\pm 2\%$ of the measurements, except near the critical temperature (approximately 132.52 K [18]). Overall, the root-mean-square deviation between calculated and experimental values of C_v is 0.48%. Also shown in Fig. 2 are the deviations of the measurements of Henry [8] and Eucken and Hauck [7] from the equation of state. There is only one data point (288.144 K, 0.1 MPa) of Henry which lies within the temperature range of this study. It is close to an ideal-gas state. The heat capacity agrees with the equation of state within 0.1%. The results from Eucken and Hauck are suitable for comparison at elevated pressures as high as 19.6 MPa. The agreement of their 16 values with the equation of state is within 9%. These deviations exhibit a strong bias. Unfortunately, their data also exhibit internal scatter of approximately $\pm 4\%$. Thus, 14 of their 16 results are in poor agreement with this study.

5. ASSESSMENT OF UNCERTAINTIES

Uncertainty in the C_v values arises from several sources, primarily from the temperature measurement and from the amount of substance in the calorimeter. In the discussion which follows, the uncertainty has been expressed in terms of the expanded uncertainty given by $\pm 2\sigma$, i.e., twice the estimated standard uncertainty. The platinum resistance thermometer has been calibrated by another research group at NIST, leading to an uncertainty of ± 0.002 K due to the calibration. Other factors, including gradients on the bomb, radiation from the exposed head of the thermometer, and time-dependent drift of the ice point resistance, give an overall uncertainty of $\sigma_t = \pm 0.03$ K for the absolute temperature measurement. Uncertainty estimates of the relative temperature, however, are derived differently. The temperatures assigned to the beginning (T_1) and to the end (T_2) of a heating interval are determined by extrapolation of a linear drift (approximately $-0.0005\ \mathrm{K \cdot min^{-1}}$) to the midpoint time of the interval. This procedure leads to an uncertainty of ± 0.002 K for T_1 and T_2, and, consequently, ± 0.004 K for the temperature rise, $\Delta T = T_2 - T_1$. For a typical experimental value of ΔT of 4 K, this corresponds to an uncertainty of $\pm 0.1\%$. The energy applied to the calorimeter is computed from the integral of the product of the applied potential and the applied current during the heating interval; its uncertainty is $\pm 0.01\%$. The energy applied to the evacuated calorimeter has been measured in repeated experiments and fit to a function of temperature [12]; its uncertainty is $\pm 0.02\%$. The number of moles of substance was determined within $\pm 0.2\%$ from the product of the bomb volume $V_b(p, T)$ and the estimated density [17] $\rho(p, T)$. A correction for PV work on the bomb leads to an additional

$\pm 0.02\%$ uncertainty. For pressure measurements, the uncertainty due to the piston gauge calibration ($\pm 0.05\%$) is added to the cross term $[(\sigma_t)(dP/dT)_\rho]$ to yield an overall maximum probable uncertainty which varies from 0.07 to 0.6%, which increases in accord with the slope of the (p, ρ, T) isochore to a maximum at the highest density and lowest pressure of the study. However, the pressure uncertainty does not appreciably contribute to the overall uncertainty for molar heat capacity. The law of propagation of uncertainty is applied to combine the various sources of experimental uncertainty. In this way, one would obtain a combined uncertainty of $\pm 2\%$ for gas and $\pm 0.5\%$ for liquid C_v values.

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NOMENCLATURE

C_v	Molar heat capacity at constant volume, $J \cdot mol^{-1} \cdot K^{-1}$
C_v^0	Molar heat capacity in the ideal-gas state, $J \cdot mol^{-1} \cdot K^{-1}$
V_{bomb}	Volume of the calorimeter containing sample, cm^3
P	Pressure, MPa
ΔP	Pressure rise during a heating interval, MPa
T	Temperature, K
T_1, T_2	Temperature at start and end of heating interval, K
ΔT	Temperature rise during a heating interval, K
Q	Calorimetric heat energy input to bomb and sample, J
Q_0	Calorimetric heat energy input to empty bomb, J
N	Moles of substance in the calorimeter, mol
ρ	Fluid density, $mol \cdot dm^{-3}$

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