

consistent with his results. For example, at a pH of 1.1, at 25 °C and concentrations of CuSO<sub>4</sub> of 0.4, 0.16, and 0.08 M, the changes in the experimental RI were 96, 96, and 83 × 10<sup>-5</sup>, respectively.

### Pressure Effects

As noted above, it has been shown that the effect of pressure on the RI of a mixed electrolyte solution such as seawater (ionic strength maximum around 0.85 *m*) can be predicted by eq 1 to 0.0001 or better (7). There does not seem to be any RI data for other mixed electrolyte solutions under pressure. However, on the basis of the seawater results it might be expected that reasonable estimates of the RI would be obtained at moderate concentrations (to 1 or 2 *m*, say). When data on *p*<sub>0</sub> and Δ*f*(*n*) are available (or data to calculate them) the value of the RI at a pressure *p* is simply obtained from eq 1, using ψ<sub>w</sub><sup>(*p*)</sup> from eq 3 and then eq 2. Extensions to the mixed solutions are made using eq 7 and 9 as well. Values of *n* for NaCl and MgSO<sub>4</sub> at 25 °C and pressures to 400 bar were calculated for a range of concentrations. The values were fitted to *p* at each concentration (linear fit with standard deviation 2 × 10<sup>-5</sup>). The piezo-optic coefficient, (∂*n*/∂*p*)<sub>T</sub>, was thus the slope of the lines. Comparison of this coefficient with direct experimental values (9) gives an indirect check on the reliability of *n* at the elevated pressures. The results are summarized in Table IX from which the value of *n* for a given concentration at any pressure up to 400 bar can be calculated. At moderate concentrations the agreement with experiment is good, but at 4–6 *m* the values of *n* predicted at 400 bar could be in error by 4 × 10<sup>-4</sup> for the wavelengths 6328–5461 Å. As the differences in the given wavelength and 5893 Å increase, the

errors, arising from the assumption that Δ*f*(*n*) is independent of wavelength naturally increase. Thus, for λ 4358 Å the errors at the higher concentrations apparently become as great as 8 × 10<sup>-4</sup>. It should be noted that the experimental concentrations are only accurate to 0.1 *m* and we have included extra *n* and (∂*n*/∂*p*)<sub>T</sub> values to indicate the possible errors in *n* and (∂*n*/∂*p*)<sub>T</sub> from this source. While not being very significant for NaCl, the greater sensitivity of the parameters to concentration for MgSO<sub>4</sub> gives larger experimental uncertainties for this salt. At low concentrations the experimental data have been supplemented with estimates of (∂*n*/∂*p*)<sub>T</sub> made from other, more restrictive models (i.e., models not so easily applicable to multicomponent solutions) (8). These values, too, are in accord with our results.

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## A Simple Formula for the Heat Capacity of Polyatomic Gases, with Constants for 143 Substances

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**A simple empirical formula,  $c_v \sim x^2/(1 + x^2)$ , is suggested for the representation of ideal-gas heat capacities. There are only two empirical constants,  $B$  and  $\tau$ , contained in the definition  $x = B(\hat{T} - \tau)$ ; both have a physical interpretation. The suggested form has the advantages of simplicity and fidelity over a large temperature range. Fitted constants for 143 substances are presented.**

Ideal-gas heat capacities are commonly represented by polynomials in the absolute temperature *T*, with coefficients empirically fitted to the data for each substance. A typical form is

$$c_p^0 = a + bT + cT^2 + dT^3 \quad (1)$$

where *c*<sub>p</sub><sup>0</sup> is the zero-pressure heat capacity at constant pressure in cal/(mol K) and *T* is in kelvins. The constants *a*, *b*, *c*, and *d* are tabulated for 102 substances by Hougen, Watson, and Ragatz (7); there are, of course, many such tabulations. The polynomial representation is quite convenient, the integrations for enthalpy and entropy being very simple. The representation

is also accurate, provided that the temperature limits of the range over which the polynomial was fitted are not exceeded.

An alternative empirical representation, the subject of this paper, is the form *c*<sub>p</sub><sup>0</sup> ~ *y*, with

$$y = x^2/(1 + x^2) \quad (2)$$

where *x* is a linear function of temperature. The function *y*(*x*) is plotted in Figure 1. The rationale is that the increase in *y* with *x* corresponds to the excitation of vibrational degrees of freedom with increasing temperature: thus *y* = 0 corresponds to no vibrational excitation and *y* = 1 corresponds to full vibrational excitation. In terms of the reduced ideal-gas heat capacity at constant volume  $\hat{c}_v \equiv c_v^0/R$ , the explicit form is then

$$y = \frac{\hat{c}_v - c_\alpha}{c_\omega - c_\alpha} = \frac{x^2}{1 + x^2} \quad (x \geq 0) \quad (3)$$

$$y = \frac{\hat{c}_v - c_\alpha}{c_\omega - c_\alpha} = 0 \quad (x < 0)$$

where *c*<sub>α</sub> is the constant-volume heat capacity with translational and rotational degrees of freedom only (*y* = 0), *c*<sub>ω</sub> is the con-

**Table I. Heat Capacity Constants for Various Substances. The Tabulated Error is the Average Absolute Percent Error in  $c_v^0$  <sup>a</sup>**

Substance	<i>n</i>	<i>T<sub>c</sub></i> , K	<i>B</i>	$\tau$	$\bar{T}$ range	Error	<i>w</i> , cm <sup>-1</sup>	Ref
Hydrogen (normal) H <sub>2</sub>	2	32.98	0.0268	15.2647	10.92–60.64	0.42	3661	6
Nitrogen N <sub>2</sub>	2	126.20	0.1591	2.4173	0.79–17.43	0.09	2359	6
Oxygen O <sub>2</sub>	2	154.58	0.2935	1.3238	0.65–7.76	0.09	1566	6
Fluorine F <sub>2</sub>	2	144.31	0.5233	0.8986	1.39–5.54	0.41	820	14
Chlorine Cl <sub>2</sub>	2	417.00	2.1997	0.1758	0.48–1.54	0.17	564	17
Bromine Br <sub>2</sub>	2	584.00	6.2207	0.1435	0.42–1.20	0.19	279	17
Hydrogen fluoride HF	2	461.00	0.3560	1.0665	0.11–3.25	0.22	3850	16
Carbon monoxide CO	2	132.92	0.1793	2.0258	0.38–7.52	0.11	2203	15
Nitric oxide NO	2	180.00	0.2515	0.7418	1.52–8.33	0.81	2128	15
Hydrogen chloride HCl	2	324.70	0.3589	1.1963	0.15–6.16	0.28	2689	16
Water H <sub>2</sub> O	3	647.86	0.5357	0.2451	0.15–3.09	0.35	3591	6
Nitrous oxide N <sub>2</sub> O	3	309.57	0.5661	-0.1475	0.79–4.41	0.46	1626	17
Carbon dioxide CO <sub>2</sub>	3	304.20	0.5930	0.0769	0.16–3.29	1.71	1525	15
Sulfur dioxide SO <sub>2</sub>	3	430.70	1.0261	0.1170	0.72–3.17	0.23	1248	17
Ammonia NH <sub>3</sub>	4	405.60	0.4880	0.1493	0.12–4.93	0.88	2956	16
Ethyne (acetylene) C <sub>2</sub> H <sub>2</sub>	4	308.33	0.3543	-0.7364	0.97–3.24	1.70	2587	15
Cyanogen C <sub>2</sub> N <sub>2</sub>	4	399.75	0.6384	-0.7570	0.75–2.50	0.27	1862	2
Methane CH <sub>4</sub>	5	190.55	0.2413	0.7661	0.31–8.40	0.65	2348	9
Methyl chloride CH <sub>3</sub> Cl	5	416.25	0.5494	0.0656	0.72–3.36	1.36	2253	16
Freon F22 CHClF <sub>2</sub>	5	369.20	0.7535	-0.0489	0.39–2.50	1.15	1457	17
PF-methane CF <sub>4</sub>	5	227.60	0.6833	0.1851	0.44–4.39	0.93	990	1
Freon F21 CHCl <sub>2</sub> F	5	451.70	0.9954	-0.0948	0.32–1.67	1.21	1349	17
Freon F13 CClF <sub>3</sub>	5	302.10	0.9333	0.0170	0.66–3.60	0.25	962	17
Silicon tetrafluoride SiF <sub>4</sub>	5	259.09	0.9216	-0.0027	0.39–13.51	0.36	836	14
Chloroform CHCl <sub>3</sub>	5	536.40	1.0855	-0.2510	0.51–2.80	0.65	1469	15
Freon F12 CCl <sub>2</sub> F <sub>2</sub>	5	384.95	1.3584	-0.0041	0.37–3.55	0.47	843	17
Freon F11 CCl <sub>3</sub> F	5	471.20	1.4332	-0.1319	0.42–1.72	0.85	977	17
Carbon tetrachloride CCl <sub>4</sub>	5	556.30	2.6707	-0.0035	0.18–2.46	0.27	619	17
Ethene C <sub>2</sub> H <sub>4</sub>	6	282.36	0.3679	0.0877	1.06–21.25	1.33	2282	14
Methanol CH <sub>3</sub> OH	6	512.58	0.5987	-0.0040	0.53–1.95	0.86	2545	15
Hydrazine H <sub>2</sub> N <sub>2</sub>	6	653.15	0.8797	-0.0217	0.08–1.53	3.36	2207	15
Methanethiol CH <sub>4</sub> S	6	470.00	0.5544	-0.1923	0.58–2.13	0.91	2521	14
Propadiene C <sub>3</sub> H <sub>4</sub>	7	393.00	0.5255	-0.2324	0.76–3.82	1.15	2224	14
Propyne C <sub>3</sub> H <sub>4</sub>	7	402.38	0.5055	-0.3255	0.74–3.73	0.81	2367	14
Sulfur hexafluoride SF <sub>6</sub>	7	318.70	1.3145	0.1455	0.31–3.14	0.45	721	11
Uranium hexafluoride UF <sub>6</sub>	7	505.80	2.7929	-0.0758	0.20–1.98	0.18	538	3
Ethane C <sub>2</sub> H <sub>6</sub>	8	305.33	0.3866	-0.0262	0.33–2.95	0.98	2348	15
PF-ethane C <sub>2</sub> F <sub>6</sub>	8	292.90	0.8024	-0.2046	0.93–5.12	0.52	1085	16
Freon 114 C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	8	418.90	1.4913	-0.0909	0.53–1.22	0.36	835	17
Cyclopropane C <sub>3</sub> H <sub>6</sub>	9	397.80	0.6424	0.1448	0.69–2.01	2.25	1841	8
Propene C <sub>3</sub> H <sub>6</sub>	9	365.00	0.4567	-0.2084	0.82–3.29	1.19	2376	15
Ethanol C <sub>2</sub> H <sub>5</sub> OH	9	516.20	0.6264	-0.1865	0.53–1.94	1.25	2450	16
2-Propanone C <sub>2</sub> H <sub>6</sub> O	9	508.20	0.7879	-0.1163	0.54–1.97	0.34	1917	16
Ethanethiol C <sub>2</sub> H <sub>6</sub> S	9	499.00	0.6116	-0.2920	0.55–2.00	1.05	2426	15
2-Thiapropane C <sub>2</sub> H <sub>6</sub> S	9	503.00	0.5939	-0.3409	0.54–1.99	0.52	2518	15
1,3-Butadiene C <sub>4</sub> H <sub>6</sub>	10	425.00	0.5881	-0.2605	0.71–2.35	1.81	2149	15
1-Butyne C <sub>4</sub> H <sub>6</sub>	10	463.60	0.5712	-0.3585	0.64–3.24	1.01	2413	15
Propane C <sub>3</sub> H <sub>8</sub>	11	369.82	0.4901	-0.1438	0.27–2.43	1.34	2243	15
Cyclobutane C <sub>4</sub> H <sub>8</sub>	12	460.00	0.6977	0.0265	0.62–2.17	1.67	1960	12
1-Butene C <sub>4</sub> H <sub>8</sub>	12	419.60	0.5228	-0.2959	0.71–2.86	1.25	2386	15
cis-2-Butene C <sub>4</sub> H <sub>8</sub>	12	435.55	0.5491	-0.1886	0.68–2.76	1.27	2358	15
trans-2-Butene C <sub>4</sub> H <sub>8</sub>	12	428.61	0.5080	-0.3567	0.70–3.50	0.86	2509	15
Isobutylene C <sub>4</sub> H <sub>8</sub>	12	417.89	0.5062	-0.3590	0.71–2.87	1.00	2454	15
1-Propanol C <sub>3</sub> H <sub>7</sub> OH	12	536.71	0.6390	-0.2705	0.51–1.86	0.92	2497	16
2-Propanol C <sub>3</sub> H <sub>7</sub> OH	12	508.31	0.6449	-0.2483	0.54–1.97	1.43	2343	16
2-Thiapropane C <sub>3</sub> H <sub>8</sub> S	12	553.00	0.6687	-0.3240	0.49–1.81	0.89	2458	15
Benzene C <sub>6</sub> H <sub>6</sub>	12	562.89	0.8954	-0.0266	0.53–2.13	1.73	1866	15
Hexafluorobenzene C <sub>6</sub> F <sub>6</sub>	12	516.67	1.2831	-0.1936	0.53–2.90	0.27	1197	4
PF-Cyclobutane C <sub>4</sub> F <sub>8</sub>	12	388.37	1.0066	-0.2168	0.51–1.80	0.29	1147	10
Cyclopentene C <sub>5</sub> H <sub>8</sub>	13	506.00	0.7633	0.0262	0.59–1.98	1.52	1971	15
1-Pentyne C <sub>5</sub> H <sub>8</sub>	13	493.40	0.5984	-0.4045	0.60–3.04	0.93	2451	15
2-Butanone C <sub>4</sub> H <sub>8</sub> O	13	535.60	0.6321	-0.3745	0.51–1.87	0.40	2519	16
n-Butane C <sub>4</sub> H <sub>10</sub>	14	425.16	0.5201	-0.3116	0.59–2.82	1.20	2430	15
2-Methylpropane C <sub>4</sub> H <sub>10</sub>	14	408.13	0.5202	-0.2677	0.49–2.94	1.64	2333	15
Cyclopentane C <sub>5</sub> H <sub>10</sub>	15	511.70	0.7541	0.0097	0.58–2.35	1.74	2017	15
1-Pentene C <sub>5</sub> H <sub>10</sub>	15	464.74	0.5718	-0.3386	0.64–2.58	1.09	2417	15
1-Butanol C <sub>4</sub> H <sub>9</sub> OH	15	562.93	0.6724	-0.3025	0.49–1.78	0.87	2489	16
2-Methyl-2-propanol C <sub>4</sub> H <sub>9</sub> OH	15	506.20	0.6255	-0.3367	0.59–1.98	1.32	2406	16
3-Thiapropane C <sub>4</sub> H <sub>10</sub> S	15	557.00	0.6741	-0.3508	0.49–1.80	1.10	2457	15
Toluene C <sub>7</sub> H <sub>8</sub>	15	591.72	0.8749	-0.1059	0.50–2.03	1.41	2011	15
Octafluorotoluene C <sub>7</sub> F <sub>8</sub>	15	534.47	1.3791	-0.1471	0.51–2.81	0.61	1152	5
Cyclohexene C <sub>6</sub> H <sub>10</sub>	16	560.41	0.8570	-0.0694	0.53–2.14	1.57	1944	15
2-Pentanone C <sub>5</sub> H <sub>10</sub> O	16	564.00	0.6704	-0.3740	0.48–1.77	0.47	2501	16

Table I (continued)

Substance	<i>n</i>	<i>T<sub>c</sub></i> , K	<i>B</i>	$\tau$	$\hat{T}$ range	Error	<i>w</i> , cm <sup>-1</sup>	Ref
3-Pentanone C <sub>5</sub> H <sub>10</sub> O	16	561.00	0.6479	-0.4420	0.49-1.78	0.32	2574	16
2-Methylbutane C <sub>5</sub> H <sub>12</sub>	17	460.39	0.5821	-0.2923	0.54-2.61	1.26	2351	15
2,2-Dimethylpropane C <sub>5</sub> H <sub>12</sub>	17	433.75	0.5711	-0.2805	0.46-2.77	1.74	2258	15
<i>n</i> -Pentane C <sub>5</sub> H <sub>12</sub>	17	469.70	0.5724	-0.3340	0.53-2.55	1.12	2440	15
Cyclohexane C <sub>6</sub> H <sub>12</sub>	18	553.50	0.8786	-0.0031	0.54-2.71	0.61	1873	15
Methylcyclopentane C <sub>6</sub> H <sub>12</sub>	18	532.73	0.7430	-0.1055	0.56-2.82	1.43	2132	15
1-Hexen C <sub>6</sub> H <sub>12</sub>	18	503.98	0.6052	-0.3699	0.59-2.98	1.20	2476	15
1-Pentanol C <sub>5</sub> H <sub>11</sub> OH	18	586.00	0.7021	-0.3163	0.47-1.71	0.84	2481	16
<i>m</i> -Xylene C <sub>8</sub> H <sub>10</sub>	18	616.97	0.8620	-0.1680	0.48-1.94	1.10	2128	15
<i>p</i> -Xylene C <sub>8</sub> H <sub>10</sub>	18	616.20	0.8546	-0.1693	0.48-1.95	1.01	2144	15
<i>o</i> -Xylene C <sub>8</sub> H <sub>10</sub>	18	630.30	0.8606	-0.2042	0.47-1.90	0.92	2177	15
Ethylbenzene C <sub>8</sub> H <sub>10</sub>	18	617.09	0.8848	-0.1567	0.48-1.94	1.41	2074	15
2-Hexanone C <sub>6</sub> H <sub>12</sub> O	19	587.00	0.9725	-0.2097	0.47-1.70	0.85	1794	16
3-Hexanone C <sub>6</sub> H <sub>12</sub> O	19	582.82	0.6803	-0.4247	0.47-1.72	0.39	2547	16
<i>n</i> -Hexane C <sub>6</sub> H <sub>14</sub>	20	507.40	0.6256	-0.3298	0.39-1.97	0.97	2411	15
2-Methylpentane C <sub>6</sub> H <sub>14</sub>	20	497.45	0.6645	-0.2465	0.40-2.01	1.35	2226	15
2,2-Dimethylbutane C <sub>6</sub> H <sub>14</sub>	20	488.73	0.6781	-0.2192	0.41-2.05	0.42	2143	15
2,3-Dimethylbutane C <sub>6</sub> H <sub>14</sub>	20	499.93	0.7034	-0.1777	0.40-2.00	2.10	2113	15
Methylcyclohexane C <sub>7</sub> H <sub>14</sub>	21	572.12	0.8747	-0.0809	0.52-2.62	0.72	1945	15
Ethylcyclopentane C <sub>7</sub> H <sub>14</sub>	21	569.46	0.7934	-0.1310	0.52-2.11	1.41	2134	15
1,1-Dimethylcyclopentane C <sub>7</sub> H <sub>14</sub>	21	547.00	0.7782	-0.1272	0.55-2.19	1.34	2090	15
<i>cis</i> -1,2-Dimethylcyclopentane C <sub>7</sub> H <sub>14</sub>	21	565.00	0.7956	-0.1334	0.53-2.12	1.37	2111	15
<i>cis</i> -1,3-Dimethylcyclopentane C <sub>7</sub> H <sub>14</sub>	21	551.00	0.7715	-0.1424	0.54-2.18	1.39	2123	15
<i>trans</i> -1,3-Dimethylcyclopentane C <sub>7</sub> H <sub>14</sub>	21	553.00	0.7743	-0.1418	0.54-2.17	1.39	2123	15
<i>trans</i> -1,2-Dimethylcyclopentane C <sub>7</sub> H <sub>14</sub>	21	553.00	0.7743	-0.1418	0.54-2.17	1.39	2123	15
<i>n</i> -Propylbenzene C <sub>9</sub> H <sub>12</sub>	21	638.30	0.8834	-0.2005	0.47-1.88	1.24	2148	15
1-Propylbenzene C <sub>9</sub> H <sub>12</sub>	21	631.10	0.8903	-0.1832	0.47-1.90	1.43	2107	15
1-Heptene C <sub>7</sub> H <sub>14</sub>	21	537.23	0.6563	-0.3499	0.55-2.23	1.04	2434	15
2-Heptanone C <sub>7</sub> H <sub>14</sub> O	22	611.50	0.7317	-0.3653	0.49-1.64	0.59	2485	16
<i>n</i> -Heptane C <sub>7</sub> H <sub>16</sub>	23	540.20	0.6641	-0.3316	0.37-1.85	1.06	2418	15
2-Methylhexane C <sub>7</sub> H <sub>16</sub>	23	530.31	0.6692	-0.3138	0.38-1.89	1.00	2356	15
3-Ethylpentane C <sub>7</sub> H <sub>16</sub>	23	540.57	0.6788	-0.3113	0.37-1.85	0.75	2368	15
2,2-Dimethylpentane C <sub>7</sub> H <sub>16</sub>	23	520.44	0.7307	-0.2218	0.38-1.92	1.14	2117	15
2,3-Dimethylpentane C <sub>7</sub> H <sub>16</sub>	23	537.29	0.7621	-0.1713	0.37-1.86	2.56	2096	15
2,4-Dimethylpentane C <sub>7</sub> H <sub>16</sub>	23	519.73	0.7248	-0.2317	0.38-1.92	2.30	2132	15
3,3-Dimethylpentane C <sub>7</sub> H <sub>16</sub>	23	536.34	0.7620	-0.1984	0.37-1.86	1.36	2093	15
2,2,3-Trimethylbutane C <sub>7</sub> H <sub>16</sub>	23	531.11	0.7595	-0.1860	0.38-1.88	1.21	2079	15
Ethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	609.00	0.9052	-0.1167	0.49-2.46	0.82	2000	15
1,1-Dimethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	591.00	0.9092	-0.0843	0.50-2.54	0.64	1933	15
<i>cis</i> -1,2-Dimethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	606.00	0.9094	-0.1042	0.49-2.48	0.82	1981	15
<i>cis</i> -1,3-Dimethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	591.00	0.8959	-0.1022	0.50-2.54	0.60	1961	15
<i>cis</i> -1,4-Dimethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	598.00	0.8867	-0.1154	0.50-2.51	0.79	2005	15
<i>trans</i> -1,2-Dimethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	596.00	0.8961	-0.1133	0.50-2.52	0.89	1977	15
<i>trans</i> -1,3-Dimethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	598.00	0.8867	-0.1154	0.50-2.51	0.79	2005	15
<i>trans</i> -1,4-Dimethylcyclohexane C <sub>8</sub> H <sub>16</sub>	24	590.00	0.8943	-0.1051	0.51-2.54	0.84	1961	15
1-Octane C <sub>8</sub> H <sub>16</sub>	24	566.60	0.6907	-0.3480	0.53-2.12	1.02	2439	15
<i>n</i> -Octane C <sub>8</sub> H <sub>18</sub>	26	568.76	0.6971	-0.3314	0.35-1.76	1.14	2426	15
2-Methylheptane C <sub>8</sub> H <sub>18</sub>	26	559.57	0.7262	-0.2760	0.36-1.79	1.18	2291	15
4-Methylheptane C <sub>8</sub> H <sub>18</sub>	26	561.67	0.7459	-0.2515	0.36-1.78	1.65	2239	15
3-Ethylhexane C <sub>8</sub> H <sub>18</sub>	26	565.42	0.7106	-0.3125	0.35-1.77	0.88	2365	15
2,2-Dimethylhexane C <sub>8</sub> H <sub>18</sub>	26	549.80	0.7487	-0.2456	0.36-1.82	0.84	2183	15
2,3-Dimethylhexane C <sub>8</sub> H <sub>18</sub>	26	563.42	0.7864	-0.1935	0.35-1.77	2.43	2130	15
2,4-Dimethylhexane C <sub>8</sub> H <sub>18</sub>	26	553.45	0.7614	-0.2349	0.36-1.81	2.34	2161	15
2,5-Dimethylhexane C <sub>8</sub> H <sub>18</sub>	26	549.99	0.7532	-0.2211	0.36-1.82	2.00	2171	15
3,3-Dimethylhexane C <sub>8</sub> H <sub>18</sub>	26	561.95	0.8037	-0.2019	0.36-1.78	1.86	2079	15
3,4-Dimethylhexane C <sub>8</sub> H <sub>18</sub>	26	568.78	0.8104	-0.1668	0.35-1.76	2.96	2087	15
3-Methyl-3-ethylpentane C <sub>8</sub> H <sub>18</sub>	26	576.51	0.8115	-0.2003	0.35-1.73	1.64	2112	15
2-Methyl-3-ethylpentane C <sub>8</sub> H <sub>18</sub>	26	567.82	0.7455	-0.2676	0.35-1.76	1.79	2261	15
2,2,4-Trimethylpentane C <sub>8</sub> H <sub>18</sub>	26	543.89	0.7660	-0.2170	0.37-1.84	1.10	2111	15
2,3,3-Trimethylpentane C <sub>8</sub> H <sub>18</sub>	26	573.49	0.8453	-0.1592	0.35-1.74	2.25	2017	15
2,3,4-Trimethylpentane C <sub>8</sub> H <sub>18</sub>	26	566.34	0.8075	-0.1926	0.35-1.77	2.93	2085	15
<i>n</i> -Nonane C <sub>9</sub> H <sub>20</sub>	29	594.56	0.7269	-0.3295	0.34-1.68	1.20	2432	15
2,2,5-Trimethylhexane C <sub>9</sub> H <sub>20</sub>	29	568.00	0.7972	-0.2090	0.35-1.76	1.45	2118	15
<i>n</i> -Decane C <sub>10</sub> H <sub>22</sub>	32	617.40	0.7543	-0.3259	0.32-1.62	1.25	2433	15
<i>n</i> -Undecane C <sub>11</sub> H <sub>24</sub>	35	638.73	0.7546	-0.3529	0.47-2.35	1.24	2517	15
<i>n</i> -Dodecane C <sub>12</sub> H <sub>26</sub>	38	658.30	0.7790	-0.3463	0.45-2.28	1.19	2512	15
<i>n</i> -Tridecane C <sub>13</sub> H <sub>28</sub>	41	675.80	0.7995	-0.3421	0.44-2.22	1.19	2513	15
<i>n</i> -Tetradecane C <sub>14</sub> H <sub>30</sub>	44	694.00	0.8210	-0.3368	0.43-2.16	1.19	2513	15
<i>n</i> -Pentadecane C <sub>15</sub> H <sub>32</sub>	47	706.80	0.8362	-0.3339	0.42-2.12	1.19	2513	15
<i>n</i> -Hexadecane C <sub>16</sub> H <sub>34</sub>	50	717.00	0.8481	-0.3321	0.42-2.09	1.19	2513	15

<sup>a</sup> Average absolute percent error for the 143 substances: 1.08.

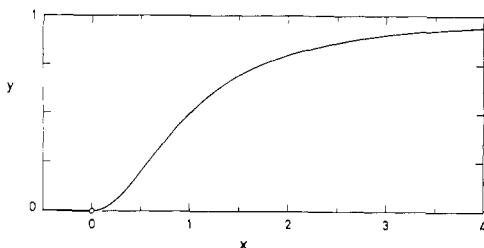


Figure 1. The function  $y(x)$ .

stant-volume heat capacity with all translational, rotational, and vibrational degrees of freedom ( $y = 1$ ) and

$$x = B(\hat{T} - \tau) \quad (4)$$

where  $\hat{T} \equiv T/T_c$  is the reduced temperature. The two parameters  $B$  and  $\tau$  are empirically fitted constants analogous to the coefficients in eq 1.

The (normalized) limiting heat capacities  $c_\alpha$  and  $c_\omega$  are

$$c_\alpha = \begin{cases} 3/2 & \text{monatomic molecules} \\ 5/2 & \text{linear molecules} \\ 3 & \text{nonlinear molecules} \end{cases} \quad (5)$$

$$c_\omega = \begin{cases} 3/2 & \text{monatomic molecules} \\ 3n - 5/2 & \text{linear molecules} \\ 3n - 3 & \text{nonlinear molecules} \end{cases} \quad (6)$$

where  $n$  is the number of atoms per molecule. No explicit account of internal rotation is taken in these limiting values. The values for monatomic molecules are included only to indicate that  $\hat{c}_v = 3/2 = \text{const}$  for this case ( $y = \text{finite}$ ).

The reduced heat capacity at constant pressure  $\hat{c}_p \equiv c_p^0/R$  is of course

$$\hat{c}_p = \hat{c}_v + 1 \quad (7)$$

The normalizations used here for temperature and heat capacity are primarily for numerical convenience and play no role in the accuracy with which eq 3 represents heat-capacity data. Changing the critical temperature used for normalization, for example, will not alter the numerical result, provided that  $B$  and  $\tau$  are accordingly adjusted.

Equation 3 has been fitted to heat-capacity data for 143 substances, minimizing the sum of the squared errors, yielding the values for the parameters  $B$  and  $\tau$  given with related information in Table I. The average absolute error for all substances tabulated is 1.08%. Figure 2 shows a plot of the experimental data in  $y(x)$  coordinates, where  $x$  was determined from the best-fit value of  $B$  and  $\tau$ , for selected substances with the same overall average absolute error of 1.08%.

For comparison, the overall average absolute error reported by Passut and Danner (12) for a five-constant polynomial representation of heat capacity for 89 substances was 0.44%. (It should be remarked that their constants were obtained by simultaneous fitting to numerical enthalpy, entropy, and heat-capacity data to obtain a thermodynamically consistent model.)

The constants  $B$  and  $\tau$  can also be determined from two experimental (or estimated) heat capacity data points. Let the two data points be represented by subscripts 1 and 2, i.e., be  $c_{v1}^0(\hat{T}_1)$  and  $c_{v2}^0(\hat{T}_2)$ . Then eq 4 and 3 yield, respectively

$$\begin{aligned} x_1 &= [(c_{v1} - c_\alpha)/(c_\omega - c_{v1})]^{1/2} \\ x_2 &= [(c_{v2} - c_\alpha)/(c_\omega - c_{v2})]^{1/2} \end{aligned} \quad (8)$$

and

$$\begin{aligned} B &= (x_2 - x_1)/(\hat{T}_2 - \hat{T}_1) \\ \tau &= (x_2 \hat{T}_1 - x_1 \hat{T}_2)/(x_2 - x_1) \end{aligned} \quad (9)$$

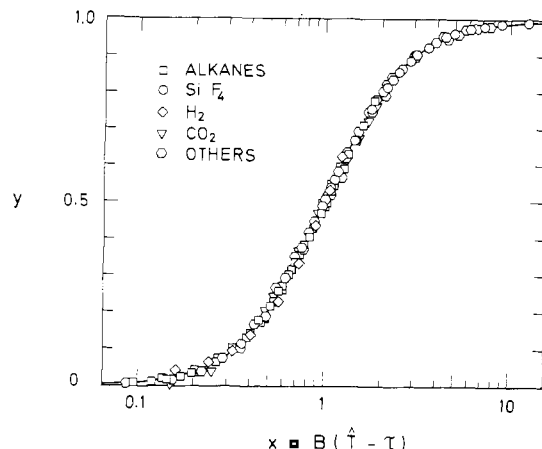


Figure 2. Experimental data for 11 substances reduced according to the best-fit values of  $B$  and  $\tau$ . The substances shown are  $H_2$ ,  $CO_2$ ,  $SiF_4$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $C_8H_{18}$ ,  $CCl_4$ ,  $C_2H_4$ ,  $N_2H_4$ , and  $UF_6$  and have the same overall average error as the substances listed in Table I.

The numerical results of this procedure are similar to those shown in Table I, provided that  $x_2$  and  $x_1$  are sufficiently different from each other and, of course, that they fall within the region of vibrational excitation  $x > 0$ .

The sensitivity of the predicted heat capacity to uncertainty in the values of the constants  $B$  and  $\tau$  can be inferred from the defining eq 2-4, which yield

$$\frac{\delta \hat{c}_v}{\hat{c}_v} = \frac{c_\omega - c_\alpha}{c_\omega x^2 + c_\alpha} \frac{2x^2}{1 + x^2} \left[ \frac{\delta B}{B} - \frac{B\tau}{B} \frac{\delta \tau}{\tau} \right] \quad (10)$$

For  $x$  not small compared to unity

$$\delta \hat{c}_v / \hat{c}_v \sim (\delta B/B) - B\tau(\delta \tau/\tau) \quad (11)$$

(For  $x$  small,  $\hat{c}_v$  is less sensitive, since it approaches the constant value  $c_\alpha$ ). Typically,  $B\tau \sim 10^{-1}$ . Thus, the sensitivity of  $\hat{c}_v$  to uncertainty in  $B$  is unity and vice versa; the sensitivity of  $\hat{c}_v$  to uncertainty in  $\tau$  is an order-of-magnitude lower. Roughly stated, the tabulated values of  $B$  have an uncertainty in the order of 1%; the uncertainty in  $\tau$  is greater.

The parameters  $\tau$  and  $B$  have physical interpretations. The characteristic reduced temperature  $\tau$  is that temperature at which vibrational excitation begins, for example, the temperature at which the ratio of specific heats for a diatomic gas rises above 7/5. (Note that  $\tau$  is a very low temperature for all polyatomic molecules with  $n > 3$ , except for methane.) The "stretching factor"  $B$  can be related to a characteristic vibrational frequency for the molecule. One way to do this is to compare eq 2 with the corresponding expression for a linear diatomic oscillator, which is

$$y = \eta^2 / \sinh^2 \eta \quad (12)$$

where  $\eta = h\nu/2kT$ ,  $\nu$  being the fundamental frequency. Expanding the denominator in powers of  $\eta$  and neglecting terms higher than  $\eta^4$  yields

$$y = 3\eta^{-2}/(3\eta^{-2} + 1) \quad (13)$$

This is identical with eq 3 if we take  $x^2 = 3\eta^{-2}$ ; at the high temperature limit appropriate to the small  $\eta$  assumption made above,  $x \approx B\hat{T}$  and one obtains  $Bh\nu/kT_c \approx 2(3^{1/2})$  or

$$B\nu/T_c = \text{constant} \quad (14)$$

The agreement between eq 2 and 12, as represented for example by the quality of the results for diatomic gases shown in Table I, is better than might be inferred from the above derivation which is based on a high-temperature approximation. The constant above has thus been arbitrarily chosen to yield the

fundamental frequency of nitrogen exactly; in terms of wavenumber  $w$ , eq 14 then becomes

$$w = (2.973 \text{ cm}^{-1} \text{ K}^{-1}) T_c / B \quad (15)$$

The constant  $2(3^{1/2})$  found in the preceding would yield wavenumber values about 20% higher.

The values of the characteristic wavenumber found from eq 15 and listed in Table I agree roughly with the appropriate bond frequencies listed in Reid and Sherwood (14), in general being close to but smaller than the stretching wavenumber, and larger than the bending wavenumbers. Some correspondence can also be found between the calculated wavenumber and vibrational spectra, as given for example by Stull and Prophet (17). Estimates of  $c_v^0(T)$  can thus be made on the basis of an estimated bond frequency for the molecule in question, by determining  $B$  from equation 13 and, for example, setting  $\tau = 0$ .

The parameter  $B$  is also a measure of the fractional vibrational excitation at the critical temperature (which is  $\hat{T} = 1$  here). From eq 3 and 4, provided that the excitation temperature is not too large, the fractional excitation  $y_c$  corresponds to

$$y_c \sim B^2 / (1 + B^2) \quad (16)$$

In order to apply the basic heat-capacity equation (eq 3), integrals for internal energy (or enthalpy) and the temperature-dependent part of the entropy are required. The conventional integrals are

$$H^* \equiv RT_c \int \hat{c}_p d\hat{T} \quad (17)$$

$$S^* \equiv R \int \hat{c}_p (d\hat{T}/\hat{T}) \quad (18)$$

for enthalpy and entropy, respectively. Integration of eq 3 yields, for  $x \geq 0$

$$H^*/RT_c = (1/B)[(c_\omega + 1)x - (c_\omega - c_\alpha) \tan^{-1} x] \quad (19)$$

$$\frac{S^*}{R} = \frac{(c_\alpha + 1) + (c_\omega + 1)(B\tau)^2}{1 + (B\tau)^2} \ln(x + B\tau) + \frac{c_\omega + c_\alpha}{1 + (B\tau)^2} \left[ \frac{1}{2} \ln(x^2 + 1) - B\tau \tan^{-1} x \right] \quad (20)$$

where an additive constant  $\tau$  has been dropped from the first integral.

An indication of the accuracy of the above expressions for ideal-gas enthalpy and entropy was obtained by comparing them with the thermodynamically consistent results of Passut and Danner. Ten substances were selected for comparison, having nearly the same overall average error (1.06%) in the heat capacity as the entire set of 143 substances in Table I. The enthalpy and entropy differences from an arbitrary reference state of 250 K to four different states (500, 750, 1000, 1250 K) were calculated from the present model and from the Passut-Danner model. The average absolute percent deviation is arbitrarily defined to be

$$\% \text{ dev} = \frac{100}{N} \sum \left| \frac{X_T - X_{PD}}{X_{PD}} \right| \quad (21)$$

where  $N = 4$ ,  $X_T$  is the calculation from the present model and  $X_{PD}$  is the calculation from the Passut-Danner model. The results are summarized in Table II.

## Discussion

The accuracy of the correlation presented here can be improved somewhat by rewriting eq 2 as

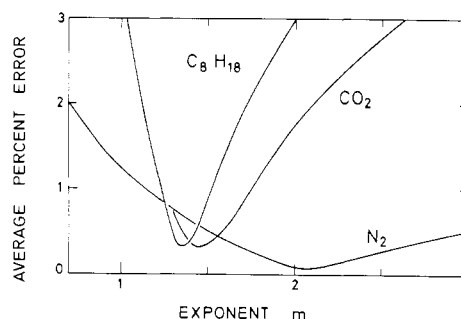
$$y = x^m / (1 + x^m) \quad (22)$$

The exponent  $m$  has an optimum value somewhat less than 2. The fit for difficult substances can be considerably improved,

**Table II. Deviation in Heat Capacity, Enthalpy, and Entropy for Ten Representative Substances**

	Heat capacity	Enthalpy change	Entropy change
Av % dev	1.06 <sup>a</sup>	0.49 <sup>b</sup>	0.37 <sup>b</sup>
Max % dev	1.73 <sup>a</sup>	0.77 <sup>b</sup>	0.58 <sup>b</sup>
Min % dev	0.23 <sup>a</sup>	0.15 <sup>b</sup>	0.15 <sup>b</sup>

<sup>a</sup> Compared to experimental data. <sup>b</sup> Defined by eq 21.



**Figure 3.** Average percent absolute error as a function of the exponent  $m$  in eq 22.  $C_8H_{18}$  is 3,4-dimethylhexane.

as shown in Figure 3. The enthalpy and entropy integrals become cumbersome, however, when  $m$  is not an integer.

The motive for this work was to seek a simple correlation for heat capacity. The resulting correlation has only two empirical constants and is reasonably accurate, but not as accurate as the four-constant and five-constant polynomial representations. The advantages of the simple correlation appear to include suitability to heat capacity estimation from minimal data, analytical convenience in the study of the behavior of large numbers of substances, and applicability outside of the fitted temperature range. (Unrealistic predictions outside of the appropriate temperature range can of course be a source of difficulty with polynomial representations.)

After the preliminary version of this paper was written, the writer learned of a recent correlation due to Wilhoit (19), which combines certain features of the simple correlation given here and the polynomial representations; it has the form

$$\frac{\hat{c}_p - (c_\alpha + 1)}{c_\omega - c_\alpha} = z^2 \left[ 1 + (z - 1) \sum_{k=0}^3 a_k z^k \right] \quad (23)$$

where

$$z = T / (T + D) \quad (24)$$

The empirical constants are  $a_0$ ,  $a_1$ ,  $a_2$ , and  $a_3$  and the "scaling factor"  $D$ . This correlation appears to yield accurate results over a large temperature range and is perhaps the most interesting of the existing high-precision correlations.

## Acknowledgments

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## Glossary

$a_k$	constant coefficient
$B$	constant in the definition $x = B(\hat{T} - \tau)$
$c_p^0$	constant pressure ideal-gas capacity
$c_v^0$	constant volume ideal-gas heat capacity
$\hat{c}_p$	reduced heat capacity = $c_p^0/R$
$\hat{c}_v$	reduced heat capacity = $c_v^0/R$
$c_\alpha$	reduced low-temperature heat capacity
$c_\omega$	reduced high-temperature heat capacity

$D$	constant "scaling factor"
$h$	Planck's constant
$H^*$	ideal-gas enthalpy
$k$	Boltzmann's constant; an index
$m$	constant exponent
$N$	number of data points
$R$	gas constant
$S^*$	temperature-dependent part of ideal-gas entropy
$T$	absolute temperature
$T_c$	absolute thermodynamic critical temperature
$\hat{T}$	reduced temperature = $T/T_c$
$w$	equivalent wavenumber, $\text{cm}^{-1}$
$x$	independent variable = $B(\hat{T} - \tau)$
$X$	computed property
$y$	dependent variable = $(\hat{c}_v - c_\alpha)/(c_\omega - c_\alpha)$
$y_c$	value of $y$ at $T = T_c$
$z$	independent variable = $T/(T + D)$

#### Greek Letters

$\alpha$	subscript denoting low temperature
$\eta$	reduced reciprocal temperature = $h\nu/2kT$
$\nu$	molecular vibration frequency
$\tau$	constant in the definition $x = B(\hat{T} - \tau)$

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## Thermodynamic Properties of Lanthanide Trihalide Molecules

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**The thermodynamic properties of lanthanide trihalide molecules have been calculated for the temperature range 298.15-2000 K using the methods of statistical mechanics. The necessary molecular data are incomplete, and the missing parameters have been estimated in a systematic manner.**

There has been considerable recent interest in the high-temperature thermodynamic properties of the lanthanide trihalides with particular emphasis on vapor pressure and sublimation pressure measurements (17). In most of these studies a "second law" treatment of the data was used to obtain enthalpies of vaporization or sublimation, although a "third law" treatment was used in some cases. However, the molecular parameters required to calculate the free energy functions  $(- [G^\circ_T - H^\circ_{298.15}] / T)$  for the gaseous molecules were developed on a case-by-case basis which makes systematic comparisons difficult. Free energy functions for the lanthanum trihalides have been published (14), but significant molecular data have become available more recently (10, 11, 15, 20, 24).

Because of an interest in systematic trends in properties of  $\text{LnX}_3$  molecules and in view of the advantages of the third law treatment, it was decided to calculate their thermodynamic functions using the best data currently available and employing uniform methods for interpolation and extrapolation in the absence of published data.

#### Method

The calculations were performed using STRETCH-TDF, a FORTRAN computer program (5) which employs the usual statistical-mechanical formulas (rigid rotor, harmonic oscillator approximation). The electronic contributions were calculated separately using QEL, an APL program written for that purpose, since the STRETCH-TDF program does not include electronic levels in the polyatomic molecule calculation mode. STRETCH-TDF inputs are molecular weight, symmetry number, moments of inertia, and vibrational frequencies together with their degeneracies. The QEL inputs are the energies and multiplicities of the electronic states of the molecule, including the multiplicity of the ground state. A description of the method may be found in the introduction to the JANAF Thermochemical Tables (23).

#### Molecular Geometry

The molecular structures of  $\text{LnX}_3$  molecules have been the subject of recent investigations (10, 11, 13, 15, 20, 24), but the picture is far from being complete. Infrared spectra of  $\text{LnF}_3$  molecules trapped in inert matrices have been interpreted by some investigators (24) as supporting a planar  $D_{3h}$  geometry, but others (10, 11) interpret similar data as supporting a pyramidal  $C_{3v}$  geometry. Molecular beam experiments (13) on a number of trifluorides support a pyramidal geometry for some but not all of the molecules studied. Earlier electron diffraction studies (7) were interpreted as supporting a planar geometry,