Empirical Heat Capacity Equations of Various Gases

By Hugh M. Spencer

Since the publication of the second article of this series,[1] new or more satisfactory values of the thermodynamic functions in the hypothetical ideal gaseous state of twenty-three substances have been derived from spectroscopic data. Those of the normal paraffin hydrocarbons[2] belong in the latter category, both because they are based on more adequate data, and, for the present purpose of obtaining empirical equations representing their heat capacities, because they include values of the heat capacities. The older data for seven gases have been corrected to correspond to use of the new values of the fundamental constants,[3] and equations are here presented for all of them except hydrogen, for which the old equation represents the new values as well as a new equation. Equations are here presented for a number of gases which were not included in Part II, because either it was considered they would not be of sufficient interest, or the temperature range was considered too small. This seems to be untrue. For the cyanogen halides additional values of the heat capacities at 291.1, 298.1°K. and at temperatures above 500°K. have been calculated using the same wave numbers and constants used by Stevenson.[4] The latter data were obtained in order to avoid the use of the heat constant data. The results are given in Table I.

Table I

Molal Heat Capacities in the Hypothetical Ideal Gaseous State

T°K.	ClCN	BrCN	ICN
	C_p° (cal. mole^{-1}. deg.$^{-1}$)		
291.1	10.63	11.05	11.50
298.1	10.70	11.12	11.55
600	12.48	12.68	12.85
700	12.83	12.98	13.11
800	13.12	13.24	13.34
900	13.35	13.46	13.55
1000	13.56	13.64	13.72

Table II presents the equations and the percentage deviations of such equations representing the heat capacities of the various gases in the forms

$$C_p^\circ = a + bT + cT^2 \quad (1)$$

$$C_p^\circ = a + bT + c'/T^2 \quad (2)$$

$$C_p^\circ = a + bT + cT^2 + dT^3 \quad (3)$$

The equations are least square solutions of all th: heat capacity data. The comments previously

Table II

Compound	Source	Range, °K.	a	$b \times 10^3$	$c \times 10^7$	$c' \times 10^{-5}$	$d \times 10^9$	—% Deviation— Max.	Av.
Acetone	5	298.1 -1500	5.371	49.227	−151.82			1.74	0.85
Acetone	5	298.1 -1500	2.024	64.401	−342.85		7.082	0.41	.20
Allene[a]	6	250 -1000	3.566	40.265	−159.55			0.66	.42
Benzene[b]	7	298.16–1500	−0.283	77.936	−262.96			4.99	1.92
Benzene[b]	7	298.16–1500	−9.478	119.930	−807.02		20.426	0.31	0.16
n-Butane[b]	2	298.16–1500	4.357	72.552	−221.45			1.74	.76
n-Butane[b]	2	298.16–1500	−0.012	92.506	−479.98		9.706	0.44	.13
cis-2-Butene[b]	8	298.16–1500	2.047	64.311	−198.34			1.51	.78
cis-2-Butene[b]	8	298.16–1500	−1.456	80.319	−402.67		7.708	0.65	.13
Carbon dioxide[b]	3	298.16–1500	6.214	10.396	− 35.45			1.41	.77
Carbon dioxide[b]	3	298.16–1500	5.152	15.224	− 96.81		2.313	0.30	.14
Carbon monoxide[b]	3	298.16–1500	6.420	1.665	− 1.96			1.17	.55
Cyanogen bromide[a]	4	250 -1000	11.654	2.141		−1.028		0.47	.20
Cyanogen chloride[a]	4	250 -1000	11.304	2.441		−1.159		.69	.27
Cyanogen iodide[a]	4	250 -1000	11.882	1.954		−0.805		.29	.11
Cyclopropane[a]	9	250 -1000	−3.562	65.107	−263.49			1.19	.62
Deuterium[a]	10	298.1 -1500	6.830	0.210	4.68			0.78	.39
Deuterium hydride[a]	10	298.1 -1500	6.991	−0.274	5.98			.47	.24
Ethane[b]	2	298.16–1500	2.195	38.282	−110.01			.91	.43
Ethane[b]	2	298.16–1500	1.279	42.464	−164.20		2.035	.57	.20
n-Heptane[b]	2	298.16–1500	8.850	120.974	−374.78			1.89	.84
n-Heptane[b]	2	298.16–1500	0.747	157.986	−854.29		18.003	0.47	.15
n-Hexane[b]	2	298.16–1500	7.313	104.906	−323.97			1.85	.82
n-Hexane[b]	2	298.16–1500	0.428	136.352	−731.38		15.295	0.48	.15

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[1] (a) H. M. Spencer and J. L. Justice, This Journal, **56**, 2311 (1934), I; (b) H. M. Spencer and G. N. Flannagan, *ibid.*, **64**, 2511 (1942), II.

[2] K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944).

[3] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[4] D. P. Stevenson, *J. Chem. Phys.*, **7**, 171 (1939).

[5] I. N. Godnev, A. Payukhina and A. Sverdlin, *J. Phys. Chem.* (U. S. S. R.), **14**, 374 (1940). See H. Zeise, *Z. Elektrochem.*, **48**, 425 (1942).

[6] J. W. Linnett and W. H. Avery, *J. Chem. Phys.*, **6**, 686 (1938).

[7] K. S. Pitzer and D. W. Scott, This Journal, **65**, 803 (1943).

[8] R. B. Scott, W. J. Ferguson and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **33**, 1 (1944).

[9] G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 610 (1940).

[10] H. L. Johnston and E. A. Long, *ibid.*, **2**, 389 (1934).

TABLE II (*Concluded*)

Compound	Source	Range, °K.	a	b × 10³	c × 10⁷	c' × 10⁻⁵	d × 10⁹	% Deviation Max.	Av.
Hydrogen sulfide[g,a]	11, 12	298.1 -1800	6.864	3.852	7.85		−0.634	0.90	0.36
Mesitylene[b]	7	298.16–1500	3.042	124.059	−397.43			2.38	1.00
Mesitylene[b]	7	298.16–1500	−6.012	165.412	−933.20		20.114	0.41	0.15
Methane[b]	3	298.16–1500	3.381	18.044	− 43.00			1.80	.52
Methane[b]	3	298.16–1500	4.171	14.450	2.67		−1.722	1.03	.41
Nitrogen[b]	3	298.16–1500	6.524	1.250	− 0.01			1.15	.60
n-Octane[b]	2	298.16–1500	10.381	137.054	−425.64			1.89	.85
n-Octane[b]	2	298.16–1500	1.064	179.611	−976.98		20.699	0.50	.16
Oxygen[b]	3	298.16–1500	6.148	3.102	− 9.23			0.65	.24
n-Pentane[b]	2	298.16–1500	5.780	88.843	−273.26			1.84	.80
n-Pentane[b]	2	298.16–1500	0.099	114.794	−609.47		12.623	0.43	.13
Propane[b]	2, 13	231.09–1500	2.258	57.636	−175.94			1.76	.64
Propane[b]	2	298.16–1500	−1.209	73.734	−386.66		7.961	0.31	.10
Propylene[c]	14	270 -510	2.974	45.024	−113.76			0.16	.04
Pyridine[d]	15	291.15–1000	−3.016	88.083	−386.65			1.02	.61
Silicon tetrachloride[e]	16	273.1 -573.1	23.494	2.942		−2.380		0.21	.07
Stannic chloride[h,e]	16	273.1 -573.1	25.115	0.925		−1.632		0.08	.02
Sulfur trioxide[f]	17	298.16–1200	6.077	23.537	− 96.87			1.53	.84
Sulfur trioxide[f]	17	298.16–1200	3.603	36.310	−288.28		8.649	0.19	.10
Titanic chloride[e]	16	273.1 -573.1	24.612	1.541		−1.940		0.12	.03
Toluene[b]	7	298.16–1500	0.436	94.254	−312.58			3.87	1.51
Toluene[b]	7	298.16–1500	−8.930	137.033	−866.80		20.807	0.30	0.14
Triborine triamine[a]	18	298.1 -1000	−0.115	91.476	−399.23			1.29	.73
Water[b]	3	298.16–1500	7.256	2.298	2.83			0.74	.45
m-Xylene[b]	7	298.16–1500	1.956	109.147	−355.83			3.16	1.27
m-Xylene[b]	7	298.16–1500	−7.634	152.950	−923.33		21.306	0.35	0.11
o-Xylene[b]	7	298.16–1500	4.603	104.476	−336.16			2.63	1.08
o-Xylene[b]	7	298.16–1500	−3.890	143.270	−838.75		18.869	0.32	0.10
p-Xylene[b]	7	298.16–1500	1.846	108.594	−352.00			2.84	1.16
p-Xylene[b]	7	298.16–1500	−7.051	149.234	−878.51		19.767	0.43	0.12

[a] "I. C. T." constants were used. [b] Defined calorie = 4.1833 int. j. and Birge's (1941) constants were used. [c] R = 1.9869 cal. deg.$^{-1}$ mole^{-1} was used. [d] Birge's (1941) constants were used. [e] Birge's (1929) constants were used. [f] Hirshfelder's constants reported by J. E. and M. G. Mayer, "Statistical Mechanics," J. Wiley and Sons, Inc., New York, N. Y., 1940, were used. [g] Contrary to the statement in note *m* of Part II, the rotational distortion correction was not included in deriving the cubic equation. [h] At 20° C_p° = 23.49. 23.84, as given in the original publication, is evidently a typographical error.

made[1] concerning the usefulness of empirical heat capacity equations, the choice of their form, and their unreliability for extrapolation apply to the present communication.

The constants of the quadratic and cubic equations for the normal paraffin hydrocarbons vary regularly for $n \geqq 5$ and $n \geqq 6$, respectively. Consequently we may write

$$C_p^\circ = (5.780 + 1.534m) + (88.843 + 16.070m) \times 10^{-3}T - (273.26 + 50.79m) \times 10^{-7}T^2 \quad (4)$$

$$C_p^\circ = (0.428 + 0.318p) + (136.352 + 21.629p) \times 10^{-3}T - (731.38 + 122.80p) \times 10^{-7}T^2 + (15.295 + 2.702p) \times 10^{-9}T^3 \quad (5)$$

where $m = n - 5$, $p = n - 6$, and n = the number of carbon atoms.

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Identification of Sulfobenzoic Acids

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We appreciate having Dr. Veibel point out (p. 1867) that *m*-sulfobenzoic acid forms a benzylthiuronium salt under the conditions of his experiments whereas it does not form readily in the strongly acidic solutions used in our work. It is regretted that reference to Dr. Veibel's prior work was not made. However, the chief point of our "Note" was that under certain conditions it is possible to determine which one of the three isomeric sulfobenzoic acids is present in a solution by the large differences in the solubilities of their benzylthiuronium salts.

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(11) P. C. Cross, *J. Chem. Phys.*, **3**, 168 (1935).
(12) E. B. Wilson, Jr., *ibid.*, **4**, 526 (1936).
(13) K. S. Pitzer, *ibid.*, **12**, 310 (1944).
(14) D. Telfair, *ibid.*, **10**, 167 (1942).
(15) C. H. Kline, Jr., and J. Turkevich, *ibid.*, **12**, 300 (1944).
(16) R. C. Herman, *ibid.*, **6**, 406 (1938).
(17) W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley, *ibid.*, **12**, 408 (1944).
(18) B. L. Crawford, Jr., and J. T. Edsall, *ibid.*, **7**, 223 (1939).