

Simple Expressions for the Heat Capacities of Gases

Bryce L. Crawford Jr. and Robert G. Parr

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Simple Expressions for the Heat Capacities of Gases

BRYCE L. CRAWFORD, JR., AND ROBERT G. PARR

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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A table of constants is given whereby one may at once write down, knowing the vibrational frequencies, the best approximation of the form $C_p^\circ = A_0 + A_1T + A_2T^2$ to the heat capacity of a gas with translational, rotational, and vibrational (harmonic) degrees of freedom.

THE heat capacities of gases (in the limit of zero pressure) are now quite frequently calculated from a knowledge of the vibrational frequencies, and estimates of any restricting potentials. This calculation is scarcely a difficult one if one wishes to find the heat capacity at a single temperature. However, in several common types of thermodynamic problem it is convenient to have a simple algebraic expression for the heat capacity as a function of temperature; even though the simple expression is only approximate, its convenience in use compensates for its inaccuracy. Such simple expressions are often fitted to values calculated for a few temperatures from the exact expressions.

Having observed that the necessary "fitting" could be done once for all, we proceeded to carry this out for the Einstein functions. Table I presents constants with whose aid one can at once write down, for any rigid molecule, the expression

$$C_p^\circ = A_0 + A_1T + A_2T^2 \quad (1)$$

which will give the best possible (least-square) approximation in this form over the temperature range from 250° to 1500°K.

It is clear that similar tables could be calculated to give the "best" constants for other approximating forms, such as $B_0 + B_1T + B_2T^{-2}$; and, perhaps more valuable, similar tables for the contribution of hindered internal rotations.

USE OF THE TABLE

The table gives, for each frequency ω , the contributions a_0 , $a_1 \times 10^{-3}$, $a_2 \times 10^{-6}$ to the constants A_0 , A_1 , A_2 in Eq. (1). One must add up the contributions of the several vibrational frequencies, giving double or triple weight to doubly

or triply degenerate frequencies, and including a translational-rotational contribution $a_0 = 6.954$ for linear or $a_0 = 7.948$ for non-linear molecules. The constants used here give C_p° in cal./mole deg.; absolute temperatures (degrees Kelvin) should be used in (1).

In the first part of Table I ($150 \text{ cm}^{-1} \leq \omega \leq 600 \text{ cm}^{-1}$) and in the last ($\omega > 3000 \text{ cm}^{-1}$), the values given for the a_i are accurate to the last place; in the middle part, the values may be in error by one or two units in the last place. The two needed universal constants were taken to be $(hc/k) = 1.4385 \text{ cm deg.}$ and $R = 1.9869 \text{ cal./mole deg.}$ Since the significant parameter in the calculation is not ω but $\alpha = (hc/k)(\omega/1500)$, any change in the accepted values of (hc/k) can be compensated by the use of an adjusted value of ω in entering the table; thus if (hc/k) should increase by 5 percent, one would adjust all frequencies of the molecule of interest by 5 percent upward, and use Table I as given. A change in the accepted value of R will affect the value of C_p° from Eq. (1) directly; hence if R should increase 5 percent, one may compensate by increasing the final constants A_0 , A_1 , A_2 by 5 percent each.

It is unlikely that values of ω higher than those in Table I will be of interest. For ω less than 150 cm^{-1} , the a_i can be calculated from the series (20); a few terms will suffice.

EXAMPLES

Thus, the equation for the heat capacity of ethylene may be found from the vibrational frequencies¹ as follows, using linear interpolation in Table I:

¹ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 326.

ω (cm ⁻¹)	a_0	a_1	a_2
Trans.-rotn.	7.948	—	—
825	-.151	3.365	-1.391
943	-.402	3.620	-1.460
949.2	-.415	3.630	-1.462
995	-.492	3.690	-1.471
1050	-.579	3.741	-1.471
1342.4	-.816	3.573	-1.275
1443.5	-.834	3.400	-1.158
1623.3	-.815	3.009	-.922
2989.5	-.143	.181	.443
3019.3	-.132	.147	.454
3105.5	-.103	.057	.484
3272.3	-.05	-.10	.52

$$C_p^\circ = 3.016 + 28.313 \times 10^{-3}T - 8.709 \times 10^{-6}T^2$$

The accuracy of this approximation is shown in Table II.

The accuracy will of course depend on the distribution of frequencies for the molecule concerned; in general, we may expect the approximation to err by less than 2 percent. As a relatively unfavorable example, we consider carbon dioxide:²

ω (cm ⁻¹)	a_0	a_1	a_2
Trans.-rotn.	6.954	—	—
667.3 (twice)	.287	2.789	-1.182
1336.9	-.813	3.581	-1.280
2349.3	-.450	1.240	-0.004

$$C_p^\circ = 6.265 + 10.399 \times 10^{-3}T - 3.648 \times 10^{-6}T^2$$

The accuracy is again shown in Table II.

CALCULATION OF THE TABLE

The Normal Equations

The true heat capacity of a perfect gas is given by

$$C_p(T) = \sum_{\omega} c(\omega, T), \quad (2)$$

where the parameters ω may be regarded as generalized to include translation, rotation, etc., as well as the frequencies of vibration. We desired to approximate this in the range 250 deg. $\leq T \leq 1500$ deg. by a function

$$\Gamma(T) = A_0 + A_1T + A_2T^2; \quad (3)$$

our criterion is that

$$I = \int_{250}^{1500} (C - \Gamma)^2 dT = \text{minimum}. \quad (4)$$

It seems worth while to give the fundamental theorem we use: that if we have a set of functions

$$\gamma(\omega, T) = a_0(\omega) + a_1(\omega) \times 10^{-3}T + a_2(\omega) \times 10^{-6}T^2 \quad (5)$$

² Frequencies from reference 1, p. 274.

each approximate to one of the set $c(\omega, T)$, so that for each ω

$$i(\omega) = \int_{250}^{1500} (c - \gamma)^2 dT = \text{minimum}, \quad (6)$$

then the function Γ satisfying (4) is

$$\Gamma(T) = \sum_{\omega} \gamma(\omega, T). \quad (7)$$

The proof is easily written out.

We have for the vibrational contributions to (2)

$$c(\omega, T) = c(x) = Rx^2 e^x (e^x - 1)^{-2}, \quad (8)$$

where R is the gas constant and

$$x = hc\omega/kT = 1.4385(\omega/T). \quad (9)$$

The requirement (6) on the approximate functions γ leads to the "normal equations" determining the a_k :

$$a_0(\omega)\Delta T^{(k+1)} + a_1(\omega)\Delta T^{(k+2)} + a_2(\omega)\Delta T^{(k+3)} = I_k(\omega); \quad k=0, 1, 2. \quad (10)$$

Here

$$\Delta T^{(k)} = (10^{-3k}/k)(1500^k - 250^k) \quad (11)$$

and

$$I_k(\omega) = 10^{-3(k+1)} \int_{250}^{1500} c(\omega, T) T^k dT. \quad (12)$$

Equations (10) can be solved to give

$$\begin{aligned} a_0(\omega) &= 29.3184I_0(\omega) \\ &\quad - 70.9632I_1(\omega) + 37.4784I_2(\omega), \\ a_1(\omega) &= -70.9632I_0(\omega) \\ &\quad + 186.7776I_1(\omega) - 103.2192I_2(\omega), \\ a_2(\omega) &= 37.4784I_0(\omega) \\ &\quad - 103.2192I_1(\omega) + 58.9824I_2(\omega), \end{aligned} \quad (13)$$

so that we need only evaluate the $I_k(\omega)$.

Calculation for $\omega \leq 600$ cm⁻¹

For small values of ω , it is convenient to calculate the $I_k(\omega)$ from their series expansions. Equations (8), (9), and (12) combine to give

$$I_k(\omega) = (1.5\alpha)^{k+1} \int_{\alpha}^{6\alpha} c(x) x^{-k-2} dx, \quad (14)$$

where

$$\alpha = 1.4385(\omega/1500) = 1.4385\mu. \quad (15)$$

Now expansion of (8) gives

$$c(x) = R \sum_{n=0}^{\infty} (1-n)(B_n/n!) x^n, \quad (16)$$

where the B_n are the Bernoulli numbers: $B_0=1$, $B_1=-\frac{1}{2}$, $B_2=\frac{1}{6}$, $B_3=0$, $B_4=-1/30$, \dots . Substituting (16) in (14) and integrating term by term, one obtains

$$I_k(\omega) = R(1.5)^{k+1} \sum_{n=0}^{\infty} (1-n)(B_n/n!) C_{n-k-1} \alpha^n, \quad (17)$$

where

$$C_n = (1/n)(6^n - 1). \quad (18)$$

Introduction of (15) and $R=1.9869$ cal./mole deg. into (17) yields

$$\begin{aligned} I_0(\omega) &= 2.483625 - 2.569660\mu^2 \\ &\quad + 3.81077\mu^4 - 6.78961\mu^6 \\ &\quad + 12.64625\mu^8 - 23.78977\mu^{10} \\ &\quad + 44.8567\mu^{12} - 84.6271\mu^{14} + \dots, \\ I_1(\omega) &= 2.173172 - 1.381264\mu^2 \\ &\quad + 1.39581\mu^4 - 2.12039\mu^6 \\ &\quad + 3.68842\mu^8 - 6.69087\mu^{10} \\ &\quad + 12.3356\mu^{12} - 22.9198\mu^{14} + \dots, \quad (19) \\ I_2(\omega) &= 2.224914 - 0.963623\mu^2 \\ &\quad + 0.59820\mu^4 - 0.70407\mu^6 \\ &\quad + 1.10641\mu^8 - 1.91167\mu^{10} \\ &\quad + 3.42655\mu^{12} - 6.25086\mu^{14} + \dots. \end{aligned}$$

Values of the $I_k(\omega)$ calculated from (19) for $0.10 \leq \mu \leq 0.40$ are given in Table I, along with the $a_k(\omega)$ found from them.

For values of $\mu = \omega/1500$ less than 0.10, the $a_k(\omega)$ may be calculated from the series

$$\begin{aligned} a_0(\omega) &= 1.9869 - 13.4345\mu^2 \\ &\quad + 35.0941\mu^4 - 74.9783\mu^6 + \dots, \\ a_1(\omega) &= 23.8265\mu^2 - 71.4641\mu^4 \\ &\quad + 158.4446\mu^6 - \dots, \quad (20) \\ a_2(\omega) &= -10.5706\mu^2 + 34.0304\mu^4 \\ &\quad - 77.1265\mu^6 + \dots. \end{aligned}$$

Calculation for $\omega > 3000 \text{ cm}^{-1}$

At the upper end, we may use

$$(1 - e^{-x})^{-2} = \sum_{n=0}^{\infty} (n+1)e^{-nx} \quad (21)$$

to expand (8); then our integrals become, with a change of variable,

$$I_k(\omega) = R(1.5)^{k+1} \sum_{n=1}^{\infty} n^k \int_{n\alpha}^{6n\alpha} y^{-k} e^{-y} dy. \quad (22)$$

TABLE I.

μ	$\omega \text{ (cm}^{-1}\text{)}$	I_0	I_1	I_2	a_0	a_1	a_2
0.00	0	2.48362	2.17317	2.22491	1.987	.000	.000
0.10	150	2.45830	2.15950	2.21534	1.856	.231	-.102
.11	165	2.45308	2.15666	2.21334	1.829	.278	-.123
.12	180	2.44739	2.15357	2.21116	1.801	.329	-.145
.13	195	2.44125	2.15022	2.20880	1.770	.383	-.169
.14	210	2.43467	2.14662	2.20625	1.737	.441	-.195
.15	225	2.42766	2.14278	2.20353	1.702	.502	-.221
.16	240	2.42023	2.13869	2.20063	1.665	.566	-.249
.17	255	2.41239	2.13437	2.19755	1.626	.633	-.279
.18	270	2.40415	2.12982	2.19430	1.586	.702	-.309
.19	285	2.39553	2.12503	2.19087	1.544	.774	-.341
.20	300	2.38653	2.12003	2.18728	1.501	.848	-.373
.21	315	2.37717	2.11480	2.18352	1.457	.924	-.406
.22	330	2.36747	2.10937	2.17960	1.411	1.002	-.440
.23	345	2.35744	2.10372	2.17552	1.364	1.082	-.474
.24	360	2.34708	2.09787	2.17127	1.317	1.163	-.509
.25	375	2.33642	2.09183	2.16687	1.268	1.244	-.544
.26	390	2.32547	2.08559	2.16231	1.218	1.327	-.580
.27	405	2.31423	2.07917	2.15760	1.169	1.411	-.616
.28	420	2.30273	2.07256	2.15274	1.118	1.495	-.652
.29	435	2.29098	2.06578	2.14773	1.067	1.579	-.687
.30	450	2.27898	2.05883	2.14258	1.016	1.663	-.723
.31	465	2.26676	2.05171	2.13729	.964	1.747	-.759
.32	480	2.25432	2.04443	2.13186	.912	1.831	-.794
.33	495	2.24169	2.03700	2.12619	.861	1.915	-.829
.34	510	2.22886	2.02942	2.12039	.809	1.997	-.863
.35	525	2.21585	2.02169	2.11476	.757	2.079	-.897
.36	540	2.20268	2.01383	2.10880	.706	2.160	-.931
.37	555	2.18935	2.00583	2.10271	.655	2.240	-.964
.38	570	2.17588	1.99770	2.09650	.604	2.319	-.996
.39	585	2.16228	1.98945	2.09018	.553	2.396	-1.027
.40	600	2.14857	1.98108	2.08373	.503	2.472	-1.058
.45	675	2.07852	1.93761	2.04980	.263	2.824	-1.196
.50	750	2.00687	1.89185	2.01336	+.044	3.124	-1.308
.55	825	1.93457	1.84432	1.97472	-.151	3.365	-1.391
.60	900	1.86236	1.79545	1.93417	-.320	3.547	-1.445
.65	975	1.79081	1.74561	1.89197	-.462	3.672	-1.471
.70	1050	1.72036	1.69513	1.84839	-.579	3.741	-1.471
.75	1125	1.65133	1.64428	1.80367	-.671	3.758	-1.448
.80	1200	1.58393	1.59331	1.75804	-.740	3.730	-1.404
.85	1275	1.51833	1.54241	1.71169	-.788	3.663	-1.342
.90	1350	1.45462	1.49176	1.66481	-.819	3.563	-1.267
.95	1425	1.39285	1.44152	1.61759	-.834	3.436	-1.181
1.00	1500	1.33307	1.39182	1.57019	-.836	3.288	-1.087
1.05	1575	1.27528	1.34276	1.52275	-.827	3.123	-.988
1.10	1650	1.21946	1.29444	1.47541	-.809	2.945	-.885
1.15	1725	1.16559	1.24694	1.42829	-.784	2.759	-.780
1.20	1800	1.11365	1.20034	1.38151	-.753	2.569	-.675
1.25	1875	1.06362	1.15470	1.33519	-.717	2.377	-.572
1.30	1950	1.01545	1.11007	1.28941	-.678	2.185	-.471
1.35	2025	.96910	1.06649	1.24424	-.637	1.996	-.374
1.40	2100	.92452	1.02398	1.19975	-.595	1.812	-.281
1.45	2175	.88168	.98257	1.15602	-.551	1.632	-.192
1.50	2250	.84052	.94229	1.11311	-.508	1.458	-.107
1.55	2325	.80101	.90315	1.07107	-.464	1.291	-.028
1.60	2400	.76310	.86517	1.02995	-.421	1.132	+.046
1.65	2475	.72674	.82835	.98977	-.380	.982	.114
1.70	2550	.69188	.79268	.95056	-.341	.840	.177
1.75	2625	.65848	.75816	.91236	-.302	.706	.235
1.80	2700	.62649	.72479	.87518	-.265	.581	.288
1.85	2775	.59586	.69256	.83904	-.231	.466	.335
1.90	2850	.56655	.66146	.80395	-.198	.359	.377
1.95	2925	.53853	.63147	.76991	-.167	.259	.415
2.00	3000	.51173	.60257	.73692	-.139	.168	.447
2.1	3150	.4617	.5480	.6741	-.09	.01	.50
2.2	3300	.4158	.4973	.6152	-.04	-.12	.53
2.3	3450	.3742	.4508	.5606	-.01	-.22	.56
2.4	3600	.3366	.4082	.5102	+.02	-.30	.57
2.5	3750	.3023	.3690	.4633	+.04	-.36	.57
2.6	3900	.2712	.3330	.4200	+.06	-.41	.57
2.8	4200	.2177	.2702	.3438	+.09	-.46	.54
3.0	4500	.1741	.2182	.2798	+.10	-.47	.50
3.5	5250	.0983	.1258	.1639	+.10	-.39	.36
4.0	6000	.0545	.0710	.0937	+.07	-.28	.24
5.0	7500	.0161	.0215	.0286	+.02	-.08	.07

These can be integrated by parts and in terms of the exponential integral

$$-E_i(-x) = \int_x^{\infty} e^{-x} x^{-1} dx \quad (23)$$

TABLE II. Accuracy of approximate formulas for ethylene and carbon dioxide.

	$T(^{\circ}\text{K})$	250	500	750	1000	1250	1500
Ethylene	C_p° true ^a	9.346	15.165	19.471	22.501	24.691	26.276
	C_p° calc. ^b	9.550	14.995	19.352	22.620	24.763	25.890
Carbon Dioxide	C_p° true	8.325	10.664	12.063	12.938	13.493	13.854
	C_p° calc.	8.637	10.553	12.012	13.016	13.564	13.656

^a "True" values are calculated from Eq. (2).^b "Calc." values are computed from equations of the form (5).

to give

$$I_0(\omega) = R(1.5\alpha)[(e^{\alpha}-1)^{-1} - (e^{6\alpha}-1)^{-1}], \quad (24)$$

$$I_1(\omega) = R(1.5\alpha)^2 \sum_{n=1}^{\infty} n[-E_i(-n\alpha) + E_i(-6n\alpha)], \quad (25)$$

$$I_2(\omega) = R(1.5\alpha)^3 \{ e^{-\alpha}\alpha^{-1}(1-e^{-\alpha})^{-2} - e^{-6\alpha}(6\alpha)^{-1}(1-e^{-6\alpha})^{-2} - \sum_{n=1}^{\infty} n^2[-E_i(-n\alpha) + E_i(-6n\alpha)] \}. \quad (26)$$

For $\omega > 3000 \text{ cm}^{-1}$, it is sufficient to take

$$I_0 \cong R(1.5\alpha)(e^{\alpha}-1)^{-1}, \quad (27)$$

$$I_1 \cong R(1.5\alpha)^2 \sum_{n=1}^5 n[-E_i(-n\alpha)], \quad (28)$$

$$I_2 \cong 1.5R^{-1}e^{\alpha}(I_0)^2 - R(1.5\alpha)^3 \times \sum_{n=1}^5 n^2[-E_i(-n\alpha)]. \quad (29)$$

These equations were used to calculate the I_k and a_k in the last part of Table I.

Calculation for Intermediate ω

As always, there is the intermediate range ($600 \text{ cm}^{-1} < \omega \leq 3000 \text{ cm}^{-1}$) where neither series is convenient; we evaluated these $I_k(\omega)$ by nu-

merical integration. It is convenient to calculate by Gregory's formula³ a set of integrals

$$J_k(\omega_i, \omega_{i+1}) = \int_{\alpha_i}^{\alpha_{i+1}} c(x)x^{-k-2}dx; \quad i=1, 2, \dots \quad (30)$$

The α_i are an appropriate sequence of values of α . The $I_k(\omega)$ then follow from relations of the form

$$I_k(\omega) = (1.5\alpha)^{k+1} \sum_{\omega_i=\alpha}^{\omega_{i+1}=6\alpha} J_k(\omega_i, \omega_{i+1}). \quad (31)$$

Values of the $I_k(\omega)$ for $0.40 < \mu \leq 2.00$ computed in this manner, using the table of Einstein functions given by Taylor and Glasstone,⁴ are given in Table I, with the corresponding a_k .

Accuracy

The series expansions at either end were carried out far enough so that the last digit in the I_k should be off not more than 1; the a_k should be good to the last digit given. In the intermediate range the last digit given for the I_k is not significant, and the a_k may be off 1 or 2 in the last place.

The I_0 can of course be evaluated in closed form in terms of the heat-content function. We evaluated it by the same methods used for I_1 and I_2 chiefly to provide a check.

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³ Cf. for example, Margenau and Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 459.

⁴ Taylor and Glasstone, *Treatise on Physical Chemistry, Volume I* (D. Van Nostrand Company, Inc., New York, 1942), p. 655.