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Representation of the Ideal-Gas Thermodynamic Properties of Water

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An equation, in the form of a summation of simple harmonic oscillator functions, for dimensionless isobaric heat capacity (specific isobaric heat-capacity divided by the specific ideal-gas constant, c_P/R) for water at zero pressure has been fitted to the values published by Woolley. The equation has a very good agreement with the values to which it has been fitted. Comparisons are made with other equations. Equations for ideal-gas dimensionless enthalpy and the ideal-gas dimensionless Gibbs function (specific enthalpy and specific Gibbs function divided by the product of specific ideal-gas constant and thermodynamic temperature respectively, h/RT and g/RT), obtained by appropriate manipulation of the equation for c_P/R, are also given.

KEY WORDS: Water; correlation; ideal-gas thermodynamic properties.

1. INTRODUCTION

When one uses a pressure, P, density, ρ, temperature, T, equation of state ($P = P(\rho, T)$) to obtain the characteristic function for the specific Helmholtz function, $f = f(\rho, T)$, an additional function of temperature is required. This additional function of temperature is most conveniently provided by properties of the fluid in the ideal-gas limit. For water, Woolley [1] has calculated from spectroscopic data accurate values of c_P/R in the ideal-gas limit.

The purpose of the equation described, for which coefficients have been determined using the Woolley values of c_P/R, is to provide for water the function of temperature indicated above with high precision. Thus the

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$f = f(\rho, T)$ equation in which it might be employed would not have any significant error imposed from this source for the Helmholtz function or any other thermodynamic property obtained from this characteristic function. In addition, the equation can be used to provide ideal-gas properties of natural isotopic mixture (ordinary water substance) for other purposes.

Woolley also gives a 16 term polynomial in temperature to represent his values of c_P/R. He gives two further constants to obtain h/RT and g/RT. The proposed equation is compared with the values of Woolley, the equation of Woolley, and also an equation based on that of Pollak [2].

2. THE PROPOSED EQUATION

Statistical mechanics (see, for instance, Wilson [3]) indicates that for water, c_P/R could be represented by contributions due to translation, rotation, and three vibrational modes. The translational part is constant while the rotational and vibrational modes are functions of temperature. Although this model does not include the more detailed calculation in the Woolley values, it provides a method for representing the Woolley values by an equation with a small number of terms.

At temperatures for which density measurements exist and for which thermodynamic properties are normally required for steam, changes in c_P/R with temperature are mainly attributable to changes in vibrational contributions represented by the equation of the simple harmonic oscillator. The equation considered here is a summation of simple harmonic oscillator functions:

$$\frac{c_P}{R} = b_0 + \sum_{i=1}^{5} b_i \frac{x_i^2 \exp(-x_i)}{(1-\exp(-x_i))^2} \tag{1}$$

where $x_i = \beta_i/T$.

Coefficients b_i for i from 0 to 5 and β_i for i from 1 to 5 have been determined by nonlinear least-squares fitting to the values of Woolley. The range of fitting was restricted to values of T from 130 to 2000 K so that a good fit could be obtained over this temperature range with a small number of terms. The decision on the upper limit was assisted by Woolley indicating that his c_P/R values "should be considered to be of satisfactory reliability up to 2000 K." The number of data points used was 56 and included 8 at temperatures below 250 K from Table I given by Woolley for light isotopic water, which are identical, where given, at temperatures up to 250 K to those of the natural isotopic mixture in his Table II, from which

Table I. Coefficients for Equations (1)–(3)

i	β_i (K)	b_i
−2		0.134865
−1		−5.005143 K
0		4.00632
1	833	0.012436
2	2289	0.97315
3	5009	1.2795
4	5982	0.96956
5	17800	0.24873

the remaining points were obtained. For simplicity, integer values of β_i were used. A process of refitting to reduce the number of significant figures in the coefficients b_i to six or less was applied. The values of the final coefficients are given in Table I.

From Eq. (1), the dimensionless ideal-gas enthalpy h/RT is given by

$$\frac{h}{RT} = \frac{b_{-1}}{T} + b_0 + \sum_{i=1}^{5} b_i \frac{x_i \exp(-x_i)}{1 - \exp(-x_i)} \tag{2}$$

and the dimensionless ideal-gas Gibbs function, g/RT, by

$$\frac{g}{RT} = \ln\left(\frac{P}{P_0}\right) + b_{-2} + \frac{b_{-1}}{T} + b_0(1 - \ln(T)) + \sum_{i=1}^{5} b_i \ln(1 - \exp(-x_i)) \tag{3}$$

where P_0 is an arbitrary reference pressure. The arbitrary constants b_{-1} and b_{-2} result from integration when Eqs. (2) and (3) are obtained from Eq. (1). The values of b_{-1} and b_{-2} given in Table I have been determined so that Eqs. (2) and (3) give the same values of h/RT and g/RT, respectively, as the equation of Woolley, as used by Haar et al. [4], at a temperature of 273.16 K and pressure $P = P_0$.

3. COMPARISON WITH DATA AND OTHER EQUATIONS

In Tables II and III and Figs. 1 and 2, the c_P/R values of Woolley are compared with the equations of Woolley, Pollak, Eq. (1), and Eq. (1) with

Table II. Ideal-Gas c_P/R Data and Comparison of Data with Values from the Equations

T (K)	c_P/R data[a]	Deviation, c_P/R (data) minus c_P/R (equation): Pollak equation	Woolley equation	Eq. (1)	Eq. (1) (term $i = 5$ omitted)
10.00	2.95227[b]	− 9.34508	1869.21485	− 1.05405	− 1.05405
20.00	3.43043[b]	− 4.38072	142.43593	− 0.57589	− 0.57589
30.00	3.68197[b]	− 2.64392	23.65799	− 0.32435	− 0.32435
40.00	3.82947[b]	− 1.76139	4.83815	− 0.17685	− 0.17685
50.00	3.91803	− 1.23791	0.85051	− 0.08829	− 0.08829
60.00	3.96553[b]	− 0.90553	− 0.04039	− 0.04079	− 0.04079
70.00	3.98847	− 0.68346	− 0.18932	− 0.01786	− 0.01786
80.00	3.99878[b]	− 0.52762	− 0.16435	− 0.00758	− 0.00758
90.00	4.00323[b]	− 0.41337	− 0.11225	− 0.00319	− 0.00319
100.00	4.00517	− 0.32665	− 0.06856	− 0.00136	− 0.00136
110.00	4.00611[b]	− 0.25913	− 0.03852	− 0.00058	− 0.00058
120.00	4.00667	− 0.20564	− 0.01981	− 0.00023	− 0.00023
130.00	4.00709[b]	− 0.16279	− 0.00901	− 0.00008	− 0.00008
140.00	4.00749[b]	− 0.12822	− 0.00325	− 0.00000	− 0.00000
150.00	4.00790	− 0.10025	− 0.00051	0.00003	0.00003
160.00	4.00835	− 0.07761	0.00056	0.00004	0.00004
170.00	4.00887	− 0.05933	0.00079	0.00004	0.00004
180.00	4.00948[b]	− 0.04466	0.00064	0.00003	0.00003
190.00	4.01022[b]	− 0.03297	0.00038	0.00002	0.00002
200.00	4.01114	− 0.02374	0.00014	− 0.00000	− 0.00000
210.00	4.01230[b]	− 0.01655	− 0.00002	− 0.00000	− 0.00000
220.00	4.01373	− 0.01106	− 0.00012	− 0.00001	− 0.00001
230.00	4.01549[b]	− 0.00695	− 0.00015	− 0.00003	− 0.00003
240.00	4.01763[b]	− 0.00396	− 0.00014	− 0.00004	− 0.00004
250.00	4.02022	− 0.00185	− 0.00009	− 0.00002	− 0.00002
270.00	4.02682	0.00040	0.00001	− 0.00000	− 0.00000
273.15	4.02803	0.00056	0.00000	− 0.00002	− 0.00002
273.16	4.02803	0.00056	− 0.00000	− 0.00002	− 0.00002
298.15	4.03966	0.00092	0.00004	− 0.00001	− 0.00001
300.00	4.04068	0.00091	0.00007	0.00001	0.00001
320.00	4.05268	0.00043	0.00004	0.00001	0.00001
350.00	4.07473	− 0.00043	− 0.00002	0.00002	0.00002
370.00	4.09189	− 0.00084	− 0.00006	0.00002	0.00002
400.00	4.12085	− 0.00100	− 0.00007	0.00002	0.00002
420.00	4.14198	− 0.00086	− 0.00005	0.00002	0.00002
450.00	4.17588	− 0.00039	− 0.00001	0.00002	0.00002
470.00	4.19967	− 0.00002	0.00001	0.00000	0.00000
500.00	4.23680	0.00053	0.00006	0.00001	0.00001
550.00	4.30153	0.00107	0.00006	− 0.00001	− 0.00001
600.00	4.36891	0.00104	0.00001	− 0.00002	− 0.00002
650.00	4.43839	0.00056	− 0.00004	− 0.00001	− 0.00001
700.00	4.50970	− 0.00010	− 0.00006	− 0.00002	− 0.00002
750.00	4.58269	− 0.00065	− 0.00005	− 0.00001	− 0.00001

Table II. continued.

T (K)	c_P/R data[a]	Deviation, c_P/R (data) minus c_P/R (equation): Pollak equation	Woolley equation	Eq. (1)	Eq. (1) (term $i = 5$ omitted)
800.00	4.65716	−0.00094	−0.00001	−0.00000	−0.00000
850.00	4.73283	−0.00092	0.00002	0.00000	0.00000
900.00	4.80936	−0.00062	0.00004	0.00001	0.00001
950.00	4.88636	−0.00015	0.00004	0.00002	0.00002
1000.00	4.96339	0.00034	0.00002	0.00002	0.00002
1050.00	5.04004	0.00072	−0.00001	0.00001	0.00001
1100.00	5.11594	0.00091	−0.00003	0.00000	0.00001
1150.00	5.19073	0.00086	−0.00002	−0.00000	0.00001
1200.00	5.26410	0.00054	−0.00001	−0.00001	0.00001
1250.00	5.33580	0.00004	0.00001	−0.00002	0.00001
1300.00	5.40564	−0.00051	0.00005	−0.00001	0.00004
1350.00	5.47344	−0.00094	0.00006	−0.00001	0.00007
1400.00	5.53910	−0.00099	0.00006	0.00000	0.00012
1450.00	5.60252	−0.00040	0.00002	0.00000	0.00018
1500.00	5.66368	0.00122	−0.00003	0.00001	0.00026
1550.00	5.72255	0.00424	−0.00009	0.00001	0.00035
1600.00	5.77914	0.00909	−0.00013	0.00001	0.00047
1650.00	5.83348	0.01624	−0.00014	0.00001	0.00061
1700.00	5.88561	0.02618	−0.00012	0.00001	0.00078
1750.00	5.93559	0.03946	−0.00005	0.00001	0.00099
1800.00	5.98346	0.05659	0.00001	−0.00001	0.00122
1850.00	6.02933	0.07820	0.00008	−0.00002	0.00151
1900.00	6.07326	0.10488	0.00011	−0.00002	0.00185
1950.00	6.11533	0.13725	0.00004	−0.00001	0.00224
2000.00	6.15563	0.17595	−0.00017	0.00002	0.00271
2500.00	6.47950	1.06605	0.00137	0.00295	0.01316
3000.00	6.70860	3.42255	−0.00951	0.01647	0.03979
3500.00	6.92450	8.18552	0.04684	0.08015	0.12044
4000.00	7.05240	16.32048	−0.18064	0.09574	0.15463

[a]From Woolley [1], Table 2.
[b]From Woolley [1], Table 1.

the final term, $i = 5$, omitted. The coefficients used here for the Woolley equation are those given by Haar et al. [4]. It may also be noted that this results in deviations of c_P/R from the data which are different from those listed by Woolley for temperatures greater than 1500 K. Pollak, as part of an $f = f(\rho, T)$ equation for steam, gives a polynomial in temperature for the dimensionless ideal-gas isochoric heat capacity. The coefficients for this equation were redetermined by fitting to the values of Woolley over a temperature range similar to that used by Pollak.

Table III. Root-Mean-Square Deviations from Woolley Data

Temperature range	Root-mean-square deviation		
T(min) T(max) (K) (K)	Woolley equation	Eq. (1)	Eq. (1) (term $i = 5$ omitted)
270–1300	0.000 038 4	0.000 014 4	0.000 015 6
270–2000	0.000 061 3	0.000 013 7	
200–2000	0.000 070 9	0.000 014 7	
140–2000	0.000 477 6	0.000 017 1	

It is evident from Fig. 1 that the polynomial equations deviate from the data outside the range of the fit. In the case of the equation of Woolley, large deviations occur at low temperatures (50 to 150 K) and high temperatures (3000 to 4000 K, from a smooth line through the widely spaced data points), possibly within the range of temperatures used in his fit.

Equation (1) gives a good representation of the Woolley values of c_P/R over the range of temperature used in the fit. In Table II, the deviations from the data are given. For the temperature range 250 to 2000 K, the deviations of c_P/R are 2×10^{-5} or less and from 140 to 240 K do not exceed 4×10^{-5}. As T tends to zero, c_P/R from Eq. (1) tends to b_0 so

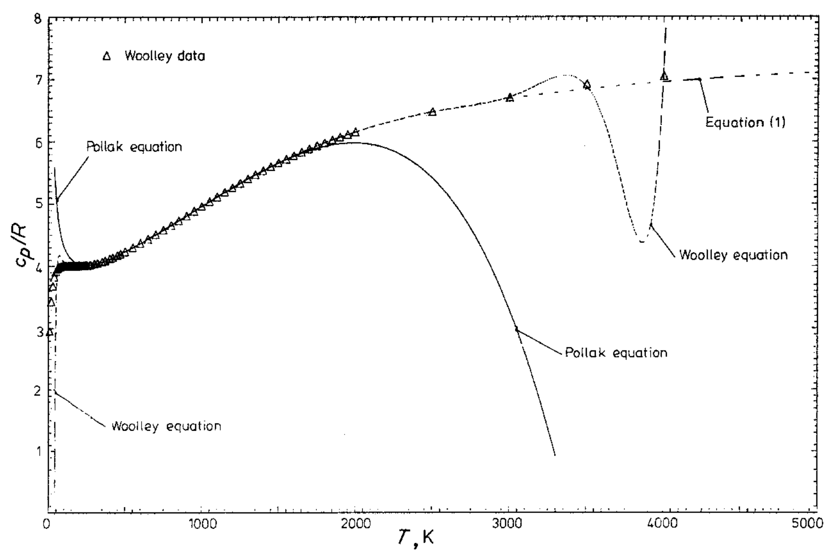

Fig. 1. Dimensionless isobaric heat capacity, c_P/R, Woolley data, equations of Pollak and Woolley, and Eq. (1) vs temperature T.

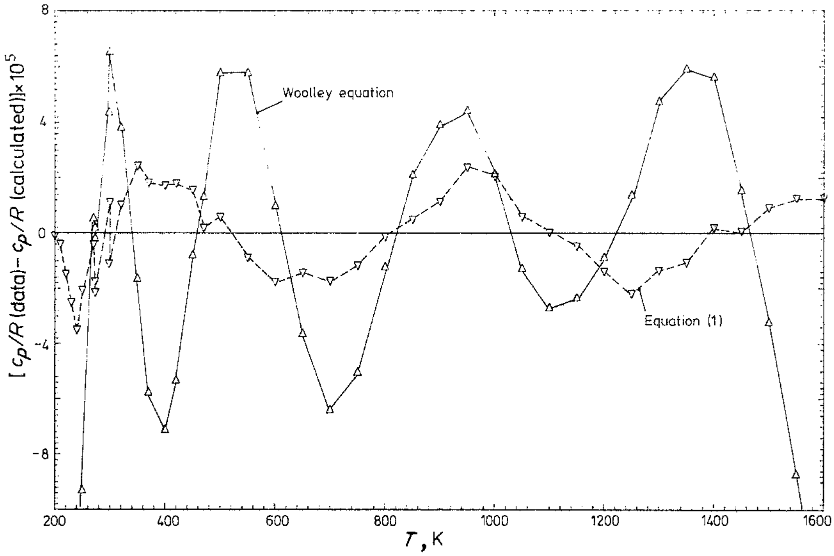

Fig. 2. Deviation of c_P/R, Woolley data minus values calculated from the Woolley equation and Eq. (1) vs temperature T.

that at temperatures less than 120 K deviations become relatively large. This results from the fact that no attempt was made to use data at temperatures below 130 K or impose a lower value of b_0 in the fit. Including the data at temperatures below 130 K was detrimental to the fit at higher temperatures with the number of terms used. Inclusion of an additional term, involving two more constants, could have resulted in better representation for $T < 130$ K, but it was considered that the additional complication was not justified for these low temperatures, which are of little practical importance. Extrapolation to high temperatures (2000 to 4000 K) is reasonable. Again, as indicated earlier, to maintain goodness of fit over the "practical temperature range," data in this temperature range was not used. It should be noted that the omission of the final term ($i = 5$) from Eq. (1) has no effect on the fifth decimal place of c_P/R at temperatures below 1100 K, as will be seen by comparing the last two columns of Table II. Thus for some purposes, this simplification might be made. Figure 2 and Table III emphasize the very good agreement of Eq. (1) with the Woolley values.

Values of dimensionless isobaric heat capacity, enthalpy, and Gibbs function obtained from Eqs. (1)–(3) are given in Table IV, together with deviations from these of values obtained from the Woolley equation. Close agreement is evident over the temperature range $T = 200$ to 2000 K.

Table IV. Ideal-Gas Properties from Eqs. (1)–(3) and Comparison with Values from the Equation of Woolley

T	c_P/R	$\Delta(c_P/R)^a$	h/RT	$\Delta(h/RT)^a$	g_0/RT	$\Delta(g_0/RT)^a$
50	4.00632	0.93880	3.90622	0.04969	− 11.63173	0.04308
100	4.00653	− 0.06720	3.95629	0.00989	− 14.35865	0.00097
150	4.00787	− 0.00054	3.97322	− 0.00012	− 15.96644	− 0.00001
200	4.01114	0.00014	3.98223	0.00002	− 17.11080	0.00000
250	4.02024	− 0.00007	3.98878	0.00000	− 18.00013	0.00000
300	4.04067	0.00005	3.99554	0.00000	− 18.72795	− 0.00000
400	4.12083	− 0.00009	4.01584	− 0.00000	− 19.87990	− 0.00000
500	4.23679	0.00005	4.04804	− 0.00001	− 20.77925	0.00000
600	4.36893	0.00003	4.09036	0.00000	− 21.52091	0.00000
700	4.50972	− 0.00005	4.14012	0.00000	− 22.15509	0.00000
800	4.65716	− 0.00001	4.19548	− 0.00000	− 22.71149	0.00000
900	4.80935	0.00003	4.25520	− 0.00000	− 23.20906	0.00000
1000	4.96337	0.00000	4.31831	− 0.00000	− 23.66063	0.00000
1100	5.11594	− 0.00003	4.38391	− 0.00000	− 24.07527	0.00000
1200	5.26411	0.00001	4.45113	− 0.00000	− 24.45959	0.00000
1300	5.40565	0.00006	4.51916	0.00000	− 24.81855	0.00000
1400	5.53910	0.00005	4.58730	0.00000	− 25.15595	0.00000
1500	5.66367	− 0.00004	4.65495	0.00001	− 25.47476	0.00000
1600	5.77913	− 0.00014	4.72165	− 0.00000	− 25.77732	0.00000
1700	5.88560	− 0.00013	4.78703	− 0.00001	− 26.06553	0.00000
1800	5.98347	0.00002	4.85082	− 0.00001	− 26.34097	0.00000
1900	6.07328	0.00012	4.91283	− 0.00001	− 26.60491	0.00000
2000	6.15561	− 0.00019	4.97294	− 0.00001	− 26.85844	0.00000
2100	6.23110	− 0.00123	5.03108	− 0.00004	− 27.10248	0.00000
2200	6.30038	− 0.00290	5.08723	− 0.00013	− 27.33783	0.00001
2300	6.36402	− 0.00446	5.14137	− 0.00028	− 27.56517	0.00002
2400	6.42257	− 0.00452	5.19355	− 0.00047	− 27.78510	0.00003
2500	6.47655	− 0.00158	5.24381	− 0.00058	− 27.99813	0.00005
2600	6.52640	0.00484	5.29219	− 0.00051	− 28.20475	0.00008
2700	6.57254	0.01282	5.33877	− 0.00016	− 28.40535	0.00009
2800	6.61533	0.01674	5.38361	0.00040	− 28.60033	0.00009
2900	6.65510	0.00734	5.42677	0.00085	− 28.79000	0.00006
3000	6.69213	− 0.02598	5.46834	0.00059	− 28.97469	0.00004
3100	6.72669	− 0.08933	5.50838	− 0.00121	− 29.15465	0.00004
3200	6.75900	− 0.17462	5.54697	− 0.00526	− 29.33015	0.00014
3300	6.78926	− 0.24733	5.58416	− 0.01160	− 29.50141	0.00039
3400	6.81766	− 0.23602	5.62002	− 0.01869	− 29.66865	0.00084
3500	6.84435	− 0.03332	5.65463	− 0.02261	− 29.83206	0.00146
3600	6.86947	0.47428	5.68803	− 0.01666	− 29.99183	0.00204
3700	6.89315	1.31906	5.72028	0.00737	− 30.14811	0.00222
3800	6.91551	2.26236	5.75144	0.05468	− 30.30108	0.00145
3900	6.93665	2.43648	5.78157	0.11678	− 30.45087	− 0.00077
4000	6.95666	− 0.27638	5.81069	0.15032	− 30.59761	− 0.00429
4100	6.97562	− 10.25910	5.83888	0.03951	− 30.74144	− 0.00713
4500	7.04237	− 403.83873	5.94299	− 11.38721	− 31.28986	0.27168
5000	7.10942	− 6354.75536	6.05641	− 241.21563	− 31.92204	8.72552

[a]Value from Eq. (1), (2), or (3) minus value from Woolley equation. $g_0 = g$ at $P = P_0$.

4. CONCLUSIONS

The equation reproduces accurately the c_P/R values of Woolley for the temperature range 130 to 2000 K, extrapolates sensibly outside this temperature range, and has a relatively small number of terms.

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