elements we have used 1.36,[6] 31.23, 45.78, 49.03, and 7.6 E. U.[7] per mole, respectively, for carbon, hydrogen, nitrogen, oxygen and sulfur. With the exception for carbon and sulfur, the values are the same as in our first paper.[1]

Except in the case of β-thiolactic acid, we believe the error involved in the $T\Delta S$ term does not exceed ±300 calories. In this particular case this uncertainty is increased to ±450 calories. The absolute accuracy of the free energies of these compounds is still restricted by uncertainties in the combustion values and the heats of formation of the auxiliary substances used. Rossini[8] has recently pointed out that the accepted value for the heat of formation of carbon dioxide is uncertain to the extent of 100 calories. This alone would introduce an uncertainty of 1200 calories in the free energy of the largest molecules we have considered. Fortunately, for intercomparison, uncertainties of this type will tend to cancel.

Summary

1. The heat capacities of four sulfur containing organic compounds have been measured over the temperature range 90 to 298° K.
2. The entropies of these four compounds have been calculated from the heat capacity data.
3. The standard free energies of formation of these compounds have been calculated.

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[6] Jacobs and Parks, THIS JOURNAL, **56**, 1513 (1934).

[7] Kelley, *Bur. Mines, Bull.*, No. 350, p. 59, 1932.

[8] Rossini, *Bur. Standards J. Research*, **13**, 21 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF ENGINEERING RESEARCH, UNIVERSITY OF MICHIGAN]

A New Approximate Equation for Heat Capacities at High Temperatures

BY JOHN CHIPMAN AND M. G. FONTANA

The classical form of expression for the heat capacity of a substance at elevated temperature is

$$C_p = a + bT + cT^2 + dT^3 + \dots \qquad (1)$$

The failure of equations of this type to represent actual heat content data has been pointed out by Maier and Kelley,[1] who proposed the expression

$$C_p = a + bT - cT^{-2} \qquad (2)$$

This same equation has been arrived at from theoretical considerations by Bronson, Chisholm and Dockerty,[2] who have shown that it is applicable to certain metals in the range 0 to 500°.

For purposes of practical thermodynamic calculations it is desirable to limit the number of terms to three and from this viewpoint each of the above expressions may be regarded as a special case of a more general formula

$$C_p = a + bT + cT^n \qquad (3)$$

The success of this expression in reproducing experimental data depends upon the value of n employed. It is desirable that a single value of n be selected which will be applicable, at least approximately, to a wide variety of substances and it is essential that the equation be readily integrated for expressing heat content and free energy.

If we consider the best available data on the heat capacities of solid substances at temperatures ranging from 0° upward, we find a marked curvature in the lower ranges and a nearly linear relationship at the higher temperatures. Values of n greater than unity are incompatible with this experimental fact. On the other hand, Equation 2 is in many instances far too strongly curved at the lower temperatures to afford an accurate representation of the data.

A comparison of equations employing values of n of $^1/_2$, $-^1/_2$, -1, and -2 has indicated that for the majority of substances for which accurate data are available an expression in which $n = -^1/_2$ conforms most closely to the experimental points. Accordingly we propose the equation

$$C_p = a + bT + cT^{-1/2} \qquad (4)$$

and the corresponding expressions for heat content and free energy

$$H = H_0 + aT + {}^1/_2bT^2 + 2cT^{1/2} \qquad (5)$$

$$F = H_0 - aT \ln T - {}^1/_2bT^2 + 4cT^{1/2} + IT \qquad (6)$$

Some of the data which were used in arriving at the selected value of n are discussed below with special reference to the choice between Equations 2 and 4. Among the most accurate of all high temperature data are those of W. P. White[3]

[1] Maier and Kelley, THIS JOURNAL, **54**, 3243 (1932).

[2] Bronson, Chisholm and Dockerty, *Can. J. Research*, **8**, 282 (1933).

[3] White, *Am. J. Sci.*, [4] **28**, 334 (1909); **47**, 1 (1919).

on a number of silicates. In Table I the second column gives White's determinations of the total heat content of pseudowallastonite. Using the data at 700 and 1400° and Parks and Kelley's[4] heat capacity of 20.06 cal. per degree per mole at 0°, Maier and Kelley devised the following equation which is represented in the third column of the table.

$$H - H_{273.1} = 25.48T + 2.066 \times 10^{-3}T^2 + 4.881 \times 10^5T^{-1} - 8900 \quad (7)$$

TABLE I

HEAT CONTENT OF CALCIUM SILICATE ABOVE 0°

Temp., °C.	White's data	Calcd. Eq. 7	Diff., %	Calcd., Eq. 8	Diff., %
100	2140	2200	+2.8	2165	+1.2
300	7125	7230	+1.5	7124	0.0
500	12600	12660	+0.5	12590	− .1
700	18350	18350	.0	18350	.0
900	24290	24250	− .16	24320	+ .13
1100	30390	30340	− .16	30430	+ .13
1300	36630	36610	− .06	36660	+ .08
1400	39800	39800	.0	39800	.0

An equation of the type of 5 based upon the same three points is given below and its solution gives the fifth column of the table. The comparison indicates that Equation 8 fits the data better than Equation 7, particularly at the lower temperatures.

$$H - H_{273.1} = 40.98T - 0.31 \times 10^{-3}T^2 - 686T^{1/2} + 168 \quad (8)$$

The heat content of graphite at elevated temperatures is known with considerable accuracy from the determinations of Magnus[5] and of Schläpfer and Debrunner[6] which are in very close agreement. The experimental data of the latter are quoted in Table II along with the first and last points of the former which serve to illustrate the agreement between the two sets of data. The heat contents calculated from the two following equations are shown in the third and fifth columns. The first of these two equations is due to Kelley.[7] The second is of the form of Equation 4 and appears to fit the data much more perfectly.

$$\beta\text{-Graphite:}\quad C_p = 2.673 + 2.617 \times 10^{-3}T - 1.169 \times 10^5T^{-2} \quad (9)$$

$$\beta\text{-Graphite:}\quad C_p = 9.62 - 0.44 \times 10^{-3}T - 130T^{-1/2} \quad (10)$$

Not only does Equation 10 fit the experimental data of Table II more precisely than does Equation 9, but its extrapolation to higher temperatures is more nearly in accord with the direct determinations of Worthing.[8] In Fig. 1, the solid line represents, with an average deviation of less than 0.05 calorie per degree, the atomic heat capacity of graphite computed from the calorimetric data by the investigators cited above. The broken line represents Worthing's experimental data; the points are calculated from Equations 9 and 10 and from an equation of the form of (1) proposed by Eastman.[9] It is evident that the extrapolation of this last equation and of Equation 9 beyond the range for which each was

TABLE II

HEAT CONTENT OF BETA GRAPHITE ABOVE 0°

Temp., °C.	Obsd.	Calcd., Eq. 9	Diff., %	Calcd., Eq. 10	Diff., %
98.4	218	232	+6.4	219	+0.5
99.0	222[a]	234	+5.4	221	−0.5
326	993	1011	+1.8	1006	+1.2
332	1023	1034	+1.1	1022	−0.1
457	1567	1554	−0.8	1576	+ .6
700	2735	2705	−1.1	2728	− .3
816	3321	3315	−0.2	3322	.0
887	3687	3707	+ .5	3694	+ .2
900.2	3775[a]	3782	+ .2	3764	− .2
902	3768	3792	+ .6	3773	+ .1
905	3786	3809	+ .6	3791	+ .1
1100	4829	4967	+2.8	4845	+ .3

[a] Data of Magnus.

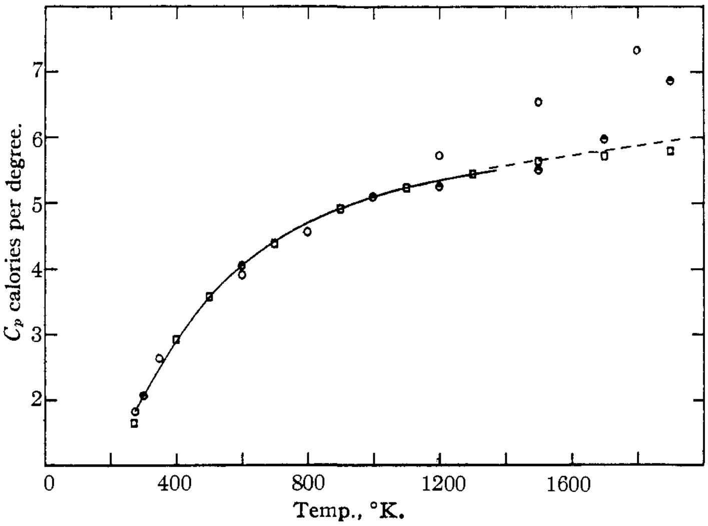

Fig. 1.—Heat capacity of graphite: ○, Eq. 9. □, Eq. 10. ●, Cubic equation. Solid and broken lines, experimental data.

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(4) Parks and Kelley, *J. Phys. Chem.*, **30**, 1175 (1926).

(5) Magnus, *Ann. Physik*, [4] **70**, 303 (1923).

(6) Schläpfer and Debrunner, *Helv. Chim. Acta*, **7**, 31 (1924).

(7) Kelley, "High-Temperature Specific-Heat Equations for Inorganic Substances," *Bur. Mines, Bull.*, 371 (1934).

(8) Worthing, *Phys. Rev.*, **12**, 199 (1918).

(9) Eastman, *Bur. Mines, Circular*, 6125 (1929).

intended (1600 and 1375°K., respectively) is not at all trustworthy. On the other hand, extrapolation of Equation 10 leads to results which are in good agreement with Worthing's data.

The heat content of magnesia has been studied by Wilkes[10] up to very high temperatures. His results were employed by Kelley[7] in his compilation of heat content data and are reproduced in the second column of Table III. The data may be represented by Equations 11 and 12, the first of which is due to Kelley while the second is of the form of Equation 4. The deviations from the observed data shown in Table III are considerably smaller in the case of Equation 12.

TABLE III

HEAT CONTENT OF MAGNESIA ABOVE 0°

Temp., °C.	Obsd.	Calcd., Eq. 11	Diff., %	Calcd., Eq. 12	Diff., %
100	920	920	0.0	902	−2.0
200	1900	1938	+2.0	1897	−0.2
300	2950	3010	+2.0	2952	+ .1
400	4030	4116	+2.1	4053	+ .6
600	6330	6403	+1.1	6356	+ .4
800	8730	8764	+0.4	8747	+ .2
1000	11200	11190	− .1	11200	.0
1200	13700	13660	− .3	13700	.0
1500	17510	17480	− .2	17500	− .1
1600	18780	18780	.0	18780	.0
1800	21280	21410	+ .6	21350	+ .3

TABLE IV

HEAT CAPACITY OF HYDROGEN, AND CARBON MONOXIDE, AND CARBON DIOXIDE

	Hydrogen			Carbon monoxide			Carbon dioxide		
T, °K.	Spectr.	Eq. 13	Diff.	Spectr.	Eq. 14	Diff.	Spectr.	Eq. 15	Diff.
300	6.90	6.94	+0.04	6.96	6.81	−0.15	8.91	8.73	−0.18
400	6.97	6.93	− .04	7.01	7.04	+ .03	9.89	9.95	+ .06
500	6.99	6.95	− .04	7.12	7.22	+ .10	10.68	10.79	+ .11
600	7.01	7.00	− .01	7.28	7.37	+ .09	11.32	11.43	+ .11
700	7.03	7.05	+ .02	7.45	7.50	+ .05	11.86	11.91	+ .05
800	7.08	7.12	+ .04	7.63	7.62	− .01	12.31	12.31	.00
900	7.14	7.20	+ .06	7.79	7.74	− .05	12.69	12.66	− .03
1000	7.22	7.27	+ .05	7.94	7.85	− .09	13.01	12.93	− .08
1200	7.41	7.44	+ .03	..	..	....	13.50	13.41	− .09
1300	..	..	....	8.27	8.15	− .12	...	...	....
1500	7.72	7.71	− .01	8.42	8.33	− .09	14.00	13.94	− .06
1750	7.96	7.94	− .02	8.56	8.56	.00	14.3	14.30	.00
2000	8.18	8.17	− .01	8.67	8.77	+ .10	14.5	14.58	+ .08

$$\text{MgO:}\quad C_p = 10.86 + 1.197 \times 10^{-3}T - 2.087 \times 10^{5}T^{-2} \qquad (11)$$

$$\text{MgO:}\quad C_p = 16.68 - 0.40 \times 10^{-3}T - 135T^{-1/2} \qquad (12)$$

In setting up heat capacity equations for use in thermodynamic computations, it is convenient to employ a form which is capable of representing the heat capacity of gases as well as that of solids. For this purpose and in the range 298–2000°K., the time-honored power series of Equation 1 is superior to the Maier–Kelley expression. Although no simple algebraic expression is adequate for gaseous specific heats, Equation 4 can be applied to limited temperature ranges without unduly large errors. The following expressions for hydrogen, carbon monoxide and carbon dioxide are based upon the data of Johnston and Davis,[11] and of Kassel.[12]

$$H_2\text{:}\quad C_p = 5.76 + 1.04 \times 10^{-3}T + 15T^{-1/2} \qquad (13)$$

$$\text{CO:}\quad C_p = 7.74 + 0.74 \times 10^{-3}T - 20T^{-1/2} \qquad (14)$$

$$CO_2\text{:}\quad C_p = 17.67 + 0.20 \times 10^{-3}T - 156T^{-1/2} \qquad (15)$$

The heat capacities calculated from these expressions are compared with the spectroscopic values in Table IV. The magnitude of the errors involved in the use of these equations may be estimated by using them to compute the free energy of each gas at higher temperatures from the values at 298.1°K. and comparing with the spectroscopic data. For hydrogen and carbon monoxide a comparison with the data of Giauque and his co-workers[13] is shown in Table V. The deviations in all cases are below 0.01 calorie per

TABLE V

VALUES OF $-(F° - E_0°)/T$ FOR HYDROGEN AND CARBON MONOXIDE

	Hydrogen			Carbon monoxide		
T, °K.	Spectr.	Calcd.	Diff.	Spectr.	Calcd.	Diff.
298.1	27.191	27.191	0.000	40.364	40.364	0.000
400	29.193	29.194	+ .001	42.408	42.406	− .002
500	30.720	30.719	− .001	43.963	43.960	− .003
750	33.512	33.505	− .007	46.813	46.816	+ .003
1000	35.507	35.499	− .008	48.876	48.884	+ .008
1250	37.069	37.063	− .006	50.513	50.520	+ .007
1500	38.360	38.358	− .002	51.880	51.884	+ .004
2000	40.440	40.439	− .001	54.095	54.090	− .005
2500	42.100	42.100	.000	55.860	55.855	− .005

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(10) Wilkes, *J. Am. Ceram. Soc.*, **15**, 72 (1931).

(11) (a) Johnston and Davis, THIS JOURNAL, **56**, 271 (1934). (b) Davis and Johnston, *ibid.*, **56**, 1045 (1934).

(12) Kassel, *ibid.*, **56**, 1838 (1934).

(13) (a) Giauque, *ibid.*, **52**, 4816 (1930); (b) Clayton and Giauque, *ibid.*, **54**, 2610 (1932); correction, **55**, 5071 (1933).

degree in the values of $(F^\circ - E_0^\circ)/T$, which is ample accuracy for most practical thermodynamic purposes.

Summary

The following form of expression is proposed for the approximate representation of heat capacities of solids and gases at high temperatures

$$C_p = a + bT + cT^{-1/2}$$

It is shown that for several typical substances for which accurate data are available, the heat capacity, heat content, and free energy may be represented with sufficient accuracy for thermodynamic computations by this expression and its integrated forms.

ANN ARBOR, MICH. RECEIVED OCTOBER 24, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Kinetic Salt Effect in the Fourth Order Reaction $BrO_3^- + Br^- + 2H^+ \longrightarrow$. Ionization Quotients for HSO_4^- at 25°

BY WILLIAM C. BRAY AND HERMAN A. LIEBHAFSKY

In the present investigation of the rate law, $-d(BrO_3^-)/dt = k(BrO_3^-)(Br^-)(H^+)^2$, initial rates of the reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \quad (I)$$

have been measured at 25°, and in the presence of added perchlorate, in order to obtain values of k that may be compared directly with those obtained by Young and Bray[1] in their study of the reaction

$$BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + 3H_2O \quad (II)$$

in perchloric acid solutions. One of the reasons for undertaking this work was to determine whether, at low ionic strength, the specific rate, k, increases rapidly in the manner required by the conclusions of Young and Bray. It also seemed desirable to re-examine the earlier results in sulfate solutions of Skrabal and Weberitsch[2] (Reaction I) and of Bray and Davis[3] (Reaction II), and to analyze them by a method which distinguishes between the change of k due to the presence of HSO_4^- and that due to variation in ionic strength.

In each experiment all the bromine liberated in the time allowed was determined iodimetrically in the reaction flask by means of an accurately standardized 0.02 M sodium thiosulfate solution. The reaction, I, was stopped by adding a solution which contained the necessary amount of phosphate buffer and a large excess of potassium iodide. This method of determining bromine in the presence of bromate is not new, and the precautions necessary for accurate iodimetric analysis need not be described in detail.

The volume of each mixture was usually 250 cc. and was smaller only when the concentrations of the reacting substances were rather high. The flasks used had closely fitting glass stoppers, which were sealed with paraffin in the long-time experiments with very dilute solutions. The gas space above the solution was not large. The stock solutions of sodium bromate, hydrobromic acid, sodium bromide and magnesium perchlorate and the distilled water were brought to the temperature of 25° before mixing. The perchlorate solution was prepared by neutralizing a measured quantity of very concentrated perchloric acid solution with magnesium oxide, diluting to a definite volume, and adjusting the concentration of hydrogen ion to a value equal to or slightly greater than 10^{-7} molal.

With the above procedure it was possible to determine accurately the quantity of bromine liberated before the concentration of any reactant had decreased by a large percentage amount, and, therefore, to calculate k by means of the fourth order differential equation. Average rather than initial concentrations were used, and all concentrations were expressed as moles per liter. This "method of constant rates" has been discussed by a number of investigators,[4] and methods of obtaining exact values of k have been described by De Lury[4b] and by Skrabal and Weberitsch.[2] Since in our experiments the product of the initial concentrations never exceeded the product of the average concentrations by more than 10.5%, the error in k due to our method of calculation never

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[1] Young and Bray, THIS JOURNAL, **54**, 4284 (1932).

[2] Skrabal and Weberitsch, *Monatsh.*, **36**, 211 (1915).

[3] Bray and Davis, THIS JOURNAL, **52**, 1427 (1930).

[4] See, for example, (a) Lash Miller and Bray, *J. Phys. Chem.*, **7**, 92 (1903); (b) De Lury, *ibid.*, **7**, 239 (1903); (c) **10**, 423 (1906); (d) Skrabal and Weberitsch, Ref. 2.