before it was only probable, that phosphorus and arsenic fit into the scheme of discussion given for silicon, germanium, and tin, all the elements showing the anticipated additivity of covalent radii when bonded to carbon, but exhibiting a characteristic shortening of radius when bonded to fluorine and chlorine. Brockway and Wall,[2] Brockway and Jenkins,[4] and Brockway[9] discussed this shortening in terms of double bond character pointing out that it is not due to the relative electronegativities or to the existence of dipole moments in the bonds, and eliminating the possibility that it is due to ionic character of the bonds. Gregg, Hampson, G. I. Jenkins, Jones and Sutton,[10] however, from a consideration of (a) series of halides of the same element and (b) series of compounds of the same halogen with different elements, point out that the case may be more complex.

We wish to express our gratitude to Professor L. Pauling for the interest which he has taken in this work, and to Dr. S. Weinbaum for assistance with the calculations.

Summary

By electron diffraction investigation of the gases, the structures of trimethylphosphine and trimethylarsine have been determined. The molecules are pyramidal with the phosphorus and arsenic atoms at the respective apices.

Trimethylphosphine has a bond angle of 100 ± 4° with the P–C bond = 1.87 ± 0.02 Å.; trimethylarsine has a bond angle of 96 ± 5° with the As–C bond = 1.98 ± 0.02 Å. These distances agree with the sums of the covalent radii given by Pauling and Huggins. From these results a firmer basis is obtained for the discussion of the bond shortening in the corresponding chlorides.

PASADENA, CALIF. RECEIVED JANUARY 25, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 395]

A Low Temperature Calorimeter. The Heat Capacity and Entropy of Thallium from 14 to 300°K. Low Temperature Studies. No. 3

BY J. F. G. HICKS, JR.[1]

A portion of the low temperature program in progress in this Laboratory has been devoted to the measurement of specific heats. This present paper is the first in this series of investigations.

The heat capacity of thallium has been measured by several previous investigators[2] and of this work the data of Clusius and Vaughen are the most complete. However, their method of measurement was not particularly well adapted to precision work above 150°K., and therefore in this region they report only three points. Although the change in heat capacity with temperature from 150 to 300°K. is small, the heat capacity is large and variations of 2% produce a significant effect upon the entropy at 298°K.

The calculations of Latimer, Schutz and Hicks[3] of the entropy of aqueous thallous ion indicated that the thermochemical data on thallium and its compounds were of unusual self-consistency. However, the entropy of thallous ion depended much upon the entropy of metallic thallium. Since that time a revised value of the entropy of thallous ion[4] derived from more recent heat of solution and e. m. f. data has appeared. The entropy of thallium as redetermined in the present work has been lowered by only 1%, which lowering does not produce a change larger than experimental error in the new value for thallous ion. It was felt, however, that the heat capacity data were of sufficient interest to justify presentation of a complete study over the temperature range 14 to 300°K.

Material.—The sample of thallium used in these measurements was obtained from the American Smelting and Refining Company, Denver, Colorado, and was not subjected to further purification. It was cast to fit the calorimeter by melting *in vacuo* in an iron mold and stored under water prior to loading. The ingots consisted of large (of millimeter size) crystals.

Qualitative analysis using standard methods failed to disclose the presence of other elements and photographs of the arc spectrum[5] set the upper limit of impurities (including indium and gallium) at one part in 10,000 of thallium.

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(1) National Research Council Fellow in Chemistry, 1933–1935. Paper II, THIS JOURNAL, **59**, 1962 (1937).

(2) Clusius and Vaughen, *ibid.*, **52**, 4686 (1930); see this paper for references to earlier work.

(3) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

(4) Brown, Smith and Latimer, THIS JOURNAL, **59**, 921 (1937).

(5) The author is indebted to Mr. P. A. Cole of the M. I. T. Physics Department for the spectroscopic examination.

Precipitation[6] as Tl_2PtCl_6 yielded 99.97 and 100.06% Tl and as TlI, 99.91% Tl. The density at 20.7° was 11.878 g./cc.

Weight of sample on loading 844.631 g. *in vacuo*
Weight of sample on unloading 844.682 g. *in vacuo*
Tl = 204.39, Sample = 4.1324 ± 0.0004 gram atoms

Apparatus.—The apparatus was similar to that used by Latimer and Greensfelder[7] with the following exceptions: the hydrogen liquefier was not built in and the calorimeter contained an internal resistance thermometer heater patterned after the design of Southard and Brickwedde.[8] The thermometer has the laboratory designation R197 and was compared directly with a helium gas thermometer.[9] A copper-constantan thermocouple was soldered to the outside of the calorimeter for use as a control.

Figure 1 is a diagram of the calorimeter proper. The outer wall of the calorimeter is a 0.2-mm. copper cylinder, 10 cm. long by 4 cm. in diameter, having a volume of 95 cc. The inner coaxial copper cylinder of 1-mm. wall and 1.3 cm. i. d. contains the separate unit R197 frozen into contact by means of stopcock grease. The telescoping copper tubes from which the core of the calorimeter and the case of R197 were made were polished carefully to a smooth, tight fit before fabrication of the separate units. This technique enables rapid assembly, convenience in checking the resistance thermometer at fixed temperature points in other apparatus, insurance against damage to the thermometer during loading and unloading of the calorimeter, and interchangeability of thermometer units.

The radial vanes in the calorimeter were made from specially drawn 0.2-mm. wall hard temper copper tubing. The 12 segments, each having a cross section of a 30° wedge cut by two concentric circles were soft-soldered to each other and to the inner and outer cylinders comprising the calorimeter walls. The external surfaces of the vane tubing and the internal surfaces of the calorimeter barrel were tinned and the vanes inserted in the barrel while the whole assembly was kept above the melting point of solder. Excess solder squeezed out by this process was readily wiped off. A reëntrant, removable top of 0.2 mm. thick monel metal provided easy access to the body of the calorimeter and at the same time enabled the top to be sealed to the body with soft solder while the contents of the calorimeter could be kept cool. The portions of the calorimeter body above the radial vanes and which received the removable top were made of monel and were joined to the copper barrel by means of silver solder. The outside surface was gold plated. Since the thermal conductivity of the calorimeter contents is usually low compared with that of the calorimeter itself, the substitution of the poorer conducting monel for copper does not affect the rate of attainment of the steady thermal states.

The empty calorimeter as calibrated weighed 339.56 g. Other calorimeters used in this type of work[7] have weighed about 80 g. The present method of attaching the thermometer unit requires a more rugged construction than otherwise, but a lighter construction could have been used.

Discussion of Procedure.—Data were taken in the usual manner and corrections for non-adiabatic conditions taken into account.[10] The difference in heat input arising from the rapidly changing resistance when the current was switched on was about 0.3% for the maximum current used.

Above 200°K., where radiation becomes an important factor in energy transfer, it is necessary to know the surface temperature of the calorimeter. Usually it is not convenient (with internal heater-thermometer) to measure the surface temperature for each specific heat run. In these cases the surface temperature is assumed to be given by linear interpolation between the end-points of the heating interval. In order to show that the surface temperature may be obtained with sufficient accuracy by this method, the calorimeter containing naphthalene was heated while the temperature of the surface was measured by means of the attached thermocouple. The results for three typical high temperature runs are shown in Fig. 2. The steep straight line confined by arrows is determined by the drift curves and the end-points of the heating interval; the circles are experimental points. The area included between the circles and the solid line is proportional to the correction which must be applied to the heat input to take into account non-linear heating of the surface. In the most unfavorable case (300°K. and 0.11 amp.) this area amounted to 1.5 degree minutes and led to a correction to the heat of 0.1%. Other corrections were treated according to the method of Gibson and Giauque.[10]

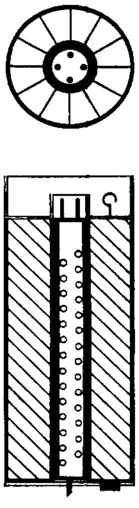

Fig. 1.—Calorimeter showing vanes, removable top and resistance thermometer-heater.

In any system where heat is flowing, temperature gradients must be present. The observer is interested in the "mean spacial" temperature of the calorimeter and contents and it is evident that the thermometer reading will be precisely that only when no heat is flowing. Therefore, in a non-adiabatic method a possible source of error in measuring the temperature interval is the heat leak along the thermometer lead wires. This heat leak produces a thermometer reading which does not indicate the mean temperature of the calorimeter and contents; an effect which produces too small a temperature rise and consequently heat capacities which are too large. The magnitude of this error was measured with carbon tetrachloride in the calorimeter. Resistances were recorded with the carbon tetrachloride in the transition and with the shield at the same temperature. Then the shield was heated to successively higher temperatures up to 20° above the calorimeter and resistances noted as a function of shield temperature. The procedure was repeated at the melting point.

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(6) Prof. S. G. Simpson of the Analytical Division of the Chemistry Department, M. I. T., kindly performed the quantitative analyses.

(7) Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

(8) Southard and Brickwedde, *ibid.*, **55**, 4378 (1933).

(9) Blue and Hicks, *ibid.*, **59**, 1962 (1937).

(10) Gibson and Giauque, *ibid.*, **45**, 93 (1923). For a more complete discussion of the sources of error considered in this paper see: Walter P. White, "The Modern Calorimeter," The Chemical Catalog Company, New York, N. Y., 1928, pp. 137 et. seq.

The results indicate that thermometer readings may show a difference from the mean calorimetric temperature when the shield and calorimeter are 3° or more apart, but that this difference is within experimental error. A high heat capacity was purposely chosen for this experiment so that heat transfer from the surroundings would keep the change in mean temperature of the calorimeter at a minimum.

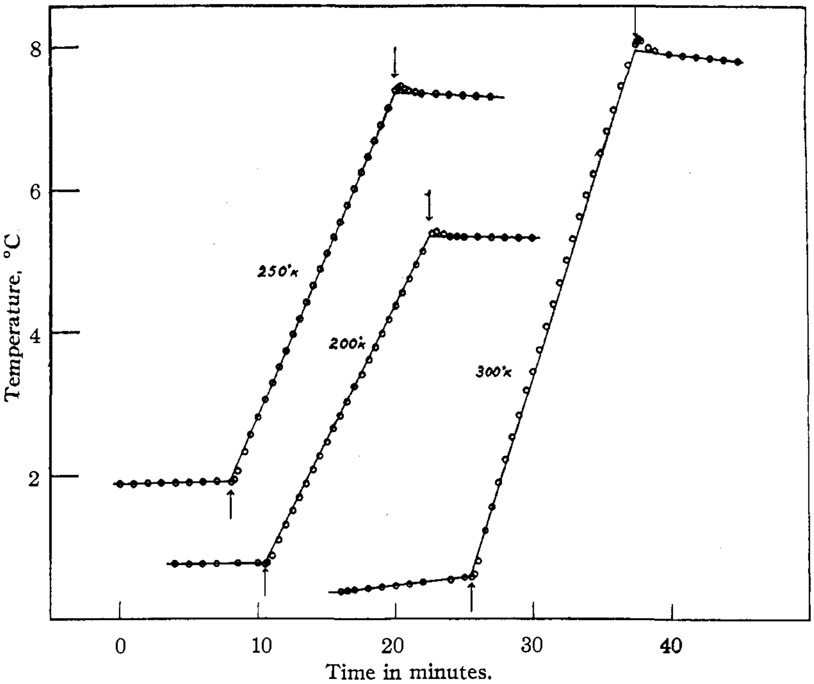

Fig. 2.—Calorimeter heating curves.

Another possible source of error arises from the wires attaining a temperature above that of the shield (lead wires are in thermal contact with the shield) during the heating period. Thus it is possible for heat to leak out along them without ever being absorbed by the calorimeter. Data on this point are not available, but rough calculations based upon the conductivity of the wires, glass seals, and the platinum tubes which are soldered to the heavy copper case, indicate heat loss from this source to be negligible. Such an error would lead to high results.

The heat capacity measurements of the empty calorimeter and of the calorimeter containing naphthalene were made with alternate points having twice the heating rate of the included one. The results are independent of any heating rate used with this calorimeter.

The resistance thermometer is sensitive to at least 0.001° between 300 and 50°K. Below 40°K., however, dR/dT drops rapidly[9] until at 12°, 0.01° is hardly detectable. The over-all accuracy of measurement of the heat capacity of the substance in the calorimeter is believed to be ±0.3% above 40°K. Below this temperature, the accuracy decreases with decreasing temperature so that at 12° the errors may be as high as 5%. The higher average accuracy of the empty calorimeter points is probably due to the elimination of the temperature gradient between the calorimeter wall and the substance.

The resistance of the thermometer at the ice-point was measured before assembling and after dismantling the apparatus. Over a three-year period the spread of ice-point resistances of R197 is one in 40,000.

Resistances were measured by comparing the potential drop across the thermometer with that across a standard resistance in series. A calibrated Leeds and Northrup volt box of 150,000 ohms with a 300-ohm tap was used in the heater potential measurements. The heating current was measured by means of the potential drop produced across a standard resistance. A Meylan 0.1 second stop watch calibrated against the time standard of General Radio Corp., Cambridge, served to measure the heating interval. The calorie used in this work equals 4.1833 int. joules. The e. m. f.'s were read on either an Eppley microvolt potentiometer or a Leeds and Northrup Wenner potentiometer. Both instruments had a range of 0.11 volt to 1 microvolt on the dials and were calibrated during the period of this work.

Measurements.—As a means of comparing the data obtained with this calorimeter with those obtained with others, the heat capacity of naphthalene (Bureau of Standards Standard Sample No.

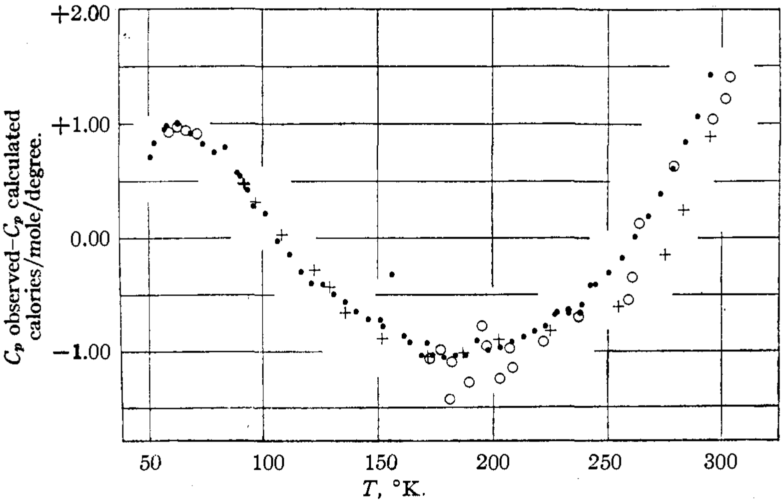

Fig. 3.—Naphthalene: ●, Southard and Brickwedde; +, Huffman, Parks and Daniels; ○, this research.

38b[8]) was determined at various temperatures above 60°K. The sample weighed 52.5 g. and the heat capacity of the empty calorimeter was about three times that of this sample. Because of this fact, the errors in this determination are magnified. The data are presented in Table I. Figure 3 shows a deviation plot in order to compare the data of Southard and Brickwedde,[8] and Huffman, Parks and Daniels[11] with the data of this research. The ordinate is molal $C_p(C_{10}H_8)$ observed $-C_p$ calculated from the straight line, $0.1231T + 1.840$.

TABLE I

NAPHTHALENE

T, °K.	C_p in cal. mole^{-1} degree^{-1}	T, °K.	C_p in cal. mole^{-1} degree^{-1}
58.48	9.96	207.07	26.35
62.24	10.47	208.19	26.32
66.17	10.93	222.07	28.26
71.04	11.50	237.51	30.38
172.21	21.97	259.35	33.22
177.13	22.65	261.00	33.62
180.89	22.68	263.76	34.44
182.02	23.15	279.20	36.84
189.49	23.89	295.92	39.31
195.32	25.10	301.58	40.18
196.96	25.13	303.59	40.62
202.83	25.56		

The empty-calorimeter data were smoothed by means of an arbitrary Debye function. The difference between observed and calculated values is plotted *vs.* T in Fig. 4. The region enclosed by the two curves denotes ±0.2% spread in the points. Every calorimetic measurement was made with helium in the calorimeter.

Table II presents the heat capacity data for thallium. The measurements are listed chronologically and are all on the one calorimeter loading. Between Series I and II and between II and III the calorimeter was warmed to room temperature and again cooled. No points have been discarded for any reason whatever. At each point, assuming the temperature to be correct, a value of the heat capacity was calculated from the equation $C = 6D\left(\frac{94}{T}\right)$.[12] Observed − calculated values are plotted (open circles) *vs.* T in Fig. 5. The dots in Fig. 5 represent Clusius and Vaughen's[2] data treated in a similar manner using the same function.

The entropy obtained graphically from a log T

TABLE II

THALLIUM

T, °K.	ΔT	C_p cal. mole^{-1} degree^{-1}	T, °K.	ΔT	C_p cal. mole^{-1} degree^{-1}
	Series I			Series II	
300.53	7.073	6.328	49.98	2.593	5.035
58.27	1.886	5.295	53.13	3.661	5.183
60.77	3.182	5.365	57.10	4.254	5.247
64.13	4.028	5.391	61.19	4.017	5.315
68.05	4.122	5.517	65.07	3.786	5.448
72.01	4.236	5.586	139.14	7.349	5.994
76.25	4.518	5.628	146.45	7.121	6.046
80.60	4.344	5.653	186.23	7.819	6.172
83.85	4.585	5.693	214.21	8.887	6.181
88.38	4.402	5.755	223.42	8.726	6.181
92.81	4.249	5.791	233.72	8.520	6.203
97.05	4.110	5.840	242.04	8.349	6.262
101.85	5.355	5.857	269.33	5.929	6.244
107.10	5.177	5.891	281.50	5.752	6.322
112.57	5.855	5.915			
118.65	6.279	5.936			
125.24	7.083	5.981			
131.77	6.883	5.978			
139.04	7.589	6.067			
146.73	7.393	6.043		Series III	
154.41	8.084	6.082	14.56	2.356	1.526
162.04	7.133	6.091	17.24	2.640	2.016
169.85	8.552	6.122	20.39	3.374	2.579
178.25	8.342	6.133	23.99	3.768	3.084
186.34	8.141	6.162	27.85	4.058	3.561
193.64	7.977	6.144	31.87	3.874	3.984
201.99	8.788	6.145	35.99	4.128	4.275
211.03	8.599	6.140	39.93	3.706	4.559
219.11	7.452	6.194	43.82	3.925	4.729
227.22	9.005	6.194	48.04	4.505	4.921
235.43	8.851	6.178	52.81	5.099	5.098
244.28	8.671	6.203			
251.97	8.502	6.240			
261.01	9.405	6.227			
269.73	8.208	6.211			
278.17	8.483	6.282			
288.34	10.587	6.166			
298.35	9.253	6.354			

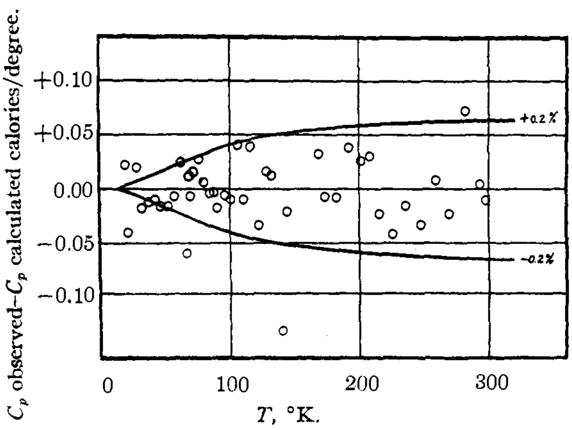

Fig. 4.—Heat capacity of empty calorimeter.

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[11] Huffman, Parks and Daniels, THIS JOURNAL, **52**, 155 (1930).

[12] "Six Place Tables of the Debye Energy and Specific Heat Functions," James A. Beattie, *J. Math. Phys.* (*M. I. T.*), VI, No. 1 (1926).

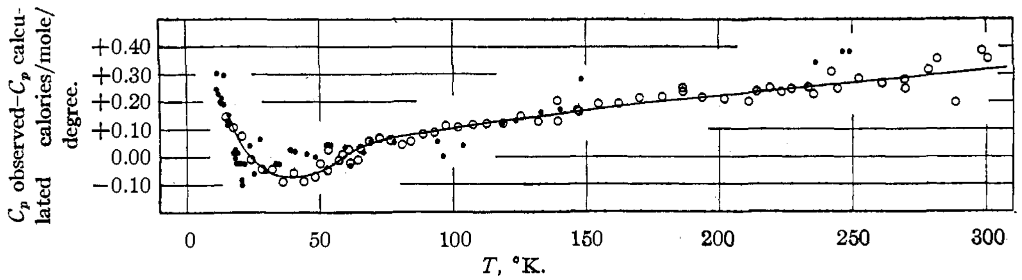

Fig. 5.—Heat capacity of thallium: ●, Clusius and Vaughen; ○, this research.

plot of the data of Table II and those of Keesom and Kok[13] is $S^\circ_{298.2} = 15.35 \pm 0.05$ e. u.

Figure 6 is included because it emphasizes the discrepancies in the low temperature specific heat data for thallium.

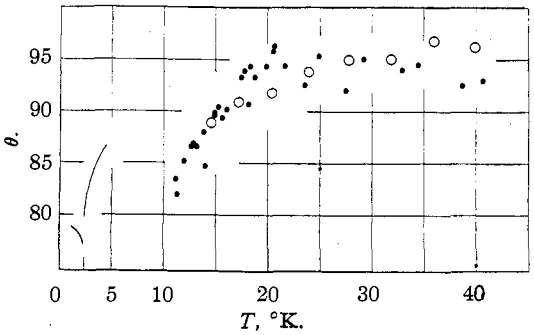

Fig. 6.—θ vs. T for thallium: ●, Clusius and Vaughen; ○, this research; the solid curve is from the data of Keesom and Kok.

The Entropy of Thallous Ion.—The e. m. f. data on the reaction[14] $Tl(s) + AgCl(s) = Ag(s) + Tl^+ + Cl^-$ were fitted to the following equation[15] by the method of least squares

$$E^{\circ\prime}_w - A(s)\sqrt{m} - E^\circ_0 = 0.000007 + 0.008403w - 0.000457w^2 + 0.000040w^3 + m(0.0794 + 0.0264w - 0.0012w^2)$$

where $A(w)$ is the Debye–Hückel limiting law expression for activity coefficients, $w = (t - 12.5)/12.5$, m = molality, $E^\circ_0 = E$ standard at 25° and $E^{\circ\prime}_w$ is the $E^{\circ\prime}$ of reference 12. $dE^\circ/dT = 6.722 \times 10^{-4}$, from the above expression, is 1% higher than that obtained by Cowperthwaite, La Mer and Barksdale.[14] The higher temperature coefficient leads to an entropy change for the above reaction of 15.5 e. u. Using this value, 15.4 for S_{Tl}, 23.0 for S_{AgCl}, 10.2 for S_{Ag} and 13.5 for S_{Cl^-}, the entropy of aqueous Tl^+ at unit activity and 298°K. is 30.2, compared with 30.1 of reference 4.

The author thanks Professor F. G. Keyes, Dr. R. W. Blue, Dr. H. T. Gerry and Dr. C. C. Stephenson for their helpful discussions and Mr. J. G. Hooley for his measurements on naphthalene.

Summary

A calorimeter suitable for low temperature heat capacity measurements has been described and the method discussed. The heat capacity of thallium has been determined from 14 to 300°K. and the entropy at 298.2°K. computed. It is 15.35 ± 0.05 e. u. Measurements on the heat capacity of naphthalene also have been presented as a means of comparing this method with those of other investigators. A check calculation of the entropy of thallous ion has been included, and found to agree with the previous value of 30.1 e. u.

CAMBRIDGE, MASS. RECEIVED DECEMBER 23, 1937

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(13) Keesom and Kok, *Physica*, **1**, 175 (1933–34).

(14) Cowperthwaite, La Mer and Barksdale, THIS JOURNAL, **56**, 544 (1934).

(15) Professor George Scatchard of this Laboratory suggested the form of this equation.