

3. The reaction described can be used as a qualitative test for natural or artificial stannic oxide.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

AN EQUATION FOR THE REPRESENTATION OF HIGH-TEMPERATURE HEAT CONTENT DATA¹

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High temperature heat content data have commonly been represented by the empirical equation

$$Q_{273.1}^T = \left[aT + \frac{b}{2} T^2 + \frac{c}{3} T^3 + \dots \right]_{273.1}^T \quad (1)$$

because the manipulation of such power series is easy and rapid. However, it is well known that this form of equation is not particularly satisfactory for the purpose. A reasonable number of terms often cannot be made to fit the data with sufficient accuracy; moreover, the resulting derived equation for specific heat

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

may have a maximum in the temperature range under consideration due to the signs and magnitudes of the coefficients, but such a maximum does not correspond to known physical facts. These difficulties are most apparent where the specific heats are still far below the Dulong and Petit equipartition value of 6 calories per gram atom at 0°. Obviously, a better form of equation is desirable, but the choice is limited by several conditions: namely, (1) the equation selected should be usable in conjunction with conventionally accepted methods in thermodynamic calculations, (2) differentiation and integration under the conditions imposed by thermodynamic calculations should be analytic and reasonably easy to perform, and (3) derived values should be consistent with the available facts.

The Pacific Experiment Station of the United States Bureau of Mines is interested in the correlation of high temperature thermal data on metallurgically important elements and compounds, and has investigated several forms of equations for the representation of these data. It is apparent that at high temperatures specific heats of normally behaving substances

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in the solid or liquid state increase nearly linearly with the temperature, and that a subtractive term is needed which will be effective at temperatures lower than that where the equipartition value of specific heat is reached. Consequently, the following equations are proposed

$$C_p = a + bT - cT^{-2} \quad (3)$$

$$Q_{273.1}^T = \left[aT + \frac{b}{2} T^2 + cT^{-1} \right]_{273.1}^T \quad (4)$$

The conditions mentioned above are satisfied by equation (4), and trial on the data for several substances has shown that it gives a satisfactory representation, as may be seen from the following examples.

The data on zinc oxide recently were reviewed by Maier,⁴ who has represented the available figures by the expression

$$Q_0^t = 9.35t + 4.34 \times 10^{-3}t^2 - 1.574 \times 10^{-6}t^3$$

This equation is equivalent to

$$Q_{273.1}^T = [6.63T + 5.63 \times 10^{-3}T^2 - 1.574 \times 10^{-6}T^3]_{273.1}^T \quad (5)$$

based on the specific heat value 9.35 cal. per degree per gram formula weight at 0°, and the total heats obtained by White and Day⁵ for 700 and 1300°. If equation (5) is differentiated, the resulting C_p equation has a maximum at 920°, which is without physical significance. Using the same three data for determining the constants in equation (4), there is obtained

$$Q_{273.1}^T = 11.40T + 0.726 \times 10^{-3}T^2 + 1.824 \times 10^6T^{-1} - 3835 \quad (6)$$

The comparison of equations (5) and (6) with the actual experimental data on zinc oxide is shown in Table I.

TABLE I
HEAT CONTENT OF ZINC OXIDE ABOVE 0°

Temp., °C.	Observed heat content	Observer	Equa- tion (5)	Diff., %	Equa- tion (6)	Diff., %
98	984	Regnault	957	-2.7	988	+0.4
99	995	Magnus	967	-2.8	998	+ .3
259	2886	Magnus	2686	-6.9	2780	-3.7
550	6033	Magnus	6193	+2.7	6262	+3.8
700	8132	White and Day	8132	0.0	8132	0.0
900	10677	White and Day	10783	+1.0	10692	+ .1
1100	13306	White and Day	13443	+1.0	13320	+ .1
1300	16009	White and Day	16009	0.0	16009	.0

It is seen that White and Day's data are represented with great exactness and furthermore that the agreement with the less accurate lower temperature data is very much better with equation (6) than with equation (5).

⁴ Maier, U. S. Bureau of Mines Bulletin 324, "Zinc Smelting from a Chemical and Thermodynamic Viewpoint," pp. 18-20.

⁵ See Maier and Ralston, THIS JOURNAL, 48, 364 (1926).

The heat content of calcium silicate in the form of pseudowollastonite has been measured by White⁶ up to 1400°, and Parks and Kelley⁷ have measured specific heats at low temperatures on the same sample. A smooth curve through the results of the latter investigators gives $C_p, 273.1 = 20.06$ cal. per degree per gram formula weight, a value far removed from the equipartition figure of about 30. Using this datum and White's total heat figures at 700 and 1400°, the following expressions are obtained and a comparison is made in Table II.

$$Q_{273.1}^T = 12.82T + 14.90 \times 10^{-3}T^2 - 4.020 \times 10^{-6}T^3 - 4530 \quad (7)$$

$$Q_{273.1}^T = 25.48T + 2.066 \times 10^{-3}T^2 + 4.881 \times 10^3T^{-1} - 8900 \quad (8)$$

TABLE II
HEAT CONTENT OF CALCIUM SILICATE ABOVE 0°

Temp., °C.	White's data	Equation (7)	Diff., %	Equation (8)	Diff., %
100	2140	2120	-0.9	2700	+2.8
300	7125	6950	-2.5	7230	+1.5
500	12600	12430	-1.3	1.660	+0.5
700	18350	18350	0.0	18350	.0
900	24290	24530	+1.0	24250	-.2
1100	30390	30760	+1.2	30340	-.2
1300	36630	36870	+0.7	36610	-.1
1400	39800	39800	.0	39800	.0

Here, again, equation (8) is much more satisfactory than equation (7). At only one point, 100°, does equation (7) fit better, but this particular experimental value may be low, as the curve given by Parks and Kelley indicates.

The proposed equations are by no means perfect, but appear to be definitely better than the older forms; they require no additional data and are as easily handled as the ordinary power series expressions, in conjunction with which they readily may be used, if desired. Also, all the data investigated so far (which are for metals, oxides and silicates) are adequately represented by the three constant equations, there being no necessity for adding more terms, as is often the case when the power series expressions are used. It is preferable to obtain the constants in the manner indicated by solving simultaneously one specific heat equation, into which has been substituted the true specific heat at 273.1°K., and two total heat equations. This makes the resulting equations consistent with both the high temperature and low temperature thermal data. Where no true specific heat measurements exist, three total heat equations must be solved for the constants. No difficulty is encountered in writing heat of reaction and free energy equations, which are of the form

⁶ White, *Am. J. Sci.*, [4] **28**, 334 (1909); **47**, 1 (1919).

⁷ Parks and Kelley, *J. Phys. Chem.*, **30**, 1175 (1926).

$$\Delta H_T = \Delta H_0 + \Delta aT + \frac{\Delta b}{2} T^2 + \Delta cT^{-1} \quad (9)$$

$$\Delta F_T^\circ = \Delta H_0 - \Delta aT \ln T - \frac{\Delta b}{2} T^2 + \frac{\Delta c}{2} T^{-1} + IT \quad (10)$$

Summary

The equation $Q_{273.1}^T = \left[aT + \frac{b}{2} T^2 + cT^{-1} \right]_{273.1}^T$ is suggested for the representation of high temperature thermal data and is shown to be superior to the ordinary power series expression. The suggested equation is readily usable in all thermodynamic calculations, involves no additional labor and may be employed in conjunction with power series expressions, if desired.

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APPARATUS FOR QUANTUM YIELDS OF GAS REACTIONS BY ACTINOMETRY

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By proper use of actinometry it is possible to avoid most of the difficulties of radiometric procedures, also the disadvantage that radiometric errors can be estimated only by the original investigator and only before his apparatus is dismantled. When quantum yields are referred to a reproducible standard under identical conditions, systematic errors tend to cancel out. If, later, the given actinometer is restandardized, it is easy to recalculate all quantum yields previously referred to it.

In this Laboratory the quantum yields of uranyl oxalate have been determined within 5% over the range 435 to 254 $m\mu$,¹ also 278 to 208 $m\mu$,² thus providing the basis for an advance in actinometric procedure. We have constructed an apparatus (Figs. 1, 2) for quantitative study of photochemical gas reactions attended by pressure changes. It could easily be modified for studies of gas reactions without pressure change, or of liquid systems.

Light from a vertical mercury vapor lamp O (Fig. 1) was resolved by the conventional train between the quartz condenser, Q_c , and the exit slit, E, cut to fit the image of the spectral line furnishing the monochromatic radiation. A shutter was placed between O and Q_c . A small elliptical quartz lens of short focus, Q_e , lessened the divergence of the issuing beam.

Two quartz cells, each the frustum of a rectangular pyramid, had identical dimensions and a volume approximately 40 cc. All seams were fused. The gas cell, C_g , shown in detail in Fig. 2, had a capillary inlet, I. The acti-

¹ Leighton and Forbes, *THIS JOURNAL*, **52**, 3139 (1930).

² Brackett and Forbes, data to be published.