

sitions of the individual carbon and nitrogen atoms) are summarized in Table VII. It will be noticed that the cadmium compound is not intermediate between the zinc and mercury compounds, but is built on a slightly larger scale than even the mercury compound. It will also be seen that, since the potassium atoms are situated relatively to the cyanide groups substantially as in potassium cyanide,<sup>6</sup> the distances between their centers in each case may properly be compared. The agreement is surprisingly close; indeed, if the bivalent atoms of the complex cyanide are simply removed and replaced by twice as many potassium atoms in the proper position, the structure of potassium cyanide is almost quantitatively reproduced.

TABLE VII  
DISTANCES

Substance	$d_{100}$	K to CN	Zn, Cd, or Hg to CN
$K_2Zn(CN)_4$	12.54 Å.	3.20 Å.	2.61 Å.
$K_2Cd(CN)_4$	12.84	3.28	2.67
$K_2Hg(CN)_4$	12.76	3.25	2.65
KCN	$\frac{1}{2} \times 13.10$	3.28	..

### VII. Summary

By means of spectral photographs and unsymmetrical Laue photographs, the structures of  $K_2Zn(CN)_4$ ,  $K_2Cd(CN)_4$  and  $K_2Hg(CN)_4$  have been determined. In the interpretation of the data the highly useful theory of space-groups has been employed, and it was not necessary to make any quantitative assumptions as to the "normal decline" of intensity. The results show that these compounds have the structure summarized at the end of Section V, represented by Fig. 4, and discussed in Section VI. A remarkable fact is that these complex cyanides have the same structure as magnetite ( $Fe_3O_4$ ) and spinel ( $MgAl_2O_4$ ).

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### NOTE

**A Simple Formula for the Calculation of the Specific Heats of Solids.**—The most important present day theories for the specific heat of solids agree in one respect, namely, that for a large class of solids,  $C_v$  is the same function of the temperature, divided by a constant which is characteristic of the substance. In other words

$$C_v = f\left(\frac{T}{\theta}\right) \quad (1)$$

where  $T$  is the absolute temperature,  $\theta$  is the characteristic temperature for each substance and  $f$  has the same form for all the substances under consideration. This is Equation 5 in the treatment of specific heats given by Lewis and Gibson.<sup>1</sup>

<sup>1</sup> Lewis and Gibson, THIS JOURNAL, 39, 2558 (1917).

Usually the function  $f$  is very complicated in form; for example, the equations of Einstein, Nernst and Lindemann, and Debye are very difficult to evaluate, while Lewis and Gibson make no attempt to obtain an analytic expression for the form of  $f$ . It is the purpose of this note to present a simple analytic formula which has been found to represent specific heats with sufficient accuracy for many calculations.

**The Specific Heat Formula.**—A simple form of the function of the previous equation which has been found to fit the experimental values is

$$C_v = 2.91 + 2.89 \tanh 2.95 \log \frac{T}{\theta} \quad (2)$$

where  $C_v$  is given in calories per gram-atom. It will readily be seen that Equation 2 is a modification of the equation  $y = \tanh x$  after a transformation of axis. The values of the numerical constants have been adjusted by the method of least squares to the values of  $C_v$  given in Table I of the paper by Lewis and Gibson.<sup>2</sup> No theoretical significance is claimed for Equation 2. It recommends itself, however, because of its analytic simplicity. It is of interest to note that the above formula is symmetrical about the axis  $C_v = \frac{3}{2} R = 2.95$ , while the actual experimental curve is apparently not quite symmetrical.

In the following table the values of  $C_v$  calculated from the above formula are compared with those of Lewis and Gibson. The greatest difference is seen to occur where  $\log \theta$  has the largest negative values, *i. e.*, at the lowest temperatures. The agreement at higher temperatures is well within the experimental error.

TABLE I  
SPECIFIC HEATS

Log $\frac{T}{\theta}$	$C_v$ Calc.		$C_v$ Lewis		Log $\frac{T}{\theta}$	$C_v$ Calc.		$C_v$ Lewis	
	$C_v$ Calc.	$C_v$ Lewis	$C_v$ Lewis	$C_v$ Calc.		$C_v$ Calc.	$C_v$ Lewis	$C_v$ Lewis	$C_v$ Calc.
-0.6	0.18	0.11	+0.09	0.4	5.30	5.26	+0.04		
-0.5	0.31	0.21	+0.10	0.5	5.51	5.49	+0.02		
-0.4	0.52	0.43	+0.09	0.6	5.64	5.65	-0.01		
-0.3	0.87	0.84	+0.03	0.7	5.71	5.72	-0.01		
-0.2	1.38	1.43	-0.05	0.8	5.74	5.76	-0.02		
-0.1	2.08	2.19	-0.11	0.9	5.77	5.78	-0.01		
0.0	2.91	2.98	-0.07	1.0	5.78	5.79	-0.01		
0.1	3.74	3.78	-0.04	1.1	5.79	5.80	-0.01		
0.2	4.44	4.43	+0.01	1.2	5.79	5.81	-0.02		
0.3	4.95	4.91	+0.04						

**The Entropy Equation.**—Since the entropy equation is obtained by integration of the specific heat equation we may write

$$S_v = \int \left( 2.91 + 2.89 \tanh 2.95 \log \frac{T}{\theta} \right) d \ln \frac{T}{\theta} \quad (3)$$

<sup>2</sup> Ref. 1, p. 2561.

Evaluating the constant of integration by putting the entropy equal to the Lewis-Gibson value 1.62 when  $\log \frac{T}{\theta} = 0$ , we obtain

$$S_v = 6.70 \log \frac{T}{\theta} + 5.18 \log \cosh 2.95 \log \frac{T}{\theta} + 1.62. \quad (4)$$

In the following table the calculated entropies are compared with those obtained graphically by Lewis and Gibson.<sup>2</sup> The agreement is good.

TABLE II  
COMPARISON OF ENTROPIES

$\log \frac{T}{\theta}$	$S_v$ Calc.	$S_v$ Lewis	$S_v - S_v$ Calc.-Lewis	$\log \frac{T}{\theta}$	$S_v$ Calc.	$S_v$ Lewis	$S_v - S_v$ Calc.-Lewis
-0.6	0.08	0.04	+0.04	+0.4	5.60	5.59	+0.01
-0.5	0.15	0.07	+0.08	+0.5	6.85	6.82	+0.03
-0.4	0.24	0.15	+0.09	+0.6	8.12	8.08	+0.04
-0.3	0.40	0.30	+0.10	+0.7	9.43	9.41	+0.02
-0.2	0.65	0.53	+0.12	+0.8	10.76	10.74	+0.02
-0.1	1.05	0.98	+0.07	+0.9	12.07	12.07	0.00
0.0	1.62	1.62	0.00	+1.0	13.40	13.40	0.00
+0.1	2.39	2.41	-0.02	+1.1	14.74	14.74	0.00
+0.2	3.33	3.37	-0.04	+1.2	16.08	16.08	0.00
+0.3	4.42	4.42	0.00				

**The Method of Calculation.**—The values of  $\tanh$  and  $\log \cosh$  are readily obtained from tables of hyperbolic functions.<sup>3</sup> The remainder of the labor is only in multiplication and addition, the former of which can be carried out with sufficient precision for the purpose with a 20-inch slide rule. In fact all of the calculated values given in the two tables were very readily obtained in this manner.

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<sup>3</sup> The "Smithsonian Mathematical Tables" hyperbolic functions are quite suited for this purpose.