3.   Drying on the water-bath or "drying to constant weight" cannot yield homogeneous products, and therefore,

4.   Many of the empirical formulas of such compounds given in the literature are necessarily incorrect.

5.   The affinity and manner of union of water of composition do not differ largely from the affinity and manner of union of ammonia.

6.   Water of crystallization, conforming to the law of definite proportions, must be held in definite molecular structures, through the agency of valency, as in other compounds.

7.   Tetravalent oxygen, necessary to express these structures, is loosened at temperatures above 100°, therefore salts usually expel water of crystallization below this temperature and water of composition above this temperature.

8.   Finding dissimilar molecules of water in hydrated salts, leads to a conception of their structure.

URBANA, ILLINOIS.
May 29, 1907.

THE SPECIFIC HEAT OF SOLIDS AT CONSTANT VOLUME, AND THE LAW OF DULONG AND PETIT.

BY GILBERT NEWTON LEWIS.

The study of the relation between the specific heat of gases at constant volume and at constant pressure has led to a number of important theoretical conclusions, but in the case of solids and liquids we have been familiar hitherto only with the specific heat at constant pressure.   To determine experimentally the specific heat at constant volume of a liquid or solid would be a difficult undertaking.   Fortunately it is possible, assuming nothing more than the validity of the two laws of thermodynamics, to calculate this important quantity from existing data.

The internal energy at constant temperature is nearly independent of the volume, in the case of a gas, but may vary considerably with the volume in the case of a liquid or solid.   Except in rare cases it increases with increasing volume.   The difference between the specific heats at constant pressure and constant volume is chiefly due to this change of internal energy with the volume, as I have shown in a previous paper[1] where the following purely thermodynamic equation was obtained.

$$c_p - c_v = \left(\frac{\partial v}{\partial T}\right)_P \left[P + \left(\frac{\partial E}{\partial v}\right)_T \right] \qquad (1)$$

c_p and c_v are the two specific heats.   E and v are respectively the in-

[1] Lewis.   The Development and Application of a General Equation for Free Energy and Physico-Chemical Equilibrium Equation 38.   Pr. Am. Acad., **35**, 1 (1899) ; J. physic. Chem., **32**, 364 (1900).

ternal energy and the volume of one gram of the substance at the absolute temperature T and the pressure P.

Besides this equation we have the fundamental thermodynamic equation connecting the pressure and temperature of any substance, namely,

$$P + \left(\frac{\partial E}{\partial v}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v \tag{2}$$

Combining these two equations, we have,

$$c_p - c_v = T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v$$

Now by the principles of partial differentials,

$$\left(\frac{\partial P}{\partial T}\right)_v = - \frac{\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T}$$

Hence

$$c_p - c_v = - T \frac{\left(\frac{\partial v}{\partial T}\right)_P^2}{\left(\frac{\partial v}{\partial P}\right)_T} \tag{3}$$

The coefficient of compressibility α and the coefficient of thermal expansion β as commonly used are defined by the equations,

$$\alpha = - \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T, \text{ and, } \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

Combining these equations with (3) we have,

$$c_p - c_v = \frac{T\beta^2 v}{\alpha} \tag{4}$$

This exact thermodynamic equation enables us from the specific heat at constant pressure to calculate the specific heat at constant volume for any substance when its coefficients of compressibility and of thermal expansion are known.

According to the theory of van der Waals the specific heat at constant volume for any unassociated substance should be the same in the liquid and the gaseous states, and this conclusion has been very generally accepted.[1] Equation (4) gives a means of testing this view directly, and I hope soon to discuss this interesting question more at length. In the present paper the above principles will be employed in the calculation of the specific heats at constant volume of the solid elements. The importance of this application of equation (4), in view of the law of Dulong and Petit, was called to my attention by Prof. A. A. Noyes.

If in equation (4) the gram atom is used as unit of mass in place of the gram, c_p and c_v must be replaced by C_p and C_v, the corresponding atomic heats, and v must be replaced by V, the atomic volume. If the unit of pressure chosen is the megadyne per square centimeter, or the

[1] See Nernst, Theoretische Chemie (Edit 4), p. 240.

megabar, and the unit of volume is the cubic centimeter, then C_p and C_v will have the dimensions of megergs per degree. If we prefer to express these in calories per degree the factor 41.78 must be introduced, and equation (4) becomes :

$$C_p - C_v = \frac{T\beta^2 V}{41.78\, a}$$

The accompanying table contains the results obtained by applying equation (5) to all the solid elements for which a and β are known, with the exception of the non-metals of atomic weight lower than 35. The latter are the elements which deviate radically from the law of Dulong and Petit. The values given are all for 20°, since for this temperature the very careful determinations of compressibility made by T. W. Richards and his collaborators are available. From their work[1] the first three columns of the table are taken directly. The first gives the approximate atomic weight of the elements ; the second, the atomic volumes in cc.; the third, the coefficients of compressibility, pressure being measured in megadynes per sq. cm. The fourth column gives the coefficients of thermal expansion. These are taken from the tables of Landolt and Börnstein, interpolated as well as possible for 20°. The fifth column contains the values of $C_p - C_v$, in calories per degree, calculated by equation (5). The sixth column contains the atomic heats at constant pressure, expressed in calories per degree. The values obtained by Gaede[2] for Sb, Pb, Cd, Cu, Pt, Zn, and Sn, in the neighborhood of 20°, are taken directly from his work. The other values are taken from the tables of Landolt and Börnstein, interpolated for 20° by means of the temperature coefficients obtained by Richarz and Wigand.[3] In some cases a certain amount of choice was possible in selecting the most probable value of the specific heat. But this choice was made in every case before the final calculations were made, in order to make sure that the selection was without prejudice. The seventh column (Δ_1) shows the deviations of the several values of C_p from the mean. The eighth column gives the values of the atomic heat at constant volume in calories per degree. The last column (Δ_2) shows the deviations of the several values of C_v from the mean. In the last five columns only one decimal place is given. For a number of elements another place would be without significance, owing to the unreliability of the data for a and C_p.

The table shows that the mean value of C_v for the nineteen elements is three-tenths of a unit below the mean of C_p. The average deviation of the individual values from the mean is considerably less for C_v than for C_p. Probably except in the case of sodium and potassium the values

[1] Publication of the Carnegie Institution, 76 (1907).

[2] Physik. Z. 4, 105 (1902).

[3] Ann. d. Phys. (4) 22, 64 (1907).

J. LIVINGSTONE R. MORGAN AND H. K. BENSON

	At. wt.	2 V	3 $a \times 10^6$	4 $\beta \times 10^6$	5 $C_p - C_v$	6 C_p	7 Δ_1	8 C_v	9 Δ_v
Na...............	23.0	23.7	15.4	72.	0.5	6.9	0.7	6.4	0.5
Mg	24.4	13.3	2.7	25.	0.2	6.0	0.2	5.8	0.1
Al	27.1	10.1	1.3	23.	0.2	5.8	0.4	5.7	0.3
K...............	39.1	45.5	31.5	83.	0.6	7.1	0.9	6.5	0.6
Fe.	55.9	7.1	0.40	10.	0.1	6.0	0.2	5.9	0.0
Ni	58.7	6.7	0.27	13.	0.2	6.1	0.1	5.9	0.0
Cu.	63.6	7.1	0.54	16.	0.2	5.8	0.4	5.6	0.3
Zn.	65.4	9.5	1.5	29.	0.3	6.0	0.2	5.6	0.2
Pd	107.	9.3	0.38	11.	0.2	6.1	0.1	5.9	0.0
Ag.	107.9	10.3	0.84	19.	0.3	6.1	0.1	5.8	0.1
Cd.	112.5	13.0	1.9	28.	0.3	6.2	0.0	5.9	0.5
Sn.	119.	16.2	1.7	22.	0.3	6.4	0.2	6.1	0.2
Sb	120.	17.9	2.2	11.	0.1	6.0	0.2	5.9	0.0
I	127.	25.7	13.	84.	0.9	6.9	0.7	6.0	0.1
Pt	195.	9.1	0.21	9.	0.2	6.1	0.1	5.9	0.0
Au.........	197.	10.2	0.47	14.	0.3	6.2	0.0	5.9	0.0
Tl	204.	17.2	2.6	28.	0.3	6.4	0.2	6.1	0.2
Pb.	207.	18.2	2.2	29.	0.4	6.3	0.1	5.9	0.0
Bi	208.	21.2	2.8	13.	0.1	6.3	0.1	6.2	0.3
Average....						6.2	0.26	5.9	0.15
Average excluding the first four						6.2	0.18	5.9	0.09

of Δ_2 are in no case greater than the possible error in C_v due to experimental errors. If the first four elements are excluded the mean value of C_p for the remaining fifteen is 6.2, and the average deviation from this mean is 0.18. The mean value of C_v is 5.9, and the average deviation is 0.09, only one-half the average deviation from C_p. This result is certainly not accidental. The law of Dulong and Petit may therefore be modified and stated as follows: *Within the limits of experimental error the atomic heat of constant volume, at 20°, is the same for all the solid elements whose atomic weights are greater than that of potassium.*

Whether this law will also be true for other temperatures cannot be ascertained until the change of compressibility with the temperature has been investigated. C_p in many cases increases rapidly with the temperature, but the term $C_p - C_v$ probably increases also. It is not unlikely therefore that C_v may be nearly independent of the temperature.

RESEARCH LABORATORY OF PHYSICAL CHEMISTRY.
Massachusetts Institute of Technology, June 25, 1907.

MOLTEN HYDRATED SALTS AS SOLVENTS FOR THE FREEZING POINT METHOD[1].
BY J. LIVINGSTONE R. MORGAN AND H. K. BENSON.
Received June 11, 1907.

The depression of the freezing point of a solvent by the addition to it of a soluble substance has been employed now for a number of years as a

[1] Abstract from the Dissertation (Columbia 1907) of H. K. Benson.