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# The Experimental Determination of the Surface Tension of Magnesium Oxide

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A simple thermodynamic theory is presented which permits the determination of the surface tension, energy and entropy of a solid. The necessary measurements are all calorimetric. Results are presented for magnesium oxide.

## I. Introduction

There appear to be no valid experimental determinations of the thermodynamic quantities of the surface of solids in the literature. For many purposes it would be desirable to have values of these quantities, especially the surface tension. A simple theory is presented whereby these quantities can be directly and unambiguously determined from experimental data. The necessary measurements are an area determination of a finely divided solid and the difference in the heats of solution and in the heat capacities of this finely divided sample and a sample composed of very large crystals. Data are presented for magnesium oxide.

## II. Theory

We wish to determine the heat content, *h*, the surface tension, $\gamma$, and the surface entropy, *s*. The above refer to 1 cm.$^2$ of surface. The area of the solid is denoted by *A*, and will be considered invariant. The heat content can be simply obtained from

$$h_{298} = \Delta H_{298}/A \qquad (1)$$

where $\Delta H$ is the difference in the heats of solution of a solid of area *A* and a solid which has essentially no area. This method of determination has been used in the past. Perhaps the best known of these studies is that of Lipsett, Johnson and Maass,[2] who attempted the determination of the surface energy of NaCl. Their results are probably high, since the method they used for area determination is known now to give a low answer.

The surface entropy and the temperature dependence of the surface heat content can be obtained as follows. Giauque[3] has shown that the entropy of a small crystal approaches zero at 0° K. provided the infinite crystal does likewise. Thus if $\Delta C_p$ is the difference in the heat capacity of an infinite crystal and that of the small crystals

$$s = 1/A \int_0^T \Delta C_p/T \, dT \qquad (2)$$

and

$$h = h_{298} + 1/A \int_{298}^T \Delta C_p dT \qquad (3)$$

The surface tension is

$$\gamma = h - Ts \qquad (4)$$

Thus, the above measurements are sufficient to determine all of the thermodynamic quantities. Since the theory is basic thermodynamics, the only question which can arise concerning the results is the reliability of the experimental measurements.

### III. Materials and Experimental

The MgO used in these experiments was made by the method of De Schulten.[4] Although this is not the best method for the manufacture of MgO, it was used since it would permit a comparison of our results with the measurements of Giauque and Archibald[5] who had previously carried out all the necessary measurements except that of the area of the finely divided sample.

The area was determined from the adsorption of $N_2$ at 77.3°K. The area was computed by the method of Brunauer, Emmett and Teller,[6] and Harkins and Jura[7] and found to be 86 m.$^2$g.$^{-1}$. The specific heats were determined by Dr. R. E. Todd of the U.S. Bureau of Mines.

Spectrographic analysis was made by Mr. Conway of the Radiation Laboratory. This analysis showed that there was less than 0.01% of Al and Fe, between 0.01 and 0.1% Ca, and no evidence of K. The quantitative determinations of Mg and Si and carbonate were made by Mr. Koch. The results of the analysis showed that the sample was 0.59% $SiO_2$, 1.01% $MgCO_3$, 96.09% MgO, and 2.31% $Mg(OH)_2$. The $SiO_2$ was introduced into the sample when the precipitated hydroxide was removed from the fritted glass disk which was used as a filter.

The observed specific heat of the sample was corrected for all the impurities. The correction for the $SiO_2$ was so small that it was immaterial as to what crystalline form the silica may have had. The correction for this impurity was obtained from the data of Anderson.[8] The data of Giauque and Archibald[5] were used for the $Mg(OH)_2$ while the data of Anderson[9] were used for the carbonate. Within experimental error, the specific heats obtained were in agreement with those previously obtained by Giauque and Archibald.[5] From 50°K., the lowest temperature in this determination, to about 80°K., the present results were about 1% higher than the earlier results. Above this temperature, the present results were about 0.3% lower than those in the earlier work. It is felt that this is a satisfactory agreement.

The crystal structure of the sample was determined by Prof. David Templeton. The X-ray diffraction agreed with the published lattice parameters, and gave no indication of any anomalies.

Since there was such good agreement in the specific heats, the heat of solution of the present sample was not redetermined. The earlier value of Giauque[3] was used.

## IV. Results and Discussion

Figure 1 shows the surface energy and surface tension as a function of temperature from 0°K. to room temperatures. These values are based on a difference in the heats of solution of 888 cal. mole$^{-1}$ at 25° as given by Giauque.[3] The $\Delta C_p$ were determined from the results of this investigation and the single crystal heat capacity data of Parks and Kelley.[10] The surface tension decreases from 1040 to 1000 ergs cm.$^{-2}$ in the temperature interval, 0° to 298°K. The heat content increases

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(2) S. G. Lipsett, F. M. G. Johnson and O. Maass, THIS JOURNAL, **49**, 925, 1940 (1927); **50**, 2701 (1928).

(3) W. F. Giauque, *ibid.*, **71**, 3192 (1949).

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(5) W. F. Giauque and R. C. Archibald, THIS JOURNAL, **59**, 561 (1937).

(6) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

(7) W. D. Harkins and G. Jura, *ibid.*, **66**, 1366 (1944).

(8) C. T. Anderson, *ibid.*, **58**, 568 (1936).

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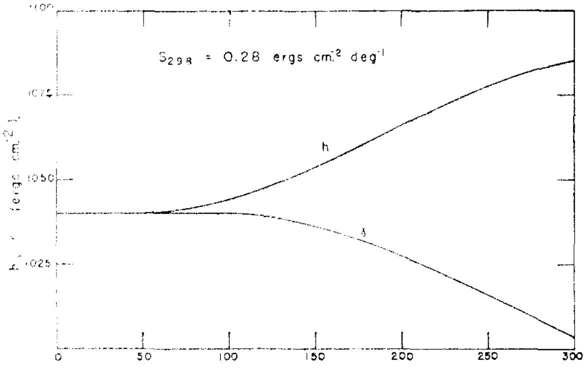

Fig. 1.—The heat content, *h*, and surface tension, $\gamma$, of MgO as a function of temperature.

from 1040 to 1090 ergs cm.$^{-2}$ in the same interval. The value of the surface entropy at 298°K. is 0.28 ergs cm.$^{-2}$ deg.$^{-1}$.

In the above experiments, there is one step in the procedure which conceivably could affect the final results. The magnesium oxide was transferred through the air when it was placed in the calorimeter. A certain amount of water would be adsorbed in this transfer. Normally, the adsorption of water would decrease the surface energy, the exact amount would depend on the solid and the amount of adsorbed water. The question arises as to how much water has been adsorbed by the sample, and the effect of this water on the values of the surface energy. Heat of immersion experiments are capable of giving a direct measure of the decrease in the surface energy by adsorption.[11] In this system, the heat of immersion results must be interpreted with care, since solubility and compound formation also occur.

Before the heat of immersion experiments are performed, it is essential to know the amount of water which has been adsorbed. As the transfer was performed, no estimate could be made. If we assume that one-half a mono-layer of water is adsorbed, and compute the heat capacity of the magnesium oxide on the assumption that the heat capacities are additive, we find that the heat capacity of the fine oxide is reduced to that of the infinite crystal. Therefore, since the heat capacity of the solid cannot be less than this, it is apparent that this is the maximum amount of water which could have been adsorbed.

The measured difference in the heats of immersion of the magnesium oxide and that which was permitted to adsorb an amount of water vapor which was computed to give one-half coverage was 600 ergs cm.$^{-2}$, uncorrected for any other processes which might have occurred. This figure is abnormally high for a change in surface energy, but corresponds to a heat of formation of magnesium hydroxide from magnesium oxide. The value obtained from the heat of immersion data for this heat is 17 ± 4 kcal. mole$^{-1}$. The literature value is 20 kcal. mole$^{-1}$. Thus it appears reasonable that any water which was adsorbed in the transfer formed magnesium hydroxide. The amount of hydroxide formed is so small, that no correction need be made for the change in composition of the solid. At the present time, it is not possible to state how much difference there might be between the heat capacity of the pure oxide, and that in which the surface is contaminated with the hydroxide. The similarity of the molecules would suggest that the difference is small.

There are no other measurements of the thermodynamics of surfaces with which the above may be compared. However, it is possible to make comparison with theoretical computations. Lennard-Jones and Taylor[12] using the simple Born theory for the lattice energy of ionic solids, computed a value of 1360 ergs cm.$^{-2}$ for the surface energy of the 100 face of MgO. The above calculation assumes that the interionic distance in the surface is the same as in the bulk. Later, Lennard-Jones and Dent[13] recomputed the surface energies of the alkali halides, correcting for a decrease in the interionic distance in the surface, and found that the values of the surface energy were decreased by 15–20%. If it is assumed that the same reduction would occur with MgO which has the same lattice structure, one can say that the calculated value of the surface energy of the 100 face of MgO is between 1360 and 1090 ergs cm.$^{-2}$, at 0°K. The measured value of 1040 ergs cm.$^{-2}$ at this temperature appears to be in good agreement with theory if it is assumed that only the 100 face of the MgO is present in the sample. It is known that the only crystallographic face which is present in normal crystals with the MgO (NaCl) structure is the 100 face. It is not unreasonable to assume that the 100 face predominates in the powdered sample. It might be possible to show that this is true by the use of electron microscopy. To date our efforts to obtain a photograph with this sample have been unsuccessful.

The error present in this work, due to an unknown quantity of adsorbed water, can be removed by improved equipment and technique. Both of these are now being done. The present data, if necessary, will be corrected in the future. At this time, an extensive discussion of the various theories by which the surface quantities can be estimated would be of less value than at the time when more data are available.

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[11] W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1919 (1944).

[12] J. E. Lennard-Jones and P. A. Taylor, *Proc. Royal Soc.* (*London*), **109A**, 476 (1925).

[13] J. E. Lennard-Jones and B. E. Dent, *Phil. Mag.*, [7] **8**, 530 (1929).