[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

An Example of the Difficulty in Obtaining Equilibrium Corresponding to a Macrocrystalline Non-volatile Phase. The Reaction $Mg(OH)_2 \rightleftarrows MgO + H_2O(g)$

BY W. F. GIAUQUE

Recently Torgeson and Sahama[1] measured the heat of solution of magnesium hydroxide in hydrochloric acid solution. They selected conditions of experiment, including final concentrations, to correspond to the work of Shomate and Huffman,[2] on the heat of solution of magnesium oxide.

Combining the results they obtain

$$Mg(OH)_2(c) = MgO(c) + H_2O(l)$$
$$\Delta H_{298.16°K} = 8850 \pm 25 \text{ cal. mole}^{-1}$$

Torgeson and Sahama prepared their $Mg(OH)_2$ by reaction of MgO with steam(saturated) at 150 p. s. i. Shomate and Huffman prepared MgO by heating $Mg(OH)_2$ in a silica flask for one hundred hours, during which the temperature was raised from 400 to 1000°. Torgeson and Sahama consider both substances to have been crystalline and we see little reason to doubt that they were approximately macrocrystalline with respect to their properties.

Giauque and Archibald[3] measured the heats of solution of $Mg(OH)_2$ and MgO in hydrochloric acid solution and obtained a result of $\Delta H_{298.16} = 9739 \pm 25$ cal. mole.$^{-1}$ for Reaction 1, however, with the MgO in a different physical state.

They prepared crystals of $Mg(OH)_2$ with an average diameter of 0.2 mm. by slowly cooling a solution of $MgCl_2$ in concentrated potassium hydroxide from 210°. There is no reason for believing that the $Mg(OH)_2$ used by Torgeson and Sahama was appreciably different in its macroscopic properties from the visible crystals used by Giauque and Archibald.

The MgO prepared by Giauque and Archibald was made by dehydrating the above $Mg(OH)_2$ crystals, *in vacuo*, at a relatively low temperature. Decomposition was attempted at 200°, but was so slow that the temperature was raised to 300°, and for a short period to 350° at the end of ten days of heating *in vacuo*. This treatment decomposed 95% of the material, which was in the form of a fine powder. The above data lead to the result

$$MgO(\text{crystalline}) = MgO \text{ (finely divided)} \qquad (2)$$
$$\Delta H_{298.16} = 888 \text{ cal. mole}^{-1}$$

Giauque and Archibald[3] were not primarily interested in the properties of either MgO or $Mg(OH)_2$ and were using these substances only as a means of determining the entropy of $H_2O(g)$ by use of the third law of thermodynamics and the decomposition equilibrium

$$Mg(OH)_2 = MgO + H_2O(g)$$

For this reason they considered it desirable to prepare and investigate the heat content and heat capacity of MgO under approximately the same conditions as those existing during their study of the decomposition pressures.

The heat capacity of the finely divided MgO was found to be higher than that of the crystalline material, which had been investigated by Parks and Kelley.[4] ΔC_p was about 1% at ordinary temperatures and this increased to about 6% at 90°K.

Giauque and Archibald were aware that the heat content of the powder should be somewhat higher than that of large crystals, due to increased surface energy, but had no idea that the difference would be a large quantity such as 888 cal. mole.$^{-1}$ We believe that it would be proper to describe the MgO powder prepared at about 300° as colloidal.

Our attention has been called to an equivalent result of Taylor and Wells[5] who decomposed $Mg(OH)_2$ at various temperatures, with a heating period of two and one-half hours.

Taking the heat of solution results at their lowest and highest temperatures

$$MgO_{(\text{formed at } 1425°)} = MgO_{(\text{formed at } 450°)} \qquad (3)$$
$$\Delta H_{298.1°K} = (36{,}670 \pm 70) - (35{,}720 \pm 30) = 950 \text{ cal. mole}^{-1}$$

This value and the 888 cal. mole.$^{-1}$ value given above agree within the limits of error of the measurements. Taylor and Wells[5] made X-ray diffraction patterns of their various samples and found no change in crystal structure. They ascribed their results as due "mainly to differences in surface."

The Decomposition Pressure of $Mg(OH)_2$.—The principal purpose of this paper is to ask the following question: How often have experimenters recorded equilibrium data which did not correspond to the macrocrystalline properties of the phases present?

Giauque and Archibald[3] studied the decomposition pressure of $Mg(OH)_2$ with unusual care at 463.1 and 485.0°K., waiting as long as two weeks for equilibrium. The equilibrium pressures at these temperatures were approached from both below and above, with results which were identical to an unusually high degree of accuracy. Moreover, there can be no reasonable doubt that they obtained an equilibrium value for the phases present, since the entropy of $H_2O(g)$ calculated from their calorimetric and equilibrium data, and the third law of thermodynamics, agrees very closely

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[1] Torgeson and Sahama, THIS JOURNAL, **70**, 2156 (1948).

[2] Shomate and Huffman, *ibid.*, **65**, 1625 (1943).

[3] Giauque and Archibald, *ibid.*, **59**, 561 (1937).

[4] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[5] Taylor and Wells, *Bur. Standards J. Res.*, **21**, 133 (1938). R. P. 1121.

with the result which is known accurately from band spectroscopy.

Let us assume that the results of Torgeson and Sahama[1] had been available to Giauque and Archibald, and that the entropy of crystalline MgO had been used in their calculations, the resultant free energy would have differed by the following amount

$$\mathrm{MgO(crystals)} = \mathrm{MgO(fine\ powder)}$$

$$\Delta F = \Delta H - T\Delta S \qquad (4)$$

$$\Delta F_{474^\circ\mathrm{K}} = (\sim 900) - 474 \times (\sim 0.2) = 800 \text{ cal. mole}^{-1}$$

where F, H and S refer to free energy, heat content and entropy.

We have used 474°K. as the average temperature of the experimental results and have estimated roughly that the finely divided MgO had a larger entropy by about 0.2 cal. deg.$^{-1}$ mole.$^{-1}$

This means, that had the pressure of H_2O been calculated from the calorimetric results on the macroscopic MgO, decomposition pressures greater by some 130%, than the values which were observed with a reproducibility of 0.1%, would have been expected.

Discussion of the Results—The above facts cannot be explained by assuming that the H_2O was in equilibrium with surface material on particles, which had macroscopic thermodynamic properties inside, since all of the material was dissolved when the heat of solution was measured. Similarly the $\int_0^T C_p \, d \ln T$ corresponds to the average entropy per mole of interior and surface material.

We conclude that the MgO came to complete equilibrium throughout the particles and thus had the same free energy per mole in the interior as on the surface.

It is often assumed that the excess of some property such as heat content, heat capacity or entropy of a system with considerable surface can be allocated to the surface. This idea is based on the assumption that the substance in the interior has retained the properties of the substance in bulk. This assumption would certainly not hold in the present case. Strictly speaking it is never possible to consider the properties within a particle as separable from those of the surface material. If such an approximation is made, as a matter of convenience, the equilibrium proved in the present case implies that

$$F = H(\text{inside}) - TS(\text{inside}) = H(\text{surface}) - TS(\text{surface}) \qquad (5)$$

By a thermodynamic artifice it is possible to obtain an approximate value for the free energy of small drops of liquid. In this case consideration of the increase in free energy of the interior material due to pressure caused by the surface tension, leads to the well known formula, $dF = 2V\, d(\gamma/r)$ which gives the change of free energy with size.[6] V represents the molal volume, and r and γ are the radius and surface tension, respectively, of the drop.

A similar consideration may be applied roughly to the MgO particles leading to the equation

$$\Delta F(\text{in calories}) \times 4.8 \times 10^7 = 2\gamma V \text{ ergs}/r$$

$$V = 11.1 \text{ cm.}^3 \text{ mole}^{-1}$$

from which

$$\frac{2\gamma}{r} = \frac{800 \times 4.8 \times 10^7}{11.1} = 35 \times 10^8 \text{ dynes cm.}^{-2}$$

If one assumes spherical particles, this is equivalent to an inside pressure of 3500 atmospheres. We have no information concerning either γ or r of the finely divided material obtained in the equilibrium measurements. A search was made for a sample of the material used but it was probably discarded. It would have been interesting to obtain an electron-microscopic photograph of the material. If the particles were large enough to be seen in an ordinary microscope, they would have to possess some open type of structure, such as a loose aggregation of small units. It is difficult to see how such a reversible equilibrium, as that observed, could have been reached unless the unit particles had assumed something approximating a spherical shape.

It is, however, not any exact knowledge of particle dimensions which interests us here, but rather the fact that the usual tests of attainment in a chemical equilibrium are no guarantee that it corresponds, even approximately, to the thermodynamic properties of macroscopic phases.

It is not difficult to see why the dehydration of crystalline $Mg(OH)_2$ should produce particles of MgO which become detached before they reach macroscopic dimensions, and it is difficult to escape the conclusion that this is a fairly commonplace occurrence in other cases, although usually in lesser degree.

For example it seems probable that anhydrous salts, or the lower hydrates of salts, formed by the decomposition of multihydrated forms, in the absence of a solution, can be expected to produce finely divided material. The higher free energies of substances in this form should give lower decomposition pressures than do macroscopic phases.

(6) *E. g.*, "Thermodynamics and the Free Energy of Chemical Substances," Lewis and Randall, McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 252. Lewis and Randall make an impractical statement on p. 248 with respect to surface effects as follows: "If we start with a given amount of liquid and increase its surface, the molal free energy in the body of the liquid does not necessarily change, and if we maintain equilibrium the total free energy in the surface formed must be the same as in the body of the liquid. Therefore the molal free energy multiplied by the total number of moles remains constant, but the total free energy is increased by $\gamma d\sigma$." We believe that it is impossible to devise a procedure in which the surface, and thus the surface energy, of a system is changed, under equilibrium conditions, without an equivalent change in the free energy of the substance or substances of which the system is composed. The total free energy of any system at equilibrium is always equal to the free energy per mole times the number of moles, summed over all components.

When the equilibrium decomposition pressure is sufficiently close to the saturation pressure, so that adsorption is considerable, equilibrium may be facilitated among solid phases. However, when the dissociation pressure of water is very small compared to that of the saturated solution, the attainment of macroscopic equilibrium may be excessively slow, and a rather definite metastable equilibrium can exist as a consequence.

When very fine particles are themselves non-volatile, and lack a reconstituting mechanism, such as some equilibrium volatile compound which can transport material from them, they can only be expected to give equilibrium results consistent with their own free energy. At sufficiently high temperatures, sintering will produce macroscopic properties but the $Mg(OH)_2$ dissociation pressure would reach considerable values at temperatures below those required to sinter the MgO produced. We conclude that many measurements on systems involving equilibrium between gases and dry solid phases should be accepted with considerable caution in correlating thermodynamic data.

Summary

It is shown that the true dissociation pressure in the reaction $Mg(OH)_2(cry.) = MgO(cry.) + H_2O(g)$, as determined from the third law of thermodynamics, is some 130% higher than accurately measured values which were reproducible to 0.1%.

The above result is attributed to the colloidal nature of the magnesium oxide produced under equilibrium conditions.

Giauque and Archibald have shown previously that the third law gives accurate agreement with the measured equilibrium pressures, when the entropy and heat content are measured on the actual finely divided magnesium oxide in equilibrium. Thus the colloidal particles approached essentially zero entropy at very low temperatures and evidently approximated a perfect crystalline structure.

For the finely divided material obtained during equilibrium dissociation, MgO(cry.) = MgO (finely divided); $\Delta H_{25} = 888$ cal. mole.$^{-1}$

It is concluded that neither reproducibility of equilibrium measurements based on approach from each side nor agreement with the third law of thermodynamics, can be accepted as proof that an equilibrium corresponds to the thermodynamic properties of macrocrystalline phases.

It seems impossible to escape the conclusion that many equilibrium measurements involving gases and finely divided dry solid phases, produced by the evolution of gases, or formed by reaction with gases, do not correspond to the properties of macroscopic materials.

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The Infrared Spectrum of Dimethylcadmium

BY H. S. GUTOWSKY[1]

In a previous publication,[2] the infrared and Raman spectra of dimethylmercury and dimethylzinc were presented and interpreted as supporting a linear C–M–C structure of D_{3h}' symmetry, with essentially free internal rotation of the methyl groups. Similar data for dimethylcadmium are of interest in verifying this interpretation and in providing force constants which, with those for mercury and zinc, afford a basis for relating molecular properties to atomic parameters of the Group IIb metals.

Experimental

Preparation of Sample.—Attempts to produce dimethylcadmium by heating dimethylmercury with cadmium metal were unsuccessful. The sample used was prepared by Mr. A. R. Bader, under the direction of Professor E. G. Rochow, from cadmium iodide and methylmagnesium bromide in ether solution. Their coöperation in furnishing the sample is gratefully acknowledged. It was purified by bulb to bulb distillation in a vacuum system until it was infrared spectroscopically free from ether.

Infrared Spectrum.—The region from 430 to 650 cm.$^{-1}$ was observed with a KRS-5 prism in conjunction with a lithium fluoride mirror using the Harvard spectrometer.[3] The gaseous sample of dimethylcadmium was at its room temperature vapor pressure of 3.6 cm., in a 30-cm. cell with potassium bromide windows. The region from 625 to 5000 cm.$^{-1}$ was run at the same pressure in a 5-cm. sodium chloride cell on a Baird Associates spectrometer. The observed spectrum is summarized in Table I. Its general appearance is similar to that of dimethylzinc,[2] with the exception that the structure of the bands at 1140 and 1305 cm.$^{-1}$ in dimethylcadmium is not nearly as distinct as the corresponding bands in dimethyl zinc.

Frequency Assignment

A generally satisfactory frequency assignment has been made, using D_{3h}' symmetry. The Raman data of Fehér, Kolb and Leverenz[4] are in-

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[2] H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949).

[3] For a detailed listing of pertinent literature and the general methods used in this investigation see ref. (2).

[4] F. Fehér, W. Kolb and L. Leverenz, *Z. Naturforsch.*, **2a**, 454 (1947).