LETTERS TO THE EDITOR

Paramagnetic Saturation in a Single Crystal

Jean Becquerel and one of us developed a method, which allows one to study the paramagnetic saturation in the direction of the optical axis of crystals by observations of the Faraday-effect.[1] If the basic level is doubly degenerate, the magnetic moment belonging to this level in the direction of the axis can be determined from the curvature of the graph which represents the magnetic rotation as a function of H/T.

This method has been applied to several (mostly natural) crystals, but as yet no check with direction susceptibility measurements has been obtained, the only available data on saturation curves being measurements on crystal powders.[2]

We now have determined the magnetization of a monoaxial single crystal of dysprosium ethylsulphate as a function of temperature and field strength, in two directions: the optical axis and a secondary axis perpendicular to it.

We found that at the temperatures of liquid helium the magnetization curve in the first direction has the form of a hyperbolic tangent, with a magnetic moment of 5.7 Bohr-magnetons. This is in excellent agreement with the optical measurements, which gave 5.66 Bohr-magnetons. In the direction perpendicular to the axis a susceptibility of about 1.2×10^{-3} was found which was almost independent of the temperature, and which showed merely a beginning of saturation at the highest fields. This is exactly what is to be expected theoretically for a doubly degenerate basic level, if the crystalline field shows a deviation from cylindric symmetry. Whether the susceptibility varies in the plane perpendicular to the axis has not yet been investigated.

At higher temperatures other levels than the basic level are occupied. At 14° the susceptibilities differ about 10 percent, a beginning of saturation being observable in the direction of the axis; at 20° the difference is but 3 percent. At 64° the ratio of the susceptibilities has increased to 1.30. This ratio slowly increases further to 1.33 at about 200°, and decreases then to about 1.25 at 290°. The susceptibility in the direction of the axis is always the larger. Between 20° and 290° the susceptibility perpendicular to the axis follows approximately Curie's law, with a magneton number of about $9\frac{1}{2}$ Bohr-magnetons. The susceptibility in the direction of the axis follows a more complicated law.

The investigations will be continued and extended and we also hope soon to give the accurate absolute values.

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[1] Comm. Leyden 193[a], 204[a], 211[b], 211[c], 218[a].
[2] Comm. Leyden 173[e], 222.

Molecular Rotation in Ice at 10°K. Free Energy of Formation and Entropy of Water

In two brief notes Mecke and Baumann[1a, b] have announced an interpretation of several of the rotation-vibration bands of the water molecule. With the assistance of these data we have made a preliminary calculation of the entropy and free energy of water by means of the Sackur-Tetrode equation. Although there are still small uncertainties in the molecular constants, we may nevertheless obtain quite accurate values. These and other values have been compared with the low temperature calorimetric measurements on ice. It has been possible to show that the facts are consistent with lack of equilibrium between ortho and para water in ice and indicate rotation of ortho water in ice.

Although small deviations occur in comparing the spectroscopic data with the relation $I_1 + I_2 = I_3$ which holds for the principal moments of inertia of planar molecules, we prefer to accept this equation with $I_2 = 1.907 \times 10^{-40} \mathrm{g \cdot cm^2}$ molecule^{-1}, and $I_3 = 2.985 \times 10^{-40}$. The absolute entropy of gaseous water is found to be 47.92 cal.$\cdot$deg.$^{-1}\cdot$mole^{-1} at 298.1°K and 1 atmosphere. In making this calculation the symmetry number of water was taken as 2. The entropy value which corresponds to that usually used in thermodynamic calculations, namely the absolute entropy less the effect of nuclear spin, is found to be $47.92 - R \ln 4 = 45.17$ e.u.

Combining this value with H_2, $S_{298.1} = 31.23$ e.u.[2] and O_2, $S_{298.1} = 49.03$ e.u.[3] we obtain $\Delta S_{298.1} = -10.58$ e.u. Rossini[4] gives $\Delta H_{298.1} = -68,313$ cal.$\cdot$mole^{-1} for the formation of liquid water from the elements. For gaseous water

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[1] Mecke and Baumann (a) Naturwiss. **20**, 657 (1932). (b) Phys. Zeits. **33**, 833 (1932).
[2] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).
[3] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).
[4] Rossini, Bur. Standards J. Research **6**, 1 (1931).

$\Delta H_{298.1} = -57,823$ cal.·mole^{-1}. Thus for $H_2 + \frac{1}{2}O_2 = H_2O$, $\Delta F_{298.1} = -54,669$. This may be compared with the value $\Delta F_{298.1} = -54,676$ calculated by Eastman[5] from the reactions $HgO = Hg + \frac{1}{2}O_2$ and $HgO + H_2 = Hg + H_2O$.

In addition we obtain values from the equilibrium data of von Falkenstein[6] and of Korvezee[7] on the reaction $2HCl + \frac{1}{2}O_2 = H_2O + Cl_2$. These data have been combined with Rossini's calorimetric heats of formation of H_2O [4] and of HCl [8] from the elements and with the free energies of HCl, Cl_2 [9] and O_2 [10] obtained from spectroscopic data. The preliminary values are $H_2O(g)$, $S_{298.1} = 45.1 \pm 0.1$ e.u. and $\Delta F_{298.1} = -54,650$.

From the low temperature heat capacity measurements on ice by Simon[11] combined with the well-known heats of fusion and vaporization the entropy of the gas at 298.1°K and 1 atmosphere is calculated by the usual third law method to be 44.23 e.u. The heat capacity measurements, which are very reliable, extend to 10°K and were extrapolated below this temperature. The large difference between the values is believed to be due to the persistence of rotation of water molecules in ice below 10°K.

Near its melting point ice has a dielectric constant[12] comparable with the very high value obtained for liquid water. As the temperature is decreased to about 100°K, the dielectric constant decreases to the low values which might be expected of a nonpolar substance. This is evidently due to loss of rotation of the electric moment, as would be expected from the interaction of the dipoles. However, clockwise and counterclockwise rotations about the symmetry axis of the molecule involve no rotation of electric moment and would be expected to persist to much lower temperatures.

As in other molecules with two identical atoms having nuclear spin, water consists of two noncombining types of molecules. The analysis of Mecke and Baumann shows that the rotational level characterized by $j = 0$, is symmetric with respect to rotation for the ground state. From this it follows that when water is cooled to sufficiently low temperatures, lack of equilibrium will leave $\frac{3}{4}$ of the molecules with $j = 1$, while $\frac{1}{4}$ will have $j = 0$. The nonpolar rotation mentioned above would apply only to the molecules trapped in the state $j = 1$. Thus if this rotation persists at 10°K, a correction of $\frac{3}{4} R \ln 2 = 1.03$ should be added to the entropy obtained from the heat capacity measurements. The corrected third law value then is $S_{298.1} = 44.23 + 1.03 = 45.26$ e.u. in excellent agreement with the values given above. The resultant value of $\Delta F_{298.1} = -54,696$.

Several additional methods of investigating the lack of equilibrium and its accompanying phenomena are immediately obvious. Work on the equilibrium reaction $MgO + H_2O = Mg(OH)_2$ and on several crystalline hydrates has been in progress for sometime by a group in this laboratory. Experiments have been started on the effects of allowing ice to remain at low temperatures for varying periods of time. The first experiments will cover observations on the melting point. Optical observations and further heat capacity measurements at low temperatures are other methods of approach.
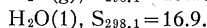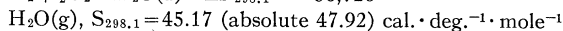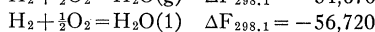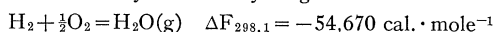
For comparison the several values given above are tabulated in Table I.

TABLE I. *Free energy of formation and entropy of gaseous water.*

$\Delta F_{298.1}$ cal.·mole^{-1}	$S_{298.1}$ cal.·deg.$^{-1}$·mole^{-1}	
$-54,669$	45.17	Band spectra
$-54,676$	45.19	$H_2 + HgO = Hg + H_2O$, cell
$-54,650$	45.1	$2HCl + \frac{1}{2}O_2 = H_2O + Cl_2$, equilibrium
$-54,696$	45.26	Third law of thermodynamics

More exact calculations on the above and on several other reactions involving water at high temperatures are in progress.

Preliminary values may be given as

$H_2 + \frac{1}{2}O_2 = H_2O(g)$ $\Delta F_{298.1} = -54,670$ cal.·mole^{-1}
$H_2 + \frac{1}{2}O_2 = H_2O(l)$ $\Delta F_{298.1} = -56,720$
$H_2O(g)$, $S_{298.1} = 45.17$ (absolute 47.92) cal.·deg.$^{-1}$·mole^{-1}
$H_2O(l)$, $S_{298.1} = 16.9$.

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[5] Eastman, Circular 6125 U. S. Dept. Comm. Bur. of Mines.

[6] von Falkenstein, Zeits. f. physik. Chemie 59, 313 (1907).

[7] Korvezee, Rec. trav. chim. 50, 1092 (1931).

[8] Rossini, Bur. Standards J. Research 9, 583 (1932).

[9] Giauque and Overstreet, J. Am. Chem. Soc. 54, 1731 (1932).

[10] Johnston and Walker, J. Am. Chem. Soc., in press.

[11] Simon, Handbuch d. Physik X, 363.

[12] Int. Crit. Tab. 6, 79.

The Plasticity of Rocksalt and Its Dependence upon Water

For years it has been known, that, if rocksalt crystals be placed in water and allowed to remain there for a short while, they become quite plastic. Also their tensile strengths when measured while in this plastic condition are found to be abnormally high (Joffe effect), sometimes 10 times as high as the values found before the crystals were made plastic. These peculiarities of rocksalt have furnished the themes for a great number of investigations, which have been carried on chiefly in Germany and in Russia. The German group of investigators may be said to be headed by Polanyi and Ewald, and the Russian group by Joffé.

As a result of these varied experiments two distinct views are being entertained regarding the action of the water upon the salt and the mechanism of the resulting increases of plasticity and of tensile strength. One view, that taken by Joffe, is that the water simply heals up the many minute fissures which are upon the dry surfaces of the crystals. With these fissures closed up, that is, with perfect surfaces, premature breaking or tearing is pre-