

$\Delta H_{298.1} = -57,823$ 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 Eastman⁵ 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 Falkenstein⁶ and of Korvezee⁷ 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 Simon¹¹ 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 constant¹² 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.

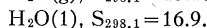
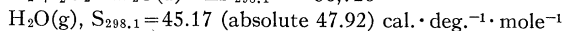
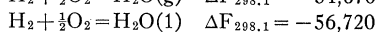
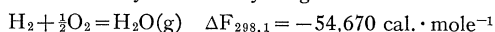
For comparison the several values given above are tabulated in Table I.

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



W. F. GIAUQUE
MURIEL F. ASHLEY

Department of Chemistry,
University of California,
Berkeley, California,
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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-

vented and as a result the salt is more plastic than when dry and has a strength more nearly approaching the calculated values. According to the other view, the water is supposed actually to enter into the crystal lattice, and, acting perhaps as a lubricant, make the crystal more plastic. Then as a result of any plastic deformation or "working" of the crystal which has thus been made possible, a sudden increase in the tensile strength sets in. The water causes the plastic limit to be lowered below the breaking point, and a subsequent deformation produces the increase in the strength of the crystal.

The fact that the water is supposed to act upon the salt either upon the surface of the crystal or within its interior, suggests a new method of approach to this problem. This consists simply in making a piece of salt plastic, removing its surfaces, and then testing by means of infrared absorption for the presence of water in the remaining piece of salt. A prism of salt, about $5 \times 12 \times 40$ mm, is made plastic in water, removed and its surfaces thoroughly dried. It is then coated with molten paraffin and its two ends split off leaving the crystal about 30 mm long and with fresh cleavage planes for ends. Assuming that rock-salt is transparent in the near infrared and that the two ends (fresh cleavage planes) are free from water, the infrared transmission is measured from 1.5μ to about 4.0μ . If the water in making the salt plastic has acted only upon the surfaces (Joffe) no absorption should be found around 3μ where water has its strongest bands. If it has actually entered the crystal (Polanyi and Ewald) the absorption of the water must show up and be proportional, roughly at least, to the length of the salt crystal

used. As a result of a long series of experiments upon some fifty-odd samples of salt, it has been found that plastic salt always shows definitely the presence of water within its interior, and, that the absorption is proportional to the length of crystal used.

It was found that crystals of salt taken from various sources reacted quite differently to tests of this kind. Some specimens even in their normal brittle condition contained a noticeable amount of water. Some became very plastic quite easily, while others would only become slightly plastic. A given sample was measured "dry" and no absorption found, and then again after having been made plastic or "wet." After heating this wet crystal in an oven for about 24 hours at 150°C the absorption which had been found while the crystal was wet could not be found. This piece of "dried" salt was again made wet and absorption again found. This process could be repeated a number of times. In each of these cases the presence or absence of the water absorption depended only upon the degree of brittleness or plasticity of the salt. The presence of water on the inside of the crystal is characteristic of the plastic condition. It is believed that the water actually enters the crystal along the crevices between the minute mosaic blocks postulated by Zwicky and Smekal for crystals of this type. A further discussion of this problem and the results obtained will appear in a later number of this journal.

R. BOWLING BARNES

Johns Hopkins University,
Baltimore, Maryland,
December 9, 1932

An Anomaly in the Columbium K Absorption Limit

During some work on the matching of the transmission curves of various pairs of thin metallic foils for x-rays a peculiar curve was observed at the K absorption edge of columbium. The shape of the foot of the K absorption edge of columbium was very different from that of rhodium, palladium, silver, cadmium, molybdenum.

The accompanying curves are a plot of a transmitted continuous spectrum as a function of the wave-length; thus a low ordinate corresponds to a high-absorption coefficient, and a high ordinate represents a low-absorption coefficient. The molybdenum curve shows a perfectly normal K absorption edge and is similar to the curve obtained from each of the other elements investigated except columbium. The dotted line shows the curve normally expected of columbium, judging from similar curves of the other elements; but as it appears in the diagram, the actual curve is anomalous.

The anomalous part of the curve was run on two different days. In order to be sure there was nothing peculiar about the impinging beam or the outfit, the two curves were taken simultaneously alternating between molybdenum and columbium for each setting of the spectrometer. Anything peculiar to the outfit or impinging beam would have shown up in the molybdenum curve. (Fig. 1.)

CECIL J. BURBANK

Department of Physics
Stanford University, California
December 7, 1932

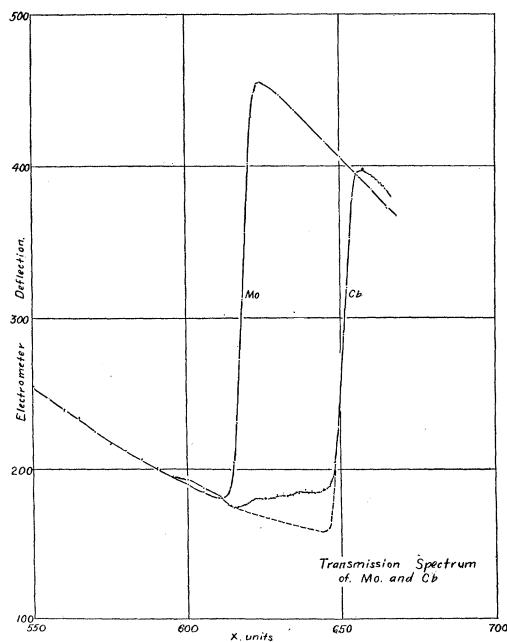


FIG. 1.