lieve, to absorption of H_2O from the glass and from unavoidable contamination with the atmosphere. We estimate that these values of ΔH_B are at least ten calories too low, since the D_2O remained in the apparatus for forty-eight hours, although closed to the atmosphere, except during addition of potassium chloride and stirring. At the conclusion of the experiments S^{25}_{25} = 1.10641 or 98.6% D_2O; Δt = 3.760 (calcd.).

The discrepancy between our experimental value and that calculated by the Seltz equation may be due to the fact that the latter treatment neglects the role of the equilibrium, $H_2O + D_2O = 2HDO$.[10]

[10] E. S. Gilfillan, Jr., THIS JOURNAL, **56**, 2201 (1934).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Transition Point of Sodium Sulfate Decadeuterate

BY HUGH S. TAYLOR

The transition point of sodium sulfate, a quadruple point involving sodium sulfate decahydrate, the anhydrous salt, saturated solution and vapor has been shown by Richards and Wells[1] to be 32.383 ± 0.001° on the International hydrogen scale of temperature. They concluded that this fixed point was equally as reliable as the ice point and more reliable than the boiling point of water unless the most careful precautions were exercised in the latter case. The extraordinary reproducibility of the transition point was attributed to the very small influence of the external pressure, the ready purification of the substance and "the certainty of obtaining a definite crystal form and homogeneity probably greater than with water, because, in the crystal growth, it is far easier to obtain independent and freely growing crystals."

The discovery of the isotopic forms both of hydrogen and of oxygen has revealed that a fourth parameter is involved in the reproducibility of such fixed points, namely, the constancy of isotopic concentration ratios of the several elements in the system under study. The isolation of deuterium oxide revealed that a disturbance of the hydrogen isotope ratio might produce deviations from the ice point amounting to 3.82°.[2] It was of interest, therefore, to ascertain the corresponding variation in the transition point of sodium sulfate when deuterium oxide was the solvent used. We have accordingly determined this transition point, producing the material from anhydrous sodium sulfate and deuterium oxide in the weight ratios given by Na_2SO_4 and $10D_2O$. The water used had a density d^{25}_{25} 1.10784, and was, therefore, better than 99.9% pure D_2O. It is probable that, in this water, prepared by the electrolytic process, the oxygen isotope ratio was normal since, in each stage of the electrolysis, this ratio should have been normalized to that of the carbon dioxide gas which was used to convert alkali hydroxide to carbonate. A thermometer reading in 0.1° was used and calibrated by means of the sodium sulfate decahydrate transition. Experiment showed that the deviation produced in the transition point was 2.10° and that the transition point with the deuterium oxide as solvent was 34.48 ± 0.02°. It is of interest to note that the magnitude of the deviation, approximately one-half that obtaining at the ice point, is sufficiently small that, assuming proportionality between deuterium concentration and deviation, the transition point of sodium sulfate in pure protium water solutions would be within the accuracy of the determination of Richards and Wells. With water from the equilibriated electrolyte in hydrogen–oxygen cells, containing one atom of deuterium to approximately 1600 of hydrogen, the deviation from 32.383° in the transition point would again be scarcely outside the limits of accuracy set by the original investigators. The data cited by Gilfillan[3] for the freezing point of $H^1_2O^{18}$, −0.1 ± 0.05°, indicate quite definitely that disturbance of the oxygen isotope ratio will be equally ineffective in significantly altering the value of the transition point.

Summary

The transition point of sodium sulfate in pure deuterium water has been found to be 34.48°.

The influence of isotope ratio on the accepted value for the sodium sulfate decahydrate transition has been discussed.

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[1] Richards and Wells, *Z. physik. Chem.*, **43**, 465 (1903).

[2] Taylor and Selwood, THIS JOURNAL, **56**, 998 (1934).

[3] Gilfillan, THIS JOURNAL, **56**, 2201 (1934).