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Thermal expansivity and refractive index determinations for some hydrosol systems and their similarity to properties ascribed to "anomalous" water

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THERMAL EXPANSIVITY AND REFRACTIVE INDEX DETERMINATIONS FOR SOME HYDROSOL SYSTEMS AND THEIR SIMILARITY TO PROPERTIES ASCRIBED TO "ANOMALOUS" WATER

BY

GERALD WAYNE CHAPPUE, 1947-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN PHYSICS

1971

Approved by

James L. Kassner, Jr. (Advisor) Barbara F. Hamell

Charles Hatfield

ABSTRACT

The characteristic thermal expansion and refractive index of aqueous dispersions of SiO_2 and NaOH were determined for samples contained in quartz micro-capillaries. Comparison is made with the expansivity and refractive properties of anomalous water or polywater as reported by other investigators. The similarity between the properties and behavior of various hydrosol systems and those ascribed to anomalous water is cited as a serious challenge to the hypothesized existence of an allotropic modification of water.

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Barbara Howell, Thesis Advisor

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I. INTRODUCTION

Water exists wherever there is life. Indeed we do not know of life where water is not present. For creatures like ourselves, water is the most crucial of chemical compounds since the human body is no less than 90% water. The importance of this substance, the most abundant compound in nature, is undeniable and this fact has not gone unnoticed.

During the past several years the scientific community has devoted increasingly larger amounts of time and effort to a study of water, partly because of the profound role water plays in biogenesis and evolutionary mechanisms as well as its involvement in the most intimate and crucial life processes. Increased concern for water has also been derivative from the meteorological, oceanographical, and vast ecological problems which face a people whose survival is dependent upon its aquisition and utilization of water.

The properties of water have been so uniquely determined that three basic units of measurement based on these properties have been established and given international acceptance:

(1) Mass. The gram is defined as the mass of one cubic centimeter of water at 4°C.

(2) Temperature. The Celsius (Centigrade) degree is one hundredth of the interval between the freezing and boiling temperature of water at one atmosphere of pressure.

(3) Heat. The calorie is defined as the amount of heat necessary to raise the temperature of one gram of water by one degree Celsius.

Our knowledge of the molecular configuration of the single water molecule is rather complete. In the vapor phase, water is essentially a monomeric system with occasional dimers and trimers.[1] Similarly, the structure of ordinary ice is rather well understood. The molecules of ice 1_h form what is essentially a single polymer molecule in which the oxygen acts as if its valence were four, similar to carbon atoms in diamond.[2]

Unfortunately, when the liquid state of water is considered, the situation is entirely different. The present understanding of the structure of liquid water is incomplete and inadequate. Intense controversy has existed in this area for some time, and seeming paradoxes characterize the field. One such puzzling question, which has received recent widespread attention and is the subject of this paper, is whether or not there exists an allotropic modification of water, described in the literature as *anomalous* water.

Considerable effort has been expended by researchers in this laboratory to understand and describe this supposedly allotropic form of water. As part of this effort, the author has found the characteristic thermal expansion and refractive index of various hydrosols and compared these findings with the behavior ascribed to anomalous water.

II. HISTORICAL OUTLINE OF RESEARCH CONCERNING MODIFIED FORMS OF WATER AND THE ENSUING CONTROVERSY

Within the investigations of water and its properties mentioned above, there have been over the years an increasing number of observations and measurements which were so unusual that they were not in accord with any of the several current theories and consequently tended to be disregarded until recently. These stubborn observations appear occasionally throughout the literature and form a necessary prelude to an understanding of the present controversy.

A. EARLIEST INVESTIGATIONS OF ANOMALOUS PHENOMENA

Lear[3] reports that an American scientist, Walter Patrick, working during the 1st World War, made very significant advances in developing a defense against the lethal gas introduced as a battlefield weapon by Germany. The device he invented used silica gel, an absorbent material that trapped various liquids, vapors, and gases. Post-war research by Patrick led him to do experiments on the removal of trapped water vapor from the gel by evaporation. Patrick observed that some of the water trapped in the micro-confines of silica gel remained in the gel in a liquid state at temperatures significantly above the temperature where water normally becomes a vapor. This unusual behavior of liquids within narrow confines such as those in silica gel became the topic of a doctoral thesis written by one of Patrick's students, a Russian immigrant named J.L. Shereshefsky.[4]

Shereshefsky's thesis, published in 1928, described his experiments in which he found that the vapor pressure of water contained in micro-capillaries was significantly lower than expected, even after taking into account corrections for the curvature of the container.

Shereshefsky's observations, Lear[3] reports, were largely ignored until, in 1937, a Soviet investigator, K.M. Chmutov, announced in the Soviet literature that he had repeated the earlier experiments using a flat plate and a curved lens instead of micro-capillaries and had obtained similarly inexplicable results. Both Shereshefsky and Chmutov published other papers which were to be ignored until 1962, when a paper by a chemistry student, N.N. Fedyakin[5] of the Institute of Light Industry in Kostroma, appeared in the Soviet *Colloid Journal* . In the paper, entitled "Changes in the Structure of Water During Condensation in Capillaries", Fedyakin described his discovery of *offspring* or *daughter* columns that formed in ultra-fine capillaries at the expense of a *mother* column of pure ordinary water. The offspring, Fedyakin reasoned, could not be identical in its properties with those of the mother; the transfer of the liquid itself indicating the saturated vapor pressure over the offspring must be lower than the pressure over the original column. In the same paper, Fedyakin described preliminary thermal expansion experiments on the anomalous daughter columns providing data for the thermal region 0-30 °C in which he observed that the expansion was approximately 1.5 times that of normal water. These experiments were conducted on samples contained in micro-capillaries of pyrex or quartz for which the volume expansion relative to that of water was negligible allowing the determination of bulk expansion by linear measurement.

At the invitation of B.V. Deryagin of the Institute of Physical Chemistry, Academy of Sciences U.S.S.R., Fedyakin went to Moscow to collaborate with Deryagin in the Division of Surface Phenomena which Deryagin headed. Experiments continued within Deryagin's laboratory and the papers which resulted were given neither wide distribution nor a serious consideration by most scientists. Then in July of 1967, Deryagin was invited to present a paper at the Gordon Research Conference on the Chemistry of Interfaces at Meriden, New Hampshire and chose to speak on his investigation with Fedyakin, et al. of a strange substance which by then he had begun to call *modified* water. According to Deryagin, modified water displays other unusual behavior besides the lowered vapor pressure and increased linear expansion coefficient. Modified samples examined in his laboratory reportedly had a boiling point far above that of ordinary water, and in addition, refused to freeze no matter how low the temperature dropped. Lear[3] reports that the paper was not met with apathy, but rather started a controversy which sent perhaps a third of the conference members to their own laboratories to duplicate Deryagin's work. Many simply refused to take Deryagin seriously, others were more than skeptical and still others were determined to vindicate the Russian's work by their own experiments. The lines were thus drawn for the ensuing controversy. Now, some four years later, there are still members in both camps, with some few having reversed their positions. Those who support Deryagin now think that a polymer of water has been discovered whose physical properties differ from those of ordinary water as radically as do the properties of polyethylene from free ethylene gas molecules. Most opponents to this hypothesis claim that the experimentally observed properties of modified water result not from polymer bonding, but rather from impurities and contaminants present in the samples.

B. MANUFACTURE OF MODIFIED SAMPLES

The samples prepared by Fedyakin[5] were the result of the first deliberate attempts to manufacture a modified species of water for investigation. His subsequent collaboration with Deryagin resulted in the development of an apparatus[6] designed to facilitate the production of modified samples. The apparatus consisted of a double-walled cylindrical glass vacuum chamber with an optically flat observation window at one end. A reservoir, which could be maintained at a different temperature than the coolant circulated between the double walls of the chamber, held the liquid sample under investigation. Thermocouples within the chamber and reservoir allowed continuous thermal monitoring and vapor pressure determination.

With vapor pressures in the range of 95 to 98%, Deryagin reported that columns appeared within a fraction of an hour after air was evacuated from the chamber. By releasing and reforming the vacuum inside the chamber repeatedly, columns were seen to form in the majority of the capillaries.[6] Deryagin noted, however, that if a capillary was wetted with a thin layer of ordinary water, the effect was that of poisoning and columns could not be made to form. This, he reasoned, occured since there was no vapor contact with the quartz surface which he felt played a determining role in the initial stage of formation of the anomalous condensate.[6,7]

Most samples manufactured in the Russian laboratory, as well as many of those produced by researchers in England and America, have been produced in apparatus similar to that described above. More commonly now, a simple modification which employs an inexpensive vacuum desiccator instead of the specially constructed chamber is being used by non-Russian investigators. In particular, Howell of this laboratory used several such vacuum desiccators for sample preparation. To counter charges of apparatus-handling contamination, plastic vacuum desiccators designed to eliminate silicon greases were used as well as specially constructed wire supports on which the capillaries were suspended in order to minimize the contact between capillaries and their container.

Other methods for producing modified water samples have been used by a few investigators. For example, Page and Jakobsen[8] of Battelle Memorial Institute have had some success with 2mm. diameter capillaries which are one to two orders of magnitude larger than those used in other laboratories. Fowkes and Lovejoy[9] of Lehigh University did not use capillaries at all, but rather 100-mesh fused silica powder which had been cleaned, heated, and vacuum sealed in flasks was used to produce samples reportedly as large as 1 gram. In this laboratory, Howell[10] worked with Cab•O•Sil, a commercial preparation of SiO_2 manufactured by the Cabot Corporation which has a negligible impurity level and a high surface area. Use of Cab•O•Sil resulted in the production of samples closely resembling those made in capillaries by her and other investigators.

Although critical attention was given to ambient conditions during production of the modified samples in the early work of Deryagin,[6,11] subsequent investigations led him to report that short periods of supersaturation before the undersaturated equilibrium conditions were established induced formation of columns in a much larger percentage of the chambered capillaries. Similarly, Brummer and Cocks[12] of Tyco Laboratories reported that sudden variations in the ambient conditions induced the appearance of modified columns more predictably than did carefully controlled capillary environments.

C. ALLEGED PHYSICAL PROPERTIES AND CHARACTERISTIC BEHAVIOR OF MODIFIED SAMPLES

An overview of the literature describing the findings of various investigators will serve to further identify the modified substance which is the subject of this paper. As stated above, most laboratories employed similar methods and apparatus in the production of the anomalous or modified samples. Subsequent quantitative measurements were often performed on equipment specially designed in the individual laboratories for the immediate experiment.

1. VAPOR PRESSURE

The earliest experiments of Fedyakin,[5] in which he noted the growth of daughter columns of liquid in sealed capillaries at the expense of a mother column, led him to infer that the vapor pressure of the modified samples was significantly lower than that of ordinary water. To estimate equilibrium vapor pressure, Deryagin, et al.[6,13,14] made graphs of the dependence of the rate of change of column length upon the relative vapor pressure p/p_s , where p is the ambient vapor pressure and p_s is the equilibrium saturation vapor pressure of ordinary water. The point of intersection of the extrapolated functions with the vertical axis at 0°C gives the equilibrium value p_a/p_s , where p_a is the equilibrium vapor pressure of anomalous or modified water. For modified columns produced in the apparatus described above, Deryagin reported p_a/p_s =0.93. Deryagin noted that p_a/p_s

values obtained in their laboratory did not exhibit any appreciable dependence upon capillary radius, indicating that the reduced vapor pressure was truly a bulk phenomenon in the modified samples. Deryagin[15] felt, however, that the lack of dependence upon capillary radius of p_a/p_s values indicated that the capillary walls essentially acted to ensure the appearance of a nucleus for the growth of modified columns. He also suggested the possibility that an absorption layer of some definite structure and thickness might serve as such a viable nucleus.

Fedyakin[5] noted in his early work that columns of condensate with depressed vapor pressures were also found to form when condensation of the vapors of methyl alcohol, acetic acid, and acetone occurred. In later work, Deryagin, et al.[6,16-22] characterized the modified water samples as a two-component system consisting of ordinary water and of a second, anomalous component which was found to be practically non-volatile at room temperature.[6,16,17] This property of essential non-volatility for the anomalous samples at room temperature was utilized both for component separation by distillation as well as determination of the equilibrium vapor pressure of water vapor above the surface of modified samples.[18,23]

2. VISCOSITY

Viscosity determinations were made from measurements of the velocity of sample column movement within a capillary under the action of a small pressure gradient. Using this method, Deryagin[2,7,24] reported viscosities elevated many times above those expected for ordinary water and consequently he argued that such an increase coupled with the sharply depressed vapor pressure is difficult to understand without assuming that it arises from a modified liquid structure for the water samples.[6]

3. REFRACTIVE INDEX

For their earliest attempts to determine the refractive index of modified samples, Deryagin, et al.[2,11,20] employed a capillary micro-method which measured the refraction of light passing through capillaries containing modified columns. Values ranged from 1.335 for very slightly modified samples to 1.48-1.5 for samples of greatest modification; this compared to the value of 1.33 for ordinary water demonstrates the degree of modification of samples. Lippincott, et al.[25] of the University of Maryland, using samples produced in their own laboratory, also reported a refractive index of 1.48 by matching the sample to liquids of known refractive index. Fedyakin, et al.,[26] Lippincott, et al.,[25] and Willis, et al.[27] reported that a portion of their modified samples were birefrigent with a refractive index somewhat lower than that cited above.

4. DENSITY

Owing to the extremely small quantities (one micro-gram or less[2]) of modified samples available, considerable difficulty was experienced by Deryagin, et al.[6,19,28] when attempting to determine the characteristic density. A column of ethylene tetrachloride and vaseline oil was prepared and allowed to stand until a vertical density gradient formed (the density ranged from 0.97 at the top to 1.50 at the bottom). The column was calibrated with standard salt solutions of known density and then modified samples were forced from their capillaries into the density gradient column. Claiming an accuracy of approximately 0.1%, Deryagin reported modified samples with density values of 1.2 to 1.4 g/cm^3. Assuming that the molar refraction of modified samples is the same as that of normal water, Lippincott, et al.[25] calculated the density of their samples of greatest modification from the Lorentz-Lorenz equation and arrived at the value of 1.39 gm/cm^3, in close agreement with the maximum value reported by Deryagin, et al.[2,11,29]

5. SURFACE TENSION

In an effort to refute the hypothesis that organic compounds give rise to the alleged properties of modified samples, Deryagin et al.[2,21,28] measured the surface tension of samples of varying degrees of modification. Their results showed that significant increases in the surface tension (values exceeding that of ordinary water by several percent) resulted for modified samples, even for those with only slight modification. For example, in samples containing concentrations of modified water on the order of 20%, the surface tension was increased by three percent.[2]

Deryagin used his surface tension data to argue strongly that the properties of modified water can not be attributed to small concentrations of organic impurities. Most such impurities are surface-active and would tend to depress the surface tension rather than elevate it; those organics which are surface-inactive could change the surface tension only slightly. Deryagin[21,28] argued that only a few substances could elevate values of the surface tension by as much as three percent and then only if they were present in high concentrations (cf. also Zhvirblis quoting Rebinder[29]).

Deryagin[2] suggested that the elevated surface tension explained another of the puzzling behavior displayed by some of the modified samples. Deryagin reported that according to Zakhavayeva of his laboratory, if a column of modified water exists close to either of the open ends of a capillary placed in an atmosphere of unsaturated water vapor, the column slowly begins to move toward that end, gradually gaining velocity, and has been observed even to spring out of the capillary itself.

6. PHASE SEPARATIONS

Another unusual phenomenon cited by various investigators is the appearance of distinct phases coexisting in the modified column below 0°C. In early work, Deryagin, et al.[6,11,16,17] reported the appearance of two distinct phases in their microscopic observations at sub-zero temperatures. The investigators subsequently reported that the column seemed to contain droplets of one liquid inside another forming a unique emulsion of water in water.

Further investigation showed that the second phase which appeared as droplets was solid rather than liquid. Deryagin[22] then theorized that modified samples at negative temperatures separated into a liquid phase, being a saturated solution of ordinary water in the anomalous or modified component, and a solid phase which was apparently solidified solvent. No such separation occurs for the most highly modified samples which instead undergo a transition to a glassy state at -30 to -40°C.[22,28] Modified samples produced at Los Alamos Scientific Laboratory by Rabideau and Florin[30] were reported to have displayed similar phase separations in the temperature region described above. Willis, Rennie, Smart, and Pethica[27] of Unilever Research Laboratory also reported that samples manufactured in their laboratory demonstrated phase separations at low temperatures not unlike those of the Russian scientists. The Unilever researchers also noted that some samples showed the two-phase appearance even at room temperature; others contained what appeared to be small crystals (cf. also Brummer and Cocks[12] and Everett, Haynes, and McElroy[31]).

7. THERMAL EXPANSION

Water is unique among liquids in the way that its molecular structure is evidenced in its physical properties. Certain of these structure-dependent properties are so radically different from those of other liquids that water is often characterized by these peculiar properties. Among the best known and most unusual in the anomaly concerning the thermal expansion, typified by a maximum density at 3.97°C. This anomalous expansion is generally acknowledged to be a result of the hydrogen bonded, diamond-like structure of ice I_h which has a lower density than liquid water and is not completely broken down in liquid water. One would expect dilute water solutions to retain this volume minimum in their thermal expansion curves. In the earliest work of Fedyakin[5] cited above where he reported the reduced vapor pressure of daughter columns formed in capillaries, Fedyakin also published preliminary data on the thermal expansion of those columns for positive temperatures between 0 and 30°C.

Plotting the relative increase in column length of a capillary-contained sample as a function of temperature, Fedyakin reported that the modified columns had an expansion coefficient approximately 1.5 times that of ordinary water in the range 0 to 30°C (cf. also Deryagin, et al.[6,14]). Suspecting that the micro-confinement of samples biased his observations, Fedyakin[32] experimented with capillaries of various sizes filled with ordinary water and looked for the characteristic expansion. Subsequent expansion curves demonstrated a pronounced radial dependence for capillaries smaller than about one micron (cf. also Deryagin[33]). For larger capillaries, the thermal expansion was the same as that for bulk samples, including the maximum density at 3.97°C.[2,15]

Thereafter, working with fused quartz capillaries of constant cross-section which have a negligible expansion coefficient over the thermal range considered, Fedyakin, Deryagin, et al.[11,15] determined the bulk expansion of modified samples by measuring the linear expansion of columns and computing the change in length divided by the length at 0°C, $(l-l_o)/l_o$. Further investigations were conducted by Deryagin, et al.[6,16] within the temperature interval from -100 to +50°C permitting a study not only of the thermal expansion, but also of the phase transitions and separations at negative Celsius temperatures.

Figure 1 shows a graph of the relative change in column length l in comparison with its length l_o at 0°C as a function of temperature t.[6] Curve *1* corresponds to a column of ordinary water, introduced into the capillary in liquid form. The sample demonstrated the expected expansion including the maximum density at 3.97°C and after supercooling crystallized into ordinary ice which melted at exactly 0°C upon heating. A modified column (curve *2*) produced by the condensation of incompletely saturated vapor in the capillary behaved very differently. The maximum density was shifted to the region of negative temperatures and the phase transition was markedly unlike that of ordinary water.

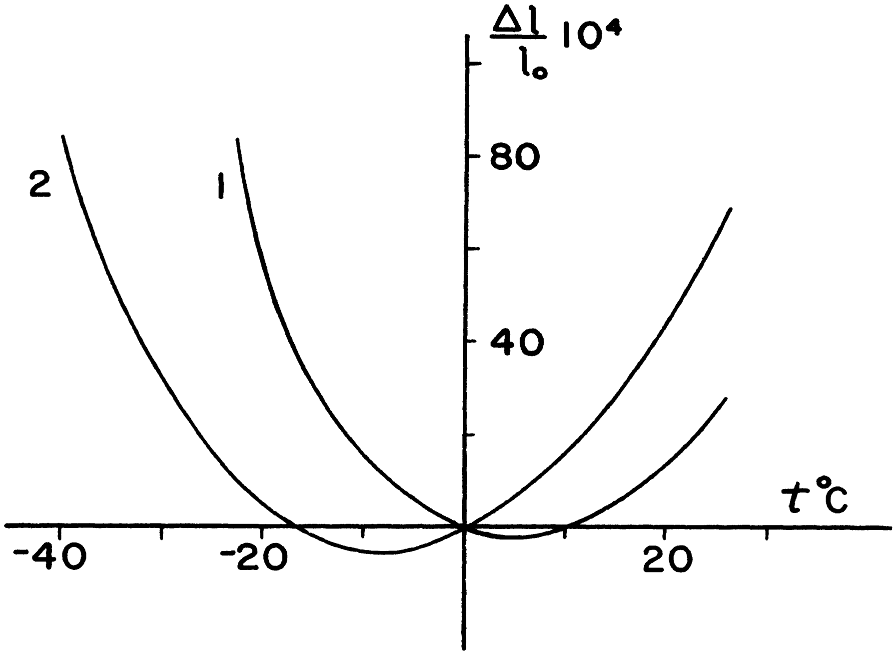

Figure 1. Thermal Expansion Curves for Ordinary Water and Modified Water (Ordinary Water, Curve *1*).

Although it is not shown in Fig. 1, Deryagin reported that at about -50°C, the modified column became turbid and experienced an abrupt elongation which was substantially smaller than that of ordinary water upon freezing. After the abrupt expansion the expansion curve becomes almost horizontal and the column length changes very little both upon further cooling and upon heating by 10 to 20°C. When the capillary is warmed to higher temperatures, the column length gradually begins to decrease along an increasingly steeper curve. Microscopic observation during this cooling and heating cycle revealed the separation into two phases at negative Celsius temperatures as described above. With increasing temperature, the number and dimensions of the droplike inclusions decreased as if they were melting away. Deryagin[2] reported that the solidified inclusions were pure ice, but because they existed in an environment of modified water, the last ice particles melted at a certain negative temperature rather than exactly at 0°C.

Figure 2 shows a series of thermal expansion curves for samples of water of various degrees of modification.[6,28] The hysteresis loops were attributed to the tendency of comparatively small volumes to supercool. The sample of greatest modification (curve *1*) possesses the greatest coefficient of expansion for temperatures greater than 0°C, exceeding the average coefficient of expansion of ordinary water in the same temperature interval by severalfold. The same sample exhibits no volume minimum or hysteresis loop but rather the expansion curve shows a sharp inflection at about -30°C and becomes almost parallel to the horizontal axis. The column of greatest modification shown in curve *1* was produced by prolonged evaporation under vacuum of a primary modified column (i.e. a column produced upon condensation of under-saturated vapors in quartz capillaries). Curves *2* and *5* represent subsequent dilutions of this column by allowing the column to contact ordinary water; curves *3*, *4* , *6*, are primary columns of differing degrees of modification; curve *7* is ordinary water.

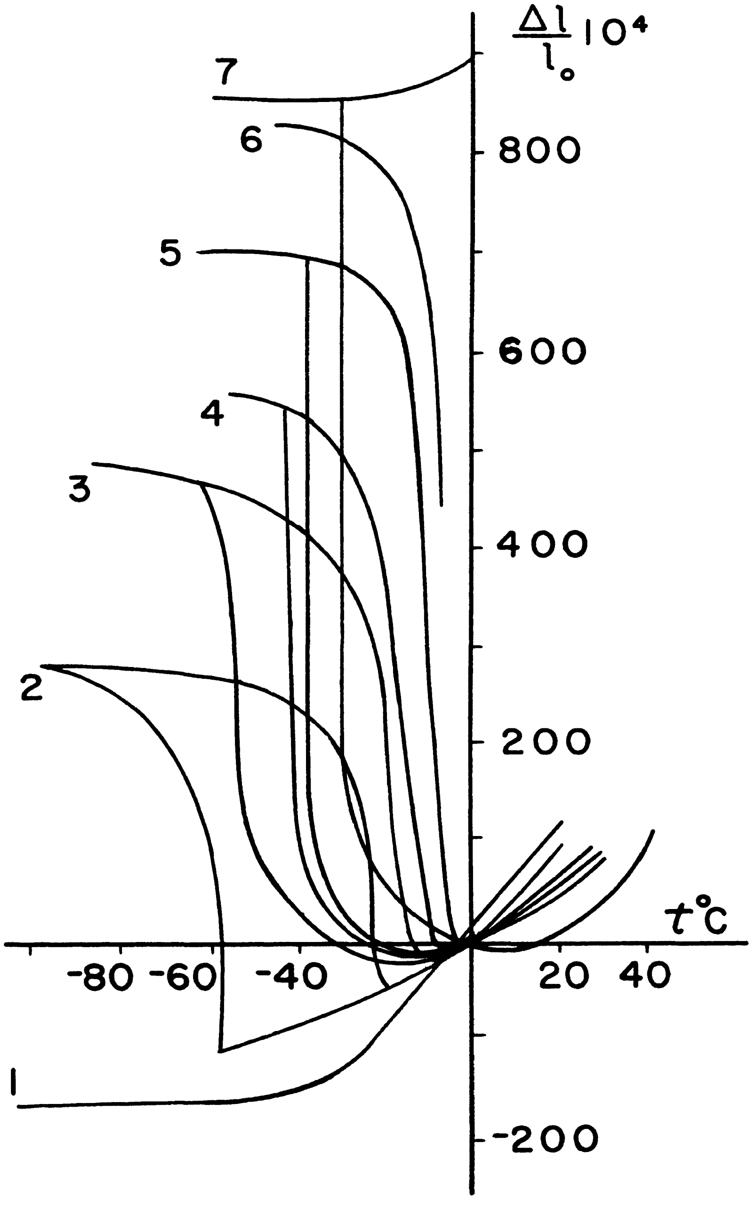

Figure 2. Thermal Expansion Curves for Modified Water with Different Concentrations of Anomalous Component (from 100% anomalous component, curve *1*, through 0% (ordinary water), curve *7*).

To investigate the stability of the physical properties of modified samples, in particular, the thermal expansivity, Deryagin, et al. tried heating samples to 400°C and holding them at that temperature for prolonged periods,[34] storing samples in capillaries for as long as one year,[28] and distilling samples from one end of a capillary to the other.[34] Subjecting modified samples to the above failed to cause a change in their properties. In the instance of distillation within a capillary, samples were distilled through a thermal barrier of 300°C or more to eliminate the possibility of film transfer along the capillary walls. Even this reportedly[34] did not alter the distinguishing features of the thermal expansion curves.

Observations such as those cited led Deryagin to conclude that modified molecules are stable and continue to exist even in the vapor phase. Further evidence of this was reported when the Russian investigators[2,34] found that distillation across a thermal barrier of more than 700-800°C resulted in a condensate whose properties were indistinguishable from those of normal water.

Fabuss[35] of Lowell Technological Institute ran extensive investigations on the thermal expansivity of modified samples and obtained data in close agreement with that of Deryagin, et al.. In particular, he identified the temperature of disappearance of the droplike inclusions during the warming branch of the thermal hysteresis loop to be -15 to -5°C, depending on the degree of sample modification. Willis, et al.[27] also produced columns with a thermal expansivity in good agreement with those of Deryagin et al.. Rabideau and Florin[30] reported that samples from their laboratory demonstrated a maximum density at negative Celsius temperatures close to those reported by the Russian investigators. For most samples, the temperature of maximum density was reported to be between -5 and -11°C, with the lower temperatures obtained for partially concentrated samples.

8. MOLECULAR WEIGHT

Using a cyroscopic technique and hypothesizing that modified water was a two-component system consisting of ordinary water and of a second, anomalous component, Deryagin, et al.[18,22] estimated the molecular weight of this anomalous component. The method makes use of the equation $\mu_a = (KCA)/\Delta t$ in which $\Delta t = t_b$, the temperature of final melting; $K = 1.86$, the cyroscopic constant of water; $C = 10^3$, a proportionality constant; and μ_a is the molecular weight of the anomalous component. The ratio, $A = m_a/m_n$ (m_a and m_n are the masses of anomalous and normal components respectively in modified water) is found from measured volume changes during melting and known density values. This method yielded a value for the average molecular weight of the anomalous component of approximately 180, which was proposed as a first estimate (an upper estimate) in need of refinement but which serves to underline the fact that modified or anomalous water differs significantly from normal water. Later work by Deryagin, et al.[2,23] utilized Raoult's Law which Deryagin had previously shown was applicable for p/p_s greater than or equal to 0.94 (where p is the equilibrium pressure of water vapor above the surface of a modified sample; p_s is the pressure of saturated vapor at test temperature). The reduction of the vapor pressure of a modified sample containing a known amount of the anomalous component was measured and yielded average molecular weight values of the anomalous component of 200 ±50 and 180 ±50. Commenting on the fact that mass spectrometric investigations on positive ions have not yet revealed the presence of polymer molecules,[27,36] Deryagin[28] proposed that modified water complexes degrade to monomer when charged by the electron beam in the mass spectrometer and cited the 700-800°C dissociation temperature reported above in support of his hypothesis (cf. also Zhvirblis[29] quoting Tal'roze). Using Raoult's law, Brummer and Cocks[12] estimated the molecular weight of the anomalous component to be 50.

9. SPECTRAL ANALYSIS

In addition to the mass spectrometric analysis cited above, several investigators have analyzed modified samples with a variety of spectrographic tools. Willis, et al.[27] of Unilever Research Laboratory investigated modified samples with nuclear magnetic resonance and infrared techniques and although their results were of poor quality, their analysis detected only the characteristic features of normal water. Rabideau and Florin[30] also ran NMR analysis of capillary-contained samples and observed the proton resonance for ordinary water. Their analysis, however, failed to confirm the broad resonance 300 hz. downfield from that of bulk water which had been attributed to the anomalous component of modified water by other investigators.[37,38] Although an apparent broad absorption signal was observed approximately 300 hz. downfield from the ordinary proton resonance, a similar resonance hump was found for empty capillaries. The similarity between this background signal and that of protons in silica gel[39] led Rabideau and Florin to suggest that the possibility of surface-absorbed water should be considered when ascribing characteristic behavior to modified samples on the basis of such investigations.

Using distilled samples of less than maximal modification, Bellamy, Osborn, Lippincott, and Bandy[40] confirmed some of the reported properties of modified water. They reported spectroscopic data in the near infrared region, as well as publishing a Raman spectrum and discussed possible structures consistent with their data. In later work Lippincott, et al.[25] did more extensive infrared and Raman spectroscopic analysis and concluded that an anomalous species of water did indeed exist which demonstrated properties largely consistent with those reported by Deryagin, et al.. Infrared spectra for samples of modified water produced by Lippincott and workers were compared with approximately 100,000 infrared spectra in the ASTM-DOW SIRCH program and were reported to be unique, different from any known substance. Samples that were produced at different times from those first tested as well as samples which were analyzed, allowed to age, and then reanalyzed show close conformity to the original spectral data. Raman spectra were also made for capillary-contained samples and were strikingly different from those of ordinary water or ice.

Rousseau and Porto[41] repeated work of Lippincott, et al. using infrared with very similar results. Raman scattering was tried but revealed nothing conclusive due to an intense flourescent background which could not be explained by those investigators. Rousseau and Porto also noted that in one Raman experiment, at a relatively high incident laser power, the modified sample burned, that is, the sample turned dark brown, nearly black, in color. Kurtin, et al.[39] also produced samples for which the infrared spectra were in close agreement with those of Lippincott, et al..

Howell[42] of this laboratory reported having reproduced the infrared spectra of Lippincott, et al.[25] by analyzing samples which had contacted glass. Howell suggested that the spectra published by Lippincott as evidence for an allotropic modification of water might rather be a result of impurities leached from the capillary surface, and therefore

Lippincott's spectra would substantiate neither the presence nor absense of an anomalous of water.

10. MISCELLANEOUS PROPERTIES AND BEHAVIOR

Only nominal information can be found in the literature concerning certain other alleged physical properties and characteristic behavior of modified water. Early research by Deryagin, et al.[26] reported qualitative findings on the electrical conductivity of modified samples measured by introducing platinum wire electrodes into the sample capillary. Deryagin's conductivity experiments indicated that dissolved ionic substances were not present in large enough quantities to be responsible for the reported properties of reduced vapor pressure, increased viscosity, etc.. Data on the dielectric properties of samples produced by Kurtin, et al.[39] have also been reported. These measurements support their arguments that the modified substance is basically a hydrosol.

Some investigators[30,40,43] commented on an unusual tendency of modified water to creep up the walls of the capillary tube in which it is contained.

Deryagin and Churayev[28] reported that the average heat of vaporization for maximally modified water is 6 ±1 kcal/mole (at 200°C) which is significantly lower than the value of 9.7 kcal/mole (at 100°C) for ordinary water.

Deryagin, et al.,[26,28] Willis, et al.,[27] Rabideau and Florin,[30] and Brummer and Cocks[12] reported that upon evaporation of modified columns within capillaries, a non-volatile optically anisotropic residue remained. Because the quantities of this gel-like residue observed were extremely small, no rigorous analysis of it has been yet performed (cf. p.33 of this paper for a partial analysis of this residue).

Rabideau and Florin[30] attempted to describe quantitatively the residue from modified samples by weighing, and reported that residues which approximated 1% of the total weight of the modified samples were obtained. This residue was cited by Rabideau and Florin as evidence of non-volatile impurities present in the sample. Deryagin and Churayev[28] stated that the residue was evidently a high-molecular mass fraction of the anomalous component in the modified sample. These Russian authors also reported that in some instances, the non-volatile residue remaining at high temperatures was as much as 15% of the original sample volume.

D. PROPOSED MECHANISMS AND STRUCTURES FOR AN ALLOTROPIC MODIFICATION OF WATER

Russian investigators under the directorship of B.V. Deryagin have long been concerned with the study of liquid-solid interfaces and the structural modifications which arise within the liquid in close proximity to a solid boundary and cause such boundary liquids to differ markedly in their physical properties from those of the bulk phase. Such modifications have been generally found to be short range and reversible, extending from the surface into the liquid no more than a few molecular layers. Investigations beginning with those of Fedyakin[5] led the Russian scientists[2,26] and others[1,25] to report, however, a different type of structural modification, an irreversible modification extending not one or two layers, but rather hundreds of layers into the bulk, even up to tens of microns.

Since Fedyakin's first paper was published in 1962, several investigators have strongly argued that such long-range structural reordering and the subsequent formation of new molecular complexes was responsible for the physical properties of what had come to be called modified or anomalous water. As a consequence, the samples were said to represent a true allotropic modification of water.

To refute this hypothesis, the charge was made that the action of small volumes of water on the glass capillary surface approximated that of an alkali (early experiments performed by Deryagin, et al.[13,28] used extremely small glass capillaries approximately one micron in diameter which were left in the vacuum apparatus for lengths of time up to several weeks or even months). Even though the solubility of fused quartz in water is small, the lixiviation hypothesis had to be answered.

To substantiate earlier results, Deryagin[11] reproduced similar samples, this time in capillaries 10-30 times as large as those used originally and in an apparatus that caused columns to grow in less than an hour. The capillaries were freshly drawn from fused quartz tubing and the samples produced in them were subjected to conductivity checks to determine if large enough ionic quantities were present to offer a credible explanation for the anomalous properties of the samples. On the basis of his conductivity experiments, Deryagin, et al.[2,6,17,28] rejected the hypothesis of lixiviation, reporting that even after storing samples in their capillaries for periods up to six months, the modified samples failed to contain dissolved substances in a sufficient quantity to account for the observed properties. Their conclusion, reiterated many times since that time, was that the physical properties of the condensed liquid differed so markedly from those of the bulk liquid that they could only be explained in terms of structural differences in the two phases.[26,28] This modified phase, Deryagin reasoned, had a structure which was more compact than the liquid structure in the bulk phase and that this compactness caused the various anomalous properties.[3,33] The part played by the capillary walls was essentially to ensure the appearance of a nucleus of the new phase.[15] Deryagin, et al.[7] proposed that the molecules of water vapor interacted with the silica surface and with each other, resulting in the formation of a network of hydrogen bonds of an unusual nature which characterize the anomalous liquid. Having observed the fact that upon evaporation the physical properties of modified samples deviate more extensively from those of ordinary water, Deryagin, et al.[2,6,11] reported that some samples appear to have a greater degree of anomaly because the samples contain some kind of molecules of water which are less volatile than the normal H_2O molecules. Thus, anomalous water was believed to represent a two-component system consisting of two types of molecules.

As "proof" that samples of maximum modification consist only of the polymeric molecules $(H_2O)_n$ and contain no perceptible amounts of organic impurities, Deryagin, et al.[2,28] cite: (i) distillation data for modified samples across high thermal barriers for which the condensate was indistinguishable from ordinary water;[34] (ii) the absence of significant quantities of organic impurities in some modified samples (reported by Zhvirblis[29]); and (iii) the increased surface tension observed for modified samples.[21]

Lear[3] reports that among the scientists who attempted to sustantiate and reproduce the findings of Deryagin, et al., Fowkes of Lehigh University began a series of investigations based on the assumption that subsurface electrical forces were responsible for the observed properties of modified samples. From earlier work, Fowkes had found that such forces could arise from quantities of impurity in the pyrex or quartz substrate, particularly random atoms of sodium.

While it is very unlikely that sodium atoms would carry negative charges, Fowkes reportedly proposed that negatively charged sodium atoms build up an opposite charge immediately above the quartz surface. These charges, Fowkes hypothesized, could pull vapor molecules into a more compact configuration than is usual. If, however, the sodium atoms were removed (e.g. by washing the surface with acid), then modified samples could no longer form. Lear reported that subsequent investigations both by Deryagin and Fowkes confirmed that such an acid washing destroyed the ability of glass capillaries to produce modified samples. Fowkes[9] later reported that the sodium ions he had supposed were important in the production of modified water were found to be present in such samples, but he did not reiterate his earlier hypothesis.

In contraposition to Deryagin, Erlander[44] of Ambassador College in California reported that modified water was not an anomaly due to the structure of the container wall since the physical properties of modified samples are independent of capillary radius. He also suggested that clusters of modified water molecules have a structure similar to that of ice-II, that is, rhombohedral crystalline.

Several other investigators have concluded that water can exist in a previously unknown allotropic form and have proposed suitable structures. For example, Lippincott, et al.[25] concluded that the modified material is a true high polymer of H_2O monomer units and suggested that the descriptive name of *polywater* be used for modified samples. The basic structural unit in this polywater, according to Lippincott, is an extremely strong O-H-O three-center bond, isoelectronic with the biflouride ion. Possible structures composed of monomer H_2O with extended networks of strong O-H-O bonds were suggested:[25] (i) a planar network of regular hexagonal rings; (ii) a highly branched planar long chain polymer; and, regarded as less likely but still possible, (iii) a three-dimensional network of O-H-O bonds in a tetrahedral configuration (a structure related to hexagonal ice or metastable cubic ice). Other investigators proposed models of: (iv) tetrahedral clusters of $(H_2O)_4$;[45] (v) planar sheets of square tetramers of $(H_2O)_4$;[40] and (vi) rhombic dodecahedrons of $(H_2O)_{14}$.[46]

Employing extensive CNDO/2 quantum mechanical calculations, Allen and Kollman[47] of Princeton concluded that the three dimensional array of planar networks of cyclic hexamers, (i), was the most likely structure for anomalous water (cf. also Allen and Kollman[48] and Bates and Lippincott[49]). Goel, Murthy, and Rao[50] of the Indian Institute of Technology also did CNDO/2 molecular orbital calculations and found the cyclic hexamer structure, (i), relatively unstable in favor of the highly branched open chain hexamer, (ii).

Mechanisms for the formation of modified samples were proposed and discussed by Petsko[38] and Allen and Kollman.[47]

An ever increasing number of scientists have rejected the above arguments and have offered in their place evidence that the hypothesis of an allotropic modification of water is unnecessary to fully describe modified samples.

E. PROPOSED ALTERNATIVES TO HYPOTHESIZED EXISTENCE OF AN ALLOTROPIC MODIFICATION OF WATER

The opposition to the claimed discovery of an allotropic modification of water report having found foreign impurities in modified samples in quantities large enough to account for the alleged properties and observed behavior.

Taking special care to maintain clean apparatus during manufacture of modified samples, Rabideau[51] reported that after concentration, the same refractive index, density, and freezing behavior as for modified water was observed for his samples. He subjected samples to electron microprobe analysis and found 6% Na, 4% B, as well as C, Mg, P, O, Si, and lesser amounts of Cl. Using isotope dilution mass spectrometry, Rabideau concluded that one third to one half of the sample was O, Na, B, Si, and Cl. In other work, Rabideau and Florin[30] state that many of the physical properties ascribed to modified water can be duplicated with salt solutions; specifically, a phase separation at negative temperatures, increased viscosity, a shifted temperature of maximum density, increased density, increased refractive index, and a lowered vapor pressure can all be produced in aqueous salt solutions. This agrees with work of Lippincott, et al.[40] who reported that their Raman spectra for anomalous samples differed from those of ordinary water in ways very similar to those produced by dissolved salts.

Rabideau and Florin[30] also analyzed the gel residue left upon vacuum evaporation of water from a modified sample. Using electron microprobe methods they found the major constituents of the residue were sodium (at least 6%), boron (at least 4%), and oxygen. Chlorine and silicon were found, but these were small weight fractions of the residue. Comparison with standard salt solutions led the authors to state that the presence of sodium, boron, and oxygen accounted for at least one third of the residue weight.

Analyzing samples produced in their laboratory for silica, Rousseau and Porto[41] ruled out the possibility that modified water was a silica gel since silica was not present in amounts greater than 1%. A significant amount of sodium, however, was detected. Subsequent neutron activation experiments found the sodium content to be between 20-60% by weight. An X-ray milliprobe was used to search for other contaminants and the following were found: Ca (1%), K (3%), Cl (15%), and SO_4^{2-} (15%). While accurate quantitative information could not be obtained, these investigators also analyzed samples with a spark source mass spectrometer and found significant amounts of Na, K, C, O, and Cl, while lesser amounts of Ca, B, Si, N, and S were detected.

According to Page and Jakobsen,[8] the presence of acetates and formates in modified samples would be inconsistent with the published infrared spectra. Although they were not able to perform conclusive analysis of the contaminants present, the Battelle scientists did report that silicon, aluminum, and boron were present in significant quantities. Without answering Page and Jakobsen, Rousseau[52] stated that sodium formate or sodium acetate in aqueous solution could reproduce the thermal expansivity and freezing behavior of modified water.

National Bureau of Standards scientists, Stromberg and Grant,[53] produced modified samples and analyzed them using electron microprobe methods. They found silicon present in trace quantities in a particulate manner as well as quantities of sodium. Halogens and carbon were not found, but the investigators reported that modified samples could not be produced in apparatus which had been previously cleaned of all greases and vacuum sealants.

Similarly, the conclusion of Barnes, et al.[54] was that when sufficient precautions are taken to eliminate the appropriate contaminants, the capillary products become indistinguishable from ordinary water.

Electron microprobe analysis by Kurtin, et al.[39] indicated the presence of substantial quantities of potassium and chlorine. Smaller amounts of sodium and sulfur were also found. Silicon was not reported to be present in an appreciable amount.

Davis[55] of Purdue University employed Electron Spectroscopy for Chemical Analysis (ESCA) to analyze modified samples which had been concentrated by distillation and reported that 12-15% of the substance consisted of carboxyl groups. Sodium, potassium, sulfate, carbonate, chloride, nitrate, borates, and silicates with traces of other impurities containing organic carbon reportedly made up some 95% of Davis' samples. More recent ESCA investigations done by Davis[56] in collaboration with Rousseau of Bell Telephone Laboratories and Board of Hewlett-Packard reported high concentrations of sodium, potassium, sulfate, chloride, nitrate, borates, silicates, and carbon-oxygen compounds with trace amounts of other impurities but very little water.

The quantities of contaminant substances found by Davis, et al. are greater than those reported for modified samples by other investigators, but even those who have argued that the anomalous substance was a true allotropic form of water have reported the presence of contaminants in modified samples. For example, Lippincott, et al.[57] reported that sodium nitrate was the most abundant impurity in samples they examined. Silicon was not found in significant quantities but Lippincott suggested it had a catalytic role in the formation of modified samples.

Zhvirblis[29] reports that 25 samples produced by Deryagin were sent to Tal'roze for mass spectrometric analysis. These samples reportedly contained organic substances, including lipids and phospholipids, in amounts commensurate with the amount of the original sample. Zhvirblis commented that these organic substances are fats and compounds of fats with phosphoric acid and its derivatives which occur in animal tissue and, in particular, are released by humans along with perspiration. Rousseau[58] believes that modified water is most likely a mixed aqueous salt solution with carboxylic-acid salts being the main determinant of the infrared spectra and the freezing data. According to Rousseau, the major organic constituent of human perspiration, (sodium lactate), is a carboxylic-acid salt which has an infrared spectrum qualitatively similar to that reported by Lippincott, et al.[25] for anomalous water.

It was reported by Zhvirblis[29] that Deryagin later submitted more carefully prepared samples to Tal'roze and that these samples had an organic level significantly lower than the earlier samples. Still, the reports of significant impurity levels in samples by several investigators must be carefully heard. In particular, similarity in the identification of major contaminants deserves consideration.

Among evidence cited by Deryagin[34] as most conclusive for the existence of an allotropic modification of water, investigations are reported in which modified samples were distilled across thermal barriers without loss of their peculiar properties. According to Sosman,[59] however, both silica sols and borate solutions can withstand such distillations. Despite the lack of significant quantities of silica in some samples, a number of investigators have commented that the observed behavior and properties of modified samples were consistent with those of gels and sols.

Among scientists who have cited the similarities between modified samples and sol systems, Willis, et al.[27] reported that NMR data taken in their laboratories on modified samples demonstrate the characteristic behavior of many types of gels where the structural molecules are present in concentrations less than about 5%.

Burton[60] reported that certain properties of modified samples are demonstrated by silica solutions, in particular, the two-phase behavior at negative Celsius temperatures, thermal conductivity, and depressed freezing points.

Bascom[61] of the Navel Research Laboratory reportedly hypothesized that modified water is a silica sol produced by the corrosive action of small amounts of water on the pristine glass or fused quartz of freshly drawn capillaries. According to Bascom, glass and fused quartz surfaces have inclusions of alkalis which could be dissolved by droplets of condensed water. These droplets could thus become extremely corrosive to the surface and sols would then be formed by their action.

In particular, Bascom reportedly suggested that the sol forming hypothesis could account for the otherwise unexplained fact that modified samples form from condensed vapor but not when ordinary water is induced into the capillary.

Bascom, together with Brooks and Worthington[62] of NRL have also proposed that silicates are responsible for the anomalous properties reported for modified samples. The NRL researchers reported that electron probe analysis revealed sodium and silica in easily detectable amounts and cited these substances as important, if not the principal constituents of the gel-like sample residue.

Kurtin, et al.[39] produced modified samples which demonstrated the physical properties of modified water described by Deryagin, et al.. When investigated, the behavior of these samples was reported to be similar to that of hydrosols (aqueous systems containing highly dispersed particulate matter). These investigators reported, for example, that the dielectric properties of modified samples were remarkedly similar to those of colloidal suspensions cited in the literature.[63] Significant quantities of particulate matter were also found in these samples by scanning electron microscopy.[39] According to these investigators, freshly drawn capillaries contain, on a submicroscopic scale, a large, highly reactive free surface which could serve as a source for potential sol formers.

Because of the repeated and persistent reports of the presence of contaminants in modified samples, some investigators have attempted to reproduce the findings of Deryagin, et al. by artificially manufacturing modified samples through the use of impurities.

Rabideau and Florin[30] made a 1% aqueous solution of sodium tetraborate decahydrate and induced the solution into freshly drawn quartz capillaries. The refractive index and vapor pressure of these synthesized samples paralleled those of anomalous samples from the same laboratory. Other behavior reported for modified samples, for example, the gel-like residue and negative Celsius temperature of maximum density were also observed for the borax solution. A sodium metaborate solution was then prepared from equimolar quantities of sodium hydroxide and boric acid. Thermal expansion data for a capillary-contained sample showed a gradual decrease of column length as the liquid was cooled to -50°C, a behavior reported by Deryagin[6,28] as characteristic of the most anomalous of modified samples.

Infrared studies of sodium metaborate decahydrate samples also showed similarities between that substance and modified water. Although the authors did not propose that the modified samples were entirely made up of this compound, or even that it is the chief component of anomalous water, they did emphasize a need for caution in ascribing the observed behavior to an allotropic modification of water.

Howell[10] reported that freshly drawn fused silica capillaries often contain extremely fine particles of silica which can serve as nuclei for the formation of liquid water and lead to the production of silica sols. In this laboratory, Howell[10,42] was able to reproduce the vapor pressure behavior of modified water using a mixture of silica gel in water. Aqueous solutions containing sodium, silicon, and oxygen demonstrated an elevated surface tension of the same magnitude as that of Deryagin's[28] modified samples. Solutions of a similar composition were able to produce appropriate values for the boiling point and heat of vaporization.

There are some few other references to modified or anomalous water in the literature. Most of these can be found by checking bibliographies for the works cited in this paper. The research here referenced, however, serves to characterize the elusive substance which has come to be called anomalous water.

In an effort to clarify the somewhat ambiguous findings of other investigators and to resolve the debate concerning the alleged existence of anomalous water as a true allotropic modification of ordinary water, Howell,[10,42] Bolander, Kassner, and Zung,[45] and others of this laboratory have done extensive research. As part of this effort, the author has measured the thermal expansivity and refractive index of various hydrosols and compared these with properties reported in the literature as characteristic of anomalous water.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

The research about which this paper centers required the preparation of samples synthetically modified by the addition of inorganic contaminants to pure water and the determination of the thermal expansion and refractive index of these samples. Special care was taken in the sample preparation to eliminate all impurities except those specifically desired.

A. PREPARATION OF PURE WATER

Water used in the experiments described was carefully obtained in the following manner to insure purity and the subsequent repeatibility of measurements. Filtered tapwater was distilled in a Barnsted type still, then in a Corning model AG2 still, and was stored in a clean tin-lined reservoir. Following Allen,[64] water from the storage reservoir was then processed in a distillation apparatus consisting of three successive pyrex boiling pots and condensation units. Reflux columns above each of the three boiling pots were filled with stainless steel chips allowing the number of effective distillations to be increased many-fold. Steam generators were fitted into each pot to prevent superheating of the distillate. The first pot contained $KMnO_4$ (10 gm/l.), to oxidize organic impurities so they can be readily removed by distillation, and KOH, to assure alkalinity and maintain a pH of 8 or 9 (about 7 gm/l.). H_3PO_4 was added to the second pot (10 ml/3 l.) to form insoluble phosphates from the heavier elements still present in the condensate of the first pot. The H_3PO_4 notably reduced the Pb ion in the distillate as determined spectrographically. The third stage consisted of a clean boiling flask which contained only condensed distillate from the second flask and from which the product was collected in a clean vented storage reservoir.

B. THERMAL EXPANSIVITY

The bulk thermal expansivity of liquids, in particular water and aqueous solutions, has been measured for samples contained in microcapillaries.[5,6,14,16] Since the expansivity for such confined samples has been shown not to have radial dependence in capillaries larger than about one micron,[32,33] determination of thermal expansion curves characterizing a substance can be made for extremely small quantities by this method. If samples for which the expansion is to be measured are confined in capillaries for which the expansion is negligible in the temperature range considered, bulk expansion properties can be determined by a linear measurement of relative change in sample column length with temperature.

Capillaries for the containment of samples under investigation were produced from 4 *mm*. fused quartz tubing which had been cleaned by repeated rinsing with distilled water and dried. Capillaries were drawn in a propane-oxygen torch and when not used immediately, were sealed at both ends to protect them from contamination. Capillaries used for expansivity measurements were between 30 and 70 microns in diameter, their size being at least an order of magnitude greater than the size cited by Deryagin, et al.[2,15] for which expansivity is radially dependent. Only capillaries with constant cross-section were used in the measurements described below. Samples of pure water, aqueous solutions of SiO_2, and aqueous solutions of reagent grade NaOH with SiO_2 were introduced into freshly drawn capillaries by capillary action. The aqueous solutions were prepared by weighing component substances on a Mettler H20 single-pan balance and combining them with a Virtis-45 homogenizer.

When a suitable quantity of sample had been drawn into the capillary, the column was forced into the center portion and both ends were sealed with the torch. Capillary-contained samples were readied for the expansivity determination by securing them in a pyrex T-tube as shown in Figure 3.

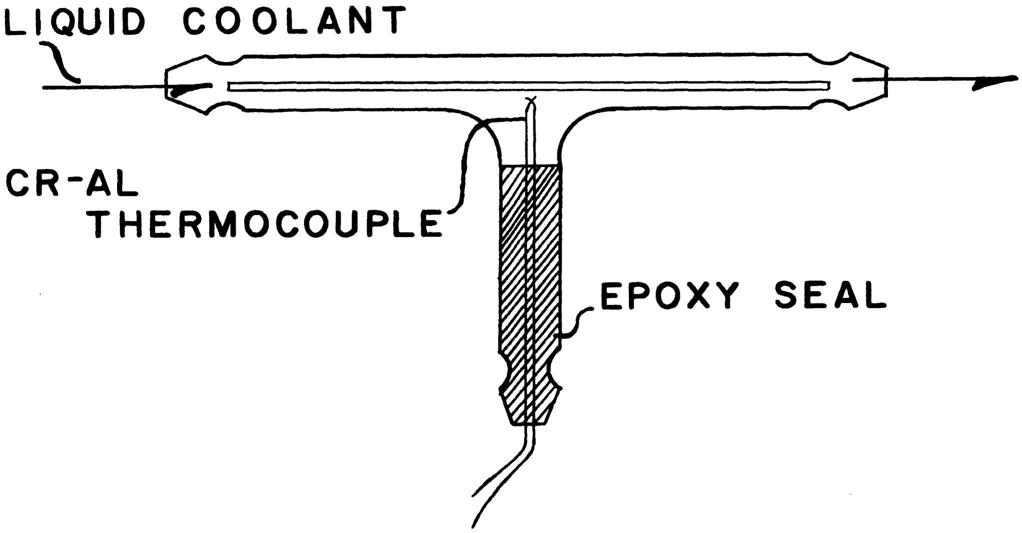

Figure 3. Capillary Container-Thermocouple Assembly.

Small amounts of quick setting epoxy on either end of the capillary were used for this purpose. Care was exercised to ensure that the sample capillary was positioned parallel to the axis of the tube and that the column-containing segment of the capillary was free from visual obstruction.

Environmental temperature at the site of the capillary-contained sample was monitored by means of a chromel-alumel junction thermocouple referenced by an ice-water bath at equilibrium. Visual readout was through a Hickok model DP110 digital milli-voltmeter. Accuracy for temperature readings was found to be ±0.2°C.

In order that expansivity measurements could be made over the thermal region from +30 to -40°C, a regulatable constant-temperature circulatory system was constructed. This system consisted of a cold reservoir bath, heater, thermoregulator, and circulator pump. Toluene was chosen as a suitable refrigerant for the thermal range under consideration because of its low melting point (-95.2°C) and relatively high boiling point (111.8°C).

The reservoir bath was cooled by a Cincinnati model A-80-2 dual compressor refrigerator. A 110 watt copper-clad heating element was inserted into the bath to warm and thermally stabilize the liquid coolant. The refrigerator was set for maximum cooling and allowed to run continuously while a particular temperature was maintained by the thermo-regulator connected to both a reservoir temperature monitor and the heater. The system was completed by a small Badger Ind. model A-5 circulatory pump which continuously cycled coolant from the bath through the glass T-tube in which the capillary was mounted and returned it to the reservoir. In this manner a very stable thermal environment could be selected and maintained for the capillary-contained sample under investigation.

In order to prevent the formation of frost on the exterior of the glass T-tube at negative temperatures, which would make visual observation of the sample impossible, additional environmental control was necessary. The T-tube containing a mounted capillary and sample, after being connected to the circulatory pump with Tygon tubing, was placed inside a clear plexiglass box, open at one end and fitted with a gas inlet port at the opposite end (Figure 4). Suitable supports held the capillary-thermocouple assembly firmly in place.

A stoppered dewar filled with liquid nitrogen was connected to the inlet with tubing which contained a heat exchanger. As the liquid nitrogen slowly boiled, the N_2 gas was warmed and allowed to pass through the box so that a dry nitrogen environment continuously surrounded the capillary assembly and prevented condensation and frost.

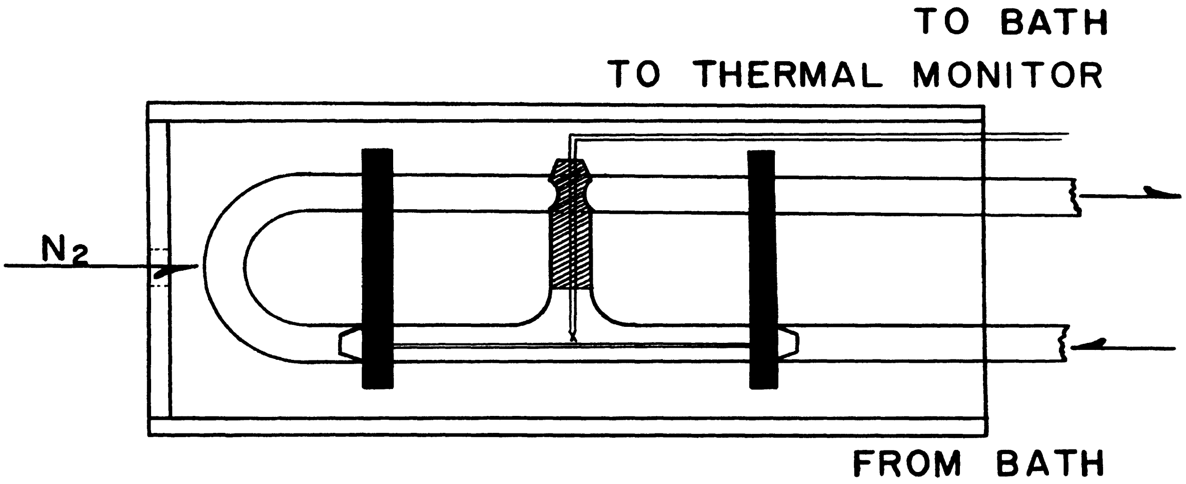

Figure 4. Environmental Cell for Capillary Container-Thermocouple Assembly.

In preparation for expansion measurements on a particular sample, the assembly shown in Figure 4 was mounted in the position ordinarily occupied by the film negative carrier of a Simmon PH-129-B photographic enlarger. The enlarger and the position occupied by the capillary-thermocouple assembly are shown in Figure 5. With the capillary-thermocouple assembly positioned as shown, the refrigerant circulatory system, thermocouple monitor, and liquid nitrogen dewar connected as described above, the apparatus was readied for use.

Measurements were begun on a capillary contained sample after first warming the reservoir bath to approximately 30°C. The circulatory system was started, room lights turned off, and the projected image of the sample column brought into sharp focus on a projection board placed beneath the enlarger head. Although the columns were transparent, a sharp image could be formed because the interior and exterior capillary surfaces and the curved column menisci project as opaque lines. Using a stylus point to mark the precise location of the column menisci, the length of the projected column image was then recorded on a mylar sheet overlayed on the projection board.

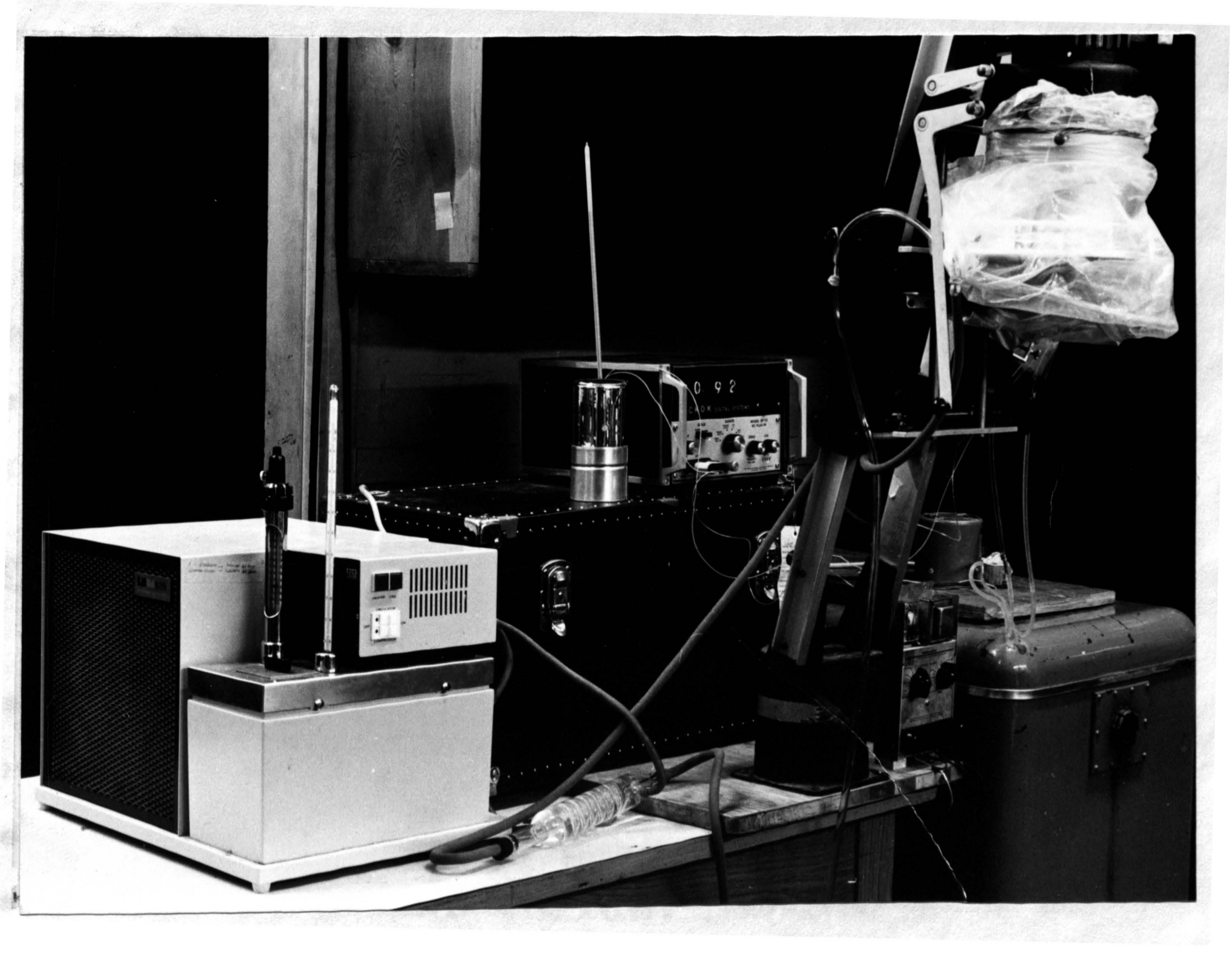

Figure 5. Assembled Thermal Expansivity Apparatus.

Having finished the preparations described above, the refrigerant system was subsequently made operative and as the coolant forming the capillary environment dropped in temperature, additional measurements of the column length were made, special care being taken to record the reference length l_o at 0^oC. When the refrigerant had been cooled to the minimum temperature allowed by the refrigerator, the heating coil was turned on and the refrigerator unit turned off to allow the refrigerant bath to warm. During this warming period, measurements of column length were made again, completing the cooling-heating cycle depicted in the thermal expansion graphs, Figures 6-11, in which the hysteresis loops were obtained. In this way a column elongation contour for a capillary-contained sample was made.

The suitability of quartz as the sample container for expansivity measurements is apparent upon comparison of the relative change in volume per degree Celsius for water and for the volume of a fused quartz capillary.

C. REFRACTIVE INDEX

Refractive index determinations for the various samples under investigation were performed on an optical refractometer of the Abbe type,[65] an instrument whose essential features are a telescope, a refractometer prism, and two Amici compensating prisms. The principle of the instrument is based on the determination of the grazing angle for the refractometer prism, which is measured through the liquid sample medium. The scale on which the magnitude of this angle is read is calibrated directly in the dimensionless units of refractive index. Reproducibility of individual readings on the scale was claimed by the manufacturer to be

±0.0002 units of refractive index. The refractive index of a sample is read directly from the calibrated scale to three decimal places and interpolated to the fourth.

Because the refractive indices of some liquids change as much as 0.0004 units per degree Celsius, accurate temperature control must be maintained. For the measurements reported here, the thermal jacket surrounding the refractometer prism was kept at 25.0 ±0.1°C. Since the refractive index for a substance is not independent of the wavelength of incident radiation, data reported in this paper was standardized on the D-line of sodium light, 5893 A.. Use of an ordinary microscope substage lamp for illumination of the refractometer was possible because the refractometer telescope contained two Amici prisms which are constructed with special glasses so that light of the sodium D-line is not deviated but all other light is deviated when the relative positions of the two Amici prisms are properly adjusted.

IV. EXPERIMENTAL RESULTS AND CONCLUSIONS CONCERNING THE ANOMALOUS WATER CONTROVERSY

A. THERMAL EXPANSIVITY RESULTS

A summary of the findings of the thermal expansion measurements is presented in Figs. 6-11. The data represents averaged values and the curves are drawn smoothly through the data points.

The thermal expansion characteristic of triply distilled water was found on this apparatus to test the accuracy of the method and its suitability for expansion determinations on other samples. The thermal expansion hysteresis curve for distilled water is shown in Fig. 6. Relative change in column length l with respect to column length l_0 at 0°C is shown on the vertical axis, temperature in degrees Celsius on the horizontal axis. This curves compares favorably with curve *1*, Fig. 1 and curve *7*, Fig. 2 from the Russian laboratories. For temperatures above 0°C, the curves coincide; below 0°C the curves differ only in the extent to which supercooling takes place, a parameter not strictly dependent on molecular composition of the substance, but rather on the quantity and purity of the substance as well as the dimensions of the sample container (pure water should freeze at 0°C but demonstrates a tendency to supercool when confined in microcapillaries).[28]

Fig. 7 shows the characteristic expansion curve for a sample produced from the condensation of undersaturated water vapors on Cab•O•Sil and subsequently collected by distillation. Thermal expansion of this distillate differs significantly from ordinary water in the degree of elongation upon solidification and the temperature of maximum density.

In Figs. 8-10, the characteristic expansion curves are drawn for triply distilled water containing a single impurity, a commercial preparation of SiO_2 manufactured by the Cabot Corp. (Cab•O•Sil has a specified 99.8% SiO_2 content). Figs. 8, 9, and 10 represent sample SiO_2 impurity concentrations by weight of 0.1%, 1.0%, and 10% respectively. The temperature of maximum density (minimum column length) differs little from that of pure water in each of the curves. The samples all melted at exactly 0°C as does distilled water, although the amount of column elongation upon solidification was significantly less for the more impure sample (Fig. 10). Other distinguishing features of the expansion curves are essentially the same as are those for pure water (Fig. 6).

Telescopic observation of capillaries containing the 10% SiO_2 aqueous solution (Fig. 10) during the cooling-heating cycle revealed that freezing followed by thawing causes an irreversible change in the sample. As the sample was warmed from -40°C the total column length varied little with temperature. Between -0.5°C and 0°C channels of air formed at each end of the column and progressed toward the column center. Although the sample was induced into the capillary as a liquid, the freeze-thaw cycle caused it to assume a gel-like appearance.

Fig. 11 shows the effect of adding a second impurity to the SiO_2-H_2O system. The sample contains 5% NaOH and 5% SiO_2 by weight in aqueous solution. The differences from samples in Figs. 6-10 and the similarities to the nominally modified water (Fig. 2, curves *5*,*6*) reported by Deryagin[28] are striking. The temperature of maximum density (minimum column length) has been displaced to the region of negative Celsius temperatures and has a value almost identical to that reported by Deryagin. Values of $(l - l_0)/l_0$ for positive temperatures are also nearly coincident with those of Fig. 2, curve *5*. In the region of positive temperatures, the expansion coefficient for the synthesized sample is more than twice that of distilled water, a distinguishing feature of anomalous samples reported by Russian investigators.[6,28]

When heated from negative Celsius temperatures, solidified samples of pure water melt at exactly 0°C. Samples containing NaOH and SiO_2 behave much differently when heated. As these samples are gradually warmed from -40°C the column lengths gradually begin to decrease along a steeper and steeper, but still smooth dependence, until the hysteresis loop closes. Deryagin, et al.[6,28] reported a similar anomaly in the melting behavior of modified samples produced by vapor condensation in quartz micro-capillaries.

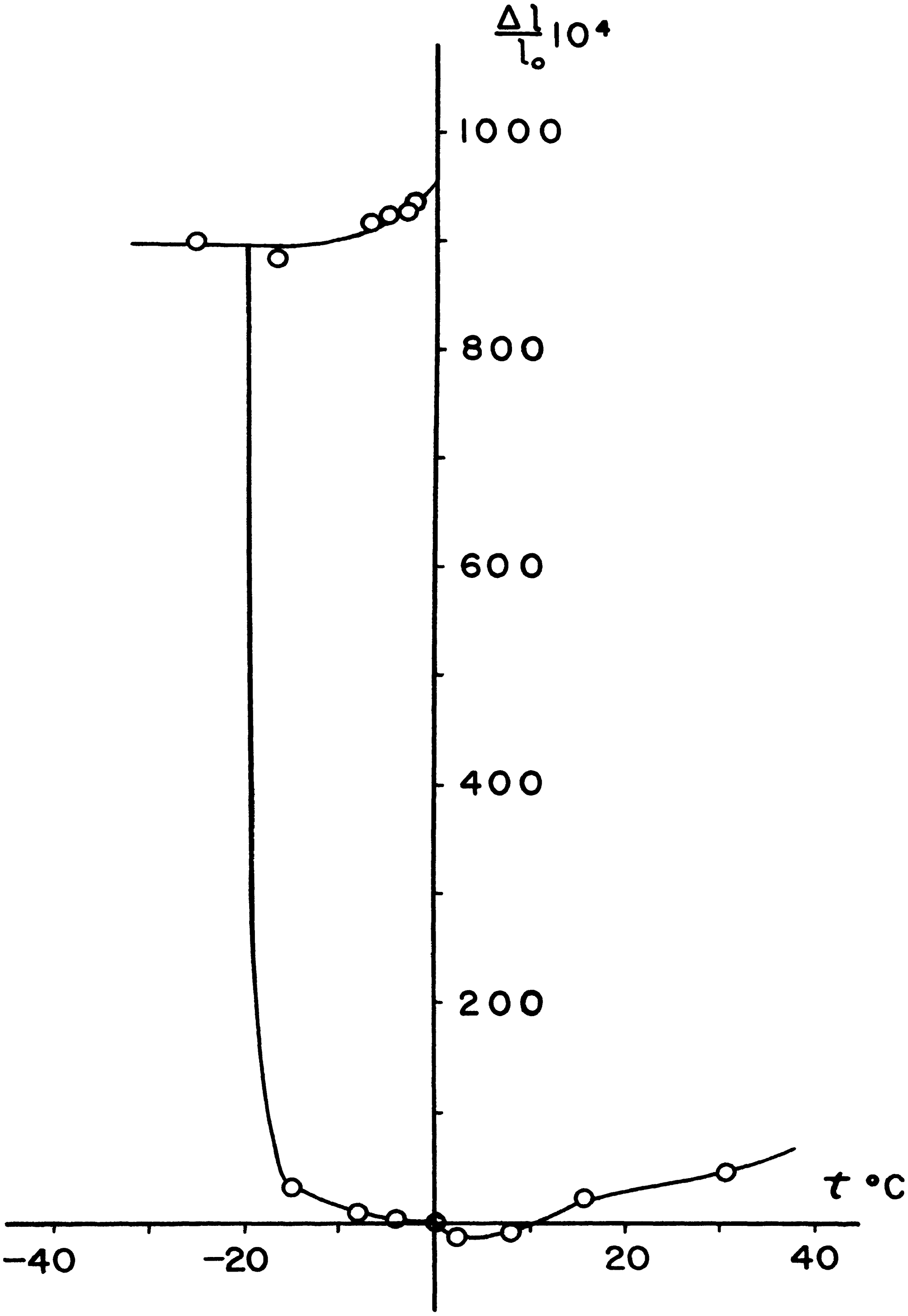

Figure 6. Characteristic Thermal Expansion of Distilled Water.

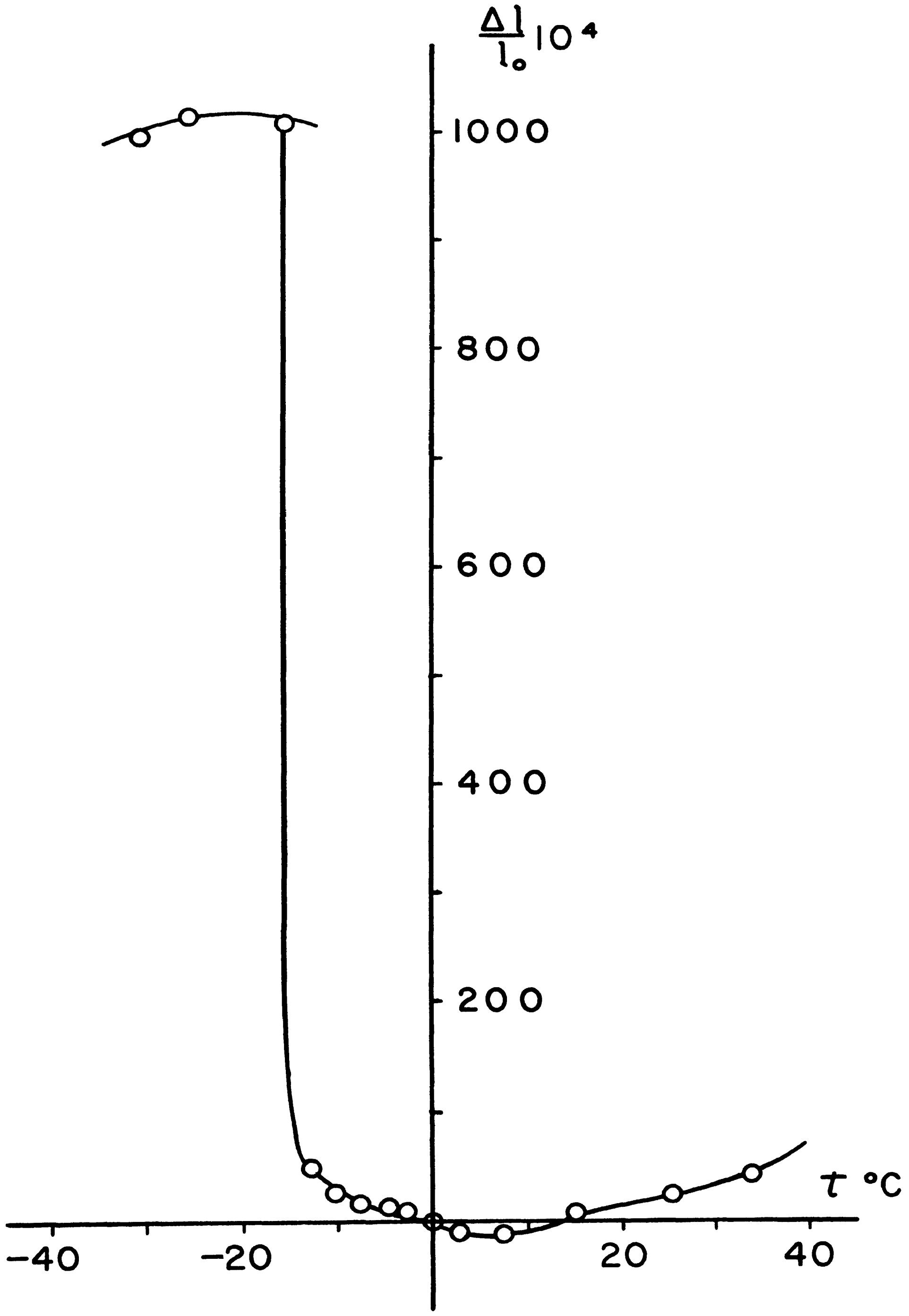

Figure 7. Characteristic Thermal Expansion of Condensed Product Distilled from Cab•O•Sil.

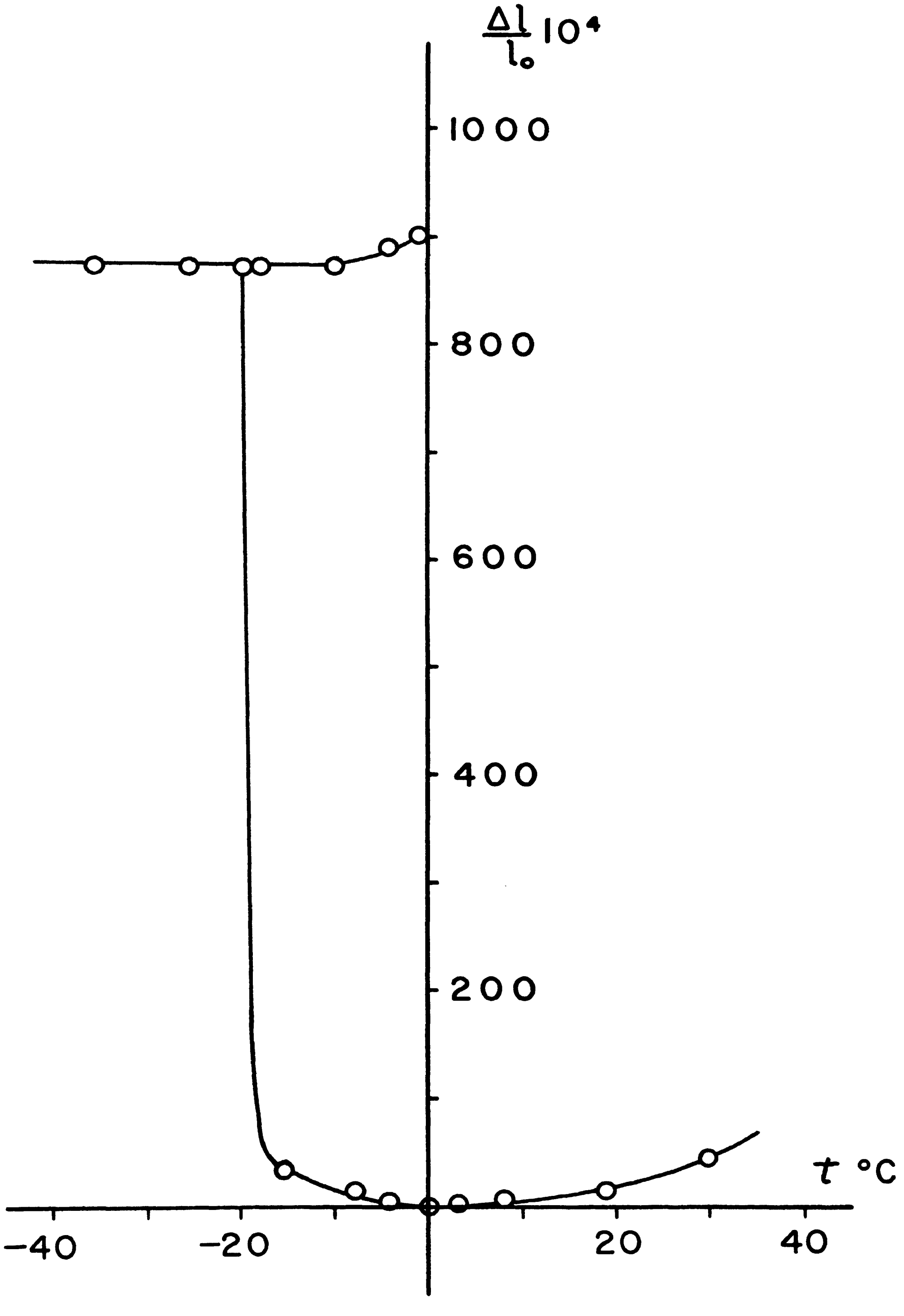

Figure 8. Characteristic Thermal Expansion of 0.1% SiO_2 Aqueous Solution.

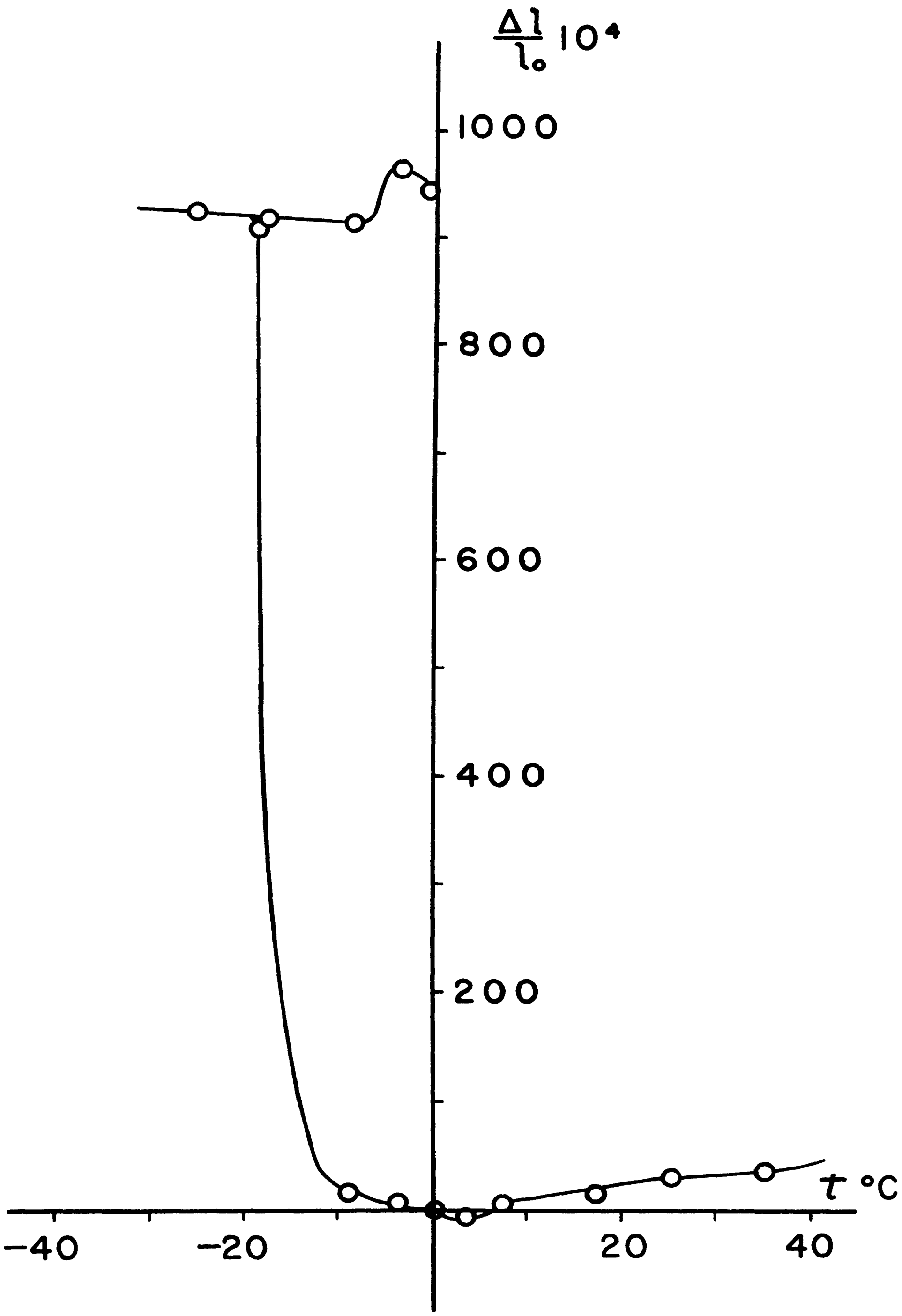

Figure 9. Characteristic Thermal Expansion of 1.0% SiO_2 Aqueous Solution.

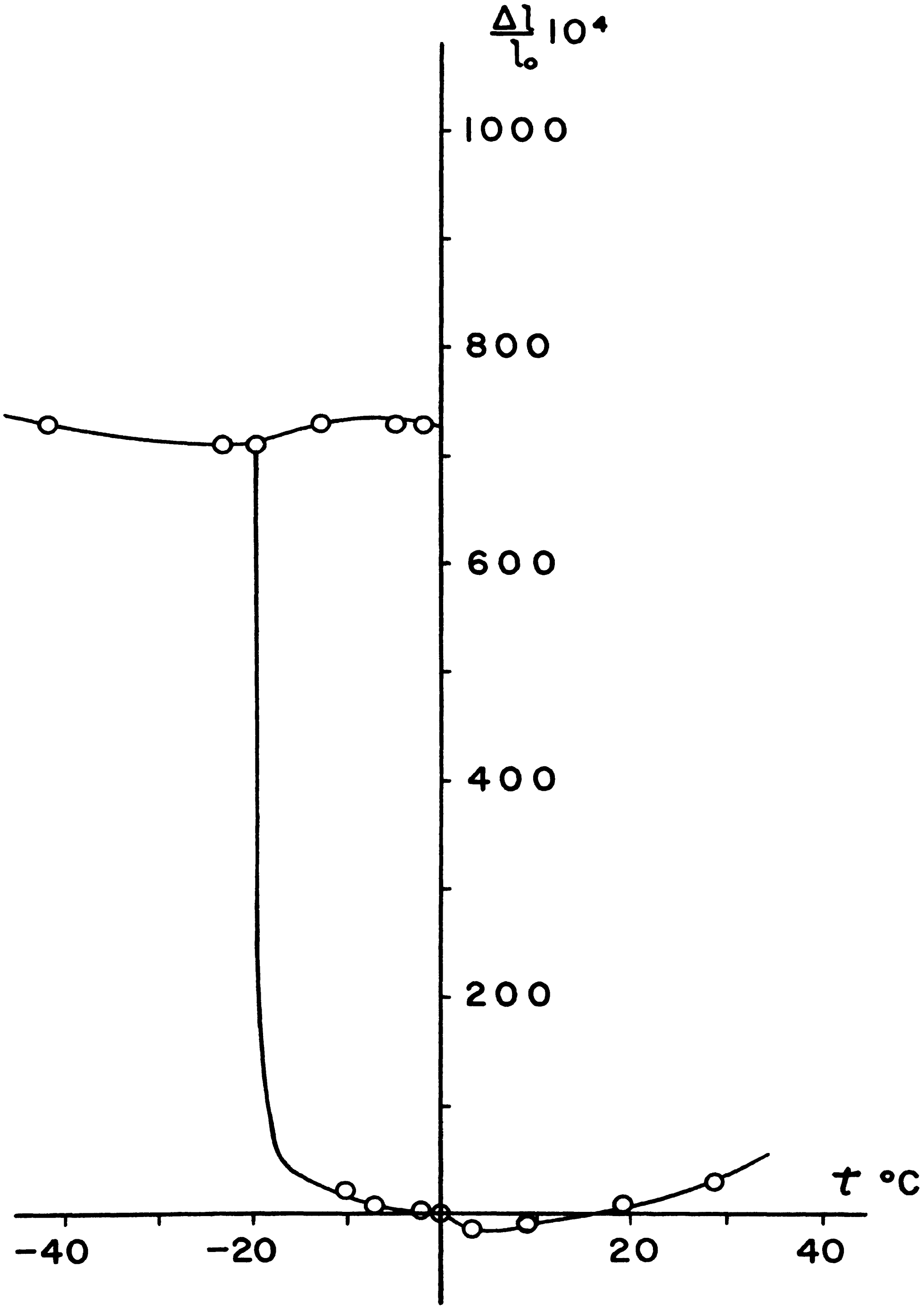

Figure 10. Characteristic Thermal Expansion of 10% SiO_2 Aqueous Solution.

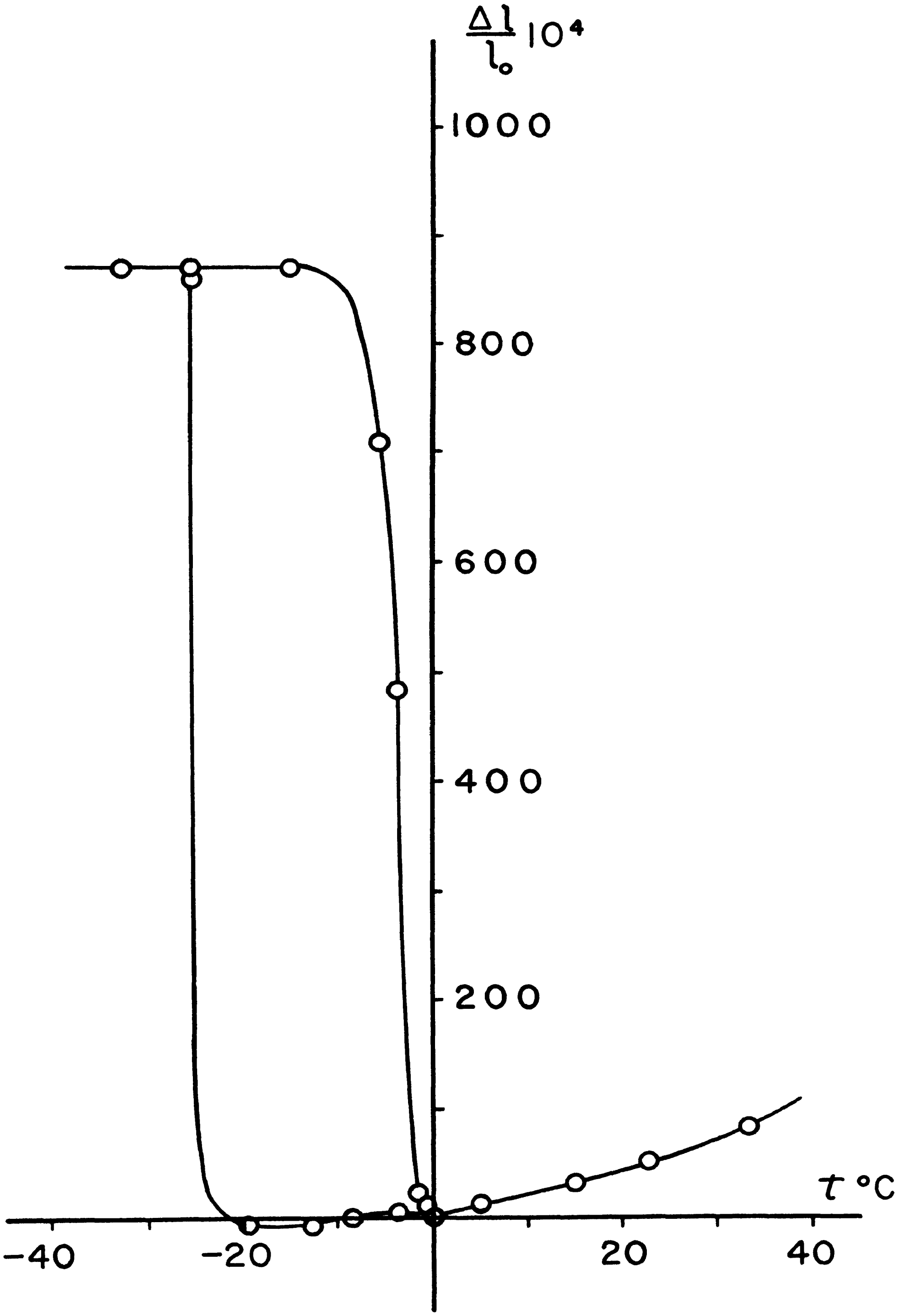

Figure 11. Characteristic Thermal Expansion of 5% SiO_2 - 5% NaOH Aqueous Solution.

B. REFRACTIVE INDEX RESULTS

Values obtained for the refractive index of samples as measured with an Abbe refractometer are given in Table I. The refractive index of pure water was also measured for comparison with the known value of 1.333. No refractive index determination was made for the condensed product distilled from Cab•O•Sil because sufficient quantities were not available. Values given in Table I were recorded at 25°C for the sodium D-line, 5893 A (cf. p. 49).

Table I

Refractive Indices of Aqueous SiO_2 Systems

Substance	n_D^{25}
Water, Pure	1.333
0.1% SiO_2-H_2O	1.334
1.0% SiO_2-H_2O	1.335
10% SiO_2-H_2O	1.340
5% SiO_2- 5% NaOH-H_2O	1.351

Deryagin, et al.[11,20] reported values ranging continuously from 1.33 to 1.48-1.5, depending on the extent of sample modification. The addition of certain impurities to ordinary water results in an elevation of the refractive index values. In particular, samples containing both NaOH and SiO_2 have characteristic indices commensurate with those of nominally modified water cited by the Russian investigators.[11,20]

C. CONCLUSIONS

As can readily be seen from a review of the literature concerned with what has come to be called anomalous water, the characterization of properties, structure, and mechanism are by no means unambiguous. Occasionally, direct contradictions can be found in the published findings of the several investigators who have attempted quantifiable elucidation of this puzzling substance, and final resolution of the controversy yet remains to be done. It soon becomes obvious that not all researchers are even working with the same material. Indeed, because only such small quantities of modified material have been produced, it is difficult to choose a standard by which to decide whether other samples are truly modified water.

Deryagin[28] has commented that the presence of disperse particles in modified samples can account for hardly a single property ascribed to anomalous water. The experience of this and other investigators, however, prompts a serious reconsideration of this comment and the entire controversy.

The author does not propose that the substance known as anomalous or polywater is necessarily a single inorganic compound dissolved in water nor that it is primarily a dispersion of sodium salts and silica. The findings reported in this work, when considered with the evidence of other investigators, strongly suggest, however, that those properties and behavior which characterize anomalous or modified water can be explained without assuming the existence of an allotropic modification of water. If conclusive evidence has not yet been published, the results cited herein should bias the argument.

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