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* Dr. Gast died on 16 May 1973.

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Anomalous Heat Capacities of Supercooled Water and Heavy Water

Abstract. *Emulsification makes it possible to supercool water to the homogeneous nucleation temperature. Accordingly, the heat capacities of water and deuterium oxide have been determined from the respective equilibrium melting points to −38° and to −34°C, respectively. Two methods, drift calorimetry and differential scanning calorimetry, have been used. Both methods reveal a striking rise in the constant-pressure heat capacity below −20°C. This indication of an apparently cooperative behavior should serve to test current theories of water, most notably perhaps, the pair potential model of Ben-Naim and Stillinger. Some implications of possible meteorological significance are mentioned.*

One of the most fundamental thermodynamic properties of water, its heat capacity, has not, to our knowledge, been reported for temperatures much below 0°C. Since an understanding of the relation between thermal energy and "geometrical" structure is vital to an understanding of the nature of water, and since measurements made on supercooled water in capillaries have shown that structural anomalies become more pronounced with decreasing temperature (*1–3*), we have sought to measure the constant-pressure heat capacity, C_p, of this substance to the lowest possible temperatures.

It is possible to study gram-sized samples of clean water to ~ −20°C under certain circumstances. Hallett has reported viscosities obtained from measurements on bulk water to −23.8°C (*4*). Accurate measurements at temperatures much lower than this are made possible by the use of samples of water so small that the chances of heterogeneous nucleation are greatly reduced. Such samples may be examined individually, as in the capillary studies of water density (*1–3*), or en masse, as in studies of emulsified water (*5, 6*). Particularly stable emulsions, in which water can be held without crystallizing for long periods at temperatures approaching the homogeneous nucleation temperature, −40°C, have been developed by Rasmussen and MacKenzie (*5*). These emulsions have proved very suitable for low-temperature heat capacity studies; they are made by dispersing water in heptane supersaturated with sorbitan tristearate (Span 65), one of a number of commercially available water-insoluble surfactants (*7*). Water droplet diameters in the range 1 to 5 μm are readily achieved with a standard blender.

Emulsions containing 40 to 50 percent water (by volume) have been used in both of the heat capacity studies presented in this report. Two different calorimetric methods were used. At the Cryobiology Research Institute, the total heat capacity of the calorimeter chamber containing the emulsion was determined by conventional drift calorimetry. The differences in heat capacities between supercooled water and ice were calculated at 5°C intervals. At Purdue University, data were obtained by differential scanning calorimetry (DSC); both the Perkin-Elmer DSC-1B and the more recent and much-refined DSC-2 instruments have been employed. In DSC measure-

Table 1. Heat capacities of water and deuterium oxide (in calories per mole per degree Celsius).

Temperature (°C)	C_p (water)					C_v (water) (av. DSC)	C_p (deuterium oxide)	
	Av. DSC-1B	DSC-2	Av. of the two DSC's	Drift calorimeter	Bulk water (DSC)		Av. DSC-2	Drift calorimeter
4						18.1	20.3	21.0
0	18.3	18.3	18.3	17.7	18.4			21.0
− 3	18.2	18.0	18.1	17.6	18.3	18.0	20.1	21.1
− 8	18.1	18.0	18.0	17.5	18.2	17.9	20.5	20.9
− 13	18.1	18.2	18.1	17.5	19.0	17.9	21.2	21.4
− 18	18.3	19.0	18.6	17.8	18.9	18.0	22.0	22.3
− 23	18.8	20.1	19.5	18.8		17.9	24.2	24.4
− 28	19.3	22.5	20.9	21.0		17.8	26.3	29.2
− 33	22.1	25.1	23.6	25.0		17.7	30.9	
− 38	27.0	28.9	28.0			17.8		

ments a voltage proportional to the heat capacity of the sample is recorded continuously during a rapid temperature scan. Because of the short time scale of this type of measurement, it was possible to reach −38°C for water (−34°C for deuterium oxide) before crystallization of the sample commenced. The accuracy of the two methods appears to be comparable.

The amount of water in the sample under study was determined by measurement of the heat absorbed at 0°C on fusion of a totally frozen sample; the differences in the heat capacities of supercooled water and ice were obtained from a comparison of the data from measurements on supercooled and frozen emulsions.

Our results are shown in Fig. 1 in the form obtained from the experiments, namely, as a plot of C_p (water) $- C_p$ (ice), denoted by ΔC_p, versus temperature T. It is reasonable to regard this difference as the approximate contribution to the total constant-pressure heat capacity due to the structural changes which occur with changing temperature. The contributions are unique to the liquid state, since the changes in vibrational frequency induced by changing temperature are relatively minor. Although this "configurational" heat capacity changes little over the first 15°C of supercooling, an astonishing near-exponential increase with decreasing temperature becomes evident with further supercooling. The differences which exist between our two sets of measurements are of little consequence when viewed against the remarkable aspects of the energetics of water which they reveal. Data for pure water and pure deuterium oxide are presented in Table 1 as total constant-pressure heat capacities, based on the results in Fig. 1 and the heat capacities of ice given in (*8*).

That the heat capacity anomaly is characteristic of water rather than an artifact arising from the state of subdivision is readily argued. Were the structuring responsible for the changes observed to be restricted to a surface layer (we cannot reasonably suppose that such a layer extends inward from a surface a distance as great as 10 nm), the measurements would necessarily reflect the ordering of, for example, 1.2 percent of the volume of a droplet 5 μm in diameter. The essential agreement of data on emulsion expansivity and proton chemical shift (see below) with data obtained from capillary studies (in which one dimension is macroscopic) further supports our contention. Additional evidence is obtained from measurements in the presence of salts, substances known to destroy the structure peculiar to pure water. Repetition of the DSC measurements on a 0.89*M* NaCl solution, in which some "bulk water" solvent structure evidently remains, revealed a less pronounced C_p increase, displaced to lower temperatures. For a 7.14*M* NaCl solution the rise in C_p has all but disappeared from DSC measurements down to the homogeneous nucleation temperature of this solution (−63°C). All of these effects suggest "bulk" water behavior rather than surface phenomena.

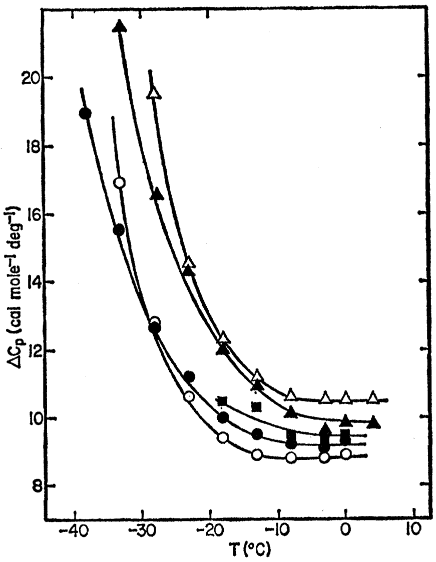

Fig. 1. Differences between the heat capacities of ice and supercooled water and of deuterium oxide ice and supercooled deuterium oxide as a function of temperature. The drift calorimeter results of D.H.R. and A.P.M. are presented as open circles for emulsified water and open triangles for emulsified deuterium oxide. The DSC results of C.A.A. and J.C.T. are presented as solid circles for emulsified water, solid triangles for emulsified deuterium oxide, and solid squares for bulk (50-mg sample) water.

Dilatometric studies on aqueous emulsions (*9*) and proton magnetic resonance (PMR) chemical shift studies on aqueous emulsions and on water in capillaries (*10*) will be reported elsewhere. The dilatometric data confirm the results obtained by Schufle (*1*) and Zheleznyi (*3*) on water in capillaries to −30° and to −34°C, respectively. The PMR data on water in capillaries deviate a little from corresponding values for bulk and emulsified water. The differences persist in large-diameter capillaries and are thought therefore to reflect experimental or data reduction (susceptibility correction) problems rather than real structural effects. Details of these effects will be given in separate communications in which our differing analyses and our further interpretations of these and related measurements will be presented (*9*, *10*).

We should note here, however, that, at constant volume, it seems that little or no heat capacity (C_v) anomaly would be observed. We can, perhaps, show this best with the aid of the standard thermodynamic expression:

$$C_p = C_v + \frac{\alpha^2 T}{\kappa} \qquad (1)$$

together with the expansivity (α) data (*9*) and compressibility (κ) data of very approximate validity extrapolated to −40°C from Kell's (*11*) extrapolation to −20°C (by multiparameter fits) from data taken above 0°C.

According to preference, such behavior could be interpreted as indicating either (i) that the anomaly really lies only in the volumetric behavior but must appear in C_p according to Eq. 1, or (ii) that the C_p anomaly is fundamental to the energetics of water, but, because the excitations determining the value of C_p involve a significant (negative) volume change, restriction of total volume to some constant value largely represses the excitations and forces less interesting heat capacity behavior on the system. On the other hand, a striking pressure-temperature anomaly should be manifested in constant volume experiments. The presence of such an anomaly in the results of some computer simulation studies now in progress (*12*) should provide an important test of the adequacy of the modified pair potential of Ben-Naim and Stillinger being used in those calculations.

In either case, the particular form of the temperature dependence observed for α and ΔC_p provides a challenge to the theorist. There is little doubt that the ability to explain this behavior should be required of any model that claims to represent essential features of such an important liquid.

Finally, we may make a point of possible meteorological significance. A cloud of water droplets supercooled, for example, to −35°C contains considerably less heat than might have been expected on the basis of the accepted "normal" constant-pressure heat capacity of water. The capacity of such a cloud to extract heat from an object passing through it must, at the same time, be rather greater than would previously have been estimated. The frequency of occurrence of cloud temperatures low enough to furnish heat capacities significantly larger than normal values, lower, that is, than −25°C, is, however, not known to us.

D. H. RASMUSSEN, A. P. MACKENZIE
Cryobiology Research Institute,
Madison, Wisconsin 53704

C. A. ANGELL, J. C. TUCKER
Department of Chemistry,
Purdue University,
West Lafayette, Indiana 47907

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Dopamine-β-Hydroxylase Deficits in the Brains of Schizophrenic Patients

Abstract. *Postmortem brain specimens from 18 schizophrenic patients and 12 normal controls were assayed for dopamine-β-hydroxylase (DBH), the enzyme responsible for the final step in norepinephrine biosynthesis. There was a significant reduction in the DBH activity of the schizophrenic group in all brain regions examined. Enzyme deficits in hippocampus and diencephalon were somewhat larger than that in pons-medulla. Since various extraneous factors, such as nonspecific deterioration, drug treatment, duration of hospitalization, cause of death, sex, and age could be ruled out, the deficits in DBH may be associated with the schizophrenic disease process. These findings are consistent with the hypothesis that noradrenergic "reward" pathways are damaged in schizophrenia.*

Recently, we proposed a neurochemical model of schizophrenia in which the fundamental symptoms and chronic course of the disease are assumed to result from a progressive deterioration of central noradrenergic pathways (*1*). Our work is based on Bleuler's (*2*) concept of the disease. To emphasize the inadequacy of central integrative processes, Bleuler coined the term "schizophrenia": "In every case we are confronted with a more or less clear-cut splitting of the psychic functions. If the disease is marked, the personality loses it unity. . . ." According to Bleuler, fragmentation of schizophrenic behavior and personality arises mainly from the fact that the thoughts, feelings, and actions "are not related and directed by any unifying concept of purpose or goal." In the related view of Rado (*3*), the crucial defect is in the organizing action of pleasure or reward; thus, schizophrenic "disorders may be viewed as so many experiments of Nature, showing what happens to central integration in the person whose pleasure resources are inherently deficient."

Research findings in many different fields (*4*) have resulted in the identification of central noradrenergic pathways tentatively associated with pleasure or reward and, hence, with the organization and control of goal-directed thinking and behavior (*5*). Thus, if the analyses of Bleuler and Rado are correct, it would be necessary only to posit the deterioration of this noradrenergic system to explain the chronic disturbance of goal-directed thinking and behavior in schizophrenia. In our model, it accordingly has been assumed that noradrenergic reward pathways and their rich terminal systems in diencephalon and limbic forebrain are the sites of critical damage. We report here postmortem studies of enzymes in human brain that were designed to evaluate the validity of this assumption. The finding that dopamine-β-hydroxylase (DBH) activity is significantly reduced in the brains of schizophrenic subjects is consistent with our proposal that the noradrenergic reward system is damaged in schizophrenia.

Damage to central noradrenergic neurons can be estimated by measuring the DBH in various regions of the brain. The DBH catalyzes the β-hydroxylation of dopamine (*6*), the last step in the biosynthesis of norepinephrine, and is "distributed in brain with a regional pattern of activity that parallels levels of norepinephrine" (*7*). Electrolytic or chemical damage to central noradrenergic tracts causes similar reductions in brain norepinephrine and DBH (*8*). Indeed, the enzyme is used as a marker in immunofluorescence studies to visualize the noradrenergic pathways (*9*). These and other results lead to the conclusion that "in brain, as in the periphery, DBH is intraneuronal and primarily restricted to those nerve cells synthesizing norepinephrine" (*8*). As a first approach, we therefore assumed that measurements of DBH in postmortem samples of human brain could serve as an indicator of the integrity of noradrenergic systems.

Brain specimens were obtained from eight male and ten female patients with a diagnosis of chronic schizophrenia who died at Norristown State Hospital, Norristown, Pennsylvania, at a mean age of 71.2 years (range, 45 to 97). The average duration of hospitalization of these patients was 34.4 years (range, 5 to 60). Control material was obtained through the Medical Examiner's Office, New York City, from six male and six female subjects with no known psychiatric history, who died suddenly in accidents or from heart attacks at an average age of 57.2 years (range, 26 to 80). Care was taken to exclude drug addicts, alcoholics, and suicides from the control group. Also excluded from statistical analysis was one control case with head injury who died after 12 days in coma; at autopsy, anoxic necrosis of the brain was found.

The pons-medulla, diencephalon, and