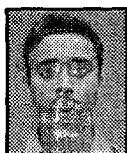


"Water"- Most Atypical Liquid !!!

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Devendra Suresh Pakhare : I plan to do my post graduation course abroad in the same or a related field. After that I plan to indulge in some research work and gain experience which would help me in efficiently completing my management studies. With a blend of my management and technical knowledge would try to add to the betterment of this field of oleo chemicals and surfactants.

Janetri Tushar Dave : I aspire to pursue a career in cosmetic industry. After graduation I plan on doing research in cosmetology. This is my first article for the Bombay Technologist Journal. Working on this article has provided me with cumulative lessons. The research work for this topic has provided me with immense amount of food for thought. I look forward to write more articles for the next issues of this journal.

Abstract

Water one of the most abundant compounds on the planet and one of the most crucial compounds to life on earth, is one of the oddest. It exhibits physical characteristics that are completely anomalous from other molecules with similar size and structure. The most unbelievable fact is that water exhibits 64 different types of anomalous behavior. Another important fact is that it has 14 different phases, solid water contributing to 12 different phases alone. For convenience 64 anomalies are categorized under 5 sub groups. Namely phase, density, thermodynamic, material, and physical anomalies. In this paper, the various phase anomalies are discussed along with a few prominent phases of water.

Keywords: High-density ice, Low-density ice, Hexagonal ice, Cubic ice.

I. Introduction

Water is an apparently simple molecule (H_2O) with a highly complex character. As a gas it is one of lightest known, as a liquid it is much denser than expected and as a solid it is much lighter than expected. Much of the behavior of liquid water is quite different from what is found with other liquids, giving rise to the term 'the anomalous properties of water'. As liquid water is so common-place in our everyday lives, it is often regarded as a 'typical' liquid. In reality water is most atypical as a liquid, behaving as a quite different material at low temperatures to that when it is hot. It has been stated that life depends on these anomalous properties of water. In particular, the large heat capacity, high thermal conductivity and high water content in organisms contribute to thermal regulation and prevent local temperature fluctuations, thus allowing homeostasis. The high latent heat of evaporation gives resistance to dehydration and considerable evaporative cooling. Water is an excellent solvent due to its polarity, high dielectric constant and small size, particularly for polar and ionic compounds and salts. Water ionizes and allows easy proton exchange between molecules, so contributing to the richness of the ionic interaction.

At $4^\circ C$ water expands on heating or cooling. This density maximum together with the low ice density results in

- Fulfilling the necessity of fresh water body along with its surface to stay close to $4^\circ C$ before any freezing can occur,
- The freezing of rivers, lakes and ocean from the top, hence permitting survival of the basal ecology, insulating the water from further freezing, reflecting back sunlight into space and

allowing rapid thawing, and

- Density driven thermal convection causing seasonal mixing in deeper temperate waters carrying life-providing oxygen into the depths.

The large heat capacity of the oceans and seas allows them to act as heat reservoirs such that sea temperatures vary only a third as much as land temperature and so control our climate. The compressibility of water reduces the sea level by about 40 m giving us 5% more land. Water's high surface tension plus its expansion on freezing encourages the erosion of rocks to give soil for our agriculture.

Noticeable amongst the anomalies of water are the antagonistic properties of hot and cold water, with the anomalous behavior more accentuated at low temperatures where the properties of super cooled water often diverge from those of hexagonal ice. As cold liquid water is heated it shrinks, it becomes less easy to compress, its refractive index increases, the speed of sound within it increases, gases become less soluble and it is easier to heat and conducts heat better. In contrast as hot liquid water is heated it expands, it becomes easier to compress, its refractive index reduces, the speed of sound within it decreases, gases become more soluble and it is harder to heat and a poorer conductor of heat. With rise in pressure, cold-water molecules move faster but hot water molecules move slower. Hot water freezes faster than cold water and ice melts when compressed except at high pressures when liquid water freezes when compressed. No other material is commonly found as solid, liquid and gas.

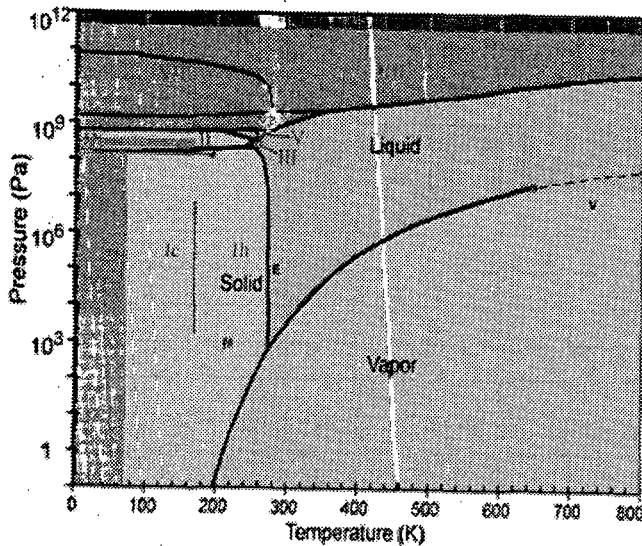


Fig. 1. Phase diagram of water

2. Hexagonal Ice (Ice Ih)

Hexagonal ice (ice Ih) (see phase diagram of water) is the form of all natural snow and ice on Earth, as evidenced in the six-fold symmetry in ice crystals grown from water vapor (i.e. snow flakes). Hexagonal ice possesses a fairly open low-density structure, where the packing efficiency is low ($\sim 1/3$) compared with simple cubic ($\sim 1/2$) or face centered cubic ($\sim 3/4$) structures. The crystals may be thought of as consisting of sheets lying on top of each other. The basic structure consists of a hexameric box where planes consist of chair-form hexamers (the two horizontal planes, opposite) or boat-form hexamers (the three vertical planes, opposite). In this diagram the hydrogen bonding is shown ordered whereas in reality it is random. The water molecules have a staggered arrangement of hydrogen bonding with respect to three of their neighbors, in the plane of the chair-form hexamers. The fourth neighbor (shown as vertical links opposite) has an eclipsed arrangement of hydrogen bonding. Twenty of the 14-molecule tetrahedral units, together containing 280 molecules of water, can form a 3 nm diameter icosahedral structure. The icosahedral structure has two forms – Expanded structure (ES) and Compressed structure (CS).

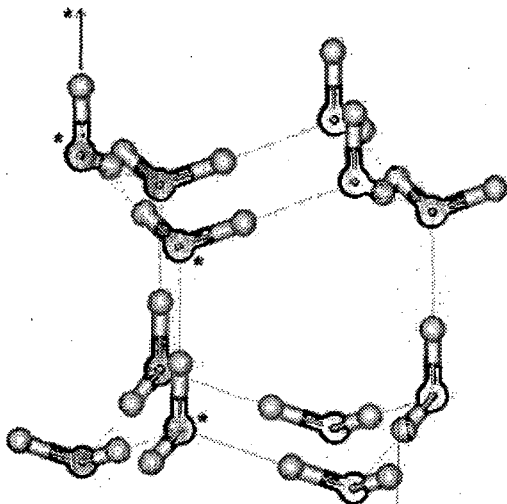


Fig. 2. Hexagonal Ice Structure I

3. Cubic Ice

Ice Ic is a metastable form of ice that can be formed, by condensation of water vapor, at ambient pressure but low temperatures (less than -80°C , see Phase diagram), or below about -38°C in small droplets ($\sim 6 \mu\text{m}$ diameter)^[12] or by reducing the pressure on high-pressure ices at 77 K. Often found are transitional states between hexagonal and cubic ice depending on the formation and history of the cubic ice^[6]. Cubic ice has a slightly higher vapor pressure than ice Ih and may naturally form in the upper atmosphere and is often found in freezing confined (porous) aqueous systems. There is evidence that it may be the preferred phase for ice formed from water droplets smaller than 15 nm radius at 160-220 K. Larger cubic ice crystals convert, irreversibly but extremely slowly in the temperature range 170-220 K, to hexagonal ice with up to 50 J mol^{-1} heat evolution. It consists of a face centered cubic lattice with half the tetrahedral holes filled. The starred molecules show the unit cell positions. The $(\text{H}_2\text{O})_{10}$ cluster, shown in red, has been found in a super-molecular structure.

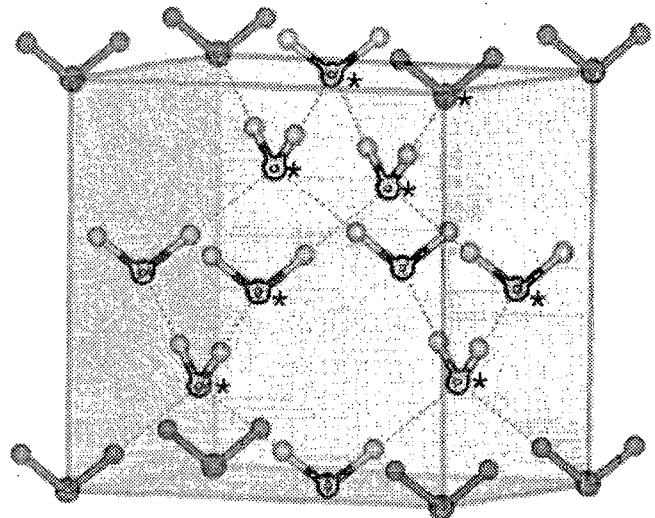


Fig. 3. Cubic Ice

4. Phase Anomalies

4.1 High melting point (0°C , compare CHCl_3 , -63°C)

In ice (Ih), all water molecules participate in four hydrogen bonds (two as donor and two as acceptor) and are held relatively static. In liquid water, some of the weaker hydrogen bonds must be broken to allow the molecules to move around. The large energy required for breaking these bonds must be supplied during the melting process and only a relatively minor amount of energy is reclaimed from the change in volume ($P\Delta V = -0.166 \text{ J mol}^{-1}$). The free energy change ($\Delta G = \Delta H - T\Delta S$, where $\Delta H = \Delta U + P\Delta V$) must be zero at the melting point. As temperature is increased, the amount of hydrogen bonding in liquid water decreases and its entropy increases. Melting will only occur when there is sufficient entropy change to provide the energy required for the bond breaking. The low entropy (high organization) of liquid water causes this melting point to be high. Although ice is very difficult to superheat above its (equilibrium) melting point, tiny amounts of ice (Ih) have been superheated to 290 K (without melting) for very short periods ($> 250 \text{ ps}$)^[7] with the limit of superheating ($> 1 \text{ ns}$) established at about 330 K.

4.2 High Boiling Point (100°C, compare CHCl_3 61°C)

The boiling point of water is 150K higher than that expected by extrapolation of the boiling of other group 6A hydrides. It is also much higher than O_2 (90 K) or H_2 (20 K). There is considerable hydrogen bonding in liquid water resulting in high cohesion (water's cohesive energy density is 2.6 times that of methanol), which prevents water molecules from being easily released from the water's surface. The cohesive density of water is 2.6 times that of methanol. This causes a reduction in the vapour pressure. As boiling point cannot occur until the vapour pressure equals the external pressure, a higher temperature is required. The pressure/temperature range of liquidity for water is much larger than for most other materials. For ambient pressure the liquid range of water is 100°C where as for H_2S and H_2Se it is about 25°C.

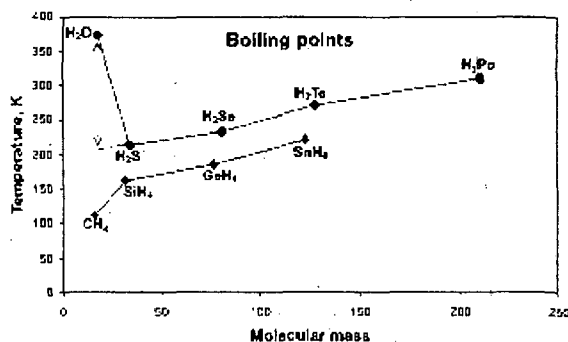


Fig. 4. Comparison of Boiling Points

4.3 High Critical Point (374°C, compare CH_3CH_3 32°C)

The critical point of water is over 250 K higher than that expected by extrapolation of the critical points of other Group 6A hydrides, here shown compared with Group 4A hydrides. e.g. the critical point of water (647 K, 22.06 MPa 322 kg m^{-3}) is far higher than that of ethanol (514 K, 6.14 MPa 276 kg m^{-3}), which too has hydrogen bonds (but in chains not 3-dimensional) and is much larger and more massive.

The critical point can only be reached when the interactions between the water molecules fall below a certain threshold level. Due to the strength and extent of the hydrogen bonding, much energy is needed to cause this reduction in molecular interaction and this requires higher temperatures. Even close to the critical point, a considerable number of hydrogen bonds remain, albeit bent, elongated and no longer tetrahedrally arranged.^[9]

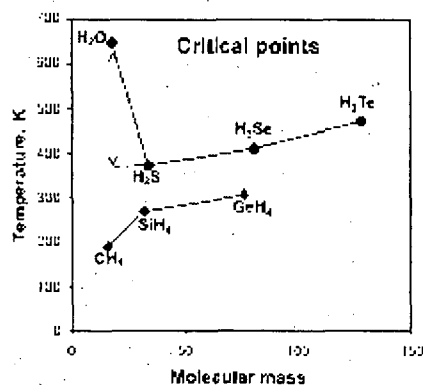


Fig. 5. Comparison of Critical Points

Ammonia and hydrogen fluoride also have somewhat raised values as they form molecular clustering, albeit with three donor H-atoms and one lone pair acceptor group or one donor H-atom and three lone pair acceptor groups, respectively giving a maximum of two hydrogen bonds per molecule, on an average. Although solid HF forms stronger hydrogen bonds, these form linear zigzag chains with no rings or polygons and hence its three-dimensional structure is weaker. The hydrogen bonds in solid NH_3 can form three-dimensional arrangements but are distorted and weakened. Water has two donor H-atoms and two lone pair acceptor groups with close to tetrahedral angles giving the possibility of four hydrogen bonds per molecule with little distortion.

The critical points (C.Pt.), boiling points (B.Pt.) and melting points (M.Pt.) of the molecules isoelectronic with water shows water to have higher values.

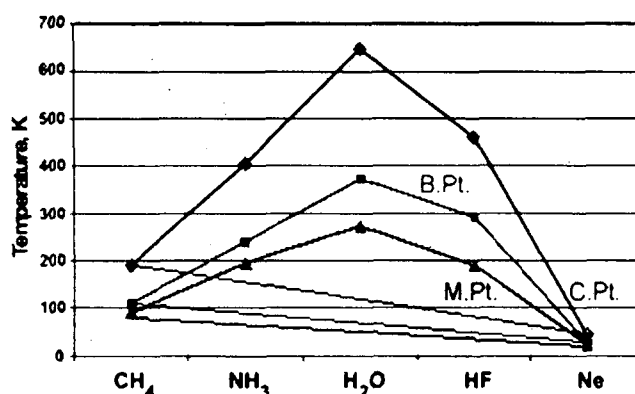


Fig. 6

4.4 Solid Water Exists in a Wider Variety of Stable (and metastable) Crystal and Amorphous Structures than other Materials

The ability for water to form extensive networks of hydrogen bonds increases the number of solid phases possible. The phase diagram shows the preferred physical states of matter at different temperatures and pressure. Within each phase the material uniform w.r.t. its chemical composition and physical state. At typical temperature and pressure (marked as E in diagram) water is a liquid, but it becomes a solid if temperature is lowered below 273K and gaseous (that is steam) if its temperature is raised above 273K, at same pressure. Each line represented a phase. Change in temperature or pressure causes the phases to abruptly change. A triple point is where three lines join, symbolizing 3 phases coexisting at that point. A slight change in pressure or temperature at this point distorts or disturbs the equilibrium. A critical point is one where the properties of two phases become indistinguishable from each other. The open structure of hexagonal ice ($19.65 \text{ cm}^3 \text{ mol}^{-1}$), which contains only about $7.5 \text{ cm}^3 \text{ mol}^{-1}$ of water molecules, gives plenty of scope for different arrangements of the water molecules as the structure is compressed. For comparison, hydrogen sulfide has only four distinct solid phases.^[13]

4.5 The Structure of Liquid Water Changes at High Pressure

Liquid water undergoes a significant change in structure at high pressure (about 200 Mpa), in a similar manner to the formation of

the high-density crystalline and amorphous ice phases. e.g. ice-five (ice V) is formed from liquid water at 500 Mpa by lowering its temperature to 253K. Ice-seven (ice VII) is formed from liquid water above 3 Gpa by lowering its temperature to ambient temperature. Viscosity of water decreases with increases in pressure (at temperature below 33°C). In water increases in pressure causes deformation, which reduces strength of the hydrogen bonded network, which is also partially responsible for viscosity. High pressure increases the self-diffusion of water at low temperature. The compressibility and structural properties of water change above about 200 Mpa. When liquid water is put under pressure (below about 200 Mpa) the water molecules approach their neighbours more closely, as expected from increase in density. If pressure increased from 200 to 400 Mpa the average distance between the neighbouring water molecules increases. These effects appear due to an increase in inter-penetration of hydrogen bonded networks at about 200 Mpa (at 290K); inter-penetration of hydrogen bonded clusters being preferred over more extreme bending or breaking of hydrogen bonds. Other changes also occur around 200 Mpa, such as the loss of the density maximum and the discontinuity in fast sound in liquid water.

This structuring for liquid water at high pressures is consistent to that found by neutron scattering^[16] and indicates that liquid water structuring at high pressure has similarity to that of its high pressure ice phases^[8].

4.6 Super Cooled Water has Two Phases and a Second Critical Point

As water is super cooled it converts mainly into its Expanded Structure (ES) at ambient pressures, which at low enough temperatures (< -38°C) may result in it forming metastable low-density amorphous ice (LDA; although normally it will form hexagonal ice at this temperature). If the pressure on LDA is increased above about 200 MPa then LDA undergoes a 30% collapse forming metastable high-density amorphous ice (HDA) but notably in a continuous process without breaking the hydrogen bonds^[17]. This phase change cannot continue to higher temperatures (so creating a second critical point) as neither of these phases is stable in the presence of liquid water although they may convert into their metastable super cooled liquid forms. The presence of these low- and higher-density forms of liquid (super cooled) water leads to the breakdown of Stokes-Einstein relationship (Stokes-Einstein relationship ($D \times \zeta = \text{constant} \times T$; where D =diffusivity, $\text{m}^2 \text{s}^{-1}$; ζ =dynamic viscosity, $\text{kg m}^{-1} \text{s}^{-1}$; the constant has the units $\text{kg m s}^{-2} \text{K}^{-1}$; and T =absolute temperature, K) in super cooled water^[3] occurring far above the glass-transition temperature, in contrast to many super cooled liquids where this behavior is found only at temperatures just above this transition.

4.7 Liquid Water is Easily Super Cooled but Glassified with Difficulty

Water freezing is not simply the reverse of ice melting^[5]. Melting is a single step process that occurs at the melting point as ice is heated. Freezing of liquid water on cooling involves ice crystal nucleation and crystal growth that generally is initiated a few degrees below the melting point for pure water. Nucleation is the onset of a

phase transition in a small region. Phase transition is the formation of a bubble or of a crystal from a liquid. Creation of liquid droplets in saturated vapour or the creation gaseous bubbles in saturated liquid is also characterized by nucleation. Liquid water below its melting point is super cooled water. It may be expected that the directional hydrogen bonding capacity of water would reduce its tendency to super cool as it would prefer the regular structuring in cold liquid leading to a crystalline state. Liquid water is easily super cooled down to about -25°C and with more difficulty down to about -38°C. Further super cooling is possible, down to about -41°C under normal atmospheric pressure in form of tiny droplets (~5 μm diameter). Water super cooled down to -37.5°C, is sustained in storm clouds. Anomalously at the limit of this super cooling (also known as the homogeneous freezing point) the water activity is always 0.305 lower than that of water melting at the same temperature^[10].

Liquid water may be maximally super cooled to about -92°C at 210 MPa. It should be noted that bulk water never forms a glass as the glass transition temperature ($T_g = \sim 136 \text{ K}$) for water is far lower, relative to its melting point ($T_m = 273 \text{ K}$) than expected. Hence the ratio $T_m/T_g \sim 2$ rather than $T_m/T_g \sim 1.3-1.5$ as for more typical liquids. Thus super cooled bulk water (i.e. not affected by surfaces or solutes) always crystallizes before its temperature can be sufficiently lowered, independent of the cooling rate. Water glass may only be produced by extremely rapid cooling (10^5 K s^{-1}) of tiny volumes of water (< ~100 μm diameter).

As water is cooled, the cluster equilibrium shifts towards the more open structure (e.g. ES) with higher viscosity. In order for crystallization to occur at least 3 - 4 unit cells worth of water molecules have to come together in the correct orientation. The formation of whole or part icosahedral clusters interferes with this process whilst not allowing cluster crystallization due to their fivefold symmetry. Lowering the temperature further, which should encourage crystallization, is partially counteracted by the increase in icosahedral clustering. The presence of clusters is, in principle, in agreement with computer simulation studies requiring the presence of metastable states. Methods that break the hydrogen bonding in these clusters, such as ultrasonics, causes the super cooled water to immediately freeze. There is a recent comprehensive review of the properties of super cooled water.

4.8 Liquid Water Exists at very Low Temperatures and Freezes on Heating

The transformation into a highly viscous deeply super cooled liquid water phase on warming amorphous LDA to about 136 K may indicate an extension of 'normal' super cooled liquid water with structural similarities. This ultraviscous deeply super cooled water has a consistency variously described as "soft toffee" or "molten sherbet" and has a million-fold greater self-diffusion (at the still very low value of $2.2 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ at 150 K) than crystalline ice. The hundred-fold higher viscosity than that expected from its diffusivity may indicate the presence of long-lived crystallites within the deeply super cooled liquid.

Deeply super cooled water can be produced from glassy amorphous ice between -123°C and -149°C^[15] and may coexist with cubic ice

up to -63°C . This behavior is particularly anomalous as the liquid (deeply super cooled water) is a 'strong' liquid (compared with super cooled water that is a 'fragile' liquid) that changes to crystalline solid (cubic ice) on increasing the temperature whilst keeping the pressure constant. Deeply super cooled water exists in the liquid state where it appears to be too cold to diffuse sufficiently quickly to crystallize noticeably. A possible explanation of this low-temperature-range liquid water may be the formation of strands of icosahedral structures. This model can also explain the high viscosity and strong (that is, low specific heat) liquid behavior of this extremely super cooled water¹¹. The unusual behavior of this liquid (that is, deeply super cooled water), by solidifying on heating, has been found with other liquids (for example, methyl cellulose and some cyclodextrin solutions.)

Also, deeply super cooled liquid water may be formed when amorphous ices are 'annealed' at temperatures above 136 K.

This deeply super cooled liquid water is a good solvent for inert gas (Xenon) atoms but a very poor solvent for salt (LiCl). At higher temperatures (~ 165 K) LiCl becomes very soluble, at high concentrations forming a deeply super cooled solution, as its interactions with ultraviscous water overcome the strong water-water interactions present at lower temperatures. The metastable phase diagram above is mainly guesswork, based on the few data available. The red dot represents the position of the proposed second critical point of water. Note that liquid water also changes structures at about 200 MPa.

4.9 Liquid Water may be Easily Superheated

Liquid water can be easily superheated above its boiling point away from its surface with the atmosphere. This may be particularly important while heating foods and drinks in a microwave oven where explosive production of steam from the superheated water may cause severe injuries. Superheating also causes the boiling point of water to vary, in much the same way as its freezing point. Irregular boiling, that is, 'bumping' is also accompanied along with it. Liquid water may be superheated to about $+240^{\circ}\text{C}$ to $+280^{\circ}\text{C}$ in capillaries or small droplets within high-boiling immiscible solvents. Superheating is also apparent at low temperatures but at negative pressures (i.e. stretched water). Water may be superheated by reducing the pressure to below -100 MPa at 20°C ¹⁴. Superheating is facilitated by dissolved gas that may increase its hydrogen-bonded order but prevented by the presence of gas bubbles or nanobubbles (that is, cavities) which act as initiation sites for vaporization. Water vapour (gas) may easily be cooled below its condensation temperature (dew point) for its partial pressure (i.e. its boiling point) in the absence of dust, or other particles or surfaces that help the nucleation process. An interesting, if unrelated effect (the Leidenfrost effect), is that water droplets remain far longer on a hotplate just above 200°C than if the hotplate was just above 100°C .

4.10 Hot Water may Freeze Faster than Cold Water; The Mpemba Effect

The ability of hot water to freeze faster than cold seems counter-intuitive as it would seem that hot water must first become cold water and therefore the time required for this will always delay its

freezing relative to cold water. However experiments show that hot water (for example, 90°C) does often (but by no means always) appear to freeze faster than the same amount of cold water (for example, 18°C) under otherwise identical conditions.¹²

Experiments show the degree of super cooling is greater, under some circumstances, in initially-cold water than initially-hot water. The initially-hot water appears to freeze at a higher temperature (less super cooling) but less of the apparently frozen ice is solid and a considerable amount is trapped liquid water. Initially-cold water freezes at a lower temperature to a more completely solid ice with less included liquid water; the lower temperature causing intensive nucleation and a faster crystal growth rate. If the freezing temperature is kept about -6°C then the initially-hot water is most likely to (apparently) freeze first. If freezing is continued, initially-cold water always completely freezes before initially-hot water.

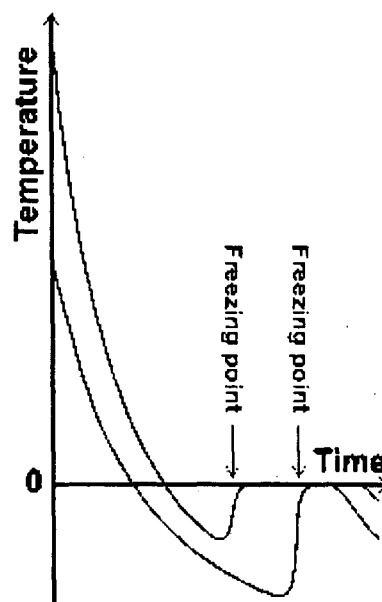


Fig. 7.

4.11 Warm Water Vibrates Longer than Cold Water

In case of a typical liquid an increase in temperature causes an increase in energy and molecular interactions, leading to a decrease in the lifetime of an excited molecular vibration. For example, the lifetime of the excited liquid HCl stretch vibration decreases from 2.1 ns at 173 K to 1.0 ns at 248 K.

In liquid water, the excited OH-stretch vibration has a lifetime of 0.26 ps at 298 K and this lifetime increases to 0.32 ps at 358 K¹¹. The reason for this is due to the effects of the hydrogen-bonded network. The OH-stretch vibration normally relaxes by transferring energy to an overtone of the H-O-H bending vibration. However, as the temperature increases the hydrogen bonds of water get weaker, which leads to an increase of the frequency of the stretch vibration and a decrease of the frequency of the bending.

5. Conclusion

These were a few anomalies of water. But beyond this a lot of research has been done and a lot demands to be excavated in this field so as to explore the properties of a molecule of water. Due to

these exceptional properties of water, it is being recruited commercially by using a variety of approaches. The journey through this paper so far summarizes the micro views of this hidden inherent behavior of water.

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