

BREAKING THROUGH EDITORIAL



The Latent Heat Saga

Peter Graneau

An outstanding scientific and technological achievement of the twentieth century has been the evolution of nuclear energy which forms part of the mix of energy sources on which the continued growth of our civilization depends. In the twenty-first century we may be blessed with the arrival of another source of energy, of similar magnitude, which is more benign than nuclear energy and does not have the disadvantages of fossil fuels, that is their declining availability and their pollution of the atmosphere. The potentially new energy of the present century is hydrogen bond energy stored in ordinary liquid water. It is hard to believe that we can speak of new energy when its existence should have been recognized long ago during two centuries of water science. So far no sizeable attempt has been made to utilize this hydrogen bond energy for the generation of electricity or the propulsion of motor vehicles.

Notwithstanding the great abundance of water on the surface of the earth and its scientific appeal for over two thousand years, water has somehow managed to conceal part of its internal energy with the confusing concept of "latent heat." This latent or concealed heat is said to have been discovered 250 years ago, but still shrouds itself in mystery. How can something be discovered and remain a mystery? The story is told by the German scientist Stefan Emeis¹ in a recent issue of a meteorological journal.

In 1758, Scottish chemist and professor at the University of Glasgow, Joseph Black, measured the temperature of a block of ice as it was steadily heated through the melting point of 0°C. First the temperature of the ice slowly increased until it reached 0°C. Continued heating had no effect on the thermometer until all the ice had been converted to liquid water. Black called the traceless disappearance of heat in the melting process the latent heat (of fusion). He made the same type of measurement of the reverse process of freezing water. As he extracted heat from warm water, the temperature of the liquid would drop gradually until it reached 0°C. At this point the temperature stopped falling below the freezing temperature while further heat was subtracted from the water. Not until all the water was converted to ice did the ice temperature fall below 0°C. The heat that disappeared without any temperature change in the cooling process Black also called latent heat (of solid-

ification), because it seemed to be the same amount of heat that had disappeared in melting. With today's terminology, the melting and freezing operations are described as reversible phase transitions involving the same latent heats.

Professor Black also investigated the liquid to gas (vapor or steam) phase transition, which is known as evaporation, and the reverse process of condensation. Again he found that the disappearing latent heat of evaporation was equal to the latent heat of condensation. The two reversible phase transitions at 0°C and 100°C were, however, very different in the quantity of heat involved. It took about eight times as much heat energy to convert one gram of liquid to steam than the latent heat of transforming one gram of ice to liquid water. At both phase transitions, energy was apparently not conserved and it was stored for an indefinite time at an unknown location between melting and freezing as well as between evaporation and condensation of the water.

At the time of the discovery of latent heat, little was known about the chemical bonding of atoms. The issue of storing and liberating bond energy in phase transitions never arose. Had the latent heat been discovered 100 years later, in the middle of the nineteenth century, it would have immediately clashed with the new concept of energy conservation which was slowly becoming the overriding principle of physics today. The conservation of energy ultimately replaced the conservation of the caloric heat medium. But this had to wait for Prescott Joule's experiments proving that heat could do mechanical work. In 1850 Joule's mechanical equivalent of heat came to 4.16 J/cal. The unit of energy was named "Joule (J)" in honor of Prescott Joule's major contributions to modern thermodynamics.

The notion of the latent heat of water survived the introduction of Joule's mechanical equivalent of heat because the cohesion of liquid water was not yet recognized as resulting from a chemical bond between two water molecules (H₂O). Such a bond was first suggested by the Nobel chemist Gilbert Lewis in 1923. It has become known as the hydrogen bond of water. Gilbert defined it as a chemical bond between an oxygen atom in one water molecule and a hydrogen atom in a neighboring molecule. This should not be confused with the covalent O-H bond inside the water molecule. Each liquid water molecule is now believed to be able to form up to

four hydrogen bonds to neighboring molecules. This gives rise to a very complex structure of ordinary water which is continuously subject to thermally and mechanically activated changes. Hydrogen bonding has been extensively discussed in the literature of water science.

Chemists have believed the breaking of hydrogen bonds in water is always a thermal process. This was finally disproved in 1994,² when our high-speed photography of water arcs established bond rupture by mechanical tension in an arc plasma column. At the same time it was shown that far more hydrogen bond energy from water can be liberated in an arc than had been expended in the formation of the arc. Breaking hydrogen bonds with tension in the arc column appeared to be a greatly more efficient process than liberating the same amount of bond energy with heat. The strength of water arc explosions revealed hydrogen bond energy which was at least 100 times as great as the tensile force energy expended in breaking the bonds. Black's introduction of the latent heat of water was undoubtedly helpful in the eighteenth century, before the notion of chemical bond energy was developed. While studying chemical bonds between atoms it was found that the bonds store potential energy, which became known as bond energy or chemical energy. This is in fact the same kind of energy as that gained from the combustion of fossil fuels. The chemical bond energy is set free when the bond is ruptured. It first appears as kinetic energy of the particles which are being separated by the bond fracture. A typical definition of chemical bond energy is³: "There is present, within the molecule, chemical energy which is related to the forces which hold the atoms together in the molecule. This is referred to as chemical energy."

Although this definition refers to inter-atomic bonds within the molecule, it will be appreciated that similar forces and energy hold atoms together in the hydrogen bond between two molecules of liquid water. Therefore hydrogen bonds do store chemical bond energy. When one of these bonds is broken, its stored chemical energy must be set free as kinetic energy of the separated particles. The flaw of chemistry—as taught today—is to assume that evaporation is the only process by which the hydrogen bond can be broken. As already pointed out, it takes the mechanical equivalent of the latent heat of evaporation to break the bond by thermal action. This action is probably a complex multiple collision process. However, when the bond is ruptured by mechanical tension, a quantity of energy much less than the latent heat is required. Breaking the bond in this manner allows the stored energy of repulsion to be realized as kinetic energy of the separated particles, which could be employed to generate electricity.

It is not easy to apply tension to intermolecular bonds in liquid water. One way of achieving water tension is to pass a concentrated electrical current pulse through water. It is well known that the passage of similar current pulses through a wire will explode the wire into small fragments. Water is a dielectric substance, but it will break down when a high voltage is applied between two separated, submerged metal electrodes which are connected to the terminals of a charged capacitor. Dielectric breakdown of liquids and gases produces conducting plasmas. The current pulse in the wire and that in the water arc plasma column creates longitudinal, electrodynamic Ampere tension⁴ which splits a wire into metal fragments and a water arc column into fog droplets.

The creation of fog droplets proves the tensile rupture of hydrogen bonds. The released hydrogen bond energy then drives the water arc explosion.^{2,4}

Another way of applying tension to the bonds between water molecules is to slide a fluid or solid substance over the water surface. Adhesion between water and another medium leads to drag forces on the water molecules and to tensile forces between adjacent water molecules. The phenomenon is often called boundary layer drag. The same forces impede the motion of ships through water and could be described as friction. It is also the method by which wind, storm, and hurricane forces shear clouds of tiny fog droplets off the ocean surface. A sample calculation has shown⁵ that the removal of a 16 μm thick layer of tiny fog droplets, per second, from the ocean surface would be of the right order of magnitude to drive a powerful Atlantic hurricane.

Horizontal wind over the ocean surface drives waves in the wind direction. When the crests of waves break, white caps appear which indicate hydrogen bond rupture without which white droplets and films of water cannot be brought into existence and seen. The bond energy liberated in this process is probably quite small, but it is likely to influence the foam motion in some way. The effect will be greatly magnified in a hurricane.⁵

In a large tropical storm, the horizontal air flow causes boundary layer drag and inter-molecular water tension in the wind direction. Therefore the molecular explosions, resulting from tension breaks of hydrogen bonds, will all cooperate in the wind direction. Hence more wind so strengthened produces more bond explosions in the wind direction. This is positive energy feedback which is the likely cause of the self-intensification of hurricanes. It is a more credible mechanism with which to explain the build-up of the cyclonic storm than the deposition of latent heat of condensation in the violent storm cloud.⁶ Therefore hydrogen bond energy is suspected to be the most significant contribution to the devastating force of hurricanes.

Since latent heat and hydrogen bond energy are clearly associated with phase changes of water, there should exist some interdependence between the two measures of inter-molecular energy. Not all physical chemistry books of water science ignore this important interdependence. An example is G.S.H. Lock's work on the *Latent Heat Transfer: An Introduction to Fundamentals*,⁷ which was published in 1994. In general, Lock recognized the stored energy in hydrogen bonds, but he found that any quantitative correspondence between the bond energy and latent heat was approximate. He did not mention the problems which arise when trying to replace the latent heat figures with hydrogen bond energy figures.

Uncertainty in the relationship of latent heat and bond energy stems from the fact that, in the liquid water state, the number of hydrogen bonds per water molecule fluctuates all the time due to thermal agitation of the liquid. The average number of bonds per molecule is believed to fall between two and three. This average is known to depend on the water temperature. Similarly, the total hydrogen bond energy per unit volume is also temperature dependent and not easily related to the latent heat of evaporation.

The latent heat concept, introduced in 1758 by Professor Black, seemed to constitute an empirical fact, even though it did not comply with heat conservation of the prevailing

caloric theory. Black himself was not convinced of the caloric heat model and, therefore, he could easily reconcile himself with the violation of heat conservation. It took another hundred years before energy conservation assumed the important role it now plays in physics. Up to this time, no good reason existed to challenge the latent heat model and the strange disappearance of considerable amounts of energy for a long period of time.

The growing understanding of chemical bonding should have forced the issue. But chemical bonding was a difficult subject at a time when grasping the structure of atoms was still in its infancy. How could one confidently discuss interatomic bond energy when negatively charged electrons refused to combine with the positive charges of the atomic nucleus?

Before the mystery of the electron structure of atoms was resolved by the quantum mechanics of Heisenberg, Schrödinger and Dirac in the early 1930s, Gilbert Lewis had already proposed that chemical bonding was largely controlled by the outer electrons of atoms. In the upheaval of physics and chemistry by quantum mechanics, little attention was paid to the storage of potential energy in chemical bonds. So it came to pass that, in 1923, physical chemists embraced the hydrogen bond between water molecules without so much as mentioning the storage of hydrogen bond energy.

Now in the early twenty-first century, chemical bond energy of chemical compounds is well established in the scientific literature. Yet hydrogen bond energy seems to have been forgotten. The huge amount of energy consumed by the activities of human society is, foremost, dependent on the availability of chemical bond energy stored in fossil fuels. The burning of these fuels pollutes the atmosphere and may be responsible for global warming. Hydrogen bond energy from water could be substituted for the heat of burning fuels, if only the majority of chemists were made aware of the existence of this form of energy in the great amounts of water on the surface of the earth.

What has not helped is that the term "bond energy" has been used for two quite different physical quantities. In the present editorial it is being employed for the chemical energy stored in a chemical bond between two atoms. This chemical bond energy has already been defined above as the chemical energy present (stored) in molecules. It equally applies to chemical bonds between two molecules as, for example, to the hydrogen bonds in water. What is important in this definition is that it concerns stored potential energy which can be liberated and transformed to another form of energy like kinetic energy or electricity.

The second definition of "bond energy" is quoted widely in chemical texts. R.H. Petrucci⁸ states it as follows: "Energy is released when atoms join together through a chemical bond and must be absorbed if bonded atoms are to be separated. Let us define bond energy as the quantity of energy required to break one mole of chemical bonds in a gaseous species."

Two differing definitions of bond energy are what has made this subject so prone to confusion. Petrucci does not say whether his definition of bond energy also applies to liquids and particularly to hydrogen bond energy in water. Many chemists appear to believe that something like the Petrucci definition also holds for liquids, because no alter-

native has been proposed. The heat energy required to break the hydrogen bonds in water is then equal to the latent heat of vaporization. This is one connection between the latent heat of water and hydrogen bonding.

Another connection between latent heat and hydrogen bonding is found in the condensation of water. According to the Petrucci definition of bond energy, the condensing water molecules should donate the latent heat of condensation to the environment instead of devoting it to the formation of hydrogen bonds. The most likely source of both the stored energy in bonds and the energy donated to the environment is the restructuring of the outer electron configurations as the two molecules approach each other under the influence of their increasing attractive force which is caused by the quantum properties of the electrons themselves. As the molecules approach each other, the electron potential energy is reduced and some converted to latent heat and given to the environment and the rest is stored as bond energy of repulsion between the positive nuclei of the bonded pair of molecules.

Starting with evaporation, sensible heat from liquid water or other elements of the environment has to be transformed to the mechanical work for undoing hydrogen bonds. This aspect of water science was not understood when Black defined the latent heat of evaporation. It caused him to speak of concealed (latent) heat which ceased to exist, but would reappear, miraculously, later during condensation of gaseous water molecules. The conversion of heat to mechanical work was quantified a hundred years after Black introduced the latent heat, and became known as the mechanical equivalent of heat (4.18 J/cal). The mechanical work is not lost. It can be converted, for example, to gravitational energy by lifting weights, or to kinetic and pressure energy in a steam engine. Therefore the conversion of heat to mechanical work does not conflict with energy conservation.

Returning once more to evaporation and the process of breaking hydrogen bonds, this can be achieved in two different ways. When boiling water, and also in evaporation at sub-boiling temperatures, heat in the form of complex angular and linear vibrations can be of sufficient intensity so as to rupture inter-molecular bonds. This is the common approach to this problem in laboratory experiments. When wind blows over the ocean surface we also rupture hydrogen bonds, not by heating, but by drag forces in the air-water interface. This mechanism is verified by the formation of water mist and foam at the surface of the sea. Inter-layer friction or drag forces create tensile stress in the water surface. With sufficient wind speed, this tensile stress will lead to hydrogen bond fractures.

Tensile stress in water can also be produced by passing an arc current through a column of water. Under these circumstances it has been found² that the tensile (mechanical) rupture of hydrogen bonds requires far less energy than the kinetic energy of the resulting explosion. The indications are that the ratio of tensile fracture energy to kinetic expansion energy is less than 1:100. It is in this way that the large energy magnification can occur at the ocean surface underneath the hurricane cloud. It pumps as much power into a single storm as is generated, simultaneously, in all the electric power plants installed on earth.

With the latent heat concept firmly implanted on the teaching of meteorology, hurricane experts have struggled to

argue that storm self-intensification is an example of positive energy feed-back by latent heat liberation during condensation of water at various altitudes in the storm cloud. We have shown that this is unlikely to be a true explanation of storm self-intensification because condensation requires a strong thermal gradient to exist in order to extract the liberated heat. However the liberated heat in a rising column of air reduces the thermal gradient and thus lowers the condensation rate. This negative feedback is very unlikely to be the true mechanism of hurricane self-intensification. Condensation is also known to be more prevalent in still conditions rather than in windy ones. This makes hurricanes a very unlikely place of intense condensation. Besides, the thermal cloud expansion due to the liberation of the heat of condensation does little to accelerate the fog in the forward direction of cyclonic motion.

The latent heat has been a useful idea from 1758 to about the middle of the nineteenth century. In this span of time it helped to account for heat transferred from one phase to another. It applied to water and other substances. When chemical bonding and un-bonding became a factor of changing phases, it should have been realized that the energy transferred in phase changes had to be either heat or electron bonding energy, but not both at the same time. For one reason or another, and mainly because of the upheaval of physics and chemistry by the introduction of quantum mechanics, we have arrived at the beginning of the twenty-first century before a reconciliation of hydrogen bond energy and the latent heat of water is being attempted.

There is really no doubt that it takes energy to undo the hydrogen bonds during evaporation of water. The sensible heat which is subtracted from the liquid phase defines the latent heat of evaporation and produces the well-known evaporation cooling effect. The latent heat in conjunction with the stored bond energy of repulsion is the mechanism for thermally separating the hydrogen bonds. We have experimental data for the heat subtracted from the liquid and this is how we know the latent heat of evaporation. Evaporation can be a very gentle process in which bonds are broken, but the separated molecules can have little or no kinetic energy. In contrast, rupturing the hydrogen bond with mechanical tension is followed by a sharp pulse of repulsion (explosion) between the separated molecules, which has been proved with water arc experiments.²

During the past century writers of chemistry texts have recognized the imprecise language of latent heat and particularly the latent heat of water. The most unsettling aspect was, of course, the disappearance and reappearance of large quantities of heat during phase changes of water, which meant that the energy had to be stored by some non-thermal mechanism. Replacing the words "latent heat" by "enthalpy change" proved to be a way around these difficulties.

The enthalpy of a quantity of atoms or molecules is primarily the internal energy of the particles. For a monatomic gas this is a combination of the kinetic energy of the linear motion of the atoms and the internal energy stored by the interactions of the electrons with the nuclei. However, for polyatomic gases we have to take account of their rotational and vibrational kinetic energy as well. A large contribution to the internal energy and the enthalpy change is usually the chemical energy stored in chemical bonds. Take the example

of water molecules. Much of their enthalpy is the chemical energy inside the H₂O molecules. But this is the same in the gas and the liquid phase and does not contribute to the enthalpy change of phase transformation. On the other hand, hydrogen bond energy is present only in the liquid phase and it is a major part of the enthalpy change of water. Hence the linguistic replacement of latent heat by enthalpy change did finally focus on hydrogen bond energy in the phenomena of evaporation and condensation. But this is not the end of the story.

When water evaporates, sensible heat of the liquid does mechanical work in undoing hydrogen bonds. If this occurs at 50°C, this heat is taken from the liquid water and cools it by evaporation. If, however, the water boils at 100°C, the heat of evaporation is derived from an external source (e.g., flame) and passed through the liquid water to the vaporization sites. The liquid temperature then remains constant. These are the only mechanisms of hydrogen bond rupture normally described in textbooks. They liberate the previously stored hydrogen bond energy and pass it on to the newly formed vapor molecules.

Our research on water arc explosions² revealed that hydrogen bonds may also be broken by tensile stress rather than thermal action. The mechanical work expended on tension breaks to produce a certain amount of liberated kinetic vapor energy is generally less than 1% of the thermal bond breaking work. This is a most important discovery for the efficient extraction of hydrogen bond energy from water to drive electricity generators. Unfortunately, the same efficient hydrogen bond rupture mechanism also drives hurricanes to wreak their awe-inspiring devastation.

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