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The (In)Difference of Water

Water is an astonishing substance whose unique properties are crucial for the conditions on our planet, making it possible for life as we know it to exist. We might ask, is water an "indifferent" substance? There are a number of ways such a question might be answered.

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In chemical science, the concept of "indifference" might be applied to molecules in several different ways:

- An "indifferent" molecule might be one that lacks any electric charge (here, the technical term is *electrically neutral*). In an electrically neutral molecule, the number of protons in the nuclei of the composite atoms is equal to the number of electrons in the molecule. The opposite notion is an ionized molecule or compound – a chemical unit with an unbalanced number of protons and electrons.
- Alternatively, an "indifferent" molecule might be one that is inactive or non-reactive (in other words, *chemically inert*). The opposite here is a chemically reactive or aggressive substance. Often laboratory work involves working in an "inert atmosphere" or carrying out a reaction in an "inert solvent." Such precautions are designed to prevent the substances being tested from undergoing unwanted chemical reactions with molecules in the medium in which the reaction happens to take place (e.g. with oxygen or water vapor present in the air).
- Or, an "indifferent" molecule might be taken to be one in which the concentrations of hydrogen ions and hydroxide ions are equal (in other words, *pH neutral*). pH is a logarithmic scale used to specify the acidity or basicity of an aqueous solution, with 7 taken as the "balanced" center of the scale.

These three notions are interrelated. Moreover, they are all linked together in Polish chemistry terminology, via the word *obojętny* ("indifferent") – which can sometimes mean *electrically neutral*, *chemically inert*, or *pH neutral*, often giving rise to a certain confusion.

Indifferent water, take one: pH always equal to 7?

Ultrapure water is a conductor of electricity. This is due to a phenomenon known as the auto-dissociation of water, whereby certain H-O bonds become broken, forming hydrogen (H^+) and hydroxide (OH^-) ions. We should hasten to point out that free H^+ ions do not exist in aqueous solutions. Rather, interacting with the free electron pairs of the oxygen atoms in water molecules, they form hydronium ions (H_3O^+) and other oxonium ions stabilized by hydrogen bonds or fluctuations of the H^+ ions between several water molecules – e.g. the Zundel cation ($H_5O_2^+$), the Eigen cation ($H_9O_4^+$), the Zundel cation solvated by four H_2O molecules ($H_{13}O_6^+$), etc. (see Fig. 1). "Solvation" means the interaction of a chemical entity (ion, molecule, atom) with molecules of the surrounding solvent, leading to the formation of a so-called solvation en-

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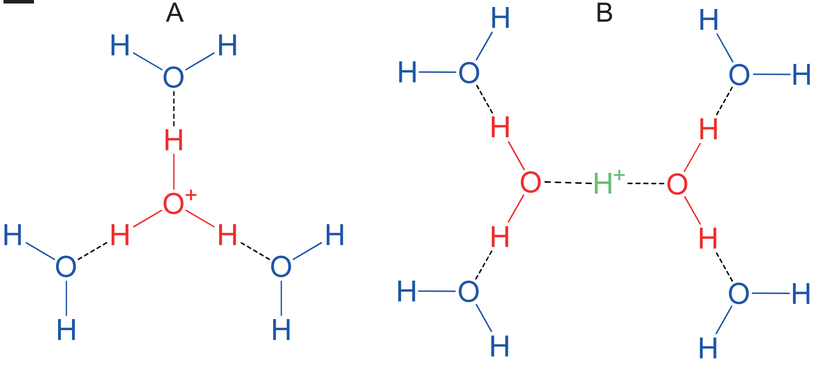

Fig. 1
The Eigen cation (A) and solvated Zundel cation (B)

velope around it. Crucial roles in the solvation process are played by hydrogen bonds and weak electrostatic interactions.

OH^- anions also undergo strong solvation, forming $H_3O_2^-$, $H_{11}O_6^-$, and other ions. However, for the sake of clarity, let us describe the auto-dissociation reaction of water using the simplest formula:

$$H_2O \rightleftharpoons H^+ + OH^-$$

At 25°C, the concentration of H^+ ions (including all its solvated forms) in pure water is 10^{-7} mol/dm^3. The concentration of OH^- ions is obviously the same. And so we can conclude that in one sense at least, water is indeed "indifferent": in the sense of *pH-neutral*. However, let us now take a closer look at pH – a logarithmic scale used to specify the acidity or basicity of an aqueous solution:

$$pH = -\log a_{H^+}$$

where a_{H^+} is the hydrogen ion activity.

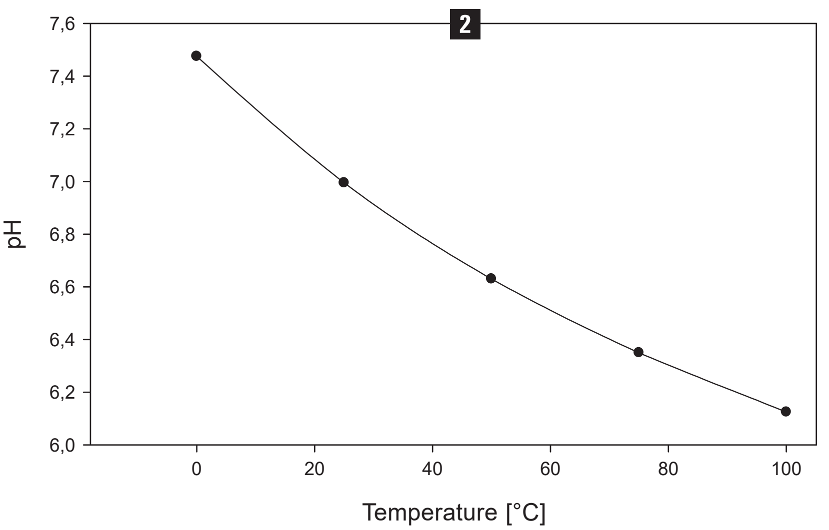

Fig. 2
pH of water as a function of temperature

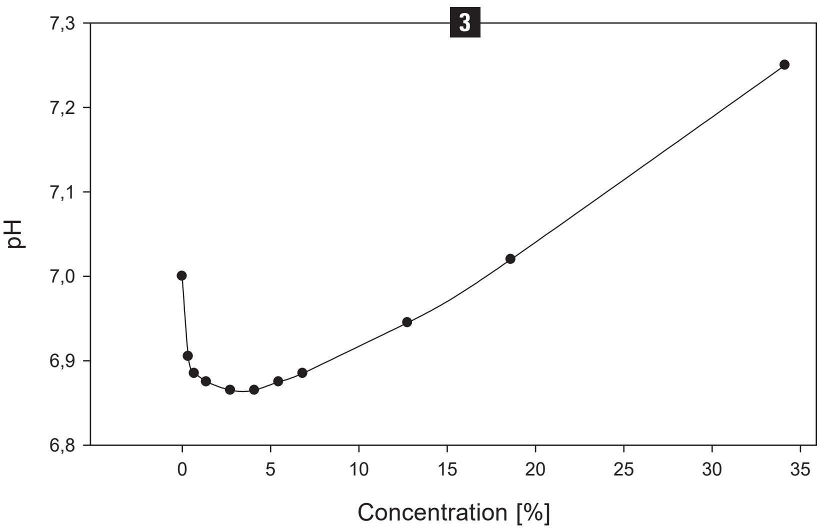

Fig. 3
pH of water as a function of sodium chloride concentration in solution at 25°C

The activity of an ion is related to its concentration, but this relationship is not linear. The activity of any ion also depends on the presence of other ions in the same solution. For very dilute solutions, it can be assumed that the activity of an ion is equal to its concentration. For pure water at 25°C, the pH value is therefore 7. This leads many non-chemists to erroneously conclude that a *pH-neutral* solution is any solution with pH = 7. Why is this erroneous? Firstly, because the process of auto-dissociation of water depends on the temperature. Since it is an endothermic reaction (the disintegration of the water molecule involves the absorption of heat), an increase in temperature shifts the equilibrium of the reaction toward the products (in keeping with Le Chatelier's principle). It follows that in hot water the concentration of H^+ ions is higher than in cold water, so hot pH-neutral water has a pH < 7. How big are these effects? Surprisingly, quite significantly so. The graph in Fig. 2 shows the pH of water as a function of temperature. As can be seen, between 0 and 100°C the change in pH of neutral water is 1.5 units. At 250°C, pure water at a pressure of 25 MPa has pH as low as 5.5!

As we have mentioned, however, the activity of H^+ ions is also affected by the presence of other ions in the solution. So let's try to analyze the effect of a salt – sodium chloride – on the pH value. Sodium chloride is a neutral salt, which means that when it is introduced into water, it does not undergo the hydrolysis reaction and so it does not disturb the balance between the H^+ and OH^- ions. However, the introduction of sodium chloride into water does cause the appearance of new ions in the system: Na^+ cations and Cl^- anions. These ions influence the inter-ion interactions in the solution – for example, one can imagine electrostatic interactions between a solvated H^+ ion and a chloride anion. In addition, these ions compete as centers of solvation. Figure 3 plots the change in pH based on the percentage of salt concentration. Thus, a physiological solution of salt (about 0.9%) will have a pH of about 6.85, whilst still remaining pH-neutral.

By a similar token, "pure" water in the laboratory usually exhibits a pH different from 7 – a fact that invariably astounds students. The most common methods of water purification are distillation or deionization. Routine laboratory procedures do not isolate the water from the air during and so it becomes saturated rather quickly with atmospheric gases and possible contaminants present in the laboratory atmosphere. The pH value of distilled water is therefore about 4.5–5, mainly due to the presence of carbon dioxide in the air. Carbon dioxide is an acidic oxide, and in aqueous solutions, it forms a certain amount of H^+ ions:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

which cause a lowering of the pH. For this reason, the term "acid rain" is somewhat misleading since any

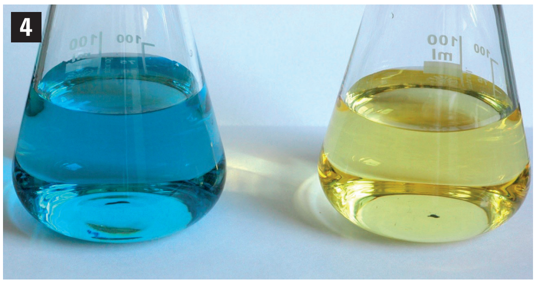

Fig. 4
Deionized (left) and distilled (right) water with bromothymol blue – an indicator changing color from yellow to blue at pH about 6

rain is acidic; it's just that those that fall near industrial centers are slightly more so. This is due to the presence of anthropogenic (i.e., man-made) acidic oxides – NO_x and SO_2. Deionized water is obtained in a two-stage process. In the first stage, water is deprived of most ionic and organic impurities by reverse osmosis, which involves selective penetration of H_2O molecules through polymeric membranes. In the second stage, water is passed through a bed of granular polymer called ionite (or ion-exchange resin), which exchanges all cations present in the treated water into H^+ and anions into OH^-. In theory, the water leaving the deionizer should have pH = 7, but in our personal experience, it is most often slightly alkaline (pH = 7.2-7.6), which is most likely due to a certain number of Na^+ ions not being captured by the ion exchanger. This means that, if we assume the "indifference" or electrical neutrality of the solution, there will be a certain excess of OH^- ions in the deionized water (Fig. 4).

Deionized water stored in contact with air quickly becomes acidic due to the dissolution of CO_2. The preparation of ultra-pure water (mainly for applications in the semiconductor industry) involves multiple ion exchange and filtration in a reverse osmosis system, sorption of contaminants on activated carbon, oxidation of organic contaminants by UV-C irradiation (and ozonation), ultrafiltration, and removal of gaseous pollutants using membrane filters. In the past, water for special applications was purified by multiple distillations in quartz and platinum (or gold) apparatus and by hours of heating in gold flasks under a constant flow of noble gas.

In summary, truly pure water is electrically neutral, yet does not always have a pH = 7. In most cases, however, the "pure" water used in the laboratory is neither electrically neutral nor pH-neutral.

Indifferent water, take two: affinities and dislikes

Everyone probably remembers from chemistry classes at school a demonstration in which sodium (or another alkali metal) was reacted with water: a rapid, almost violent process, often ending with the ignition of the metal or a small explosion (Fig. 5).

The O-H bond is strong (with bond energy of 463 kJ/mol), but many substances react spontaneously (and often violently) with water. In other words, water is not "indifferent" in the sense of *chemically inert*. The table below lists examples of compounds that "dislike" water in this way, often reacting quite vigorously with it. Some of these reactions have been

Fig. 5
Metallic potassium violently reacting with water

Group of compounds	Examples	Example reaction
Reactive metals	Li, Na, K, Cs, Ca, Eu	$2Cs + 2H_2O \longrightarrow 2CsOH + H_2\uparrow$
Metal hydrides	NaH, $LiAlH_4$	$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3\downarrow + 4H_2\uparrow$
Amides, nitrides, phosphides	$NaNH_2$, Li_3N, Zn_3P_2	$Zn_3P_2 + 6H_2O \longrightarrow 3Zn(OH)_2\downarrow + 2PH_3\uparrow$
Organometallic compounds	CH_3MgCl, C_4H_9Li	$C_4H_9Li + H_2O \longrightarrow LiOH + C_4H_{10}\uparrow$
Anhydrous halides of certain metals	$TiCl_4$, $AlBr_3$, $SnCl_4$	$TiCl_4 + 2H_2O \longrightarrow TiO_2\downarrow + 4HCl\uparrow$
Halides of non-metals	$OPCl_3$, $SiCl_4$, BF_3	$OPCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl\uparrow$
Acyl anhydrides and halides	$(CH_3CO)_2O$, CH_3COCl	$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$
Oxides of certain metals and non-metals	SO_2, P_2O_5, Na_2O_2, CaO	$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

Fig. 6
Reaction of $TiCl_4$ with water – note the fog, comprised of hydrolysis products

or are of practical importance – e.g. hydrolysis products of $TiCl_4$ have been used to produce smokescreens (unfortunately with corrosive properties) during military operations (Fig. 6), and peroxide reactions have been used to produce oxygenated water.

Generally, the non-inertness of water is quite a nuisance for chemists and forces them often to rigorously and cumbersomely maintain reactants under anhydrous conditions. Over the years, many ways of storing water-sensitive substances have been developed – bottles with special closures (Fig. 7), ampoules (Fig. 8), isolating materials under a layer of kerosene or mineral oil, etc. Research work involving such reagents is more cumbersome because it requires the use of glove boxes, argon-vacuum lines, and other techniques. Often the preparations, including the necessary drying of solvents and apparatus, take more time than the actual experiment. Unfortunately, substances that react violently with water have also been the cause of many laboratory accidents and pose a hazard to firefighters combatting laboratory and chemical plant fires.

Of course, the reactivity of water is not limited to violent reactions. Slow reactions are also quite a problem – to mention just electrochemical corrosion or hydrolysis of active drugs in complex preparations.

Fig. 7
A bottle closed by a silicone-Teflon membrane (called a septum cap) which protects the contents from humidity and oxygen from the air, enabling reagents to be drawn out with a syringe (the bottle contains anhydrous dimethyl sulfoxide – DMSO)

It should be emphasized, however, that if water were chemically inert, there could be no life on Earth – as photosynthesis, the hydrolysis of nutrients (lipids, proteins, sugars), and many other biochemical processes would be impossible. So, we are quite fortunate that water is not "indifferent" in the sense of chemically inert.

Indifferent water, take three: verging on quackery

We should stress, however, that water itself (as a molecule) is electrically neutral. Of course, it can dissociate into ions (see part one), but then it essentially ceases to be water. Ions formed from water molecules as a result of electron detachment (H_2O^+) or electron attachment (H_2O^-) are impermanent. Detaching an electron from a water molecule requires an energy input of 1220 kJ/mol. It is easier to force water to absorb an electron, the energies required for this process being an order of magnitude smaller. Apart from the laboratory, ionized water also exists in the natural world – out in space, such as in interstellar dust or cometary plumes. It is detected by radio astronomers on the basis of characteristic signals in the GHz and THz bands.

However, ionized water is a topic of much debate within the "alternative medicine" community. Swindlers exploiting human credulity peddle various systems for the production of "ionized water" (or "alkaline water," "living water"), allegedly with positive health effects on the human body. The pseudo-scientific explanations for its alleged action include "the presence of free electrons" and "enrichment with OH-groups." It should be emphasized, however, that physics and chemistry inexorably show these revelations to be fraudulent: the solution as a whole must remain electrically neutral, and free electrons are strong reducers. As a result, free electrons immediately react with hydronium ions, resulting in water and hydrogen, and "enriching" of water with OH^- ions must be accompanied by the presence of counter-ions (cations). Hence, alternative medicine aficionados should consider whether it would not be simpler just to drink water similarly "enriched," for instance, with a chemical drain cleaner.

The conclusions are simple – water is "indifferent" in the sense of electrically neutral, although it can be ionized (it remains a philosophical question as to whether then it is still water). However, ionized water is impermanent and all miraculous health products allegedly containing "living water" should be dismissed as nothing but fairy-tales.

By way of a summary

The complex properties of water, often illogical or surprising at first sight, support the very possibility of life on Earth and a number of processes occurring in our environment. So is it "indifferent"? Well, yes and no. We could sum up our discussion here as follows: "indifferent" in the sense of *chemically inert* – no, in the sense of *electrically neutral* – yes (though it can be ionized), and in the sense of *pH-neutral* – yes (though not always at pH 7). All in all, water is an amazing substance that still holds many secrets and surprises in store for us. ■

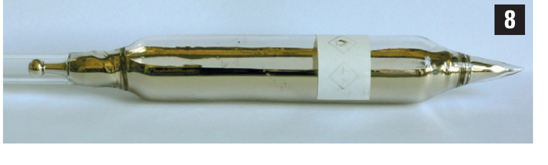

Fig. 8
A glass ampoule containing caesium – a metal violently reacting with moisture in air and oxygen