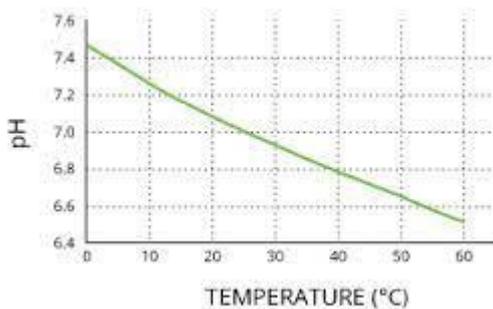


Why does pH of water reduces with increases in temperature? Can heat generate H+ ions?

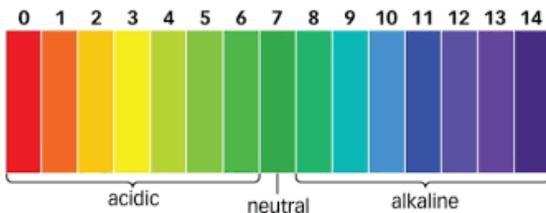
*Problem statement: "I'm trying to calculate the right quantity of OH dosing to keep the pH in a High-pressure steam drum at 10. The water comes from the deaerator and increases 120 °C, until 280 °C, 77 bar. I know that pH goes down when the temperature goes up. I would calculate, knowing the water flow and the inlet pH, the right Mass of OH to pump. I can't find the formula with pH and temperature." Someone from LinkedIn*

In my time the pH meter did not have built-in auto temperature compensation. I was told to check pH by adjusting the sample temperature to 25 degc. None explained why? Later when pH meters came with auto temperature compensation life became easy. But like me, many may not have questioned what does the pH meter compensates for?



pH increases with temperature

Basics: Water exists in weak ionic forms consisting of H and OH ions,  $H_2O \rightleftharpoons H^+ + OH^-$ . The total number of ions under standard conditions of temperature is fixed at  $10^{-14}$  moles/lit. The ionic product of water,  $K_w = [OH^-] \times [H^+] = 10^{-14} [mole/lit]^2$  at 25 degc. When both H and OH ions are equal at  $10^{-7}$  moles / lit water is neutral,  $pH = -\text{LOG} [10^{-7}] = 7$ , When H increases OH ions decreases because the total number ions are fixed at  $10^{-14}$ moles/lit. This is the background why pH scale starts at 0 and end ends at 14



One line answer to the question is that heating does not make water more acidic. Then what happens?

Explanation:



Ionization of water is an endothermic equilibrium reaction. Its forward reaction is endothermic that is when water dissociates into ions, the equilibrium is on the right. Its reverse reaction is an exothermic reaction, equilibrium directed to the left.

When water is heated its dynamic equilibrium between water and its ions is disturbed. The applied heat increases the reverse reaction of water ionization on the left side of equilibrium because water's reverse ionization is exothermic. According to LeChatellier's principle, this is opposed by water. To counter the heat supply water speeds up its forward endothermic reaction. The equilibrium shifts on right. More H and OH ions are produced. So, to sum up when water becomes hot both H and OH ions increase. Heating does not selectively increase H ions.

Question: Then why do I see a lower pH in my boiler feed water?

| T (°C) | $K_w$ ( $\text{mol}^2 \text{dm}^{-6}$ ) | pH   |
|--------|---|------|
| 0      | $0.114 \times 10^{14}$                  | 7.47 |
| 25     | $1.008 \times 10^{14}$                  | 7.00 |
| 50     | $5.476 \times 10^{14}$                  | 6.63 |
| 100    | $51.3 \times 10^{14}$                   | 6.14 |

The answer is the ionic constant of water changes with temperature as you can see in the above table. The problem is that we are all familiar with 7 being the pH of pure water, that anything else feels really strange. Remember that to calculate the neutral value of pH from  $K_w$ . If that changes, then the neutral value for pH changes as well. At 100°C, the pH of pure water is 6.14, which is "neutral" on the pH scale at this higher temperature. A solution with a pH of 7 at this temperature is slightly alkaline because its pH is a bit higher than the neutral value of 6.14. Similarly, you can argue that a solution with a pH of 7 at 0°C is slightly acidic, because its pH is a bit lower than the neutral value of 7.47 at this temperature. Hence, there is an excess of  $\text{H}^+$  ions vs.  $\text{OH}^-$  ions.