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HYDROGEN-ION CONCENTRATION AND $p_{\rm H}$ —AN EXPLANATION.*

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A brief explanation of the terms "Hydrogen-ion concentration" and " $p_{\rm H}$." They cannot be used interchangeably. A means of calculation and diagram illustrating the numerical value of the two terms.

In presenting this paper it is the writer's intention to explain the terms "Hydrogen-ion concentration" and " $p_{\rm H}$." Primarily the paper is intended for those uninformed on the subject, and repetition may occur for the sake of clarity and emphasis.

Ions are electrically charged atoms or groups of atoms in solution. Solutions containing hydrogen ions (H^+) or hydroxyl ions (OH^-) , therefore, have an acid or alkaline reaction respectively, depending upon which of the two ions are greater in number. In acid and alkaline solutions we have to deal with the dissociation or splitting off of hydrogen (H^+) and hydroxyl (OH^-) groups. This dissociation gives us the active acidity or alkalinity of the solution. Therefore, the term hydrogen in the solution, and, since the ions carry electrical charges, hydrogen-ion concentration may be measured by electrical methods. Certain indicators have been found that give different shades of colors in solutions differing in hydrogen-ion concentration, and they are very reliable in this measurement.

With considerable effort F. Kolrausch and A. Heydeweyller obtained some very pure distilled water and upon measuring the electrical conductivity found it to have a dissociation constant of 10^{-14} . Water dissociates as illustrated in the following equation:

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

Knowing then that the dissociation constant of water is 10^{-14} (let this be designated as k_w), and known also the manner in which it dissociates, the hydrogen and hydroxyl-ion concentrations may be figured according to the law of mass action. This law may be stated as follows: When the temperature remains constant the product of the active masses on one side of a chemical equation when divided by the product of the active masses on the other side is a constant. Going back then to the above equation and working according to the law just stated we have the following:

$$H^{+} \times OH^{-} = k_{w}$$

H⁺ × OH⁻ = 10⁻¹⁴

From this it is readily seen that $10^{-14} = 10^{-7} \times 10^{-7}$. Therefore the concentration of II⁺ is 10^{-7} and OH⁻ is 10^{-7} , and both concentrations being equal we have the point of neutrality.

WHAT IS " $p_{\rm H}$ "?

To begin with it may be well to state that " $p_{\rm H}$ " is not a symbol for hydrogenion concentration. The advantages in using the $p_{\rm H}$ scale, which suggestion was made by Sørensen, are legion and it was readily and universally accepted. The cumbersome mathematical expressions of hydrogen-ion concentration are reduced

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to logarithms, and are easily handled although woefully misunderstood or perhaps not understood at all. Remember then that $p_{\rm H}$ is a reduction to, or an expression in logarithms of the hydrogen-ion concentration. It is therefore the logarithm of $\frac{1}{H^+}$. In the other words it is the logarithm of the normality of a solution, in regard to hydrogen, divided by the logarithm of the factor for the ionized hydrogen which has previously been measured. For example:

$$H^{+} = 3.81 \times \text{an } N/1,000,000 \text{ hydrogen solution}$$

or
$$H^{+} = 3.81 \times 0.000001 \text{ or } H^{+} = 3.81 \times 10^{-6}$$

or
$$p_{H} = \log \frac{N/1,000,000}{3.81} = \frac{6}{0.5809} = 6 - 0.5809 = 5.4191.$$

Reversing the process it will be seen from the above figures that the hydrogen-ion concentration may be figured easily from any given $p_{\rm H}$. Given, for instance, the $p_{\rm H}$ 8.25, the hydrogen-ion concentration may be calculated as follows:

$$8.25 = 9 - 0.75 = 5.623 \times 10^{-9} = H^+.$$

As has been stated, the dissociation constant of water is 10^{-14} (H⁺ = 10^{-7}) and OH⁻ = 10^{-7}). Therefore to maintain an equilibrium, if the H⁺ increases the OH⁻ must decrease and conversely so, for the product of H⁺ × OH⁻ must always equal 10^{-14} . The following diagram will serve to illustrate the dissociation relationship between H⁺ and OH⁻. The exponents on the reader's left may be considered as $p_{\rm H}$ and on the right as $p_{\rm OH}$.

H + =	10-0	OH-	$= 10^{-14}$
H +	1	OH-	13
Η+	2	OH-	12
H+	3	OH-	11
Η+	4	OH^-	10
H+	5	OH-	9
H^+	G	OII-	8
		7	
H +	8	OH~	6
H +	9	OH-	5
H^+	10	OH-	4
H+	11	OH -	3
H+	12	OH-	2
H +	13	OH-	1
H+	14	OH-	0

Do not overlook the fact that a solution that is $p_{\rm H}$ 1 is ten times the hydrogenion concentration of a solution that is $p_{\rm H}$ 2, etc.

The methods for determining $p_{\rm H}$, both electrometric and colorimetric are widely discussed in chemical and pharmaceutical literature. There are also two standard works on this subject, namely, "The Determination of Hydrogen Ions," by Clark and "Hydrogen-Ion Concentration," by Michaelis (now in English as well as German).

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IMPORTANCE OF H-ION CONCENTRATION.

Solutions may contain buffer substances, that is, substances that are not readily changed upon the addition of acid or alkali and act to repress the liberation of free hydrogen or hydroxyl ions. For this reason the addition of 10 cc. of HCl does not assure one that the entire 10 cc. will be dissociated, or that the ionized hydrogen can be assumed without measurement. Acids do not ionize or dissociate to the same extent, and the same holds true for alkalies. Though the total acidity or alkalinity of two N/10 solutions, for example, may be the same, the active acidity may not even be approximate. The determination of the H-ion concentration, therefore, is the only accurate guide to the acid and alkaline nature of substances.

The determination of $p_{\rm H}$ has been applied to practically all fields of industry and research with good results. A few of the varied industries are those of Baking, Canning, Tanning, Candy, Pharmaceutical, Sewage Disposal, Paper, Water Supply, Ceramics, Electroplating, Paints and Dyes, etc.

The pharmaceutical applications of hydrogen-ion concentration are many and deal with the regulation of intravenous solutions to prevent irritation, the preservative action in tinctures, syrups, gland products and the like; and the prevention of discoloration in chemicals and solutions. There are many other possibilities in this field and careful observations in pharmaceutical work may reveal important facts. The writer has examined a great many samples of Sodium Iodide and has found a variation in $p_{\rm H}$ of from 4.9 to 9.8, the acid samples showing a fairly rapid discoloration after being in solution and standing a few weeks. Sodium Salicylate was found varying from $p_{\rm H}$ 5.9 to 7.7 and Calcium Chloride from $p_{\rm H}$ 7.45 to 8.30. In fact, the chemicals purchased from the most reliable sources show wide variations, and only careful examination in regard to H-ion concentration, as well as other details, will result in uniform pharmaceutical products. Some variation must be allowed, since there are such a great number of "outside" influences in the manufacture of chemicals and pharmaceuticals that affect the H-ion concentration. The extremes are the important things to guard against and application of the methods of p_{II} determination will bring the variations to comparatively narrow limits.

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