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**CALCIUM CARBONATE SATURATION INDEX
AND ALKALINITY INTERPRETATIONS**

By
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By *T. E. Larson and A. M. Buswell*

THE-calcium carbonate solubility equilibrium is highly important in many phases of water chemistry. It is directly associated with scale formation in many types of equipment, from tea kettles to boiler feed water heaters, and with incrustation of well screens, filter sand, meters and water taps. In physiological chemistry it is significant in relation to bone calcification and to blood equilibriums. In geochemistry the deposition of carbonates is also related to this equilibrium.

The equilibrium balance is affected by many natural reactions in water, before, during or after the process of treatment. Photosynthesis in surface supply reservoirs removes CO_2 , resulting in a pH increase which has been known to precipitate CaCO_3 . Aeration of well waters whether from mechanical means or mere exposure to air alters the equilibrium by loss or absorption of CO_2 . Treatment with coagulants always changes the free CO_2 . "Air binding" in filters, due to drop in pressure, tends to draw out CO_2 and shift the equilibrium. Chlorine treatment and de-aeration are not without effect. Anti-corrosion treatment whether by lime, soda ash, silicates, chromates or phosphates more or less affects this equilibrium. Bacterial growths in the mains may either consume CO_2 , or, in some cases, produce CO_2 , directly or indirectly. Bacterial action can convert the basic ammonium ions into acidic nitrite or nitrate ions. Corrosive action itself has a direct influence by the production of hydroxyl ions which alter the equilibrium, significantly to precipitate CaCO_3 at the point of corrosion in hard high alkalinity waters. A change in temperature naturally changes the status of the relationship.

Many other conditions could be listed, but these serve to illustrate the importance of the subject. The reverse consideration is perhaps of still greater importance. How does this equilibrium affect the reactions and treatments mentioned? In many cases, attention to, and control of, this

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equilibrium will aid or increase the effectiveness of the treatments and the resultant quality of the water.

Various equations have been proposed for calculating the carbonate equilibrium, ranging from the early simple relation of Tillmans (1) and Greenfield and Baker (2) to the more rigorous work of Johnston (3, 4), Langelier (5) and others. None of these equations is sufficiently fundamental to be applicable over wide ranges of temperature and concentrations and, even in the average range, their apparent applicability is frequently due to compensating errors. For the sake of comparison, the calculated saturation pH of a water of 20.0 ppm. Ca, 12.2 ppm. Mg, 300 ppm. alkalinity (as CaCO_3), 92 ppm. Na, and 320 ppm. residue at 25°C is 7.8 by the Langelier calculation and 7.57 by corrected constants. At 80°C . the respective saturation pH values are 6.9 and 7.07. Likewise, for a water of 41.3 ppm. Ca, 16.0 ppm. Mg, 352 ppm. alkalinity (as CaCO_3), 267 ppm. Cl, 20 ppm. SO_4 , 230 ppm. Na, and 800 ppm. residue, the calculated saturation pH is 7.6 at 25°C . by the Langelier calculation but 7.20 if the corrected constants are used. At 80°C . the respective saturation pH values are 6.7 and 6.69.

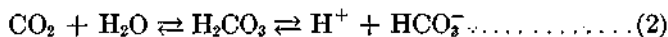
This discussion, therefore, is intended to extend the general applicability of the saturation equation without including prohibitively complicated considerations. This permits accumulation of more accurate data for comparative purposes, not only for various plants, but also for various points in the distribution system supplied by the same plant.

The constants involved in developing a saturation equation represent the law of mass action applied to the following equilibriums:



$$K_w = (\text{H}^+)(\text{OH}^-) = \gamma_{\text{H}^+}[\text{H}^+]\gamma_{\text{OH}^-}[\text{OH}^-] \dots \dots \dots (1a)$$

$$K'_w = [\text{H}^+][\text{OH}^-] \dots \dots \dots (1b)$$



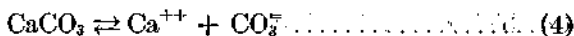
$$K_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = \frac{\gamma_{\text{H}^+}[\text{H}^+]\gamma_{\text{HCO}_3^-}[\text{HCO}_3^-]}{\text{CO}_2} \dots \dots \dots (2a)$$

$$K'_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{\text{CO}_2} \dots \dots \dots (2b)$$



$$K_2 = \frac{(\text{H}^+)(\text{CO}_3^{2-})}{(\text{HCO}_3^-)} = \frac{\gamma_{\text{H}^+}[\text{H}^+]\gamma_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}]}{\gamma_{\text{HCO}_3^-}[\text{HCO}_3^-]} \dots \dots \dots (3a)$$

$$K'_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \dots \dots \dots (3b)$$



$$K_s = (\text{Ca}^{++})(\text{CO}_3^{--}) = \gamma_{\text{Ca}^{++}}[\text{Ca}^{++}]\gamma_{\text{CO}_3^{--}}[\text{CO}_3^{--}] \dots \dots \dots (4a)$$

$$K'_s = [\text{Ca}^{++}][\text{CO}_3^{--}] \dots \dots \dots (4b)$$

where parentheses represent activities and brackets represent concentrations in moles per liter.

The activity concept assumes complete dissociation of salts in dilute solutions, a condition which obeys the law of mass action only at infinite dilution. Deviations from the ideal condition are corrected for by considering "effective" concentrations or activities. The activity coefficient γ_x may be defined as a measure of the extent of deviation, or the ratio of the "effective" concentration to the actual concentration, $\gamma_x = (x)/[x]$. Hence at infinite dilution, the activity is equal to the concentration and the activity coefficient is 1.0.

The activity coefficient, γ_x , may be calculated by:

$$\log \gamma_x = -\nu_x^2 \sqrt{\mu} / (1 + A\sqrt{2\mu}) \dots \dots \dots (5)$$

where ν_x is the valence of x and μ is the ionic strength of the solution. The latter is defined as one-half the summation of the productions of the molal concentrations of the ions in solution and the square of their respective valences, $\frac{1}{2} \sum m_x \nu_x^2 + m_y \nu_y^2 + \dots$. In general, the simplified expression (5) for natural waters of less than 500 ppm. mineral content may be used; $\mu = 0.000025$ times the total mineral content.

A is a constant dependent on ionic diameter and is calculated from the experimental data for various equilibriums. In water works practice this value may generally be taken as 1.0 for simplicity, although this may be quite, far from the correct value.

Since total alkalinity (in equivalents per liter) is equal to:

$$[\text{Alky.}] + [\text{H}^+] = 2[\text{CO}_3^{--}] + [\text{HCO}_3^-] + [\text{OH}^-] \dots \dots \dots (6)$$

then:

$$[\text{CO}_3^{--}] = \frac{1}{2}[\text{Alky.}] - \frac{1}{2}[\text{HCO}_3^-] \dots \dots \dots (7)$$

when $[\text{H}^+]$ and $[\text{OH}^-]$ are too small to be significant ($\text{pH} < 10.5$). From Eq. 3b:

$$[\text{CO}_3^{--}] = \frac{K'_2[\text{HCO}_3^-]}{[\text{H}^+]} \dots \dots \dots (8)$$

and combining Eqs. 7 and 8:

$$[\text{HCO}_3^-] = \frac{[\text{Alky.}]}{1 + 2K'_2/[\text{H}^+]} \dots \dots \dots (9)$$

Combining Eqs. 8 and 9:

$$[\text{CO}_3^{=}] = \frac{K'_2[\text{Alky.}]}{[\text{H}^+](1 + 2K'_2/[\text{H}^+])} \dots\dots\dots(10)$$

and substituting in Eq. 4b:

$$K'_s = [\text{Ca}^{++}] \frac{K'_2[\text{Alky.}]}{[\text{H}^+](1 + 2K'_2/[\text{H}^+])} \dots\dots\dots(11)$$

If $-\log K = pK$, then at saturation equilibrium:

$$p[\text{H}^+] = pK'_s - pK'_2 - \log [\text{Ca}^{++}] - \log [\text{Alky.}] + \log (1 + 2K'_2/[\text{H}^+]) \dots(12)$$

The last term may be omitted if the pH is below about 9.0, but involves a correction of 0.05 to 0.5 as the pH increases from about 9.0 to 10.3.

This equation in the various forms, as suggested by Tillman (1), Lange-lier (5), and Strochecker (6), has served a very useful purpose. In many cases, however, it is not sufficiently rigorous. Its shortcomings have not always been detected, since compensating errors frequently give apparent checks with experimental data when in reality the results are incorrect. The purpose of the present paper is to correct the activity factors for salinity in accordance with the most recent data and to indicate the correct constants at various temperatures.

Salinity Corrections

The second ionization constant, K_2 , for carbonic acid is commonly taken to be that indicated by MacInnes (7) and has been considered authentic until recent date. The value of K'_2 , however, has been obtained (5, 8) by $pK'_2 = pK_2 - .382 \sqrt{\mu}$. This is contrary to the experimental data and was used by MacInnes for extrapolation purposes only. A closer approximation for these data would be $pK'_2 = pK_2 - 1.382 \sqrt{\mu}$. More recently Harned and Sholes (13) have provided a more correct value for K_2 , whereby K'_2 is calculated by $pK'_2 = pK_2 - \frac{2\sqrt{\mu}}{1 + 1.4\sqrt{\mu}}$

The first ionization constant, K_1 , as commonly used, is likewise from MacInnes (7). The value of K'_1 , however, has been obtained (8) by $pK'_1 = pK_1 - .119 \sqrt{\mu}$. This also is contrary to the experimental data in which this equation merely represents that used for extrapolation purposes. A more nearly correct equation should be $pK'_1 = pK_1 - \frac{\sqrt{\mu}}{1 + 1.4\sqrt{\mu}}$. More recently Shedlovsky and MacInnes (10) have indi-

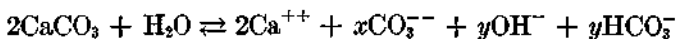
cated close agreement with the above constant and also show the variation with temperature.

The ionization constant for water K_w should be taken from the excellent work of Harned and collaborators (9, 11) wherein $pK'_w = pK_w - \frac{\sqrt{\mu}}{1 + 1.4\sqrt{\mu}}$.

The solubility product for calcium carbonate, K_s , is that of Johnston and Frear (3), and K'_s is assumed to vary as $pK'_s = pK_s - 4\sqrt{\mu}$ (5). This is contrary to the experimental data used in the determination of this constant (3, 16). It appears that K'_s of the experimental data would more nearly be approximated by $pK'_s = pK_s - \frac{4\sqrt{\mu}}{1 + 3.9\sqrt{\mu}}$ (see Eq. 13 and footnote).

Temperature Corrections

The temperature correction for the solubility product of calcium carbonate is given by Langelier as $pK'_{s(t)} = pK_{s(25^\circ C)} - \log r$ (5) and later corrected to $pK'_{s(t)} = pK_{s(25^\circ C)} - 2 \log r$ (12). Neither of these expressions is correct. These were taken from the Johnston and Frear summary (3) which gives the value, r , as the ratio of the "solubility" (not the solubility product) at $t^\circ C.$ to that at $25^\circ C.$ Since calcium carbonate hydrolyzes as follows:



only the CO_3^{--} of the alkalinity present can be used in the solubility product calculations. At $16^\circ C.$ at equal $[OH^-]$ and $[HCO_3^-]$, the $[CO_3^{--}]$ is only 46 per cent of the total alkalinity (4). Therefore, the value, r , should not and cannot be used as the ratio of the "solubility product" at $t^\circ C.$ to that at $25^\circ C.$

With the recent data on the temperature variation for K_1 (10), and K_2 (13) as well as for K_w (9), it is now possible to calculate correctly the temperature variation for K_s from $0-50^\circ C.$ It would be desirable to have further data for K_1 and K_2 to 70 or $85^\circ C.$

Using the data of Johnston and Frear (3) and applying:

$$K'_s = \frac{\gamma_{Ca^{++}}\gamma_{HCO_3^-}[Ca^{++}][HCO_3^-]^2 K'_2}{PK_1c} \dots \dots \dots (13)$$

from Eqs. 2b, 3b and 4b, or:

$$pK'_s = pK'_2 - pK'_1 - pP - pc + p[Ca^{++}] + 2p[HCO_3^-] + \frac{3\sqrt{\mu}}{1 + 4.86\sqrt{\mu}},$$

the average value for pK_s becomes 8.34 or $K_s = 4.55 \times 10^{-9}$. For these data pK'_s varies as $\frac{3\sqrt{\mu}}{1 + 4.86\sqrt{\mu}}$ *. This is assumed by analogy to the data by Shedlovsky and MacInnes on calcium chloride solutions (14). The data for c , the solubility of CO_2 at a partial pressure, P , of one atmosphere, was taken from Bohr (15). The values for K_1 and K_2 were taken from the more recent data presented in Table 1. It is interesting to note that the ratio of these values (9200) at 25°C. agrees remarkably well with that (9100) obtained by Walker, Bray and Johnston (16).

Also, using the data for K_1 , K_2 and c (15), as given in the listed references, and the ratio of the calcium solubility, as given by Johnston (3), where $\log r = \frac{830}{T} - 2.78$, the variation of pK_s with temperature is calculated as given in Table 1.

Alkalinity Interpretation

It has been proposed (5, 8, 9); and correctly so, that free CO_2 and the forms of alkalinity be determined by calculation from the following equations:

Hydroxide concentration (as $CaCO_3$) (from Eq. 1b):

$$\text{ppm. } [OH^-] = 50,000 \frac{K_w'}{[H^+]} \dots \dots \dots (14)$$

where $pH = \log \frac{1}{[H^+]} = \log \frac{1}{[H^+]} + \frac{.5\sqrt{\mu}}{1 + 1.5\sqrt{\mu}}$

* In the saturation equation as derived, however, $[Ca^{++}]$ and $[CO_3^{--}]$ are involved. Therefore K_s must vary as $\gamma_{Ca^{++}}$ and $\gamma_{CO_3^{--}}$. The equation for pK'_s can be obtained from the identity:

$$(Ca^{++})(HCO_3^-)^2 = (Ca^{++})(CO_3^{--}) \times \frac{(H^+)(HCO_3^-) \times (HCO_3^-)}{(CO_3^{--})(H^+)}$$

Then:

$$\gamma_{Ca^{++}} \gamma_{HCO_3^-}^2 = \gamma_{Ca^{++}} \gamma_{CO_3^{--}} \times \frac{\gamma_{H^+} \gamma_{HCO_3^-}}{\gamma_{CO_3^{--}}} \times \frac{\gamma_{HCO_3^-}}{\gamma_{H^+}}$$

and:

$$\frac{3\sqrt{\mu}}{1 + 4.86\sqrt{\mu}} = \frac{4\sqrt{\mu}}{1 + 4\sqrt{\mu}} \times \frac{1\sqrt{\mu}}{1 + 1.4\sqrt{\mu}} \times 1$$

therefore:

$$pK'_{CaCO_3} = pK_{CaCO_3} - \frac{4\sqrt{\mu}}{1 + 3.9\sqrt{\mu}} \text{ (approx.)}$$

in the range where $\sqrt{\mu} = 0.05 - 0.1$.

Any deviation from the assumption concerning the equality of γ_{H^+} and $\gamma_{HCO_3^-}$ would cause only an insignificant error in the data for which K_s is to be used.

Bicarbonate concentration (as CaCO₃) (from Eqs 6 and 8):

$$\text{ppm. [HCO}_3^-] = 50,000 \frac{\frac{[\text{Alky.}]}{50,000} + [\text{H}^+] - \frac{K_w}{[\text{H}^+]}}{1 + \frac{2K_2'}{[\text{H}^+]}} \quad (15)$$

where [Alky.] = ppm, alkalinity (as CaCO₃).

Carbonate concentration (as CaCO₃) (from Eqs. 8 and 15):

$$\text{ppm. [CO}_3^{2-}] = \frac{K_2'}{[\text{H}^+]} \times \text{ppm. [HCO}_3^-] \quad (16)$$

TABLE 1
Values for K₁, K₂, K_s and K_w

t°C.	K _w × 10 ¹⁴ *	K ₁ × 10 ^{7†}	K ₂ × 10 ^{11‡}	K _s × 10 ^{9§}
0	0.115	2.61	2.36	9.50
10	0.298	3.34	3.24	7.07
20	0.681	4.05	4.20	5.25
25	1.008	4.31	4.69	4.55
30	1.460	4.52	5.13	4.03
40	2.916	[4.85]¶	6.03	[3.06]
50	5.469	[5.05]	6.73	[2.37]
60	9.637	[5.08]	[7.20]	[1.83]
70		[5.00]	[7.51]	[1.38]
80		[4.84]	[7.55]	[1.06]

* See reference 9.

† See reference 10.

‡ See reference 13.

§ Recalculated from references 3, 16, 10, 13 and Eq. 13.

|| Value is 4.86 in reference 3.

¶ Brackets indicate extrapolated values.

Free carbon dioxide concentration (as CO₂) (from Eq. 2b):

$$\text{ppm. CO}_2 = \frac{.88 [\text{H}^+][\text{Alky.}]}{K_1'} \quad (17)$$

$$\log \text{CO}_2 = \log \frac{.88}{K_1'} + \log [\text{Alky.}] - \text{pH} - .5 \sqrt{\mu} \quad (17a)$$

$$\log \text{CO}_2 = \log \frac{.88}{K_1'} + \log [\text{Alky.}] - \text{pH} + .5 \sqrt{\mu} \quad (17b)$$

In these determinations care should be taken to note serious discrepancies which may arise in certain ranges from inconsistent use of hydrogen ion activity (H^+) or concentration $[H^+]$ and appropriate constants. If pH is to be obtained at values greater than 10.0, it is advisable to standardize the glass electrode against a standard buffer solution in this range.

A glaring example of the fallacy of the simple methods for the calculation (17) of the forms of alkalinity is noted in Fig. 1. The pH on the left

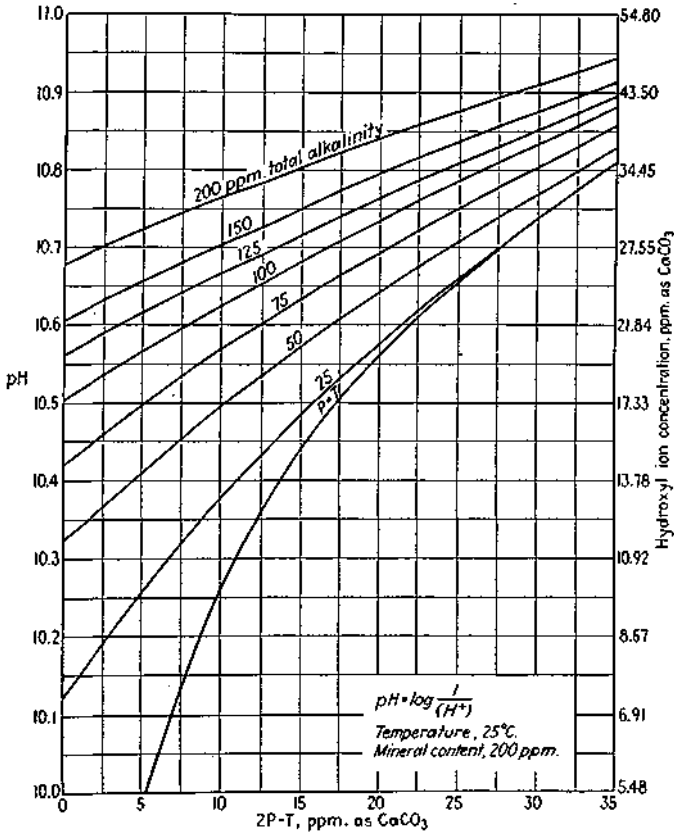


FIG. 1. Relation of "So-Called" Caustic Alkalinity to pH and $[OH^-]$

and the corresponding true hydroxyl ion concentration on the right may be compared with the "2P - T" values (caustic alkalinity) indicated on the abscissa for the various curves for total alkalinity. In this connection it is evident that the federal drinking water standards committee should limit causticity to a definite hydroxyl ion concentration rather than to a given value for causticity. Since the hydroxyl ion concentration

varies considerably for a small error in pH in this range and since the pH varies appreciably with temperature and total mineral content, a constant hydroxyl ion concentration may be represented by $P = aT + b$, where a and b are constants, dependent on the limitation on the hydroxyl ion concentration, and where P and T represent the phenolphthalein and methyl orange alkalinities.

It may be of interest to boiler water analysts that the true $[OH^-]$ and pH can be calculated from the phenolphthalein and methyl orange alkalinities or their more accurate equivalents from strontium chloride or barium chloride methods, providing the boiler water is of less than about 1,200 ppm. mineral content:

$$[OH^-] = \sqrt{\left(\frac{K'_w}{2K'_2} \times 10^4\right)^2 + (2T - P) \frac{K'_w}{2K'_2} \times 10^4 \times \left(\frac{2P - T}{2}\right)^2} + \frac{1}{2}(2P - T) - \frac{K'_w}{2K'_2} \times 10^5 \dots \dots \dots (18)$$

$$pH = pK'_w + \log \left[\sqrt{\left(\frac{K'_w}{K'_2} \times 10^4\right)^2 + \left(\frac{2T - P}{10}\right) \frac{K'_w}{K'_2} \times 10^4 + \left(\frac{2P - T}{20}\right)^2} + \frac{2P - T}{10} - \frac{K'_w}{K'_2} \times 10^4 \right] - 4.00 + \frac{.5 \sqrt{\mu}}{1 + 1.5 \sqrt{\mu}} \dots \dots \dots (18a)$$

(from Eqs. 9 and 14) where $T = [OH^-] + [HCO_3^-] + [CO_3^{2-}]$ and $P = \frac{1}{2}[CO_3^{2-}] + [OH^-] - [HCO_3^-]$ or $[HCO_3^-] = \frac{1}{3}T - 2P + [OH^-]$; and P , T , and $[OH^-]$ are expressed in parts per million as $CaCO_3$.

Free Carbon Dioxide

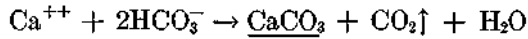
Free CO_2 is often confused with excess or "aggressive" CO_2 . A certain amount of free CO_2 is necessary to maintain calcium carbonate in solution. The total free CO_2 minus the necessary free CO_2 as calculated from the saturation pH comprises the excess CO_2 :

$$ppm. \text{ excess } \dot{C}O_2 = \frac{.88 [Alky.]}{K'_1} \left([H^+] - \frac{K'_2 [Ca^{++}][Alky.]}{K'_2 \times 2 \times 10^9} \right) \dots (19)$$

(from Eqs. 12 and 17) where $[Ca^{++}]$ and $[Alky.]$ are expressed in parts per million (as Ca and $CaCO_3$ respectively).

Many data are presented in the literature on the removal of free CO_2 by aeration. To the authors' knowledge no successful effort has been made to correlate the amount of CO_2 removal with the efficiency of the iron precipitation. Very often it is apparent that considerably more

than the excess CO_2 is removed by vigorous aeration. The result is a shift of the equilibrium



to the right thereby supersaturating the water with or precipitating calcium carbonate. From the standpoint of corrosion prevention the disadvantage of introducing excessive dissolved oxygen may overcome the advantage of calcium carbonate supersaturation. This would be particularly true at dead ends of low circulation. From the standpoint of iron removal, precipitation of finely divided calcium carbonate may hinder rather than aid in the flocculation and settling of iron prior to filtration. This criticism is logical since a large excess of negatively charged calcium carbonate particles would tend to adsorb the positively charged ferric hydroxide particles ($\text{pH} > 7.1$), and remain in colloidal suspension. Since 1.0 ppm. ferrous iron requires only 0.14 ppm. oxygen for conversion to ferric hydroxide and since the original ferrous bicarbonate thereby releases only 1.6 ppm. CO_2 , it is evident that many waters receive excessive aeration and would be more readily filtered if controlled aeration were practiced. This reasoning would be more applicable to waters of High alkalinity than to those of low alkalinity.

Saturation Index

The saturation pH may be calculated from Eq. 12 by converting $p[\text{H}^+]$ to pH and $\log \frac{K'_s}{K'_2}$ to $\log \frac{K_s}{K_2}$ and combining the corrections for salinity.

$$\text{pH} = \log \frac{K_s}{K_2} - \log [\text{Ca}^{++}] - \log [\text{Alky.}] + 9.30 + \frac{2.5 \sqrt{\mu}}{1 + 5.3 \sqrt{\mu} + 5.5 \mu} \quad (12a)$$

where $[\text{Ca}^{++}]$ and $[\text{Alky.}]$ are expressed in parts per million (as Ca and CaCO_3 , respectively).

Since the total free CO_2 calculation is limited in accuracy by the sensitivity of the pH determination, the saturation index, I , as calculated from Eq. 12a is used to denote the presence, (-), or lack, (+), of excess CO_2 .

The saturation index may be calculated as follows:

$$I = \text{pH} + \log [\text{Ca}^{++}] + \log [\text{Alky.}] - \log \frac{K_s}{K_2} - 9.30 - \frac{2.5 \sqrt{\mu}}{1 + 5.3 \sqrt{\mu} + 5.5 \mu} \quad (12b)$$

where pH is the actual pH measured experimentally.

Although the presence of sulfates increases the ionic strength, μ , 1.46 times the increase produced by chlorides in similar concentration (in

ppm.), it is significant that high sulfate waters are generally also of high calcium concentration, whereas high chloride waters generally are accompanied by a high sodium concentration. The calcium content offsets the corrosive tendencies as indicated by the increase in μ by the addition of salts. Therefore, the high chloride waters are more notorious for their corrosive action than high sulfate waters.

It is advisable to measure pH at the temperature at which the equation is to be applied, and to choose the constants for this temperature. Increasing the temperature tends to precipitate CaCO_3 and yield a false pH. Theoretically a state of + saturation should not exist. Its existence is due to a condition of incomplete reaction, a condition which is more likely to prevail at relatively low calcium and carbonate ion concentrations. Since pH varies directly as pK_1 , however, the saturation index at any temperature should vary from that at 25° by the difference between $p \frac{K_1 K_s}{K_2}$ at that temperature and $p \frac{K_1 K_s}{K_2}$ at 25°C . The variation amounts to .015. unit per degree (Table 2).

TABLE 2
Variation of Saturation Index With Temperature

Temp. °C.	0	10	20	30	40	50	60	70	80
$K_1 K_3 / K_2 \times 10^5$	10.5	7.28	5.07	3.55	2.46	1.78	1.29*	.92*	.68*
$p(K_1 K_s / K_2)$	3.98	4.14	4.29	4.45	4.61	4.75	4.89*	5.04*	5.17*

* Extrapolated.

Summary

A correlating discussion has been given on the different forms of alkalinity and their relation to free and excess CO_2 and the saturation index. The activity concept has been extended to produce more nearly correct results for calculations for waters of greater than 500 ppm. mineral content.

More recent and corrected data for the fundamental constants involved have been indicated and the correct variation of the solubility product of calcium carbonate with temperature has been calculated. A method has been included for calculation of pH from phenolphthalein and methyl orange alkalinity determinations. The relation between "aggressive" CO_2 and the saturation index is indicated.

The authors wish to acknowledge the comments of Dr. John Johnston and Dr. D. A. MacInnes, who confirmed the authors' opinions concerning the misinterpretation of their respective data (4, 7).

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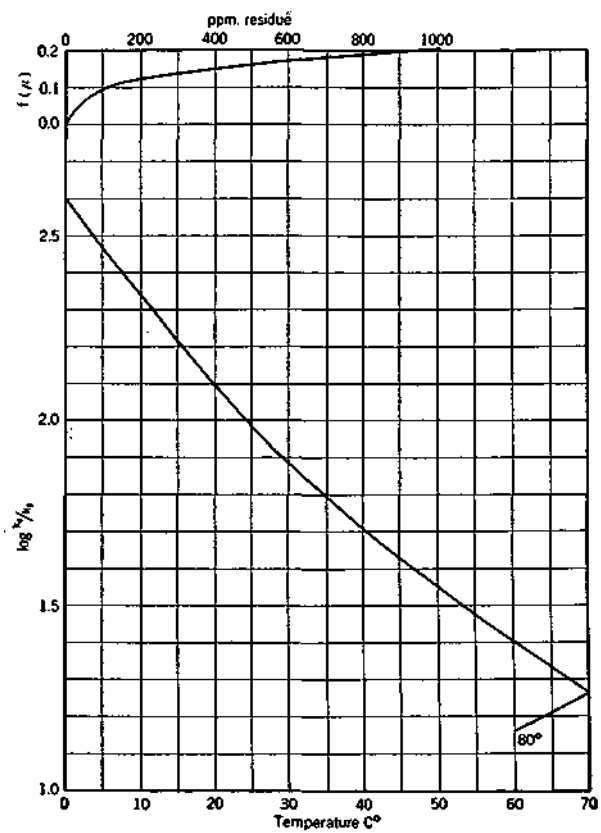


FIGURE 2

ABOVE: relation of salinity factor to mineral content.

BELOW : relation of log K_s/K₂ to temperature.