Calcium Carbonate Saturation in Ground Water, From Routine Analyses

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By WILLIAM BACK

GEOCHEMISTRY OF WATER

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UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOCHEMISTRY OF WATER

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ABSTRACT

A method is developed to calculate, from standard ground-water analyses, the calcium-ion concentration under conditions of assumed equilibrium as an indication of the extent of departure from equilibrium attained between calcium carbonate and ground-water solutions. These calculations require an acceptable value for the equilibrium constants (K values) for calcium carbonate and the bicarbonate ion. The results of four methods used to obtain the K values as a function of temperature show close agreement within the temperature range of 0° to 50° C. Theoretical calcium-ion concentrations are calculated for 25 chemical analyses of water samples collected from limestone terranes. The greatest source of error is in the reported pH values from laboratory measurements. More precise field data are required before reliable geologic inferences can be extended to limestone areas in general.

INTRODUCTION

PURPOSE

The purpose of this study is twofold; the first objective is to introduce a method to compute a theoretical calcium-ion concentration as a measure of the saturation of calcium carbonate attained in ground water, and the second is to demonstrate the application of this method to a series of ground-water analyses. A comparison of the calcium concentration as shown by the chemical analysis with the value obtained by calculating what the concentration would be if the ground water were saturated with calcium carbonate provides a basis for determining the extent to which ground water may be in equilibrium with calcium carbonate (calcite in this study).

The basic assumption is that an excess of available solid-phase calcium carbonate exists within the environment under consideration. This method is valid only in normal ground water and cannot be applied to more concentrated solutions. Table 1 contains chemical analyses of 25 samples of ground water from areas underlain by limestone in Kentucky and Texas, selected from existing publications (Walker, 1956; Harvey, 1956; Petitt, 1956).

DEPENDENCE OF EQUILIBRIUM CONSTANTS ON TEMPERATURE

A comparison of values for the equilibrium constants (K values) for H_2CO_3, HCO_3^- and $CaCO_3$ for temperatures from 0° to 100°C determined by several different methods is shown in plate 1. The ionization constants for H_2CO_3 were measured by Shedlovsky and MacInnes (1935) for 0° to 38°C and Harned and Davis (1943) for 0° to 50°C. The ionization constants for HCO_3^- were measured by MacInnes and Belcher (1933, 1935) for 25° and 38°C and by Harned and Scholes (1941) for 0° to 50°C. Larson and Buswell (1942) extrapolated the data of Shedlovsky and MacInnes and of Harned and Scholes to extend the temperature range to 80°C. Langelier (1946) further extrapolated the data to include temperatures to 100°C. The source of data he used is not stated, but evidently it is Harned's work.

Measurements for the equilibrium constant of $CaCO_3$ in the form of either calcite or aragonite have not been made for 0° to 100°C; therefore several methods have been used to obtain these necessary values. Langelier (1936, p. 1512) computed the solubility products of $CaCO_3$ for temperatures from 0° to 90°C from the data of Frear and Johnston (1929, p. 2083). The temperature correction is given by Frear and Johnston as log $r = (830/T) - 2.78$, where r is the ratio of solubility of $CaCO_3$ at t°C to that at 25°C. (In Langelier's table 4, p. 1512, there are two misprints; for temperatures 25°C and 70°C read 8.32 and 8.67, respectively). Langelier (*in* Hoover, 1938, p. 1806) later modified the temperature correction to $pK_{CaCO_3} = 8.32 - [2 (830/T) - 2.78]$. The values obtained from this equation are given in his discussion of Larson and Buswell's paper (1942, p. 1680). However, Larson and Buswell (p. 1671) state that neither at these expressions is correct because r is the ratio of the solubility and not the ratio of the solubility product at t°C to that at 25°C. The criticism relates to Langelier's more simplified treatment, which neglects the hydrolysis effects in the temperature corrections.

The method used by Garrels and Dreyer (1952) to calculate the equilibrium constants is based on the thermodynamic relationships

of free energy and the heat of formation of the calcium and carbonate species ions, as expressed in the following equations:

$$-\Delta F_i^\circ = nE_i^\circ F \qquad (1)$$

$$E_i^\circ + \frac{\Delta H_i^\circ}{nF} = T\frac{dE_i^\circ}{dT} \qquad (2)$$

where ΔF_i° is the free energy of formation of the ion; E_i° is the standard electrode potential for the formation of the calcium or carbonate ion; ΔH_i° is the heat of formation of the ion; n is the number of electrons transferred in the ionization; F is the Faraday, expressed in calories per mole; and T is the absolute temperature. By this method E_i° is calculated from equation 1, the free-energy value at 25°C being obtained from Latimer (1952) and from the number of electrons involved in the chemical reaction. This value of E_i° is substituted into equation 2 along with the experimental value for the heat of ionization measured at one temperature to obtain the value of $\frac{dE_i^\circ}{dT}$ expressed in volts per degree. If it is assumed that the term $\frac{dE_i^\circ}{dT}$ is constant within the temperature range of interest of 25° to 65°C, the value of E_i° can be computed from equation 2 for temperatures other than the reference temperature for the heat of ionization. These values can then be substituted into equation 1 to calculate the free-energy values over the temperature range from 25° to 65°C. The equilibrium constant can be computed from the temperature-corrected free energy by

$$\Delta F^\circ(t) = -RT \, ln \, K$$

A third series of values for equilibrium constants were computed for this paper by a method based on the equation

$$\left[\frac{\partial(\Delta F_R)}{\partial T}\right]_P = -\Delta S_R$$

Values for ΔF° in kilocalories and S° in calories per degree are listed by Latimer, 1952. For example, the calculation follows for the reaction

$$HCO_3^- = H^+ + CO_3^-$$
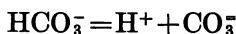
$$\Delta F_R = \Delta F_{H^+} + \Delta F_{CO_3^-} - \Delta F_{HCO_3^-}$$

From Latimer (p. 30 and p. 128), for 25°C,

$$\Delta F_R = [0.0 - 126.22] - [-140.31] = +14.09$$

The similar entropy relationship is as follows:

$$\Delta S_{Reaction} = \Delta S_{Products} - \Delta S_{Reactants}$$

$$\Delta S_R = \Delta S_{H^+} + \Delta S_{CO_3^=} - \Delta S_{HCO_3^-}$$

$$\Delta S_R = [0.0 - 12.7] - [22.7] = -35.4 \text{ cal} = -0.0354 \text{ kcal}$$

By integration

$$\Delta F_R = -T\Delta S_R + \text{constant of integration}$$
$$+14.09 = -(298)(-.0354) + C$$
$$C = +3.54$$

For various temperatures, such as 0°C=273°K

$$\Delta F_R = -[(273)(-.0354)] + 3.54$$
$$\Delta F_R = +13.20$$

and

$$\Delta F_R = -RT \, ln \text{ K} + 13.20 = -(1.98)(2.30)(273) \log K_{HCO_3^-}$$

$$+13.20 = -1.242 \log K_{HCO_3^-}$$

$$\log K_{HCO_3^-} = -10.63$$

$$K_{HCO_3^-} = 10^{-10.63}$$

The values obtained from the equilibrium constants of $CaCO_3$, H_2CO_3, and HCO_3^- by the various methods agree closely for the temperatures from 0° to 50°C. Above 50°C the agreement is poorer. A comparison of these values provides an estimate of the amount of discrepancy that can be expected in calculations based on various assumptions about the effect of temperature on the equilibrium constants.

Harned's values for constants of HCO_3^-, H_2CO_3, and H_2O and Larson and Buswell's values for $CaCO_3$ were used for calculations in this paper and are replotted at an expanded scale on figure 1.

CALCULATION OF THE ACTIVITY OF THE IONS

In the reaction

$$CaCO_3 = Ca^{++} + CO_3^=$$
$$\frac{\alpha_{Ca^{++}} \cdot \alpha_{CO_3^=}}{\alpha_{CaCO_3}} = K_{CaCO_3} \qquad (3)$$

Where the α terms represent activities and α_{CaCO_3} is unity. By definition

$$\alpha_{Ca^{++}} = m_{Ca^{++}} \cdot \gamma_{Ca^{++}} \qquad (4)$$
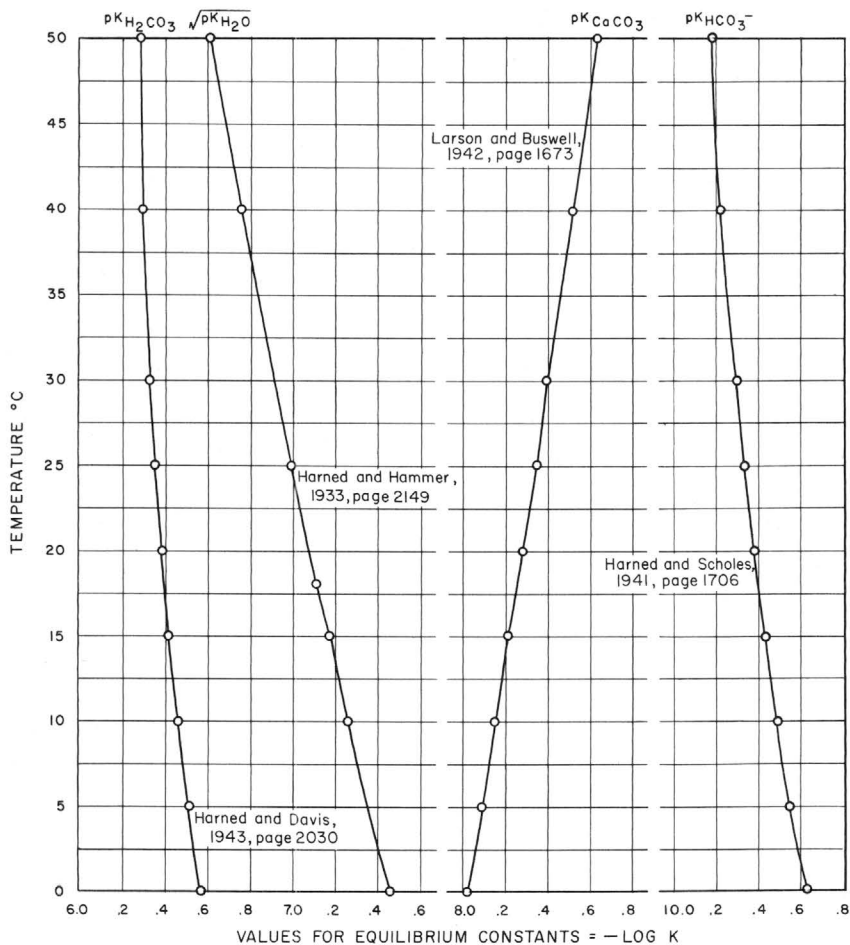
FIGURE 1.—Equilibrium constants used in the calculations of activity of calcium and bicarbonate ions.

where m is molality and γ is the activity coefficient. Values for γCa^{++} are read from the graph in figure 2. Temperature corrections for the activity coefficients were not made for this paper. Klotz (1950, p. 331–332) tabulated the activity coefficients computed by Kielland (1937) from the first approximation of the Debye–Hückel equation.

To read the value of the activity coefficient for the calcium and bicarbonate ions from figure 2, the ionic strength, μ, of the solution is computed from the following equation:

$$\mu = \frac{1}{2} \Sigma m_i z_i^2 \tag{5}$$
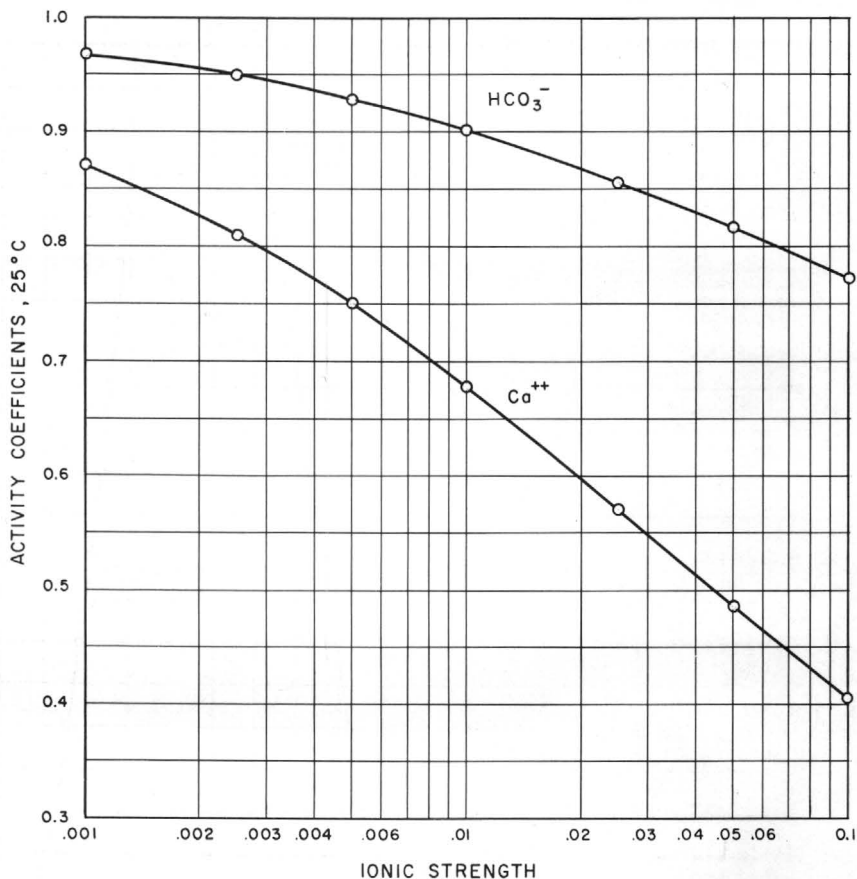
FIGURE 2.—Activity coefficients for calcium and bicarbonate ions.

where m is the molality of the ion, i, which has a charge z in the solution. In most ground waters $m_{CO_3^=}$ is too small to be determined by the usual analysis. However, $\alpha_{CO_3^=}$ can be computed from the HCO_3^- concentration and the pH.

From the reaction

$$HCO_3^- \rightleftharpoons CO_3^= + H^+$$
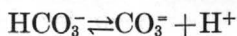
and the law of mass action

$$\frac{\alpha_{CO_3^=} \cdot \alpha_{H^+}}{\alpha_{HCO_3^-}} = K_{HCO_3^-} \qquad (6)$$

and by transposition and application of equation 1

$$\alpha_{CO_3^=} = \frac{m_{HCO_3^-} \cdot \gamma_{HCO_3^-} \cdot K_{HCO_3^-}}{\alpha_{H^+}} \qquad (7)$$

In equation 7, a value for $m_{HCO_3^-}$ is obtained directly from the analyses, table 1. $\gamma_{HCO_3^-}$ is read from the graph in figure 2, and $K_{HCO_3^-}$ is read from figure 1 at the temperature of the ground water. α_{H^+} is obtained from the pH; that is, a pH of 7.9 means that α_{H^+} is $10^{-7.9}$. Therefore, by transposition of equation 3,

$$\alpha_{Ca^{++}} = \frac{K_{CaCO_3}}{\alpha_{CO_3^-}}$$

The activity of the calcium ion under equilibrium conditions can be calculated by reading the value for the equilibrium constants at the temperature of the ground water from figure 1. The molality is obtained by use of equation 4 and converted to concentration in parts per million.

APPLICATION OF THE METHOD TO GROUND-WATER SAMPLES

The theoretical activity of the calcium ion under assumed equilibrium conditions was calculated for 25 ground-water analyses. The calculated calcium-ion concentration, in parts per million, is shown in table 2 with the values obtained by chemical analysis. The results expressed by the ratio

$$\frac{\text{Analyzed Ca}^{++} \text{ (ppm)} - \text{calculated Ca}^{++} \text{ (ppm)}}{\text{Analyzed Ca}^{++} \text{ (ppm)}}$$

are plotted on figure 3 against the ionic strength of the ground water.

FIGURE 3.—Ratio of difference between the analyzed and calculated values to the analyzed value for calcium-ion concentration plotted with the ionic strength.

TABLE 1.—*Selected chemical analyses of*

[Analyses sample Nos. 1-8 (Walker, 1956), 9-13 (Harvey, 1956), 14-25 (Petitt, 1956). Parts per million

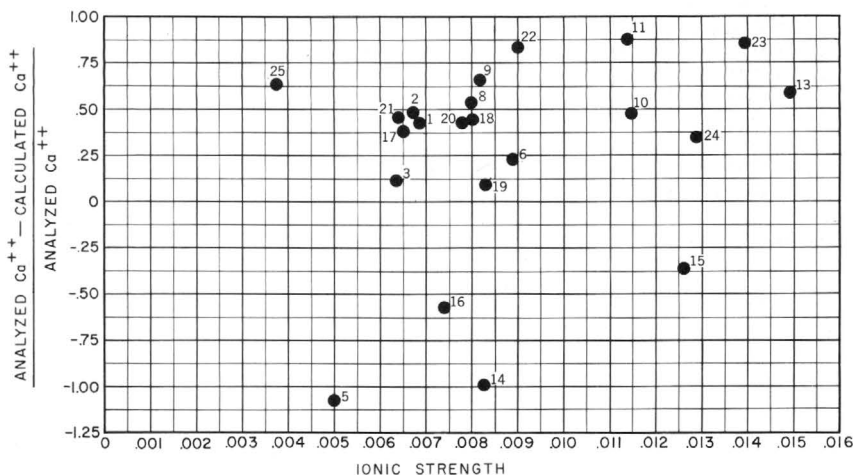| Sample No.	Location	Depth of wells (feet)	Stratigraphic unit	Date of collection	Temperature (°F)	Silica (SiO₂)	Total iron (Fe)	Calcium (Ca)	Magnesium (Mg)
1	8720-3645-51	90	Mississippian limestone.	6- 7-50	62	8.2	0.19	69 / 1.72	11 / .45
2	8720-3650-19	60	_____do_____	6- 7-50	60	10	.12	64 / 1.60	12 / .49
3	8725-3645-24	65	_____do_____	6- 7-50	60	8.0	.27	40 / 1.00	24 / .99
4	8725-3645-41	23	_____do_____	1-25-50	54	4.6	.16	62 / 1.55	4.5 / .18
5	8625-3645-55	(¹)	_____do_____	6- 7-50	58	13	.86	48 / 1.20	4.1 / .17
6	8725-3645-157	73	_____do_____	3- 7-50	58	7.2	.19	31 / .77	22 / .90
7	8725-3650-15	65	_____do_____	6- 7-50	63	7.0	.59	6.2 / .15	3.5 / .14
8	8730-3645-6	93	_____do_____	6- 7-50	63	7.8	.12	62 / 1.55	24 / .99
9	8730-3745-32	180	Pennsylvanian shale and limestone.	3-30-50	57	5.6	.37	74 / 1.85	13 / .53
10	8730-3750-66	125	_____do_____	3-30-50	57	9.6	4.4	86 / 2.15	32 / 1.32
11	8735-3745-6	110	Quaternary alluvium___	12-29-49	56	12	4.5	92 / 2.29	31 / 1.27
12	8735-3745-77	209	Pennsylvanian shale and limestone.	3-29-50	55	21	6.8	8.0 / .20	3.9 / .16
13	8735-3745-138	60	Quaternary alluvium___	3-29-50	56	11	13	92 / 2.29	48 / 1.97
14	H-5-1 Uvalde Co.	350	Cretaceous limestone____	11- 2-45	72	11	.08	74 / 1.85	9.5 / --------
15	I-4-37 Uvalde Co.	1,493	_____do_____	11- 2-45	80	14	.12	88 / 2.20	29 / --------
16	I-3-133 Medina Co.	1,500	_____do_____	11- 2-45	76	14	.08	66 / 1.65	16 / --------
17	261 Bexar Co.	703	_____do_____	6-21-50	74	16	.00	50 / 1.25	17 / --------
18	283 Bexar Co.	1,361	_____do_____	5-14-52	81	17	.01	65 / 1.62	19 / --------
19	D-12 Bexar Co.	360	_____do_____	4- 8-54	71	10	-------	78 / 1.95	16 / --------
20	G-43 Bexar Co.	426	_____do_____	3-17-50	72	14	.01	63 / 1.58	18 / --------
21	J-85 Bexar Co.	720	_____do_____	12-13-48	75	24	.00	50 / 1.25	14 / --------
22	E-38 Hays Co.	325	_____do_____	1-28-46	66	10	.05	58 / 1.45	33 / --------
23	G-58 Hays Co.	500	_____do_____	9-28-53	74	10	-------	100 / 2.50	39 / --------
24	H-19 Hays Co.	765	_____do_____	10-28-49	75	13	.02	72 / 1.80	43 / --------
25	K-14 Hays Co.	44	_____do_____	1-19-54	70	7.2	.08	44 / 1.10	1.6 / --------

¹ Spring.

ground water from Kentucky and Texas

(upper number), molality x 10^3 (lower number). Analytical results in parts per million except as indicated]

Sodium (Na)	Potassium (K)	Bicarbonate (HCO₃)	Sulfate (SO₄)	Chloride (Cl)	Fluoride (F)	Nitrate (NO₃)	Dissolved solids residue on evaporation at 180° C	Ionic strength	Hardness as CaCO₃	Specific conductance (micromhos at 25°C)	pH
2.8		227	25	5.8	.2	3.4	240	0.0069	217	393	7.8
.12		3.72	.26	.16		.05					
7.6		228	15	13	.5	4.3	231	.0067	209	388	7.9
.33		3.74	.16	.37		.07					
4.2		204	29	3.5	2.0	.1	211	.0064	198	352	7.9
.18		3.34	.30	.10		0					
.2		190	9.3	2.8	.2	4.6	189	.0053	173	320	7.3
.01		3.11	.10	.08		.07					
20		190	8.2	3.5	.3	12	200	.0050	137	317	7.5
.87		3.11	.08	.10		.19					
75		282	68	5.6	4.5	11	357	.0089	168	607	8.0
3.26		4.62	.71	.16		.18					
94		214	48	5.5	.6	.5	274	.0055	30	431	7.7
4.09		3.51	.50	.15		.01					
7.5		302	11	5.5	.7	1.4	267	.0080	253	477	7.8
.33		4.95	.11	.15		.02					
24		326	2.6	6.8	.3	13	308	.0082	238	527	7.9
1.04		5.34	.03	.19		.21					
15		398	45	4.4	.2	0	388	.0115	346	639	7.6
.65		6.52	.47	.12	0	0					
11		414	27	8.5	.1	2.1	390	.0114	357	680	8.0
.48		6.78	.28	.24		.03					
9.4		46	11	3.6	.1	2.5	86	.0016	36	110	7.6
.41		.75	.11	.10		.04					
49		639	.8	2.1	.4	5.9	524	.0149	427	897	7.5
2.13	7	10.47	.01	.06		.09					
24	7	277	19	24	.4	4.1	319	.0082	224	570	7.0
		4.54									
17	9.5	254	142	20	.6	3.	470	.0126	338	722	7.1
		4.16									
4.8	3.4	244	16	18	.2	3.8	263	.0074	230	438	7.0
		4.00									
5.2	.8	190	32	13	.3	3.5	246	.0065	195	490	7.8
		3.17									
10	1.6	238	35	18	.3	5.0	296	.0080	240	498	7.6
		3.90									
6.1	.9	298	13	13		5.6	313	.0083	260	531	7.4
		4.89									
10	3.6	233	34	20	.6	3.8	287	.0078	231	484	7.7
		3.82									
13	.4	176	35	19	.4	2.5	244	.0064	182	425	7.9
		2.89									
3.0	3.0	280	38	12	1.8	.0	301	.0090	280	540	8.2
		4.59									
7.8	1.4	330	122	15		14	491	.0139	410	654	8.0
		5.41									
17	5.2	283	129	22	3.6	.0	490	.0129	356	725	7.6
		4.64									
4.9	1.0	151	2.0	3.8		2.5	147	.0038	116	261	8.2
		2.48									

If we assume no errors of measurement or calculation, those samples that plot above the zero line are supersaturated with calcium carbonate and those that plot below the zero line are undersaturated. Samples 4, 7, and 12 are not plotted because of the low value of the ratio.

TABLE 2.—*Analyzed and calculated calcium-ion concentration, in parts per million*

Sample No.	Analyzed	Calculated	Anal-calc / Anal
1	69	40	+0. 42
2	64	33	+0. 48
3	40	36	+. 10
4	62	179	−1. 9
5	48	98	−1. 0
6	31	24	+. 23
7	6. 2	49	−6. 9
8	62	29	+. 53
9	74	25	+. 66
10	86	45	+. 48
11	92	11	+. 88
12	8	297	−36.
13	92	38	+. 59
14	74	150	−1. 0
15	88	121	−. 37
16	66	155	−. 57
17	50	31	+. 38
18	65	36	+. 44
19	78	71	+. 09
20	63	36	+. 43
21	50	27	+. 46
22	58	11	+. 81
23	100	14	+. 86
24	72	47	+. 34
25	44	16	+. 64

EVALUATION OF ERRORS

Before it can be concluded that any single sample is undersaturated or supersaturated, the possible errors must be evaluated. The greatest source of error is the pH measurement. The pH values reported in the table of analyses were determined in the laboratory. These laboratory determinations may not be representative of the pH of the water in the aquifer because of instrument error and of changes in the carbon dioxide content and the temperature. The samples were collected by standard sampling techniques. However, even if the greatest care is used in collecting samples, changes occur within the water that cannot be compensated for in the laboratory. For greatest accuracy, the pH and HCO_3^- content should be measured in the field, although the effect of errors in the bicarbonate determination is far less than the errors in pH determination. No samples were

collected during the present study, and the chemical analyses used were obtained from published ground-water reports.

Although the water samples analyzed in the laboratory may not truly represent conditions within the aquifer, it seems reasonable to assume that whatever chemical changes have occurred within the samples may be in the same direction and of the same magnitude for most samples collected under similar conditions from the same geologic and hydrologic system. That is, from the published data we may not be able to conclude that any one sample is exactly in equilibrium with calcium carbonate, but it may be possible to compare the relative degree of saturation of a group of samples. Even this comparison, which can be refined by study of more carefully collected field data, will provide a basis for a better understanding of the hydrology of limestone terranes.

The significance of an error in the pH determination is shown by considering, for example, analysis 3, which shows a reported pH of 7.9 and a concentration ratio of $+0.10$. If the pH were in error as much as 0.2 unit, the concentration ratio might be as high as $+0.45$ (pH 8.1) or as low as -0.42 (pH 7.7).

Factors other than the pH that effect the computed values for equilibrium constants are those of temperature and concentration of the ions in the water. From figure 2 it is seen that an increase in temperature will increase the value for the equilibrium constant for HCO_3^-, and increase the computed value for α_{CO_3}. Accordingly, with the other components remaining fixed in the following equations:

$$\alpha_{CO_3^=} = \frac{m_{HCO_3^-} \cdot \gamma_{HCO_3^-} \cdot K_{HCO_3^-}}{\alpha_{H^+}}$$

and

$$\alpha_{Ca^{++}} = \frac{K_{CaCO_3}}{\alpha_{CO_3^=}}$$

an error that results in a temperature measurement higher than the true temperature will increase $K_{HCO_3^-}$ and the computed value of $\alpha_{Ca^{++}}$ to make the water appear to be more saturated with calcium carbonate. For example, sample 3 has a recorded temperature of 60°F, and the calculated calcium concentration is 36 ppm. If we assume an error of plus or minus 5°F, at 65°F the theoretical calcium concentration would be 31 ppm and at 55°F the value would be 42 ppm. The corresponding concentration-ratio values are $+0.22$ (65°F) and -0.05 (55°F).

The possible error introduced by the laboratory analysis and computation of the ionic strength has virtually no effect on the value

of the activity coefficients and therefore involves no significant change
in the calculated values. The error due to standard analytical pro-
cedures arises primarily through the determination of calcium and
bicarbonate. The potentially most serious error in using the reported
calcium value for a comparison, is that any strontium present shows
up as calcium. Fortunately, many strontium determinations have
indicated that generally it is present in only small amounts. More
work is currently being done on the strontium content of water.

A far more serious analytical misrepresentation is the reported
value for bicarbonate. This value is alkalinity expressed as bicar-
bonate, and therefore represents all constituents that contribute to
the alkalinity of the water. These may include carbonate as well as
bicarbonate, in addition to borates, phosphates, and silicates, which
are generally present in minor amounts. Again by using sample 3
as an example, if we assume that 10 percent of the reported value for
bicarbonate is due to the presence of other weak acids, the true
bicarbonate value would be 184 ppm. In most waters the contribu-
tion to alkalinity by the weak acids would be far less than the 10
percent assumed.

However, if loss of carbon dioxide occurred, the reported value for
bicarbonate would be too low. This effect also could easily amount
to 10 percent, so that the true value on sample 3 would be 224 ppm.

A few calculations indicate that this range of values reflects a
change in the ionic strength small enough to have no effect on the
value for the activity coefficient to be used. Therefore, the change
in the theoretical calcium-ion concentration will result from the new
value for molality of the bicarbonate ion. The calculated calcium
values are 40 and 32, assuming respectively 184 and 224 ppm of
bicarbonate. The corresponding concentration ratios are 0.0 and
+0.20. The amount of error introduced in the analysis of calcium
and bicarbonate content by standard methods and in the determina-
tion of equilibrium constants, activity coefficients, and temperature
can be kept within narrow limits so far as the calculation of relative
equilibrium is concerned.

SUMMARY

A change in temperature, ionic strength, or pH, according to the
direction of change, can shift the conditions of equilibrium with
calcium carbonate and cause the water to precipitate or to dissolve
calcite or aragonite or both. Such changes can be brought about
by bacterial action, by movement of the water to another environ-
ment of different temperature and pressure, or by mixing with water
from another source which has a different temperature and ionic
strength.

In summary, this paper suggests a method to obtain calculated values for the calcium ion from standard chemical analyses of water, in order to determine the extent of departure from calcium carbonate saturation.   However, additional analyses of samples collected under more carefully controlled conditions and more accurate determinations of pH are necessary before reliable geologic inferences can be extended to limestone areas in general.

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