Procedures for Determining the Neutralizing Capacity of Wood during Hydrolysis with Mineral Acid Solutions

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Those anions present in wood that are associated with inorganic cations neutralize part of the mineral acid added to wood to catalyze hydrolysis. The resulting reduced hydronium ion concentration proportionally reduces the rates of hemicellulose and cellulose hydrolysis. Hydronium ion concentration is a fundamental variable in the kinetics of hydrolysis. In this study procedures were developed for determining the neutralizing capacity of wood and hydrolysis residues so that hydronium ion concentration can be accurately determined in low pH hydrolysis solutions at reaction conditions. The neutralizing capacity of wood was found to depend on the reaction conditions employed. All anions in wood associated with inorganic cations are not active in neutralization even under the most severe prehydrolysis conditions. Hydronium ion concentrations in hydrolysates calculated from wood neutralizing capacities agreed well with those determined by a kinetic method.

Introduction

Proposed and existing processes for the conversion of wood to ethyl alcohol invariably involve a one- or two-stage hydrolysis procedure for hydrolyzing the wood hemicelluloses and cellulose to monomeric sugars. These sugars are then fermented to ethanol. Either enzymes or mineral acids are used to catalyze the hydrolysis of the glycosidic linkages between the anhydrosugar units of the wood polymers. Acid hydrolysis has been much studied and is presently used industrially in the USSR. It is, at present, thought to be more practical than enzymatic hydrolysis. Sulfuric acid is invariably used since it is the cheapest mineral acid.

When a mineral acid solution is added to wood, paper, or other lignocellulosic materials, the hydronium ion concentration in the solution is found to decrease (Kirby, 1948; McLean, 1940; Saeman, 1945; Veeraraghavan et al., 1982). This decrease, which will here be called neutralization, is principally due to an ion-exchange reaction between the inorganic cations associated with the bound and free anions contained in the wood and the hydronium ions in the applied solution. The reaction for the bound anions can be written in a simplified manner as follows:

$$\text{wood–COO}^-\text{M}^+ + \text{H}^+ \rightarrow \text{wood–COO}^-\text{H}^+ + \text{M}^+$$

M^+ is the inorganic cation. This neutralization is important because it is, in most instances, the major factor involved in establishing the hydronium ion concentration (acidity) in the reacting solution. Hydronium ion concentration directly affects the rates of hydrolysis of the wood carbohydrate polymers and consequently directly affects process calculations and the size of processing equipment used.

This neutralization of mineral acid by wood should be distinguished from the usual neutralizing effect of wood. Wood contains small amounts of soluble organic acids and an appreciable quantity of bound carboxylic acid groups (Subramanian et al., 1983). It is thus naturally acidic and can be neutralized by treatment with alkali.

The reduction in hydronium ion concentration when a mineral acid solution is applied to wood depends on both the acid concentration and the amount of solution applied, If large quantities of acid are applied, as either concentrated or dilute solution, there will be little effect. However, under commercial conditions where it is desirable to minimize both the amount and concentration of the applied solution, the effect may be quite large.

Direct measurement of pH, either at reacting or ambient temperature, would be desirable. However, such measurements are quite inaccurate at the low pH values (about 1.5) commonly encountered in mineral acid prehydrolysis. Thus we, in this work, determine the hydronium ion concentration by difference, that is, by subtracting the acid consumed by the wood from the amount of acid applied.

Attempts to measure the acid consumption of wood directly, by adding a known quantity of acid to a weighed wood sample, removing an aliquot, and back-titrating with base, were unsuccessful. The presence of colored extractives prevented the use of an indicator, and the weak organic acids present resulted in an uninterpretable potentiometric titration curve. As discussed below, we found that the reduction in acidity was primarily due to the exchange reaction of hydronium ions with the inorganic cations in the wood and that satisfactory estimates of the final hydronium ion concentration could be based on measurements of the mineral constituents of the substrate.

Source of the Neutralizing Capacity of Wood

Considering the chemical constitution of wood, its interaction with acid solution might be expected to result in two types of reactions affecting the acidity of the solution: (1) replacement of bound inorganic cations with bound hydronium ions (i.e., ion exchange); (2) hydrolysis of esters to produce ionized acids We will first consider the participation of the cations.

The principal cations of wood are potassium, calcium, magnesium, and sodium (BeMiller, 1967). Many others, some of which are essential to plant growth, are present in small amounts. The cations are bound to both inorganic and organic anions in the wood. Those associated with organic anions are largely present as salts of the 4-*O*-methylglucuronic acid groups attached to the xylan hemicellulose polymer, but some woods also contain significant amounts of crystalline calcium oxalate (Schorger, 1926; Krasowski and Marton, 1982). The principal inorganic anions are sulfates, phosphates, and chloride.

The effectiveness of the cation exchange in reducing the hydronium ion concentration of the applied solution depends on the final pH and the p*K* of the associated acid.

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Salts of 4-*O*-methylglucuronic acid stoichiometrically exchange with hydronium ions at a pH of 1.5 or less (which includes the acidity range considered in this study). Since the p*K* of this acid is about 3, the organic salt is almost completely converted to the undissociated acid at pH 1.5. Thus each equivalent of 4-*O*-methylglucuronic acid salt neutralizes an equivalent of acid. At this same pH, however, only about 65% of the anions of salts of divalent oxalic acid are effective in cation exchange because the p*K* of the first ionization of this acid is 1.2. For salts of the other acids mentioned the approximate neutralizing capacities at this pH level are phosphate, 1.4; sulfate, 0.7; and chloride, 0 equiv of H^+/mol. It must he emphasized that the neutralizing effect of the anions decreases as the pH of the solution increases. Above pH levels of 4, where the 4-*O*- methylglucuronic acid is almost completely ionized, they have no effect.

The change in acidity incurred by the second reaction type, the hydrolysis of esters, also depends on the acidity of the solution in which the reaction occurs. To contribute to the hydronium ion concentration, it is necessary that the liberated acid be ionized. If the p*K* of the liberated acid is greater than the pH in which the reaction occurs, the liberated acid will be undissociated and the hydrolysis reaction will not affect the acidity. Since the p*K*'s of acetic acid and 4-*O*-methylglucuronic acid are 4.8 and 3.0, respectively, the hydrolysis of their esters will not contribute to the acidity of a solution at pH 1.5. However, if hydrolysis occurs in a solution of pH greater than 5, the reactions will increase the acidity. It is well-known that on heating wood in water the pH drops due to the formation of acetic acid. In water prehydrolysis of wood there is a significant induction period in which acids are released (Springer, 1968).

From the above discussion it can he concluded that at high acidities the anions associated with inorganic cations are the only wood constituents that alter the hydronium ion concentration of the applied acid solution. Further, all anions are not equally effective, since the cations originally present in salts of strong acids or moderately strong acids are not completely replaced with protons. However, most of the cations in wood are combined as salts of 4-*O*-methylglucuronic acid groups. Because the quantity of salts of strong acids is usually quite small, ignoring their effect will, for most North American wood species, lead to errors in the neutralizing capacity of less than 10%. Thus, a satisfactory estimate of the total potential neutralizing capacity can he obtained from a knowledge of the total inorganic cation content of the wood.

Results and Discussion

Measuring the Cation Content. Among several analytical methods considered, two were found suitable for determining the cation equvalents in wood and hydrolysis residues. In one commonly used wet-ashing method the sample is solubilized by using a nitric-perchloric acic mixture, and the individual cations in the resulting solution are determined by plasma emission spectrophotometry (Liegel et al., 1980). The total neutralizing capacity of the anions asscoiated with the inorganic cations is then obtained by summing the individual cation contributions. In the second method the sample is dry-ashed by a standard method (Moore and Johnson, 1967) and the neutralizing capacity of the ash determined. This is done by adding a known quantity of sulfuric acid to the ash and back-titrating with sodium hydroxide.

The two methods would be expected to give the same value only if salts of strong acids were not present. The sum of the equivalents of cations that are determined by the first or wet-ashing method would be greater than the neutralizing capacity of the wood if such salts were present. In the dry-ashing method, salts of strong inorganic acids would not fully contribute to the neutralizing capacity of the ash. For example, if $CaCl_2$ were present, the Ca^{2+} ions would he determined by the webashing method and would he assumed to completely exchange with the applied hydronium ions; however, this exchange would not occur. In the dry-ashing method the $CaCl_2$ present after dry-ashing would not neutralize the applied acid, and a correct value for neutralizing capacity would he determined. If salts of strong organic acids were present, however—forexample, calcium oxalate—the dry-ashing method would yield the same value as the webashing method. This value would he higher than the neutralizing capacity of the wood. On dry-ashing, calcium oxalate would be converted to calcium oxide, which would contribute to the basicity of the ash. Both procedures would he unaffected by the presence of silica, since it would contribute neither to ash basicity nor to cation content.

Table I. Analysis of Southern Red Oak (*Quercus falcata* Michx.) Wood Samples

	sample 1[a,b]		sample 2[a]	
	%[c]	mequiv/kg	%[c]	mequiv/kg
glucan	40.3		37.8	
mannan	2.9		2.1	
xylan	19.3		18.4	
galactan	*b*		1.1	
arabinan	*b*		0.71	
uronic anhydride	2.9		3.3	
acetyl	3.7		4.3	
lignin	21.8		21.9	
ash	0.24		0.72	
extractives	5.5		6.7	
neutralizing capacity				
method 1[d]		42 ± 7		131 ± 22
method 2[e]		35 ± 1		118 ± 3

[a] Sample 1 was used for ampoule studies; sample 2 for digester studies. [b] The analtyical procedure does not distinguish galactan from glucan nor arabinan from mannan. [c] Except where indicated, units are percent of OD wood. [d] Sample digested with nitric–perchloric acid mixture and cations determined by plasma emission spectrophotometry (Liegel et al., 1980). Neutralizing capacity taken as the sum of equivalents of cations [e] Sample ashed (Moore and Johnson, 1967) and neutralizing capacity of the ash determined by titration.

The results from the two procedures together with their 95% confidence limits are compared in Table I, which also indudes other analytical data for the wood samples used in this study. The ash content and neutralizing capacity of the two southern red oak samples differed in part due to the fact that sample 1 contained only heartwood whereas sample 2 contained both sapwood and heartwood. Lower values for neutralizing capacity may have been obtained from the dry-ashing procedure because salts of strong inorganic acids are present in the wood. The difference is, however, much greater than might be expected and may be due in whole or part to losses occurring during dry-ashing. With the dry-ashing procedure it is difficult to avoid some volatilization of sodium and potassium and some other loss of material (Phifer and Maginnis, 1960). Although the wet method is perferable, it should be recognized that the resulting value will be high if salts of strong acids are present.

We used both methods in our prehydrolysis studies: the wet method in a bench-scale study and the dry-ashing method in a pilot-scale study (Scott et al., 1983; Harris et al., 1984). Since the wet method is thought to be more accurate, only it was used in making the comparison with the subsequently described kinetic method.

Accessibility of Cations. At ambient temperature all ash-forming constituents cannot be readily acid-leached from finely divided wood; even after severe hydrolysis wood residues contain significant amounts of cations. The anions associated with these cations, which are evidently inaccessible, do not participate in neutralization. The quantity of cations removed during acid-leaching, prehydrolysis, or hydrolysis depends on wood particle size, concentration of the acid solution, and temperature and time of reaction, as indicated by the several experiments described below.

An acid-leaching procedure was used to remove cations from a wood sample for use in the hydrolysis experiment described in a subsequent section. Wood (sample 1, Table I) was ground to pass a USS No. 12 screen (<1.68 mm), and 0.1 kg was placed in a 35-mm-diameter glass column with a sintered glass bottom. Five liters of 0.02 N HCl was passed through the column over 16 h, always keeping the liquid level above the wood. The material was then washed with distilled water until it was chloride-free, and a sample was analyzed by the wet-ashing procedure. The cation content was reduced from 42 to 8 mequiv/kg; that is, after leaching, 20% of the potential neutralizing capacity remained.

In other experiments, thin disks (0.25 mm thick and 3 mm in diameter) cut with the small dimension across the grain so that every lumen was open were immersed in dilute H_2SO_4 solutions for 16 h, removed, washed, and analyzed by using the wet-shing procedure for cation content. For wood disks cut from sample 1 (Table I), using 0.4% H_2SO_4 w/w, 69% of the cations were removed, reducing the content from 42 to 13 mequiv/kg. Seventy-six percent of the cations were removed when a 0.8% H_2SO_4 solution was used.

The ash-forming constituents are more difficult to remove from larger particles. Chips 9.5 mm in length were prepared from sample 2 (Table I), vacuum-impregnated with sulfuric acid solution, and kept submerged (at atmospheric pressure) for 3 days. The acid solution was then replaced. The chips were kept submerged for an additional 3 days, with decantation and replacement of the solution after 24 and 48 h. The dry-shing titration procedure was used to analyze the original wood and the treated chips. The treatment reduced the cation content 56% (from 118 to 52 meq/kg) when a 0.47% H_2SO_4 w/w solution was used and 75% (from 118 to 30 meq/kg) when a 0.73% H_2SO_4 w/w solution was used.

Some but not all of the cations inaccessible at ambient temperature became accessible during hydrolysis at 170 or 190°C (Figure 1). Approximately half of the remaining cations were removed during the first few minutes of hydrolysis at 170°C, but the remainder were removed only slowly and incompletely over the period studied. This implies that the acidity of the solution must decrease as hydrolysis proceeds. The importance of this variation depends upon the pH level at which the reaction is occurring. At conditions optimal for commercial prehydrolysis (pH ≈ 1.4) (Scott et al., 1983) this variation in acidity is relatively small. The fact that not all of the anions associated with the cations present in the wood will participate in neutralization, even at reaciton temperatures, is a new and significant finding.

The cations removed by pretreatment prior to hydrolysis are readily accessible during hydrolysis if no pretreatment is used (Figure 1). Untreated chips (9.5 mm, sample 2, Table I) with a cation content of 118 mequiv/kg were vacuum-impregnated with 2.5% H_2SO_4 w/w solution. Impregnation conditions were adjusted so that the quantity

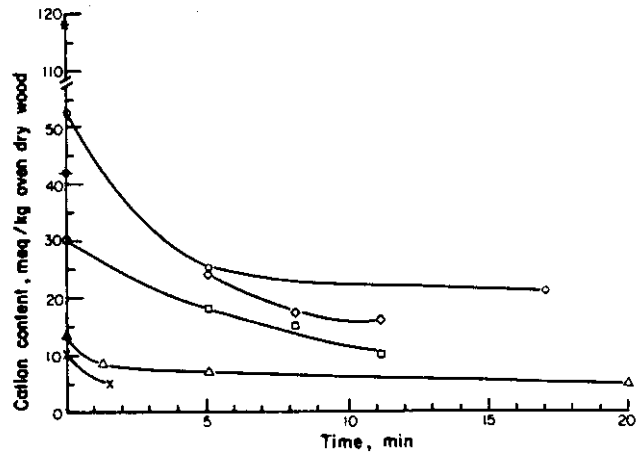

Figure 1. Variation of cation content with time of hydrolysis far various wood samples. Key: 9.5-mm chips–sample 2, Table I(118 mequiv/kg); *, initial untreated wood, «, pretreated by thorough impregnation with 0.47% H_2SO_4, reaction temperature 170 °C;), pretreated by thorough impregnation with 0.73% H_2SO_4, reaction temperature 170 °C: W, rapidly impregnated with 2.5%, H_2SO_4, reaction temperature 170°C, 3-mm disks–sample 1, Table I (42 mequiv/kg); «, initial untreated wood, •, pretreated with 0.40% H_2SO_4, reaction temperature 170 °C; X, pretreated 0.80% H_2SO_4, reaction temperature 190°C.

of acid absorbed would result in about the same final pH as that in other chip runs. The impregnated chips were hydrolyzed immediately, and only a short time was available for the acid to equilibrate. Nevertheless, after hydrolysis the residues had cation contents ranging from 16 to 24 mequiv/kg; at least 80% of the cations were quickly released into solution.

The total quantity of cations released to the solution can be used to calculate the hydronium ion concentration prevailing during reaction.

Calculation of Hydronium Ion Concentration, [H⁺]. The calculation of hydronium ion concentration is detailed in the Appendix. Since sulfuric acid was used, the dissociation of the bisulfate ion must be considered. Its dissociation decreases as temperature and acid concentration are increased (Lietzke et al., 1961). Over the range of conditions of this study as much as 10% of the bisulfate ion was dissociated, and it was necessary to include its contribution to the acidity. The correlation of Lietzke et al. (1961) was used to calculate the extent of dissociation. The concentration of soluble organic products in the hydrolyzing solution was ignored in the calculation.

Values of $[H^+]$ calculated by this procedure were compred to results obtained from a kinetic method for determining hydronium ion concentration described below.

Determining Acidity by Measurement of Hydrolysis Rate. The initial rate of xylan removal from hardwoods is constant up to about 50-60% removal. Although this weight-loss rate constant, k, is somewhat species dependent (Springer, 1968), it responds to temperature and acidity changes similarly to a first-order chemical reaction rate constqnt. For aspen reacted in dilute acid solution at a given temperature, k can be correlated with acidity by the relationship $\ln k = a \ln [H^+] + b$, where a and b are constants (Springer, 1966). This relationship can be used inversely to obtain the acidity by measuring the rate, that is, $[H^+] = \exp [(\ln k - b)/a]$.

To relate the weight-loss rate constant for the removal of xylan from southern red oak to hydronium ion concentration, measurements of k were made at 120°C and three acidity levels (0.1, 0.2, and 0.4% H_2SO_4 added). The substrate was the finely divided, low cation content ma-

Table II. Initial Weight-Loss Rate Constants for Southern Red Oak at 120 °C

appl acid concn, %	liquid-to-solid ratio	rate constant k, min^{-1}	neutralizing capacity,[a] mequiv/kg OD wood: wood	neutralizing capacity,[a] mequiv/kg OD wood: residue[b]	[H$^+$] concn, mol/kg of water: A[c]	[H$^+$] concn, mol/kg of water: B[d]
		Sample No. 1, Table I–De-Ashed				
0.100	2.97	0.00240			0.0096	
0.100	3.09	0.00247			0.0097	
0.200	2.81	0.00485	8	4	0.0198	
0.200	3.03	0.00456			0.0199	
0.400	2.75	0.00825			0.0404	
0.400	2.89	0.00990			0.0405	
		Sample No. 1. Table I				
0.201	3.11	0.00327			0.0115	0.0133
0.201	3.42	0.00303	42	8	0.0124	0.0123
0.201	5.37	0.00370			0.0155	0.0153
					av 0.0131	0.0136
		Sample No. 2. Table I				
0.401	3.05	0.00449			0.0177	0,0189
0.401	3.19	0.00485	131	49	0.0187	0.0205
0.401	3.26	0.00427			0.0192	0.0178
					av 0.0185	0.0191

[a] Analysis by wet-ashing procedure. [b] Separate duplicate samples used to determine residual cations at longest reaction time of the group. Neutralizing capacity based on original material. [c] Calculated by procedure in Appendix. [d] From rate measurement, [H$^+$] = exp [(ln (k) + 1.7712)/0.9152].

terial prepared from sample 1 (Table I) by leaching the finely ground wood with 0.02 N HCl at room temperature as previously described. This contained 8 mequiv/kg of cations, measured by wet-ashing, 50% of which dissolved during hydrolysis. Reactions were carried out in 5-mm glass ampoules by using experimental and analytical procedures previously described (Springer, 1963, 1966, 1968). Results are presented in Table II.

From these data the relationship between the rate of xylan weight loss, k, and [H$^+$] was established Although the amount of cations released during reaction from this low-ash wood was small (4 mequiv/kg), it nevertheless consumed some acid and lowered the acidity slightly. The values of [H$^+$] listed in Table II, calculated by the procedure given in the Appendix, were used to relate k to [H$^+$]. The resulting equation, ln (k) = 0.9152 ln [H$^+$] - 1.7712, is shown graphically in Figure 2 (solid line) along with the experimental points. It differs, over this range of acid concentrations, by less than 10% from the correlation found previously for aspen reacting in hydrochloric acid solutions where the neutralization effect was negligible (Springer, 1966).

Initial rate constants, k were determined for two wood samples containing their original cation content (Table II). Also listed in Table II are the hydronium ion concentrations calculated from the cations released (A), determined by the wet-ashing procedure, and the acid concentrations inferred from the rate measurements (B). For this comparison only the wet-ashing procedure was used, since it is thought to be more accurate. The estimations of [H$^+$] based on the cations released (A) average slightly lower than the values obtained kinetically (B) for both wood samples; however, the observed differences are not statistically significant. These slight differences, if real, might indicate that not all cations are effective in neutralization (i.e., that some strong acid salts are present). However, the inaccessibility of some of the cations and their gradual release during the reaction period may also be a factor, for this gradual release results in a gradual decrease in the average acidity during hydrolysis. The value based on the cations released is an estimate of the acidity at the end of the reaction period, whereas the kinetic value is an averaged, and therefore higher, value.

Both measurements indicate that the actual hydronium ion concentration is much lower than that which would

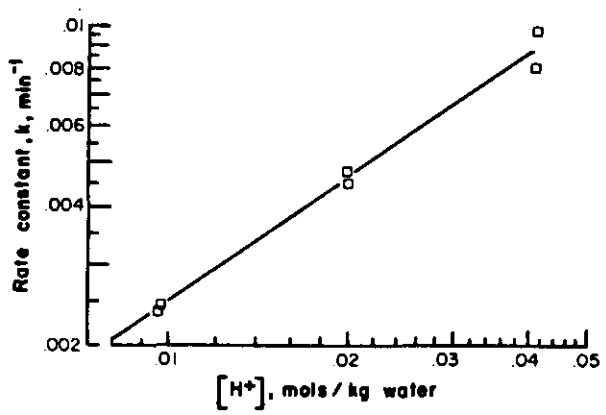

Figure 2. Variation of rate of initial xylan weight loss with acidity for low-ash content southern red oak. Equation: k = exp(0.9152 ln [H$^+$] - 1.7112).

prevail if no neutralization occurred. A 0.201% H_2SO_4 w/w solution with no cation exchange would have a [H$^+$] molality of 0.0212 at 120 °C, whereas the average value from the three rate measurements for sample 1 is 0.0136 m. Values for the 0.401% w/w acid solution and sample 2 are 0.0419 and 0.0191 m, more than a 50% reduction in catalyst concentration resulting from the neutralizing capacity of the wood.

The data of this study thus indicate that the anions associated with the inorganic cations of wood significantly lower the acidity of applied mineral acid solutions and cannot be ignored. Correcting for the effect of these anions by assuming that all their associated cations released into the solution are a direct index of the extent of neutralization results in values for [H$^+$] that, while they appear to be slightly lower, differ by less than 10% from those measured kinetically.

Conclusions

On dilute mineral acid hydrolysis or prehydrolysis of wood, most of the inorganic cations present in the wood are exchanged for hydronium ions in the solution, and the hydronium ion concentration of the solution is thereby reduced. Due to inaccessibility or other factors, some cations are very resistant to exchange, and a small quantity will be present in even the most severely hydrolyzed wood. At low pH the difference between the cations in the initial

wood and those in the hydrolyzed residue can be used to calculate the hydronium ion concentration in the solution during hydrolysis. Through the use of standard analytical methods, two procedures were developed to determine the quantity of cations in a wood or hydrolysis residue sample. When the most accurate procedure was used, the hydronium ion concentration calculated from cations released into the solution agreed closely with that measured kinetically.

Appendix

Calculation of Hydronium Ion Concentration, $[H^+]$. (Molal concentration units of mol/kg of water are used; i.e., $[X]$ = concentration of X in mol/kg of water.)

Basis: 100 kg of OD wood.

Given: concentration of added acid = CA, % H_2SO_4; liquid-to-solid ratio = LS, kg/kg; neutralizing capacity of wood = EQW, mequiv/kg OD wood; neutralizing capacity of residue = EQR, mequiv/kg OD wood.

Then: EQ = equivalents of cations released to solution = (EQW - EQR)/10; SS = sum of the concentrations of sulfate and bisulfate ions in solution = CA/[9.8(1 – 0.01 × CA)]mol/1000 g of water; CS = concentration of cations in solution = EQ/ [LS × (100 - CA)]equiv/1000 g of water.

Sulfur balance: $[HSO_4^-] + [SO_4^{2-}]$ = SS; charge balance ($[OH^-]$«$[SO_4^{2-}]$), $[HSO_4^-] + 2[SO_4^{2-}] - [H^+]$ = CS; bisulfate dissociation quotient, $Q = [H^+][SO_4^{2-}]/[HSO_4^-]$.

These equations combine to the quadratic equation in $[H^+]$:

$$[H^+]^2 + (Q + CS - SS)[H^+] + Q(CS - 2 \times SS) = 0$$

With numerical values for CS, SS, and Q the coefficients may be evaluated and the equation solved for its one real positive root that is the value of $[H^+]$. The bisulfate dissocietion quotient, Q, is evaluated by using the following relationships from Lietzke et al. (1961):

$$\ln Q = \ln K + 4S\left[\frac{I^{1/2}}{1 + AI^{1/2}}\right]$$

where K = bisulfate dissociation equilibrium constant = $\exp(-1283.108/T + 12.31995 - 0.0422322T)$, T = temperature, kelvin; S = Debye-Hückel limiting slope at temperature T, for a singly charged ion = $2^{1/2} \times 1.290 \times 10^6/(DT)^{3/2}$; D = dielectric constant for water = $78.54(1 - 0.004579(t - 25) + 11.9 \times 10^{-6}(t - 25)^2 + 28.0 \times 10^{-9}(t - 25)^3)$; t = temperature, °C; I = ionic strength = $0.5([H^+] + [HSO_4^-] + 4[SO_4^{2-}] + CS)$; A = an empirical constant = 0.4.

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Registry No. H_2SO_4, 7664-93-9; H^+, 12408-02-5.

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