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THE CALCULATION OF AQUIFER CHEMISTRY IN HOT-WATER GEOTHERMAL SYSTEMS

By ALFRED H. TRUESDELL and WENDY SINGERS,
Menlo Park, Calif., Chemistry Division, D.S.I.R., New Zealand

Abstract.—The temperature and chemical conditions (pH, gas pressure, and ion activities) in a geothermal aquifer supplying a producing bore can be calculated from the enthalpy of the total fluid (liquid + vapor) produced and chemical analyses of water and steam separated and collected at known pressures. Alternatively, if a single water phase exists in the aquifer, the complete analysis (including gases) of a sample collected from the aquifer by a downhole sampler is sufficient to determine the aquifer chemistry without a measured value of the enthalpy. The assumptions made are that the fluid is produced from a single aquifer and is homogeneous in enthalpy and chemical composition. These calculations of aquifer chemistry involving large amounts of ancillary information and many iterations require computer methods. A computer program in PL-1 to perform these calculations is available from the National Technical Information Service as document PB-219 376.

In active hydrothermal systems that have been drilled, mineral alteration and deposition can be related to observed temperatures and fluid compositions. Chemical analyses of water and steam produced from many types of geothermal systems are now available. However, analyses of fluids collected at the surface do not describe the chemistry of fluids as they occur at depth. The chemical differences between the fluids at the surface and in the deep aquifer are due to the decrease of pressure and temperature during production. Adiabatic expansion during passage up the drill hole may result in steam separation, cooling, and an increase in the concentration of the solutes in the water phase. Loss of dissolved CO₂ and H₂S from the water to the vapor increases the pH value of the water. The increase in pH and solute concentration and the decrease in temperature may cause the water to become supersaturated with calcite or silica minerals and may result in scaling of well casings. The continued production of a geothermal system is likely to decrease the reservoir pressures enough to form steam in the aquifer (Mahon, 1970). The resulting decrease in gas pressures, increase in aquifer pH, and temperature lowering may cause increased calcite deposition in the casing and possibly in the aquifer. Potential mineral deposition may be calculated if the chemistry of aquifer fluids is known.

Underground water temperatures may be calculated from known mineral solubility or ion exchange reactions that control water compositions; for example, quartz solubility (Fournier and Rowe, 1966; Mahon, 1966), Na:K ratios (White,

1965; Ellis, 1970), or Na:K:Ca ratios (Fournier and Truesdell, 1973). The assumptions underlying these calculations have been discussed by White (1970).

Thus, for practical reasons as well as to increase our knowledge of natural systems, it is of interest to calculate the chemical properties of geothermal fluids before they are changed during production. This is the purpose of the computer program described here.

ACKNOWLEDGMENTS

The computer program is a further development of the method of Ellis (1967, 1970) and was partly written in the laboratories of the Chemistry Division, Department of Scientific and Industrial Research (D.S.I.R.), New Zealand, while the author was on a training grant from the U.S. Geological Survey. The calculations have been discussed with A. J. Ellis, W. A. J. Mahon, Werner Giggenbach, and R. B. Glover of the D.S.I.R., New Zealand, and Ivan Barnes, L. J. P. Muffler, R. O. Fournier, and D. E. White of the U.S. Geological Survey. The program was initially written in Elliot-Algol.

ASSUMPTIONS

These calculations assume that fluid from a geothermal well (1) is produced from a single aquifer, (2) does not gain or lose significant heat or matter during passage up the well and through surface pipes to sampling points, and (3) maintains chemical equilibrium at each point of steam-water separation.

The first assumption that the fluid is produced from a single aquifer must be judged in each situation. In general, wells in which discharge enthalpy and silica contents indicate the same aquifer temperature are most probably from a single aquifer and existed in that aquifer as a single liquid phase. Two or more aquifers may, however, contribute fluids to a producing bore. This circumstance can be deduced from the drilling log, the ratios of gaseous components in the steam (Glover, 1970), or a comparison of the water composition with that of other wells in the field (Mahon, 1970).

The second assumption is most probably true for the well-studied and long-producing Wairakei, New Zealand, geothermal system in which the composition of produced fluids has been nearly constant over a decade of observation and in

which the mass of scale deposited is negligible (Mahon, 1970; Grindley, 1965, p. 58). Here also the conductive heat flow is small compared with the heat delivered to the surface in the fluid (Dawson and Dickinson, 1970; Grindley, 1965). This assumption is probably true also for many but not all other hot-water geothermal systems.

The assumption of chemical equilibrium is more difficult to justify. It has been observed that, in the aquifer, saturation with quartz is exactly maintained (Mahon, 1970), and most equilibria involving species dissolved in the aquifer water phase should be more rapid than saturation equilibria with a solid phase. However, during passage up the well and through the separator, CO₂ may not maintain an equilibrium distribution between the steam and water, as shown by Glover (1970), who found at Wairakei that the distribution coefficient for CO₂ between vapor and liquid water was about 70 rather than the equilibrium value of 460 (Ellis and Golding, 1963). The calculated total CO₂ based on analyses of the separated steam may be low by 2 percent or less. This would not significantly change the calculated CO₂ pressures or aquifer pH.

The difference between the actual total pressure in the aquifer and the saturated water-vapor pressure at the aquifer temperature is assumed to have a negligible effect on the equilibrium constants. The constants used in the program all refer to saturated water-vapor pressure conditions.

CHEMICAL AND PHYSICAL CHANGES ON PRODUCTION

The calculations performed in the program can be best illustrated by following the chemical and physical changes in the fluid produced from a representative aquifer. Analyses of water and gas samples from well 20 of the Wairakei, New Zealand, geothermal field are used as an example. The changes are discussed in the order that they occur; that is, from inaccessible conditions to the separated water and steam as analyzed. The program works backwards along the line of these changes and reconstructs the inaccessible states.

The calculated conditions prior to entering the bore are given in table 1. Note that the pH of 6.34 is nearly the neutral pH at the temperature 246°C and that virtually all boric and silicic acids and nearly all carbonic acid and hydrogen sulfide are undissociated. A substantial proportion of total sulfate exists as bisulfate ion, fluoride as neutral hydrogen fluoride, and ammonia as ammonium ion. Ion pairs such as NaCl, KCl, NaSO₄ and CaSO₄ are more stable than at low temperatures (see tables 4 and 5) and are present in moderate amounts. The enthalpy (enthalpy refers to specific enthalpy throughout) of the fluid is slightly less than that of water in equilibrium with steam (table 1), and a gas phase is probably not present.

The aquifer fluid flows toward and into the well along a gradient of decreasing pressure resulting from the lower density of the two-phase steam-water mixture in the well. The decrease in pressure causes steam separation and a decrease in temperature. These processes continue in the well and in the

Table 1.—*Aquifer fluid adjacent to hole 20, Wairakei, New Zealand*
[1 cal = 4.184 abs J]

Temperature	°C	246
Pressure	bars abs	37.6
Enthalpy ¹	cal/g	252.8
pH ²	6.34
CO ₂ partial pressure.....	bars	0.79
H ₂ S partial pressure.....	do	0.0093

<i>Dissolved constituents</i>	<i>Concentrations in mmol/1,000 g H₂O</i>
Li ⁺	1.5
Na ⁺	38.3
K ⁺	4.1
Rb ⁺025
Cs ⁺014
Ca ⁺²43
Mg ⁺²0
F ⁻29
Cl ⁻	42.9
Br ⁻05
I ⁻002
SO ₄ ⁻²079
H ₃ BO ₃	1.74
H ₂ BO ₃002
H ₂ CO ₃ ⁰ +CO ₂ aq	7.89
HCO ₃ ⁻35
CO ₃ ⁻²00001
H ₄ SiO ₄ ⁰	7.85
H ₃ SiO ₄ ⁻006
H ₂ SiO ₄ ⁻²00001
NH ₄ ⁺002
NH ₃ aq011
H ₂ Saq25
HS ⁻022
HF ⁰050
H ₂ SO ₄ ⁻0023
HCl ⁰00006
NaCl ⁰	1.27
KCl ⁰097
MgSO ₄ ⁰0
CaSO ₄ ⁰025
KSO ₄ ⁻015
NaSO ₄ ⁻15
CaCO ₃ ⁰0002
MgOH ⁺0

¹Saturated-water enthalpy is 254.6 cal/g.

²Neutral pH is 5.6 at 246°C.

steam-water separator, which was operated at a pressure of 16.3 bars absolute and a temperature of 202°C. With the decrease of pressure and temperature, the fluid separates into 10.1 percent steam with an enthalpy of 667.4 cal/g and 89.9 percent water with an enthalpy of 206.1 cal/g. (1 cal=4.184 abs J.) The total enthalpy remains 252.8 cal/g (0.101X667.4+0.899X206.1) because no significant amount of heat has been lost in the passage up the well. The gases originally dissolved in the water have largely exsolved into the gas phase (experimental distribution coefficients for CO₂ and H₂S, tables 4 and 5, greatly favor the gas phase, particularly near 200°C). From the separator, the steam is collected and analyzed for CO₂ and H₂S. Collection and analysis methods

Table 2.—Analysis as reported on water and steam from well 20, Wairakei, New Zealand

Temperature of steam separation	°C.	202
Temperature of water separation	°C.	99 and 202
CO ₂ in high pressure steam	mmol/100 mol H ₂ O.	142
H ₂ S in high pressure steam	mmol/100 mol H ₂ O.	4.5
Water pH measured at 20°C		8.0

Dissolved constituents	Concentrations in water as analyzed at 20°C in mg/kg	Dissolved constituents	Concentrations in water as analyzed at 20°C in mg/kg
Li	14.8	Br	5.4
Na	1,260	I	.4
K	228	SO ₄	35
Rb	3.0	B	26
Cs	2.5	HCO ₃	7.7
Ca	25	CO ₃	0
Mg	0	SiO ₂	650
F	8.8	NH ₃	.3
Cl	2,164	H ₂ S	0

for steam and water are given in Ellis, Mahon, and Ritchie (1968). The gas analysis is given in table 2. The steam and water leave the separator in separate lines, and the water enters a silencer, which discharges to the atmosphere. In the silencer an additional 20 percent of the original water is flashed to steam, and the remaining water flows out the weir box where it is sampled. The proportions of steam and water at each separation point are calculated from an enthalpy balance with the assumption of constant enthalpy. The water sample in a capped polyethylene bottle is cooled and taken to the laboratory where it is analyzed and the pH is measured. The amount of CO₂ and H₂S dissolved in the water after separation is negligible relative to that which partitions into the gas phase and is not analyzed. The enthalpy of the whole fluid is calculated from measurements of the flows of steam and water under controlled conditions.

The properties of the water as analyzed are given in table 2. The steam and water analyses were made by the staff of the Chemistry Division, D.S.I.R., New Zealand. The water analysis has been recalculated in table 3 to show what species were present in the analyzed solution at 20°C. The water composition differs substantially from the composition of the aquifer fluid. The separation of steam has increased the concentration of mineral constituents that are insoluble in steam (compare Li⁺ in the tables). The separation of CO₂ and H₂S into the steam phase has increased the pH by 1.7 units.

The pH increase and temperature decrease have increased the ionization of weak acids, particularly boric acid, silicic acid, and carbonic acid. Ion pairs are generally less stable at lower temperatures (tables 4 and 5) and are thus less in evidence. The most important change is the partition of acid gases (CO₂, H₂S) into the steam with the resultant increase in pH. The aquifer pH, the activity coefficient of H⁺, and the potassium contents can be combined to calculate a K:H concentration ratio of 10^{3.83} which is similar to the extrapo-

Table 3.—Calculated composition at 20°C of separated well water from well 20, Wairakei, New Zealand

[Water pH measured at 20°C is 8.0]

Dissolved constituents	Concentrations in mmol/1,000 g H ₂ O	Dissolved constituents	Concentrations in mmol/1,000 g H ₂ O
Li ⁺	2.1	H ₃ SiO ₄ ⁻	.25
Na ⁺	54.9	H ₂ SiO ₄ ⁻²	.00009
K ⁺	5.85	NH ₄ ⁺	.017
Rb ⁺	.035	NH ₃ ^o	.0006
Cs ⁺	.019	H ₂ S	.0
Ca ⁺²	.62	HS ⁻	.0
Mg ⁺²	.0	HF ^o	<.000005
F ⁻	.47	HSO ₄ ⁻	<.000005
Cl ⁻	61.3	HCl ^o	<.000005
Br ⁻	.068	NaCl ^o	.05
I ⁻	.003	KCl ^o	.005
SO ₄ ⁻²	.315	MgSO ₄ ^o	.0
H ₃ BO ₃ ⁻	2.26	CaSO ₄	.007
H ₂ BO ₃ ⁻	.15	KSO ₄ ⁻	.005
H ₂ CO ₃ ^o +CO ₂ aq	.003	NaSO ₄ ⁻	.04
HCO ₃ ⁻	.126	CaCO ₃ ^o	.0002
CO ₃ ⁻²	.001	MgOH ⁺	.0
H ₄ SiO ₄ ^o	10.6		

lated, pressure-corrected experimental value of 10^{3.92} for water in equilibrium with K-mica, K-feldspar, and quartz near 250°C (Hemley, 1959; R. O. Fournier, oral. commun., 1972; Ellis and McFadden, 1972). This similarity suggests that mineralogical buffer systems are the major control on the pH of this aquifer fluid.

DATA REQUIRED

Data necessary to the calculation of aquifer chemistry consist of (1) a chemical analysis of the water separated from the water-steam mixture produced from the well, (2) the content of carbon dioxide and hydrogen sulfide in the separated steam, (3) the pressures of water and steam separation and the atmospheric pressure, and (4) the enthalpy of the whole fluid. The water analysis must include the pH, the temperature of pH measurement, and concentrations of all major dissolved constituents, particularly those that form weak acids or bases at low or high temperatures (HCO₃⁻, SO₄⁻², BO₃⁻, F⁻, SiO₂, and so forth. A silica analysis is essential because the temperature of the aquifer is calculated by assuming that the aquifer water phase is saturated with quartz (Mahon, 1966).

The CO₂ and H₂S contents of separated steam must be known because both of these gases dissolve in water to form weak acids and their separation from water raises the pH. The pressure of steam separation is introduced because the separation and collection of steam for gas analysis is most efficiently done at high pressure (to achieve a maximum gas to H₂O ratio) and the collection of water is usually from the silencer at atmospheric pressure (Ellis, Mahon and Ritchie, 1968). If the sample is from a downhole sampler, the water analysis and the CO₂ and H₂S contents are sufficient to

calculate the aquifer chemistry, provided that the fluid sampled was a single liquid phase.

AQUIFER TEMPERATURE CALCULATION

The temperature of an aquifer feeding a geothermal well is measured infrequently, and the measurements when made are uncertain. It has been shown (Fournier and Rowe, 1966; Mahon, 1966, 1970) to be preferable to calculate the aquifer temperature from the silica content of the discharge, assuming equilibrium with quartz in the aquifer, rather than to measure the temperature directly. The original silica content in the deep water must be calculated from analytical data allowing for concentration from steam separation and for the presence of steam in the aquifer. The calculation of the aquifer temperature requires enthalpy values of saturated steam and water at that temperature, and therefore an iteration procedure is necessary.

If the pH of the aquifer fluid is greater than about 7, some silica is present as silicate ions, and the indicated temperature from total silica will be too high. In this instance, concentrations of ionic silica species are calculated and subtracted from total silica concentrations because the silica concentration used for the temperature estimate is specifically $\text{SiO}_2(\text{aq})$.

CALCULATION OF THE EFFECTS OF STEAM SEPARATION AND EXCESS ENTHALPY

The enthalpies of the total fluid and of water and steam at the pressure and temperature of the aquifer and at each point of separation are necessary for calculating the proportion of water and steam separated and the degree of concentration of the dissolved mineral constituents in the water and of the dissolved gases in the steam. For these calculations, the program uses thermodynamic data for pure water from Keenan, Keyes, Hill, and Moore (1969). The effect of the low mineral contents (<0.3 wt percent NaCl) of most geothermal waters on the thermodynamic properties of water is negligible (J. L. Hass, written commun., 1971). The content of dissolved gases in steam from most geothermal discharges is low (<2 percent), and their effect on the thermodynamic properties has been neglected.

With the assumption of constant total enthalpy, the fraction of water or steam in the fluid can be calculated for any temperature (t) from the equations,

$$\text{fraction water} = \frac{\text{enthalpy of steam at } t - \text{fluid enthalpy}}{\text{enthalpy of vaporization at } t}$$

$$\text{and fraction steam} = \frac{\text{fluid enthalpy} - \text{enthalpy of water at } t}{\text{enthalpy of vaporization at } t}$$

If the enthalpy of the fluid is the same or lower than that of water saturated with steam at the aquifer temperature, then no steam is present in the aquifer, and the concentrations of mineral constituents owing to later steam separation are

calculated from the following:

$$\begin{aligned} \text{Original concentration} &= \text{concentration in complete discharge} \\ &= (\text{analyzed concentration in water}) \times (\text{fraction of water in separator 1}) \times (\text{fraction of water in separator 2}) \times (\text{fraction of water in silencer}). \end{aligned}$$

If, however, the enthalpy of the fluid is higher than that of steam-saturated water at the aquifer temperature, the presence of steam in the aquifer is indicated. The presence of steam causes the mineral constituents in the original waters as calculated above to be too low, so that the following correction factor is applied:

$$\begin{aligned} \text{Concentration in original water} \\ &= \frac{\text{concentration in complete discharge}}{\text{fraction of water in the aquifer}} \end{aligned}$$

The presence of steam is often the result of lowered pressure owing to extensive production. Because CO_2 and H_2S are strongly partitioned into the steam phase, the development of steam in the aquifer may result in a decrease in gas pressures and an increase in aquifer pH with the possibility of carbonate scale deposition in the aquifer and in the well casing.

Because of instrumental inaccuracies, measurement of the enthalpy of drillhole discharges is necessarily somewhat approximate; therefore, samples with fluid enthalpies within ± 23 cal/g (50 Btu/lb) of the enthalpy of water in equilibrium with steam at the aquifer temperatures are recalculated assuming exact equilibrium.

GAS PARTIAL PRESSURES

If the gas (CO_2 , H_2S) contents of the sampled steam and the fraction of steam in the fluid at the sampling point are known, the total gas contents of the aquifer fluids may be calculated. If a single liquid phase exists in the aquifer, the gas partial pressures may be calculated directly from experimental data on the solubility of gas in water at high temperatures (Ellis and Golding, 1963; Kozintseva, 1964). If both steam and water exist in the aquifer, a large fraction of the gas partitions into the aquifer steam phase, and the partial pressure of the gas is a quadratic function of the total gas content.

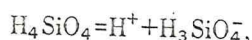
CHEMICAL MODEL

The calculation of the chemistry of the aquifer fluids requires knowledge of the total content of all solution components and of the dissociation constants of all weak acids and bases and all ion pairs. The total contents of components other than gases and hydrogen ions are easily calculated from the water analysis with allowance for the effects of steam separation and of steam in the aquifer as described earlier. The contents of dissolved gases in the water may be calculated from their solubilities, their contents in the separated steam, the steam fraction, and if there is excess enthalpy, from the fractions of steam and water in the aquifer. For the calculation

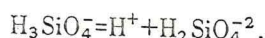
of the total content of hydrogen ion, the state of ionization of all weak acids and bases under the conditions of analysis must first be ascertained. This is done through the calculations of a chemical model (Garrels and Thompson, 1962; Ellis, 1967).

SOLUTION OF MASS ACTION AND MASS BALANCE EQUATIONS

In the chemical model for the water as analyzed, the analytical concentrations, experimental dissociation constants, mass balances, and the measured pH are used to calculate the distribution of weak acid species and experimental dissociation constants, and mass balance equations are used to calculate that of ion pairs. Weak acids dissociate to form hydrogen ions by equations such as those for silicic acid as follows:



and



The concentration of each species is determined by the total concentration, the pH, the activity coefficients of the species, and the equilibrium constants for distribution of species at chemical equilibrium. For the preceding reactions we can write the equilibrium equations as follows:

$$K_1 = \frac{m_{H_3SiO_4^-} \gamma_{H_3SiO_4^-} 10^{-pH}}{m_{H_4SiO_4} \gamma_{H_4SiO_4}}$$

$$K_2 = \frac{m_{H_2SiO_4^{2-}} \gamma_{H_2SiO_4^{2-}} 10^{-2pH}}{m_{H_3SiO_4^-} \gamma_{H_3SiO_4^-}}$$

The mass balance equation for total silica (silicic acid and silicate ions) is

$$m_{Si \text{ total}} = m_{H_4SiO_4} + m_{H_3SiO_4^-} + m_{H_2SiO_4^{2-}}$$

The mass action equations can be combined with the mass balance equation to solve for $m_{H_4SiO_4}$.

$$m_{H_4SiO_4} = \frac{m_{Si \text{ total}}}{1 + \gamma_{H_4SiO_4} \left(\frac{K_1 10^{pH}}{\gamma_{H_3SiO_4^-}} + \frac{K_1 K_2 10^{2pH}}{\gamma_{H_2SiO_4^{2-}}} \right)}$$

The value of $m_{H_4SiO_4}$ is then substituted into the mass action equations to solve for $m_{H_3SiO_4^-}$ and $m_{H_2SiO_4^{2-}}$. Activity coefficients are calculated from the extended Debye-Huckel equation as described later, and the ionic strength is calculated by iteration. Calculation of the concentration of ion pairs is accomplished by a slightly different procedure, which is illustrated by the calculation of the calcium ion species. The mass action expressions,

$$K_1 = \frac{m_{Ca^{+2}} \gamma_{Ca^{+2}} m_{SO_4^{2-}} \gamma_{SO_4^{2-}}}{m_{CaSO_4} \gamma_{CaSO_4}}$$

and

$$K_2 = \frac{m_{Ca^{+2}} \gamma_{Ca^{+2}} m_{CO_3^{2-}} \gamma_{CO_3^{2-}}}{m_{CaCO_3} \gamma_{CaCO_3}}$$

are combined with the mass balance expression,

$$m_{Ca \text{ total}} = m_{Ca^{+2}} + m_{CaSO_4} + m_{CaCO_3}$$

to produce an expression for free (uncomplexed) Ca^{+2} ion,

$$m_{Ca^{+2}} = \frac{m_{Ca \text{ total}}}{1 + \gamma_{Ca^{+2}} \left(\frac{m_{SO_4^{2-}} \gamma_{SO_4^{2-}}}{K_1 \gamma_{CaSO_4}} + \frac{m_{CO_3^{2-}} \gamma_{CO_3^{2-}}}{K_2 \gamma_{CaCO_3}} \right)}$$

The value of $m_{Ca^{+2}}$ may be substituted into the mass action expressions to solve for the ion pairs. In these equations Ca total is from the analysis, the dissociation constants depend only on temperature, and the activity coefficients are calculated from the ionic strength, which changes slowly during iteration. The molalities of the anions (SO_4^{2-} , CO_3^{2-}) are corrected in each iteration loop by summing the calculated species (for example, $m_{SO_4^{2-}} + m_{HSO_4^-} + m_{KSO_4^+}$...) and comparing the sum with the analytical concentration of total anion. If the sum calculated differs from the analytical concentration by more than 0.1 percent, the free anion concentration is corrected by an amount depending on the difference. When all anions have been checked (and corrected if necessary), the program iterates if corrections have been made to any of them. Thus, the program leaves the loop when the concentrations of all species satisfy the mass balances to 0.1 percent.

TOTAL IONIZABLE HYDROGEN ION CONTENT

The total content of hydrogen ions in an aqueous solution includes not only free ions but also those in combination in weak acids and in water itself. Only part of these can be ionized under the range of conditions found in natural waters.

This part, the total "ionizable" hydrogen ion content, is calculated by summing the contents of H^+ ion and of all the undissociated and partly dissociated weak acids— HCO_3^- , HBO_2 , H_2S , NH_4^+ , HSO_4^- , HF , HCl , $H_3SiO_4^-$, $H_4SiO_4^-$, (two times), and H_2CO_3 (two times). When the total ionizable hydrogen ion content has been corrected for electrolyte concentration changes due to steam separation and the presence of aquifer steam as discussed earlier, the H_2S and CO_2 originally dissolved in the water are added (the CO_2 two times as H_2CO_3).

AQUIFER CHEMICAL MODEL

The aquifer chemical model is calculated using the analysis corrected for steam separation and aquifer steam contents, values of dissociation constants at the aquifer temperature and saturated water vapor pressure, and the total ionizable hydrogen ion content. The method of calculation of the chemical model is the same as before except that the pH is now a dependent rather than an independent variable. Because almost all of the hydrogen ion occurs in complexes, changes in the calculated pH cause relatively large changes in the anion mass balances, and the program converges very slowly. A change in the criteria of convergence from 1 percent to 0.1 percent of the anion mass balances doubles the number of

iterations and changes the final calculated pH by 0.1 to 0.15 units.

The correctness of the calculated model is dependent on the existence and validity of high-temperature quartz solubility values, gas solubility constants, and dissociation constants for the weak acids and bases and ion pairs present in the water. The data used in the program are given in tables 4 and 5 with their sources. They are of uneven quality, and as better data become available, the program can be easily updated. Tabular data are interpolated by a program written by P. C. Doherty of the U.S. Geological Survey. Single-ion activity coefficients have been calculated from the extended Debye-Hückel equation, with a small hydration coefficient (the "B." of Helgeson, 1969) assumed constant with temperature. This equation differs little from that suggested by Davies (1962). The ionic strength (I) of most geothermal waters is moderate ($<0.03m$), and the ionic activity coefficients are not very sensitive to the ion size (\bar{a}) and hydration parameters chosen. The equation used is:

$$\log \gamma_i = \frac{-A z_i^2 I^{1/2}}{1 + \bar{a}_i B I^{1/2}} + 0.04 I.$$

The constants A and B are from a tabulation by Helgeson (1967) and are for molal units. Values of \bar{a} are taken from Kielland (1937).

Table 4.—Solubility constants and dissociation constants in KA(I) and KT(I) arrays, analytical expressions

Reaction	Analytical expression if used (T in K , t in $^{\circ}C$)	Log K		Note	Reference
		25°	250°		
1..... $H_2CO_3 \text{ app} = H^+ + HCO_3^-$	$\text{Log } K = -2382.3/T + 8.153 - 0.02194T$	-6.38	-7.88	(1)	Ryzhenko (1963).
2..... $H_2S = H^+ + HS^-$	$\text{Log } K = -3279.0/T + 11.17 - 0.02386T$	-6.94	-7.6		D'yachkova and Khodakovskiy (1968).
3..... $HBO_2 + OH^- = H_2BO_3^-$	$\text{Log } K = 1573.21/T + 28.6059 + 0.012078T - 13.2258 \log T$	+4.76	+1.98	(2)	Mesmer, Baes, and Sweeton (1972).
4..... $H_3SiO_4 = H^+ + H_2SiO_4^-$	See table 5	-9.63	-9.63	(3)	Cobble (1964); Ryzhenko (1967).
5..... $HF = H^+ + F^-$do	-3.18	-5.80	(4)	Ellis (1963).
6..... $HSO_4^- = H^+ + SO_4^{2-}$	$\text{Log } K = -557.2461/T + 5.3505 - 0.0183412T$	-1.99	-5.31		Lietzke, Stoughton, and Young (1961).
7..... $H_2O = H^+ + OH^-$	$\text{Log } K = -4470.99/T + 6.0875 - 0.01706T$	-13.995	-11.38		Harned and Owen (1958, p. 645).
8..... $NH_3(H_2O) = NH_4^+ + OH^-$	See table 5	-4.75	-6.00		Wright, Lindsay, and Druga (1961).
9..... $HCl = H^+ + Cl^-$do	-6.10	-6.67		Helgeson (1969).
10..... $NaCl = Na^+ + Cl^-$do	+1.60	-0.25	(5)	Pearson, Copeland, and Benson (1963); Dunn and Marshall (1969); Hanna, Pethybridge, and Prue (1971).
11..... $KCl = K^+ + Cl^-$do	+1.59	-1		Helgeson (1969); Hanna, Pethybridge, and Prue (1971).
12..... $MgSO_4 = Mg^{2+} + SO_4^{2-}$do	-2.25	-5.7	(6)	Do.
13..... $CaSO_4 = Ca^{2+} + SO_4^{2-}$do	-2.30	-4.1	(3)	Do.
14..... $KSO_4 = K^+ + SO_4^{2-}$do	-0.83	-2.35	(3)	Quist and others (1963); Truesdell and Hostettler (1968).
15..... $NaSO_4 = Na^+ + SO_4^{2-}$do	-0.83	-2.35	(6)	Do.
16..... $CaCO_3 = Ca^{2+} + CO_3^{2-}$do	-2.30	-5.90	(3)	Helgeson (1969).
17..... $MgOH^+ = Mg^{2+} + OH^-$do	-2.60	-4.65	(3)	Do.
18..... $H_3SiO_4 = H^+ + H_2SiO_4^-$	$\text{Log } K = -3450/T + 6.34 - 0.0216T$	-11.7	-11.5		Naymov, Ryzhenko, and Kodakovskii (1971).
19..... $HCO_3^- = H^+ + CO_3^{2-}$	$\text{Log } K = -2730.7/T + 5.338 - 0.02199T$	-9.12	-11.34		Ryzhenko (1963).
KS..... $H_2S \text{ gas} = H_2S \text{ aq}$	$K = 357 + 15.688t - 0.038253t^2$	+2.86	+3.28		Kozintseva (1964).
K..... $CO_2 \text{ gas} + H_2O = H_2CO_3 \text{ app}$	See table 5	+3.21	+3.72	(1)	Ellis and Golding (1963).

¹ H_2CO_3 apparent includes H_2CO_3 and CO_2 aqueous.

² H_2BO_3 given in print out as BO_2 . Reaction written by Mesmer, Baes, and Sweeton (1972) as $B(OH)_3 + OH^- = B(OH)_4^-$.

³ Extrapolated above 200°C.

⁴ Extrapolated above 200°C. Agrees with Ryzhenko (1965) to 200°C.

⁵ Extrapolated below 100°C.

⁶ Assumed identical to K KSO_4 .

Table 5.—*Log K(pK), and CO₂ and quartz solubility, data in tabular form interpolated by look-up subroutine*
[For reaction equations and source of data, see table 4]

°C	(4) H ₄ SiO ₄ ^o	(5) HF ^o	(8) NH ₃ (H ₂ O) ^o	(9) HCl ^o	(10) NaCl ^o	(11) KCl ^o	(12) MgSO ₄ ^o	(13) CaSO ₄ ^o	(14) KSO ₄ ⁻	(16) CaCO ₃ ^o	(17) MgOH ⁺	CO ₂ solubility	Quartz solubility ¹ (p/m)
0	10.2	2.96	4.87	-7.5	-1.65	-1.65	2.05	2.3	0.65	3.0	2.58	700	2.4
10	9.94	3.00	4.80	-6.8	-1.63	-1.62	2.10	2.3	.71	3.05	2.58	1000	3.6
25	9.63	3.18	4.75	-6.1	-1.60	-1.59	2.25	2.3	.83	3.20	2.60	1630	6.6
35	9.48	3.25	4.70	-5.7	-1.40	-1.50	2.35	2.35	.90	3.27	2.63	2100	8.6
50	9.30	3.40	4.70	-5.0	-1.20	-1.40	2.60	2.40	1.00	3.40	2.7	2900	13.5
75	9.11	3.64	4.75	-3.8	-.90	-1.20	2.90	2.55	1.15	3.65	2.9	4000	27
100	9.03	3.85	4.85	-2.9	-.55	-1.00	3.20	2.7	1.30	3.90	3.1	5200	48
125	9.03	4.09	4.97	-2.0	-.55	-.90	3.55	2.9	1.45	4.15	3.33	6000	80
150	9.10	4.34	5.10	-1.23	-.45	-.75	3.90	3.1	1.60	4.50	3.6	6600	125
175	9.23	4.59	5.33	-.60	-.30	-.60	4.40	3.35	1.78	4.85	3.85	6800	190
200	9.36	4.89	5.53	-.07	-.15	-.40	4.80	3.6	1.93	5.20	4.1	6400	265
225	9.48	5.3	5.73	.30	.05	-.20	5.25	3.8	2.10	5.55	4.35	5900	367
250	9.63	5.8	6.0	.67	.25	.10	5.7	4.1	2.35	5.90	4.65	5300	490
275	9.83	6.2	6.3	.95	.60	.30	6.1	4.3	2.55	6.20	4.9	4600	615
300	10.2	6.8	6.75	1.2	.95	.6	6.4	4.5	2.75	6.45	5.15	3900	680
325	10.5	7.1	7.25	1.6	1.35	1.0	6.7	4.75	2.9	6.65	5.45	3100	720
350	11.0	7.4	8.0	2.5	2.0	1.7	7.0	5.0	3.1	7.0	5.7	2100	(750)

¹ Quartz solubility in water at saturated water vapor pressure. 0°–240°C from Morey, Fournier, and Rowe (1962); 260°–325°C from Kennedy (1950). An incorrect 350° value is included because the look-up subroutine requires a monotonic function.

The algol version of this program (Truesdell and Singers, 1973) has just been published.

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