GEOCHEMICAL TECHNIQUES IN GEOTHERMAL DEVELOPMENT: AN UPDATE

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ABSTRACT:
The ultimate goal of geochemical studies of geothermal systems is to understand the physical-chemical processes responsible for their origin and evolution. The chemical composition of fluids (separated vapor and water), collected from fumaroles, hot springs and drilled wells at the Earth’s surface (25°C) is determined in the laboratory. Using the chemical geothermometers, conservation of mass, energy and alkalinity, and distribution coefficients for gaseous species, the chemical concentrations are converted to the reservoir conditions in order to predict the state of water-rock interaction and reservoir processes like boiling, condensation, mixing with other fluids, mineral dissolution-precipitation, etc.

The most widely used chemical geothermometers are the cation-exchange and silica (quartz) solubility geothermometers. According to the cation-exchange theory, the cation ratio (e.g., Na⁺/K⁺) in a solution is a function of temperature, the type of minerals and the Na⁺/K⁺ ratio in the mineral phases. The Na⁺/K⁺ ratio of reservoir rocks, which are in equilibrium with the fluid, is not known and is not included in any cation-exchange geothermometer. Similarly, it is also against the basic laws of solution chemistry that the cation ratio is only a function of temperature.

Although quartz geothermometer based on the experimental quartz solubility data has many limitations, it is the only reliable geochemical tool to estimate the geothermal reservoir temperature. A computer program is written to estimate the temperature and vapor fraction in the reservoir, using four representative types of regression equations for the quartz solubility data along the saturation curve. On considering the analytical errors in the silica and enthalpy determinations, the estimated reservoir temperatures using the quadratic regression equation of P(MPa) and 1/T(K) are accurate within ±20°C up to 370°C.

The fundamental limitations of geochemical modeling approaches of geothermal systems are: (i) high uncertainty in the analytical data, (ii) incorrect method for the determination of carbonic (bicarbonate and carbonate) species, (iii) little use of alkalinity which is a conservative parameter in chemical reactions, and (iv) lack of internally consistent thermodynamic data for the equilibrium constants of chemical reactions at the reservoir conditions of P and T.

1. INTRODUCTION
Geochemical studies of geothermal systems during their exploration and exploitation contemplate the determination of reservoir parameters like temperature, pressure, state of water-rock interaction, mineral deposition potential of fluid, natural heat flow, fluid flow
pattern, recharge zone, upflow permeability, injection feasibility, size of the reservoir, etc. Similarly, the chemical and isotopic compositions of fluid from drilled wells together with natural manifestations in the region are used to trace the fluid origin and the physical-chemical processes occurring in the reservoir and during the ascent of fluid to the surface.

A chemical modeling computer program is an efficient, fast, accurate and systematic way to interpret water chemistry in nature as well as in the laboratory, and to trace the reaction mechanisms and processes for the evolution of water-bodies. Nordstrom et al. (1979) reviewed over 30 chemical modeling programs and concluded that every modeling program had been developed for specific purposes with its own individual capacities and limitations. Fundamental limitations were the form of alkalinity input and non-carbonic alkalinity correction, and pH calculation, which are still not resolved completely in the improved versions of commercial computer-programs (Verma 2000a, Verma and Truesdell 2001). Similarly, the results of interlab comparisons for geothermal water analysis data suggested a need to consider the effect of analytical uncertainty on the chemical modeling results (Verma and Santoyo 2002, Verma et al. 2002a). Another limitation of geochemical modeling is lack of internally consistent thermodynamic data for the conditions of temperature and pressure, which exist in a geothermal system (Verma 2000b, 2003a, 2003b).

The first step in the geochemical modeling approaches is to determine the deep reservoir fluid composition from the surface natural manifestation and well discharge chemistry. We measure the dissolved species including pH in separated water at weirbox and the non-condensable gaseous species in vapor phase at separator. The chemical composition of reservoir fluid is reconstructed as a mixture of separated water and vapor. It comprises the calculation of temperature, pH and chemical composition of both vapor and liquid phases in the reservoir. The concentration calculation of the total discharge dissolved species (like Na\(^+\), K\(^+\), Cl\(^-\), etc.) is performed using mass and enthalpy balance equations; however, the reservoir pH is calculated through the conservation of alkalinity (Verma 2000c, 2002a, Verma and Truesdell 2001). For gaseous species the knowledge of their distribution coefficients and pH is necessary.

A computer program, SteamTables in Visual Basic 6.0 is developed to calculate 23 thermodynamic properties of vapor-liquid of pure water in the range of temperature 190 to 2000 K and pressure 5 \(10^8\) to 10000 MPa (Verma 2003c). It is programmed as an ActiveX component, so it can be used in any computer program including MS-Excel.

An approach of chemical modeling of geothermal systems, which is basically the evaluation of reservoir fluid-mineral equilibrium-state, is presented. Similarly, a summary of the results of interlab comparisons of geothermal waters, conducted by the International Association of Geochemistry and Cosmochemistry (IAGC) and International Atomic Energy Agency, Vienna (IAEA), is discussed. These results establish a need for improving analytical quality of chemical data and consideration of propagation of errors in the results of geochemical modeling of geothermal systems. The results of interlab calibration of silica for geothermal waters, conducted among Mexican laboratories is also discussed (Verma et al. 2002a). Additionally, a revised titration method for the analysis of carbonic species (bicarbonate and carbonate) is presented (Verma 2003d). Using the SteamTables, an algorithm is developed to calculate deep geothermal reservoir temperature and vapor
fraction from quartz geothermometry (Verma 2003e, 2003f). The methodology is discussed in respect to developing the reservoir conceptual models during the exploration and exploitation of geothermal systems.

2. STEAM TABLES FOR PURE WATER

Thermodynamic properties of water are of vital importance to understand the physical-chemical and geological processes in the Earth, since water plays a fundamental role in rock weathering, mineral dissolution-deposition, mass transport, etc. In the electricity industry, water has a special role in the process of energy generation. Different types of heat resources like coal, oil, natural gas, geothermal energy or nuclear fuel heat water to convert to vapor, which is used to move turbines in generating electrical energy. Thus, the steam tables of pure water are useful to model the thermal and mass transport and physical-chemical processes during the generation of electricity. In the geothermal industry, the enthalpies of water and vapor are used in the geochemical modeling calculations.

Verma (2003c) wrote a computer program in Visual Basic 6.0. to calculate the values of 23 properties of water for liquid and vapor phases in the temperature range from 190 to 2000 K and pressure range from $5 \times 10^8$ to 10,000 MPa, using the most recent formulation, IAPWS-95, which was approved by the International Association for the Properties of Water and Steam (Wagner and Pruβ 2002). The steam table program (SteamTables) is an ActiveX component, so it can be used in any computer program. Here we explain its use in a MS-Excel Workbook and in a computer program in Visual Basic 6.0 to calculate temperature and vapor fraction in a geothermal reservoir through quartz geothermometry.

2.1 PVT Characteristics of Water

Figure 1 shows the PT relation for pure water according to the IAPWS-95 formulation (Verma 2003c). The saturation curve is the locus of data points for the values of $T$ and $P$ where liquid and vapor coexist in equilibrium: it starts from the ice-water-vapor triple point and terminates at the critical point ($T=T_C$, $P=P_C$). The supercritical fluid region, existing at $T>T_C$ (critical) and $P>P_C$ is shown by dashed lines, which do not represent phase changes but depend on arbitrary definition of what constitutes liquid and vapor phases (Smith and van Ness 1975).

It is possible to draw a path (e.g., the path 1 from A to B) from the liquid region to the vapor region that does not cut a phase boundary. This path represents a gradual phase transition from the liquid to vapor, rather than the path 2 from A to B that passes through the boundary (saturation curve) resulting in abrupt changes in the water properties. There is no phase change on moving from the liquid region to the fluid region, similarly from the fluid region to the vapor region (Smith and van Ness 1975). Thus there should exist a phase change within the fluid region, as water is liquid at point A and vapor at point B. Verma (2000d, 2002b) presented numerical simulation studies for heating different masses of water in a constant volume reaction vessel. He suggested that a gradual phase change boundary was the critical isochor (i.e., total specific volume $V = 0.003106 \text{ m}^3/\text{kg}$ or density $\rho = 322.0 \text{ kg/m}^3$) in the fluid region. In other words a supercritical fluid is composed of
Figure 1: PT characteristics of water (Verma 2003c). T.P.- represents the ice-water-vapor triple point and C.P.-as the critical point. T\(_C\) and P\(_C\) are the critical temperature and pressure, respectively. The critical isochor is a locus of data points for the critical density (322.0 kg/m\(^3\)).

... compressed liquid or superheated vapor depending on the conditions of pressure and temperature. Thus the whole steam tables are divided in five regions: i. along the sublimation curve, ii. along the saturation curve, iii. along the critical isochor, iv. in superheated steam region and v. in the compressed liquid region.

2.2 Description of SteamTables

The computer program SteamTables is written as an ActiveX component in the library MyProgram.DLL (Dynamic Link Library) and is a class module written in Visual Basic 6.0 (Verma 2003c). An ActiveX component is a server application that exposes its functionality through an interface consisting of properties, methods and events. Programmers may access a class module within their projects in any language that supports OLE (Object Link Embedding) in the Windows environment. The ActiveX programming also avoids name conflicting among various variables as the object variables are identified together with object name. The input parameters are T and/or P. If the values of temperature or pressure are higher than their respective upper limits (i.e., T=2000 K and P=10,000 MPa), it adjusts to the maximum value; whereas it adjusts T and P to zero when they are lower than the respective lower limits (i.e., T=190 K and P=5 \times 10^8 MPa). In case T
(or P) is zero; it calculates T (or P) along the sublimation curve, saturation curve or critical isocho, depending on the given value of P (or T), respectively. One should take care that both T and P are never lower than their respective lower limits. Additionally, the values of T and P are checked for validity for the compressed liquid and super heated steam region. If the values of T and P are for the solid (ice) region, it assigns –1 for all the thermodynamic properties of water and vapor (see Table 1). Similarly, if the values of T and P correspond to the liquid region, it assigns –1 for all the properties of vapor phase and vice versa.

A test program (SteamTablesIAPWS95) using the ActiveX component, SteamTables is written in Visual Basic 6.0 to display the thermodynamic properties of liquid-vapor for pure water. The program package can be installed on a computer in the Windows environment by running the setup program and following the instructions. The program (SteamTablesIAPWS95) together with the ActiveX component, SteamTables in library MyProgram.DLL is installed in the default directory (e.g., C:\ProgramFiles\SteamTablesIAPWS95). Figure 2 shows a data entry form of the test application. On entering the value of T and/or P and pressing calculate, it calculates all the thermodynamic properties for liquid and vapor phases of pure water.

2.3 Use of SteamTables in MS-Excel

Verma (2003c) described the procedure to use the Steamtables ActiveX component in an workbook in MS-Excel. It consists of four functions: Temperature(Press), Pressure(Temp), State(Temp, Press) and WtrStmTbls(Temp, Press, Nphs, Nprop). The functions are stored in “PERSONAL.XLS”, which makes the functions availability for any workbook in MS-Excel. The function, Temperature(press) calculates the value of T along the sublimation curve, saturation curve or the critical isocho, depending on the value of Press. Similarly, Pressure(Temp) calculates the value of P along the sublimation curve, saturation curve or the critical isocho, depending on the value of Temp. To perform this, press the function button from MS-Excel Toolbar and select user defined function “PERSONAL.XLS!Pressure” and provide the value of temperature as an input parameter. The function, State(Temp, Press) defines the location of the data point along the sublimation curve, saturation curve, critical isocho, compressed liquid region and superheated steam region.

The function WtrStmTbls(Temp, Press, Nphs, Nprop) has four input parameters, where Nphs is an integer parameter and stands for phase (1= Liquid phase and 2= Vapor phase) and Nprop represents for the water property number (as given in Table 1), needed to be calculated. Here it is needed to provide both Temp and Press (i.e., the program does not calculate the value of P from T and vice versa). The SteamTables stores the values of all the thermodynamic properties of water. It does not recalculate untill Temp or Press is changed.

For example, to calculate the liquid enthalpy along the saturation curve at 100ºC, one should calculate first temperature in K (Temp=100+273.15) in a MS-Excel cell, then pressure along the saturation curve (Press=pressure(Temp)) is calculated in another cell. These values of Temp and Press, together with the values of Nphs=1 and Nprop= 5 (see
Figure 2: Interface form of the test program (SteamTablesIAPWS-95) to display properties of ActiveX component SteamTables (Verma 2003c).

Table 1: List of thermodynamic properties of water for liquid and vapor phases, calculated in the temperature (190 to 2000 K) and pressure ($5 \times 10^8$ to 10000 MPa) range (Verma 2003c).

<table>
<thead>
<tr>
<th>Num.</th>
<th>Property</th>
<th>Unit</th>
<th>Num.</th>
<th>Property</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Volume (V)</td>
<td>m$^3$/kg</td>
<td>13</td>
<td>Velocity of sound (VelS)</td>
<td>m/s</td>
</tr>
<tr>
<td>2</td>
<td>Density (D)</td>
<td>kg/m$^3$</td>
<td>14</td>
<td>Partial derivative of P with T at constant V (dPdT)</td>
<td>MPa/K</td>
</tr>
<tr>
<td>3</td>
<td>Compressibility factor ($Z_0$)</td>
<td>dimensionless</td>
<td>15</td>
<td>Partial derivative of T with V at constant P (dTdV)</td>
<td>K kg/m$^3$</td>
</tr>
<tr>
<td>4</td>
<td>Internal energy (U)</td>
<td>kJ/kg</td>
<td>16</td>
<td>Partial derivative of P with T at constant V (dVdT)</td>
<td>m$^3$/kg MPa</td>
</tr>
<tr>
<td>5</td>
<td>Enthalpy (H)</td>
<td>kJ/kg</td>
<td>17</td>
<td>Joule-Thomson coefficient (JTC)</td>
<td>K/MPa</td>
</tr>
<tr>
<td>6</td>
<td>Gibbs free energy (G)</td>
<td>kJ/kg</td>
<td>18</td>
<td>Isothermal throttling coefficient (IJTC)</td>
<td>KJ/(kg MPa)</td>
</tr>
<tr>
<td>7</td>
<td>Helmholtz free energy (A)</td>
<td>kJ/kg</td>
<td>19</td>
<td>Viscosity (Vis)</td>
<td>µPa S</td>
</tr>
<tr>
<td>8</td>
<td>Entropy (S)</td>
<td>kJ/(kg K)</td>
<td>20</td>
<td>Thermal conductivity (ThrmCond)</td>
<td>W/(m K)</td>
</tr>
<tr>
<td>9</td>
<td>Heat capacity at constant pressure ($C_p$)</td>
<td>kJ/(kg K)</td>
<td>21</td>
<td>Surface tension (Surften)</td>
<td>N/m</td>
</tr>
<tr>
<td>10</td>
<td>Heat capacity at constant volume ($C_v$)</td>
<td>kJ/(kg K)</td>
<td>22</td>
<td>Prandtl number (PrdNum)</td>
<td>dimensionless</td>
</tr>
<tr>
<td>11</td>
<td>Coefficient of thermal expansion (CTE)</td>
<td>l/K</td>
<td>23</td>
<td>Dielectric constant (DielCons)</td>
<td>dimensionless</td>
</tr>
<tr>
<td>12</td>
<td>Isothermal compressibility ($Z_{iso}$)</td>
<td>1/MPa</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1) should be given as input parameters to obtain the liquid enthalpy at 100°C. Now, the values of \( N_{phs} \) and \( N_{prop} \) are only changed, the program will provide the value of the properties without recalculating, which saves the execution time. Thus, the thermodynamic properties of water, through these functions, can be calculated efficiently in any MS-Excel Workbook.

3. CHEMICAL THERMODYNAMICS: A State Function

Verma (2002a, 2003b, 2003e) discussed the importance of the definition of a state function to understand the temperature and pressure behavior of an equilibrium constant of a chemical reaction. Thermodynamic variables (e.g., temperature, pressure, volume, Gibb’s free energy, internal energy, enthalpy or entropy represented by \( T \), \( P \), \( V \), \( G \), \( U \), \( H \) or \( S \), respectively) including the equilibrium constant of a reaction, solubility, viscosity, thermal conductivity, etc. are state functions. A state function does not depend on the past history of the substance or on the path it has followed in reaching a given state (Kestin 1966, Smith and van Ness 1975, Chatterjee 1991). It should be single valued and continuously differentiable unless there is a phase transition. On fixing the values of any two state functions (for example \( T \) and \( P \)), the values of all the other state functions are uniquely defined.

The equilibrium constant (\( K \)) for a chemical reaction may be expressed as

\[
\log K = \frac{1}{2.303} \left( \frac{-\Delta G_{F,T,P}}{RT} \right) = \frac{1}{2.303} \left( \frac{-\Delta H_{F,T,P}^{r}}{RT} \right) + \frac{1}{2.303} \left( \frac{-\Delta S_{T,P}^{r}}{RT} \right)
\]

where \( R \) is gas constant, \( P \) is pressure and \( T \) is absolute temperature. The sub-index \( F \) stands for formation. In a small range of \( T \) and \( P \), the values of Gibb’s free energy (\( \Delta G_{F,T,P}^{r} \)) or enthalpy (\( \Delta H_{F,T,P}^{r} \)) and entropy (\( \Delta S_{T,P}^{r} \)) for the first order of approximation are constant and the variation of \( \log K \) with \( 1/T \) or \( P \) is a straight line. There could be positive or negative deviation from the linear trend at extreme temperatures, but the function should always be single valued (i.e., the trend of \( \log K \) may be asymptotic).

Figure 3(a) shows four sets of possible trends of \( \log K \) with the inverse of \( T \) at different values of \( P \). The variation of \( \log K \) may be one of four sets of curves shown in Figure 3(a). The value of \( \log K \) increases with \( T \), while decreases with \( P \) for sets 1 and 2. In the case of sets 3 and 4 the behavior of \( \log K \) is the opposite. Let us consider two other behaviors of \( \log K \) as shown with curves I and II in Figure 3(b). In case I there are two values of \( \log K \) at a given \( T \), whereas in case II there are two values of \( T \) for a value of \( \log K \). Thus, \( K(T) \) in case I and \( T(K) \) in case II are not single valued functions.

Similarly, \( dT/dK \to \infty \) in case I and \( dK/dT \to \infty \) in case II. It means that \( T \) or \( K \) are not continuously differentiable. In other words, neither \( T \) nor \( K \) are a thermodynamic state functions in the respective cases. Figure 3(c) presents the behavior of \( \log K \) with \( 1/T \) at two pressures \( P_1 \) and \( P_2 \). The functions are crossing at temperature \( T_1 \). Then at \( T=T_1 \), \( dP/dK \to \infty \) and \( dP/dT \to \infty \). It means that \( P \) is not a state function. Figure 3(d) shows a point of inflection in the variation of \( \log K \) with \( 1/T \) at constant \( P \). Mathematically, a point of inflection in a function is singular and the second derivative of the function is
discontinuous at the point of inflection. Additionally, \( \frac{dK}{dT} = 0 \) or \( \frac{dT}{dK} = \infty \) at the point of inflection in the case of the behavior shown in Figure 3(d). This is very much similar to the behavior of electromagnetic fields in Physics which never cross and are parallel for small displacement.

It is well known that T, P and K are state functions. Therefore, the behaviors of log K presented in Figures 3(b), 3(c) and 3(d) are against the basic laws of thermodynamics. Thus, the permissible behaviors of log K with 1/T are as given in Figure 3(a).

4. STRUCTURE AND CLASSIFICATION OF GEOTHERMAL SYSTEMS

Verma (2002a) presented the structure and classification of geothermal systems, which are well described in many textbooks (Ellis and Mahon 1977, Henley et al. 1984, Nicholson 1993). Geothermal systems are generally found in a wide range of geological settings at the active tectonic plate boundaries such as subduction zones (e.g., Pacific Rim), spreading zones (e.g., Mid Atlantic) and rift zones (e.g., East Africa) and within orogenic belts (e.g., Mediterranean, Himalayas) and are defined and classified on the basis of their geological, hydrological, and heat transfer characteristics (Nicholson 1993). Thus, there exist many types of classifications. However, all the geothermal systems have four common basic components: heat source, fractured rock reservoir, working fluid (water) and caprock.

Figure 3: A schematic diagram for the variation of logarithm of the equilibrium constant of a reaction (log K) with inverse of T(K). According to the definition of state function, the behavior of log K is only valid as described in Figure 3(a) (after Verma 2003b, 2003e).
Nicholson (1993) presented a broad classification based on the reservoir equilibrium state, fluid type and temperature as following

1. Convective geothermal systems (dynamic systems)
   a. High temperature: liquid- and vapor-dominated
   b. Low temperature
2. Conductive geothermal systems (static systems)
   a. Low temperature
   b. Geo-pressurized

The high-temperature geothermal systems are often volcanogenic, with the heat provided by intrusive masses of rhyolitic-andesitic composition and associated with calderic or graben structures like Los Azufres, Los Humeros, and Cerro Prieto, Mexico. High temperature chloride springs are found within the geothermal field. The features of these systems are: recharge by meteoric waters, heat input at depth, convective upflow, deep mixing with meteoric cold water, transfer of steam to the surface and its interaction with groundwater, and the flow of deep fluid direct to the surface or its dilution and outflow to some hydraulic base level like a river or lake. These are also known as vertical flow geothermal systems.

Some systems are formed on the flanks of young volcanoes (e.g., Ahuachapan, El Salvador; Kamojang, Indonesia). In these systems the same basic processes occur, but the chloride water springs are found several kilometers from the hot upflow part of the system. These are known as lateral flow geothermal systems.

White et al. (1971) classified them as the vapor- and liquid-dominated geothermal systems in order to understand the production characteristics and reservoir geochemistry. Some authors consider the presence of both vapor and liquid (White et al. 1971, Verma 1997) in a vapor-dominated reservoir, while others accept the existence of only superheated steam (Donaldson and Grant 1981, Economides and Miller 1984). The PVT characteristics of water are helpful to enlighten the definition of vapor- and liquid-dominated geothermal systems.

4.1 Thermodynamic Definition of Vapor and Liquid Dominating Geothermal Reservoirs

Verma (1997) demonstrated that there was no unanimous definition of vapor- and liquid-dominated geothermal reservoirs. If superheated steam reservoirs are vapor-dominated, then compressed liquid systems will be liquid-dominated. Why should two-phase reservoirs be considered liquid-dominated? A two-phase reservoir can produce only vapor or liquid, depending on well taping. If both phases can be present together in the vapor-and liquid-dominated reservoirs, the proportion of phases becomes important to distinguish between the vapor- and liquid-dominated geothermal reservoirs.

According to the PVT characteristics of water, a geothermal system can be classified as vapor- or liquid-dominated depending on whether the specific volume of the fluid in the reservoir is smaller or greater than the critical volume, respectively. Both types of reservoirs can produce vapor only at the wellhead. Thus, it is incorrect to define the type of
geothermal reservoir by the characteristics of geothermal fluid at the wellhead. It is necessary to calculate the deep reservoir fluid specific volume from the fluid characteristics at the wellhead to classify a geothermal system.

To relate the production fluid characteristics with the type of reservoir, let us assume a geothermal reservoir as a constant volume container of 1000 ml. There are two extreme cases when the container is completely filled with saturated vapor or liquid at a given temperature (say 300°C). Figure 4 shows the pressure variation on extracting fluid from the container for the two cases. Pressure decreases substantially when the container is filled with vapor only. It means that there should be an entry of some fluid in order to maintain the pressure constant. It is assumed here that there is sufficient heat transfer from the rock to the fluid for converting into vapor. Thus, a vapor-dominated reservoir also has a liquid phase in the reservoir. There is one more point to be emphasized that the conversion of liquid into vapor means extensive boiling. So, there should be highly concentrated geothermal brine in some part of the reservoir, if it is producing only vapor.

5. ANALYTICAL DATA QUALITY

Ellis (1976) conducted the first international interlab comparison of chemical analysis of geothermal waters. In 1985 the International Atomic Energy Agency, Vienna (IAEA) initiated interlab calibrations of geothermal waters within the framework of the “Coordinated Research Program on the Application of Isotope and Geochemical Techniques in Geothermal Exploration”. Verma and Santoyo (2002) reassessed the first four IAEA interlab calibrations for geothermal waters (Giggenbach et al. 1992, Gerardo-Abaya et al. 1998, Alvis-Isidro et al. 1999, 2000). Eight water samples (i.e., two samples in each calibration) were analyzed among the geochemistry laboratories involved in geothermal developments around the world. The analyzed parameters were electrical conductivity, pH, Na+, K+, Ca2+, Mg2+, Cl-, SO42-, HCO3-, F-, SiO2, B and As.

Figure 5 shows a relation between concentration and percentage error for all the chemical parameters. The percentage error increases with decreasing concentration for all the chemical parameters except for SiO2. The analytical error is of the same order of magnitude for concentration if it is lower than 1 ppm. The overall error in the analytical data for geothermal waters is ±13% and there is no appreciable improvement in the analytical quality in the successive interlab calibrations, probably due to the existence of systematic errors in the measurements from some laboratories (Verma and Santoyo 2002). There were some serious problems with sampling and analytical procedures for SiO2 and HCO3-.

There is an average error of 10% for concentration >10 ppm, 20% for concentration between 10 to 1 ppm and >80% for concentration <1 ppm for all the parameters except SiO2 and HCO3-. There is the need of running some common commercial standards for each species together with samples in the participating laboratories to the interlaboratory calibration program (Verma et al. 2002a). The propagation of errors must be considered in developing geochemical models of geothermal systems.
Figure 4. Pressure variation on extracting fluid from a container (1000 ml) completely filled with saturated vapor or liquid at 300°C (Verma 2002a)

Figure 5. A relation between analytical value and percentage error for all the chemical parameters analyzed under the IAEA interlaboratory calibration program. The data points with circles around them were not included in deriving the trends.
5.1 Interlab Comparison of \( \text{SiO}_2 \)

Verma et al. (2002a) conducted an interlaboratory comparison of silica analysis, using four commercial standards, prepared by diluting “9947 Titrisol silica standard, Merck, Germany”, were distributed as samples among the three Mexican geochemical laboratories. One of the laboratories analyzed the samples using both atomic absorption and colorimetric methods. The four sets of data are designated randomly as Lab I to IV. The samples were labeled in random order for each laboratory and the only information provided to the laboratories was the maximum expected silica concentration (2500 ppm).

Figure 6 shows the results of silica interlab comparison. Lab I and Lab IV analyzed the samples after dilution, whereas Lab II and III analyzed without dilution. The values for lower concentration samples are on the 45° line for all the laboratories, whereas there is a wide dispersion among the higher concentration samples. The results are similar to the IAEA calibration data. Lab IV has a systematic positive error whereas Lab I has a systematic negative error. Values from Labs II and III have a random distribution. In other words, the analytical error at high \( \text{SiO}_2 \) concentrations is not related with silica deposition during storage and transportation because the commercial standards used are created taking these factors into consideration. The interlaboratory calibration program should be continued to insure a high level of analytical quality by the participating laboratories. Reliable analytical results are crucial for geochemical modeling of hydrothermal systems.

![Figure 6: Relationship between the real and measured silica concentrations. The analytical technique used by individual laboratory is denoted by AA for atomic absorption spectrometry and CO for colorimetry (Verma et al. 2002a)](image-url)
5.2 Interlab Comparison of HCO\textsubscript{3} and Revised Analytical Method

Figure 7 presents a relation between % S.D. (coefficient of variation) and mean value of bicarbonate concentration of samples, distributed during the IAGC and IAEA interlab comparisons. The error increases when decreasing the concentration and it is \(\sim\) 25\% for 50 ppm and \(\sim\) 60\% for 25 ppm of bicarbonate. Thus, there is a considerable analytical error in the measurement of bicarbonates. Another interpretation is that there are two sets of water samples: high (>50 ppm) and low (<50 ppm) concentration groups. For the high concentration group there is always an error of \(\sim\) 7\%, whereas for the low concentration group there is higher error and it is independent of the amount of bicarbonate in the samples. That is, the determination of bicarbonate is inappropriate for the low concentration samples, applying the titration method.

Verma (2003d) presented a revised analytical method for the determination of carbonate and bicarbonate in geothermal waters. The backward titration from the carbonic acid equivalence point (H\textsubscript{2}CO\textsubscript{3}EP) to the original pH after CO\textsubscript{2} removal, as had been practiced earlier in geothermal industry in order to estimate the contribution of silicic and boric alkalinitities to the total alkalinity, is incorrect because the amount of standard base (NaOH) added is equivalent to silicic and boric alkalinitities plus some OH\textsuperscript{-} alkalinity.

The revised method consists of the determination of total alkalinity (alk) with respect to H\textsubscript{2}CO\textsubscript{3}EP. In presence of boric and silicic species, the alk is expressed as

\[
\text{alk} = [\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{H}_3\text{SiO}_4^-] \\
= [\text{H}^+] + [\text{H}^+] + C_T (\alpha_1 + 2\alpha_2) + C_{TB} (\alpha_{1b}) + C_{TSi} (\alpha_{1si})
\]  

(2)

where square brackets [ ] represent the molal concentration of the species. \(C_T\), \(C_{TB}\) and \(C_{TSi}\) are the total concentration of carbonic, boric and silicic acids, respectively. Similarly, \(\alpha_1\) and \(\alpha_2\) represent the fractions of the corresponding species formed by losing one and two protons, respectively, and \(\alpha \)'s are only the function of pH at a given temperature.

By knowing initial pH, silica (CTSi), boron (CT) and total (alk) alkalinitities, the concentration of total dissolved CO\textsubscript{2} (CT) is calculated through the above equation. Then, the concentration of individual carbonic species is calculated using the following equations

\[
H_2CO_3 = C_T \cdot \alpha_0, \quad HCO_3^- = C_T \cdot \alpha_1 \quad \text{and} \quad CO_3^{2-} = C_T \cdot \alpha_2
\]  

(3)

To illustrate the determination of bicarbonate and carbonate in natural waters containing other alkalinitities like boric and silicic, etc. together with carbonic alkalinity, a water sample from Alchichica Lake is taken here. Figure 8 shows the titration curves for 20 ml of the sample with the HCl 0.0931 N and NaOH 0.0990 N solutions. It requires 9.15 ml of HCl to reach the H\textsubscript{2}CO\textsubscript{3}EP. The total amount of the acid (HCl) added to the titrand is 12 ml. It can be observed that the H\textsubscript{2}CO\textsubscript{3}EP for the backward titration is at pH=6.3. This is due to the presence of boric and silica acid in the titrand. The volume of NaOH added to reach back to the H\textsubscript{2}CO\textsubscript{3}EP is 3.0 ml. Therefore the excess HCl through the backward titration is 3.19 ml (3.0×0.0990/0.0931), whereas 2.85 ml is excess HCl according to the forward titration. Thus, the average alkalinity (alk) is 41.802±0.791 meq/l (8.98×0.0931×1000/20.0).
Figure 7: Relation between % S.D. (coefficient of variation) and mean value for bicarbonate in geothermal waters, distributed during the IAGC (0) and IAEA (1-11) interlab comparisons (Verma 2003d).

Figure 8: Titration curve for 20 ml of water from the Alchichica Lake, Puebla, Mexico. In forward titration the excess HCl 0.0931 N is 2.85 ml, whereas the compensating NaOH 0.0990 N is 3.0 ml in order to get back to $H_2CO_3 EP$ during backward titration (Verma 2003d).
Substituting the value of alk (41.802 meq/l) and concentrations of boron (C_{TB}=18 ppm = 0.0017 mmole) and silica (C_{TSi}=12 ppm = 0.0002 mmole) in equation 2, we get the concentration of total dissolved carbonic species (C_T = 39.0637 mmole). The equilibrium constants for boric and silicic acid are taken from Henley et al. (1984) in order to calculate the values of \( \alpha_{1B} \) and \( \alpha_{1Si} \), respectively. By knowing the value of C_T and initial pH, the concentration of the carbonic species is calculated from the equation 3 as follows

\[
H_2CO_3 = C_T \cdot \alpha_0 = 0.0735 \text{ mmole} = 0.0735 \times 62 = 4.5 \text{ ppm}
\]

\[
HCO_3^- = C_T \cdot \alpha_1 = 36.8220 \text{ mmole} = 36.8220 \times 61 = 2246.1 \text{ ppm}
\]

\[
CO_3^2- = C_T \cdot \alpha_2 = 2.1682 \text{ mmole} = 2.1682 \times 60 = 130.1 \text{ ppm}
\]

Thus the method is applicable to measure carbonic species in geothermal waters, which have silicic and boric alkalinities. It is clear that the analytical errors in the measurements of boron and silica also contribute to the errors in the measurements of carbonic species according to this method.

6. CALCULATION OF GEOTHERMAL RESERVOIR FLUID PARAMETERS

The procedure for back calculating the deep reservoir physical-chemical parameters from the chemistry of surface manifestations like springs, fumaroles and drilled wells is based on the conservation of mass, enthalpy and alkalinity, and distribution coefficients of gaseous species (Verma 2002a). As the geothermal fluid flows up in a well, it flashes within the well and in the separator. The separated water is flashed further in the weir box at the atmospheric pressure or passed through a cooling coil attached to the separator to collect the sample. Samples of water from the weir box and steam from the separator are, generally, collected to analyze geochemical constituents.

During the formation of natural manifestations (hot springs and fumaroles) the geothermal reservoir fluid undergoes many processes like boiling, mixing, dissolution-precipitation and losing some part of the geothermal components. Thus, the reconstruction of deep fluid composition from natural manifestations has certain limitations.

6.1 Conservation of mass and enthalpy

As the geothermal fluid ascends to the surface it separates into vapor and liquid. Assuming adiabatic steam separation (i.e., heat loss or gain by the fluid from its surroundings is negligible) the distribution of reservoir fluid enthalpy between the liquid and vapor phases is expressed by

\[
H_{res} = y H_v + (1 - y) H_l
\]  

(4)

where \( H \) is enthalpy, \( y \) is the fraction of vapor by weight in the separator and sub-indices res, v and l stand for reservoir, vapor and liquid, respectively. Similar equation can be written for the concentration of any chemical species i as

\[
C_{i, res} = y C_{i,v} + (1 - y) C_{i,l}
\]  

(5)

The non-volatile species like Na\(^+\), Cl\(^-\), etc. resides only in the liquid phase (i.e., their concentration in the vapor phase is zero). In this way the equations 1 and 2 are sufficient to
calculate the concentration of reservoir fluid from the separated water concentration and vice versa. But in case of volatile species like CO$_2$, H$_2$S, N$_2$, CH$_4$, etc. there is a need to know the distribution coefficient for the species between the liquid and vapor phases. The distribution coefficient B for a species, i is defined as the concentration ratio of the species in the vapor and liquid phases.

\[ B_i = \frac{C_{vi}}{C_{li}} \]  

(6)

Giggenbach (1980) derived the regressions equations for the distribution coefficient of certain gaseous species of geothermal interest valid from 100 to 340ºC (Table 2). Thus, the reconstruction of deep reservoir chemical composition in the vapor and liquid phases is possible through the conservation of mass and enthalpy and knowing the values of the distribution coefficient of gaseous species. The approach is applicable only for the species, which do not convert to other aqueous species like N$_2$, H$_2$, CH$_4$, etc. However, there is also need to know alkalinity and pH in case of species like CO$_2$ and H$_2$S which transform to other aqueous species. For example, it is well known on adding CO$_2$ to an aqueous solution, some CO$_2$ converts to HCO$_3^-$ and CO$_3^{2-}$ and vice versa. For knowing the distribution of total CO$_2$ we have to consider alkalinity and pH.

6.2 Fluid Geothermometry

Geothermometry is presently an integral part of almost all the geochemical investigations for the exploration and development of geothermal resources. There are two types of geothermometers: chemical and isotope geothermometers. The chemical geothermometers are further subdivided as water or solute geothermometers and steam or gas geothermometers. The application of water geothermometers will only be discussed here. Two types of water geothermometers have been devised: the cation-exchange geothermometers and the silica (quartz) solubility geothermometers.

6.2.1 Cation exchange geothermometers

Verma (2002a) discussed that the concept of cation-exchange geothermometry was violating the fundamental laws of chemical thermodynamics. A cation-exchange reaction between Na$^+$ and K$^+$ can be written in general as following

\[ zNa^+ + Na_{1-z}K_xX = zK^+ + Na_xK_{1-z}X \]  

(7)

where the capital X represents an anion and z denotes the stoichiometric coefficient. The equilibrium constant for this reaction is given by

\[ K = \exp\left( -\frac{\Delta G_f^T}{RT} \right) = \left( \frac{a_{Na,K_{1-z}X}}{a_{Na^+}a_{K_xX}} \right)^z \]  

(8)

where ‘a’ is the activity of respective species. The activity coefficient is considered to be unity in case of dilute solution. Similarly, the activity of solid phases is also taken as unity in developing the geothermometers. Thus, the equilibrium constant is reduced to
Table 2. Regression equations for the distribution constant (B) of gaseous species (Giggenbach 1980). The parameter t is temperature in °C.

<table>
<thead>
<tr>
<th>Species</th>
<th>Regression Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>log ( B_{NH_3} ) = 1.4113 − 0.00292 ( t )</td>
</tr>
<tr>
<td>H₂S</td>
<td>log ( B_{H_2S} ) = 4.057 − 0.00981 ( t )</td>
</tr>
<tr>
<td>CO₂</td>
<td>log ( B_{CO_2} ) = 4.7593 − 0.01092 ( t )</td>
</tr>
<tr>
<td>CH₄</td>
<td>log ( B_{CH_4} ) = 6.0783 − 0.1383 ( t )</td>
</tr>
<tr>
<td>H₂</td>
<td>log ( B_{H_2} ) = 6.2283 − 0.01403 ( t )</td>
</tr>
<tr>
<td>N₂</td>
<td>log ( B_{N_2} ) = 6.4426 − 0.01416 ( t )</td>
</tr>
</tbody>
</table>

\[
K = \left( \frac{[K^+]^{z}}{[Na^+]^{1-z}} \right)
\]

(9)

where square brackets [ ] represent the molal concentration of the species. We will further be presenting the concentration without square brackets. The mixed-minerals like Na\(_z\)K\(_{1-z}\)X are not pure phases, so their activity cannot be considered as unity. To avoid the situation the end members of mixed-minerals are considered. It means that we are indirectly considering the solubility of NaX and KX. Then, the concentration Na\(^+\)/K\(^+\) ratio will not only depend on temperature, but also on the type and concentration of anion X\(^-\).

Additionally, to reach the solubility equilibrium, the concentration of Na\(^+\) and K\(^+\) will be very high that can be observed in lake and ocean waters.

According to the cation-exchange theory, the Na\(^+\)/K\(^+\) ratio in a solution is a function of temperature, type of minerals and Na\(^+\)/K\(^+\) ratio in the mineral phases (Garrels and Christ 1965). The Na\(^+\)/K\(^+\) ratio of reservoir rocks, which are in equilibrium with the fluid, is not known and is not included in any cation-exchange geothermometer.

Additionally, Fournier (1989) simplified the equations for various cation-exchange geothermometers to the Na\(^+\)/K\(^+\) geothermometer. Then he plotted \( \log (Na^+/K^+) \) versus 1000/T for base exchange between albite and adularia, albite and microcline and Na\(^-\) and K\(^+\)-montmorillonites together with the values of \( \log (Na^+/K^+) \) for the empirical equations (Figure 9). There is a wide range of values for \( \log (Na^+/K^+) \) at a given temperature and vice versa. For example, at temperature 100°C, \( \log (Na^+/K^+) \) varies in the range 0.95 to 2.25 for different equations. Similarly, for \( \log (Na^+/K^+) \)=1.00, the temperature range is 90 to 410°C. Thus, one can get a wide range of temperature values using different geothermometer equations for a given ratio of Na\(^+\)/K\(^+\).

In summary the cation exchange geothermometers are merely empirical and different geothermometer equations provide different values of temperature. There are no fundamental criteria to justify superiority of one equation over others. There is a need to re-evaluate the concepts of cation-exchange geothermometer including the reservoir rock-types.
6.2.2 Quartz solubility geothermometer

Verma (2003e) derived a quadratic regression equation in P (in MPa) and 1/T (in K) for the quartz solubility data along the saturation curve. The dissolution of quartz results in the formation of silicic acid according to the following reaction

$$\text{SiO}_2(qz) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$$ (10)

The equilibrium constant for the reaction is

$$K_{qc} = \exp \left( \frac{-\Delta G_f^{T,P}}{RT} \right) = \frac{a_{\text{H}_4\text{SiO}_4}}{a_{qz} \cdot a_{\text{H}_2\text{O}}} \equiv a_{\text{H}_4\text{SiO}_4} \equiv [\text{H}_4\text{SiO}_4]$$ (11)

If we assume water and solid quartz as pure phases, the equilibrium constant is equal to the activity of $\text{H}_4\text{SiO}_4$. Further, on assuming the activity coefficient for $\text{H}_4\text{SiO}_4$ as unity, the equilibrium constant ($K_{qc}$) reduces to the molal concentration of $\text{H}_4\text{SiO}_4$. In the case of pure water solution, the undissociated silicic acid species ($\text{H}_4\text{SiO}_4$) is the dominating species, therefore the total dissolved silicic species concentration ($\text{SiO}_2(aq)$) is equal to $[\text{H}_4\text{SiO}_4]$ and may be written as

$$\log \text{SiO}_2(aq) = \frac{1}{2.303} \left( -\frac{\Delta G_f^{T,P}}{RT} \right) = -\frac{1}{2.303} \left( \frac{\Delta H_f^{T,P}}{RT} \right) + \frac{1}{2.303} \left( \frac{\Delta S_f^{T,P}}{R} \right)$$ (12)

The log $\text{SiO}_2(aq)$ in equation 12 is a inverse function of T. Therefore, a quadratic function for log $\text{SiO}_2(aq)$ is considered here in order to counter effect the contribution of T and P, since P and T play inverse role on the physico-chemical properties of a substance. The second order equation for log $\text{SiO}_2(aq)$ as a function of 1/T and P is obtained through the least square curve fitting for all the experimental values of log $\text{SiO}_2(aq)$ along the saturation curve (Verma 2003e)
concentration provides an incorrect value of reservoir temperature, which could be highly irrecoverable. Therefore, the application of quartz geothermometer to the total discharge silica concentrations in the reservoir. There may also be some loss of vapor within a geothermal reservoir. Geothermal reservoir conditions are generally along the liquid-vapor saturation and there is high dispersion in the experimental data above 300ºC. This is associated with the analytical limitations in the quartz solubility determinations at >300ºC (Verma 2000d).

A computer program to calculate temperature and vapor fraction in a geothermal reservoir using quartz geothermometer is written in Visual Basic 6.0. Four representative types of regression equations are programmed (Table 3): (a) a quadratic regression equation of \( 1/T(K) \) and P(MPa) (Verma 2003d), (b) a linear equation relating log SiO2 to the inverse of absolute T (Verma 2002a), (c) a polynomial of absolute T including logarithmic terms (Gunnarsson and Arnórsson 2000) and (d) temperature as a polynomial of SiO2 including logarithmic terms (Fournier and Potter 1982).

Geothermal reservoir conditions are generally along the liquid-vapor saturation and there may be any proportion of liquid-vapor from 0 to 100% in the reservoir. Silica dissolves only in the liquid phase. The total discharge fluid from a well represents both liquid and vapor phases in the reservoir. There may also be some loss of vapor within a geothermal reservoir. Therefore, the application of quartz geothermometer to the total discharge silica concentration provides an incorrect value of reservoir temperature, which could be highly

\[
\log SiO_{2(aq)}(ppm) = 5.8983 - 1894.6/T + 0.27348 P + 1.3577 \times 10^5 / T^2 \\
- 153.23 P/T - 3.3112 \times 10^{-3} P^2
\]  

(13)

Figure 10 shows the four representative types of theoretical curves together with the experimental data. It can be observed that there is a good agreement between the experimental and theoretical solubility data up to the critical point of water (374ºC), in the case of the quadratic regression equation. The log SiO2 data above 300ºC is associated with the analytical limitations in the quartz solubility determinations at >300ºC (Verma 2000d).

\[
\log SiO_{2(aq)}(ppm) = 5.8983 - 1894.6/T + 0.27348 P + 1.3577 \times 10^5 / T^2 \\
- 153.23 P/T - 3.3112 \times 10^{-3} P^2
\]  

(13)

Figure 10: Experimental quartz solubility data along the liquid-vapor saturation curve. Four Representative regression equations (Verma 2003e, 2003f).

\[
\log SiO_{2(aq)}(ppm) = 5.8983 - 1894.6/T + 0.27348 P + 1.3577 \times 10^5 / T^2 \\
- 153.23 P/T - 3.3112 \times 10^{-3} P^2
\]  

(13)
distinct from the real reservoir temperature, depending on the amount of vapor present or lost from liquid phase within the reservoir. Here an algorithm based on the conservation of enthalpy and silica is developed to estimate temperature and vapor fraction in a geothermal reservoir.

Similarly, according to equation 5 the conservation of silica is stated as

$$SiO_{2,TD} = (1 - y) \cdot SiO_{2,l}$$  \hspace{1cm} (14)

where \(SiO_{2,TD}\) is the total discharge concentration of silica and \(SiO_{2,l}\) is the silica concentration in liquid phase in the reservoir. From equation 14, the fraction of vapor in the reservoir is

$$y = 1 - \frac{SiO_{2,TD}}{SiO_{2,l}}$$  \hspace{1cm} (15)

Let the temperature in the reservoir be \(T\). The value of \(T\) (and the corresponding saturated pressure (\(P\)) in case of the quadratic regression equation of \(1/T\) and \(P\)) is substituted in the regression equations given in Table 3 to calculate the silica concentration. This silica concentration (\(SiO_{2, poly}\)) is substituted for \(SiO_{2,l}\) in equation 15 to calculate \(y\). The value of \(y\) together with the values of \(H_l\) and \(H_v\) at \(T\) are used to calculate the reservoir enthalpy (\(H_{res}\)) from equation 4. \(H_{res}\) must be equal to the measured reservoir enthalpy (\(H_R\)), if \(T\) is equal to the reservoir temperature. Since we do not know the correct value of reservoir temperature, the values of \(H_{res}\) calculated for each temperature and plotted in an enthalpy versus temperature plot to find the temperature for which \(H_{res} = H_R\).

An alternative approach is applying the Newton-Raphson method, which is extensively used in the geochemical modeling computer programs (Bethke 1996). The equations 14 and 15 can be rewritten as residual functions of \(T\) and \(y\)

$$R_1(T, y) = H_l \cdot (1 - y) + H_v \cdot y - H_R = 0$$
$$R_2(T, y) = SiO_{2,poly} \cdot (1 - y) - SiO_{2,TD} = 0$$  \hspace{1cm} (16)

### Table 3: Quartz solubility regression equations, programmed in QrtzGeotherm (Verma 2003f)

<table>
<thead>
<tr>
<th>Equation</th>
<th>Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (\log SiO_2 (\text{in ppm}) = 5.8983 + 1894.6/T(\text{in K}) + 0.27348P(\text{in MPa}) + 1.3577 \times 10^5/T - 153.23 P^{1/2} - 3.3112 \times 10^{-1} P^2)</td>
<td>Quadratic of (1/T) and (P)</td>
<td>Verma (2003d)</td>
</tr>
<tr>
<td>2. (\log SiO_2 (\text{in ppm}) = \frac{1117.34(\pm 13.05)}{T(\text{in K})} + 4.78(\pm 0.03))</td>
<td>Linear of (1/T)</td>
<td>Verma (2002a)</td>
</tr>
<tr>
<td>3. (\log SiO_2 (\text{in m}) = -34.188 + 197.47/T(\text{in K}) - 5.851 \times 10^{-6} T^2 + 12.245 \log T)</td>
<td>Polynomial of (T)</td>
<td>Gunnarsson &amp; Arnórsson (2000)</td>
</tr>
<tr>
<td>4. (t(\text{in } ^\circ C) = -42.198 + 0.28831S(\text{in ppm}) - 3.6686 \times 10^{-4} S^2 + 3.1665 \times 10^{-3} S^3 + 77.034 \log S)</td>
<td>Polynomial of (SiO_2)</td>
<td>Fournier &amp; Potter (1982)</td>
</tr>
</tbody>
</table>
The increments $\Delta T$ and $\Delta y$ in $T$ and $y$, respectively, are determined by

$$
\frac{\partial R_1}{\partial T} \Delta T + \frac{\partial R_1}{\partial y} \Delta y = -R_1 \quad \text{and} \quad \frac{\partial R_2}{\partial T} \Delta T + \frac{\partial R_2}{\partial y} \Delta y = -R_2
$$

(17)

To solve the equations 17 for $\Delta T$ and $\Delta y$, the determinant $D$ of the coefficient matrix (the Jacobian) is determined

$$
D = \frac{\partial R_1}{\partial T} \frac{\partial R_2}{\partial y} - \frac{\partial R_1}{\partial y} \frac{\partial R_2}{\partial T}
$$

(18)

Then the roots of equations 17 are following

$$
\Delta T = \left( \frac{R_2 \frac{\partial R_1}{\partial y} - R_1 \frac{\partial R_2}{\partial T}}{D} \right) \quad \text{and} \quad \Delta y = \left( \frac{R_1 \frac{\partial R_2}{\partial T} - R_2 \frac{\partial R_1}{\partial y}}{D} \right)
$$

(19)

We update the estimated roots accordingly

$$
(T)^{i+1} = (T) + \Delta T \quad \text{and} \quad (y)^{i+1} = (y) + \Delta y
$$

(20)

where $i$ is iteration number, varying from 0 to $i_{\text{max}}$. The iteration process is stopped as the sum of square of residual functions is smaller than a preselected value for obtaining desire accuracy in the roots or the number of iteration exceeds $i_{\text{max}}$.

Figure 11 shows the user interface. The input parameters are well number, total discharge enthalpy $H_R$, separator pressure, atmospheric pressure, silica at weirbox and the total discharge silica concentration. If the total discharge silica concentration is given, there is no need to provide the values of separator pressure, atmospheric pressure and silica at weirbox. Otherwise, it calculates first the total discharge silica concentration on pressing the button “StartCalc”.

From the total discharge silica concentration, the reservoir enthalpy from 100 to 374ºC is calculated using the first algorithm and the regression equations given in Table 3. The values are plotted in an enthalpy versus temperature graph in an OLE (Object Link Embedding) container, which permits the user to edit the graph parameters using MS-Excel by a double click on any part of the OLE container. A precaution is that the workbook, StartData.xls should not be closed after the chart editing in MS-Excel.

On pressing the button “Continue”, it shows a frame for selecting the quartz solubility regression equations and another frame for providing initial guess of temperature and vapor fraction in the geothermal reservoir. It is compulsory to provide the value of guess temperature between 100 to 370ºC. The value of initial vapor fraction is automatically assigned to zero, if it is not provided. It is recommended to look at the graph for the intersection between the curves $H=H_R$ and $H=H_{res}$ in order to choose an initial temperature near the correct reservoir temperature. Then the program calculates the correct values of reservoir temperature and vapor through second algorithm.
On pressing the button “Calculate”, it shows the values of temperature and vapor fraction calculated using the selected equations. The three buttons, NewCalc, Save and End are for conducting a new calculation, saving the calculated results and ending the execution of the program, respectively.

Table 4 presents the silica concentration in total discharge, reservoir enthalpy and measured downhole temperature for wells M-50, M-53 and M-90 at Cerro Prieto. These wells were selected to illustrate different features of the calculation procedure of the computer program. The calculated values of temperature and vapor fraction in the reservoir are also given in Table 4. The negative values of vapor fraction indicate that steam was lost within the reservoir.

Figure 12 illustrates the procedure to calculate the reservoir temperature using quartz geothermometers. For M-50, the intersection between $H=H_R$ and $H=H_{res}$ are 300 and 313°C for all the regression equations, whereas the downhole measured temperature is 310°C. Thus, there is a good agreement between the results from all the regression equations. It can be noticed that there is an exponential increase in $H_{res}$ calculated from all the regression equations, near the critical point of water. This is associated with getting the thermodynamic properties of water and vapor closer to that of the critical point. Similarly, there are some analytical problems in measuring quartz solubility near the critical point (Verma, 2000d). Therefore, the use of quartz geothermometer is limited up to 370°C.
Table 4: Well data from the Cerro Prieto geothermal system (Verma and Santoyo 1997) and an application of the quartz regression equations to estimate the reservoir parameters considering the conservation of mass and enthalpy.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>M-50</td>
<td>1362</td>
<td>310</td>
<td>674</td>
<td>-0.009</td>
<td>305.2</td>
<td>0.010</td>
<td>300.7</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>300.7</td>
<td>0.043</td>
<td>312.6</td>
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<td></td>
<td>0.006</td>
<td>301.5</td>
</tr>
<tr>
<td>M-53</td>
<td>1588</td>
<td>339</td>
<td>652</td>
<td>-0.007</td>
<td>339.0</td>
<td>0.129</td>
<td>313.1</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>313.1</td>
<td>0.010</td>
<td>330.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.159</td>
<td>317.7</td>
</tr>
<tr>
<td>M-90</td>
<td>1396</td>
<td>345</td>
<td>639</td>
<td>0.029</td>
<td>301.8</td>
<td>0.043</td>
<td>298.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>298.3</td>
<td>-0.002</td>
<td>309.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.042</td>
<td>298.5</td>
</tr>
</tbody>
</table>

In the case of well M-53, the measured temperature is 339ºC. The calculated temperature using the Gunnarsson and Arnórsson’s regression equation is 331ºC (Table 4), which is closer to the measured temperature. If we look in Figure 12(b), the curves, \(H=H_R\) and \(H=H_{\text{res}}\) never intersect for the quadratic regression equation. However, they are very close near to 341ºC. An error of 1% in the measurement of enthalpy (or total discharge silica concentration) will produce an intersect between the curves in the range of temperature 339-343ºC. The measured temperature 339ºC is within this temperature range.

For well M-90, there is an intersect between the curves, \(H=H_R\) and \(H=H_{\text{res}}\) at 302ºC (Figure 12(c)) in case of the quadratic equation, but the measured temperature is 345ºC. Similarly, the other regression equations provide quite incorrect values of reservoir temperature (Table 3). However, an error of 5% in the measurement of enthalpy and total discharge silica concentration may produce an intersection around 358ºC for the quadratic regression equation, which is closer to the measured temperature (345ºC).

Thus, the approach implemented in the computer program QrtzGeotherm, to estimate the reservoir temperature through quartz solubility geothermometer provides a visualization of all the probable temperatures. In the case of Cerro Prieto, the measured downhole temperature for each well was available; therefore, the results are compared to select the best choice of the two temperature values. This can also be done with other techniques like using other geothermometers and measuring pressure and temperature independently in each well.

### 6.3 pH Calculation Through Alkalinity

There are three types of equations for an aqueous solution: *mass balance, charge balance* and *proton balance*. But out of the three equations two are independent and the third can be derived as an algebraic sum of the other two equations (Verma and Truesdell 2001). Theoretically, a solution should be electrically neutral, but the electro-neutrality condition is rarely satisfied, even in best quality analyses. Thus, the alkalinity approach is safer for the pH calculation of hydrothermal fluids (Verma 2002a).

A base-neutralizing capacity (BNC) or acid-neutralizing capacity (ANC) is the equivalent sum of all the acids or bases that can be titrated with a strong base or acid to a preselected equivalence point (Stumm and Morgan 1981). The BNC and ANC are more commonly...
Figure 12: An illustration of the calculation of geothermal reservoir temperature for the wells, M-50, M-53 and M-90 at Cerro Prieto.
known as alkalinity and acidity, respectively. Both of these terms are defined for certain pertinent equivalence points (EPs) for the system. Acidity is the negative of alkalinity for the same reference EP. In carbonate systems there are three equivalence points called the H$_2$CO$_3$EP, NaHCO$_3$EP and Na$_2$CO$_3$$^2$EP. Alkalinity could be defined with respect to either EP. However, the geothermal fluids also have other weak acids and bases and the alkalinity is defined as

\[
alk = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4]^- + [H_3SiO_4] + [HS^-] - [NH_4^+] - [H^+]
\]

where the \( \alpha \)'s identify the ionization fraction (Stumm and Morgan 1981) and \( C_T \) is the total dissolved concentration of the subscripted constituent, i.e., carbonic acid (car), boric acid (B), silicic acid (Si), hydrogen sulfide (S) and ammonia (N), respectively. Chemical speciation can be reconstructed introducing pH, alkalinity and total dissolved concentrations of relevant constituents in equation 21.

It is important to point out here that we are interested in the dissolution-exsolution of NH$_3$, but not of NH$_4^+$ or its salts like NH$_4$Cl (Verma and Truesdell 2001). Therefore, we defined the alkalinity with respect to the NH$_3$EP in equation 21. The procedure of writing the alkalinity expression for different types of reactions in a system is explained by Stumm and Morgan (1981). Thus, the alkalinity defined here does not change upon dissolution or exsolution of CO$_2$ (H$_2$CO$_3$) and other gases, such as H$_2$S and NH$_3$. On the other hand, the addition or removal of CaCO$_3$ or other carbonate minerals, and Ca(OH)$_2$ or other hydroxides, will increase or decrease alkalinity.

Verma (2002a) presented the stepwise geochemical calculations for well M-19A, Cerro Prieto, Mexico (Table 5). The calculated results are presented up to three decimal places for comparison purposes, although the accuracy of these results depends on the quality of analytical data. The speciation of carbonic, silicic and boric species may be obtained with knowing pH and concentration of one of the species. For example, the concentrations of all carbonic species are calculated from the analytical values of pH and HCO$_3^-$. Similarly, the speciation of silicic and boric species is obtained from their total concentration and pH. Then, the alkalinity is determined using equation 21. This water is heated up to 100°C to get the chemical speciation of flashed water at the weirbox. Alkalinity does not change on heating a solution.

The fraction of lost vapor at the weirbox is calculated through the conservation of enthalpy and mass. The concentrations of dissolved gaseous species like H$_2$S, NH$_3$, H$_2$, CH$_4$, etc. are not measured in the flashed water. From the concentration of dissolved CO$_2$ (H$_2$CO$_3$) as calculated above in the flashed water at the weirbox, the concentration of CO$_2$ in the lost vapor could be calculated from equations 3 and 6, considering equilibrium between the water and vapor phases. The data are reported in the column “lost vapor” in Table 5. On mixing the flashed water and lost vapor, the speciation of separated water at 100°C is calculated and reported as “lost vapor correction” at the weirbox. Then, this water is heated to 168.060°C (i.e., corresponding to the separator pressure 7.55 bar) to get the chemical speciation of separated water at the separator.