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A Simplified Statistical Treatment of Geochemical Data by Graphical Representation[1]

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Abstract

In the course of a mineral exploration sponsored by the United Nations Development Programme in two selected zones of Guatemala, a stream sediment reconnaissance was carried out, and graphical methods of interpretation were attempted in the search for a simplified statistical treatment of about 25,000 geochemical results. The data were grouped by drainage and lithological units, and the frequency distributions of the abundance of Cu, Pb, Zn and Mo were studied in the form of cumulative frequency curves. The four elements appear to be approximately lognormally distributed. Background, coefficients of deviation and threshold levels were graphically estimated. Examples are given of simple and complex populations. Mineral associations were studied by correlation diagrams.

Contents

Introduction

THE United Nations Mineral Exploration Programme in Guatemala relied heavily on geochemical prospecting. During one year (1967) 60 percent of the total Project area was covered systematically by a geochemical reconnaissance carried out in the drainage systems. Nine thousand stream sediment samples were collected over about 12,000 km² (rounded figures). All the samples were analyzed for copper and zinc, and the total number thinned out to approximately 4,000 before being run for lead and molybdenum. Finally about 25,000 geochemical results were available for compilation and interpretation. As they accumulated, it became apparent that high-contrast anomalies which are obvious targets for follow-up operations would not be encountered but rather more subtle features not so easy to pinpoint and interpret.

The interpretation phase of the survey was characterized by two essential features: the great amount of data to be analyzed and the lack of precision of these data.

Sampling and analytical methods must sacrifice precision for speed due to the nature of geochemical prospecting, and the first consequence of this fact is that an isolated result has little meaning in geochemistry. It must be part of a population as numerous and homogeneous as possible. Indeed in all kinds of phenomena, individual inaccuracies shade off progressively when observation is extended to larger and larger populations.

The first phase of geochemical interpretation is to condense large masses of numerical data and extract from them the essential information. The most objective and reliable way to do it (and sometimes the only one) is statistically. Large sets of numbers, cumbersome and difficult to interpret, may be reduced to a useful form by the use of descriptive statistics. This is best done by the graphical representation of the frequency distribution of a given set of data; then the average value, an expression of the degree of variation around the average, and the limit above which the anomalies start are immediately and precisely determined as well as the existence of one or several populations in the surveyed area.

This treatment of the data also simplifies the comparison of the geochemical behavior of an element in various geological surroundings or of several elements in the same lithological unit.

I am grateful to Mr. Henry H. Meyer, Project Manager of the Guatemala and El Salvador Mineral

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Surveys, and to Mr. Stephen S. Steinhauser for technical criticism and much helpful discussion.

Difficulty of Statistical Approach in Stream Sediment Surveys

A reliable statistical interpretation requires that a great quantity of data be treated and that these data be homogeneous.

In drainage reconnaissance surveys, the first condition is easily filled but not the second. As a matter of fact, the importance of sampling technique is sometimes overlooked in this type of prospecting. But even if given the appropriate attention, too many types of rivers and too many lithological units are generally sampled to result in a homogeneous collection of samples. The best way to limit the inconvenience of the heterogeneity of the samples (particularly pH, organic content and grain size) is to split the survey area into drainages and lithological units, when possible, and to make the statistical interpretation for each of them separately. However, even if this is done, the same degree of precision cannot be achieved as in the case of a soil survey where good homogeneity is possible.

Adjustment to a Lognormal Distribution

Definitions

When dealing with a large mass of geochemical data, the first step is to find what sort of distribution pattern best fits the various sets of observations. And, thus far, the lognormal distribution pattern appears to be the one most applicable to the results of most geochemical surveys (Ahrens, 1957).

In geochemical prospecting, we study the content of trace elements in various natural materials, and to say that the values are lognormally distributed means that the logarithms of these values are distributed following a normal law (or Gauss' law) well known as the bell-shaped curve (Monjallon, 1963).

Many natural or economic phenomena can be expressed by a value varying between zero and infinity, represented by a skewed distribution curve. If, instead of the actual value of the variable itself, we plot its logarithm in abscissae, the frequency curve takes a symmetrical, bell-shaped form, typical of the normal distribution. This happens when a phenomenon is subject to a proportional effect, that is to say when independent initial causes of variations of the studied value take effect in a multiplicative way. It is the case, for instance, for the distribution of trace elements in rocks, for the area of the different countries of the world, for the income of individuals in a country, for the grain size in samples of sedimentary rocks, and others (Coulomb, 1959; Cousins, 1956).

In all these examples, the character studied follows the lognormal law, which is probably more common than the normal one.

It is interesting to note here that the lognormal law fits very well in the case of low-grade deposits like gold but for high-grade deposits, iron for instance, the experimental distributions are generally negatively skewed because of the limitation towards the high values. G. Matheron gives a thermodynamic interpretation of the proportional effect in the case of ore deposits and relates it to the Mass Action Law (Matheron, 1962). To the extent in which geochemical anomalies are extrapolations of ore deposits this theory should apply to geochemical prospecting.

Construction of the Cumulative Frequency Curve

A lognormal distribution curve is defined by two parameters: one dependent on the mean value, and the other dependent on the character of value-distribution. This latter parameter is a measure of the range of distribution of values, that is whether the distribution covers a wide or narrow range of values. The two parameters can be determined graphically as will be explained on following pages. For practical purposes, we work on cumulative frequency curves, and their construction shall be explained by means of a concrete example.

The various steps of this construction are the following:

(a) Selection of a precise set of data ("population") as large and homogeneous as possible.

(b) Grouping of the values into an adequate number of classes.

(c) Calculating the frequency of occurrence in each class and plotting it against the class limits; this gives a diagram called the "histogram."

(d) Smoothing the histogram to get the frequency curve.

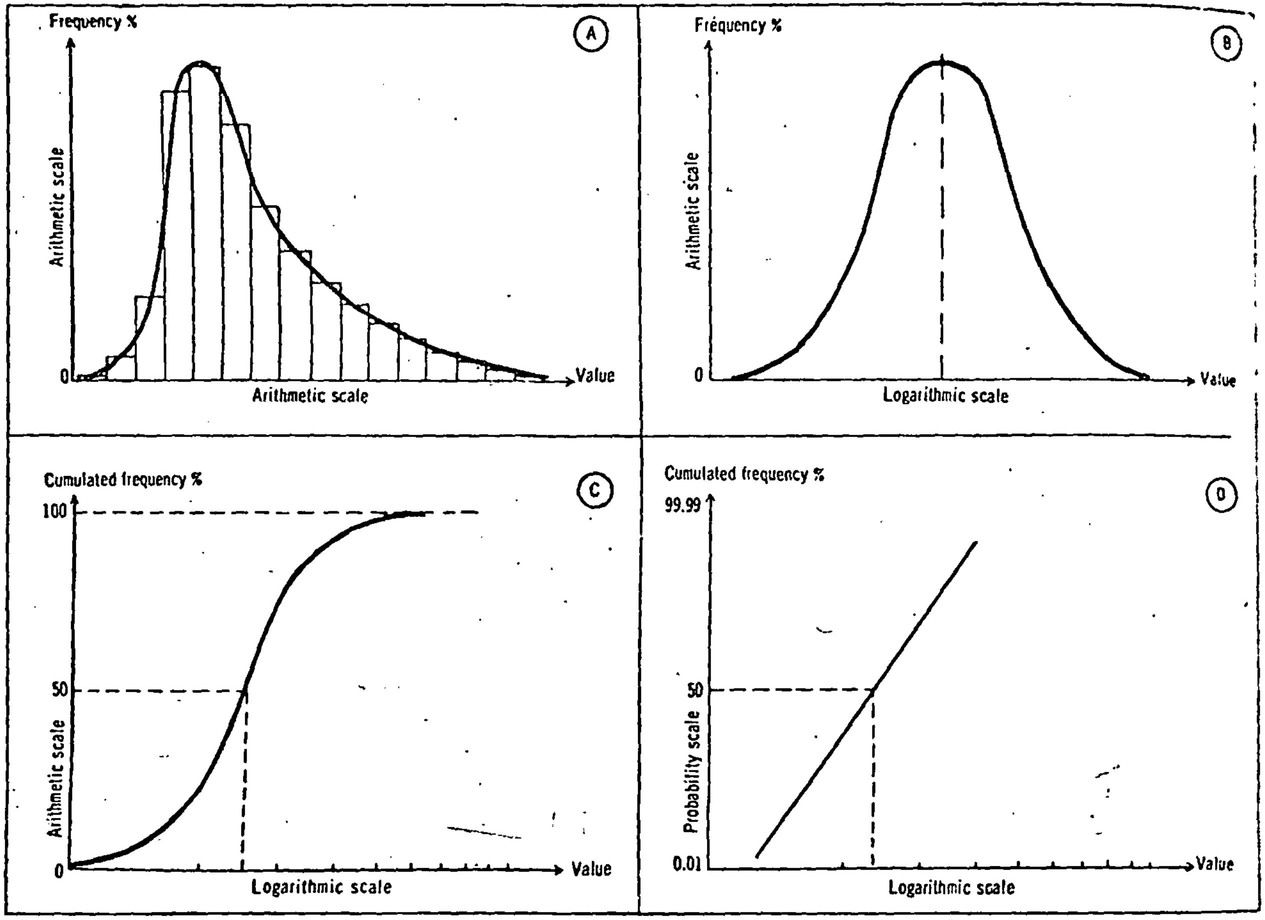
(e) Plotting the cumulated frequencies as ordinates gives the cumulative frequency curve, which is the integral of the frequency curve.

(f) By replacing the arithmetic ordinate scale with a probability scale the cumulative frequency curve is represented by one or more straight lines. Examples of lognormal frequency curves are shown in Figure 1.

Some brief comments on the different steps follow:

(a) The larger the population to be analyzed, the more precise and reliable the results. If necessary, as few as 50 values may be treated statistically but

Figure 1. Lognormal distribution curves



the confidence limits must be calculated to see if the analysis is meaningful.

(b) A correct grouping of the values is mandatory if some precision is to be achieved in the statistical interpretation; too few classes will result in shading out important features of the curve; too many in losing significant details amidst a cloud of erratic ones. The results are distributed in classes, the modulus of which should be proportional to the precision of the analyses: the more precise the analyses, the smaller the modulus. The logarithmic interval must be adapted to the variation amplitude of the values and to the precision of the analytical methods (Miesh, 1967).

In statistics, working with 15 to 25 intervals (or classes) is recommended. As a rule, the width of a class, expressed logarithmically, must be kept equal to or smaller than half of standard deviation (Shaw, 1964).

For geochemical purposes, it is convenient to work with 10 to 20 points on the cumulative frequency line, that is to say with 9 to 19 intervals or classes. There are three variables to consider: the number of points (n) necessary to construct a correct line: the range of distribution of the values (R), expressed as the ratio of the highest to the lowest value of the population; and the width of the classes expressed logarithmically (log. int.) which has to be selected in function of the two first parameters. These three variables are linked by the relation:

$$\text{log. int.} = \frac{\log R}{n}$$

In most of the cases R varies from 6 to 300 (experimental average values), then, with (n) varying from 10 to 20, log R from 0.78 to 2.48, the extreme values for the logarithmic interval will be:

$$\text{log. int.} = \frac{0.78}{20} = 0.039$$

$$\text{log. int.} = \frac{2.48}{10} = 0.25$$

The 0.10 was selected as the best suited logarithmic interval for the classes because it suits most distribution, giving reasonable number of classes and a good definition of the curve. In case of very reduced dispersion of the values around the mean, it may be necessary to use 0.05, and if the dispersion is specially large, 0.2 will be chosen. When the logarithmic interval is selected, it is easy to calculate a table giving the class limits in ppm. The only precaution is to avoid starting with a round value so that no analytical results will fall on the limit of two classes. The most useful and commonly employed in geochemical work is the 0.1 log. int. classs table, a part of which is given below:

class limit (log) ..	0.07, 0.17, 0.27, 0.37, 0.47, 0.57
class limit (ppm) .	1.17, 1.48, 1.86, 2.34, 2.95, 3.72

It can be extended in both directions as far as necessary.

(c-d) After selecting the class table, the values are grouped and the frequency calculated for each class (in percentage); then the frequencies are plotted against the class limits (the latter being logarithmically calculated, ordinary arithmetic-arithmetic paper must be used), giving a histogram which is smoothed to a frequency curve. But histograms are often misleading, being strongly affected by slight changes in class intervals, and frequency curves are difficult to draw and handle: for instance, it is necessary to determine the inflexion points of the curve in order to evaluate the standard deviation. Practically, the histogram-frequency curve step is skipped and the cumulative frequency directly constructed. However, note here an advantage of the histogram: it clearly illustrates the effect of the sensitivity of the analytical method and more precisely the bias brought to the low values by the use of colorimetric scales of standards. As a matter of fact, experience shows that there is an inevitable concentration of the readings, whoever the analyst, on the values actually represented in the colorimetric scale. For instance, in the case of copper, the lower part of the standard colorimetric scale reads 0,2,4,7 . . . ppm. Usually this results in an excess of 2, 4 and 7 values, and a conspicuous lack of 1, 3, 5 ppm values. This is of importance for a correct construction of the frequency curve, and the raw values must often be corrected by extrapolating the general shape of the curve.

(e-f) By plotting the cumulated frequencies as ordinates instead of the frequencies, one obtains the integral curve of the preceding. It has the form of a straight line when using the appropriate graphpaper (probability-log), and it is the one used in geochemical presentation and interpretation of the results. Then two questions have to be answered: where to start accumulating the frequencies, and where to plot the cumulated frequencies?

As for the first point, the normal procedure followed by many authors is to start cumulating the

Figure 2 - Cumulative Frequency Distribution for Zn and Cu

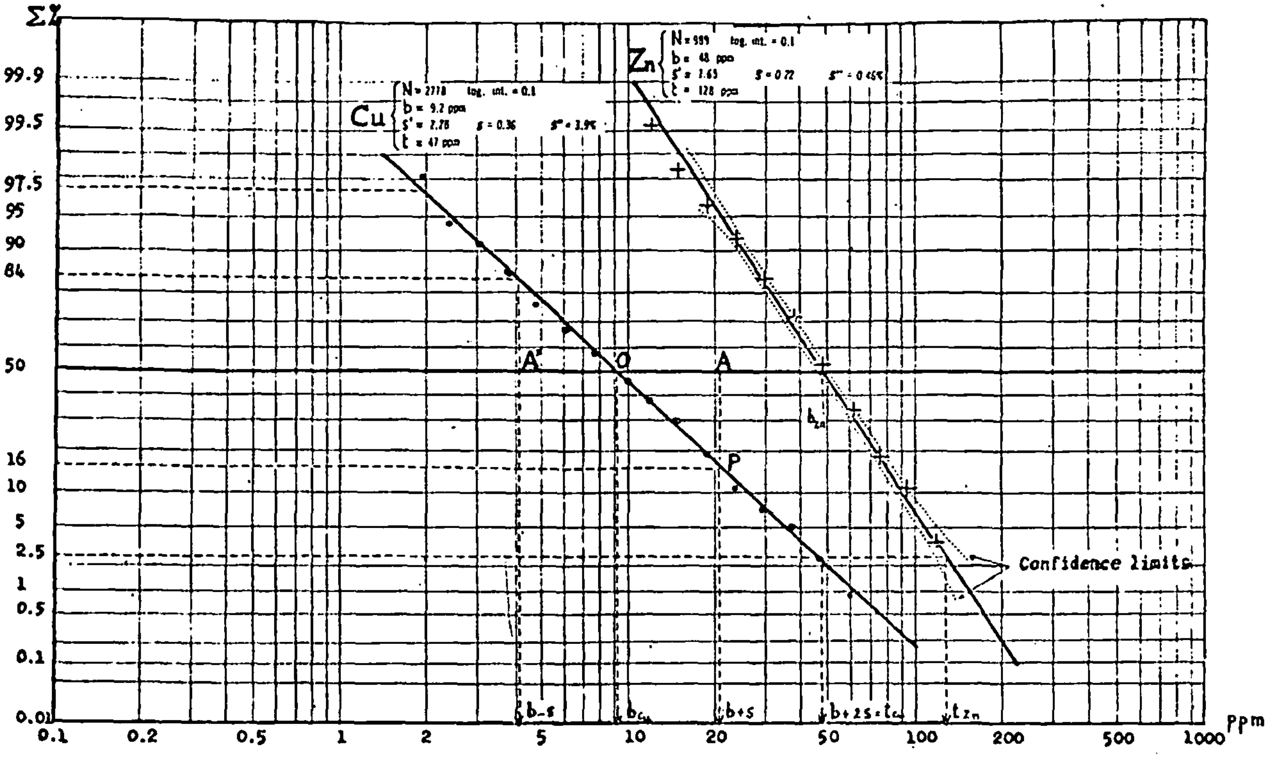
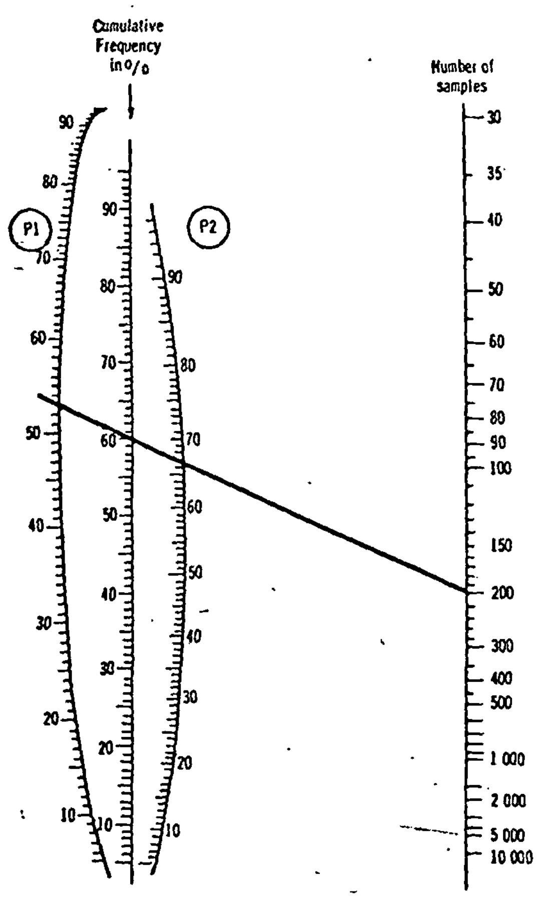


Figure 3. Confidence limits (P_1, P_2) at 0.05 probability level



Source: A. Lierzou, Initiation pratique à la statistique, Gauthier Villars, Paris, 1961.

frequencies from the lowest values toward the highest (Fig. 1) (Hubaux, 1961; Tennant and White, 1959). However, one has to consider a property of the probability scale used as ordinates: the values zero and 100% are rejected at the infinite; it does not matter for zero because zero% never occurs, but in each case the last cumulated frequency is 100%, and this value is impossible to plot, lost for the curve. Then considering the lack of precision in the low values and the importance of the high ones for the determination of the threshold level, I consider it much better to *cumulate the frequencies from the highest to the lowest values*; thus, the 100% will correspond to the lowest class and be eliminated.

As for the second point, the curve being an integral one, the ordinates must be plotted at class limits and not at class center; then, since one cumulates the frequencies from the highest values to the lowest, cumulated frequencies are to be plotted against the lower class limits. Using the class center will entail an error of excess on the central tendency parameters (background and threshold) but not on the dispersion parameter (coefficient of deviation). This error, or difference, varies with the type of classes used and is easily calculated (6% for the 0.05 logarithmic class interval, 12% for the 0.1 log. int. and 26% for the 0.2 log. int.). If the class limit is used, curves constructed from different log. int. classes can be directly compared without correction.

Let us take a concrete example: the distribution of Zn in the quaternary alluvial deposits of Block I (Fig. 2). There are 989 results ranging from 10 to 230 ppm.

$$\text{population}: N = 989 \quad \text{range}: R = \frac{230}{10} = 23$$

The best class interval is selected as explained above:

$$\text{log. int.} = \frac{\log R}{n} = \frac{1.36}{14} = 0.097$$

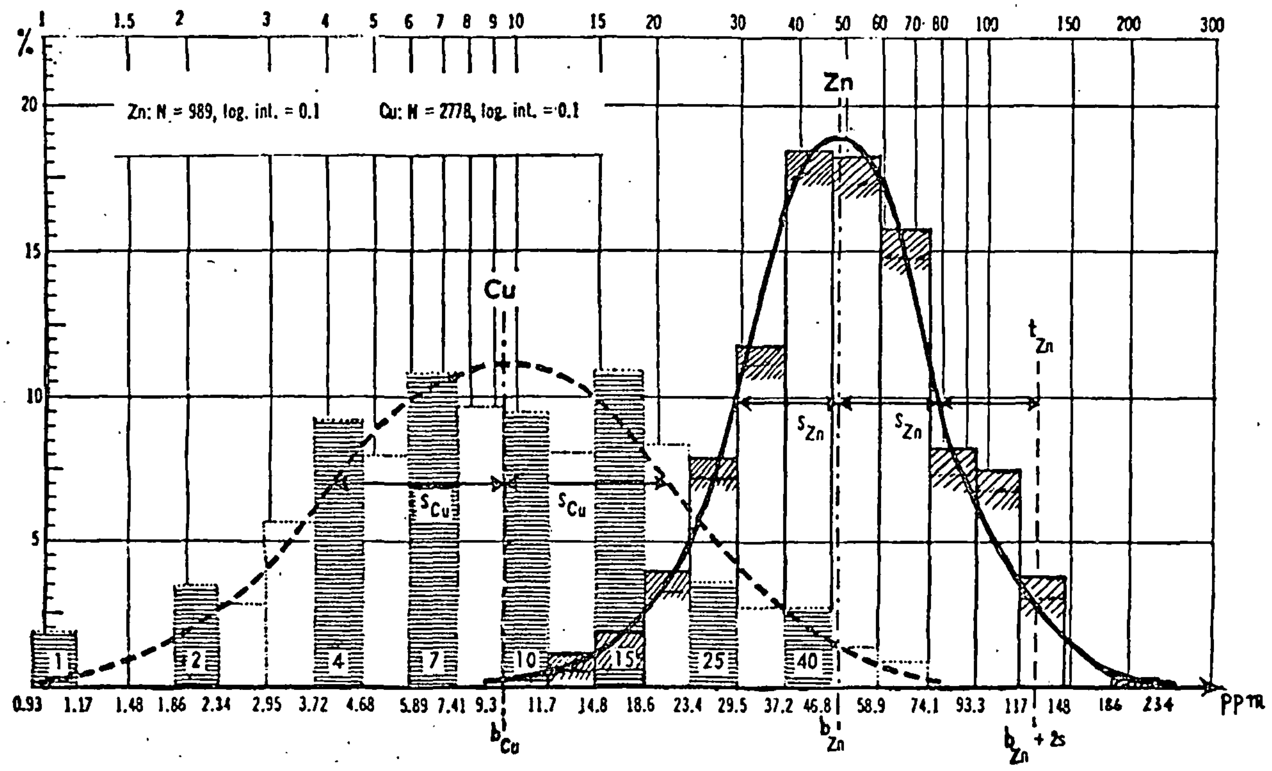
A 0.1 log. interval will give 14 intervals, which is acceptable. Usually, the histogram-frequency curve step is skipped and the cumulative frequency diagram directly constructed.

In Figure 2, the points fit fairly well along a straight line, suggesting a lognormal distribution of zinc in the alluvial deposits. Actually, the points never fit the line exactly, but this does not matter provided they stay in a channel delimited by the confidence limits usually taken at the 5% probability level. This confidence interval has been drawn on Figure 2 by using a graph (Fig. 3), which avoids fastidious calculation and gives a fairly good precision for the cumulative frequency values between 5% and 95%. The width of the confidence channel is inversely proportional to the importance of the population considered: the bigger the population, the narrower the confidence interval. To check that a distribution fits a lognormal pattern, one should use the Pearson's test (Rodionov, 1965; Vistelius, 1960), but this longer operation is generally not warranted in this type of interpretation and, for practical purposes, the graphical control described above is satisfactory.

Comparison with Histograms

For comparison purposes the cumulative frequency curve for Cu in the Motagua drainage (Fig. 2) was also constructed, then, in Figure 4, the corresponding histograms and frequency curves for Cu and Zn. Figures 2 and 4 present the same data in two different ways. Before enumerating and com-

Figure 4. Histogram and frequency curve for Zn and Cu



menting on the advantages of the former presentation over the latter, an interesting feature of the histogram should be mentioned: in the case of colorimetric determinations made in the lower range of sensitivity of the analytical method, the histogram shows clearly the bias introduced in the readings by the human factor and by the accuracy and sensitivity limits of the method. This effect is illustrated for copper in Figure 4, where the classes including a colorimetric standard are shaded and the value of the standard itself is given as a larger figure (1, 2, 4 . . . ppm); the cumulation of the frequency reduces this effect, particularly if it is started from the high values, but it may be necessary to bring some corrections to the low value frequencies in order to construct a precise distribution curve.

Comparing Figures 2 and 4, one sees immediately that it is easier to compare two straight lines than two overlapping bell-shaped curves; many more populations can be presented on the same diagram by using cumulative frequency curves than by using histograms. Cumulative frequency curves are of easier construction and more precise than ordinary frequency curves; it is simpler to draw a line that fits a set of points than to draw a bell-shaped curve with inflexion points.

Information Given by Cumulative Frequency Curves

The main purpose in constructing the cumulative frequency curve for a given population is to check if it fits a lognormal distribution, and if it does, to estimate graphically its basic parameters: background (*b*), coefficients of deviation (*s*, *s'*, *s''*) and threshold level (*t*).

(*b*) gives an idea of the average concentration level of the elements in a given surrounding.

(*s*) expresses the scatter of the values around (*b*): it corresponds to the spread of the values and their range, from the lowest to the highest.

(*t*) is a complex notion which might be termed "conditional": statistically it depends on the probability level chosen; geologically, and for practical purposes, it is supposed to be the upper limit of the fluctuations of (*b*): it depends on (*b*) and (*s*). The values equal to or higher than (*t*) are considered anomalous.

Adjustment to the lognormal law is generally the case when soil samples are considered: in the drainage reconnaissance survey in Guatemala, we found that trace element contents in stream sediments appear also to be lognormally distributed.

Background

A straight line denotes a single population lognormally distributed. In this simple case, the background value (b) is given by the intersection of the line with the 50% ordinate. In the examples given in Figure 2, we have:

background value for copper .. b (Cu) = 9.2 ppm
background value for zinc .... b (Zn) = 48 ppm

Of course, these values must be rounded off; it will be illusory to imply a precision far out of reach of the analytical methods. In the illustrated example, 10 and 50 ppm are taken as reasonably good approximations of the background levels.

In the case of a perfect frequency distribution curve, the background thus calculated corresponds to the mode (most frequent) and median (50% of the values above, 50% below it) values, and is *the geometric mean* of the results. This geometric mean is a more significant value that the arithmetic mean. It is also a more stable statistic, less subject to change with the addition of new data and less affected by high values.

Deviation

Before explaining how to determine graphically the deviation coefficient, an essential property of the normal distribution (i.e., fitting the "bell-shaped" curve) must be recalled here:

(b) being the median value and (s) the standard deviation then:

> 68.26% of the population falls between $b - s$ and $b + s$
> 95.44% of the population falls between $b - 2s$ and $b + 2s$
> 99.74% of the population falls between $b - 3s$ and $b + 3s$

This holds true in the case of the lognormal distribution since the logarithms of the values are normally distributed. Then, rounding off the above-mentioned percentages and taking (b) as the background, we can say that 68% of the population falls between $b - s$ and $b + s$ or that 32% is outside these limits. The distribution curve being symetrical around an axis of abscissa (b) (Fig. 4), 16% of the values will fall above $b + s$ and 16% below $b - s$. In Figure 2, the values $b + s$ and $b - s$ will be obtained by projecting the intersection of the distribution line with the ordinates 16 and 84% on the abscissa axis. Working with logarithms, one has to consider the ratios and not the absolute values thus established. Taking the same example of Cu (Fig. 2), one determines the points P (at the 16% ordinate) and A. OA is the geometrical expression of the deviation: it is inversely proportional to the slope of the line. We call it the *geometric deviation* (s'); it has no dimension: *it is a factor* obtained by dividing the value read in A by the value read in O:

$$s' = \frac{21}{9.2} = 2.28$$

Then multiplying or dividing the background value by the geometric deviation will give the upper and lower limits of a range including 68% of the population (from $b - s$ to $b + s$, or $A'A$ on the figure). Multiplying or dividing by the square of the geometric deviation gives a range including about 95% of the values ($b - 2s$ to $b + 2s$).

Because all the reasoning is made on logarithms, it is also necessary to express the deviation by a logarithm: the *coefficient of deviation* (s) is the logarithm (base 10) of the geometric deviation (s').

$$s' = 2.28$$

$$s = \log s' = 0.36$$

It will be seen later that it might be interesting to consider a third deviation index: the *relative deviation* (s'') sometimes called *coefficient of variation*. It is expressed as a percentage:

$$s'' = 100\,\frac{s}{b}$$

$$s'' = 100\,\frac{0.36}{9.2} = 3.9\%$$

Threshold

After the background and the coefficient of deviation, the third important parameter is the threshold level (t), which is a function of the two former. It has been seen that in the case of symmetrical distribution (either normal or lognormal) 95% of the individual values fall between $b + 2s$ and $b - 2s$, that is to say that only 2.5% of the population exceeds the upper limit $b + 2s$. This upper limit is conventionally taken as the threshold level (t) above which the values are considered as anomalies:

$$\log t = (\log b) + 2s$$

or to avoid using logarithms:

$$t = b \times s'^2$$

$$t = 9.2 \times 5.2 = 47.8 \text{ ppm}$$

Practically, (t) as well as (b), is read directly on the graph as the abscissa of the intersection of the distribution line with the 2.5% ordinate. In this example one reads 47 ppm, and the slight difference is due to the rounding off of the exact

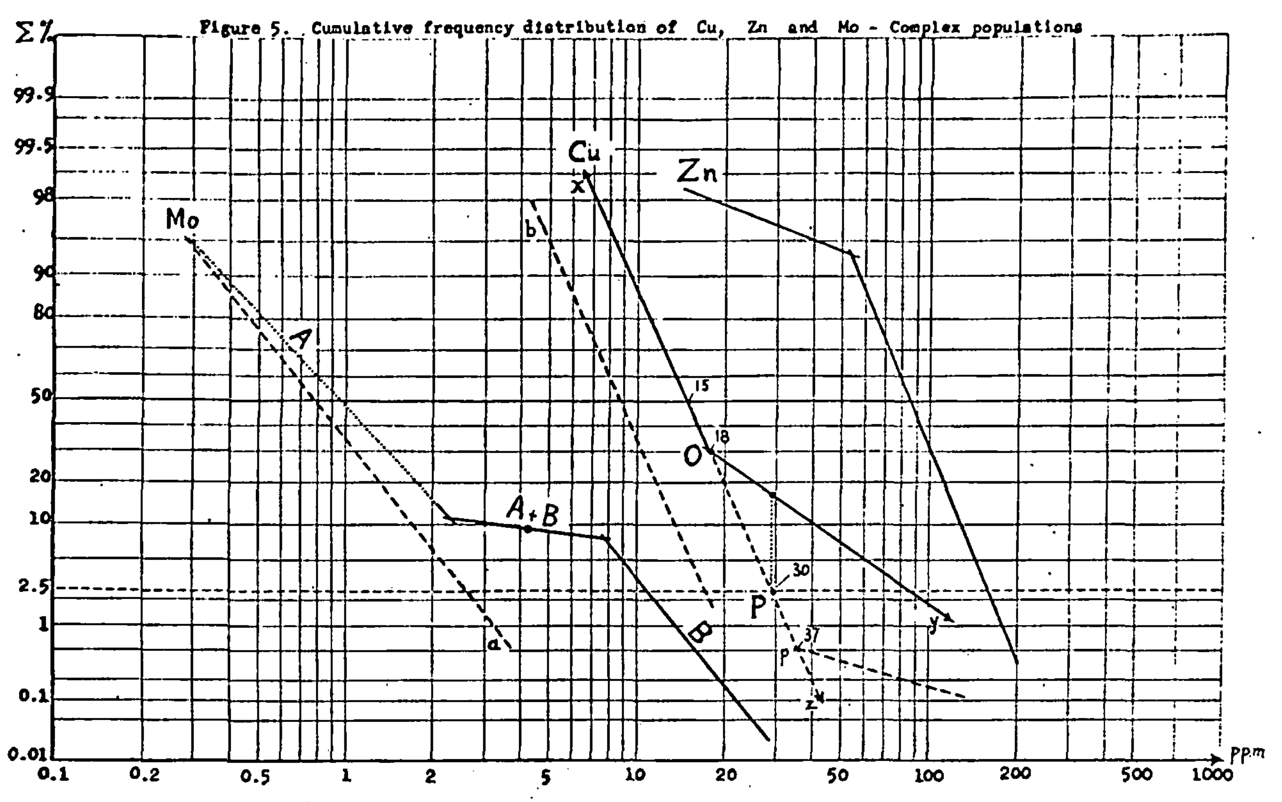


Figure 5. Cumulative frequency distribution of Cu, Zn and Mo - Complex populations

ordinate 2.28% to 2.5%. This shows the importance of the deviation in the estimation of the threshold; two populations may have the same background but, nevertheless, different thresholds if their coefficients of deviation are different. In Figure 2, the threshold is five times the background for Cu and only 2.7 times for Zn.

In all the foregoing, I have considered the simplest case: a single lognormal population, the diagrammatic expression of which is a straight line. However, when constructing cumulative frequency curves, a broken line is frequently obtained suggesting that the set of data considered consists of a complex population or of different ones. Whenever possible in practice, the interpretation is made on sets of data selected so as not to include more than two different distributions; for instance, a lithological unit may include two types of mineralization showing up in soil or sediment samples; one representative of the normal or background content of the material sampled, and the other, a superimposed mineralization related to ore.

Examples

The three main cases of non-homogeneous distribution that are the most likely to occur are, in decreasing frequency order:

a. an excess of high values in the considered population;

b. a mixture of two populations in a given set of data; and

c. an excess of low values in the considered population.

These three cases are represented graphically in Figures 5. They correspond to real distributions encounetred in the Guatemalan drainage survey and appear as solid lines with slope breaks on the diagram. Some indications are given below showing how to interpret such lines.

Copper Distribution (in a lithological unit). The cumulative frequency line (Fig. 5) shows a break to a flatter slope at the 30% level. This is the case when there is an excess of high values in the population; the histogram will give a frequency curve skewed to the right, in the direction of the high values (positive skewness). If the population was lognormally distributed, the main branch *Ox* should extend as a straight line in *Oz* whereas, in this case, *Oz* is lifted to *Oy* which means that instead of having 2.5% of the values 30 ppm or greater, there are 17% of them. The abscissa of the breaking point, *O*, (in this case 18 ppm) indicates the limit above which there is a departure from the norm (i.e., from the lognormal distribution), an excess of high values. In this case, background and coefficients of deviation are calculated with the main branch *Ox*. The abscissa of the breaking point may be conveniently taken as threshold value if the break occurs above the normal threshold level of 2.5%. If, however, the break occurs below 2.5% level (at point *p* for instance) the threshold should be taken as usual (abscissa of point *P*). Positively broken distribution lines are the more interesting because they indicate an excess over the background mineralization.

Molybdenum Distribution (in a lithological unit). The cumulative distribution line shows two breaks: first a positive, then a negative one. Such a graph is the expression of a dual distribution, suggesting the existence of two distinct populations in the set of data considered. It gives a double-peaked histogram. We shall consider here only the most frequent case of a main "background" population mixed with a smaller one of higher average value, the two of them being lognormally distributed. On the diagram (Fig. 5), branch A corresponds to the main or normal population, branch B to the anomalous population and the central branch $A + B$ to a mixture of the two. By splitting the data at a value taken around the middle of $A + B$ (at 4 ppm for instance), it is possible to separate the total population into two elementary ones appearing as *a* and *b* on the diagram. The general background will be taken with branch *A* and the threshold as the abscissa of the middle of branch $A + B$, though the threshold of population *a* may also be considered, but we have not enough examples of such complex distributions to make definite recommendations, and we lacked computing facilities to calculate theoretical distributions. The coefficients of deviation must be calculated separately for distributions *a* and *b*.

Zinc Distribution (in a drainage unit). The negatively broken line on Figure 5 is the expression of an excess of low values in an essentially lognormal distribution; in this case, the histogram is skewed to the left, toward these low values (negative skewness). Provided their proportion is not too high (20% or less or instance), they do not interfere in the interpretation, which is done on the main branch of the distribution line in the usual way. This excess of low values may be due to the inclusion in the population of a low-background lithological unit or, more often, to poor sampling (for instance, collecting an important set of sediment samples that are too coarse).

When the results do not fit a lognormal distribution, an explanation may generally be found among these three factors: (1) lack of homogeneity in sampling, (2) complex geology (imprecision in the lithological boundaries), and (3) analytical errors.

It should also be kept in mind that some elements in some surroundings may not be lognormally distributed.

Advantages of Cumulative Frequency Curves

Plotting the distribution of an element in a selected unit as cumulative frequency curve on probability graph paper is the easiest and most precise way to present a great amount of data (for instance, presenting Figure 5 as histograms and frequency curves will result in an overloaded and illegible diagram). All the characteristic parameters of the distribution can be estimated without cumbersome calculations. Comparison between various populations are easy and complex distributions are clearly identified. Furthermore, the adjustment to a lognormal distribution can be checked graphically.

Comparing the geochemical features of the various units of a survey area is important in assessing their mineral potential. This is conveniently done by plotting the corresponding distributions on the same diagram—for instance Cu distribution in three or four different drainages in the case of a stream sediment reconnaissance. Distribution heterogeneities will be spotted and the corresponding units selected for further investigations. On a broader scale, the geochemical behavior of trace elements in a given geological environment from different countries or metallogenic provinces can be readily compared. This is an approach to a better understanding of the distribution laws of trace elements in naturally occurring materials.

The Coefficients of Deviation

A lognormal distribution is completely determined by two parameters: the geometric mean (*b*) and the coefficient of deviation (*s*). It has been seen that the *absolute deviation* can be expressed as a geometric factor s' or, more commonly, as a logarithmic coefficient *s*. The term "deviation" is preferred to "dispersion" which might be more expressive, because there is no genetic implication in the concept of statistical dispersion whereas there is one in the notion of geochemical dispersion; however, many people use the term "dispersion" in statistical interpretation of geochemical data.

The coefficient of deviation is a dispersion index specific for the distribution of a given element in a given environment and expresses the degree of homogeneity of this distribution. When rocks are considered, a similarity in the coefficient of deviation, together with similar average values, may indicate similar geochemical processes in their formation.

It is possible that a given value of *s* corresponds to each type of mineralization in a lithological unit. Confirming this assumption would require very extensive geological-statistical studies encompassing all metallogenic cases.

There is also a relationship between the background (*b*) and the coefficient of deviations (*s*) which is the expression of the geochemical law which states that the dispersion of an element is inversely proportional to its abundance. This is expressed very clearly by the relative dispersion s'' (or relative deviation), a percentage related to b and s as follows:

$$s'' = 100\,\frac{s}{b}$$

The higher the background, the lower the relative deviation. This is best shown on a log/log correlation diagram by plotting s'' as abscissa and b as ordinate. Figure 6, for instance, shows the variation of s'' in function of b in the different lithological units of Blocks I and II, for Cu, Zn, Pb and Mo. The diagram has been constructed by taking, for each element, the extreme values for b and s'', thus determining parallelograms including all the individual values. One sees immediately that there is an inverse linear relationship between b and s'' (which is evident from the definition of s'') and that the average absolute deviation s (graphically estimated in Fig. 6) also decreases when the abundance of the element increases.

The weighted mean values of b, s and s'' for each element have been calculated separately for Blocks I and II:

Block I	b	s	s''	Block II	b	s	s''
Zn	55.	0.23	0.42	Zn	70.	0.17	0.24
Cu	8.	0.34	4.2	Cu	8.	0.30	3.8
Pb	6.8	0.32	4.7	Pb	5.8	0.30	5.2
Mo	0.38	0.37	97.5	Mo	0.35	0.40	125.

The fact that the absolute deviation for Pb is equal to or slightly lower than that for copper is due to two factors: (1) the sensitivity limit of the analytical method for lead, which entailed a number of assumptions and extrapolations in the interpretation—determination of b and s, and (2) the existence of some Pb mineralized zones in the survey area where b was high and s low.

Figure 6. Correlation diagram b/s" for blocks I and II

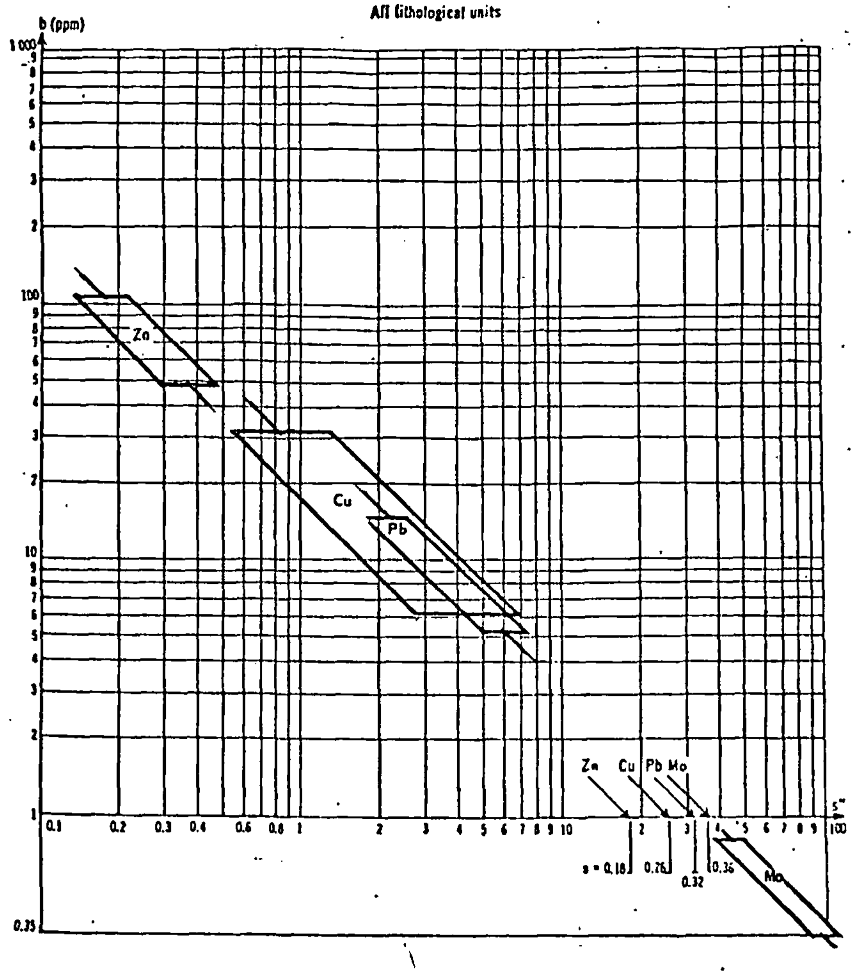
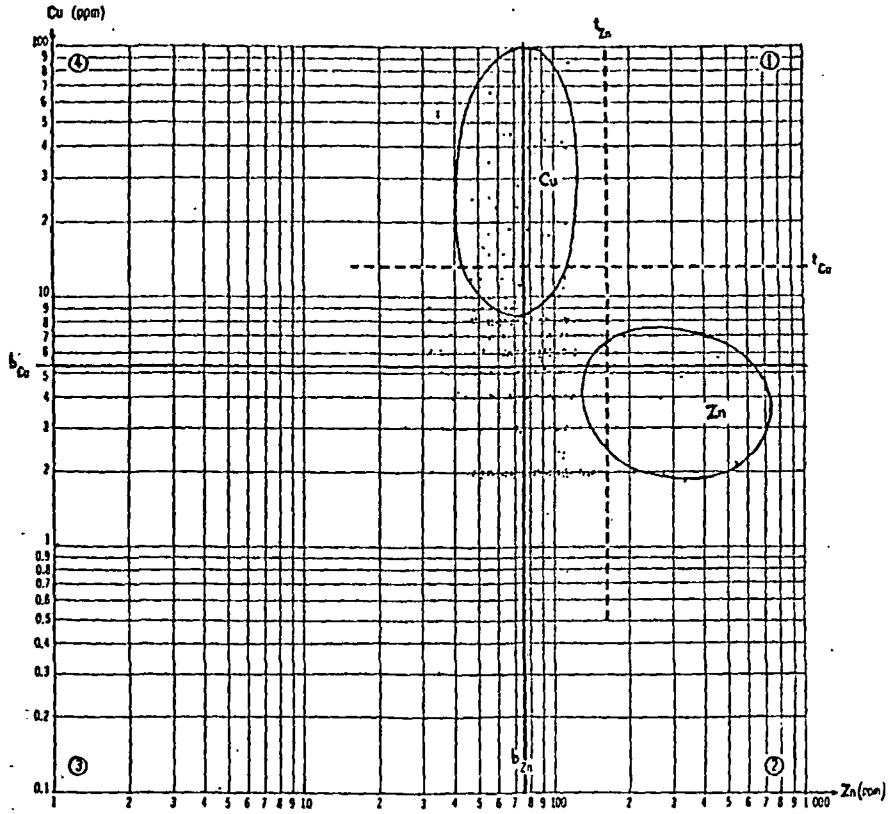


Figure 7. Correlation diagram Cu/Zn



$$\left.\begin{array}{l} n_1 = 98 \\ n_2 = 88 \\ n_3 = 70 \\ n_4 = 105 \end{array}\right\} \begin{array}{l} N_1 = n_1 + n_3 = 168 \\ N_2 = n_2 + n_4 = 193 \end{array} \Bigg\} \rho = \sin\left[\frac{\pi}{2} \cdot \frac{N_1 - N_2}{N_1 + N_2}\right] = -0.11$$

In Figure 6, it is also interesting to note the variations of the dispersion of the same element in different lithological units which is particularly noticeable for copper; the width of each parallelogram indicates the range of variation of s for each element.

The coefficient of deviation is a very important character of the distribution of an element in a given surrounding; it is probably related to the type of geochemical dispersion, mechanical or chemical, and consequently might give an indication of the type of anomaly encountered: syngenetic or epigenetic. It appears that a higher coefficient of deviation indicates a preponderantly mechanical dispersion, but this has not been proved. Much remains to be done in this field.

Correlation Diagrams

In the case of a polymetallic mineralization, with two or more elements lognormally distributed, there is generally a positive correlation between them; for instance between lead and zinc, a sample high in Pb is commonly also high in Zn. This geologic concept of a relationship between two types of mineralization (only qualitative and rather vague) may be substituted by a precise factor, the coefficient of correlation ρ, which gives a rigorous measure of their degree of dependency. In the case of geochemical prospecting, ρ measures the degree of dependency of two lognormal variables namely the tenors of two elements in a sample population (Matheron, 1962).

The coefficient ρ always falls between -1 and $+1$. $\rho = 0$ means a complete independence between the two elements, $\rho = \pm 1$ indicates a functional relationship, direct or inverse, between them (it is a linear relationship between the logarithms of the tenors).

Simplified Calculation of ρ.—There is a graphical way to estimate ρ, slightly less precise but much faster than the complete statistical calculation: constructing a *correlation cloud* in full log. coordinates (Fig. 7, 8). Each sample of the population under study is plotted following its two coordinates: its tenor in element A and its tenor in element B and the total population appears as a cloud of points.

Practically, this presentation of the data is very convenient because it gives a geometric image of the distribution laws. The axes passing by the gravity center (b_A, b_B), that is to say by the point whose coordinates are the background values for the two considered elements, are then drawn. In Figure 7, the axes will pass through the point ($b_{Cu} = 5.3$ ppm, $b_{Zn} = 75$ ppm). The points falling in each quadrant are summed up and counted as follows:

N_1 = number of points in first and third quadrants
N_2 = number of points in second and fourth quadrants.

Then ρ is given by the formula:

$$\rho = \sin\left[\frac{\pi}{2}\cdot\frac{N_1 - N_2}{N_1 + N_2}\right]$$

Practically, ρ is never equal to ± 1 (which would be the case if all the points were on a straight line) and the points form an elliptical cloud. Two cases may happen:

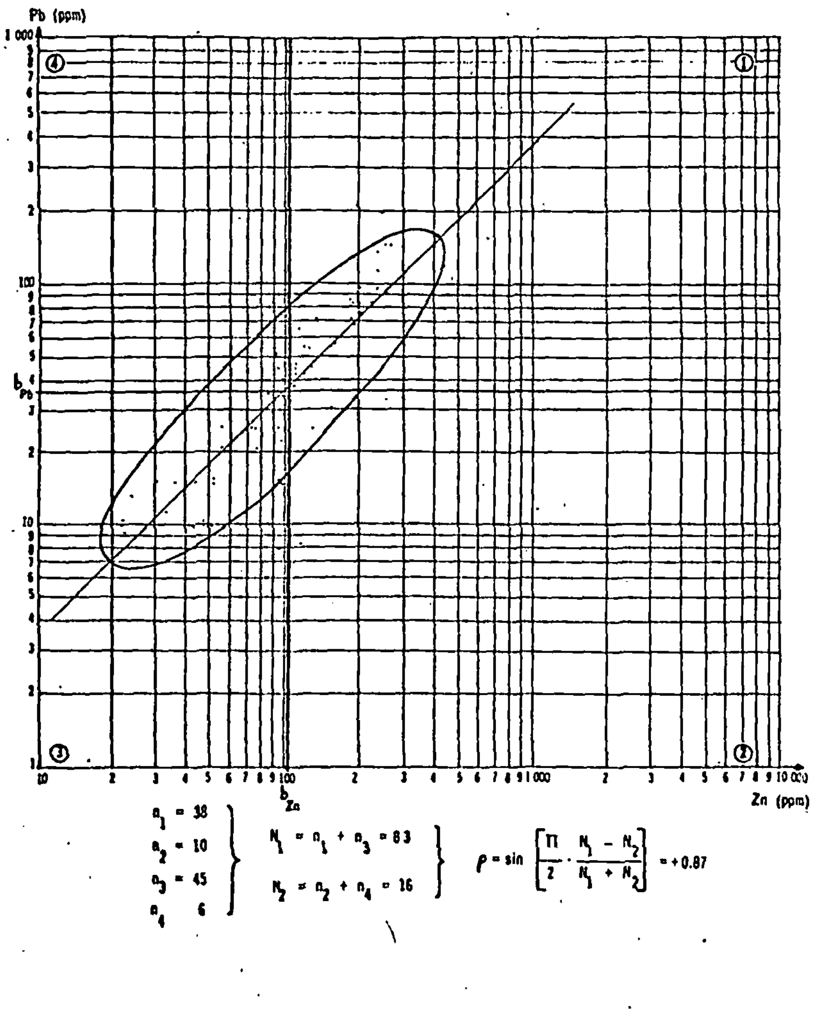
(1) either ρ is equal or near to zero: the elliptical cloud has its axes parallel to the coordinate axes and the two variables are independent,

(2) or ρ is clearly different from zero and the cloud is an ellipse whose axes are inclined relative to the coordinates. The slope of the main axis has the same sign as ρ (if $\rho > 0$ the two elements vary in the same direction; if $\rho < 0$ the two elements vary inversely).

The correlation cloud is in fact a two dimensional histogram; it is the best and simplest way to establish whether a population is homogeneous or heterogeneous: in the first case, the points tend to group in a single elliptical cloud; in the second, they split into 2 or several attraction centers and form several elliptical clouds more or less overlapping. G. Matheron points out that the relation expressed by ρ is an expression of the Mass Action Law if $\rho = \pm 1$ (or of the order of ± 0.95) (Matheron, 1962); then it is likely that a geologically based chemical equilibrium exists between the two elements considered.

In geochemical prospecting, correlation coefficients

Figure 8. Correlation diagram Pb/Zn



may be used to assess mineral associations of elements in natural samples. The correlation diagram shows whether two elements are spatially associated and if one may be used as a pathfinder for the other.

Let us consider two examples: the relationship of Cu/Zn in the drainage of the Suchiate River (Fig. 7) and the relationship of Pb/Zn in the Rio Grande drainage (Fig. 8).

The first example, in Figure 7, is intended only to illustrate the lack of relationship between two types of mineralization. The cloud of points has no definite shape, but it can be divided into three zones: one around the intersection point of the axes, including the majority of the points which are spread more or less equally among the four quadrants; an elliptical one, marked Cu, in the range high-Cu/background-Zn values; and a third one, including only a few high-Zn/background-Cu points. This shows that, in the Suchiate drainage, there is no relationship whatsoever between the Cu and Zn mineralization, that the Cu anomaly is more important than that for Zn and that the two anomalies are well separated spatially. All this is expressed by the coefficient of correlation:

$$\rho = -0.11$$

Its low absolute value indicates a nearly complete independence of the two mineralizations, with a tendency to inverse relationship (negative value).

On the contrary, Figure 8 shows an example of direct relationship between two types of mineralization. In the Rio Grande drainage, Pb and Zn are associated: the correlation cloud is an elongated ellipse whose main axis has a 45° slope and the correlation coefficient $\rho = +0.87$. In this drainage, lead and zinc anomalies will have the same pattern and will be spatially related. In similar geological conditions, one element may be used as a pathfinder for the other.

Conclusion

In the Guatemalan geochemical reconnaissance, the statistical analysis of the data, although elementary, was useful in outlining subdued anomalous patterns in a complex geochemical surrounding, but much more information can certainly be extracted from the analytical results by a more thorough, computer-oriented, treatment.

The graphical methods described above have the great advantage of being quick, cheap and easy to use in the field without any special mathematical knowledge. It is a convenient and synthetic way to present a great amount of geochemical data, and I think it might be useful to any geologist involved in geochemical prospecting.

United Nations Mineral Survey,
Guatemala City, Guatemala,
January 20; March 28, 1969

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WATSPEC: A COMPUTER PROGRAM FOR DETERMINING THE EQUILIBRIUM SPECIATION OF AQUEOUS SOLUTIONS

by

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EDITORS' PREFACE

The publication of the Technical Bulletins by the British Geomorphological Research Group arises out of a common need, expressed by the Group as a whole, to have a source of standardised information relating to increasingly sophisticated methods of data collection and data handling. The demand for such Bulletins is three-fold: for comparability of results among workers in the field; for the dissemination of information concerning techniques, particularly where this speeds up and facilitates the execution of a research programme, and for manuals which stress particularly the uses and limitations of the techniques in the field of geomorphology.

The authors and editor have endeavoured to ensure accuracy and where necessary the manuscripts are being forwarded before publication to interested commercial firms for critical evaluation. In other respects the authors alone are responsible for the views expressed.

EDITOR:-

Dr. T.C. Atkinson, School of Environmental Sciences,
University of East Anglia,
Norwich, NR4 7TJ,
England.

INTRODUCTION

This monograph describes the development and use of a computer program for interpreting chemical data from the aqueous environment; rivers, lakes, groundwaters and the ocean. The need for such a program arises because standard chemical analyses only tell the <u>gross</u> chemical makeup of a natural water sample (i.e. the <u>total</u> amount of calcium, magnesium, sulphate etc. in solution) rather than the concentrations of the individual free ions. Furthermore, such analyses do not immediately reveal the thermodynamic state (or saturation level) of a water sample with respect to various common minerals such as calcite, dolomite, gypsum and the clay minerals. In order to find out the detailed chemical makeup of a water sample, and its thermodynamic state some sort of iterative mathematical juggling is required to obtain the values of more fundamental variables from those which are usually measured in the laboratory or field. In most cases this juggling is best done by a computer.

The computer program given here, WATSPEC, is a relatively simple water chemistry manipulator. It has a wide range of applicability, and can be used to analyse water sample data from the most dilute waters to those 2 or 3 times more saline than seawater. The most commonly occurring cationic and anionic species are included as input variables. The program uses a simple computational algorithm which can be easily understood and so adapted to suit individual needs.

The chemical and mathematical bases of WATSPEC are explained in some detail in the following sections assuming very little background knowledge on the part of the reader. It is hoped that in this way WATSPEC can act as an introduction to the basic chemistry necessary for a proper understanding of the chemical processes which occur in natural waters. Naturally, in a work of this length, some fundamental concepts must be left unexplained or only partially explained. For more detail the reader is directed towards the excellent texts of Garrels and Christ (1965) and Stumm and Morgan (1970).

Before proceeding with a detailed description of WATSPEC and its theoretical foundations, a word of caution is in order. Like all computer 'package' programs, WATSPEC is a tool which should not be used blindly. This is particularly important here because a great deal of basic chemistry is hidden within the program. Some understanding of this chemistry is essential before one can reliably use and interpret the program's output. The thermodynamic data and solution chemistry used in WATSPEC is the result of many decades of experimental and theoretical development work by many authors. The theoretical approach used is one of a number of possible approaches: although it is one which is popular, which makes considerable physical sense, and which can be applied successfully to many situations. The user should bear in mind that WATSPEC is essentially an equilibrium thermodynamic model of the aqueous phase. The validity of the assumption of equilibrium should always be examined before results from WATSPEC are interpreted. Finally, WATSPEC accounts only for commonly observed inorganic species. The presence of significant amounts of other more unusual inorganic species may invalidate the results. The presence of dissolved organic material may have similar effects.

WHY THE COMPUTER?

In this application the computer is basically a time-saving device. In principle the calculations performed by WATSPEC could be performed 'by hand': indeed, in the past, this was the only means available. One might, therefore, ask the more fundamental question: why not use the raw data for interpretation? In some circumstances this is possible; considerable insight into natural chemical processes can be gained from an examination of changes in total species concentrations (e.g. total hardness), from cation or anion ratios (e.g. total Mg to total Ca ratio) and other directly measured variables such as pH. However, in some ways this is like trying to understand the mechanics of a car engine from its outside: WATSPEC breaks a water sample down into its constituent parts. Most chemical species are present in solution in a number of forms; as free ions, or as various ion pairs, loosely combined with other species. In addition, the thermodynamic behaviour of a species in solution is determined by its activity rather than by its concentration. (The relation between concentration and activity will be defined later).

WATSPEC determines the detailed composition of a solution, the concentrations and activities of all species. Once the detailed composition of a solution is known it is possible to determine in a fundamental and precise way the level of saturation of the solution with respect to any mineral. Saturation level then determines whether the solution has the thermodynamic potential for further dissolution or for precipitation of that mineral, and additionally allows one to conjecture about the past and future evolution of the water sample. In some cases it is possible to determine saturation levels either experimentally or graphically: but such methods lack generality and usually have other drawbacks.

Computer analysis also facilitates the calculation of other derived variables used in water sample interpretation. WATSPEC, for example, calculates the carbon dioxide partial pressure of the sample (strictly the partial pressure of a CO_2 gas phase which would be in equilibrium with the water sample) and determines the charge balance error, a useful parameter for detecting errors in chemical analysis.

Finally, computer programs like WATSPEC form the basis for more complicated programs which can be used to synthesize or model natural processes such as mixing of waters of different composition, mineral precipitation and dissolution, incongruent solution (i.e. simultaneous dissolution of one mineral and precipitation of another), evaporation and CO_2 degassing.

UNITS

The results of chemical analyses can be expressed in many different ways: parts per million, milligrams per litre, equivalents or milliequivalents per litre, molarity and molality beir the most common. WATSPEC accepts input in millimoles per litre of solution (i.e. millimolarity) and conversion of input data into these units is essential. It would be possible to modify WATSPEC to accept and translate any type of input units. I have chosen not to do this partly in order to keep WATSPEC simple and straightforward, and partly because some personal data manipulation keeps one 'in touch' with the data and able to detect and correct gross errors early in the analysis.

Perhaps the most fundamental concentration variable is the mole fraction. In aqueous solutions its analogue is molality defined as the number of moles of solute per Kg of water. A mole is a mass unit equal to the gram-formula-weight (GFW). The prefi 'm' is commonly used for molality, so that $mHCO_3$ denotes the bicarbonate molality and mX would denote the molality of a general species 'X'. Formality and molarity are closely related to molality. The three are defined below:

$$\text{molality (m)} = \frac{\text{mass of solute in gms}}{\text{GFW (mass of water in Kg)}} \quad \ldots.(1)$$

$$\text{formality (f)} = \frac{\text{mass of solute in gms}}{\text{GFW (mass of solution in Kg)}} \quad \ldots.(2)$$

$$\text{molarity (M)} = \frac{\text{mass of solute in gms}}{\text{GFW (volume of solution in litres)}} \quad ..(3)$$

These three quantities are related (since mass of solution = mass of water + total mass of solutes) by the following:

$$M = \rho f \quad \ldots.(4)$$

$$m = \frac{M}{\rho(1-S)} = \frac{f}{1-S} \quad \ldots.(5)$$

where ρ = density of solution (gm/cc or Kg/l)

and $S = \frac{\text{total mass of solutes}}{\text{total mass of solution}}$

For most aqueous solutions the density is close to 1 (e.g. the density of seawater is about 1.035 Kg/l) and the solution itself is dominantly water so that S is very much less than 1. In these circumstances M, m and f are almost equal.

Direct chemical analysis (e.g. by titration) usually gives the result as molarity or in units easily converted to molarity (such as parts per million or milligrams per litre).

has therefore been chosen for data input. However, WATSPEC uses molality for internal calculations. A conversion is necessary and this requires a knowledge of both S and ρ. WATSPEC calculates S and uses equation (5) to convert the input into molalities. If density is not specified then it is assumed by WATSPEC to be 1. In this case the calculations are only approximate (since $\rho \neq 1$ in general) although the approximation is a very good one.

In geomorphology and hydrology chemical data are often given in parts (of the specific ion) per million (of solution), parts per million $CaCO_3$ equivalent, or milligrams per litre. Parts per million (ppm) is a direct concentration variable defined by

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \qquad \ldots.(6)$$

However, solution mass is rarely measured and chemical analyses are usually based on volume. Frequently units reported as ppm are in reality milligrams per litre

$$\text{mg/l} = \frac{\text{mass of solute in mg}}{\text{volume of solution in litres}} \qquad \ldots.(7)$$

To convert ppm to mg/l one must multiply the concentration in ppm by the density (gm/cc or Kg/l). The two are only identical when the solution density is 1. To convert mg/l to millimolarity one need only divide the concentration in mg/l by the gram formula weight of the solute.

In carbonate waters concentrations are often expressed as ppm-$CaCO_3$ equivalent (ppm*). To convert ppm* to ppm one generally multiplies ppm* by the ratio

$$\frac{\text{gram formula weight of solute species}}{\text{gram formula weight of } CaCO_3}$$

although there is an important exception to this rule (see below). The GFW of $CaCO_3$ is 100.08835 gms. Frequently ppm* is reported when the units actually employed are milligrams-$CaCO_3$ equivalent per litre (mg/l*). Division of mg/l* by 100.08835 converts these units to millimolarity. Alkalinity (which will be defined later, *but which is roughly equivalent to bicarbonate ion concentration*) is sometimes expressed as ppm*. Taking alkalinity to be equal to bicarbonate ion concentration, one would expect the conversion from ppm* to ppm to be effected by multiplying ppm* by $\frac{61.01732}{100.08835} = 0.60963$ (61.01732 is the GFW of HCO_3^-). This is not the ase, however, and the correct factor is 1.21927. This anomaly rises because the dissolution of calcite may be written as the eaction

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{++} + 2HCO_3^- \qquad \ldots.(8)$$

ccording to (8) dissolution of one mole of $CaCO_3$ leads to two oles of HCO_3^-. The appropriate conversion factor in this case is herefore 2(0.60963) = 1.21927. Using the factor 0.60963 is quite a common error and leads to an underestimate of the alkalinity and a large positive charge balance error.

The final commonly-used concentration measure is equivalents (or milli-equivalents) per litre of solution. This is defined as the number of gram-equivalents per litre of solution where one gram-equivalent is the number of grams of substance which will react with or produce one gram of hydrogen. Frequently equivalent per litre are almost identical to molarities (i.e. except for a factor 1.00797, the GFW of hydrogen), but there can be large differences in some cases. For example, one mole of carbonic acid (H_2CO_3) produces 2 moles of hydrogen so its equivalent weight and formula weight differ by a factor of approximately 2.

THERMODYNAMIC BACKGROUND

(1) Activities and Activity Coefficients

Most chemical calculations involve activities rather than concentrations. The activity, or effective concentration of a species, is a measure of the thermodynamic concentration or chemical potential of that species. Activity is denoted here by the prefix 'a' and activities and molalities are related by a factor called the activity coefficient (γ_X):

$$aX = \gamma_X mX \qquad \ldots.(9)$$

The activity coefficent of a charged species in solution is generally less than 1 and decreases as the total dissolved solids of the solution increases (although there are important exceptions to this generalization). The reason for this can be seen with a simple picture of ions in solution. By virtue of electrostatic attraction any charged species will attract oppositely charged species. Sometimes these will become attached to the original ion for a significant time period and form an ion pair (see below), but in general the original ion can be pictured as moving about with an attendant cloud of oppositely charged ions. This cloud tends to shield the ion from the bulk of the solution so that it is partly hidden from other species in solution: its apparent or effective concentration as far as other species are concerned is therefore less than its true concentration. This shielding effect is accounted for by the activity coefficient. For uncharged species the cloud will not occur and the shielding which produces activity coefficients below 1 will not result. As an empirical result, based largely on gas solubility studies, activity coefficients for uncharged species are taken to be slightly greater than 1. For some uncharged ion pairs, however, this has been questioned. $CaSO_4^0$ and $MgCO_3^0$ appear to behave like dipoles in aqueous solutions and have activity coefficients less than 1 (Reardon and Langmuir, 1976). WATSPEC does not incorporate this recent result.

(2) Law of Mass Action

Activities determine the direction of chemical reactions through the fundamental law of mass action. Consider as an example the reaction where species A and B (reactants) react to produce species C and D (products):

$$A + B \rightarrow C + D$$

All chemical reactions are reversible. Thus, if A,B,C and D are all present, species C and D will also react together to produce A and B:

$$C + D \rightarrow A + B$$

The two reactions will, in general, occur together. The composite or net reaction is said to be in equilibrium when the forward (i.e. A + B → C + D) and backward (i.e. C + D → A + B) reactions proceed at the same rate so there is no net production of reactants or products.

The net direction (i.e. forward or backward) of a chemical reaction is determined by the relative chemical potentials of reactants compared with products. Chemical potential (capacity to react) is analagous in many ways to mechanical potential energy (or capacity to do work). The chemical potential (prefix μ) of species X depends on the (natural) logarithm of its activity

$$\mu X = RT \ln(aX) + \text{constant} \qquad \ldots.(10)$$

where R is the gas constant and T is temperature in °K. Just like potential energies, chemical potentials are additive. The chemical potential of A and B is therefore $\mu A + \mu B$. The reaction is in equilibrium when the chemical potential of A + B is equivalent to that of C + D. In terms of activities (through equation (10)) this leads to the mathematical statement

$$\ln(aC) + \ln(aD) - \ln(aA) - \ln(aB) = \text{constant}$$

which can also be written as

$$\frac{aC\ aD}{aA\ aB} = K \qquad \ldots.(11)$$

where K is the equilibrium constant for the reaction. Equation (11) is a statement of the law of mass action. Since the relation between chemical potential and activity involves temperature (see equation (10)) equilibrium constants are in general functions of temperature. As a direct result of equation (11), if a species occurs n times in a reaction (e.g., $nX = Y + Z$) then the activity of that species must be raised to the power n in the law of mass action.

As a specific example consider the reaction between carbonate and hydrogen ions to form bicarbonate ion, or vice-versa:

$$CO_3^{--} + H^+ = HCO_3^-$$

(Note: the equality sign is used to indicate that no particular reaction direction is specified. By convention species on the left are called reactants and those on the right are called products). At equilibrium, the law of mass action necessitates that

$$\frac{aHCO_3^-}{aCO_3^{--}\ aH^+} = \text{constant} = K_{HCO_3^-} \qquad \ldots.(12)$$

(at 25°C the value of $K_{HCO_3^-}$ is $10^{10.329}$). When aCO_3^{--} and aH^+ are such that $aH^+\ aCO_3^{--} > \frac{aHCO_3^-}{K_{HCO_3^-}}$ the reaction (12) will proceed from left to right. Hydrogen and carbonate ion activities (and concentrations) will decrease and bicarbonate ion activity (and concentration) will increase until equilibrium is reached.

By convention, the law of mass action is always written in the form

$$K = \frac{\text{products}}{\text{reactants}}$$

In the example above HCO_3^- is the product species and $K_{HCO_3^-}$ is the association or formation constant for HCO_3^-. If the reaction were written $HCO_3^- = H^+ + CO_3^{--}$ then the corresponding equilibrium constant would be the inverse of $K_{HCO_3^-}$ and would be called the dissociation constant for HCO_3^-.

(3) Ion Pairs

Equation (11) is the basis for separating measured concentrations into their constituent parts, and for calculating saturation levels. Most dissolved species exist in solution both as free ions or in association with other species as ion pairs. In addition, most chemical analysis procedures (excluding some direct electrochemical techniques) do not distinguish between free ions and ion pairs. Thus, for example, calcium in solution occurs as the free ion Ca^{++} or as pairs with sulphate ($CaSO_4^0$), carbonate $CaCO_3^0$), bicarbonate ($CaHCO_3^+$), hydroxyl ($CaOH^+$) and other ions (the four mentioned here are the most important calcium ion pairs in natural waters and are the only Ca^{++} pairs considered in WATSPEC). Thus, the total calcium concentration (or molality), which is what would be measured by titration with EDTA for instance, is actually the sum of the constituent concentrations

$$mCa^T = mCa^{++} + mCaSO_4^0 + mCaCO_3^0 + mCaHCO_3^{\ +} + mCaOH^+ \qquad \ldots.(13)$$

In many situations a significant proportion of calcium may exist in the paired form. Wigley (1971) gives examples in which the free ion accounts for from 70.6 to 94.5% of the total calcium concentration, lower values corresponding to cases where sulphate was present in substantial amounts.

(4) Calculating the Concentrations of Individual Species

In natural waters it is generally assumed that dissolved (or aqueous phase) species are in mutual equilibrium within the solution, although the solution as a whole may not be in equilibrium with other phases such as solid minerals or gases with which it is in contact. Equilibrium within a single phase is termed homogeneous equilibrium, while that between different phases is termed heterogeneous equilibrium. The assumption of homogeneous equilibrium within the aqueous phase is a fundamental one. WATSPEC (and other computer programs similar to it) only gives the equilibrium chemical speciation of a water sample. Such programs are therefore only equilibrium models of the real situation, although generally very good models: they are collectively called aqueous models.

The assumption of homogeneous equilibrium is used to calculate the detailed speciation. For example, the free ions Ca^{++} and SO_4^{--} and the ion pair $CaSO_4^0$ will be in equilibrium (although calcium and sulphate species need not be in equilibrium with, for example, the mineral gypsum). The appropriate mass action equations can therefore be used to relate the ion pair activities to the free ion activities:

$$\frac{aCaSO_4^0}{aCa^{++}\ aSO_4^{--}} = K_{CaSO_4^0} \qquad \ldots.(14)$$

$$\frac{aCaCO_3^0}{aCa^{++}\ aCO_3^{--}} = K_{CaCO_3^0} \qquad \ldots.(15)$$

etc. In (14) and (15) the Ks are association constants for the ion pairs (i.e. the inverse of the dissocation constants). The activities in (14) and (15) can be replaced by products of activity coefficients and molalities (see equation (9)). If the results are then substituted into equation (13) one eventually obtains

$$mCa^{++} = mCa^{T}\left\{1 + \frac{\gamma_{Ca^{++}}\ \gamma_{SO_4^{--}}\ mSO_4^{--}\ K_{CaSO_4^0}}{\gamma_{CaSO_4^0}} + \frac{\gamma_{Ca^{++}}\ \gamma_{CO_3^{--}}\ mCO_3^{--}\ K_{CaCO_3^0}}{\gamma_{CaCO_3^0}} + \frac{\gamma_{Ca^{++}}\ \gamma_{HCO_3^-}\ mHCO_3^-\ K_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}} + \frac{\gamma_{Ca^{++}}\ \gamma_{OH^-}\ mOH^-\ K_{CaOH^+}}{\gamma_{CaOH^+}}\right\}^{-1} \qquad \ldots.(16)$$

Similar results can be written for all of the other species, relating total molalities (e.g. mCa^T) to the molalities of key species (e.g. mCa^{++}). WATSPEC accepts as input data total molalities of calcium, magnesium, sodium, potassium, chloride, carbonate, sulphate, aluminium, iron, strontium, barium, lithium, nitrate, silicate, borate, bromide, sulphide and ammonium species. Carbonate species are determined by alkalinity (see below). The key species here is HCO_3^-. In this and in all other cases the key species is that which dominates over other species related to it in 'normal' natural waters. For example $Al(OH)_4^-$, $H_4SiO_4^0$ and $H_3BO_3^0$ are the key species for aluminium, silicate and borate.

Equations like the equilibrium relations (14) and (15), and *the restated mass balance criterion (16) (which is derived from* the mass balance equation (13)) together form a complicated set of non-linear algebraic equations which is solved by WATSPEC to calculate the molalities of all the individual species in solution. The method which WATSPEC uses to solve these equations is described below in the section on Iterative Methods.

(5) Extended Debye-Hückel Equation

In order to use equations like (14), (15) and (16) it is necessary to know all the activity coefficients, and all the equilibrium constants. *The former are determined by the temperature* and ionic strength of the solution; the latter are, in general, known functions of temperature and pressure. Ionic strength is a measure of the total concentration of charged ions in solution. It is defined by

$$I = \frac{1}{2}\sum_{i=1}^{n} mX_i\ (Z_i)^2 \qquad \ldots.(17)$$

where Z_i is the charge on species X_i, mX_i is the molality of species X_i and the summation is over all charged species. For dilute solutions (ionic strength less than 0.1; for reference, the ionic strength of seawater is approximately 0.7) activity coefficients of charged species can be determined using the Extended Debye-Hückel equation (see, for example, Stumm and Morgan, 1970, p.83)

$$-\log\ \gamma_i = \frac{A\ Z_i^2\ \sqrt{I}}{1 + a_i B\sqrt{I}} \qquad \ldots.(18)$$

where A and B are known functions of temperature and a_i is a parameter called the effective ion radius (which has known values determined from experimental data for most common ions). This equation, and the following modification of it, depends on an empirical rule called the MacInnes convention which gives excellent results up to high ionic strength. For ionic strengths above 0.1 it is necessary to further 'extend' the Debye-Hückel equation empirically (introducing another parameter, b_i) to

$$-\log\ \gamma_i = \frac{A\ Z_i^2\ \sqrt{I}}{1 + a_i\ B\sqrt{I}} + b_i\ I \qquad \ldots.(19)$$

Equation (19), which WATSPEC uses, is based on measured activity coefficients and is valid up to ionic strengths of two or more (i.e. for solutions up to about three times as concentrated as seawater). The parameters a_i and b_i are determined empirically. They differ from ion to ion, and the value of a_i which is appropriate when using equation (19) is not necessarily the same as that which would be used with equation (18). For many species the value of b_i is zero. a_i and b_i values used in WATSPEC are those determined by Truesdell and Jones (1974) and used in WATEQ and WATEQF (Plummer et al, 1976).

Equation (19) generally gives a decreasing activity coefficient for increasing ionic strength up to moderate ionic strengths as predicted by the simple shielding explanation given earlier. At very high ionic strengths activity coefficients may begin to increase with increasing ionic strength, both in practice and according to the predictions of (19).

For uncharged species (such as, for example, the ion pairs $CaSO_4^o$ and $CaCO_3^o$) WATSPEC determines the activity coefficients using the empirical relation

$$\gamma = 10^{0.1I} \qquad \ldots.(20)$$

except for <u>free carbon dioxide</u> (defined below) where WATSPEC uses a more complex relationship, determined by Wigley and Plummer (1976), and for the activity coefficient of water where WATSPEC uses

$$\gamma_{H_2O} = aH_2O = 1 - .017(XTOT),$$

XTOT being the sum of the molalities of all dissolved species. (Note that the <u>molality</u> of H_2O is 1 by definition).

(6) <u>Alkalinity and Carbonate Systems</u>

It has already been noted that <u>alkalinity</u> is one of the input variables for WATSPEC, and that this is a measure of (and often approximately equal to) the bicarbonate ion concentration. Alkalinity is an important variable in carbonate systems, and these systems are most easily examined experimently by determining alkalinity and pH.

Consider a solution containing dissolved carbonate species. For simplicity I will omit ion pairs (such as $CaCO_3^o$, $CaHCO_3^+$, $MgHCO_3^+$ etc.) from the following discussion. The carbonate species then are: CO_2^o (dissolved carbon dioxide, alternatively written as $CO_{2,aq}$); $H_2CO_3^o$ (carbonic acid); HCO_3^- (bicarbonate ion) and CO_3^{--} (carbonate ion). At equilibrium these species are related by the chemical reactions

$$CO_2^o + H_2O = H_2CO_3^o$$

$$H^+ + HCO_3^- = H_2CO_3^o$$

$$CO_3^{--} + H^+ = HCO_3^-$$

for which the following mass action equations may be written

$$\frac{aH_2CO_3^o}{aCO_2^o \; aH_2O} = K_{CO_2^o} \qquad \ldots.(21)$$

$$\frac{aH_2CO_3^o}{aH^+ \; aHCO_3^-} = K_{H_2CO_3^o} \qquad \ldots.(22)$$

$$\frac{aHCO_3^-}{aCO_3^{--} \; aH^+} = K_{HCO_3^-} \qquad \ldots.(23)$$

The molality of water is unity so that, ignoring activity coefficients, the above is a set of three equations in five unknowns. Thus, any two will be enough to specify the whole set: e.g. H^+ and CO_3^{--}, together with (21), (22) and (23) determine HCO_3^-, CO_2^o and $H_2CO_3^o$.

Hydrogen ion activity can be directly measured as pH which is defined by

$$pH = -\log(aH^+) \qquad \ldots.(24)$$

The other variables are difficult to measure individually, and instead it is easier to measure alkalinity (ALK), defined for this system only (see below for a more general definition) by

$$ALK = mHCO_3^- + 2mCO_3^{--} + mOH^- - mH^+ \qquad \ldots.(25)$$

Note that mOH^- and mH^+ are related by

$$\frac{aH^+ \; aOH^-}{aH_2O} = K_{H_2O} \qquad \ldots.(26)$$

Equations (25) and (26) introduce two new variables (ALK and mOH^-) enlarging the set of equations to five with seven variables. Their advantage is that <u>alkalinity</u> is easily measured by titration with a strong acid. Thus, the carbonate system is completely determined by specifying pH and alkalinity, although the calculations become a little more complicated than the outline given above when activity coefficients and ion pairs are included.

In practice it is not necessary to know both CO_2^o and $H_2CO_3^o$ and they are invariably combined as one variable, the <u>free carbon dioxide content</u>:

$$mH_2CO_3^* = mCO_2^0 + mH_2CO_3^0$$

The notation used here, which follows Stumm and Morgan (1970), is a little misleading because CO_2^0 dominates over $H_2CO_3^0$ by a factor of about 1000. The notation is, however, well established.

The free carbon dioxide content is, in turn, frequently replaced by the CO_2 partial pressure of a hypothetical coexisting gas phase: PCO_2. PCO_2 and $H_2CO_3^*$ are related by Henry's Law:

$$aH_2CO_3^* = K_H \; PCO_2 \qquad \ldots.(27)$$

where K_H is a function only of temperature and which is usually given in units which determine PCO_2 in atmospheres. To go one step further it is often useful to employ the 'p' notation used in the definition of pH (viz. 'p' ≡ '-log') so that

$$pPCO_2 = -\log(PCO_2) \qquad \ldots.(28)$$

This notation is useful because PCO_2 is generally a small quantity. For the atmosphere $pPCO_2 \approx 3.5$ and for most groundwaters $pPCO_2$ ranges from 1.0 to 3.0.

The alkalinity definition given above (equation (25)) is only valid in an idealized carbonate system. There are, in fact, three different types of alkalinity; carbonate alkalinity, titration alkalinity and total alkalinity. The latter two are of concern here. Total alkalinity is a measure of the ability of a water to neutralize acids which are stronger than carbonic acid. In theory it can be determined by titration with a strong acid (0.1N HCl is often used) to the carbonic acid equivalence point (see Stumm and Morgan, 1970, for further details). In practice such titration is usually to the methyl orange end-point (pH ≈ 4.5), and not all theoretically neutralizable weak acid species are neutralized during titration because of slow chemica reaction rates. It is necessary, therefore, to distinguish a pra tical titration alkalinity from the ideal concept of total alkalinity.

WATSPEC accepts titration alkalinity (in milliequivalents per litre of solution) as input. For the species considered by WATSPEC titration alkalinity is defined by

$$\begin{aligned}ALK^* = {} & mHCO_3^- + mCaHCO_3^+ + mMgHCO_3^+ + mNaHCO_3^- + 2(mCO_3^{--} + mCaCO_3^0 \\ & + mMgCO_3^0 + mNaCO_3^-) + mH_3SiO_4^- + 2mH_2SiO_4^{--} + mH_2BO_3^- + mAlOH^{++} + \\ & + 2(mAl(OH)_2^+) + 4(mAl(OH)_4^-) + mHS^- + 2mS^{--} + mNH_{3,aq} + mOH^- + \\ & mCaOH^+ + mMgOH^+ + mSrOH^+ + mBaOH^+ + mLiOH^0 - (mH^+ + mHCl^0 + \\ & mHSO_4^- + 2mH_2SO_4^0) \qquad \ldots.(29)\end{aligned}$$

This expression only differs from the total alkalinity for the WATSPEC aqueous model in that iron-hydroxide species, which react slowly, have been neglected. Other programs use different definitions of titration alkalinity. For example, WATEQ uses

$$\begin{aligned}ALK^* = {} & mHCO_3^- + mCaHCO_3^+ + mMgHCO_3^+ + mNaHCO_3^- + 2(mCO_3^{--} + mCaCO_3^0 + \\ & mMgCO_3^0 + mNaCO_3^-) + mH_3SiO_4^- + 2mH_2SiO_4^{--} + mH_2BO_3^- + mAl(OH)_4^- + mHS^- \\ & + 2mS^{--} + mOH^- + mLiOH^0 - mH^+ \qquad \ldots.(30)\end{aligned}$$

The difference between ALK* as defined by equations (29) and (30) is usually very small.

(7) Mineral Saturation Indices

WATSPEC calculates saturation indices with respect to a number of minerals. This term, an abbreviation of 'degree of saturation' index, is a measure of the thermodynamic state of a solution relative to equilibrium with a specified solid-phase mineral. To illustrate, I will consider the mineral calcite. For a solution to be in equilibrium with solid-phase calcite the following reaction must be in equilibrium:

$$CaCO_{3,s} = Ca^{++} + CO_3^{--} \qquad \ldots.(31)$$

where subscript 's' denotes solid-phase. (Note that this is only a hypothetical reaction and doesn't precisely describe the mechanism by which calcite dissolves or precipitates: see Plummer and Wigley, 1976, and Plummer et al, 1977). The mass action equation for (31) is

$$aCa^{++} \; aCO_3^{--} = K_C$$

since solid-phase mineral activities are taken by convention to be unity. If the product $aCa^{++} \, aCO_3^{--}$ (called the ion activity product or IAP) is less than K_C then the 'reaction' (31) will proceed from left to right (i.e. dissolution will occur if one neglects any kinetic limitations to reaction progress), and if IAP > K_C then precipitation will occur. Equilibrium, or saturation corresponds to IAP = K_C, and the index

$$SI_C = \log\left\{\frac{IAP}{K_C}\right\} \qquad \ldots.(32)$$

is a measure of departure from equilibrium. Equation (32) defines the saturation index (SI) for calcite. $SI_C < 0$ means IAP < K_C and undersaturation with respect to calcite; while $SI_C > 0$ means IAP > K_C and the solution will be supersaturated with respect to calcite. Other saturation indices are defined in a similar way. Note that saturation indices only determine the thermodynamic potential for dissolution and precipitation: In practice, slow reaction kinetics may allow a solution to maintain a super- or undersaturated state for a very long period of time.

(8) Charge Balance

A balance between the total number of positive charges on positively charged ions and the total number of negative charges on negatively charged ions is an essential condition for any water sample. This charge balance condition can be written mathematically as

$$\sum_{i=1}^{n} mX_i \; Z_i = 0 \qquad \ldots.(33)$$

where Z_i is the charge on species X_i with molality mX_i and summation is over all charged species. Because of chemical analysis errors, and/or the existence of species which may be present in a sample but not measured, some imbalance of charge will invariably occur when one compares the total number of positive and negative charges. The probable level of charge imbalance depends on the completeness and accuracy of the chemical analysis procedures used: the acceptable level depends on what use is to be made of, or what implications are to be drawn from the data. Conclusions drawn from data which shows appreciable charge imbalance must be regarded as rather suspect.

Charge imbalance is often measured using the charge balance error which is defined by

$$CBE = \left\{ \frac{\sum^{C} mX_i \; Z_i - \sum^{A} mX_i \; Z_i}{\sum^{C} mX_i \; Z_i + \sum^{A} mX_i \; Z_i} \right\} 100\% \qquad \ldots.(34)$$

In equation (34) superscripts C and A over the summations indicate summation over cations and anions. CBE values outside the range ± 5% are usually sufficient for one to discard the data, or at least to examine it closely for errors in chemical analysis or conversion of units, or for omitted species. For instance, the possible error in converting alkalinity from ppm-$CaCO_3$-equivalent to other units mentioned earlier can produce CBE values up to 33%. Even larger errors can arise from neglecting to analyse for species such as sulphate or chloride when these species are actually present.

Because sulphate concentration is difficult and time consuming to determine, it is sometimes estimated 'by difference'. The method is to assume that any charge imbalance is due to (unanalysed) sulphate. This is definitely not a recommended procedure since the charge balance criterion is automatically fulfilled and no longer provides a check on the quality of the data.

(9) Reduction-Oxidation Reactions

Certain species can occur in different oxidation states: for example, iron occurs as Fe^{++} and Fe^{+++}. Reactions involving different oxidation states are called reduction-oxidation (or redox) reactions. Such reactions are conceptually analagous to acid-base reactions. In the same way that acids and bases may be interpreted as proton (or hydrogen ion) donors and receivers, reductants and oxidants can be defined as electron donors and receivers.

The following example has been taken from Stumm and Morgan (1970, p. 301)

reduction: $O_2 + 4H^+ + 4e^- = 2H_2O$ ....(35)

oxidation: $4Fe^{++} = 4Fe^{+++} + 4e^-$ ....(36)

redox reaction: $O_2 + 4Fe^{++} + 4H^+ = 4Fe^{+++} + 2H_2O$ ....(37)

This splits the simultaneous oxidation of Fe^{++} to Fe^{+++} and reduction of O_2 to H_2O (equation 37) into two parts (equations 35 and 36). Oxidation and reduction reactions always occur in pairs, as redox reactions, so that free electrons (e^- in (35) and (36)) do not actually occur in solution. Nevertheless, when redox reactions are split up in this way the electron can be considered as a 'virtual species' whose concentration determines the potential for oxidation or reduction and the relative concentrations of oxidized and reduced forms (such as Fe^{+++} and Fe^{++}) of any given species. Just as the proton activity is conveniently determined in logarithmic form by pH,

$$pH = -\log(aH^+),$$

so the electron activity is determined by the pe,

$$pe = -\log(e^-),$$

where e^- is the electron activity. The pe is a key variable in determining the relative amounts at equilibrium of all species which can occur in different oxidation states. Large positive pe implies strongly oxidizing conditions with a predominance of oxidized forms, while small or negative pe implies strongly reducing conditions with a preponderance of reduced forms. Examples of redox pairs or couples are Fe^{+++} and Fe^{++}; dissolved O_2 and H_2O; SO_4^{--} and dissolved H_2S; HCO_3^- and dissolved CH_4; and NO_3^- and dissolved NH_3. In all these pairs the oxidized form is given first.

In the field or laboratory pe can be determined by measuring the redox potential (Eh) which is the potential difference (in volts) between an inert (Au or Pt) electrode immersed in the solution and a standard hydrogen electrode. pe and Eh are related by

$$pe = \frac{Eh}{1.98422 \; 10^{-4} \; T}$$

where T is in °K. Eh is actually measured with a probe containing an inert electrode and a reference electrode (usually calomel) which has a known potential relative to the standard hydrogen electrode. The reference electrode potential must be added to the measured potential difference to obtain the Eh. Because the reference potential depends on temperature, a temperature correction may be necessary.

Eh is less commonly measured than pH for a number of reasons including:

(i) quite often either or both species in a redox pair occur in very low concentrations so that many important details of the speciation of a water sample can be determined without needing Eh data,

(ii) since many redox reactions are slow, the concentrations of many oxidizable and/or reducible species are frequently far from the values predicted by equilibrium thermodynamics,

(iii) Eh is a difficult parameter to measure electrochemically. Furthermore, to quote Stumm and Morgan (1970, p 350), 'Even when reproducible results are obtained .... quantitative interpretation with respect to solution composition is often not justified'.

Because of point (iii) WATSPEC (following WATEQ and WATEQF) can calculate Eh from the details of certain redox pair concentrations (specifically the SO_4^{--}, H_2S pair, and the dissolved O_2, H_2O pair). Even when using this method one should note that these pairs need not be in equilibrium; the O_2, H_2O pair is frequently not in equilibrium.

The redox pairs which WATSPEC considers are the five pairs given above. WATSPEC also considers a number of other species related to the individual pair members; species such as $Fe(OH)_3^0$, $FeSO_4^+$, HS^-, NH_4^+ and *many* others. For all these pairs and associated species, except for the ammonium species, concentrations are determined by using equilibrium thermodynamic data and the law of mass action for reactions such as equation (35) and equation (36). Since free electrons do not actually exist such mass action equations can only be interpreted in terms of the relative activities or concentrations of different oxidation states. By convention the reaction

$$2H^+ + 2e^- = H_2,gas$$

is arbitrarily assigned an equilibrium constant value of 1 and equilibrium constants for other redox reactions are determined relative to this value.

Two quantitative examples may help to clarify the issue and to illustrate the type of calculations which WATSPEC performs. Reaction (35) above may be written as

$$\frac{1}{2} H_2O = \frac{1}{4} O_2,aq + H^+ + e^- \qquad \ldots.(38)$$

where subscript 'aq' denotes the dissolved species. The equilibrium constant for this reaction at 25°C is $10^{-21.495}$. One can use this to calculate the pe of a solution which is in equilibrium with the atmospheric oxygen concentration. The partial pressure of oxygen in the atmosphere at sea-level is 0.21 atmospheres. Gas-phase partial pressures and aqueous phase activities are related by Henry's Law, which, for a gas 'X' is

$$aX = K_H\ PX$$

Here PX is the gas-phase pressure and K_H is the Henry's Law constant for species X. For oxygen at 25°C, K_H is $10^{-2.86}$, so that the equilibrium oxygen activity in the aqueous phase is $2.9\ 10^{-4}$. Now, from equation (38),

$$\frac{(aO_2,aq)^{\frac{1}{4}}\ aH^+\ e^-}{(aH_2O)^{\frac{1}{2}}} = 10^{-21.495} \qquad \ldots.(39)$$

Using $aO_2,aq = 2.9\ 10^{-4}$ and $aH_2O = 1$, and taking negative logarithms of both sides of equation (39) gives

$$pH + pe \approx 21.495 - \frac{1}{4}(3.5376) \approx 20.61$$

The pe of a solution in equilibrium with *atmospheric* oxygen therefore depends on the pH. At pH = 7.5 the pe is 13.11.

As a second example I will consider reaction (36) above and calculate the ratio of the activities of the free ions Fe^{+++} and Fe^{++} at equilibrium in a solution with pe = 13.11. Reaction (36) can be written as

$$Fe^{++} = Fe^{+++} + e^-$$

for which the equilibrium constant at 25°C is $10^{-13.013}$. The law of mass action gives

$$\frac{aFe^{+++}\ e^-}{aFe^{++}} = 10^{-13.013} \qquad \ldots.(40)$$

so that

$$\log\left\{\frac{aFe^{+++}}{aFe^{++}}\right\} = pe - 13.013$$

At pe = 13.11 the ratio aFe^{+++} to aFe^{++} would therefore be 1.25 (note: log(1.25) ≈ 0.097) if redox equilibrium existed. Actual water samples are often not in equilibrium with the atmospheric oxygen reservoir and these examples are only given to illustrate calculation procedures.

ITERATIVE METHODS

WATSPEC calculates the detailed chemical composition of a water sample (i.e. the concentrations of all free ions and ion pairs) from a knowledge of the total concentrations of various species. WATSPEC works within the limited framework of an aqueous model containing up to 18 total concentrations (70 individual species) and assuming homogeneous equilibrium between all species. Other similar programs consider more species, but WATSPEC has been designed to be a compromise between extreme generality and conciseness and simplicity. WATSPEC considers the most common species found in natural waters and the program is small enough and fast enough to be used on quite small computers. Although developed independently by the present author (the earliest version was written in 1970) the program has been modified to parallel WATEQF (Plummer et al, 1976) a program which is an expanded version of WATEQ (Truesdell and Jones, 1974).

The problem of finding individual species concentrations from total concentrations is often referred to as a 'chemical equilibrium problem'. WATSPEC solves this problem by using an equilibrium constant approach which was pioneered by Brinkley (1947). The basic equations are those of mass balance (e.g. equation (13); there are 18 such equations in WATSPEC) and a number of mass action equations (e.g. equations (12), (14), (15) etc.; WATSPEC uses 53 mass action equations). An early application of this approach was to determine the detailed chemical composition of seawater (Sillén, 1961; Garrels and Thompson, 1962). More recently, general computer programs have been developed by Ingri et al (1967) with HALTAFALL, Morel and Morgan (1972) with REDEQL, and others, and the field has been reviewed by Zeleznik and Gordo (1968), Dyrssen et al (1968), van Zeggeren and Story (1970) and Wolery and Walters (1975).

HALTAFALL, REDEQL and some other very general programs are limited by not including a general formulation of activity coefficients. Such programs are most useful in cases where the ionic strength of the sample is known and where empirical equilibrium constants, incorporating activity coefficients within them, can be specified. In many natural waters, however, the range of possible constituents is known and extreme flexibility of input components is not required. In addition, ionic strengths are not known a priori and can cover a wide range. For computer analysis of natural waters, therefore, a built-in formulation of activity coefficients is highly desirable. This need for less generality in one sense and increased generality in another has led to the development of a large number of programs specifically designed for the study of chemical equilibrium problems in natura waters. Examples of such programs are those used by Wigley (1971) Langmuir (1971), Thrailkill (1972) and van Breeman (1973), and the programs WATEQ (Truesdell and Jones, 1974), WATEQF (Plummer et al, 1976) and SOLMNEQ (Kharaka and Barnes, 1973). There are many others, both published and unpublished and of varying degrees of complexity.

To illustrate the chemical equilibrium problem and the method of solution employed by WATSPEC, I will consider a simple example in which there are only two major species (cation 'C', and anion 'A') and a single ion pair ('P'). In this case routine chemical analysis would determine the total molalities, mC^T and mA^T. The species in solution are (assuming singly charged major species) C^+ and A^- and the uncharged pair P whose activity is related to that of C^+ and A^- by the mass action equation

$$\frac{aP}{aC^+ \; aA^-} = \frac{\gamma_P \; mP}{\gamma_{C^+} \, mC^+ \quad \gamma_{A^-} \, mA^-} = K \qquad \ldots.(41)$$

The following mass balance relations must also hold

$$mC^T = mC^+ + mP \qquad \ldots.(42)$$

$$mA^T = mA^+ + mP \qquad \ldots.(43)$$

(cf. equation (13)). Since the activity coefficients are determined by the ionic strength, which in turn depends on mC^+ and mA^-, equations (41), (42) and (43) constitute a set of three equations in three unknowns which can be solved for the unknowns mC^+, mA^- and mP.

Unfortunately the ionic strength (and, hence, the activity coefficients) depends on the unknown concentrations. Either equation (41) must be replaced by a much more complicated equation, or one must solve the set of equations by an iterative method, even in this simple example. One such method is to use a first guess of the unknown concentrations, mC^+ and mA^-, and use these guesses to estimate ionic strength. This gives a first estimate for the activity coefficients which allows one to solve the equations to find a better estimate of mC^+, mA^- and mP. These values can be used to determine a better ionic strength estimate and the procedure can be repeated (iterated) over and over until negligible changes occur between each iteration.

In general, the main need for using an iterative solution is not due to the activity coefficient terms in equation (41), since activity coefficients are relatively insensitive to moderate errors in ionic strength (and hence in mC^+ and mA^-). In any realistic problem there is a much larger set of equations (over 70 in WATSPEC) and some sort of iterative method is necessary even without the ionic strength/activity coefficient difficulty.

To illustrate this, I will simplify equation (41) further by assuming all activity coefficients have the value one. Equation (41) becomes

$$mP = K \, mC^+ \, mA^- \qquad \ldots.(41a)$$

In this case (41a), (42) and (43) actually have an analytical solution given by

$$mC^+ = \frac{-1 + K\,(mC^T - mA^T) + \sqrt{(1-K(mC^T-mA^T))^2 + 4\,K.A^T}}{2K} \quad \ldots.(44)$$

and similar results for mA^- and mP. To make the problem less abstract I will take arbitrary numerical values of mC^T, mA^T and K:

$$mC^T = mA^T = 1$$

$$K = \tfrac{1}{2}$$

Substitution into (44) gives

$$mC^+ = \sqrt{3} - 1 = 0.732051\ldots.$$

To solve the problem by iteration on a computer (necessary ecause an analytical solution will generally not be possible) here are a number of different possible approaches. I will consider two only, a brute force method, which is perhaps the most bvious one, and a continued fraction method, which is the method mployed by WATSPEC. In the following the subscript denotes the rder of the iteration. In both methods we start with first uesses of

$$mC_1^+ = mC^T \quad \ldots.(45)$$

$$mA_1^- = mA^T \quad \ldots.(46)$$

n the brute force method, these estimates yield a first estimate f mP

$$mP_1 = K\,mC_1^+\,mA_1^-$$

hen (42) and (43) can be applied directly to give second estiates of mC^+ and mA^-:

$$mC_2^+ = mC^T - mP_1 = mC^T - K\,mC_1^+\,mA_1^-$$

$$mA_2^- = mA^T - mP_1 = mA^T - K\,mC_1^+\,mA_1^-$$

n general the (n+1)-th estimate can be found from the n-th estiate using

$$mC_{n+1}^+ = mC^T - K\,mC_n^+\,mA_n^- \quad \ldots.(47)$$

$$mA_{n+1}^- = mA^T - K\,mC_n^+\,mA_n^- \quad \ldots.(48)$$

In the continued fraction method equations (42) and (43) are rst juggled a little to give (cf. equation (16))

$$mC^+ = mC^T \left\{1 + \frac{mP}{mC^+}\right\}^{-1} = mC^T \left\{1 + K\,mA^-\right\}^{-1} \quad \ldots.(49)$$

$$mA^- = mA^T \left\{1 + \frac{mP}{mA^+}\right\}^{-1} = mA^T \left\{1 + K\,mC^+\right\}^{-1} \quad \ldots.(50)$$

If the same first estimates are used as before (equations (45) and (46)) then second estimates will be given by

$$mC_2^+ = mC^T \left\{1 + K\,mA^T\right\}^{-1}$$

$$mA_2^- = mA^T \left\{1 + K\,mC^T\right\}^{-1}$$

and the general iteration relations are (compare and contrast with (47) and (48))

$$mC_{n+1}^+ = mC^T \left\{1 + K\,mA_n^-\right\}^{-1} \quad \ldots.(51)$$

$$mA_{n+1}^- = mA^T \left\{1 + K\,mC_n^+\right\}^{-1} \quad \ldots.(52)$$

The name of this method comes from substituting successively for A_n^-, C_{n-1}^+, etc. in (51) to give a continued fraction

$$mC_{n+1}^+ = \cfrac{mC^T}{1 + K\,\cfrac{mA^T}{1 + K\,\cfrac{mC^T}{1 + K\,\cfrac{mA^T}{1 + K\,mC^T.}}}}$$

The table below compares the results of the two iteration schemes outlined above for the example with $mC^T = mA^T = 1$ and $K = \tfrac{1}{2}$. Iteration 7 should be compared with the exact analytic result, $mC^+ = .732051\ldots.$

Iteration number, n	1	2	3	4	5	6	7
mC_n^+ (brute force)	1	0.5	0.875	.617188	.809540	.672323	.773991
mC_n^+ (continued fraction)	1	0.666667	0.75	.727273	.733333	.731707	.732143

After seven iterations the brute force method is still out by .041940 while the continued fraction method is only out by .000092 It takes the brute force method 27 iterations before its error is less than this latter value.

It should be obvious from this example that the speed with which the correct answer is approached (and hence the computer time used in getting a satisfactory answer) depends critically on the type of iteration scheme used: in fact, in some circumstances, the brute force method never gets to a satisfactory answer! WATSPEC uses the continued fraction method, modified slightly to include activity coefficients, and is quite efficient in its use of computer time. Other methods are available, some of which are mathematically quite sophisticated and are a little more efficient than the continued fraction method. More detailed discussions of the numerical aspects of chemical equilibrium problems are given by van Zeggeren and Story (1970), Wolery and Walters (1975) and others.

HOW TO USE WATSPEC

WATSPEC is written in standard FORTRAN IV. The program accepts up to 18 total concentrations as input. Other input data required are temperature and pH (both essential) and density (optional). Eh can be specified in any of 5 ways, or omitted. Output is selective and contains a summary of input details, pe, P_{CO_2}, P_{O_2} and P_{CH_4} (as negative logarithms), ionic strength, total dissolved solids, total inorganic carbon molality, ion balance error, excess cation charge, species molalities for 69 species, and mineral saturation indices for 40 minerals. A source listing and sample input and output are given in Appendix C.

Input is given on 2, 3, 4 or 5 cards per sample. The number of samples which may be analysed at any one time is arbitrary and need not be specified. A card with 99 in columns 1 and 2 must be placed after the last sample to indicate the end of the data. The simplest data input requires two cards per sample; a (possibl blank) indicator card to indicate the extent of the data, and a major species card giving details of total concentrations of the species, calcium, magnesium, sodium, potassium, chloride and sulphate, together with titration alkalinity, pH and temperature (If any major species concentrations are unknown then they may be left blank or specified as zero on the major species card. Due allowances should be made in interpreting the output). More extensive data input requires more input cards (up to 5 per sample).

CARD 1: Indicator card (Format; (2I1,F10.0))

Column 1 gives the value of FLAG1 which indicates the presence (FLAG1 = 1) or absence (FLAG1 = blank, 0, 2-8) of reduction-oxidation data. Reduction-oxidation data, if available, is given on a separate card (CARD 3).

Column 2 gives the value of FLAG2. FLAG2 is the number of minor species cards (i.e. species not included on CARD 2). Minor species data are given on CARDS 4 and (if necessary) 5. (If there is no reduction-oxidation data these will be the 3rd and 4th cards). Each minor species card can have up to 6 minor species so FLAG2 can be 0 (or blank), 1 or 2.

Columns 3 to 12 give solution density in gms/cc or Kg/litr If density is unknown then this may be left blank or assig ed any value less than 1.0; in both cases WATSPEC assumes density = 1.0.

The simplest data input will therefore require a blank carc for CARD 1.

CARD 2: Major species card (Format; (9F6.0))

Temperature (°C), pH and seven major species total concentrations are given on this card. All concentrations must be as millimolarities (millimoles per litre of solution) except for titration alkalinity which is in milliequivalent per litre of solution. The data must be in the following order. Temperature, pH, total calcium, total magnesium, total sodium, total potassium, total chloride, titration alkalinity and total sulphate. Unknown values must be eithe left blank or specified as zero.

CARD 3: Optional Eh card (Format; (I1,2F10.0))

Eh may be specified in any of five different ways. The type of Eh input is specified by the value of FLAG3 given in column 1. FLAG3 may have the values 1 to 5. Columns 2 to 11 (ZZZ) give the value of the Eh variable. Columns 12 to 21 (EZ) are only used if FLAG3 = 3.

FLAG3 = 1: ZZZ is the electrochemically measured field Eh value in volts, corrected for sample temperatur

FLAG3 = 2: ZZZ is the uncorrected field Eh (Calomel reference).

FLAG3 = 3: ZZZ is the uncorrected field Eh (Calomel reference). With this option EZ (columns 12 to 21) must also be specified. EZ is the Eh of a standard Zobell's solution measured at the same temperature as the sample.

FLAG3 = 4: ZZZ is the negative logarithm of the oxygen concentration (in moles of O_2 per litre of solution). Eh is calculated using the water-oxygen redox pair (see equation (38) in the text).

FLAG3 = 5: ZZZ is the negative logarithm of the total sulphide concentration (in moles of H_2S per litre of solution). Eh is calculated using the sulphide-sulphate redox pair.

CARDS 4 and 5: Optional minor species cards (Format; (6(I2,G10.4)))

Details of minor species total concentrations are given on CARDS 4 (if less than or equal to six minor species) and 5. All these concentrations must be specified in millimoles per litre of solution (same units as CARD 2). Data must be given as pairs of numbers with the species number (I2) followed by the concentration (G10.4), with up to six pairs per card. Species may be in any order. The species numbers and the appropriate molal reference formulae are: 8, Al; 9, Fe; 10, Sr; 11, Ba; 12, Li; 13, NO_3; 14, SiO_2; 15, B; 16, Br; 17, H_2S; 18, NH_4. The G input format is a general format which accepts both F and E input formatted data.

Input of data on species which participate in redox rections requires further explanation. Data on minor species cards akes precedence over data on the Eh card in calculation of specation. This is significant for the sulphide-sulphate and ammonia itrate redox pairs. If Eh data of any form are given then sulhide species can be calculated from sulphate and pe. This is hat WATSPEC does, unless total sulphide is given on a minor pecies card. In this case WATSPEC uses the minor species data. rerun of WATSPEC with total sulphide omitted from the minor pecies cards would be needed to calculate the sulphide speciaion implied by sulphate and pe. If Eh data of any form is given hen the ammonia-nitrate redox pair could be used to calculate mmonium species from nitrate and pe, or nitrate from total mmonia and pe. WATSPEC performs these calculations if they are ossible and prints out the results, but does so independently f the main speciation calculations because this particular redox air is rarely in equilibrium. Only direct nitrate and/or ammonia oncentrations (on minor species cards) are used in the main peciation calculations; implied concentrations are never used.

WATSPEC is not infallible. The program may fail if thermoynamically inconsistent or incomplete data are given as input. ailure is unlikely in the 'normal' pH range of natural waters. approximately pH 5 to 11); and the program will accept some irly bizarre (though thermodynamically sensible) inputs such negative alkalinity at very low pH (i.e. below 4.5). WATSPEC ll detect and signal the presence of the following probable consistencies in the input data:

) Input of total iron with no Eh data given. In such a case there is no way to calculate the relative amounts of Ferrous (Fe^{++}) to Ferric (Fe^{+++}) species. WATSPEC automatically gives a warning and then calculates iron speciation using the arbitrarily chosen pe value of 10.0.

) Input of total sulphide with no Eh data given. Since total sulphate should almost invariably be an input variable, Eh could be calculated using the sulphide-sulphate redox pair (redox input option 5). The fact that this option has not been specified probably indicates an input error and WATSPEC signals this and then proceeds to the next sample.

) No convergence after 50 iterations. In the event of this extremely unlikely occurrence WATSPEC signals the fact, outputs all details as at the 50-th iteration and then proceeds to the next sample.

(4) Negative bicarbonate ion molality. If alkalinity and pH are thermodynamically inconsistent (e.g. very low pH and large positive alkalinity) then WATSPEC will generally discover this at the first iteration by obtaining a negative value for $mHCO_3^-$. If so, WATSPEC signals a warning and then proceeds to the next sample.

(5) Density less than 1.0. If density on CARD 1 is neither specified as greater than or equal to 1.0, nor left blank, then WATSPEC will print out a warning and change density to 1.0.

Subroutine PRINT in WATSPEC only prints out a selection of the data generated by the program. The program can easily be modified by the user to print out other details. For example, the user may wish to know individual species activities rather than molalities. To obtain this information one need only replace the X in line D 52 (WRITE(6,70) etc.) by A. Activities will be then printed instead of molalities, although the output will still show the heading '*****   INDIVIDUAL SPECIES MOLALITIES   ***'.

Finally, 99.99 and -99.99 are used in the output to indicate that there was insufficient data to calculate a given parameter. For example, if no Eh data is given, then pe, $-\log(PO_2)$ and $-\log(PCH_4)$ will be printed out as 99.99; and if any component of a mineral has zero concentration, or is unspecified, then the saturation index for that mineral will be printed out as -99.99.

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APPENDIX A

Key to species, minerals and reactions

In WATSPEC species molalities are labelled X(I), I=1,72, activities are labelled A(I), I=1,74, and total concentrations are Z(I), I=1,18. X(I), A(I) and Z(I) are keyed together so that X(I) and A(I) refer to the same species and Z(I) is the corresponding total concentration. For example; X(1) is the molality of Ca^{++}, and Z(1) is the total calcium molality; X(9) is the molality of $Fe(OH)_3^0$, and Z(9) is the total iron molality. Z(I) is also used for input total concentrations as millimolarity, but these are converted to molalities early in the program. A listing of species is given in Table A1. Numbers 67, 69 and 70 are not used, nor are X(I) equivalents to A(73) and A(74). A(75) is only used in subroutine PRINT where it is assigned the fixed value 1.

All equilibrium constant values are calculated for the given temperature in subroutine EQUCON and are denoted by K(I), I=1,77 (although not all values of I are used). The constants are keyed to the species, and are all association constants (except for K(73)). For example; X(6) is HCO_3^- and K(6) is the association constant for HCO_3^-; X(19) is the ion pair $CaOH^+$ and K(19) is the association constant for $CaOH^+$. The chemical reactions for all equilibrium constants are given in Table A1. K(77) is the Henry's Law constant for CO_2.

Mineral dissociation constants (KMIN(I), I=1,40) are determined for the given temperature in subroutine EQUCON. Mineral names and dissociation equations are listed in Table A2. In practice KMIN values are not actually calculated and WATSPEC only uses the logarithmic equivalents, PKMIN(I) where $pK \equiv -\log(K)$.

WATSPEC calculates the temperature dependence of species and mineral equilibrium constants using either the van't Hoff equation (see Garrels and Christ, 1965) or using an analytic expression. The thermodynamic data used in WATSPEC come from a number of sources and are the same as those used in WATEQF (Plummer et al, 1976) with the following exceptions:

(1) The Debye-HÜckel constants (A and B in equ.(19)) are calculated using a quadratic fit to data in the range 0°C to 100°C. The fit is accurate to within .0003 for A and to within .0001 for B. It is invalid above 100°C.

(2) The activity coefficient of $H_2CO_3^*$ is that calculated by Wigley and Plummer (1976).

(3) The dissociation constant for gypsum is that given by Wigley (1973). The WATEQF value will be used by default if line B 46 (PKMIN(17)=   etc) in subroutine EQUCON is removed or bypassed.

WATSPEC does not account for the pressure dependence of equilibrium constants.

For calcite two options are available in the literature (see Jacobson and Langmuir, 1974). WATSPEC chooses to include the ion pair $CaHCO_3^+$ in its calculations and uses the appropriate dissociation constant for calcite.

TABLE A1

NUMBER	SPECIES	REACTION
1	Ca^{++}	
2	Mg^{++}	
3	Na^+	
4	K^+	
5	Cl^-	
†6	HCO_3^-	$CO_3^{--} + H^+ = HCO_3^-$
7	SO_4^{--}	
8	$Al(OH)_4^-$	$Al^{+++} + 4OH^- = Al(OH)_4^-$
9	$Fe(OH)_3^0$	$Fe^{++} + 3H_2O = Fe(OH)_3^0 + 3H^+ + e^-$
10	Sr^{++}	
11	Ba^{++}	
12	Li^+	
13	NO_3^-	
14	$H_4SiO_4^0$	
15	$H_3BO_3^0$	
16	Br^-	
17	H_2S_{aq}	
18	NH_4^+	
19	$CaOH^+$	$Ca^{++} + OH^- = CaOH^+$
†20	$CaCO_3^0$	$Ca^{++} + CO_3^{--} = CaCO_3^0$
†21	$CaHCO_3^+$	$Ca^{++} + HCO_3^- = CaHCO_3^+$
22	$CaSO_4^0$	$Ca^{++} + SO_4^{--} = CaSO_4^0$
†23	$MgOH^+$	$Mg^{++} + OH^- = MgOH^+$
†24	$MgCO_3^0$	$Mg^{++} + CO_3^{--} = MgCO_3^0$

TABLE A1 - continued

†25	$MgHCO_3^+$	$Mg^{++} + HCO_3^- = MgHCO_3^+$
26	$MgSO_4^0$	$Mg^{++} + SO_4^{--} = MgSO_4^0$
27	$NaCl^0$	$Na^+ + Cl^- = NaCl^0$
28	$NaCO_3^-$	$Na^+ + CO_3^{--} = NaCO_3^-$
29	$NaHCO_3^0$	$Na^+ + HCO_3^- = NaHCO_3^0$
30	$NaSO_4^-$	$Na^+ + SO_4^{--} = NaSO_4^-$
31	KCl^0	$K^+ + Cl^- = KCl^0$
†32	KSO_4^-	$K^+ + SO_4^{--} = KSO_4^-$
33	HCl^0	$H^+ + Cl^- = HCl^0$
34	CO_3^{--}	
†35	HSO_4^-	$H^+ + SO_4^{--} = HSO_4^-$
36	$H_2SO_4^0$	$2H^+ + SO_4^{--} = H_2SO_4^0$
†37	$H_3SiO_4^-$	$H_4SiO_4^0 = H_3SiO_4^- + H^+$
†38	$H_2SiO_4^{--}$	$H_4SiO_4^0 = H_2SiO_4^{--} + 2H^+$
39	Al^{+++}	
40	$AlOH^{++}$	$Al^{+++} + OH^- = AlOH^{++}$
41	$Al(OH)_2^+$	$Al^{+++} + 2OH^- = Al(OH)_2^+$
42	$AlSO_4^+$	$Al^{+++} + SO_4^{--} = AlSO_4^+$
43	$Al(SO_4)_2^-$	$Al^{+++} + 2SO_4^{--} = Al(SO_4)_2^-$
†44	$H_2BO_3^-$	$H_3BO_3^0 = H^+ + H_2BO_3^-$
45	Fe^{+++}	$Fe^{++} = Fe^{+++} + e^-$
46	$FeCl^{++}$	$Fe^{++} + Cl^- = FeCl^{++} + e^-$
47	$FeCl_3^0$	$Fe^{++} + 3Cl^- = FeCl_3^0 + e^-$
48	$FeOH^{++}$	$Fe^{++} + H_2O = FeOH^{++} + H^+ + e^-$
49	$Fe(OH)_2^+$	$Fe^{++} + 2H_2O = Fe(OH)_2^+ + 2H^+ + e^-$
50	$Fe(OH)_4^-$	$Fe^{++} + 4H_2O = Fe(OH)_4^- + 4H^+ + e^-$
51	$FeSO_4^+$	$Fe^{++} + SO_4^{--} = FeSO_4^+ + e^-$

TABLE A1 - continued

52	Fe^{++}	
53	$FeCl_2^+$	$Fe^{++} + 2Cl^- = FeCl_2^+ + e^-$
54	$FeOH^+$	$Fe^{++} + H_2O = FeOH^+ + H^+$
55	$Fe(OH)_2^0$	$Fe^{++} + 2H_2O = Fe(OH)_2^0 + 2H^+$
56	$FeOOH^-$	$Fe^{++} + 2H_2O = FeOOH^- + 3H^+$
57	$FeSO_4^0$	$Fe^{++} + SO_4^{--} = FeSO_4^0$
58	$SrOH^+$	$Sr^{++} + OH^- = SrOH^+$
59	$BaOH^+$	$Ba^{++} + OH^- = BaOH^+$
60	$LiOH^0$	$Li^+ + OH^- = LiOH^0$
61	$LiSO_4^-$	$Li^+ + SO_4^{--} = LiSO_4^-$
†62	HS^-	$H_2S_{aq} = H^+ + HS^-$
63	S^{--}	$HS^- = H^+ + S^{--}$
†64	$NH_{3,aq}$	$NH_4^+ = NH_{3,aq} + H^+$
65	$NH_4SO_4^-$	$NH_4^+ + SO_4^{--} = NH_4SO_4^-$
66	$O_{2,aq}$	$0.5\ H_2O = 0.25\ O_{2,aq} + H^+ + e^-$
67		
†68	$H_2CO_3^*$	$H^+ + HCO_3^- = H_2CO_3^*$
69		
70		
71	H^+	
72	OH^-	
73	H_2O	$H_2O = H^+ + OH^-$
74	e^-	$SO_4^{--} + 10H^+ + 8e^- = H_2S_{aq} + 4H_2O$
75		$HCO_3^- + 9H^+ + 8e^- = CH_{4,g} + 3H_2O$
76		$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$

† denotes analytic expression used in calculating equilibrium constant.

TABLE A2

NUMBER	MINERAL	REACTION
1	Calcite	$CaCO_3 = Ca^{++} + CO_3^{--}$
2	Aragonite	$CaCO_3 = Ca^{++} + CO_3^{--}$
3	Anhydrite	$CaSO_4 = Ca^{++} + SO_4^{--}$
4	Magnesite	$MgCO_3 = Mg^{++} + CO_3^{--}$
5	Halite	$NaCl = Na^{+} + Cl^{-}$
6	Strontianite	$SrCO_3 = Sr^{++} + CO_3^{--}$
7	Celestite	$SrSO_4 = Sr^{++} + SO_4^{--}$
8	Barite	$BaSO_4 = Ba^{++} + SO_4^{--}$
9	Witherite	$BaCO_3 = Ba^{++} + CO_3^{--}$
10	Siderite	$FeCO_3 = Fe^{++} + CO_3^{--}$
11	Thenardite	$Na_2SO_4 = 2Na^{+} + SO_4^{--}$
12	Brucite	$Mg(OH)_2 = Mg^{++} + 2OH^{-}$
13	Gibbsite	$Al(OH)_3 = Al^{+++} + 3OH^{-}$
14	Chalcedony	$SiO_2 + 2H_2O = H_4SiO_4^{0}$
15	Quartz	$SiO_2 + 2H_2O = H_4SiO_4^{0}$
16	Dolomite	$CaMg(CO_3)_2 = Ca^{++} + Mg^{++} + 2CO_3^{--}$
17	Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{++} + SO_4^{--} + 2H_2O$
18	Nesquehonite	$MgCO_3 \cdot 3H_2O = Mg^{++} + CO_3^{--} + 3H_2O$

TABLE A2 - continued

19	Mirabilite	$Na_2SO_4 \cdot 10H_2O = 2Na^{+} + SO_4^{--} + 10H_2O$
20	Mackinawite	$FeS + H^{+} = Fe^{++} + HS^{-}$
21	Huntite	$CaMg_3(CO_3)_4 = 3Mg^{++} + Ca^{++} + 4CO_3^{--}$
22	Goethite	$FeO(OH) + H_2O = Fe^{+++} + 3OH^{-}$
23	Boehmite	$AlO(OH) + H_2O = Al^{+++} + 3OH^{-}$
24	Hematite	$Fe_2O_3 + 6H^{+} + 2e^{-} = 2Fe^{++} + 3H_2O$
25	Albite	$NaAlSi_3O_8 + 8H_2O = Na^{+} + Al(OH)_4^{-} + 3H_4SiO_4^{0}$
26	Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2 + 10H_2O = K^{+} + 3Mg^{++} + Al(OH)_4^{-} + 3H_4SiO_4^{0} + 6OH^{-}$
27	Adularia (K-Feldspar)	$KAlSi_3O_8 + 8H_2O = K^{+} + Al(OH)_4^{-} + 3H_4SiO_4^{0}$
28	Muscovite (K-Mica)	$KAl_3Si_3O_{10}(OH)_2 + 12H_2O = K^{+} + 3Al(OH)_4^{-} + 3H_4SiO_4^{0} + 2H^{+}$
29	Anorthite	$CaAl_2Si_2O_8 + 8H_2O = Ca^{++} + 2Al(OH)_4^{-} + 2H_4SiO_4^{0}$
30	Talc	$Mg_3Si_4O_{10}(OH)_2 + 10H_2O = 3Mg^{++} + 4H_4SiO_4^{0} + 6OH^{-}$
31	Kaolinite	$Al_2Si_2O_5(OH)_4 + 7H_2O = 2Al(OH)_4^{-} + 2H_4SiO_4^{0} + 2H^{+}$
32	Halloysite	$Al_2Si_2O_5(OH)_4 + 7H_2O = 2Al(OH)_4^{-} + 2H_4SiO_4^{0} + 2H^{+}$
33	Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8 + 10H_2O = 5Mg^{++} + 2Al(OH)_4^{-} + 3H_4SiO_4^{0} + 8OH^{-}$
34	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2 + 12H_2O = 2Al(OH)_4^{-} + 4H_4SiO_4^{0} + 2H^{+}$
35	Hydromagnesite	$Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O = 4Mg^{++} + 3CO_3^{--} + 2OH^{-} + 3H_2O$
36	Magnetite	$Fe_3O_4 + 8H^{+} + 2e^{-} = 3Fe^{++} + 4H_2O$

TABLE A2 - continued

37	Pyrite	$FeS_2 + 2H^+ + 2e^- = Fe^{++} + 2HS^-$
38	Greigite	$Fe_3S_4 + 4H^+ + 2e^- = 3Fe^{++} + 4HS^-$
39	Illite	$K_{.6}Mg_{.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 + 11.2H_2O = .6K^+ + .25Mg^{++} + 2.3\ Al(OH)_4^- + 3.5H_4SiO_4^0 + 1$
40	Ca-montmorillonite	$Ca_{.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12H_2O = .17Ca^{++} + 2.33\ Al(OH)_4^- + 3.67\ H_4SiO_4^0 + 2H^+$

NOTE: A number of these minerals form solid solution series and only idealized formulae have been used.

APPENDIX B

Glossary of symbols used in WATSPEC

A(I)	activity of I-th species (I ≠ 75)
A(75)	1, used in subroutine PRINT
AA	Debye-Hückel constant, A in equation (19)
A1(I)	coefficient for calculation of K(I2)
A2(I)	coefficient for calculation of K(I2)
A3(I)	coefficient for calculation of K(I2)
B(I)	extended Debye-Hückel parameter, b_i in equation (19)
BB	Debye-Hückel constant, B in equation (19)
C	temporary variable label
CATXS	excess cation charge
CHG(I)	charge on species I
CHH(I)	charge on species I
CTOT	total inorganic carbon molality
DELH(I)	enthalpy values for calculating K(I) using van't Hoff equation
DENS	solution density (Kg/litre or gm/cc)
E	electron activity (= A(74))
ELIMIT	test criterion for convergence
ERROR	charge balance error (equation (34))
EZ	Eh of standard Zobell's solution
F(I)	activity coefficient of I-th species
FLAG1	flag for signalling redox input
FLAG2	flag for signalling minor species input
FLAG3	flag for type of redox input
G	temporary variable label
GFW(I)	gm. formula weight of I-th species
GMH2O	mass of water in one litre of solution (in gms)
GMSOLN	mass of solution in one litre of solution (in gms)
ITER	counter for number of iterations
I1(I)	K(I1) are calculated using van't Hoff equation
I2(I)	K(I2) are calculated from analytic expressions
IS1(I)	species number used in calculating IAP and SI
IS2(I)	species number used in calculating IAP and SI
IS3(I)	species number used in calculating IAP and SI

and SI

IO1(I)	species number for determining order of output
IO2(I)	mineral number for determining order of output
K(I)	association constant for I-th species
K(77)	Henry's Law constant for CO_2
KMIN(I)	dissociation constant for I-th mineral (not used)
NDATA	number of input data sets analysed
NX(I)	minor species number for input
N1(I)	coefficient used in calculating IAP and SI
N2(I)	coefficient used in calculating IAP and SI
N3(I)	coefficient used in calculating IAP and SI
N4(I)	coefficient used in calculating IAP and SI
PE	pe ($\equiv$ -log(E))
PH	pH
PK(I)	-log(K(I))
PK25(I)	PK(I) or PKMIN(I) at 25°C
PKHO2	-log (Henry's Law constant for O_2)
PKMIN(I)	-log(KMIN(I))
PPCH4	-log(CH_4 partial pressure in atmospheres)
PPCO2	-log(CO_2 partial pressure in atmospheres)
PPO2	-log(O_2 partial pressure in atmospheres)
R(I)	effective ion radius, a_i in equation (19)
SI(I)	saturation index for mineral I
SUMAN	total anion charge
SUMCAT	total cation charge
T	temperature in °K
TDS	total dissolved solids (gms per litre of solution)
TEMP	temperature in °C
TEST	CTOT value stored from previous iteration
TKEEP	temperature of previous input data set
U	ionic strength
X(I)	molality of I-th species
XTOT	total solution molality
X13	NO_3^- molality implied by Eh and NH_4^+
X18	NH_4^+ molality implied by Eh and NO_3^-
Y	temporary variable label
Z(I)	total molarity or molality keyed to X(I)
ZZZ	Eh input variable value
Z17	total sulphide as specified on Eh card, used in subroutine PECALC

APPENDIX C

Program listing and input and output examples

WATSPEC has been developed on an ICL 1903T computer. On this computer, which is relatively small and slow, a typical execution time for a single sample is 3 seconds. Compilation takes approximately 40 seconds so that the total execution time for ten samples would be about 70 seconds. WATSPEC has also been run successfully on an IBM 370/165 computer. Compilation time on this machine is approximately 5 seconds, and execution time is about 0.2 seconds per sample (using the G compiler). Storage space required is approximately 19K on the ICL 1903T and 50K on the 370/165.

WATSPEC is written in single precision, and this accuracy is certainly adequate on ICL 1900 series computers (which have 11 figure accuracy for real arthimetic). On IBM 360 and 370 series computers (which have 7 figure accuracy in single precision) double precision may be necessary. All test cases run on an IBM 370/165 in single precision did, in fact, give identical results to those obtained on the ICL 1903T, but this may not be the case if the convergence test criterion, ELIMIT, is reduced.

The program listing given over is followed by output for two examples. The first is a water sample with a very detailed set of chemical data including all major species, density, Eh data and nine minor species. Five input cards are required. The sample itself has a chemical composition similar to that of sea-water (although the Eh value is unrealistic). The second sample only contains information on pH, temperature and four of the major species (viz. calcium, magnesium, sulphate and alkalinity) This is an example which is close to the minimum amount of data needed to specify the character of a water sample. Only two input cards are required. The first card is a blank card which tel the program that there are no Eh or minor species data, and that density is unknown. WATSPEC automatically assigns a value 1.0 for the density in this case. The input cards are shown over. Note that the last card, containing 9 in columns 1 and 2, is required to indicate an end to the data input. Cards 1 to 5 specify data for sample 1, and cards 6 and 7 specify data for sample 2.

Input cards

CARD

```
1:   12 1.03
2:   10.   7.5   10.   50.   483.5 10.   550.   2.5   30.
3:   1 0.2
4:    8 .1   E-03 9 .5   E-0410 .9   E-0111 .2   E-0412 .2   E-0113 .5   E-02
5:   14 .7   E-0115 .4   E-0016 .8   E-00
6:   (blank card)
7:   5.    7.    12.   1.5   0.    0.    0.    4.    12.5
8:   99
```

The Program listing follows:

see opposite page

```
C          **********          W A T S P E C          **********
C**********
C  WATSPEC IS AN AQUEOUS MODEL FOR DETERMINING EQUILIBRIUM CHEMICAL
C  SPECIATION IN NATURAL WATERS. IT ACCEPTS UP TO 18 TOTAL SPECIES
C  CONCENTRATIONS AS INPUT. EH INPUT CAN BE INCLUDED IN ANY OF 5
C  DIFFERENT WAYS, OR MAY BE OMITTED. WATSPEC ACCOUNTS FOR UP TO 70
C  AQUEOUS-PHASE SPECIES AND COMPUTES SATURATION INDICES FOR 40 MINERALS
C**********
C  INPUT DETAILS : EACH SAMPLE REQUIRES 2, 3, 4 OR 5 CARDS.
C  CARD 1 (2I1,F10.0)
C    FLAG1 = 1 IF SAMPLE INCLUDES REDUCTION-OXIDATION DATA (CARD 3)
C    FLAG2 = NUMBER OF MINOR SPECIES CARDS (CARDS 4 AND/OR 5)
C            (6 MINOR SPECIES PER CARD SO FLAG2 = 0, 1 OR 2)
C    DENS = DENSITY (GM/CC OR KG/LITRE) : IF DENS IS MISSING OR INPUT
C           AS LESS THAN 1.0, WATSPEC PUTS DENS = 1.0
C  CARD 2 (9F6.0) : TEMP (DEG C), PH AND MAJOR SPECIES.
C    Z(I),I=1,7 = MAJOR SPECIES TOTAL CONCENTRATIONS IN MILLIMOLES PER
C                 LITRE OF SOLUTION (MILLIEQUIVALENTS FOR TITRATION
C                 ALKALINITY) : SPECIES ORDER, 1 = CALCIUM,
C                 2 = MAGNESIUM, 3 = SODIUM, 4 = POTASSIUM, 5 = CHLORIDE
C                 6 = TITRATION ALKALINITY, 7 = SULPHATE
C  CARD 3 (I1,2F10.0) : OXIDN-REDN DATA (OMIT IF FLAG1 NOT EQUAL TO 1).
C    THERE ARE 5 INPUT OPTIONS INDICATED BY FLAG3. ZZZ IS THE
C    APPROPRIATE DATA VALUE. EZ IS LEFT BLANK UNLESS FLAG3 = 3. EH
C    VALUES IN VOLTS.
C     FLAG3 VALUE      **  ZZZ  **
C         1             MEASURED EH, TEMPERATURE CORRECTED
C         2             MEASURED EH, NOT TEMPERATURE CORRECTED
C         3             MEASURED EH, NOT TEMPERATURE CORRECTED. EZ MUST BE
C                       SPECIFIED WITH THIS OPTION. EZ = EH OF STANDARD
C                       ZOBELLS SOLUTION
C         4             OXYGEN CONCENTRATION AS -LOG(MOLES OF O2 PER LITRE
C                       OF SOLUTION)
C         5             TOTAL SULPHIDE AS -LOG(MOLES OF H2S PER LITRE
C                       OF SOLUTION)
C  CARDS 4 AND 5 (6(I2,G10.4) : MINOR SPECIES. OMIT IF NO MINOR SPECIES
C    DATA. DATA INPUT IS IN PAIRS WITH SPECIES NUMBER FOLLOWED BY TOTAL
C    CONCENTRATION IN MILLIMOLES PER LITRE OF SOLN : SPECIES NUMBERS
C    8 (ALUMINIUM), 9 (IRON), 10 (STRONTIUM), 11 (BARIUM), 12 (LITHIUM),
C    13 (NITRATE), 14 (SILICATE AS SIO2), 15 (BORATE AS B),16 (BROMIDE),
C    17 (SULPHIDE AS H2S), 18 (AMMONIA AS NH4+).
C    IF SULPHIDE IS ENTERED ON CARD 4 OR 5 THIS VALUE WILL BE USED FOR
C    CALCULATION OF SPECIATION EVEN IF MEASURED EH DATA IS GIVEN ON
C    CARD 3. TO FIND SPECIATION WITH SULPHIDE DETERMINED BY MEASURED
C    EH DATA OMIT SULPHIDE FROM CARD 4.
C**********
C  END OF DATA : A CARD WITH 99 IN COLUMNS 1 AND 2 SHOULD ALWAYS BE
C  INCLUDED AFTER THE LAST DATA CARD TO DENOTE END OF DATA
C**********
C  THIS VERSION OF WATSPEC IS DATED FEB 1977.
C**********
      DIMENSION R(72),B(72),IPAIR(21),IR1(21),IR2(21),GFW(18),NX(11)     A   1
     1,CHH(72)                                                           A   2
      INTEGER CHG,CHH,FLAG1,FLAG2,FLAG3                                  A   3
      REAL K,KMIN                                                        A   4
      COMMONA(75),F(72),X(72),Z(72),AA,BB,CHG(72),CTOT,DENS,FLAG3,GMH20, A   5
     1PPCH4,EZ,PE,PH,T,TEMP,TDS,U,ZZZ,K(77),KMIN(40),PK(77),PKMIN(40)    A   6
      DATA IPAIR/19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,35,58,59,  A   7
     160,61,68/,IR1/4*1,4*2,4*3,4,4,71,71,10,11,12,12,71/,IR2/72,34,6,7, A   8
     272,34,6,7,5,34,6,7,5,7,5,7,3*72,7,6/,CHH/2,2,1,1,-1,-1,-2,-1,0,2,  A   9
     32,1,-1,0,0,-1,0,1,1,0,1,0,1,0,1,0,0,-1,0,-1,0,-1,0,-2,-1,0,-1,-2,  A  10
     43,2,1,1,-1,-1,3,2,0,2,1,-1,1,2,1,1,0,-1,0,1,1,0,-1,-1,-2,0,-1,5*0, A  11
     51,-1/,GFW/40.08,24.312,22.99,39.102,35.453,61.017,96.062,26.981,   A  12
     655.847,87.62,137.34,6.939,62.005,60.085,10.811,79.909,34.08,       A  13
     718.039/,R/5.,5.5,4.,2*3.5,5.4,5.,4.5,0.,5.,5.,6.,3.,0.,2.5,4.,0.,  A  14
     80.,6.,0.,6.,0.,6.5,0.,4.,0.,0.,5.4,0.,5.4,0.,5.4,0.,5.4,4.5,0.,4., A  15
     95.4,9.,2*5.4,2*4.5,0.,9.,5.,0.,5.,2*5.4,5.,6.,5.,5.,0.,5.,0.,5.,   A  16
     *5.,0.,5.,3.5,5.,0.,5.,5*0.,9.,3.5/,B/.165,.2,.075,2*.015,0.,-.04,  A  17
     165*0./,ELIMIT/1.E-06/,NDATA/0/,TKEEP/1000./                        A  18
10    DO 20 I=1,72                                                       A  19
      CHG(I)=CHH(I)                                                      A  20
      Z(I)=0.                                                            A  21
```

```
      X(I)=0.
      A(I)=0.
   20 F(I)=1.
      NDATA=NDATA+1
      READ(5,220) FLAG1,FLAG2,DENS
      IF((FLAG1.EQ.9).AND.(FLAG2.EQ.9))GO TO 130
      READ(5,230) TEMP,PH,(Z(I),I=1,7)
      IF(FLAG1.EQ.1)READ(5,240)FLAG3,ZZZ,EZ
      IF(FLAG2.GE.1)READ(5,250)((NX(I),Z(NX(I))),I=1,6)
      IF(FLAG2.GE.2)READ(5,250)((NX(I),Z(NX(I))),I=1,6)
      WRITE(6,170) NDATA
      IF((DENS.GT.0.).AND.(DENS.LT.1.))WRITE(6,210)DENS
      IF((DENS.GE.0.).AND.(DENS.LT.1.))DENS=1.0
      T=TEMP+273.15
      IF(ABS(TEMP-TKEEP).GT.0.1)CALL EQUCON
      TKEEP=TEMP
      PPCH4=99.99
      PE=99.99
      CTOT=1000.
      TDS=0.
      GMSOLN=1000.*DENS
      DO 30 I=1,18
   30 TDS=TDS+Z(I)*GFW(I)/1000.
      GMH20=GMSOLN-TDS
      DO 40 I=1,18
      Z(I)=Z(I)/GMH20
   40 X(I)=Z(I)
      IF((Z(17).GT.0.).AND.(FLAG1.NE.1)) GO TO 120
      A(71)=10.**(-PH)
      X(71)=A(71)
      X(72)=K(73)/A(71)
      A(73)=1.
C***** FIRST ESTIMATE OF HCO3- ACTIVITY.
      X(6)=(Z(6)+X(71)-X(72))/(1.+Z(1)*K(21)+Z(2)*K(25)+Z(3)*K(29)+
     12.*(1.+Z(1)*K(20)+Z(2)*K(24)+Z(3)*K(28))/(K(6)*A(71)))
      IF(X(6).LT.0.0)GO TO 120
      ITER=0
   50 IF(ITER.GE.50) GO TO 120
C***** CALCN OF IONIC STRENGTH AND ACTIVITY COEFFICIENTS.
      U=0.
      DO 60 I=1,72
   60 U=U+.5*X(I)*CHG(I)*CHG(I)
      XTOT=0.
      DO 70 I=1,72
      C=SQRT(U)*CHG(I)*CHG(I)*AA
      IF(CHG(I).EQ.0)F(I)=10.**(0.1*U)
      IF(CHG(I).NE.0)F(I)=10.**(-C/(1.+BB*SQRT(U)*R(I))+U*B(I))
      IF(I.NE.71) A(I)=F(I)*X(I)
   70 XTOT=XTOT+X(I)
      C=TEMP*TEMP
      F(68)=10.**(U*(33.5-.109*TEMP+.0014*C-U*(1.5+.015*TEMP-.0004*C))
     1/T)
C***** ACTIVITIES OF H20, OH- AND CO3--.
      A(73)=1.-.017*XTOT
      A(72)=K(73)*A(73)/A(71)
      X(72)=A(72)/F(72)
      A(34)=A(6)/(K(6)*A(71))
C***** TEST FOR CONVERGENCE.
      TEST=CTOT
      CTOT=X(6)+X(20)+X(21)+X(24)+X(25)+X(28)+X(29)+X(34)+X(68)
      IF((ABS(TEST-CTOT)/CTOT).LT.ELIMIT)GO TO 110
      ITER=ITER+1
C***** CALCULATION OF PE, O2, CH4 AND SULPHIDE SPECIES.
      IF(FLAG1.EQ.1)CALL PECALC
C***** SILICATE SPECIES.
      A(14)=Z(14)/(1./F(14)+(K(37)/F(37)+K(38)/F(38))/A(71))
      A(37)=K(37)*A(14)/A(71)
      A(38)=K(38)*A(14)/(A(71)*A(71))
C***** BORATE SPECIES.
      A(15)=Z(15)/(1./F(15)+K(44)/(F(44)*A(71)))
      A(44)=K(44)*A(15)/A(71)
C***** ALUMINIUM SPECIES.
```

```
     1(F(40)*A(72))+K(41)/F(41))+A(7)*(K(42)/F(42)+K(43)*A(7)/F(43)))
      C=A(39)*A(72)
      A(8)=K(8)*C*A(72)**3
      A(40)=K(40)*C
      A(41)=K(41)*C*A(72)
      A(42)=K(42)*A(39)*A(7)
      A(43)=K(43)*A(39)*A(7)*A(7)
      IF((FLAG1.NE.1).AND.(Z(9).GT.0.)) PE=10.
      IF((FLAG1.NE.1).AND.(Z(9).EQ.0.)) GO TO 80
C***** IRON SPECIES.
      E=10.**(-PE)
      A(74)=E
      C=A(71)/A(73)
      G=C*C
      A(52)=E*Z(9)/(E/F(52)+K(9)/(F(9)*C*G)+K(45)/F(45)+K(46)*A(5)/F(46)
     1+K(47)*A(5)**3/F(47)+K(48)/(F(48)*C)+K(49)/(F(49)*G)+K(50)/(F(50)*
     2G*G)+K(51)*A(7)/F(51)+K(53)*A(5)*A(5)/F(53)+K(54)*E/(F(54)*C)
     3+K(55)*E/(F(55)*G)+K(56)*E/(F(56)*G*A(71))+K(57)*E*A(7)/F(57))
      Y=A(52)/E
      A(9)=K(9)*Y/(C*G)
      A(45)=K(45)*Y
      A(46)=K(46)*Y*A(5)
      A(47)=K(47)*Y*(A(5)**3)
      A(48)=K(48)*Y/C
      A(49)=K(49)*Y/G
      A(50)=K(50)*Y/(G*G)
      A(51)=K(51)*Y*A(7)
      A(53)=K(53)*Y*A(5)*A(5)
      A(54)=K(54)*A(52)/C
      A(55)=K(55)*A(52)/G
      A(56)=K(56)*A(52)/(G*A(71))
   80 A(57)=K(57)*A(52)*A(7)
C***** NITRATE AND AMMONIUM SPECIES. REDOX EQUILIBRIUM IS NOT ASSUMED
C***** FOR THESE SPECIES.
      IF(Z(18).GT.0.) A(18)=Z(18)/(1./F(18)+K(64)/(F(64)*A(71))+K(65)
     1/(F(65)*A(7)))
      IF(FLAG1.EQ.1)C=10.**(PK(76)+10.*PH+8.*PE+3.*ALOG10(A(73)))
      IF((Z(13).GT.0.).AND.(FLAG1.EQ.1))X18=A(13)/(C*F(18))
      IF((Z(18).GT.0.).AND.(FLAG1.EQ.1))X13=A(18)*C/F(13)
      IF(A(18).GT.0.)A(64)=K(64)*A(18)/A(71)
      IF(A(18).GT.0.)A(65)=K(65)*A(18)/A(7)
C***** ALL OTHER ION PAIRS.
      DO 90 I=1,21
   90 A(IPAIR(I))=K(IPAIR(I))*A(IR1(I))*A(IR2(I))
      A(36)=K(36)*A(71)*A(71)*A(7)
      DO 100 I=1,65
  100 X(I+7)=A(I+7)/F(I+7)
C***** KEY SPECIES.
      IF(X(1).GT.0.)X(1)=Z(1)/(1.+(X(19)+X(20)+X(21)+X(22))/X(1))
      IF(X(2).GT.0.)X(2)=Z(2)/(1.+(X(23)+X(24)+X(25)+X(26))/X(2))
      IF(X(3).GT.0.)X(3)=Z(3)/(1.+(X(27)+X(28)+X(29)+X(30))/X(3))
      IF(X(4).GT.0.)X(4)=Z(4)/(1.+(X(31)+X(32))/X(4))
      IF(X(5).GT.0.)X(5)=Z(5)/(1.+(X(27)+X(31)+X(33)+X(46)+3.*X(47)+2.*
     1X(53))/X(5))
      IF(X(7).GT.0.)X(7)=Z(7)/(1.+(X(22)+X(26)+X(30)+X(32)+X(35)+X(36)
     1+X(42)+2.*X(43)+X(51)+X(57)+X(61)+X(65))/X(7))
      IF(X(10).GT.0.)X(10)=Z(10)/(1.+X(58)/X(10))
      IF(X(11).GT.0.)X(11)=Z(11)/(1.+X(59)/X(11))
      IF(X(12).GT.0.)X(12)=Z(12)/(1.+(X(60)+X(61))/X(12))
      C=X(37)+2.*X(38)+X(44)+X(8)+X(62)+2.*X(63)+X(72)+X(60)-X(71)
      C=X(37)+2.*X(38)+X(44)+X(40)+2.*X(41)+4.*X(8)+X(62)+2.*X(63)+X(64)
     1+X(72)+X(19)+X(23)+X(58)+X(59)+X(60)-X(71)-X(33)-X(35)-2.*X(36)
      X(6)=(Z(6)-C)/(1.+(X(21)+X(25)+X(29)+2.*(X(20)+X(24)+X(28)+X(34)))
     1/X(6))
      GO TO 50
  110 IF((FLAG1.EQ.1).AND.(Z(18).GT.0.)) WRITE(6,140) X13
      IF((FLAG1.EQ.1).AND.(Z(13).GT.0.)) WRITE(6,150) X18
      IF((FLAG1.NE.1).AND.(Z(9).GT.0.)) WRITE(6,160)
      CALL PRINT
      GO TO 10
  120 IF(ITER.GT.50) WRITE(6,180)
```

```
      IF(X(6).LT.0.) WRITE (6,190)
      IF((Z17.GT.0.).AND.(FLAG1.NE.1)) WRITE (6,200)
      IF(ITER.GT.50) CALL PRINT
      GO TO 10
  130 CONTINUE
  140 FORMAT(//,'  NH3 AND PE DATA GIVEN : NH3, PH AND PE IMPLY NO3- MOL
     1ALITY =',E11.4)
  150 FORMAT(//,'  NO3 AND PE DATA GIVEN : NO3, PH AND PE IMPLY NH4+ MOL
     1ALITY =',E11.4)
  160 FORMAT(//,'  FE TOTAL > ZERO BUT NO EH DATA CARD : PE ARBITRARILY
     1ASSUMED EQUAL TO 10.0')
  170 FORMAT(1H1,' *****  SAMPLE NUMBER',I4)
  180 FORMAT(//,'  NOT CONVERGED AFTER 50 ITERATIONS.  RESULTS AT THIS S
     1TAGE ARE .....')
  190 FORMAT(1X,'   SAMPLE REJECTED : HCO3 < 0, POSSIBLE PH OR ALKALINIT
     1Y ERROR')
  200 FORMAT(1X,'   POSSIBLE DATA INPUT ERROR : TOTAL SULPHIDE SPECIFIED
     1 BUT NO EH DATA CARD')
  210 FORMAT(1X,'   WARNING, DENSITY SPECIFIED AS',F6.3,'  :  VALUE CHAN
     1GED TO 1.0')
  220 FORMAT(2I1,F10.0)
  230 FORMAT(9F6.0)
  240 FORMAT(I1,2F10.0)
  250 FORMAT(6(I2,G10.4))
      STOP
      END


      SUBROUTINE EQUCON
C***** THIS SUBROUTINE CALCULATES ALL EQUILIBRIUM CONSTANTS AND
C***** DEBYE-HUCKEL CONSTANTS.
      DIMENSION I1(39),I2(15),PK25(78),DELH(78),A1(15),A2(15),A3(15)
      INTEGER CHG,FLAG1,FLAG2,FLAG3
      REAL K,KMIN
      COMMONA(75),F(72),X(72),Z(72),AA,BB,CHG(72),CTOT,DENS,FLAG3,GMH20,
     1PPCH4,EZ,PE,PH,T,TEMP,TDS,U,ZZZ,K(77),KMIN(40),PK(77),PKMIN(40)
      DATA I1/8,9,19,22,26,27,28,29,30,31,33,36,40,41,42,43,45,46,47,48,
     149,50,51,53,54,55,56,57,58,59,60,61,63,65,66,73,74,75,76/,I2/6,20,
     221,23,24,25,32,35,37,38,44,62,64,68,77/
      DATA PK25/-33.938, 26.571, -1.4  , -2.309, -2.238,  1.602, -1.268,
     1     .25 , -0.72 ,  1.585,  6.1  ,  1.   , -8.998,-18.235, -3.2  ,
     2   -5.1  , 13.013, 11.6  , 11.925, 15.473, 20.173, 34.894,  8.886,
     3   10.919,  9.319, 20.57 , 29.458, -2.2  , -0.82 , -0.64 , -0.2  ,
     4   -0.64 , 12.918, -1.11 , 21.495, 13.998,-40.644,-30.741,-119.077
     5 ,  8.215,  4.548,  8.24 , -1.582, 11.41 ,  5.974,  9.756, 13.32 ,
     6   10.55 ,   .179, 11.41 , 32.77 ,  3.523,  4.005, 17.02 ,  4.759,
     7    5.211,  1.113,  4.631, 30.51 , 41.2  , 33.41 ,-24.15 , 18.   ,
     8   63.53 , 20.57 , 49.09 , 19.33 , 62.29 , 36.91 , 32.82 , 90.61 ,
     9   42.43 , 37.82 ,-32.67 , 18.48 , 17.97 , 40.31 , 45.   /
      DATA DELH/ -9.32 ,    .0 ,  1.19 ,  1.5  ,  1.27 ,    .0 ,  8.911,
     1      .0 ,  1.1  ,    .0 , 18.63 , 10.   ,  1.99 ,    .0 ,  2.29 ,
     2    3.07 ,  9.7  , 18.152,    .0 , 20.115,    .0 ,    .0 , 15.92 ,
     3      .0 , 13.218, 28.565, 32.995,   .56 ,  1.15 ,  1.75 ,  4.832,
     4      .0 , 12.1  ,    .0 , 33.457, 13.345,-65.44 ,-57.435,-187.055
     5 , -2.959, -3.769, -6.169,   .918,  2.361, -1.054,  6.141,  6.95 ,
     6   -5.328, -0.572,   .85 , 14.47 ,  4.615,  6.22 , -8:29 ,   .261,
     7   -4.551, 18.987,    .0 ,-25.76 , 25.555, 11.905,-49.65 , 25.896,
     8      .0 , 30.82 , 67.86 , 17.53 , 45.065, 49.15 , 44.68 , 54.76 ,
     9      .0 ,-25.52 ,-68.86 , 11.3  ,    .0 , 54.684, 58.373/
      DATAA1/-6.498,-27.393,-2.95,.684,.991,2.319,3.106,-5.3505,6.368,39
     1.478,28.6059,11.17,.6322,-14.8435,-14.0184/,A2/.02379,.05617,.0133
     2,.0051295,.00667,-.011056,0.,.0183412,-.016346,-.065927,.012078,-.
     302386,-.001225,.032786,.015264/,A3/2902.39,4114.,0.,0.,0.,0.,-673.
     46,557.25,-3405.9,-12355.1,1573.21,-3279.,-2835.76,3404.71,2385.73/
      DO 10 I=1,39
      PK(I1(I))=PK25(I)+DELH(I)*(25.-TEMP)/(T*1.3642378)
   10 IF(I1(I).NE.76) K(I1(I))=10.**(-PK(I1(I)))
      DO 20 I=1,15
      PK(I2(I))=-A1(I)-A2(I)*T-A3(I)/T
      IF(I.EQ.6)PK(I2(I))=PK(I2(I))-2.29812E-05*T*T
      IF(I.EQ.11)PK(I2(I))=PK(I2(I))+13.2258*ALOG10(T)+PK(73)
   20 K(I2(I))=10.**(-PK(I2(I)))
```

```
      DO 30 I=1,39
   30 PKMIN(I+1)=PK25(I+39)+DELH(I+39)*(25.-TEMP)/(T*1.3642378)
      PKMIN(1)=-13.543+.0401*T+3000./T
      PKMIN(17)=4.6535-TEMP*(.004545-.000101*TEMP)
      AA=.48863+TEMP*7.48E-4+TEMP*TEMP*3.85E-6
      BB=.32415+TEMP*1.65E-4+TEMP*TEMP*2.0E-7
      RETURN
      END


      SUBROUTINE PECALC
C***** THIS SUBROUTINE CALCULATES PE, O2, CH4 AND SULPHIDE SPECIES.
      INTEGER CHG,FLAG1,FLAG2,FLAG3
      REAL K,KMIN
      COMMONA(75),F(72),X(72),Z(72),AA,BB,CHG(72),CTOT,DENS,FLAG3,GMH20,
     1PPCH4,EZ,PE,PH,T,TEMP,TDS,U,ZZZ,K(77),KMIN(40),PK(77),PKMIN(40)
      C=ALOG10(A(73))
      IF(FLAG3.EQ.1)EH=ZZZ
      IF(FLAG3.EQ.2)EH=ZZZ+.244+.00086*(25.-TEMP)
      IF(FLAG3.EQ.3)EH=ZZZ+.429+.0024*(25.-TEMP)-EZ
      IF(FLAG3.LT.4) PE=EH/(1.98422E-04*T)
      IF(FLAG3.NE.5) GO TO 10
      Z17=10.**(-ZZZ)/(GMH20/1000.)
      A(17)=Z17/(1./F(17)+K(62)*(1./F(62)+K(63)/(F(63)*A(71)))/A(71))
      PE=(-ALOG10(A(17))-4.*C+ALOG10(A(7))-10.*PH-PK(74))
   10 IF(FLAG3.EQ.4) A(66)=10.**(-ZZZ)*F(66)/(GMH20/1000.)
      IF(FLAG3.EQ.4)PE=PK(66)-.5*C-PH+.25*ALOG10(A(66))
      IF(A(7).GT.0.)G=-PK(74)+ALOG10(A(7))-10.*PH-8.*PE-4.*C
      IF((A(7).GT.0.).AND.(G.GT.-75.))A(17)=10.**G
      IF(Z(17).GT.0.)A(17)=Z(17)/(1./F(17)+K(62)*(1./F(62)+K(63)/(F(63)*
     1A(71)))/A(71))
      A(62)=K(62)*A(17)/A(71)
      A(63)=K(63)*A(62)/A(71)
      G=4.*(PE-PK(66)+.5*C+PH)
      IF((FLAG3.NE.4).AND.(G.GT.-75.))A(66)=10.**G
      PPCH4=8.*PE+3.*C+PK(75)+9.*PH-ALOG10(A(6))
      RETURN
      END


      SUBROUTINE PRINT
C***** THIS SUBROUTINE CALCULATES SATURATION INDICES AND OTHER OUTPUTS.
      DIMENSION IS1(38),IS2(38),IS3(38),IS4(38),N1(38),N2(38),N3(38),
     1N4(38),SI(40),IO1(69),IO2(40)
      INTEGER CHG,FLAG1,FLAG2,FLAG3
      REAL K,KMIN
      COMMONA(75),F(72),X(72),Z(72),AA,BB,CHG(72),CTOT,DENS,FLAG3,GMH20,
     1PPCH4,EZ,PE,PH,T,TEMP,TDS,U,ZZZ,K(77),KMIN(40),PK(77),PKMIN(40)
      DATA IS1/3*1,2,3,2*10,2*11,52,7,2,39,2*14,2*1,2,7,52,1,45,39,52,3,
     13*4,1,2,4*8,2,3*74/,N1/23*1,2,5*1,3,4*2,4,3*-2/,IS2/2*34,7,34,5,
     234,7,7,2*34,3,2*72,2*73,2,7,34,3,62,2,2*72,71,5*8,72,2*71,72,71,72
     3,3*71/,N2/10*1,2*2,3,2*-2,3*1,2,1,3*3,-6,3*1,3,2,6,2*2,8,2*2,-8,-2
     4,-4/,IS3/15*75,34,3*73,71,34,15*73,2*62/,N3/15*0,2*2,3,10,-1,4,
     52*-1,3,-8,-10,-8,-12,-8,-10,2*-7,-10,-12,3,4,2,4/,IS4/23*75,74,
     610*14,34,3*52/,N4/23*0,-2,4*3,2,4,2*2,3,4,3,3,1,3/
      DATA IO1/72,34,6,7,5,1,19,20,21,22,2,23,24,25,26,3,28,29,30,27,4,3
     12,31,11,59,10,58,12,60,61,14,37,38,39,40,41,8,42,43,45,48,49,9,50,
     246,53,47,51,52,54,55,56,57,18,64,65,13,71,36,35,33,17,62,63,16,15,
     344,68,66/, IO2/27,25,3,29,2,8,23,12,1,40,7,14,33,16,13,22,38,17,5,
     432,24,21,35,39,31,28,20,4,36,19,18,26,37,34,15,10,6,30,11,9/
      A(75)=1.
      PPO2=99.99
      SUMCAT=0.
      SUMAN=0.
      DO 10 I=1,40
   10 SI(I)=-99.99
      DO 20 I=1,38
   20 IF((A(IS1(I)).GT.0.).AND.(A(IS2(I)).GT.0.).AND.(A(IS3(I)).GT.0.).
     1AND.(A(IS4(I)).GT.0.))SI(I)=N1(I)*ALOG10(A(IS1(I)))+N2(I)*ALOG10(A
     2(IS2(I)))+N3(I)*ALOG10(A(IS3(I)))+N4(I)*ALOG10(A(IS4(I)))+PKMIN(I)
      IF(SI(26).GT.-99.99)SI(26)=SI(26)+3.*ALOG10(A(2))+6.*ALOG10(A(72))
      IF(SI(28).GT.-99.99)SI(28)=SI(28)+2.*ALOG10(A(71))
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      IF(SI(33).GT.-99.99)SI(33)=SI(33)+5.*ALOG10(A(2))                 D 32
      IF((A(2).GT.0.).AND.(A(4).GT.0.).AND.(A(8).GT.0.).AND.(A(14).GT.0.D 33
     1))SI(39)=.25*ALOG10(A(2))+.6*ALOG10(A(4))+2.3*ALOG10(A(8))+3.5*   D 34
     2ALOG10(A(14))+1.2*ALOG10(A(71))-11.2*ALOG10(A(73))+PKMIN(39)      D 35
      IF((A(1).GT.0.).AND.(A(8).GT.0.).AND.(A(14).GT.0.))SI(40)=.17*ALOGD 36
     110(A(1))+2.33*ALOG10(A(8))+3.67*ALOG10(A(14))+2.*ALOG10(A(71))-   D 37
     212.*ALOG10(A(73))+PKMIN(40)                                        D 38
      DO 30 I=1,72                                                       D 39
      IF(CHG(I).GT.0)SUMCAT=SUMCAT+CHG(I)*X(I)                           D 40
   30 IF(CHG(I).LT.0)SUMAN=SUMAN-CHG(I)*X(I)                             D 41
      DO 40 I=1,18                                                       D 42
   40 Z(I)=Z(I)*GMH2O/1000.                                              D 43
      WRITE(6,50) (Z(I),I=1,18)                                          D 44
      PKHO2=2.860-2.8*(25.-TEMP)/(T*1.3642378)                           D 45
      IF(A(66).GT.0.) PPO2=-ALOG10(A(66))-PKHO2                          D 46
      PPCO2=-ALOG10(A(68))-PK(77)                                        D 47
      CATXS=SUMCAT-SUMAN                                                 D 48
      ERROR=100.*CATXS/(SUMCAT+SUMAN)                                    D 49
      WRITE(6,60) PH,PE,TEMP,DENS,PPCO2,PPO2,PPCH4,U,TDS,CTOT,ERROR,     D 50
     1CATXS,A(73)                                                        D 51
      WRITE(6,70)(X(IO1(I)),I=1,69)                                      D 52
      WRITE(6,80)(SI(IO2(I)),I=1,40)                                     D 53
   50 FORMAT(//,' *****  INPUT DATA (MOLES PER LITRE OF SOLUTION : EQUIVD 54
     1ALENTS PER LITRE FOR ALKALINITY)',/,                               D 55
     2' CATOT',E12.4,' MGTOT',E13.4,' NATOT',E11.4,' KTOT',E12.4,        D 56
     3' CLTOT',E12.4,' ALK',E14.4,/,' SO4TOT',E11.4,' ALTOT',E13.4,      D 57
     4' FETOT',E11.4,' SRTOT',E11.4,' BATOT',E12.4,' LITOT',E12.4,/,     D 58
     5' NO3TOT',E11.4,' SIO2TOT',E11.4,' BTOT',E12.4,' BRTOT',           D 59
     6E11.4,' H2STOT',E11.4,' NH4TOT',E11.4)                             D 60
   60 FORMAT(//,' PH =',F6.2,'  PE =',F6.2,'  TEMP =',F6.2,'DEG C   D    D 61
     1ENSITY =',F6.3,'GM/CC', /,' -LOG(PCO2) =',F5.2,'  -LOG(PO2) =',    D 62
     2F6.2,'  -LOG(PCH4) =',F6.2, /,' IONIC STRENGTH =',F8.5,'   TOTA    D 63
     3L DISS SOLIDS =',F6.2,'GM/LITRE SOLN   TOTAL INORG CARBON MOLALITY D 64
     4 =',E11.4, /,'  ION BALANCE ERROR =',F6.2,'PERCENT   CATION EXCES  D 65
     5S =',E11.4,'(CHARGE*MOLES)   H2O ACTIVITY =',F7.4)                 D 66
   70 FORMAT(//,' *****  INDIVIDUAL SPECIES MOLALITIES  ***',//,21X,'OH- D 67
     1  ',E11.4,' CO3-- ',E11.4,' HCO3- ',E11.4,' SO4-- ',E11.4,' C      D 68
     2L-   ',E11.4,/,' CA++  ',E11.4,' CAOH+ ',E11.4,' CACO30',E11.4,    D 69
     3' CAHCO3',E11.4,' CASO40',E11.4,19X,/,' MG++  ',E11.4,' MGOH+      D 70
     4',E11.4,' MGCO30',E11.4,' MGHCO3',E11.4,' MGSO40',E11.4,/,         D 71
     5' NA+   ',E11.4,19X,' NACO3-',E11.4,' NAHCO3',E11.4,' NASO4-',     D 72
     6E11.4,' NACLO ',E11.4,/,' K+    ',E11.4,57X,' KSO4- ',E11.4,       D 73
     7' KCLO  ',E11.4,/,' BA++  ',E11.4,' BAOH+ ',E11.4,/,' SR++  ',     D 74
     8E11.4,' SROH+ ',E11.4,/,' LI+   ',E11.4,' LIOHO ',E11.4,38X,       D 75
     9' LISO4-',E11.4,/,' H4SIO4',E11.4,' H3SIO4',E11.4,' H2SIO4'        D 76
     *,E11.4,/,' AL+++ ',E11.4,' ALOH++',E11.4,' ALOH2+',E11.4,' AL      D 77
     1OH4-',E11.4,' ALSO4+',E11.4,' ALSO42',E11.4,/,' FE+++ ',E11.4,     D 78
     2' FEOH++',E11.4,' FEOH2+',E11.4,' FEOH30',E11.4,' FEOH4-',         D 79
     3E11.4,' FECL++',E11.4,/,21X,'FECL2+',E11.4,' FECL30',E11.4,21X,    D 80
     4'FESO4+',E11.4,/,' FE++  ',E11.4,' FEOH+ ',E11.4,' FEOH2O',E11.    D 81
     54,' FEOOH-',E11.4,' FESO40',E11.4,/,' NH4+  ',E11.4,' NH3AQ ',     D 82
     6E11.4,40X,'NH4SO4',E11.4,' NO3-  ',E11.4,/,' H+    ',E11.4,40X,    D 83
     7'H2SO40',E11.4,' HSO4- ',E11.4,' HCLO  ',E11.4,/,' H2SAQ ',E11.    D 84
     84,' HS-   ',E11.4,' S--   ',E11.4,40X,'BR-   ',E11.4,/,' H3BO30    D 85
     9',E11.4,' H2BO3-',E11.4,40X,'H2CO3*',E11.4,' O2AQ  ',E11.4)        D 86
   80 FORMAT(//,' *****  MINERAL SATURATION INDICES  ***',//' ADULARIA'  D 87
     1,F7.2,' ALBITE  ',F7.2,' ANHYDRIT',F7.2,' ANORTHIT',F7.2,' ARA     D 88
     2GONIT',F7.2,' BARITE  ',F7.2,' BOEHMITE',F7.2,/,' BRUCITE ',F7.    D 89
     32,' CALCITE ',F7.2,' CA-MONT ',F7.2,' CELESTIT',F7.2,' CHALCED     D 90
     4N',F7.2,' CHLORITE',F7.2,' DOLOMITE',F7.2,/,' GIBBSITE',F7.2,'     D 91
     5 GOETHITE',F7.2,' GREIGITE',F7.2,' GYPSUM  ',F7.2,' HALITE  ',F    D 92
     67.2,' HALLOYST',F7.2,' HEMATITE',F7.2,/,' HUNTITE ',F7.2,' HYD     D 93
     7ROMAG',F7.2,' ILLITE  ',F7.2,' KAOLINIT',F7.2,' K-MICA  ',F7.2,    D 94
     8' MACKINAW',F7.2,' MAGNESIT',F7.2,/,' MAGNETIT',F7.2,' MIRABIL     D 95
     9T',F7.2,' NESQUEHO',F7.2,' PHLOGOPT',F7.2,' PYRITE  ',F7.2,' P     D 96
     *YROPHYL',F7.2,' QUARTZ  ',F7.2,/,' SIDERITE',F7.2,' STRONTNT',F    D 97
     17.2,' TALC    ',F7.2,' THENARDT',F7.2,' WITHERIT',F7.2)            D 98
      RETURN                                                             D 99
      END                                                                D100
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 *****  SAMPLE NUMBER   1

 NO3 AND PE DATA GIVEN : NO3. PH AND PE IMPLY NH4+ MOLALITY = 0.5865E 18

 *****  INPUT DATA (MOLES PER LITRE OF SOLUTION : EQUIVALENTS PER LITRE FOR ALKALINITY)
 CATOT  0.1000E-01  MGTOT   0.5000E-01  NATOT 0.4835E 00  KTOT  0.1000E-01  CLTOT  0.5500E 00  ALK    0.2500E-02
 SO4TOT 0.3000E-01  ALTOT   0.1000E-06  FETOT 0.5000E-07  SRTOT 0.9000E-04  BATOT  0.2000E-07  LITOT  0.2000E-04
 NO3TOT 0.5000E-05  SIO2TOT 0.7000E-04  BTOT  0.4000E-03  BRTOT 0.8000E-03  H2STOT 0.0000E 00  NH4TOT 0.0000E 00


 PH =  7.50   PE =  3.56   TEMP = 10.00DEG C   DENSITY = 1.030GM/CC
 -LOG(PCO2) = 2.66   -LOG(PO2) = 44.20   -LOG(PCH4) = 65.87
 IONIC STRENGTH = 0.66321   TOTAL DISS SOLIDS = 35.74GM/LITRE SOLN   TOTAL INORG CARBON MOLALITY = 0.2573E-02
  ION BALANCE ERROR =  0.03PERCENT   CATION EXCESS = 0.3977E-03(CHARGE*MOLES)   H2O ACTIVITY = 0.9808


 *****  INDIVIDUAL SPECIES MOLALITIES  ***

                      OH-    0.1531E-06  CO3--  0.6184E-05  HCO3-  0.1911E-02  SO4--  0.1621E-01  CL-    0.5506E 00
 CA++   0.8935E-02  CAOH+  0.7089E-08  CACO30 0.2928E-05  CAHCO3 0.2833E-04  CASO40 0.1091E-02
 MG++   0.4456E-01  MGOH+  0.2422E-06  MGCO30 0.1158E-04  MGHCO3 0.2925E-03  MGSO40 0.5426E-02
 NA+    0.4762E 00                     NACO3- 0.5573E-05  NAHCO3 0.2138E-03  NASO4- 0.7295E-02  NACLO  0.2536E-02
 K+     0.9860E-02                                                           KSO4-  0.1498E-03  KCLO   0.4830E-04
 BA++   0.2012E-07  BAOH+  0.2136E-14
 SR++   0.9052E-04  SROH+  0.1535E-10
 LI+    0.1984E-04  LIOHO  0.1156E-11                                        LISO4- 0.2776E-06
 H4SIO4 0.7020E-04  H3SIO4 0.2088E-06  H2SIO4 0.5672E-11
 AL+++  0.4861E-12  ALOH++ 0.1491E-10  ALOH2+ 0.9218E-09  ALOH4- 0.9964E-07  ALSO4+ 0.2490E-12  ALSO42 0.5676E-13
 FE+++  0.1779E-16  FEOH++ 0.3151E-12  FEOH2+ 0.3486E-09  FEOH30 0.2531E-08  FEOH4- 0.6375E-09  FECL++ 0.3142E-16
                    FECL2+ 0.7997E-16  FECL30 0.1577E-17                     FESO4+ 0.5292E-16
 FE++   0.4266E-07  FEOH+  0.6906E-10  FEOH20 0.1753E-14  FEOOH- 0.8391E-16  FESO40 0.4038E-08
 NH4+   0.0000E 00  NH3AQ  0.0000E 00                                        NH4SO4 0.0000E 00  NO3-   0.5029E-05
 H+     0.4162E-07                                        H2SO40 0.2641E-18  HSO4-  0.9622E-08  HCLO   0.1417E-14
 H2SAQ  0.1453E-62  HS-    0.5914E-62  S--    0.2341E-67                                        BR-    0.8046E-03
 H3BO30 0.3867E-03  H2BO3- 0.1562E-04                                        H2CO3* 0.1013E-03  O2AQ   0.9534E-47


 *****  MINERAL SATURATION INDICES  ***

 ADULARIA   0.18 ALBITE    -0.84 ANHYDRIT  -0.74 ANORTHIT  -5.10 ARAGONIT  -0.41 BARITE    -0.91 BOEHMITE  -0.58
 BRUCITE   -4.48 CALCITE   -0.10 CA-MONT    0.18 CELESTIT  -1.32 CHALCEDN  -0.37 CHLORITE   0.61 DOLOMITE   0.44
 GIBBSITE  -1.13 GOETHITE   3.30 GREIGITE-218.64 GYPSUM    -0.55 HALITE    -2.47 HALLOYST  -2.93 HEMATITE  10.03
 HUNTITE   -2.25 HYDROMAG  -2.37 ILLITE     0.90 KAOLINIT   1.33 K-MICA     0.80 MACKINAW -58.30 MAGNESIT   0.25
 MAGNETIT   7.76 MIRABILT  -1.68 NESQUEHO  -2.74 PHLOGOPT  -5.82 PYRITE   -91.83 PYROPHYL  -3.19 QUARTZ     0.18
 SIDERITE  -3.52 STRONTNT   0.89 TALC      -0.00 THENARDT  -3.29 WITHERIT  -0.68
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*****  SAMPLE NUMBER   2


*****  INPUT DATA (MOLES PER LITRE OF SOLUTION : EQUIVALENTS PER LITRE FOR ALKALINITY)
 CATOT  0.1200E-01  MGTOT   0.1500E-02  NATOT 0.0000E 00  KTOT  0.0000E 00  CLTOT  0.0000E 00  ALK    0.4000E-02
 SO4TOT 0.1250E-01  ALTOT   0.0000E 00  FETOT 0.0000E 00  SRTOT 0.0000E 00  BATOT  0.0000E 00  LITOT  0.0000E 00
 NO3TOT 0.0000E 00  SIO2TOT 0.0000E 00  BTOT  0.0000E 00  BRTOT 0.0000E 00  H2STOT 0.0000E 00  NH4TOT 0.0000E 00


 PH =  7.00   PE = 99.99   TEMP =  5.00DEG C   DENSITY = 1.000GM/CC
 -LOG(PCO2) = 1.77   -LOG(PO2) = 99.99   -LOG(PCH4) = 99.99
 IONIC STRENGTH = 0.03904   TOTAL DISS SOLIDS =  1.96GM/LITRE SOLN   TOTAL INORG CARBON MOLALITY = 0.5068E-02
 ION BALANCE ERROR = -4.88PERCENT   CATION EXCESS =-0.2004E-02(CHARGE*MOLES)   H2O ACTIVITY = 0.9995


*****  INDIVIDUAL SPECIES MOLALITIES  ***


                  OH-    0.2387E-07 CO3--  0.1784E-05 HCO3-  0.3875E-02 SO4--  0.8822E-02 CL-    0.0000E 00
 CA++   0.8599E-02 CAOH+  0.2250E-08 CACO30 0.4226E-05 CAHCO3 0.9594E-04 CASO40 0.3324E-02
 MG++   0.1100E-02 MGOH+  0.1736E-08 MGCO30 0.3683E-06 MGHCO3 0.2382E-04 MGSO40 0.3786E-03
 NA+    0.0000E 00                   NACO3- 0.0000E 00 NAHCO3 0.0000E 00 NASO4- 0.0000E 00 NACLO  0.0000E 00
 K+     0.0000E 00                                                       KSO4-  0.0000E 00 KCLO   0.0000E 00
 BA++   0.0000E 00 BAOH+  0.0000E 00
 SR++   0.0000E 00 SROH+  0.0000E 00
 LI+    0.0000E 00 LIOHO  0.0000E 00                                     LISO4- 0.0000E 00
 H4SIO4 0.0000E 00 H3SIO4 0.0000E 00 H2SIO4 0.0000E 00
 AL+++  0.0000E 00 ALOH++ 0.0000E 00 ALOH2+ 0.0000E 00 ALOH4- 0.0000E 00 ALSO4+ 0.0000E 00 ALSO42 0.0000E 00
 FE+++  0.0000E 00 FEOH++ 0.0000E 00 FEOH2+ 0.0000E 00 FEOH30 0.0000E 00 FEOH4- 0.0000E 00 FECL++ 0.0000E 00
                   FECL2+ 0.0000E 00 FECL30 0.0000E 00                   FESO4+ 0.0000E 00
 FE++   0.0000E 00 FEOH+  0.0000E 00 FEOH20 0.0000E 00 FEOOH- 0.0000E 00 FESO40 0.0000E 00
 NH4+   0.0000E 00 NH3AQ  0.0000E 00
 H+     0.1153E-06                                                       NH4SO4 0.0000E 00 NO3-   0.0000E 00
 H2SAQ  0.0000E 00 HS-    0.0000E 00 S--    0.0000E 00 H2SO40 0.4420E-17 HSO4-  0.3016E-07 HCLO   0.0000E 00
 H3BO30 0.0000E 00 H2BO3- 0.0000E 00                                                        BR-    0.0000E 00
                                                                         H2CO3* 0.1066E-02 O2AQ   0.0000E 00

*****  MINERAL SATURATION INDICES  ***

 ADULARIA -99.99 ALBITE   -99.99 ANHYDRIT  -0.36 ANORTHIT -99.99 ARAGONIT  -0.33 BARITE   -99.99 BOEHMITE -99.99
 BRUCITE   -7.19 CALCITE    0.00 CA-MONT  -99.99 CELESTIT -99.99 CHALCEDN -99.99 CHLORITE -99.99 DOLOMITE  -1.08
 GIBBSITE -99.99 GOETHITE -99.99 GREIGITE -99.99 GYPSUM    -0.07 HALITE   -99.99 HALLOYST -99.99 HEMATITE -99.99
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Computer

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WATEQ, A COMPUTER PROGRAM FOR CALCULATING CHEMICAL EQUILIBRIA OF NATURAL WATERS

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Abstract.—The computer program, WATEQ, calculates the equilibrium distribution of inorganic aqueous species of major and important minor elements in natural waters using the chemical analysis and *in situ* measurements of temperature, pH, and redox potential. From this model, the states of reaction of the water with solid and gaseous phases are calculated. Thermodynamic stabilities of aqueous species, minerals, and gases have been selected from a careful consideration of all available experimental data. The program is written in PL-1 for IBM 360 computers.

The chemistry of water-rock interactions is determined in part by possible reactions with regard to the states of the water (undersaturated or supersaturated with respect to a solid phase or to a gas at a certain pressure). The reaction states may be calculated from an equilibrium chemical model of the water and from the stabilities of phases with which it may react. The examination of reaction states may suggest the origin of dissolved constituents and assist in the prediction of the chemical effects of ground-water production, recharge, and irrigation. Although the use of inorganic equilibrium models for the processes of mineral solution and precipitation cannot produce a complete description of these processes, an equilibrium model is a useful reference. It can indicate which processes are impossible for a given water-rock system and suggest which processes may control water compositions and which processes are so hindered by kinetic factors that the water compositions are indifferent to them.

Calculations of the states of saturation of natural waters with minerals are complicated by the consideration of all the factors which affect the activity of the ions involved in the solution equilibria. One simple approach for multicomponent water solutions is to assume the existence of complexes whose formation is described by mass-action expressions and to assume that the activity coefficients of simple ions and complexes can be described by equations depending only on the temperature and a function of the water composition, the ionic strength. The number of possible ions, complexes, and minerals and the use of iteration for the solution of simultaneous equations and for the calculation of activity coefficients practically necessitate the use of computer methods.

This report is an attempt to provide a general computer program, for the calculation of chemical equilibria in natural waters at low temperatures, that may be expanded and updated by the user as additional stability data on complexes and minerals become available. The complete computer program is available from the National Technical Information Service, Springfield, VA 22151, as document No. PB-220 464 at a cost of $1.45 per microfiche and $4.85 per paper copy. The study was financed in part by the Defense Advanced Research Projects Agency of the Department of Defense under Order 1813, Amendment 1.

Acknowledgments.—Our thanks are extended to Ivan Barnes, whose earlier program suggested the format, and to C. L. Christ, J. Haas, G. M. Lafon, F. J. Pearson, Jr., Y. Karaka and E. A. Jenne for data and for corrections to the program. We are especially grateful to Manuel Nathenson for checking the thermodynamic data. The thermodynamic approach has been influenced by Garrels and Christ (1965), Sillen and Martell (1964), and Denbigh (1955). Many readers find the approach familiar, and they may wish to omit the next sections in which the minimum thermodynamic theory necessary to explain the calculations is presented.

MASS-ACTION EQUILIBRIUM EQUATIONS

In a mixture at equilibrium, the activities of the chemical species present are related by a set of mass-action equilibrium equations (Garrels and Christ, 1965, p. 6, 342; Denbigh, 1955, p. 138, 307). For each possible reaction of the form,

$$aA+bB=cC+dD, \tag{1}$$

in which lowercased letters are the stoichiometric coefficients of the chemical species represented by the uppercased letters, there is a mass action equation of the form,

$$K=\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \tag{2}$$

In this equation, K is the mass action or equilibrium constant, and the brackets represent activities. For equilibria involving low-pressure gases, the partial pressure of the gas may be used instead of activity, and for gas-aqueous solution equilibria, activities and partial pressures may be used in the same equation.

The equilibrium constants may be derived from experimental measurement of concentrations in a series of equilibrium mixtures of different total concentration with extrapolation to infinite dilution. Alternatively, the experimental concentrations may be corrected to activities by means of calculated activity coefficients (see later discussion). Useful compilations of experimentally derived equilibrium constants have been made by Sillen and Martel (1964), Barnes, Helgeson, and Ellis (1966), Ellis (1967) and Helgeson (1969).

The equilibrium constant for a reaction may also be derived from the standard free energy change of that reaction. For the reaction given by equation 1, the sum of the standard free energies of formation, ΔG°_f, of the products times their stoichiometric coefficients less that of the reactants times their stoichiometric coefficients is the standard free energy change of reaction:

$$\Delta G^\circ_r = c\Delta G^\circ_f,\ C + d\Delta G^\circ_f,\ D - (a\Delta G^\circ_f,\ A + b\Delta G^\circ_f,B)\ . \qquad (3)$$

This standard free energy change of reaction is related to the equilibrium constant of the reaction by the equation,

$$\Delta G^\circ_r = -2.303\ RT \log K \qquad (4)$$

In which R is the gas constant and T is the absolute temperature. By the use of these equations, experimental equilibrium data may be related to thermochemical data derived from calorimetric measurements. Useful compilations of standard free energies of formation (and other thermochemical data) have been made by the National Bureau of Standards (Rossini and others, 1952; Wagman and others, 1968 and 1969) and by Latimer (1952), Garrels and Christ (1965), Robie and Waldbaum (1968) and Helgeson (1969).

No single source of equilibrium constants or thermochemical data is of sufficient scope or of recent enough publication to include all the data relevant to near-surface rock-water reactions. The data contained in WATEQ (table 1) are from a compilation in preparation by the authors of this program and Manuel Nathenson.

The effect of temperature and pressure on mass action equations will be considered in a later section.

Table 1.—*Reactions and thermodynamic data*

[Log K_{298} (logarithm of equilibrium constant at 298 K) and $\Delta H_{r,298}$ (heat of reaction at 298 K), unless otherwise noted, are calculated from free energies and enthalpies. Data source values are given for the reactions as considered by the original reference, not necessarily as printed here. R and W refer to Robie and Waldbaum (1968); 270-3 and 270-4 refer to Wagman and others (1968) and (1969), respectively. S°, standard state of entropy. Sources for ΔG_f and ΔH_f of individual ion species in solution are all from 270-3 or 270-4, except that Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, and Li^+ are from Latimer (1952), $H_4SiO_4^\circ$ is from Helgeson (1969), and H^+ plus e^- are 0 by definition. ΔG and ΔH values are given in calories]

Reaction No.	Mineral or species name	Reaction	log K	ΔH_r	Data source
0	Fe^{+2}	$Fe^{+2} = Fe^{+3} + e^-$	-13.013	9,700	ΔG_f and ΔH_f from 270-4.
1	$FeOH^{+2}$	$Fe^{+2} + H_2O = FeOH^{+2} + e^- + H^+$	-15.473	20,115	$Fe^{+3} + H_2O = FeOH^{+2} + H^+$, log $K = -2.46$; Lamb and Jacques as quoted in Langmuir (1969), ΔH_f from 270-4.
2	$FeOH^+$	$Fe^{+2} + H_2O = FeOH^+ + H^+$	- 9.319	13,218	From ΔH_r and ΔS_r of magnetite hydrolysis (Sweeton and Baes, 1970).
3	$Fe(OH)_3^-$	$Fe^{+2} + 3H_2O = Fe(OH)_3^- + 3H^+$	-29.458	32,995	Do.
4	$FeSO_4^+$	$Fe^{+2} + SO_4^{-2} = FeSO_4^+ + e^-$	- 8.886	15,920	ΔG_f and ΔH_f from 270-4.
5	$FeCl^{+2}$	$Fe^{+2} + Cl^- = FeCl^{+2} + e^-$	-11.600	18,152	Do.
6	$FeCl^+$	$Fe^{+2} + 2Cl^- = FeCl_2^+ + e^-$	-10.919	--------	ΔG_f from 270-4.
7	$FeCl_3^\circ$	$Fe^{+2} + 3Cl^- = FeCl_3^\circ + e^-$	-11.925	--------	Do.
8	$FeSO_4^\circ$	$Fe^{+2} + SO_4^{-2} = FeSO_4^\circ$	2.200	560	Log $K = 2.20$, $\Delta H_r = 560$ (Izatt and others, 1969).
9	Siderite	$FeCO_3 = Fe^{+2} + CO_3^{-2}$	-10.55	-5,328	Langmuir (1969), ΔH_f from R and W.
10	Magnesite	$MgCO_3 = Mg^{+2} + CO_3^{-2}$	- 8.029	-6,169	Do.
11	Dolomite	$CaMg(CO_3)_2 = Ca^{+2} + Mg^{+2} + 2CO_3^{-2}$	-17.000	-8,290	Log $K_{298} = -17.0$ (Berner, 1967). $\Delta H_r = -8{,}290$ (Helgeson, 1969).
12	Calcite	$CaCO_3 = Ca^{+2} + CO_3^{-2}$	- 8.370	-3,190	Log $K_{298} = -8.37$ (Berner, 1967). $\Delta H_r = -3{,}190$ (Helgeson, 1969).

Table 1. *Reactions and thermodynamic data*—Continued

Reaction No.	Mineral or species name	Reaction	log K	ΔH_r	Data Source
13	..... $H_3SiO_4^-$	$H_4SiO_4^\circ - H_3SiO_4^- + H^+$	- 9.930	8,935	Log K=-9.929, ΔH_r=8.935 from log $K(T)$ expression (Ryzhenko, 1967).
14	..... $H_2SiO_4^{-2}$	$H_4SiO_4^\circ = 2H^+ + H_2SiO_4^{-2}$	-21.619	29,714	Log K=-21.617, ΔH_r=29,714 from log $K(T)$ expression (Ryzhenko, 1967).
15	..... HPO_4^{-2}	$H^+PO_4^{-3} = HPO_4^{-2}$	12.346	-3,530	ΔC_f and ΔH_f from 270-3.
16	..... $H_2PO_4^-$	$2H^+ + PO_4^{-3} = H_2PO_4^-$	19.553	-4,520	Do.
17	..... Anhydrite	$CaSO_4 = Ca^{+2} + SO_4^{-2}$	- 4.637	-3,769	ΔC_f and ΔH_f from R and W.
18	..... Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{+2} + SO_4^{-2} + 2H_2O$	- 4.848	261	Do.
19	..... Brucite	$Mg(OH)_2 = Mg^{+2} + 2OH^-$	-11.204	850	ΔC_f and ΔH_f from R and W.
20	..... Chrysotile	$Mg_3Si_2O_5(OH)_4 + 5H_2O = 3Mg^{+2} + 2H_4SiO_4^\circ + 6OH^-$	-51.800	27,585	Log K=-51.8 (Hostetler and Christ, 1968), ΔH_f from R and W.
21	..... Aragonite	$CaCO_3 = Ca^{+2} + CO_3^{-2}$	-8.305	-2,959	ΔC_f and ΔH_f from R and W.
22	..... MgF^+	$Mg^{+2} + F^- = MgF^+$	1.820	4,674	Log K=1.82, ΔH_r=24 (Sillen and Martell, 1964).
23	..... $CaSO_4^\circ$	$Ca^{+2} + SO_4^{-2} = CaSO_4^\circ$	2.309	1,650	Log K=2.309, ΔH_r=1,650 (Bell and George, 1953).
24	..... $MgOH^+$	$Mg^{+2} + OH^- = MgOH^+$	2.600	2,140	Log K=2.6 (Hostetler, 1963); ΔH_r=2,140 (Helgeson, 1969).
25	..... H_3BO_3	$H_3BO_3 = H^+ + H_2BO_3^-$	-9.240	3,224	Log K=4.757-log KW, ΔH_r=-10,121 -$(\Delta H_r)_{KW}$ from log $K(T)$ expression (Mesmer and others, 1972).
26	..... NH_3°	$NH_4^+ = NH_3^\circ + H^+$	-9.252	12,480	ΔC_f and ΔH_f from 270-3.
27	..... Forsterite	$Mg_2SiO_4 + 4H_2O = 2Mg^{+2} + 2H_4SiO_4 + 4OH^-$	-27.694	4,870	ΔC_f and ΔH_f from R and W.
28	..... Diopside	$CaMgSi_2O_6 + 6H_2O = Ca^{+2} + Mg^{+2} + 2H_4SiO_4^\circ + 4OH^-$	-36.106	21,100	Do.
29	..... Clinoenstatite	$MgSiO_3 + 3H_2O = Mg^{+2} + H_4SiO_4^\circ + 2OH^-$	-16.658	6,675	Do.
30	..... $NaHPO_4^-$	$Na^+ + HPO_4^{-2} = NaHPO_4^-$	1.200	----------	Log K=1.20 obtained by calculation from data of Smith and Alberty (1956) by using $K_{equiv} = \gamma NaHPO_4^- / (\gamma Na^+ \gamma HPO_4^{-2})$ and K_{approx} and by assuming $\gamma HPO_4^{-2} = \gamma SO_4^{-2} = 0.25$, $\gamma Na^+ = 0.75$, and $\gamma NaHPO_4^- = \gamma Na^+$.
31	..... Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2 + 22H_2O = 2Ca^{+2} + 5Mg^{+2} + 8H_4SiO_4^\circ + 14OH^-$	-139.426	90,215	ΔC_f and ΔH_f from R and W.
32	..... $KHPO_4^-$	$K^+ + HPO_4^{-2} = MgHPO_4^\circ$	1.090	----------	Log K=1.09 obtained by calculation from data of Smith and Alberty (1956) in a similar manner to $NaHPO_4^-$.
33	..... $MgHPO_4^\circ$	$Mg^{+2} + HPO_4^{-2} = MgHPO_4^\circ$	2.870	3,300	Log K=2.87 (Sillen and Martell, 1964), ΔH_r=3,300 by analogy to $CaHPO_4^\circ$ data of Chughtai, Marshall, and Nancollas (1968).
34	..... $CaHPO_4^\circ$	$Ca^{+2} + HPO_4^{-2} - CaHPO_4^\circ$	2.739	3,300	Log K=2.739, ΔH_r=3,300 (Chughtai and others, 1968).
35	..... HCO_3^-	$H_2CO_3^\circ = HCO_3^- + H^+$	-6.379	1,976	Log K=-6.379, ΔH_r=1,976 from log $K(T)$ expression (Ryzhenko, 1963).
36	..... Sepiolite	$Mg_2Si_3O_{7.5}OH \cdot 3H_2O + 4.5H_2O = 2Mg^{+2} + 3H_4SiO_4^\circ + 4OH^-$	-40.079	26,532	ΔC_f=-1,105,600; S°=90.1 (Christ and others, 1973).
37	..... Talc	$Mg_3Si_4O_{10}(OH)_2 + 10H_2O = 3Mg^{+2} + 4H_4SiO_4^\circ + 6OH^-$	-60.933	45,065	ΔG_f from Hostetler and others (1971): ΔH_f from R and W.
38	..... Hydromagnesite ..	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O = 5Mg^{+2} + 4CO_3^{-2} + 2OH^- + 4H_2O$	-36.762	-25,520	ΔG_f and ΔH_f from Robie and Hemingway (1972).
39	..... Adularia	$KAlSi_3O_8 + 8H_2O = K^+ + Al(OH)_4^- + 3H_4SiO_4^\circ$	-20.573	30,820	ΔG_f and ΔH_f from R and W.

Table 1.—*Reactions and thermodynamic data*—Continued

Reaction No.	Mineral or species name	Reaction	log *K*	ΔH_r	Data source
40	Albite	$NaAlSi_3O_8 + 8H_2O = Na^+ + Al(OH)_4^- + 3H_4SiO_4^0$	-18.002	25,896	Do.
41	Anorthite	$CaAl_2Si_2O_8 + 8H_2O = Ca^{+2} + 2Al(OH)_4^- + 2H_4SiO_4^0$	-19.424	17,530	ΔG_f and ΔH_f from R and W.
42	Analcime	$NaAlSi_2O_6 \cdot H_2O + 5H_2O = Na^+ + Al(OH)_4^- + 2H_4SiO_4^0$	-12.701	18,206	Do.
43	K-mica	$KAl_3Si_3O_{10}(OH)_2 + 12H_2O = K^+ + 3Al(OH)_4^- + 3H_4SiO_4^0 + 2H^+$	-49.102	67,860	Do.
44	Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2 + 10H_2O = K^+ + 3Mg^{+2} + Al(OH)_4^- + 3H_4SiO_4^0 + 6OH^-$	------------	----------	No data.
45	Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 + 11.2H_2O = 0.6K^+ + 0.25Mg^{+2} + 2.3Al(OH)_4^- + 3.5H_4SiO_4^0 + 1.2H^+$	-40.267	54,684	ΔG_f and ΔH_f from Helgeson (1969).
46	Kaolinite	$Al_2Si_2O_5(OH)_4 + 7H_2O = 2Al(OH)_4^- + 2H_4SiO_4^0 + 2H^+$	-36.921	49,150	Kaolinite $+ 6H^+ = 2Al^{+3} + 2H_4SiO_4 + H_2O$; log *K*=7.185 (Kittrick, 1966); ΔH_f from R and W.
47	Halloysite	$Al_2Si_2O_5(OH)_4 + 7H_2O = 2Al(OH)_4^- + 2H_4SiO_4^0 + 2H^+$	-32.830	44,680	ΔG_f and ΔH_f from R and W.
48	Beidellite	$(Na,K,\frac{1}{2}Mg)_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12H_2O = 0.33(Na,K,\frac{1}{2}Mg)^+ + 2.33Al(OH)_4^- + 3.67H_4SiO_4^0 + 2H^+$	-45.272	60,355	ΔG_f and ΔH_f from Helgeson (1969) for Na end member.
49	Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8 + 10H_2O = 5Mg^{+2} + 2Al(OH)_4^- + 3H_4SiO_4^0$	-89.563	54,760	ΔG_f and ΔH_f taken as average of Helgeson (1969) and Zen (1972).
50	Alunite	$KAl_3(SO_4)_2(OH)_6 = K^+ + 3Al^{+3} + 2SO_4^{-2} + 6OH^-$	-85.334	29,820	ΔG_f and ΔH_f from Hemley and others (1969).
51	Gibbsite (crystalline)	$Al(OH)_3 = Al^{+3} + 3OH^-$	-32.774	14,470	ΔG_f and ΔH_f from R and W.
52	Boehmite	$AlO(OH) + H_2O = Al^{+3} + 3OH^-$	-33.416	11,905	Do.
53	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2 + 12H_2O = 2Al(OH)_4^- + 4H_4SiO_4^0 + 2H^+$	-48.314	----------	ΔG_r=65,900 from data in tables 4 and 5 in Reesman and Keller (1968).
54	Phillipsite	$Na_{0.5}K_{0.5}AlSi_3O_8 \cdot H_2O + 7H_2O = 0.5Na^+ + 0.5K^+ + Al(OH)_4^- + 3H_4SiO_4^0$	-19.874	----------	Log *K*=0.7 for reaction phillipsite$+ 0.5K^+ =$K-feldspar$+ 0.5Na^+ + H_2O$: ΔG_f of K-feldspar from R and W; (Hess, 1966).
55	Erionite	$NaAlSi_{3.5}O_9 \cdot 3H_2O + 6H_2O = Na^+ + Al(OH)_4^- + 3.5H_4SiO_4^0$	------------	----------	No data.
56	Clinoptilolite	$(K,Na)AlSi_5O_{12} \cdot 3.5H_2O + 8.5H_2O = (K,Na)^+ + Al(OH)_4^- + 5H_4SiO_4^0$	------------	----------	Do.
57	Mordenite	$(Na,K)AlSi_{4.5}O_{11} \cdot 3H_2O + 8H_2O = (Na,K)^+ + Al(OH)_4^- + 4.5H_4SiO_4^0$	------------	----------	Do.
58	Nahcolite	$NaHCO_3 = Na^+ + HCO_3^-$	-0.548	3,720	ΔG_f and ΔH_f from Latimer (1952).
59	Trona	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O = 2H_2O + 3Na^+ + CO_3^{-2} + HCO_3^-$	-0.795	-18,000	From data on natron (this study), nahcolite (Latimer, 1952), and trona-nahcolite-soda in equilibrium at 21.1°C (Linke and Seidell, 1965, p. 925).
60	Natron	$Na_2CO_3 \cdot 10H_2O = 2Na^+ + CO_3^{-2} + 10H_2O$	-1.311	15,745	$Na_2CO_3 \cdot 10H_2O = Na_2CO_3 \cdot H_2O + 9H_2O$ (g); ΔG_r=20,435; ΔH_r=113,218 (Waterfield and others, 1968); ΔG_f and ΔH_f of thermonatrite computed in this study.
61	Thermonatrite	$Na_2CO_3 \cdot H_2O = 2Na^+ + CO_3^{-2} + H_2O$	0.125	-2,802	$Na_2CO_3 \cdot H_2O = Na_2CO_3 + H_2O$ (g); ΔG_r=2,944; ΔH_r=14.037; Waterfield and others (1968); ΔG_f of Na_2CO_3 from ΔH_f of Latimer (1952) and S° of Waterfield and others (1968).
62	Fluorite	$CaF_2 = Ca^{+2} + 2F^-$	-9.046	1,530	ΔG_f and ΔH_f from R and W.
63	Ca montmorillonite	$Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12H_2O = 0.17Ca^{+2} + 2.33Al(OH)_4^- + 3.67H_4SiO_4^0 + 2H^+$	-45.027	58,373	ΔG_f and ΔH_f from Helgeson (1969).
64	Halite	$NaCl = Na^+ + Cl^-$	1.582	918	ΔG_f and ΔH_f from R and W.
65	Thenardite	$Na_2SO_4 = 2Na^+ + SO_4^{-2}$	0.179	572	Do.

Table 1.—*Reactions and thermodynamic data*—Continued

Reaction No.	Mineral or species name	Reaction	log *K*	ΔH_r	Data source
66	Mirabilite	$Na_2SO_4 \cdot 10H_2O = 2Na^+ + SO_4^{-2} + 10H_2O$	-1.114	18,987	Do.
67	Mackinawite	$FeS + H^+ = Fe^{+2} + HS^-$	-4.648	----------	Log K=-17.566 (Berner, 1967).
68	CO_3^{-2}	$HCO_3^- = H^+ + CO_3^{-2}$	-10.330	3,550	ΔG_f and ΔH_f from 270-3.
69	$NaCO_3^-$	$Na^+ + CO_3^{-2} = NaCO_3^-$	1.268	8,911	Log K=-1.268 (Garrels and others, 1961), ΔH_r=-8,911 (Lafon, 1969).
70	$NaHCO_3^\circ$	$Na^+ + HCO_3^- = NaHCO_3^\circ$	-0.250	----------	Log K=0.25 (Garrels and Thompson, 1962).
71	$NaSO_4^-$	$Na^+ + SO_4^{-2} = NaSO_4^-$	0.226	2,229	Log K=0.226, ΔH_r=308 from log $K(T)$ expression (Lafon and Truesdell, 1971).
72	KSO_4^-	$K^+ + SO_4^{-2} = KSO_4^-$	0.847	3,082	Log K=0.847, ΔH_r=3,082 from log $K(T)$ expression (Truesdell and Hostetler, 1968).
73	$MgCO_3^\circ$	$Mg^{+2} + CO_3^{-2} = MgCO_3^\circ$	3.398	58	Log K=3.398 (Garrels and others, 1961); ΔH_r=58 (Lafon, 1969).
74	$MgHCO_3^-$	$Mg^{+2} + HCO_3^- = MgHCO_3^+$	0.928	10,370	$MgHCO_3^+ = MgCO_3^\circ + H^+$, log K=-7.86 (Hostetler, 1963); ΔH_r=+10,370 (Lafon, 1969).
75	$MgSO_4^\circ$	$Mg^{+2} + SO_4^{-2} = MgSO_4^\circ$	2.238	4,920	Log K=-2.238 (Hanna and others, 1971); ΔH_r=-4,920 (Helgeson, 1969).
76	$CaOH^+$	$Ca^{+2} + OH^- = CaOH^+$	1.400	1,190	Log K=1.40; ΔH_r=1,190 (Sillen and Martell, 1964).
77	$CaHCO_3^+$	$Ca^{+2} + HCO_3^- = CaHCO_3^+$	1.260	6,331	Log K=-1.26 (Garrels and Thompson, 1962); ΔH_r=-6,331 (Lafon, 1969).
78	$CaCO_3^\circ$	$Ca^{+2} + CO_3^{-2} = CaCO_3^\circ$	3.200	3,130	Log K=-3.2 (Garrels and Thompson, 1962); ΔH_r=-3,130 (Helgeson, 1969).
79	$Na_2CO_3^\circ$	$2Na^+ + CO_3^{-2} = Na_2CO_3^\circ$	0.672	-------	Log K=-0.672 (Garrels and Christ, 1965, p. 109).
80	$AlOH^{+2}$	$Al^{+3} + OH^- = AlOH^{+2}$	8.998	1,990	$Al^{+3} + H_2O = AlOH^{+2} + H^+$; log K=-5.00 (*Hem and others* 1973). ΔH_r=1,990 (Helgeson, 1969).
81	$Al(OH)_2^+$	$Al^{+3} + 2OH^- = Al(OH)_2^+$	18.235	----------	$Al^{+3} + 2H_2O = Al(OH)_2^+ + 2H^+$; log K=-9.76 (Hem and others, 1973).
82	$Al(OH)_4^-$	$Al^{+3} + 4OH^- = Al(OH)_4^-$	33.938	-9,320	$Al(OH)_3$ (microcryst)=$Al^{+3} + 3OH$, log K=32.65; $Al(OH)_3$ (microcryst) +$H_2O = Al(OH)_4^- + H^+$; log K=-12.71. (Hem and Roberson, 1967); ΔH_f from 270-3.
83	AlF^{+2}	$Al^{+3} + F^- = AlF^{+2}$	7.010	----------	Log K=7.01 (Hem, 1968).
84	AlF_2^+	$Al^{+3} + 2F^- = AlF_2^+$	12.750	20,000	Log K=12.75 (Hem, 1968), ΔH_f from 270-3.
85	AlF_3°	$Al^{+3} + 3F^- = AlF_3^\circ$	17.020	2,500	Log K=17.02 (Hem, 1968), ΔH_f from 270-3.
86	AlF_4^-	$Al^{+3} + 4F^- = AlF_4^-$	19.720	--------	Log K=19.72 (Hem, 1968).
87	$AlSO_4^+$	$Al^{+3} + SO_4^{-2} = AlSO_4^+$	3.200	2,290	Log K=3.2 (Hem, 1968): ΔH_r=2,290 (Izatt and others, 1969).
88	$Al(SO_4)_2^-$	$Al^{+3} + 2SO_4^{-2} = Al(SO_4)_2^-$	5.100	3,070	Log K=5.1 (Hem, 1968): ΔH_r=3,070 (Izatt and others, 1969).
89	HSO_4^-	$H^+ + SO_4^{-2} = HSO_4^-$	1.987	4,910	Log K=-1.987, ΔH_r=4,910 from log $K(T)$ expression (Lietzke and others, 1961).
90	SO_4^{-2}/H_2S	$SO_4^{-2} + 10H^+ + 8e^- = H_2S^+ + 4H_2O$	40.644	65,410	ΔG_f and ΔH_f from 270-3.
91	HS^-	$H_2S = H^+ + HS^-$	6.994	5,300	Do.
92	S^{-2}	$HS^- = H^+ + S^{-2}$	-12.918	12,100	Do.
93	H_2O/O_2(gas)	$0.5H_2O = 0.25O_2(g) + H^+ + e^-$	-20.780	34,157	Definition.
94	HCO_3^-/CH_4(gas)	$HCO_3^- + 8e^- + 9H^+ = CH_4 + 3H_2O$	30.711	57,135	ΔG_f and ΔH_f from 270-3.

Table 1.—*Reactions and thermodynamic data*—Continued

Reaction No.	Mineral or species name	Reaction	Log K	ΔH_r	Data source
95	OH apatite	$Ca_5(PO_4)_3(OH)+3H_2O=5Ca^{+2}+3HPO_4^{-2}+4OH^-$	-59.421	17,225	OH apatite $=5Ca^{+2}+3PO_4^{-3}+OH^-$; log $K=-54.408$ (Brown, 1960); ΔH_f from R and W.
96	F apatite	$Ca_5(PO_4)_3F+3H_2O=5Ca^{+2}+3HPO_4^{-2}+3OH^-+F^-$	67.243	19,695	ΔG_f and ΔH_f from Robertson (1966).
97	Chalcedony	$SiO_2+2H_2O=H_4SiO_4^\circ$	-3.523	4,615	Log K and ΔH_r obtained from data of R. O. Fournier and J. J. Rowe (in Fournier, 1973).
98	Magadiite	$NaSi_7O_{13}(OH)_3 \cdot 3H_2O+H^++9H_2O=Na^++7H_4SiO_4^\circ$	-14.300	----------	Log $K=-14.3$ (Bricker, 1969).
99	Cristobalite	$SiO_2+2H_2O=H_4SiO_4^\circ$	-3.587	5,500	ΔG_f and ΔH_f from R and W.
100	Silica gel	$SiO_2+2H_2O=H_4SiO_4^\circ$	-3.018	4,440	Do.
101	Quartz	$SiO_2+2H_2O=H_4SiO_4^\circ$	-4.006	6,220	Do.
102	$Fe(OH)_2^+$	$Fe^{+2}+2H_2O=Fe(OH)_2^++2H^++e^-$	-20.173	----------	$FeOH^{+2}+H_2O=Fe(OH)_2^++H^+$; log $K=-4.7$, Lamb and Jacques as quoted in Langmuir (1969).
103	$Fe(OH)_3^\circ$	$Fe^{+2}+3H_2O=Fe(OH)_3^\circ+3H^++e^-$	-26.571	----------	$Fe(OH)_3^\circ=Fe(OH)_2^++OH^-$; log $K=7.6$, Hem and Cropper as quoted in Langmuir (1969).
104	$Fe(OH)_4^-$	$Fe^{+2}+4H_2O=Fe(OH)_4^-+4H^++e^-$	-34.894	----------	Rough estimate from $Fe^{+3}+4OH^-=Fe(OH)_4^-$; log $K=34.11$ in 3 M $NaClO_4$ solution (Langmuir, 1969).
105	$Fe(OH)_2^\circ$	$Fe^{+2}+2H_2O=Fe(OH)_2^\circ+2H^+$	-20.570	28,565	From ΔH_r and ΔS_r of magnetite hydrolysis (Sweeton and Baes, 1970).
106	Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O=3Fe^{+2}+2PO_4^{-3}+8H_2O$	-36.000	----------	Vivianite $=3Fe^{+2}+2PO_4^{-3}+8H_2O$: log $K=-36$ (Nriagu, 1972b).
107	Magnetite	$Fe_3O_4+8H^+=3Fe^{+3}+4H_2O+e^-$	-9.565	-40,660	ΔG_f and ΔH_f from R and W.
108	Hematite	$Fe_2O_3+6H^+=2Fe^{+3}+3H_2O$	-4.008	-30,845	Do.
109	Maghemite	$Fe_2O_3+6H^+=2Fe^{+3}+3H_2O$	6.386	----------	Maghemite $+3H_2O=2Fe^{+3}+6OH^-$; log $K=-77.6$ (Doyle as quoted in Langmuir, 1969).
110	Goethite	$FeO(OH)+H_2O=Fe^{+3}+3OH^-$	-41.200	25,555	2 goethite = hematite + H_2O; $\Delta G_r=545$ (Langmuir, 1971); ΔH_f from R and W.
111	Greenalite	$Fe_3Si_2O_5(OH)_4+5H_2O=3Fe^{+2}+2H_4SiO_4^\circ+6OH^-$	----------	----------	No data.
112	$Fe(OH)_3$ (amorphous)	$Fe(OH)_3+3H^+=Fe^{+3}+3H_2O$	4.891	----------	$Fe(OH)_3$ (amorphous) $=Fe^{+3}+3OH^-$; log $K=-37.1$ (Langmuir, 1969).
113	Annite	$KFe_3AlSi_3O_{10}(OH)_2+10H_2O=K^++3Fe^{+2}+Al(OH)_4^-+3H_4SiO_4^\circ$	-85.645	62,480	ΔG_f and ΔH_f from Helgeson (1969).
114	Pyrite	$FeS_2+2H^++2e^-=Fe^{+2}+2HS^-$	-18.479	11,300	ΔG_f and ΔH_f from R and W.
115	Montmorillonite (Belle Fourche)	$(H,Na,K)_{0.28}Mg_{0.29}Fe^{+3}_{0.23}Al_{1.58}Si_{3.93}O_{10}(OH)_2+10.04H_2O=0.28(H,Na,K)^++0.29Mg^{+2}+0.23Fe^{+3}+1.58Al(OH)_4^-+3.93H_4SiO_4^\circ+0.23Fe^{+3}$	-34.913	----------	Recalculated from data in table 2 of Kittrick (1971a) assuming hydrogen montmorillonite was dissolved in equilibrium with $Fe(OH)_3$ (amorph) rather than hematite.
116	Montmorillonite (Aberdeen)	$(H,Na,K)_{0.42}Mg_{0.45}Fe^{+3}_{0.34}Al_{1.47}Si_{3.82}O_{10}(OH)_2+9.16H_2O+0.84H^+=0.42(H,Na,K)^++0.45Mg^{+2}+0.34Fe^{+3}+1.47Al(OH)_4^-+3.82H_4SiO_4^\circ$	-29.688	----------	Recalculated from data in table 2 of Kittrick (1971b) assuming hydrogen montmorillonite was dissolved in equilibrium with $Fe(OH)_3$ (amorph) rather than hematite.
117	Huntite	$CaMg_3(CO_3)_4=3Mg^{+2}+Ca^{+2}+4CO_3^{-2}$	29.968	25,760	ΔG_f and ΔH_f from Hemingway and Robie (1972).
118	Greigite	$Fe_3S_4+4H^++2e^-=3Fe^{+2}+4HS^-$	18.959	----------	Log K 70.63 (Berner, 1967).

Table 1.—*Reactions and thermodynamic data*—Continued

Reaction No.	Mineral or species name	Reaction	Log *K*	ΔH_r	Data source
119	FeS (precipitate)	$FeS+H^+=Fe^{+2}+HS^-$	-3.915	—	Log K=-16.833 (Berner, 1967).
120	FeH_2PO_4	$Fe^{+2}+H_2PO_4=FeH_2PO_4^+$	2.700	—	Log K=2.7 (Nriagu, 1972b).
121	$CaPO_4^-$	$Ca^{+2}+PO_4^{-3}=CaPO_4^-$	6.459	3,100	Log K=6.459, ΔH_r=3,100 (Chughtai and others, 1968).
122	$CaH_2PO_4^+$	$Ca^{+2}+H_2PO_4^-=CaH_2PO_4^+$	1.408	3,400	Log K=1.408, ΔH_r=3,400 (Chughtai and others, 1968).
123	$MgPO_4^-$	$Mg^{+2}+PO_4^{-3}=MgPO_4^-$	6.589	3,100	Log K adjusted from $CaPO_4^-$ by using analogy between $CaHPO_4^-$ and $MgHPO_4^\circ$; that is, log K=6.459+(2.87-2.74)=6.589, ΔH_r=3,100 by analogy with $CaPO_4^-$.
124	$MgH_2PO_4^+$	$Mg^{+2}+H_2PO_4^-=MgH_2PO_4^+$	1.513	3,400	Log K adjusted from $CaH_2PO_4^-$ by using analogy between $CaHPO_4^-$ and $MgHPO_4^\circ$; that is, log K=1.408+(2.87-2.74)=1.513, ΔH_r=3,400 by analogy with $CaH_2PO_4^-$.
125	$LiOH^\circ$	$Li^++OH^-=LiOH^\circ$	0.200	4,832	ΔG_r=-273, ΔH_r=4,832 obtained by fitting best straight line in log K vs. $1/T$ plot of data in Sillen and Martell (1964).
126	$LiSO_4^-$	$Li^++SO_4^{-2}=LiSO_4^-$	0.640	—	Log K=0.64 (Sillen and Martell, 1964).
127	NO_3^-/NH_4^+	$NO_3^-+10H^++8e^-=NH_4^++3H_2O$	119.077	-187,055	ΔG_f and ΔH_r from 270-3.
128	Laumontite	$CaAl_2Si_4O_{12}\cdot 4H_2O+8H_2O=Ca^{+2}+2Al(OH)_4^-+4H_4SiO_4^\circ$	-31.053	39,610	ΔG_f and ΔH_f from Zen (1972).
129	$SrOH^+$	$Sr^{+2}+OH^-=SrOH^+$	0.820	1,150	Log K=0.82, ΔH_r=1,150 (Sillen and Martell, 1964).
130	$BaOH^+$	$Ba^{+2}+OH^-=BaOH^+$	0.640	1,750	Log K=0.64, ΔH_r=1,750 (Sillen and Martell, 1964).
131	$NH_4SO_4^-$	$NH^++SO_4^{-2}=NH_4SO_4^-$	1.110	—	Log K=1.110 (Sillen and Martell, 1964).
132	HCl°	$H^++Cl^-=HCl^\circ$	-6.100	18,630	Log K=-6.1, ΔH_r=18,630 (Helgeson, 1969).
133	$NaCl^\circ$	$Na^++Cl^-=NaCl^\circ$	-1.602	—	Log K=-1.602 (Hanna and others, 1971).
134	KCl°	$K^++Cl^-=KCl^\circ$	-1.585	—	Log K=-1.585 (Hanna and others, 1971).
135	$H_2SO_4^\circ$	$2H^++SO_4^{-2}=H_2SO_4^\circ$	-1.000	—	$H^++HSO_4^-=H_2SO_4^\circ$; log K=-3, (Sillen and Martell, 1964).
136	H_2O/O_2 (aqueous)	$0.5H_2O=0.25\ O_2(aq)+H^++e^-$	-11.385	—	Eh=0.70 from equation (1) of Sato (1960).
137	H_2CO_3	$CO_2(g)+H_2O=H_2CO_3$	-1.452	-5,000	ΔG_f and ΔH_f from 270-3.
138	$FeHPO_4^\circ$	$Fe^{+2}+HPO_4^{-2}=FeHPO_4^\circ$	3.600	—	Log K=-3.6 (Nriagu, 1972b).
139	$FeHPO_4^+$	$Fe^{+2}+HPO_4^{-2}=FeHPO_4^++e^-$	-7.613	—	$Fe^{+3}+HPO_4^{-2}=FeHPO_4^+$; log K=5.4 (Nriagu, 1971).
140	$Al(OH)_3$ (amorphous)	$Al(OH)_3=Al^{+3}+3OH^-$	-31.611	12,990	ΔG_f and ΔH_f from Latimer (1952).
141	Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2+8H_2O+2H^+=2Ca^{+2}+2Al(OH)_4^-+3H_4SiO_4^\circ$	-11.695	10,390	ΔG_f and ΔH_f from Zen (1972).
142	Strontianite	$SrCO_3=Sr^{+2}+CO_3^{-2}$	-11.789	2,361	ΔG_f and ΔH_f from R and W.
143	Celestite	$SrSO_4=Sr^{+2}+SO_4^{-2}$	-6.349	-1,054	Do.
144	Barite	$BaSO_4=Ba^{+2}+SO_4^{-2}$	-9.773	6,141	ΔG_f and ΔH_f from R and W.
145	Witherite	$BaCO_3=Ba^{+2}+CO_3^{-2}$	-13.335	6,950	Do.
146	Strengite	$FePO_4\cdot 2H_2O=Fe^{+3}+PO_4^{-3}+2H_2O$	-26.400	-2,030	Log K=-26.4 (Nriagu, 1972b); ΔH_f from R and W.
147	Leonhardite	$Ca_2Al_4Si_8O_{24}\cdot 7H_2O+17H_2O=2Ca^{+2}+4Al(OH)_4^-+8H_4SiO_4^\circ$	-69.756	90,070	ΔG_f and ΔH_f from R and W.
148	$Na_2SO_4^\circ$	$2Na^++SO_4^{-2}=Na_2SO_4^\circ$	1.512	-2,642	Log K=1.512, ΔH_r=2,642 from log $K(T)$ expression in Lafon and Truesdell (1971).

Table 1.—*Reactions and thermodynamic data*—Continued

Reaction No.	Mineral or species name	Reaction	log K	ΔH_r	Data source
149	Nesquehonite	$MgCO_3 \cdot 3H_2O = Mg^{+2} + CO_3^{-2} + 3H_2O$	4.999	-4,619	ΔG_f and ΔH_f from Robie and Hemingway (1972).
150	Artinite	$MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O = 2Mg^{+2} + CO_3^{-2} + 2OH^- + 3H_2O$	-17.980	498	ΔG_f and ΔH_f from Hemingway and Robie (1972).
151	H_2O/O_2 (aqueous)	$0.5H_2O = 0.25O_2(aq) + H^+ + e^-$	-21.495	33,457	ΔG_f and ΔH_f from 270-3.
152	H_2O	$H_2O = H^+ + OH^-$	-13.998	13,345	Do.
153	Sepiolite (precipitate)	$Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O + 4.5H_2O = 2Mg^{+2} + 3H_4SiO_4^\circ + 4OH^-$	-37.212	———	Log K=-37.212 (Wollast and others, 1968).
154	Diaspore	$AlOOH + H_2O = Al^{+3} + 3OH^-$	-35.121	15,405	ΔG_f and ΔH_f from 270-3.
155	Wairakite	$CaAl_2Si_4O_{12} \cdot 2H_2O + 10H_2O = Ca^{+2} + 2Al(OH)_4^- + 4H_4SiO_4^\circ$	-26.708	26,140	ΔG_f and ΔH_f from Zen (1972).
156	$FeH_2PO_4^{+2}$	$Fe^{+2} + H_2PO_4^- = FeH_2PO_4^{+2} + e^-$	-7.583	———	$Fe^{+3} + H_2PO_4^- = FeH_2PO_4^{+2}$; log K= -5.43 (Nriagu, 1972b).

ACTIVITY COEFFICIENTS

In the limit of infinite dilution, a consequence of the definition of the standard state for ions in solution is that all ionic activities approach ionic concentrations and activity coefficients (defined as the ratios of activities to concentrations) approach unity. This property is useful in experimental studies where mass action expressions are written in which concentrations may be extrapolated to infinite dilution to yield equilibrium constants, but the property gives no clue to activity coefficients in real solutions of finite concentration. In real solutions of more than a few components, it is necessary to use single-ion activities and single-ion activity coefficients. These are formally defined by the equation,

$$a_i = \gamma_i m_i, \tag{5}$$

in which a_i, γ_i, and m_i are respectively the activity, the activity coefficient, and the molality of the *i*th ion. The convention that activities are dimensionless requires that single-ion activity coefficients have dimensions of molality $^{-1}$.

Single-ion activities and single-ion activity coefficients cannot be defined thermodynamically or exactly measured or calculated because measurement of the activity (and therefore the chemical potential) of a single-charged ion would require the measurement of the finite free energy change of the solution resulting from a finite change in concentration of the single charged ion while the concentrations of all other ions and the electrical potential of the phase are held constant. This measurement obviously cannot be made. We must, therefore, use nonthermodynamic models to evaluate single-ion activity coefficients. The reader should be aware of the additional uncertainties introduced by this approach.

Two models have been used in WATEQ for the calculation of single-ion activity coefficients, the Debye-Hückel equation and the MacInnes assumption. These are not the only models available but are perhaps the most widely used and are generally consistent with the functions used to correct experimental determinations to infinite dilution. The Debye-Hückel theory provides an equation which describes single-ion activity coefficient behavior of ions in dilute solutions and which can be extended with adjustable parameters to more concentrated solutions. The MacInnes assumption provides information on the behavior of single-ion activities at higher concentrations with which to fit the parameters of the extended Debye-Hückel equation.

The Debye-Hückel theory

The Debye-Hückel theory considers the effect, on the free energy of a single ion, of electrical interactions with other ions by assuming that oppositely charged ions can be considered as forming a spherical shell around the ion. This assumption is valid only for very dilute solutions, and activity coefficients derived from the theory deviate increasingly from experimental results as the concentration increases. The original equation (Robinson and Stokes, 1955, p. 229) states that,

$$\log \gamma = -\frac{A z^2 \sqrt{I}}{1 + Ba\sqrt{I}} \tag{6}$$

where A and B are constants depending only on the dielectric constant, density, and temperature; z is the ionic charge; and I is the ionic strength (defined as half the sum of the products of the molality and the square of the charge of all ions in the solution) and contains one parameter, a, the "hydrated ion size" that must be estimated from experimental data. The extended form of the equation (Robinson and Stokes, 1955, p. 231),

$$\log \gamma = -\frac{A z^2 \sqrt{I}}{1 + Ba\sqrt{I}} + bI, \tag{7}$$

adds a second adjustable parameter, *b*, which allows for the effect of the decrease in concentration of solvent in concentrated solutions. This equation is used in WATEQ for major ions with *a* and *b* values calculated from experimental mean salt single-ion activity coefficients (see "The MacInnes Assumption") and for minor ions with values of *a* from Kielland (1937) and *b* set to zero. The constants *A* and *B* are calculated from the dielectric constant, density, and temperature by the equations (Hamer, 1968)

$$A = \frac{1.82483 \times 10^6 d^{1/2}}{(\epsilon T)^{3/2}} \text{ moles}^{-1/2} (10^3 \text{ g H}_2\text{O})^{1/2} \tag{8}$$

and

$$B = \frac{50.2916 \times 10^8 d^{1/2}}{(\epsilon T)^{1/2}} \text{ cm}^{-1} \text{ mole}^{-1/2} (10^3 \text{ g H}_2\text{O})^{1/2} \tag{9}$$

where *d* is the density of water (Keenan and Keyes, 1936), *T* is the absolute temperature, and ϵ is the dielectric constant of water (Malmberg and Maryott, 1956; Akerlof and Oshery, 1950).

The MacInnes assumption

In order to assign the adjustable parameters in equation 7, it is necessary to know the variation of single-ion activity coefficients with ionic strength in a single solution. Experimental values are available for the mean molal activity coefficients, $\gamma\pm$, of many salts, and if the activity coefficient of one ion can be calculated, then others may be derived from it. The MacInnes assumption (MacInnes, 1939) that the single-ion activity coefficients of K^+ and Cl^- are equal to each other and to the mean activity coefficient of KCl allows this to be done. By definition,

$$\gamma_+ \gamma_- \equiv \gamma_\pm^2 . \tag{10}$$

If

$$\gamma_{\pm \text{KCl}} = \gamma_{K^+} = \gamma_{Cl^-} , \tag{11}$$

then

$$\gamma_{Na^+} = \frac{\gamma_\pm^2 \text{NaCl}}{\gamma_\pm \text{KCl}}, \tag{12}$$

$$\gamma_{Ca^{+2}} = \frac{\gamma_\pm^3 \text{CaCl}_2}{\gamma_\pm^2 \text{KCl}}, \tag{13}$$

and

$$\gamma_{Br^-} = \frac{\gamma_\pm^2 \text{KBr}}{\gamma_\pm \text{KCl}}, \tag{14}$$

and so forth.

In deriving these mean salt activity coefficients, one must be careful to avoid solutions in which the ions are highly associated. In calculating $\gamma_{SO_4^{-2}}$, for example, $\gamma_{\pm K_2SO_4}$ cannot be used because of the formation of the KSO_4^- ion pair. In this calculation, the most reasonable values of $\gamma_{SO_4^{-2}}$ can be obtained from $\gamma_{\pm Cs_2SO_4}$, $\gamma_{\pm CsCl}$, and $\gamma_{\pm KCl}$ by the relation,

$$\gamma_{SO_4^{-2}} = \frac{\gamma_\pm^3 \text{Cs}_2\text{SO}_4 \cdot \gamma_\pm^2 \text{KCl}}{\gamma_\pm^4 \text{CsCl}} . \tag{15}$$

Even here, the results must be used with caution because Cs^+ and Cl^- may be weakly associated and $\gamma_{SO_4^{-2}}$ values derived in this way may be somewhat too high at high ionic strengths.

Values of *a* and *b* for major ions obtained from computer fitting of calculated mean salt activity coefficients as well as values of *a* for minor ions derived from Kielland (1937) are shown in table 2.

Table 2.—*Parameters of the Debye-Hückel equation*

Major ions[1]	*a*	*b*
Ca^{+2}	5.0	0.165
Mg^{+2}	5.5	.20
Na^+	4.0	.075
K^+	3.5	.015
Cl^-	3.5	.015
SO_4^{-2}	5.0	−.04
HCO_3^-	5.4	.0
CO_3^{-2}	5.4	.0

Minor ions[2]	*a*
$H_2BO_3^-$, NH_4^+	2.5
NO_3^-	3.0
OH^-, F^-, HS^-	3.5
$MgHCO_3^+$, $H_3SiO_4^-$	4.0
MgF^+, $Al(OH)_4^-$, AlF_4^-, $AlSO_4^+$, $Al(SO_4)_2^-$, HSO_4^-	4.5
$FeOH^{+2}$, $FeOH^+$, $FeSO_4^+$, $FeCl^{+2}$, $FeCl_2^+$, PO_4^{-3}, HPO_4^{-2}, S^{-2}, $LiSO_4^-$, Sr^{+2}, $SrOH^+$, Ba^{+2}, $BaOH^+$, NH_4SO_4	5.0
$H_2SiO_4^{-2}$, $CaPO_4^-$, $CaH_2PO_4^+$, $MgPO_4^-$, $MgH_2PO_4^+$, $NaCO_3^-$, $NaSO_4^-$, KSO_4^-, $H_2PO_4^-$, $NaHPO_4^-$, $KHPO_4^-$, $AlOH^{+2}$, $Al(OH)_2^+$, AlF^{+2}, AlF_2^+, $Fe(OH)_4^-$, $FeHPO_4^+$, $FeH_2PO_4^+$	5.4
Fe^{+2}, $CaOH^+$, $CaHCO_3^+$, Li^+	6.0
Fe^{+3}, Al^{+3}, H^+	9.0

[1] *a* and *b* values calculated from experimental mean salt single-ion activity coefficients.

[2] *a* values from Kielland (1937); *b* values set to zero.

Single-ion activity coefficients have been calculated for concentrated single-salt solutions by use of the Stokes-Robinson equation (Bates and others, 1970). Where comparisons are possible, these values agree reasonably with activity coefficients based on mean salt calculations. In table 3, values of single-ion activity coefficients used in WATEQ are compared with mean salt coefficients and with those calculated by Bates and others (1970).

The use of any model of single-ion activity coefficients based on experimental measurements made on single salt solutions requires the assumption that, at a given temperature, activity coefficients in simple solutions are equal to those in complex solutions of the same ionic strength. This assumption is reasonable in dilute solutions, but limited experimental work in concentrated (>1 molal) mixed electrolyte solutions indicates that it is not always true. The extent of deviation from ionic strength dependence is small except for ions that differ greatly in size and hydration such as H^+ and Cs^+. However, for models in which all ion associations are considered (as in WATEQ), these deviations have proved to be insignificant (Pytkowicz and Kester, 1969; Yeatts and Marshall, 1972). For further discussion and comparison of activity coefficient equations, see Truesdell and Jones (1969).

Table 3.—*Single-ion activity coefficients at 25° C from a two-parameter equation used in WATEQ compared with mean salt, Stokes-Robinson, and other single-ion activity coefficients*

Ionic strength		0.01	0.1	0.5	1.0	2.0	3.0	4.0
γ_{Na^+}	DH[1]	0.903	0.782	0.708	0.715	0.789	0.901	1.043
	MS[2]	.904	.786	.713	.716	.779	.896	1.062
	SR[3]		.783	.701	.697	.756	.870	1.038
γ_{K^+}	DH[1]	.900	.763	.642	.600	.570	.562	.563
	MS[2]	.901	.770	.649	.604	.573	.569	.577
	SR[3]		.773	.659	.623	.610	.626	.659
$\gamma_{Ca^{+2}}$	DH[1]	.670	.389	.266	.247	.289	.376	.509
	MS[2]	.680	.382	.266	.251	.291	.385	.553
	SR[3]		.380	.234	.210	.220	.265	.340
	Davies[4]	.661	.372	.288				
$\gamma_{Mg^{+2}}$	DH[1]	.674	.406	.292	.297	.389	.554	.822
	MS[2]	.685	.400	.289	.293	.380	.567	.945
	SR[3]		.390	.247	.230	.265	.350	.470
γ_{Cl^-}	DH[1]	.900	.763	.642	.600	.570	.562	.563
	MS[2]	.901	.770	.649	.604	.573	.569	.577
	SR[3]		.773	.661	.620	.590	.586	.591
$\gamma_{SO_4^{-2}}$	DH[1]	.667	.371	.205	.155	.112	.091	.077
	MS[2]	.653	.368	.214	.155	.108	.085	.070
$\gamma_{HCO_3^-}$	DH[1]	.905	.788	.692	.654	.623	.606	.596
	WBJ[5]	.904	.790	.692	.654	.627	.600	.580
$\gamma_{CO_3^{-2}}$	DH[1]	.671	.386	.229	.184	.150	.135	.126
	WBJ[5]	.668	.388	.230	.183	.154	....	.....

[1] From parameters of Debye-Hückel equation (table 2).

[2] Mean salt.

[3] In chloride solutions (Bates and others, 1970); γ_{Cl^-} from NaCl solution.

[4] No adjustable parameters (Davies, 1962).

[5] From Walker, Bray, and Johnson (1927).

SOLUTION OF MASS ACTION AND MASS BALANCE EQUATIONS

Computation of solution species distribution is accomplished by means of a chemical model (Garrels and Thompson, 1962) which uses analytical concentrations, experimental solution equilibrium constants, mass balance equations, and the measured pH. The distribution of anionic weak acid species is calculated first from total analyzed concentrations, the pH, and activity coefficients of individual species, as illustrated by silicate equilibria,

$$H_4SiO_4 = H^+ + H_3SiO_4^- \qquad (16)$$

and

$$H_3SiO_4^- = H^+ + H_2SiO_4^{-2}. \qquad (17)$$

The concentration of each species is calculated from the total or analytical concentration, the pH, and the activity coefficients of the species. From the preceding equations,

$$K_1 = \frac{m_{H_3SiO_4^-}\, \gamma_{H_3SiO_4^-}\, 10^{-pH}}{m_{H_4SiO_4}\, \gamma_{H_4SiO_4}}, \qquad (18)$$

and

$$K_2 = \frac{m_{H_2SiO_4^{-2}}\, \gamma_{H_2SiO_4^{-2}}\, 10^{-pH}}{m_{H_3SiO_4^-}\, \gamma_{H_3SiO_4^-}}. \qquad (19)$$

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

$$m_{Si\ total} = m_{H_4SiO_4} + m_{H_3SiO_4^-} + m_{H_2SiO_4^{-2}}. \qquad (20)$$

The mass action equations can be combined with the mass balance equation to solve for $m_{H_4SiO_4}$, as follows:

$$m_{H_4SiO_4} = \frac{m_{Si\ total}}{1 + \gamma_{H_4SiO_4}\left(\frac{K_1\, 10^{pH}}{\gamma_{H_3SiO_4^-}} + \frac{K_1 K_2\, 10^{2pH}}{\gamma_{H_2SiO_4^{-2}}}\right)}; \qquad (21)$$

$m_{H_4SiO_4}$ is then substituted into the mass action equations to solve for $m_{H_3SiO_4^-}$ and $m_{H_2SiO_4^{-2}}$. The activity coefficients are calculated from the ionic strength by an iterative procedure. The same method is employed for phosphate, borate, and sulfide species and for the carbonate-bicarbonate distribution from pH and the alkalinity determination, after correction for other weak acid radicals (if the alkalinity has been corrected during the chemical analysis, this step may be bypassed in the program). The concentration of H_2CO_3 is calculated from the re-computed bicarbonate molality and the first dissociation constant of carbonic acid.

Calculation of the concentrations of ion pairs is accomplished by a procedure similar to that for weak acid species, but the analyzed or computed values for the anion concentrations are utilized in place of the pH and equilibrium association constants are employed. The calculations may be illustrated for the calcium ion species. The major ion-pairing reactions are

$$Ca^{+2} + OH^{-2} = CaOH^{+}, \quad (22)$$

$$Ca^{+2} + HCO_3^{-} = CaHCO_3^{+}, \quad (23)$$

$$Ca^{+2} + CO_3^{-2} = CaCO_3^{\circ}, \quad (24)$$

and

$$Ca^{+2} + SO_4^{-2} = CaSO_4^{\circ}. \quad (25)$$

From equations 22–25, equilibrium constants for the association reactions are

$$K_1 = \frac{a_{CaOH^+}}{a_{Ca^{+2}}\, a_{OH^-}}, \quad (26)$$

$$K_2 = \frac{a_{CaHCO_3^+}}{a_{Ca^{+2}}\, a_{HCO_3^-}}, \quad (27)$$

$$K_3 = \frac{a_{CaCO_3^\circ}}{a_{Ca^{+2}}\, a_{CO_3^{-2}}}, \quad (28)$$

and

$$K_4 = \frac{a_{CaSO_4^\circ}}{a_{Ca^{+2}}\, a_{SO_4^{-2}}}. \quad (29)$$

From these quations the expressions,

$$m_{CaOH^+} = \frac{K_1\, a_{OH^-}\, m_{Ca^{+2}}\, \gamma_{Ca^{+2}}}{\gamma_{CaOH^+}}, \quad (30)$$

$$m_{CaHCO_3^+} = \frac{K_2\, a_{HCO_3^-}\, m_{Ca^{+2}}\, \gamma_{Ca^{+2}}}{\gamma_{CaHCO_3^{+2}}}, \quad (31)$$

$$m_{CaCO_3^\circ} = \frac{K_3\, a_{CO_3^{-2}}\, m_{Ca^{+2}}\, \gamma_{Ca^{+2}}}{\gamma_{CaCO_3^\circ}}, \quad (32)$$

and

$$m_{CaSO_4^\circ} = \frac{K_4\, a_{SO_4^{-2}}\, m_{Ca^{+2}}\, \gamma_{Ca^{+2}}}{\gamma_{CaSO_4^\circ}} \quad (33)$$

may be substituted into the mass balance equation for calcium as follows:

$$m_{Ca\ total} = m_{Ca^{+2}} + m_{CaOH^+} + m_{CaHCO_3^+} + m_{CaCO_3^\circ} + m_{CaSO_4^\circ}$$

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

$$m_{Ca^{+2}} = \frac{m_{Ca\ total}}{1 + \gamma_{Ca^{+2}}\left(\dfrac{K_1 a_{OH^-}}{\gamma_{CaOH^+}} + \dfrac{K_2 a_{HCO_3^-}}{\gamma_{CaHCO_3^+}} + \dfrac{K_3 a_{CO_3^{-2}}}{\gamma_{CaCO_3^\circ}} + \dfrac{K_4 a_{SO_4^{-2}}}{\gamma_{CaSO_4}}\right)} \quad (34)$$

In actuality, these computations in WATEQ also include phosphate species. The computed concentration of free calcium ion, $m_{Ca^{+2}}$, is substituted back into the mass action expressions to solve for the concentrations of ion pairs. The concentrations assigned to ion pairs and weak acids reduce the concentrations of the free ions and change the ionic strength and therefore the activity coefficients. The corrected values are calculated by iteration. In each iteration, the program reduces, if necessary, the molalities of the free anions HCO_3^- CO_3^{-2}, SO_4^{-2}, Cl^-, F^-, and PO_4^{-3} and recalculates the ionic strength and the activity coefficients. Then the calculations of free Ca^{+2} and Ca complexes along with similar calculations for Na, K, Mg, Fe, and H complexes are repeated. When the sums of all weak acids, complex ions, and free ions for all anions agree with the analytical values within 0.5 percent, the iteration is stopped.

ION RATIOS

When the chemical model is complete, it is useful to calculate molal concentration ratios and ion activity ratios for plotting on water composition and mineral stability diagrams, respectively. Comparison of these ratios with those of related waters can suggest possible origins of dissolved constituents and possible controls by mineral reactions. A number of these ratios are calculated in WATEQ.

ACTIVITY PRODUCTS AND SOLUBILITY PRODUCTS

The equilibrium of a solid phase with an aqueous solution can be characterized by a mass action equation. For a solid of formula AX which dissolves to form ions A^+ and X^-, this expression is

$$K = \frac{a_{A^+}\, a_{X^-}}{a_{AX}}, \quad (35)$$

where *K* is the equilibrium constant of solubility. If the solid is a pure substance, not a solid solution, its activity is equal to one because it is in its standard state (Garrels and Christ, 1965, p. 5), and the expression for the equilibrium constant reduces to the "solubility product,"

$$K_{SP} = a_{A^+}\, a_{X^-}. \quad (36)$$

In hydrolysis reactions, water is considered explicitly as part of the reaction. In the solution of quartz to form silicic acid, for example,

$$SiO_{2\,(quartz)}+2H_2O=H_4SiO_4, \tag{37}$$

the water is written as part of the reaction, and its activity appears in the equilibrium expression.

A water sample when collected is usually no longer in contact with mineral phases, and these phases may not be accessible to observation. It is of interest then to determine with what mineral phases the water is saturated or nearly so. The calculated activities of the dissolved ions in a water may be combined to produce the appropriate activity product which may be compared with the solubility equilibrium constant to show the degree of saturation of the water with each mineral considered.

This comparison may be made by means of the ratio of the activity product to the equilibrium solubility product which is given in the program as "AP/K" and "LOG AP/K" and by means of the free energy change of the reaction ΔG_r (which is zero at equilibrium) and is given as "DELGR" in the program. These quantities are related by the expression

$$\Delta G_r=2.303RT\log(AP/K). \tag{38}$$

Some mineral formulas contain a relatively large number of atoms, and the ΔG_r values for these minerals will deviate from zero more rapidly with dilution of concentration than will those values for minerals with simple formulas. This deviation can be illustrated by comparing the activity product of dolomite, $a_{Ca^{+2}}a_{Mg^{+2}}a^2_{CO_3^{-2}}$ with that of calcite, $a_{Ca^{+2}}a_{CO_3^{-2}}$. If a water initially saturated with both minerals is diluted with pure water, ΔG_r dolomite will be twice ΔG_r calcite. To correct this, ΔG_r values are divided by the number of negative charges in the formula of the mineral and presented as (for want of a better label) "PER EQUIV" ΔG_r.

The compilation of a consistent set of stability constants for minerals suffers from several uncertainties. The standard enthalpy of formation and standard entropy of most minerals have been measured by calorimetric methods, and the standard free energy of formation calculated from these quantities is often referenced to the free energies of formation of the elements rather than to the free energies of formation of the ions formed on solution of the mineral. The combination of such values with those for solution species involving aqueous ions may lead to erroneous stability constants. The use of experimental solubility products or resulting free energy values is free from this inconsistency. The main uncertainty in the use of these data lies in the precise definition of reactants and products involved in the experiment and in the difficulty of reversing the equilibrium.

Because of these uncertainties, the logarithms of the maximum and minimum solubility products are calculated in WATEQ and presented in addition to the logarithm of the most probable value for visual comparison with the logarithm of the activity product. Because of space limitations only the most probable solubility product is used in calculating values of AP/K, *log* (AP/K), ΔG_r, and ΔG_r per equivalent. Enthalpy values and solubility products used in the program, together with the sources of all data, are given in table 1.

EFFECTS OF TEMPERATURE AND PRESSURE

In the relationships developed in the previous sections, temperature and pressure have been assumed to be constant and their effect on the equilibria has not been discussed. The great majority of experimental determinations of equilibrium constants and of free energy values has been made at 25°C and, particularly for solution equilibria, data at other temperatures may be entirely lacking. If experiments have been made over a wide range of temperatures or if complete thermochemical data are available for all species of a reaction, then the equilibrium constant may be expressed as a power function of the absolute temperature

$$\log K=A+BT+C/T+D\log T, \tag{39}$$

in which one or more coefficients may be zero. Where this type of expression was available in the literature, it has been used in WATEQ (table 4). If experimental determinations at only two or three temperatures are available, a linear dependence of log K with the reciprocal of the absolute temperature may be indicated (that is, B and D are zero in eq. 39) which is equivalent to a constant value of the enthalpy (heat content) change of the reaction, ΔH. This is expressed by the Van't Hoff relation,

$$\log K=\log K_{Tr}-\frac{\Delta H_{Tr}}{2.3R}\left(\frac{1}{T}-\frac{1}{Tr}\right), \tag{40}$$

$$-\frac{1}{2.303RT}\int_{T_r}^{T}\Delta C^{\circ}_{p,r}(T)\,dT+\frac{1}{2.303R}\int_{T_r}^{T}\Delta C^{\circ}_{p,r}(T)\,d\ln T$$

in which Tr is the reference temperature (298.15 K (= 25°C) in WATEQ) and the constants A and C in equation 39 are equal to

→ [illegible] heat capacity of reaction

$$\log K_{Tr}+\frac{\Delta H_{Tr}}{2.3RT}\text{ and }\frac{\Delta H_{Tr}}{2.3R},$$

respectively.

The enthalpy change of reaction can be obtained by determining the slope of a plot of experimental values of log K versus $(1/T)$, from tabulated values of the standard enthalpy of formation of the species in the reaction by using a relation analogous to equation 3 or from direct measurements. The enthalpy of reaction at 25°C has been calculated for most of the equilibria used in WATEQ (table 1), and equation 40 is used to calculate the value of the equilibrium constant for the

$$\frac{AP}{K}=\frac{Q}{K}$$

$$DELGR=\Delta G_R$$

Table 1. *Analytical expressions for log K(T) used in WATEQ*

[*T*, in kelvins]

Identifier	Reaction	Expression for log $K(T)$	Reference
KT(13)	$H_4SiO_4^\circ = H_3SiO_4^- + H^+$	$6.368-0.016346\,T-3405.9/T$	Ryzhenko (1967).
KT(14)	$H_4SiO_4^\circ = H_2SiO_4^{-2} + 2H^+$	$39.478-0.065927\,T-12355.1/T$	Do.
KT(25)	$H_3BO_3^\circ = H_2BO_3^- + H^+$	$1573.21/T+28.6059+0.012078\,T -13.2258 \log T + \log KW$	Mesmer, Baes, and Sweeton (1972).
KT(26)	$NH_4^+ = NH_3^\circ + H^+$	$0.6322-0.001225\,T-2835.76/T$	Wright, Lindsay, and Druga (1961).
KT(35)	$H_2CO_3^\circ = HCO_3^- + H^+$	$8.153-0.02194\,T-2382.3/T$	Ryzhenko (1963).[1]
KT(68)	$HCO_3^- = H^+ + CO_3^{-2}$	$5.388-0.02199\,T-2730.7/T$	Do.
KT(72)	$K^+ + SO_4^{-2} = KSO_4^-$	$3.106-673.6/T$	Truesdell and Hostetler (1968).
KT(89)	$H^+ + SO_4^{-2} = HSO_4^-$	$-5.3505+0.0183412\,T+557.2461/T$	Lietzke, Stoughton, and Young (1961).
KT(91)	$H_2S^\circ = H^+ + HS^-$	$11.17-0.02386\,T-3279/T$	D'yachkova and Khodakovskiy (1968).

[1] In more recent practice, the expressions based on the original work of Harned and co-workers (Harned and Owen, 1958) have been utilized, despite being limited to 50°C maximum temperature.

temperature of the water. For a few reactions in which data at temperatures other than 25°C were not available, the 25°C value of the equilibrium constant is used at all temperatures.

The effect of pressure has not been calculated in WATEQ because the necessity of inputing a measured pH value virtually limits WATEQ to surface and near-surface waters and because much necessary data is not available for ion pairs. Correlations suggested by Ellis and McFadden (1972) allow the calculation of the pressure effect on equilibria involving only minerals and simple ions (not ion pairs) to be made for temperatures to 250°C. These calculations suggest that pressure effects are not large for pressures less than a few hundred atmospheres.

REDOX REACTIONS

Oxidation-reduction equilibria have been treated in the same manner as other reactions in WATEQ. To achieve this, the measured Eh value, or the Eh value calculated from the measured concentration of dissolved oxygen, is converted to the negative logarithm of the conventional activity of the electron (or pE) by the relation,

$$pE \equiv Eh/(2.303RT/F), \tag{41}$$

in which F is the faraday and $2.303RT/F$ is the Nernst slope. pE is related to the conventional activity of the electron by

$$a_{e^-} = 10^{-pE} \tag{42}$$

This equation is similar to that assumed for pH, and because both measurements have an unknown liquid junction potential, the relations of pE to electron activity and of pH to hydrogen ion activity are equally uncertain. It is necessary, however, to use these relations despite the uncertainty. The standard free energy and enthalpy of the hydrated electron in aqueous solution are zero by convention. The conventional electron activity thus ranges from 10^{-20} to 10^{+20} while the actual electron activity is about 10^{-60} to 10^{-100}. These conventions are discussed by Sillén and Martell (1964) and by Truesdell (1968).

An advantage of the use of electron activity is that it is not necessary to set up separate redox equilibrium expressions. For example, the equilibrium between Fe^{+2} and Fe^{+3} is expressed by a conventional equilibrium constant,

$$K = \frac{a_{Fe^{+3}}\, a_{e^-}}{a_{Fe^{+2}}} \tag{43}$$

and the value of the equilibrium constant may be calculated from G_f°, Fe^{+3}, and G_f°, Fe^{+2} (G_f°, electron = 0 by convention). Other redox equilibria are treated similarly, and the method of calculation of the concentration of ion pairs involving iron is the same as that involving metals that are not redox active.

In natural waters that contact the atmosphere the dissolved oxygen (DOX) content may have been measured in addition to or in place of the Eh. If the dissolved oxygen has been measured, it is read into the program after the normal data as a statement, "DOX = (parts per million of dissolved oxygen),". Two values of pE are calculated in WATEQ from the relation,

$$pE = -\log K - pH - 0.5 \log a_{H_2O} + 0.25 \log a_{DOX}, \tag{44}$$

in which log K values are from thermodynamic data ("PE CALC O") and from the empirical Eh-pH relation for waters in contact with the atmosphere (Sato, 1960). ("EMPIR PE O") and DOX activities are on a molal scale. If a DOX measurement is given without an Eh value, the value of PE CALC O is used throughout the program. If instead, EMPIR PE O is to be adopted, the statement "TEMPOX = 1" is added to the optional data.

Separate analyses of reduced and oxidized species allow the calculation of pE values which may be compared with each other or the measured pE to estimate the degree of internal redox equilibrium. Two such pairs are sulfide-sulfate and ammonia-nitrate. The equilibrium between sulfide and sulfate can be written,

$$H_2S+4H_2O=SO_4^{-2}+10H^++8e^-, \qquad (45)$$

and the mass action expression can be rearranged to give

$$pE=(\log K+\log a_{SO_4^{-2}}-\log a_{H_2S}-10pH-4\log a_{H_2O})/8. \qquad (46)$$

Similarly, the equilibrium between ammonium and nitrate yields the expression

$$pE=(-\log K+\log a_{NO_3^-}-\log a_{NH_4^+}-10pH-3\log a_{H_2O})/8. \qquad (47)$$

These quantities, PE CALC S and PE CALC N, are calculated in WATEQ.

GAS PARTIAL PRESSURES

Although gas partial pressures are seldom measured in natural waters, in some solutions they may be calculated from the gas solubility constants and the water analysis. The partial pressures of CO_2, O_2, and CH_4 are calculated from the following equations,

$$\log P_{CO_2}=\log K+\log a_{HCO_3^-}+\log a_{H^+}-\log a_{H_2O}, \qquad (48)$$

$$\log P_{O_2}=\log K'+2\log a_{H_2O}+4pH+4pE, \qquad (49)$$

$$\log P_{CH_4}=\log K''+\log a_{HCO_3^-}-9pH-9pE-3\log a_{H_2O}. \qquad (50)$$

ACTIVITY OF WATER

The activity of water is calculated in WATEQ by the approximate relation (Garrels and Christ, 1965, p. 66)

$$a_{H_2O}=1-0.017\Sigma m_i, \qquad (51)$$

where Σm_i is the sum of the molalities of dissolved anions, cations, and neutral species. The equation yields reasonable values if Σm_i is less than molal.

INPUT

Input to WATEQ consists of a complete chemical analysis of the water sample and field measurements of its temperature and pH. If available, measurements of Eh and dissolved oxygen as well as some trace element analyses may be included. In order to allow the inclusion of optional data, the last space on the first card is coded with ISTDATA which is the number of cards containing the necessary data including the normal chemical analysis and the sample description. Cards after the chemical analysis are used for optional data. A blank card must be included after each data set to separate data sets. The required data is coded in free field (that is, one space between each number) in the order indicated below. See list of identifiers in the complete computer program for detailed descriptions. Sample sets of data are given with the resulting printout after the program.

Card 1 . . . . Sample Description (79 spaces) and ISTDATA (space 80).
Card 2 . . . . TEMP, PH, EHM (in volts, code 9.9 if data is not available), FLAG (='PPM', 'MG/L', 'MEQ/L' or 'MOL').
Card 3 . . . . Chemical analysis in PPM, MG/L, and MEQ/L or MOL/L (set FLAG) in the order Ca, Mg, Na, K, Cl, SO_4, HCO_3, Fe, H_2S, CO_3, SiO_2, NH_4, B, PO_4, Al, F, NO_3.
Succeeding cards . . . . Other data (identifier, equality sign, numerical value, and comma) including: "DENS=□" (if not specified, density is set equal to 1); if alkalinity is corrected for noncarbonate alkalinity "CORALK=1," (omitted if not corrected); electrical potential (volts) of the Eh cell including the calomel reference electrode "EHMC=□,"; electrical potential (volts) of the Eh cell with Zobell's solution for calibration, "EMFZSCE=□,"; parts per million of dissolved oxygen, "DOX=□,"; and certain trace elements including Li (I=80), Sr (I=87), Ba (I=89) in the form, "CUNITS(I)=□,". A semicolon in place of a comma follows the last data statement.
Last card . . . . Blank.

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WATEQ2—A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters

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The protection of ecosystems, upon which our health and lives depend (1), requires that we understand natural processes and develop the capability to predict the effect of changes, such as the addition of pollutants, on these ecosystems. The prediction of trace-element behavior in ecosystems requires a multicomponent model by which one can: 1) calculate aqueous speciation of the trace elements among both natural organic and inorganic ligands; 2) evaluate solubility hypotheses; 3) account for sorption-desorption processes; and 4) incorporate chemical kinetics. This paper documents a chemical model that partially accomplishes the first two of these four goals. The present model has evolved from WATEQ, the earlier water-mineral equilibria model written in Pl/1 by Truesdell and Jones (2, 3), and from WATEQF, the Fortran version of Plummer et al. (4). These models, in turn, drew on the preceding model of Barnes and Clarke (5). The related PL/1 model, SOLMNEQ (6), drew on the models of Barnes and Clarke (5) and a prepublication version of Truesdell and Jones (2) as well as the thermodynamic data treatment of Helgeson (7) and Helgeson et al. (8)

The WATEQ program contains an extensive thermodynamic data base which was carefully selected for use with low-temperature natural waters (9, 2). Activity coefficients for the major ions are calculated from a computer fit of an extended Debye-Hückel equation containing two adjustable parameters (2, 3). These activity coefficients are considered more reliable than the standard Debye-Hückel equation or the Davies equation for high ionic strength solutions (up to 1-3 molal). The method of calculation in WATEQ is back-substitution for the cations and successive approximation for the anions with convergence on mass balance for anions. WATEQF changed to the more rapid back-substitution method for anion mass balance convergence. In addition, manganese speciation is included in WATEQF, and an option for calculating activity coefficients by either the Debye-Hückel or the Davies equation is provided. WATEQ2 retains most of these features, and additional modifications are explained below.

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We have added ten additional elements (Ag, As, Cd, Cs, Cu, Mn, Ni, Pb, Rb, and Zn), complexes of Br and I, several metastable solids, some sparingly soluble salts, and several ion pairs of major constituents to the model. Other changes include reorganization of the computer code into a series of external subroutines and changing the mode of convergence to decrease the number of iterations required.

Because of the interactive nature of aqueous solute speciation calculations, it would be desirable to enter at once into the chemical model the reactions and thermodynamic data for all elements whose inclusion might affect the computed activity or equilibrium solubility of other solute species. However, our experience is that the greatest reliability is obtained by adding only the data for one element, or for one ligand group, at a time; then test data sets and real world water sample analyses are run before making further additions to or changes in the model.

Various associates, whom we have frequently called on for specialized knowledge and information, have materially assisted in this modeling effort. Collaborative studies have often provided the impetus to add some specific element, ligand group, or group of solid phases to the model. Apparent oversaturation with one or more solid phases of an element has often prompted us to seek out and add data for additional solute complexes or more soluble solid phases. The partitioning of an unexpectedly large portion of an element into a particular complex has led us to make an expanded compilation for the complex or to consult with colleagues to assist in selecting best values. Colleague criticisms (constructive and kind for the most part) of studies in press and in preparation have prompted us to make specific tests and proceed immediately with some change or addition, which would otherwise have awaited a "more opportune time." L. N. Plummer provided frequent consultation and supplied a prepublication copy of the reactions and associated thermodynamic data for the manganese section of the WATEQF chemical model (4). B. F. Jones and A. H. Truesdell have also been particularly helpful on many occasions.

In our effort to collect the appropriate data and develop the requisite understanding of geochemical processes, we have developed some adjunct computer programs. These include AACALC (Atomic Absorption and emission spectrometry CALCulation), EQLIST (EQuilibrium computation LISTing), and EQPRPLOT (EQuilibrium computation PRinting and PLOTing). AACALC (FORTRAN) reduces atomic absorption or emission spectrometry data to concentrations, EQLIST (PL/1) constructs tables from the WATEQ2 (input) card file, and EQPRPLOT (FORTRAN) constructs ratio and scatter plots of dissolved constituents, activity products (AP), or activity product to solubility product ratios (AP/K) via computer terminal printer or tape-driven plotter.

Additions and Modifications to the Model

The thermochemical reaction values vary according to the way the reaction is written. Therefore, all reactions in the present model which have been added or revised, together with the selected thermochemical values, and operational-information to facilitate input and output of the data, are available in an adjunct report (10).

Elements. Rather large sets of solute complexes and mineral phases have been added for Ag, As, Cd, Cu, Mn, Ni, Pb, and Zn. Additionally, Cs and Rb have been added to the model.

The merit of including Cs and Rb in the model, in spite of the near absence of solute complexes or pure solids, is that in the future the activities of the uncomplexed alkali metal ions can be used to compute their probable substitution into certain silicate minerals and to examine ion-exchange processes. Alkali metals complex with OH^-, Cl^-, and NO_3^- only at such high ionic strengths that the basic assumptions of a multicomponent ion-association model are no longer valid. In addition, thermodynamic data for these complexes are highly uncertain. For these reasons, such complexes have been dropped from the model. Similarly, there are data on alkali metal compounds such as Rb_2S which might have been included. However, the pure alkali metal sulfides are known to be highly unstable and/or deliquescent (11) and are rarely found as minerals. Therefore, they have not been included in the model.

The manganese sections of WATEQF (4) were heavily utilized in preparing a similar section for WATEQ2 (10). The solute portion was utilized in its entirety, but the $MnOH^+$ and $Mn(OH)_3^-$ association reactions were expressed in terms of H_2O and H^+ instead of OH^-, and the $HMnO_2^-$ complex, a duplication of the $Mn(OH)_3^-$ complex, was excluded. The following subset of the mineral species was selected: pyrolusite, birnessite, nsutite, bixbyite, hausmannite, pyrochroite, manganite, rhodochrosite, $MnCl_2 \cdot 4H_2O$, MnS(green), $MnSO_4$, $Mn_2(SO_4)_3$, $Mn_3(PO_4)_2$ and $MnHPO_4$. The following subset was excluded: MnO, $Mn(OH)_3$, $MnCl_2$, $MnCl_2 \cdot H_2O$, $MnCl_2 \cdot 2H_2O$, Mn_2SiO_4 and $MnSiO_3$. To the selected set were added six minerals for which thermochemical data are unknown, in order to obtain log AP values of the individual minerals for different waters. The six minerals are: cryptomelane ($K_{08}Mn^{2+}_{0.6}Mn^{4+}_{8}O_{17}$), hollandite ($Ba_{0.78}Fe^{2+}_{0.57}Mn^{2+}_{0.59}Mn^{4+}_{7}O_{16}$), psilomelane ($Ba_{0.78}Ca_{0.19}K_{0.03}Mn^{2+}Mn^{4+}_{7}O_{16} \cdot 2.5H_2O$), todorokite ($Ca_{0.393}Mg_{0.473}Mn^{2+}_{1.134}Mn^{4+}_{5}O_{12} \cdot 2H_2O$), lithiophorite ($Li_2Al_8Mn^{2+}_{2}Mn^{4+}_{10}O_{35} \cdot 14H_2O$), and rancieite ($Ca_{0.44}Mn^{2+}_{0.56}Mn^{4+}_{4}O_9 \cdot 3H_2O$).

Aqueous Complexes. All solute reactions are written as association (formation) reactions whereas the solid reactions are written as dissociation (dissolution) reactions. For mass balancing purposes, all solute reactions are written in terms of the free form of the parent species, so that all constants are for overall rather than stepwise reactions.

Polysulfides and Sulfide. The polysulfide complexes of Ag and Cu have been added to the model in an attempt to reduce the apparent oversaturation with $Ag_2S(s)$ calculated for San Francisco Bay waters (12). Calculation of the activity of polysulfide ions requires the assumptions: 1) the quantity of S_8° (free sulfur) is not a limitation on its reaction with bisulfide (HS^-) to form polysulfides; and 2) polysulfides are in equilibrium with bisulfide.

In addition to the sulfide complexes of the added trace elements, the $Fe(HS)_2^\circ$ and $Fe(HS)_3^-$ complexes (13) have been included to increase the rigor of the sulfide speciation. The sulfide reactions have been rewritten in terms of HS^- rather than S^{2-} since HS^- is the dominant sulfide ion in most waters.

Sulfate. Various published values for the association constants and association enthalpies of metal sulfate ion pairs and triplets (14, 15, 16, 17) show good agreement (± 10%) except for $NaSO_4^-$. Log K values for the formation of $NaSO_4^-$ range from the 0.226 value of Lafon and Truesdell (18) to the 1.17 value of Pytkowicz and Kester (19), as cited by Fisher (20). If the one low value of Lafon and Truesdell (18) and the high values of Fisher and Fox (21) and Fisher (20) are dropped, the remaining four values average 0.70 ± 0.05 (22, 23, 24, 25) which is identical to the value selected by Smith and Martell (26), who may have used the same evaluation technique. G. M. Lafon (Johns Hopkins U., personal communication, 1978) has suggested that the low value should be discounted and that the formation of a sodium sulfate ion triplet is unlikely. Most of the other association constants were obtained from R. M. Siebert and C. L. Christ (Continental Oil Co., U. S. Geol. Survey, personal communication, 1976) after comparing their values with those reported in the literature. Enthalpy values were also selected from the preliminary data of R. M. Siebert and C. L. Christ which had been evaluated by the Fuoss equation (27). Careful checking with published literature values showed no serious discrepancies and it was felt that using data from one source would help maintain internal consistency. The ion triplet $Fe(SO_4)_2^-$ was one exception. The log K for this complex is the average of the results of Izatt *et al*. (25) and Mattoo (28) which differ by less than 1%. The enthalpy of association has not been published but it has been estimated by assuming that the difference between it and $FeSO_4^+$ is equal to the difference between $Al(SO_4)_2^-$ and $AlSO_4^+$. Although the reliability of this estimation cannot easily be determined, it certainly is better than assuming $\Delta H_r = 0$.

Fluoride. For equilibrium calculations in acid solutions, stability constants are needed for HF°, HF_2^-, and $(HF)_2^\circ$ species. These species become important when the pH drops below 4.5 and fluoride concentration rises above 5×10^{-4}*M*. Several measurements have been made on the dissociation of HF° at 298.15°K and the agreement is excellent (29-37). The weighted mean value of log K = 3.169 ± 0.010 (1σ, unweighted) given in Ball *et al*. (10) was calculated from these investigations after dropping the high value of Patel *et al*. (34) and the low value of Vasil'ev and Kozlovskii (37) which is necessary in order to maintain consistency with the kinetic data of Kresge and Chiang (38, 39).

For the reaction:

$$HF^\circ + F^- \rightleftarrows HF_2^- \tag{1}$$

the stability constant has a larger uncertainty owing to the competing HF° association equilibrium. Reported log K values range from 0.49 to 0.70 (29, 30, 32, 33, 35, 36) and the weighted mean value is 0.58 ± 0.05.

Aqueous HF dimers have been shown to exist by Warren (35) who measured a log K of 0.43 ± 0.05 for the reaction:

$$2HF^\circ \rightleftarrows (HF)_2^\circ. \tag{2}$$

Enthalpy values for the calculation of temperature dependence are not available for reaction 2. The log K for the dissociation of HF° and for reaction 1 have been measured between 0 and 100°C by Broene and DeVries (29), Ellis (30) and Hamer and Wu (33). Vasil'ev and Kozlovskii (37) have also obtained enthalpy data for these reactions by calorimetric titration. The average $\Delta H = -3.46 \pm 0.75$ kcal mol^{-1} for HF° dissociation and $\Delta H = 1.09 \pm 0.30$ kcal mol^{-1} for reaction 1.

Silicate minerals are more soluble in natural waters having high fluoride concentrations and low pH values than in other waters. High concentrations of dissolved silica may be maintained by the formation of hexafluorosilicic acid:

$$Si(OH)_4^\circ + 6F^- + 4H^+ \rightleftarrows SiF_6^{2-} + 4H_2O. \tag{3}$$

The equilibrium constant for this reaction has been measured at 25°C by Roberson and Barnes (40) and the enthalpy is estimated from the data of Wagman *et al*. (41). Reaction 3 is important in many applications: a) chemical processes involving volcanic gases and condensates (40), b) chemical reactions in acid, halogen-rich hot springs (42, 43), c) waters receiving effluent from phosphate processing plants (44), d) fluoridation of water supplies (45), e) analytical chemistry, such as in the determination of either fluoride or dissolved silica (46) and f) the formation and hydrothermal alteration of ore deposits (47, 48, 49).

The log K and ΔH for the formation of the aqueous complexes CaF^+, FeF^{2+}, FeF_2^+, FeF_3°, $BF(OH)_3^-$, $BF_2(OH)_2^-$ and $BF_3(OH)^-$ have been evaluated by Nordstrom and Jenne (50) and are in good agreement with those selected by Smith and Martell (26) who used a different evaluation procedure. This addition to WATEQ2 makes a fairly complete inventory of aqueous fluoride complexes.

Neutral and Polymeric Aluminum and Iron. The association constants and enthalpies of aluminum and iron hydroxides have been evaluated by comparing the critically selected data of Baes and Mesmer (51) with that of R. M. Siebert and C. L. Christ (personal communication, 1976). Differences between the two data sets are negligible and the final selection was from Baes and Mesmer (51) because data on more complexes are found there. Important new species added to the model are the polynuclear complexes $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$. Some controversy has arisen over the existence of $Fe(OH)_3^\circ$ and $Al(OH)_3^\circ$. Baes and Mesmer (51) have indicated that although the formation constant of $Al(OH)_3^\circ$ is only known from one measurement (52) and has a large uncertainty, it is real, with a log K $\leq$ -15.0 for the reaction

$$Al^{3+} + 3H_2O \rightleftarrows Al(OH)_3^\circ + 3H^+ . \qquad (4)$$

Baes and Mesmer (51) also suggest that the log K for

$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3^\circ + 3H^+ \qquad (5)$$

is less than -12 and this agrees with the generally accepted value of -13.6 (53). Recently, Byrne (54) and Kester et al. (55) have presented evidence for the existence of $Fe(OH)_3^\circ$ and reconfirmed the value of the log K. We have therefore included both neutral species in the model.

Others. Equilibrium association constants calculated from free energy data (41) for two aqueous arsenic fluoride species, AsO_3F^{2-} and $HAsO_3F^-$, were so high that the two species accounted for virtually all the As^{5+} in several water samples, practically irrespective of the fluoride concentration. The E^H calculated from the activities of As^{3+} and As^{5+} under these conditions was near -4 volts, i.e. well below that at which water decomposes (0 to -0.83 volts from pH 0 to 14). From the original data of Dutt and Gupta (56) the log K = 2.832 for

$$H_3AsO_4^\circ + F^- = HAsO_3F^- + H_2O \qquad (6)$$

and log K = -3.037 for

$$H_3AsO_4^\circ + F^- = AsO_3F^{2-} + H^+ + H_2O . \qquad (7)$$

Thus, there appears to have been a computational error in converting the stability data of Dutt and Gupta (56) to standard free energies of formation.

Equilibrium log K_r° values calculated from free energy data (41) for two lead hydroxychlorides (PbOHCl, $Pb_2(OH)_3Cl$) did not agree with those of the original authors (57). However, revised ΔG_f° data (10) from NBS (B. R. Staples, Nat'l Bur. Stand., personal communication, 1978) agree very well with the original data.

Organic Ligands. The model has been expanded to permit sensitivity analyses of naturally occurring organic ligands. These composite ligand groups are referred to as fulvate and humate. The model defaults to molecular weights of 650 and 2000, respectively, for these two ligand groups. Reported molecular weights for these substances vary widely (S. A. Jacobs and E. A. Jenne, unpub. data, 1978). Therefore, if a concentration for either substance is used as input data, without an accompanying analytically determined molecular weight, a warning message is printed, and all pertinent output data are flagged. Reported equilibrium constants for these metal-ligand complexes also vary widely and should therefore be user supplied. In the absence of supplied values, the model defaults to data from Smith and Martell (26) for oxalic acid (10).

Solid Phases. Sulfates. Solubility product constants and free energies of formation for the jarosite mineral group (jarosite, natrojarosite, and hydronium jarosite or carphosiderite, as the hydrogen form is termed in the older literature) have been compiled by Nordstrom (58). Considerable discrepancies occur between different investigations because the solution equilibria are very complicated: several strong complexes are formed and attempts are seldom made to account for the effect of hydroxide and sulfate complexation of the cations involved on apparent solubility. There is also a lack of consistency between values for the jarosite solubility product constant, partly because different complexes were used. Of the four investigations made on jarosite, Brown's results (59, 60) must be discounted because of very large uncertainties in the results. A mean value of -98.80 ± 1.1 for the log K_{sp} has been selected for WATEQ2 from the works of Zotov et al. (61), Vlek et al. (62) and Kashkai et al. (63). If the dissolution reaction is written as:

$$6H^+ + KFe_3(SO_4)_2(OH)_6(s) \rightleftarrows K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \qquad (8)$$

then the log K is -14.8 ± 1.1. The log K for natrojarosite, written in the same manner as reaction 8, is -11.2 ± 1.0 from the work of G. Clifton (Continental Material Co., personal communication, 1977) and agrees with the value obtained by Kashkai et al. (63). Only one log K value is available for hydronium jarosite (63). The ΔH for the reaction 8 has been estimated to be -31.28 kcal mol^{-1} by utilizing the data of Zotov et al. (61) for the entropy of jarosite, the previously cited investigations for the mean ΔG_f° value and Wagman et al. (41, 64) for the enthalpies of the ions. The enthalpy for natrojarosite dissolution is derived from the entropy and free energy values given by G. Clifton (personal communication, 1977) and for hydronium jarosite a linear correlation between free energies and enthalpies was assumed for the jarosite group since no data are available.

We have observed melanterite, $FeSO_4 \cdot 7H_2O$, to be one of the common sulfate minerals produced by the oxidation of pyrite during weathering. Unfortunately, its solubility and related thermodynamic properties are not well established. The log K for melanterite dissolution has been derived from the free energies of formation of the constituent species and the greatest source of uncertainty lies with the ΔG_f° for Fe^{2+}. We prefer the value of -21.8 ± 0.5 (65) which results in a log K of -2.47. The enthalpy of dissolution is 2.86 kcal mol^{-1} based on $\Delta H_f^\circ = -22.1$ kcal mol^{-1} for Fe^{2+} from Larson and Hepler (65).

The log K and ΔH° values in Ball et al. (10) for the dissolution of epsomite have been obtained from the free energy and enthalpy data given in Wagman et al. (41) and Parker et al. (66). For the log K and ΔH° of potassium alum solubility, values were obtained from the free energies and enthalpies of Wagman et al. (41) and Kelly et al. (67).

Fluorite. The solubility and related thermodynamic properties of fluorite have had large uncertainties, i.e. 2 to 3 orders of magnitude. Nordstrom and Jenne (50) utilized simultaneous multiple regression analysis (68) to evaluate these thermochemical data. The revised log K (10) agrees quite well with the upper limit of fluorite ion activity product calculations of many geothermal waters in the western United States. Although a total uncertainty of ± 0.5 was assigned to the log K (to include analytical and computational errors), more recent investigations indicate that the log K falls between -10.5 and -11.0 (69, 70, 71) so that the uncertainty in the log K at 298.15°K is ±0.25. At this level of deviation the analytical and computational uncertainties inherent in the calculations of the ion activity product are likely to be greater than those in the thermodynamic properties.

Other alkaline earth fluorides (BaF_2, SrF_2) have been added to the model. However, they are less likely than their respective sulfates or carbonates to be solubility limiting phases.

Others. Thermochemical data for the ferrous chlorite, greenalite ($Fe_3Si_2O_5(OH)_4$), and phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$) dissolution were taken from Plummer et al. (4) who used the free energy values of Eugster and Chow (72) for greenalite and Bird and Anderson (73) for phlogopite.

Solubility calculations were added for two allophanes, for which the equilibrium constants and formulae are a function of pH. Paces (74) found cold ground waters collected from springs in granitic rocks of the Bohemian Massif of Czechoslovakia to be supersaturated with respect to kaolinite while being unsaturated with respect to amorphous silica. He interpreted this as an indication that a metastable aluminosilicate more soluble than kaolinite was controlling the concentrations of alumina and silica in these waters. This aluminosilicate was further hypothesized to be of varied chemical composition, controlled by the mole fraction of silica and dissolved by the reaction:

$$[Al(OH)_3]_{(1-x)}[SiO_2]_x(s) + 3(1-x)H^+ \rightleftarrows (1-x)Al^{3+} + xH_4SiO_4^\circ + (3-5x)H_2O \, . \qquad (9)$$

In equation 9, x is the mole fraction of silica and is equal to 1.24 - 0.135pH. This expression describes the linear variation between pure amorphous hydrous alumina and silica as a function of pH (75). The equilibrium constant for this substance was calculated by combining two endmember constants from the literature and incorporating the pH-dependence equation into the resulting expression, yielding an expression for the equilibrium solubility (75) of:

$$\log K = -5.7 + 1.68pH. \qquad (10)$$

Under field conditions the solubility of this material should be lower due to the large difference in the speed of crystallization of amorphous alumina versus amorphous silica. In fact, a best-fit line to field samples from the Sierra Nevada is described by the equation (75):

$$\log K = -5.4 + 1.52pH. \qquad (11)$$

Copper ferrites have been included in the model, but have as yet not been found to be equilibrium controls on copper or iron solubility. The calculated activity products for the two minerals, cuprous ferrite and cupric ferrite, are characteristically several orders of magnitude oversaturated when compared to their respective equilibrium constants in a wide variety of surface waters.

Ponnamperuma et al. (76) describe a ferrosoferric hydroxide ($Fe_3(OH)_8$), offering evidence that most iron (II) in reduced soils other than acid sulfate soils is present in this form. Using a log K of 17.56 from Ponnamperuma et al. (76) for the reaction:

$$2Fe(OH)_3(s) + Fe^{2+} + 2OH^- \rightleftarrows Fe_3(OH)_8(s) \qquad (12)$$

and log K values for the ionization of water and ferric hydroxide dissolution, we calculate a log K of 20.222 for the reaction:

$$Fe_3(OH)_8(s) + 8H^+ \rightleftarrows 2Fe^{3+} + Fe^{2+} + 8H_2O \, . \qquad (13)$$

Biedermann and Chow (77) describe a ferric hydroxy-chloride ($Fe(OH)_{2.7}Cl_{0.3}$) which has been seen to precipitate from sea water, having a log K of 3.04 ± 0.05 (51) for the reaction:

$$Fe(OH)_{2.7}Cl_{0.3}(s) + 2.7H^+ \rightleftarrows Fe^{3+} + 2.7H_2O + 0.3Cl^- . \qquad (14)$$

Chien and Black (78) calculate a log K of -114.4 for the fluorocarbonato apatite reaction:

$$Ca_{9.5}Na_{.36}Mg_{.144}(CO_3)_{1.2}F_{2.48}(PO_4)_{4.8}(s) \rightleftarrows 9.5Ca^{2+} + 0.36Na^{+} + 0.144Mg^{2+} + 1.2CO_3^{-} + 2.48F^{-} + 4.8PO_4^{3-} \ . \qquad (15)$$

These reactions have been added to the model.

Morey et al. (79) have calculated an equilibrium constant for amorphic silica which best fits their field data. The log K for this reaction of -2.71 has also been added.

Redox Couples. The model calculates the redox potential of the couples: H_2O_2/O_2, H_2O/O_2, Fe^{2+}/Fe^{3+}, NO_2^-/NO_3^-, S^{2-}/SO_4^{2-}, and As^{3+}/As^{5+}, given the requisite concentrations of the couple members. Dissolved oxygen is all that is required for calculation of both the H_2O/O_2 and H_2O_2/O_2 couples. The H_2O/O_2 couple is kinetically inhibited and is grossly out of equilibrium except at elevated temperatures (80). Therefore, the option of using pE from dissolved oxygen for redox speciation has been dropped from the model.

Recent studies (81) show that when the following three conditions are fulfilled, the platinum electrode provides a reliable and accurate estimate of the ferrous-ferric redox potential, $E^H_{Fe^{2+}/Fe^{3+}}$, in acid mine drainage waters. The conditions are: 1) large volumes of water must flow past the electrodes during emf measurement; 2) water samples must be properly filtered ($\leq$ 0.1 μm membrane) and preserved for ferrous-ferric iron analyses; and 3) activities of Fe^{2+} and Fe^{3+} rather than concentrations must be used to compute the potential of the ferrous-ferric couple. Other studies (R. E. Stauffer, E. A. Jenne, J. W. Ball, unpub. data, 1974) show that when a flow-through cell is used for emf measurements of geothermal waters, the platinum electrode potential mirrors decreasing dissolved sulfide and then increasing dissolved oxygen values in the downstream drainage of individual hot springs.

As alluded to above, input data for total iron, Fe(II) and/or Fe(III) are accepted by the model, with solute modeling calculations done using whatever data are input. If either Fe(II) or Fe(III) are present, Fe(total) is ignored; if Fe(II) only is present, speciation is done among Fe(II) complexes only, and likewise for Fe(III). To accomplish this, the reactions of the iron section have been extensively rewritten (10) and a procedure, named SPLIT_IRON, has been added, which performs the mass balance calculations separately for Fe(II) and Fe(III) when they are input separately. An E^H value is calculated from the computed activities of Fe^{2+} and Fe^{3+} and may, by user option, be used to distribute other redox species in lieu of an input E^H value. If only Fe(total) is input, the input E^H value is used to distribute all redox species including Fe^{2+} and Fe^{3+}; if there is only Fe(total) input, and no input E^H value, all Fe calculations are bypassed.

Standard Deviations. In order to evaluate the effect on the modeling calculations of errors in the analytical input data, propagated standard deviations are now computed for a subset of the solid phase activity products considered in the model. Arrangements have also been made to enter and output standard deviations for thermodynamic data.

A new procedure named ERRCALC was written to calculate the propagated standard deviation. The basic equation for the activity product of a solid phase is:

$$\log_{10}AP = Ax + By \qquad (16)$$

where AP is the activity product, x and y are the log activities of the constituent ions in solution, and A and B are the number of ions of each species making up the solid. From Bevington (81, p. 60) we construct the following equation to calculate the standard deviation in the $\log_{10}$ of the activity product, which in practice is the sum of the $\log_{10}$ of the activities of the constituent ions:

$$\sigma^2_{\log_{10}AP} = A^2\sigma^2_x + B^2\sigma^2_y \ . \qquad (17)$$

Unfortunately, the standard deviation in the $\log_{10}$ of the activity of the species is not known; rather the known quantity is the standard deviation in the input analytical value. Therefore, a second equation is required for x and y as the $\log_{10}$ of another number. From Bevington (82, p. 63-64),

$$\text{for:}\quad x = a\ln(\pm bu) \qquad (18)$$

$$\sigma_x = a\frac{\sigma_u}{u} \qquad (19)$$

where u and x are the activity and $\log_{10}$ of the activity, respectively, of the species, and a and b are weighting constants. If a is set equal to 1/2.303 (i.e., 1/ln (10)), equation 18 becomes

$$x = \log_{10}(\pm bu) \qquad (18a)$$

and equation 19 becomes:

$$\sigma_x = \frac{1}{2.303}\,\frac{\sigma_u}{u} \ . \qquad (19a)$$

The standard deviation in the activity of the species is also unknown, but we have defined the propagated standard deviation to be strictly in terms of errors in analytical input data, so that the relative standard deviation of input data and computed activities are, under this definition, equal:

$$\frac{\sigma_v}{v} = \frac{\sigma_u}{u} \qquad (20)$$

where u is the activity of the species, v is the analytical concentration of the species from which the activity of the species was derived and σ_u and σ_v are the respective standard deviations. Substituting from equation 20 to equation 19a we obtain:

$$\sigma_x = \frac{1}{2.303}\left(\frac{\sigma_v}{v}\right). \tag{19b}$$

Deriving an analogous expression for σ_y in terms of w and substituting it and the right side of 19b into 17 we obtain:

$$\sigma^2_{\mathrm{Log}_{10}AP} = A^2\left(\frac{\sigma_v}{2.303v}\right)^2 + B^2\left(\frac{\sigma_w}{2.303w}\right)^2 \tag{17a}$$

where σ_w and w are the analogously obtained values for σ_y.

The sigma values thus computed are printed along with the results of the activity product calculations under the heading SIGMA(A), the uncertainty ascribed to the analytical values used. The uncertainties ascribed to the thermodynamic data are labeled SIGMA(T).

Sigma values are routinely obtained for analyses performed in our laboratory. However, we are utilizing a considerable amount of literature data to evaluate the role of various solid phases as effective solubility controls. These data rarely contain either sigma values or the data from which they can be calculated. Therefore, we have resorted to use of twice the uncertainty resulting from rounding of the analytical values as a minimum estimate of the analytical uncertainty. These are not distinguished in the model from true sigma values.

Other Modifications. All new reactions which include OH^- are written in terms of H_2O and H^+, following the convention of Baes and Mesmer (51). If the reactions are written in terms of OH^-, errors in the dissociation of water and in its temperature dependence are encountered. These errors are thus avoided since A_{H^+} is a directly measured quantity. This also has the advantage of making the propagated standard deviations for different solid phases more comparable than if some are written in terms of OH^- and some in terms of H_2O and H^+. Most of the preexisting reactions which include OH^- were similarly modified to conform to this convention.

Other features of WATEQF (4) which have been incorporated into WATEQ2 include: 1) revised set of analytical expressions for the effect of temperature on the stability constant (10); 2) printed table of log K values for which analytical expressions exist, following the listing of the input thermochemical data (10); 3) check on the charge balance computed from input data, with aborting of the calculations if the balance is off by >30%; 4) revised anion mass balance calculation, allowing for faster convergence; and 5) improved set of headings used in the printed results of the solute modeling calculations.

Specific conductance calculated from input major constituent data using the method of Laxen (83) has been added to the model as a check on analytical input data. Differing input and calculated specific conductances indicate that one or more errors may exist in the analytical input data.

A mass balance section for the hydrogen sulfide species was added to the anion mass balance calculations when we observed that strong HS^- complexing of some trace metals sometimes rendered cation mass balance convergence impossible.

Activity coefficients were originally calculated using the extended Debye-Hückel equation and whenever a new complex was added to the program it was necessary to estimate the å parameter. This problem was overcome by substituting the more general Davies equation which has adequate reliability at low ionic strengths and is usually more accurate at high ionic strengths (84). Since acid mine waters can have ionic strengths approaching that of sea water, it is desirable to use a theory for activity coefficients that can reach somewhat above 0.1 molal, the usual upper limit for extended Debye-Hückel calculations. The Davies equation is considered satisfactory to 0.5 molal. The extended Debye-Hückel equation with fit parameters (2, 3) has been retained for the major ions, Ca, Mg, Na, K, Cl and SO_4, and the Debye-Hückel equation is used to calculate the polysulfide activity coefficients, for which å parameters have been estimated by Cloke (85).

There are inconsistencies in the model for the calculation of activity products for the "clays." Exchangeable cations are disregarded for the low exchange capacity kaolinite, halloysite, chlorite, and moderate capacity illite. For certain expansible layer silicates and two zeolites, the $\log_{10}$ of the activity of selected cations is added into the sum of the activity products. The mineral phases treated in this manner, and the solute cations considered as exchangeable cations, are beidellite ($[A_{Mg^{2+}}]^{\frac{1}{2}} + A_{Na^+} + A_{K^+}$), clinoptilolite and mordenite ($A_{Na^+} + A_{K^+}$), Belle Fourche montmorillonite and Aberdeen montmorillonite ($A_{H^+} + A_{Na^+} + A_{K^+}$). Note that the square root of the divalent cation is used in the sum in keeping with the practice in the ion exchange literature (86). Revision of the calculation of exchangeable cation contribution to the activity product has been delayed pending the pertinent reviews of Kittrick (87), as well as that of Bassett et al. (88) presented at this symposium.

Modifications in the Code

The PL/1 language computer code has been extensively altered in the process of building it into WATEQ2; in fact, minor alterations are far too numerous to mention here. Several errors in the original code were corrected and some major changes, noted below, were made to improve program execution and ease of use and to broaden its usefulness. The input and output aspects of program operation are given, along with the thermodynamic data base, in a supplementary report (10).

Arrays which must be increased in size when species are added are now automatically adjustable in dimension merely by supplying appropriate input data. The results of solute and mineral calculations will not appear if the activity or activity product, respectively, has not been calculated. This eliminates extraneous non-information and shortens the listing considerably, an advantage especially when a simple laboratory solution is considered and/or a low-speed remote computer terminal is utilized.

Some data are entered into the model as "carried-only" data, primarily for plotting using a subsequent computer program. However, as the model evolves, some of these carried-only data become input to the model itself or to adjunct calculations. Specific conductance, which was initially carried-only data, is now compared to a computed "specific conductance" as a quality-of-analysis screening technique.

The listing of the results of the mineral equilibrium calculations has been drastically altered, with the deletion of ΔG_r, ΔG_r per equivalent cation, and all values in base 10 form. Information now printed for each species for which an activity product is calculated includes log AP/K, SIGMA (Analytical), SIGMA (Thermodynamic), log AP/K_{min}, and log AP/K_{max}. As discussed previously, SIGMA(A) is the propagated standard deviation in the analytical values and SIGMA(T) is the standard deviation in the thermodynamic data. The $\log_{10}K_{min}$ and $\log_{10}K_{max}$ values have been changed from ± 5% of the $\log_{10}K$ value (2) to experimentally determined values which may represent a less soluble or more soluble form of the solid phase than that selected as the "best" value.

WATEQ2 consists of a main program and 12 subroutines and is patterned similarly to WATEQF (4). WATEQ2 (the main program) uses input data to set the bounds of all major arrays and calls most of the other procedures. INTABLE reads the thermodynamic data base and prints the thermodynamic data and other pertinent information, such as analytical expressions for effect of temperature on selected equilibrium constants. PREP reads the analytical data, converts concentrations to the required units, calculates temperature-dependent coefficients for the Debye-Hückel equation, and tests for charge balance of the input data. SET initializes values of individual species for the iterative mass action-mass balance calculations, and calculates the equilibrium constants as a function of the input temperature. MAJ_EL calculates the activity coefficients and, on the first iteration only, does a partial speciation of the major anions, and performs mass action-mass balance calculations on Li, Cs, Rb, Ba, Sr and the major cations. TR_EL performs these calculations on the minor cations, Mn, Cu, Zn, Cd, Pb, Ni, Ag, and As. SUMS performs the anion mass action-mass balance calculations, and tests the results against input concentration values for the anions CO_3^{2-}, SO_4^{2-}, F^-, PO_4^{3-}, Cl and S^{2-}, and prints the results of each set of iterative calculations. MAJ_EL, TR_EL and SUMS are executed repetitively until mass balance to within 0.1% of the input concentrations is achieved for the six anions, or until 40 iterations have elapsed. If convergence is not reached in 40 iterations, a warning message is printed and execution continues just as through convergence had been reached. SOLUTES performs computations not related to the mass balance calculations, such as E^H, specific conductance, pO_2 and pCH_4 calculations, prints out all the solute data, and performs necessary logarithm conversions for use in subsequent calculations. RATIO calculates and prints mole ratios calculated from analytical molality and log activity ratios. APCALC calculates thermodynamic activity products for the various mineral species considered by WATEQ2. OUTPNCH generates a card deck of a subset of the calculated activities, activity products and input concentrations for subsequent use with plotting programs. ERRCALC, discussed previously, uses input analytical standard deviations to calculate the propagated standard deviation in the log of the activity products for a subset of minerals considered. PHASES prints the results of the activity product and error calculations, and computes and prints the saturation state of each mineral with respect to a thermodynamic equilibrium constant for each reaction considered.

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Abstract

The computerized aqueous chemical model of Truesdell and Jones (2, 3), WATEQ, has been greatly revised and expanded to include consideration of ion association and solubility equilibria for several trace metals, Ag, As, Cd, Cu, Mn, Ni, Pb and Zn, solubility equilibria for various metastable and(or) sparingly soluble equilibrium solids, calculation of propagated standard deviation, calculation of redox potential from various couples, polysulfides, and a mass balance section for sulfide solutes. Revisions include expansion and revision of the redox, sulfate, iron, boron, and fluoride solute sections, changes in the possible operations with Fe (II, III, and II + III), and updating the model's thermodynamic data base using critically evaluated values (81, 50, 58) and new compilations (51, 26; R. M. Siebert and

C. L. Christ, unpublished data 1976). Mechanical revisions include numerous operational improvements in the computer code.

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