

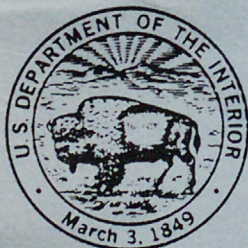
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BALANCE —
A COMPUTER PROGRAM FOR CALCULATING
MASS TRANSFER FOR GEOCHEMICAL
REACTIONS IN GROUND WATER

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U.S. GEOLOGICAL SURVEY
Water-Resources Investigations 82—14





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By David L. Parkhurst, L. Niel Plummer, and Donald C. Thorstenson

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ABSTRACT

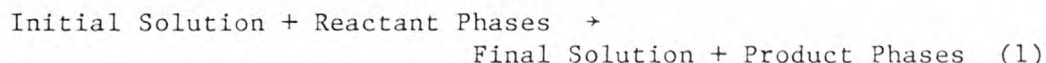
BALANCE is a Fortran computer program designed to define and quantify chemical reactions between ground water and minerals. Using (1) the chemical compositions of water samples from two points along a flow path and (2) a set of mineral phases hypothesized to be the reactive constituents in the system, the program calculates the mass transfer (amounts of the phases entering or leaving the aqueous phase) necessary to account for the observed changes in composition between the two water samples. Additional constraints can be included in the problem formulation to account for mixing of two end-member waters, redox reactions, and, in a simplified form, isotopic composition. The computer code and a description of the input necessary to run the program are presented. Three examples typical of ground-water systems are described.

DESCRIPTION OF THE PROGRAM

BALANCE is a Fortran computer program designed to help define and quantify chemical reactions between ground water and minerals. Data required to run the program are: (1) the chemical compositions of two water samples, generally assumed to represent points along a flow path, and (2) the chemical compositions of a set of minerals, organic substances, or gases, which we will call phases, selected as the reactants or products in the system. Implicit in this treatment is the assumption that only these selected phases participate in the chemical reactions that determine the composition of the final water.

The program calculates the mass transfer (amounts of phases entering or leaving the aqueous phase) necessary to account for the observed

changes in composition between the two solutions. The purpose of BALANCE is to derive balanced reactions of the form:



A "reaction model" is defined by the selected phases and the calculated amount of each phase necessary to satisfy equation 1. In general, many reaction models can account for an observed change in water chemistry. BALANCE alone cannot determine if any one, unique set of phases governs the reactions in the ground-water system.

BALANCE models are not constrained by any thermodynamic criteria and may imply reactions that are thermodynamically impossible. Methods for identifying reaction models that do not satisfy thermodynamic or other criteria are presented in Plummer and others (1982). In the ideal case, all but one reaction model can be eliminated, leaving one unique chemical model consistent with the available data.

The program BALANCE is designed specifically for mineral-water interactions, but essentially BALANCE solves any set of linear equations formulated by the user. The report includes discussions of several processes which can be formulated as linear equations: (1) mass balance on elements, (2) mixing end-member waters, (3) oxidation-reduction reactions, and (4) simple isotope balance. Following these discussions, the input necessary to run the program and three examples in a carbonate system are presented.

Elements

In order to use BALANCE, the chemical composition of two waters must be known. Only the total concentrations of each element are required for models in which redox reactions are not considered. BALANCE accepts two kinds of concentration data as input: (1) the total concentration of each element in the initial and final solutions, or (2) the difference in total concentration for each element between the final and initial solutions (final - initial). If data are unavailable for some element, reasonable assumptions may describe the change in concentration for that element. For example, if the total concentration of iron is not known but can be assumed to be very low, then it may be reasonable to assume that iron is essentially conserved in any reaction and that the difference in iron concentration between the initial and final solution is zero. The problem of missing analytical data is discussed more thoroughly in Plummer and others (1982).

Phases

The phases to be used in the calculations are selected by the user on the basis of the geology, hydrology, or mineralogy of the system. These "plausible" phases generally are mineral solids but may also include gases, ion exchangers, or (in the special case of mixing) other aqueous solutions. For the purposes of this program, a phase represents a set of chemical elements that enter or leave the initial solution in fixed ratios. The objective in selecting phases is to provide a source or sink for each element in the initial and final solutions. The result is a set of linearly independent equations which can be solved simultaneously to yield values that describe the amount of each phase participating in the reaction.

In general, the number of phases must equal the number of elements in order to solve the set of equations. Although the calculated mass transfer for one or more phases might be zero, indicating that the phase(s) did not participate in the reaction, the phase(s) must still be included in the input to BALANCE in order to perform the calculations.

Element Mass Balance Equations

The equations for mass balance on elements are:

$$\sum_{p=1}^P \alpha_p b_{p,k} = m_{T,k}(\text{final}) - m_{T,k}(\text{initial}) = \Delta m_{T,k} \quad (2)$$

for each element $k = 1$ to J .

where the notation is defined as follows: P is the number of total reactant and product phases in the net reaction, α_p is the calculated mass transfer of the p^{th} phase, $b_{p,k}$ denotes the stoichiometric coefficient of the k^{th} element in the p^{th} phase, $m_{T,k}$ is the total molality of the k^{th} element in solution, and J is the number of elements included in the calculation. In problems with only element mass balance equations (no redox or mixing), $P = J$.

Mixing

This program also allows for the following type of problem: Two end-member waters mix in unknown proportions and, in addition, phases dissolve and precipitate to produce a final water. In this problem,

the two initial solutions are treated exactly like other phases and α_1 is the fraction of initial solution 1 and α_2 is the fraction of initial solution 2 which combine, along with mineral reactions, to produce the final solution. In addition to the element mass balance equations, an additional equation is automatically included to ensure the sum of the two fractions is equal to 1.

$$\alpha_1 + \alpha_2 = 1.0 \quad (3)$$

For a mixing problem, the number of phases (other than solutions) that must be included is equal to the number of elements minus one, $P = J - 1$.

Redox

When studying systems involving oxidation and reduction, it is necessary to conserve electrons in chemical reactions. Each mole of electrons released in oxidizing certain species must be consumed by reducing other species. We use the electron counting convention from the program PHREEQE (Parkhurst and others, 1980) to ensure conservation of electrons. (See also Plummer and others, 1982.) The convention defines a redox state for a solution as:

$$RS = \sum_{i=1}^I m_i v_i \quad (4)$$

where RS is the redox state of the solution, m_i is the molality of the i^{th} aqueous species, v_i is the "operational valence" of the i^{th} species, and I is the total number of species.

A redox species is defined as a species of any element which can occur in more than one oxidation state in natural aqueous environments. The rules for determining the operational valence of aqueous species are: (1) use the formal elemental valence for aqueous redox species, (2) use zero for non-redox species, (3) use the sum of the operational valences of species which associate to form redox complexes, (4) assign zero to the valences of H and O in aqueous species, (5) use zero for H^+ and OH^- , (6) use -2.0 for $H_2O(aq)$ and +4.0 for $O_2^0(aq)$. The operational value of a phase is defined in the same way as for a dissolved complex. Table 1 lists examples of the operational valence of selected species and minerals.

Using these definitions, a linear equation ensuring the conservation of electrons can be formulated. The redox state is included in

Table 1.-Definition of v_i and u_p for selected aqueous species and minerals^{1/}

Species	v_i	Mineral	u_p
Ca^{2+}	0.0	CaCO_3	4.0
Mg^{2+}	0.0	$\text{CaMg}(\text{CO}_3)_2$	8.0
Na^+	0.0	5 percent Fe-Dolomite ^{2/}	8.1
K^+	0.0	NaCl	0.0
Fe^{2+}	2.0	CaSO_4	6.0
Fe^{3+}	3.0	FeOOH	3.0
Cl^-	0.0	Fe_2O_3	6.0
SO_4^{2-}	6.0	FeCO_3	6.0
H_2S^0	-2.0	FeS	0.0
HS^-	-2.0	FeS_2	0.0
HCO_3^-	4.0	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	6.0
CH_4^0	-4.0	" CH_2O "	0.0
CaHCO_3^+	4.0	KAlSi_3O_8	0.0
H_2CO_3^0	4.0	$\text{Al}(\text{OH})_3$	0.0
N_2^0	0.0	KOH	0.0
NO_3^-	5.0	H_2S gas	-2.0
NH_4^+	-3.0	CH_4 gas	-4.0
$\text{Fe}(\text{OH})_2^+$	3.0	CO_2 gas	4.0
FeSO_4^0	8.0	H_2 gas	-2.0
H^+, OH^-	0.0	O_2 gas	4.0
H_2^0	-2.0	N_2 gas	0.0
O_2^0	4.0	NH_3 gas	-3.0
H_2O	0.0	CaF_2	0.0

^{1/} The list is obviously incomplete but should serve as an example for other species and minerals that may be considered.

^{2/} $\text{Ca}_{1.05}\text{Mg}_{0.90}\text{Fe}_{0.05}(\text{CO}_3)_2$.

BALANCE input as an "element". In this report we have chosen the letters "RS" to designate this pseudo-element.

$$\sum_{p=1}^P u_p \alpha_p = RS(\text{final}) - RS(\text{initial}) = \Delta RS \quad (5)$$

where u_p is the operational valence of the p^{th} phase and RS denotes the redox state of the solution. If we consider RS to be another element, then the same equalities hold for the number of phases and the number of elements. For non-mixing problems, $P = J$ (including RS) and for mixing $P = J - 1$.

Results

The results of running the program BALANCE are a set of numbers indicating the moles of each phase which react with the initial solution to produce the final solution (positive for dissolution, negative for precipitation). In the mixing case, the numbers for solution 1 (α_1) and solution 2 (α_2) are the mixing fractions for the two solutions.

Error Messages

Two error messages may be printed by the program. If the number of phases does not match the number of elements, the number of phases counted by the program is printed, followed by the number of elements counted, with the message, "NUMBER OF PHASES DOES NOT MATCH NUMBER OF EQUATIONS". If the linear equations are found to be linearly dependent, then "THE PHASE RULE HAS BEEN VIOLATED" is printed. If the selected phases do not include a source or sink for each element or if they include minerals whose compositions can be derived by linear combinations of other minerals in the set, this error message will be printed. For example, if CaCO_3 , MgCO_3 , and $\text{CaMg}(\text{CO}_3)_2$ are chosen as phases, an error will result because:



In BALANCE, a division by zero often occurs before this message is printed which may result in an abnormal termination of the program. Although the reason may not be immediately obvious to the user, the cause of the latter error message nearly always lies in the choice of the mineral phases.

PROGRAM INPUT

The program BALANCE requires three types of input to run: (1) A title, (2) a set of elements and their total concentrations or changes in concentrations, and (3) a set of minerals defined in terms of their elemental stoichiometry (and operational valence for redox problems). In the description that follows the Fortran format for each card is given in parentheses. The input is as follows:

TYPE 1: TITLE (20A4) The title is any name or description of 80 characters or less (one card).

TYPE 2: Solution data. Only one of the following type 2 forms of input may be used for a single simulation.

2.a. ENAME, EDELTA (A2,F8.3)

ENAME - The standard element abbreviation (e.g. K, NA, or CL). The abbreviation must be left justified and if redox is considered, RS must be one of the elements.

EDELTA - The difference in total concentration of the element between the final and the initial solution (final - initial). The units used may be molal, mmolal, or μ molal. No distinction is made between molarity and molality. The same units must be used for all elements.

2.b. ENAME, SFINAL, SINIT (A2,F8.3,F10.3)

ENAME - Same as above.

SFINAL - The total concentration of the element in the final solution in mole, mmole or μ mole units, provided the same unit is used for all elements.

SINIT - The total concentration of the element in the initial solution.

2.c. ENAME, SFINAL, SINIT1, SINIT2 (A2,F8.3,F10.3,F10.3)

ENAME - Same as above.

SFINAL - Same as above.

SINIT1 - The total concentration of the element in one of the two end-member solutions which mix to form SFINAL.

SINIT2 - The total concentration of the element in the other end-member solution assumed to mix in forming SFINAL.

BALANCE calculates the fractions of the two initial solutions, with or without additional reaction, which combine to form the final solution.

Any number of elements for which there are data may be included (one element per card) but a mineral source or sink must be included for each element. All elements for a single simulation must use a single type (2.a., 2.b., or 2.c.) of input.

Note: The final card of type 2 input must be blank.

TYPE 3: Phase data. PNAME, (PELT(J), PCOEF(J), J=1,7) (A8,2X,7(A2,F8.3))

PNAME - An eight character name for the phase.

PELT - The standard abbreviation for a constituent element of the phase (must be left justified and identical to ENAME used in type 2 input). Seven sets of PELT and PCOEF (see below) can be read on this card but only those necessary to define the mineral need to be entered. RS must be included if redox is being considered. Omission of an element or RS implies zero.

PCOEF - Read as a pair with PELT, this is the stoichiometric coefficient for the element in the phase. For RS, PCOEF is the operational valence of the phase. (See table 1 for examples.)

A number of phases equal to the number of elements must be entered for types 2.a and 2.b. For mixing cases, the number of phases must be one less than the number of elements. Elements in the phases which are not included in the list of elements will be ignored in the calculations.

Note: The final card in type 3 input must be blank.

Sequential mass balance calculations may be run by repeating the input sequence starting with the title.

EXAMPLES

Three examples are presented below to demonstrate how to code problems for BALANCE and to show some of the varieties of reactions and data that can be considered.

Example 1

The observed analytical data for initial and final waters for example 1 are given in table 2:

Table 2.-Analytical data for example 1 ^{a/}

<u>Element</u>	Total concentration (mmol/kg H ₂ O)	
	<u>Final Water</u>	<u>Initial water</u>
Calcium	3.230	1.118
Magnesium	2.668	0.950
Sulfur	4.000	0.0
Carbon	4.294	4.464

Note that accompanying the increases in total dissolved calcium, magnesium, and sulfur (sulfate in this case), total inorganic carbon decreases in the final water. The four elements for which analytical data are given allow four phases to be included in testing reaction models. The four phases chosen for this example are calcite (CaCO₃), dolomite (CaMg(CO₃)₂), gypsum (CaSO₄·2H₂O), and CO₂ gas.

The mass balance equations (equation 2) for this choice of phases are given as follows:

$$\Delta m_{T,Ca} = 3.230 - 1.118 = 1\alpha_{\text{calcite}} + 1\alpha_{\text{dolomite}} + 1\alpha_{\text{gypsum}} \quad (7)$$

$$\Delta m_{T,Mg} = 2.668 - 0.950 = 1\alpha_{\text{dolomite}} \quad (8)$$

$$\Delta m_{T,S} = 4.000 - 0.0 = 1\alpha_{\text{gypsum}} \quad (9)$$

$$\Delta m_{T,C} = 4.294 - 4.464 = 1\alpha_{\text{calcite}} + 2\alpha_{\text{dolomite}} + 1\alpha_{\text{CO}_2} \quad (10)$$

^{a/} Although the analytical data of table 2 are realistic, they were generated from thermodynamic data using the equilibrium model PHREEQE (Parkhurst and others, 1980). Both solutions are constructed to be in equilibrium with dolomite and calcite, but undersaturated with gypsum.

Table 3 lists the input data set for BALANCE. Card 1 is the title card. Cards 2-5 define the element concentrations in the final and initial water using type 2.b input (as defined earlier). Card 6 is a blank card denoting the end of type 2 input. Cards 7-10 define the selected phases for the reaction model, type 3 input, and card 11 is blank denoting the end of type 3 input. BALANCE will accept successive reaction model data sets but only one data set is given in table 3.

Table 4 gives the results computed by BALANCE including the linear matrix of coefficients used to solve the reaction model and the computed mass transfers of the selected phases (DELTA PHASES). Note that the coefficients of the array are the same as the coefficients in the mass balance equations in equations 7-10. The units of DELTA PHASES in table 4 are mmol/kg H₂O (\cong mmol/L). Negative values indicate precipitation between the initial and final water and positive values indicate dissolution.

The results of table 4 show that if calcite, dolomite, gypsum, and CO₂ are the minerals reacting in the ground-water between the initial and final solution, then the reaction is incongruent dissolution of dolomite (dolomite dissolution with calcite precipitation) accompanying the dissolution of gypsum in a system closed to CO₂ gas.

Example 2

This example assumes that an observed final water composition has resulted from the mixing of two end-member (initial) solutions with subsequent reactions. The final observed water and the two initial solutions are summarized in table 5. As with example 1, the water chemistry was constructed using PHREEQE (Parkhurst and others, 1980).

The end-member waters are (1) a calcium bicarbonate water in equilibrium with calcite at a P_{CO_2} of 10^{-2} atm, and (2) seawater. The final water has been constructed to be in equilibrium with calcite and dolomite. In this example, we are interested in computing the fractions of solutions 1 and 2 in the mixture and the amounts of subsequent mineral-water reactions. The phases chosen for these calculations are calcite, dolomite, gypsum, CO₂ gas, NaCl, and Ca²⁺-Na⁺ ion exchange. Note that because this is a mixing problem, the number of phases (6) is one less than the number of elements (7). The ion exchange reaction is written

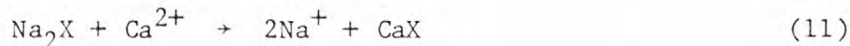


Table 3.-Card images of input data set for example 1

CARD #	COLUMN	1 0	2 0	3 0	4 0	5 0	6 0	7 0	8 0
1	EXAMPLE #1: NON-REDOX REACTION (TYPE 2.B INPUT)								
2	CA 3.230 1.118								
3	MG 2.668 0.950								
4	S 4.000 0.0								
5	C 4.294 4.464								
6									
7	CALCITE CA 1.0 C 1.0								
8	DOLOMITE CA 1.0 MG 1.0 C 2.0								
9	CO2 GAS C 1.0								
10	GYP SUM CA 1.0 S 1.0								
11									

Table 4.-Printout listing results for example 1

EXAMPLE #1: NON-REDOX REACTION (TYPE 2.B)

DELTA		CALCITE	DOLOMITE	CO2 GAS	GYPSUM
2.112	CA	1.000	1.000	0.0	1.000
1.718	MG	0.0	1.000	0.0	0.0
4.000	S	0.0	0.0	0.0	1.000
-0.170	C	1.000	2.000	1.000	0.0

DELTA PHASES

CALCITE	-3.6060
DOLOMITE	1.7180
CO2 GAS	0.0000
GYPSUM	4.0000

Table 5.-Analytical data for example 2

Element	Final water	End-member waters (mmol/kg H ₂ O)	
		Solution 1	Solution 2
Calcium	11.567	1.651	10.661
Magnesium	9.156	0.0	55.083
Sodium	145.626	0.0	485.418
Potassium	3.174	0.0	10.579
Chloride	170.025	0.0	566.751
Sulfur	8.778	0.0	29.259
Carbon	3.029	3.635	2.138

Table 6 lists the card deck to solve example 2. Card 1 is the title card. Cards 2-8 define the total concentrations of the elements in the final water and in the end-member solutions 1 and 2. Card 9 is blank. Cards 10-15 define the stoichiometry of the mineral reactions included in the model and card 16 is blank.

Table 7 gives the results computed by BALANCE which indicates that the final water contains 70 percent calcium bicarbonate water (solution 1) and 30 percent seawater (solution 2). In addition to mixing, the water has dissolved 14.58 mmol of calcite and precipitated 7.37 mmol of dolomite per kg H₂O. None of the other phases considered in this example have contributed significantly to the evolution of the final water.

Example 3

This example uses observed chemical data from the Floridan aquifer and is similar to the modeling considered by Plummer and others (1982). The analytical data for the initial and final waters, including data on the sulfur isotopes, are summarized in table 8.

In calculating the mass transfer in the evolution of the initial water to the final water, three types of linear equations are solved simultaneously: (1) chemical mass balance, (2) conservation of electrons, and (3) a linear sulfur isotope balance equation. These equations are developed below for a reaction model that assumes the following set of seven phases: calcite (CaCO₃), dolomite (CaMg(CO₃)₂), gypsum (CaSO₄·2H₂O), organic matter (CH₂O), carbon dioxide (CO₂), ferric hydroxide (FeOOH), and pyrite (FeS₂). It is important to note that these choices of phases are arbitrary. Other sets of phases will also lead to valid reaction models. That is, all the mass balance and redox criteria included in BALANCE can be satisfied by other sets of phases.

Table 6.-Card images of input data set for example 2

CARD #	1 0	2 0	3 0	4 0	5 0	6 0	7 0	8 0
1	EXAMPLE #2: MIXING WITH NON-REDOX REACTIONS (TYPE 2.C INPUT)							
2	CA11.56664	1.651	10.6611					
3	MG9.156023		55.083283					
4	NA145.6255		485.4183					
5	K 3.173669		10.57890					
6	CL170.0254		566.75133					
7	S 8.777783		29.25928					
8	C 3.02943	3.635	2.137485					
9								
10	CALCITE	CA 1.0	C 1.0					
11	DOLOMITE	CA 1.0	MG 1.0	C 2.0				
12	CO2 GAS	C 1.0						
13	ION EXCH	CA -1.0	NA 2.0					
14	GYPSUM	CA 1.0	S 1.0					
15	NACL	NA 1.0	CL 1.0					
16								

Table 7.-Printout listing results for example 2

EXAMPLE #2: MIXING WITH NON-REDOX REACTIONS (TYPE 2.C INPUT)

FINAL		INIT1	INIT2	CALCITE	DOLOMITE	CO2 GAS	ION EXCH	GYPSUM	NACL
11.567	CA	1.651	10.661	1.000	1.000	0.0	-1.000	1.000	0.0
9.156	MG	0.0	55.083	0.0	1.000	0.0	0.0	0.0	0.0
145.626	NA	0.0	485.418	0.0	0.0	0.0	2.000	0.0	1.000
3.174	K	0.0	10.579	0.0	0.0	0.0	0.0	0.0	0.0
170.025	CL	0.0	566.751	0.0	0.0	0.0	0.0	0.0	1.000
8.778	S	0.0	29.259	0.0	0.0	0.0	0.0	1.000	0.0
3.029	C	3.635	2.137	1.000	2.000	1.000	0.0	0.0	0.0
1.000	MIX	1.000	1.000	0.0	0.0	0.0	0.0	0.0	0.0

DELTA PHASES

INIT1	0.7000
INIT2	0.3000
CALCITE	14.5816
DOLOMITE	-7.3689
CO2 GAS	0.0000
ION EXCH	0.0000
GYPSUM	0.0000
NACL	0.0001

Table 8.-Analytical data for example 3a/

Element	Final water	Initial water	Δ concentration (Final - initial)
Calcium	1.647	0.848	0.799
Magnesium	1.193	0.230	0.963
Carbon	2.845	2.055	0.790
Total Sulfur	1.649	0.025	1.624
Sulfate	1.614	0.025	
Sulfide	0.035	0.0	
Iron	~0.0	~0.0	~0.0
$\delta^{34}\text{S}(\text{SO}_4)$	24.9	14.0	-
$\delta^{34}\text{S}(\text{H}_2\text{S})$	-32.9	-	-

1. Chemical mass balance

Using the values of $\Delta m_{T,k}$ (in mmol/kg H_2O) from table 8, the mass balance equations (equation 3) for Ca, Mg, C, S, and Fe are:

$$\Delta m_{T,\text{Ca}} = 0.799 = \alpha_{\text{calcite}} + \alpha_{\text{dolomite}} + \alpha_{\text{gypsum}} \quad (12)$$

$$\Delta m_{T,\text{Mg}} = 0.963 = \alpha_{\text{dolomite}} \quad (13)$$

$$\Delta m_{T,\text{C}} = 0.790 = \alpha_{\text{calcite}} + 2\alpha_{\text{dolomite}} + \alpha_{\text{CH}_2\text{O}} + \alpha_{\text{CO}_2} \quad (14)$$

$$\Delta m_{T,\text{S}} = 1.624 = \alpha_{\text{gypsum}} + 2\alpha_{\text{pyrite}} \quad (15)$$

$$\Delta m_{T,\text{Fe}} = 0.0 = \alpha_{\text{FeOOH}} + \alpha_{\text{pyrite}} \quad (16)$$

2. Conservation of electrons

Because our problem involves changes in oxidation state, one equation of the form of equation 5, must be included. In this system, carbon, sulfur, and iron are the only redox elements we have included.

a/ All concentrations of elements are given in mmol/kg H_2O and are taken from Back and Hanshaw (1970). Isotope values are in permil (‰) by Rightmire and others (1974) and Rye and others (1981).

Using equation 4, RS for the initial solution is given by $RS = 4(2.055) + 6(0.025) + 0 = 8.370$. In the final solution, $RS = 4(2.845) + 6(1.614) - 2(0.035) = 20.994$, where each redox state of sulfur is considered. ΔRS is then equal to $20.994 - 8.370 = 12.624$ and equation 5 is as follows:

$$\Delta RS = 12.624 = 4\alpha_{\text{calcite}} + 8\alpha_{\text{dolomite}} + 6\alpha_{\text{gypsum}} + 0\alpha_{\text{CH}_2\text{O}} + 4\alpha_{\text{CO}_2} + 3\alpha_{\text{FeOOH}} + 0\alpha_{\text{pyrite}} \quad (17)$$

Note that the pyrite and organic matter terms drop out of the electron conservation equation because their operational valence is zero (table 1). The coefficient for the dolomite term, 8, is the product of the operational valence of carbon in dolomite, 4, and the stoichiometric coefficient of carbon in dolomite, 2.

3. Linear isotope equation

Linear isotope balance equations may be included with the mass balance and electron balance equations provided the reaction is either congruent (that is, mineral dissolution only), or, if incongruent, the fractionation between solution and solid can be neglected. Along our flow path, the measured fractionation is approximately 55‰ in the reduction of sulfate to sulfide. Because of this large difference in isotopic composition of sulfate and sulfide, we will ignore the small fractionation between dissolved total sulfide and pyrite of perhaps 1 to 2‰. The general form for the linear sulfur isotope balance equation is

$$\sum_{p=1}^P \alpha_{p\text{bs},p} \delta^{34}\text{S}_p = \Delta^{34}\text{S} \quad (18)$$

$$\text{where,} \quad \Delta^{34}\text{S} = (m_{\text{T,S}} \delta^{34}\text{S}_{\text{T}})_{\text{final}} - (m_{\text{T,S}} \delta^{34}\text{S}_{\text{T}})_{\text{initial}} \quad (19)$$

and the subscript T denotes total sulfur (sulfide plus sulfate). In this example, the isotope equation is as follows:

$$\Delta^{34}\text{S} = \alpha_{\text{gyp}} \delta^{34}\text{S}_{\text{gyp}} + 2\alpha_{\text{pyrite}} \delta^{34}\text{S}_{\text{pyrite}} \quad (20)$$

The isotopic composition of dissolved sulfur, $\delta^{34}\text{S}_{\text{T}}$, in the final water is given by

$$\delta^{34}\text{S}_T = \frac{m_{\text{T},\text{SO}_4^{2-}} \delta^{34}\text{S}_{\text{SO}_4^{2-}} + m_{\text{T},\text{H}_2\text{S}} \delta^{34}\text{S}_{\text{H}_2\text{S}}}{S_T} \quad (21)$$

Using the isotopic composition and total concentrations of sulfate and sulfide in the final water (table 8), the calculated $\delta^{34}\text{S}_T$ is 23.673‰. Because dissolved sulfides are not present in the initial water, $\delta^{34}\text{S}_T$ for this water is that of sulfate alone (14‰). Using these values of $\delta^{34}\text{S}_T$ and the total concentrations of sulfur in the final and initial waters (1.649 and 0.025, respectively), $\Delta^{34}\text{S}$ from equation 19 is 38.687. Using a $\delta^{34}\text{S}$ value of +22‰ for dissolving gypsum (Rightmire and others, 1974) and -32.9‰ for precipitating pyrite (table 8), the linear sulfur isotope equation (equation 20) is

$$22.0\alpha_{\text{gyp}} - 65.8\alpha_{\text{pyrite}} = 38.687 \quad (22)$$

Equations 12 to 17 and 22 are linear and may be solved simultaneously, using BALANCE, to yield values for the seven unknowns, α_p .

Table 9 lists the card deck to solve the problem. Card 1 is the title card. Cards 2-8 define the delta values (final - initial) for the elements, redox state, RS, and sulfur isotope, DS. Card 9 is blank. Cards 10-16 define the stoichiometry, redox state, and sulfur isotopic data for the phases. Card 17 is blank.

Table 10 gives the results computed by BALANCE, indicating

$$\alpha_{\text{calcite}} = -1.842, \alpha_{\text{dolomite}} = 0.963, \alpha_{\text{gypsum}} = 1.678, \alpha_{\text{CH}_2\text{O}} = 0.171, \\ \alpha_{\text{CO}_2} = 0.535, \alpha_{\text{FeOOH}} = 0.027, \text{ and } \alpha_{\text{pyrite}} = -0.027. \text{ This}$$

particular choice of phases gives the net reaction between initial and final water as follows:

Initial water + 1.678 gypsum + 0.963 dolomite +

0.171 CH₂O + 0.535 CO₂ + 0.027 FeOOH →

Final water + 1.842 calcite + 0.027 pyrite. (23)

Table 9.-Card images of input data set for example 3

```

CARD #                                COLUMN
      1 0      2 0      3 0      4 0      5 0      6 0      7 0      8 0
+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '
1  EXAMPLE #3:  REDOX REACTIONS WITH LINEAR ISOTOPE BALANCE (TYPE 2.A INPUT)
2  CA      0.799
3  MG      0.963
4  S       1.624
5  C       0.790
6  FE      0.0
7  RS     12.624
8  DS     38.687
9
10 DOLOMITE  CA 1.000  MG 1.000  C  2.000  RS 8.000
11 CALCITE   CA 1.000  MG 0.000  C  1.000  RS 4.000
12 CO2 GAS   C  1.000  RS 4.000
13 GYPSUM    CA 1.000  S  1.000  RS 6.000  DS 22.000
14 "CH2O"    C  1.000  RS 0.000
15 GOETHITE  FE 1.000  RS 3.000
16 PYRITE    FE 1.000  S  2.000  RS 0.000  DS -65.800
17
+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '+++++++ '
      1 0      2 0      3 0      4 0      5 0      6 0      7 0      8 0

```


Table 10.-Printout listing results for example 3

DELTA		DOLOMITE	CALCITE	CO2 GAS	GYPSUM	"CH2O"	GOETHITE	PYRITE
0.799	CA	1.000	1.000	0.0	1.000	0.0	0.0	0.0
0.963	MG	1.000	0.0	0.0	0.0	0.0	0.0	0.0
1.624	S	0.0	0.0	0.0	1.000	0.0	0.0	2.000
0.790	C	2.000	1.000	1.000	0.0	1.000	0.0	0.0
0.0	FE	0.0	0.0	0.0	0.0	0.0	1.000	1.000
12.624	RS	8.000	4.000	4.000	6.000	0.0	3.000	0.0
38.687	DS	0.0	0.0	0.0	22.000	0.0	0.0	-65.800

DELTA PHASES

DOLOMITE	0.9630
CALCITE	-1.8419
CO2 GAS	0.5348
GYPSUM	1.6779
"CH2O"	0.1711
GOETHITE	0.0269
PYRITE	-0.0269

HOW TO RUN BALANCE ON THE USGS AMDAHL COMPUTER

In order to run BALANCE on the USGS Amdahl 470V/7 computer the first card of the job must be a legitimate JOB card as defined in the Computer Center Division's user's manual.

```
//AAllyyyxx JOB (....),'user name',CLASS=x
```

The following Job Control Language (JCL) statements will execute the program BALANCE:

```
// EXEC FORTRUN,PROG=BALANCE,ULIB='BFJONES.PGMLIB'
```

Insert input data deck here

```
//
```

Attachment A contains a listing of the Fortran source code for BALANCE. This code is stored in a catalogued partitioned data set named BFJONES.CARDS. The member name is BALANCE. Chapter two of the USGS Computer User's manual gives the JCL necessary to obtain listings and card decks for a partitioned data set.

The cards for the test problems in this report are stored in a card image file named PARK.BALANCE.TEST. This is a catalogued sequential data set and can be listed or punched using the JCL from the user's manual. By using the following JCL statements it is possible to run the test cases directly from the disk, without making a deck of the test cases. The cards for the run stream are:

```
// EXEC FORTRUN,PROG=BALANCE,ULIB='BFJONES.PGMLIB'  
//SYSIN DD DSN=PARK.BALANCE.TEST,DISP=SHR  
//
```

All jobs should end with // in the first two columns of the last card.

REFERENCES

- Back, William, and Hanshaw, B. B., 1970, Comparison of chemical hydrology of the carbonate peninsulas of Florida and Yucatan: *Journal of Hydrology*, v. 10, p. 330-368.
- Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, PHREEQE - a computer program for geochemical calculations: U.S. Geological Survey Water-Resources Investigations 80-96, 210 p.
- Plummer, L. N., Parkhurst, D. L., and Thorstenson, D.C., 1982, Development of reaction models for ground-water systems: *Geochimica et Cosmochimica Acta* (in press).
- Rightmire, C. T., Pearson, F. J., Jr., Back, William, Rye, R. O., and Hanshaw, B. B., 1974, Distribution of sulfur isotopes of sulfates in ground waters from the principle artesian aquifer of Florida and the Edwards Aquifer of Texas, United States of America, in isotope techniques in ground-water hydrology, 2. vol. II: International Atomic Energy Association, Vienna, p. 191-207.
- Rye, R. O., Back, William, Hanshaw, B. B., Rightmire, C. T., and Pearson, F. J., Jr., 1981, The origin and isotopic composition of dissolved sulfide in groundwater from carbonate aquifers in Florida and Texas: *Geochimica et Cosmochimica Acta*, v. 45, p. 1941-1950.

Attachment A: Program listing of BALANCE

PROGRAM BALANCE

THIS PROGRAM CALCULATES THE MASS TRANSFER OF AN INPUT SET OF PHASES, NECESSARY TO PRODUCE AN OBSERVED FINAL SOLUTION OR OBSERVED CHANGES IN CONCENTRATION.

INPUT:

- 1 TITLE (20A4)
- 2 SOLUTION INPUT (A2,F8.3,2F10.3)
ONE CARD FOR EACH ELEMENT CONSIDERED. ONLY ONE OF THE FOLLOWING THREE TYPES OF INPUT MAY BE USED FOR A SINGLE SIMULATION.
 - 2.A. ELEMENT NAME, DELTA ELEMENT CONCENTRATION.
 - 2.B. ELEMENT NAME, FINAL SOLUTION CONCENTRATION, INITIAL SOLUTION CONCENTRATION.
 - 2.C. ELEMENT NAME, FINAL SOLUTION CONCENTRATION, INITIAL SOLUTION CONCENTRATION, ADDITIONAL AQUEOUS PHASE CONCENTRATION.
- 3 BLANK CARD ENDS SOLUTION INPUT.
- 4 PHASE INPUT
CARD 4.A. IS REQUIRED FOR EACH PHASE. CARD 4.B. IS USED FOR ANY PHASE WHICH CONTAINS MORE THAN 7 ELEMENTS. MFLAG MUST BE EQUAL TO 1 TO USE CARD 4.B. FOR A PARTICULAR PHASE.
 - 4.A. PHASE NAME, MFLAG, COMPOSITION (ELEMENT NAME, COEFFICIENT IN PHASE). (A8,1X,11,7(A2,F8.3))
 - 4.B. COMPOSITION (ELEMENT NAME, COEFFICIENT IN PHASE). (8(A ,F .
USE CARD 4.B. ONLY IF PHASE CONTAINS MORE THAN 7 ELEMENTS AND MFLAG=1 IN PREVIOUS CARD.
- 5 BLANK CARD ENDS SOLUTION INPUT.

THE NUMBER OF ELEMENT CARDS MUST EQUAL THE NUMBER OF PHASES UNLESS TYPE 2.C INPUT IS USED. IN THAT CASE THE NUMBER OF PHASES PLUS ONE (THE OTHER AQUEOUS PHASE) MUST EQUAL THE NUMBER OF ELEMENTS.

INPUT FOR MORE SIMULATIONS MAY FOLLOW. SIMPLY REPEAT THE INPUT PROCESS.

D.PARKHURST, N.PLUMMER, AND D.THORSTENSON
REVISED MARCH, 1982

REAL * 8 TNAME, PELT(20,15), BLANK	1010
REAL * 8 ENAME(20), HEAD, DELTA1, DINIT1, DINIT2, DMIX, FINAL	1020
REAL * 8 DBLANK	1030
REAL * 8 PNAME(20)	1040
DIMENSION EDELTA(20), PCOEF(20,15), TITLE(20)	1050
DIMENSION A(20,20), DELTA(20), SINIT(20), SFINAL(20), SMIX(20)	1060
DATA BLANK/' '/, DBLANK/' '/, DELTA1/'DELTA'/, DINIT1/'INIT1'	1070
1/, DINIT2/'INIT2'/, DMIX/'MIX'/, FINAL/'FINAL'/	1080

30	CONTINUE	1090
C		1100
C	INPUT TITLE	1110
C		1120
	READ(5,15,END=1000) (TITLE(I),I=1,20)	1130
15	FORMAT(20A4)	1140
	PRINT 25,(TITLE(I),I=1,20)	1150
25	FORMAT(1H1,///1X,20A4///)	1160
C		1170
C	BEGIN INPUT WITH ELEMENTS FOR MASS BALANCE EQUATIONS	1180
C		1190
	I=0	1200
	ISOLN=0	1210
	IMIX=0	1220
20	CONTINUE	1230
	I=I+1	1240
	READ (5,10,END=1000) ENAME(I),SFINAL(I),SINIT(I),SMIX(I)	1250
10	FORMAT(A2,F8.3,2F10.3)	1260
	IF (SINIT(I).GT.0.0) ISOLN=1	1270
	IF(SMIX(I).GT.0) IMIX=1	1280
	EDELTA(I)=SFINAL(I)-SINIT(I)	1290
	IF(ENAME(I).NE.BLANK) GO TO 20	1300
	NELTS=I-1	1310
	NEQ=NELTS+IMIX	1320
C		1330
C		1340
C	ZERO ARRAYS PELT AND A	1350
C		1360
	DO 35 J=1,20	1370
	DO 35 I=1,15	1380
	PELT(J,I)=BLANK	1390
35	CONTINUE	1400
	DO 200 I=1,20	1410
	DO 200 J=1,20	1420
	A(I,J)=0.0	1430
200	CONTINUE	1440
C		1450
C	ARRANGE ARRAY FOR MIXING IF IMIX=1	1460
C		1470
	HEAD=DELTA1	1480
	IF (IMIX.EQ.0) GO TO 220	1490
	IF (ISOLN.GT.0) GO TO 230	1500
	PRINT 250	1510
250	FORMAT(1X,70('*')/1X,'A MIXING SOLUTION WAS ENTERED BUT NO',	1520
1	' INITIAL SOLUTION WAS ENTERED.')	1530
	STOP	1540
C		1550
230	CONTINUE	1560
	PNAME(1)=DINIT1	1570
	PNAME(2)=DINIT2	1580

HEAD=FINAL	1590
ENAME(NEQ)=DMIX	1600
EDELTA(NEQ)=1.0	1610
A(NEQ,1)=1.0	1620
A(NEQ,2)=1.0	1630
DO 240 I=1,NELTS	1640
A(I,1)=SINIT(I)	1650
A(I,2)=SMIX(I)	1660
EDELTA(I)=SFINAL(I)	1670
PELT(I,1)=ENAME(I)	1680
PELT(I,2)=ENAME(I)	1690
240 CONTINUE	1700
C	1710
C INPUT PHASE DATA	1720
C	1730
220 CONTINUE	1740
I=2*IMIX	1750
40 CONTINUE	1760
I=I+1	1770
READ 50,PNAME(I),(PELT(I,J),PCOEF(I,J),J=1,7)	1780
50 FORMAT(A8,2X,7(A2,F8.3))	1790
IF(PNAME(I).NE.DBLANK) GO TO 40	1800
NMINS=I-1	1810
IF(NMINS-IMIX.EQ.NELTS) GO TO 60	1820
PRINT 70,NMINS,NELTS	1830
70 FORMAT(1X,100('*'))//1X,'NUMBER OF PHASES DOES NOT MATCH NUMBER OF	1840
1EQUATIONS',2I4)	1850
STOP	1860
C	1870
C PUT COEFFICIENTS INTO ARRAY A	1880
C	1890
60 CONTINUE	1900
J1=2*IMIX+1	1910
DO 80 I=1,NEQ	1920
TNAME=ENAME(I)	1930
DO 90 J=J1,NMINS	1940
DO 160 K=1,15	1950
IF(PELT(J,K).NE.TNAME) GO TO 160	1960
A(I,J)=PCOEF(J,K)	1970
160 CONTINUE	1980
90 CONTINUE	1990
A(I,NEQ+1)=EDELTA(I)	2000
80 CONTINUE	2010
C	2020
C PRINT OUT ARRAY WHICH IS TO BE SOLVED	2030
C	2040
PRINT 100,HEAD,(PNAME(I),I=1,NMINS)	2050
100 FORMAT(4X,A5,10X,11A10)	2060
PRINT 110	2070
110 FORMAT(1X)	2080

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