

THE PHASE RULE AS APPLIED TO COMPLEX AQUEOUS EQUILIBRIA

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ABSTRACT

Stability diagrams such as Pourbaix diagrams are useful tools to the hydrometallurgist looking for a possible leaching window. However, ores, concentrates, industrial and domestic wastes are multi-phase complex systems and thus the representation of the several equilibria occurring inside the pulp could be cumbersome. In this case solving the equations provided by the related equilibria-mass balance constraints could be an alternative approach. The Phase Rule - besides its physical meaning - provides the degrees of freedom, i.e., the number of variables which should be set or known in order to obtain a mathematically sound set of equations. Its correct application requires all the independent reactions and special constraints to be known. Although an easy task and a simple problem, it could prove to be problematic when dealing with complex systems. An algorithm - relying on matrix algebra - has been proposed which, applied to the case of a system involving neutral and charged species, results on the proper independent reactions and special constraints. These could then be used in conjunction with a stable technique [1] - such as arithmetic-geometric equality - for solving the resulting non-linear equations. Some examples are herein reviewed.

Key words: Phase rule, Algorithm, Solubility, Independent reactions.

INTRODUCTION

Like many others concepts in Thermodynamics, the Phase Rule is both simple and powerful, but its judicious application requires skill and a clear understanding of the terms involved. Its usual statement reads:

$$F = C - P + 2 \quad (1)$$

where:

F = number of degrees of freedom

P = number of phases

C = number of components.

and its importance to the study of systems at equilibria can be assessed if one recalls that F, the so-called degrees of freedom, is meant to indicate the number of thermodynamic variables, among temperature, pressure and composition of the phases (or more precisely activities values) involved, which should be provided in order to completely describe the thermodynamic state of the system. Thus, once F variables are specified and/or measured, all the remaining variables can be obtained from equations of state and/or thermodynamic relationships. Although the meaning of P, the number of phases, seems clear, sometimes the proper value of C eludes a careless inspection. As put by Denbigh [2]: "the number of components, in the sense of the phase rule, ... is in fact the minimum number of substances which must be available in the laboratory in order to prepare any arbitrary equilibrium mixture of the system". Things are further complicated when special relationships between the thermodynamic variables, not included in the phase rule formal derivation, arise. An algorithm is proposed, which applied to the case of a system involving neutral and charged species results in the proper number of components and the independent reactions between the species.

PHASE RULE DERIVATION

In order to set up the algorithm, we first recall that in an algebraic sense a system of m unknowns and n independent equations (no one can be recast as a combination of the others) there are $m-n$ actually independent variables, i.e. , $m-n$ degrees of freedom. Thus the phase rule can be seen as the result of the application of this principle:

[degrees of freedom] equals [number of unknowns, i.e. temperature, pressure and composition of each phase] minus [number of independent equations between the unknowns, i.e., thermal equilibrium condition, mechanical equilibrium condition, distribution of species equilibrium, chemical equilibrium condition] (2)

and

$$F = (S - R) - P + 2 \quad (3)$$

Here S is the number of chemical species present in the system and R is the number of chemical equilibria between them. A chemical species means any substance (element, compound, ion) detected and/or deemed to be important. This introduces a degree of arbitrariness and a trade-off between simplicity (small number of species, simplified calculations) and complexity (large number of species, high level of details, demanding calculations) should be sought. Thus, for a reactive system $C = S - R$, this relationship can be used as the basis of an algorithm which results in the number of components, the number of independent reactions and the independent reactions themselves.

THE EXPANDED ATOM MATRIX

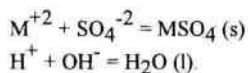
Once one has decided which are the species present at equilibrium, a matrix [3] can be formed by determining how many "basic structural units" are required to create each species. Here "basic structural units" would mean atoms and, since charged species are present, electrons.

As an example, let us take into consideration a system resulting from the addition of n^0 moles of pure MSO_4 to 1000 grams of pure water and let us further assume that the species present at equilibrium are M^{+2} , SO_4^{-2} , H^+ , OH^- , $\text{H}_2\text{O}(l)$, and $\text{MSO}_4(s)$ [4]. The first five species all make up a single phase and some undissolved sulfate remains as a separate phase. The expanded atom matrix (table I) would read:

Table I: Expanded atom matrix.

LINE #	SPECIES		STRUCTURAL UNITS					Reaction of formation
			M	O	S	H	e	
1	EQUILIBRIUM	M ⁺²	1				-2	M = M ⁺² + 2 e
2		SO ₄ ⁻²		4	1		2	S + 4 O + 2 e = SO ₄ ⁻²
3		H ⁺				1	-1	H = H ⁺ + e
4		H ₂ O(l)		1		2		2 H + O = H ₂ O
5		MSO ₄ (s)	1	4	1			M + S + 4 O = MSO ₄
6		OH ⁻		1		1	1	O + H + e = OH ⁻
	BEGINNING	H ₂ O(l)		1		2		
		MSO ₄ (s)	1	4	1			

where we choose to write two matrices, the upper one corresponding to the equilibrium condition and, separated by a double line, the lower matrix representing conditions at the very moment of mixing H₂O and MSO₄. For sake of simplicity we assume that "pure water" implies in the absence of H⁺ and OH⁻ ions. For this simplified system, it is apparent that two independent reactions between the various species are:



Also, if L_i denotes the i -eseme line of the matrix, the before-mentioned equilibria imply, respectively,

$$(1) \times L_1 + (1) \times L_2 = (1) \times L_5 \quad (4)$$

$$(1) \times L_3 + (1) \times L_6 = (1) \times L_4 \quad (5)$$

i.e., as far as matrix algebra is concerned, if one line can be written as a linear combination of others, that would indicate a reaction between the species. Thus, any algorithm resulting in the number of dependent lines of the expanded atom matrix would, in turn, indicate the number of independent reactions [3].

A Gauss-Jordan-like algorithm is proposed. Through this algorithm linear combinations of lines are employed in order to replace the numerical values below the a_{ij} "diagonal" by zeroes [5]. Eventually, a certain number of lines will be reduced to zero, exposing the dependent ones. The same procedure applied to column "Species" will display the corresponding independent reactions. For example, the expanded atom matrix (table II):

Table II.: expanded atom matrix for equilibrium conditions.

M^{+2}	1				-2
SO_4^{-2}		4	1		2
H^+				1	-1
$H_2O(l)$		1		2	
$MSO_4(s)$	1	4	1		
OH^-		1		1	1

upon which the following operations are applied:

$-1 \times L_5 + L_1 \implies L_5$	a ₁₁ pivot
$-4 \times L_4 + L_2 \implies L_4$	a ₂₂ pivot
$L_5 + L_2 \implies L_5$	a ₂₂ pivot
$-4 \times L_6 + L_2 \implies L_6$	a ₂₂ pivot
interchange L_5 and L_6	an all zero line was found at L_5
interchange L_3 and L_5	a ₃₃ pivot was found equal to zero
$-1 \times L_4 + L_3 \implies L_4$	a ₃₃ pivot
$-4 \times L_5 + L_4 \implies L_5$	a ₄₄ pivot

can be recast as table III.

Table III. Expanded atom matrix after application of Gauss-Jordan method.

M^{+2}	1				-2
SO_4^{-2}		4	1		2
$SO_4^{-2} - 4 OH^-$			1	-4	-2
$4 H_2O - 4 OH^-$				4	-4
$4 H_2O - 4 OH^- - 4 H^+$					
$M^{+2} + SO_4^{-2} - MSO_4$					

As can be seen, L_5 and L_6 have been reduced to "all zero lines", corresponding to two independent reactions:



and then $R = 2$, $r(\text{rank of the matrix}) = S - R = C = 4$.

Although in this case the results were apparent from the beginning, it seems that this procedure would be very useful when dealing with more complex systems.

STRUCTURAL UNITS BALANCE CLOSURE

Since all the species present at equilibrium (M^{+2} , $MSO_4(s)$, SO_4^{-2} , $H_2O(l)$, H^+ , OH^-) and also the species from which the system is formed (H_2O , MSO_4) can be built from the various structural units, equations stating the conservation of each structural unit can be written. In the following n_i and m_j denote number of moles of i and molality of j (as for simplicity, the mass of water was taken as being equal to 1000 grams, then molality and number of moles will be numerically equal). Thus (refer to Table I for the stoichiometric coefficients):

a) conservation of M

$$1 \cdot n^0 = 1 \cdot n_{MSO_4} + 1 \cdot m_{M^{+2}} \quad (6)$$

b) conservation of O

$$1 \cdot 1000 / M_{H_2O} + 4 \cdot n^0 = 1 \cdot m_{OH^-} + 4 \cdot n_{MSO_4} + 1 \cdot n_{H_2O} + 4 \cdot m_{SO_4^{2-}} \quad (7)$$

c) conservation of S

$$1 \cdot n^0 = 1 \cdot n_{MSO_4} + 1 \cdot m_{SO_4^{2-}} \quad (8)$$

d) conservation of H

$$2 \cdot 000 / M_{H_2O} = 1 \cdot m_{OH^-} + 2 \cdot n_{H_2O} + 1 \cdot m_{H^+} \quad (9)$$

e) conservation of electrons or the electroneutrality condition

$$0 = 1 \cdot m_{OH^-} + 2 \cdot m_{SO_4^{2-}} + 1 \cdot m_{H^+} - 2 \cdot m_{M^{+2}} \quad (10)$$

Some comments should be made regarding these balances. Not all five balances will be independent. As a matter of fact it can be easily shown that:

$$\text{balance (e)} = 2 \times \text{balance (b)} - \text{balance (d)} - 2 \times \text{balance (a)} - 6 \times \text{balance (c)}$$

Whenever possible balances (b) and (d) should not be used directly because they involve mathematical operations with terms of significantly different orders of magnitude, thus increasing the chances of round-off errors. Since the sole source of M^{+2} and SO_4^{-2} ions is the decomposition of MSO_4 , according to $MSO_4 = M^{+2} + SO_4^{-2}$, then

$$m_{SO_4^{2-}} = m_{M^{+2}} \quad (11)$$

This restriction can be retrieved by subtracting balance (a) from (c).

In addition, H^+ and OH^- come from H_2O decomposition only, $H_2O = H^+ + OH^-$, which results in

$$m_{H^+} = m_{OH^-} \quad (12)$$

or, alternately, by combining balance (a), balance (c) and balance (e).

Thus, generally speaking, special relationships between activities of species, such as equations (11) and (12), can be seen as the result of manipulations applied to the structural balance closures.

DEGREES OF FREEDOM ACCORDING TO GIBBS' PHASE RULE

From $F = C - P + 2 = (S - R) - P + 2$ and with

$$S = 6 (M^{+2}, MSO_4(s), SO_4^{-2}, H_2O(l), H^+, OH^-)$$

$$R = 2 (H_2O = OH^- + H^+; M^{+2} + SO_4^{-2} = MSO_4)$$

$$P = 2 (\text{aqueous liquor}; MSO_4(s))$$

result four degrees of freedom, meaning that four thermodynamic variables should be specified (or measured) in order to make possible the calculation of all remaining ones. However, one should recall that according to equation (2) any independent equation between the thermodynamic variables should decrease the number of degrees of freedom by one. Also, in deriving equation (3) only thermal, pressure, distribution and chemical equilibrium restrictions have been taken into consideration. Thus equation (11) and equation (12) which are special constraints (additional relationships), and have not been contemplated, effectively decrease the number of degrees of freedom by two, i.e., the remaining degrees of freedom equals two. Then, by specifying a value for temperature and pressure (1 atm), a set of four unknowns: $(m_{OH^-}, m_{SO_4^{2-}}, m_{H^+}, m_{M^{2+}})$ and four equations results:

$$m_{SO_4^{2-}} = m_{M^{2+}} \quad (11)$$

$$m_{H^+} = m_{OH^-} \quad (12)$$

$$H_2O(l) = H^+ + OH^- \quad K_T^1 = (\gamma_{H^+} \cdot m_{H^+}) \cdot (\gamma_{OH^-} \cdot m_{OH^-}) \quad (13)$$

$$MSO_4(s) = M^{2+} + SO_4^{2-} \quad K_T^2 = (\gamma_{M^{2+}} \cdot m_{M^{2+}}) \cdot (\gamma_{SO_4^{2-}} \cdot m_{SO_4^{2-}}) \quad (14)$$

which can be solved numerically (activities of $H_2O(l)$ and $MSO_4(s)$ have been taken as equal to one).

THE ADDITIONAL CONSTRAINTS

It has been shown that mass balance closures can yield additional constraints. Thus, a procedure other than trial and error or simple inspection should be made available to uncover them. At least in principle, one could think of combining the mass balance equations in order to eliminate unwanted species. Let us take the MSO_4/H_2O example, equations (6) to (9). Each equation can be multiplied by a numerical coefficient α_i ($i=1$ to p , where p is the number of elements), i.e.:

$$\begin{aligned}
 1 \cdot n^0 &= 1 \cdot n_{MSO_4} + 1 \cdot m_{M^{2+}} && \times \alpha_1 \\
 1 \cdot 1000 / M_{H_2O} + 4 \cdot n^0 &= 1 \cdot m_{OH^-} + 4 \cdot n_{MSO_4} + 1 \cdot n_{H_2O} + 4 \cdot m_{SO_4^{2-}} && \times \alpha_2 \\
 1 \cdot n^0 &= 1 \cdot n_{MSO_4} + 1 \cdot m_{SO_4^{2-}} && \times \alpha_3 \\
 2 \cdot 1000 / M_{H_2O} &= 1 \cdot m_{OH^-} + 2 \cdot n_{H_2O} + 1 \cdot m_{H^+} && \times \alpha_4
 \end{aligned}$$

Having done that the resulting equations can be added together and in the final equation only m_{OH^-} , $m_{SO_4^{2-}}$, m_{H^+} , $m_{M^{2+}}$ (the unknowns) might remain, i.e., the coefficients corresponding to the "unwanted" species, n_{H_2O} , n_{MSO_4} , n^0 , $1000 / M_{H_2O}$ should be equal to zero. Then, a matrix on α_i can be defined as in table IV.

Table IV. α matrix on MSO_4/H_2O system.

α_1	α_2	α_3	α_4
1	4	1	0
0	1	0	2
1	4	1	0
0	1	0	2

By applying the same Gauss-Jordan-like procedure depicted before, one can find this matrix rank. When r is equal to p , the determinant of the square matrix is different from zero, and then there will be a solution which corresponds to $\alpha_i = \text{zero}/\text{determinant} = \text{zero}$, a trivial one which is of no interest. This case will be discussed later. In general $r < p$, meaning that the problem is un-determined and $p-r$ multipliers can be arbitrarily chosen, the remaining ones being calculated from them. Also, there will be $p-r$ independent relationships among the unknowns. In the example, $r = 2$ and $p = 4$, so there are two independent equations on the α_i matrix and two independent relationships among m_{OH^-} , $m_{SO_4^{2-}}$, m_{H^+} , $m_{M^{2+}}$. Thus, choosing $\alpha_4 = 0$, $\alpha_3 = 1$, then $\alpha_2 = 0$, $\alpha_1 = -1$ and so equation (11) is retrieved. On the other hand for $\alpha_4 = 1$, $\alpha_3 = 8$, then $\alpha_2 = -2$, $\alpha_1 = 1$ and equation (12) results. Any other arbitrary choice of α 's would produce equations which are linear combinations of the previous ones. Of course, the electro-neutrality condition is linearly dependent on (11) and (12).

Let us now consider a system formed from 1000 g of H_2O and n^0 moles of BeO , where the species $Be(OH)_2(s)$, Be^{+2} , Be_2O^{+2} , H^+ , OH^- , $H_2O(l)$ are present in equilibrium [4]. Mass balances of Oxygen, Hydrogen, Beryllium are:

$$n^0 + 1 \cdot 1000 / M_{H_2O} = 2 \cdot n_{Be(OH)_2} + 1 \cdot m_{Be_2O_3} + 1 \cdot n_{H_2O} + 1 \cdot m_{OH^-} \quad (15)$$

$$2 \cdot 1000 / M_{H_2O} = 2 \cdot n_{Be(OH)_2} + 2 \cdot n_{H_2O} + 1 \cdot m_{OH^-} + 1 \cdot m_{H^+} \quad (16)$$

$$1 \cdot n^0 = 1 \cdot n_{Be(OH)_2} + 2 \cdot m_{Be_2O_3} \quad (17)$$

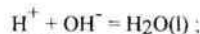
and the resulting α_i , $i=1$ to p , matrix obtained by determining that the coefficients of n^0 , $1000 / M_{H_2O}$, $n_{Be(OH)_2}$, n_{H_2O} are equal to zero is on table V.

Table V. α matrix on Be/H₂O system.

	α_1	α_2	α_3
	1	0	1
	1	2	0
	2	2	1
	1	2	0

As before, r (equal to two) is smaller than p (equal to 3) and then again the system remains undetermined. Here one multiplier can be set. For example choosing α_1 equal to 1 results $\alpha_3 = -1$, $\alpha_2 = -.5$ and the electro-neutrality condition is retrieved.

Finally, let us look at a couple of wrongly stated problems. First of all, consider the case where the species at equilibrium, Cr^{+3} , $Cr(OH)_3(s)$, $Cr_2O_7^{-2}$, H^+ , OH^- , $H_2O(l)$ [4] have, supposedly, been obtained from 1000 g of H_2O and n^0 moles of Cr_2O_3 . It is apparent that this proposition is not a feasible one because there is not a reduction process which balances the oxidation of chromium, from Cr^{+2} (in Cr_2O_3) to Cr^{+6} (in $Cr_2O_7^{-2}$). The rank of the expanded atom matrix is found to be equal to four, and then there should be two independent reactions, say



On the other hand the mass balances reads:

$$2 \cdot 1000 / M_{H_2O} = 3 \cdot n_{Cr(OH)_3} + 2 \cdot n_{H_2O} + 1 \cdot m_{OH^-} + 1 \cdot m_{H^+} \quad (18)$$

$$1 \cdot 1000 / M_{H_2O} + 3 \cdot n^0 = 3 \cdot n_{Cr(OH)_3} + 1 \cdot n_{H_2O} + 1 \cdot m_{OH^-} + 7 \cdot m_{Cr_2O_7^{-2}} \quad (19)$$

$$2 \cdot n^0 = 1 \cdot n_{Cr(OH)_3} + 1 \cdot m_{Cr_2O_3} + 2 \cdot m_{Cr_2O_7^{-2}} \quad (20)$$

which defines a α_i , $i=1$ to 3, matrix (table VI):

Table VI. α matrix on $\text{Cr}^{+3}/\text{Cr}_2\text{O}_7^{-2}/\text{H}_2\text{O}$ system.

α_1	α_2	α_3
2	1	0
0	3	2
2	1	0
3	3	1

of rank equal to 2. Then there will be $p-r = 3 - 2 = 1$ independent relationship among $m_{\text{Cr}^{+3}}$, $m_{\text{Cr}_2\text{O}_7^{-2}}$, m_{OH^-} , m_{H^+} , which can be found by setting arbitrarily one of the α 's. For example, if $\alpha_2 = -2$ results $\alpha_1 = 1$, $\alpha_3 = 3$ or, adding the equations together :

$$-m_{\text{OH}^-} + m_{\text{H}^+} - 8m_{\text{Cr}_2\text{O}_7^{-2}} + 3m_{\text{Cr}^{+3}} = 0 \quad (21)$$

Taking into consideration that the electro-neutrality condition should be met, one finds $m_{\text{Cr}_2\text{O}_7^{-2}}$ equal to zero, i.e., $\text{Cr}_2\text{O}_7^{-2}$ is not present at all.

A different conclusion would be reached when the species Cr^{+2} , $\text{Cr}(\text{OH})_2(\text{s})$, $\text{Cr}_2\text{O}_7^{-2}$, H^+ , OH^- , $\text{H}_2\text{O}(\text{l})$ are said to be obtained from mixing only 1000 g of H_2O and n^0 moles of Cr_2O_3 . The mass balances are:

$$2 \cdot 1000 / M_{\text{H}_2\text{O}} = 2 \cdot n_{\text{Cr}(\text{OH})_2} + 2 \cdot n_{\text{H}_2\text{O}} + 1 \cdot m_{\text{OH}^-} + 1 \cdot m_{\text{H}^+} \quad (22)$$

$$1 \cdot 1000 / M_{\text{H}_2\text{O}} + 3 \cdot n^0 = 2 \cdot n_{\text{Cr}(\text{OH})_2} + 1 \cdot n_{\text{H}_2\text{O}} + 1 \cdot m_{\text{OH}^-} + 7 \cdot m_{\text{Cr}_2\text{O}_7^{-2}} \quad (23)$$

$$2 \cdot n^0 = 1 \cdot n_{\text{Cr}(\text{OH})_2} + 1 \cdot m_{\text{Cr}^{+2}} + 2 \cdot m_{\text{Cr}_2\text{O}_7^{-2}} \quad (24)$$

and the α_i , $i=1$ to 3, matrix (table VII):

Table VII. α matrix on $\text{Cr}^{+2}/\text{Cr}_2\text{O}_7^{-2}/\text{H}_2\text{O}$ system.

α_1	α_2	α_3
2	1	0
0	3	2
2	1	0
2	2	1

with a rank equal to three. Thus, the determinant of the matrix is different of zero pointing to a trivial solution $\alpha_j = \text{zero/determinant}$ and implying that a relationship among $m_{Cr^{3+}}$, $m_{FeO^{2+}}$, n_{H^+} , m_{H^+} would not exist. Of course, this paradox (the electro-neutrality condition must prevail) is due to the fact that the problem, as posed, is not feasible.

CONCLUSIONS

The proposed algorithm allows the direct determination of the independent reactions in a hydrometallurgical system, and it makes apparent the mathematical relationships that govern the equilibria. Besides removing any ambiguities regarding the phase Rule its application results in a logical procedure that eliminates trial and error approaches which are very time demanding specially in complex systems.

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