

1996

Linear Algebra Used to Determine Independent Half-Cell Equations

D. H. Coleman

Ralph E. White

University of South Carolina - Columbia, white@cec.sc.edu

Follow this and additional works at: https://scholarcommons.sc.edu/eche_facpub

 Part of the [Chemical Engineering Commons](#)

Publication Info

Published in *Journal of the Electrochemical Society*, Volume 143, Issue 6, 1996, pages 1781-1783.

© The Electrochemical Society, Inc. 1996. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in Coleman, D.H., & White, R.E. (1996). Linear Algebra Used to Determine Independent Half-Cell Equations. *Journal of the Electrochemical Society*, 143(6): 1781-1783.

Publisher's Version: <http://dx.doi.org/10.1149/1.1836903>

This Article is brought to you by the Chemical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.

Linear Algebra Used to Determine Independent Half-Cell Equations

D. H. Coleman* and R. E. White**

Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA

ABSTRACT

A method is presented for determining a set of independent half-cell equations. The difference between half-cell equations and half-cell reactions is discussed. The method is applied to two electrochemical examples: electrodeposition/electro-oxidation of copper and electrochemical reduction and oxidation of nitrate and nitrite in a caustic solution.

Introduction

One method of determining an independent set of chemical equations has been referred to by Smith and Missen as chemical stoichiometry.¹⁻³ This method can be used to obtain a set of independent chemical equations given a list of species found in the system. If used for an electrochemical system, the method developed by Smith and Missen generates a set of overall cell equations. In an electrochemical system, however, it would be more useful if a set of half-cell equations could be generated directly. More recently, Alberty presented a method for calculating half-cell equations.⁴ His method, however, relies on knowing the half-cell equation before using chemical stoichiometry, in order to decide the number of electrons for each species in the matrix. In his examples, he showed the half-cell equations first, then showed that linear algebra could be used to derive these half-cell equations. In the species matrices, the number of electrons was determined either by knowing the half-cell equation prior to the calculations, or, alternatively, by keeping track of the relative number of electrons for each species present. For simple systems this is not a problem. In more complex systems, it would be easier if one did not have to balance the number of electrons explicitly. This can be accomplished by keeping track of the total number of electrons (rather than the relative number). A computer program can keep this information in a database for use in any system, given a list of the species present. A modified chemical stoichiometry method has been developed here that allows independent half-cell equations to be generated directly from a list of the species found in a solution. This process has been used to generate and verify a set of independent half-cell equations that have been used in other modeling work done in our research group.⁵

Half-Cell Equations Method

Chemical stoichiometry can be used to determine a set of independent half-cell equations for a closed system by treating the electrons of the half-cell reaction as another species. While redox equations can be determined by using a charge number constraint (see Ref. 2 for details) this charge number constraint does not give a set of half-cell chemical equations. However, keeping track of the total

number of electrons each species has does allow for half-cell equations.

A simple example of half-cell chemical equation determination is for the aqueous copper sulfate system. The species present are Cu, Cu⁺, Cu²⁺, and SO₄²⁻. These species and an electron, which is treated as a species here, appear as column vectors in the matrix **A**, as shown in Table I.

In keeping with the notation of Smith and Missen, the matrix in Table I is called a formula-vector matrix, **A**. The total number of species is *N*, and for the copper sulfate system, *N* = 5 (four chemical species plus *e*⁻). Note that there are only three true elements (Cu, S, O) but the electron is treated as though it is an element (and a species).

A set of independent equations is found by performing row operations on **A** to develop a new row reduced matrix **A**^{*}. This is easily done using symbolic math software, such as *Mathematica*.⁶ The **A**^{*} matrix for the copper sulfate system is shown in Table II. From **A**^{*}, the rank of the matrix **A** is read as the number of ones in the diagonal unit submatrix. The number of independent equations, *R*, is then *R* = *N* - Rank (**A**). For the copper sulfate system, *R* = 5 - 3 = 2.

The stoichiometric coefficients for each independent equation are read from the column vectors of **A**^{*} to the right of the unit submatrix. Each column represents the coefficients of the left-hand side of each equation. The species corresponding to each coefficient is read left to right from the species above the unit submatrix. The right-

Table I. **A** matrix for the CuSO₄ system.

	<i>e</i> ⁻	Cu ⁺⁺	SO ₄ ²⁻	Cu ⁺	Cu
<i>e</i> ⁻	1	27	50	28	29
Cu	0	1	0	1	1
S	0	0	1	0	0
O	0	0	4	0	0

Table II. **A**^{*} for the CuSO₄ system.

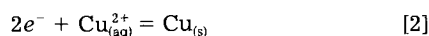
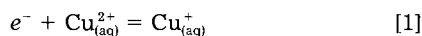
	<i>e</i> ⁻	Cu ⁺⁺	SO ₄ ²⁻	Cu ⁺	Cu
1	0	0	1	2	
0	1	0	1	1	
0	0	1	0	0	
0	0	0	0	0	

*Electrochemical Society Student Member.

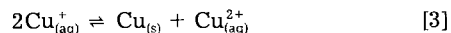
**Electrochemical Society Active Member

hand side of each equation corresponds to the species at the top of each column vector to the right of the unit sub-matrix, and has a coefficient of 1 (see Ref. 2 for further details).

The equations that can be written down directly from Table II for the copper sulfate system are



Equations 1 and 2 are two independent half-cell equations which can be written for the entire system. Note, however, that this does not give the mechanism of reaction. In fact there may be three different reactions occurring, the two electrode reactions above (Eq. 1 and 2) and a disproportionation reaction in the solution⁷



This equation is obtained from 2(Eq. 1) - Eq. 2. Two independent equations but three possible reactions, further illustrates the importance of a reaction mechanism for nonequilibrium studies. If the chemical stoichiometry alone were used to decide which equations were reactions and should be in a kinetic model, only two would be found for the copper sulfate system. At least three reactions should be in such a model of this system. Of course, one could assume that the disproportionation reaction was negligible, but this is an assumption made to simplify the analysis and not to reflect reality.

This illustrates one of the differences between chemical equations and chemical reactions. There may be reactions occurring that are not independent in the sense of equations (not linearly independent when written as Eq. 1-3 above) but they are independent reactions because they occur in a different location or by a different mechanism. A thermodynamic model of a system requires an independent set of equations (like Eq. 1 and 2 above), since where or how a reaction occurs is not important. Only the thermodynamic state of the system is important. In kinetic models, however, an independent set of reactions is needed. This may or may not correspond to an independent set of equations as written above, but always corresponds to an independent set of equations once location and mechanism of the reaction are taken into account in writing the equation. The equations for a kinetic model would not look the same as those above (Eq. 1-3) but rather would include kinetic information and, implicitly, the location of reaction. In the copper sulfate example, the system is the whole cell, but reactions are occurring in three separate locations (anode, cathode, and bulk). Thus, there are not two independent reactions for the system. Rather, there are five independent reactions for the system; two at each electrode and one in the bulk (assuming Eq. 1 and 2 occur at both the cathode and the anode and reaction 3 occurs in the bulk solution). Note that the reactions at the anode and cathode can be different reactions, because different materials are often used for the anode and the cathode.

Another illustration may help to clarify some of these points and also leads to another difference between chemical equations and chemical reactions. This method for half-cell equation calculation was used for the nitrate/nitrite system.⁵ The species formula-vector matrix, **A**, and row reduced matrix, **A***, appear in Tables III and IV, respectively. The method verifies that the half-cell equations below are an independent set of equations.

The resulting equations which can be written directly from Table IV by using the Smith and Missen method are

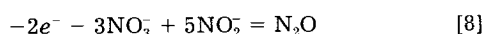
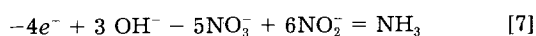
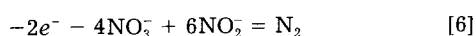
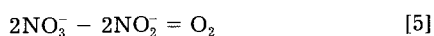
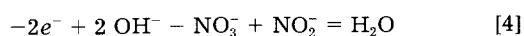
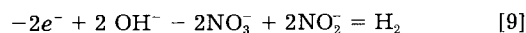


Table III. **A** for the nitrate/nitrite system.

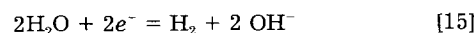
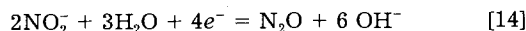
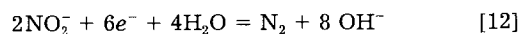
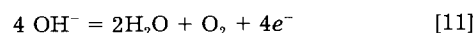
	e^-	OH^-	NO_3^-	NO_2^-	Na^+	H_2O	O_2	N_2	NH_3	N_2O	H_2
e^-	1	10	32	24	10	10	16	14	10	22	2
Na	0	0	0	0	1	0	0	0	0	0	0
O	0	1	3	2	0	1	2	0	0	1	0
H	0	1	0	0	0	2	0	0	3	0	2
N	0	0	1	1	0	0	0	2	1	2	0

Table IV. **A*** for the nitrate/nitrite system.

e^-	OH^-	NO_3^-	NO_2^-	Na^+	H_2O	O_2	N_2	NH_3	N_2O	H_2
1	0	0	0	0	-2	0	-2	-4	-2	-2
0	1	0	0	0	2	0	0	3	0	2
0	0	1	0	0	-1	2	-4	-5	-3	-2
0	0	0	1	0	1	-2	6	6	5	2
0	0	0	0	1	0	0	0	0	0	0



Solving Eq. 4 for NO_3^- and then substituting this into Eq. 5-9 yields upon rearrangement



Although this method does allow calculation of half-cell equations, it is not possible to differentiate between anodic and cathodic equations if all of the species in the whole cell are used. In fact, for the nitrate/nitrite system shown here, only six equations are independent but seven half-cell reactions have been described.⁵ Equation (or reaction) 10 actually occurs at both the cathode and the anode, thus giving seven half-cell reactions but only six half-cell equations. One could calculate the half-cell equations for each electrode by treating each half-cell separately and including in the calculations only those species found in each half-cell. This is only strictly valid when each half-cell can be treated as a closed system, where no species enter or leave the half-cell.

This example also illustrates that in addition to the number of independent chemical equations being different than the independent reactions, chemical equations can be written in a way that does not represent a reaction. For example, Eq. 9 is not thought to be the reaction which generates hydrogen, yet it is a valid equation. Equation 15 is much more likely to be a reaction that generates hydrogen.

In addition, no mention of homogeneous chemical reactions have been given for the nitrate/nitrite system, even though they could be occurring. If there were homogeneous chemical reactions occurring, they could be represented by a combination of the above equations (Eq. 10-15).

Chemical stoichiometry using linear algebra is useful for thermodynamic studies and for balancing equations, but a knowledge of the system of interest is still important for deciding which reactions are likely to occur (or which equations are likely to be reactions). The number of independent chemical equations gives the minimum number of equations that would need to be in a system model. However, this number does not necessarily represent the total number of chemical reactions due to location or mechanistic differences. The question may arise as to whether determining an independent set of equations is useful. The answer is yes, because many systems studied can be represented by the same independent set of equations as determined from linear algebra. Electrochemical models often neglect (at least as a first model) homogeneous

reactions. In this case, both the examples given in this article generated a complete set of equations that could be used in modeling the system. This may be especially useful in modeling a complex system that is not well understood. A further assumption used in such a model could be that reactions occur by one mechanism (in many systems this is the case).

In summary, an equation is a mathematical equality. It may or may not be a reaction. Whereas a reaction is a chemical process. A reaction can be represented by a chemical equation, but there are details in the reaction (e.g., location and mechanism) that are not always shown by a balanced chemical equation.

Linear algebra can be used to determine an independent set of chemical or electrochemical equations, but some knowledge of the system itself must be used in conjunction with this method to determine the proper equations to use as reactions in a model of the system.

Manuscript submitted June 15, 1995; revised manuscript received March 19, 1996.

The University of South Carolina assisted in meeting the publication costs of this article.

REFERENCES

1. W. R. Smith and R. W. Missen, *Chemical Engineering Education*, Winter, 26 (1979).
2. W. R. Smith and R. W. Missen, *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*, Wiley, New York (1982).
3. R. W. Missen and W. R. Smith, *J. Chem. Ed.*, **66**, 217 (1989).
4. R. A. Alberty, *This Journal*, **140**, 3488 (1993).
5. D. H. Coleman, R. E. White, and D. T. Hobbs, *ibid.*, **142**, 1152 (1995).
6. Wolfram Research, Inc., *Mathematica*, Version 2.2, Wolfram Research, Inc., Champaign, IL (1994).
7. J. S. Newman, *Electrochemical Systems*, 2nd ed., p. 190, Prentice-Hall, Englewood Cliffs, NJ (1991).

The High Temperature Phase Diagram of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ and Its Implications

Yuan Gao* and J. R. Dahn*

Department of Physics, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

ABSTRACT

Using thermal gravimetric analysis, we recently showed that there is a temperature dependent phase transition in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ which involves oxygen loss. The temperature of the phase transition, T_{ci} , depends linearly on x over the range from $x = 0$ to $x = 0.20$. Here we discuss the origin of the phase transition and show that it is caused by the disproportionation of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ into Li_2MnO_3 , oxygen, and $\text{Li}_{1+x'}\text{Mn}_{2-x'}\text{O}_4$ where $x' < x$. X-ray diffraction measurements of samples quenched from above T_{ci} show that this produces Li_2MnO_3 . Furthermore, the weight loss of the samples above T_{ci} can be accounted for by a simple model which describes the disproportionation reaction. Calculations of the rate of change of sample mass with temperature, dM/dT , agree well with the measured data. A phase diagram for the maximum attainable x in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ is presented as a function of temperature for samples heated in air. These results show that the optimum method for preparing materials with low specific surface area and large values of x is a two-step method. The first step involves heating materials with x about equal to zero to about 850 to 900°C to lower the surface area, and the second involves reacting this intermediate with additional lithium salt near 600°C, which avoids Li_2MnO_3 formation. Such materials with x near 0.15 show excellent capacity retention vs. cycle number in secondary lithium coin cells even at 55°C.

Introduction

Lithium-ion cells are the state-of-the-art power sources for consumer electronics. They are used in laptop computers, cellular phones, and camcorders. They have excellent cycle life (1000 cycles typically) and high energy density (120 Wh/kg typically), so they are being considered for electric vehicle applications as well. The current commercial products being marketed today use LiCoO_2 as the positive electrode material and a carbon or graphite as the negative electrode material. However cobalt is a relatively rare and expensive transition metal, and consequently manufacturers are searching for inexpensive replacements for LiCoO_2 .

One possible replacement for LiCoO_2 is LiMn_2O_4 . Mn is about 20 times less expensive than Co per unit weight. However, there are problems associated with the direct replacement of LiCoO_2 by LiMn_2O_4 . For example, it was initially difficult to prepare LiMn_2O_4 with long charge-discharge cycle life. Recently Thackeray and co-workers¹ showed that the cycle life of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ with $x = 0.1$ is significantly better than that of materials with $x = 0.0$ though the specific capacity is decreased. Similar results were also found by Tarascon *et al.*² Furthermore, the operating voltage of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ cells is higher than LiCoO_2 ,

so special electrolytes needed to be developed³ to obtain good cycling behavior.

Nevertheless, the preparation of high quality $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ is complicated. Tarascon and co-workers⁴ have shown using TGA experiments that $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ loses oxygen when heated and that oxygen deficient samples have inferior electrochemical properties. We have recently reported careful TGA studies⁵ of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ as a function of x and have identified a phase transition associated with oxygen loss whose temperature is linearly dependent on x . The temperature of this transition, T_{ci} , can be used to measure x , once a calibration curve has been determined. We also showed the effects of oxygen deficiencies in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ on its electrochemical behavior.⁶ Other workers have measured the TGA profile of LiMn_2O_4 as a function of oxygen partial pressure.⁷ However, the origin of the phase transition at T_{ci} , whose temperature depends on x , has not been identified in any of these prior works.

Here we show that the x -dependent phase transition arises from a disproportionation of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ into Li_2MnO_3 , oxygen, and $\text{Li}_{1+x'}\text{Mn}_{2-x'}\text{O}_4$ with $x' < x$. The transition is reversible, but only if samples are cooled through it very slowly. By considering the implications of the disproportionation reaction we have developed a two-step heating process to make pure single-phase $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ samples with low specific surface area and with x as large as 0.20. These materials show excellent charge-discharge cycling characteristics even at 55°C in lithium coin cells.

* Electrochemical Society Active Member.