Calculation Cover Sheet

Complete only applicable items.

2. Calculation Title MING Parameter Input: EMMA Model Redox Half Reaction Equation Delta G Corrections for pH			
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	Print Name	Signature	Date
7. Originator	Darren M. Jolley		7/22/98
8. Checker	Paul Domski		7/22/98
9. Lead Design Engineer	Jerry A. McNeish		7.23.98
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Originator: Darren M. Jolley

Checker: Paul Domski

Lead Discipline Engineer: Jerry A. McNeish

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1.0 Purpose

The purpose of this calculation is to provide appropriate input parameters for use in MING V 1.0 (CSCI 30018 V1.0). This calculation corrects the Grogan and McKinley (1990) values for ΔG so that the data will function in the MING model. The Grogan and McKinley (1990) ΔG data are presented for a pH of 12 whereas the MING model requires that the ΔG be reported at standard conditions (i.e. pH of 0).

2.0 Method

Any redox reaction can be written in the general form (Pankow, 1991):

for which a standard free energy of reaction (ΔG_r°) can be specified. The ΔG_r° can be derived from standard free energies of formation (ΔG_f°):

$$\Delta G_r^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$$

or from an equilibrium constant (K):

$$\Delta G_r^\circ = -RT \ln K$$

ΔG_f° values are defined for standard conditions which, for solutes, corresponds to unit activity. Grogan and McKinley (1990) in their modeling approach report ΔG_{act} 's for a pH of 12. The ΔG_{act} values are normalized by the number of electrons involved in the half reaction above ($\Delta G/a$). In order for the MING model to utilize this dataset in its calculations, the $\Delta G_{normalized}$ values must be corrected and reported at standard conditions (for purposes of this calculation pH = 0). The corrections have to be made by using the following relationships found in Grogan and McKinley (1990):

$$\Delta G_{act} = \Delta G_{normalized} * e^-$$

and

$$\Delta G_{cor} = \Delta G_{act} - b * 5.707 * pH$$

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Where $5.707 \text{ kJ mol}^{-1} = RT \ln 10$ at 25°C

3.0 Assumptions

There are no assumptions used in this calculation.

4.0 Use of Computer Software

The calculations were done using Microsoft Excel 97 on a Dell PowerEdge 2200 with dual Pentium II - 266 MHz chips, 128 MB of RAM, in a Windows NT 4.0 operating system

Excel is an appropriate application because in this data reduction calculation only simple mathematical expressions are needed to derive the final results

The only software routine found in the Microsoft Excel 97 package that was used in this calculation was the SUM function which included use of the (), *, /, +, and - operands.

5.0 Calculation

See Section 6.0

CRWMS M&O/Performance Assessment Operations Calculation

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6.0 Results

Half reaction [(DG act) = DG cor + b*RT*pH] RT ln 10 = 5.707	DG normalized	e-	DG act (ph=12)	b (moles of H+)	pH	DG cor
2e- + 2H+ + H2O2 = 2H2O	-101.7	2	-203.4	2	12	-340.368
3e- + 4H+ + NO2- = 2H2O + .5N2	-56.1	3	-168.3	4	12	-442.236
4e- + 4H+ + O2 = 2H2O	-50.1	4	-200.4	4	12	-474.336
5e- + 6H+ + NO3- = 3H2O + 0.5N2	-37.9	5	-189.5	6	12	-600.404
2e- + 2H+ + NO3- = H2O + NO2-	-10.6	2	-21.2	2	12	-158.168
8e- 9H+ + NO3- = 3H2O + NH3	-1.4	8	-11.2	9	12	-627.556
6e- + 7H+ + NO2- = 2H2O + NH3	1.8	6	10.8	7	12	-468.588
4e- + 4H+ + <HCHO> = H2O + CH4	29.1	4	116.4	4	12	-157.536
2e- + H+ + S = HS-	40.2	2	80.4	1	12	11.916
6e- + 7H+ + SO2 = 3H2O + HS-	44.5	6	267	7	12	-212.388
2e- + 2H+ + <HCOH> = <HCH2OH>	46.1	2	92.2	2	12	-44.768
8e- + 9H+ + SO42- = 4H2O + HS-	53	8	424	9	12	-192.356
8e- + 10H+ + CO32- = 3H2O + CH4	56.3	8	450.4	10	12	-234.44
2e+ 3H+ + Fe(OH)-3 = 3H2O + Fe	57.1	2	114.2	3	12	-91.252
6e- + 8H+ + SO42- = 4H2O + S	57.3	6	343.8	8	12	-204.072
6e- + 8H+ + CO32- = 3H2O + <CH2>	59.3	6	355.8	8	12	-192.072
8e- + 10H+ + 2SO42- = 5H2O + S2O32-	59.4	8	475.2	10	12	-209.64
8e- + 11H+ + 2CO32- = 4H2O + CH3COO-	61.4	8	491.2	11	12	-262.124
5e- + 7H+ + CO32- = 3H2O + <CH>	61.6	5	308	7	12	-171.388
14e- + 19H+ + 3CO32- = 7H2O + CH3CH2COO-	61.7	14	863.8	19	12	-437.396
6e- + 8H+ + CO32- = 3H2O + CH3CH2COO-	62.1	6	372.6	8	12	-175.272
e- + H+ .5H2	68.5	1	68.5	1	12	0.016
6e- + 8H+ + CO32- = 2H2O + <HCH2OH>	71	6	426	8	12	-121.872
8e- 8H+ + Fe3O4 = 4H2O + 3Fe	76.5	8	612	8	12	64.128
4e- + 6H+ + CO32- = 2H2O + <HCHO>	83.5	4	334	6	12	-76.904
2e- + 4H+ + CO32- = H2O + <HCOO>	96.1	2	192.2	4	12	-81.736
e- + H2O + FeO(OH) = Fe(OH)3-	99.9	1	99.9	0	12	99.9
2e- + 5H2O + Fe3O4 = H+ + 3Fe(OH)3-	134.7	2	269.4	1	12	337.884

Note: Because there are non-Q data used as inputs, this calculation is defined as TBV.

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7.0 References

Pankow J. F., 1991, Aquatic Chemistry Concepts, Lewis Publishers, Chelsea, Michigan, 683p., (Chapter 19).

Grogan H. A., and McKinley I. G., 1990, An Approach to Microbiological Modeling: Application to the Near Field of a Swiss Low/Intermediate-Level Waste Repository, NAGRA Technical Report 89-06, (page 18 and Appendix 1)

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