

ELECTRONIC ANNEX EA4: SYNOPSIS OF THERMODYNAMIC CALCULATIONS USED TO CALCULATE THE STABILITY FIELD FOR SIDERITE

Consider the thermal decomposition of siderite (FeCO_3) to magnetite (Fe_3O_4), CO_2 and CO , according to the reaction:



The Standard Gibbs free energy of reaction (ΔG_{rxn}^\ominus) is given by the difference in the standard Gibbs free energies of formation of the products and the reactants:

$$\Delta G_{rxn}^\ominus = \Delta G_{\text{Fe}_3\text{O}_4}^\ominus + 2 \cdot \Delta G_{\text{CO}_2}^\ominus + \Delta G_{\text{CO}}^\ominus - 3 \cdot \Delta G_{\text{FeCO}_3}^\ominus \quad (2)$$

Typically the term ‘*standard conditions*’ refers to state at which the extensive variables of pressure and temperature have the values of 1 bar (P_0) and 298.15 K (T_0) respectively. To calculate Gibbs free energy of the reaction under a different pressure (P_1) and temperature (T_1) it is necessary to use the fundamental thermodynamic identity:

$$\partial(\Delta G_{rxn}) = -\Delta S_{rxn} \cdot \partial T + \Delta V_{rxn} \cdot \partial P + \sum_i \mu_i \cdot \partial N_i \quad (3)$$

Where ΔS_{rxn} is the entropy change on reaction ($= S_{\text{Fe}_3\text{O}_4} + 2 \cdot S_{\text{CO}_2} + S_{\text{CO}} - 3 \cdot S_{\text{FeCO}_3}$), ΔV_{rxn} is the volume change on reaction ($= V_{\text{Fe}_3\text{O}_4} + 2 \cdot V_{\text{CO}_2} + V_{\text{CO}} - 3 \cdot V_{\text{FeCO}_3}$), and μ_i and N_i are the chemical potential and molarity of the i^{th} component in the system respectively. If we assume a closed system for which N is fixed (hence $\partial N_i = 0$) and equation (3) can be integrated and rearranged to give the result:

$$\Delta G_{rxn}^{P_1, T_1} = \Delta G_{rxn}^\ominus - \int_{T_0}^{T_1} \Delta S_{rxn} \cdot \partial T + \int_{P_0}^{P_1} \Delta V_{rxn} \cdot \partial P \quad (4)$$

Evaluation of the entropy integral proceeds by first recasting it in terms of the isobaric heat capacities (C_P) of the reactants and products from the relationship:

$$S^{T_1} = S^\ominus + \int_{T_0}^{T_1} \frac{C_P}{T} \cdot \partial T \quad (5)$$

Hence, equation (4) can be rewritten as:

$$\int_{T_0}^{T_1} \Delta S_{rxn} \cdot \partial T = \Delta S_{rxn}^\ominus (T_1 - T_0) + \int_{T_0}^{T_1} \int_{T_0}^{T_1} \frac{C_p^{Fe_3O_4} + 2C_p^{CO_2} + C_p^{CO} - 3C_p^{FeCO_3}}{T} \cdot \partial T \cdot \partial T \quad (6)$$

Tables of isobaric heat capacities have been compiled for just about every chemical compound known and can be usefully approximated by a polynomial expression of the form:

$$C_P \simeq a + b \cdot T + \frac{c}{T^2} + \frac{d}{\sqrt{T}} \quad (7)$$

Substituting equation (7) into equation (6) we have:

$$\int_{T_0}^{T_1} \Delta S_{rxn} \cdot \partial T = \Delta S_{rxn}^\ominus \cdot \Delta T - \Delta a \left(\Delta T - T_1 \cdot \log_e \left[\frac{T_1}{T_0} \right] \right) + \frac{\Delta b \cdot \Delta T}{2} + \frac{\Delta c \cdot \Delta T^2}{2 \cdot T_1 \cdot T_0} + 2 \cdot \Delta D \left(\sqrt{T_1} - \sqrt{T_0} \right) \quad (8)$$

where $\Delta T = T_1 - T_0$, and $\Delta i = (i_{Fe_3O_4} + 2 \cdot i_{CO_2} + i_{CO} - 3 \cdot i_{FeCO_3})$ for $i = a, b, c, d$. To evaluate the volume integral term in equation (4) requires consideration the phases of each species. For solids, under the range of pressures relevant to the discussion here, no significant error is incurred by simply assuming that $\left(\frac{\partial V}{\partial P}\right)_T \cong 0$, such that:

$$\int_{P_0}^{P_1} \Delta V_{rxn} \cdot \partial P = (P_1 - P_0) \cdot (V_{Fe_3O_4}^\ominus - 3 \cdot V_{FeCO_3}^\ominus) + \int_{P_0}^{P_1} (2 \cdot V_{CO_2} + V_{CO}) \cdot \partial P \quad (9)$$

where $V_{Fe_3O_4}^\ominus$ and $V_{FeCO_3}^\ominus$ are the molar volumes of magnetite and siderite respectively. For gas species such as CO_2 and CO it is necessary to use an equation-of-state (EOS). If both CO_2 and CO were to behave ideally (i.e., no intermolecular forces are present) the application of the ideal gas EOS, $V = \frac{n \cdot R \cdot T}{P}$, gives:

$$\int_{P_0}^{P_1} (2 \cdot V_{\text{CO}_2} + V_{\text{CO}}) \cdot \partial P = R \cdot T \cdot \left(2 \cdot \log_e \left[\frac{P_1^{\text{CO}_2}}{P_0^{\text{CO}_2}} \right] + \log_e \left[\frac{P_1^{\text{CO}}}{P_0^{\text{CO}}} \right] \right) \quad (10)$$

Since in general real gases do not behave ideally equation (10) is not applicable except under very low pressures. Nevertheless, to preserve the simplicity of the ideal gas solution, it is convenient to replace the pressure term for a real gases with an “effective pressure” or fugacity such that:

$$\int_{P_0}^{P_1} V \cdot \partial P = R \cdot T \cdot \log_e \left[\frac{f_{P_1}}{f_{P_0}} \right] \quad (11)$$

Where f_{P_0} and f_{P_1} are the fugacities for the real gas at pressures P_0 and P_1 respectively. Hence equation (10) can be rewritten in terms of the fugacities of CO and CO₂, that is:

$$\int_{P_0}^{P_1} (2 \cdot V_{\text{CO}_2} + V_{\text{CO}}) \cdot \partial P = R \cdot T \cdot \left(2 \cdot \log_e \left[\frac{f_{P_1}^{\text{CO}_2}}{f_{P_0}^{\text{CO}_2}} \right] + \log_e \left[\frac{f_{P_1}^{\text{CO}}}{f_{P_0}^{\text{CO}}} \right] \right) \quad (12)$$

Appropriate values for the CO₂ and CO fugacities can then be estimated from a real gas EOS. For the purposes of our calculations the Peng-Robertson-Gasem cubic EOS (Gasem et al., 2001) is sufficient for our purposes and requires only three input parameters for each species – the critical temperature (T_c), the critical pressure (P_c) and the accentric factor (ω). The form of this EOS is:

$$P = \frac{R \cdot T}{(V - b)} - \frac{a \cdot \alpha}{V(V + b) + V(V - b)} \quad \text{where} \quad \begin{cases} a = \frac{0.45724 \cdot R^2 \cdot T^2}{P_c} \\ b = \frac{0.07780 R \cdot T_c}{P_c} \\ \alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) \cdot \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \end{cases} \quad (13)$$

Using the relation $\partial(V \cdot P) = V \cdot \partial P + P \cdot \partial V$ the volume integral $\int_{P_0}^{P_1} V \cdot \partial P$ can be rewritten:

$$\int_{P_0}^{P_1} V \cdot \partial P = P_1 \cdot V_1 - P_0 \cdot V_0 - \int_{V_0}^{V_1} P \cdot \partial V \quad (14)$$

Applying equation (13) we have:

$$\int_{P_0}^{P_1} V \cdot \partial P = P_1 \cdot V_1 - P_0 \cdot V_0 - \int_{V_0}^{V_1} \left(\frac{R \cdot T}{(V-b)} - \frac{a \cdot \alpha}{V(V+b) + V(V-b)} \right) \cdot \partial V \quad (15)$$

This can be solved algebraically to give:

$$\begin{aligned} \int_{P_0}^{P_1} V \cdot \partial P = P_1 \cdot V_1 - P_0 \cdot V_0 - R \cdot T \cdot \log_e \left[\frac{V_1 - b}{V_0 - b} \right] \\ + \frac{a \cdot \alpha}{b \cdot 2\sqrt{2}} \cdot \log_e \left[\frac{V_1 + b(1 - \sqrt{2})}{V_1 + b(1 + \sqrt{2})} \cdot \frac{V_0 + b(1 + \sqrt{2})}{V_0 + b(1 - \sqrt{2})} \right] \end{aligned} \quad (16)$$

From the form of equation (11) we can easily see that:

$$\begin{aligned} \log_e \left[\frac{f_{P_1}}{f_{P_0}} \right] = \frac{P_1 \cdot V_1 - P_0 \cdot V_0}{R \cdot T} - \log_e \left[\frac{V_1 - b}{V_0 - b} \right] \\ + \frac{a \cdot \alpha}{b \cdot R \cdot T \cdot 2\sqrt{2}} \cdot \log_e \left[\frac{V_1 + b(1 - \sqrt{2})}{V_1 + b(1 + \sqrt{2})} \cdot \frac{V_0 + b(1 + \sqrt{2})}{V_0 + b(1 - \sqrt{2})} \right] \end{aligned} \quad (17)$$

Since all real gases approach ideal behavior at very low pressures we know that in the limit $\lim_{P_0 \rightarrow 0} \left(\frac{f_0}{P_0} \right) = 1$, hence taking $f_0 \rightarrow 0$ in equation (17) the fugacity f of a given gas at a pressure P can be written as:

$$\log_e [f_P] = \frac{P \cdot V}{R \cdot T} - 1 + \log_e \left[\frac{R \cdot T}{V - b} \right] + \frac{a \cdot \alpha}{b \cdot R \cdot T \cdot 2\sqrt{2}} \cdot \log_e \left[\frac{V + b(1 - \sqrt{2})}{V + b(1 + \sqrt{2})} \right] \quad (18)$$

Replacing P by the definition of pressure from equation (13) we obtain the fugacity expression for a gas described by the Peng-Robinson-Gasem EOS, which is:

$$\begin{aligned} \log_e [f_P] = \frac{b}{V - b} + \log_e \left[\frac{R \cdot T}{V - b} \right] + \frac{a \cdot \alpha}{R \cdot T} \left(\frac{1}{b \cdot 2\sqrt{2}} \cdot \log_e \left[\frac{V + b(1 - \sqrt{2})}{V + b(1 + \sqrt{2})} \right] \right) \\ - \frac{V}{V(V + b) + b(V - b)} \end{aligned} \quad (19)$$

The volume term, V , at the temperature, T , can be numerically determined from the real solution of the Peng-Robertson-Gasem EOS when expressed as a cubic polynomial in V , that is:

$$P \cdot V^3 + (Pb + RT) \cdot V^2 + (a\alpha + 2R \cdot T - 3Pb^3) \cdot V + (Pb^3 - RTb^2 - a\alpha b) = 0 \quad (20)$$

Putting this all together we can write:

$$\begin{aligned} \Delta G_{rxn}^{P_1, T_1} = & \Delta G_{rxn}^{\ominus} - \Delta S_{rxn}^{\ominus} \Delta T + \Delta a \left(\Delta T - T_1 \cdot \log_e \left[\frac{T_1}{T_0} \right] \right) - \frac{\Delta b \cdot \Delta T}{2} - \frac{\Delta c \cdot \Delta T^2}{2 \cdot T_1 \cdot T_0} \\ & - 2 \cdot \Delta d \left(\frac{\Delta T}{\sqrt{T_0}} - 2 \left\{ \sqrt{T_1} - \sqrt{T_0} \right\} \right) + (P_1 - P_0) \cdot (V_{\text{Fe}_3\text{O}_4}^{\ominus} - 3 \cdot V_{\text{FeCO}_3}^{\ominus}) \quad (21) \\ & + R \cdot T \cdot \left(2 \cdot \log_e \left[\frac{f_{P_1}^{\text{CO}_2}}{f_{P_0}^{\text{CO}_2}} \right] + \log_e \left[\frac{f_{P_1}^{\text{CO}}}{f_{P_0}^{\text{CO}}} \right] \right) \end{aligned}$$

At this point it is import to realize that the value $\Delta G_{rxn}^{P_1, T_1}$ represents the Gibbs free energy of reaction for the decomposition of siderite to magnetite, CO₂ and CO where all species are at a pressure P_1 , and temperature T_1 . Such conditions are in fact physically impossible to realize since both CO₂ and CO would mix, each occupying the same volume space so that their pressures would fall to $\frac{2}{3}P$ and $\frac{1}{3}P$ respectively. To take this practicality into account we can use the relationship between the Gibbs free energy and the thermodynamic equilibrium constant of the reaction K_{rxn} , for which we have:

$$\Delta G_{rxn} = \Delta G_{rxn}^{P_1, T_1} + R \cdot T \cdot \log_e [K_{rxn}] \quad (22)$$

The thermodynamic equilibrium constant is given by:

$$K_{rxn} = (\mathbb{F}_{\text{CO}_2})^2 \cdot \mathbb{F}_{\text{CO}} \quad (23)$$

where \mathbb{F}_{CO_2} and \mathbb{F}_{CO} are mixture fugacities of CO₂ and CO. Determination of these mixture fugacities is complex and it is convenient at this point to make use of the Lewis and Randall fugacity mixing rule (Lewis and Randall, 1961). This allows us to approximate the fugacity of a real gas i in a non-ideal gas mixture as the product of the mole fraction of i in the mixture and the fugacity i would have if it were the only gas present. Hence for gas i at a partial pressure P_i in a gas mixture at a total pressure P , the mixture fugacity of i is given by:

$$\mathbb{F}^i = \frac{P_i}{P} \cdot f_i^P \quad (24)$$

where f_i^P is the pure gas fugacity of i at pressure P . Substituting in to equation (22) we have:

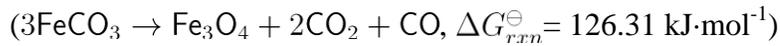
$$\begin{aligned}\Delta G_{rxn} &= \Delta G_{rxn}^{P_1, T_1} + R \cdot T \cdot \log_e \left[\left(\frac{\frac{2}{3} \cdot f_{\text{CO}_2}^{P_1}}{f_{\text{CO}_2}^{P_1}} \right)^2 \cdot \left(\frac{\frac{1}{3} \cdot f_{\text{CO}}^{P_1}}{f_{\text{CO}}^{P_1}} \right) \right] \\ &= \Delta G_{rxn}^{P_1, T_1} + R \cdot T \cdot \log_e \left[\frac{4}{27} \right]\end{aligned}\quad (25)$$

The stability field for siderite decomposition according to equation (1) in P - T space can thus be determined by solving equation (25) in P - T space subject to condition that $\Delta G_{rxn} = 0$, where the value of $\Delta G_{rxn}^{P_1, T_1}$ is given by equation (21). Values of the necessary thermodynamic parameters are provided by most recent version of the HP98 dataset (Holland and Powell, 1998; Powell et al., 1998) and are reproduced for reference in Table EA-4-1.

Gas constants for the Peng-Robinson-Gasem EOS are taken from the pure component databases of the Phase Equilibria computer code developed at the Technical University of Hamburg-Harburg (Pfohl et al., 1999) and are shown Table EA-4-2.

Table EA-4-1. Thermodynamic data from THERMOCALC 3.26

Species	ΔH^θ (J)	S^θ (J·K ⁻¹)	V (J·bar ⁻¹)	a	b	C	d
FeCO₃	-7.61440E+05	9.5000E+01	2.938E+00	1.684E+02	0.000E+00	0.0000E+00	-1.4836E+03
Fe₃O₄	-1.11551E+06	1.4610E+02	4.452E+00	2.625E+02	-7.204E-03	-1.9262E+06	-1.6557E+03
CO₂	-3.93510E+05	2.1370E+02	0.000E+00	8.780E+01	-2.644E-03	7.0640E+05	-9.9890E+02
CO	-1.10530E+05	1.9767E+02	0.000E+00	4.570E+01	-9.700E-05	6.6270E+05	-4.1470E+02

**Table EA-4-2. Gas constants for the Peng-Robinson-Gasem EOS***

Species	P_c (bar)	T_c (K)	ω
CO₂	73.80	304.10	0.225
CO	35.00	132.90	0.066

*(Pfohl et al., 1999)

REFERENCES

- Gasem, K. A. M., Gao, W., Pan, Z., and Robinson, R. L. J. (2001) A modified temperature dependence for the Peng-Robinson equation of state. *Fluid Phase Equilib.* **181**, 113-125.
- Holland, T. and Powell, R. (1998) An internally-consistent thermodynamic dataset for phases of petrological interest. *J. Metamorph. Geol.* **16**, 309-343.
- Lewis, G. N. and Randall, M. (1961). *Thermodynamics, 2nd Edition*. McGraw-Hill, New York.
- Pfohl, O., Petkov, S., and Brunner, G. (1999). *PE: a scientific computer program for the calculation of fluid-phase equilibria, Scientific Computing in Chemical Engineering*. . Springer-Verlag, Berlin Heidelberg.
- Powell, R., Holland, T., and Worley, B. (1998) Calculating phase diagrams involving solid solutions via non-linear equations with examples using THERMOCALC. *J. Metamorph. Geol.* **16**, 577-588.