Rate of change at equilibrium

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ABSTRACT

A general procedure to evaluate derivatives of thermodynamic quantities with respect to equilibrium conditions (external variables, parameters) at equilibrium is outlined. An example calculation is given.

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1. Introduction

A powerful feature of the Thermo-Calc software [1] is the possibility to obtain analytical derivatives of thermodynamic quantities with respect to equilibrium conditions. It has been possible to evaluate such derivatives for a very long time using the Thermo-Calc equilibrium calculation engine [2], but the method used has never been published.

The present work outlines a general procedure to evaluate such derivatives, i.e. derivatives taken at equilibrium states with respect to parameters representing equilibrium conditions. Or, in other words, the rate of change at equilibrium of thermodynamic properties relative the change of an external parameter. These derivatives are constrained since they are evaluated at equilibrium; the internal variables are interdependent.

The problem is sometimes referred to as optimum sensitivity analysis. Smith and Nissen [3] present in-depth results on this subject matter in their general book on chemical reaction equilibrium analysis and is recommended as further reading. So-bieszczanski-Sobieski and Riley [4] have performed this type of analysis within the field of structural mechanics.

The structure of this paper is as follows. First a general formulation for the optimization problem of finding an equilibrium state is given. Then the general procedure of evaluating derivatives at equilibrium is outlined. Finally, a simple example is given to illustrate the method.

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2. Calculating thermodynamic equilibria

There are numerous articles and books where methods for calculating thermodynamic equilibria are discussed, see, for example, Lukas et al. [5] and Hillert [6]. Here the method of Lagrange multipliers will be considered. With the Calphad formalism, the internal variables of a system are normally temperature $\tilde{T}$, pressure $\tilde{P}$, number of moles formula units of each phase α, n^α, and the site fractions $y_k^{\alpha s}$ of constituents k on sublattices s in phase α. The tilde (˜) signifies that these temperature and pressure variables are internal, as opposed to external, and the reason for this distinction will become clear below. The total Gibbs energy G of a system is given by

$$G = \sum_\alpha n^\alpha G_m^\alpha \left(\tilde{P}, \tilde{T}, y^\alpha \right) \tag{1}$$

where G_m^α is Gibbs energy of phase α per mole formula unit.

The equilibrium state is found by minimizing Eq. (1) subject to "internal" and "external" constraints.

Internal constraints are

$$0 \le y_k^{\alpha s} \le 1 \tag{2}$$

$$\sum_k y_k^{\alpha s} = 1 \tag{3}$$

$$n^\alpha \ge 0 \tag{4}$$

and may also include constraints on charge neutrality. In the following the internal constraints will not be considered; it is assumed that they are satisfied. It will also be assumed that one site

fraction on each sublattice is eliminated so that the constraint given by Eq. (3) does not give rise to internal derivatives.

The external constraints are the equilibrium conditions. The natural external variables of Gibbs energy are P, T and the number of moles of each component N_i. In this paper we will only consider equilibrium conditions corresponding to these variables. The external constraint corresponding to mass balance with regards to component i is then formulated as

$$N_i - \tilde{N}_i(n^\alpha, ..., n^\omega, y^\alpha, ..., y^\omega) = 0 \tag{5}$$

where $\tilde{N}_i$ is a function yielding the total number of moles of component i in the system.

The corresponding constraints on temperature and pressure are $P - \tilde{P} = 0$ and $T - \tilde{T} = 0$, which are trivially satisfied.

In the following internal variables will be denoted with v and external variables with z. The optimization problem of finding the equilibrium state may then be formulated as

$$\text{minimize} \quad G(v_1, ..., v_n) \tag{6}$$

$$\text{subject to constraints} \quad g_i(v_1, ..., v_n, z_i) = 0, \quad i = 1, ..., m \tag{7}$$

In general the number of constraints m is equal to $C + 2$ where C is the number of components. When determining a specific equilibrium state the external variables z are held constant. To find the solution, form the Lagrangian

$$\mathcal{L} = G + \sum_{i=1}^{m} \lambda_i g_i \tag{8}$$

where the λ_i are the multipliers. The equilibrium state is then found by satisfying the system of equations

$$\begin{cases} \dfrac{\partial \mathcal{L}}{\partial v_j} = \dfrac{\partial G}{\partial v_j} + \sum_{i=1}^{m} \lambda_i \dfrac{\partial g_i}{\partial v_j} = 0, & j = 1, ..., n \\[2ex] \dfrac{\partial \mathcal{L}}{\partial \lambda_i} = g_i = 0, & i = 1, ..., m \end{cases} \tag{9}$$

3. Evaluating a derivative with respect to an equilibrium condition

Given an equilibrium found by solving the optimization problem (Eq. (9)) for a given set of z_i external variable values, consider a function h

$$h(v_1, ..., v_n) \tag{10}$$

and evaluate how h will change subject to a change in equilibrium condition z_k, i.e. evaluate the derivative

$$\frac{dh}{dz_k} = \sum_{j=1}^{n} \frac{\partial h}{\partial v_j} \frac{dv_j}{dz_k} \tag{11}$$

The partial derivatives $\partial h / \partial v_j$ are given directly by the expression for h. The interdependence of the v, λ and z variables is found by differentiating the system of equations (Eq. (9)) with respect to z_k:

$$\sum_{r=1}^{n} \frac{\partial^2 \mathcal{L}}{\partial v_j \partial v_r} \frac{dv_r}{dz_k} + \sum_{s=1}^{m} \left(\frac{\partial^2 \mathcal{L}}{\partial v_j \partial \lambda_s} \frac{d\lambda_s}{dz_k} + \frac{\partial^2 \mathcal{L}}{\partial v_j \partial z_s} \frac{dz_s}{dz_k} \right) = 0,$$
$$j = 1, ..., n \tag{12}$$

$$\sum_{r=1}^{n} \frac{\partial^2 \mathcal{L}}{\partial \lambda_i \partial v_r} \frac{dv_r}{dz_k} + \frac{\partial^2 \mathcal{L}}{\partial \lambda_i \partial z_i} \frac{dz_i}{dz_k} = 0, \quad i = 1, ..., m \tag{13}$$

where it has been utilised that $\partial \mathcal{L}/\partial v_j = f(v, z, \lambda)$ and $\partial \mathcal{L}/\partial \lambda_i = f(v, z_i)$

For dz_i / dz_k we have that

$$\frac{dz_i}{dz_k} = \delta_{ik} \tag{14}$$

where δ_{ik} is Kronecker's delta, i.e. $\delta_{ik} = 1$ if $i = k$ and zero otherwise. This is the case since all z_i are held constant except z_k.

Using (Eqs. (8) and 14), (Eqs. (12) and 13) can be rewritten as

$$\sum_{r=1}^{n} \left(\frac{\partial^2 G}{\partial v_j \partial v_r} + \sum_{i=1}^{m} \lambda_i \frac{\partial^2 g_i}{\partial v_j \partial v_r} \right) \frac{dv_r}{dz_k} + \sum_{s=1}^{m} \left(\frac{\partial g_s}{\partial v_j} \frac{d\lambda_s}{dz_k} + \lambda_s \frac{\partial^2 g_s}{\partial v_j \partial z_s} \delta_{sk} \right)$$
$$= 0, \quad j = 1, ..., n \tag{15}$$

$$\sum_{r=1}^{n} \frac{\partial g_i}{\partial v_r} \frac{dv_r}{dz_k} + \frac{\partial g_i}{\partial z_i} \delta_{ik} = 0, \quad i = 1, ..., m \tag{16}$$

The system of equations, (Eqs. (15) and 16), is the Hessian of the Lagrangian. At a solution point values can be inserted for all multipliers λ and all derivatives except for $d\lambda_s/dz_k$ and dv_j/dz_k, the values of which can be found by solving the resulting linear system of equations. Moving the unknowns to the right hand side, the system of equations can be written in matrix form as $Aw = b$ where

$$A = \begin{bmatrix} \left(\dfrac{\partial^2 G}{\partial v_1^2} + \sum_{i=1}^{m} \lambda_i \dfrac{\partial^2 g_i}{\partial v_1^2} \right) & \cdots & \left(\dfrac{\partial^2 G}{\partial v_1 \partial v_n} + \sum_{i=1}^{m} \lambda_i \dfrac{\partial^2 g_i}{\partial v_1 \partial v_n} \right) & \dfrac{\partial g_1}{\partial v_1} & \cdots & \dfrac{\partial g_m}{\partial v_1} \\ \vdots & & & & & \vdots \\ \left(\dfrac{\partial^2 G}{\partial v_n \partial v_1} + \sum_{i=1}^{m} \lambda_i \dfrac{\partial^2 g_i}{\partial v_n \partial v_1} \right) & \cdots & \left(\dfrac{\partial^2 G}{\partial v_n^2} + \sum_{i=1}^{m} \lambda_i \dfrac{\partial^2 g_i}{\partial v_n^2} \right) & \dfrac{\partial g_1}{\partial v_n} & \cdots & \dfrac{\partial g_m}{\partial v_n} \\ \dfrac{\partial g_1}{\partial v_1} & \cdots & \dfrac{\partial g_1}{\partial v_n} & 0 & \cdots & 0 \\ \vdots & & & & & \vdots \\ \dfrac{\partial g_m}{\partial v_1} & \cdots & \dfrac{\partial g_m}{\partial v_n} & 0 & \cdots & 0 \end{bmatrix} \tag{17}$$

$$w = \begin{bmatrix} \dfrac{dv_1}{dz_k} & \cdots & \dfrac{dv_n}{dz_k} & \dfrac{d\lambda_1}{dz_k} & \cdots & \dfrac{d\lambda_m}{dz_k} \end{bmatrix}^T \tag{18}$$

$$b = \left[-\sum_{s=1}^{m} \lambda_s \frac{\partial^2 g_s}{\partial v_1 \partial z_s} \delta_{sk} \quad \cdots \quad -\sum_{s=1}^{m} \lambda_s \frac{\partial^2 g_s}{\partial v_n \partial z_s} \delta_{sk} \quad -\frac{\partial g_1}{\partial z_1} \delta_{1k} \quad \cdots \quad -\frac{\partial g_m}{\partial z_m} \delta_{mk} \right]^T \quad (19)$$

4. Example calculation

For simplicity a hypothetical isobarothermal binary system $A - B$ with two regular solutions α and β each with a single sublattice are considered. Here, site fractions y_i are identical to mole fractions x_i. We will determine how the mole fraction of the α phase f^α varies with the amount of B, i.e. df^α/dN_B.

We have that, cf. Eq. (1),

$$G = n^\alpha G_m^\alpha + n^\beta G_m^\beta \quad (20)$$

The molar Gibbs energy of the α phase and the partial derivatives with respect to x_A^α are given by

$$G_m^\alpha = x_A^\alpha {}^\circ G_A^\alpha + \left(1 - x_A^\alpha\right) {}^\circ G_B^\alpha + RT\left[x_A^\alpha \ln x_A^\alpha + \left(1 - x_A^\alpha\right) \ln\left(1 - x_A^\alpha\right)\right]$$

$$+ x_A^\alpha \left(1 - x_A^\alpha\right) L_{AB}^\alpha \quad (21)$$

$$\frac{\partial G_m^\alpha}{\partial x_A^\alpha} = {}^\circ G_A^\alpha - {}^\circ G_B^\alpha + RT\left[\ln x_A^\alpha - \ln\left(1 - x_A^\alpha\right)\right] + \left(1 - 2x_A^\alpha\right) L_{AB}^\alpha \quad (22)$$

$$\frac{\partial^2 G_m^\alpha}{\partial x_A^{\alpha 2}} = \frac{RT}{x_A^\alpha \left(1 - x_A^\alpha\right)} - 2L_{AB}^\alpha \quad (23)$$

and similarly for the β phase.

The internal variables of the system, corresponding to the v in (Eqs. (15) and 16), are n^α, x_A^α, n^β and x_A^β. The external variables, corresponding to the z in (Eqs. (15) and 16), are N_A and N_B. All of T, $\tilde{T}$, P and $\tilde{P}$ are disregarded since an isobarothermal system is considered.

Regarding the multipliers λ we have, at the solution point, that

$$\frac{\partial \mathcal{L}}{\partial n^\alpha} = \frac{\partial G}{\partial n^\alpha} + \sum \lambda_i \frac{\partial g_i}{\partial n^\alpha} = G_m^\alpha - \sum \lambda_i x_i^\alpha = 0 \quad (24)$$

$$G_m^\alpha = \sum \lambda_i x_i^\alpha \quad (25)$$

Thus, at equilibrium we may identify the multipliers with the chemical potentials μ_i.

The constraints are

$$g_{N_A} \equiv g_A = N_A - \tilde{N}_A = N_A - n^\alpha x_A^\alpha - n^\beta x_A^\beta = 0 \quad (26)$$

$$g_{N_B} \equiv g_B = N_B - \tilde{N}_B = N_B - n^\alpha \left(1 - x_A^\alpha\right) - n^\beta \left(1 - x_A^\beta\right) = 0 \quad (27)$$

In the system of equations, (Eqs. (15) and 16), many terms are zero for the present case, viz.

$$\lambda_s \frac{\partial^2 g_s}{\partial v_j \partial z_s} \delta_{sk} = 0$$

$$\frac{\partial^2 G}{\partial n^{\alpha 2}} = 0$$

$$\frac{\partial^2 g_A}{\partial n^{\alpha 2}} = \frac{\partial^2 g_B}{\partial n^{\alpha 2}} = 0$$

$$\frac{\partial^2 g_A}{\partial x_A^{\alpha 2}} = \frac{\partial^2 g_B}{\partial x_A^{\alpha 2}} = 0$$

and correspondingly for the β phase. Also, for the present case, all second derivatives taken with respect to a variable of the α phase and a variable of the β phase are zero.

The system of equations, (Eqs. (15) and 16), become

$$\left(\frac{\partial^2 G}{\partial n^\alpha \partial x_A^\alpha} + \mu_A \frac{\partial^2 g_A}{\partial n^\alpha \partial x_A^\alpha} + \mu_B \frac{\partial^2 g_B}{\partial n^\alpha \partial x_A^\alpha}\right) \frac{dx_A^\alpha}{dz_k} + \frac{\partial g_A}{\partial n^\alpha} \frac{d\mu_A}{dz_k} + \frac{\partial g_B}{\partial n^\alpha} \frac{d\mu_B}{dz_k} = 0 \quad (28)$$

$$\left(\frac{\partial^2 G}{\partial n^\alpha \partial x_A^\alpha} + \mu_A \frac{\partial^2 g_A}{\partial n^\alpha \partial x_A^\alpha} + \mu_B \frac{\partial^2 g_B}{\partial n^\alpha \partial x_A^\alpha}\right) \frac{dn^\alpha}{dz_k}$$

$$+ \frac{\partial^2 G}{\partial x_A^{\alpha 2}} \frac{dx_A^\alpha}{dz_k} + \frac{\partial g_A}{\partial x_A^\alpha} \frac{d\mu_A}{dz_k} + \frac{\partial g_B}{\partial x_A^\alpha} \frac{d\mu_B}{dz_k} = 0 \quad (29)$$

$$\frac{\partial g_A}{\partial n^\alpha} \frac{dn^\alpha}{dz_k} + \frac{\partial g_A}{\partial x_A^\alpha} \frac{dx_A^\alpha}{dz_k} + \frac{\partial g_A}{\partial n^\beta} \frac{dn^\beta}{dz_k} + \frac{\partial g_A}{\partial x_A^\beta} \frac{dx_A^\beta}{dz_k} + \frac{\partial g_A}{\partial N_A} \frac{dN_A}{dz_k} = 0 \quad (30)$$

For (Eqs. (28) and 29) there are corresponding equations for the β phase and for Eq. (30) there is a corresponding equation for g_B.

Using (Eqs. (20), (26) and 27), (Eqs. (28)–30) become

$$\left(\frac{\partial G_m^\alpha}{\partial x_A^\alpha} - \mu_A + \mu_B\right) \frac{dx_A^\alpha}{dz_k} - x_A^\alpha \frac{d\mu_A}{dz_k} - \left(1 - x_A^\alpha\right) \frac{d\mu_B}{dz_k} = 0 \quad (31)$$

$$\left(\frac{\partial G_m^\alpha}{\partial x_A^\alpha} - \mu_A + \mu_B\right) \frac{dn^\alpha}{dz_k} + n^\alpha \frac{\partial^2 G_m^\alpha}{\partial x_A^{\alpha 2}} \frac{dx_A^\alpha}{dz_k} - n^\alpha \frac{d\mu_A}{dz_k} + n^\alpha \frac{d\mu_B}{dz_k} = 0 \quad (32)$$

$$-x_A^\alpha \frac{dn^\alpha}{dz_k} - n^\alpha \frac{dx_A^\alpha}{dz_k} - x_A^\beta \frac{dn^\beta}{dz_k} - n^\beta \frac{dx_A^\beta}{dz_k} + \frac{dN_A}{dz_k} = 0 \quad (33)$$

Similar to Eq. (33), the equation for g_B differentiated with respect to z_k becomes

$$-\left(1 - x_A^\alpha\right) \frac{dn^\alpha}{dz_k} + n^\alpha \frac{dx_A^\alpha}{dz_k} - \left(1 - x_A^\beta\right) \frac{dn^\beta}{dz_k} + n^\beta \frac{dx_A^\beta}{dz_k} + \frac{dN_B}{dz_k} = 0 \quad (34)$$

In matrix form the system of equations becomes

$$\begin{bmatrix} 0 & c_{12} & 0 & 0 & c_{15} & c_{16} \\ c_{21} & c_{22} & 0 & 0 & c_{25} & c_{26} \\ 0 & 0 & 0 & c_{34} & c_{35} & c_{36} \\ 0 & 0 & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & 0 & 0 \\ c_{61} & c_{62} & c_{63} & c_{64} & 0 & 0 \end{bmatrix} \begin{bmatrix} dn^\alpha/dz_k \\ dx_A^\alpha/dz_k \\ dn^\beta/dz_k \\ dx_A^\beta/dz_k \\ d\mu_A/dz_k \\ d\mu_B/dz_k \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -dN_A/dz_k \\ -dN_B/dz_k \end{bmatrix} \quad (35)$$

The square coefficient matrix is symmetric, i.e. $c_{ij} = c_{ji}$. We have that

$$c_{12} = c_{21} = \frac{\partial G_m^\alpha}{\partial x_A^\alpha} - \mu_A + \mu_B, \quad c_{22} = n^\alpha \frac{\partial^2 G_m^\alpha}{\partial x_A^\alpha}$$

$$c_{34} = c_{43} = \frac{\partial G_m^\beta}{\partial x_A^\beta} - \mu_A + \mu_B, \quad c_{44} = n^\beta \frac{\partial^2 G_m^\beta}{\partial x_A^{\beta 2}}$$

$$c_{15} = c_{51} = -x_A^\alpha, \quad c_{25} = c_{52} = -n^\alpha$$

$$c_{35} = c_{53} = -x_A,^\beta \quad c_{45} = c_{54} = -n^\beta$$

$$c_{16} = c_{61} = -\left(1 - x_A^\alpha\right), \quad c_{26} = c_{62} = n^\alpha$$

$$c_{36} = c_{63} = -\left(1 - x_A^\beta\right), \quad c_{46} = c_{64} = n^\beta$$

Assume the following parameter values [J/mol]:

$${}^\circ G_A^\alpha = {}^\circ G_B^\beta = 0$$

$${}^\circ G_A^\beta = {}^\circ G_B^\alpha = 10,000$$

$$L_{AB}^\alpha = -10,000$$

$$L_{AB}^\beta = -5000$$

At a temperature of 1000 K and with equilibrium conditions $N_A = 0.4$, $N_B = 0.6$ [mol] the equilibrium state is two phase $\alpha + \beta$ and

$n^\alpha = 0.41444, \quad n^\beta = 0.58556$

$x_A^\alpha = 0.63664, \quad x_A^\beta = 0.23251$

$\mu_A = -5074.6, \quad \mu_B = -2470.6$

With $z_k \equiv N_B$ the solution to the linear system of equations yields $dn^\alpha/dN_B = -0.5753$ and $dn^\beta/dN_B = 1.5753$ while the other derivatives are zero, as they should be.

The mole fraction of the α phase is given by

$$f^\alpha = \frac{n^\alpha}{n^\alpha + n^\beta} \tag{36}$$

The derivative of f^α with respect to N_B is, cf. Eq. (11),

$$\frac{df^\alpha}{dN_B} = \frac{\partial f^\alpha}{\partial n^\alpha}\frac{dn^\alpha}{dN_B} + \frac{\partial f^\alpha}{\partial n^\beta}\frac{dn^\beta}{dN_B} = \frac{n^\beta}{\left(n^\alpha + n^\beta\right)^2}\frac{dn^\alpha}{dN_B} - \frac{n^\alpha}{\left(n^\alpha + n^\beta\right)^2}\frac{dn^\beta}{dN_B} \tag{37}$$

In this case $df^\alpha/dN_B = -0.98977$.

5. Summary and discussion

A general method to evaluate partial derivatives of thermodynamic functions with respect to variables corresponding to equilibrium conditions has been described. These derivatives have been possible to evaluate in Thermo-Calc for a very long time, but the method used has never been published although this is a very powerful feature of the program. An example of their use is found in a model suggested by Larsson and Reed [7,8] for simulating diffusion controlled growth under local equilibrium conditions. This model is completely dependent on the availability of such derivatives and triggered the interest of one of the present authors (HL) in this subject.

Appendix A. Supplementary data

Supplementary data associated with this paper can be found in the online version at http://dx.doi.org/10.1016/j.calphad.2015.10.002.

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