Calculating thermodynamic equilibria

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1 Thermodynamic equilibrium

A general reference is the book by Hillert [1]

The 1st law relates the change in internal energy in a system to the interactions with the surroundings

$$\begin{aligned} dU &= dQ + dW + \sum \mu_i dN_i \\ dW &= -PdV \\ dU &= dQ - PdV + \sum \mu_i dN_i \end{aligned} \tag{1}$$

where U is the internal energy, Q is heat, W is work, μ_i is the chemical potential and N_i is the number of moles of component i. P is pressure and V is volume. Here, only pressure-volume work will be considered.

The 2nd law dictates the changes that are possible in an isolated system

$$dS_{ip} \geq 0 \tag{2}$$

Entropy S will increase for any spontaneous internal process (ip) in an isolated system

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$$dS = dQ/T + dS_{ip} \tag{3}$$

Driving force D is given by

$$D = T\frac{dS_{ip}}{d\xi} \tag{4}$$

where $\Delta\xi$ is the extent of an internal process. In view of the second law, the sign of D and ξ must be the same for a spontaneous process.

Write dQ as

$$dQ = TdS - TdS_{ip} = TdS - Dd\xi \tag{5}$$

The combined law

$$dU = TdS - PdV + \sum \mu_i dN_i - Dd\xi \tag{6}$$

Gibbs energy

$$G = U - TS + PV \tag{7}$$

$$dG = VdP - SdT + \sum \mu_i dN_i - Dd\xi \tag{8}$$

Consider a closed system at constant P and T made up of two subsystems. Transfer a component k internally from subsystem $\prime$ (prime) to subsystem $\prime\prime$ (double prime). This is an internal process. For the system as a whole $dG = -Dd\xi$. For $\prime$, $d\xi = -dN_k$. For $\prime\prime$, $d\xi = dN_k$. thus,

$$-D = \frac{\partial G}{\partial \xi} = \frac{\partial G'}{\partial\left(-N_k\right)} + \frac{\partial G''}{\partial N_k} = -\mu_k' + \mu_k'' \tag{9}$$

$$D = \mu_k' - \mu_k'' \tag{10}$$

At equilibrium, $\mu_k' = \mu_k''$.

Since $D = -\partial G/\partial \xi$ and $Dd\xi \geq 0$, G is minimized at equilibrium.

2 Mathematical statement of thermodynamic equilibrium

External variables are those that are controlled from outside the system. As the system approaches equilibrium, the internal variables gradually change.

Consider these as the external variables: P, T, N_k

The internal variables are: $\tilde{P}$, $\tilde{T}$, $\tilde{x}_k^r$, $\tilde{n}^r$

The tilde ($\tilde{}$) is used to distinguish between internal and external quantities, but may be dropped when there is no risk of confusion. $\tilde{x}_k^r$ is the mole fraction of component k in phase r. $\tilde{n}^r$ is the number of moles of phase r. The chosen set of external variables are the natural variables of Gibbs energy-

In order to find the thermodynamic equilibrium for a given set of values of the external variables, minimize

$$G\left(\tilde{P}, \tilde{T}, \tilde{x}_k^r, \tilde{n}^r\right) = \sum_r \tilde{n}^r G_m\left(\tilde{P}, \tilde{T}, \tilde{x}_k^r\right) \tag{11}$$

subject to the following constraints

$$g_P = P - \tilde{P} = 0 \tag{12}$$

$$g_T = T - \tilde{T} = 0 \tag{13}$$

$$g_i = N_i - \tilde{N}_i = N_i - \sum_r \tilde{n}^r \tilde{x}_i^r \tag{14}$$

$$0 \leq \tilde{x}_k^r \leq 1 \tag{15}$$

$$\tilde{n}^r \geq 0 \tag{16}$$

$$\sum_{k=1}^{n} \tilde{x}_k^r = 1 \tag{17}$$

The constraints on P and T are trivially satisfied. The inequalities are assumed to be satisfied. In general, the set of constraints may also include a constraint on charge.

After also replacing $\tilde{x}_n^r$ with $1 - \sum_{k=1}^{n-1} \tilde{x}_k^r$, the simplified optimization problem is (dropping the tilde)

$$\text{minimize} \qquad G\left(n^r, x_k^r\right) = \sum_r n^r G_m^r\left(x_k^r\right) \tag{18}$$

$$\text{subject to} \qquad g_i = N_i - \sum_r n^r x_i^r \qquad i = 1, \cdots, n \tag{19}$$

Form the Lagrangian $\mathcal{L}$ and introduce the multipliers λ_i

$$\mathcal{L}\left(n^r, x_k^r, \lambda_i\right) = G + \sum \lambda_i g_i \tag{20}$$

The solution to the contrained optimization problem is then given by

$$\frac{\partial \mathcal{L}}{\partial n^t} = 0 = \frac{\partial G}{\partial n^t} + \sum_{i=1}^{n} \lambda_i \frac{\partial g_i}{\partial n^t} = G_m^t - \sum_{i=1}^{n} \lambda_i x_i^t \tag{21}$$

$$\frac{\partial \mathcal{L}}{\partial x_j^t} = 0 = \frac{\partial G}{\partial x_j^t} + \sum_{i=1}^{n} \lambda_i \frac{\partial g_i}{\partial x_j^t} = n^t \frac{\partial G_m^t}{\partial x_j^t} + \sum_{i=1}^{n} \lambda_i \frac{\partial g_i}{\partial x_j^t} \tag{22}$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_i} = 0 = g_i \tag{23}$$

$$\tag{24}$$

Finally it may be noted that within the Calphad framework the more general site fractions y_j^{rs} on sublattices s in phase r are used rather than mole fractions x_k^r. It should also be noted that a constituent of a phase may not necessarily be a component of the system. Further, in general n^r refers to the number of moles of formula units of a phase, which in general will be different from the number of moles of components that make up the phase.

3 Solving optimizaton problems numerically

A general reference is the book by Nocedal and Wright [2].

The problem is

$$\begin{aligned} \text{minimize} \quad & F(v_1, \cdots, v_n) && (25) \\ \text{subject to} \quad & g_i(v_1, \cdots, v_n, z_i) = 0 \qquad i = 1, \cdots, m && (26) \end{aligned}$$

The v_j can be identified with the internal variables and the z_i with the external.

Form the Lagrangian

$$\mathcal{L} = F + \sum \lambda_i g_i \tag{27}$$

Solve

$$\mathcal{L}'_j = \frac{\partial \mathcal{L}}{\partial v_j} = \frac{\partial F}{\partial v_j} + \sum_i \lambda_i \frac{\partial g_i}{\partial v_j} = F'_j + \sum_i \lambda_i g'_{ij} = 0 \qquad j = 1, \cdots, n \tag{28}$$

$$\mathcal{L}'_i = \frac{\partial \mathcal{L}}{\partial \lambda_i} = g_i = 0 \qquad i = 1, \cdots, m \tag{29}$$

Given an initial guess, expand

$$\mathcal{L}'_j \simeq \mathcal{L}'_{j0} + \sum_k \frac{\partial F'_j}{\partial v_k} \Delta v_k + \sum_i \sum_k \lambda_i \frac{\partial g'_{ij}}{\partial v_k} \Delta v_k + \sum_i g'_{ij} \Delta \lambda_i = 0 \tag{30}$$

$$\mathcal{L}'_i \simeq g_{i0} + \sum_k g'_{ik} \Delta v_k = 0 \tag{31}$$

The resulting linear system of equations has the form

$$\begin{bmatrix} (F'' + g'') & g' \\ g'^T & 0 \end{bmatrix} \begin{bmatrix} \Delta v \\ \Delta \lambda \end{bmatrix} = \begin{bmatrix} -\mathcal{L}'_0 \\ -g_0 \end{bmatrix} \tag{32}$$

Form a squared residual

$$r = \sum_j |\mathcal{L}'_j|^2 + \sum_i |\mathcal{L}'_i|^2 \tag{33}$$

Do a line search along the direction given by the solution to the linear system of equations, i.e. , for a scalar θ, find the value of θ that minimize

$$r = \sum_j |\mathcal{L}'_j\left(v + \theta\Delta v, \lambda + \theta\lambda\right)|^2 + \sum_i |\mathcal{L}'_i\left(v + \theta\Delta v\right)|^2 \tag{34}$$

and then update the variables

$$\begin{aligned} v &\rightarrow v + \theta\Delta v \\ \lambda &\rightarrow \lambda + \theta\Delta\lambda \end{aligned}$$

4 Home assignment

Write a simple program, using for example Matlab, which can compute thermodynamic equilibria for binary systems consisting of two regular solution phases. The equilibrium conditions are pressure, temperature and the number of moles of each component. Compare results with calculations using an existing software, for example Thermo-Calc.

Use negative interaction parameters.

The selection of the set of stable phases does not need to be fully automatic.

References

[1] M Hillert. Phase Equilibria, Phase Diagrams and Phase Transformations – Their Thermodynamic Basis. 2nd Edition.Cambridge University Press, Cambridge, UK, 2008.

[2] J Nocedal, SJ Wright. Numerical Optimization. Springer Science+Business Media, New York, USA, 2006.