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) to subsystem $''$ (double prime). This is an internal process. For the system as a whole $dG = -Dd\xi$. For $'$, $d\xi = -dN_k$. For $''$, $d\xi = dN_k$. 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 (˜) 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)

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

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

Single constraint:
maximize f(x, y)
subject to g(x, y) = c.
Lag(x,y,λ)=f(x,y)-+λ.(g(x,y)-c)

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

In optimization, the method of Lagrange multipliers is a strategy for finding the local maxima and minima of a function subject to equality constraints.
maximize f(x1,..,xn)
subject to g(x1,..,xn) = c.
Then:
Lag(x1,..,xn,λ1,..,λM)=f(x1,..,xn)-SUM[K=1..M](λK.gK(x1,..,xN))
note: the constant term of each constraint has been subsumed in the function gk so the kth constraint is gk=0

λ term may be either added or subtracted
If f(x0, y0) is a maximum of f(x, y) for the original constrained problem, then there exists λ0 such that (x0, y0, λ0) is a stationary point for the Lagrange function (stationary points are those points where the partial derivatives of lambda are zero).
However, not all stationary points yield a solution of the original problem.
Thus, the method of Lagrange multipliers yields a necessary condition for optimality in constrained problems. Sufficient conditions for a minimum or maximum also exist.intuition that at a maximum, f(x, y) cannot be increasing in the direction of any neighboring point where g = 0. If it were, we could walk along g = 0 to get higher, meaning that the starting point wasn't actually the maximum.
We can visualize contours of f given by f(x, y) = d for various values of d, and the contour of g given by g(x, y) = 0.
Suppose we walk along the contour line with g = 0.
We are interested in finding points where f does not change as we walk, since these points might be maxima. There are two ways this could happen: First, we could be following a contour line of f, since by definition f does not change as we walk along its contour lines. This would mean that the contour lines of f and g are parallel here. The second possibility is that we have reached a "level" part of f, meaning that f does not change in any direction.

Solution:
To check the first possibility, since the gradient of a function is perpendicular to the contour lines, the contour lines of f and g are parallel if and only if the gradients of f and g are parallel. Thus we want points (x, y) where g(x, y) = 0 and
curl[x,y](f) = λ.curl[x,y](g) ==
(df/dx,df/dy) = λ(dg/dx,dg/dy)
The constant λ is required because although the two gradient vectors are parallel the magnitudes of the gradient vectors are generally not equal.
This constant is called the Lagrange multiplier.

this method also solves the second possibility:
if f is level, then its gradient is zero, and setting λ = 0 is a solution regardless of g.
To incorporate these conditions into one equation, we introduce an auxiliary function:
Single constraint:
maximize f(x, y)
subject to g(x, y) = c.

Lag(x,y,λ)=f(x,y)-+λ.(g(x,y)-c) and solve: Curl [x,y] Lag(x,y,λ)= 0 (I think c) solving three equations in three unknowns. This is the method of Lagrange multipliers. *=> curl[λ](x,y,z)=0 implies g(x,y)=0 so:

curl[x,y,λ] Lag(x,y,λ)=0 <=> {[g(x,y)=0] &[curl[x,y]f(x,y) = g(x,y)=0 curl[x,y]g(x,y)]}
The constrained extrema of f are critical points of the Lagrangian , but they are not necessarily local extrema of it.

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

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

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

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

https://en.wikipedia.org/wiki/Linear_least_squares_(mathematics)

Xb=y [n,m].[n,1]=[n,1] does not have solution, so to find the best fitting solution we do quaratic minimization b^=arg[b]min S(b) and S is objective function (here it is called r)

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

Wolfe conditions
From Wikipedia, the free encyclopedia
In the unconstrained minimization problem, the Wolfe conditions are a set of inequalities for performing inexact line search, especially in quasi-Newton methods, first published by Philip Wolfe in 1969.[1][2]
In these methods the idea is to find min f(x)

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

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.