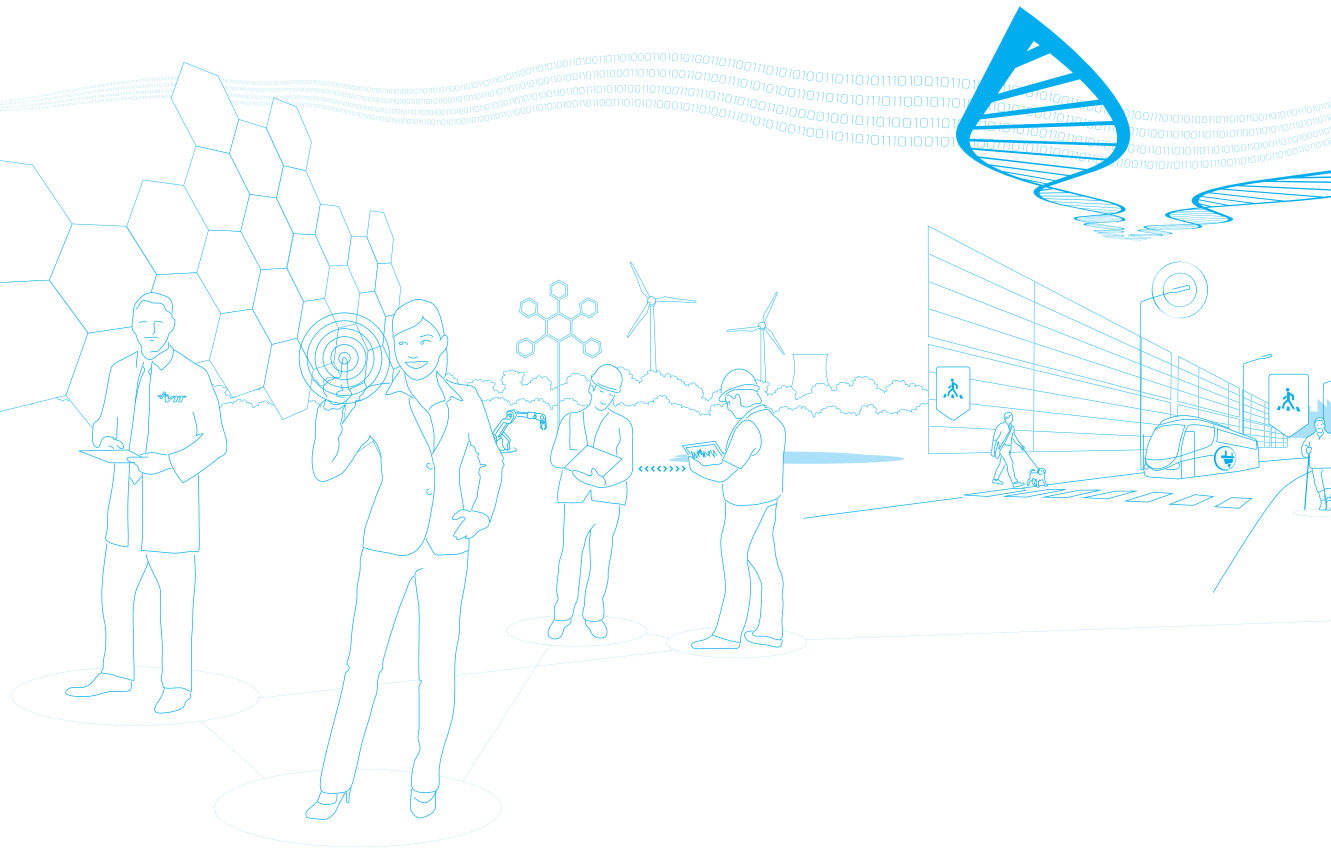




Introduction to constrained Gibbs energy methods in process and materials research

Pertti Koukkari



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Monifaasisysteemien laskenta rajoitettua Gibbs'in energian minimointia käyttäen.
Pertti Koukkari. Espoo 2014. VTT Technology 160. 100 p. + app. 11 p.

Abstract

In process and materials chemistry, digitalization with computational methods has been a long-time continuing process. The methodology based on numerical methods in reaction kinetics as well as for fluid phase thermodynamics applying equations of state has been well established. During the last two decades, however, multi-phase technology based on the minimization of Gibbs free energy has made progress in such fields of process and materials chemistry, where the conventional methods have not been applicable. Recent advancements also include introduction of such new Gibbs'ian algorithms, which, in addition to complex equilibrium problems, facilitate modelling of time-dependent dynamic changes in multi-phase systems.

Within the said period, VTT has been an active performer in the development of multiphase Gibbs'ian techniques. The research work performed at VTT has led to several new algorithms with practical industrial applications. The particular focus has been the development of the Constrained Gibbs Free energy minimization technique, where instead of material balances and stoichiometric relations derived thereof, also immaterial physical conditions are applied as constraints in the free energy minimizing calculation.

In this report, the method of constrained Gibbs energy minimization for calculating chemical equilibria in arbitrary multiphase systems is derived using basic thermodynamic concepts. The method of Lagrange undetermined multipliers is introduced for a simple system of an ideal gas phase and a number of condensed phases, constrained by the number of moles of the system components. The use of additional constraints in the Gibbs energy minimization procedure is facilitated by applying the concept of generalised work-coefficients as the Lagrange multipliers of immaterial components in the system. The thus introduced method of immaterial constraints in Gibbs energy minimization is illustrated with a number of simple practical examples such as electrochemical Donnan equilibria applied for pulp suspensions, surface equilibria and systems constrained by reaction kinetics via the extent of chemical reactions. A few examples of non-equilibrium and parametric phase diagrams calculated with the immaterial constraints are also given. Finally, the applicability of the method for biochemical systems is shortly discussed.

Keywords

Gibbs free energy, constrained minimization, immaterial constraint, work-coefficient, extent of reaction, paraequilibrium

Monifaasisysteemien laskenta rajoitettua Gibbsin energian minimointia käyttäen

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Tiivistelmä

Laskennallisten menetelmien käyttö prosessi- ja materiaalitekniikassa on jatkunut useiden vuosikymmenien ajan uusien numeeristen tekniikoiden käyttöönoton seurattessa tietokoneiden laskentatehon kasvua. Etenkin reaktiokinetiikkaan, virtaustekniikkaan ja termodynamiikan tilanyhtälöihin perustuvat menetelmät ovat saavuttaneet vahvan jalansijan myös näiden alojen teollisuudessa. Lisäksi kahden viimeksi kuluneen vuosikymmenen aikana termodynaamiset monifaasisystemien menetelmät, jotka perustuvat tilanyhtälöiden asemesta systeemin vapaan energian (Gibbsin energian) minimointiin, ovat voittaneet alaa etenkin sellaisissa prosessi- ja materiaalitekniikan tasapainosovelluksissa, joissa perinteiset tilanyhtälömenetelmät ovat osoittautuneet riittämättömiksi. Termodynaamisen tasapainolaskennan ohella on kehitetty Gibbsin energiaan nojaavia algoritmeja, jotka mahdollistavat myös kiinteistä rajoitettujen ajasta riippuvien monifaasisysteemien simuloinnin.

VTT:llä 1990-luvun puolivälistä jatkuneessa tutkimustyössä on kehitetty erityinen rajoitetun vapaan energian laskentateknikka osittaisten ja ajan suhteen rajoitettujen kemiallis-termodynaamisten systeemien kvantitatiiviseen tarkasteluun. Menetelmä perustuu termodynaamisen vapaaenergiafunktion käyttöön, ja sen minimin numeeriseen ratkaisuun systeemiä tai sen osaa kulloinkin rajoittavien ehtojen voimassaollessa. Uuden lähestymistavan ero perinteiseen Gibbsin energian minimointiin nähden on menetelmän kyky käyttää ainetase-rajoittimien lisäksi fysikaalisesti perusteltuina rajoittimina systeemin aineettomia ehtoja.

Tässä julkaisussa monifaasisysteemeille soveltuva rajoitetun Gibbsin energian menetelmä johdetaan termodynaamisista perussuureista. Vapaa energia minimoidaan soveltamalla Lagrangen määräämättömien kertoimien tekniikkaa yksinkertaiselle monifaasisysteemille, jota rajoitetaan suljetun systeemin ainetaseella. Aineettomien rajoitusten käyttö minimoinnissa on tämän jälkeen esitetty yleistettyjen työkerroimien ja vastaavien työkoordinaattien avulla, jolloin Lagrange-kertoimet antavat ratkaisuna aineettomien systeemikomponenttien kemialliset potentiaalit. Tällä tavoin laajennetulla vapaaenergian laskentateknikalla on havaittu olevan runsaasti sovelluksia, joista yksinkertaisin esimerkein kuvataan rajoitetun vapaaenergiatekniikan käyttö sähkökemiallisen Donnan-potentiaalin määräämiseen kuitususpensioissa sekä edelleen sen soveltaminen reaktiokineettisesti rajoitettujen monifaasisysteemien ja kemiallisten reaktorien laskentaan. Materiaalitekniikan sovelluksista käsitellään monikomponenttisysteemien pintaenergiälaskenta sekä partiaalisten ja koostumusrajoitteisten faasisapasainojen laskeminen. Lopuksi arvioidaan vielä lyhyesti mahdollisuuksia soveltaa termodynaamista laskentaa biokemiallisille systeemeille.

Avainsanat Gibbs free energy, constrained minimization, immaterial constraint, work-coefficient, extent of reaction, paraequilibrium

Preface

These notes on multiphase chemical thermodynamics have evolved during ca 20 years of university short course lecturing while simultaneously developing advanced thermodynamic methods for various problems, often with practical industrial significance. The notes have been used as supporting material for teaching computational thermodynamics as an intensive course. During this period of time, the adaptation of the modern computational approach has created a completely new way to treat multicomponent and multi-phase problems in chemical thermodynamics. The new opportunities offered by modern computers and data processing have encouraged both long-standing compilation of comprehensive thermodynamic databases and development of new algorithms for thermodynamic problem solution.

The worldwide community of expert thermochemists has developed a contemporary methodology, which is based on active use of computational techniques in connection with the classical Gibbs'ian theory on multiphase systems. The advances are eminent within both the international academic community and in industry when the rigorous and systematic approach of chemical thermodynamics has been connected with the performance in data-processing of the present-day computers. Novel extensive models have been developed for complex mixtures for high-temperature slags and melts as well as for concentrated aqueous solutions while simultaneously the multicomponent methodology has been successfully applied for interrelated material properties. Use of Gibbs'ian thermodynamics in process modelling and simulation has become a part of the development of best available and new emerging technologies striving for improved sustainability.

Concurrent thermodynamic databanks cover fields for many classes of substances ranging from organic and biochemical systems to various inorganic and metallurgical materials. The systematic data storage and management in connection with the increasing numerical capability of modern computers enables the treatment of the thermochemistry of complex systems as a whole. Thus, accurate theoretical studies of the phase stability and equilibria of systems with a great number of chemical components can be made. Recent advancements also include introduction of such new algorithms, which facilitate modelling of time-dependent dynamic changes in multi-phase systems.

The text will serve as an introduction to the calculation basis of well-defined thermochemical systems when the actual equilibrium calculation is made with the

multi-component Gibbs energy minimization technique. The basic thermodynamic functions as well as the formulation of the chemical potentials used in these calculations will be presented shortly for the introduction of the $\min(G)$ principle. The focus is, however, not in the conventional Gibbs'ian technique nor in its most widely spread applications of calculating global chemical equilibria and equilibrium phase diagram for ideal and non-ideal thermodynamic systems, but in the application of the Gibbs energy minimization method for problems which are subjected to other conditions than those directly derived from the stoichiometry or the mass balance of the system under consideration.

The minimization of Gibbs energy is solved by using the method of Lagrange with mass balance constraints of the independent components as the subsidiary conditions. Following this, the use of complementary, immaterial constraints is introduced and their physical significance in connection with the general Gibbs equation is outlined. A number of examples with immaterial constraints are explained in more detail.

The first 5 Chapters are devoted to fundamental concepts and equations. The fundamental concepts are briefly presented through conventional mathematical techniques of classical thermodynamics and without illustrations. By following the simple calculus, the systematic route from fundamental concepts of work and heat to Entropy and Gibbs free energy should become evident. [Temperature, pressure and amount of matter are then chosen as the independent variables]. Other well-known thermodynamic potentials are not considered, as the Gibbs free energy is by far the most useful when applying computational methods and as there are a great number of comprehensive texts introducing potentials with alternative choices of independent variables.

No specific treatment of the excess Gibbs energy models of various systems is given. Their detailed presentation would be beyond the scope of this kind of text and for a general reader it is more important to understand the broad idea of the division of the chemical potential to its ideal and non-ideal (excess) parts in all kind of real systems. An exception is made in terms of the introduction of Equation of States (EOS) into the Gibbs'ian multiphase domain, as this has rarely been done and will provide new opportunities for the multiphase modelling of organic systems. Chapters 6-8 deal with Gibbs free energy minimization and its relation with the conventional expression of chemical equilibrium.

The constrained Gibbs free energy method (CFE) is explained in Chapter 9. Chapters 10-15 involve applications of the CFE method. In Chapter 16 the conventions of biochemical thermodynamics are presented and their connection with CFE is shortly explained.

As for notation, the formalism of generalized work coordinates and work coefficients, originally introduced by Haase has been used quite extensively. Though this approach may appear less specific and less familiar, it is well-founded for the later introduction of the constrained Gibbs energy method, where the different work terms appear as formally equivalent.

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List of abbreviations

CFE	constrained Gibbs (free) energy minimization
EOS	equation of state
KKT	Karush-Kuhn-Tucker (inequality) conditions for optimization problems
LCE	local chemical equilibrium
NIST	National Institute of Standards and Technology (USA) (www.nist.gov)
NLP	non linear programming
$\min(G)$	minimum of Gibbs energy or Gibbs energy minimization
RCCE	rate controlled constrained equilibrium method
SGTE	Scientific Group Thermodata Europe (www.sgte.org)
VL	Vapour-liquid system
VLE	Vapour liquid equilibrium

List of symbols

A	surface or interfacial area	m^2
A_k	molar surface area	$\text{m}^2 \cdot \text{mol}^{-1}$
A_0	unit (molar) area	$\text{m}^2 \cdot \text{mol}^{-1}$
A_r	affinity of reaction r	J
B	magnetic flux density	T
C_P, C_V	heat capacity at constant P or V	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
E	energy	J
F	Faraday constant	$\approx 96485 \text{ C} \cdot \text{mol}^{-1}$
G	Gibbs free energy	J
G'	free energy function matching system specific constraints	J
H	enthalpy	J
I	ionic strength of aqueous solution	$\text{mol} \cdot \text{dm}^{-3}$
K_a, Q_a	equilibrium constant and reaction quotient based on activities	
L_j	thermodynamic work coefficient j	
l_j	thermodynamic work co-ordinate j	
M	molar magnetisation	$\text{J} \cdot \text{T}^{-1} \cdot \text{mol}^{-1}$
P	pressure	$\text{Pa} = \text{N} \cdot \text{m}^{-2}$
Q	heat	J
R	gas constant	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
S	entropy	$\text{J} \cdot \text{K}^{-1}$

T	temperature	K, °C
U	internal energy	J
W	work	J
Z	arbitrary extensive property	
\mathbf{A}	$(M \times N)$ matrix of stoichiometric coefficients	
a_{kj}	stoichiometric coefficient between component j and species k . Element of \mathbf{A}	
a_k	activity of species k	
\mathbf{b}	$(M \times 1)$ column vector of molar amounts of components	mol
b_j	molar amount of component j	mol
c_k	molar concentration of species	mol · dm ⁻³
\hat{f}_k	fugacity	Pa = N · m ⁻²
L	Lagrangian function	
M	number of components in the system	
m	magnetic moment	J·T ⁻¹
m_k	molal concentration of species	mol · kg _{H₂O} ⁻¹
N	number of species in the system	
NC	number of components in the system	
\mathbf{n}	$(N \times 1)$ column vector of molar amount of species	mol
n_k	amount of species	mol
q^α, Q^α	charge total charge of region α	C
R	number of reactions	
x_k	mole fraction of species	
u_k	constant mole fraction of substitutional species k	
q^α, Q^α	charge total charge of region α	C
z_k	charge number of species k	
A	frequency factor	s ⁻¹
E_a	activation energy	J·mol ⁻¹

k	chemical reaction rate constant ($p =$ order of reaction)	$\text{mol}^{1-p} \cdot (\text{dm}^{-3})^{p-1} \cdot \text{s}^{-1}$
R	number of reactions	
r	chemical reaction rate	$\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$
t	time	s
γ_k	activity coefficient of species k	
φ_k	electrochemical potential	V
ϕ	electric potential	V
$\hat{\phi}_k$	fugacity coefficient	
λ_j	Lagrange multiplier j	
Λ	Donnan distribution coefficient	
μ_k	chemical potential of species k	J mol^{-1}
$\nu_{k,r}$	stoichiometric coefficient of species k in reaction r	
π_j	chemical potential of component j	J mol^{-1}
Π	volume constraining osmotic or other pressure	$\text{Pa} = \text{N} \cdot \text{m}^{-2}$
σ	surface tension	J m^{-2}

The used subscripts and superscripts are explained in the text.

1. Introduction

During the last decades quite some effort has been laid on computational thermodynamics with main focus on its equilibrium applications in materials science and complex multiphase chemistry, in particular for studies of global chemical equilibria and construction of phase diagrams. Then, there still appear little or no treatments of computational multiphase thermodynamics with emphasis in process simulation. However, applications in this field have extensively been developed during the last 20 years, while the advantages of using Gibbs'ian thermodynamic methods in process models have also become more evident. In chemical engineering there is a much longer tradition in process simulation with extensive use of thermodynamic equations of state for different conditions. Such methods are successful for processes where a limited number of fluids appear as major phases. For more complex systems with brines and solid phases, mineral processing, metallurgy, steelmaking as well as in pulp and paper chemistry more degrees of freedom are needed and it has proven advisable to use Gibbs free energy models. The accuracy of such models, due to their ability to reproduce the rich multi-phase chemistry and thermodynamic state properties is often astonishing, even when applied to complex industrial processes.

The use of state properties also allows for linking between various phenomena, whether physical, chemical or even biological. The simulation model appears useful, if it may bring together quantitative and interdisciplinary relations and dependencies. Particularly in macroscopic systems, where thermal, electrical or mechanical functions affect the chemical or biochemical changes, the state properties based on Gibbs energy provide a general methodology to be applied for quantitative calculations.

Yet, the conventional global equilibrium methods are not always applicable, as the systems often are constrained by other factors than their (internal) molar abundancy, the other constraining factors including effects due to e.g. electrochemical, -magnetic, interfacial or mechanical work. Such conditions can be taken into account by using conserved immaterial components in the Gibbs'ian calculation system. The immaterial components may represent a physical entity (such as surface area) or be deduced as virtual aids from a given physical condition (e.g. partitionless phase transformation). Their introduction with the *Constrained Free Energy method (CFE)* enables the use of work-related constraints into the con-

temporary Gibbs energy minimization routines. This method also allows for systematic and rigorous simulation of various partial equilibria, including those constrained by reaction kinetics while the assumption of local chemical equilibrium (LCE) is valid for the 'unconstrained' reactions. The significance of the CFE method is thus quite considerable, as its applications range in materials science from complex surface tension calculations to metallurgical paraequilibria and in process simulation from electrochemical Donnan equilibria (e.g. in pulp suspensions) to the use of Gibbs'ian methods in kinetically controlled chemical reactor engineering.

Applying multi-phase thermodynamics in process simulation inherently provides treatment of non-isothermal systems in process modelling as the free energy data will be used as temperature dependent. By applying the constrained minimization method the extent of reaction can be introduced to the thermodynamic calculation as an additional time-dependent parameter, the calculation then resulting with the non-zero affinities of the kinetically constrained reactions (at the global equilibrium all affinities of chemical reactions must of course be zero). For chemical reactors, the non-isothermal CFE simulation allows for the effect of the changing temperature on incremental reaction rates. Heat exchange between the system (often called as the control volume of simulation) and its surroundings is also straightforward to include by using an appropriate heat transfer model. Thus, the chemical change becomes simulated as a thermodynamic 'natural process', and the result of the calculation can be verified to follow the basic laws of the thermodynamic theory.

The text pursues to serve as an introduction to the usage of the advanced Gibbs free energy techniques in process and materials research. The focus is thus on the basic methods. As for more sophisticated treatments, the reader is referred to a number of former publications while several industrial applications have also been described earlier (Koukkari 2009).

The formalism used in this text follows that of Haase (Haase 1990), whose excellent introductory part of 'Fundamental concepts' is recommended for more extensive studies on macroscopic thermodynamics. Some features have also been adapted from the classic books of Lawden (Lawden 2005) and Guggenheim (Guggenheim 1977). However, in the present text the basic concepts of chemical thermodynamics have been gathered while keeping in focus their further use in Gibbs energy minimization calculations and in particular their significance when introducing the constrained Gibbs energy minimization method.

2. Basic concepts

In Figure (2.1) a *volume element* of a chemical reactor in correspondence with its surroundings is shown. In the following, the thermodynamic equations to interpret any chemical processes in the control volume are compiled. The basic laws of thermodynamics will be followed, yet without their axiomatic representation

The volume element in Figure 2.1 may, when calculations concerning its thermochemical behaviour are done, be treated as a *thermodynamic system*. A system which is so separated from the outside world that no matter can pass through the system boundary is called *closed*. A system, which may exchange matter with its surroundings is called *open*. Respectively, expressions "closed region" or "open region" may be used. The term isolated is used of a system which is cut off from all exchange with the surroundings and thus applies to a system, which does not exchange heat or other forms of energy with its surroundings.

The variables which describe the system macroscopically are called *state variables*. For the thermodynamic application, the internal variables such as internal energy, temperature, pressure, volume, amounts of different substances etc. are the most meaningful. The state variables are represented by macroscopic measurable quantities. The thermodynamic theory also gives consistent mathematical relations for these quantities, thus providing the basis for chemical calculus.

An *intensive variable* is independent of the quantity of matter considered and has a definite value at each point of the materially filled space. An *extensive quantity* is proportional to the quantity of matter in the region considered and is increased by n times when the amount of all substances present is increased n times at a fixed value of the intensive variables. For example, temperature (T) and pressure (P) are intensive variables; volume (V) is an extensive quantity.

With changing internal variables (e.g. varying chemical composition) the system of Figure 2.1 experiences a process called *state change*. The processes that actually take place are called *natural processes*. The process is called *reversible* if the conceptual change can be reversed and the system returned to its original state without changes remaining in the surroundings of the system. All actual processes are *irreversible*, that is, a system cannot be recycled with a set of state changes without having an effect on the surroundings of the system. The concept of a reversible process is, for example, useful to distinguish between practical variables, such as different kinds of work (Haase 1990).

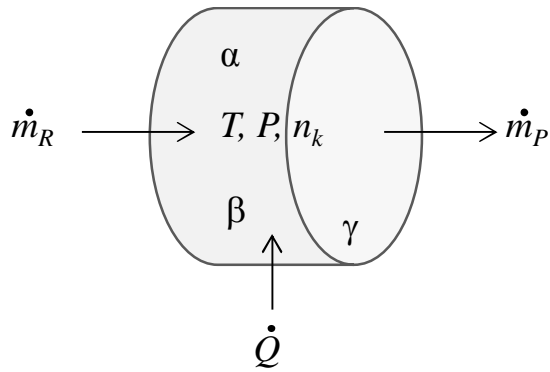


Figure 2.1. Volume element of a chemical reactor with mass flow of reactants (subscript R) and products (subscript P); \dot{Q} denotes time-dependent heat flux. The Greek letters indicate presence of separate regions (phases).

3. Work, heat and enthalpy

3.1 Generalised work

The fundamental concepts of work are most often used for the illustration of the macroscopic thermodynamic theory. Work is the measurable entity, which leads to the more abstract concepts of thermodynamic potentials, and serves also to introduce the fundamental principle of conservation of mass and energy. As the work appears in several forms, it is often useful to use a single generalized concept for it. The notation of Haase is systematic and used below in somewhat simplified expressions. The generalised *reversible deformation* work $[W]$ is then defined for a closed system as follows:

$$dW_l^\alpha = \sum_i L_i^\alpha dl_i^\alpha \quad (3.1)$$

where L_i is the generalized work-coefficient with intensive character and l_i is the corresponding generalized work-co-ordinate with extensive character. [The super-script α refers to the region or phase under consideration]. Familiar examples of work are: $dW_l = -PdV + \sigma dA$ for an isotropic system with infinitesimal compression or expansion work (P = pressure, V = volume) and work due to surface tension (σ = surface tension, A = surface area).

The general expression of work $[W]$ performed for the region (phase) α is:

$$dW^\alpha = dW_l^\alpha + dW_{diss}^\alpha + dW_a^\alpha \quad (3.2)$$

where W_{diss} is the *dissipative work* due to such effects as friction, turbulence, electric conduction etc. Alternatively for an arbitrary infinitesimal change in a system of several regions:

$$dW = dW_l + dW_a + dW^* \quad (3.3)$$

where W_a is the *external work* done on the system, caused by external force fields and bringing about changes in the external co-ordinates of the system. In the latter

expression, W^* includes the *dissipative work* due to such effects as friction, turbulence, electric conduction etc. For a system of several regions it may also contain reversible portions in addition to the dissipation effects (Haase 1990).

It is worth emphasizing that several kinds of reversible work may be utilized in computational chemical thermodynamics. From the point of view of 'purely' chemical systems, the reversible compression/expansion work $-PdV$ is yet often the most interesting. For this reason and also for its familiarity in classical textbooks it will also be most frequently used below. However, several other forms of internal or external work (electrochemical, surface, electric-magnetic) will have salient effects on the multiphase chemistry of the interrelated properties of functional materials and thus they become more important in the latter parts of the text.

3.2 Energy and heat

For the closed system, the following relations between energy, work and heat hold:

$$W = \Delta E \quad (\text{adiabatic change}) \quad (3.4)$$

$$W \neq \Delta E \quad (\text{non - adiabatic change}) \quad (3.5)$$

$$Q \equiv \Delta E - W \quad (\text{non - adiabatic change}) \quad (3.6)$$

where E designates the *energy* of the system and Q is called the *heat* supplied to the system from the surroundings. Thus the *adiabatic change* takes place in a thermally insulated system.

Accordingly, the change in energy ΔE is:

$$\Delta E = Q + W \quad (3.7)$$

$$dE = dQ + dW \quad (3.8)$$

where dQ and dW are inexact differentials, as heat and work are not functions of state, but concepts which indicate how the change of state will occur, i.e. they will describe the interaction of the system with its surroundings during the course of the change. The values of Q and W thus are dependent on the path of the integration and cannot be defined by the properties of the initial and final state.

Further, the energy of a system is divided to its *kinetic*, *potential*, and *internal* parts:

$$E = E_{kin} + E_{pot} + U \quad (3.9)$$

where

$$U = \sum_{\alpha} U^{\alpha} \quad (3.10)$$

with U denoting the internal energy of the system. It will be obvious that for multi-phase thermodynamic treatment, the interest will be in the internal changes of the system, and consequently the internal energy is the focal quantity in what follows.

Thus for an internal state change in a closed system ($W_a=0$, $\Delta E = \Delta U$):

$$\Delta U = Q + W = Q + W_l + W^* \quad (3.11)$$

from which particular cases such as $\Delta U = W^*$ for the adiabatic change with constant work-co-ordinates follow. This balance also sets the first law of thermodynamics for a closed system without chemical changes. Considering a system with merely reversible deformation work, the infinitesimal change in the internal energy becomes:

$$dU = dQ + dW_l ; \quad dU = dQ - PdV \quad (3.12)$$

where the latter form is for systems with reversible compression or expansion work. The sign conventions for work and heat are illustrated in Figure 3.1.

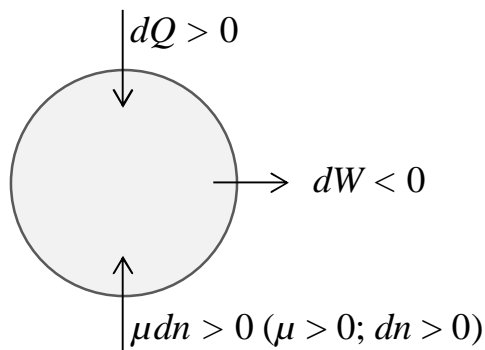


Figure 3.1. The sign conventions for the first law of thermodynamics. The term μdn relates to chemical potentials and exchange of matter (see Chapter 4).

3.3 Enthalpy

For any region α a new state variable H^{α} can be defined in terms of the internal energy and the reversible deformation work:

3. Work, heat and enthalpy

$$H = \sum_{\alpha} H^{\alpha} \quad (3.13)$$

$$H^{\alpha} \equiv U^{\alpha} - (-P^{\alpha}V^{\alpha}) = U^{\alpha} + P^{\alpha}V^{\alpha} \quad (3.14)$$

Equation (3.14) is valid for the isotropic region (α) with no electrification and magnetization (the negative pressure $-P^{\alpha}$ thus being the sole work-coefficient of the region). *Enthalpy* (H) of the system is of extensive character. To define its relation to work and heat, consider an internal state change in a closed system with constant pressure. Then, omitting superscripts, from (3.1) there is:

$$dW_l = -PdV$$

$$W_l = -P\Delta V \quad (\text{constant } P)$$

and

$$\Delta U = Q + W = Q + W_l + W^*$$

from which

$$\begin{aligned} \Delta H &= \Delta(U + PV) \\ &= \Delta U + P\Delta V = Q + W_l + W^* + P\Delta V = Q - P\Delta V + W^* + P\Delta V \\ \Delta H &= Q + W^* \quad (\text{const. } P) \end{aligned} \quad (3.15)$$

The same reasoning applies for all systems with constant work-coefficients, which means that the energy appearing as heat or other than expansion work will equal ΔH in such systems which are free to expand or to contract as the process occurs. Thus, changes in these systems due to Q (heat exchange with the surroundings) or W^* (work due to dissipation effects or, e.g. electrochemical processes) reflect in the *enthalpy state function*, which is so extensively used in all practical calculations involving interrelated chemical and thermal phenomena. Typical examples of systems with constant work coefficients are kilns and furnaces, which most often are operated at ambient pressure. For systems that involve reactors with changing pressure and with heat losses the definition of enthalpy from (3.14) is used together with the appropriate properties of ΔU .

3.4 Partial molar quantities

Changes in multicomponent systems, which involve chemical reactions, will necessitate the expression of properties in terms of the amounts of matter and as related to their molar composition. Within a single region, for an arbitrary extensive property Z (e.g. volume, internal energy, enthalpy) there is:

$$Z = Z(T, L_i, n_k) \quad (3.16)$$

[(index α omitted for sake of brevity)] with the temperature T , the work-coefficients L_i and the amounts n_k of the substances contained in the region have been chosen as the independent variables (L_i will often be replaced by P , when only PV work is considered). The *partial molar quantity* of substance k for the considered region is defined as:

$$Z_k \equiv \left(\frac{\partial Z}{\partial n_k} \right)_{T, L_i, n_{j \neq k}} \quad (3.17)$$

The mole fraction of species k is:

$$x_k \equiv \frac{n_k}{\sum_k n_k} = \frac{n_k}{n} \quad (3.18)$$

The molar quantity is:

$$Z_m \equiv \frac{Z}{n} \quad (3.19)$$

and the generalized density of Z :

$$Z_V \equiv \frac{Z}{V} \quad (3.20)$$

Further, the extensive quantity is received from its partial molar contributors:

$$Z = \sum_k n_k Z_k \quad (3.21)$$

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This relation follows mathematically from Euler's theorem valid for homogenous functions of first degree and thus the extensive quantities (Z) are made up additively by a contribution Z_k from unit amounts of each substance k .

Finally, from (1) the total differential of Z in terms of the temperature, pressure and amounts of substances:

$$dZ = \left(\frac{\partial Z}{\partial T} \right) dT + \left(\frac{\partial Z}{\partial P} \right) dP + \sum_k Z_k dn_k \quad (3.22)$$

where the summation is taken over all substances (n_k) within the region. The partial molar quantities are then as defined in Equation (3.17). While the partial derivatives in terms of temperature and pressure are of so outstanding importance for many observations in classical thermodynamics involving changes due to heat and work, the partial molar quantities are of no less significance in systems with chemical and phase changes. They become particularly useful when the extensive property (Z) represents a thermodynamic potential of a multi-component multi-phase system such as the Gibbs free energy.

3.5 Heat capacity

Considering the absorption of heat into a region (with no work done on or by the system) either constant volume or constant pressure may be assumed. Consequently, the heat capacity for such a region can be defined either by the internal energy or by the enthalpy, as follows:

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{V, n_k} \quad (3.23)$$

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_{P, n_k} \quad (3.24)$$

Thus, applying (3.22) for enthalpy:

$$dH = \left(\frac{\partial H}{\partial T} \right) dT + \left(\frac{\partial H}{\partial P} \right) dP + \sum_k H_k dn_k$$

Using heat capacity (C_P), partial molar enthalpies (H_k) and assuming a system with constant pressure this becomes:

$$dH = C_p dT + \sum_k H_k dn_k \quad (3.25)$$

for the simple chemical system. Using (3.15) in (3.25) gives:

$$\Delta H = \int_I^II C_p dT + \int_I^II \sum_K H_k dn_k = Q + W^* \quad (3.26)$$

$$\Delta H = \int_I^II C_p dT + \int_I^II \sum_K H_k dn_k = Q \quad (3.27)$$

Here, the integration is performed between two arbitrary states with different temperatures T_I and T_{II} , producing the enthalpy balance of a thermodynamic system with constant pressure. The latter expression is valid for such closed system, in which chemical reactions may occur but no work is done on the system ($W^* = 0$). This relation forms the basis for the calculation of non-isothermal processes, as the balance may be written to an arbitrary volume or system element. If the heat transfer from the element to its surroundings is known (by measurement or from a heat transfer function) and the composition can be deduced from a (thermo)chemical solution procedure, such as Gibbs energy minimization, the temperature of the system can be solved. While the molar enthalpies as well as heat capacities are functions of temperature and the chemical composition, the solution of T will most often be iterative, balancing the left and right hand sides of (3.27) by solving both composition and temperature to match the known heat transfer to or from the element.

3.6 Enthalpy and heat in open systems

When processes of practical importance are quantitatively described, it is often necessary to define the streams of matter in terms of open systems. This will then need some additional notation, which will specify the exchange of matter and heat across the system boundaries. A short review of the notation for open systems, consistent with the rest of the text has been collected in Appendix A.

The term 'work' is actually indeterminate for open regions. However, expressing W for the work that would be done to region if it were closed there is (Haase 1990, p.17):

$$dW = \sum_i L_i dl_i + dW_{diss} + dW_a \quad (3.28)$$

when all the individual terms to the right have definite meanings also for open regions. This applies for the actual work-coefficients (L_i) and the work-coordinates

3. Work, heat and enthalpy

(l_i). The dissipative work and the work due to external force fields affecting the open region in question may be calculated from their outside sources (electric-magnetic work, lifting work in a gravitational field, acceleration work etc.).

The heat absorbed by an open phase from surroundings during an infinitesimal state change is (cf. 3.8)

$$dQ \equiv dE - dW - \sum_k H_k d_e n_k \quad (3.29)$$

Here the relation (A1, see Appendix A) has been used for the infinitesimal increase of matter either due to material transport or chemical reactions:

$$dn_k = d_r n_k + d_e n_k \quad (A.1)$$

where the subscript e refers to exchange of matter either between neighbouring regions or with the surroundings of the entire system and subscript r refers to chemical reactions within the system.

In (3.29) the enthalpy 'carry-over' due to exchange of matter between the region and its surroundings has been taken into account. For such internal changes with $dE=dU$ and $dW_a=0$,

$$dQ = dU - \sum_i L_i dl_i - dW_{diss} - \sum_k H_k d_e n_k \quad (3.30)$$

or, in the more usual isotropic system without electrical or magnetic effects:

$$dQ = dU + PdV - \sum_k H_k d_e n_k \quad (3.31)$$

At constant pressure one has, for the entire system, by (3.15) and (3.25):

$$dU - PdV = d(U + PV) = dH = C_p dT + \sum_k H_k dn_k$$

Using this and (A1) in (3.31) the following relation is received:

$$dQ = C_p dT + \sum_k H_k d_r n_k \quad (3.32)$$

which then reduces to Equation (3.27) for an isotropic closed system with no exchange of matter from either outside or from neighbouring regions ($d_e n_k = 0$).

Thus the 'heat' absorbed by the open region is balanced by the temperature change of the system and enthalpy change due to the chemical reactions within the system.

4. Entropy and its properties

4.1 Entropy and chemical potential

The state function *entropy* (S) at constant amounts of substances n_k^α is defined by using internal energy and volume as the complete set of independent variables for the system where no chemical or phase changes take place. Then, the differential form of entropy is as follows:

$$TdS = dU + PdV \quad (4.1)$$

Substituting dQ from Equation (3.12) to (4.1) there is

$$dS = \frac{dQ}{T} \quad (4.2)$$

which connects the quantity of heat to the state properties U and S and the temperature T appears as the integrating factor for dQ . This relation is due to the second law of thermodynamics and thus the entropy differential (4.1) presents a fundamental equation which combines the first and second laws.

Further from (4. 1)

$$T \left(\frac{\partial S}{\partial U} \right)_{V_i, n_k} = 1 \quad (4.3)$$

$$T \left(\frac{\partial S}{\partial V} \right)_{U, n_k} = P \quad (4.4)$$

Note that if the general form of reversible work $dW_l^\alpha = \sum_i L_i^\alpha dl_i^\alpha$ is used instead of $-PdV$, equation (4. 4) takes the form

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$$T^\alpha \left(\frac{\partial S^\alpha}{\partial l_i^\alpha} \right)_{U, l_j, n_k} = -L_i \quad (4.5)$$

which defines different work-coefficients in terms of the entropy state function. Thus, all work processes have an effect on the entropy state function.

Equation (4. 1) represents the entropy change in a system, where yet no chemical changes take place. When they do occur, the variable amounts of substances as well contribute to the entropy function. Then, by analogy with the work-coefficients (L_i) there is

$$\mu_k^\alpha \equiv -T^\alpha \left(\frac{\partial S^\alpha}{\partial n_k^\alpha} \right)_{U, l_j, n_{j \neq k}} \quad (4.6)$$

And thus the differential of the entropy may be generalized for chemically reacting systems:

$$T^\alpha dS^\alpha = dU^\alpha + P^\alpha dV^\alpha - \sum_k \mu_k^\alpha dn_k^\alpha \quad (4.7)$$

Here again only $-PdV$ work in each region has been taken into account. This is often called the *generalized Gibbs equation*. The internal energy is a homogeneous function of degree one in terms of the extensive variables S^α , V^α and n_k^α , and thus from Euler's theorem:

$$T^\alpha S^\alpha = U^\alpha + P^\alpha V^\alpha - \sum_k \mu_k^\alpha n_k^\alpha \quad (4.8)$$

where μ_k 's refer to the chemical composition of the system and each μ_k^α is called the *chemical potential* of substance k in the respective phase $[\alpha]$. The relation between entropy and chemical potential is given by the definition of μ_k^α in Equation (4. 6). The result (4. 8) results as a conceptual integration over the quantity of material present while keeping all intensive quantities such as temperature, pressure and composition constant.

Replacing the $-PdV$ work term with the general work-coefficients and work-coordinates the Gibbs equation becomes

$$T^\alpha dS^\alpha = dU^\alpha - \sum_i L_i^\alpha dl_i^\alpha - \sum_k \mu_k^\alpha dn_k^\alpha \quad (4.9)$$

and in the Euler form

$$T^\alpha S^\alpha = U^\alpha - \sum_i L_i^\alpha l_i^\alpha - \sum_k \mu_k^\alpha n_k^\alpha \quad (4.10)$$

The more general expressions obviously become important for systems, which, in addition to the reversible deformation work include other kinds of reversible work (e.g. surface work, electrification or magnetization).

4.2 Properties of entropy

The entropy of a system is an extensive quantity:

$$S = \sum_\alpha S^\alpha \quad (4.11)$$

For the arbitrary state change $I \rightarrow II$:

$$\Delta S = S_{II} - S_I = \Delta_a S + \Delta_i S \quad (4.12)$$

where (again) the subscript a refers to exchange between the system and its surroundings and subscript i to an internal process within the system. In terms of differentials:

$$dS = d_a S + d_i S \quad (4.13)$$

The properties of entropy are found by experience as follows:

$$\Delta_a S = 0 \quad (\text{thermally insulated system}) \quad (4.14)$$

$$\Delta_i S = 0 \quad (\text{reversible change}) \quad (4.15)$$

$$\Delta_i S > 0 \quad (\text{irreversible change}) \quad (4.16)$$

$$\Delta_i S < 0 \quad (\text{impossible change}) \quad (4.17)$$

Thermal insulation means prevention of mass and heat exchange with the surroundings. Thus $\Delta_a S$ represents the entropy change of the system due to mass and heat exchange with the outside world and thus it may appear either positive or negative. $\Delta_i S$ is the entropy increase of the system due to processes taking

4. Entropy and its properties

place inside the system, being either positive or zero. The subscripts a and i are respectively used for heat as $d_a Q$ and $d_i Q$ (see Appendix A).

Whereas ΔS and $\Delta_a S$ can during an arbitrary state change be positive, negative or zero, there always is $\Delta_i S \geq 0$. This condition follows from the second law of thermodynamics¹ and thus for irreversible changes the entropy production is always positive.

¹ The change in internal energy U e.g. in an isothermal constant volume system is ΔU , which in the surroundings leads to the respective entropy change $\Delta U/T$. The total entropy change (of the universe) is then

$$\Delta S(\text{total}) = \Delta S - \frac{\Delta U}{T} = \Delta_a S + \Delta_i S - \frac{\Delta U}{T}$$

As $\Delta_a S$ must be equal with $\Delta U/T$, the 2nd law of thermodynamics then states that $\Delta_i S \geq 0$ (for more detailed treatments see Haase 1990 or e.g. Atkins 2007).

5. Gibbs energy of the system

The thermochemical *Gibbs energy* (G) is deduced from Equation (4. 10) as follows:

$$\sum_k \mu_k^\alpha n_k^\alpha = U^\alpha + \sum_i L_i^\alpha l_i^\alpha - T^\alpha S^\alpha \quad (5.1)$$

$$= H^\alpha - T^\alpha S^\alpha \quad (5.2)$$

$$\equiv G^\alpha \quad (5.3)$$

and with the summation of all phase contributions the extensive state function (G) is received:

$$G = \sum_\alpha G^\alpha \quad (5.4)$$

The partial molar Gibbs energy is (see 3.17 and 3.21):

$$\mu_k = \left(\frac{\partial G}{\partial n_k} \right)_{n_{i \neq k}} = \mu_k(T, P, n_k) \quad (5.5)$$

$$G = \sum_k n_k \mu_k = \sum_\alpha \sum_k n_k^\alpha \mu_k^\alpha \quad (5.6)$$

The Gibbs energy is deduced from the generalized Gibbs equation, its complete set of independent variables being T and P (or, more generally L_i) with the amount of matter (n_k^α), as expressed in (5.6) on the right hand side. It is an extensive state property, which is received from the internal energy with the respective

5. Gibbs energy of the system

change of variables (from V to P (from L_i to L_i), and from S to T). For any problem dealing with chemical and phase changes, where temperature and pressure as intensive variables are either easily held constant or can be effortlessly measured, this choice is obviously the most practical.

The functionality of the Gibbs energy can be deduced by using its definition (5.2) and considering the respective change of G at constant temperature and pressure, $\Delta G(T,P)$. By using (3.14) and (5.2)- (5.4) there is $\Delta G(T,P) = \Delta U + P\Delta V - T\Delta S$. Here $P\Delta V$ deducts the expansion work at constant pressure and $- T\Delta S$ the heat transferred to the surroundings in a constant temperature reversible process (cf. 4.12), thus leaving that part of the energy which yet may be utilized for useful (non-expansion) work. A significant contribution to the Gibbs (free) energy is deduced from the changes in the chemical composition of the system, but also will include effects arising from e.g. electric-magnetic, mechanical or interfacial work.

From Equations (5.1) and (4. 9), the differential form of Gibbs energy is

$$dG^\alpha = - S^\alpha dT^\alpha - \sum_I l_i^\alpha dL_i^\alpha + \sum_k \mu_k^\alpha dn_k^\alpha \quad (5.7)$$

$$dG^\alpha = - S^\alpha dT^\alpha + V^\alpha dP^\alpha + \sum_k \mu_k^\alpha dn_k^\alpha \quad (5.8)$$

The latter form is valid for the isotropic system with e.g. no effects due to electrification or magnetization. For the partial molar quantities, from (5.5) and (5.2) one has

$$\mu_k^\alpha = H_k^\alpha - T^\alpha S_k^\alpha \quad (5.9)$$

Equation (5.9) is of great importance in computational thermodynamics, as it forms the starting point for Gibbs energy calculations. The tabulated values mostly appear in the form of molar enthalpies and entropies of chemical substances, or, as temperature-dependent formulas of heat capacities, from which entropies and enthalpies easily can be derived. Thus the convention of Gibbs energy calculations is most conveniently based on Equations (5.6) and (5.9). The use of enthalpy and heat capacity data or adequate temperature-dependent Gibbs energy formulas also allows for direct calculation of heat balances and enthalpic processes, which in industrial practice often appear as non-isothermal.

6. Entropy and Gibbs function at chemical equilibrium

As defined above, entropy is an extensive function of internal energy U , the work co-ordinate l_i , and amount of substance n_k . For the isotropic, 'chemical' system without electric and magnetic effects the work co-ordinate may be replaced by volume V :

$$S = S(U, V, n_k) \quad (6.1)$$

The sources of entropy are given in the following sentence (see Appendix B to derive it):

$$T^\alpha dS^\alpha = d_a Q^\alpha + T^\alpha \sum_k S_k^\alpha d_a n_k^\alpha + dW_{diss}^\alpha + d_i Q^\alpha + T^\alpha \sum_k S_k^\alpha d_u n_k^\alpha - \sum_k \mu_k^\alpha d_r n_k^\alpha \quad (B.6)$$

With the subscript notation of Appendices A and B the right hand terms are obvious giving the sources of entropy as the heat exchange between the system and its surroundings ($d_a Q$), the transport of entropy due to exchange of matter between the system and its surroundings ($d_a n_k$), dissipative work, heat transfer within the system ($d_i Q$), the transport of entropy between the regions of the system ($d_u n_k$) and, finally due to entropy production in chemical reactions.

To keep the further treatment simple a single isotropic phase without electric or magnetic polarization is considered below and superscripts will be omitted for brevity. The condition for chemical equilibrium is then received for the homogeneous single phase (closed) system [which may, however be generalized for heterogeneous and continuous systems].

The criteria of *equilibrium* are listed e.g. by Haase as follows:

1. The macroscopic kinetic energy of the whole system is constant
2. No exchange of matter takes place with the outside world
3. No work is done on the total system
4. No heat flows out of the surroundings into the system
5. The total volume of the system is constant.

6. Entropy and Gibbs function at chemical equilibrium

At equilibrium, the system experiences no changes, and all state functions will be constant. Then, for entropy the condition $dS=0$ may be derived e.g. from (B.6) using the above conditions.

First, when considering the single isotropic phase one has $d_u n_k=0$ (no transfer of material from the neighbouring regions) and $d_i Q=0$ (no heat transfer within the system). For the closed system $d_a n_k=0$, and excluding dissipative work, $dW_{diss}=0$. [Note that the latter two exclusions are also in accordance with the equilibrium conditions 2 and 3 as listed above]. Thence from (B.6) for the homogenous, closed system:

$$TdS = d_a Q - \sum_k \mu_k d_r n_k \quad (6.2)$$

In (4.13) the entropy change due to interaction between the system and the surroundings and due to processes taking place inside the system was expressed as:

$$dS = d_a S + d_i S \quad (4.13)$$

then evidently from this and (6.2):

$$Td_a S = d_a Q \quad (6.3)$$

$$Td_i S = -\sum_k \mu_k d_r n_k \quad (6.4)$$

At equilibrium, the closed system is in the same temperature as its surroundings, and no heat transfer takes place [equilibrium condition 4.]. Thus, $d_a Q = 0$ and from (6.3) and (4.13) there is:

$$Td_a S = d_a Q = 0 \quad (\text{at equilibrium}) \quad (6.5)$$

From (6.4), (4.13) and (6.5) the chemical equilibrium condition for the closed system thus becomes

$$TdS = Td_i S = -\sum_k \mu_k d_r n_k = -\sum_k \mu_k dn_k = 0 \quad (\text{at equilibrium}) \quad (6.6)$$

The latter expression being valid since for the single phase closed system one may write $d_r n_k = dn_k$ [no mass transfer to/from surroundings or between phases]. Furthermore, from conditions (6.3) and (6.4), one must have $dU = dW + dQ = 0$,

and directly from condition (6.5), $dV=0$ (thermal and mechanical equilibrium) for the closed system. The equilibrium conditions in terms of entropy then are:

$$dS = 0 \quad (6.7)$$

$$dU = 0, \quad dV = 0 \quad (6.8)$$

which may be compared with Equations (6.1) and (4.7).

As was stated above, in systems with chemical or phase changes the Gibbs energy, being a function of temperature, pressure and chemical composition, is most often the practical tool to solve equilibrium situations. There is:

$$G = G(T, P, n_k) \quad (6.9)$$

$$G = \sum_{\alpha} G^{\alpha} \quad (5.4)$$

$$dG^{\alpha} = -S^{\alpha} dT^{\alpha} + V^{\alpha} dP^{\alpha} + \sum_k \mu_k^{\alpha} dn_k^{\alpha} \quad (5.8)$$

For a single isotropic phase the superscripts may be omitted and, at equilibrium, the closed system is at constant temperature and pressure ($dT = dP = 0$):

$$dG = \sum_k \mu_k dn_k = 0 \quad (\text{at equilibrium}) \quad (6.10)$$

which is equivalent with the condition (6.6). [Note that the equilibrium condition for a system consisting of several regions or phases is analogous with an additional summation over all regions $[\alpha]$]. Then the equilibrium temperature and pressure must also be uniform throughout the system. The equilibrium criteria in terms of the Gibbs energy become:

$$dG = 0 \quad (6.11)$$

$$dT = 0, \quad dP = 0 \quad (6.12)$$

Evidently, (6.7) and (6.11) are equivalent and represent extremum points for S and G ($dS = 0, dG = 0$). By using the definition of Gibbs energy ($G = H - TS = U + PV - TS$) and the properties of entropy as defined above, there is

6. Entropy and Gibbs function at chemical equilibrium

$$dG = dU + PdV + VdP - TdS - SdT \quad (6.13)$$

$$dG = dQ - PdV + PdV + VdP - Td_a S - Td_i S - SdT \quad (6.14)$$

for the isotropic closed system, $dQ = Td_a S$ (see eq. 6.3), and at equilibrium, $dT = 0$ and $dP = 0$:

$$dG = -Td_i S \leq 0 \quad (6.15)$$

At equilibrium, following the second law of thermodynamics the Gibbs free energy reaches its minimum (T, P const.). Having a system at constant T and P , solution of condition (6.10) then provides the equilibrium composition of the closed system at the given conditions.

The practical balance or equilibrium calculation is usually performed for the closed system or such (closed) system element as described in Figure (1) according to the above principles.

7. Basis for Gibbs energy calculations

7.1 Conventions for pure substances and ideal mixtures

The Gibbs energy of the system is given by (5.6):

$$G = \sum_{\alpha} \sum_k n_k^{\alpha} \mu_k^{\alpha} \quad (5.6)$$

For any calculation to minimize G in terms of the system composition (n_k 's), the actual numeric values of the partial molar Gibbs energies (μ_k 's) of the possible system components should be known. Thus for each species k , the chemical potential $\mu_k = \mu_k(T)$ must be written. All such species that can be stable under the given conditions should be taken into account in the evaluation of the system Gibbs energy. The minimum of G then can be reached by numerical computer methods, e.g. by using the Lagrangian-multiplier technique (Eriksson 1975).

Though the Gibbs energy is the salient function, it is yet customary to store the thermodynamic data in the form of standard enthalpies and entropies. The standard condition for pure substance data are $T=298.15$ K and $P(\text{total}) = 1$ bar (100 kPa). The convention used in the thermodynamic routines then derives the chemical potentials of pure species through the conventionally tabulated values of the enthalpy of formation, heat capacity and entropy of formation (Eriksson 1975, Roine 1999, Hack 2008). Thence, for each species k at constant pressure:

$$H(T) = H_f(298) + \int_{298}^T C_p dT + \sum (\Delta H_t) \quad (7.1)$$

$$S(T) = S_f(298) + \int_{298}^T \left(\frac{C_p}{T} \right) dT + \sum \left(\frac{\Delta H_t}{T_t} \right) \quad (7.2)$$

$$G_f(T) = H(T) - TS(T) \quad (7.3)$$

and then, by agreement and for the calculations,

7. Basis for Gibbs energy calculations

$$\mu_k^{\circ}(T) = G_f^{\circ}(T) \quad (7.4)$$

where the simplified notation refers to each pure species k at 1 bar pressure². Then in (7.1–7.4)

$H_f(298)$ = enthalpy of formation of species at 298.15 K

$S_f(298)$ = entropy of the species at 298.15 K

ΔH_t = enthalpy change of phase transformation

$C_p(T)$ = heat capacity of the species

$\mu_k^{\circ}(T, P)$ = chemical potential of pure species k .

Thus the thermodynamic data is characteristically established on the basis of the *standard element reference state* (SER). Then room temperature (298.15 K) and the total pressure of 1 bar are introduced as standard conditions and the enthalpy of formation $H_f(298)$ of the state of the elements which are stable under these conditions is set to zero by convention. The entropy $S_f(298)$ is taken as its absolute value and the heat capacity $C_p(T)$ at constant pressure is presented with a polynomial, e.g. as follows:

$$C_p(T) = c_1 + c_2T + c_3T^2 + \frac{c_4}{T^4} \quad (7.5)$$

Through (7.4) the chemical potential of the pure species k is fixed to $G_f(T)$, which may be called the *Gibbs energy of formation* of the pure species k at temperature T .

The calculation of the numeric values of chemical potentials in multicomponent and multiphase mixtures then follows established physico-chemical methods. For example, a simple ideal gas - pure condensed phases system becomes:

$$\mu_k(T, P) = \mu_k^{\circ}(T, P) + RT \ln P_k \quad (\text{ideal gas}) \quad (7.6)$$

$$\mu_k(T) = \mu_k^{\circ}(T) \quad (\text{pure condensed phases}) \quad (7.7)$$

² The superscript \circ has been kept for the chemical potential of the pure species, as it will be essential in any further treatment of the chemical potentials of mixtures).

Where P_k is the partial pressure of gaseous species k and $\mu_k^o(T, P)$ has been used for the standard state of both gaseous and condensed species. For the pure condensed phases, the chemical potential is assumed to be independent of pressure.

Using (7.6) and (7.7) in (5.6) the overall Gibbs energy of the gas-condensed system is reached. Other conventions to define numerical values for μ_k 's of the pure substances could be used, but the calculation result should be the same, provided that consistency of the thermodynamic data is maintained.

For other ideal mixture phases than gases the chemical potential is given by an equation similar to (7.6), where the logarithmic term is given in terms of the ideal concentration variable, instead of the partial pressure. For the ideal Raoultian solution, for example, there is

$$\mu_k = \mu_k^o(T, P) + RT \ln x_k \quad (7.8)$$

where x_k is the mole fraction of species k in the solution. For the Raoultian mixture the standard value of the chemical potential $\mu_k^o(T, P)$ remains that of the pure substance k . When other concentration scales (e.g. molality, molar concentrations) are used for the chemical potentials of mixtures, one should take care to define one's standard states according to the appropriate scale.

7.2 Non-ideal mixtures

In *non-ideal mixtures* the logarithmic concentration factor of the chemical potential is generally replaced by the respective activity (a_k) term. Thus, for a non-ideal mixture there is,

$$\mu_k(T, P) = \mu_k^o(T, P) + RT \ln a_k \quad (7.9)$$

$$\mu_k(T, P) = \mu_k^o(T, P) + RT \ln \gamma_k x_k, \quad \lim \gamma_k = 1 (x_k \rightarrow 0) \quad (7.10)$$

where $a_k = \gamma_k x_k$. From (7.10) it is evident that the activity coefficient (γ_k), being a function of temperature, pressure and composition is used as a non-ideal correction factor to give the activity in terms of the concentrations. By separating the ideal and non-ideal parts of the chemical potential, one may write in general

$$\mu_k(T, P) = \mu_k^{id}(T, P) + \mu_k^e(T, P) \quad (7.11)$$

The superscripts *id* and *e* refer to ideal and non-ideal parts of the chemical potential. The μ_k^e is called *the partial molar excess Gibbs energy* of each non-ideal species k . The excess Gibbs energies in different systems are generally given in terms of activities and the respective activity coefficients. The activity then is the

7. Basis for Gibbs energy calculations

product of the composition factor and the activity coefficient. The current Gibbs energy minimization routines allow a number of ways for the user to describe the non-ideality of the calculation system, generally in terms of the excess Gibbs energies. In Table 7.1, examples of the non-ideal systems (solution models) covered in the well-known Gibbs energy minimization routine ChemApp have been listed. The listing is by far not 'complete' as additional excess Gibbs energy models are continuously being programmed to ChemApp as well as to other respective software packages. In Figure 7.1, a simplified data flowsheet of the Gibbs'ian calculation is presented.

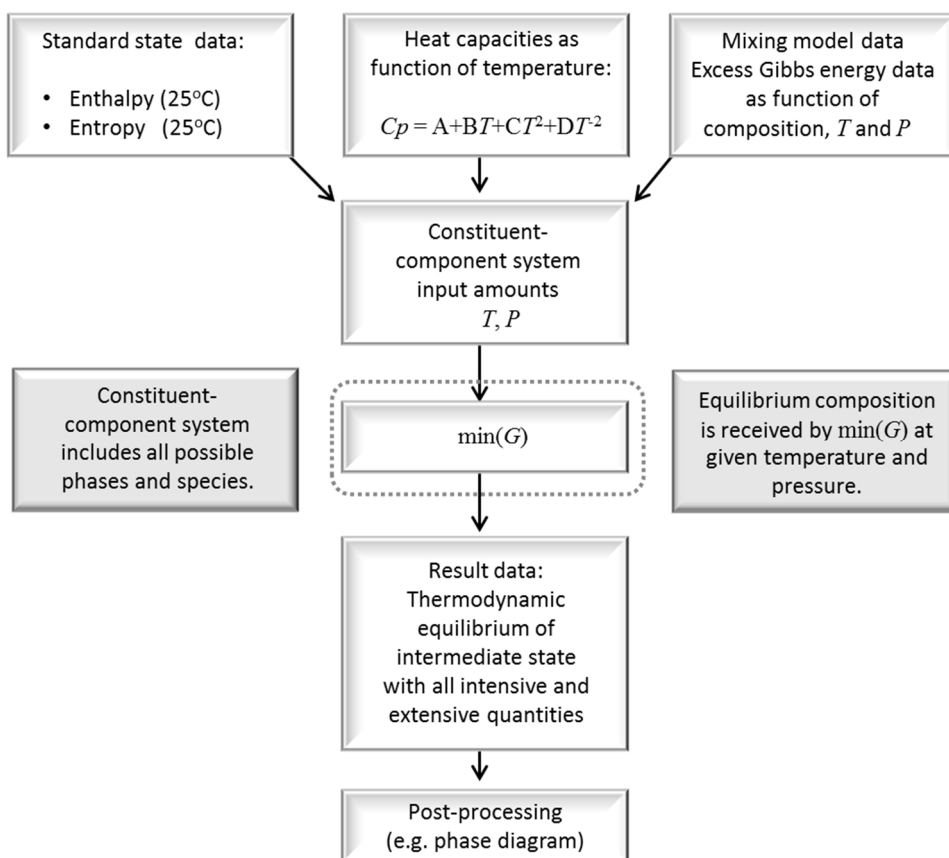


Figure 7.1. Data flowsheet for Gibbs energy minimization calculations.

Table 7.1. Examples of solution models available in ChemApp/ChemSheet (adapted from Petersen and Hack, 2007).

Model	Application area
Redlich-Kister-Muggianu Kohler-Toop Hoch-Arpshofen	For general use with substitutional or associated solution phases
Compound energy formalism Two-sublattice order/disorder formalism* Species chemical potential/bond energy formalism* Extended compound energy formalism	Solid phases with sublattice descriptions
Two-sublattice ionic formalism*	Ionic liquids
Two-sublattice equivalent fraction formalism Two-sublattice equivalent fraction formalism as a polynomial Guts formalism	Molten salts
Gaye-Kapoor-Frohberg cell model* Modified quasi-chemical formalism	Ionic oxidic mixtures with or without non-oxidic solutes
Quadruplet quasichemical model	Condensed non-aqueous solutions
Binary defect formalism*	Binary condensed phases with a narrow stoichiometry range
Wagner	Metallic dilute solutions
Davies formalism* Helgeson-Tanger-Shock formalism (ideal)* Helgeson-Tanger-Shock formalism (Debye-Hückel)* Helgeson-Tanger-Shock formalism (Davies)*	Dilute aqueous solutions
Pitzer formalism* Modified Pitzer formalism Specific ion-interaction formalism* Helgeson-Tanger-Shock formalism (Pitzer)*	Concentrated aqueous solutions
Revised Helgeson-Kirkham-Flowers (HKF) model*	Aqueous solutions up to 5 kbar and 1300 K
C-H-O-S-N-Ar multicomponent fluid model*	Fluid mixtures up to 1 Mbar and 6000 K; important for many geological and environmental systems
Virial equation with Tsonopoulos' second virial coefficient correlation	Non-ideal gas

* Magnetic contributions not permitted.

7.3 Use of Equation of State (EOS) data

In addition to the excess Gibbs energies as listed e.g. in Table 7.1, it is also possible to perform vapour-liquid equilibrium calculations by using the multi-component Gibbs'ian approach. In general the VL (vapour-liquid) equilibria are presented in terms of equations of state, where the non-ideality of a system is given by using fugacities. Thus, the classical vapour-liquid equilibrium (VLE) is defined as:

7. Basis for Gibbs energy calculations

$$\hat{f}_k^V = \hat{f}_k^L \quad k = 1, 2, \dots, N \Rightarrow y_k \hat{\phi}_k^V P = x_k \hat{\phi}_k^L P \quad k = 1, 2, \dots, N \quad (7.12)$$

where y and x are the vapour and liquid molar fractions, \hat{f}_k is the *fugacity* and $\hat{\phi}_k$ is the *fugacity coefficient* of a species in a mixture phase (hat indicating the property in a mixture) and P is the total pressure. For example in the *phi-phi model*, the fugacity coefficients express the fugacity of both the real vapour and the liquid phase(s) relative to the ideal gas phase. Then the chemical potential of a species in a vapour or liquid mixture can be given as:

$$\mu_k = \mu_k^\circ + RT \ln \frac{x_k \hat{\phi}_k^L P}{P^\circ} = \mu_k^\circ + RT \ln a_k \quad (7.13)$$

where μ_k° is the standard chemical potential of a pure ideal gas species and P° is the reference pressure (= 1 bar) at the given temperature (T).

The equation of state can be expressed as functions of $P(V, T)$ or $V(P, T)$. The fugacity of a species in mixture phase can be calculated from:

$$\ln \hat{\phi}_k = \ln \frac{\hat{f}_k}{x_k P} = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_k} \right)_{T, P, n_{j \neq k}} - \frac{RT}{V} \right] dV - \ln \frac{PV}{RT} \quad (7.14)$$

$$\ln \hat{\phi}_k = \ln \frac{\hat{f}_k}{x_k P} = \int_0^P \left[\left(\frac{\partial V}{\partial n_k} \right)_{T, P, n_{j \neq k}} - \frac{RT}{P} \right] dP \quad (7.15)$$

Here, the former equation is suitable for EOS of type $P(V, T, n_k)$, while the latter is suitable for $V(P, T, n_k)$. The most prominent use of an equation of state is to predict the state of gases and liquids. As the ideal gas equation becomes increasingly inaccurate at higher pressures and lower temperatures, it also fails e.g. to predict condensation from a gas to a liquid. Therefore, a number of much more accurate equations of state have been developed for gases and liquids (solids), typical examples are *van der Waals*, *Soave*, *Soave-Redlich-Kwong* and *Peng-Robinson* EOS (see e.g. Tester & Modell 1997). There is no single equation of state that accurately predicts the properties of all substances under all conditions. Yet, by using (7.11) in connection with either (7.12) or (7.13), the EOS-approach can be incorporated into the Gibbs'ian model and combined with a multi-phase equilibrium calculation.

7.4 Overview of the Lagrange method for Gibbs energy minimization

A number of methods can be used to minimise the Gibbs energy of the multi-component thermochemical system (Eriksson 1971, Walas 1985, Smith & Missen 1991). The solution strategy can be based on independent chemical reactions in mutual equilibria or on independent system components, the chemical potentials of which must give the phase-independent values of the chemical potentials of the reactants and products at equilibrium. The former, sometimes called as the stoichiometric approach, results with group of nonlinear equations and requires a new set of reaction equations to be described each time a new component is introduced to the system. The latter (sometimes referred to as the 'non-stoichiometric' method) is somewhat easier to systematize while introducing new components with the respective new possible constituents. The equilibrium condition is then searched by finding the minimum of the Gibbs free energy of the system, most often by applying the Lagrange method of undetermined multipliers. During the last few decades the resulting non-linear equations have been successfully linearized for several computer programs and thus the latter ('non-stoichiometric') method has become the most widespread technique for computational free energy procedures.

In this chapter the basics of the Lagrange multiplier method is described in terms of a simple system, which consists of pure condensed phases and ideal gas phase. The treatment of such a simple system is but introductory as regards the numerical minimization procedures; yet it serves to elucidate the mathematical procedure of the Lagrange method by which the undetermined multipliers are solved as the component potentials. This feature will then be essential while developing the aspects of the constrained Gibbs energy minimization for systems including complementary immaterial conditions.

The following description of the pure solid phases – one gaseous mixture phase system is essentially that of Eriksson (1971). A respective treatment for systems with several mixture phases can be found in Eriksson (1975). See also e.g. Smith & Missen 1991, Walas 1985, Hack 2008).

The system consists of s condensed substances and of a gaseous mixture phase with m constituents. The amount of matter (in mol) of the gas phase are denoted with n_k^g and the condensed with n_k^c , respectively. The Gibbs energy of the system may be written as

$$G = RT \cdot \sum_{k=1}^m n_k^g \left[\left(\frac{\mu^\circ}{RT} \right)_k^g + \ln P + \ln x_k^g \right] + \sum_{k=1}^s n_k^c \left(\frac{\mu^\circ}{RT} \right)_k^c \quad (7.16)$$

The chemical elements present form the most obvious set of independent components for the thermochemical system. Other stoichiometric combinations of the elements may equally well be used as components, supposing that they can be combined to form the appropriate constituents of the system. The number of com-

7. Basis for Gibbs energy calculations

ponents is denoted by NC . The mass balance constraints for the components of the system then are:

$$\sum_{k=1}^m a_{kj}^g n_k^g + \sum_{k=1}^c a_{kj}^c n_k^c = b_j, \quad j = 1, \dots, NC. \quad (7.17)$$

where

$a_{kj}^{g,c}$ = number of atoms of the j^{th} element in a molecule of the k^{th} substance in the system (superscripts g and c again refer to the gas and condensed phases, respectively)

b_j = the amount of j^{th} element in the system.

The mass balances are the necessary constraints for the minimization problem.

The amounts of substances and the chemical potentials of the standard state can be expressed more concisely in the form of matrices:

$$\mathbf{n} = (n_1, \dots, n_{m+s}) = (n_1^g, \dots, n_m^g, n_1^c, \dots, n_s^c) \quad (7.18)$$

$$\boldsymbol{\mu}^\circ = (\mu_1^\circ, \dots, \mu_{m+s}^\circ) = (\mu_1^{\circ g}, \dots, \mu_m^{\circ g}, \mu_1^{\circ c}, \dots, \mu_s^{\circ c}) \quad (7.19)$$

The Gibbs energy then is written as a function of the amounts of substances [mole numbers] (n_k):

$$F(\mathbf{n}) = \frac{G}{RT} = \sum_{k=1}^{m+s} n_k \left(\frac{\mu^\circ}{RT} \right)_k + \ln P \sum_{k=1}^m n_k + \sum_{k=1}^m n_k \ln \frac{n_k}{\sum_{k=1}^m n_k} \quad (7.20)$$

The mass-balance constraints may, respectively, be presented as a $(m+s) \times NC$ matrix A :

$$\mathbf{A} = \begin{pmatrix} a_{1,1}^g & \cdot & \cdot & \cdot & a_{1,NC}^g \\ \cdot & \cdot & & & \\ \cdot & & \cdot & & \\ \cdot & & & \cdot & \\ a_{m,1}^g & \cdot & \cdot & \cdot & a_{m,NC}^g \\ a_{1,1}^c & \cdot & \cdot & \cdot & a_{1,NC}^g \\ \cdot & \cdot & & & \\ \cdot & & \cdot & & \\ \cdot & & & \cdot & \\ a_{s,1}^g & \cdot & \cdot & \cdot & a_{s,NC}^g \end{pmatrix} \quad (7.21)$$

The total amount of each element can be presented in vector form as \mathbf{b} :

$$\mathbf{b} = (b_1, \dots, b_{NC}) \quad (7.22)$$

The mass balance constraints then become defined with a single vector function $\psi(\mathbf{n})$:

$$\psi(\mathbf{n}) = \left(\sum_{k=1}^{m+s} a_{kj} n_k - b_j \right)_{j=1}^{NC} = \mathbf{A}^T \mathbf{n} - \mathbf{b} = 0 \quad (7.23)$$

The Gibbs energy minimization is then equivalent to minimization of the function $F(\mathbf{n})$ in Equation (7.20) with the limiting condition of $\psi(\mathbf{n}) = 0$. The minimization can be performed with the Lagrange method of undefined multipliers. With this method, the minimum of the Gibbs energy is subjected to the mass balance relations (7.23), which are used as subsidiary conditions. The new objective function to be minimised in terms of the amounts of matter n_k is written as

$$L(\mathbf{n}, \boldsymbol{\lambda}) = F - \lambda_j \left(\sum_{k=1}^{m+s} a_{kj} n_k - b_j \right)_{j=1}^{NC} \quad (7.24)$$

where $\boldsymbol{\lambda} = (\lambda_1, \dots, \lambda_{NC})$ are the Lagrange undefined multipliers. The minimum of $L(\mathbf{n}, \boldsymbol{\lambda})$ gives the minimum of F while the mass balance condition (7.23) holds. The respective partial derivatives in terms of the amounts (n_k) and in terms of the Lagrange multipliers (λ_j) must be zero. Concisely, the equations to be solved are as follows:

7. Basis for Gibbs energy calculations

$$\left(\frac{\partial F}{\partial n_k} \right)_{T,p,n_i} - \sum_{j=1}^{NC} \lambda_j a_{kj} = 0 \quad (k = 1, 2, \dots, m + s) \quad (7.25)$$

$$\psi(\mathbf{n}) = 0 \quad (7.26)$$

Firstly, the derivatives of function F must be obtained. For the gaseous species, $k = 1, \dots, m$ and the derivative becomes:

$$\begin{aligned} \left(\frac{\partial F}{\partial n_k} \right)_{T,p,n_i} &= \left(\frac{\mu^\circ}{RT} \right)_k + \ln P + \ln \frac{n_k}{\sum_{k=1}^m n_k} + n_k \cdot \frac{\sum_{k=1}^m n_k}{n_k} \cdot \frac{\sum_{k=1}^m n_k - n_k}{\left(\sum_{k=1}^m n_k \right)^2} + \sum_{i=1, i \neq k}^m n_i \cdot \frac{\sum_{k=1}^m n_k}{n_i} \cdot \frac{-n_i}{\left(\sum_{k=1}^m n_k \right)^2} \\ &= \left(\frac{\mu^\circ}{RT} \right)_k + \ln P + \ln \frac{n_k}{\sum_{k=1}^m n_k} + 1 - \sum_{i=1}^m \frac{n_i}{\sum_{k=1}^m n_k} \\ &= \left(\frac{\mu^\circ}{RT} \right)_k + \ln P + \ln \frac{n_k}{\sum_{k=1}^m n_k} \end{aligned} \quad (7.27)$$

For the pure condensed phases, $k = m + 1, \dots, m + s$, the derivation is more simple, as there are only the terms due to the standard chemical potentials:

$$\left(\frac{\partial F}{\partial n_k} \right)_{T,p,n_i} = \left(\frac{\mu^\circ}{RT} \right)_k \quad (7.28)$$

If the total amount of moles in the gas phase is denoted by $N = \sum_{k=1}^m n_k$, from Equations (7.25), (7.27) and (7.28) together with (7.23) the following set of equations is received:

$$\left(\frac{\mu^\circ}{RT} \right)_k + \ln P + \ln \frac{n_k}{N} - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \quad k = 1, \dots, m \quad (7.29)$$

$$\left(\frac{\mu^\circ}{RT} \right)_k - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \quad k = m + 1, \dots, m + s \quad (7.30)$$

$$\sum_{k=1}^{m+s} a_{kj} n_k - b_j = 0, \quad j = 1, \dots, NC \quad (7.31)$$

The number of equations is $m + s + NC$, which also hold $m + s + NC$ variables, viz. n_k with $k = 1, \dots, m+s$ and λ_j , with $j = 1, \dots, NC$.

Due to the thermochemical generality of the minimization problem, a wide variety of equilibrium systems can be treated with the said equations. However, though Equations 7.30 and 7.31 are linear, there are no efficient algorithms which could be generally used for the non-linear equations (7.29). To ensure robust computational solution, the problem can be linearized by using e.g. Taylor expansion by using a value point $n_k(0) = y_k$ as initial values. Then, an iterative solution based on these initial estimates becomes viable, providing in general a well-behaved numerical solution. The details of the linearization technique are presented in Appendix D.

The Equations 7.29–7.31 form the mathematical basis for solving the equilibrium amounts of constituents for a system of s condensed species (pure substances) and an ideal gas phase with m constituents (see also D.10 and D.15 from Appendix D). The method can be generalised for systems with a number of non-ideal mixture phases. For these, of course, the contribution from their excess Gibbs energies must be taken into account. This will increase the numerical complexity of the problem but does not add conditions in terms of the system components and constraints.

While the $\min(G)$ has been solved for any control volume, the standard thermodynamic relations can be used to deduce the extensive and intensive state properties of the thus defined system (Figure 7.2). This feature is one of the main advantages of the use of Gibbs'ian technique in process simulation.

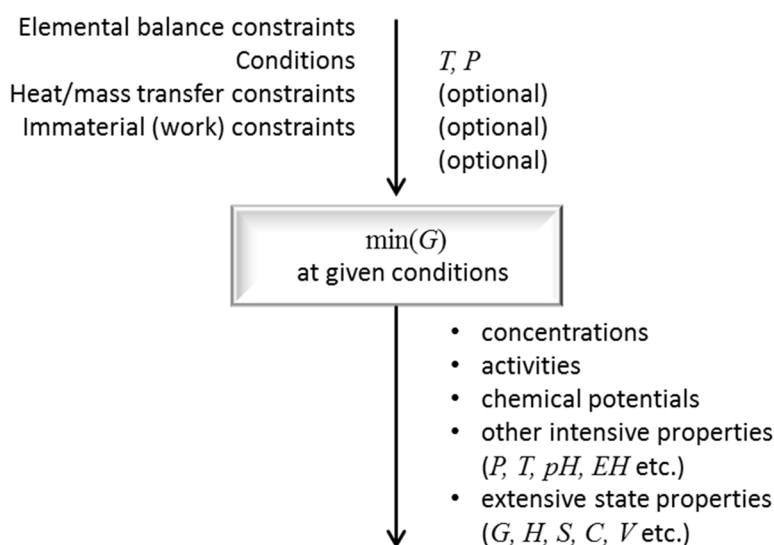


Figure 7.2. The block diagram for the Gibbs'ian thermochemical method. With the Gibbs energy simulation all the thermodynamic state quantities can be systematically derived from the fundamental relations.

7. Basis for Gibbs energy calculations

From equation (7.30) it is noticed that the linear combination of the Lagrange multipliers $\left(\sum_{j=1}^{NC} a_{kj}\lambda_j\right)$ will always give the chemical potentials μ_k^0 of the pure substances ($k > m+1$). The result, in fact, is even more general as can be seen from equation (7.25), where the same linear combination of the stoichiometric factors and Lagrange multipliers are connected with the partial molar Gibbs energies, i.e. the chemical potentials of all system constituents. Thus the Lagrange multipliers of the $\min(G)$ solution represent the chemical potentials of the independent system components at equilibrium:

$$\left(\frac{\mu}{RT}\right)_k = \sum_{j=1}^{NC} a_{kj}\lambda_j \quad k = 1, \dots, m+s \quad (7.32)$$

Using the above relation in the definition of the Gibbs function by Equation (5.6) together with the mass balance relations (7.31), the total Gibbs energy of the system is received in terms of the Lagrange multipliers as

$$\frac{G}{RT} = \sum_{j=1}^{NC} b_j\lambda_j \quad k = 1, \dots, m+s \quad (7.33)$$

These two important results will be extensively used, when additional, immaterial constraints with the respective virtual components are introduced to the Gibbs'ian system.

8. Law of mass action for the chemical equilibrium

The state of chemical equilibrium corresponds to the minimum of thermodynamic potential with respect to the chemical composition of the system, ie. to the amount of moles of different chemical substances. The proportions of the active masses of the substances then arrange according to the *equilibrium law of mass action*. This is usually presented by using the equilibrium constant, K_a .

It is customary to write for a single reaction between reactants (R) and products (P):



$$\Delta_r G = \sum_{\text{Products}} \nu \mu - \sum_{\text{Reactants}} \nu \mu = \Delta_r G^\circ + RT \ln \frac{\prod_{\text{Products}} a^\nu}{\prod_{\text{Reactants}} a^\nu} \quad (8.2)$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q_a \quad \left(Q_a = \frac{\prod_{\text{Products}} a^\nu}{\prod_{\text{Reactants}} a^\nu} \right) \quad (8.3)$$

where Q_a is used for the reaction quotient, defined in terms of the activities of the reactants and products during the course of the reaction. At equilibrium $\Delta_r G = 0$, and the reaction quotient then is equivalent with the equilibrium constant (K_a):

$$\ln K_a = -\frac{\Delta_r G^\circ}{RT} \quad (8.4)$$

The same will follow in general, as there exists a function $G = G(T, P, n_i)$. The function G has a minimum at the chemical equilibrium.

8. Law of mass action for the chemical equilibrium

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_k} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_k} dP + \sum_{k=1}^N \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_{j \neq k}} dn_k \quad (8.5)$$

At the minimum $dG = 0$ (extremum point), in the thermal equilibrium $dT = 0$, mechanical equilibrium $dP = 0$. The chemical equilibrium requires the condition:

$$dG = \sum_{k=1}^N \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_{j \neq k}} dn_k = 0 \quad (8.6)$$

when it is necessary to find the minimum of the function $G = G(T,P,n_k)$, in terms of the amount of matter (n_k -values). Equations (8.6) then stands for Equation (8.4) in the general case (law of mass action, see example of Appendix C).

One may also describe the whole chemical change as a set of stoichiometric reactions, each of which gains the advancement (extent of reaction) ξ_r . Then there is $dn_k = \sum_r \nu_{kr} d\xi_r$, (ν_{kr} being the stoichiometric coefficient of constituent k in the r^{th} chemical reaction) and the equilibrium condition is:

$$dG = \sum_r \sum_{k=1}^N \left(\frac{\partial G}{\partial n_k}\right)_{T,P} \nu_{kr} d\xi_r = 0 \quad (8.7)$$

From this, the two frequently used conditions for the chemical equilibrium are deduced:

$$dG = - \sum_r A_r d\xi_r = 0 \quad (T,P \text{ constant}) \quad (8.8)$$

and

$$\left(\frac{\partial G}{\partial \xi_r}\right)_{T,P,\xi_s} = 0 \quad (8.9)$$

The above equations also define the *thermodynamic affinity* of a chemical reaction. In general, affinity can be presented as

$$-A_r = \left(\frac{\partial G}{\partial \xi_r} \right)_{T,P,\xi_{s \neq r}} = \sum_{k=1}^N \left(\frac{\partial n_k}{\partial \xi_r} \right)_{T,P,\xi_{s \neq r}} \left(\frac{\partial G}{\partial n_k} \right)_{T,P,n_{i \neq k}} = \sum_{k=1}^N \nu_{kr} \left(\frac{\partial G}{\partial n_k} \right)_{T,P,n_{i \neq k}} \quad ; \quad r = 1, 2, \dots, R \quad (8.10)$$

with R here being the number of independent reactions in the system. Using the chemical potentials the affinity is

$$A_r = -\Delta_r G = \sum_{\text{Reactants}} \nu_{kr} \mu_k - \sum_{\text{Products}} \nu_{kr} \mu_k \quad (8.11)$$

If $A_r > 0$ the reaction will occur spontaneously. The concept of affinity is useful when dealing with kinetically constrained systems, as it provides a thermodynamically well-defined property for the development of computational tools consistent with the Gibbs energy approach for global equilibrium.

9. The minimization problem with immaterial constraints

When additional energy or work terms affect the Gibbs free energy, [$G = G(T, P, n_k)$] it is customary to transform the total differential of the Gibbs function to read as follows:

$$dG = S dT + V dp + \sum \mu_k dn_k + \sum z_k F \varphi_k dn_k + \sigma \sum (A_k dn_k) + \dots \quad (9.1)$$

The two last terms now refer to additional energy effects, expressed instead of the generalized work terms (L_i and l_i factors) by their specific symbols, which in this case are electrochemical potential (φ_k) and surface energy (σ), with F being the Faraday constant, and z_k the charge number, and A_k the partial molar surface area of species k . As the Gibbs energy is an additive extensive function, further terms due to either systemic or external force fields can be entered, respectively.

As presented in Chapter 7.4 Gibbs energy minimization involves optimization of the non-linear G -function with linear constraints and can be performed by the Lagrange method of undetermined multipliers. In the conventional method the amounts of matter (mass balances) appear as necessary constraints. To incorporate the additional phenomena, a method with analogous immaterial constraints is needed (see e.g. Koukkari and Pajarre 2006¹, 2011, Koukkari et al. 2007). The Gibbs energy is again calculated as the sum of all molar Gibbs energies, weighted by the respective amount of matter. The sum then contains all constituents as they may be chemical species in different phases, including e.g. molecular adsorption and surface layers, organic isomer groups, transformed biochemical metabolites or even such virtual species, which have only been introduced to adapt the calculation procedure to solve a certain physical problem.

$$G = \sum_k^N n_k \mu_k \quad (9.2)$$

The summation covers all species and phases and thus (9.2) is equivalent with (5.6). It was already stressed in Chapter 7 that the objective function of the mini-

mization problem is nonlinear because the chemical potentials are complex functions of the amounts of matter. The detailed mathematical form for the chemical potentials/molar Gibbs energies depend on the applied phase models. The linear constraints denote the balance equations set on the components forming the constituents of the system. Using matrix notation, these limitations are expressed as follows:

$$\mathbf{A}^T \mathbf{n} = \mathbf{b} \quad (9.3)$$

As already presented in in Chapter 7.4 \mathbf{A} is the conservation matrix, \mathbf{n} the molar amount vector for the constituents and \mathbf{b} is the vector for the amount of the components (in moles) of the Gibbs'ian system.

Together, Equations (9.2) and (9.3) constitute the problem for the Non-Linear Programming (NLP) to be solved:

$$\min G(\mathbf{n}) \text{ s.t. } \mathbf{A}^T \mathbf{n} = \mathbf{b} \quad ; \quad n_k \geq 0 \quad \forall k \quad (9.4)$$

The global minimum represents the equilibrium state with the lowest energy reachable with the given set of constraints. The constraints typically refer to elemental amounts of a closed thermodynamic system, but, as stipulated above, they can also include conservation of various attributes or entities. The solution may also be referred to as a constrained equilibrium. While the constraints are always linear, the NLP $\min(G)$ problem can then be linearized with the same procedure, which was described in Chapter 7.4.

The Lagrangian objective function to be minimized then becomes as follows

$$L = G - \sum_j^{NC} \pi_j \left[\sum_{\alpha}^{\Omega} \sum_k^N a_{kj} n_k^{\alpha} - b_j \right] \quad (9.5)$$

where π_j are the undetermined Lagrange multipliers used to include the constraints into the objective function L , and NC is the number of components in the system. [cf Equation (9.5). Here and henceforth the π_j ($= RT\lambda_j$) are used for the Lagrange multipliers to emphasize their role as thermodynamic potentials of the system components]. As shown above, the solution of the variational problem then provides both the Lagrange multipliers and the equilibrium amounts of constituents. The summation includes all system components, whether elemental abundances or immaterial or even virtual entities. Using (5.5) and the extremum condition $\frac{\partial L}{\partial n_k} = 0$ for (9.5) it follows that the chemical potential of each chemical species

remains the linear combination of the Lagrange multipliers as defined by the elements of the conservation matrix:

9. The minimization problem with immaterial constraints

$$\mu_k = \sum_{j=1}^{NC} a_{kj} \pi_j \quad (k = 1, 2, \dots, N) \quad (9.6)$$

Deducing the total Gibbs energy in terms of the Lagrange multipliers and the total amounts of the components becomes respectively

$$G = \sum_{j=1}^{NC} b_j \pi_j \quad (9.7)$$

These equations correspond the formerly deduced (7.32) and (7.33) in the simple Gibbs'ian system. However, by taking into account such non-material entities which may be interpreted as system components, a more general utilization of the same relations becomes viable. Then (9.7) can be divided in two parts as follows

$$G = \sum_{j=1}^{NC'} b_j \pi_j + \sum_{j=NC'+1}^{NC} b_j \pi_j \quad (9.8)$$

The 'stoichiometric part' ($j \leq NC'$) of the conservation matrix A defines entirely the amounts of elements and electrons (mass balance) of the given system. The additional components ($NC' < j \leq NC$) descend from various immaterial sources affecting the Gibbs free energy of the system. To be applicable in the minimization problem, a conservation sentence, which is analogous with the mass balance must be written for such immaterial entities. For example, conservation of charge, surface area and partial volumes can be expressed in this way, and thus their contribution to the minimization procedure is straightforward. The respective conjugate potentials become electrochemical potential, surface energy (surface tension) and osmotic pressure. The physical meaning of the Lagrange multipliers is then evident as the equilibrium potentials of the components of the system, irrespective to their 'material content'. In the conventional Gibbs energy minimization method they give the chemical potentials of the elements or other stoichiometrically defined components of the equilibrium system. More generally they represent the energy contribution of any appropriate property to the molar Gibbs energy of a constituent.

The introduction of immaterial constraints into the minimization problem then reduces to finding the appropriate form for the conservation matrix A when the additional terms affect the chemical composition of the system. In general, A is of the following form (cf. Chapter 7.4, Equation 7.21)

$$\mathbf{A} = \begin{pmatrix} a_{1,1}^{(1)} & \cdots & a_{1,NC'}^{(1)} & \cdots & a_{1,NC}^{(1)} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ a_{N_1,1}^{(1)} & \cdots & a_{N_1,NC'}^{(1)} & \cdots & a_{N_1,NC}^{(1)} \\ a_{N_1+1,1}^{(2)} & \cdots & a_{N_1+1,NC'}^{(2)} & \cdots & a_{N_1+1,NC}^{(2)} \\ \vdots & \cdots & \vdots & \ddots & \vdots \\ a_{N,1}^{(\Omega)} & \cdots & a_{N,NC'}^{(\Omega)} & \cdots & a_{N,NC}^{(\Omega)} \end{pmatrix} \quad (9.9)$$

In the conventional minimization technique, the components represent elemental building blocks of the constituents and the matrix elements a_{kj} are the respective stoichiometric coefficients. In Equation (9.9) the matrix elements for the material phase constituents remain equivalent with the conventional approach, and as stated above the Lagrange multipliers (π_j) then represent the chemical potentials of the independent (material) components at $\min(G)$

The additional column with subscript $NC'+1$ gives a new conservation equation. The respective matrix element $a_{k,NC'+1} = 0$ for all those constituents k which are not affected by the additional constraint, whereas it is not zero for those constituents which are affected by this constraint. The mass balance of the total system remains unaltered if the molecular mass of the additional component, M_{m+1} , is chosen to be zero. Thus, by using immaterial components, additional conservation conditions can be included into the minimization of the objective function. Each immaterial component also brings a new potential into the solution in the form of the corresponding Lagrange multiplier.

In Table 9.1, characteristic examples of the immaterial constraints with their conjugate potentials applicable in $\min(G)$ problems have been collected. The constraints have been written in terms of the conserved quantity and the conjugate potential is given as the respective derivative. The table also lists some practical conditions, where the immaterial constraining becomes useful. Characteristic calculation examples of thermodynamically meaningful systems with immaterial components will be presented in the following chapters.

9. The minimization problem with immaterial constraints

Table 9.1. Immaterial constraints and their conjugate potentials used in CFE models.

System	Constraint	Matrix element	Conjugate potential	Practical examples
Chemical equilibrium systems	$\sum_{k=1}^N a_{kj} n_k = b_j$	a_{kj}	$\pi_j = \frac{\partial G}{\partial b_j}$	Multiphase chemical equilibrium Phase diagrams
Systems with area constraints	$\sum_{k=1}^{N_k} A_k n_k^s = A$	$\frac{A_k}{A_0}$	$\pi_{area} = \frac{\partial G}{\partial b_{(area)}} = \sigma A_0$	Surface and interface systems, sorption phenomena
Systems with volume constraints	$\sum_{k=1}^{N_F} V_k n_k^F = V_F$	$\frac{V_k}{V_0}$	$\pi_F = \frac{\partial G}{\partial b_{(V_F)}} = \Pi \bar{V}_F$	Osmotic systems, fibers and membranes
EOR-controlled complex systems	$\sum_{k=1}^N a_{kr} n_k = b_{(r)}$	v_{kr}	$\pi_{(r)} = \frac{\partial G}{\partial b_{(r)}} = \frac{\partial G}{\partial \xi_i} = -Aff_i$	Reactive systems Partial and 'super' equilibria
Para-equilibrium systems	$u_k = \frac{n_k}{\sum_M n_M} = const.$	$\frac{n_{Fe}}{n_M} a_{k,M} - a_{k,Fe}$	$\frac{\partial G}{\partial \xi} = \sum_{M^*} a_{k,M^*} \left(\frac{\partial G}{\partial b_{M^*}} \right) = \sum_{M^*} a_{k,M^*} \pi_{M^*}$	Paraequilibria, co-precipitation
System with external magnetic field	$B = const.$	$\frac{\Delta_M \mu_i}{f(B) M_0}$	$\pi_M \equiv \frac{\partial G}{\partial b_M} = f(B) M_0$	Magnetic phase stability
Electrochemical (Donnan) multi-phase systems	$\sum_{k=1}^{N_\alpha} z_k n_k^\alpha = Q^\alpha$	z_k	$\pi_{(q^\alpha)} = \frac{\partial G}{\partial b_{(q^\alpha)}} = F \Delta \phi^\alpha$	Electrochemical membrane systems, Pulp suspensions
Constant contribution pH	$pH = const.$	$N_{H,k}$	$\pi_{Ha} \equiv RT \ln 10 pH_a$	Biochemical systems (pH = 7 at standard state)
Constant contribution ionic strength	$I = \frac{1}{2} \sum_k z_k^2 c_k = const.$	z_k^2	$\pi_I \equiv \frac{-\alpha RT \sqrt{I}}{1 + B\sqrt{I}} = \frac{RT}{z_k^2} \ln \gamma_k$	Biochemical systems with constant ionic strength

9. The minimization problem with immaterial constraints

A_k	=	molar surface area of constituent k
A_0	=	unit area
A	=	total area of system (symbol A is often used also for the thermodynamic affinity, in this table A_{ff} = affinity)
σ	=	surface energy
V_k	=	molar surface area of constituent k
V_0	=	unit volume
V	=	total volume of a phase or subvolume within the system
Π	=	volume constraining osmotic or other pressure
z_k	=	charge number of species k
Q^a	=	total charge of a subvolume or a phase
F	=	Faraday constant
$\Delta\phi$	=	electric potential difference in a phase
u_k	=	constant amount fraction of species k
$\Delta_M \mu_i$	=	molar Gibbs energy change due to magnetization
B	=	magnetic flux density
M_0	=	unit magnetization
$\nu_{kr(i)}$	=	stoichiometric coefficient for species k in reaction $r(i)$
ξ_i	=	advancement of reaction i
A_{ff_i}	=	affinity of reaction i
R	=	gas constant
T	=	temperature
I	=	ionic strength of aqueous solution
m_k	=	molality of solute k
α, B	=	constants related to aqueous electrolyte activity theories
γ_k	=	activity coefficient of solute k

10. Surface energies of mixtures

In Equation (9.1) the last term shown on the right hand side includes the surface energy (σ) and the surface area (A) of the thermodynamic system. The *surface energy*, often also named as *surface tension* is known to be a function of temperature, pressure and composition $\sigma = \sigma(T, P, n_k)$. The composition of the surface layer in general differs from that of the bulk, due to molecular rearrangement in the vicinity of the interface. In classical thermodynamics, the surface layer is then conventionally treated as a separate phase, for which e.g. the chemical potentials of the surface species are well defined (Guggenheim 1977, Butler 1932). It is then easy to follow this convention while introducing a simple example of the use of immaterial (work term related) constraints in Gibbs energy minimization. The Gibbs'ian method for surface energies was first outlined by Pajarre et al. in 2006. In this text the notation by Koukkari et al. (2007) is mainly followed.

A surface monolayer in equilibrium with the bulk mixture is assumed, the surface curvature effects are omitted. Separating the contributions of the bulk (b) and surface (s) compositions, the Gibbs energy at constant temperature and pressure can be written as follows:

$$G = \sum_{k=1}^{N_b} \mu_k^b n_k^b + \sum_{k=1}^{N_s} \mu_k^s n_k^s + \sigma \sum_{k=1}^{N_s} A_k n_k^s \quad (10.1)$$

The same species (constituents) are assumed to be present in the bulk and surface phases, the subscripts then denoting the same chemical species irrespective of the phase considered. The surface tension is a function of temperature and composition, $\sigma = \sigma(T, x_k)$. Each constituent of the surface phase occupies a characteristic molar surface area A_k . The equilibrium condition for the surface system is that of a constant surface area (A), which in terms of the partial molar areas and amounts of constituents is:

$$\sum_{k=1}^{N_s} A_k n_k^s = A \quad (10.2)$$

Taking formally into account the bulk phase contributions and by using unit area A_0 with dimensions $\text{m}^2\text{mol}^{-1}$ as a normalisation constant, a condition analogous to Equations (7.23.) and (9.3) can be written (summation is but formal over all species and phases):

$$\sum_{\alpha=1}^Q \sum_{k=1}^N \left[\left(\frac{A^\alpha}{A_0} \right) n_k^\alpha - \frac{A^\alpha}{A_0} \right] = 0 \quad (10.3)$$

The molar surface area for any bulk species is zero ($N = N_s + N_b$). This equation gives the condition for the constant surface area which then is applied in the exchange matrix of the surface system, the surface area being the additional system component. The respective Lagrange function of the surface system becomes:

$$L = \sum_{k=1}^{N_b} \mu_k^b n_k^b + \sum_{k=1}^{N_s} \mu_k^s n_k^s + \sigma \sum_{k=1}^{N_s} A_k^s n_k^s - \sum_{j=1}^{NC'} \pi_j \left(\left(\sum_k a_{kj}^b n_k^b + \sum_k a_{kj}^s n_k^s \right) - \beta_j \right) \quad (10.4)$$

where β_j is used for the 'generalised' constraints and the number of system components $NC' = NC + 1$, including the surface area component. For NC' one obtains: $\beta_{NC'=NC+1} = A^s / A_0$, and $a_{k,NC+1}^s = A_k^s / A_0$ for each of the surface species. To preserve the mass balance of the system, the additional surface area component needs to be immaterial, i.e. it needs to have zero molecular mass. Using the partial derivatives of L and the condition that the equilibrium chemical potential of a species is a quantity independent of the phase ($\mu_k^b = \mu_k^s = \mu_k$), the surface tension of the mixture is obtained with the additional Lagrange multiplier:

$$\sigma \cdot A_0 = \pi_{NC'=NC+1} \quad (10.5)$$

To perform the calculations within the framework of a standard Gibbs energy minimising program, such as ChemApp, the input data must be arranged in terms of the standard state and the excess Gibbs energy data of chemical potentials of the system constituents. For this purpose, the chemical potentials of species k in the bulk and surface phases can be written in terms of their activities as follows

$$\mu_k^b = \mu_k^\circ + RT \ln a_k^b \quad (10.6)$$

$$\mu_k^s = \mu_k^{\circ,s} + RT \ln a_k^s - A_k^s \sigma \quad (10.7)$$

where the superscript $^\circ$ refers to the standard state, a_k^b is the activity of the constituent k in the bulk phase and a_k^s , respectively, in the surface phase. By applying

Eqs. (10.6) and (10.7) for the case of a pure one component system, a relationship between the standard states of the bulk and surface phase can be derived.

$$\mu_k^{\circ,s} = \mu_k^{\circ} + A_k^s \sigma_k \quad (10.8)$$

This approach for surface systems was outlined already by Butler in 1932. Equations (10.6)–(10.8) then indicate that the necessary input for a Gibbsian surface energy model must include not only standard state and activity (excess Gibbs energy) data for the constituents of the bulk and surface phases, but also the data for surface tensions of the pure substances (σ_k) as well as their molar surface areas (A_k^s). The surface tensions of pure substances, especially liquids at ambient temperatures, are usually well known and can be easily adapted as input data for the calculations. For high temperature systems the data is well available for pure metals as liquids, but for molecular components, such as oxides and salts, the available data is much less extensive. The value of the normalisation constant A_0 can be chosen arbitrarily, but for practical reasons it is advantageous if the ratio A_k^s/A_0 is a value close to unity, being of the same order of magnitude as the stoichiometric coefficients appearing in the conservation matrix.

A simple binary alloy system (liquid Ag–Pb) is given as a calculation example in Figure 10.1. (see details in Koukkari and Pajarre, 2011) Thermodynamic and thermophysical data required to do the calculations, as well as the change to the stoichiometry matrix used for the surface phase are also presented in the Figure. The model result is compared to measured data from Joud et al. (1973) and Metzger (1959).

Normal standard state values can be used for the bulk phase (although for the purpose of just calculating surface tension and surface equilibrium composition they could also be set to zero), while the standard state values for the surface phase need to be adjusted using Eq. (10.8). The excess Gibbs energy for the bulk is calculated with a standard Gibbs energy model (here the Redlich–Kister polynomial) the data for which are also given in Figure 10.1. The excess Gibbs energy for the surface phase is derived from that of the bulk phase by using a correction as follows: $G_{\text{surface}}^{\text{Excess}} = \beta \cdot G^{\text{Excess}}$. The scaling factor β is used to for the effect which the reduced coordination number of metal atoms in the surface has on the excess Gibbs energy; following Tanaka et al. (1996) the value 0.83 for β has been used.

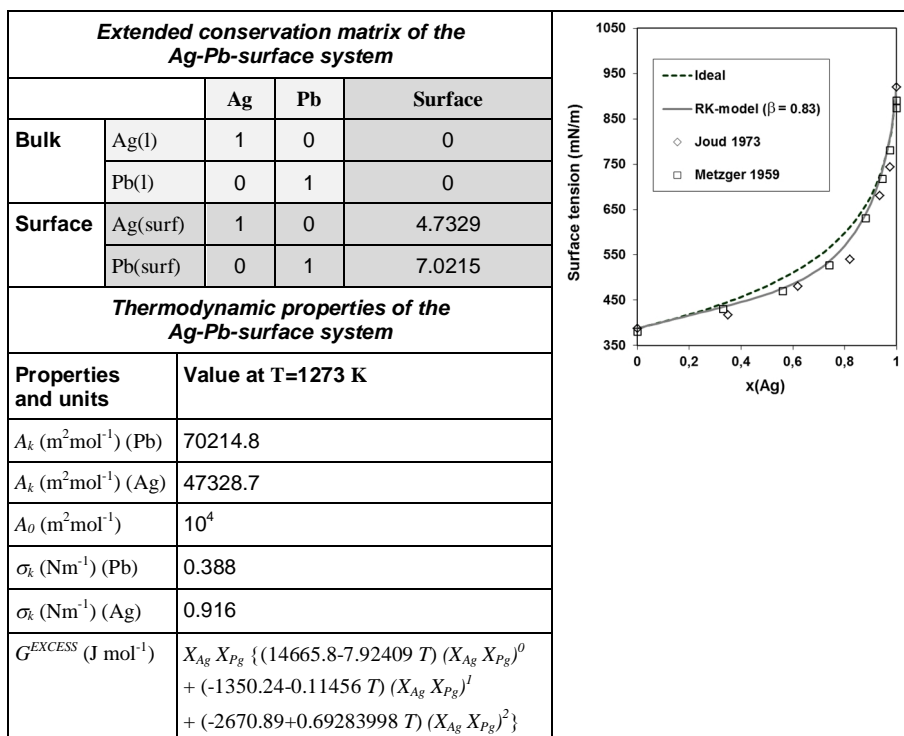


Figure 10.1. Calculation of the surface tension of a non-ideal binary system. The excess Gibbs energy (G^E) is included as the Redlich-Kister polynomial (RK-model) and the $G^E(\text{surface}) = 0.83G^E(\text{bulk})$ as deduced from the reduced coordination number between atoms in the surface region (Tanaka et al. 1996). Experimental values are from Joud et al. (1973) and Metzger (1959).

The method applies to liquid mixtures, such as binary and ternary alloys, steel (Fe-alloys) with its surface active trace components (oxygen, nitrogen, sulphur), silicon (boron, oxygen etc.), molten salts and, organic mixtures as well as to water-organic solutions (Tang et al. 2009, Heikkinen et al. 2010, Pajarre and Koukkari, 2009). The recently extended formalism, which allows for the calculation of interfacial energy and composition of two immiscible condensed phases (Pajarre et al. 2013) increases the applicability of the method and for example provides data of interfacial properties for mesoscale and phasefield studies of alloy and steel microstructures.

11. Electrochemical potential and Donnan equilibria in multiphase systems

In Equation (9.1) the term including the electrochemical potential presents a further condition which can be introduced to Gibbs'ian calculations by using appropriate immaterial constraints. The practical significance is apparent for aqueous electrochemical solutions. The one including ion exchange phenomena in pulp suspensions is discussed below.

When two aqueous solutions, in two separate compartments are at the same temperature and pressure and separated by a semi-permeable interface which allows transport of some ions but not others nor the solvent, the so-called Donnan equilibrium is established in the system. This condition is most typical for membrane-separated aqueous systems – yet it also approximates the chemical behaviour of aqueous pulp suspensions, in which the fibres absorb water from the external filtrate solution and ion-exchange processes between the swelling 'fibre phase' and external solution take place (Lindgren et al. 2001; Koukkari et al. 2002, 2004). The system contains two aqueous phases with water as solvent and mobile and immobile ions as solute species. In a multi-phase system, gas as well as precipitating solids may also be present. Both compartment systems containing the aqueous solutions remain electrically neutral. The essential feature of the Donnan equilibrium is that due to the macroscopic charge balance in the separate parts, the immobility of some of the ions will cause an uneven distribution for the mobile ions. This distribution strongly depends on pH of the system in cases, where dissociating molecules in one of the compartments may release mobile hydrogen ions (being fixed acidic groups typically present e.g. in the fibrils of cellulose fibers), while their respective (large or bound) counter anions remain immobile due to the separating membrane interface.

By applying the electroneutrality condition together with other physical conditions of the membrane system, the constraint potential approach allows the calculation of multi-phase Donnan equilibria by way of Gibbs energy minimization. Thus, the distribution of ions in the two compartments, together with formation of possible precipitating phases can be calculated.

In Table 11.1 an extract of the exchange matrix for a two-compartment Donnan system is presented. For the two solution phases present, the notation ' and '' has

been used. The constancy of the amount of water in the second compartment is ascertained by setting the respective matrix element to unity. By assuming zero molecular weight for this additional system component ($\text{H}_2\text{O}''$), the mass for the constituent H_2O in the second solution volume (solvent $''$) is obtained from the respective system components O (for oxygen) and H (for hydrogen). The electronic charge of aqueous ions is introduced to both aqueous phases in terms of the negative charge numbers (column e^-). An additional electroneutrality condition has been set for the secondary aqueous phase $''$, denoted in the matrix as system component q'' and arbitrarily chosen with the opposite sign as compared with aqueous electrons. Cations are represented as Me^{z+} and mobile anions as X^{z-} . The immobile anion (Ac^-) is a constituent for the secondary aqueous phase $''$ and it is related to the additional neutral system component Ac .

Table 11.1. Sub-matrix showing the Donnan equilibrium system with two aqueous solution phases. Gas and solid species are omitted for brevity.

		H	O	Me	X	e^-	$\text{H}_2\text{O}''$	q''	Ac
1 st solution (')	H_2O	2	1	0	0	0	0	0	0
	H^+	1	0	0	0	-1	0	0	0
	Me^{z+}	0	0	1	0	-z	0	0	0
	X^{z-}	0	0	0	1	z	0	0	0
2 nd solution ('')	H_2O	2	1	0	0	0	1	0	0
	H^+	1	0	0	0	-1	0	1	0
	Me^{z+}	0	0	1	0	-z	0	z	0
	X^{z-}	0	0	0	1	z	0	-z	0
	Ac^-	0	0	0	0	1	0	-1	1
	HAc	1	0	0	0	0	0	0	1

With the given matrix conditions, by using (7.8) and (9.6) for the chemical potentials of charged species at equilibrium

$$\mu_k^{\circ'} = \mu_k^{\circ''} + RT \ln a_k^{\circ''} = \mu_k^{\circ'} + z_k \pi_{q''} = \mu_k^{\circ'} + RT \ln a_k^{\circ'} + z_k \pi_{q''} \quad (11.1)$$

where the standard state potentials $\mu_k^{\circ'}$ and $\mu_k^{\circ''}$ are equal while the respective activities ($a_k^{\circ'}$ and $a_k^{\circ''}$) are different. The additional term ($z_k \pi_{q''}$) deduced from Eq. (9.6) is due to the supplementary electroneutrality constraint that holds for the secondary aqueous phase. Eq. (11.1) can then be compared with the general electrochemical equilibrium of charged species

$$\mu_k^{\circ''} + RT \ln a_k'' = \mu_k^{\circ'} + RT \ln a_k' + z_k F \Delta\varphi \quad (11.2)$$

indicating that the Gibbs energy minimization, when solving the π_j -values, gives the electrochemical potential difference between the two phases as

$$F(\varphi'' - \varphi') = F \Delta\varphi = \pi_{q''} \quad (11.3)$$

For the ion-exchanging membrane system as described above $\Delta\varphi$ is often called the Donnan potential.

Furthermore, the additional constraint set for the incompressible solvent water gives in terms of its molar volume $V_{\text{H}_2\text{O}}^{\text{m}}$:

$$\pi_{\text{H}_2\text{O}''} = (p' - p'')V_{\text{H}_2\text{O}}^{\text{m}} = RT \ln \left(\frac{a_{\text{H}_2\text{O}}''}{a_{\text{H}_2\text{O}}'} \right) \quad (11.4)$$

in which the difference $(p' - p'')$ is the osmotic pressure difference between the two liquid parts of the system.

From (11.2) and (11.3), one may solve for the activities of the mobile ions:

$$\left(\frac{a_k''}{a_k'} \right)^{1/z_k} = \exp \left(\frac{\pi_{q''}}{RT} \right) = \exp \left(\frac{F \Delta\varphi}{RT} \right) \equiv \Lambda \quad (11.5)$$

where the symbol Λ has been introduced for the Donnan distribution coefficient, which is used to describe the uneven distribution of the mobile ions in solvent systems separated by a membrane. The Gibbs'ian multicomponent approach can thus be applied to determine the difference in water activity between the two aqueous phases and thus to define the expected pressure difference in membrane systems, as well as to calculate the distribution coefficient for such mobile ions, for which the non-selective Donnan equilibrium assumption is valid.

Gibbs energy data for calculations can be obtained from conventional sources for standard phase constituents. However, the standard chemical potentials for the acid group species HAc and Ac^- must be deduced from dissociation constants (K_a)-data by using the relation $\ln K_a = -\Delta G^\circ / (RT)$. As only the dissociation inside the secondary compartment is considered, the reference chemical potential of $\mu_{\text{Ac}^-}^{\circ''}$ is then obtained from the K_a -value. For the aqueous system, molalities are typically used and the activity coefficients for the solution species are calculated e.g. from an extended Debye-Hückel model or by using Pitzer interaction parameters.

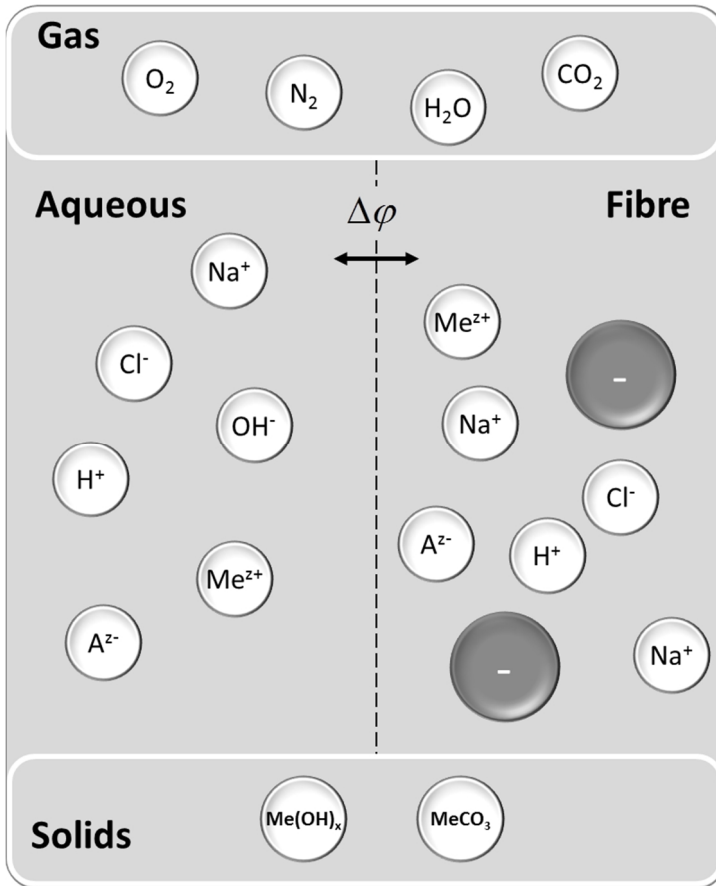


Figure 11.1. A schematic presentation of the pulp suspension as a typical Donnan equilibrium system. The large anions in the compartment of right hand side are immobile.

In Figure 11.1 typical pulp suspension is schematically presented in terms of the main species occurring in the ion-exchange (Donnan) model. The per weight consistency of the pulp suspension at the wet end of contemporary paper machines is typically 1–2 per cent of fibre, the rest being water. The water content of the fibre is ca 1:1 on weight basis and thus 1–2 wt-% of water is present in the fibre phase. This amount can be measured for different pulps by standard methods as the water retention value (wrv) and forms the basis for the pulp suspension model. According to the Donnan theory, pH will be different in the external aqueous solution and in the internal (fibre) solution; yet it can be only measured for the external solution. Instead, through sampling, the cations can be quantitatively detected for both the external solution and for the fibre phase, the latter then also containing the possible precipitated salts.

The advantage of the multi-phase Gibbsian approach is in its ability to take into account not only the multi-component ion exchange equilibria but also other chemical and phase changes in the system. In Figure 11.2, this is illustrated by showing the distribution of Ca^{2+} -ions in an aqueous suspension of typical thermomechanical pulp. Thus, effects of precipitating phases and that of gaseous components can be included, as well as possible reactive solute effects, such as chelants. The method has been extensively used for practical studies and process simulations of various unit processes in pulp- and paper-making.

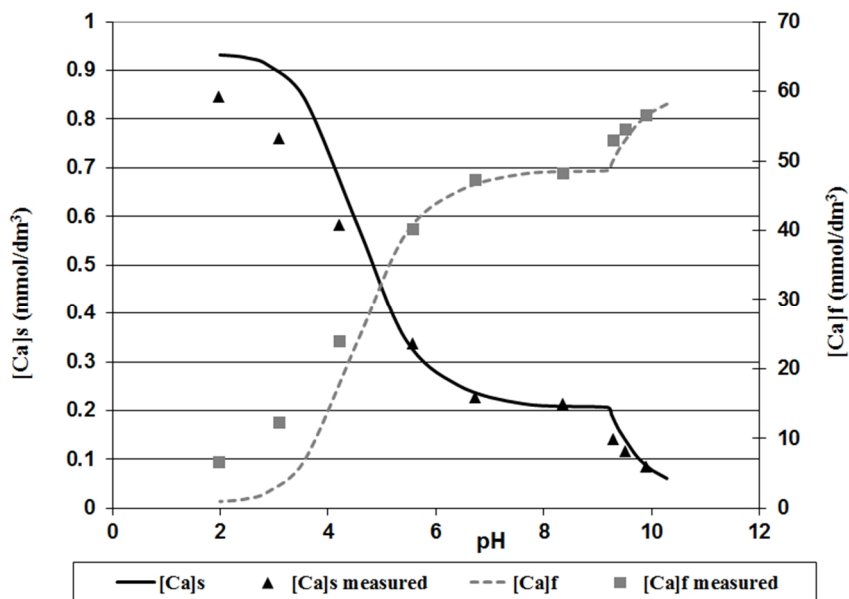


Figure 11.2. The solute concentrations in the two aqueous phases for Ca^{2+} -ions in thermomechanical pulp as calculated with the Gibbs'ian model (s = external solution, f = fibre phase, containing also the contribution of the solid precipitates within pH-range 9–10). The experimental data is from Mäenpää (2001).

12. 'Resistances to change' in systems with metastable equilibria

To introduce further applications of the constrained Gibbs energy method with reaction kinetics, first a simple system is considered, where equilibrium is constrained by a passive kinetic inhibition. This example was presented already by J.W. Gibbs in his publication "On the Equilibrium of Heterogeneous Substances". To contrast with free equilibrium, "which does not depend upon possible resistances to change" Gibbs also considers kinetic restrictions present in a system, stating as an example the system consisting of the components of water, i.e. S_{aq} , S_{H} and S_{O} (note the notation in mass units). "In respect to a mixture of vapour of water and free hydrogen and oxygen (at ordinary temperatures) we may not write

$$9S_{\text{aq}} = 1S_{\text{H}} + 8S_{\text{O}} \quad (12.1)$$

but water is to be treated as an independent substance, and no necessary relation will subsist between the potential for water and the potentials for hydrogen and oxygen" (The Scientific Papers of J. Willard Gibbs, 1993). In other words normally the equation



holds together with the equation received from Eq. (9..6):

$$\mu_{\text{H}_2\text{O}} = 2\pi_{\text{H}} + \pi_{\text{O}} \quad (12.3)$$

but in the case of passive kinetic inhibitions it does not: H_2O , H_2 and O_2 can coexist in a metastable state in which H_2 does not react with O_2 to give additional H_2O , and the chemical potential of water is an independent quantity. For such a case, one may include the restriction as an additional 'passive resistant' component into the stoichiometric matrix, as presented in Table 12.1 a–b.

Table 12.1a-c. Setting passive resistance and reaction rate constraints into the $\text{H}_2/\text{O}_2/\text{H}_2\text{O}$ reactive system.

Table 12.1a

Free equilibrium

	H	O
H_2O	2	1
H_2	2	0
O_2	0	2
$\text{H}_2\text{O(l)}$	2	1

Table 12.1b

Passive resistance

	H	O	H_2O^*
H_2O	0	0	1
H_2	2	0	0
O_2	0	2	0
$\text{H}_2\text{O(l)}$	0	0	1

Table 12.1c

Reaction constraints

	H	O	H_2O^*
H_2O	2	1	1
H_2	2	0	0
O_2	0	2	0
$\text{H}_2\text{O(l)}$	2	1	1
ξ_+	0	0	1
ξ_-	0	0	-1

Whereas Table 12.1a represents the free equilibrium situation, Table 12.1b gives H_2O as an independent component, its chemical potential being used for example in Eq. (9.6) as $\pi_{\text{H}_2\text{O}^*}$.

In Figure 12.1, the passive resistance ($\text{H}_2/\text{O}_2/\text{H}_2\text{O}$ -system as described in Table 12.1b) has been used in Gibbs energy minimization to calculate the water evaporation as function of temperature (20–65°C, total pressure 101 kPa). As no reaction [other than $\text{H}_2\text{O(l)} \leftrightarrow \text{H}_2\text{O(g)}$] is allowed, the partial pressure of H_2 only slightly decreases with raising temperature due to the respectively increasing water vapour in the gas phase. This simple example merely shows the utilisation of Gibbs's 'passive resistance' concept, i.e. the extension of the stoichiometric matrix of the system with an additional constraint, for the calculation of metastable phase equilibria. In what follows, the matrix extension method with rate-controlled chemical reactions is then introduced as a useful method in multi-phase reactor calculations.

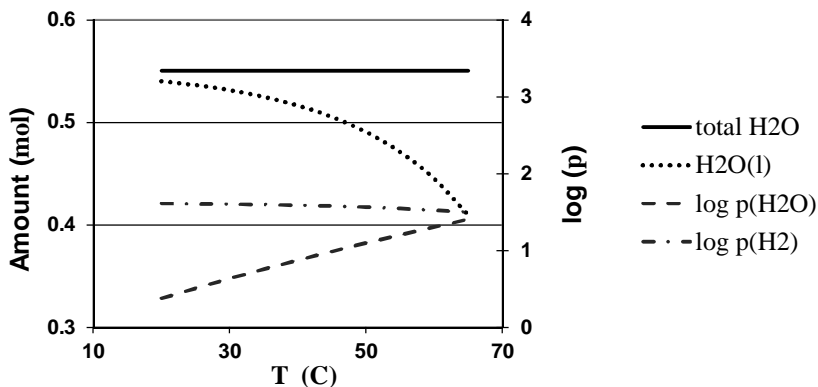


Figure 12.1. Use of the 'passive resistance' in Gibbs energy minimization. Input: 0.55 mol H_2O , 0.25 mol O_2 and 0.175 mol H_2 , 101 kPa total pressure (see Hack 2008, pp. 359–367).

13. Immaterial constraints related to extents of reaction

In Table 12.1c, the constrained $H_2/O_2/H_2O$ -system is introduced in a somewhat different form. The H_2O species have been actually connected with components H and O; it is thus assumed that their stoichiometry is defined in terms of hydrogen (2) and oxygen (1) and one H_2O^* component. While having done so, the additional H_2O^* component must be assumed immaterial, i.e. its molecular mass is regarded as zero. The chemical potential from (9.6) for the water species then becomes:

$$\mu_{H_2O} = 2\pi_H + \pi_O + \pi_{H_2O^*} \quad (13.1)$$

As regards the 'passive resistance' concept, this formulation leads to equivalent results while doing the $\min(G)$ calculation. What makes a difference in Table 12.1c is its 3x6 structure, where two additional rows indicated by ξ_+ and ξ_- are introduced as virtual constituents into the system. By using the virtual species together with immaterial components the extent of kinetically controlled reactions (and thus incremental reaction rate effects) can be incorporated into the multi-component, multi-phase Gibbs energy minimization calculation.

The functionality of the virtual species is to increase or decrease the amount of a real species in the system according to a given reaction stoichiometry as defined by the stoichiometric matrix. As the given mass of the immaterial component is zero, adding the virtual species does not affect the mass balance of the system. By defining the standard chemical potential of the virtual species as zero at all temperatures (which means that its enthalpy, entropy and heat capacity are also zero) it can be ensured that the also energy balances remain unaffected while for example calculating a non-isothermal system. In the case of the stoichiometry of Table 12.1c, the controlled reaction is that of (12.2), i.e. formation or decomposition of water from oxygen and hydrogen. Addition of immaterial virtual species ξ_+ will increase the amount of water in the system. Respectively addition of the immaterial virtual species ξ_- will decompose water into hydrogen and oxygen. While doing the Gibbs'ian calculation, all non-constrained reactions will reach equilibrium. In this simple case, the only other reaction allowed is the phase change $H_2O(l) \leftrightarrow H_2O(g)$.

13. Immaterial constraints related to extents of reaction

From the matrix in Table 12.1c, by using again (9.6) in (8.2) the Gibbs energy of the reaction ($\Delta_r G$) is received for the decomposition of water (12.2):

$$\Delta_r G = 2\pi_{\text{H}} + \pi_{\text{O}} - (2\pi_{\text{H}} + \pi_{\text{O}} + \pi_{\text{H}_2\text{O}^*}) = -\pi_{\text{H}_2\text{O}^*} \quad (13.2)$$

Keeping in mind that the π_j -values are solved in the $\min(G)$ procedure and that they represent the chemical potentials of the independent components of the thermodynamic system in the Gibbs energy minimum, it is interesting to note that the $\pi_{\text{H}_2\text{O}^*}$ gives the negative of $\Delta_r G$ of a non-equilibrium reaction. As stated above in Chapter 8, this is the thermodynamic affinity of a chemical reaction, which becomes zero at equilibrium.

The incremental calculation of the progress of a kinetically constrained system is then quite simple. The original input for the system is defined as for any thermodynamic calculation in terms of the initial amounts of substances and the conditions of the $G = G(T, P, n_i)$ system. The extent of a known chemical change is deduced from the appropriate increment (typically by solving a reaction rate equation) and then introduced to the sequential calculation as the value (mol) of the virtual species. During the minimization procedure, the amounts of reactant and product species of the constrained reactions will adjust according to the incremental changes as obtained from the reaction rate equations and the rest of the system will reach the constrained equilibrium.

The example of Figure 13.1 shows the result of the constrained $\min(G)$ calculation for the system of Table 12.1, supposing gradual H_2O decomposition to O_2 and H_2 at 25 °C, 101 kPa total pressure. In this case, the total amount of water decreases in accordance with decomposition of liquid H_2O (water is mainly liquid in these conditions). The increase of the partial pressure of H_2 is shown to indicate the formation of gaseous reaction products. As the $\min(G)$ procedure solves the chemical potentials of the system components as Lagrange multipliers, the Table shows a listing of the respective computed $\pi_{\text{H}_2\text{O}^*}$ from the program ChemSheet for the 9 calculation steps, compared with the $\Delta_r G$ of reaction (12.2). The result also verifies the meaning of Equation (8.2) in the Gibbs energy minimization.

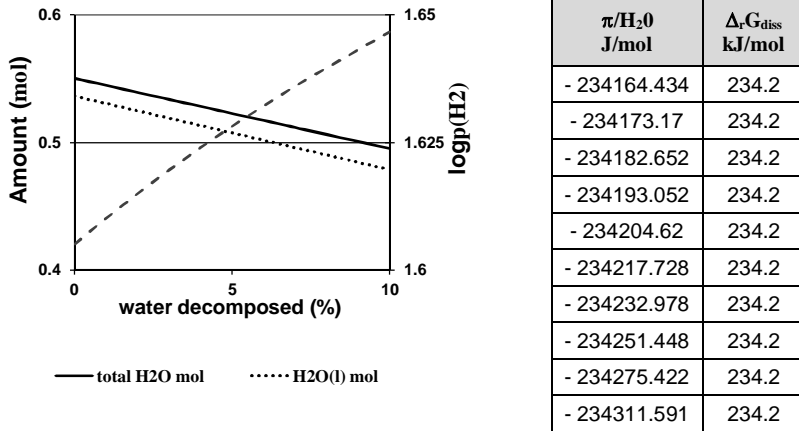


Figure 13.1. Use of the incremental reaction constraint in Gibbs energy minimization. Input: 0.55 mol H₂O, 0.25 mol O₂ and 0.175 mol H₂. The rate of H₂O decomposition is given as input of the virtual species ξ - with the formula $\xi = 0.055 - 0.055 * \log_{10}(1 - (t-10))$ [mol]; t is dimensionless (time) parameter with increment of unity; 25 °C, 101 kPa (cf. Hack 2008).

14. Use of actual reaction kinetics in Gibbs'ian calculations

14.1 Rate controlled Gibbs energy methods

A few approaches to combine reaction kinetics with Gibbs energy minimization have previously been published. Based on the early work of Keck and Gillespie (1971), Keck (1990) presented the rate-controlled constrained equilibrium (RCCE) method for use in fuel combustion calculations (Janbozorgi et al. 2009). All fast reactions are assumed to reach equilibrium, while the kinetically 'slow' reactions proceed according to their rate expressions. The rate equations are integrated so that the time-evolution can be simulated and the solution is used as a set of 'passive resistance' constraints in the Gibbs energy calculation. The extents of reaction are then introduced from an external group of differential equations into the Gibbs'ian algorithm. To include the extent of reaction (and its related changes in the thermodynamic properties) into the thermodynamic system, Koukkari (1993) suggested the *Ratemix* algorithm, which provides a discretized change of the reaction advancement within the Gibbs'ian calculation. The use of reaction rates as constraints was then refined to a more general approach by Pajarre and Koukkari (Pajarre 2001, Koukkari et al. 2001, Koukkari & Pajarre 2006¹⁻²) as one key application of the Constrained Free Energy (CFE) method (see also e.g. Blomberg & Koukkari 2011 and Koukkari et al. 2011). In what follows, the CFE approach of introducing reaction rate constraints into Gibbs energy minimising programs is described using three simple examples.

The introduction of reaction rate constraining into the Gibbs'ian thermochemical calculation does not indicate for any deduction of kinetic data from thermodynamic principles. The method merely makes it possible to calculate such 'dynamic chemical states' for which it is possible to distinguish rate controlling reactions while the rest of the system may reach partial equilibrium. For such systems the net reaction rate(s) can be combined with the thermodynamic affinity, while the assumption of the local or partial thermodynamic equilibrium is valid. This condition presumes that irrespective of a given concentration of chemical species in the reacting system at a given time, the thermodynamic intensive variables such as temperature remain defined. Consequently the chemical potential may be deduced for each species during the course of such chemical change. There are a large number of

interesting phenomena in chemistry, physics and biology well within this assumption, and it is thus of interest to have a method, by which the chemical potential can be followed in a complex thermodynamic system during an arbitrary chemical change.

The simplest means of using reaction rates as constraints in the thermodynamic system is to define the time-dependent input as a discrete increment of a given reactant. Suggesting a chemical reaction



The typical reaction rate (r) is given in terms of a reaction rate coefficient (k) and concentration $[X]$ as follows:

$$\frac{d[X]}{dt} = r = -k \cdot F([X]) \Rightarrow \Delta[X] = r \cdot \Delta t \Rightarrow \Delta n_X = V \cdot \Delta[X] \quad (14.2)$$

The increment Δn_X is then used as the mole number input of the virtual species ξ in the Gibbs'ian system. During the course of the reaction the sequential increments $\Delta n_X(t)$ can be solved in succession from (14.2) until the final reactant concentration (or chemical equilibrium) has been reached. The sequential $\min(G)$ calculation results with the respective constrained minima and their system properties, including amount of matter of other species in the system under the assumption of the partial equilibrium.

As the thermodynamic $\min(G)$ calculation inherently uses the activities of species, one may take advantage of the reaction quotients by using the net reaction rates, which for elementary reactions are defined as follows (McQuarrie 1999):

$$r = k \prod_{\text{reactants}} a_{\text{reactants}}^{v_{\text{reactants}}} \left[1 - e^{-A/RT} \right] = k \prod_{\text{reactants}} a_{\text{reactants}}^{v_{\text{reactants}}} \left[1 - \frac{Q}{K} \right] \quad (14.3)$$

where

$$\frac{\prod_{\text{products}} a_k^{v_k}}{\prod_{\text{Reactants}} a_k^{v_k}} \equiv Q \quad (\Delta_r G \neq 0) \quad ; \quad \frac{\left[\prod_{\text{products}} a_k^{v_k} \right]_{eq}}{\left[\prod_{\text{Reactants}} a_k^{v_k} \right]_{eq}} \equiv K \quad (\Delta_r G = 0) \quad (14.4)$$

The *affinity* is denoted by A and the *reaction quotient* by Q as these are their established symbols and there is seldom a context where they could be confused with surface area and heat (see also Equations of Chapter 8 and Table 9.1). In

applied process engineering the Equation (14.3) appears often as a useful approximation even for non-elementary reactions, giving an appropriate method for which the experimental (net) rate coefficient k can be adjusted with proper kinetic data.

In practical computation problems it is of course possible to use other than thermodynamically deduced expressions for the reaction kinetics, such as concentration-based, net or global reaction rate expressions deduced from mechanistic models as well as purely empirical formulations. In the following chapters a few simple examples are explained in more detail.

14.2 Example 1. A simple reaction kinetic system

The decomposition of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2) is a gas phase reaction occurring with a finite rate in close to ambient temperatures



The rate of N_2O_4 decomposition can be approximated as a first order reaction as follows:

$$\frac{d[N_2O_4]}{dt} = r = -k \cdot [N_2O_4] \quad (14.6)$$

The extended conservation matrix of the simple system is presented in Table 14.1. The matrix includes nitrogen as an inert gas (not participating in the reaction) and the immaterial component R connected with either forward or reverse reaction via the virtual invariant phases denoted by R_+ and R_- . The gaseous species have been indicated as (g), the virtual constituents appear formally as separate (pure) condensed phases in the Gibbs energy minimization.

Table 14.1. The extended conservation matrix of the N_2O_4 dissociation system.

	N	O	R
N_2 (g)	2	0	0
N_2O_4 (g)	2	4	1
NO_2 (g)	1	2	0
R_+	0	0	1
R_-	0	0	-1

The incremental decomposition of N_2O_4 from Equation (14.6) is then given as input of R_- in a sequential calculation. The value of the first order reaction rate constant k_1 ($= A \exp[-E_a/(RT)]$) is from the NIST database (<http://kinetics.nist.gov/kinetics/>); the frequency factor $A \sim 1.E06 \mu s^{-1}$ and activation energy $E_a \sim 40 \text{ kJ mol}^{-1}$ T -range 270–320 K, $P = 1 \text{ bar}$; N_2 assumed to be the inert gas present).

The first mode (Figures 14.1 a–b) allows the virtual phase to be ‘formed’ when the equilibrium composition has been reached and thus the calculated Gibbs energy remains at the equilibrium value. The alternative mode is to prevent the ‘formation’ of virtual species in the calculation by using the DORMANT option (the activity of a phase or a constituent is calculated but finally the phase or substance is removed from the $\min(G)$ system) and thus the Gibbs energy curve $G = G(\xi)$; $0 \leq \xi \leq 1$ is received as the result (lower Figures 14.1 c and d). The energy and mass of the virtual species are zero by definition and thus its presence remains but virtual without any effect on the physical system.

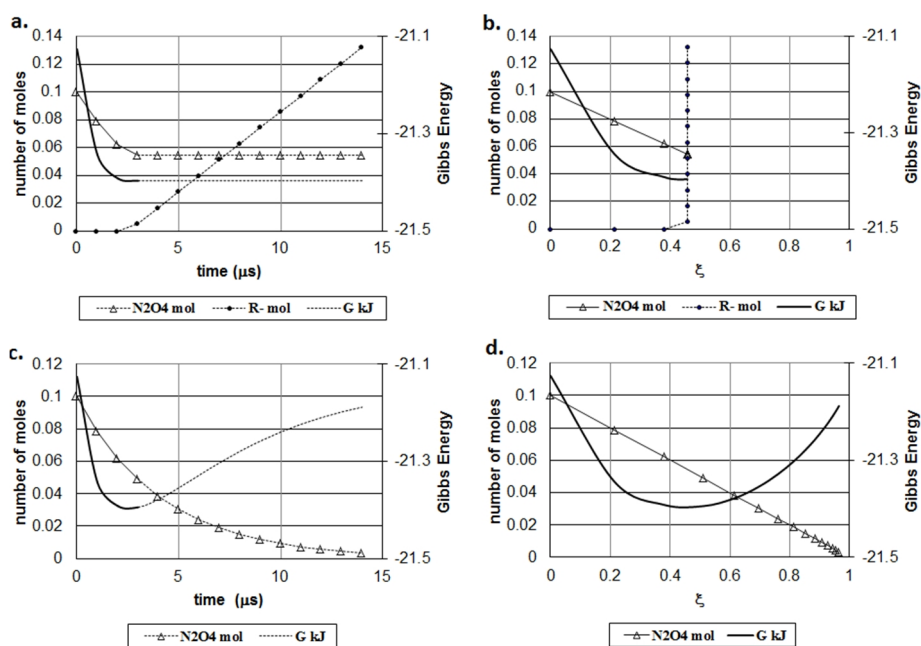


Figure 14.1a–d. Use of the virtual invariant phase with reaction rate constraints in Gibbs energy minimization in the $N_2/N_2O_4/NO_2$ –system, presented either in terms of the relative extent of reaction (ξ) or time scale. Model input: N_2 2.0 mol (inert); N_2O_4 1.0 mol; $P = 101$ kPa, $T = 40$ °C. When the virtual species (R-) appears ‘Entered’ in the calculation, the system reaches equilibrium at $\xi \sim 0.46$ without further change in composition or Gibbs energy (a-b). When R- is set ‘Dormant’ in the calculation, the chemical change continues and the full $G = G(\xi)$ and $G = G(t)$ curves are produced (c–d).

14.3 Example 2. Use of reaction quotient and/or affinity in the reaction rate expression

The absorption of CO₂ into water is described with the simple reaction



for which the reaction rate is $r = -dn_{\text{CO}_2(\text{g})}/dt$. This can be expressed in terms of the affinity (or reaction quotient) as follows:

$$r = k_1 a_{\text{CO}_2(\text{g})} - k_{-1} a_{\text{CO}_2(\text{aq})} = k a_{\text{CO}_2(\text{g})} \left(1 - \frac{Q}{K} \right) = k a_{\text{CO}_2(\text{g})} \left(1 - e^{\frac{-A}{RT}} \right) \quad (14.8)$$

where the affinity A is as in Equation (14.3). In Figure 14.2 a calculation result together with measured values for a pH change in a simulated papermaking solution (a dilute aqueous solution consisting of dissolved CaSO₄ and CaCO₃ fines and the respective solute species) is shown. The pH drop is due to absorption of CO₂ from the ambient air to the clear solution. The net reaction rate coefficient k has been 'curve-fitted' with the measured pH data. Thus the calculated curve only shows the applicability of the supposed rate equation to the data used for the fitting parameter. From the thermodynamic point of view the example however shows the attainment of the thermodynamic absorption limit in terms of the pH of the solution. (It may be needless to say that the thermodynamic calculation bears the major advantage of giving all the measurable thermodynamic quantities, among them pH itself, without additional elaboration in the kinetic model). The use of the affinity, as received from the Gibbs'ian method can be used to recognize the thermodynamic curb in the reaction rate calculation.

Table 14.2. The extended conservation matrix of the CO₂ absorption system.

	O	H	C	e ⁻	R
O ₂ (g)	2				
CO ₂ (g)	2		1		1
H ₂ O(g)	1	2			
H ₂ O	1	2			
H ⁺ (aq)		1		-1	
OH ⁻ (aq)	1	1		1	
CO ₂ (aq)	2		1		
HCO ₃ ⁻ (aq)	3	1	1	1	
CO ₃ ²⁻ (aq)	3		1	2	
R ⁺					1
R ⁻					-1

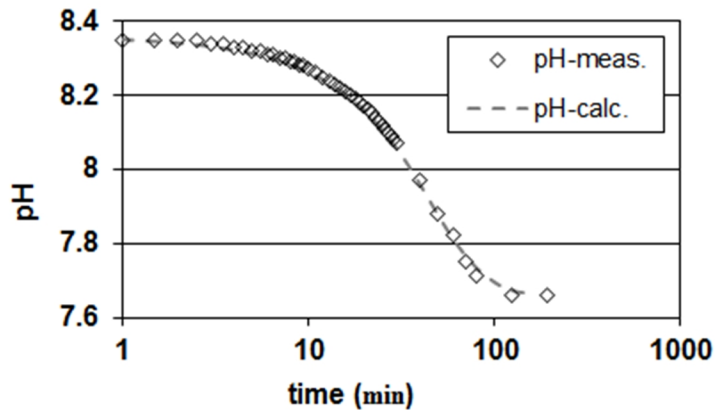
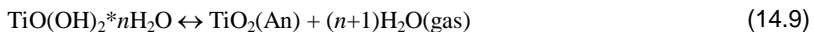


Figure 14.2. The extended conservation matrix of the CO_2 dissolving system, calculation performed by using the reaction quotient rate expression.

14.4 Example 3. Anatase-rutile transformation

This example presents the formation of titanium dioxide in a calciner, which is one of the final stages of the industrial sulfate process producing titania pigment. To simplify the treatment here, the feed is supposed to consist merely of titanium oxyhydrate [without moisture including sulphuric acid and sulfate residues]. The chemical composition of the oxyhydrate is approximated as $\text{TiO}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. In a calcination process the temperature of the hydrate is raised to ca 1000 °C, the slurry becomes dried and finally the hydrate decomposes, leaving titanium dioxide as a solid product. From the oxy-hydrate, at relatively low temperatures (ca 200 °C) the less stable xenotime form anatase, $\text{TiO}_2(\text{An})$, is formed first, and only in the high temperature zone of the furnace end, the thermodynamically stable tetragonal rutile $\text{TiO}_2(\text{Ru})$ appears as the desired product. The reactions are as follows:



As rutile is the more stable form of the two titanium dioxide species Gibbs free energy minimization would at all temperatures result in rutile and water. This would lead to a 100 % rutilisation of the titania already at temperatures, where the Ti-oxyhydrate is but calcined by reaction (14.9). It is however well-known from practical experience, that the rutilisation reaction (14.10) is slow and only takes place with a finite rate at elevated temperatures (above 850 °C). Any simulation of the calcination process must take this feature into account.

The extended matrix of the calcination system is shown in Table 14.3. Note that the system components do not need to be elements but can be freely chosen from

appropriate stoichiometric combinations. The reaction constraints have been set to control the formation of rutile, $\text{TiO}_2(\text{Ru})$, affecting the reaction (14.10) above.

Table 14.3. The extended matrix of $\text{TiO}(\text{OH})_2$ calcination with three system components.

	TiO_2	H_2O	R
$\text{H}_2\text{O-gas}$	0	1	0
$\text{TiO}(\text{OH})_2$	1	1	0
$\text{TiO}_2(\text{An})$	1	0	0
$\text{TiO}_2(\text{Ru})$	1	0	1
R+	0	0	1
R-	0	0	-1

The reaction rate can be presented in the form of rutile fraction x , which is measured as function of time at constant temperature and pressure. For example, the following formula used:

$$x = 1 - (1 - k \cdot t)^3 \quad (14.11)$$

Here, x is the fraction of rutile in the reaction mixture, t is time (hours) and k is the reaction rate constant (h^{-1}). This formula was used in the multi-component system to calculate the respective molar amount for R_+ , which determines the kinetic conversion rate from anatase to rutile.

The input data of the calculation system have been collected to Table 14.4. The parameters for the rate constant are again given in terms of the Arrhenius equation [$k = A \exp(-E_a/RT)$], with A as the frequency factor and E_a as the activation energy.

Table 14.4. Input data for the $\text{Ti}(\text{OH})_2$ calcination model.

$\text{TiO}(\text{OH})_2$	R+	Temperature	Pressure	A	E_a
mol	mol	$^\circ\text{C}$	atm	h^{-1}	kJ mol^{-1}
1.0	Eqn(14.11)	995–1045	1	1.8E17	442

The thermodynamic (Gibbs energy) data for the species are received from standard sources or estimated from thermogravimetric studies for the amorphous oxy-hydrate species. The calculation is then performed in 60 steps with 10 minute intervals to match the experimental data of McKenzie (1975), which covers in total 10 hours at 995°C . For each step, the Gibbs energy of the system is minimised and as a result the composition as well as the Gibbs energy of the system becomes calculated.

Figure 14.3 (left) shows the anatase-rutile transformation curves for the $\text{TiO}(\text{OH})_2\text{-O}_2$ -system at three different temperatures. The curves represent the

degree of rutilisation (rising from zero to 1) and the total, decreasing Gibbs energy of the system during the course of the reaction. At each temperature, the Gibbs energy is a monotonically descending curve as a function of time, reaching its minimum value at equilibrium. As the Gibbs energy model inherently calculates other thermodynamic properties, such as heat capacities, enthalpies and entropies, it is often advantageous to use Gibbs energy based modeling in process calculations. As an example, the exotherm of the rutilisation reaction has been deduced from the Gibbs energy model at the three reaction temperatures and is presented in Figure 14.3 (right).

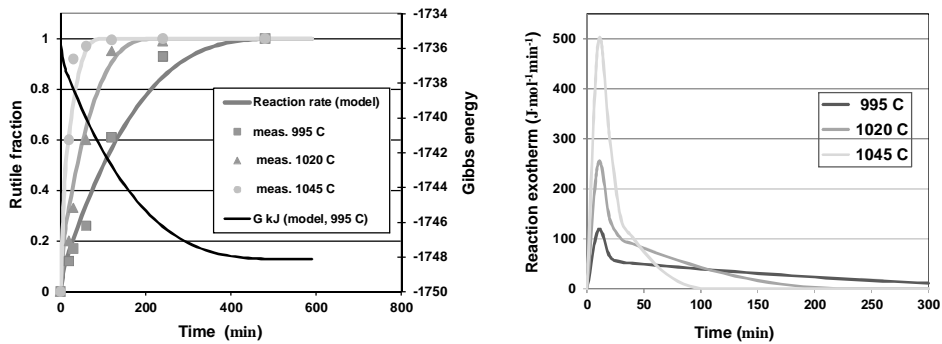


Figure 14.3. The kinetics of rutilisation in three temperatures. The time-dependent Gibbs energy is shown as a monotonically descending curve $G = G(t)$.

14.5 Features of the virtual species in kinetically constrained calculations

In Table 14.5, the key properties of the chemical constituents of the unconstrained system and virtual constituents have been listed. The chemical constituents are those with a true stoichiometric formula, such as e.g. H_2O consisting of one oxygen and two hydrogen atoms, bearing a molecular mass in the respective ratio of its elemental components. The virtual constituent in the conservation matrix appears with zero molecular mass and with zero standard chemical potential, having a stoichiometric factor of +1 for the forward and -1 for the reverse reaction. These properties (zero mass and zero energy) make the virtual species to appear as mathematical aids in the thermochemical calculation, without affecting the energy or mass balance of the thermodynamic system.

Table 14.5. Properties of the virtual species in constrained Gibbs energy systems.

Type of constituent	Stoichiometric elements	Standard state data	Molecular mass
Chemical	a_{kj} in $\sum_j a_{kj} X_j$	$\mu_k^\circ = h_k^\circ - TS_k^\circ$	$M_k = \sum_j a_{kj} M_j$
Virtual (forward)	+1	$\mu_k^\circ \equiv 0$	$M_k \equiv 0$
Virtual (reverse)	-1	$\mu_k^\circ \equiv 0$	$M_k \equiv 0$

The above treatment has been presented for a single reaction in a most simple system. In the general case of several reactions, the following two equations can be deduced from (8.2) and (9.6) for the chemical potentials of the constrained system:

$$\sum_k v_k \mu_k = 0 \quad (\text{equilibrium reactions}) \quad (14.12)$$

$$\sum_k v_k \mu_k = \sum_k v_k \sum_{j=NC+1}^{NC} a_{kj} \pi_j \neq 0 \quad (\text{constrained non-equilibrium reactions}) \quad (14.13)$$

Here, v_k is the stoichiometric number of a species k in a given reaction and the summation goes over the reactant and product species. In (14.13), index j refers as usual to the system components of the Gibbs'ian calculation, NC' has been used for actual chemical components, NC is the total number of components and thus includes the virtual components present for the suggested kinetic constraints.

When compared with (8.10) it is evident that Equation (14.13) gives the affinity of the kinetically constrained non-equilibrium reactions and may also be written as:

$$A_r = - \sum_{j=1}^{NC} \sum_{k=1}^N v_{k_r}^* \left(\frac{\partial G}{\partial b_j} \right) = - \sum_{k=1}^N v_{k_r} \mu_{k_r} \quad r=1,2,\dots,R \quad (14.14)$$

where the notation $v_{k_r}^* = v_{k_r} a_{k_r,j}$ has been adapted for brevity and to emphasize that the two expressions (8.10) and (14.14) are equivalent.

While the minimization is performed, the physically reasonable solution requires that all constituent amounts n_k receive a non-negative value. This condition incorporates the inequality conditions

$$\mu_k^\circ - \sum_j a_{kj} \pi_j = 0; \quad \forall k \quad ; \quad n_k > 0 \quad (14.15)$$

$$\mu_k^\circ - \sum_j^{NC} a_{kj} \pi_j > 0; \quad \forall k; \quad n_k = 0 \quad (14.16)$$

Together with the conservation constraints (9.3), the conditions (14.15) and (14.16) represent the Karush-Kuhn-Tucker (KKT) conditions for the Gibbs energy minimization problem (Smith and Missen 1991), here written for pure invariant phases. (see Smith and Missen for the respective conditions written for mixture phases) As the virtual constituents always appear as pure invariants, the simple expressions (14.15) and (14.16) will yet be sufficient for the use of these conditions while applying the kinetic constraints in the minimization algorithm.

While the Lagrange multiplier (chemical potential) for the constraint component affecting reactant(s) is negative ($\pi_{\text{reactant}} < 0$), based on Equations (8.2) and (14.3) it follows that the corresponding affinity > 0 and the net reaction will proceed spontaneously. The inequality condition (14.16) then holds for the Gibbs'ian calculation. When any of the constraint multipliers becomes zero, the respective constraint entity becomes ineffective. When all of them are zero, also affinities of all reactions are zero and the system has reached chemical equilibrium. Thus, the algorithm provides inherently the thermodynamic equilibrium condition for the kinetically constrained calculation.

It is typical for the Gibbs energy minimizing algorithms that metastability of a phase can be taken into account by suppressing a more stable phase or a given phase constituent from the final calculation, even though it might appear in the given stoichiometric system. In those cases, the algorithms indicate the greater activity of a certain phase, but provide the final calculation for the suppressed metastable system. For example in the ChemApp program (Petersen and Hack 2007), the respective identification is 'Dormant' for the suppressed phase (constituent) and 'Entered' for the phases allowed to be formed. For the dormant species, however, the activities are calculated using the final (metastable) state as a reference.

Thus with the 'dormancy' of a phase, it is straightforward to follow and control the affinity for the formation of metastability in the system. This feature is extensively used in many conventional minimization algorithms. As was already indicated in the above example 1 (Chapter 14.2.), it is also of practical advantage when performing calculations with the virtual constituents in a constrained Gibbs energy system.

For an equilibrium system the Equation (14.15) can be considered defining a value of the chemical potential also for a species that is not present in the system. It follows that the virtual invariant phases, for which the standard term is zero, can be used for the calculation of alternative reactivity options in systems which apply reaction rate constraints. The chemical potential of a pure invariant equals zero, when the pure phase appears as 'Entered' and (14.15) is valid for a stable phase (the Lagrange multiplier $\pi_{j=R} = 0$, respectively). When (14.16) is valid, the phase is not stable and chemical potential of the virtual phase is less than zero. If the calculation is performed in the 'Dormant' mode, the chemical potential of a virtual feed phase may be less than zero and a forced calculation beyond the equilibrium point becomes possible. This behaviour is presented in Figure 14.4.

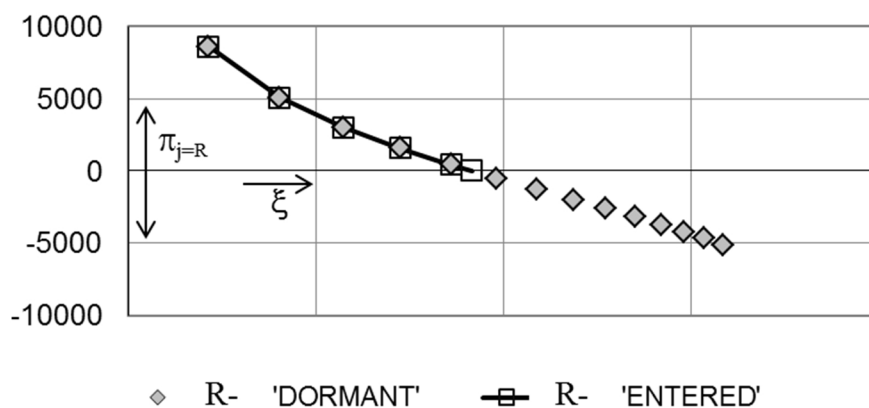


Figure 14.4. Affinity of the kinetically constrained reaction calculated as the Lagrange multiplier ($\pi_{j=R}$, $\text{J}\cdot\text{mol}^{-1}$) of the virtual component. Virtual phase as 'Entered' reveals the equilibrium point at $\xi \approx 0.45$ ($\pi_{j=R} = 0$). The virtual phase as 'Dormant' leads to a forced calculation beyond the equilibrium point ($\pi_{j=R} < 0$).

15. Non-equilibrium and parametric phase diagrams

15.1 Uses of phase diagrams

Phase diagrams are extensively used in chemistry and materials science for depicting stability conditions for multi-component systems. Before the computational era, voluminous books were dedicated to mere phase diagrams, while then one of the leading motivations for computational thermodynamics has been the development of automated methods to present the wanted equilibrium system as a phase diagram. The phase diagrams in general are graphical projections of the multi-component Gibbs energy surfaces, presented in terms of (generalised) potentials and state variables. Typical examples are T - X (temperature-composition), H - X (enthalpy-composition) and P - X (pressure-composition) diagrams. The elements of the construction of such diagrams is well presented in standard textbooks, a more advanced treatment is given e.g. by Hillert (2008).

The introduction of virtual components and constituents provides new aspects to phase diagram calculations. As the virtual component can be used as an additional parameter in the Gibbs energy calculation, the result then becomes visible directly in the respective phase diagrams. The CFE becomes helpful when specific physical conditions, advancement of chemical reactions or e.g. external field effects will contribute to the phase stabilities.

15.2 Paraequilibrium diagrams

In steel and alloy solidification the driving forces for phase transformations are set by thermodynamics, while the actual changes in phase composition are often controlled by diffusion and convection. The different mobilities of species in the solidifying structure will depend on temperature and composition and thus the conditions lead to several different solidification patterns, which also are of practical interest. Typical cases involve the formation of carbides in steelmaking, as the thermodynamically favoured reactions between interstitial carbon and substitutional metals (e.g. chromium, nickel) in high quality steels would lead to presence of a number of carbide compounds in the respective equilibrium phase diagrams.

However, in a practical solidifying process (such as continuous casting) their formation is often avoided by the chosen cooling rate, the physical reason being that small interstitial atoms (carbon, oxygen, nitrogen) with their greater mobility may equilibrate between the melt and solid fractions, while the substitutional metal atoms remain immobile between these regions. Furthermore, the phase transformation from $\alpha \rightarrow \beta$ may occur without any change in their mutual fractions between the reactant (parent) phase and the product phase. In such conditions, a *partitionless transformation* as defined by Hillert (p. 144) will occur. This leads to a condition, where the use of composition based constraints in the Lagrangian problem will give the respective results in $\min(G)$ calculations for an arbitrary number of restricted phases and constituents (Kozeschnik 2000) and can be used to produce the respective *paraequilibrium phase diagrams*.

A simple example consisting of a BCC – FCC (body centered cubic – face centered cubic) Fe-Ni-C system is presented as an example in Table 15.1. A virtual component *Ni-FCC has been introduced with matrix elements u_{Ni} and u_{Fe} as new stoichiometric entities. Their meaning as the complementary constraints is to control the ratio of Ni and Fe as metallic elements during any phase transformation and thus they are defined as follows:

$$u_{Fe} = \frac{n_{Fe}}{n_{Ni} + n_{Fe}} \quad (15.1)$$

$$u_{Ni} = \frac{n_{Ni}}{n_{Ni} + n_{Fe}} \quad (15.2)$$

i.e. the fractions of Fe and Ni in the parent phase, predestined to remain as constant in both phases during any phase transformation.

By using these definitions for the molar balance of the virtual component *Ni-FCC:

$$b \cdot *_{Ni_{FCC}} = -u_{Ni} \cdot n_{Fe:C|FCC} - u_{Ni} \cdot n_{Fe|FCC} + u_{Fe} \cdot n_{Ni:C|FCC} + u_{Fe} \cdot n_{Ni|FCC} \quad (15.3)$$

$$b \cdot *_{Ni_{FCC}} = -u_{Ni} \cdot n_{Fe}^{FCC} + u_{Fe} \cdot n_{Ni}^{FCC} = 0 \quad (15.4)$$

as the amount of any such virtual component must be zero. It then follows that the ratio of Fe and Ni in the FCC phase equals the by definition constant ratio of the u -fractions. It is then evident from the matrix that the chemical potentials of Fe and Ni can be expressed in terms of the u_{Me} -coefficients as follows:

$$u_{Fe} \mu_{Fe|FCC} + u_{Ni} \mu_{Ni|FCC} = u_{Fe} \mu_{Fe|BCC} + u_{Ni} \mu_{Ni|BCC} \quad (15.5)$$

while instead, carbon is in equilibrium between the phases:

$$\mu_{C|FCC} = \mu_{C|BCC} \tag{15.6}$$

The weighted average of chemical potentials of iron and the alloying components metals remains the same in all phases. With several metallic components and several paraequilibrium phases, a new virtual component will be needed for each combination. With known stoichiometry and composition of the parent phase, the u -factors are, however, easily deduced and the extension of the matrix can be performed algorithmically during the computational procedure. When the number of phases (N) or the number of metallic components (M) is larger than two the number of required constraint components is given by (N-1)*(M-1) (Pelton et al. 2014).

Table 15.1. Introduction of the virtual component into the Fe/Ni/C paraequilibrium system.

Phase	Constituent	Fe	Ni	C	*Ni_FCC
FCC	Fe:C	1	0	1	$-u_{Ni}$
	Fe	1	0	0	$-u_{Ni}$
	Ni:C	0	1	1	u_{Fe}
	Ni	0	1	0	u_{Fe}
BCC	Fe:C	1	0	3	0
	Fe	1	0	0	0
	Ni:C	0	1	3	0
	Ni	0	1	0	0

The practical significance of paraequilibrium presentation becomes evident eg. from Figure 15.1, as the number of possible phases in the given compositional range becomes reduced to those, which also refer to experimental evidence in e.g. steelmaking conditions (Kozeschnik 2000, Hillert 2008).

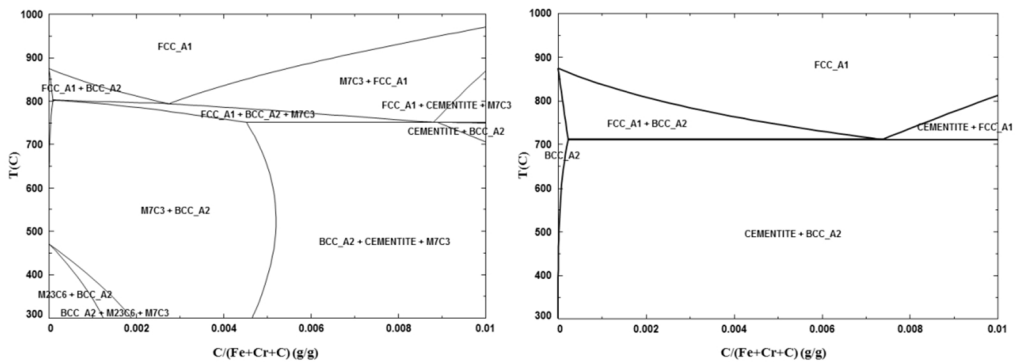


Figure 15.1. Phase diagram for Fe-Cr-C system. Left: no compositional constraints; right: partitionless phase transformation (paraequilibrium) for Fe and Cr with free mobility of carbon [Cr/((Cr+Fe)+C) (g/g) = 0.0280, P = 1 atm, courtesy of Hack, 2012].

15.3 Partial equilibria in reactive systems (isoaffinity diagrams)

As already shown in Chapter 13 the immaterial constraining can be connected with the advancement of selected chemical reactions, resulting with the non-zero non-equilibrium affinity of the said reaction as one of the Lagrange multipliers. If such kinetically constrained reaction occurs in phase α the immaterial constraining can be connected with the advancement of selected chemical reactions, resulting phase diagrams where the chemical change appears with a given (non-equilibrium) extent of reaction, while the respective phase composition is at partial equilibrium.

Relative slowness of chemical reaction rates can often prevent equilibration in chemically reactive fluid mixtures, particularly at low temperatures and in conditions where the phase separation is to take place in a short residence time (e.g. Maurer 1996). A typical case is reactive distillation, quite extensively utilised in the chemical industry. The well-known ethanol-acetic acid, water - ethylacetate system serves as a viable example (Toikka et al. 2009) and was chosen to illustrate the respective calculation by using the constrained Gibbs energy technique. The chemical reaction is



which may be abbreviated as follows:



The extended matrix, including the virtual constituent for the extent of reaction is presented in Table 15.2.

Table 15.2. Introduction of the virtual component into the ethanol-acetic acid vapour-liquid system.

		H ₂ O	EtOH	AA	R
Vap	Ethanol		1		
	Acetic acid			1	
	Acid dimer			2	
	Water	1			
	Ethyl acetate	-1	1	1	1
Liq	Ethanol		1		
	Acetic acid			1	
	Water	1			
	Ethyl acetate	-1	1	1	1
Virtual	ξ_+				1

The virtual constituent (ξ_+) will control the extent of the esterification reaction, while the rest of the system consisting of vapour and liquid phases is otherwise free to reach equilibrium; the dimerization in the gas phase alike is an equilibrium reaction.

The partial equilibrium calculation can be performed e.g. for the dew and bubble points by using the extent of reaction in the liquid phase as a parameter (Figure 15.2).

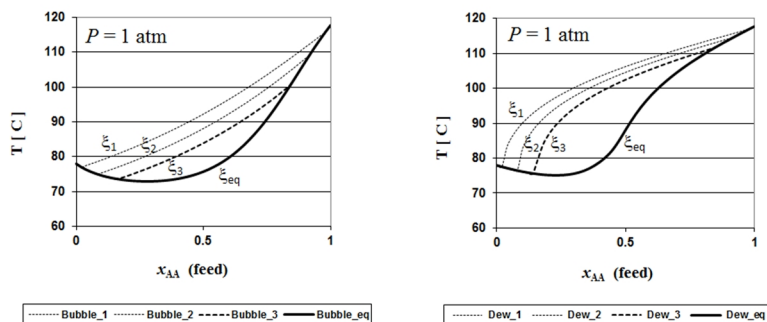


Figure 15.2. Calculated bubble and dew points of the two phase esterification system with the reaction advancement as a parameter.

As physical components of the model system those corresponding to ethanol, acetic acid, and water were selected. The same result can be obtained with the elements (C, H and O) as physical components. Additional immaterial constraint was applied to the ethyl acetate species allowing the control of the advancement of the esterification reaction. The standard state chemical potentials from HSC (A. Roine, Outokumpu, HSC Chemistry® for Windows, Version 4.1, (1999)) were adjusted by using the vapour pressure data from several sources (for these see references in Koukkari and Pajarre 2011). The vapour phase was regarded as an ideal gas including the acetic acid dimer, while the liquid mixture is modelled using the UNIFAC data (e.g. Poling, et al. 2001).

It may be more relevant to compare the vapor and liquid phase not with the same reaction advancement of the esterification, but the two phases with equal affinity for the reaction (Maurer 1996). The respective isoaffinity calculation is straightforward in the CFE-method, as the Lagrange multiplier adjacent to the extent of a kinetically constrained reaction provides directly the non-equilibrium affinity (Koukkari et al. 2011). The technique then allows for construction of metastability surfaces as 'isoaffinity diagrams' for various reactive separation processes. Even though such conditions may frequently appear in practical engineering processes, there seems to be little confirming data for isoaffinity curves from controlled experimental arrangements.

15.4 Parametric diagrams for magnetic systems

The CFE method provides a practical approach to phase diagrams with additional (immaterial) parameters. The effect of diameter onto the phase behaviour of alloy nanoparticles has been discussed by Lee et al. (2005) while it has been shown that the lowering of the melting point of small particles can be interpreted with the increasing surface energy factor. As for macroscopic media, the immaterial effect may be due to external fields (or more generally, external work). Quite recently Ludtka et al. (2005) were considering the phase change between austenite and ferrite, while the remains of austenitic constituent was removed by treatment of the steels with high intensity magnetic field. They also presented the respective phase diagram calculated by the Thermocalc program, for which the appropriate changes in the standard Gibbs energy of the ferrite phase had been made.

From the point of view of the CFE method the magnetic field strength may be included in terms of an immaterial component, which then may be used as a parameter in analogy with the extent of reaction in case of isoaffinity diagrams.

It is customary to write the chemical potential (Yamaguchi et al. 1997) of a two component (X,Y) compound subject to magnetisation as follows :

$$\mu(X_a Y_b) = a \pi(X) + b \pi(Y) = \mu^{\circ(B=0)}(X_a Y_b) + RT \ln a(X_a Y_b) + MB \quad (15.9)$$

where B is the magnetic flux density and M is magnetisation (assumed independent of the magnetic field for simplicity). If the magnetic component is introduced to the Lagrangian system as an additional constraint, the respective chemical potential solved by the minimization algorithm is μ^* :

$$\mu^*(X_a Y_b) = a \pi(X) + b \pi(Y) + v_M \pi_M = \mu^{\circ(B=0)}(X_a Y_b) + RT \ln a(X_a Y_b) \quad (15.10)$$

It follows that

$$v_M \pi_M = -MB \quad (15.11)$$

Then, introducing a normalisation factor in terms of the magnetization units $M_0 = J/(\text{mol T})$

$$v_M = -\frac{M}{M_0} \quad (15.12)$$

and

$$\pi = B \cdot M_0 \quad (15.13)$$

Then the magnetic flux can be used directly as a parameter in the input of a $\text{min}(G)$ routine with a capability of using the virtual components.

The magnetic effect on chemical or phase transformations is often negligible due to the high field intensities required to reach any substantial chemical effect. However, for ferromagnetic materials the external field effects may be significant and can be used e.g. in high-strength steelmaking for transformation of residual austenite to ferrite. Even such transformations will require high field intensities, the experimentally estimated effect on the Gibbs energy being relatively small. For the austenite-ferrite transformation the ΔG -value due to the magnetic field was estimated to be $12.6 \text{ J}/(\text{molT})$ (Ludtka et al. 2005). The extended system with the magnetic contribution introduced with a virtual component-constituent combination is presented in Table 15.3.

Table 15.3. Introduction of the magnetization component into a simple austenite-ferrite system.

Phase	Species	System component		
		Fe	C	M
BCC-Fer	Fe:C	1	1	-12.6
	Fe:Va	1	0	0
FCC-Aus	Fe:C	1	1	0
	Fe:Va	1	0	0
Fe₃C	Fe ₃ C	3	1	0
M	M	0	0	1

The ΔG due to the external magnetic field can be set to positive value (for example in ChemSheet calculations) with the magnetic flux intensity as a parameter. This will directly affect the chemical potential of the ferritic iron (BCC/Fe:C). For example with magnetic field of 20 T chemical potential of Fe:C is changed by $252 \text{ J}\cdot\text{mol}^{-1}$. The respective parametric phase diagram is shown in Figure 15.3 below.

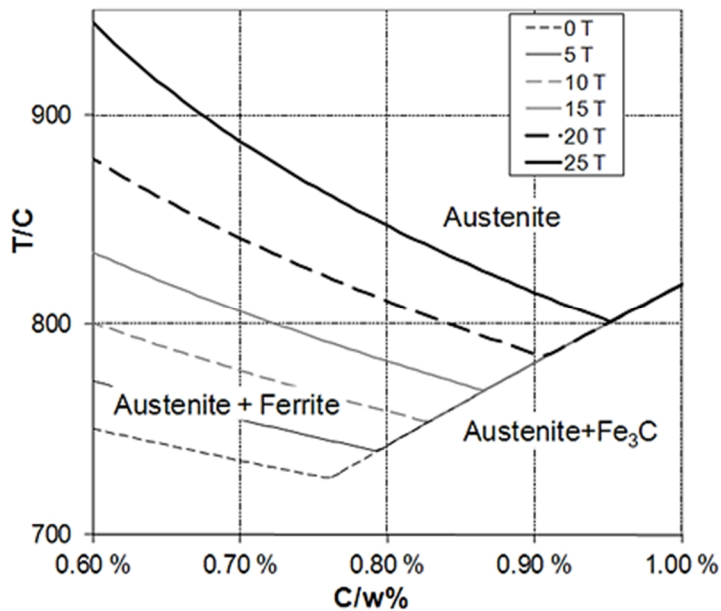


Figure 15.3. The effect of external magnetic field on the ferrite-austenite phase transformation (Pajarre 2014). The result is in fair agreement with those reported by Ludtka et. al. (2005) and e.g. Choi et. al. (2000).

16. Conventions used in biochemical thermodynamics

A new emerging field for the Gibbs'ian applications exists in biochemical thermodynamics. In biochemistry, with a multitude of metabolite species and correspondingly a vast number of optional reaction mechanisms, the application of thermodynamic feasibility analysis often offers a time-saving approach for computational studies. Then, one may utilise the constrained Gibbs energy approach e.g. for energetic studies of the operable pathways.

In biochemistry, the conventions regarding the expressions of species and components are somewhat different from those used in traditional physical chemistry. The focus is on dilute aqueous solutions where reactants like ATP, composed of ATP_4^- , HATP_3^- , H_2ATP_2^- , exist in a pH range varying from 5 to 9. The pH is considered to be an independent variable controlled by a buffer solution. The consumption or production of hydrogen ions is not included when writing biochemical equations such as $\text{ATP} + \text{H}_2\text{O} \leftrightarrow \text{ADP} + \text{P}_i$. Biochemical equations do not balance hydrogen atoms or electric charges, but they balance atoms of other elements. When water is a reactant, its concentration is not used in the expression of the apparent equilibrium constant, yet its standard Gibbs energy of formation is used in the calculation of the apparent equilibrium constant.

Alberty (2001), and recently e.g. Fleming et al. (2009) have formulated the thermodynamic conventions to be applicable in biochemistry. The transformed Gibbs energy (G') is introduced, for which in addition to temperature and pressure, pH is used as an additional independent variable. The standard chemical potentials of aqueous species are transformed taking into account the effect of hydrogen ions by a mathematical transform and by including a 'standard activity' assuming constant ionic strength. In what follows, these features are interpreted by using the concept of immaterial components of the system.

For a homogeneous system, from (5.8)

$$dG = -SdT + VdP + \sum_k \mu_k dn_k \quad (16.1)$$

The amount of hydrogen component $n_c(\text{H})$ in a biochemical reaction system is

$$n_c(\text{H}) = \sum_{k=1}^N N_{\text{H}}(k)n_k \quad (16.2)$$

where $N_{\text{H}}(k)$ is used for the number of hydrogen atoms in each constituent (k).

The transformed Gibbs energy that has the chemical potential of hydrogen ions as a natural variable is defined by a Legendre transform (see Alberty 2001):

$$G' = G - n_c(\text{H})\mu(\text{H}^+) \quad (16.3)$$

From which

$$dG' = dG - n_c(\text{H})d\mu(\text{H}^+) - \mu(\text{H}^+)dn_c(\text{H}) \quad (16.4)$$

and further the fundamental equation for the transformed Gibbs energy becomes

$$dG' = -SdT + VdP + \sum_{k=1}^{N-1} \mu'_k dn_k - n_c(\text{H})d\mu(\text{H}^+) \quad (16.5)$$

The transformed chemical potential for any species (k) is here given by

$$\mu'_k = \mu_k - N_{\text{H}}(k)\mu(\text{H}^+) \quad (16.6)$$

To derive the standard transformed chemical potentials, use (7.9) in the form

$$\mu_k(T) = \mu_k^{\circ}(T) + RT \ln a_k = \mu_k^{\circ}(T) + RT \ln \gamma_k + RT \ln \frac{c_k}{c^{\circ}} \quad (16.7)$$

Here, the concentration of species k and the reference concentration are given with the symbols c_k and c° , respectively. Combining (16.6) and (16.7) there is

$$\mu'_k \equiv \mu_k^{\circ} + RT \ln \frac{c_k}{c^{\circ}} \quad (16.8)$$

Where the standard transformed chemical potential is

$$\mu_k^{\circ} \equiv \mu_k^{\circ} + RT \ln \gamma_k - N_{\text{H}}(k)\mu_{\text{H}} \quad (16.9)$$

The activity coefficients are calculated from the ionic strength of the solution (I) using the Extended Debye-Hückel equation:

$$\ln \gamma_k = \frac{-\alpha z_k^2 \sqrt{I}}{1 + B\sqrt{I}} = z_k^2 \frac{\pi_1}{RT} \quad (16.10)$$

Following Alberty, the value of the constant B is $1.6 \text{ M}^{-1/2}$ for ionic strengths less than 0.35 M ($\text{mol} \cdot \text{dm}^{-3}$). The temperature dependent constant αRT has the value $2.91482 \text{ kJ mol}^{-1} \text{ M}^{-1/2}$ at 25°C . The charge independent ionic strength contribution is defined as a new constant:

$$\pi_1 \equiv \frac{-\alpha RT \sqrt{I}}{1 + B\sqrt{I}} \quad (16.11)$$

The chemical potential contribution of the hydrogen component is fixed by the chemical potential of the compound because the system contains a compound that is made up of only hydrogen components and that compound is guaranteed to exist in the biochemical system. The constant chemical potential of the hydrogen component can thus be expanded as follows

$$\mu_{\text{H}} \equiv \mu_{\text{H}}^\circ + RT \ln a_{\text{H}} = \mu_{\text{H}}^\circ - RT \ln 10 pH_a \quad (16.12)$$

The standard state chemical potential of the hydrogen ion is zero for all temperatures and pressures at a one molar reference concentration, which enables labeling the remaining as the activity based pH contribution as:

$$\pi_{\text{Ha}} \equiv RT \ln 10 pH_a \quad (16.13)$$

The definition of the transformed standard state chemical potential (Equation 16.9) can be expressed in terms of the constant contributions defined by equations (16.12) and (16.13). The signs of the contributions have been chosen such that they are consistent with the equilibrium chemical potentials in Gibbs energy minimization.

$$\mu_k' \equiv \mu_k^\circ + z_k^2 \pi_1 + N_{\text{H}}(k) \pi_{\text{Ha}} \quad (16.14)$$

Equations (16.11) and (16.13) represent constant contributions to the chemical potentials of solutes in systems where pH and ionic strength can be assumed not to change. Equation (16.14) captures the concept of transformed Gibbs energies suitable for implementing appropriate Legendre transforms in any Gibbs energy framework.

Biochemical reactions are subdued to both thermodynamic and kinetic constraints. Constrained Gibbs energy minimization pursues to embrace both restrictions. Applications range from conceptual investigation of physical phenomena

16. Conventions used in biochemical thermodynamics

like ion partitioning inside a nanopore in a cell membrane to pathway analysis in relation to industrial bioconversion of lignocellulosic material.

Figures (16.1) and (16.2) present applications of Gibbs'ian thermodynamics in biochemical systems. In Figure (16.1) a comparison of a ChemSheet calculation with results reported by Alberty (1991) is shown. In Figure (16.2), the Constrained Gibbs energy method has been used to study the thermodynamic feasibility of the glycolysis metabolic pathway. The use of kinetic constraining together with Gibbs energy minimization gives the consistent descending energy diagram.

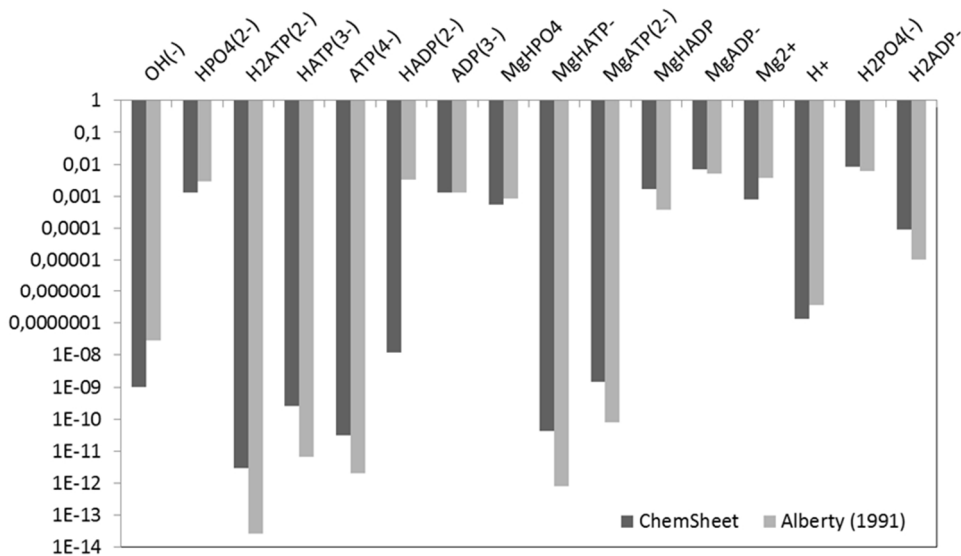


Figure 16.1. Molar concentrations (mol·dm⁻³) of ATP hydrolysis species calculated by ChemSheet. The comparison is with the early results of Alberty (1991).

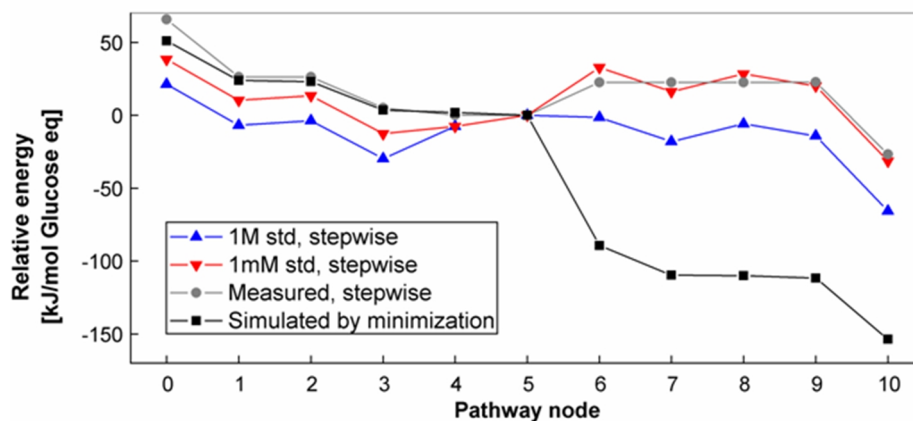


Figure 16.2. Energy diagrams of the ten reactions of glycolysis (the metabolic pathway that converts glucose $C_6H_{12}O_6$, into pyruvate, $CH_3COCOO^- + H^+$). The energy curves are aligned vertically at reference node 5. The first two curves show cumulative reaction energies for two alternative standard states, while the third uses measured concentrations from Kümmel et al. (2006). The fourth curve represents the evolution of the local system as calculated by the constrained Gibbs minimization (adapted from Blomberg in, Koukkari (2009), pp. 138–145).

17. Concluding remark

Multiphase thermodynamic methods deal with systems that undergo chemical changes in processes which include several condensed phases in connection with the gas or vapour phase. The systems characteristically comprise of saturated solutions and mixtures, fibre containing suspensions or aqueous compartments separated with membranes. In high temperatures, gas-solid-suspensions together with melts with segregating deposits or inclusions may occur. Thus, the range of practical applications is from chemistry and environmental issues of various process and manufacturing industry to energy and power production. In all these fields, different problems related to material properties and their functionality can also be handled with multiphase methods. New areas for the usage of multicomponent chemistry are emerging in biorefining and biochemistry.

Computational chemical thermodynamics thus provides an evolving methodology for experts working in both research and industry while developing advanced processes and materials. The Gibbs free energy is the key concept in this approach and the minimization of the Gibbs energy as the consequence of the first and second laws of thermodynamics is the prevalent technology. For this reason the focus of the text has been kept solely on Gibbs energy, the derivation of which was presented shortly from the fundamental concepts.

The scope of applications of the Gibbs energy minimization technique can be substantially widened by the adoption of the constrained Gibbs'ian method. The CFE method allows for the use of the general Gibbs equation in terms of the Lagrange multipliers; thus providing a simple mathematical theory with an extensive field of applications. The novel CFE technique is fully consistent with the traditional $\min(G)$ methodology, quite often allowing for its implementation in the conventional minimization programs. The examples given in the text appear simple, yet they pursue to concisely illustrate the basic features of the method as well as its applicability within a diverse range of problems.

The advantage of the Gibbs'ian approach is its generic applicability with great functional flexibility. It provides the combined and interdependent treatment of chemical and energy changes and allows for deep insight into theoretical concepts when necessary. Rich chemistry including major and minor species in process simulation is available and their combination with the interrelated thermodynamic state properties is often the key to gain control of the complex system as a whole. A benefit not to be underrated in practical applications is the direct validation of

calculation results by using thermodynamic relationships in connection with laboratory or process measurement. This is also supported by the inherent connection of the thermodynamic method with well-defined state properties, which also makes it straightforward to connect the thermodynamic concepts with other physical models.

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Appendix A: Notation for heterogenous and open systems

The system, which is exchanging matter with its surroundings is called open. When processes of practical importance are calculated by using thermochemical theory, one often needs to define process streams in terms of open systems. In addition, the description of the thermochemical changes in terms of their entropy production requires some basic concepts of open thermodynamic systems. For these reasons, a short review of the notation for open systems is given. For open and heterogeneous systems the following notation can be used:

$$dn_k^\alpha = d_r n_k^\alpha + d_e n_k^\alpha \quad (\text{A.1})$$

$$d_e n_k^\alpha = d_a n_k^\alpha + d_u n_k^\alpha \quad (\text{A.2})$$

$$d_r n_k^\alpha = \sum_r v_{kr}^\alpha d\xi_r \quad (\text{A.3})$$

$$dm = \sum_\alpha \sum_k M_k dn_k^\alpha \quad (\text{A.4})$$

$$dQ^\alpha = d_a Q^\alpha + d_i Q^\alpha \quad (\text{A.5})$$

$$dQ = \sum_\alpha d_a Q^\alpha \quad (\text{A.6})$$

where

$d_e n_k^\alpha =$ the infinitesimal increase amount n_k of substance k due to exchange of matter either with neighboring regions or with the surroundings of the entire system

$d_r n_k^\alpha =$ the infinitesimal increase of amount n_k due to chemical reactions within the region

$v_{kr}^\alpha =$ stoichiometric coefficient of species k in reaction r

$\xi_r =$ extent of reaction r (mol)

$m =$ total mass of the system

$M_k =$ molar mass of species k

$d_a n_k^\alpha =$ mass exchange with the surroundings of the entire system

- $d_a Q^\alpha =$ heat exchange with the surroundings of entire system
- $d_u n_k^\alpha =$ mass transfer from other phases to the phase in question
- $d_i Q^\alpha =$ heat transfer from other phases to the phase in question
(cf. $d_i n_k = d_u n_k + d_r n_k$)

Appendix B: The sources of entropy (relation between entropy and heat)

The following equations describe the relation between the entropy change of an arbitrary heterogeneous system and the heat supplied to the different individual parts of the system from the surroundings. The most general case is the non-isothermal change in the individual parts [phases] of the system and also between the system and the outside world.

The increase of the amount n_k^α (substance k in phase α) is:

$$dn_k^\alpha = d_r n_k^\alpha + d_a n_k^\alpha + d_u n_k^\alpha \quad (\text{B.1})$$

with the notation as explained above in Appendix A:

$d_r n_k^\alpha =$ infinitesimal increase of amount n_k due to chemical reactions within the region

$d_a n_k^\alpha =$ transport of matter due to mass exchange with the surroundings of the entire system

$d_u n_k^\alpha =$ transport of matter due to mass transfer to or from neighboring phases to the phase in question

The heat supplied to phase $[\alpha]$ during an infinitesimal state change was above given by Equation (3.30)

$$dQ^\alpha = dU^\alpha - \sum_i L_i^\alpha dl_i^\alpha - dW_{diss}^\alpha - \sum_k H_k^\alpha d_e n_k^\alpha \quad (\text{B.2})$$

From (A.1) and (A.5):

$$dQ^\alpha = dU^\alpha - \sum_i L_i^\alpha dl_i^\alpha - dW_{diss}^\alpha - \sum_k H_k^\alpha (d_a n_k^\alpha + d_u n_k^\alpha) \quad (\text{B.3})$$

$$dQ^\alpha = d_i Q^\alpha + d_a Q^\alpha \quad (\text{B.4})$$

The generalized Gibbs equation for the entropy differential is:

$$T^\alpha dS^\alpha = dU^\alpha - \sum_i L_i^\alpha dl_i^\alpha - \sum_k \mu_k^\alpha dn_k^\alpha \quad (\text{B.5})$$

Combining (B.1), (B.2) and (B.3) with the relation $\mu_k^\alpha = H_k^\alpha - T^\alpha S_k^\alpha$ [see Equations (5.7) and (5.8)] yields

$$T^\alpha dS^\alpha = d_a Q^\alpha + T^\alpha \sum_k S_k^\alpha d_a n_k^\alpha + dW_{diss} + d_i Q^\alpha + T^\alpha \sum_k S_k^\alpha d_u n_k^\alpha - \sum_k \mu_k^\alpha d_r n_k^\alpha \quad (\text{B.6})$$

Equation (B.6) identifies the entropy factors of an arbitrary state change in the open heterogeneous system. Evidently, the entropy change is a combination due to heat and material exchange between the individual parts [phases] of the system and that exchange between the system and the surroundings. In addition, the chemical reactions and the dissipative work contribute to the entropy state function.

Appendix C: Example: Solution of CO/CO₂/O₂ equilibrium with the Lagrange-method

The minimum of the Gibbs energy of the ideal gas CO/CO₂/O₂ system is solved with the Lagrange method of undetermined multipliers. The Lagrangian function to be minimized is formed with the mass balances of carbon and oxygen as the additional conditions.

Stoichiometric matrix:

Constituent/System Component	C	O
CO	1	1
O ₂	0	2
CO ₂	1	2

Mass balances (CO=1, O₂ = 2, CO₂ = 3):

$$\phi_1 = n_1 + n_3 - b' = 0 \text{ (carbon balance)} \quad (\text{C.1})$$

$$\phi_2 = n_1 + 2n_2 + 2n_3 - b'' = 0 \text{ (oxygen balance)} \quad (\text{C.2})$$

where b' and b'' indicate the total amounts of carbon and oxygen in the system.

Gibbs energy:

$$G = \sum_k n_k \mu_k \quad (\text{C.3})$$

where

$$\mu_k(T) = \mu_k^\circ(T) + RT \ln a_k \quad (\text{C.4})$$

$$a_k = \frac{n_k}{n}; \quad n = n_1 + n_2 + n_3 \quad (\text{C.5})$$

as the activity of each constituent is derived from its mole fraction in the ideal gas.

For brevity, the notation $g_k^\circ = \frac{\mu_k^\circ}{RT}$; $g = \frac{G}{RT}$ is adapted and for the thus modified Gibbs energy there is

$$g = \sum_k n_k \left[g_k^\circ + \ln \left(\frac{n_k}{n} \right) \right] \quad (\text{C.6})$$

The Lagrangian:

The Lagrangian function (ψ) is now received from g and from the mass balances as given above for carbon and oxygen. The Lagrange undetermined multipliers (λ_1, λ_2) are connected with the mass balance conditions:

$$\psi = \sum_k n_k \left[g_k^\circ + \ln \left(\frac{n_k}{n} \right) \right] + \lambda_1 \cdot \phi_1 + \lambda_2 \cdot \phi_2 \quad (\text{C.7})$$

$$\psi = \sum_k n_k \left[g_k^\circ + \ln \left(\frac{n_k}{n} \right) \right] + \lambda_1 \cdot (n_1 + n_3 - b') + \lambda_2 \cdot (n_1 + 2n_2 + 2n_3 - b'') \quad (\text{C.8})$$

The minimum of the Lagrangian is now identical with the minimum of the function g . By using the undetermined multipliers as additional variables the amount of matter of the constituents at equilibrium can be solved. The minimum condition is:

$$\frac{\partial \psi}{\partial n_k} = 0 ; \quad \frac{\partial \psi}{\partial \lambda_1} = 0 ; \quad \frac{\partial \psi}{\partial \lambda_2} = 0 \quad (\text{C.9})$$

$$\frac{\partial \psi}{\partial n_1} = g_1^\circ + \ln \frac{n_1}{n} + \lambda_1 + \lambda_2 = 0 \quad (\text{C.10})$$

$$\frac{\partial \psi}{\partial n_2} = g_2^\circ + \ln \frac{n_2}{n} + 2 \cdot \lambda_2 = 0 \quad (\text{C.11})$$

which with three constituents k gives five equations for the five variables ($n_1, n_2, n_3, \lambda_1, \lambda_2$).

From the partial derivatives $\frac{\partial \psi}{\partial n_k} = 0$, there is:

$$\frac{\partial \psi}{\partial n_3} = g_3^\circ + \ln \frac{n_3}{n} + \lambda_1 + 2 \cdot \lambda_2 = 0 \quad (\text{C.12})$$

by eliminating the undetermined multipliers the following relation can be solved:

$$g_3^\circ - g_1^\circ - 0.5 \cdot g_2^\circ = -\ln \left(\frac{n_3}{n} \right) + \ln \left(\frac{n_1}{n} \right) + 0.5 \cdot \ln \left(\frac{n_2}{n} \right) \quad (\text{C.13})$$

which is the same as the formula of the equilibrium constant

$$\frac{\Delta G^\circ}{RT} = -\ln K_a \quad (\text{C.14})$$

for the stoichiometric reaction $\text{CO} + 0.5\text{O}_2 \leftrightarrow \text{CO}_2$ (cf. equation 8.4).

The derivatives of the Lagrangian in terms of the multipliers (λ_1, λ_2) give two additional equations in terms of the mass balance conditions (b', b''). Using these together with the above result the equilibrium amounts for n_1, n_2 and n_3 can be solved.

Appendix D: Linearization of the Lagrangian equations

The min(G) problem of Chapter 7.4 is solved e.g. in the programs Solgasmix and ChemApp by linearizing the m non-linear Equations (7.29):

$$\left(\frac{\mu^\circ}{RT}\right)_k + \ln P + \ln \frac{n_k}{N} - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \quad k = 1, \dots, m \quad (\text{D.1})$$

The linearization can be done with the Taylor formula for the logarithmic function:

$$\ln x \approx \ln y + \frac{x - y}{y} = \ln y + \frac{x}{y} - 1. \quad (\text{D.2})$$

Where y is the value point of the Taylor expression. In iterative methods, y is the value of an initial guess from which a series of calculations towards a final convergence point is commenced. From Equation (D.1) one gets

$$\left(\frac{\mu^\circ}{RT}\right)_k + \ln P + \ln n_k - \ln N - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \quad k = 1, \dots, m \quad (\text{D.3})$$

Now, applying the iterative Taylor approach, a set of initial guesses are set as $n_k(0) = y_k$, $k = 1, \dots, m$ and with $\sum_{k=1}^m y_k = Y$, where the vector $y = (y_1, \dots, y_{m+s})$ is the value of the initial guess and thus,

$$\left(\frac{\mu^\circ}{RT}\right)_k + \ln P + \ln y_k + \frac{n_k}{y_k} - 1 - \ln Y - \frac{N}{Y} + 1 - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \quad k = 1, \dots, m \quad (\text{D.4})$$

By combination of terms,

$$\left(\frac{\mu^\circ}{RT}\right)_k + \ln P + \ln \frac{y_k}{Y} + \frac{n_k}{y_k} - \frac{N}{Y} - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \quad k = 1, \dots, m \quad (\text{D.5})$$

Then, n_k can be solved in terms of the y_k 's:

$$n_k = y_k \left[-\left(\frac{\mu^\circ}{RT}\right)_k - \ln P - \ln \frac{y_k}{Y} + \frac{N}{Y} + \sum_{j=1}^{NC} a_{kj} \lambda_j \right], \quad k = 1, \dots, m \quad (\text{D.6})$$

Adapting from Eriksson, the following notation may be used:

$$f_k = y_k \left[\left(\frac{\mu^\circ}{RT} \right)_k + \ln P + \ln \frac{y_k}{Y} \right], \quad k = 1, \dots, m \quad (\text{D.7})$$

This quantity (f_k) is a function of temperature, pressure and the initial guess for each y_k . Then, with f_k , the n_k 's can be solved from

$$n_k = y_k \left[\frac{N}{Y} + \sum_{j=1}^{NC} a_{kj} \lambda_j \right] - f_k, \quad k = 1, \dots, m \quad (\text{D.8})$$

where then, the term N/Y remains as an unknown variable, common for each equation on n_k . The number of unknowns then reduces to the amounts of condensed phases n_k , $k = m+1, \dots, m+s$, the Lagrange multipliers λ_j , $j = 1, \dots, NC$ and the ratio N/Y . When these are solved, the amounts for the gaseous mixture phase can be calculated by (D.8).

A summation over all the gaseous species gives from (D.8):

$$\sum_{k=1}^m n_k = \sum_{k=1}^m y_k \left[\frac{N}{Y} + \sum_{j=1}^{NC} a_{kj} \lambda_j \right] - \sum_{k=1}^m f_k \quad (\text{D.9})$$

which further gives

$$\sum_{j=1}^{NC} \lambda_j \sum_{k=1}^m a_{kj} y_k = \sum_{k=1}^m f_k \quad (\text{D.10})$$

With a new abbreviated notation

$$C_j = \sum_{k=1}^m a_{kj} y_k - b_j, \quad j = 1, \dots, NC \quad (\text{D.11})$$

another calculable quantity C_j is derived to serve as a correction factor for cases where the initial guess does not match the mass balance relations. The total amounts of elements can be solved in terms of C_j 's and then solved from D.3 as follows:

$$\sum_{k=1}^{m+s} a_{kj} n_k + C_j - \sum_{k=1}^m a_{kj} y_k = 0, \quad j = 1, \dots, NC \quad (\text{D.12})$$

Here, replacing n_k 's from Equation D.8:

$$\sum_{k=1}^m a_{kj} \left(y_k \left[\frac{N}{Y} + \sum_{j=1}^{NC} a_{kj} \lambda_j \right] - f_k \right) + \sum_{k=m+1}^{m+s} a_{ij} n_k + C_j - \sum_{k=1}^m a_{kj} y_k = 0, \quad j=1, \dots, NC \quad (D.13)$$

which may be rearranged to

$$\left[\frac{N}{Y} - 1 \right] \sum_{k=1}^m a_{kj} y_k + \sum_{k=1}^m a_{kj} y_k \sum_{i=1}^{NC} a_{ki} \lambda_i - \sum_{k=1}^m a_{kj} f_k + \sum_{k=m+1}^{m+s} a_{ij} n_k + C_j = 0, \quad j=1, \dots, NC \quad (D.14)$$

Note that while Equation (D14) is valid for all system components ($j=1, \dots, NC$), it includes another summation over all system components, denoted by subscript i for clarity. Further rearrangement gives

$$\sum_{i=1}^{NC} \lambda_i \sum_{k=1}^m a_{kj} a_{ki} y_k + \left[\frac{N}{Y} - 1 \right] \sum_{k=1}^m a_{kj} y_k + \sum_{k=m+1}^{m+s} a_{ij} n_k = \sum_{k=1}^m a_{kj} f_k - C_j, \quad j=1, \dots, NC \quad (D.15)$$

and by combining the summation over a_{kj} 's and a_{ki} 's with the following notation may also be used (see Eriksson, 1973):

$$r_{ji} = r_{ij} = \sum_{k=1}^m a_{ki} a_{kj} y_k \quad (i, j=1, \dots, NC) \quad (D.16)$$

The coefficients r_{ij} are defined by the stoichiometry of the system and the initial guess, and thus their values can be calculated for the iteration.

Equations 7.30, D.10 and D.15 then form a set of $s+NC+1$ linear equations, with equal amounts of variables. The linear equations are as follows

$$\left(\frac{\mu^\circ}{RT} \right)_k - \sum_{j=1}^{NC} a_{kj} \lambda_j = 0, \quad k = m+1, \dots, m+s \quad (7.30)$$

$$\sum_{j=1}^{NC} \lambda_j \sum_{k=1}^m a_{kj} y_k = \sum_{k=1}^m f_k \quad (D.10)$$

$$\sum_{i=1}^{NC} \lambda_i \sum_{k=1}^m a_{kj} a_{ki} y_k + \left[\frac{N}{Y} - 1 \right] \sum_{k=1}^m a_{kj} y_k + \sum_{k=m+1}^{m+s} a_{ij} n_k = \sum_{k=1}^m a_{kj} f_k - C_j, \quad j=1, \dots, NC \quad (D.15)$$

The solution can be reached by, e.g. the Gaussian elimination method. From the solution of D.1-D.3 and D.15, the amounts of matter in the condensed phases n_k , $k = m+1, \dots, m+s$ and the Lagrange multipliers λ_j , $j = 1, \dots, l$ are calculated. The amounts for the gaseous phases are received from D.9, and $N/Y-1$ is applied as the convergence criterion.

The Equations 7.30–7.32 and D.15 form the mathematical basis for solving the equilibrium amounts of constituents for a system of s condensed species (pure substances) and an ideal gas phase with m constituents. The reader is referred to Eriksson (1975) and e.g. Smith & Missen for the generalization of the Lagrange method for more complex systems.

Title	Introduction to constrained Gibbs energy methods in process and materials research
Author(s)	Pertti Koukkari
Abstract	<p>In process and materials chemistry, digitalization with computational methods has been a long-time continuing process. The methodology based on numerical methods in reaction kinetics as well as for fluid phase thermodynamics applying equations of state has been well established. During the last two decades, however, multiphase technology based on the minimization of Gibbs free energy has made progress in such fields of process and materials chemistry, where the conventional methods have not been applicable. Recent advancements also include introduction of such new Gibbs'ian algorithms, which, in addition to complex equilibrium problems, facilitate modelling of time-dependent dynamic changes in multi-phase systems.</p> <p>Within the said period, VTT has been an active performer in the development of multiphase Gibbs'ian techniques. The research work performed at VTT has led to several new algorithms with practical industrial applications. The particular focus has been the development of the Constrained Gibbs Free energy minimization technique, where instead of material balances and stoichiometric relations derived thereof, also immaterial physical conditions are applied as constraints in the free energy minimizing calculation.</p> <p>In this report, the method of constrained Gibbs energy minimization for calculating chemical equilibria in arbitrary multiphase systems is derived using basic thermodynamic concepts. The method of Lagrange undetermined multipliers is introduced for a simple system of an ideal gas phase and a number of condensed phases, constrained by the number of moles of the system components. The use of additional constraints in the Gibbs energy minimization procedure is facilitated by applying the concept of generalised work-coefficients as the Lagrange multipliers of immaterial components in the system. The thus introduced method of immaterial constraints in Gibbs energy minimization is illustrated with a number of simple practical examples such as electrochemical Donnan equilibria applied for pulp suspensions, surface equilibria and systems constrained by reaction kinetics via the extent of chemical reactions. A few examples of non-equilibrium and parametric phase diagrams calculated with the immaterial constraints are also given. Finally, the applicability of the method for biochemical systems is shortly discussed.</p>
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Nimeke	Monifaasisysteemien laskenta rajoitettua Gibbsin energian minimointia käyttäen
Tekijä(t)	Perti Koukkari
Tiivistelmä	<p>Laskennallisten menetelmien käyttö prosessi- ja materiaalitekniikassa on jatkunut useiden vuosikymmenien ajan uusien numeeristen tekniikoiden käyttöönoton seurattessa tietokoneiden laskentatehon kasvua. Etenkin reaktiokinetiikkaan, virtaustekniikkaan ja termodynamiikan tilanyhtälöihin perustuvat menetelmät ovat saavuttaneet vahvan jalansijan myös näiden alojen teollisuudessa. Lisäksi kahden viimeksi kuluneen vuosikymmenen aikana termodynaamiset monifaasisimenetelmät, jotka perustuvat tilanyhtälöiden asemesta systeemin vapaan energian (Gibbsin energian) minimointiin, ovat voittaneet alaa etenkin sellaisissa prosessi- ja materiaalitekniikan tasapainosovelluksissa, joissa perinteiset tilanyhtälömenetelmät ovat osoittautuneet riittämättömiksi. Termodynaamisen tasapainolaskennan ohella on kehitetty Gibbsin energiaan nojaavia algoritmeja, jotka mahdollistavat myös kineettisesti rajoitettujen ajasta riippuvien monifaasisysteemien simuloinnin.</p> <p>VTT:llä 1990-luvun puolivälistä jatkuneessa tutkimustyössä on kehitetty erityinen rajoitetun vapaan energian laskentateknikka osittaisten ja ajan suhteen rajoitettujen kemiallis-termodynaamisten systeemien kvantitatiiviseen tarkasteluun. Menetelmä perustuu termodynaamisen vapaaenergiakäytön käyttöön, ja sen minimin numeeriseen ratkaisuun systeemiä tai sen osaa kulloinkin rajoittavien ehtojen voimassaollessa. Uuden lähestymistavan ero perinteiseen Gibbsin energian minimointiin nähden on menetelmän kyky käyttää ainetase-rajoittimien lisäksi fysikaalisesti perusteltuina rajoittimina systeemin aineettomia ehtoja.</p> <p>Tässä julkaisussa monifaasisysteemeille soveltuva rajoitetun Gibbsin energian menetelmä johdetaan termodynaamisista perussuureista. Vapaa energia minimoidaan soveltamalla Lagrangen määräämättömien kertoimien tekniikkaa yksinkertaiselle monifaasisysteemille, jota rajoitetaan suljetun systeemin ainetaseella. Aineettomien rajoitusten käyttö minimoinnissa on tämän jälkeen esitetty yleistettyjen työkerroimien ja vastaavien työkoordinaattien avulla, jolloin Lagrange-kertoimet antavat ratkaisuna aineettomien systeemikomponenttien kemialliset potentiaalit. Tällä tavoin laajennetulla vapaaenergian laskentatekniikalla on havaittu olevan runsaasti sovelluksia, joista yksinkertaisin esimerkein kuvataan rajoitetun vapaaenergiatekniikan käyttö sähkökemiallisen Donnan-potentiaalin määräämiseen kuitususpensioissa sekä edelleen sen soveltaminen reaktiokineettisesti rajoitettujen monifaasisysteemien ja kemiallisten reaktorioiden laskentaan. Materiaalitekniikan sovelluksista käsitellään monikomponenttisyysteemien pintaenergiakäytön laskenta sekä partiaalisten ja koostumusrajoitteisten faasitasapainojen laskeminen. Lopuksi arvioidaan vielä lyhyesti mahdollisuuksia soveltaa termodynaamista laskentaa biokemiallisille systeemeille.</p>
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Introduction to constrained Gibbs energy methods in process and materials research

It has become increasingly important to manage the complexity of multicomponent and multiphase chemical systems in both process and materials science. The development of clean, resource and energy efficient technologies entails sophisticated control of the chemical details, often during the time course of a dynamic process interacting with its surroundings. In materials research, exclusive structure-property relations of end products will require both accuracy of their molecular composition and understanding of the cross-functional interactions when their performance is activated with ambient conditions or even by external force fields.

The novel Constrained Gibbs Free energy (CFE) technique developed by VTT provides a quantitative methodology for such chemical or biochemical processes which are affected by specific physical functions deciphered as thermodynamic work. Based on computational multiphase thermodynamics, CFE deals with the complexity of matter in systems involving changes in energy and in chemical or phase composition. The salient feature of the method is its ability to incorporate the contribution from generalised work to a multiphase free energy computation, which facilitates quantifiable solutions of intricate chemical problems in systems affected by either internal or external forces due e.g. to surface tension, charge and electric-magnetic factors. The same principle can also be applied to non-equilibrium processes, allowing for the inclusion of chemical reaction rates as affinity related constraints in the thermodynamic multiphase analysis.

The scope of CFE applicability ranges from functional behaviour of nanosize particles to features of dynamic superequilibria in large scale industrial and environmental processes. Thus the method gives an exceptionally large array of potential uses in the fields of materials and process chemistry as well as in the development of sustainable technology.

The present introductory text provides an overview of the basic principles of the constrained Gibbs free energy minimisation in the context of classical thermodynamics for both students and experts interested in problem solving in process or materials research.

Related reports:

Koukkari, P. (ed.). Advanced Gibbs Energy Methods for Functional Materials and Processes – ChemSheet 1999–2009. Espoo, 2009. VTT Research Notes 2506. ISBN 978-951-38-7330-1. 145 p. <http://www.vtt.fi/inf/pdf/tiedotteet/2009/T2506.pdf>.

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