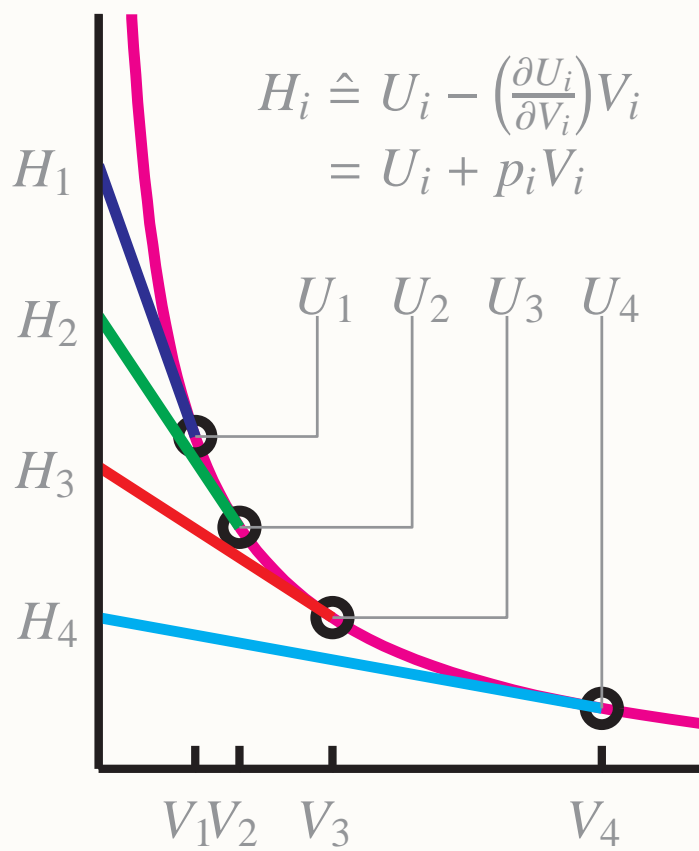


# 46 W T

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$$\min_{S,N}(H)_p \Leftrightarrow \min_{S,V,N}(U)$$

T      H      -W



# 46 Workouts in Thermodynamics

... for semiadvanced studies

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## Foreword

The topics included in this text are intended for PhD students coming from the departments of chemical and mechanical engineering, material science, physics and chemistry alike—students who want to boost their thermodynamics knowledge and learn about practical calculations to support their own research activities. This means that the student should acquire the theoretical insight, and the necessary hands-on training, to solve thermodynamic equilibrium problems in a generic manner. Much emphasis is therefore put on the understanding of Euler functions and Legendre transformations put into a thermodynamic context, but besides this a thorough understanding of common equations of state, residual functions and equilibrium calculations is also required. To make the best out of the material it is important that the student has some prior knowledge in multivariate calculus, linear algebra and optimisation theory. He and she must also know how to computerise mathematical algorithms into modern script languages like Matlab, Maple, Python, etc.



## CHAPTER 1

**Thermodynamic Concepts**

The use of abstractions and theoretical models is very important for the progress of learning, and especially so in the field of natural sciences. Obviously, the ability to share complex ideas and thoughts with other people is unevenly shared out<sup>a</sup>, but a sound awareness of this issue will nevertheless increase the technical understanding of the subject at hand, and reduce misunderstandings. For this reason we shall revise some of the concepts used in applied thermodynamics analysis<sup>b</sup>, ranging in complexity from trivial definitions to abstract idioms. A thermodynamic state description is always idealized to some extent, and a thorough understanding of the basic concepts is one of the key premises for digesting the material presented in this book.

§ 1 Explain the following concepts: System (control volume), system boundary and environment (surroundings).

**S** . A thermodynamic *system* is a bounded part of the universe. The system *boundary* defines an abstract, or, in some cases, a physical distinction<sup>c</sup> from the *environment*. An *open* system can exchange mass with the environment while a *closed* system cannot. An *isolated* system does neither exchange mass nor energy. A control *surface* is synonymous to a system boundary for an open system, and a control *volume* is synonymous to an open system. The world outside the system is called the *environment* or *surroundings*. An *adiabatic* boundary acts as a perfect isolator while a *diabatic* boundary acts as a perfect heat conductor. A *reservoir* is a thermodynamic system that interacts with other systems without changing its state description. Recipients like air, sea, and soil make reservoirs for you and me, but not for mankind. Likewise, the water (behind a dam) is a reservoir for the turbine, but not for the energy company. □

<sup>a</sup> It was, I presume, the politicians' poor gifts in this respect that made the late Professor Gustav Lorentzen write his article: "Should the Parliament suspend the second law of thermodynamics?" (original title "Bør Stortinget oppheve termodynamikkens 2. lov?") as a contribution to the (already) heated debate on thermal power plants in Norway. <sup>b</sup> James A. Beattie and Irwin Oppenheim. *Principles of Thermodynamics*. Elsevier, 1979. <sup>c</sup> The system boundary is instrumental in the active control of the system's mass and energy, or, alternatively, in the passive observation of these quantities. The boundary itself is a mathematical surface with zero thickness. Intensive properties which are defined on this surface are common to the system and the environment. This presumption is similar to the continuum hypothesis used in fluid dynamics.

§ 2 Explain the difference between intensive and extensive properties. Where do the specific and molar properties fit in?

P . An *intensive* property is independent of the system size. Examples are the temperature, pressure and density of a fluid. A property that is proportional to the system size is called *extensive*<sup>a</sup> in volume and energy. The difference between a *specific* and a *molar* property is simply that the first is given on a mass basis (per kilogramme) while the second is given on a mole basis (per mol). □

§ 3 Explain the following concepts: State, property, process and path.

P . The thermodynamic *state* is uniquely defined in terms of the thermodynamic state *properties*<sup>b</sup> which at the same time act as state functions. This makes the state definition circular and it must be emphasised that the state properties depend only on the current state, and that the evolution (history) of the system is irrelevant for its measured (or derived) properties. In short, a simple thermodynamic system has no memory effect like the viscosity of a tixotropic paint or other examples of rheology. This makes the definition of state rather simple, but in practise the proper identification of state variables is one of the great challenges in thermodynamics. A thermodynamic *process* describes the state change along an abstract *path* taking the system from one state to another. The path contains a full state description of the process viz. state change history. A *cycle* is equivalent to a closed path in which the state variables take on the same values periodically. A *dynamic* state depends on time while a *static* state does not. A *quasi-static* state is something intermediate; the state changes dynamically, but the system remains at equilibrium all the time<sup>c</sup>. The thermodynamic equilibrium is static on a macroscopic scale while it is highly dynamic on a molecular level. This implies that the equilibrium principles must be reformulated if the system is of small size i.e. when the particle number  $n \rightarrow 0$ . At this limit the intensive properties like temperature, pressure and chemical potential lose their usual meaning. A dynamic process which is time invariant, such as steady fluid flow, is called *stationary*. The state change of a *reversible* process can be reversed anytime by making an infinitesimal change to the environment. An *irreversible* process is not influenced by the surroundings at all, or it needs at least a finite stimulus to change or reverse its direction. A stone in free fall undergoes an irreversible change of state when it hits the ground, while a submarine with an accurately balanced buoyancy undergoes a reversible change of state. □

§ 4 Explain the following concepts: Material phase, phase boundary, equi-

<sup>a</sup> The two concepts *intensive* and *extensive* are explained somewhat vaguely here and will later be rigorously defined as the *homogeneous* properties of *zeroth* and *first order* respectively.

<sup>b</sup> Note that transport properties like heat and mass diffusion coefficients depend on the thermodynamic but do not take part in the state description. <sup>c</sup> The state is actually drifting along the equilibrium manifold.

librium, state of aggregation and stability. Where does transport theory and kinetics fit in?

**E** . A material *phase* is a homogeneous subsystem that is separated from the rest by a phase *boundary*. The densities of energy and component masses are uniform within the subsystem, but vary discontinuously across the phase boundary. The fields of temperature, pressure and chemical potentials, however, are uniform across the phase boundary. A phase can be lumped into a single region in space, or it can be dispersed into e.g. smog particles in air or droplets of fat in milk. A *homogeneous* system contains only one single phase, while a *heterogeneous* system is made up of two or more phases. A material phase may exist in two possible states of *aggregation*; crystalline or non-crystalline (the latter as fluid or glass). The equilibrium state is achieved at  $t \rightarrow \infty$ . If the system returns to the same state after an arbitrarily large perturbation the equilibrium is *stable*. A *metastable* equilibrium is conditionally stable for small perturbations, while an *unstable* equilibrium is not stable at all, not even for infinitesimal perturbations. The unstable equilibrium cannot be realised in any physical system, but it does nevertheless provide important theoretical knowledge. *Transport theory* is a discipline of physics that studies the transfer of mass, energy and momentum which occur far away from thermodynamic equilibrium. Kinetics is about forces and bodies in motion. *Chemical kinetics* is another field of science that aims at chemical reactions and phase transitions. In general, transport phenomena must be formulated (and solved) as partial differential equations, while thermodynamic equilibrium problems can be expressed as algebraic equations<sup>a</sup>. □

### § 5 Explain the thermodynamic meanings of heat, work and energy.

**H** & . Heat and work are closely related mechanisms for transferring *energy* between the system and its surroundings. *Work* is an energy transfer that is related to the displacement of matter against an external force, for example by a rotating shaft, electrons moving across a voltage drop, water flowing through a turbine. *Heat* is the microscopic equivalent of work and does not naturally bring about any net displacement of matter. Heat can be partially converted into work, but only if a large number of microscopic fluctuations are aligned into one macroscopic displacement. The second law of thermodynamics tells that this conversion is not possible without losing some heat to the environment<sup>b</sup>. Energy dissipation is a phrase which is used to stress that spontaneous energy processes always proceed towards a lower energy potential. Conventionally, delivered work and supplied heat are considered positive when seen from the system point of view. □

§ 6 What is the definition of a “mole” in thermodynamics? How does this quantity correspond with mass?

<sup>a</sup> Distributed versus lumped state description. <sup>b</sup> I.e. to a thermal reservoir having the same temperature as the environment.



M & . The *mass* of a system is closely related to the inertia forces acting on an accelerated body (Newton's second law), and it is also a principle factor of the gravitational potential. It remains an unsolved problem in theoretical physics to prove that the two definitions are equivalent. A *mole* is the number<sup>a</sup> of atoms that make exactly 0.012 kg of the carbon isotope <sup>12</sup>C. In everyday context this is known as Avogadro's number<sup>b</sup>  $A_v = 6.022136736 \cdot 10^{23}$ . *Molal* and *molar* are concentration units given as moles per kilogramme solvent and moles per litre solution respectively. They do not play any significant roles in thermodynamics, but they are important to the physical chemistry of dilute solutions. □

§ 7 Define the following thermodynamic state changes: Isothermal, isobaric, isochoric, isentropic, isenthalpic, isopiestic and isotonic. What is an isopleth in this context?

I . The descriptions mentioned above define processes which occur at constant temperature, pressure, volume, entropy, enthalpy, vapour pressure, and osmotic pressure respectively. An isopleth is a generic term originally used in meteorology to cover any of the aforementioned state changes. □

§ 8 Give a mathematical understanding of: State variable, state function, total differential and exact differential.

S . An example *state function* is  $f(x, y) = xy + c$  where  $x$  and  $y$  are *state variables*. Here,  $df = y dx + x dy$  is the *total differential* of  $f$  and the right hand side is then said to be *exact*. Replacing  $+$  by  $-$  yields  $y^2 dg = y dx - x dy$  where  $dg$  is the total differential of  $g(x, y) = xy^{-1} + c$ , but  $y dx - x dy$  is *inexact* since it can no longer be written as a total differential. Small changes sometimes make large effects! More about this in Chapter **Prelude**. □

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<sup>a</sup> The mole depends on the kilogramme prototype in Paris, not the other way around. Atomic masses are measured in so-called *atomic mass units* where the mass of a single atom <sup>12</sup>C-isotope is defined as 12 amu independent of the mole concept (however, it is of course not purely coincidental that 12 pops up both places). <sup>b</sup> Count Lorenzo Romano Amedeo Carlo Avogadro di Quaregna e Cerreto, 1776–1856. Italian chemist.



## CHAPTER 2

## Legendre Transformation

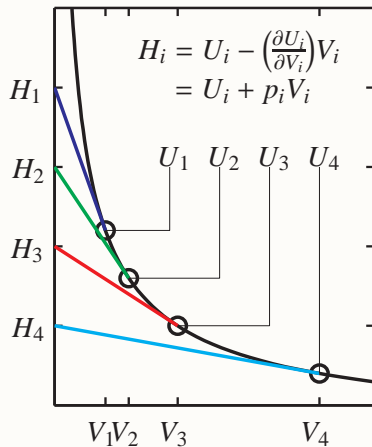


FIGURE 2.1 Legendre transformation of  $U$  into  $H$ .

The transformation properties of canonical potentials<sup>a</sup> make one of the pillars of modern thermodynamics<sup>b,c</sup>, but what practical merits does a mathematical formalism bring to the engineering student? Why is it not sufficient to remember that  $U$  is suitable for dynamic simulation,  $H$  for stationary simulation, etc? Well, if a feasible solution is at hand this is a quite adequate strategy, but if a new solution is sought the theoretical insight must be deeper. Here, the Legendre<sup>d</sup> transformation comes in as a key to increased understanding, and with it a simple formula is provided which let us replace the free variable of a function with the corresponding function derivative<sup>e</sup>. E.g. the variable  $V$  in internal energy  $U(S, V, N)$  can be replaced by  $(\partial U/\partial V)_{S,N}$ , see Figure 2.1. The

new variable can be interpreted as the negative pressure  $\pi$  and the resulting transformed function, called enthalpy  $H(S, \pi, N)$ , is in many cases more versatile than  $U$  itself. Even more so because it will be proved (later) that  $H$  has the same information content as  $U$ . This makes the Legendre transformation a strong point in the theories of thermodynamics and mechanics. Mathematically, the Legendre transformation  $f_i$  of the function  $f_o$  is defined by:

$$(2.1) \quad f_i(\xi_i, x_j, x_k, \dots, x_n) \hat{=} f_o(x_i, x_j, x_k, \dots, x_n) - \xi_i x_i$$

$$\xi_i \hat{=} \left( \frac{\partial f_o}{\partial x_i} \right)_{x_j, x_k, \dots, x_n}$$

Repeated transformations are easy:

$$(2.2) \quad f_{ij}(\xi_i, \xi_j, x_k, \dots, x_n) \hat{=} f_i(\xi_i, x_j, x_k, \dots, x_n) - \xi_j x_j$$

$$\xi_j \hat{=} \left( \frac{\partial f_i}{\partial x_j} \right)_{\xi_i, x_k, \dots, x_n}$$


<sup>a</sup> The functions  $U(S, V, N)$ ,  $H(S, p, N)$ ,  $A(T, V, N)$ , etc. <sup>b</sup> Herbert Callen. *Thermodynamics and an Introduction to Thermostatistics*. Wiley, 2nd edition, 1985. <sup>c</sup> Michael Modell and Robert C. Reid. *Thermodynamics and Its Applications*. Prentice Hall, 2nd edition, 1983. <sup>d</sup> Adrien-Marie Legendre, 1752–1833. French mathematician. <sup>e</sup> Quite remarkably this proves to be advantageous in many cases.

The Definitions 2.1 and 2.2 are readily combined into the alternative formula

$$(2.3) \quad f_{ij}(\xi_i, \xi_j, x_k, \dots, x_n) = f_o(x_i, x_j, x_k, \dots, x_n) - \xi_i x_i - \xi_j x_j$$

but the (re)interpretation of  $\xi_i$  and  $\xi_j$  needs more attention. Whereas Eqs. 2.1 and 2.2 seem to imply a sequential procedure for the Legendre transformation this is really not required because  $(\partial f_i / \partial x_j)_{\xi_i, x_k, \dots, x_n}$  and  $(\partial f_o / \partial x_j)_{x_i, x_k, \dots, x_n}$  take on the same value  $\xi_j$  in Eq. 2.3, see Paragraph 10 on the facing page for more details. The state descriptions  $(x_i, x_j, \dots, x_n)$ ,  $(\xi_i, x_j, \dots, x_n)$  and  $(\xi_i, \xi_j, \dots, x_n)$  are the *canonical* variables of the functions  $f_o$ ,  $f_i$  and  $f_{ij}$ . The knowledge of just one variable set is sufficient to define an arbitrary Legendre transform. Even better, the Legendre transformation is independent of the order of differentiation because  $f_{ij} = f_{ji}$ . Mathematically we say that the Legendre operator<sup>a</sup> commutes.

§ 9 Make a table of all possible Legendre transforms of internal energy. Identify the *canonical* variables for each of the transforms using the definitions<sup>b</sup>  $\tau \hat{=} (\partial U / \partial S)_{V,N}$ ,  $\pi \hat{=} (\partial U / \partial V)_{S,N}$  and  $\mu \hat{=} (\partial U / \partial N)_{S,V}$ .

 E For a thermodynamic function with  $m = \dim(\mathbf{n})+2$  variables there are  $2^m - 1$  Legendre transforms. Given a single component system this means there will be  $2^3 - 1 = 7$  different transformations possible. By using Definition 2.1 on each of the variables in turn we get:

$$(2.4) \quad A(\tau, V, N) = U(S, V, N) - \left(\frac{\partial U}{\partial S}\right)_{V,N} S \hat{=} U - \tau S$$

$$(2.5) \quad H(S, \pi, N) = U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{\pi,N} V \hat{=} U - \pi V$$

$$(2.6) \quad X(S, V, \mu) = U(S, V, N) - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \hat{=} U - \mu N$$

Using Definitions 2.2 on pairs of two variables there are three more transforms emerging:

$$(2.7) \quad G(\tau, \pi, N) = U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S,N} V - \left(\frac{\partial U}{\partial S}\right)_{V,N} S \hat{=} U - \pi V - \tau S$$

$$(2.8) \quad Y(S, \pi, \mu) = U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S,N} V - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \hat{=} U - \pi V - \mu N$$

$$(2.9) \quad \Omega(\tau, V, \mu) = U(S, V, N) - \left(\frac{\partial U}{\partial S}\right)_{V,N} S - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \hat{=} U - \tau S - \mu N$$

 Finally, by using Eq. 2.2 repeatedly on all three variables the result is the null

<sup>a</sup> There is no dedicated symbol for this operator. <sup>b</sup> Here,  $\tau$  is used for temperature and  $\pi$  for *negative* pressure in order to stress that these are transformed properties. The chemical potential is given the (usual) symbol  $\mu$ .

potential:

$$\begin{aligned}
 O(\tau, \pi, \mu) &= U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S,N} V - \left(\frac{\partial U}{\partial S}\right)_{V,N} S - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \\
 &\triangleq U - \pi V - \tau S - \mu N \\
 (2.10) \quad &\equiv 0 \qquad \square
 \end{aligned}$$

Most of the energy transforms have dedicated names: Internal energy  $U(S, V, N)$  is used for closed systems and is in many respects the base function of thermodynamics. Helmholtz energy  $A(\tau, V, N)$  is central for fluid state description. Gibbs energy  $G(\tau, \pi, N)$  has traditionally been the focus of chemical thermodynamics and physical metallurgy. Enthalpy  $H(S, \pi, N)$  is important for the understanding of fluid flow calculations in engineering thermodynamics. The grand canonical potential  $\Omega(\tau, V, \mu)$  is used for the description of open systems discussed in statistical mechanics. The null potential  $O(\tau, \pi, \mu)$  has received very little attention in the literature and has no internationally accepted name, even though the function has several interesting properties as we shall see later. Left behind are the two functions  $X(S, \pi, \mu)$  and  $Y(S, V, \mu)$  which are without practical importance.

§ 10 The variable  $\xi_j$  was defined as  $(\partial f_i / \partial x_j)_{\xi_i, x_k, \dots, x_n}$  in Eq. 2.2, but from Eq. 2.3 an alternative definition would be  $(\partial f_o / \partial x_j)_{x_i, x_k, \dots, x_n}$ . Prove that the two definitions are equivalent.

D I. Note that the variables  $x_k, \dots, x_n$  are common to both  $f_i$  and  $f_o$  and may hence be omitted to make the text simpler. The current study is therefore restricted to the functions  $f_o(x_i, x_j)$  and  $f_i(\xi_i, x_j)$ . It is natural to start with Eq. 2.1 which is differentiated with respect to  $x_j$ :

$$\begin{aligned}
 \left(\frac{\partial f_i}{\partial x_j}\right)_{\xi_i} &= \left(\frac{\partial f_o}{\partial x_j}\right)_{\xi_i} - \left(\frac{\partial(\xi_i x_i)}{\partial x_j}\right)_{\xi_i} \\
 (2.11) \quad &= \left(\frac{\partial f_o}{\partial x_j}\right)_{\xi_i} - \xi_i \left(\frac{\partial x_i}{\partial x_j}\right)_{\xi_i}
 \end{aligned}$$

Further progress requires the derivative of  $f_o$ . This quantity must be determined indirectly and the simplest(?) way is to first calculate the total differential of  $f_o(x_i, x_j)$ ,

$$\begin{aligned}
 df_o &= \left(\frac{\partial f_o}{\partial x_i}\right)_{x_j} dx_i + \left(\frac{\partial f_o}{\partial x_j}\right)_{x_i} dx_j \\
 (2.12) \quad &= \xi_i dx_i + \left(\frac{\partial f_o}{\partial x_j}\right)_{x_i} dx_j
 \end{aligned}$$

where  $\xi_i$  is defined in Eq. 2.1. At constant  $\xi_i$  Eq. 2.12 gives:

$$(2.13) \quad \left(\frac{df_o}{dx_j}\right)_{\xi_i} = \xi_i \left(\frac{dx_i}{dx_j}\right)_{\xi_i} + \left(\frac{\partial f_o}{\partial x_j}\right)_{x_i}$$

The differential quotients take on the values of the corresponding partial deriva-

tives (one degree of freedom). Substitution of Eq. 2.13 into Eq. 2.11 yields:

$$(2.14) \quad \left(\frac{\partial f_i}{\partial x_j}\right)_{\xi_i} = \left(\frac{\partial f_o}{\partial x_j}\right)_{x_i}$$

The conclusion is that the differentiation of  $f_i$  with respect to the untransformed variable  $x_j$  yields the same derivative as the original function  $f_o$ .  $\square$

§ 11 Make use of the result from Paragraph 10 on the previous page to show that the chemical potential has four equivalent definitions  $\mu \hat{=} (\partial U/\partial N)_{S,V} \hat{=} (\partial H/\partial N)_{S,\pi} \hat{=} (\partial A/\partial N)_{\tau,V} \hat{=} (\partial G/\partial N)_{\tau,\pi}$ . Put up a similar table of alternative definitions for temperature  $\tau$  and negative pressure  $\pi$ .

I I. Let  $f_o = U(S, V, N)$  be the base function for the transformations. The text asks for the derivatives with respect to the mole number  $N$  and it is tacitly understood that only  $S$  and  $V$  shall be transformed. From the Eqs. 2.4 and 2.5 we have  $f_1 = A(\tau, V, N)$  and  $f_2 = H(S, \pi, N)$  which on substitution into Eq. 2.14 gives:

$$(2.15) \quad \left(\frac{\partial A}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

$$(2.16) \quad \left(\frac{\partial H}{\partial N}\right)_{S,\pi} = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

The transform  $f_{12} = f_{21} = G(\tau, \pi, N)$  in Eq. 2.7 can be reached either via  $A$  or  $H$ . Inserted into Eq. 2.14 the two alternatives become:

$$(2.17) \quad \left(\frac{\partial G}{\partial N}\right)_{\tau,\pi} = \left(\frac{\partial A}{\partial N}\right)_{\tau,V}$$

$$(2.18) \quad \left(\frac{\partial G}{\partial N}\right)_{\tau,\pi} = \left(\frac{\partial H}{\partial N}\right)_{S,\pi}$$

Note that all the Eqs. 2.15–2.18 have one variable in common on the left and right hand sides ( $V$ ,  $S$ ,  $\tau$  and  $\pi$  respectively). For multicomponent systems this variable has a vectorial nature, compare  $x_k, \dots, x_n$  in Paragraph 10. To conclude this session the following is true for any single component system:

$$(2.19) \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{\tau,V} \hat{=} \left(\frac{\partial H}{\partial N}\right)_{S,\pi} \hat{=} \left(\frac{\partial G}{\partial N}\right)_{\tau,\pi} \hat{=} \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Performing the same kind of operations on temperature and negative pressure:

$$(2.20) \quad \tau = \left(\frac{\partial H}{\partial S}\right)_{\pi,N} \hat{=} \left(\frac{\partial X}{\partial S}\right)_{V,\mu} \hat{=} \left(\frac{\partial Y}{\partial S}\right)_{\pi,\mu} \hat{=} \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

$$(2.21) \quad \pi = \left(\frac{\partial A}{\partial V}\right)_{\tau,N} \hat{=} \left(\frac{\partial X}{\partial V}\right)_{S,\mu} \hat{=} \left(\frac{\partial \Omega}{\partial V}\right)_{\tau,\mu} \hat{=} \left(\frac{\partial U}{\partial V}\right)_{S,N} \quad \square$$

§ 12 The Legendre transform was differentiated with respect to an untransformed variable in Paragraph 10. It remains to determine the derivative with respect to a transformed variable. Show that  $(\partial f_i/\partial \xi_i)_{x_j, x_k, \dots, x_n} = -x_i$ .

D II. Analogously to Paragraph 10 the variables  $x_k, \dots, x_n$  are omitted to make the analysis simpler. The basis for the operation is  $f_i(\xi_i)$ ,

$x_j) = f_o(x_i, x_j) - \xi_i x_i$  taken from Eq. 2.1. The equation is first differentiated with respect to  $\xi_i$ . Be aware that the chain rule of differentiation

$$\left(\frac{\partial f_o}{\partial \xi_i}\right)_{x_j} = \left(\frac{\partial f_o}{\partial x_i}\right)_{x_j} \left(\frac{\partial x_i}{\partial \xi_i}\right)_{x_j}$$

is used in the last line below:

$$\begin{aligned} \left(\frac{\partial f_i}{\partial \xi_i}\right)_{x_j} &= \left(\frac{\partial f_o}{\partial \xi_i}\right)_{x_j} - \left(\frac{\partial(\xi_i x_i)}{\partial \xi_i}\right)_{x_j} \\ &= \left(\frac{\partial f_o}{\partial \xi_i}\right)_{x_j} - x_i - \xi_i \left(\frac{\partial x_i}{\partial \xi_i}\right)_{x_j} \\ (2.22) \qquad &= \left(\frac{\partial f_o}{\partial x_i}\right)_{x_j} \left(\frac{\partial x_i}{\partial \xi_i}\right)_{x_j} - x_i - \xi_i \left(\frac{\partial x_i}{\partial \xi_i}\right)_{x_j} \end{aligned}$$

From the Eq. 2.3 we can write  $(\partial f_o / \partial x_i)_{x_j} = \xi_i$  which is readily substituted into Eq. 2.22. The result is

$$(2.23) \qquad \left(\frac{\partial f_i}{\partial \xi_i}\right)_{x_j} = -x_i$$

which leads to the conclusion: The derivative of  $f_i$  with respect to a transformed variable  $\xi_i$  gives back the original variable  $x_i$ , but with an induced sign shift. The variable  $x_i$  in  $f_o(x_i, x_j)$  corresponds in other words to  $\xi_i$  in  $f_i(\xi_i, x_j)$  in a natural way<sup>a</sup>. Due to the simple relationship in Eq. 2.23 the variables  $(\xi_i, x_j)$  are said to be the canonical variables of the transform  $f_i(\xi_i, x_j)$ . □

**§ 13** Make use of Paragraph 12 on the facing page to prove that  $V = (\partial H / \partial \pi)_{S,N} = (\partial G / \partial \pi)_{\tau,N} = (\partial Y / \partial \pi)_{S,\mu}$ . Put up a table of similar identities for the entropy  $S$  and the mole number  $N$ .

I                      II. Starts once more with  $f_o = U(S, V, N)$  and defines the transform  $f_2 = H(S, \pi, N) = U - \pi V$ . Inserted into Eq. 2.23 this formula yields<sup>b</sup>  $(\partial H / \partial \pi)_{S,N} = -V$ . A systematic application of Eq. 2.23 on all the the energy transforms of Paragraph 9 on page 6 yields<sup>c</sup>:

$$(2.24) \qquad -V = \left(\frac{\partial H}{\partial \pi}\right)_{S,N} \hat{=} \left(\frac{\partial G}{\partial \pi}\right)_{\tau,N} \hat{=} \left(\frac{\partial Y}{\partial \pi}\right)_{S,\mu}$$

$$(2.25) \qquad -S = \left(\frac{\partial A}{\partial \tau}\right)_{V,N} \hat{=} \left(\frac{\partial G}{\partial \tau}\right)_{\pi,N} \hat{=} \left(\frac{\partial \Omega}{\partial \tau}\right)_{V,\mu}$$

$$(2.26) \qquad -N = \left(\frac{\partial X}{\partial \mu}\right)_{S,V} \hat{=} \left(\frac{\partial Y}{\partial \mu}\right)_{S,\pi} \hat{=} \left(\frac{\partial \Omega}{\partial \mu}\right)_{\tau,V} \quad \square$$

<sup>a</sup> The variables  $x$  and  $\xi$  are said to be conjugated.    <sup>b</sup> The symbol  $\pi = -p$  is used here to signify the pressure variable. This choice is quite deliberate to avoid the eternal discussion about the sign convention of  $p$ . In the literature it is common practise that  $-p$  is simply replaced by  $p$  in the transformations, leaving the question of sign to the reader as an intellectual obstacle. Note, however, that it does not matter whether  $-p$  or  $p$  are held constant during the differentiation.    <sup>c</sup> The sharp-minded student will miss  $-S = (\partial O / \partial \tau)_{\pi,\mu}$ ,  $V = (\partial O / \partial \pi)_{\tau,\mu}$  and  $-N = (\partial O / \partial \mu)_{\tau,p}$ . These relations have no clear thermodynamic interpretation, however, because  $\tau, \pi, \mu$  are experimentally dependent quantities, see also Paragraph 16 on page 11.

§ 14 Make use of the Paragraphs 11 and 13 on pages 8 and 9 to find the total differentials of all the energy transforms mentioned in Paragraph 9.

D . The total differentials of the energy transforms can be put up using the results from Eqs. 2.19–2.21 and 2.24–2.26 as the starting point:

$$(2.27) \quad dU(S, V, N) = \tau dS + \pi dV + \mu dN$$

$$(2.28) \quad dA(\tau, V, N) = -S d\tau + \pi dV + \mu dN$$

$$(2.29) \quad dH(S, \pi, N) = \tau dS - V d\pi + \mu dN$$

$$(2.30) \quad dX(S, V, \mu) = \tau dS + \pi dV - N d\mu$$

$$(2.31) \quad dG(\tau, \pi, N) = -S d\tau - V d\pi + \mu dN$$

$$(2.32) \quad dY(S, \pi, \mu) = \tau dS - V d\pi - N d\mu$$

$$(2.33) \quad d\Omega(\tau, V, \mu) = -S d\tau + \pi dV - N d\mu$$

$$(2.34) \quad dO(\tau, \pi, \mu) = -S d\tau - V d\pi - N d\mu \quad \square$$

§ 15 Show from Paragraph 12 on page 8 that the repeated use of a Legendre transformation gives back the original function.

I . With the basis in Definition 2.1 and Eq. 2.23 the inverse Legendre transformation can be written,

$$(2.35) \quad f_i - \left( \frac{\partial f_i}{\partial \xi_i} \right)_{x_j} \xi_i = f_i - (-x_i) \xi_i \equiv f_o$$

but it is not entirely clear what variable set should be attached to  $f_o$ . To understand the problem a small example is needed, and from Eq. 2.4 it follows:

$$(2.36) \quad U(S, V, N) - \left( \frac{\partial U(S, V, N)}{\partial S} \right)_{V, N} S = U(S, V, N) - \tau S \triangleq A(\tau, V, N)$$

To go the other way around we have to calculate the Legendre transformation of  $A(\tau, V, N)$  with respect to the variable  $\tau$ , that is:

$$(2.37) \quad A(\tau, V, N) - \left( \frac{\partial A(\tau, V, N)}{\partial \tau} \right)_{V, N} \tau = A(\tau, V, N) - (-S)\tau \equiv U(-S, V, N)$$

This yields the original function  $U$  back, but the canonical variable set has been changed from  $S, V, N$  to  $-S, V, N$ ! In order to get back to where we started the Legendre transformation must be employed two more times:

$$(2.38) \quad U(-S, V, N) - \left( \frac{\partial U(-S, V, N)}{\partial (-S)} \right)_{V, N} (-S) = U(-S, V, N) - (-\tau)(-S) \triangleq A(-\tau, V, N)$$


$$(2.39) \quad A(-\tau, V, N) - \left( \frac{\partial A(-\tau, V, N)}{\partial (-\tau)} \right)_{V, N} (-\tau) = A(-\tau, V, N) - S(-\tau) \equiv U(S, V, N)$$

 Clearly, the repeated use of a Legendre transformation results in the cyclic

operation<sup>a</sup>:

$$\begin{array}{ccc}
 U(S, V, N) & \xrightarrow{S} & A(\tau, V, N) \\
 \uparrow -\tau & & \downarrow \tau \\
 A(-\tau, V, N) & \xleftarrow{-S} & U(-S, V, N)
 \end{array} \quad \square$$

§ 16 Show that a Legendre transformation of internal energy  $U(S, V, N)$  with respect to all the canonical variables  $S, V, N$  ends up in the null potential  $O(\tau, \pi, \mu) = 0$ . Show next that the total differential of  $O$  is identical to the Gibbs–Duhem equation, see also Paragraph 24 on page 22 in Chapter 3.

N . The differential of the null potential in Eq. 2.10 is of course 0. However, this result is valid for the entire definition domain and it must logically enforce some kind of restriction on the intensive degrees of freedom of the system. Mathematically, the  $O$ -function forms a hyperplane in  $\dim(\mathbf{n}) + 2$  dimensions. This feature is made visible by differentiating  $O(\tau, \pi, \mu)$  in Eq. 2.10:  $dU - \tau dS - S d\tau - V d\pi - \pi dV - \mu dN - N d\mu = 0$ . Recognises  $\tau dS + \pi dV + \mu dN$  as the total differential of internal energy and simplifies the expression: 

$$(2.40) \quad S d\tau + V d\pi + N d\mu = 0$$

This result is identical to the Gibbs–Duhem’s Eq. 3.23 on page 22 which plays an important role in consistency checks of thermodynamic measurements. A consistency check means that Eq. 2.40 says something about the dependencies of  $\tau, \pi, \mu$ . If a series of measurements are conducted independently such that experimental values are provided for all the variables  $\tau, \pi, \mu$ , then the Gibbs–Duhem equation raises the opportunity to check the quality of the measurements in the sense that Eq. 2.40, or Eq. 2.10 for that sake, must be fulfilled. In practise this shows up in the chemical potential<sup>b</sup> being expressed as a function of temperature and negative pressure, i.e.  $f(\tau, \pi, \mu) = 0$ .  $\square$

§ 17 Make a complete table of all Maxwell relations that originates from the Leibnitz<sup>c</sup> rule  $\partial^2 f / \partial x_i \partial x_j = \partial^2 f / \partial x_j \partial x_i$  when applied to the functions  $U, A, H, Y, G, \Omega, X$  and  $O$ . Restrict yourself to single component systems!

M . First, the meaning of a Maxwell<sup>d</sup> relation is illustrated using  $U(S, V, N)$  as the base function. From the definitions of  $\tau$  and  $\pi$  it follows:

$$\begin{aligned}
 \left( \frac{\partial^2 U}{\partial S \partial V} \right)_N &= \left( \frac{\partial^2 U}{\partial V \partial S} \right)_N \Rightarrow \left[ \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_{S,N} \right]_{V,N} = \left[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right)_{V,N} \right]_{S,N} \\
 &\Rightarrow \left( \frac{\partial \pi}{\partial S} \right)_{V,N} = \left( \frac{\partial \tau}{\partial V} \right)_{S,N}
 \end{aligned}$$

<sup>a</sup> A one-step reversal is possible if the transformed canonical variables are defined as  $(x, y) = (-(\partial g / \partial z)_y, y)$  and not  $(x, y) = ((\partial g / \partial z)_y, y)$  as in the current text. <sup>b</sup> For single component or multicomponent systems at fixed concentration. <sup>c</sup> . <sup>d</sup> James Clerk Maxwell, 1831–1879. Scottish physicist.

Cyclic permutation of the variables  $S$ ,  $V$  and  $N$  yields in a similar way:

$$\begin{aligned} \left(\frac{\partial^2 U}{\partial S \partial N}\right)_V &= \left(\frac{\partial^2 U}{\partial N \partial S}\right)_V &\Rightarrow & \left(\frac{\partial \mu}{\partial S}\right)_{V,N} = \left(\frac{\partial \tau}{\partial N}\right)_{S,V} \\ \left(\frac{\partial^2 U}{\partial V \partial N}\right)_S &= \left(\frac{\partial^2 U}{\partial N \partial V}\right)_S &\Rightarrow & \left(\frac{\partial \mu}{\partial V}\right)_{S,N} = \left(\frac{\partial \tau}{\partial N}\right)_{S,V} \end{aligned}$$

By systematically comparing the second derivatives of all the Legendre transforms mentioned in Paragraph 9 on page 6, we get the result shown below. See also Paragraph 14 on page 10 for a table of total differentials and first derivatives. Note that the Maxwell relations which originate from the null potential  $O(\tau, \pi, \mu)$  are physically inaccessible and therefore excluded from the table.

$$\begin{aligned} \left(\frac{\partial \pi}{\partial S}\right)_{V,N} &= \left(\frac{\partial \tau}{\partial V}\right)_{S,N} & \left(\frac{\partial \mu}{\partial S}\right)_{V,N} &= \left(\frac{\partial \tau}{\partial N}\right)_{S,V} & \left(\frac{\partial \mu}{\partial V}\right)_{S,N} &= \left(\frac{\partial \tau}{\partial N}\right)_{S,V} \\ -\left(\frac{\partial S}{\partial V}\right)_{\tau,N} &= \left(\frac{\partial \pi}{\partial \tau}\right)_{V,N} & -\left(\frac{\partial S}{\partial N}\right)_{\tau,V} &= \left(\frac{\partial \mu}{\partial \tau}\right)_{V,N} & \left(\frac{\partial \pi}{\partial N}\right)_{\tau,V} &= \left(\frac{\partial \mu}{\partial V}\right)_{\tau,N} \\ -\left(\frac{\partial \tau}{\partial \pi}\right)_{S,N} &= \left(\frac{\partial V}{\partial S}\right)_{\pi,N} & \left(\frac{\partial \tau}{\partial N}\right)_{S,\pi} &= \left(\frac{\partial \mu}{\partial S}\right)_{\pi,N} & -\left(\frac{\partial V}{\partial N}\right)_{S,\pi} &= \left(\frac{\partial \mu}{\partial \pi}\right)_{S,N} \\ \left(\frac{\partial \tau}{\partial V}\right)_{S,\mu} &= \left(\frac{\partial \pi}{\partial S}\right)_{V,\mu} & -\left(\frac{\partial \tau}{\partial \mu}\right)_{S,V} &= \left(\frac{\partial N}{\partial S}\right)_{V,\mu} & -\left(\frac{\partial \pi}{\partial \mu}\right)_{S,V} &= \left(\frac{\partial N}{\partial V}\right)_{S,\mu} \\ \left(\frac{\partial S}{\partial \pi}\right)_{\tau,N} &= \left(\frac{\partial V}{\partial \tau}\right)_{\pi,N} & -\left(\frac{\partial S}{\partial N}\right)_{\tau,\pi} &= \left(\frac{\partial \mu}{\partial \tau}\right)_{\pi,N} & -\left(\frac{\partial V}{\partial N}\right)_{\tau,\pi} &= \left(\frac{\partial \mu}{\partial \pi}\right)_{\tau,N} \\ -\left(\frac{\partial \tau}{\partial \pi}\right)_{S,\mu} &= \left(\frac{\partial V}{\partial S}\right)_{\pi,\mu} & -\left(\frac{\partial \tau}{\partial \mu}\right)_{S,\pi} &= \left(\frac{\partial N}{\partial S}\right)_{\pi,\mu} & \left(\frac{\partial V}{\partial \mu}\right)_{S,\pi} &= \left(\frac{\partial N}{\partial \pi}\right)_{S,\mu} \\ -\left(\frac{\partial S}{\partial V}\right)_{\tau,\mu} &= \left(\frac{\partial \pi}{\partial \tau}\right)_{V,\mu} & \left(\frac{\partial S}{\partial \mu}\right)_{\tau,V} &= \left(\frac{\partial N}{\partial \tau}\right)_{V,\mu} & -\left(\frac{\partial \pi}{\partial \mu}\right)_{\tau,V} &= \left(\frac{\partial N}{\partial V}\right)_{\tau,\mu} \end{aligned} \quad \square$$

§ 18 Prove the Gibbs–Helmholtz equation  $(\partial(G/\tau)/\partial(1/\tau))_{\pi,N} \equiv H$ . See if you can generalise this result.

G –H . Plain differentiation and substitution of  $(\partial G/\partial \tau)_{\pi,N} = -S$  and  $G + TS = H$  confirms that the equation is correct, but there is more to it than that. From the mathematical identity

$$\frac{\partial(y/x)}{\partial(1/x)} \equiv y + \frac{1}{x} \frac{\partial y}{\partial(1/x)} \equiv y - x \frac{\partial y}{\partial x}$$

we can conclude that

$$(2.41) \quad \left(\frac{\partial(f_o/x_i)}{\partial(1/x_i)}\right)_{x_j, x_k, \dots, x_n} \equiv f_o - \xi_i x_i \hat{=} f_i$$

for the Legendre transform in Eq. 2.1. The identity applies equally well to  $f_{ij}$  and to any of the higher transforms, which means Eq. 2.41 provides an alternative way of calculating the *numerical* value of the Legendre transform. The *definition* of the transformation is of course not altered. Another useful equation is  $(\partial(A/\tau)/\partial(1/\tau))_{V,N} \equiv U$ . The analogy does not stop here and a whole world of similar equations can be built on the same principle. Quite interestingly, the differentiation of these equations is also comparatively simple. The derivative of the Gibbs–Helmholtz equation may serve as an example:

$$(2.42) \quad \left(\frac{\partial H}{\partial \pi}\right)_{\tau,N} = \left(\frac{\partial^2(G/\tau)}{\partial \pi \partial(1/\tau)}\right)_N = \left(\frac{\partial(V/\tau)}{\partial(1/\tau)}\right)_{\pi,N}$$



Note that the enthalpy is differentiated with respect to a non-canonical variable. This subject is taken up again in Chapter [Constant Composition](#) but then in a different setting (systematic elimination of total differential variables).  $\square$



*Amaryllis Hippeastrum equestre* (Christmas 2004).

## CHAPTER 3

**Euler's Theorem on Homogeneous Functions**

The thermodynamic state is mathematically described by the mapping  $f : \mathbb{R}^{n+2} \rightarrow \mathbb{R}$  where  $n \geq 0$ <sup>a</sup> stands for the number of chemical components in the system (assumed macroscopically homogenous). The definition domain is quite arbitrary, but the theory is relieved from the fact that  $f$  is observed to be linear along vectorial directions departing from the origin. The practical consequence of the linearity<sup>b</sup> will be elucidated when we start investigating the mathematical properties of  $f$ , but first we need to state that the function  $f(x_1, \dots, x_n)$  is homogeneous of order  $k \in \mathbb{Z}$  provided the parametrised function  $f(\lambda \mathbf{x})$  is *proportional* to  $\lambda^k$  in the direction of  $\mathbf{x} = (x_1, \dots, x_n)$ . Here, the parameter  $\lambda \in \mathbb{R}$  is a dimensionless measure of the distance from the origin to the coordinate tuple  $\lambda \mathbf{x} \in \mathbb{R}^n$ . More precisely, the function  $f(x_1, \dots, x_n, \xi_{n+1}, \dots, \xi_m)$  is homogeneous of order  $k$  in the variables  $x_1, \dots, x_n$  if the following criteria are satisfied:

$$(3.1) \quad \begin{aligned} F &= \lambda^k f \\ f &\hat{=} f(x_1, \dots, x_n, \xi_{n+1}, \dots, \xi_m) \\ F &\hat{=} f(X_1, \dots, X_n, \xi_{n+1}, \dots, \xi_m) \end{aligned}$$

$$(3.2) \quad X_i \hat{=} \lambda x_i$$

It is tacitly understood that  $f$  does not have any homogeneity (at least not of order  $k$ ) in the variables  $\xi_{n+1}, \dots, \xi_m$ . Strange at the first sight maybe, but grouping the variables into disjoint subsets is quite natural in physics. For example the kinetic energy of an  $n$ -particle ensemble  $E_k(\mathbf{m}, \mathbf{v}) \hat{=} \frac{1}{2} \sum_i^n m_i v_i^2$  is homogeneous of order 1 with respect to the masses  $m_i$  and homogeneous of order 2 with respect to the velocities  $v_i$ . Pushed to the extreme one can say that  $f = xyz$  is homogeneous of order 1 in  $x$  if  $y, z$  are taken to be constant *parameters* (the same argument holds circularly for  $y$  and  $z$ ), and homogeneous of order 3 in  $x, y, z$  if all quantities are treated as free function variables.

Of particular interest to us are the energy functions<sup>c</sup>  $U, A, \dots, O$  with state variables belonging to  $S, V, N$  or  $\tau, \pi, \mu$ . The energy functions, and entropy, volume and mole number, are homogeneous functions of order 1, while tem-

<sup>a</sup> An empty chamber has no chemical components but is still a thermodynamic system.

<sup>b</sup> Herbert Callen. *Thermodynamics and an Introduction to Thermostatistics*. Wiley, 2nd edition, 1985. <sup>c</sup> From Eqs. 3.1–3.2 the total Gibbs energy is  $G(N, \tau, \pi) = |N|g(1 \text{ mol}, \tau, \pi)$ , or, alternatively,  $G = Ng(\tau, \pi)$ . The latter form is accepted in thermodynamic literature and  $g$  is then referred to as the molar Gibbs energy (or specific Gibbs energy if a mass basis is being used).

perature, pressure<sup>a</sup> and chemical potential are homogeneous functions of order 0. In a thermodynamic context these quantities are referred to as *extensive* and *intensive* state variables respectively<sup>b</sup>.

§ 19 The Gibbs energy of a binary mixture is homogeneous of order 1 in the mole numbers  $N_1$  and  $N_2$  (at fixed  $T$  and  $p$ ). Make a contour diagram illustrating the function  $G = aN_1x_2 + N_1 \ln x_1 + N_2 \ln x_2$  where  $N_2$  is plotted along the ordinate axis and  $N_1$  along the abscissa. Show that the isopleths corresponding to constant  $G$  (the contour lines) are equidistant for evenly distributed Gibbs energy values. Use  $a = 2.4$  in your calculations.

C . Gibbs energy is nonlinear in  $N_1, N_2$  and the isopleths must be calculated iteratively:  $N_{2,k+1} = N_{2,k} - (G_k - G)/\mu_2$ , where  $\mu_2 = ax_1^2 + \ln x_2$  is the partial derivative of  $G$  with respect to  $N_2$ . A fixed value is selected for  $N_1$  and  $N_2$  is iterated till  $G$  has converged ( $G_{k \rightarrow \infty} = G$ ), see the Matlab-program 1.2 in Appendix F. The calculated result is shown in Figure 3.1 on the facing page. Note that each isopleth defines a *non-convex* region which can be interpreted as a fundamental thermodynamic instability. The corresponding two-phase region (the symmetry of the model reduces the phase equilibrium criterion to  $\mu_1 = \mu_2$ ) can be calculated from the total differential of  $G$ , rewritten here into the tangent of the isopleth:

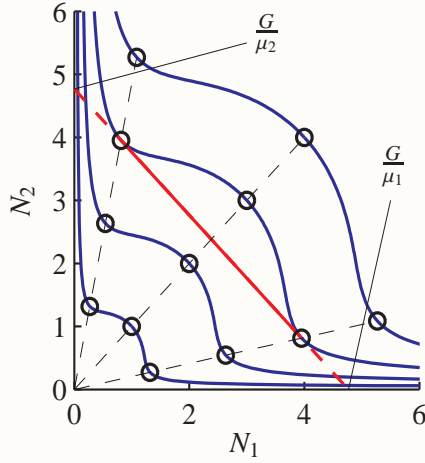
$$\left(\frac{dN_2}{dN_1}\right)_{T,p,G} = -\frac{\mu_1}{\mu_2}$$



It can be proved (do this) that the tangent intersects with the  $y$  and  $x$ -axes at  $G/\mu_2$  and  $G/\mu_1$  respectively. This indicates that the phase equilibrium condition is fulfilled whenever two points on the same isopleth has common tangents (remember that  $G$  takes on constant values along each isopleth such that the criterion is reduced to  $\mu_1 = \mu_2$ ).  $\square$

Further contemplations on homogeneity should always be based on the proper identification of the canonical state variables of the function. This is not an absolute issue, however, because the thermodynamic state of any system is uniquely determined if *any* of its possible variable sets is fully specified. For example  $U$  is extensive in  $S, V, N$  while  $G$  is extensive in  $N$  at given  $\tau$  and  $\pi$ , but we can alternatively state the opposite and say that  $U$  is extensive in  $N$  at given  $\tau$  and  $\pi$  and that  $G$  is extensive in  $S, V, N$ . There are plenty of alternative state descriptions, but a combination of three arbitrary state variables is not always sufficient. A simple counter-example is the redundant specification  $H, \tau, N^c$ . To avoid problems of this kind we shall therefore make use of canonical

<sup>a</sup> Here,  $\tau$  and  $\pi$  are used for temperature and negative pressure respectively, as already introduced in Chapter 2. In this context it is important to stress that the properties (in common with the chemical potential  $\mu$ ) are intensive quantities. <sup>b</sup> A physical quantity is *extensive* if it is proportional to the system size and *intensive* if it is insensitive to the system size. <sup>c</sup> E.g. the ideal gas enthalpy can be written  $H^{ig} = H(\tau, N)$ . At given  $\tau, N$  the system is underspecified because there is no way we can fix the pressure. If we try to specify  $H$  in addition to  $\tau$  and  $N$  this will be a redundant (or even a contradictory) statement.



**FIGURE 3.1** Contour diagram of Gibbs energy (solid lines). Equidistant values (open circles) are made visible along 3 rays (dotted lines) from the origin. The two-phase region is spanned by the two outermost rays. One of the isopleths indicates the phase equilibrium condition in the shape of a convex hull construction.

variables if nothing else is stated.

We shall also avoid the general description of multicomponent functions in Eq. 3.1, and rather go for a detailed analysis of the simpler two-variable functions  $f(x, \xi)$  and  $f(X, \xi)$ . The results will later be generalised in Chapter [General Theory](#) and nothing is spoilt by taking it easy here. In order to exploit the function properties it is appropriate to make use of the total differential of  $F = f(X, \xi)$  expressed in  $X$  and  $\xi$ -coordinates:

$$dF = \left(\frac{\partial F}{\partial X}\right)_{\xi} dX + \left(\frac{\partial F}{\partial \xi}\right)_X d\xi$$

The variable  $X$  is defined as a function of  $x$  and  $\lambda$  in Eq. 3.2 and by substituting the total differential of  $X$ , or more precisely  $dX = \lambda dx + x d\lambda$ , we get:

$$(3.3) \quad dF = \left(\frac{\partial F}{\partial X}\right)_{\xi} x d\lambda + \left(\frac{\partial F}{\partial X}\right)_{\xi} \lambda dx + \left(\frac{\partial F}{\partial \xi}\right)_X d\xi$$

An alternative would be to make use of  $F = \lambda^k f$  from Eq. 3.1 as the starting point for the derivation:

$$dF = k\lambda^{k-1} f d\lambda + \lambda^k df$$

Substitution of the total differential of  $f$  expressed in  $x$  and  $\xi$ -coordinates gives:

$$(3.4) \quad dF = k\lambda^{k-1} f d\lambda + \lambda^k \left(\frac{\partial f}{\partial x}\right)_{\xi} dx + \lambda^k \left(\frac{\partial f}{\partial \xi}\right)_x d\xi$$

Note that Eq. 3.3 and Eq. 3.4 are two alternative expressions for the same differential  $dF(\lambda, x, \xi)$ . Comparing the equations term-by-term reveals three relations of great importance to thermodynamic methodology:

C  $d\lambda$ . Comparing the  $d\lambda$ -terms reveals that  $(\partial F/\partial X)_{\xi} x = k\lambda^{k-1} f$ . Multiplication on both sides by  $\lambda$  gives  $(\partial F/\partial X)_{\xi} \lambda x = k\lambda^k f$ , which upon substitution

of Eq. 3.1 and Definition 3.2 can be transformed to:

$$(3.5) \quad \left(\frac{\partial F}{\partial X}\right)_{\xi} X = kF$$

The closed form of Eq. 3.5 indicates that there is a general solution to the undetermined integral  $F(X, \xi) = \int (dF)_{\xi} = \int (\partial F / \partial X)_{\xi} dX$ . The result is known as Euler's first theorem<sup>a</sup> on homogeneous functions, or simply as the Euler integration of  $F$ .  $\square$

C  $dx$ . Comparing the  $dx$ -terms reveals that  $(\partial F / \partial X)_{\xi} \lambda = \lambda^k (\partial f / \partial x)_{\xi}$ . Dividing on each side by  $\lambda$  leads to:

$$(3.6) \quad \left(\frac{\partial F}{\partial X}\right)_{\xi} = \lambda^{k-1} \left(\frac{\partial f}{\partial x}\right)_{\xi}$$

The derivative of  $F$  with respect to  $X$  can be written on the form  $G(X, \xi) = \lambda^{k-1} g(x, \xi)$  which implies that  $\partial F / \partial X$  is a homogeneous function of order  $k - 1$ . Differentiation with respect to  $X$  therefore reduces the homogeneity of  $F$  by one order.  $\square$

C  $d\xi$ . Comparing the  $d\xi$ -terms reveals that the homogeneity of the derivative with respect to  $\xi$  is unchanged:

$$(3.7) \quad \left(\frac{\partial F}{\partial \xi}\right)_X = \lambda^k \left(\frac{\partial f}{\partial \xi}\right)_x$$

This implies that the derivative of  $F$  with respect to  $\xi$  is a new homogeneous function of degree  $k$ . Differentiation with respect to  $\xi$  therefore conserves the homogeneity in  $X$ .  $\square$

R . It should be stressed that the Euler integration in Eq. 3.5 is not limited to one particular value of  $X$ . In fact, any scaled variable  $x = \lambda^{-1}X$  satisfies the equation:

$$\left(\frac{\partial f}{\partial x}\right)_{\xi} x = kf$$

The validity of this statement is ensured by first combining Eqs. 3.5 and 3.6, and thereafter substituting Eq. 3.1 and Definition 3.2. This result emphasises the practical importance of Euler's theorem as outlined in Eq. 3.5.  $\square$

G . The general properties of homogeneous functions will be elucidated in Chapter **General Theory**, but to get an impression of the overall picture we shall briefly mention what changes are required in Eqs. 3.5–3.7 to

<sup>a</sup> Leonhard Euler, 1707–1783. Swiss mathematician.

make these valid for multivariate functions:

$$(3.8) \quad \sum_{i=1}^n X_i \left( \frac{\partial F}{\partial X_i} \right)_{X_{j \neq i}, \xi_l} = kF$$

$$(3.9) \quad \left( \frac{\partial F}{\partial X_i} \right)_{X_{j \neq i}, \xi_l} = \lambda^{k-1} \left( \frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}, \xi_l}$$

$$(3.10) \quad \left( \frac{\partial F}{\partial \xi_k} \right)_{X_j, \xi_{l \neq k}} = \lambda^k \left( \frac{\partial f}{\partial \xi_k} \right)_{x_j, \xi_{l \neq k}} \quad \square$$

§ 20 Internal energy  $U = U(S, V, N)$  is an extensive function in the variables  $S, V$  and  $N$ . The total differential of  $U$  is  $dU = \tau dS + \pi dV + \mu dN$ . Explore the homogeneity associated with the functions  $\tau$  and  $\pi$  and  $\mu$ .

I . The variables  $\tau, \pi$  and  $\mu$  mentioned above must be identified. Mathematically, the total differential of  $U(S, V, N)$  can also be written:

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \left( \frac{\partial U}{\partial N} \right)_{S,V} dN$$

Compared with the differential given in the text this means that  $\tau \hat{=} (\partial U / \partial S)_{V,N}$  and  $\pi \hat{=} (\partial U / \partial V)_{S,N}$  and  $\mu \hat{=} (\partial U / \partial N)_{S,V}$ , see also Paragraph 9 on page 6 in Chapter 2. Substitution of  $k = 1$  and  $X_i = S$  and  $X_j \in \{V, N\}$  and  $\xi_l = \emptyset^a$  in Eq. 3.9 yields:

$$(3.11) \quad \tau(S, V, N) \hat{=} \left( \frac{\partial U(S,V,N)}{\partial S} \right)_{V,N} = \lambda^0 \left( \frac{\partial u(s,v,n)}{\partial s} \right)_{v,n} = \tau(s, v, n)$$

The function  $\tau(S, V, N)$  is obviously homogeneous of order 0 in the variables  $S, V, N$  because it is independent of the scaling factor  $\lambda$ . In common speech the temperature is said to be an intensive variable and is taken to be independent of the system size<sup>b</sup>. Differentiation of  $U$  with respect to  $V$  and  $N$  yield in a similar manner,

$$(3.12) \quad \pi(S, V, N) \hat{=} \left( \frac{\partial U(S,V,N)}{\partial V} \right)_{S,N} = \lambda^0 \left( \frac{\partial u(s,v,n)}{\partial v} \right)_{s,n} = \pi(s, v, n)$$

$$(3.13) \quad \mu(S, V, N) \hat{=} \left( \frac{\partial U(S,V,N)}{\partial N} \right)_{S,V} = \lambda^0 \left( \frac{\partial u(s,v,n)}{\partial n} \right)_{s,v} = \mu(s, v, n)$$

where the (negative) pressure and the chemical potential are intensive variables as well. □

§ 21 Internal energy  $U = U(S, V, N)$  is an extensive function in the variables  $S, V$  and  $N$ . The total differential of  $U$  is  $dU = \tau dS + \pi dV + \mu dN$ . What is the correct integral form of  $U$ ? Make a physical reasoning about this integral.

E . Substitution of  $k = 1$  and  $X_i \in \{S, V, N\}$  and  $\xi_l = \emptyset$  in Eq. 3.8 together with the definitions from Paragraph 20 i.e.  $\tau \hat{=} (\partial U / \partial S)_{V,N}$  and  $\pi \hat{=} (\partial U / \partial V)_{S,N}$  and  $\mu \hat{=} (\partial U / \partial N)_{S,V}$  yields Euler's equation applied to ✎

<sup>a</sup> Actually an empty set. Here it is used to denote a missing variable or an empty vector.

<sup>b</sup> Valid only if the system is sufficiently big i.e. the number of particles is large enough to fix the temperature!

internal energy:

$$(3.14) \quad U = \tau S + \pi V + \mu N$$

The paragraph does not question us about multicomponent mixtures, but Eq. 3.14 is quite general and can in (analogy with Eq. 3.8) be extended to:

$$(3.15) \quad U = \tau S + \pi V + \sum_{i=1}^n \mu_i N_i \hat{=} \tau S + \pi V + \boldsymbol{\mu}^T \mathbf{n} \quad \square$$

**R** . The total differential of internal energy for a single component system is  $dU = \tau dS + \pi dV + \mu dN$ . The differential can be integrated without actually solving any partial differential equation because  $\tau, \pi, \mu$  are intensive (mass independent) variables. Physically, this means that the system can be built from zero size<sup>a</sup> in a manner that keeps  $\tau, \pi, \mu$  constant during the process. This process is achieved by agglomerating a large number of small systems at fixed temperature, (negative) pressure and chemical potential. When these subsystems are collected into one big system there will be no changes to the intensive properties because the requirements for *thermodynamic equilibrium* are intrinsically fulfilled, see also Chapter 8.  $\square$

**§ 22** Gibbs energy  $G(\tau, \pi, N)$  is an extensive function of the mole number  $N$  at a given temperature  $\tau$  and (negative) pressure  $\pi$ . The total differential of  $G$  is  $dG = -S d\tau - V d\pi + \mu dN$ . Explore the homogeneity associated with the functions  $S$  and  $V$ .

**E** . Applies the same procedure as was used in Paragraph 20 on the previous page. First of all the functions  $S, V$  and  $\mu$  mentioned in the text must be identified. Mathematically, the total differential of  $G(\tau, \pi, N)$  is:

$$dG = \left(\frac{\partial G}{\partial \tau}\right)_{\pi, N} d\tau + \left(\frac{\partial G}{\partial \pi}\right)_{\tau, N} d\pi + \left(\frac{\partial G}{\partial N}\right)_{\tau, \pi} dN$$

Compared to the differential in the text this yields  $-S(\tau, \pi, N) = (\partial G / \partial \tau)_{\pi, N}$  and  $-V(\tau, \pi, N) = (\partial G / \partial \pi)_{\tau, N}$  and  $\mu = (\partial G / \partial N)_{\tau, \pi}$ . From Eq. 3.10 we can deduce that both volume and entropy are homogeneous functions of order 1 in the mole number at specified temperature and (negative) pressure, i.e. they are extensive variables. From Eq. 3.9 it is seen that the chemical potential (still) is a homogeneous function of order 0, see also Eq. 3.13.  $\square$



**§ 23** Homogeneity causes a whole range of remarkable results. One formula obtained by differentiating Eq. 3.5 is:

$$X d\left(\frac{\partial F}{\partial X}\right)_{\xi} - k\left(\frac{\partial F}{\partial \xi}\right)_X d\xi = (k - 1)\left(\frac{\partial F}{\partial X}\right)_{\xi} dX$$

<sup>a</sup> A system of zero size has by definition null internal energy, i.e.  $U = 0$ . The meaning of “zero size” refers in this context to zero volume, zero mass and zero entropy. Note, however, that it is not sufficient to say zero mass because even an evacuated volume will have a radiation energy which is proportional to  $T^4$ !



For  $k = 1$  this implies that  $(\partial^2 F / \partial X \partial X)_\xi = 0$  and  $(\partial F / \partial \xi)_X = (\partial^2 F / \partial X \partial \xi)_X$ . Verify these results and give a physical explanation for the behaviour.

H . The left side of Eq. 3.5 is differentiated and the right side is replaced by the total differential of  $F$ :

$$X d\left(\frac{\partial F}{\partial X}\right)_\xi + \left(\frac{\partial F}{\partial X}\right)_\xi dX = k\left(\frac{\partial F}{\partial X}\right)_\xi dX + k\left(\frac{\partial F}{\partial \xi}\right)_X d\xi$$

For  $k = 1$  the equation reduces to  $X d(\partial F / \partial X)_\xi = (\partial F / \partial \xi)_X d\xi$ . Note that  $X$  and  $d\xi$  are arbitrary. To proceed we must know the differential of  $\partial F / \partial X$ , but because  $F$  is a function of  $X$  and  $\xi$  this can be written as the total differential

$$d\left(\frac{\partial F}{\partial X}\right)_\xi = \left(\frac{\partial^2 F}{\partial X \partial X}\right)_\xi dX + \left(\frac{\partial^2 F}{\partial X \partial \xi}\right)_\xi d\xi$$

where  $dX$  is also arbitrary. Substituted into the equation above, and plugging in  $k = 1$ , this gives the intermediate result:


$$(3.16) \quad X\left(\frac{\partial^2 F}{\partial X \partial X}\right)_\xi dX + X\left(\frac{\partial^2 F}{\partial X \partial \xi}\right)_\xi d\xi = \left(\frac{\partial F}{\partial \xi}\right)_X d\xi$$

The trick is to recognise that  $X$ ,  $dX$  and  $d\xi$  are independent variables. This implies the existence of two non-trivial relations connected to Eq. 3.16 (one equation in three variables leaves two non-trivial relations), irrespective of the actual values of  $X$  and  $\xi$ :

$$(3.17) \quad \left(\frac{\partial^2 F}{\partial X \partial X}\right)_\xi = 0$$

$$(3.18) \quad X\left(\frac{\partial^2 F}{\partial X \partial \xi}\right)_\xi = \left(\frac{\partial F}{\partial \xi}\right)_X \quad \square$$

From a physical point of view any extensive function  $F(X, \xi)$  can be expressed on the form  $F = \beta(\xi)X$ . This stems from the fact that  $F(0, \xi) = 0$  in addition to  $\partial^2 F / \partial X \partial X = 0$ , see Eq. 3.17<sup>a</sup>.

The derivative of  $F$  with respect to  $\xi$  is therefore an extensive function  $\beta'(\xi)X$  where the second derivative of  $F$  with respect to both  $X$  and  $\xi$  is equal to the intensive function  $\beta'(\xi)$ . The numerical value of  $\partial F / \partial \xi$  is easily obtained by Euler integration of  $\partial^2 F / \partial X \partial \xi$  as shown in Eq. 3.18. 

G . In the general case  $\mathbf{x}$  and  $\xi$  would be vectorial quantities. If  $F(\mathbf{x}, \xi)$  is extensive in  $\mathbf{x}$  it can be shown that the differential in Paragraph 23 on the facing page takes the form,

$$(3.19) \quad \mathbf{x}^T d\left(\frac{\partial F}{\partial \mathbf{x}}\right)_\xi - \left(\frac{\partial F}{\partial \xi}\right)_\mathbf{x} d\xi = 0$$

where the differential of  $\partial F / \partial \mathbf{x}$  is written:

$$(3.20) \quad d\left(\frac{\partial F}{\partial \mathbf{x}}\right)_\xi = \left(\frac{\partial^2 F}{\partial \mathbf{x} \partial \mathbf{x}}\right)_\xi d\mathbf{x} + \left(\frac{\partial^2 F}{\partial \mathbf{x} \partial \xi}\right)_\xi d\xi$$

<sup>a</sup> It should be remarked that it is the second derivative *function* which is zero. It is not sufficient to say that the second derivative has a zero value at one particular point!

The two quantities  $d\mathbf{x}$  and  $d\xi$  are independent and by substitution of the differential 3.20 in Eq. 3.19 it follows that:

$$(3.21) \quad \left(\frac{\partial^2 F}{\partial \mathbf{x} \partial \mathbf{x}}\right)_{\xi} \mathbf{x} = \mathbf{0}$$

$$(3.22) \quad \left(\frac{\partial^2 F}{\partial \xi \partial \mathbf{x}}\right) \mathbf{x} = \left(\frac{\partial F}{\partial \xi}\right)_{\mathbf{x}}$$



Note that Eq. 3.22 is a *generalisation* of 3.18 whereas Eq. 3.17 represents a *specialisation* of 3.21. That means the second derivative of  $F(X, \xi)$  with respect to  $X$  is zero for all single-variable functions, while the corresponding Hessian  $F(\mathbf{x}, \xi)$  for multivariate systems is singular in the direction of  $\mathbf{x}$ . This is Euler's second theorem on homogeneous functions.  $\square$

§ 24 Substitute for  $U = U(S, V, N)$  in Paragraph 23 on page 20 and show that  $S d\tau + V d\pi + N d\mu = 0$ . Do you know the name of this equation in thermodynamics? Does it make any difference if you plug in  $G = G(\tau, \pi, N)$  rather than  $U(S, V, N)$ ?

**G –D**. Substitution of  $F = U(\mathbf{x}, \xi)$  in Eq. 3.19 where  $\mathbf{x}^T = (S, V, N)$  and  $\xi = \emptyset$ , reduces the expression to  $\mathbf{x}^T d(\partial U / \partial \mathbf{x}) = 0$ . From the definitions of  $\tau, \pi, \mu$  in Paragraph 20 on page 19 we can write,

$$(3.23) \quad S d\tau + V d\pi + N d\mu = 0$$



better known as the Gibbs–Duhem equation. Alternatively, if  $F = G(\mathbf{x}, \xi)$  where  $\mathbf{x} = N$  and  $\xi^T = (\tau, \pi)$ , then Eq. 3.19 takes the form:

$$N d\left(\frac{\partial G}{\partial N}\right)_{\tau, \pi} - \left(\frac{\partial G}{\partial \tau}\right)_{\pi, N} d\tau - \left(\frac{\partial G}{\partial \pi}\right)_{\tau, N} d\pi = 0$$

The partial derivatives of  $G$  with respect to  $N, \tau$  and  $\pi$  are recognised as  $\mu, -S$  and  $-V$  in Paragraph 22 on page 20. The expression can therefore be reformulated as  $N d\mu + S d\tau + V d\pi = 0$  which is identical to the Gibbs–Duhem equation. In fact, all Legendre transforms of  $U$  winds up into the same Gibbs–Duhem equation.  $\square$

The paragraph does not ask for any extensions, but in analogy with Eqs. 3.8 and 3.15 the Gibbs–Duhem equation may be extended to a multicomponent form:

$$(3.24) \quad S d\tau + V d\pi + \sum_{i=1}^n N_i d\mu_i \hat{=} S d\tau + V d\pi + \mathbf{n}^T d\boldsymbol{\mu} = 0$$

Note that the Gibbs–Duhem equation is an inevitable consequence of the homogeneous derivative properties of extensive functions and not only those of thermodynamic origin. The homogeneity, which effectively removes one degree of freedom in the function expression, shows up as a mutual dependency in the  $n$  derivatives (of  $U$ ). As a result only  $n - 1$  of the intensive state variables are independent. In single component systems this means that any arbitrary in-

tensive variable can be expressed as a function of (at most) two other intensive variables, see also Paragraph 29 on page 25.

**L** . It is important to realise that the information content of  $U$  is conserved during the Legendre transformation to  $H, A, \dots, O$ . The knowledge of e.g. Gibbs energy  $G(\tau, \pi, N)$  really implies a full knowledge of  $U(S, V, N)$ , and vice versa. The Gibbs–Duhem equation can therefore be derived from any of the energy functions. In particular this also applies to the differential of the null-potential  $O(\tau, \pi, \mu)$  which is identical to Eq. 3.23, see Paragraph 16 on page 11.  $\square$

**§ 25** Use the result from Paragraph 23 on page 20 to determine the second derivatives  $(\partial^2 G / \partial N \partial N)_{\tau, \pi}$  and  $(\partial^2 Y / \partial S \partial S)_{\pi, \mu}$  and  $(\partial^2 \Omega / \partial V \partial V)_{\tau, \mu}$  where  $G = G(\tau, \pi, N)$  and  $Y = Y(S, \pi, \mu)$  and  $\Omega = \Omega(\tau, V, \mu)$ .

**L** . The three functions  $G, Y$  and  $\Omega$  are extensive in  $N, S$  and  $V$  respectively, i.e. in one single variable. This makes Eq. 3.17 valid and the substitution of the definitions for  $\tau, \pi, \mu$  yields:

$$(3.25) \quad \left( \frac{\partial^2 G}{\partial N \partial N} \right)_{\tau, \pi} = \left( \frac{\partial \mu}{\partial N} \right)_{\tau, \pi} = 0$$

$$(3.26) \quad \left( \frac{\partial^2 Y}{\partial S \partial S} \right)_{\pi, \mu} = \left( \frac{\partial \tau}{\partial S} \right)_{\pi, \mu} = 0$$

$$(3.27) \quad \left( \frac{\partial^2 \Omega}{\partial V \partial V} \right)_{\tau, \mu} = \left( \frac{\partial \pi}{\partial V} \right)_{\tau, \mu} = 0 \quad \square$$

**§ 26** Show that the Hessian of  $A = A(\tau, V, N)$  has one single *independent* element when the temperature  $\tau$  is taken to be a constant parameter. Use Eq. 3.21 as your point of departure.

Helmholtz energy is extensive in  $V, N$  at the given temperature  $\tau$ . With due reference to Eq. 3.21 the Hessian of  $A$  can be expressed as a function of only one independent variable because the matrix, in addition to being symmetric, must satisfy the homogeneity relation:

$$\left( \frac{\partial^2 A}{\partial \mathbf{x} \partial \mathbf{x}} \right)_{\tau} \mathbf{x} \hat{=} \begin{pmatrix} \left( \frac{\partial \pi}{\partial V} \right)_{\tau, N} & \left( \frac{\partial \pi}{\partial N} \right)_{\tau, V} \\ \left( \frac{\partial \mu}{\partial V} \right)_{\tau, N} & \left( \frac{\partial \mu}{\partial N} \right)_{\tau, V} \end{pmatrix} \begin{pmatrix} V \\ N \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

The notion about symmetry is valid to all Hessians of thermodynamic origin and leads in this case to  $(\partial \pi / \partial N)_{\tau, V} = (\partial \mu / \partial V)_{\tau, N}$ . Altogether there are 4 matrix elements and 3 connecting relations.

**H** . The solution of the homogeneous(!) system of equations can be formulated in an infinite number of ways where one possibility is:

$$(3.28) \quad \frac{N}{V} \left( \frac{\partial \mu}{\partial N} \right)_{\tau, V} \begin{pmatrix} \frac{N}{V} & -1 \\ -1 & \frac{V}{N} \end{pmatrix} \begin{pmatrix} V \\ N \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Note that the second derivative of Helmholtz energy with respect to the mole number is different from zero in Eq. 3.28, while the corresponding second derivative of Gibbs energy is zero in Eq. 3.25:

$$\begin{aligned}\left(\frac{\partial\mu}{\partial N}\right)_{\tau,\pi} &= 0 \\ \left(\frac{\partial\mu}{\partial N}\right)_{\tau,V} &\neq 0\end{aligned}$$

This emphasises that a proper understanding of the many peculiarities of the energy functions is important, and it also stresses that it is essential to know which variables are held constant during the differentiation.  $\square$

**§ 27** Find analytical expressions for  $(\partial G/\partial\tau)_{\pi,N}$  and  $(\partial G/\partial\pi)_{\tau,N}$  based on an Euler integration of the partial molar entropy and partial molar volume.

**P** . Replaces  $F$  by  $G(\xi, \mathbf{n})$  in Eq. 3.22 where  $\xi^T = (\tau, \pi)$  and  $\mathbf{n}^T = (N_1, \dots, N_n)$ . This gives without difficulty:

$$\begin{pmatrix} \left(\frac{\partial G}{\partial\tau}\right)_{\pi,N} \\ \left(\frac{\partial G}{\partial\pi}\right)_{\tau,N} \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial^2 G}{\partial\tau\partial\mathbf{n}^T}\right)_{\pi} \\ \left(\frac{\partial^2 G}{\partial\pi\partial\mathbf{n}^T}\right)_{\tau} \end{pmatrix} \mathbf{n} = - \begin{pmatrix} \left(\frac{\partial S}{\partial\mathbf{n}^T}\right)_{\tau,\pi} \\ \left(\frac{\partial V}{\partial\mathbf{n}^T}\right)_{\tau,\pi} \end{pmatrix} \mathbf{n} \hat{=} - \begin{pmatrix} \bar{\mathbf{s}}^T \mathbf{n} \\ \bar{\mathbf{v}}^T \mathbf{n} \end{pmatrix}$$

The partial derivatives of  $S$  and  $V$  on the right hand side are called the partial molar entropy and partial molar<sup>a</sup> volume respectively. These quantities (and similar partial molarities) occur so frequently in the thermodynamic theory of mixtures that they are given a differential operator of their own, see Paragraph **Partial Differentials**. A more compact writing is therefore  $S = \mathbf{n}^T \bar{\mathbf{s}}$  and  $V = \mathbf{n}^T \bar{\mathbf{v}}$ .  $\square$

**§ 28** Show that  $G(S, V, N)$  really is an extensive function of the variables  $S, V, N$ , verifying the conjecture which was made in the introduction to this chapter (on page 16).

**P** . From the definition  $G(\tau, \pi, N) \hat{=} U - \tau S - \pi V$  where  $U = U(S, V, N)$  and  $\tau \hat{=} (\partial U/\partial S)_{V,N}$  and  $\pi \hat{=} (\partial U/\partial V)_{S,N}$  it follows that we can express Gibbs energy as a function of  $S, V, N$  because the right side of the equation only includes  $U$  and functions derived from  $U$ :

$$G(S, V, N) = U(S, V, N) - \tau(S, V, N)S - \pi(S, V, N)V$$


We know from before that  $\tau, \pi$  and  $U, S, V$  are intensive and extensive variables respectively. From this it follows,

$$\begin{aligned}G(S, V, N) &= \lambda u(s, v, n) - \lambda\tau(s, v, n)s - \lambda\pi(s, v, n)v \\ &\hat{=} \lambda g(s, v, n)\end{aligned}$$

<sup>a</sup> A partial molar quantity is defined as  $\bar{\mathbf{f}} = (\partial F/\partial\mathbf{n})_{\tau,\pi}$  independent of whether  $F$  has  $\tau, \pi, N_1, \dots, N_n$  as canonical variables or not (it is only for Gibbs energy there is a correspondence between the two variable sets).

which clearly states that  $G$  is homogeneous in accordance with the conjecture. Note that the last equation tacitly exploits the homogeneity relations  $S = \lambda s$ ,  $V = \lambda v$  and  $N = \lambda n$ .  $\square$

§ 29 Can you from Paragraph 25 on page 23 tell how many thermodynamic variables that are needed to determine the intensive state of a system?

T . A thermodynamic system is in general described by  $n + 2$  independent state variables. The intensive state is, however, determined once  $n + 1$  (intensive) variables are fixed. This fact is illustrated by Eqs. 3.25–3.27 where the derivative with respect to the remaining extensive variable is zero when the other variables are intensive and constant during the differentiation. In fact, the (single) extensive variable determines the system size but has no influence on  $\tau, \pi$  and  $\mu$ . For a single component system we can describe the intensive state in three different ways: 

$$\tau = \tau(\pi, \mu)$$

$$\pi = \pi(\tau, \mu)$$

$$\mu = \mu(\tau, \pi)$$

$\square$



?? *Aeschna grandis* (Trondheim 2004).



## CHAPTER 4

**Postulates and Definitions**

The unifying theory which embraces this book depends on four postulates only, but as in every axiomatic system there is a considerable degree of freedom in how the postulates are stated (according to the incompleteness theorems of Gödel<sup>a</sup>). First of all we must select a merit function among the four basic quantities  $U$ ,  $S$ ,  $V$  and  $N$ . The volume is familiar to all of us while the mole number is getting a little more vague (although molecular entities are no doubt countable). On the other hand energy (work) and entropy (heat) are pure abstractions. Among the latter two concepts most people find it easier to accept energy as a state variable rather than entropy because macroscopic work is more directly quantified than heat. The pros and cons of the merit functions are summarised below:

$U(S, V, N)$ . The variables are strictly positive (+), but  $S$  is a rather difficult concept (-). Equilibrium is described as a minimum energy state (++) □

$U(U, V, N)$ . The variables have simple physical interpretations (+), but are not strictly positive (-) because  $U$  has no absolute zero point. Equilibrium is described as a state of maximum disorder (-). □

$U(S, U, N)$ . The variables are not strictly positive (-),  $S$  is an abstract concept (-) and the equilibrium state has no clear physical interpretation (-). However, all the variables tell something about the *internal* state of the system (+), while the function value is a measure for an *external* property (+). □

$U(S, V, U)$ . No contemplations—neither positive nor negative. □

The thermodynamic equilibrium corresponds with a state of minimum energy which justifies the choice of  $U(S, V, N)$  as the basis function. The four postulates can then be stated as:

$$\begin{aligned} \text{Internal energy: } U &= U(S, V, \mathbf{n}) \\ \text{Heterogeneous system: } U_{\text{tot}} &= \sum_i U_i(S_i, V_i, \mathbf{n}_i) \\ \text{Equilibrium state: } U_{\text{eq}} &= \min_{S_i, V_i, \mathbf{n}_i} U_{\text{tot}} \\ \text{Zero entropy: } \lim_{T \rightarrow 0} S &= 0 \end{aligned}$$

<sup>a</sup> Kurt Gödel, 1906–1978. Austrian–American logician.

We can build upon these postulates by defining four closely related energy functions from the Legendre transform of internal energy;

$$\begin{aligned}
 \text{Internal energy:} \quad U(S, V, \mathbf{n}) &= U && \hat{=} TS - pV + \sum_{i=1}^n \mu_i N_i \\
 \text{Helmholtz energy:} \quad A(T, V, \mathbf{n}) &= U - TS && \hat{=} -pV + \sum_{i=1}^n \mu_i N_i \\
 \text{Enthalpy:} \quad H(S, -p, \mathbf{n}) &= U + pV && \hat{=} TS + \sum_{i=1}^n \mu_i N_i \\
 \text{Gibbs energy:} \quad G(T, -p, \mathbf{n}) &= U - TS + pV && \hat{=} \sum_{i=1}^n \mu_i N_i
 \end{aligned}$$

two Massieu functions dedicated isolated and open stationary systems respectively (the functions have no special symbols);

$$\begin{aligned}
 S(U, V, \mathbf{n}) &= T^{-1}U + T^{-1}pV - T^{-1}\sum_{i=1}^n \mu_i N_i \\
 S(H, -p, \mathbf{n}) &= T^{-1}H - T^{-1}\sum_{i=1}^n \mu_i N_i
 \end{aligned}$$

some extra definitions with roots in physical chemistry;

$$\begin{aligned}
 \text{Temperature:} \quad T &= \left(\frac{\partial U}{\partial S}\right)_{V, \mathbf{n}} \hat{=} \left(\frac{\partial H}{\partial S}\right)_{p, \mathbf{n}} \hat{=} \dots \\
 \text{Pressure:} \quad -p &= \left(\frac{\partial U}{\partial V}\right)_{S, \mathbf{n}} \hat{=} \left(\frac{\partial A}{\partial V}\right)_{T, \mathbf{n}} \hat{=} \dots \\
 \text{Chemical potential:} \quad \mu_i &= \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_{j \neq i}} \hat{=} \left(\frac{\partial A}{\partial N_i}\right)_{T, V, N_{j \neq i}} \hat{=} \dots
 \end{aligned}$$

$$\text{Heat capacity:} \quad C_V = T \left(\frac{\partial S}{\partial T}\right)_{V, \mathbf{n}} \hat{=} \left(\frac{\partial U}{\partial T}\right)_{V, \mathbf{n}}$$

$$\text{Heat capacity:} \quad C_P = T \left(\frac{\partial S}{\partial T}\right)_{p, \mathbf{n}} \hat{=} \left(\frac{\partial H}{\partial T}\right)_{p, \mathbf{n}}$$

$$\text{Isothermal expansivity:} \quad \alpha \hat{=} V^{-1} \left(\frac{\partial V}{\partial T}\right)_{p, \mathbf{n}} = v^{-1} \left(\frac{\partial v}{\partial T}\right)_{p, \mathbf{n}}$$

$$\text{Isobaric compressibility:} \quad -\beta \hat{=} V^{-1} \left(\frac{\partial V}{\partial p}\right)_{T, \mathbf{n}} = v^{-1} \left(\frac{\partial v}{\partial p}\right)_{T, \mathbf{n}}$$

$$\begin{aligned}
 \text{Maxwell relations:} \quad \frac{\partial^2 F}{\partial X_i \partial X_j} &= \frac{\partial^2 F}{\partial X_j \partial X_i} \stackrel{\text{e.g.}}{\Rightarrow} \left(\frac{\partial^2 U}{\partial S \partial V}\right)_{\mathbf{n}} = \left(\frac{\partial^2 U}{\partial V \partial S}\right)_{\mathbf{n}} \\
 &\stackrel{\text{def}}{\Rightarrow} -\left(\frac{\partial p}{\partial S}\right)_{V, \mathbf{n}} = \left(\frac{\partial T}{\partial V}\right)_{S, \mathbf{n}}
 \end{aligned}$$

$$\begin{aligned}
 \text{Partial molarity:} \quad \bar{f}_i &= \left(\frac{\partial F}{\partial N_i}\right)_{T, p, N_{j \neq i}} \stackrel{\text{e.g.}}{\Rightarrow} \bar{g}_i = \mu_i \\
 &\Rightarrow \mu_i = \bar{h}_i - T \bar{s}_i
 \end{aligned}$$



a diagram illustrating the connections (Figure 4.1); and finally a table of all

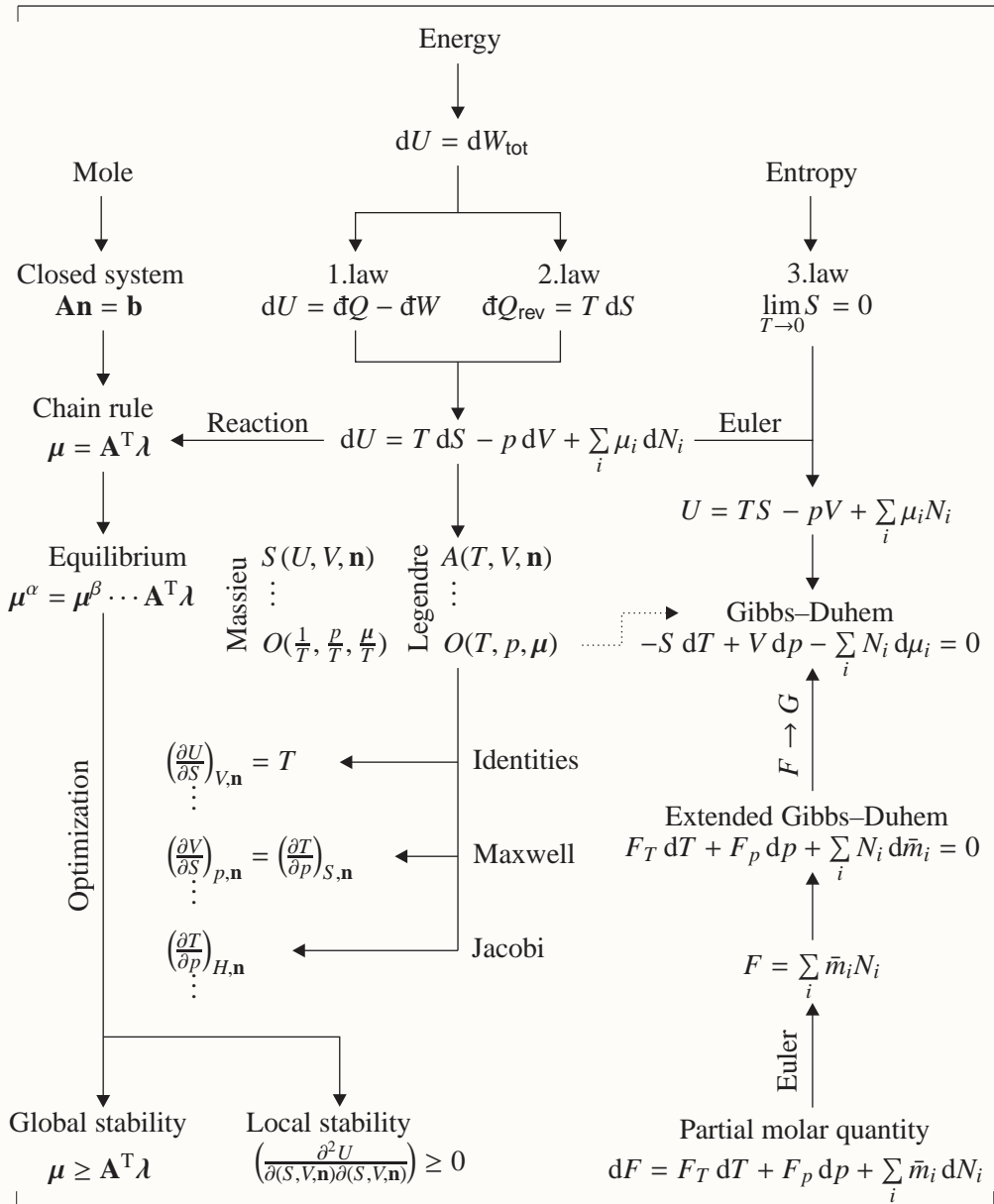


FIGURE 4.1 Formal relationships in thermodynamics

Legendre transforms of internal energy for a single component system (summarises much of what has already been stated):

Symbol	Variables	Derivatives	Euler form	Legendre form
$U$	$S, V, N$	$\tau, \pi, \mu$	$\tau S + \pi V + \mu N$	$U$
$A$	$\tau, V, N$	$-S, \pi, \mu$	$\pi V + \mu N$	$U - \tau S$
$H$	$S, \pi, N$	$\tau, -V, \mu$	$\tau S + \mu N$	$U - \pi V$
$X$	$S, V, \mu$	$\tau, \pi, -N$	$\tau S + \pi V$	$U - \mu N$
$G$	$\tau, \pi, N$	$-S, -V, \mu$	$\mu N$	$U - \tau S - \pi V$
$\Omega$	$\tau, V, \mu$	$-S, \pi, -N$	$\pi V$	$U - \tau S - \mu N$
$Y$	$S, \pi, \mu$	$\tau, -V, -N$	$\tau S$	$U - \pi V - \mu N$
$O$	$\tau, \pi, \mu$	$-S, -V, -N$		$U - \tau S - \pi V - \mu N$

## CHAPTER 5

**Thermofluids**

The theory of continuum mechanics is critical for the understanding of transport phenomena and rheology of macroscopic material phases, which is one reason the topic has established itself as an important research area. Limiting the scope to “thermofluids” makes the scenery smaller, but it is still too wide for a book dedicated applied thermodynamics. We shall therefore narrow the focus even further and study primarily the *laminar flow of compressible single phases with or without chemical reactions*<sup>a</sup>, and in particular we shall do so using Euler control volumes and *macroscopic* theory only. Even this limited scope includes complex topics like momentum and energy balances, mass and heat diffusion, reaction kinetics, viscous stresses, equation of states, thermodynamic equilibrium and entropy production. The total picture is indeed very complicated, but the system behaviour should still agree with thermodynamic equilibrium theory if, or when, the fluid has come to a rest. It is therefore assumed that the static state is fully described by the density fields

Internal energy	$u$
Extents of reaction	$r_i$
Reaction invariants	$c_i$

and a thermodynamic equation of state  $s(u, n_1, n_2, \dots)$  capable of describing the (frozen kinetics) equilibrium manifold

$$s(u, r_1, r_2, \dots, c_1, c_2, \dots) = \max_{\mathbf{r}, \mathbf{c}} [s(u, n_1, n_2, \dots)]$$

where  $\mathbf{r}$  and  $\mathbf{c}$  are vectorised mass relations of  $n_1, n_2, \dots$ <sup>b</sup>. From basic thermodynamic theory the equilibrium value of  $s$  must fulfil  $u = \tau s + \pi + \sum_i \mu_i n_i$ , see also Eq. 5.1 below. The potential strengths  $\tau$ ,  $\pi$  and  $\mu_i$  are defined elsewhere in Chapter 2 on page 8,

Temperature	$\tau \hat{=} \left(\frac{\partial U}{\partial S}\right)_{V, N_1, N_2, \dots}$
Negative pressure	$\pi \hat{=} \left(\frac{\partial U}{\partial V}\right)_{S, N_1, N_2, \dots}$
Chemical potentials	$\mu_i \hat{=} \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_{j \neq i}}$

where  $U = Vu$ ,  $S = Vs$  and  $N_i = Vn_i$  and subscript  $i$  indicates a component specific mixture property. Thus,  $\mu_i$  and  $n_i$  denote the chemical potential and the

<sup>a</sup> No external force fields so far. <sup>b</sup>  $n_i = c_i$  if there are no chemical equilibrium reactions in the system.

composition of component  $i \in [1, N]$  in the mixture. More fundamental to the theoretical development are the homogeneous properties of thermodynamic energy functions. E.g. internal energy  $U$  is a homogeneous function in terms of  $S, V, N_i$  and Euler's theorem of integration applies to the free variables as shown in Chapter 3. The volumetric energy (same as energy density) becomes

$$(5.1) \quad u = \tau s + \pi + \sum_i \mu_i n_i$$

Taking the differential  $du = d(V^{-1}U) = V^{-1}(dU - u dV)$  and inserting the total differential  $dU = \tau dS + \pi dV + \sum_i \mu_i dN_i$ , makes the pressure term vanish:

$$(5.2) \quad du = \tau ds + \sum_i \mu_i dn_i$$

This equation shall later be used to calculate an entropy balance for the system, see Section 3.5 on page 44. Homogeneity also means that the Gibbs–Duhem equation  $s d\tau + d\pi + \sum_i n_i d\mu_i = 0$  must hold both in time and space coordinates, see also Chapter 3, page 22. This is really a bold statement because *simple* thermodynamic systems cannot depend explicitly on time or spatial position. Thus, if there is any reason to suspect the validity of the Gibbs–Duhem equation the whole thermodynamic fundament of this chapter must be reconsidered. For an infinitesimal Euler control volume it must in particular hold that

$$(5.3) \quad \begin{aligned} s \frac{\partial \tau}{\partial t} + \frac{\partial \pi}{\partial t} + \sum_i n_i \frac{\partial \mu_i}{\partial t} &= 0 \\ s \nabla \tau + \nabla \pi + \sum_i n_i \nabla \mu_i &= \mathbf{0} \end{aligned}$$

where  $\nabla$  is the spatial gradient operator. Secondly, it is assumed that the dynamic state can be fully described by the stress–strain relation

$$\mathbf{P} = \mathbf{\Pi}[\text{grad}(\mathbf{v}), \text{grad}(\widetilde{\mathbf{v}})] - \pi(u, c_1, c_2, \dots) \mathbf{I}$$

from which it follows that  $\mathbf{P} = -\pi \mathbf{I}$  in the absence of velocity gradients. The only explicit coupling with the thermodynamic equilibrium state is therefore due to  $\pi$ . Note also that the mass average velocity  $\mathbf{v}$  defined in  $\rho \mathbf{v} \hat{=} \sum_i \rho_i \mathbf{v}_i$  with  $\rho_i \hat{=} w_i n_i$  is considered to be a sufficient variable for the stress–strain relation, and that the presence of molecular diffusion shall not complicate this picture.

The fields are functions of both time and spatial position, i.e.  $\varphi(t, \mathbf{x})$ , but at a given instant of time their values are spatially fixed. It is then permissible to study *virtual displacements* of heat and matter independent of what physical processes take place in the time domain. This abstraction shall prove invaluable in merging the thermodynamic state description with fluid mechanics theory. But, first it must be appreciated that, although thermodynamics has a plethora of amenable variables, it suffices to discuss the canonical variable

sets only. In this context “canonical” means that the Legendre transform

$$\mathcal{L}_x f(x, y, \dots) \rightsquigarrow g(f_x, y, \dots) \hat{=} f - f_x x$$

quite naturally defines a new variable  $f_x \hat{=} (\partial f / \partial x)_{y, \dots}$  which replaces  $x$  in the original variable list. In the case just mentioned  $f$  has canonical variables  $x, y, \dots$  while the transform  $g$  has canonical variables  $f_x, y, \dots$ . The two variables  $x$  and  $f_x$  are sometimes referred to as conjugated variables. What is written here would not be of much interest was it not for the fact that the Legendre transform is a reversible operation. Hence, any of the two aforementioned variable sets can be used to express the thermodynamic state, e.g. as  $g(x, y, \dots)$  or  $f(f_x, y, \dots)$ , without deteriorating the system description. E.g. let Gibbs energy be defined by the Legendre transform

$$\mathcal{L}_{S,V} U(S, V, N_1, N_2, \dots) \rightsquigarrow G(\tau, \pi, N_1, N_2, \dots)$$

The transformed variables  $\tau, \pi, N_1, N_2, \dots$  are just as informative as  $S, V, N_1, N_2, \dots$  and it is permissible to write  $dU = U_\tau d\tau + U_\pi d\pi + \sum_i \bar{u}_i dN_i$  where  $U_\tau$  and  $U_\pi$  have obvious meanings and

$$\bar{u}_i \hat{=} \left( \frac{\partial U}{\partial N_i} \right)_{\tau, \pi, N_{j \neq i}}$$

$U$  is in this case a homogeneous function in  $N_1, N_2, \dots$  at fixed temperature and (negative) pressure. Thus, Euler’s theorem of integration<sup>a</sup> applies to the component mole numbers,

$$U = \sum_i N_i \left( \frac{\partial U}{\partial N_i} \right)_{\tau, \pi, N_{j \neq i}} = \sum_i N_i \bar{u}_i$$

or, on a volumetric basis

$$(5.4) \quad u \hat{=} \sum_i \bar{u}_i c_i$$

This equation is quite noteworthy in that it integrates a partial differential equation in one single step, but to do so in a physical situation all the  $\bar{u}_i$  must be known at the outset. Virtual displacement of matter in fixed thermodynamic fields satisfies these conditions and we shall later make extensive use of Eq. 5.4 and similar expressions for  $V, H, G$  and  $S$ .

### 1. Tensor versus matrix notation

The understanding of tensors and their transformation properties is central to the fluid mechanics theory and is a required asset for any text on the subject. Quite unfortunately, however, the convention adopted for tensor indices is in conflict with the same indices used to denote component specific properties in thermodynamics. It is of course conceivable to use one set of indices for the spatial coordinates and another set for the thermodynamic variables, but

<sup>a</sup> The same procedure applies to any other extensive variable like volume, enthalpy, etc.

after giving this idea a second thought it is maybe better to distinguish the two worlds rather than forcing them to look similar. The theory covered in this

**TABLE 5.1** Tensors used in fluid mechanics and some matrix analogues with relevance to thermodynamics texts. Common indices in a tensor product implies summation over that index (the Einstein summing convention).

This text	Tensor	Matrix	Size
$\mathbf{v} \cdot \mathbf{T}$	$T_{ij}v_i$	$\mathbf{v}^T \mathbf{T}$	$j$
$\mathbf{T} \cdot \mathbf{v}$	$T_{ij}v_j$	$\mathbf{T} \mathbf{v}$	$i$
$\mathbf{T} \cdot \mathbf{S}$	$T_{ik}S_{kj}$	$\mathbf{T} \mathbf{S}$	$i \times j$
$\mathbf{T} : \mathbf{S}$	$T_{ij}S_{ij}$	$\text{trace}(\mathbf{T}^T \mathbf{S})$	1
$\text{grad}(a)$	$\nabla_i a$	$\partial a / \partial \mathbf{x}$	$i$
$\text{grad}(\mathbf{v})$	$\nabla_j v_i$	$\partial \mathbf{v} / \partial \mathbf{x}$	$i \times j$
$\text{div}(\mathbf{v})$	$\nabla_i v_i$	$\text{trace}(\partial \mathbf{v} / \partial \mathbf{x})$	1
$\text{div}(\mathbf{T})$	$\nabla_j T_{ij}$	–	$i$
$\text{div}(\text{grad}(a))$	$\nabla_i \nabla_i a$	$\text{trace}(\partial^2 a / \partial \mathbf{x} \partial \mathbf{x})$	1
$\mathbf{v} \star \mathbf{v}$	$v_i v_j$	$\mathbf{v} \mathbf{v}^T$	$i \times j$
$\mathbf{T} + \widetilde{\mathbf{T}}$	$T_{ij} + T_{ji}$	$\mathbf{T} + \mathbf{T}^T$	$i \times j$

chapter therefore benefits from a “tensor light” notation which should be quite obvious to anyone with background in fluid mechanics. However, rather than using del-notation ( $\nabla$ ) to differentiate spatial variables it is suggested to use literal operators (grad, div, etc.) in order to make the distinction between fluid mechanics and thermodynamics even more pronounced. Throughout the text it is also necessary to deal with the abstract vector spaces of thermodynamics but for this purpose matrix notation is better suited. Everything that has to do with tensorial flow and transport of matter in  $\mathbb{R}^3$  will be using  $\cdot$ ,  $:$ ,  $\star$ , div and grad notation, while operations connected to the general vector space  $\mathbb{R}^n$  will be using matrix notation. Pure tensor notation (with Einstein summing convention) does not find much use in this text. A comparison of the different options is included in Table 5.1.

## 2. Reaction invariants

The reaction variables mentioned at the beginning of this chapter provide the opportunity to distinguish between the (fast) equilibrium reactions on one side, and the (slow) kinetic reactions and (true) reaction invariants on the other side. This time scale separation is essential to avoid numerical stiffness when the rate of a chemical reaction approaches infinity (equilibrium reaction). Our mathematical remedy in this respect is to transform fast

differential equations into algebraic couplings. Here it means that the equation of state  $s(u, n_1, n_2, \dots)$  must be transformed into an equilibrium manifold  $s(u, r_1, r_2, \dots, c_1, c_2, \dots)$ . Rather than including source terms for each mole variable  $N_1, N_2, \dots$  that takes part in a chemical reaction, it can be put up closed algebraic formulae for  $N_1, N_2, \dots$  in terms of  $R_1, R_2, \dots, C_1, C_2, \dots$ . Thus, it is sufficient to track the extents of kinetic reactions, and the reaction invariants, rather than keeping an eye on every single species in the mixture. Let us continue by writing the mass conservation of a closed system (fixed  $C_1, C_2, \dots$ ) using reaction stoichiometry notation:

$$(\mathbf{dn})_c = \begin{pmatrix} \mathbf{Q}_e & \mathbf{Q}_r \end{pmatrix} \begin{pmatrix} \mathbf{de} \\ \mathbf{dr} \end{pmatrix} \hat{=} \mathbf{dn}_e + \mathbf{dn}_r$$

Here  $\mathbf{n} = (n_1, n_2, \dots) \hat{=} V^{-1}(N_1, N_2, \dots)$  are the molar densities of the thermodynamic model,  $\mathbf{e}$  and  $\mathbf{r}$  are the extents of equilibrium and kinetic reactions, and  $\mathbf{c}$  are the densities of reaction invariants. The vector dimensions are such that  $\dim(\mathbf{n}) \geq \dim(\mathbf{r}) + \dim(\mathbf{c})$ . The stoichiometry matrices  $\mathbf{Q}_e$  and  $\mathbf{Q}_r$  are orthogonal representations of the equilibrium reactions and the kinetic reactions respectively. The reaction stoichiometry can be expanded into a full orthogonal basis  $[\mathbf{Q}_e \mathbf{Q}_r \mathbf{Q}_c]$  where  $\mathbf{Q}_c \hat{=} \text{null}[\mathbf{Q}_e \mathbf{Q}_r]^T$ . From this it follows that  $[\mathbf{Q}_r \mathbf{Q}_c]^T \mathbf{de} = \mathbf{0}$  and furthermore that  $\mathbf{c} \hat{=} \mathbf{Q}_c^T \mathbf{n}$  and  $\mathbf{r} \hat{=} \mathbf{Q}_r^T \mathbf{n}$  are conserved quantities for the equilibrium reactions. Of interest to our thermodynamic approach is that energy, volume and mass can be handled in a uniform way:

$$\mathbf{Q}^T \mathbf{y} = \mathbf{x}$$

where

$$\mathbf{Q}^T = \begin{pmatrix} 1 & 0 & \mathbf{0} \\ 0 & 1 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{Q}_r^T \\ \mathbf{0} & \mathbf{0} & \mathbf{Q}_c^T \end{pmatrix}; \quad \mathbf{x} = V \begin{pmatrix} u \\ 1 \\ \mathbf{r} \\ \mathbf{c} \end{pmatrix}; \quad \mathbf{y} = V \begin{pmatrix} u \\ 1 \\ \mathbf{n} \end{pmatrix}$$

In a simulation context  $\mathbf{x}$  holds the variables controlled by the flow solver, while  $\mathbf{y}$  holds the variables controlled by the thermodynamic equilibrium package. The key to success lies in merging these two variables seamlessly. From a thermodynamic point  $\mathbf{y}$  is the canonical variable set of entropy. Euler integration over the control volume, at fixed field strengths, yields

$$S = \tau^{-1}(U - \pi V - \boldsymbol{\mu}^T \mathbf{n}) = \mathbf{g}_y^T \mathbf{y}$$

where  $\mathbf{g}_y$  is the gradient function of  $S$ :

$$\mathbf{g}_y = \frac{\partial S}{\partial \mathbf{y}} = \tau^{-1} \begin{pmatrix} 1 \\ -\pi \\ -\boldsymbol{\mu} \end{pmatrix}$$

Provided there is a significant time scale separation between the fast reactions on one side and the kinetic reactions on the other side, it is meaningful to calculate the equilibrium condition from Lagrange multiplier theory<sup>a</sup>:

$$\mathbf{g}_y = \mathbf{Q}\mathbf{g}_x \quad \Leftrightarrow \quad \mu = \mathbf{Q}_r\lambda_r + \mathbf{Q}_c\lambda_c$$

The equilibrium potential  $\mu$  is clearly in the column spaces of  $\mathbf{Q}_r$  and  $\mathbf{Q}_c$  so what happened to the column space of  $\mathbf{Q}_e$ ? Pre-multiplications of the rightmost equation by  $\mathbf{Q}_e^T$ ,  $\mathbf{Q}_r^T$  and  $\mathbf{Q}_c^T$  reveal the following conditions:

$$(5.5) \quad \begin{aligned} \mathbf{Q}_e^T\mu &= \mathbf{0} \\ \lambda_r &\hat{=} \mathbf{Q}_r^T\mu \rightarrow \mathbf{0} \quad (t \rightarrow \infty) \\ \lambda_c &\hat{=} \mathbf{Q}_c^T\mu \neq \mathbf{0} \end{aligned}$$

From basic optimisation theory it can be decided that the chemical potential vector is orthogonal to the stoichiometry matrix at equilibrium. This is always true for the fast reactions above. It is conditionally true for the slow reactions at infinite reaction time. For the reaction invariants it will never come true except by coincidence. The numerical solution to the equilibrium problem can be found by iterating a Newton–Lagrange<sup>b</sup>  $\mathbf{S}_{yy} = \partial\mathbf{g}_y/\partial\mathbf{y}^T$  is the Hessian matrix of the entropy function  $S(\mathbf{y})$ :

$$(5.6) \quad \begin{pmatrix} \mathbf{S}_{yy} & \mathbf{Q} \\ \mathbf{Q}^T & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{y} \\ -\mathbf{g}_x \end{pmatrix} = \begin{pmatrix} -\mathbf{g}_y \\ \mathbf{x} \end{pmatrix}$$

At this point it is tempting to go for a detailed analysis of the equilibrium problem rather than a plain simultaneous solution. Symbolic inversion yields

$$(5.7) \quad \begin{pmatrix} -\mathbf{g}_x \\ \mathbf{y} \end{pmatrix} = \begin{pmatrix} -\mathbf{S}_{xx} & \mathbf{C}_{12} \\ \mathbf{C}_{12}^T & \mathbf{C}_{22} \end{pmatrix} \begin{pmatrix} \mathbf{x} \\ -\mathbf{g}_y \end{pmatrix}$$

where  $\mathbf{S}_{xx}$  and  $\mathbf{C}_{ij}$  are unknown<sup>c</sup> sub-matrices. To find these,  $\mathbf{Q}$  can be extended into a full orthogonal basis  $[\mathbf{Q}\mathbf{N}]$  where  $\mathbf{N} = \text{null}(\mathbf{Q}^T)$  i.e.  $\mathbf{Q}^T\mathbf{N} = \mathbf{0}$ . Back-substitution into the Newton–Lagrange equations gives the solution<sup>d</sup>

$$\mathbf{C}_{22} = \mathbf{N}(\mathbf{N}^T\mathbf{S}_{yy}\mathbf{N})^{-1}\mathbf{N}^T$$

<sup>a</sup> The nature of Lagrange multipliers is peculiar to thermodynamic theory. E.g.  $\lambda_c$  is interpreted as the chemical potentials of the reaction invariants:  $\mathbf{Q}_c^T\mu = \mathbf{Q}_c^T\mathbf{Q}_r\lambda_r + \mathbf{Q}_c^T\mathbf{Q}_c\lambda_c = \lambda_c$

<sup>b</sup> The knowledgeable reader may insist on using  $\delta\mathbf{y}$  and  $\delta\mathbf{g}_x$  rather than  $\mathbf{y}$  and  $\mathbf{g}_x$  on the left side. But,  $\mathbf{S}_{xx}$  is singular in the direction of  $\mathbf{y}$  which means  $\mathbf{S}_{xx}\delta\mathbf{y} = \mathbf{S}_{xx}\mathbf{y}$ , and because the constraints are linear  $\mathbf{g}_x$  does not show up in the coefficient matrix. The equation system is therefore valid both as an update scheme and a condition for the final solution. <sup>c</sup> Note that the Hessian has one singular direction  $\mathbf{S}_{yy}\mathbf{y} = \mathbf{0}$  caused by the homogeneous nature of  $S(\mathbf{y})$ . Inverting  $\mathbf{S}_{yy}$  directly is therefore not an option. <sup>d</sup> Actually, a few algebraic steps are required here. Back-substitution immediately gives  $\mathbf{I} = \mathbf{S}_{yy}\mathbf{C}_{22} + \mathbf{Q}\mathbf{C}_{12}$ ,  $\mathbf{0} = \mathbf{S}_{yy}\mathbf{C}_{12}^T - \mathbf{Q}\mathbf{S}_{xx}$ ,  $\mathbf{0} = \mathbf{Q}^T\mathbf{C}_{22}$  and  $\mathbf{I} = \mathbf{Q}^T\mathbf{C}_{12}^T$ . From the last two equations it is evident that  $\mathbf{C}_{22} = \mathbf{N}\mathbf{U}$  and  $\mathbf{C}_{12}^T = \mathbf{Q} + \mathbf{N}\mathbf{V}$ . Solving for  $\mathbf{U}$  and  $\mathbf{V}$  using the first two equations is relatively easy leading to the solution listed in the main text.



$$\begin{aligned}\mathbf{C}_{12}^T &= \mathbf{Q} - \mathbf{C}_{22}\mathbf{S}_{yy}\mathbf{Q} \\ \mathbf{S}_{xx} &= \mathbf{Q}^T\mathbf{S}_{yy}\mathbf{C}_{12}^T\end{aligned}$$

The true benefits of using a second order Newton–Lagrange scheme are more visible then it comes to perturbation analysis. Let  $\alpha \geq 0$  be a distance parameter along the curve  $\mathbf{x}(\alpha) \in \mathbb{R}^{N+2}$ :

$$\begin{aligned}\mathbf{x}(\alpha) &= \mathbf{x} + \alpha \frac{\partial \mathbf{x}}{\partial \alpha} + \frac{1}{2}\alpha^2 \frac{\partial^2 \mathbf{x}}{\partial \alpha^2} + \dots \\ &\triangleq \sum_{k=0} \frac{\alpha^k}{k!} \partial_\alpha^k \mathbf{x}\end{aligned}$$

The compact notation  $\partial_\alpha^k$  is not essential but it makes the forthcoming text less verbose. More important is that each point on the curve represents a unique equilibrium state, and that the solution vectors  $\mathbf{y}(\alpha)$  and  $\mathbf{g}_x(\alpha)$  are functions of  $\alpha$ . However, because Eq. 5.6 on the facing page is generally valid the parameter form of the equilibrium equations can be written without much pondering:

$$\begin{pmatrix} \mathbf{S}_{yy}(\alpha) & \mathbf{Q} \\ \mathbf{Q}^T & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{y}(\alpha) \\ -\mathbf{g}_x(\alpha) \end{pmatrix} = \begin{pmatrix} -\mathbf{g}_y(\alpha) \\ \mathbf{x}(\alpha) \end{pmatrix}$$

Quite unexpectedly this problem has an analytic solution. The secret is that  $\mathbf{S}_{yy}(\alpha)\mathbf{y}(\alpha) = \mathbf{S}_{yy}\mathbf{y}$  due to the homogeneous properties of  $S^a$ . The only complication that remains is  $\mathbf{g}_y(\alpha)$ . By introducing the expansion

$$\begin{aligned}\mathbf{g}_y(\alpha) &= \mathbf{g}_y + \alpha \partial_\alpha^1 \mathbf{g}_y + \frac{1}{2}\alpha^2 \partial_\alpha^2 \mathbf{g}_y + \dots \\ &= \mathbf{g}_y + \alpha \mathbf{S}_{yy} \partial_\alpha^1 \mathbf{y} + \frac{1}{2}\alpha^2 [\mathbf{S}_{yyy}(\partial_\alpha^1 \mathbf{y})^2 + \mathbf{S}_{yy}(\partial_\alpha^2 \mathbf{y})] + \dots\end{aligned}$$

it turns out that the path derivatives can be calculated, one at a time, using the same coefficient matrix as in Eq. 5.7!

$$\begin{pmatrix} -\partial_\alpha^k \mathbf{g}_x \\ \partial_\alpha^k \mathbf{y} \end{pmatrix} = \begin{pmatrix} -\mathbf{S}_{xx} & \mathbf{C}_{12} \\ \mathbf{C}_{12}^T & \mathbf{C}_{22} \end{pmatrix} \begin{pmatrix} \partial_\alpha^k \mathbf{x} \\ -\mathbf{f}_k \end{pmatrix}$$

It is assumed that all  $\partial_\alpha^k \mathbf{x}$  are known at the outset. The generating function  $\mathbf{f}_k$  is recursively calculated from the previous  $k - 1$  solutions, and the  $k - 2$ 'th derivative of  $\mathbf{S}_{yy}$ , as shown in Table 5.2. Two special cases are worth mentioning:  $k = 0$  corresponds with the equilibrium calculation in Eq. 5.6, and  $k = 1$  with the first order perturbation of this equilibrium state. Physically, it means that

$$\begin{aligned}\mathbf{g}_x &= \left( \frac{\partial S}{\partial \mathbf{x}} \right)_{\text{eq}} \\ \mathbf{S}_{xx} &= \left( \frac{\partial \mathbf{g}_x}{\partial \mathbf{x}^T} \right)_{\text{eq}} = \left( \frac{\partial^2 S}{\partial \mathbf{x} \partial \mathbf{x}^T} \right)_{\text{eq}}\end{aligned}$$

<sup>a</sup> The expansion reads:  $\mathbf{S}_{yy}(\alpha)\mathbf{y}(\alpha) = \mathbf{S}_{yy}\mathbf{y} + \alpha[\mathbf{S}_{yy}\partial_\alpha^1 \mathbf{y} + \mathbf{S}_{yyy}\mathbf{y}\partial_\alpha^1 \mathbf{y}] + \frac{1}{2}\alpha^2[2\mathbf{S}_{yyy}(\partial_\alpha^1 \mathbf{y})^2 + \mathbf{S}_{yy}(\partial_\alpha^2 \mathbf{y}) + \mathbf{S}_{yyy}\mathbf{y}(\partial_\alpha^1 \mathbf{y})^2 + \mathbf{S}_{yyy}\mathbf{y}(\partial_\alpha^2 \mathbf{y})] + \dots$  By substituting  $\mathbf{S}_{yyy}\mathbf{y} = -\mathbf{S}_{yy}$ ,  $\mathbf{S}_{yyy}\mathbf{y} = -2\mathbf{S}_{yyy}$ , etc. the higher order terms vanish. Hence, the only term that survives the expansion is  $\mathbf{S}_{yy}\mathbf{y}$  (which is also  $\mathbf{0}$  but that is a different story).

**TABLE 5.2** Taylor expansion of equilibrium gradient. The “matrix” products follow no particular convention, but they should nevertheless be quite legitimate.

$k$	$\mathbf{f}_k$
0	$\mathbf{g}_y$
1	$\mathbf{0}$
2	$\mathbf{S}_{yyy}(\partial_\alpha^1 \mathbf{y})^2$
3	$\mathbf{S}_{yyyy}(\partial_\alpha^1 \mathbf{y})^3 + 3\mathbf{S}_{yyy}(\partial_\alpha^1 \mathbf{y})(\partial_\alpha^2 \mathbf{y})$
4	$\mathbf{S}_{yyyyy}(\partial_\alpha^1 \mathbf{y})^4 + 6\mathbf{S}_{yyyy}(\partial_\alpha^1 \mathbf{y})^2(\partial_\alpha^2 \mathbf{y}) + 4\mathbf{S}_{yyy}(\partial_\alpha^1 \mathbf{y})(\partial_\alpha^3 \mathbf{y}) + 3\mathbf{S}_{yyy}(\partial_\alpha^2 \mathbf{y})^2$

Although theoretically correct the matrices above are not suited for direct calculations. Virtually all equations of (fluid) state use  $T, V, N_i$  as free variables, and there are simply no viable alternatives for the  $U, V, N_i$  case! Not unexpected the Legendre transform is the cure of this illness, as many others, and listed below are examples on (congruent) transformations of the Hessian of  $A$  into the Hessians of  $U$  and  $G$ :

$$\mathbf{U}_{S_{VN}, S_{VN}} = \mathbf{C} \begin{pmatrix} -\mathbf{A}_{\tau, \tau}^{-1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}_{V, V} & \mathbf{A}_{V, N} \\ \mathbf{0} & \mathbf{A}_{N, V} & \mathbf{A}_{N, N} \end{pmatrix} \mathbf{C}^T, \quad \mathbf{C} \triangleq \begin{pmatrix} 1 & \mathbf{0} & \mathbf{0} \\ \mathbf{A}_{V, \tau} & 1 & \mathbf{0} \\ \mathbf{A}_{N, \tau} & \mathbf{0} & \mathbf{I} \end{pmatrix}$$

$$\mathbf{G}_{\tau \pi N, \tau \pi N} = \mathbf{C} \begin{pmatrix} \mathbf{A}_{\tau, \tau} & \mathbf{0} & \mathbf{A}_{\tau, N} \\ \mathbf{0} & -\mathbf{A}_{V, V}^{-1} & \mathbf{0} \\ \mathbf{A}_{N, \tau} & \mathbf{0} & \mathbf{A}_{N, N} \end{pmatrix} \mathbf{C}^T, \quad \mathbf{C} \triangleq \begin{pmatrix} 1 & -\mathbf{A}_{\tau, V} & \mathbf{0} \\ \mathbf{0} & 1 & \mathbf{0} \\ \mathbf{0} & -\mathbf{A}_{N, V} & \mathbf{I} \end{pmatrix}$$

The Hessian of  $G$  is needed because  $-\bar{\mathbf{s}} \triangleq G_{N, \tau}$  and  $-\bar{\mathbf{v}} \triangleq G_{N, \pi}$  find some use throughout this text. The Hessian of  $U$  is an intermediate result needed to calculate the Hessian of  $S$  (implicit differentiation):

$$\tau^3 \mathbf{S}_{U_{VN}, U_{VN}} = \mathbf{C} \mathbf{U}_{S_{VN}, S_{VN}} \mathbf{C}^T, \quad \mathbf{C} \triangleq \begin{pmatrix} 1 & \mathbf{0} & \mathbf{0} \\ -\pi & \tau & \mathbf{0} \\ -\mu & \mathbf{0} & \tau \mathbf{I} \end{pmatrix}$$

### 3. Conservation laws

The conservations of mass, energy and momentum are central to fluid mechanics and shall therefore be outlined in some detail. However, our approach shall be quite naive and based on macroscopic thermodynamic principles rather than a concise microscopic kinetic theory. Let  $\Phi$  be an integral property of the control volume  $\mathcal{V}$ , and  $\varphi$  the corresponding density which is supposed to vary throughout  $\mathcal{V}$ . Now, if  $\mathcal{V}$  is an Euler control volume, the total differential of  $\Phi$  is

$$d\Phi = d \int_{\mathcal{V}} \varphi dV = dt \int_{\mathcal{V}} \frac{\partial \varphi}{\partial t} dV$$

because the integration limits are fixed in time. The convective flux of  $\Phi$  through the control surface  $\mathcal{A}$  at a given instance of time is

$$\int_{\mathcal{A}} \varphi(\mathbf{v} \cdot \mathbf{u}) \, dA = \int_{\mathcal{V}} \operatorname{div}(\varphi \mathbf{v}) \, dV$$

where  $\mathbf{u}$  is an outward unit vector normal to the surface element  $dA$ , and  $\mathbf{v}$  is the local velocity at which  $\varphi$  is being transported (an application of Gauss's divergence theorem has taken place from left to right). If  $\Phi$  is a conserved property then  $d\Phi / dt$  must balance the flux through the control surface,

$$\int_{\mathcal{V}} \frac{\partial \varphi}{\partial t} \, dV + \int_{\mathcal{V}} \operatorname{div}(\varphi \mathbf{v}) \, dV = 0$$

or, because the integration domain is arbitrary

$$(5.8) \quad \frac{\partial \varphi}{\partial t} = -\operatorname{div}(\varphi \mathbf{v})$$

All this may seem trivial but getting the flux expressions right can be quite tricky. Let us start the discussion by studying the transport of thermodynamic quantities. E.g. the flux of internal energy is  $\bar{u}_i n_i \mathbf{v}_i$  for each component being present in the system. The physical argument was carried out in connection with Eq. 5.4 on page 33 and it will here be taken for granted that Euler integration of the energy density is possible. The introduction of molecular diffusion  $n_i \mathbf{v}_i \hat{=} \mathbf{j}_i + n_i \mathbf{v}$  gives rise to

$$(5.9) \quad \begin{aligned} \sum_i \bar{u}_i n_i \mathbf{v}_i &= \sum_i \bar{u}_i \mathbf{j}_i + \mathbf{v} \sum_i \bar{u}_i n_i \\ &\hat{=} \mathbf{j}_u + u \mathbf{v} \end{aligned}$$

The flux is seen to consist of one convective term  $u \mathbf{v}$  and an (optional) molecular diffusion term  $\mathbf{j}_u$ <sup>a</sup>. Expressions similar to the one above hold for all densities of thermodynamic origin:

$$(5.10) \quad \sum_i \bar{v}_i n_i \mathbf{v}_i = \sum_i \bar{v}_i \mathbf{j}_i + 1 \mathbf{v} \hat{=} \mathbf{j}_v + 1 \mathbf{v}$$

$$(5.11) \quad \sum_i \bar{s}_i n_i \mathbf{v}_i = \sum_i \bar{s}_i \mathbf{j}_i + s \mathbf{v} \hat{=} \mathbf{j}_s + s \mathbf{v}$$

$$(5.12) \quad \sum_i \bar{h}_i n_i \mathbf{v}_i = \sum_i \bar{h}_i \mathbf{j}_i + h \mathbf{v} \hat{=} \mathbf{j}_h + h \mathbf{v}$$

$$(5.13) \quad \sum_i \bar{g}_i n_i \mathbf{v}_i = \sum_i \bar{g}_i \mathbf{j}_i + g \mathbf{v} \hat{=} \mathbf{j}_g + g \mathbf{v}$$

Note that  $1 \mathbf{v}$  is deliberately used in the first equation to emphasise that this line is not misprinted—the volume density is really unity everywhere in the control volume! In the last equation  $\mu_i$  can be substituted for  $\bar{g}_i$ . This redundancy is caused by a clash of two independent definitions and is quite inevitable from a thermodynamic standpoint.

<sup>a</sup> We shall later learn that similar diffusion terms are ignored for both the momentum and the kinetic energy fluxes.

**3.1. Mass.** Let  $R_{i \in [1, R]}$  and  $C_{i \in [1, C]}$  define the extents of kinetic reactions and the moles of reaction invariants as explained in Section 2. It is important to realise that all  $C_i$  are conserved independently of any reactions in the control volume, while  $R_i$  are conserved only for infinitesimally small time lapses i.e. for frozen kinetics only. This knowledge is sufficient for putting up a mass balance, but there is one complicating factor:  $C_i$  and  $R_i$  refer to *virtual* components which are not useful for defining e.g. molecular diffusion fluxes. It is therefore necessary to formulate the mass balance in terms of the model variables  $N_i$  which are physically present in the mixture. From identifying the molar density  $n_i \hat{=} V^{-1}N_i$  as the state property  $\varphi$  in Eq. 5.8 it follows that

$$\frac{\partial n_i}{\partial t} = -\operatorname{div}(n_i \mathbf{v}_i) + [\mathbf{Q}_c \frac{\partial \mathbf{e}}{\partial t}]_i + [\mathbf{Q}_r \dot{\mathbf{r}}]_i \quad i \in [1, N]$$

Note that  $\frac{\partial \mathbf{e}}{\partial t}$  and  $\dot{\mathbf{r}}$  represent two different modes<sup>a</sup> of time changes—the first is a differential change in the extents of equilibrium reactions, while the other is the rate at which the extents of kinetic reactions will change. Next, let the mass average velocity be defined by  $\rho \mathbf{v} \hat{=} \sum_i \rho_i \mathbf{v}_i$  and the molar diffusion flux<sup>b</sup> relative to the mass centre by  $n_i \mathbf{v}_i \hat{=} \mathbf{j}_i + n_i \mathbf{v}$ . The divergence term can then be written

$$\operatorname{div}(n_i \mathbf{v}_i) = \operatorname{div}(\mathbf{j}_i) + \operatorname{grad}(n_i) \cdot \mathbf{v}_i + n_i \operatorname{div}(\mathbf{v}_i)$$

At this point it is favourable to collect all the  $i \in [1, N]$  mass balances into one matrix equation:

$$(5.14) \quad \frac{\partial \mathbf{n}}{\partial t} = -\operatorname{div}(\mathbf{J}) - \operatorname{grad}(\mathbf{n}) \cdot \mathbf{v} - \mathbf{n} \operatorname{div}(\mathbf{v}) + \mathbf{Q}_c \frac{\partial \mathbf{e}}{\partial t} + \mathbf{Q}_r \dot{\mathbf{r}}$$

Pre-multiplication of Eq. 5.14 with  $[\mathbf{Q}_r \mathbf{Q}_c]^T$  reveals<sup>c</sup> the mass balance in its final form:

$$\frac{\partial \begin{pmatrix} \mathbf{r} \\ \mathbf{c} \end{pmatrix}}{\partial t} = -\operatorname{div} \begin{pmatrix} \mathbf{J}_r \\ \mathbf{J}_c \end{pmatrix} - \operatorname{grad} \begin{pmatrix} \mathbf{r} \\ \mathbf{c} \end{pmatrix} \cdot \mathbf{v} - \begin{pmatrix} \mathbf{r} \\ \mathbf{c} \end{pmatrix} \operatorname{div}(\mathbf{v}) + \begin{pmatrix} \dot{\mathbf{r}} \\ \mathbf{0} \end{pmatrix}$$

The mole numbers  $C_i$  of the reaction invariants are conserved in the reactions (slow and fast), and so must the accompanying masses be. Mathematically this implies that the vector of molecular weights  $\mathbf{w}$  (of each species  $N_i$ ) has to be in the column space of  $\mathbf{Q}_c$ . Pre-multiplication of Eq. 5.14 with  $\mathbf{w}^T$  therefore yields<sup>d</sup> the total mass balance of the system:

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\operatorname{grad}(\rho) \cdot \mathbf{v} - \rho \operatorname{div}(\mathbf{v}) \\ &= -\operatorname{div}(\rho \mathbf{v}) \end{aligned}$$

<sup>a</sup> That is to say  $\mathbf{e}$  is a state variable while  $\mathbf{r}$  is not. <sup>b</sup> When combined with  $\rho_i \hat{=} w_i n_i$  these definitions imply that  $\sum_i w_i \mathbf{j}_i = \mathbf{0}$ . <sup>c</sup>  $\mathbf{J}_r \hat{=} \mathbf{Q}_r^T \mathbf{J}$ ,  $\mathbf{J}_c \hat{=} \mathbf{Q}_c^T \mathbf{J}$ ,  $\mathbf{Q}_r^T \mathbf{Q}_c = \mathbf{0}$ ,  $\mathbf{Q}_c^T \mathbf{Q}_r = \mathbf{0}$ ,  $\mathbf{Q}_r^T \mathbf{Q}_r = \mathbf{I}$ ,  $\mathbf{Q}_c^T \mathbf{n} \hat{=} \mathbf{r}$  and  $\mathbf{Q}_c^T \mathbf{c} \hat{=} \mathbf{c}$ . <sup>d</sup>  $\mathbf{w}^T \mathbf{n} = \rho$ ,  $\mathbf{w}^T \mathbf{Q}_c \propto \mathbf{Q}_c^T \mathbf{Q}_c = \mathbf{0}$  and  $\mathbf{w}^T \mathbf{Q}_r \propto \mathbf{Q}_c^T \mathbf{Q}_r = \mathbf{0}$ .

Yet another inner product, prepared exclusively for the entropy balance in Section 3.5, is:

$$\begin{aligned}
 \boldsymbol{\mu}^T \frac{\partial \mathbf{n}}{\partial t} &\hat{=} \sum_i \mu_i \frac{\partial n_i}{\partial t} = - \sum_i \mu_i \operatorname{div}(\mathbf{j}_i) - \sum_i \mu_i \operatorname{div}(n_i \mathbf{v}) + \boldsymbol{\mu}^T \mathbf{Q}_e \frac{\partial e}{\partial t} + \boldsymbol{\mu}^T \mathbf{Q}_r \dot{\mathbf{r}} \\
 (5.15) \qquad \qquad \qquad &= - \sum_i \mu_i \operatorname{div}(\mathbf{j}_i + n_i \mathbf{v}) + \boldsymbol{\lambda}_r^T \dot{\mathbf{r}}
 \end{aligned}$$

The chemical equilibrium conditions from Eq. 5.5 have been substituted in line two of this equation, and there is a slightly unusual mix of summations and matrix multiplications to have the equation fit better into its future context.

**3.2. Momentum.** The momentum density  $\sum_i n_i w_i \mathbf{v}_i$  is a tensorial property conserved (element-wise) in each spatial direction. Substitution of the diffusion flux  $n_i \mathbf{v}_i \hat{=} \mathbf{j}_i + n_i \mathbf{v}$  where  $\sum_i w_i \mathbf{j}_i = \mathbf{0}$  and  $\rho \hat{=} \sum_i n_i w_i$  yields:

$$\sum_i n_i w_i \mathbf{v}_i \hat{=} \sum_i (w_i \mathbf{j}_i + w_i n_i \mathbf{v}) \hat{=} \rho \mathbf{v}$$

Clearly, molecular diffusion has no influence on the momentum density<sup>a</sup>, but as shown below this will not be the case for the momentum flux. The momentum flux associated with the transport of component  $i$  in the  $x$ -direction is  $w_i n_i v_{x,i} \mathbf{v}_i$ , and considering all directions simultaneously the flux expression becomes  $w_i n_i (\mathbf{v}_i \star \mathbf{v}_i)$ . From the definitions above the total momentum flux can be written

$$\begin{aligned}
 \sum_i w_i n_i (\mathbf{v}_i \star \mathbf{v}_i) &\hat{=} \sum_i w_i n_i^{-1} (\mathbf{j}_i + n_i \mathbf{v}) \star (\mathbf{j}_i + n_i \mathbf{v}) \\
 &= \sum_i w_i (n_i^{-1} \mathbf{j}_i \star \mathbf{j}_i + \mathbf{j}_i \star \mathbf{v} + \mathbf{v} \star \mathbf{j}_i + n_i \mathbf{v} \star \mathbf{v}) \\
 &\hat{=} \rho [1 + \mathcal{O}(\frac{\varepsilon}{v})] (\mathbf{v} \star \mathbf{v})
 \end{aligned}$$

Neglecting the momentum of diffusion introduces an error  $\sim \frac{\varepsilon}{v} \rho (\mathbf{v} \star \mathbf{v})$ , i.e. something very small unless  $\varepsilon \sim v$ . Thus, for large flow velocities the situation is similar to that discussed more thoroughly in Section 3.3. Next, according to the principle of momentum conservation it can be argued that

$$\int_{\mathcal{V}} \frac{\partial \rho \mathbf{v}}{\partial t} dV = \int_{\mathcal{A}} \sum_i w_i n_i (\mathbf{v}_i \star \mathbf{v}_i \cdot \mathbf{u}) dA + \int_{\mathcal{A}} (\mathbf{P} \cdot \mathbf{u}) dA$$

where  $\mathbf{P}$  is the local stress tensor<sup>b</sup> at a point on the control surface. Substitution of the momentum flux gives

$$\begin{aligned}
 \frac{\partial \rho \mathbf{v}}{\partial t} &\simeq - \operatorname{div}[\rho (\mathbf{v} \star \mathbf{v})] - \operatorname{div}(\mathbf{P}) \\
 &= - \operatorname{div}[\rho (\mathbf{v} \star \mathbf{v})] - \operatorname{div}(\boldsymbol{\Pi}) + \operatorname{grad}(\pi)
 \end{aligned}$$

These are the equations of motion for the centre of mass. They also form a sound basis for the conservation of kinetic energy, see Section 3.3.

<sup>a</sup> This is the reason why we are troubled with the *mass average velocity* most of the time.

<sup>b</sup> Force per unit area in six tangential and three normal directions ( $3 \times 3$  tensor).

**3.3. Kinetic energy.** The kinetic energy density is  $\frac{1}{2} \sum_i n_i w_i v_i^2$ . The definitions  $v_i^2 \hat{=} \mathbf{v}_i \cdot \mathbf{v}_i$  and  $n_i \mathbf{v}_i \hat{=} \mathbf{j}_i + n_i \mathbf{v}$  lead to

$$n_i v_i^2 = n_i (\mathbf{v}_i \cdot \mathbf{v}_i) = n_i^{-1} (\mathbf{j}_i + n_i \mathbf{v}) \cdot (\mathbf{j}_i + n_i \mathbf{v})$$

Further algebraic manipulation yields

$$\begin{aligned} n_i v_i^2 &= n_i^{-1} (\mathbf{j}_i + 2n_i \mathbf{v}) \cdot \mathbf{j}_i + n_i (\mathbf{v} \cdot \mathbf{v}) \\ &= (\mathbf{v}_i + \mathbf{v}) \cdot \mathbf{j}_i + n_i (\mathbf{v} \cdot \mathbf{v}) \\ &= \mathbf{j}_i \cdot \mathbf{v}_i + \mathbf{j}_i \cdot \mathbf{v} + n_i (\mathbf{v} \cdot \mathbf{v}) \end{aligned}$$

The total kinetic energy summed over all components (considering that  $\sum_i w_i \mathbf{j}_i = \mathbf{0}$  and  $\sum_i n_i w_i = \rho$  and  $\mathbf{v} \cdot \mathbf{v} = v^2$ ) is

$$\begin{aligned} \sum_i n_i w_i v_i^2 &= \sum_i w_i (\mathbf{j}_i \cdot \mathbf{v}_i) + \mathbf{v} \cdot \sum_i w_i \mathbf{j}_i + \mathbf{v} \cdot \mathbf{v} \sum_i n_i w_i \\ &= \sum_i w_i (\mathbf{j}_i \cdot \mathbf{v}_i) + \rho v^2 \\ &= \rho [1 + O(\frac{\varepsilon}{v})] v^2 \end{aligned}$$

Neglecting the kinetic energy of diffusion introduces an error  $\sim \frac{\varepsilon}{v} \rho v^2$  which is small unless  $\varepsilon \sim v$ . At large flow velocities the kinetic energy density can therefore be written  $e \simeq \frac{1}{2} \rho v^2$ . So far so good, but to find a balance equation<sup>a</sup> for  $e$  it is necessary to go back to the momentum balance in Section 3.2

$$\frac{\partial \rho \mathbf{v}}{\partial t} \simeq -\text{div}[\rho(\mathbf{v} \star \mathbf{v}) + \mathbf{P}]$$

Plain differentiation followed by the elimination of the total mass balance  $\partial \rho / \partial t = -\text{div}(\rho \mathbf{v})$  yields

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \text{grad}(\mathbf{v}) \cdot \mathbf{v} - \text{div}(\mathbf{P})$$

The vector equation above is contracted into a scalar equation by taking the inner product over  $\mathbf{v}$

$$\rho(\mathbf{v} \cdot \frac{\partial \mathbf{v}}{\partial t}) = -\rho[\mathbf{v} \cdot \text{grad}(\mathbf{v})] \cdot \mathbf{v} - \mathbf{v} \cdot \text{div}(\mathbf{P})$$

<sup>a</sup> Although not needed till Chapter 3.4, the kinetic energy flux is  $v_i^2 w_i n_i \mathbf{v}_i$  per component in the system. From the definitions  $v_i^2 n_i \mathbf{v}_i \hat{=} \mathbf{k}_i + v^2 n_i \mathbf{v}$  and  $v_i^2 \hat{=} \mathbf{v}_i \cdot \mathbf{v}_i$  and  $v^2 \hat{=} \mathbf{v} \cdot \mathbf{v}$  the kinetic energy can be summed over all components (note that  $\rho = \sum_i w_i n_i$ ) to obtain

$$\sum_i v_i^2 w_i n_i \mathbf{v}_i = \sum_i w_i \mathbf{k}_i + \mathbf{v} \sum_i v^2 w_i n_i = \sum_i w_i \mathbf{k}_i + \rho v^2 \mathbf{v} = \rho v^2 [1 + O(\frac{\varepsilon}{v})] \mathbf{v}$$

Here,  $\varepsilon$  is defined as a representative diffusion velocity. For large flow velocities we get

$$\lim_{v_i \rightarrow v} \sum_i w_i \mathbf{k}_i = \lim_{v_i \rightarrow v} \sum_i w_i n_i v^2 [(\frac{v_i}{v})^2 \mathbf{v}_i - \mathbf{v}] = v^2 \sum_i w_i \mathbf{j}_i = \mathbf{0}$$

So what is large? It is reasonable to assume that the diffusional velocities  $\mathbf{v}_i - \mathbf{v}$  are of ‘‘chemical’’ nature and quite independent of the flow conditions. Hence,  $v_i - v = \pm \varepsilon$  and  $\mathbf{v}_i - \mathbf{v} = \pm \varepsilon (v^{-1} \mathbf{v})$ . By neglecting the kinetic energy of diffusion we make an error  $\sum_i w_i \mathbf{k}_i = \sum_i n_i w_i v^2 [(\frac{v_i}{v})^2 \mathbf{v}_i - \mathbf{v}] \sim \sum_i n_i w_i v^2 [(1 \pm \frac{\varepsilon}{v})^3 - 1] \mathbf{v} \sim \frac{3\varepsilon}{v} \sum_i n_i w_i v^2 \mathbf{v} \sim \frac{3\varepsilon}{v} \rho v^2 \mathbf{v}$  i.e. something very small compared to  $\rho v^2 \mathbf{v}$  unless  $\varepsilon \sim v$ .

The left term, and the first term on the right side, can be reinterpreted using the product rule of differentiation backward:

$$\frac{\rho}{2} \frac{\partial v^2}{\partial t} = -\frac{\rho}{2} \text{grad}(v^2) \cdot \mathbf{v} - \mathbf{v} \cdot \text{div}(\mathbf{P})$$

Further simplification is possible by doing the same backward operations on the div and grad operators

$$\frac{1}{2} \frac{\partial \rho v^2}{\partial t} - \frac{v^2}{2} \frac{\partial \rho}{\partial t} = -\frac{1}{2} \text{div}(\rho v^2 \mathbf{v}) + \frac{v^2}{2} \text{div}(\rho \mathbf{v}) - \text{div}(\mathbf{P} \cdot \mathbf{v}) + \mathbf{P} : \text{grad}(\mathbf{v})$$

Finally, the mass balance  $\partial \rho / \partial t = -\text{div}(\rho \mathbf{v})$  can be used to simplify the equation to:

$$(5.16) \quad \begin{aligned} \frac{\partial e}{\partial t} &\simeq -\text{div}(e \mathbf{v}) - \text{div}(\mathbf{P} \cdot \mathbf{v}) + \mathbf{P} : \text{grad}(\mathbf{v}) \\ &= -\text{div}(e \mathbf{v}) - \text{div}(\mathbf{\Pi} \cdot \mathbf{v}) + \mathbf{\Pi} : \text{grad}(\mathbf{v}) + \mathbf{v} \cdot \text{grad}(\pi) \end{aligned}$$

**3.4. Total energy.** The total energy of a system is composed of kinetic and internal energy contributions. An approximate expression for the kinetic energy density is known from Section 3.3, while Eq. 5.4 on page 33 is an exact representation of the internal energy density:

$$\int_{\mathcal{V}} \frac{\partial}{\partial t} \sum_i n_i (\bar{u}_i + \frac{1}{2} w_i v_i^2) dV \simeq \int_{\mathcal{V}} \frac{\partial(u+e)}{\partial t} dV$$

There is also an (approximate) expression for the convective flux of kinetic energy, see footnote on Page 42, the flux of internal energy (Eq. 5.9) and the volume flux due to the transport of matter (Eq. 5.10). In addition the First Law of thermodynamics states that

$$(dU)_{V,C_1,C_2,\dots} = \delta Q + \delta W$$

where  $\delta Q$  is the heat and  $\delta W$  is mechanical work *added to* the system. In our case  $\delta W$  can be interpreted as the viscous strain (rate) work done at the control surface. Next, it must be assumed that both heat and viscous work can be added to the control volume independent of virtual displacements of matter. If this argument holds<sup>a</sup> it is correct to add a heat flux  $\mathbf{q}$  and a flux of viscous

<sup>a</sup> This is not trivial. In many textbooks there is a so-called total heat flux which incorporates pure conduction (our  $\mathbf{q}$ ) plus all kinds of coupled heat transport (Soret, Dufour, etc.). Secondly, the definition of strain rate work is based on an analogy with elastic deformation work in solid state mechanics. While the latter is something that is quite easily defined for a closed volume, the strain rate work is not because viscous forces depend on velocity gradients inside the body rather than pure elastic strains (and hence the control volume cannot be closed in a thermodynamic sense). It is also worth a moment of reflection why the thermodynamic pressure is let out of the pressure tensor and rather included as a convection term.

work  $\mathbf{\Pi} \cdot \mathbf{v}$  to the balance equation:

$$\begin{aligned} \int_{\mathcal{V}} \frac{\partial(u+e)}{\partial t} dV &= \int_{\mathcal{A}} \sum_i n_i (\bar{u}_i - \pi \bar{v}_i + \frac{1}{2} w_i v_i^2) (\mathbf{v}_i \cdot \mathbf{u}) dA \\ &+ \int_{\mathcal{A}} (\mathbf{\Pi} \cdot \mathbf{v}) (\mathbf{v} \cdot \mathbf{u}) dA \\ &+ \int_{\mathcal{A}} (\mathbf{q} \cdot \mathbf{u}) dA \end{aligned}$$

This equation is on the same form as explained on Page 39, and Gauss's divergence theorem applies to the integrals on the right hand side:

$$\frac{\partial}{\partial t}(u + e) \simeq -\operatorname{div}(u\mathbf{v} - \pi\mathbf{v} + e\mathbf{v}) - \operatorname{div}(\mathbf{j}_u + p\mathbf{j}_v) - \operatorname{div}(\mathbf{\Pi} \cdot \mathbf{v}) - \operatorname{div}(\mathbf{q})$$

A balance equation for the total energy is not very useful because no grand models are available for  $u + e$ . Subtracting the kinetic energy balance in Eq. 5.16, and defining the enthalpy density as  $h = u - \pi$ , leaves something much more tractable:

$$\frac{\partial u}{\partial t} \simeq -\operatorname{div}(h\mathbf{v}) - \operatorname{div}(\mathbf{q} + \mathbf{j}_h) - \mathbf{\Pi} : \operatorname{grad}(\mathbf{v}) - \mathbf{v} \cdot \operatorname{grad}(\pi)$$

**3.5. Entropy.** The entropy density and the corresponding time derivative can easily be calculated once  $u$  and  $n_i$  are known, see Eqs. 5.1 and 5.2 on page 32:

$$\tau \frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \sum_i \mu_i \frac{\partial n_i}{\partial t}$$

The balance equations for internal energy, matter and entropy are

$$\begin{aligned} \frac{\partial u}{\partial t} &\simeq -\operatorname{div}(h\mathbf{v}) - \operatorname{div}(\mathbf{j}_h + \mathbf{q}) - \mathbf{\Pi} : \operatorname{grad}(\mathbf{v}) - \mathbf{v} \cdot \operatorname{grad}(\pi) \\ \frac{\partial n_i}{\partial t} &= -\operatorname{div}(n_i\mathbf{v}) - \operatorname{div}(\mathbf{j}_i) + [\mathbf{Q}_e \frac{\partial \mathbf{e}}{\partial t}]_i + [\mathbf{Q}_r \dot{\mathbf{r}}]_i \\ \frac{\partial s}{\partial t} &\hat{=} -\operatorname{div}(s\mathbf{v}) - \operatorname{div}(\mathbf{j}_s) - \operatorname{div}(\tau^{-1}\mathbf{q}) + \dot{s}_{\text{irr}} \end{aligned}$$

The first equations are explained in Section 3.4 and 3.1, while the last one is new. Its first two terms on the right hand side follow directly from Gauss's divergence theorem applied to the convective entropy flux defined in Eq. 5.11 on page 39. The last two terms, however, are motivated from the Second Law of thermodynamics which states that

$$(dS)_{V,C_1,C_2,\dots} = \frac{\delta Q}{T} + \dot{s}_{\text{irr}}$$

Hence, by defining the heat flow as independent of virtual mass displacements (the control *volume* is fixed), it is correct to add the convective term  $\tau^{-1}\mathbf{q}$  on the right hand side of the balance equation. The next step is to isolate the entropy



production from the equations above<sup>a</sup>. With the aid of Eq. 5.15 we get:

$$\begin{aligned}
 \tau \dot{s}_{\text{irr}} &= -\text{div}(h\mathbf{v}) - \text{div}(\mathbf{q} + \mathbf{j}_h) - \mathbf{\Pi} : \text{grad}(\mathbf{v}) - \mathbf{v} \cdot \text{grad}(\pi) \\
 &\quad + \sum_i \mu_i \text{div}(n_i \mathbf{v} + \mathbf{j}_i) - \lambda_{\text{T}}^{\text{T}} \dot{\mathbf{r}} \\
 (5.17) \quad &\quad + \tau \text{div}(s\mathbf{v} + \mathbf{j}_s + \tau^{-1} \mathbf{q})
 \end{aligned}$$

Further simplification is possible provided the last two lines are reinterpreted adequately<sup>b</sup>. Backward use of the rule of product differentiation makes the chemical potential sum be written

$$\begin{aligned}
 \sum_i \mu_i \text{div}(n_i \mathbf{v} + \mathbf{j}_i) &= \sum_i \text{div}(n_i \mu_i \mathbf{v} + \mu_i \mathbf{j}_i) - \sum_i (n_i \mathbf{v} + \mathbf{j}_i) \cdot \text{grad}(\mu_i) \\
 &\hat{=} \text{div}(g\mathbf{v} + \mathbf{j}_g) - \sum_i (n_i \mathbf{v} + \mathbf{j}_i) \cdot \text{grad}(\mu_i)
 \end{aligned}$$

and similarly for the entropy flux

$$\tau \text{div}(s\mathbf{v} + \mathbf{j}_s + \tau^{-1} \mathbf{q}) = \text{div}(\tau s\mathbf{v} + \tau \mathbf{j}_s + \mathbf{q}) - (s\mathbf{v} + \mathbf{j}_s + \tau^{-1} \mathbf{q}) \cdot \text{grad}(\tau)$$

The last two equations are finally substituted into the expression for  $\tau \dot{s}_{\text{irr}}$ . The result is quite appealing

$$(5.18) \quad \tau \dot{s}_{\text{irr}} = -(\mathbf{j}_s + \tau^{-1} \mathbf{q}) \cdot \text{grad}(\tau) - \sum_i \mathbf{j}_i \cdot \text{grad}(\mu_i) - \mathbf{\Pi} : \text{grad}(\mathbf{v}) - \lambda_{\text{T}}^{\text{T}} \dot{\mathbf{r}}$$

because three terms drop out as a consequence of the definitions of Gibbs energy and partial molar quantities, and the Gibbs–Duhem equation:

$$\begin{aligned}
 \text{div}[(g - h + \tau s)\mathbf{v}] &= 0 \\
 \text{div}(\mathbf{j}_g - \mathbf{j}_h + \tau \mathbf{j}_s) &\hat{=} \text{div}[\sum_i (\mu_i - \bar{h}_i - \tau \bar{s}_i) \mathbf{j}_i] = 0 \\
 \mathbf{v} \cdot [\text{grad}(\pi) + \sum_i n_i \text{grad}(\mu_i) + s \text{grad}(\tau)] &= 0
 \end{aligned}$$

Everything looks fine at this point but there is one serious caveat in Eq. 5.18: The right hand side of the equation is sensitive to changes in the reference velocity of diffusion while  $\tau \dot{s}_{\text{irr}}$  in Eq. 5.17 is not! It is only when  $\mathbf{v}$  is interpreted as the average mass velocity (which has been the case so far) that  $\text{grad}(\pi)$  drops out in Eq. 5.18. To understand this matter clearly we first rewrite<sup>c</sup> the diffusion

<sup>a</sup> The diffusion fluxes are arbitrarily related to the mass average velocity, so what happens to  $\tau \dot{s}_{\text{irr}}$  if another reference velocity is chosen? The answer is “no change” because the diffusion fluxes are paired with convective terms making  $\tau \dot{s}_{\text{irr}}$  insensitive to the reference velocity. E.g. for the entropy flux we can write  $s\mathbf{v} + \mathbf{j}_s \hat{=} \sum_i \bar{s}_i (n_i \mathbf{v} + \mathbf{j}_i) \hat{=} \sum_i s_i n_i \mathbf{v}_i$  which depends on absolute velocities only. <sup>b</sup> As is often the case in the real world: The proof of the pudding lies in its eating! <sup>c</sup> There are many ways to Rome and this is but one of them:  $\mathbf{j}_i \hat{=} n_i \mathbf{v}_i - n_i \mathbf{v} \hat{=} n_i \mathbf{v}_i - \rho^{-1} n_i \sum_j w_j n_j \mathbf{v}_j$ . Substitute the definition  $n_j \mathbf{v}_j \hat{=} \mathbf{j}_{m,j} + n_j \mathbf{v}_m$  for diffusion relative to the average molar velocity. Further manipulation yields  $\mathbf{j}_i = \mathbf{j}_{m,i} + n_i \mathbf{v}_m - \rho^{-1} n_i \sum_j w_j (\mathbf{j}_{m,j} + n_j \mathbf{v}_m) = \mathbf{j}_{m,i} - \rho^{-1} n_i \sum_j w_j \mathbf{j}_{m,j}$

equation  $\mathbf{j}_i \hat{=} n_i \mathbf{v}_i - n_i \mathbf{v}$  into

$$(5.19) \quad \mathbf{j}_i = \mathbf{j}_{m,i} - \frac{n_i}{\rho} \sum_j w_j \mathbf{j}_{m,j}$$

where  $\mathbf{j}_{m,i} \hat{=} n_i(\mathbf{v}_i - \mathbf{v}_m)$  and subscript  $m$  stands for average molar velocity. Plugging the equation above into Eq. 5.18 while keeping in mind that  $\tau \dot{s}_{\text{irr}}$  does not change, and using Gibbs–Duhem Eq. 5.3 to get rid of  $\text{grad}(\tau)$  and  $\text{grad}(\mu_i)$ , it turns out that

$$\tau \dot{s}_{\text{irr}} = \tau \dot{s}_{\text{irr}}(\mathbf{j}_{m,i}) - \frac{1}{\rho} (\sum_j w_j \mathbf{j}_{m,j}) \cdot \text{grad}(\pi)$$

The term  $\tau \dot{s}_{\text{irr}}(\mathbf{j}_{m,i})$  indicates that Eq. 5.18 still applies but this time as the functional of  $\mathbf{j}_i \curvearrowright \mathbf{j}_{m,i}$  and  $\mathbf{j}_s \curvearrowright \mathbf{j}_{m,s}$ . This is an important result because diffusion models are normally written in terms of  $\mathbf{j}_{m,i}$  and not  $\mathbf{j}_i$ .

#### 4. Phenomenological models

So far we have been fiddling around with definitions, exact thermodynamic relations and absolute conservation laws. Now it is time for putting some flesh on the bones, and in particular it is necessary to fill in the missing links in Section 3.1–3.4. These are the quantities  $\mathbf{q}$ ,  $\dot{\mathbf{r}}$ ,  $\mathbf{j}_i$ ,  $\mathbf{\Pi}$  and  $u$ , which must be calculated from phenomenological models. Three of them shall be discussed in this section while the last one, the equation of state, belongs to a section of its own, see Chapter [Equation of State](#).

**4.1. Heat conduction.** Fourier’s law is frequently used to describe the heat flow in isotropic fluids:

$$\mathbf{q} = -\kappa(\tau, \pi, \mathbf{n}) \text{grad}(\tau)$$

The thermal conductivity  $\kappa$  approaches in many cases a constant value. If this assumption is not good enough there are tons of empirical and semi-empirical correlations available in the literature, both for pure component fluids and mixtures.

**4.2. Reaction kinetics.** A general understanding of reaction kinetics is lacking and there is little theoretical guidance on how to put up a kinetic rate term. From a thermodynamic point of view, however, the rate must go to zero when the reaction approaches an equilibrium state. It is therefore reasonable to demand an expression similar to

$$R\tau\dot{\mathbf{r}} = -\mathbf{R}(\tau, \pi, \mathbf{n})\lambda_{\mathbf{r}}$$

where  $\mathbf{R}$  is a positive definite matrix (state function). This choice guarantees positive entropy production at all possible reaction conditions.

**4.3. Molecular diffusion.** The understanding of molecular diffusion is also intricate, and e.g. the Maxwell–Stefan formulation reads

$$\mathbf{f}_i = \sum_j \frac{x_j \mathbf{j}_{m,j} - x_j \mathbf{j}_{m,i}}{n D_{ij}}, \quad D_{ij} = D_{ji}$$

where  $D_{ij}$  are empirical state dependent diffusion coefficients and  $\mathbf{f}_i$  is the generalised force acting on component  $i$  in the mixture:  $R\tau\mathbf{f}_i = \text{grad}_\tau(\mu_i) - \frac{w_i}{\rho} \text{grad}(\pi)$ . It is missing a lengthy discussion of irreversible thermodynamics at this point— $\text{grad}_\tau(\mu_i)$  is a terrible concept which definitely should be avoided! Anyway, on matrix form the generalised forces can be written:

$$R\tau\mathbf{F} = \text{grad}_\tau(\boldsymbol{\mu}) - \rho^{-1} \mathbf{w} \text{grad}(\pi)$$

The diffusion fluxes are stated in an implicit manner which means the Maxwell–Stefan equations must be inverted each time  $\mathbf{j}_{m,i}$  are needed. To come closer an explicit formula the equations are first re-casted into the matrix form:

$$\begin{aligned} n\mathbf{F} &= \mathbf{B}\mathbf{J}_m \\ n\mathbf{B} &\hat{=} n^D\mathbf{D} - (\mathbf{D}\mathbf{n})^D \end{aligned}$$

The bad news are that  $\mathbf{B}$  is singular. The good news are that the singular directions are known<sup>a</sup>:

$$\begin{aligned} n\mathbf{B}^T \mathbf{e} &= \mathbf{0} \\ n\mathbf{B}\mathbf{n} &= \mathbf{0} \end{aligned}$$

Hence,  $n\mathbf{B} + \mathbf{n}\mathbf{e}^T$  shifts the zero eigenvalue to  $n$  and the flux equation can be inverted without problems<sup>b</sup>:

$$\mathbf{J}_m = n[n(n\mathbf{B} + \mathbf{n}\mathbf{e}^T)^{-1} - n^{-1}\mathbf{n}\mathbf{e}^T]\mathbf{F} \hat{=} n\mathbf{B}^+\mathbf{F}$$

The diffusion fluxes relative to the mass average velocity are calculated by means of Eq. 5.19. The matrix equivalent to this equation is:

$$\mathbf{J} = \mathbf{J}_m - \rho^{-1} \mathbf{n}\mathbf{w}^T \mathbf{J}_m = (\mathbf{I} - \rho^{-1} \mathbf{n}\mathbf{w}^T) \mathbf{J}_m$$

**4.4. Viscous stress.** Finally, a model for the stress tensor must be supplied. The simpler the better really, because even the simplest conceivable model

$$\begin{aligned} \Pi_{ij} &= \mathbf{K}_{ij} : \mathbf{T} \\ 2\mathbf{T} &\hat{=} \text{grad}(\widetilde{\mathbf{v}}) + \text{grad}(\mathbf{v}) \end{aligned}$$

<sup>a</sup> In a little more detail:  $n\mathbf{B}^T \mathbf{e} = \mathbf{D}\mathbf{n}^D \mathbf{e} - (\mathbf{D}\mathbf{n})^D \mathbf{e} = \mathbf{D}\mathbf{n} - \mathbf{D}\mathbf{n} = \mathbf{0}$  and  $n\mathbf{B}\mathbf{n} = n^D \mathbf{D}\mathbf{n} - (\mathbf{D}\mathbf{n})^D \mathbf{n} = n^D \mathbf{D}\mathbf{n} - n^D \mathbf{D}\mathbf{n} = \mathbf{0}$  <sup>b</sup>  $\mathbf{B}^+$  is similar to the Moore–Penrose inverse, but rather than aiming at the minimum norm of the solution vector it preserves the eigenvectors of  $\mathbf{B}$ .

requires the evaluation of a fourth order tensor  $\mathbf{K}$  with 81 coefficients! Here, Stoke's postulates come in very handy: Assume  $\mathbf{\Pi}$  is a symmetric tensor without directional preferences. Based on symmetry arguments it can then be proved that the 81 coefficients collapse into just two independent quantities  $\mu$  and  $\lambda$ :

$$\mathbf{\Pi} = \lambda \operatorname{div}(\mathbf{v})\mathbf{I} + \mu\mathbf{T}$$

Like everything else the bulk viscosity  $\lambda$  and the shear viscosity  $\mu$  are functions of the thermodynamic state. However,  $\lambda$  is hard to measure experimentally and the Stokes law  $3\lambda + 2\mu = 0$  is often used.

## 5. Governing equations

The conservations of reaction invariants, momentum and energy are the work horses of fluid dynamics, and in the Sections 3.1–3.4 we arrived at the following formulae (the equations have been rewritten slightly to fit into the current context):

$$\begin{aligned}\frac{\partial \mathbf{r}}{\partial t} &= -\mathbf{r} \operatorname{div}(\mathbf{v}) - \operatorname{grad}(\mathbf{r}) \cdot \mathbf{v} - \operatorname{div}(\mathbf{J}_r) + \dot{\mathbf{r}} \\ \frac{\partial \mathbf{c}}{\partial t} &= -\mathbf{c} \operatorname{div}(\mathbf{v}) - \operatorname{grad}(\mathbf{c}) \cdot \mathbf{v} - \operatorname{div}(\mathbf{J}_c) \\ \rho \frac{\partial \mathbf{v}}{\partial t} &\simeq -\operatorname{div}(\mathbf{\Pi}) - \rho \operatorname{grad}(\mathbf{v}) \cdot \mathbf{v} + \operatorname{grad}(\pi) \\ \frac{\partial u}{\partial t} &\simeq -h \operatorname{div}(\mathbf{v}) - \operatorname{grad}(u) \cdot \mathbf{v} - \operatorname{div}(\mathbf{q}) - \operatorname{div}(\mathbf{j}_h) - \mathbf{\Pi} : \operatorname{grad}(\mathbf{v})\end{aligned}$$

The following non-trivial definitions apply to these equations:  $\mathbf{j}_h \hat{=} \mathbf{h}^T \mathbf{J}$ ,  $\mathbf{J}_r \hat{=} \mathbf{Q}_r^T \mathbf{J}$  and  $\mathbf{J}_c \hat{=} \mathbf{Q}_c^T \mathbf{J}$ . This is as far the general theory goes. To obtain an equation closure it must be supplied phenomenological models for heat,

$$\mathbf{q} = -\kappa \operatorname{grad}(\tau)$$

reaction kinetics,

$$R\tau\dot{\mathbf{r}} = -\mathbf{R}\lambda_r$$

molecular diffusion,

$$\begin{aligned}\mathbf{J} &= (\mathbf{I} - \rho^{-1} \mathbf{n}\mathbf{w}^T) \mathbf{J}_m \\ \mathbf{J}_m &= n[n(n\mathbf{B} + \mathbf{n}\mathbf{e}^T)^{-1} - n^{-1} \mathbf{n}\mathbf{e}^T] \mathbf{F} \\ R\tau\mathbf{F} &= \operatorname{grad}_\tau(\mu) - \rho^{-1} \mathbf{w} \operatorname{grad}(\pi) \\ n\mathbf{B} &= \mathbf{n}^D \mathbf{D} - (\mathbf{D}\mathbf{n})^D\end{aligned}$$

viscous stress (Stoke's law is conveniently used)

$$\begin{aligned}\mathbf{\Pi} &= \mu\mathbf{T} - \frac{2}{3}\mu \operatorname{div}(\mathbf{v})\mathbf{I} \\ 2\mathbf{T} &= \operatorname{grad}(\widetilde{\mathbf{v}}) + \operatorname{grad}(\mathbf{v})\end{aligned}$$

and a thermodynamic equilibrium manifold

$$\text{grad}(\mathbf{g}_y) = \mathbf{S}_{yy} \text{grad}(\mathbf{y})$$

$$\text{grad}(\mathbf{y}) = \mathbf{C}_{12}^T \text{grad}(\mathbf{x})$$

The second last equation is responsible for the coupling to the scalar fields (using the chain rule):

$$\text{grad} \begin{pmatrix} \tau \\ \pi \\ \boldsymbol{\mu} \end{pmatrix} = -\tau^2 \begin{pmatrix} 1 & 0 & \mathbf{0} \\ \pi & -\tau & \mathbf{0} \\ \boldsymbol{\mu} & \mathbf{0} & -\tau \end{pmatrix}^{-1} \text{grad}(\mathbf{g}_y)$$

These are the governing differential equations for the system, but in addition the thermodynamic equilibrium state must be determined for each time step and at each point in space. The equilibrium calculation is needed for the algebraic coupling of the system as told above. Basically, it requires an underlying phase model, see Chapters [Equation of State](#) and [Activity Models](#), but the mathematics of the equilibrium problem can be stated without emphasis on the model details: Each Legendre transform has a unique equilibrium formulation, and using  $u, r_1, r_2, \dots, c_1, c_2, \dots$  as state variables the equilibrium state can be expressed as

$$\max S(U, V, C_1, C_2, \dots)$$

constrained by

$$U_{k+1} = V_k \left( u + \frac{\partial u}{\partial t} \delta t \right)_k$$

$$V_{k+1} = V_k$$

$$C_{i,k+1} = V_k \left( c_i + \frac{\partial c_i}{\partial t} \delta t \right)_k$$

This description fits right into the heart of Section 2 which means the outcome of the calculation will be the Lagrange multiplier vector  $\mathbf{g}_x$ . The multipliers keep all the information needed to update  $\tau$ ,  $\pi$  and  $\mu_i$  in the next time step, but what about the step size? Is there any guiding principles we have forgot to mention? Yes there is, and what is really nice is that the entropy balance in Section 3.5 can be used as a “norm” for the time step:

$$\frac{\max(S)_{k+1} - \max(S)_k}{\left( V \frac{\partial s}{\partial t} \delta t \right)_k} \simeq 1$$

I.e. the exact entropy difference between two successive time steps  $k + 1$  and  $k$  should not be allowed to deviate too much from the linearisation made in step  $k$ . This criterion can be used to control the consistency of the thermodynamic state, but it says of course nothing about the accuracy of the velocity field.



?? *Eriophorum vaginatum* (Ål in Hallingdal 2002).

## CHAPTER 6

**Residual Functions**

For a thermodynamic system it makes little difference whether it is composed of one or many components, provided the composition<sup>a</sup> is constant over time and in space. The thermodynamic state has then 3 degrees of freedom as discussed in Chapter **Constant Composition**. The situation worsens, however, if the molar composition is allowed to vary. As the number of independent variables increases the notion of components becomes less important, and because it is not our intention to restrict the theory to a limited number of chemical systems we shall hereafter use generic indices  $i \in [1, n]$  instead of component names. At the same time the thermodynamic potentials are at best described as abstract hyperplanes in  $> 3$  vectorial dimensions. The thermodynamics of mixtures is thereby cast into a formal subject, at least when compared to its constant composition counterpart.

The virial equation shall later be used as a recurring example, but to serve as a suitable starting point we shall first extend the results from Chapter **Constant Composition** to multicomponent theory. Ideal gas has a comparatively simple composition dependency and with reference to the Eqs. **Ideal Gas  $U$ –Ideal Gas  $S$**  we can write:

$$(6.1) \quad \Delta_f H^{\text{ig}}(T_o, \mathbf{n}) = \sum_{i=1}^n N_i \Delta_f h_i^{\circ}(T_o)$$

$$(6.2) \quad C_V^{\text{ig}}(T, \mathbf{n}) = \sum_{i=1}^n N_i c_{v,i}^{\circ}(T)$$

$$(6.3) \quad C_P^{\text{ig}}(T, \mathbf{n}) = \sum_{i=1}^n N_i c_{p,i}^{\circ}(T)$$

$$(6.4) \quad S^{\text{ig}}(T_o, p_o, \mathbf{n}) = \sum_{i=1}^n N_i s_i^{\circ}(T_o, p_o) - R \sum_{i=1}^n N_i \ln \left( \frac{N_i}{N} \right)$$

Note that  $\Delta_f h_i^{\circ}$ ,  $c_{v,i}^{\circ}$ ,  $c_{p,i}^{\circ}$  and  $s_i^{\circ}$  are standard state contributions of the same kind as  $\mu_i^{\circ}$  in Eq. **Ideal Gas  $\mu$** . For systems of constant composition  $U$ ,  $H$  and  $S$  are the most prominent functions, but in mixtures the chemical potential becomes increasingly more important. However, this quantity does not lean itself to the canonical differentiation of  $U$  or  $H$  because  $\mu_i \hat{=} (\partial U / \partial N_i)_{S, V, N_{j \neq i}} = (\partial H / \partial N_i)_{S, p, N_{j \neq i}}$  requires that  $S$  is a free variable. To avoid this problem we can use

<sup>a</sup> It is important to distinguish between mass and molar composition. The onset of chemical reactions may change the mole numbers in a system without affecting the mass variables i.e. the atoms or invariant groups of atoms.



either Gibbs<sup>a</sup> or Helmholtz<sup>b</sup> energy as our point of departure because  $\mu_i = (\partial G / \partial N_i)_{T,p,N_{j \neq i}} = (\partial A / \partial N_i)_{T,V,N_{j \neq i}}$  is calculated by explicit differentiation<sup>c</sup>. Whether  $G$  or  $A$  finds use as the basic function depends on the actual equation of state (more about this subject later).

§ 30 Express the ideal gas Gibbs energy using Eqs. 6.1–6.4. Make  $s_i^\circ$  and  $\Delta_f h_i^\circ$  the standard state of  $G^{ig}$ . Remember to include the temperature integrals of  $c_{p,i}^\circ$ ! Show by differentiation that the chemical potential is  $\mu_i^{ig}(T, p, \mathbf{n}) = \mu_i^\circ(T, p_\circ) + RT \ln[N_i p / (N p_\circ)]$ . Identify the function  $\mu_i^\circ$ .

A . The Gibbs energy  $G = H - TS$  of an ideal gas mixture follows from Eqs. Ideal Gas  $H$  and Ideal Gas  $S$ :

$$(6.5) \quad G^{ig}(T, p, \mathbf{n}) = \Delta_f H^{ig}(T_\circ, \mathbf{n}) + \int_{T_\circ}^T C_p^{ig}(T, \mathbf{n}) dT - T \left\{ S^{ig}(T_\circ, p_\circ, \mathbf{n}) + \int_{T_\circ}^T \frac{C_p^{ig}(T, \mathbf{n})}{T} dT - NR \ln\left(\frac{p}{p_\circ}\right) \right\}$$

Substitute Eqs. 6.1, 6.3 and 6.4 into Eq. 6.5 and differentiate with respect to  $N_i$ :

$$(6.6) \quad \begin{aligned} \mu_i^{ig}(T, p, \mathbf{n}) &= \left( \frac{\partial G^{ig}}{\partial N_i} \right)_{T,p,N_{j \neq i}} \\ &= \Delta_f h_i^\circ(T_\circ) + \int_{T_\circ}^T c_{p,i}^\circ(T) dT - T \left\{ s_i^\circ(T_\circ, p_\circ) - R \ln\left(\frac{N_i}{N}\right) - \sum_{k=1}^n N_k R \frac{N}{N_k} \frac{\delta_{ik} N - N_k}{N^2} \right. \\ &\quad \left. + \int_{T_\circ}^T \frac{c_{p,i}^\circ(T)}{T} dT - R \ln\left(\frac{p}{p_\circ}\right) \right\} \end{aligned}$$

Note the Kronecker-symbol  $\delta_{ik}$  which finds use in the equation above. It has the value 1 if  $i = k$  and 0 if  $i \neq k$ . Simplification of Eq. 6.6 yields,

$$(6.7) \quad \mu_i^{ig}(T, p, \mathbf{n}) = \mu_i^\circ(T, p_\circ) + RT \ln\left(\frac{N_i p}{N p_\circ}\right)$$

where the standard chemical potential  $\mu_i^\circ$  is defined as:

$$(6.8) \quad \mu_i^\circ(T) = \Delta_f h_i^\circ(T_\circ) + \int_{T_\circ}^T c_{p,i}^\circ(T) dT - T s_i^\circ(T_\circ, p_\circ) - T \int_{T_\circ}^T \frac{c_{p,i}^\circ(T)}{T} dT \quad \square$$

§ 31 Show that  $U^{ig} - TS^{ig} + pV^{ig} = \sum_{i=1}^n \mu_i^{ig} N_i$ .

A . First, Eq. 6.7 is substituted on the right hand side. The left hand side follows then from  $H^{ig} = U^{ig} + NRT$ .  $\square$

<sup>a</sup> Josiah Willard Gibbs, 1839–1903. American physicist. <sup>b</sup> Hermann Ludwig Ferdinand von Helmholtz, 1821–1894. German physician and physicist. <sup>c</sup> Most thermodynamic models, including both equations of state and activity coefficient models are explicit in  $T$  but not in  $S$ .



## 1. Gibbs energy

The canonical variables of Gibbs energy include temperature and pressure. This makes it possible to compare the chemical potential of a real fluid component with reference to the same component in the ideal gas state, maintained at the same temperature and pressure. The outcome of this comparison is the so-called residual Gibbs energy:

$$(6.9) \quad G^{r,p}(T, p, \mathbf{n}) \triangleq G(T, p, \mathbf{n}) - G^{ig}(T, p, \mathbf{n})$$

In the limit of  $p \rightarrow 0$  all fluids behave ideally (in the context of energy contribution):


$$(6.10) \quad \lim_{p \rightarrow 0} \left\{ G^{r,p} = 0, \left( \frac{\partial G^{r,p}}{\partial p} \right)_{T, \mathbf{n}} = B'_2, \dots, \left( \frac{\partial^n G^{r,p}}{\partial p \dots \partial p} \right)_{T, \mathbf{n}} = (n-1)! B'_{n+1} \right\}$$

These limits conform with the virial expansion in Chapter [Equation of State](#), and with the Legendre transform in Chapter 2 which interprets  $(\partial G / \partial p)_{T, \mathbf{n}}$  as the system volume quite independent of whether the fluid is ideal or real. By exploiting Eq. 6.10 it is permissible to rewrite Eq. 6.9 into<sup>a</sup>:

$$(6.11) \quad G^{r,p}(T, p, \mathbf{n}) = \int_0^p (V - V^{ig}) d\pi = \int_0^p (V(\pi) - \frac{NRT}{\pi}) d\pi$$

A corresponding expression for the chemical potential  $\mu_i = (\partial G / \partial N_i)_{T, p, N_{j \neq i}}$  is defined for all conceivable Gibbs energy functions, including  $G^{r,p}$ . This means we can define the residual chemical potential as  $\mu_i^{r,p} \triangleq \mu_i - \mu_i^{ig}$ , that is

$$(6.12) \quad \begin{aligned} \mu_i^{r,p}(T, p, \mathbf{n}) &\triangleq \left( \frac{\partial G^{r,p}}{\partial N_i} \right)_{T, p, N_{j \neq i}} \\ &= \int_0^p \left[ \left( \frac{\partial V}{\partial N_i} \right)_{T, \pi, N_{j \neq i}} - \frac{RT}{\pi} \right] d\pi \triangleq \int_0^p (\bar{v}_i - \frac{RT}{\pi}) d\pi \end{aligned}$$

where  $\bar{v}_i \triangleq (\partial V / \partial N_i)_{T, \pi, N_{j \neq i}}$  is the *partial molar volume* of component  $i$ . The translation of Eq. 6.11 into Eq. 6.12 requires that  $G^{r,p}$  is differentiated at constant pressure<sup>b</sup>. The system pressure enters only the limit of the integral and we need only to worry about the kernel, but here the pressure does vary during the integration! This is an unusual situation and it is important to realise that the total differential of  $V(\pi)$  is defined locally as 

$$(dV)_{T, \pi, N_{j \neq i}} = \left( \frac{\partial V}{\partial N_i} \right)_{T, \pi, N_{j \neq i}} dN_i$$

for all pressures  $\pi \in [0, p]$ . The local pressure  $\pi$  is constant at each point in the integration and the only degree of freedom comes from the composition variation. Hence, the chemical potential must be integrated over the volume

<sup>a</sup> Note that  $\pi$  is used as the integration variable to avoid conflict with  $p$  which appears in the upper limit of the integral. <sup>b</sup> Note, however, that the derivative of  $G^{r,p}$  at constant pressure  $p$  requires knowledge of the derivative of  $V - V^{ig}$  at all pressures  $\pi \in [0, p]$  in the integration domain.

derivative as indicated in Eq. 6.12. One final remark: It is customary to rewrite the residual potential as

$$(6.13) \quad RT \ln \varphi_i \hat{=} \mu_i^{\text{r,p}}(T, p, \mathbf{n})$$



where  $\varphi_i(T, p, \mathbf{n})$  is the *fugacity coefficient* of component  $i$ . It measures the departure between a real fluid and an ideal gas at the same system conditions  $T, p, \mathbf{n}$ . The fugacity coefficient is traditionally given due attention in American literature, and for gases at low pressures and phase equilibria calculated by the  $K$ -value method it has certain benefits, but in the general context it causes more trouble than cure — the fugacity coefficient does neither increase the basic understanding nor does it improve the numeric behaviour of thermodynamic algorithms.

§ 32 Show that  $\mu_i = \mu_i^{\text{ig}} + \mu_i^{\text{r,p}} = \mu_i^\circ + RT \ln[N_i \varphi_i p / (N p^\circ)]$ . Calculate the limit  $\lim_{p \rightarrow 0} \varphi_i = 1$ . What is  $\varphi_i$  for a component in the ideal gas state?

A . The chemical potential is derived from Eqs. 6.7 and 6.12. The latter equation gives  $\lim_{p \rightarrow 0} \mu_i^{\text{r,p}} = 0$  and hence  $\lim_{p \rightarrow 0} \varphi_i = 1$ . For ideal gas  $\bar{v}_i^{\text{ig}} = RT/\pi$  and  $\mu_i^{\text{r,p,ig}} = 0$  independent of pressure and  $\varphi_i^{\text{ig}} = 1$  (always). □

§ 33 Derive  $G^{\text{r,p}}$  for the 2nd virial equation  $pV^{2,\text{vir}} = NRT + Bp$ . Differentiate to find  $RT \ln \varphi_k^{2,\text{vir}}$ . Make use of  $B = N \sum_i \sum_j x_i x_j B_{i,j}$  where  $B_{i,j} = B_{j,i}$ .

A . The residual Gibbs energy is determined by direct substitution of the 2nd virial equation into Eq. 6.11:

$$(6.14) \quad G^{\text{r,p,2,vir}} = \int_0^p \left( \frac{NRT}{\pi} + B - \frac{NRT}{\pi} \right) d\pi = Bp$$

In order to find  $RT \ln \varphi_k$  we must differentiate  $G^{\text{r,p}}$  and hence  $B$  with respect to  $N_k$ , but the differentiation of (mole)fractions causes something known as “code bloat” in computer science. The work load is reduced considerably by rearranging the virial function into  $NB = \sum_i \sum_j N_i N_j B_{i,j}$  which gives the implicit formulation:

$$\left( \frac{\partial NB}{\partial N_k} \right)_{T, N_i \neq k} = \sum_i \sum_j \left( \frac{\partial N_i N_j}{\partial N_k} \right)_{N_i \neq k} B_{i,j}$$

Differentiate both sides using the Kronecker-delta:

$$B + N \left( \frac{\partial B}{\partial N_k} \right)_{T, N_i \neq k} = \sum_i \sum_j \left( \delta_{ik} N_j + N_i \delta_{jk} \right) B_{ij} = \sum_j N_j B_{kj} + \sum_i N_i B_{ik}$$

Recognises the symmetry  $B_{kj} = B_{jk}$  and changes the summation index  $j$  to  $i$  (or vice versa). This operation reveals two identical contributions on the right hand side. The partial derivative of  $B$  is therefore

$$\bar{b}_i \hat{=} \left( \frac{\partial B}{\partial N_k} \right)_{T, N_i \neq k} = 2 \sum_i \frac{N_i}{N} B_{ik} - \frac{B}{N}$$

The residual potential is calculated from Eq. 6.14 on the facing page as shown below:

$$RT \ln \varphi_k^{2.\text{vir}} = \left( \frac{\partial G^{r,p,2.\text{vir}}}{\partial N_k} \right)_{T,p,N_i \neq k} = p \left( \frac{\partial B}{\partial N_k} \right)_{T,N_i \neq k} \hat{=} p \bar{b}_i$$

We can alternatively put the partial derivative of  $B$  into Eq. 6.12 on page 53 and integrate with the same result<sup>a</sup>.  $\square$

## 2. Helmholtz energy at fixed pressure

To make calculations with residual Gibbs energy we must employ an equation of state on the form  $V = V(T, p, \mathbf{n})$ . This limits practical applications to the second virial equation  $V = NRT/p + Bp$ . However, there is a rapid development of equation of states on the form  $p = p(T, V, \mathbf{n})$  which calls for the canonical variable *volume* rather than *pressure*. This invites us to use Helmholtz energy rather than Gibbs energy as the basic function.

Traditionally, the definition of the fugacity coefficient in Eq. 6.13 is not changed in the transposition from  $G$  to  $A$ . This causes a problem with the chemical potential because  $\varphi_i$  describes the departure between the real fluid and ideal gas at given pressure — not at given volume. The result is a non-canonical description which is discussed here mainly because it has accumulated in the engineering literature.

**2.1. Physical derivation.** Our goal is to describe the difference in Helmholtz energy between a real fluid and ideal gas at a given *temperature and pressure*. To achieve this we have to find the difference between two state functions applied to two different states. The task is simplified by splitting the expression in two terms: The first term compares the two functions in the same state while the second term compares the ideal gas in two different states:


$$\begin{aligned} A^{r,p}(T, V(p), \mathbf{n}) &\hat{=} A(T, V(p), \mathbf{n}) - A^{1g}(T, V^{1g}(p), \mathbf{n}) \\ (6.15) \quad &\equiv A(T, V(p), \mathbf{n}) - A^{1g}(T, V(p), \mathbf{n}) \\ &+ A^{1g}(T, V(p), \mathbf{n}) - A^{1g}(T, V^{1g}(p), \mathbf{n}) \end{aligned}$$

It must be emphasised that volume is a function of pressure  $p$ . The pressure is by definition the same in the ideal gas and the real fluid, i.e.  $p^{1g} = p$ . It implies, however, that the two fluids have different volumes because  $V \neq V^{1g}$  at given  $p$ . From Chapter 2 we know that  $(\partial A / \partial V)_{T,\mathbf{n}} = -p$ . This relation holds for any Helmholtz energy function whether it is an ideal gas or a real fluid. In analogy


<sup>a</sup> It is worth while to mention that  $\bar{b}_i$  is the (pressure independent) residual of the 2nd virial partial molar volume:  $\bar{v}_i^{2.\text{vir}} - RT/\pi = \bar{b}_i(T)$ .

to Eq. 6.11 on page 53 we can write,

$$\begin{aligned}
 A^{r,p}(T, V(p), \mathbf{n}) &= \int_{\infty}^{V(p)} (\pi^{ig} - \pi) dv - \int_{V^{ig}(p)}^{V(p)} \pi^{ig} dv \\
 (6.16) \qquad \qquad \qquad &= \int_{\infty}^{V(p)} \left( \frac{NRT}{v} - \pi \right) dv - NRT \ln z(p)
 \end{aligned}$$

 where the ideal gas volume is given by  $V^{ig} = NRT/p$ , and the *compressibility factor*  $z$  is defined as  $z \hat{=} pV/(NRT) = V/V^{ig}$ . Eq. 6.16 may look trivial but please note that the volume is an implicit variable in the integral. The implicit form of  $A^{r,p}(T, V(p), p, \mathbf{n})$  prevents the calculation of chemical potentials by canonical differentiation with respect to  $T, V, \mathbf{n}^a$ , and we must rather look at:

$$\mu_i = \left( \frac{\partial A}{\partial N_i} \right)_{T, V, N_{j \neq i}} \quad \wedge \quad \mu_i^{ig} = \left( \frac{\partial A^{ig}}{\partial N_i} \right)_{T, V^{ig}, N_{j \neq i}}$$

 Then replaced in the definition of the residual chemical potential  $\mu_i^{r,p} \hat{=} \mu_i - \mu_i^{ig}$  this yields:

$$\begin{aligned}
 \mu_i^{r,p} &= \left( \frac{\partial A}{\partial N_i} \right)_{T, V(p), N_{j \neq i}} - \left( \frac{\partial A^{ig}}{\partial N_i} \right)_{T, V^{ig}(p), N_{j \neq i}} \\
 &= \left( \frac{\partial A^{r,p}}{\partial N_i} \right)_{T, V(p), V^{ig}(p), N_{j \neq i}}
 \end{aligned}$$

Note that  $V(p)$  is constant in one of the derivatives while  $V^{ig}(p)$  is constant in the other two. This means that both  $V(p)$  and  $V^{ig}(p)$  must be constant while differentiating  $A^{r,p}$ , which really implies that  $z(p) = V^{ig}/V$  is a constant factor. The residual chemical potential is therefore

$$(6.17) \quad \mu_i^{r,p}(T, V(p), \mathbf{n}) = \int_{\infty}^{V(p)} \left[ \frac{RT}{v} - \left( \frac{\partial \pi}{\partial N_i} \right)_{T, v, N_{j \neq i}} \right] dv - RT \ln z(T, V(p), \mathbf{n})$$

Even though this description is mathematically correct it cannot be explained on a rational basis because it relies on two different volumes which are both constant in the same differentiation.

**§ 34 Find  $A^{r,p}$  for the 2nd virial equation when  $pV^{2, \text{vir}} = NRT + Bp$ .**

**A** . The residual Helmholtz energy is calculated by inserting the 2nd virial equation in Eq. 6.16. The answer is simple:

$$(6.18) \quad A^{r,p,2, \text{vir}} = \int_{\infty}^V \left( \frac{NRT}{v} - \frac{NRT}{v-B} \right) dv - NRT \ln \left( \frac{V}{V-B} \right) = 0$$

Quite curiously, there is no difference between Helmholtz energy for the 2nd virial gas and ideal gas at a *given pressure*. In other words: The volume con-

<sup>a</sup> If the fugacity coefficient is (re)defined as the departure between ideal gas and real fluid at a *given volume* rather than *given pressure* the derivation of chemical potential is simplified, see Section 3 on page 58.

tribution to  $A^{2.\text{vir}}$  happens to be just  $RT \ln z^{2.\text{vir}}$ . This does not say that all thermodynamic departures cancel. E.g.  $G^{\text{r,p,2.vir}}$  was calculated as  $Bp$  in Eq. 6.14 on page 54, and you should verify that the 2nd virial equation substituted in Eq. 6.17 gives the same answer as in Eq. 6.12 on page 53. Moreover, even though  $A^{\text{r,p,2.vir}}$  is zero it does not imply that  $\mu_i^{\text{r,p,2.vir}}$  is zero (remember that  $A^{\text{r,p}}$  is a non-canonical function).  $\square$

**2.2. Rational derivation.** The derivation of  $A^{\text{r,p}}$  in the last section was not straightforward and it is desirable to find a more rational explanation. Here, Eq. 6.15 is first differentiated with respect to the mole number  $N_i$ :

$$(6.19) \quad \left(\frac{\partial A^{\text{r,p}}}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \mu_i - \left(\frac{\partial A^{\text{ig}}}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

This time we have to face that constant  $V$  is not synonymous with constant  $V^{\text{ig}}$ . In fact, differentiation of  $A^{\text{ig}}$  with respect to  $N_i$  requires the change of  $V^{\text{ig}}$  with  $N_i$  while  $V$  is constant. The total differential of  $A^{\text{ig}}$  is,

$$(6.20) \quad (dA^{\text{ig}})_{T,N_{j\neq i}} = \left(\frac{\partial A^{\text{ig}}}{\partial N_i}\right)_{T,V^{\text{ig}},N_{j\neq i}} dN_i + \left(\frac{\partial A^{\text{ig}}}{\partial V^{\text{ig}}}\right)_{T,\mathbf{n}} dV^{\text{ig}} = \mu_i^{\text{ig}} dN_i - p^{\text{ig}} dV^{\text{ig}}$$

where  $^{\text{ig}}$  is stated explicitly to make things a little clearer in the next turn. Keeping the condition  $p^{\text{ig}} = p$  in mind we can, on the basis of Eq. 6.20, write:

$$(6.21) \quad \left(\frac{\partial A^{\text{ig}}}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \mu_i^{\text{ig}} - p \left(\frac{\partial V^{\text{ig}}}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

Combined with Eq. 6.19 this gives:

$$(6.22) \quad \mu_i - \mu_i^{\text{ig}} = \left(\frac{\partial A^{\text{r,p}}}{\partial N_i}\right)_{T,V,N_{j\neq i}} - p \left(\frac{\partial V^{\text{ig}}}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

Eq. 6.16 is finally differentiated:

$$(6.23) \quad \left(\frac{\partial A^{\text{r,p}}}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \int_{\infty}^V \left[ \frac{RT}{v} - \left(\frac{\partial p}{\partial N_i}\right)_{T,v,N_{j\neq i}} \right] dv + \frac{NRT}{V^{\text{ig}}} \left(\frac{\partial V^{\text{ig}}}{\partial N_i}\right)_{T,V,N_{j\neq i}} - RT \ln z$$

$NRT/V^{\text{ig}}$  is recognised as  $p^{\text{ig}} = p$  in Eq. 6.23. This makes the term  $(\partial V^{\text{ig}}/\partial N_i)_{T,V,N_{j\neq i}}$  disappear when the Eqs. 6.22 and 6.23 are combined. The residual chemical potential  $\mu_i^{\text{r,p}} \hat{=} \mu_i - \mu_i^{\text{ig}}$  is thereby the same as in Eq. 6.17 on the facing page.

**2.3. Connection with Gibbs energy.** A third alternative is to use Gibbs energy as the basic function, which by the way is the most natural choice because the residual chemical potential is defined at constant system pressure. Substituting  $G = A + pV$  into  $G^{\text{r,p}} \hat{=} G - G^{\text{ig}}$  gives:

$$(6.24) \quad G^{\text{r,p}} = A(T, V(p), \mathbf{n}) + pV(p) - [A^{\text{ig}}(T, V^{\text{ig}}(p), \mathbf{n}) + pV^{\text{ig}}(p)]$$

Furthermore,  $pV = zNRT$  and  $pV^{1g} = NRT$ . When substituted into the equation above, together with Eqs. 6.15 and 6.16 on page 55, we get:

$$(6.25) \quad \begin{aligned} G^{r,p} &= A^{r,p} + NRT(z - 1) \\ &= \int_{\infty}^{V(p)} \left( \frac{NRT}{v} - \pi \right) dv - NRT \ln z(p) - NRT[z(p) - 1] \end{aligned}$$

It remains to differentiate the last expression with respect to the mole number of component  $i$ . This proves to be a quite tedious task, and we shall first find the partial derivative of  $z \hat{=} pV/NRT$ :

$$z_i \hat{=} \left( \frac{\partial z}{\partial N_i} \right)_{T,p,N_{j \neq i}} = \frac{p\bar{v}_i}{NRT} - \frac{pV}{N(NRT)} = \frac{p\bar{v}_i}{NRT} - \frac{z}{N}$$

Next, the integral in Eq. 6.25 must be differentiated. The upper limit depends clearly on the composition at fixed pressure, while the total differential of  $\pi$  at the local volume  $v$  is:

$$(d\pi)_{T,v,N_{j \neq i}} = \left( \frac{\partial \pi}{\partial N_i} \right)_{T,v,N_{j \neq i}} dN_i$$

Analogous to the derivation of residual Gibbs energy on page 53, the variable  $v$  is an integration variable and does not represent a new degree of freedom in the integral. The result from the partial differentiation is therefore:

$$\begin{aligned} \mu_i^{r,p} &= \int_{\infty}^{V(p)} \left[ \frac{RT}{v} - \left( \frac{\partial \pi}{\partial N_i} \right)_{T,v,N_{j \neq i}} \right] dv + \left( \frac{NRT}{V(p)} - p \right) \bar{v}_i \\ &\quad - RT \ln z - \frac{z_i NRT}{z} + RT(z - 1) + z_i NRT \end{aligned}$$

Substitution of  $z_i$  makes most of the terms cancel and the final result is identical with Eq. 6.17 on page 56.

**§ 35** Show that  $G^{r,p,2.vir} = NRT(z - 1) = Bp$  when  $pV^{2.vir} = NRT + Bp$ .

**A** . From Eq. 6.25 we know the general expression  $G^{r,p} = A^{r,p} + NRT(z - 1)$ . Combined with  $A^{r,p,2.vir} = 0$  from Eq. 6.18 on page 56 this yields  $G^{r,p,2.vir} = NRT(z - 1)$ . Substitution of  $z^{2.vir} = 1 + Bp/NRT$  makes  $G^{r,p,2.vir} = Bp$  in accordance with Eq. 6.14 on page 54. The results from the earlier sections are indeed consistent.  $\square$

### 3. Helmholtz energy at fixed volume

The problems experienced in the last section were initiated by the disastrous choice of using pressure as a free variable in the Helmholtz function. If the residual Helmholtz energy is redefined to

$$A^{r,v}(T, V, \mathbf{n}) \hat{=} A(T, V, \mathbf{n}) - A^{1g}(T, V, \mathbf{n})$$

we are back into the canonical world, and the derivation follows closely that of the residual Gibbs energy on page 53. The alternative residual function can be written

$$A^{r,v} = \int_{\infty}^V \left( \frac{NRT}{v} - p(v) \right) dv$$

and the corresponding chemical potential:

$$\mu_i^{r,v} \hat{=} \left( \frac{\partial A^{r,v}}{\partial N_i} \right)_{T,V,N_{j \neq i}} = \int_{\infty}^V \left[ \frac{RT}{v} - \left( \frac{\partial p}{\partial N_i} \right)_{T,v,N_{j \neq i}} \right] dv$$

§ 36 Derive an expression for  $A^{r,v}$  and the corresponding first derivatives  $\partial A^{r,v} / \partial(T, V, \mathbf{n})$  for a fluid which conforms with the Redlich–Kwong equation of state  $p^{\text{rk}} = RT/(v - b) - a/\sqrt{T}v(v + b)$ . Use the mixing rules  $b(\mathbf{x}) = \sum_i b_i x_i$  and  $a(\mathbf{x}) = \sum_i \sum_j \sqrt{a_i a_j} x_i x_j$  where  $b_i$  and  $a_i$  are component specific parameters. Estimate  $b_i$  and  $a_i$  from the critical conditions  $(\partial p / \partial v)_T = 0$  and  $(\partial^2 p / \partial v \partial v)_T = 0$ , see also Paragraph Van der Waal.

R –K . Let us estimate  $a$  and  $b$  for a pure fluid first. The equation of state is purposely reshaped into a *cubic* polynomial:

$$v^3 - \frac{RT}{p}v^2 + \left( \frac{a}{pT^{1/2}} - b^2 - \frac{RTb}{p} \right)v - \frac{ab}{pT^{1/2}} = 0$$

At the critical point this equation must fulfil  $(v - v_c)^3 = 0$ , that is  $v^3 - 3vv_c + 3v^2v_c^2 - v_c^3 = 0$ . When compared term-by-term the two polynomials define a set of equations that can be solved for  $a$  and  $b$  (and  $v_c$ ):

$$3v_c = \frac{RT_c}{p_c}, \quad 3v_c^2 = \frac{a}{p_c T_c^{1/2}} - b^2 - \frac{RT_c b}{p_c}, \quad v_c^3 = \frac{ab}{p_c T_c^{1/2}}$$

The second equation is combined with the other two to yield  $2v_c^3 - (v_c + b)^3 = 0$ , which is solved for the positive root  $b = (2^{1/3} - 1)v_c$ . In terms of the critical temperature and pressure (for any component  $i$ ) this is equivalent to:

$$\begin{aligned} b_i &= \Omega_b \frac{RT_{c,i}}{p_{c,i}} & a_i &= \Omega_a \frac{R^2 T_{c,i}^{5/2}}{p_{c,i}} \\ \Omega_b &\hat{=} \frac{2^{1/3} - 1}{3} & \Omega_a &\hat{=} \frac{1}{9(2^{1/3} - 1)} \end{aligned}$$

In the remaining text we can choose to express our-self in (extensive) mole numbers and volume, or (intensive) mole fractions and molar volume. Here, the extensive form is chosen to emphasise the homogeneous properties of the thermodynamic functions. The total Helmholtz energy for the fluid is,

$$A^{r,v,\text{rk}} = \int_{\infty}^V \left( \frac{NRT}{v} - p^{\text{rk}} \right) dv = NRT \ln \left( \frac{V}{V-B} \right) + \frac{A}{B} \ln \left( \frac{V}{V+B} \right)$$

and the corresponding first derivatives are:

$$\begin{aligned} \left(\frac{\partial A^{r,v,rk}}{\partial T}\right)_{V,\mathbf{n}} &= NR \ln\left(\frac{V}{V-B}\right) + \frac{A_T}{B} \ln\left(\frac{V}{V+B}\right) \\ \left(\frac{\partial A^{r,v,rk}}{\partial V}\right)_{T,\mathbf{n}} &= NRT \frac{B}{V(V-B)} - \frac{A}{V(V+B)} \\ \left(\frac{\partial A^{r,v,rk}}{\partial N_i}\right)_{T,V,N_{j \neq k}} &= RT \ln\left(\frac{V}{V-B}\right) + NRT \frac{b_i}{V-B} + \frac{1}{B} \left(A_i - \frac{Ab_i}{B}\right) \ln\left(\frac{V}{V+B}\right) - \frac{Ab_i}{B(V+B)} \end{aligned}$$

The coefficients are defined below (note that  $\alpha_i$  has units similar to  $\alpha_i^{\text{vdw}}$ ):

$$B \hat{=} \sum_i b_i N_i$$

$$A \hat{=} \sum_i \sum_j \left(\frac{a_i a_j}{T}\right)^{1/2} N_i N_j = \left(\sum_i \alpha_i^{1/2} N_i\right)^2$$

$$A_T \hat{=} -\frac{A}{2T}$$

$$A_i \hat{=} 2\alpha_i^{1/2} \sum_j \alpha_j^{1/2} N_j = 2(\alpha_i A)^{1/2}$$

$$\alpha_i \hat{=} \frac{a_i}{T^{1/2}}$$

□



## CHAPTER 7

**Multicomponent Phase Equilibrium**

At thermodynamic equilibrium the system has reached a state of minimum energy. This far-reaching postulate is of tremendous importance for our understanding of matter and energy, but it remains to discuss *which* of the energy functions that are being minimised. In Chapter **Single Reaction** it has been proved that Gibbs energy of a closed system decreases (due to chemical reactions) till the minimum value  $G_{\text{eq}} = \min_{\mathbf{n}} G(T, p, \mathbf{n})$  is reached. This is generally true when the temperature and pressure are constant. If the volume is kept constant and the pressure is varied the Helmholtz energy will be minimised. Chapter **Vapor–Liquid Equilibrium** illustrates this for the case of a simple vapour–liquid equilibrium. The other energy functions  $U$ ,  $H$ , etc. are minimised at constant values of their respective *canonical* variables.

In general we shall investigate a closed system consisting of  $\pi = \alpha, \beta, \dots, \psi, \omega$  phases<sup>a</sup> and a set of  $i = 1, 2, \dots, n$  components which are common to all the phases. Reacting systems with (maybe) disjoint sets of the components in each of the phases is taken up in Chapter **Phase Reactions**. For the special case of constant temperature and pressure  $(dG)_{T,p,\mathbf{n}} = \sum_{\pi=\alpha}^{\omega} \sum_{i=1}^n \mu_i^{\pi} dN_i^{\pi} = 0$  is a *necessary* condition for thermodynamic equilibrium. From the mass balance it follows that  $\sum_{\pi=\alpha}^{\omega} N_i^{\pi} = N_i$  and even  $\sum_{\pi=\alpha}^{\omega} dN_i^{\pi} = 0$  because the total moles  $N_i$  are constant. The main concern of this chapter is a two-phase system where  $\alpha$  and  $\beta$  may include vapour–liquid, liquid–liquid, solid–liquid and solid–solid equilibrium. The thermodynamic equilibrium criterion is then simplified to:

$$(dG)_{T,p,\mathbf{n}} = \sum_{i=1}^n \mu_i^{\alpha} dN_i^{\alpha} + \sum_{i=1}^n \mu_i^{\beta} dN_i^{\beta} = 0$$

$$dN_i^{\alpha} + dN_i^{\beta} = 0$$

Elimination of  $dN_i^{\beta}$  makes  $(dG)_{T,p,\mathbf{n}} = \sum_{i=1}^n (\mu_i^{\alpha} - \mu_i^{\beta}) dN_i^{\alpha} = 0$ . In the vicinity of an equilibrium point all the  $dN_i^{\alpha}$  are independent quantities<sup>b</sup> and the equilibrium relationship is equivalent to:

$$(7.1) \quad \mu_i^{\alpha} = \mu_i^{\beta}, \quad \forall i \in [1, n]$$

<sup>a</sup> Phase  $\alpha$  is usually the low temperature phase and  $\beta, \dots, \psi, \omega$  are phases that become stable at successively increasing temperatures. <sup>b</sup> At equilibrium  $dN_i^{\alpha}$  are *fluctuations* beyond our control. These fluctuations are quite inevitable from the laws of quantum mechanics and will be observed in every physically acceptable system. Thermodynamic equilibria are in other words dynamic, not static.

§ 37 Show that the necessary criteria for multiphase equilibrium at given total entropy  $S$ , total volume  $V$  and total composition  $N_i$  for each component  $i$ , are  $T^\alpha = T^\beta = \dots = T^\omega$ ,  $p^\alpha = p^\beta = \dots = p^\omega$  and  $\mu^\alpha = \mu^\beta = \dots = \mu^\omega$ . It is assumed that all the components  $i \in [1, n]$  are present in all the phases  $\alpha, \beta, \dots, \omega$ . Hint: start from

$$\begin{aligned} U_{\text{eq}} &= \min_{\mathbf{s}, \mathbf{v}, \mathbf{n}_i} U(\mathbf{s}, \mathbf{v}, \mathbf{n}_1, \dots, \mathbf{n}_n) \\ \mathbf{e}\mathbf{s} &= S \\ \mathbf{e}\mathbf{v} &= V \\ \mathbf{e}\mathbf{n}_i &= N_i, \quad \forall i \in [1, n] \end{aligned}$$

where  $\mathbf{e} \hat{=} [1 \ 1 \dots 1]$ ,  $\mathbf{s}^T \hat{=} [S^\alpha \ S^\beta \dots S^\omega]$ ,  $\mathbf{v}^T \hat{=} [V^\alpha \ V^\beta \dots V^\omega]$  and  $\mathbf{n}_i^T \hat{=} [N_i^\alpha \ N_i^\beta \dots N_i^\omega]$  are phase vectors with as many elements as there are phases in the system.

P . The internal energy of the system is minimised in the equilibrium state. In this (stationary) state the differential of  $U$  must be zero for all *feasible* variations in  $S^\pi$ ,  $V^\pi$  and  $N_i^\pi$ :

$$(dU)_{S, V, \mathbf{n}} = \sum_{\pi=\alpha}^{\omega} dU^\pi = \sum_{\pi=\alpha}^{\omega} (T^\pi dS^\pi - p^\pi dV^\pi + \sum_{i=1}^n \mu_i^\pi dN_i^\pi) = 0$$

Note that  $U$  has no absolute minimum. Due to its extensive properties it will  $\rightarrow \pm\infty$  when the system size  $\rightarrow \infty$ . The variations in  $S^\pi$ ,  $V^\pi$  and  $N_i^\pi$  must therefore be constrained such that the total entropy, volume and mole numbers (of each component) are conserved:

$$\begin{aligned} \sum_{\pi=\alpha}^{\omega} dS^\pi &= 0 \\ \sum_{\pi=\alpha}^{\omega} dV^\pi &= 0 \\ \sum_{\pi=\alpha}^{\omega} dN_i^\pi &= 0; \quad \forall i \in [1, n] \end{aligned}$$

From these  $n + 2$  balance equations we can eliminate  $dS^\omega$ ,  $dV^\omega$  and  $dN_i^\omega$  for all the components  $i \in [1, n]$ . Substituted into the differential of  $U$ :

$$(dU)_{S, V, \mathbf{n}} = \sum_{\pi=\alpha}^{\psi} ((T^\pi - T^\omega) dS^\pi - (p^\pi - p^\omega) dV^\pi + \sum_{i=1}^n (\mu_i^\pi - \mu_i^\omega) dN_i^\pi) = 0$$


In the neighbourhood of an equilibrium point the quantities  $dS^\alpha, \dots, dS^\psi$  and  $dV^\alpha, \dots, dV^\psi$  and  $dN_\alpha^1, \dots, dN_n^\psi$  are truly independent variables. If  $(dU)_{S, V, \mathbf{n}} = 0$  then it must be true that:

$$\begin{aligned} T^\alpha &= T^\beta = \dots = T^\psi = T^\omega \\ p^\alpha &= p^\beta = \dots = p^\psi = p^\omega \end{aligned}$$

$$\begin{aligned}\mu_1^\alpha &= \mu_1^\beta = \cdots = \mu_1^\psi = \mu_1^\omega \\ &\vdots \\ \mu_n^\alpha &= \mu_n^\beta = \cdots = \mu_n^\psi = \mu_n^\omega\end{aligned}\quad \square$$

Despite the fact that temperature, pressure and chemical potentials are uniform at thermodynamic equilibrium we cannot specify these variables directly. The Gibbs–Duhem’s equation

$$\mathbf{s} dT - \mathbf{v} dp + [\mathbf{n}_1 \mathbf{n}_2 \cdots \mathbf{n}_n] d\boldsymbol{\mu} = \mathbf{0}$$

removes one degree of freedom per phase. The number of independent intensive variables in a system is therefore  $F = \dim(\mathbf{n}) + 2 - \dim(\mathbf{e})$ , or in other words  $F = N + 2 - P$ , also known as the Gibbs phase rule for un-reacting systems. 

### 1. Direct substitution

Vapour–liquid equilibria are frequently calculated by an iterative method which is due to Rachford and Rice<sup>a</sup>. This is also known as the  $K$ -value method because the equilibrium relations are solved as a set of  $K$ -value problems on the form

$$(7.2) \quad x_i^\beta \hat{=} K_i x_i^\alpha, \quad \forall i \in [1, n]$$

where  $x_i^\alpha$  and  $x_i^\beta$  are the mole fractions of component  $i$  in  $\alpha$  (liquid) and  $\beta$  (vapour) respectively. We shall later learn that there is a one-to-one relationship between  $K_i$  and the chemical potentials of component  $i$  in the two phases. This tells us that the  $K$ -value method can be applied even when  $\alpha$  and  $\beta$  are two arbitrary phases, but prior to the discussion of exotic phase equilibria we shall derive a calculation scheme (algorithm) for Eq. 7.2. The total mass balance is  $N^\alpha + N^\beta = N$  and the component balances can be written  $x_i^\alpha N^\alpha + x_i^\beta N^\beta = N_i$ . Elimination of  $N^\beta$  produces  $x_i^\alpha N^\alpha + x_i^\beta (N - N^\alpha) = N_i$  and a subsequent substitution of  $x_i^\beta$  from Eq. 7.2 yields:

$$(7.3) \quad x_i^\alpha = \frac{N_i}{N^\alpha + K_i(N - N^\alpha)} = \frac{z_i}{z^\alpha + K_i z^\beta}$$

The corresponding expression for  $x_i^\beta$  is

$$(7.4) \quad x_i^\beta = \frac{K_i N_i}{N^\alpha + K_i(N - N^\alpha)} = \frac{K_i z_i}{z^\alpha + K_i z^\beta}$$

where  $z^\alpha \hat{=} N^\alpha / (N^\alpha + N^\beta)$  and  $z^\beta \hat{=} N^\beta / (N^\alpha + N^\beta)$  are the phase fractions and  $z_i \hat{=} N_i / N$  is the total (feed) mole fraction of component  $i$ . Note that the right hand sides of Eqs. 7.3 and 7.4 contain a single unknown variable  $z^\alpha$ , or equivalently  $z^\beta = 1 - z^\alpha$ . Definition-wise  $\sum_i^n x_i = 1$  in both phases and it is possible to solve for  $z^\alpha$  from Eq. 7.3 or 7.4, but practical experience

<sup>a</sup> H. H. Rachford and J. D. Rice. *Trans. Am. Inst. Min., Metall. Pet. Eng.*, 195:327–328, 1952.

proves that the algorithm is more stable when the symmetric condition  $f(z^\alpha) = \sum_{i=1}^n (x_i^\alpha - x_i^\beta) = 0$  is being used. Summing up  $x_i^\alpha$  and  $x_i^\beta$  from Eqs. 7.3 and 7.4 yields

$$f(z^\alpha) = \sum_{i=1}^n \frac{(1-K_i)z_i}{z^\alpha + K_i z^\beta} = \sum_{i=1}^n f_i z_i = 0$$

$$f_i \hat{=} \frac{1-K_i}{z^\alpha + K_i z^\beta}$$

which is easily solved with respect to  $z^\alpha$  using a Newton–Raphson iteration:

$$(7.5) \quad z^{\alpha,k+1} = z^{\alpha,k} - \left(\frac{\partial f}{\partial z^\alpha}\right)^{-1} f = z^{\alpha,k} + \left(\sum_{i=1}^n f_i^2 z_i\right)^{-1} f$$

The recursion formula makes a new  $z^{\alpha,k+1}$  available, which on substitution into Eqs. 7.3 and 7.4 produces new values of  $x_i^\alpha$  and  $x_i^\beta$ . These updates (hopefully) improve the  $K_i$ -values, and subsequent iterates in Eq. 7.5 converge finally to the equilibrium state.

§ 38 Computerise the function  $[\mathbf{x}^\alpha, \mathbf{x}^\beta, z^\alpha] = \text{TpKvalue}(\mathbf{n}, \mathbf{k})$  using Eq. 7.5 as your reference algorithm.

R –R . See Matlab function 2.2 in Appendix F. Note that the function interface is more elaborate than has been asked for in the text. The syntax has notably been extended to  $\text{TpKvalue}(\mathbf{n}, \mathbf{k}, u, \mathbf{U}, v, \mathbf{V})$  where  $\mathbf{U}$  and  $\mathbf{V}$  are data structures transmitting model specific parameters used by  $u$  and  $v$ . This makes it possible to iterate on non-ideal equilibrium states by supplying two fugacity (activity) coefficient models  $u$  and  $v$ . The update of  $K_i$  assumes for each iteration that  $\ln \mathbf{k}^{k+1} = \ln \mathbf{k} + u(\mathbf{x}^\alpha, \mathbf{U}) - v(\mathbf{x}^\beta, \mathbf{V})$ . Constant  $K_i$  values will be assumed if the functions  $u$  and  $v$  are expelled from the argument list. □

Note that  $\partial f / \partial z^\alpha < 0$  in Eq. 7.5 except for the degenerated case  $K_i = 1 \forall i \in [1, n]$  then  $\partial f / \partial z^\alpha = 0$ . A fixed derivative sign means that there is at most one solution in the domain  $z^\alpha \in [0, 1]$ . Similar to the Newton method, which is derived in Section 2, the number of floating point operations in the update of  $x^\alpha$  is proportional to  $n$ , i.e. the computation time increases linearly with the number of components in the system. These are the strengths of the  $K$ -value method, but it has also an inherent weakness in that *non-ideal* equilibria must be solved by nested iteration. First, Eq. 7.5 is solved with respect to  $z^\alpha$  at given or estimated  $K_i$  (inner loop). The phase compositions are then updated by the Eqs. 7.3 and 7.4 before new  $K_i$ -values can be calculated (outer loop). The double iteration procedure is repeated until the phase compositions  $x_i^\alpha$  and  $x_i^\beta$  have converged. The Newton method in Section 2 is without this flaw because  $\Delta\mu_i$  (equivalent to  $K_i$ ) is updated in every iteration avoiding the outer loop<sup>a</sup>.

<sup>a</sup> Also applies to the  $K$ -value problem if disregarding the monotonic form of  $f(z^\alpha)$ .

## 2. Newton's method

Contrary to the  $K$ -value method of Rachford–Rice, the Newton method works at constant mass balance in every iteration. This requires a feasible starting point where  $\mathbf{n}^\alpha + \mathbf{n}^\beta = \mathbf{n}$  is fulfilled. The Newton iteration of Eq. 7.1 is then,

$$\begin{aligned} \mu_i^\alpha + \sum_{j=1}^n \left( \frac{\partial \mu_i^\alpha}{\partial N_j^\alpha} \right)_{T,p,N_{l \neq j}} \Delta N_j^\alpha &= \mu_i^\beta + \sum_{j=1}^n \left( \frac{\partial \mu_i^\beta}{\partial N_j^\beta} \right)_{T,p,N_{l \neq j}} \Delta N_j^\beta \\ -\Delta N_j^\beta &= \Delta N_j^\alpha \end{aligned}$$

or on matrix form:

$$\begin{aligned} \boldsymbol{\mu}^\alpha + \mathbf{G}^\alpha \Delta \mathbf{n}^\alpha &= \boldsymbol{\mu}^\beta + \mathbf{G}^\beta \Delta \mathbf{n}^\beta \\ -\Delta \mathbf{n}^\beta &= \Delta \mathbf{n}^\alpha \end{aligned}$$

Matrix  $\mathbf{G} \hat{=} \{(\partial^2 G / \partial N_i \partial N_j)_{T,p}\}$  is the Hessian<sup>a</sup> of Gibbs energy and  $\Delta \mathbf{n} = \mathbf{n}^{k+1} - \mathbf{n}^k$  is the composition difference between two (subsequent) iterations  $k + 1$  and  $k$ . The Newton equations can be combined into

$$(\mathbf{G}^\alpha + \mathbf{G}^\beta) \Delta \mathbf{n}^\alpha = -(\boldsymbol{\mu}^\alpha - \boldsymbol{\mu}^\beta)$$

or even better:  $\Delta \mathbf{n}^\alpha = -\mathbf{H}^{-1} \Delta \boldsymbol{\mu}$  where  $\mathbf{H} \hat{=} \mathbf{G}^\alpha + \mathbf{G}^\beta$  and  $\Delta \boldsymbol{\mu} \hat{=} \boldsymbol{\mu}^\alpha - \boldsymbol{\mu}^\beta$ . It must be realised, however, that the algorithm has to be guided. In particular the mole number updates must be checked for  $\mathbf{n}^{\alpha,k+1} = \mathbf{n}^{\alpha,k} + \Delta \mathbf{n}^\alpha > \mathbf{0}$  and  $\mathbf{n}^{\beta,k+1} = \mathbf{n}^{\beta,k} - \Delta \mathbf{n}^\alpha > \mathbf{0}$ . If the relations are violated it is mandatory to shorten the step size according to

$$(7.6) \quad \Delta \mathbf{n}^\alpha = -\tau \mathbf{H}^{-1} \Delta \boldsymbol{\mu}$$

where  $\tau \in \langle 0, 1 \rangle$  is calculated such that all the updated mole numbers are positive. In this way we can ensure that the mass balance is fulfilled in every iteration. The Newton method converges to a state where  $\Delta \boldsymbol{\mu} = \mathbf{0}$ , but note that the phase models have not been taken into account yet. It must therefore be anticipated that  $\Delta \boldsymbol{\mu}$  is calculated from an equation of state, or an activity model, that describes the system with sufficient accuracy.

The calculation of  $\mathbf{H}$  may be approximated by the Hessian of an ideal mixture. The convergence properties will deteriorate close to the solution compared to the rigorous implementation of  $\mathbf{H} = \mathbf{G}^\alpha + \mathbf{G}^\beta$ , but the simplicity of the model makes it interesting in its own right. In summary it means that ideal mixing is assumed in the calculation of  $\mathbf{H}$  while  $\Delta \boldsymbol{\mu}$  is calculated rigorously.

<sup>a</sup> Ludwig Otto Hesse, 1811–1874. German mathematician.

From the definition of an ideal mixture we can write,

$$\begin{aligned}\mathbf{G}^{\text{id}}_{ij} &= \left(\frac{\partial \mu_i^{\text{id}}}{\partial N_j}\right)_{T,p,N_{k \neq j}} = \frac{\partial}{\partial N_j} \left(\mu_i^{\star} + RT \ln \frac{N_i}{N}\right)_{T,p,N_{k \neq j}} \\ &= \frac{NRT}{N_i} \left(\frac{\partial(N_i/N)}{\partial N_j}\right)_{N_{k \neq j}} \\ &= RT \left(\frac{\delta_{ij}}{N_i} - \frac{1}{N}\right)\end{aligned}$$

where the Kronecker<sup>a</sup>  $\delta_{ij} = 1$  if  $i = j$  and  $\delta_{ij} = 0$  else. On matrix form this formula is written — see also Paragraph **Hessian** in Chapter **Prelude**:

$$\begin{aligned}\mathbf{G}^{\text{id}} &= RT(\mathbf{n}^{-\text{D}} - N^{-1}\mathbf{e}\mathbf{e}^{\text{T}}) \\ \mathbf{e} &= (1, 1, \dots, 1)^{\text{T}}\end{aligned}$$

Here,  $\mathbf{n}^{-\text{D}}$  is an (inverted) diagonal matrix having  $1/N_i$  along the main diagonal. The simple structure of this matrix makes it possible to calculate  $\mathbf{H}^{-1}$  with an analytical formula as shown below. From the definition  $\mathbf{H} \triangleq \mathbf{G}^{\alpha} + \mathbf{G}^{\beta}$  it follows:

$$\mathbf{H}^{\text{id}} = RT[(\mathbf{n}^{\alpha})^{-\text{D}} + (\mathbf{n}^{\beta})^{-\text{D}} - ((N^{\alpha})^{-1} + (N^{\beta})^{-1})\mathbf{e}\mathbf{e}^{\text{T}}]$$

The matrix  $(\mathbf{n}^{\alpha})^{-\text{D}} + (\mathbf{n}^{\beta})^{-\text{D}}$  has diagonal elements  $(N_i^{\alpha})^{-1} + (N_i^{\beta})^{-1} = N_i/(N_i^{\alpha} N_i^{\beta})$  and the factor  $(N^{\alpha})^{-1} + (N^{\beta})^{-1}$  can be rewritten to  $(N^{\alpha} + N^{\beta})/(N^{\alpha} N^{\beta})$ . This makes the following factorisation of  $\mathbf{H}^{\text{id}}$  possible:

$$\mathbf{H}^{\text{id}} = RT \frac{N^{\alpha} + N^{\beta}}{N^{\alpha} N^{\beta}} \left[ \text{diag} \left( \frac{N^{\alpha} N^{\beta}}{N_i^{\alpha} N_i^{\beta}} \frac{N_i}{(N^{\alpha} + N^{\beta})} \right) - \mathbf{e}\mathbf{e}^{\text{T}} \right]$$

or,

$$(7.7) \quad \begin{aligned}\frac{N^{\alpha} + N^{\beta}}{RT} \mathbf{H}^{\text{id}} &= \frac{1}{z^{\alpha} z^{\beta}} (\mathbf{D}^{-1} - \mathbf{e}\mathbf{e}^{\text{T}}) \\ \mathbf{D}^{-1} &\triangleq \text{diag} \left( \frac{z_i}{x_i^{\alpha} x_i^{\beta}} \right)\end{aligned}$$

where  $z^{\alpha}$  and  $z^{\beta}$  are phase fractions,  $x_i^{\alpha}$  and  $x_i^{\beta}$  are component mole fractions, and  $z_i$  is the feed mole fraction of component  $i$ . Eq. 7.7 indicates that  $\mathbf{H}$  is a rank one update of  $\mathbf{D}$ . The inverse of  $\mathbf{H}$  can then be calculated from the Sherman–Morrison formula  $(\mathbf{D}^{-1} - \mathbf{e}\mathbf{e}^{\text{T}})^{-1} = \mathbf{D} + (1 - \mathbf{e}^{\text{T}}\mathbf{D}\mathbf{e})^{-1}\mathbf{D}\mathbf{e}\mathbf{e}^{\text{T}}\mathbf{D}$ , or, equivalently, if we define  $\mathbf{d} \triangleq \mathbf{D}\mathbf{e}$ :

$$(7.8) \quad \frac{RT}{N^{\alpha} + N^{\beta}} (\mathbf{H}^{\text{id}})^{-1} = z^{\alpha} z^{\beta} (\mathbf{D} + (1 - \mathbf{e}^{\text{T}}\mathbf{d})^{-1}\mathbf{d}\mathbf{d}^{\text{T}})$$

From Eqs. 7.6 and 7.8 it is possible to express the simplified two-phase Newton method as

$$(7.9) \quad \frac{\Delta \mathbf{n}^{\alpha}}{N^{\alpha} + N^{\beta}} = -z^{\alpha} z^{\beta} (\mathbf{D} + \frac{1}{1 - \mathbf{d}^{\text{T}}\mathbf{e}} \mathbf{d}\mathbf{d}^{\text{T}}) \frac{\Delta \mu}{RT}$$

Note that  $z^{\alpha}$ ,  $z^{\beta}$ ,  $\mathbf{d}$ ,  $\mathbf{D}$  and  $\Delta \mu / RT$  are dimensionless variables. This makes the iteration sequence independent of the system size for a given total composition

<sup>a</sup> Leopold Kronecker, 1823–1891. German mathematician.


z. We may therefore scale the system<sup>a</sup> such that  $N^\alpha + N^\beta = 1$  without affecting the mole fractions in the phases  $\alpha$  and  $\beta$ .

§ 39 The Sherman–Morrison formula is widely applicable and not at all limited to thermodynamic problems. Verify the formula by proving that  $\mathbf{H}^{-1}\mathbf{H} = \mathbf{I}$ . Attempt to find a more general formula valid for  $(\mathbf{A} - \mathbf{u}\mathbf{v}^T)^{-1}$ .

S  $-\mathbf{M}$  . Pure substitution. The general formula for rank one updates is:  $(\mathbf{A} - \mathbf{u}\mathbf{v}^T)^{-1} = \mathbf{A}^{-1} + \mathbf{A}^{-1}\mathbf{u}(1 - \mathbf{v}^T\mathbf{A}^{-1}\mathbf{u})^{-1}\mathbf{v}^T\mathbf{A}^{-1}$ .  $\square$

§ 40 Computerise the function  $[\mathbf{x}^\alpha, \mathbf{x}^\beta, z^\alpha] = \text{TpNewton}(\mathbf{n}, \mathbf{k})$  using Eq. 7.9 as your reference algorithm.

N . See Matlab function 2.3 in Appendix F. Note that the function interface is more elaborate than has been asked for in the text. The syntax has notably been extended to  $\text{TpNewton}(\mathbf{n}, \mathbf{k}, u, \mathbf{U}, v, \mathbf{V})$  where  $\mathbf{U}$  and  $\mathbf{V}$  are data structures transmitting model specific parameters used by  $u$  and  $v$ . This makes it possible to iterate on non-ideal equilibrium states by supplying two fugacity (activity) coefficient models  $u$  and  $v$ . The update of  $\Delta\boldsymbol{\mu}$  assumes that for each iteration  $\Delta\boldsymbol{\mu} = \Delta\boldsymbol{\mu}^{\text{ld}} + \Delta\boldsymbol{\mu}^{\text{r,p}}$  where  $\Delta\boldsymbol{\mu}^{\text{ld}} = \ln \mathbf{k} + \ln \mathbf{x}^\alpha - \ln \mathbf{x}^\beta$  and  $\Delta\boldsymbol{\mu}^{\text{r,p}} = u(\mathbf{x}^\alpha, \mathbf{U}) - v(\mathbf{x}^\beta, \mathbf{V})$ . Constant  $\Delta\boldsymbol{\mu}^{\text{r,p}} = \mathbf{0}$  will be assumed if the functions  $u$  and  $v$  are expelled from the argument list.  $\square$

It should be mentioned that the number of floating point operations in the update is proportional to  $n$ . Hence, the computation time increases linearly with the number of components in the mixture. However, if we had not spent time on the Sherman–Morrison formula, but rather used numerical inversion of  $\mathbf{H}$  in each iteration, the computation time would be proportional to  $n^3$ . 

### 3. Chemical potential versus $K$ -value

The Rachford–Rice procedure spends time on calculating  $K$ -values while the Newton method deals directly with chemical potentials. However, because the two methods aim at solving the same problem there must be a rational connection between them. The purpose of this section is to show that (and how) Eq. 7.1 on page 61 can be used to derive some useful relations between  $K_i$  and  $\Delta\mu_i$ .

**3.1. Equal fugacity models in both phases.** For fluid  $p(V, T)$  equations of state  $\mu_i^\circ(T, p_\circ)$  is defined as the chemical potential of a pure ideal gas at the temperature  $T$  and pressure  $p_\circ$ . The same standard state applies to both of the phases and from  $\mu_i^\alpha = \mu_i^\beta$  it is conventionally written

$$\mu_i^\circ + RT \ln \left( \frac{\varphi_i^\alpha x_i^\alpha p}{p_\circ} \right) = \mu_i^\circ + RT \ln \left( \frac{\varphi_i^\beta x_i^\beta p}{p_\circ} \right)$$

<sup>a</sup> This is just another example on the special properties of extensive functions.

where the left side stands for  $\mu_i^\alpha$  and the right side stands for  $\mu_i^\beta$ . The quantity  $\Delta\mu_i/RT$  which appears in Eq. 7.9 is then

$$(7.10) \quad \frac{\Delta\mu_i}{RT} \triangleq \frac{\mu_i^\alpha - \mu_i^\beta}{RT} = \ln\left(\frac{K_i^{\text{eos}} x_i^\alpha}{x_i^\beta}\right)$$

where  $K_i^{\text{eos}}$  is defined as the ratio between the fugacity coefficients  $\varphi_i^\alpha$  and  $\varphi_i^\beta$ :

$$(7.11) \quad K_i^{\text{eos}} = \frac{\varphi_i^\alpha}{\varphi_i^\beta}$$

The  $K$ -value concept<sup>a</sup> is therefore quite misleading —  $K_i(T, p, \mathbf{x}^\alpha, \mathbf{x}^\beta)$  is in fact a non-linear function in temperature, pressure and the compositions of both phases.

§ 41 Find experimental data for a typical hydrocarbon vapour–liquid system and see how close the RK equation of state matches the measurements. Calculate the phase diagram using TpKvalue or TpNewton.

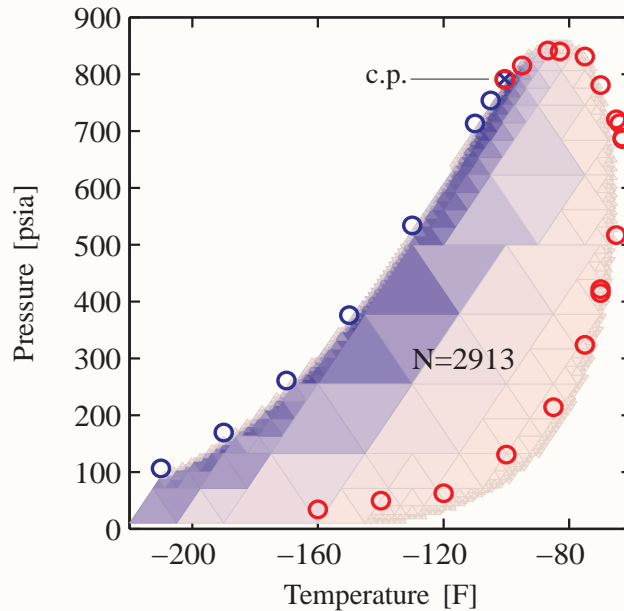
N . The phase diagram of a typical, albeit synthetic, natural gas<sup>b</sup> is illustrated in Figure 7.1 on the next page. The plot is given a high colour density where the liquid and vapour phases coexist in approximately equal amounts, and a light colour near the single-phase region (vapour or liquid). The dense ridge running along the left edge of the diagram combined with the shallow basin to the right is typical for methane-rich natural gases. The bubble point is dominated by the large methane content while the dew point is determined by the trace components comprising the “heavy tail” of the gas.

The Newton method does an excellent job in this case<sup>c</sup>, but note that the dew-point calculations are sensitive to the start estimate. Increasing the liquid composition of the medium components by less than one tenth of a mole fraction causes the rightmost part of the phase boundary to be left out. The  $K$ -value method has even larger problems in this part of the diagram, and needs some type of guidance which is not implemented here. □

In the days before the modern computer technology it was mandatory to make physical simplifications before any numerical calculation was attempted. One of these simplifications is known as the Lewis mixing rule. Under certain circumstances the fugacity coefficient  $\varphi_i$  will be almost independent of the mixture composition. This is always true for an ideal gas mixture and it is valid to a high degree of approximation for real gases at low pressures or high temperatures. The approximation also holds at high pressures if  $\Delta V^{\text{ex}} \approx 0$  in

<sup>a</sup> As an equilibrium constant of some kind. <sup>b</sup> Mario H. Gonzalez and Anthony L. Lee. *J. Chem. Eng. Data*, 13(2):172–176, April 1968. <sup>c</sup> Far better than anticipated. In fact, it does a better job than for a rigorous implementation of the Hessian. The reason for this somewhat strange behaviour is that the eigenvalues of the simplified Hessian are strictly positive while the eigenvalues of the rigorous Hessian change sign wherever thermodynamic instability occurs, see Chapter 8. This is known to cause numerical problems in Newton methods. <sup>c</sup> Mario H. Gonzalez and Anthony L. Lee. *J. Chem. Eng. Data*, 13(2):172–176, April 1968.





**FIGURE 7.1** Phase diagram of Nitrogen–Methane–Ethane–Propane– $n$ -Butane put together from a total of 6093 triangular patches. Experimental dew and bubble points are taken from<sup>a</sup>.

the entire pressure and composition region. In the case of  $\varphi_i(T, p, \mathbf{x}) \approx \varphi_i^*(T, p)$  then  $K_i$  will be constant in Eq. 7.11 (at a given temperature and pressure). The  $K$ -value method is then superior to the Newton iteration because it solves the entire equilibrium problem in  $\mathbb{R}^1$  and not in  $\mathbb{R}^n$ .

§ 42 Show that the Lewis mixing rule is exact if  $V^{\text{ex}} = 0$  over the entire composition and pressure  $[0, p]$  range.

L .  $V^{\text{ex}} = 0$  means that  $V = \sum_{i=1}^n v_i(T, p)N_i$ . The fugacity coefficient is defined by the Eqs. 6.12 and 6.13, see page 53. Substituted for the Lewis rule we get

$$RT \ln \varphi_i^{\text{Lewis}} = \int_0^p \left( v_i(T, p) - \frac{RT}{p} \right) dp = f(T, p)$$

which shows that  $\varphi_i$  depends on temperature and pressure only (because the partial molar volume is independent of composition).  $\square$

**3.2. Equal activity models in both phases.** In Eq. 7.11 it is common that  $\alpha$  is the liquid phase and  $\beta$  the vapour phase, but it is important to understand that this is just one out of many possibilities. We could alternatively let  $\alpha$  and  $\beta$  be two near-critical fluids (fluid means something in between vapour and liquid) or two sub-cooled liquid phases. There are also examples on gas–gas equilibria in the literature. In a thermodynamic sense there is no fundamental

difference between a vapour phase and a liquid phase<sup>a</sup>, but it is easy to decide whether the phases are of the same *type* by looking at the pure component states in the system. If the chemical potentials of the *pure* components are the same in both phases, at the temperature and pressure of the system, it can be concluded that the phases are of the same nature. If this is the case it is no longer necessary to integrate all the way from the ideal gas in Eq. 7.11 but rather use the pure component properties as a reference. In practise this means that the *fugacity coefficients* can be replaced by *activity coefficients*:

$$K_i^{\text{eos}} = \frac{\varphi_i^\alpha}{\varphi_i^\beta} \hat{=} \frac{\gamma_i^\alpha \varphi_i^{\star,\alpha}}{\gamma_i^\beta \varphi_i^{\star,\beta}}$$

Provided the same activity model is used to describe both phases the  $K_i$ -values are

$$\varphi_i^{\star,\alpha} = \varphi_i^{\star,\beta} \quad \Rightarrow \quad K_i^{\text{eos}} = K_i^{\text{ex}} = \frac{\gamma_i^\alpha}{\gamma_i^\beta}$$

because the pure component reference  $\varphi_i^\star$  is the same in both phases.

§ 43 Find experimental data for a ternary liquid–liquid system with known NRTL, van Laar or Margules model parameters. Select a system which has a fairly large solubility region and a critical end-point inside the ternary region. Use TpNewton to calculate the phase diagram.

C – – . The phase diagram of cyclohexane–cyclopentane–methanol<sup>b</sup> is illustrated in Figure 7.2 on the facing page. It is a classic liquid–liquid diagram—quite symmetric and with a critical end-point inside the triangle. The diagram was successfully calculated using TpNewton, see Matlab program 1.4 in Appendix F. In this case the measurements were used as start values and the calculations converge without difficulties. The agreement between the measured and the calculated values is otherwise extremely good. Still, the  $K$ -value method experiences serious problems close to the critical point. □

**3.3. Mixed use of fugacity and activity models.** In some cases it may be appropriate to employ an equation of state for the vapour phase and an activity model for the condensed phase. The standard state of the two phases will be different and the phase diagram will in general not be “closed” at the critical point. On the other hand, hybrid models have greater flexibility and are favourable in the modelling of complex liquids and crystal phases. The starting point is Eq. 7.1 on page 61 which in this case gives:

$$(7.12) \quad \mu_i^\star(T, p) + RT \ln(\gamma_i x_i^\alpha) = \mu_i^\circ(T, p_\circ) + RT \ln\left(\frac{\varphi_i x_i^\beta p}{p_\circ}\right)$$

<sup>a</sup> It is intuitive that the density of the vapour phase has to be lower than the density of the liquid phase, but this is wrong. At high pressures the system H<sub>2</sub>–He will in fact invert because the vapour phase is dominated by He which has a higher molecular weight than H<sub>2</sub>. <sup>b</sup> Ternary systems. In *Liquid–Liquid Equilibrium Data Collection*, volume V, part 2., DECHEMA, Frankfurt/Main, 1980. p. 115.

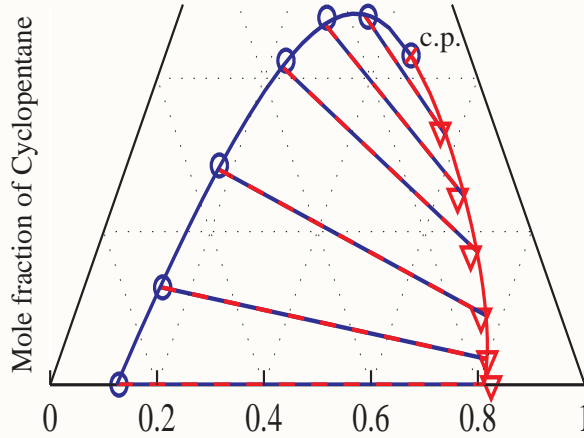


FIGURE 7.2 Phase diagram of Methanol–Cyclopentane–Methanol–Cyclopentane–Methanol at 298.15 K and 760 mmHg.

The left hand side denotes  $\mu_i^\alpha$  and the right hand side  $\mu_i^\beta$ . The standard state of  $\beta$  is assumed to be pure ideal gas at the temperature  $T$  and standard pressure  $p^\circ$ . The reference state of phase  $\alpha$  is in principle a function of temperature, pressure and composition, but in most cases a pure component reference is used where  $\lim \gamma_i = 1.0$  as  $p \rightarrow p_i^{\text{sat}}$ , i.e. the reference pressure is set equal to the saturation pressure of component  $i$ :

$$(7.13) \quad \mu_i^*(T, p_i^{\text{sat}}) = \mu_i^\circ + RT \ln \left( \frac{\varphi_i^{\text{sat}} p_i^{\text{sat}}}{p^\circ} \right)$$

In order to calculate  $\mu_i^*$  at  $p \neq p_i^{\text{sat}}$  it is necessary to integrate  $(\partial \mu_i^* / \partial p)_{T,n} = v_i^*$  from the saturation pressure  $p_i^{\text{sat}}$  to the system pressure  $p$ . The pure component volume  $v_i^*$  is usually a weak function of pressure, which makes it sensible to use  $v_i^* \approx v_i^{\text{sat}}(T)$  or maybe  $v_i^* \approx v_i(T^\circ, p^\circ)$  because most condensed phases (liquid as well as solids) are comparatively incompressible<sup>a</sup>. A useful estimate of  $\mu_i^*(T, p)$  is

$$(7.14) \quad \mu_i^*(T, p) = \mu_i^*(T, p_i^{\text{sat}}) + \int_{p_i^{\text{sat}}}^p v_i^* dp \approx \mu_i^*(T, p_i^{\text{sat}}) + v_i^{\text{sat}}(p - p_i^{\text{sat}})$$

which is substituted into Eq. 7.13 and finally combined with the equilibrium relation in Eq. 7.12. The result is:

$$\mu_i^\circ + RT \ln \left( \frac{\varphi_i^{\text{sat}} p_i^{\text{sat}} \gamma_i x_i^\alpha}{p^\circ} \right) + v_i^{\text{sat}}(p - p_i^{\text{sat}}) \approx \mu_i^\circ + RT \ln \left( \frac{\varphi_i x_i^\beta p}{p^\circ} \right)$$

$\Delta \mu_i / RT$  from the Newton algorithm in Eq. 7.9 may now be written on the same form as in Eq. 7.10 provided  $K_i$  is calculated as

$$(7.15) \quad K_i^{\text{vle}} = \frac{\varphi_i^{\text{sat}} p_i^{\text{sat}} \gamma_i}{\varphi_i p} \exp \left( \frac{v_i^{\text{sat}}(p - p_i^{\text{sat}})}{RT} \right)$$

<sup>a</sup> Provided we stay clear off the critical point.

The exponential term is known as the Poynting<sup>a</sup>-factor of  $K_i$ . This factor is often neglected at low pressures, but only if  $K_i \neq 1$ . If this is not true the Poynting-factor may dominate  $K_i$  down to 5 – 10 bar.

**R**      . For an approximately pure liquid component  $i$  it is reasonable to set  $\varphi_i = \varphi_i^{\text{sat}}$ ,  $\gamma_i = 1$  and  $p = p_i^{\text{sat}}$ . The mixture is by definition ideal and  $K_i$  appears to be a simple function of temperature and pressure:

$$K_i^{\text{raoult}} = \lim_{x_i \rightarrow 1} K_i^{\text{vle}} = \frac{p_i^{\text{sat}}}{p} \quad \square$$

**H**      . In the same mixture it may also be appropriate to use a *hypothetical* vapour pressure  $H_{ji}$  for all diluted components  $j$ , the value of which is chosen such that the phase equilibrium is reproduced faithfully:

$$K_j^{\text{henry}} = \lim_{x_j \rightarrow 0} K_j^{\text{vle}} = \frac{H_{ji}}{p} \quad \square$$

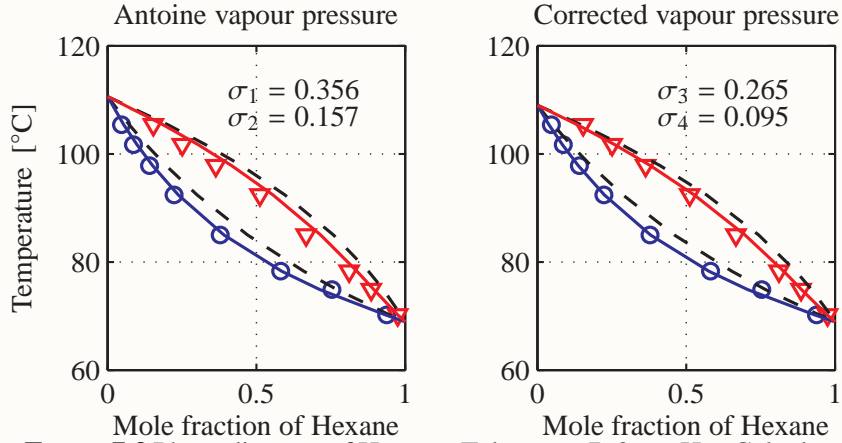
§ 44 Find experimental data for a close to ideal binary vapour–liquid system with known NRTL, Wilson, van Laar or Margules model parameters. Use `TpKvalue` or `TpNewton` to calculate the phase diagram. Comment on the practical applicability of Raoult’s law versus the accuracy of pure component data.

**H**      . The phase diagram of hexane–toluene<sup>b</sup> is illustrated in Figure 7.3 on the facing page. The calculations make use of the Matlab program 1.5 in Appendix F. The system is almost ideal, but there are nevertheless some notable deviations between the experimental and the calculated values. Correcting for non-ideality makes some improvement (compare  $\sigma_1$  and  $\sigma_2$  in the left subfigure), but the largest error is actually hidden in the vapour pressure of toluene. By increasing the vapour pressure 2% the agreement is improved even further (compare  $\sigma_3$  and  $\sigma_4$  in the right subfigure), while the Raoult’s law still shows a significant deviation. This shows that Raoult’s law is of limited value even for nearly ideal systems. In fact, the pure component parameters are maybe more important for the mixture properties than the phase model itself. □

**3.4. Mixed use of activity models in the phases.** When  $\alpha$  and  $\beta$  are condensed phases it is often appropriate to neglect the influence of pressure on the system properties. This is quite typical for metallurgical melts and refractory systems where the process conditions are close to atmospheric. In general, pressure explicit equations of state are not conceivable for these systems and activity models are often used for both phases:

$$(7.16) \quad \mu_i^{*,\alpha}(T) + RT \ln(\gamma_i^\alpha x_i^\alpha) = \mu_i^{*,\beta}(T) + RT \ln(\gamma_i^\beta x_i^\beta)$$

<sup>a</sup> John Henry Poynting, 1852–1914. English physicist. <sup>b</sup> Aliphatic hydrocarbons: C<sub>4</sub>–C<sub>6</sub>. In *Vapor–Liquid Equilibrium Data Collection*, volume I, part 6a., DECHEMA, Frankfurt/Main, 1980. p. 593.



**FIGURE 7.3** Phase diagram of Hexane–Toluene at 760 mmHg. Calculated curves show Raoult’s law (stippled) and van Laar activity (solid). The right subfigure shows the effect of increasing the vapour pressure of toluene by 2%. The sum-of-squares are denoted  $\sigma_1$ – $\sigma_4$ .

The reference state is usually chosen such that  $\lim \gamma_i = 1$  for  $x_i \rightarrow 1$ . At the melting<sup>a</sup> point  $T_i$  the following is true:

$$(7.17) \quad \mu_i^{*,\alpha}(T_i) = \mu_i^{*,\beta}(T_i)$$

In order to find  $\mu_i^{*,\beta}$  at  $T \neq T_i$  it is necessary to integrate  $(\partial \mu_i^{*,\beta} / \partial T)_{p,n} = -s_i^{*,\beta}$  from the melting temperature  $T_i$  to the system temperature  $T$ . The molar entropy of phase change depends on the temperature, but as a first approximation it can be assumed that  $\Delta s_i^* = (h_i^{*,\beta} - h_i^{*,\alpha}) / T_i$  is approximately constant for the phase transition  $\alpha \rightarrow \beta$ :

$$\begin{aligned}
 \mu_i^{*,\beta}(T) &= \mu_i^{*,\beta}(T_i) - \int_{T_i}^T s_i^{*,\beta} dT \\
 &= \mu_i^{*,\alpha}(T_i) - \int_{T_i}^T s_i^{*,\beta} dT + \int_{T_i}^T s_i^{*,\alpha} dT - \int_{T_i}^T s_i^{*,\alpha} dT \\
 &= \mu_i^{*,\alpha}(T) - \int_{T_i}^T \Delta s_i^* dT \\
 (7.18) \quad &\approx \mu_i^{*,\alpha}(T) - \frac{\Delta h_i^*}{T_i}(T - T_i)
 \end{aligned}$$

Note that Eq. 7.17 is used in the transposition from the first to the second line. The integral which is added and subtracted in the second line puts the expression on the wanted form after it has been combined with Eq. 7.16:

$$\mu_i^{*,\alpha}(T) + RT \ln(\gamma_i^\alpha x_i^\alpha) \approx \mu_i^{*,\alpha}(T) + RT \ln(\gamma_i^\beta x_i^\beta) - \frac{\Delta h_i^*}{T_i}(T - T_i)$$

<sup>a</sup> Or phase transition point if the two phases are solid.

$\Delta\mu_i/RT$  required by the Newton algorithm in Eq. 7.9 can finally be written as in Eq. 7.10 provided  $K_i$  is calculated as:

$$(7.19) \quad K_i^{\text{sle}} = \frac{\gamma_i^\alpha}{\gamma_i^\beta} \exp \left[ \frac{\Delta h_i^*}{R} \left( \frac{1}{T_i} - \frac{1}{T} \right) \right]$$

§ 45 Find experimental data for a binary alloy (or a binary salt) with full solubility in the solid phase. Choose a system with fitted Margules or Redlich–Kister model parameters. Calculate the phase diagram using TpNewton or TpKvalue. How important is the temperature dependency of  $\Delta s_i^*$  in this context?

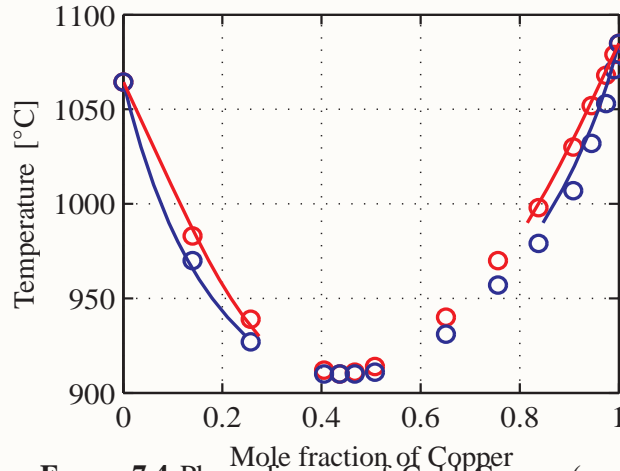
G –C . Figure 7.4 on the next page illustrates the high-temperature portion of the Gold–Copper<sup>a</sup> phase diagram, see Matlab program F1.6. The agreement between the measured and calculated values is generally good even though it is not possible to calculate the entire diagram — neither with TpNewton nor with TpKvalue. The problem is quite persistent, and although the starting values are chosen judiciously there is a substantial region around the congruence point where things go wrong. The flaw is due to the (large) negative deviations from ideality which is observed in the two phases. This does in turn cause an oscillatory iteration sequence. Quite surprisingly, maybe, because the phase calculations in Figure 7.2 on page 71 converges nicely over the entire composition range. However, the latter system benefits from having a positive deviation from ideality. The ideal Hessian matrix will then over-estimate the curvature of the energy surface and yield a conservative step size in TpNewton (and a safe, albeit very slow, convergence). With negative deviations from ideality the curvature is under-estimated and the step size may eventually grow so large that the iterations start oscillating around the solution point<sup>b</sup>. □

Concerning the accuracy of the calculations it is not easy to argue that  $\Delta s_i^*$  varies over the temperature domain. The simplification which is part of the pure component reference is dominated by the activity model, and the calculated phase diagram looks very promising. But, a single phase diagram is not sufficient to claim any kind of thermodynamic consistency. To do this we have to verify all types of calorimetric quantities, vapour pressures, cryoscopic measurements, etc. A systematic study at this level would indeed reveal the noted inconsistency, as well as several minor ones.

While azeotropes are common for vapour–liquid phase diagrams, the analogous phenomena of congruent melting is quite rare among the alloys — at least when disconnected from stoichiometry compound formation and phase separations in the solid phase<sup>c</sup>. It has nevertheless been chosen to present such an exotic system here to stress the fact that phase diagrams are classified according to their morphology, and that the calculation method is quite indepen-

<sup>a</sup> H. Okamoto, D. J. Chakrabarti, D. E. Laughlin, and T. B. Massalski. *Bull. Alloy Phase Diagrams*, 8(5):454–473, 1987. <sup>b</sup> An exact Hessian would stabilise the Newton method.

<sup>c</sup> The Gold–Copper system exhibits solid phase separation at  $T < 400$  °C.

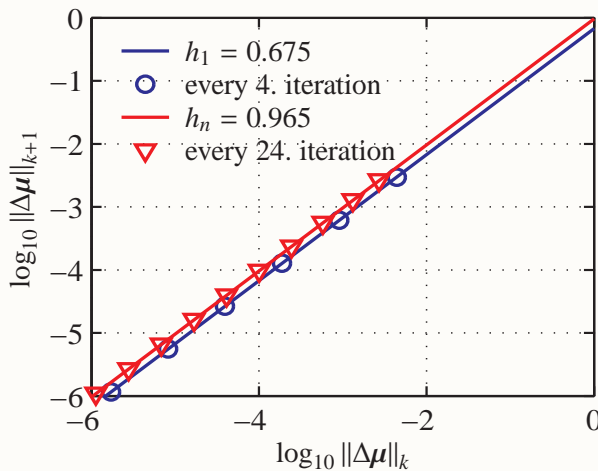


**FIGURE 7.4** Phase diagram of Gold-Copper (negative deviations from ideality). Both TpNewton and TpKvalue has convergence problems close to the azeotrope.

dent of the phase models. The thermodynamics of equilibrium systems makes no difference between vapour, liquid and solid phases in this regard<sup>a</sup>, but note that the number of model parameters can be quite substantial for a solid phase compared to what is expected for vapour and liquid phases. In the above case there are six binary parameters for the solid, but only three for the liquid.

#### 4. Convergence properties

A sequence of iterative calculations has (convergence) order  $m$  and (convergence) factor  $h$  if the sequence approximates  $\lim_{k \rightarrow \infty} \log \|\mathbf{x}^{k+1} - \mathbf{x}^\infty\| = \log(h) + m \log \|\mathbf{x}^k - \mathbf{x}^\infty\|$ . The  $K$ -value method is typically of first order, but



**FIGURE 7.5** Convergence properties of the Newton method when using an ideal Hessian in the calculation of the bottom ( $h_1$ ) and top ( $h_n$ ) tie-lines in Figure 7.2. The latter is close to the critical point. Solid lines illustrate 1st order convergence. Note that  $h \rightarrow 1$  for the near-critical point.

close to the critical point the convergence factor  $h \rightarrow 1$  and  $\mathbf{x}^{k+1} \simeq \mathbf{x}^k$ . Thus,

<sup>a</sup> Even though the equilibrium conditions 7.11, 7.15 and 7.19 look quite differently.

convergence is severely hampered and it may be difficult to decide whether the sequence converges or not. The iteration should therefore be accelerated along the most prominent eigendirection of the Jacobian. This is known as the *Dominant Eigenvalue Method*, see Appendix D.



The Newton method is of second order—details concerning the convergence factor is discussed in Appendix C. This means that the number of significant digits will double in each iteration provided that iteration  $k$  is sufficiently close to the solution point. The local convergence properties are irreplaceable, but the method needs quite good start estimates. Note also that the simplifications in Section 2 makes  $m = 1$  unless for ideal mixtures where the Hessian is exact. Figure 7.5 illustrates what influence the simplification has on the calculation of the bottom and top tie-lines of Figure 7.2. The iteration sequence approaches the  $45^\circ$  line which is typical for first order methods, and close to the critical point the convergence factor creeps toward 1, in the sense that  $h_n = 0.965$  is pretty close to unity in this context.



## CHAPTER 8

**Material Stability**

The question of material stability is crucial to the understanding of complex phase behaviour, and, as an indispensable analysis tool, to the calculation of thermodynamic equilibrium states. It turns out, however, that the subject is quite complex and that a full theoretical contemplation requires a rather abstract notation. In order to achieve a good understanding of the basic concepts without sacrificing too much physical insight we shall therefore restrict the analysis to  $U$ , and possibly its Legendre transforms  $A$ ,  $H$  and  $G$ , but it is stressed that similar analyses could be carried out based on  $S$ ,  $V$ , etc.

**1. Global stability**

The starting point is a closed system withheld at constant entropy, volume and composition, the internal energy of which is  $U(\mathbf{x})$  where  $\mathbf{x}^T = (S, V, N_1, \dots, N_n)$ . The system can be a single phase, it is maybe easier to grasp the theory then, but this is not required. No changes are needed for multi-phase systems. A new phase with state vector  $\mathbf{y} \in \Omega \mid \mathbf{0} < \mathbf{y} < \mathbf{x}$  is tentatively formed within the system boundary. Of particular interest to us is the change in internal energy  $\Delta U(\mathbf{x}, \mathbf{y}) \hat{=} U(\mathbf{y}) + U(\mathbf{x} - \mathbf{y}) - U(\mathbf{x})$  caused by the phase formation. A perturbation in  $U(\mathbf{x})$  combined with an Euler integration of  $U(\mathbf{y})$  yields<sup>a</sup>:

$$(8.1) \quad \begin{aligned} \Delta U(\mathbf{x}, \mathbf{y}) &= U_{\mathbf{y}} \cdot \mathbf{y} - U_{\mathbf{x}} \cdot \mathbf{y} + \frac{1}{2!} U_{\mathbf{xx}} \cdot \mathbf{y} \cdot \mathbf{y} - \frac{1}{3!} U_{\mathbf{xxx}} \cdot \mathbf{y} \cdot \mathbf{y} \cdot \mathbf{y} + \dots \\ &\hat{=} \tilde{U} + \sum_{k=2} \frac{(-1)^k}{k!} \delta^k U \end{aligned}$$

The following shorthand notation has been adopted to ease the writing<sup>b</sup>:

$$\delta^k U = U_{\mathbf{x}}^k \cdot \mathbf{y}^k = U_{\mathbf{x} \dots \mathbf{x}} \cdot \mathbf{y} \cdots \mathbf{y} = \sum_{j=1}^n \cdots \sum_{i=1}^n \frac{\partial^k U}{\partial x_i \cdots \partial x_j} y_i \cdots y_j$$

The tangent plane function  $\tilde{U} \hat{=} (U_{\mathbf{y}} - U_{\mathbf{x}}) \cdot \mathbf{y}$  defined in 8.1 is instrumental to the *global* stability analysis elucidated below, while  $\delta^2 U$ ,  $\delta^3 U$ , etc. are factors closely related to the *local* instabilities known as spinodal, critical, and tricritical points. The exact conditions for these states are quite elaborate and will be pursued in the next section.

<sup>a</sup> Direct Euler integration is also possible:  $\Delta U = (U_{\mathbf{y}} - U_{\mathbf{x}-\mathbf{y}}) \cdot \mathbf{y} - (U_{\mathbf{x}} - U_{\mathbf{x}-\mathbf{y}}) \cdot \mathbf{x}$  <sup>b</sup> The inner product  $\cdot$  binds to the left operand thereby avoiding nested parentheses.

To prove that the system is in global equilibrium it must be verified that  $\Delta U(\mathbf{x}, \mathbf{y}) \geq 0$ ,  $\forall \mathbf{y} \in \Omega$ , but it is not needed to scan the entire function domain; the system is globally stable if all the *stationary* values of  $\Delta U$  fulfil the positive sign restriction. A necessary condition for the stationary state is  $(\partial \Delta U / \partial \mathbf{y}) = \mathbf{0}$  which in the current context translates to  $U_{\mathbf{y}} = U_{\mathbf{x}-\mathbf{y}}$ <sup>a</sup>. Substituted into the Euler integrated form of  $\Delta U$ , see footnote on the previous page, this gives the ultimate stability criterion  $(U_{\mathbf{y}} - U_{\mathbf{x}}) \cdot \mathbf{x} \geq 0$  and the equilibrium state is correctly located as the lowest of all feasible tangent planes. However, it does not hint at *how* or *where* the calculations should be started. Note that there may be several phases  $\mathbf{y}_i$  and each phase has in general a finite *region of attraction*<sup>b</sup>.

To investigate this problem further let  $\{\mathbf{y}_0, \mathbf{y}_1, \dots, \mathbf{y}_m\}$  be the set of all stationary states<sup>c</sup>. But, how can we determine this set? There is no definite answer and we shall therefore look explicitly for regions where the stability criterion is violated. Let  $s_i \in [0, 1]$  be a distance parameter and  $\Delta U(s_i) = U(s_i \mathbf{y}_i) + U(\mathbf{x} - s_i \mathbf{y}_i) - U(\mathbf{x})$  the parametrised internal energy change. The values  $s_i = 0$  and  $s_i = 1$  correspond to the system  $\mathbf{x}$  and to the stationary state  $\mathbf{y}_i$  respectively. A Taylor series of  $\Delta U$  in the parameter  $s_i$  can be written

$$\begin{aligned} \Delta U(s_i) &= s_i(U_{\mathbf{y}_i} - U_{\mathbf{x}}) \cdot \mathbf{y}_i + \frac{1}{2} s_i^2 U_{\mathbf{x}-\alpha_i \mathbf{y}_i}^2 \cdot \mathbf{y}_i^2 \\ &\hat{=} s_i \tilde{U}_i + \frac{1}{2} s_i^2 Q(\mathbf{x}, \alpha_i \mathbf{y}_i) \end{aligned}$$

where the quadratic  $Q$  is a representative for Lagrange's Taylor Series Remainder. If the Hessian<sup>d</sup>  $U_{\mathbf{x}-\alpha_i \mathbf{y}_i}^2$  is positive (semi)definite for all  $\alpha_i \in [0, 1]$  it follows that  $Q$  is non-negative. Hence, if  $\Delta U(\mathbf{y}_i) < 0$  it must be true that  $\tilde{U}_i < 0$ . The reverse is also true because  $\lim_{s_i \rightarrow 0} \Delta U / s_i = \tilde{U}_i$ . The question of global stability can therefore be resolved by calculating  $\min \tilde{U}$  in each region of attraction<sup>e</sup>:

$$\begin{aligned} \text{stable} & \quad \tilde{U} \geq 0 \quad \forall \mathbf{y}_i \in \Omega \\ \text{metastable} & \quad \tilde{U} < 0 \quad \exists \mathbf{y}_i \in \Omega \end{aligned}$$

In case the tangent plane distance is everywhere non-negative the system is stable, and in the opposite case the energy can be lowered by using  $\mathbf{y}_i$  as a start estimate for the new phase, see Section 3 on page 82.

## 2. Local stability

Assume that  $\mathbf{x}$  is now a one-phase system in Eq. 8.1 and that  $\tilde{U} = 0$  for some incipient phase  $\mathbf{y} \rightarrow \mathbf{0}$ . If at the same time  $\delta^2 U \rightarrow 0^+$  the system is stable to local perturbations, but if  $\delta^2 U \rightarrow 0^-$  the system is intrinsically unstable and an increase in  $\mathbf{y}$  will eventually lead to  $\tilde{U} < 0$ . If  $\delta^2 U = 0$  the system will be stabilised by the incipient phase  $\mathbf{y}$  when  $\delta^3 U \rightarrow 0^+$ , and de-stabilised when  $\delta^3 U \rightarrow 0^-$ . These thoughts can obviously be generalised but they are not very

<sup>a</sup> This is also recognised as the general phase equilibrium criterion. <sup>b</sup> The extent of the region depends also on the numerical algorithm in use. <sup>c</sup> Any value  $\mathbf{y} \propto \mathbf{x}$  represent a so-called trivial solution and is excluded from the set. <sup>d</sup> Ludwig Otto Hesse, 1811–1874. German mathematician. <sup>e</sup> Normally unknown at the outset — global stability constitutes a tough problem.

conclusive because  $\mathbf{y} \rightarrow \mathbf{0}$  does not tell how far  $\mathbf{y}$  is from  $\mathbf{x}$  in a thermodynamic sense<sup>a</sup>. We shall therefore redo Eq. 8.1 into a Taylor series with one single reference composition  $\mathbf{x}$  rather than using two distinct compositions  $\mathbf{x}$  and  $\mathbf{y}$ . The motivation for doing so is to understand what happens if (or when) some of the lower order terms in the series vanish, and to gain full control over the zero (phase) size limit. The total energy of the composite system is:

$$(8.2) \quad U(\mathbf{x}, \mathbf{y}) = U(\mathbf{y}) + U(\mathbf{x} - \mathbf{y})$$

To proceed we need Taylor expansions for  $U(\mathbf{y})$  and  $U(\mathbf{x} - \mathbf{y})$  both started at the same composition  $\mathbf{x}$ , or, more precisely, somewhere along vector  $\mathbf{x}$ . The trial state vector is first decomposed into one component along  $\mathbf{x}$  and another component  $\bar{\mathbf{x}}$  defined such that  $-\alpha x_i < \bar{x}_i < -\alpha x_i + x_i$ :

$$\mathbf{y} \hat{=} \alpha \mathbf{x} + \bar{\mathbf{x}}, \quad \alpha \in \langle 0, 1 \rangle$$

Next, remember that  $U, U_{\mathbf{x}}, U_{\mathbf{xx}}, \dots$  are homogeneous functions of order 1, 0, -1, ... This means the expansion can be started *anywhere* along vector  $\mathbf{x}$  provided the derivatives<sup>b</sup> are properly scaled:

$$(8.3) \quad \begin{aligned} U(\mathbf{y}) &= \alpha U(\mathbf{x}) + \alpha^0 U_{\mathbf{x}} \cdot \bar{\mathbf{x}} + \frac{1}{2} \alpha^{-1} U_{\mathbf{xx}} \cdot \bar{\mathbf{x}} \cdot \bar{\mathbf{x}} + \frac{1}{3!} \alpha^{-2} U_{\mathbf{xxx}} \cdot \bar{\mathbf{x}} \cdot \bar{\mathbf{x}} \cdot \bar{\mathbf{x}} + \dots \\ &= \alpha U(\mathbf{x}) + \sum_{k=1} \frac{1}{k!} \alpha^{1-k} U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k \end{aligned}$$

The expansion of  $U(\mathbf{y})$  is also valid for  $U(\mathbf{x} - \mathbf{y})$  if the new variable  $\beta$  is defined such that

$$\mathbf{x} - \mathbf{y} = \mathbf{x} - (\alpha \mathbf{x} + \bar{\mathbf{x}}) = (1 - \alpha) \mathbf{x} - \bar{\mathbf{x}} \hat{=} \beta \mathbf{x} - \bar{\mathbf{x}}$$

Hence, by replacing  $\alpha \rightarrow \beta$  and  $\bar{\mathbf{x}} \rightarrow -\bar{\mathbf{x}}$  we get the expression

$$(8.4) \quad U(\mathbf{x} - \mathbf{y}) = \beta U(\mathbf{x}) + \sum_{k=1} \frac{1}{k!} \beta^{1-k} U_{\mathbf{x}}^k \cdot (-\bar{\mathbf{x}})^k$$

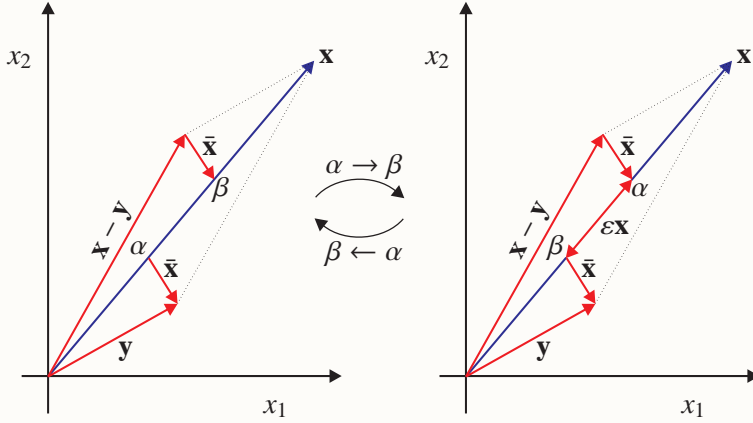
for free. From Eqs. 8.2, 8.3 and 8.4 the expansion of the total energy reads<sup>c</sup>:

$$(8.5) \quad U(\mathbf{x}, \mathbf{y}) = U(\mathbf{x}) + \sum_{k=2} \frac{1}{k!} [\alpha^{1-k} - (-\beta)^{1-k}] U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k$$

The first index  $k = 1$  is skipped because  $\alpha^0 - \beta^0 = 0$  for all  $\alpha, \beta \in \langle 0, 1 \rangle$ , that is to say the Taylor series gives no clue about the tilt of the energy surface<sup>d</sup>. Of special concern here is the term  $\alpha^{1-k} - (-\beta)^{1-k}$  which is strictly positive for the even indices  $k = 2, 4, \dots$  and of variable sign for the odd indices  $k = 3, 5, \dots$ . The sign of an odd-powered term can therefore be switched by exchanging the values of  $\alpha$  and  $\beta$ . Whenever the leading terms of the series vanishes this implies that the even and odd terms must vanish in pairs. A concise reasoning is given below.

<sup>a</sup> We do not know whether  $\mathbf{y}$  approaches the trivial solution  $\mathbf{y} \propto \mathbf{x}$  or not. <sup>b</sup> Note that the derivatives are by default evaluated in state  $\mathbf{x}$ . <sup>c</sup> Where  $\alpha + \beta = 1$  according to the definitions

<sup>d</sup> The energy gained by one phase is to a first approximation lost by the other phase.



**FIGURE 8.1** The effect of exchanging the (Taylor expansion) phase sizes  $\alpha$  and  $\beta$  in a tentative two-phase system. The overall state vector  $\mathbf{x}$  is fixed (closed system). The difference between the two sub-figures lies in the  $\varepsilon\mathbf{x}$  contribution.

Consider a Taylor series where  $n$  is an odd, non-zero, term and all the terms  $2, 3, \dots, n-1$  are zero. If the sign of the  $n$ 'th term is switched the value of the leading approximation changes from positive to negative, or the other way around. This behaviour has no physical counterpart and it can be concluded that  $U_{\mathbf{x}}^n \cdot \bar{\mathbf{x}}^n$  must vanish as well. However, as illustrated in Figure 8.1, exchanging the values of  $\alpha$  and  $\beta$  will in general change  $\bar{\mathbf{x}}$  to  $\bar{\mathbf{x}} + \varepsilon\mathbf{x}$  and it must be proved that this change does not distort the lower order terms:

**P** . Assume that  $n$  is an odd number  $3, 5, \dots$  and that  $U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k = 0$  for all  $k \in [2, n)$ . We shall prove that adding an arbitrary vector  $\varepsilon\mathbf{x}$  to  $\bar{\mathbf{x}}$  does not change any of the terms  $U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k$  for  $k \in [2, n]$ . Using binomial coefficients we can write

$$U_{\mathbf{x}}^n \cdot (\varepsilon\mathbf{x} + \bar{\mathbf{x}})^n = \sum_{k=0}^n \binom{n}{k} \varepsilon^{n-k} U_{\mathbf{x}}^n \cdot \mathbf{x}^{n-k} \cdot \bar{\mathbf{x}}^k$$

The derivatives are known to be homogeneous functions of order  $1, 0, -1, \dots$  which implies the reduction scheme:

$$\begin{aligned} U_{\mathbf{x}}^n \cdot \mathbf{x}^{n-k} &= (2-n)(2-n-1) \cdots (2-k-1) U_{\mathbf{x}}^k \\ &= U_{\mathbf{x}}^k \prod_{i=n}^{k+1} (2-i) \end{aligned}$$

Combining the two equations yields the intermediate result

$$U_{\mathbf{x}}^n \cdot (\bar{\mathbf{x}} + \varepsilon\mathbf{x})^n = \sum_{k=0}^n c_k U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k$$

where  $c_k$  have values:

$$c_k = \varepsilon^{n-k} \binom{n}{k} \prod_{i=n}^{k+1} (2-i), \quad k \in [0, n)$$

$$c_n \equiv 1$$

Remember that  $U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k = 0$  for all  $k \in [2, n)$ . Furthermore,  $c_0 = c_1 = 0$  for  $k < 2$  because  $(2 - i) = 0$  somewhere in the product sum. Hence, we can conclude that only the  $n$ 'th term survives the summation:

$$U_{\mathbf{x}}^n \cdot (\varepsilon \mathbf{x} + \bar{\mathbf{x}})^n = U_{\mathbf{x}}^n \cdot \bar{\mathbf{x}}^n, \quad \forall \varepsilon > 0 \quad \square$$

In retrospect it is easy to see that  $\varepsilon \mathbf{x}$  vanishes due to the first order homogeneity of  $U$  implemented in a Taylor series without any first order term. Anyway, the conclusion is that  $U_{\mathbf{x}}^{n-1} \cdot \bar{\mathbf{x}}^{n-1}$  and  $U_{\mathbf{x}}^n \cdot \bar{\mathbf{x}}^n$  must vanish in pairs of even and odd indices if the leading terms  $k \in [2, n - 2)$  are zero<sup>a,b</sup>. Rather than  $U_{\mathbf{x}}^{n-1} \cdot \bar{\mathbf{x}}^{n-1}$  and  $U_{\mathbf{x}}^n \cdot \bar{\mathbf{x}}^n$  we could as well talk about  $\delta^{n-1}U$  and  $\delta^n U$  because they must also vanish in the same circumstances. Therefore, when  $\delta^2 U \geq 0$  for all feasible  $\mathbf{y}$  the phase is intrinsically stable (but it can still be metastable in the global scope). When  $\delta^2 U < 0$  for some vector  $\mathbf{y}$  the phase is intrinsically unstable and if  $\delta^2 U = 0$  the phase is said to be at a spinodal point. If  $\delta^3 U = 0$  for the same vector  $\mathbf{y}$  the state is called critical. In the same manner higher order critical points can be defined where  $U_{\mathbf{x}}^{n-1} \cdot \mathbf{y}^{n-1} = U_{\mathbf{x}}^n \cdot \mathbf{y}^n = 0$  for  $n = 5, 7, \dots$ . To conclude this section we state our findings in a condensed way:

unstable	$\delta^2 U < 0$	for some $\mathbf{y}$
critical	$\delta^2 U = 0$	for some $\mathbf{y}$
	$\delta^3 U = 0$	
tricritical	$\delta^2 U = 0$	for some $\mathbf{y}$
	$\delta^3 U = 0$ , $\delta^4 U = 0$ $\delta^5 U = 0$	
tetracritical	$\delta^2 U = 0$	for some $\mathbf{y}$
	$\delta^3 U = 0$ , $\delta^4 U = 0$ , $\delta^5 U = 0$ $\delta^6 U = 0$ , $\delta^7 U = 0$	

In theory it is easy to put  $\delta^2 U$ ,  $\delta^3 U$ , etc. to zero, but what about reality? Matrix algebra can be used to analyse  $\delta^2 U$ , but is not helpful with the higher order terms. To get an idea of the numerical complexity it is legitimate to calculate the number of different terms involved. The partial derivative  $U_{\mathbf{x}}^k$  contains  $n^k$  elements, but only a fraction<sup>c</sup> of these are independent. One obvious reason is

<sup>a</sup> Michael Modell and Robert C. Reid. *Thermodynamics and Its Applications*. Prentice Hall, 2nd edition, 1983. <sup>b</sup> There is a textbook alternative<sup>a</sup> to the analysis outlined above. Let  $\alpha \rightarrow 0$  in Eq. 8.5. Because  $\beta = 1 - \alpha \gg \alpha$  the simplified equation is  $\lim_{\alpha \rightarrow 0} \left( \frac{\Delta U}{\alpha} \right) = \sum_{k=2} \frac{1}{k!} U_{\mathbf{x}}^k \cdot \left( \frac{\bar{\mathbf{x}}}{\alpha} \right)^k$ . Here,  $\Delta U(\mathbf{x}, \mathbf{y})$  is a homogeneous function in  $\alpha$  for a constant perturbation vector  $\frac{\bar{\mathbf{x}}}{\alpha}$  and the original system  $\mathbf{x}$  acts as a thermodynamic reservoir making it possible to study the properties of the incipient phase  $\mathbf{y}$  in isolation. Consider again a Taylor series where all the terms  $2, 3, \dots, n - 1$  (even number) are approaching zero. If the direction of  $\bar{\mathbf{x}}$  is flipped so will the sign of the  $n$ 'th term and it can be argued that  $U_{\mathbf{x}}^n \cdot \bar{\mathbf{x}}^n$  must vanish. However, changing the direction of  $\bar{\mathbf{x}}$  severely changes the composition of the incipient phase  $\mathbf{y}$ , and it is not clear (to me) that this has been properly accounted for in the analysis. I therefore find this argumentation weaker than my own. <sup>c</sup> E.g. for  $k = n = 10$  there are  $10^{10}$  elements, but only 43758 independent ones!

the commutative symmetry of the partial derivative:

$$\frac{\partial^k U}{\partial x_k \partial x_j \dots \partial x_i} = \frac{\partial^k U}{\partial x_i \partial x_j \dots \partial x_k}$$

Thus, the sampling of  $k$  indices *without regard to order* from a population of  $n = \dim(\mathbf{x})$  components (with replacement of the indices) gives rise to

$$\binom{n+k-1}{k} \equiv \frac{(n+k-1)!}{k!(n-1)!}$$

potentially different terms in  $U_{\mathbf{x}}^k$ . However, the homogeneity of  $U$  reduces the number further because

$$U_{\mathbf{x}}^k \cdot \mathbf{x} = (2 - k)U_{\mathbf{x}}^{k-1}$$

For each derivative  $U_{\mathbf{x}}^k$  there exists as many relations as there are independent terms in  $U_{\mathbf{x}}^{k-1}$ , hence the number of independent terms in  $U_{\mathbf{x}}^k$  is cut off to

$$\binom{n+k-1}{k} - \binom{n+k-2}{k-1} \equiv \frac{(n+k-2)!}{k!(n-2)!}, \quad k, n \geq 2$$

Some numbers have been calculated below and we immediately recognise the 2-variable case as particularly interesting — only one extra term is needed to describe each derivative, no matter the value of  $k$ . This finding becomes even more interesting in Section 4 where we shall find that the 2-variable case is sufficient in all but some highly degenerate cases (e.g. critical azeotropes).

	$k = 2$	$k = 3$	$k = 4$	$\dots$	$k$
$n = 2$	1	1	1	$\dots$	$\frac{1}{1}$
$n = 3$	3	4	5	$\dots$	$\frac{k+1}{1}$
$n = 4$	6	10	15	$\dots$	$\frac{(k+1)(k+2)}{2}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
$n$	$\frac{(n-1)n}{2}$	$\frac{(n-1)n(n+1)}{6}$	$\frac{(n-1)n(n+1)(n+2)}{24}$	$\dots$	$\frac{(n+k-2)!}{k!(n-2)!}$

### 3. The tangent plane test

In theory it is possible to formulate a tangent plane test based on the internal energy, but most models have canonical variables  $T, V, N$  or  $T, p, N$  and it is more practical to formulate the test in terms of Helmholtz energy or Gibbs energy. Assume therefore that we have a phase (assembly) characterised by

$$A = \mathbf{g}^T \mathbf{x}$$

where  $A$  is the Helmholtz energy and  $\mathbf{x}^T = (V, \mathbf{n}^T)$ . The system temperature  $T$  is constant. If the phase (assembly) is stable then  $\tilde{A} \geq 0$  for all feasible values of the trial state vector  $\mathbf{y}$ :

$$(8.6) \quad \tilde{A}(\mathbf{x}, \mathbf{y}) = [\mathbf{g}(\mathbf{y}) - \mathbf{g}(\mathbf{x})]^T \mathbf{y} > 0$$

Note the difference in notation from Eq. 8.1. In the current situation it is more natural to use  $\mathbf{g}$  for the gradient rather than  $A_{\mathbf{x}}$  in conformity with the notation used in linear algebra.

**3.1. Lagrange formulation.** To verify that  $\tilde{A} \geq 0$  for all feasible  $\mathbf{y} \in \Omega$  we can do little more than investigate the outcome of the minimisation problem

$$\min_{\mathbf{y}}(\tilde{A})_T \quad \forall \quad \mathbf{a}^T \mathbf{y} = c$$

for several trial values of  $\mathbf{y}$ . This minimisation problem is linearly constrained<sup>a</sup> and the method of Lagrange multipliers is ideally suited:

$$L(\mathbf{x}, \mathbf{y}, \lambda) = \tilde{A} - \lambda(\mathbf{a}^T \mathbf{y} - c)$$

The stationary point of  $L$  is given by  $\partial L / \partial \mathbf{y} = \mathbf{0}$ , or when written out in some more detail:

$$\begin{aligned} \mathbf{0} &= \frac{\partial \tilde{A}}{\partial \mathbf{y}} - \frac{\partial \lambda(\mathbf{a}^T \mathbf{y} - c)}{\partial \mathbf{y}} \\ &= \mathbf{H}(\mathbf{y})\mathbf{y} + \mathbf{g}(\mathbf{y}) - \mathbf{g}(\mathbf{x}) - \lambda \mathbf{a} \\ (8.7) \quad &= \mathbf{g}(\mathbf{y}) - \mathbf{g}(\mathbf{x}) - \lambda \mathbf{a} \end{aligned}$$

The stationary value of  $\tilde{A}$  can be calculated from Eqs. 8.6 and 8.7:

$$(8.8) \quad \tilde{A}_o = \mathbf{g}(\mathbf{y})^T \mathbf{y} - \mathbf{g}(\mathbf{x})^T \mathbf{y} = \lambda \mathbf{a}^T \mathbf{y} = \lambda c$$

Hence, the phase is stable if  $\lambda c \geq 0$  at every stationary point of  $L(\mathbf{x}, \mathbf{y}, \lambda)$ , and metastable if  $\lambda c < 0$ . If metastability occurs the Helmholtz energy can be lowered by including the incipient phase  $\mathbf{y}$  on the expense of  $\mathbf{x}$ , but a natural question is: How big should we make this new phase? The definite answer lies of course in the subsequent equilibrium calculation, but we have to start the iterations somewhere. With minimum effort we can study the second order variation of  $\tilde{A}$  along the (optimum) state vector  $\mathbf{y}$ ,

$$\tilde{A}(\mathbf{x}, \mathbf{y}) = \alpha \mathbf{g}(\mathbf{y})^T \mathbf{y} - \alpha \mathbf{g}(\mathbf{x})^T \mathbf{y} + \frac{\alpha^2}{2!} \mathbf{y}^T \mathbf{H}(\mathbf{x}) \mathbf{y} + \dots$$

where  $\alpha \in [0, \alpha_{\max})$  is a step length parameter under our control. A minimum in Helmholtz energy requires that  $\partial \tilde{A} / \partial \alpha = 0$  and plain differentiation gives the following phase size estimate

$$(8.9) \quad \alpha_o = \frac{\mathbf{g}(\mathbf{y})^T \mathbf{y} - \mathbf{g}(\mathbf{x})^T \mathbf{y}}{\mathbf{y}^T \mathbf{H}(\mathbf{x}) \mathbf{y}} \triangleq \frac{-\lambda c}{Q(\mathbf{x}, \mathbf{y})}$$

In the limit of incipient phase stability  $\alpha_o$  will approach the true equilibrium value, but deep inside the phase boundary we may expect  $\alpha_o > \alpha_{\max}$ . We must therefor keep a close eye with the estimate in Eq. 8.9 and restrict  $\alpha$  if appropriate. Note also that the estimate breaks down if the phase (assembly)  $\mathbf{x}$  is unstable in the direction of  $\mathbf{y}$  i.e. when  $Q(\mathbf{x}, \mathbf{y}) < 0$ . A more elaborate line search is then definitely needed.

<sup>a</sup> The constraint specification  $\mathbf{a}^T \mathbf{y} = c$  is arbitrary, but nevertheless crucial to the problem formulation because  $\tilde{A}$  is a homogeneous function, and as such experiences a singular Hessian matrix in the direction of  $\mathbf{y}$ . Adding a rank-one constraint makes the Hessian invertible (loosely speaking).

This is as far as the general theory goes, the next question is how to proceed with actual calculations. A Newton iteration started at a feasible point  $\mathbf{y}_0 \neq \mathbf{x}$  yields the recurrence formula,

$$\begin{pmatrix} \mathbf{y} \\ -\lambda \end{pmatrix}_{k+1} = \begin{pmatrix} \mathbf{H}(\mathbf{y}) & \mathbf{a} \\ \mathbf{a}^T & \mathbf{0} \end{pmatrix}_k^{-1} \begin{pmatrix} \mathbf{g}(\mathbf{x}) - \mathbf{g}(\mathbf{y}) \\ c \end{pmatrix}_k$$

but to continue we need the constraint vector  $\mathbf{a}$ . The most intuitive choice is to fix the volume of the incipient phase such that  $\mathbf{y}_1 = \mathbf{x}_1 = V$  and let the mole numbers vary freely. This corresponds to  $\mathbf{a}^T = \mathbf{e}_1^T = (1, 0, \dots)$  and  $\lambda$  being a vector with one single element interpreted as the difference in negative pressure  $\pi$  between the two states  $\mathbf{x}$  and  $\mathbf{y}$ . Inserting  $\mathbf{a} = \mathbf{e}_1$  into Eq. 8.7 gives the solution

$$\begin{aligned} p(\mathbf{x}) - p(\mathbf{y}) &= \pi \\ \boldsymbol{\mu}(\mathbf{x}) - \boldsymbol{\mu}(\mathbf{y}) &= \mathbf{0} \end{aligned}$$

There is no mechanical equilibrium in this case although the conditions for chemical equilibrium are fulfilled<sup>a</sup>. The stationary value of  $\tilde{A}_o$  in Eq. 8.8 simplifies to

$$\tilde{A}_o = \pi \mathbf{e}_1^T \mathbf{y} = \pi y_1 = \pi V$$

because  $\mathbf{y}_1 = \mathbf{x}_1 = V$ . Knowing only one stationary point we can argue that the phase (assembly)  $\mathbf{x}$  is metastable if  $-\pi > 0$  and possibly<sup>b</sup> stable if  $-\pi \leq 0$ . Finally, for  $\mathbf{a} = \mathbf{e}_1$  the phase size estimate simplifies to (see Eq. 8.9 on the preceding page)

$$\alpha_o = \frac{-\pi V}{Q(\mathbf{x}, \mathbf{y})}$$

**3.2. Direct substitution.** The Lagrange formulation is very neat in the general case, but if the mixture is nearly ideal the direct substitution of variables becomes a viable alternative. The minimisation problem is for a change written

$$\min_{\mathbf{y}} (\tilde{G})_{T,p} \quad \vee \quad \mathbf{e}^T \mathbf{y} = 1$$

where  $\mathbf{y}$  represents the mole numbers in the mixture. Let  $\mathbf{y}_{1,\dots,n-1}$  be the  $n-1$  first components of  $\mathbf{y}$  and let  $\mathbf{S}$  be a matrix that maps this vector onto  $\mathbf{y}$ :

$$\mathbf{y} = \mathbf{e}_n + \begin{pmatrix} \mathbf{I} \\ -\mathbf{e}^T \end{pmatrix} \mathbf{y}_{1,\dots,n-1} \hat{=} \mathbf{e}_n + \mathbf{S} \mathbf{y}_{1,\dots,n-1}$$

The variation in  $\mathbf{y}$  is easily calculated as  $\delta \mathbf{y} = \mathbf{S} \delta \mathbf{y}_{1,\dots,n-1}$  and because  $\mathbf{e}^T \mathbf{S} = \mathbf{0}^T$  it follows that  $\mathbf{e}^T \delta \mathbf{y} = 0$ . Clearly, the mapping conserves the total number of moles in the mixture and the minimisation problem can *de facto* be written

<sup>a</sup> The situation will change if another  $\mathbf{a}$  is chosen. E.g.  $\mathbf{a}^T = (0, 1, \dots, 1)$  releases the chemical equilibrium and fixes the mechanical equilibrium. <sup>b</sup> If we are going to rely on one single solution point, we should really check for intrinsic stability first. This topic will be covered in the next section.



on an unconstrained form as  $\min_{\mathbf{y}_{1,\dots,n-1}}(\tilde{G})_{T,p}$ . The chain rule of differentiation yields

$$\left(\frac{\partial \tilde{G}}{\partial \mathbf{y}_{1,\dots,n-1}}\right) = \left(\frac{\partial \mathbf{n}^T}{\partial \mathbf{y}_{1,\dots,n-1}}\right) \left(\frac{\partial \tilde{G}}{\partial \mathbf{y}}\right) = \mathbf{S}^T[\boldsymbol{\mu}(\mathbf{y}) - \boldsymbol{\mu}(\mathbf{x})] = \mathbf{0}$$

If we can assume that the mixture behaves ideally then  $\boldsymbol{\mu}(\mathbf{y}) - \boldsymbol{\mu}(\mathbf{x}) = \Delta\boldsymbol{\mu} + \ln(\mathbf{y})$ , where  $\Delta\boldsymbol{\mu}$  is a constant vector at the given temperature and pressure. The condition for a stationary point is  $\mathbf{S}^T[\Delta\boldsymbol{\mu} + \ln(\mathbf{y})] = \mathbf{0}$ , or when written out in full:  $\Delta\boldsymbol{\mu}_{1,\dots,n-1} - \Delta\boldsymbol{\mu}_n \mathbf{e} + \ln(\mathbf{y}_{1,\dots,n-1}) - \ln(\mathbf{y}_n) \mathbf{e} = \mathbf{0}$ . Direct substitution of the  $n - 1$  first variables gives the update formula:

$$\mathbf{y}_{1,\dots,n-1}^{(k+1)} = \mathbf{y}_n^{(k)} \exp(\Delta\boldsymbol{\mu}_n) \exp(-\Delta\boldsymbol{\mu}_{1,\dots,n-1})$$

The calculation converges in one step for ideal mixtures whereas the Lagrange formulation would require several iterations (typically 5–10). Another nice feature is that the mole numbers are guaranteed to be positive due to the exponential on the right hand side.

§46 Write a modified update scheme for the direct substitution of mole numbers in an ideal gas at fixed temperature. The volume is a free variable and can be set to any value.

I . Assume that, in the previous derivation, Helmholtz energy is used to replace Gibbs energy and  $\mathbf{S}^T \hat{=} (\mathbf{I} \mathbf{0})$  where the last column (of zeros) corresponds to the (constant) variable  $V$ . Because the iteration is now conducted at constant volume rather than at constant pressure all the mole variables will be updated simultaneously:  $\mathbf{n}^{(k+1)} = \mathbf{n}^{(k)} \exp(-\Delta\boldsymbol{\mu})$ . □

#### 4. Intrinsic stability criteria

Intrinsic stability of a phase requires that the quadratic  $U_{\mathbf{xx}} \cdot \mathbf{y} \cdot \mathbf{y} \geq 0$  for all  $\mathbf{y} \in \Omega$ . This is a classical problem formulation known from courses in linear algebra, the solution of which can be stated in several equivalent ways:

- (1) The eigenvalues of  $U_{\mathbf{xx}}$  are non-negative.
- (2) The pivots in the Cholesky factorisation of  $U_{\mathbf{xx}}$  are non-negative.
- (3) The principal sub-determinants of  $U_{\mathbf{xx}}$  are non-negative.
- (4)  $U_{\mathbf{xx}}$  is a semi-definite matrix of rank  $n - 1$ .

The second formulation is apt to simple matrix algebra and defines for this reason the route followed here. For a single component system a step-by-step elimination<sup>a</sup> of the rows in  $U_{\mathbf{xx}}$  yields

$$(8.10) \quad \begin{pmatrix} U_{SS} & U_{SV} & U_{SN} \\ U_{VS} & U_{VV} & U_{VN} \\ U_{NS} & U_{NV} & U_{NN} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ \alpha & 1 & 0 \\ \beta & 0 & 1 \end{pmatrix} \begin{pmatrix} U_{SS} & U_{SV} & U_{SN} \\ 0 & A_{VV} & A_{VN} \\ 0 & A_{NV} & A_{NN} \end{pmatrix}$$

<sup>a</sup> Because  $U_{\mathbf{xx}}$  is a symmetric matrix of rank  $n - 1$  we can write the full Cholesky factorisation of an intrinsically stable, single component system, as  $U_{\mathbf{xx}} = \mathbf{L}\mathbf{L}^T$  where  $\mathbf{L}^T = \begin{pmatrix} u & u\alpha & u\beta \\ 0 & a & ay \end{pmatrix}$  and  $u = \sqrt{U_{SS}}$  and  $a = \sqrt{A_{VV}}$

$$(8.11) \quad = \begin{pmatrix} 1 & 0 & 0 \\ \alpha & 1 & 0 \\ \beta & \gamma & 1 \end{pmatrix} \begin{pmatrix} U_{SS} & U_{SV} & U_{SN} \\ 0 & A_{VV} & A_{VN} \\ 0 & 0 & G_{NN} \end{pmatrix}$$

where the following parameters have been used:

$$\alpha \hat{=} \frac{U_{VS}}{U_{SS}}, \quad \beta \hat{=} \frac{U_{NS}}{U_{SS}}, \quad \gamma \hat{=} \frac{A_{NV}}{A_{VV}}$$

Note that the last pivot in the elimination ( $G_{NN}$  in this case) will always be 0 due to the homogeneous nature of  $U$ . To prove that Eqs. 8.10–8.11 are correct we must prove that the Cholesky<sup>a</sup> factorisation of a thermodynamic Hessian (in the extensive variables) is equivalent to a series of Legendre transformations applied to the original function<sup>b</sup>. It is possible to prove this in general terms, but to make the theory amenable to the casual reader we shall carry out a less general factorisation. From Chapter 2 we know that  $A(T, V, N)$  is related to  $U(S, V, N)$  such that  $A_X = U_X$  then assuming constant temperature and entropy respectively. This relation holds for any  $X \in \{V, N\}$ . The differentials of  $A_X$  at constant temperature, and of  $U_X$  with no restrictions on the variables, are:

$$(8.12) \quad (dA_X)_T = A_{XV} dV + A_{XN} dN$$

$$(8.13) \quad dU_X = U_{XS} dS + U_{XV} dV + U_{XN} dN$$

In order to compare the two differentials it is necessary that the (differential) entropy is eliminated in the second equation such that the temperature is held constant. Using the definition  $T \hat{=} U_S$  it follows that

$$(8.14) \quad 0 = (dU_S)_T = U_{SS} dS + U_{SV} dV + U_{SN} dN$$

From Eq. 8.14 it is straightforward to eliminate  $dS$  in Eqs. 8.13, and furthermore to collect similar terms into

$$(dU_X)_T = \left( U_{XV} - U_{XS} \frac{U_{SV}}{U_{SS}} \right) dV + \left( U_{XN} - U_{XS} \frac{U_{SN}}{U_{SS}} \right) dN$$

The last equation is compared term-by-term with Eq. 8.12 which yields

$$(8.15) \quad A_{XY} = U_{XY} - U_{XS} \frac{U_{SY}}{U_{SS}}$$

for any  $Y \in \{V, N\}$ . Substitution of  $X, Y \in \{V, N\}$  into the formula above verifies the first step in the Cholesky factorisation 8.10–8.11. Furthermore, because the differentiation outlined in Eqs. 8.12–8.15 is valid for any Legendre sequence  $U(S, V, N) \rightarrow A(T, V, N) \rightarrow G(T, -p, N)$  etc., an induction proof verifies that the factorisation can be completed as indicated<sup>c</sup>. The intrinsic stability of a

<sup>a</sup> André-Louis Cholesky, 1875–1918. French mathematician. <sup>b</sup> The marvels of thermodynamics are quite fascinating! <sup>c</sup> The factorisation of positive *semi*-definite matrices has not yet been discussed. The question is where the zero pivots of  $U_{xx}$  show up when a stable phase changes (continuously) into an unstable one. The outcome is that the last pivot changes its sign before the second last pivot, which changes its sign before the third last pivot, etc. This holds for all non-degenerated states. In the current case  $G_{NN} = 0$  is the last pivot and the sign shift will therefore show up in  $A_{VV}$  first, before it eventually also shows up in  $U_{SS}$ .

phase can then be stated in terms of just 1 second derivative, rather than  $n(n+1)/2$  as would be expected from matrix theory alone<sup>a</sup>. It is also true that the transformation sequence is arbitrary, and that the factorisation could start out with  $U_{VV}$  or  $U_{NN}$  rather than  $U_{SS}$ . Thus, for a one-component system the stability conditions can be written in 6 different ways,

$$\begin{aligned} U_{SS} > 0, & \quad A_{VV} > 0 \\ U_{SS} > 0, & \quad A_{NN} > 0 \\ U_{VV} > 0, & \quad H_{SS} > 0 \\ U_{VV} > 0, & \quad H_{NN} > 0 \\ U_{NN} > 0, & \quad X_{SS} > 0 \\ U_{NN} > 0, & \quad X_{VV} > 0 \end{aligned}$$

where  $X$  denotes the unnamed energy function  $X(S, V, \mu)$ . These relations are equivalent to those derived from the principal sub-determinants of the original Hessian. The left column is clearly related to the rank-one determinants (main diagonal elements), and with the help of Eq. 8.15 the rank-two determinants can be written:

$$\begin{aligned} U_{SS}U_{VV} - U_{SV}U_{VS} &= U_{SS}A_{VV} = H_{SS}U_{VV} > 0 \\ U_{SS}U_{NN} - U_{SN}U_{NS} &= U_{SS}A_{NN} = X_{SS}U_{NN} > 0 \\ U_{VV}U_{NN} - U_{VN}U_{NV} &= U_{VV}H_{NN} = X_{VV}U_{NN} > 0 \end{aligned}$$

There is also one final rank-three criterion, and several rank-two criteria coming from the Legendre transforms, but they are all zero because the Hessian is singular for whatever values of  $S$ ,  $V$  and  $N$ . The rank-two criteria listed in the right column above are therefor conclusive and are violated *simultaneously* at the limit of material stability. This stability limit is often referred to as the spinodal. The rank-one criteria define a new spinodal inside the outer one.

A final note on quadratic forms is appropriate. We know that for a stable system the quadratic  $U_{\mathbf{x}\mathbf{x}} \cdot \mathbf{y} \cdot \mathbf{y} \geq 0$  for all  $\mathbf{y} \in \Omega$ . This has been stressed many times already, but so far it has been just a theoretical result. To give a practical demonstration we can calculate the inner product from the factorisation in Eq. 8.11:

$$U_{SVN}^2 \cdot \mathbf{y}^2 = U_{SS} \left( y_S + \frac{U_{VS}}{U_{SS}} y_V + \frac{U_{NS}}{U_{SS}} y_N \right)^2 + A_{VV} \left( y_V + \frac{A_{NV}}{A_{VV}} y_N \right)^2 + G_{NN} (y_N)^2$$

Clearly, the quadratic is non-negative only if the leading factors  $U_{SS}$  and  $A_{VV}$  are positive. The Euler properties of  $U$  makes  $G_{NN} = 0$  so the quadratic is always zero in the direction of  $\mathbf{x}$ , but otherwise it should be strictly positive.

<sup>a</sup> This does not imply that only 1 coefficient in the original matrix is needed for the stability analysis. The Legendre transforms will effectively bring all the coefficients into action.

For a multicomponent system the quadratic is generalised to

$$U_{\mathbf{x}}^2 \cdot \mathbf{y}^2 = \sum_{i=1} U_{x_i x_i}^{(i-1)} \left( y_i + \sum_{j>i} \left( U_{x_i x_i}^{(i-1)} \right)^{-1} U_{x_i x_j}^{(i-1)} y_j \right)^2$$

where  $U^{(i-1)}$  is used to denote the  $(i - 1)$ 'th Legendre transform of internal energy and  $U^{(0)} \hat{=} U$ . With regard to the leading factors  $U_{x_i x_i}^{(i-1)}$  in this formula the picture gets quite complex, and already for a binary system there will be 24 different possibilities. The most common formulation is:

$$\begin{aligned} U_{SS} &= \left( \frac{\partial T}{\partial S} \right)_{V, N_1, N_2} \hat{=} \frac{T}{C_V} > 0 \\ A_{VV} &= - \left( \frac{\partial p}{\partial V} \right)_{T, N_1, N_2} \hat{=} \frac{1}{V\beta} > 0 \\ G_{N_1 N_1} &= \left( \frac{\partial \mu_1}{\partial N_1} \right)_{T, p, N_2} > 0 \end{aligned}$$

## References

This chapter provides references to theoretical thermodynamics and experimental data in physical chemistry used within the book. There are also some references to selected books and articles which shed light on the more esoteric sides of thermodynamics. The latter references contain a mix of scientific and controversial literature.

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- [5] Michael Modell and Robert C. Reid. *Thermodynamics and Its Applications*. Prentice Hall International Series in the Physical and Chemical Engineering Sciences. Prentice Hall, Inc., Englewood Cliffs, New Jersey, second edition, 1983.



## Biographies

In technical literature there is a plethora of *eponymes* which makes a vital part of the scientific language. Some examples are: The Raoult's law, Gibbs–Duhem equation, Boltzmann constant, Helmholtz energy, etc. To provide a historical meaning of these terms I have collected a series of short and subjective biographies about the most prominent contributors to physics and chemistry (and of course thermodynamics). The sources of information are: Aschehoughs store konversasjonsleksikon (1974), Encyclopædia Britannica (1985), [www.wikipedia.org](http://www.wikipedia.org) (*the free encyclopedia*) and [www.gap-system.org/~history](http://www.gap-system.org/~history) (*School of Mathematics and Statistics University of St. Andrews, Scotland*). The thumb nail pictures have been downloaded from various public domain sources on the internet.

- [1] **Niels Henrik Abel, 1802–1829. Norwegian mathematician.**
- [2] **Jožef Stefan alias Joseph Stefan, 1835–1993. Slovenian physicist and poet.**
- [3] **William Thomson alias Lord Kelvin, 1824–1907. Irish physicist.**
- [4] **André Marie Ampère, 1775–1836. French physicist.**
- [5] **Stefan Banach, 1892–1945. Polish mathematician.**
- [6] **Ludwig Boltzmann, 1844–1906. Austrian physicist.**
- [7] **George Brayton, 1830–1892. American engineer.**
- [8] **Nicolas Leonard Sadi Carnot, 1796–1832. French engineer.**
- [9] **André-Louis Cholesky, 1875–1918. French mathematician.**
- [10] **Count Lorenzo Romano Amedeo Carlo Avogadro di Quaregna e Cerreto, 1776–1856. Italian chemist.**
- [11] **John Ericsson, 1803–1889. Swedish engineer.**
- [12] **Leonhard Euler, 1707–1783. Swiss mathematician.**
- [13] **Michael Faraday, 1791–1867. English physicist.**
- [14] **Josiah Willard Gibbs, 1839–1903. American physicist.**
- [15] **Ludwig Otto Hesse, 1811–1874. German mathematician.**

- [16] **Carl Gustav Jacob Jacobi, 1804–1851. German mathematician.**
- [17] **Leopold Kronecker, 1823–1891. German mathematician.**
- [18] **Adrien-Marie Legendre, 1752–1833. French mathematician.**
- [19] **James Clerk Maxwell, 1831–1879. Scottish physicist.**
- [20] **Sir Isaac Newton, 1642–1727 by the Julian calendar. English physicist and mathematician.**
- [21] **Nikolaus August Otto, 1832–1891. German engineer.**
- [22] **Max Karl Ernst Ludwig Planck, 1858–1947. German physicist.**
- [23] **John Henry Poynting, 1852–1914. English physicist.**
- [24] **William John Macquorn Rankine, 1820–1872. Scottish physicist.**
- [25] **Robert Stirling, 1790–1878. Scottish reverend.**
- [26] **Brook Taylor, 1685–1731. English mathematician.**
- [27] **Hermann Ludwig Ferdinand von Helmholtz, 1821–1894. German physician and physicist.**



## APPENDIX A

 **$T, s$  and  $p, v$ -Diagrams for Ideal Gas Cycles**

The aim of this chapter is to present a complete set of  $T, s$  and  $p, v$  diagrams for an idealised heat engine using ideal gas as a work medium. For simplicity, we shall assume a constant heat capacity<sup>a</sup>  $c_p = 3.5R$  in all the calculations. All together, twelve coordinate systems are required in order to describe the six thermodynamic cycles of Otto<sup>b</sup> ( $s, v$ ), Stirling<sup>c</sup> ( $T, v$ ), Brayton<sup>d</sup> ( $s, p$ ), Ericsson<sup>e</sup> ( $T, p$ ), Carnot<sup>f</sup> ( $T, s$ ) and Rankine<sup>g</sup> ( $p, v$ ). In order to draw all these diagrams the exact knowledge of the  $T(s, v)$ ,  $T(s, p)$ ,  $p(s, v)$  and  $p(T, v)$  isopleths must exist. The starting points are

$$\begin{aligned}\frac{s^{ig}-s_o}{R} &= \ln \frac{p_o}{p} + \frac{c_p}{R} \ln \frac{T}{T_o}, \\ \frac{s^{ig}-s_o}{R} &= \ln \frac{v}{v_o} + \frac{c_v}{R} \ln \frac{T}{T_o},\end{aligned}$$

which can be inverted to

$$\begin{aligned}T = T(s, v) : \quad \frac{T^{ig}}{T_o} &= \left(\frac{v_o}{v}\right)^{\gamma-1} \exp\left(\frac{s-s_o}{c_v}\right). \\ T = T(s, p) : \quad \frac{T^{ig}}{T_o} &= \left(\frac{p}{p_o}\right)^{\frac{\gamma-1}{\gamma}} \exp\left(\frac{s-s_o}{c_p}\right). \\ p = p(s, v) : \quad \frac{p^{ig}}{p_o} &= \left(\frac{v_o}{v}\right)^{\gamma} \exp\left(\frac{s-s_o}{c_v}\right).\end{aligned}$$

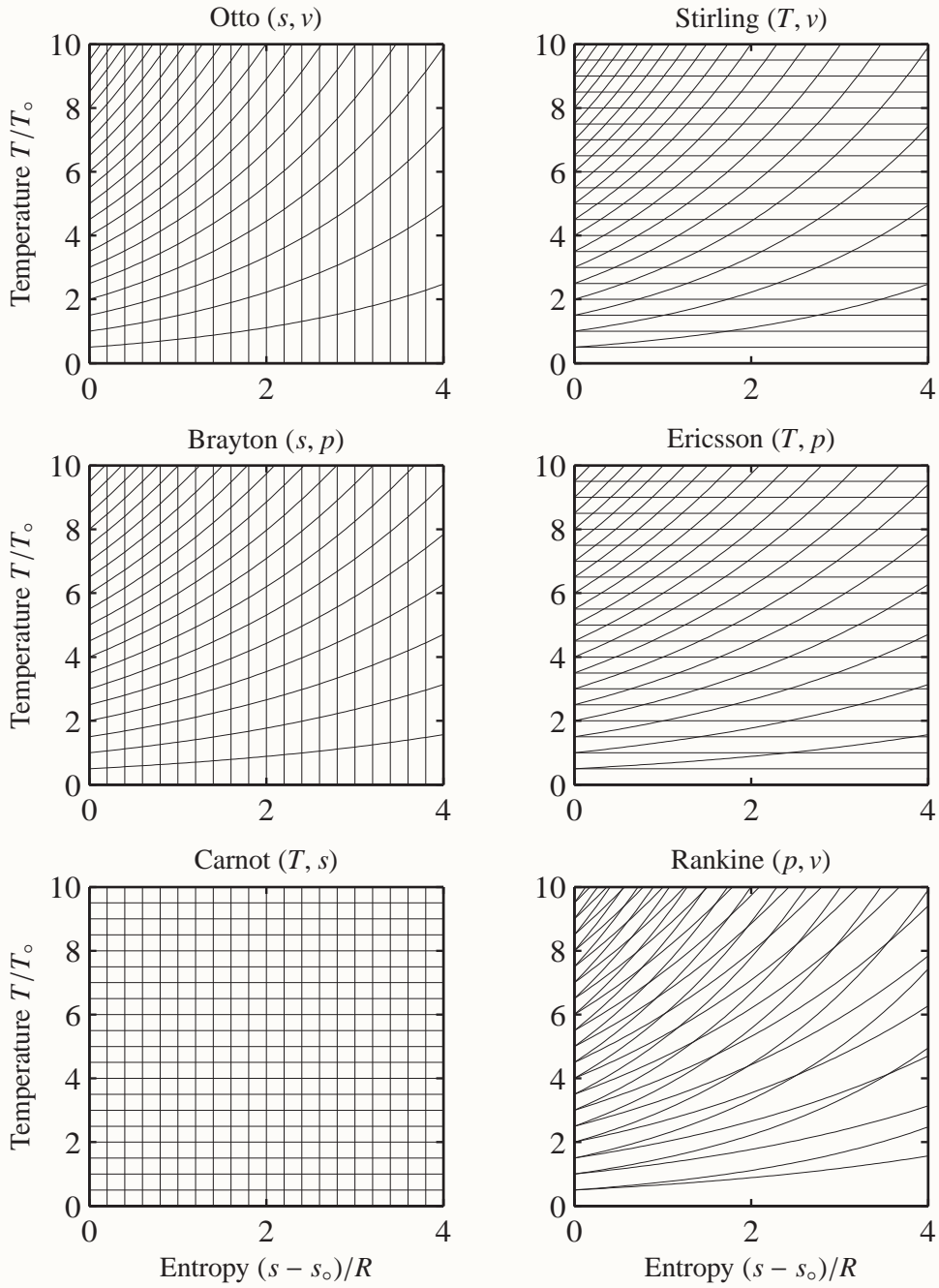
Additionally, the ideal gas equation of state on the form

$$p = p(T, v) : \quad \frac{p^{ig}}{p_o} = \left(\frac{v_o}{v}\right)\left(\frac{T}{T_o}\right)$$

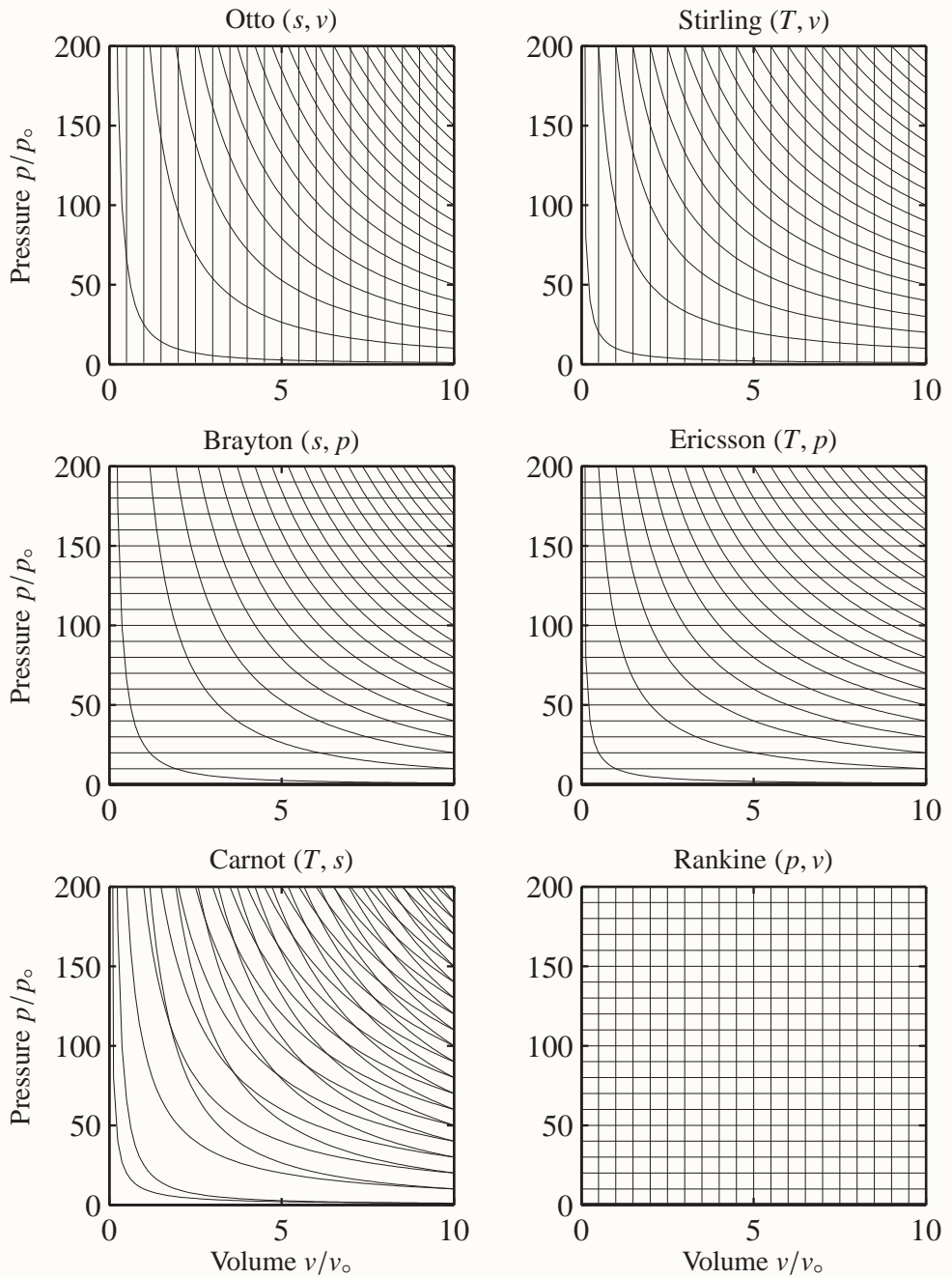
is also needed. The actual calculations are outlined in Matlab code 1.7 on page 120, and the final diagrams are shown in Figures A.1 and A.2 on the next page.

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<sup>a</sup> Assuming diatomic molecules with fully developed translational and rotational degrees of freedom gives  $c_p = 3.5R$  and  $\gamma = 7/5 = 1.4$  <sup>b</sup> Nikolaus August Otto, 1832–1891. German engineer. <sup>c</sup> Robert Stirling, 1790–1878. Scottish reverend. <sup>d</sup> George Brayton, 1830–1892. American engineer. <sup>e</sup> John Ericsson, 1803–1889. Swedish engineer. <sup>f</sup> Nicolas Leonard Sadi Carnot, 1796–1832. French engineer. <sup>g</sup> William John Macquorn Rankine, 1820–1872. Scottish physicist.



**FIGURE A.1**  $T, s$  diagrams with ideal gas ( $\gamma = 1.40$ ) used as work medium (equidistant isopleths).



**FIGURE A.2**  $p, v$  diagrams using ideal gas ( $\gamma = 1.40$ ) as work medium. The isopleths are equidistant except for the lowest isotherm and isentrope which start at  $p/p_0 = 1 \neq 0$  to avoid division by zero.



## APPENDIX B

**SI units and Universal Constants**

The SI convention (*Système International d' Unités*) has its roots in the French Revolution and the contemporary will of breaking with old traditions. The central idea of using a metric (decimal) measuring system for length and mass was adopted by the French Academy in 1790, and put to work in 1795. On 20 May 1875 the Meter Convention was signed in Paris by 18 member countries<sup>a</sup>.

SI unit	sym	Description
Ampère <sup>b</sup>	A	That constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 m apart in vacuum, would produce between these conductors a force equal to $2 \cdot 10^{-7} \text{ N m}^{-1}$ .
Candela	cd	Luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540 \cdot 10^{12} \text{ Hz}$ and that has a radiant intensity in that direction of $1/683 \text{ W}$ per steradian.
Gram	g	One thousand of the mass of the international kilogramme prototype in Paris (probably about to change).
Kelvin <sup>c</sup>	K	The fraction $1/273.16$ of the thermodynamic temperature of the triple point of water.
Metre	m	Length of the path travelled by light in vacuum during a time interval of $1/299,792,458$ of a second.
Mole	mol	Amount of substance of a system which contains as many elementary entities as there are atoms in $0.012 \text{ kg}$ of $^{12}\text{C}$ . When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Second	s	Duration of $9,192,631,770$ periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the $^{133}\text{Cs}$ atom.

<sup>a</sup> Quite remarkably Norway was among these early pioneers.

The SI consists of seven base units and two supplementary units related to the geometry of objects (radian and steradian). An infinite number of coherent units for power, force, energy, and so on can be defined as multiple products of these base units. The use of optional prefixes (kilo, Mega, milli, etc.) makes it possible for the researcher to report measurements that are close to unity, or whatever is considered to be “normal” or practical ( $\mu\text{g}$ , kPa, mm, ns, etc.). An issue closely related to the base units is the formulation of universal constants in physical theories. The ones of special interest to thermodynamics are:

Constant name	sym	expr	value <sup>a</sup>	mult	units
Atomic mass unit	$amu$	$\frac{0.001}{ A_v }$	1.6605402(1)	$10^{-27}$	kg
Avogadro <sup>b</sup> number	$A_v$		6.0221367(4)	$10^{+23}$	$\text{mol}^{-1}$
Boltzmann <sup>c</sup> constant	$k$		1.380658(1)	$10^{-23}$	$\text{J K}^{-1}$
Elementary charge	$e$		1.60217733(5)	$10^{-19}$	C
Faraday <sup>d</sup> constant	$F$	$A_v e$	96485.309(3)		$\text{C mol}^{-1}$
Permeability of vacuum	$\mu_o$	$\frac{4\pi}{10^7}$	1.2566370...	$10^{-6}$	$\text{N A}^{-2}$
Permittivity of vacuum	$\epsilon_o$	$\frac{1}{\mu_o c^2}$	8.8541878...	$10^{-12}$	$\text{F m}^{-1}$
Planck <sup>e</sup> constant	$h$		6.6260755(4)	$10^{-34}$	J s
Speed of light in vacuum	$c$		299792458		$\text{m s}^{-1}$
Standard acceleration	$g$		9.80665		$\text{m s}^{-2}$
Stefan <sup>f</sup> –Boltzmann <sup>c</sup>	$b$	$\frac{2\pi^5 k^4}{15h^3 c^2}$	5.67051(0)	$10^{-8}$	$\text{W m}^{-2} \text{K}^{-4}$
Universal gas constant	$R$	$A_v k$	8.314510(7)		$\text{J mol}^{-1} \text{K}^{-1}$

The evolution of the measuring units, and not to forget the history of metrology as a scientific subject, is a very fascinating story which deserves a volume much larger than this text. Here, we can merely appreciate the outcome of the huge scientific efforts leading to the current SI. The system is not entirely fixed, however, and it should be noted that the *working* definitions of length, time, amount, etc. have changed considerably throughout time and that changes are still to come<sup>g</sup>.

The SI-system is the *de facto* standard in scientific texts but there are still other measuring systems around. The Anglo-American systems are among these, and there are systems derived from the SI-system which are used on special occasions ( $\text{\AA}$  and bar for instance). Since it is not likely that man will

<sup>b</sup> André Marie Ampère, 1775–1836. French physicist. <sup>c</sup> William Thomson alias Lord Kelvin, 1824–1907. Irish physicist. <sup>a</sup> E. Richard Cohen and Barry N. Taylor. *Physics Today*, pages 5–9, aug 1999. <sup>b</sup> Count Lorenzo Romano Amedeo Carlo Avogadro di Quaregna e Cerreto, 1776–1856. Italian chemist. <sup>c</sup> Ludwig Boltzmann, 1844–1906. Austrian physicist. <sup>d</sup> Michael Faraday, 1791–1867. English physicist. <sup>e</sup> Max Karl Ernst Ludwig Planck, 1858–1947. German physicist. <sup>f</sup> Jožef Stefan alias Joseph Stefan, 1835–1993. Slovenian physicist and poet. <sup>g</sup> Mass is notably the last of the measuring units that is based on an international prototype. All the other units have been replaced by exact definitions which can be reproduced in any laboratory at any time without the inflict of maintaining a physical prototype.

ever agree on one common set of units<sup>a</sup> we must be able to convert between the different sets on demand. To ease our troubles in this respect we shall describe an algorithm doing exactly this<sup>b</sup>. Assume for simplicity that there are only three fundamental units available: Metre [m], second [s] and gram [g]. The question to be answered is: How can these units be replaced by e.g. inch [in], acceleration of free fall [ $g_a$ ] and pound gravity per square inch [psia] as the input units required by a computer program? A mathematical statement of the problem consists of the recursive definitions

$$\begin{aligned} 1 \text{ kg} &\hat{=} 1000 \text{ g} & 1 \text{ lb} &\hat{=} 0.45359237 \text{ kg} \\ 1 \text{ in} &\hat{=} 0.0254 \text{ m} & 1 g_a &\hat{=} 9.80665 \text{ m s}^{-2} \\ 1 \text{ psia} &\hat{=} 1 g_a \text{ lb in}^{-2} \end{aligned}$$

closed by the identities  $1 \text{ m} \equiv 1 \text{ m}$ ,  $1 \text{ s} \equiv 1 \text{ s}$  and  $1 \text{ g} \equiv 1 \text{ g}$ . Treating the symbols m, kg and s as algebraic entities makes it feasible to write  $\ln(1) + \ln(m) \equiv \ln(1) + \ln(m)$  etc. for each of the identities. Converting all the definitions to logarithmic form yields the following system of linear equations

$$\begin{pmatrix} \ln \mathbf{u} \\ \ln \mathbf{x} \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \ln \mathbf{c} \end{pmatrix} + \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \ln \mathbf{u} \\ \ln \mathbf{x} \end{pmatrix},$$

where

$$\begin{aligned} \mathbf{u}^T &= (m \quad s \quad g), \\ \mathbf{x}^T &= (\text{kg} \quad \text{lb} \quad \text{in} \quad g_a \quad \text{psia}), \\ \mathbf{c}^T &= (1000 \quad 0.45359237 \quad 0.0254 \quad 9.80665 \quad 1), \end{aligned}$$

and the exponents are

$$\mathbf{B} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & -2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathbf{A} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 \end{pmatrix}.$$

A straightforward rearrangement of the equations leads to the simple solution

$$\left( \mathbf{B} \quad (\mathbf{A} - \mathbf{I}) \right) \begin{pmatrix} \ln \mathbf{u} \\ \ln \mathbf{x} \end{pmatrix} = -\ln \mathbf{c}.$$

In the equation above  $\mathbf{A}$  is a square, maybe singular, matrix. The matrix  $\mathbf{A} - \mathbf{I}$ , however, is non-singular for any consistent choice of the units. It can thus be

<sup>a</sup> Fortunately I should say, because else it would be a terribly boring world. Wherever you go and whatever you do everything looks just the same — the very idea scares me. We could as well decide that there should be only one kind of fish and one kind of meat in the world, and maybe that is exactly where we are heading. . . <sup>b</sup> In a consistent manner without using redundant conversion tables.

concluded that the derived units  $\mathbf{x}$  are unique functions of the base units  $\mathbf{u}$ :

$$\ln \mathbf{x} = -(\mathbf{A} - \mathbf{I})^{-1} (\mathbf{B} \ln \mathbf{u} + \ln \mathbf{c}) .$$

The entire range of derived units can easily be generated by redefining the current choice of the base units. Here, we shall assume that the variables are suitably arranged such that  $\mathbf{x}^T = (\mathbf{y}^T \ \mathbf{v}^T)$ , where  $\mathbf{y}$  is a vector of intermediate variables and  $\mathbf{v}^T \hat{=} (\ln \ g_a \ \text{psia})$  is our new vector of base units. Furthermore, let  $\mathbf{A} - \mathbf{I}$  be partitioned into  $(\mathbf{A}_1 \ \mathbf{A}_2)$  such that the row dimension of  $\mathbf{A}_2$  is equal to  $\dim(\mathbf{v}) = \dim(\mathbf{u})$ . The equation can then be rearranged into

$$\left( \mathbf{B} \quad \underbrace{\mathbf{A}_1 \ \mathbf{A}_2}_{\mathbf{A}-\mathbf{I}} \right) \begin{pmatrix} \ln \mathbf{u} \\ \ln \mathbf{y} \\ \ln \mathbf{v} \end{pmatrix} = -\ln \mathbf{c} ,$$

and the alternative solution written

$$\begin{pmatrix} \ln \mathbf{u} \\ \ln \mathbf{y} \end{pmatrix} = -\left( \mathbf{B} \ \mathbf{A}_1 \right)^{-1} (\mathbf{A}_2 \ln \mathbf{v} + \ln \mathbf{c}) .$$

When the numbers from the last page are plugged into the expression above the answer comes out on logarithmic form, but exponentiation on both sides reveals the following conversion factors:

$$\mathbf{u} \begin{cases} 1 \text{ m} & = 39.370078 \dots \text{in}^1 \\ 1 \text{ s} & = 19.649136 \dots \text{in}^{0.5} \text{g}_a^{-0.5} \\ 1 \text{ g} & = 0.0022046 \dots \text{in}^2 \text{g}_a^{-1} \text{psia}^1 \end{cases}$$

$$\mathbf{y} \begin{cases} 1 \text{ kg} & = 2.2046226 \dots \text{in}^2 \text{g}_a^{-1} \text{psia}^1 \\ 1 \text{ lb} & = 1.0000000 \dots \text{in}^2 \text{g}_a^{-1} \text{psia}^1 \end{cases}$$

These conversion factors are valid for a measuring system where in,  $\text{g}_a$  and psia make the selected basis.



## APPENDIX C

**Newton Iteration**

Let  $\mathbf{x}$  be a state vector of the (gradient) function  $\mathbf{g}(\mathbf{x})$ , and  $\mathbf{H}(\mathbf{x})$  the corresponding Jacobian<sup>a</sup> (Hessian<sup>b</sup> if  $\mathbf{g}$  is a gradient). The Newton<sup>c</sup> iteration from  $k \rightsquigarrow k+1$  is defined as

$$\mathbf{x}^{k+1} = \mathbf{x}^k - (\mathbf{H}^k)^{-1} \mathbf{g}^k.$$

Suppose that a stable stationary point  $\mathbf{g}^\infty = \mathbf{0} \wedge \det \mathbf{H}^\infty \neq 0$  exists. The Taylor<sup>d</sup> expansion of  $\mathbf{g}$  in the vicinity of  $\mathbf{x}^\infty$  is

$$\mathbf{g}^k = \mathbf{g}^\infty + \sum_i \left( \frac{\partial \mathbf{g}}{\partial x_i} \right)^\infty (x_i^k - x_i^\infty) + \mathcal{O}(x^2) \simeq \mathbf{H}^\infty (\mathbf{x}^k - \mathbf{x}^\infty).$$

In the same spirit the Taylor expansion of  $\mathbf{H}^{-1}$  can be written

$$(\mathbf{H}^k)^{-1} = (\mathbf{H}^\infty)^{-1} + \sum_i \left( \frac{\partial \mathbf{H}^{-1}}{\partial x_i} \right)^\infty (x_i^k - x_i^\infty) + \mathcal{O}(x^2).$$

Implicit differentiation of  $\mathbf{I} \equiv \mathbf{H}\mathbf{H}^{-1}$  leads to  $\partial \mathbf{H}^{-1} / \partial x_i = -\mathbf{H}^{-1} (\partial \mathbf{H} / \partial x_i) \mathbf{H}^{-1}$  for all  $x_i \in \mathbf{x}$ . Inserted into the Taylor expansion of  $\mathbf{H}^{-1}$  it follows that

$$(\mathbf{H}^k)^{-1} \simeq (\mathbf{H}^\infty)^{-1} - (\mathbf{H}^\infty)^{-1} \sum_i \left( \frac{\partial \mathbf{H}}{\partial x_i} \right)^\infty (x_i^k - x_i^\infty) (\mathbf{H}^\infty)^{-1}.$$

At a point  $\mathbf{x}^k$  close to  $\mathbf{x}^\infty$  the Taylor expansions of  $\mathbf{g}$  and  $\mathbf{H}$  are sufficiently accurate to help us understand the local convergence conditions of the iteration sequence, hence from the Newton update  $\mathbf{x}^{k+1} = \mathbf{x}^k - (\mathbf{H}^k)^{-1} \mathbf{g}^k$  we may write

$$\mathbf{x}^{k+1} = \mathbf{x}^k - \left[ \mathbf{I} - (\mathbf{H}^\infty)^{-1} \sum_i (x_i^k - x_i^\infty) \left( \frac{\partial \mathbf{H}}{\partial x_i} \right)^\infty \right] (\mathbf{x}^k - \mathbf{x}^\infty).$$

Making the variable shift  $\mathbf{y} \hat{=} \mathbf{x} - \mathbf{x}^\infty$  in the last equation

$$\mathbf{y}^{k+1} = (\mathbf{H}^\infty)^{-1} \sum_i y_i^k \left( \frac{\partial \mathbf{H}}{\partial x_i} \right)^\infty \mathbf{y}^k,$$

and multiplying on both sides with  $\mathbf{H}^\infty$ , leaves an expression amenable to an-

<sup>a</sup> Carl Gustav Jacob Jacobi, 1804–1851. German mathematician. <sup>b</sup> Ludwig Otto Hesse, 1811–1874. German mathematician. <sup>c</sup> Sir Isaac Newton, 1642–1727 by the Julian calendar. English physicist and mathematician. <sup>d</sup> Brook Taylor, 1685–1731. English mathematician.

alytical operations. The  $j$ 'th element of  $\mathbf{H}^\infty \mathbf{y}^{k+1}$  is

$$\begin{aligned} (\mathbf{H}^\infty \mathbf{y}^{k+1})_j &= \sum_i y_i^k \sum_k \left( \frac{\partial^3 f}{\partial x_i \partial x_j \partial x_k} \right)^\infty y_k^k = \sum_i \sum_k y_i^k \left[ \frac{\partial}{\partial x_j} \left( \frac{\partial^2 f}{\partial x_i \partial x_k} \right) \right]^\infty y_k^k \\ &= (\mathbf{y}^k)^\top \left( \frac{\partial \mathbf{H}}{\partial x_j} \right)^\infty \mathbf{y}^k, \end{aligned}$$

which on back-substitution into the formula for  $\mathbf{y}^k$  yields:

$$(C.1) \quad \mathbf{y}^{k+1} = (\mathbf{H}^\infty)^{-1} \begin{pmatrix} (\mathbf{y}^k)^\top \left( \frac{\partial \mathbf{H}}{\partial x_1} \right)^\infty \mathbf{y}^k \\ \vdots \\ (\mathbf{y}^k)^\top \left( \frac{\partial \mathbf{H}}{\partial x_n} \right)^\infty \mathbf{y}^k \end{pmatrix}.$$

This equation is analogous to Banach's Fix Point Theorem<sup>a</sup> for linear operators. It is readily observed that  $\|\mathbf{y}^{k+1}\| \propto \|\mathbf{y}^k\|^2$  because the matrices  $\mathbf{H}^\infty$  and  $(\partial \mathbf{H} / \partial x_i)^\infty$  are constant by definition. Quite interestingly, quadratic convergence is the case even when an eigenvalue of  $\mathbf{H}^\infty$  is several order of magnitudes smaller than the rest. The Newton iteration converges then along the eigenvector corresponding to  $\lambda_{\min}$  (almost fixed direction), but the convergence rate will still be of second order. The convergence region may be very small, however, as is seen from the norm estimate given below:

$$\|\mathbf{y}^{k+1}\| \leq \|(\mathbf{H}^\infty)^{-1}\| \sqrt{\sum_j \left[ (\mathbf{y}^k)^\top \left( \frac{\partial \mathbf{H}}{\partial x_j} \right)^\infty \mathbf{y}^k \right]^2} \leq \lambda_{\min}^{-1} \sqrt{n} \max(\lambda_j) \|\mathbf{y}^k\|^2.$$

Here,  $\max(\lambda_j)$  denotes the largest (absolute) eigenvalue of all the  $(\partial \mathbf{H} / \partial x_j)^\infty$  matrices. Unambiguous convergence requires that  $\|\mathbf{y}^k\| > \|\mathbf{y}^{k+1}\|$  in each step, and from the conservative estimate of  $\|\mathbf{y}^{k+1}\|$  it can be concluded that<sup>b</sup>

$$(C.2) \quad \|\mathbf{y}^0\| < \frac{\lambda_{\min}}{\sqrt{n} \max(\lambda_j)}.$$

This inequality defines a (conservative) convergence region around  $\mathbf{x}^\infty$ . Note the appearance of  $\sqrt{n}$  in the denominator. This factor is a mathematical necessity although in most cases it makes the condition too strict.

Opposite to common belief the Newton iteration does not converge "fast" from the first iteration on. It is a second order method all right, but it usually takes 3-5 iterations before convergence really sets in. This is illustrated in the table below where the convergence factor  $\alpha = \lambda_{\min}^{-1} \sqrt{n} \max(\lambda_j)$  is taken to be constant and the starting point is selected such that  $\|\mathbf{y}^0\| = 0.9\alpha$ . It is only from iteration 5 and onwards we get the feeling of rapid convergence, although the sequence is of second order during the entire iteration:

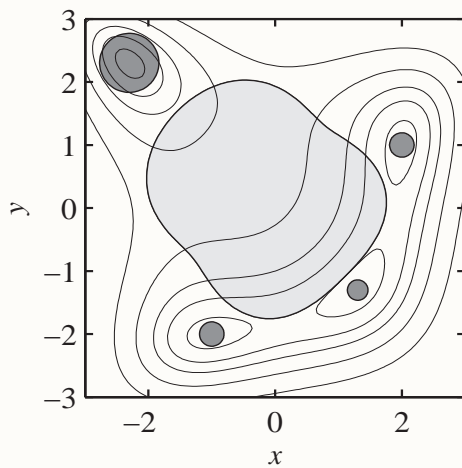
<sup>a</sup> Stefan Banach, 1892–1945. Polish mathematician. <sup>b</sup> An other approach to this problem is to claim that  $\mathbf{H} \approx \mathbf{H}^\infty + \sum_j (\partial \mathbf{H} / \partial x_j)^\infty y_j$  is non-singular in the iteration domain. A conservative criterion is  $\lambda_{\min} - \sum_j |\lambda_j| y_j > 0$  and from  $\sum_j y_j \leq \sqrt{n} \|\mathbf{y}\|$  it follows that  $\lambda_{\min} > \sqrt{n} \max(\lambda_j) \|\mathbf{y}\|$ .

0	1	2	3	4	5	6	7	8
.90	.81	.66	.43	.18	.034	1.2e-3	1.39e-6	1.93e-12

O . Let  $g(x) = (a - x)(b - x)$ . The stationary points of this function are  $x_1 = a$  and  $x_2 = b$ . The Jacobian is  $H(x) = 2x - (a + b)$ . At the two stationary points  $H^\infty$  becomes  $\pm(a - b)$ . The second derivative is the constant  $\partial H/\partial x = 2$  and from Eq. C.1 we can write for all  $x \in \mathbb{R}$ :

$$y^{k+1} = \pm \frac{y^k 2y^k}{a-b} = \pm \frac{2}{a-b} (y^k)^2.$$

From this update formula it follows that the convergence region is  $|y^k| < \left| \frac{a-b}{2} \right|$  because any values larger than this will be magnified on the right hand—a conclusion that is in full agreement with the estimate given in Eq. C.2 (the latter equation happens to be an exact condition in this case).  $\square$



**FIGURE C.1** Contour diagram shown along with the regions of convergence for the function  $4z(x, y) = p^2 + q^2$  (here  $p = x^2 - 3 - y$  and  $q = 3 - y^2 - x$ ). The small patches indicate conservative estimates of the convergence regions and the big patch is where the Hessian is indefinite ( $\lambda_{\min} < 0$ ).

T . Let  $z(x, y) = \frac{1}{4}(p^2 + q^2)$  where  $p = x^2 - 3 - y$  and  $q = 3 - y^2 - x^a$ . The gradient vector and the Hessian matrix for this function can be expressed like

$$-\mathbf{g} = \begin{pmatrix} \frac{1}{2}q - xp \\ \frac{1}{2}p + yq \end{pmatrix},$$

$$\mathbf{H} = \begin{pmatrix} \frac{1}{2} + 2x^2 + p & y - x \\ y - x & \frac{1}{2} + 2y^2 - q \end{pmatrix},$$

and the third derivatives are

$$\mathbf{H}_x = \begin{pmatrix} 24x & -4 \\ -4 & 4 \end{pmatrix}, \quad \mathbf{H}_y = \begin{pmatrix} -1 & 1 \\ 1 & 6y \end{pmatrix}.$$

<sup>a</sup> The expressions  $p$  and  $q$  describe parabolas symmetric about the  $y$  and  $x$  axes respectively. The indicated sum of squares have zeros where the two parabolas intersect.

The stationary points are calculated in Matlab script 1.8 from Appendix F, together with the eigenvalues of the Hessian as well as the third derivative matrices:

$x$	$y$	$\lambda_{\min}$	$\max(\lambda_j)$	$\frac{\lambda_{\min}}{\max(\lambda_j)}$
2	1	2.338	12.09	0.193
1.303	-1.303	1.289	7.960	0.162
-1	-2	2.338	12.09	0.193
-2.303	2.303	6.5	13.88	0.468

Put into Eq. C.2 this gives the convergence radii indicated to the right (the  $\sqrt{n}$ -term has been left out). Figure C.1 gives a graphical picture of the situation. Note carefully that the estimated convergence regions are circular whilst the true geometries are much more complicated (of fractal nature—only the indefinite region is depicted here).  $\square$

## APPENDIX D

**Direct Substitution**

Let vector  $\mathbf{x}^\infty$  be a solution point for  $\mathbf{x}^\infty = \mathbf{f}(\mathbf{x}^\infty)$ . The recurrence formula according to Banach's fix-point theorem is

$$\mathbf{x}^{k+1} = \mathbf{f}(\mathbf{x}^k).$$

The conditions of convergence and the convergence rate shall next be outlined. At a point sufficiently close to the solution it is permissible to write

$$\begin{aligned} \mathbf{f}(\mathbf{x}^k) &= \mathbf{f}(\mathbf{x}^\infty) + \left(\frac{\partial \mathbf{f}}{\partial \mathbf{x}}\right)^\infty (\mathbf{x}^k - \mathbf{x}^\infty) + \mathcal{O}(\|\Delta \mathbf{x}^k\|^2) \\ &\simeq \mathbf{f}(\mathbf{x}^\infty) + \mathbf{J}(\mathbf{x}^k - \mathbf{x}^\infty). \end{aligned}$$

Combine the two equations while using the convergence criterion  $\mathbf{x}^\infty = \mathbf{f}(\mathbf{x}^\infty)$

$$\mathbf{x}^{k+1} = \mathbf{x}^\infty + \mathbf{J}(\mathbf{x}^k - \mathbf{x}^\infty) = \mathbf{y} + \mathbf{J}\mathbf{x}^k.$$

The first elements in the iteration sequence read

$$\begin{aligned} \mathbf{x}^1 &= \mathbf{y} + \mathbf{J}\mathbf{x}^0 \\ \mathbf{x}^2 &= \mathbf{y} + \mathbf{J}\mathbf{x}^1 = \mathbf{y} + \mathbf{J}\mathbf{y} + \mathbf{J}^2\mathbf{x}^0 \\ \mathbf{x}^3 &= \mathbf{y} + \mathbf{J}\mathbf{x}^2 = \mathbf{y} + \mathbf{J}\mathbf{y} + \mathbf{J}^2\mathbf{y} + \mathbf{J}^3\mathbf{x}^0 \\ &\vdots \end{aligned}$$

Expand the  $k$ 'th term and substitute the convergence criterion  $\mathbf{x}^\infty = \mathbf{f}(\mathbf{x}^\infty)$

$$\begin{aligned} \mathbf{x}^{k+1} &= (\mathbf{I} + \mathbf{J} + \mathbf{J}^2 + \dots + \mathbf{J}^k)\mathbf{y} + \mathbf{J}^{k+1}\mathbf{x}^0 \\ &= (\mathbf{I} + \mathbf{J} + \mathbf{J}^2 + \dots + \mathbf{J}^k)(\mathbf{I} - \mathbf{J})\mathbf{x}^\infty + \mathbf{J}^{k+1}\mathbf{x}^0 \\ &= (\mathbf{I} - \mathbf{J}^{k+1})\mathbf{x}^\infty + \mathbf{J}^{k+1}\mathbf{x}^0 \\ &= \mathbf{x}^\infty + \mathbf{J}^{k+1}(\mathbf{x}^0 - \mathbf{x}^\infty). \end{aligned}$$

Eigenvalue decomposition of  $\mathbf{J}$  (assumed diagonalisable) yields  $\mathbf{J} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}$ . Let the eigenvalues be sorted in ascending order such that  $|\lambda_1| < |\lambda_2| < \dots < |\lambda_n|$ . The last two eigenvalues are supposedly well separated such that  $\lambda_{n-1}^k \ll \lambda_n^k$  for finite  $k$ 's. In the limit of  $k \rightarrow \infty$  only one eigenvector  $\mathbf{q}_n$  corresponding to the largest eigenvalue  $\lambda_n$  will survive in  $\mathbf{J}^{k+1}$  meaning that

$$(D.1) \quad \lim_{k \rightarrow \infty} \mathbf{x}^{k+1} = \mathbf{x}^\infty + c\lambda_n^{k+1}\mathbf{q}_n$$

where  $c = \sum_{i=1}^n \mathbf{S}_{n,i}^{-1}(\mathbf{x}_i^0 - \mathbf{x}_i^\infty)$ . With this notation the difference between two successive iterations  $k$  and  $k + 1$  becomes

$$\begin{aligned}\Delta \mathbf{x}^{k+1} &= c \lambda_n^k (\lambda_n - 1) \mathbf{q}_n, \\ \Delta \mathbf{x}^{k+2} &= c \lambda_n^k (\lambda_n^2 - \lambda_n) \mathbf{q}_n.\end{aligned}$$

Combining the two last equations leaves

$$\Delta \mathbf{x}^{k+2} = \Delta \mathbf{x}^{k+1} \frac{\lambda_n^2 - \lambda_n}{\lambda_n - 1} = \Delta \mathbf{x}^{k+1} \lambda_n.$$

Hence, the convergence rate is clearly of first order because the norm

$$(D.2) \quad \|\Delta \mathbf{x}^{k+2}\| = \lambda_n \|\Delta \mathbf{x}^{k+1}\|$$

of two successive update vectors will approach a constant value  $\lambda_n$  (in the limit  $k \rightarrow \infty$ ). Clearly, if  $|\lambda_n| \geq 1$  the process will not converge at all. It also follows that  $\lambda_n$  can be estimated from two successive updates taking the inner product with  $\Delta \mathbf{x}^{k+1}$  on both sides:

$$(D.3) \quad \lambda_n = \lim_{k \rightarrow \infty} \frac{(\Delta \mathbf{x}^{k+1})^T \Delta \mathbf{x}^{k+2}}{(\Delta \mathbf{x}^{k+1})^T \Delta \mathbf{x}^{k+1}}.$$

Close to the solution point the eigenvector  $\mathbf{q}_n$  will experience small changes from one iteration to the next and the iterations will creep along  $\mathbf{q}$  at a constant rate  $1 - \lambda_n$ . Note that in the limit  $\lambda_n \rightarrow 1$  the iteration progress becomes infinitely slow. The dominant eigenvalue acceleration method tries to remedy this flaw by forming an accelerated step every 4th iteration (or so). From Eq.D.1 we get

$$\begin{aligned}\mathbf{x}^\infty &= \mathbf{x}^{k+1} - c \lambda_n^{k+1} \mathbf{q}, \\ \mathbf{x}^\infty &= \mathbf{x}^k - c \lambda_n^k \mathbf{q}.\end{aligned}$$

Eliminating  $c \lambda_n^k \mathbf{q}$  from the equations above yields the approximation

$$\mathbf{x}^\infty \approx \frac{\mathbf{x}^{k+1} - \lambda_n \mathbf{x}^k}{1 - \lambda_n},$$

where  $\lambda_n$  is estimated from the last three iterates  $\mathbf{x}^{k-1}, \mathbf{x}^k, \mathbf{x}^{k+1}$  as explained in Eq.D.3. Unless there is a weird coupling between the iterate  $\mathbf{x}^k, \mathbf{x}^{k+1}$  and the eigenvalue  $\lambda_n$ , the step taken will be proportional to the ratio  $1/(1 - \lambda_n)$ . Apparently, the dominant eigenvalue method will converge at a higher rate than the direct substitution method when  $\lambda_n$  approaches unity (the convergence rate will be something like  $\sqrt{2}$ ).

## APPENDIX E

**Nine Concepts of Mathematics**

We shall in this appendix propose working definitions of mathematical concepts commonly used in the engineering, and in the applied physics, literature. The first five of the definitions deal with vague concepts like: Expressions, functions, mappings, transformations and operators. They are by no means strict, at least not so to the taste of a mathematician, but on the other hand no universally accepted definitions seem to exist. The reader is therefore left in an equivocal state until somebody more skilled than the present author comes up with precise definitions<sup>a</sup>, and the rest of the world starts to follow them.

**E** . A combination of numbers, variables and operators that can be evaluated according to grammatical rules. Two expressions with the same semantic meaning (scientific units for example) can be combined into a *relation* using logical  $<$ ,  $>$ ,  $=$ , etc. An *equation* is a relation that is true ( $=$ ) for zero or more values of the variables (the solutions). An equation that is true regardless of any particular value of the variables is called an *identity*<sup>b</sup>.  $\square$

**F** . A point-to-point rule  $f$  which assigns, to each element  $x \in D$  in the definition domain  $D \subseteq X$ , exactly one element  $y = f(x) \in R$  in the function range  $R \subseteq Y$ .  $X$  and  $Y$  are two sets, typically  $\mathbb{Z}$ ,  $\mathbb{Q}$ ,  $\mathbb{R}$  or  $\mathbb{C}$ . A common notation is  $f : X \rightarrow Y$  where  $f$  can be the rule of correspondence belonging to a *mapping*, a *transformation* or an *operator*. One also speaks of  $f$  taking the argument  $x$ , or that  $f(x)$  is the function value of  $x$ , or that  $y$  is the dependent variable and  $x$  is the independent variable. The set of ordered pairs  $\{(x, y)\} \in X \times Y$  is called the graph of  $f$ . In common speech  $f$  and  $f(x)$  are used interchangeably but this should be avoided. Strictly speaking  $f(x)$  denotes a point in  $Y$  whereas  $f$  is the rule of correspondence, or vice versa, but not with both meanings at the same time. The abstraction is a matter of preference as long as it is applied consistently. An explicit function is written  $y = f(x)$  whereas an implicit function is written  $F(x, y) = 0$ . The inverse of  $f$  is defined as  $x = f^{-1}(y)$ . In the general case this is a multi-valued equation which may, or may not, be a function. If  $f : X \rightarrow Y$  and  $g : Y \rightarrow Z$ , then  $f \circ g : X \rightarrow Z$  is called the composite of  $f$  and  $g$ .  $\square$

<sup>a</sup> In the meanwhile you should check out <http://en.wikipedia.org> <sup>b</sup> E.g. the relation  $x \ln(x) < 0$  is true for  $x < 1$ , the equation  $x \ln(x) = e$  has the solution  $x = e$ , and the identity  $\ln(\exp(x)) \equiv x$ .

**M** . The abstract operation of bringing a *domain*  $D \subseteq X$  onto its *image*  $R = f(D) \subseteq Y$  using a point-to-point rule  $f$ . In the special case that  $X$  and  $Y$  are number sets, mapping and function are often used interchangeably, but the set operation is the one favoured here. From the definition of the function there must to each element  $x \in D$  correspond one single element  $y \in R$ , and for each  $y \in R$  there shall correspond at least one element  $x \in D$ . If  $Y = X$  one says that  $f$  maps the set  $X$  into itself. If  $Y = R$ , that is if  $Y$  coincides with the range of  $f$ , then  $f$  maps  $X$  onto  $Y$  and is said to be a *surjection*. If  $x_1 \neq x_2 \Rightarrow y_1 \neq y_2$  then  $f$  is an *injection*, or a one-to-one mapping. If the mapping is both one-to-one and onto  $f$  is said to be a *bijection*. One also speaks about a correspondence or an invertible mapping.  $\square$

**T** . A mapping  $A$  from one *vector space*  $X$  onto itself, or into a different vector space  $Y$ . The notation  $y = Ax$  is frequently used. A transformation can be one-to-one and thereby invertible as in  $x = A^{-1}y$  where  $A$  is any  $n \times n$  non-singular matrix<sup>a</sup>. A transformation which remains unchanged if it is applied twice i.e.  $AAx = Ax$  is called *idempotent*<sup>b</sup>. A *projection* is an idempotent transformation for which  $Y$  is a subspace of  $X$  and is thus non-invertible<sup>c</sup>.  $\square$

**O** . A mapping  $A$  from one function space  $X$  to a related function space  $Y$ . The domain of  $A$  is denoted  $D(A)$  and the range  $R(A)$  is defined as  $\{A(x) \mid x \in D\}$ . If  $Y = X$  then  $A$  is called an operator on  $X$ . If  $D(A) = X$  then  $A$  is called an everywhere defined operator. If  $x_1 \neq x_2 \Rightarrow Ax_1 \neq Ax_2$  then the inverse operator  $A^{-1}$  can be defined such that  $x = A^{-1}Ax$ . A zero operator assigns the element  $0 \in Y$  to every  $x \in X$ . An identity operator assigns the element  $x \in X \subseteq Y$  to every element  $x \in X$ . If  $A$  is an everywhere defined operator such that  $AA = A$ , then  $A$  is called a projection operator. The operator  $A$  is *linear* if it fulfils  $A(\alpha \star x_1 + \beta \star x_2) = \alpha \star A(x_1) + \beta \star A(x_2)$ <sup>d</sup>. The binary *infix* operator  $\star : S \times S \rightarrow S$  takes two elements from  $S$  and returns a single element of  $S$ . The element in  $S$  assigned to  $(x, y) \in S \times S$  is denoted  $x \star y$ . The operator  $\star$  is *commutative* if  $x \star y = y \star x$ , *associative* if  $x \star (y \star z) = (x \star y) \star z$  and *distributive* over the operator  $\circ$  if  $x \star (y \circ z) = (x \star y) \circ (x \star z)$ .  $\square$

**G** . An associative operator  $\circ$  defined on a non-empty set  $G$  such that to each  $x, y \in G$  there exist a third element  $z = x \circ y \in G$ . The notation  $\langle G, \circ \rangle$  is used to signify that the *semigroup* is closed under  $\circ$ :

$$x \circ (y \circ z) = (x \circ y) \circ z.$$

The semigroup can be extended to a *group* if a neutral element  $e \in G$  and an

<sup>a</sup> Other examples include congruence  $CAC^T$  and Legendre  $f - x \frac{\partial f}{\partial x}$  transformations. <sup>b</sup> The similarity transformation  $SAS^{-1}$  is one example. <sup>c</sup> The least square projection  $A^T(AA^T)^{-1}A$  brings vector  $y$  onto the subspace  $A^T x$ . <sup>d</sup> For instance  $\mathcal{D}_x y = \frac{\partial y}{\partial x} \triangleq \lim_{\Delta x \rightarrow 0} \frac{\Delta y}{\Delta x}$ ,  $\mathcal{I}_x y = \int y dx$ , and  $\mathcal{L}_x y = y - x \frac{\partial y}{\partial x}$ .



inverse element  $x^{-1} \in G$  exist such that

$$\begin{aligned}x \circ e &= e \circ x = x, \\x \circ x^{-1} &= x^{-1} \circ x = e.\end{aligned}$$

This group is ordinarily called a *multiplicative* group, in which case the operator  $\circ$  is often replaced by  $\star$  and  $e$  is given the meaning of 1 in some sense. If also

$$x \circ y = y \circ x,$$

the group is an *abelian*<sup>a</sup> or commutative group. This group is ordinarily called an *additive* group, in which case the operator  $\circ$  is replaced by  $+$  and  $x^{-1}$  by  $-x$ , and  $e$  is given the meaning of 0 in some sense.  $\square$

**R** . A ring  $\langle R, +, \star \rangle$  is an additive abelian group  $\langle R, + \rangle$  combined with a semigroup  $\langle R, \star \rangle$  which is closed under a second operation called multiplication. The product  $\star$  of three elements  $x, y, z \in R$  must fulfil

$$\begin{aligned}x \star (y \star z) &= (x \star y) \star z, \\x \star (y + z) &= x \star y + x \star z, \\(x + y) \star z &= x \star z + y \star z.\end{aligned}$$

Note that, combined with the underlying properties of the abelian group, this is sufficient to prove that

$$x \star 0 = 0 \star x = 0.$$

Multiplication is not necessarily commutative, but if this is the case, i.e. if

$$x \star y = y \star x$$

the ring is said to be commutative. If in addition,

$$x \star 1 = 1 \star x = x$$

where 1 is a unique identity element, then  $\langle R, +, \star \rangle$  is called a ring with identity. To each regular element  $x$  corresponds an inverse element  $x^{-1}$ . Elements that do not have inverses are called singular. If  $\forall x \neq 0$  are regular the ring is a *division* ring.  $\square$

**F** . A field  $\mathbb{F}$  is a commutative division ring, e.g.  $\mathbb{Q}, \mathbb{R}$  and  $\mathbb{C}$ .  $\square$

**V** . Let  $\langle V, + \rangle$  be an additive abelian group defined over the number field  $\mathbb{F}$ . This means that for each  $x, y, z, 0 \in V$  the following prop-

<sup>a</sup> Niels Henrik Abel, 1802–1829. Norwegian mathematician.

erties are all true:

$$\begin{aligned}x + y &\in V, \\(x + y) + z &= x + (y + z), \\x + y &= y + x, \\x + 0 &= x, \\(-x) + x &= 0.\end{aligned}$$

If the next properties are also true for given  $\alpha, \beta, 1 \in \mathbb{F}$ , then  $V$  is said to be a *vector space* over  $\mathbb{F}$ :

$$\begin{aligned}\alpha \star x &\in V, \\\alpha \star (\beta \star x) &= (\alpha\beta) \star x, \\\alpha \star (x + y) &= \alpha \star x + \alpha \star y, \\(\alpha + \beta) \star x &= \alpha \star x + \beta \star x, \\1 \star x &= x.\end{aligned}$$

Note in particular that  $0$  means a vector whereas  $\alpha, \beta, 1$  are scalars. These are different mathematical entities which even belong to different spaces unless  $X = \mathbb{F}$ . Note also that  $\star$  behaves differently from scalar multiplication. For this reason the product of  $\alpha$  times  $\beta$  is simply written  $\alpha\beta$  and not  $\alpha \star \beta$ . A vector space equipped with the concept of length is called a *normed* vector space if the following properties can be verified:

$$\begin{aligned}\|x\| &\geq 0, \\\|\alpha x\| &= |\alpha| \|x\|, \\\|x + y\| &\leq \|x\| + \|y\|. \quad \square\end{aligned}$$

## APPENDIX F

**Code Snippets**

The graphs (figures with quantitative axes) from the main text are programmed in Matlab with due reference to Section 1 below. The reader is thereby given an excellent opportunity to re-examine important details of the calculations, and to make changes of her own. Note, however, that some of the calculations require access to the user defined functions presented in Section 2 on page 123. These functions must be available in the Matlab search path before calculations are attempted.

A “script” is here given the semantic meaning of Matlab’s interpretive programming environment, but this does not mean that everything is tied entirely up to Matlab. The code snippets are rather simple and can easily be translated into other programming languages (Ruby, Python, etc.), provided the (other) language has a suitable graphics driver. However, it may prove difficult to find a language that gives a more compact computer code than Matlab does due to its matrix–vector oriented grammar.

**1. Interactive code****1.1. Legendre transformation of internal energy.**

```
%Plot internal energy of ideal gas                                     %
g = 5/3;                                                             % Cp/Cv
v = logspace(-2,0.3,100);                                           % dimensionless volume
u = v.^(1-g);                                                       % internal energy
plot(v,u,'-k'), hold on;                                           % plot U(V) at constant S
axis([0,0.5,1,11])                                                %
%                                                                    %
%Plot points of transformation                                       %
h = [9,7,5,3];                                                      % equi-distant enthalpy
v = (h/g).^(1/(1-g));                                              % back-calculated volume
u = v.^(1-g);                                                       % back-calculated internal energy
V = [zeros(size(v));v];                                           % volume axis for H and U
U = [h;u];                                                         % H and U values
plot(v,u,'ok',V,U)                                               %
%                                                                    %
%Plot enthalpy values                                              %
set(gca,'XTick',v)
set(gca,'XTickLabel',['V1';'V2';'V3';'V4'])
set(gca,'YTick',h(end:-1:1))
```

```

set(gca,'YTickLabel',['H4';'H3';'H2';'H1'])
%
%Annotate transformation figure
vu = linspace(.18,v(end),length(v));
V = [v;vu;vu];
U = [u;u;h(2)*ones(size(u))];
plot(V,U,'k','LineWidth',0.2); hold off;
text(vu(1)-0.02,h(2)+0.3,'U1'); text(vu(2)-0.02,h(2)+0.3,'U2')
text(vu(3)-0.02,h(2)+0.3,'U3'); text(vu(4)-0.02,h(2)+0.3,'U4')
text(0.130,h(1)+1.0,'umdudv'); text(0.130,h(1)+0.0,'umpv')
printps('UigTransform',5,6)

```

### 1.2. Contour diagram of Gibbs energy.

```

a = 2.4; % energy parameter / R*T
n = [0.01:0.01:1]'; % mole number vector
N1 = [n,2*n,3*n,4*n]; % mole numbers component 1
N2 = N1; % mole numbers component 2
G = ones(size(N1)); % Gibbs energy
dG = G; % Gibbs energy difference
%
%Calculate equidistant iso-G-curves. Iterate on N2 while keeping
%N1 fixed until the Gibbs energies are the same in each column
%of the G-matrix. The last value, which corresponds to an equi-
%molar mixture, is used as target
while max(max(abs(dG./G)))>1e-6
    X1 = N1./(N1+N2); % mole fraction 1
    X2 = N2./(N1+N2); % mole fraction 2
    Gex = a*N1.*X2; % excess Gibbs
    Gid = N1.*log(X1) + N2.*log(X2); % ideal Gibbs
    G = Gex + Gid; % total Gibbs
    Mu1 = a*X2.*X2 + log(X1); % chemical potential # 1
    Mu2 = a*X1.*X1 + log(X2); % chemical potential # 2
% G = N1.*Mu1 + N2.*Mu2; % alternative expression
    dG = G - ones(size(n))*G(end,:); % energy difference
    N2 = N2 - dG./Mu2; % simultaneous iteration of all points
end
%
%Calculate two-phase equilibrium (very simple because of the
%symmetry).
n1 = 1; n2 = 6;
mu1 = 0; mu2 = 1;
%
%Iterate on n2 while keeping n1 fixed until the two chemical pot-
%entials are equal.
while abs(mu1-mu2)>1e-6
    nt = n1 + n2; % total mole number
    x1 = n1./nt; % mole fraction 1
    x2 = n2./nt; % mole fraction 2

```

```

mu1 = a*x2.*x2 + log(x1);           % chemical potential # 1
mu2 = a*x1.*x1 + log(x2);           % chemical potential # 2
dmudn = (2*a*x1*x2-1)/nt + ...      % derivative of mu1 -
        (2*a*x1*x1-x1/x2)/nt;      % derivative of mu2
n2 = n2 - (mu1-mu2)/(dmudn);        % Newton iteration
end
%
%Show iso-curves
plot(N1,N2,'b',N2,N1,'b'), hold on; % symmetric diagram
axis([0,6,0,6]); box off; xlabel('N1'); ylabel('N2')
%
%Show two-phase equilibrium region
y = G(1,:)/mu2;                     % y-axis intersections
x = G(1,:)/mu1;                     % x-axis intersections
plot([0,y(3)], [x(3),0], '--r')     % equilibrium tangent
plot([y(3)*x1,y(3)*x2], [x(3)*x2,x(3)*x1], '-r') % equilibrium
%
%Show equidistant points (on the iso-curves) along three different
%rays running from origo
plot(y*x1,y*x2,'ok',x*x2,x*x1,'ok') % equil. points
plot(N1(end,:),N2(end,:), 'ok')     % diagonal points
plot([0,y]*x1,[0,y]*x2, '--k', 'LineWidth',0.2) % left ray
plot([0,x]*x2,[0,x]*x1, '--k', 'LineWidth',0.2) % right ray
plot([0,N1(end,:)],[0,N2(end,:)], '--k', 'LineWidth',0.2) % diag
%
%Annotations.
plot([0,3],[y(3),5.5], 'k', 'LineWidth',0.2); % y-axis intersection
text(3.1,5.5, 'Gdivmu2'); % label
plot([x(3),5.5],[0,3], 'k', 'LineWidth',0.2), hold off; % x-axis
text(5.3,3.4, 'Gdivmu1'); % label
printps('IsoGibbsCurves',6,6)

```

### 1.3. Phase diagram: Synthetic natural gas.

```

%Experimental data for synthetic natural gas taken from Gonzales,
%M.H. and Lee,A.L. J.Chem.Eng.Data, 13(2), 172-176, (1968), valid
%for mixture number 9 (nitrogen, methane, ethane, propane, n-butane).
%
global x y k rk liq vap              % global flash data
%
z = [1.6 94.5 2.6 0.81 0.52]';      % feed fraction
x = z./[10 10 1.5 1.05 1.01]';     % initial liquid composition
y = z - x;                          % initial vapor composition
k = ones(size(x));                  % same reference state in both phases
%
%Bubble point measurements
pbul = [753.8 713.0 533.7 375.9 261.1 169.6 106.4 37.2];
tbub = -[105 110 130 150 170 190 210 250 ];
%

```

```

%Dew point measurements
pdew = [ 34.4  49.4  62.4 130.6 214.1 323.8 421.7 414.6 516.9 ...
        688.4 685.8 713.4 720.6 780.9 830.9 839.9 841.4 815.0 ...
        791.6 790.0];
tdew =-[160  140  120  100  85  75  70  70  65  ...
        63  63  64  65  70  75  83  86.8 95  ...
        100.5 100.5];

%
%Critical point
tc = -100.5;
pc = (790.9+791.6)/2;

%The Redlich-Kwong equation of state is used for both phases
vap.tc = [126.2 190.6 305.3 369.8 425.1]'; % Tc [K]
vap.pc = [ 34.0 46.0 48.7 42.5 38.0]'; % Pc [bar]
vap.phase = 'vapor'; % phase label
liq.tc = vap.tc; % critical temperatures [K]
liq.pc = vap.pc; % critical pressures [bar]
liq.phase = 'liquid'; % phase label
rk = @FugacityRedlichKwong; % function pointer

%
%Calculate the smallest phase fraction in each selected T,p-frame
t =-[220 100 160; 160 40 100; 150 30 90]; % temperature frames
p = [ 10 10 500; 500 500 10; 500 500 990]; % pressure frames
n = 1; % total number of recursive function calls
axis([-220,-60,0,900]); box on; grid on; hold on; % plot range
for j=1:size(t,1) % iterate over T,p-frames
    l = [0 0 0]; % initialize liquid phase fraction
    for i=1:size(t,2) % iterate over frame (triangle) vertexes
        vap.t = 273.15 + (t(j,i)-32)/1.8; % temperature [K]
        liq.t = vap.t; % temperature [K]
        vap.p = p(j,i)/14.50377; % pressure [bar]
        liq.p = vap.p; % pressure [bar]
        [a,b,c] = tpnewton(x,y,k,rk,liq,rk,vap); % flash calculation
    % [a,b,c] = tpkvalue(x,y,k,rk,liq,rk,vap); % flash calculation
        l(i) = 2*min(c,1-c); % 2 x smallest phase fraction [0,1]
    end %
    n = dac(t(j,:),p(j,:),l,n); % number of function calls
    disp(['Frame #',num2str(j),' => ',num2str(n),' evaluations'])%
end %
H = get(gcf,'Children'); % get handle to all subplots
set(H,'XTick',-[200 160 120 80]); % change ticks on x-axis
plot(tdew,pdew,'or',tbub,pbub,'ob','MarkerSize',6); % exp. data
plot(tc,pc,'xb','MarkerSize',6) % critical point
plot([tc-30,tc-5],[pc,pc],'-k','LineWidth',0.2); grid % c.p.loc.
text(tc-40,pc,'cp'); text(-130,300,['N=',num2str(n)]); % N calls
xlabel('Temperature(F)'); ylabel('Pressure(psia)'); hold off %

```

```
printps('NaturalGas',8,8)
```

#### 1.4. Phase diagram: Cyclohexane–Cyclopentane–Methanol.

```
%Experimental data for Cyclohexane(1)-Cyclopentane(2)-Methanol(3)
%taken from the "DECHEMA Chemistry Data Series", Vol.V, Part 2,
%p.115. T = 25 C, p = 1 bar.
x1 = [87.09 72.59 54.02 34.76 24.28 16.50];
x2 = [00.01 12.71 28.61 42.30 47.93 48.05];
x3 = 100 - x1 - x2;
y1 = [17.52 16.59 14.99 12.85 11.54 10.47];
y2 = [00.01 03.30 08.86 16.97 24.50 33.13];
y3 = 100 - y1 - y2;
%
x = [x1;x2;x3];           % initial composition liquid phase 1
y = [y1;y2;y3];           % initial composition liquid phase 2
k = ones(size(x));        % same ref.state in both phases
%
%The NRTL activity model is used for both liquid phases
liq = @ActivityNRTL;      % function name
s.alpha = [0 .2 .2; .2 0 .2; .2 .2 0]; % non-random parameter
s.tau = [ 0.0 -97.419 544.82; ... % matrix of interaction
         -56.868  0.0  361.38; ... % coefficient
         318.02  234.33  0.0]; % parameters [K]
s.t = 298.15;             % temperature [K]
%
%Calculate tie lines for the 2-phase liquid-liquid equilibria. Do
%also collect the iteration history to say something about the
%convergence properties. NB! use only each 4*i'th iteration point
%in order to avoid a cramped plot.
for i=1:max(size(x))
    [x(:,i),y(:,i),l,dm]=tpnewton(x(:,i),y(:,i),k(:,i),liq,s,liq,s);
% [x(:,i),y(:,i),l,dm]=tpkvalue(x(:,i),y(:,i),k(:,i),liq,s,liq,s);
    dmx = log10(dm(6:4*i:end-1)); % norm of k iteration (x-axis)
    dmy = log10(dm(7:4*i:end)); % norm of k+1 iteration (y-axis)
    h = sum(dmy-dmx)/length(dmx); %converg. factor (first order)
    if i==1 % iteration history of the first calculation point
        plot([0 -6],[0 -6]+h,'b',dmx,dmy,'ob') % regression line
    elseif i==max(size(x)) % iteration history of n'th calc. point
        plot([0 -6],[0 -6]+h,'r',dmx,dmy,'vr') % regression line
    end
    hold on
    disp(['Convergence factor pt ',num2str(i),': ',num2str(10^h)])
end
axis([-6 0 -6 0]); box on; grid on
xlabel('logk'); ylabel('logk1')
legend('h1','p1','hn','pn',2); legend boxoff, hold off
printps('FirstOrderNewtonIteration',8,6);
%
```

```

%Show some experimental points belonging to the phase diagram %
plot(x3/100,x2/100,'ob',y3/100,y2/100,'vr'), hold on; %
axis([0 1 0 0.43]); box off; grid off; %
xlabel('methanol'); ylabel('cyclopentane'); %
set(gca,'YTick',[]); set(gca,'YColor','w'); % invisible y-axis
set(get(gca,'YLabel'),'Color','k'); % awake visibility of label
plot([0 0 1 0.5],[0.5 0 0 0.5],'-k','LineWidth',0.8);% new frame
plot(.46,.43,'ob',.46,.43,'xr'); text(.46,.46,'cp') % crit.point
plot([x(3,:);y(3,:)],[x(2,:);y(2,:)],'b'); % tie-lines
plot([x(3,:);y(3,:)],[x(2,:);y(2,:)],'--r'); % tie-lines
%
%Append the estimated critical end point to the composition array
x(:,end+1) = [.11 .43 .46]';
y(:,end+1) = [.11 .43 .46]';
%
%Expand the composition arrays to obtain more points on the curve
a = linspace(1,1/99,5); % interpolation vector
x = kron(x(:,1:end-1),a)+kron(x(:,2:end),1-a); %liquid 1
y = kron(y(:,1:end-1),a)+kron(y(:,2:end),1-a); %liquid 2
k = ones(size(x));
%
%Calculate additional 2-phase liquid - liquid equilibria in order
%to get a smooth phase diagram.
for i=1:max(size(x))
    [x(:,i),y(:,i)] = tpnewton(x(:,i),y(:,i),k(:,i),liq,s,liq,s);
% [x(:,i),y(:,i)] = tpkvalue(x(:,i),y(:,i),k(:,i),liq,s,liq,s);
end
plot(x(3,:),x(2:,:),'b'); plot(y(3,:),y(2:,:),'r'); % envelope
%
%Draw isoplethes at constant composition in triangular Gibbs-plot
g = 0.2:0.2:0.8;
plot([g;g-g],[g-g;g],':k','LineWidth',0.2);
plot([g-g;1-g],[g;g],':k','LineWidth',0.2);
plot([g;g],[g-g;1-g],':k','LineWidth',0.2); hold off
for h=get(gca,'Children')
    arr = fields(get(h));
    if any(strmatch('XData',arr,'exact')) % transform line-objects
        x = get(h,'XData'); % old x-values
        y = get(h,'YData'); % old y-values
        set(h,'XData',x+0.5*y); % transformed x-values
        set(h,'YData',y*sqrt(3)/2); % transformed y-values
    elseif any(strmatch('Position',arr,'exact')) % text-objects
        x = get(h,'Position');
        set(h,'Position',[x(1)+0.5*x(2),x(2)*sqrt(3)/2,x(3)]); % xyz
    end
end
end
printps('CyclohexaneCyclopentaneMethanol',9,4.5);

```



### 1.5. Phase diagram: Hexane-Toluene.

%Experimental data for Hexane(1) - Toluen(2) taken from the %"Dechema Data Series". Temperatures are in Celcius, pressures in %mmHg.

```

t = [105.4 104.4 103.1 101.7 100.3 98.0 97.8 95.8...
     93.6 92.4 91.6 89.2 85.0 82.8 80.0 78.3...
     77.0 76.3 74.9 72.7 71.4 70.2];
x1 = [.047 .057 .071 .087 .104 .125 .141 .172 ...
      .201 .224 .240 .290 .379 .439 .516 .582 ...
      .639 .659 .754 .822 .885 .938];
y1 = [.154 .176 .212 .251 .301 .331 .364 .424 ...
      .471 .512 .531 .592 .667 .717 .766 .812 ...
      .833 .851 .886 .921 .954 .975];

%
p = 760; % system pressure
t = [105.4 101.7 97.8 92.4 85.0 78.3 74.9 70.2]; % Celcius
x1 = [.047 .087 .141 .224 .379 .582 .754 .938]; % liquid
y1 = [.154 .251 .364 .512 .667 .812 .886 .975]; % vapor

%
c1 = [6.91058 1189.64 226.280]; % published Antoine Hexane
c2 = [6.95087 1342.31 219.187]; % published Antoine Toluene
t1 = c1(2)/(c1(1)-log10(p))-c1(3); % nbp Hexane
t2 = c2(2)/(c2(1)-log10(p))-c2(3); % nbp Toluene
k = [c1(1)-c1(2)./(t+c1(3));... % log10(p/mmHg) Hexane
     c2(1)-c2(2)./(t+c2(3))]; % log10(p/mmHg) Toluene
k = 10.^k/p; % K-values Hexane & Toluene
x = [x1;1-x1]; % initialize liquid mole fractions
y = [y1;1-y1]; % initialize vapour mole fractions

%
%Assume ideal liquid mixture and ideal gas phase.This is equival-
%ent to assuming Raoult's law (constant K-values)
for i=1:length(t)
    [x(:,i),y(:,i)] = tpkvalue(x(:,i)+y(:,i),k(:,i));
end
ss = norm(x(1,:)-x1) + norm(y(1,:)-y1);

%
%Show experimental points
subplot('position',[.1 .12 .36 .80])
plot(x1,t,'ob',y1,t,'vr'), hold on;
axis([0,1,60,120]); box on; grid on;

%
%Show calculated results
plot([0,x(1,:),1],[t2,t,t1],'--k');
plot([0,y(1,:),1],[t2,t,t1],'--k');
text(0.4,112,['ss1=',num2str(ss,3)])

%
%The van Laar activity model is used in the liquid phase

```

```

liq = @ActivityBinVanLaar;           % activity coefficients
vap = @ActivityRaoult;              % ideal mixture
s.a12 = 0.2222;                     % published model parameter A12
s.a21 = 0.4306;                     % published model parameter A21
for i=1:length(t)
% [x(:,i),y(:,i)] = tpnewton(x(:,i),y(:,i),k(:,i),liq,s,vap,[]);
  [x(:,i),y(:,i)] = tpkvalue(x(:,i),y(:,i),k(:,i),liq,s,vap,[]);
end
ss = norm(x(1,:)-x1) + norm(y(1,:)-y1);
%
%Show calculated results
plot([0,x(1,:),1],[t2,t,t1],'b');
plot([0,y(1,:),1],[t2,t,t1],'r'), hold off;
text(0.4,107,['ss2=',num2str(ss,3)])
title('published'); xlabel('hexane'); ylabel('celcius')
%
%The Antoine pressure is quite off for toluene. Redo the calcula-
%tions after adjusting the pressure 2.0 percent
off = 0.020;                         % offset in Antoine vapor pressure
c2(1) = c2(1) + off;                  % adjusted Antoine Toluene
t2 = c2(2)/(c2(1)-log10(p))-c2(3);    % nbp Toluene
k(2,:) = k(2,:)*10^off;              % adjusted K-value Toluene
%
%Raoults law.
for i=1:length(t)
% [x(:,i),y(:,i)] = tpnewton(x(:,i)+y(:,i),k(:,i));
  [x(:,i),y(:,i)] = tpkvalue(x(:,i)+y(:,i),k(:,i));
end
ss = norm(x(1,:)-x1) + norm(y(1,:)-y1);
%
%Show experimental points
subplot('position',[.62 .12 .36 .80])
plot(x1,t,'ob',y1,t,'vr'), hold on;
axis([0,1,60,120]); box on; grid on
%
%Show calculated results
plot([0,x(1,:),1],[t2,t,t1],'--k');
plot([0,y(1,:),1],[t2,t,t1],'--k');
text(0.4,112,['ss3=',num2str(ss,3)])
%
%van Laar activity.
for i=1:length(t)
% [x(:,i),y(:,i)] = tpnewton(x(:,i),y(:,i),k(:,i),liq,s,vap,[]);
  [x(:,i),y(:,i)] = tpkvalue(x(:,i),y(:,i),k(:,i),liq,s,vap,[]);
end
ss = norm(x(1,:)-x1) + norm(y(1,:)-y1);
%
```

```
%Show calculated results
plot([0,x(1,:),1],[t2,t,t1],'b')
plot([0,y(1,:),1],[t2,t,t1],'r'), hold off;
text(0.4,107,['ss4=',num2str(ss,3)])
title('corrected'); xlabel('hexane'); xlabel('hexane')
printps('HexaneToluene',11,5.5);
```

### 1.6. Phase diagram: Gold–Copper.

```
%Experimental data for Gold(1)-Copper(2) taken from Okamoto et al
%Bulletin of Alloy Phase Diagrams, 8 (5) 454-473 (1987). Solidus
%and liquidus temperatures are in Celcius.
x2 = [140 257 405 437 467 508 651 756 838 908 945 974 991];
tliq = [983 939 912 910 911 914 940 970 998 1030 1052 1068 1079];
tsol = [970 927 910 910 910 911 931 957 979 1007 1032 1053 1071];
x2 = x2/1000; % mole fractions of copper
t1 = 1064.43; % melting point of gold [C]
h1 = 12677; % enthalpy of fusion for gold [J/mol]
t2 = 1084.87; % melting point of copper [C]
h2 = 13012; % enthalpy of fusion for copper [J/mol]
%
plot(x2,tliq,'or',x2,tsol,'ob'); hold on; grid; % phase diagram
plot(0,t1,'or',0,t1,'ob',1,t2,'or',1,t2,'ob') % melting points
xlabel('copper'); ylabel('celcius'); box on; grid on
%
%Excess enthalpy and entropy (Redlich-Kister) parameters
hsc = [-11053 -22878 8000 4000]; % solid-solution enthalpy
ssc = [ 2.4 -2.4 0 0]; % solid-solution entropy
hlc = [-21748 -16614 9541 0]; % liquid phase enthalpy
slc = [ 0 0 0 0]; % liquid phase entropy
%
%The Redlich-Kister activity model is used for both phases
liq = @ActivityBinRedlichKister; % liquid activity coefficients
sol = @ActivityBinRedlichKister; % solid activity coefficients
R = 8.314511984; % universal gas constant [J/mol*K]
%
%Good initial temperatures and phase compositions are needed
txy = [1050,0.01,0.03;1030,0.04,0.06;1010,0.06,0.08;
990,0.09,0.11; 980,0.12,0.15; 970,0.14,0.17;
960,0.16,0.19; 950,0.18,0.22; 940,0.21,0.25;
930,0.24,0.28; NaN, NaN, NaN;
990,0.86,0.82;1008,0.88,0.86;1020,0.90,0.88;
1040,0.92,0.94;1050,0.94,0.96;1065,0.96,0.98]';
%
for i=1:size(txy,2)
T = txy(1,i) + 273.15; % temperature [K]
x = txy(2,i); % solid phase Cu-composition
y = txy(3,i); % liquid phase Cu-composition
g = hsc/R/T - ssc/R; % excess Gibbs energy coefficients
```

```

    u = struct('a12',g(1),'b12',g(2),'c12',g(3),'d12',g(4)); %
    g = hlc/R/T - slc/R; % excess Gibbs energy coefficients
    v = struct('a12',g(1),'b12',g(2),'c12',g(3),'d12',g(4)); %
    k = exp([h1/R*(1/(t1+273.15)-1/T);h2/R*(1/(t2+273.15)-1/T)]);
% [x,y,l] = tpkvalue([1-x;x],[1-y;y],k,sol,u,liq,v);
[x,y,l] = tpnewton([1-x;x],[1-y;y],k,sol,u,liq,v);
txy(2,i) = x(2); % store calculated solid Cu-composition
txy(3,i) = y(2); % store calculated liquid Cu-composition
end
txy = [[t1 0 0]',txy,[t2 1 1]']; % insert melting points
plot(txy(2,:),txy(1:,:),'-b',txy(3,:),txy(1:,:),'-r'); hold off;
printps('GoldCopper',8,6);

```

### 1.7. Ideal gas cycles: Coordinate systems.

%Common parameter settings.

```

m = 3; %Number of subplots, vertically
n = 2; %Number of subplots, horisontally
cp = 7/2; %Isobaric heat capacity [Cp/R]
cv = cp - 1; %Isochoric heat capacity [Cv/R]
g = cp/cv; %Isentropic exponent [Cp/Cv]
%

```

%Axes limits

```

Slim = [0 4]; % (S-S0)/R
Tlim = [0 10]; % T/T0
Plim = [0 200]; % P/P0
Vlim = [0 10]; % V/V0
%

```

%

%Calculate and plot TS-diagrams.

```

np = 81; % total number of points along the isoplethes
i = 1:4:np; % points selected for plotting
e = ones(1,np); % unity vector
s = linspace(min(Slim),max(Slim),np); % entropy axis
t = linspace(min(Tlim),max(Tlim),np); % temperature axis
tv = exp(s/cv); % temperature profile along isochore
tp = exp(s/cp); % temperature profile along isobar
%

```

```

subplot(m,n,1), plot(s,tv'*t(i),'k-',e'*s(i),t,'k-')
title('Otto(SV)')
ylabel('Temperature')
axis([Slim Tlim])
%

```

%

```

subplot(m,n,2), plot(s,tv'*t(i),'k-',s,e'*t(i),'k-')
title('Stirling(TV)')
axis([Slim Tlim])
%

```

%

```

subplot(m,n,3), plot(s,tp'*t(i),'k-',e'*s(i),t,'k-')
title('Brayton(SP)')
ylabel('Temperature')

```

```

axis([Slim Tlim])
%
subplot(m,n,4), plot(s,tp'*t(i),'k-',s,e'*t(i),'k-')
title('Ericsson(TP)')
axis([Slim Tlim])
%
subplot(m,n,5), plot(s,e'*t(i),'k-',e'*s(i),t,'k-')
title('Carnot(TS)')
ylabel('Temperature')
xlabel('Entropy')
axis([Slim Tlim])
%
subplot(m,n,6), plot(s,tp'*t(i),'k-',s,tv'*t(i),'k-')
title('Rankine(PV)')
xlabel('Entropy')
axis([Slim Tlim])
printps('TSdiagrams',13.1,17.8)
%
%Calculate and plot PV-diagrams.
v = linspace(min(Vlim),max(Vlim),np); % volume axis
v(1) = 1/np; % override first point - avoid divide by zero
p = linspace(min(Plim),max(Plim),np); % pressure axis
p(1) = 1; % override first point - avoid divide by zero
vr = e./(v+eps); % reciprocal volume axis
ps = (vr/min(vr)).^g; % pressure profile along isentrope
pt = vr/min(vr); % temperature profile along isotherm
%
subplot(m,n,1), plot(v,ps'*p(i),'k-',e'*v(i),p,'k-')
title('Otto(SV)')
ylabel('Pressure')
axis([Vlim Plim])
%
subplot(m,n,2), plot(v,pt'*p(i),'k-',e'*v(i),p,'k-')
title('Stirling(TV)')
axis([Vlim Plim])
%
subplot(m,n,3), plot(v,ps'*p(i),'k-',v,e'*p(i),'k-')
title('Brayton(SP)')
ylabel('Pressure')
axis([Vlim Plim])
%
subplot(m,n,4), plot(v,pt'*p(i),'k-',v,e'*p(i),'k-')
title('Ericsson(TP)')
axis([Vlim Plim])
%
subplot(m,n,5), plot(v,ps'*p(i),'k-',v,pt'*p(i),'k-')
title('Carnot(TS)')

```

```

ylabel('Pressure')
xlabel('Volume')
axis([Vlim Plim])
%
subplot(m,n,6), plot(e'*v(i),p,'k-',v,e'*p(i),'k-')
title('Rankine(PV)')
xlabel('Volume')
axis([Vlim Plim])
printps('PVdiagrams',13.1,17.8)

```

### 1.8. Convergence region of Newton iteration.

```

n = 100; % number of points
x = linspace(-3,3,n); % spanned x-axis
y = linspace(-3,3,n)'; % spanned y-axis
e = ones(n,1); % unity vector
P = e*(x.*x) - 3 - y*e'; % parabola symmetric about y-axis
Q = -(y.*y)*e' - e*x + 3; % parabola symmetric about x-axis

%Calculate and plot indefinite region
for i=1:n
    for j=1:n
        H = [2*x(i)*x(i)+P(i,j)+1/2,y(j)-x(i);... % Hessian row 1
             y(j)-x(i),2*y(j)*y(j)-Q(i,j)+1/2]; % Hessian row 2
        F(i,j) = min(eig(H)); % smallest eigenvalue
    end
end
[c,h] = contour(x,y,F,[0 0],'k'); % contour line of lambda=0
xlabel('x'); ylabel('y'); hold on % hold current plot
h = patch(c(1,2:end),c(2,2:end),[.9 .9 .9]); % neg eigenvalue(s)
%set(h,'EdgeColor','none'); % erase patch border

%Show minima of f(x,y) and the corresponding convergence regions
for xy=[[2 1];[1.3 -1.3];[-1 -2];[-2.3 2.3]]' % find four minima
    d = xy; % update vector
    while norm(d)>1e-8 % iterate till a small norm
        z = xy(1); % x-coordinate
        w = xy(2); % y-coordinate
        p = z*z - w - 3; % parabola symmetric about the y-axis
        q = -w*w - z + 3; % parabola symmetric about the x-axis
        g = [z*p-q/2;-w*q-p/2]; % gradient vector
        H = [2*z*z+p+1/2,w-z;w-z,2*w*w-q+1/2]; % Hessian matrix
        d = -H\g; % update vector
        xy = xy + d; % new x and y-values
    end
    Hx = [6*z,-1;-1,1]; % x-derivative of Hessian
    Hy = [-1,1;1,6*w]; % y-derivative of Hessian
    lmin = min(eig(H)); % smallest eigenvalue of H
    lmax = max(max(abs(eig(Hx))),max(abs(eig(Hy)))); % Hx and Hy
end

```

```

r      = lmin/lmax;                % radii of convergence
disp(['x=',num2str(z),' y=',num2str(w), ...           %
      ' lmin=',num2str(lmin),' lmax=',num2str(lmax), ... %
      ' r=',num2str(r)])          %
fi     = linspace(0,2*pi,100); % span circle (polar coordinates)
z      = z + r*cos(fi);           % corresponding x-values
w      = w + r*sin(fi);           % corresponding y-values
h      = patch(z,w,[.5 .5 .5]); % conv region in x,y-coordinates
% set(h,'EdgeColor','none');      % erase patch border
end

%Add a few contour lines to illustrate the objective function
F = P.*P + Q.*Q;                  % grid of objective function values
set(gcf,'DefaultLineLineWidth',0.2)
contour(x,y,F,[1 4 8 16 32],'k'); hold off % plot contour lines
printps('NewtonConvergence',6,6)

```

## 2. Functions

A function is a program body with a separate name-space which can be referred to from a script, see Section 1 on page 111 of this appendix, or from another Matlab function. User defined functions behave similarly to the built-in log, exp, sin, etc., but in order to be recognised by Matlab they must reside somewhere in the search path as \*.m files. You must therefore be sure to copy the functions to your home directory before use.

### 2.1. Linear programming.

```

%Simplex algorithm applied to solve a limited LP - problem. The
%syntax is [x,A,it] = lp(A,x0,c) where:
%
% min(c'*x)
% A*x(k+1)=A*x(k)
% x>0
%
% A = m x n coefficient matrix, rank(A)=m>1.
% x0 = initial basis solution vector (feasible)
% c = cost vector
% x = final solution vector
% it = number of iterations spent in this function
%
%Copyright Tore Haug-Warberg 2003 (course TMT4140, KP8108, NTNU)
%
function [x,A,it] = lp(A,x0,c)
%
[m,n] = size(A);                % assumed full-rank
x      = x0;                      % assumed feasible
%

```

```

for it=1:m*n          % restrict number of iterations for simplex
    f = find(x==0)';          % free variables
    b = find(x >0)';          % basis variables
    if length(b)<m; error('Degenerated'); end          %
    A(:,[b,f]) = [eye(length(b)),inv(A(:,b))*A(:,f)]; % new basis
    i = find([c(f)'-c(b)']*A(:,f)<0);          % negative cost elements
    if length(i)<1; return; end          % converged
    H = [A(:,f(i))./(x(b)*ones(1,length(i)))];
    [h,j] = max(max(H));
    if h<1; error('Unbounded'); end
    x(f(i(j))) = 1/h;
    x(b) = x(b).*(ones(size(b')) - H(:,j))/h);
end
error('Not converged')

```

## 2.2. Two-phase equilibrium: K-value method.

%Solve two-phase equilibria using Rachford-Rice iteration. Note  
 %that the non-idealities are solved for directly - no inner/outer  
 %loop strategy. Three cases are distinguished in the function in-  
 %terface: [x,y,l,varargout] = TpKvalue(varargin)

```

%
% 1) varargin = z,k          constant K-values
% 2) varargin = z,k,f,p      same model in both phases
% 3) varargin = x,y,k,f,p,g,q  different models in each phase
%
% x,y,z = liquid, vapor, feed (total) mole fraction vectors      %
% k      = reference state K-value vector (ideal mixture)         %
% f,g    = liquid, vapor activity or equation-of-state model      %
% p,q    = liquid, vapor parameter struct                         %
% l      = liquid phase fraction (mole liquid per mole feed)     %
%

```

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```

%
function [x,y,l,varargout] = TpKvalue(varargin)
%
if nargin==7
    [nl,nv,k,f,p,g,q] = deal(varargin{:});
    z = nl + nv;
    nl = nl/sum(z);
    nv = nv/sum(z);
    z = nl + nv;
else
    [z,k] = deal(varargin{1:2});
    z = z./sum(z);
    nl = z./(1+k);
    nv = z - nl;
    if nargin==2; f=@ActivityRaoult; p=[]; end
    if nargin==4; [f,p]=deal(varargin{3:4}); end

```



```

    g = f;
    q = p;
end
if nargout > 3          % optional output then > 3 return variables
    varargout = {[]};    % prepare output cell array
end
%
tol = 1.e-6;           % convergence tolerance
maxit = 100;           % maximum number of iterations
l = 0.5;               % initial liquid fraction
dl = 1.0;              % liquid fraction increment
it = 0;                % iteration counter
%
%if min(z)<0; l=0; x=z*0; y=z*0; return; end
%if min(k)<0; l=0; x=z*0; y=z*0; return; end
%if min(k)>1; l=0; x=z*0; y=z ; return; end
%if max(k)<1; l=1; y=z*0; x=z ; return; end
%
while abs(dl)>tol && l>tol && l<1-tol && it<maxit
    it = it + 1;          % increment counter
    x = nl/sum(nl);      % mole fraction liquid
    y = nv/sum(nv);      % mole fraction vapor
    kval = k.*exp(feval(f,x,p)-feval(g,y,q)); % K-values
    dnum = 1 + (1-l)*kval; % denominator
    fi = (1-kval)./dnum; % function contribution
    fun = z'*fi;         % function value
    dfdl = -z'*(fi.*fi); % function derivative
    dl = -fun/(dfdl-abs(fun)*0.1-eps); % avoid divide by zero
    l = l + max(-0.9*l,min((1-l)*0.9,dl)); % control step size
    nl = z./dnum;        % new liquid composition
    nv = z.*kval./dnum;  % new vapor composition
    if nargout > 3      % output of iteration variable
        varargout(1) = {[varargout{1},dl]}; % collect variable
    end
end
end
%
if it == maxit; l=0; x=z*0; y=z*0; end
if l >= 1-tol; l=1; x=z ; y=z*0; end
if l <= tol; l=0; y=z ; x=z*0; end

```

### 2.3. Two-phase equilibrium: Newton's method.

%Solve two-phase equilibria using Newton - Raphson iteration. The %Hessian is approximated by ideal mixture theory. The gradient, %however, can incorporate non-ideal behaviour. Three cases are %distinguished in [x,y,l,varargout] = TpNewton(varargin):

```

%
% 1) varargin = z,k          constant K-values
% 2) varargin = z,k,f,p     same model in both phases

```

```

% 3) varargin = x,y,k,f,p,g,q      different models in each phase
%
% x,y,z = liquid, vapor, feed (total) mole fraction vectors      %
% k      = reference state K-value vector (ideal mixture)        %
% f,g    = liquid, vapor activity or equation-of-state model     %
% p,q    = liquid, vapor parameter struct                        %
% l      = liquid phase fraction (mole liquid per mole feed)    %
%
%Copyright Tore Haug-Warberg 2004 (course TMT4140, KP8108, NTNU)
%
function [x,y,l,varargout] = TpNewton(varargin)
%
if nargin==7
    [nl,nv,k,f,p,g,q] = deal(varargin{:});
    z = nl + nv;
    nl = nl/sum(z);
    nv = nv/sum(z);
    z = nl + nv;
else
    [z,k] = deal(varargin{1:2});
    z = z./sum(z);
    nl = z./(1+k);
    nv = z - nl;
    if nargin==2; f=@ActivityRaoult; p=[]; end
    if nargin==4; [f,p]=deal(varargin{3:4}); end
    g = f;
    q = p;
end
if nargout > 3      % optional output then > 3 return variables
    varargout = {[]};      % prepare output cell array
end
%
maxit = 10000;      % maximum number of iterations
tol    = 1.e-6;      % convergence tolerance
dm     = ones(length(k),1); % chemical potential difference
s      = 1;          % relative step length
it     = 0;          % iteration counter
%
while norm(dm)>tol & s>tol & it<maxit
    it = it + 1;
    x  = nl/sum(nl);
    y  = nv/sum(nv);
    dm = log(y./x./k) + feval(g,y,q) - feval(f,x,p);
    d  = (x.*y)./z;
    dn = -sum(nv)*sum(nl)*(d.*dm+d*(d'*dm)/(1-sum(d)));
    s  = min(0.8/abs(min(min(dn./nv),min(-dn./nl))),1);
    nv = nv + s*dn;

```

```

nl = z - nv;
if nargout > 3                % optional output of iteration norm
    varargout(1) = {[varargout{1},norm(dm)]};    % collect norm
end
end
if s==1 & it<maxit            % last step was of full length
    l = sum(nl);                % converged liquid phase fraction
else                            % constrained step
    l = min(1,max(0,round(sum(nl))));    % phase fraction is 0 or 1
    x = z*l;                    % liquid fraction
    y = z*(1-l);                % vapor fraction
end
end

```

#### 2.4. Phase diagram: Recursive calculation.

%Recursive Divide-And-Conquer calculation of a T,p-phase diagram.  
 %The triangular grid is refined until its elementary cells are  
 %within the specifications and the phase boundary is sufficiently  
 %accurate.

```

%
function n = dac(t,p,l,n)
%
global x y k rk liq vap
%
dt = max(diff(abs([t,t(1)])));    % max temperature difference
dp = max(diff(abs([p,p(1)])));    % max pressure difference
%dl = max(diff(abs([l,l(1)])));    % max phase fraction difference
%
if any(l) && not(all(l)) && dt>1 && dp>5 || dt>30 || dp>200
    u = [(t(1)+t(2))/2 (t(2)+t(3))/2 (t(1)+t(3))/2]; % new T-range
    v = [(p(1)+p(2))/2 (p(2)+p(3))/2 (p(1)+p(3))/2]; % new P-range
    z = [0 0 0]; % initialize phase fractions
    for i=1:length(z) % calculate phase fraction at each vertex
        vap.t = 273.15 + (u(i)-32)/1.8; % temperature [K]
        liq.t = vap.t; % temperature [K]
        vap.p = v(i)/14.50377; % pressure [bar]
        liq.p = vap.p; % pressure [bar]
        [a,b,c] = tpnewton(x,y,k,rk,liq,rk,vap); % flash calculation
    % [a,b,c] = tpkvalue(x,y,k,rk,liq,rk,vap); % flash calculation
        z(i) = 2*min(c,1-c); % 2 x smallest phase fraction [0,1]
    end
    n=dac([t(1) u(1) u(3)], [p(1) v(1) v(3)], [l(1) z(1) z(3)],n+1);
    n=dac([u(1) t(2) u(2)], [v(1) p(2) v(2)], [z(1) l(2) z(2)],n+1);
    n=dac([u(3) u(2) t(3)], [v(3) v(2) p(3)], [z(3) z(2) l(3)],n+1);
    n=dac([u(1) u(2) u(3)], [v(1) v(2) v(3)], [z(1) z(2) z(3)],n+1);
    return
end
if any(l)
    rgb = [1.0*(1-sum(l)/3) 0.9*(1-sum(l)/3) 0.9+0.1*sum(l)/3];

```

```

    patch(t,p,rgb,'EdgeColor',rgb*0.9,'LineWidth',0.2);
end

```

### 2.5. Fugacity coefficients: Redlich–Kwong.

%Multicomponent Redlich-Kwong fugacity coefficients. The syntax is  
 %lnf = FugacityRedlichKwong(n,s) where:

```

%
%   n = mole number vector
%   s = parameter struct: phase, t[K], p[bar], tc[K] and pc[bar]
% lnfi = logarithm of fugacity coefficients
%
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%

```

```

function [lnfi] = FugacityRedlichKwong(n,s)
%
bar = 1e5; t = s.t;      p = s.p*bar;
tc = s.tc; pc = s.pc*bar; x = n/sum(n);
%
rgas = 8.314511984;
omegab = (2^(1/3)-1)/3;
omega = 1/27/omegab;
brk = omegab*rgas*tc./pc;
ark = omega*rgas^2*tc.^2./pc./sqrt(t./tc);
b = brk'*x;
a = (sqrt(ark))*x^2;
ai = 2*sqrt(a*ark);
%
v = roots([1,-rgas*t/p,a/p-b^2-rgas*t*b/p,-a*b/p]);
v = v(find(imag(v)==0));
if isempty(findstr(s.phase,'l')); v=max(v); else v=min(v); end
%
lnfi = log(v/(v-b)) + brk/(v-b) + ...
      (ai-a*brk/b)*log(v/(v+b))/b/rgas/t - ...
      a*brk/b/(v+b)/rgas/t - log(p*v/rgas/t);

```

### 2.6. Activity coefficients: van Laar.

%Binary van Laar activity coefficients. The syntax is  
 %lng = ActivityBinVanLaar([n1;n2],s), where:

```

%
% n1 = mole numbers
% n2 = mole numbers
% s = parameter struct i.e. a12 and a21
% lng = logarithm of activity coefficients
%
%Copyright Tore Haug-Warberg 2003 (course SIK3035, NTNU)
%
function [lng] = ActivityBinVanLaar(n,s)
%

```

```
x = n/sum(n);
lng1 = s.a12/(1+s.a12*x(1)/s.a21/x(2))^2;
lng2 = s.a21/(1+s.a21*x(2)/s.a12/x(1))^2;
lng = reshape([lng1,lng2],size(x));
```

### 2.7. Activity coefficients: Redlich–Kister.

%Binary Redlich-Kister activity coefficients. The syntax is  
%lng = ActivityBinRedlichKister([n1;n2],s), where:

```
%
% n1 = mole numbers
% n2 = mole numbers
% s = parameter struct i.e. a12, b12, c12, d12
%lng = logarithm of activity coefficients
%
%Copyright Tore Haug-Warberg 2005 (course TMT4140, NTNU)
%
function [lng] = ActivityBinRedlichKister(n,s)
%
x = n/sum(n);
f = s.a12 + s.b12*x(2) + s.c12*x(2)^2 + s.d12*x(2)^3;
dfdx = s.b12 + 2*s.c12*x(2) + 3*s.d12*x(2)^2;
lng1 = (f - dfdx*x(1))*x(2)^2;
lng2 = (f + dfdx*x(2))*x(1)^2;
lng = reshape([lng1,lng2],size(x));
```

### 2.8. Activity coefficients: NRTL.

%Multicomponent NRTL activity coefficients.The syntax is  
%lng = ActivityNRTL(n,s) where:

```
%
% n = mole number vector
% s = parameter struct i.e. alpha[-], tau[K] and t[K]
%lng = logarithm of activity coefficients
%
%Copyright Tore Haug-Warberg 2003 (course TMT4140, NTNU)
%
function [lng] = ActivityNRTL(n,s)
%
T = s.tau/s.t; A = s.alpha; G = exp(-T.*A);
x = n./sum(n); y = G'*x; z = (T.*G)'*x./y;
e = ones(size(x));
%
lng = z + G.*(T-e*z')*(x./y);
```

### 2.9. Activity coefficients: Raoult.

%Ideal activity coefficients.

```
function [lng] = ActivityRaoult(x,p)
lng = zeros(size(x));
return
```

### 2.10. PostScript: Print current graphics.

%Print current graphics using the PostScript-driver. The syntax  
%is `printps(file,dimx,dimy)`, where `file` is a valid file name (the  
%file extension `.eps` is added automatically), and `dimx` and `dimy`  
%are figure sizes in centimeter. The background is made transpar-  
%ent (including all the childrens of the plot).

```
%  
function printps(file,dimx,dimy)  
%  
dir = '..\graphics\CMYK\';  
%  
set(gcf,'PaperUnits','centimeter');  
set(gcf,'PaperPosition',[0,0,dimx,dimy]);  
set(gcf,'PaperSize',[dimx,dimy])  
set(gcf,'Color','none')  
set(gcf,'InvertHardCopy','off')  
for h = get(gcf,'Children')  
    set(h,'Color','none')  
end  
%  
disp(['print -depsc2 -cmyk -noui ',dir,file,'.eps'])  
print(gcf,'-depsc2', '-cmyk', '-noui',[dir,file,'.eps'])
```

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