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Lecture notes in KP8108 Advanced Thermodynamics

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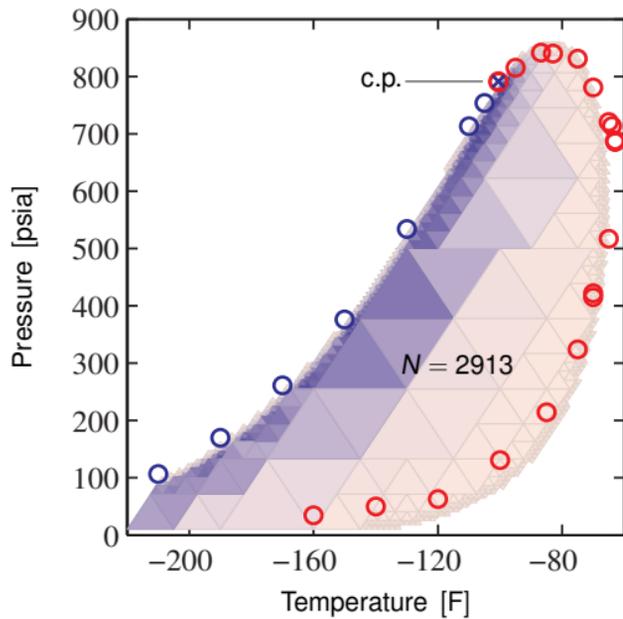
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▶ Exercise 1

▶ Table of contents

▶ Exercise 153



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

Part-Contents

	Titlepage	1
1	List of symbols	6
2	Thermodynamic concepts	21
3	Prelude	54
4	The Legendre transform	105
5	Euler's Theorem on Homogeneous Functions	167
6	Postulates and Definitions	221
7	Equations of state	239
8	State changes at constant composition	340
9	Closed control volumes	417
10	Dynamic systems	488
11	Open control volumes	532

Part-Contents (2)

12	Gas dynamics	588
13	Departure Functions	653
14	Simple vapour-liquid equilibrium	696
15	Multicomponent Phase Equilibrium	746
16	Chemical equilibrium	818
17	Simultaneous reactions	869
18	Heat engines	944
19	Entropy production and available work	1011
20	Plug flow reactor	1068
21	Material Stability	1160
22	Thermofluids	1214
24	T, s and p, v -Diagrams for Ideal Gas Cycles	1271

Part-Contents (3)

25	SI units and Universal Constants	▶ 1279
26	Newton–Raphson iteration	▶ 1295
27	Direct Substitution	▶ 1309
28	Linear Programming	▶ 1318
29	Nine Concepts of Mathematics	▶ 1337
30	Code Snippets	▶ 1355



◀ **Part 2** ▶

Thermodynamic concepts

◀ see also Part-Contents ▶



Contents

New issues

◀ 2 Thermodynamic ...

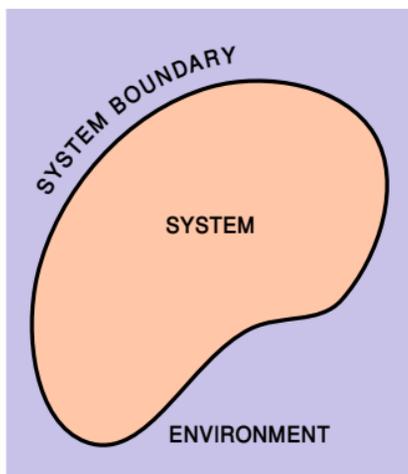
- 1 System
- 2 State
- 3 Process
- 4 Extensive vs. intensive
- 5 Equilibrium
- 6 Heat and work

Thermodynamics



◀ 2 Thermodynamic ...

- 1** Thermodynamics describes natural phenomena in idealised terms.
- 2** The scope of the description can vary, and must be adapted to our needs at any given time.
- 6** We can then use the model to perform thought experiments that reveal certain characteristics of the system's behaviour.



Explain in your own words what is meant by the concepts: system, boundary and environment or surroundings.

§ 001 System

◀ 2 Thermodynamic ...

- 1** A *system* is a limited part of the universe with a *boundary* that may be a mathematical surface of zero thickness, or a physical barrier between it and the *surroundings*¹.
- 2** A *reservoir* is a system that can interact with other systems without undergoing any change in its state variables. These reservoirs, and other *simple* systems, have properties that are spatially and directionally uniform (the system is homogeneous with isotropic properties).
- 6** A real-world system will never be perfectly uniform, nor completely unaffected by its surroundings, but it is nevertheless possible to make some useful simplifying assumptions.

¹ We must be able to either actively control the system's mass and composition, impulse (or volume) and energy, or passively observe and calculate the conserved quantities at all times. All transport properties ρ must satisfy $\lim_{x \rightarrow 0^+} \rho = \lim_{x \rightarrow 0^-} \rho$ so that ρ is the same for the system and the surroundings *across* the control surface. In physics,

Properties

- 1** The state of a thermodynamic system is determined by the system's properties — and vice versa.
- 3** For example, the energy of the system is given by the formula $U = (\partial U/\partial X_1) X_1 + (\partial U/\partial X_2) X_2 + \dots$ once the state variables X_i and the derived properties $(\partial U/\partial X_i)$ are known.
- 6** $(\partial U/\partial X_i)$ can then be calculated from the function $U(X_1, X_2, \dots)$ through partial differentiation with respect to X_i .
- 7** The measurements are no longer directly visible to us, but are instead encoded in the shape of model parameters (that describe the observations to some degree at least).

Variables

- 1** State variables only relate to the current state of the system.
- 2** In other words, they are independent of the path taken by the system to reach that state.
- 7** The state of the system can be changed through what we call a process.
- 8** Terms such as isothermal, isobaric, isochoric, isentropic, isenthalpic, isopiestic and isotonic are often used to describe simple physical processes.

Variables (2)

◀ 2 Thermodynamic ...

9 Without considering how to bring about these changes in practice, the terms refer to various state variables that are kept constant, such that the state change takes place at constant temperature, pressure, volume, entropy, enthalpy, (vapour) pressure or osmotic pressure respectively.

Explain in your own words what is meant by the terms:
state, property, process and path.

§ 002 The state concept

◀ 2 Thermodynamic ...

- 1** A thermodynamic *state* is only fully defined once all of the relevant thermodynamic properties are known.
- 3** In *simple* systems, the properties are (by definition) independent of location and direction, but correctly identifying the system's state variables is nevertheless one of the main challenges in thermodynamics.
- 9** A *cycle* is the same as a closed path. The cycle can either be temporal (a periodic process) or spatial (a cyclic process). In a *steady state*, the variables do not change with time, whereas in *dynamic* systems they change over time. Between these two extremes you have a *quasi-static* state: the state changes as a function of time, but in such a way that the system is at all times in thermodynamic equilibrium, as described in greater detail in Paragraph 4.

§ 002 The state concept (2)

◀ 2 Thermodynamic ...

11 A state that is in thermodynamic equilibrium appears static at the macroscopic level, because we only observe the average properties of a large number of particles, but it is nonetheless dynamic at the molecular level.

14 In a theoretical *reversible* process, it is possible to reverse any change of state by making a small change to the system's interaction with its surroundings.

17 Let us assume, for example, that the movement creates friction in the pulley. You will then need a small, but measurable, change in mass in order to set the weights in motion one way or the other.

§ 002 The state concept (3)

◀ 2 Thermodynamic ...

18 The total energy of the system is conserved, but the mechanical energy is converted into internal (thermal) energy in the process — so it is irreversible..

Extensive / intensive

◀ 2 Thermodynamic ...

- 1** Experimentally it has been shown that the size of a system is proportional to some of its properties. These are called extensive properties, and include volume, mass, energy, entropy, etc.
- 3** Intensive properties, meanwhile, are independent of the size of the system, and include temperature, pressure and chemical potential.
- 8** The system's mass is a fundamental quantity, which is closely related to inertia, acceleration and energy. An alternative way of measuring mass is by looking at the number of moles of the various chemical compounds that make up the system.
- 12** Systems of variable mass contain a minimum number of independent components that together make up the chemical composition of the system.

Extensive / intensive (2)

◀ 2 Thermodynamic ...

14 Only the composition at equilibrium can be described in these simple terms, which is because we are forced to specify as few as possible variables that depend on mass or the number of moles.

Explain in your own words what is meant by a property being intensive or extensive. If you divide an extensive property by the number of moles in the system or its mass, you get a molar or specific property respectively. Show that the property obtained is intensive.

§ 003 Size

◀ 2 Thermodynamic ...

- 1** In thermodynamics, size is not only a measure of the volume of a system, but also of any properties related to its mass.
- 3** Properties that can be doubled in this way, such as entropy S , volume V and the number of moles N , are proportional to the size of the system, and are referred to as *extensive* variables.
- 10** Certain pairs of extensive and intensive variables combine to form a product with a common unit (most commonly energy), and feature in important relationships such as $U = TS - pV + \mu_1 N_1 + \mu_2 N_2 + \dots$.
- 11** These pairs of T and S , p and V , and μ_i and N_i are called *conjugate* variables.

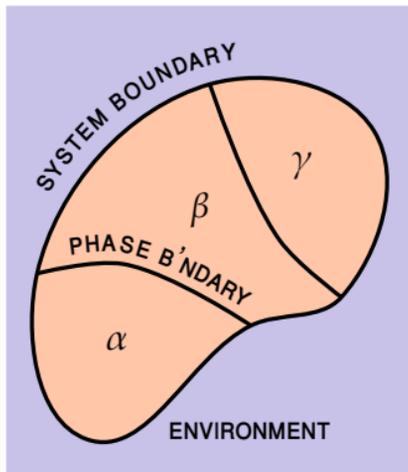
§ 003 Size (2)

◀ 2 Thermodynamic ...

15. Dividing one extensive property by another gives you a new, intensive variable that represents the ratio between the two properties. Then $\rho \hat{=} f/g = a/b$ is independent of x , in other words ρ is intensive.

Degrees of freedom

- 1** Let us consider a thermodynamic system that does not change with time, which means that it must be in equilibrium.
- 8** The general principles of equilibrium mean that the energy of the system will be minimised with respect to all the degrees of freedom that form the basis for the system description.
- 10** The degrees of freedom are at all times controlled by the physical nature of the system, and this determines which extremal principle to apply.



Explain in your own words the following terms associated with equilibrium and equilibrium states: phase, phase boundary, aggregate state, equilibrium and stability.

§ 004 Equilibrium

◀ 2 Thermodynamic ...

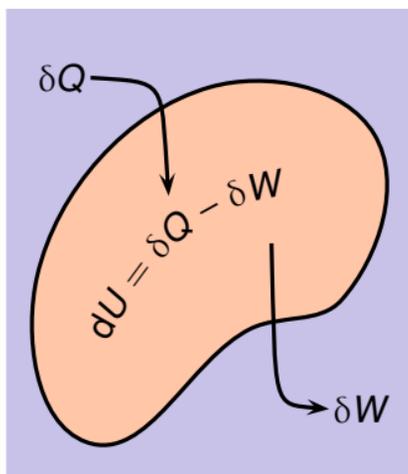
- 1** Equilibrium is the state attained by the system when $t \rightarrow \infty$.
- 14** If the system returns to the same equilibrium state after exposure to a large random perturbation (disturbance), the equilibrium is said to be *stable*.
- 15** A *metastable* equilibrium is stable when exposed to minor perturbations, but it becomes unstable in the event of major displacements.
- 19** If the stability limit is exceeded, the system will split into two or more equilibrium phases (from the mechanical analogy in the figure it is equally likely that the ball will fall to the right as to the left).

(In)exact differential

- 1** State variables are variables that form part of a state function.
- 2** A state function always produces an exact differential, but not all differentials in physics are exact².
- 3** One example from thermodynamics is $(dU)_n = \delta Q - \delta W$, which describes the energy balance for a closed system. Here the energy U is a state function with the total differential $(dU)_n$.
- 4** For any change $\delta Q - \delta W$ there is a unique value of $(dU)_n$.
- 6** For any change $(dU)_n$ there are in principle an infinite number of combinations of δQ and δW , since only the difference between heat and work is observable.

(In)exact differential (2)

² Let e.g. $f(x, y) = xy + c$ be a state function with x and y as its state variables. Here $df = y dx + x dy$ is the total differential of the function. The right side of the equation is then called exact. If as a pure thought experiment we change the plus operator on the right side to minus, the differential becomes non-exact. It is possible to transform the left-hand side into $y^2 dg = y \delta x - x \delta y$, where y^2 is an integrating factor for the differential and dg is the total differential of $g(x, y) = xy^{-1} + c$, but the new differential $y \delta x - x \delta y$ remains non-exact, since it cannot be expressed as the total differential of any known function.



Explain in your own words the meaning of the terms: heat, work and energy. Are all three state variables?

§ 005 Heat and work

◀ 2 Thermodynamic ...

- 1** Heat and work are two closely related *mechanisms* for transporting *energy* between the system and its surroundings.
- 2** Transporting energy affects the state of the system, but the heat and work are not themselves accumulated in the system. ■■■

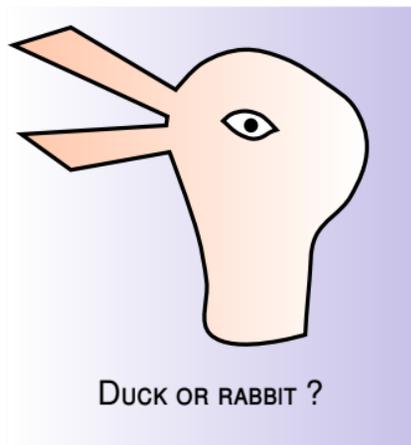
Das Ding an sich

◀ 2 Thermodynamic ...

- 1 Last but not least, we need to know the *purpose* of our analysis.
- 7 Mathematics provides us with a useful tool, but that does not mean that models and reality are two sides of the same coin, and hence that we, by carefully eliminating “all” assumptions, can reach an absolutely true answer.
- 8 Mathematical descriptions allow us to understand some characteristic events that surround us, but they do not give us the whole picture.

Das Ding an sich (2)

◀ 2 Thermodynamic ...



9 Immanuel Kant³ unified the most important strands of rationalism and empiricism with his interpretation of *das Ding an sich*. Science is based on observable events taking place in a world where time and space are assumed to be independent of us, but from a philosophical point of view Kant argues that we may be unable to see all the aspects of whatever we are observing.

14 Thermodynamics is really a subject that describes *das Ding für uns*⁴ as opposed to *das Ding an sich*.

Das Ding an sich (3)

◀ 2 Thermodynamic ...

16 The solid circles show calorimetric readings for the mixing enthalpy $\Delta_{\text{mix}}h$ of the system $\text{H}_2\text{O}-\text{D}_2\text{O}$ at varying compositions (mole fractions x) of the two compounds.

18 The line fits the data points very well, and we can therefore conclude that this simple model adequately represents the readings taken.

20 Based on our understanding of nature, isotopes are chemically identical, but in this case the mixing enthalpy measured is equivalent to a fall in temperature of 0.43 K for an equimolar mixture of the two isotopes, which is much greater than expected.

27 The reaction product HDO is not stable either since it decomposes instantaneously to H_2O and D_2O , which prevents us from observing the substance in its pure state.

Das Ding an sich (4)

◀ 2 Thermodynamic ...

29 In reality all scientific knowledge is based on theoretical models of one kind or the other, and therefore does not imply that we have any exact understanding of *das Ding an sich*.

30 The foundations of phenomenological thermodynamics are too weak to state hard facts about the *true* nature of the systems it describes, but strangely enough thermodynamic theory can still be used to falsify claims that break the laws upon which it is founded⁶.

32 Thermodynamic analysis is capable of confirming prior assumptions, or of demonstrating new relationships between existing results, but the calculations are not necessarily correct even if the model appears to correspond with reality.

Das Ding an sich (5)

◀ 2 Thermodynamic ...

34 It is also worth remembering that even a small one-component system has maybe 10^{15} – 10^{20} microscopic degrees of freedom that are modelled with only three thermodynamic state variables⁷.

36 It is therefore necessary to develop our ability to recognise what is important for the modelling, so that we can perform the right calculations, rather than trying to look (in vain) for the very accurate description.

³ Immanuel Kant, 1724–1804. German philosopher and logician.

⁴ Referred to as *Erscheinung* in Kant's thesis.

⁵ D. V. Fenby and A. Chand. *Aust. J. Chem.*, 31(2):241–245, 1978.

⁶ The *perpetuum mobile* is the most famous example of this. In Norway it is in fact impossible to apply for patent protection for a perpetual motion machine, cf. the Norwegian Industrial Property Office's *Guidelines for processing patent applications*. The online (2010) version of *Part C: Preliminary examination; Chapter II Contents of the patent application, except requirements; 3.3.6 Insufficient clarity excludes inventions*

physical laws to be broken — this applies e.g. to perpetual motion machines.”

⁷ Systems with many components are obviously even more complex

Looking back

◀ 2 Thermodynamic ...

- 1 System
- 2 State
- 3 Process
- 4 Extensive vs. intensive
- 5 Equilibrium
- 6 Heat and work

◀ **Part 4** ▶

The Legendre transform

◀ see also Part-Contents ▶

Contents

- 1 Canonical potentials**
- 2 Manifolds**
- 3 Inversion**
- 4 Maxwell relations**
- 5 Gibbs–Helmholtz equation**

Energy

1 From a pragmatic point of view it is convenient to remember that U is useful for dynamic simulation, H for stationary simulation, etc. If a feasible solution to the problem already exists then this is perfectly adequate, but when seeking a new solution we need a deeper theoretical understanding.

5 Here, the Legendre¹ transformation is the key, as it provides a simple formula that allows us replace the free variable of a function with the corresponding partial derivative. For example, the variable V in internal energy $U(S, V, N)$ can be replaced by $(\partial U/\partial V)_{S,N}$, see Figure 4.1.

Energy (2)

◀ 4 The ...

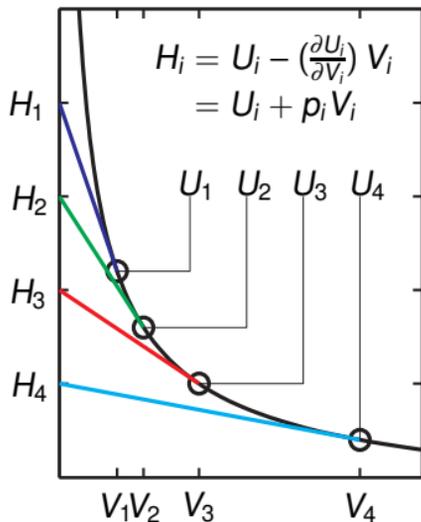


Figure 4.1: Legendre transformation of internal energy to enthalpy.

Energy (3)

6 The new variable can be interpreted as the negative pressure π and the resulting transformed function, called enthalpy $H(S, \pi, N)$, is in many cases more versatile than U itself. In fact, as we will see later, H has the same information content as U .

¹ Adrien-Marie Legendre, 1752–1833. French mathematician.

Transformation rules

1 Mathematically, the Legendre transformation ϕ_i of the function f is defined by:

$$\begin{aligned}\phi_i(\xi_i, x_j, x_k, \dots, x_n) &\hat{=} f(x_i, x_j, x_k, \dots, x_n) - \xi_i x_i, \\ \xi_i &\hat{=} \left(\frac{\partial f}{\partial x_i}\right)_{x_j, x_k, \dots, x_n}.\end{aligned}\quad (4.1)$$

2 As mentioned above, one example of this is the transformation of internal energy to enthalpy:

$$\begin{aligned}H &\hat{=} U_V(S, \pi, N) = U(S, V, N) - \pi V \\ \pi &\hat{=} \left(\frac{\partial U}{\partial V}\right)_{S, N} = -p\end{aligned}$$

Note that the volume derivative of U is the *negative* pressure π , because U diminishes when the system *performs* work on the surroundings— not vice versa.

Transformation rules (2)

3 To begin to get an understanding of the Legendre transform we shall first write out the differential

$$d\phi_i = df - x_i d\xi_i - \xi_i dx_i ,$$

and then substitute in the total differential of the initial function f expressed as: $df = \xi_i dx_i + \sum_{j \neq i}^n (\partial f / \partial x_j)_{x_i, x_k, \dots, x_n} dx_j$.

4 The simplification is obvious:

$$d\phi_i = -x_i d\xi_i + \sum_{j \neq i}^n \left(\frac{\partial f}{\partial x_j} \right)_{x_i, x_k, \dots, x_n} dx_j .$$

Transformation rules (3)

5 If we now consider ϕ_i as a function of the derivative ξ_i rather than of the original variable x_i , the total differential of ϕ_i can be written

$$d\phi_i = \left(\frac{\partial\phi_i}{\partial\xi_i}\right)_{x_j, x_k, \dots, x_n} d\xi_i + \sum_{j \neq i}^n \left(\frac{\partial\phi_i}{\partial x_j}\right)_{\xi_i, x_k, \dots, x_n} dx_j .$$

6 Comparing the last two equations term-by-term gives us the important transformation properties $(\partial\phi_i/\partial\xi_i)_{x_j, x_k, \dots, x_n} = -x_i$ and $(\partial\phi_i/\partial x_j)_{\xi_i, x_k, \dots, x_n} = (\partial f/\partial x_j)_{x_i, x_k, \dots, x_n} \hat{=} \xi_j$.

Transformation rules (4)

◀ 4 The ...

7 The latter shows that further transformation is straightforward:

$$\begin{aligned} \phi_{ij}(\xi_i, \xi_j, x_k, \dots, x_n) &\hat{=} \phi_i(\xi_i, x_j, x_k, \dots, x_n) - \xi_j x_j, & (4.2) \\ \xi_j &\hat{=} \left(\frac{\partial \phi_i}{\partial x_j} \right)_{\xi_i, x_k, \dots, x_n} \\ &= \left(\frac{\partial f}{\partial x_j} \right)_{x_i, x_k, \dots, x_n}. \end{aligned}$$

Repeated transformation

1 Combining Eqs. 4.1 and 4.2 gives the alternative, and conceptually simpler, expression

$$\phi_{ij}(\xi_i, \xi_j, x_k, \dots, x_n) = f(x_i, x_j, x_k, \dots, x_n) - \xi_i x_i - \xi_j x_j, \quad (4.3)$$

where the sequential structure of the Legendre transforms in 4.1 and 4.2 has been replaced by a simultaneous transformation of two (or more) variables.

5 Moreover, as the Legendre transform is independent of the order of differentiation, we know that $\phi_{ij} = \phi_{ji}$. Mathematically we say that the Legendre operator² commutes.

6 The three sets of variables (x_i, x_j, \dots, x_n) , (ξ_i, x_j, \dots, x_n) and $(\xi_i, \xi_j, \dots, x_n)$ are particularly important, and are often referred to as the *canonical* variables of the functions f , ϕ_i and $\phi_{ij} = \phi_{ji}$.

Repeated transformation (2)

◀ 4 The ...

² Mathematical operators are often allocated their own symbols, but in thermodynamics it is more usual to give the transformed property a new function symbol.

Canonical potentials

- 1** In thermodynamics, we refer to canonical potentials, meaning those that contain *all* of the thermodynamic information about the system.
- 5** Here we will show that the Legendre transforms of internal energy give us a canonical description of the thermodynamic state of a system.
- 6** Essentially, what we need to show is that $U(S, V, \mathbf{n})$, $A(T, V, \mathbf{n})$, $H(S, -p, \mathbf{n})$, etc. have the unique property that we can recreate *all* of the available information from any single one of them.
- 7** This is not trivial, as we will see that $U(T, V, \mathbf{n})$ and $H(T, -p, \mathbf{n})$, for instance, do not have this property.

§ 019

◀ § 18

▶ § 20

◀ 4 The ...

Derive all of the possible Legendre transforms of internal energy. State carefully the *canonical* variables in each case. Use the definitions³ $\tau \hat{=} (\partial U / \partial S)_{V,N}$, $\pi \hat{=} (\partial U / \partial V)_{S,N}$ and $\mu \hat{=} (\partial U / \partial N)_{S,V}$ to help you.

³ Let τ and π denote temperature and negative pressure respectively. This is to emphasize that they are transformed quantities, like the chemical potential μ . In this notation, all intensive derivatives of internal energy are denoted by lower case Greek letters.

§ 019 Energy functions

1 For a single-component system this means that there are $2^3 - 1 = 7$ possible transformations.

3 By using Eq. 4.1 on each of the variables in turn we get three of the transforms:

$$A(\tau, V, N) = U(S, V, N) - \left(\frac{\partial U}{\partial S}\right)_{V,N} S \hat{=} U - \tau S, \quad (4.4)$$

$$H(S, \pi, N) = U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S,N} V \hat{=} U - \pi V, \quad (4.5)$$

$$X(S, V, \mu) = U(S, V, N) - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \hat{=} U - \mu N. \quad (4.6)$$

§ 019 Energy functions (2)

4 By using Eq. 4.3 on pairs of variables we can obtain three more transforms:

$$\begin{aligned} G(\tau, \pi, N) &= U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S,N} V - \left(\frac{\partial U}{\partial S}\right)_{V,N} S \\ &\hat{=} U - \pi V - \tau S, \end{aligned} \quad (4.7)$$

$$\begin{aligned} Y(S, \pi, \mu) &= U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S,N} V - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \\ &\hat{=} U - \pi V - \mu N, \end{aligned} \quad (4.8)$$

$$\begin{aligned} \Omega(\tau, V, \mu) &= U(S, V, N) - \left(\frac{\partial U}{\partial S}\right)_{V,N} S - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \\ &\hat{=} U - \tau S - \mu N. \end{aligned} \quad (4.9)$$

§ 019 Energy functions (3)

5 Finally, by using Eq. 4.2 on all three variables successively we can obtain the null potential, which is also discussed on page 199 in Chapter 5:

$$\begin{aligned}O(\tau, \pi, \mu) &= U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S, N} V - \left(\frac{\partial U}{\partial S}\right)_{V, N} S - \left(\frac{\partial U}{\partial N}\right)_{S, V} N \\ &\hat{=} U - \pi V - \tau S - \mu N \\ &\equiv 0\end{aligned}\tag{4.10}$$

H A U G

- 1** Several of the Legendre transforms of energy have their own names:
- 2** Internal energy $U(S, V, N)$ is used when looking at changes to closed systems, and is in many respects the fundamental relationship of thermodynamics.
- 3** Helmholtz energy $A(\tau, V, N)$ is central to describing the properties of fluids.
- 4** Gibbs energy $G(\tau, \pi, N)$ has traditionally been the transform that is of most interest in chemical thermodynamics and physical metallurgy.
- 5** Enthalpy $H(S, \pi, N)$ is important for describing thermodynamic processes in chemical engineering and fluid mechanics. ■

§ 020

◀ § 19

▶ § 21

◀ 4 The ...

The variable ξ_j in Eq. 4.2 can be defined as either $(\partial\phi_i/\partial x_j)_{\xi_i, x_k, \dots, x_n}$ or $(\partial f/\partial x_j)_{x_i, x_k, \dots, x_n}$. Use implicit differentiation to prove that the two definitions are equivalent.

§ 020 Differentiation I

1 It is natural to start with Eq. 4.1, which we differentiate with respect to x_j :

$$\left(\frac{\partial \phi_j}{\partial x_j}\right)_{\xi_i} = \left(\frac{\partial (f - \xi_i x_i)}{\partial x_j}\right)_{\xi_i}, \quad (4.11)$$

where $(\partial \xi_i / \partial x_j)_{\xi_i}$ is by definition zero.

4 Hence, at constant ξ_j :

$$\begin{aligned} d(f - \xi_i x_i)_{\xi_i} &= \left(\frac{\partial f}{\partial x_i}\right)_{x_j} dx_i + \left(\frac{\partial f}{\partial x_j}\right)_{x_i} dx_j - \xi_i dx_i \\ &\hat{=} \xi_i dx_i + \left(\frac{\partial f}{\partial x_j}\right)_{x_i} dx_j - \xi_i dx_i \\ &= \left(\frac{\partial f}{\partial x_j}\right)_{x_i} dx_j \end{aligned}$$

§ 020 Differentiation I (2)

6 The full derivative takes the same value as the corresponding partial derivative (only one degree of freedom). Substitution into Eq. 4.11 yields

$$\left(\frac{\partial \phi_i}{\partial x_j}\right)_{\xi_i} = \left(\frac{\partial f}{\partial x_j}\right)_{x_i} \hat{=} \xi_j \quad (4.13)$$

leading to the conclusion that differentiation of ϕ_i with respect to the untransformed variable x_j gives the same derivative as for the original function f .

§ 021

◀ § 20

▶ § 22



◀ 4 The ...

Use the result from Paragraph 20 on page 122 to show that the chemical potential has four equivalent definitions: $\mu \hat{=} (\partial U/\partial N)_{S,V} \hat{=} (\partial H/\partial N)_{S,\pi} \hat{=} (\partial A/\partial N)_{\tau,V} \hat{=} (\partial G/\partial N)_{\tau,\pi}$. Specify the equivalent alternative definitions for temperature τ and negative pressure π .

§ 021 Identities I

1 Let $f = U(S, V, N)$ be the function to be transformed. The question asks for the derivatives with respect to the mole number N and it is tacitly implied that only S and V are to be transformed.

2 From the Eqs. 4.4 and 4.5 we have $\phi_1 = A(\tau, V, N)$ and $\phi_2 = H(S, \pi, N)$, which on substitution into Eq. 4.13 give:

$$\left(\frac{\partial A}{\partial N}\right)_{\tau, V} = \left(\frac{\partial U}{\partial N}\right)_{S, V}, \quad (4.14)$$

$$\left(\frac{\partial H}{\partial N}\right)_{S, \pi} = \left(\frac{\partial U}{\partial N}\right)_{S, V}. \quad (4.15)$$

3 The transform $\phi_{12} = \phi_{21} = G(\tau, \pi, N)$ in Eq. 4.7 can be reached either via A or H .

§ 021 Identities I (2)

4 Inserted into Eq. 4.13 the two alternatives become:

$$\left(\frac{\partial G}{\partial N}\right)_{\tau,\pi} = \left(\frac{\partial A}{\partial N}\right)_{\tau,V} , \quad (4.16)$$

$$\left(\frac{\partial G}{\partial N}\right)_{\tau,\pi} = \left(\frac{\partial H}{\partial N}\right)_{S,\pi} . \quad (4.17)$$

7 So, in conclusion, the following is true for any single-component system:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{\tau,V} \hat{=} \left(\frac{\partial H}{\partial N}\right)_{S,\pi} \hat{=} \left(\frac{\partial G}{\partial N}\right)_{\tau,\pi} \hat{=} \left(\frac{\partial U}{\partial N}\right)_{S,V} . \quad (4.18)$$

8 By performing the same operations on temperature and negative pressure we obtain:

$$\tau = \left(\frac{\partial H}{\partial S}\right)_{\pi,N} \hat{=} \left(\frac{\partial X}{\partial S}\right)_{V,\mu} \hat{=} \left(\frac{\partial Y}{\partial S}\right)_{\pi,\mu} \hat{=} \left(\frac{\partial U}{\partial S}\right)_{V,N} , \quad (4.19)$$

$$\pi = \left(\frac{\partial A}{\partial V}\right)_{\tau,N} \hat{=} \left(\frac{\partial X}{\partial V}\right)_{S,\mu} \hat{=} \left(\frac{\partial \Omega}{\partial V}\right)_{\tau,\mu} \hat{=} \left(\frac{\partial U}{\partial V}\right)_{S,N} \quad (4.20)$$

§ 021 Identities I (3)

§ 022

◀ §21

▶ §23



◀ 4 The ...

The Legendre transform was differentiated with respect to the original variable x_j in Paragraph 20. However, the derivative with respect to the transformed variable ξ_j remains to be determined. Show that $(\partial\phi_i/\partial\xi_i)_{x_j, x_k, \dots, x_n} = -x_j$.

§ 022 Differentiation II

1 Let us start with $\phi_i(\xi_i, x_j) = f(x_i, x_j) - \xi_i x_i$ from Eq. 4.1 and differentiate it with respect to ξ_i . Note that the chain rule of differentiation

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

has been used to obtain the last line below:

$$\begin{aligned} \left(\frac{\partial \phi_i}{\partial \xi_i}\right)_{x_j} &= \left(\frac{\partial f}{\partial \xi_i}\right)_{x_j} - \left(\frac{\partial(\xi_i x_i)}{\partial \xi_i}\right)_{x_j} \\ &= \left(\frac{\partial f}{\partial \xi_i}\right)_{x_j} - x_i - \xi_i \left(\frac{\partial x_i}{\partial \xi_i}\right)_{x_j} \\ &= \left(\frac{\partial f}{\partial x_i}\right)_{x_j} \left(\frac{\partial x_i}{\partial \xi_i}\right)_{x_j} - x_i - \xi_i \left(\frac{\partial x_i}{\partial \xi_i}\right)_{x_j}. \end{aligned} \quad (4.21)$$

§ 022 Differentiation II (2)

3 From Eq. 4.3 we know that $(\partial f / \partial x_i)_{x_j} = \xi_i$, which can easily be substituted into Eq. 4.21 to produce

$$\left(\frac{\partial \phi_i}{\partial \xi_i}\right)_{x_j} = -x_i, \quad (4.22)$$

which leads to the following conclusion: The derivative of ϕ_i with respect to a transformed variable ξ_i is the original variable x_i , but with the sign reversed.

Non-canonical differentiation

- 1** The Eq. 4.22 is strikingly simple, and leads to a number of simplifications in thermodynamics.
- 2** The properties explained in the previous paragraph are of prime importance. Before we move on, however, we should investigate what happens if we do *not* describe the Legendre transform in terms of canonical variables.
- 3** Differentiating $\phi_i = f - \xi_i x_i$ with respect to the original variable x_i gives:

$$\left(\frac{\partial \phi_i}{\partial x_i}\right)_{x_{j \neq i}} = \left(\frac{\partial f}{\partial x_i}\right)_{x_{j \neq i}} - \left(\frac{\partial \xi_i}{\partial x_i}\right)_{x_{j \neq i}} x_i - \xi_i = -\left(\frac{\partial^2 f}{\partial x_i \partial x_i}\right)_{x_{j \neq i}} x_i,$$

§ 023

◀ § 22

▶ § 24



◀ 4 The ...

Use the results obtained in Paragraph 22 to prove that the derivatives $(\partial H/\partial\pi)_{S,N}$, $(\partial G/\partial\pi)_{\tau,N}$ and $(\partial Y/\partial\pi)_{S,\mu}$ are three equivalent ways of expressing the volume V of the system. Specify the corresponding expressions for the entropy S and the mole number N .

§ 023 Identities II

1 Let us start out once more from $f = U(S, V, N)$ and define⁴ the transform $\phi_2 = H(S, \pi, N) = U - \pi V$. Inserted into Eq. 4.22, this gives us $(\partial H / \partial \pi)_{S, N} = -V$.

2 Systematically applying Eq. 4.22 to all of the energy functions in Paragraph 19 on page 117 yields⁵:

$$-V = \left(\frac{\partial H}{\partial \pi}\right)_{S, N} \hat{=} \left(\frac{\partial G}{\partial \pi}\right)_{\tau, N} \hat{=} \left(\frac{\partial Y}{\partial \pi}\right)_{S, \mu} , \quad (4.23)$$

$$-S = \left(\frac{\partial A}{\partial \tau}\right)_{V, N} \hat{=} \left(\frac{\partial G}{\partial \tau}\right)_{\pi, N} \hat{=} \left(\frac{\partial \Omega}{\partial \tau}\right)_{V, \mu} , \quad (4.24)$$

$$-N = \left(\frac{\partial X}{\partial \mu}\right)_{S, V} \hat{=} \left(\frac{\partial Y}{\partial \mu}\right)_{S, \pi} \hat{=} \left(\frac{\partial \Omega}{\partial \mu}\right)_{\tau, V} . \quad (4.25)$$

§ 023 Identities II (2)

⁴ The symbol $\pi \hat{=} -p$ is used here as the pressure variable. This is quite deliberate, in order to avoid the eternal debate about the sign convention for p . As used here, τ , π and μ are subject to the same transformation rules. This means that the same rules apply to e.g. $(\partial H/\partial\pi)_{S,N} = -V$ and $(\partial A/\partial\tau)_{V,N} = -S$, whereas the traditional approach using $(\partial H/\partial p)_{S,N} = V$ and $(\partial A/\partial T)_{V,N} = -S$ involves different rules for p and T derivatives. Note, however, that it makes no difference whether $-p$ or p is kept constant during the differentiation.

⁵ Sharp students will note the absence of $-S = (\partial O/\partial\tau)_{\pi,\mu}$, $V = (\partial O/\partial\pi)_{\tau,\mu}$ and $-N = (\partial O/\partial\mu)_{\tau,p}$. These relations have no clear thermodynamic interpretation, however, because experimentally τ, π, μ are dependent variables, see also Paragraph 26 on page 157.

§ 024

◀ § 23

▶ § 25



◀ 4 The ...

Use the results from Paragraphs 21 and 23 on pages 125 and 133 to find the total differentials of all the energy functions mentioned in Paragraph 19.

§ 024 Differentials I

1 The total differentials of the energy functions can be stated by taking the results from Eqs. 4.18–4.20 and 4.23–4.25 as a starting point:

$$dU(S, V, N) = \tau dS + \pi dV + \mu dN, \quad (4.26)$$

$$dA(\tau, V, N) = -S d\tau + \pi dV + \mu dN, \quad (4.27)$$

$$dH(S, \pi, N) = \tau dS - V d\pi + \mu dN, \quad (4.28)$$

$$dX(S, V, \mu) = \tau dS + \pi dV - N d\mu, \quad (4.29)$$

$$dG(\tau, \pi, N) = -S d\tau - V d\pi + \mu dN, \quad (4.30)$$

$$dY(S, \pi, \mu) = \tau dS - V d\pi - N d\mu, \quad (4.31)$$

$$d\Omega(\tau, V, \mu) = -S d\tau + \pi dV - N d\mu, \quad (4.32)$$

$$dO(\tau, \pi, \mu) = -S d\tau - V d\pi - N d\mu. \quad (4.33)$$

Manifolds

- 1** In what has been written so far we note that all of the state variables τ , S , π , V , μ and N appear in conjugate pairs such as τdS , $-S d\tau$, πdV , $-V d\pi$, μdN or $-N d\mu$.
- 3** The obvious symmetry reflects Eq. 4.22, which also implies that the Legendre transform is “its own inverse”.
- 4** However, this is only true if the function is either strictly convex or strictly concave, as the relationship breaks down when the second derivative $f(x_i, x_j, x_k, \dots, x_n)$ is zero somewhere within the domain of definition of the free variables (see also Section 4.3).

Manifolds (2)

5 This is illustrated in Figure 4.2 based on the transformation of the third order polynomial

$$f(x) = x(1 - x^2) \Rightarrow \xi(x) \hat{=} \left(\frac{\partial f}{\partial x}\right) = 1 - 3x^2.$$

The Legendre transformation of f to $\phi \hat{=} f - \xi x$ can be expressed in two different ways:

$$\phi(x) = 2x^3 \Rightarrow \phi(\xi) = \pm 2 \left(\frac{1-\xi}{3}\right)^{3/2}. \quad (4.34)$$

6 Moreover, both x and f can be expressed as functions of the transformation variable ξ :

$$x = \pm \left(\frac{1-\xi}{3}\right)^{1/2} \Rightarrow f(\xi) = \pm \left(\frac{1-\xi}{3}\right)^{1/2} \left(\frac{2+\xi}{3}\right),$$

This means that in total we have to consider three functions involving x , and three involving ξ : $f(x)$, $\phi(x)$, $\xi(x)$, $f(\xi)$, $\phi(\xi)$ and $x(\xi)$.

Manifolds (3)

7 In order to retain the information contained in $f(x)$, we need to know either $\phi(x)$ and $\xi(x)$, or $f(\xi)$ and $x(\xi)$, or simply $\phi(\xi)$. In principle, the latter is undoubtedly the best option, and this is the immediate reason why $\phi(\xi)$ is said to be in canonical form.

8 Nevertheless, there is an inversion problem when ϕ is interpreted as a function of ξ rather than x .

10. Instead, they are examples of what we call manifolds (loosely speaking folded surfaces defined by a function) as illustrated in Figures 4.2c–4.2d⁶.

⁶ A function is a point-to-point rule that connects a point in the domain of definition with a corresponding point in the function range.

Consistency requirements

1 Finally, let us look at what differentiating ϕ with respect to ξ implies. From Section 22, we know that the answer is $-x$, but

$$\left(\frac{\partial\phi}{\partial\xi}\right) = \mp\left(\frac{1-\xi}{3}\right)^{1/2}$$

initially gives us a manifold in ξ with two solutions, as shown in Figure 4.2.

2 It is only when we introduce $x(\xi)$ from Eq. 4.34 that the full picture emerges: $(\partial\phi/\partial\xi) = -x$.

5 If the three values have been independently measured, then the relation $(\partial\phi/\partial\xi) = -x$ can be used to test the experimental values for consistency.

Consistency requirements (2)

6 The existence of these kinds of tests, which can involve a variety of physical measurements, is one of the great strengths of thermodynamics.

Figure a–b). The function $f = x(1 - x^2)$ and its Legendre transform $\phi = 2x^3$ defined as the intersection of the tangent bundle of f and the ordinate axis. Note that f shows a maximum and a minimum while ϕ has no extrema.

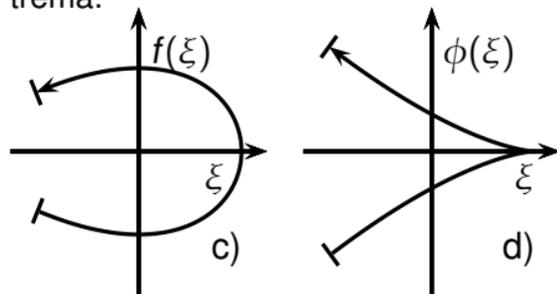
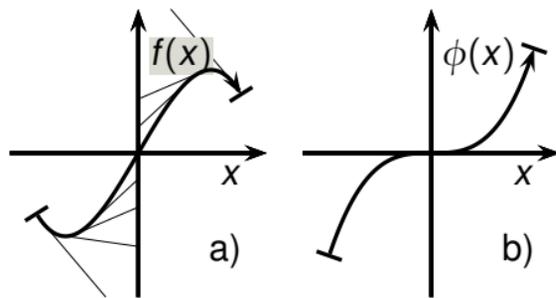


Figure c–d). The same two functions shown as parametric curves with $\xi \hat{=} (\partial f / \partial x) = 1 - 3x^2$ along the abscissa. The fold in the plane(s) is located at the inflection point $(\partial^2 f / \partial x \partial x) = 0$.

Figure 4.2: The Legendre transformation of $f = x(1 - x^2)$ to $\phi = f - \xi x$ where $\xi \hat{=} (\partial f / \partial x) = 1 - 3x^2$. The two domains of definition are $x \in [-\sqrt{2/3}, \sqrt{2/3}]$ and $\xi \in [-1, 1]$. Together, the four graphs demonstrate how an explicit function of x , i.e. $f(x)$ or $\phi(x)$, is turned into an implicit manifold when expressed in terms of ξ , i.e. $f(\xi)$ or $\phi(\xi)$.

Vapour–liquid

1 In view of these practical considerations, we cannot claim that Legendre transforms are globally invertible, but it is true to say that they are locally invertible on curve segments where the sign of $(\partial^2 f / \partial x \partial x)$ remains unchanged. We shall therefore take the precaution of treating each curve segment as a separate function.

8 For instance, in vapor–liquid equilibrium calculations we shall designate one of the curve segments as being *vapour* and the other as being *liquid*, although there is no thermodynamic justification for this distinction, other than the fact that $(\partial^2 A / \partial V \partial V)_{T,N} = 0$ somewhere along the isotherm.

From ϕ to f ?

◀ 4 The ...

- 1** In this section we will explain how, and under what conditions, it is possible to convert the Legendre transform ϕ back to the original function f .
- 2** This operation will be based on the transformation rule set out in Eq. 4.1

$$\phi(y) \hat{=} f - \left(\frac{\partial f}{\partial x}\right) x, \quad (4.35)$$

where the properties of the variable y are, as yet, unknown.

From ϕ to f ? (2)

◀ 4 The ...

3 What we need to know is whether the same transformation rule applies to the inverse transform of $\phi(y)$, such that

$$f \stackrel{?}{=} \phi - \left(\frac{\partial\phi}{\partial y}\right) y, \quad (4.36)$$

and, if so, what y is (we have an inkling that $y = (\partial f/\partial x)$, but we need to prove it).

4 Substituting Eq. 4.36 into Eq. 4.35, rearranging the expression slightly, and applying the chain rule, gives us:

$$-\left(\frac{\partial\phi}{\partial y}\right) y = -\left(\frac{\partial\phi}{\partial x}\right) \left(\frac{\partial x}{\partial y}\right) y \stackrel{?}{=} \left(\frac{\partial f}{\partial x}\right) x. \quad (4.37)$$

From ϕ to f ? (3)

◀ 4 The ...

5 Next we substitute Eq. 4.35 into Eq. 4.37:

$$\begin{aligned}
 -\left(\left(\frac{\partial f}{\partial x}\right) - \left(\frac{\partial^2 f}{\partial x \partial x}\right) x - \left(\frac{\partial f}{\partial x}\right)\right) \left(\frac{\partial x}{\partial y}\right) y &\stackrel{?}{=} \left(\frac{\partial f}{\partial x}\right) x \\
 \left(\frac{\partial^2 f}{\partial x \partial x}\right) x \left(\frac{\partial x}{\partial y}\right) y &\stackrel{?}{=} \left(\frac{\partial f}{\partial x}\right) x \\
 \left(\frac{\partial x}{\partial y}\right) y &\stackrel{?}{=} \left(\frac{\partial f}{\partial x}\right) \left(\frac{\partial^2 f}{\partial x \partial x}\right)^{-1}. \quad (4.38)
 \end{aligned}$$

Integration

- 1** For the inverse transform to exist, it must be true that $(\partial^2 f / \partial x \partial x) \neq 0$. This is a necessary condition.
- 2** It is also worth adding that in general, partial differential equations do not have an analytical solution. However, thermodynamic problems are often unusually simple, and that is also the case here.
- 3** Let us define $\xi \hat{=} (\partial f / \partial x)$, which gives us

$$\left(\frac{\partial x}{\partial y}\right) y \stackrel{?}{=} \xi \left(\frac{\partial \xi}{\partial x}\right)^{-1} .$$

Integration (2)

◀ 4 The ...

4 Introducing the logarithmic variables $d \ln y \hat{=} dy / y$ and $d \ln \xi \hat{=} d\xi / \xi$ produces an elegant solution to the problem (note how the chain rule is used in reverse in the second-last line):

$$\begin{aligned} \left(\frac{\partial x}{\partial \ln y}\right) &= \left(\frac{\partial \ln \xi}{\partial x}\right)^{-1} \\ \left(\frac{\partial \ln \xi}{\partial x}\right) \left(\frac{\partial x}{\partial \ln y}\right) &= 1 \\ \left(\frac{\partial \ln \xi}{\partial \ln y}\right) &= 1 \end{aligned} \tag{4.39}$$

Solution criteria

1 The most general solution can be expressed as $y = c\xi \hat{=} c(\partial f/\partial x)$, where c is an arbitrary factor. It is natural to choose $c = 1$, which means that $y \equiv \xi$, as we know from our earlier discussion of the Legendre transform, but any value of $c \in \mathbb{R}_+$ will give the same result, as the inverse transform in Eq. 4.36 is insensitive to scaling.

2 We say that x and ξ are the natural (or canonical) variables of the functions $f(x)$ and $\phi(\xi)$, as they allow transformation in both directions without the loss of any information.

4 In the context of thermodynamics, this means that e.g. $A(T, V, \mathbf{n})$ can be inverse transformed to $U(S, V, \mathbf{n})$, provided that $(\partial^2 U/\partial S \partial S)_{V, \mathbf{n}} \neq 0$.

Solution criteria (2)

5 However, the transformation rule is symmetrical, and the same requirement must also apply in the other direction: $U(S, V, \mathbf{n})$ can only be transformed into $A(T, V, \mathbf{n})$ if $(\partial^2 A / \partial T \partial T)_{V, \mathbf{n}} \neq 0$.

6 The two requirements may appear contradictory, but in actual fact they are overlapping, because:

$$\left(\frac{\partial^2 U}{\partial S \partial S}\right)_{V, \mathbf{n}} = \left(\frac{\partial T}{\partial S}\right)_{V, \mathbf{n}} = \left(\frac{\partial S}{\partial T}\right)_{V, \mathbf{n}}^{-1} = -\left(\frac{\partial^2 A}{\partial T \partial T}\right)_{V, \mathbf{n}}^{-1}$$

7 In states in which one of the derivatives tends to zero, and the other one tends to infinity, the system is on the verge of being unstable.

8 Depending on the variables involved, this relates to either thermal (T, S), mechanical (p, V) or chemical (μ_i, N_i) stability.■

§ 025

◀ §24

▶ §26

◀ 4 The ...

Use the result from Paragraph 22 on page 129 to show that performing two Legendre transformations on f , first with respect to x_i and then with respect to ξ_i , returns the original function.

§ 025 Inverse transform

1 Given Definition 4.1 and Eq. 4.22, the inverse Legendre transformation can be written

$$\phi_i - \left(\frac{\partial \phi_i}{\partial \xi_i}\right)_{x_j} \xi_i = \phi_i - (-x_i) \xi_i \equiv f, \quad (4.40)$$

but it is not entirely clear what variable set should be used to define f .

2 To understand the nature of the problem, let us consider the following example. From Eq. 4.4 it follows that:

$$U(S, V, N) - \left(\frac{\partial U(S, V, N)}{\partial S}\right)_{V, N} S = U(S, V, N) - \tau S \hat{=} A(\tau, V, N). \quad (4.41)$$

3 To approach it from the opposite direction, we have to calculate the Legendre transform of $A(\tau, V, N)$ with respect to the variable τ :

$$A(\tau, V, N) - \left(\frac{\partial A(\tau, V, N)}{\partial \tau}\right)_{V, N} \tau = A(\tau, V, N) - (-S)\tau \equiv U(-S, V, N). \quad (4.42)$$

§ 025 Inverse transform (2)

4 This clearly returns the original function U , but the set of canonical variables has changed from S, V, N to $-S, V, N$. In order to get back to where we started, we must perform two further Legendre transformations:

$$U(-S, V, N) - \left(\frac{\partial U(-S, V, N)}{\partial(-S)}\right)_{V, N} (-S) = U(-S, V, N) - (-\tau)(-S) \\ \hat{=} A(-\tau, V, N), \quad (4.43)$$

$$A(-\tau, V, N) - \left(\frac{\partial A(-\tau, V, N)}{\partial(-\tau)}\right)_{V, N} (-\tau) = A(-\tau, V, N) - S(-\tau) \\ \equiv U(S, V, N). \quad (4.44)$$

5 In other words, performing repeated Legendre transformations reveals a closed cycle, where the original information contained in U is retained, as shown in the figure below:⁷

§ 025 Inverse transform (3)

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

⁷ In practice it may be easier to use the canonical variables $(x, y) = (-(\partial g/\partial z)_y, y)$ for the inverse transformation, rather than $(x, y) = ((\partial g/\partial z)_y, y)$ as has been done here.

Invertibility

- 1** This example shows that the Legendre transform is (locally) invertible, which means that we can choose whatever energy function is most suitable for our purposes.
- 2** Moreover, Eq. 4.10 tells us that the Legendre transform of U with respect to all of the state variables S , V and N is a function with very special properties. The function, which is known as the null potential, is identical to zero over the entire definition domain, and as such it has no inverse.

§ 026

◀ §25

▶ §27

◀ 4 The ...

Show that performing a Legendre transformation of internal energy $U(S, V, N)$ with respect to all the canonical variables S, V, N gives the null potential $O(\tau, \pi, \mu) = 0$. Next, show that the differential of O is identical to the Gibbs–Duhem equation; see also Paragraph 34 in Chapter 5.

§ 026 Null potential

- 1 However, since this result is valid for the entire domain of definition it must have a bearing on the degrees of freedom of the system.
- 3 Mathematically, the O -function forms a hyperplane in $\dim(\mathbf{n}) + 2$ dimensions.

Seven samurai

- 1** We have in this chapter introduced seven energy functions: U , H , A , G , X , Y and O , and six state variables: S , V , N , t , p and μ .
- 2** On reflection it is clear that only four of these variables are independent, because the discussion has relied entirely on the fact that internal energy U is a function of S , V and N .
- 3** All of the other variables have been defined at a later stage either as partial derivatives or as transformed functions of U .

§ 027

◀ § 26

▶ § 28

◀ 4 The ...

Set out all of the Maxwell relations that can be derived by applying the Leibniz⁸ rule $\partial^2 f / \partial x_i \partial x_j = \partial^2 f / \partial x_j \partial x_i$ to the functions U, A, H, Y, G, Ω, X and O , restricting yourself to single-component systems.

⁸ Gottfried Wilhelm von Leibniz, 1646–1716. German mathematician.

§ 027 Maxwell relations

1 Let us begin by illustrating what is meant by a Maxwell⁹ relation using $U(S, V, N)$ as our starting point. From the definitions of τ and π it follows that:

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

2 Similarly, cyclic permutation of the variables S , V and N yields:

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

3 By systematically comparing the second derivatives of all of the Legendre transforms mentioned in Paragraph 19 on page 117, we get the results shown below.

§ 027 Maxwell relations (2)

5 Note that the Maxwell relations which are derived from the null potential $O(\tau, \pi, \mu)$ have no physical interpretation, as experimentally τ, π, μ are dependent variables.

⁹ James Clerk Maxwell, 1831–1879. Scottish physicist.

Alternative procedure

1 We are familiar with the key characteristics of Legendre transforms, having looked at topics like transformation geometry, differentiation rules, inverse transforms and Maxwell relations. We shall now focus on the simple rule used in Figure 4.1, which shows that the Legendre transform is equal to the intersection of the tangent bundle of the original function and the ordinate axis.

2 The subject becomes even more interesting now, as we are going to prove another rule, which is even simpler, although not so easy to derive. The key to this is a simple change in variables from y and x in $(\partial y/\partial x)$ to y/x and $1/x$ in the expression $(\partial(y/x)/\partial(1/x))$. ■

§ 028

◀ §27

▶ §29

◀ 4 The ...

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

§ 028 Gibbs–Helmholtz

1 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

$$\left(\frac{\partial(f/x_i)}{\partial(1/x_i)}\right)_{x_j, x_k, \dots, x_n} \hat{=} f - \xi_i x_i \hat{=} \phi_i, \quad (4.46)$$

cf. the Legendre transform in Eq. 4.1. The identity applies generally, including to ϕ_{ij} and to any other derived transforms.

4 One of the classic applications of the Gibbs–Helmholtz equation is in calculating the temperature derivative of the equilibrium constant, as shown in Chapter 16, where $\ln K \hat{=} -\Delta_{rx} G_o / RT$ is shown to be an almost linear function of $1/T$ with a slope of $\Delta_{rx} h_o / R$.

Continued differentiation

1 It remains to be shown that it is straightforward to differentiate the Gibbs–Helmholtz equation. To illustrate this, let us use the derivative of the equation given in the worked example above:

$$\left(\frac{\partial H}{\partial \pi}\right)_{\tau, N} = \left(\frac{\partial}{\partial \pi} \left(\frac{\partial(G/\tau)}{\partial(1/\tau)}\right)_{\tau, N}\right)_{\tau, N} = \left(\frac{\partial}{\partial(1/\tau)} \left(\frac{\partial(G/\tau)}{\partial \pi}\right)_{\tau, N}\right)_{\tau, N} = \left(\frac{\partial(V/\tau)}{\partial(1/\tau)}\right)_{\tau, N}.$$

Note that the enthalpy has been differentiated with respect to negative pressure, which is a canonical variable; the result follows an easily recognisable pattern.

3 Finally, it is worth adding that every time we derive an expression of the form $y - x(\partial y/\partial x)$ we can choose to replace it with $(\partial(y/x)/\partial(1/x))$.

Part 5

Euler's Theorem on Homogeneous Functions

[← see also Part-Contents](#)



Contents

State description

◀ 5 Euler's ...

- 1** The thermodynamic state of a so-called *simple* system is described mathematically by the mapping $f : \mathbb{R}^{n+2} \rightarrow \mathbb{R}$ where $n \geq 0$ stands for the number of chemical components¹ in the system.
- 3** Apart from this constraint, the domain of definition of a multicomponent system is infinitely large, but the mathematical treatment is considerably simplified by the fact that it can be verified experimentally that f is linear along all state vectors starting at the origin.
- 4** The practical consequences of this linearity² will be clarified when we start investigating the mathematical properties of f , but let us first formalise our statement by stating that the function $f(x_1, \dots, x_n)$ is homogeneous of order $k \in \mathbb{Z}$ provided that the parametrised function $f(\lambda \mathbf{x})$ is *proportional* to λ^k in the direction of $\mathbf{x} = (x_1, \dots, x_n)$.

State description (2)

◀ 5 Euler's ...

6 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:

$$F(X_1, \dots, X_n, \xi_{n+1}, \dots, \xi_m) = \lambda^k f(x_1, \dots, x_n, \xi_{n+1}, \dots, \xi_m), \quad (5.1)$$

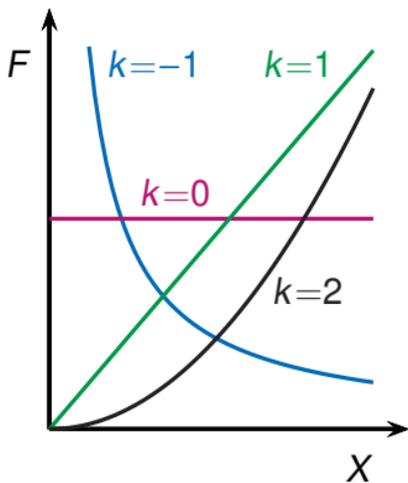
$$X_i \triangleq \lambda x_i. \quad (5.2)$$

¹ An empty chamber has no chemical components, but it nevertheless constitutes a thermodynamic system of electromagnetic radiation with two degrees of freedom.

² Herbert Callen. *Thermodynamics and an Introduction to Thermostatistics*. Wiley, 2nd edition, 1985.

Homogeneity

1



Note that F has exactly the same function definition as f . Hence, it is only by convention that we distinguish the two forms. We may therefore write:

$$F \stackrel{X}{\rightleftharpoons} f$$

2 It is then assumed that ξ_{n+1}, \dots, ξ_m do not take part in the homogeneity of f . That means the scaling law in Eq. 5.1 is valid for *all* choices of ξ_{n+1}, \dots, ξ_m .

Homogeneity (2)

◀ 5 Euler's ...

7 Taking this a step further, 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 of the quantities are treated as free function variables.

From our daily lives

◀ 5 Euler's ...

- 1** Of particular interest to us are the energy functions³ U, A, \dots, O with state variables belonging to S, V, N or τ, π, μ .
- 2** The energy functions, and entropy, volume and mole number, are homogeneous functions of order 1, while temperature, pressure⁴ and chemical potential are homogeneous functions of order 0.
- 3** In the context of thermodynamics these quantities are referred to as *extensive* and *intensive* state variables respectively⁵.

From our daily lives (2)

◀ 5 Euler's ...

³ In thermodynamics it is common to write $F = X\langle f \rangle$ in this case, where X is a physical quantity, i.e. a quantity with an associated unit of measurement. We could look, for example, at the total number of moles for all components in the system while it is kept at a constant composition (constant mole fractions). In this case $F(X) = \lambda f(x)$ where $X = \lambda x$ and $X = \{X\}[X]$. Here, $\{ \}$ denotes the magnitude of X and $[\]$ denotes its unit of measurement. Let us now choose $x = X/\{X\}$ i.e. $\lambda = \{X\}$. It is then possible to write $F(X) = \{X\} \cdot f(X/\{X\}) = \{X\}[X] \cdot f(X/\{X\})/[X] = X \cdot f(X/\{X\})/[X]$. It is for instance quite common to write the total Gibbs energy for the system as $G(\tau, \pi, N) = Ng(\tau, \pi, \mathbf{x})$ where \mathbf{x} is a vector of mole fractions, or, alternatively, as $G = Ng(\tau, \pi)$ if $\mathbf{x} = [1]$. The function $g = \langle f \rangle$ denotes *molar* Gibbs energy in both cases. Correspondingly, we can write $U = Nu(s, v)$, $H = Nh(s, \pi)$ etc. for the other molar energies.

⁴ Here, τ and π are used for temperature and negative pressure respectively, as already introduced in Chapter 4. In this context we want to stress that the properties (in common with the chemical potential μ) are intensive quantities.

⁵ A physical quantity is *extensive* if it is proportional to the system size and *intensive* if it is insensitive to the system size.

Differential in X and ξ

◀ 5 Euler's ...

1 We are not initially aiming to embark on a general discussion of the multicomponent functions in Eq. 5.1. Instead, we will start with a detailed analysis of the simpler two-variable functions $f(x, \xi)$ and $F(X, \xi)$.

3 In order to exploit the function properties, it makes sense to use the total differential of F expressed in X and ξ -coordinates:

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

4 The variable X is defined as a function of x and λ in Eq. 5.2, and by substituting the total differential of X , or more precisely $dX = \lambda dx + x d\lambda$, we obtain

$$dF = \left(\frac{\partial F}{\partial X}\right)_{\xi} x d\lambda + \left(\frac{\partial F}{\partial X}\right)_{\xi} \lambda dx + \left(\frac{\partial F}{\partial \xi}\right)_{X} d\xi . \quad (5.3)$$

Differential in λ and f

1 An alternative would be to make use of $F = \lambda^k f$ from Eq. 5.1 as the starting point for the derivation:

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

2 Substitution of the total differential of f expressed in x and ξ -coordinates gives:

$$dF = k\lambda^{k-1} f d\lambda + \lambda^k \left(\frac{\partial f}{\partial x}\right)_\xi dx + \lambda^k \left(\frac{\partial f}{\partial \xi}\right)_x d\xi . \quad (5.4)$$

3 Note that Eq. 5.3 and Eq. 5.4 are two alternative expressions for the same differential $dF(\lambda, x, \xi)$.

4 Comparing the equations term-by-term reveals three relations of great importance to thermodynamic methodology:

Case $d\lambda$

◀ 5 Euler's ...

1 Comparing the $d\lambda$ terms reveals that $(\partial F/\partial X)_\xi x = k\lambda^{k-1}f$. Multiplying both sides by λ gives $(\partial F/\partial X)_\xi \lambda x = k\lambda^k f$, which if we substitute in Eq. 5.1 and Definition 5.2 can be transformed into:

$$\left(\frac{\partial F}{\partial X}\right)_\xi X = kF. \quad (5.5)$$

3 The result is known as Euler⁶'s first theorem for homogeneous functions, or simply as the Euler integration of F .

⁶ Leonhard Euler, 1707–1783. Swiss mathematician.

Case dx

◀ 5 Euler's ...

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

$$\left(\frac{\partial F}{\partial X}\right)_\xi = \lambda^{k-1} \left(\frac{\partial f}{\partial x}\right)_\xi . \quad (5.6)$$

3 Hence, $(\partial F/\partial X)_\xi$ is a homogeneous function of order $k - 1$.

4 Differentiation with respect to X therefore reduces the order of homogeneity of F by one.

Case $d\xi$

◀ 5 Euler's ...

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

$$\left(\frac{\partial F}{\partial \xi}\right)_X = \lambda^k \left(\frac{\partial f}{\partial \xi}\right)_X, \quad (5.7)$$

3 Differentiation with respect to ξ therefore conserves the homogeneity in X .

Note

◀ 5 Euler's ...

- 1** It should be stressed that the Euler integration in Eq. 5.5 is not limited to one particular interpretation of X .
- 2** In fact, any scaled variable $x = \lambda^{-1}X$ satisfies the equation:

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

Extended notation I

◀ 5 Euler's ...

1 The general properties of homogeneous functions will be explained further in Chapter **General Theory**, but to get a sense of the overall picture we shall briefly mention what changes are required in Eqs. 5.5–5.7 to make them valid for multivariate functions:

$$\sum_{i=1}^n X_i \left(\frac{\partial F}{\partial X_i} \right)_{X_{j \neq i}, \xi_l} = kF \quad , \quad (5.8)$$

$$\left(\frac{\partial F}{\partial X_i} \right)_{X_{j \neq i}, \xi_l} = \lambda^{k-1} \left(\frac{\partial f}{\partial X_i} \right)_{X_{j \neq i}, \xi_l} \quad , \quad (5.9)$$

$$\left(\frac{\partial F}{\partial \xi_k} \right)_{X_{j, \xi_l \neq k}} = \lambda^k \left(\frac{\partial f}{\partial \xi_k} \right)_{X_{j, \xi_l \neq k}} \quad . \quad (5.10)$$

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 for τ , π and μ .

§ 029 Intensive functions

◀ 5 Euler's ...

1 The variables τ, π and μ mentioned above must first be defined. Mathematically, the total differential of $U(S, V, N)$ is:

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

3 Substitution of $k = 1$, $X_i = S$, $X_j \in \{V, N\}$ and $\xi_l = \emptyset^7$ in Eq. 5.9 yields:

$$\tau(S, V, N) \triangleq \left(\frac{\partial U(S, V, N)}{\partial S}\right)_{V, N} = \lambda^0 \left(\frac{\partial u(s, v, n)}{\partial s}\right)_{v, n} = \tau(s, v, n) . \quad (5.11)$$

4 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 λ .

§ 029 Intensive functions (2)

◀ 5 Euler's ...

6 Similarly, differentiation of U with respect to V and N yields

$$\pi(S, V, N) \hat{=} \left(\frac{\partial U(S, V, N)}{\partial V} \right)_{S, N} = \lambda^0 \left(\frac{\partial u(s, v, n)}{\partial v} \right)_{s, n} = \pi(s, v, n), \quad (5.12)$$

$$\mu(S, V, N) \hat{=} \left(\frac{\partial U(S, V, N)}{\partial N} \right)_{S, V} = \lambda^0 \left(\frac{\partial u(s, v, n)}{\partial n} \right)_{s, v} = \mu(s, v, n), \quad (5.13)$$

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

⁷ Actually an empty set. Here it is used to denote a missing variable or an empty vector.

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 ? Explain the physical significance of this integral.

§ 030 Euler integration

◀ 5 Euler's ...

1 Substituting $k = 1$, $X_i \in \{S, V, N\}$ and $\xi_I = \emptyset$ into Eq. 5.8, together with the definitions from Paragraph 29 on page 182 i.e. $\tau \hat{=} (\partial U / \partial S)_{V, N}$, $\pi \hat{=} (\partial U / \partial V)_{S, N}$ and $\mu \hat{=} (\partial U / \partial N)_{S, V}$ yields Euler's equation applied to internal energy:

$$U = \tau S + \pi V + \mu N. \quad (5.14)$$

2 We are not being asked about multicomponent mixtures, but Eq. 5.14 is quite general and can (by analogy with Eq. 5.8) be extended to:

$$U = \tau S + \pi V + \sum_{i=1}^n \mu_i N_i \hat{=} \tau S + \pi V + \boldsymbol{\mu}^T \mathbf{n} \quad (5.15)$$

Remark

◀ 5 Euler's ...

1 The total differential of internal energy for a single component system is $dU = \tau dS + \pi dV + \mu dN$.

3 Physically, this means that the system can be built up from zero size⁸ in a manner that keeps τ, π, μ constant during the process.

5 When these subsystems are merged into one big system there will be no changes in the intensive properties, because the requirements for *thermodynamic equilibrium* are automatically fulfilled, see also Chapter 21 on page 1162.

⁸ By definition, a system of zero size has zero internal energy, i.e. $U = 0$. In this context, “zero size” refers to zero volume, zero mass and zero entropy. Note, however, that it is not sufficient to assume zero mass, because even an evacuated volume will have radiation energy proportional to T^4 !

§ 031

◀ § 30

▶ § 32

◀ 5 Euler's ...

Gibbs energy $G(\tau, \pi, N)$ is an extensive function of the mole number N at a given temperature τ and (negative) pressure π . 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 .

§ 031 Extensive functions

◀ 5 Euler's ...

1 First of all the functions S , V and μ must be defined. Mathematically, the total differential of $G(\tau, \pi, N)$ is:

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

3 Comparing this with the differential in the problem formulation yields $-S(\tau, \pi, N) = (\partial G / \partial \tau)_{\pi, N}$, $-V(\tau, \pi, N) = (\partial G / \partial \pi)_{\tau, N}$ and $\mu = (\partial G / \partial N)_{\tau, \pi}$.

5 From Eq. 5.9 it can be seen that the chemical potential is (still) a homogeneous function of order 0, see also Eq. 5.13.



The Gibbs energy of a binary mixture is given as a homogeneous function 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. Let $x_1 \hat{=} N_1/(N_1 + N_2)$ and $x_2 \hat{=} N_2/(N_1 + N_2)$.

Show that the isopleths corresponding to constant G (the contour lines) are equidistant for a series of evenly distributed Gibbs energy values. Use $a = 2.4$ in your calculations.

§ 032 Gibbs energy I

◀ 5 Euler's ...

- 1** The function is nonlinear in N_1 and N_2 , and the isopleths must be calculated iteratively using e.g. Newton–Raphson's method: $N_{2,k+1} = N_{2,k} - (G_k - G)/\mu_2$, where $\mu_2 = ax_1^2 + \ln x_2$ is the partial derivative of G with respect to N_2 .
- 2** A fixed value is selected for N_1 , and N_2 is iterated until $G_{k \rightarrow \infty}$ has converged to G , see the Matlab-program 1.4 in Appendix 30.
- 4** Note that each isopleth defines a *non-convex* region, which can be interpreted as a fundamental thermodynamic instability.

§ 032 Gibbs energy I (2)

◀ 5 Euler's ...

5 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:

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

7 This indicates that the phase equilibrium condition is fulfilled whenever two points on the same isopleth have common tangents (remember that G takes constant values along each isopleth such that the criterion is reduced to $\mu_1 = \mu_2$).

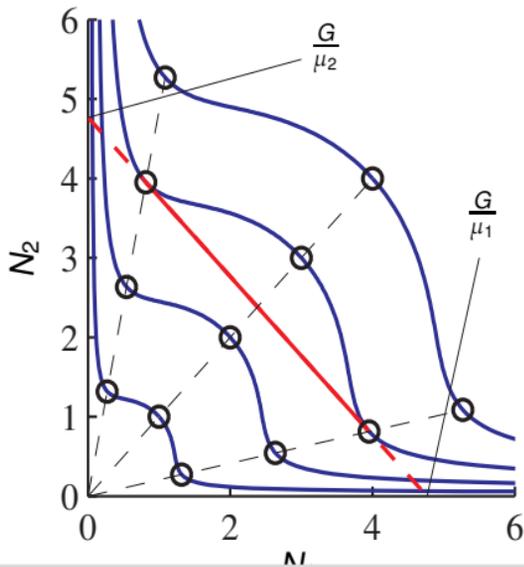


Figure 5.1: Contour diagram of Gibbs energy (solid lines). Equidistant values (open circles) are made visible along 3 rays (dotted lines) from the origin. The two-phase region is spanned by the two outermost rays. One of the isopleths indicates the phase equilibrium condition in the shape of a convex hull construction.

Homogeneity causes a whole range of remarkable results. One formula obtained by differentiating Eq. 5.5 is:

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

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 them.

§ 033 Homogeneity

◀ 5 Euler's ...

1 The left-hand side of Eq. 5.5 is differentiated and the right-hand side is replaced by the total differential of F :

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

2 For $k = 1$ the expression reduces to $X d(\partial F/\partial X)_{\xi} = (\partial F/\partial \xi)_X d\xi$. To proceed we need the differential of $\partial F/\partial X$, and because F is a function of X and ξ it can be written as the total differential

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

5 Substituted into the equation above (letting $k = 1$), this yields the intermediate result:

$$X \left(\frac{\partial^2 F}{\partial X \partial X}\right)_{\xi} dX + X \left(\frac{\partial^2 F}{\partial X \partial \xi}\right) d\xi = \left(\frac{\partial F}{\partial \xi}\right)_X d\xi . \quad (5.16)$$

§ 033 Homogeneity (2)

◀ 5 Euler's ...

7 This implies that two non-trivial relations follow from Eq. 5.16 (one equation in three variables gives two non-trivial relations), irrespective of the actual values of X , dX , ξ and $d\xi$:

$$\left(\frac{\partial^2 F}{\partial X \partial X}\right)_\xi = 0, \quad (5.17)$$

$$X \left(\frac{\partial^2 F}{\partial X \partial \xi}\right) = \left(\frac{\partial F}{\partial \xi}\right)_X \quad (5.18)$$

Parametric form

◀ 5 Euler's ...

- 1** From a physical point of view any extensive function $F(X, \xi)$ can be expressed in the form $F = \beta(\xi)X$.
- 2** This stems from the fact that $F(0, \xi) = 0$ in addition to $\partial^2 F / \partial X \partial X = 0$, see Eq. 5.17⁹ The derivative of F with respect to ξ is therefore an extensive function $\beta'(\xi)X$ where the second derivative of F with respect to both X and ξ is equal to the intensive parameter $\beta'(\xi)$. ■

⁹ It should be noted that it is the second derivative *function* which is zero. It is not sufficient to say that the second derivative is zero at a given point.

Extended notation II

◀ 5 Euler's ...

1 If $F(\mathbf{x}, \xi)$ is extensive in \mathbf{x} it can be shown that the differential in Paragraph 33 on page 194 takes the form:

$$\mathbf{x}^T d\left(\frac{\partial F}{\partial \mathbf{x}}\right)_\xi - \left(\frac{\partial F}{\partial \xi}\right)_\mathbf{x} d\xi = 0, \quad (5.19)$$

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

$$d\left(\frac{\partial F}{\partial \mathbf{x}}\right)_\xi = \left(\frac{\partial^2 F}{\partial \mathbf{x} \partial \mathbf{x}}\right) d\mathbf{x} + \left(\frac{\partial^2 F}{\partial \mathbf{x} \partial \xi}\right) d\xi. \quad (5.20)$$

3 The two quantities $d\mathbf{x}$ and $d\xi$ are independent, and by substituting the differential 5.20 into Eq. 5.19 it follows that:

$$\left(\frac{\partial^2 F}{\partial \mathbf{x} \partial \mathbf{x}}\right)_\xi \mathbf{x} = \mathbf{0}, \quad (5.21)$$

$$\left(\frac{\partial^2 F}{\partial \xi \partial \mathbf{x}}\right) \mathbf{x} = \left(\frac{\partial F}{\partial \xi}\right)_\mathbf{x}. \quad (5.22)$$

6 This is Euler's second theorem for homogeneous functions.

Substitute $U = U(S, V, N)$ into Paragraph 33 on page 194 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 $U(S, V, N)$?

§ 034 Gibbs–Duhem

◀ 5 Euler's ...

1 Substituting $F = U(\mathbf{x}, \xi)$ into Eq. 5.19 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 τ, π and μ in Paragraph 29 on page 182 we can write

$$S d\tau + V d\pi + N d\mu = 0, \quad (5.23)$$

3 Alternatively, if $F = G(\mathbf{x}, \xi)$ where $\mathbf{x} = N$ and $\xi^T = (\tau, \pi)$, then Eq. 5.19 takes the form:

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

4 The partial derivatives of G with respect to N, τ and π have been identified as $\mu, -S$ and $-V$ in Paragraph 31 on page 188.

5 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.

§ 034 Gibbs–Duhem (2)

◀ 5 Euler's ...

6 In fact, all Legendre transforms of U end up giving the same Gibbs–Duhem equation.

Comment

◀ 5 Euler's ...

1 We have not been asked for any extensions, but by analogy to Eqs. 5.8 and 5.15 the Gibbs–Duhem equation may be extended to a multicomponent form:

$$S d\tau + V d\pi + \sum_{i=1}^n N_i d\mu_i \hat{=} S d\tau + V d\pi + \mathbf{n}^T d\boldsymbol{\mu} = 0. \quad (5.24)$$

4 The homogeneity, which effectively removes one degree of freedom in the function expression, shows up as a mutual dependency in the n th derivatives (of U).

6 In single component systems this means that any arbitrary intensive variable can be expressed as a function of (at most) two other intensive variables, see also Paragraph 39 on page 214.

- 1** It is important to realise that the information contained in U is conserved during the Legendre transformation to H, A, \dots, O .
- 2** For example, knowing the Gibbs energy $G(\tau, \pi, N)$ really implies full knowledge of $U(S, V, N)$, and vice versa.
- 3** The Gibbs–Duhem equation can therefore be derived from any of the energy functions.
- 4** In particular this also applies to the differential of the null-potential $O(\tau, \pi, \mu)$ which is identical to Eq. 5.23, see Paragraph 26 on page 157.

Use the result from Paragraph 33 on page 194 to determine the second derivatives $(\partial^2 G / \partial N \partial N)_{\tau, \pi}$, $(\partial^2 Y / \partial S \partial S)_{\pi, \mu}$ and $(\partial^2 \Omega / \partial V \partial V)_{\tau, \mu}$, where $G = G(\tau, \pi, N)$ and $Y = Y(S, \pi, \mu)$ and $\Omega = \Omega(\tau, V, \mu)$.

§ 035 Linear potentials

◀ 5 Euler's ...

- 1** The three functions G , Y and Ω are extensive in N , S and V respectively, i.e. in one variable each.
- 2** This makes Eq. 5.17 valid and the substitution of the definitions for τ , π and μ yields:

$$\left(\frac{\partial^2 G}{\partial N \partial N}\right)_{\tau, \pi} = \left(\frac{\partial \mu}{\partial N}\right)_{\tau, \pi} = 0, \quad (5.25)$$

$$\left(\frac{\partial^2 Y}{\partial S \partial S}\right)_{\pi, \mu} = \left(\frac{\partial \tau}{\partial S}\right)_{\pi, \mu} = 0, \quad (5.26)$$

$$\left(\frac{\partial^2 \Omega}{\partial V \partial V}\right)_{\tau, \mu} = \left(\frac{\partial \pi}{\partial V}\right)_{\tau, \mu} = 0. \quad (5.27)$$

Show that the Hessian of $A = A(\tau, V, N)$ has only one *independent* element when the temperature τ is taken to be a constant parameter. Use Eq. 5.21 as your starting point.

Example

◀ 5 Euler's ...

- 1** Helmholtz energy is extensive in V, N at any given temperature τ .
- 2** Bearing in mind Eq. 5.21 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 relation:

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

- 3** The fact that the matrix, like all Hessians, must be symmetric, in this case leads to $(\partial \pi / \partial N)_{\tau, V} = (\partial \mu / \partial V)_{\tau, N}$.
- 4** Altogether there are 4 matrix elements, with 3 associated relations.

§ 036 Hessians

◀ 5 Euler's ...

1 The solution of the homogeneous (!) system of equations can be formulated in an infinite number of ways, one of which is:

$$\frac{N}{V} \left(\frac{\partial \mu}{\partial N} \right)_{\tau, V} \begin{pmatrix} \frac{N}{V} & -1 \\ -1 & \frac{V}{N} \end{pmatrix} \begin{pmatrix} V \\ N \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \quad (5.28)$$

2 Note that the second derivative of Helmholtz energy with respect to the mole number is non-zero in Eq. 5.28, while the corresponding second derivative of Gibbs energy is zero in Eq. 5.25:

$$\text{fra 5.25: } \left(\frac{\partial \mu}{\partial N} \right)_{\tau, \pi} = 0,$$

$$\text{og fra 5.28: } \left(\frac{\partial \mu}{\partial N} \right)_{\tau, V} \neq 0.$$

§ 037

◀ § 36

▶ § 38

◀ 5 Euler's ...

Find analytical expressions for $(\partial G/\partial \tau)_{\tau, N}$ and $(\partial G/\partial \pi)_{\tau, N}$ by using the Euler method to integrate the partial molar entropy and partial molar volume.

§ 037 Partial molarity

◀ 5 Euler's ...

1 Replace F by $G(\xi, \mathbf{n})$ in Eq. 5.22, where $\xi^T = (\tau, \pi)$ and $\mathbf{n}^T = (N_1, \dots, N_n)$. This gives, without much difficulty:

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

2 The partial derivatives of S and V on the right hand side are called the partial molar entropy and partial molar¹⁰ volume respectively.

4 A more compact notation is therefore $S = \mathbf{n}^T \bar{\mathbf{s}}$ and $V = \mathbf{n}^T \bar{\mathbf{v}}$.

¹⁰ A partial molar quantity is defined as $\bar{f} = (\partial F / \partial n)_{\tau, \pi}$, irrespective of whether or not F has $\tau, \pi, N_1, \dots, N_n$ as canonical variables (it is only for Gibbs energy that there is a correspondence between the two sets of variables).

Show that $G(S, V, N)$ is really an extensive function of the variables S , V and N , thus verifying the conjecture set out in the introduction to this chapter (on page 190).

§ 038 Proof

◀ 5 Euler's ...

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

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

2 We already know that τ and π are intensive variables, whereas U , S and V are extensive variables.

§ 038 Proof (2)

◀ 5 Euler's ...

3 From this it follows that

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

which clearly demonstrates that G is homogeneous, in accordance with the conjecture. ■

Starting from Paragraph 35 on page 204, can you tell how many thermodynamic variables are needed to determine the intensive state of a system?

§ 039 The state concept

◀ 5 Euler's ...

- 1** A thermodynamic system is normally described by $n + 2$ independent state variables.
- 2** However, the intensive state can be determined once $n + 1$ (intensive) variables are known.
- 4** In fact, the (single) extensive variable determines the system size but has no influence on τ, π and μ .
- 5** For a single-component system we can describe the intensive state in three different ways:

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

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

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

Part 7

Equations of state

[← see also Part-Contents](#)

Contents

1 Ideal gas law

- 1 Helmholtz potential
- 2 Gibbs potential
- 3 Grand canonical potential

2 Molecules

- 1 Translation
- 2 Vibration
- 3 Rotation
- 4 Other intra-molecular degrees of freedom

3 Photons

4 Phonons

5 Free electrons

Contents (2)

6 Virial

7 Van der Waals

8 Murnaghan

State description

[◀ 7 Equations ...](#)

- 1** Although thermodynamics builds on some basic, fundamental principles of physical science, which form part of a well-defined mathematical theory, it is essentially an empirical science.
- 3** That is how it was in the past, and that is how it will continue to be in the future, because with the exception of a handful of simplifications used in statistical mechanics¹ there are no precise models, and there will always be the need for essentially physical models with *adjustable* parameters.
- 6** In this chapter we learn about a variety of useful concepts, such as ideal gases, virial development, the Einstein–Debye phonon model and van der Waals theory, but first of all we need to define the concept of an equation of state.

State description (2)

◀ 7 Equations ...

7 Let us start with any canonical differential, e.g. of internal energy

$$dU = T dS - p dV + \sum_{i=1}^n \mu_i dN_i, \quad (7.1)$$

defined using the canonical variables S, V, N_i .

8 If we know the fundamental *state functions* referred to as the equations of state of the system

$$T = T(S, V, \mathbf{n}), \quad (7.2)$$

$$p = p(S, V, \mathbf{n}), \quad (7.3)$$

$$\mu_i = \mu_i(S, V, \mathbf{n}), \quad (7.4)$$

then Eq. 7.1 can be integrated using Euler's 1st theorem to give $U = TS - pV + \sum_{i=1}^n \mu_i N_i$, as shown in Paragraph 30 in Chapter 5. However,

State description (3)

[◀ 7 Equations ...](#)

in practice this doesn't work, because the relationships defined by 7.2–7.4 only exist as implicit functions².

9 It is therefore more normal to start with

$$(dG)_{T,p} = \sum_{i=1}^n \mu_i dN_i \quad (7.5)$$

or alternatively

$$(dA)_T = -pdV + \sum_{i=1}^n \mu_i dN_i, \quad (7.6)$$

but it is still difficult to accurately describe the chemical potential of the compounds in a multi-component mixture.

11 The exceptions to this are ideal (gas) mixtures for which we can obtain exact solutions using statistical mechanics.

State description (4)

[◀ 7 Equations ...](#)

17 The alternative to the above approach is to derive the thermodynamic functions in non-canonical coordinates:

$U(T, V, n)$ rather than $U(S, V, n)$

$H(T, V, n)$ rather than $H(S, p, n)$

⋮

$S(T, p, n)$ rather than $S(H, p, n)$

This is particularly useful if you only need to obtain U , H or S , but not A or G .

¹ Above all crystalline phases, ideal gases and dilute electrolytes.

² Only very rarely can entropy be written as an explicit (independent) variable in the state functions.

Ideell (perfect) gas

[◀ 7 Equations ...](#)

1. An ideal gas consists of individual particles (atoms, molecules or radicals) that move freely and independently in space, without any kind of interaction.
5. In spite of this massive simplification, the total energy of the gas is not equal to zero, as the particles have their kinetic energy (translation), moment of inertia (rotation), internal degrees of freedom (vibration, internal rotation, torsion, electronic excitation) and chemical binding energy.
7. Ideal gases are only valid as a special case of the true thermodynamic state when pressure approaches zero, and can never be measured directly in a real (physical) system.

The ideal gas law

◀ 7 Equations ...

1 It is not a new idea that the world is composed of more or less distinct material points, but the experiments that underpin the ideal gas law as we know it today are more recent:

Name	Observation	Year
Boyle	$(PV)_{T,N} = c_1$	1662
Charles	$(V/T)_{p,N} = c_2$	1787
Gay-Lussac	$(P/T)_{V,N} = c_4$	1809
Avogadro	$(V/N)_{T,p} = c_5$	1811

3 It was only in 1834 that Émile Clapeyron successfully formulated the ideal gas law in the simple form:

$$p^{ig} = \frac{NRT}{V} . \quad (7.7)$$

The ideal gas law (2)

[◀ 7 Equations ...](#)

5 We can see that the unit of the product $p \cdot V$ is the same as for A , which means that there may be a deeper relationship between pressure–volume and the energy functions.

vmode (bug):

Gibbs–Duhem I

◀ 7 Equations ...

1 The quickest way to obtain a useful result is to apply the Gibbs–Duhem Eq. 5.23 described in Chapter 5. For a thermodynamic system with only one chemical component, the following applies:

$$s d\tau + v d\pi + d\mu = 0.$$

2 This differential has no general solution, as s and v are quite arbitrary functions of the material state, but for a change of state that is assumed to be *isothermal*, then $d\tau = 0$ and $v^{\text{ig}} \hat{=} V/N = RT/p \hat{=} -RT/\pi$, giving us

$$(d\mu^{\text{ig}})_T = \frac{RT}{\pi} d\pi,$$

or:

$$\mu^{\text{ig}}(T, p) - \mu^\circ(T) = RT \int_{p^\circ}^p \frac{d\pi}{\pi} = RT \ln\left(\frac{p}{p^\circ}\right).$$

Gibbs–Duhem I (2)

◀ 7 Equations ...

Euler's homogeneous function theorem

◀ 7 Equations ...

1 The Helmholtz energy of a single-component system can therefore be written as the integral $A = -pV + \mu N$.

5 From Chapter 4 on Legendre transforms we know the general equations $S = -(\partial A / \partial T)_{V,N}$ and $U = A + TS$, which means that it also follows that:

$$U^{\text{ig}} = N \left[\mu_{\circ} - T \left(\frac{\partial \mu_{\circ}}{\partial T} \right) \right] - NRT = Nh_{\circ} - NRT.$$

6 In other words, the internal energy of the gas depends on the system's size N and temperature T through the constant of integration³ called μ_{\circ} .

³ The *internal* energy U^{ig} is inevitably independent of both pressure and volume: ideal gases are a collection of free material points without any form of interaction. It is only the *internal* degrees of freedom of the particles that contribute to their energy, and these are also what determine the integration constant μ_{\circ} .

Gibbs–Duhem II

[◀ 7 Equations ...](#)

1 Our next challenge is to generalise this result into one that is similarly valid for a multi-component system. In order to do that, we must write the ideal gas law in its extended form

$$p^{\text{ig}} = \sum_i \frac{N_i RT}{V} \quad (7.8)$$

so that we can identify the components that constitute the mixture.

5 The Gibbs–Duhem equation from Chapter 5 follows directly from the fact that U is a homogeneous function to which Euler's theorem applies when expressed using the variables S , V and \mathbf{n} .

Gibbs–Duhem II (2)

◀ 7 Equations ...

7 Let us substitute for $\pi \hat{=} -p^{\text{ig}}$ while keeping $\tau \hat{=} T$ constant as shown below:

$$-V \sum_i \frac{N_i RT}{-V^2} dV - V \sum_i \frac{RT}{V} dN_i + \sum_i N_i (d\mu_i)_T^{\text{ig}} = 0,$$

$$\text{or } \sum_i \left(RT \frac{dV}{V} - RT \frac{dN_i}{N_i} + (d\mu_i)_T \right) = 0.$$

8 The simplest solution for an expression with a sum equal to zero is to assume that each individual term is equal to zero:

$$\frac{(d\mu_i)_T^{\text{ig}}}{RT} = -\frac{dV}{V} + \frac{dN_i}{N_i}; \quad \forall i \in [1, n].$$

Gibbs–Duhem II (3)

[◀ 7 Equations ...](#)

13 Integrating the differential gives us

$$\frac{1}{RT} (\mu_i^{\text{ig}}(T, V, \mathbf{n}) - \mu_i^\circ(T)) = -\ln \frac{V}{V^\circ} + \ln \frac{N_i}{N_i^\circ} .$$

Note that the constant of integration μ_i° , which will hereafter be called the *standard state* of component i , is a function of temperature.

Standard potential

[◀ 7 Equations ...](#)

1 The normal convention is to assume a pure-component standard state where $V_o/N_i^o = RT/p_o$ and where $p_o = 1$ bar, or, in older reference works, where $p_o = 1$ atm.

3 Bearing in mind this fundamental understanding of what μ_i^o means, the chemical potential of the component can be expressed as

$$\mu_i^{\text{ig}}(T, V, \mathbf{n}) = \mu_i^o(T, p_o) + RT \ln\left(\frac{N_i RT}{p_o V}\right). \quad (7.9)$$

Here we should particularly note that $(d\mu_i^{\text{ig}})_{T,V,\mathbf{n}} = 0$ must be true for all values of p_o .

Standard potential (2)

[◀ 7 Equations ...](#)

10 Essentially, standard states are presented in three different ways in the literature:

$$\mu_i^\circ(T, p_o) = \mu_i^\circ(T, p_o) \quad (7.10)$$

$$\mu_i^\circ(T, p_o) = \Delta_f h_i^\circ(T) - Ts_i^\circ(T, p_o) \quad (7.11)$$

$$\mu_i^\circ(T, p_o) = \Delta_f h_i^\circ(T_o) + (h_i^\circ(T) - h_i^\circ(T_o)) - Ts_i^\circ(T, p_o). \quad (7.12)$$

11 These equations follow from the definition $G \hat{=} U + pV - TS \hat{=} H - TS$ from Chapter 4 applied to the standard state as defined in the above paragraph.

Standard potential (3)

◀ 7 Equations ...

14 All of the formation properties (enthalpy, volume, entropy, etc.) of any given compound $A_a B_b \dots Z_z$ in an ideal gas state are defined analogously by

$$\Delta_f h_{A_a B_b \dots Z_z}^\circ \hat{=} h_{A_a B_b \dots Z_z}^{\text{ig}} - ah_A^\alpha - bh_B^\beta - \dots - zh_Z^\zeta,$$

where α , β and ζ indicate the phases (configurations) of the various elements.

17 For example, hydrogen bromide would have the formula $(\text{H}_2)_{0.5}(\text{Br}_2)_{0.5}$, giving the enthalpy of formation

$$\Delta_f h_{\text{HBr}}^\circ = h_{\text{HBr}}^{\text{ig}} - 0.5h_{\text{H}_2}^{\text{ig}} - 0.5h_{\text{Br}_2}^{\text{liq}}.$$

at $T_o = 298.15 \text{ K}$ and $p_o = 1 \text{ bar}$.

Standard potential (4)

◀ 7 Equations ...

19 Hence, in the above equation $h_{\text{H}_2}^{\text{lg}} = h_{\text{Br}_2}^{\text{liq}} = 0$ and the enthalpy of formation $\Delta_f h_{\text{HBr}}^\circ \equiv h_{\text{HBr}}^{\text{lg}}$ is given relative to this arbitrary reference.

22 There are therefore many ways of reporting the standard state, but for all of them it is true that

$$h_i^\circ(T) - h_i^\circ(T_o) = \int_{T_o}^T c_{p,i}^\circ(T) dT, \quad (7.13)$$

$$s_i^\circ(T) - s_i^\circ(T_o) = \int_{T_o}^T c_{p,i}^\circ(T) d \ln T. \quad (7.14)$$

23 One of these equations (it doesn't matter which) can be viewed as a definition of c_p° , while the other one follows from the total differential $dh = T ds + v dp + \sum \mu_i dN_i$, which for constant pressure and composition gives us $(dh)_{p,n} = T ds$.

The superposition principle

◀ 7 Equations ...

1 In practice, all thermodynamic reference works are based on a large number of carefully recorded measurements supported by one or more theoretical calculations, which together produce figures for $\Delta_f h_i^\circ(T_o)$, $s_i^\circ(T_o, p_o)$ and $c_{p,i}^\circ(T)$.

3 The enthalpy of formation is generally measured using calorimetry, whereas the heat capacity of an ideal gas component essentially adheres to the superposition principle ⁴

$$c_{p,i}^\circ = c_{v,i}^{\text{trans}} + c_{v,i}^{\text{rot}} + c_{v,i}^{\text{vib}} + c_{v,i}^{\text{elec}} + R$$

and can be calculated from spectrometric measurements.

⁴ The gas constant R in the above equation is a result of the definition of $H \triangleq U + pV$, which for an ideal gas gives us $H^{\text{ig}} \triangleq U^{\text{ig}} + (pV)^{\text{ig}} = U^{\text{ig}} + NRT$. If we then differentiate with respect to temperature we get $c_{p,i}^\circ = c_{v,i}^\circ + R$.

Euler integration

[← 7 Equations ...](#)

1 It is easy to lose one's way in the details of these calculations. It is therefore worth reiterating that using Euler's theorem to integrate equations 7.8 and 7.9 always works, and that the Helmholtz energy of the gas can be expressed in the following general form:

$$\begin{aligned}
 A^{\text{ig}}(T, V, \mathbf{n}) &= \pi^{\text{ig}} V + \sum_i N_i \mu_i^{\text{ig}} \\
 &= - \sum_i N_i RT + \underbrace{\sum_i N_i \mu_i^\circ(T, p_o)}_{G^\circ(T, p_o)} + \sum_i N_i RT \ln \left(\frac{N_i RT}{p_o V} \right) .
 \end{aligned}$$

2 Note that, in this expression, the standard state term is a conventional Gibbs energy function, because T and p_o have been selected as the state variables of μ_i° , rather than T and V_o . ■

Note 7.10

◀ 7 Equations ...

1 In summary, the following equations apply to ideal gas mixtures:

$$A^{\text{ig}}(T, V, \mathbf{n}) = \sum_i N_i \mu_i^{\circ}(T, p_{\circ}) + \sum_i N_i RT \left[\ln \left(\frac{N_i RT}{p_{\circ} V} \right) - 1 \right] \quad (7.15)$$

$$-S^{\text{ig}}(T, V, \mathbf{n}) = \sum_i N_i s_i^{\circ}(T, p_{\circ}) + \sum_i N_i R \ln \left(\frac{N_i RT}{p_{\circ} V} \right) \quad (7.16)$$

$$U^{\text{ig}}(T, \mathbf{n}) = H^{\text{ig}}(T, \mathbf{n}) - NRT \quad (7.17)$$

$$H^{\text{ig}}(T, \mathbf{n}) = \sum_i N_i h_i^{\circ}(T). \quad (7.18)$$

$\mu(T, p, \mathbf{n})$

◀ 7 Equations ...

1 In our case, it is possible to calculate Gibbs energy by using the Euler method to integrate the chemical potential in Eq. 7.9, and substituting in the ideal gas law from Eq. 7.7

$$\mu_i^{\text{ig}}(T, p, \mathbf{n}) = \mu_i^\circ(T, p_\circ) + RT \ln\left(\frac{N_i p}{N p_\circ}\right), \quad (7.19)$$

which gives us:

$$G^{\text{ig}}(T, p, \mathbf{n}) = \sum_{i=1}^n \mu_i^{\text{ig}} N_i = \sum_{i=1}^n \mu_i^\circ N_i + RT \sum_{i=1}^n N_i \ln\left(\frac{N_i}{N}\right) + NRT \ln\left(\frac{p}{p_\circ}\right). \quad (7.20)$$

3 Alternatively, we can calculate the Gibbs energy as a Legendre transform of Helmholtz energy (or vice-versa).

7 This significantly complicates the practical application of Legendre transforms.

$n(T, V, \mu)$

◀ 7 Equations ...

1 An alternative way of expressing Eq. 7.19 is:

$$N_i^{\text{ig}}(T, V, \mu) = \frac{p_o V}{RT} \exp\left(\frac{\mu_i - \mu_i^o}{RT}\right). \quad (7.21)$$

5 Substituted into the ideal gas law, Eq. 7.21 gives us an adequate equation of state for the grand potential $\Omega(T, V, \mu)$:

$$p^{\text{ig}}(T, \mu) = \frac{RT}{V} \sum_{i=1}^n N_i^{\text{ig}} = p_o \sum_{i=1}^n \exp\left(\frac{\mu_i - \mu_i^o}{RT}\right). \quad (7.22)$$

6 The total differential of Ω for a one-component system was derived in Chapter 4, see Paragraph 24 on page 136.

7 For an n -component system, we can state that

$$(d\Omega)_{T, \mu} = -p dV. \quad (7.23)$$

n(T, V, μ) (2)

◀ 7 Equations ...

8 The differential $(d\Omega)_{T,\mu}$ can be integrated directly, as long as the function of state $p(T, V, \mu)$ is expressed explicitly. Eq. 7.22 is explicit, and if we integrate using Euler's method at a given T and μ we obtain

$$\Omega^{\text{ig}}(T, V, \mu) = -p^{\text{ig}}V = -p_o V \sum_{i=1}^n \exp\left(\frac{\mu_i - \mu_i^o}{RT}\right). \quad (7.24)$$

9 It may at first sight appear that p_o is a free variable in the above equations, but if we change p_o , then $\mu_i^o(T, p_o)$ varies accordingly, always keeping the value of Ω^{ig} unchanged (show this).

11 The intensive state is evidently given when $n + 1$ intensive variables have been determined, while the extensive state requires $n + 2$ variables.

12 This is a general result, which is not limited to ideal gases⁵.

⁵ In contrast to e.g. $U^{\text{ig}} = U(T, \mathbf{n})$, which only applies to ideal gases.

§ 040

◀ § 39

▶ § 41

◀ 7 Equations ...

Derive the partial derivatives of $\Omega^{\text{ig}}(T, V, \mu_j)$ with respect to T , V and μ_j . Show that the results can be interpreted as $-S^{\text{ig}}$, $-p^{\text{ig}}$ and $-N_j^{\text{ig}}$, without discussing the properties of the Legendre transform.

§ 040 Grand canonical potential

◀ 7 Equations ...

1 Instead of differentiating $p^{\text{ig}}V$ in Eq. 7.24 we will use the fact that $-\Omega^{\text{ig}} = p^{\text{ig}}V = \sum_i N_i^{\text{ig}}RT = N^{\text{ig}}RT$. If we differentiate $N_i^{\text{ig}}(T, V, \mu)$ in Eq. 7.21 we get:

$$\left(\frac{\partial N_i^{\text{ig}}}{\partial T}\right)_{V, \mu} = N_i^{\text{ig}} \frac{RTs_i^\circ - R(\mu_i - \mu_i^\circ)}{(RT)^2} - \frac{N_i^{\text{ig}}}{T} = \frac{N_i^{\text{ig}}}{RT} (\bar{s}_i^{\text{ig}} - R),$$

$$\left(\frac{\partial N_i^{\text{ig}}}{\partial V}\right)_{T, \mu} = \frac{N_i^{\text{ig}}}{V},$$

$$\left(\frac{\partial N_i^{\text{ig}}}{\partial \mu_j}\right)_{T, V, \mu_{k \neq j}} = \frac{\delta_{ij} N_i^{\text{ig}}}{RT}.$$

3 Here we have made use of the relationship $-s_i^\circ = -(\partial \mu_i^\circ / \partial T)_{p, n}$, which also means that $-s_i^\circ = -(\partial \mu_i^\circ / \partial T)_{V, \mu}$.

§ 040 Grand canonical potential (2)

◀ 7 Equations ...

5 Apart from this fundamental observation, the simplification of $RTs_i^\circ - R(\mu_i - \mu_i^\circ)$ in the first partial differential equation relies on an understanding of certain principles of thermodynamics.

6 In the general case, $\mu_i = \bar{h}_i - T\bar{s}_i$. In the special case of ideal gases, $\bar{h}_i^{\text{ig}} = \bar{h}_i^\circ$, and hence $Ts_i^\circ - (\mu_i - \mu_i^\circ) = T\bar{s}_i^{\text{ig}}$.

7 We are now ready to derive the partial differentials of Ω^{ig}

$$\left(\frac{\partial \Omega^{\text{ig}}}{\partial T}\right)_{V,\mu} = -RT \sum_{i=1}^n \left(\frac{\partial N_i^{\text{ig}}}{\partial T}\right)_{V,\mu} - NR = -\sum_{i=1}^n N_i(\bar{s}_i^{\text{ig}} - R) - NR = -S^{\text{ig}},$$

$$\left(\frac{\partial \Omega^{\text{ig}}}{\partial V}\right)_{T,\mu} = -RT \sum_{i=1}^n \left(\frac{\partial N_i^{\text{ig}}}{\partial V}\right)_{T,\mu} = -RT \sum_{i=1}^n \frac{N_i}{V} = -p^{\text{ig}},$$

$$\left(\frac{\partial \Omega^{\text{ig}}}{\partial \mu_j}\right)_{T,V,\mu_{k \neq j}} = -RT \sum_{i=1}^n \left(\frac{\partial N_i^{\text{ig}}}{\partial \mu_j}\right)_{T,V,\mu_{k \neq j}} = -\sum_{i=1}^n N_i^{\text{ig}} \delta_{ij} = -N_j^{\text{ig}}$$

Molecular contributions

[◀ 7 Equations ...](#)

1 Without further introduction, let us assume that the relationship between the particles' microstates and Helmholtz energy is

$$\frac{A}{NRT} = -\ln Q,$$

where Q is the total partition function of the system⁶⁷.

7 The molecular partition function q approximates to the product of $q \approx q^{\text{trans}} q^{\text{vib}} q^{\text{rot}} \dots$ over the (assumed) number of independent terms.

8 In principle, this is all we need to know about the gas, but in order to calculate the necessary properties, we must first know the quantum mechanical description of each individual input to the model.

⁶ D. F. Lawden. *Principles of Thermodynamics and Statistical Mechanics*. John Wiley & Sons, 1987.

⁷ Robert P. H. Gasser and W. Graham Richards. *An Introduction to Statistical Thermodynamics*. World Scientific Publishing Co. Pte. Ltd., 2nd edition, 1995.

Free translation

[◀ 7 Equations ...](#)

- 1** A particle-in-a-box has three identical degrees of translational freedom.
- 3** In a cubic box, each direction will have its own quantum number j_x , j_y and j_z , which is given the same unit of energy $\varepsilon = h^2/8ml^2$.
- 4** The associated partition function⁸ can be written

$$q^{\text{trans}} = \sum_{j_x=1}^{\infty} \sum_{j_y=1}^{\infty} \sum_{j_z=1}^{\infty} \exp\left(\frac{-(j_x^2 + j_y^2 + j_z^2)\varepsilon}{kT}\right).$$

- 5** For high quantum numbers $j^2 = j_x^2 + j_y^2 + j_z^2 \gg 0$ is a virtually continuous function over (an eighth of) the surface of a sphere with a radius of j .

Free translation (2)

◀ 7 Equations ...

6 The surface area of the octant of the sphere is $\pi j^2/2$, which leads us to the integral

$$\begin{aligned}
 \lim_{kT \gg \varepsilon} q^{\text{trans}} &= \frac{\pi}{2} \int_0^{\infty} j^2 \exp\left(\frac{-j^2 \varepsilon}{kT}\right) dj \\
 &= \frac{\pi}{2} \left(\frac{kT}{\varepsilon}\right)^{3/2} \underbrace{\int_0^{\infty} x^2 e^{-x^2} dx}_{\sqrt{\pi}/4}, \quad x^2 \triangleq \frac{j^2 \varepsilon}{kT}, \\
 &\rightarrow \frac{(2\pi mkT)^{3/2} V}{h^3}.
 \end{aligned}$$

Free translation (3)

[◀ 7 Equations ...](#)

7 When going from summation to integration, it has been assumed that $kT \gg \varepsilon_x$. Combining this with $j^2 \gg 0$ gives us $j^2 \varepsilon / kT < 1$ over much of the area of integration, which ensures that the integral is a good approximation of the sum.

⁸ Per Chr. Hemmer. *Statistisk mekanikk*. Tapir Forlag, 1970. In Norwegian.

§ 041

◀ § 40

▶ § 42

◀ 7 Equations ...

Calculate the typical translational temperature $\varepsilon/k = h^2/8m l^2 k$ for the light gases hydrogen, helium and neon. Assume that the lengths of the sides of the box are ≥ 1 nm. Comment on the answer.

§ 041 Particle-in-a-box

[◀ 7 Equations ...](#)

1 The table below gives the values for ε/k and the standard boilingpoint of these three low-boiling-point compounds.

	$\frac{M_w}{\text{g/mol}}$	$\frac{\varepsilon/k}{\text{K}}$	$\frac{T_b}{\text{K}}$
H ₂	2.0159	1.19	20.39
He	4.0026	0.60	4.224
Ne	20.179	0.12	27.09

2 The length of the sides of the box is $l = 1$ nm (which is right at the limit of the range of validity of classical thermodynamics).

3 Except in the case of He, ε/k is reassuringly far below the boiling point of the compounds, and in practice all gases have a virtually continuous spectrum of translational energies⁹.

⁹ Note that $\varepsilon \propto l^{-2}$. If the length of the box is changed to e.g. 10 nm, then ε/k will be reduced by a factor of 100. This means that even He behaves in the classical manner

Sackur–Tetrode S

◀ 7 Equations ...

1 For an ensemble of n particles-in-a-box without fixed locations, the total partition function becomes $Q^{\text{trans}} = \frac{1}{n!} (q^{\text{trans}})^n$.

2 This results in a function for communal entropy that only depends on the system's volume and the mass and number of particles, while the geometry and bonds are irrelevant:

$$Q^{\text{trans}} = \frac{(q^{\text{trans}})^n}{n!} \xrightarrow{n \rightarrow \infty} \frac{e^n (q^{\text{trans}})^n}{n^n} \xrightarrow{\epsilon \ll kT} \left(\frac{e}{n}\right)^n \left[\frac{V(2\pi mkT)^{3/2}}{h^3}\right]^n .$$

3 Let us substitute in $n = N_A N$, $m = N_A^{-1} M_w$, $k = N_A^{-1} R$ and $\ln e = 1$.

Sackur–Tetrode S (2)

[◀ 7 Equations ...](#)

4 Differentiating gives us a set of canonical equations of state for Helmholtz energy:

$$\frac{p^{\text{trans}} V}{NRT} = 1 ,$$
$$\frac{\mu^{\text{trans}}}{RT} = 1 - \ln \left[\frac{V(2\pi M_w RT)^{3/2}}{NN_A^4 h^3} \right] .$$

... which is also known as the Sackur¹⁰–Tetrode¹¹ equation.

¹⁰ O. Sackur. *Ann. Physik*, 36:398, 1911.

¹¹ H. Tetrode. *Ann. Physik*, 38:434, 1912. Correction in 39 (1912) 255.

§ 042

◀ § 41

▶ § 43

◀ 7 Equations ...

Use the Sackur–Tetrode equation to estimate $s_{298.15\text{ K}, 1\text{ bar}}^{\circ}$ for all of the noble gases. Compare your answer with experimental values.

§ 042 Sackur–Tetrode

[◀ 7 Equations ...](#)

- 1** A convincing comparison of measured and calculated values is shown in Table 7.1.
- 2** These calculations are more precise than experimental results, but the theory cannot be tested on multi-atomic molecules, because the internal degrees of freedom of the molecules also contribute energy.

Figure 7.1: Comparison of experimental standard entropies with the Sackur-Tetrode equation (the margin of error for R , N_A , h and M_w is less than 0.01 cal/mol K).

	$\frac{M_w}{\text{g/mol}}$	$\frac{s}{\text{cal/K mol}}^{122}$	$\frac{s^{\text{trans}}}{\text{cal/K mol}}$		$\frac{M_w}{\text{g/mol}}$	$\frac{s}{\text{cal/K mol}}^{132}$	$\frac{s^{\text{trans}}}{\text{cal/K mol}}$
He	4.0026	-	30.11	Kr	83.80	39.17 ± 0.1	39.18
Ne	20.179	35.01 ± 0.1	34.93	Xe	131.29	40.70 ± 0.3	40.52
Ar	39.948	36.95 ± 0.2	36.97	Rn	222.0	-	42.08

¹⁴² Gilbert Newton Lewis and Merle Randall. *Thermodynamics*. McGraw-Hill Book Company, Inc., 2nd edition, 1961.

Free vibration

◀ 7 Equations ...

1 The atoms in a molecule are held together by forces which, when subjected to small perturbations, allow the atoms to vibrate as if their centres of were connected by elastic springs.

2 The partition function for a *harmonic oscillator* of this kind, with a characteristic frequency ν , quantum number j and energy factor $\varepsilon = h\nu = h\omega/2\pi \hat{=} \hbar\omega$, is

$$q^{\text{vib}} = \sum_{j=0}^{\infty} \exp\left[-\frac{(j+\frac{1}{2})\varepsilon}{kT}\right] = \exp\left(\frac{-\varepsilon}{2kT}\right) \sum_{j=0}^{\infty} \exp\left(\frac{-j\varepsilon}{kT}\right).$$

3 The summation can be written as a geometric series $q^{\text{vib}} = \sqrt{u} \sum_{j=0}^{\infty} u^j = \sqrt{u}/(1-u)$ where $u \hat{=} e^{-x} \hat{=} \exp(-\varepsilon/kT)$.

Free vibration (2)

◀ 7 Equations ...

4 If we divide the numerator and denominator by $\sqrt{e^{-x}}$, we get

$$q^{\text{vib}} = \frac{\sqrt{u}}{1-u} \rightarrow \frac{\sqrt{e^{-x}}}{1-e^{-x}} = \frac{1}{\sqrt{e^x} - \sqrt{e^{-x}}}.$$

5 We can obtain a canonical equation of state if we substitute $2 \sinh(x/2) = \sqrt{e^x} - \sqrt{e^{-x}}$.

6 When inserted into $x = \varepsilon/kT$ this produces

$$\frac{\mu^{\text{vib}}}{RT} = -\ln q^{\text{vib}} = \ln \left[2 \sinh \left(\frac{h\nu}{2kT} \right) \right].$$

7 Differentiating twice with respect to temperature gives us

$$\frac{c_v^{\text{vib}}}{R} = \frac{\left(\frac{h\nu}{2kT} \right)^2}{\sinh^2 \left(\frac{h\nu}{2kT} \right)}. \quad (7.25)$$

§ 043

◀ § 42

▶ § 44

◀ 7 Equations ...

The heat capacity of a harmonic oscillator has an upper temperature limit of $\lim_{T \rightarrow \infty} c_V^{\text{vib}} = R$. Show this.

§ 043 Harmonic oscillator

[◀ 7 Equations ...](#)

1 The power series expansion of $\sinh(x) = x + \frac{1}{3!}x^3 + O(x^5)$ applied to $kT \gg h\nu$ gives:

$$\lim_{kT \gg h\nu} \frac{c_v^{\text{vib}}}{R} = \lim_{x \ll 1} \frac{x^2}{\left(x + \frac{1}{3!}x^3 + \dots\right)^2} = 1.$$

2 A harmonic oscillator has two equally important energy contributions (kinetic and potential energy), which gives us $c_v \rightarrow R/2 + R/2 = R$ as the upper temperature limit.

3 In a multi-atomic molecule with many vibration frequencies, the contributions of each individual oscillator must be summed (linearly) in accordance with the equipartition principle.

Einstein C_P

◀ 7 Equations ...

- 1** The table below shows the characteristic vibrational temperatures $\varepsilon/k = h\nu/k = hc/\lambda k$ for a few di- and multi-atomic molecules.
- 2** Unlike the contributions from translation and rotation, the vibrational state is only fully developed at high temperatures:

	$g_{1,2,3,\dots}$	$\frac{\lambda_{1,2,3,\dots}^{-1}}{\text{cm}^{-1}}$	$\frac{\varepsilon/2k}{\text{K}}$
H ₂	1	4162	ca. 3000
CH ₄	3, 2, 1, 1	1306, 1534, 2916, 3019	900–2200
HCl	1	2885	ca. 2100
H ₂ O	1, 1, 1	1595, 3657, 3756	1100–2700

Einstein C_P (2)

[◀ 7 Equations ...](#)

3 One of the striking features of the oscillator equations is that the ground state (with the quantum number $j = 0$) makes a positive contribution to the total energy.

4 If we ignore the ground state, the partition function simplifies to

$$q^{\text{Einstein}} \rightarrow \frac{1}{1 - \exp\left(\frac{-\epsilon}{kT}\right)} = \frac{1}{1 - e^{-x}} .$$

5 The heat capacity can then be expressed as Einstein's¹⁵ equation:

$$C_V^{\text{Einstein}} = \frac{x^2 e^x}{(e^x - 1)^2} . \quad (7.26)$$

Einstein C_P (3)

[◀ 7 Equations ...](#)

6 Our intuition tells us that the Eqs. 7.25 and 7.26 are equivalent, because the ground state only makes a constant (temperature-independent) energy contribution. The explanation for this is by no means obvious at first glance, but if we compare the equations, we can see that it is the case (show this).

¹⁵ Albert Einstein, 1879–1955. German physicist.

Free rotation

[◀ 7 Equations ...](#)

- 1** A rotating system with a fixed distribution of mass is called a rigid rotor. The moment of inertia of the rotor determines how much kinetic energy it stores at any given frequency.
- 2** In quantum mechanics, the moment of inertia of isolated atoms is zero, whereas diatomic (linear) molecules have degenerate moments of inertia about two of their axes of rotation and a zero moment of inertia about the third axis.
- 3** In multi-atomic (non-linear) molecules, the moments of inertia about each axis of rotation are different, unless the symmetry of the molecule dictates otherwise.

Free rotation (2)

[◀ 7 Equations ...](#)

4 The partition function for a linear molecule with a moment of inertia I , quantum number j and energy factor $\varepsilon = \hbar^2/2I \hat{=} h^2/8\pi^2I$ can be expressed

$$q^{\text{rot},2\text{D}} = \frac{1}{\sigma} \sum_{j=0}^{\infty} (2j+1) \exp\left[-\frac{j(j+1)\varepsilon}{kT}\right],$$

where σ corrects for any rotational symmetry of the molecule ($\sigma_{\text{H}_2\text{O}} = 2$, $\sigma_{\text{NH}_3} = 3$, $\sigma_{\text{CH}_4} = 12$).

5 There is no analytical limit to the above summation, but expanding the power series¹⁶ gives us $q^{\text{rot}} = \frac{kT}{\varepsilon} \left(1 + \frac{\varepsilon}{3kT} + \frac{1}{15}\left(\frac{\varepsilon}{kT}\right)^2 + \frac{4}{315}\left(\frac{\varepsilon}{kT}\right)^3 + \dots\right)$ provided that $0.3kT > \varepsilon$.

Free rotation (3)

◀ 7 Equations ...

7 The rotational behaviour of multi-atomic (non-linear) molecules is more complex than that of linear molecules, and we will therefore simply state the partition function without further explanation¹⁷:

$$\lim_{kT \gg \epsilon} q^{\text{rot},3\text{D}} = \frac{(8\pi^2 kT)^{3/2}}{\sigma h^3} .$$

$$\mathbf{M} = \sum_i M_i (\mathbf{y}_i^T \mathbf{y}_i \mathbf{I} - \mathbf{y}_i \mathbf{y}_i^T) \sim \mathbf{Q} \Lambda \mathbf{Q}^T .$$

8 Here $\mathbf{y}_i = \mathbf{x}_i - \widehat{\mathbf{x}}$ represents the molecular coordinates of each of the atoms i measured in relation to the molecule's centre of mass $\widehat{\mathbf{x}} = \sum_i M_i^{-1} M_i \mathbf{x}_i$.

¹⁶ Gilbert Newton Lewis and Merle Randall. *Thermodynamics*. McGraw-Hill Book Company, Inc., 2nd edition, 1961.

¹⁷ Note the close analogy between $\sigma^{\text{rot},3\text{D}}$ and σ^{trans} . Both of the terms include a kinetic energy contribution, and so there are clear similarities.

§ 044

◀ § 43

▶ § 45

◀ 7 Equations ...

Determine the moment of inertia of an H_2O molecule if the bond angle is 104.5° and the O–H distance is 0.958 \AA .

§ 044 Moment of inertia

◀ 7 Equations ...

- 1** Let us number the atoms H(1), H(2) and O(3).
- 2** Their respective atomic weights are $M_1 = 1.00794 \text{ g mol}^{-1}$, $M_2 = 1.00794 \text{ g mol}^{-1}$ and $M_3 = 15.9994 \text{ g mol}^{-1}$.
- 3** The molecule can be oriented in an infinite number of ways, and the coordinates given below are simply based on an arbitrary choice (origin at O(3) and H(1) along the x axis):

$$\frac{\mathbf{x}_1}{[\text{Å}]} = \begin{pmatrix} -0.958 \\ 0 \\ 0 \end{pmatrix}, \quad \frac{\mathbf{x}_2}{[\text{Å}]} = \begin{pmatrix} 0.958 \cdot \sin\left(\frac{14.5 \cdot 2\pi}{360}\right) = 0.240 \\ 0.958 \cdot \cos\left(\frac{14.5 \cdot 2\pi}{360}\right) = 0.927 \\ 0 \end{pmatrix}, \quad \frac{\mathbf{x}_3}{[\text{Å}]} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

§ 044 Moment of inertia (2)

[◀ 7 Equations ...](#)

4 From this information, the inertia tensor follows

$$\frac{\mathbf{M}}{[\text{g mol}^{-1} \text{Å}^2]} = \begin{pmatrix} 0.818 & -0.262 & 0 \\ -0.262 & 0.954 & 0 \\ 0 & 0 & 1.772 \end{pmatrix}.$$

5 Diagonalising $\mathbf{M} \rightsquigarrow \mathbf{Q}\mathbf{\Lambda}\mathbf{Q}^T$ gives us the eigenvalues $\lambda_1 = 0.615$, $\lambda_2 = 1.156$ and $\lambda_3 = 1.772$, which have the same units as \mathbf{M} itself.

6 The moment of inertia can now be calculated as $I = \sqrt[3]{0.615 \cdot 1.156 \cdot 1.772} = 1.080 \text{ g mol}^{-1} \text{Å}^2 = 1.794 \cdot 10^{-47} \text{ kg m}^2$.

Non-linear molecules

[← 7 Equations ...](#)

1 Finally, the canonical equation of state describing the rotation of non-linear molecules can be written

$$\mu^{\text{rot},3\text{D}} = -RT \ln \frac{(8\pi^2 IRT)^{3/2}}{\sigma N_A^3 h^3},$$

as long as we understand that $I = \sqrt[3]{\lambda_1 \lambda_2 \lambda_3}$ represents the *molar* moment of inertia.

2 Most molecules, with the exception of hydrogen (isotopes), therefore have a relatively high moment of inertia, which means that the upper temperature limit is as low as $T \lesssim 50$ K:

Non-linear molecules (2)

◀ 7 Equations ...

Ref. ¹⁸	σ	$\frac{\lambda_r \cdot 10^{47}}{\text{kg m}^2}$			$\frac{I \cdot 10^{47}}{\text{kg m}^2}$	$\frac{\epsilon/k}{\text{K}}$	$\frac{T_b}{\text{K}}$
H ₂	2	0.460	0.460	0	0.460	87.6	20.39
CH ₄	12	5.313	5.313	5.313	5.313	7.6	111.66
HCl	1	2.641	2.641	0	2.641	15.3	188.15
H ₂ O	2	1.022	1.920	2.942	1.794	22.5	373.15

3 This gives us the classical heat capacity values of R and $3/2R$ for linear and non-linear molecules respectively.

¹⁸ G. M. Barrow. *Physical Chemistry*. McGraw-Hill, 3rd edition, 1979.

Internal degrees of freedom

[◀ 7 Equations ...](#)

- 1** Vibration and rotation are the “classical” contributions to the intramolecular energy function.
- 2** For simple molecules, these contributions can be added together, provided that the amplitude of vibration is small and doesn't disturb the molecule's centre of mass (harmonic oscillator).
- 3** However, the general description of the molecule is far more complex, and must take into account anharmonic vibration or internal rotational and torsional fluctuations.
- 4** In hydrocarbons, e.g. CH_3 , groups will rotate freely around the bond axis, whereas double bonds such as $\text{CH}_2 = \text{CH}_2$ only allow torsional fluctuations.

Electron excitation

[◀ 7 Equations ...](#)

- 1** Electron excitation is a phenomenon that typically occurs at high temperatures, and the outer electrons in a stable molecule will (gradually) be excited at temperatures $\gtrsim 3000$ K.
- 2** In radicals, excitation can occur at $\lesssim 1000$ K, because their electrons are more weakly bonded.

Quantum spin

[◀ 7 Equations ...](#)

- 1** The spin of elementary particles can also contribute to the energy state of a molecule.
- 2** In the case of hydrogen, nuclear spin (cf. parahydrogen and ortho-hydrogen) plays a key role at temperatures $\lesssim 400$ K.
- 3** Similarly, electron spin is significant if the molecule has unpaired electrons (cf. NO, O₂ and NO₂).

Photon gas

◀ 7 Equations ...

- 1** Thermal radiation (in a closed control volume) can be treated as a thermodynamic system, provided that we're not interested in the spectral distribution¹⁹ of the radiation.
- 2** In this case it is actually possible to set up the canonical equations of state²⁰ for internal energy

$$p^{\text{rad}} = \frac{1}{4} \sqrt[3]{\frac{3}{4b} \left(\frac{S}{V}\right)^4},$$

$$T^{\text{rad}} = \sqrt[3]{\frac{3S}{4bV}},$$

hvor

$$b = \frac{8\pi^5 k^4}{15h^3 c^3} = 7.56591 \dots \cdot 10^{-16} \frac{\text{J}}{\text{m}^3 \text{K}^4}.$$

Photon gas (2)

[◀ 7 Equations ...](#)

6 Using Euler's method to do a simplified integration with respect to only S and V gives us the internal energy of the radiation space:

$$U^{\text{rad}}(S, V) = T^{\text{rad}}S - p^{\text{rad}}V = \frac{3}{4} \sqrt[3]{\frac{3S^4}{4bV}}.$$

7 By eliminating S we can obtain the Stefan²¹–Boltzmann²² law of radiation $U^{\text{rad}} = bVT^4$. Alternatively, we can replace T with p , which gives us $U^{\text{rad}} = 3pV$.

¹⁹ An energy distribution function which has frequency as a free variable.

²⁰ Herbert Callen. *Thermodynamics and an Introduction to Thermostatistics*. Wiley, 2nd edition, 1985.

²¹ Jožef Stefan alias Joseph Stefan, 1835–1993. Slovenian physicist and poet.

²² Ludwig Boltzmann, 1844–1906. Austrian physicist.

§ 045

◀ § 44

▶ § 46

◀ 7 Equations ...

One of the most important fission reactions in a uranium bomb can be written ${}_0^1\text{n} + {}_{92}^{235}\text{U} \rightarrow {}_{56}^{142}\text{Ba} + {}_{36}^{91}\text{Kr} + {}_0^1\text{n}$.
 The energy released is $3.5 \cdot 10^{-11}$ J per fission event.
 Calculate T^{rad} and p^{rad} if 1% of the atoms take part in the fission reaction.

§ 045 Atomic bomb

[◀ 7 Equations ...](#)

- 1** The density of the ^{235}U isotope is 19.1 g cm^{-3} and its molar mass is $235.04 \text{ g mol}^{-1}$.
- 2** If 1% of the mass is involved in the reaction, the energy density will be $u \hat{=} V^{-1}U = 0.01 \cdot 6.0221 \cdot 10^{23} \cdot 3.5 \cdot 10^{-11} \cdot 19.1 \cdot 10^6 / 235.04 = 1.71 \cdot 10^{16} \text{ J m}^{-3}$.
- 3** From $u = bT^4 = 3p$ we can obtain $T^{\text{rad}} = 6.9 \cdot 10^7 \text{ K}$ and $p^{\text{rad}} = 5.7 \cdot 10^{10} \text{ bar}$.
- 4** These figures are representative for the uranium bomb *Little Boy*, which was dropped on Hiroshima on 6 August 1945.

Debye A

[◀ 7 Equations ...](#)

- 1** At each lattice point there is a particle (atom, group of atoms or molecule) oscillating in the force field of the neighbouring particles.
- 5** Together all of the particles vibrate within a wide spectrum of frequencies (called phonons), right up to the critical frequency ω_{\max} , which is an indirect measure of the total number of degrees of freedom in the system:

$$\int_0^{\omega_{\max}} g(\omega) d\omega = 3n.$$

- 6** The function $g(\omega)$ indicates the multiplicity for each frequency, and the next important assumption in the Debye model is $g(\omega) \propto \omega^2$.

Debye A (2)

◀ 7 Equations ...

9 The partition function can now be expressed in a modified Einstein model

$$Q^{\text{Debye}} = \prod_{\omega}^{\omega_{\text{max}}} \frac{1}{[1 - \exp(-\frac{\hbar\omega}{kT})]^{g(\omega)}},$$

where the ω represent all of the discrete frequencies in the crystal.

10 At the limit value $n \rightarrow \infty$ there will be a continuum of frequencies, and the Helmholtz energy can be expressed as

$$\lim_{n \rightarrow \infty} A^{\text{Debye}} = \frac{9NRT}{\omega_{\text{max}}^3} \int_0^{\omega_{\text{max}}} \omega^2 \ln \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right] d\omega.$$

Debye C_P

[◀ 7 Equations ...](#)

1 When expressed in the dimensionless form it makes sense to introduce a characteristic vibrational temperature $\theta_D \hat{=} \hbar\omega_{\max}/k$ also referred to as the Debye temperature. The chemical potential then becomes

$$\frac{\mu^{\text{Debye}}}{RT} = 9 \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} x^2 \ln(1 - e^{-x}) dx ,$$

where $x = \hbar\omega/kT \hat{=} \theta_D/T$.

Debye C_P (2)

◀ 7 Equations ...

3 If we differentiate the partition function twice with respect to temperature, it gives us

$$\frac{c_v^{\text{Debye}}}{R} = 9 \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx ,$$

but note that these expressions are two independent *approximations* of the partition function.

4 This introduces a thermodynamic inconsistency where $c_v^{\text{Debye}} \neq -T \partial^2 \mu^{\text{Debye}} / \partial T \partial T$.

Debye C_P (3)

◀ 7 Equations ...

5 There is no analytical solution to the above integral, but at the upper temperature limit $\theta_D/T \rightarrow 0$ and expanding the power series $e^x = 1 + x + \mathcal{O}(x^2)$ gives us

$$\lim_{T \rightarrow \infty} \frac{c_v^{\text{Debye}}}{R} = 9 \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4(1+x+\dots)}{(x+\dots)^2} dx \approx 9 \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} x^2 dx = 3.$$

6 This result shows that each atom (molecule) in the lattice oscillates in 3 independent directions if the temperature is sufficiently high.

7 Many metals (Pb, Sn, Cd, Ag, ...) are essentially in this state at room temperature. The limit value is also referred to as the Dulong–Petit²³ law.

8 For the lower temperature limit, $\theta_D/T \rightarrow \infty$ and the integral is a constant.

Debye C_P (4)

[◀ 7 Equations ...](#)

9 This has a practical application in the proportional relationship

$$\lim_{T \rightarrow 0} \frac{C_v^{\text{Debye}}}{R} \propto T^3$$

when determining the entropy of a substance by calorimetry.

10 Instead of the highly time-consuming and difficult process of measuring near 0 K, all you need to do is measure the heat capacity down to 15 – 20 K.

²³ Alexis T. Petit and Pierre L. Dulong. *Ann. Chim. Phys.*, 10:395, 1819.

Fermions in metals

◀ 7 Equations ...

1 One of the characteristics of fermions is that they cannot share the same one-particle state (the Pauli²⁴ exclusion principle).

3 In a metal, the electron energy levels will therefore be filled up from the lowest level up to the Fermi level equivalent to the chemical potential (μ_o) of the electrons in the conduction band.

4 The internal energy of these electrons can be expressed

$$\frac{U^{\text{elec}}}{NRT} = \frac{u_o}{RT} + \frac{\pi^2}{4} \cdot \frac{kT}{\mu_o} + \dots$$

5 The chemical potential of electrons is a relatively abstract concept, and an alternative to this value is the Fermi temperature $T_F \hat{=} \frac{\mu_o}{k}$, which for normal metals is approximately 10^5 K.

Fermions in metals (2)

[◀ 7 Equations ...](#)

6 Differentiating U^{elec} gives us the lower temperature limit for the electronic contribution to the heat capacity of metals:

$$\lim_{T \rightarrow 0} \frac{c_v^{\text{elec}}}{R} = \frac{\pi^2 T}{2T_F} \propto T.$$

7 This is in contrast to crystalline phases with covalent bonds where $\lim_{T \rightarrow 0}(c_v) \propto T^3$ due to the phonon contribution.

8 The practical implication of this is that the heat capacity of metals is dominated by the fermion contribution at sufficiently low temperatures ($T \lesssim 5 \text{ K}$).

²⁴ Wolfgang Ernst Pauli, 1900–1958. Austrian physicist.

Second virial coefficient

[◀ 7 Equations ...](#)

1 The virial equation relates to ideal gases. Expand the power series p/RT in molar density $\rho = N/V$:

$$\frac{p^{\text{vir}} V}{NRT} = \sum_{k=1}^{\infty} B_k(T) \left(\frac{N}{V}\right)^{k-1} = 1 + B_2(T) \frac{N}{V} + \dots \quad (7.27)$$

3 This is the normal way to express the virial development of gases, but it is also possible to invert the series from $p(\rho)$ to $\rho(p)$ as shown below.

4 Here the series has been truncated after the second term, which means that the index ₂ can be left off the symbol B :

$$\frac{pV^{2.\text{vir}}}{NRT} = 1 + \frac{BN}{V} + \dots \simeq 1 + \frac{Bp}{RT} + \dots$$

Second virial coefficient (2)

[◀ 7 Equations ...](#)

- 5** Multiplying both sides by NRT/p gives the volume-explicit form $V^{2,\text{vir}} = NRT/p + BN$, which reveals that B is a correction factor for the molar volume of the gas.
- 6** Experimentally $B = \lim_{p \rightarrow 0} (V - RT/p)$ is used, but this limit tells us nothing about how B varies with temperature.
- 7** In practice $B < 0$ for $T < T_B \approx 6T_C$, where T_B is known as the Boyle²⁵ temperature.

Second virial coefficient (3)

[◀ 7 Equations ...](#)

8 Statistical mechanics explains the theoretical relationship between B and the associated pair potential $\phi(r)$ for the interaction between two molecules in the gas phase:

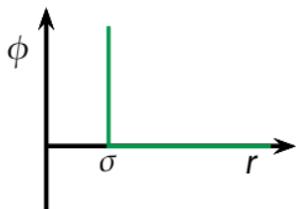
$$B(T) = 2\pi N_A \int_0^{\infty} \left(1 - e^{\frac{-\phi(r)}{kT}}\right) r^2 dr . \quad (7.28)$$

²⁵ Robert Boyle, 1627–1691. English chemist and philosopher.

Hard spheres

◀ 7 Equations ...

1



Let us assume that $\phi = 0$ for $r > \sigma$ and $\phi = \infty$ for $r \leq \sigma$.

2 That means viewing the molecules as hard spheres, with no pairwise interaction.

3 Substituting this into the integral for B gives us

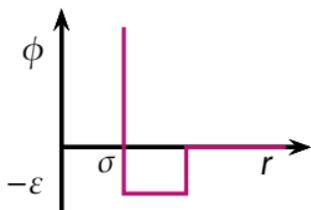
$$B^{\text{hs}} = N_A \int_0^{\sigma} r^2 dr = \frac{2\pi N_A \sigma^3}{3}$$

4 The hard sphere potential produces a reasonable approximation of a real system at high temperatures, but it doesn't explain why B is temperature-dependent.

Potential well

◀ 7 Equations ...

1



Let us assume that $\phi = 0$ for $r > \alpha\sigma$, $\phi = -\epsilon$ for $\sigma < r \leq \alpha\sigma$ and $\phi = \infty$ for $r \leq \sigma$.

2 That means viewing the molecules as hard spheres with pairwise interaction within the potential well.

3 Substituting this simple potential into the integral for B (where $\alpha > 1$), demonstrates that $B(T)$ is a strongly temperature-dependent function with the hard-sphere potential as its upper temperature limit:

$$\begin{aligned}
 B^{\text{sw}} &= B^{\text{hs}} + 2\pi N_A \int_{\sigma}^{\alpha\sigma} \left(1 - e^{\frac{\epsilon}{kT}}\right) r^2 dr \\
 &= B^{\text{hs}} \left[1 + (\alpha^3 - 1)\left(1 - e^{\frac{\epsilon}{kT}}\right)\right].
 \end{aligned}$$

Potential well (2)

[◀ 7 Equations ...](#)

4 Another connection between ε , T_B and α is revealed if you solve the equation $B^{\text{SW}}(T_B) = 0$:

$$\frac{\varepsilon}{kT_B} = \ln \frac{\alpha^3}{\alpha^3 - 1} \quad \Leftrightarrow \quad \alpha^3 = \frac{e^{\frac{\varepsilon}{kT_B}}}{e^{\frac{\varepsilon}{kT_B}} - 1}$$

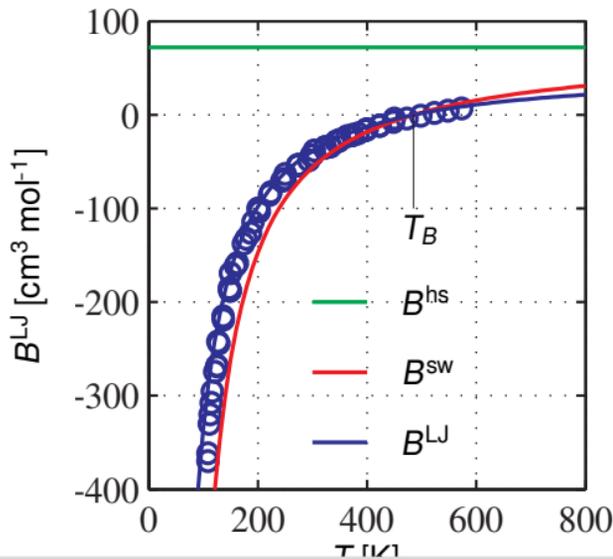
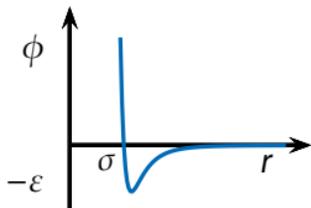


Figure 7.2: The second virial coefficient of methane calculated using the hard sphere, well and Lennard-Jones 6:12-potential where $\sigma = 3.85 \text{ \AA}$ and $\varepsilon = 1.96 \cdot 10^{-21} \text{ J}$. Both B^{sw} and B^{LJ} satisfy the lower temperature limit $\lim_{T \rightarrow 0} B = -\infty$, whilst the upper temperature limit $\lim_{T \rightarrow \infty} B = 0^+$ is only fulfilled for B^{LJ} (this can only be seen once you reach $T \gtrsim 10^4 \text{ K}$).

Lennard-Jones²⁸

◀ 7 Equations ...

1

Let us assume that $\phi = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$ for $r > 0$.

3 The exponent 6 has a theoretical basis in the London²⁶ theory of dispersion forces involving instantaneous dipoles, whilst the exponent 12 is empirical.

4 B^{LJ} cannot be determined analytically, and numerical integration is therefore required.

7 A typical temperature progression is shown in Figure 7.2 along with the experimental data for methane²⁷.

²⁵ John Edward Lennard-Jones, 1894–1954. English mathematician and physicist.

²⁶ Fritz London, 1900–1954. German–american physicist.

²⁷ J. H. Dymond and E. B. Smith. *The Virial Coefficients of Pure Gases and Mixtures*.

Oxford University Press, 1968.

The van der Waals equation

◀ 7 Equations ...

1 For a given vector \mathbf{x} consisting of the mole fractions x_1, x_2, \dots, x_n the van der Waals²⁹ equation of state can be expressed as

$$p^{\text{VdW}}(T, v, \mathbf{x}) = \frac{RT}{v-b(\mathbf{x})} - \frac{a(\mathbf{x})}{v^2}, \quad (7.29)$$

where $a(\mathbf{x}) = \sum_i \sum_j a_{ij} x_i x_j$ tells us something about the *attractive* forces between the molecules and $b(\mathbf{x}) = \sum_i b_i x_i$ represents the *hard-sphere volume*.

2 This means that there must be a relationship between the van der Waals equation and the virial equation in Section 7.6. We can demonstrate this relationship by expanding the power series $p^{\text{VdW}} V / NRT$ at the limit $V \rightarrow \infty$ (ideal gas):

$$\frac{p^{\text{VdW}} V}{NRT} = \frac{1}{1-b(\frac{N}{V})} - \frac{a}{RT} \left(\frac{N}{V}\right)$$

The van der Waals equation (2)

[◀ 7 Equations ...](#)

$$= 1 + b \left(\frac{N}{V}\right) + b^2 \left(\frac{N}{V}\right)^2 + \dots + b^n \left(\frac{N}{V}\right)^n - \frac{a}{RT} \left(\frac{N}{V}\right).$$

3 If we compare the coefficients in this series with the ones in Eq. 7.27, we find that $B_2^{vdw} = b - a/RT$, $B_3^{vdw} = b^2$, $B_4^{vdw} = b^3$ etc.

6 It is beyond the scope of this chapter to discuss all of the implications of the van der Waals equation here, but we will at the very least note one important property: the parameters a_{ij} and b_i can be obtained by measuring the critical point of each individual compound experimentally.

²⁹ Johannes Diderik van der Waals, 1837–1923. Dutch physicist.

§ 046

◀ § 45

▶ § 47

◀ 7 Equations ...

Show that the parameters $b = RT_c/8p_c$, $v_c = 3b$ and $a = 27(RT_c)^2/64p_c$ meet the criteria for a mechanical-critical point defined by $(\partial p/\partial v)_{T,x} = 0$, $(\partial^2 p/\partial v^2)_{T,x} = 0$ and $p(T_c, v_c) = p_c$.

Cubic equations of state

◀ 7 Equations ...

1 If you multiply both sides of the equation by $v^2(v - b)$ you can rewrite the equation of state 7.29 in the form $p(v - b)v^2 = RTv^2 - a(v - b)$, or as

$$v^3 - v^2\left(b + \frac{RT}{p}\right) + v\frac{a}{p} - \frac{ab}{p} = 0. \quad (7.30)$$

3 This shows that (at constant pressure) the van der Waals equation can be treated as a *cubic* equation with volume as a free variable. From the problem statement, we know that the pV isotherm has a degenerate extreme point³⁰ as its critical point.

4 This implies that the equation of state must have three coincident roots $(v - v_c)^3 = 0$, or in its expanded form:

$$v^3 - v^2 3v_c + v 3v_c^2 - v_c^3 = 0. \quad (7.31)$$

³⁰ Both a maximum and a minimum (a horizontal point of inflection).

§ 046 Critical points

[◀ 7 Equations ...](#)

- 1** The two Eqs. 7.30 and 7.31 have the same algebraic structure, which allows us to compare the coefficients term by term.
- 2** This gives rise to the following set of equations:

$$3v_c = b + \frac{RT_c}{p_c} ,$$

$$3v_c^2 = \frac{a}{p_c} ,$$

$$v_c^3 = \frac{ab}{p_c} ,$$

which must be solved with respect to a , b and v_c .

§ 046 Critical points (2)

◀ 7 Equations ...

5 The solution to the above set of equations can be expressed

$$\frac{3}{8} = \frac{v_c p_c}{RT_c}, \quad (7.32)$$

$$b = \frac{1}{3} v_c, \quad (7.33)$$

$$a = 3p_c v_c^2, \quad (7.34)$$

which can in turn be rewritten in the form used in the problem statement.

6 We should note that the *critical* compressibility factor $z_c^{\text{vdW}} \triangleq p_c v_c / RT_c = \frac{3}{8}$ behaves as a universal constant because v_c is a dependent variable in the solution.

7 Experimentally this is no more than a rough approximation as $0.25 < z_c < 0.35$ for most molecular compounds.

§ 047

◀ § 46

▶ § 48

◀ 7 Equations ...

Pressure is an intensive property (homogeneous function of degree zero), which implies that $p(T, v, \mathbf{x}) = p(T, V, \mathbf{n})$.
Rewrite the van der Waals Eq. 7.29 in this form.

§ 047 VDW in the extensive form

[◀ 7 Equations ...](#)

- 1** Dimensional analysis shows that if $v \rightarrow V$ and $\mathbf{x} \rightarrow N\mathbf{x}$ in Eq. 7.29, then homogeneity will be preserved.
- 2** Consequently, the equation of state can be written in the form

$$p^{\text{VdW}}(T, V, \mathbf{n}) = \frac{NRT}{V - Nb(\mathbf{x})} - \frac{N^2 a(\mathbf{x})}{V^2} \quad (7.35)$$

§ 048

◀ §47

▶ §49

◀ 7 Equations ...

Show that, in its reduced form, the van der Waals equation can be written as $p_r = 8T_r / (3v_r - 1) - 3/v_r^2$. Draw the function for $T_r \in \{0.75, 1, 1.5\}$. Identify all of the asymptotes to the graph. Specify the physical range of the function.

§ 048 Corresponding state

◀ 7 Equations ...

1 Rewrite the van der Waals equation in its reduced form by substituting Eqs. 7.33 and 7.34 into Eq. 7.29:

$$p^{\text{VdW}} = \frac{RT}{v - \frac{1}{3}v_c} - \frac{3p_c v_c^2}{v^2} . \quad (7.36)$$

2 Then divide by p_c and define reduced pressure as $p_r \hat{=} p/p_c$ and reduced volume as $v_r \hat{=} v/v_c$:

$$p_r^{\text{VdW}} = \frac{\left(\frac{RT}{p_c v_c}\right)}{v_r - \frac{1}{3}} - \frac{3}{v_r^2} . \quad (7.37)$$

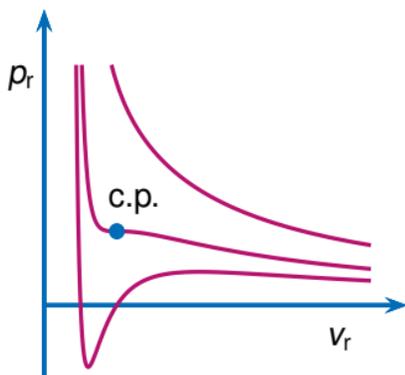
3 Finally substitute in $R/(p_c v_c) = 1/(z_c T_c) = 8/(3T_c)$ from Eq. 7.32 and define reduced temperature as $T_r \hat{=} T/T_c$.

§ 048 Corresponding state (2)

◀ 7 Equations ...

4 This gives us the van der Waals equation as formulated in the problem statement:

$$p_r^{\text{VdW}} = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \quad (7.38)$$



5 The physical range is defined by $v_r \in \left\langle \frac{1}{3}, \infty \right\rangle$. Note that the equation contains no arbitrary model parameters.

7 For the lowest isotherm ($T_r = 0.75$) there are up to three possible solutions for $p_r = p_r(v_r)$. This results in a phase transition for the system as described in Chapter 14 on vapour–liquid equilibria.

Condensed phases

◀ 7 Equations ...

1 According to Murnaghan³¹'s equation, isobaric expansivity α and isothermal compressibility β are two *independent* state functions of temperature and pressure respectively.  also see Section 8.6 on page 385.

4 Two commonly used functions for α and β are:

$$\alpha(T) = a_1 + a_2 T + \frac{a_3}{T^2} ,$$

$$\beta(p) = \frac{b_1}{1+b_2 p} .$$

5 Let us start by integrating $\alpha(T)$ at a given reference pressure p_o between the reference temperature T_o and an arbitrary system temperature T . This gives us: $\ln[v(T, p_o)/v(T_o, p_o)] = a_1(T - T_o) + \frac{1}{2}a_2(T^2 - T_o^2) - a_3(T^{-1} - T_o^{-1}) = (T - T_o)[a_1 + \frac{1}{2}a_2(T + T_o) + a_3(TT_o)^{-1}]$.

Condensed phases (2)

◀ 7 Equations ...

6 Next we integrate $\beta(p)$ at constant T between the reference pressure p_o and an arbitrary system pressure p . This gives us: $\ln[v(T, p)/v(T, p_o)] = -b_2^{-1} b_1 \ln[(1 + b_2 p)/(1 + b_2 p_o)]$.

7 We can now integrate $(d\mu)_{T,N} = v dp$ between the two states T, p and T, p_o . This produces $\mu^{\text{mur}}(T, p) = \mu_o(T, p_o) + \int_{p_o}^p v(T, p) dp$ which with a little bit of effort can be rewritten as

$$\begin{aligned} \mu^{\text{mur}}(T, p) &= \mu_o(T, p_o) + v(T, p_o) \int_{p_o}^p \left(\frac{1+b_2 p}{1+b_2 p_o}\right)^{-b_1/b_2} dp \\ &= \mu_o(T, p_o) + v(T, p_o) \frac{1+b_2 p_o}{b_2-b_1} \left[\left(\frac{1+b_2 p}{1+b_2 p_o}\right)^{1-b_1/b_2} - 1 \right] \\ &= \mu_o(T, p_o) + \frac{b_1}{b_2-b_1} \frac{v_o}{\beta_o} \left[\frac{\beta_o}{\beta} \frac{v}{v_o} - 1 \right], \end{aligned}$$

where $\beta_o \hat{=} \beta(p_o)$ and $v_o \hat{=} v(T, p_o)$.

³¹ F. D. Murnaghan. *Proc. Natl. Acad. Sci. U. S. A.*, 30:244–247, 1944.

§ 049

◀ § 48

▶ § 50

◀ 7 Equations ...

Murnaghan's equation is derived by integrating the expansivity with respect to T at a given p_0 , and then integrating the compressibility with respect to p at constant T , but this provides no guarantee that our starting point was thermodynamically consistent. Use differentiation to show that $\alpha = f(T)$ and $\beta = g(p)$ genuinely represent a consistent basis for a model.

§ 049 The Murnaghan model

◀ 7 Equations ...

1 For the model to be consistent, the third-order Maxwell equation

$$\frac{\partial^2 v}{\partial T \partial p} = \frac{\partial^2 v}{\partial p \partial T}$$

must hold. Substituting in $(\partial v / \partial T)_p = vf(T)$ and $(\partial v / \partial p)_T = -vg(p)$ gives us

$$-\left(\frac{\partial v}{\partial T}\right)_p g(p) \stackrel{?}{=} \left(\frac{\partial v}{\partial p}\right)_T f(T),$$

where $f(T)$ and $g(p)$ are functions of different state variables.

4 If we rewrite the last equation slightly we get

$$vf(T)g(p) \stackrel{?}{=} vg(p)f(T).$$

Here the right-hand side is identical to the left-hand side, so the test has been satisfied.

§ 050

◀ §49

▶ §51

◀ 7 Equations ...

Assume that thermal expansivity is constant, i.e. that $a_2 = 0 \text{ K}^{-2}$ and $a_3 = 0 \text{ K}$. Find an expression for $(\partial c_p / \partial p)_{T,N}$ that is true for this simplified Murnaghan model. What is the sign of the derivative?

§ 050 Murnaghan C_P

◀ 7 Equations ...

1 The fact that c_p is pressure-dependent can be derived as shown below.

2 Note the Maxwell relationship used at the start of the equation:

$$\begin{aligned}
 \left(\frac{\partial c_p^{\text{mur}}}{\partial p}\right)_{T,N} &= \frac{\partial}{\partial p} \left[T \left(\frac{\partial s}{\partial T}\right)_{p,N} \right]_{T,N} = T \frac{\partial}{\partial T} \left[\left(\frac{\partial s}{\partial p}\right)_{T,N} \right]_{p,N} \\
 &= -T \frac{\partial}{\partial T} \left[\left(\frac{\partial v}{\partial T}\right)_{p,N} \right]_{p,N} \\
 &\hat{=} -T \left(\frac{\partial(v\alpha)}{\partial T}\right)_{p,N} \\
 &= -T v \alpha^2 \\
 &\leq 0
 \end{aligned}$$

§ 051

◀ § 50

▶ § 52

◀ 7 Equations ...

For a one-component system to be thermodynamically stable, it must satisfy the conditions $\beta > 0$ and $c_p > 0$.
Are these conditions (always) met for Murnaghan's equation?

§ 051 Thermal instability

◀ 7 Equations ...

- 1** The first condition is satisfied for all T and p if $b_1 > 0$ and $b_2 > 0$.
- 2** With respect to the second condition, in Paragraph 50 we showed that $(\partial c_p^{\text{mur}} / \partial p)_{T,N} < 0$ for all $V > 0$.
- 3** Since $c_p < \infty$, there will always be a pressure $p < \infty$ at which $c_p^{\text{mur}} = 0$, unless

$$\int_{p_0}^{\infty} v^{\text{mur}} dp \stackrel{?}{<} \infty.$$

- 4** It can be demonstrated that this is not the case, and that Murnaghan's model therefore does not satisfy the requirement for thermal stability at all T, p .

Part 13

Departure Functions

◀ see also Part-Contents ▶

Contents

1 $G^{r,p}(T, p, n)$

2 $A^{r,p}(T, p, n)$

- 1 Physical derivation
- 2 Rational derivation
- 3 Connection with Gibbs energy

3 $A^{r,v}(T, V, n)$

Multicomponent thermodynamics

- 1** From a thermodynamic point of view, it makes little difference whether a system is composed of one, two or many components, provided that their relative proportions are constant in time and space.
- 4** The situation becomes much more complicated, however, if the components that vary with mass are included in the system description.
- 5** The number of degrees of freedom increases, and the thermodynamic functions describe abstract hyperplanes in more than three spatial dimensions.
- 6** This makes it difficult to visualise the mathematical description, and as we do not want to restrict the theory to any specific chemical system, we shall hereafter use generic indices $i \in [1, n]$ instead of component names.

Multicomponent thermodynamics (2)

9 In ideal gases, the composition dependence is relatively simple, and by referring to the Eqs. 8.40–8.42 on 390 we can write:

$$\Delta_f H^{\text{IG}}(T_o, \mathbf{n}) = \sum_{i=1}^n N_i \Delta_f h_i^{\circ}(T_o), \quad (13.1)$$

$$C_V^{\text{IG}}(T, \mathbf{n}) = \sum_{i=1}^n N_i c_{v,i}^{\circ}(T), \quad (13.2)$$

$$C_P^{\text{IG}}(T, \mathbf{n}) = \sum_{i=1}^n N_i c_{p,i}^{\circ}(T), \quad (13.3)$$

$$S^{\text{IG}}(T_o, p_o, \mathbf{n}) = \sum_{i=1}^n N_i s_i^{\circ}(T_o, p_o) - R \sum_{i=1}^n N_i \ln\left(\frac{N_i}{N}\right). \quad (13.4)$$

10 Note that $\Delta_f h_i^{\circ}$, $c_{v,i}^{\circ}$, $c_{p,i}^{\circ}$ and s_i° are contributions from the standard state of the same kind as μ_i° in Eq. 7.19 on page 262.

§ 103

◀ § 102

▶ § 104

◀ 13 Departure ...

Express the Gibbs energy of an ideal gas based on Eqs. 13.1–13.4. Calculate the standard state contribution of G^{IG} by using s_i° , $\Delta_f h_i^\circ$ and $c_{p,i}^\circ(T)$. Show by differentiation that the chemical potential can be expressed as $\mu_i^{\text{IG}}(T, p, \mathbf{n}) = \mu_i^\circ(T, p_\circ) + RT \ln[N_i p / (N p_\circ)]$. Identify the function μ_i° .

§ 103 Ideal gas Gibbs energy

1 The Gibbs energy $G = H - TS$ of an ideal gas mixture can be derived from Eqs. 8.41 and 8.42:

$$G^{\text{ig}}(T, p, \mathbf{n}) = \Delta_{\text{f}}H^{\text{ig}}(T_0, \mathbf{n}) + \int_{T_0}^T C_P^{\text{ig}}(T, \mathbf{n}) dT - T \left\{ S^{\text{ig}}(T_0, p_0, \mathbf{n}) + \int_{T_0}^T \frac{C_P^{\text{ig}}(T, \mathbf{n})}{T} dT - NR \ln\left(\frac{p}{p_0}\right) \right\}. \quad (13.5)$$

§ 103 Ideal gas Gibbs energy (2)

2 Let us substitute Eqs. 13.1, 13.3 and 13.4 into Eq. 13.5 and differentiate with respect to N_j :

$$\begin{aligned}
 \mu_i^{\text{ig}}(T, p, \mathbf{n}) &= \left(\frac{\partial G^{\text{ig}}}{\partial N_i} \right)_{T, p, N_{j \neq i}} \\
 &= \Delta_f h_i^\circ(T_o) + \int_{T_o}^T c_{p,i}^\circ(T) dT - T \left\{ s_i^\circ(T_o, p_o) \right. \\
 &\quad - R \ln \left(\frac{N_j}{N} \right) - \sum_{k=1}^n N_k R \frac{N}{N_k} \frac{\delta_{ik} N - N_k}{N^2} \\
 &\quad \left. + \int_{T_o}^T \frac{c_{p,i}^\circ(T)}{T} dT - R \ln \left(\frac{p}{p_o} \right) \right\}. \tag{13.6}
 \end{aligned}$$

3 The above equation contains Kronecker's delta, which has the value 1 if $i = k$ and 0 in all other cases.

§ 103 Ideal gas Gibbs energy (3)

4 By simplifying Eq. 13.6 we can state the chemical potential as

$$\mu_i^{\text{IG}}(T, p, n) = \mu_i^\circ(T, p_o) + RT \ln\left(\frac{N_i p}{N p_o}\right), \quad (13.7)$$

where the standard chemical potential μ_i° is defined as:

$$\mu_i^\circ(T) = \Delta_f h_i^\circ(T_o) + \int_{T_o}^T c_{p,i}^\circ(T) dT - T s_i^\circ(T_o, p_o) - T \int_{T_o}^T \frac{c_{p,i}^\circ(T)}{T} dT \quad (13.8)$$

§ 104

◀ § 103

▶ § 105

◀ 13 Departure ...

Use a specific example to show that $U^{\text{ig}} - TS^{\text{ig}} + pV^{\text{ig}} = \sum_{i=1}^n \mu_i^{\text{ig}} N_i$.

§ 104 Ideal gas internal energy

- 1** It provides valuable experience to know that the general relations we meet in thermodynamics are valid under special circumstances as well.
- 3** First, Eq. 13.7 is substituted into the right-hand side of the equation given in the paragraph text.
- 4** The left-hand side then follows by inserting $H^{Ig} = U^{Ig} + NRT$.

Gibbs residual $G^{r,p}$

- 1** The canonical variables of Gibbs energy include temperature and pressure.
- 3** Using what we already know about G^{ig} allows us to define the residual Gibbs energy: as

$$G^{r,p}(T, p, \mathbf{n}) \hat{=} G(T, p, \mathbf{n}) - G^{ig}(T, p, \mathbf{n}). \quad (13.9)$$

- 4** As $p \rightarrow 0$, all fluids have virtually ideal properties.
- 5** This approximation means that

$$\lim_{p \rightarrow 0} \left\{ G^{r,p} = 0, \left(\frac{\partial G^{r,p}}{\partial p} \right)_{T, \mathbf{n}} = B'_{2'}, \dots, \left(\frac{\partial^n G^{r,p}}{\partial p \dots \partial p} \right)_{T, \mathbf{n}} = (n-1)! B'_{n+1} \right\}. \quad (13.10)$$

Gibbs residual $G^{r,p}$ (2)

[◀ 13 Departure ...](#)

6 This is consistent with the virial theorem in Chapter 7 on page 242, and with the Legendre transform in Chapter 4, from which it follows that $(\partial G/\partial p)_{T,n}$ is the system volume regardless of whether the fluid is ideal or real.

7 By taking the limits from Eq. 13.10 it is possible to rewrite Eq. 13.9 as¹:

$$G^{r,p}(T, p, n) = \int_0^p (V - V^{ig}) d\pi = \int_0^p \left(V(\pi) - \frac{NRT}{\pi} \right) d\pi . \quad (13.11)$$

¹ Note that π is used as the integration variable in order to avoid confusion with p , which appears in the upper limit of the integral.

Residual chemical potential

1 An equivalent expression for the chemical potential $\mu_i = (\partial G / \partial N_i)_{T, p, N_{j \neq i}}$ is true for all conceivable Gibbs energy functions, including $G^{r,p}$.

2 This allows us to define the residual chemical potential as $\mu_i^{r,p} \triangleq \mu_i - \mu_i^{\text{ig}}$, or

$$\begin{aligned} \mu_i^{r,p}(T, p, \mathbf{n}) &\triangleq \left(\frac{\partial G^{r,p}}{\partial N_i} \right)_{T, p, N_{j \neq i}} \\ &= \int_0^p \left[\left(\frac{\partial V}{\partial N_i} \right)_{T, \pi, N_{j \neq i}} - \frac{RT}{\pi} \right] d\pi \triangleq \int_0^p \left(\bar{v}_i - \frac{RT}{\pi} \right) d\pi, \end{aligned} \quad (13.12)$$

where $\bar{v}_i \triangleq (\partial V / \partial N_i)_{T, \pi, N_{j \neq i}}$ is the *partial molar volume* of the component i .

The derivative of an integral

- 1** Since the system pressure is only present in the limit of the integral, we need only worry about the derivative of the kernel, but there the pressure does vary (locally) throughout the integration!
- 2** This is an unusual situation, and it is important to realise that the corresponding 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 $\pi \in [0, p]$.

- 3** What is unusual in this respect is that there are two different physical interpretations of pressure—one being the system pressure in the upper limit of the integral and the other being the integration variable π .

The derivative of an integral (2)

- 4** However, there is a given local pressure π at each stage of the integration, so the only remaining degree of freedom comes from variation in the composition of component i .
- 5** Hence, the chemical potential must be integrated over the volume derivative as shown in Eq. 13.12.
- 6** For historical reasons it is customary to rewrite the residual potential as

$$RT \ln \varphi_i \hat{=} \mu_i^{r,P}(T, p, \mathbf{n}), \quad (13.13)$$

where $\varphi_i(T, p, \mathbf{n})$ is the *fugacity coefficient* of component i .

§ 105

◀ § 104

▶ § 106

◀ 13 Departure ...

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

§ 105 The fugacity coefficient

- 1** The chemical potential can be derived by combining Eqs. 13.7 and 13.12.
- 2** The latter equation gives us $\lim_{p \rightarrow 0} \mu_i^{r,p} = 0$ and hence $\lim_{p \rightarrow 0} \varphi_i = 1$.
- 3** For an ideal gas $\bar{v}_i^{ig} = RT/p$, which means that $\mu_i^{r,p,ig} = 0$ regardless of the pressure.
- 4** Hence $\varphi_i^{ig} = 1$.

§ 106

◀ § 105

▶ § 107

◀ 13 Departure ...

Derive $G^{r,P}$ for the 2nd virial equation if $pV^{2.\text{vir}} = NRT + Bp$.

Differentiate to find $RT \ln \varphi_k^{2.\text{vir}}$. Use the quadratic mixing rule for $B = N \sum_i \sum_j x_i x_j B_{ij}$ where $B_{i,j} = B_{j,i}$.

§ 106 Virial Gibbs energy I

1 The residual Gibbs energy can be determined by directly substituting the 2nd virial equation into Eq. 13.11:

$$G^{r,P,2.vir} = \int_0^p \left(\frac{NRT}{\pi} + B - \frac{NRT}{\pi} \right) d\pi = Bp. \quad (13.14)$$

2 In order to find $RT \ln \varphi_k$ we must differentiate $G^{r,P}$, and hence B , with respect to N_k , but differentiating with respect to (mole) fractions has an unfortunate tendency to cause what is known as “code bloat” in computing.

§ 106 Virial Gibbs energy I (2)

3 We can considerably reduce the amount of writing that we need to do by using $NB = \sum_i \sum_j N_i N_j B_{i,j}$, which, even though it is an implicit expression, is much better suited for differentiation:

$$\left(\frac{\partial NB}{\partial N_k}\right)_{T, N_{l \neq k}} = \sum_i \sum_j \left(\frac{\partial N_i N_j}{\partial N_k}\right)_{N_{l \neq k}} B_{ij}.$$

4 Differentiate both sides and substitute in Kronecker's delta, where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$:

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

5 We can simplify the right-hand side considerably by substituting $B_{kj} = B_{jk}$ and simultaneously changing one of the summation indices from j to i .

§ 106 Virial Gibbs energy I (3)

6 This gives us two identical terms on the right-hand side, so the partial derivative of B can now be written

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

7 The residual potential can be calculated from Eq. 13.14 on page 671, as shown below:

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

8 Alternatively, we can achieve the same result by substituting the partial derivative of B into Eq. 13.12 on page 665 and integrating².

² It is worth noting that \bar{b}_i is the (pressure-independent) departure function of the partial molar volume from the 2nd virial equation: $\bar{v}_i^{2,\text{vir}} - RT/\pi = \bar{b}_i(T)$.

Helmholtz residual $A^{r,p}$ I

- 1** Our goal is to describe the difference in Helmholtz energy between a real fluid and an ideal gas at a given *temperature and pressure*.
- 3** We can simplify our task by splitting the expression into 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:

$$\begin{aligned} A^{r,p}(T, V(p), \mathbf{n}) &\hat{=} A(T, V(p), \mathbf{n}) - A^{ig}(T, V^{ig}(p), \mathbf{n}) \\ &\equiv A(T, V(p), \mathbf{n}) - A^{ig}(T, V(p), \mathbf{n}) \\ &\quad + A^{ig}(T, V(p), \mathbf{n}) - A^{ig}(T, V^{ig}(p), \mathbf{n}). \end{aligned} \quad (13.15)$$

- 4** It should be emphasised that volume is a function of pressure p . It implies, however, that the two fluids have different volumes, since $V \neq V^{ig}$ at a given p .

Helmholtz residual A^{r,P} I (2)

6 From Chapter 4 we know that $(\partial A / \partial V)_{T,n} = -p$. Analogously to Eq. 13.11 on page 664 we can therefore write³

$$\begin{aligned} A^{r,P}(T, V(p), \mathbf{n}) &= \int_{\infty}^{V(p)} (\pi^{ig} - \pi) dV - \int_{V^{ig}(p)}^{V(p)} \pi^{ig} dV \\ &= \int_{\infty}^{V(p)} \left(\frac{NRT}{V} - \pi \right) dV - NRT \ln z(p), \end{aligned} \quad (13.16)$$

where the ideal gas volume is given by $V^{ig} = NRT/p$, and the *compressibility factor* z is defined as $z \hat{=} V/V^{ig} = pV/(NRT)$.

³ This follows from $\lim_{V \rightarrow \infty} \left\{ A - A^{ig} = 0, \left(\frac{\partial A - A^{ig}}{\partial V} \right)_{T,n} = 0, \dots, \left(\frac{\partial^n A - A^{ig}}{\partial V^n \partial V} \right)_{T,n} = 0 \right\}$ in accordance with the virial theorem.

Problems

1 The implicit form of the function $A^{r,P}(T, V(p), p, \mathbf{n})$ prevents us from calculating the chemical potential by differentiation with respect to the canonical variables T, V, \mathbf{n} .

3 so we must instead use

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

4 If we substitute this into the residual chemical potential $\mu_i^{r,P} \hat{=} \mu_i - \mu_i^{\text{ig}}$ we get

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

Problems (2)

- 5** Note that $V(p)$ is constant in one of the partial derivatives, while $V^{ig}(p)$ is constant in the other one.
- 6** This means that both $V(p)$ and $V^{ig}(p)$ must be kept constant when differentiating $A^{r,p}$, which in turn implies that $z(p) = V(p)/V^{ig}(p)$ is a constant factor.
- 7** The residual chemical potential can therefore be expressed

$$\mu_i^{r,p}(T, V(p), \mathbf{n}) = \int_{\infty}^{V(p)} \left[\frac{RT}{v} - \left(\frac{\partial \pi}{\partial N_i} \right)_{T, v, N_{j \neq i}} \right] dv - RT \ln z(T, V(p), \mathbf{n}). \quad (13.17)$$

Problems (3)

8 Although this derivation is mathematically correct, it is hard to explain logically, as it relies on there being two different volumes (both of which remain constant, in line with the definition) during the same differentiation.

⁴ If we redefine the fugacity coefficient to mean the difference between an ideal gas and a real fluid at a *given volume* rather than a *given pressure*, it becomes easier to derive the chemical potential; see Section 13.3 on page 689.

§ 107

◀ § 106

▶ § 108

◀ 13 Departure ...

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

§ 107 Virial Helmholtz energy

1 The residual Helmholtz energy is calculated by inserting the 2nd virial equation into Eq. 13.16, which gives us this surprising result:

$$A^{r,p,2,\text{vir}} = \int_{\infty}^V \left(\frac{NRT}{v} - \frac{NRT}{v-B} \right) dv - NRT \ln \left(\frac{V}{V-B} \right) = 0. \quad (13.18)$$

2 So there is no difference between Helmholtz energy for the 2nd virial equation and that for an ideal gas at the *same pressure*.

3 In other words: The volume term in $A^{2,\text{vir}}$ happens to be equal to $RT \ln z^{2,\text{vir}}$.

6 Moreover, even though $A^{r,p,2,\text{vir}}$ is zero, this does not imply that $\mu_i^{r,p,2,\text{vir}}$ is also zero.

8 It is important to remember that $A^{r,p}$ is a non-canonical function.

Helmholtz residual $A^{r,p}$ II

- 1** At this point it may be helpful to offer an alternative, more intuitive derivation of $A^{r,p}$.
- 2** Let us first differentiate Eq. 13.15 with respect to the mole number N_i :

$$\left(\frac{\partial A^{r,p}}{\partial N_i}\right)_{T,V,N_{j \neq i}} = \mu_i - \left(\frac{\partial A^{ig}}{\partial N_i}\right)_{T,V,N_{j \neq i}} \quad (13.19)$$

- 3** This time we face the problem that constant V does not necessarily imply constant V^{ig} .
- 4** In fact, in order to differentiate A^{ig} with respect to N_i , we need to know how V^{ig} varies with N_i when V is kept constant.

Helmholtz residual A^{r,p} II (2)

5 At a given temperature and at fixed amounts of all components j , except i , the differential of A^{ig} is

$$(dA^{ig})_{T, N_{j \neq i}} = \left(\frac{\partial A^{ig}}{\partial N_i}\right)_{T, V^{ig}, N_{j \neq i}} dN_i + \left(\frac{\partial A^{ig}}{\partial V^{ig}}\right)_{T, n} dV^{ig} = \mu_i^{ig} dN_i - p^{ig} dV^{ig}, \quad (13.20)$$

where ig is stated explicitly in order to make the next step a little bit clearer.

6 If we bear in mind the condition $p^{ig} = p$, we can simplify Eq. 13.20 to

$$\left(\frac{\partial A^{ig}}{\partial N_i}\right)_{T, V, N_{j \neq i}} = \mu_i^{ig} - p \left(\frac{\partial V^{ig}}{\partial N_i}\right)_{T, V, N_{j \neq i}}. \quad (13.21)$$

7 Combined with Eq. 13.19 this gives us:

$$\mu_i - \mu_i^{ig} = \left(\frac{\partial A^{r,p}}{\partial N_i}\right)_{T, V, N_{j \neq i}} - p \left(\frac{\partial V^{ig}}{\partial N_i}\right)_{T, V, N_{j \neq i}}. \quad (13.22)$$

Helmholtz residual $A^{r,p}$ II (3)

8 Finally, Eq. 13.16 is differentiated:

$$\left(\frac{\partial A^{r,p}}{\partial N_i}\right)_{T,V,N_{j \neq i}} = \int_{\infty}^V \left[\frac{RT}{v} - \left(\frac{\partial p}{\partial N_i}\right)_{T,v,N_{j \neq i}} \right] dv + \frac{NRT}{V^{ig}} \left(\frac{\partial V^{ig}}{\partial N_i}\right)_{T,V,N_{j \neq i}} - RT \ln z. \quad (13.23)$$

9 You will recognise $NRT/V^{ig} = p^{ig} = p$ in Eq. 13.23.

10 This means that the term $(\partial V^{ig}/\partial N_i)_{T,V,N_{j \neq i}}$ disappears when the Eqs. 13.22 and 13.23 are combined.

11 The residual chemical potential $\mu_i^{r,p} \hat{=} \mu_i - \mu_i^{ig}$ is thus the same as in Eq. 13.17 on page 677.

Helmholtz residual $A^{r,P}$ III

1 A third option is to use Gibbs energy as our starting point, which is a natural thing to do, since the residual chemical potential has the same canonical variables as Gibbs energy.

2 Substituting $G = A + pV$ into $G^{r,P} \triangleq G - G^{ig}$ gives us:

$$G^{r,P} = A(T, V(p), \mathbf{n}) + pV(p) - [A^{ig}(T, V^{ig}(p), \mathbf{n}) + pV^{ig}(p)] . \quad (13.24)$$

3 Furthermore, $pV = zNRT$ and $pV^{ig} = NRT$. When we substitute these into the above equation, and combine it with Eqs. 13.15 and 13.16 on page 674, we get:

$$\begin{aligned} G^{r,P} &= A^{r,P} + NRT(z - 1) \\ &= \int_{\infty}^{V(p)} \left(\frac{NRT}{v} - \pi \right) dv - NRT \ln z(p) - NRT[z(p) - 1] . \quad (13.25) \end{aligned}$$

Helmholtz residual $A^{\text{r,p}}$ III (2)

- 4** Our one remaining task is to differentiate this expression with respect to the mole number of component i .
- 5** It is evident that we will need to obtain the partial derivative of $z \triangleq pV/NRT$, so let us start by doing that:

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

- 6** This is where things start to get tricky: how can we differentiate the integral?
- 7** The upper limit clearly depends on the composition at fixed pressure, while the differential of π at a given volume v is:

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

Helmholtz residual A^{r,p} III (3)

- 8** It is important to note that v is an integration variable in Eq. 13.25, and that it remains constant during the above differentiation.
- 9** Partial differentiation therefore gives us:

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

- 10** If we substitute in z_i , most of the terms cancel, and the final result is identical to Eq. 13.17 on page 677.

§ 108

◀ § 107

▶ § 109

◀ 13 Departure ...

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

§ 108 Virial Gibbs energy II

- 1** From Eq. 13.25 we know the general expression $G^{r,p} = A^{r,p} + NRT(z - 1)$.
- 2** Combined with $A^{r,p,2.vir} = 0$ from Eq. 13.18 on page 680 this gives us $G^{r,p,2.vir} = NRT(z - 1)$.
- 3** Substituting in $z^{2.vir} = 1 + Bp/NRT$ gives $G^{r,p,2.vir} = Bp$ in accordance with Eq. 13.14 on page 671.
- 4** The results from the various sections are thus internally consistent.

(T, p, \mathbf{n}) vs (T, V, \mathbf{n})

- 1** The problems we experienced in the previous section were caused by the disastrous decision to use pressure as a free variable in the Helmholtz function.
- 2** If we redefine the residual Helmholtz energy as

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

we are back into the world of canonical variables, and we can use the same approach as the one used for residual Gibbs energy on page 663.

(T, p, n) vs (T, V, n) (2)

3 The alternative departure function can be written

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

while the associated chemical potential is

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

§ 109

◀ § 108

▶ § 110

◀ 13 Departure ...

Derive an expression for $A^{r,v}$ and the first derivatives $\partial A^{r,v} / \partial (T, V, \mathbf{n})$ for a fluid that conforms to 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. Finally, state b_i and a_i as functions of T_c and p_c ; also see Paragraph 46 on page 319.

§ 109 Redlich–Kwong⁵

1 Let us first estimate a and b for a pure fluid. For this purpose we will rewrite the equation of state as a *cubic* polynomial of volume:

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

2 At the critical point this equation must fulfil $(v - v_c)^3 = 0$, or $v^3 - 3vv_c + 3v^2v_c^2 - v_c^3 = 0$.

3 If compared term-by-term (see Paragraph 46 in Chapter 7), the two polynomials can be used to produce three equations, which can then be solved for a , b and v_c :

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

4 Combining the middle equation with the other two yields $2v_c^3 - (v_c + b)^3 = 0$, which can be solved for the positive root $b = (2^{1/3} - 1)v_c$.

§ 109 Redlich–Kwong⁶ (2)

5 If expressed in terms of the critical temperature and pressure (for any component i), this is equivalent to:

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

6 We can now choose whether to express the rest of the derivation in terms of extensive properties (mole number and volume) or intensive properties (mole fraction and molar volume).

7 Here, the extensive properties have been chosen, in order to emphasise the homogeneity of the thermodynamic functions.

§ 109 Redlich–Kwong⁷ (3)

8 The total Helmholtz energy of the fluid is thus

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

and the associated first derivatives are:

$$\left(\frac{\partial A^{r,v,RK}}{\partial T} \right)_{V,n} = NR \ln \left(\frac{V}{V-B} \right) + \frac{A_T}{B} \ln \left(\frac{V}{V+B} \right),$$

$$\left(\frac{\partial A^{r,v,RK}}{\partial V} \right)_{T,n} = NRT \frac{-B}{V(V-B)} + \frac{A}{V(V+B)},$$

$$\left(\frac{\partial A^{r,v,RK}}{\partial N_i} \right)_{T,V,N_{j \neq k}} = RT \ln \left(\frac{V}{V-B} \right) + NRT \frac{b_i}{V-B} + \frac{1}{B} \left(A_i - \frac{Ab_i}{B} \right) \ln \left(\frac{V}{V+B} \right) - \frac{Ab_i}{B(V+B)}.$$

§ 109 Redlich–Kwong⁸ (4)

9 The coefficients of the equation are defined below (note that α_i has the same units as a_i^{vdW}):

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

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

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

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

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

⁸ Otto Redlich and J. N. S. Kwong. *Chem. Rev. (Washington, D. C.)*, 44:233–244, 1949.

Part 14

Simple vapour–liquid equilibrium

← see also Part-Contents



Contents

- 1 Saturation pressure**
- 2 Saturation volume**
- 3 Enthalpy of vaporization**
- 4 Critical exponents**
- 5 Maxwell equal area rule**

Phase equilibrium

◀ 14 Simple ...

1 Most of the above-mentioned processes require complex descriptions of multicomponent systems involving various phases, but we can nevertheless study the *typical* characteristics of vapour–liquid equilibria based on the behaviour of a realistic one-component system.

3 How to go about that is precisely what this chapter is about. The conditions for thermodynamic equilibrium along a *continuous* phase boundary curve in the T, p, μ space are:

$$\begin{aligned}
 T^v &= T^{\text{liq}} & dT^v &= dT^{\text{liq}} \\
 p^v &= p^{\text{liq}} \quad \Rightarrow & dp^v &= dp^{\text{liq}} \\
 \mu^v &= \mu^{\text{liq}} & -s^v dT^v + v^v dp^v &= -s^{\text{liq}} dT^{\text{liq}} + v^{\text{liq}} dp^{\text{liq}}
 \end{aligned}$$

Clausius–Clapeyron equation

◀ 14 Simple ...

1 It is normal to combine the three differentials into a single equation, which is referred to as the Clapeyron¹ equation

$$\left(\frac{dp}{dT}\right)_{\Delta\mu=0} = \frac{s^v - s^{liq}}{v^v - v^{liq}} \hat{=} \frac{\Delta_{\text{vap}}s}{\Delta_{\text{vap}}v} = \frac{\Delta_{\text{vap}}h}{T\Delta_{\text{vap}}v},$$

8 At low pressures the volume of liquid is negligible, since $\lim_{p \rightarrow 0}(T\Delta_{\text{vap}}v) = Tv^{ig} = T\frac{RT}{p}$. This means that

$$\left(\frac{\partial p}{\partial T}\right)_{\Delta\mu=0, p \rightarrow 0} = \frac{p\Delta_{\text{vap}}h}{RT^2}, \quad (14.1)$$

11 If we integrate we get the Clausius²–Clapeyron vapour pressure equation, where $b = \Delta_{\text{vap}}h/R$ is assumed to be constant over the relevant temperature range:

$$\ln\left(\frac{p}{p^\circ}\right)^{\text{C-C}} = a - \frac{b}{T}. \quad (14.2)$$

¹ Émile Clapeyron. 1799–1864. French engineer and mathematician.

Measured vapour pressure

◀ 14 Simple ...

1 If $p \gg 0$ then we cannot assume ideal gas behaviour, and if $p \rightarrow p_c$ then the volume of liquid is no longer negligible. This undermines the theoretical

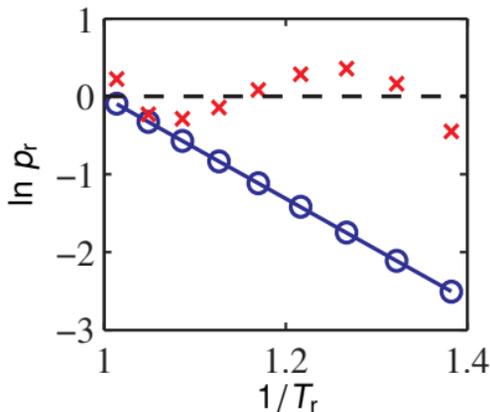


Figure 14.1: Vapour pressure of CO_2 , where \circ is the measured value and \times is the deviation.

Measured vapour pressure (2)

◀ 14 Simple ...

basis for the Clausius–Clapeyron equation, but the non-linear contributions largely cancel each other out, so Eq. 14.2 still gives a reasonable approximation of the vapour pressure.

4 To begin to understand why the vapour pressure can be plotted as a straight line even at high pressures, let us look at the van der Waals equation of state

$$p^{\text{VdW}} = \frac{NRT}{V-Nb} - \frac{aN^2}{V^2}$$

Measured vapour pressure (3)

◀ 14 Simple ...

6 The chemical potential can be expressed as $\mu^{\text{VdW}} = \mu^{\text{Ig}} + \mu^{\text{r,v}}$, where the residual term is defined as being

$$\begin{aligned}\mu^{\text{r,v}} &\hat{=} \int_{\infty}^V \left(\frac{RT}{V} - \left(\frac{\partial p}{\partial N} \right)_{T,V} \right) dV \\ &= \int_{\infty}^V \left(\frac{RT}{V} - \frac{RT}{V-Nb} - \frac{NRTb}{(V-Nb)^2} + \frac{2aN}{V^2} \right) dV \\ &= RT \ln \left(\frac{V}{V-Nb} \right) + \frac{NRTb}{V-Nb} - \frac{2aN}{V},\end{aligned}$$

and the ideal gas contribution is

$$\mu^{\text{Ig}} = \mu^{\circ}(T, p^{\circ}) + RT \ln \left(\frac{NRT}{Vp^{\circ}} \right).$$

Van der Waals equation

◀ 14 Simple ...

1 Combining the equations gives us the following expression for a van der Waals fluid:

$$\mu^{\text{VdW}} = \mu^\circ(T, p^\circ) + RT \ln\left(\frac{NRT}{p^\circ(V-Nb)}\right) + \frac{NRTb}{V-Nb} - \frac{2aN}{V}.$$

2 If we use the generalised parameters $3b = v_c$, $a = 3p_c v_c^2$ and $8p_c v_c = 3RT_c$ from Section 46 on page 319, we can express the pressure and chemical potential in dimensionless form:

$$\frac{p^{\text{VdW}}}{p_c} \hat{=} p_r^{\text{VdW}} = \frac{8T_r}{3v_r-1} - \frac{3}{v_r^2}, \quad (14.3)$$

$$\frac{\mu^{\text{VdW}}}{RT_c} \hat{=} \mu_r^{\text{VdW}} = \mu_r^\circ - T_r \ln p_r^\circ + T_r \ln\left(\frac{8T_r}{3v_r-1}\right) + \frac{T_r}{3v_r-1} - \frac{9}{4v_r}. \quad (14.4)$$

Van der Waals A

◀ 14 Simple ...

1 It is worth noting that these two equations represent a complete set of equations of state for Helmholtz energy.

2 Integration using the Euler method gives us $A = -pV + \mu N$, which expressed in dimensionless form becomes $\frac{A}{NRT_c} = -\frac{pV}{NRT_c} + \frac{\mu}{RT_c}$. Rewriting this in reduced variables:

$$a_r^{\text{VdW}} \hat{=} \frac{A^{\text{VdW}}}{NRT_c} = -\frac{3}{8} p_r^{\text{VdW}} v_r + \mu_r^{\text{VdW}} \quad (14.5)$$

Vapour-liquid equilibrium

◀ 14 Simple ...

1 At thermodynamic equilibrium, T , p and μ have the same values in both the vapour and liquid phases.

2 Since the van der Waals equation is expressed in terms of $p_r(T_r, v_r)$, the equilibrium equations have to be solved simultaneously in T_r, v_r coordinates.

4 The fact that the pressure is the same in both phases means that

$$\frac{8T_r}{3v_r^{\text{liq}}-1} - \frac{3}{(v_r^{\text{liq}})^2} = \frac{8T_r}{3v_r^{\text{v}}-1} - \frac{3}{(v_r^{\text{v}})^2},$$

which can be solved for temperature:

$$8T_r = 6 \frac{x^2 - y^2}{\frac{2x}{3-x} - \frac{2y}{3-y}}. \quad (14.6)$$

5 Here $x \in [1, 3)$ and $y \in \langle 0, 1]$ are reduced (molar) densities defined by $x \hat{=} (v_r^{\text{liq}})^{-1}$ and $y \hat{=} (v_r^{\text{v}})^{-1}$.

Vapour–liquid equilibrium (2)

◀ 14 Simple ...

6 Similarly, the fact that the chemical potential is the same in both phases means that

$$T_r \ln\left(\frac{8T_r}{3v_r^{\text{liq}}-1}\right) + \frac{T_r}{3v_r^{\text{liq}}-1} - \frac{9}{4v_r^{\text{liq}}} = T_r \ln\left(\frac{8T_r}{3v_r^{\text{v}}-1}\right) + \frac{T_r}{3v_r^{\text{v}}-1} - \frac{9}{4v_r^{\text{v}}} .$$

7 If we substitute in the temperature from Eq. 14.6 and rewrite the equation in terms of molar density, the equilibrium equation can be expressed as

$$\ln\left(\frac{x(3-y)}{y(3-x)}\right) + \left(1 - \frac{6}{x+y}\right) \frac{3(x-y)}{(3-x)(3-y)} = 0 . \quad (14.7)$$

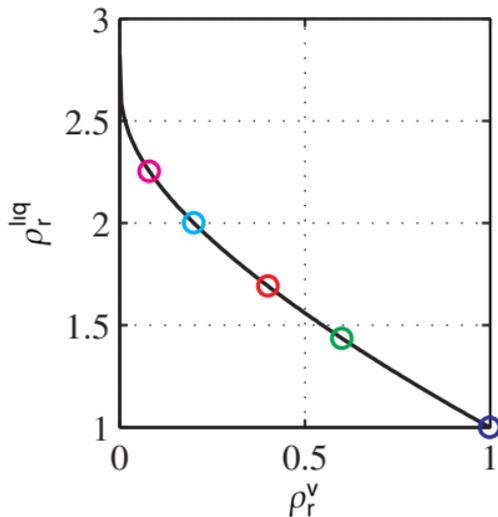
Pressure–potential diagram

[◀ 14 Simple ...](#)

- 1** In order to determine the saturation state of the fluid, we need to solve Eq. 14.7 for $y = y(x)$ or $x = x(y)$.
- 3** The solution is shown graphically in Figure 14.2 on the next page along with a parametrised $p_r(v_r), \mu_r(v_r)$ diagram³.
- 6** Note that the slope of the graph asymptotically approaches -1 as it nears the critical point, where $x_c = y_c = 1$. The average density of the two phases therefore has the constant value $\frac{1}{2}(x + y) \simeq 1$.
- 8** Experimentally it has been demonstrated that the value of $x + y$ is not quite constant, but nevertheless it is virtually a linear function of T_r (hence it is also referred to as the rectilinear density) over a wide range of temperatures.

³ The volume increases from the top right corner down to the bottom left corner of the figure.

Molar density



Pressure–chem.pot.

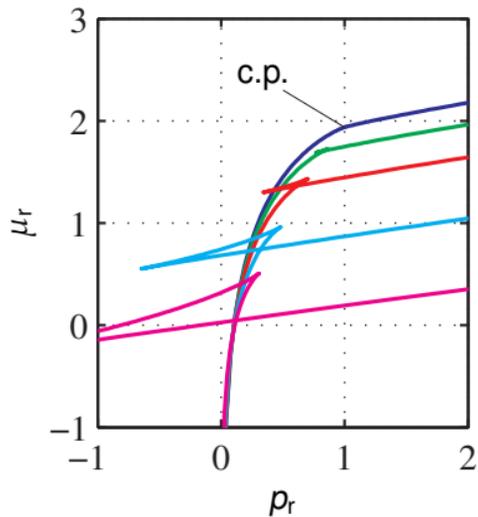


Figure 14.2: ρ_r^v, ρ_r^{liq} saturation graph, with the associated isotherms, expressed in p_r, μ_r coordinates (drawn with volume as the parameter).

Limit $p_r^{\text{VdW}}(T_r \ll 1)$

◀ 14 Simple ...

1 At low temperatures the reduced densities can be expressed as $x = 3 - \alpha$ and $y = \beta$, where α and β are small positive numbers. When substituted into the equilibrium Eq. 14.7 this gives us

$$0 = \ln\left(\frac{(3-\alpha)(3-\beta)}{\beta\alpha}\right) + \left(1 - \frac{6}{3-\alpha+\beta}\right) \frac{3(3-\alpha-\beta)}{\alpha(3-\beta)} \simeq \ln\left(\frac{9}{\beta\alpha}\right) - \frac{3}{\alpha},$$

if only the dominant terms are included.

2 The asymptotic solution $\lim_{T_r \rightarrow 0}(\beta) = \frac{9}{\alpha} \exp\left(\frac{-3}{\alpha}\right)$ shows that the vapour density declines exponentially with falling temperature.

5 Combining these latter two equations allows us to eliminate α , giving us the temperature-explicit form $\lim_{T_r \rightarrow 0} \ln p_r^{\text{VdW}} = \ln 27 - \frac{27}{8} T_r^{-1}$, which conforms to the Clausius–Clapeyron vapour pressure Eq. 14.2, with a slope of $-b = -\frac{27}{8} = -\frac{\Delta_{\text{vap}} h_r}{R}$.

Limit $p_r^{\text{VdW}}(T_r \rightarrow 1)$

◀ 14 Simple ...

1 Near the critical point, the reduced densities can be expressed as $x = 1 + \alpha$ and $y = 1 - \beta$, where α and β are small positive numbers. If we substitute these values into the equilibrium Eq. 14.7 we get

$$\ln\left(\frac{(1+\alpha)(2+\beta)}{(1-\beta)(2-\alpha)}\right) + \left(1 - \frac{6}{2+\alpha-\beta}\right) \frac{3(\alpha+\beta)}{(2-\alpha)(2+\beta)} = 0.$$

3 We can ignore all higher order terms of the kind $\alpha\beta$, α^2 and β^2 :

$$\begin{aligned} 0 &= \alpha + \frac{1}{2}\beta - \left(-\beta - \frac{1}{2}\alpha\right) + \left(1 - \frac{6}{2+\alpha-\beta}\right) \frac{3(\alpha+\beta)}{4+2\beta-2\alpha-\alpha\beta} \\ &\simeq 1 + \left(1 - \frac{6}{2+\alpha-\beta}\right) \frac{1}{2+\beta-\alpha} \\ &= 4 - (\beta - \alpha)^2 + 2 + (\beta - \alpha) - 6 \\ &\simeq \beta - \alpha. \end{aligned} \tag{14.8}$$

Limit $p_r^{\text{VdW}}(T_r \rightarrow 1)$ (2)

◀ 14 Simple ...

4 This implies that $\lim_{T_r \rightarrow 1}(\alpha) = \beta$, which shows that the vapour and liquid densities are symmetrical about the point $x_c = y_c = 1$.

7 By substituting into the temperature Eq. 14.6 we can obtain the limit value

$$\lim_{T_r \rightarrow 1} 8T_r^{\text{VdW}} = 6 \frac{(1+\alpha)^2 - (1-\alpha)^2}{\frac{2(1+\alpha)}{2-\alpha} - \frac{2(1-\alpha)}{2+\alpha}} = 2(4 - \alpha^2), \quad (14.9)$$

which can in turn be substituted into the van der Waals equation, to give us

$$\lim_{T_r \rightarrow 1} p_r^{\text{VdW}} = \frac{8T_r}{\frac{3}{x}-1} - 3x^2 = \frac{2(4-\alpha^2)}{\frac{3}{1+\alpha}-1} - 3(1+\alpha)^2 = 1 - \alpha^2. \quad (14.10)$$

Limit $p_r^{\text{vdW}}(T_r \rightarrow 1)$ (3)

◀ 14 Simple ...

■ If α^2 is eliminated from the last two equations, the saturation pressure can instead be written as a logarithmic function with temperature as its free variable:

$$\lim_{T_r \rightarrow 1} \ln(p_r^{\text{vdW}}) = \ln(4T_r - 3) \simeq 4(T_r - 1).$$

10 If we combine this with the Clausius–Clapeyron vapour pressure Eq. 14.2 we get the slope $\lim_{T_r \rightarrow 1} \partial \ln p_r / \partial (1/T) = -4T_r^2 \geq -4$.

Vapour pressure curve

◀ 14 Simple ...

- 1** The conclusion is that the slope of the vapour pressure curve varies in the range $-4 < -b < -\frac{27}{8}$.
- 3** The van der Waals equation therefore gives us a qualitatively accurate representation of the vapour pressure curve, although from experience we know that the model is insufficiently accurate for quantitative purposes.
- 5** The one-phase region is not adequately represented either, but once again it is qualitatively accurate, as seen in Figure 14.3⁴.

⁴ W. Duschek, R. Kleinrahm, and W. Wagner. *J. Chem. Thermodynamics*, 22:841–864, 1990.

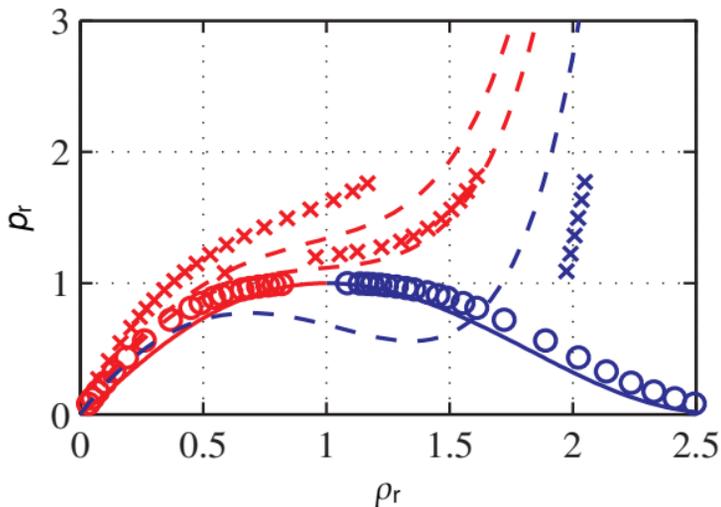


Figure 14.3: The saturation pressure of CO_2 along with selected isotherms in the one-phase region (280 K, 313 K and 330 K respectively). Note the symmetry of the saturation pressure p_r^{sat} around the critical density $\rho_{r,c} = 1$.

Critical phenomena

◀ 14 Simple ...

- 1** At sufficiently low temperatures, the molar density of a liquid approaches a constant value of $\lim_{T_r \rightarrow 0}(x) = 3$.
- 2** As the temperature increases, the liquid phase gradually becomes less significant, until it ceases to exist entirely at the critical point where $\lim_{T_r \rightarrow 1}(x) = \lim_{T_r \rightarrow 1}(y) = 1$.
- 3** In this state there is no fundamental difference between a gas and a liquid.
- 4** This idea is supported by Eq. 14.8, which shows that the density of the two phases is symmetrical about $x_c = y_c = 1$ close to the critical point.

Limit $v_r^{\text{vdW}}(T_r \ll 1)$

◀ 14 Simple ...

1 As previously mentioned, when the temperature approaches zero, the specific volume of the liquid tends to a ratio of $\lim_{T_r \rightarrow 0}(v_r^{\text{vdW}}) = \frac{1}{3}$.

Limit $v_r^{\text{VdW}}(T_r \rightarrow 1)$

◀ 14 Simple ...

1 Close to the critical point, the reduced density of the liquid can be expressed as $x \hat{=} (v_r^{\text{liq}})^{-1} = 1 + \alpha$ where α is a small number, and from Eq. 14.9 we can then derive the asymptotic temperature function:

$$\lim_{T_r \rightarrow 1} (v_r^{\text{liq}})^{\text{VdW}} = \lim_{T_r \rightarrow 1} \frac{1}{1+\alpha} = \frac{1}{1+\sqrt{4-4T_r}} \simeq 1 - 2\sqrt{1-T_r}.$$

Enthalpy of vaporization

◀ 14 Simple ...

1 The enthalpy of the van der Waals fluid can be expressed as $H^{\text{VdW}} = H^{\text{ig}} + H^{r,v}$ where the residual term is

$$\begin{aligned}
 H^{r,v} &= \int_{\infty}^V \left[V \left(\frac{\partial p}{\partial V} \right)_{T,N} + T \left(\frac{\partial p}{\partial T} \right)_{V,N} \right] dV \\
 &= \int_{\infty}^V \left[V \left(\frac{-NRT}{(V-Nb)^2} + \frac{2aN^2}{V^3} \right) + T \left(\frac{NR}{V-Nb} \right) \right] dV \\
 &= \frac{N^2 RTb}{V-Nb} - \frac{2aN^2}{V} .
 \end{aligned}$$

2 We can substitute in the generalised parameters $3b = v_c$, $a = 3p_c v_c^2$ and $8p_c v_c = 3RT_c$, and then rewrite the enthalpy expression in dimensionless form:

$$h_r^{\text{VdW}} \hat{=} \frac{H^{\text{ig}} + H^{r,v}}{NRT_c} = h_r^{\text{ig}} + \frac{T_r}{3v_r - 1} - \frac{9}{4v_r} .$$

Enthalpy of vaporization (2)

◀ 14 Simple ...

3 The ideal gas contribution cancels out when calculating the enthalpy of vaporization:

$$\begin{aligned}\Delta_{\text{vap}} h_r^{\text{VdW}} &= \frac{T_r}{3v_r^y - 1} - \frac{9}{4v_r^y} - \frac{T_r}{3v_r^{\text{liq}} - 1} + \frac{9}{4v_r^{\text{liq}}} \\ &\hat{=} (y - x) \left(\frac{3T_r}{(3-x)(3-y)} - \frac{9}{4} \right).\end{aligned}$$

Limit $\Delta_{\text{vap}} h_r^{\text{VdW}}(T_r \ll 1)$

◀ 14 Simple ...

1 In practice, the low-temperature limit $\lim_{T_r \rightarrow 0}(\Delta_{\text{vap}} h_r^{\text{VdW}}) = \frac{27}{8}$ can never be reached, because most liquids freeze at a temperature of $T_r \approx 0.7$. Table 14.4 on the following page therefore gives a comparison with the heat of vaporization⁵ measured at the normal boiling point.

⁵ Robert C. Reid, John M. Prausnitz, and Thomas K. Sherwood. *The Properties of Gases and Liquids*. McGraw-Hill, 3rd edition, 1977.

Figure 14.4: Enthalpy of vaporization at the normal boiling point compared with $\Delta_{\text{vap}}h_r^{\text{VdW}} = \frac{27}{8} = 3.375$ calculated from the van der Waals equation.

	$\frac{T_b}{[\text{K}]}$	$\frac{T_c}{[\text{K}]}$	$\frac{\Delta_{\text{vap}}h}{[\text{cal/mol}]}$	$\frac{\Delta_{\text{vap}}h}{RT_c}$	$\frac{\Delta_{\text{vap}}h^{\text{VdW}}}{[\text{cal/mol}]}$
N ₂	77.35	126.2	1333	5.32	846
Ar	87.27	150.8	1560	5.21	1011
O ₂	90.17	154.6	1630	5.31	1037
CH ₄	111.66	190.4	1955	5.17	1277
Kr	119.74	209.4	2309	5.55	1404
H ₂ O	373.15	647.3	9717	7.55	4341

Limit $\Delta_{\text{vap}} h_r^{\text{VdW}}(T_r \rightarrow 1)$

◀ 14 Simple ...

1 Close to the critical point, the reduced densities can be expressed as $x = 1 + \alpha$ and $y = 1 - \beta$, where α and β are small positive numbers:

$$\Delta_{\text{vap}} h_r^{\text{VdW}} = -(\alpha + \beta) \left(\frac{3T_r}{(2-\alpha)(2+\beta)} - \frac{9}{4} \right).$$

2 Now let us substitute in $\lim_{T_r \rightarrow 1}(\beta) = \alpha$ and $\lim_{T_r \rightarrow 1}(4T_r) = 4 - \alpha^2$ from Eq. 14.9:

$$\lim_{T_r \rightarrow 1} \Delta_{\text{vap}} h_r^{\text{VdW}} = -2\alpha \left(\frac{3T_r}{4 - \alpha^2} - \frac{9}{4} \right) = 6 \sqrt{1 - T_r}.$$

Critical exponents

◀ 14 Simple ...

- 1** In Section 48 on page 325 we showed that the van der Waals equation can be written in its reduced form without the use of any arbitrary model parameters.
- 5** This results in a useful form of the equation of state, which we have used in this chapter to analyse the fluid's behaviour in a number of interesting limit cases.
- 6** Nevertheless, Figure 14.3, to give a specific example, shows that the theory is by no means universally applicable.
- 7** In this section we will look in greater detail at what happens close to the critical point, and quantify to what extent the van der Waals equation fails to predict experimental results.

Critical exponents (2)

[◀ 14 Simple ...](#)

8 It has been theoretically proven — and experimentally confirmed — that the energy surface close to the critical point of a vapour–liquid equilibrium is of a universal form, which is parametrised by what we call an *order parameter*.

15 For vapour–liquid equilibria, it is natural to use $|\rho_r - 1|$ as an order parameter, provided that it produces symmetrical phase transitions⁶, which it indeed does.

17 Outside the two-phase region (using values along the fluid's critical isochore moving towards the critical point) it is possible to observe a gradual phase transition in the fluid.

18 The closer we get to the critical point, the more anomalous the behaviour of the fluid.

Critical exponents (3)

◀ 14 Simple ...

22. In the literature for this field, which incidentally covers a large and exciting range of research⁷, the critical anomalies of the fluid are expressed using divergence formulae:

$$\text{One phase, } \rho_r = 1 : \quad c_v \propto (T_r - 1)^{-\alpha}, \quad (14.11)$$

$$\text{One phase, } \rho_r = 1 : \quad \left(\frac{\partial \rho_r}{\partial p_r}\right)_{T_r} \propto (T_r - 1)^{-\gamma}, \quad (14.12)$$

$$\text{Critical, } T_r = 1 : \quad |\rho_r - 1| \propto |\rho_r - 1|^{+\delta}, \quad (14.13)$$

$$\text{Two phases, } T_r < 1 : \quad |\rho_r - 1| \propto (1 - T_r)^{+\beta}. \quad (14.14)$$

⁶ The theory applies to all phase equilibria that have a single (scalar) order parameter. For example, ferromagnetic materials display relatively analogous behaviour, which is described by the order parameter $|M_r - 1|$, where M is the magnetisation of the substance.

⁷ Kenneth G. Wilson received the Nobel prize in 1982 for his contribution to the development of renormalisation groups applied to, amongst other things, critical phase tran-

Isochoric heat capacity (α)

◀ 14 Simple ...

1 Eliminating s gives us $c_v = -RT_r(\partial^2 a_r / \partial T_r \partial T_r)_{v_r}$. In other words, the heat capacity of the fluid gives us the second derivative of Helmholtz energy.

4 For a van der Waals fluid, we can obtain the Helmholtz energy by combining Eq. 14.5 with equations 14.3 and 14.4.

5 Double differentiation of a_r with respect to T_r gives us

$$c_v^{\text{VdW}} = -RT_r \left(\frac{\partial^2 \mu_r^\circ}{\partial T_r \partial T_r} + \frac{1}{T_r} \right) = c_p^\circ - R = c_v^\circ(T).$$

9 We can therefore conclude that $\alpha^{\text{VdW}} = 0$ in Eq. 14.11.

Bulk modulus (γ)

◀ 14 Simple ...

1 The van der Waals equation expressed in reduced T_r, v_r coordinates was discussed in Section 48. Here we need the same equation, but this time as a function of T_r and ρ_r :

$$\rho_r^{\text{VdW}} = \frac{8T_r}{3v_r-1} - \frac{3}{v_r} \hat{=} \frac{8T_r\rho_r}{3-\rho_r} - 3\rho_r^2$$

2 Let us differentiate the pressure with respect to density, and rearrange the resulting equation in such a way as to isolate $T_r - 1$ in one of the numerators:

$$\lim_{\rho_r \rightarrow 1} \left(\frac{\partial \rho_r}{\partial \rho_r} \right)_{T_r}^{\text{VdW}} = 24 \left(\frac{T_r-1}{(3-\rho_r)^2} + \underbrace{\frac{1}{(3-\rho_r)^2} - \frac{\rho_r}{4}}_0 \right) = 6(T_r - 1)$$

3 The exponent of the expression on the right side of the equation is 1 which means that $\gamma^{\text{VdW}} = 1$ (not -1) in Eq. 14.12. ■

Critical isotherm (δ)

◀ 14 Simple ...

- 1** We will start out from the van der Waals equation expressed as a function of T_r and ρ_r , just as we did for the bulk modulus.
- 2** Along the critical isotherm, the equation of state can be factored as follows:

$$\lim_{T_r \rightarrow 1} (p_r^{\text{VdW}} - 1) = \frac{3}{3 - \rho_r} (\rho_r - 1)^3$$

- 3** That gives us $\delta^{\text{VdW}} = 3$ in Eq. 14.13. In other words, the critical isotherm describes a third-degree curve with its origin at the critical point. ■

Phase envelope (β)

◀ 14 Simple ...

1 Based on our discussion of phase equilibrium problems in Section 14.1, and with particular reference to Eq. 14.10, it follows that:

$$2(\rho_r - 1) = \pm(1 - T_r)^{0.5}.$$

2 The vapour pressure curve describes a parabola with the order parameter $\rho_r - 1$, which means that $\beta^{\text{vdW}} = 0.5$ in Eq. 14.14.

Figure 14.5: Critical exponents measured experimentally for selected compounds compared with the classical values calculated from the van der Waals equation of state.

System	α	γ	δ	β
Van der Waals	0	1	3	0.5
Ising 3D ⁸²	0.110(1)	1.237(2)	4.789(2)	0.326(5)
Heisenberg 3D ⁹²	-.1336(2)	1.3960(9)	4.783(3)	0.3689(3)
Ni, Fe, Gd ₂ BrC, Gd ₂ IC, Tl ₂ Mn ₂ O ₇ , ... ¹⁰²	-.1336(2)	1.3960(9)	4.783(3)	0.3689(3)
³ He, ⁴ He, Xe, CO ₂ , H ₂ O, O ₂ ¹¹²	0.10(0)	1.19(0)	4.35(0)	0.35(5)

¹²² J. M. H. Levelt Sengers and J. V. Sengers. *Phys. Rev. A*, 12(6):2622–2627, 1975.

Critical point measurements

◀ 14 Simple ...

- 1** Table 14.5 gives a summary of what we have learned so far about phase transitions and how they relate to the van der Waals equation.
- 3** What is surprising is that the experimental values do not diverge; instead they suggest that physical quantities exhibit certain universal behaviour during phase transitions.
- 8** What we can say for sure is that there is no equation with an analytical solution that accurately describes critical phenomena in nature. In other words, the critical exponents are neither integers ($z \in \mathbb{Z}$) nor simple fractions ($q \in \mathbb{Q}$).
- 13** The simplest special case is a gas in which the molecules are constantly moving around without colliding or interacting with each other in any way. That is what we mean by an ideal gas.

Critical point measurements (2)

◀ 14 Simple ...

15 The second special case is a system in which the molecules (or atoms) are arranged in a repeating lattice with long-range order. That is what we mean by a crystalline structure.

17 The third special case only arises in conjunction with phase transitions.

18 Here the correlation length varies over several orders of magnitude, which means that this phenomenon is much more significant than the contributions from the intermolecular forces in the fluid.

19 At the critical point, the correlation length is of the same order of magnitude as the system itself, or at least big enough to interfere with the wavelength of visible light.

Critical point measurements (3)

◀ 14 Simple ...

27 The conclusion is that theory and practice agree, but that the van der Waals equation (like other equations of state with analytical solutions) produces inaccurate estimates of the critical exponents.

28 However, the principle that the critical phenomena display universal scaling behaviour holds true, and there is in fact a general rule that applies to phase transitions in all substances, as stated in equations 14.11–14.14. Moreover, we also know that

$$\alpha = 2 - \beta(\delta + 1)$$

$$\gamma = \beta(\delta - 1)$$

§ 110

◀ § 109

▶ § 111

◀ 14 Simple ...

At 101 K nitrogen has the following saturation state: $p = 8.344$ bar, $\rho^{\text{liq}} = 24.360 \text{ mol dm}^{-3}$ and $\rho^{\text{v}} = 1.222 \text{ mol dm}^{-3}$. The critical point exists at $p_c = 34.000$ bar, $\rho_c = 11.210 \text{ mol dm}^{-3}$ and $T_c = 126.2$ K. Calculate the saturation state expressed in reduced coordinates and draw your result onto the graph $p_r^{\text{vdW}} = f(T_r, v_r)$; also see Section 48 on page 325. Comment on the discrepancy between the calculated volumes of vapour and liquid and the experimental values.

§ 110 Maxwell equal area rule I

[◀ 14 Simple ...](#)

- 1** The results calculated from the Van der Waals equation have been drawn in reduced coordinates in Figure 14.6 on the following page using the Matlab program 30:1.8.
- 2** Note that the equation overestimates the volume of N_2 in the liquid phase.
- 5** Also note that the areas above and below the phase boundary line ($T_r = 0.8$) based on experimental values are roughly equal.

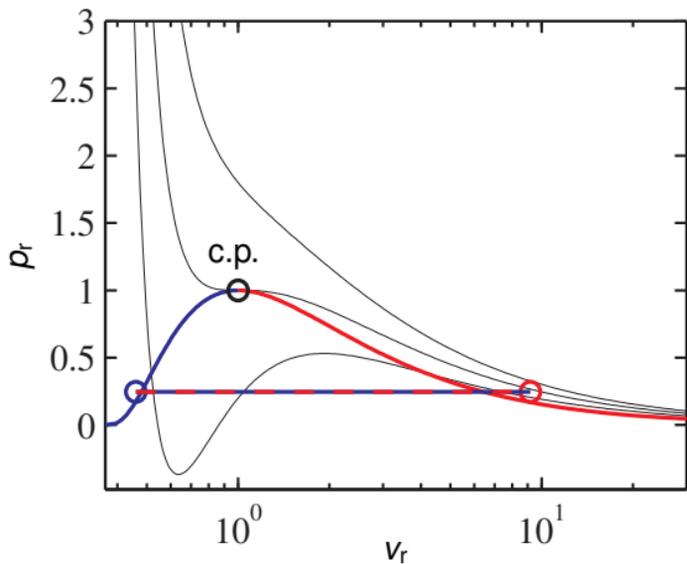


Figure 14.6: The van der Waals equation of state expressed in p_r, v_r coordinates for $T_r = \{0.8, 1.0, 1.2\}$. The horizontal line shows the experimentally established two-phase region for nitrogen at $T_r = 0.8$.

§ 111

◀ § 110

▶ § 112

◀ 14 Simple ...

The Maxwell equal area rule can be expressed as $\int_{V^{\text{liq}}}^{V^{\text{v}}} (p - p_{\text{sat}}) (dV)_{T,N} = 0$ and be plotted on a figure equivalent to 14.6, but with the ordinary volume and pressure along the axes. Show that this equation actually holds for a one-component phase equilibrium.

§ 111 Maxwell equal area rule II

◀ 14 Simple ...

1 The integral along this isotherm can be expressed as follows:

$$\begin{aligned}
 \int_{V^{\text{liq}}}^{V^{\text{v}}} (p - p_{\text{sat}}) (dV)_{T_{\text{sat}}, N} &= - \int_{V^{\text{liq}}}^{V^{\text{v}}} \left[\left(\frac{\partial A}{\partial V} \right)_{T, n} + p_{\text{sat}} \right] dV \\
 &= A^{\text{liq}} - A^{\text{v}} - p_{\text{sat}} (V^{\text{v}} - V^{\text{liq}}) \\
 &\stackrel{?}{=} 0.
 \end{aligned} \tag{14.15}$$

3 Since the system only has one chemical component, it must also be true that $A = -pV + \mu N$. Moreover, when the vapour and liquid phases are in equilibrium, $p^{\text{liq}} = p^{\text{v}} = p_{\text{sat}}$. Hence the equality in 14.15 can be simplified to

$$(\mu N)^{\text{liq}} \stackrel{?}{=} (\mu N)^{\text{v}}. \tag{14.16}$$

§ 111 Maxwell equal area rule II (2)

◀ 14 Simple ...

It then follows that

$$\mu^{\text{liq}} = \mu^{\text{v}},$$

which is identical to the phase equilibrium criterion for a one-component system.

§ 112

◀ § 111

▶ § 113

◀ 14 Simple ...

The necessary conditions for thermodynamic equilibrium in a closed system with only one chemical component, at a given temperature T , total volume $V = V^v + V^{liq}$ and total composition $N = N^v + N^{liq}$, are

$$A_{eq} = \min_{\mathbf{v}, \mathbf{n}} A(T, \mathbf{v}, \mathbf{n}),$$

$$\mathbf{e}\mathbf{v} = V,$$

$$\mathbf{e}\mathbf{n} = N.$$

Here $\mathbf{e} \hat{=} [1 \ 1]$, $\mathbf{v}^T \hat{=} [V^v \ V^{liq}]$ and $\mathbf{n}^T \hat{=} [N^v \ N^{liq}]$. As was mentioned at the start of this chapter, $p^v = p^{liq}$ and $\mu^v = \mu^{liq}$ are necessary conditions for equilibrium.

§ 112

◀ § 111

▶ § 113

(2)

◀ 14 Simple ...

Show that this is the case. Illustrate the energy surface using a ρ, A diagram where $\rho_r \hat{=} v_r^{-1} \in \langle 0, 3 \rangle$.

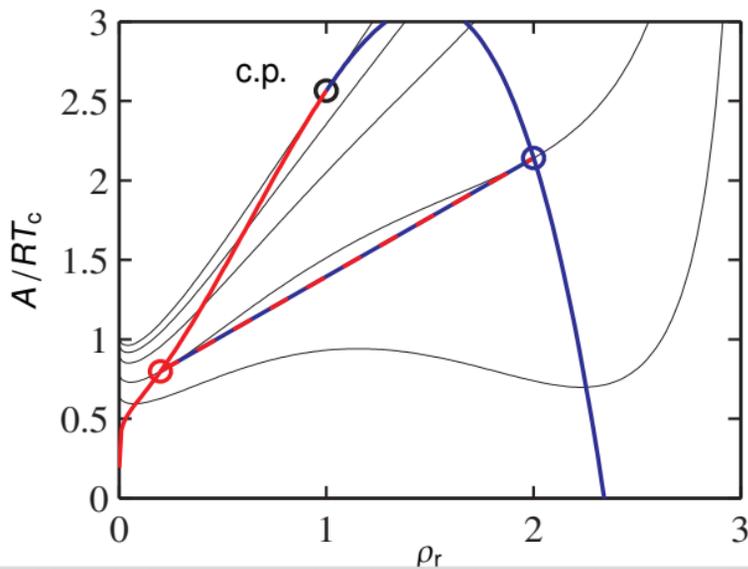


Figure 14.7: Helmholtz energy for the isotherms shown in Figure 14.2 on page 708. The equilibrium state (the tangent plane at minimum energy) is given for the second lowest isotherm. Note that the standard state has been chosen for the purposes of clarity, and varies for each isotherm. The parabolic curve indicates the system's phase boundaries.

§ 112 Minimum of Helmholtz energy

◀ 14 Simple ...

1 A necessary—but not sufficient—condition for thermodynamic equilibrium is that $(dA)_T = 0$ for variations in the extensive variables V^v, N^v and V^{liq}, N^{liq} . Taking the total differential for both phases gives us

$$\begin{aligned}(dA)_T &= (dA)_T^v + (dA)_T^{liq} \\ &= -p^v dV^v + \mu^v dN^v - p^{liq} dV^{liq} + \mu^{liq} dN^{liq} \\ &= 0.\end{aligned}$$

2 The limits on the volume and mole number of the closed system mean that $dV^{liq} = -dV^v$ and $dN^{liq} = -dN^v$. Substituted into the differential of A that gives us

$$(dA)_T = -(p^v - p^{liq}) dV^v + (\mu^v - \mu^{liq}) dN^v = 0.$$

§ 112 Minimum of Helmholtz energy (2)

[◀ 14 Simple ...](#)

- 3** Since dV^v and dN^v are independent variables, then it must be the case that $p^v = p^{liq}$ and $\mu^v = \mu^{liq}$, which is what we needed to show.
- 4** Figure 14.7 shows selected isotherms in the requested ρ, A diagram, along with the saturation curve of the fluid (see Matlab-program 30:1.10).

Tangent plane

◀ 14 Simple ...

- 1** Note that the minimum free energy along each isotherm is not in any way related to the equilibrium state.
- 2** Helmholtz energy is a function of the standard state of the fluid, and since standard state properties do not have absolute values, the minimum of the function won't be an absolute value either.
- 4** The equilibrium state is therefore characterised by having two points on a single isotherm that can be connected by a line that is entirely below the rest of the function surface (the graph).
- 5** From a geometrical point of view, this condition will be met if the two points have a common tangent.

Part 15

Multicomponent Phase Equilibrium

← see also Part-Contents

Contents

1 Direct substitution

2 Newton–Raphson iteration

3 Chemical potential versus K -value

- 1 Equal fugacity models in both phases
- 2 Equal activity models in both phases
- 3 Mixed use of fugacity and activity models
- 4 Mixed use of activity models in the phases

4 Convergence properties

Minimum energy

◀ 15 Multicomponent ...

- 1 At thermodynamic equilibrium the system has reached a state of minimum energy.
- 3 In Chapter 16 on page 820 it is for example 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.
- 5 If the volume is kept constant and the pressure is varied the Helmholtz energy will be minimised.
- 6 Chapter 14 on page 698 illustrates this for the case of a simple vapour-liquid equilibrium.

ω phases

◀ 15 Multicomponent ...

1 In general we shall investigate a closed system consisting of $\pi = \alpha, \beta, \dots, \psi, \omega$ phases¹ and a set of $i = 1, 2, \dots, n$ components which are common to all the phases.

3 For the special case of constant temperature and pressure $(dG)_{T,p,n} = \sum_{\pi=\alpha}^{\omega} \sum_{i=1}^n \mu_i^{\pi} dN_i^{\pi} = 0$ is a *necessary* condition for thermodynamic equilibrium.

4 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.

ω phases (2)

◀ 15 Multicomponent ...

6 The thermodynamic equilibrium criterion is then simplified to:

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

$$dN_i^\alpha + dN_i^\beta = 0.$$

Elimination of dN_i^β makes $(dG)_{T,p,n} = \sum_{i=1}^n (\mu_i^\alpha - \mu_i^\beta) dN_i^\alpha = 0$.

7 In the vicinity of an equilibrium point all the dN_i^α are independent quantities² and the equilibrium relationship is equivalent to:

$$\mu_i^\alpha = \mu_i^\beta, \quad \forall i \in [1, n]. \quad (15.1)$$

¹ Phase α is usually the low temperature phase and $\beta, \dots, \psi, \omega$ are phases that become stable at successively increasing temperatures.

² At equilibrium dN_i^α 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.

§ 113

◀ § 112

▶ § 114

◀ 15 Multicomponent ...

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

$$U_{\text{eq}} = \min_{\mathbf{s}, \mathbf{v}, \mathbf{n}_i} U(\mathbf{s}, \mathbf{v}, \mathbf{n}_1, \dots, \mathbf{n}_n),$$

$$\mathbf{e}\mathbf{s} = S,$$

$$\mathbf{e}\mathbf{v} = V,$$

$$\mathbf{e}\mathbf{n}_i = N_i, \quad \forall i \in [1, n],$$

§ 113

◀ § 112

▶ § 114

(2)

◀ 15 Multicomponent ...

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.

§ 113 Phase equilibrium

◀ 15 Multicomponent ...

1 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^π , V^π and N_i^π :

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

4 The variations in S^π , V^π and N_i^π must therefore be constrained such that the total entropy, volume and mole numbers (of each component) are conserved:

$$\sum_{\pi=\alpha}^{\omega} dS^\pi = 0,$$

$$\sum_{\pi=\alpha}^{\omega} dV^\pi = 0,$$

§ 113 Phase equilibrium (2)

◀ 15 Multicomponent ...

$$\sum_{\pi=\alpha}^{\omega} dN_i^{\pi} = 0, \quad \forall i \in [1, n].$$

6 Substituted into the differential of U :

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

8 If $(dU)_{S,V,n} = 0$ then it must be true that:

$$\begin{aligned} T^{\alpha} &= T^{\beta} = \dots = T^{\psi} = T^{\omega}, \\ p^{\alpha} &= p^{\beta} = \dots = p^{\psi} = p^{\omega}, \\ \mu_1^{\alpha} &= \mu_1^{\beta} = \dots = \mu_1^{\psi} = \mu_1^{\omega}, \\ &\vdots \\ \mu_n^{\alpha} &= \mu_n^{\beta} = \dots = \mu_n^{\psi} = \mu_n^{\omega}. \end{aligned}$$

§ 113 Phase equilibrium (3)

Gibbs' phase rule

◀ 15 Multicomponent ...

- 1 Despite the fact that temperature, pressure and chemical potentials are uniform at thermodynamic equilibrium we cannot specify these variables directly.
- 2 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.

- 3 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.

K -values

◀ 15 Multicomponent ...

- 1** Vapour–liquid equilibria are frequently calculated by an iterative method which is due to Rachford and Rice³.
- 2** 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

$$x_i^\beta \hat{=} K_i x_i^\alpha, \quad \forall i \in [1, n], \quad (15.2)$$

where x_i^α and x_i^β are the mole fractions of component i in α (liquid) and β (vapour) respectively.

- 3** 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.
- 5** The total mass balance is $N^\alpha + N^\beta = N$ and the component balances can be written $x_i^\alpha N^\alpha + x_i^\beta N^\beta = N_i$.

K -values (2)

◀ 15 Multicomponent ...

6 Elimination of N^β produces $x_i^\alpha N^\alpha + x_i^\beta (N - N^\alpha) = N_i$ and a subsequent substitution of x_i^β from Eq. 15.2 yields:

$$x_i^\alpha = \frac{N_i}{N^\alpha + K_i(N - N^\alpha)} = \frac{z_i}{z^\alpha + K_i z^\beta} \quad (15.3)$$

³ H. H. Rachford and J. D. Rice. *Trans. Am. Inst. Min., Metall. Pet. Eng.*, 195:327–328, 1952.

Rachford–Rice

◀ 15 Multicomponent ...

1 The corresponding expression for x_i^β is

$$x_i^\beta = \frac{K_i N_i}{N^\alpha + K_i(N - N^\alpha)} = \frac{K_i z_i}{z^\alpha + K_i z^\beta}, \quad (15.4)$$

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 .

2 Note that the right hand sides of Eqs. 15.3 and 15.4 contain a single unknown variable z^α , or equivalently $z^\beta = 1 - z^\alpha$.

Rachford–Rice (2)

◀ 15 Multicomponent ...

4 Summing up x_i^α and x_i^β from Eqs. 15.3 and 15.4 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^α using a Newton–Raphson iteration:

$$z^{\alpha,k+1} = z^{\alpha,k} - \left(\frac{\partial f}{\partial z^\alpha}\right)^{-1} f = z^{\alpha,k} + \left(\sum_{i=1}^n f_i^2 z_i\right)^{-1} f. \quad (15.5)$$

5 The recursion formula makes a new $z^{\alpha,k+1}$ available, which on back-substitution into Eqs. 15.3 and 15.4 produces new values of x_i^α and x_i^β .

Rachford–Rice (3)

◀ 15 Multicomponent ...

6 These updates (hopefully) improve the K_j -values, and subsequent iterates in Eq. 15.5 converge finally to the equilibrium state.

§ 114

◀ § 113

▶ § 115

◀ 15 Multicomponent ...

Computerise the function $[\mathbf{x}^\alpha, \mathbf{x}^\beta, z^\alpha] = \text{TpKvalue}(\mathbf{n}, \mathbf{k})$
using Eq. 15.5 as your reference algorithm.

§ 114 Rachford-Rice

◀ 15 Multicomponent ...

- 1 See Matlab function 2.6 in Appendix 30.
- 3 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 .
- 5 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.

Algorithm

[◀ 15 Multicomponent ...](#)

- 1** A fixed derivative sign means that there is at most one solution in the domain $z^\alpha \in [0, 1]$.
- 5** First, Eq. 15.5 is solved with respect to z^α at given or estimated K_i (inner loop).
- 6** The phase compositions are then updated by the Eqs. 15.3 and 15.4 before new K_i -values can be calculated (outer loop).
- 7** The double iteration procedure is repeated until the phase compositions x_i^α and x_i^β have converged.

Newton–Raphson

◀ 15 Multicomponent ...

- 1** Contrary to the K -value method of Rachford–Rice, the Newton⁴–Raphson⁵s method fulfills the mass balance in every iteration.
- 2** This requires a feasible starting point where $\mathbf{n}^\alpha + \mathbf{n}^\beta = \mathbf{n}$ is fulfilled.
- 3** The Newton–Raphson iteration of Eq. 15.1 is then,

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

$$-\Delta N_j^\beta = \Delta N_j^\alpha,$$

or on matrix form:

$$\mu^\alpha + \mathbf{G}^\alpha \Delta \mathbf{n}^\alpha = \mu^\beta + \mathbf{G}^\beta \Delta \mathbf{n}^\beta,$$

$$-\Delta \mathbf{n}^\beta = \Delta \mathbf{n}^\alpha.$$

⁴ Sir Isaac Newton, 1642–1727 by the Julian calendar. English physicist and mathematician.

Algorithm

◀ 15 Multicomponent ...

1 The matrix $\mathbf{G} \hat{=} \{(\partial^2 G / \partial N_i \partial N_j)_{T,p}\}$ is the Hessian⁶ 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 .

2 The Newton–Raphson equations can be combined into

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

or even better: $\Delta \mathbf{n}^\alpha = -\mathbf{H}^{-1} \Delta \mu$ where $\mathbf{H} \hat{=} \mathbf{G}^\alpha + \mathbf{G}^\beta$ and $\Delta \mu \hat{=} \mu^\alpha - \mu^\beta$.

4 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 $\mathbf{n}^{\beta,k+1} = \mathbf{n}^{\beta,k} - \Delta \mathbf{n}^\alpha > \mathbf{0}$.

Algorithm (2)

◀ 15 Multicomponent ...

5 If the relations are violated it is mandatory to shorten the step size according to

$$\Delta n^\alpha = -\tau \mathbf{H}^{-1} \Delta \mu, \quad (15.6)$$

where $\tau \in \langle 0, 1 \rangle$ is calculated such that all the updated mole numbers are positive.

6 In this way we can ensure that the mass balance is fulfilled in every iteration.

7 The Newton–Raphson method converges to a state where $\Delta \mu = \mathbf{0}$, but note that the phase models have not been taken into account yet.■

⁶ Ludwig Otto Hesse, 1811–1874. German mathematician.

Ideal mixture Hessian

◀ 15 Multicomponent ...

1 In summary it means that ideal mixing is assumed in the calculation of \mathbf{H} while $\Delta\mu$ is calculated rigorously. From the definition of an ideal mixture we can write,

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

where the Kronecker⁷ delta function $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ else.

Ideal mixture Hessian (2)

◀ 15 Multicomponent ...

4 On matrix form this formula is written — see also Paragraph 12 on page 81 in Chapter 3 on page 56:

$$\mathbf{G}^{\text{d}} = RT(\mathbf{n}^{-\text{D}} - N^{-1}\mathbf{e}\mathbf{e}^{\text{T}}),$$

$$\mathbf{e} = (1, 1, \dots, 1)^{\text{T}},$$

5 Here, $\mathbf{n}^{-\text{D}}$ is an (inverted) diagonal matrix having $1/N_i$ along the main diagonal.

7 From the definition $\mathbf{H} \hat{=} \mathbf{G}^{\alpha} + \mathbf{G}^{\beta}$ it follows:

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

⁷ Leopold Kronecker, 1823–1891. German mathematician.

Sherman–Morrison

◀ 15 Multicomponent ...

1 The matrix $(\mathbf{n}^\alpha)^{-D} + (\mathbf{n}^\beta)^{-D}$ 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 $(N^\alpha + N^\beta) / (N^\alpha N^\beta)$.

2 This makes the following factorisation of \mathbf{H}^{d} possible:

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

or,

$$\begin{aligned} \frac{N^\alpha + N^\beta}{RT} \mathbf{H}^{\text{d}} &= \frac{1}{z^\alpha z^\beta} (\mathbf{D}^{-1} - \mathbf{e}\mathbf{e}^T), \\ \mathbf{D}^{-1} &\hat{=} \text{diag} \left(\frac{z_i}{x_i^\alpha x_i^\beta} \right), \end{aligned} \quad (15.7)$$

where z^α and z^β are phase fractions, x_i^α and

3 As usual x_i^β are component mole fractions, and z_i is the feed mole fraction of component i .

Sherman–Morrison (2)

◀ 15 Multicomponent ...

- 4** Eq. 15.7 indicates that \mathbf{H} is a rank one update of \mathbf{D} .
- 5** The inverse of \mathbf{H} can then be calculated from the Sherman–Morrison formula $(\mathbf{D}^{-1} - \mathbf{e}\mathbf{e}^T)^{-1} = \mathbf{D} + (1 - \mathbf{e}^T\mathbf{D}\mathbf{e})^{-1}\mathbf{D}\mathbf{e}\mathbf{e}^T\mathbf{D}$, or, equivalently, if we define $\mathbf{d} \hat{=} \mathbf{D}\mathbf{e}$:

$$\frac{RT}{N^\alpha + N^\beta} (\mathbf{H}^{\text{d}})^{-1} = z^\alpha z^\beta (\mathbf{D} + (1 - \mathbf{e}^T \mathbf{d})^{-1} \mathbf{d} \mathbf{d}^T). \quad (15.8)$$

Simplified algorithm

◀ 15 Multicomponent ...

1 From Eqs. 15.6 and 15.8 it is possible to express the simplified two-phase Newton–Raphson method as

$$\frac{\Delta n^\alpha}{N^\alpha + N^\beta} = -z^\alpha z^\beta \left(\mathbf{D} + \frac{1}{1 - \mathbf{d}^T \mathbf{e}} \mathbf{d} \mathbf{d}^T \right) \frac{\Delta \mu}{RT} . \quad (15.9)$$

2 Note that z^α , z^β , \mathbf{d} , \mathbf{D} and $\Delta \mu / RT$ are dimensionless variables.

3 This makes the iteration sequence independent of the system size for a given total composition \mathbf{z} .

4 We may therefore scale the system⁸ such that $N^\alpha + N^\beta = 1$ without affecting the mole fractions in the phases α and β .

⁸ This is just another example on the special properties of extensive functions.

§ 115

◀ § 114

▶ § 116

◀ 15 Multicomponent ...

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 $(\mathbf{A} - \mathbf{u}\mathbf{v}^T)^{-1}$.

§ 115 Sherman–Morrison

◀ 15 Multicomponent ...

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

§ 116

◀ § 115

▶ § 117

◀ 15 Multicomponent ...

Computerise the function $[\mathbf{x}^\alpha, \mathbf{x}^\beta, z^\alpha] = \text{TpNewton}(\mathbf{n}, \mathbf{k})$
using Eq. 15.9 as your reference algorithm.

§ 116 Newton–Raphson iteration

◀ 15 Multicomponent ...

- 1 See Matlab function 2.7 in Appendix 30.
- 3 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 .
- 4 This makes it possible to iterate on non-ideal equilibrium states by supplying two fugacity (activity) coefficient models u and v .

K_i versus μ_i

◀ 15 Multicomponent ...

- 1** The Rachford–Rice procedure spends time on calculating K -values while the Newton–Raphson method deals directly with chemical potentials.
- 2** However, because the two methods aim at solving the same problem there must be a rational connection between them.
- 3** The purpose of this section is to show that (and how) Eq. 15.1 on page 750 can be used to derive some useful relations between K_i and $\Delta\mu_i$.

Fugacity / fugacity

◀ 15 Multicomponent ...

1 For fluid $p(V, T)$ equations of state $\mu_i^\circ(T, p_o)$ is defined as the chemical potential of a pure ideal gas at the temperature T and pressure p_o .

2 The same standard state applies to both of the phases and from $\mu_i^\alpha = \mu_i^\beta$ it is conventionally written

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

where the left side stands for μ_i^α and the right side stands for μ_i^β .

Fugacity / fugacity (2)

◀ 15 Multicomponent ...

3 The quantity $\Delta\mu_i/RT$ which appears in Eq. 15.9 is then

$$\frac{\Delta\mu_i}{RT} \hat{=} \frac{\mu_i^\alpha - \mu_i^\beta}{RT} = \ln\left(\frac{K_i^{\text{eos}} x_i^\alpha}{x_i^\beta}\right), \quad (15.10)$$

where K_i^{eos} is defined as the ratio between the fugacity coefficients φ_i^α and φ_i^β :

$$K_i^{\text{eos}} = \frac{\varphi_i^\alpha}{\varphi_i^\beta}. \quad (15.11)$$

4 In the context of being an equilibrium constant the K -value 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.

§ 117

◀ § 116

▶ § 118

◀ 15 Multicomponent ...

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 T_pK value or T_p Newton.

§ 117 Natural gas

◀ 15 Multicomponent ...

- 1** The phase diagram of a typical, albeit synthetic, natural gas⁹ is illustrated in Figure 15.1 on the following page.
- 2** The calculations are shown in Matlab program 30:1.22.
- 3** 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).

⁹ Mario H. Gonzalez and Anthony L. Lee. *J. Chem. Eng. Data*, 13(2):172–176, April 1968.

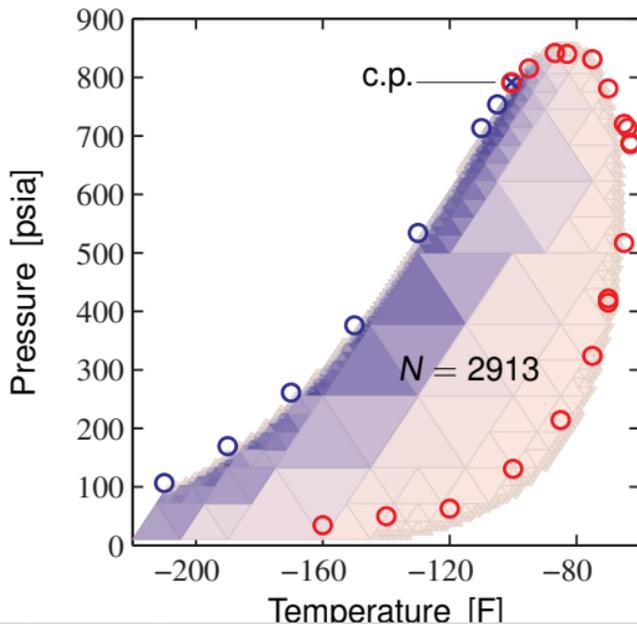


Figure 15.1: Phase diagram of nitrogen–methane–ethane–propane– n -butane put together from a total of 6093 triangular patches using a recursive *divide-and-conquer* algorithm (each triangle is split into four smaller ones until all the vertices are in the same phase domain).

§ 118

◀ § 117

▶ § 119



◀ 15 Multicomponent ...

Show that the Lewis mixing rule is exact if Amagat¹⁰s law $V^{\text{ex}} = 0$ is valid over the entire composition and pressure $[0, p]$ range.

¹⁰ Émile Hilaire Amagat, 1841–1915. French chemist.

§ 118 Lewis¹¹ mixing rule

◀ 15 Multicomponent ...

1 $V^{\text{ex}} = 0$ means that $V = \sum_{i=1}^n v_i(T, p)N_i$.

2 The fugacity coefficient is defined by the Eqs. 13.12 and 13.13, see page 665. 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 φ_i depends on temperature and pressure only because the partial molar volume is independent of composition.

¹⁰ Gilbert Newton Lewis, 1875–1946. American chemist.

Activity / activity

◀ 15 Multicomponent ...

- 1** In Eq. 15.11 it is common that α is the liquid phase and β the vapour phase, but this is just one out of many possibilities.
- 2** We could alternatively assume that α and β are two near-critical fluids being something in between a vapour and a liquid, or two well-defined liquid phases.
- 7** If this is the case it is no longer necessary to integrate all the way from the ideal gas in Eq. 15.11 but rather use the pure component properties as a reference.
- 8** In practise this means that the *fugacity coefficients* can be replaced by *activity coefficients*:

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

Activity / activity (2)

◀ 15 Multicomponent ...

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

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



§ 119

[◀ § 118](#)[▶ § 120](#)[◀ 15 Multicomponent ...](#)

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.

§ 119 Phase separation

◀ 15 Multicomponent ...

- 1** The phase diagram of cyclohexane–cyclopentane–methanol¹² is illustrated in Figure 15.2 on the next page.
- 3** The diagram was successfully calculated using TpNewton, see Matlab program 1.23 in Appendix 30.
- 6** Still, the K -value method experiences serious problems close to the critical point.

¹² Ternary systems. In *Liquid–Liquid Equilibrium Data Collection*, volume V, part 2., DECHEMA, Frankfurt/Main, 1980. p. 115.

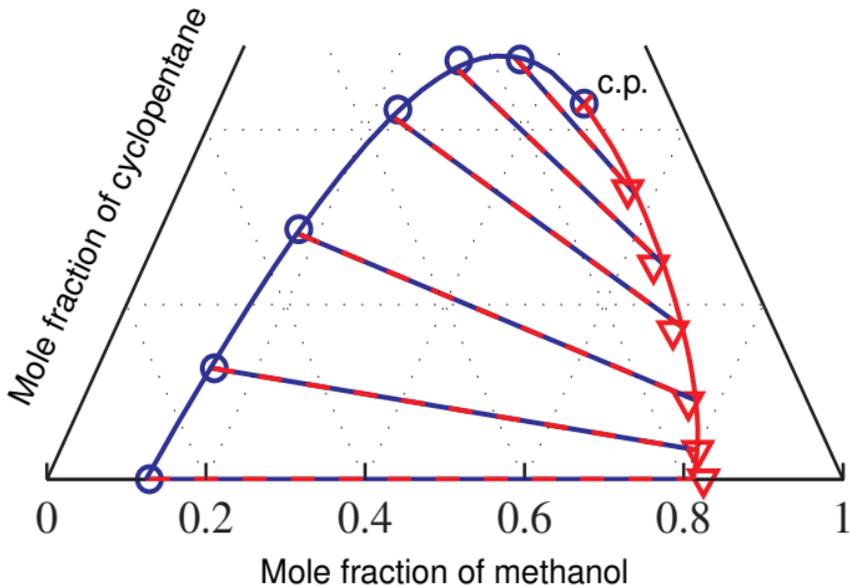


Figure 15.2: Phase diagram of cyclohexane–cyclopentane–methanol at 298.15 K and 760 mmHg. The iterations are started at interpolated points in the diagram (ensure safe convergence).

Fugacity / activity

◀ 15 Multicomponent ...

- 1** 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.
- 2** The standard state of the two phases will be different and the phase diagram will in general not be “closed” at the critical point.
- 4** The starting point is Eq. 15.1 on page 750 which in this case gives:

$$\mu_i^*(T, p) + RT \ln(\gamma_i x_i^\alpha) = \mu_i^\circ(T, p_\circ) + RT \ln\left(\frac{\varphi_i x_i^\beta p}{p_\circ}\right). \quad (15.12)$$

- 6** The standard state of β is assumed to be pure ideal gas at the temperature T and standard pressure p_\circ .

Fugacity / activity (2)

◀ 15 Multicomponent ...

7 The reference state of phase α 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 :

$$\mu_i^*(T, p_i^{\text{sat}}) = \mu_i^\circ + RT \ln \left(\frac{\varphi_i^{\text{sat}} p_i^{\text{sat}}}{p^\circ} \right). \quad (15.13)$$

Pure component reference

◀ 15 Multicomponent ...

1 In order to calculate μ_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^{sat} to the system pressure p .

2 The pure component volume v_i^* is usually a weak function of pressure, and it makes sense 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 (in the form of a liquid¹³ or maybe a solid phase) are comparatively incompressible in this regard.

3 A useful estimate of $\mu_i^*(T, p)$ is therefore

$$\mu_i^*(T, p) = \mu_i^*(T, p_i^{\text{sat}}) + \int_{p_i^{\text{sat}}}^p v_i^* dp \approx \mu_i^*(T, p_i^{\text{sat}}) + v_i^{\text{sat}}(p - p_i^{\text{sat}}). \quad (15.14)$$

¹³ Provided the state of the liquid is sufficiently removed from the critical point.

Chemical potential

◀ 15 Multicomponent ...

1 which is substituted into Eq. 15.13 and finally combined with the equilibrium relation in Eq. 15.12. The result is:

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

2 $\Delta\mu_i/RT$ from the Newton–Raphson algorithm in Eq. 15.9 may now be written on the same form as in Eq. 15.10 provided K_i is calculated as

$$K_i^{\text{vle}} = \frac{\varphi_i^{\text{sat}} p_i^{\text{sat}} \gamma_i}{\varphi_i p} \exp\left(\frac{v_i^{\text{sat}}(p - p_i^{\text{sat}})}{RT}\right), \quad (15.15)$$

The exponential term is known as the Poynting¹⁴ factor of K_i .

¹⁴ John Henry Poynting, 1852–1914. English physicist.

Raoult¹⁵ s law

◀ 15 Multicomponent ...

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

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

¹⁴ François-Marie Raoult, 1830–1901. French chemist.

Henry¹⁶s law

◀ 15 Multicomponent ...

1 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:

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

¹⁵ William Henry, 1775–1836. English chemist.

§ 120

◀ § 119

▶ § 121

◀ 15 Multicomponent ...

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.

§ 120 Ideal mixture

◀ 15 Multicomponent ...

- 1 The phase diagram of hexane–toluene¹⁷ is illustrated in Figure 15.3 on the next page.
- 2 The calculations make use of the Matlab program 1.24 in Appendix 30.
- 4 Correcting for non-ideality makes some improvement (compare σ_1 and σ_2 in the left subfigure), but the largest error is actually hidden in the vapour pressure of toluene.
- 5 By increasing the vapour pressure 2% the agreement is improved even further (compare σ_3 and σ_4 in the right subfigure), while Raoult's law still shows a significant deviation from the measurements.

¹⁷ Aliphatic hydrocarbons: C_4 – C_6 . In *Vapor–Liquid Equilibrium Data Collection*, volume I, part 6a,. DECHEMA, Frankfurt/Main, 1980. p. 593.

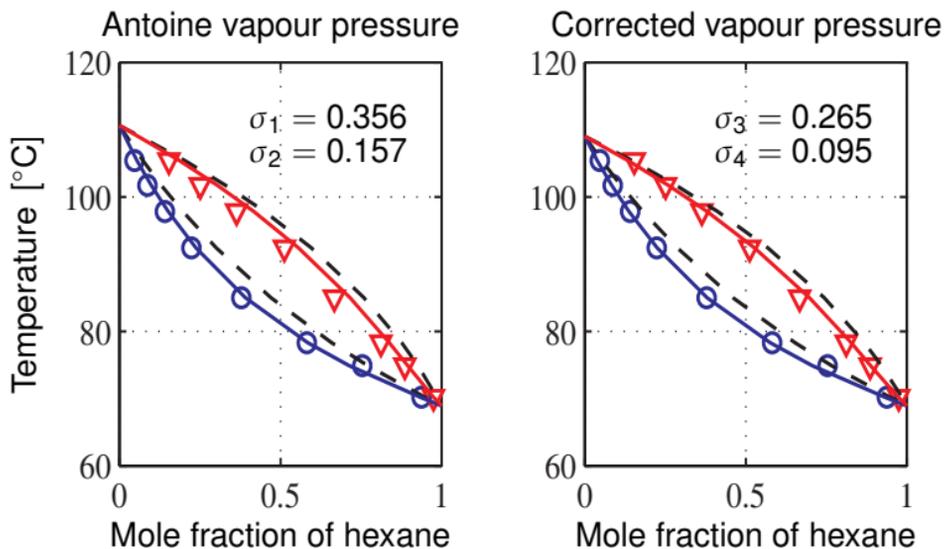


Figure 15.3: Phase diagram of hexane–toluene at 760 mmHg. Calculated curves show Raoult's law (stipled) and van Laar activity (solid). The right subfigure shows the effect of increasing the vapour pressure of toluene by 2%. The sum-of-squares are denoted σ_1 , σ_2 , σ_3 and σ_4 .

Acitivity / activity

◀ 15 Multicomponent ...

- 1** When α and β are condensed phases it is often appropriate to neglect the influence of pressure on the system properties.
- 2** This is quite typical for metallurgical melts and refractory systems where the process conditions are close to atmospheric. At the melting point¹⁸ T_i the following is true:

$$\mu_i^{\alpha,\star}(T_i) = \mu_i^{\beta,\star}(T_i). \quad (15.17)$$

¹⁸ Or phase transition point if the two phases are solid.

Pure component reference

◀ 15 Multicomponent ...

1 In order to find $\mu_i^{\star,\beta}$ at $T \neq T_i$ it is necessary to integrate $(\partial\mu_i^{\star,\beta}/\partial T)_{p,n} = -s_i^{\star,\beta}$ from the melting temperature T_i to the system temperature T .

2 The molar entropy of phase change depends on the temperature, but as a first approximation it can be assumed that $\Delta s_i^{\star} = (h_i^{\star,\beta} - h_i^{\star,\alpha})/T_i$ is approximately constant for the phase transition $\alpha \rightarrow \beta$:

$$\begin{aligned}\mu_i^{\beta,\star}(T) &= \mu_i^{\beta,\star}(T_i) - \int_{T_i}^T s_i^{\beta,\star} dT \\ &= \mu_i^{\alpha,\star}(T_i) - \int_{T_i}^T s_i^{\beta,\star} dT + \int_{T_i}^T s_i^{\alpha,\star} dT - \int_{T_i}^T s_i^{\alpha,\star} dT \\ &= \mu_i^{\alpha,\star}(T) - \int_{T_i}^T \Delta s_i^{\star} dT\end{aligned}$$

Pure component reference (2)

◀ 15 Multicomponent ...

$$\approx \mu_i^{\alpha, \star}(T) - \frac{\Delta h_i^{\star}}{T_i} (T - T_i). \quad (15.18)$$

Chemical potential

◀ 15 Multicomponent ...

- 1** Note that Eq. 15.17 is used in the transposition from the first to the second line.
- 2** 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. 15.16:

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

- 3** $\Delta\mu_i/RT$ required by the Newton–Raphson algorithm in Eq. 15.9 can finally be written as in Eq. 15.10 provided K_i is calculated as:

$$K_i^{\text{sle}} = \frac{\gamma_i^\alpha}{\gamma_i^\beta} \exp \left[\frac{\Delta h_i^*}{R} \left(\frac{1}{T_i} - \frac{1}{T} \right) \right]. \quad (15.19)$$

§ 121

◀ § 120

▶ § 122

◀ 15 Multicomponent ...

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 T_p Newton or T_p Kvalue. How important is the temperature dependency of Δs_i^* in this context?

§ 121 Metallurgy

◀ 15 Multicomponent ...

- 1** Figure 15.4 on page 806 illustrates the high-temperature portion of the gold–copper¹⁹ phase diagram, see Matlab program 30:1.25.
- 2** 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 $TpKvalue$.
- 3** 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.
- 8** The Hessian matrix for the assumed ideal mixture will then overestimate the curvature of the energy surface and therefore yield a conservative step size in $TpNewton$ (and a safe, albeit very slow, convergence).

§ 121 Metallurgy (2)

◀ 15 Multicomponent ...

9 With negative deviations from ideality the curvature of the energy surface is under-estimated and the step size may eventually grow so large that the iterations start oscillating around the solution point²⁰.

¹⁹ H. Okamoto, D. J. Chakrabarti, D. E. Laughlin, and T. B. Massalski. *Bull. Alloy Phase Diagrams*, 8(5):454–473, 1987.

²⁰ An exactly calculated Hessian would stabilise the Newton–Raphson method.

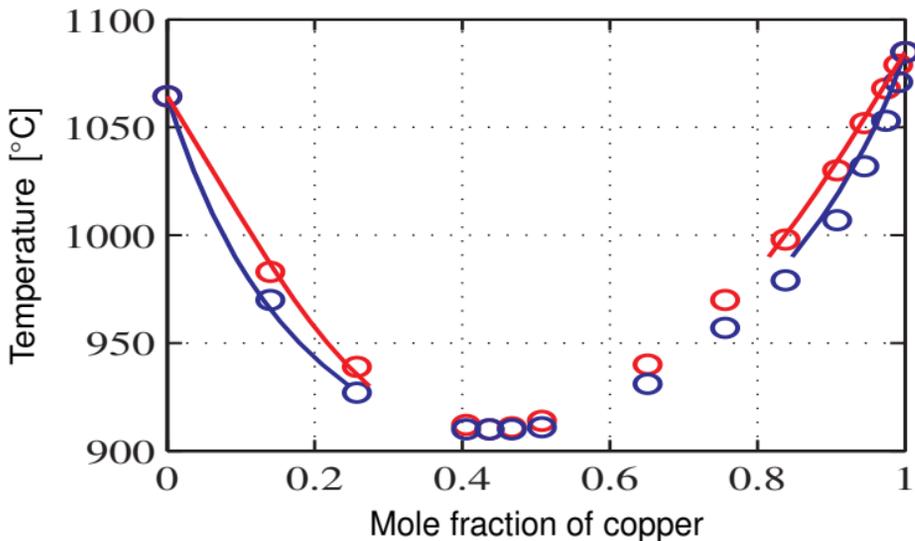


Figure 15.4: Phase diagram of gold–copper showing a negative deviation from ideality. Both $T_{p\text{Newton}}$ and $T_{pK\text{value}}$ has convergence problems close to the azeotrope.

First order convergence



◀ 15 Multicomponent ...

- 1** The K -value method is typically of first order, but close to the critical point the convergence factor $h \rightarrow 1$ which means $\mathbf{x}^{k+1} \simeq \mathbf{x}^k$.
- 3** Thus, convergence is severely hampered and it may be difficult to decide whether the sequence converges or not.
- 4** To broaden the applicability of first order methods it has been suggested to accelerate the iteration step along the strongest eigendirection of the Jacobi²¹ matrix. This is known as the *Dominant Eigenvalue Method*, see Appendix 27.

²¹ Carl Gustav Jacob Jacobi, 1804–1851. German mathematician.

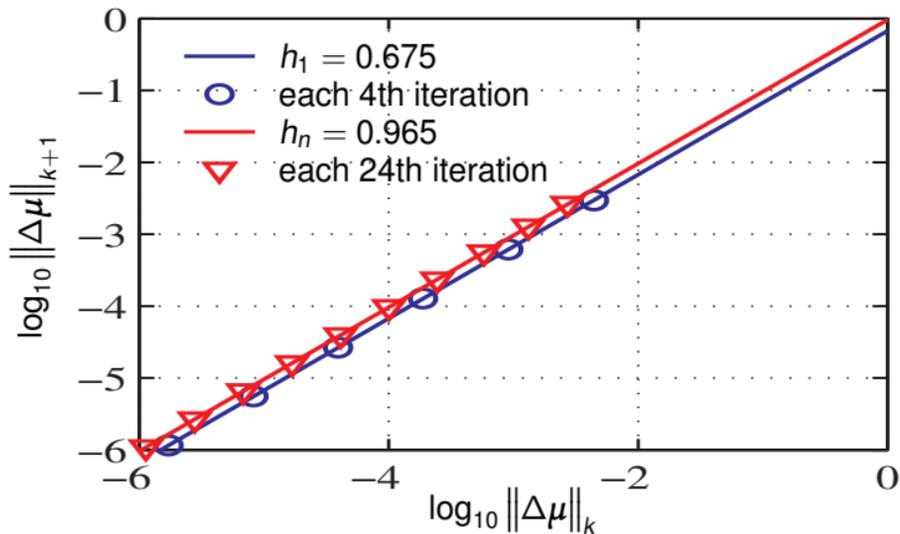


Figure 15.5: Convergence properties of the quasi Newton–Raphson method when using an ideal Hessian in the calculation of the bottom (h_1) and top (h_n) tie-lines in Figure 15.2. The latter is close to the critical point. Solid lines illustrate 1st order convergence. Note that $h \rightarrow 1$ for the near-critical point.

Second order convergence

[◀ 15 Multicomponent ...](#)

- 1** The Newton–Raphson method is of second order—details concerning the convergence factor is discussed in Appendix 26.
- 2** This means that the number of significant digits will double in each iteration provided that iteration k is sufficiently close to the solution point.
- 4** But, the simplifications in Section 15.2 makes $m = 1$ unless for ideal mixtures where the Hessian is exact.
- 5** Figure 15.5 illustrates what influence the simplification has on the calculation of the bottom and top tie-lines of Figure 15.2.

Second order convergence (2)

◀ 15 Multicomponent ...

6 The iteration sequence approaches a line with slope 1, which is typical for first order methods, and for the near-critical point the convergence factor also approaches 1, in the sense that $h_n = 0.965$ is pretty close to unity in this context.

◀ **Part 21** ▶

Material Stability

◀ see also Part-Contents ▶

Contents

- 1 Global stability**
- 2 Local stability**
- 3 The tangent plane test**
 - 1 Lagrange formulation
 - 2 Direct substitution
- 4 Intrinsic stability criteria**

Note 21.1

[◀ 21 Material ...](#)

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

Note 21.2

1 Let us start with a closed system held at constant entropy, volume and composition, the internal energy of which is $U(\mathbf{x})$, where $\mathbf{x}^T = (S, V, N_1, \dots, N_n)$. It is perhaps easier to grasp the theory by looking at a single-phase system. However, this is not a requirement, and no changes are needed for multi-phase systems. Let us consider what happens when a new phase, with state variables $\mathbf{y} \in \Omega \mid \mathbf{0} < \mathbf{y} < \mathbf{x}$, is 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 $U(\mathbf{y})$ yields¹:

$$\begin{aligned} \Delta U(\mathbf{x}, \mathbf{y}) &= U_{\mathbf{y}} \cdot \mathbf{y} - U_{\mathbf{x}} \cdot \mathbf{y} + \frac{1}{2!} U_{\mathbf{xx}} \cdot \mathbf{y} \cdot \mathbf{y} - \frac{1}{3!} U_{\mathbf{xxx}} \cdot \mathbf{y} \cdot \mathbf{y} \cdot \mathbf{y} + \dots \\ &\hat{=} \tilde{U} + \sum_{k=2} \frac{(-1)^k}{k!} \delta^k U \end{aligned} \quad (21.1)$$

Note 21.2 (2)

◀ 21 Material ...

For convenience, the following shorthand notation has been adopted²:

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

¹ Direct Euler integration is also possible: $\Delta U = (U_{\mathbf{y}} - U_{\mathbf{x}-\mathbf{y}}) \cdot \mathbf{y} - (U_{\mathbf{x}} - U_{\mathbf{x}-\mathbf{y}}) \cdot \mathbf{x}$

² The inner product \cdot binds to the operand on the left, thereby avoiding nested parentheses.

Note 21.3

◀ 21 Material ...

1 The tangent plane distance function $\tilde{U} \hat{=} (U_{\mathbf{y}} - U_{\mathbf{x}}) \cdot \mathbf{y}$ defined in 21.1 is fundamental to the *global* stability analysis set out below, while the factors $\delta^2 U$, $\delta^3 U$, etc. are closely related to the *local* instabilities known as spinodal, critical, and tricritical points. The exact conditions for these states are quite involved, and will be discussed in the next section.

Note 21.4

◀ 21 Material ...

1 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 necessary to scan the entire function domain; the system is globally stable if all the *stationary* values of ΔU have a positive sign. A necessary condition for the stationary state is $(\partial \Delta U / \partial \mathbf{y}) = \mathbf{0}$, which in the current context translates to $U_{\mathbf{y}} = U_{\mathbf{x}-\mathbf{y}}$ ³. Substituted into the integrated form of ΔU (see footnote on page 1163 on Euler integration), this gives the final stability criterion $(U_{\mathbf{y}} - U_{\mathbf{x}}) \cdot \mathbf{x} \geq 0$, which correctly identifies the equilibrium state as the lowest of all feasible tangent planes. However, this does not give us any clue as to *how* or *where* we should start our calculations. Note that there may be several phases \mathbf{y}_i and in general each phase has a finite *region of attraction*⁴.

³ Also referred to as the general condition for phase equilibrium.

⁴ The extent of the region also depends on the numerical algorithm being used.

Note 21.5

◀ 21 Material ...

1 To investigate this problem further let $\{\mathbf{y}_0, \mathbf{y}_1, \dots, \mathbf{y}_m\}$ be the set of all stationary states⁵. But, how can we determine this set? There is no definitive answer, so we shall specifically look for regions where the stability criterion is violated. Let $s_i \in [0, 1]$ be a distance parameter and let $\Delta U(s_i) = U(s_i \mathbf{y}_i) + U(\mathbf{x} - s_i \mathbf{y}_i) - U(\mathbf{x})$ be 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 ΔU 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 represents Lagrange's Taylor Series Remainder. If the Hessian⁶ $U_{\mathbf{x}-\alpha_i \mathbf{y}_i}^2$ is positive (semi)definite for all $\alpha_i \in [0, 1]$ it follows

Note 21.5 (2)

◀ 21 Material ...

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 attraction⁷:

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

If the tangent plane distance is everywhere non-negative, the system is stable, and if this is not the case, the energy can be lowered by using \mathbf{y}_i as an initial estimate for the new phase, see Section 21.3 on page 1185.

⁵ Any value $\mathbf{y} \propto \mathbf{x}$ represents a so-called trivial solution and is excluded from the set.

⁶ Ludwig Otto Hesse, 1811–1874. German mathematician.

⁷ Normally unknown at the outset—global stability constitutes a difficult problem.

Note 21.6

[◀ 21 Material ...](#)

1 Assume that \mathbf{x} is now a single-phase system in Eq. 21.1 and that $\tilde{U} = 0$ for some vector $\mathbf{y} \rightarrow \mathbf{0}$ describing a new incipient phase that is formed within the system boundary. If moreover $\delta^2 U \rightarrow 0^+$, the system is stable to local perturbations, whereas 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 new phase \mathbf{y} when $\delta^3 U \rightarrow 0^+$, and de-stabilised when $\delta^3 U \rightarrow 0^-$. This can obviously be generalised, but it is not very conclusive, because $\mathbf{y} \rightarrow \mathbf{0}$ does not tell us how far \mathbf{y} is from \mathbf{x} in a thermodynamic sense⁸. We shall therefore rewrite Eq. 21.1 as a Taylor series with one single reference composition \mathbf{x} , rather than using two distinct compositions \mathbf{x} and \mathbf{y} . This is to understand what happens if (or when) some of the lower order terms

Note 21.6 (2)

◀ 21 Material ...

in the series vanish, and to properly understand the zero phase fraction lines. The total energy of the composite system is:

$$U(\mathbf{x}, \mathbf{y}) = U(\mathbf{y}) + U(\mathbf{x} - \mathbf{y}) \quad (21.2)$$

⁸ We do not know whether \mathbf{y} approaches the trivial solution $\mathbf{y} \propto \mathbf{x}$ or not.

Note 21.7

◀ 21 Material ...

1 To proceed we need Taylor expansions for $U(\mathbf{y})$ and $U(\mathbf{x} - \mathbf{y})$, both starting at the same composition \mathbf{x} , or, more precisely, somewhere along vector \mathbf{x} . The trial vector of state variables 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 $1, 0, -1, \dots$. This means that the expansion can be started *anywhere* along vector \mathbf{x} provided that the derivatives⁹ are properly scaled:

$$\begin{aligned} U(\mathbf{y}) &= \alpha U(\mathbf{x}) + \alpha^0 U_{\mathbf{x}} \cdot \bar{\mathbf{x}} + \frac{1}{2} \alpha^{-1} U_{\mathbf{xx}} \cdot \bar{\mathbf{x}} \cdot \bar{\mathbf{x}} + \frac{1}{3!} \alpha^{-2} U_{\mathbf{xxx}} \cdot \bar{\mathbf{x}} \cdot \bar{\mathbf{x}} \cdot \bar{\mathbf{x}} + \dots \\ &= \alpha U(\mathbf{x}) + \sum_{k=1} \frac{1}{k!} \alpha^{1-k} U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k \end{aligned} \quad (21.3)$$

⁹ Note that by default the derivatives are evaluated in state \mathbf{x} .

Note 21.8

◀ 21 Material ...

1 The expansion of $U(\mathbf{y})$ is also valid for $U(\mathbf{x} - \mathbf{y})$ if the new variable β 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

$$U(\mathbf{x} - \mathbf{y}) = \beta U(\mathbf{x}) + \sum_{k=1} \frac{1}{k!} \beta^{1-k} U_{\mathbf{x}}^k \cdot (-\bar{\mathbf{x}})^k \quad (21.4)$$

for free. From Eqs. 21.2, 21.3 and 21.4 the expansion of the total energy reads¹⁰:

$$U(\mathbf{x}, \mathbf{y}) = U(\mathbf{x}) + \sum_{k=2} \frac{1}{k!} [\alpha^{1-k} - (-\beta)^{1-k}] U_{\mathbf{x}}^k \cdot \bar{\mathbf{x}}^k \quad (21.5)$$

The first index $k = 1$ is skipped because $\alpha^0 - \beta^0 = 0$ for all $\alpha, \beta \in \langle 0, 1 \rangle$, i.e. the Taylor series is independent of the slope of the energy surface¹¹. Of particular interest here is the term $\alpha^{1-k} - (-\beta)^{1-k}$, which is strictly

Note 21.8 (2)

[◀ 21 Material ...](#)

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 α and β . Whenever the leading terms of the series vanish, this implies that the even and odd terms vanish in pairs. A concise explanation is given below.

¹⁰ Where $\alpha + \beta = 1$, as defined above.

¹¹ The energy gained by one phase is, to a first approximation, the same as that lost by the other phase.

Note 21.9

[◀ 21 Material ...](#)

1 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 vice versa. This behaviour has no physical interpretation, and it can be concluded that $U_{\mathbf{x}}^n \cdot \bar{\mathbf{x}}^n$ must vanish as well. However, as illustrated in Figure 21.1 on the following page, exchanging the values of α and β 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:

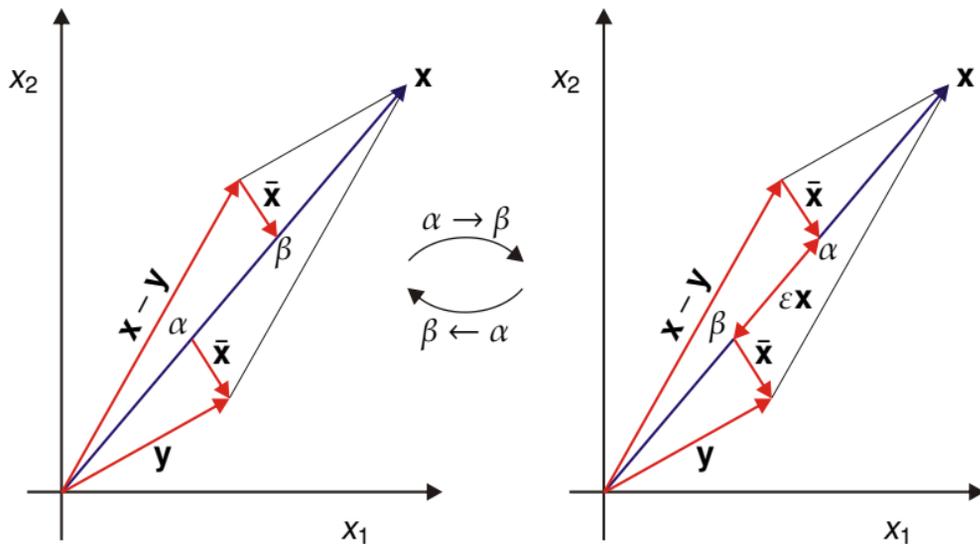


Figure 21.1: The effect of exchanging the (Taylor expansion) phase sizes α and β in a trial two-phase system. The overall vector of state variables \mathbf{x} is fixed (closed system). The difference between the two sub-figures lies in the $\epsilon \mathbf{x}$ term.

Proof

◀ 21 Material ...

1 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 following reduction scheme:

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

Proof (2)

◀ 21 Material ...

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 the 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. Hence, we can conclude that only the n 'th term survives the summation:

$$U_{\mathbf{x}}^n \cdot (\varepsilon \mathbf{x} + \bar{\mathbf{x}})^n = U_{\mathbf{x}}^n \cdot \bar{\mathbf{x}}^n, \quad \forall \varepsilon > 0 [0.8]$$

Note 21.10

◀ 21 Material ...

1 In retrospect it is easy to see that $\varepsilon \mathbf{x}$ vanishes due to the first order homogeneity of U when 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 zero¹²¹³.

¹² Michael Modell and Robert C. Reid. *Thermodynamics and Its Applications*. Prentice Hall, 2nd edition, 1983.

¹³ There is a textbook alternative¹² to the analysis outlined above. Let $\alpha \rightarrow 0$ in Eq. 21.5. As $\beta = 1 - \alpha \gg \alpha$ the equation simplifies to $\lim_{\alpha \rightarrow 0} \left(\frac{\Delta U}{\alpha} \right) = \sum_{k=2} \frac{1}{k!} U_{\mathbf{x}}^k \cdot \left(\frac{\bar{\mathbf{x}}}{\alpha} \right)^k$. Here, $\Delta U(\mathbf{x}, \mathbf{y})$ is a homogeneous function in α 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 new 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, the sign of the n 'th term will also switch, and it can be shown 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 new phase \mathbf{y} , and it is not clear (to me) that this has been properly accounted

Note 21.11

◀ 21 Material ...

1 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 just 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 globally metastable). 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 will summarise our findings:

unstable $\delta^2 U < 0$ for some \mathbf{y}

critical $\delta^2 U = 0$
 $\delta^3 U = 0$ for some \mathbf{y}

tricritical $\delta^2 U = 0 \quad \delta^4 U = 0$
 $\delta^3 U = 0 \quad \delta^5 U = 0$ for some \mathbf{y}

tetracritical $\delta^4 U = 0 \quad \delta^6 U = 0 \quad \delta^8 U = 0$
 $\delta^3 U = 0 \quad \delta^5 U = 0 \quad \delta^7 U = 0$ for some \mathbf{y}

Note 21.11 (2)

◀ 21 Material ...

Note 21.12

◀ 21 Material ...

1 In theory it is easy to set $\delta^2 U$, $\delta^3 U$, etc. to zero, but what about in reality? Matrix algebra can be used to analyse $\delta^2 U$, but it is not helpful for the higher order terms. To get an idea of the numerical complexity it is useful to calculate the number of different terms involved. The partial derivative $U_{\mathbf{x}}^k$ contains n^k elements, but only a fraction¹⁴ of these are independent. One obvious reason for this is the commutative symmetry of the partial derivative:

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

¹⁴ E.g. for $k = n = 10$ there are 10^{10} elements, but only 43758 independent ones!

Note 21.13

◀ 21 Material ...

1 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 exist 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 limited to

$$\binom{n+k-1}{k} - \binom{n+k-2}{k-1} \equiv \frac{(n+k-2)!}{k!(n-2)!}, \quad k, n \geq 2$$

Note 21.14

◀ 21 Material ...

1 From the numbers calculated in the table below we can immediately identify the 2-variable case as particularly interesting—only one extra term is needed to describe each derivative, regardless of the value of k . This finding becomes even more interesting in Section 21.4, where we will find that the 2-variable case is sufficient in all but some highly degenerate cases (e.g. critical azeotropes).

	$k = 2$	$k = 3$	$k = 4$...	k
$n = 2$	1	1	1	...	$\frac{1}{1}$
$n = 3$	3	4	5	...	$\frac{k+1}{1}$
$n = 4$	6	10	15	...	$\frac{(k+1)(k+2)}{2}$
\vdots	\vdots	\vdots	\vdots	\ddots	\vdots
n	$\frac{(n-1)n}{2}$	$\frac{(n-1)n(n+1)}{6}$	$\frac{(n-1)n(n+1)(n+2)}{24}$...	$\frac{(n+k-2)!}{k!(n-2)!}$

Note 21.14 (2)

◀ 21 Material ...

Note 21.15

◀ 21 Material ...

1 In theory it is possible to formulate a tangent plane test based on internal energy, but most models use the 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) defined 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 vector of state variables \mathbf{y} :

$$\tilde{A}(\mathbf{x}, \mathbf{y}) = [\mathbf{g}(\mathbf{y}) - \mathbf{g}(\mathbf{x})]^T \mathbf{y} > 0 \quad (21.6)$$

Note 21.15 (2)

[◀ 21 Material ...](#)

Note the difference in notation from Eq. 21.1. Here it is more natural to use \mathbf{g} for the gradient rather than $A_{\mathbf{x}}$, in keeping with the notation used in linear algebra.

Note 21.16

◀ 21 Material ...

1 To verify that $\tilde{A} \geq 0$ for all feasible $\mathbf{y} \in \Omega$ our best option is to investigate the outcome of the minimisation problem

$$\min_{\mathbf{y}}(\tilde{A})_{\mathcal{T}} \quad \vee \quad \mathbf{a}^T \mathbf{y} = c$$

for several trial values of \mathbf{y} . This minimisation problem is linearly constrained¹⁵ and the method of Lagrange multipliers is the perfect tool:

$$L(\mathbf{x}, \mathbf{y}, \lambda) = \tilde{A} - \lambda(\mathbf{a}^T \mathbf{y} - c)$$

¹⁵ The constraint specification $\mathbf{a}^T \mathbf{y} = c$ is arbitrary, but nevertheless crucial to the formulation of the problem, because \tilde{A} is a homogeneous function, and as such has a singular Hessian matrix in the direction of \mathbf{y} . Adding a rank-one constraint makes the Hessian invertible (loosely speaking).

Note 21.17

◀ 21 Material ...

1 The stationary point of L is given by $\partial L / \partial \mathbf{y} = \mathbf{0}$, or when written out in more detail:

$$\begin{aligned}\mathbf{0} &= \frac{\partial \tilde{A}}{\partial \mathbf{y}} - \frac{\partial \lambda(\mathbf{a}^T \mathbf{y} - c)}{\partial \mathbf{y}} \\ &= \mathbf{H}(\mathbf{y})\mathbf{y} + \mathbf{g}(\mathbf{y}) - \mathbf{g}(\mathbf{x}) - \lambda \mathbf{a} \\ &= \mathbf{g}(\mathbf{y}) - \mathbf{g}(\mathbf{x}) - \lambda \mathbf{a}\end{aligned}\tag{21.7}$$

The stationary value of \tilde{A} can be calculated from Eqs. 21.6 and 21.7:

$$\tilde{A}_o = \mathbf{g}(\mathbf{y})^T \mathbf{y} - \mathbf{g}(\mathbf{x})^T \mathbf{y} = \lambda \mathbf{a}^T \mathbf{y} = \lambda c\tag{21.8}$$

Note 21.18

◀ 21 Material ...

1 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, Helmholtz energy can be lowered by including the new phase \mathbf{y} at the expense of \mathbf{x} , but this begs the question: how big should we make this new phase? The final answer lies, of course, in the subsequent equilibrium calculation, but we have to start the iterations somewhere. It requires only a minimum of effort to study the second order variation of \tilde{A} along the (optimum) vector of state variables \mathbf{y} ,

$$\tilde{A}(\mathbf{x}, \mathbf{y}) = \alpha \mathbf{g}(\mathbf{y})^T \mathbf{y} - \alpha \mathbf{g}(\mathbf{x})^T \mathbf{y} + \frac{\alpha^2}{2!} \mathbf{y}^T \mathbf{H}(\mathbf{x}) \mathbf{y} + \dots$$

Note 21.18 (2)

◀ 21 Material ...

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 simple differentiation gives the following phase size estimate

$$\alpha_o = \frac{\mathbf{g}(\mathbf{y})^T \mathbf{y} - \mathbf{g}(\mathbf{x})^T \mathbf{y}}{\mathbf{y}^T \mathbf{H}(\mathbf{x}) \mathbf{y}} \hat{=} \frac{-\lambda c}{Q(\mathbf{x}, \mathbf{y})} \quad (21.9)$$

Note 21.19

[◀ 21 Material ...](#)

1 At the limit of phase stability α_o will approach the true equilibrium value, but deep inside the phase boundary we may expect $\alpha_o > \alpha_{\max}$. We must therefore keep a close eye on the estimate in Eq. 21.9 and restrict α if appropriate. Also note 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 essential.

Note 21.20

1 This is as far as the general theory goes; the next question is how to proceed with actual calculations. A Newton iteration starting at a feasible point $\mathbf{y}_0 \neq \mathbf{x}$ yields the recurrence formula,

$$\begin{pmatrix} \mathbf{y} \\ -\lambda \end{pmatrix}_{k+1} = \begin{pmatrix} \mathbf{H}(\mathbf{y}) & \mathbf{a} \\ \mathbf{a}^T & 0 \end{pmatrix}_k^{-1} \begin{pmatrix} \mathbf{g}(\mathbf{x}) - \mathbf{g}(\mathbf{y}) \\ c \end{pmatrix}_k$$

but to continue we need the constraint vector \mathbf{a} . The most intuitive choice is to fix the volume of the new phase such that $\mathbf{y}_1 = \mathbf{x}_1 = V$ and to let the mole numbers vary freely. This corresponds to $\mathbf{a}^T = \mathbf{e}_1^T = (1, 0, \dots)$ and λ being a vector with one single element interpreted as the difference in negative pressure π between the two states \mathbf{x} and \mathbf{y} . Inserting $\mathbf{a} = \mathbf{e}_1$ into Eq. 21.7 gives the solution

$$p(\mathbf{x}) - p(\mathbf{y}) = \pi$$

Note 21.20 (2)

◀ 21 Material ...

$$\mu(\mathbf{x}) - \mu(\mathbf{y}) = 0$$

Note 21.21

◀ 21 Material ...

1 There is no mechanical equilibrium in this case, although the conditions for chemical equilibrium are fulfilled¹⁶. The stationary value of \tilde{A}_o in Eq. 21.8 simplifies to

$$\tilde{A}_o = \pi \mathbf{e}_1^T \mathbf{y} = \pi \mathbf{y}_1 = \pi V$$

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 possibly¹⁷ stable if $-\pi \leq 0$. Finally, for $\mathbf{a} = \mathbf{e}_1$ the phase fraction estimate simplifies to (see Eq. 21.9 on page 1190)

$$\alpha_o = \frac{-\pi V}{Q(\mathbf{x}, \mathbf{y})}$$

¹⁶ The situation will change if a different \mathbf{a} is chosen. E.g. $\mathbf{a}^T = (0, 1, \dots, 1)$ releases the chemical equilibrium and fixes the mechanical equilibrium.

¹⁷ If we are going to rely on a single solution point, we should really check for intrinsic stability first. This topic will be covered in the next section.

Note 21.22

◀ 21 Material ...

1 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 can now be 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} :

$$\mathbf{y} = \mathbf{e}_n + \begin{pmatrix} \mathbf{I} \\ -\mathbf{e}^T \end{pmatrix} \mathbf{y}_{1,\dots,n-1} \hat{=} \mathbf{e}_n + \mathbf{S} \mathbf{y}_{1,\dots,n-1}$$

Note 21.23

◀ 21 Material ...

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, this operation conserves the total number of moles in the mixture and the minimisation problem can *de facto* be written in an unconstrained form as $\min_{\mathbf{y}_{1,\dots,n-1}}(\tilde{G})_{T,p}$. The chain rule of differentiation yields

$$\left(\frac{\partial\tilde{G}}{\partial\mathbf{y}_{1,\dots,n-1}}\right) = \left(\frac{\partial\mathbf{n}^T}{\partial\mathbf{y}_{1,\dots,n-1}}\right)\left(\frac{\partial\tilde{G}}{\partial\mathbf{y}}\right) = \mathbf{S}^T[\boldsymbol{\mu}(\mathbf{y}) - \boldsymbol{\mu}(\mathbf{x})] = \mathbf{0}$$

Note 21.24

◀ 21 Material ...

1 If we can assume that the mixture behaves ideally then $\mu(\mathbf{y}) - \mu(\mathbf{x}) = \Delta\mu + \ln(\mathbf{y})$, where $\Delta\mu$ is a constant vector at the given temperature and pressure. The condition for a stationary point is $\mathbf{S}^T[\Delta\mu + \ln(\mathbf{y})] = \mathbf{0}$, or when written out in full: $\Delta\mu_{1,\dots,n-1} - \Delta\mu_n \mathbf{e} + \ln(\mathbf{y}_{1,\dots,n-1}) - \ln(\mathbf{y}_n) \mathbf{e} = \mathbf{0}$. Direct substitution of the first $n - 1$ variables gives the update formula:

$$\mathbf{y}_{1,\dots,n-1}^{(k+1)} = \mathbf{y}_n^{(k)} \exp(\Delta\mu_n) \exp(-\Delta\mu_{1,\dots,n-1})$$

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 always positive due to the exponential on the right hand side.

§ 153

◀ § 152

▶ § 1

◀ 21 Material ...

Write a modified update formula 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.

§ 153 Ideal gas

◀ 21 Material ...

1 Assume that, in the previous derivation, Helmholtz energy is used to replace Gibbs energy and $\mathbf{S}^T \triangleq [\mathbf{I} \ \mathbf{0}]$, where the last column (of zeros) corresponds to the (constant) variable V . Because the iteration is now performed at constant volume rather than at constant pressure, all of the mole variables will be updated simultaneously: $\mathbf{n}^{(k+1)} = \mathbf{n}^{(k)} \exp(-\Delta\mu)$.

Note 21.25

[◀ 21 Material ...](#)

1 Intrinsic stability of a phase requires that the quadratic $U_{xx} \cdot \mathbf{y} \cdot \mathbf{y} \geq 0$ for all $\mathbf{y} \in \Omega$. This is a classical formulation of a problem familiar from courses in linear algebra, the solution to which can be stated in several equivalent ways:

- 1** The eigenvalues of U_{xx} are non-negative.
- 2** The pivots in the Cholesky factorisation of U_{xx} are non-negative.
- 3** The principal sub-determinants of U_{xx} are non-negative.
- 4** U_{xx} is a semi-definite matrix of rank $n - 1$.

Note 21.26

◀ 21 Material ...

1 The second formulation is suited to simple matrix algebra and for this reason it is the route followed here. For a single-component system a step-by-step elimination¹⁸ of the rows in U_{xx} yields

$$\begin{pmatrix} U_{SS} & U_{SV} & U_{SN} \\ U_{VS} & U_{VV} & U_{VN} \\ U_{NS} & U_{NV} & U_{NN} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ \alpha & 1 & 0 \\ \beta & 0 & 1 \end{pmatrix} \begin{pmatrix} U_{SS} & U_{SV} & U_{SN} \\ 0 & A_{VV} & A_{VN} \\ 0 & A_{NV} & A_{NN} \end{pmatrix} \quad (21.10)$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ \alpha & 1 & 0 \\ \beta & \gamma & 1 \end{pmatrix} \begin{pmatrix} U_{SS} & U_{SV} & U_{SN} \\ 0 & A_{VV} & A_{VN} \\ 0 & 0 & G_{NN} \end{pmatrix} \quad (21.11)$$

where the following parameters have been used:

$$\alpha \hat{=} \frac{U_{VS}}{U_{SS}}, \quad \beta \hat{=} \frac{U_{NS}}{U_{SS}}, \quad \gamma \hat{=} \frac{A_{NV}}{A_{VV}}$$

¹⁸ Because U_{xx} is a symmetric matrix of rank $n - 1$ we can write the full Cholesky

Note 21.27

[◀ 21 Material ...](#)

1 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. 21.10–21.11 are correct, we must prove that the Cholesky¹⁹ factorisation of a thermodynamic Hessian (in the extensive variables) is equivalent to a series of Legendre transformations applied to the original function²⁰. It is possible to prove this in general terms, but to make the theory more accessible to the casual reader we shall carry out a less general factorisation. From Chapter 4 we know that $A(T, V, N)$ is related to $U(S, V, N)$ such that $A_X = U_X$, assuming constant temperature and entropy respectively. This relation holds for any $X \in \{V, N\}$.

Note 21.27 (2)

◀ 21 Material ...

The differentials of A_X at constant temperature, and of U_X with no restrictions on the variables, are:

$$(dA_X)_T = A_{XV} dV + A_{XN} dN \quad (21.12)$$

$$dU_X = U_{XS} dS + U_{XV} dV + U_{XN} dN \quad (21.13)$$

¹⁹ André-Louis Cholesky, 1875–1918. French mathematician.

²⁰ The marvels of thermodynamics are quite fascinating!

Note 21.28

◀ 21 Material ...

1 In order to compare the two differentials it is necessary to eliminate the (differential) entropy in the second equation such that the temperature is held constant. Using the definition $T \hat{=} U_S$ it follows that

$$0 = (dU_S)_T = U_{SS} dS + U_{SV} dV + U_{SN} dN \quad (21.14)$$

From Eq. 21.14 it is straightforward to eliminate dS in Eq. 21.13, and furthermore to collect similar terms into

$$(dU_X)_T = \left(U_{XV} - U_{XS} \frac{U_{SV}}{U_{SS}} \right) dV + \left(U_{XN} - U_{XS} \frac{U_{SN}}{U_{SS}} \right) dN$$

Note 21.29

◀ 21 Material ...

1 The above equation can be compared term-by-term with Eq. 21.12, which yields

$$A_{XY} = U_{XY} - U_{XS} \frac{U_{SY}}{U_{SS}} \quad (21.15)$$

for any $Y \in \{V, N\}$. Substitution of $X, Y \in \{V, N\}$ into the formula above verifies the first step of the Cholesky factorisation 21.10–21.11. Furthermore, because the differentiation outlined in Eqs. 21.12–21.15 is valid for any Legendre sequence $U(S, V, N) \rightarrow A(T, V, N) \rightarrow G(T, -p, N)$ etc., proof by induction verifies that the factorisation can be completed as indicated²¹.

²¹ The factorisation of positive *semi*-definite matrices has not yet been discussed. The question is where the zero pivots of U_{xx} appear 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 does, which in turn changes its sign before the third last pivot, etc. This holds for all non-degenerate states. In the current case $G_{NN} = 0$ is the last pivot and the sign shift will therefore show up in A_{NN} first, before it eventually also shows up in U_{SS} .

Note 21.30

1 The intrinsic stability of a 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 alone²². It should also be noted that the transformation sequence is arbitrary, and that the factorisation could start with U_{VV} or U_{NN} rather than U_{SS} . Thus, for a single-component system the stability conditions can be written in 6 different ways,

$$U_{SS} > 0, \quad A_{VV} > 0$$

$$U_{SS} > 0, \quad A_{NN} > 0$$

$$U_{VV} > 0, \quad H_{SS} > 0$$

$$U_{VV} > 0, \quad H_{NN} > 0$$

$$U_{NN} > 0, \quad X_{SS} > 0$$

$$U_{NN} > 0, \quad X_{VV} > 0$$

Note 21.30 (2)

◀ 21 Material ...

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-hand column is clearly related to the determinants of the submatrices of order one (main diagonal elements), and with the help of Eq. 21.15 the determinants of the submatrices of order two can be written:

$$U_{SS}U_{VV} - U_{SV}U_{VS} = U_{SS}A_{VV} = H_{SS}U_{VV} > 0$$

$$U_{SS}U_{NN} - U_{SN}U_{NS} = U_{SS}A_{NN} = X_{SS}U_{NN} > 0$$

$$U_{VV}U_{NN} - U_{VN}U_{NV} = U_{VV}H_{NN} = X_{VV}U_{NN} > 0$$

²² 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 of the coefficients into action.

Note 21.31

[◀ 21 Material ...](#)

1 There is also one final criterion relating to the whole matrix, and several additional criteria from the Legendre transforms, but they are all zero because the Hessian is singular for any values of S , V and N . The criteria given in the right-hand column above are therefore conclusive and are violated *simultaneously* at the limit of material stability. This limit of stability is often referred to as the spinodal. The criteria derived from the submatrices of order one define a new spinodal inside the outer one.

Note 21.32

◀ 21 Material ...

1 A final note on quadratic forms is appropriate. We know that for a stable system the quadratic $U_{\mathbf{xx}} \cdot \mathbf{y} \cdot \mathbf{y} \geq 0$ for all $\mathbf{y} \in \Omega$. This has been stressed many times already, but so far it has only been a theoretical result. To give a practical demonstration we can calculate the inner product from the factorisation in Eq. 21.11:

$$U_{SVN}^2 \cdot \mathbf{y}^2 = U_{SS} \left(y_S + \frac{U_{VS}}{U_{SS}} y_V + \frac{U_{NS}}{U_{SS}} y_N \right)^2 + A_{VV} \left(y_V + \frac{A_{NV}}{A_{VV}} y_N \right)^2 + G_{NN} (y_N)^2$$

Note 21.33

◀ 21 Material ...

1 Clearly, the quadratic is non-negative only if the leading factors U_{SS} and A_{VV} are positive. The Euler properties of U make $G_{NN} = 0$ so the quadratic is always zero in the direction of \mathbf{x} , but otherwise it should be strictly positive. For a multicomponent system the quadratic can be generalised to

$$U_{\mathbf{x}}^2 \cdot \mathbf{y}^2 = \sum_{i=1} U_{x_i x_i}^{(i-1)} \left(y_i + \sum_{j>i} (U_{x_j x_j}^{(i-1)})^{-1} U_{x_i x_j}^{(i-1)} y_j \right)^2$$

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 even for a binary system there are 24 different possibilities. The most common formulation is:

$$U_{SS} = \left(\frac{\partial T}{\partial S} \right)_{V, N_1, N_2} \hat{=} \frac{T}{C_V} > 0$$

Note 21.33 (2)

◀ 21 Material ...

$$A_{VV} = - \left(\frac{\partial p}{\partial V} \right)_{T, N_1, N_2} \hat{=} \frac{1}{V\beta} > 0$$
$$G_{N_1 N_1} = \left(\frac{\partial \mu_1}{\partial N_1} \right)_{T, p, N_2} > 0$$