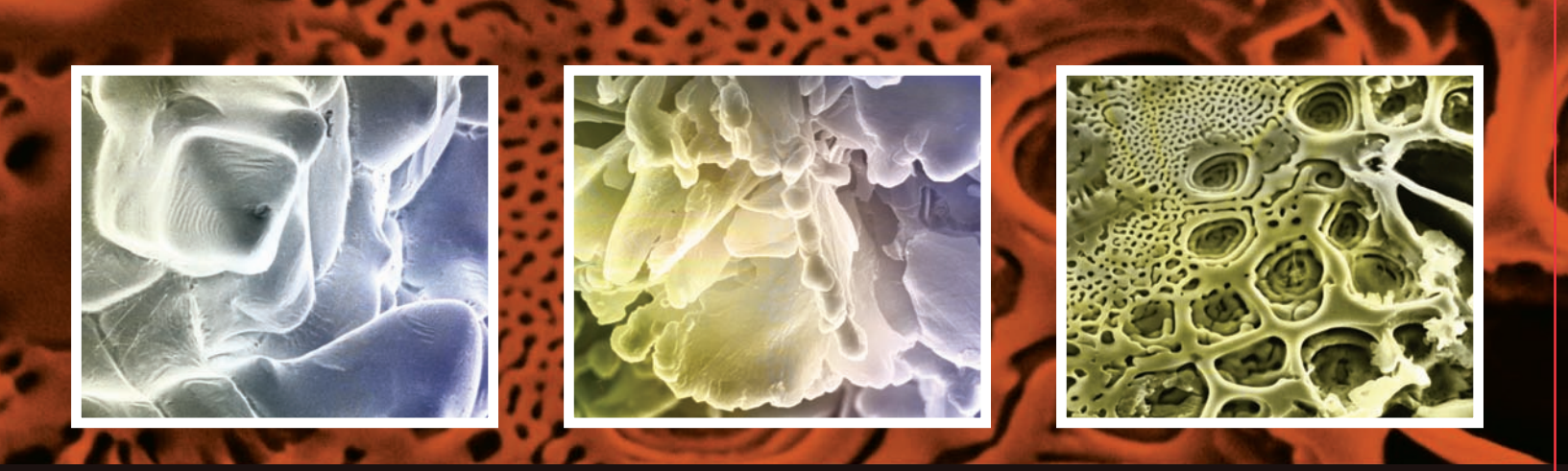


Solidification and Crystallization Processing in Metals and Alloys

Hasse Fredriksson and Ulla Åkerlind

WILEY

Solidification and Crystallization Processing in Metals and Alloys

Solidification and Crystallization Processing in Metals and Alloys

Hasse Fredriksson
KTH, Royal Institute of Technology, Stockholm, Sweden

and

Ulla Åkerlind
University of Stockholm, Stockholm, Sweden

WILEY
A John Wiley & Sons, Ltd., Publication

This edition first published 2012

Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

Library of Congress Cataloging-in-Publication Data

Fredriksson, Hasse.
Solidification and crystallization processing in metals and alloys / Hasse Fredriksson and Ulla Åkerlind.
p. cm.
Includes bibliographical references and index.
ISBN 978-1-119-99305-6 (cloth)
1. Metal crystals–Growth. I. Åkerlind, Ulla. II. Title.
TN690.F73 2012
669′.94–dc23
2011014030

A catalogue record for this book is available from the British Library.

ISBN: 978-1-119-99305-6
Set in 10/12pt, Times by Thomson Digital, Noida
Printed in [Country] by [Printer]

Contents

Preface

The present book is the third and last book in a series of three:

1. Materials Processing during Casting, Wiley 2006
2. Physics of Functional Materials, Wiley 2008
3. Solidification and Crystallization Processing in Metals and Alloys, Wiley 2012

Solidification and Crystallization Processing in Metals and Alloys represents a deeper interpretation of the solidification and crystallization processes than that treated in the book *Materials Processing during Casting*, written for the undergraduate level. The aim of the present book is to analyze the solidification and crystallization processes from a general point of view and in accordance with generally accepted results and experimental evidence of modern research in the field. Hence, the book does not treat applications on casting other than as occasional examples.

The book may be useful and suitable as a text book on courses at the Master and PhD level. The mathematical level is not discouragingly high. Ordinary basic courses in Mathematics at university level are enough. On the other hand, genuine knowledge of Physics is often required. The second book, *Physics of Functional Materials*, or any other Physics book with any other equivalent content, will cover this want for those who need it. Numerous citations to the second book are given in the present book.

Solidification and Crystallization Processing in Metals and Alloys starts with a chapter of basic thermodynamics. Chapter 1 is a review of the thermodynamics that later will be applied on metals and alloys. It may be a tough and abstract introduction. Alternatively, it can be studied in connection with later applications. Energy conditions play an important role for understanding the driving forces of solidification processes in metals and alloys. These topics are treated in Chapter 2. The structure and properties of interfaces between two phases and the nucleation of embryos and forming of stable nuclei are closely related to crystallization processes. The basic outlines of these fields are given in Chapters 3 and 4, respectively.

After these four basic and general chapters, Chapters 5 and 6 follow, where the mechanisms of the solidification and crystallization processes in vapours and liquids are extensively discussed. Heat transport during solidification processes is treated in Chapter 7, which also includes an orientation about modern methods of thermal analysis. Chapter 8 deals with crystal growth controlled by heat and mass transport.

The rest of the book is devoted to the structures of the solid phases that form during different types of solidification processes, i.e. faceted and dendritic structures (Chapter 9), eutectic structures (Chapter 10), peritectic structures (Chapter 11) and structure of Metallic Glasses (Chapter 12).

Solidification and Crystallization Processing in Metals and Alloys contains many solved examples in the text and exercises for students at the end of each chapter. Answers to all the exercises are given at the end of the book. In a 'Guide to Exercises' full solutions to all the exercises are given on the Internet at http://www.wiley.com/go/fredriksson3

Acknowledgements

This book is based on lectures and exercises presented to PhD and Master students over the years. We want to express our sincere thanks to them for their engagement and for the fruitful discussions we

have had with them about different scientific topics in the field. The communication with them helped us to identify the items that were difficult for them to understand. In this way, we could try to explain better and improve the book.

We are most grateful to MSc Per Olov Nilsson for many fruitful mathematical discussions and general support through the years. We also wish to express our sincere thanks to Dr Jonas Åberg, Thomas Bergström (Casting of Metals, KTH, Stockholm), Dr Gunnar Edvinsson (University of Stockholm), Dr Bengt Örjan Jonsson (KTH), Dr Hani Nasser and Dr Sathees Ranganathan (Casting of Metals, KTH) for their valuable support concerning practical matters such as annoying computer problems and application of some special computer programs. We also thank Dr Lars Åkerlind warmly for patient assistance with checking parts of the manuscript.

We are very grateful for financial support from the Iron Masters Association in Sweden and the Foundation of Sven and Astrid Toresson, which made it possible for us to fulfill the last part of this project.

In particular, we want to express our sincere gratitude to Karin Fredriksson and Lars Åkerlind. Without their constant support and great patience through the years this book would never have been written.

Finally, we want to thank each other for a more than 10 years long and pleasant cooperation. It has been the perfect symbiosis. Neither of us could have written this trilogy without the other. We complemented each other well. One of us (guess who) contributed many years of research in the field and an ever-lasting enthusiasm to his devoted subject. The other one contributed with some Mathematics and Physics together with many years experience of book production and teaching Physics at university level and also plenty of *time* for the extensive project.

Hasse Fredriksson
Ulla Åkerlind
Stockholm, May 2010

1

Thermodynamic Concepts and Relationships

Solidification and Crystallization Processing in Metals and Alloys, First Edition. Hasse Fredriksson and Ulla Åkerlind.

1.1 Introduction

Solidification or crystallization is a process where the atoms are transferred from the disordered liquid state to the more ordered solid state. The rate of the crystallization process is described and controlled by kinetic laws. These laws give information of the movements of the atoms during the rearrangement. In most cases a driving force is involved that makes it possible to derive the rate of the solidification process.

The aim of this book is to study the solidification processes in metals and alloys. The laws of thermodynamics and other fundamental physical laws, which control the solidification, rule these processes.

In this preparatory chapter the basic concepts and laws of thermodynamics are introduced. They will be the tools in following chapters. In particular, this is true for the second chapter, where the driving forces of solidification for pure metals and binary alloys are derived and the relationship between energy curves of solid metals and metal melts and their phase diagrams is emphasized.

1.2 Thermodynamic Concepts and Relationships

1.2.1 First Law of Thermodynamics. Principle of Conservation of Energy

One of the most fundamental laws of physics is the law of conservation of energy. So far, it is known to be valid without any exceptions. When applied in thermodynamics it is called the first law of thermodynamics and is written

$$Q = U + W \tag{1.1}$$

where
Q = heat energy added to a closed system
U = the internal energy of the system or the sum of the kinetic and potential energies of the atoms
W = work done by the system.

Differentiating Equation (1.1) gives the relationship

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W = \mathrm{d}U + p\mathrm{d}V \tag{1.2}$$

The added heat $\mathrm{d}Q$ is used for the increase $\mathrm{d}U$ of the internal energy of the system and for the external work $p\mathrm{d}V$ against the surrounding pressure p when the volume of the system increases by the amount $\mathrm{d}V$.

1.2.2 Enthalpy

The enthalpy of a closed system is defined as

$$H = U + pV \tag{1.3}$$

The enthalpy H can be described as the 'heat content' of the system. In the absence of phase transformations we have

$$H = \int_0^T nC_\mathrm{p}\mathrm{d}T \tag{1.4}$$

where
H = enthalpy of the system
n = number of kmol
C_p = molar heat capacity of the system (J/kmol).

When the heat content of a system is changed the enthalpy changes by the amount ΔH. When the system *absorbs* heat from the surroundings the heat content of the system is *increased* and ΔH *is positive*.

When the system *emits* heat to the surroundings and *reduces* its heat content, ΔH is *negative*. The amount of heat absorbed by the surroundings is $(-\Delta H)$, which is a positive quantity.

Differentiating Equation (1.3) gives

$$dH = dU + p dV + V dp \tag{1.5}$$

By use of Equation (1.2) we obtain

$$dH = dQ + V dp$$

At constant pressure, the heat absorbed by a system equals its enthalpy increase:

$$(dH)_p = (dQ)_p \tag{1.6}$$

1.2.3 Second Law of Thermodynamics. Entropy

Second Law of Thermodynamics

By experience it is known that heat always is transferred spontaneously from a warmer to a colder body, never the contrary.

It is possible to transfer heat into mechanical work but never to 100%. Consider a closed system (no energy exchange with the surroundings) which consists of an engine in contact with two heat reservoirs. If an amount Q_1 of heat is emitted from reservoir 1 at a temperature T_1 to the engine and an amount Q_2 of heat is absorbed by reservoir 2 at temperature T_2, the energy difference $Q_1 - Q_2$ is transferred into mechanical work in the ideal case.

The reversed process is shown in Figure 1.1. It can be described as follows.

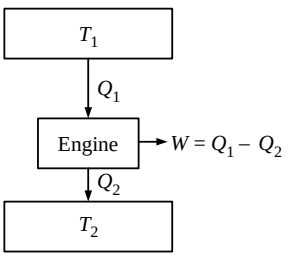


Figure 1.1 Engine in contact with two heat reservoirs. $T_1 > T_2$. The energy law gives $Q_1 = Q_2 + W$.

- Heat can be transferred from a colder body to a warmer body only if work or energy is supplied.

This is one of many ways to express the second law of thermodynamics.

In practice, heat is transferred into mechanical work in heat engines. The process in such a machine can theoretically be described by the Carnot cycle (Figure 1.2a). Fuel is burned and the combustion gas runs through the following cycle in the engine

1. The gas absorbs the amount Q_1 of heat and expands isothermally at temperature T_1.
2. The gas expands adiabatically. The temperature decreases from T_1 to T_2.
3. The gas is compressed isothermally at temperature T_2 and emits the amount Q_2 of heat.
4. The gas is compressed adiabatically. The temperature changes from T_2 back to T_1.

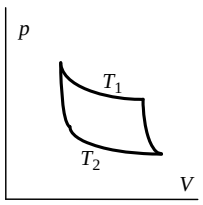


Figure 1.2a The Carnot cycle. The enclosed area represents the work done by the heat engine during a cycle.

Calculations of the expansion and compression works show that

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{1.7}$$

In the ideal case, the efficiency η of the Carnot cycle is

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{1.8}$$

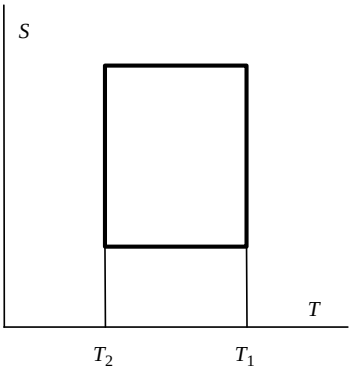


Figure 1.2b The Carnot cycle. The enclosed area represents the work done by the heat engine during a cycle.

Entropy

A very useful and important quantity in thermodynamics is the entropy S. Entropy is defined by the relationship

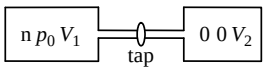
$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} \tag{1.9}$$

As an example we represent the Carnot cycle in a TS diagram (Figure 1.2b). Horizontal lines represent the isothermal expansion and compression. The vertical lines illustrate the adiabatic steps of the cycle. The area of the rectangle equals the work done by the gas. A reversible adiabatic process is also called *isentropic*.

Entropy Change at an Isothermal Irreversible Expansion of a Gas

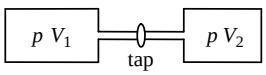
In many solidification processes the entropy change is of great interest. As a first example we will consider the isothermal, irreversible expansion of an ideal gas and calculate the entropy change.

Example 1.1



Calculate the change in entropy when n kmol of an ideal gas with the pressure p_0 and the volume V_1 expands irreversibly to the volume $V_1 + V_2$ in the way shown in the figure.

Solution:



There are no forces between the molecules in the gas and therefore there is no change of internal energy when the gas expands. No change of internal energy means no temperature change.

When the tap is opened, the gas expands isothermally from volume V_1 to $V_1 + V_2$. The first law of thermodynamics and the definition of entropy give

$$\Delta S = \int \frac{\mathrm{d}q}{T} = \int_{V_1}^{V_1+V_2} \frac{p\mathrm{d}V}{T} \tag{1'}$$

Using the general gas law $pV = nRT$ to eliminate T we obtain

$$\Delta S = \int_{V_1}^{V_1+V_2} \frac{nR\mathrm{d}V}{V} = nR \ln \frac{V_1 + V_2}{V_1} \tag{2'}$$

Answer: The entropy increases by the amount $nR \ln \dfrac{V_1 + V_2}{V_1}$.

The final state in Example 1.1 is far more likely than the initial state. When the tap is opened the molecules move into the empty container until the pressures in the two containers are equal rather than that no change at all occurs. Hence, the system changes spontaneously from one state to another, more likely state and the entropy increases.

All experience shows that the result in Example 1.1 can be generally applied. The following statements are generally valid:

- If a process is reversible the entropy change is zero.

$$\Delta S = 0.$$

- The entropy increases in all irreversible processes.

$$\Delta S > 0.$$

Entropy of Mixtures

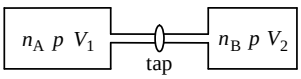
Entropy Change at Mixing Two Gases

As a second example of deriving entropy changes we will calculate the entropy change when two gases mix.

Example 1.2

A short tube and a closed tap connect two gases A and B of equal pressures, each in a separate closed container. When the tap is opened the two gases mix irreversibly. No changes in pressure and temperature are observed.

Calculate the total change of entropy as a function of the initial pressure p and the final partial pressures when the two gases mix. The data of the gases are given in the figure.

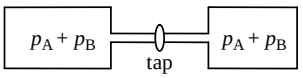


n = number of kmol
p = pressure
V = volume
The temperature T is constant.

Solution:

When the tap is opened the two gases mix by diffusion. The diffusion goes on until the composition of the gas is homogeneous. It is far more likely that the gases mix by diffusion than that the gases remain separate. Hence, the total entropy change is expected to be positive.

In a gas, the distances between the molecules are large and the interaction between them can be neglected. The diffusion of each gas is independent of the other. The total entropy change can be regarded as the sum of the entropy change of each gas after its separate diffusion from one container into the other.



After the diffusion the gases are mixed and the pressure is equal in the two containers. The temperature T is constant.

$$\Delta S^{\text{mix}} = \Delta S_A^{\text{mix}} + \Delta S_B^{\text{mix}} \tag{1'}$$

n_A kmol of gas A change their pressure from p to p_A where p_A is its final partial pressure. In the same way n_B kmol of gas B change their pressure from p to p_B.

The initial pressure and the final total pressure are equal as no pressure change is observed.

$$p = p_A + p_B \tag{2'}$$

Using the result of Example 1.1 we obtain

$$\Delta S_A^{\text{mix}} = n_A R \ln \frac{V_1 + V_2}{V_1} \tag{3'}$$

and

$$\Delta S_B^{\text{mix}} = n_B R \ln \frac{V_1 + V_2}{V_2} \tag{4'}$$

The partial pressures can be calculated with the aid of Boyle's law applied on each gas:

$$pV_1 = p_A(V_1 + V_2) \tag{5'}$$

and

$$pV_2 = p_B(V_1 + V_2) \tag{6'}$$

The ratio of the volumes from Equations (5′) and (6′) are inserted into Equations (3′) and (4′) and we obtain

$$\Delta S_{\mathrm{A}}^{\mathrm{mix}} = n_{\mathrm{A}} R \ln \frac{p}{p_{\mathrm{A}}} \tag{7′}$$

and

$$\Delta S_{\mathrm{B}}^{\mathrm{mix}} = n_{\mathrm{B}} R \ln \frac{p}{p_{\mathrm{B}}} \tag{8′}$$

The total entropy change is

$$S^{\mathrm{mix}} = \Delta S_{\mathrm{A}}^{\mathrm{mix}} + \Delta S_{\mathrm{B}}^{\mathrm{mix}} = n_{\mathrm{A}} R \ln \frac{p}{p_{\mathrm{A}}} + n_{\mathrm{B}} R \ln \frac{p}{p_{\mathrm{B}}} \tag{9′}$$

The ratio of the pressures is >1 and the entropy change is therefore positive, as predicted above.

Answer: The total entropy change when the gases mix is

$$n_{\mathrm{A}} R \ln \frac{p}{p_{\mathrm{A}}} + n_{\mathrm{B}} R \ln \frac{p}{p_{\mathrm{B}}}, \quad \text{where} \quad p = p_{\mathrm{A}} + p_{\mathrm{B}}.$$

Entropy Change at Mixing Two Liquids or Solids

Diffusion occurs not only in gases but also in liquids and solids. The entropy change ΔS^{mix} or simply S^{mix}, owing to mixing of two compounds in a melt or a solid can be calculated if we make a minor modification of Equation (9′) in Example 1.2.

Instead of the partial pressures of the two gases we introduce the mole fractions x_{A} and x_{B}:

$$x_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{p_{\mathrm{A}} + p_{\mathrm{B}}} \quad \text{and} \quad x_{\mathrm{B}} = \frac{p_{\mathrm{A}}}{p_{\mathrm{A}} + p_{\mathrm{B}}}$$

Equation (9′) can then be written as

$$S^{\mathrm{mix}} = -n_{\mathrm{A}} R \ln x_{\mathrm{A}} - n_{\mathrm{B}} R \ln x_{\mathrm{B}} \tag{1.10}$$

By use of the relationship $n = n_{\mathrm{A}} + n_{\mathrm{B}}$ where n is the total number of kmole we obtain

$$S^{\mathrm{mix}} = -nR(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \tag{1.11}$$

The molar entropy of mixing will then be

$$S_{\mathrm{m}}^{\mathrm{mix}} = -R(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \tag{1.12}$$

Equations (1.11) and (1.12) are directly applicable on mixtures of gases but also on liquids and solids. These applications will be discussed later.

Entropy and Probability

The two examples given above indicate that entropy in some way is related to probability. The probability function can be found by the following arguments.

Consider N molecules in a container with the volume V (Figure 1.3). The molecules do not interact at all. Each molecule is free to move within the volume V. The probability of finding it within a unit volume is the same everywhere. Hence the probability of finding a molecule within a volume V_1 is V_1/V. The probability of finding two molecules within the same volume V_1 equals the

product of their probabilities $(V_1/V)^2$. The probability of finding N molecules within a particular volume V_1 is $(V_1/V)^N$.

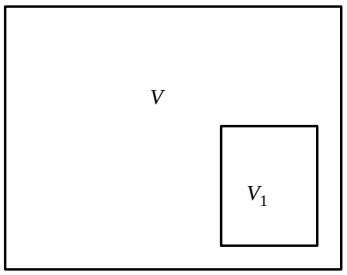


Figure 1.3 Volume element.

Equation (2′) in Example 1.1 on page 4 and Equation (9′) on page 6 give us the clue to relating entropy and probability. We have seen above that the overall probability is the *product* of the probabilities of independent events. We also know that the entropy of two systems is the *sum* of their entropies. It is striking that the logarithmic function converts the multiplicative property of probability to the additive property of entropy.

These arguments led the physicists Maxwell and Boltzmann in 1877 to suggest a relationship between entropy and probability. Boltzmann interpreted entropy as a measure of the order, or rather disorder, of a system. The more probable a state of a system is and the greater its disorder is, the higher will be its entropy.

Boltzmann derived an alternative expression of entropy by using statistical thermodynamics.

$$S = k_B \ln P \tag{1.13}$$

where
k_B = Boltzmann's constant
P = probability of the state.

Equation (1.13) is the fundamental relationship between entropy and probability. P is called the statistical weight of the state, i.e. its configuration.

Consider a binary system, a gas or a liquid, of two components B and C. N_B atoms of B and N_C atoms of C are arranged at random among $N = N_B + N_C$ sites. This can be done in many different ways and is equivalent to mixing the two components. The statistical weight P is the number of alternative ways to arrange the B and C atoms among the N sites. Statistical considerations give the result

$$P = \frac{N!}{N_B! N_C!} = \frac{N!}{N_B!(N - N_B)!} \tag{1.14}$$

We use Stirling's formula

$$\lim N! \to \sqrt{2\pi}\, N^{N+1/2} e^{-N} \quad \text{when} \quad n \to \infty$$

for the very high numbers N, N_B and $N_C = N - N_B$ and obtain

$$P = \frac{N^{N+1/2}}{N_B^{N_B+1/2}(N - N_B)^{N-N_B+1/2}} \frac{e^{-N}}{e^{-N_B} e^{-(N-N_B)}} \tag{1.15}$$

The last factor in Equation (1.15) is equal to 1. The term 1/2 in the exponents can be neglected in comparison with N and N_B. Taking the logarithm of both sides of Equation (1.15) we obtain

$$\ln P = N \ln N - N_B \ln N_B - (N - N_B)\ln(N - N_B) \tag{1.16}$$

If we introduce the mole fractions

$$x_B = \frac{N_B}{N} \quad \text{and} \quad x_C = \frac{N - N_B}{N} \quad \text{and the relationship} \quad x_B + x_C = 1$$

Equation (1.16) can, after some calculations, be transformed into

$$\ln P = N(-x_B \ln x_B - x_C \ln x_C) \tag{1.17}$$

Instead of N we introduce n, the number of kmol with the aid of the relationship:

$$n = \frac{N}{N_A} \tag{1.18}$$

where N_A is Avogadro's number, i.e. the number of molecules of 1 kmol. Hence, we obtain

$$\ln P = nN_A(-x_B \ln x_B - x_C \ln x_C) \tag{1.19}$$

Instead of N_A we introduce R/k_B into Equation (1.18), where k_B is Boltzmann's constant.

$$k_B \ln P = -nR(x_B \ln x_B + x_C \ln x_C) \tag{1.20}$$

According to Equation (1.13) $k_B \ln P$ equals the entropy change S^{mix} when the two components B and C mix. Hence, we obtain

$$S^{mix} = -nR(x_B \ln x_B + x_C \ln x_C) \tag{1.21}$$

Equation (1.21) is valid for homogeneously mixed solids and liquids.

Equation (1.21) is identical with Equation (1.11) on page 6 derived in an entirely different way. The conclusion is that the concept of entropy as a function of probability is in complete agreement with the classical theory and does not lead to any contradictions.

Entropy Change during Solidification

Freezing and boiling causes changes in the molecular order and are therefore expected to lead to changes in entropy.

At freezing and melting the system is in equilibrium and the temperature is constant. Energy is transferred reversibly and isothermally in the shape of heat between the system and its surroundings.

At constant pressure the heat *absorbed* by a system equals its enthalpy *increase*:

$$(\Delta Q_{tr})_p = (\Delta H_{tr})_p \tag{1.22}$$

and the entropy change will be

$$\Delta S = \frac{\Delta H_{tr}}{T_{tr}} \tag{1.23}$$

Subscript 'tr' stands for transformation.

At *solidification* the system *emits* heat and the phase transition is exothermic. In this case the enthalpy change is negative and *the entropy change is negative.* The system changes from a disordered state (liquid) to a more ordered state (solid). The disorder decreases.

In the case of melting the opposite is valid. The phase transition is endothermic and the entropy change is positive. Heat has to be added to the system and its disorder increases.

1.2.4 Gibbs' Free Energy

Consider a system in thermal equilibrium with its surroundings at the temperature T. A spontaneous change of state of the system always leads to an increase of the entropy of the system. This can be expressed mathematically by Clausius' inequality

$$dS - \frac{dQ_{reversible}}{T} \geq 0 \tag{1.24}$$

If the process is reversible the sign of equality is valid. In the case of an irreversible process the upper sign has to be used. Heat transfer at constant pressure is of special interest in chemistry and metallurgy. If there is no other work than expansion work, $dQ_{rev} = dH$ and Equation (1.24) can be written as

$$T dS - dH \geq 0 \tag{1.25}$$

Equation (1.25) is valid if either of the following two conditions is fulfilled

1. The enthalpy of the system is constant.

$$dS_{H,p} \geq 0 \tag{1.26}$$

2. The entropy of the system is constant.

$$dH_{S,p} \leq 0 \tag{1.27}$$

The conditions 1 and 2 can be expressed in a simpler and understandable way by introduction of another thermodynamic function, the *Gibbs' free energy* or *Gibbs' function*

$$G = H - TS \tag{1.28}$$

When the state of the system changes at constant temperature the change of G equals

$$dG = dH - TdS \tag{1.29}$$

Equation (1.25) can be expressed in terms of the Gibbs' function as

$$dG_{T,p} \leq 0 \tag{1.30}$$

- At constant temperature and pressure spontaneous processes always occur in the direction of decreasing G.

The deviation of the thermodynamic function G of a system from its equilibrium value can be regarded as the driving force in chemical and metallurgical reactions. At equilibrium

$$dG_{T,p} = 0 \tag{1.31}$$

and the driving force is zero. This condition will be applied later in this chapter.

Gibbs' free energy is a most useful instrument for studying the driving forces of various processes, for example chemical reactions, solution processes, melting/solidification and evaporation/condensation processes.

1.2.5 Intensive and Extensive Thermodynamic Quantities

Consider a single-component system, for example a pure metal, which consists of a certain amount of the pure substance. The system can be described by a number of quantities such as volume V, pressure p, absolute temperature T, number of kmol n of the pure element, internal energy U and entropy S.

The quantities of the system can be divided into two groups

- *intensive* quantities, which are independent of the amount of matter;
- *extensive* quantities, which are proportional to the amount of matter.

The pressure p, the temperature T are intensive quantities while volume, energy and entropy of the system are examples of extensive quantities.

A single-component system may consist of several phases, e.g. solid and liquid phases. A single-component system can be regarded as a special case of a multiple-component system. Phases in single- and multiple-component systems will be discussed in Section 1.5.1.

Extensive quantities, which refer to 1 kmol, will normally be denoted by capital letters with no index, otherwise with an index or by the product if the capital letter and the number of kmol.

In metallurgy an index 'm' for molar (1 kmol) is often used. We will also use this principle of designation. As we strictly use the SI system the concept *molar* is used in the sense of 1 kmol.

Gibbs' free energy G is an extensive thermodynamic quantity that will be frequently used in this and the following chapters, especially in Chapter 2.

1.3 Thermodynamics of Single-Component Systems

A single-component system may consist of only one phase, for example a solid, a liquid or a gas depending on the temperature. At certain temperatures discontinuous phase transformations occur when the system changes from one phase to another.

Examples of such transformations are melting of solid metals and evaporation of liquids. In this section we will study this type of processes in single-component systems. The results are general but will entirely be applied on the special single-component systems, which consist of *pure metals*.

At the transformation temperatures two phases are in equilibrium with each other. The conditions for equilibrium will be set up in terms of thermodynamics and the influence of some parameters on the transformation temperatures will be studied.

1.3.1 Clausius–Clapeyron's Law

The general expression for equilibrium between two arbitrary phases α and β in contact with each other is

$$G^{\alpha} = G^{\beta} \tag{1.32}$$

The Gibbs' free energies can be regarded as functions of the independent variables pressure p and temperature T.

A change of one of the independent variables results in changes of G^{α} and G^{β}. If the equilibrium is to be maintained a simultaneous and corresponding change of the other independent variable must occur. There must be a relationship between Δp and ΔT. In order to find it we use the condition for maintaining the equilibrium of the system:

$$\mathrm{d}G^{\alpha} = \mathrm{d}G^{\beta} \tag{1.33}$$

Gibbs' free energy is defined as

$$G = H - TS = U + pV - TS \tag{1.34}$$

The total differential of G is

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T \tag{1.35}$$

By use of the first law of thermodynamics, $\mathrm{d}Q = \mathrm{d}U + p\mathrm{d}V$ and the definition of entropy, $\mathrm{d}S = \mathrm{d}Q/T = (\mathrm{d}U + p\mathrm{d}V)/T$, Equation (1.35) can be reduced to

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T \tag{1.36}$$

Equation (1.36) is applied on the two phases α and β and the results are introduced into Equation (1.33).

$$V^{\alpha}\mathrm{d}p - S^{\alpha}\mathrm{d}T = V^{\beta}\mathrm{d}p - S^{\beta}\mathrm{d}T \tag{1.37}$$

or

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{V^{\beta} - V^{\alpha}}{S^{\beta} - S^{\alpha}} = \frac{\Delta V^{\alpha \to \beta}}{\Delta S^{\alpha \to \beta}} \quad \text{Clausius–Clapeyron's law} \tag{1.38}$$

where
$\Delta V^{\alpha \to \beta}$ = difference between the volumes of the β and α phases, i.e. $V^{\beta} - V^{\alpha}$
$\Delta S^{\alpha \to \beta}$ = difference between the entropies of the β and α phases, i.e. $S^{\beta} - S^{\alpha}$.

Equation (1.38) is the *Clausius–Clapeyron's law*, which is the desired relationship between the changes in pressure and temperature in a two-phase system at equilibrium. It will be applied on the melting and boiling processes below.

1.3.2 Equilibrium between Liquid and Solid Phases. Influence of Pressure and Crystal Curvature on Melting Point

Influence of Pressure on Melting Point

Consider a solid metal at the melting point in equilibrium with the corresponding metal melt. If the pressure p_0 is increased by an amount $\mathrm{d}p$ to $p = p_0 + \Delta p$, a new equilibrium is developed and the temperature is changed by the amount $\mathrm{d}T$.

The temperature change or the change of melting point as a function of the pressure change can be found if we apply Clausius–Clapeyron's law on the liquid–solid system. Solidification means that a liquid phase α is transformed into a solid phase β at the melting-point temperature.

If we apply Equation (1.38) on 1 kmol of the liquid, which solidifies, we obtain

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{\Delta V_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}}}{\Delta S_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}}} \tag{1.39}$$

Subscript 'm' stands for molar (1 kmol).

If $\Delta S_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}}$ is substituted by $\Delta H_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}} / T_{\mathrm{M}}$ (compare Equation (1.23) on page 8) in Equation (1.39) we obtain

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{T_{\mathrm{M}} \Delta V_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}}}{\Delta H_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}}} = \frac{T_{\mathrm{M}} \left(V_{\mathrm{m}}^{\mathrm{s}} - V_{\mathrm{m}}^{\mathrm{L}} \right)}{- H_{\mathrm{m}}^{\mathrm{fusion}}} \tag{1.40}$$

or

$$\Delta T_{\mathrm{M}} = T_{\mathrm{M}}(p) - T_{\mathrm{M}}(p_0) = \frac{T_{\mathrm{M}} \left(V_{\mathrm{m}}^{\mathrm{L}} - V_{\mathrm{m}}^{\mathrm{s}} \right)}{H_{\mathrm{m}}^{\mathrm{fusion}}} \Delta p \tag{1.41}$$

where
ΔT_{M} = change of melting point, i.e. $T_{\mathrm{M}}(p) - T_{\mathrm{M}}(p_0)$
p_0 = normal pressure, usually 1 atm
p = pressure p equal to $p_0 + \Delta p$
$T_{\mathrm{M}}(p)$ = melting-point temperature at pressure p
$\Delta V_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}}$ = difference in molar solid and liquid volumes at temperature T_{M}, i.e. $V^{\mathrm{s}} - V^{\mathrm{L}}$
$-\Delta H_{\mathrm{m}}^{\mathrm{L} \to \mathrm{s}}$ = molar heat of fusion $H_{\mathrm{m}}^{\mathrm{fusion}} = -(H^{\mathrm{s}} - H^{\mathrm{L}})$.

As the molar volume of a metal melt normally is larger than that of the solid metal and the heat of fusion is positive, an *increase* of the pressure leads to an *increase* of the melting point.

The pressure dependence on the melting-point temperature in metal melts is very small. Moderate changes of the pressure during the casting and solidification processes hardly influence the liquidus

temperature at all. The effect can normally be neglected except for pressures of the magnitude $\geq 10^2$ atm.

Influence of Crystal Curvature on Melting Point

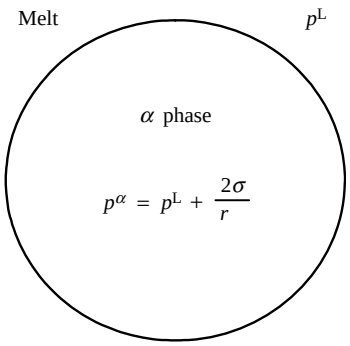


Figure 1.4a Spherical particle in a melt. Curvature K equals $1/r$.

It is a common practical situation that one phase has a much smaller volume than the other phase while the phases still are at equilibrium with each other. An example of such a case is shown in Figure 1.4a.

A small spherical α phase particle or a gas pore with radius r is floating freely in a melt of pressure p^L. The surface tension between particle and melt causes the pressure inside the particle to be higher than outside in the melt. The pressure inside the melt is obtained by a mechanical equilibrium study, which gives the result

$$p^\alpha = p^L + \frac{2\sigma}{r} \tag{1.42}$$

where σ is the surface tension between the melt and the α phase.

Equation (1.42) is a special case of Laplace's formula that states that there will be a pressure difference, owing to surface tension at a point on a curved surface between two phases

$$p^\alpha = p^L + \sigma\left(\frac{1}{r_{max}} + \frac{1}{r_{min}}\right) \tag{1.43}$$

where r_{max} and r_{min} are the maximum and minimum radii of curvature of the particle that is no longer necessarily spherical. We introduce the concept *curvature*, which is denoted by K and defined by the relationship

$$K = \frac{1}{2}\left(\frac{1}{r_{max}} + \frac{1}{r_{min}}\right) \tag{1.44}$$

Equation (1.43) can then be written as

$$p_K^\alpha = p^L + 2\sigma K \tag{1.45}$$

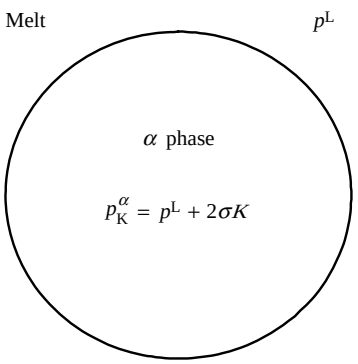


Figure 1.4b Spherical particle in a melt. Curvature K equals $1/r$.

Equation (1.45) is introduced into Figure 1.4b. At a planar surface K is zero and $p_K^\alpha = p^L$.

The pressure p_K^α will therefore change when the solid surface is curved instead of planar. This pressure change $p_K^\alpha - p_0^\alpha$ is accompanied by a corresponding change of the melting point of the solid. The difference in melting-point temperature can be calculated with the aid of Equation (1.41) while the following conditions are assumed to be valid:

1. the α phase and the melt are in equilibrium with each other
2. the melt maintains a constant pressure p^L independent of the particle curvature.

According to Equation (1.45) the pressure p_0^α at a planar interface equals the constant liquid pressure p^L. It is also identical with the pressure p_0 in Equation (1.41). Hence, we obtain

$$T_M(p_K^\alpha) - T_M(p_0^\alpha) = \frac{T_M\left(V_m^\alpha - V_m^L\right)}{H_m^{fusion}}\left[(p^L + 2\sigma K) - p^L\right]$$

or

$$T_M\left(p_K^\alpha\right) - T_M\left(p_0^\alpha\right) = \frac{T_M\left(V_m^\alpha - V_m^L\right)}{H_m^{fusion}} 2\sigma K \tag{1.46}$$

where
$T_M(p_K^\alpha)$ = melting point at curvature K of the particle and constant liquid pressure p^L
$T_M(p_0^\alpha)$ = melting point at curvature 0 and constant liquid pressure p^L
σ = surface tension
K = average curvature of the particle
V_m^α = molar volume of the α phase at the melting point
V_m^L = molar volume of the melt at the melting point.

K is positive when the curvature is convex. This is the case for a growing dendrite tip in a metal melt. As the volume change in Equation (1.46) is negative, there will be a *decrease* in melting-point temperature in the neighbourhood of a growing dendrite tip. The more curved the dendrite tip is, the lower will be the melting point.

1.3.3 Equilibrium between Liquid and Gaseous Phases. Influence of Pressure on Boiling Point. Bubble Formation in Melts

Influence of Pressure on Boiling Point

Clausius–Clapeyron's law (Equation (1.38) on page 11) is also valid for evaporation and condensation. It can be used for calculation of the change in boiling-point temperature of a liquid and its vapour in equilibrium with each other, caused by a change of pressure of the two phases. Boiling means that a liquid phase L is transformed into a gaseous phase g at the boiling-point temperature.

If we apply Equation (1.38) on 1 kmol of the liquid, which evaporates, we obtain

$$\frac{dT}{dp} = \frac{\Delta V_m^{L\to g}}{\Delta S_m^{L\to g}} \tag{1.47}$$

If $\Delta S_m^{L\to g}$ is substituted by $\Delta H_m^{L\to g}/T_B$ in Equation (1.47) we obtain

$$\frac{dT}{dp} = \frac{T_B \Delta V_m^{L\to g}}{\Delta H_m^{L\to g}} = \frac{T_B\left(V_m^g - V_m^L\right)}{H_m^{evap}} \tag{1.48}$$

or

$$\Delta T_B = T_B(p) - T_B(p_0) = \frac{T_B\left(V_m^g - V_m^L\right)}{H_m^{evap}}\Delta p \tag{1.49}$$

where
ΔT_B = change of boiling-point temperature
p_0 = normal pressure, usually 1 atm
p = pressure equal to $p_0 + \Delta p$
$\Delta V_m^{L\to g}$ = difference in molar gaseous and liquid volumes at boiling-point temperature T_B
$\Delta H_m^{L\to g}$ = molar heat of evaporation H_m^{evap}.

As the molar volume of the vapour is very much larger than that of the liquid, an *increased* pressure corresponds to an *increase* of the boiling-point temperature and vice versa.

The boiling point change is of the magnitude 10^4 times larger than the melting point change for the same change of pressure and can not be neglected.

Equation (1.49) can be simplified by neglecting the molar volume of the liquid in comparison with that of the vapour. If we replace the quantities ΔT and Δp by the corresponding differentials and assume, somewhat doubtfully, that the gas behaves like an ideal gas, we obtain for a temperature T close to the boiling point

$$dT = \frac{T}{H_m^{evap}} V_m^g dp = \frac{T}{H_m^{evap}} \frac{RT}{p} dp \tag{1.50}$$

or

$$\frac{dp}{p} \approx \frac{H_m^{evap}}{R}\frac{dT}{T^2} \tag{1.51}$$

It is reasonable to assume that the heat of evaporation is approximately independent of pressure and temperature.

$$\int_{p_0}^{p}\frac{dp}{p} \approx \frac{H_m^{evap}}{R}\int_{T_B}^{T}\frac{dT}{T^2} \tag{1.52a}$$

or

$$\ln\frac{p}{p_0} = \frac{H_m^{evap}}{R}\left(\frac{1}{T_B} - \frac{1}{T}\right) \tag{1.52b}$$

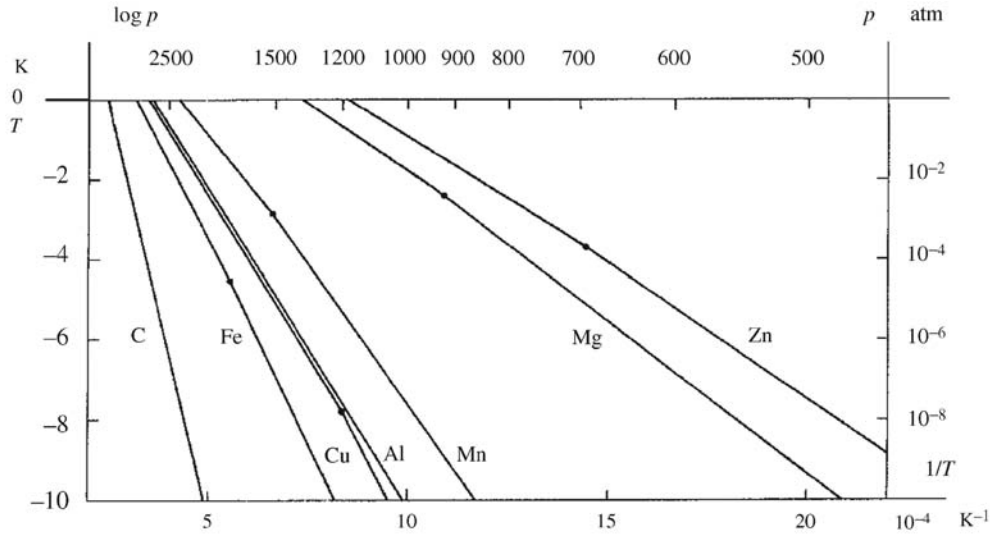


Figure 1.5 Vapour pressure as a function of $1/T$ for some common elements.

The melting points of the metals are marked by small black dots.

The rectangle represents four different axes. The functions and the corresponding scales are found in the corners. Reproduced from Elsevier © 1983.

Figure 1.5 shows $\ln p$ as a function of $1/T$ for some common elements. The straight lines in the figure shows that the approximations we made above seem to be justified and acceptable.

Equation (1.52b) can alternatively be written as

$$\Delta T_B = T_B(p) - T_B(p_0) = \frac{RT_B(p)T_B(p_0)}{H_m^{evap}}\ln\frac{p}{p_0} \tag{1.53}$$

which gives the change of boiling-point temperature as a function of pressure. The molar heat of evaporation is positive. At $p = p_0$ the boiling point is $T_B(p_0)$. An increase of the pressure leads to a positive value of ΔT, i.e. the boiling point increases. A decrease of the pressure results in a decrease of the boiling point.

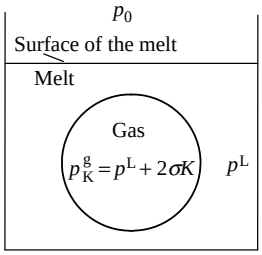


Figure 1.6a Pressure inside a spherical gas pore in a melt. Curvature K equals $1/r$ where r is the radius of the gas pore. p_0 is the pressure above the surface.

Bubble Formation in Melts

The condition for bubble formation in a liquid is that the pressure inside the bubble $\geq$ the pressure of the surrounding liquid.

To treat bubble formation we substitute the α phase in Figure 1.4a by a gas phase of pressure $p = p_K^g$ (Figure 1.6a). The pressure inside a bubble with the curvature K (page 12) is derived in the same way as on page 12. In analogy with Equation (1.45) we obtain the total pressure inside the bubble equals

$$p_K^g = p^L + 2\sigma K \tag{1.54}$$

where $p^L = p_0 + \rho g h$.

The smaller the bubble is when it is formed, the larger will be p_K^g, which facilitates bubble formation. If we replace p by p_K^g in Equation (1.53) we obtain

$$\Delta T_B = T_B(p_K^g) - T_B(p_0) = \frac{RT_B(p_K^g)T_B(p_0)}{H_m^{evap}} \ln \frac{p^L + 2\sigma K}{p_0} \tag{1.55}$$

The third term in Equation (1.55) is always positive. This leads to the obvious conclusion that a gas bubble with a higher internal pressure than the surroundings can only be formed *above* the normal boiling temperature T_B (p_0) of the melt. Energy for evaporation must be supplied, or else the boiling will stop.

The equilibrium between phases will be discussed more generally in the following sections.

If the pressure p_0 is kept low by pumping away the gas above the surface of the melt (Figure 1.6b), the pressure p^L, which equals $p_0 + \rho gh$, will also go down and the boiling-point temperature becomes strongly reduced. The consequence is that the bubble-formation condition is easier to fulfil and the boiling starts at a much lower temperature than normally.

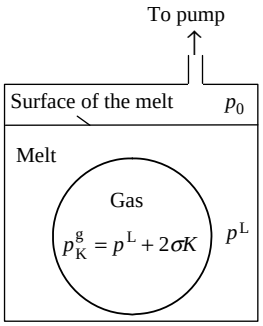


Figure 1.6b Pressure inside a spherical gas pore in a melt. Curvature K equals $1/r$ where r is the radius of the gas pore. h is the depth of the bubble below the surface.

1.3.4 Molar Gibbs' Free Energy of a Pure Metal

The Gibbs' free energy of a single phase, for example a pure metal, is defined by Equation (1.28) on page 9. If we apply this definition to the Gibbs' free energy of 1 kmol of the pure metal and use an index m, which stands for molar, we obtain

$$G_m = H_m - TS_m \tag{1.56}$$

Each metal has its own characteristic values of the thermodynamic quantities. The values of the molar enthalpy and the molar entropy of the solid metal are different from those of the liquid metal. The values of H_m are fairly constant but S_m varies with the temperature for each phase.

Figures 1.7 and 1.8, which show the functions

$$G_m^s = H_m^s - TS_m^s \tag{1.57a}$$

$$G_m^L = H_m^L - TS_m^L \tag{1.57b}$$

confirm the statements above. We can conclude that the thermodynamic quantities vary with temperature, as the curves are non-linear.

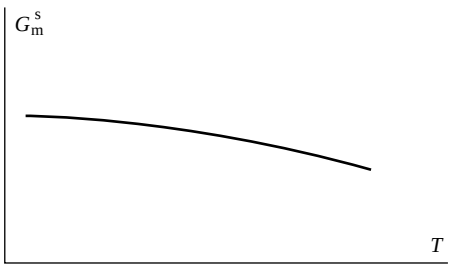


Figure 1.7 The molar Gibbs' free energy of a solid metal A as a function of temperature.

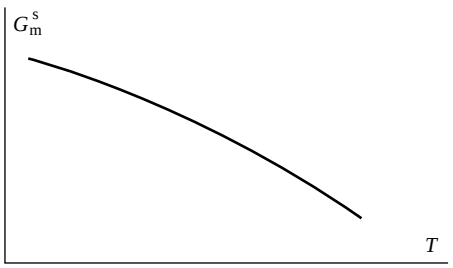


Figure 1.8 The molar Gibbs' free energy of a liquid metal A as a function of temperature.

Often, a reference temperature T_{ref} is used instead of zero and relative values ΔH and ΔS are introduced:

$$\Delta H_m^i = \int_{T_{ref}}^{T} C_p(T)\mathrm{d}T \quad \text{and} \quad \Delta S_m^i = \int_{T_{ref}}^{T} \frac{C_p(T)}{T}\mathrm{d}T \tag{1.58a+b}$$

Calculation of Molar Enthalpy and Entropy of Solids and Liquids

The curves in Figures 1.7 and 1.8 are calculated from Equations (1.57a) and (1.57b) in combination with the relationships

$$H_{\mathrm{m}}^{\mathrm{i}} = \int_0^T C_{\mathrm{p}}(T)\mathrm{d}T \quad \text{and} \quad S_{\mathrm{m}}^{\mathrm{i}} = \int_0^T \frac{C_{\mathrm{p}}(T)}{T}\mathrm{d}T \tag{1.59a+b}$$

where i = s and L, respectively.

The entropy of the liquid phase is normally larger than that of the solid. For this reason the curve in Figure 1.8 is steeper than that in Figure 1.7.

1.4 Thermodynamics of Multiple-Component Systems

Both single- and multiple-component systems may be *homogeneous*, i.e. appear as a single phase with uniform composition and physical properties, or *heterogeneous*, i.e. consist of several phases with different physical properties. At the phase boundaries these properties change abruptly. In multiple-component systems the composition of each phase must be specified.

Below, we will introduce a number of new thermodynamic concepts and relationships between them, which will be used on binary alloys in the remaining sections in this chapter and in Chapter 2. They are generally valid for many quantities in multiple-component systems, for example volume V, enthalpy H, entropy S and Gibbs' free energy G and also for several other thermodynamic functions.

To make the description below as short and surveyable as possible and avoid boring repetitions we use the volume V as a principle example throughout this section, when new concepts and relationships are introduced. However, we want to point out strongly that the concepts and relationships are also valid for other thermodynamic quantities.

- In all definitions, concepts and relationships the enthalpy H, the entropy S or the Gibb's free energy G can replace the volume V.

Independent Thermodynamic Variables of Multiple-Component Systems

As a multiple-component system we will consider an alloy to make the description below realistic. Alloys can be described by the following independent variables

- temperature;
- pressure;
- composition.

The thermodynamic quantities of a multiple-component system, for example an alloy, changes very little when the pressure is changed and the influence of pressure can be neglected in most cases.

The influence of temperature on thermodynamic variables, for example the Gibbs' free energy, is often strong and must definitely be taken into consideration.

The composition of a system is expressed as concentration of its components. Usual measures are number of kmol, mole fraction and atomic per cent (at%).

1.4.1 Partial Molar Thermodynamic Quantities

Consider a system, which consists of components A, B . . . c where c corresponds to the number of components. Index i refers to component i of the system where i = A, B, . . . c. The number of kmol of component i in the alloy is n_{i}.

Each system has its own characteristic thermodynamic quantities such as volume V and entropy S. In addition, it is convenient and useful to define so-called *partial molar thermodynamic quantities*

or shortly *molar quantities* for multiple-component systems. A partial molar quantity is the corresponding molar quantity of each component instead the molar quantity of the total system. As an example we use the volume V.

$$\text{Partial molar quantity } \overline{V}_i = \frac{\partial V}{\partial n_i} \tag{1.60}$$

The definition is general and can be applied on *any* thermodynamic quantity. It is applied in Table 1.1 below on four of the most important and frequent basic thermodynamic quantities.

By use of basic mathematics we will derive some important and useful relationships. They are derived below for the volume but are valid for all extensive thermodynamic quantities. Examples are given in Table 1.1.

Table 1.1 Some partial molar thermodynamic quantities (V, S, H and G)

Partial molar volume	Partial molar entropy	Partial molar enthalpy	Partial molar Gibbs' free energy
$\overline{V}_i = \frac{\partial V}{\partial n_i}$	$\overline{S}_i = \frac{\partial S}{\partial n_i}$	$\overline{H}_i = \frac{\partial H}{\partial n_i}$	$\overline{G}_i = \frac{\partial G}{\partial n_i}$

When the numbers of kmol of the components are changed by dn_A, $dn_B \ldots dn_c$, the volume dV of the system changes by the amount

$$dV = \frac{\partial V}{\partial n_A} dn_A + \frac{\partial V}{\partial n_B} dn_B + \cdots + \frac{\partial V}{\partial n_c} dn_c. \tag{1.61}$$

If we introduce the partial molar volume we obtain

$$dV = \overline{V}_A dn_A + \overline{V}_B dn_B + \cdots + \overline{V}_c dn_c \cdots \tag{1.62}$$

Systems with Constant Composition

At constant pressure and temperature the intensive quantities $\overline{V}_i$ remain constant. The total volume of a system, which consists of $n_A, n_B, \ldots n_c$ kmol of the components A, B . . . c, is found by integrating Equation (1.62).

$$V = n_A \overline{V}_A + n_B \overline{V}_B + \cdots + n_c \overline{V}_c \tag{1.63}$$

If Equation (1.63) is divided by the total number of kmol $(n_A + n_B + \cdots n_c)$ the molar volume V_m of the alloy (subscript m stands for molar) as a function of the mol fractions is obtained:

$$V_m = x_A \overline{V}_A + x_B \overline{V}_B + \cdots + x_c \overline{V}_c \tag{1.64}$$

Systems with Variable Composition

If we differentiate Equation (1.63) for the case that the composition of the system may change we obtain

$$\begin{aligned} dV = &\left(n_A d\overline{V}_A + n_B d\overline{V}_B + \cdots + n_c d\overline{V}_c\right) \\ &+ \left(\overline{V}_A dn_A + \overline{V}_B dn_B + \cdots + \overline{V}_c dn_c\right) \end{aligned} \tag{1.65}$$

From a comparison between Equations (1.62) and (1.65) we can conclude that the first bracket in Equation (1.65) must be zero. If we divide it with $(n_A + n_B + \cdots n_c)$ we obtain

$$x_A d\overline{V}_A + x_B d\overline{V}_B + \cdots + x_c d\overline{V}_c = 0 \tag{1.66}$$

where $d\overline{V}_A, d\overline{V}_B, \ldots, d\overline{V}_c$ are the changes in volume in the individual partial molar quantities when p and T are constant.

Graphical Construction of Partial Molar Quantities for Binary Systems

If we apply Equation (1.66) on a binary system, where x_B is regarded as the independent composition variable, we can derive some useful relationships. From Equation (1.66) it follows that

$$x_A \frac{\partial \overline{V}_A}{\partial x_B} + x_B \frac{\partial \overline{V}_B}{\partial x_B} = 0. \tag{1.67}$$

This relationship was first derived by Duhem. If we take the derivative of the binary version of Equation (1.64) with respect to x_B we obtain

$$\frac{\partial V_m}{\partial x_B} = \frac{\partial x_A}{\partial x_B}\overline{V}_A + x_A \frac{\partial \overline{V}_A}{\partial x_B} + \overline{V}_B + x_B \frac{\partial \overline{V}_B}{\partial x_B}$$

Since $x_A + x_B = 1$ and $\partial x_A/\partial x_B = -1$ and Equation (1.67) is valid we obtain

$$\frac{\partial V_m}{\partial x_B} = \overline{V}_B - \overline{V}_A \tag{1.68}$$

If we combine Equations (1.64) and (1.68) to an equation system we can solve the partial molar volumes as functions of x_A, x_B, $\overline{V}_m$ and its partial derivatives with respect to x_A and x_B. The solution is

$$\overline{V}_A = V_m - x_B \frac{\partial V_m}{\partial x_B} = V_m + (1 - x_A)\frac{\partial V_m}{\partial x_A} \tag{1.69}$$

$$\overline{V}_B = V_m + (1 - x_B)\frac{\partial V_m}{\partial x_B} \tag{1.70}$$

where $V_m = x_A\overline{V}_A + x_B\overline{V}_B$ according to Equation (1.64).

Equations (1.69) and (1.70) are called *Gibbs–Duhem's equations*.

Both V_m, $\overline{V}_A$ and $\overline{V}_B$ obviously varies with x_B. This is shown in Figure 1.9, which also shows a useful graphical way to construct the partial molar volumes $\overline{V}_A$ and $\overline{V}_B$ when the $x_B V_m$ curve is known. The construction is based on Equations (1.69) and (1.70).

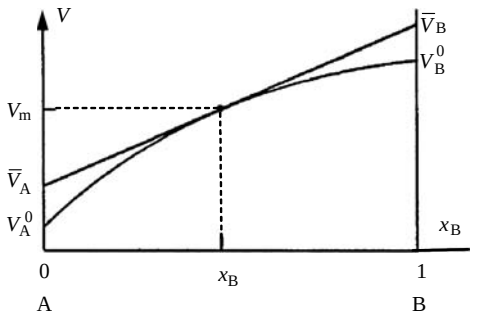


Figure 1.9 Molar volume V_m of a binary alloy as a function of the mole fraction x_B.

$$\overline{V}_A = V_m - x_B \frac{\partial V_m}{\partial x_B}$$

$$\overline{V}_B = V_m + (1 - x_B)\frac{\partial V_m}{\partial x_B}$$

The intersections V_A^0, respectively V_B^0, between the vertical axes and the V_m curve represent the molar volumes of pure elements A and B, respectively, at a given temperature.

As we have emphasized before, the theory of partial molar quantities given above and completely analogous formulas are valid for all thermodynamic functions.

1.4.2 Relative Thermodynamic Quantities and Reference States. Relative Partial Molar Thermodynamic Quantities or Partial Molar Quantities of Mixing

In the case of potential energy it is well known that a zero level has to be defined. This is also true for thermodynamic quantities. An example is the entropy S. Its zero level appears as an integration