

SVEIN STØLEN TOR GRANDE

CHEMICAL THERMODYNAMICS OF MATERIALS

MACROSCOPIC AND MICROSCOPIC ASPECTS



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Chemical Thermodynamics of Materials

Macroscopic and Microscopic Aspects

Svein Stølen

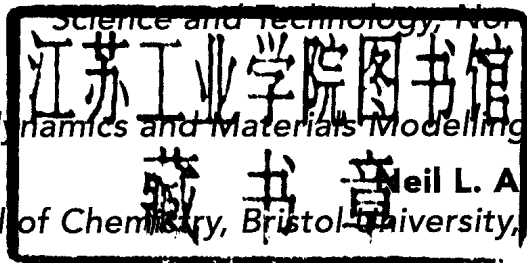
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with a chapter on *Thermodynamics and Materials Modelling* by

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Preface

Why write yet another book on the thermodynamics of materials? The traditional approach to such a text has been to focus on the phenomenology and mathematical concepts of thermodynamics, while the use of examples demonstrating the thermodynamic behaviour of materials has been less emphasized. Moreover, the few examples given have usually been taken from one particular type of materials (metals, for example). We have tried to write a comprehensive text on the chemical thermodynamics of materials with the focus on cases from a variety of important classes of materials, while the mathematical derivations have deliberately been kept rather simple. The aim has been both to treat thermodynamics macroscopically and also to consider the microscopic origins of the trends in the energetic properties of materials that have been considered. The examples are chosen to cover a broad range of materials and at the same time important topics in current solid state sciences.

The first three chapters of the book are devoted to basic thermodynamic theory and give the necessary background for a thermodynamic treatment of phase diagrams and phase stability in general. The link between thermodynamics and phase diagrams is covered in Chapter 4, and Chapter 5 gives the thermodynamic treatment of phase stability. While the initial chapters neglect the effects of surfaces, a separate chapter is devoted to surfaces, interfaces and adsorption. The three next chapters on trends in enthalpy of formation of various materials, on heat capacity and entropy of simple and complex materials, and on atomistic solution models, are more microscopically focused. A special feature is the chapter on trends in the enthalpy of formation of different materials; the enthalpy of formation is the **most** central parameter for most thermodynamic analysis, but it is still neglected in **most** thermodynamic treatments. The enthalpy of formation is also one of the **focuses** in a chapter on experimental methods for obtaining thermodynamic **data**. **Another** special feature is the final chapter on thermodynamic and materials **modelling**, contributed by Professor Neil Allan, University of Bristol, UK – **this is a topic not** treated in other books on chemical thermodynamics of materials.

The present text should be suitable for advanced undergraduates or graduate students in solid state chemistry or physics, materials science or mineralogy. Obviously we have assumed that the readers of this text have some prior knowledge of chemistry and chemical thermodynamics, and it would be advantageous for students to have already taken courses in physical chemistry and preferably also in basic solid state chemistry or physics. The book may also be thought of as a source of information and theory for solid state scientists in general.

We are grateful to Neil Allan not only for writing Chapter 11 but also for reading, commenting on and discussing the remaining chapters. His effort has clearly improved the quality of the book. Ole Bjørn Karlsen, University of Oslo, has also largely contributed through discussions on phase diagrams and through making some of the more complex illustrations. He has also provided the pictures used on the front cover. Moreover, Professor Mari-Ann Einarsrud, Norwegian University of Science and Technology, gave us useful comments on the chapter on surfaces and interfaces.

One of the authors (TG) would like to acknowledge Professor Kenneth R. Poeppelmeier, Northwestern University, for his hospitality and friendship during his sabbatical leave during the spring semester 2002. One of the authors (S²) would like to express his gratitude to Professor Fredrik Grønvold for being an inspiring teacher, a good friend and always giving from his great knowledge of thermodynamics.

Svein Stølen

Tor Grande

Oslo, October 2003

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Thermodynamic foundations

1.1 Basic concepts

Thermodynamic systems

A thermodynamic description of a process needs a well-defined **system**. A thermodynamic system contains everything of thermodynamic interest for a particular chemical process within a boundary. The **boundary** is either a real or hypothetical enclosure or surface that confines the system and separates it from its **surroundings**. In order to describe the thermodynamic behaviour of a physical system, the interaction between the system and its surroundings must be understood. Thermodynamic systems are thus classified into three main types according to the way they interact with the surroundings: **isolated systems** do not exchange energy or matter with their surroundings; **closed systems** exchange energy with the surroundings but not matter; and **open systems** exchange both energy and matter with their surroundings.

The system may be homogeneous or heterogeneous. An exact definition is difficult, but it is convenient to define a **homogeneous system** as one whose properties are the same in all parts, or at least their spatial variation is continuous. A **heterogeneous system** consists of two or more distinct homogeneous regions or **phases**, which are separated from one another by surfaces of discontinuity. The boundaries between phases are not strictly abrupt, but rather regions in which the properties change abruptly from the properties of one homogeneous phase to those of the other. For example, Portland cement consists of a mixture of the phases β -Ca₂SiO₄, Ca₃SiO₅, Ca₃Al₂O₆ and Ca₄Al₂Fe₂O₁₀. The different homogeneous phases are readily distinguished from each

other macroscopically and the thermodynamics of the system can be treated based on the sum of the thermodynamics of each single homogeneous phase.

In colloids, on the other hand, the different phases are not easily distinguished macroscopically due to the small particle size that characterizes these systems. So although a colloid also is a heterogeneous system, the effect of the surface thermodynamics must be taken into consideration in addition to the thermodynamics of each homogeneous phase. In the following, when we speak about heterogeneous systems, it must be understood (if not stated otherwise) that the system is one in which each homogeneous phase is spatially sufficiently large to neglect surface energy contributions. The contributions from surfaces become important in systems where the dimensions of the homogeneous regions are about $1\ \mu\text{m}$ or less in size. The thermodynamics of surfaces will be considered in Chapter 6.

A homogeneous system – solid, liquid or gas – is called a **solution** if the composition of the system can be varied. The **components** of the solution are the substances of fixed composition that can be mixed in varying amounts to form the solution. The choice of the components is often arbitrary and depends on the purpose of the problem that is considered. The solid solution $\text{LaCr}_{1-y}\text{Fe}_y\text{O}_3$ can be treated as a quasi-binary system with LaCrO_3 and LaFeO_3 as components. Alternatively, the compound may be regarded as forming from La_2O_3 , Fe_2O_3 and Cr_2O_3 or from the elements La, Fe, Cr and O_2 (g). In La_2O_3 or LaCrO_3 , for example, the elements are present in a definite ratio, and independent variation is not allowed. La_2O_3 can thus be treated as a single component system. We will come back to this important topic in discussing the Gibbs phase rule in Chapter 4.

Thermodynamic variables

In thermodynamics the state of a system is specified in terms of macroscopic **state variables** such as volume, V , temperature, T , pressure, p , and the number of moles of the chemical constituents i , n_i . The laws of thermodynamics are founded on the concepts of internal energy (U), and entropy (S), which are functions of the state variables. Thermodynamic variables are categorized as intensive or extensive. Variables that are proportional to the size of the system (e.g. volume and internal energy) are called **extensive variables**, whereas variables that specify a property that is independent of the size of the system (e.g. temperature and pressure) are called **intensive variables**.

A **state function** is a property of a system that has a value that depends on the conditions (state) of the system and not on how the system has arrived at those conditions (the thermal history of the system). For example, the temperature in a room at a given time does not depend on whether the room was heated up to that temperature or cooled down to it. The difference in any state function is identical for every process that takes the system from the same given initial state to the same given final state: it is independent of the path or process connecting the two states. Whereas the internal energy of a system is a state function, work and heat are not. Work and heat are not associated with one given state of the system, but are defined only in a transformation of the system. Hence the work performed and the heat

adsorbed by the system between the initial and final states depend on the choice of the transformation path linking these two states.

Thermodynamic processes and equilibrium

The state of a physical system evolves irreversibly towards a time-independent state in which we see no further macroscopic physical or chemical changes. This is the state of **thermodynamic equilibrium**, characterized for example by a uniform temperature throughout the system but also by other features. A **non-equilibrium state** can be defined as a state where irreversible processes drive the system towards the state of equilibrium. The rates at which the system is driven towards equilibrium range from extremely fast to extremely slow. In the latter case the isolated system may appear to have reached equilibrium. Such a system, which fulfils the characteristics of an equilibrium system but is not the true equilibrium state, is called a **metastable** state. Carbon in the form of diamond is stable for extremely long periods of time at ambient pressure and temperature, but transforms to the more stable form, graphite, if given energy sufficient to climb the activation energy barrier. Buckminsterfullerene, C_{60} , and the related C_{70} and carbon nanotubes, are other metastable modifications of carbon. The enthalpies of three modifications of carbon relative to graphite are given in Figure 1.1 [1, 2].

Glasses are a particular type of material that is neither stable nor metastable. Glasses are usually prepared by rapid cooling of liquids. Below the melting point the liquid become supercooled and is therefore metastable with respect to the equilibrium crystalline solid state. At the glass transition the supercooled liquid transforms to a glass. The properties of the glass depend on the quenching rate (thermal history) and do not fulfil the requirements of an equilibrium phase. Glasses represent **non-ergodic** states, which means that they are not able to explore their entire phase space, and glasses are thus not in internal equilibrium. Both stable states (such as liquids above the melting temperature) and metastable states (such as supercooled liquids between the melting and glass transition temperatures) are in internal equilibrium and thus **ergodic**. Frozen-in degrees of freedom are frequently present, even in crystalline compounds. Glassy crystals exhibit translational periodicity of the molecular

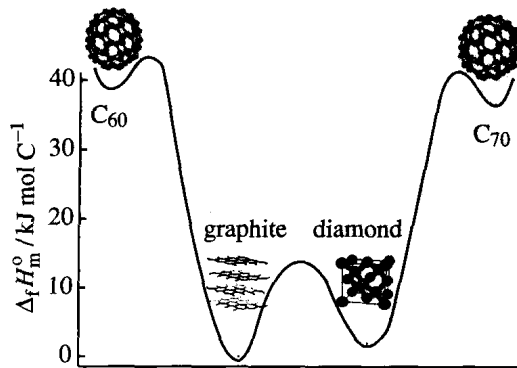


Figure 1.1 Standard enthalpy of formation per mol C of C_{60} [1], C_{70} [2] and diamond relative to graphite at 298 K and 1 bar.

centre of mass, whereas the molecular orientation is frozen either in completely random directions or randomly among a preferred set of orientations. Strictly spoken, only ergodic states can be treated in terms of classical thermodynamics.

1.2 The first law of thermodynamics

Conservation of energy

The first law of thermodynamics may be expressed as:

Whenever any process occurs, the sum of all changes in energy, taken over all the systems participating in the process, is zero.

The important consequence of the first law is that energy is always conserved. This law governs the transfer of energy from one place to another, in one form or another: as heat energy, mechanical energy, electrical energy, radiation energy, etc. The energy contained within a thermodynamic system is termed the **internal energy** or simply the **energy** of the system, U . In all processes, reversible or irreversible, the change in internal energy must be in accord with the first law of thermodynamics.

Work is done when an object is moved against an opposing force. It is equivalent to a change in height of a body in a gravimetric field. The energy of a system is its capacity to do work. When work is done on an otherwise isolated system, its capacity to do work is increased, and hence the energy of the system is increased. When the system does work its energy is reduced because it can do less work than before. When the energy of a system changes as a result of temperature differences between the system and its surroundings, the energy has been transferred as **heat**. Not all boundaries permit transfer of heat, even when there is a temperature difference between the system and its surroundings. A boundary that does not allow heat transfer is called **adiabatic**. Processes that release energy as heat are called **exothermic**, whereas processes that absorb energy as heat are called **endothermic**.

The mathematical expression of the first law is

$$\sum dU = \sum dq + \sum dw = 0 \quad (1.1)$$

where U , q and w are the internal energy, the heat and the work, and each summation covers all systems participating in the process. Applications of the first law involve merely accounting processes. Whenever any process occurs, the net energy taken up by the given system will be exactly equal to the energy lost by the surroundings and vice versa, i.e. simply **the principle of conservation of energy**.

In the present book we are primarily concerned with the work arising from a change in volume. In the simplest example, work is done when a gas expands and drives back the surrounding atmosphere. The work done when a system expands its volume by an infinitesimal small amount dV against a constant external pressure is

$$dw = -p_{\text{ext}} dV \quad (1.2)$$

Table 1.1 Conjugate pairs of variables in work terms for the fundamental equation for the internal energy U . Here f is force of elongation, l is length in the direction of the force, σ is surface tension, A_S is surface area, Φ_i is the electric potential of the phase containing species i , q_i is the contribution of species i to the electric charge of a phase, E is electric field strength, p is the electric dipole moment of the system, B is magnetic field strength (magnetic flux density), and m is the magnetic moment of the system. The dots indicate scalar products of vectors.

Type of work	Intensive variable	Extensive variable	Differential work in dU
<i>Mechanical</i>			
Pressure–volume	$-p$	V	$-pdV$
Elastic	f	l	$f dl$
Surface	σ	A_S	σdA_S
<i>Electromagnetic</i>			
Charge transfer	Φ_i	q_i	$\Phi_i dq_i$
Electric polarization	E	p	$E \cdot dp$
Magnetic polarization	B	m	$B \cdot dm$

The negative sign shows that the internal energy of the system doing the work decreases.

In general, dw is written in the form (intensive variable)·d(extensive variable) or as a product of a force times a displacement of some kind. Several types of work terms may be involved in a single thermodynamic system, and electrical, mechanical, magnetic and gravitational fields are of special importance in certain applications of materials. A number of types of work that may be involved in a thermodynamic system are summed up in Table 1.1. The last column gives the form of work in the equation for the internal energy.

Heat capacity and definition of enthalpy

In general, the change in internal energy or simply the energy of a system U may now be written as

$$dU = dq + dw_{pV} + dw_{\text{non-e}} \quad (1.3)$$

where dw_{pV} and $dw_{\text{non-e}}$ are the expansion (or pV) work and the additional non-expansion (or non- pV) work, respectively. A system kept at constant volume cannot do expansion work; hence in this case $dw_{pV} = 0$. If the system also does not do any other kind of work, then $dw_{\text{non-e}} = 0$. So here the first law yields

$$dU = dq_V \quad (1.4)$$

where the subscript denotes a change at constant volume. For a measurable change, the increase in the internal energy of a substance is

$$\Delta U = q_V \quad (1.5)$$

The temperature dependence of the internal energy is given by the **heat capacity at constant volume** at a given temperature, formally defined by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (1.6)$$

For a constant-volume system, an infinitesimal change in temperature gives an infinitesimal change in internal energy and the constant of proportionality is the heat capacity at constant volume

$$dU = C_V dT \quad (1.7)$$

The change in internal energy is equal to the heat supplied only when the system is confined to a constant volume. When the system is free to change its volume, some of the energy supplied as heat is returned to the surroundings as expansion work. Work due to the expansion of a system against a constant external pressure, p_{ext} , gives the following change in internal energy:

$$dU = dq + dw = dq - p_{\text{ext}} dV \quad (1.8)$$

For processes taking place at constant pressure it is convenient to introduce the **enthalpy** function, H , defined as

$$H = U + pV \quad (1.9)$$

Differentiation gives

$$dH = d(U + pV) = dq + dw + Vdp + pdV \quad (1.10)$$

When only work against a constant external pressure is done:

$$dw = -p_{\text{ext}} dV \quad (1.11)$$

and eq. (1.10) becomes

$$dH = dq + Vdp \quad (1.12)$$

Since $dp = 0$ (constant pressure),

$$dH = dq_p \quad (1.13)$$

and

$$\Delta H = q_p \quad (1.14)$$

The enthalpy of a substance increases when its temperature is raised. The temperature dependence of the enthalpy is given by the **heat capacity at constant pressure** at a given temperature, formally defined by

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (1.15)$$

Hence, for a constant pressure system, an infinitesimal change in temperature gives an infinitesimal change in enthalpy and the constant of proportionality is the heat capacity at constant pressure.

$$dH = C_p dT \quad (1.16)$$

The heat capacity at constant volume and constant pressure at a given temperature are related through

$$C_p - C_V = \frac{\alpha^2 VT}{\kappa_T} \quad (1.17)$$

where α and κ_T are the **isobaric expansivity** and the **isothermal compressibility** respectively, defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (1.18)$$

and

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (1.19)$$

Typical values of the isobaric expansivity and the isothermal compressibility are given in Table 1.2. The difference between the heat capacities at constant volume and constant pressure is generally negligible for solids at low temperatures where the thermal expansivity becomes very small, but the difference increases with temperature; see for example the data for Al_2O_3 in Figure 1.2.

Since the heat absorbed or released by a system at constant pressure is equal to its change in enthalpy, enthalpy is often called heat content. If a phase transformation (i.e. melting or transformation to another solid polymorph) takes place within