

Microscopic Kinetic and Thermodynamics

Notes of the course

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Thermodynamics of equilibrium in condensed phases

1.1 Physical properties

When one think at the study of condensed matter, the first thing that might come to his mind is the evaluation of the properties of a material intended as its characteristics. That is indeed true to some extent, but still one question that the reader thinking at it should ask himself is: what is a matherial property? This question may seem daunting at first sight, nevertheless an incredible simple and elegant answer can be given to it in the following terms

Definition 1.1.1: Physical property

A physical property is a relation between two measurable quantities.

If one is not completely obscure to physics may find out that this definition fits for the description of quantities like the conductivity σ , connecting external field \mathbf{E} and density current \mathbf{J} , or elasticity constant K and so on. Therefore, this concept may seem to lead us in the right track to understand what a physical property is but to have the picture complete we shall need to define exactly what quantities can be related by such properties. We are going to classify them in **generalized forces** and **conjugate responses** which are related in the following way

Definition 1.1.2: Measurable quantities

We classify the measurable quantities between generalized forces ψ_i and conjugate response ξ_i which are related by the following relation

$$\psi_i d\xi_i = \delta w, \quad (1.1)$$

where δw is the differential of work per unit volume done on the system.

One can also see this definition, or distinction, on a more physical level by thinking at the generalized forces ψ as stimuli that, acting on the system, generates a response ξ . Exactly like pressure P generate

a variation of volume from the system dV that so create work PdV .

This framework also allow us to rewrite the first principle of Thermodynamics in a simpler manner since we have given a general form to the work δw on the system. In particular, using the Einstein implicit summation formalism, we will have

$$du = Tds + \psi_i d\xi_i, \quad (1.2)$$

where we can also think at the temperature as a generalized force with entropy as a response. Thus, we will write from now on X_i for all the generalized forces, including temperature, and Y_i for the responses having Eq. (1.2) written as

$$du = X_i dY_i, \quad (1.3)$$

that will work as our **generalized first principle of thermodynamics**.

During the course we will also see how this definition of physical property also allow us to distinguish two main categories: **equilibrium properties**, that appear in a system at equilibrium such as the spring constant, and **transport properties**, that appear do to irreversible thermodynamic such has the conductivity. The main difference between the two can be thought to be the fact that in one case the material is still, in the other case average currents are present that, even if are in a stationary state, create transport of matter inside the material.

Constitutive relation

Once defined what a physical quantity is in general we can go and see how they look like, which is something that can be done in a first approximation making the assumption that a linear relation between forces and response are present. In this way we can assume that a general way to write down such linear relation in general is the following

$$Y_i - Y_i^0 = \mathcal{K}_{ij}(X_j - X_j^0). \quad (1.4)$$

The latter is called **constitutive relation** and effectively relates forces with responses through the tensor \mathcal{K} which, therefore, contains all the physical properties. Obviously this is only a first order approximation used to evaluate the variation of the two quantities from a starting state $(\mathbf{X}^0, \mathbf{Y}^0)$, nevertheless still allow us to have a first simple way of looking at the physical properties. In fact, inside Eq. (1.4) we are able to write down the entries of \mathcal{K} simply using

$$\mathcal{K}_{ij} = \left. \frac{\partial Y_i}{\partial X_j} \right|_{X_j=X_j^0}, \quad \mathcal{K} = \begin{pmatrix} \nabla_{\mathbf{k}} Y_1 \\ \vdots \\ \nabla_{\mathbf{k}} Y_N \end{pmatrix}. \quad (1.5)$$

This tensor is the main object of interest in a first approximation and understanding its properties can lend us a huge help on a general ground. Luckily the definition we have given leave us a lot of space to work with and one can readily go and see easily how the following is true

Theorem 1.1.1: Symmetry of \mathcal{K}

The physical property tensor \mathcal{K} is a symmetric one, therefore we have

$$\mathcal{K}_{ij} = \mathcal{K}_{ji}. \quad (1.6)$$

Proof: We can consider the free energy function g , we know it's defined as the Legendre transform of the internal energy which in our generalized case makes us obtain the following

$$g = u - X_i Y_i, \quad dg = -Y_i dX_i. \quad (1.7)$$

Since g is assumed to be continuous we can use the Schwartz theorem and say that the order of the derivation doesn't matter having so that

$$\frac{\partial^2 g}{\partial X_i \partial X_j} = \frac{\partial^2 g}{\partial X_j \partial X_i}, \quad (1.8)$$

which, using Eq. (1.5), turns out as

$$\mathcal{K}_{ij} = \mathcal{K}_{ji}. \quad (1.9)$$

☺

So, before even starting to look into the actual form of \mathcal{K} we already now that has certain symmetries, but it's also not so difficult to give a concrete form to this tensor by assuming the forces into play inside our system. In particular, we are going to assume that inside a solid state system the work is mainly given by the following expression

$$\delta w = \mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B} + \boldsymbol{\sigma} \cdot d\boldsymbol{\varepsilon}. \quad (1.10)$$

Where electric and magnetic work are presents along with the one given by the stress $\boldsymbol{\sigma}$ and strain $\boldsymbol{\varepsilon}$. The last two are symmetric rank two tensors that kind of generalize pressure and variation of volume. This allows us to see the various general force and responses that we need to relate, making us have a general form for the \mathcal{K} tensor that look as in Fig. (1.1). Inside that general form we can see how all the quantities are related to each others somehow, This means that the presence of an electric field not only can cause the creation of an electric polarization, generated by the on-diagonal blocks called **principal effects**, but also a magnetic one or a change in shape. These phenomenons are due to the presence of off-diagonal blocks, called **cross effects** or **interaction effects**, inside the tensor that relate the force also to non-conjugate responses. For this reason can be important to look at some of them, also to understand some important properties of these tensors.

c specific heat, $T(0)$. Relates the temperature and the heat transmitted to the solid per unit volume at constant \mathbf{E} , \mathbf{H} and $\boldsymbol{\sigma}$. It's important to notice that is a scalar quantity, the only one inside \mathcal{K} , and so can be also written as $T(0)$ ¹.

k dielectric constant, $T_S(2)$. Relates the polar vectors \mathbf{E} and \mathbf{D} , it's known from classical electromagnetism. Also, being on the diagonal one can see that needs to be symmetric $\mathbf{k} = \mathbf{k}^\dagger$, so it's a rank two symmetric tensor, $T_S(2)$ ², and as such has 6 independent components.

μ magnetic permeability, $T_S(2)$. Relate two axial vectors \mathbf{H} and \mathbf{B} , and it's also known from classical electromagnetism. The same consideration done on \mathbf{k} are valid also on him being on the diagonal.

¹To identify different type of tensor we will use the notation $T(n)$, which means tensor of rank n .

²If a tensor is symmetric the subscript S is used.

	T	E	H	σ
s	c/T	p	q	α
D	p'	k	λ	d
B	q'	λ'	μ	Q
ε	α'	d'	Q'	s

Figure 1.1: General form of the \mathcal{K} tensor that defines the constitutive relations inside the material. The different blocks are composed by tensors of different ranks and symmetries, but the overall structure needs to be symmetric.

s elastic compliance, $T_S(4)$. It generalizes Hooke's law relating stress with deformation which are rank two tensors, making it a rank four that write down the relation of the two as

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}. \quad (1.11)$$

Also, in this case the tensor is symmetric since ε and σ are having so $s_{ijkl} = s_{klij}$, this make so that the total number of independent variables in the tensor are 21. The inverse of this tensor, **c**, is called **elastic stiffness**.

p electrocaloric effect, $T(1)$. Describes how an external electric field can generate heat inside a material changing entropy and so temperature. Since \mathcal{K} is symmetric we need to have **p** = **p'**.

p' pyroelectric effect, $T(1)$. Describe the electric polarization generated by variation of the material's temperature.

q magnetocaloric effect, $T^{ax}(1)$. Describes the variation of temperature generated by an external magnetic field. Also, since we will have that $T\mathbf{q} = \mathbf{H}$ we will need **q** to be a pseudo-vector, therefore the tensor is called an axial one³.

q' pyromagnetic effect. $T^{ax}(1)$. Describe Magnetization induced by temperature changes, and from symmetry we once again have **q** = **q'**.

³We will describe axial tensor with the upscript ax , mathematically are objects that are not invariant to parity transformations.

Symmetry is important

In the simple description of the constitutive relation that we give previously inside a simple linear approximation was already simple to grasp how the symmetry of \mathcal{K} helped us in the understanding of some phenomena. For example, we found out that if the \mathbf{p} entries are non-zero we have electrocaloric effect, and with it also \mathbf{p}' needs to be non-zero having so also the pyroelectric effect. Therefore, only by simple symmetry we see how several effects are related to each others, but we can go deeper and the way to do that rely on a simple but incredibly clever principle thought by Nuemann that assume the following

Theorem 1.1.2: Nuemann principle

The symmetry of any physical property of a material can not be lower than the symmetry of its atomic-level structure.

Proof: This is not really a proof of the principle, it's more an explanation of the logic on which is based. The idea is that if I make a rotation to the system and the atomic structure doesn't change, due to symmetry, therefore I have the exact same material and interactions. This implies that, if the latter was true, also all the properties of the material should not have changed. Mathematically, this translates to the invariance of the mathematical object to the action of the group elements inside the point group of the crystal. ☺

To understand to what extent the utility of this principle we can look at some cases of application to some quantities. For example, let's imagine having a crystal with inversion as a symmetry and see what happens to rank ones tensors. Therefore, let's assume to have the tensor $\mathbf{p} = (p_x, p_y, p_z)$ if the system have inversion symmetry the following needs to be true

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} -p_x \\ -p_y \\ -p_z \end{pmatrix}. \quad (1.12)$$

This clearly makes so that the only possible solution to the equation to make the vector invariant is $\mathbf{p} = \mathbf{0}$, meaning that in a crystal with inversion symmetry no $T(1)$, or $T(0)$, properties can be present. This is already a powerful result that let us know which materials can possibly show some properties. Another interesting thing to see is looking at the presence of rotational symmetries which allow us to have the following result

Corollary 1.1.1

If a rotation symmetry is inside the point group of the crystal the $T(1)$ properties can only have non-zero entries only in the direction of the axis of rotation called **polar direction**.

Proof: Let the group C_n be a subgroup of the point group, and we assume that the rotation axes is in z direction, so that if we need to make a $T(1)$ invariant respect to the rotation we will require the following

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \cos(2\pi/n)p_x + \sin(2\pi/n)p_y \\ \cos(2\pi/n)p_y - \sin(2\pi/n)p_x \\ p_z \end{pmatrix}. \quad (1.13)$$

To solve the equation it's easy to see how $p_x = p_y = 0$ while only the component in the polar direction can be non-zero. ☺

The same principle can be applied to other rank tensors, and becomes really important for rank two ones \mathbf{T} where the requirement for respecting a ceratain symmetry \mathbf{R} simply becomes

$$\mathbf{T} = \mathbf{R}\mathbf{T}\mathbf{R}^{-1}. \quad (1.14)$$

Applied to general matrix using specific high symmetry point groups allows for a huge simplification of the independent components inside the tensor. The simplest, and probably most important, case is the one of a crystal with cubic symmetry, which bring the possibilities to one

Corollary 1.1.2

Inside a cubic crystal all the $T(2)$ properties are isotropic, therefore have only one independent component and can be written as $\mathbf{A} = A\mathbf{1}$.

I'm not going to do the computations, but in reality are really easy since you only need to impose two 90° rotations on different axis.

Note

This particular case forms also a counterexample to prove how the Neumann principle doesn't work backwards, meaning that it's possible how a physical property shows greater symmetry than the crystal itself. In fact, in this case the $T(2)$ becomes a scalar which is invariant under any type of rotational symmetry, while the cubic crystal has only C_4 at best.

Time symmetry

One last type of symmetry was left out by the latter discussion, in fact inside magnetic crystals the orientation of the magnetic moment may add another degree of symmetry. If we assume that all magnetic phenomena can be associated to the presence of moving charge, and so currents, then also the **time reversal symmetry** Θ becomes important. In particular one can call **i-tensors** the ones that are invariant under Θ and **c-tensors** the others we will have that the magnetic field is inside the latter, having

$$\mathbf{H}(-t) = -\mathbf{H}(t). \quad (1.15)$$

The same thing can be applied to the \mathcal{K} matrix and add also time-symmetry to the Nuemann principle. In particular the physical quantity needs to be compatible with the properties of the quantities that relates, for example let's consider \mathbf{X} and \mathbf{Y} both i or c-tensors we can write

$$\Theta\mathbf{Y} = \pm\mathbf{Y} = \pm\mathcal{K}\mathbf{X} = \Theta\mathcal{K}\mathbf{X}. \quad (1.16)$$

Which simply translates to no further restrictions to the properties of the physical quantities. Instead, if we have that \mathbf{X} and \mathbf{Y} are opposite time reversal tensors, in that case the relation between the two becomes

$$\Theta\mathbf{Y} = -\mathbf{Y} = -\mathcal{K}\mathbf{X} = \Theta\mathcal{K}\mathbf{X}. \quad (1.17)$$

This leads to the fact that $\Theta\mathcal{K} = -\mathcal{K}$ giving rise an increase of the symmetry inside the tensor. Also, if we assume that \mathcal{K} is a c-tensor in the specific case we are looking we obtain $\mathcal{K} = -\mathcal{K}$ saying to us that the tensor needs to be identically zero.

The properties that relate different time-symmetry tensors are, therefore, special and takes the name of **special magnetic properties**. Some examples of such properties are the magnetocaloric effect p_i , magnetoelectric polarization λ_{ij} and piezomagnetism Q_{ijkl} .

1.2 Unary heterogeneous systems

To start the approach to the thermodynamic study of material it's better to first approach simple systems, and in this field the simplest case that one can think of are **unary systems**. The latter are simply defined as systems where only one element is present, such as Carbon, Silicon or also more complicated ones such as water or SiO_2 . In fact, also system composed by molecules can be thought as unary as long as we work in a range where the smallest component is stable and no spontaneous dissociation appears.

Definition 1.2.1: Unary systems

A system is said to be unary if it is composed by only one main component, which can be a molecule or an atom, that is stable inside the working range of the analysis.

Our aim in working with this system is to start to understand how they present themselves in nature in different ambient. Basically we will explain how to predict if a material at a certain pressure and temperature is in gases, solid or liquid state, comprehending how to read and construct a **phase diagram** for these simple cases.

For the readers that has never seen, or heard of, a phase diagram some examples for the cases of Carbon and Water are reported in Fig. (1.2). These type of plots are made to clearly show the state in which the material presents itself in the selected region of phase space. In our case we selected the (P, T) representation, where it is possible to see at what pressure and temperature the two materials are in a solid state or transform to a liquid one etc. Nevertheless, the real points of interest inside the graph are the lines that mark the boundaries between phases. They are called **coexistence lines** and are a special subspace of phase space where both phases can coexist at equilibrium. A condition that allows us to model what happens in that region and predict their form and, therefore, the boundaries that describe the phase diagram. At last, of great interest are also the points at the intersection of two lines, called **triple points**, where three states of matter coexist at the same time, which we will see is the maximum number of states that can coexist in a unary system.

Equilibrium conditions

To draw a phase diagram of a system we need to predict the positions of the coexistence line, finding out the subset of phase space where two, or more, phases of matter are in equilibrium with each other and

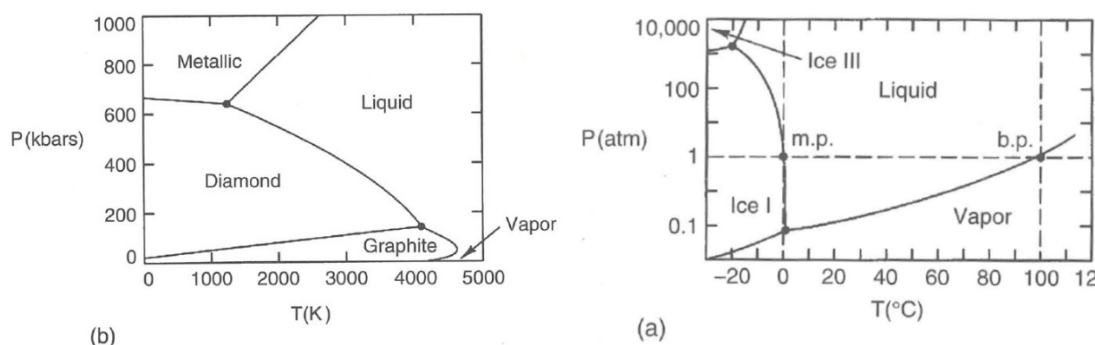


Figure 1.2: Phase diagrams of simple unary systems: Carbon(a) and Water(b). Both are reported in a P vs T graph, where we can clearly see the triple points and the coexistence lines.

can, therefore, coexist. To do that is needless to say that we need to define what being in equilibrium means, and in particular finding out the physical conditions that tells us when two phases of matter are in equilibrium with each others. In order to do that simple thermodynamic considerations allow us to arrive to the following results.

Theorem 1.2.1: Equilibrium conditions

Inside a unary system two phases α, β of matter can coexist at equilibrium, creating a heterogeneous system, only if the relation for **thermal**, **mechanical** and **chemical** equilibrium are satisfied, namely:

$$T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu^\alpha = \mu^\beta. \quad (1.18)$$

Proof: Let's imagine to start with the system composed by α and β being an open one inside an environment. After some time the studied system will evolve to an equilibrium state within the environment, which nevertheless will not depend on it. This is something that we can easily understand since, for the zeroth principle of thermodynamics, if we close the system when in equilibrium, basically eliminating the environment, the state of the α and β unary system will remain untouched. Basically the evolution of the open system leads to an equilibrium situation that is analogous to the case of a closed one, meaning that at equilibrium we can consider $\alpha \cup \beta$ as closed having that the following conditions must be true

$$U^\alpha + U^\beta = \text{const}, \quad V^\alpha + V^\beta = \text{const}, \quad N^\alpha + N^\beta = \text{const}. \quad (1.19)$$

Basically the total energy, volume and number of particle must remain constant in a closed system, as we know. Now, inside equilibrium we can also write down the first principle of thermodynamics, in the normal form, as follows

$$du = Tds - PdV + \mu dn. \quad (1.20)$$

Where u is the energy density, s the entropy per unit volume and n the number of mole. With this equation we can rewrite it to obtain the differential of the entropy as

$$ds = \frac{du}{T} + \frac{P}{T}dV - \frac{\mu}{T}dn, \quad (1.21)$$

this is really useful since being at equilibrium is implicitly saying to us that the entropy should be at a maximum. In fact, from classical thermodynamics we know that system evolves towards maximum entropy, so that the differential of the total entropy of the system must be zero at its maximum $ds^\alpha + ds^\beta = 0$. If we now use Eq. (1.21) and the relations Eq. (1.19) we can easily see that the following is true

$$\left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) du^\alpha + \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) dV^\alpha - \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} \right) dn^\alpha = 0, \quad (1.22)$$

which can be respected only if the conditions in Eq. (1.18) are true. ☺

These conditions are essential for the study of the phenomenon of coexistence that we are interested in since gives us a mathematical way of imposing the presence of the phases we are interested in. Nevertheless, are not the only tools that we need to arrive at a solution. In fact, equilibrium conditions can be formulated also on the base of others quantities such as the different **thermodynamic potentials**. The major ones that we are going to use the most are reported synthetically inside Tab. (1.1), the latter is not a mathematical precise definition of them, which is obtained through Legendre transform, but that is outside the scope of the course. Between the different types of potential defined we will focus on a

Table 1.1: Table with the major thermodynamic potential giving their: definition, differential and major cases in which are used in a quick way.

Name	Definition	Differential	Utility
Enthalpy	$H = U + PV$	$dH = Tds + VdP + \mu dn$	isobare study, since $dH = \delta Q$.
Helmoltz ener.	$F = U - TS$	$dF = -SdT - PdV + \mu dn$	isocore-isotherm study.
Gibbs free ener.	$G = U - TS + PV$	$dG = -SdT + VdP + \mu dn$	isobare-isotherm study.

particular one, the **Gibbs free energy** G . The reasons for it are several, for example one can see from its differential how taking the Gibbs energy per number of mole, \bar{G} , is equal to the chemical potential

$$\mu = \left. \frac{\partial G}{\partial n} \right|_{T,P} = \left. \frac{\partial(n\bar{G})}{\partial n} \right|_{T,P} = \bar{G} \left. \frac{\partial n}{\partial n} \right|_{T,P} = \bar{G}. \quad (1.23)$$

Nevertheless, this is still not the major reason why we are interested in it. The main reason is that using that we can give another powerful equilibrium condition based on it.

Theorem 1.2.2: Gibbs equilibrium condition

Every system, not at equilibrium, constrained to constant pressure and temperature will evolve in order to minimize the Gibbs free energy per unit mole, reaching an equilibrium where \bar{G} is at its minimum.

Proof: We can take the differential of \bar{G} , which is equal to μ , by using the total one and eliminating the part on the variation of the number of mole, having

$$d\mu = -SdT + VdP. \quad (1.24)$$

Now, this differential is exact only if we have a reversible transformation. In a non equilibrium situation the differential changes to an unknown form that still we know have Eq. (1.24) as upper limit. In fact, if one use the second principle of thermodynamics for a general transformation in the derivation of the differential will obtain

$$d\mu \leq -SdT + VdP. \quad (1.25)$$

Now, if we assume that the system is kept at constant P and T that relation becomes simply $d\mu \leq 0$, meaning that μ can only decrease as the system evolve reaching equilibrium when found its minimum.

☺

This equilibrium condition is really powerful to us, since all we need to do is found out the functions $\mu^i(P, T)$ for all the possible phases that we are interested into for our system and confront them. We will have that the one with the lower chemical potential will be the one that shows up in that position of the phase diagram, also if we have two phases with same μ than that means a coexistence line will pass on that point. This process is really simple and is clearly explained with the example given in Fig. (1.3) where all that was sad before is present.

As a last remark it could be interesting to understand how the values of μ can be computed inside a system, in particular using experimental results. The idea is starting from the differential Eq. (1.24)

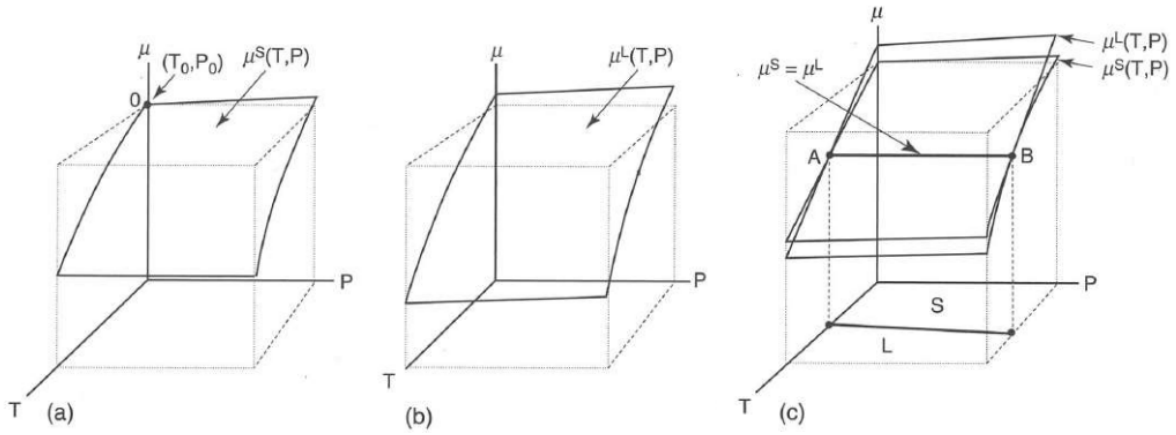


Figure 1.3: Graphical representation of the chemical potential for a solid phase(a), liquid phase(b) and the superposition of the two to see which one prevails on the other for the equilibrium phase(c). It's possible to see how in the part of the phase diagram where $\mu^S = \mu^L$ a coexistence line appear.

and try to write down expressions for S and V . To do that we need first to write down the differential of those two quantities, starting from S

$$dS = \left. \frac{\partial S}{\partial P} \right|_T dP + \left. \frac{\partial S}{\partial T} \right|_P dT. \quad (1.26)$$

We need to simplify it and the first thing that we can say is that μ is a continuous function, therefore the Schwartz theorem apply having

$$\frac{\partial^2 \mu}{\partial P \partial T} = - \left. \frac{\partial S}{\partial P} \right|_T = \frac{\partial^2 \mu}{\partial T \partial P} = \left. \frac{\partial V}{\partial T} \right|_P = V\alpha. \quad (1.27)$$

Where the definition of **thermal expansion coefficient** $\alpha = V^{-1} \partial V / \partial T|_P$ was used. The remaining partial derivative in Eq. (1.26) is simply the **specific heat** at constant pressure c_P , having so that the final form is

$$dS = -V\alpha dP + \frac{c_P}{T} dT. \quad (1.28)$$

Analogous considerations can be done for the volume, using also the **bulk modulus** β having so that its final form will be instead

$$\frac{dV}{V} = -\beta dP + \alpha dT. \quad (1.29)$$

In this way both $V(P, T)$ and $S(P, T)$ can be computed since α , β and c_P can be easily obtained experimentally and then the differential can be integrated through known numerical routines. For example, one can easily compute a so-called **isobaric section**, basically a slice of phase diagram at constant pressure P_0 , using two consecutive integrations

$$S(T, P_0) = S(T_0, P_0) + \int_{T_0}^T \frac{c_P(T')}{T'} dT', \quad (1.30)$$

$$\mu(T, P_0) = \mu(T_0, P_0) - \int_{T_0}^T S(T') dT'. \quad (1.31)$$

Clausius-Clapeyron equation

Now we want to completely focus on the coexistence lines and try to describe them better. In particular our main goal is to find a way to predict their form so that we will be able to draw them on the phase diagram having so, directly, all the information needed. It is renown that a solution to this is present in literature and comes with the name of **Clausius-Clapeyron equation**.

Theorem 1.2.3: Clausius-Clapeyron equation

A coexistence line between two phases α and β of a system has a slope in the P vs T plane that is given by the following relation

$$\frac{dP}{dT} = \frac{1}{T} \frac{\Delta H^{\alpha \rightarrow \beta}}{\Delta V^{\alpha \rightarrow \beta}}. \quad (1.32)$$

Proof: Since we are on a coexistence line we know that the equilibrium conditions of Eq. (1.18) must be valid, therefore $d\mu^\alpha = d\mu^\beta$ along with dT and dP , leading to

$$-S^\alpha dT + V^\alpha dP = -S^\beta dT + V^\beta dP \quad (1.33)$$

Rearranging and assuming that the study is done in an isobare condition, meaning that $dH = TdS$, we will have the wanted result.

$$\frac{dP}{dT} = \frac{1}{T} \frac{H^\beta - H^\alpha}{V^\beta - V^\alpha} = \frac{1}{T} \frac{\Delta H^{\alpha \rightarrow \beta}}{\Delta V^{\alpha \rightarrow \beta}}. \quad (1.34)$$

☺

This is a really known equation that can tell us some interesting information about the system. For example, if we have the phase diagram of a transition from solid to liquid, we know that ΔH needs to be positive since the heat is transferred inside the material during melting. Therefore, if experimentally we have that the coexisting line has a positive slope, this means that the system is expanding, while it's becoming smaller if the slope is negative. The latter case is something that can be clearly seen in the phase diagram of water, which is known it's a peculiar case where the volume reduces going from solid to liquid.

The equation can also be solved exactly for some simple cases of which the most important is the case of liquid-gases coexistence lines where a really simple result can be found out.

Corollary 1.2.1 Vapor pressure curves

A coexistence line between a liquid and gases phases can be described analytically by the following equation

$$P = c \exp\left(-\frac{\Delta H}{RT}\right), \quad (1.35)$$

where c is a constant.

Proof: We can use Eq. (1.32) assuming that $\Delta V^{\alpha \rightarrow \beta} \approx V^{\text{gas}}$ since gases have much larger volume than liquid. Then by using the equation of perfect gas one can obtain the differential equation

$$\frac{dP}{P} = \frac{\Delta H}{R} \frac{dT}{T^2}, \quad (1.36)$$

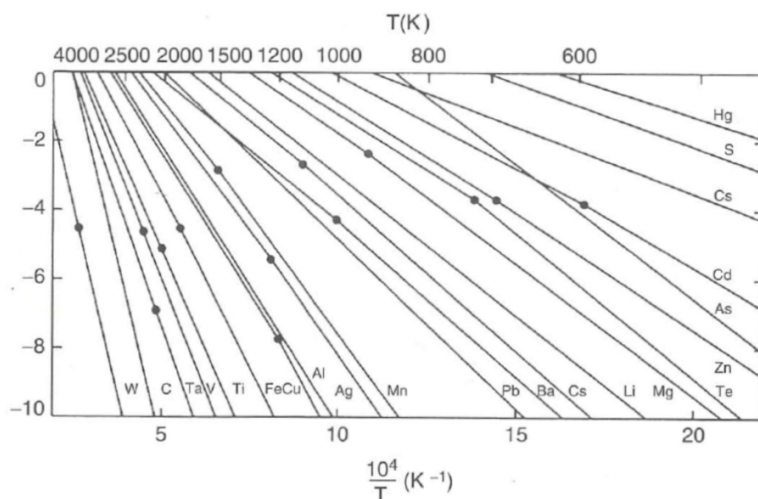


Figure 1.4: Compilation of vapor pressure for the elements with $\log P$ on the y-axis. A change in slope (marked by the dot) corresponds to the melting point, which is also a triple point here because of the coexistence with the vapor phase.

where ΔH has usually a small dependence on T and can therefore be assumed constant. Thus, the equation can be integrated directly giving the wanted result. ☺

This equation allow us to describe up to a good precision the wanted lines where gasses are involved. To make an example of how good of an approximation this is we can have a look to Fig. (1.4) where the coexistence lines all respect the exponential relation given by Eq. (1.35) being straight lines that changes slope on the melting point, in correspondence of a change in ΔH going from liquid-gass to solid-gass one.

Note

Fig. (1.4) also tells us that the difficulty in having sublimation instead melting for a material is not in the different amount of heat that we need to give in the two processes, since the slopes changes really little, but only in the needs of a much higher temperature for the former process to even start.