

Metals

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1 10-03-25: — Introduction

Pre-requisites: It's important to understand the **phase transformations** in alloys under development. We'll also focus on the **quantitative treatments** and most importantly on the **sustainability** of the metals production.

We should already know the atomic structure of metals, crystalline structures, dislocations, boundaries, and other defects. We need to know how to read and understand a phase diagram. Also we need to know the basic principles of thermodynamics and kinetics. Like for example diffusion, concentration gradient, flux and so on.

1.1 Thermodynamics and phase diagrams:

Some terminology:

- Component: element of the periodic table or compound.
- Phase: portion of a system that has uniform physical and chemical characteristics.
- System: mixture of one or more phases.

Some thermodynamic properties:

- Temperature
- Pressure
- Composition

The stability of the system is given from the **Gibbs free energy** G :

$$G = H - TS \quad (1)$$

This is the most useful equation, because we can actually control both T and P. In this course we will assume that the variations of P are small, so we consider it constant.

Thermodynamic quantities are extensive quantities, so they depend on the amount of material. We can define the **molar Gibbs free energy** g as:

$$G_m = \frac{G}{N} \quad (2)$$

In the case it contains more phases, G total will be the sum:

$$G = \sum_{\varphi} N_{\varphi} G^{\varphi} \quad (3)$$

The composition is described as a molar fraction of the total (all expressed in moles):

$$x_{\varphi} = \frac{N_{\varphi}}{N_{tot}} \quad (4)$$

Moreover, the equilibrium is reached when the Gibbs free energy is minimized. This means that we can find it by finding a local minima (metastable) or a global minima (stable):

$$dG = 0, \text{ and } d^2G \geq 0 \quad (5)$$

Interestingly, we never know the actual integral value of G, we always work with differences of it, unless we define a reference state.

Reference state: Don't think is very relevant, but in case you want to investigate further: *Thermodynamics and free energy curves.pptx*, slide 7.

Single component systems (pure metals): We can consider a system made out of a single element, constant pressure. For each phase we can define the Gibbs free energy. But how can I obtain valuable information from this? I can just change T, and rewrite calculating H and S.

$$H = H_{\text{ref}} + \int_{T_{\text{ref}}}^T C_p dT, \text{ with } C_p = \left(\frac{\partial H}{\partial T} \right)_P \quad (6)$$

$$S = S_{\text{ref}} + \int_{T_{\text{ref}}}^T C_p d \ln T, \text{ with } C_p = \left(\frac{\partial S}{\partial T} \right)_P \quad (7)$$

Where we will need to obtain the values of different c using fitting of real data. So recap: we fit the data obtaining c , then we calculate S and H and then we obtain the amount of G at different T.

These plots have T on the X-axis and C_p on the Y-axis (there's a small digression on the magnetic behaviour of Iron and a big spike in the plot).

If we for example plot the total Gibbs energy and the T, we get that some crystalline structures are more stable than others at different temperatures.

Coordinate system: The plots can be plotted assuming the reference state as the **BCC** at every temperature with pressure 1bar. Remember by the way that each one of the plots with changing temperature, is just a slice, one line of the full diagram phase T and P.

DoF: Remember that the number of degrees of freedom is:

$$\nu = c - f + 2 \quad (8)$$

1.2 Driving force of solidification

By comparing different Gibbs energies at different temperatures of the liquid and solid phase, we obtain the melting point. However, under certain conditions (fast cooling), the solidification happens at a couple hundred degrees lower. The bigger is the difference between the Gibbs energies, the bigger is the driving force (the energy gain) of the transition. The different differences, are obtained from the calculations between solid and liquid phases.

Remember that usually the ΔH is called L as in *Latent heat of fusion*.

1.3 Binary systems

Alloys made of 2 different components. We have two different possibilities:

- Same crystal structure: Homogeneous, because of substitutional solid solution.
- Not same crystal structure: Heterogenous, because both can create substitutional solid solutions inside the other and not mix.

Other cases:

- Interstitial solid solutions

- Different phase, which has a crystal structure that is not A nor B.

Either way, the new plot of representation is a plot that has the Gibbs energy (T and P constant) on the Y-axis and the percentage of composition on the X-axis. At each end of the plot we have a 100% of the given component. The attributes of the mix and the single components is the '*linear interpolation*', but I guess that in future the true behaviour will not be a straight line.

Entropy of mixing: Using:

$$S = k_B \ln(\omega_{\text{conf}}) \quad (9)$$

Where we can describe the amount of entropy as the number of different configurations a system can assume. Before mixing we had only 1 configuration of atoms in different position (atoms of the same element are indistinguishable), while after mixing we have different possible configurations and thus a higher entropy. The value of ω is:

$$\omega_{\text{config}} = \frac{(N_A + N_B)!}{N_A! N_B!} \quad (10)$$

With the different N are the number of atoms of different elements:

$$N_A = X_A N_a \quad (11)$$

Sterling's equation: SKIP, it is an approx.: $\ln(N) \sim N \ln(N) - N$. So now we have all the data to calculate the ΔS :

$$\Delta S_{\text{mix}} = S_2 = k_B \ln(\omega_{\text{conf}}) = -R(X_A \ln(X_A) + X_B \ln(X_B)) \quad (12)$$

The derivation is often asked at the exam.

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The real case is different from the ideal one, in fact, the ΔG_{mix} strongly depends on the temperature, with higher energies we obtain higher differences. Remember that it is always negative in the ideal case. Mixing is always thermodynamically favorable.

But to obtain this type of ideal solution we must use specific alloys, so we need to add complexity to the model, to better simulate real data: Regular Solution Model.

2.1 Regular Solution Model

We first of all assume that the bonding energies do not change with the composition, and P & V remain constant when mixing (this is expressed by the relation: $\Delta U = \Delta H$). We also assume that the the bonding energies between different atoms are fixed:

- A-A bonds with energy ε_{AA}
- B-B bonds with energy ε_{BB}
- A-B bonds with energy ε_{AB}

This simplify a little the calcs, because:

$$\Delta H = \Delta E + \Delta(PV) \quad (13)$$

There are also formulas to get the number of atoms from the number of bonds and viceversa, skipped.

Now follows a demonstration of the calculation of internal energy after mixing, which mainly considers the 2 original values and correlates it to the number of bonds, essentially summing them all over. More information *1 - Thermodynamics and free energy curves2.pdf @ pag.20*.

The final result is this:

$$\Omega = N_a z \varepsilon \quad (14)$$

$$\Delta H_{\text{mix}} = \Omega X_A X_B \quad (15)$$

We can have different combinations of high/low temperature and $\Omega \leq 0$. This illustrates how actually the ΔH might not be negative, meaning it is not thermodynamically favorable. The sign depends on whether the bonds between same atoms is stronger or weaker compared to bonds between different atoms. The void zone is called **Miscibility gap**. This gap is always present, even if the ΔH is negative, this is because, there always states more favorable (energetically).

2.2 Chemical potential

This tells us how much chemical potential energy a pure element has and how much it lowers whenever creating a solution: usually the solution will have the lowest free energy. This chemical energy is related to the crystal structure, so like the energy contained in the element.

If we mix 2 components which have different crystal structure, the situation becomes even more complicated, we must consider *'how much a certain component in a certain crystal structure is stable in the OTHER crystal structure'*. We then obtain 2 different curves, each one describing one

or the other free energy for every crystal structure considered. Whenever this happens it results more convenient to have BOTH phases together, so both minima. To understand the amount of one phase respect to the other we can use the '*Legge della Leva*'. ~ Rizzi

The tangent line used passes through the 2 minima, and we project our composition down the line. This is applied only inside the miscibility gap, outside it follows the free energy curve.