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Entropy Models and their Predictions of Phase Stability for High-Entropy Alloys

Bacheloroppgave i Kjemi
Veileder: Per-Olof Åstrand
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Abstract

A new class of alloys was proposed in 2004, with its distinction derived from its high configurational entropy. In the original paper, they gave credit to this entropy term in stabilizing the alloy, and thus they named the alloys High-Entropy Alloys (HEAs). In the last 20 years, attention has grown around these remarkable alloys and their qualities, but with it a growing critical viewpoint has amassed against their seemingly simplified postulation.

This thesis briefly discusses the creation of individual HEAs and thermodynamics of complex crystal structures, though its focus remains on the stabilization effect that the entropy term has on the alloys, with different models to calculate it.

As is shown, the ideal configurational entropy is a far too simple model to be able to consistently predict phase stability for HEAs. The excess entropy terms that have been proposed to be relevant are vibrational, electronic, magnetic, and deviation in the configurational entropy.

Data shown in this thesis indicates that vibrational and non-ideal configurational are the most important among these, each potentially contributing a deviation of around 20% from the ideal entropy. Calculating these parameters are computationally challenging, however, and this paper suggests using machine learning to predict future stable HEAs until better models are made.

Sammendrag

En ny kategori av legeringer ble foreslått i 2004, med sin distinksjon om at de har høy konfigurasjonell entropi. I den opprinnelige artikkelen pekte forfatterne på nettopp nettopp denne entropi-termen som stabiliserings-mekanismen til legeringene, og de kalte dem derfor for høy-entropiske legeringer (HEAs, fra High-Entropy Alloys).

Denne oppgaven vil diskutere termodynamikken bak HEAs, og de ulike modellene for å kvantisere dette, samt stabiliseringseffekten som entropien har på legeringene.

Det blir vist at den ideelle konfigurasjonelle entropien er en altfor enkel modell til å konsekvent kunne forutsi fasestabilitet hos HEAs. De overflødige entropi-termene som er relevante å ta med er foreslått å være vibrasjonell, elektronisk, magnetisk, og avvik i den ideelle konfigurasjonelle entropien.

Denne oppgaven framlegger data som indikerer at den vibrasjonelle og ikke-ideelle konfigurasjonelle entropien er viktigst blandt disse, samt at hver av disse kan bidra til å gi rundt 20% avvik fra den ideelle entropien. Å beregne disse parametrene viser seg dog å være utfordrene, og derfor anbefaler denne oppgaven å se videre på maskinlæring for å forutsi fremtidige HEAs, frem til bedre modeller blir fremstilt.

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Symbols & abbreviations

| | | |
|-----|----------------------|--|
| HEA | High-Entropy Alloy | |
| SS | Single solid | |
| IM | Intermetallic | |
| k | Boltzmann's constant | $1.381 \cdot 10^{-27} \text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$ |
| R | Molar gas constant | $8.314 \text{J mol}^{-1} \text{K}^{-1}$ |
| N | Avogadro constant | $6.022 \cdot 10^{23}$ |

1 Introduction

The ever-lasting effect of new knowledge will forever outweigh the more temporary impact of political revolutions or economic trends. One of the most driving fields of science, with this respect, has been that of metallurgy. The discovery of new materials may happen accidentally — like the discovery of steel —, or conscientiously — like the tin bronze that initiated the bronze age.^[1] At times, these revelations have even been so important as to give its name to the whole era they initiated.

With todays greater understanding of material sciences, it is easier to create alloys with specific qualities for intended purposes. This, in effect, makes metallurgic progress track our developments, instead of the other way around. The booming aircraft industry in the 1900s, for instance, gave rise to a number of aluminium alloys with increasing yield strength (see figure 1.1). Similarly today, the green industries and information technology drives the metallurgic field in search of novel materials with specific qualities. One contender for these necessities is High-Entropy Alloys (HEAs).

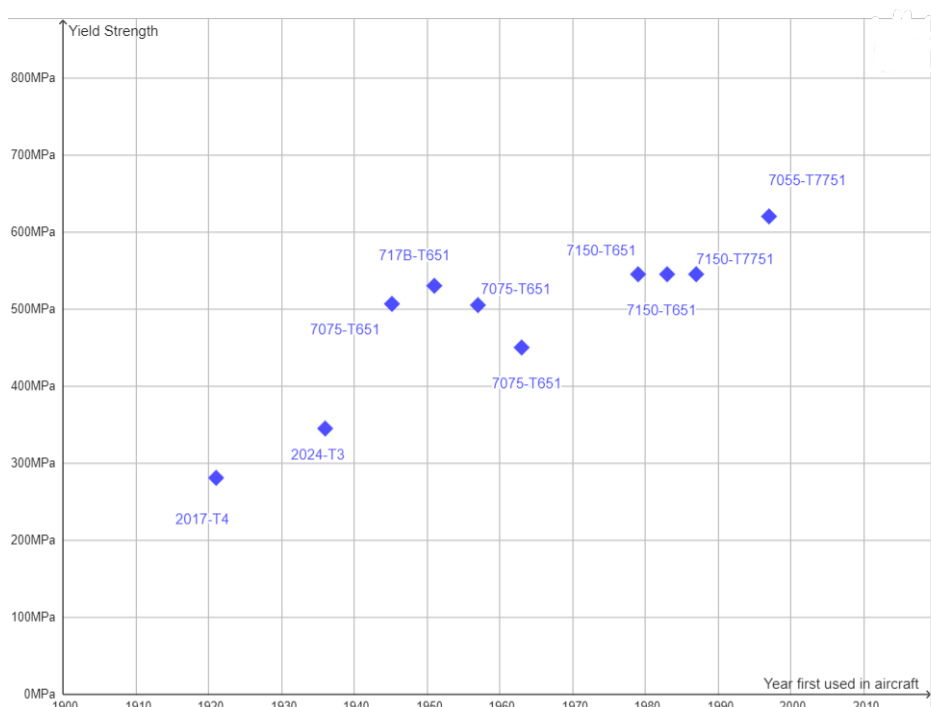


Figure 1.1: Aluminium alloys introduced in aircraft, plotted against its yield strength. Adapted from Polmear.^[2]

The field of HEAs is fairly young. The exact term was first properly described in 2004.^[3;4] Since then, the number of publications regarding HEAs has steadily risen each year (see figure 1.2).

In the original paper of 2004, Yeh et al. defined HEAs as

those [alloys] composed of five or more principal elements in equimolar ratios [...] with the concentration of each element being between 35 and 5 at.-%.^[4]

This, albeit contradictory, definition was made to broaden the field from the easily defined equimolar part. A typical way of crafting new HEAs is then to start with a known stable compound, and gradually adding or subtracting one element at a time, Because there practically speaking are an infinite amount of possible HEAs made in this way, they have the potential of having many different properties; notably superconductivity, irradiation and corrosion resistance, yield strength, thermal stability, and hydrogenation capability.^[6-8] This makes HEAs

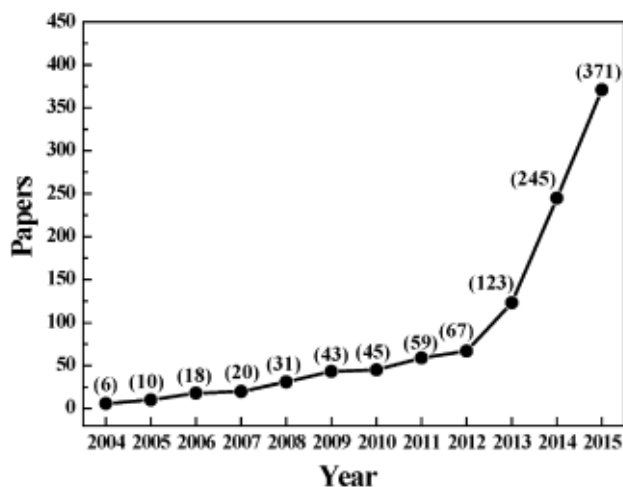


Figure 1.2: Number of publications related to high-entropy alloys from 2004 until 2015. Reused with permission from Yeh.^[5]

suitable in use for a number of important industries and needs, such as in nuclear plants, solar cells, hydrogen storage, etc.^[9–11]

In order to predict the properties of a crafted alloy, one needs good calculable theoretical models. There are a number of theorized effects of HEA structures that give them the possibility to carry the aforementioned properties. These are the high mixing entropy, the severe lattice distortion, the cocktail effects, and sluggish diffusion.^[3] While the modelling of each of these deserves a discussion, this thesis will focus on the mixing entropy.

The entropy effect is the distinctive property of HEAs, and is even included in the formal definition in some later theses.^[12] It is then essential to have a proper physical model for it, not only to affirm the identity of the material, but to also be able to predict the phase stabilities and properties of different compositions.

A number of such models have been proposed, with varying degrees of complexity.^[3] The problem herein stems from the complexity of the material itself. It has numerous different interpretations, and physicists and chemists attempt to find out which contributions to the entropy term are necessary, and which ones to scrap.

Potential candidates are the configurational, vibrational, magnetic, and electronic contributions. We shall take a look at each of these individually, compare their magnitudes, and hopefully separate the useful from the superfluous. We do this by first studying the theory behind HEAs, and some useful thermodynamics, before discussing some useful data obtained from previous studies.

2 Theory

2.1 High-Entropy Alloys

The formal definition of a high entropy alloys is disputed. As mentioned above, it was introduced as a composition of more than 4 different elements i , with the molar fraction x_i as $0.05 < x_i < 0.35$. However, more recently, another proposed definition has become more popular. This defines HEAs as materials with $\Delta S > 1.6R$, where R is the molar gas constant $R = 8.3145 \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \text{ mol}^{-1}$ [12], and ΔS is the difference in entropy from mixing the components in the alloy.

The high mixing entropy stems from the increased multiplicity in the crystal when adding each element. As the entropy stabilization effect is dependent on temperature one would expect the alloys to have a high thermal stability [9;13], as is shown for many HEAs. We shall see in the following subsection how this can be calculated.

In addition to this condition, one can include the constraint that the material has to be single-phase, solid solution (SS). This, simply coming from the fact that this is usually the wanted phase for the material. The common alternative is that the alloy transitions to an intermetallic (IM), where there is ordering within the solid.

HEAs typically fit the models of body-centered cubic (BCC), face-centered cubic (FCC), or sometimes hexagonally close-packed (HCP). [14]. An important presumption in the materials is that no particular configurational regularity exists within the lattice, something that in fact can be observed. [15]

2.2 Thermodynamics

In Gibbs free energy-model we assume constant temperature and pressure, to define the following thermodynamic relation:

$$G = H - TS \quad (2.1)$$

Here, H is enthalpy, T is the absolute temperature, S represents the entropy, and G is the Gibbs free energy. In the common case of minimizing G , one finds the state of which the system is most lenient towards. Therefore, it is common practice to use the following relation,

$$\Delta G = G_2 - G_1 = \Delta H - T\Delta S, \quad (2.2)$$

where the Δ represents difference of some property after a given change in the system. If G then should be lowered for a spontaneous change in the system, it is equivalent to saying that ΔG should be negative. The absolute temperature in eqn. (2.2) is always positive, so a positive change in entropy for a given change is favourable for it to occur spontaneously.

The spontaneity comes in play when the alloy is finished casting, and starts cooling. Gradually, the entropy term will have less impact because of the sinking temperature. This can often give rise to separate phases within the alloy, and avoiding this is ultimately the goal. [3] To explain this, the terms enthalpy and entropy will need elaboration, as they are ubiquitous in the following discussion.

Entropy is the degree of multiplicity in a system, as defined by Boltzmann and Gibbs, through Boltzmann's law:

$$S = k \ln W \quad (2.3)$$

Where k is the Boltzmann constant $k = 1.38065 \cdot 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$, and W is the multiplicity of the system, meaning the numbers of possible microstates it has (see e.g Dill and Bromberg [16]).

In a solution with r components, each with N_i number of particles out of a total of N , the increase in entropy from mixing said components together can then be calculated: First, one

assumes that the particles occupy discrete points on a lattice. If we assume that the lattice is filled in the case of condensed matter, it would contain the same indistinguishable particle on every point. In other words, the configurational multiplicity of pure solids is 1, meaning the entropy (from eqn. (2.3)) is 0. If one were to mix said solids together, the multiplicity would have to be calculated:

$$W = \prod_{i=1}^r \frac{N!}{N_i!} \quad (2.4)$$

This is based on the $N!$ number of ways the particles can be distributed on the lattice. The denominator takes into account that the particles from each component are indistinguishable amongst themselves, and each component with N_i particles can be arranged in $N_i!$ ways that are indistinguishable. For the logarithm of the multiplicity, we get:

$$\ln W = \ln \prod_{i=1}^r \frac{N!}{N_i!} = \ln N! - \sum_{i=1}^r \ln N_i! \quad (2.5)$$

As N is typically large, on the scale of Avogadro's number, using Stirling's approximation (see figure 2.1), that for large N , $\ln N! \approx N \ln N - N$, is valid:

$$\ln W \approx N \ln N - \sum_{i=1}^r N_i \ln N_i \quad (2.6)$$

Further, one can exploit that $\sum_{i=1}^r N_i = N$:

$$\ln W \approx \sum_{i=1}^r N_i \ln N - N_i \ln N_i = \sum_{i=1}^r N_i \ln \frac{N}{N_i} = - \sum_{i=1}^r N_i \ln \frac{N_i}{N} \quad (2.7)$$

When the starting substrates then are all pure, i.e $S_1 = 0$, the ΔS_{mix} is only dependent on the finished product.

$$\Delta S_{\text{mix}} = k \left(- \sum_{i=1}^r N_i \ln \frac{N_i}{N} \right) \quad (2.8)$$

Or, more commonly:

$$\Delta S_{\text{mix}} = -nR \sum_{i=1}^r x_i \ln x_i, \quad (2.9)$$

where n is moles of particle i . This model, in addition to using the Stirling's approximation (see figure 2.1), assumes ideal behaviour of the solution, which comes with certain assertions.

The vibrational entropy is a component of the total entropy that emerges if one includes the vibrational motion within systems. For a molecule, this can mean the harmonically approximated oscillations within different bonds, and for metallics it can include the multiplicity of possible phonon-waves within the material.

To possibly calculate, some new variables are introduced, Helmholtz free energy F , internal energy U , and the partition function Q .

$$F = U - TS \quad (2.10)$$

$$F = -kT \ln Q \quad (2.11)$$

There are now two methods of solving for the entropy; Either by combining eqn. (2.10) with eqn. (2.11) to get eqn. (2.12) or by differentiating F with respect to temperature (assuming U is not temperature-dependent):

$$S = k \ln Q + \frac{U}{T} \quad (2.12)$$

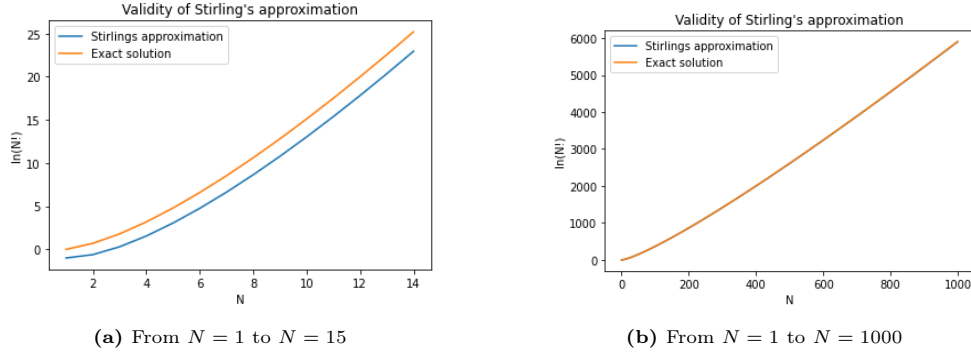


Figure 2.1: Stirling's approximation, $\ln N! \approx N \ln N$, plotted together with the exact solution, showing the validity of the approximation for large N .

$$S = - \left(\frac{\partial F}{\partial T} \right) \quad (2.13)$$

The partition function is the sum of the probabilities of a system being in a possible state:

$$Q = \sum_j^t e^{-\frac{E_j}{kT}} \quad (2.14)$$

Here, the energy of a given state j is represented by E_j , with t being the number of possible states for a molecule. If the system then has multiple energy-dependencies, we can write

$$Q = \sum_j^t e^{-\frac{E_{1j} + E_{2j}}{kT}}$$

$$Q = \sum_j^t \left(e^{-\frac{E_{1j}}{kT}} e^{-\frac{E_{2j}}{kT}} \right)$$

$$Q = q_1 q_2 \quad (2.15)$$

The partition function can be further divided into different energy contributors, and these can both represent other particles, or other energy states. Quantum mechanics makes the following contributions calculable and typically used.

$$Q = q_{\text{translation}} q_{\text{vibration}} q_{\text{rotation}} q_{\text{electronic}} \quad (2.16)$$

This implies that one can separately calculate each contribution to the Helmholtz energy, and thus the entropy, if one can define and calculate its partition function.

$$F = -kT \ln (q_{\text{translation}} q_{\text{vibration}} q_{\text{rotation}} q_{\text{electronic}}) \quad (2.17)$$

The most important takeaways from these for our purposes:^[17]

$$F_{\text{vib}} = -kT \ln q_{\text{vib}} \quad (2.18)$$

$$F_{\text{elec}} = -kT \ln q_{\text{elec}} \quad (2.19)$$

Finding accurate partition functions for large systems proves complicated, however. For example, a common way to calculate the vibrational partition function is to use the density of states of phonons. An example of a simpler method could be to use the Einstein model for solids.

In the Einstein model, one assumes that each atom vibrates independently, in all three directions.^[18] This means that for N particles in the system, there will be a total number of $3N - 6$ vibrational modes $\approx 3N$ for purposes with large N , such as ours. One can then calculate the energy for each vibrational mode, considering only nearest-neighbour interactions.

Using harmonic oscillator for quantum vibrations, and the sum of a geometric series, the vibrational partition function for a diatomic becomes

$$q_{\text{vib}} = \frac{e^{-\frac{h\nu}{2kT}}}{1 - e^{-\frac{h\nu}{kT}}} \quad (2.20)$$

h being Planck's constant, and

$$v = \frac{1}{2\pi} \sqrt{\frac{k_c}{\mu}} \quad (2.21)$$

k_c is here the spring constant in the chemical bonds, or the vibrational mode, and μ is the reduced mass of the two particles. In Einsteins model, we then have $3N$ such partition functions, and the total vibrational partition function for the solid will be:

$$Q_{\text{vib}} = \prod_{i=1}^{3N} q_i^{\text{vib}} \quad (2.22)$$

Combining this with eqn. (2.18) yields the following:

$$\begin{aligned} F_{\text{vib}} &= -kT \ln \prod_{i=1}^{3N} q_i^{\text{vib}} \\ F_{\text{vib}} &= -kT \sum_{i=1}^{3N} \ln \frac{e^{-\frac{h\nu_i}{2kT}}}{1 - e^{-\frac{h\nu_i}{kT}}} \\ F_{\text{vib}} &= \frac{h}{2} \sum_{i=1}^{3N} \nu_i + kT \sum_{i=1}^{3N} \ln \left(1 - e^{-\frac{h\nu_i}{kT}} \right) \end{aligned} \quad (2.23)$$

The final expression can then be used to find the vibrational entropy, by eqn. (2.13):

$$S_{\text{vib}} = - \left(\frac{\delta F}{\delta T} \right) = k \sum_{i=1}^{3N} \left(\frac{h\nu_i e^{-\frac{h\nu_i}{kT}}}{kT \left(1 - e^{-\frac{h\nu_i}{kT}} \right)} - \ln \left(1 - e^{-\frac{h\nu_i}{kT}} \right) \right)$$

Now applying Bragg-Williams approximation, for an r -component equiatomic solid:

$$S_{\text{vib}} = k \frac{6N}{r(r+1)} \sum_{i=1}^{\frac{r(r+1)}{2r}} \left(\frac{h\nu_i e^{-\frac{h\nu_i}{kT}}}{kT \left(1 - e^{-\frac{h\nu_i}{kT}} \right)} - \ln \left(1 - e^{-\frac{h\nu_i}{kT}} \right) \right) \quad (2.24)$$

The last equation is exploiting that there are a possible number of $\frac{r(r+1)}{2}$ different nearest-neighbour bonds in the solid. Using Bragg-Williams approximation, this would mean that there would be an average of $\frac{6N}{r(r+1)}$ units of that bond in the solid. Summing these up should then yield the total contribution from all modes.

In both configurational and vibrational entropy calculations there are now models introduced that both apply the Bragg-Williams approximation. What this approximation means, in principle, is that the mixing would happen in the same way as mixing r boxes of identical balls, but with r different colors. At any location of this mixture, one would expect the probability of finding a ball of a given color to be given solely by the fraction of that colors' presence in the

mixture. This is the Bragg-Williams approximation, which approximates a solution by saying the probability of finding any particle at a given matrix point is simply given by its number density.^[16]

What this approximation disregards, then, is all unique properties of said particles that give them a site preference within the matrix, such as electron-affinity, size or otherwise shape, particle interactions, etc. A detailed model for entropy in HEAs will include these in the calculation.

One way of doing this is to use Monte Carlo simulations. If so, one first assumes a structure of the system. This structure, with all its particles, is then reorganized in a computer in a step-wise manner, based on probabilities. The probabilities of, say a switch of the configuration of two atoms, is calculated based on an energy change of the two states. Equilibrium is then obtained when the number of changes back and forth is equal.

This does not mean that the probability of a change must be 0.5 at equilibrium, but rather, it can be represented by the following equation:

$$n_i p_{i \rightarrow j} = n_j p_{j \rightarrow i} \quad (2.25)$$

where i and j are two different states, and p is the probability of some change of state.^[19] When reaching a state that satisfies this condition for all possible changes, the system is in equilibrium. At that point, measurements can be made to calculate the realistic configurational entropy, along with other values.^[20] The ideal configurational analogy to this would be to set $p = 1/z$ for all p , where z is the number of possible state changes, meaning they are all just as likely.

The way Monte Carlo simulations can deviate from this ideality, however, is to base the probabilities on parameters of already acquired data about the particles, $p = e^{-\frac{\Delta E}{kT}}$. Here, ΔE represents the difference in energy between the final state and the initial state.^[17] The choice of parameters and their effect on the energy levels — and thus the probabilities of state changes — is then left up for discussion. Another analogy to the ideal configurational entropy in this case would be that the change of energy for any given state change would be 0, making all $p = 1$.

3 Discussion

There is yet to be a model that satisfactorily predicts the formation of single phase HEAs.^[21] The problem stems from the very nature of HEAs, namely its complexity.

As Troparevsky et al. points out, one should for instance calculate every combination of components and their individual phase stability, in order to accurately compare their competitiveness with SS phase of the HEA.^[22] This, of course, is an unrealistic prospect, and approximative models must be made, the problem being that with every simplification of each parameter, the predictions lose their accuracy.

The foremost discussion should be to what degree entropy needs to be weighted. From eqn. (2.1), we know that entropy may be in competition with enthalpy in deciding whether a state is stable. If either entropy or temperature is low enough, enthalpy would be the dominant decider. In this case, entropy calculation could be neglected, and nothing but the mixing enthalpy would have to be calculated, as is the case with most other alloys.

An important point is made on this by Miracle and Senkov, who emphasizes that systems with large negative enthalpy values of SS phase are likely to have just as large for the IM phase.^[3] Calculations of mixing enthalpy for HEAs typically lies between $+5 \text{ kJmol}^{-1}$ and -20 kJmol^{-1} (see table 3.1).^[23;24] This can be compared to the ideal configurational entropy for an equiatomic alloy with r components using eqn. (2.9):

$$\frac{\Delta S_{\text{mix}}}{n} = -Rr \frac{1}{r} \ln \frac{1}{r} = 8.314 \ln r \text{ JK}^{-1} \text{mol}^{-1} \quad (3.1)$$

With r between 4 and 8, and temperatures ranging from 100K to 1500K, this free energy contribution is between 1.15 kJmol^{-1} and 25.9 kJmol^{-1} . While it should be acknowledged that the real configurational entropy most likely will yield lower values than this ideal version, it is still in the same scale as the mixing enthalpy, and can not be ignored.

Table 3.1: Examples of calculated values of ΔH_{mix} for various HEAs, at temperatures around 1700K adapted from Yang and Zhang, with calculated ideal entropy of mixing.^[23]

| Alloy | Structure | $\Delta H_{\text{mix}} [\text{kJmol}^{-1}]$ | $1700\text{K} \cdot \Delta S_{\text{ideal}} [\text{kJmol}^{-1}]$ |
|------------------------------|-----------|---|--|
| CoCrFeNiAl | BCC | -12,32 | 22.75 |
| CoCrFeNiCuAl ₃ | BCC | -10.56 | 23.57 |
| CoCrFeNiCu _{0.5} Al | BCC | -7.93 | 24.96 |
| CoCrFeNiCu | FCC | 3.20 | 22.75 |
| Ti _{0.5} CoCrFeNiCu | FCC | -3.70 | 24.96 |
| CoFeNiCuV | FCC | -1.78 | 22.75 |

Secondly, one should determine which entropy-terms need to be included, based on their magnitudes. Ideal configurational entropy is calculated from eqn. (2.9). Beyond this, Wang et al. found the excess entropy contribution to be $0.9R$ and $0.7R$ at 300K for equiatomic NiCoFeCr and NiCoCr, respectively.^[25] This is compared to their ideal configurational entropies of $1.39R$ and $1.10R$. The differences here suggests that the excess entropy is imperative to include, and the following question becomes what constitutes the excess entropy.

$$S = S_{\text{ideal}} + S_{\text{excess}} \quad (3.2)$$

The possible contributors are the deviation between real and ideal configurational entropy, or vibrational, electronic, or magnetic entropy. To find the deviation between real and ideal configurational entropy, an atomistic Monte Carlo simulation can be used.

Liu et al. found with this method a lattice constant for CoCrFeNi that were 0.2% off the experimental value, meaning the final modelled structure could very well be realistic. With the same model and alloy, they calculated a configurational entropy of $1.329R$ at temperature 1373 K. This is remarkably close to, about 4% less than, the ideal configurational entropy.^[20] This means in principle that each atom within the structure should have a very close to equal chance of having any other atom next to it (see figure 3.1).

In the same article, Liu et al. models the effect of changing mixing enthalpy and atomic size differences. They created 4 hypothetical alloys, each created by replacing one of the atoms in CoCrFeNi with a fictional atom Me. They then adjusted the values for the size difference, measured as δ (where $\delta < 0$ or $\delta > 0$ respectively indicates a reduction or increase in atomic size from the original atom), for one set of simulations, and adjusted the mixing enthalpy for another set. The results shown in figure 3.2 tell the story of how these parameters affect the true configurational entropy of alloys.

The curves in figure 3.2a all clearly indicate some ideal size difference where the entropy is close to that of the ideal configurational entropy, i.e $S/S_{\text{ideal}} \approx 1.0$. An argument for this is that large atomic size differences would distort the lattice, and cause some atoms to have preferences for specific lattice sites. this creates a certain regularity in the alloy, which serves to decrease the entropy.

The mixing enthalpy is a good indication of how likely the constituents of the alloy is to bind together. A high mixing enthalpy can make it less likely for atoms to interact with other components, making it separate. A too negative mixing enthalpy, on the other hand, can make

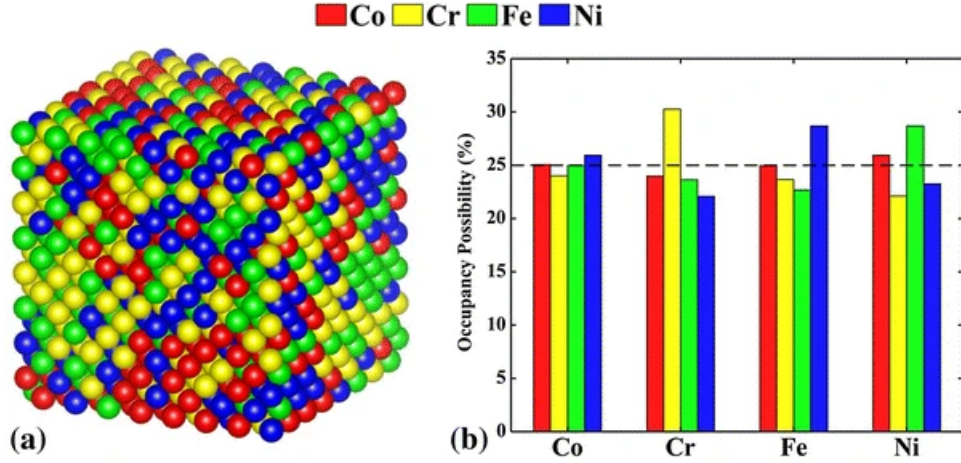
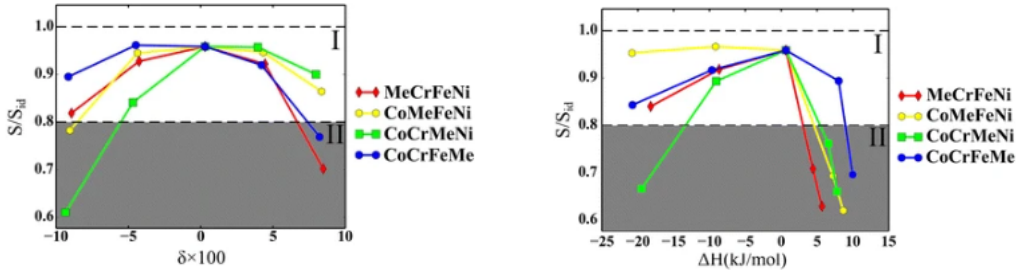


Figure 3.1: a) A representative structure of equiatomic CoCrFeNi. b) Probability of first-nearest neighbour being the given atoms. Reused with permission from Liu et al.^[20]



(a) Ratio of measured and ideal configurational entropy, as a function of size difference δ .

(b) Ratio of measured and ideal configurational entropy, as a function of mixing enthalpy

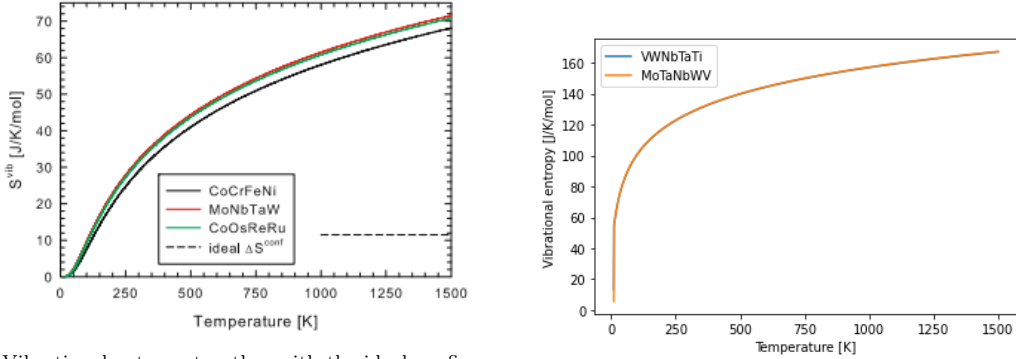
Figure 3.2: Variation in ratio between measured and ideal configurational entropy, as functions of size difference (a) and mixing enthalpy (b). Calculations done from atomistic Monte Carlo simulations for 4 hypothetical alloys, reused with permission from Liu et al.^[20]

some atoms interact too strongly, creating intermetallics, and reducing the overall entropy.^[23] This result is also well depicted in the simulation of Liu et al (see figure 3.2b).

Another thing Monte Carlo simulations vividly demonstrates, is the dependency of W on temperature. When the temperature is high, the multiplicity of the system increases, because an increasing amount of states become accessible. This is something that the ideal configurational entropy fails to acknowledge.^[26]

According to Miracle and Senkov, the vibrational entropy is dominant in the total entropy of the HEAs (see figure 3.3a). However, they argue, it is equally dominant in the IM phase of the alloys they calculated for, meaning that its stabilization-effect on the SS-phase would be limited.^[3]

Others, on the other hand, can be cited in saying that the vibrational entropy of mixing is crucial. Gao et al. predicts a positive value of this parameter for one alloy, and a negative for another.^[28] These are plotted by Gao et al. in another article (see figure 3.4) together with a third alloy that has a neutral mixing entropy of vibration.^[27]



(a) Vibrational entropy together with the ideal configurational entropy, reused with permission from Gao et al. [27]

(b) Vibrational entropy, approximated using Einstein's model

Figure 3.3: Vibrational entropy plotted for temperature ranging from 1K to 1500K.

Although the average mixing entropy of vibration for possible HEAs might then be close to 0, the variation in each individual case could very well be the deciding factor in creating the stable SS phase. This fact has been known in binary alloy-crafting for some time. Already in 2002, van de Walle and Ceder published vibrational entropy differences on the scale of 0.1 and 0.2 R, both theoretical and experimental, and concluded that it has dramatic impact on the phase stability predictions of binary alloys. [29]

Knowing, then, that vibrational mixing entropy is a generally important parameter for phase stability in alloys, a pressing question becomes whether or not the vibrational mixing entropy increases with increasing the number of components. If so, it would have to be incorporated into the identity of HEAs who is at present solely characterized by its configurational component. After all, the vibrational entropy of the materials in figure 3.4(a,b) would be about 20% of the ideal configurational at room temperature; clearly substantial amounts.

Körmann et al. found an increase of S_{vib} with increasing the number of equimolar components r for one set of materials. [30] They explained this phenomenon, however, not as a consequence of having more components r , but as a consequence of the increased volume of the alloy from its gradually distorted lattice — something which is known to increase the vibrational entropy. Indeed, for another set of alloys with more stable volume, the vibrational entropy was equally stable.

The simple Einstein model also supports that the number of components r does not directly impact the vibrational entropy, in the same way it does for configurational. If one looks at eqn. (2.24), one finds that increasing r does not impact the scale of the entropy. Rather, a change would come from introducing a new element with different force constants or masses.

Körmann et al. also commented on the effect of the newly added components' mass, claiming that decreasing the average mass of the alloy would increase the vibrational entropy. This can also be supported by the Einstein model, which is made clear when derivating the entropy with respects to v_i :

$$\frac{\partial S_{\text{vib}}}{\partial v_i} = -\frac{h^2}{kT^2} \frac{6N}{r(r+1)} \sum_{i=1}^{\frac{r(r+1)}{2}} \frac{e^{-\frac{h v_i}{kT}}}{\left(1 - e^{-\frac{h v_i}{kT}}\right)^2} \quad (3.3)$$

Eqn. (3.3) shows that the change of vibrational entropy with respects to change in v_i is negative for all possible values of v_i and T . This means that an average increase in spring constant k_c or, notably, a decrease in average reduced mass μ (see eqn. 2.21), increases the entropy.

One view in the HEA field seems to be that the electronic entropy of mixing is truly negligible, i.e only the electronic ground state is occupied. [27] Meanwhile, the magnetic entropy seems to

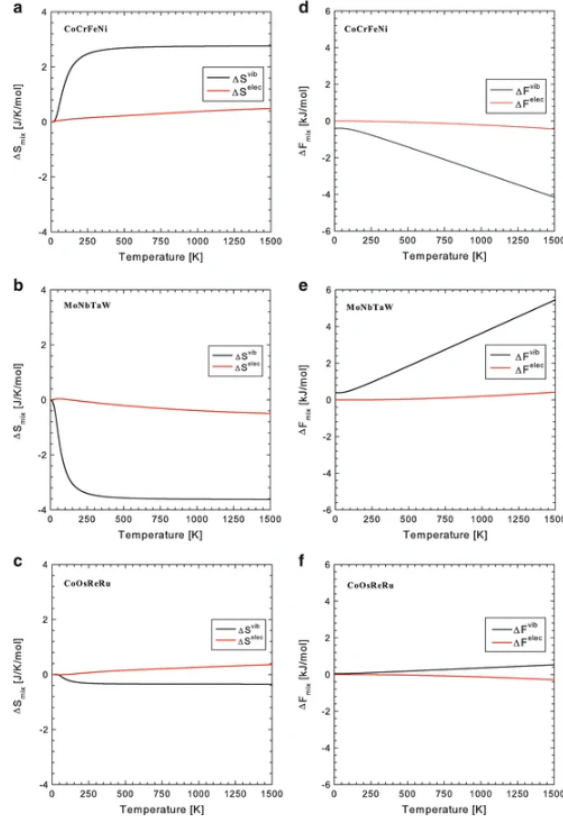


Figure 3.4: Vibrational and electronic entropy of mixing by temperature (a-c), with their Helmholtz free energy contribution by temperature (d-f), reused with permission from Gao et al.^[27]

be up for discussion when the HEAs contain elements with magnetic properties. Wang et al. claims that for NiCoFeCr, magnetic entropy would be dominant among the excess entropy terms in the range 300 K to 1000 K.^[25] This is, albeit, an alloy containing three ferromagnetic materials, Ni, Co and Fe, but it is certainly notable, and should motivate elaboration for different alloys. There are more than one way of quantifying it, but one is by using the following expression:

$$\Delta S_{\text{mag}} = \int_{B_0}^{B_1} \left(\frac{\partial M}{\partial T} \right)_{B,p} dB \quad (3.4)$$

where M is the magnetization of the alloy, and B is the strength of the electric field applied on the alloy.^[31] This can then be measured experimentally, by measuring changes in magnetization for different T and B .

There are other methods of predictions besides the ones discussed above, that deserve mentioning.

Density Functional Theory (DFT) is currently the standard for predicting thermodynamic properties and phase stability in HEAs. This method uses state functionals of electrons within systems to calculate parameters for the entire system. It is, unfortunately, not only too computationally demanding to be explained further here, but also to be used in large scale in the HEA field.^[32] One exciting prospect is utilizing machine learning to calculate the vibrational entropy. Manzoor and Aidhy used machine learning to predict S_{vib} following another prediction of the force constants c_i within HEAs. First taking 96 hours to computationally calculate their parameters with DFT as reference points, they later found well matching force constants and vibrational entropy for HEAs in a matter of seconds.^[32]

The HEA field is already semi-empirically based, with trial and error as a method of ultimately finding a good prediction-model for stable phases. While a computer's machine learning might not be as romantic as the mechanistic approach, it might be wise in this case to follow Manzoor and Aidhy's idea, which have already given good results.^[32] From there, one can instead move backwards, and build a theory that matches the numbers.

4 Conclusion

20 years has past since Yeh et al. published their first article explicitly defining HEAs. What may have seemed at the time a simple definition and mechanic has since then been increasingly complex, with more parameters, terms, suggested mechanics, and semi-empirical equations being launched each year, to better predict the phase stability of the exciting alloys.

It has been shown that the entropy, in particular, is a complex subject in the field. The ideal solution approximation gives an alluringly simple calculation for the configurational entropy. While we have shown that this term indeed is dominating the total entropy in the system, the excess term is too large to leave out.

In systems that has temperature $T < 1000$ K, large absolute mixing enthalpy, or substantial atomic size difference, especially, the configurational entropy will be much lower than what the ideal approximation predicts. A better approach then would be to simulate the system using Monte Carlo simulations.

For high temperatures, Wang et al. considers the magnetic entropy to be the dominant term in the excess entropy.^[25] Their measuring was only for one intentional set of alloys, however, and this should be looked at further for other alloys.

Another discovery is the change in vibrational entropy that can arise when mixing the components. Data indicates that its magnitude can be up to 20% of the ideal configurational, and can either contribute to stabilize the SS phase, or induce separation to IMs. Whether this is solely from size and mass changes in the system, or if it is some intrinsic effect in adding more components is still up for debate.

The Einstein model of solids was introduced, as an example of a simplified model for one of the entropy terms, namely the vibrational. This model gave no indications of any direct correlations between number of equimolar components and the vibrational entropy of the solids, something that Körmann et al.'s data supported.^[30]

Regardless, these terms, namely the configurational and vibrational components, are the dominant factors when calculating the entropy of HEAs, and serves as equally important predictors of phase stability with the mixing enthalpy.^[20] For now, the models of calculating these excess entropy terms are too computationally demanding for it to be used in large scale search of new stable HEAs. This thesis therefore recommends further look into machine learning as a possible method of prediction, and in time when more data is acquired, better theoretical models can be made.

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