# Thermal Physics Project

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## Abstract

Using the data from the Heat Capacities of a $Cu_3Au$ initially ordered sample, the effect on the entropy of the order-disorder (OD) transition is investigated. Following a similar analysis to the Artur Benisek and Edgar Dachs (BD) [1] study, the final results on the total entropy change of the OD phase transition are compared with the ideal entropy of mixing. It was found that the total entropy change of the disordering transition at $711.11K$ gave an excess entropy of $-0.172$ (in units of R) when compared to the ideal entropy of mixing.

## Contents

# 1 Background Theory

## 1.1 Entropy and Ideal Entropy of Mixing

In thermodynamics, entropy is defined as the amount of reversible work into the system divided by the temperature of the reservoir from which heat was taken. In a differential form, it means that [2]:

$$dS = \frac{dQ_{\text{rev}}}{T}$$

However, entropy is also a measure of ignorance. In terms of statistical mechanics, entropy is defined as [2]:

$$S = k\ln(\Omega)$$

Where k is the Boltzmann's constant and $\Omega$ is the number of microstates (ways of arranging the system) associated with a particular macrostate. The larger the number of microstates, the larger the ignorance we have about the system (We can only macrostate quantities like the temperature but not the exact arrangement of atoms that give that temperature). The ideal entropy of mixing is of particular interest in this study. This entropy change refers to the change in entropy caused by mixing two ideal gases that occupy initial volumes $V_A$ and $V_B$, and they end up sharing the total volume $V_A + V_B$. This entropy change is given by [2]:

$$\Delta S^{\text{ideal}} = -R(\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \tag{1}$$

Where $\chi_A$ and $\chi_B$ are the molar fractions of the gases. While this formula is initially derived only for ideal gases, it can also be used as an upper limit for the configurational entropy change in some transitions in solids. Consider a binary solid crystal formed by N atoms, initially in ordered (determined) positions with N available positions in a lattice. Of those N atoms, there are $\chi_A N$ atoms of type A and $\chi_B N$ atoms of type B. There is only one way of arranging the atoms, the one that defines the solid. After a particular process, the atomic distribution of the solid becomes disordered, meaning that the positions of the atoms on the lattice become fully random[1]. Hence, after the phase transition, we need to place $N\chi_A$ atoms of A and $N\chi_B$ atoms of B in a lattice of N sites entirely randomly. Then there are $\Omega$ distinct ways of doing so, where $\Omega$ is given by:

$$\Omega = \frac{N!}{(N\chi_A)!(N\chi_B)!} \tag{2}$$

These are the number of microstates associated with the macrostate of having N partices arragned in a lattice of N sites. Hence, the entropy change is given by (the entropy of

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[1] This restriction can be stated in mathematical terms by imposing that all the individual partitions are equally likely

the initial sample is zero as there is only one way of arranging such the atoms in the ordered way):

$$\Delta S^{\mathrm{conf}} = k \ln\left(\frac{N!}{(N\chi_A)!(N\chi_B)!}\right) \tag{3}$$

$$\Delta S^{\mathrm{cong}} = k \ln(N!) - kln((N\chi_A)!) - kln((N\chi_B)!) \tag{4}$$

$$\Delta S^{\mathrm{conf}} \approx -Nk(\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \tag{5}$$

Where the last step is possible thanks to sterling's approximation. Taking $N$ to be Avogadro's Number, the latter equation gives:

$$\Delta S^{\mathrm{conf}} \approx \Delta S^{\mathrm{ideal}} \tag{6}$$

Hence, the ideal entropy of mixing poses an upper limit for the configurational entropy change of the process described above. However, it is a theoretical limit as it assumes a perfectly ordered sample at the beginning and a perfectly disordered distribution at the end. These conditions mean that when the configurational entropy change is measured experimentally, it will be smaller than the ideal entropy of mixing.

## 1.2 Use Heat Capacities

We can use Heat capacities to measure how the entropy changes. The definition of Heat capacity states [2]:

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \tag{7}$$

Meaning that the heat capacity tells how much heat it is required to input to the system to raise the temperature by 1K while the pressure is constant.

On the other hand, the Enthalpy is defined as [2]:

$$H = U + VP \tag{8}$$

And the differential version is obtained as follows:

$$\begin{aligned} dH &= d(U + VP) \\ &= dU + PdV + VdP \\ &= dQ - PdV + PdV + VdP \\ &= dQ + VdP \end{aligned}$$

If the process occurs at constant pressure, then:

$$dH = dQ$$

Therefore it is easy to see that:

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P \tag{9}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \tag{10}$$

On the other hand, for reversible processes the differential version of the entropy can be written as [2]:

$$dH = TdS + VdP \tag{11}$$

Hence, it is possible to rewrite the expression for the Heat capacity at constant pressure as:

$$C_P = T\left(\frac{dS}{dT}\right)_P \tag{12}$$

Equation 12 can be used to obtain the entropy change between a range of temperatures, moving $T$ to the left side and integrating both sides with respect of $T$ the expression gives:

$$\Delta S = \int_{T_0}^{T_f} \frac{C_P}{T} dT \tag{13}$$

Where $\Delta S$ gives the entropy change that the system has undergone between $T_0$ and $T_f$

## 1.3 The use of entropy change

The measurement of entropy changes is helpful in studying the properties of materials as changes in entropy hint at a change in the structure and properties of the materials. In this particular example, the change in entropy tells us that the structure of the initial $Cu_3Au$ sample is changing. This can already be seen from the heat capacity data, and it is precisely what the peak in the heat capacity tells.

## 1.4 Order-disorder transitions and $Cu_3Au$

At low Temperatures, the $Cu_3Au$ alloy presents a stable $L1_2$ ordered structure with $Au$ atoms at the corners and $Cu$ atoms in the face centres. However, at around $660K$, this material undergoes a phase transition, in which some atoms change their position, leading to a disordered face centred cubic (fcc) structure [1, 3]. A disordered atomic distribution means that the lattice sites are occupied by $Au$ and $Cu$ atoms with stoichiometric probability [4]. Despite having a disordered atomic distribution after the phase transition, the $Cu_3Au$ still shows some short-ranged order [1, 3], which can be decreased by increasing the temperature.

The disordering process entrails an entropy change in the system. However, this entropy change does not only have a configurational origin; it also has a vibrational origin. When the alloy transitions between an ordered $L1_2$ structure to a disordered fcc structure, there is an obvious increase in entropy due to the new ways of arranging the atoms in the lattice. This entropy change of configurational origin will be denoted as $\Delta S^{\mathrm{dis}}_{\mathrm{conf}}$. On the other hand, there is an 0.8% decrease in volume in the transition from an $L1_2$ structure to an fcc structure [1]. Such decrease causes the frequency of vibrations to be slowed down. Hence, there is an entropy change associated with the change in frequency of vibrations, which will be denoted as $\Delta S^{\mathrm{dis}}_{\mathrm{vib}}$. When investigating the total entropy change of the OD phase transition, the final result of the entropy change will include both (if derived from heat capacity data), in other words:

$$\Delta S^{\mathrm{dis}} = \Delta S^{\mathrm{dis}}_{\mathrm{conf}} + \Delta S^{\mathrm{dis}}_{\mathrm{vib}} \tag{14}$$

# 2 Methods

## 2.1 Data Collection

The BD research paper provided the data for this project. It consisted of measurements of the Heat Capacity ($C_p$) of a $Cu_3Au$ sample across different temperatures in units of the universal gas constant R. The measurements were taken from $300K$ to about $718.11K$ in the original article. However, for this study, only temperatures between $500K$ and $718.11K$ have been considered. The data was collected at approximately $0.08K$ intervals giving a total of 2616 data points (not taking into account those between $300K$ and $500K$). The background heat capacity was subtracted from the raw data of the BD research paper, giving the quantity $\Delta C_P$. Such subtraction was done to avoid including anything unrelated to the OD transition into the data.

The original paper gave in its supplementary material the uncertainties on the data[2]:

$$\sigma_{C_p} = C_p \cdot (-0.198 + 9.4 \cdot 10^{-4} \cdot T - 9.2 \cdot 10^{-7} \cdot T^2) \quad (15)$$

$$\sigma_T = T \cdot (0.001 - 9 \cdot 10^{-7} \cdot T) \quad (16)$$

Assuming the uncertainties in the baseline (values subtracted to get $\Delta C_P(T)$) are small, the uncertainties on $\Delta C_P(T)$ are the same as the uncertainties of $C_P(T)$.

The following plot shows the relationship of $\Delta C_P(T)$ and $T$:

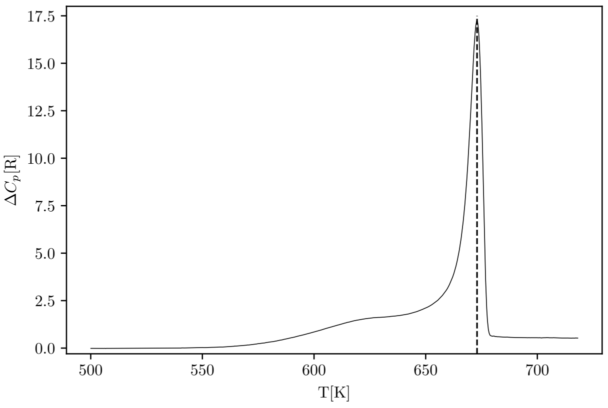

Figure 1: Graph of $\Delta C_P$ in units of R vs the Temperature $T$ measured in Kelvins. The dashed line represents the maximum the Heat capacity at about 675K.

The graph shows a peak in the heat capacity around $680K$ as was expected. Note that all quantities like $\Delta C_P$ or $\Delta S^{\text{dis}}$ (which will be obtained in the following sections) are specific quantities (they are given in units of R).

## 2.2 Entropy of Disordering

The total change on entropy of the disordering process can be calculated using the relation $dS = \frac{C_P}{T} dT$. Hence, the integral of $\int_{T_0}^{T_f} \frac{\Delta C_P}{T} dT$ gives the total entropy change of the disordering process. $\Delta C_P$ is used instead of $C_P$ to avoid adding anything that has nothing to do with the disordering process.

The scaled data (the usual heat capacity data divided by the Temperature) is presented in the following graph to show its relationship with Temperature:

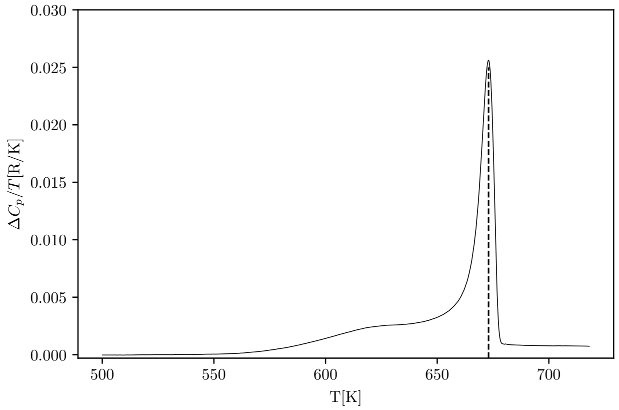

Figure 2: Graph of $\frac{\Delta C_P}{T}$ in units of $\frac{R}{K}$ vs the Temperature $T$ measured in Kelvins. The dashed lines represent the maximum Heat capacity over temperature at about 675K.

The area under the curve obtained in Figure 2 gives the entropy change due to the disordering process. If the disordering process starts at $T = 500K$ and it ends at around $700K$ (Actually the process continues, but the data was not provided for temperatures over $711.11K$), Then the definite integral $\int_{500K}^{T_f} \frac{\Delta C_P}{T} dT$ will give the entropy change of the process up to the temperature $T_f$. Hence, the total entropy change in the disordering process will be given by letting $T_f = T_{Max} = 711.11K$. However, as there is an interest in knowing how the change in entropy evolves with Temperature (How does the entropy change evolve as you go through the disordering process), $T_f$ is defined as a variable that ranges from all the temperatures available.

Given that the data for $\frac{\Delta C_P}{T}$ is discrete, it is not possible to solve the integral analytically. However, numerical solutions are still possible. The mid point rule was used to calculate the value of the integral $\int_{500K}^{T_f} \frac{\Delta C_P}{T} dT$ for different $T_f$.

The mid point rule states that:

$$\int_a^b f(x)dx \approx \sum_i f(x_i)\delta(x_i) \text{ Where: } \delta(x_i) = x_{i+1} - x_i$$

The mid point method breaks the function into rectangles of width $\delta_{x_i}$ to calculate the area below it.

Using the mid point rule the integral ($\Delta S^{\text{dis}}$) was calculated for different values of $T_f$. The relation between the entropy of disorder and the temperature is shown in the plot below:

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[2] The uncertainty on the temperature was provided directly by the authors of the BD paper as it was wrong in the supplementary materials

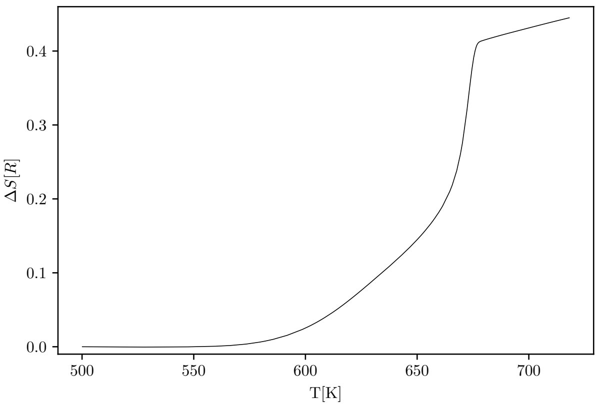

Figure 3: Graph of the entropy change of the disordering process vs Temperature

The figure shows that the real increase happens around 660-690, which agrees with what it was expected given the shape of Figure 2. The total entropy change encapsulates both the vibrational entropy change and configurational entropy change discussed in the background section. Hence, $\Delta S^{\text{dis}} = \Delta S^{\text{dis}}_{\text{vib}} + \Delta S^{\text{dis}}_{\text{conf}}$. The total entropy change of the disrodering process is given by the value on the right edge of the graph, as this value accounts for the entropy change due to the disordering process between $500K$ and $700K$

## 2.3 Uncertainties

It can be seen from Equations 15 that the uncertainties in $C_P$ range from 0 to 0.3. In relative terms, they range from 4% to 0.026% (using the original data). In the case of temperatures, the errors range from $0.2K$ to $0.3K$, and in relative terms, they are not even a 1% of the measured values. In conclusion, the uncertainties of $C_P$ and $T$ are minimal. This makes that the overall uncertainty in the entropy change will also be small, or at least sufficiently small, so that they do not make a difference when comparing the total entropy change with the ideal entropy of mixing. Furthermore, the provided data show only minor deviations from a smooth function. Given that the area under $\frac{\Delta Cp}{T}$ graph gives the entropy change, the slight positive deviations of the data will counterweight the small negative deviations in the sum, making the deviations even smaller in the entropy case.

# 3 Results And Discussion

## 3.1 Heat Capacity

The graph obtained in Figure 1 reflects exactly the phase transition that the background section mentions. It can be seen that there is a peak of around $675K$ and that the effect of disordering becomes effective at around $560K$; before that, the Heat capacities stays almost constant and near 0.

The provided data contains some negative $\Delta C_p$ values in low temperatures, but those arise from errors in the subtraction of the baseline. After a conversation with Dr Poon, it was discovered that the given values had been subtracted a baseline by hand instead of taking the baseline from literature values. This could result in minor discrepancies between our study and the key paper. The value used by Dr Poon seems to be higher than the one used in the BD paper, leading to slightly smaller values in the final result.

## 3.2 Entropy of Disordering

Figure 3 gives the entropy change of disordering across different temperatures. It can be seen from the graph that up to $560K$ there is no entropy change, which agrees with the data of the heat capacities that were zero at that range. Furthermore, it can be seen that the minor errors in that area (that gave some negative values in $\Delta C_p$) have almost no effect on the final result as the expected result in that region (0, as the alloy, has not yet started the disordering) is obtained from the entropy graph. The shape of the graph makes sense given the data of Figure 2. The rapid increase of the entropy between $660K$ and $680K$ is explained by the lambda type peak present in both Figures 2 and 1. Hence, even a simple integration method as the mid-point rule is enough to capture this phase transition's essential behaviour (in terms of entropy change).

## 3.3 Ideal Entropy mixing

The total entropy of disordering can be compared to the ideal entropy of mixing. The ideal entropy of mixing is given by the equation:

$$\Delta S^{\text{ideal}} = -R(\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \tag{17}$$

In units of R the Equation 17 gives:

$$\Delta S^{\text{ideal}} = -(\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \tag{18}$$

For this particular case, 18 gives $\Delta S^{\text{ideal}} = 0.562$ in units of R, given that $\chi_A = 0.75$ and $\chi_B = 0.25$. The total entropy change ($\Delta S^{\text{dis}}$) of the OD transition between $500K$ and $711.11K$ was calculated to be 0.445 in units of R.
Comparing this result to the ideal entropy of mixing it is possible to get an excess entropy:

$$\Delta S^{\text{excess}} = \Delta S^{\text{dis}} - \Delta S^{\text{ideal}} = -0.117 \tag{19}$$

In an ideal scenario, where the initial sample is fully ordered at the beginning of the process and the sample becomes fully disordered at its end, the configurational entropy change would have been given by the ideal entropy of mixing as explained in the background theory. Only the vibrational change would be left in the entropy excess if this is the case. In such scenario, Equation 19 would be:

$$\Delta S^{\text{excess}} \approx \Delta S^{\text{dis}}_{\text{vib}} \tag{20}$$

Hence, the excess entropy would likely be positive in this case.

However, it is not the case that the initial sample is fully ordered at the start, and also it is mentioned in the BD article that even after the phase transition, there is some short-range order in the fcc structure. This contributes to the configurational entropy being smaller than in the ideal scenario. Hence, the excess entropy is negative as the configurational entropy obtained with the integration is insufficient to compensate for the subtraction of the ideal entropy of mixing. While there is still another positive term in the equation (the vibrational entropy change), this is not enough to compensate for the defect of the configurational entropy change (The vibrational component can be found independently, and other studies have found that this value is significantly less than the configurational contribution, accounting for about 13% of the total entropy change [1, 3]). The value of the excess entropy can become more positive if a greater range of temperatures is considered. Increasing the temperature has the effect of decreasing the short-range ordering present in the fcc structure [1]. Hence, it makes the configurational entropy change closer to the ideal entropy of mixing. Given the conditions in which the experiment was performed, it is more plausible to state that increasing the temperature will generally reduce the difference between the ideal entropy of mixing and the total entropy change, making the excess tend towards zero. However, the excess could become positive by increasing the temperature if the configurational entropy change becomes similar to the ideal entropy of mixing and if the vibrational change can compensate for the difference between them. This analysis assumes that the vibrational entropy change is both positive and almost constant as the temperature raises, this hypothesis has been found to be reasonable above $700K$ [1, 3].

### 3.4 Further Studies

This section explores what further studies could be carried away to find more precise conclusions.

The first possibility is considering a greater range of temperatures for the Heat capacity data. This data could be used to calculate the configurational entropy change at larger temperatures as the vibrational part can be calculated independently (other studies have found that the vibrational entropy change does not change much as the temperature is increased above $700K$ [3]. Hence, getting a larger range of temperatures would allow to calculate the total entropy change at larger temperatures and hence calculate the configurational entropy change, which could then be compared to the ideal entropy of mixing. Overall, this comparison would estimate how disordered the $Cu_3Au$ sample is at different temperatures.

There are other possibilities to consider. In this analysis and the one proposed in BD, the total entropy change is assumed to be given by contributions of a vibrational and a configurational origin only. However, other studies in $Cu_3Au$ suggest that this might be a too simplistic approach, as other contributions might be non-negligible [5], specially a change in entropy or electronic origin [5]. If the assumption that other contributions are not negligible is taken to be true, then it would not change the analysis done in this paper up to the point where it was concluded than in ideal conditions (starting with a fully ordered sample and ending with a fully disordered sample) would give an excess entropy ($\Delta S^{\text{dis}} - \Delta S^{\text{ideal}}$) equal to the vibrational change contribution ($\Delta S_{\text{vib}}^{dis}$). Equation 20 would need to be corrected to:

$$\Delta S^{\text{excess}} \approx \Delta S_{\text{vib}}^{dis} + \Delta S_{\text{electronic}}^{dis} \tag{21}$$

The sign of this new corrected version is not that easy to interpret because while the first term has been determined in different studies to be positive[1, 3], the second term could be negative, as suggested by other studies[5]. This also makes the analysis of the sign obtained in our study more difficult as the sign in ideal conditions is unknown. However, it is still true that the configurational entropy change will tend to the ideal entropy of mixing. Overall, the conclusion that increasing the temperature will make the excess more positive is still valid as the difference between the configurational and the ideal entropy of mixing will decrease. The conclusion holds only if the vibrational and electronic changes do not vary much with the increase of temperature, which is a reasonable assumption. Hence, further studies could try to measure the electronic contribution independently for different temperatures, then the original hypothesis of only including the vibrational and configurational changes could be adequately challenged.

## 4 Conclusion

The analysis shows that the total entropy change from the OD transition of $Cu_3Au$ is smaller than the ideal entropy of mixing at $711.11K$, giving an excess entropy of $-0.117$. This result was explained in terms of the conditions that make the configurational entropy change tend towards the ideal entropy of mixing (perfect order and disorder in each of the transition limits) not being met. Therefore, the overall result of the study is plausible in light of the relevant theory. Finally, other possible hypotheses were presented about the contributions to the total entropy change. Those hypotheses would not change the conclusion of this study (as the reasons to explain the discrepancy between the ideal entropy of mixing and the total entropy change would still be valid). However, they could be a good starting point for future studies as determining the contributions from different origins independently at different temperatures is required to get a precise value of the configurational entropy change (which is hard to measure directly).

## References

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