Thermodynamics Hand-in Project

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November 2024

1 Introduction

Entropy (ΔS) is a fundamental concept in thermodynamics that quantifies the degree of disorder within a system. On a microscopic level, it is characterized by the number of possible microstates a system can adopt. More microstates correspond to more possible configurations of the system, leading to greater disorder and, consequently, higher entropy. Understanding entropy provides insight into changes occurring at the atomic and molecular levels which is essential for designing materials with desired thermal and structural properties, highlighting the critical role entropy plays in material studies.

A notable example is the order-disorder (OD) transformation of the Cu_3Au crystalline alloy presented in Benisek and Dachs 2015 (BD). Cu_3Au maintains an ordered $L1_2$ structure below 680K, with gold atoms occupying the corners of the unit cell and copper atoms positioned at the face centers. Above 680 K, the structure transitions into a disordered cubic arrangement (fcc), characterized by short-range order and increased entropy [1]. This report aims to investigate this OD phase transition and track the entropy change by using the specific heat capacity across its transition at 680K.

2 Background Theory[1]

Practical measurement of entropy change during transitions is commonly assessed by analyzing the specific molar heat capacity, c_p. If one has the c_p data of a phase transition it can be used to calculate the total excess entropy change, Δs, using eq. (1) below.

$$\Delta s = \int_{T_0}^{T} \frac{c_p}{T'} \, dT', \qquad (1)$$

where the integral is taken over the entire temperature range of the transition. In the given data, Δc_p is provided, which represents the excess molar specific heat capacity associated with the OD transition of Cu_3Au. This value reflects the additional energy absorbed or released by the system due to the transition. Using this isolates the excess entropy change resulting directly from the OD transition.

When two elements are mixed, as in Cu_3Au, the change in entropy is significant because the number of possible microstates are increased. The entropy of two materials, A and B, when ideally mixed together can be quantified by eq. (2).

$$\Delta s_{\text{mix}} = -R(x_A \ln x_A + x_B \ln x_B), \qquad (2)$$

where x_a and x_b represent the molar fractions of A and B, and R is the molar gas constant.

The negative sign indicates that Δs_{mix} will be positive, highlighting that mixing always increases the disorder of a system, leading to higher entropy. This value is maximized when the two materials mix completely and randomly.

3 Method

The plots for Δc_p vs. T and $\frac{\Delta c_p}{T}$ vs. T were created by importing the data into pandas DataFrames and using Matplotlib for visualization. This initial analysis was straightforward and provided valuable insight into the behavior of the heat capacity.

Calculating and presenting the total change in excess entropy Δs was more complex, as it required the numerical integration of the $\frac{\Delta c_p}{T}$ vs. T

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[1]Written using the 2024 *Thermal Physics* notes [2]

curve over the entire temperature range to evaluate the phase transition, as outlined in the background.

The primary numerical integration method used was *scipy.integrate.quad*, alongside the integration method recommended in the guidance notes for comparison. The quadrature method implemented by *quad* is based on the Clenshaw-Curtis quadrature, an adaptive integration technique that iteratively subdivides the interval and refines it until the integral converges [3]. The choice to use *quad* was due to its adaptive nature, making it well-suited for capturing sharp changes and peaks in experimental data with high precision. It simplifies integration by handling numerical calculations internally and provides an error estimate, aiding in the validation of results.

However, this is an error on the validity of the method and not on Δs itself. In order to evaluate an error on the value, consider that Δc_p must approach zero after the OD phase change is completed. To propagate an error on Δs we consider the worst-case scenario and use the lowest possible value of $\frac{\Delta c_p}{T}$ and calculate the maximum deviation in Δs across the entire integration range used, this is quantified by eq. (3). The equation will estimate the maximum error by considering the largest possible shift in the area under the curve (which is what Δs is). It is important to note this will overestimate and provide a purely systematic error on Δs as the random noise between Δc_p points could not be considered due to lack of data. There is also no error for temperature as no instrument uncertainty was provided.

$$\delta(\Delta s) = \frac{\Delta c_{\text{p,min}}}{T_{\text{min}}} \Delta T \qquad (3)$$

where ΔT is the positive difference between the bounds of the integration and $\Delta c_{\text{p,min}}$, T_{min} are the corresponding lowest values of specific heat capacity and temperature.

To facilitate the use of *quad*, a *UnivariateSpline* was employed to interpolate the experimental data, effectively converting discrete data points into a continuous, smooth polynomial function suitable for integration. A smoothing factor of $s = 1$ was chosen, as higher values were observed to excessively over fit the data, leading to deviations from the actual values. This selection was supported by comparative plots that demonstrate the effects of different smoothing factors on the fit,

as shown in fig. 1.

The starting temperature when applying eq. (1) was selected at a point where the curve appeared flat below the peak, approximately aligning with the minimum temperature. This approach ensures that T_0 is sufficiently below the phase transition temperature to represent the ordered state, while T_{max} extends beyond the transition into the disordered state. The chosen range captures the full transition, from the ordered state through to where entropy changes stabilize past the transition at 680 K.
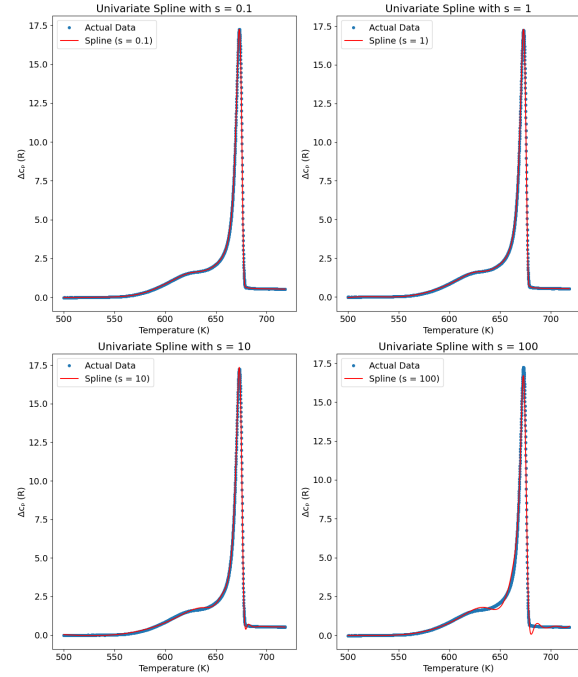

Figure 1: Comparative plot showing the fit of different smoothing factors in *UnivariateSpline*. As observed, $s = 10$ and $s = 100$ begin to overfit the data, introducing additional features not present in the original data, leading to poor fits. Thus, higher values were not considered. Both $s = 0.1$ and $s = 1$ provide similar fits that align well with the data, making either value a suitable choice.

4   Results and Discussion

In fig. 2 the Δc_p vs. T curve demonstrates the heat absorbed by the system during phase change, while the $\frac{\Delta c_p}{T}$ vs. T graph shows the rate of change
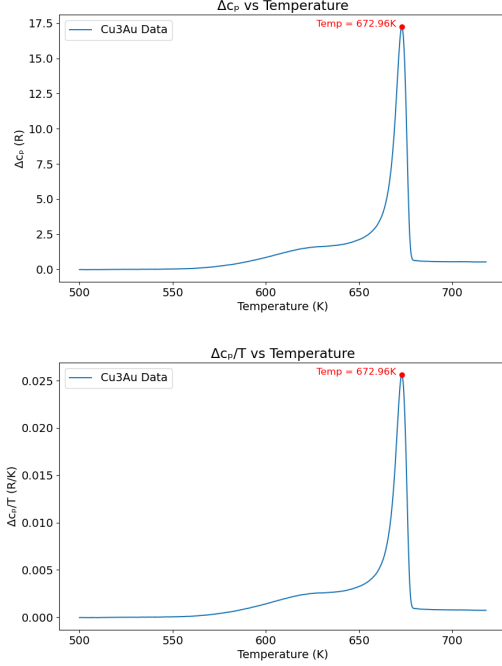
Figure 2: Δc_p vs T and $\frac{\Delta c_p}{T}$ versus T for Cu$_3$Au. The peaks in both graphs indicate the temperature at which the OD phase transition occurs, verifying that the transition takes place at the expected temperature of approximately 680K.

in entropy across the temperature range. Moreover, the area under the curve $\frac{\Delta c_p}{T}$ vs. T up to some temperature T will give the total excess molar entropy up to that point.

Three main regions are evident in fig. 3 throughout the entire OD transition. The first region extends up to 600 K, where minimal entropy change is observed, indicating that the structure remains largely ordered and retains the expected L1$_2$ configuration. Majority of the entropy in this state is vibrational and not due to changes in atomic structure. The sharp increase after 600 K marks the onset of the OD transition, where long-range order breaks down, leading to a transition to a disordered fcc structure. This steep rise signifies a significant increase in configurational entropy, with the atoms becoming more randomly distributed leading to an increase in long-range disordering as the atoms begin to move from their ordered L1$_2$ lattice positions. Beyond the transition, in the high-temperature region, the curve
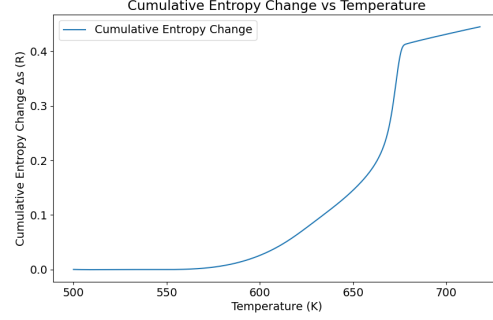

Figure 3: The plot illustrates Δs in units of R as a function of temperature, spanning over the entire temperature range. The curve shows an initial low entropy change up to approximately 600K, followed by a steep rise just past 650K, peaking near the OD transition temperature of 680 K, and leveling off beyond that in the high-temperature region to a constant increase.

plateaus, indicating that the majority of the transition has occurred and the system approaches maximum disorder.

The total entropy change across the OD transition estimated from the graph is $\Delta s \approx 0.4R$. This value is confirmed by numerical integration of eq. (1) over the range $T_0 = 500.04K$ to $T = 718.11K$ which yields $\Delta s_{quad} = 0.4451R$, with an error of the order 10^{-9} from $scipy.quad$, which confirms the stability and reliability of the result. The integration range was selected based on the minimum and maximum values of the given data set, which were validated by referencing fig. 2 with the conditions outlined in the methods section. The alternative integration method, outlined in the guidance notes, was also applied in the same range, producing $\Delta s_{rec} = 0.4450R$. The close alignment between these results affirms the validity of both techniques and the accuracy of the calculated Δs. Lastly, eq. (3) yielded $\delta(\Delta s) = 9.6678 \times 10^{-3}$ which then results in the following final value for Δs

$$\Delta s_{\mathrm{quad}} = \Delta s_{\mathrm{rec}} = 0.45(1)R. \qquad (4)$$

Comparing eq. (4) to Table 3 in BD, which reports the cumulative entropy as a function of temperature, a comparison can be made at $T = 700K$ and $T = 750K$, where BD's values are $\Delta s = 0.41(4)R$ and $\Delta s = 0.46(4)R$, respectively. The

calculated Δs aligns well with these values within the uncertainties and considering that the integration did not extend to exactly the same temperature points. Although, it does verify that the chosen temperature range for integration was reasonable and has produced the correct results.

Finally, the ideal entropy of mixing is considered due to the 3:1 mix of Copper and Gold in Cu_3Au, respectively. This can be calculated simply using eq. (2) with $x_A = 0.75$ and $x_B = 0.25$ where element A is Copper and element B is Gold, which yields $\Delta s_{mix} = 0.56R$. It is noticed that this value is significantly higher than the one calculated in eq. (4).

One reason for this discrepancy is that in section 3.5 BD mentions that the cooper and gold system approaches the ideal entropy of mixing at $T = 800K$, whereas the provided data only extends up to $T \approx 720$. This limitation in temperature range could partially explain why the observed entropy change is lower than the theoretical value. In so, a higher temperature range upto at least $T = 800K$ would provide a closer value to the ideal one— this is further supported by BD using a temperature range up to $T = 900K$.

Moreover, the fact that the interpreted value is less than the ideal value suggests that even at higher temperatures, a complete random distribution was not fully reached; some level of short-range order likely persisted, preventing the system from reaching total configurational entropy. The entropy of mixing assumes ideal, complete, and random mixing, which is not achievable in real-life systems. This incomplete disorder could be due to the intermolecular forces between copper and gold atoms. These forces may cause the atoms to favor certain arrangements because of the nature of the metallic bonding, which results in a lower observed molar entropy change compared to the ideal prediction.

5   Conclusions

The results show that the total molar entropy change during the OD phase transition in Cu_3Au is $\Delta s = 0.45(1)R$ aligning with BD's reported values of $\Delta s = 0.41(4)R$. This consistency validates the integration method used over $500.04K$ to $718.11K$. However, the calculated Δs is lower than the ideal entropy of mixing, $\Delta s_{mix} = 0.56R$,

representing a lack of full random mixing of the alloy. The difference can be explained by non-ideal behavior due to real interactions between the atoms, resulting in partial ordering and preventing complete disorder. This could be tackled by using a larger temperature range for the Δc_p measurements, as done in BD's paper.

The observed entropy change includes both configurational and vibrational components, providing insight into the disorder and energy distribution within the system. This allows us to further understand the OD phase transition of Cu_3Au and its thermal and structural properties which are useful in real world applications of the material.

References

[1] A. Benisek and E. Dachs, "The vibrational and configurational entropy of disordering in cu3au", Journal of Alloys and Compounds **632**, 585–590 (2015).

[2] W. C. K. Poon, *Thermodynamics: from the steam engine to a theory of everything* (learn page for 'thermal physics [phys09061/09019/09021]', 2024).

[3] W. M. Gentleman, "Implementing clenshaw-curtis quadrature, i methodology and experience", Commun. ACM **15**, 337–342 (1972).