Cu_3Au order-disorder entropy changes

Thermodynamics Hand-in Project

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1 Introduction

Cu_3Au is an alloy that undergoes an order-disorder (OD) transition from a $L1_2$ ordered face-centred cubic (fcc) with Cu occupying the face centre to a disordered state in temperature range $560K$ to $675K$[1], as shown in figure 1. This report aims to calculate the experimental and theoretical values of the entropy change ΔS during this OD transition and attempt to account for any discrepancies. The entropy change of a material is important as other physical behavioural quantities like the isobaric expansivity and C_V may be predicted via the Maxwell's relations.

1.1 Background theory

1.1.1 Entropy changes in OD transitions

The total change in entropy from our OD transition is given by[3]

$$\Delta S^{OD} = \Delta S^{vib} + \Delta S^{config} + \Delta S^{mag} + \Delta S^{elec}$$

where ΔS^{vib} is the vibrational entropy change, ΔS^{mag} is the magnetic entropy change and ΔS^{elec} is the electronic entropy change from disordering. Finally ΔS^{config} corresponds to the theoretical entropy of mixing and represents the entropy change when particles are rearranged from ordered fcc to a disordered state where there are still 4 atoms per lattice but their specific positions are now unknown. Figure 1 below shows the ordered fcc structure of Cu_3Au where 1/4 of a Cu atom occupies the face centre and 1/8 of an Au atom occupies the vertices, summing up to give 4 atoms per lattice.

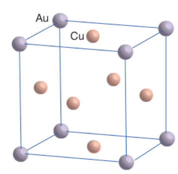

Figure 1: Ordered fcc Cu_3Au[4]

1.1.2 Measuring C_P

Here we outline the method for finding ΔS given data C_P and temperature T. We define

$$C_P = \frac{\mathrm{d}Q_p}{\mathrm{d}T} = \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_p$$

where state function H is the enthalpy. Since $H = U + PV$:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$$

and dividing by $\mathrm{d}T$:

$$\frac{\mathrm{d}H}{\mathrm{d}T} = T\frac{\mathrm{d}S}{\mathrm{d}T} + V\frac{\mathrm{d}P}{\mathrm{d}T}.$$

If $\Delta P = 0$ then:

$$C_P(T) = T\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_P.$$

Rearranging and integrating gives us the change in entropy:

$$\Delta S^{OD} = \int_{(1)}^{(2)} \frac{C_P(T)}{T}\mathrm{d}T.$$

1.1.3 Ideal entropy of mixing

Consider a box with separator, containing n_A moles at V_A of gas A on one side and n_B moles at V_B of gas B on the other. We set $\Delta T = 0$, $\Delta P = 0$ and proceed to mix gases A and B.

The **entropy of mixing** is:

$$\begin{aligned}\Delta S &= \Delta S_A + \Delta S_B \\ &= n_i R \ln\left(\frac{V_f}{V_i}\right) \\ &= n_A R \ln\left(\frac{V_A + V_B}{V_A}\right) + n_B R \ln\left(\frac{V_A + V_B}{V_B}\right).\end{aligned}$$

Since P and T are fixed, the ideal state equation $PV = nRT$ implies that:

$$\frac{V_A + V_B}{V_A} = \frac{n_A + n_B}{n_A}$$

and so we define **inverse mole fractions** as:

$$x_A = \frac{n_A}{n_A + n_B}$$

and

$$x_B = \frac{n_B}{n_A + n_B}.$$

After substituting and dividing through by $n_A + n_B$ we find the **molar specific entropy of mixing**:

$$\Delta s_{mix} = -R(x_A \ln x_A + x_B \ln x_B).$$

In the context of Cu_3Au we have that:

$$\begin{aligned}\Delta S_{mix} &= \Delta S^{config} \\ &= -4R(x_{Cu} \ln x_{Cu} + x_{Au} \ln x_{Au}) \\ &= 18.7 J\text{mol}^{-1} K\end{aligned}$$

where this is per 1 mole of Cu_3Au and that $x_{Cu} = \frac{3}{4}$ and $x_{Au} = \frac{1}{4}$.

2 Data analysis

2.1 Visualisations

The temperature T and heat capacity C_P data are from Benisek and Dachs.[1]
Using the following Python code we can plot figures 2 and 3.

```
import pandas as pd
import matplotlib.pyplot as plot

df = pd.read_csv("data.csv")

x = df["temp"]
y1 = df["cp"]
y2 = df["cp"] / x

plt.plot(x, y1)
plt.show()
```

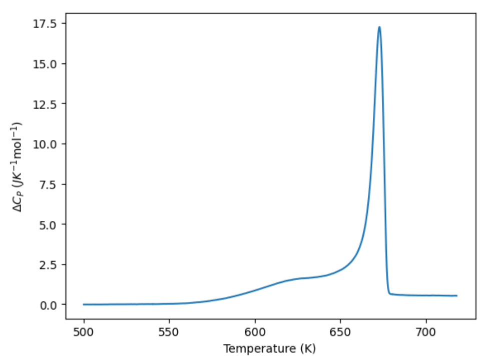

Figure 2: ΔC_P $(JK^{-1}\text{mol}^{-1})$ against T (K)

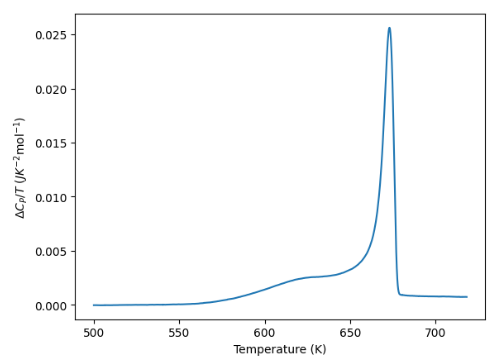

Figure 3: $\dfrac{\Delta C_P}{T}$ $(JK^{-2}\text{mol}^{-1})$ against T (K)

It can be shown that there is a peak near $T = 680K$ using the following code:

```
import numpy as np

i1 = np.argmax(y1)    # finds index of max value
print(x[i1])

i2 = np.argmax(y2)
print(x[i2])
```

which gives the following outputs:

```
> 672.96
> 672.96
```

The slight difference in temperatures ($673K$ compared to $680K$) are the result of either experimental precision or that our peak occures in a range of values rather than a specific temperature.

2.2 Calculating ΔS^{OD}

From before we have the following integral on endpoints $[a, b]$:

$$\begin{aligned}\Delta S^{OD} &= \int_a^b \frac{C_P(T)}{T}\mathrm{d}T \\ &\approx \sum_i \frac{C_P(t_i)}{t_i}\delta t_i\end{aligned}$$

where given the ith datum of data we have that $\delta t_i = t_{i+1} - t_i$ for $t_i \in [a, b]$ and holds $\forall i \in \{1, \ldots, n\}$. Here n corresponds to the number of data entries. This sum may be found using the following code:

```python
df_int = pd.concat([x,y2], axis = 1)
df_cut = df_int[df_int.temp.between(560, 675)]
df_cut.columns = ['temp','cpt']

temp = df_cut["temp"].tolist()
cpt = df_cut["cpt"].tolist()
l = len(temp)

total_area = 0
for i in list(range(1, l)):
    base = temp[i]-temp[i-1]
    height = cpt[i]
    area = base*height
    total_area += area
print(total_area) # in units R
```

which gives the following output:

```
> 0.38718425519279304
```

This choice of endpoints $[560K, 675K]$ is suggested by Benisek and Dachs:

$$\begin{aligned}\Delta S^{OD} &= \int_{560}^{675} \frac{C_P(T)}{T}\mathrm{d}T \\ &\approx 0.39R \\ &= 3.24JK^{-1}\mathrm{mol}^{-1}\end{aligned}$$

where $R = 8.31JK^{-1}\mathrm{mol}^{-1}$ is the molar gas constant. Choosing another set of endpoints:

$$\begin{aligned}\Delta S^{OD} &= \int_{550}^{700} \frac{C_P(T)}{T}\mathrm{d}T \\ &\approx 3.58JK^{-1}\mathrm{mol}^{-1}\end{aligned}$$

and so after taking averages of the two we claim:

$$\Delta S^{OD} = 3.41JK^{-1}\mathrm{mol}^{-1}.$$

2.3 Physical interpretations

Summarising our results we have that:

$$\Delta S^{OD} = \Delta S^{vib} + \Delta S^{config} + \Delta S^{mag} + \Delta S^{elec}$$

for

$$\Delta S^{config} = 18.7J\text{mol}^{-1}K \quad \text{and} \quad \Delta S^{OD} = 3.41JK^{-1}\text{mol}^{-1}.$$

This suggests that some of the other entropies (vibrational, magnetic and electronic) are negative valued, confirmed via Paras and Allanore.[3] They also note that Cu_3Au undergoes multiple stages of transitions before disordering. ($I \to II \to D$) Furthermore we have that $Cu_3Au(I)$ is an orderd fcc and $Cu_3Au(II)$ a tetragonal structure consisting of 18 $Cu_3Au(I)$ unit cells.[2] The disordered fcc state (D) for temperatures greater than $T = 675K$ can be thought of as a solid "solution" of Cu and Au atoms where entropy change is computed via ideal entropy of mixing.

3 Conclusions

This report calculates the ideal entropy of mixing and compares it to numerically integrated entropy value from experimental data. It is then concluded that the discrepancies between these two value were due to other entropy values. We also remark that improved quenching techniques and experiemental data with higher precision will result in a better data analysis.

References

[1] Artur Benisek and Edgar Dachs. "The vibrational and configurational entropy of disordering in Cu3Au". In: *Journal of Alloys and Compounds* 2015 (May 2015), pp. 585–590. DOI: 10.1016/j.jallcom.2014.12.215.

[2] H. Okamoto. "The Au−Cu (Gold-Copper) system". In: *Journal of Phase Equilibria* 8 (Oct. 1987), pp. 454–474. DOI: 10.1007/BF02893155.

[3] J. Paras and Antoine Allanore. "Contribution of electronic entropy to the order-disorder transition of Cu3Au". In: *Physical Review Research* 3 (June 2021). DOI: 10.1103/PhysRevResearch.3.023239.

[4] Mark Weller, Tina Overton, and Jonathan Rourke. *Inorganic Chemistry*. OUP Oxford, 2018.