Investigation of the Lindemann Criterion and the Melting Point in Complex Alloys

Ryan Warren[1],*

[1]School of Mathematics and Physics, University of Portsmouth, Portsmouth PO1 3HF, UK

*Corresponding author: ryan.warren1167@gmail.com

Abstract - Despite various theories, the understanding of melting points remains incomplete. This project extends the Lindemann melting criterion to $A_{1-x}B_x$ alloys in an attempt to predict the melting temperatures of complex alloys. Frederick Lindemann developed a theory to predict melting temperatures over 100 years ago, with the assumption that melting occurs when a critical fraction of root-mean-square displacement of a crystal and interatomic spacing, known as the Lindemann coefficient, η, is exceeded. 100 years later, Melvin Vopson developed a relationship between element groups and this coefficient, assigning a different value of this coefficient to 12 element groups on the periodic table. Presented here is an extension of this generalised Lindemann melting criterion to extend to binary alloys, finding fair agreement with experimental data by applying effective parameters for atomic mass, Lindemann coefficient, interatomic spacing and Debye temperature, assuming these parameters take weighted averages and applying a correction to the resulting plot.

Keywords - Lindemann criterion; Melting point; Metallic alloys

1   Introduction

Despite being a crucially fundamental topic, and containing an abundance of theories, melting points are not understood theoretically very well. Many attempts have been made to consolidate this knowledge, with no completely reliable predictions. With easy to calculate, or well-known, parameters and a reliable model of melting temperatures, a way of identifying the composition of complex alloys could be made, or a way of predicting melting temperatures of these complex alloys would be possible and extremely useful in streamlining industrial processes.

For over 100 years, the most widely accepted theory of understanding melting points came from Fredrick Lindemann in 1910, who proposed a phenomenological theory relating the melting point of a material to the interatomic distances of the material and the temperature of the material's highest mode of vibration, often referred to as the Debye temperature, θ_D [1], by postulating that a material will melt when thermal vibrations are large enough to allow adjacent atoms to occupy the same space. This approach is incomplete, however, with an accuracy of around 20% [2], leading to the conclusion that some crucial parameter is missing within Lindemann's theory; a hidden mechanism lying within his postulation.

More recently, in 2020, Melvin Vopson [2] identified a previously unknown relationship between element groups and their associated Lindemann criterion,η. This coefficient was assigned a constant

value by Lindemann, but is in fact not constant. In Vopson's work, a different Lindemann coefficient was applied to different element groups on the periodic table, based on a trend connecting the melting points of elements in each group and their interatomic distances, Debye temperatures and atomic masses. Through this generalised Lindemann coefficient, Vopson was able to reduce this error for some elements to under 1%, unveiling the curtain to expose some part of the missing mechanism Lindemann had missed over 100 years prior.

With this project I hope to extend Vopson's work to apply to A1-xBx alloys, such as CuNi, CsRb and AuCu using the generalised Lindemann melting criterion, through the assumption that atomic mass, Lindemann coefficient, interatomic spacing and Debye temperature for constituent elements in a binary alloy can be taken as weighted averages to create effective parameters for the combined compound. Results will then be compared with existing experimental data to calculated values predicted by this extension to the generalised Lindemann melting coefficient.

2   Theory and Methodology

The phenomenological Lindemann coefficient is given by ref [3] as the fraction between the vibration amplitude of a material and its interatomic spacing, a:

$$u^2 = (\eta a)^2 \tag{1}$$

This shows that a material should melt when the root-mean-square vibration amplitude reaches a certain fraction (the Lindemann coefficient) of the material's interatomic spacing, as postulated by Gilvarry [3]. At the melting point, temperature is considered far greater than absolute zero, and quantum effects can be considered negligible. For these simplifications, the mean-square vibration amplitude is then given by ref [4]:

$$u^2 = \frac{9k_B T}{4\pi^2 M v^2} \tag{2}$$

where k_B is the Boltzmann constant, M is the mass of the atom, T is the temperature and v is the vibrational frequency of the crystal structure of the atom. Combining (1) with (2) and rearranging for temperature yields:

$$T = \frac{\eta^2 a^2 4\pi^2 M v^2}{9k_B} \tag{3}$$

The atomic mass number, A, of an element is related to the mass of the atom is related by $M = A/N_A$ where N_A is Avogadro's constant in order to work with atomic masses of elements instead of the mass of a singular atom. In addition, the vibrational frequency, v, can be considered equal to the Debye frequency, v_D , when T is equal to T_m where T_m is the melting temperature of the atom, since it is fair to assume that at the temperature of melting, the crystal structure has the highest allowed amplitude and frequency, justifying the introduction of the relationship between Debye frequency and Debye temperature. The Debye temperature is related to the Debye frequency by the relation $hv_D = k_B\theta_D$ [5] Where h is Planck's constant. Given these assumptions, the equation for melting temperature of a mono-atomic crystal can be given as:

$$T_{m,monoatomic} = \xi A \eta^2 a^2 \theta_D^2 \tag{4}$$

where ξ is a constant approximately equal to $2.29 \cdot 10^{20} \frac{mol}{JKs}$, defined by $\xi = \frac{4\pi^2 k_B}{9N_A h^2}$ in order to simplify the form of the equation. The effective weight of an alloy is given by a weighted average of the atomic weights of the constituent elements. For an $A_{1-x}B_x$ alloy this is given by:

$$A_{eff} = (1 - x)A_A + xA_B \tag{5}$$

where x is the proportion of element B in the alloy. It is also assumed that the effective Debye temperatures and generalised Lindemann coefficients of the alloys are weighted averages of these parameters for each of the constituent elements as a postulation for the effective parameters for the Lindemann coefficient and Debye temperature.

$$\eta_{eff} = (1 - x)\, \eta_A + x\eta_B \tag{6}$$

$$\theta_{D,eff} = (1 - x)\, \theta_{D,A} + x\theta_{D,B} \tag{7}$$

Although the Debye temperature does vary with temperature, its values are usually only given in academic articles at absolute zero, or at room temperature. For the purposes of this paper, it is assumed that the values for Debye temperature are that of at room temperature, $\theta_D(\text{RT})$, given that this is closer in value to the melting point than at absolute zero, though this does pose some problems for the accuracy of the results in certain scenarios, as described in the results. In addition, the lattice constant (and thus the interatomic spacing) is a function of the proportions of each element, but is assumed to be approximately equal to their weighted average, an assumption which is based on data from ref [6].

$$a_{eff} = (1 - x)\, a_A + xa_B \tag{8}$$

Combining equation (4) with equations (5), (6), (7) and (8) yields the following:

$$T_m = \xi A_{eff}\eta_{eff}^2 a_{eff}^2 \theta_{D,eff}^2 \tag{9}$$

It was expected that Equation (9) should have given an expression of the melting point of a binary alloy, however, after plotting values using the initial equations, (5), (6), (7), (8) and (9), the observation was made that the calculated graphs of CsRb appeared to be a 2π Rad rotation of the expected graph about the point $\left(0.5, \frac{T_{m,A}+T_{m,B}}{2}\right)$.
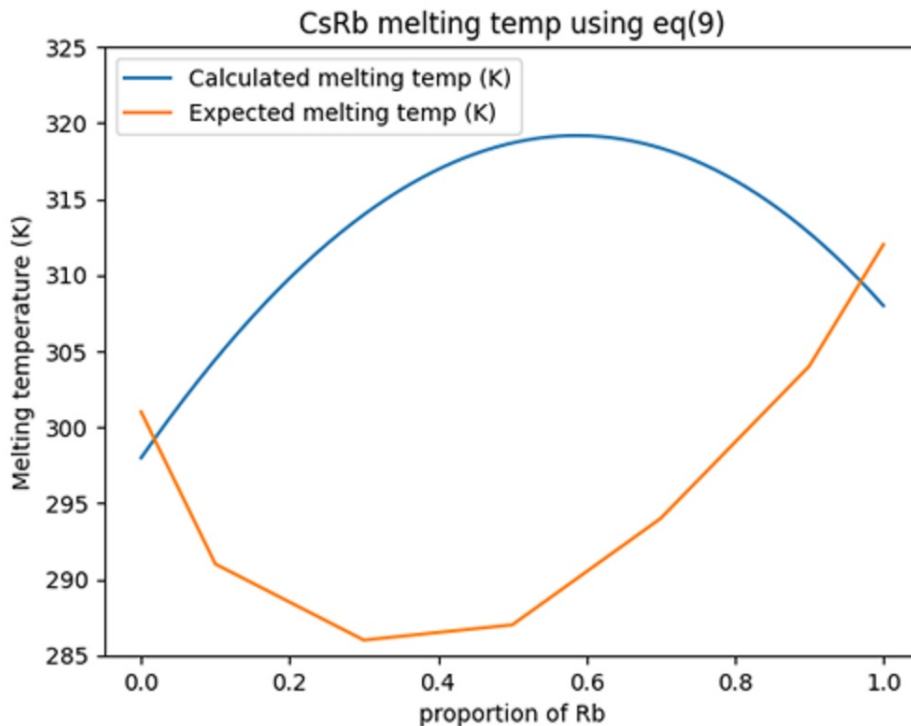

Figure 1: Plot of melting temperature against proportion of Rb. Shows the justification behind assuming weighted averages were wrong and applying graph transformation.

In order to reflect this observation in equation (9), the transformation $-f(-x+1) + T_{m,A} + T_{m,B}$ was made to rotate the plot about the centre of the calculated graph (blue). This transformation yields the following:

$$A_{eff} = (x-1) A_B + x A_A \tag{10}$$

$$\eta_{eff} = (x-1) \eta_B + x \eta_A \tag{11}$$

$$\theta_{D,eff} = (x-1) \theta_{D,B} + x \theta_{D,A} \tag{12}$$

$$eff = (x-1) a_B + x a_A \tag{13}$$

$$T_m = \xi A_{eff} \eta_{eff}^2 a_{eff}^2 \theta_{D,eff}^2 + T_{m,A} + T_{m,B} \tag{14}$$

This Observation means there is an error somewhere in the weighted average or melting temperature calculations which could not be resolved within the span of this project. Nonetheless, the altered equation (14) can still be used to estimate melting points of binary alloys, with equations (10), (11), (12) and (13) making up the variables. Equation (4) can also still be used to find the mono-atomic melting points of element A, Tm, A, and element B, Tm, B for equation (14) which sets the correction in the y-axis.

3   Results

Figure 1 shows melting temperature against the proportion of element B for CsRb using equation (9) and respective dependent equations, (5-8). The values for monoatomic interatomic spacing, Debye temperature at room temperature and atomic masses are gathered from ref [7], whilst values for the generalised Lindemann melting coefficient are gathered from ref [2] as an assigned value for each elemental group. Expected values of melting temperature as a function of element proportion for CsRb are gathered from ref [8] and [2]. There is little correlation between plotted data and expected values, except for those at the monatomic melting points of each constituent element in the alloy. On observation, Figure 1 appears as a 180^0 rotation of the expected graph, showing that an initial calculation was very likely incorrect, but motivates the reasoning behind the translation of plots, and thus the alteration of equation (9), yielding equations (10-14)
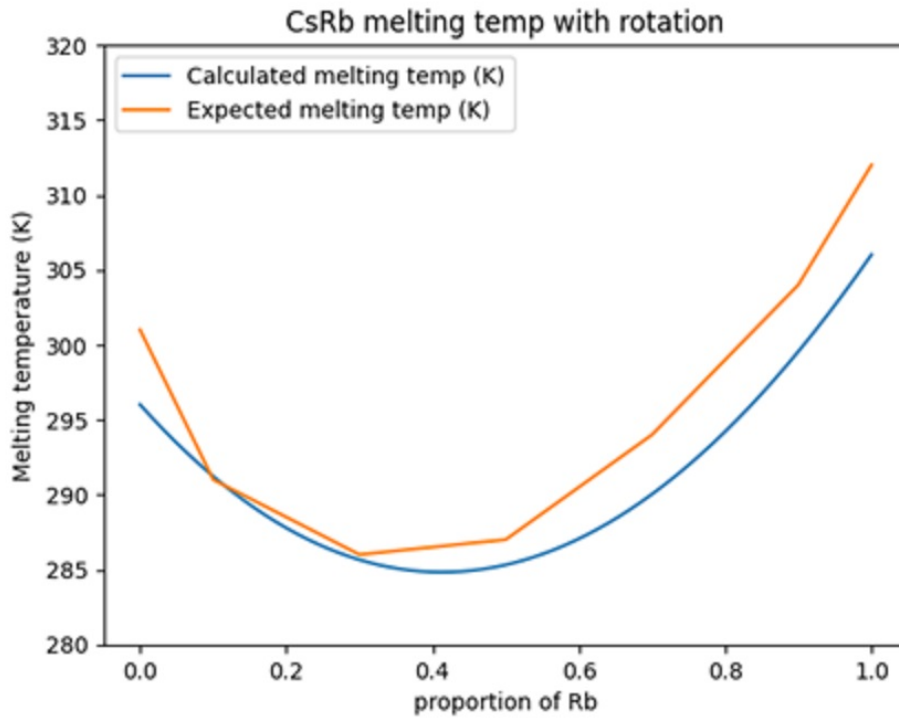
Figure 2: Replotted data of melting temperature vs proportion of Rb using equations (10-14).

The results in Figure 2 show much better correlation between calculated and expected melting points, after which, the eutectic nature of CsRb can be seen very clearly compared to before. A eutectic system, such as CsRb, is a system of elements whereby the melting temperature of the mixed system is lower than that of either constituent element and is driven by the Gibbs free energy [9], though that is beyond the scope of this project.
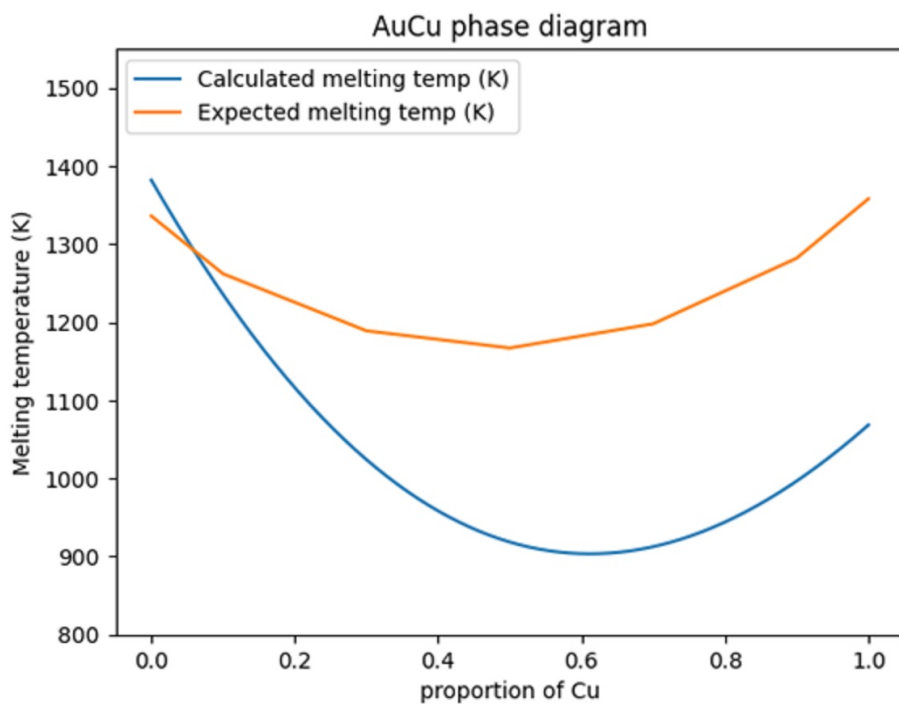

Figure 3: Phase diagram of AuCu alloy

Figure 3 presents the phase diagram of AuCu. Data points of the expected melting temperatures of AuCu at different values are extracted from ref [10] and [2]. Once again, it can be deduced from the calculated data points that AuCu is indeed a eutectic system. The larger errors from 100% copper

are likely due to uncertainties in both the atomic spacing, as well as the Debye temperature, since literature does not usually ever provide Debye temperatures closer to the melting points of these elements.
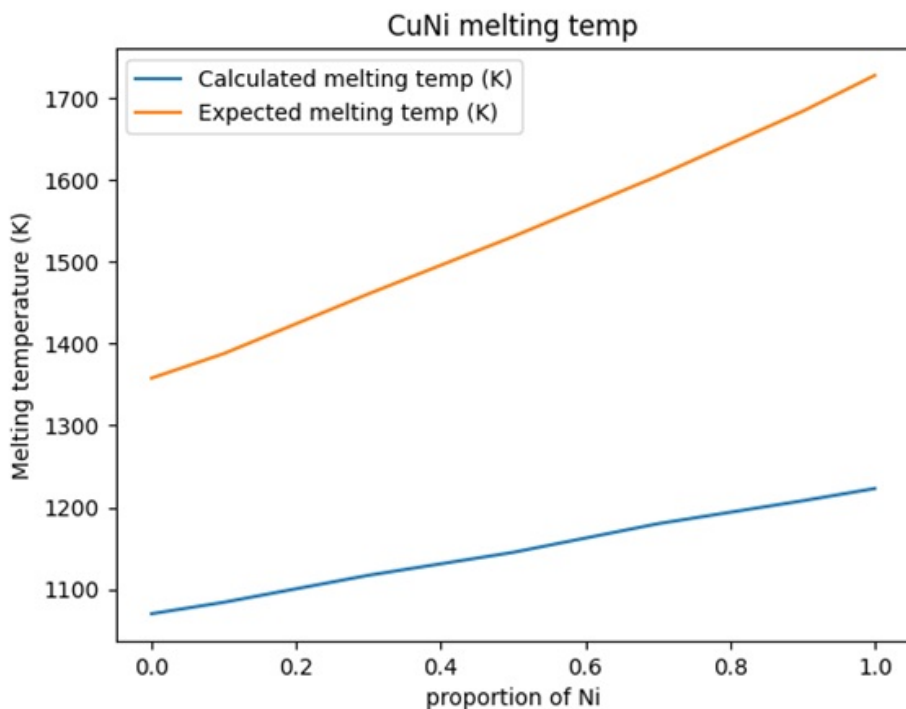

Figure 4: Phase diagram of CuNi

Figure 4, showing the phase diagram of CuNi. Data points for the expected line are taken from ref [8] and [2]. The large error is again likely due to inaccuracies in Debye temperature and interatomic spacing for both Cu and Ni, being 1000K off the value at which the Debye temperature was taken to be for these results. The plot does, however, keep the linear correlation between both elements and would likely show better with greater availability of Debye temperatures for different absolute temperatures.

Proportion (x)	A_{eff}(g/mol)	η_{eff}	a_{eff} (pm)	$\theta_{D, eff}$ (K)	T_m (exp.) (K)	T_m (calc.) (K)	T_m (% difference)
0	132.91	0.139	523.5	43	301	297.0	1.3
0.1	128.17	0.139	519.52	44.6	291	292.2	0.41
0.3	118.68	0.139	511.56	47.8	286	286.7	0.24
0.5	109.19	0.139	503.6	51.0	287	286.3	0.24
0.7	99.70	0.139	495.64	54.2	294	291.0	1.0
0.9	90.21	0.139	487.68	57.4	304	300.6	1.1
1	85.47	0.139	483.7	59	312	307.0	1.6

Table 1: Effective parameters for $Cs_{1-x}Rb_x$ and melting temperatures over proportion, from equations (5-8) and (10-14).

Proportion (x)	A$_{eff}$(g/mol)	η$_{eff}$	a$_{eff}$ (pm)	θ$_{D, eff}$ (K)	T$_m$ (exp.) (K)	T$_m$ (calc.) (K)	T$_m$ (% difference)
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0.7	99.70	0.139	495.64	54.2	294	291.0	1.0
0.9	90.21	0.139	487.68	57.4	304	300.6	1.1
1	85.47	0.139	483.7	59	312	307.0	1.6

Table 2: Effective parameters for $Au_{1-x}Cu_x$ and melting temperatures over proportion.

Proportion (x)	A$_{eff}$(g/mol)	η$_{eff}$	a$_{eff}$ (pm)	θ$_{D, eff}$ (K)	T$_m$ (exp.) (K)	T$_m$ (calc.) (K)	T$_m$ (% difference)
0	63.55	0.108	256.0	310	1357	1069	26.9
0.1	63.06	0.1083	255.3	313.5	1388	1084	28.0
0.3	62.09	0.1089	253.9	320.5	1461	1112	31.4
0.5	61.12	0.1095	252.5	327.5	1531	1147	33.5
0.7	60.15	0.1101	251.1	334.5	1605	1175	36.6
0.9	59.18	0.1107	249.7	341.5	1684	1208	39.4
1	58.69	0.111	249	345	1728	1222	41.4

Table 3: Effective parameters for $Cu_{1-x}Ni_x$ and melting temperatures over proportion.

As mentioned, literature does not provide Debye temperatures for monatomic elements over a wide range of temperatures. This error propagates into the generalised Lindemann melting criterion, usually for elements whose melting points are not likeable to room temperature, where θ_D is taken at. Furthermore, interatomic spacing was taken to be a linear function with respect to element proportions, but is not strictly the case, although it is the closest approximation that could be found for the purposes of this project and unfortunately poses some issues with uncertainty.

Data points for expected melting temperatures over element proportion are taken from secondary sources, and thus have associated errors which may somewhat affect the accuracy of percentage errors between calculated and experimental values. Caesium-137 is also a radioactive material, but despite this a well-fitting Lindemann coefficient is assigned to this monatomic element, and so it is used in caution of this fact.

Equation (4) is very sensitive to deviations in interatomic spacing [2], experimental values of interatomic spacing contain a variety of extraneous variables, which are expected to propagate heavily when applied to equation (14). With the assumption that interatomic spacing is a linear function with respect to element proportion, the deviations from this assumption compound and could contribute to some of the larger errors. The uncertainty of effective parameters for Debye temperature and interatomic spacing is:

$$\sigma_{a_{eff}} = \sqrt{\sigma_{a_A}^2 + \sigma_{a_B}^2} \tag{15}$$

$$\sigma_{\theta_{D,eff}} = \sqrt{\sigma_{\theta_{D,A}}^2 + \sigma_{\theta_{D,B}}^2} \tag{16}$$

The uncertainty for the calculated melting temperature is therefore

$$\frac{\sigma_{T_M}}{T_m} = 2\sqrt{\left(\frac{\sigma_{a_{eff}}}{a}\right)^2 + \left(\frac{\sigma_{\theta_{D,eff}}}{\theta}\right)^2} \tag{17}$$

For example, a relative uncertainty of 10% for Debye temperatures of elements A and B, as well as 5% uncertainty for interatomic spacing for elements A and B yields a resulting uncertainty of 32%.

A paper by Nguyen Toan [8] provides a similar method of calculating melting temperatures for different proportions of constituent elements through a similar method, still based off the Lindemann melting criterion, with the difference of using the number of atoms in a given lattice cell for each constituent element. Unlike the assumptions I had made during this project, this paper shows a stronger link between melting temperature over element proportions and lattice structure. During this project, I did not consider this in my theory. If this project were to be completed again, or improved, a method of incorporating this into formalisms could be made. However, during this project, values for the Lindemann coefficient were taken with the knowledge that the Lindemann coefficient is dependent on the atomic number of each element contained within the binary alloy. Combining the generalised Lindemann melting criterion and the paper by Toan, an even greater understanding of binary alloy melting points could be made.

The three chosen binary alloys for this project also all contain the same lattice structure (FCC) as their constituent partner. A generalisation of this formula would require an identification of alloys with different lattice structures and incorporate this in the theory.

Through the observed data, the extent to which the aims have been achieved has been varied. It is inconclusive to me whether the initial assumption of weighted averages for each effective variable is strictly true based on the need to rotate the graph, as outlined in my theory and methodology. However an altered equation was able to be formulated from this rotation, and with this new alteration, the results from it are found to be within reasonable agreement with experimental results within the uncertainty which both the interatomic spacing and Debye temperature gives with the current assumptions of this project. This work attempts to further the generalised Lindemann criterion and finds that more work needs to be done to discover a conclusive extension of the generalised Lindemann melting criterion for complex alloys.

Overall, phase diagrams, whereby all of the required parameters are fulfilled to obtain results for melting temperatures, for binary alloys are hard to find or locked behind paywalls. A conclusive statement about the effectiveness of this method of calculating melting points for A1-xBx alloys may require a greater sample of data for Debye temperatures as a function of temperature, interatomic spacing as a function of element proportion and alloys, with varied lattice characteristics, melting temperatures as a function of element proportion, which would likely require a lot of time.

Though not within the scope of this project, these plots can also be used to determine the eutectic point of the binary alloy, by requiring that it occur at the minimum point of the plot, given by the derivative of melting temperature for the binary alloy with respect to element proportion. These eutectic points are important for industrial applications[], such as for welding, and provide a good reason for the research of these melting points in complex alloys.

Despite these limitations, the method for predicting melting temperatures of binary alloys shows great promise, whereby all results are within an order of magnitude of expected results and still present crucial characteristics about the alloy, such as if it's a eutectic system or not. However, to be sure of its accuracy and effectiveness, an analysis or more binary alloys should be made. A refinement of this method could be useful for industrial applications, such as in the development of solder [12]. Additionally, further approaches to improving the theory of monatomic melting temperatures would be useful to align this work better with results, for example through a computational approach [13]. These improvements with the method outlined in this work could also enable an extension of the theory to apply to ternary alloys and further, furthering the development towards a complete, if not perfectly understood, model of melting temperatures for all compounds.

4 Conclusions

Through an extension of the Lindemann melting criterion onto A1-xBx alloys using the generalised Lindemann melting criterion and assuming each variable took a weighted average in a binary alloy, the extension was used to plot data of 3 binary alloys to observe the relationship between melting temperatures and constituent element proportions and compare these results to existing data from literature to determine the effectiveness of this method. When plotting the initial assumptions, an observation was made that the experimental data and calculated data were off by a rotation of 180° about the centre of the calculated plot, likely indicating an error in my initial calculations which were unable to be rectified in the span of this project. However, after plotting the adjusted formula to compare to experimental results, fair agreement was made between the two, especially for the binary alloy CsRb. The extension of these results to many binary alloys relies on a refinement of the generalised Lindemann melting criterion and understanding of melting points of elements which are not solid metallic elements, and is therefore inapplicable to heavy elements, radioactive elements and semiconductor elements, such as silicon, though it would be interesting to see results for a binary doped semiconductor. It would likely be necessary to explore the hidden mechanisms behind the Lindemann melting criterion in order to gain a full understanding of melting temperatures of complex alloys, however the work outlined in this project could nonetheless create a useful tool for industrial purposes if the parameters of the extended melting temperature equation were further developed for various binary alloys. The results of this project are generally in line with other theoretically calculated phase diagrams. A refined theory of melting for binary alloys should better understand the relationship between element proportions and the effective parameters of equation (9) to better understand the true relationship which correlates them for solid metals, as well as for more complicated solids if a consensus is to be reached for the theory of melting of binary alloys.

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