

MTEN 6005 Project Assignment #2 – Calculating the Triple Point of a Pure Element

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1. Introduction

In Part I of the MTEN 6005 project, students were asked to plot the specific heat capacity, enthalpy, and entropy of a pure element as a function of temperature using data from the NIST-JANAF thermochemical tables. Using the plots, the latent heat of fusion and latent heat of vaporization were calculated to determine the energy required to initiate solid-to-liquid and liquid-to-vapor phase transformations respectively. Part II of the project assignment extended the findings of Part I by determining the triple point of a pure element (i.e. the pressure and temperature state where solid, liquid, and vapor phases of the pure element can exist in equilibrium). This report identifies the triple point of pure nickel and summarizes the methods used to calculate it.

2. Methods

The following section outlines the methodology used to calculate the triple point of nickel. Emphasis is placed on the thermodynamic principles and numerical techniques utilized to arrive at the triple point using only knowledge of the element's specific heat capacity and fundamental material properties such as molar volume. Table 1 summarizes the material properties used for based on the NIST-JANAF thermochemical table for pure nickel.

Table 1. NIST-JANAF data for Nickel [1] & Additional Assumptions

Standard State Pressure (P°)	0.1 MPa
Enthalpy Reference Temperature (T_r)	298.15 K
C_p Lambda Maximum Transition Temp. (T_λ)	631.000 K
Melting Temperature (T_m)	1728.000 K
Vaporization Temperature (T_v)	3156.584 K
Fugacity	1 bar
Ideal Gas Constant (R)	8.341 J mol ⁻¹ K ⁻¹
Molar Volume at T_r (V_m)	6.5888 m ³ mol ⁻¹

The following assumptions were made when defining the Gibbs free energy of nickel:

- The solid and liquid phases are incompressible (i.e. molar volume is constant)
- Nickel behaves as an ideal gas upon vaporization for all temperatures and pressures

2.1 Deriving Standard State Enthalpy and Entropy

Equation 1 and Equation 2 present two forms of the Shomate equation that were used to curve fit NIST-JANAF heat capacity data to define specific heat capacity as a function of temperature for each phase of nickel from 0 K to 6000 K. In this temperature range, nickel experiences three phase transformations, a solid-solid, solid-liquid, and liquid-vapor transformation, occurring at their respective temperatures reported in Table 1.

$$C_p = a + bT + cT^2 + dT^3 \quad (1)$$

$$C_p = a + bT + cT^2 + dT^3 + \frac{e}{T^2} \quad (2)$$

To calculate the polynomial coefficients for each phase, MATLAB's `fitttype` and `fit` function were used. The `fitttype` function defined the form of the polynomial the `fit` function calculated coefficients for [2, 3]. Equation 1, a simplified form of the Shomate equation that excludes the fifth polynomial term, was used to define specific heat capacity from 0 K to T_λ as `fit` was unable to calculate coefficients for the full Shomate equation due to the highly nonlinear nature of heat capacity in this temperature range. Equation 2 was used to define specific heat capacity for the remaining temperature ranges. Note that specific heat from 0 K to 6000 K was defined as a piecewise function due to the discontinuities that occur at phase transformations.

$$H - H^\circ(T_r) = \int_{T_r}^T C_p dT \quad (3)$$

$$S^\circ - S^\circ(T_r) = \int_{T_r}^T \frac{C_p}{T} dT \quad (4)$$

Equations following the form of Equation 3 and Equation 4 were used to derive enthalpy and entropy as a function of temperature using the curve-fit Shomate equations for heat capacity. MATLAB's `integral` function was used to calculate enthalpy and entropy numerically for each temperature range to easily work with the piecewise heat capacity function. Note that this changed the limits of the integral depending on which portion of the heat capacity curve was being integrated due to discontinuities at phase transformations. The latent heat of fusion and latent heat of vaporization were manually added to the heat capacity function at their respective phase transformation temperatures as these results were previously calculated in Part I of this project. MATLAB's `integral` function was unable to numerically integrate entropy from 0 K to 100 K, so for the purposes of this report, entropy was only defined from 100 K to 6000 K. This

simplification was made as entropy data from 0 K to 100 K was not critical to calculating nickel's triple point. Table 2 reports values used from NIST-JANAF and Part I of the project to complete these calculations.

Table 2. NIST-JANAF data and Part I results used in enthalpy and entropy calculations

$H^\circ(T_r)$	0. kJ mol ⁻¹
$S^\circ(100\text{ K})$	7.454 J K ⁻¹ mol ⁻¹
Latent Heat of Fusion (L_f)	17.155 kJ mol ⁻¹
Latent Heat of Vaporization (L_v)	377.552 kJ mol ⁻¹

Following numerical integration, MATLAB's `spline` and `ppval` functions were used to define enthalpy and entropy as functions of temperature for the solid, liquid, and vapor phases. Although nickel can only exist as a solid, liquid, or vapor in specific temperature intervals at standard state pressure, functions for enthalpy and entropy for the solid, liquid, and vapor phases needed to be defined for the entire temperature range to calculate the triple point using the Gibbs free energy of each phase.

2.2 Defining Gibbs Free Energy at the Triple Point

Using the enthalpy and entropy functions defined for each phase, the Gibbs free energy as a function of temperature and pressure can be defined for solid, liquid, and vapor phases respectively.

$$G_{solid}(T, P) = H^\circ_{solid}(T) - TS^\circ_{solid}(T) + V_m(P - P^\circ) \quad (5)$$

$$G_{liquid}(T, P) = H^\circ_{liquid}(T) - TS^\circ_{liquid}(T) + V_m(P - P^\circ) \quad (6)$$

$$G_{vapor}(T, P) = H^\circ_{vapor}(T) - TS^\circ_{vapor}(T) + RT \ln\left(\frac{P}{P^\circ}\right) \quad (7)$$

Equations 5-7 can be used to calculate the Gibbs free energy of the solid, liquid, and vapor phase of nickel as a function of temperature and pressure. Therefore, these equations are used to determine nickel's equilibrium for a given temperature and pressure. Note that this formulation of Gibbs free energy makes several simplifying assumptions: (1) that nickel is incompressible in the solid and liquid phase, (2) there is no difference in molar volume between the solid and liquid phase, and (3) nickel vapor behaves as an ideal gas.

At the triple point, where solid, liquid, and vapor phases coexist at equilibrium, Equation 8 must be satisfied.

$$G_{solid}(T, P) = G_{liquid}(T, P) = G_{vapor}(T, P) \quad (8)$$

If Equation 8 is not satisfied, it implies there is at least one phase that has a lower energy state than the others, meaning it will be the thermodynamically favored equilibrium of the material and the three phases will not coexist at equilibrium. To find the specific temperature and pressure where all three phases can coexist, we must solve for the conditions where the Gibbs free energies of all three phases are simultaneously equal. This requires finding the values of T and P that satisfy Equation 8, which can be rewritten as two independent constraint equations. The relationship between solid, liquid, and vapor phases described in Equation 8 can be used to introduce two constraining functions to solve for the triple point using the method of Lagrange multipliers.

$$g(T, P) = G_{solid}(T, P) - G_{liquid}(T, P) \text{ and } g(T, P) = 0 \quad (9)$$

$$h(T, P) = G_{solid}(T, P) - G_{vapor}(T, P) \text{ and } h(T, P) = 0 \quad (10)$$

Equation 9 and Equation 10 are used to define the Lagrangian function, Equation 11, which sets up the constrained optimization problem that needs to be solved to identify nickel's triple point,

$$\mathcal{L}(T, P, \lambda, \mu) = f(T, P) + \lambda g(T, P) + \mu h(T, P) \quad (11)$$

where $f(T, P)$ is the objective function, $g(T, P)$ and $h(T, P)$ are constraint functions, and λ and μ are Lagrange multiples. Recognize, with this setup, an arbitrary objective function can be defined as the two constraint functions are sufficient to define the system of equations needed to solve for the four unknowns T, P, λ , and μ (two constraint functions, each with two partial derivatives). Therefore, for simplicity, calculations in MATLAB were carried out using $f(T, P) = 0$. By solving this system of equations, what is being calculated is the combination of temperature and pressure that satisfy Equation 8.

To solve the system equation for T and P , MATLAB's `fmincon` function was used. This function is specifically designed to find the minimum of constrained nonlinear multivariable functions numerically [4]. In this case, since $f(T, P) = 0$, `fmincon` is not solving for a true minimum, rather it is simply solving for the conditions that satisfy the two constraint equations (which is a root-finding problem).

3. Results

The following section presents the results of Part II of the project. Both results from Section 2.1 and Section 2.2 are presented to discuss the individual components that led to the determining nickel's triple point. When possible, calculated results are compared against reference thermochemical tables to validate the accuracy of the MATLAB script written.

Figure 1 is a plot of specific heat capacity as a function of temperature. NIST-JANAF data points are plotted alongside the curve fit Shomate equations used to estimate the specific heat capacity function used in subsequent calculations for enthalpy and entropy. As mentioned, two different forms of the Shomate equation were used depending on the temperature range the function was being evaluated for. From 0 K to T_λ , corresponding to the red curve in Figure 1, Equation 1 was used due to the highly nonlinear nature of nickel's heat capacity. For $T > T_\lambda$, Equation 2 was used. As highlighted in the graph, the Shomate equations were curve fit in a piecewise manner to accommodate the discontinuities in specific heat associated with phase transformations. This is represented visually by the different color lines plotted on Figure 1, each corresponding to one temperature range within that piecewise function.

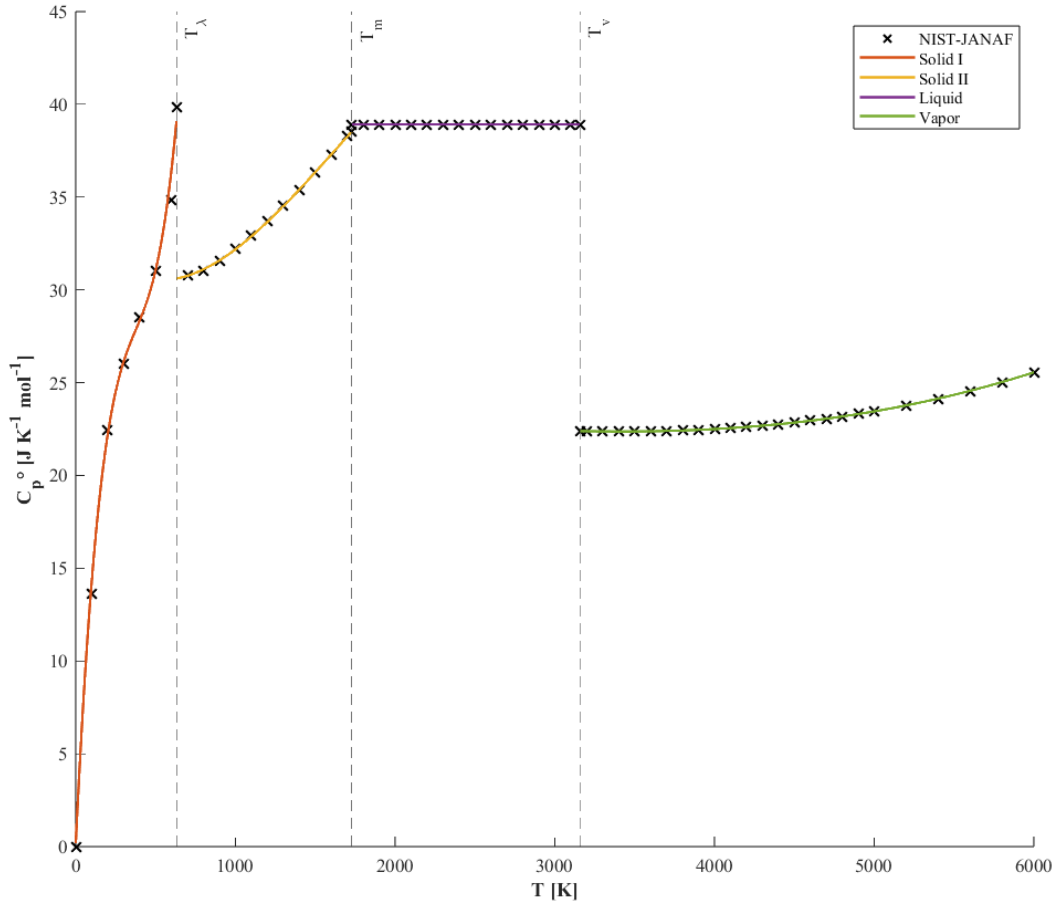


Figure 1. Specific Heat Capacity vs Temperature, Ni

Figure 2 is a plot of enthalpy as a function of temperature. Like specific heat, NIST-JANAF data points are plotted alongside the calculated curves for reference. Note that Equation 3 was used to calculate the enthalpy function for each phase; these curves are not functions calculated through

regression of known data points like specific heat capacity is. Figure 3 is a plot of entropy as a function of temperature and was calculated similarly to enthalpy using Equation 4.

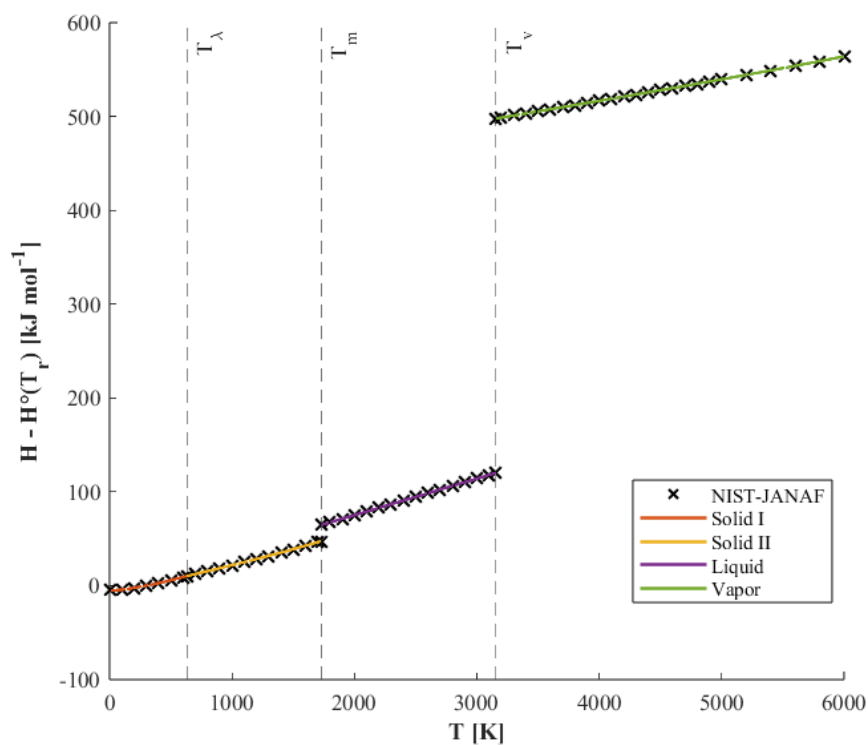


Figure 2. Enthalpy vs Temperature, Ni

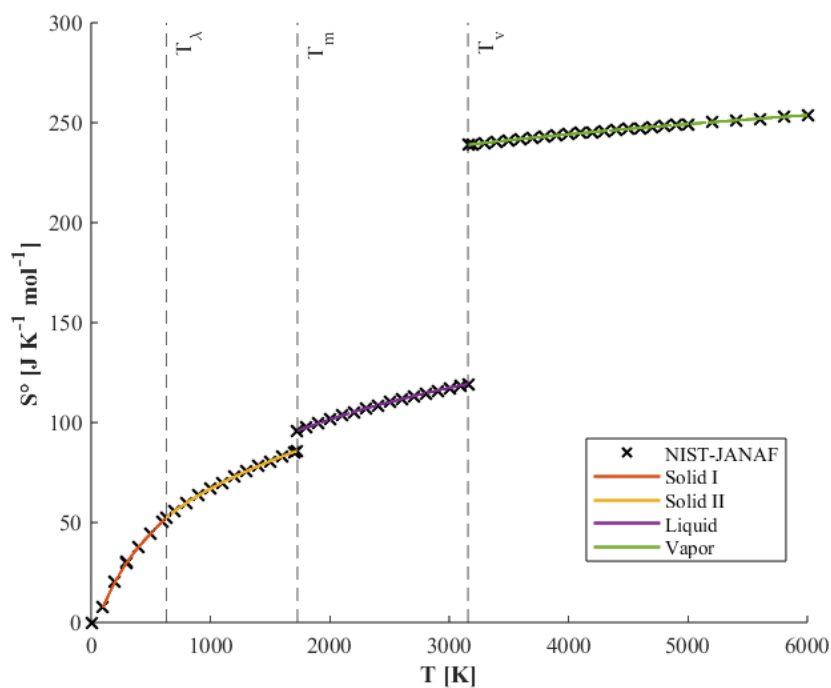


Figure 3. Entropy vs Temperature, Ni

Figure 4 and Figure 5 depict the MATLAB spline curve-fit functions for enthalpy and entropy for the solid, liquid, and vapor phases of nickel. These are plotted alongside NIST-JANAF enthalpy and entropy data for reference. These spline functions are the enthalpies and entropies used to define the Gibbs free energy for solid, liquid, and vapor phases (Equation 5-7) that are ultimately used to calculate the triple point.

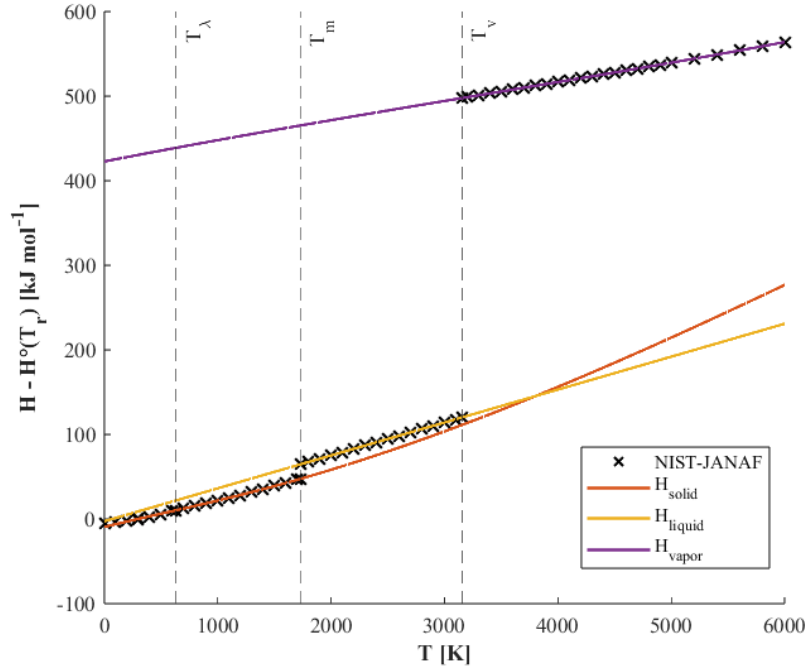


Figure 4. MATLAB Spline curve-fit for H_{solid} , H_{liquid} , H_{vapor}

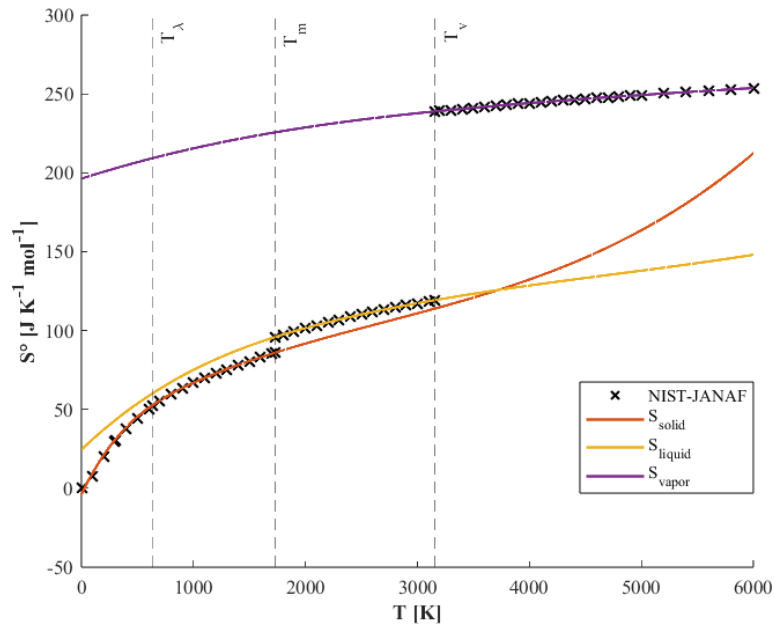


Figure 5. MATLAB Spline curve-fit for S_{solid} , S_{liquid} , S_{vapor}

Table 3. Calculated triple point for Ni

T_t	1728 K
P_t	0.4642 Pa
$G_{solid} = G_{liquid} = G_{vapor}$	-101.03 kJ mol ⁻¹

Table 3 reports the calculated triple point of Ni by solving the system of equations derived from Equations 9-11 using MATLAB's `fmincon` function. The function met the default stopping criteria and converged in six iterations.

4. Discussion

Part II of the MTEN 6005 project took a vastly different approach to evaluating thermodynamic properties of a material compared to Part I. Figure 1 provides the key result that enabled this difference in approach—curve fitting specific heat capacity to a polynomial expression rather than simply plotting known data points. The Shomate equation, in a partial form and its full form, showed excellent agreement with critically evaluated experimental measurements reported in the NIST-JANAF thermochemical database. These results confirm that the Shomate equations can be used to mathematically model specific heat capacity, so long as the discontinuities are taken into consideration.

Using this mathematical model, two fundamental thermodynamic properties can be derived, enthalpy and entropy. Equation 3 and 4 were used to derive these thermodynamic properties, and the results are compared to values reported by NIST-JANAF in Figure 2 and Figure 3. Unsurprisingly, the functions derived using the Shomate equations showed excellent agreement with data reported by NIST-JANAF, confirming that the calculations for enthalpy and entropy were executed correctly in MATLAB. Comparing the specific heat capacity, enthalpy, and entropy graphs, an observation of interest is the contrast in behavior at T_λ . Specific heat capacity has a sharp discontinuity at this temperature, of which the left-hand side corresponds to nickel's maximum specific heat. Enthalpy and entropy are smooth and continuous at this phase transformation, which suggests that the two solid-phases of nickel can be treated as the same phase when considering enthalpy or entropy specifically.

Knowing that the ultimate aim of Part II is to determine the triple point of nickel, the standard state enthalpy and standard state entropy of the solid, liquid, and vapor phases were calculated using the results presented in Figure 2 and Figure 3, respectively, so the Gibbs free energy of the solid, liquid, and vapor phase could be defined. This was accomplished by using a spline fit to extended fragments of the solid, liquid, and vapor curves shown in Figure 2 and Figure 3 over the entire temperature search space, 0 K to 6000 K. The `spline` fit function was selected to define the enthalpy and entropy of the solid, liquid, and vapor phases because of its ease-of-use in

MATLAB. However, a physics-based approach could have been pursued by using the `fittype` and `fit` functions to calculate a polynomial of the same form as the Shomate equation being integrated using Equation 3 or Equation 4. The spline fits matched the trends of the NIST-JANAF data well from 0 K to 3000 K; however, it is clear that if equilibrium states above 3000 K are to be calculated, the spline approximation should not be used as the trend of the solid phase relative to the liquid phase is no longer reasonable. Because this project is only calculating a triple point, which generally exists around the melting temperature of a substance ($T_m = 1728$ K for Ni), analysis was completed using the spline approximation.

The constrained nonlinear multivariable system of equations formulated using Equation 9-11 was solved using MATLAB's `fmincon` function, which is designed to solve constrained optimization problems using a numerical Lagrange multiplier method. Although this was not a true minimization problem in the way the constraining functions were defined, `fmincon` can still be used to solve the constrained system of equations. The `fmincon` function converged on a triple point at $T_t = 1728$ K and $P_t = 0.4642$ Pa which corresponds to a Gibbs free energy of $G = -101.03$ kJ mol⁻¹. To understand if this triple point was physically reasonable for a pure metal, the triple point of other pure metals were referenced. Table 4 highlights that the triple point of pure metals tends to exist at very low pressures and at or within a few degrees of their melting temperature.

Table 4. Triple point comparison of pure metals [6]

Element	T_m (K)	T_t (K)	P_t (Pa)
Mercury (Hg)	234	234	1.65×10^{-4}
Palladium (Pd)	1828	1825	3.5
Platinum (Pt)	2041	2045	0.20
Titanium (Ti)	1941	1941	5.3
Zinc (Zn)	693	692.5	65
Nickel (Ni) – <i>This Study</i>	1728	1728	0.4642

The results of this study follow this general trend, suggesting that the calculated triple point for nickel is plausible. The calculated triple point temperature is equal to nickel's melting temperature which is consistent with the trend $T_t = T_m$ exhibited by other metals. However, the calculated triple point pressure of 0.4642 Pa shows some inconsistency with trends exhibited by other metals. For the elements listed in Table 4, as you move down the periodic table, the triple point pressure decreases. This implies that Ni, being in the same group as Pd and Pt, should have a higher triple point pressure than both of these elements. Instead, the calculated pressure for nickel falls between these two values, though it remains in the same order of magnitude as other transition metals.

Several sources of error may contribute to this discrepancy. First, the ideal gas assumption applied to the vapor phase is likely inadequate for nickel. Due to nickel's relatively large atomic size and high electron count, non-negligible intermolecular forces and non-ideal behavior must be accounted for, which are not captured by the ideal gas model used.

Second, the use of the spline fits to derive enthalpy and entropy for the solid, liquid, and vapor phases used to formulate the Gibbs free energy equations may be introducing error. While the spline function in MATLAB provides smooth interpolation between data points, it may be misrepresenting the trend as it does not incorporate the underlying physics governing thermodynamic properties. A more physics-based approach, such as integrating the Shomate equation, may better capture the fundamental behavior of these properties and improve the accuracy of the Gibbs free energy functions used to calculate the triple point.

5. Conclusion

This report identified the triple point of pure nickel using thermodynamic principles and numerical methods. By curve fitting NIST-JANAF specific heat capacity data to the Shomate equation and deriving enthalpy and entropy functions through numerical techniques, the Gibbs free energy of the solid, liquid, and vapor phases were formulated as functions of temperature and pressure. The method of Lagrange multipliers was employed to solve for the conditions where all three phases coexist in equilibrium, resulting in a calculated triple point of $T_t = 1728$ K and $P_t = 0.4642$ Pa.

The calculated triple point temperature is consistent with expected trends for pure metals, where the triple point temperature typically equals, or is within a few degrees of, the melting temperature. However, the calculated pressure exhibits some inconsistency with triple point trends of pure metals, falling between the triple point pressures of palladium and platinum rather than exceeding both. A possible explanation for this inconsistency is the simplifying assumptions made in the analysis, particularly the ideal gas assumption for the vapor phase and the use of spline fits rather than integrating the Shomate equation to define enthalpy and entropy for phases from 0 K to 6000 K. Despite these sources of error, the calculated triple point for nickel is physically reasonable and demonstrates that thermodynamic properties can be effectively modeled using polynomial expressions and numerical methods.

References

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