New Kinetic Theory and New Equations for Lattice and Electronic Heat Capacities, Enthalpies and Entropies of Solids: Application to Tungsten

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New equations for heat capacities, entropies and enthalpies were applied to the experimental constant volume and constant pressure heat capacity data of tungsten. The heat capacity $C_{P\,\max}$ was predicted to be 24.96 J/molK at 400 K. The temperatures Θ_V and Θ_P were found to be 78.5 K. The relationships between dimension and Θ_V and Debye temperature were given. Tungsten shows the dimensionality crossover from 3 to 2 at about 80 K. Temperature dependences of Debye temperature, Θ_V and Θ_P and non-monotonic behavior were discussed. The heat capacity and entropy values predicted by the proposed models were compared with the values predicted by the Debye models. The results have shown that the proposed models fit the data better than the Debye models. The enthalpy values predicted by the proposed models were compared with the values predicted by the polynomial model and good fitting was obtained. The proposed models have shown that the constant pressure heat capacity data can be used to calculate enthalpies, entropies and heat capacities of tungsten.

1. Introduction

Einstein introduced the first quantum statistical model with single oscillator for the temperature dependences of heat capacities of solids [1]. The values obtained from this model lie below the experimental heat capacities at low temperatures [2–4].

Nernst and Lindemann's two oscillator model has improved the fitting of heat capacity data in comparison with Einstein's model. However, this model could not well describe the heat capacities in the region $T < 100$ K [5].

Einstein and Nernst-Lindemann's models have used the discrete oscillation frequencies, and the resulting theoretical curves obtained by these models show a plateau behavior in the $T \to 0$ K limit. In the model given by Debye, atomic system is considered to be a three dimensional, elastic and isotropic continuum [6]. The heat capacity equation is given by [2–4, 6, 7]:

$$C_V = 9R\left(\frac{T}{\Theta_{\mathrm{D}}(T)}\right)^3 \int\limits_0^{x_{\mathrm{D}}} \frac{x^4\,\mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x, \tag{1}$$

where Θ_{D} is Debye temperature, $x = \Theta_{\mathrm{D}}(T)/T$ and R is gas constant.

The entropy equation in the Debye model is given by [2, 3, 6]:

$$S = 3R\left(\frac{4}{x_{\mathrm{D}}^3} \int\limits_0^{x_{\mathrm{D}}} \frac{x^3\,\mathrm{d}x}{\mathrm{e}^x - 1} - \ln\left(1 - \mathrm{e}^{-x_{\mathrm{D}}}\right)\right). \tag{2}$$

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The analytical solutions of integrals in Eq. (1) and Eq. (2) are not known. Therefore, at the intermediate temperatures, the values of heat capacities and entropies must be obtained by numerical integration.

At very low temperatures, where $T \ll \Theta_{\mathrm{D}}$, the following equation is obtained from Eq. (1):

$$C_V \cong \frac{12\pi^4 R}{5}\left(\frac{T}{\Theta_{\mathrm{D}}(T)}\right)^3. \tag{3}$$

Equation (3) is assumed to be valid from 0 K up to lattice temperatures of order $\theta_{\mathrm{D}}(0)/50$, where $\Theta_{\mathrm{D}}(0)$ is the Debye temperature at $T \to 0$ K. Θ_{D} depends on temperature. Therefore, it is often impossible to provide good fittings of Eq. (1) to the given heat capacity data sets with a single Debye temperature over the entire temperature range [3, 8]. These non-Debye behaviors have been given in terms of C_V/T^3 functions [9–11]. These curves show a non-monotonic behavior in the low temperature region, which cannot be explained with the Debye's model.

The departure from Eq. (3) in the temperature interval $\theta_{\mathrm{D}}(0)/50 \leq T \leq \theta_{\mathrm{D}}(0)/10$ was assumed to be due to the deviation of frequency distribution. For this region, the equation based on Taylor series expansion has been proposed [3, 8, 12]. Different models based on Thirring and exponential series expansions have also been given for the intermediate to high temperature regions, respectively [5]. However, these models are more complex and seven or eight empirical parameters should be determined.

The heat capacity of a free electron gas in three dimensions for $T \ll T_{\mathrm{F}}$ has been given in [7]:

$$C_{\mathrm{el}} = 3R\frac{\pi^2}{6}\frac{T}{T_{\mathrm{F}}}, \tag{4}$$

where T_{F} is the Fermi temperature. For high temperatures, the following equation has been given in [3]:

$$C_{el} = \frac{3}{2} R z \left[1 - \frac{1}{6 (2\pi)^{3/2}} \left(\frac{T_F}{T} \right)^{3/2} \cdots \right], \qquad (5)$$

where z is the number of free electrons per atom. For intermediate values of (T/T_F), C_{el} must be computed numerically.

At low temperatures, the heat capacity of solids may be written as:

$$C_V = \gamma T + A T^3, \qquad (6)$$

where γ and A are characteristic constants of the solid [7]. A plot of C_V/T versus T^2 should be a straight line with slope A and intercept γ and allows the determination of Debye temperature $\Theta_D(0)$ through $A = 12\pi^4 Rs/5\Theta_D^3(0)$.

In this study, the heat capacity, enthalpy and entropy equations proposed in [13] will be applied to the constant volume and constant pressure heat capacity data of tungsten. The temperature and dimension dependence of Debye temperature and the deviation from monotonicity will be explained. The results obtained from the proposed Debye and polynomial equations will be compared.

2. Heat capacity, entropy and enthalpy equations

The heat capacity equation at constant volume,

$$C_V = 3R \frac{T^n}{T^n + \Theta_V^n(T)}, \qquad (7)$$

the heat capacity equation at constant pressure,

$$C_P = C_{Pmax} \frac{T^n}{T^n + \Theta_p^n(T)}, \qquad (8)$$

and the electronic heat capacity equation

$$C_{el} = \frac{3}{2} R \frac{T^n}{T^n + T_E^n(T)}, \qquad (9)$$

were given in Ref. 13.

If $n = 3$, the following equation can be written at low temperature:

$$C_V = 3R \left(\frac{T}{\Theta_V(T)} \right)^3. \qquad (10)$$

From Eq. (3) and Eq. (10), the following equation is obtained:

$$\Theta_V(T) = \Theta_D(T) \left(\frac{5}{4\pi^4} \right)^{1/3}. \qquad (11)$$

The electronic molar entropy equation,

$$S_{el,n} = \frac{3}{2n} R \ln \left(\left(\frac{T}{T_E(T)} \right)^n + 1 \right), \qquad (12)$$

the lattice molar entropy equation at constant volume,

$$S_{V,n} = \frac{3}{n} R \ln \left(\left(\frac{T}{\Theta_V(T)} \right)^n + 1 \right), \qquad (13)$$

and the lattice molar entropy equation at constant pressure

$$S_{P,n} = \frac{C_{Pmax}}{n} \ln \left(\left(\frac{T}{\Theta_P(T)} \right)^n + 1 \right), \qquad (14)$$

were given in Ref. 13.

The lattice molar enthalpy equations at constant pressure for $n = 1$, $n = 2$ and $n = 3$,

$$H_{p,n=1} = C_{Pmax} \left(T + \Theta_P \ln \left(\frac{\Theta_P}{T + \Theta_P} \right) \right), \qquad (15)$$

$$H_{p,n=2} = C_{Pmax} \left(T - \Theta_P \cot \left(\frac{T}{\Theta_P} \right) \right), \qquad (16)$$

$$H_{P,n=3} = C_{Pmax} \left(-\frac{\pi}{6\sqrt{3}} \Theta_P + T - \frac{\Theta_P}{3} \ln (\Theta_P + T) \right.$$
$$\left. + \frac{\Theta_P}{6} \ln \left(\Theta_P^2 - \Theta_P T + T^2 \right) - \frac{\Theta_P}{\sqrt{3}} \cot \left(\frac{2T - \Theta_P}{\sqrt{3}\Theta_P} \right) \right), \qquad (17)$$

the lattice molar enthalpy equations at constant volume for $n = 1$, $n = 2$ and $n = 3$, and

$$H_{V,n=1} = 3R \left(T + \Theta_V \ln \left(\frac{\Theta_V}{T + \Theta_V} \right) \right), \qquad (18)$$

$$H_{V,n=2} = 3R \left(T - \Theta_V \cot \left(\frac{T}{\Theta_V} \right) \right), \qquad (19)$$

$$H_{V,n=3} = 3R \left(-\frac{\pi}{6\sqrt{3}} \Theta_V + T - \frac{\Theta_V}{3} \ln (\Theta_V + T) \right.$$
$$\left. + \frac{\Theta_V}{6} \ln \left(\Theta_V^2 - \Theta_V T + T^2 \right) - \frac{\Theta_V}{\sqrt{3}} \cot \left(\frac{2T - \Theta_V}{\sqrt{3}\Theta_V} \right) \right), \qquad (20)$$

the electronic molar enthalpy equations for $n = 1$, $n = 2$ and $n = 3$

$$H_{el,n=1} = \frac{3}{2} R \left(T + T_E \ln \left(\frac{T_E}{T + T_E} \right) \right), \qquad (21)$$

$$H_{el,n=2} = \frac{3}{2} R \left(T - T_E \cot \left(\frac{T}{T_E} \right) \right), \qquad (22)$$

$$H_{el,n=3} = \frac{3}{2} R \left(-\frac{\pi}{6\sqrt{3}} T_E + T - \frac{T_E}{3} \ln (T_E + T) \right.$$
$$\left. + \frac{T_E}{6} \ln \left(T_E^2 - T_E T + T^2 \right) - \frac{T_E}{\sqrt{3}} \cot \left(\frac{2T - T_E}{\sqrt{3}T_E} \right) \right), \qquad (23)$$

were given in Ref. 13.

3. Results and discussion

The heat capacity data of tungsten at constant volume and constant pressure for the temperature range from 1 K to 400 K were obtained from Ref. 14 and are shown in Fig. 1. The value of C_{Pmax} was predicted to be 24.96 J/molK at 400 K from Eq. (8). The values of Θ_V and Θ_P were found to be 78.5 K. The value of $\Theta_D(0)$ was found to be 383 K from C_V versus T^2 plot. The heat capacity values calculated using $\Theta_D = 383$ K in Eq. (1) and the heat capacity values calculated by using $\Theta_V = 78.5$ K and $n = 3$ in Eq. (7) are shown in Fig. 1.

The $\Theta_D(T)$ values were calculated from the numerical solution of Eq. (1). Temperature dependence of $\Theta_D(T)$
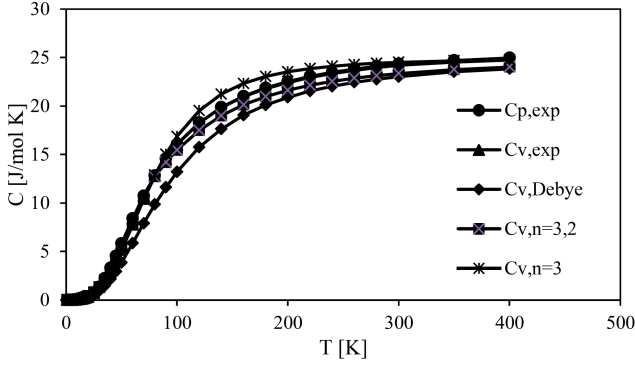
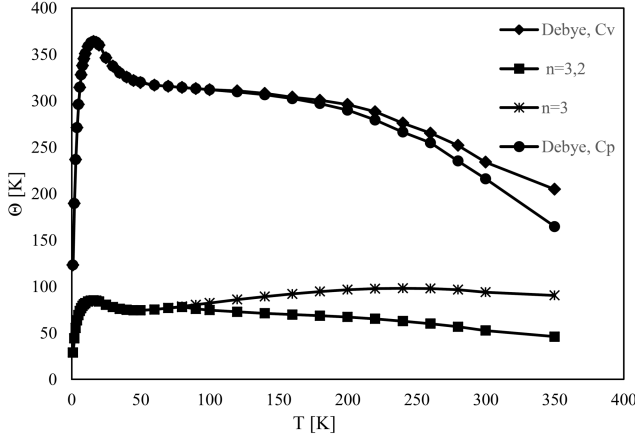Fig. 1. Temperature dependence of heat capacity of tungsten.

Fig. 2. Temperature dependence of $\Theta_D(T)$ and $\Theta_V(T)$ of tungsten.

Fig. 3. Temperature dependence of n of tungsten.
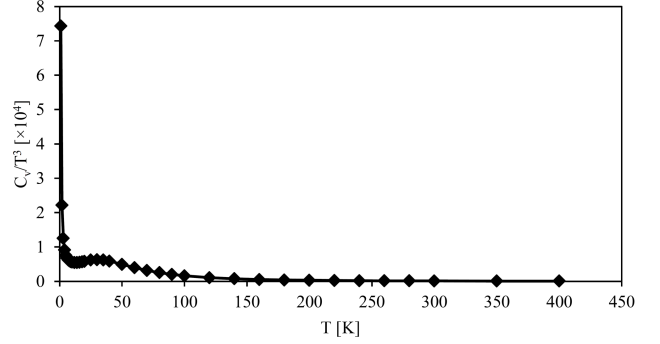
Fig. 4. C_V/T^3 versus T for tungsten.

for tungsten is shown in Fig. 2. The value of $\Theta_D(T)$ increases monotonously from 123 K to the maximum 364 K with increasing temperature from 1 K to 16 K and then decreases towards 165 K at about 350 K.

The following equation is obtained from Eqs. (7) and (11):

$$ n = \frac{\log\left(\frac{3R}{C_V} - 1\right)}{\log\left(\Theta_{D(T)}\left(5/4\pi^4\right)^{1/3}/T\right)}. \qquad (24) $$

The temperature and $\Theta_D(T)$ dependence of n for tungsten is shown in Fig. 3. The value of n is about 3 from 1 K to 18 K. It then decreases and passes through a minimum of 2.92 at about 40 K and then increases to 3 at 50 K. n exhibits a crossover from 3 to 2 at about 80 K. After 80 K, n takes the value of about 2. Figure 2 and Eq. (24) show that $\Theta_D(T)$ depends on temperature and n.

The following equation is obtained from Eq. (7):

$$ \Theta_V(T) = T\left(\frac{3R}{C_V} - 1\right)^{1/n}. \qquad (25) $$

The $\Theta_V(T)$ values were calculated by using $n = 3$ at all temperatures, and by using $n = 3$ from 1 K to 80 K and
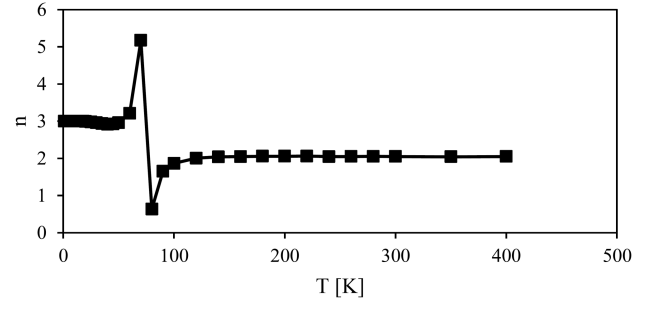
by using $n = 2$ from 80 K to 400 K in Eq. (25). Figure 2 shows that the temperature dependence of $\Theta_V(T)$, obtained by using $n = 3$ from 1 K to 80 K and by using $n = 2$ from 80 K to 400 K, is similar to $\Theta_D(T)$. However, the $\Theta_V(T)$ values obtained by using $n = 3$ at all temperatures are different.

Figure 4 shows the non-monotonic behavior of the C_V/T^3 function at low temperatures. n was taken to be 3 in this function. It is seen from Eqs. (3) and (10) that the C_V/T^3 is inversely proportional to $\Theta_D^3(T)$ and $\Theta_V^3(T)$. Therefore, the C_V/T^3 function shows the inverse behavior to $\Theta_D^3(T)$ and $\Theta_V^3(T)$.

The root mean square error of prediction (RMSEP) is obtained from the following equation:

$$ \mathrm{RMSEP}(C) = \sqrt{\frac{1}{m}\sum_{i=1}^{m}\left(C_{V\,\mathrm{pred}} - C_{V\,\mathrm{exp}}\right)^2}, \qquad (26) $$

where C_{exp} is the experimental heat capacity at constant volume and constant pressure, C_{pred} is the predicted heat capacity at constant volume and constant pressure and m is the number of heat capacities. The values of RMSEP obtained for the proposed models by using $\Theta_V(T) = \Theta_P(T) = 78.5$ K and $n = 3$ from 1 K to 80 K and $n = 2$ from 80 K to 400 K were found to be 0.5063 and 0.5654 for constant volume and constant pressure heat capacities, respectively. The value of RMSEP obtained for the Debye model was found to be 1.437. These results show that the proposed model obtained by using $n = 3$ from 1 K to 80 K and $n = 2$ from 80 K to 400 K fits the experimental data better than the other

models and tungsten exhibits dimensionality crossover from 3 to 2 at about 80 K.

The values of entropies of tungsten obtained from the Debye model, the proposed and the polynomial models are shown in Fig. 5.
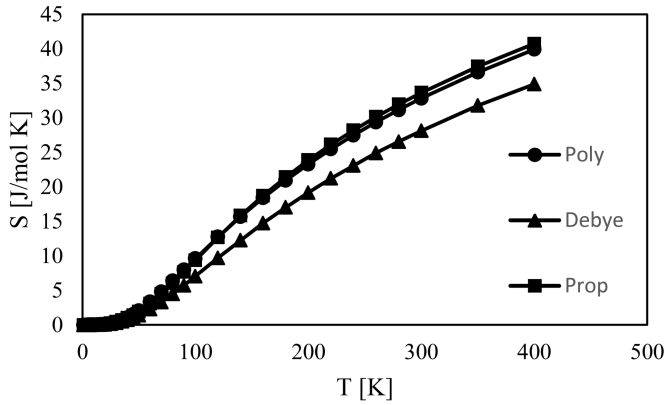

Fig. 5. Temperature dependence of entropy of tungsten.

The RMSEP values for entropy are obtained from the following equation:

$$\text{RMSEP}(S) = \sqrt{\frac{1}{m} \sum_{i=1}^{m} \left(S_{\text{pred}} - S_{\text{poly}} \right)^2}, \qquad (27)$$

where S_{poly} is the entropy obtained from the polynomial model and S_{pred} is the entropy obtained from the proposed and the Debye models. The values of RMSEP obtained for the proposed and the Debye models were found to be 0.3795 and 2.4858, respectively. These results and Fig. 5 show that the proposed model fits the data better than the Debye model.

Enthalpy equation cannot be obtained from the Debye model. The enthalpy values of tungsten obtained from the proposed and polynomial models are shown in Fig. 6.
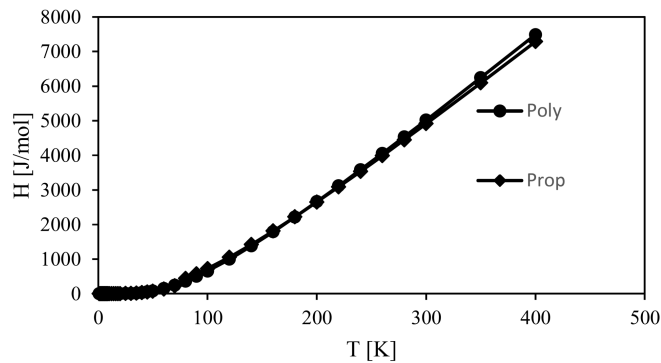

Fig. 6. Temperature dependence of enthalpy of tungsten.

The RMSEP value for enthalpy is obtained from the following equation:

$$\text{RMSEP}(H) = \sqrt{\frac{1}{m} \sum_{i=1}^{m} \left(H_{\text{pred}} - H_{\text{poly}} \right)^2}, \qquad (28)$$

where H_{poly} is the enthalpy obtained from polynomial model and H_{pred} is the enthalpy obtained from the proposed model. The value of RMSEP was found to be 54.71. This result and Fig. 6 show that the proposed model fits the data very well. The value of $\Theta_V(T)$ is equal to the value of $\Theta_P(T)$ and $C_{P\text{max}}$ is approximately equal to $3R$. Therefore, the RMSEP values of entropy and enthalpy obtained for constant volume and constant pressure are approximately equal to each other.

4. Conclusions

The values of Θ_V and Θ_P were found to be 78.5 K for tungsten. Tungsten shows the dimensionality crossover from $n = 3$ to $n = 2$ at about 80 K. The temperature and n dependence of $\Theta_D(T)$ and the non-monotonic behavior were discussed. The relationship between n and $\Theta_V(T)$ was given. The heat capacity and entropy values predicted by the proposed models were compared with the values predicted by the Debye models. The results have shown that the proposed models fit the data better than the Debye models. The enthalpy values predicted by the proposed models were compared with the values predicted by the polynomial model.

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