MM6010 - Assignment 1

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1 Question 1

The chemical contribution to Gibbs energy of cementite(Fe_3C) can be approximated using Meyer-Kelly polynomial. In the temperature range of interest Gibbs energy can be expressed as,

$$G^{\circ,cem} - 3H_{Fe}^{SER} - H_{C}^{SER} = a + bT + cTlnT + d_2T^2 + d_4T^4 + d_{-1}T^{-1}, \tag{1}$$

From eq 1, the other thermodynamic properties can be calculated.

$$\Delta H = a - c\,\mathrm{T} + \frac{2\,d_{-1}}{\mathrm{T}} - d_2\,\mathrm{T}^2 - 3\,d_4\,\mathrm{T}^4, \tag{2}$$

$$\Delta S = \frac{d_{-1}}{\mathrm{T}^2} - c\,(\ln(\mathrm{T}) + 1) - 2\,d_2\,\mathrm{T} - b - 4\,d_4\,\mathrm{T}^3, \tag{3}$$

$$Cp = -c - 2\,d_2\,\mathrm{T} - \frac{2\,d_{-1}}{\mathrm{T}^2} - 12\,d_4\,\mathrm{T}^3, \tag{4}$$

The code snippet that calculates the chemical part of the thermodynamic properties at various temperatures is given below.

```
if((temp>0)&&(temp<=43))
    a   = 11369.937746;
    b   = -5.641259263;
    c   = 0.0;
    d_4 = -8.333*10^(-6);
    d_2 = 0.0;
    d_1 = 0.0;
else
    if ((temp>43)&&(temp<=163))
        a   = 11622.647246;
        b   = -59.537709263;
        c   = 15.74232;
        d_4 = 0.0;
        d_2 = -0.27565;
        d_1 = 0.0;
    else
        if ((temp>163)&&(temp<=2000))
            a   = -10195.860754;
            b   = 690.949887637;
            c   = -118.47637;
            d_4 = 0.0;
            d_2 = -0.0007;
            d_1 = 590527;
        end
    end
end

enthalpy_ch = a - c*temp - 3*d_4*(temp^4) - d_2*temp^2 + 2*d_1*temp^(-1);
entropy_ch  = -b -c*(1 + log(temp)) - 4*d_4*temp^3 - 2*d_2*temp + d_1*temp^(-2);
cp_ch       = -c -12*d_4*temp^3 - 2*d_2*temp -2*d_1*temp^(-2);
```

For the magnetic contribution of the thermodynamic properties, Inden-Hillert-Jarl model [1] has been used. This gives the functional form of C_p and G,

$$C_p^{ferro} = 2\,K_{\mathrm{ferro}}\,R\left(\tau^m + \frac{\tau^{3\,m}}{3} + \frac{\tau^{5\,m}}{5}\right), for\ \tau \leq 1 \tag{5}$$

$$C_p^{para} = 2\,K_{\mathrm{para}}\,R\left(\tau^{-n} + \frac{\tau^{-3\,n}}{3} + \frac{\tau^{-5\,n}}{5}\right), for\ \tau \geq 1 \tag{6}$$

This can be integrated to find the values of other thermodynamic quantities. The code snippet that calculates the magnetic part of the thermodynamic properties at various temperatures is given below.

```
if (temp<=Tc)
    cp_mo = 2*K_ferro*R*(tau^m + tau^(3*m)/3 + tau^(5*m)/5);
    enthalpy_mo = 2*K_ferro*R*temp*((tau^m)/(m+1) + tau^(3*m)/(3*(3*m+1)) + tau
    ^(5*m)/(5*(5*m+1)));
    enthalpy_mo = -(R*Tc*(71*K_ferro/120 + 79*K_para/140) - enthalpy_mo);
    entropy_mo  = 2*K_ferro*R*((tau^m)/m + tau^(3*m)/(3*(3*m)) + tau^(5*m)/(5*(5*m
    )));
    entropy_mo  = -(R*log(1+beta) - entropy_mo);
else
    cp_mo       = 2*K_para*R*(tau^(-n) + tau^(-3*n)/3 + tau^(-5*n)/5);
    enthalpy_mo = 2*K_para*R*((temp*tau^(-n) - Tc)/(-n+1) + (temp*tau^(-3*n)-Tc)
    /(3*(-3*n+1)) + (temp*tau^(-5*n)-Tc)/(5*(-5*n+1)));
    enthalpy_mo = enthalpy_mo + 2*K_ferro*R*Tc*(1/(m+1) + 1/(3*(3*m+1)) + 1/(5*(5*
    m+1)));
    enthalpy_mo = -(R*Tc*(71*K_ferro/120 + 79*K_para/140) - enthalpy_mo);
    entropy_mo  = 2*K_para*R*((tau^(-n)-1)/(-n) + (tau^(-3*n) -1)/(3*(-3*n)) + (
    tau^(-5*n)-1)/(5*(-5*n)));
    entropy_mo  = entropy_mo + 2*K_ferro*R*(1/m + 1/(3*(3*m)) + 1/(5*(5*m)));
    entropy_mo  = -(R*log(1+beta) - entropy_mo);
end
```

Finally both the contributions can be added to calculate the total quantity. The output of the code is given below.

```
temp = 200
Enthalpy = 17056.7929 J mfu^{-1}
Entropy  = 64.7829 J K^{-1}
Cp       = 90.0825 J mfu^{-1} K^{-1}

temp = 400
Enthalpy = 38553.6228 J mfu^{-1}
Entropy  = 138.186 J K^{-1}
Cp       = 119.3122 J mfu^{-1} K^{-1}

temp = 500
Enthalpy = 51001.2987 J mfu^{-1}
Entropy  = 165.9348 J K^{-1}
Cp       = 120.2085 J mfu^{-1} K^{-1}
```

2 Question 2

The specific heat is calculated and plotted as a function of temperature in Fig. 1. Since, there is a magnetic transformation occurring at $T = 485K$, the specific heat is not differentiable at that temperature, which is evident from the graph.

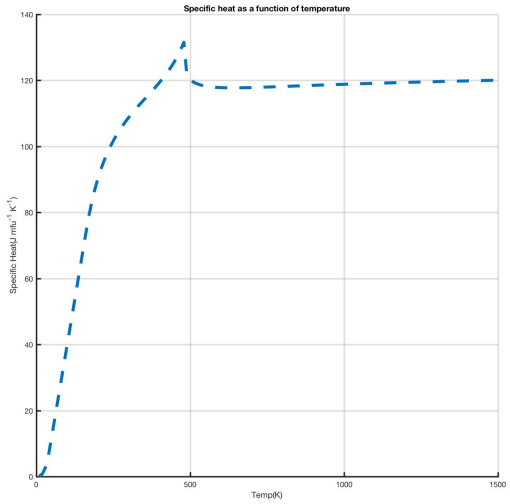

Figure 1: Specific heat as a function of temperature

3 Question 3

The magnetic contribution to Gibbs energy at the Curie temperature can be calculated using the following code snippet.

```
tau = 1;
gibbs_energy = -K_para*R*Tc*((tau^(-4)/10) + (tau^(-14)/315) + (tau^(-24)/1500));
```

The output of the snippet is given below.

```
Gibbs_mo = -124.6148 J mfu^{-1}
```

References

[1] Mats Hillert and Magnus Jarl. "A model for alloying in ferromagnetic metals". In: *Calphad* 2.3 (1978), pp. 227 –238. ISSN: 0364-5916. DOI: https://doi.org/10.1016/0364-5916(78)90011-1. URL: http://www.sciencedirect.com/science/article/pii/0364591678900111.