

Series 4 Solution

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Exercise 1: C Interstitials in Fe

In a compact body-centered cubic structure, the maximum radius allowed for an interstitial is given by:

$$r_{\text{int}} = \frac{1}{2}a - R$$

$$a = \frac{4}{\sqrt{3}}R \quad \text{the measured along the close-packed directions, } \langle 111 \rangle.$$

where a is the cell parameter, and R is the atomic radius of iron. We also have

$$r_{\text{int}} = \frac{1}{2} \left(\frac{4}{\sqrt{3}}R \right) - R = 0.192 \text{ \AA}$$

The atomic radius of carbon (Table II.1 of Chapter 2 lecture notes) is 0.77 \AA . Thus, the linear elastic distortion of the interstitial site occupied by a carbon atom is $> 300\%$. The linear elastic distortion of the cell parameter $a=2.86 \text{ \AA}$ is 20% if the surrounding atoms are not readjusted to accommodate this considerable strain.

$$\epsilon = \frac{0.77 - 0.192}{2.86}$$

In reality, this distortion is transmitted to all adjacent cells. Nevertheless, such a distortion limits the solubility of the carbon in α iron at $0.02\text{wt}\%$ (measured experimentally and calculated from this exercise), i.e., $0.073\text{at}\%$, which is 1.5 atoms for 1000 atomic cells.

In the face-centered cubic structure (γ iron), the maximum radius allowed for an interstitial is given again by:

$$r_{\text{int}} = \frac{1}{2}a - R$$

We have, in this case:

$$a = \frac{4}{\sqrt{2}}R \quad \text{close-packed direction } \langle 110 \rangle$$

$$r_{\text{int}} = \frac{\sqrt{2}}{2}R - R = 0.52 \text{ \AA}$$

The elastic distortion of the interstitial site caused by the carbon is about 48% . The maximum elastic distortion of the cell parameter $a=3.59 \text{ \AA}$ is 6.9% , much less than that in the BCC network. As such, the solubility of the carbon in the γ iron can be as high as $\sim 0.8\text{wt}\%$.

Exercise 2: Equilibrium density of vacancies

Let us consider a network of $N+n$ atomic sites. The equilibrium at constant P and T implies that G is minimum. The presence of n new vacancies implies a variation in the free enthalpy necessary for the formation of vacancies and a variation in the configurational (mix) entropy due to the distribution of vacancies on the network, as there is an increase in disorder.

$$G = H - TS$$

For n defects:

$$\Delta G = n\Delta H_V^F - nT\Delta S_V^F - TS_m$$

By definition, the entropy is given by the logarithm of the number of possible configurations $\Delta\Gamma$ of the system. The Boltzmann constant gives us the proper units. For the distribution of n vacancies on $N+n$ sites, the number of combinations is provided by the binomial coefficient,

$$\binom{N+n}{n}$$

In the general case of n_i particles distributed on N sites, $\sum_i n_i = N$, we have:

$$\binom{N}{n_1 n_2 n_3 \dots} = \frac{N!}{n_1! n_2! n_3! \dots}$$

Thus:

$$S_m = k \ln \Delta\Gamma = k \ln \left(\frac{(N+n)!}{n! N!} \right)$$

If N is large, we can use the Stirling formula $\ln N! = N \ln N - N$

$$\Delta G = n\Delta H_V^F - nT\Delta S_V^F - kT((N+n)\ln(N+n) - N \ln N - n \ln n - (N+n) + N + n)$$

If ΔG is minimum, it then implies $\frac{\partial \Delta G}{\partial n} = 0$

$$\Delta H_V^F - T\Delta S_V^F - kT \left(\ln(N+n) + \frac{n}{N+n} - \ln n + \frac{N}{N+n} + \frac{n}{N+n} - 1 \right) = 0$$

$$\ln \frac{n}{N+n} = \ln C_V = \frac{-\Delta G_V^F}{kT} \quad \text{and finally:}$$

$$C_V = e^{\frac{-\Delta G_V^F}{kT}} = e^{\frac{\Delta S_V^F}{T}} e^{\frac{-\Delta H_V^F}{kT}} = C_0 e^{\frac{-\Delta H_V^F}{kT}}$$

Exercise 3: Thermal expansion of aluminum

We systematically observe that the thermal expansion measured on a massive sample is more significant than that resulting solely from the crystalline lattice. This difference is due to the presence and formation of vacancies. Considering the expansion along one of the sample's dimensions, we can say that its length, L , is the sum of the spaces due to the vacancies and the atomic spaces:

$$L = (n_a + n_v) a$$

where a is the interatomic distance, n_a is the number of atoms, and n_v is the number of vacancies.

All these quantities depend on the temperature T . Thus, at ambient temperature T_0 :

$$L(T_0) = (n_a + n_v(T_0)) \cdot a(T_0)$$

We can nevertheless admit that the quantity of vacancies at T_0 is negligible compared to higher temperatures. We shall verify it later. Thus:

$$L(T_0) \approx (n_a) \cdot a(T_0)$$

The variation in the length of the sample is given by:

$$\Delta L = L - L_0 = (n_a + n_v(T)) \cdot a(T) - n_a \cdot a(T_0)$$

Macroscopically, $\Delta L = \alpha \cdot L_0$

where α is the linear coefficient of thermal expansion measured by dilatometry.

But $a(T) = \alpha' \cdot \Delta T \cdot a(T_0) + a(T_0)$ where $\alpha' \cdot \Delta T$ is the thermal expansion measured on the lattice cell (by x-ray, for example) and therefore,

$$\Delta L = \alpha' \Delta T n_a a(T_0) + \alpha' \Delta T n_v(T) a(T_0) + n_a a(T_0) + n_v(T) a(T_0) - n_a a(T_0) = a(T_0) \cdot (\alpha' \Delta T n_a + \alpha' \Delta T n_v(T) + n_v(T))$$

The variation of the lattice parameter $\Delta a = a(T) - a(T_0)$ is given by:

$$\Delta a = \alpha' \cdot \Delta T \cdot a(T_0)$$

$$\frac{\Delta L}{L(T_0)} - \frac{\Delta a}{a(T_0)} = \frac{a(T_0) \cdot (\alpha' \Delta T n_a + \alpha' \Delta T n_v(T) + n_v(T))}{n_a \cdot a(T_0)} - \alpha' \Delta T = \frac{\alpha' \Delta T n_v(T)}{n_a} + \frac{n_v(T)}{n_a}$$

Since $\alpha \cdot \Delta T \approx 10^{-2}$ and $\frac{n_v}{n_a}$ are small, we can neglect the expansion associated with vacancy sites; this gives the concentration of defects CV directly at the temperature T .

$$\frac{\Delta L}{L(T_0)} - \frac{\Delta a}{a(T_0)} \approx \frac{n_v(T)}{n_a}$$

Remembering that: $C_V = C_0 e^{\frac{-(\Delta H_V^F)}{k \cdot T}}$

$$\frac{n_V(T = 673 \text{ K})}{n_a} = C_0 e^{\frac{-\Delta H_V^F}{k \cdot 673}} = 7.633 \cdot 10^{-6}, \quad \frac{n_V(T = 873 \text{ K})}{n_a} = C_0 e^{\frac{-\Delta H_V^F}{k \cdot 873}} = 2.94 \cdot 10^{-4}$$

$$\Delta H_V^F = \frac{\ln\left(\frac{7.633 \cdot 10^{-6}}{2.94 \cdot 10^{-4}}\right)}{\frac{1}{k} \left(\frac{1}{873} - \frac{1}{673}\right)}, \quad k = 8.617 \cdot 10^{-5} \text{ [eV/atom]}$$

$$\Delta H_V^F = 0.92 \text{ [eV/atom]}$$

We calculate ΔH_V^F since ΔG_V^F depends on temperature, and its derivation for temperature would not be appropriate.