

MME 4518 Phase Transformations

MIDTERM 1

NAME SURNAME: KEY

16.03.2016

Dear Friends, there are 2 types of bonuses in this exam, intrinsic and extrinsic ☺

- You have 100 minutes.
- Answers without unit **WILL NOT** get credit!
- Please check the tables and cheat sheets (3 pages in total) You may need them.
- Mobile phone usage is absolutely forbidden!
- Answers of each question must be on the relevant question page.
- Constants that you may need are;

R: $8.314 \text{ J}/(\text{mol K})$; $N_A: 6.022 \times 10^{23} \text{ atoms/mol}$; $k: 1.38 \times 10^{-23} \text{ m}^2 \text{ kg} / (\text{s}^2 \text{ K})$

- 1) Why a rain droplet is spherical in shape (5 pts), and why a single crystal material is not? (10 pts)
Please explain in detail.

Rain droplet wants to minimize its own energy. Sphere is the shape with minimum energy.

When a crystal material becomes sphere, its total energy does not minimize. Some (crystallographic) planes have high energy (the ones with low atomic density), some have low energy which have high atomic densities. Therefore it forms its own shape according to its crystal structure and atomic densities of planes.

2) (a) (5 pts) Prove that

$$G = X_A (G_A + \Omega X_B^2 + RT \ln X_A) + X_B (G_B + \Omega X_A^2 + RT \ln X_B)$$

(b) Use this equation to drive an equation for the change in the internal energy of the system (5 pts).

a)

$$G = X_A G_A + \Omega X_B^2 X_A + RT X_A \ln X_A + X_B G_B + \Omega X_A^2 X_B + RT X_B \ln X_B$$

$$X_A G_A + X_B G_B = G_0$$

$$\Rightarrow G = G_0 + \Omega X_A X_B (X_A + X_B) + RT (X_A \ln X_A + X_B \ln X_B)$$

$$X_A + X_B = 1 \Rightarrow G = G_0 + \underbrace{\Omega X_A X_B}_{\Delta H_{\text{mix}}} + \underbrace{RT (X_A \ln X_A + X_B \ln X_B)}_{-T \Delta S_{\text{mix}}}$$

$$\Rightarrow G = G_0 + \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \Rightarrow \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

$$b) \Delta H = \Delta E + \Delta PV$$

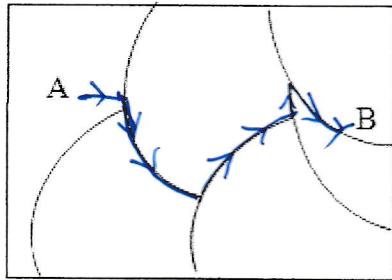
substituting this term instead of ΔH

$$\Rightarrow \Delta E = \frac{\Delta G + T \Delta S}{\Delta PV}$$

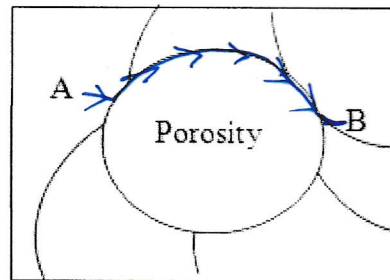
this answer will be accepted. But I was expecting this one;

$$\Delta H_{\text{mix}} = N_0 z X_A X_B \Delta E \Rightarrow \Delta E = \frac{\Delta G + T \Delta S_{\text{mix}}}{N_0 z X_A X_B}$$

- 3) There are 2 different nickel materials; a fully dense polycrystalline, and a partially dense polycrystalline with some porosity. Nickel atoms will diffuse from position A to position B.
- (a) Please draw the most dominant diffusion paths of the nickel atoms at 200°C in each case (8 pts) and explain.
- (b) What changes if the temperature will be 1200°C (9 pts)? Please explain the reasons for each case.



(1)



(2)

a) Since temp. is not high, they will prefer grain boundaries or surfaces if possible. They are open structures compared to lattice and diffusion in open structures is easier.

b) At high temp, diffusion speed/probability through lattice, gb, and surface will be almost same. Therefore atoms will select the shortest distance. In (1) they will directly go from A to B by lattice diffusion. In (2) the shortest distance is again surface diffusion.

- 4) Carbon content of 0.5 wt% is reached at 556 μm away from the surface of $\gamma\text{-Fe}$ after 8 hours carburization process with a surface concentration of 1,5 wt%. What is the carburization temperature? (10 pts) What kind of defect is produced in iron by this process? (3 pts)

$$C_x = 0.5 \% \quad x = 556 \times 10^{-6} \text{ m} \quad C_x = C_s - (C_s - C_0) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C_0 = 0 \% \text{ (pure iron)}$$

$$0.5 = 1.5 - (1.5 - 0) \operatorname{erf}(z)$$

$$C_s = 1.5 \%$$

$$\frac{1}{1.5} = \operatorname{erf}(z) = 0.667$$

for	$\frac{\operatorname{erf}(z)}{z}$	z	}	$x = 0.6885$
	0.6778	0.7		
	0.6667	x		
	0.6420	0.65		

$$\frac{x}{2\sqrt{Dt}} = 0.6885 \Rightarrow \sqrt{Dt} = \frac{556 \times 10^{-6} \text{ m}}{1.377} = 403.7 \times 10^{-6}$$

$$\sqrt{D} = \frac{403.7 \times 10^{-6}}{169.7} = 2.378 \times 10^{-6} \Rightarrow D \approx 5.6 \times 10^{-12} \text{ m}^2/\text{s}$$

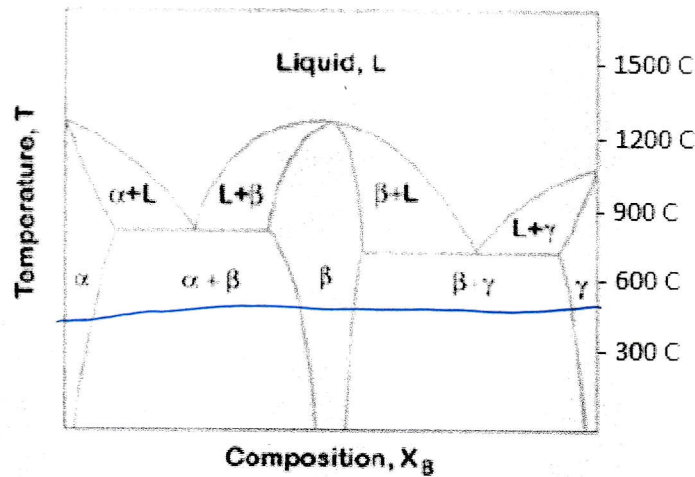
from table, it is close to 900°C diffusion coeff. $\Rightarrow T \approx 900^\circ\text{C}$

— Defect type is interstitial defect.

5) You are given ;

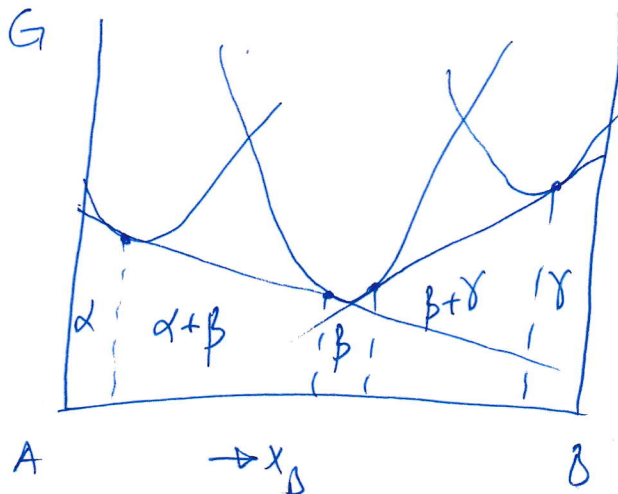
- The phase diagram of the binary compound. Assume that the compound has BCC lattice in all compositions.
- Positron annihilation measurement results, such that there are 4 vacancies are present in 10^6 lattice points for the same compound at equilibrium.
- The activation energy of vacancy formation, 80 kJ/mol.

Please draw the free energy-composition curve of the material for this vacancy condition. (25 pts)



$$X_v^e = X_v^0 \exp\left(\frac{-\Delta G_a}{RT}\right) \Rightarrow 4 \times 10^{-6} = e^{-\frac{80000 \text{ J/mol}}{8.314 T}}$$

$$\Rightarrow T = 500^\circ\text{C}$$

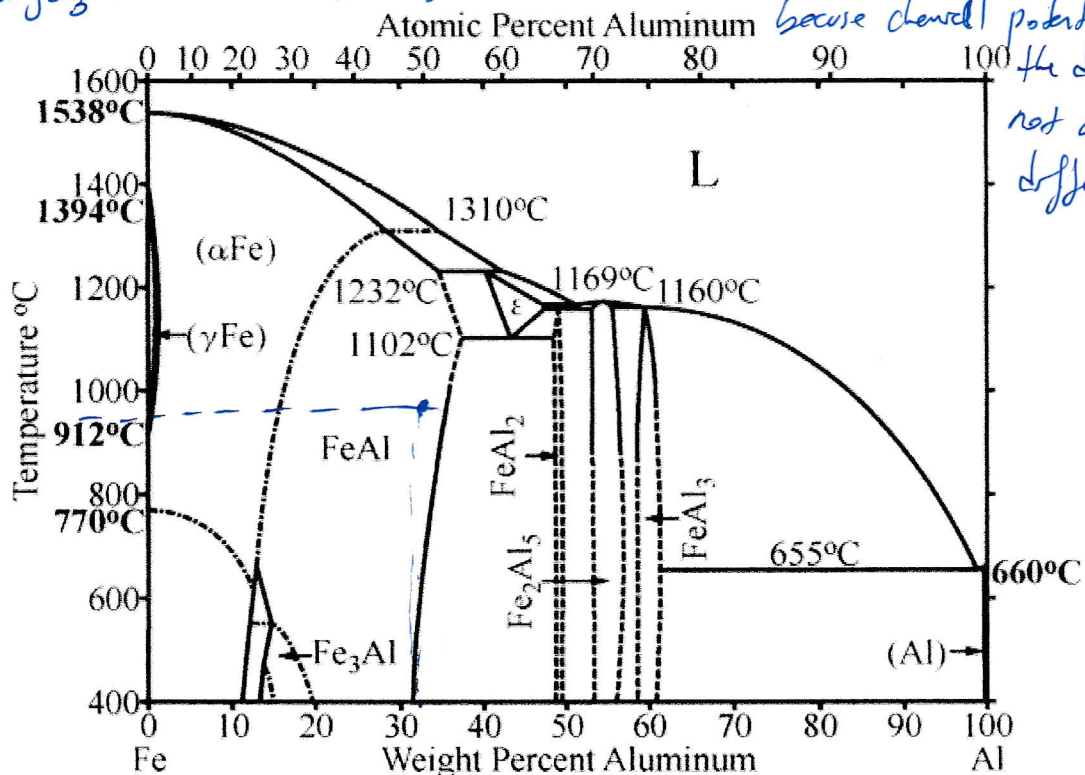


- 6) Now it is 05:00 in the morning and I am preparing you this boring question. I am sleepy, therefore some of the statements may be wrong. Please correct them if you think that it is wrong, and please explain the correct one(s). (5x5 pts)
- If I mix 300 gr iron and 100 gr aluminum nano-powders homogenously and heat up to 900°C, Fe₃Al will form at equilibrium. Because its free energy is lower than the other phases.
 - Chemical potential of Fe is higher than chemical potential of Al at 1400°C, because Fe has higher melting temperature.
 - Atoms always diffuse from high concentration regions to the low concentration regions, because they tend to make their concentrations equal everywhere.
 - Thermodynamics tells us the speed of Phase Transformations via diffusion of species. The relation for this phenomena is given by the equation below:

$$v = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

- Free energy curve of FeAl₂ is very narrow, because its phase region is also very narrow.

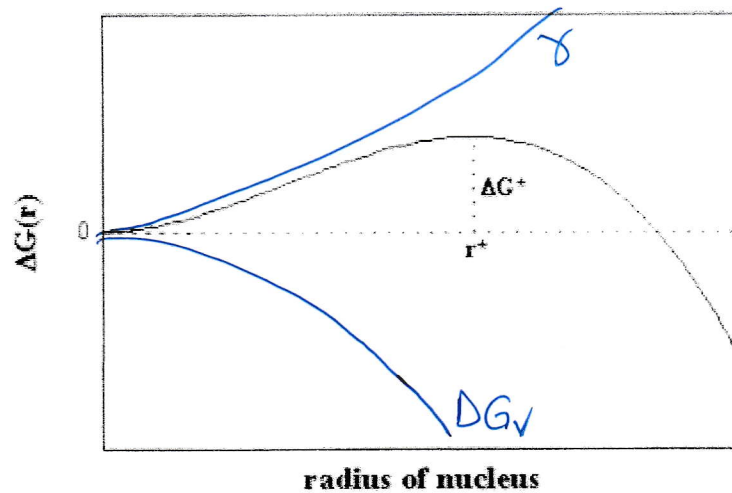
- a) At 900°C, phase diagram shows formation of FeAl at equilibrium. \Rightarrow false
 b) At 1400°C, there are millions of compositions. Missing information in the q! \Rightarrow false
 c) Not always / sometimes they may travel from low C to high C, \Rightarrow ~~false~~ (false)
 because chemical potential determines the diffusion direction, not always conc. difference.



- d) Thermodynamics doesn't tell us speed of anything. It is kinetics. \Rightarrow false
 e) Correct.

BONUS QUESTION (10 pts)

Below it is shown the free energy vs crystallite size graph during solidification of a metal. Please explain the behaviour of the curve in detail.



This curve is composed of free energy of new formed surface area curve (γ) and volume free energy curve (ΔG_v)

ΔG_v always decreases total energy of the system, whereas γ always increases. In the beginning of formation of nucleus, γ is dominated because of high $\frac{A}{V}$ ratio. After r^* , ΔG_v is dominated because

$\frac{A}{V}$ ratio is dropped below critical value.