

Part IB Paper 3: MATERIALS
Examples Paper 3/2 – Diffusion, and Phase Transformations

*Straightforward questions are marked with a †, Tripos standard questions are marked with a **

Phase Equilibrium: Thermodynamic Basis

† 1. (Revision) Describe in a few words, with examples, what is meant by each of the following:

- (a) an interstitial solid solution
- (b) a substitutional solid solution
- (c) precipitation from a solid solution
- (d) an intermetallic compound

† 2. Consider a closed system with pressure p , volume V , temperature T and entropy S undergoing an irreversible process, with the only work transfer given by $dW=pdV$. Use the 1st and 2nd laws of thermodynamics to derive the following expressions:

$$d(U + pV) \leq TdS + Vdp$$

$$d(U + pV - TS) \leq -SdT + Vdp$$

How are the quantities $(U + pV)$ and $(U + pV - TS)$ otherwise known? Explain why the second equation is most relevant to phase changes in materials processing.

3. (a) Figure 1 shows two sets of balls, initially separated so that the white balls are to the left and the black balls to the right. Write down how many distinguishable possible ways there are for this initial configuration. Now the membrane is removed and the balls can be placed anywhere in the four possible positions. Determine, by sketching or otherwise, the number of distinguishable possible ways in which the balls can now be placed. Hence determine the entropy of mixing ΔS_{mix} associated with the change from the initial to the mixed configuration, using the expression for entropy $S = k \ln w$.

(b) Explain, with reference to Gibbs function, how the above analysis can be used to understand why two liquids mix.

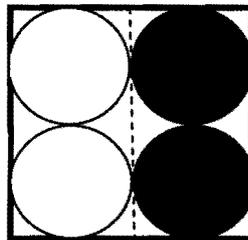


Fig. 1

4. Figure 2 shows the phase diagram for nickel and gold. Region B is a single-phase solid solution of the two metals, while region C is a two phase region, with two solid solutions, one relatively gold-rich and the other nickel-rich. Sketch the form of the Gibbs function as a function of composition which could give rise to this “miscibility gap” at, for example, a temperature of 600 °C [Hint – compare this to polymer mixing, as discussed in lectures].

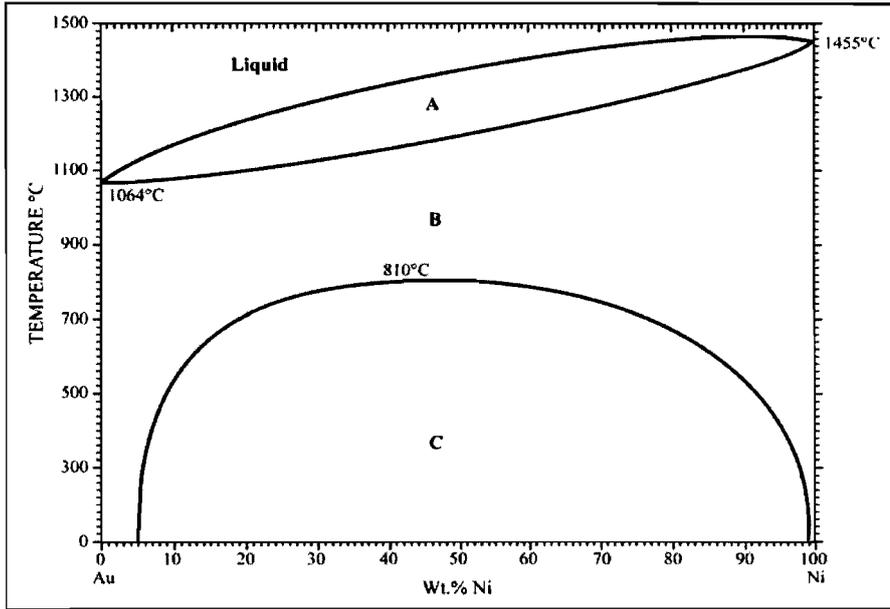


Fig. 2.

Phase Transformations: Thermodynamics

5. Figure 3 shows a sketch of the Gibbs function per mole G_α and G_β as a function of temperature T for two phases α and β of a solid.

(a) The two phases are coexisting in equilibrium at constant pressure and temperature T_e . Starting from the expression $G = H - TS$, derive an expression for the difference in entropy $\Delta S = S_\beta - S_\alpha$ between phases α to β , in terms of the equilibrium temperature and the difference in enthalpy $\Delta H = H_\beta - H_\alpha$.

(b) Now consider a change in phase at a small temperature ΔT above the equilibrium temperature, still at constant pressure and temperature. Find an expression for the driving force $\Delta G = G_\beta - G_\alpha$ associated with the phase change from α to β . Does the phase change from α to β occur above or below T_e ?

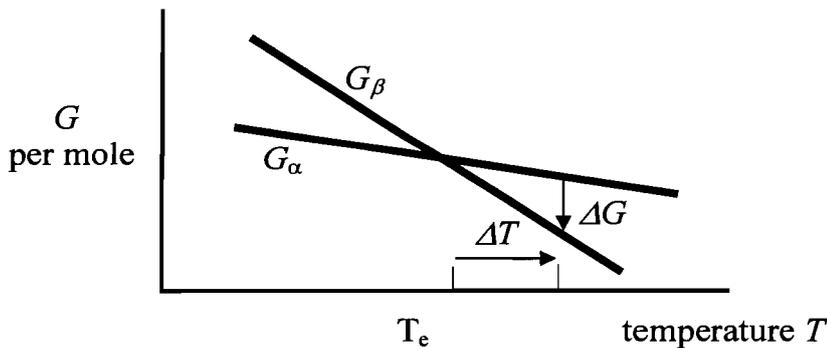


Fig. 3

6. † (a) Why is there a critical size for nucleation of a phase transformation?

(b) A certain phase transformation occurs by homogeneous nucleation of spheres when the temperature is cooled below a transformation temperature T_E . Starting from the expression for the total change in free energy associated with this nucleation event, derive an expression for the critical radius r^* above which nuclei are stable, in terms of the enthalpy change per unit volume ΔH_v , the interfacial surface energy γ , the transformation temperature T_E , and the undercooling below that temperature.

(c) Ice nucleates homogeneously as spherical particles from clean undercooled water at -40°C . Find the critical radius r^* given that the melting temperature is $T_m = 273\text{ K}$, the surface energy between liquid and solid is $\gamma = 0.025\text{ Jm}^{-2}$, and the enthalpy change *per unit mass* of ice on freezing is $\Delta H_m = 335\text{ kJkg}^{-1}$.

Estimate the number of H_2O molecules needed to make a critical-sized nucleus. Why do ponds freeze over when the temperature falls below 0°C by only a few degrees?

[The density of ice is 0.92 Mg m^{-3} . The atomic weights of hydrogen and oxygen are 1.01 and 16.00 respectively.]

Diffusion

† 7. Use your knowledge of diffusion to account for the following observations:

(a) The rate of diffusion of oxygen from the atmosphere into an oxide film is strongly dependent on the temperature and the concentration of oxygen in the atmosphere.

(b) Carbon diffuses far more rapidly than chromium through austenite.

(c) Diffusion is more rapid in polycrystalline silver with a small grain size than in coarse-grained silver.

8. In a study of slowly propagating cracks in high strength steel plates under constant stress, it was found that in a moist air environment the crack growth rate increased with temperature as follows:

Growth rate ($\mu\text{m s}^{-1}$)	0.70	2.20	8.70	29.1
Temperature ($^\circ\text{C}$)	5	25	55	87

Show, by using an Arrhenius plot, that for these conditions crack propagation is a thermally activated process and determine the activation energy.

It is believed that diffusion of one of the elements listed below is the rate-controlling mechanism. Decide which of these element is likely to be involved.

Diffusing element in α iron	Activation energy for diffusion (kJ/mol)
hydrogen	38
nitrogen	72
carbon	84
iron	285

9. (a) State Fick's first law of diffusion, defining the parameters in the equation. Fick's second law of diffusion for one-dimensional flow states that

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Outline qualitatively how this is derived.

(b) Molten aluminium is cast into a copper mould having a wall thickness of 5 mm. The coefficient of diffusion D of aluminium in copper is $2.6 \times 10^{-17} \text{ m}^2/\text{s}$ at 500°C and $1.6 \times 10^{-12} \text{ m}^2/\text{s}$ at 1000°C .

(i) Calculate the activation energy Q for the diffusion of aluminium in copper. By considering the mechanisms of diffusion, list some factors which will affect the value of Q in diffusion-controlled processes in crystalline solids.

(ii) Determine the coefficient of diffusion of aluminium in copper at 750°C .

(iii) A useful "rule-of-thumb" in diffusion problems states that the characteristic diffusion distance in time t is given by \sqrt{Dt} , where D is the diffusion coefficient for the temperature concerned. Make an order-of-magnitude estimate of the time taken for an aluminium atom to diffuse through the wall of the copper mould if the mould temperature is 750°C .

10. A thick steel plate of thickness $2w = 0.2\text{m}$ is continuously cast into a long sheet. Introduce a co-ordinate system such that x is the distance from the mid-thickness of the plate. The casting process gives a non-uniform concentration of aluminium in the steel, with a concentration profile C that can be taken to have the form

$$C(x, t = 0) = C_o + C_o \cos \frac{\pi x}{w}$$

An attempt is made to homogenise the concentration of aluminium within the casting by holding the casting at a temperature of 1000°C for one hour.

(i) Sketch the initial aluminium concentration $C(x, t = 0)$ as a function of thickness through the billet. Add to your figure rough sketches of how you expect the variation of concentration with position to evolve with time, including the end point with no variation in concentration, and explain why solutions of the form

$$C(x, t) = C_o + g(t) \cdot C_o \cos \frac{\pi x}{w}$$

with $g(0) = 1$ and $g(t \rightarrow \infty) \rightarrow 0$ are appropriate solutions to Fick's second law governing the subsequent diffusion process.

(ii) Substitute the form of solution suggested above into Fick's second law to derive a differential equation relating g and t . Hence obtain an expression for the evolution of concentration profile with time, $C(x, t)$. Confirm that the final concentration profile is uniform and of magnitude C_o .

(iii) Is the homogenisation treatment time of one hour sufficient to be successful? Assume that the diffusion constant is $D = 10^{-9} \text{ m}^2\text{s}^{-1}$.

(iv) Explain why homogenisation can occur much more rapidly with changes in concentration varying over a much shorter length scales of the order of millimetres. What else can be done to speed up homogenisation?

Phase Transformations: Kinetics

† 11. (a) For a transformation which is energetically favourable below an equilibrium temperature T_E , how does the amount of undercooling below T_E influence the rate of nucleation?

(b) A small undercooling below the equilibrium temperature of a solid state phase transformation leads to a coarse microstructure. Justify this statement and explain the consequence of increasing the undercooling.

(c) Explain why more bubbles are produced when a pint of Guinness is poured into a dirty earthenware tankard than a freshly washed glass.

12. Phase transformations in polycrystalline materials such as metals and ceramics are controlled by the rate of cooling below the transformation temperature. A TTT diagram is used to summarise the kinetics of transformation after quenching and holding at a given temperature.

Glass ceramics are made by quenching complex glasses (like $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Li}_2\text{O}$) to give an amorphous structure, and then making them crystallise ("devitrify"). The crystallisation process follows the classical theory for a diffusion controlled phase transformation. For a particular glass it is found that:

(a) no crystallisation occurs above a temperature of 1000°C ;

(b) the rate of crystallisation is a maximum at 950°C ;

(c) the rate of crystallisation is negligible below 700°C .

Sketch a diagram of temperature against crystallisation rate for this glass ceramic, and explain the shape of the curve. Show how this accounts for the shape of the curves on the corresponding TTT diagram.

Answers

3 (a). 1, 6, $k \ln(6)$

5. $\Delta G = -\Delta H (T_e - T) T_e$

6. $r^* = 1.11 \text{ nm}$; 176 molecules (approx).

8. 38 kJ/mol, hence hydrogen.

9. (b) (i) 180 kJ/mol. e.g. bond strengths, atomic sizes, crystal structure and defects.

(ii) $2.44 \times 10^{-14} \text{ m}^2/\text{s}$.

(iii) 11860 days

10. $C(x, t) = C_o + C_o \exp(-t/T) \cos \frac{\pi x}{w}$, (iii) $T = 10^6 \text{ s}$, the concentration variation has dropped negligibly from its initial amplitude, so homogenisation is not successful.

Relevant Tripos Questions from previous years

2003/1, 2 (parts), 2007/2, 2007/6, 2008/3, 2011/1, 2012/4, 2013/6

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