EMA5001 Lecture 16 Diffusional Transformation in Solids - Introduction

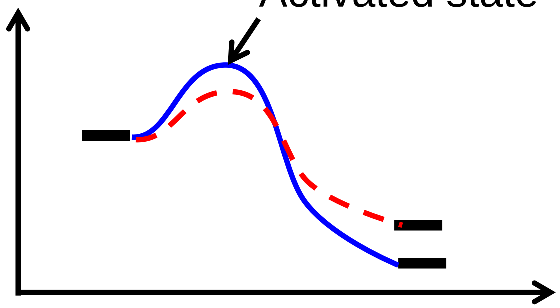
Introduction

❑ Phase transformation

- Solid-gas reaction: e.g., sublimation, oxidation of metals
- Solid-liquid conversion: e.g., solidification
- Solid-solid phase transformation: precipitation; polymorph transformation;

❑ At least one (can be both) of the following changes for solid-state phase transformation

- (Crystal) structure
  - α-Fe ↔ γ-Fe
  - Extent of ordering
- (Chemical) composition
  - Spinodal decomposition



❑ Thermodynamics vs. Kinetics

- Lowering (not necessarily minimization) of system free energy
- Overcome kinetic barriers

Characteristics of Solid-State Phase Transformation (1)

❑ Large barrier

- Volume strain energy (difference in molar volume)
- Interfacial energy (chemical term + geometric term)

❑ Slow migration (mobility) of atoms

- (Self) diffusion coefficient in solid is ~10^{-6} of that in liquid

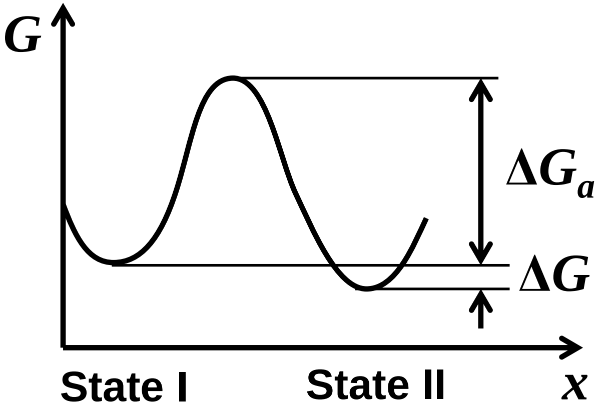
❑ Mostly heterogeneous nucleation

- All types of defects as potential heterogeneous nucleation sites
  - Vacancy
  - Dislocation
  - Grain boundary
  - Stacking fault
  - Second phase
  - Surface

Fundamentals of Materials Science (in Chinese), Pan, Tong, Tian, 1st Ed, 1998, p. 549-556

Characteristics of Solid-State Phase Transformation (2)

- **Meta-stable phase may appear**
  - Although I → II is energetically favorable
  - Too large barrier (especially at lower T) makes existence of meta-stable phase possible



- **New phase often has specific shapes**
  - Interface energy controlled – Matching of low energy interfaces
  - Strain energy controlled – Plate like

- **Various interface structures (coherent, semi-coherent, incoherent)**

- **Match of certain orientation and crystal planes between new phase and matrix**

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Classification of Solid-State Phase Transformation by Thermodynamics

❑1st order phase transformation

$$G_1 = G_2 \qquad \mu_i^1 = \mu_i^2$$

$$\left(\frac{\partial G_1}{\partial T}\right)_P \neq \left(\frac{\partial G_2}{\partial T}\right)_P \qquad \Delta V \neq 0$$

$$dG = VdP - SdT$$

$$\left(\frac{\partial G_1}{\partial P}\right)_T \neq \left(\frac{\partial G_2}{\partial P}\right)_T \qquad \Delta S \neq 0$$

Examples: most solid phase transformation including solidification, precipitation

❑2nd order phase transformation

$$G_1 = G_2 \qquad \mu_i^1 = \mu_i^2 \qquad \left(\frac{\partial G_1}{\partial T}\right)_P = \left(\frac{\partial G_2}{\partial T}\right)_P \qquad \left(\frac{\partial G_1}{\partial P}\right)_T = \left(\frac{\partial G_2}{\partial P}\right)_T$$

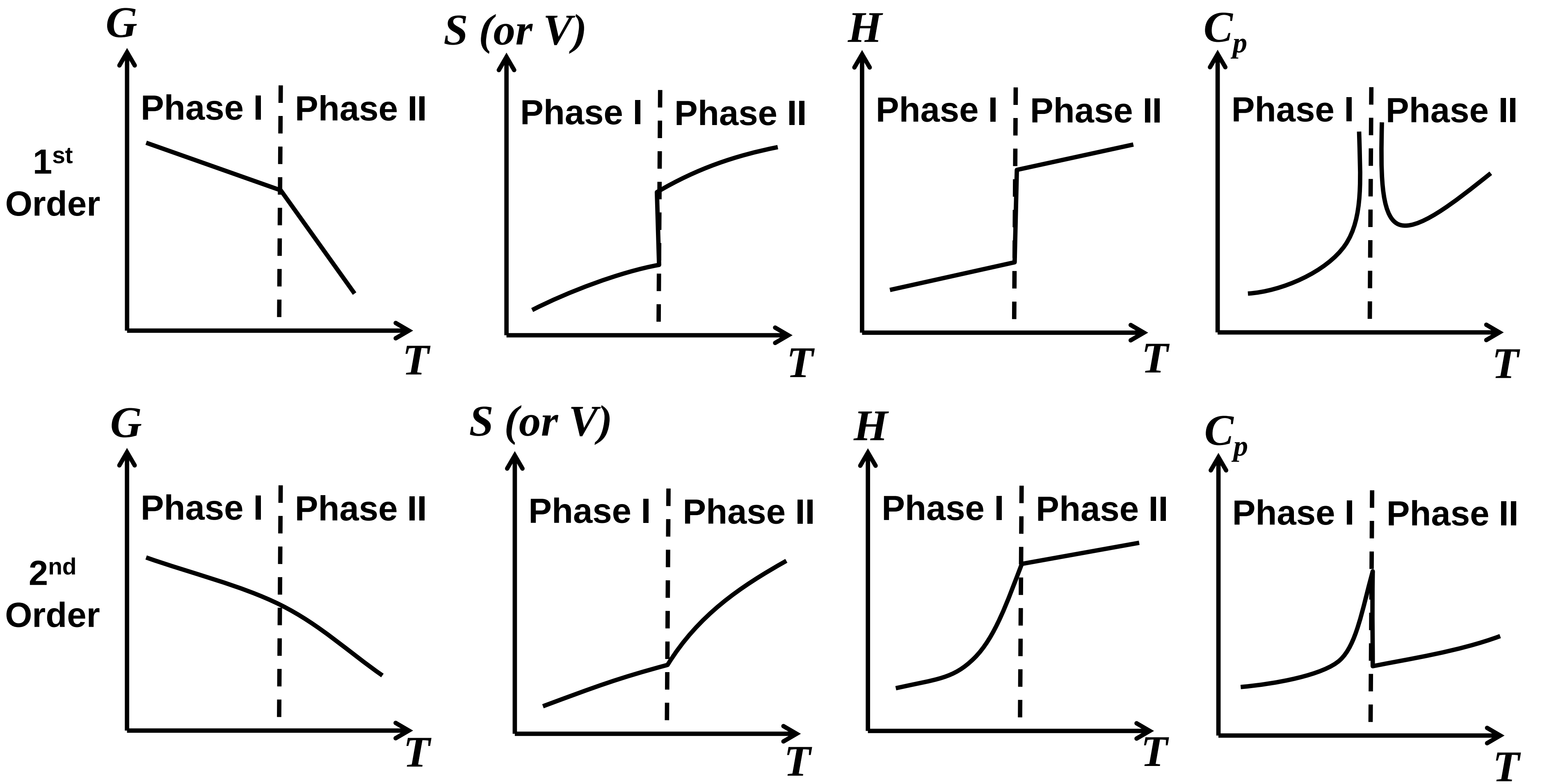
$$\left(\frac{\partial^2 G_1}{\partial T^2}\right)_P \neq \left(\frac{\partial^2 G_2}{\partial T^2}\right)_P \qquad \left(\frac{\partial^2 G_1}{\partial P^2}\right)_T \neq \left(\frac{\partial^2 G_2}{\partial P^2}\right)_T \qquad \frac{\partial^2 G_1}{\partial P \partial T} \neq \frac{\partial^2 G_2}{\partial P \partial T}$$

$$\Delta C_p \neq 0 \qquad \Delta \beta \neq 0 \qquad \Delta \alpha \neq 0$$

Examples: some order-disorder transformation

1st Order Phase Transformation vs. 2nd Order Phase Transformation

- Change of G, S, V, H, and C_p with T



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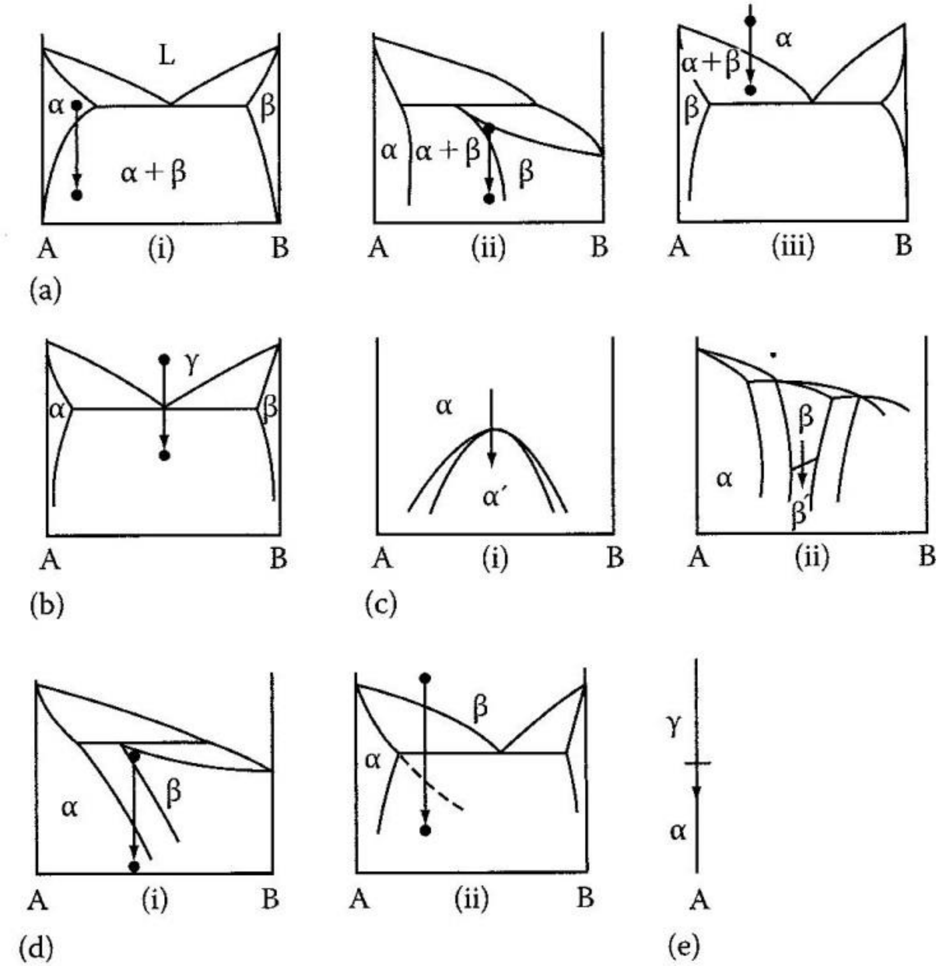
Classification of Solid-State Phase Transformation by Kinetics

- **By diffusion**
  - Diffusionless
  - Diffusion
    a) Precipitation: α' → α + β
       Change in solubility with temperature
       - γ-Fe → α-Fe + γ-Fe
    b) Eutectoid transformation: γ → α + β
       - γ-Fe → α-Fe + Fe_3C
    c) Ordering: α (disordered) → α (ordered)
       - Cu-Zn; Cu-Au
    d) Massive transformation
       - β brass → α brass at 38 atom% Zn
    e) Polymorphic changes
       - Diamond → graphite
       - γ-Fe → α-Fe



Phase Transformations in Metals & Alloys, Porter, 3rd Ed, 2008, p. 262