The Richard Stockton College of New Jersey
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CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 22: Phase transformations and nucleation

Key Concepts

- Homogeneous nucleation of a solid phase from a liquid phase (i.e. ice freezing out of water) is a simple case to consider because: there are many nucleation sites (it can happen anywhere), transport of material through a liquid is fast, a liquid-solid interface is strain free.
  - There are two important contributions to the energy that must be considered for homogeneous nucleation of a solid from a liquid:
    1. The chemical or volumetric driving force (ΔG_v or ΔG_{chem}): this is the energy difference between the liquid phase and the solid phase that wants to form. As you undercool below the transformation temperature (i.e. melting temperature), the driving for *increases*. The driving force is proportional to the volume of the nucleus formed.
    2. Upon nucleation, a new interface between the solid and liquid is formed. This interface has an associated surface energy (γ) and thus it costs energy to create it. This term is an energy penalty and reduces the driving force. The surface energy is proportional to the surface area of the nucleus formed.
  - Assuming spherical nuclei and taking these two contributions together, the total energy change upon nucleation can be written as:

    $$\Delta G_{tot} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

    This expression uses the convention that ΔG_v is a negative quantity since below the transformation temperature the formation of the more stable phase is favored.
  - When plotting this function, you will notice that a maximum exists at some critical radius (r^*). For a nucleus smaller than the critical radius, the energy can be lowered by the nucleus shrinking and disappearing. Nuclei with sizes greater than or equal to the critical radius can lower their energy by growing and are therefore stable.
  - This should make sense in terms of the interplay between the volumetric driving force and surface energy. For extremely small particles, the surface area to volume ratio is huge and thus the nuclei are not stable.
  - By taking a derivative of the total energy, we can solve for the critical radius and critical energy for nucleation (i.e. the activation barrier):

    $$r^* = \frac{2\gamma}{\Delta G_v}$$

    $$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v}$$

  - From these expressions it is clear that as you cool below the transformation temperature and ΔG_v increases, the critical radius size and the critical energy for nucleation both decrease.
- Homogeneous nucleation is typically difficult from an energetic viewpoint. To lower the barrier, the nucleating phase can form on existing surfaces to lower the surface energy cost of nucleation. This is referred to as heterogeneous nucleation and can occur on specific types of sites:

  By forming on these special sites, the nucleus can offset the cost of creating new interface by destroying an exciting high energy interface or defect.

  - The critical radius for heterogeneous nucleation is the same as for homogeneous nucleation.

– The critical energy for heterogeneous nucleation is related to the critical energy for homogeneous nucleation through the following relationship:

$$\Delta G^*_{het} = \Delta G^*_{hom} S(\theta)$$

where $S(\theta)$ is a term that accounts for the geometry of the nuclei and for the lenticular case is given by:

$$S(\theta) = \frac{1}{4}(2 - 3\cos\theta + \cos^3\theta)$$