Thermodynamics and Kinetics

A Little Justification …

- Thin film growth is intimately intertwined with thermodynamics and gas kinetics.
- Temperature and pressure are the main parameters of film growth, especially in vacuum systems.
- As most films form through the contact of a vapor with a substrate, gas and molecular kinetics have to be taken into account as well.
- The chemical reactions involved in film formation have to satisfy the rules of thermodynamics.

Thermal Equilibrium

- Two objects are in thermal equilibrium when there is no exchange of energy when they are in contact.
- Objects in thermal equilibrium are said to have the same temperature.
- An ideal gas obeys the relation:

$$\boxed{PV = nRT}$$

where *P* is pressure, *V* is volume, *T* is temperature, *n* is the number of moles and *R* is the universal gas constant (8.314 J/(mol.K))

Entropy

- Entropy (S) is the physical measure of disorder in a system.
- In a reversible process, the change in entropy ΔS of a system from an initial state, i to a final state, f is:

$$\boxed{\Delta S = \int_i^f \frac{dQ_r}{T}}$$

where Q_r is the energy transferred by the reversible process and T is the temperature.

- This means that the entropy of a closed system remains constant.

Laws of Thermodynamics

- **Zeroth Law**: If two objects are separately in equilibrium with a third object, then they are in equilibrium with each other.
- **First Law**: If a system goes from one state to another, the change in its internal energy is the energy transferred to the system plus the work done on the system.

$$\boxed{\Delta U = T\Delta S + P\Delta V}$$

where ΔU is the change in internal energy and $P\Delta V$ is the external work done

- **Second Law**: The entropy of a closed system will increase and reach a maximum when thermal equilibrium is reached.
- **Third Law**: As temperature approaches absolute zero, the entropy of the system approaches a constant minimum.

Feasibility of Reactions

- In general thermodynamics tells us which reaction is allowed to happen but not which one will happen, which depend on the reaction rates.
- The possibility of a reaction depends on the change in the **Gibbs Free Energy**, *G*.

$\boxed{\Delta G = \Delta H - T\Delta S}$ where ΔH is the change in the enthalpy

- If $\Delta G > 0$, the process is forbidden.
- If $\Delta G < 0$, it is allowed.
- If $\Delta G = 0$, there is equilibrium.

Chemical Reactions

- Consider a chemical reaction involving three substances.

$$aA + bB \rightarrow cC$$

- It can be shown that,

$$\boxed{\Delta G = RT\ln\left\{\frac{\left(a_C / a_{C,eq}\right)^c}{\left(a_A / a_{A,eq}\right)^a \left(a_B / a_{B,eq}\right)^b}\right\}}$$

where the a_i's are the activities (kind of a thermodynamic concentration).

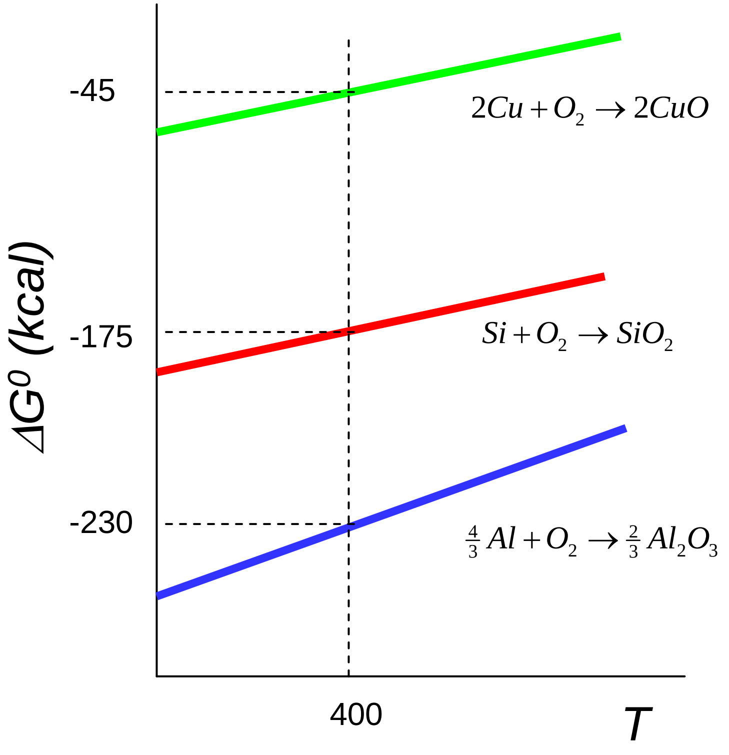
- In most cases, the activities assumed to be equal to the standard state value and taken to be one. Then,

$$\boxed{\Delta G = \Delta G^0 = RT\ln\left\{\frac{{a_{C,eq}}^c}{{a_{A,eq}}^a {a_{B,eq}}^b}\right\}}$$

where ΔG^0 is the standard state value of ΔG.

Example – Ellingham Diagrams

- Plots of ΔG^0 vs. T can be used to determine a preferred reaction.
- Consider the choice of depositing either Al or Cu on SiO_2 at 400 K.



To get the relevant reduction equations for Si, add either the Al or Cu equation to the Si equation and algebraically eliminate O_2. Apply the same factor to the free energy. Then you'll get:

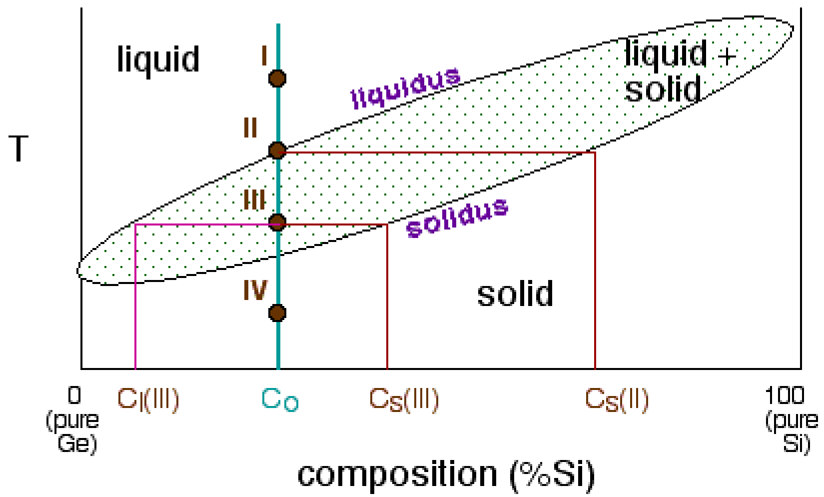
$$\tfrac{4}{3}Al + SiO_2 \rightarrow \tfrac{2}{3}Al_2O_3 + Si \qquad \Delta G^0 = -55kcal$$

$$2Cu + SiO_2 \rightarrow 2CuO + Si \qquad \Delta G^0 = +130kcal$$

Since the Al reaction has a lower free energy and will reduce SiO_2, Cu would be the better choice for metallization.

Phase Diagrams

- Phase diagrams represent the equilibrium conditions for inorganic systems as a function of pressure, temperature and composition.



Kinetics

- A system in thermodynamic non-equilibrium will try to reach equilibrium through certain driving forces.
- These forces would result in mass transport in the system to minimize the free energy.
- Phase transformations, recrystallization, compound growth and degradation are examples of the possible results.

Diffusion

- In solids, mass transport is achieved through diffusion.
- A concentration gradient creates an atomic migration within the solid.
- Fick’s first law governs one dimensional diffusion:

$$\boxed{J = -D\frac{dC}{dx}}$$

where *J* is the mass flux, *D* is the diffusion constant and *C* is the concentration

- The diffusion constant is temperature dependent.

$$\boxed{D = D_0 \exp\left(-E_D / k_B T\right)}$$

Atomistic View of Diffusion

- We would need to concentrate on how atoms can jump from one site to another in a lattice.
- For appreciable movement, the neighboring site needs to be vacant.

- An externally applied field (stress, electric) can also induce diffusion.

Nucleation

- Formation of a new phase such as a solid from vapor starts with nucleation.
- Thermodynamics will tell us if nucleation is energetically possible.
- Kinetics will tell us how fast it will be.

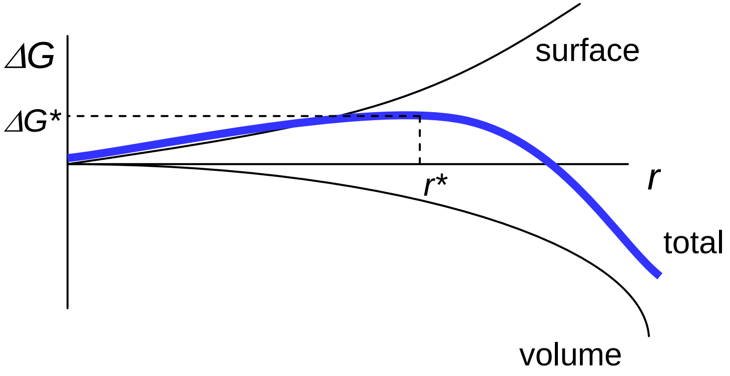
Thermodynamics of Nucleation

- The free energy needs to decrease for nucleation to be possible.
- Energy minimization happens by volume transition and surface formation.
- For homogenous nucleation:

$\boxed{\Delta G = \frac{4}{3}\pi r^3 \Delta G_v}$ where $\boxed{\Delta G_v = \frac{k_B T}{\Omega} \ln \frac{P_S}{P_V}}$ and $\boxed{\Delta G_{surf} = 4\pi r^2 \gamma}$

Volume transition can have negative free energy if there is a supersaturation of the vapor phase. Surface formation always has positive free energy.

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



Kinetics of Nucleation

- The nucleation rate is a product of three terms.

$$\boxed{\dot{N} = N^{*} A^{*} \omega}$$

where *N** is the equilibrium concentration of the stable nuclei, ω is the rate at which atoms impinge on to the nuclei of critical area *A**.

$$N^{*} = n_s \exp\left(-\Delta G^{*}/k_B T\right)$$

$$A^{*} = 4\pi\left(r^{*}\right)^2$$

$$\omega = \frac{\alpha\left(P_V - P_S\right)N_A}{\sqrt{2\pi MRT}}$$

where α is the sticking coefficient, N_A is the Avogadro’s number and *M* is the atomic weight