5. Electrode reactions that deviate from complete equilibrium
(Huggins, ch. 5)

1. Stable and metastable equilibrium
2. Selective equilibrium
3. Amorphous vs. crystalline structures
4. Deviations from equilibrium for kinetic reasons

1. Stable and Metastable Equilibrium

Stable: lowest value of the Gibbs free energy
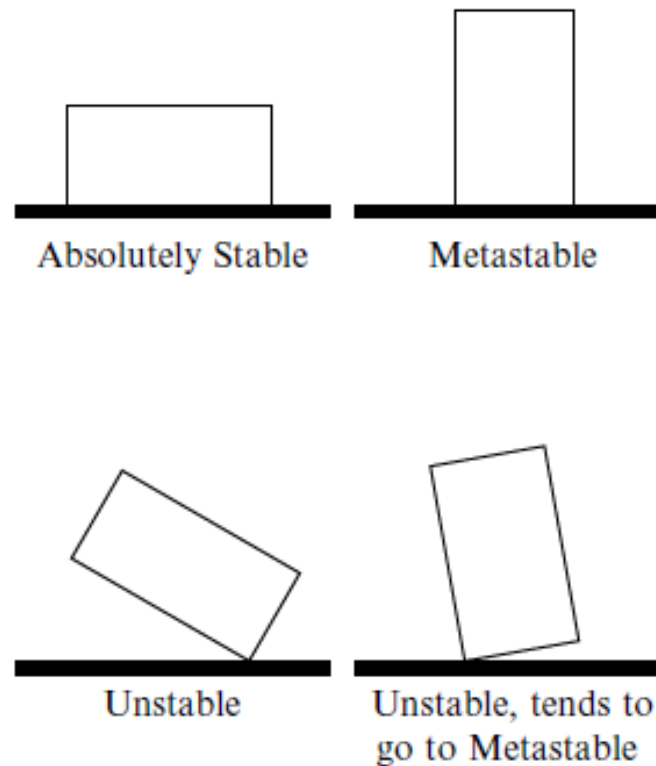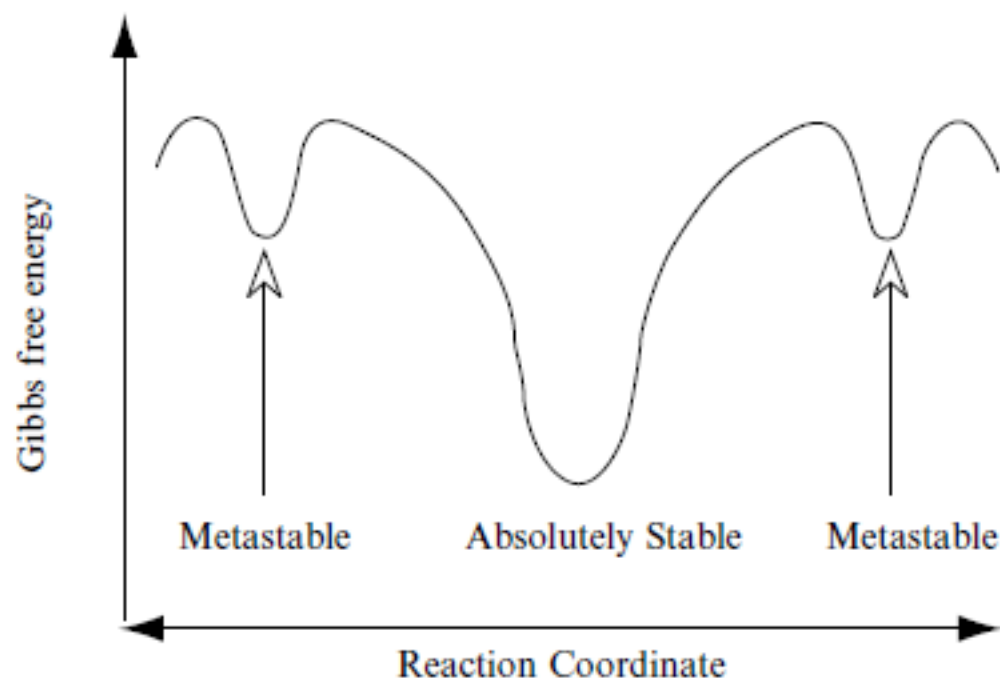Metastable: less stable than the absolute stable

Fig. 5.1 Simple mechanical model illustrating metastable and absolutely stable states

Fig. 5.2 Reaction coordinate representation of a system with metastable and absolutely stable states

2. Selective Equilibrium

-A number of the reactants in ambient temperature battery systems have crystal structures that can be described as a composite consisting of a <u>highly mobile ionic species within a relatively stable host structure</u>

→ such structures are sometimes described as having two different *sublattices*, (a) one of which has a high degree of mobility, and (b) the other is highly stable, for its structural components are rigidly bound → The guest species with high mobilities are typically rather small and move about through interstitial tunnels in the surrounding rigid host structure. The species in the mobile sublattice can readily come to equilibrium with the thermodynamic forces upon them, whereas the more tightly bound parts of the host structure cannot → 'selective equilibrium'

e.g. Li_xTiS_2 : rigid planar slabs of covalently bonded TiS_2, with mobile lithium ions in the space between them

3. Formation of Amorphous vs. Crystalline Structures

-Amorphous structures do not have regular long-range arrangements of their constituent atoms or ions. Amorphous structures are always less stable than the crystalline structure with the same composition. Thus they have less negative values of the Gibbs free energy of formation than their crystalline cousins
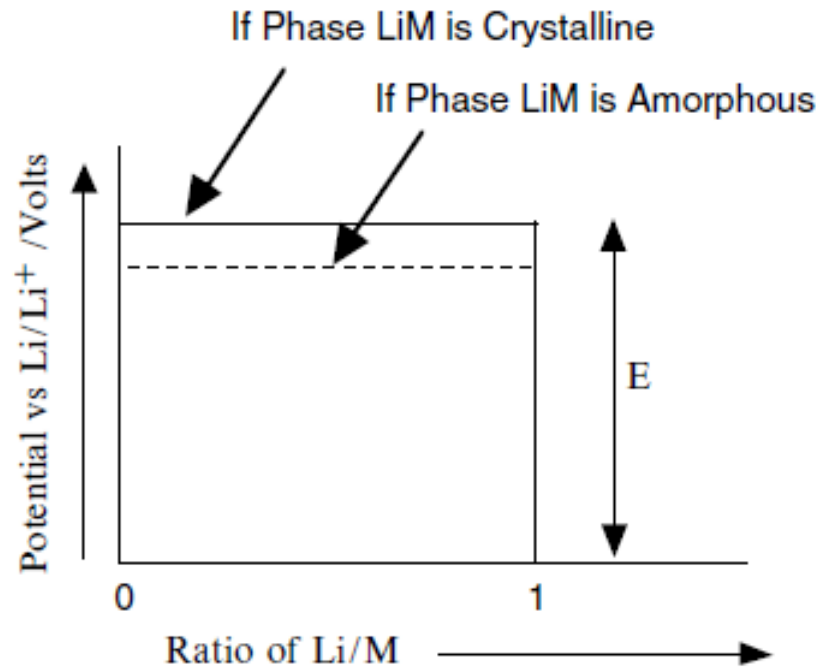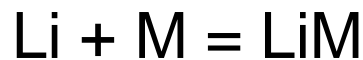
Fig. 5.3 Schematic drawing of the voltage of galvanic cell as a function of overall composition for a simple formation reaction Li + M = LiM for two cases, one in which the LiM product is crystalline, and the other in which it is amorphous

assume Li react with M to form LiM and Li_2M

The reaction for the formation of the first phase, LiM

$$Li + M = LiM$$

The plateau voltage, $\quad E = -\Delta G_f^\circ(LiM)/F$

If additional lithium can react with LiM to form the phase Li_2M

additional voltage plateau, $\quad Li + LiM = Li_2M$

The voltage of the second plateau is lower than that of the first

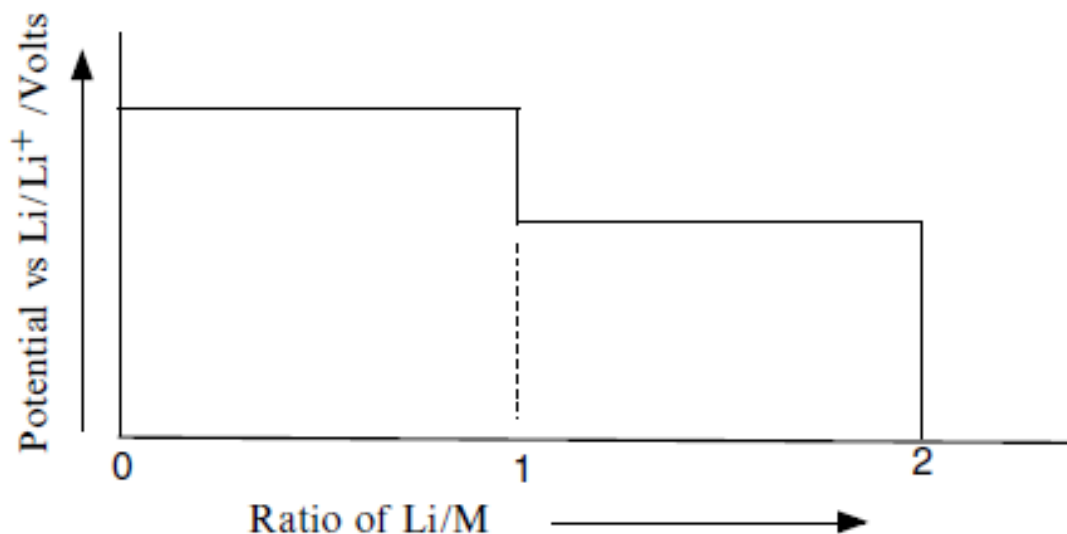$$E = -[\Delta G_f^\circ(Li_2M) - \Delta G_f^\circ(LiM)]/F$$

Fig. 5.4 Schematic titration curve for a sequence of two reactions of Li with M, first forming LiM, and then forming Li_2M

if the first phase, LiM, is amorphous, rather than crystalline? → Gibbs free energy of formation of that phase is smaller and the voltage of the first plateau is reduced.

→ The total Gibbs free energy of the two reactions by the Gibbs free energy of formation of the final phase, Li_2M → The total area under the curve is thus a constant. The interesting result is that if the voltage of the first plateau is reduced, the voltage of the second one must be correspondingly increased.
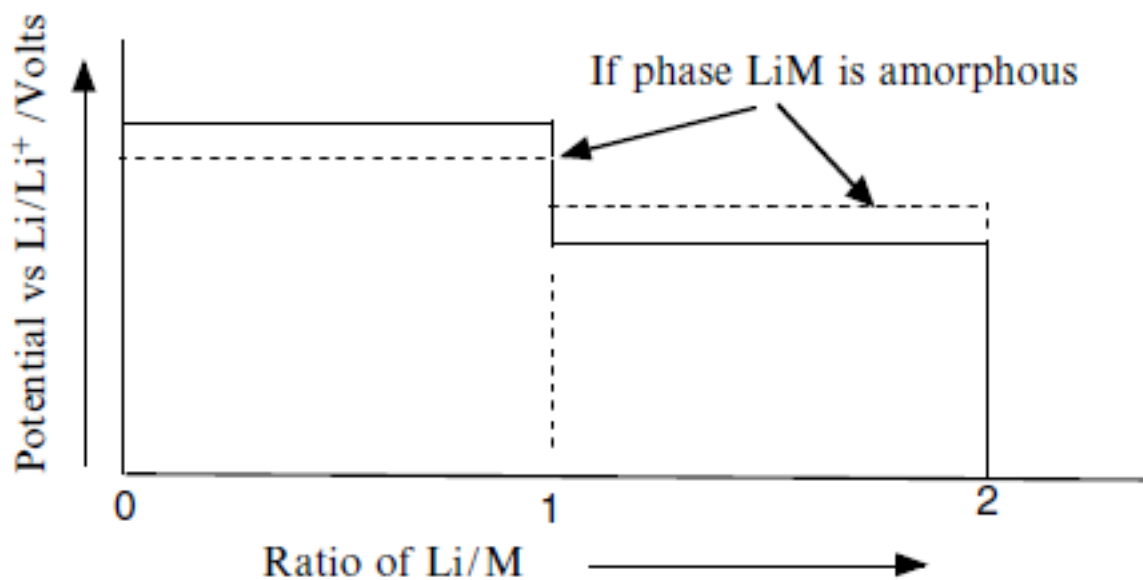
Fig. 5.5 Change in the schematic titration curve if the first product, LiM, is amorphous. The voltage of the second plateau must be higher to compensate for the reduced voltage of the first plateau

4. Deviations from Equilibrium for Kinetic Reasons

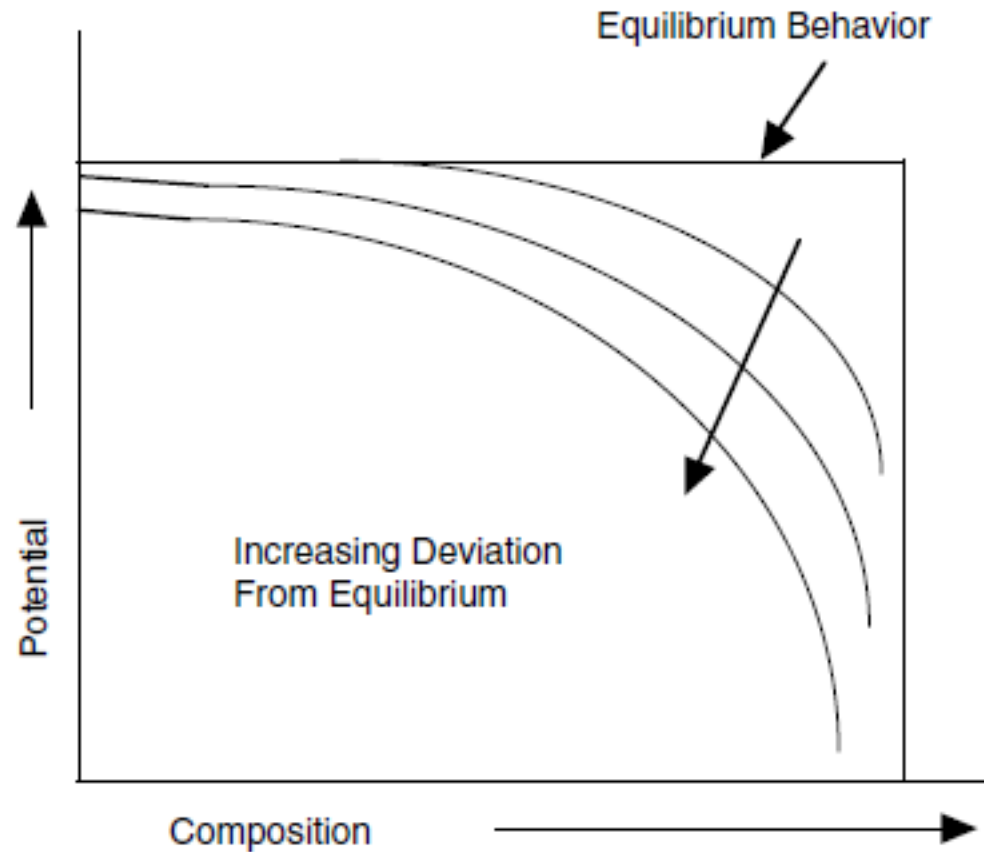Kinetic limitations: deviation from equilibrium (thermodynamics)

Fig. 5.6 Schematic representation of the influence of kinetic limitations upon both the potential and the capacity of an electrode reaction