

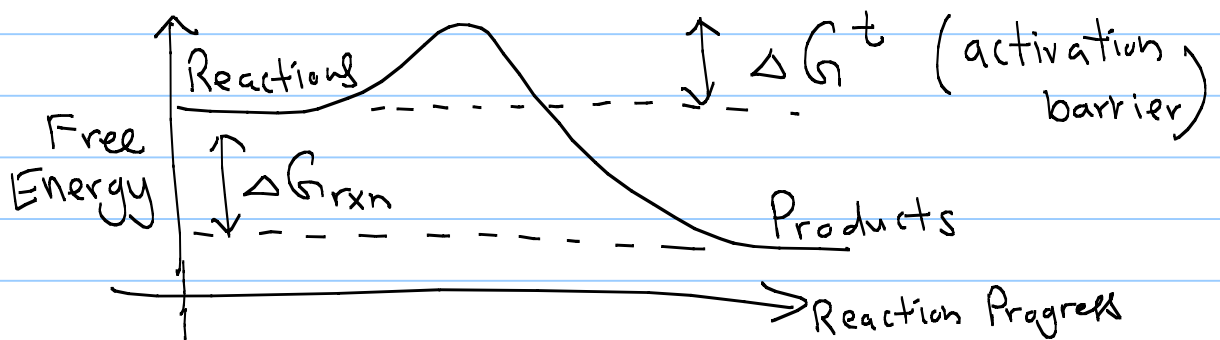
Notes: March 1st 2011 (Kelvin Soh)

Note Title

1/3/2011

Fuel Cell Reaction Kinetics

- Kinetics determine how much current we can draw from a fuel cell



- Electrochemical processes necessarily heterogeneous because of the interface between the fuel, catalyst and electrolyte.

Current $i = \frac{dQ}{dt}$ (Rate of change of charge)

$$i = n F \nu$$

i : Current

F : Faraday's constant

ν : Molar flow rate ($\frac{dN}{dt}$)

n : Number of electrons per reaction

Current density a more fundamental property than current.

$$j = \frac{i}{A} \quad ; \quad j = \frac{j}{nF} \quad (j: \text{per unit area reaction rate})$$

By applying a relative voltage, we can drive electron movement through changing the Fermi level of the electrode in the electrodes.



Several steps:

- ① Mass transport of H_2 gas to electrode
- ② Adsorption on to electrode
- ③ Separation into 2 atoms
- ④ Transfer of e^- into electrolyte
- ⑤ Mass transport away from electrode Reactant

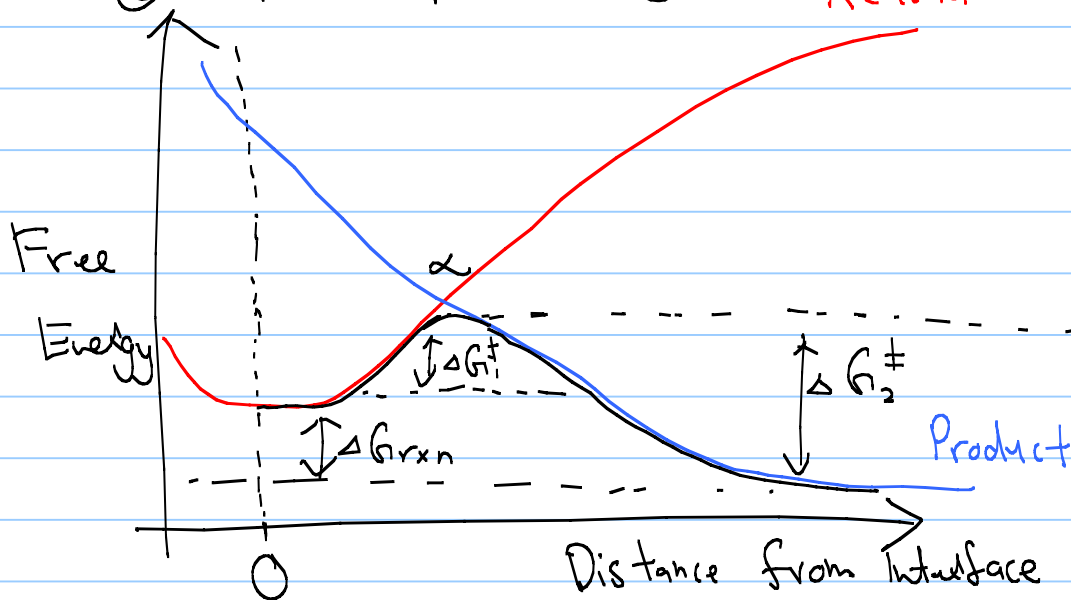
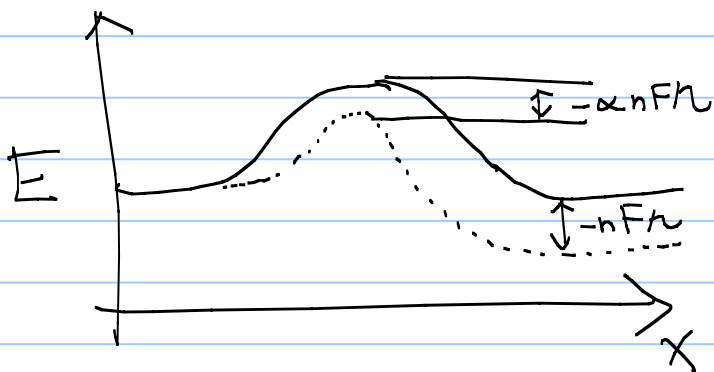


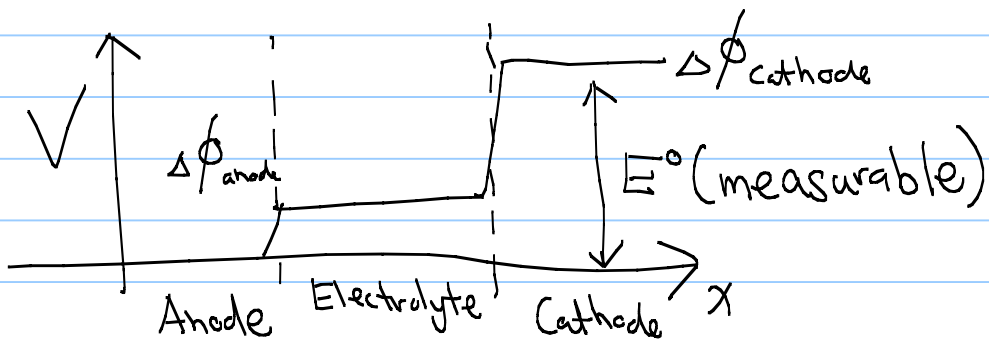
Fig
3.5

$$J = c_R^* f_1 e^{-\Delta G_1^\ddagger / RT} - c_P^* f_2 e^{-(\Delta G_2^\ddagger - \Delta G_{rxn}) / RT}$$

At equilibrium, $j_1 = j_2 = j_0$ (Dynamic equilibrium)



Obtained by introducing a voltage equivalent to overpotential



η : Difference between theoretical and real cell potential (Overpotential)

High exchange currents desirable
 \rightarrow Lower overpotential.

$$j = j_0 \left(e^{\alpha n F \eta / (RT)} - e^{- (1-\alpha) n F \eta / (RT)} \right) \quad \text{--- (1)}$$

α is transfer coefficient which describes symmetry

of activation barrier. $0 < \alpha < 1$ necessarily and $0.2 < \alpha < 0.5$

Assumption: Concentration of reactants & products ^{usually} unaffected

Without this assumption,

$$j = j_0 \left(\frac{C_R^*}{C_R^{o*}} e^{\alpha n F \eta / (RT)} - \frac{C_P^*}{C_P^{o*}} e^{-(1-\alpha) n F \eta / (RT)} \right) \quad (2)$$

① & ② is known as the Butler-Volmer equation, the cornerstone of electrochemical kinetics.