

The Use of e.m.f. Measurements with Suitable Cell for the Determination of Thermodynamic Variables.

The Equation $\Delta G = -EZF$ Shows that e.m.f. measurements can be used to determine free energy changes.

The Nernst equation $E = E^\circ + \frac{RT}{ZF} \ln a_{M^{z+}}$

is dependent on the activity of the ion taking part in the electrode reaction and

$$G_A - G_A^\circ = RT \ln a_A$$

Measurements of E for cells at various temperatures has given their temperature coefficients $(\frac{\partial E}{\partial T})_P$. Using the Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_P$$

and substituting for ΔG by $\Delta G = -EZF$

$$\Delta G = -EZF = \Delta H - TZF \left(\frac{\partial E}{\partial T} \right)_P$$

Thus, at temperature T .

$$\Delta H = TZF \left(\frac{\partial E}{\partial T} \right)_P - EZF$$

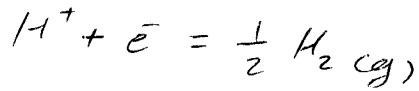
and ΔH can be calculated

$$\Delta G = \Delta H - T\Delta S$$

The kinetics of Electrode processes polarization.

polarization: The electrode potential changes from its reversible value. (if the electrode is part of a system in which a finite current is being passed, ~~it~~ it is no longer behaving thermodynamically reversibly, and it is found that the electrode potential changes from its reversible value. There are three types of polarization:

1- The hydrogen overvoltage: (η^A)
is in the discharge of hydrogen gas at a cathode from aqueous solution by the reaction.

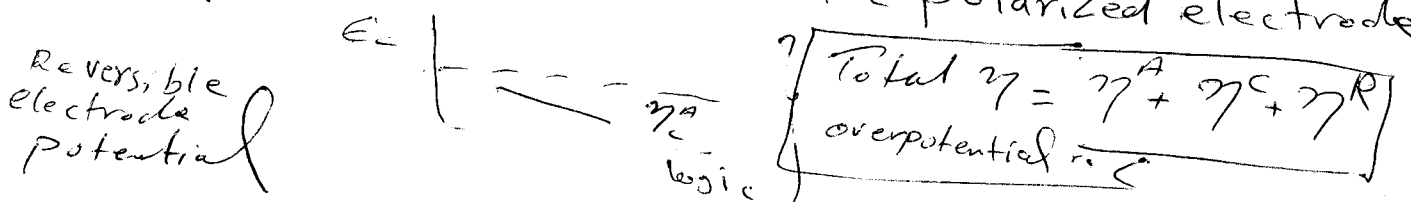


The hydrogen overvoltage varies according to the metal at which the hydrogen discharges.

2- Concentration polarization: (η^C)
irreversible behaviour of electrodes is caused by a change in concentration of the electrolyte at the surface of the electrode

3- The Resistance over potential (η^R)
The source of this polarization is an increase in the electrical resistance of the surface of the electrode. This can be caused by an oxide film deposited on the metal surface or by gas adsorbed on the metal surface.

* The overpotential at an electrode is the difference between the reversible electrode potential and the polarized electrode potential



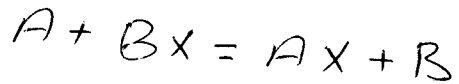
The Effects of polarization

There are two effects of polarization.

1- Decomposition Voltage.

is the voltage which must be applied in electrolysis before appreciable reactions take place in an electrolytic cell.

if the overall cell reaction is

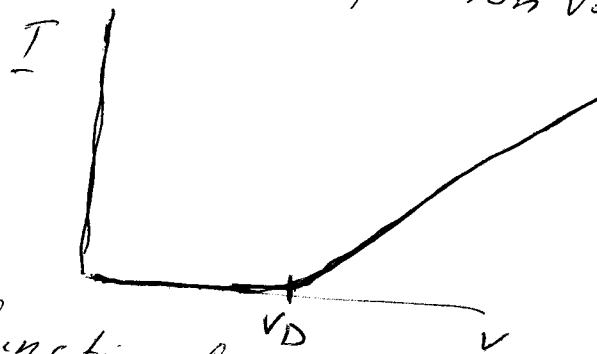


where A and B are metallic elements, X an acid.

The voltage necessary to cause this reaction to take place reversibly is $\Delta G_{\text{cell}} = -E_{\text{cell}} ZF$

Both electrodes in the cell will be polarized once a current is passed and also there will be an internal resistance "R" in the circuit. The voltage necessary to produce a current I in the cell will $\Rightarrow V = E_{\text{cell}} + |\eta_c| + |\eta_a| + IR$ where η_c and η_a are cathode and anode over potentials ~~revers~~ respectively.

* when the current first starts, the cell will be unpolarized and $I = 0$ (Zero); so that the decomposition voltage, V_D will then be equal to E_{cell} .



current I as a function of applied voltage for electrolysis, V_D is the decomposition voltage.

2- Discharge potential.

The potential at electrodes at which particular ions will discharge, and in an electrolyte containing several metal ions.

For a cathodic deposition the discharge potential

$$\text{is } E_r + \eta_c$$

EX The zinc ions will discharge at a zinc electrode when the potential of the electrode is less than $(-0.76 - 0.20)V$ because $-0.76V$ is the reversible electrode potential and $-0.20V$ is the activation overpotential for Zn^{2+} (neglecting concentration and resistance polarization).

$-0.96V$ is the discharge potential of Zn^{2+} ions under these conditions.

with hydrogen $-1.13V$