Electrochemistry

Standard EMF of a cell: $E° = E°_{cathode} - E°_{anode}$

The E° refers to standard reduction potential

The Nernst equation allows us to calculate E under nonstandard-state conditions

$$E = E° - \frac{RT}{\nu F}\ln Q = E° - \frac{0.0257}{\nu}\ln Q \qquad \text{(at 298 K)}$$

Thermodyanics of an electrochemical cell

$$\Delta G° = -\nu F E° \qquad \Delta G = -\nu F E$$

$$\left(\frac{\partial \Delta G°}{\partial T}\right)_P = -\Delta S° = -\nu F\left(\frac{\partial E°}{\partial T}\right)_P$$

$$\Delta H° = \Delta G° - T\Delta S° = -\nu F E° + \quad -\nu F T\left(\frac{\partial E°}{\partial T}\right)_P$$

By measuring E° at several temperatures, we can determine the thermodynamic parameters of an electrochemical cell.

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Equation	Conditions
$w = -P\Delta V$	Constant pressure
$w = -nRT \ln V_2/V_1$	Reversible, ideal gas, constant T
$\Delta U = q + w$	First law
$H = U + PV$	Definition
$\Delta H = \Delta U + P\Delta V$	constant P
$\Delta U = q_v$	Constant V
$\Delta H = q_P$	Constant P
$q = ms\Delta t = C\Delta t$	s and C independent of T
$\Delta U = C_V \Delta T = n\overline{C}_V \Delta T$	$\overline{C}_V$ independent of T
$\Delta H = C_P \Delta T = n\overline{C}_P \Delta T$	$\overline{C}_P$ independent of T
$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$	Ideal gas, adiabatic, reversible
$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{prods}) - \sum \nu \Delta_f H^\circ(\text{reactants})$	None
$\Delta_r H^\circ = \sum BE(\text{reactants}) - \sum BE(\text{prods})$	Only for ball-park values
$\Delta_r H^\circ_{T_2} = \Delta_r H^\circ_{T_1} + \Delta C_P (T_2 - T_1)$	C_P independent of T
$S = k \ln W$	None
$\Delta S = \frac{q_{rev}}{T}$	Reversible, constant T
$\Delta_{mix} S = nR \ln \frac{V_2}{V_1}$	Const. T
$\Delta S = \Delta H / T$	At equilibrium; constant T
$\Delta S = n\overline{C}_P \ln \frac{T_2}{T_1}$	$\overline{C}_P$ independent of T

Equation	Conditions
$G = H - TS$	Definition
$\Delta G = \Delta H - T\Delta S$	Const T
$\Delta G = nRT \ln P_2/P_1$	Ideal gas, const T
$\ln K = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$	ΔH° and ΔS° independent of.
$dP/dT = P\Delta_{vap}H/RT^2$	Ideal gas, $\Delta_{vap}H$ independ. of T
$dG = VdP - SdT$	None
$\Delta G = \Delta G^\circ + RT \ln Q$	Constant T
$\Delta G^\circ = -RT \ln K$	Constant T
$E^\circ = E^\circ_{cathode} - E^\circ_{anode}$	None (o means standard)
$E = E^\circ - \frac{RT}{\nu F} \ln Q$	
$= E^\circ - \frac{0.0257}{\nu} \ln Q$	298 K
$\Delta G^\circ = -\nu F E^\circ$ $\Delta G = -\nu F E$	None
$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_p = -\Delta S^\circ = -\nu F \left(\frac{\partial E^\circ}{\partial T}\right)_p$	None
$\Delta H^\circ = \Delta G^\circ - T\Delta S^\circ$	
$= -\nu F E^\circ + \left[-\nu F T \left(\frac{\partial E^\circ}{\partial T}\right)_p\right]$	None