The cell potential and the Gibbs energy

\[- \nu FE = \Delta_r G\]

\[\Rightarrow E = - \frac{\Delta_r G}{\nu F}\]

@ equilibrium: \(\Delta_r G = 0 \Rightarrow E = 0\)

if \(\Delta_r G < 0 \Rightarrow E > 0\) for a spontaneous reaction
if \(\Delta_r G > 0 \Rightarrow E < 0\) for a non-spontaneous reaction

and \(\Delta_r G = \Delta_r G^\Theta + RT \ln Q\)

\[\Rightarrow E = - \frac{\Delta_r G^\Theta}{\nu F} - \frac{RT}{\nu F} \ln Q = E^\Theta - \frac{RT}{\nu F} \ln Q\]

@ 25°C: 25.7 mV

@ equilibrium:

\[\ln K = \frac{\nu FE^\Theta}{RT}\]

Nernst equation

Standard cell potentials are measured relative to the standard hydrogen electrode: Pt(s) | H₂(g) | H⁺(aq) with \(E^\Theta = 0\) V

Nils Walter: Chem 260
The electrochemical series

Anode (Left): Zn$^{2+}$(aq) + 2e$^- → Zn(s); $E_R$

Cathode (Right): Cu$^{2+}$(aq) + 2e$^- → Cu(s); $E_L$

Overall (R-L): Cu$^{2+}$(aq) + Zn(s) \rightleftharpoons Cu(s) + Zn$^{2+}$(aq)

Low reduces high; high oxidizes low

$E^\ominus = E_R - E_L$

⇒ a cell reaction is spontaneous if $E_R > E_L$
The rates of reactions: Chemical kinetics
Atkins, Chapter 10

What can we learn?
→ predict how quickly a reaction mixture approaches equilibrium
→ study the reaction mechanism (understand the elementary steps)

How do we do it?
→ determine the stoichiometry and identify any side reactions
→ determine how the reagent and/or product concentrations change

A) Quenching the reaction at defined times
B) Real-time analysis by spectroscopy

Flow method

Flow diagram:
- Driving syringes
- Movable spectrometer
- Stopped-flow method
- Spectrometer
- Mixing chamber
- Stopping syringe
Kinetics can be measured when relaxing!?

Connection between kinetics and equilibrium!

@ equilibrium:
A → B is as fast as B → A

\[ K = \frac{[B]}{[A]} \]

van’t Hoff equation: T dependence of K

\[ \ln K' - \ln K = \ln \frac{K'}{K} = \frac{\Delta_r H}{R} \left( \frac{1}{T} - \frac{1}{T'} \right) \]

From the relaxation time the reaction rate can be calculated ⇒ fast reactions that reach their equilibrium quickly can be studied!
Reaction rates

Raw kinetic data: $[\text{reactant}](t)$

$\text{Initial rate } \Rightarrow \text{ faster}$

$\text{Rate} = \frac{\Delta[\text{reactant}]}{\Delta t} \quad (M^{-1}s^{-1})$

$\Rightarrow \text{Rate} = \frac{d[\text{reactant}]}{dt}$

$\text{Rates at later times } \Rightarrow \text{ slower}$

Stoichiometry and rate:

A + B $\rightarrow$ C

E.g., I$_2$ + C$_2$H$_4$ $\rightarrow$ C$_2$H$_4$I$_2$

$\Delta A = -5$
$\Delta B = -5$
$\Delta C = 5$

$2A \rightarrow C$

$\Delta A = -10$
$\Delta C = 5$

$- \frac{d[A]}{dt} = 2 \frac{d[C]}{dt}$

$\Rightarrow - \frac{1}{2} \frac{d[A]}{dt} = \frac{d[C]}{dt}$