The cell potential and the Gibbs energy

$$\boxed{-\nu FE = \Delta_r G} \Rightarrow E = -\frac{\Delta_r G}{\nu F}$$

@ 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 $\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$

@ 25°C: 25.7 mV

$$\Rightarrow \quad E = -\frac{\Delta_r G^{\ominus}}{\nu F} - \frac{RT}{\nu F} \ln Q = E^{\ominus} - \boxed{\frac{RT}{\nu F}} \ln Q$$

standard cell potential

Nernst equation

@ equilibrium:

$$\boxed{\ln K = \frac{\nu F E^{\ominus}}{RT}}$$

Standard cell potentials are measured relative to the standard hydrogen electrode: Pt(s)| H_2(g)| H^+(aq) with $E^{\ominus} = 0$ V

The electrochemical series

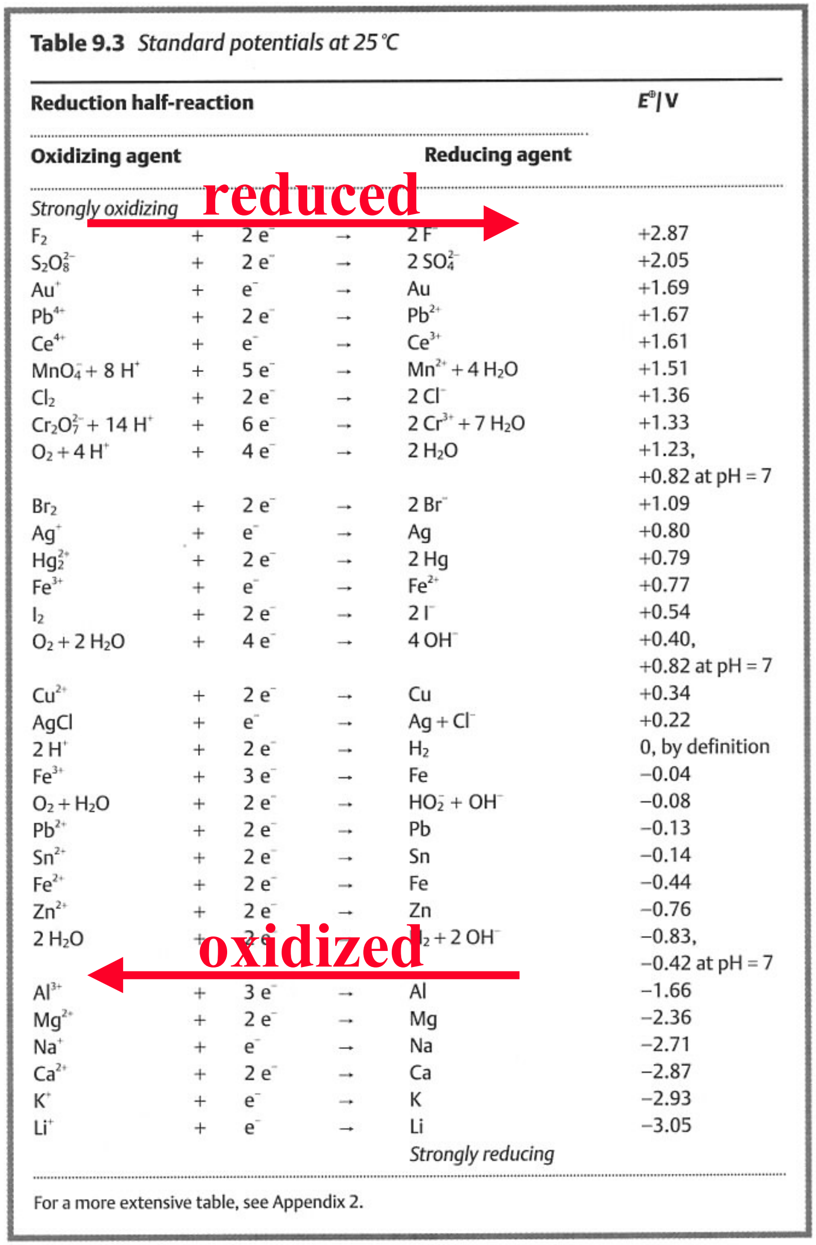
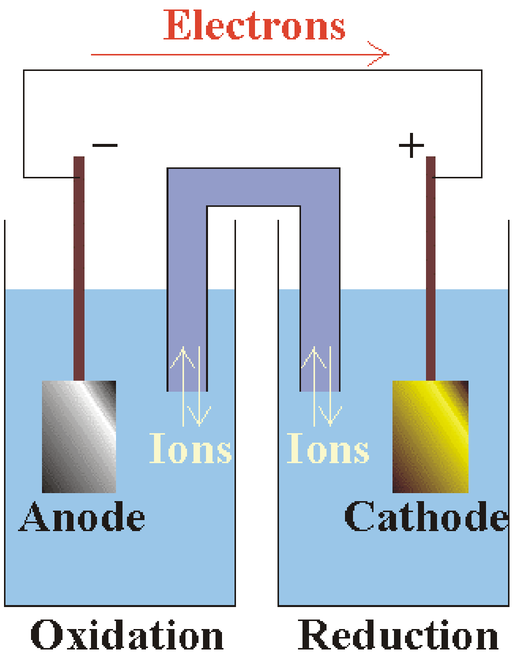


Table 9.3 *Standard potentials at 25 °C*

Reduction half-reaction **Oxidizing agent**				**Reducing agent**	$E^\ominus$/V
Strongly oxidizing					
F_2	+	2 e^-	→	2 F^-	+2.87
$S_2O_8^{2-}$	+	2 e^-	→	2 SO_4^{2-}	+2.05
Au^+	+	e^-	→	Au	+1.69
Pb^{4+}	+	2 e^-	→	Pb^{2+}	+1.67
Ce^{4+}	+	e^-	→	Ce^{3+}	+1.61
$MnO_4^- + 8\,H^+$	+	5 e^-	→	$Mn^{2+} + 4\,H_2O$	+1.51
Cl_2	+	2 e^-	→	2 Cl^-	+1.36
$Cr_2O_7^{2-} + 14\,H^+$	+	6 e^-	→	$2\,Cr^{3+} + 7\,H_2O$	+1.33
$O_2 + 4\,H^+$	+	4 e^-	→	2 H_2O	+1.23, +0.82 at pH = 7
Br_2	+	2 e^-	→	2 Br^-	+1.09
Ag^+	+	e^-	→	Ag	+0.80
Hg_2^{2+}	+	2 e^-	→	2 Hg	+0.79
Fe^{3+}	+	e^-	→	Fe^{2+}	+0.77
I_2	+	2 e^-	→	2 I^-	+0.54
$O_2 + 2\,H_2O$	+	4 e^-	→	4 OH^-	+0.40, +0.82 at pH = 7
Cu^{2+}	+	2 e^-	→	Cu	+0.34
AgCl	+	e^-	→	$Ag + Cl^-$	+0.22
2 H^+	+	2 e^-	→	H_2	0, by definition
Fe^{3+}	+	3 e^-	→	Fe	−0.04
$O_2 + H_2O$	+	2 e^-	→	$HO_2^- + OH^-$	−0.08
Pb^{2+}	+	2 e^-	→	Pb	−0.13
Sn^{2+}	+	2 e^-	→	Sn	−0.14
Fe^{2+}	+	2 e^-	→	Fe	−0.44
Zn^{2+}	+	2 e^-	→	Zn	−0.76
2 H_2O	+	2 e^-	→	$H_2 + 2\,OH^-$	−0.83, −0.42 at pH = 7
Al^{3+}	+	3 e^-	→	Al	−1.66
Mg^{2+}	+	2 e^-	→	Mg	−2.36
Na^+	+	e^-	→	Na	−2.71
Ca^{2+}	+	2 e^-	→	Ca	−2.87
K^+	+	e^-	→	K	−2.93
Li^+	+	e^-	→	Li	−3.05
				Strongly reducing	

For a more extensive table, see Appendix 2.



$$\boxed{E^\ominus = E_R^\ominus - E_L^\ominus}$$

⇒ a cell reaction is spontaneous if $E_R^\ominus > E_L^\ominus$

Cathode (**R**ight): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E_R^\ominus$

Anode (**L**eft): $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$; $E_L^\ominus$

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

Low reduces high;
high oxidizes low

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 with time (@ constant T)

A) Quenching the reaction at defined times

B) Real-time analysis by spectroscopy

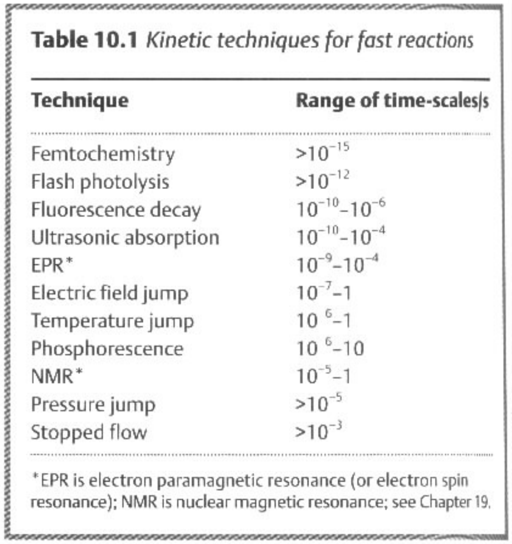
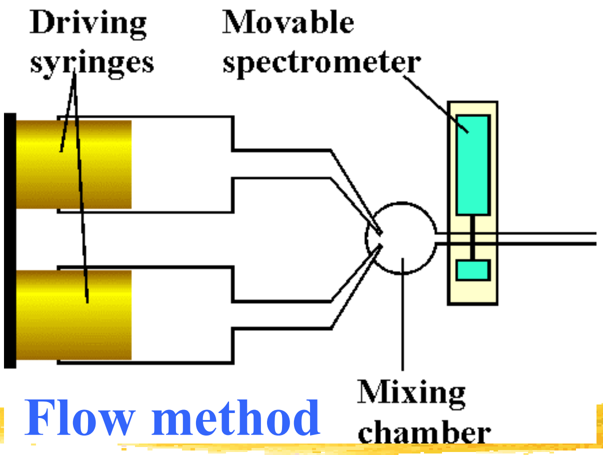


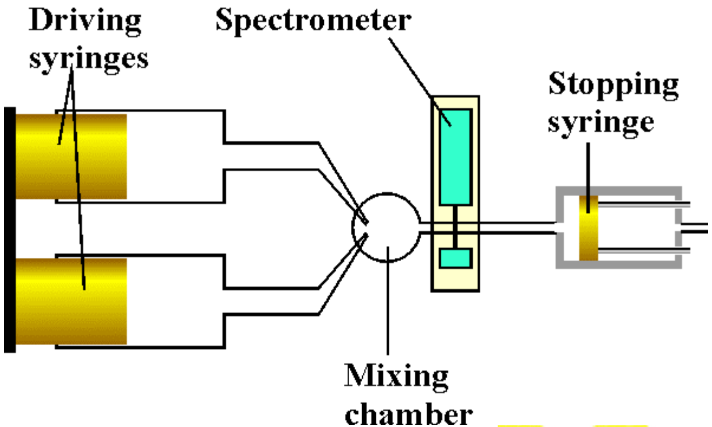
Table 10.1 *Kinetic techniques for fast reactions*

Technique	Range of time-scales/s
Femtochemistry	$>10^{-15}$
Flash photolysis	$>10^{-12}$
Fluorescence decay	10^{-10}–10^{-6}
Ultrasonic absorption	10^{-10}–10^{-4}
EPR*	10^{-9}–10^{-4}
Electric field jump	10^{-7}–1
Temperature jump	10^{6}–1
Phosphorescence	10^{6}–10
NMR*	10^{-5}–1
Pressure jump	$>10^{-5}$
Stopped flow	$>10^{-3}$

*EPR is electron paramagnetic resonance (or electron spin resonance); NMR is nuclear magnetic resonance; see Chapter 19.



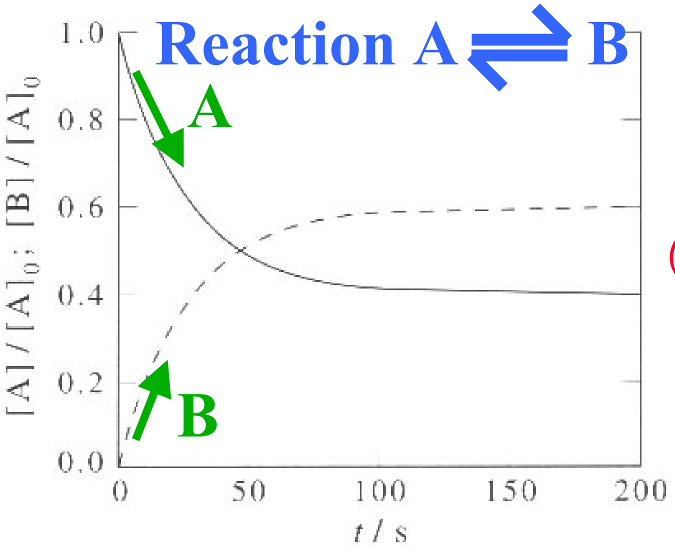
Flow method



Stopped-flow method

Kinetics can be measured when relaxing!?


Manfred Eigen: Chemistry Novel prize 1967


Reaction A $\rightleftharpoons$ B

Connection between kinetics and equilibrium!
↑

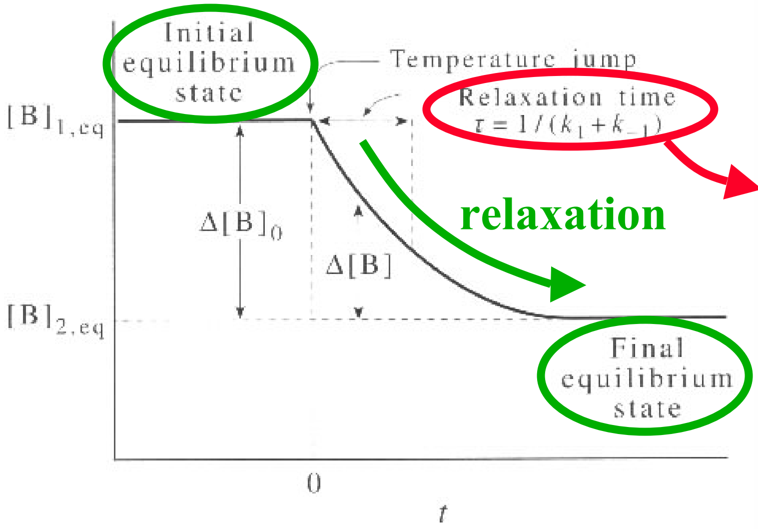
@ equilibrium:

A → B is as fast as B → A

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

van't Hoff equation:
T dependence of K

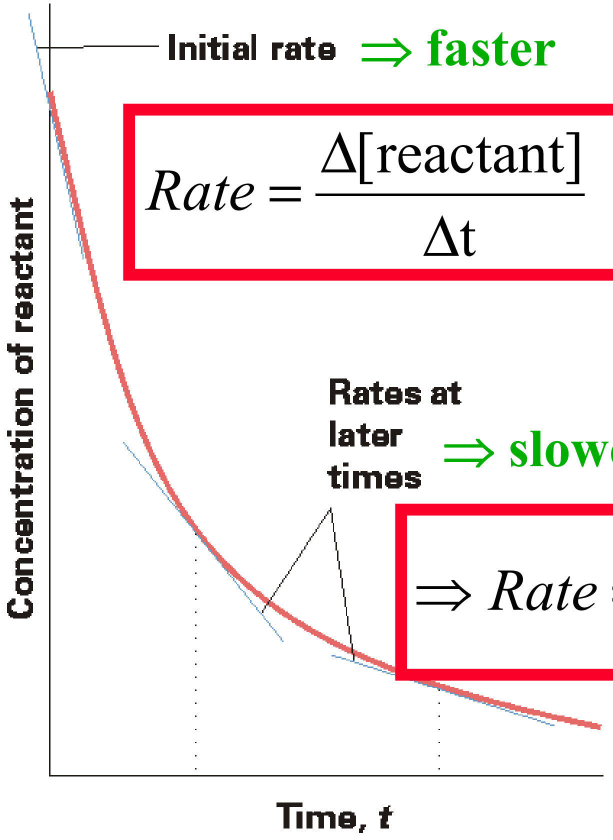
$$\ln K' - \ln K = \ln\frac{K'}{K} = \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T}-\frac{1}{T'}\right)$$



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: [reactant](t)



⇒ faster

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

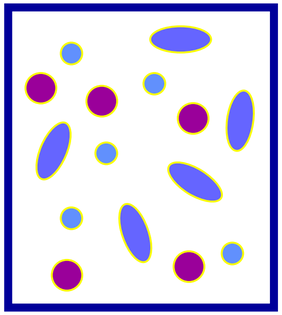
⇒ slower

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

Stoichiometry and rate:

$$A + B \rightarrow C$$

E.g., $I_2 + C_2H_4 \rightarrow C_2H_4I_2$



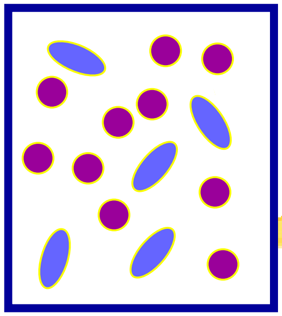
● $\Delta A = -5$

• $\Delta B = -5$

⬬ $\Delta C = 5$

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

$$2A \rightarrow C$$



● $\Delta A = -10$

⬬ $\Delta C = 5$

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