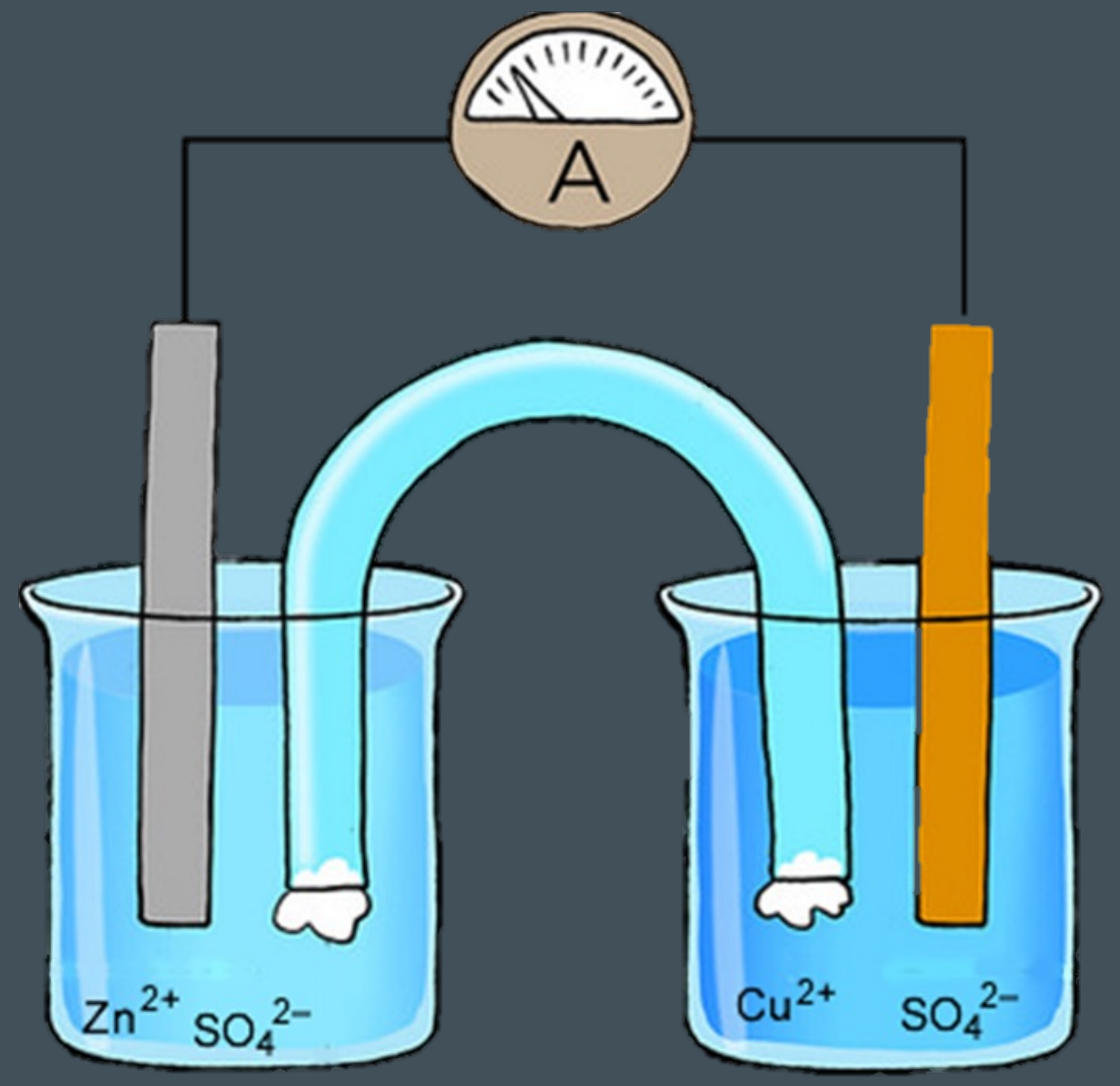
Unit 1

ELECTROCHEMISTRY

Nernst Equation - Potential and Concentration

Topics

1. Nernst Equation
2. Pourbaix Diagrams
3. Standard electrode potentials



Review: electrochemical potentials

$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$

1. Which half reaction is at the cathode?
2. Which half reaction is at the anode?
3. What is the standard cell potential?

TABLE 15-1
Standard Oxidation-Reduction Potentials and Equilibrium Constants
The values apply to temperature 25°C, with standard concentration for aqueous solutions 1*M* and standard pressure of gases 1 atm.

	$E°$	K
$Li \rightleftharpoons Li^+ + e^-$	3.05	$4 \times 10^{[illegible]}$
$Cs \rightleftharpoons Cs^+ + e^-$	2.92	$1 \times 10^{[illegible]}$
$Rb \rightleftharpoons Rb^+ + e^-$	2.92	$1 \times 10^{[illegible]}$
$K \rightleftharpoons K^+ + e^-$	2.92	$1 \times 10^{[illegible]}$
$\frac{1}{2}Ba \rightleftharpoons \frac{1}{2}Ba^{++} + e^-$	2.90	$5 \times 10^{[illegible]}$
$\frac{1}{2}Sr \rightleftharpoons \frac{1}{2}Sr^{++} + e^-$	2.89	$4 \times 10^{[illegible]}$
$\frac{1}{2}Ca \rightleftharpoons \frac{1}{2}Ca^{++} + e^-$	2.87	$2 \times 10^{[illegible]}$
$Na \rightleftharpoons Na^+ + e^-$	2.712	$4.0 \times 10^{[illegible]}$
$\frac{1}{3}Al + \frac{4}{3}OH^- \rightleftharpoons \frac{1}{3}Al(OH)_4^- + e^-$	2.35	$3 \times 10^{[illegible]}$
$\frac{1}{2}Mg \rightleftharpoons \frac{1}{2}Mg^{++} + e^-$	2.34	$2 \times 10^{[illegible]}$
$\frac{1}{2}Be \rightleftharpoons \frac{1}{2}Be^{++} + e^-$	1.85	$1 \times 10^{[illegible]}$
$\frac{1}{3}Al \rightleftharpoons \frac{1}{3}Al^{+++} + e^-$	1.67	$1 \times 10^{[illegible]}$
$\frac{1}{2}Zn + 2OH^- \rightleftharpoons \frac{1}{2}Zn(OH)_4^{--} + e^-$	1.216	$2.7 \times 10^{[illegible]}$
$\frac{1}{2}Mn \rightleftharpoons \frac{1}{2}Mn^{++} + e^-$	1.18	$7 \times 10^{[illegible]}$
$\frac{1}{2}Zn + 2NH_3 \rightleftharpoons \frac{1}{2}Zn(NH_3)_4^{++} + e^-$	1.03	2×10^{17}
$Co(CN)_6^{----} \rightleftharpoons Co(CN)_6^{---} + e^-$	0.83	1×10^{14}
$\frac{1}{2}Zn \rightleftharpoons \frac{1}{2}Zn^{++} + e^-$	.762	$6.5 \times 10^{[illegible]}$
$\frac{1}{3}Cr \rightleftharpoons \frac{1}{3}Cr^{+++} + e^-$	.74	$3 \times 10^{[illegible]}$
$\frac{1}{2}H_2C_2O_4(aq) \rightleftharpoons CO_2 + H^+ + e^-$	.49	2×10^{8}
$\frac{1}{2}Fe \rightleftharpoons \frac{1}{2}Fe^{++} + e^-$	.440	2.5×10^{7}
$\frac{1}{2}Cd \rightleftharpoons \frac{1}{2}Cd^{++} + e^-$	.402	5.7×10^{6}
$\frac{1}{2}Co \rightleftharpoons \frac{1}{2}Co^{++} + e^-$	.277	4.5×10^{4}
$\frac{1}{2}Ni \rightleftharpoons \frac{1}{2}Ni^{++} + e^-$	.250	1.6×10^{4}
$I^- + Cu \rightleftharpoons CuI(s) + e^-$	.187	1.4×10^{3}
$\frac{1}{2}Sn \rightleftharpoons \frac{1}{2}Sn^{++} + e^-$	.136	1.9×10^{2}
$\frac{1}{2}Pb \rightleftharpoons \frac{1}{2}Pb^{++} + e^-$	.126	1.3×10^{2}
$\frac{1}{2}H_2 \rightleftharpoons H^+ + e^-$	.000	1
$\frac{1}{2}H_2S \rightleftharpoons \frac{1}{2}S + H^+ + e^-$	−0.141	4.3×10^{-3}
$Cu^+ \rightleftharpoons Cu^{++} + e^-$	−0.153	2.7×10^{-3}
$\frac{1}{2}H_2O + \frac{1}{2}H_2SO_3 \rightleftharpoons \frac{1}{2}SO_4^{--} + 2H^+ + e^-$	−0.17	1×10^{-3}
$\frac{1}{2}Cu \rightleftharpoons \frac{1}{2}Cu^{++} + e^-$	−0.345	1.6×10^{-6}
$Fe(CN)_6^{----} \rightleftharpoons Fe(CN)_6^{---} + e^-$	−0.36	9×10^{-7}
$I^- \rightleftharpoons \frac{1}{2}I_2(s) + e^-$	−0.53	1×10^{-9}
$MnO_4^{--} \rightleftharpoons MnO_4^- + e^-$	−0.54	1×10^{-9}
$\frac{4}{3}OH^- + \frac{1}{3}MnO_2 \rightleftharpoons \frac{1}{3}MnO_4^- + \frac{2}{3}H_2O + e^-$	−0.57	$3 \times 10^{[illegible]}$
$\frac{1}{2}H_2O \rightleftharpoons \frac{1}{4}O_2 + H^+ + e^-$	−0.682	$3.5 \times 10^{[illegible]}$
$Fe^{++} \rightleftharpoons Fe^{+++} + e^-$	−0.771	$1.1 \times 10^{[illegible]}$
$Hg \rightleftharpoons \frac{1}{2}Hg_2^{++} + e^-$	−0.799	$3.7 \times 10^{[illegible]}$
$Ag \rightleftharpoons Ag^+ + e^-$	−0.800	$3.5 \times 10^{[illegible]}$
$H_2O + NO_2 \rightleftharpoons NO_3^- + 2H^+ + e^-$	−0.81	$3 \times 10^{[illegible]}$
$\frac{1}{2}Hg \rightleftharpoons \frac{1}{2}Hg^{++} + e^-$	−0.854	$4.5 \times 10^{[illegible]}$
$\frac{1}{2}Hg_2^{++} \rightleftharpoons Hg^{++} + e^-$	−0.910	$5.0 \times 10^{[illegible]}$
$\frac{1}{2}HNO_2 + \frac{1}{2}H_2O \rightleftharpoons \frac{1}{2}NO_3^- + \frac{3}{2}H^+ + e^-$	−0.94	$2 \times 10^{[illegible]}$
$NO + H_2O \rightleftharpoons HNO_2 + H^+ + e^-$	−0.99	$2 \times 10^{[illegible]}$
$\frac{1}{2}ClO_3^- + \frac{1}{2}H_2O \rightleftharpoons \frac{1}{2}ClO_4^- + H^+ + e^-$	−1.00	$2 \times 10^{[illegible]}$
$Br^- \rightleftharpoons \frac{1}{2}Br_2(l) + e^-$	−1.065	$1.3 \times 10^{[illegible]}$
$H_2O + \frac{1}{2}Mn^{++} \rightleftharpoons \frac{1}{2}MnO_2 + 2H^+ + e^-$	−1.23	$2 \times 10^{[illegible]}$
$Cl^- \rightleftharpoons \frac{1}{2}Cl_2 + e^-$	−1.358	$1.5 \times 10^{[illegible]}$
$\frac{7}{6}H_2O + \frac{1}{3}Cr^{+++} \rightleftharpoons \frac{1}{6}Cr_2O_7^{--} + \frac{7}{3}H^+ + e^-$	−1.36	$1 \times 10^{[illegible]}$
$\frac{1}{2}H_2O + \frac{1}{6}Cl^- \rightleftharpoons \frac{1}{6}ClO_3^- + H^+ + e^-$	−1.45	$4 \times 10^{[illegible]}$
$\frac{1}{3}Au \rightleftharpoons \frac{1}{3}Au^{+++} + e^-$	−1.50	$6 \times 10^{[illegible]}$
$\frac{4}{5}H_2O + \frac{1}{5}Mn^{++} \rightleftharpoons \frac{1}{5}MnO_4^- + \frac{8}{5}H^+ + e^-$	−1.52	$3 \times 10^{[illegible]}$
$\frac{1}{2}Cl_2 + H_2O \rightleftharpoons HClO + H^+ + e^-$	−1.63	$4 \times 10^{[illegible]}$
$H_2O \rightleftharpoons \frac{1}{2}H_2O_2 + H^+ + e^-$	−1.77	$2 \times 10^{[illegible]}$
$Co^{++} \rightleftharpoons Co^{+++} + e^-$	−1.84	$1 \times 10^{[illegible]}$
$F^- \rightleftharpoons \frac{1}{2}F_2 + e^-$	−2.65	$4 \times 10^{[illegible]}$

Review: standard potentials and equilibrium

Equivalence of electrochemical potential and Gibbs free energy

$$E = \frac{-\Delta G}{nF}$$

$$E° = \frac{-\Delta G°}{nF}$$ (standard state)

Equilibrium constant

$$-\Delta G° = RT ln(K_{eq})$$

$$K_{eq} = e^{\frac{nE°F}{RT}}$$

Temperature dependance

Hydrogen fuel cell reaction: How will the generators voltage change with temperature?

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

$$2H_2 + O_2 \xrightarrow{\Delta V} 2H_2O$$

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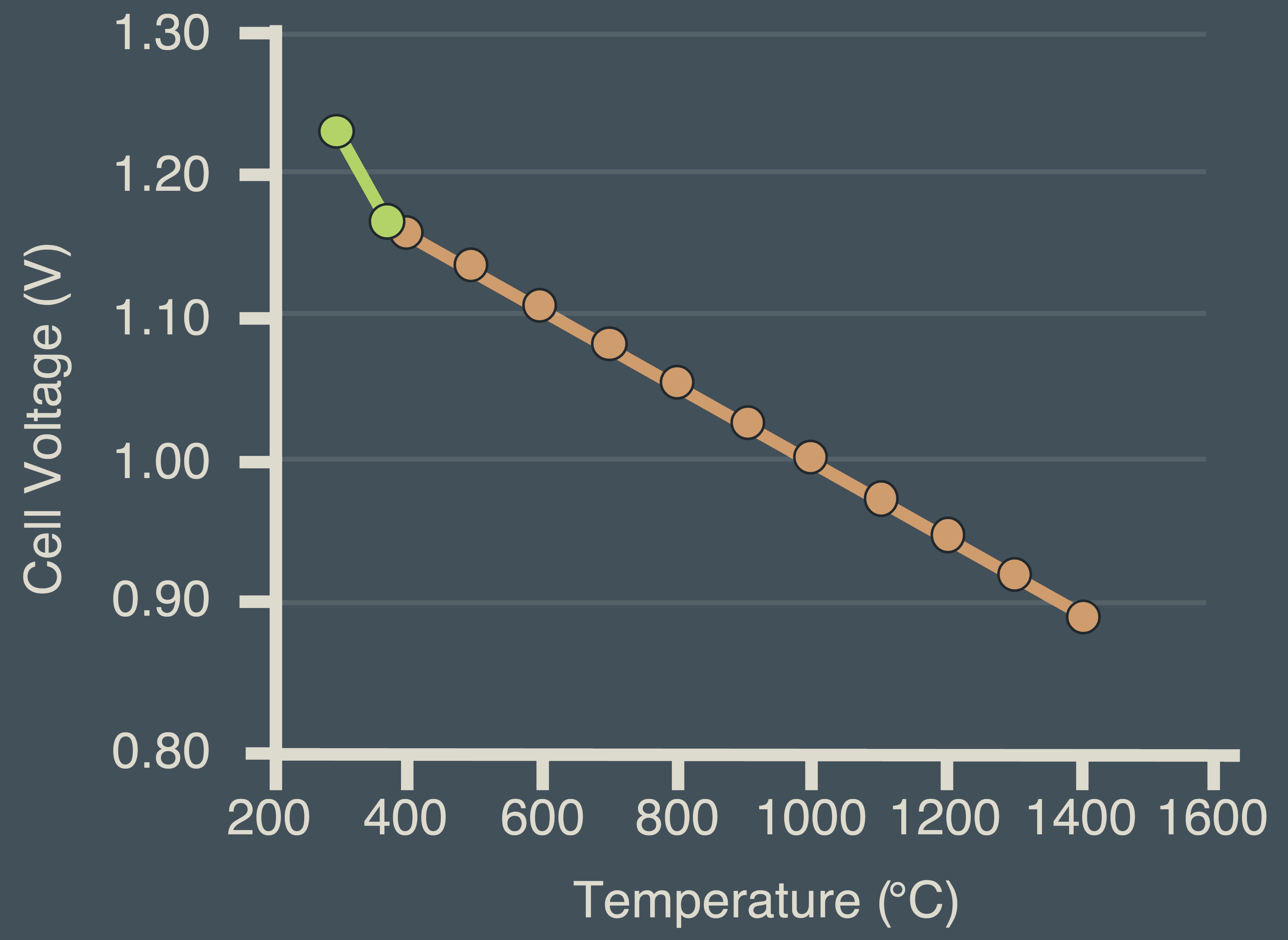
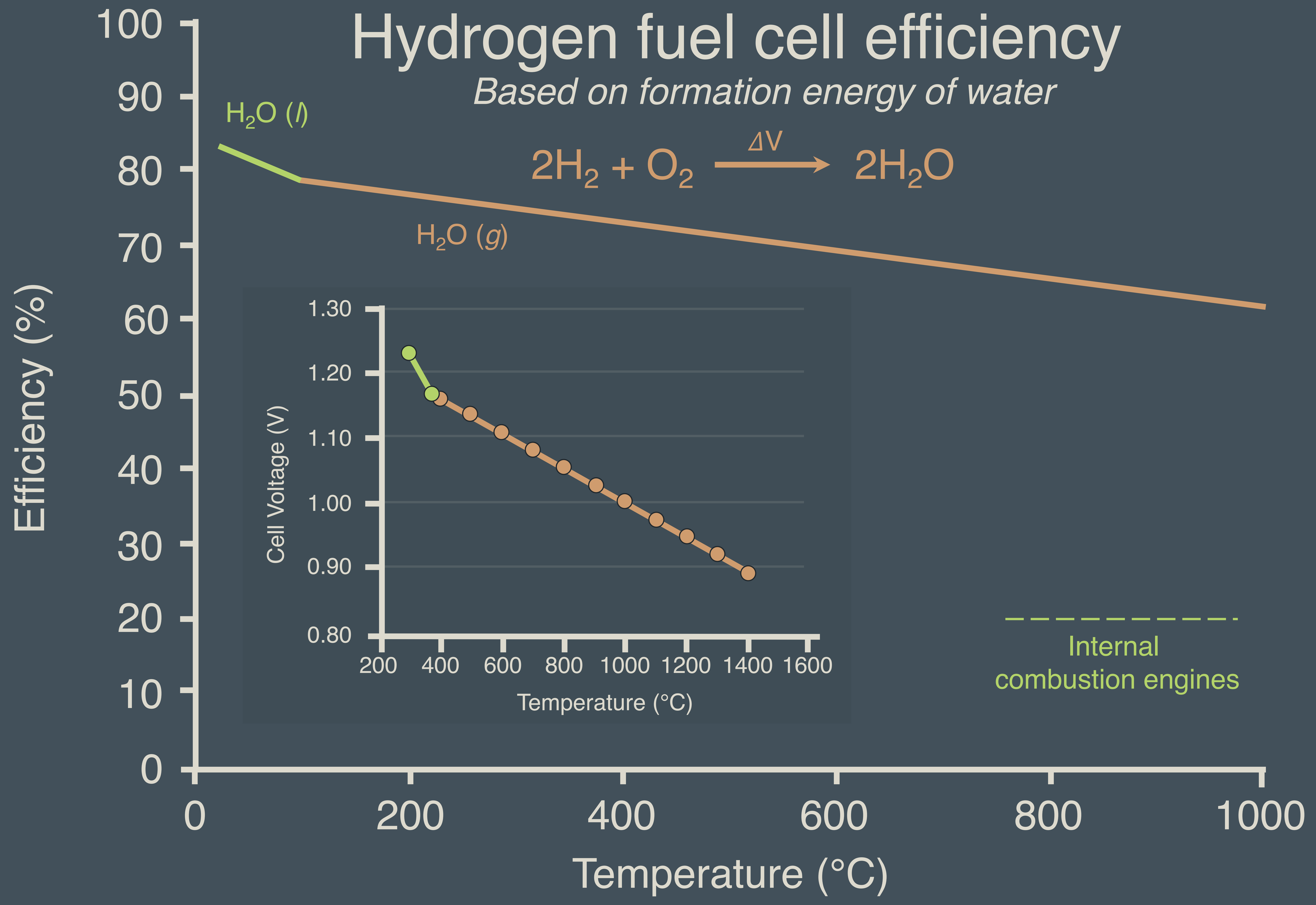


Temperature dependance

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



Efficiency

$$\epsilon = \frac{\Delta G}{\Delta H} = \frac{\Delta T}{\mathrm{T}}$$

Maximum theoretical energy efficiency heat engine

Heat engines are generally much lower efficiency at easily achievable temperature < 1000 °C

Concentration dependance

Electrochemistry uses the same equilibrium relations equations you've seen before:

Recall: $\Delta G = \Delta G° + RTlnQ$

$\Delta G = -nEF$

Nernst Equation

$$E_{cell} = E° - \frac{RT}{nF} lnQ$$

Nernst equation: chemical equilibrium

$$\Delta G = \Delta G° + RT lnQ$$

$$nEF = -\Delta G$$

Nernst Equation $E_{cell} = E° - \frac{RT}{nF} lnQ$

Consider the two half reactions:

$Co(CN)_6^{4-} \longrightarrow Co(CN)_6^{3-} + e^-$ $\Delta E° = 0.83$ V

$Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + e^-$ $\Delta E° = –0.36$ V

What is the equilibrium constant for the spontaneous reaction?

Concentration cells

$$\Delta G = \Delta G° + RT ln Q$$

$$nEF = -\Delta G$$

Nernst Equation $E_{cell} = E° - \frac{RT}{nF} ln Q$

$Cr(s) + Pb^{2+}(aq) \longrightarrow Pb(s) + Cr^{2+}(aq)$

What is the value of n in the Nernst equation?

Concentration cells

$$\Delta G = \Delta G° + RT lnQ$$

$$nEF = -\Delta G$$

Nernst Equation $E_{cell} = E° - \frac{RT}{nF} lnQ$

Zn | Zn^{2+} (2 M) || Cu^{2+}(0.0002 M) | Cu

$Zn^{2+} + 2e^- \longrightarrow Zn\ (s)$ E° = –0.76

$Cu^{2+} + 2e^- \longrightarrow Cu\ (s)$ E° = 0.34

1. What is the cell voltage at 25°C?
2. What is the concentration of Cu at equilibrium?

Concentration cells

$$\Delta G = \Delta G° + RT lnQ$$

$$nEF = -\Delta G$$

Nernst Equation $$E_{cell} = E° - \frac{RT}{nF} lnQ$$

$Fe(s) + Mn^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Mn(s)$
($E°$ = 0.77 V at 25 °C)

What is [Fe^{2+}] if [Mn^{2+}] = 0.050 M and E = 0.78 V?
(Assume T is 298 K)