# Summary Lecture 1 (glossery: see App. B, SG)

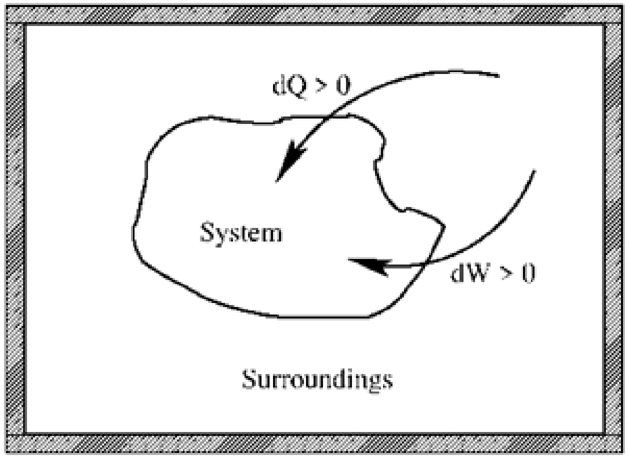
- **First law: conservation of energy**

$$dU = dW + dQ$$

$$\Delta U = \int dU = W + Q$$

$$\oint dU = 0$$

$U$ is a state function




Reversible process

- Mechanical work

$$W = -\int P_{\text{ext}}\, dV = -\int P\, dV$$

- Perfect gas

$$PV = nRT$$

Equation of state

- Perfect atomic gas

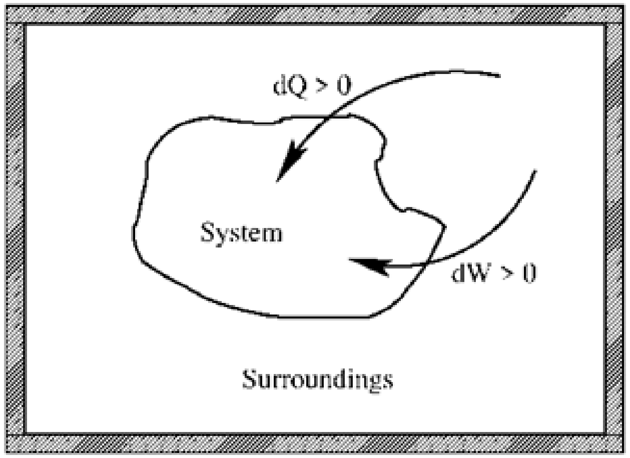
$$U = \frac{3}{2} nRT = \frac{3}{2} PV$$

# Summary Lecture 2 (second law and entropy)

**Second law:**
**for any spontaneous process**

$$\boxed{dS_{tot} = dS + dS_{sur} \geq 0}$$

$$\boxed{dS \equiv \frac{dQ^{rev}}{T}}$$




**$S$ is a state function, so independent of path**

**Alternative form: Clausius inequality:**

$$\boxed{dQ \leq TdS} \quad \begin{cases} \boxed{dQ^{rev} = TdS} & \textbf{Reversible process} \\ \boxed{dQ^{irr} < TdS} & \textbf{Irreversible process} \end{cases}$$

# Summary Lecture 2 (alternative energy functions)

**Internal energy** $\boxed{U}$

**Enthalpy** $\boxed{H \equiv U + PV}$

**Helmholtz free energy** $\boxed{A \equiv U - TS}$

**Gibbs free energy** $\boxed{G \equiv H - TS}$

**State functions**

$$\boxed{dU = TdS - PdV} \Rightarrow \boxed{dU\big|_V = TdS}$$

$$\boxed{dH = TdS + VdP} \Rightarrow \boxed{dH\big|_P = TdS}$$

$$\boxed{dA = -SdT - PdV} \Rightarrow \boxed{dA\big|_{T,V} = 0}$$

$$\boxed{dG = -SdT + VdP} \Rightarrow \boxed{dG\big|_{T,P} = 0}$$

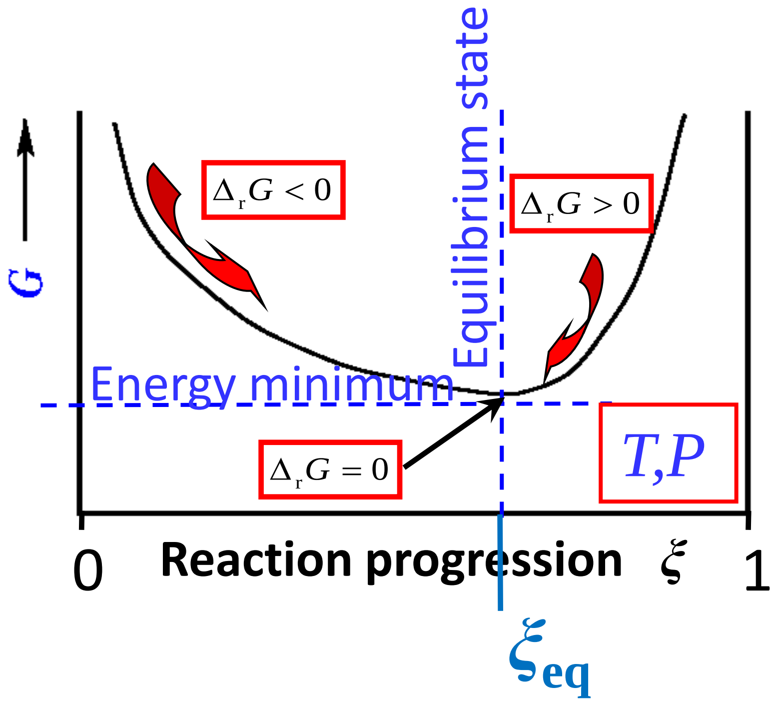
**Heat capacities**

$$\boxed{C_V \equiv \left(\frac{\partial U}{\partial T}\right)\bigg|_V} \quad \boxed{C_P \equiv \left(\frac{\partial H}{\partial T}\right)\bigg|_P}$$

# Summary Lecture 3 (chemical equilibria)

**Second law→** $\left. dG \right|_{P,T} \leq 0$

$$\Delta_r G \equiv \left( \frac{\partial G}{\partial \xi} \right)_{P,T}$$

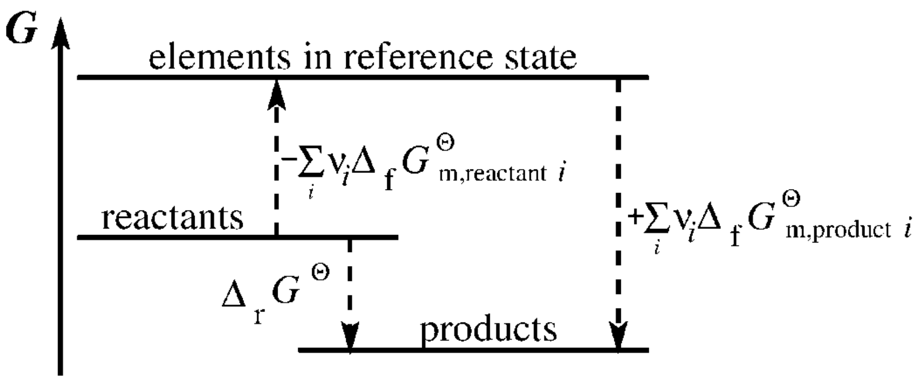



$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

| $\Delta_r G$ | reaction |
|---|---|
| $\Delta_r G < 0$ | → |
| $\Delta_r G > 0$ | ← |
| $\Delta_r G = 0$ | ↔ |

$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G^{\Theta}_{m,i} \quad \Rightarrow \quad K = \exp\left[ -\frac{\Delta_r G^{\Theta}}{RT} \right]$$

# Summary Lecture 3 (formation energies)




$$\boxed{\Delta_f G^{\ominus}_{\mathrm{m},i} = \Delta_f H^{\ominus}_{\mathrm{m},i} - T\Delta_f S^{\ominus}_{\mathrm{m},i}}$$

**At constant, chosen $T$**

**For all elements in their reference states at $T$** $\boxed{\Delta_f G^{\ominus}_{\mathrm{m},i} \equiv 0}$

**For all elements in their reference states at $T$** $\boxed{\Delta_f H^{\ominus}_{\mathrm{m},i} \equiv 0}$

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**For gaseous mixtures**

Partial pressure

$$\boxed{P_i \equiv x_i P}$$

Mole fraction

$$\boxed{x_i \equiv \frac{n_i}{n} = \frac{n_i}{\sum_j n_j}}$$

**For perfect gas mixtures**

$$\boxed{Q = \prod_i \left(\frac{P_i}{P^{\ominus}}\right)^{\nu_i}}$$

# Summary Lecture 3 (chemical equilibria)

**Second law→** $\boxed{dG|_{P,T} \leq 0}$ **(for any system)**

**Non-quilibrium $\xi$**

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

**Equilibrium $\xi_{eq}$**

$$\Delta_r G = 0$$

**Equilibrium constant: $K$**

$$\Delta_r G^{\Theta} = -RT \ln Q_{eq} \equiv -RT \ln K$$

$$K = \exp\left[-\frac{\Delta_r G^{\Theta}}{RT}\right]$$

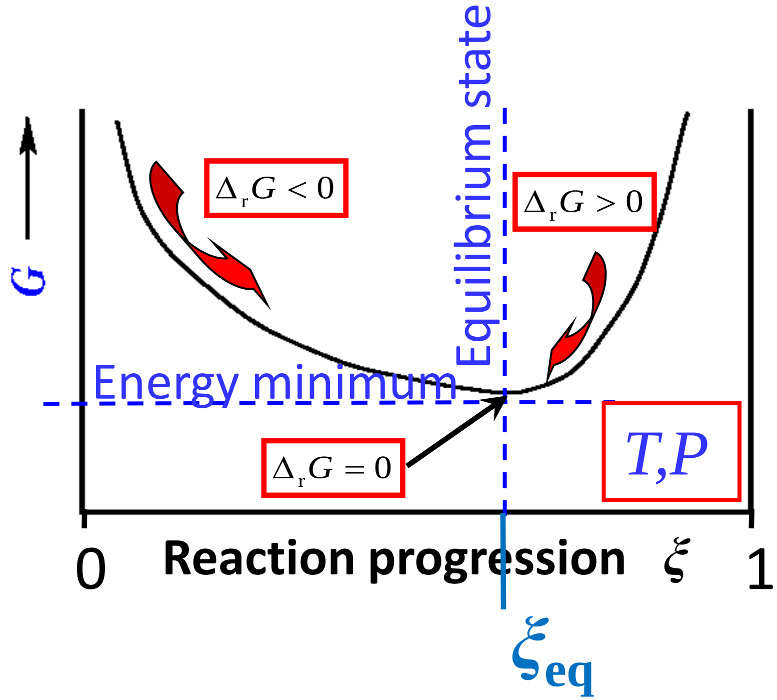
$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G^{\Theta}_{m,i}$$

$\Theta$ $\begin{cases} P = P^{\Theta} \equiv 1 \text{ bar (standard pressure)} \\ \text{component } i \text{ is pure (as if it is not in a mixture)} \end{cases}$

$$\mu_i^{\Theta} = \mu_i^{\Theta}(T)$$

# Lecture 4: Chemical reaction equilibria cont$^{d}$

# Chemical reaction equilibria: activities




$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

| $\Delta_r G$ | reaction |
|---|---|
| $\Delta_r G < 0$ | → |
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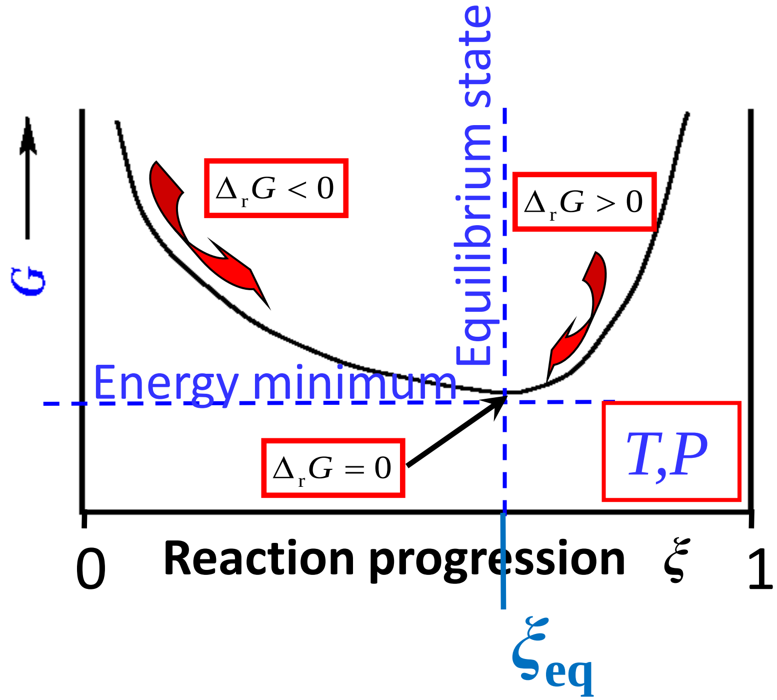
| $\Delta_r G = 0$ | ↔ |

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G^\ominus_{m,i} \Rightarrow K = \exp\left[-\frac{\Delta_r G^\ominus}{RT}\right]$$

$$RT \ln Q = ? \Rightarrow$$ **For perfect gas mixtures** $$Q = \prod_i \left(\frac{P_i}{P^\ominus}\right)^{\nu_i}$$

# Chemical reaction equilibria: activities




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

| $\Delta_r G$ | reaction |
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| $\Delta_r G < 0$ | → |
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$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G^{\Theta}_{m,i} \Rightarrow K = \exp\left[-\frac{\Delta_r G^{\Theta}}{RT}\right]$$

$$RT \ln Q = ? \Rightarrow$$

**For perfect gas mixtures** $Q = \prod_i \left(\frac{P_i}{P^{\Theta}}\right)^{\nu_i}$

**What to do with real systems?**

# Chemical reaction equilibria: activities

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

$$\boxed{RT \ln Q = ?}$$ ⇒ **For perfect gas mixtures** $$\boxed{Q = \prod_i \left( \frac{P_i}{P^{\ominus}} \right)^{\nu_i}}$$

**What to do with real systems?**

# Chemical reaction equilibria: activities

$$\Delta_r G = \Delta_r G^\Theta + RT \ln Q$$

$$RT \ln Q = ?$$

**For perfect gas mixtures**

$$Q = \prod_i \left( \frac{P_i}{P^\Theta} \right)^{\nu_i}$$

$$\Delta_r G \equiv \left( \frac{\partial G}{\partial \xi} \right)\bigg|_{T,P} = \sum_i \nu_i \mu_i = \sum_i \nu_i \mu_i^\Theta + \sum_i \nu_i RT \ln \frac{P_i}{P^\Theta}$$

**The chemical potential of perfect gas component *i***

$$\mu_i = \mu_i^\Theta + RT \ln \frac{P_i}{P^\Theta}$$

**What to do with real systems?**

# Chemical reaction equilibria: activities

**What is the chemical potential of a component *i* in real systems?**

$$\boxed{dG = -SdT + VdP + \sum_i \mu_i dn_i}$$

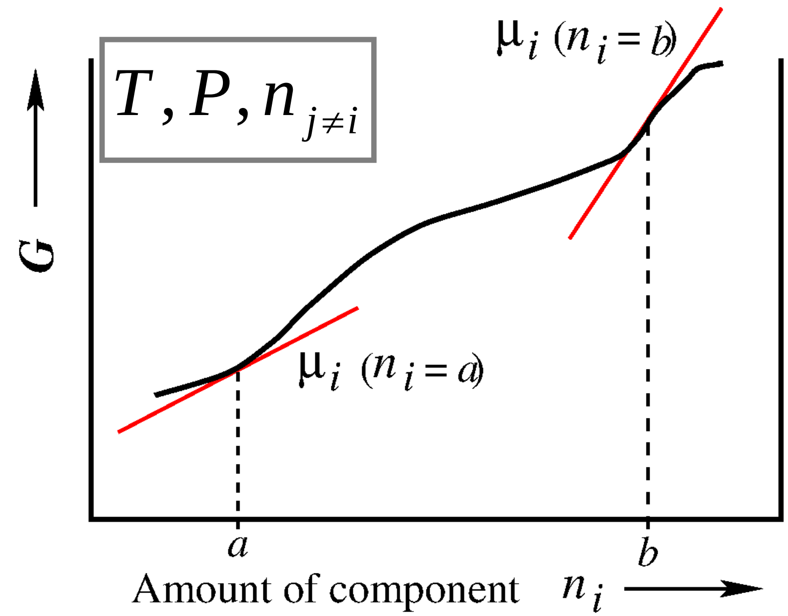
$$\Rightarrow \boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}}$$

# Chemical reaction equilibria: activities

**What is the chemical potential of a component *i* in real systems?**

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$




**Real systems**
- **real gases**
- **liquids**
- **solids**
- **solutions**

**molecules not independent; also have interactions other than hard sphere collisions**

# Chemical reaction equilibria: activities

**The chemical potential of perfect gas component *i***

$$\mu_i = \mu_i^{\Theta} + RT \ln \frac{P_i}{P^{\Theta}}$$

**Real systems** — **real gases**, **liquids**, **solids**, **solutions** — **molecules not independent; also have interactions other than hard sphere collisions**

$$\cancel{\mu_i = \mu_i^{\Theta} + RT \ln \frac{P_i}{P^{\Theta}}}$$

$$\Rightarrow \quad \boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i}$$

$$\Delta_r G = \sum_i \nu_i \mu_i^{\Theta} + \sum_i \nu_i RT \ln a_i$$

***a**$_i$* **is the activity of component *i* in a solution or mixture**

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\ominus} + RT \ln a_i}$$

**Real systems**

$$\Rightarrow \boxed{\Delta_r G = \underbrace{\sum_i \nu_i \mu_i^{\ominus}}_{\equiv \Delta_r G^{\ominus}} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}}$$

$$\Downarrow$$

$$\boxed{Q = \prod_i a_i^{\nu_i}}$$

$$\Downarrow$$

$$\boxed{K = \left( \prod_i a_i^{\nu_i} \right)_{\mathrm{eq}}}$$

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i} \Rightarrow \boxed{\Delta_\mathrm{r} G = \underbrace{\sum_i \nu_i \mu_i^{\Theta}}_{\equiv \Delta_\mathrm{r} G^{\Theta}} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}}$$

**Real systems**

$$\boxed{\Delta_\mathrm{r} G \neq 0} \qquad \boxed{\Delta_\mathrm{r} G = \Delta_\mathrm{r} G^{\Theta} + RT \ln Q} \Leftrightarrow \boxed{Q = \prod_i a_i^{\nu_i}}$$

**Equilibrium**

$$\boxed{\Delta_\mathrm{r} G = 0}$$

**Equilibrium constant**

$$\boxed{K = \exp\left[-\frac{\Delta_\mathrm{r} G^{\Theta}}{RT}\right]} \Leftrightarrow \boxed{K = \left(\prod_i a_i^{\nu_i}\right)_\mathrm{eq}}$$

# Chemical reaction equilibria: activities

$$\mu_i \equiv \mu_i^{\ominus} + RT \ln a_i$$

**Real systems**

$$\Delta_r G = \underbrace{\sum_i \nu_i \mu_i^{\ominus}}_{\sum_i \nu_i \Delta_f G_{m,i}^{\ominus} = \Delta_r G^{\ominus}} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}$$

$$Q = \prod_i a_i^{\nu_i}$$

$$\Delta_r G \neq 0$$

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

**Equilibrium**

$$\Delta_r G = 0$$

**Equilibrium constant**

$$K = \exp\left[-\frac{\Delta_r G^{\ominus}}{RT}\right]$$

$$K = \left(\prod_i a_i^{\nu_i}\right)_{\text{eq}}$$

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i}$$

**Real systems**

$$\Rightarrow \boxed{\Delta_r G = \underbrace{\sum_i \nu_i \mu_i^{\Theta}} + \sum_i \nu_i RT \ln a_i}$$

$$\boxed{\sum_i \nu_i \Delta_f G_{m,i}^{\Theta} = \Delta_r G^{\Theta}}$$

$\Theta$ $\begin{cases} P = P^{\Theta} \equiv 1 \text{ bar (standard pressure)} \\ \text{component } i \text{ is pure (as if it is not in a mixture)} \end{cases}$

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i} \Rightarrow \boxed{\Delta_r G = \underbrace{\sum_i \nu_i \mu_i^{\Theta}}_{} + \sum_i \nu_i RT \ln a_i}$$

**Real systems**

$$\boxed{\sum_i \nu_i \Delta_f G_{m,i}^{\Theta} = \Delta_r G^{\Theta}}$$

$\Theta$
- $P = P^{\Theta} \equiv 1$ bar (standard pressure)
- component $i$ is pure (as if it is not in a mixture)

$\boxed{\Delta_f G_{m,i}^{\Theta}}$ is independent of interactions in real systems

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\ominus} + RT \ln a_i}$$

$$\Delta_r G = \sum_i \nu_i \mu_i^{\ominus} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}$$

**Real systems**

$$\boxed{Q = \prod_i a_i^{\nu_i}}$$

***$a_i$* is the activity of component *$i$* in a solution or mixture**

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i} \Rightarrow \boxed{\Delta_r G = \sum_i \nu_i \mu_i^{\Theta} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}}$$

**Real systems**

$$\boxed{Q = \prod_i a_i^{\nu_i}}$$

**For perfect gas mixtures**

$$\boxed{Q = \prod_i \left(\frac{P_i}{P^{\Theta}}\right)^{\nu_i}} \Leftrightarrow \boxed{Q = \prod_i a_i^{\nu_i}}$$

⇒ **For perfect gas mixtures**

$$\boxed{a_i = \frac{P_i}{P^{\Theta}}}$$

**$a_i$ is the activity of component $i$ in a solution or mixture**

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i} \Rightarrow \boxed{\Delta_r G = \sum_i \nu_i \mu_i^{\Theta} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}}$$

**Real systems**

$$\boxed{Q = \prod_i a_i^{\nu_i}}$$

**For perfect gas mixtures** $\boxed{Q = \prod_i \left( \frac{P_i}{P^{\Theta}} \right)^{\nu_i}} \Leftrightarrow \boxed{Q = \prod_i a_i^{\nu_i}}$

⇒ **For perfect gas mixtures** $\boxed{a_i = \frac{P_i}{P^{\Theta}}}$

**Liquids and solids are virtually incompressible**

- **For pure liquids** $\boxed{a_l \approx 1}$
- **For pure solids** $\boxed{a_s \approx 1}$

# Chemical reaction equilibria: activities

$$\boxed{\mu_i \equiv \mu_i^{\ominus} + RT \ln a_i} \Rightarrow \boxed{\Delta_r G = \sum_i \nu_i \mu_i^{\ominus} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}}$$

**Real systems**

**For perfect gas mixtures**

$$\boxed{Q = \prod_i \left(\frac{P_i}{P^{\ominus}}\right)^{\nu_i}} \Leftrightarrow \boxed{Q = \prod_i a_i^{\nu_i}}$$

**For perfect gas mixtures** $\boxed{a_i = \frac{P_i}{P^{\ominus}}}$

**Liquids and solids are virtually incompressible**

**For pure liquids** $\boxed{a_l \approx 1}$

**For pure solids** $\boxed{a_s \approx 1}$

**So what about solutions?**

# Chemical reaction equilibria: Electrochemistry

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i} \Rightarrow \boxed{\Delta_r G = \sum_i \nu_i \mu_i^{\Theta} + \underbrace{\sum_i \nu_i RT \ln a_i}_{\equiv RT \ln Q}}$$

$$\boxed{Q = \prod_i a_i^{\nu_i}}$$

**For perfect gas mixtures** $\boxed{a_i = \frac{P_i}{P^{\Theta}}}$

**For pure liquids** $\boxed{a_l \approx 1}$

**For pure solids** $\boxed{a_s \approx 1}$

**So what about solutions?**
- **Neutral solutions (Lecture 5)**
- **Electrolytes (ions): Electrochemistry**

# Chemical reaction equilibria: Electrochemistry

## Electrochemistry: redox reactions; a few concepts:

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

**Reduction halfreaction**

$$\text{Oxidizing agent} + \nu e^- \longrightarrow \text{Reducing agent}$$

$$\text{Oxidant} + \nu e^- \longrightarrow \text{Reductant}$$

$$\text{Ox} + \nu e^- \longrightarrow \text{Red}$$

$$\boxed{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)}$$

**redox reactions: electron transfer**

# Chemical reaction equilibria: Electrochemistry

## Electrochemistry: redox reactions; a few concepts:

$$MnO_4^-(aq) + 8H^+(aq) + \boxed{5e^-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

**Reduction halfreaction**

Oxidizing agent + νe⁻ ⟶ Reducing agent

Oxidant + νe⁻ ⟶ Reductant

Ox + νe⁻ ⟶ Red

$$Fe^{3+}(aq) + \boxed{e^-} \rightarrow Fe^{2+}(aq)$$

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$$Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + \boxed{5e^-}$$

**Oxidation halfreaction**

Reducing agent ⟶ Oxidizing agent + νe⁻

Reductant ⟶ Oxidant + νe⁻

Red ⟶ Ox + νe⁻

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + \boxed{e^-}$$

# Chemical reaction equilibria: Electrochemistry

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

**Reduction halfreactions**

Oxidizing agent + $\nu e^-$ $\longrightarrow$ Reducing agent

Oxidant + $\nu e^-$ $\longrightarrow$ Reductant

Ox + $\nu e^-$ $\longrightarrow$ Red

$$\boxed{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)}$$

**Total reaction**

$$Ox_1 + Red_2 + \nu e^- \longrightarrow Red_1 + Ox_2 + \nu e^-$$

$$Ox_1 + Red_2 \longrightarrow Red_1 + Ox_2$$

# Chemical reaction equilibria: Electrochemistry

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

**Reduction halfreactions**

Oxidizing agent + $\nu e^-$ $\rightarrow$ Reducing agent

Oxidant + $\nu e^-$ $\rightarrow$ Reductant

Ox + $\nu e^-$ $\rightarrow$ Red

$$\boxed{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)}$$

---

**Total reaction**

$Ox_1 + Red_2 + \nu e^- \rightarrow Red_1 + Ox_2 + \nu e^-$

$Ox_1 + Red_2 \rightarrow Red_1 + Ox_2$

Reduction 1

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

Oxidation 2

$$\boxed{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-}$$

# Chemical reaction equilibria: Electrochemistry

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

**Reduction halfreactions**

Oxidizing agent + $\nu e^-$ → Reducing agent

Oxidant + $\nu e^-$ → Reductant

Ox + $\nu e^-$ → Red

$$\boxed{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)}$$

**Total reaction**

$Ox_1 + Red_2 + \nu e^- \rightarrow Red_1 + Ox_2 + \nu e^-$

$Ox_1 + Red_2 \rightarrow Red_1 + Ox_2$

Reduction 1

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

Oxidation 2

$$5x \quad \boxed{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-}$$

+

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)}$$

# Chemical reaction equilibria: Electrochemistry

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)}$$

$$Ox_1 + Red_2 \rightarrow Red_1 + Ox_2$$

**But what about the reverse reaction?**

$$\boxed{Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq)}$$

$$Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$$

$$Ox_2 + Red_1 \rightarrow Red_2 + Ox_1$$

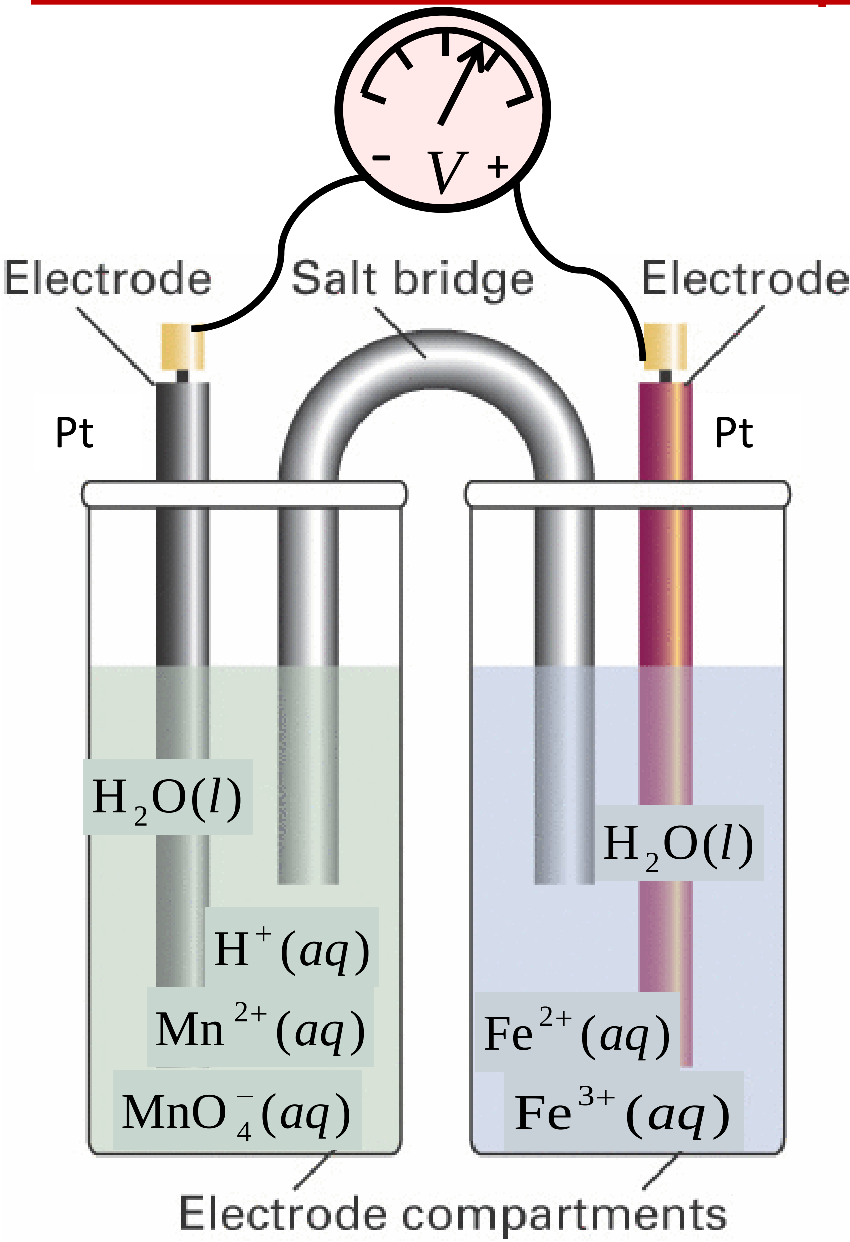
**Electrochemical Equilibrium reaction**

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \leftrightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)}$$

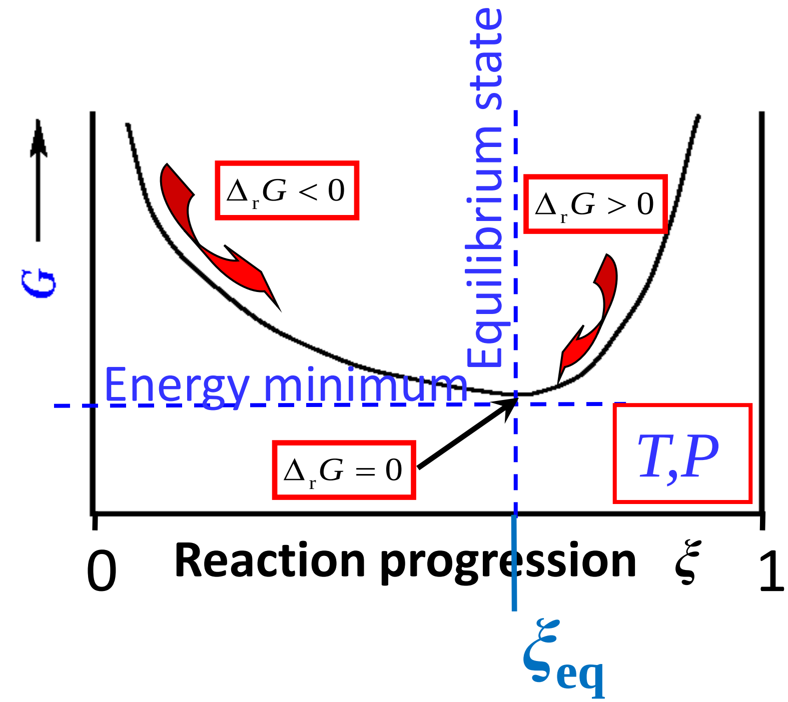
$\longrightarrow$ **Will it run spontaneously to the right or to the left?**

$\longrightarrow$ **Where is the equilibrium?**

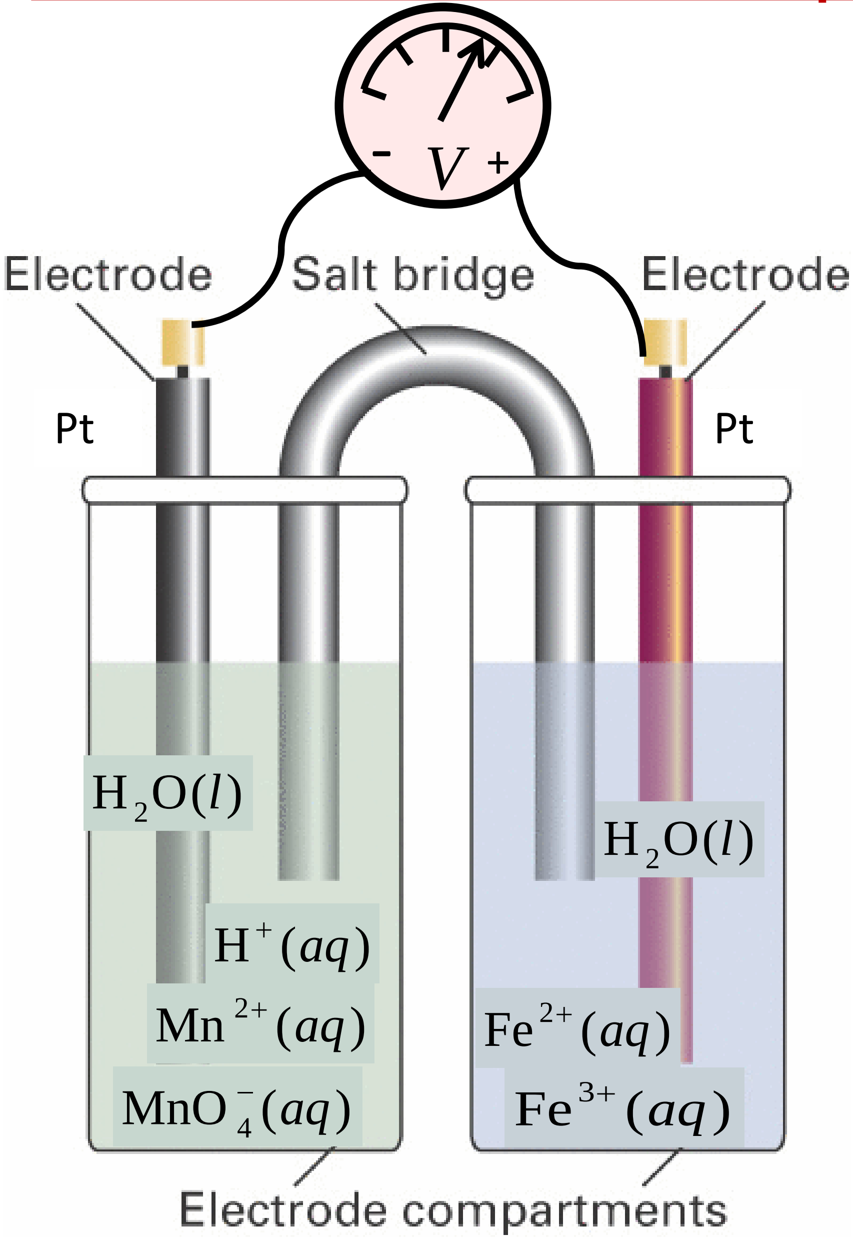
# Chemical reaction equilibria: Electrochemistry




**Voltage $V$ represents a 'driving force' like $\Delta_r G$**



# Chemical reaction equilibria: Electrochemistry




**Voltage $V$ represents a 'driving force' like $\Delta_r G$**

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

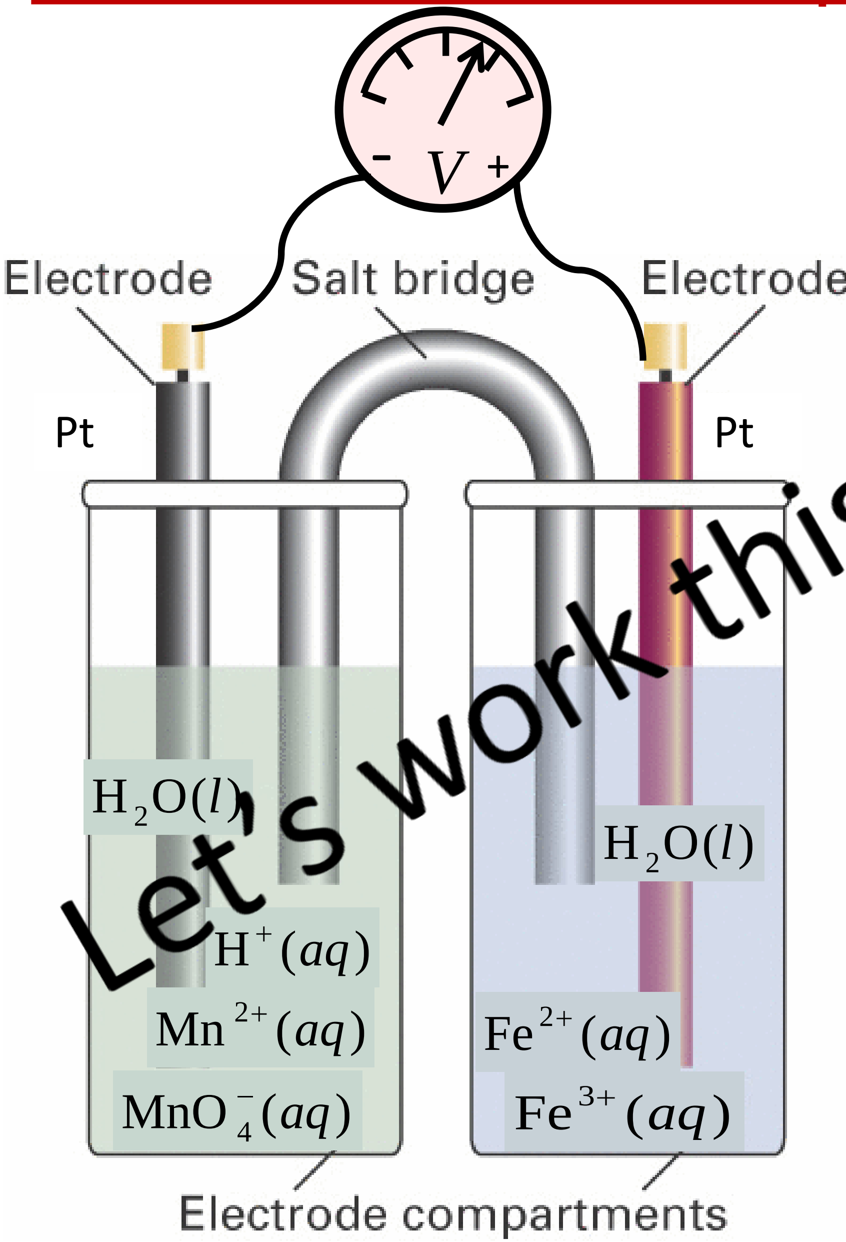
$$\boxed{\Delta_r G^{\ominus} = \sum_i \nu_i \Delta_f G_{m,i}^{\ominus}}$$

**Equilibrium:**

$$\boxed{\Delta_r G^{\ominus} = -RT \ln K}$$

**Relation between $V$ and $\Delta_r G$**

# Chemical reaction equilibria: Electrochemistry




Let's work this out in detail

**Voltage $V$ represents a 'driving force' like $\Delta_r G$**

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

$$\boxed{\Delta_r G^{\ominus} = \sum_i \nu_i \Delta_f G_{m,i}^{\ominus}}$$

**Equilibrium:**

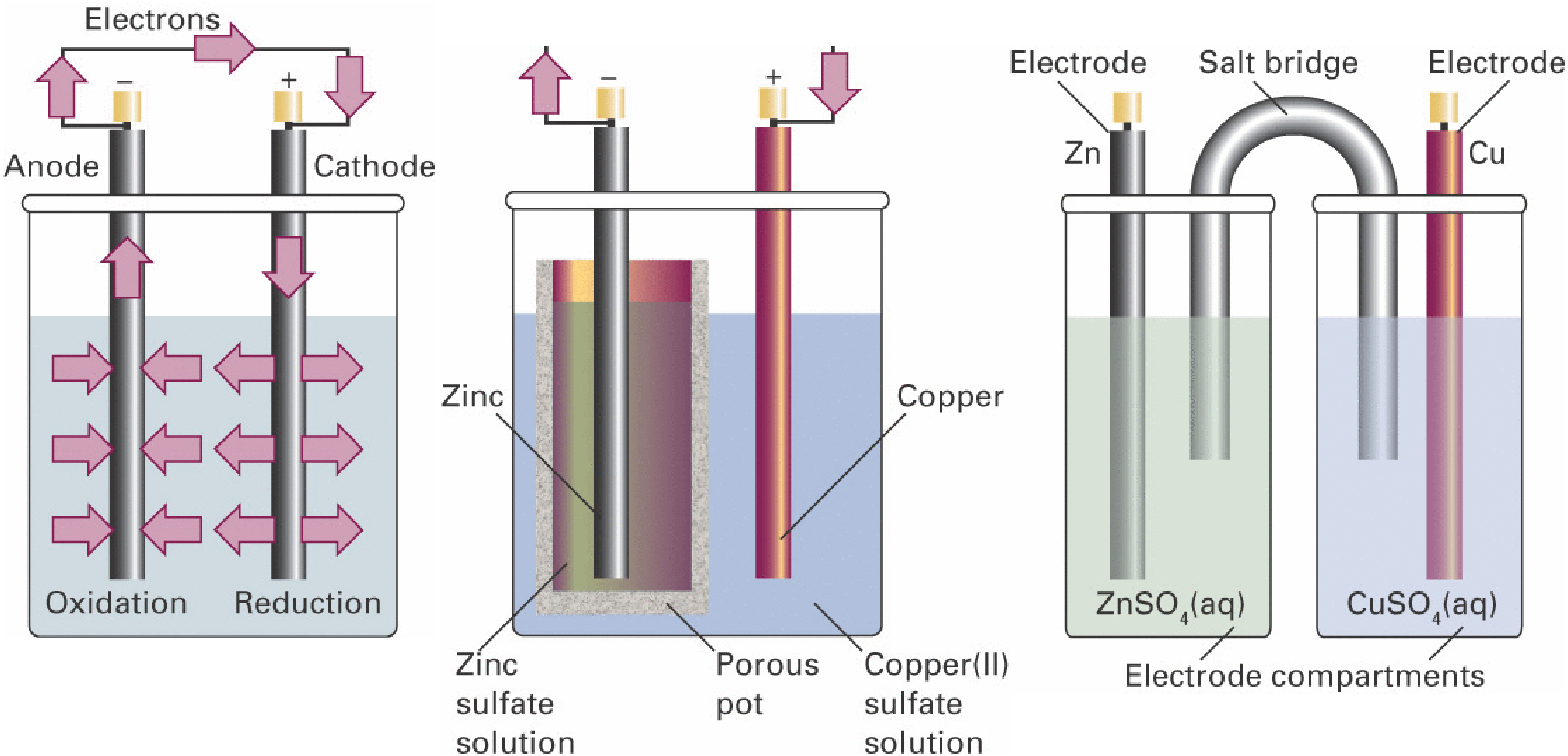
$$\boxed{\Delta_r G^{\ominus} = -RT \ln K}$$

**Relation between $V$ and $\Delta_r G$**

$$\boxed{\Delta_r G = -\nu F V = -\nu F E}$$

# Chemical reaction equilibria: Electrochemistry

## Electrochemical cells



# Chemical reaction equilibria: Electrochemistry

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

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

**Equilibrium:**

$$\boxed{\Delta_\mathrm{r} G^{\Theta} = -RT \ln K}$$

**Equilibrium:**

$$\Rightarrow \boxed{E^{\Theta} = +\frac{RT}{\nu F} \ln K}$$

$$\boxed{\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G_{m,i}{}^{\Theta} = -\nu F E^{\Theta}}$$

# Chemical reaction equilibria: Electrochemistry

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

$\Longleftrightarrow$

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

**Nernst equation**

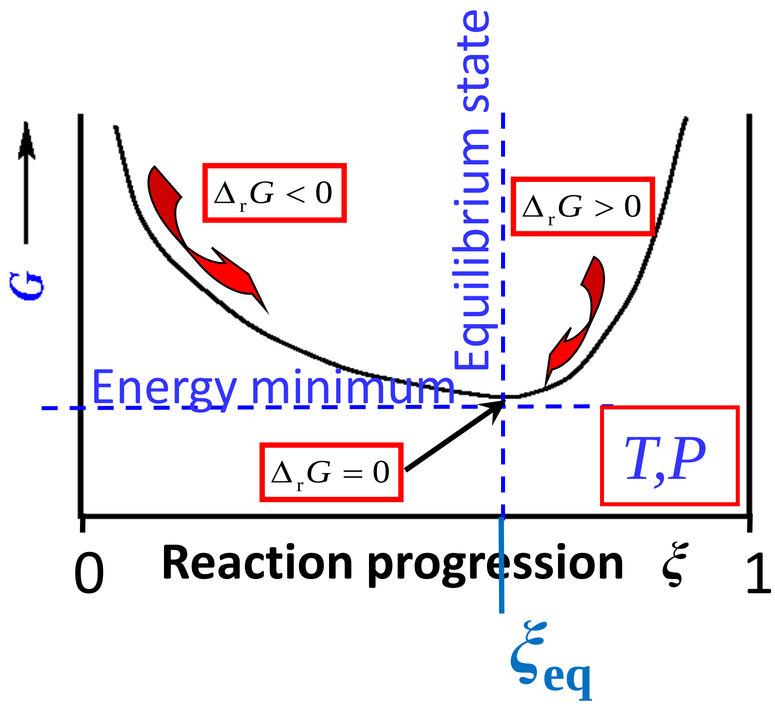
# Chemical reaction equilibria: Electrochemistry

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

$$\Delta_r G = -\nu F E$$

$$E = E^{\ominus} - \frac{RT}{\nu F} \ln Q$$

**Nernst equation**

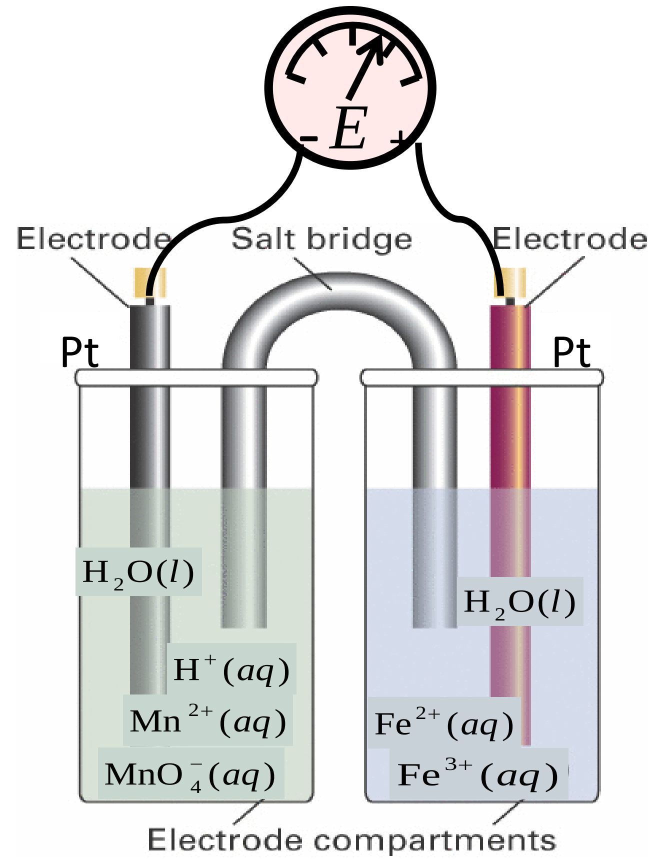



**reaction**

$\Delta_r G < 0$ $E > 0$

$\Delta_r G > 0$ $E < 0$

$\Delta_r G = 0$ $E = 0$



# Chemical reaction equilibria: Electrochemistry

**Nernst equation**

$$\boxed{E = E^{\Theta} - \frac{RT}{\nu F} \ln Q}$$ **with** $$\boxed{Q = \prod_i a_i^{\nu_i}}$$

# Chemical reaction equilibria: Electrochemistry

**Nernst equation**

$$E = E^{\Theta} - \frac{RT}{\nu F}\ln Q$$ **with** $$Q = \prod_i a_i^{\nu_i}$$

**Nernst also holds for half reactions**

$$\mathrm{MnO_4^-}(aq) + 8\mathrm{H^+}(aq) + 5e^- \rightarrow \mathrm{Mn^{2+}}(aq) + 4\mathrm{H_2O}(l)$$

$$E_{\mathrm{MnO_4^-/Mn^{2+}}} = E^{\Theta}_{\mathrm{MnO_4^-/Mn^{2+}}} - \frac{RT}{5F}\ln\frac{a_{\mathrm{Mn^{2+}}}\,a^4_{\mathrm{H_2O}}}{a_{\mathrm{MnO_4^-}}\,a^8_{\mathrm{H^+}}}$$

$$5\mathrm{Fe^{3+}}(aq) + 5e^- \rightarrow 5\mathrm{Fe^{2+}}(aq)$$

**Note: reduction half reaction**

$$E_{\mathrm{Fe^{3+}/Fe^{2+}}} = E^{\Theta}_{\mathrm{Fe^{3+}/Fe^{2+}}} - \frac{RT}{5F}\ln\frac{a^5_{\mathrm{Fe^{2+}}}}{a^5_{\mathrm{Fe^{3+}}}}$$

# Chemical reaction equilibria: Electrochemistry

**Nernst also holds for half reactions**

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

$$\boxed{5Fe^{3+}(aq) + 5e^- \rightarrow 5Fe^{2+}(aq)}$$

**Note: reduction half reactions**

# Chemical reaction equilibria: Electrochemistry

**Nernst also holds for half reactions**

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

$$\boxed{5Fe^{3+}(aq) + 5e^- \rightarrow 5Fe^{2+}(aq)}$$

**Note: reduction half reactions**

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)}$$

# Chemical reaction equilibria: Electrochemistry

**Nernst also holds for half reactions**

$$\boxed{\mathrm{MnO}_4^-(aq) + 8\mathrm{H}^+(aq) + 5e^- \rightarrow \mathrm{Mn}^{2+}(aq) + 4\mathrm{H}_2\mathrm{O}(l)}$$

$$\boxed{5\mathrm{Fe}^{3+}(aq) + 5e^- \rightarrow 5\mathrm{Fe}^{2+}(aq)}$$

**Note: reduction half reactions**

—

$$\boxed{\mathrm{MnO}_4^-(aq) + 8\mathrm{H}^+(aq) + 5\mathrm{Fe}^{2+}(aq) \rightarrow \mathrm{Mn}^{2+}(aq) + 4\mathrm{H}_2\mathrm{O}(l) + 5\mathrm{Fe}^{3+}(aq)}$$

$$\boxed{E_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}} = E^{\Theta}_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}} - \frac{RT}{5F}\ln\frac{a_{\mathrm{Mn}^{2+}}\,a^4_{\mathrm{H}_2\mathrm{O}}}{a_{\mathrm{MnO}_4^-}\,a^8_{\mathrm{H}^+}}}$$

$$\boxed{E_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} = E^{\Theta}_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} - \frac{RT}{5F}\ln\frac{a^5_{\mathrm{Fe}^{2+}}}{a^5_{\mathrm{Fe}^{3+}}}}$$

—

# Chemical reaction equilibria: Electrochemistry

## Nernst also holds for half reactions

$$E_{MnO_4^-/Mn^{2+}} = E^{\Theta}_{MnO_4^-/Mn^{2+}} - \frac{RT}{5F}\ln\frac{a_{Mn^{2+}}\,a_{H_2O}^4}{a_{MnO_4^-}\,a_{H^+}^8}$$

$$E_{Fe^{3+}/Fe^{2+}} = E^{\Theta}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{5F}\ln\frac{a_{Fe^{2+}}^5}{a_{Fe^{3+}}^5}$$

**Note: reduction half reactions**

$-$

$$E_{\text{total cell}} = E^{\Theta}_{MnO_4^-/Mn^{2+}} - E^{\Theta}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{5F}\left[\ln\frac{a_{Mn^{2+}}\,a_{H_2O}^4}{a_{MnO_4^-}\,a_{H^+}^8} - \ln\frac{a_{Fe^{2+}}^5}{a_{Fe^{3+}}^5}\right]$$

# Chemical reaction equilibria: Electrochemistry

## Nernst also holds for half reactions

$$E_{\mathrm{MnO_4^-/Mn^{2+}}} = E^{\Theta}_{\mathrm{MnO_4^-/Mn^{2+}}} - \frac{RT}{5F}\ln\frac{a_{\mathrm{Mn^{2+}}}\,a^4_{\mathrm{H_2O}}}{a_{\mathrm{MnO_4^-}}\,a^8_{\mathrm{H^+}}}$$

$$E_{\mathrm{Fe^{3+}/Fe^{2+}}} = E^{\Theta}_{\mathrm{Fe^{3+}/Fe^{2+}}} - \frac{RT}{5F}\ln\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}$$

**Note: reduction half reactions**

$-$

$$E_{\text{total cell}} = E^{\Theta}_{\mathrm{MnO_4^-/Mn^{2+}}} - E^{\Theta}_{\mathrm{Fe^{3+}/Fe^{2+}}} - \frac{RT}{5F}\left[\ln\frac{a_{\mathrm{Mn^{2+}}}\,a^4_{\mathrm{H_2O}}}{a_{\mathrm{MnO_4^-}}\,a^8_{\mathrm{H^+}}} - \ln\frac{a^5_{\mathrm{Fe^{2+}}}}{a^5_{\mathrm{Fe^{3+}}}}\right] \Rightarrow$$

$$E_{\text{total cell}} = E^{\Theta}_{\mathrm{MnO_4^-/Mn^{2+}}} - E^{\Theta}_{\mathrm{Fe^{3+}/Fe^{2+}}} - \frac{RT}{5F}\left[\ln\frac{a_{\mathrm{Mn^{2+}}}\,a^4_{\mathrm{H_2O}}\,a^5_{\mathrm{Fe^{3+}}}}{a_{\mathrm{MnO_4^-}}\,a^8_{\mathrm{H^+}}\,a^5_{\mathrm{Fe^{2+}}}}\right]$$

$$\mathrm{MnO_4^-}(aq) + 8\mathrm{H^+}(aq) + 5\mathrm{Fe^{2+}}(aq) \rightarrow \mathrm{Mn^{2+}}(aq) + 4\mathrm{H_2O}(l) + 5\mathrm{Fe^{3+}}(aq)$$

# Chemical reaction equilibria: Electrochemistry

## Nernst also holds for half reactions

$$\boxed{E_{\text{total cell}} = \underbrace{E^{\Theta}_{\mathrm{MnO_4^-/Mn^{2+}}}} - \underbrace{E^{\Theta}_{\mathrm{Fe^{3+}/Fe^{2+}}}} - \frac{RT}{5F}\left[\ln \frac{a_{\mathrm{Mn^{2+}}}\, a^4_{\mathrm{H_2O}}\, a^5_{\mathrm{Fe^{3+}}}}{a_{\mathrm{MnO_4^-}}\, a^8_{\mathrm{H^+}}\, a^5_{\mathrm{Fe^{2+}}}}\right]}$$

**Standard electrochemical potentials of redox couples are in tables as reduction half reactions**

$$\boxed{\mathrm{MnO_4^-}(aq) + 8\mathrm{H^+}(aq) + 5\mathrm{Fe^{2+}}(aq) \rightarrow \mathrm{Mn^{2+}}(aq) + 4\mathrm{H_2O}(l) + 5\mathrm{Fe^{3+}}(aq)}$$

# Chemical reaction equilibria: Electrochemistry

## Nernst also holds for half reactions

$$E_{\text{total cell}} = \underbrace{E^{\Theta}_{MnO_4^- / Mn^{2+}}} - \underbrace{E^{\Theta}_{Fe^{3+} / Fe^{2+}}} - \frac{RT}{5F}\left[ \ln \frac{a_{Mn^{2+}}\, a^4_{H_2O}\, a^5_{Fe^{3+}}}{a_{MnO_4^-}\, a^8_{H^+}\, a^5_{Fe^{2+}}} \right]$$

**Standard electrochemical potentials of redox couples are in tables as reduction half reactions**

**- sign because we need a reduction and an oxidation half reaction**

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

# Chemical reaction equilibria: ions in solution

| | $M/(\mathrm{g\ mol^{-1}})$ | $\Delta_f H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$ | $\Delta_f G^{\ominus}/(\mathrm{kJ\ mol^{-1}})$ | $S_m^{\ominus}/(\mathrm{J\ K^{-1}\ mol^{-1}})$† | $C_{p,m}^{\ominus}/(\mathrm{J\ K^{-1}\ mol^{-1}})$ |
|---|---|---|---|---|---|
| **Fluorine** | | | | | |
| $F_2(g)$ | 38.00 | 0 | 0 | 202.78 | 31.30 |
| $F(g)$ | 19.00 | +78.99 | +61.91 | 158.75 | 22.74 |
| $F^-(aq)$ | 19.00 | −332.63 | −278.79 | −13.8 | −106.7 |
| $HF(g)$ | 20.01 | −271.1 | −273.2 | 173.78 | 29.13 |
| **Gold** | | | | | |
| $Au(s)$ | 196.97 | 0 | 0 | 47.40 | 25.42 |
| $Au(g)$ | 196.97 | +366.1 | +326.3 | 180.50 | 20.79 |
| **Helium** | | | | | |
| $He(g)$ | 4.003 | 0 | 0 | 126.15 | 20.786 |
| **Hydrogen** (see also deuterium) | | | | | |
| $H_2(g)$ | 2.016 | 0 | 0 | 130.684 | 28.824 |
| $H(g)$ | 1.008 | +217.97 | +203.25 | 114.71 | 20.784 |
| $H^+(aq)$ | 1.008 | 0 | 0 | 0 | 0 |
| $H^+(g)$ | 1.008 | +1536.20 | | | |
| $H_2O(s)$ | 18.015 | | | 37.99 | |
| $H_2O(l)$ | 18.015 | −285.83 | −237.13 | 69.91 | 75.291 |
| $H_2O(g)$ | 18.015 | −241.82 | −228.57 | 188.83 | 33.58 |
| $H_2O_2(l)$ | 34.015 | −187.78 | −120.35 | 109.6 | 89.1 |
| **Iodine** | | | | | |
| $I_2(s)$ | 253.81 | 0 | 0 | 116.135 | 54.44 |
| $I_2(g)$ | 253.81 | +62.44 | +19.33 | 260.69 | 36.90 |
| $I(g)$ | 126.90 | +106.84 | +70.25 | 180.79 | 20.786 |
| $I^-(aq)$ | 126.90 | −55.19 | −51.57 | +111.3 | −142.3 |
| $HI(g)$ | 127.91 | +26.48 | +1.70 | 206.59 | 29.158 |
| **Iron** | | | | | |
| $Fe(s)$ | 55.85 | 0 | 0 | 27.28 | 25.10 |
| $Fe(g)$ | 55.85 | +416.3 | +370.7 | 180.49 | 25.68 |
| $Fe^{2+}(aq)$ | 55.85 | −89.1 | −78.90 | −137.7 | |
| $Fe^{3+}(aq)$ | 55.85 | −48.5 | −4.7 | −315.9 | |
| $Fe_3O_4(s)$ (magnetite) | 231.54 | −1118.4 | −1015.4 | 146.4 | 143.43 |
| $Fe_2O_3(s)$ (haematite) | 159.69 | −824.2 | −742.2 | 87.40 | 103.85 |
| $FeS(s, \alpha)$ | 87.91 | −100.0 | −100.4 | 60.29 | 50.54 |
| $FeS_2(s)$ | 119.98 | −178.2 | −166.9 | 52.93 | 62.17 |
| **Krypton** | | | | | |
| $Kr(g)$ | 83.80 | 0 | 0 | 164.08 | 20.786 |
| **Lead** | | | | | |
| $Pb(s)$ | 207.19 | 0 | 0 | 64.81 | 26.44 |
| $Pb(g)$ | 207.19 | +195.0 | +161.9 | 175.37 | 20.79 |
| $Pb^{2+}(aq)$ | 207.19 | −1.7 | −24.43 | +10.5 | |
| $PbO$(s, yellow) | 223.19 | −217.32 | −187.89 | 68.70 | 45.77 |
| $PbO$(s, red) | 223.19 | −218.99 | −188.93 | 66.5 | 45.81 |
| $PbO_2(s)$ | 239.19 | −277.4 | −217.33 | 68.6 | 64.64 |

$$\boxed{\Delta_r G^{\ominus} = \sum_i \nu_i \Delta_f G_{m,i}^{\ominus} = -\nu F E^{\ominus}}$$

$$\leftarrow \Delta_f G^{\ominus}_{m,H^+} \equiv \Delta_f H^{\ominus}_{m,H^+} \equiv 0 \text{ all } T$$

**Standard thermodynamic data**

**(@ 298K)**

**(Ed.11: Table 2C.7)**

# Standard electrochemical potentials $E^{\ominus}$ of redox couples

(@ 298K) alphabetical order (Ed.11: Table 6D.1b)

| Reduction half-reaction | $E^{\ominus}$/V | Reduction half-reaction | $E^{\ominus}$/V |
|---|---|---|---|
| $Ag^+ + e^- \rightarrow Ag$ | +0.80 | $I_2 + 2e^- \rightarrow 2I^-$ | +0.54 |
| $Ag^{2+} + e^- \rightarrow Ag^+$ | +1.98 | $I_3^- + 2e^- \rightarrow 3I^-$ | +0.53 |
| $AgBr + e^- \rightarrow Ag + Br^-$ | +0.0713 | $In^+ + e^- \rightarrow In$ | −0.14 |
| $AgCl + e^- \rightarrow Ag + Cl^-$ | +0.22 | $In^{2+} + e^- \rightarrow In^+$ | −0.40 |
| $Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$ | +0.45 | $In^{3+} + 2e^- \rightarrow In^+$ | −0.44 |
| $AgF + e^- \rightarrow Ag + F^-$ | +0.78 | $In^{3+} + 3e^- \rightarrow In$ | −0.34 |
| $AgI + e^- \rightarrow Ag + I^-$ | −0.15 | $In^{3+} + e^- \rightarrow In^{2+}$ | −0.49 |
| $Al^{3+} + 3e^- \rightarrow Al$ | −1.66 | $K^+ + e^- \rightarrow K$ | −2.93 |
| $Au^+ + e^- \rightarrow Au$ | +1.69 | $La^{3+} + 3e^- \rightarrow La$ | −2.52 |
| $Au^{3+} + 3e^- \rightarrow Au$ | +1.40 | $Li^+ + e^- \rightarrow Li$ | −3.05 |
| $Ba^{2+} + 2e^- \rightarrow Ba$ | +2.91 | $Mg^{2+} + 2e^- \rightarrow Mg$ | −2.36 |
| $Be^{2+} + 2e^- \rightarrow Be$ | −1.85 | $Mn^{2+} + 2e^- \rightarrow Mn$ | −1.18 |
| $Bi^{3+} + 3e^- \rightarrow Bi$ | +0.20 | $Mn^{3+} + e^- \rightarrow Mn^{2+}$ | +1.51 |
| $Br_2 + 2e^- \rightarrow 2Br^-$ | +1.09 | $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ | +1.23 |
| $BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$ | +0.76 | $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | +1.51 |
| $Ca^{2+} + 2e^- \rightarrow Ca$ | −2.87 | $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ | +0.56 |
| $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$ | −0.81 | $MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$ | +0.60 |
| $Cd^{2+} + 2e^- \rightarrow Cd$ | −0.40 | $Na^+ + e^- \rightarrow Na$ | −2.71 |
| $Ce^{3+} + 3e^- \rightarrow Ce$ | −2.48 | $Ni^{2+} + 2e^- \rightarrow Ni$ | −0.23 |
| $Ce^{4+} + e^- \rightarrow Ce^{3+}$ | +1.61 | $NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ | +0.49 |
| $Cl_2 + 2e^- \rightarrow 2Cl^-$ | +1.36 | $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$ | −0.80 |
| $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ | +0.89 | $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ | +0.96 |
| $ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$ | +1.23 | $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$ | +0.10 |
| $ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$ | +0.36 | $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ | +0.40 |
| $Co^{2+} + 2e^- \rightarrow Co$ | −0.28 | $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | +1.23 |
| $Co^{3+} + e^- \rightarrow Co^{2+}$ | +1.81 | $O_2 + e^- \rightarrow O_2^-$ | −0.56 |
| $Cr^{2+} + 2e^- \rightarrow Cr$ | −0.91 | $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ | −0.08 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ | +1.33 | $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ | +2.07 |
| $Cr^{3+} + 3e^- \rightarrow Cr$ | −0.74 | $O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$ | +1.24 |
| $Cr^{3+} + e^- \rightarrow Cr^{2+}$ | −0.41 | $Pb^{2+} + 2e^- \rightarrow Pb$ | −0.13 |
| $Cs^+ + e^- \rightarrow Cs$ | −2.92 | $Pb^{4+} + 2e^- \rightarrow Pb^{2+}$ | +1.67 |
| $Cu^+ + e^- \rightarrow Cu$ | +0.52 | $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ | −0.36 |
| $Cu^{2+} + 2e^- \rightarrow Cu$ | +0.34 | $Pt^{2+} + 2e^- \rightarrow Pt$ | +1.20 |
| $Cu^{2+} + e^- \rightarrow Cu^+$ | +0.16 | $Pu^{4+} + e^- \rightarrow Pu^{3+}$ | +0.97 |
| $F_2 + 2e^- \rightarrow 2F^-$ | +2.87 | $Ra^{2+} + 2e^- \rightarrow Ra$ | −2.92 |
| $Fe^{2+} + 2e^- \rightarrow Fe$ | −0.44 | $Rb^+ + e^- \rightarrow Rb$ | −2.93 |
| $Fe^{3+} + 3e^- \rightarrow Fe$ | −0.04 | $S + 2e^- \rightarrow S^{2-}$ | −0.48 |
| $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | +0.77 | $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ | +2.05 |
| $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$ | +0.36 | $Sc^{3+} + 3e^- \rightarrow Sc$ | −2.09 |
| $2H^+ + 2e^- \rightarrow H_2$ | 0, by definition | $Sn^{2+} + 2e^- \rightarrow Sn$ | −0.14 |
| $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ | −0.83 | $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ | +0.15 |
| $2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$ | +1.60 | $Sr^{2+} + 2e^- \rightarrow Sr$ | −2.89 |
| $2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$ | +1.63 | $Ti^{2+} + 2e^- \rightarrow Ti$ | −1.63 |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | +1.78 | $Ti^{3+} + e^- \rightarrow Ti^{2+}$ | −0.37 |
| $H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$ | +3.0 | $Ti^{4+} + e^- \rightarrow Ti^{3+}$ | 0.00 |
| $Hg_2^{2+} + 2e^- \rightarrow 2Hg$ | +0.79 | $Tl^+ + e^- \rightarrow Tl$ | −0.34 |
| $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ | +0.27 | $U^{3+} + 3e^- \rightarrow U$ | −1.79 |
| $Hg^{2+} + 2e^- \rightarrow Hg$ | +0.86 | $U^{4+} + e^- \rightarrow U^{3+}$ | −0.61 |
| $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ | +0.92 | $V^{2+} + 2e^- \rightarrow V$ | −1.19 |
| $Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$ | +0.62 | $V^{3+} + e^- \rightarrow V^{2+}$ | −0.26 |
| | | $Zn^{2+} + 2e^- \rightarrow Zn$ | −0.76 |

for all $T$(aq)

# Standard electrochemical potentials $E^{\ominus}$ of redox couples

**(@ 298K) electrochemical order (Ed.11: Table 6D.1a)**

| Reduction half-reaction | $E^{\ominus}$/V | Reduction half-reaction | $E^{\ominus}$/V |
|---|---|---|---|
| **Strongly oxidizing** | | $Cu^{2+} + e^- \rightarrow Cu^+$ | +0.16 |
| $H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$ | +3.0 | $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ | +0.15 |
| $F_2 + 2e^- \rightarrow 2F^-$ | +2.87 | $AgBr + e^- \rightarrow Ag + Br^-$ | +0.07 |
| $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ | +2.07 | $Ti^{4+} + e^- \rightarrow Ti^{3+}$ | 0.00 |
| $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ | +2.05 | $2H^+ + 2e^- \rightarrow H_2$ | 0, by definition |
| $Ag^{2+} + e^- \rightarrow Ag^+$ | +1.98 | $Fe^{3+} + 3e^- \rightarrow Fe$ | −0.04 |
| $Co^{3+} + e^- \rightarrow Co^{2+}$ | +1.81 | $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ | −0.08 |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | +1.78 | $Pb^{2+} + 2e^- \rightarrow Pb$ | −0.13 |
| $Au^+ + e^- \rightarrow Au$ | +1.69 | $In^+ + e^- \rightarrow In$ | −0.14 |
| $Pb^{4+} + 2e^- \rightarrow Pb^{2+}$ | +1.67 | $Sn^{2+} + 2e^- \rightarrow Sn$ | −0.14 |
| $2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$ | +1.63 | $AgI + e^- \rightarrow Ag + I^-$ | −0.15 |
| $Ce^{4+} + e^- \rightarrow Ce^{3+}$ | +1.61 | $Ni^{2+} + 2e^- \rightarrow Ni$ | −0.23 |
| $2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$ | +1.60 | $Co^{2+} + 2e^- \rightarrow Co$ | −0.28 |
| $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | +1.51 | $In^{3+} + 3e^- \rightarrow In$ | −0.34 |
| $Mn^{3+} + e^- \rightarrow Mn^{2+}$ | +1.51 | $Tl^+ + e^- \rightarrow Tl$ | −0.34 |
| $Au^{3+} + 3e^- \rightarrow Au$ | +1.40 | $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ | −0.36 |
| $Cl_2 + 2e^- \rightarrow 2Cl^-$ | +1.36 | $Ti^{3+} + e^- \rightarrow Ti^{2+}$ | −0.37 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ | +1.33 | $Cd^{2+} + 2e^- \rightarrow Cd$ | −0.40 |
| $O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$ | +1.24 | $In^{2+} + e^- \rightarrow In^+$ | −0.40 |
| $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | +1.23 | $Cr^{3+} + e^- \rightarrow Cr^{2+}$ | −0.41 |
| $ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$ | +1.23 | $Fe^{2+} + 2e^- \rightarrow Fe$ | −0.44 |
| $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ | +1.23 | $In^{3+} + 2e^- \rightarrow In^+$ | −0.44 |
| $Br_2 + 2e^- \rightarrow 2Br^-$ | +1.09 | $S + 2e^- \rightarrow S^{2-}$ | −0.48 |
| $Pu^{4+} + e^- \rightarrow Pu^{3+}$ | +0.97 | $In^{3+} + e^- \rightarrow In^{2+}$ | −0.49 |
| $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ | +0.96 | $U^{4+} + e^- \rightarrow U^{3+}$ | −0.61 |
| $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ | +0.92 | $Cr^{3+} + 3e^- \rightarrow Cr$ | −0.74 |
| $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ | +0.89 | $Zn^{2+} + 2e^- \rightarrow Zn$ | −0.76 |
| $Hg^{2+} + 2e^- \rightarrow Hg$ | +0.86 | $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$ | −0.81 |
| $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$ | +0.80 | $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ | −0.83 |
| $Ag^+ + e^- \rightarrow Ag$ | +0.80 | $Cr^{2+} + 2e^- \rightarrow Cr$ | −0.91 |
| $Hg_2^{2+} + 2e^- \rightarrow 2Hg$ | +0.79 | $Mn^{2+} + 2e^- \rightarrow Mn$ | −1.18 |
| $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | +0.77 | $V^{2+} + 2e^- \rightarrow V$ | −1.19 |
| $BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$ | +0.76 | $Ti^{2+} + 2e^- \rightarrow Ti$ | −1.63 |
| $Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$ | +0.62 | $Al^{3+} + 3e^- \rightarrow Al$ | −1.66 |
| $MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$ | +0.60 | $U^{3+} + 3e^- \rightarrow U$ | −1.79 |
| $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ | +0.56 | $Sc^{3+} + 3e^- \rightarrow Sc$ | −2.09 |
| $I_2 + 2e^- \rightarrow 2I^-$ | +0.54 | $Mg^{2+} + 2e^- \rightarrow Mg$ | −2.36 |
| $Cu^+ + e^- \rightarrow Cu$ | +0.52 | $Ce^{3+} + 3e^- \rightarrow Ce$ | −2.48 |
| $I_3^- + 2e^- \rightarrow 3I^-$ | +0.53 | $La^{3+} + 3e^- \rightarrow La$ | −2.52 |
| $NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ | +0.49 | $Na^+ + e^- \rightarrow Na$ | −2.71 |
| $Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$ | +0.45 | $Ca^{2+} + 2e^- \rightarrow Ca$ | −2.87 |
| $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ | +0.40 | $Sr^{2+} + 2e^- \rightarrow Sr$ | −2.89 |
| $ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$ | +0.36 | $Ba^{2+} + 2e^- \rightarrow Ba$ | −2.91 |
| $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$ | +0.36 | $Ra^{2+} + 2e^- \rightarrow Ra$ | −2.92 |
| $Cu^{2+} + 2e^- \rightarrow Cu$ | +0.34 | $Cs^+ + e^- \rightarrow Cs$ | −2.92 |
| $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ | +0.27 | $Rb^+ + e^- \rightarrow Rb$ | −2.93 |
| $AgCl + e^- \rightarrow Ag + Cl^-$ | +0.22 | $K^+ + e^- \rightarrow K$ | −2.93 |
| $Bi^{3+} + 3e^- \rightarrow Bi$ | +0.20 | $Li^+ + e^- \rightarrow Li$ | −3.05 |

# Chemical reaction equilibria: Electrochemistry

$$\boxed{\Delta_f G^{\Theta}_{H^+(aq)} \equiv 0 \text{ for all } T}$$

$$\boxed{E^{\Theta}_{2H^+/H_2} \equiv 0 \text{ for all } T}$$

# Chemical reaction equilibria: Electrochemistry

$$\boxed{\Delta_f G^{\ominus}_{\mathrm{H}^+(\mathrm{aq})} \equiv 0 \text{ for all } T}$$

$$\boxed{E^{\ominus}_{2\mathrm{H}^+/\mathrm{H}_2} \equiv 0 \text{ for all } T}$$

$$\boxed{2\mathrm{H}^+(aq) + 2e^- \rightarrow \mathrm{H}_2(g)}$$

$$\boxed{\mathrm{E}_{2\mathrm{H}^+/\mathrm{H}_2(g)} = \mathrm{E}^{\ominus}_{2\mathrm{H}^+/\mathrm{H}_2(g)} - \frac{\mathrm{RT}}{2\mathrm{F}} \ln \frac{a_{\mathrm{H}_2(g)}}{a^2_{\mathrm{H}^+}} = -\frac{\mathrm{RT}}{2\mathrm{F}} \ln \frac{a_{\mathrm{H}_2(g)}}{a^2_{\mathrm{H}^+}}}$$

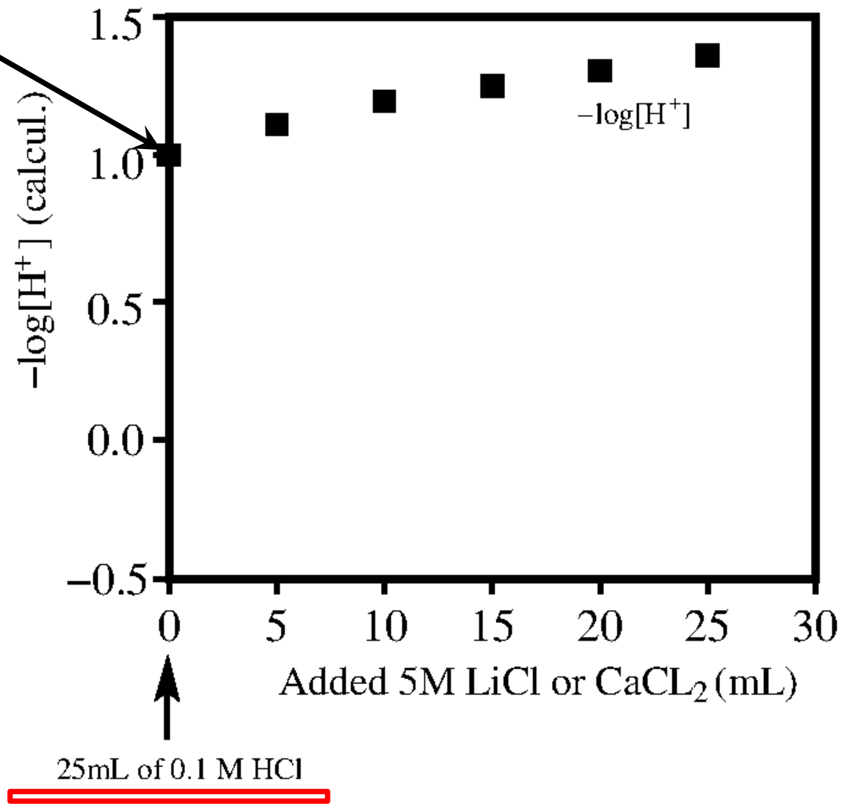
$$\Rightarrow \boxed{\mathrm{pH} \equiv -{}^{10}\log a_{\mathrm{H}^+} \approx -{}^{10}\log\left[\mathrm{H}^+\right]}$$

# Chemical reaction equilibria: Electrochemistry

## Why pH is defined via the activity

$$\boxed{\mathrm{pH} \equiv -\log a_{\mathrm{H}^+}}$$

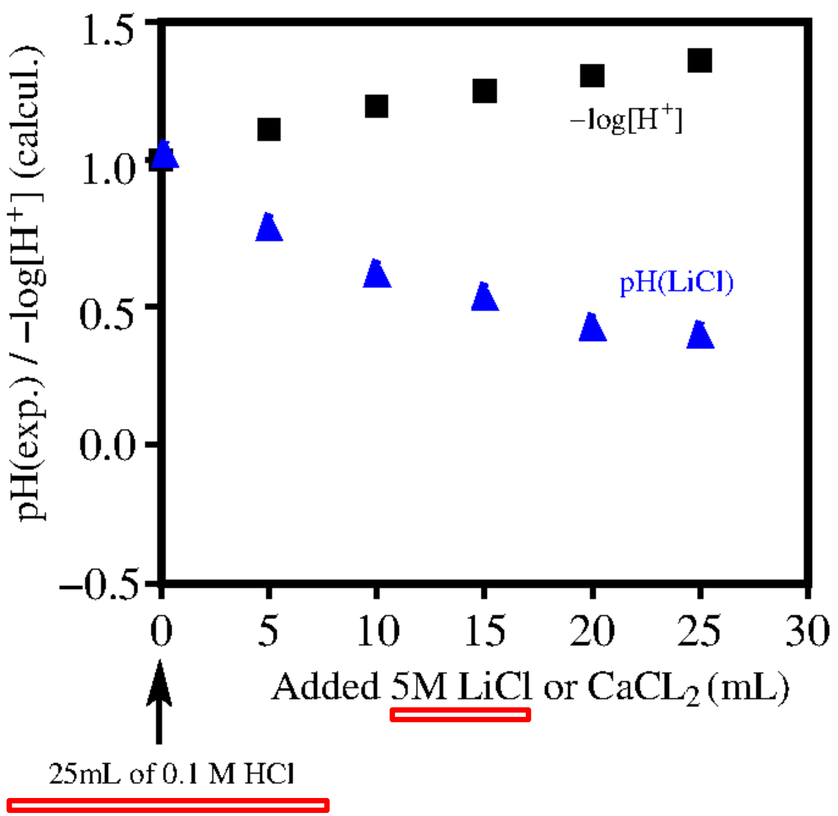
$$\boxed{-\log\left[\mathrm{H}^+\right] = -\log(0.1)}$$



# Chemical reaction equilibria: Electrochemistry

## Why pH is defined via the activity

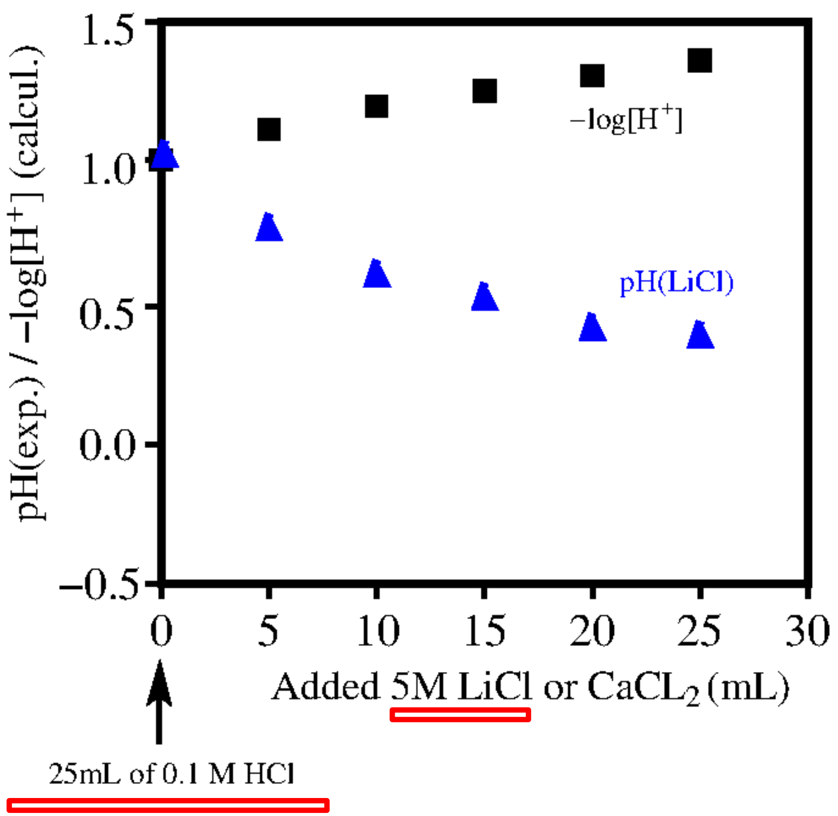
$$\boxed{pH \equiv -\log\, a_{H^+}}$$

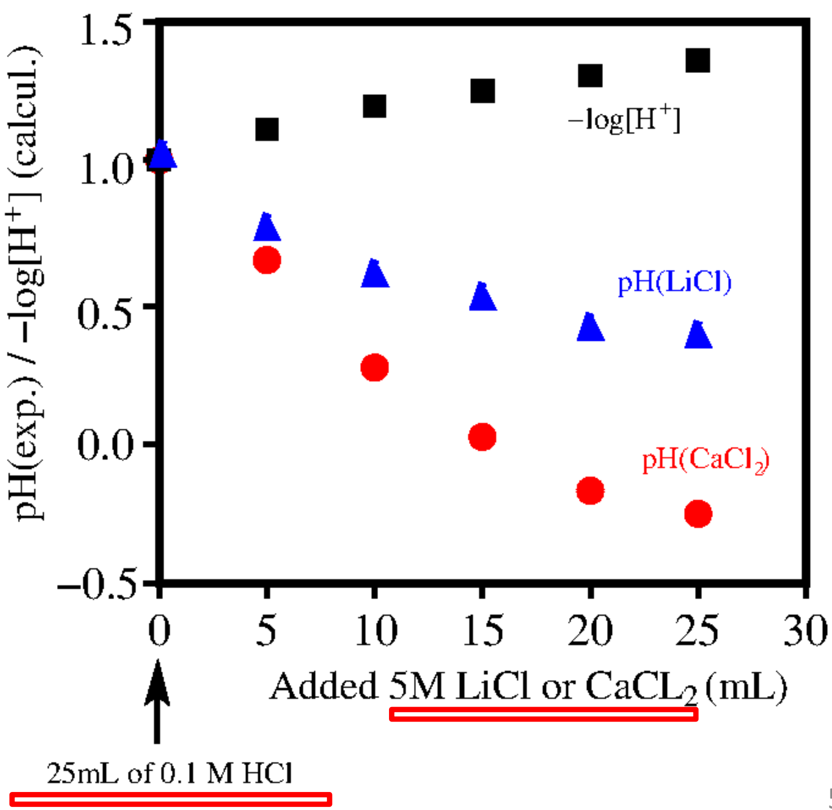


# Chemical reaction equilibria: Electrochemistry

## Why pH is defined via the activity

$$\boxed{\mathrm{pH} \equiv -\log a_{\mathrm{H}^+}}$$



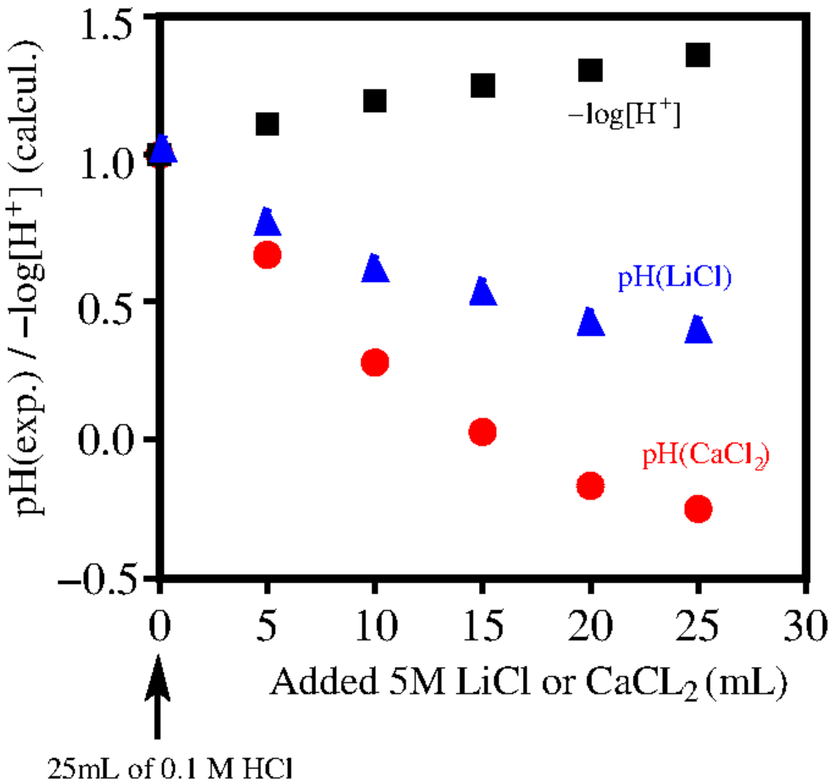



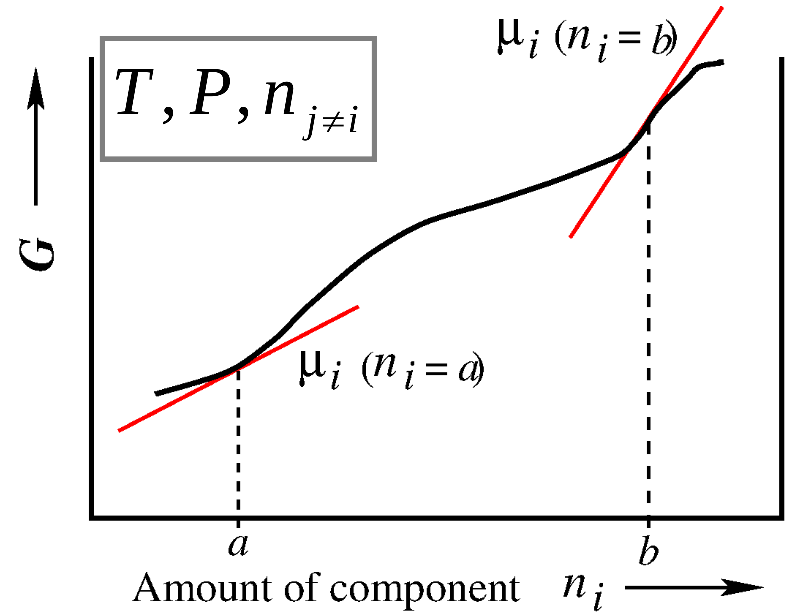
# Chemical reaction equilibria: Electrochemistry

## Why pH is defined via the activity

$$\mathrm{pH} \equiv -\log a_{\mathrm{H}^+}$$

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$




**Definition of activity:**

$$\mu_{\mathrm{H}^+} \equiv \mu^{\Theta}_{\mathrm{H}^+} + RT \ln a_{\mathrm{H}^+}$$

# Chemical reaction equilibria: Electrochemistry

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)}$$

$$\boxed{E_{\text{cell}} = E^{\Theta}_{MnO_4^-/Mn^{2+}} - E^{\Theta}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{5F}\left[\ln \frac{a_{Mn^{2+}} a_{H_2O}^4 a_{Fe^{3+}}^5}{a_{MnO_4^-} a_{H^+}^8 a_{Fe^{2+}}^5}\right]}$$

**Tables**

$$\left\{ \begin{array}{l} \boxed{E^{\Theta}_{MnO_4^-/Mn^{2+}} = +1.51\ \text{V}} \\ \boxed{E^{\Theta}_{Fe^{3+}/Fe^{2+}} = +0.77\ \text{V}} \end{array} \right\}$$

$$\boxed{E^{\Theta}_{\text{cell}} = 1.51 - 0.77 = 0.74\ \text{V}}$$

$$\Rightarrow \boxed{E_{\text{cell}} = 0.74\ \text{V} - \frac{RT}{5F}\left[\ln \frac{a_{Mn^{2+}} a_{H_2O}^4 a_{Fe^{3+}}^5}{a_{MnO_4^-} a_{H^+}^8 a_{Fe^{2+}}^5}\right]}$$

# Chemical reaction equilibria: Electrochemistry

$$\mathrm{MnO_4^-}(aq) + 8\mathrm{H}^+(aq) + 5\mathrm{Fe}^{2+}(aq) \rightarrow \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l) + 5\mathrm{Fe}^{3+}(aq)$$

$$E_{\text{cell}} = 0.74\ \mathrm{V} - \frac{RT}{5F}\left[\ln \frac{a_{\mathrm{Mn}^{2+}} a_{\mathrm{H_2O}}^4 a_{\mathrm{Fe}^{3+}}^5}{a_{\mathrm{MnO_4^-}} a_{\mathrm{H}^+}^8 a_{\mathrm{Fe}^{2+}}^5}\right]$$

$$E_{\text{cell}} \approx 0.74\ \mathrm{V} - \frac{RT}{5F}\left[\ln \frac{a_{\mathrm{Mn}^{2+}} a_{\mathrm{Fe}^{3+}}^5}{a_{\mathrm{MnO_4^-}} a_{\mathrm{H}^+}^8 a_{\mathrm{Fe}^{2+}}^5}\right]$$

**Very dilute solutions→$a_{H2O}$≈1**

$$E_{\text{cell}} \approx 0.74\ \mathrm{V} - \frac{RT}{5F}\left[\ln \frac{[\mathrm{Mn}^{2+}][\mathrm{F}e^{3+}]^5}{[\mathrm{MnO_4^-}][\mathrm{H}^+]^8[\mathrm{F}e^{2+}]^5}\right]$$

**Very dilute solutions→$a_i$≈[$i$]**

# Chemical reaction equilibria: Electrochemistry

## Activity as an effective concentration

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i}$$

$$\boxed{\mu_i \equiv \mu_i^{\Theta} + RT \ln \gamma_i \frac{c_i}{c^{\Theta}} = \underbrace{\mu_i^{\Theta} + RT \ln \frac{c_i}{c^{\Theta}}}_{\text{ideal or dilute behaviour}} + \underbrace{RT \ln \gamma_i}_{\text{deviation from ideal}}}$$

$$\boxed{a_i \equiv \gamma_i \frac{c_i}{c^{\Theta}}} \qquad \boxed{c^{\Theta} \equiv 1\,\text{mol/L}}$$

$\boxed{\gamma_i}$ **activity coefficient on the concentration scale**

**Molarity (mol/L):** $\boxed{c_i = \frac{\#\,\text{mol solute } i}{\text{volume } V \text{ solution}} = \frac{n_i}{V}}$

# Chemical reaction equilibria: Electrochemistry

## Activity as an effective concentration

$$\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i$$

**Molarity**
**(mol/L)**

$$c_i = \frac{\#\,\text{mol solute } i}{\text{volume } V \text{ solution}} = \frac{n_i}{V}$$

$$a_i = \gamma_i^{(c)} \frac{c_i}{c^{\Theta}}$$

$$c^{\Theta} \equiv 1\,\text{mol/L}$$

**Molality**
**(mol/kg)**

$$b_i = \frac{\#\,\text{mol solute } i}{\text{mass } m \text{ solvent}} = \frac{n_i}{m}$$

$$a_i = \gamma_i^{(b)} \frac{b_i}{b^{\Theta}}$$

$$b^{\Theta} \equiv 1\,\text{mol/kg}$$

**Mole fraction**
**( )**

$$x_i = \frac{\#\,\text{mol solute } i}{\text{total } \#\,\text{mol in solution}} = \frac{n_i}{n}$$

$$a_i = \gamma_i^{(x)} x_i$$

**example**

$$\text{pH} \equiv \text{-log } a_{\text{H}^+} = -\log \frac{c_{\text{H}^+}}{c^{\Theta}} - \log \gamma_{\text{H}^+}$$

# Summary Lecture 4 (chemical equilibria cont$^{d}$)

# Summary Lecture 4 (activity)

$$\mu_i \equiv \mu_i^{\ominus} + RT \ln a_i$$

**For perfect gas mixtures**

$$a_i = \frac{P_i}{P^{\ominus}}$$

**For pure liquids**

$$a_l \approx 1$$

**For pure solids**

$$a_s \approx 1$$

**For general systems:**

$$a_i = \gamma_i^{(c)} \frac{c_i}{c^{\ominus}}$$

$$a_i = \gamma_i^{(b)} \frac{b_i}{b^{\ominus}}$$

$$a_i = \gamma_i^{(x)} x_i$$

$$c^{\ominus} \equiv 1\,\mathrm{mol/L}$$

$$b^{\ominus} \equiv 1\,\mathrm{mol/kg}$$

$$\mathrm{pH} \equiv \text{-}\log a_{\mathrm{H}^+}$$

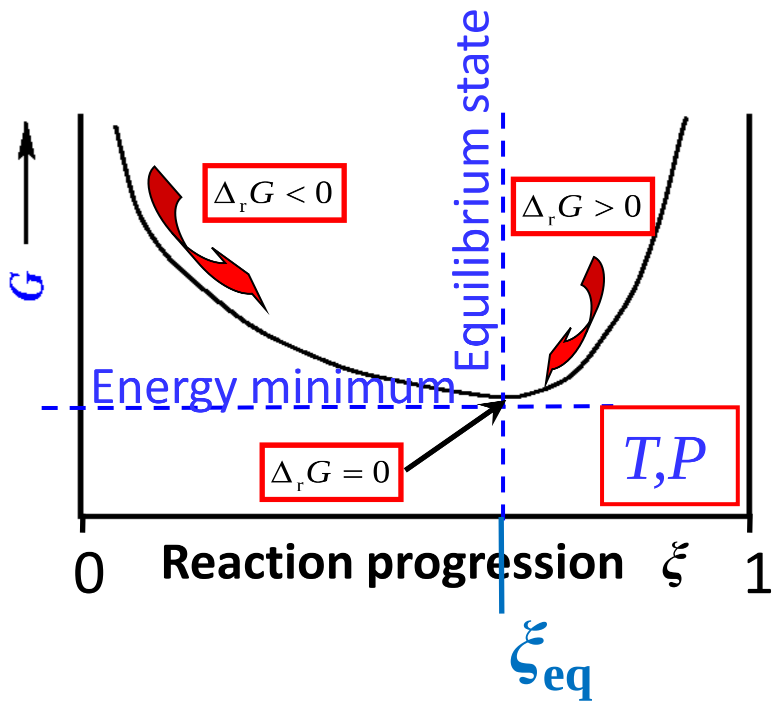
# Summary Lecture 4 (electrochemistry)

$$\boxed{\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q}$$

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

$$\boxed{E = E^{\Theta} - \frac{RT}{\nu F} \ln Q}$$

**Nernst equation**

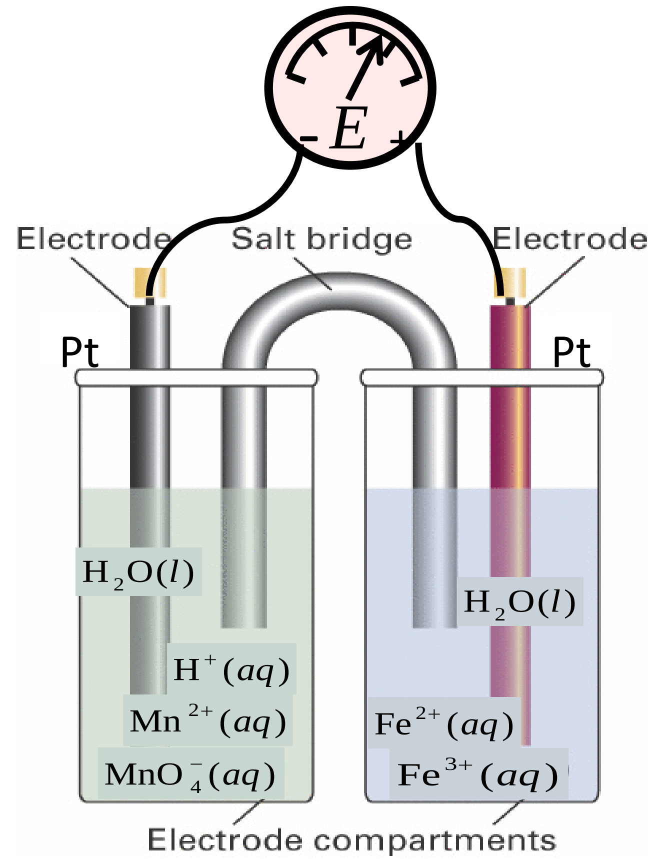



**reaction**

$\Delta_r G < 0$ $E > 0$

$\Delta_r G > 0$ $E < 0$

$\Delta_r G = 0$ $E = 0$



# Lecture 4: Final hour

# Lecture 3 and 4: Temperature dependence of $K$

$$\boxed{RT\ln K = -\Delta_r G^{\Theta}} \Rightarrow \boxed{\ln K = -\frac{\Delta_r G^{\Theta}}{RT}} \Rightarrow$$

$$\boxed{\left(\frac{\mathrm{d}\ln K}{\mathrm{d}T}\right)_P = \frac{\Delta_r G^{\Theta}}{RT^2} - \frac{1}{RT}\left(\frac{\mathrm{d}\Delta_r G^{\Theta}}{\mathrm{d}T}\right)_P}$$

$$\boxed{\mathrm{d}G^{\Theta} = -S^{\Theta}\mathrm{d}T + V^{\Theta}\mathrm{d}P}$$

$$\Rightarrow \boxed{-\frac{1}{RT}\left(\frac{\mathrm{d}\Delta_r G^{\Theta}}{\mathrm{d}T}\right)_P = +\frac{1}{RT}\Delta_r S^{\Theta}}$$

# Lecture 3 and 4: Temperature dependence of *K*

$$\left(\frac{\mathrm{d}\ln K}{\mathrm{d}T}\right)_P = \frac{\Delta_\mathrm{r} G^\Theta}{RT^2} + \frac{1}{RT}\Delta_\mathrm{r} S^\Theta = \frac{\Delta_\mathrm{r} H^\Theta - T\Delta_\mathrm{r} S^\Theta}{RT^2} + \frac{1}{RT}\Delta_\mathrm{r} S^\Theta$$

$$\Rightarrow \boxed{\left(\frac{\mathrm{d}\ln K}{\mathrm{d}T}\right)_P = \frac{\Delta_\mathrm{r} H^\Theta}{RT^2}}$$

Van 't Hoff equation

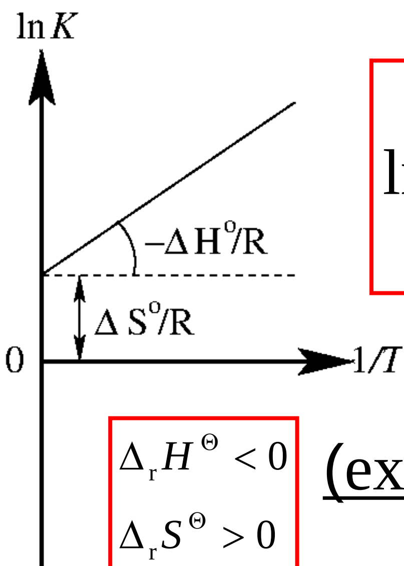
$$\Rightarrow \boxed{\ln K(T_2) - \ln K(T_1) = -\frac{\Delta_\mathrm{r} H^\Theta}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$$

$$\boxed{(\text{for constant } \Delta_\mathrm{r} H^\Theta)}$$

# Lecture 3 and 4: Temperature dependence of $K$

$$RT \ln K = -\Delta_r G^\Theta$$

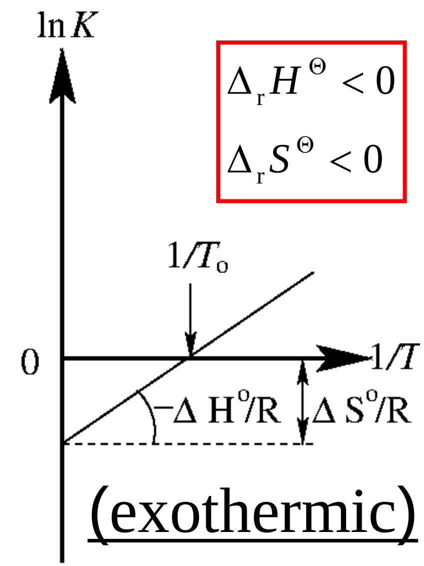
$$\ln K = \left[\frac{-\Delta_r H^\Theta}{R}\right]\frac{1}{T} + \left[\frac{\Delta_r S^\Theta}{R}\right]$$




$\Delta_r H^\Theta < 0$

$\Delta_r S^\Theta > 0$

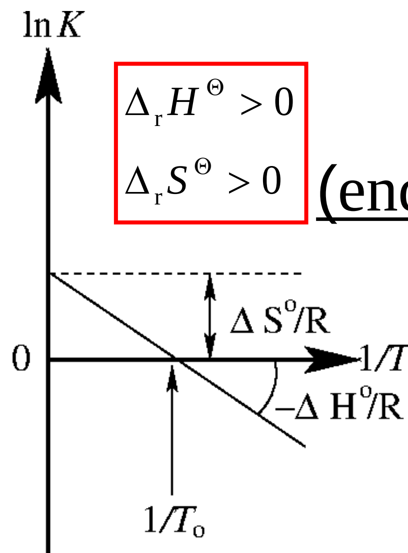
(exothermic)




$\Delta_r H^\Theta < 0$

$\Delta_r S^\Theta < 0$

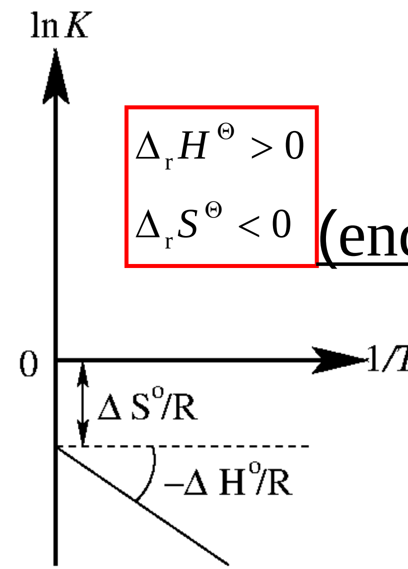
(exothermic)




$\Delta_r H^\Theta > 0$

$\Delta_r S^\Theta > 0$

(endothermic)

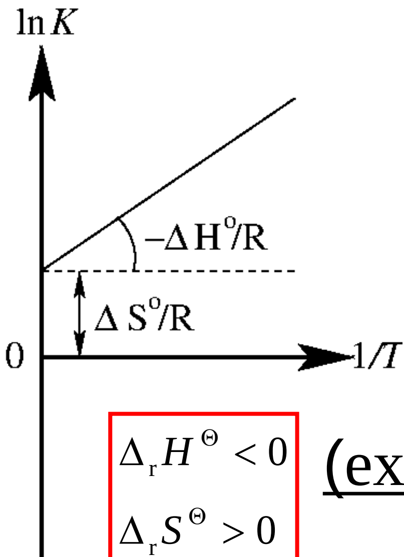



$\Delta_r H^\Theta > 0$

$\Delta_r S^\Theta < 0$

(endothermic)

# Lecture 3 and 4: Temperature dependence of *K*



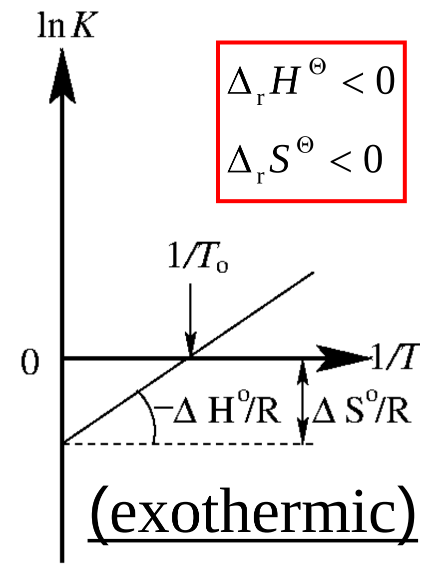

$\Delta_r H^\Theta < 0$
$\Delta_r S^\Theta > 0$

(exothermic)

at $T = T_o$:

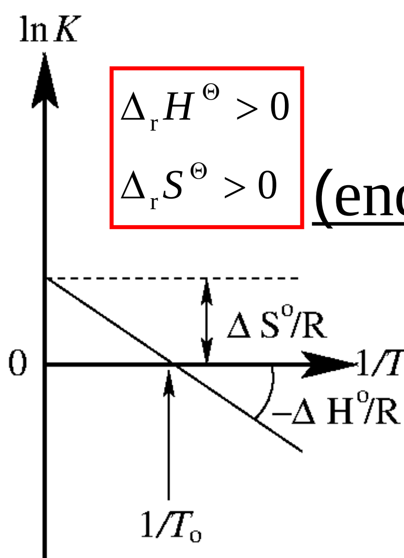
$$\boxed{\Delta_r G^\Theta = -RT_o \ln K = 0}$$

$$\left\{ \begin{array}{l} \boxed{K = 1} \\ \boxed{\Delta_r H^\Theta = T_o \Delta_r S^\Theta} \end{array} \right.$$



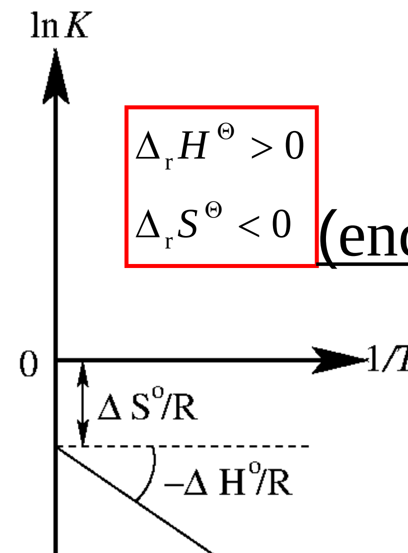

$\Delta_r H^\Theta < 0$
$\Delta_r S^\Theta < 0$

(exothermic)




$\Delta_r H^\Theta > 0$
$\Delta_r S^\Theta > 0$

(endothermic)




$\Delta_r H^\Theta > 0$
$\Delta_r S^\Theta < 0$

(endothermic)

# Lecture 3: Thermochemistry for $K$ (at temp $T$)

# Lecture 3: Thermochemistry for $\boldsymbol{K}$ (at temp $\boldsymbol{T}$)

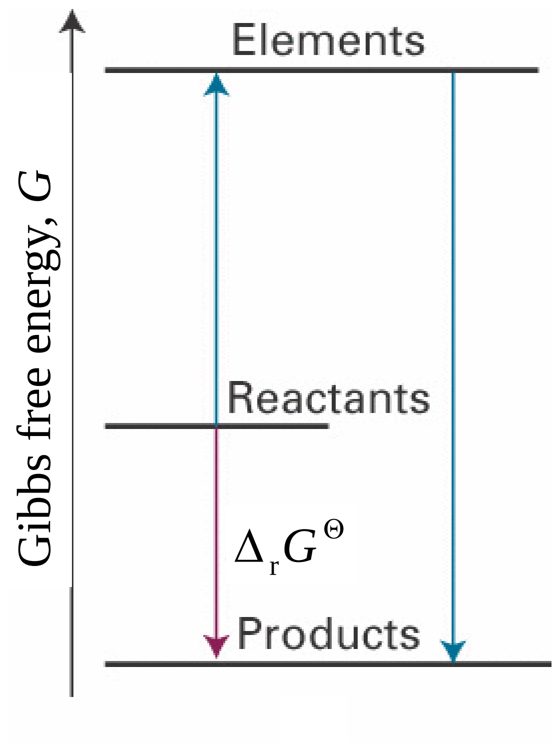
$$\boxed{RT \ln K = -\Delta_r G^{\Theta}}$$

$$\boxed{\Delta_r G^{\Theta} = \sum_i \nu_i \mu_i^{\Theta} = \sum_i \nu_i G_{m,i}^{\Theta}}$$

($\Theta$ => pure compound)

$$\boxed{\sum_i \nu_i G_{m,i}^{\Theta} = \sum_i \nu_i \Delta_f G_{m,i}^{\Theta}}$$

($G$ is a state function)




$$\boxed{RT \ln K = -\sum_i \nu_i \Delta_f G_{m,i}^{\Theta}}$$

# Lecture 3: Thermochemistry for *K* (at temp *T*)

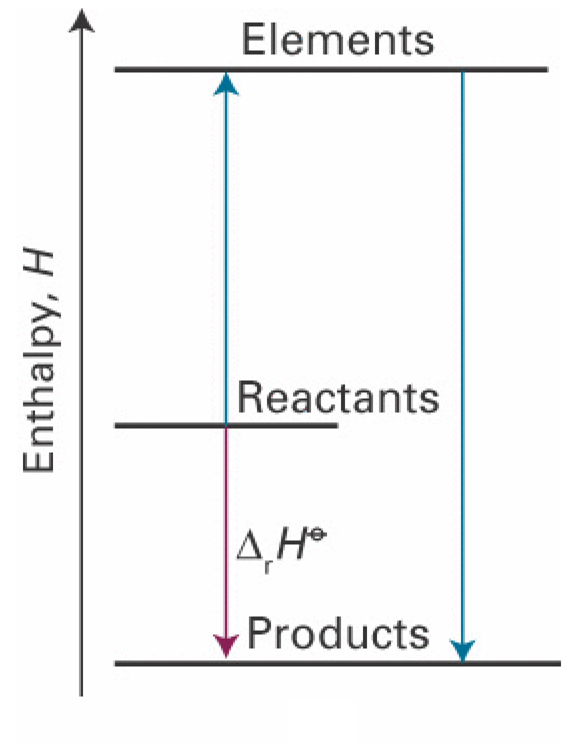
$$\boxed{RT\ln K = -\Delta_r G^{\ominus}} \quad \Rightarrow \quad \boxed{RT\ln K = -\Delta_r H^{\ominus} + T\Delta_r S^{\ominus}}$$

$$\boxed{\Delta_r H^{\ominus} = \sum_i \nu_i \Delta_f H_{m,i}^{\ominus}}$$

(*H* is a state function)

$$\boxed{\Delta_r S^{\ominus} = \sum_i \nu_i \Delta_f S_{m,i}^{\ominus}}$$

(*S* is a state function)




$$\boxed{RT\ln K = -\sum_i \nu_i \Delta_f H_{m,i}^{\ominus} + T\sum_i \nu_i \Delta_f S_{m,i}^{\ominus}}$$

Atkins: Table 2C.6-7 (ed.11)($T$ = 298 K)

| | $M/(\mathrm{g\ mol^{-1}})$ | $\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$ | $\Delta_f G^\ominus/(\mathrm{kJ\ mol^{-1}})$ | $S_m^\ominus/(\mathrm{J\ K^{-1}\ mol^{-1}})$† | $C_{p,m}^\ominus/(\mathrm{J\ K^{-1}\ mol^{-1}})$ |
|---|---|---|---|---|---|
| **Carbon** (Continued) | | | | | |
| $C_2(g)$ | 24.022 | +831.90 | +775.89 | 199.42 | 43.21 |
| $CO(g)$ | 28.011 | −110.53 | −137.17 | 197.67 | 29.14 |
| $CO_2(g)$ | 44.010 | −393.51 | −394.36 | 213.74 | 37.11 |
| $CO_2(aq)$ | 44.010 | −413.80 | −385.98 | 117.6 | |
| $H_2CO_3(aq)$ | 62.03 | −699.65 | −623.08 | 187.4 | |
| $HCO_3^-(aq)$ | 61.02 | −691.99 | −586.77 | +91.2 | |
| $CO_3^{2-}(aq)$ | 60.01 | −677.14 | −527.81 | −56.9 | |
| $CCl_4(l)$ | 153.82 | −135.44 | −65.21 | 216.40 | 131.75 |
| $CS_2(l)$ | 76.14 | +89.70 | +65.27 | 151.34 | 75.7 |
| $HCN(g)$ | 27.03 | +135.1 | +124.7 | 201.78 | 35.86 |
| $HCN(l)$ | 27.03 | +108.87 | +124.97 | 112.84 | 70.63 |
| $CN^-(aq)$ | 26.02 | +150.6 | +172.4 | +94.1 | |
| **Chlorine** | | | | | |
| $Cl_2(g)$ | 70.91 | 0 | 0 | 223.07 | 33.91 |
| $Cl(g)$ | 35.45 | +121.68 | +105.68 | 165.20 | 21.840 |
| $Cl^-(g)$ | 34.45 | −233.13 | | | |
| $Cl^-(aq)$ | 35.45 | −167.16 | −131.23 | +56.5 | −136.4 |
| $HCl(g)$ | 36.46 | −92.31 | −95.30 | 186.91 | 29.12 |
| $HCl(aq)$ | 36.46 | −167.16 | −131.23 | 56.5 | −136.4 |
| **Chromium** | | | | | |
| $Cr(s)$ | 52.00 | 0 | 0 | 23.77 | 23.35 |
| $Cr(g)$ | 52.00 | +396.6 | +351.8 | 174.50 | 20.79 |
| $CrO_4^{2-}(aq)$ | 115.99 | −881.15 | −727.75 | +50.21 | |
| $Cr_2O_7^{2-}(aq)$ | 215.99 | −1490.3 | −1301.1 | +261.9 | |
| **Copper** | | | | | |
| $Cu(s)$ | 63.54 | 0 | 0 | 33.150 | 24.44 |
| $Cu(g)$ | 63.54 | +338.32 | +298.58 | 166.38 | 20.79 |
| $Cu^+(aq)$ | 63.54 | +71.67 | +49.98 | | |
| $Cu^{2+}(aq)$ | 63.54 | +64.77 | +65.49 | | |
| $Cu_2O(s)$ | 143.08 | −168.6 | −146.0 | | 63.64 |
| $CuO(s)$ | 79.54 | −157.3 | −129.7 | | 42.30 |
| $CuSO_4(s)$ | 159.60 | −771.36 | −661.8 | | 100.0 |
| $CuSO_4\cdot H_2O(s)$ | 177.62 | −1085.8 | −918.11 | | 134 |
| $CuSO_4\cdot 5H_2O(s)$ | 249.68 | −2279.7 | −1879.7 | | 280 |
| **Deuterium** | | | | | |
| $D_2(g)$ | | | | | |
| $HD(g)$ | | | | | |
| $D_2O(g)$ | | | | | |
| $D_2O(l)$ | | | | | |
| $HDO(g)$ | | | | | |
| $HDO(l)$ | 19.022 | −289.89 | −241.86 | 79.29 | |

for all $T$(g)

for all $T$(s)

Absolute entropy

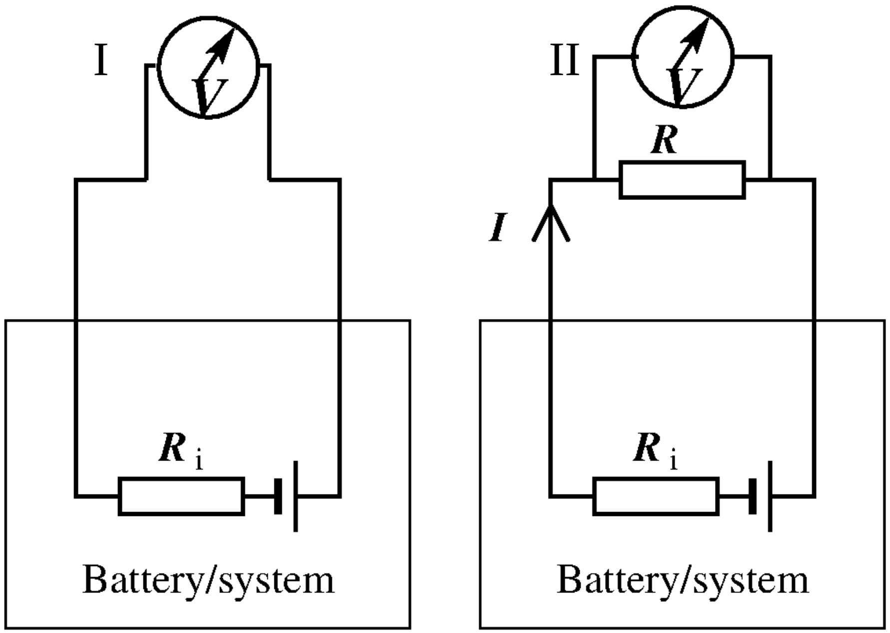
$$\Delta_r S^\ominus = \sum_i \nu_i \Delta_f S_{m,i}^\ominus = \sum_i \nu_i S_{m,i}^\ominus$$

$$\boxed{S_{m,i}^\ominus}$$

# Thermodynamics problem: My Auncle and I

# Thermodynamics problem: My Auncle and I

## The voltage across the terminals of a battery




**What is the voltage measured ?**

Possible answers:

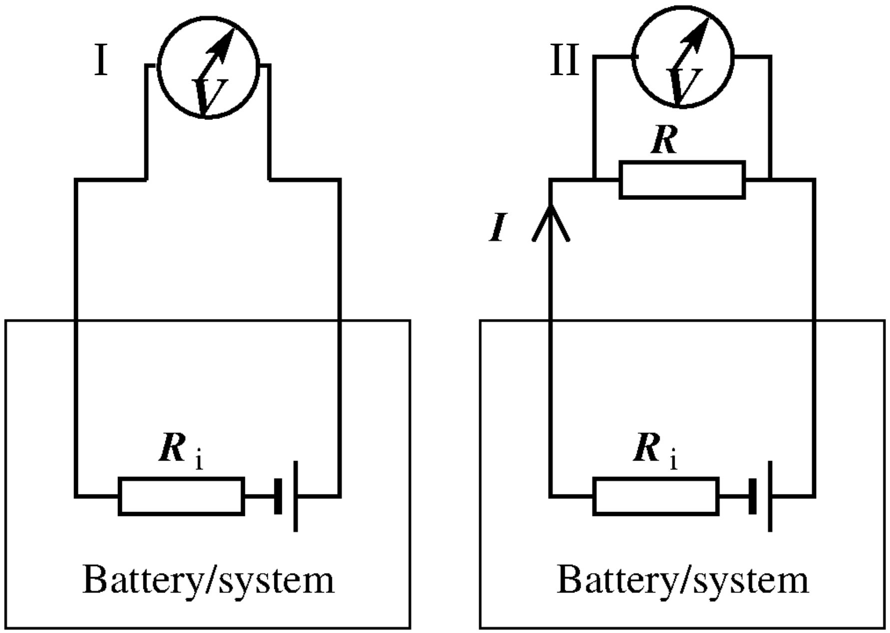
Answer 1: $V_{\mathrm{I}} = (R + R_{\mathrm{i}})V_{\mathrm{II}} / R$

Answer 2: $V_{\mathrm{I}} = R_{\mathrm{i}} V_{\mathrm{II}} / R$

Answer 3: $V_{\mathrm{I}} = R_{\mathrm{i}} V_{\mathrm{II}} / (R + R_{\mathrm{i}})$

# Thermodynamics problem: My Auncle and I

## The voltage across the terminals of a battery




What is the voltage measured ?

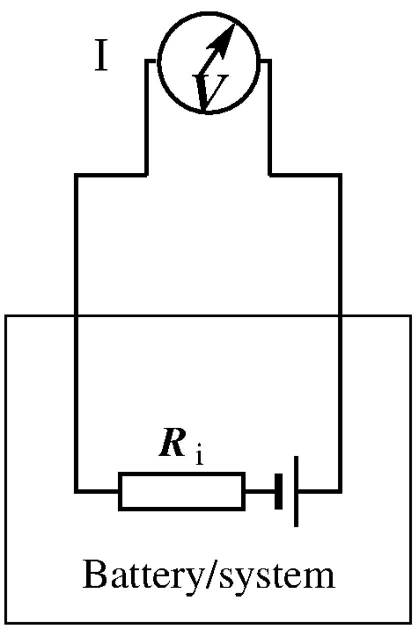
Possible answers:

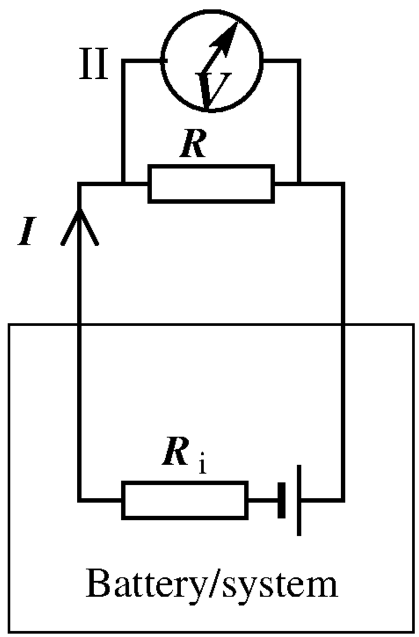
- Answer 1: $V_I = (R + R_i)V_{II} / R$
- Answer 2: $V_I = R_i V_{II} / R$
- Answer 3: $V_I = R_i V_{II} / (R + R_i)$

My auncle says: the current ***I*** runs through ***R*** , so together with Ohm's law $V_{II}$ = ***IR*** we find a lower voltage, so $V_I > V_{II}$
➔ answer 1

# Thermodynamics problem: My Auncle and I

The voltage across the terminals of a battery




What is the voltage measured ?

Possible answers:

Answer 1: $V_{\mathrm{I}} = (R + R_{\mathrm{i}})V_{\mathrm{II}} / R$

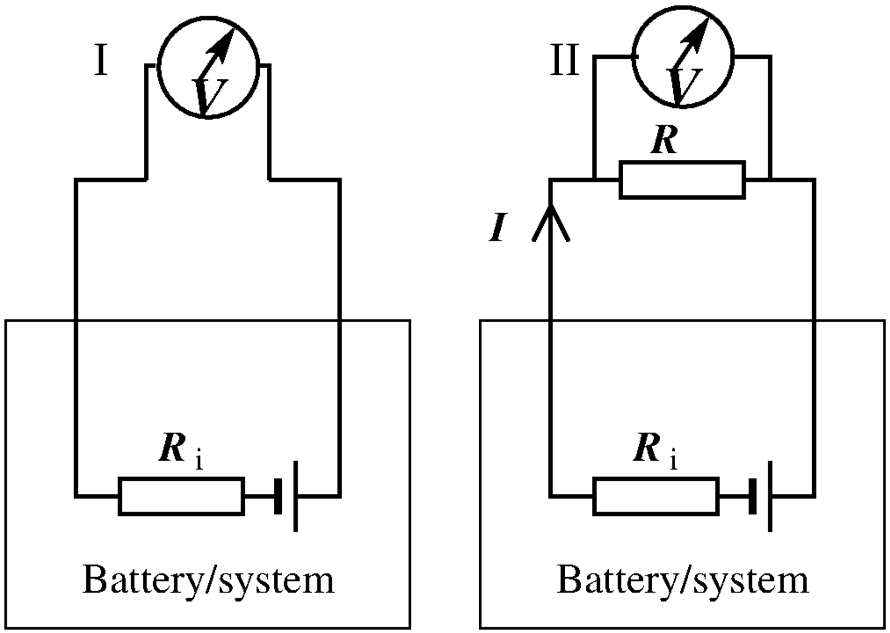
Answer 2: $V_{\mathrm{I}} = R_{\mathrm{i}} V_{\mathrm{II}} / R$

Answer 3: $V_{\mathrm{I}} = R_{\mathrm{i}} V_{\mathrm{II}} / (R + R_{\mathrm{i}})$

I say: the volt meter is a perfect volt meter, so it takes negligible current, so $V_{\mathrm{II}} / R = V_{\mathrm{I}} / R_{\mathrm{i}}$ ➔ answer 2

# Thermodynamics problem: My Auncle and I

## The voltage across the terminals of a battery




What is the voltage measured ?

Possible answers:

Answer 1: $V_{\mathrm{I}} = (R + R_{\mathrm{i}})V_{\mathrm{II}} / R$

Answer 2: $V_{\mathrm{I}} = R_{\mathrm{i}} V_{\mathrm{II}} / R$

Answer 3: $V_{\mathrm{I}} = R_{\mathrm{i}} V_{\mathrm{II}} / (R + R_{\mathrm{i}})$