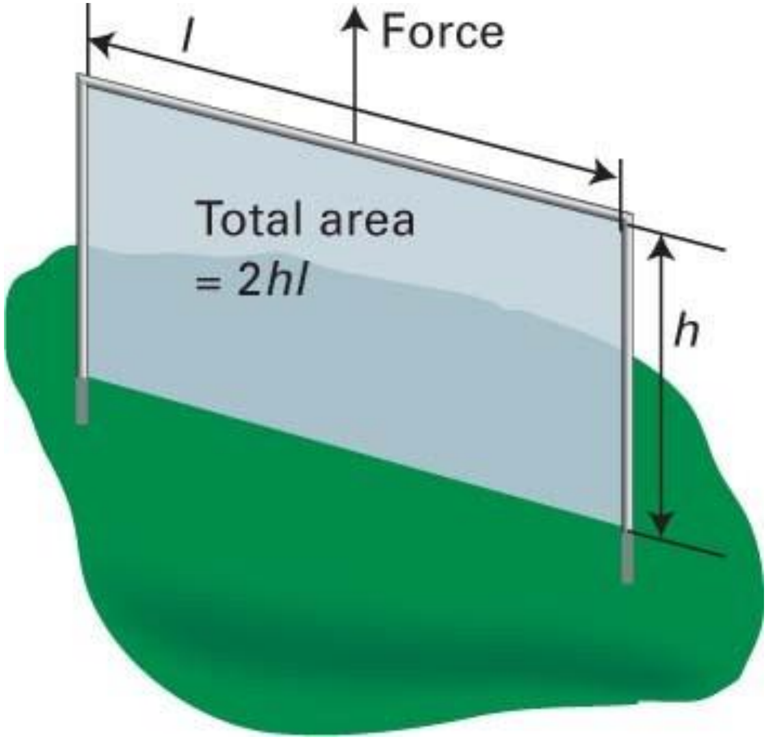
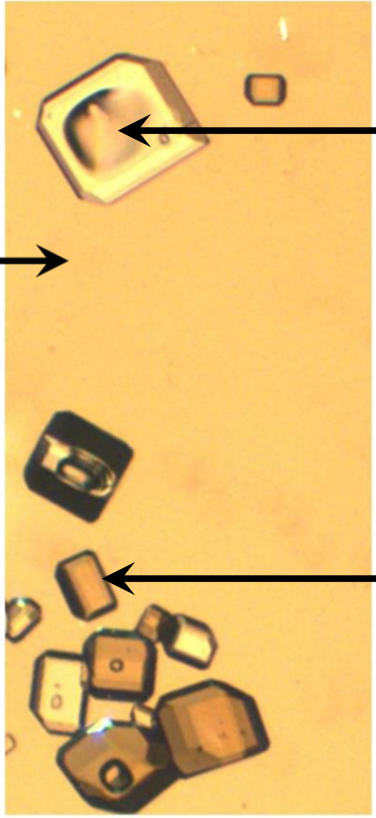
Thermodynamics of surfaces and interfaces



Atkins (ed. 12, 11): §14C.2 - 14C.4
Atkins (ed. 10): §16C.2 - 16C.4
Atkins (ed. 9): §17.8 - 17.10
Study Guide: P.19

Na_2ClO_3 crystals in a saturated solution

saturated solution

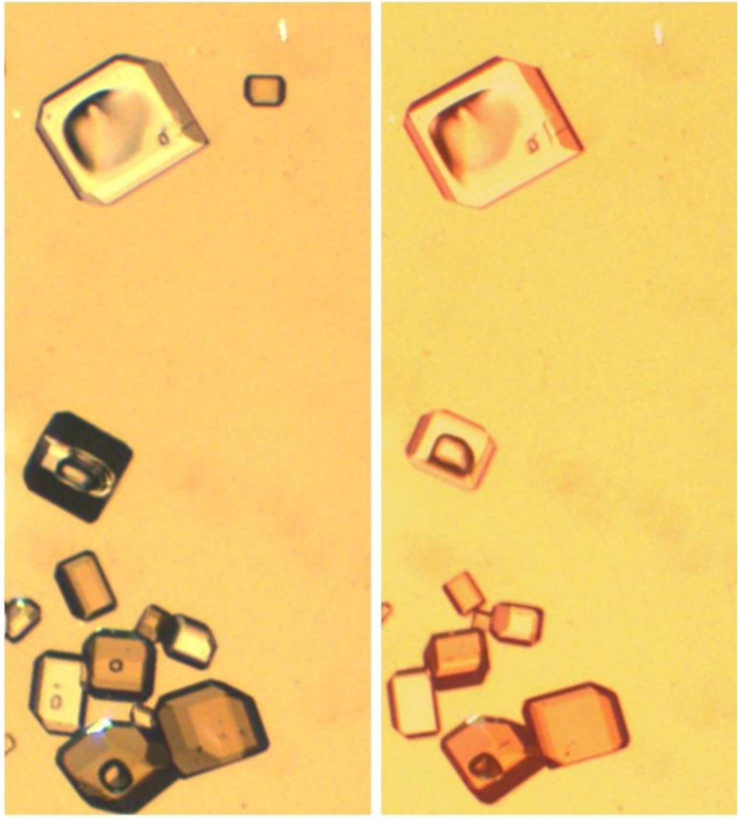


Optically left rotating crystal

Optically right rotating crystal

Optical active crystals under polarizing microscope

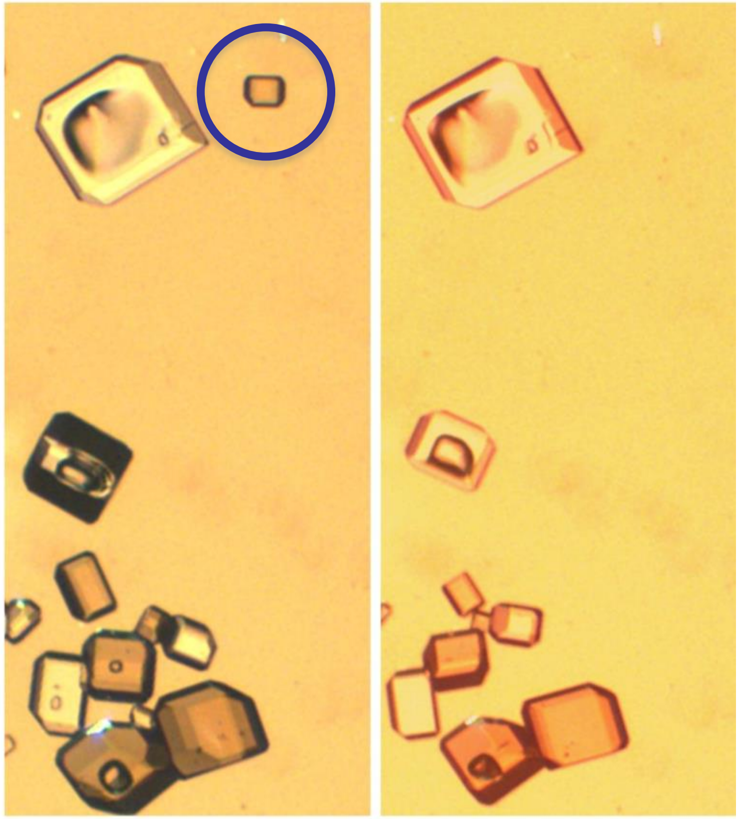
Na_2ClO_3 crystals in a saturated solution



$T = 0$ $T = 1$ day

Large crystals grow; small crystals dissolve

Na_2ClO_3 crystals in a saturated solution



$T = 0$ $T = 1$ day

Wilhelm Ostwald

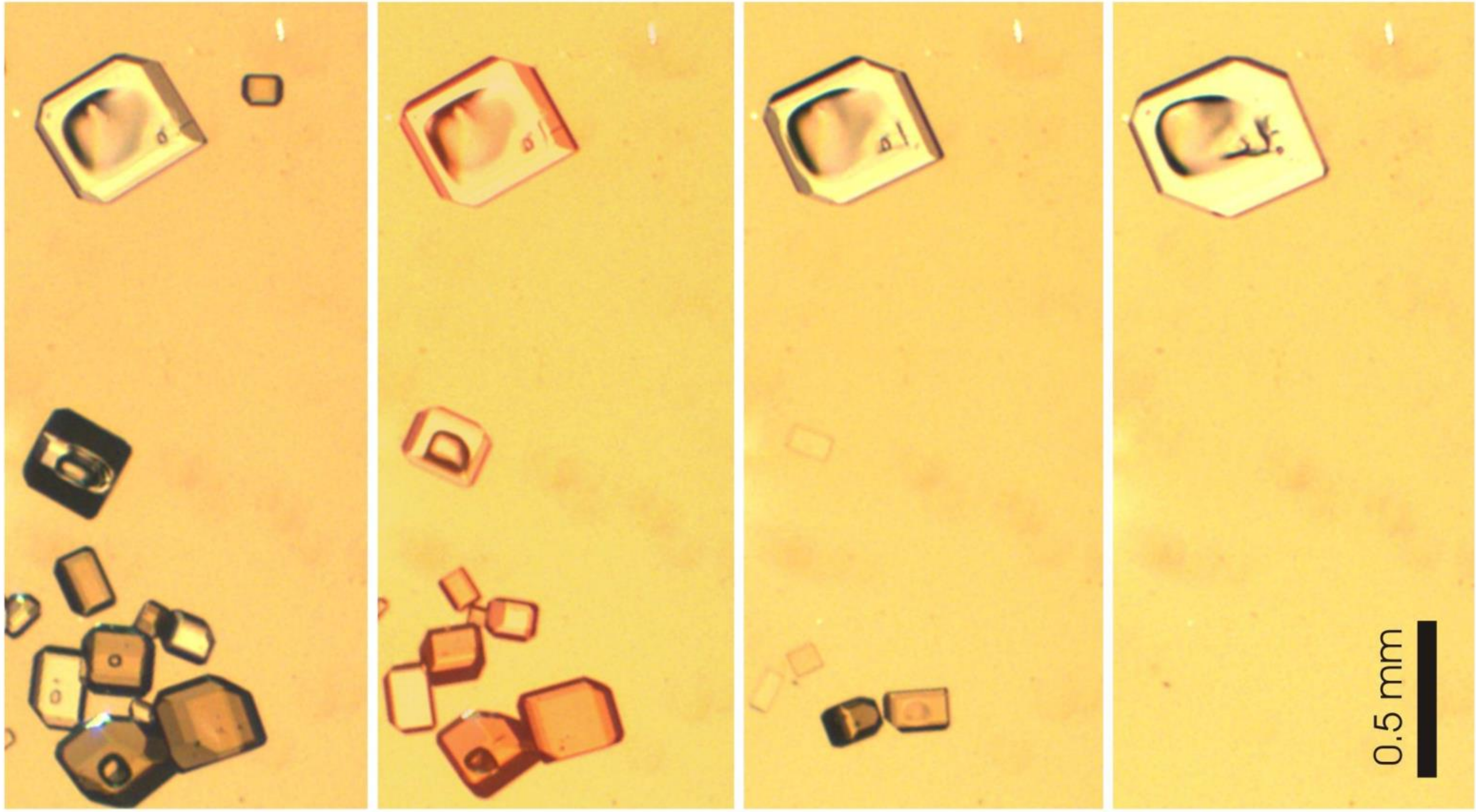
(1853-1932)

Ostwald ripening

(1896)

Large crystals grow; small crystals dissolve

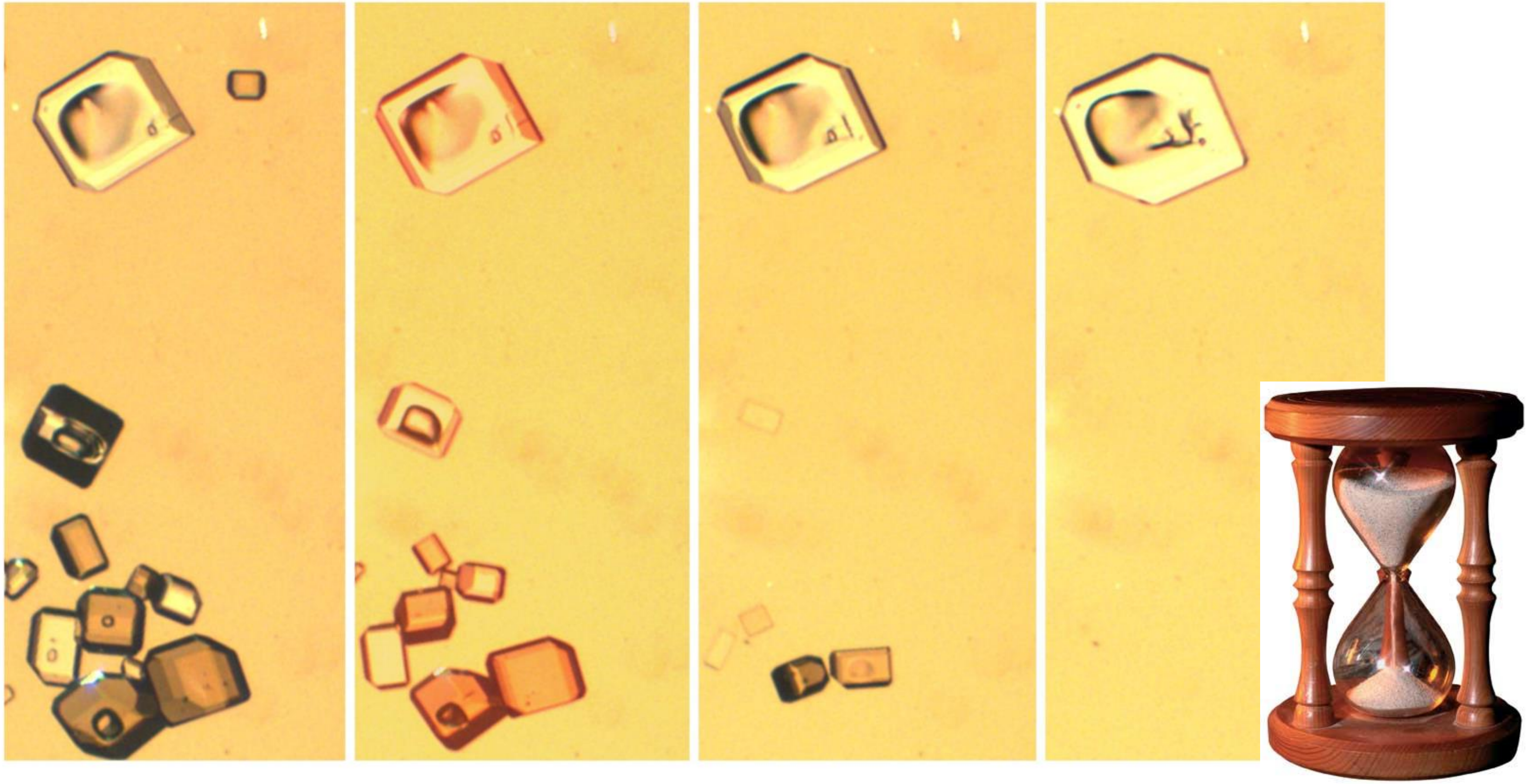
Na_2ClO_3 crystals in a saturated solution



T = 0 *T* = 1 day 10 days 30 days

Equilibrium: one single crystal of single handedness!

Na_2ClO_3 crystals in a saturated solution



$T = 0$ $T = 1$ day 10 days 30 days

Equilibrium: one single crystal of single handedness!

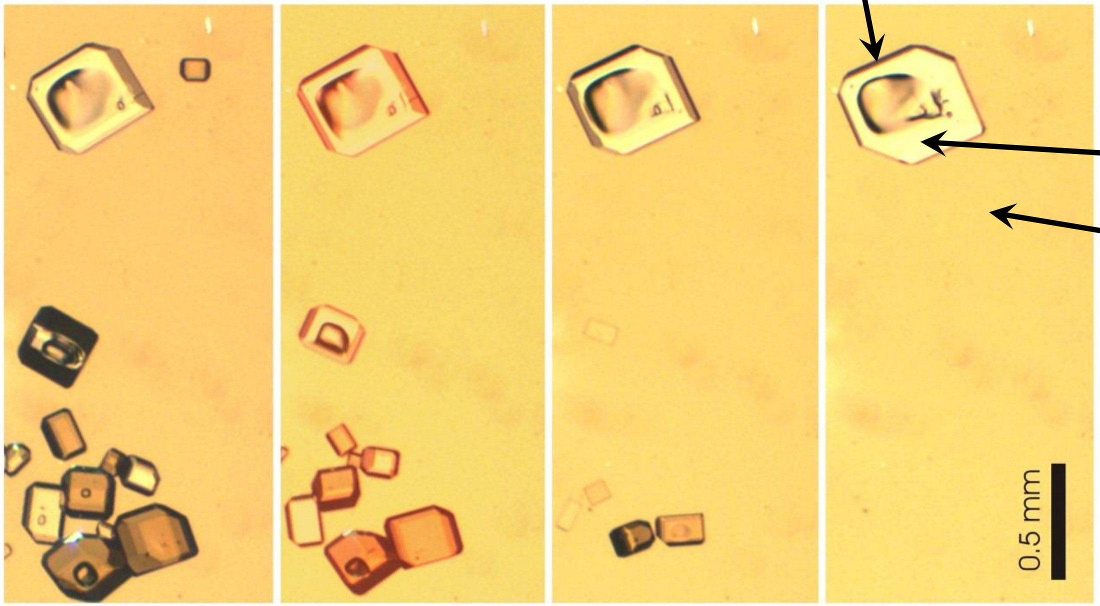
Gibbs-Thomson effect

Interfacial (free) energy between two phases

$$\boxed{dA = -SdT - PdV + dW_\sigma}$$

σ : Interfacial surface

A : Helmholtz free energy



crystal

solution

Gibbs-Thomson effect

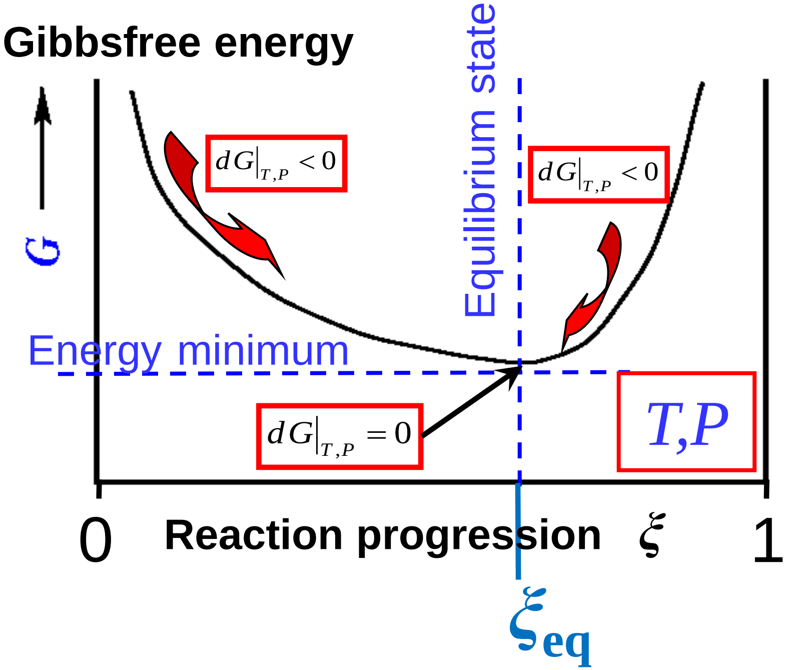
Interfacial (free) energy between two phases

$$\boxed{dA = -SdT - PdV + dW_\sigma}$$

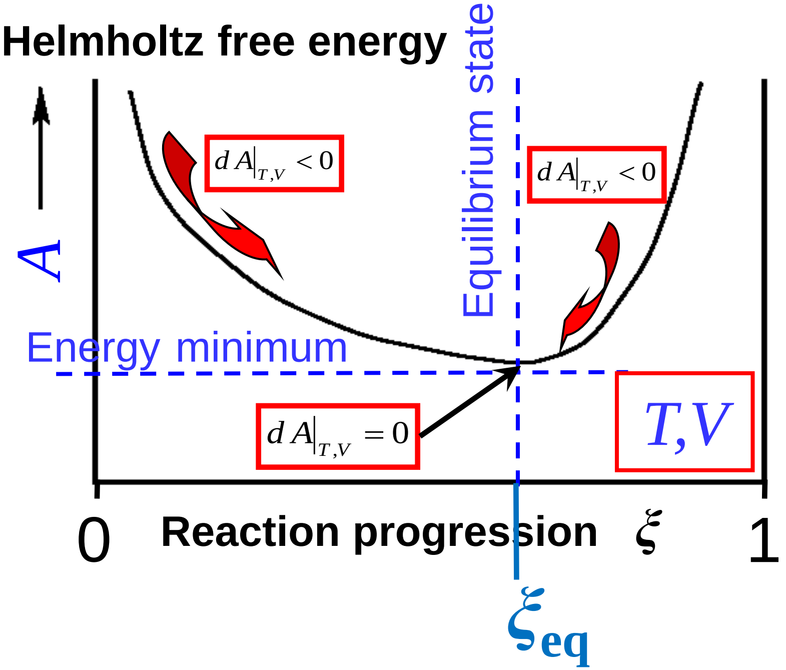
σ : Interfacial surface

A : Helmholtz free energy

Gibbsfree energy



Helmholtz free energy



Gibbs-Thomson effect

Interfacial (free) energy between two phases

$$\boxed{dA = -SdT - PdV + dW_\sigma}$$

σ : Interfacial surface

$$\boxed{dA_{T,V} = dW_\sigma \equiv \gamma d\sigma}$$

γ : Interfacial or surface tension

$\boxed{\gamma > 0}$ ➡ Interfacial tension γ tends to reduce σ

σ (m^2): surface

γ (Jm^{-2}): surface free energy

relevant for $P > 1$

Gibbs-Thomson effect

Interfacial (free) energy between two phases

$$\boxed{dA = -SdT - PdV + dW_\sigma}$$

σ : Interfacial surface

$$\boxed{dA_{T,V} = dW_\sigma \equiv \gamma d\sigma}$$

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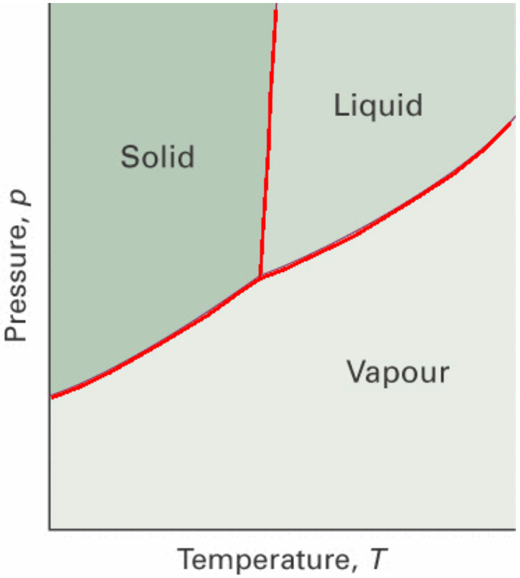
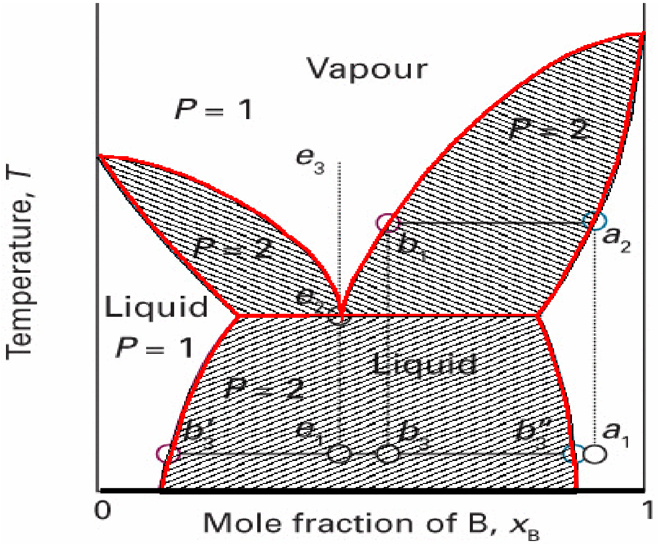
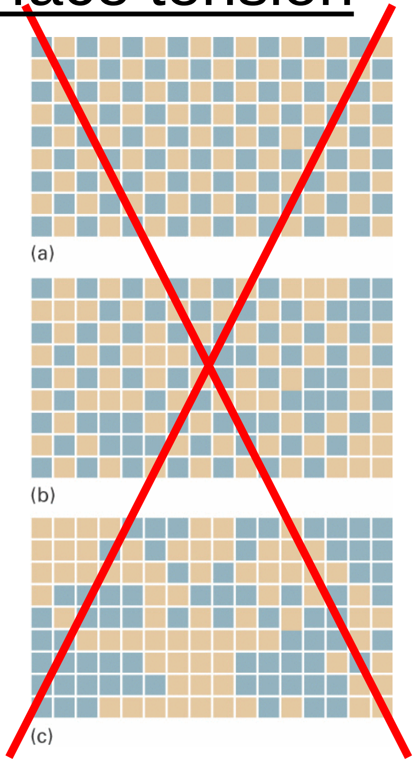


$P = 2,3$



$P = 2,3$



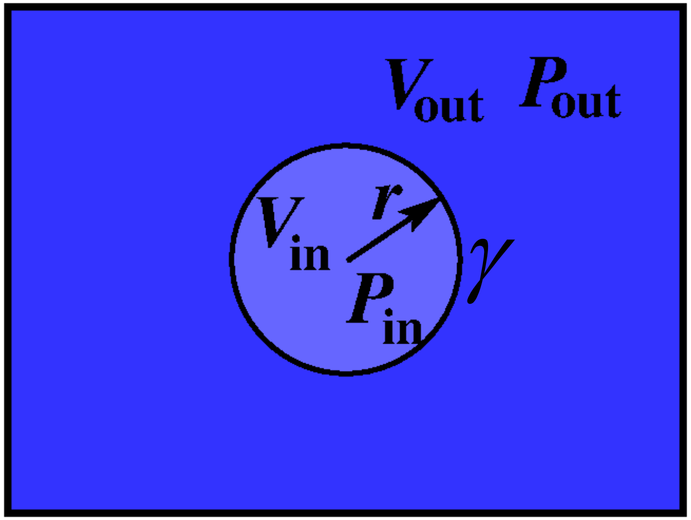
$P = 1$

Gibbs-Thomson effect: Laplace equation

Equilibrium: $$\boxed{dA = -SdT + dW_V^{\text{rev}} + dW_\sigma^{\text{rev}} = -SdT - PdV + \gamma\, d\sigma}$$

Interfacial or surface tension $\gamma > 0$ tends to reduce σ

➡ Smallest surface σ is a sphere



$$\boxed{\gamma \Rightarrow \mathrm{d}\sigma < 0}$$

$$\boxed{P_{\text{in}} \Rightarrow \mathrm{d}V_{\text{in}} > 0}$$

$$\boxed{P_{\text{out}} \Rightarrow \mathrm{d}V_{\text{in}} < 0}$$

Equilibrium: Relation between P_{in}, P_{out} and γ ?

Gibbs-Thomson effect: Laplace equation

Equilibrium: $$\boxed{dA = -SdT + dW_V^{\text{rev}} + dW_\sigma^{\text{rev}} = -SdT - PdV + \gamma\, d\sigma}$$

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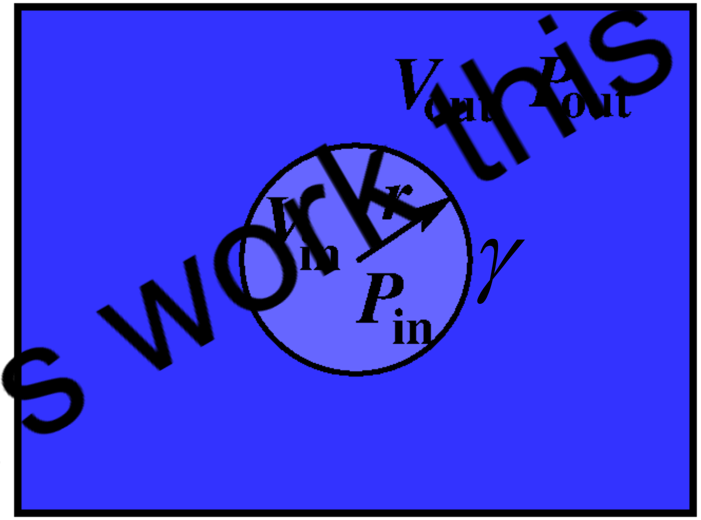


$$\boxed{\gamma \Rightarrow \mathrm{d}\sigma < 0}$$

$$\boxed{P_{\text{in}} \Rightarrow \mathrm{d}V_{\text{in}} > 0}$$

$$\boxed{P_{\text{out}} \Rightarrow \mathrm{d}V_{\text{in}} < 0}$$

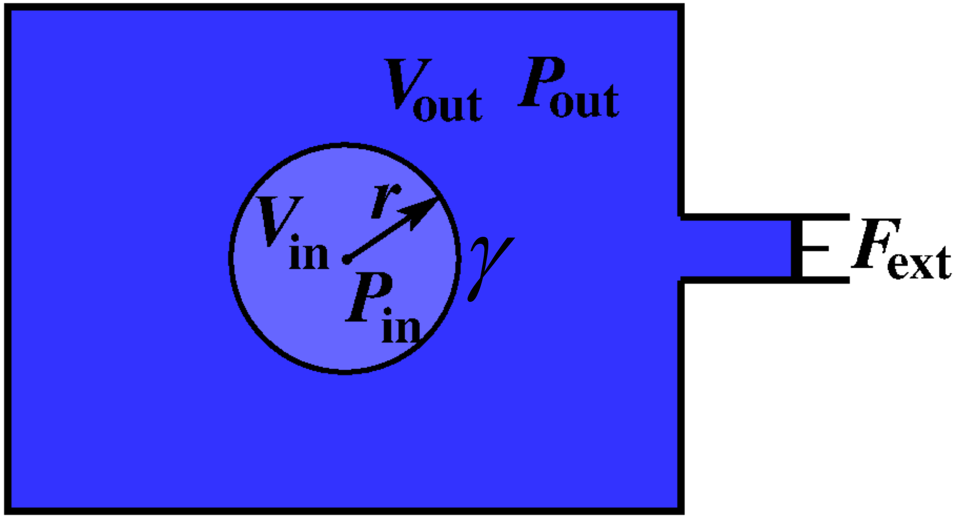
Let's work this out in detail

Equilibrium: Relation between P_{in}, P_{out} and γ ?

Gibbs-Thomson effect: Laplace equation

$$\boxed{dA = -SdT + dW_V^{\mathrm{rev}} + dW_\sigma^{\mathrm{rev}} = -SdT - PdV + \gamma\, d\sigma}$$

$$\left.\begin{array}{l} \rightarrow \boxed{dA_T = -P_{\mathrm{in}} dV_{\mathrm{in}} - P_{\mathrm{out}} dV_{\mathrm{out}} + \gamma\, d\sigma} \\ \boxed{dA_T = -P_{\mathrm{ext}} dV = -P_{\mathrm{out}} dV = -P_{\mathrm{out}}\left(dV_{\mathrm{in}} + dV_{\mathrm{out}}\right)} \end{array}\right\} \rightarrow$$



$$\rightarrow \boxed{P_{\mathrm{in}} dV_{\mathrm{in}} = P_{\mathrm{out}} dV_{\mathrm{in}} + \gamma\, d\sigma}$$

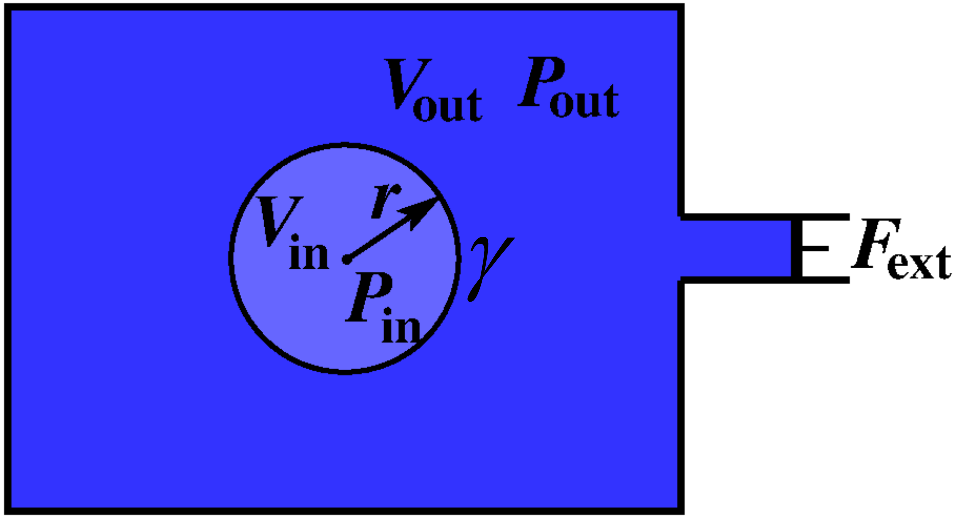
Gibbs-Thomson effect: Laplace equation

$$P_{\text{in}} dV_{\text{in}} = P_{\text{out}} dV_{\text{in}} + \gamma\, d\sigma$$

Equilibrium and isotropic γ:

$$\mathrm{d}V_{\text{in}} = \frac{\mathrm{d}V_{\text{in}}}{\mathrm{d}r}\mathrm{d}r = \frac{\mathrm{d}4\pi/3\, r^3}{\mathrm{d}r}\mathrm{d}r = 4\pi\, r^2 \mathrm{d}r$$

$$\mathrm{d}\sigma = \frac{\mathrm{d}\sigma}{\mathrm{d}r}\mathrm{d}r = \frac{\mathrm{d}4\pi\, r^2}{\mathrm{d}r}\mathrm{d}r = 8\pi\, r\mathrm{d}r$$



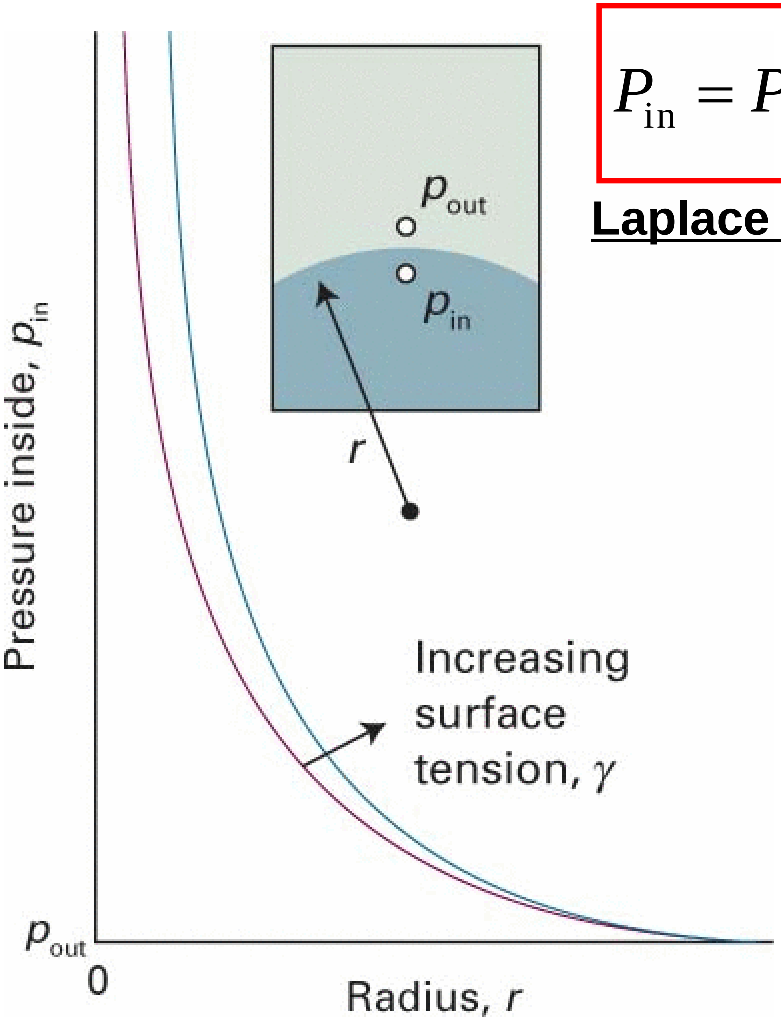
Laplace equation

$$P_{\text{in}} 4\pi\, r^2 \mathrm{d}r = P_{\text{out}} 4\pi\, r^2 \mathrm{d}r + \gamma\, 8\pi\, r\mathrm{d}r$$

$$\boxed{P_{\text{in}} = P_{\text{out}} + \frac{2\gamma}{r}}$$

Gibbs-Thomson effect: Laplace equation

Surface tension γ ($Jm^{-2} = Nm^{-1}$)

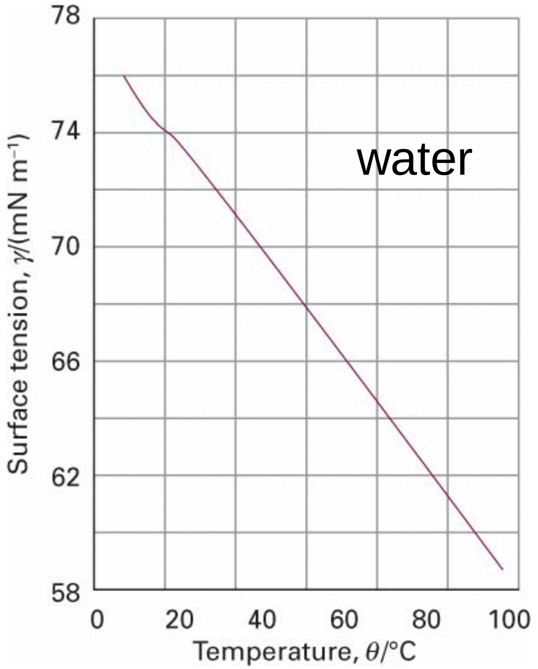


$$\boxed{P_{in} = P_{out} + \frac{2\gamma}{r}}$$

Laplace equation

(293 K, in air)	$\gamma/(mN\,m^{-1})$
Benzene	28.88
Mercury	472
Methanol	22.6
Water	72.75

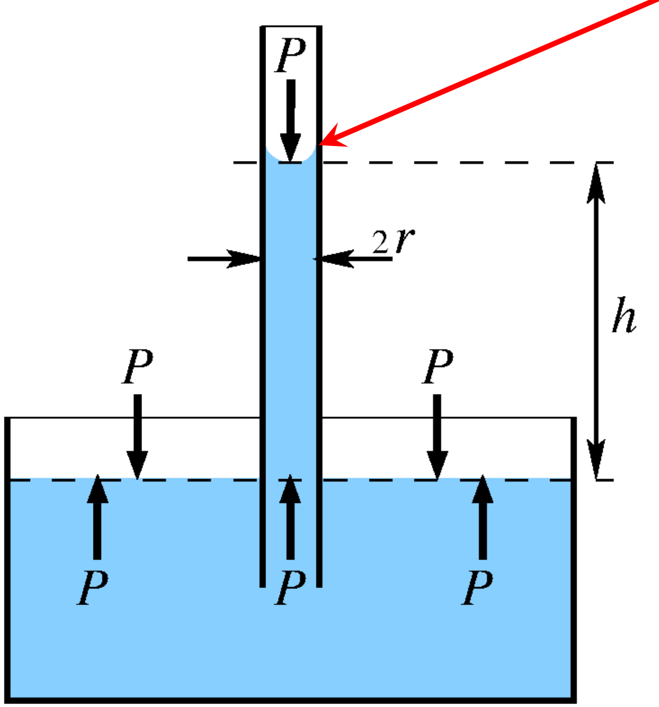
* More values are given in the *Data section*.
Note that $1\ N\,m^{-1} = 1\ J\,m^{-2}$.



Surface tension and capillary action

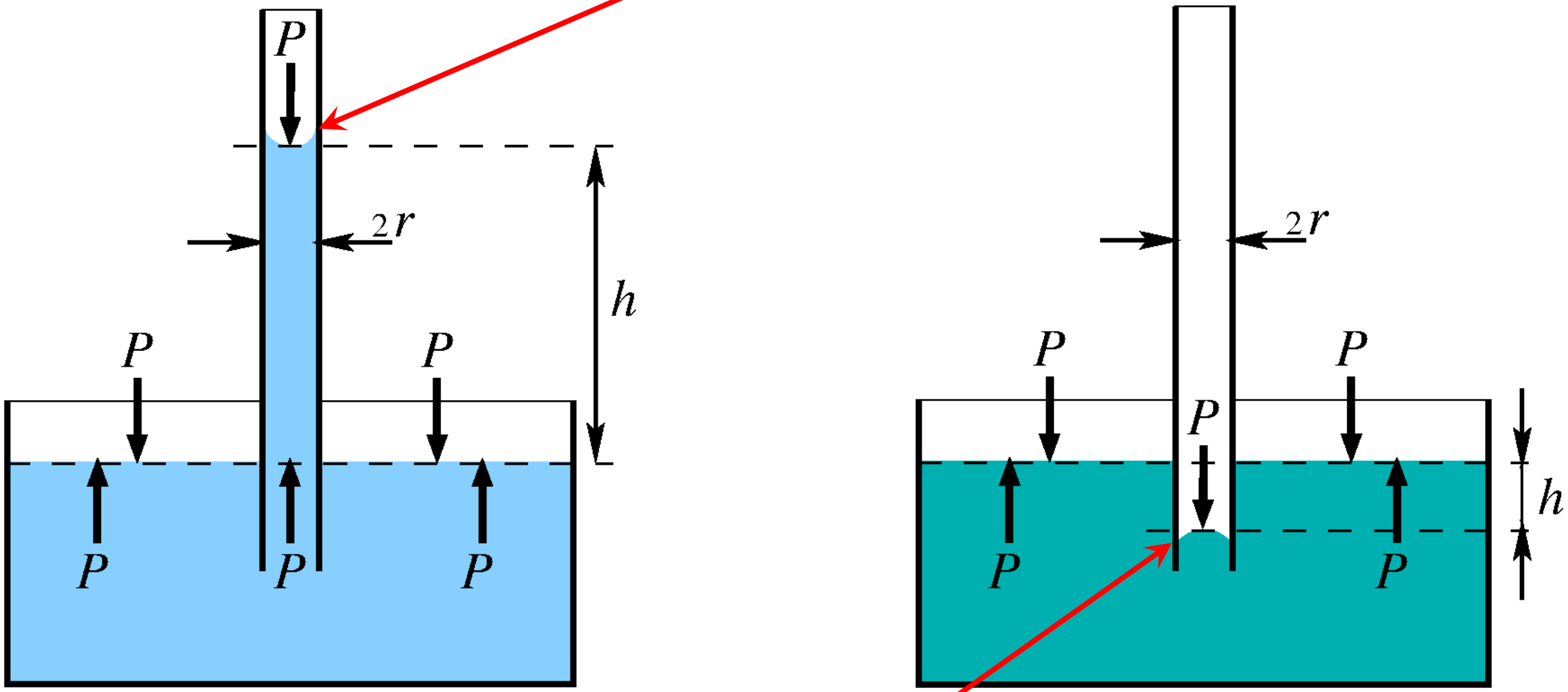
Surface tension and capillary action

Adhesive force between liquid and capillary, e.g. H_2O/glass



Surface tension and capillary action

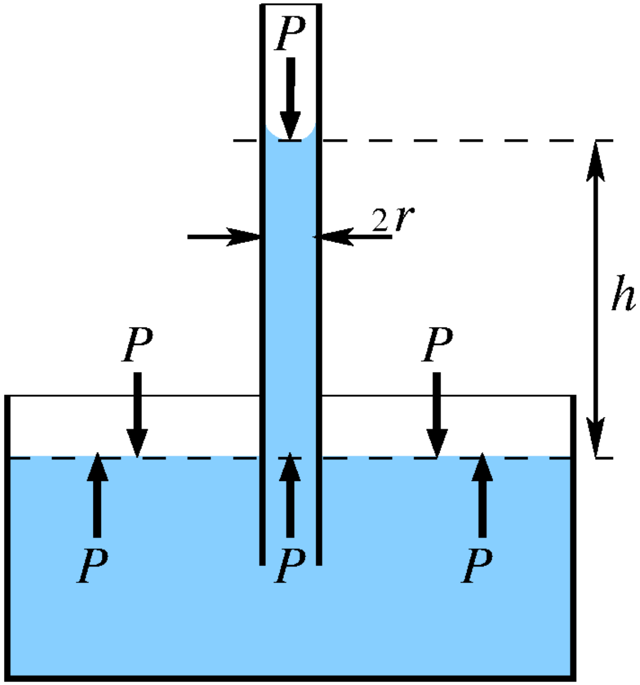
Adhesive force between liquid and capillary, e.g. H_2O/glass



Stronger cohesive force within the liquid, e.g. Hg/glass

Surface tension and capillary action

Adhesive force between liquid and capillary



Pressure of a liquid column of height h and mass density ρ

$$P(h) = \frac{F(h)}{A} = \frac{m(h)g}{A} = \frac{m(h)gh}{Ah} = \frac{m(h)gh}{V} = \rho g h$$

Surface tension and capillary action

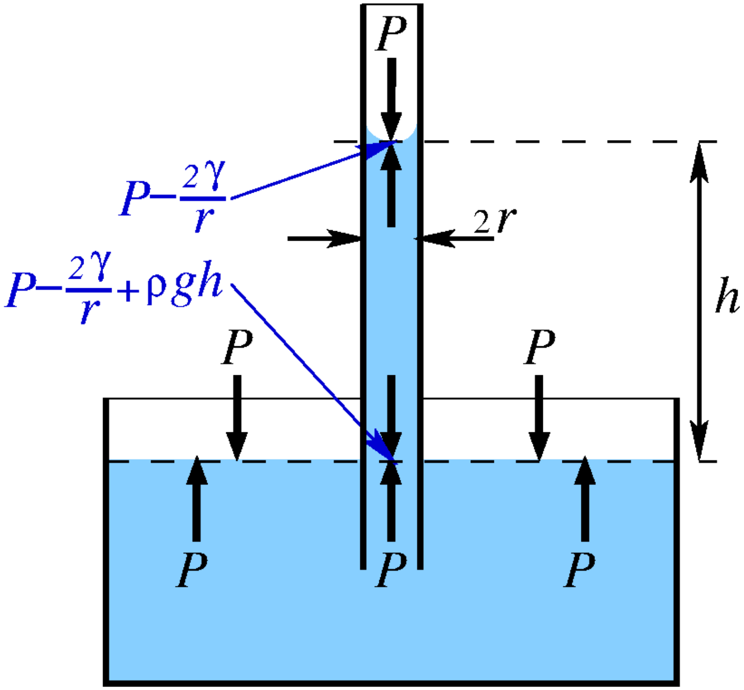
Adhesive force between liquid and capillary

Laplace equation

$$\Delta P = P_{\text{in}} - P_{\text{out}} = \frac{2\gamma}{r}$$

$$P(h) = \rho g h$$

equilibrium $P(h) = \Delta P$



$$P(h) = \frac{F(h)}{A} = \frac{m(h)g}{A} = \frac{m(h)gh}{Ah} = \frac{m(h)gh}{V} = \rho g h$$

Surface tension and capillary action

Adhesive force between liquid and capillary

Laplace equation

$$\Delta P = P_{\text{in}} - P_{\text{out}} = \frac{2\gamma}{r}$$

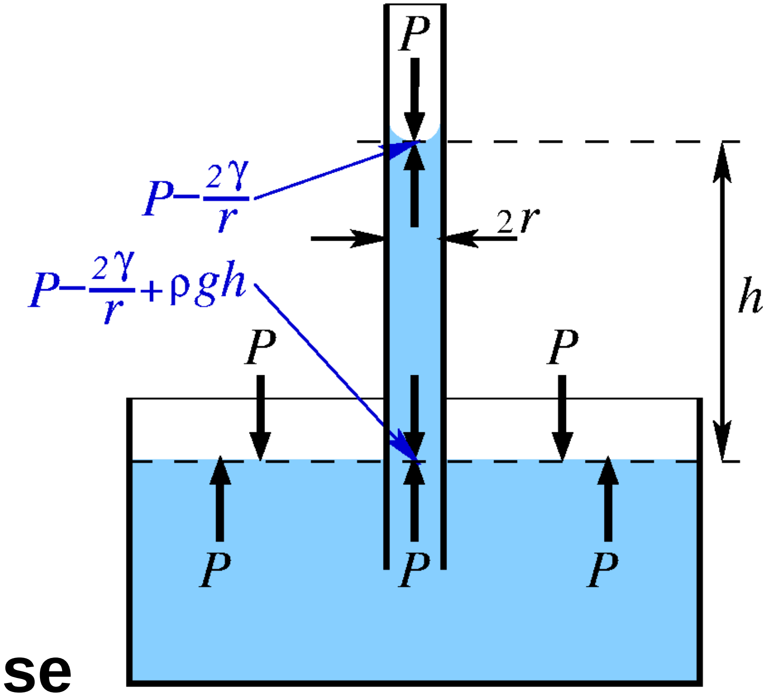
$$P(h) = \rho g h$$

equilibrium

$$P(h) = \Delta P$$

$$h = \frac{2\gamma}{\rho g r}$$

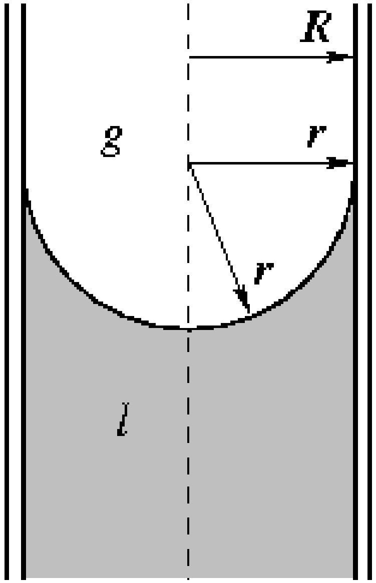
capillary rise

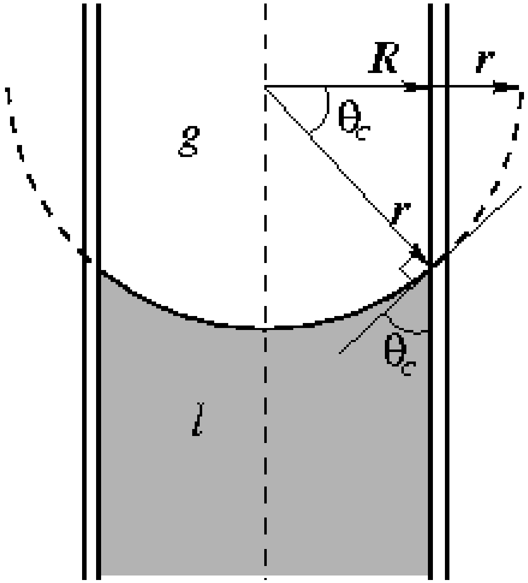


Exercise 22

Surface tension and capillary action

$$\boxed{\theta_c = 0}$$





$$\boxed{\cos\theta_c = \frac{R}{r}}$$

$$\boxed{\theta_c = 0} \qquad \boxed{r = R}$$

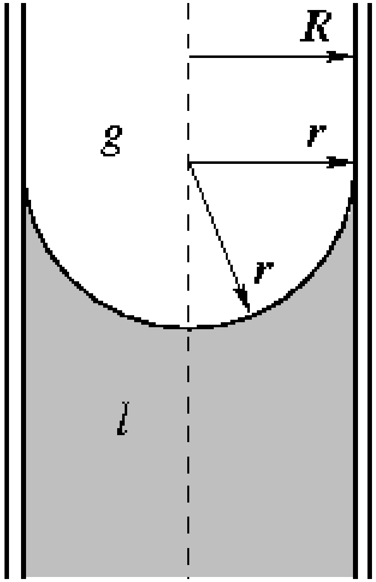
$$\boxed{h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}}$$

$$\boxed{\theta_c \neq 0} \qquad \boxed{r > R}$$

$$\boxed{h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}\cos\theta_c}$$

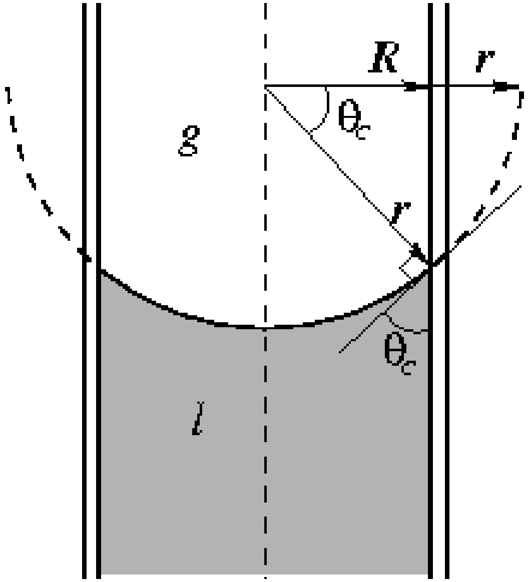
Surface tension and capillary action

equilibrium situations



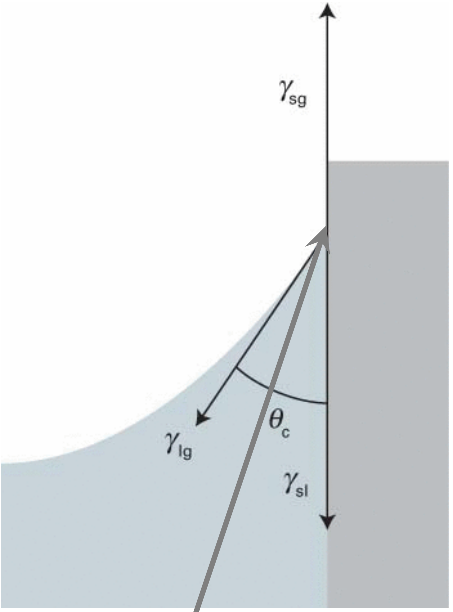
$$\boxed{\theta_c = 0}$$

$$\boxed{h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}}$$



$$\boxed{\theta_c \neq 0}$$

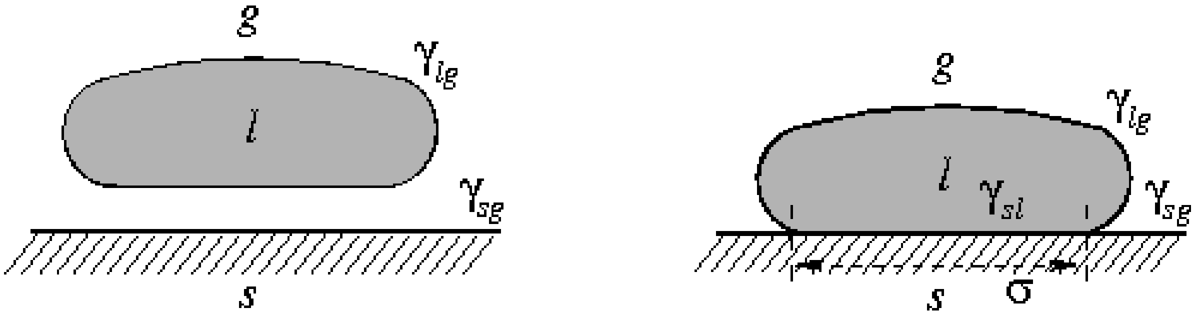
$$\boxed{h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}\cos\theta_c}$$



Each interfacial tension tries to reduce its corresponding surface

$$\boxed{\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta_c}$$

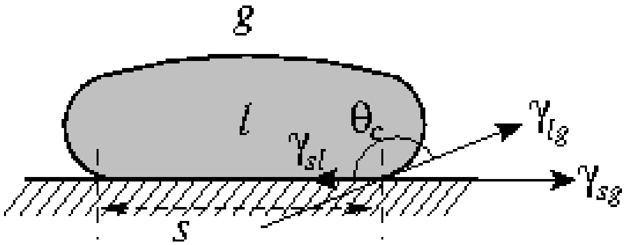
Surface tension and wetting



$$\boxed{w_{adh} = -\frac{W}{\sigma} = -\frac{\gamma_{sl}\sigma - \gamma_{sg}\sigma - \gamma_{lg}\sigma}{\sigma} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}}$$

specific work (J/m^2) of adhesion

(γ is always trying to reduce the corresponding surface)

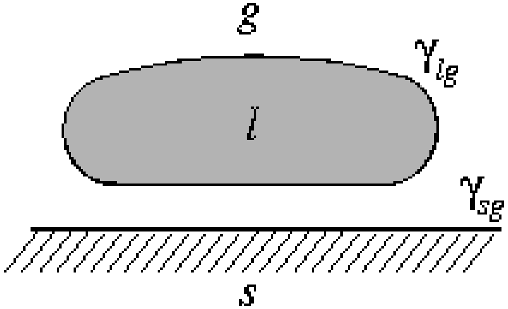


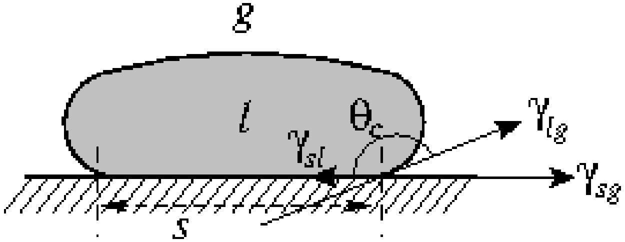
$$\boxed{\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta_c}$$

(equilibrium)

horizontal Force (N/m) balance

Surface tension and wetting





Work (J/m²)

$$w_{adh} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}$$

Force (N/m)

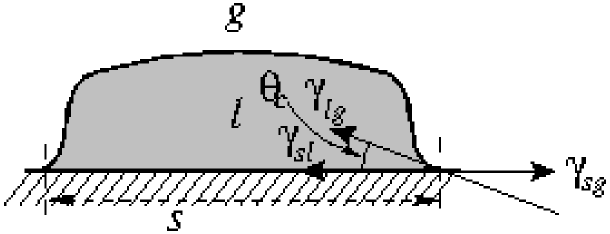
$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta_c$$

$$\left.\right\} \quad \cos \theta_c = \frac{w_{adh}}{\gamma_{lg}} - 1$$

$$0 < \frac{w_{adh}}{\gamma_{\mathrm{lg}}} < 1 \Leftrightarrow 180^\circ < \theta_c < 90^\circ$$

partial dewetting

$$1 < \frac{w_{adh}}{\gamma_{\mathrm{lg}}} < 2 \Leftrightarrow 90^\circ < \theta_c < 0^\circ$$

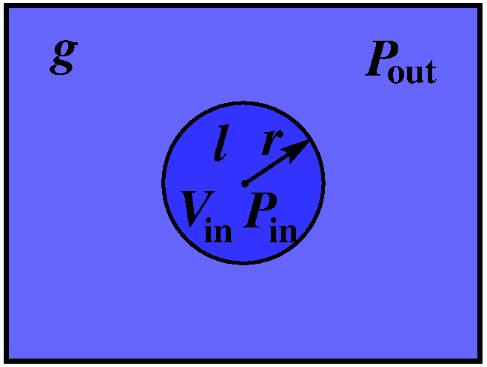


partial wetting

Kelvin equation

Kelvin equation

nucleation barrier for condensation (*g* → *l*)



$$\boxed{\Delta P = P_{\text{in}} - P_{\text{out}} = \frac{2\gamma}{r}}$$

Laplace equation

equilibrium $\boxed{\mathrm{d}\mu_g = \mathrm{d}\mu_l}$

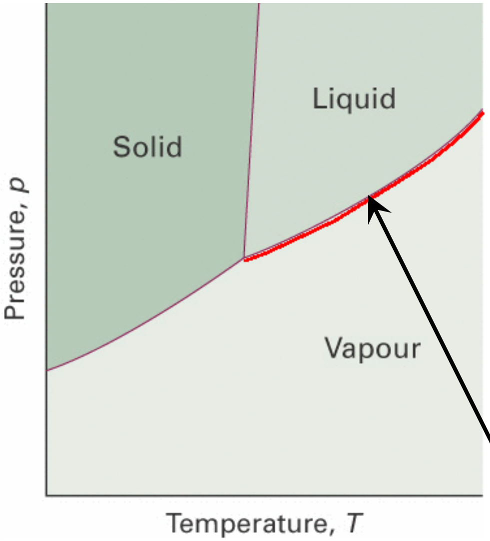
$$\boxed{d\mu_{l,g} = -S_{\mathrm{m},l,g}dT + V_{\mathrm{m},l,g}dP}$$

(pure compound)

Surface tension will change P_g

$$\boxed{\int_{P^*}^{P_g} V_{\mathrm{m},g} dP = \int_{P^*}^{P^*+\Delta P} V_{\mathrm{m},l} dP}$$

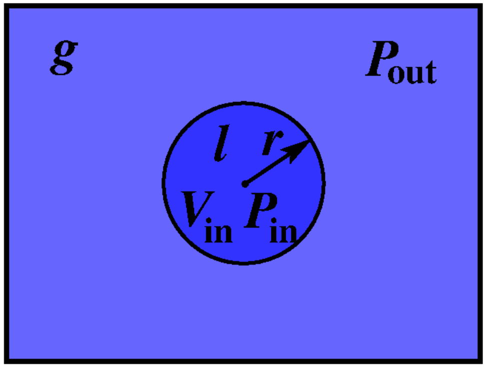
@ constant *T*



$$\boxed{P^* = P^*(T)}$$

Kelvin equation

nucleation barrier for condensation (*g* → *l*)



$$\Delta P = P_{\text{in}} - P_{\text{out}} = \frac{2\gamma}{r}$$

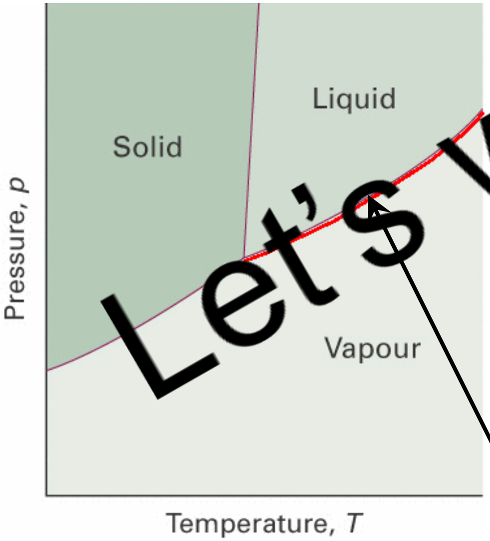
Laplace equation

equilibrium $d\mu_g = d\mu_l$

$$d\mu_{l,g} = -S_{\text{m},l,g}\,dT + V_{\text{m},l,g}\,dP$$

(pure compound)

Let's work this out in detail



Surface tension will change P_g

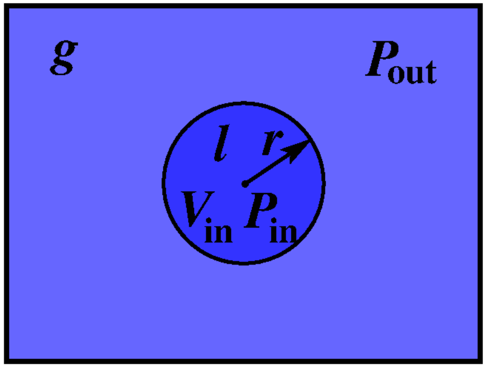
$$\int_{P^*}^{P_g} V_{\text{m},g}\,dP = \int_{P^*}^{P^*+\Delta P} V_{\text{m},l}\,dP$$

@ constant *T*

$$P^* = P^*(T)$$

Kelvin equation

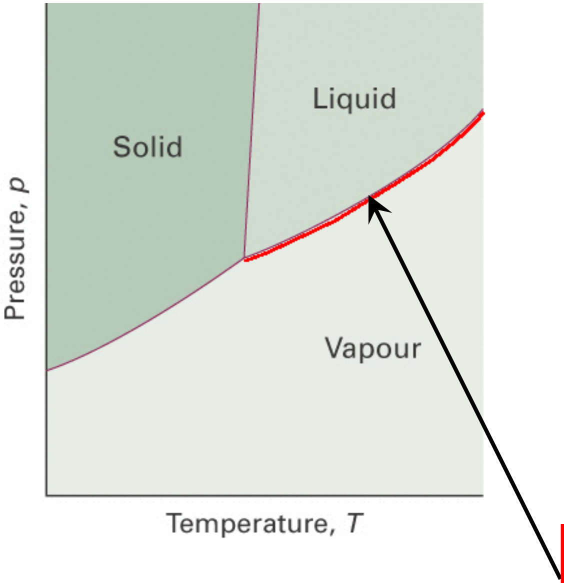
nucleation barrier for condensation (*g* → *l*)



$$\left.\begin{array}{l} \Delta P = P_{\text{in}} - P_{\text{out}} = \dfrac{2\gamma}{r} \\[2ex] \displaystyle\int_{P^*}^{P_g} V_{\text{m},g}\,dP = \int_{P^*}^{P^*+\Delta P} V_{\text{m},l}\,dP \end{array}\right\} \Rightarrow$$

$$\Rightarrow \int_{P^*}^{P_g} \frac{RT}{P}\,dP \approx V_{\text{m},l} \int_{P^*}^{P^*+\Delta P} dP$$

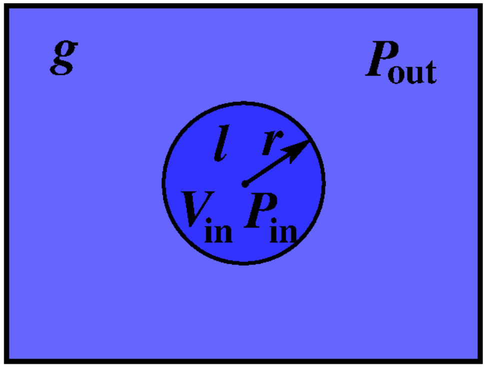
$$RT \ln \frac{P_g}{P^*} \approx V_{\text{m},l}\,\Delta P = V_{\text{m},l}\,\frac{2\gamma}{r}$$



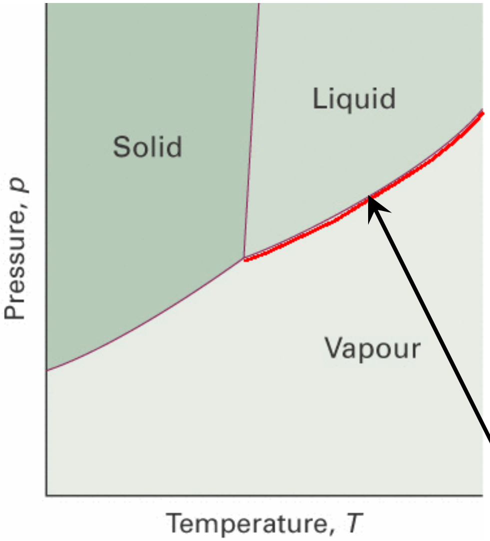
$$\boxed{P^* = P^*(T)}$$

Kelvin equation

nucleation barrier for condensation ($g \rightarrow l$)



$$\left.\begin{array}{l}\Delta P = P_{\text{in}} - P_{\text{out}} = \dfrac{2\gamma}{r} \\[2ex] RT\ln\dfrac{P_g}{P^*} \approx V_{\text{m},l}\,\Delta P = V_{\text{m},l}\,\dfrac{2\gamma}{r}\end{array}\right\} \Rightarrow$$



$$\boxed{P_g = P^* \exp\left[\frac{2\gamma V_{\text{m}}(l)}{rRT}\right]}$$

Kelvin equation

Consider an undercooled gas:

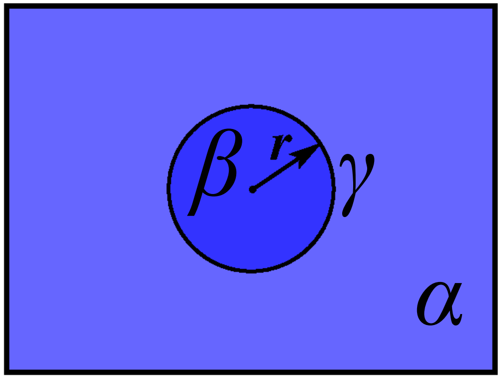
$$\boxed{\rightarrow P_g > P^*}$$

→small droplets evaporate
→condensation nucleation barrier

$$\boxed{P^* = P^*(T)}$$

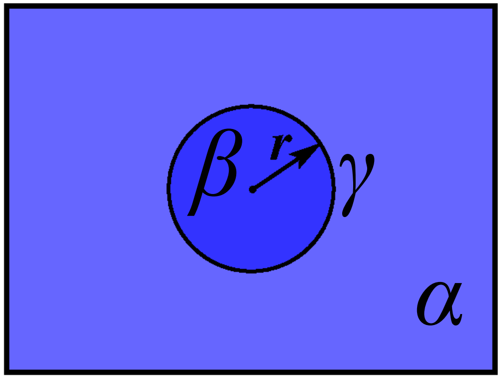
nucleation of phase $\beta(s)$ from phase $\alpha(l)$

- revert to Gibbs free energy
- classical nucleation theory
  - – spherical nucleus, radius r
  - – driving force: $\Delta\mu = \mu_\beta - \mu_\alpha$
  - – surface free energy: γ
  - – molar volume of phase β: V_m



nucleation of phase $\beta(s)$ from phase $\alpha(l)$

- revert to Gibbs free energy
- classical nucleation theory
  - spherical nucleus, radius r
  - driving force: $\Delta\mu = \mu_\beta - \mu_\alpha$
  - surface free energy: γ
  - molar volume of phase β: V_m



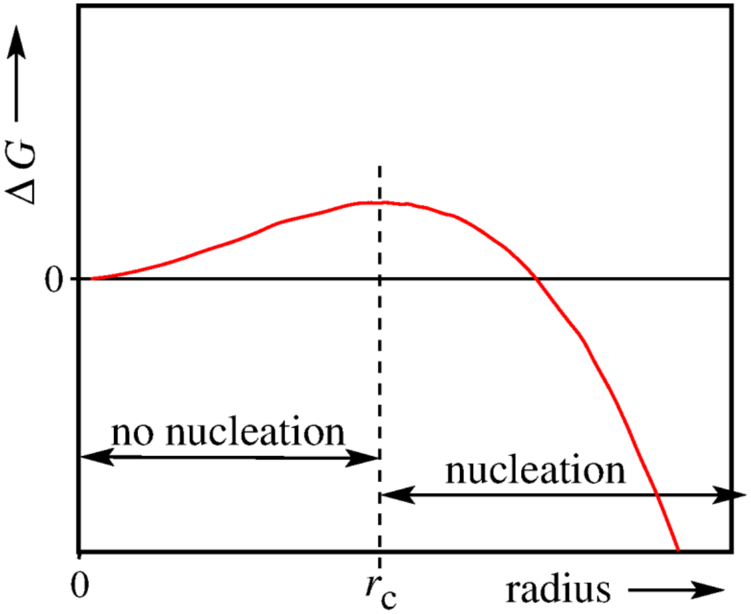
$$\left.\begin{array}{r}\boxed{\Delta G_V = n_\beta \Delta\mu = -\dfrac{\frac{4}{3}\pi r^3}{V_\mathrm{m}}\Delta\mu} \\ \boxed{\Delta G_\sigma = +4\pi r^2 \gamma}\end{array}\right\} \Rightarrow \boxed{\Delta G = -\dfrac{\frac{4}{3}\pi r^3}{V_\mathrm{m}}\Delta\mu + 4\pi r^2\gamma}$$

$$\Delta G = \underbrace{-\frac{\frac{4}{3}\pi r^3}{V_\mathrm{m}}\Delta\mu}_{\textbf{gain}} + \underbrace{4\pi r^2\gamma}_{\textbf{cost}}$$

(if $\Delta\mu = \mu_\beta - \mu_\alpha > 0$)

nucleation of phase $\beta(s)$ from phase $\alpha(l)$

$$\boxed{\Delta G = -\frac{\frac{4}{3}\pi r^3}{V_\mathrm{m}}\Delta\mu + 4\pi r^2\gamma}$$



nucleation of phase $\beta(s)$ from phase $\alpha(l)$

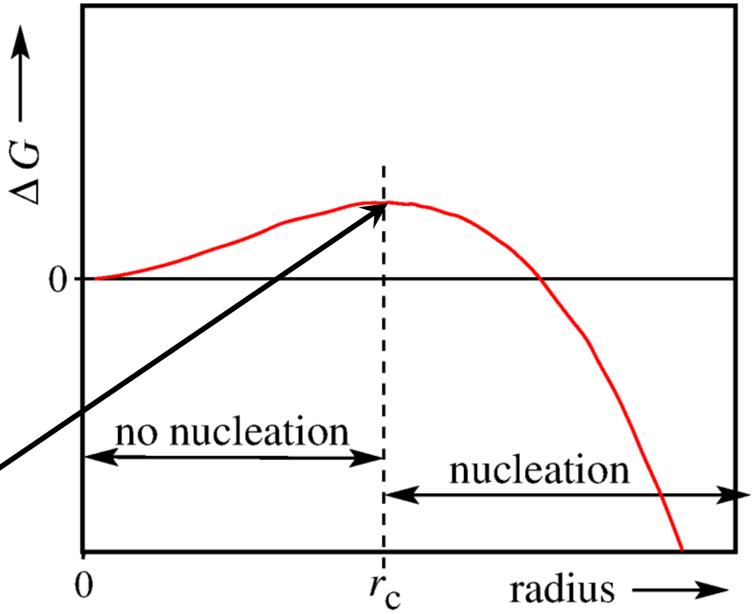
$$\Delta G = -\frac{\frac{4}{3}\pi r^3}{V_\mathrm{m}}\Delta\mu + 4\pi r^2\gamma$$

critical radius r_c:

$$\left.\frac{d\Delta G}{dr}\right|_{r_\mathrm{c}} = 0$$

$$G_c = \frac{16\pi^2 V_\mathrm{m}^2\gamma^3}{3\Delta\mu^2};\; r_c = \frac{2\gamma V_\mathrm{m}}{\Delta\mu}$$

Exercise 23



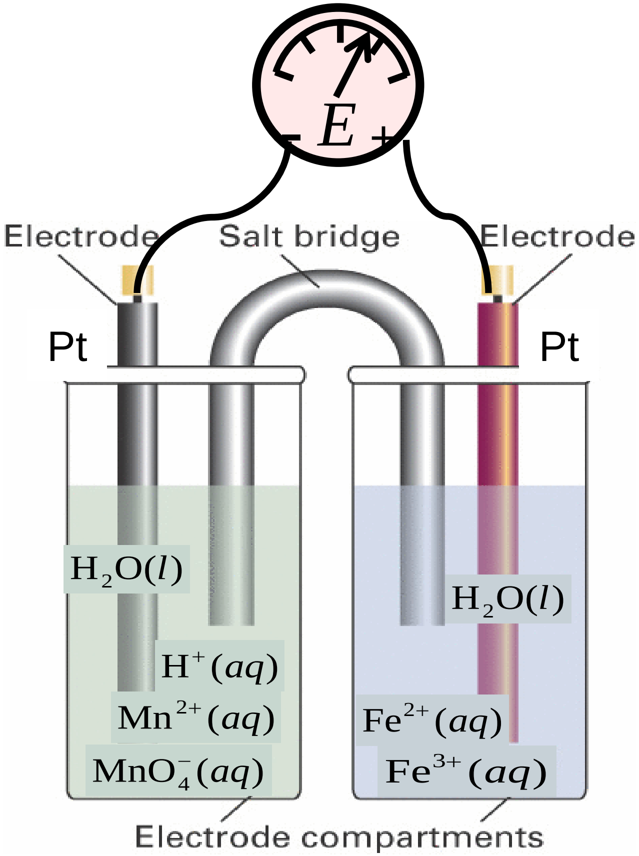
nucleation barrier depends on supersaturation ($\Delta\mu = \Delta\mu(T)$)

-low $\Delta\mu$: no nucleation

-high $\Delta\mu$: easy nucleation

Electrochemistry and electrolytic solutions

Electrochemistry and electrolytic solutions



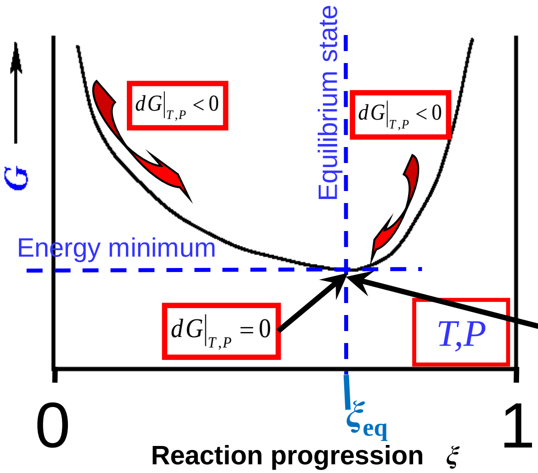
This is a partly recap from Thermodynamics (Lecture 4)

(https://www.vsc.science.ru.nl/hugom/Thermo/Thermo.html)

Chemical reaction equilibria: electrochemistry

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

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



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

Equilibrium:

$$\boxed{\Delta_r G = 0}$$

$$\boxed{\Delta_r G^\Theta = -RT\ln Q_{eq} = -RT\ln\left(\prod_i a_i^{\nu_i}\right)_{eq} \equiv -RT\ln K}$$

Chemical reaction equilibria: electrochemistry

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

$$\Big\Downarrow$$

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

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

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

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

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

solutions
- **Neutral solutions (Lecture 3)**
- **Electrolytes (ions): Electrochemistry**

Chemical reaction equilibria: electrochemistry

Electrochemistry: a few concepts

1) Aqueous dissolution of a sparingly soluble salts

$$\boxed{\mathrm{Ca_3(PO_4)_2(s)} \leftrightarrow \mathrm{3Ca^{2+}(aq)} + \mathrm{2PO_4^{3-}(aq)}}$$

(Note: the equation is overall charge neutral)

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

$$\boxed{K = \left(\prod_i a_i^{\nu_i}\right)_\mathrm{eq} = \frac{a^3_{\mathrm{Ca^{2+}(aq)}}\, a^2_{\mathrm{PO_4^{3-}(aq)}}}{a_{\mathrm{Ca_3(PO_4)_2(s)}}} \approx \frac{\dfrac{b^3_{\mathrm{Ca^{2+}(aq)}}}{(b^\Theta)^3} \cdot \dfrac{b^2_{\mathrm{PO_4^{3-}(aq)}}}{(b^\Theta)^2}}{1} = \frac{b^3_{\mathrm{Ca^{2+}(aq)}}\, b^2_{\mathrm{PO_4^{3-}(aq)}}}{(b^\Theta)^5}}$$

Solubility s of the salt:

$$\boxed{s\,(\mathrm{mol/kg}) = \frac{b_{\mathrm{Ca^{2+}(aq)}}}{3} = \frac{b_{\mathrm{PO_4^{3-}(aq)}}}{2}}$$

$$\Rightarrow \quad \boxed{K = \frac{(3s)^3 (2s)^2}{(b^\Theta)^5}} \quad \Rightarrow \quad \boxed{s = \frac{K^{1/5}}{108}\,(\mathrm{mol/kg})}$$

Chemical reaction equilibria: electrochemistry

Aqueous dissolution of a sparingly soluble salts

$$\boxed{\mathrm{Ca_3(PO_4)_2(s)} \leftrightarrow \mathrm{3Ca^{2+}(aq)} + \mathrm{2PO_4^{3-}(aq)}}$$

(Note: both sides of the equation are charge neutral)

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

$$\boxed{s = \frac{K^{1/5}}{108} \; (\mathrm{mol/kg})}$$

$$\boxed{\Delta_\mathrm{r} G^\Theta = 3\Delta_\mathrm{f} G^\Theta_{\mathrm{Ca^{2+}(aq)}} + 2\Delta_\mathrm{f} G^\Theta_{\mathrm{PO_4^{3-}(aq)}} - \Delta_\mathrm{f} G^\Theta_{\mathrm{Ca_3(PO_4)_2(s)}}}$$

(*)

$$\boxed{\Delta_\mathrm{r} G^\Theta = 3\cdot(-553.0\cdot 10^3) + 2\cdot(-1019\cdot 10^3) - (-3885\cdot 10^3) = 188.0\,\mathrm{kJ/mol}}$$

$$\Rightarrow \boxed{K = 1.11\cdot 10^{-33}} \Rightarrow \boxed{s = 2.4\cdot 10^{-9}\ \mathrm{mol/kg}}$$

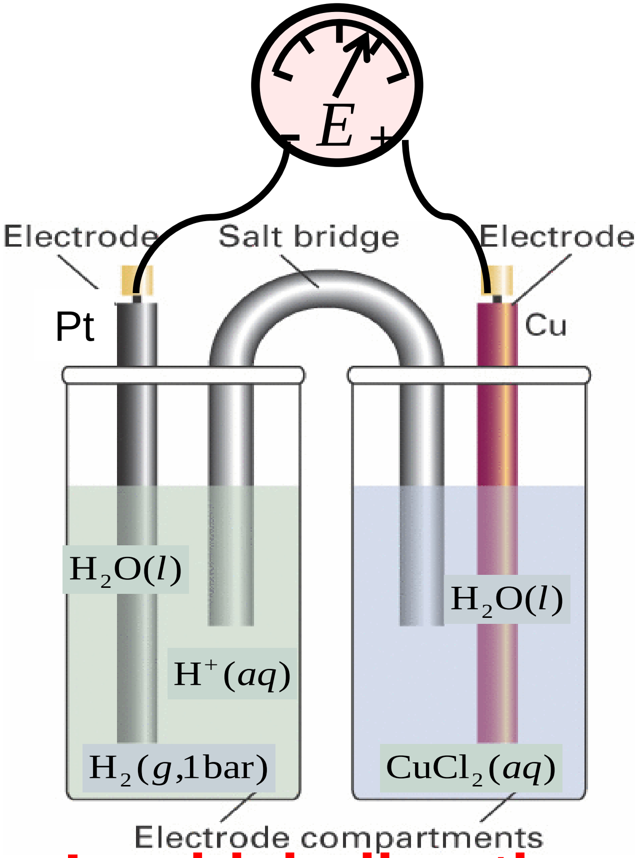
Exercise 24

(*) https://www.chm.uri.edu/weuler/chm112/refmater/thermtable.html

Chemical reaction equilibria: electrochemistry

Electrochemistry: a few concepts

2) Electrochemical cells: basic example



$$\boxed{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$$

(Reduction halfreaction)

$$\boxed{H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)}$$

(Reduction halfreaction)

$$\boxed{2H^+(aq) + Cu(s) \rightarrow H_2(g) + Cu^{2+}(aq)}$$

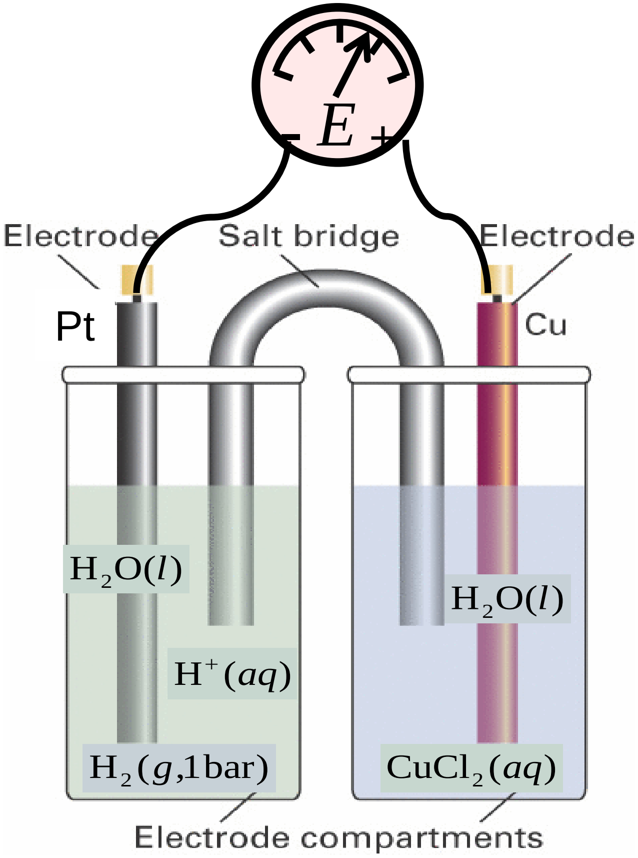
(Total cell reaction)

(Note: the equation is overall charge neutral)

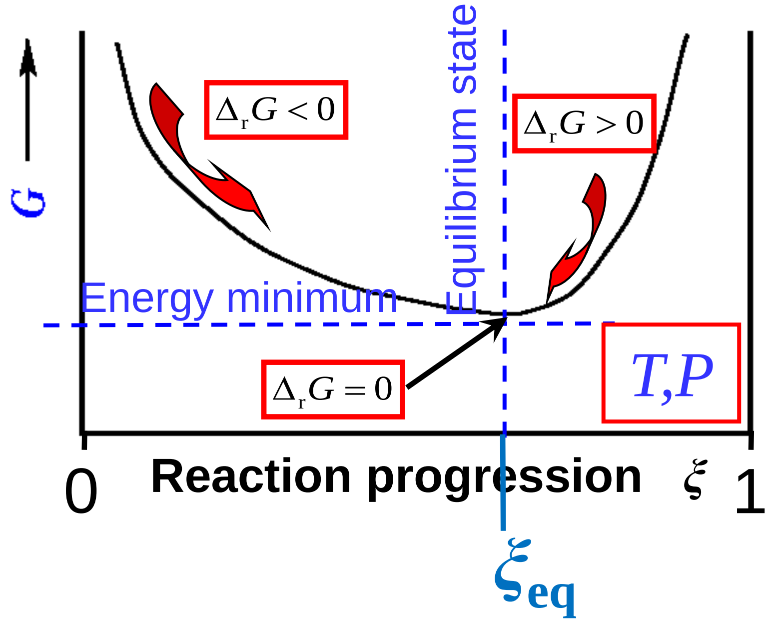
In which direction will the reaction run spontaneously?

→ **Where is the equilibrium?**

Chemical reaction equilibria: electrochemistry



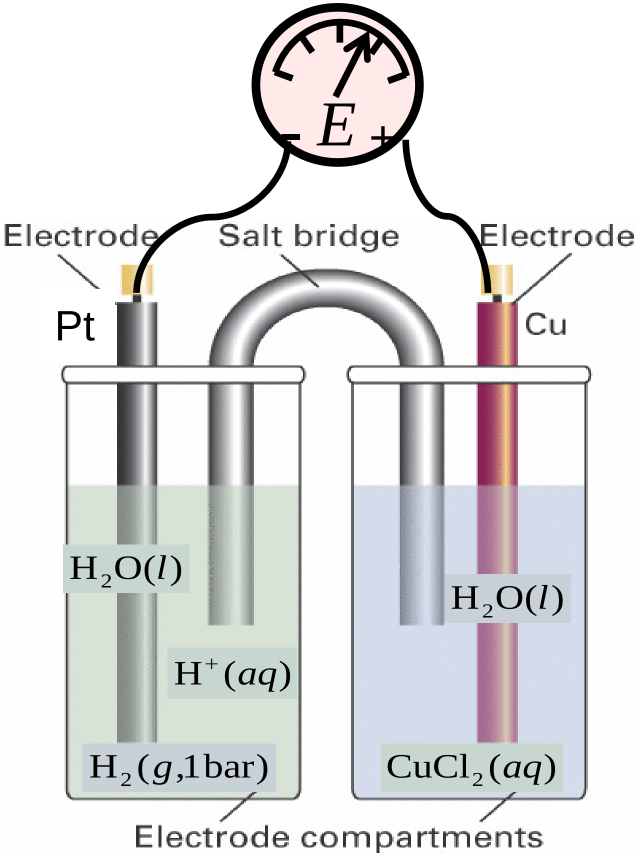
Voltage E represents a ‘driving force’ like $\Delta_r G$



Ideal volt meter has an infinitely large internal resistance

➔measures E with zero current

Chemical reaction equilibria: electrochemistry



Voltage E represents a 'driving force' like $\Delta_r G$

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

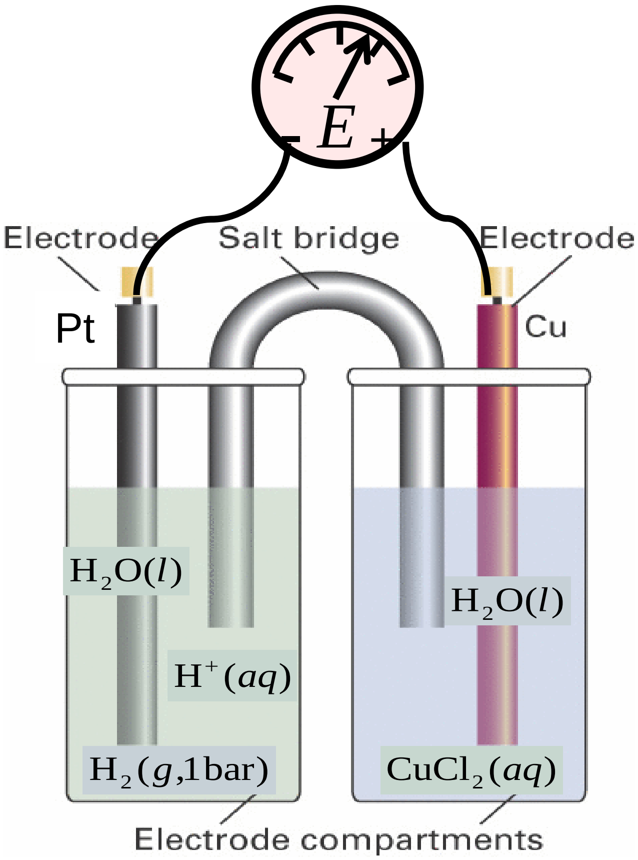
$$\boxed{\Delta_r G^\Theta = \sum_i \nu_i \Delta_f G_{m,i}^\Theta}$$

Equilibrium:

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

Relation between E and $\Delta_r G$

Chemical reaction equilibria: electrochemistry



Voltage *E* 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 *E* and $\Delta_r G$

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

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:

Equilibrium:

$$\boxed{\Delta_{\mathrm{r}} G^{\Theta} = -RT \ln K} \Rightarrow \boxed{E^{\Theta} = +\frac{RT}{\nu F} \ln K}$$

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

Number of electrons transferred in chemical equation

Faraday constant (charge of 1 mole of electrons)

Chemical reaction equilibria: electrochemistry

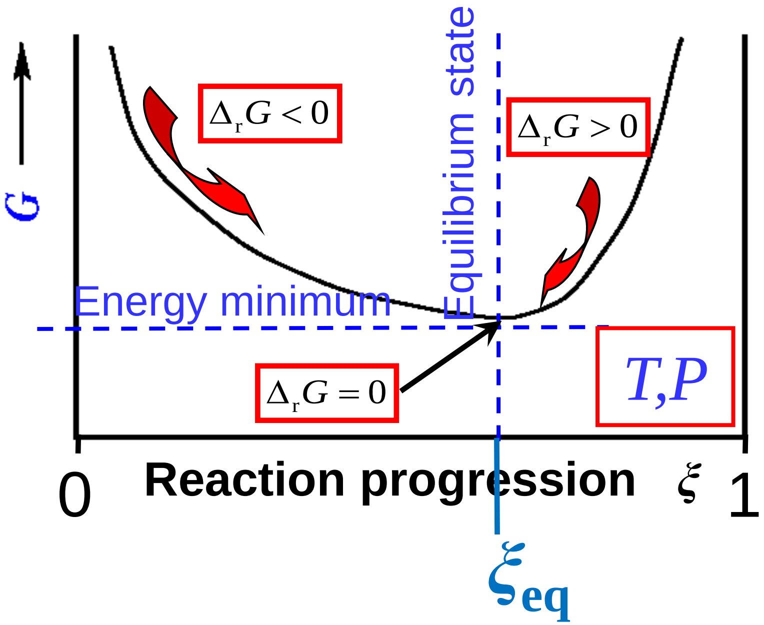
$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$$

↔

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

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

Nernst equation

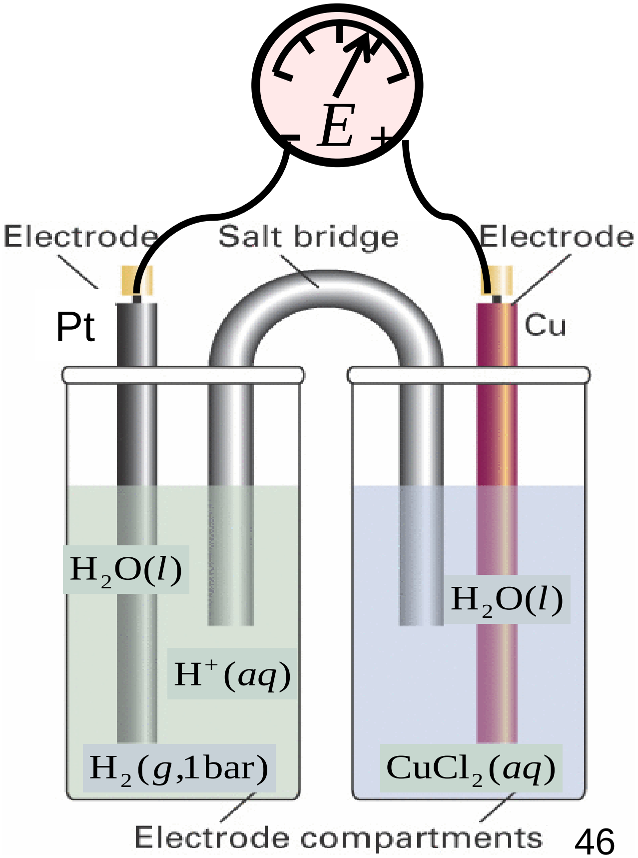


reaction

$\Delta_r G < 0$ $E > 0$ →

$\Delta_r G > 0$ $E < 0$ ←

$\Delta_r G = 0$ $E = 0$ ↔



Chemical reaction equilibria: electrochemistry

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

Nernst also holds for half reactions:

$$\mathrm{Cu}^{2+}(aq) + 2e^{-} \rightarrow \mathrm{Cu(s)}$$

$$E_{\mathrm{Cu}^{2+}/Cu} = E^{\Theta}_{\mathrm{Cu}^{2+}/Cu} - \frac{RT}{2F}\ln\frac{a_{\mathrm{Cu(s)}}}{a_{\mathrm{Cu}^{2+}(aq)}}$$

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

Note: reduction half reaction

$$E_{\mathrm{H_2(g)/2H^+}} = E^{\Theta}_{\mathrm{H_2(g)/2H^+}} - \frac{RT}{2F}\ln\frac{a_{\mathrm{H_2(g)}}}{a^2_{\mathrm{H}^+(aq)}}$$

Chemical reaction equilibria: electrochemistry

Nernst also holds for half reactions

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

$$\underline{\boxed{\mathrm{Cu}^{2+}(aq) + 2e^{-} \rightarrow \mathrm{Cu}(\mathrm{s})}} \quad -$$

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

Chemical reaction equilibria: electrochemistry

Nernst also holds for half reactions

$$\mathrm{2H^+}(aq) + \mathrm{Cu(s)} \rightarrow \mathrm{H_2}(g) + \mathrm{Cu^{2+}(aq)}$$

$$E_{\mathrm{H_2(g)/2H^+}} = E^{\Theta}_{\mathrm{H_2(g)/2H^+}} - \frac{RT}{2F}\ln\frac{a_{\mathrm{H_2(g)}}}{a^2_{\mathrm{H^+}(aq)}}$$

$$E_{\mathrm{Cu^{2+}}/Cu} = E^{\Theta}_{\mathrm{Cu^{2+}}/Cu} - \frac{RT}{2F}\ln\frac{a_{\mathrm{Cu(s)}}}{a_{\mathrm{Cu^{2+}}(aq)}}$$

$$E_{\mathrm{total\,cell}} = E^{\Theta}_{\mathrm{H_2/2H^+}} - E^{\Theta}_{\mathrm{Cu^{2+}/Cu}} - \frac{RT}{2F}\left[\ln\frac{a_{\mathrm{H_2(g)}}}{a^2_{\mathrm{H^+}(aq)}} - \ln\frac{a_{\mathrm{Cu(s)}}}{a_{\mathrm{Cu^{2+}}(aq)}}\right]$$

Chemical reaction equilibria: electrochemistry

Nernst also holds for half reactions

$$2\mathrm{H}^+(aq)+\mathrm{Cu(s)}\rightarrow \mathrm{H}_2(g)+\mathrm{Cu}^{2+}\mathrm{(aq)}$$

$$E_{\mathrm{total\,cell}}=E^{\Theta}_{\mathrm{H_2/2H^+}}-E^{\Theta}_{\mathrm{Cu^{2+}/Cu}}-\frac{RT}{2F}\left[\ln\frac{a_{\mathrm{H_2(g)}}}{a^2_{\mathrm{H^+}(aq)}}-\ln\frac{a_{\mathrm{Cu(s)}}}{a_{\mathrm{Cu^{2+}}(aq)}}\right]$$

$$\Rightarrow\quad E_{\mathrm{total\,cell}}=E^{\Theta}_{\mathrm{H_2/2H^+}}-E^{\Theta}_{\mathrm{Cu^{2+}/Cu}}-\frac{RT}{2F}\ln\frac{a_{\mathrm{H_2(g)}}a_{\mathrm{Cu^{2+}}(aq)}}{a^2_{\mathrm{H^+}(aq)}a_{\mathrm{Cu(s)}}}$$

$$\Rightarrow\quad E_{\mathrm{total\,cell}}=E^{\Theta}_{\mathrm{H_2/2H^+}}-E^{\Theta}_{\mathrm{Cu^{2+}/Cu}}-\frac{RT}{2F}\ln\frac{a_{\mathrm{H_2(g)}}a_{\mathrm{Cu^{2+}}(aq)}}{a^2_{\mathrm{H^+}(aq)}}$$

Exercise 25

$$\left.\begin{array}{l}E^{\Theta}_{\mathrm{H_2/2H^+}}\equiv 0\ \mathrm{for\ all}\ T\\ a_{\mathrm{H_2(g)}}(\mathrm{H_2}\,|\,\mathrm{Pt}\,|\,\mathrm{H^+_{aq}})\equiv\dfrac{P^{\Theta}}{P^{\Theta}}=1\end{array}\right\}\Rightarrow\quad E_{\mathrm{total\,cell}}=0-E^{\Theta}_{\mathrm{Cu^{2+}/Cu}}-\frac{RT}{2F}\ln\frac{a_{\mathrm{Cu^{2+}}(aq)}}{a^2_{\mathrm{H^+}(aq)}}$$

Chemical reaction equilibria: electrochemistry

2) Electrochemical cells: another example

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

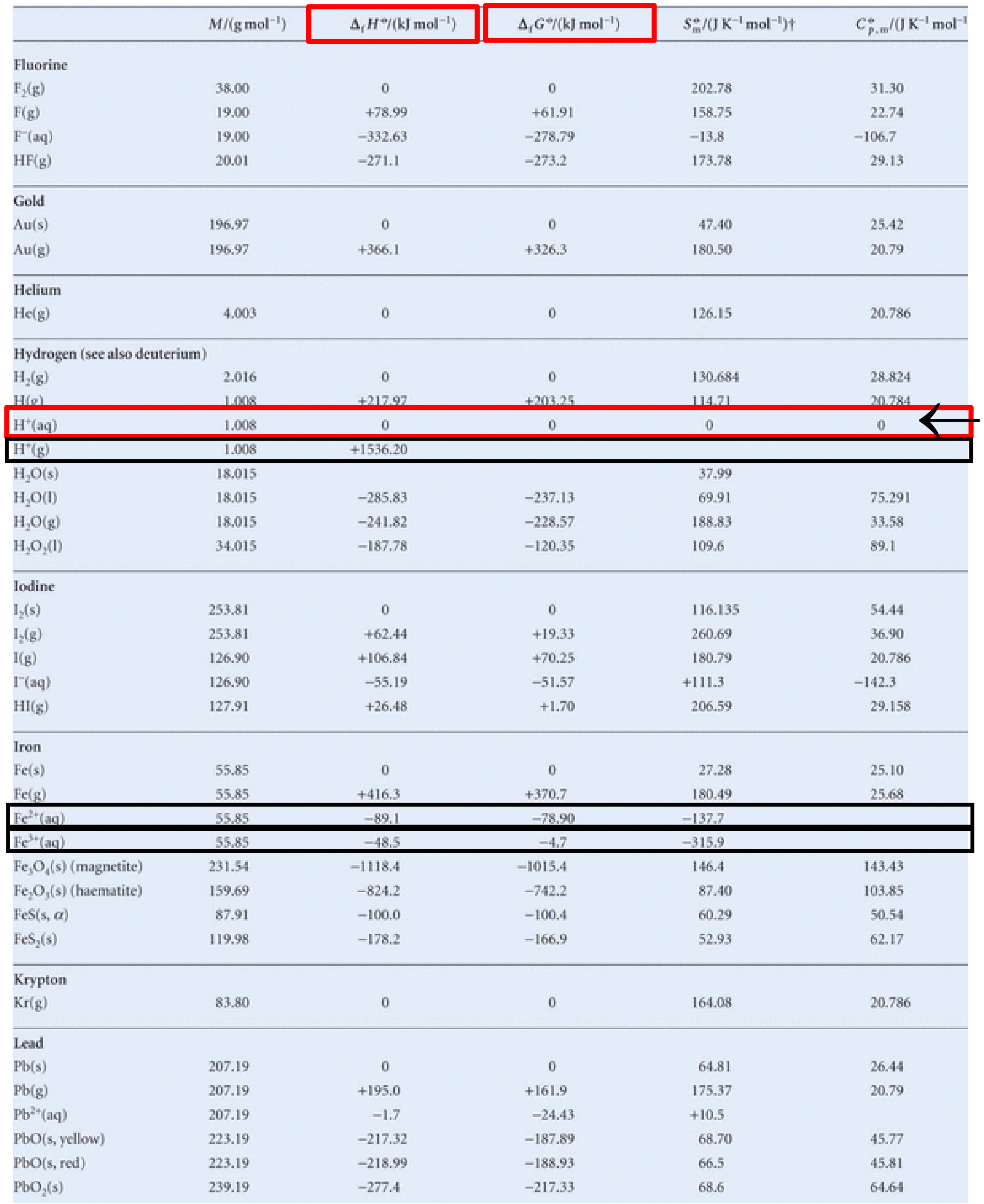
$$E_{\text{total cell}} = E^{\Theta}_{MnO_4^-/Mn^{2+}} - E^{\Theta}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{5F}\left[\ln \frac{a_{Mn^{2+}}\, a_{H_2O}^{4}\, a_{Fe^{3+}}^{5}}{a_{MnO_4^-}\, a_{H^+}^{8}\, a_{Fe^{2+}}^{5}}\right]$$

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

$$\boxed{\nu = 5}$$

- sign as we need a reduction and an oxidation half reaction

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

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

$$\leftarrow \Delta_\mathrm{f} G^\Theta_{\mathrm{m,H^+}} \equiv \Delta_\mathrm{f} H^\Theta_{\mathrm{m,H^+}} \equiv 0 \text{ all } T$$

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)

Chemical reaction equilibria: electrochemistry

3) Standard hydrogen electrode

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

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

Chemical reaction equilibria: electrochemistry

3) Standard hydrogen electrode

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

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

$$\mathrm{2H^+}(aq) + 2e^- \rightarrow \mathrm{H_2}(g)$$

$$\mathrm{E}_{\mathrm{2H^+/H_2}(g)} = \mathrm{E}^{\Theta}_{\mathrm{2H^+/H_2}(g)} - \frac{\mathrm{RT}}{\mathrm{2F}} \ln \frac{a_{\mathrm{H_2}(g)}}{a^2_{\mathrm{H^+}}} \equiv - \frac{\mathrm{RT}}{\mathrm{2F}} \ln \frac{a_{\mathrm{H_2}(g)}}{a^2_{\mathrm{H^+}}}$$

⇒ $$\mathrm{pH} \equiv -{}^{10}\log a_{\mathrm{H^+}} = -{}^{10}\log\left[\mathrm{H^+}\right] - {}^{10}\log \gamma_{\mathrm{H^+}}$$

Chemical reaction equilibria: electrochemistry

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

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

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

Very dilute solutions → $a_{\mathrm{H2O}}\approx 1$

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

Very very dilute solutions→$a_i\approx[i\,]$

Exercise 24-25

Chemical reaction equilibria: electrochemistry

Activity as an effective concentration

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

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

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

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

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

Chemical reaction equilibria: electrochemistry

Activity as an effective concentration

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

Molarity
(mol/L)

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

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

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

Molality
(mol/kg)

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

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

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

Mole
fraction ( )

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

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

example

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