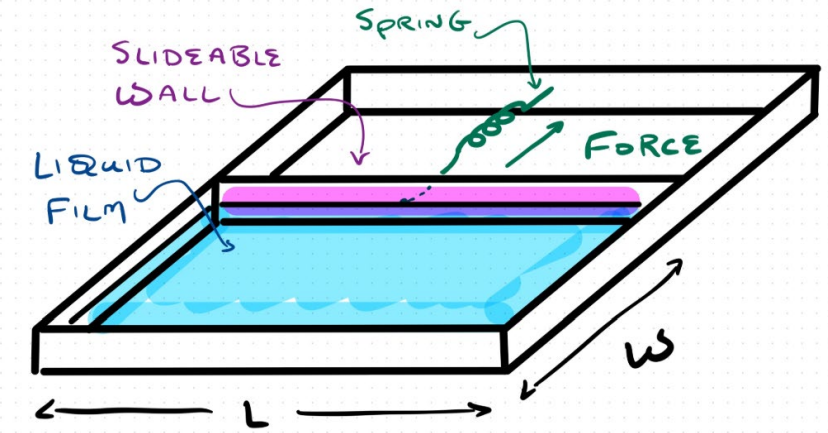
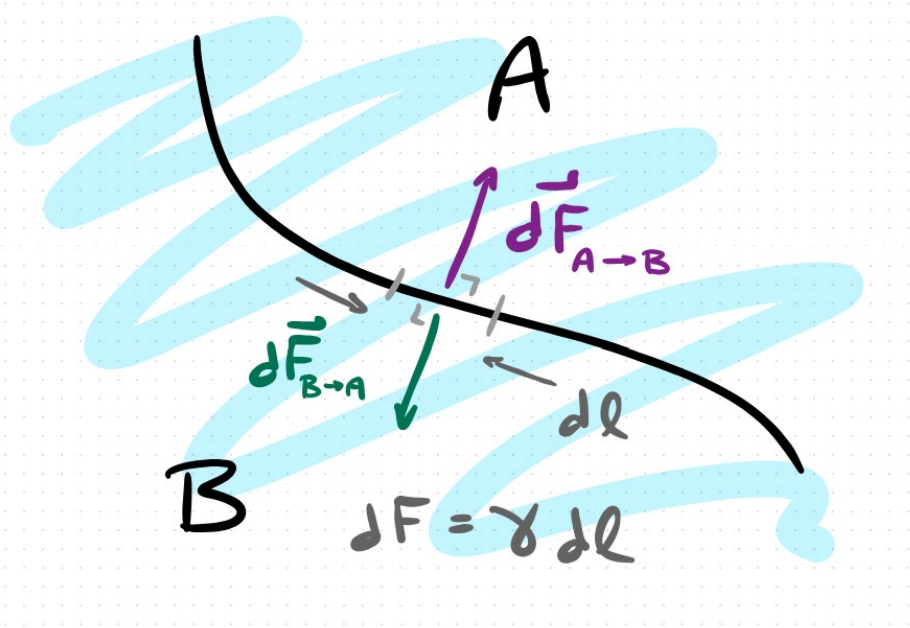
Interfacial chemistry overview

Lecture 1 – Surface tension

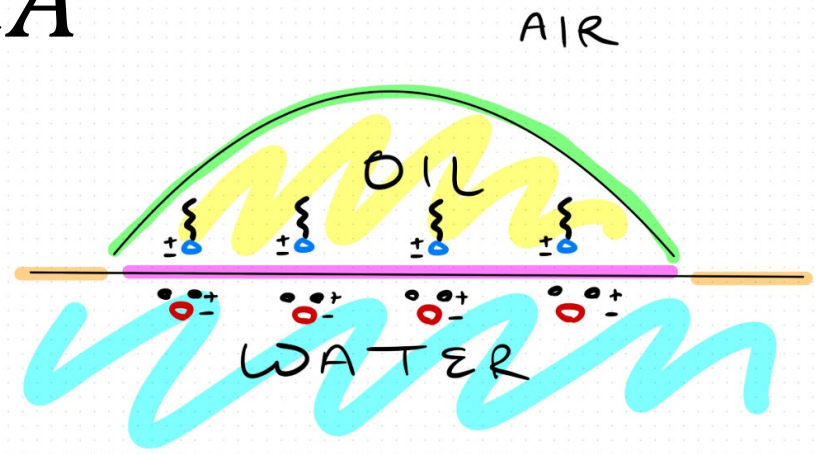
surface tension





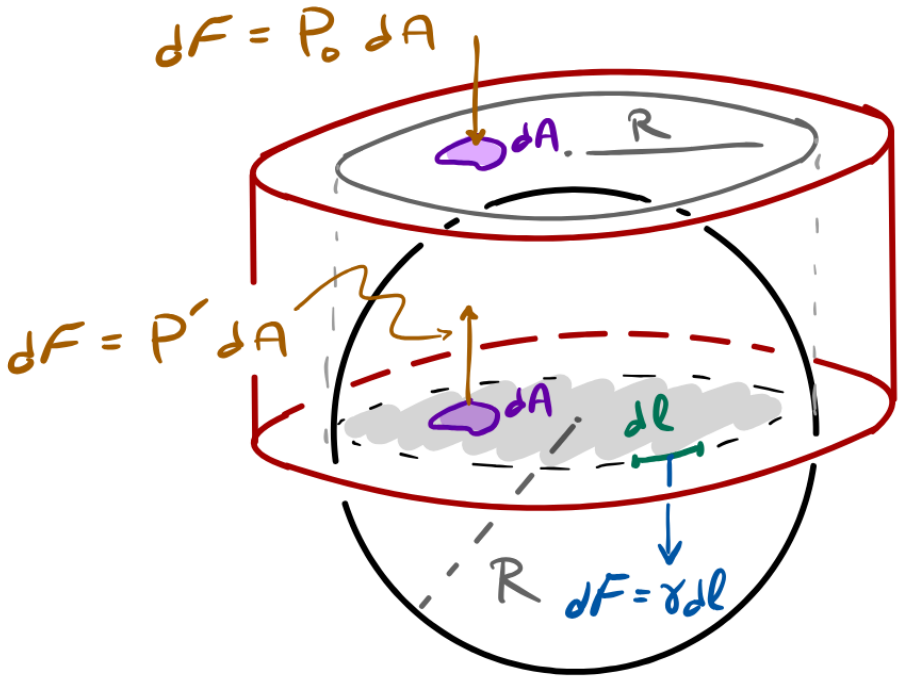
$$|d\vec{F}| = \gamma dl$$

$$dW = \gamma dA$$



Lecture 1 – Surface tension

Young-Laplace equation

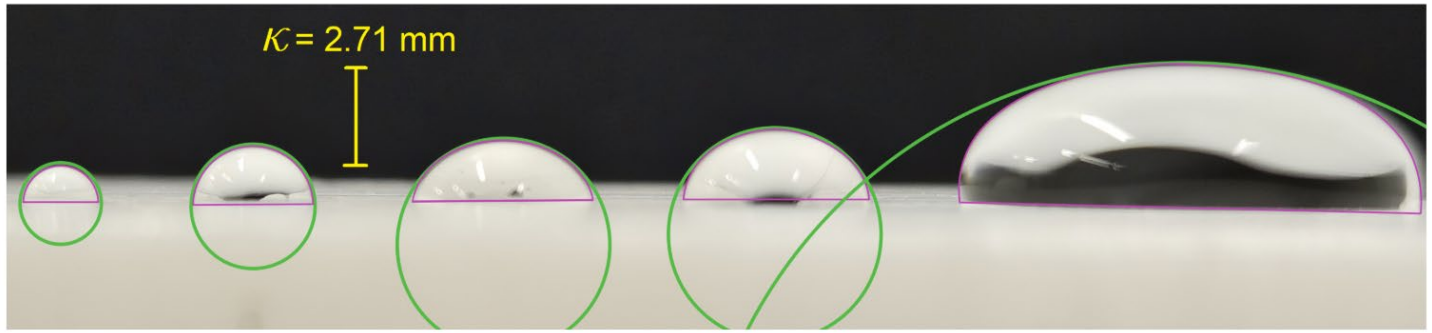


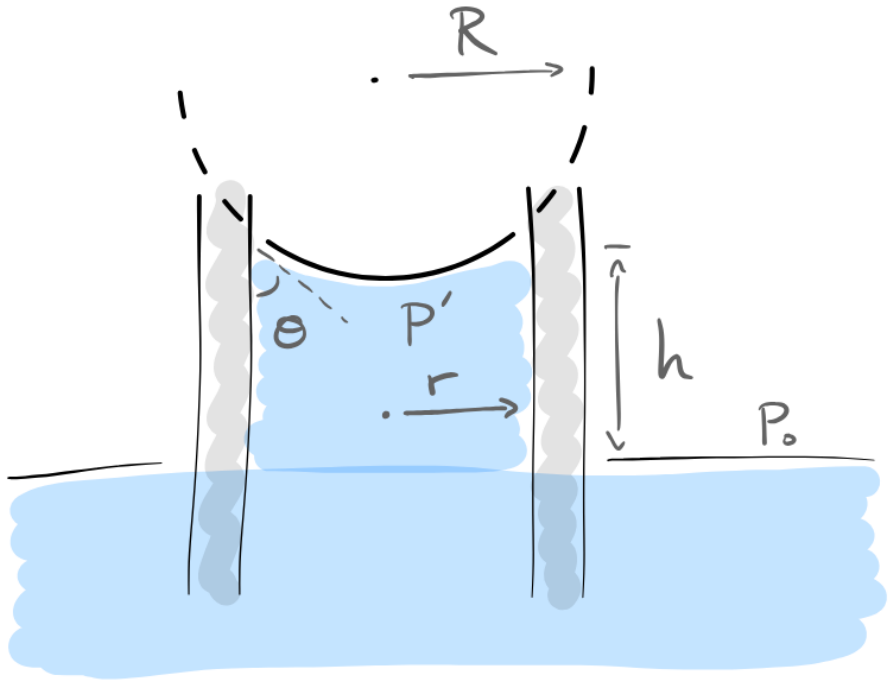
$$\Delta P = \frac{2\gamma}{R}$$

Lecture 1 – Surface tension

capillary action

$$\kappa \equiv \sqrt{\frac{\gamma}{\rho g}}$$





$$h = 2\kappa^2 \cos\theta / r$$

(Jurin's law)

Lecture 1 – Surface tension

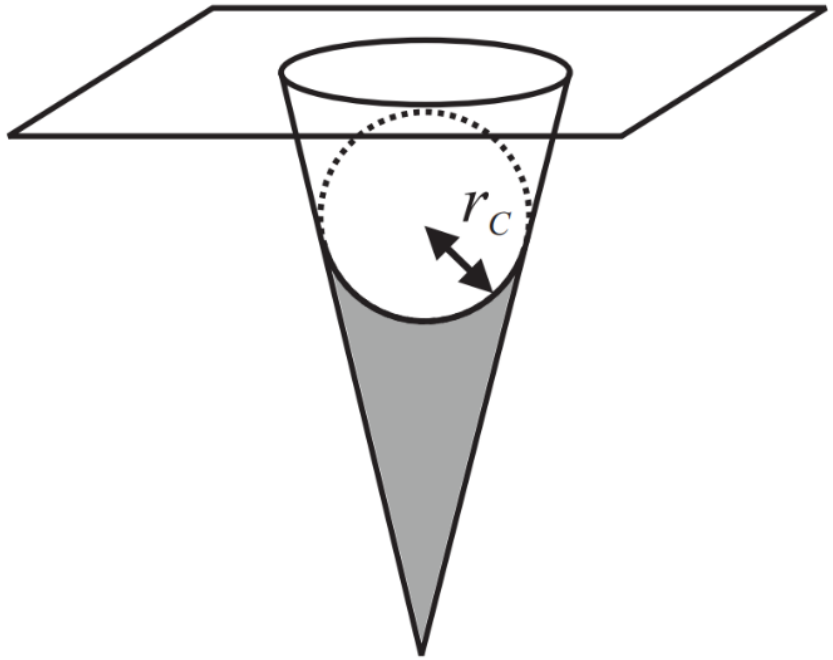
vapor pressure and the Kelvin equation

$$P_o' = P_o e^{R_o/R}$$

(Kelvin's law)

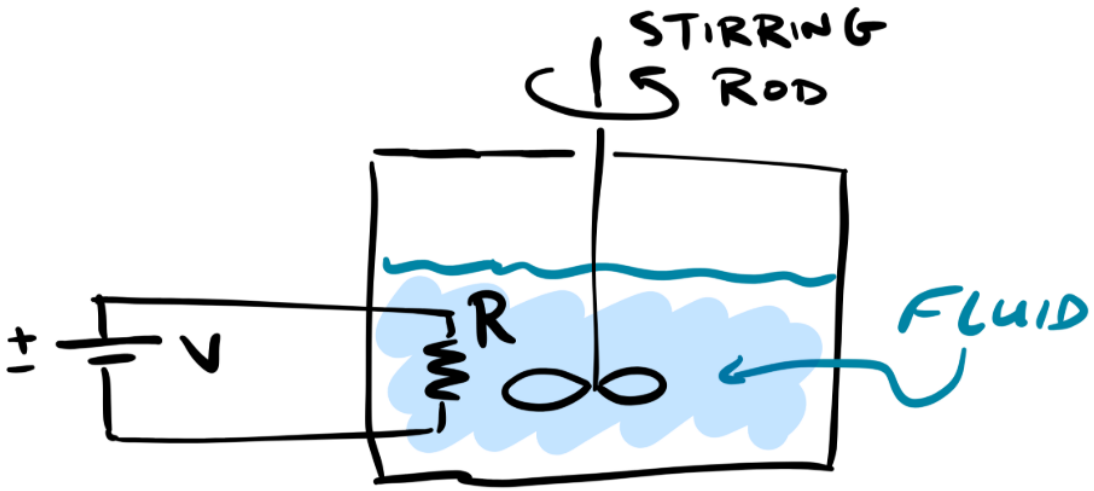
$$R_o \equiv \frac{2\gamma V_m}{\bar{R}T}$$

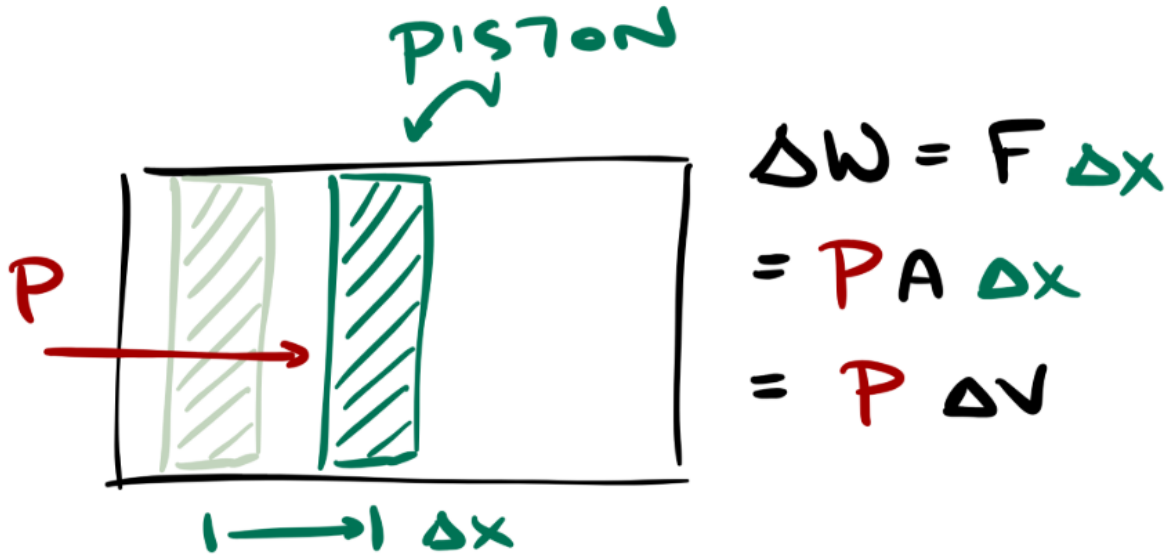
e.g. capillary condensation



Lecture 2 – Interfacial thermodynamics

work and heat





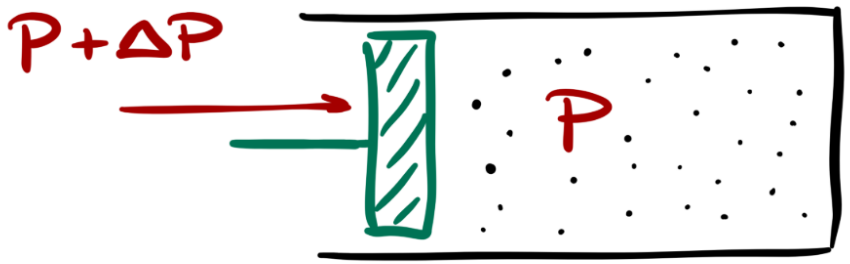
$$\Delta U = \Delta W + \Delta Q$$

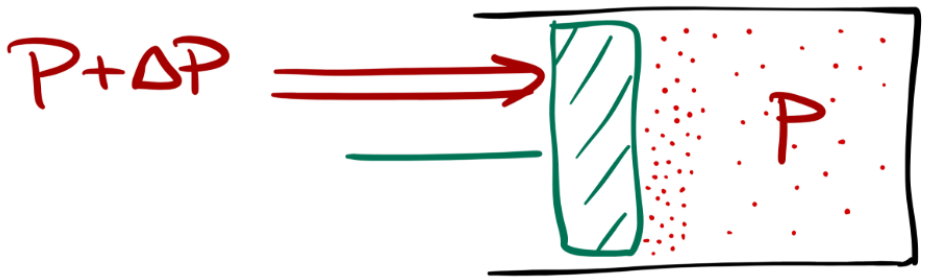
Lecture 2 – Interfacial thermodynamics

entropy

$$dU = TdS - PdV + \mu dN$$

$$T\Delta S \geq \Delta Q$$





Lecture 2 – Interfacial thermodynamics

surface tension

$$dU = TdS + \gamma\, dA$$

$$\gamma = \left(\frac{\partial U}{\partial A}\right)\Bigg|_S$$

Lecture 2 – Interfacial thermodynamics

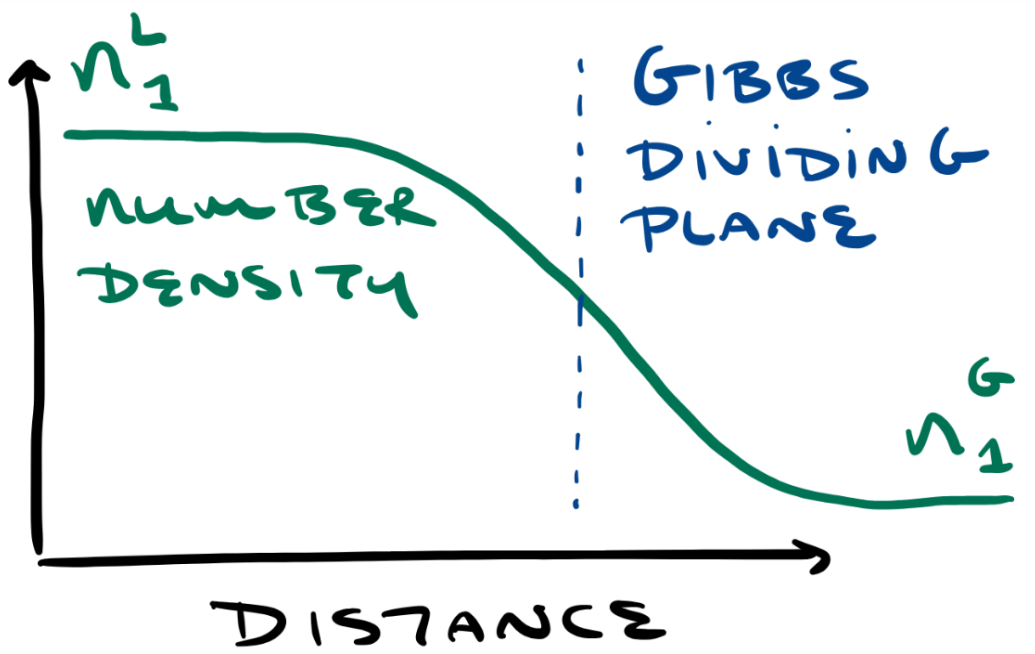
surface energy and entropy

$$s = -\partial_T \gamma$$

$$u = \gamma - T\partial_T \gamma$$

Lecture 2 – Interfacial thermodynamics

Gibbs dividing plane



$$N_i^S \equiv N_i - N_i^A - N_i^B$$

$$N_1^S \equiv 0$$

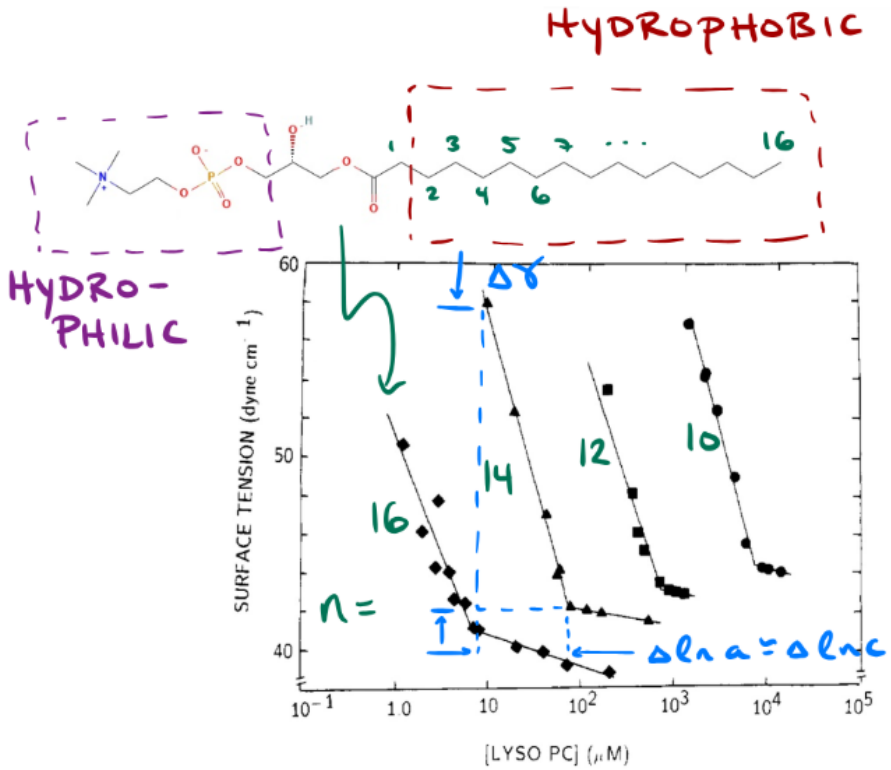
$$\Gamma_i \equiv N_i^S / A$$

Lecture 2 – Interfacial thermodynamics

Gibbs adsorption isotherm

$$d\gamma = -\Gamma d\mu^S$$

$$\Gamma = -\frac{c}{RT}\partial_c \gamma$$



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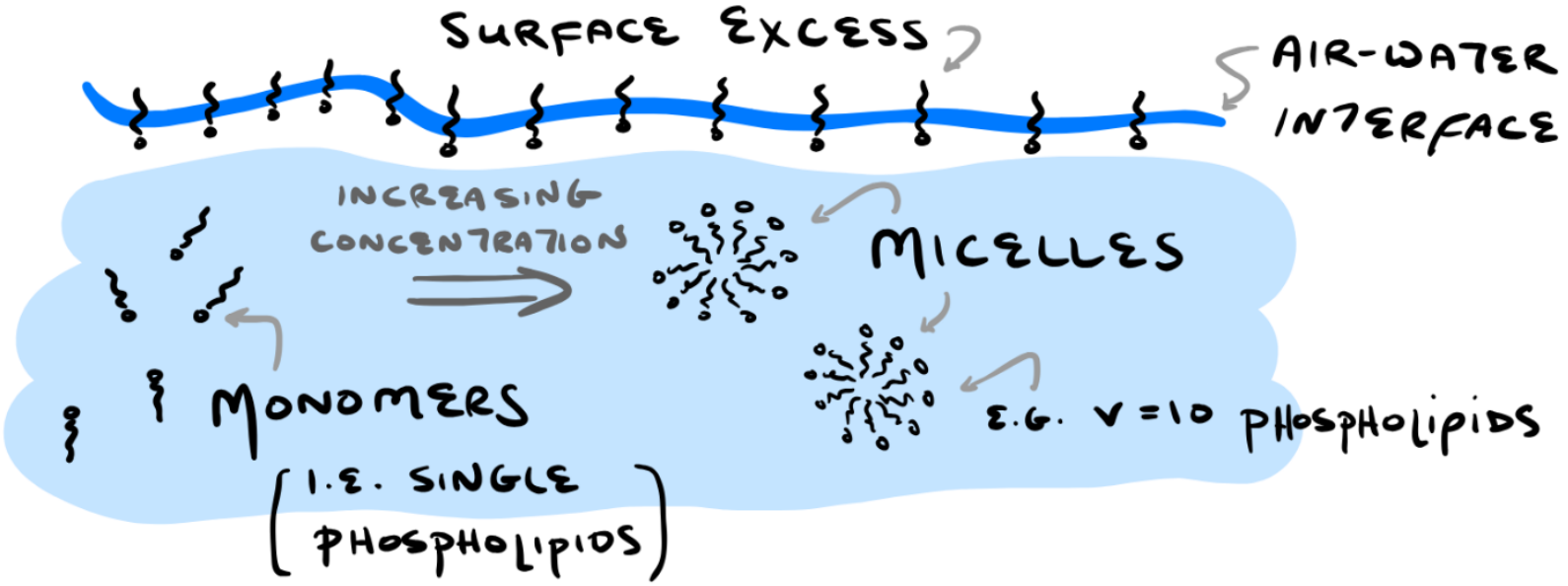
Lecture 2 – Interfacial thermodynamics

micelles

$$\nu m \longleftrightarrow M$$

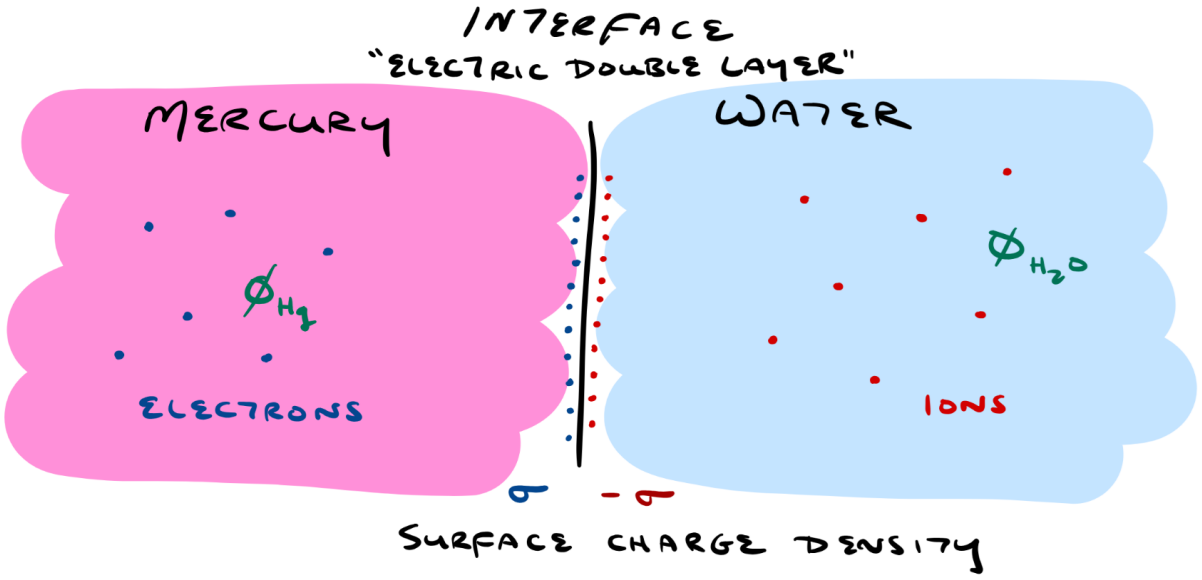


$$\frac{c^{\nu}}{c'} = \exp\left(\frac{\Delta G^{o}}{RT}\right)$$

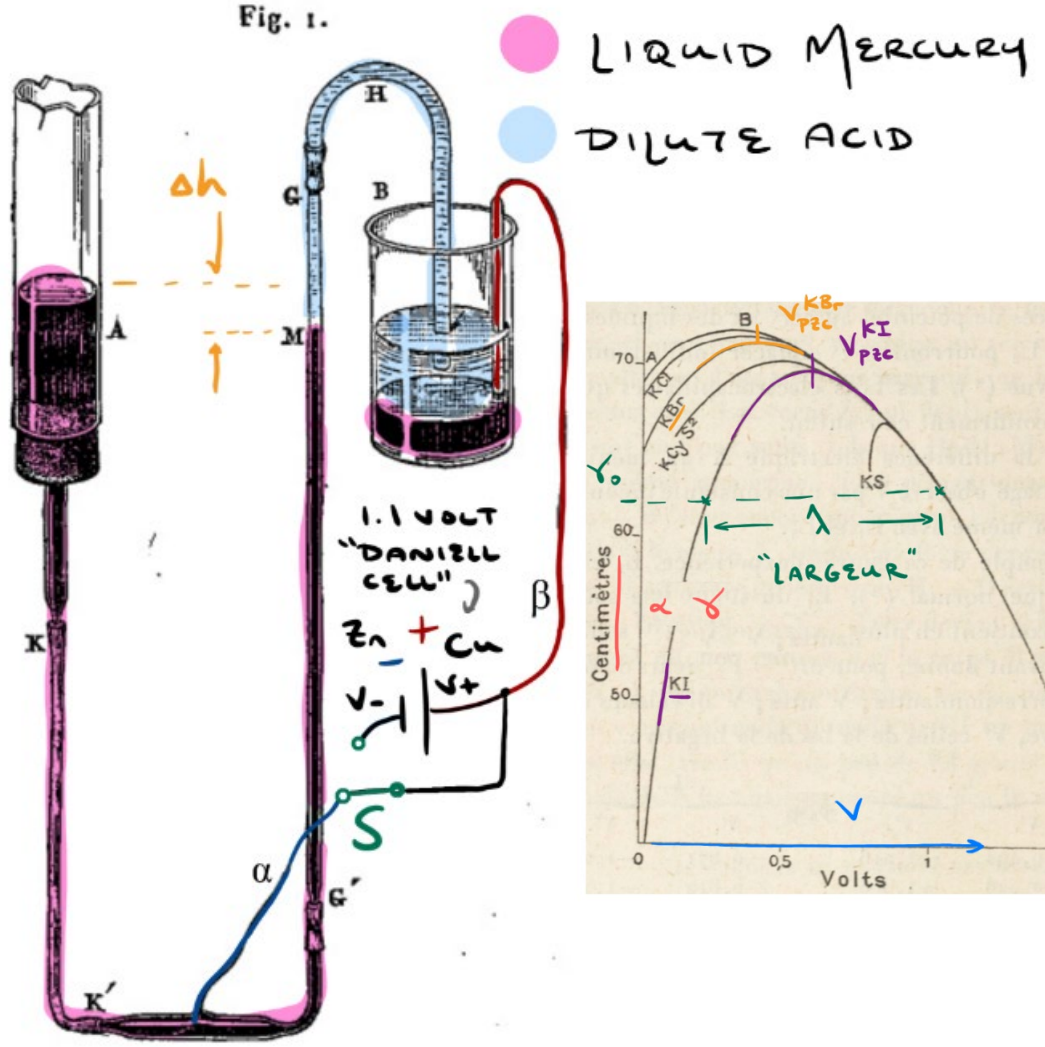
$$\ln \bar{c}_{CMC} \approx \frac{1}{\nu}\Delta G^{o}/RT$$

Lecture 3 – Interfacial electrochemistry

electrocapillarity



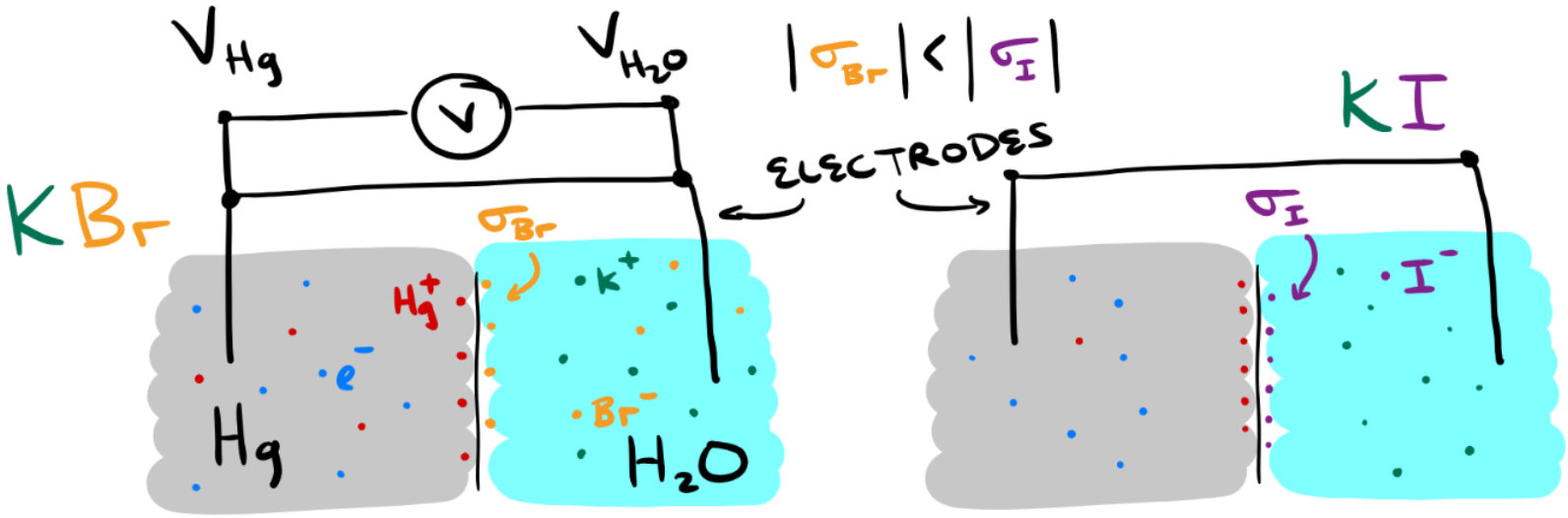
$$\frac{d\gamma}{dV} = \sigma \qquad c_A \equiv -\frac{d^2\gamma}{dV^2}$$

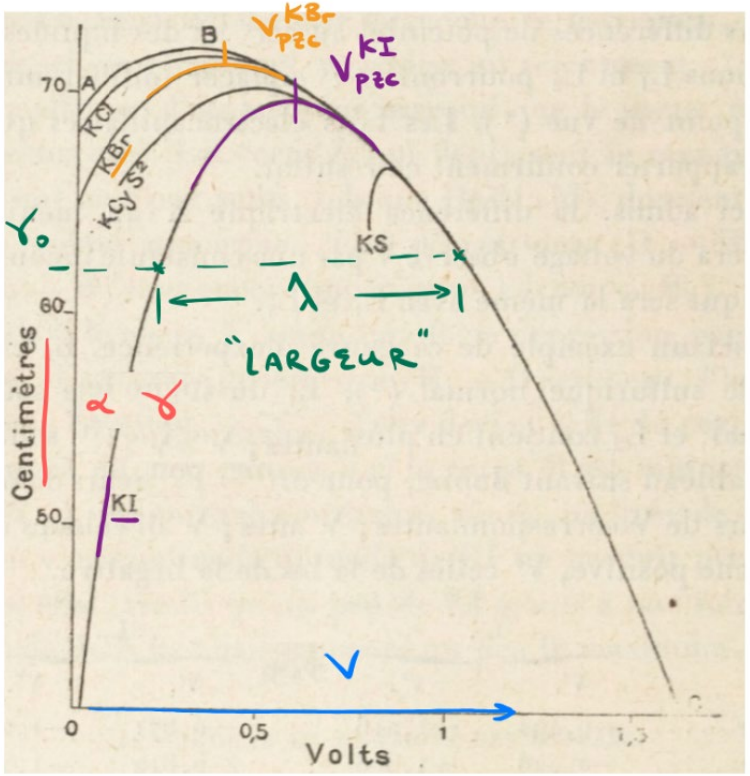


Lecture 3 – Interfacial electrochemistry

specific adsorption

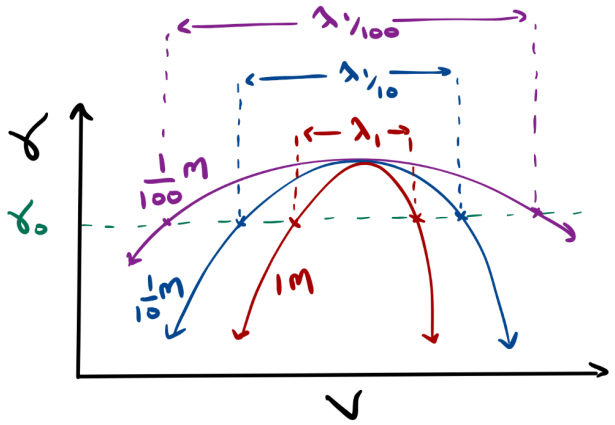
$$V = V_{H_2O} - V_{Hg} = 0$$

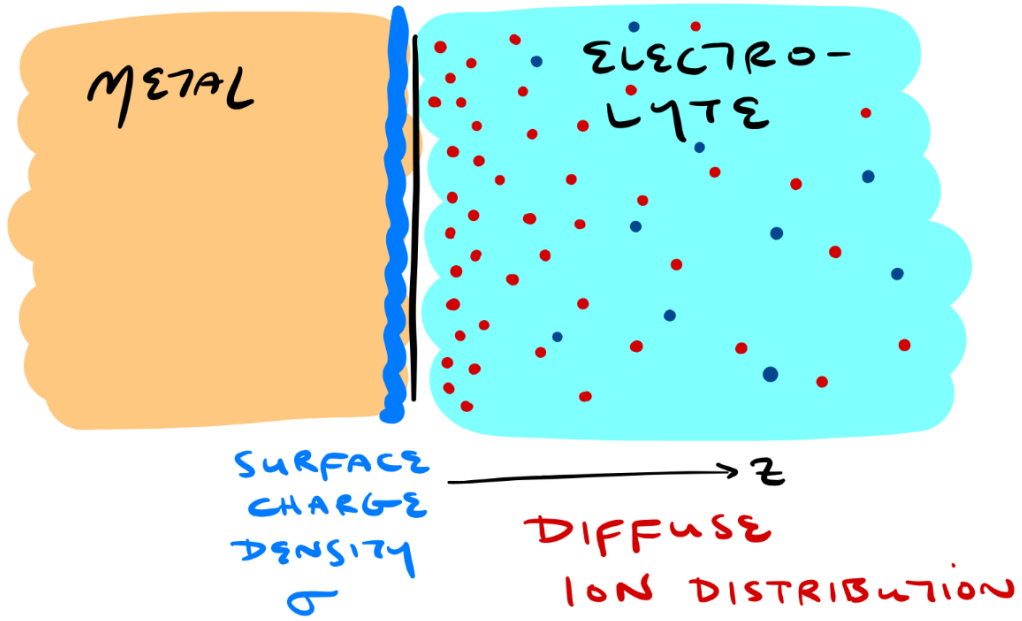




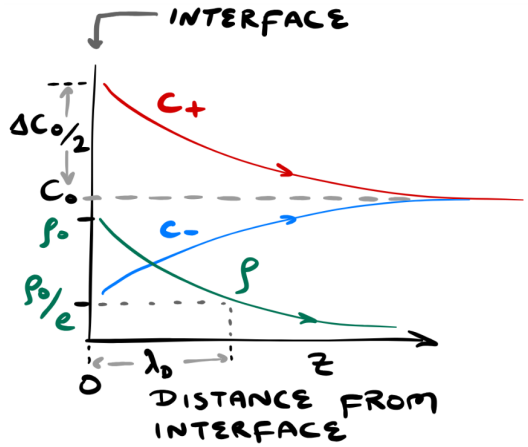
Lecture 3 – Interfacial electrochemistry

diffuse layer





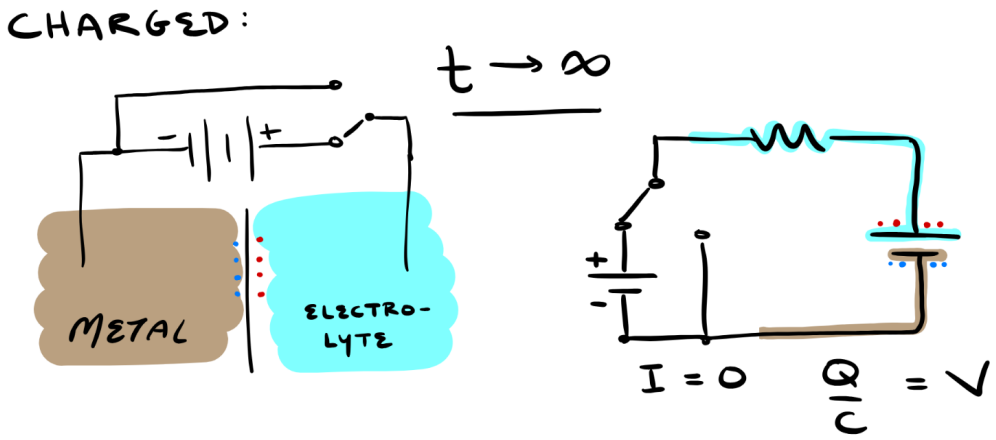
$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2c_o F^2}} \qquad c_A = \frac{\varepsilon}{\lambda_D}$$



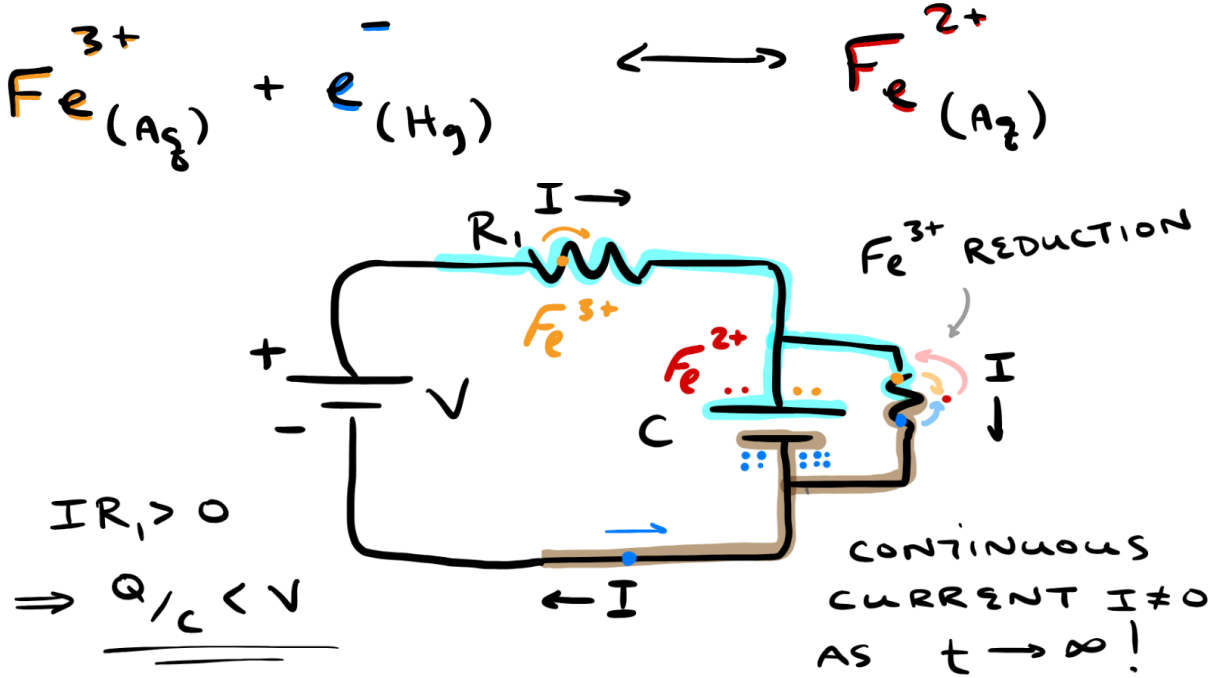
Lecture 3 – Interfacial electrochemistry

polarizable vs. nonpolarizable interfaces

polarizable

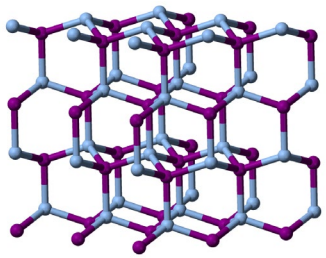


non-polarizable

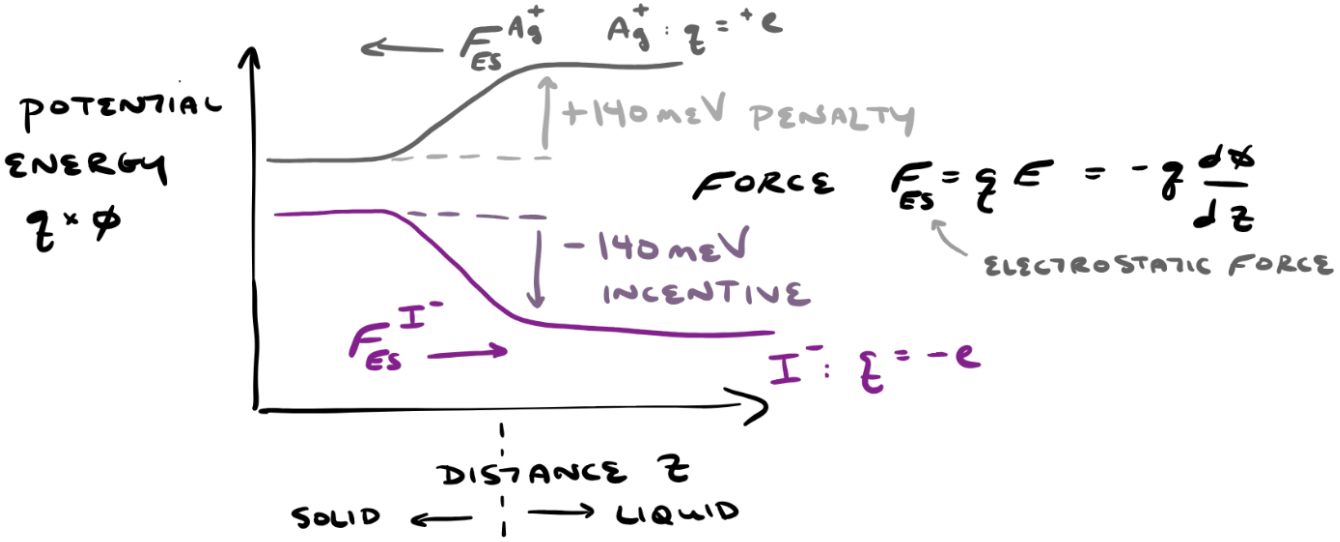


Lecture 3 – Interfacial electrochemistry

AgI electrode and the Nernst equation



$$[\mathrm{Ag}^+] = [\mathrm{Ag}^+]_{\mathrm{pzc}} e^{\frac{F\Delta\phi}{RT}}$$



$$\mathrm{AgI}_{(\mathrm{solid})} \longleftrightarrow \mathrm{Ag}_{(\mathrm{Aq})}{}^{+} + \mathrm{I}_{(\mathrm{Aq})}{}^{-}$$

$$\mathrm{Ag}_{(\mathrm{solid})}{}^{+} \longleftrightarrow \mathrm{Ag}_{(\mathrm{Aq})}{}^{+}$$