Thermodynamics of Solution Crystallization

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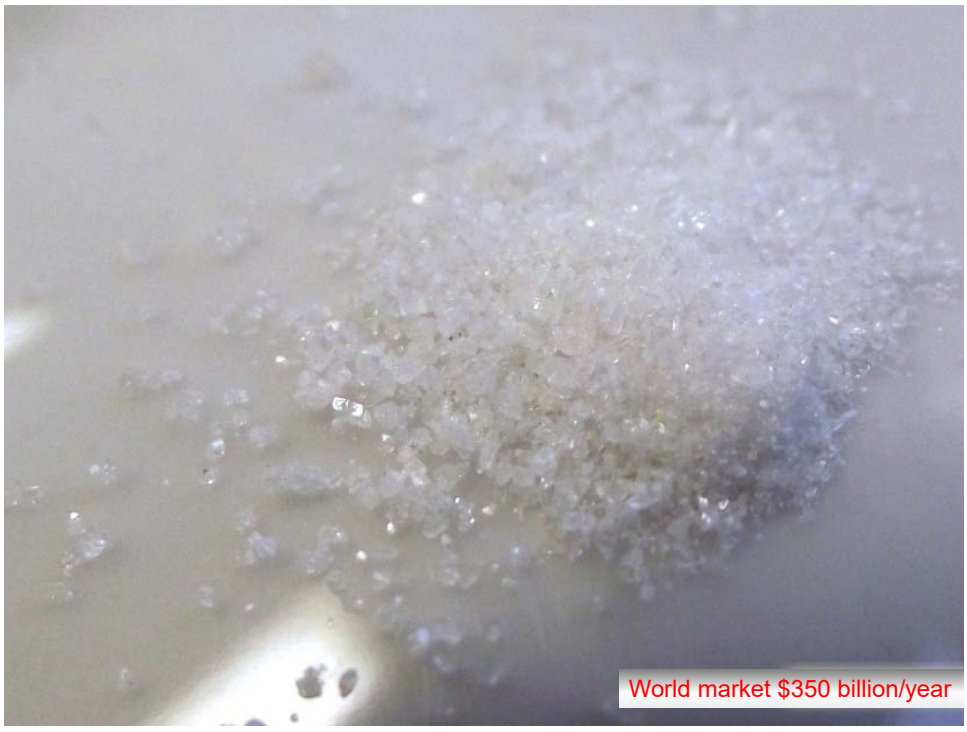
University of Houston


World market $304 billion/year


World market $350 billion/year

Flint and Quarts Crystals

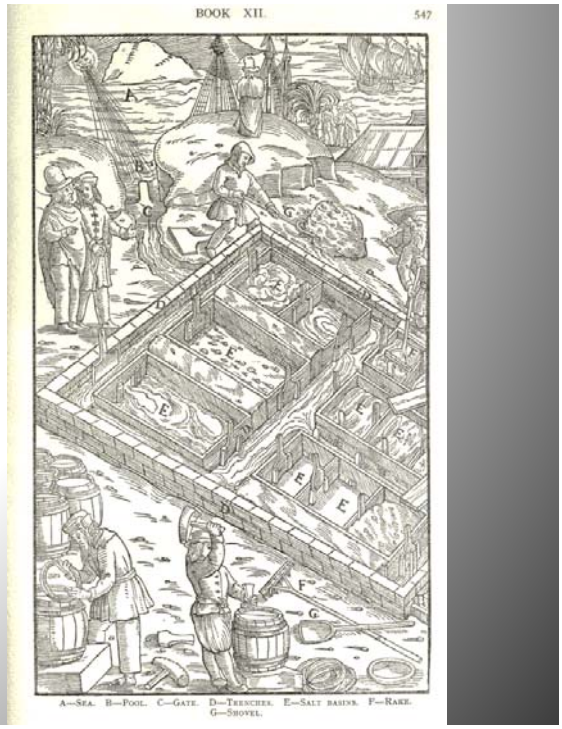
Kremuk

Hematite Drawings

Synthetic Crystals

"The history of salt-making in salt-pans, from sea water or salt springs, goes further back than human records."

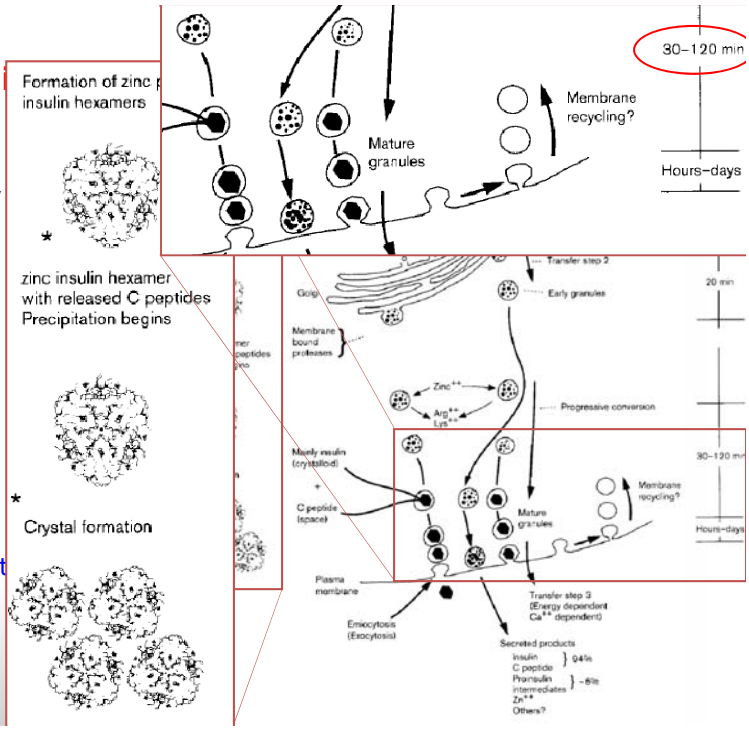
G. Agricola
De re metalica (1556)



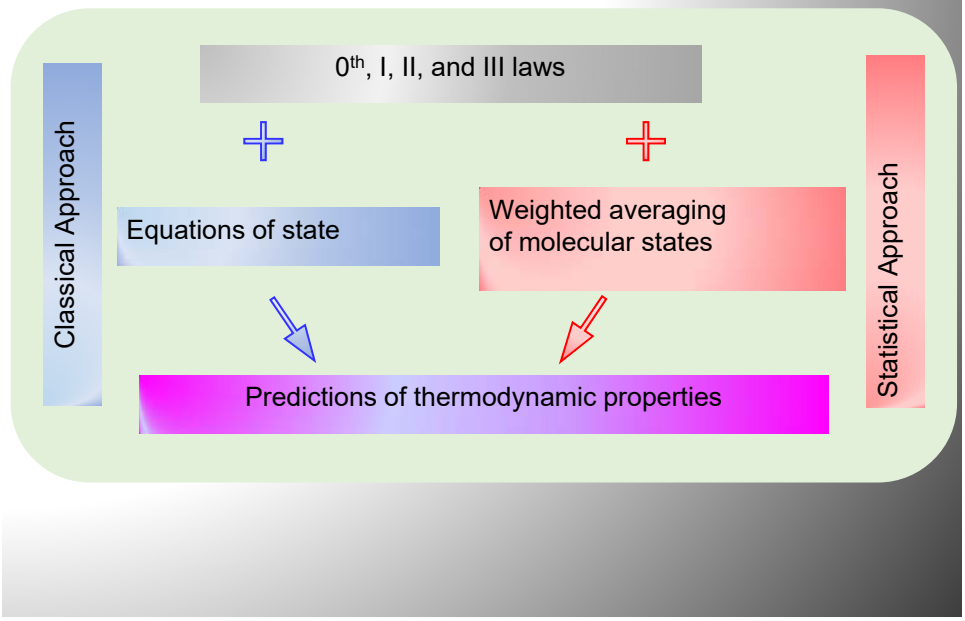
Insulin Biosynthesis

G. Dodson,
D. Steiner,
Curr. Op.Struct. Biol.
8 (1998) 189

- Single crystal per vesicle
- Fast crystal growth
- Ready response to fluctuations in conversion rate
- Crystals exclude proinsulin present in islet cells
- Slow dissolution at undersaturation

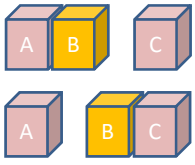


Classical and Statistical Thermodynamics



The Four Laws of Thermodynamics

0th Law



If $B \leftrightarrows A$

and $B \leftrightarrows C$

then $A \leftrightarrows C$

1st Law

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

$$\Delta U = Q + W$$

Entropy

2nd Law

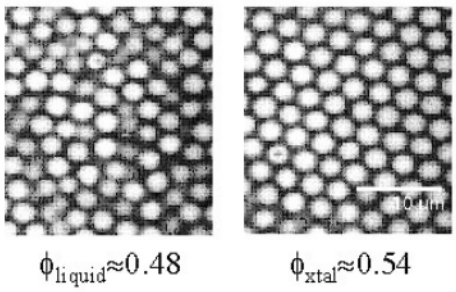
$\Delta S_{universe} \geq 0$

$\Delta S_{isolated\ system} \geq 0$

3rd Law

at T = 0 K

S = 0



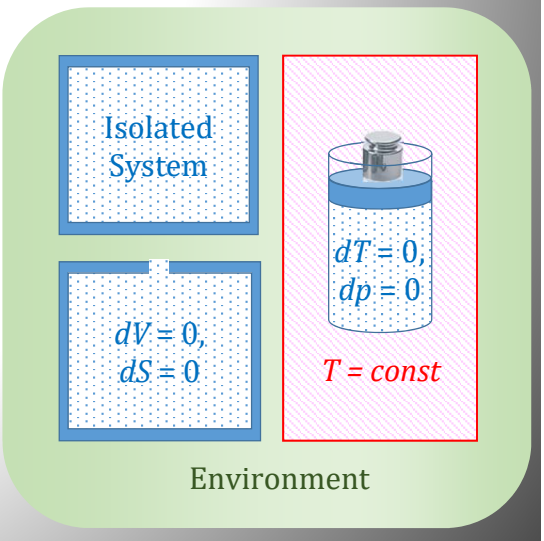
Other Formulations of the Second Law

$\Delta S_{isolated\ system} \geq 0$

$\Delta U_{S,V} \leq 0$

$\Delta G_{p,T} \leq 0$

$dG = Vdp - SdT + \sum_1^N \mu_i dn_i$



Other Formulations of the Second Law

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{reservoir} \geq 0$$

At $p = const$, $\quad dU = \delta W + \delta Q = -pdV + \delta Q$

$$\delta Q = dU + pdV = dH$$

$$\Delta Q_{system} = \Delta H_{system}$$

$$\Delta Q_{system} = -\Delta Q_{environment} = -T\Delta S_{reservoir}$$

$$\Delta S_{reservoir} = -\frac{\Delta Q_{system}}{T} = -\frac{\Delta H_{system}}{T}$$

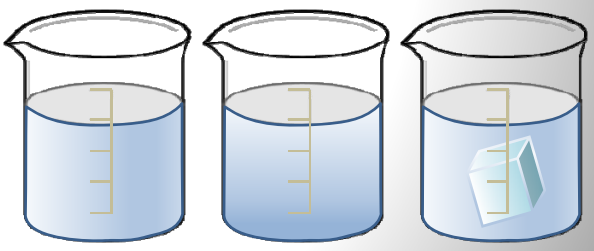
$$\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T} = -\frac{\Delta G_{system}}{T} \geq 0$$

$$\Delta G = \Delta H - T\Delta S \leq 0$$

$$\Delta G_{system} \leq 0$$

$T = const$

Homogenous and Heterogeneous Systems



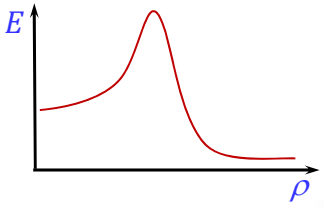
Homogeneous: properties do not change or change smoothly

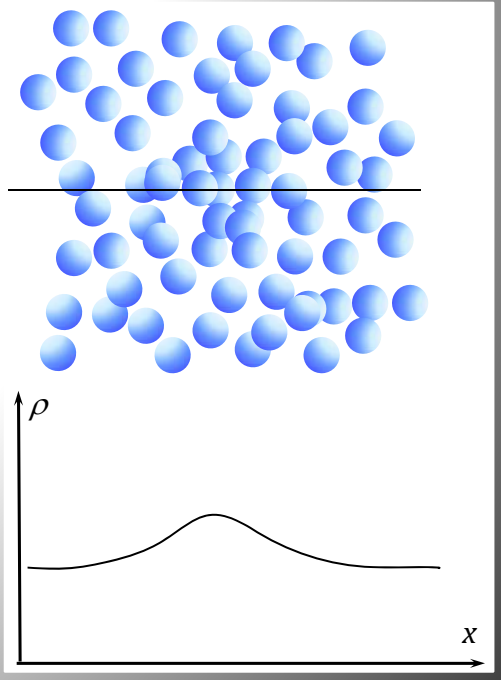
Heterogeneous: properties change abruptly

Phase: homogeneous part of a heterogeneous system

Fluctuations

The only way forward for activated processes



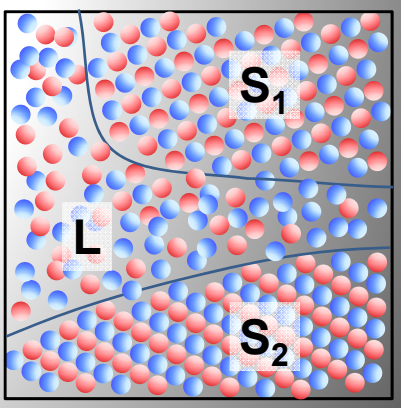


Gibbs's Phase Rule

Equilibrium between Π phases: α, β, γ, ... ω.
N components

$$T_\alpha = T_\beta = ... = T_\omega$$
$$p_\alpha = p_\beta = ... = p_\omega$$
$$\mu_{1,\alpha} = \mu_{1,\beta} = ... = \mu_{1,\omega}$$
$$\mu_{2,\alpha} = \mu_{2,\beta} = ... = \mu_{2,\omega}$$
$$...$$
$$\mu_{N,\alpha} = \mu_{N,\beta} = ... = \mu_{N,\omega}$$

$$f = N - \Pi + 2$$



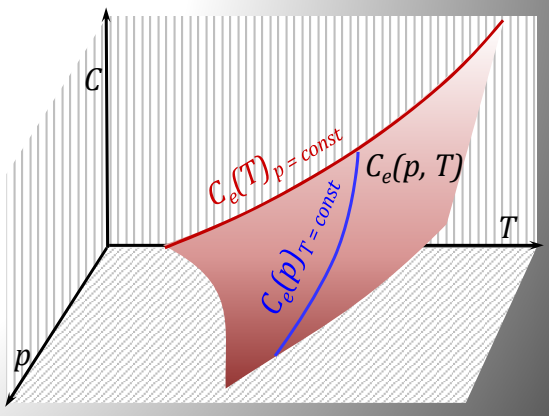
Solubility of a Crystal

$N = 2$ (solvent and solute)
$\Pi = 2$ (crystal and solution)

$f = N - \Pi + 2 = 2$

$C_e = C_e(p, T)$

$C_e = C_e(T)_{p = 1\ atm}$



Solvent and Solute

Solution: a mixture of two or more components
majority component: solvent
present at lower concentration: solutes

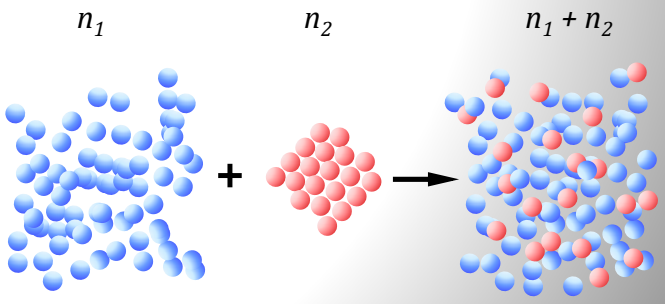
At $p = const$ and $T = const$

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$\mu_2 = \mu_2^0 + RT ln a_2 = \mu_2^0 + RT ln \gamma_2 C_2$$

$$= \mu_2^0 + RT \ln \gamma_2 + RT \ln C_2$$

Molecular-level View of the Solution



Ideal Solutions

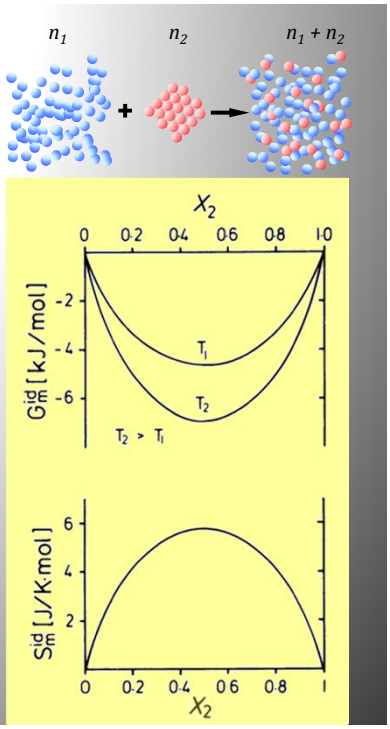
$$\Delta H = 0$$

$$S = -kB \sum_i p_i \ln p_i$$

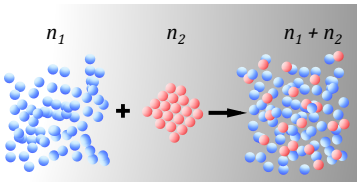
$$\frac{\Delta S}{n} = -k_B(x_1 \ln x_1 + x_2 \ln x_2) =$$

$$-k_B[(1-x_2)\ln(1-x_2) + x_2 \ln x_2]$$

$$x_2 = \frac{n_2}{n} = \frac{C_2 V M_{w1}}{V\rho - C_2 V(M_{w2} - M_{w1})} \approx \frac{C_2 M_{w1}}{\rho}$$



Regular Solution Model



$\Delta H \neq 0$

$$\frac{H_{solution}}{n} = \frac{zw_{11}x_1}{2} + \frac{zw_{22}x_2}{2} + \left(w_{12} - \frac{w_{11}+w_{22}}{2}\right)m_{12}$$

$$m_{12} = znx_2(1 - x_2)$$

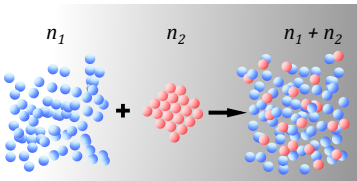
$$\chi_{12} = \frac{z}{k_B T}\left(w_{12} - \frac{w_{11}+w_{22}}{2}\right)$$

$\Delta G/nkBT$

$=(1 - x_2)\ln(1 - x_2) + x_2\ln x_2 + \chi_{12}x_2(1 - x_2)$

$$\Delta H/nkBT = \chi_{12}x_2(1 - x_2)$$

Regular Solution Model



$$\mu_2 = (\partial G/\partial n_2)_{T,P,n_1} = \frac{zw_{22}}{2} + k_B T \ln x_2 + k_B T \chi_{12}(1 - x_2)^2$$

$$\mu_2 = \mu_2^0 + RT ln a_2 = \mu_2^0 + RT \ln C_2 + RT \ln \gamma_2$$

$$RT \ln \gamma_2 = \chi_{12}(1 - x_2)^2$$

μ_2^0 : properties of pure solute

$RT \ln C_2$: entropy of dissolution

$RT \ln \gamma_2$: interactions between solute and solvent

The Crystallization Driving Force

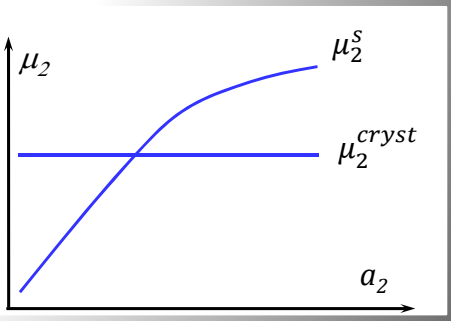
$dG = dG^{cryst} + dG^{s} =$

$\mu_2^{cryst} dn_2^{cryst} + \mu_2^{s} dn_2^{s}$

$dG = (\mu_2^{cryst} - \mu_2^{s}) dn_2$

$dn_2^{cryst} > 0$

only if $\mu_2^{cryst} < \mu_2^{s}$



If $\mu_2^{cryst} > \mu_2^{s}$ then

$dG < 0$ only if $dn_2^{cryst} < 0$: the crystal dissolves

The Crystallization Equilibrium Constant

At equilibrium

$dG = 0$ and

$\mu_2^{cryst} = \mu_2^{s} = \mu_2^{0} + RT ln a_{2,e}$

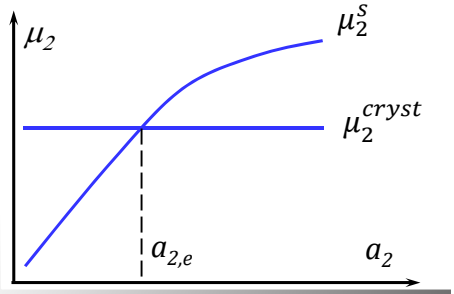
Since $\mu_2^{cryst} = \mu_2^{cryst,0}$

then $\mu_2^{cryst,0} - \mu_2^{0} = \Delta G^0$

$K_{eq} = \exp(-\Delta G^0 / RT)$

$K_{eq} = a_{2,e}^{-1}$

$\Delta G^0 = RT \ln a_{2,e}$



The Crystallization Driving Force

$$\Delta\mu = \mu_2^s - \mu_2^{cryst}$$
$$= \mu_2^0 + RT \ln a_2 - (\mu_2^0 + RT \ln a_{2,e})$$
$$= RT \ln(a_2/a_{2,e})$$
$$= RT \ln(C_2/C_{2,e}) + RT \ln(\gamma_2/\gamma_{2,e})$$

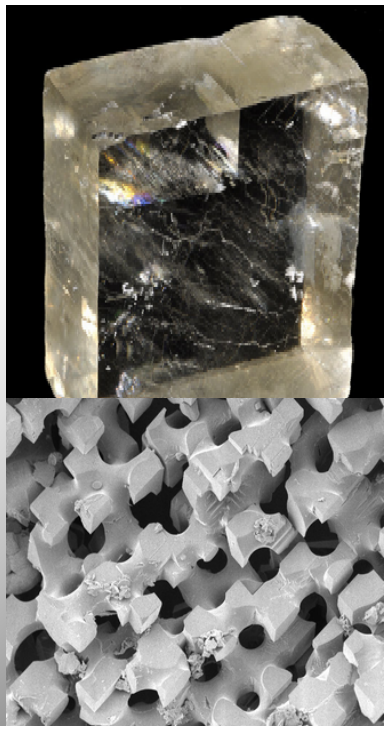
$$\Delta\mu \approx RT \ln(C_2/C_{2,e})$$

Multi-component Systems

$Ca^{2+}(s) + CO_3^{2-}(s) \rightarrow CaCO_2(cryst).$

$$K_{sp} = a_{Ca^{2+},e}\, a_{CO_3^{2-},e}$$

$$\Delta\mu = RT \ln(a_{Ca^{2+}}\, a_{CO_3^{2-}}/K_{sp})$$



Thermodynamic Effects of the Solvent

$Na^+(gas) + Cl^-(gas) \rightarrow NaCl(solid)$

$\Delta H^0 = -788$ kJ mol^{-1}

$Na^+(gas) + nH_2O \rightarrow Na^+(aq)$

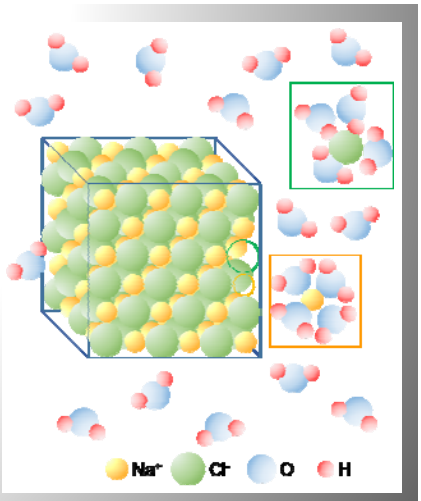
$\Delta H^0 = -406$ kJ mol^{-1}.

$Cl^-(gas) + nH_2O \rightarrow Cl^-(aq)$

$\Delta H^0 = -366$ kJ mol^{-1}

$Na^+(aq) + Cl^-(aq) \rightarrow NaCl(solid)$

$\Delta H^0 = -19$ kJ mol^{-1}



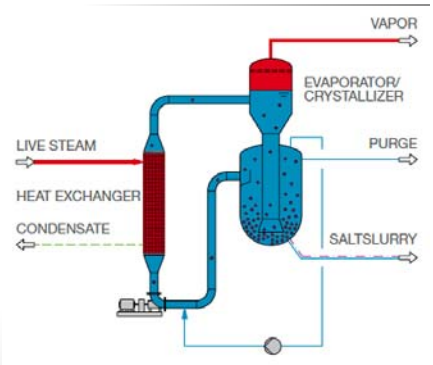
$$\Delta S^0 = \Delta S^0_{solute} + \Delta S^0_{solvation}$$

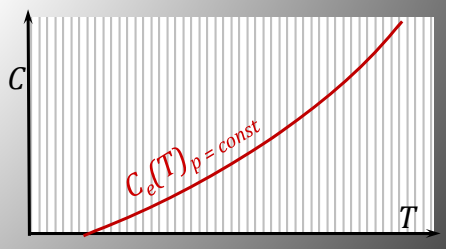
The Effect of Temperature

$$\frac{\partial(\Delta G/RT)_{p,n_i}}{\partial T} = -\frac{\Delta H}{RT^2}$$

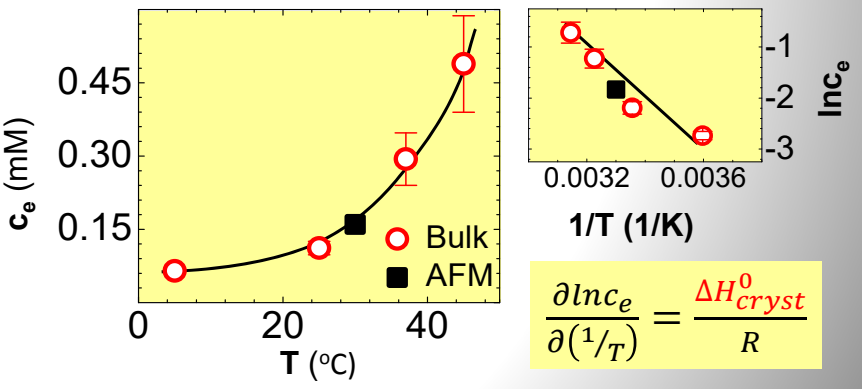
$$\Delta G^0 = RT \ln a_{2,e}$$

$$\left.\frac{\partial \ln a_{2,e}}{\partial T}\right|_{p,n_i} = -\frac{\Delta H}{RT^2}$$





Thermodynamics of Hematin Crystallization



$$\frac{\partial \ln c_e}{\partial (1/T)} = \frac{\Delta H^0_{cryst}}{R}$$

- The crystallization enthalpy ΔH^0_{cryst} = -37±8 kJ mol^{-1}
- The crystallization entropy ΔS^0_{cryst} = -49±7 J mol^{-1}K^{-1} suggests a process leading to higher disorder accompanies hematin crystallization

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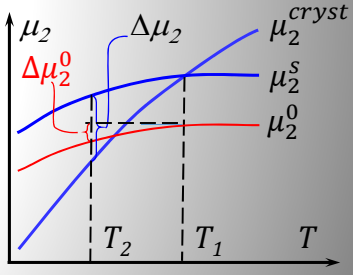
The Effect of Temperature

$$\mu_2^0(T_2) = -T_2 \int_{T_1}^{T_2} \frac{\Delta H^0}{T^2} dT$$

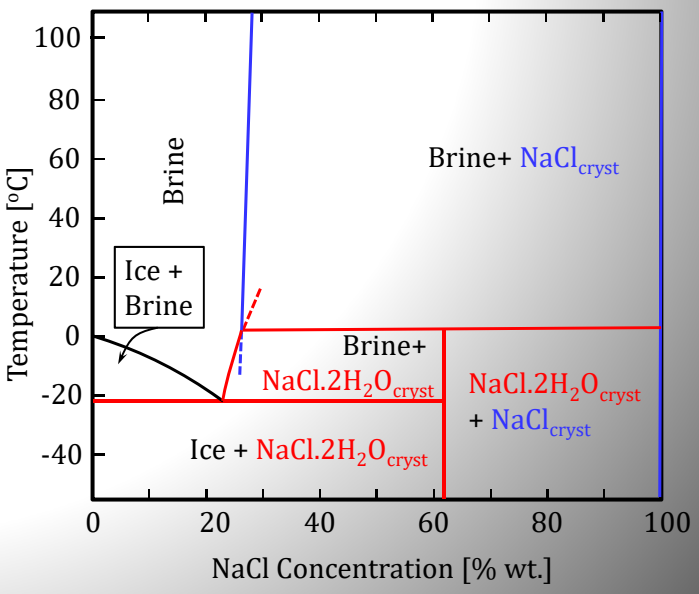
$$\Delta\mu(T_2) = \Delta\mu_2^0(T_2) + RT_2 \ln a_2(T_2) - RT_1 \ln a_2(T_1)$$

$$\Delta\mu = RT \ln(a_2/a_{2,e}(T_2))$$

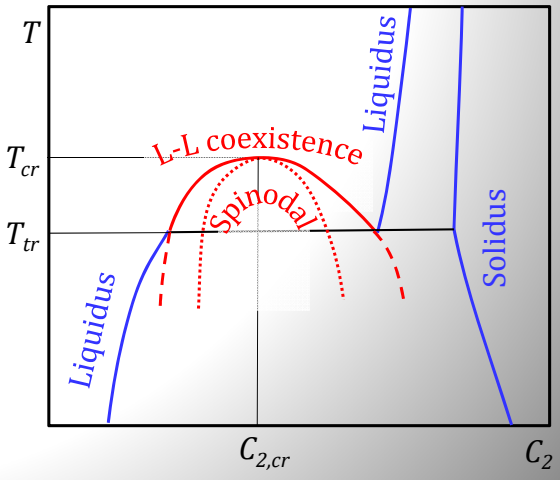
$$\Delta\mu \approx RT \ln(C_2/C_{2,e}(T_2))$$



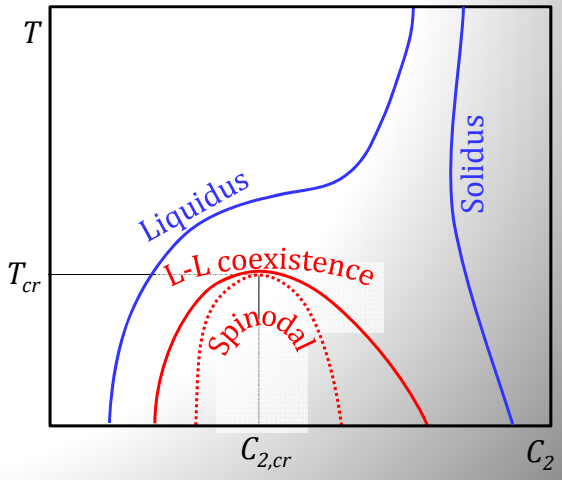
The Phase diagram of Ionic Solutes



Theoretical phase diagrams of small-molecule solutes



Theoretical phase diagrams of of protein and colloid solutions

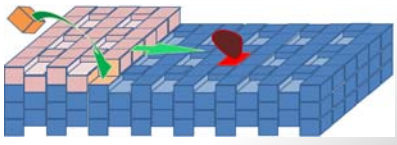


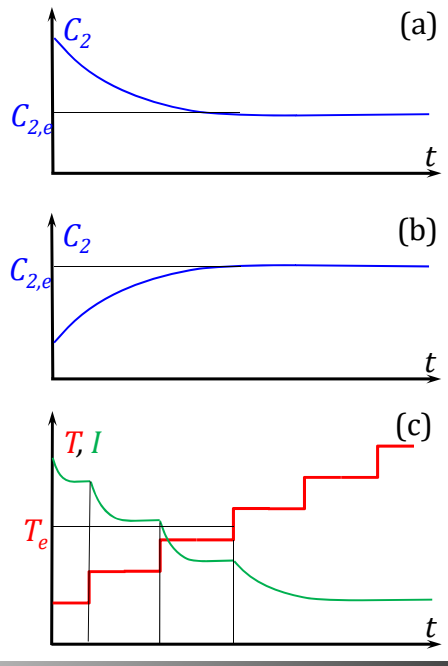
Macroscopic Methods of Solubility Determination

Crystal growth

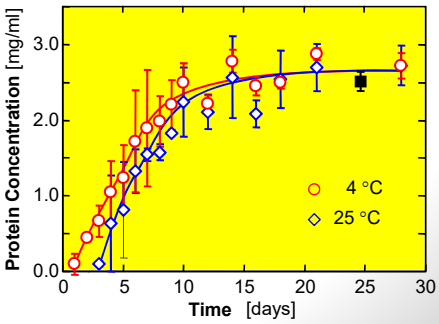
Crystal dissolution

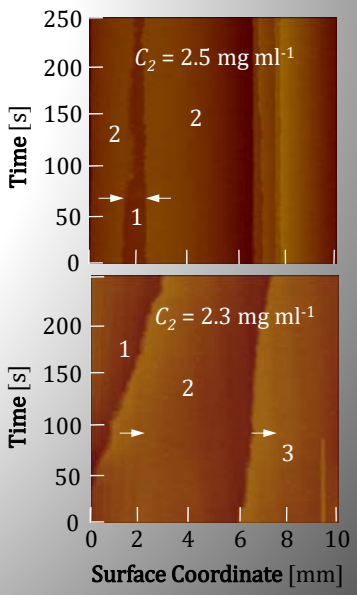
Step wise dissolution



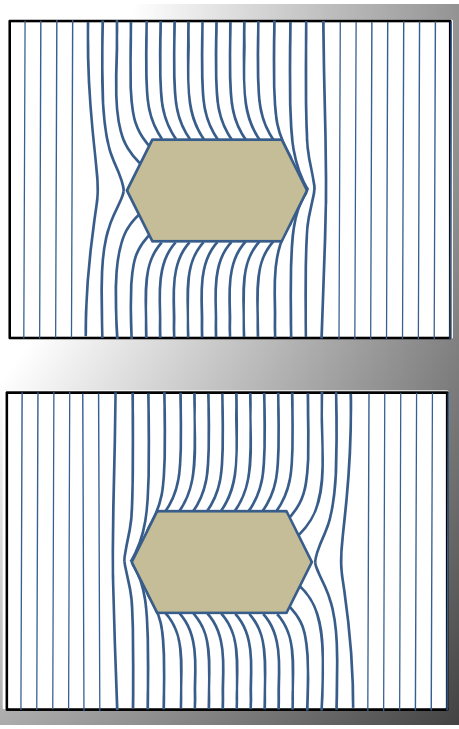


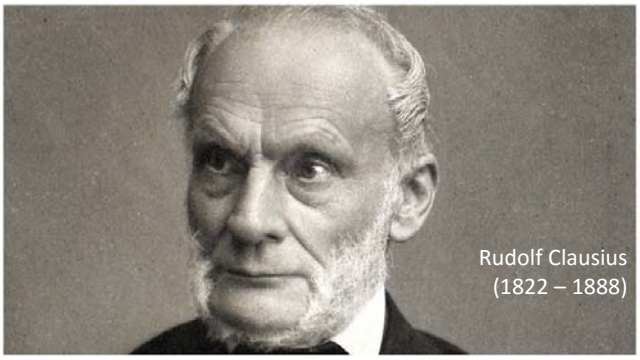
Microscopic Methods of Solubility Determination



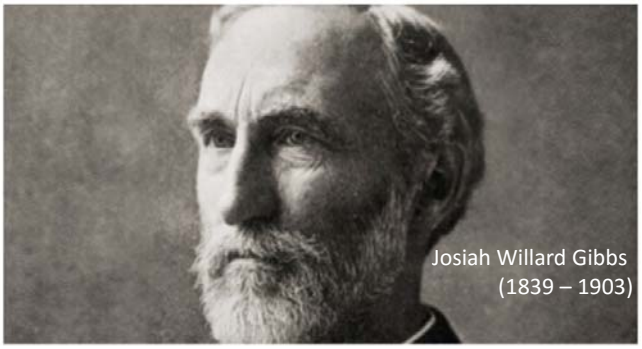


Microscopic Methods of Solubility Determination





Rudolf Clausius
(1822 – 1888)



Josiah Willard Gibbs
(1839 – 1903)