

Introductory Concepts

- Each Macro state corresponds to many Microstates
- An Ensemble is a large number of copies of a system / each comprising a different Microstate
- * An Ensemble Average of A (\bar{A})

$$\bar{A} = \sum_i p_i A_i \text{ where } \sum_i p_i = 1 \text{ (Probability)}$$

Micro Canonical Ensemble

Boundary Condition: Constant Energy

constant Volume
Fundamental Postulate: Given an isolated system in Equilibrium, Each Microstate is found with Equal Probability

Statistical Interpretation of Entropy

- S maximized at Equilibrium

$$S = k \cdot \ln(\Omega)$$

↳ where Ω = accessible microstates

$$S_{\text{total}} = S_1 + S_2 \quad \left\{ \Omega_{\text{Total}} = \Omega_1 \cdot \Omega_2 \right.$$

Distinguishable → each particle's position can be tracked

Indistinguishable → each particle is indivisible from another

Gibbs Entropy of Mixing

- Solid 1 contains n_1 atoms on N_1 sites
- Solid 2 contains n_2 atoms on N_2 sites

↳ Assume solid solution of same lattice & random distribution

$$\Delta S = S_f - S_i \quad * \text{Assump}$$

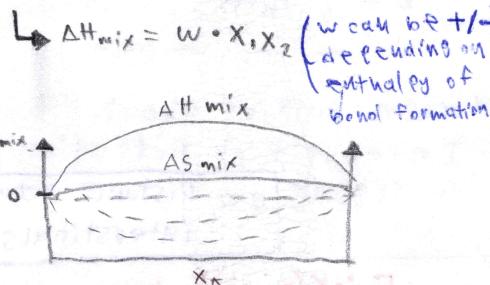
$$= k \ln \left(\frac{n!}{n_1! n_2!} \right) \quad \ln(x!) = x \ln(x) - x$$

$$= -nk \left(x_1 \ln(x_1) + x_2 \ln(x_2) \right)$$

3.022 Summary Sheet (Exam)

Regular Binary Solution Theory

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$



Common Tangent Construction

- Composition of Phases in 2-Phase Equilibrium dictated by Common Tangent Construction

- Also Dictates Chemical Potential of Each Substance

Canonical Ensemble

Boundary Condition: Temperature

$$T \quad (\text{constant})$$

Volume

- a composite system consists of N Identical Systems such that

$$\sum_i E_i = E_{\text{Total}}$$

Example:

- You have N different systems

↳ for a system with N₀ particles at 0 energy, etc.

$$\Omega = \frac{N!}{\prod_i N_i!} \quad \left\{ \begin{array}{l} \text{Microstate} \\ \text{Degeneracy for} \\ \text{given Energy} \\ \text{distribution} \end{array} \right.$$

Mechanics of Partition Function

- Probability of Macrostate $\propto \frac{N!}{\prod_i N_i!}$

- We Maximize Ω with constraint

$$\frac{\partial \ln \Omega}{\partial N_m} = 0 \quad \sum N_i = N \quad \sum N_i E_i = E$$

$$\text{Partition Function: } Z = \sum_i \exp(-E_i/kT)$$

Canonical

$$\text{Distribution: } P_i = \frac{N_i}{N} = \frac{1}{Z} \exp\left(-\frac{E_i}{kT}\right)$$

Properties and Examples of Canonical Ensemble

$$\text{Average Energy: } \bar{E} = \frac{1}{Z} \sum E_i \cdot e^{-E_i/kT} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\text{Average Extensive Variable: } \bar{B} = \frac{1}{Z} \sum B_i \cdot e^{-E_i/kT}$$

How to deal w/ system exposed to Force

1) Identify system

2) Determine Hamiltonian of Energy Levels

3) Calculate Z and canonical distribution

4) calculate system Properties

Heat Capacity

- For Condensed Matter

$$C_V = \frac{N_A}{N} \left(\frac{\partial \bar{E}}{\partial T} \right)_V$$

How to Derive Heat capacity

1. Determine System Energy Levels

2. Derive Partition Function Z

3. Calculate Mean Energy as Function of Temp

4. Calculate By taking Derivative w/ respect to Temp

11 Energy & Partition Function of N identical but Distinguishable Particles

$$E_{\text{system}} = \sum_N E_{\text{particle}}$$

$$Z_{\text{system}} = Z_{\text{particle}}^N$$

Energy & Partition Function of N Indistinguishable Particles

$$E_{\text{system}} = \sum_n E_{\text{particle}}$$

$$Z_{\text{system}} = \frac{1}{N!} Z_{\text{system}}^N$$

Heat Capacity of Monatomic Gas and Solid

• Harmonic Oscillator Model for Solid

↳ Each atom oscillates in potential well

Potential Function

$$\psi(x) = \psi(0) + \frac{1}{2} Kx^2 \rightarrow K = \left. \frac{\partial^2 \psi}{\partial x^2} \right|_{x=0}$$

Oscillator angular Frequency

$$\omega = \sqrt{K/m}$$

$$\text{Energy: } E_i = n_i \hbar \omega$$

$$\text{Partition Function: } Z = \sum_{n_i=0}^{\infty} e^{-\beta n_i \hbar \omega} = \frac{1}{1 - e^{-\beta \hbar \omega}}$$

$$\text{Mean Energy: } \bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}$$

$$\text{Heat capacity: } C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = k_B \frac{e^{\beta \hbar \omega}}{[e^{\beta \hbar \omega} - 1]^2} \cdot (\beta \hbar \omega)^2$$

Diffusion

1. Diffusion by Vacancy

2. Diffusion by Interstitial

Interstitial Diffusion:

$$\text{Atom Vibration Frequency: } \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{K}{m}}$$

$$\text{Frequency of Successful Hops: } v_h = r \cdot \exp(-E_a/kT)$$

* Number of Atoms to successfully hop from plane 1 to 2 per unit time

$$J = \frac{1}{6} v_h \cdot n_1$$

$$\text{Net Flux: } J_{\text{net}} = J_+ - J_-$$

$$= \frac{1}{6} v_h \cdot (n_1 - n_2)$$

$$= \frac{1}{6} v_h a (c_1 - c_2)$$

$$\frac{dc}{dx} \cdot da$$

$$D = \frac{1}{6} v_h a^2$$

• When talking about Interstitial Diffusion in crystals $d = \text{Distance between interstitials}$

Fick's 1st Law

$$J = -D \cdot \frac{\partial c(x,t)}{\partial x} \quad * \text{Proven Above}$$

Deriving Fick's 2nd Law

$$\bullet J(x+dx) = -D \frac{\partial c(x+dx,t)}{\partial x}$$

Net change of amount of diffusant in a section over period dt

$$J(x) \cdot A \cdot dt - J(x+dx) \cdot A \cdot dt = -\frac{\partial J}{\partial x} \cdot A \cdot dt$$

$$\frac{\partial c(x,t)}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$

Point Source Diffusion

• at $t=0$, amount a of a species diffuses on an area plane

$$c(x,t) = \frac{a}{2\pi D t} \cdot \exp\left(-\frac{x^2}{4Dt}\right)$$

$$\hookrightarrow \text{Diffusion Length} = 2\sqrt{Dt}$$

Step-Concentration Diffusion

$$\text{Initial conditions: } c(x,0) = c_0$$

↳ where $x < 0$

$$c(x,0) = 0$$

↳ where $x > 0$

$$c(x,t) = \frac{c_0}{2} \cdot [1 - \text{erf}(x/2\sqrt{Dt})]$$

$$\text{erf}(x) = \frac{2}{\sqrt{\pi t_0}} \int_0^x \exp(-n^2) dn$$

Diffusion from Extended Source

Initial condition: $c(x,0) = c_0 \quad (-h \leq x \leq h)$

$$c(x,0) = 0 \quad (x < -h, x > h)$$

$$c(x,t) = \frac{c_0}{2} \cdot \left[\text{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right) + \text{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right) \right]$$

* Linear superposition of 2 step functions

Thermo Behind Diffusion

• Average velocity of diffusing species A

$$v_a = M_a F_a \quad J_a = v_a C_a$$

$$F_a \cdot dx = -dH_a \quad \rightarrow \text{Force is Gradient of chemical potential}$$

Final Derivation:

$$J_a = M_a C_a F_a = -M_a C_a \frac{dH_a}{dx} \rightarrow D = x_a M_a \frac{dM_a}{dx_a}$$

$$D_a = M_a K T \quad \rightarrow \text{Einstein Relation}$$

Partition Function (Actual)

$$Z = \sum_E \Omega_E \exp(-\frac{E}{kT})$$

During - Petrie

$$C_V, \text{solid} = 3R \text{ @ high temp} \\ = 0 \text{ @ low temp}$$

Substitutional Vacancy

Frequency of atomic vibration: $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$

Probability of sufficient energy: $e^{-E_a/kT}$

New
Probability of finding a vacancy: $\frac{n}{N} * Z$

Equilibrium Vacancy Conc.

Entropy contribution: $\Delta S_{\text{formation}} + N\Delta S_{\text{vibration}}$

$$= N \times v \Delta S_v + K \ln \left(\frac{(N+n)!}{N! n!} \right)$$

↳ simplify using Sterling

Enthalpy contribution: $N \times v \Delta H_v$

Equilibrium vacancy: Value of $\frac{\partial G}{\partial x_v}$ that

* Energy causes defect minimizes free energy

Substitutional self-Diffusion

Successful hop frequency: $\nu_h = \frac{Z}{2\pi} \sqrt{\frac{k}{m}} \exp\left(-\frac{\Delta G - E_a}{kT}\right)$

Diffusion constant: $D = D_0 \exp\left(-\frac{E_{\text{sp}}}{kT}\right)$

(separating T dependent from non-Temp)

Vacancy Diffusion

Hopping frequency for vacancy diffusion: $\nu_h = \frac{1}{6} Z r v a^2$

$D_v = \frac{D}{x_v} = \frac{1}{6} Z r v a^2 * e^{-\frac{E_a}{kT}}$

$J = J_{\rightarrow} - J_{\leftarrow} = \frac{1}{6} \nu_h (n_1 - n_2)$

Ficks 1st Law: $\frac{1}{6} \nu_h d^2 \frac{dC}{dx} = -D \frac{dC}{dx}$

↳ refined w/ respect to Lattice Vacancy Diffusion (Binary system)

$J_A = -D_A \frac{dC_A}{dx}$ $J_B = -D_B \frac{dC_B}{dx}$

Exam 2 Summary Sheet

Concentration of lattice sites: $C_0 \approx C_A + C_B$

Net Vacancy Diffusion Flux: $J_V = J_{V,A} + J_{V,B}$
 $= (D_A - D_B) \frac{\partial C_A}{\partial x}$

Notes:

- * Edge Dislocations act as sources & sinks of Vacancies
- * This Demonstrates the Kirkendall Effect

Planes in Motion & Reference Frame

Velocity of crystal plane motion: $v = \frac{J_V}{C_0} = (D_A - D_B) \frac{\partial C_A}{\partial x}$

Interdiffusion in ionic solids: $\bar{D} = \frac{D_{Na} D_{K+}}{D_{Na} X_{Na} + D_{K+} X_K}$

- Laboratory Reference Frame considers
- 1. Diffusion
 - 2. Convective Flow

$J_A' = -D_A \frac{\partial C_A}{\partial x} + v C_A$

Darken Equation

$\bar{D} = x_B D_A + x_A D_B$ Interdiffusion of Binary alloy

↳ Diffusion co-efficient goes to pure A's value as its more dilute in B

Ionic Defect types

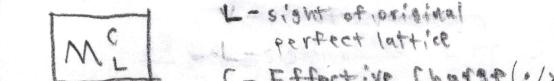
- A. Schottky Defect
↳ Anion & Cation Vacancy Pair
- B. Frenkel Defect
↳ Self-Interstitial
- C. Substitutional Atom
- D. Foreign Interstitial

Kroger-Vink Notation

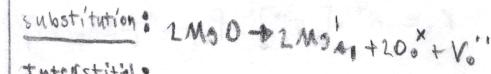
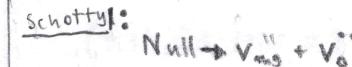
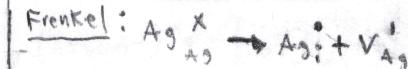
General Form: M-Atom Type or Vacancy

L-sight of original perfect lattice

C-Effective Charge (+/-)



Examples & Defect Concentration



Interstitial:

1. Mass Conservation

2. Charge Conservation

3. Each side Charge Neutral

$x_{Frenkel} = e^{-\frac{-\Delta G_f}{2kT}}$

K represents reaction coefficient

Charge Compensation in Ionic solid

Ex. TiO_2 doped w/ Al_2O_3

1. List all charged species

- Native Vacancies ($V_O^{..}, V_{Al}^{..}$)
- Foreign Substitutional (Ti^{+3}_{Al})
- Interstitials (Al^{+3}, Ti^{+4})

2. List Defect Reactions

* Balance charge

3. Combine all Equations

$$K_1 = [V_{Al}^{..}]^2 \cdot [V_O^{..}]^3 = \exp(-\Delta G_1/kT)$$

$$K_2 = [Ti^{+3}_{Al}]^3 \cdot [V_{Al}^{..}] = \exp(-\Delta G_2/kT)$$

$$K_3 = [Al^{+3}] \cdot [V_{Al}^{..}] = \exp(-\Delta G_3/kT)$$

$$K_4 = [Ti^{+4}]^3 \cdot [V_{Al}^{..}]^4 = \exp(-\Delta G_4/kT)$$

$$2[V_O^{..}] + [Ti^{+3}_{Al}] + 3[Al^{+3}] + 4[Ti^{+4}] = 3[V_{Al}^{..}]$$

5 equations; 5 variables unknown;

8 unique solution

charge comp in Non-Stoichiometric

Ex. Non-Stoichiometric TiO_x

1. List charged species

Native Vacancies: $V_O^{..}, V_{Ti}^{..}$

Electrons and Holes: e^-, h^+

3. Combine all Eqs to Solve

$$K_1 = [V_{+i}^{(1)}][V_0^{(2)}]^2 = e^{\Delta G / kT}$$

$$K_2 = n \cdot p = e^{\Delta G_2 / kT}$$

$$K_3 = n^4 \cdot [V_0^{(2)}]^2 \cdot P_{O_2} = e^{\Delta G_3 / kT}$$

$$p + 2[V_0^{(2)}] = n + 4[V_{+i}^{(1)}]$$

↳ perfect concentration depends on O₂ Partial Pressure

Brower Approximation

- Pretend one charged defect dominates all others

| | | | |
|-------------------|--------------------------------------|--------------------|-------------------------|
| $[V_{Mg}] = p$ | High O ₂ Partial Pressure | $[V_{Mg}] - [V_0]$ | Schottky Compensation |
| $[V_0^{(2)}] = n$ | Low O ₂ partial pressure | $[n] = [e]$ | Electronic Compensation |

Equilibrium constants:

$$K_1 = [V_{Mg}] \cdot [V_0] \quad K_2 = n \cdot p \quad K_3 = [V_0^{(2)}]^2 \cdot P_{O_2}$$

| | | |
|--------------------------------------|-------------------------------------|------------------------------|
| High O ₂ Partial Pressure | Low O ₂ Partial Pressure | Schottky compensation region |
|--------------------------------------|-------------------------------------|------------------------------|

$$[V_0^{(2)}] = 2K_1/p \quad n = 2[V_0^{(2)}] \quad [V_0^{(2)}] = \sqrt{K_1 \cdot p}$$

$$n = K_2/p \quad K_3 = [V_0^{(2)}]^2 \cdot P_{O_2} \quad K_3 = [V_0^{(2)}]^2 \cdot n \cdot P_{O_2}$$

$$K_3 = [V_0^{(2)}]^2 \cdot n \cdot P_{O_2}$$

$$V_0^{(2)} = \frac{1}{2} \cdot \frac{K_1}{K_2} \cdot \frac{P_{O_2}}{p} \quad [V_0^{(2)}] = \left(\frac{K_1}{16}\right) V_0 \cdot P_{O_2} \quad [V_0^{(2)}] = \sqrt{\frac{K_1}{K_2}} \cdot \frac{V_0}{P_{O_2}}$$

$$n = 2 \cdot \left(\frac{K_2}{K_1}\right)^{1/2} \cdot V_0 \cdot P_{O_2} \quad n = \left(\frac{K_2}{K_1}\right)^{1/2} \cdot V_0 \cdot P_{O_2}$$

Governing Equations

$$[V_0] \cdot p \cdot P_{O_2}^{-1/2}$$

$$n = 2[V_0^{(2)}]$$

$$[V_{Mg}] \cdot [V_0^{(2)}] = k_1$$

$$p \cdot n = K_2$$

Chemical Potential/Electrochemical

chemical Potential:

$$\bar{H}_A = H_{A,0} + kT \ln(x_A)$$

Electrochemical Potential:

$$\bar{H}_A = H_A + Z_A e \phi$$

ϕ = Electric Potential
 Z_A = FF of charge species

Thermo of Diffusion & Ion conductivity

Velocity of Diffusing Species

$$v_A = M_A F_A \quad J_A = v_A C_A$$

$$M_A = M_A T$$

$$J_A = -D_A \frac{dC_A}{dx} + C_A M_A Z_A e E(x)$$

① Diffusion - Motion driven by (chemical Potential) Gradient

② Drift - Directional motion of ions driven by Electric Field

Current Density of Drifting Ions:

$$I_A = Z_A e J_A = C_A M_A Z_A^2 e^2 E(x)$$

$$J_A = M_A C_A Z_A^2 e^2 = \frac{D_A C_A Z_A^2 e^2}{kT}$$

Total Conductivity:

$$\sigma = \sum_i \sigma_i = \sum_i \frac{D_i C_i Z_i^2 e^2}{kT}$$

Surface Energy

$$\Delta G = -S dT + V dP + \Delta G_{\text{surface}}$$

$$\Delta G_{\text{surface}} = \gamma \cdot dA \Rightarrow \gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P}$$

$$\gamma = \frac{1}{2} T E_b \quad T = \# \text{ of broken bonds per unit SA}$$

$$E_b = \text{Bond Energy}$$

(100) FCC Surface Energy:

- Area of Plane = πa^2
- # of broken bonds = $4 + \frac{8}{2} = 12$
- $T_{100} = \frac{8}{a^2} \quad \gamma_{100} \approx 4 \cdot \frac{E_b}{a^2}$

(110) FCC surface Energy:

- Area = $\sqrt{2} a^2$
- # broken bonds = $10 + \frac{3}{2} + 4/4 = 12$
- $T_{110} = \frac{12}{\sqrt{2} a^2} \quad \gamma_{110} \approx 4.24 \cdot \frac{E_b}{a^2}$

(111) FCC Surface Energy:

- Area = $\frac{\sqrt{3}}{4} a^2$
- # broken bonds = 3
- $T = \frac{6.93}{a^2} \quad \gamma_{111} = 3.46 \frac{E_b}{a^2}$

Surface Energy of planes

$$\gamma = \gamma_1 \cos(\theta) + \gamma_2 \sin(\theta)$$

Adsorption: adhesion of atoms, ions, or gas molecules to a surface

Reconstruction: atoms at the surface assume different structure than bulk materials

Surface energy & surface tension

- For system w/ fixed mol #

$$\Delta G = -SdT + VdP + \gamma dA$$

Surface Tension: $F = 2\sigma l$

$$\sigma = \gamma + A \left(\frac{\partial \gamma}{\partial A}\right)_{T,P}$$

- For system w/ many particles

$$\Delta G = -SdT + VdP + \chi dA + \eta_p dN$$

- In general Area is function of molecules

chemical: $M = \left(\frac{\partial \gamma}{\partial N}\right)_{T,P} = H^{(P)} + \gamma \left(\frac{\partial A}{\partial N}\right)_{T,P}$

For spherical particle

$$A = 4\pi r^2 \quad \left\{ \left(\frac{\partial A}{\partial N}\right)_{T,P} = \frac{2}{r} \right.$$

$$N = \frac{4}{3} \pi r^3 C_0 \quad \left. \left(\frac{\partial A}{\partial N}\right)_{T,P} = \frac{2}{C_0 r} \right\}$$

Vapor Pressure & chemical Potential

- $H - H_0 = kT \ln\left(\frac{P}{P_0}\right)$

Vapor Pressure of spherical particle

$$P = P^{(P)} \cdot \exp\left(-\frac{2\gamma}{kT C_0 r}\right)$$

Crystal Growth

| | |
|---|--|
| $\gamma_{\text{smooth}} < \gamma_{\text{rough}}$ | $S_{\text{smooth}} < S_{\text{rough}}$ |
| Jackson Crystal Growth Model | |
| • consider single layer of atoms on flat surface | |
| $\Delta G = -\Delta E_0 - \Delta E_1 + T\Delta S_+ - T\Delta S_c - P\Delta V$ | |
| $\Delta E_0 = \text{Energy decrease from bond formation w/ bulk}$ | |

- $\Delta E_1 = \text{Energy decrease from bonds made with other surface atoms}$
- $T\Delta S_+ = \text{Entropy decrease from Phase transition}$
- $-T\Delta S_c = \text{Entropy increase due to random arrangement of adsorbed atoms}$
- $-P\Delta V = \text{Volume decrease due to Phase transition}$

$$\Delta E_0 = nE_b \cdot Z_0 = 2nL_0 \left(\frac{Z_0}{2}\right)$$

$L_0 = \text{Internal energy released upon condense/freeze}$

$Z_0 = \# \text{ of bonds between adsorbed atom \& bulk crystal}$
 $Z = \text{total co-ordination \#}$

$$\Delta E_1 = \frac{1}{2} \frac{n}{N} \cdot n E_b \cdot Z_1 = N \theta^2 L_0 \left(1 - \frac{Z_0}{Z}\right)$$

$$\theta = n/N \quad Z = Z_1 + 2Z_0$$

$N_1 = \text{Average \# of bonds between adsorbed atoms}$

$$\Delta S_+ = \frac{nL}{T_+} \quad \begin{matrix} L = \text{total Enthalpy per atom} \\ T_+ = \text{phase transition temp} \end{matrix}$$

$$\Delta S_c = k \ln \left(\frac{N!}{n!(N-n)!} \right)$$

$$P\Delta V \rightarrow nKT \quad \text{Gas Condensation}$$

Faceted vs. Non-Faceted Growth

$$\text{Jackson Factor: } d = \frac{L_0}{kT} \cdot \frac{Z_1}{Z}$$

$d > 2$: A measure of Enthalpy \& Entropy contributions

- | | |
|-------------------------|-----------------------|
| (Faceted Growth) | (Non-Faceted) |
| • Energy Dominates | • Entropy Dominates |
| • Strong bonds | • weak chemical bonds |
| • Low Temp | • High Temperature |

2D Grain Growth

$$H_i = H_i^{(p)} + \frac{\gamma}{C_{\text{eff}}} \quad \begin{matrix} 1 \\ 2 \end{matrix} \quad H_2 = H_2^{(p)} - \frac{\gamma}{C_{\text{eff}}}$$

$r = \text{radius of GB curvature}$
 $C_{\text{eff}} = \# \text{ of Molecules}$
 $\gamma = \text{surface energy}$

2D Grain Boundary Growth

$$F = \frac{dH}{dx} = \frac{2\gamma}{r C_{\text{eff}} \cos \theta} \quad V = M' F = \frac{2\gamma D'}{r K T_0 \cos \theta}$$

Driving Force for Grain Growth is interface curvature

$$\text{Laplace Pressure} = \frac{2\gamma}{r} \quad (\sigma)$$

Driving force of Grain Boundary motion is Laplace Pressure

Scaling Behavior \& Grain Growth Kinetics

$$(1) 4 \Rightarrow 2 \quad \sigma: \frac{\sigma_2}{\sigma_1} = \frac{r_1}{r_2} = \frac{1}{2}$$

$$M_{gb} = \frac{D'}{K T_0 \cos \theta_B} \quad \begin{matrix} \text{Larger Grains} \\ \text{grow/shrink faster} \\ \text{relative to small grains} \end{matrix}$$

• Square of Grain size grows w/ time

$$\frac{dL^2}{dt} = \frac{8\gamma M_{gb}}{K} \quad \begin{matrix} \text{Ostwald \& Ritterkin} \\ \text{R} \end{matrix}$$

$$\bullet \text{Particles in Equilibrium with local solution environment}$$

$$H(a) = H^{(p)} + \frac{2\gamma}{C_{\text{eff}}} = H^{(p)} + \frac{2\gamma V}{a}$$

$V = \text{Volume occupied by one molecule}$

$$C(a) = C^{(p)} \cdot e^{\frac{2\gamma V}{kT_a}} \quad \begin{matrix} \text{Gibbs-Thomann} \\ \text{Equation} \end{matrix}$$

• Smaller particles locally equilibrate in more concentrated soln

Ostwald: Mean Field Approximation

- Particles exchange solute w/ bath of continuous uniform solution

$$\text{Growth of Particle of da/dt} = \frac{2C^{(p)} Y D V^2}{kT a} \cdot \left[\frac{1}{\langle a \rangle} - \frac{1}{a} \right]$$

$D = \text{diffusion coefficient in continuous phase}$
 $\langle a \rangle = \text{Average size of particles}$

• Particles larger than $\langle a \rangle$ will grow, all smaller will shrink

$$\text{Max Growth Rate: } a = 2 \langle a \rangle$$

$$\left(\frac{da}{dt} \right)_{\text{max}} = \frac{C^{(p)} Y D}{2C_0^2 K T \langle a \rangle^2}$$

Change in average particle size:

$$\frac{d\langle a \rangle}{dt} = \frac{C^{(p)} Y D V^2}{4 K T \langle a \rangle^2}$$

Wagner Theory

$$\langle a \rangle^3 |_{\text{initial}} - \langle a \rangle^3 |_{\text{final}} = \frac{3}{4} \cdot \frac{C^{(p)} Y D}{C_0^2 K T} \cdot t$$

- Bi-modal grain size starting profile can be used to result in large grains

Therm of phase change

$$\Delta G = \Delta G_{\text{volume}} + \Delta G_{\text{surface}}$$

For spherical particle:

$$\Delta G_v = -\Delta T \cdot \frac{\Delta H_m}{T_m} \cdot \frac{4\pi r^3}{3}$$

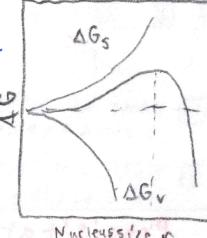
$\Delta T = \text{melting Temp}$

$\Delta T = \text{Degree of Supercooling}$

$$\Delta G_{\text{surface}} = 4\pi r^2 Y$$

Gibbs Free Energy at Nucleation

$$\Delta G = -\frac{\Delta H_m \Delta T \cdot 4\pi r^3}{T_m} + 4\pi r^2 Y$$



Critical Nucleus Size

$$r^* = \frac{2Y T_m}{\Delta H_m \Delta T}$$

Energy Barrier for Nucleation:

$$\Delta G^* = \frac{16\pi}{3} \cdot \frac{X^3 T_m^2}{\Delta H_m^2 (\Delta T)^2}$$

Density of Critical Nuclei

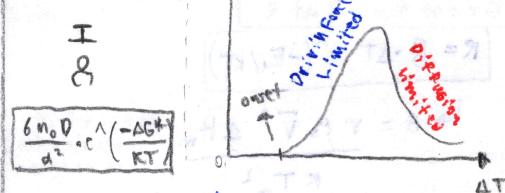
$$n_r = n_0 \cdot e^{-\left(\frac{-\Delta G}{kT}\right)}$$

$n_0 = \text{total \# of atoms}$
 $\Delta G = \text{supercooling threshold exists for Nucleation events}$

Homogenous Nucleation Rate

Nucleation Rate (I)

$$I = n_r \cdot e^{\frac{-\Delta G^*}{kT}} \cdot V_n \quad \begin{matrix} \text{Nucleation Rate} \\ I \end{matrix}$$



standard Practice

- Super cool to get Nucleation centers
- Raise temp just below T_m to get Growth

Heterogenous Nucleation

$$Y_{\text{sc}} \quad \begin{matrix} \text{cluster} \\ \theta \end{matrix} \quad Y_{\text{sc}} \quad \begin{matrix} \text{substrate} \\ \theta \end{matrix} \quad Y_{\text{sc}} = Y_{\text{sc}} + Y_{\text{sc}} \cos(\theta)$$

$$\Delta G_{\text{het}} = \left(-\frac{\Delta H_m \Delta T \cdot 4\pi r^3}{T_m} + 4\pi r^2 Y_{\text{sc}} \right) \cdot S(\theta)$$

$$S(\theta) = \frac{1}{4} (2 + \cos(\theta)) (1 - \cos(\theta))^2$$

critical nucleus size Energy Barrier for Nucleation

$$r_{\text{het}}^* = r_{\text{hom}}^* \quad \Delta G_{\text{het}}^*$$

$$\frac{2\pi r^2 Y_{\text{sc}} T_m}{3 \Delta H_m^2 (\Delta T)^2} \cdot S(\theta)$$

• Wetting on substrate reduces Energy Barrier for Nucleation

• Fast cooling & presence of secondary phase lead to smaller grain sizes

VLS nanowire Growth



- Melted gold sat urates itself w/ Si-H₄
- This silicon heterogeneously nucleates to interface

1. Done at high temp to prevent homogeneous nucleation

2. Silicon has very low gold solubility

Precipitate Growth

1. Growth from Single Component

- Faceted Precipitate (2D Nucleation) controlled

- Precipitate w/ (interface kinetic controlled) atomically rough surface

2. Growth from Binary System w/ miscibility gap (diffusion controlled)

Continuous Growth

- Plenty of surface sites for attachment
- Growth Rate determined by: atom attachment rate $\propto V_n$

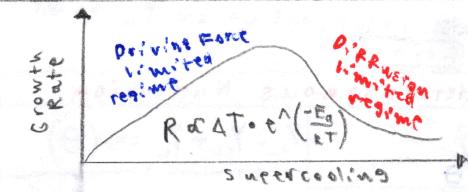
$$V_n = \frac{r \cdot \Delta G_v}{kT} e^{\frac{-E_a}{kT}} \Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

Growth Rate

$$R = B \cdot \Delta T \cdot e^{\frac{-E_a}{kT}}$$

$$\Delta B = \frac{r P_s V^2 \Delta H_m}{k T_m^2} \quad p_s = \text{surface area density of atoms}$$

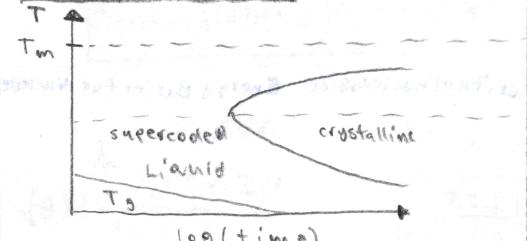
Growth Rate & TTT Diagram



NOTE: No supercooling threshold

• Both Growth & Diffusion driven by Supercooling

TTT Diagram



| Volume Gibbs Term | 2D Nucleation |
|-------------------|--|
| Surface term | $\Delta G_v = -\Delta T \cdot \frac{\Delta H_m}{T_m} \cdot \pi r^2 h$ $\Delta G_s = 2\pi r h Y$ |

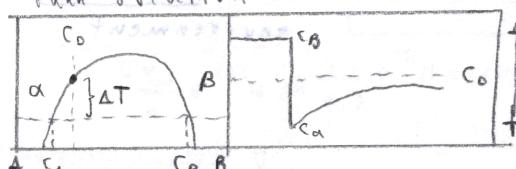
| Critical Nucleus | Energy Barrier |
|--|---|
| $r_{2D}^* = \frac{Y T_m}{\Delta H_m \Delta T}$ | $\Delta G_{2D}^* = \frac{\pi h Y^2 T_m}{\Delta H_m \Delta T}$ |

Note: 2D faceted growth has supercooling threshold

Far Screw Dislocation | $R_d (\Delta T)^2$

Growth from Binary Soln

- Precipitates have different composition than solution



$$R = \frac{1}{2} \sqrt{\frac{k D_B}{+ (C_0 - C_a)(C_B - C_a)}}$$

Note: no supercooling threshold for this method

↳ Does not apply in spinodal

Dendritic Growth

Interface Stability:

Solid A B

If $\Delta T(x_a) > \Delta T(x_b)$
stable interface
(Planar Growth)

A B

If $\Delta T(x_a) < \Delta T(x_b)$
(unstable)
(Dendritic Growth)

Bridgman-Stockbarger (Planar)

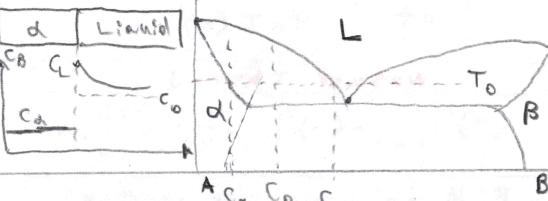


Planar interface results in Bridgman growth

Solidification of supercooled liquid



Constitutional Supercooling



$$C_B(x) = C_0 + (C_L - C_0) \cdot \exp\left(-\frac{Rx}{D}\right)$$

Growth rate determined by diffusion of solute away from interface

Stability Condition:

$$\frac{\partial T}{\partial x} > -\frac{R}{D} \cdot \frac{\partial T_L}{\partial C_B} \cdot (C_B - C_0)$$

↳ leads to supercooling zone, and dendrite due to impurity

True or False

Part 6

Nano crystals have lower melting point than bulk materials?

↳ yes, Gibbs-Thomson effect

Surface Energy & surface tension refer to same thing

↳ no, $\sigma = x + A \left(\frac{\Delta H}{kT}\right)$

Dendrites cannot form if liquid is of uniform Temp \rightarrow no, constitutional supercool

Fat is insoluble in water, can it undergo Ostwald ripening? No, solubility is a must

Dendritic growth implies surface roughness \rightarrow no, interface stability has no bearing on surface roughness

Part 5

Jackson model predicts low growth rate for 2D faceted growth No, Jackson Model is thermo exercise has no rate parameter

Vapor pressure on macro scale is same as nano scale No, Large vapor pressure product of large surface volume ratio

If phases have same chemical potential interface energy goes away No, Surface energy is a result of structure

Surface reconstruction always lowers surface energy yes, otherwise it wouldn't occur

Bubbles don't undergo Ostwald ripening No, they do

At high temp grain growth becomes limited No

Example

Reducing atomic radii increases equilibrium concentration of Schottky defect No, greater pull decreases concentration

Net vacancy flux seen in both reference frames

charge carriers balance defect reactions

Crystal Growth

- Atomically smooth vs. Rough

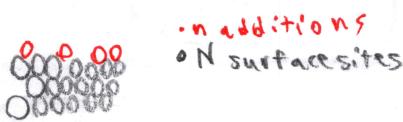
$$Y_{\text{smooth}} < Y_{\text{rough}}$$

↳ energy increases

$$\boxed{S} \quad S_{\text{smooth}} < S_{\text{rough}}$$

Jackson Crystal growth Model

- Consider single layer of atoms on flat surface



$$\Delta G = -\Delta E_0 - \Delta E_1 + TAS_+$$

$$-TAS_c - P\Delta V$$

\rightarrow $-\Delta E_0 \rightarrow$ Energy Decrease due to Bond formation with atoms in Bulk crystal

\rightarrow $-\Delta E_1 \rightarrow$ Energy Decrease from bonds made with other adsorbed atoms

$\rightarrow +T\Delta S_+ \rightarrow$ Entropy decrease from phase transition

$\rightarrow -T\Delta S_c \rightarrow$ Entropy increase due to Random Arrangement of Adsorbed atoms

$\rightarrow -P\Delta V \rightarrow$ Volume Decreases due to phase transition (for Gas Condensation)

$$\boxed{\Delta E_0} \quad \Delta E_0 = nE_b \cdot Z_0 = 2nL_0 \left(\frac{Z_0}{Z} \right)$$

$\rightarrow L_0$: Internal energy released per atom upon condensation/freezing

Z_0 : # of bonds between adsorbed atoms & crystal

Z : Total Co-ordination #

where $L_0 = \frac{1}{2} Z E_b$

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$$\boxed{\Delta E_1} = \frac{1}{2} \frac{n}{N} \cdot n E_b \cdot Z_1$$

$$= N \theta^2 L_0 \left(1 - \frac{2Z_0}{Z} \right)$$

$$\bar{\theta} = n/N$$

$Z_1 = \frac{\text{average # of bonds between adsorbed}}{\text{between adsorbed}}$

$$Z = Z_1 + 2Z_0$$

$$\boxed{\Delta S_+}$$

$$\Delta S_+ = \frac{nL}{T_+}$$

L: Enthalpy change per atom upon condensation/freezing
 T_+ : Phase Transition Temperature

$$\boxed{\Delta S_c}$$

$$= k \ln \left(\frac{N!}{n!(N-n)!} \right)$$

$$\boxed{P\Delta V}$$

$$= nKT \rightarrow$$
 for Gas Condensation

Faceted vs. Non-Faceted Growth

Jackson Factor

$$d = \frac{L_0}{kT} \cdot \frac{Z_1}{Z}$$

↳ A measure of Relative Magnitude of Enthalpy & Entropy contributions

1. Non-Faceted Growth

- $d < 2$
- Entropy Term Dominates
- Bonds are weak
- High Temperature

2. Faceted Growth

- $d > 2$
- Enthalpy Dominates
- Low Temp
- Packed Planes

2-D Grain Growth

$$\boxed{\text{Grain 1}} \qquad \qquad \boxed{\text{Grain 2}}$$

$$H_i = K_{gb} + \frac{Y}{r}$$

Flux $u - u(P) - \frac{Y}{r}$

$$F = \frac{dH}{dx} = \frac{H_1 - H_2}{dgb} = \frac{2Y}{rC_0 dgb}$$

$$v = M'F = \frac{D'}{kT} F = \frac{2Y D'}{r R + C_0 dgb}$$

$$J = v C_0 = \frac{2Y D'^2}{r k T dgb}$$

2-D Grain Growth

Driving Force of Grain Growth is Interface Curvature

Laplace Pressure (σ)

$$\sigma = \frac{\Delta G}{A \Delta X} = (H_1 - H_2) \cdot C_0 = \frac{2Y}{r}$$

$$V_{GB} = M_{gb} \sigma$$

$$M_{gb} = \frac{D'}{R T C_0 dgb}$$

* Driving Force for Grain Boundary Motion is Laplace Pressure

Scaling Behavior & Growth Kinetics

$$L_1 \left[t = t_1 \right] \Rightarrow \left[t = t_2 \right] L_2$$

Crystal Growth:

$$\sigma = \frac{2Y}{r} \Rightarrow \frac{\sigma_2}{\sigma_1} = \frac{t_1}{t_2} = \frac{L_1}{L_2} = \frac{1}{T}$$

$$V_{gb} = M_{gb} \sigma = \frac{V_{gb,2}}{V_{gb,1}} = \frac{1}{T}$$

Large grains grow or shrink slower compared to small grains

$$\frac{dL}{dt} = 2V_{gb} = \frac{4Y M_{gb}}{r} \approx \frac{4Y M_{gb}}{KL}$$

$$\frac{dL^2}{dt} \approx \frac{8Y M_{gb}}{K}$$

* Square of Grain size grows linearly w/ time

