Brief Thermodynamics Rewiew (APPWA)

Thermodynamic variables are classified as *extensive* if they scale as the volume of the system, V. Thus U, the internal energy, N, the number of particles, and S, the entropy, are extensive variables. (Here attention is restricted to a system in which there is only one kind of particle.) Variables that do not scale as the size of the system are called *intensive*. The internal energy of the system may be expressed as a function of the extensive variables [i.e., $U = U(V, N, S)$]. Thus

$$dU = \left(\frac{\partial U}{\partial V}\right)_{N,S} dV + \left(\frac{\partial U}{\partial N}\right)_{V,S} dN + \left(\frac{\partial U}{\partial S}\right)_{N,V} dS \qquad \text{(WA.1)}$$

$$= -P\,dV + \mu\,dN + T\,dS.$$

One sees by comparing the coefficients of dV, dN, and dS that P, the pressure, T, the temperature, and μ, the chemical potential, are intensive variables. Equation (WA.1) is known as the *first law of thermodynamics*. It recognizes that energy is conserved and that heat is a form of energy. The differential quantity TdS represents the heat input to a system, $P\,dV$ is the work done by the system, $-\mu\,dN$ the energy transported by particles leaving the system, and dU the increase of internal energy of the system. Since one often has control over variables other than (V, N, S) it is convenient to introduce thermodynamic potentials. The Helmholtz free energy, F, is defined as

$$F = U - TS. \qquad \text{(WA.2)}$$

Forming the differential and combining the result with Eq. (WA.1) leads to

$$dF = -P\,dV + \mu\,dN - S\,dT. \qquad \text{(WA.3)}$$

The Helmholtz free energy is useful in problems in which one controls the variables (V,N,T). If (V,N,T) are constant, $dF = 0$ at equilibrium.

The enthalpy, H, is defined by

$$H = U + PV. \qquad \text{(WA.4)}$$

Its differential leads to the formula

$$dH = T\,dS + \mu\,dN + V\,dP. \qquad \text{(WA.5)}$$

The enthalpy is used when one controls (S,N,P). If (S,N,P) are held constant, $dH = 0$ at equilibrium.

The *Gibbs free energy* is defined by

$$G = U - TS + PV = F + PV = H - TS. \qquad \text{(WA.6)}$$

Its differential results in

$$dG = \mu\,dN - S\,dT + V\,dP. \qquad \text{(WA.7)}$$

The Gibbs free energy is of use in problems where one controls (N,T,P). If (N,T,P) are held constant, $dG = 0$ at equilibrium.

From Eqs. (WA.2), (WA.4), and (WA.6), one sees that F, H, and G are all extensive variables. One may integrate Eq. (WA.1) to obtain the Euler relation

$$U = -PV + \mu N + TS, \qquad \text{(WA.8)}$$

from which it is seen that

$$G = N\mu. \qquad \text{(WA.9)}$$

The chemical potential for a one-component system is thus the Gibbs free energy per particle. From Eqs. (WA.1) and (WA.8) one obtains the *Gibbs–Duhem formula*:

$$N\,d\mu = V\,dP - S\,dT. \qquad \text{(WA.10)}$$

A number of thermodynamic relations follow from expressing Eqs. (WA.1), (WA.3), (WA.5), and (WA.7) as partial derivatives. They are

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V}, \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{N,S}, \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}, \qquad \text{(WA.11}a)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}, \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}, \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}, \qquad \text{(WA.11}b)$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{N,P}, \qquad \mu = \left(\frac{\partial H}{\partial N}\right)_{P,S}, \qquad V = \left(\frac{\partial H}{\partial P}\right)_{N,S}, \qquad \text{(WA.11}c)$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}, \qquad S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}, \qquad V = \left(\frac{\partial G}{\partial P}\right)_{N,T}. \qquad \text{(WA.11}d)$$

A pair of useful mathematical identities follow from forming the differential of a function $z(u,v)$:

$$dz = \left(\frac{\partial z}{\partial u}\right)_v du + \left(\frac{\partial z}{\partial v}\right)_u dv, \qquad \text{(WA.12)}$$

and then forming $u(z,v)$,

$$dz = \left(\frac{\partial z}{\partial u}\right)_v \left(\left(\frac{\partial u}{\partial z}\right)_v dz + \left(\frac{\partial u}{\partial v}\right)_z dv\right) + \left(\frac{\partial z}{\partial v}\right)_u dv, \qquad \text{(WA.13)}$$

Thermodynamic and Chemical Effects

Gibbs free energy: $G(N_i, T) = \sum_i N_i(T)\mu_i(T)$

Number of particles N_i
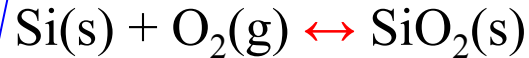Chemical potential $\mu_i = (\partial G / \partial N_i)_{T,P,Nj}$

- Reactions (materials formation), <u>free energy change</u> is:

$$\Delta G = \Delta H - T\Delta S = \Delta U + P\Delta V - T\Delta S \quad (p, T = const.)$$

or:

$$\Delta G = \Sigma G_{(products)} - \Sigma G_{(``charges")}$$

Example: $Si(s) + O_2(g) \leftrightarrow SiO_2(s)$ *sign of ΔG is important*

ΔG < 0 exhothermic   **ΔG > 0 endothermic**   **ΔG =0 equillibrium → ΔH=TΔS**

faster → (forward direction)   *faster ← (reverse direction)*   *equal rates ΣG(products) = ΣG("charges")*

_ΔG__min_ *is obtained through minimizing ΔH and/or maximizing ΔS*

Thermodynamic and Chemical Effects

- *Standard* Gibbs free energy change:

$$\Delta_r G^0(T) = \Delta_r H^0(T) - T\Delta_r S^0(T)$$

Formation of material from elemental reactants in standard states (equilibrium at 300 K and 1 atm)

equillibrium constant

$$\Delta_r G^0(T) = -RT\ln K(T) \qquad (R = 8.31 \text{ J/mole})$$

$$K(T) = \exp\left(\frac{-\Delta_r G^0}{RT}\right) = \exp\left(\frac{-\Delta_r S^0}{R}\right)\exp\left(\frac{-\Delta_r H^0}{RT}\right)$$

- Activity of a solid or a liquid:

For ideal gasses in *standard* states $a = 1$ (*at 1 atm. of pressure*).

When *not in standard state*: $a(ideal\ gas) = P(X)/1atm,$

The activity of any solid or liquid at arbitrary conditions: **$a(X) = P(X,T)/P_{eq}(X,T)$**

equillibrium p in standard state

since vapor pressures of solids are close to equllibrium, $a(X)_{solid} \sim 1$

Thermodynamic and Chemical Effects

- ***What is Gibbs free energy change in materials formation?***

  activity quotient

  $$\Delta G = \Delta_r G^0 + RTln\, \boxed{Q} = -RTlnK + RTlnQ = RTln[Q/K]$$

- For chemical reaction: $bB + cC \longleftrightarrow dD + eE$

  $$Q = \frac{a_D^d a_E^e}{a_B^b a_C^c}$$

- *Note that process is in equillibrium for $Q = K$ so $\Delta G = \Sigma G(products) - \Sigma G(\text{"charges"})$, therefore <u>K is equillibrium value of Q</u>*

  $$K(T) = \frac{\prod\limits_i P_{eq}^{m_i}[prod.](T)}{\prod\limits_i P_{eq}^{m_i}[react.](T)}$$

  For solid $\leftrightarrow$ vapor or liquid $\leftrightarrow$ vapor processes

  $$G(N_i, T) = \sum_i N_i(T)\mu_i(T)$$

- Vaporization of Si and SiO_2: $Si(s) + SiO_2(s) \longrightarrow 2SiO(g)$ will be at equillibrium if:

  $$\mu[Si(s),T] + \mu[SiO_2(g),T] = 2\mu[SiO(g),T]$$

- Equilibrium constant for this reaction is:

  $$K(T) = \frac{P_{eq}^2(SiO(g),T)}{a[Si(s),T]\,a[SiO_2(s),T]}$$

Kinetic Effects

Equilibrium constant K(t)

MATERIALS SYNHESIS

Rates and paths of thermodynamic processes are important
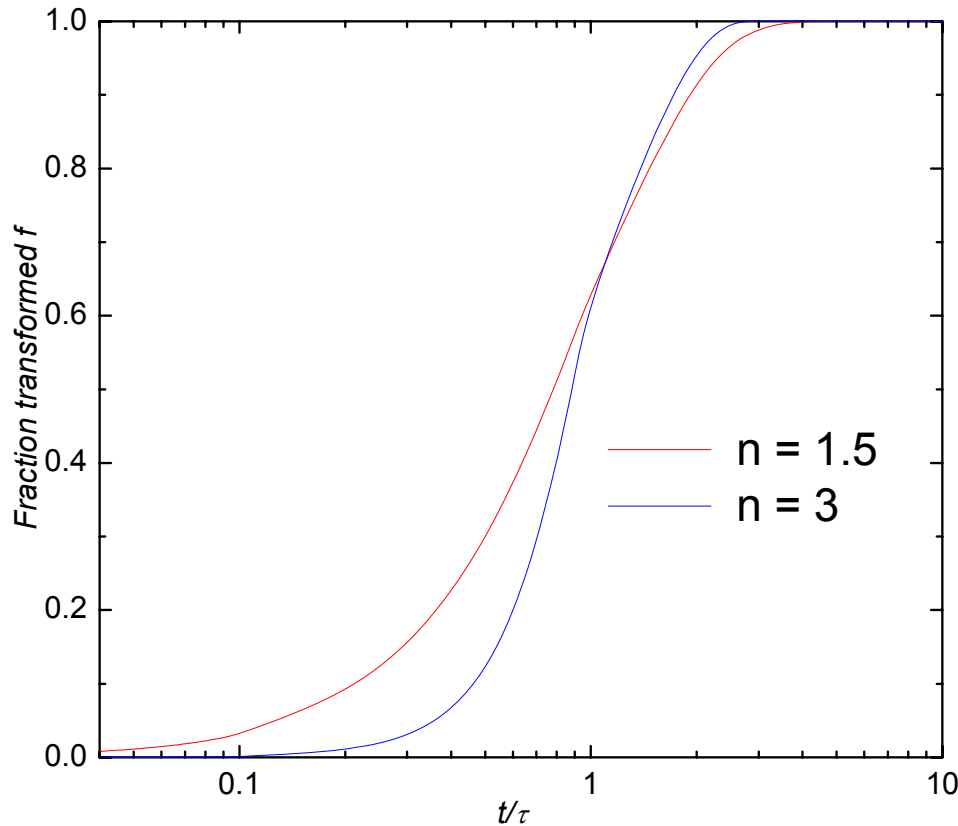
- "Higher" T, faster diffusion, lowest G can be realized more easily

Equilibrium condition for Chemical reaction: bB+cC $\longrightarrow$ dD+eE

$$k_f(T)[B(T)]_{eq}^b[C(T)]_{eq}^c = k_r(T)[D(T)]_{eq}^d[E(T)]_{eq}^e$$

$k_{f,r}$ = forward, reverse reaction rates, $[X(T)_{eq}]$ is concentration

Kinetic Effects

Nucleation and growth of the new phase is described by *Avrami equation*:

$$f(t) = 1 - e^{-(t/\tau)^n}$$

τ and n can be $\tau(T)$, $n(T)$

Time constant τ depends on density of nucleation sites

$n \sim (0.5 - 4)$

Rate of transformation:

$$R(T) = A e^{(-E_a/k_B T)} = 1/t_{0.5}$$

$t_{0.5}$ is time for 50% conversion

Kinetic Effects

- Chemical reaction: bB+cC $\longrightarrow$ dD+eE

$$K_c(t) = \frac{[D(T)]_{eq}^d [E(T)]_{eq}^e}{[B(T)]_{eq}^b [C(T)]_{eq}^c} = \frac{k_f(T)}{k_r(T)}$$

Connects thermodynamics and kinetics

- *Some processes (diffusion, vaporization) have activated reaction rates*:

$$k_f(T) = A_f e^{-\frac{E_{af}}{k_B T}} ; k_r(T) = A_r e^{-\frac{E_{ar}}{k_B T}}$$

$A_f = A_f(T),$
$A_r = A_r(T)$
$E_{af} = E_{af}(T)$
$E_{ar} = E_{ar}(T)$

- When both forward and reverse processes are activated:

$$K_c = \frac{A_f}{A_r} e^{-\frac{E_{af}-E_{ar}}{k_B T}} = e^{\frac{-\Delta_r G}{RT}} = e^{\frac{\Delta S}{R}} e^{\frac{-\Delta_r H}{RT}}$$

equilibrium constant
concentration ~ activity

.....since $\Delta_r G_0(T) = \Delta_r H_0(T) - T\Delta_r S_0(T) = -RT \ln K(T)$

Therefore enthalpy and entropy changes are:

Enthalpy changes (kinetic) effects dominant at low T
Entropy changes (thermodynamic) at high T

$$\frac{\Delta_r H(T)}{R} = \frac{E_{af} - E_{ar}}{k_B} \rightarrow \Delta_r H(T) = N_A(E_{af} - E_{ar})$$

$$\frac{\Delta_r S(T)}{R} = \ln \frac{A_f}{A_r}$$

$(N_A = R/k_B = 6.022 \cdot 10^{23} \text{mol}^{-1})$

Crystal Growth – Creation of a nucleus

- System of N atoms of the same type in V <u>in vapor</u> (can be in melt) with $n = N/V$

- *When $P_{gas} > P_{vapor}$ at T = const., droplets will begin to nucleate* (condensation)

- Vapor atom   Droplet atom

  N_V and μ_V N_D and μ_D

- Gibbs free energy change in droplet formation (σ – *surface energy*) :

(no droplet, only vapor particles)   (vapor) + (droplet, assumed spherical)

$G_i = N_V \mu_V$ $\longrightarrow$ $G_f = (N_V - N_D)\mu_V + N_D\mu_D + 4\pi\sigma r^2$

transforms to

(interface: sphere with radius r and surface energy σ)

$$\Delta G = N_D(\mu_D - \mu_V) + 4\pi\sigma r^2$$

- Introducing $N_D = 4\pi r^3/3\Omega$ it is possible to estimate: (Ω = volume of an atom in the droplet)

$$\Delta G (N_D) = -N_D\delta\mu + 4\pi\sigma[3\Omega N_D/4\pi]^{2/3} \quad (\delta\mu = \mu_V - \mu_D) \qquad \textit{Extremum values: } (\Delta G^*, N_D^*)$$

$$N_D^* = \left(\frac{32\pi}{3} \frac{\Omega^2\sigma^3}{(\delta\sigma)^3} \right) \qquad \Delta G^* = \frac{16\pi}{3} \frac{\Omega^2\sigma^3}{(\delta\mu)^2} = \frac{1}{2} N_D^* \delta\mu$$

There is some critical *size* for cluster formation

Bulk Synthesis in CMMP

Crystal Growth

- There is some critical size that a cluster of atoms must reach before it establishes itself as a nucleation site. If number of atoms in droplet is smaller, the cluster will shrink

$$\text{Critical radius } r_c = 2\sigma\Omega/\delta\mu$$

- Probability that *thermal fluctuation will nucleate a particle* of size corresponding to N_D:

$$P = A \exp [-\beta\Delta G(N_D)]$$

A = probability that N_D particles are within critical radius from each other

In crystals after nucleation atoms are adsorbed on the surface of nucleated crystallite

Crystals grow in size, but adjust their shape (facets) to lowest Gibbs free energy

If the volume is fixed, in order to minimize surface energy polyhedral facets grow

Nucleation may be homogeneous (random throughout the melt) or heterogeneous (at surfaces, particles in the melt)

Consider a crystallite:

A_i, σ_i

h_i
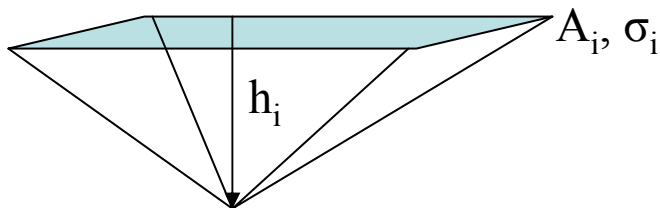
Center of the mass of polyhedron

(the higher the surface energy the more unstable the surface is)

The net surface energy is: $E_s = \Sigma\sigma_i A_i$

Volume is sum of pyramidal volumes: $V = \Sigma A_i h_i/3$

Minimizing surface energy in fixed volume:

$$\frac{\partial(E_s - \lambda V)}{\partial A_i} = 0 \Rightarrow h_i = \frac{3}{\lambda}\sigma_i$$

$\lambda = E_s/V$ (Lagrange multiplier)

Surfaces with higher σ have higher growth velocities v_i, smaller areas and are further from the center of mass

Bulk Synthesis in CMMP

Crystal Growth

- Early phase of crystal growth – crystals grow independently
- Later stages – crystallites compete for growth as the melt is depleted, smaller crystals shrink and supply atoms to larger crystals (Ostwald ripening)

- Consider two spheres with number of atoms N_1 and N_2. $N = N_1 + N_2$

- Gibbs free energy for the pair is:

$$G(N_1, N - N_1) = N\mu_D + 4\pi\sigma\left(\frac{3\Omega}{4\pi}\right)^{2/3}\left[N_1^{2/3} + \left(N - N_1\right)^{2/3}\right]$$

- $G\ (N_1, N_2)$ has maximum for $N_1 = N_2 = N/2$

- If $N_1 > N_2$ crystal 1 will grow at the expense of crystal 2 until crystal 2 disappears

- Final energy drops to: $G(N,0) = N\mu_D + 4\pi\sigma\left(\frac{3\Omega}{4\pi}\right)^{2/3} N^{2/3}$

- Example – the difference in energy between having one combined and two spheres is:

$$\Delta G = -4\pi\sigma\left(\frac{3\Omega}{4\pi}\right)^{2/3}\left[2^{1/3} - 1\right]N^{2/3}$$

Slow cooling from high T favors larger grains. Rapid cooling freezes microstructure corresponding to thermodynamic and kinetic conditions <u>at that time</u>, grain size, their number, boundaries

Bulk Synthesis in CMMP

Annealing

search for the state of lowest free energy
heating close to the melting point and slowly cooling back to room T

- At high T rates of diffusion are high, there is high mobility of atoms
- Grains of new phases may be formed in the search for lowest G
- There are two types of processes:

  a) Dislocation density decreases. Microcrystallites of new phase are formed. Driving force provided by residual elastic energy built up due to mechanical history

  b) Drive towards thermodynamical equillibrium

Assume nucleation sites are set of spheres with R_j which grow by adding layer of thickness δ and

$R_j=\delta j$, (j integer, number of layers) Γ = rate of increase in the crystallites in the sample Δ = time step Ω = sample volume
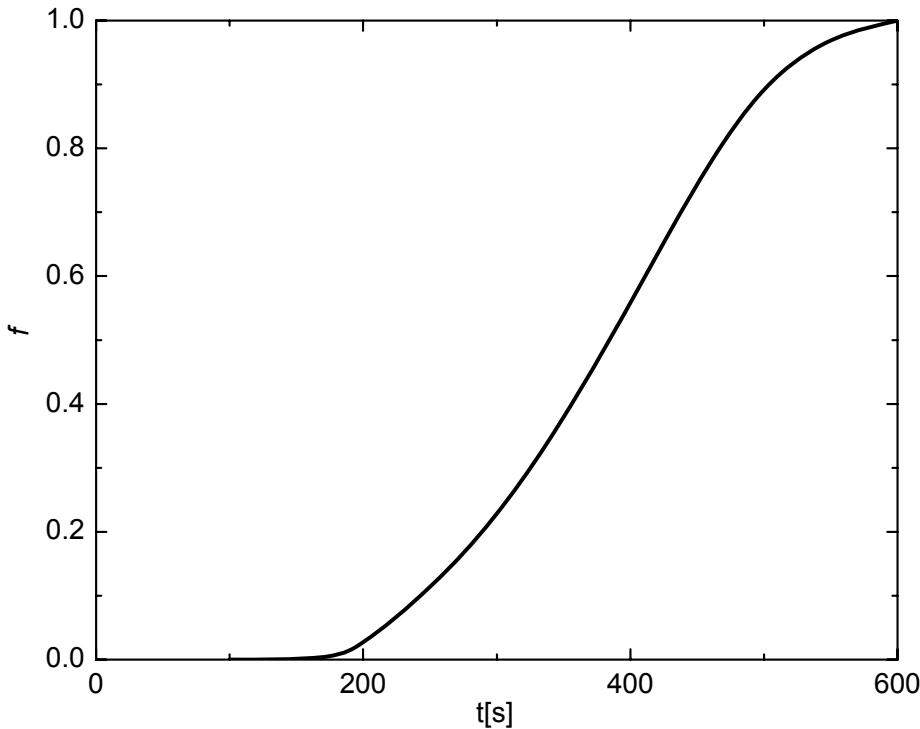
At $t = 0$ there are no crystallites $\longrightarrow$ At $t = j\Delta$ there are $N = j\Gamma\Delta$ crystallites with $R_1 \leq r \leq R_j$

Total volume occupied is: $V(t) = [4\pi/3]\Gamma\Delta\{\delta^3 + (2\delta)^3 + \ldots\ldots+ (j\delta)^3\} \sim (\pi/3)\Gamma\Delta\delta^3 j^4$ for j<<1

Since $\delta = \Delta dR/dt$, we have $V = (\pi/3)\Gamma(dR/dt)^3 t^4$ and $(dV/dt) = (4\pi/3) \Gamma[(dR/dt)t]^3$

If the volume space occupied by spherical nucleation sites is f, then $1-f$ is fraction of space not occupied and new spheres can grow only in the unoccupied space, therefore:

Annealing

$$\frac{df}{dt} = \frac{1}{\Omega}\frac{dV}{dt}(1-f) \longrightarrow f(t) = 1 - e^{-[\frac{\pi}{3}\frac{dn}{dt}(\frac{dR}{dt})^3 t^4]}$$

Johnson – Mehl equation

dn/dt number density of new crystallites nucleating per unit time.

With increase of T, *f(t)* slows down. Nucleation rate and growth rate fall since they are proportional to *supercooling* which is measured relative to T of phase transition

2. Assume system relaxing to the state of minimum surface energy by varying R.   Relaxation – set of irreversible processes, so we introduce viscous coefficient K:

1. Assume N spherical grains $V = 4\pi NR^3/3$ with surface energy $U = 4\pi NR^2\gamma$
γ: energy per unit area of the grain – liquid interface

What is surface energy minimum in fixed volume, *assuming changing number of grains – large grains swallowing smaller or grains coalescing*?

$$\left(\frac{\partial U}{\partial N}\right)_V = \frac{\partial}{\partial N}\left[4\pi N\gamma\left(\frac{3V}{4\pi N}\right)^{2/3}\right] = \frac{4\pi\gamma}{3}R^2; \frac{\partial U}{\partial R} = \frac{\partial U}{\partial N}\frac{\partial N}{\partial R} = \frac{3V\gamma}{R^2}$$

viscous coefficient

$$-K\frac{\partial R}{\partial t} - \frac{\partial U}{\partial R} = 0$$

$$\frac{\partial R}{\partial t} = \frac{3\gamma V}{KR^2}$$

$$R(t) = \left(R_0 + 9\gamma Vt/K\right)^{1/3}$$

$t^{1/3}$ growth rates can be expected for long times
For $K \rightarrow \infty$, $R \rightarrow R_0$ (radius at t=0)
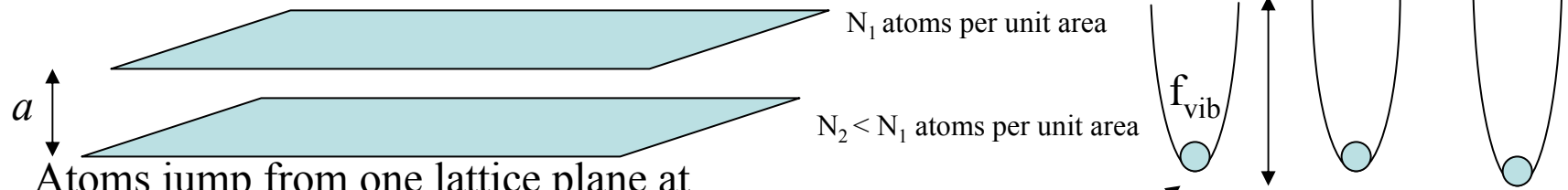
Diffusion

Thermally activated process:
Rate $R(T) = A \exp[-E_a/k_B T]$
Examples: diffusion, vaporization, vacancies and point deffects

- Diffusion - thermally activated motion which reduces concentration gradients in the solid by mass transfer (defects, interstitials, dopant atoms….). Drive towards equilibrium
- Driving force is the *increase of S* when randomness is increased and concentration gradients are minimized
- Self diffusion – for example of Si in bulk Si
- Uphill diffusion – opposite to concentration gradients - in inhomogeneous solids (eg. binary alloys) atoms move towards sites where they are more tightly bound, towards energy minimum due to gradient of chemical potential
- Vacancy mechanism of diffusion – atoms move towards neighboring vacancies
- Interstitial mechanism of diffusion – for interstitial atoms when lattice atoms and interstitial atoms exchange places
- Direct interstitial mechanism of diffusion – jump from one interstitial site to adjacent interstitial site
- Diffusion not along lattice sites but via surface, grain boundaries, dislocations – usually have higher rates at low temperatures

Diffusion

N_1 atoms per unit area

$N_2 < N_1$ atoms per unit area

f_{vib}

- Atoms jump from one lattice plane at finite T with rate:

  E_a: activation energy for the jump

  $R(T) = A \exp [-E_a/k_B T]$

  $\sim f_{vib} \exp [-E_a/k_B T]$ ⟶ f_{vib} : *atomic vibration frequency*

  R/2 of jumps are to 1st plane and R/2 to 2nd

- The net flux of atoms moving between the two adjacent planes in homogeneous solids (**Fick's laws**):

  diffusion coefficient $D(T) = a^2 R(T)/2 = a^2 f_{vib}/2 \; exp[-Ea/k_B T]$

  $J = [N_1 - N_2]R/2 = - (aR/2)(dN/dx) = (a^2 R/2)(dC/dx) = - D(dC/dx)$ **Fick's 1st law**

or:

drift velocity   mobility   chemical potential

$$\vec{J} = -D\vec{\nabla}C = C_i\vec{v}_i = -C_i\mu_i(mob)\vec{\nabla}\mu_i$$

since $N_2 = N_1 + a(dN/dx)$ and $C(x) = N(x)/a$ (concentration gradient of atoms)

If the concentration gradient (dC/dx) is not constant in time:

in 1D

$$\boxed{\frac{\partial C}{\partial t} = -\vec{\nabla} J}$$

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

Fick's 2nd law

Diffusion

Random movement of atoms from one lattice site to another – *Random walk* process

- Net flux of atoms in one dimension

$$J(x,t) = C\left(\frac{\langle X \rangle}{t}\right) - \left(\frac{\langle X^2 \rangle}{2t}\frac{\partial C}{\partial x}\right)$$

$<X>$ – average net displacement of an atom over all possible paths
$<v> = <X>/t$ - mean drift velocity of an atom

- In chemically homogeneous solid $<X>=0$, so we get Fick's 2nd law where:

$$D = \frac{\langle X^2 \rangle}{2t}$$

Einstein difusion equation

- When ions diffuse in electric field $<X>\neq0$ since they get drift velocity due to electric field E (electrical conduction): $<v>=\mu(mob)E$ so for equilibrium conditions:

$$D = \frac{k_B T}{q}\mu(mob)$$

Einstein relation

Ionic mobility

- In general it is activation process, $D(T)=D_0 \exp(-E_a/k_B T)$ or for multiple defect species:

Diffusivitiy of i-th component

$$D(T) = \sum_i D_{0i}\exp\left(-\frac{E_{ai}}{k_B T}\right) = \sum_i D_i(T)n_{di}(T)$$

Vaporization

Thermal excitation of atoms out of surface potential well into the vapor phase
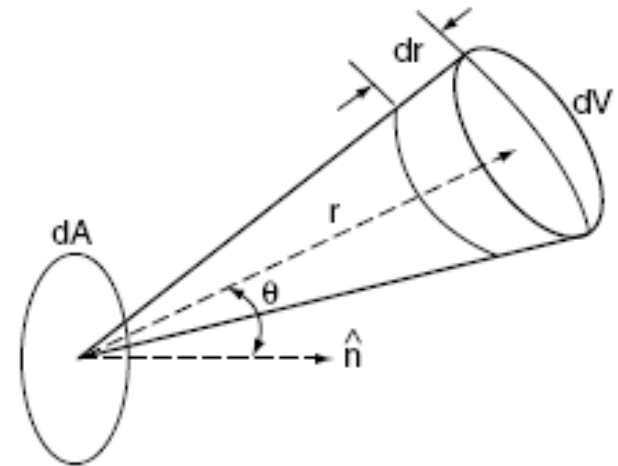Activated process, rate increases exponentially with T

- Solid – vapor equilibrium exists if

  flux of vaporized = flux of desorbed atoms:

$$J_{vap} = J_{con}$$

$$\frac{a(vapor)}{a(solid)} = K(T) = \frac{Peq}{1atm} = e^{\left(-\frac{\Delta_r G}{k_B T}\right)}$$

where $\Delta_r G = G(vapor) – G(solid)$, $K(T)$ is the equilibrium constant; $a(vapor)$ is normalized to P1atm, $a(solid) = 0$

Number of atoms in dV(gas) is $dN = ndV$ (n – atoms per unit volume)
- The volume element $dV = r^2 dr d\Omega = r^2 d\Omega vdt$ where $d\Omega$ is the solid angle surrounded by dV at dA(surface).
- The fraction f of atoms emanating from dV and striking dA is determined by solid angle $d\Omega' = dS/r^2$; dS is the projection of dA on the plane perpendicular to r, $dS = dAcos\theta$
$$df = dAcos\theta/4\pi r^2$$

Vaporization

Differential flux is therefore:

$$dF = \frac{df}{dA}\frac{dN}{dt} = \frac{nv}{4\pi}\cos\theta d\Omega$$

Integrating over angle $0 \le \theta \le \pi/2$ and using $d\Omega' = 2\pi\sin\theta d\theta$ we get net flux

$$F = \frac{n\langle v\rangle}{4}$$

From kinetic theory of gasses $\langle v\rangle = \dfrac{\int d^3v\, v e^{-\frac{\beta mv^2}{2}}}{\int d^3v\, e^{-\frac{\beta mv^2}{2}}} = \sqrt{8/\pi\beta m}$

Thus net flux is $F = P/\sqrt{2\pi mk_BT}$ since $P = nk_BT$

Therefore

$$J_{vap}(T) = \left(\frac{Peq(T)}{\sqrt{2\pi mk_BT}}\right) = \frac{1atm}{\sqrt{2\pi mk_BT}}e^{-\frac{\Delta_r G}{k_BT}} = n_s(T)f_{vib}\exp\left(-\frac{\Delta G_{des}}{k_BT}\right)$$