# Principles of Chemical Kinetics
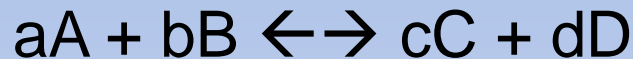
**http://eps.mcgill.ca/~courses/c220/**



slow

fast

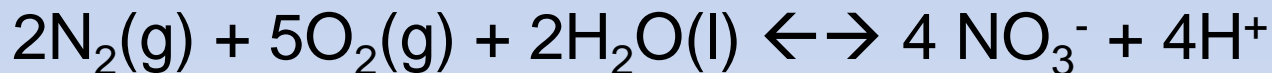very fast

# Principles of Chemical Kinetics

Thermodynamics (or the free energy of the system) tells us if the reaction is energetically feasible (or spontaneous) and in which direction it should proceed. However, …

$$aA + bB \leftrightarrow cC + dD$$

For example:

$$C_{diamond} \rightarrow C_{graphite} \qquad \Delta_{RX}G^o = -2900 \text{ J/mol}$$

Similarly,

$$2N_2(g) + 5O_2(g) + 2H_2O(l) \leftrightarrow 4\ NO_3^- + 4H^+$$

$$\Delta_{RX}G^o = 28282 \text{ J/mol and } \ln K = -\Delta_{RX}G^o /RT$$

$$K = 10^{-4.955} = a(H^+)^4\ a(NO_3^-)^4/P(N_2)^2\ P(O_2)^5$$
$$= (10^{-8})^4\ a(NO_3^-)^4/(0.78)^2\ (0.21)^5$$

$[NO_3^-]_{eq} = 7.2 \times 10^5$ M whereas the average value in the oceans is $3 \times 10^{-5}$ M

# Principles of Chemical Kinetics

What is chemical kinetics?

It is a description of the state of a reactional system as a function of time or, more precisely, of the rate of chemical changes (e.g., concentration) of the system, $d\zeta/dt$ and of the process involved.

Reactions that take place within a single phase (e.g., between molecules and ions in solution) are <span style="color:red">homogeneous reactions</span>.

Those that take place between species in two different phases (e.g., air/liquid, liquid/solid, liquid/liquid, etc.), where the reaction usually occurs at the interface of the two phases, are called <span style="color:red">heterogeneous reactions</span>.

# Rate determining step

Whether homogeneous or heterogeneous, reactions can be separated into three different steps:
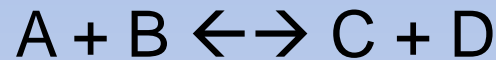
$$A + B \longleftrightarrow C + D$$

1) Transport of the reacting species towards each other or to the interface, which is generally done through diffusion:  $\rightarrow$ A    B $\leftarrow$ (transport)

2) Chemical transformation of the reacting species:  AB $\rightarrow$ CD and finally,

3) Transport or separation of the reaction products   $\leftarrow$ C D $\rightarrow$ which also generally occurs through diffusion.

The slowest step will control the rate of the reaction. Thus, two types of reactions can be distinguished in natural systems: some reactions are transport- or diffusion-controlled whereas others are purely chemically-controlled.

# Chemically-controlled reactions

The chemical transformation process may be composed of only one elementary step, but more often, it is complex and composed of a suite/sequence of simple reactions or elementary reactions. For example, let us consider the following overall reaction:

$$Hg^{2+} + 3Cl^- \longleftrightarrow HgCl_3^-$$
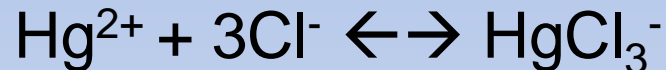
As written, this reaction would require the simultaneous encounter or collision of four separate ions. The probability of the simultaneous encounter and reaction among four separate ions is very low. It is more reasonable to imagine that the reaction takes place as a stepwise formation of complexes with increasing chloride coordination such as:

$$Hg^{2+} + Cl^- \longleftrightarrow HgCl^+$$
$$HgCl^+ + Cl^- \longleftrightarrow HgCl_2^o$$
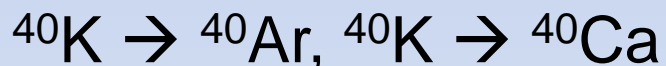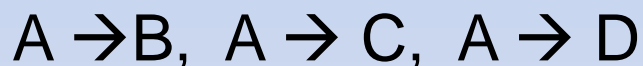$$HgCl_2^o + Cl^- \longleftrightarrow HgCl_3^-$$
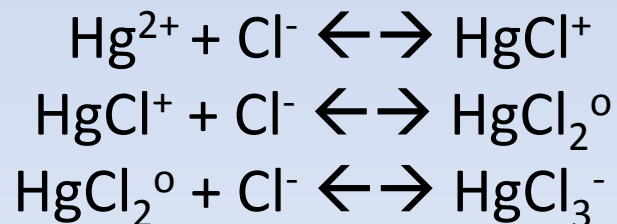
# Consecutive and concurrent reactions

The mechanism of an overall chemical reaction in solution will most often include a combination of simple unimolecular or bimolecular (rarely termolecular) steps taking place:
in series (consecutive reactions)

$A \rightarrow B \rightarrow C$

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$

$^{238}U \rightarrow ^{234}Th \rightarrow ^{230}Ra$

or in parallel (concurrent reactions)

$A \rightarrow B, \; A \rightarrow C, \; A \rightarrow D$

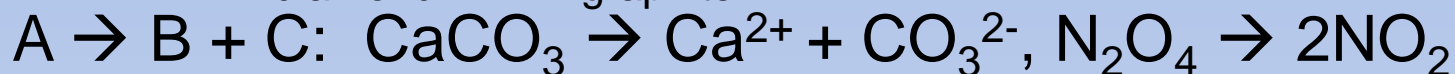$^{40}K \rightarrow ^{40}Ar, \; ^{40}K \rightarrow ^{40}Ca$

Each step may be reversible (i.e., appreciable rate in the forward and reverse directions) or irreversible. The slowest step in a sequence of elementary steps is rate-controlling for that sequence and determines the overall rate of that sequence.
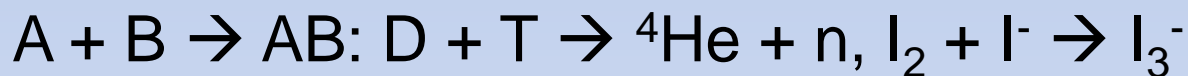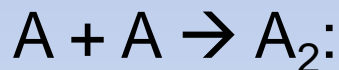
# Molecularity of a reaction

The **molecularity** of a reaction is defined as the number of molecules of reactant participating in a simple reaction constituting an elementary step.
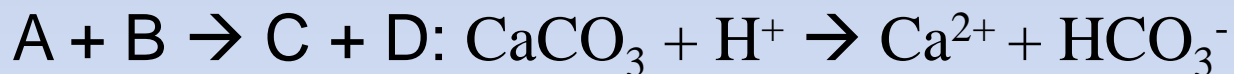
For example, **unimolecular** reactions involve a single molecule:

$A \rightarrow B$: $C_{diamond} \rightarrow C_{graphite}$, $^{14}C \rightarrow ^{14}N$, or

$A \rightarrow B + C$: $CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$, $N_2O_4 \rightarrow 2NO_2$

In **bimolecular reactions**, two identical or different species combine to give a product or products such as:

$A + A \rightarrow A_2$:

$A + B \rightarrow AB$: $D + T \rightarrow ^4He + n$, $I_2 + I^- \rightarrow I_3^-$

They are also called association reactions.

$A + B \rightarrow C + D$: $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$
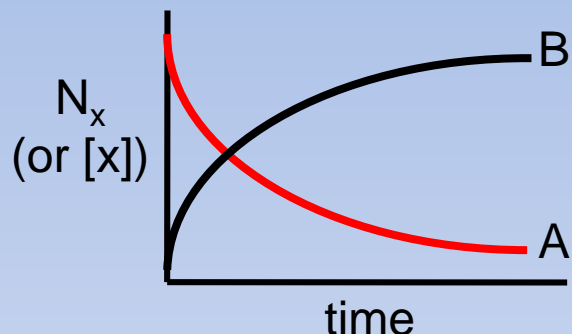
$A + A \rightarrow E + F$

They are also called exchange reactions.

**Termolecular reactions** are unusual because they require that the three species encounter/collide at the same time to yield the products.

$A + B + C \rightarrow X + ...$

# Rate Expressions for Elementary Reactions

The temporal evolution of the reaction: A → B can be represented graphically in the following manner:



where Nx = number of moles in the system. If the volume of the system is constant, then Nx can be replaced by concentration, [x].

The average reaction rate between $t_1$ and $t_2$ will be given by:

$$R_m = ([x]_2 - [x]_1)/(t_2 - t_1)$$

so that $R_m$ will always be positive, we will write:

$$R_m = -\Delta[x]_r / \Delta t = \Delta[x]_p / \Delta t = -\Delta[A] / \Delta t = \Delta[B] / \Delta t$$

In fact, what we really want to determine is the value of the rate at each point or time t, which is given by the slope of the tangent to the curve at a given point.

$$R = -d[A]/dt = d[B]/dt$$

# Polymolecular reactions

When the stoichiometry of the reactants and products are different, such as in the following reaction:

$$2A + B \rightarrow 2N$$



Then $R_B = 1/2\ R_A \rightarrow$     $-d[B]/dt = -d[A]/2dt$
and  $R_A = R_N$      $\rightarrow$     $-d[A]/dt = d[N]/dt$

the rate of the overall reaction can be described as:
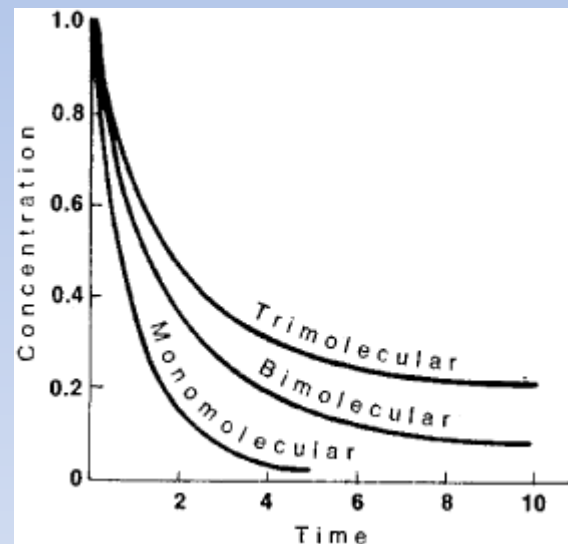
$R = -d[B]/dt = -1/2\ d[A]/dt = 1/2\ d[N]/dt$

As a general rule, for a reaction of the type:
$aA + bB + ...\ \rightarrow nN + mM + ...$
the reaction rate will be defined as:
$R = -1/a\ d[A]/dt = -1/b\ d[B]/dt = 1/n\ d[N]/dt = 1/m\ d[M]/dt$
where the letters in lowercase correspond to the **molecularity**.

At a constant temperature, the rate of a reaction is related to the concentration (probablility of encounter) of the reactants so that for:
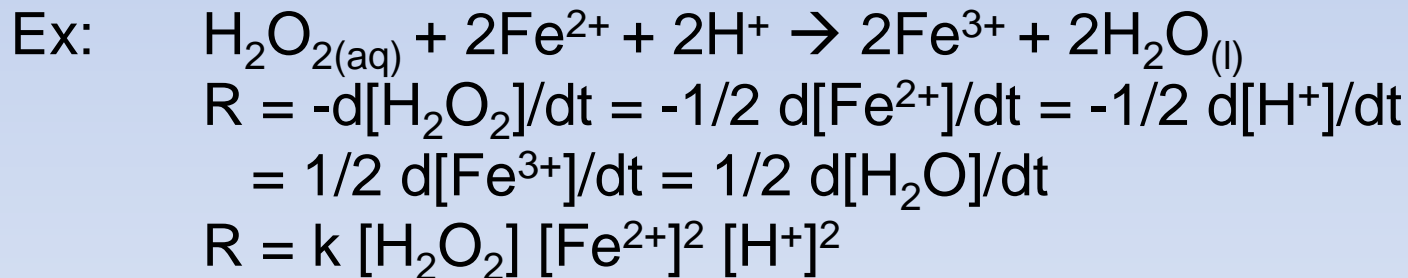
$$aA + bB + ... \rightarrow nN + mM + ...$$

$$R = -1/a \; d[A]/dt = 1/n \; d[N]/dt = k \; [A]^{\alpha} \; [B]^{\beta} \; ... = k \; \Pi \; [C_i]^{\gamma i}$$

where k = the rate constant that is characteristic of the reaction at a given temperature whereas $\alpha$ and $\beta$ are the partial orders of the reaction with respect to each reactant.

For an elementary reaction, the reaction order is also equal to the molecularity of the reaction, $\alpha = a$ and $\beta = b$ which does not hold true for complex reactions such as most reactions occurring at interfaces.
The overall reaction order is equal to the sum of the partial orders, $n = \alpha + \beta + ...$

Ex: $\quad H_2O_{2(aq)} + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O_{(l)}$
$\quad R = -d[H_2O_2]/dt = -1/2 \; d[Fe^{2+}]/dt = -1/2 \; d[H^+]/dt$
$\quad\quad = 1/2 \; d[Fe^{3+}]/dt = 1/2 \; d[H_2O]/dt$
$\quad R = k \; [H_2O_2] \; [Fe^{2+}]^2 \; [H^+]^2$

but experimental investigations have shown (as one could have guessed given the molecularity of the reaction) that it is not an elementary reaction. In fact, the order of the reaction can only be determined experimentally.

$$R = -d[H_2O_2]/dt = k \; [H_2O_2] \; [Fe^{2+}]$$

# Rate constants and kinetic expressions of simple reactions

For a monomolecular elementary reaction: A → B, the reaction rate is given by the differential equation:

$R = -d[A]/dt = d[B]/dt = k[A]$

where k is the first-order rate constant and has units of $sec^{-1}$ (or more generally $t^{-1}$) if the rate is expressed as M $sec^{-1}$

For the bimolecular reaction: A + B → product, the rate of change of [A] is given by:

$R = -d[A]/dt = -d[B]/dt = k\,[A]\,[B]$

$n = 2$, $\alpha = 1$ with respect to [A] and $\beta = 1$ with respect to [B]
and k is a second-order rate constant with units $M^{-1}\ sec^{-1}$ if the rate is still expressed as M $sec^{-1}$

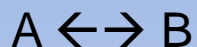For the bimolecular reaction: A + A → product, the corresponding rate equation is:

$R = -d[A]/dt = k\,[A]^2$

in which case, the rate of disappearance of A is second-order w/r to [A]

# Rate constants and kinetic expressions of complex reactions

***Reversible or opposite reactions***

A $\leftarrow\rightarrow$ B

represent a combination of two elementary unimolecular reactions. The rate expression of this reaction at constant T is:

$R = -d[A]/dt = k_1[A] - k_{-1}[B] = d[B]/dt$

at equilibrium in a closed system, at a macroscopic level:

$R = -d[A]/dt = d[B]/dt = 0$ $\rightarrow$ $[B]/[A] = k_1/k_{-1}$

The equilibrium constant for this reaction is also equal to [B]/[A] and therefore $K = k_1/k_{-1}$, the ratio of the rate constants for opposing elementary reactions is equal to the equilibrium constant ...

For opposing elementary bimolecular reactions such as:

A + B $\leftarrow\rightarrow$ C + D

the rate expression is described by:

$R = -d[A]/dt = -d[B]/dt = k_1[A][B] - k_{-1}[C][D]$

At equilibrium,
$R = d[A]/dt = d[B]/dt = d[C]/dt = d[D]/dt = 0$ and $k_1/k_{-1} = ([C][D])/([A][B]) = K$
(Ex: $O_3 \leftarrow\rightarrow O_2 + O$)

# Rate constants and kinetic expressions of complex reactions

## *Consecutive opposing reactions*

Consider a sequence of opposing elementary reactions

$A + B \longleftrightarrow C$ and $C \longleftrightarrow D$

At equilibrium, each elementary reaction and the reverse reaction must occur at the same rate. This requirement is known as **the principle of microscopic reversibility**. Consequently,

$-d[A]/dt = d[C]/dt = k_1[A]\,[B] - k_{-1}[C] = 0$,

And therefore $[C]/([A][B]) = k_1/k_{-1}$ and $d[D]/dt = k_2[C] - k_{-2}[D] = 0$
leading to $[D]/[C] = k_2/k_{-2} = K_2$ so that $[D]/([A][B]) = K_{12} = (k_1 k_2)/(k_{-1} k_{-2})$

In general, the principle of microscopic reversibility leads to the following expression:

$K_{1n} = \Pi\,(k_i/k_{-i})$ for n consecutive opposing elementary processes.

# Rate constants and kinetic expressions of complex reactions

## *Consecutive irreversible reactions*

A sequence of elementary unimolecular reactions such as:

A→ B → C

is described kinetically by:
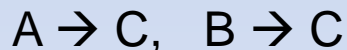
$-d[A]/dt = k_1[A]$, $d[B]/dt = k_1[A] - k_2[B]$ and $d[C]/dt = k_2[B]$

## *Concurrent or parallel reactions*

A simple case is a mechanism in which a single reactant gives different products.

A → B,   A → C,   A → D

for which the rate equation is: $-d[A]/dt = (k_1 + k_2 + k_3)[A]$

Another simple combination of unimolecular reactions involves different reactants to yield a single product:

A → C,   B → C

for which $-d[A]/dt = k_1[A]$, $-d[B]/dt = k_2[B]$
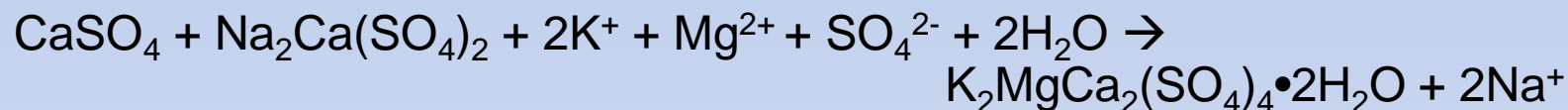and $d[C]/dt = -d[A]/dt - d[B]/dt = k_1[A] + k_2[B]$

Unlike consecutive reactions for which the slowest reaction is the rate determining step, in the case of parallel reactions, the fastest reaction determines the overall rate of the reaction.

# Rate constants and kinetic expressions of complex reactions

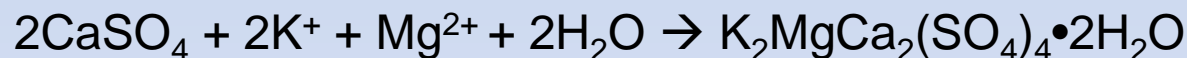A combination of concurrent bimolecular and unimolecular steps to form a common product:

A + B $\rightarrow$ C,  A $\rightarrow$ C

yields the rate equation: $d[C]/dt = k_1[A][B] + k_2[A]$

$CaSO_4 + Na_2Ca(SO_4)_2 + 2K^+ + Mg^{2+} + SO_4^{2-} + 2H_2O \rightarrow$
$$K_2MgCa_2(SO_4)_4 \cdot 2H_2O + 2Na^+$$

anhydrite + glauberite $\rightarrow$ polyhalite
(in the sequence of precipitation during the evaporation of seawater)

$2CaSO_4 + 2K^+ + Mg^{2+} + 2H_2O \rightarrow K_2MgCa_2(SO_4)_4 \cdot 2H_2O$

# Rate constants and kinetic expressions of complex reactions

There are essentially unlimited combinations of elementary reactions to yield complex mechanisms for overall reactions.

The case of opposing reactions followed by one irreversible reaction represents a mechanism encountered frequently in overall reactions:

A $\leftrightarrow$ B and B $\rightarrow$ C
$O_3$ $\leftrightarrow$ $O_2$ + O and O + $O_3$ $\rightarrow$ $2O_2$

If the opposing reactions are rapid and the second reaction is slow, a simple result is obtained by the approximation that d[B]/dt ~ 0 (near equilibrium).
This approximation is known as the **stationary-state assumption**, then:
$d[B]/dt = k_1[A] - k_{-1}[B] - k_2[B] = 0$ and $[B] = k_1[A]/(k_{-1} + k_2)$,
the rate equation becomes:
$d[C]/dt = k_2[B] = k_2 k_1[A]/(k_{-1} + k_2)$
as $k_{-1} >> k_2$ (initial assumption), $d[C]/dt = k_2 k_1[A]/k_{-1} = K_1 k_2[A]$
where $K_1 = k_1/k_{-1}$ for the equilibrium between A and B (**microscopic reversibility**)

# Rate constants and kinetic expressions of complex reactions

If a reaction is a single elementary reaction, the form of the rate expression observed experimentally will be precisely that expected from the stoichiometry of the elementary reaction

ex: $H_2CO_3 + H_2O \leftrightarrow HCO_{3^-} + H_3O^+$
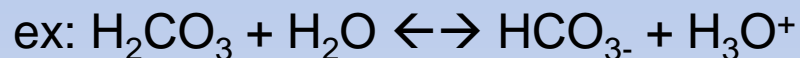
Although a number of important aqueous reactions, such as dissociations, hydrations, substitutions, and ion-pair formation reactions consist of single-step mechanisms, the bulk of solution (homogeneous) and heterogeneous reactions take place by complex mechanisms, and the overall stoichiometry of the reaction often has no relationship with the form of the observed rate equation.

# Integration of kinetic expressions

In a few cases, it is possible to integrate the rate equations to determine the exact concentration gradient with time.

Starting with the simplest case of a unimolecular irreversible reaction such as:

$$A \rightarrow B + ... \text{ where } -d[A]/dt = k[A]$$
$$(\text{radioactive decay, } {}^{14}C \rightarrow {}^{14}N + \acute{e})$$
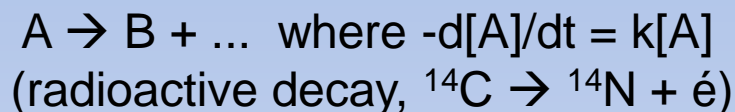
Separating the variables, we obtain: $-d[A]/[A] = kdt$

and integrating between concentrations of [A] to 0 in a time interval of o to $\infty$

$$\int_{[A]}^{o} -d[A]/[A] = \int_{0}^{\infty} kdt ,$$

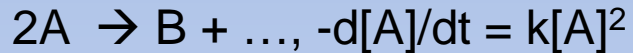we get: $-\ln [A] = kt + \text{constant}$

since $[A] = [A]_o$ at t=0
then the constant $= -\ln [A]_o$ and $\ln [A]_o/[A] = kt$ or $[A] = [A]_o e^{-kt}$

The half-time of this reaction, $t_{1/2}$, which corresponds to the time after which the concentration of the reactant is equal to half its initial value is given by:

$\ln [A]_o/([A]_o/2) = \ln 2 = kt_{1/2}$ or $t_{1/2} = \ln 2/k$

# Integration of kinetic expressions

For second-order reactions such as:

2A → B + …, -d[A]/dt = k[A]$^2$

Integrating after separating the variables, $\int_{[A]}^{0}$ -d[A]/[A]$^2$ = $\int_{0}^{\infty}$ kdt ,

we get: 1/[A] = kt + constant

since [A] = [A]$_0$ at t = 0, constant = 1/[A]$_0$

then 1/[A] – 1/[A]$_0$ = kt or ([A]$_0$ – [A])/([A][A]$_0$) = kt

The half-life for this reaction is given by:
$t_{1/2}$ = 1/k ([A]$_0$ – 0.5[A]$_0$)/(0.5[A]$_0$[A]$_0$) = 1/k (0.5[A]$_0$/(0.5[A]$_0^2$) = 1/(k[A]$_0$)

The half-life is inversely proportional to the initial concentration of the reactant.

# Pseudo-order or zeroeth-order reactions

If certain species concentrations, $[X_i]$, are kept constant over the course of the reaction, the factors $[X_i]^{\upsilon i}$ that would normally appear in the rate expression are constant and become incorporated in the rate constant.

For a process such as:

A → P where the rate law is $-d[A]/dt = k$

in which case $[A]_0 - [A] = kt$

The rate is constant and the half-life of the reaction is $t_{1/2} = [A]_0/(2k)$
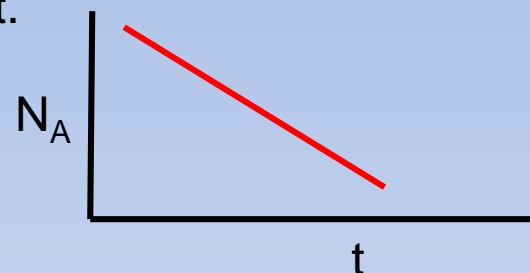


This reaction is zeroeth-order in the concentration of the reactant. In other words, the reaction rate is independent of that reactant. Often the case of heterogeneous reactions on the surface of a solid.

The rate constant may include one or many concentration terms if the concentration of the reactants is constant over the course of the reaction. These are called pseudo-order reactions.

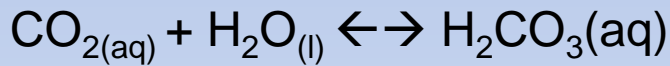# Pseudo-order or zeroeth-order reactions

The rate law for the reaction: $A + 2B + C \rightarrow P$

would normally be written: $-d[A]/dt = k\,[A]\,[B]^2\,[C]$

If the concentrations $[B]$ and $[C]$ remain constant (through being in great excess or replenished by other reactions), the apparent rate law would reduce to:
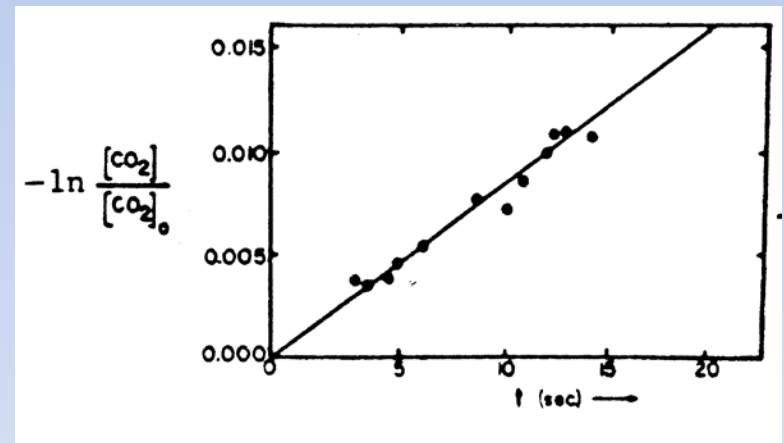
$-d[A]/dt = k'\,[A]$  where $k' = [B]^2\,[C]$

and the reaction is pseudo first-order with respect to $[A]$

$CO_{2(aq)} + H_2O_{(l)} \leftarrow\rightarrow H_2CO_3(aq)$

This reaction is rather sluggish compared to the almost instantaneous dissociation of $H_2CO_3$ to $HCO_3^-$ and $CO_3^{2-}$

$-d[CO_2]_{(aq)}/dt = k\,[CO_2]_{(aq)}\,[H_2O] = k'\,[CO_2]_{(aq)}$



The reaction follows a first-order rate law w/r to $[CO_2]_{(aq)}$ since in most natural systems $[H_2O]$ is more or less constant and not affected by the reaction.

The rate constant $k' = 2.0 \times 10^{-3}$ sec$^{-1}$ at 0°C which makes the half-life of the reaction ~ 6 minutes.
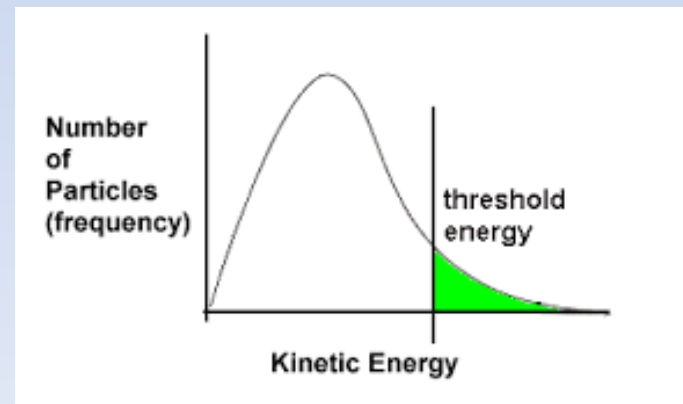
# Influence of temperature on the reaction rate

In the majority of cases, the rate of chemical reactions increases with the temperature. Arrhenius (1889) proposed that the rate constant of a reaction is exponentially related to temperature, such that:
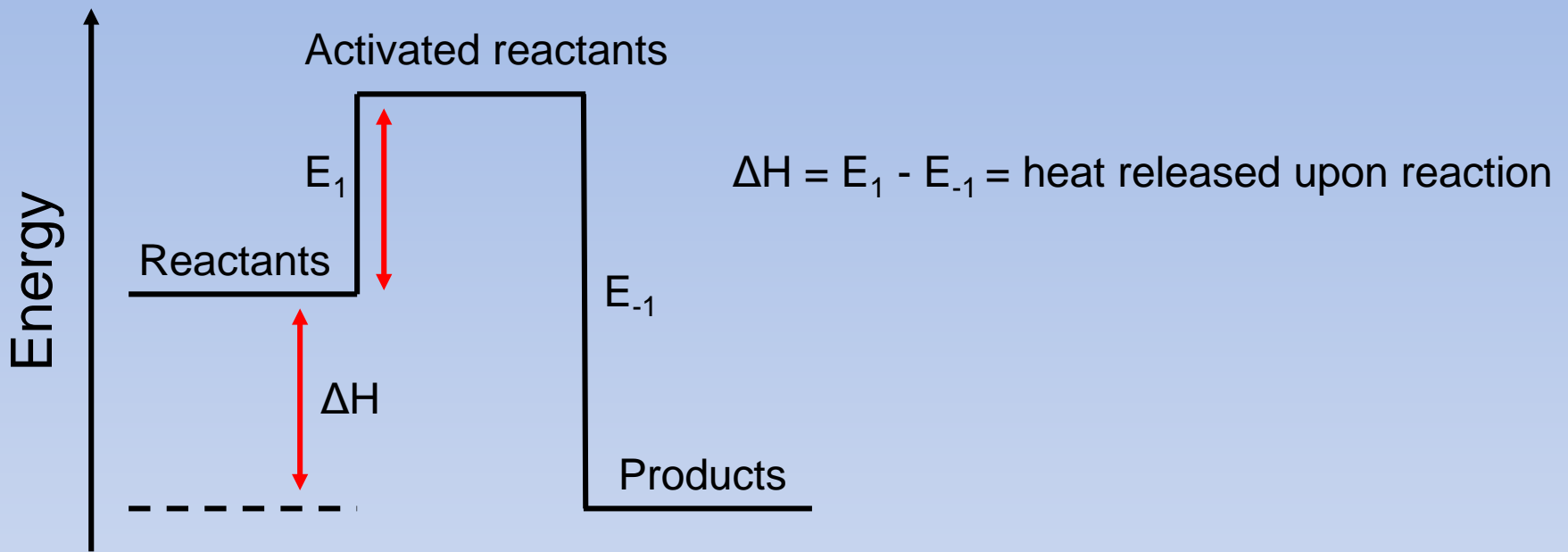
$$k = A\, e^{-\beta/RT}$$

where A and $\beta$ are constants for a given reaction. This relationship applies to all elementary reactions for which the reaction rate can be expressed by: $R = k\, \pi\, [X_i]^{n_i}$

A is a frequency factor and represents the probablility that the molecules of reactants will encounter (collide) each other (in the proper orientation)
$\beta$ is the activation energy of the reaction or the energy necessary to bring the molecules of reactants to a high enough energy state following a collision so they can react with each other. In other words, the expression is the probablility that molecules of reactants will acquire the energy necessary for them to react following an appropriate collision.
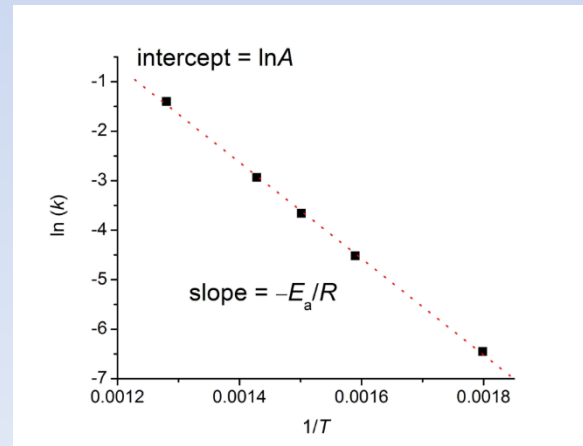
# Influence of temperature on the reaction rate

Energy

Activated reactants

$E_1$

Reactants

$E_{-1}$

$\Delta H$

Products

$\Delta H = E_1 - E_{-1}$ = heat released upon reaction

If the reaction is reversible $k_1 = A_1 e^{-E_1/RT}$ and $k_{-1} = A_{-1} e^{-E_{-1}/RT}$.

$-E_a/RT$ can be obtained from the slope of ln k vs 1/T since ln k = ln A $-$ $E_a/R$ (1/T)



intercept = ln$A$

ln ($k$)

slope = $-E_a/R$

1/$T$

# Nucleation and crystal growth

The overall process of mineral precipitation from a supersaturated solution (or a cooling melt) can be divided into a number of steps
→ nucleation and growth

The interaction between ions or molecules in solution lead to the formation of a cluster

$$X + X \rightarrow X_2$$
$$X_2 + X \rightarrow X_3$$
$$\ldots$$
$$X_{j-1} + X \rightarrow X_j \ \text{(cluster)}$$
$$X_j + X \rightarrow X_{j+1} \ \text{(nucleus)}$$



and eventually to a nucleus from which spontaneous growth can occur. The nucleation process determines the size and the size distribution of crystals produced. Subsequently, material is deposited on these nuclei and the crystal grows.



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# Nucleation and crystal growth

Nucleation will only occur when a certain degree of supersaturation is attained since an activation energy barrier must be crossed before crystal growth can occur. The free energy of formation of a nucleus, $\Delta G_T$, consists of energy gained from making bonds between ions/molecules and the work required to create a surface:

$$\Delta G_T = \Delta G_{bulk} + \Delta G_{interf}$$

where $\Delta G_{bulk}$ is the free energy of the crystal and $\Delta G_{interf}$ is the interfacial free energy. For the crystal to grow, the change in free energy gained through the formation of the mineral must exceed the interfacial energy, otherwise the nucleus is unstable and will be disrupted by molecular motion before it can grow to a stable size.

Supersaturation is the driving force for crystal growth and, within limits, the greater the supersaturation state, the faster the growth rate. Therefore, there is a degree of supersaturation at which there is a greater probability of crystal nuclei to grow than being disrupted.

$$\Delta G_{bulk} = -n\, kT \ln (IAP/K_{sp}) = -n\, kT \ln \Omega = -(4\pi\, r^3)/(3v)\, kt \ln \Omega = -(4\pi\, r^3)/(3v)\, \Delta G_V$$

where n = number of molecules or ions in the nucleus, k is Boltzman's constant, $(IAP/K_{sp}) = \Omega$ = degree of saturation, and $\Delta G_V$ is the free energy change per unit volume of crystal.

# Nucleation and crystal growth

$$\Delta G_{interf} = A\sigma$$

where $\sigma$ = interfacial energy, $A$ = surface area = $4\pi r^2$ for a spherical nucleus. Hence, the free energy of the nucleus formation can be written as:

$$\Delta G_T = 4\pi r^2 \sigma + (4\pi r^3)/3\, \Delta G_V = 4\pi r^2 \sigma + n\, kT \ln \Omega$$

The equation shows that for small values of r (small # molecules or ions) and a fixed degree of saturation, that the free energy change increases with an increase in n (or j) until some critical radius ($r_{crit}$) or cluster size ($j_{crit}$) is reached, after which the change in free energy decreases with further increase in r or j. Once nuclei of critical size are formed, crystallization can occur spontaneously.

The point of maximum free energy is a state of equilibrium (metastable) where the solution of a given $\Omega$ can be considered just saturated w/r to crystals of the size of the critical nucleus.
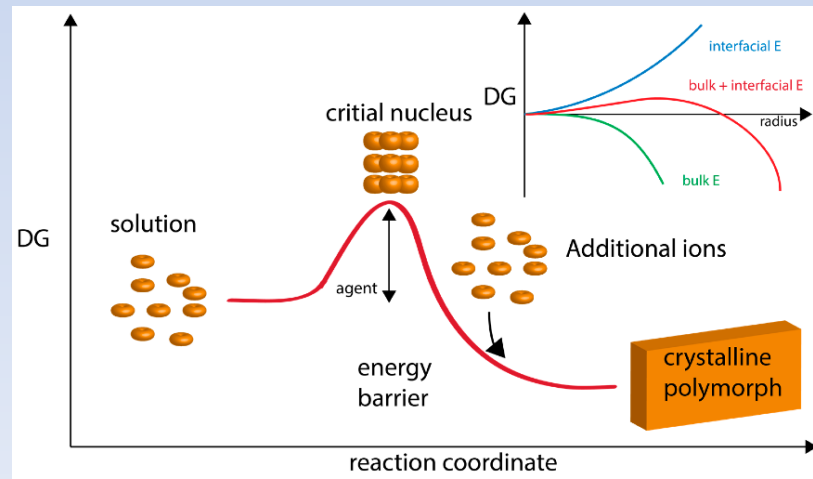
# Metastability and particle size

Finely grained particles have a greater solubility than large crystals. As a consequence, small crystals are thermodynamically less stable and should recrystallize into larger ones (Ostwald's Ripening). The increase in the free energy of the small particles results from their large interfacial energy.

The change in the free energy $\Delta G$ involved in subdividing a coarse solid suspended in an aqueous solution into a finely divided one of molar surface $S$ is given by:

$$\Delta G = 2/3\ \sigma\ S$$

where $\sigma$ is the mean free surface energy (interfacial tension) of the solid-liquid interface. Consequently,

$$(d\ln K_{sp}/dS)_T = 2\ \sigma\ /RT \quad \text{or} \quad \log K_{sp(S)} = \log K_{sp(S=0)} + 2/3\ \sigma\ S/(2.3RT)$$
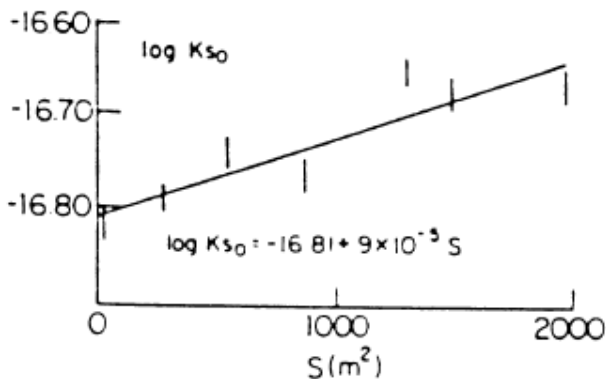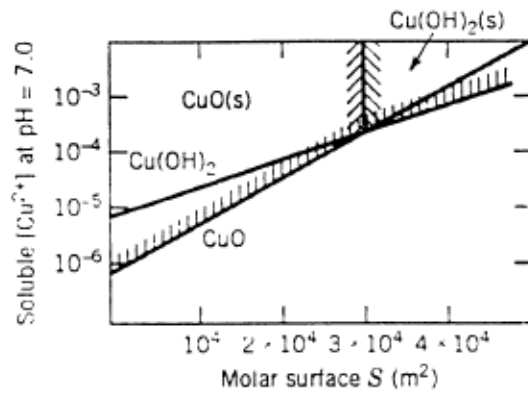


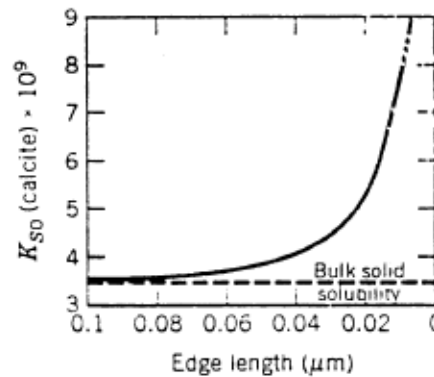Figure 7.23. Effect of molar surface on solubility product of ZnO (25°C, $I = 0$). (From Schindler. 1967.)

# Metastability and particle size
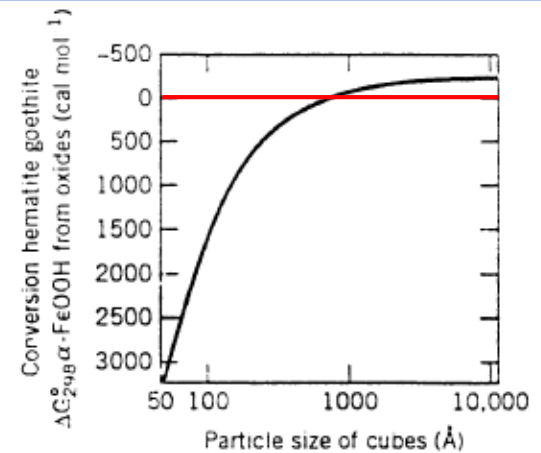


$$CuO: \quad \log {}^*K_{s0} = 7.89 + 8 \times 10^{-5}S$$

$$\sigma = 690 \pm 150 \times 10^{-7} \text{ J cm}^{-2}$$

Figure 7.24. (a) Influence of molar surface on solubility of CuO and of Cu(OH)₂ at pH = 7.0. [From data on solubility constants and surface tensions by Schindler (1967). The relations depicted have been validated experimentally only for $S < 10^4$ m².] The figure suggests that Cu(OH)₂(s) becomes more stable than CuO(s) for very finely divided CuO crystals ($S > 3 \times 10^4$ m², $d < 40$ Å). Plausibly, in precipitating Cu(II), Cu(OH)₂(s) may be precipitated ($d$ = very small), but CuO(s) becomes more stable than Cu(OH)₂ upon growth of the crystals, and an inversion of Cu(OH)₂ into the more stable phase becomes possible. (b) Change in calcite solubility with particle size, assuming cubic shape and $\bar{\gamma} = 85$ mJ m⁻². (From Morse and Mackenzie, 1990.) (c) $\Delta G°$ for the reaction $\frac{1}{2}\alpha$-Fe₂O₃ + $\frac{1}{2}$H₂O = $\alpha$-FeOOH is plotted as a function of particle size assuming equal particle size for goethite and hematite. For equal-sized hematite and goethite crystals, goethite is more stable than hematite when the particle size exceeds 760 Å but less stable than hematite at smaller particle sizes. (From Langmuir and Whittemore, 1971.)

# Nucleation and crystal growth

Theoretically, at a high supersaturation, the nucleation rate is so high that the precipitate formed consists mostly of extremely fine crystallites and, if the nucleus is smaller that one unit cell, the growing crystallite is most likely amorphous (gel-like).

In most cases, however, nucleation results in a rapid decrease in the saturation state and growth on the initially formed crystals → **homogeneous nucleation**.
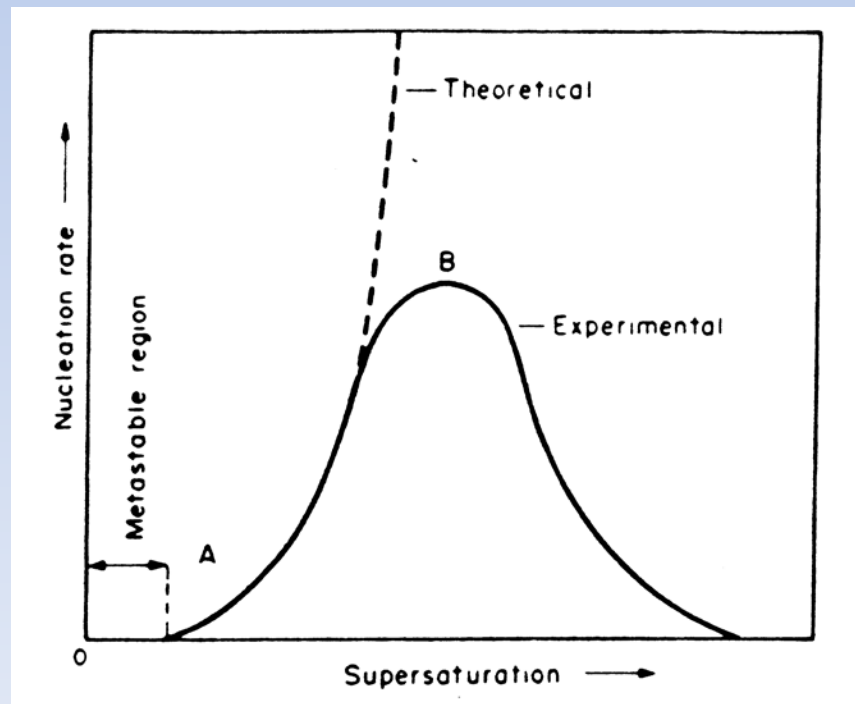
# Nucleation and crystal growth

**Heterogeneous nucleation**, however, is the predominant process by which crystals form in natural waters. It occurs when the presence of foreign solids (e.g., dust, seed, other mineral crystallites) catalyze the nucleation process by reducing the energy barrier .

If the surface of the foreign nucleus matches well (e.g., lattice type, atomic distances) with the supersaturated mineral, the interfacial energy between the two solids, $\sigma_Z$, is smaller than the interfacial energy between the mineral and the solution, $\sigma$, nucleation and growth will occur at lower supersaturations
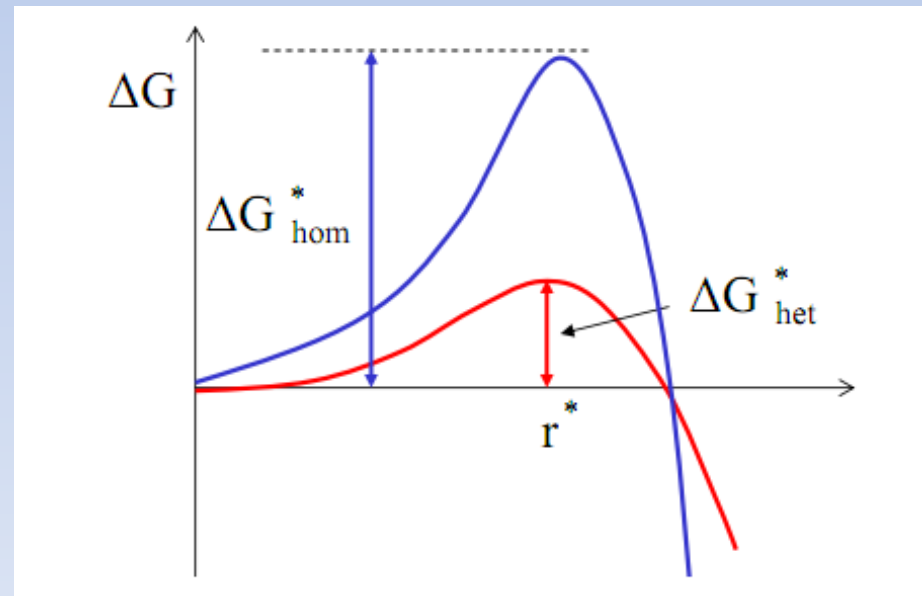
# Crystal Growth

The growth of crystals occurs through a number of steps:
(a) Transport of the solutes to the crystal interface
(b) the adsorption of the solutes at the surface (including surface nucleation, dehydration, ion-exchange, surface diffusion)
(c) incorporation of the crystal constituents into the lattice and/or removal of reactions products, if any.

Ignoring the latter, the rate of crystal growth may be limited either by transport, by surface reactions, or by a combination of both processes.
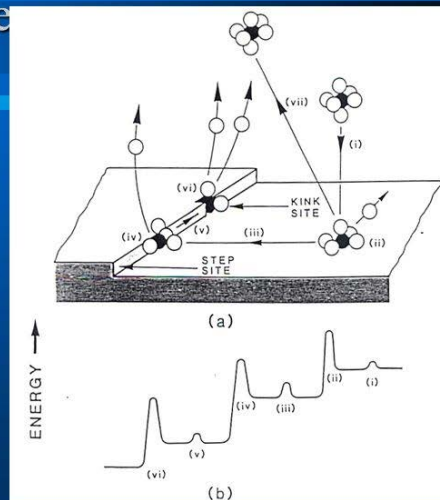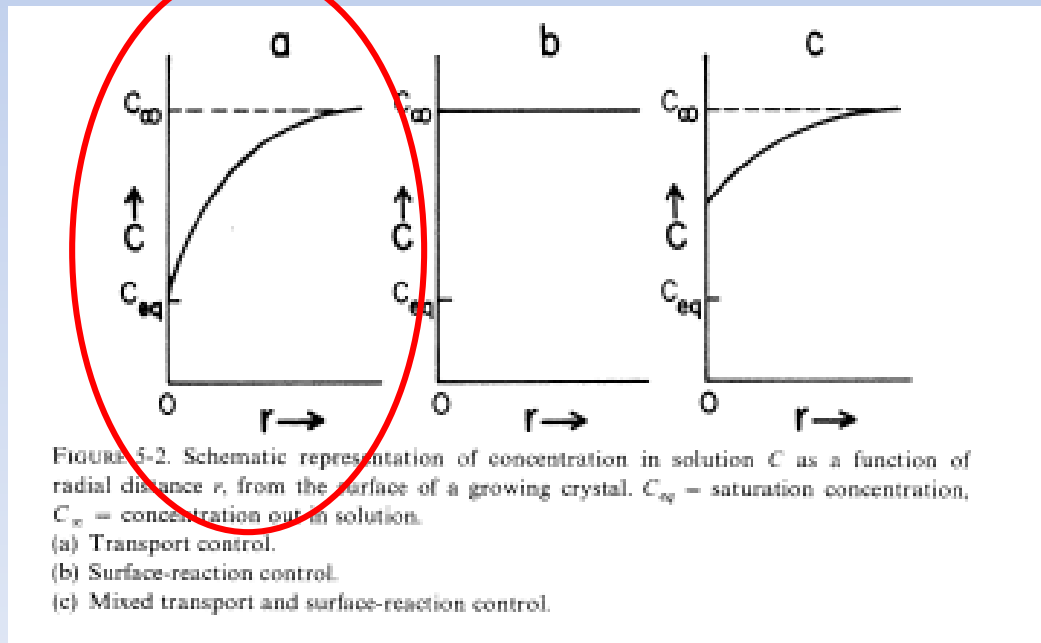
# Crystal Growth

In pure transport-controlled growth, ions are attached so rapidly to the surface of the crystal that the concentration in solution immediately adjacent to the crystal is lowered to close to the equilibrium or saturation level. Growth is then limited by the rate at which ions can migrate to the surface by diffusion or advection. The rate of growth, consequently, depends upon hydrodynamic conditions in solution, with faster growth resulting from increased flow velocities (e.g., stirring rate in solution).

FIGURE 5-2. Schematic representation of concentration in solution $C$ as a function of radial distance $r$, from the surface of a growing crystal. $C_{eq}$ = saturation concentration, $C_\infty$ = concentration out in solution.
(a) Transport control.
(b) Surface-reaction control.
(c) Mixed transport and surface-reaction control.

# Crystal Growth

Conversely, for pure surface-controlled growth, attachment of solutes through surface reactions is so slow that concentrations adjacent to the surface of the growing crystal build up to values that are nearly the same as in the bulk solution. The rate of growth is limited by surface reactions and is not affected by the increased flow velocities in the solution.
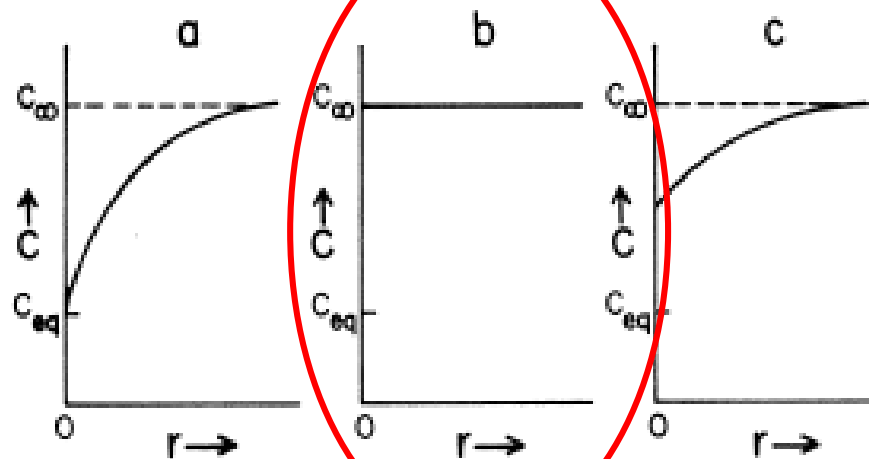


FIGURE 5-2. Schematic representation of concentration in solution $C$ as a function of radial distance $r$, from the surface of a growing crystal. $C_{eq}$ = saturation concentration, $C_{\infty}$ = concentration out in solution.
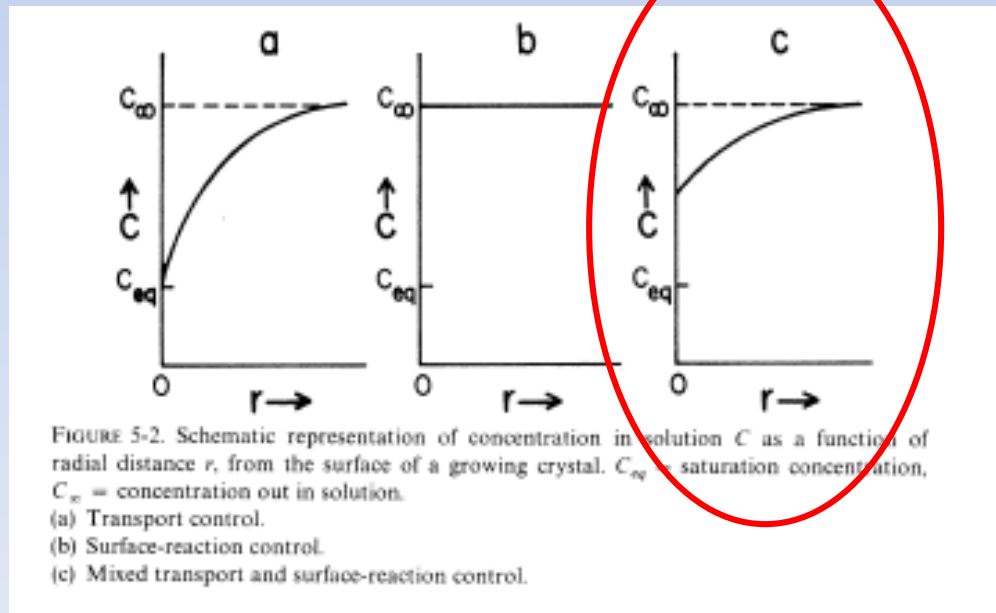(a) Transport control.
(b) Surface-reaction control.
(c) Mixed transport and surface-reaction control.

# Crystal Growth

As you can imagine, a number of intermediate situations between the two ideal conditions, where surface reactions are sufficiently fast that solute depletion occurs adjacent to the crystal surface, but transport prevents the concentration from being lowered to the saturation level.

As the rates of surface attachment are a strong function of the degree of supersaturation, the rate controlling step in the growth of a crystal may change from transport-control at high supersaturations to surface-control at low supersaturations.



FIGURE 5-2. Schematic representation of concentration in solution $C$ as a function of radial distance $r$, from the surface of a growing crystal. $C_{eq}$ = saturation concentration, $C_{\infty}$ = concentration out in solution.
(a) Transport control.
(b) Surface-reaction control.
(c) Mixed transport and surface-reaction control.

# Transport-controlled Growth

Growth via molecular diffusion constitutes a limiting situation of the transport growth-limited mechanisms (e.g., stagnant solution, no stirring)
The rate of growth of a crystal via molecular diffusion can be calculated theoretically if the crystal can be approximated to a sphere using Fick's second law of diffusion:

$\delta C_i/\delta t = D\ (\delta^2 C_i/\delta x^2) = D(\delta^2 C_i/\delta r^2 + 2/r\ (\delta C_i/\delta r))$

which states that the rate of change of the concentration of a component *i* is equal to the second derivative of the linear concentration gradient multiplied by the diffusion coefficient.

Solving this equation for a constant r and the proper boundary and initial conditions:
$C(r,0) = C_\infty = C_{bulk}$
$C(r_c,t) = C_{eq}$
$C(\infty,t) = C_\infty = C_{bulk}$

leads to $\delta r_c/\delta t = \overline{V}\ D\ (C_{bulk} - C_{eq})/r_c$
where $r_c$ is the radius of the crystal sphere, D is the molecular diffusion coefficient, $\overline{V}$ is the molar volume of the precipitate and $C_{bulk}$ and $C_{eq}$ are the solute concentrations in the bulk solution and at equilibrium with respect to the precipitate.

If advection becomes more efficient at transporting the crystal component to the surface of the growing crystal: $\delta C_i/\delta t = v\ ((\delta C_i/\delta x)$

# Fick's first law of diffusion

## Steady-State Diffusion

Flux proportional to concentration gradient = $\dfrac{dC}{dx}$
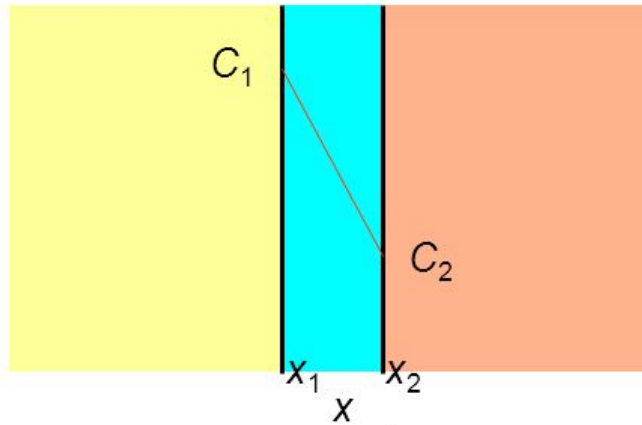


Fick's first law of diffusion
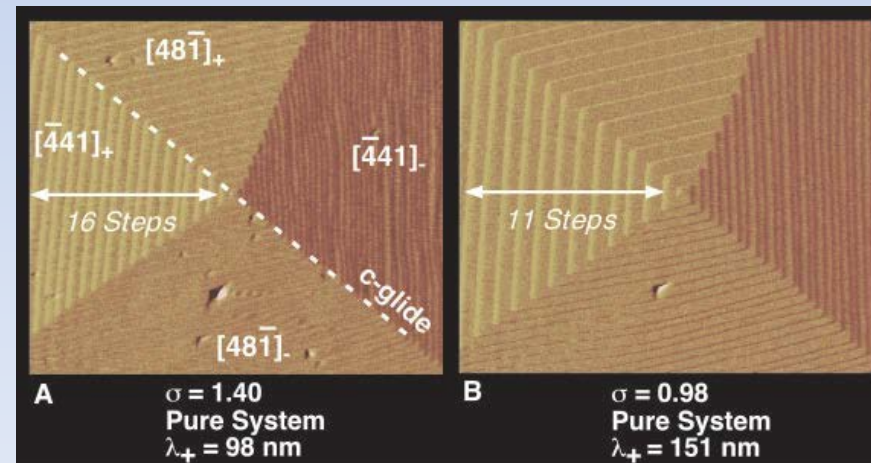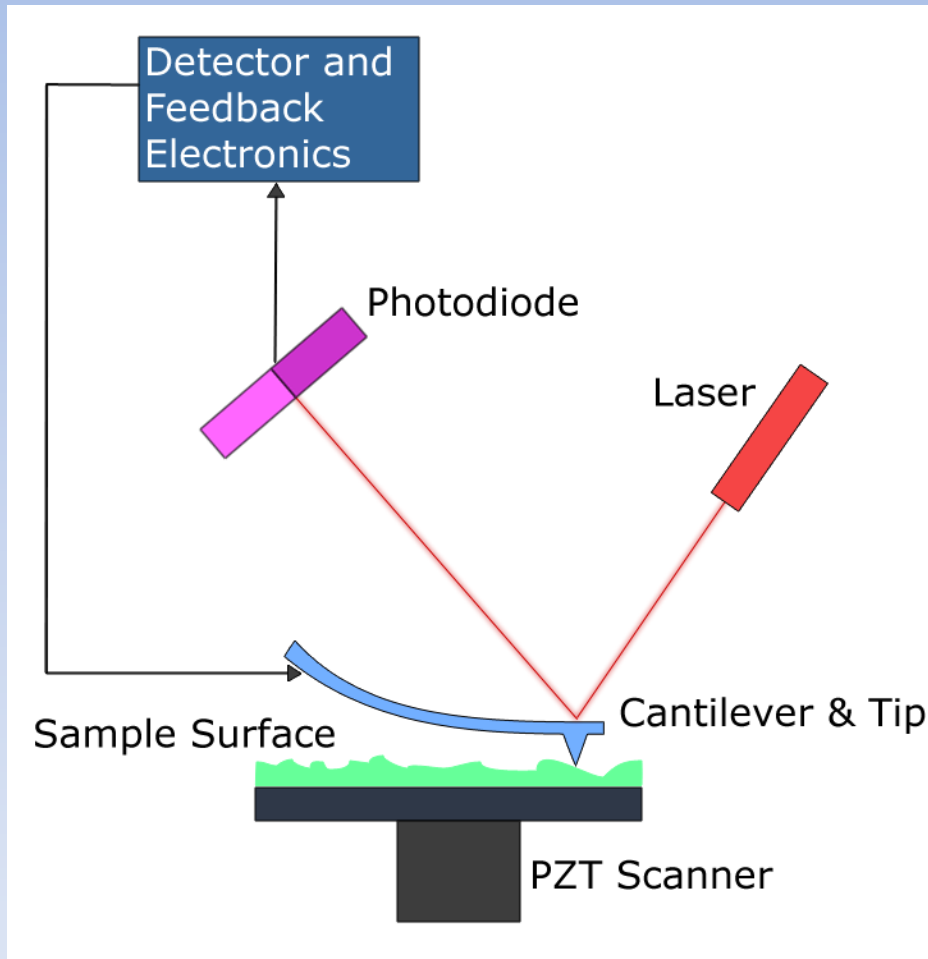
$$J = -D\frac{dC}{dx}$$

$D \equiv$ diffusion coefficient

if linear $\dfrac{dC}{dx} \cong \dfrac{\Delta C}{\Delta x} = \dfrac{C_2 - C_1}{x_2 - x_1}$

Fick's first law gives us the flux of the component, but does not tell us how the concentration of the component varies in time.

# Surface-reaction controlled growth

## Viewed by Atomic Force Microscopy



Detector and Feedback Electronics

Photodiode

Laser

Cantilever & Tip

Sample Surface

PZT Scanner



Figure 2. As supersaturation increases, two-dimensional growth of canavilan crystals sets in, seen in the appearance of small islands rising from the surface.

33 by 58 micrometers



$[48\bar{1}]_+$

$[\bar{4}41]_+$

$[\bar{4}41]_-$

16 Steps

c-glide

$[48\bar{1}]_-$

11 Steps

**A** $\sigma = 1.40$ Pure System $\lambda_+ = 98$ nm

**B** $\sigma = 0.98$ Pure System $\lambda_+ = 151$ nm

# Surface-reaction controlled growth

Many theories of surface-reaction controlled growth were developed, but we will only consider two:
1) surface-nucleation controlled growth
2) dislocation-controlled growth

In the surface-nucleation controlled growth, the rate determining step is the nucleation of a flat, two-dimensional crystal one atom thick on an otherwise atomically smooth crystal.
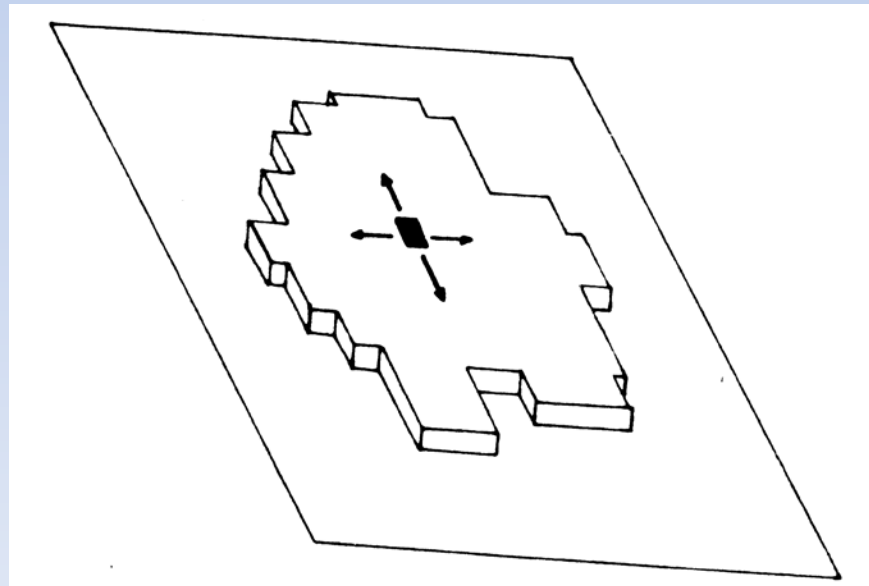
# Surface-reaction controlled growth

Surface nucleation creates atomic-sized steps on the surface where attachment of new ions is facilitated. As the number of direct bonds on the surface increases, attachment becomes energetically more attractive. Hence, holes are more energetically favorable than kinks and steps.

The attachment of ions at kinks creates new kinks, so the process of crystal growth can be visualized as the migration of kinks and steps until the surface is covered.
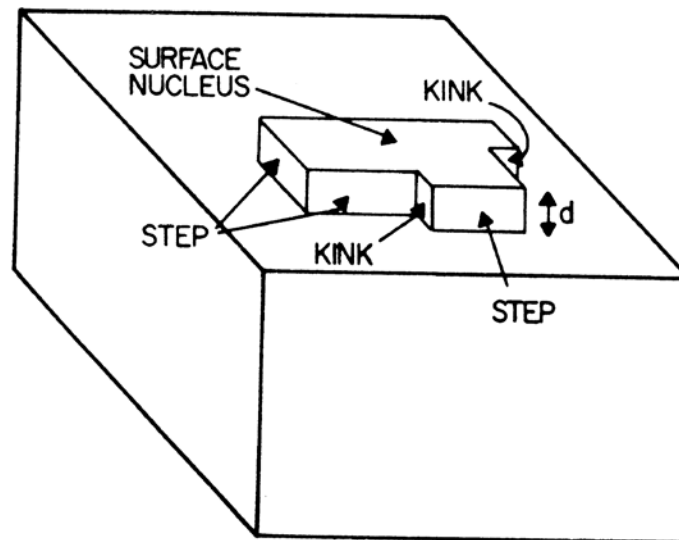
FIGURE 5-3. Idealized representation of the surface of a crystal. Dimension d represents one atom, molecule, unit cell, etc. On the flat crystal surface a flat ("two-dimensional") surface nucleus is present which exhibits monoatomic steps and kinks.

# Surface-reaction controlled growth

In order to provide steps and kinks for the next surface layer, a new nucleus must be formed on the surface. The rate at which the surface nucleus forms is the rate-determining step and can be calculated from the standard nucleation theory.

According to the mononuclear theory, the rate of growth is limited solely by surface nucleation. In other words, once a surface nucleus has formed, the rate of spreading of its steps by ion/atom attachment is so fast that the entire monoatomic crystal layer is formed before  another surface nucleus is created. Each atomic layer on the crystal is formed from only one surface nucleus. …
A more probable situation is polynuclear growth or "birth and spread" model.
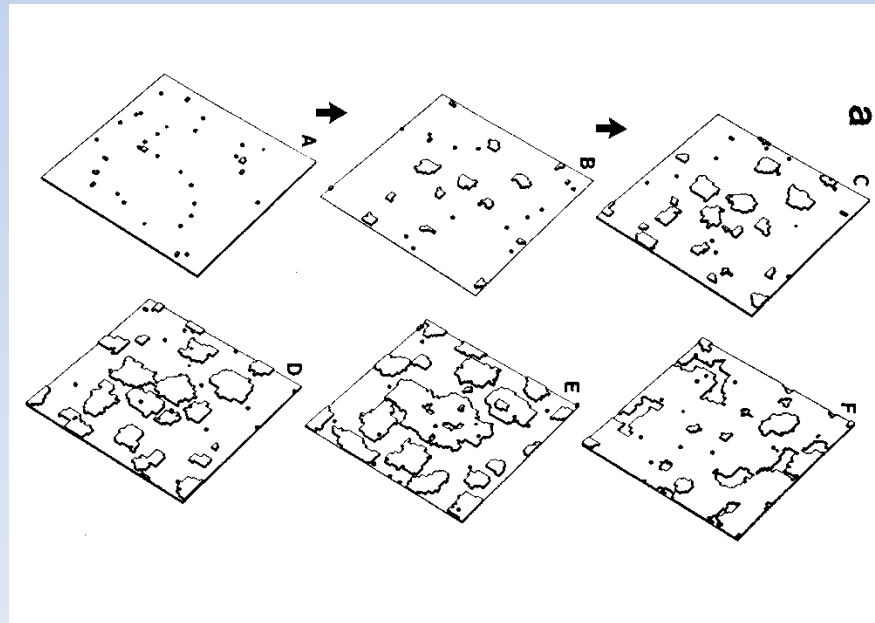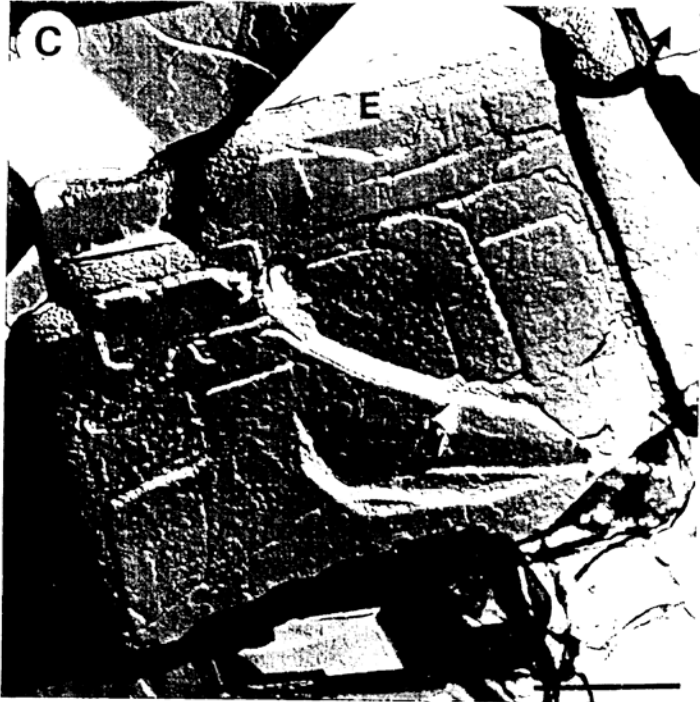
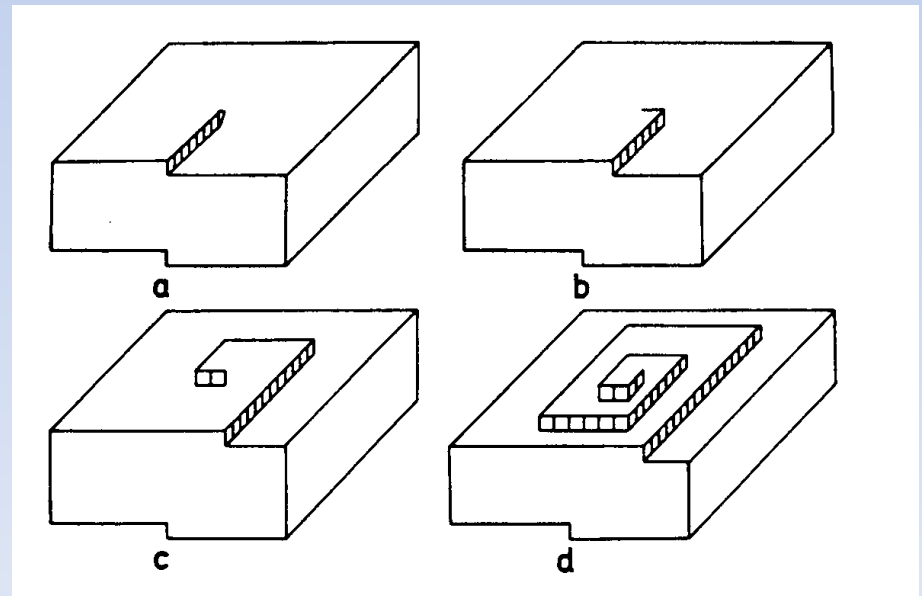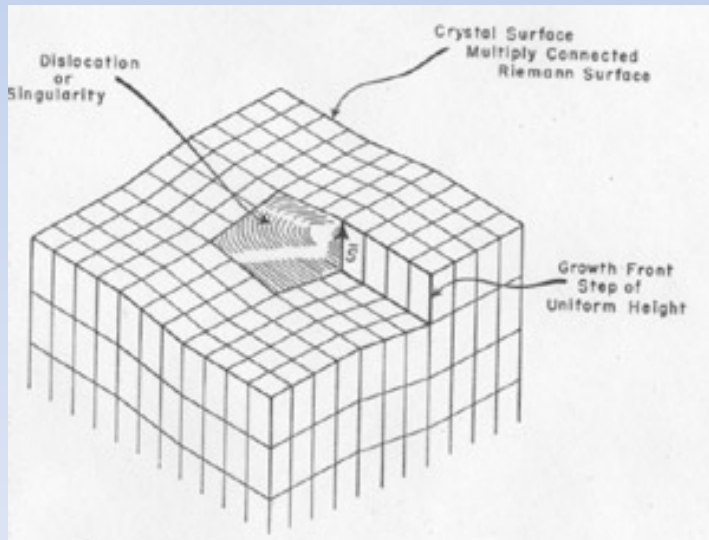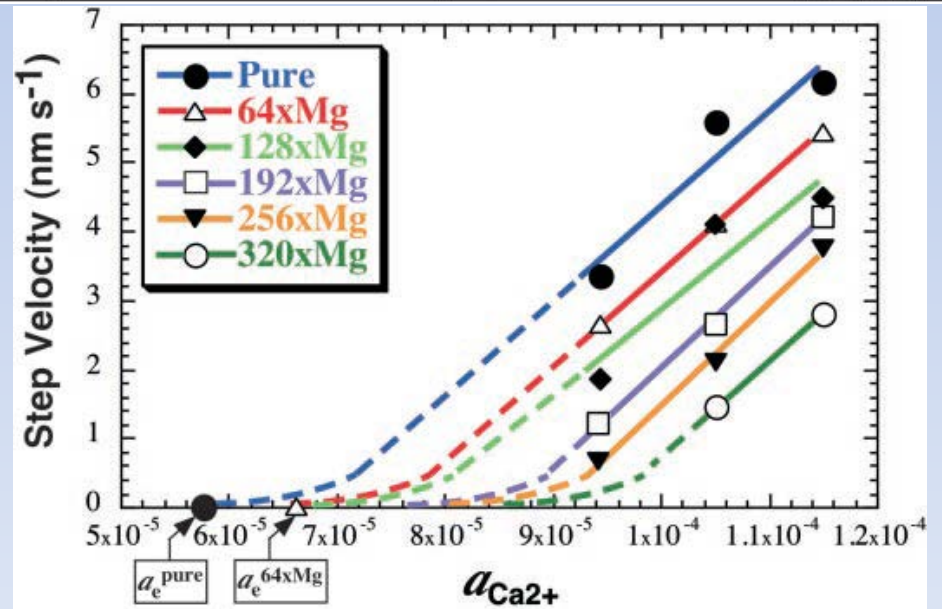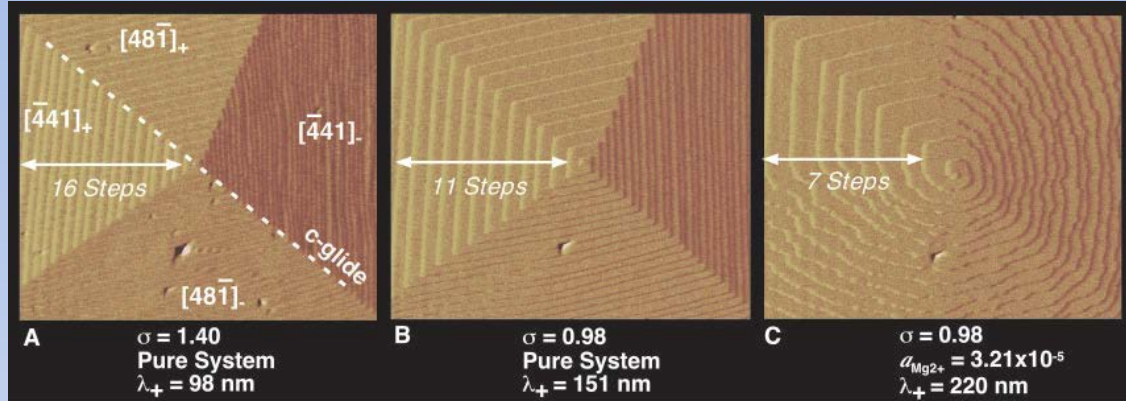# Polynuclear growth on a calcite surface



**Figure 4.5.9** TEM image of the overgrowth-coated inorganic seed crystal. Magnification is approximately 180,000X.

# Screw dislocation or spiral growth

Growth at intersections of screw dislocations with the surface of the crystal. Screw dislocations are common in all crystalline substances. Crystal growth occurs along atomic steps provided by the outcropping rows of atoms on the surface. No nucleation of new steps is required since the screw dislocation outcrops are always present. Crystal growth at the outcrops occurs as a spiral-like rotation of the steps, by continuous attachment of ions/molecules, around the screw axis and can even be maintained at very low supersaturations (impossible according to surface nucleation theories).

# Screw dislocation or spiral growth



Figure 32 (a) Computer simulated configurations of a simple cubic (100) crystal face during a growth period after instantaneous supercooling with no dislocation present (A to F is a time sequence). Note the formation and growth of a number of surface nuclei which grow together to form the first new layer and the formation of surface nuclei in the second new layer before the first layer is completely filled. ($\Delta u/kT = 2$, $\phi = 4kT$). (b) Computer simulated development of a spiral step pattern on a simple cubic (100) face with a double Burger's vector screw dislocation emergent at the center (A to D is a time sequence). Note the minor contribution of surface nuclei to the overall growth. Figures courtesy of Dr. G. H. Gilmer.

From: Davis et al. (Science 290: 2000)

# Crystal growth and dissolution

There is no universally-accepted theory for crystal growth, especially when dealing with specific growth inhibitors that are frequently encountered in natural environments. Nevertheless, as a first approximation, one can assume that surface-reaction controlled growth in the presence or absence of inhibitors follows a relation of the form:

$$\delta r_c / \delta t = k \, (C_{bulk} - C_{eq})^n$$

where n > 1.

In many respects, dissolution can be considered as the inverse of precipitation/ growth. Like precipitation, dissolution rate is controlled either by transport or by surface reactions. Also, like precipitation, dissolution can be visualized as taking place by the migration of steps and kinks, and deceleration of dissolution may occur by the adsorption of inhibitors at the kinks.