

# Kinetics

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**NUCLEAR ENGINEERING &  
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# Microscopic Diffusion

$$\bar{r}^2 = n\lambda^2$$

time ( $t$ )  
jump frequency ( $\Gamma$ )

We need to now convert this to a function of time,  $t$ . We can do this by considering the frequency of each jump,  $\Gamma$ , and the time allowed for hopping, then we get:

$$\bar{r}^2 = \Gamma t \lambda^2$$

We now need to equate this to the [macroscopic](#) diffusion,  $D$ . To do this we use Ficks second law of diffusion to describe the probability of finding a spherical shell surrounding an origin:

$$P_t = \frac{C(r,t)}{N} \frac{\exp(-r^2/4Dt)}{(4\pi Dt)^{3/2}}$$

macroscopic  
diffusion coefficient

$$\bar{r}^2 = n\lambda^2$$

# Fick's First Law of Diffusion

- Relates the flux and the concentration gradient of the diffusing specie:
- D is given in  $\text{cm}^2/\text{s}$  or  $\text{m}^2/\text{s}$
- For solids it is between 20-1500°C,  $10^{-20} < D < 10^{-4} \text{ cm}^2/\text{s}$

# Fick's First Law of Diffusion

$$J = -D \frac{\partial C}{\partial x}$$

Why do random jumps of atoms result in a net flux of atoms from regions of high concentration towards regions of low concentrations?

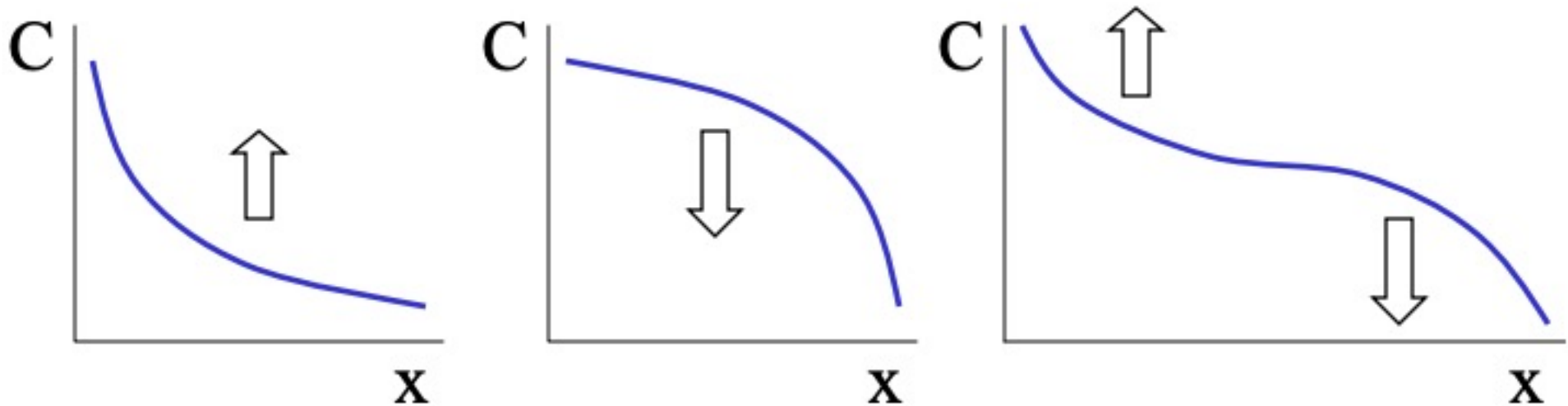


Atoms here jump randomly  
both right to left

But there are not many  
atoms here to jump to the left

# Fick's Second Law of Diffusion

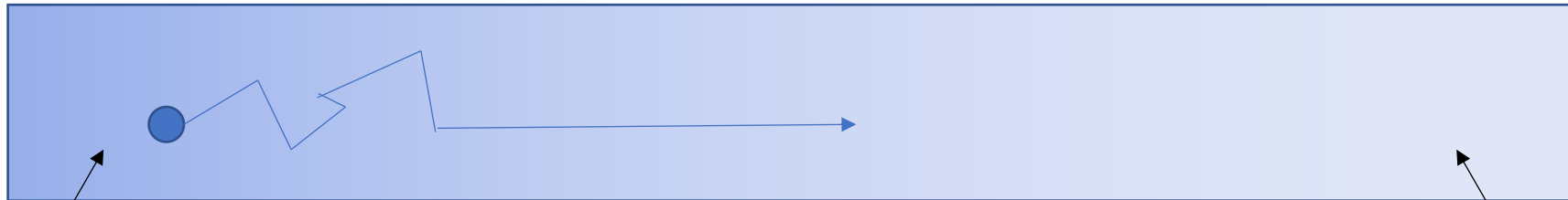
- Provides the relationship between the concentration gradient and the rate of change of concentration caused by diffusion at a given point in the system



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macroscopic  
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# Point defect properties

	Symbol	Unit	Al	Cu	Pt	Mo	W
<b>Interstitials</b>							
Relaxation volume	$V_{\text{relax}}^i$	Atomic vol.	1.9	1.4	2.0	1.1	
Formation energy	$E_f^i$	eV	3.2	2.2	3.5		
Equilibrium concentration at $T_m^*$	$C_i(T_m)$	–	$10^{-18}$	$10^{-7}$	$10^{-6}$		
Migration energy	$E_m^i$	eV	0.12	0.12	0.06		0.054
<b>Vacancies</b>							
Relaxation volume	$V_{\text{relax}}^v$	Atomic vol.	0.05	–0.2	–0.4		
Formation energy	$E_f^v$	eV	0.66	1.27	1.51	3.2	3.8
Formation entropy	$S_f^v$	k	0.7	2.4			2
Equilibrium concentration at $T_m^*$	$C_v(T_m)$	–	$9 \times 10^{-6}$	$2 \times 10^{-6}$			$4 \times 10^{-5}$
Migration energy	$E_m^v$	eV	0.62	0.8	1.43	1.3	1.8
Activation energy for self-diffusion	$Q_{\text{vSD}}$	eV $Q_a$	1.28	2.07	2.9	4.5	5.7



# Microscopic Diffusion

Both the **macroscopic** and **microscopic** equations can be equated together based on both can be defined based on the probability,  $p_t$ . To do this, we substitute  $p_t(r)$  into:

$$\bar{r}^2 = 4\pi \int_0^\infty r^4 p_t(r) dr$$

And solving, we get simply:

$$\bar{r}^2 = 6Dt$$

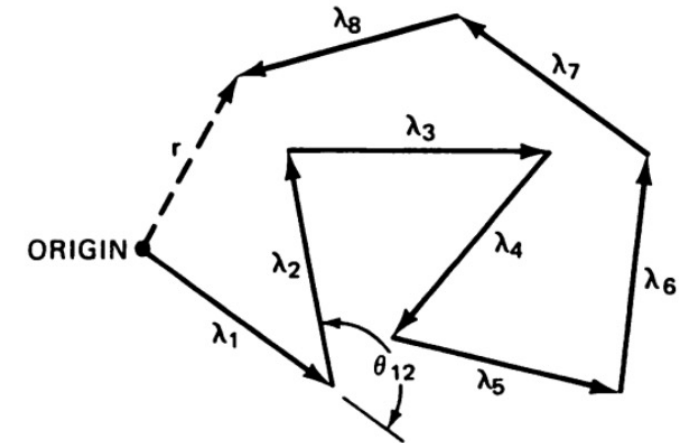


Fig. 7.4 Eight random jumps of equal length  $\lambda$ .

# Diffusion accounting for hopping mechanism

Knowing now that:

$$D = \frac{1}{6} \lambda^2 \Gamma$$

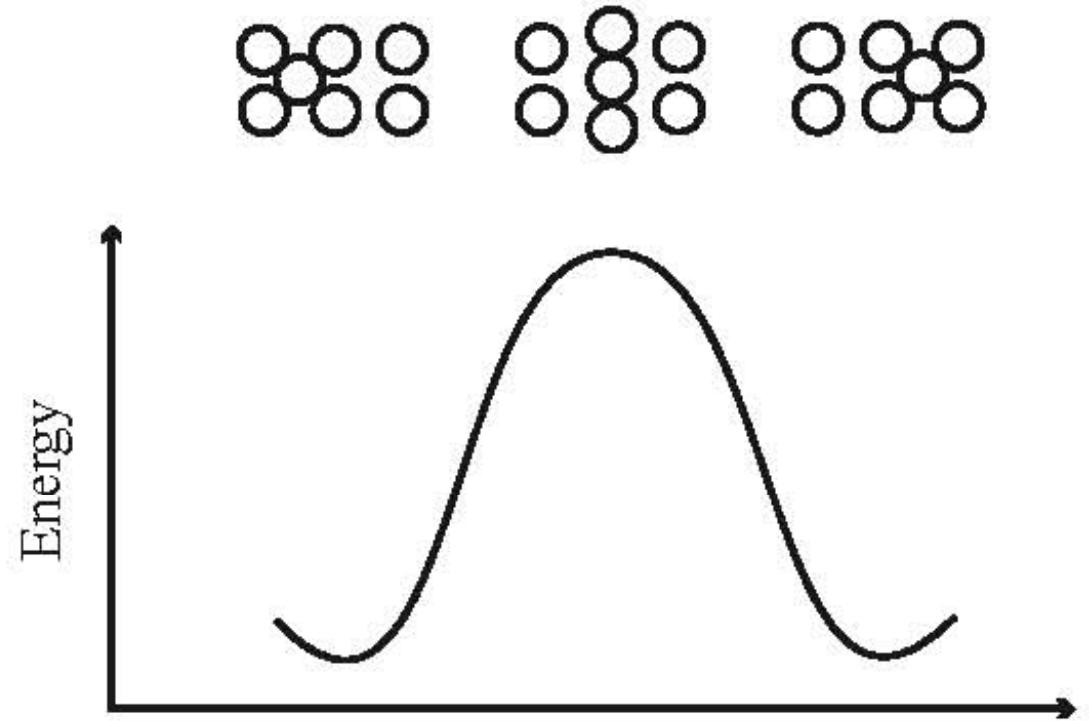
We need to determine the jump frequency for a given jump mechanism. This is dependent on the probability a jump site is open,  $\rho_j$ , the number of nearest neighbors,  $z$ , and the frequency of a given jump type,  $\omega$ :

# How to determine $\omega$

$$\omega = v \exp\left(\frac{-\Delta G_m}{k_b T}\right)$$

$$\omega = v \exp\left(\frac{-S_m}{k_b}\right) \exp\left(\frac{-\Delta H_m}{k_b T}\right)$$

$$\omega = v \exp\left(\frac{-S_m}{k_b}\right) \exp\left(\frac{-\Delta E_m}{k_b T}\right)$$



# Pulling it together to get the diffusion equations:

Diffusion of vacancies:  $D_v = \alpha a^2 \omega = \alpha a^2 v \exp\left(\frac{S_m^v}{k}\right) \exp\left(\frac{-E_m^v}{kT}\right)$

Diffusion of atoms by way of vacancies – vacancy self-diffusion:  $D_a^v = \alpha a^2 v \exp\left(\frac{S_f^v + S_m^v}{k}\right) \exp\left(\frac{-E_f^v - E_m^v}{kT}\right)$

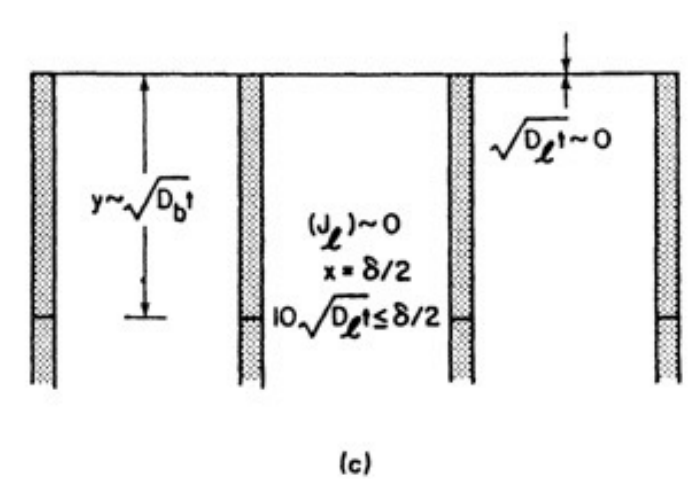
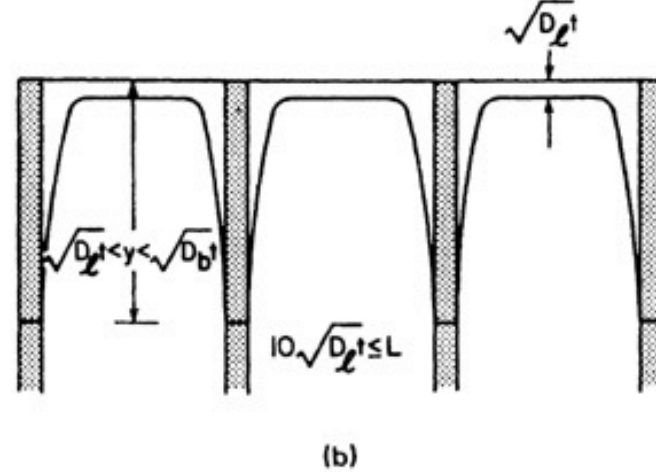
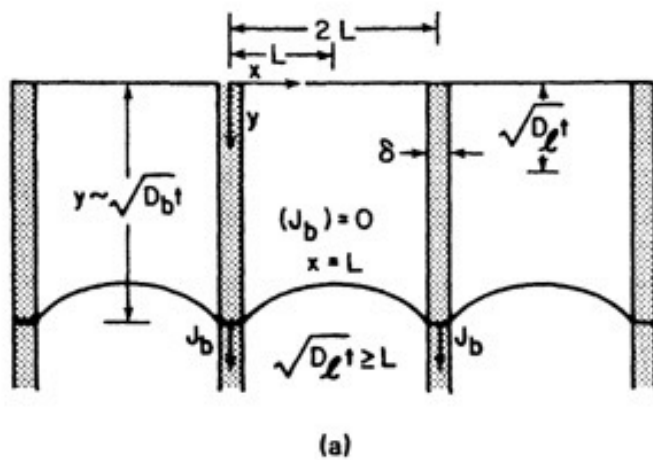
Diffusion of interstitials:  $D_i = \alpha a^2 v \exp\left(\frac{S_m^i}{k}\right) \exp\left(\frac{-E_m^i}{kT}\right)$

Diffusion of atoms by way of interstitials – interstitial self-diffusion:  $D_a^i = \alpha a^2 v \exp\left(\frac{S_f^i + S_m^i}{k}\right) \exp\left(\frac{-E_f^i + -E_m^i}{kT}\right)$



Or, more simply:

# Diffusion along high-diffusivity paths:



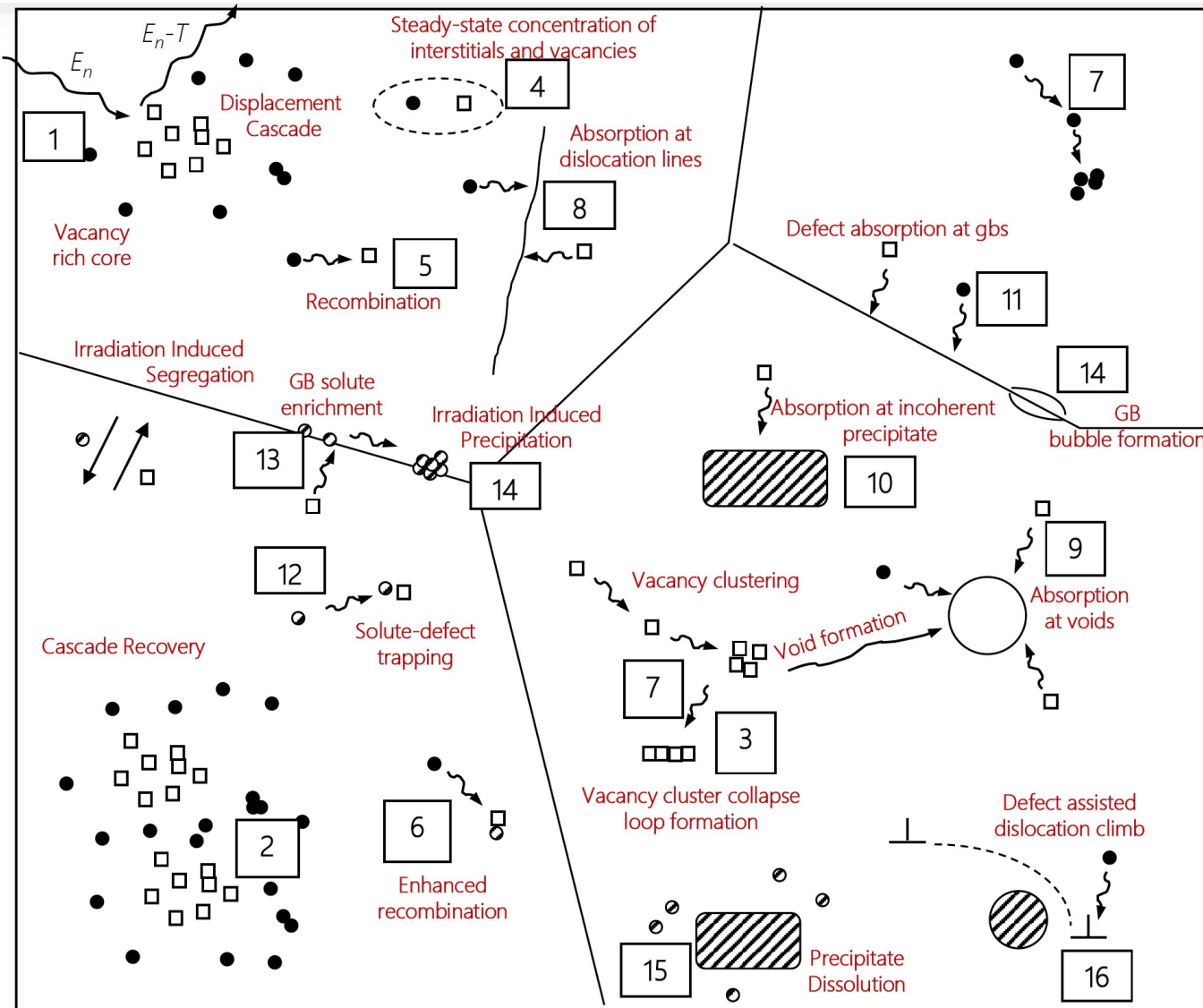
Type A: The diffusion front in the bulk and in the boundary advanced at the same speed

Type B: The diffusion in the grain boundary is faster than in the bulk

Type C: The diffusion in the bulk is negligible and grain boundary diffusion is only active

# Radiation Effects at the Grain Scale

**Goal:** Determine the kinetics of microstructure evolution under irradiation



# We now do point defect accounting

$$\text{Change} = \boxed{\text{Gain}} - \boxed{\text{Loss}}$$

- What are the possible gain terms?
- What are the possible loss terms?



# Gain Terms

- Defect production rate:

$$K_0 = \left( \frac{dpa}{s} \right) \times \varepsilon$$

- Reaction production rate:

$$R_0 = \sum_{d=1}^n Rxn_d$$

# Loss Term: Recombination

- Inherently, random walk of defects means there is a probability and thus a rate of recombination
- Must be related to the defect concentration

# Loss Term: Diffusion

- Inherently, random walk of defects means there is a probability and thus a local loss of defects due to diffusion
- Use macroscopic description for diffusion (Fick's Law):

# Total diffusion coefficient

The diffusion coefficients of the atoms in the solid are written in terms of the concentration and diffusion coefficients of the *defects*

$$D_a = f_v d_v C_v + f_i d_i C_i + f_{2v} d_{2v} C_{2v}$$

The effect of irradiation is two-fold:

Our next objective is to determine  $C_i$  and  $C_v$  during irradiation to calculate  $D_a$  from above

# Loss Terms: Sinks

- Non-perfect crystals have trapping sites for point defects where annihilation or recombination is promoted, these are defect sinks
- The effectiveness (or rate) of a sink in promoting loss is the *sink strength*,  $K_s$

# Let's play a quick game:

Change =

Gain

-

Loss

Sinks

Diffusion

Recombination

Production

Gain

Loss

$$K_0 = \left( \frac{dpa}{s} \right) \varepsilon$$

$$\frac{\partial C_{i,v}}{\partial t} = - \sum_{s=1}^{all\ sinks} K_s C_{i,v} C_s$$

$$\frac{\partial C_{i,v}}{\partial t} = K_{iv} C_i C_v$$

$$\frac{\partial C_{i,v}}{\partial t} = \nabla D_{i,v} \nabla C_{i,v}$$



# Pulling it together: Point Defect Kinetic Equations

- If we neglect clustering:

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{vs}C_vC_s + D_v\nabla^2 C_v$$

$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{is}C_iC_s + D_i\nabla^2 C_i$$

# Point Defect Kinetic Equations

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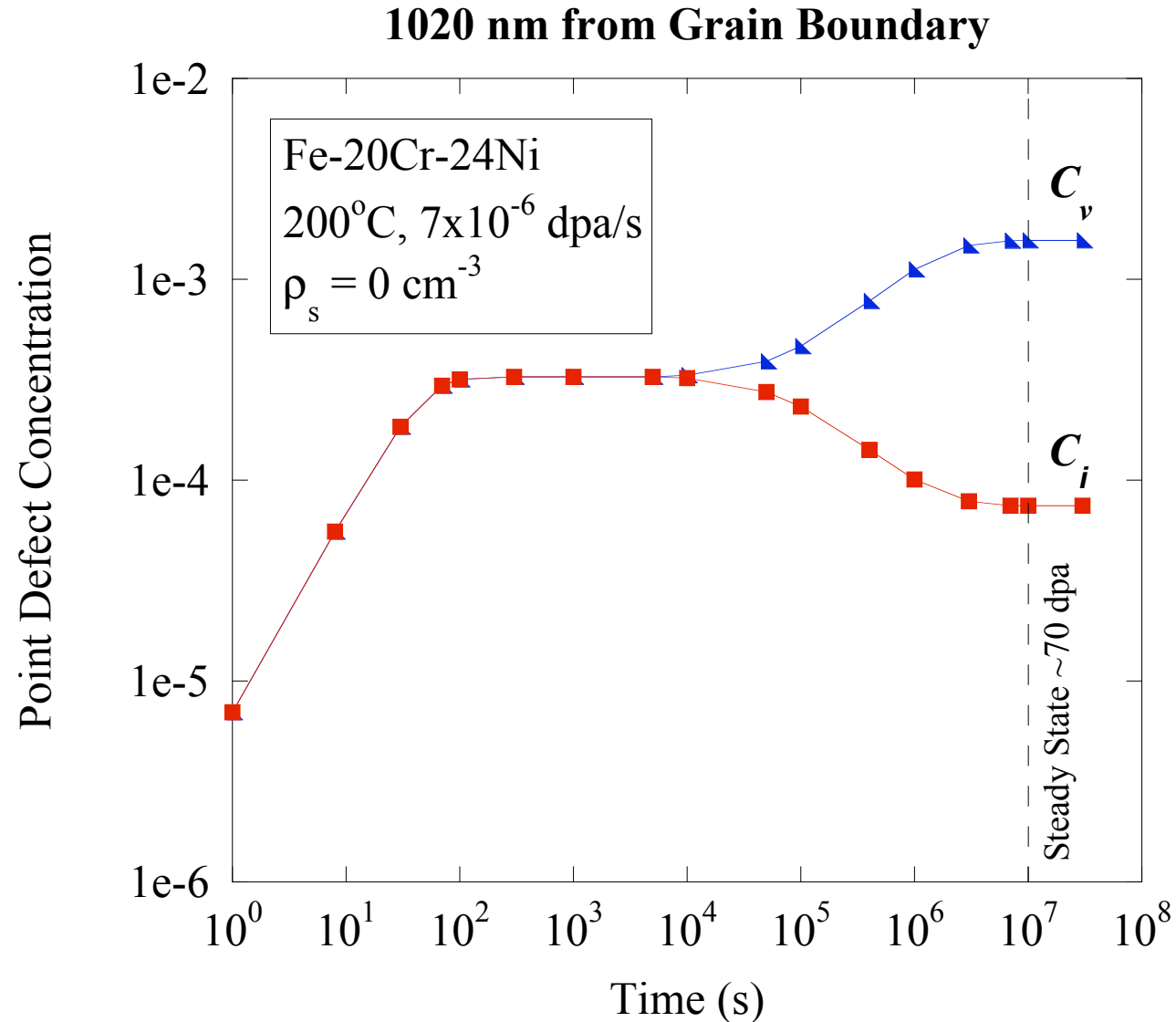
- Example of defect absorption to cavities:

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - z_v p_d D_v C_v + 4\pi R_c N_c D_v C_v$$

$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - z_i p_d D_i C_i + 4\pi R_c N_c D_i C_i$$



# Results from MIK code for Fe-20Cr-24Ni at a damage rate of $7 \times 10^{-6}$ dpa/s, $T=200^\circ\text{C}$



# To solve these, we subject these equations to limitations

1. The model applies to pure metals. No binding of defects to atomic species
2. Sink concentration and strength are time-independent
3. Other than mutual recombination, defect-defect interactions(e.g. formation of di-vacancies or di-interstitials) are ignored
4. Bias factors for diffusion of defects to sinks are set to unity (no preferential absorption of specific point defects at specific sinks)
5. Diffusion loss terms in and out of the observation volume are not considered
6. Thermal equilibrium vacancy concentration is neglected

We can now look at several cases...

# Low Temperature, Low Sink Density

1. Initially, defect concentrations build up according to  $dC/dt = K_0$  with  $C_i \sim C_v$   
so  $C_i = C_v = C = K_0 t$ 
  - Concentrations are too low for either recombination or sinks to have an effect
2. Build up will start to level off when the production rate is compensated by the recombination rate. Quasi-steady state concentrations are:

We can find the time at which the defect concentrations level off by equating this concentration with that during build:

# Low Temperature, Low Sink Density

3.  $C_i$  and  $C_v$  remain approximately equal until a time,  $t_2$ , which is the time constant for the process of interstitials reacting with sinks. Because  $D_i > D_v$ , more interstitials are lost to sinks than vacancies, which is described by:

Vacancies and interstitials build up and decay (respectively) to:

$$C_v(t) = \left[ \frac{K_0 K_{is} C_s t}{K_{iv}} \right]^{1/2}$$

$$C_i(t) = \left[ \frac{K_0}{K_{iv} K_{is} C_s t} \right]^{1/2}$$

The time at which this occurs is given by:

# Low Temperature, Low Sink Density

4. After awhile, true steady state is achieved due to interaction of vacancies with sinks. Solving for the steady state concentrations of vacancies and interstitials by setting  $dC_v/dt = dC_i/dt = 0$ , gives:

$$C_v^{ss} = -\frac{K_{is}C_s}{2K_{iv}} + \left[ \frac{K_0K_{is}}{K_{iv}K_{iv}} + \frac{K_{is}^2C_s^2}{4K_{iv}^2} \right]^{1/2}$$

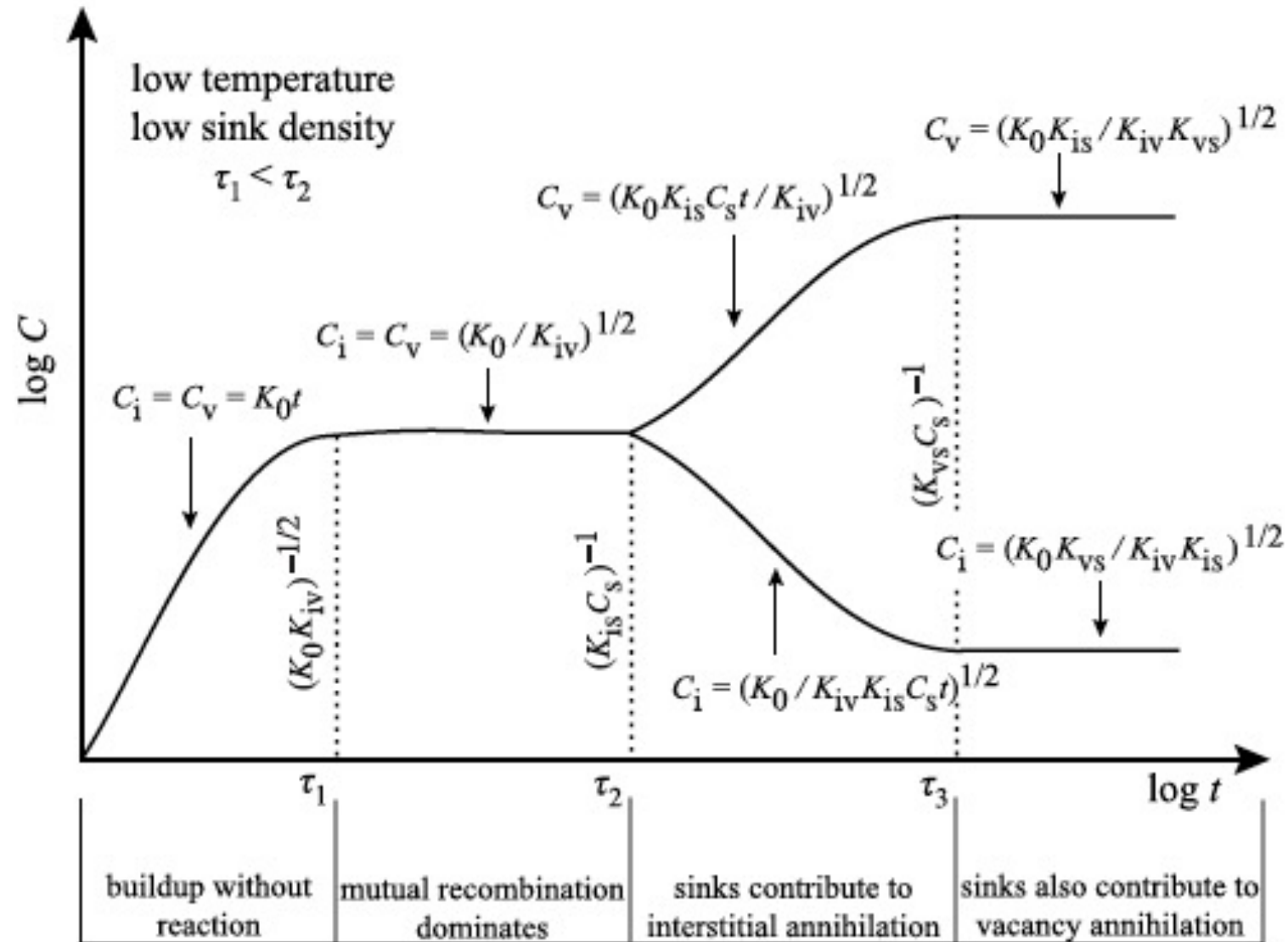
$$C_i^{ss} = -\frac{K_{is}C_s}{2K_{iv}} + \left[ \frac{K_0K_{is}}{K_{iv}K_{vs}} + \frac{K_{vs}^2C_s^2}{4K_{iv}^2} \right]^{1/2}$$

For the case of low temperature and low sink density,  $C_s$  is small:

# Low Temperature, Low Sink Density

We can solve for the time to steady state in a similar manner to that of the quasi steady state by equating the previous region (build up) to the steady state regime:

# Low Temperature, Low Sink Density



# Example calculation for BCC Fe

- Problem: Calculate the typical times of the different stages of  $C_v$  and  $C_i$  for BCC Fe using the following parameters:

293K neutron irradiation

Lattice parameter ( $a_0$ ) of 2.82 Å

Dislocation density ( $\rho_d$ ) of  $10^8 \text{ cm}^{-2}$

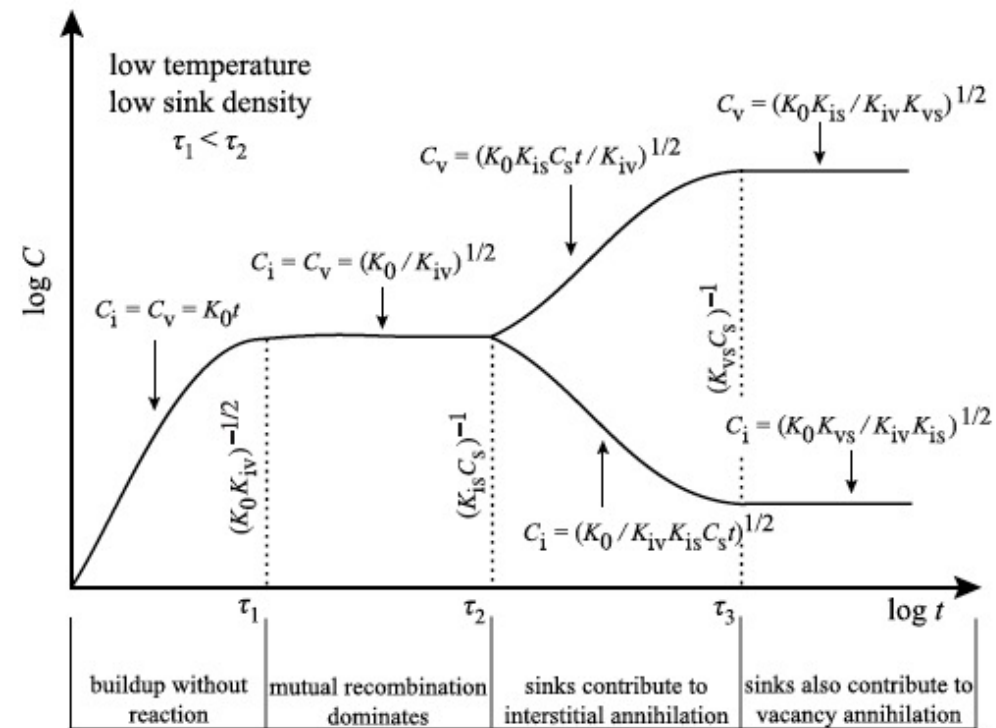
Interstitial migration energy ( $E_m^i$ ) of 0.65 eV

Vacancy migration energy ( $E_m^v$ ) of 1.5 eV

Capture radius ( $r_{iv}$ ) of  $10a_0$

Displacement rate ( $K_0$ ) of  $10^{-7} \text{ dpa/s}$

Vibration frequency ( $\nu$ ) of  $10^{13} \text{ Hz}$





# Example calculation for BCC Fe

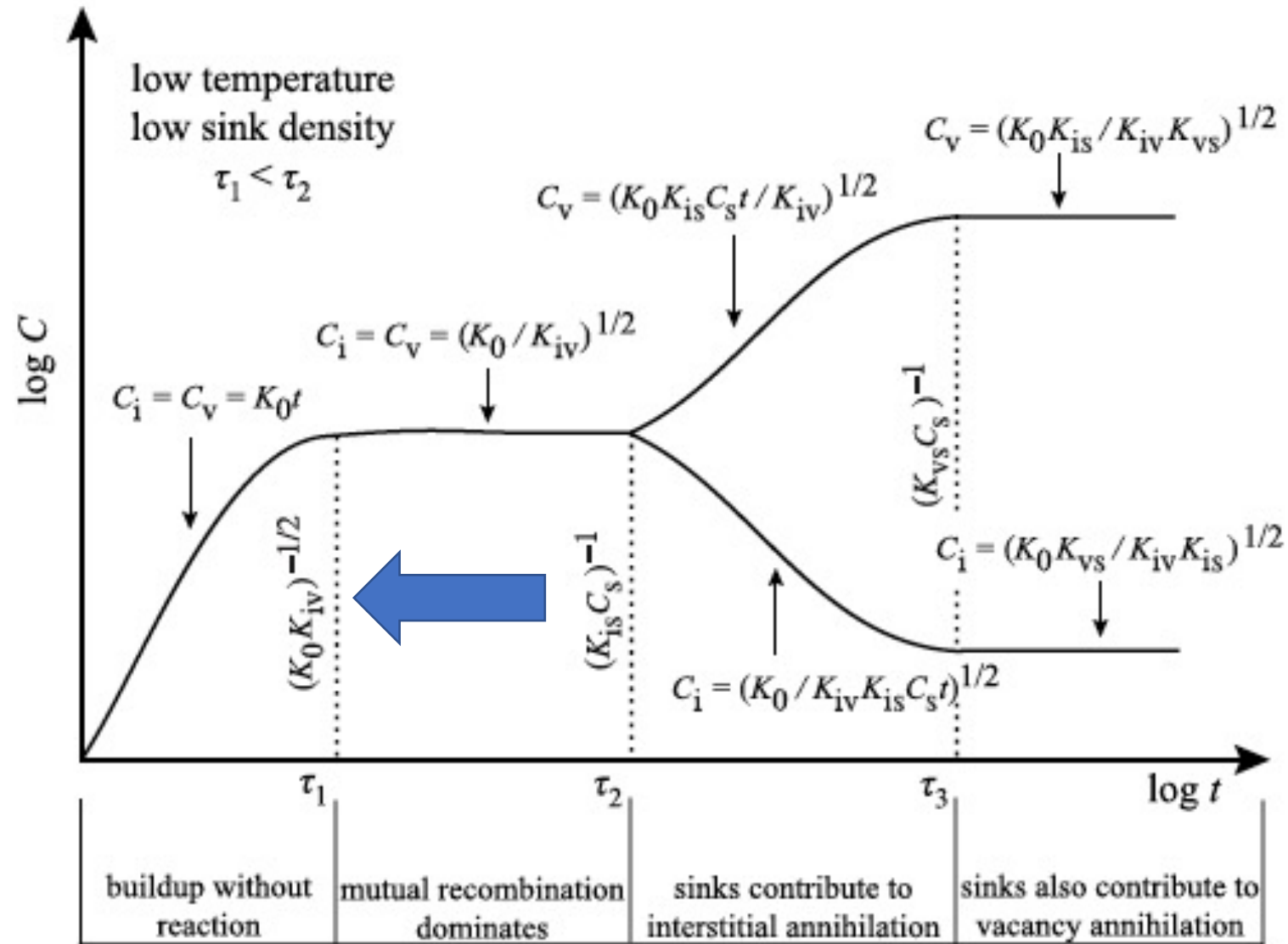
- Problem: Calculate the typical times of the different stages of  $C_v$  and  $C_i$  for BCC Fe using the following parameters:
  - Step 1: Calculate the recombination constant:
  - Now calculate the time for recombination to become significant

# Example calculation for BCC Fe

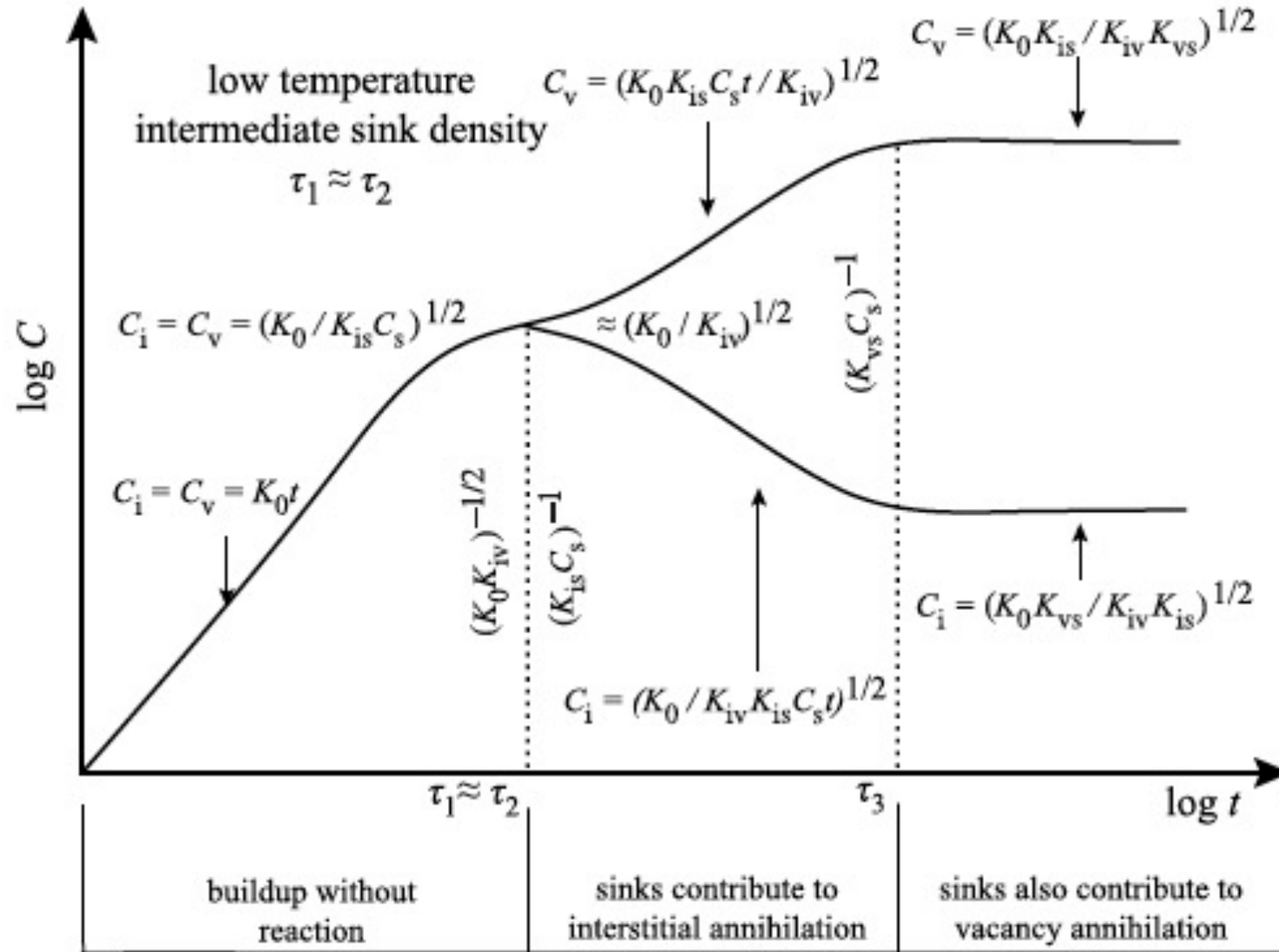
- Problem: Calculate the typical times of the different stages of  $C_v$  and  $C_i$  for BCC Fe using the following parameters:
  - Step 2: Calculate the time for interstitials to arrive sinks using  $D_i$  from before:
  - Step 3: Calculate the time when vacancies arrive at sinks to determine steady state:
    - Must calculate  $D_v$



# Low Temperature, Increasing Sink Density



# Low Temperature, Increasing Sink Density



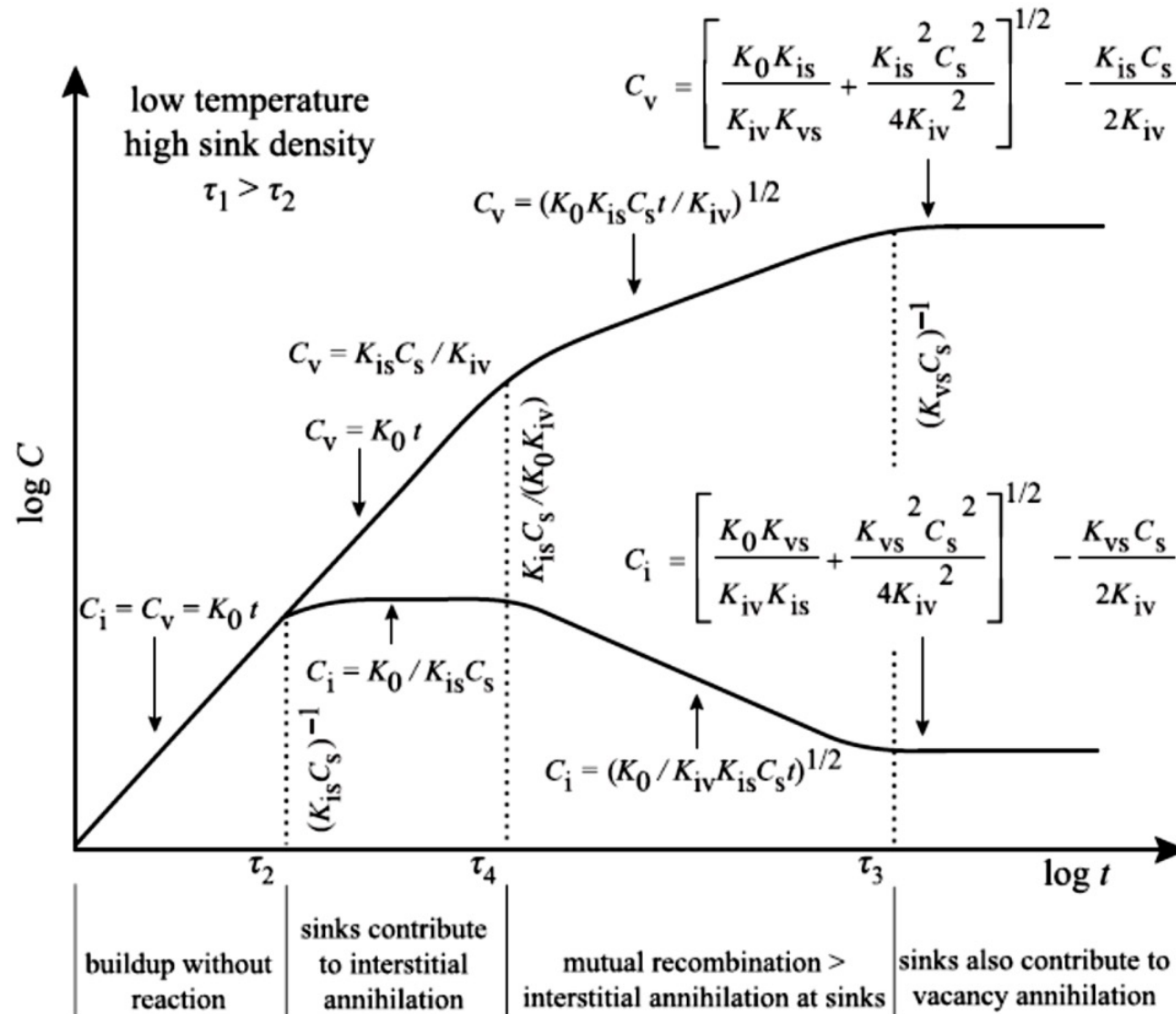
# Low T, High $C_s$

- In this case, the interstitial concentration comes into a quasi-steady state with production and annihilation at sinks:
- Equating the interstitial concentrations in the linear buildup regime with the quasi-steady state regime:

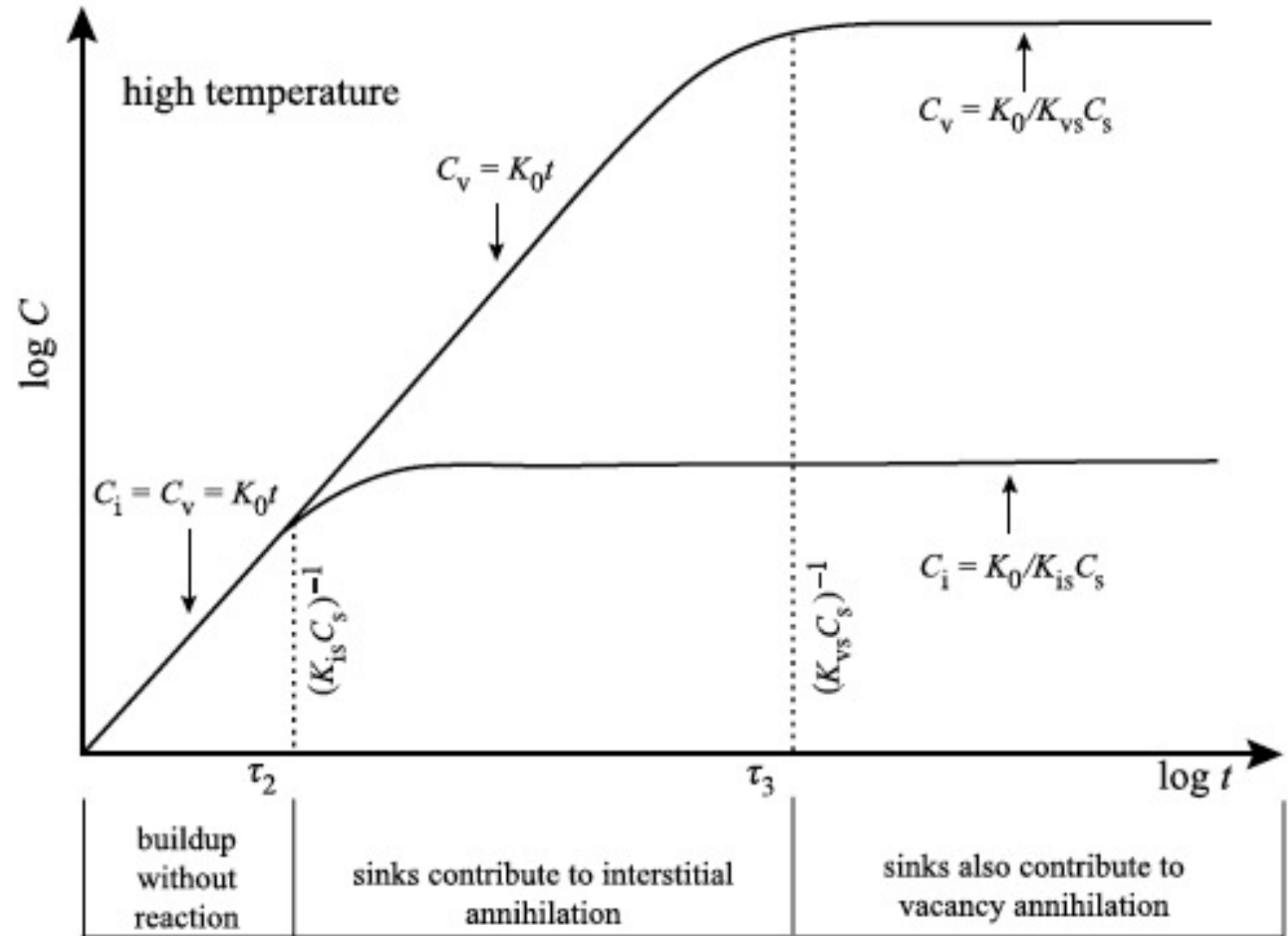
# Low T, High $C_s$

- A competition soon arises between the annihilation of interstitials at sinks and recombination with vacancies, such that:
- Yielding the time constant for the transition between the regimes where interstitials go to sinks and mutual recombination dominates:

# Low T, High $C_s$



# High Temperature





# Properties of point defect balance equations

1. If there is only one type of sink, then the net absorption rate at that sink is zero:

$$K_{is}C_i = K_{vs}(C_v - C_v^0)$$

2. Even if we have more than one type of sink, if the sinks have the same “strength” for vacancies and interstitials ( $z_i = z_v$ ), then the net flow to any sink is zero
3. In the absence of sinks and thermal vacancies,  $C_v$  can be exchanged with  $C_i$ , that is,  $C_v = C_i$  at any instant

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v \qquad \frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v$$

Since  $D_{rad} = d_iC_i + d_vC_v$  &  $C_i = C_v$ , but since  $d_i \gg d_v$ , then interstitials contribute more to atom mobility than do vacancies

4. Inclusion of sink terms violates the symmetry with respect to  $C_i$  and  $C_v$  because of different values of  $K_s$  ( $K_{vs} \neq K_{is}$ )
  - Symmetry is present in the steady state with regard to  $d_iC_i$  and  $d_vC_v$  since  $K_{is}$  and  $K_{vs}$  are proportional to  $d_i$  and  $d_v$ , respectively

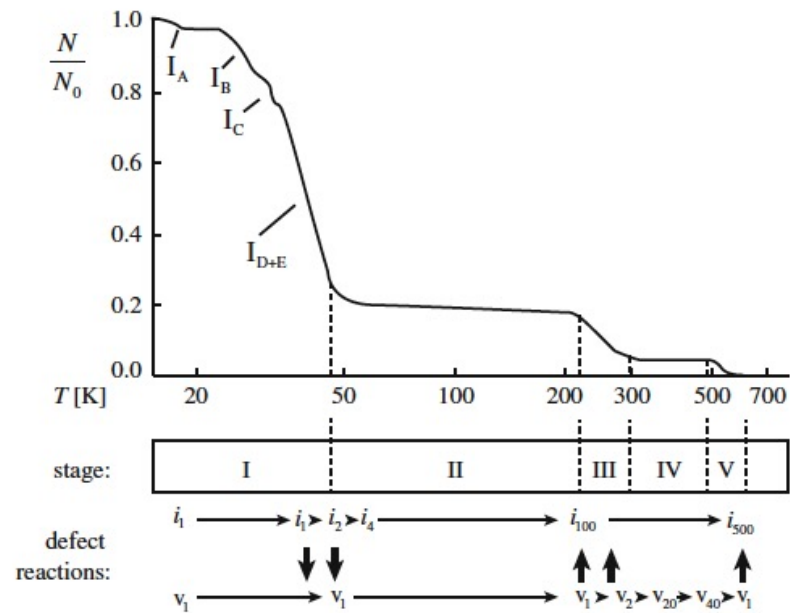


# Note on vacancy concentration

- $C_v$  must be accounted for thermal vacancies:
- Why are we ignoring this for interstitials?!

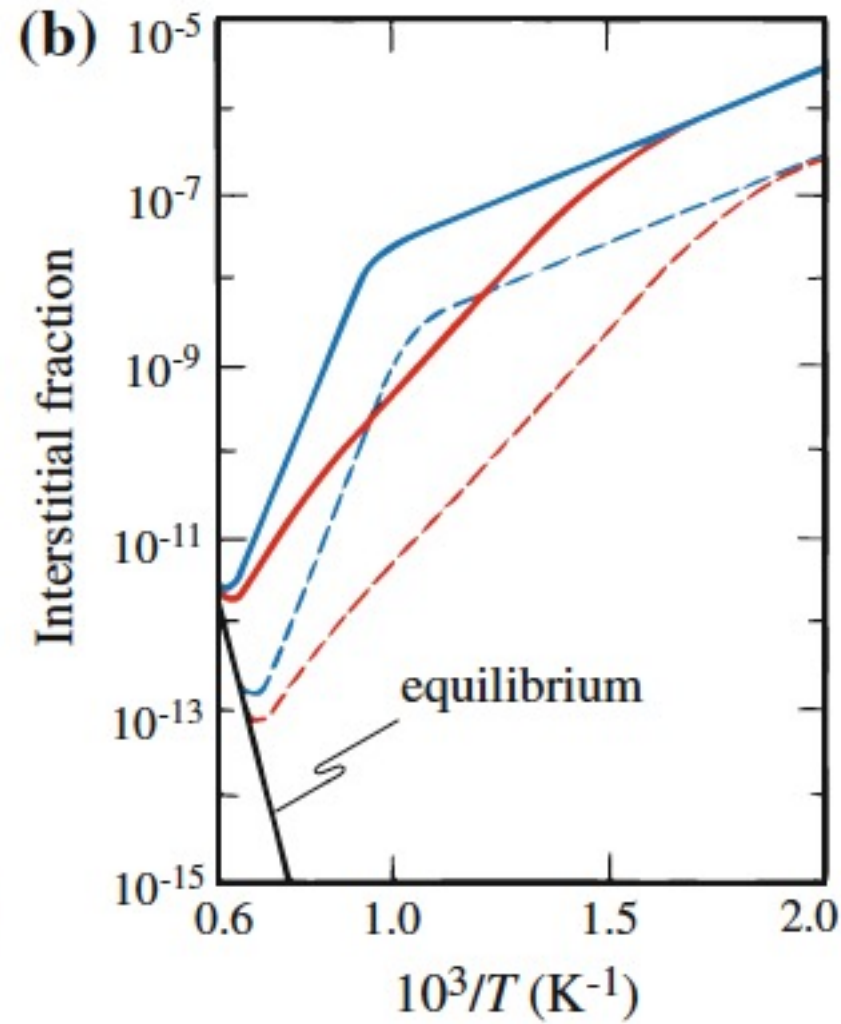
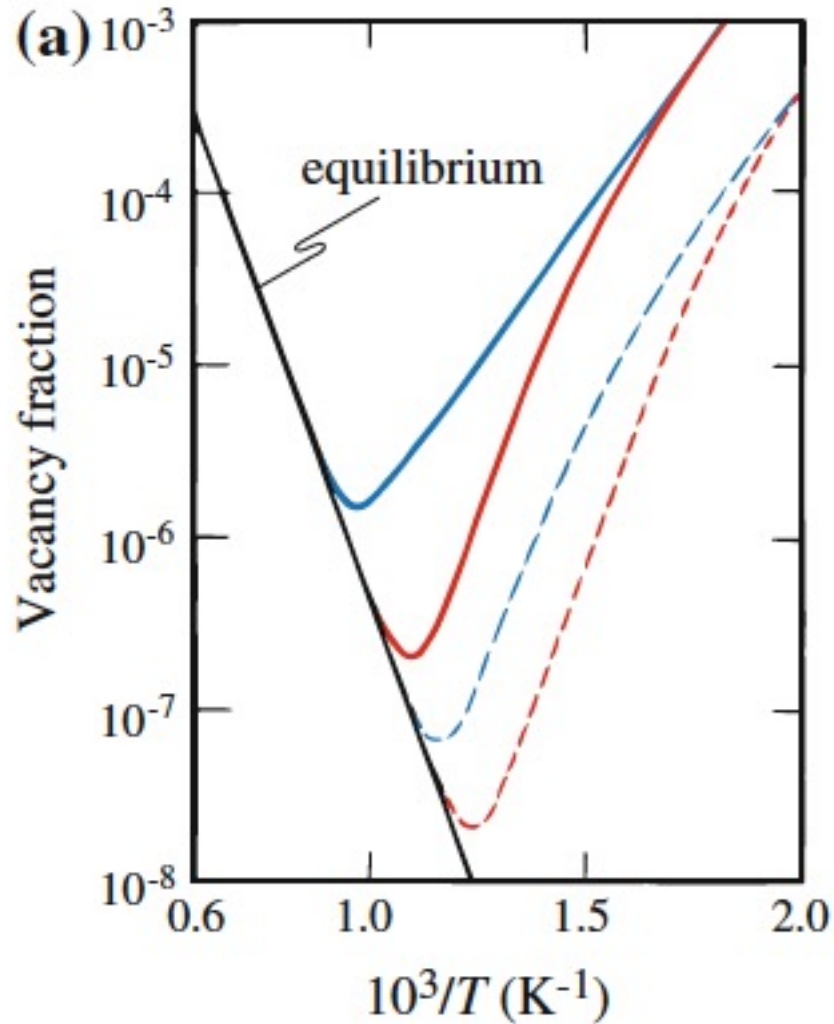
# Post-irradiation annealing

- No diffusion, no sinks, no irradiation:
- Integrating:
- Then:

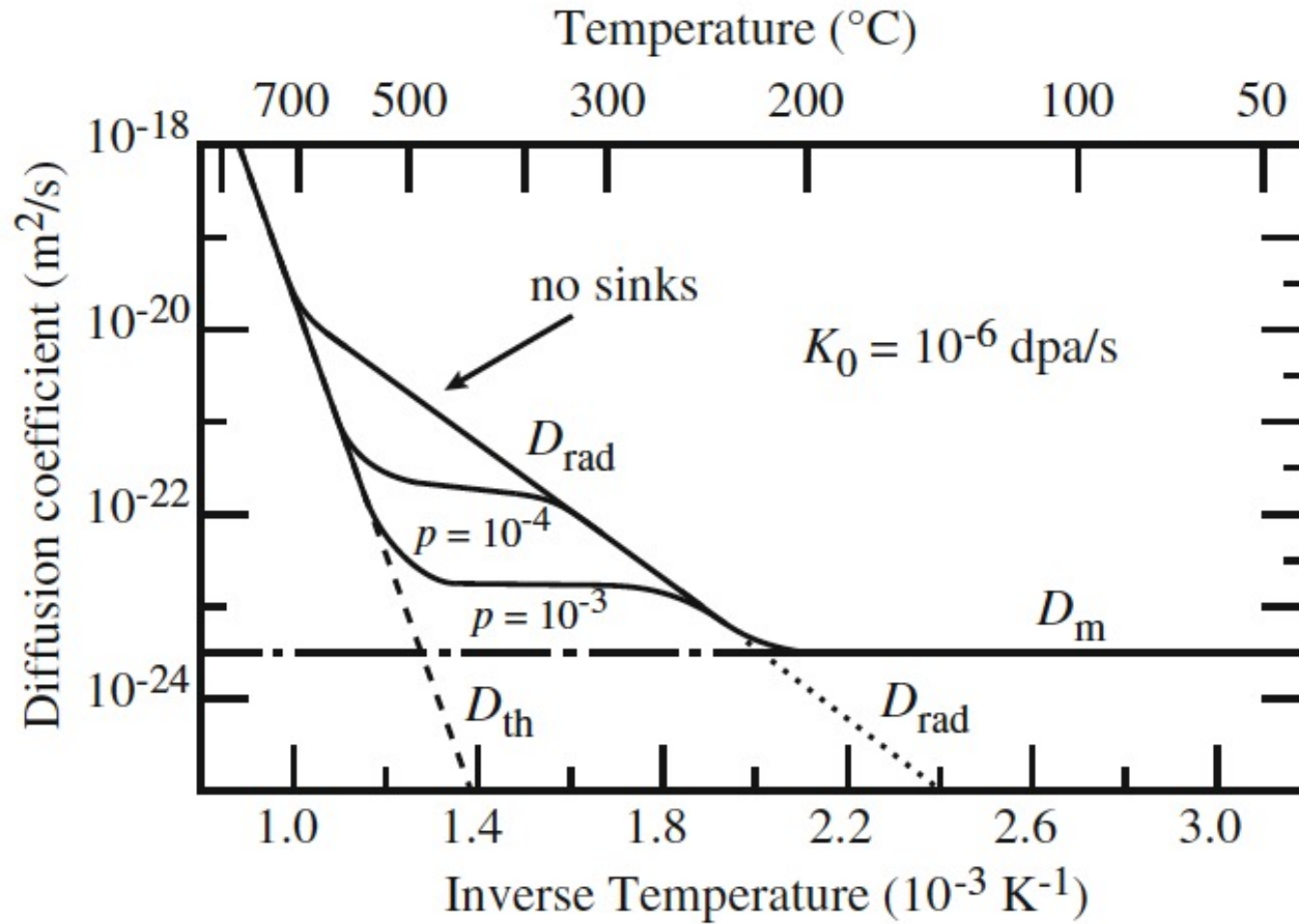


# Pulling this now together:

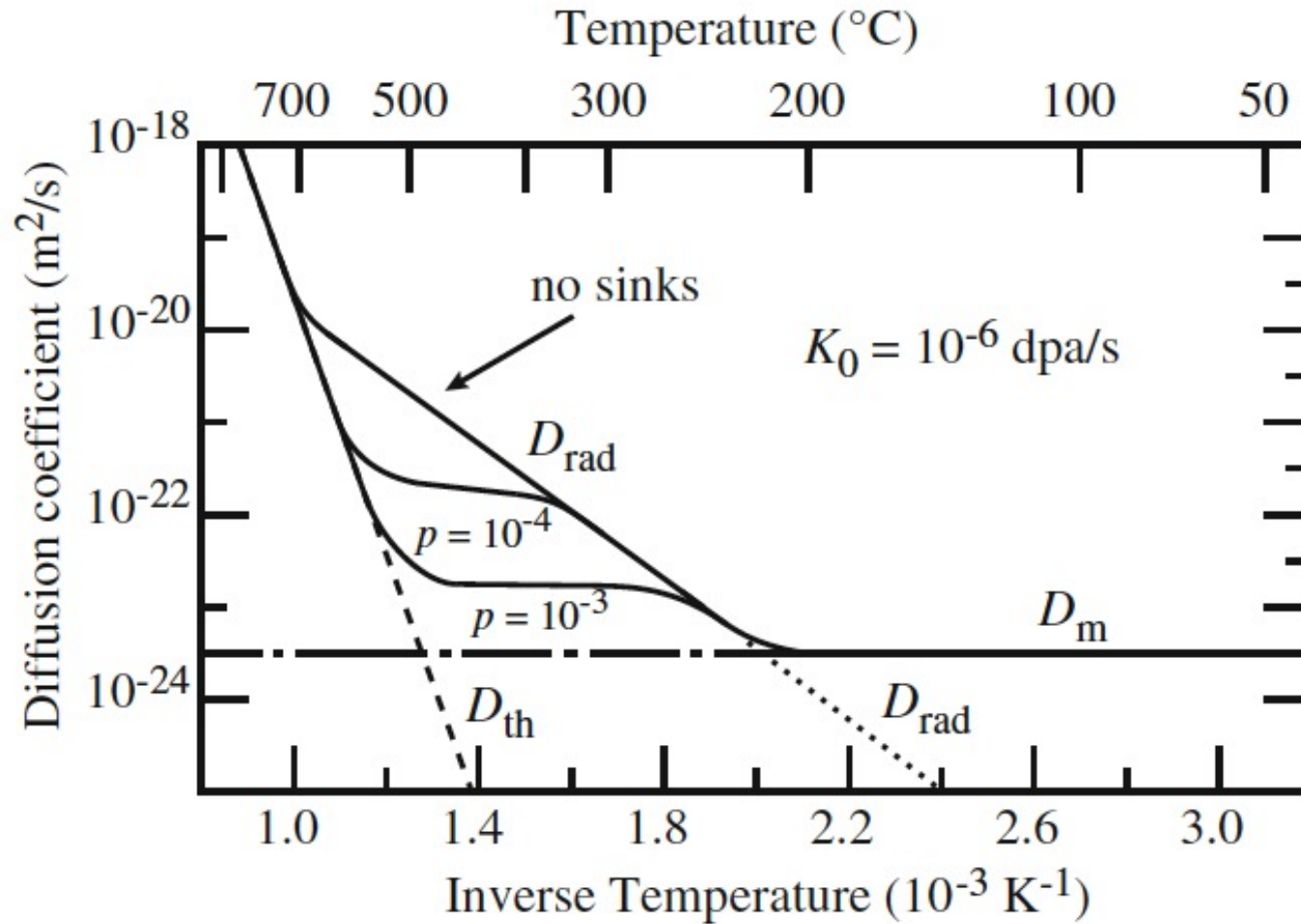
- upper solid line —  $K_0$  high  $\rho$  low
- lower solid line —  $K_0$  high  $\rho$  high
- upper dashed line —  $K_0$  low  $\rho$  low
- lower dashed line —  $K_0$  low  $\rho$  high



# Pulling this now together:



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The critical temperature below which mutual recombination will dominate, above which loss to sinks will dominate:

$$T_c = \frac{E_m^v}{k \ln \frac{2D_0^v C_s^2 K'_{is} K'_{vs}}{K_0 K'_{iv}}}$$

# Rate of Reaction

- We have now determined the relative change of  $C_i$  and  $C_v$ , but the **rates are dependent on the reaction rate constant**  $K_{AB} (s^{-1})$ , where the rate of reaction between A & B is:

$$K_{AB} C_A C_B \text{ reactions/cm}^3 s$$

- Analogous to first order chemical reactions
- We will consider two types of reactions:
  - Defect-defect reactions
  - Defect-extended sinks reactions





Questions?

