Kinetics

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Let's play a quick game:

Change =	Gain	-	Loss

Sinks

Diffusion

Recombination

Production

Gain

Loss

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

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

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

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

Point Defect Kinetic Equations

- If we neglect clustering:

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

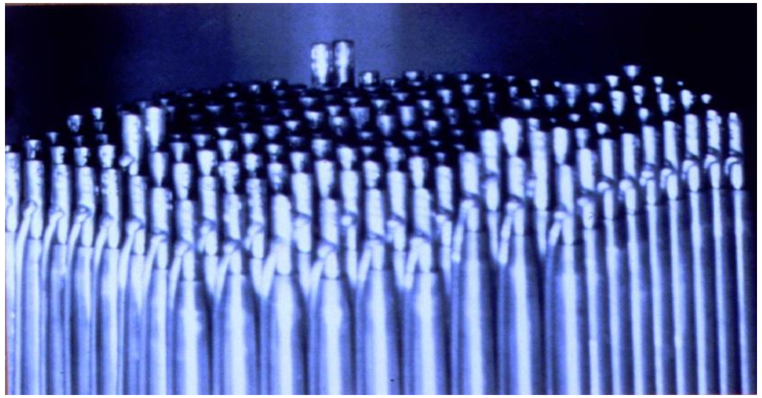
$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{is}C_iC_s + D_i\nabla^2 C_i$$

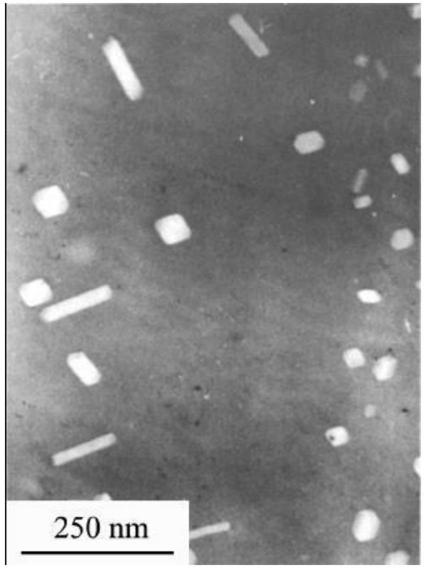
- Example of defect absorption to cavities and dislocations:

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

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

Swelling in fuel elements





Stainless Steel

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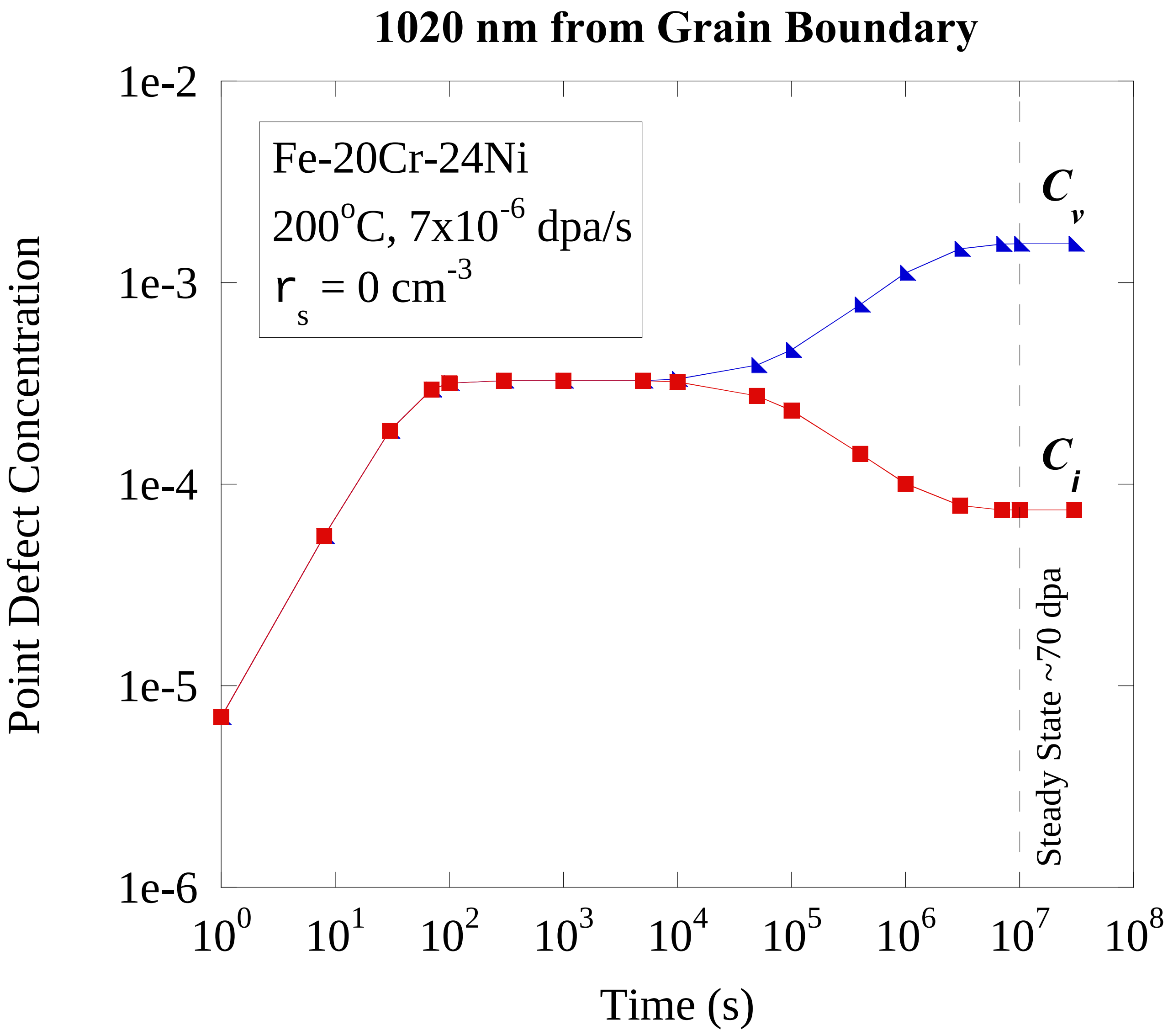
Results from MIK code for Fe-20Cr-24Ni at a damage rate of 7 x 10^{-6} dpa/s, T=200°C



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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 $dC/dt = \varepsilon K_0$ with $C_i \sim C_v$ so $C_i = C_v = C = \varepsilon K_0 t$
   - 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:

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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:

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

The time at which this occurs is given by:

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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:

$$C_v^{SS} = -\frac{K_{is}C_s}{2K_{iv}} + \left[\frac{K_0 K_{is}}{K_{iv}K_{vs}} + \frac{K_{is}^2 C_s^2}{4K_{iv}^2}\right]^{1/2}$$

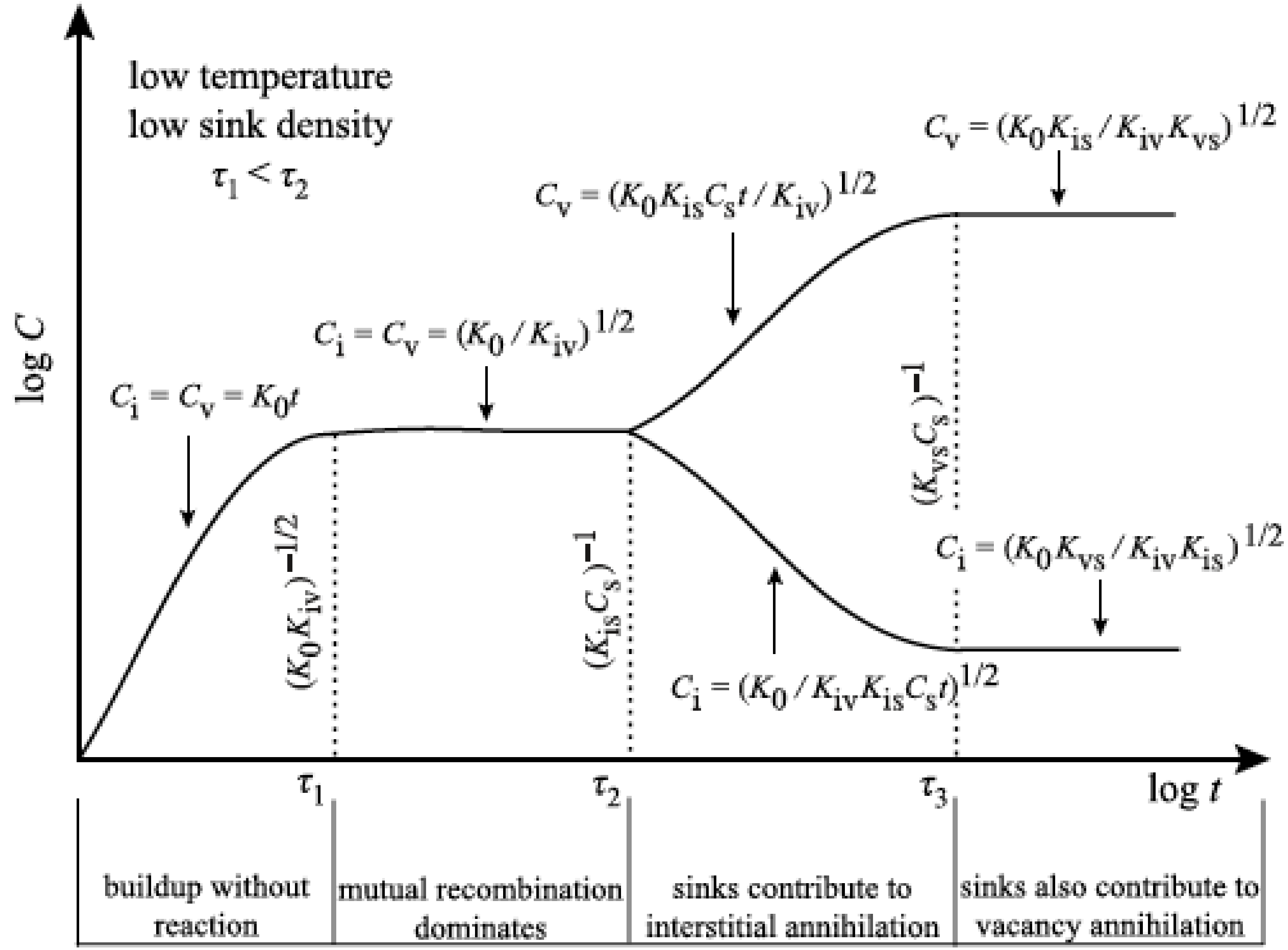
$$C_i^{SS} = -\frac{K_{is}C_s}{2K_{iv}} + \left[\frac{K_0 K_{vs}}{K_{iv}K_{is}} + \frac{K_{vs}^2 C_s^2}{4K_{iv}^2}\right]^{1/2}$$

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



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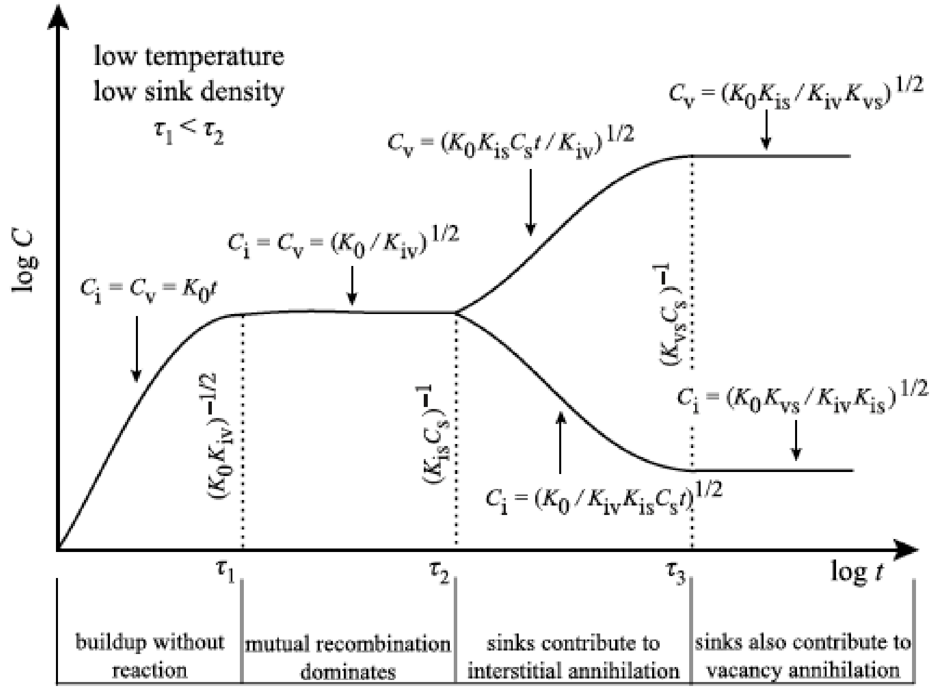
Example calculation for BCC Fe

- 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 ($\boldsymbol{a_0}$) of 2.82 Å
Dislocation density ($\boldsymbol{p_d}$) of 10^8 cm^{-2}
Interstitial migration energy ($\boldsymbol{E_m^i}$) of 0.65 eV
Vacancy migration energy ($\boldsymbol{E_m^v}$) of 1.5 eV
Capture radius($\boldsymbol{r_{iv}}$) of 10$\mathbf{a_0}$
Displacement rate ($\boldsymbol{K_0}$) of 10^{-7} dpa/s
Vibration frequency ($\boldsymbol{v}$) of 10^{13} 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

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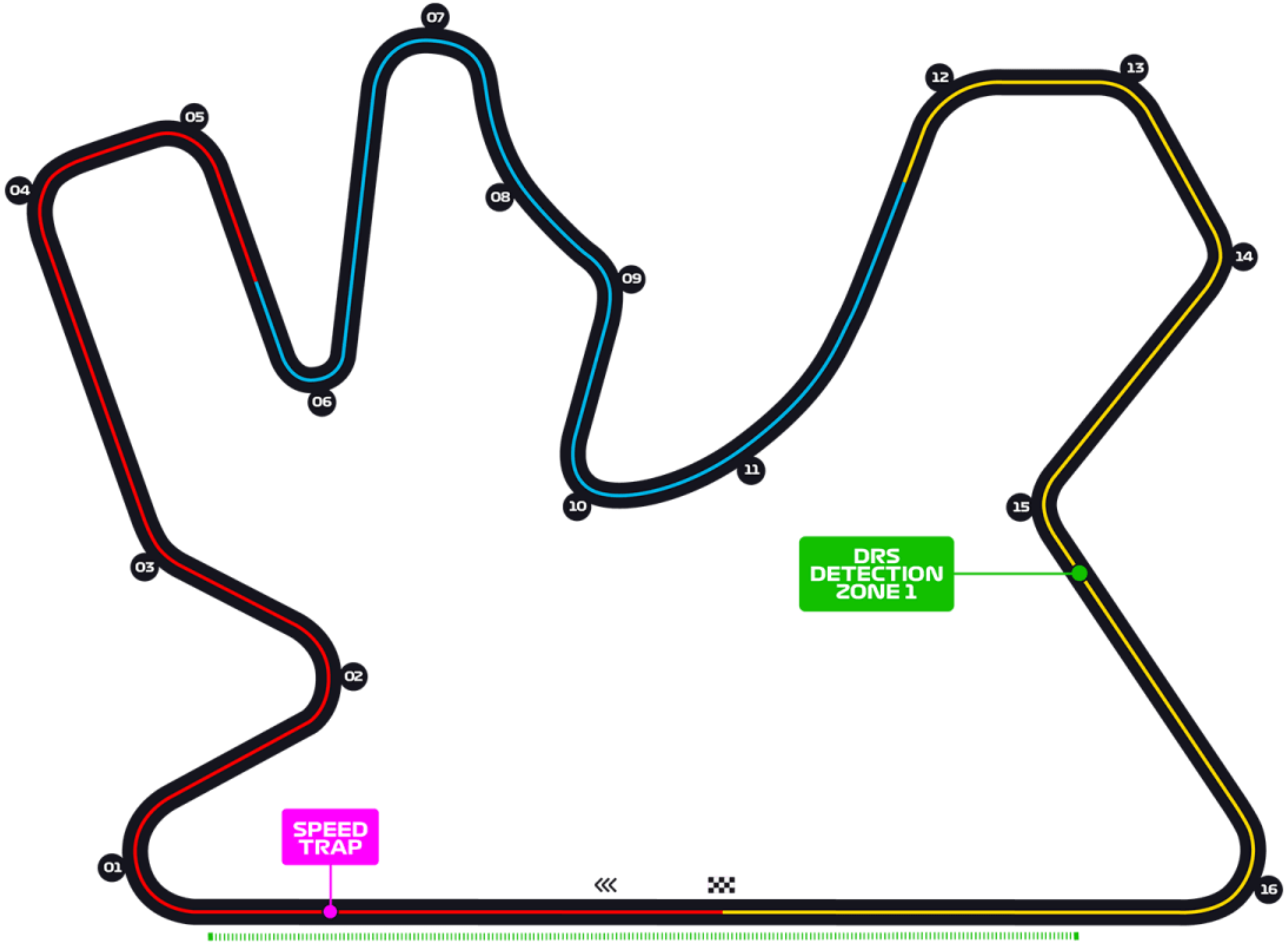
Example calculation for BCC Fe

- 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

The Losail International Circuit is 5.380 kilometers long and has 16 corners. The track was designed for motorbike racing, so it has a fast layout with many medium and high-speed corners. **What is the distance in meters from the pole position to the Turn 1 breaking point?**



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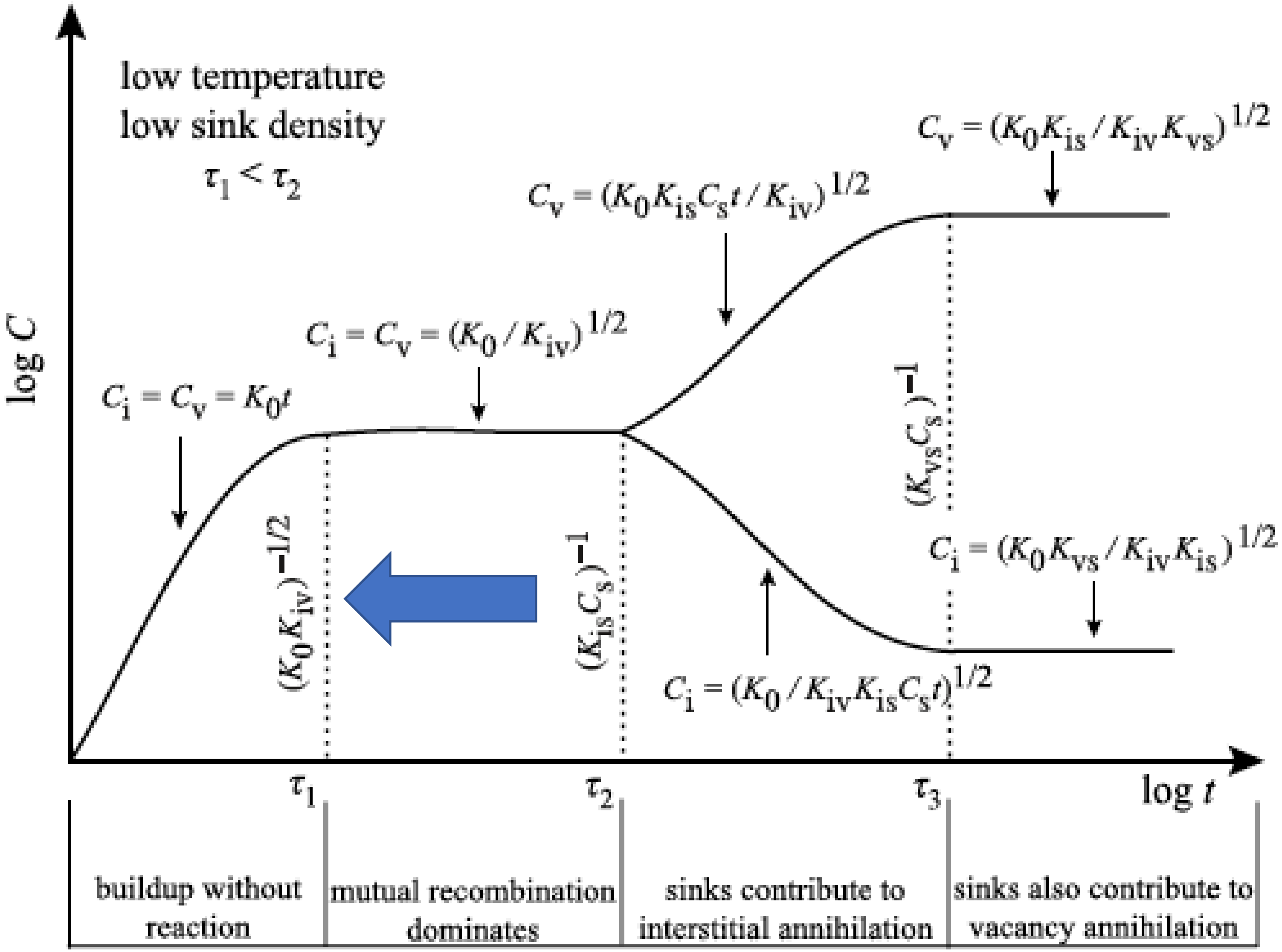
Low Temperature, Increasing Sink Density



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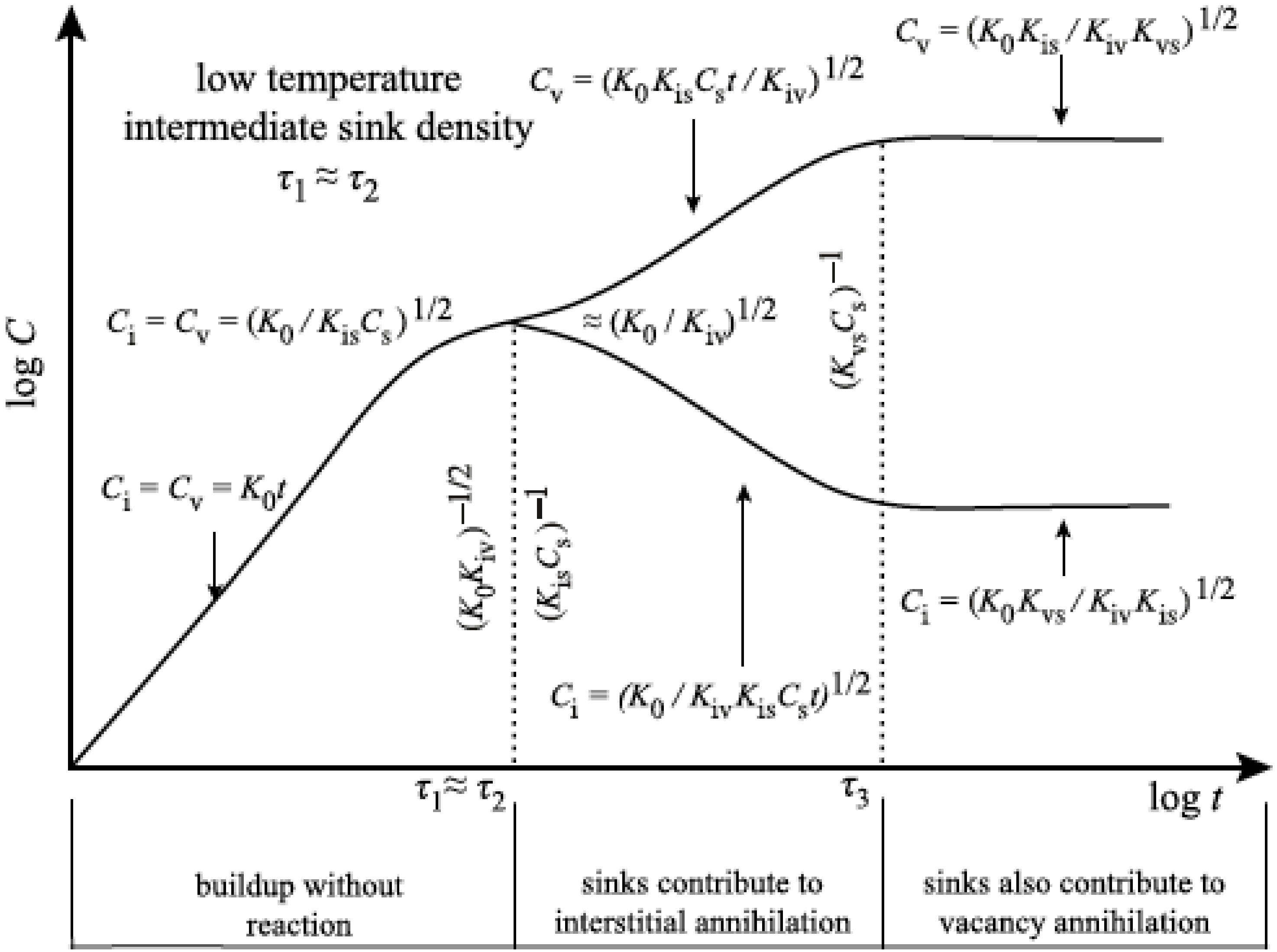
Low Temperature, Increasing Sink Density



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Low T, High C_s

- In this case, the interstitial concentration comes into a quasi-steady state with production and annihilation at sinks:

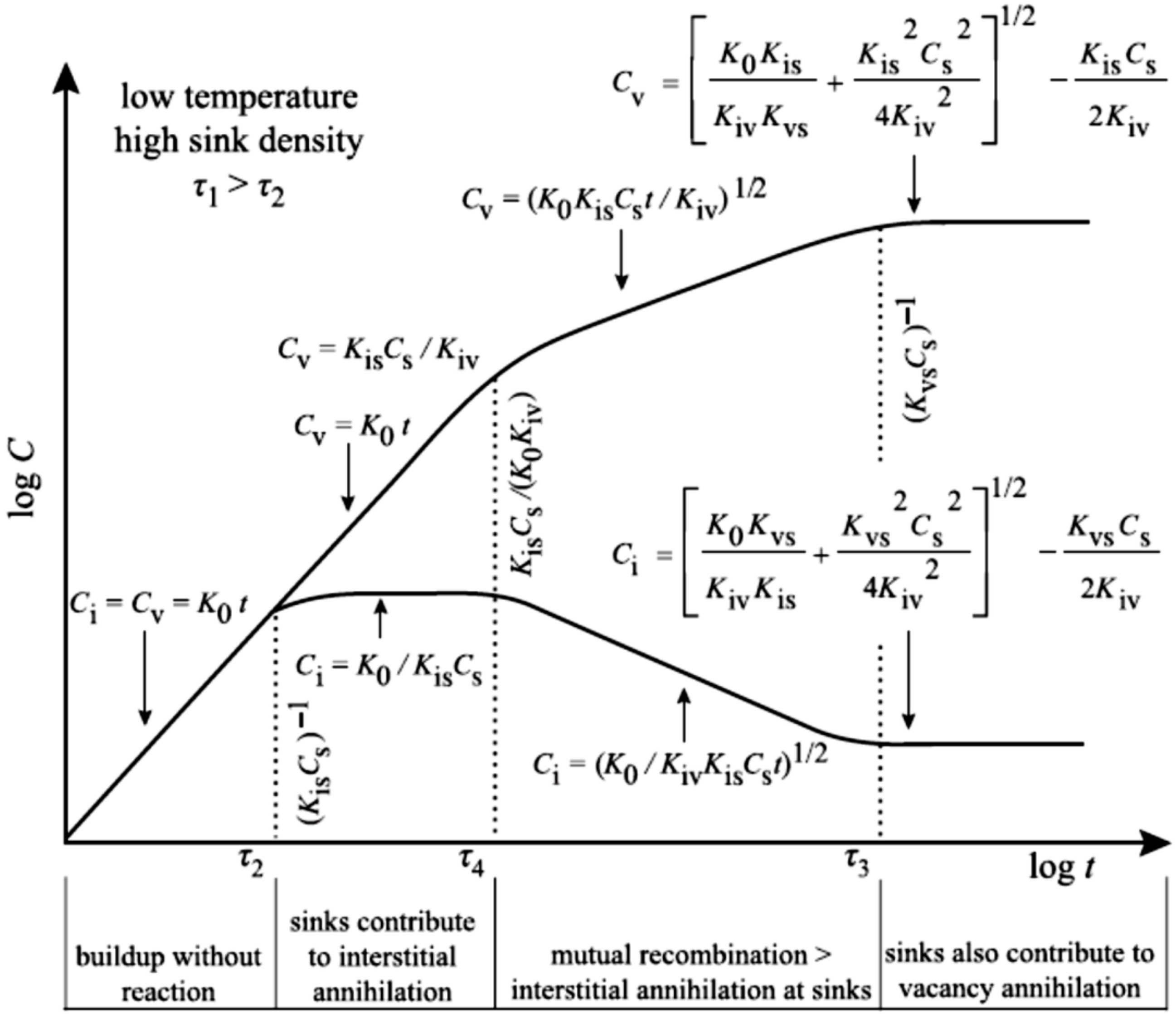
- Equating the interstitial concentrations in the linear buildup regime with the quasi-steady state regime:

Low T, High C_s

- A competition soon arises between the annihilation of interstitials at sinks and recombination with vacancies, such that:

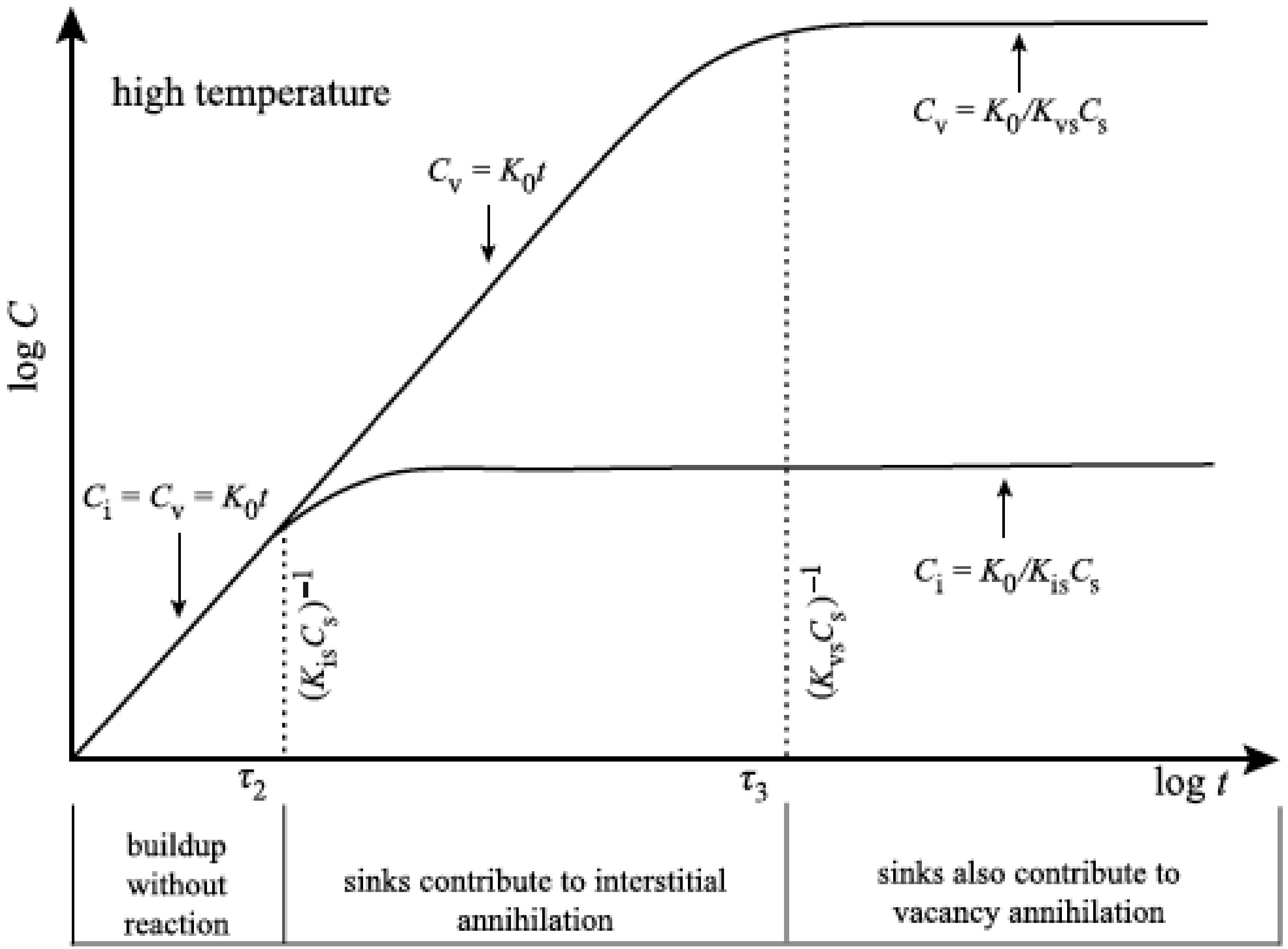
- Yielding the time constant for the transition between the regimes where interstitials go to sinks and mutual recombination dominates:

Low T, High C_s



low temperature
high sink density
$\tau_1 > \tau_2$
$C_v = \left[\frac{K_0 K_{is}}{K_{iv} K_{vs}} + \frac{K_{is}^2 C_s^2}{4K_{iv}^2}\right]^{1/2} - \frac{K_{is} C_s}{2K_{iv}}$
$C_v = (K_0 K_{is} C_s t / K_{iv})^{1/2}$
$C_v = K_{is} C_s / K_{iv}$
$C_v = K_0 t$
$C_i = C_v = K_0 t$
$C_i = K_0 / K_{is} C_s$
$K_{is} C_s / (K_0 K_{iv})$
$(K_{vs} C_s)^{-1}$
$(K_{is} C_s)^{-1}$
$C_i = \left[\frac{K_0 K_{vs}}{K_{iv} K_{is}} + \frac{K_{vs}^2 C_s^2}{4K_{iv}^2}\right]^{1/2} - \frac{K_{vs} C_s}{2K_{iv}}$
$C_i = (K_0 / K_{iv} K_{is} C_s t)^{1/2}$
log C
log t
τ_2
τ_4
τ_3
buildup without reaction
sinks contribute to interstitial annihilation
mutual recombination > interstitial annihilation at sinks
sinks also contribute to vacancy annihilation

High Temperature



Note on vacancy concentration

- C_v must be accounted for thermal vacancies:

- Why are we ignoring this for interstitials?!

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 Ci, 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 $d_i>>d_v$, 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

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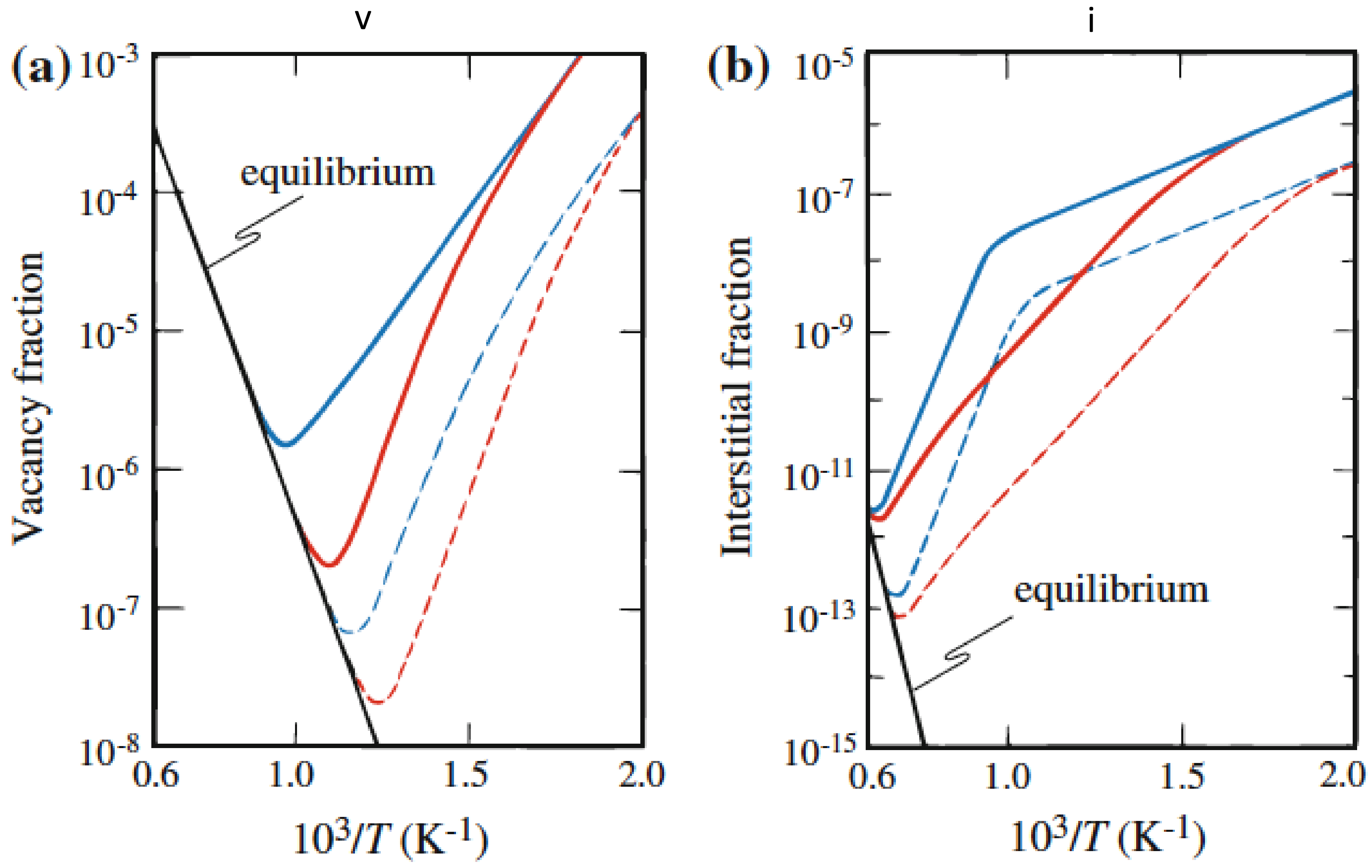
Pulling this now together:

upper solid line — K_0 high ρ low
lower solid line — K_0 high ρ high
upper dashed line — K_0 low ρ low
lower dashed line — K_0 low ρ high



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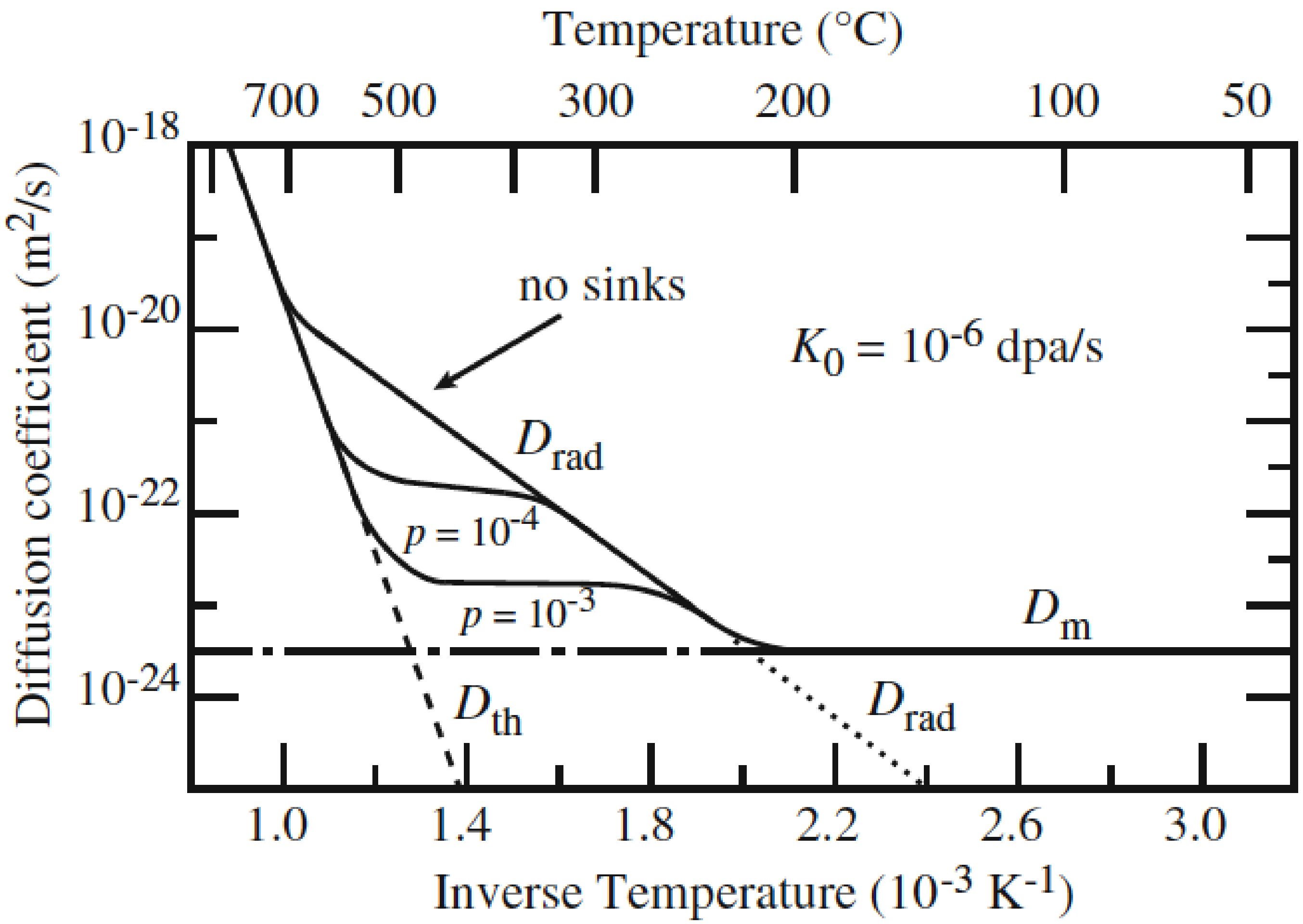

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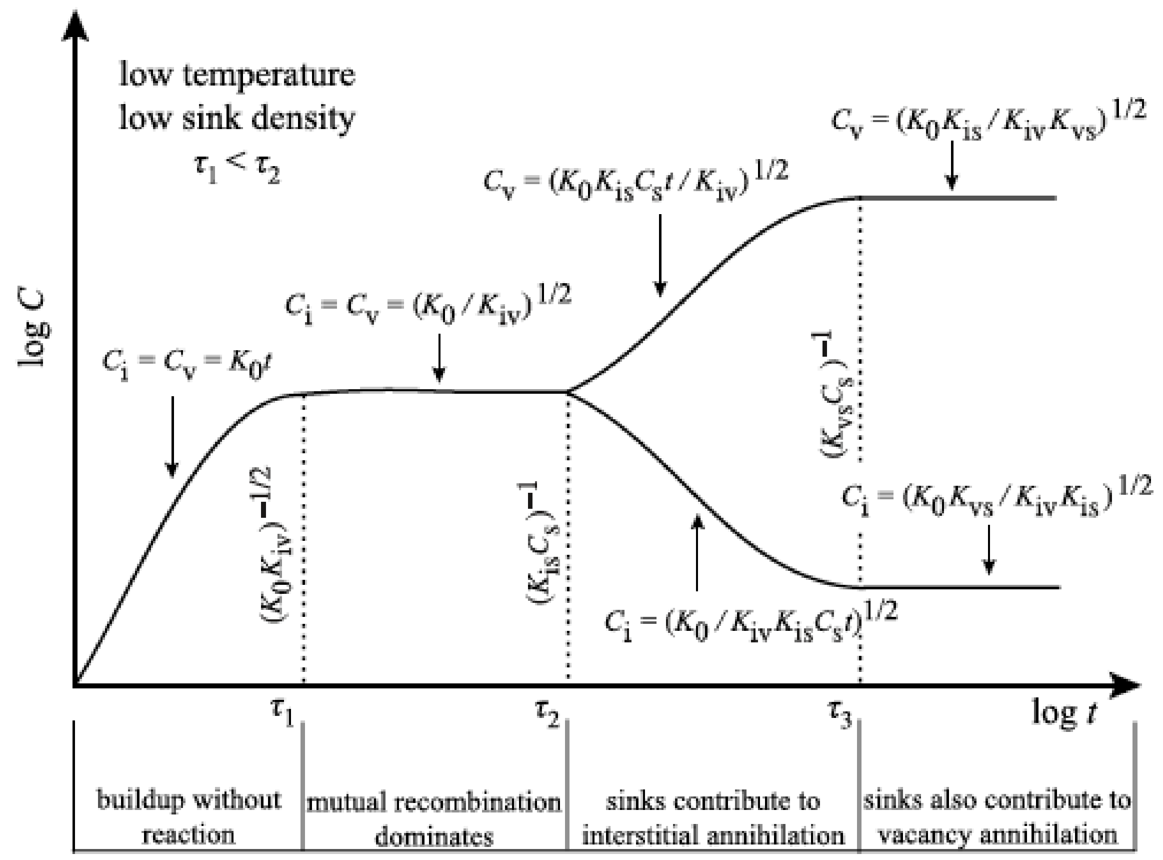
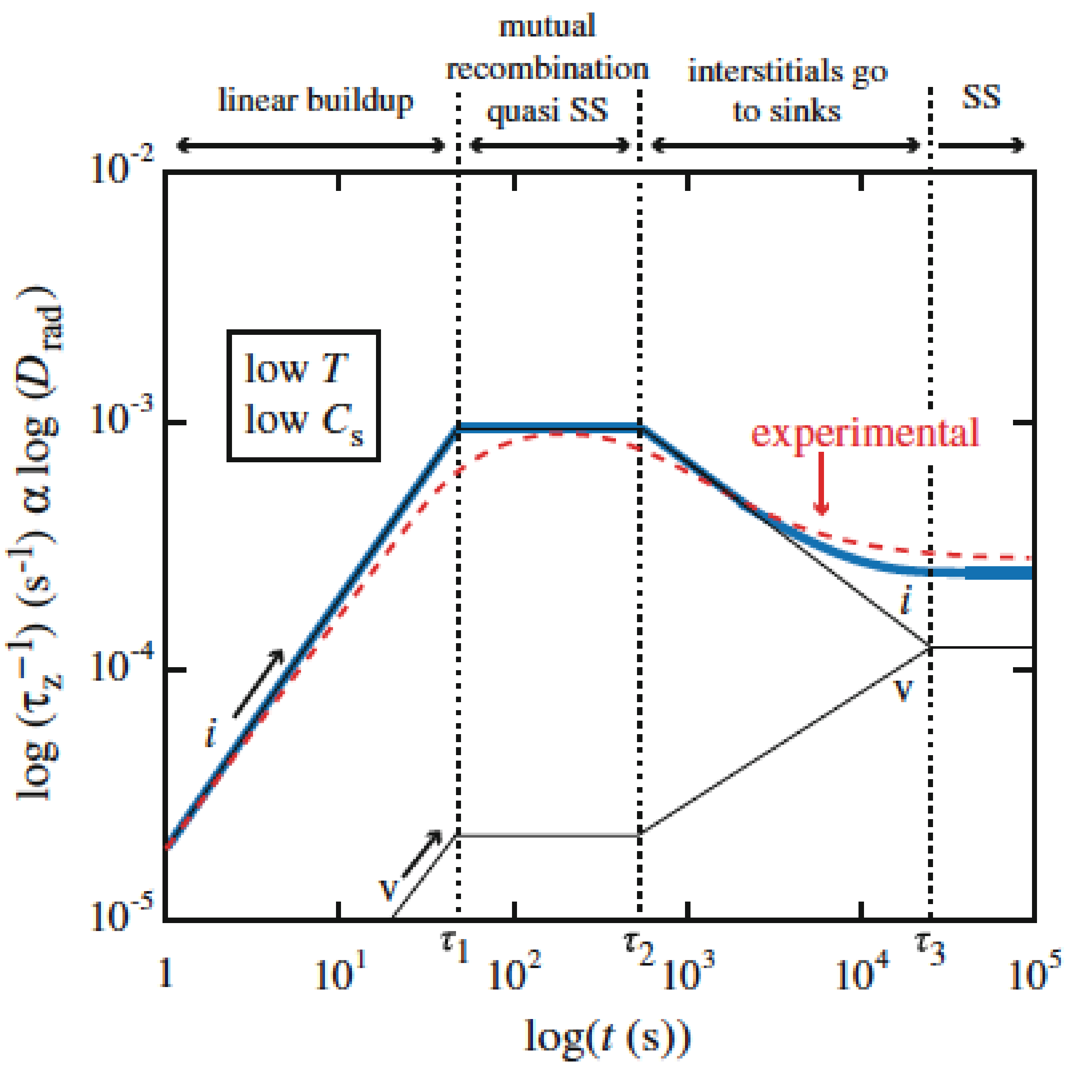
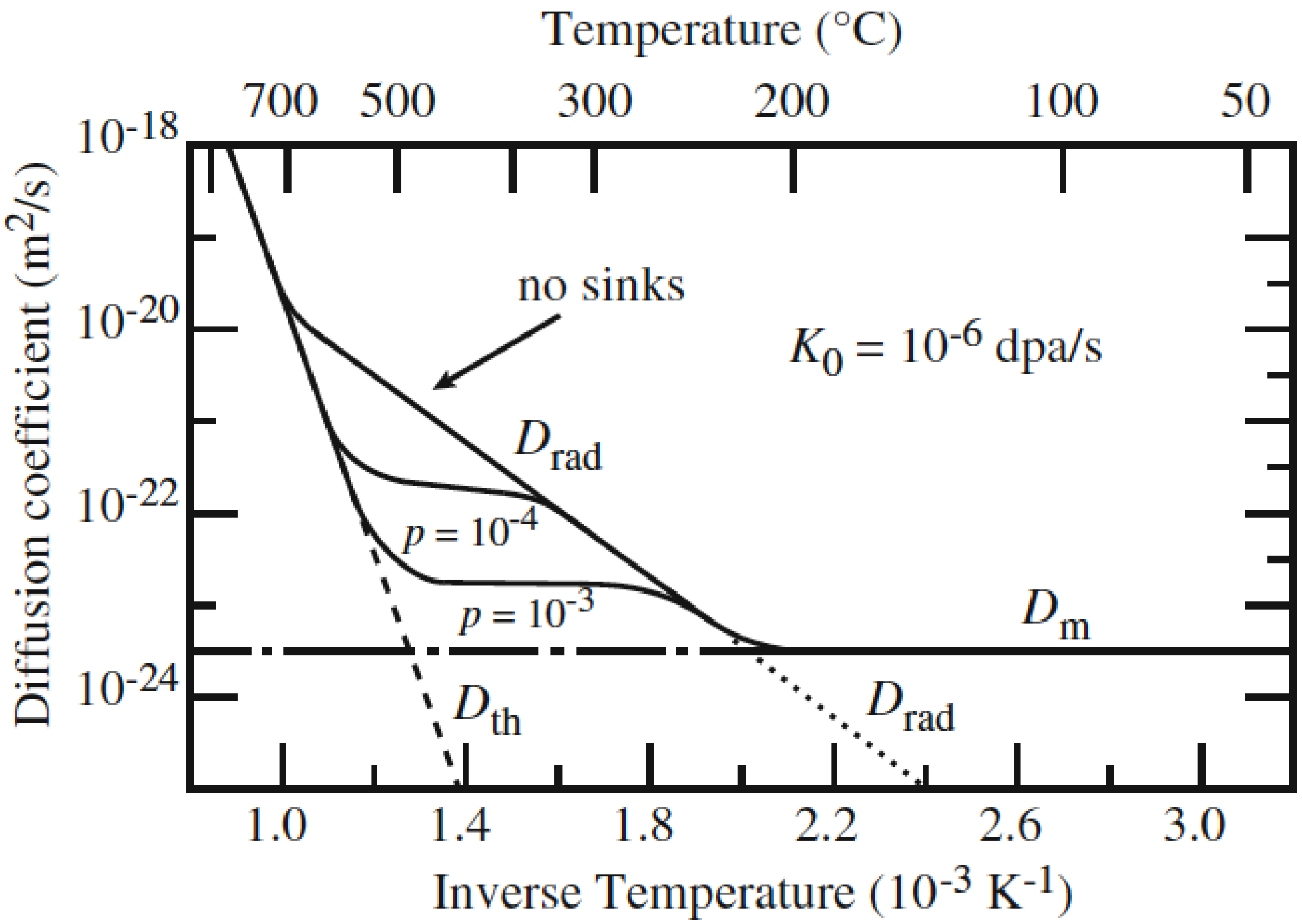




Log(D_{rad}) vs. log(t)

Pulling this now together:



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

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

Questions?