DiffusioninSolids

ISSUESTOADDRESS...

- How does diffusion occur?

- Whyis it animportant part of processing?

- Howcan therateofdiffusion be predictedforsome simplecases?

- How doesdiffusiondependonstructure and temperature?

1

Whatisdiffusion?

Phenomenonof material/mattertransportby atomic motion.

Oftenthink ofdiffusion inamedium where atomsare relatively free to move around such as liquidsandgases…

So,whydowecareaboutdiffusioninsolids?

e.g. **Materialsprocessing**
Manymaterialsare heattreated to achievenecessary properties:prefertodevelopmethods thatwillallow relatively highdiffusion rates toachievean efficient/cost-effectivelyprocess (e.g.alloying,case hardeningetc…)

2

PROCESSINGUSINGDIFFUSION(1)

- Case Hardening:
  - --Diffuse carbon atoms intothehostironatomsatt hesurface.
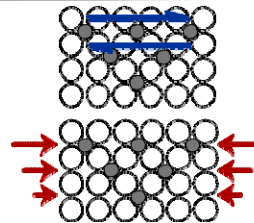 - --Exampleofinterstitial diffusionisacasehard enedgear.

- Result:The "Case" is
  - --hardtodeform:Catoms"lock" planesfromshearing.
  - --hardtocrack:Catomsputthes urfaceincompression.

Fig.5.0, *Callister6e.* (Fig.5.0 is courtesyof Surface Division,Mi dland- Ross.)

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PROCESSINGUSINGDIFFUSION(2)

- DopingSiliconwithPforn-type semiconductors:
- Process:

  1. DepositPrich layersonsurface.

     silicon

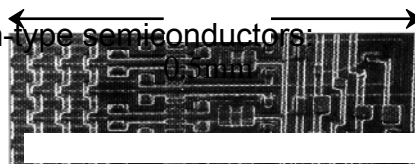   eat.H2it.

  3. Result:Doped semiconductor regions.
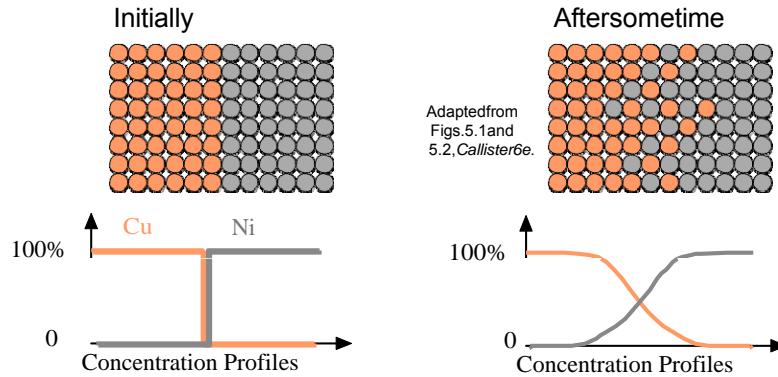
     silicon

0.5mm

magnifiedimageofacomputerchip

Fig.18.0, *Callister6e.*

light regions: Si atoms

light regions: Al atoms

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DIFFUSION: THE PHENOMENON

• Interdiffusion:Atomsofonematerialdiffusingintoanotherandviceversa.
e.g. Inanalloy,atomstendtomigratefromregionsoflargeconcentration.

Initially   Aftersometime

Adaptedfrom
Figs.5.1and
5.2,*Callister6e.*

Cu   Ni

100%

0
Concentration Profiles

100%

0
Concentration Profiles

Considerasaconcentrationgradient(atomsmovefromhighconc.to
lowconc.).

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DIFFUSION: THE PHENOMENON

• Self-
diffusion:Atomswithinonematerialexchangingpositions.(i.
e.Inanelementalsolid,atomsalsomigrate).

Labelsomeatoms

C

A

D

B

Aftersometime

C

D

A

B
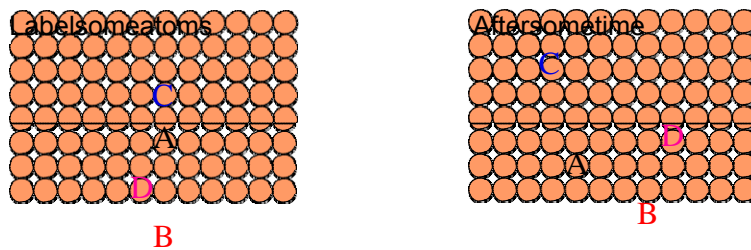
6

Diffusionmechanisms

Howdoatomsmoveinacrystallinesolid?

Fordiffusiontooccur:
1. Adjacentsite needstobe empty (vacancy or interstitial).
2. Sufficientenergy mustbeavailabletobreak bonds and overcome lattice distortion.

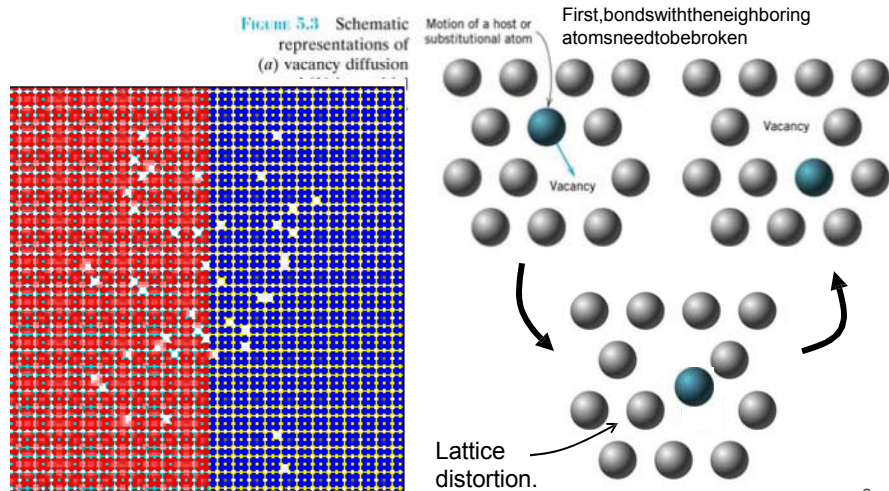There are many possiblemechanismsbut let'sconsider thesimplecases:
1. Vacancydiffusion.
2. Interstitialdiffusion.

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Vacancydiffusion

-An atom adjacenttoa vacantlattice site moves into it.

FIGURE 5.3 Schematic representations of (a) vacancy diffusion

Motion of a host or substitutional atom

First,bondswiththeneighboring atomsneedtobebroken

Vacancy

Vacancy

Lattice distortion.

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InterstitialDiffusion

-migrationfromone interstitialsite toanother (mostlyforsmall atoms thatcan be interstitial impurities: e.g.H,C, N,andO).

Position of interstitial atom before diffusion

Position of interstitial atom after diffusion

(b)
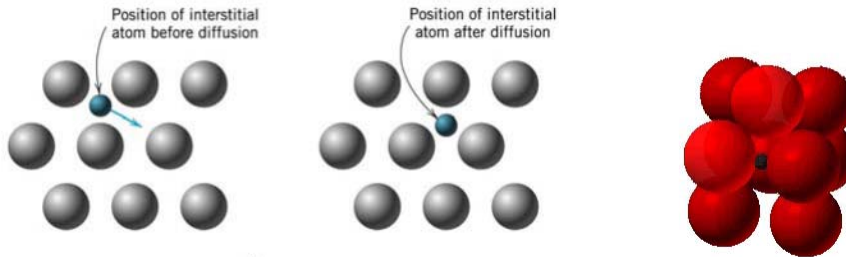
Callisterfig.5.3
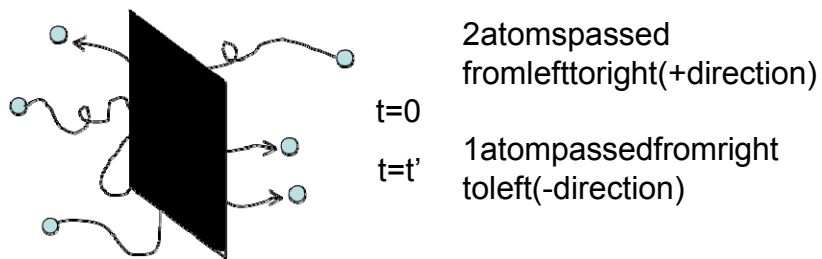
Typicallymorerapidthanvacancydiffusion.

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MODELINGDIFFUSION: FLUX

Consider atoms(ormass,M) goingthrough aplane

2atomspassed fromlefttoright(+direction)

t=0

t=t'

1atompassedfromright toleft(-direction)

Netresult:

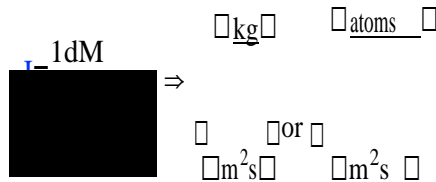$$\frac{1atom}{area \times t'} \quad \text{or} \quad \frac{M}{At'}$$

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MODELINGDIFFUSION: FLUX
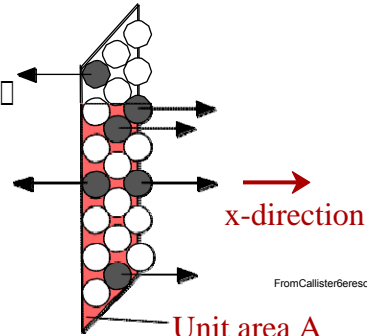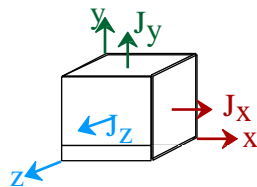
- Flux:

$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{kg}{m^2 s}\right] \ or \ \left[\frac{atoms}{m^2 s}\right]$$

- DirectionalQuantity

J_y, J_x, J_z, x, y, z

x-direction

FromCallister6eresource CD.

Unit area A through which atoms move.

- Flux can be measuredfor:
  - --vacancies
  - --host(A)atoms
  - --impurity(B)atoms

Ingeneral:diffusionflux may ormay notbe thesameovertime

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MODELINGDIFFUSION

Whatcausesnetflowofatoms?

- Concentration Profile,$C(x)$:$[kg/m^3]$

Cu flux   Niflux

Concentration of Cu $[kg/m^3]$

Concentration of Ni $[kg/m^3]$
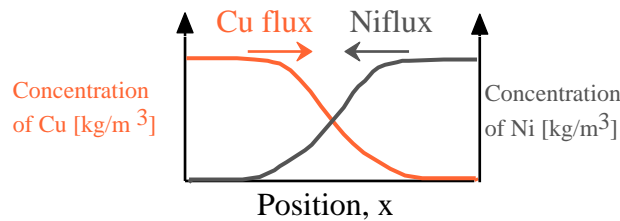
Adaptedfrom Fig.5.2(c), *Callister6e.*

Position, x

- Fick'sFirstLaw:

flux in x-dir. $[kg/m^2\text{-}s]$

Diffusion coefficient$[m^2/s]$

concentration gradient $[kg/m^4]$

$$J_x = -D\frac{dC}{dx}$$

- The steeper the concentrationprofile, the greater the flux! 12

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Steady-state diffusion

- Steady State: the concentration profile doesn't change with time.

J_x(left) → | box | → J_x(right)

Steady State:

J_x(left) $= J_x$(right)

x
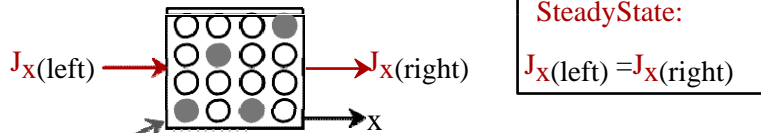
Concentration, C, in the box doesn't change w/time.

- Apply Fick's First Law:

$$J_x = -D \frac{dC}{dx}$$

- If J_x)$_{left}$ $= J_x$)$_{right}$, then

$$\left(\frac{dC}{dx}\right)_{left} = \left(\frac{dC}{dx}\right)_{right}$$

- Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position)!

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EX: STEADY-STATE DIFFUSION

- Steel plate at 700C with geometry shown:

Carbon rich gas

$C = 1.2 kg/m^3$

$C = 0.8 kg/m^3$

Steady State = straight line!

Carbon deficient gas

$D = 3 \times 10^{-11} m^2/s$

Adapted from Fig.5.4, *Callister 6e.*

0   x_1 x_2

5mm   10mm
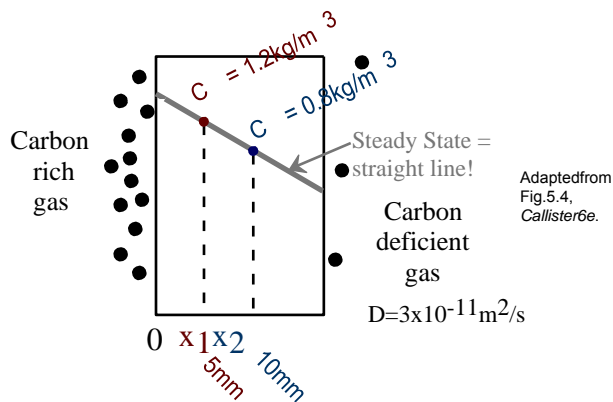
- Q: How much carbon transfers from the rich to the deficient side?

$$J = -D \frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9} \quad \frac{kg}{m^2 s}$$

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Note that we'd have to remove carbon from the right side and add to the left side to keep a constant flux.

Possible in the previous example of processing using gas source that can be added and removed but in many cases this may not be possible….

— **Nonsteady-state diffusion**

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Nonsteady-state diffusion

From Fick's 1stLaw:

$$J = -D \frac{dc}{dx}$$

Take the first derivative w.r.t. x:

$$\frac{dJ}{dx} = -\frac{d}{dx}\left(D \frac{dc}{dx} \right)$$

$J_l \longrightarrow \longrightarrow J_r$

$\overleftrightarrow{dx}$ $c = conc.$ $inside box$

Conservation of mass:

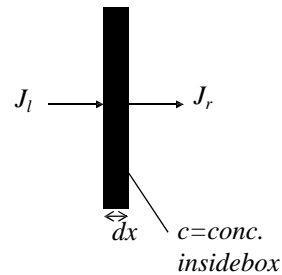$$-\frac{dc}{dt} = -\frac{J_r - J_l}{dx} = \frac{dJ}{dx}$$

i.e. fluxes to left and to right have to correspond to concentration change.
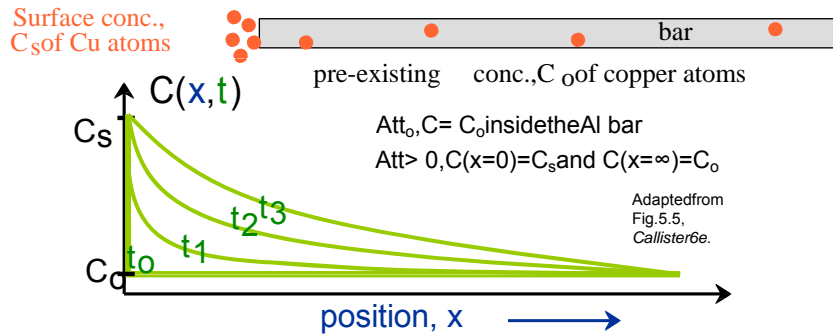
Sub into the first derivative:

$$\frac{dc}{dt} = \frac{d}{dx}\left(D \frac{dc}{dx} \right)$$ Fick's 2nd law

Partial differential equation. We'll need boundary conditions to solve…16

EX:NONSTEADY-STATE DIFFUSION

• Copper diffuses into a bar of aluminum (semi infinite solid).

Surface conc.,
C_s of Cu atoms

bar

pre-existing conc., C_o of copper atoms

$C(x,t)$

C_s

At t_o, $C = C_o$ inside the Al bar
At $t > 0$, $C(x=0) = C_s$ and $C(x=\infty) = C_o$

t_2 t_3

t_o t_1

C_o

Adapted from Fig. 5.5, *Callister 6e.*

position, x

• General solution:

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

"error function"

Values calibrated in Table 5.1, *Callister 6e.*

From Callister 6e resource CD.

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If it is desired to achieve a specific concentration C_1

i.e.

$$\frac{C(x,t) - C_o}{C_s - C_o} = \frac{C_1 - C_o}{C_s - C_o} = \text{constant}$$

which leads to:

Specified with C_1

$$\frac{x}{2\sqrt{Dt}} = \text{constant}$$

Known for given system

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Table 5.1 Tabulation of Error Function Values

z	$erf(z)$	z	$erf(z)$	z	$erf(z)$
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

Table 5.2 A Tabulation of Diffusion Data

Diffusing Species	Host Metal	$D_o(m^2/s)$	Activation Energy Q_d kJ/mol	Activation Energy Q_d eV/atom	Calculated Values $T(°C)$	Calculated Values $D(m^2/s)$
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α-Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

Source: E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.

PROCESSINGQUESTION

- Copper diffusesintoa barofaluminum.
- 10hoursat 600C givesdesiredC(x).
- Howmanyhourswould it take to get the sameC(x) if weprocessedat 500C?

   Keypoint1: $C(x,t_{500C})=C(x,t_{600C})$.
   Key point 2: Bothcaseshavethe same$C_o$andC_s.

- Result:Dt shouldbe heldconstant.

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \longrightarrow (Dt)_{500°C} = (Dt)_{600°C}$$

- Answer: $t_{500} = \dfrac{(Dt)_{600}}{D_{500}} = 110hr$

   $5.3 \times 10^{-13} m^2/s$ (10hrs)

   $4.8 \times 10^{-14} m^2/s$

   Note:values ofDare providedhere.

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Temperaturedependence

pre-exponential[m^2/s]

activationenergy [J/mol],[eV/mol]

diffusivity $\quad D = D_O \exp \left[-\dfrac{Q_d}{RT} \right]$ (seeTable5.2, *Callister6e*)

gasconstant [8.31J/mol-K]
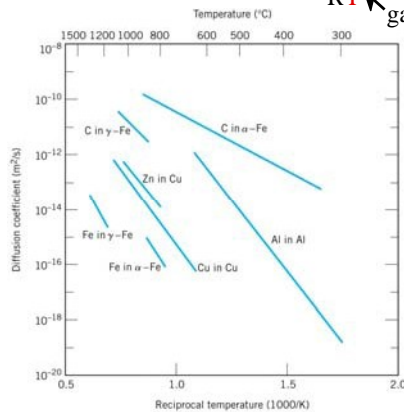
Dhasexp.dependenceonT
Recall:Vacancydoesalso!

$D_{interstitial} \gg D_{substitutional}$

|	
Cinα-Fe	Cu in Cu
Cinγ-Fe	Al in Al
	Feinα-Fe
	Feinγ-Fe
	Zn in Cu

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Diffusion:designexample

- During a steelcarburizationprocess at 1000°C, there is a drop incarbon concentrationfrom 0.5at% to0.4 at% between1mmand2mmfromthesurface(γ-Feat 1000°C).

  – Estimatetheflux ofcarbonatomsatthesurface.
  D_o=2.3x10^{-5}m^2/sforCdiffusioninγ-Fe.

  Q_d=148kJ/mol

  $\rho_{\gamma-Fe}$=7.63g/cm^3
  A_{Fe}= 55.85 g/mol

  – IfwestartwithC$_o$=0.2wt%andC$_s$=1.0wt%howlongdoesit taketoreach0.6wt%at0.75mmfromthesurfacefordifferent processingtemperatures?

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Diffusion:designexamplecont'd
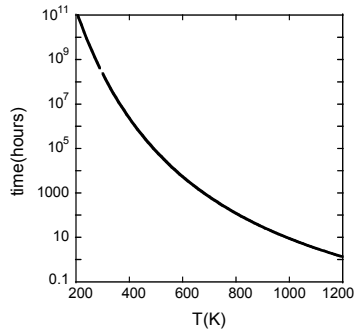
T(ºC)	t(s)	t(h)	
300	8.5x 10^{11}	2.4x10^8	➔ **27782yrs!**
900	106,400	29.6	
950	57,200	15.9	
1000	32,300	9.0	
1050	19,000	5.3	

Needtoconsiderfactorssuchascostofmaintainingfurnaceatdifferent Tforcorrespondingtimes.

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Designexample2

Metal plate

H_2 (0.1013MPa)

H_2 (0.051MPa)

N_2 (0.1013MPa)

N_2 (0.01013MPa)

Δx

Concentrations(inmol/m³)

$$C_{H_2} = 2.5 \times 10^3 \sqrt{p_{H_2}} \exp\left[-\frac{27.8kJ/mol}{RT}\right]$$

$$C_{N_2} = 2.75 \times 10^3 \sqrt{p_{N_2}} \exp\left[-\frac{37.6kJ/mol}{RT}\right]$$

Diffusioncoefficients (inm²/s)

$$D_{H_2} = 1.4 \times 10^{-7} \exp\left[-\frac{13.4kJ/mol}{RT}\right]$$

$$D_{N_2} = 3.0 \times 10^{-7} \exp\left[-\frac{76.15kJ/mol}{RT}\right]$$

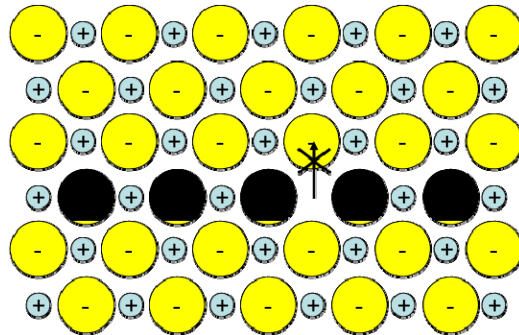Giventheaboveinfo, determinewhetherornotit will bepossibletousethismetalplateforgasseparation. Ifso,at whattemperature?

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Diffusionin ionicsolids

Needto considercoulombinteractionsbetweenions…

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Diffusionin ionicsolids

Whichdoyouexpecttodiffusefaster,cationsora
nions?

Smallercationswillusuallydiffusefaster.Butanal
ogoustochargeneutralityrequiredfordefectform
ation,eachionwillneedcounterchargetomovewit
hit(e.g.vacancy,impurityorfreeelectronsorholes
).

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STRUCTURE&DIFFUSION

Diffusion FASTER for...	Diffusion SLOWER for...
• opencrystal structures	• close-packedstructures
• lower meltingTmaterials	• highermeltingTmaterials
• materials w/secondary bonding	• materialsw/covalent bonding
• smallerdiffusingatoms	• largerdiffusing atoms
• lower densitymaterials	• higher density materials

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Conceptsto remember

- Diffusionmechanismsandphenomena.
  - Vacancy diffusion.
  - Interstitialdiffusion.
- Importance/usefulnessofunderstandingd iffusion(especiallyinprocessing).
- Steady-statediffusion.
- Nonsteady-statediffusion.
- Temperaturedependence.
- Structuraldependence(e.g.sizeofthediffusingato ms,bondingtype,crystalstructureetc.).

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