

Notes on Diffusion

- Diffusion is encountered in many physical phenomena: e.g. heat transfer, liquid transport, transport of electrons in electrical conductor. It is a fundamental feature of "transport".
- It always has units of m^2/s i.e. $(\text{length})^2 s^{-1}$.
- Its unit gives the following scaling relationship

$$6Dt = L^2 \quad \text{--- (1)}$$

↑ three dimensional nature of transport

L = diffusion distance

t = time

For example, the Eq. (1) can be used to calculate the depth of doping of silicon with, say, aluminum, deposited on its surface at a given time & temperature.

Phenomenological Form

$$D = D_0 e^{-\frac{Q}{RT}} \quad \text{--- (2)}$$

$\frac{Q}{RT}$ is dimensionless. ∴ Q - J/mole.

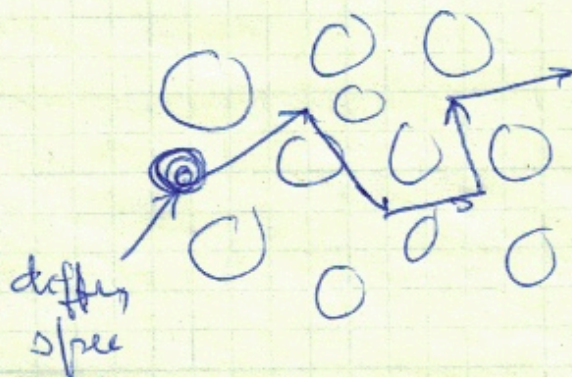
R - J/(mol.K).

D_0 m^2/s .

T = Kelvin

Physical Basis of Eq. (2)

It starts with a consideration of the physical mechanism.



The diffusing species moves by "jumps" each over a distance equal to atom-atom spacing, let us call it "a".

Then we can show that-

$$D_0 = \frac{1}{6} a^2 \Gamma \quad \text{--- (3)}$$

↑ jump frequency.

The jump frequency is the vibration frequency of the species, while remaining at its site, multiplied by the probability of a jump:

$$\Gamma = \nu \times e^{-Q/RT} \quad \text{--- (4)}$$

↑ vibration frequency - also called the Debye frequency, ~~diffusion~~ ~~rate~~ generally set equal to 10^{13} s^{-1} .

→ The probability of overcoming the activation barrier.

Schematic ~~refact~~ representation of $e^{-Q/RT}$

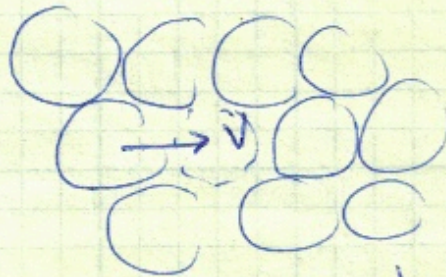


equivalent sites
separated by
an energy barrier -

Q is also sometimes called as the activation energy.

The Vacancy Mechanism

In a crystal where atoms are closely packed together, atoms are much ~~not~~ more likely to jump if there is a vacant site ~~is~~ next to them.



Now the jump frequency becomes

$$\Gamma = \nu_D e^{-\frac{Q_V}{RT}} \quad (\text{prob of finding a vacancy})$$

⚡
= molar concentration
of vacancies

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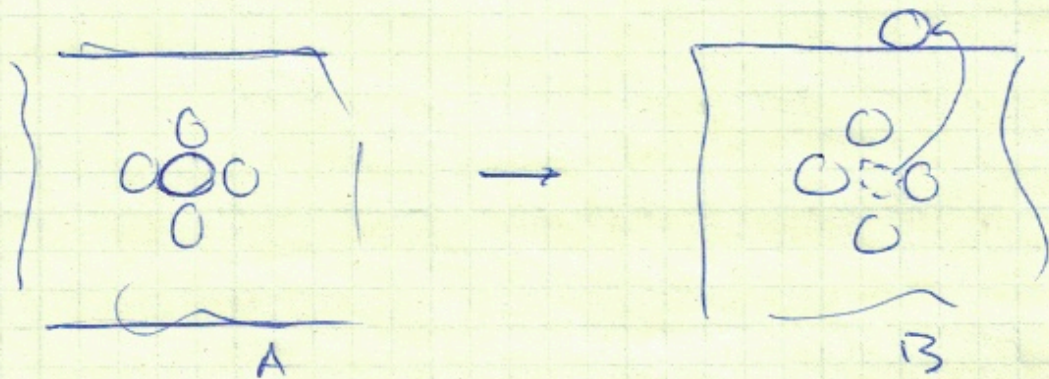
Ceramics

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Molar concentration of vacancies

Vacancies are thermodynamically equilibrated "defects", that are stabilized by their entropy.



$A \rightarrow B$ is an endothermic process. The amount of enthalpy absorbed = $\frac{1}{2}$ energy of formation.

Let this be ΔH_v (per vacancy)

Equilibrium:

$$\Delta H_v + k_B T \ln x_v = 0$$

↑ molar concentration

$$\therefore x_v = e^{\frac{-\Delta H_v}{k_B T}} \quad \text{or} \quad e^{\frac{-\Delta H_v}{RT}}$$

↑ pre-exponential factor

\therefore Eq (5) now becomes:

$$\Gamma = \sum_D e^{\frac{-Q_D}{RT}} \times e^{\frac{-\Delta H_v}{RT}} = \sum_D e^{\frac{-Q}{RT}}$$

$$Q = Q_D + \Delta H_v \quad \text{--- (6)}$$

Phenomenological Relationship of Q to the melting temperature, T_M (K)

$$Q = Q_V + \Delta H_V$$

Both Q_V and ΔH_V are likely to be related to the heat of melting, i.e. in some way to the enthalpy of formation.

Now, the heat of melting is related to the melting temperature (K) and the entropy of melting by,

$$\Delta H_M + T_M \Delta S_M = 0 \quad \text{--- (7)}$$

Let us say that

$$Q = \alpha \Delta H_M \quad \text{--- (8)}$$

where α may be close to a universal constant since the entropy of melting is likely to be the same for many materials (actually mostly metals)

$$\therefore \Delta S_M = \frac{\Delta H_M}{T_M} \text{ is a constant (approx.)} \quad \text{--- (9)}$$

Combining above we have,

$$Q = \alpha \cdot T_M \Delta S_M$$

$$\therefore \frac{Q}{RT} = \frac{\alpha T_M \Delta S_M}{RT} = \frac{\alpha \Delta S_M}{R} \cdot \left(\frac{T_M}{T} \right) \quad \text{--- (10)}$$

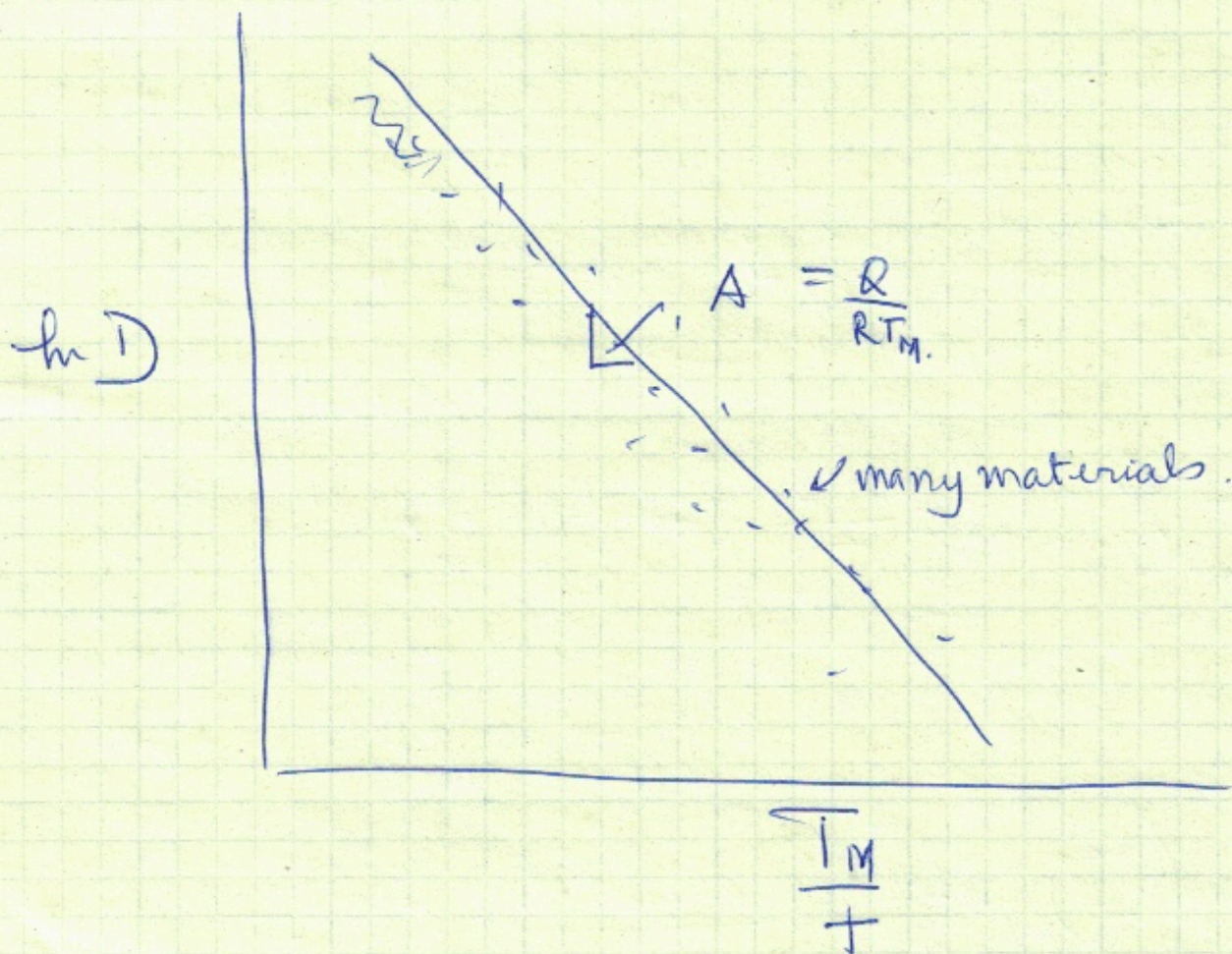
As per above discussion:

$$\alpha \frac{\Delta S_m}{R} \approx \text{universal value for vacancy diffn.}$$

$$\alpha \frac{\Delta S_m}{R} = A$$

$$\therefore D = D_0 e^{-A \cdot \frac{T_M}{T}} \quad \text{--- (11)}$$

$$\ln D = \ln D_0 - A \cdot \frac{T_M}{T}$$



Crystalline

Empirical Methods for Estimating the Diffusion Coefficient (usually applies only to pure metals - but still interesting).

$$D = D_0 e^{-\frac{Q}{RT}} = D_0 e^{-\frac{Q}{RT_M} \times \frac{T_M}{T}}$$

$$\therefore A = \frac{Q}{RT_M} \quad \text{--- (12)}$$

A for many crystalline materials has values

$$A \approx 17 \rightarrow 20 \text{ (dimensionless)}$$

At the melting point

Eq. (12) when $T = T_M$

$$D(T_M) = D_0 e^{-A} \leftarrow \text{constant}$$

\uparrow essentially constant

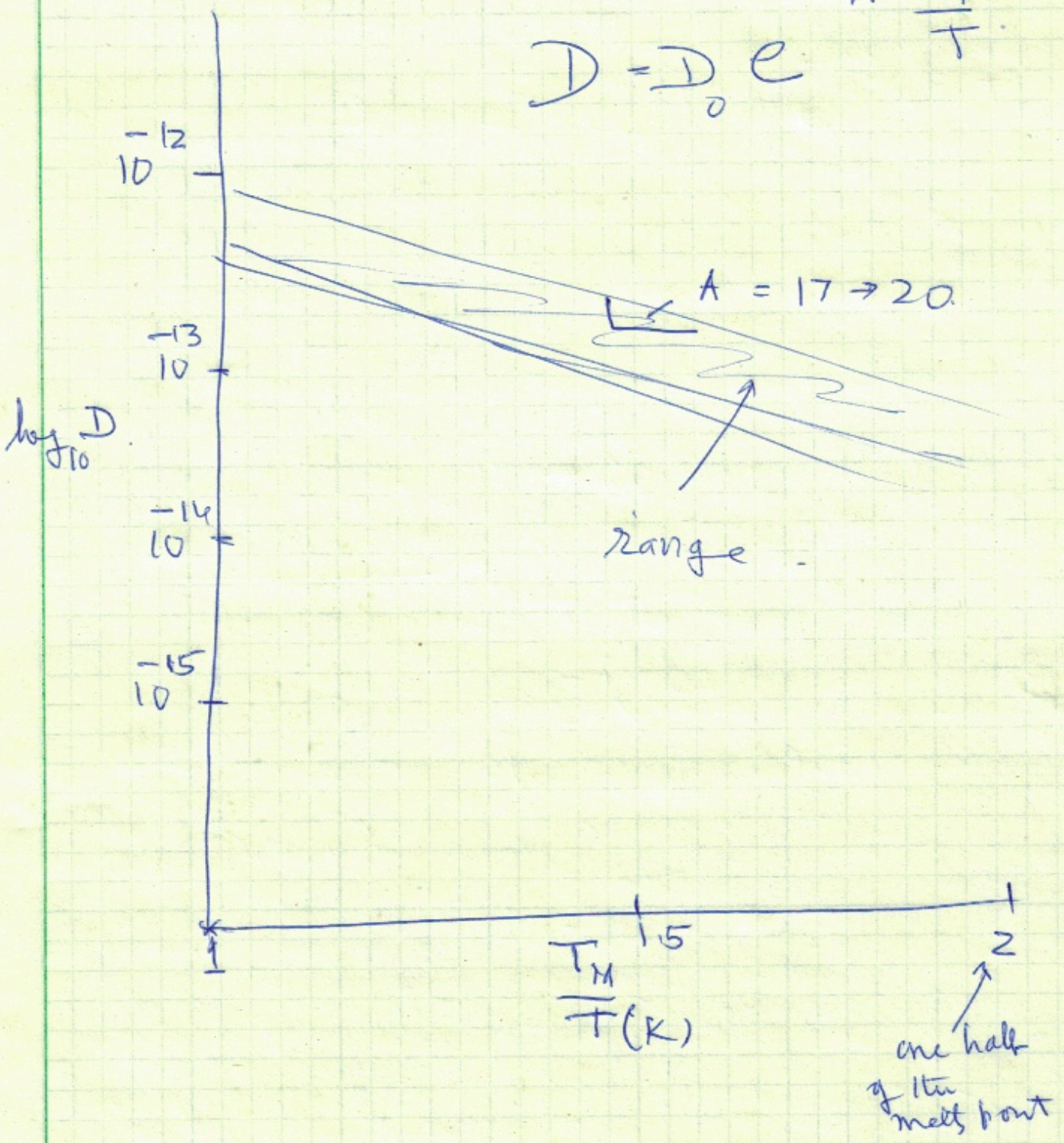
$D(T_M)$ ranges from

$$10^{-14} \rightarrow 10^{-15} \text{ m}^2/\text{s}$$
$$10^{-12} \rightarrow 10^{-13} \text{ m}^2/\text{s}$$

Therefore Now the diffusion coefficient can be obtained from the following

$$-A \frac{T_M}{T}$$

$$D = D_0 e^{-A \frac{T_M}{T}}$$



Now possible to get the diffusion coefficient for any 'metal' from its melt's T_M .

Ionic Conductance of O^{2-} in ZrO_2

- Vacancy concentration is determined by Y_2O_3 content.



one oxygen vacancy.

$$D = D_0 e^{-Q/RT}$$

- ⊕ D_0 includes the mole fraction of Y_2O_3
- ⊕ Q is only the migration barrier for O^{2-} diffusion via vacancies

Problem Calculate Q from the diffusion data given on p. 10

the original paper →

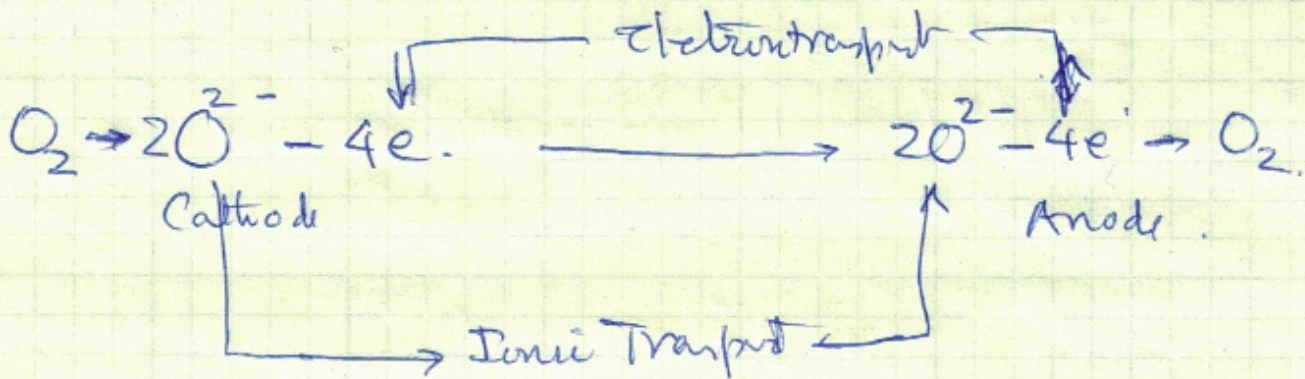
S. P. S. Badwal

Electrical Conductivity of
Single Crystal and
Polycrystalline $Y_2O_3-ZrO_2$

J. Mater. Sci.

19. (1984) 1767-1776

Electronic Current \leftrightarrow Ionic Current



⊛ Ionic transport of O^{2-} through the electrolyte determines the resistance of the electrolyte. ($\sigma_{O^{2-}}$)

Question: How is $\sigma_{O^{2-}}$ related to $D_{O^{2-}}$.

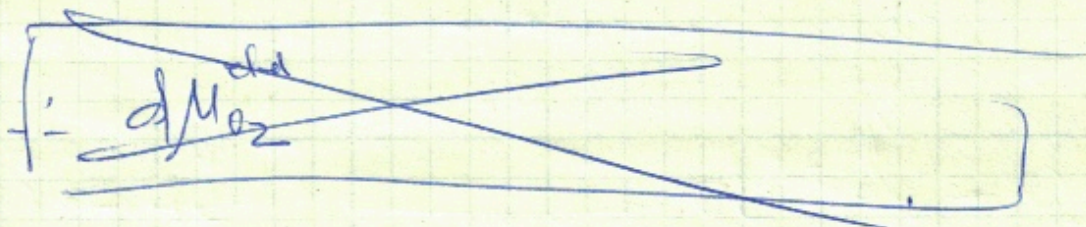
Method: Apply a potential gradient across the electrolyte and calculate the flux.

$$J = \frac{C_{O^{2-}} D_{O^{2-}}}{RT} \cdot \frac{d\mu_{O^{2-}}}{dx}$$

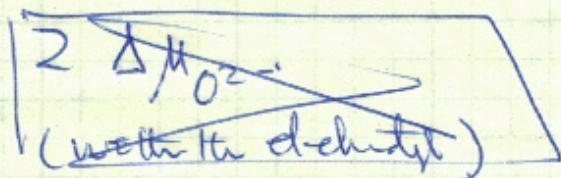
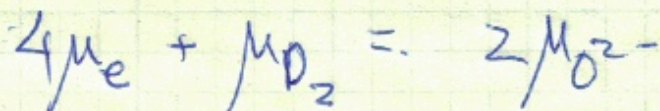
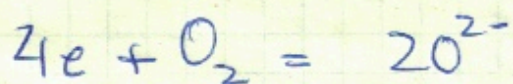
~~$\Delta \mu_{O^{2-}} = \Delta V \cdot z \cdot F$~~

~~Since $\Delta \mu_{O^{2-}}^{electr} = 4F(V_{cath} - V_{anod})$~~

~~$\mu_{O^{2-}}^{cathode} = \mu_0 + 4FV + RT \ln \frac{p_{O_2}^{cath}}{p_{O_2}^{anod}}$~~



Reaction at anode and cathode



$$2MO^{2-} = 4FV \overset{\text{volts}}{\downarrow} + RT \ln p_{O_2}$$

$$2\Delta MO^{2-} = 4F[V_{\text{cath}} - V_{\text{anode}}] + RT \ln \frac{p_{O_2}^{\text{cath}}}{p_{O_2}^{\text{anode}}}$$

∴ Gradient

$$\frac{\Delta MO^{2-}}{h} = \frac{2F \Delta V}{h} \overset{\text{voltage across the cell}}{\uparrow}$$

↑ electrolyte thickness

$$\therefore J = \frac{C_{O_2} - D_{O_2}}{RT} \cdot \frac{2F\Delta V}{h}$$

A_s = electrode surface area

$$\underbrace{I}_{\substack{\uparrow \\ \text{total current} \\ \text{electrical}}} = J \times \underbrace{2}_{\substack{\uparrow \\ \text{each ion} \\ \text{carries 2 electrons}}} \times e \times A_s$$

$$I = A_s \times 2e \times \frac{C_{O_2} - D_{O_2}}{k_B T} \times 2e \frac{\Delta V}{h}$$

$$j = \sigma_{O_2} \cdot E_e$$

\uparrow conductivity of the electrolyte
 \uparrow field

$$j = \frac{I}{A_s} = \frac{4e^2 C_{O_2} - D_{O_2}}{k_B T} \cdot E_e$$

σ_{O_2}