Under certain conditions, defects are related to the O_2 partial pressure.
↳ Brouwer diagrams: [Defect] vs. P_{O_2} at a given T.

IV. Effect of defects on material properties

1) Defects & conductivity

Defect motion in solids (e.g. by vacancy or interstitial diffusion) ⇒ mass & charge transport.

· Electrical conductivity: charge motion under an applied electric field. ∃ ionic, electronic & mixed conductivity.

Ionic conductors: In ionic crystals, defects have charge (e.g. ZrO_2) ∄ electronic σ, this is a class of materials called ionic conductors.

Ex: Y-doped ZrO_2 ⇒ vacancies : $Y_2O_3 \rightarrow 2Y'_{Zr} + 3O_O^x + V_O^{\bullet\bullet}$
⇒ $\sigma = \sum_i n_i |q_i| \mu_i =$ $\sigma = 2[V_O^{\bullet\bullet}] e \mu_{V_O}$ (1)
But vacancy diffusion is thermally activated due to temp-dependance of diffusivity, D :
$D = D_0 \exp -\left(\frac{\Delta G_m}{RT}\right)$ (2)

From eq. (1) : $[V_O^{\bullet\bullet}] \nearrow \Rightarrow \sigma \nearrow$, BUT in, e.g. CaF_2, max(σ) occurs for low dopant content.
When the vacancy content increases, ∃ defect association : $Y'_{Zr} + V_O^{\bullet\bullet} \rightarrow \{Y'_{Zr}, V_O^{\bullet\bullet}\}$
↳ Defects aren't "free" to be involved in transport processes: at high [X], ∃ enough defects for them to interact through Coulomb attraction & form defect pairs & clusters.

Defect reaction : $Y'_{Zr} + V_O^{\bullet\bullet} \rightleftharpoons \{Y'_{Zr}, V_O^{\bullet\bullet}\}^{\bullet} \Rightarrow K_{ass} = \frac{[\{Y'_{Zr}, V_O^{\bullet\bullet}\}^{\bullet}]}{[Y'_{Zr}][V_O^{\bullet\bullet}]} = z\exp\left(-\frac{\Delta G_a}{kT}\right)$

Electronic conductors: · Metallic conductors: the valence band isn't filled ⇒ e^- are easily promoted to LUMO → $\sigma \in [10^2 ; 10^8]$ $S cm^{-1}$

· Semiconductors: ∃ an energy gap between HOMO & LUMO, Eg $\in [0,5 ; 3]$ eV.

· Insulator : Eg > 3eV

The degree of overlapping of bands defines conduction mechanism. For metals σ ↘ ⇐ T ↗, for insulators & SC : T ↗ ⇒ σ ↗.