Solid State Ionics 2024 Tutorial

Fundamentals: Part 1

Defect notation to Brouwer diagrams

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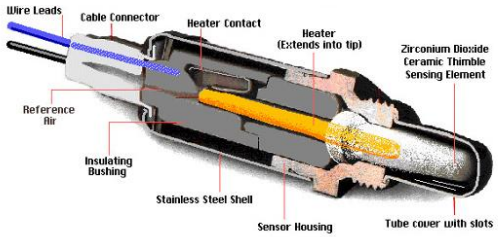
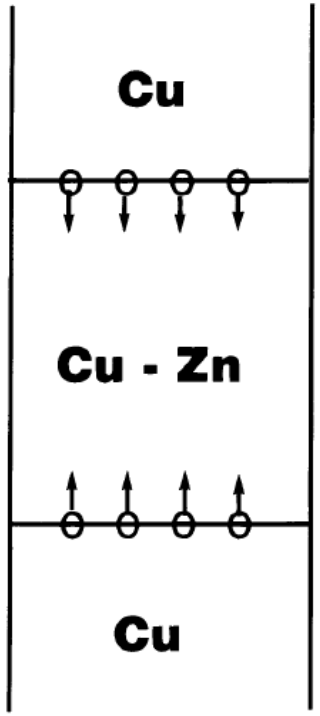
Why study defects?

Potentiometric O-sensors



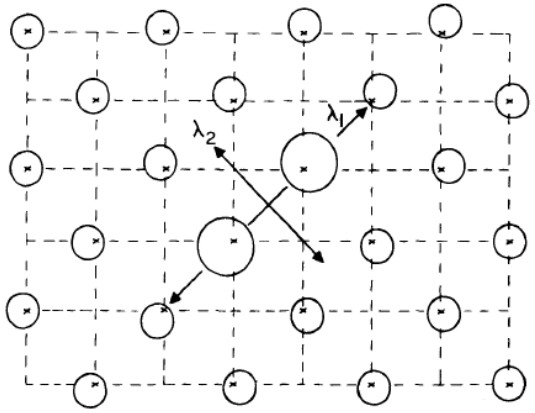
1949 - 1959



THE GOLDEN AGE OF CRYSTAL DEFECTS

(CONCEPTUALISATION)

Arthur S. Nowick

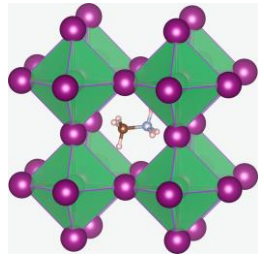


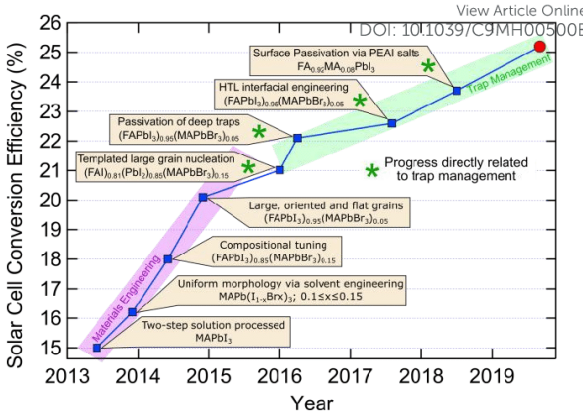
$$n + [V_M'] = p + [M_i^{\cdot}] + [F_M^{\cdot}].$$

The Golden Age of Crystal Defect *Applications*

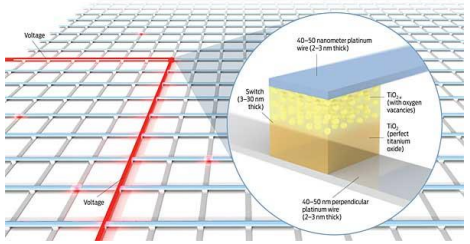
Proliferation of Li-ion batteries

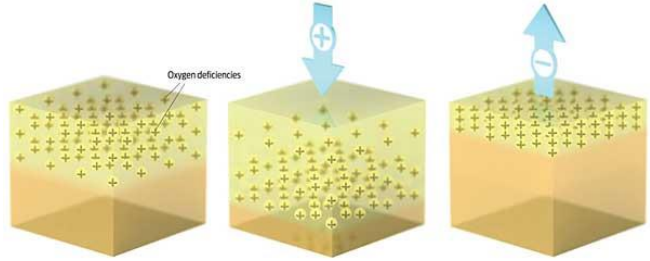
Hybrid-perovskite photovoltaic cells



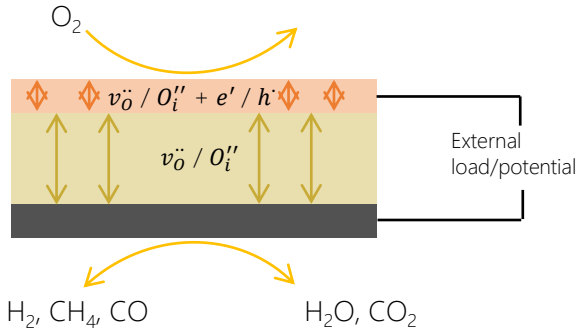


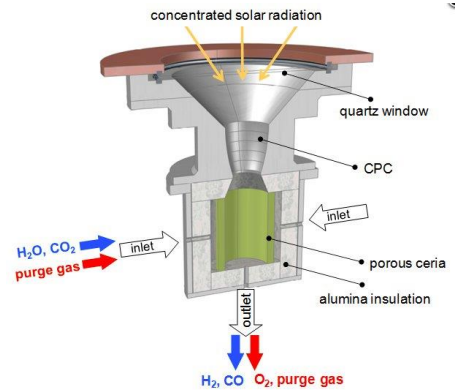
Valence-change memristor devices for neuromorphic computing





Production of hydrogen at scale – Solid oxide electrolyser cells, solar reactors





Contents

- Point defects: Definition, terminology and rationale
- Defect Chemistry: Reactions and equilibria
- Combining defect reactions: Brouwer diagrams

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- Point defects: Definition, terminology and rationale
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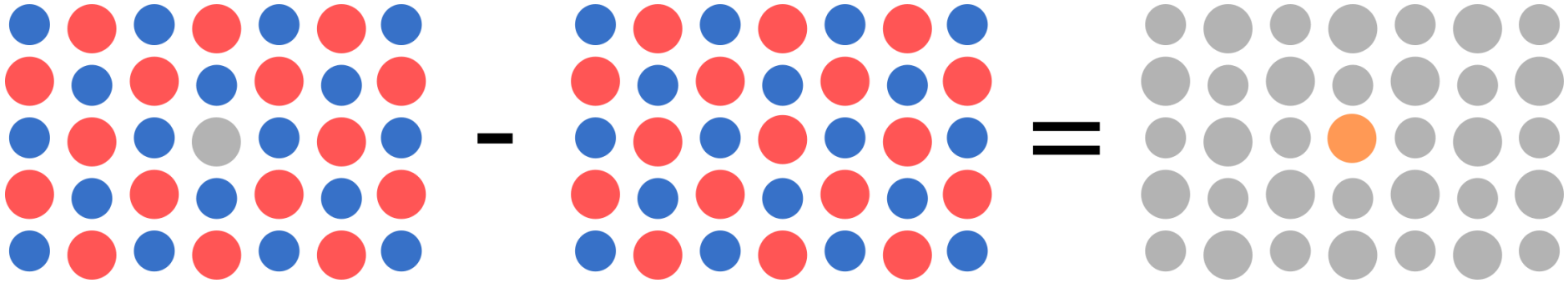
Definition

real – ideal = defect



Second definition: Atomic entity that adds to the configurational entropy of the ideal crystal

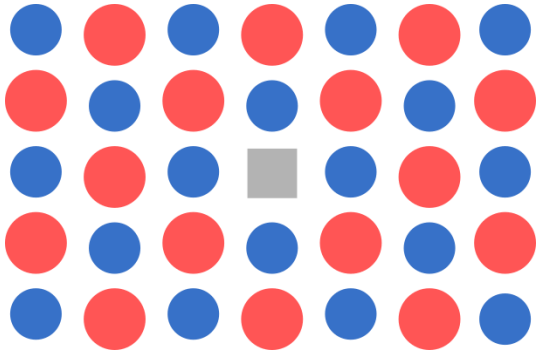
Why so important in ceramics/ionic solids?

- Charged
- Can be in high concentration

Types of point defect

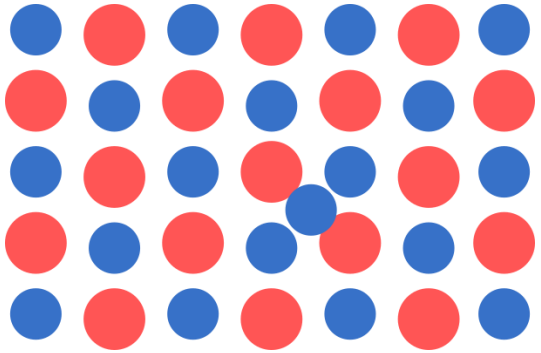
Ionic point defects

vacancy



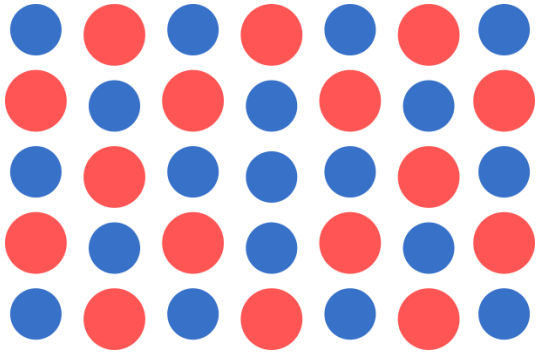
Missing ions

interstitial



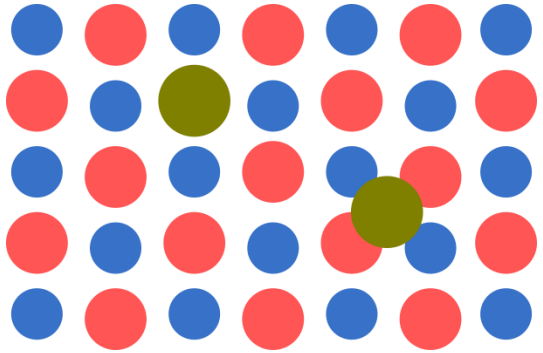
Additional ions

anti-site



Native ions sitting on the wrong site

impurity/dopant



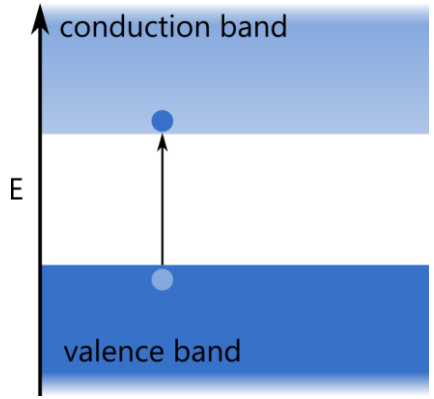
Foreign ions

Substitutionally or interstitially

Termed:

- Impurity – unintentional
- Dopant – intentional/low in concentration

Electronic point defects



Free electrons and holes

Extended defects

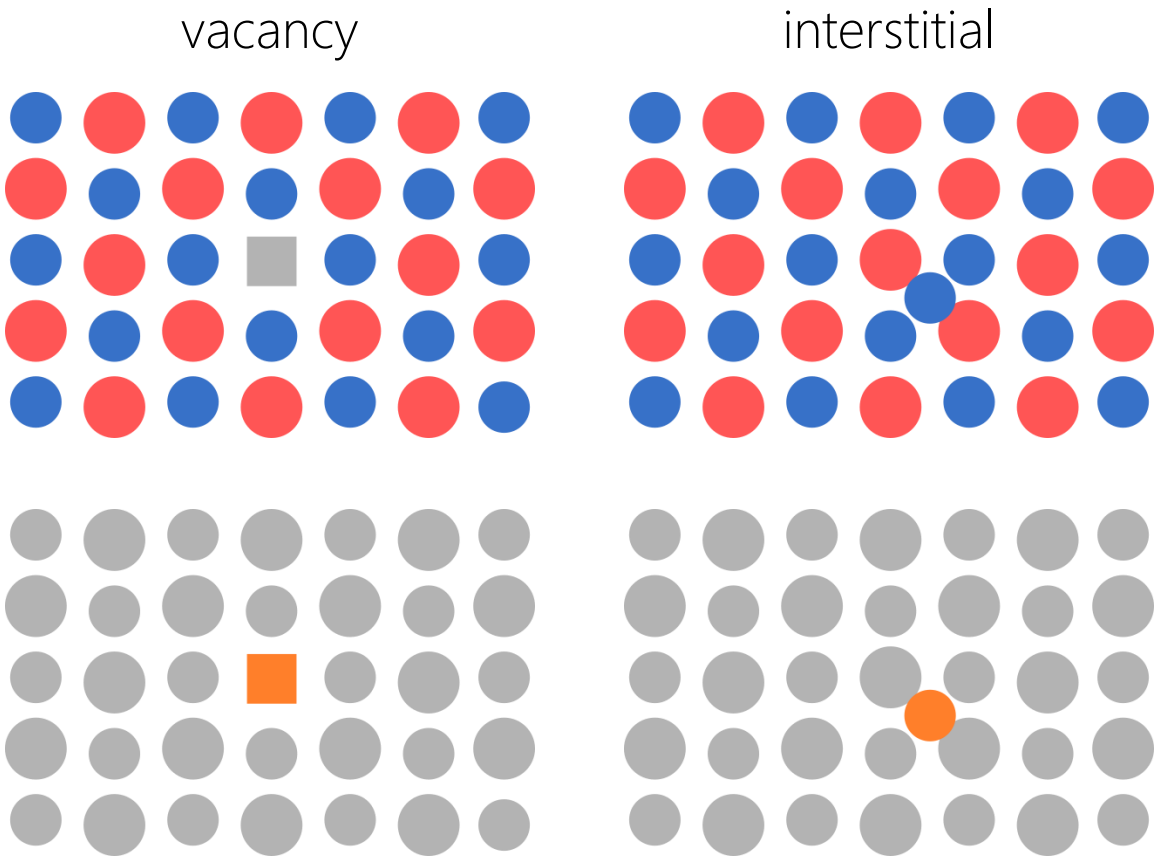
0D: Point defects

1D: Dislocations

2D: Surfaces, grain boundaries

3D: Secondary phases, pores

Why define defects? – Much simpler!



Extremely useful!

Don’t need to track a huge number of strongly interacting ions

Can only track a much smaller number of (sometimes) non-interacting defects.

If defects do interact, can treat through pair-wise interactions

Describing defects – Kröger-Vink notation

$$M_S^C$$

M (species):
atoms – e.g., Zr, Ce, O, Sr
vacancies – v
electrons – e
electron holes – h

S (site):
atoms – e.g., Zr, Ce, O, Sr
interstitial – i

C (relative charge):
positive – •
negative - ′
neutral - ×

$$[\cdots]$$

Square brackets:
Concentration of defect
For electronic defects, $[\mathrm{e}'] = \mathrm{n}$ and $[\mathrm{h}^{\cdot}] = \mathrm{p}$ is sometimes used

$$(\mathrm{X}_\mathrm{S}^{\cdot\cdot} - \mathrm{Y}_\mathrm{S}'')$$

Round brackets:
Defect-associate

Examples

- Oxygen vacancy

$$\mathrm{v}_\mathrm{O}^{\cdot\cdot}$$

- Ca^{2+} on Zr^{4+} site

$$\mathrm{Ca}_\mathrm{Zr}''$$

- Ca^{2+} and O-vacancy associate

$$(\mathrm{Ca}_\mathrm{Zr}'' - \mathrm{v}_\mathrm{O}^{\cdot\cdot})$$

- Free electron

$$\mathrm{e}'$$

Kröger, F. A. & Vink, H. J. *Solid State Phys.* 3, 307–435 (1956).

Defect notation – "bad" practice

Changing sites with species

- Oxygen vacancy

  $\mathrm{O_v}$ ✗ $\mathrm{v_O}$ ✓

- Oxygen interstitial

  $\mathrm{i_O}$ ✗ $\mathrm{O_i}$ ✓

- Ca on Zr site

  $\mathrm{Zr_{Ca}}$ ✗ $\mathrm{Ca_{Zr}}$ ✓

Using $\mathbf{V}$ and $\mathbf{I}$ instead of $\mathbf{v}$ and $\mathbf{i}$

- $\mathbf{V}$ and $\mathbf{I}$ are standard KV notation, but $\mathbf{v}$ and $\mathbf{i}$ is better

What is $\mathrm{V_I}$?

- Iodine vacancy: $\mathrm{v_I}$
- Vanadium interstitial: $\mathrm{V_i}$
- Vacant interstitial site: $\mathrm{v_i}$
- Vanadium anti-site defect on iodine-ion site: $\mathrm{V_I}$

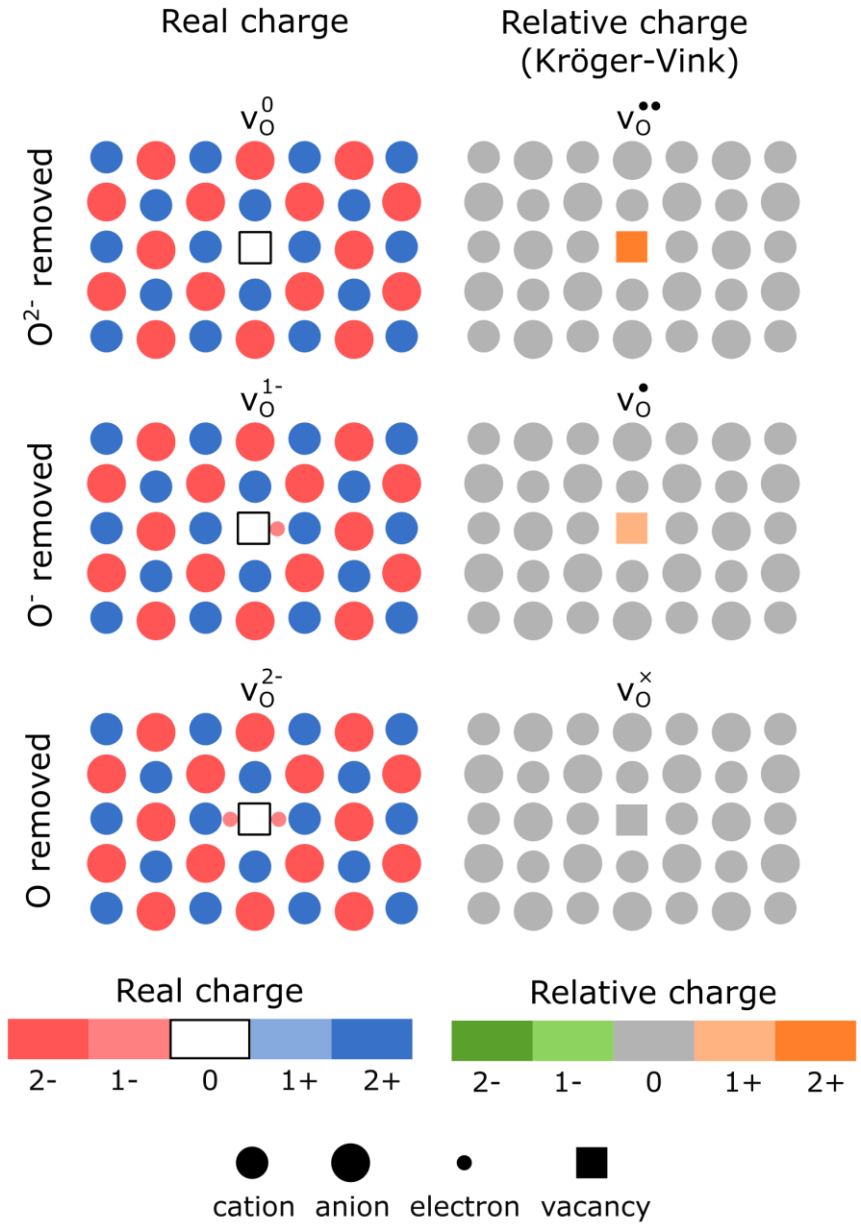
Using real instead of relative charge

- Real and relative charge are different quantities
  - Real: relative to free space
  - Relative: relative to crystal lattice

De Souza, R. & G. Harrington. *Nat. Mater.* 22: p. 794–797 (2023); Norby, T. *J. Kor. Ceram. Soc.* 47, 19–25 (2010).

Defect notation – “bad” practice

Species removed	Relative charge	Real charge	Wrong!
O^{2-}	$v_O^{\cdot\cdot}$	v_O^{0}	v_O^{2+}
O^{-}	$v_O^{\cdot}$	v_O^{-}	v_O^{+}
O	$v_O^{\times}$	v_O^{2-}	v_O^{0}



De Souza, R. & G. Harrington. *Nat. Mater.* 22: p. 794–797 (2023)

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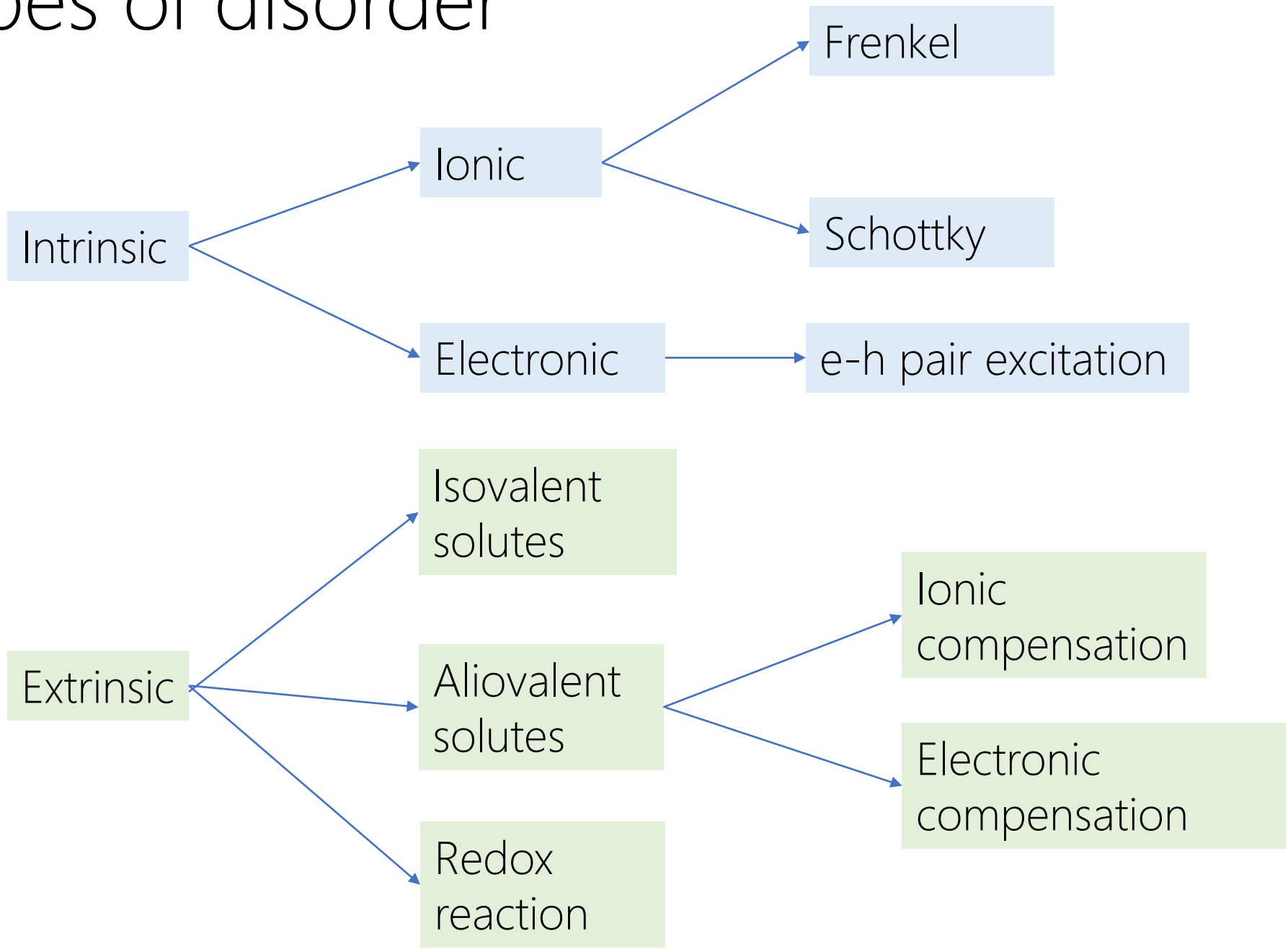
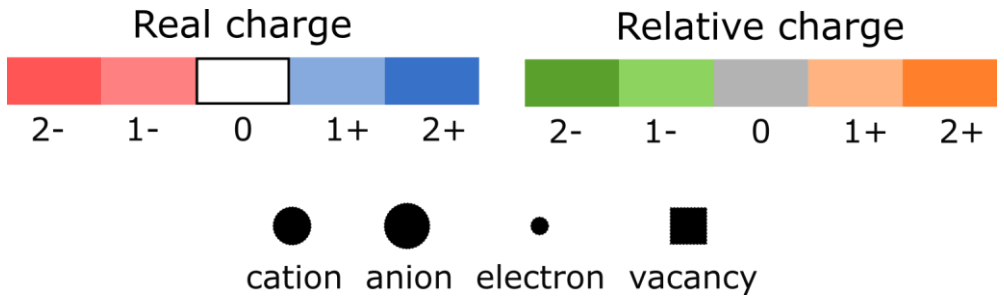
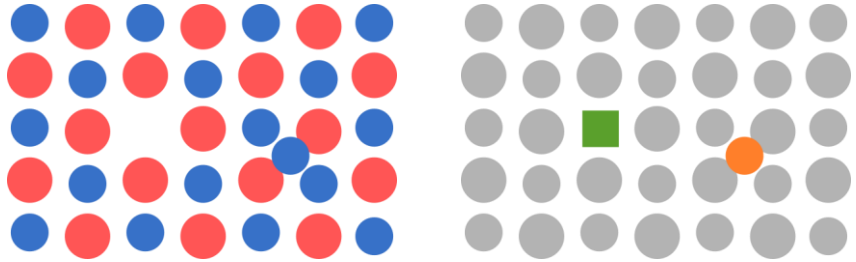
Types of disorder



Intrinsic disorder

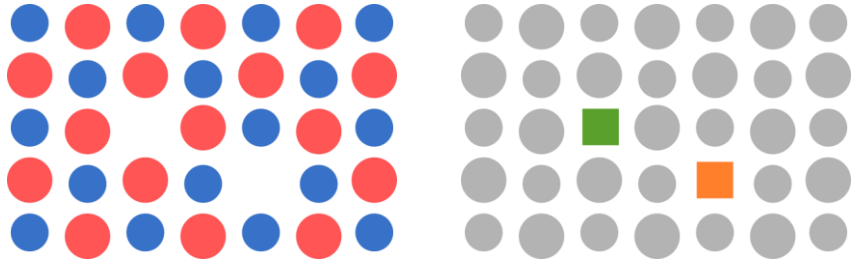


Frenkel disorder



$$M_M^{\times} \rightleftharpoons v_M'' + M_i^{\cdot\cdot}$$

Schottky disorder



$$null \rightleftharpoons v_M'' + v_O^{\cdot\cdot}$$

Intrinsic disorder: concentration of defects

$$G = G_0 + n\Delta g_f - T\Delta S_c$$

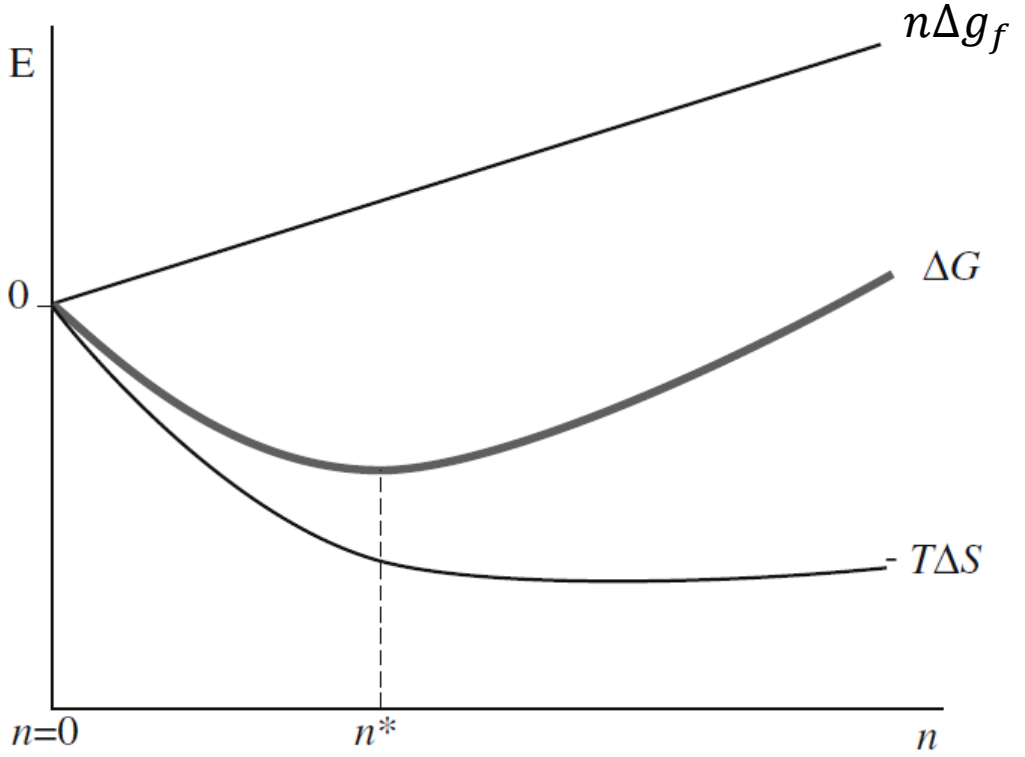
$$\Delta G = (G - G_0) = n\Delta g_f - T\Delta S_c$$

$$\Delta S_c = k \ln \Omega$$

$$\Delta S_c = k \ln \left(\frac{N!}{(N - n_v)!\, n_v!} \right) \left(\frac{N!}{(N - n_i)!\, n_i!} \right)$$

Take, $\left(\frac{\partial \Delta G}{\partial n} \right)_{T,P} = 0$ (and some maths relations/assumptions)

$$\frac{n}{N} = \exp\left(-\frac{\Delta g}{2kT} \right)$$



G: free energy

G_0: free energy of a perfect crystal

n: number of defects

N: number of sites

Δg_f: free energy change per defect pair

ΔS_c: change in configurational entropy

Expect to find point defects in pure crystals at all temperatures above 0K

See full derivation in Chiang, Birnie and Kingery, Physical Ceramics or Carter and Norton, Ceramic Materials

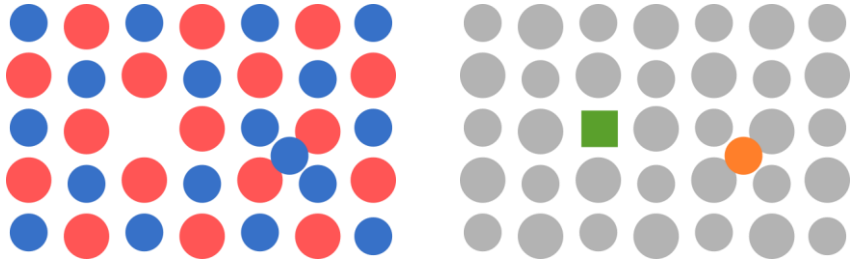
Intrinsic disorder: concentration of defects

Frenkel disorder

$$\frac{n}{N} = \exp\left(-\frac{\Delta g}{2kT}\right)$$

TABLE 11.6 Formation Enthalpy of Frenkel Defects In Some Compounds of Formula MX and MX_2

Material	ΔE_f *(*10^{-19} *J)*	ΔE_f *(eV)*
UO_2	5.448	3.40
ZrO_2	6.569	4.10
CaF_2	4.486	2.80
SrF_2	1.122	0.70
AgCl	2.564	1.60
AgBr	1.923	1.20
β-AgI	1.122	0.70

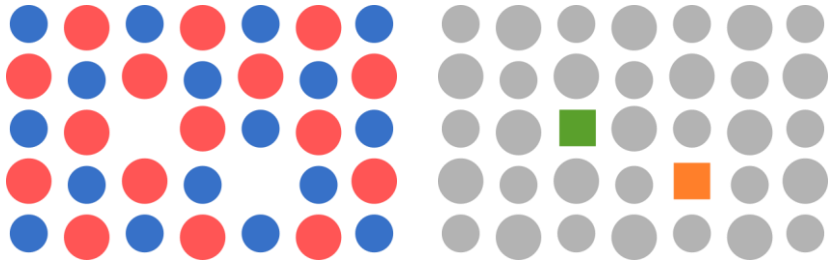


$$\mathrm{M}_M^{\times} \rightleftharpoons \mathrm{v}_M'' + \mathrm{M}_\mathrm{i}^{\cdot\cdot}$$

Schottky disorder

TABLE 11.4 The Formation Enthalpy of Schottky Defects In Some Compounds of Formula MX

Compound	ΔE_s *(*10^{-19} *J)*	ΔE_s *(eV)*
MgO	10.574	6.60
CaO	9.773	6.10
SrO	11.346	7.08
BaO	9.613	6.00
LiF	3.749	2.34
LiCl	3.397	2.12
LiBr	2.884	1.80
LiI	2.083	1.30
NaCl	3.685	2.30
NaBr	2.692	1.68
KCl	3.621	2.26
KBr	3.797	2.37
KI	2.563	1.60
CsBr	3.204	2.00
CsI	3.044	1.90



$$\mathrm{null} \rightleftharpoons \mathrm{v}_M'' + v_O^{\cdot\cdot}$$

See full derivation in Chiang, Birnie and Kingery, Physical Ceramics or Carter and Norton, Ceramic Materials

Intrinsic disorder: concentration of defects

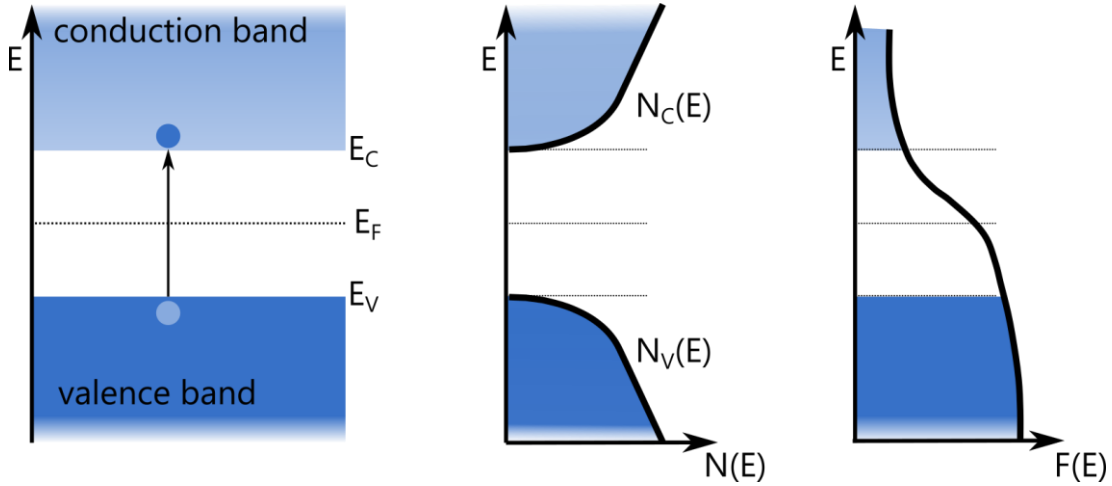
Electronic disorder

$$n = N \exp\left(-\frac{\Delta g}{2kT}\right)$$

$$\text{null} \rightleftharpoons e' + h^{\cdot}$$

Concentration of electrons/holes

$$n(E) = N(E) \cdot F(E)$$



Density of states

$N_{c,v} = 2\left(\frac{2\pi m^*_{e,h} kT}{h^2}\right)^{3/2} \approx 10^{-19}\ \text{cm}^{-3}$ (at 300K)

$m^*_{e,h}$: effective mass of electrons in CB or holes in VB

Fermi-Dirac function

$F(E) \approx \exp[-(E - E_f)/kT]$

$$\frac{n_e}{N_c} = \exp\left(-\frac{(E_c - E_f)}{kT}\right)$$

$$\frac{n_h}{N_v} = \exp\left(-\frac{(E_f - E_v)}{kT}\right)$$

For intrinsic electronic disorder:

$(E_f - E_v) = (E_c - E_f) = E_{bg}/2$

See full derivation in Chiang, Birnie and Kingery, Physical Ceramics

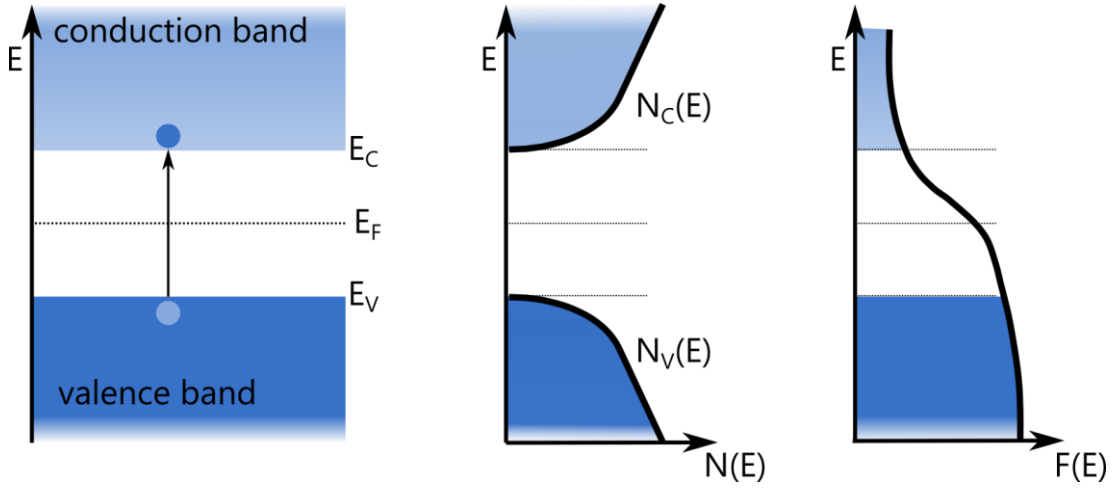
Intrinsic disorder: concentration of defects

Electronic disorder

Table 2.3 Bandgap Values for Some Semiconductors and Insulators

Compound	Band Gap (eV)	Compound	Band Gap (eV)
Si	1.11	NaF	6.7
Ge	0.66	KCl	7
Diamond	5.4	NaCl	7.3
InSb	0.17	LiF	12.0
InAs	0.36	BaF_2	8.9
InP	1.27	SrF_2	9.5
GaSb	0.68	CaF_2	10.0
GaAs	1.43	MgF_2	11.8
GaP	2.25	SrO	5.7
CdTe	1.44	MgO	7.8
CdSe	1.74	NiO	4.2
CdS	2.42	CoO	4.0
ZnSe	2.6	MnO	3.7
ZnO	3.2	FeO	2
ZnS	3.6	VO	0.3
PbSe	0.27	Fe_2O_3	3.1
PbTe	0.29	Ga_2O_3	4.6
PbS	0.34-0.37	Al_2O_3	8.8
AgI	2.8	$BaTiO_3$	2.8
AgCl	3.2	TiO_2	3.0
SiC (α)	2.9	UO_2	5.2
BN	4.8	SiO_2	8.5
		$MgAl_2O_4$	7.8

Chiang, Birnie and Kingery, Physical Ceramics



$$\frac{n_e}{N_c} = \exp\left(-\frac{(E_c - E_f)}{kT}\right)$$

$$\frac{n_h}{N_v} = \exp\left(-\frac{(E_f - E_v)}{kT}\right)$$

For intrinsic electronic disorder:

$$(E_f - E_v) = (E_c - E_f) = E_{bg}/2$$

Defect chemical reactions

- Sometimes called *quasi-chemical* reactions
- Must balance:
  - Mass
  - Charge
  - Site

- For equilibrium reactions → law of mass action

Examples: Schottky disorder

$\text{null} \rightleftharpoons \text{v}''_{\text{M}g} + \text{v}^{\cdot\cdot}_{\text{O}}$ (MgO)

$\text{null} \rightleftharpoons 2\text{v}'''_{\text{Al}} + 3\text{v}^{\cdot\cdot}_{\text{O}}$ (Al_2O_3)

$\text{null} \rightleftharpoons \text{v}''_{Ba} + \text{v}''''_{Ti} + 3\text{v}^{\cdot\cdot}_{\text{O}}$ ($BaTiO_3$)

$$\text{null} \rightleftharpoons \text{v}''_{\text{M}g} + \text{v}^{\cdot\cdot}_{\text{O}}$$

$$K_s = [\text{v}''_{\text{M}g}][\text{v}^{\cdot\cdot}_{\text{O}}]$$

$$K_s = \exp\left(-\frac{\Delta g_s}{kT}\right)$$

$$[\text{v}''_{\text{M}g}] = [\text{v}^{\cdot\cdot}_{\text{O}}] = \exp\left(-\frac{\Delta g_s}{2kT}\right)$$

Defect chemical reactions: oxidation and reduction

Reduction of an oxide:

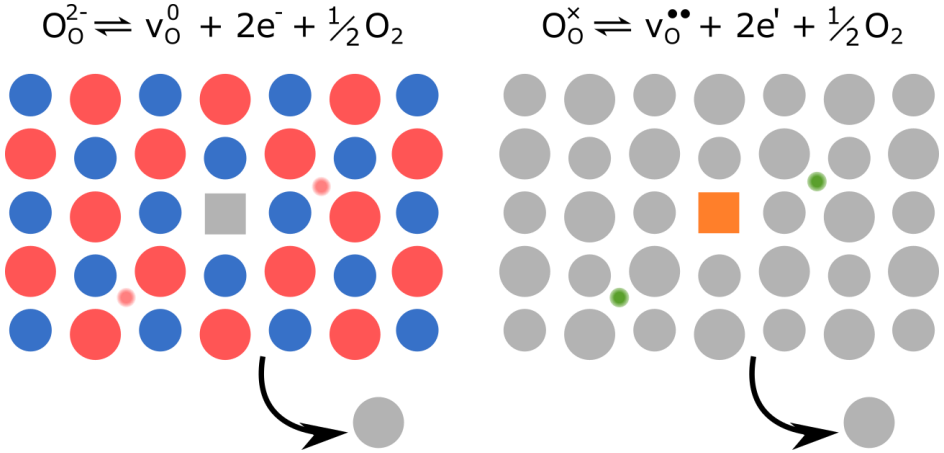
$$O_O^{\times} \rightleftharpoons \frac{1}{2}O_2(g) + v_O^{\cdot\cdot} + 2e'$$

$$K_R = n^2[v_O^{\cdot\cdot}](P_{O_2})^{1/2} = K_R^0 \exp\left(-\frac{\Delta g_R}{kT}\right)$$

Oxidation of an oxide:

$$\frac{1}{2}O_2(g) + v_O^{\cdot\cdot} \rightleftharpoons O_2^{\times} + 2h^{\cdot}$$

$$K_O = \frac{p^2}{[v_O^{\cdot\cdot}](P_{O_2})^{1/2}} = K_O^0 \exp\left(-\frac{\Delta g_O}{kT}\right)$$



Defect chemical reactions: solute incorporation

Ensure site balance (ratio)

$$NiO \xrightarrow{MgO} Ni_{Mg}^{\times} + O_O^{\times}$$

Ensure charge balance (relative)

$$Al_2O_3 \xrightarrow{MgO} 2Al_{Mg}^{\cdot} + 3O_O^{\times} \quad \times$$

$$Al_2O_3 \xrightarrow{MgO} 2Al_{Mg}^{\cdot} + 3O_O^{\times} + v_{Mg}'' \quad \checkmark$$

Multiple solute incorporation mechanisms possible

$$2MgO \xrightarrow{Al_2O_3} 2Mg_{Al}' + 2O_O^{\times} + v_O''$$ (substitutional)

$$3MgO \xrightarrow{Al_2O_3} 3Mg_i^{\cdot\cdot} + 3O_O^{\times} + 2v_{Al}'''$$ (interstitial)

$$3MgO \xrightarrow{Al_2O_3} 2Mg_{Al}' + Mg_i^{\cdot\cdot} + 3O_O^{\times}$$ (self-compensating)

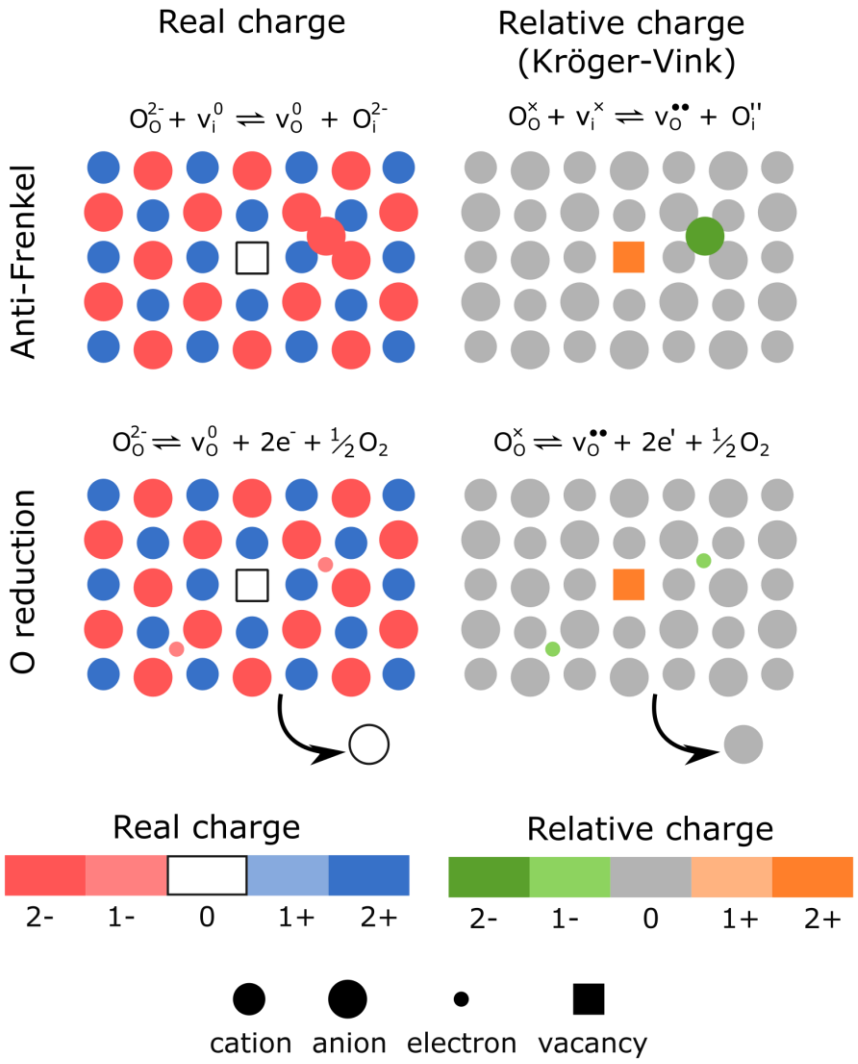
Multiple compensation mechanisms possible

- $2Nb_2O_5 \xrightarrow{TiO_2} 4Nb_{Ti}^{\cdot} + 10O_O^{\times} + v_{Ti}''''$ (ionic compensation)
- $2Nb_2O_5 \xrightarrow{TiO_2} 4Nb_{Ti}^{\cdot} + 8O_O^{\times} + O_2(g) + 4e'$ (electronic compensation

Defect notation – "bad" practice

Anti-Frenkel disorder	
Relative charge	$O_O^{\times} + v_i^{\times} \rightleftharpoons v_O^{\cdot\cdot} + O_i''$
Real charge	$O_O^{2-} + v_i^{0} \rightleftharpoons v_O^{0} + O_i^{2-}$
Wrong	$O_O^{0} + v_i^{0} \rightleftharpoons v_O^{2+} + O_i^{2-}$

Oxygen reduction reaction	
Relative charge	$O_O^{\times} \rightleftharpoons v_O^{\cdot\cdot} + 2e' + \frac{1}{2}O_2$
Real charge	$O_O^{2-} \rightleftharpoons v_O^{0} + 2e^{-} + \frac{1}{2}O_2$
Wrong	$O_O^{0} \rightleftharpoons v_O^{2+} + 2e^{-} + \frac{1}{2}O_2$



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Simultaneous defect equilibria

- In most solids, multiple defect reactions occur simultaneously
- A defect can participate in multiple defect equilibria
- How do we understand what is important?

Must consider:

1. Intrinsic ionic defects
2. Intrinsic electronic defects
3. Oxidation and reduction
4. Incorporation of solutes/impurities

Example: Intrinsic MgO

Defect equilibria	Equilibrium constants
$\mathrm{null} \rightleftharpoons \mathrm{v}''_{\mathrm{Mg}} + \mathrm{v}^{\cdot\cdot}_{\mathrm{O}}$	$\mathrm{K_s} = [\mathrm{v}''_{\mathrm{Mg}}][\mathrm{v}^{\cdot\cdot}_{\mathrm{O}}]$
$\mathrm{null} \rightleftharpoons \mathrm{e}' + \mathrm{h}^{\cdot}$	$\mathrm{K}_i = \mathrm{np}$
$\mathrm{O}^{\times}_2 \rightleftharpoons \frac{1}{2}\mathrm{O}_2(\mathrm{g}) + \mathrm{v}^{\cdot\cdot}_{\mathrm{O}} + 2\mathrm{e}'$	$\mathrm{K_R} = \mathrm{n}^2[\mathrm{v}^{\cdot\cdot}_{\mathrm{O}}]\left(\mathrm{P}_{\mathrm{O}_2}\right)^{1/2}$

Example: Intrinsic MgO

- Have a total of 4 defect species $\mathrm{v}''_{\mathrm{Mg}}$, $\mathrm{v}^{\cdot\cdot}_{\mathrm{O}}$, e', $\mathrm{h}^{\cdot}$
- Only 3 independent equilibrium equations
- Need one more:

$$2[\mathrm{v}''_{\mathrm{Mg}}] + \mathrm{n} = 2[\mathrm{v}^{\cdot\cdot}_{\mathrm{O}}] + \mathrm{p} \qquad \text{(electroneutrality condition)}$$

At this point, we are technically done….

Brouwer approximations

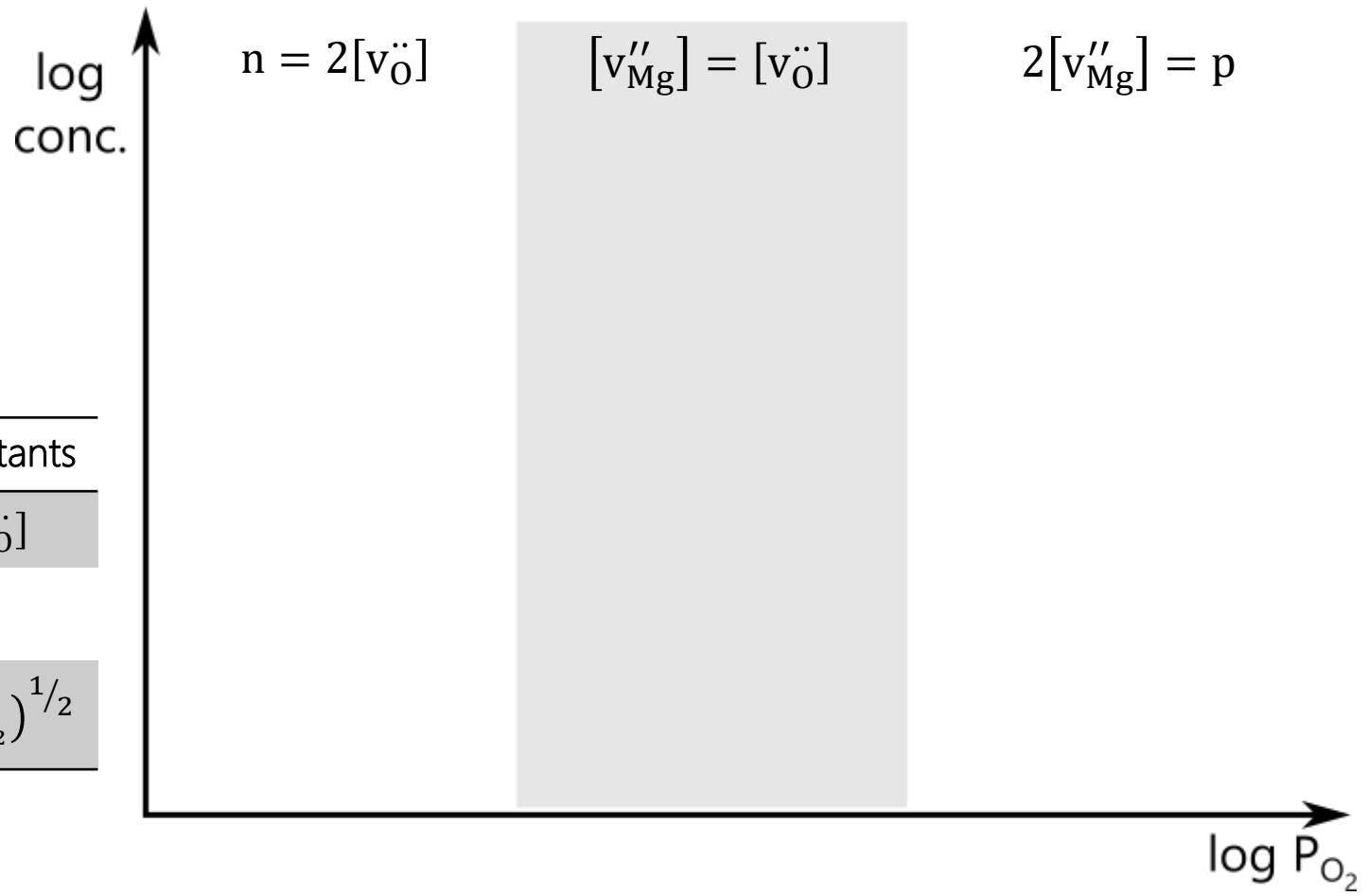
- Assume one positive defect and one negative defect dominate.

$$2[v''_{Mg}] + n = 2[v^{\cdot\cdot}_{O}] + p$$

1. $n = 2[v^{\cdot\cdot}_{O}]$
2. $2[v''_{Mg}] = p$
3. $[v''_{Mg}] = [v^{\cdot\cdot}_{O}]$
4. $n = p$

Defect equilibria	Equilibrium constants
$null \rightleftharpoons v''_{Mg} + v^{\cdot\cdot}_{O}$	$K_s = [v''_{Mg}][v^{\cdot\cdot}_{O}]$
$null \rightleftharpoons e' + h^{\cdot}$	$K_i = np$
$O_2^{\times} \rightleftharpoons \frac{1}{2}O_2(g) + v^{\cdot\cdot}_{O} + 2e'$	$K_R = n^2[v^{\cdot\cdot}_{O}](P_{O_2})^{1/2}$

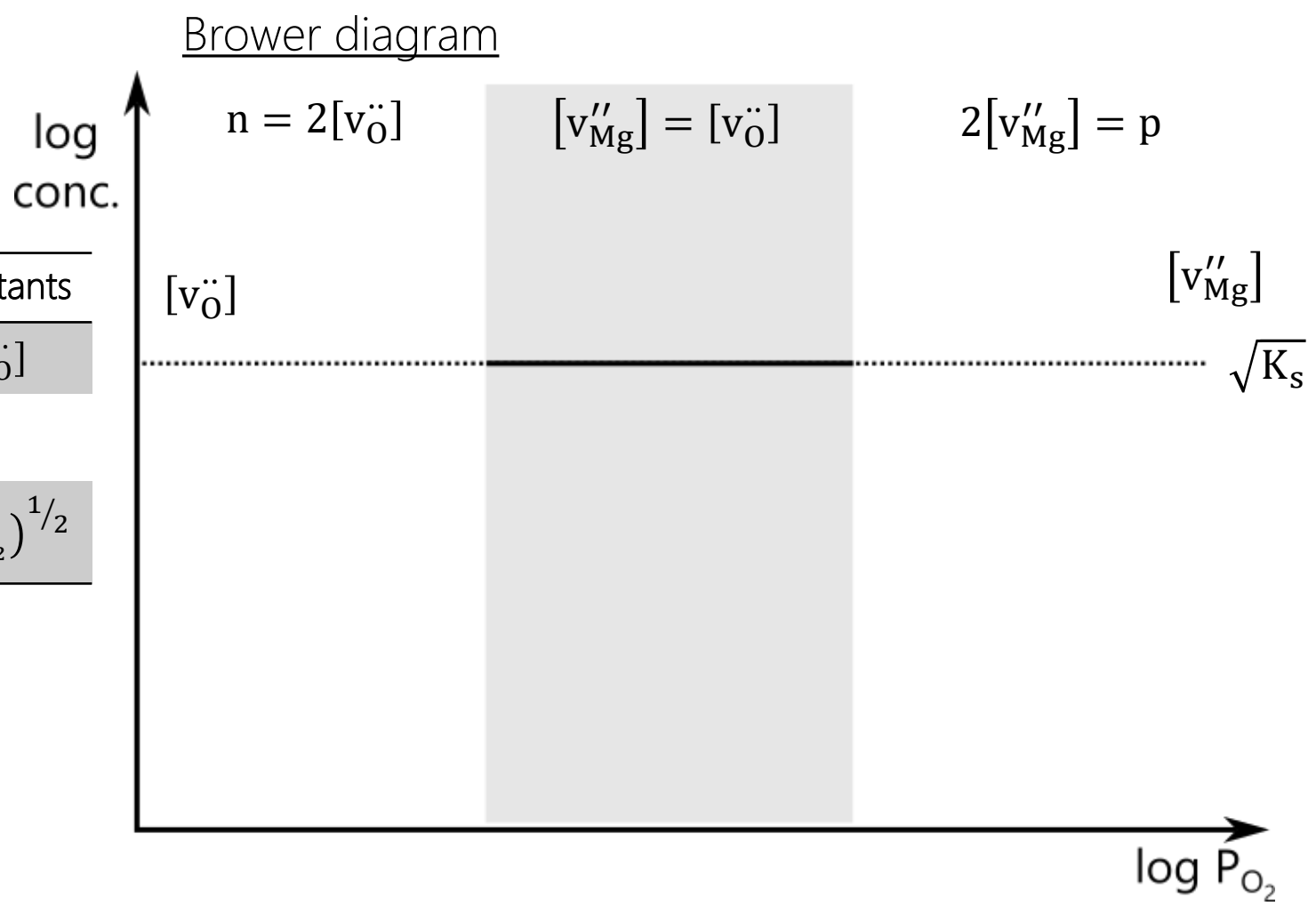
Brower diagram



Brouwer approximations

1. $n = 2[v_O^{\cdot\cdot}]$
2. $2[v_{Mg}''] = p$
3. $[v_{Mg}''] = [v_O^{\cdot\cdot}]$
4. $n = p$

Defect equilibria	Equilibrium constants
$null \rightleftharpoons v_{Mg}'' + v_O^{\cdot\cdot}$	$K_s = [v_{Mg}''][v_O^{\cdot\cdot}]$
$null \rightleftharpoons e' + h^{\cdot}$	$K_i = np$
$O_2^{\times} \rightleftharpoons \frac{1}{2}O_2(g) + v_O^{\cdot\cdot} + 2e'$	$K_R = n^2[v_O^{\cdot\cdot}](P_{O_2})^{1/2}$



Brouwer approximations

1. $n = 2[v_O^{\cdot\cdot}]$
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Defect equilibria	Equilibrium constants
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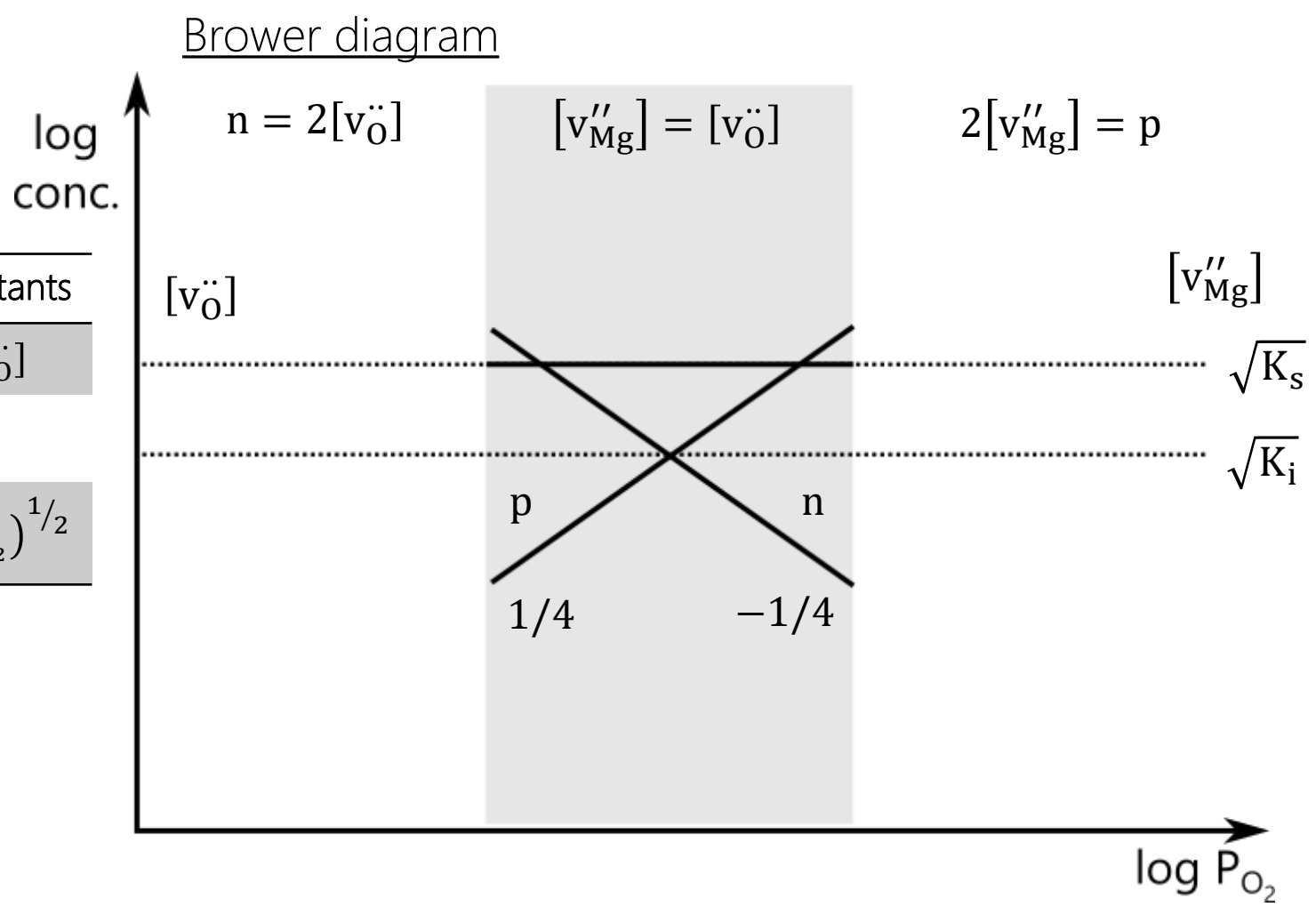
$O_2^{\times} \rightleftharpoons \frac{1}{2}O_2(g) + v_O^{\cdot\cdot} + 2e'$	$K_R = n^2[v_O^{\cdot\cdot}](P_{O_2})^{1/2}$

$$n = K_R^{1/2} K_s^{-1/4} P_{O_2}{}^{-1/4}$$

$$\log n \propto -\frac{1}{4}\log P_{O_2}$$

Brower diagram



Brouwer approximations

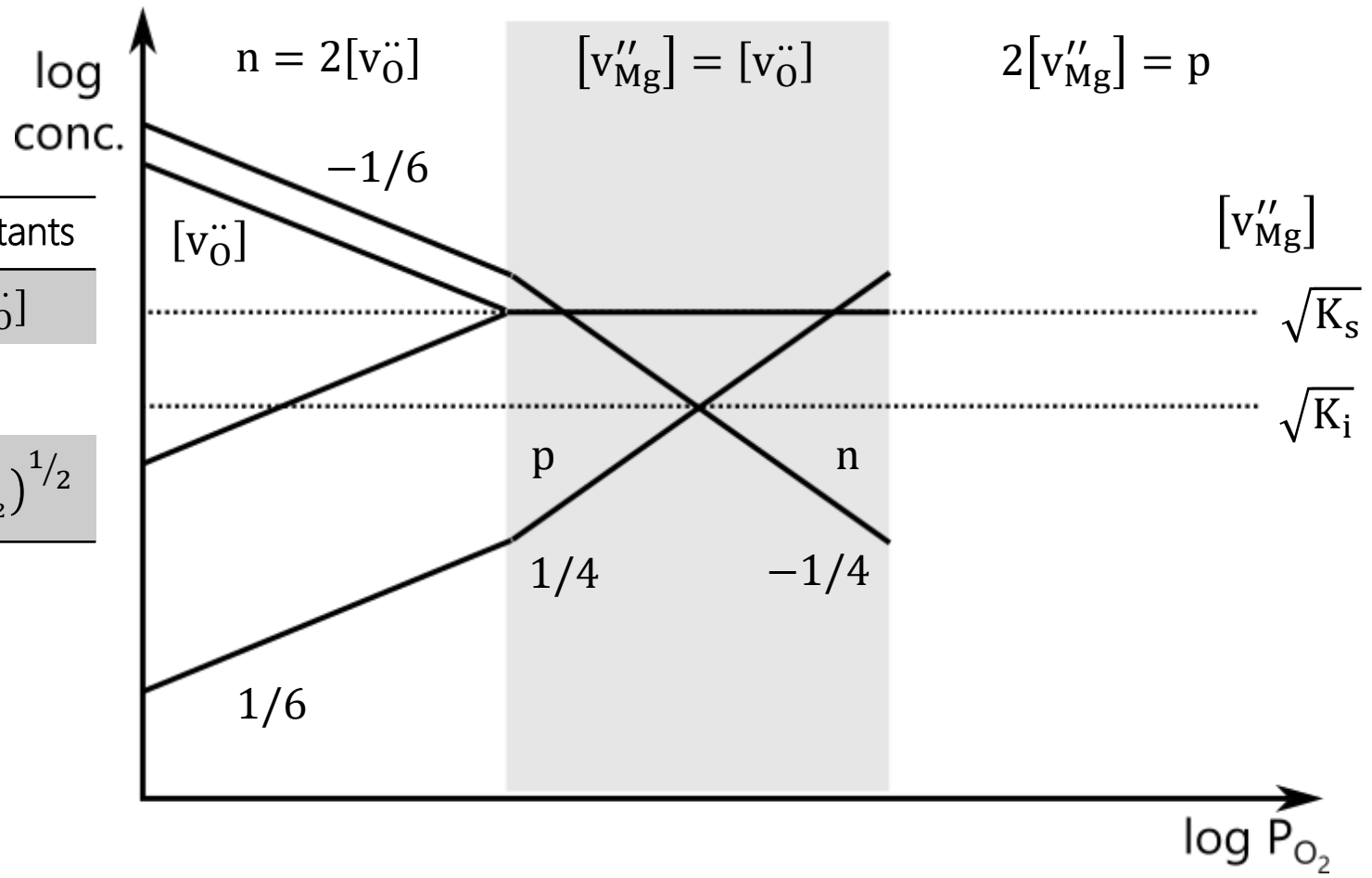
1. $n = 2[v_O^{\cdot\cdot}]$
2. $2[v_{Mg}''] = p$
3. $[v_{Mg}''] = [v_O^{\cdot\cdot}]$
4. $n = p$

Defect equilibria	Equilibrium constants
$null \rightleftharpoons v_{Mg}'' + v_O^{\cdot\cdot}$	$K_s = [v_{Mg}''][v_O^{\cdot\cdot}]$
$null \rightleftharpoons e' + h^{\cdot}$	$K_i = np$
$O_2^{\times} \rightleftharpoons \frac{1}{2}O_2(g) + v_O^{\cdot\cdot} + 2e'$	$K_R = n^2[v_O^{\cdot\cdot}](P_{O_2})^{1/2}$

$$n = 2[v_O^{\cdot\cdot}] = (2K_R)^{1/3} P_{O_2}{}^{-1/6}$$

$$\log n \propto -\frac{1}{6}\log P_{O_2}$$

Brower diagram



Brouwer approximations

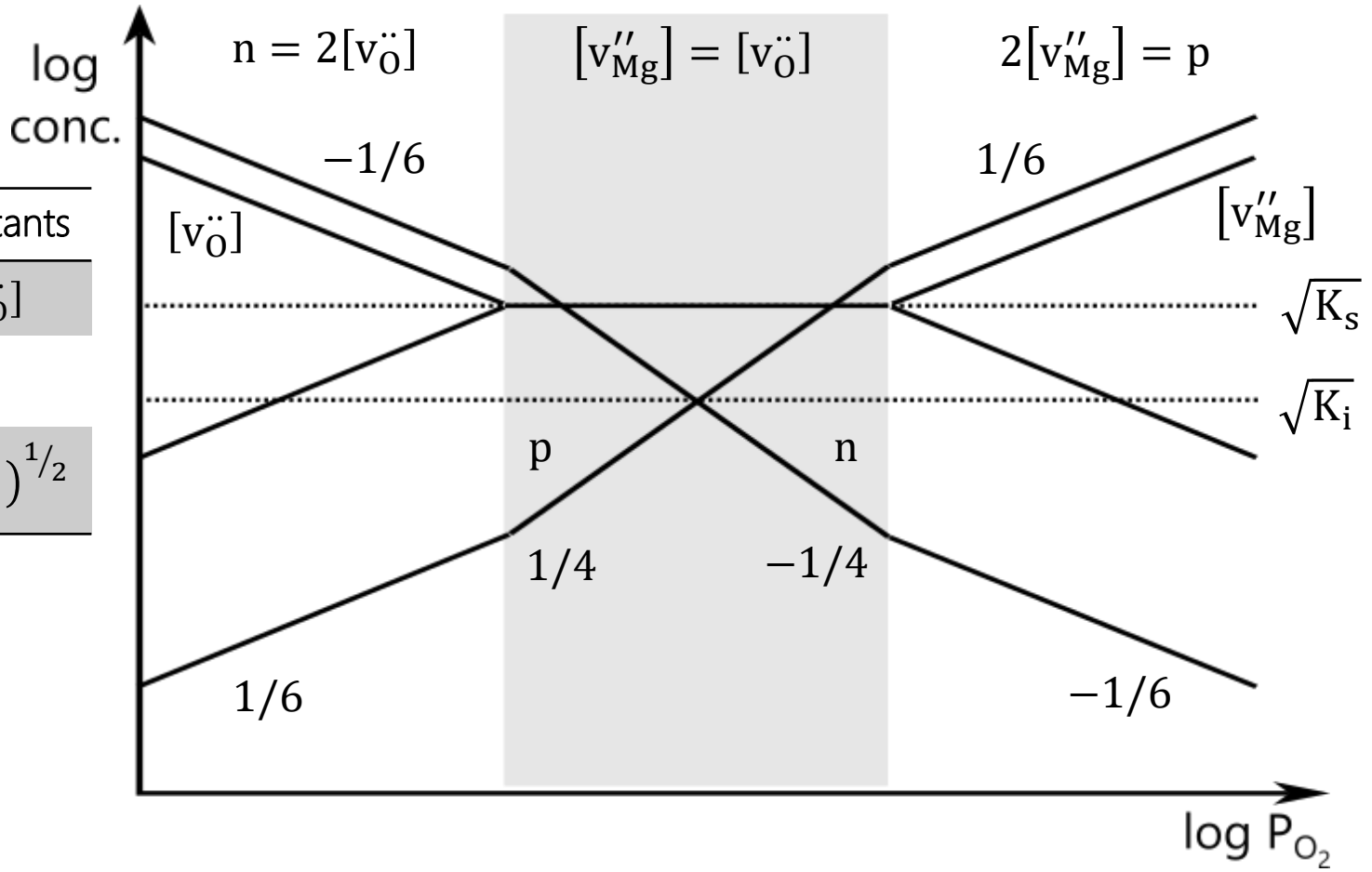
1. $n = 2[v_O^{\cdot\cdot}]$
2. $2[v_{Mg}''] = p$
3. $[v_{Mg}''] = [v_O^{\cdot\cdot}]$
4. $n = p$

Defect equilibria	Equilibrium constants
$null \rightleftharpoons v_{Mg}'' + v_O^{\cdot\cdot}$	$K_s = [v_{Mg}''][v_O^{\cdot\cdot}]$
$null \rightleftharpoons e' + h^{\cdot}$	$K_i = np$
$O_2^{\times} \rightleftharpoons \frac{1}{2}O_2(g) + v_O^{\cdot\cdot} + 2e'$	$K_R = n^2[v_O^{\cdot\cdot}](P_{O_2})^{1/2}$

$$p = 2[v_{Mg}'']$$

$$\log p \propto \frac{1}{6}\log P_{O_2}$$

Brower diagram



Brouwer approximations

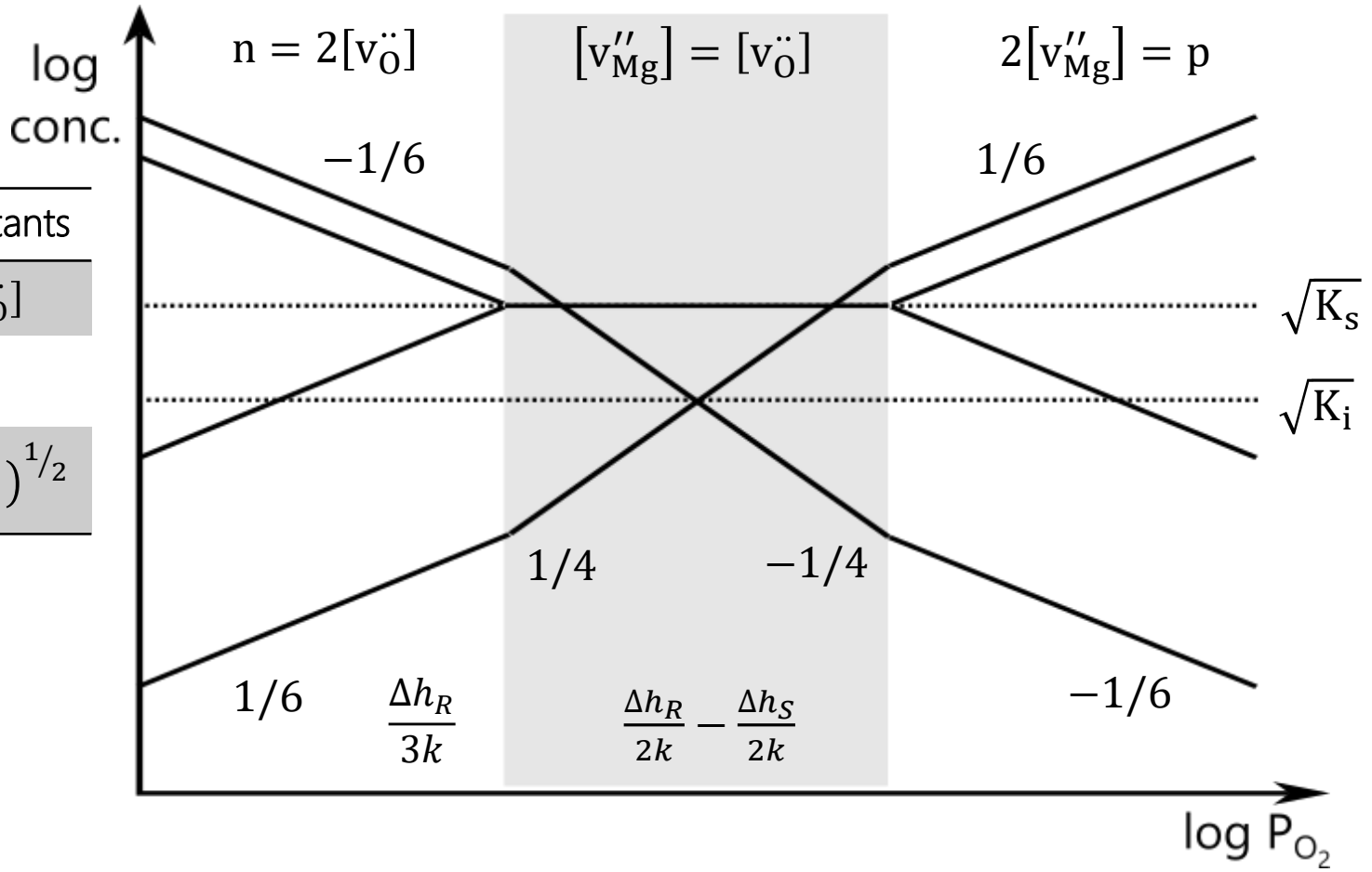
1. $\mathrm{n} = 2[\mathrm{v_O^{\cdot\cdot}}]$
2. $2[\mathrm{v''_{Mg}}] = \mathrm{p}$
3. $[\mathrm{v''_{Mg}}] = [\mathrm{v_O^{\cdot\cdot}}]$
4. $\mathrm{n} = \mathrm{p}$

Defect equilibria	Equilibrium constants
$\mathrm{null} \rightleftharpoons \mathrm{v''_{Mg}} + \mathrm{v_O^{\cdot\cdot}}$	$\mathrm{K_s} = [\mathrm{v''_{Mg}}][\mathrm{v_O^{\cdot\cdot}}]$
$\mathrm{null} \rightleftharpoons \mathrm{e'} + \mathrm{h^{\cdot}}$	$\mathrm{K}_i = \mathrm{np}$
$\mathrm{O_O^{\times}} \rightleftharpoons \frac{1}{2}\mathrm{O_2(g)} + \mathrm{v_O^{\cdot\cdot}} + 2\mathrm{e'}$	$K_R = \mathrm{n}^2[\mathrm{v_O^{\cdot\cdot}}](P_{O_2})^{1/2}$

Temperature dependence:

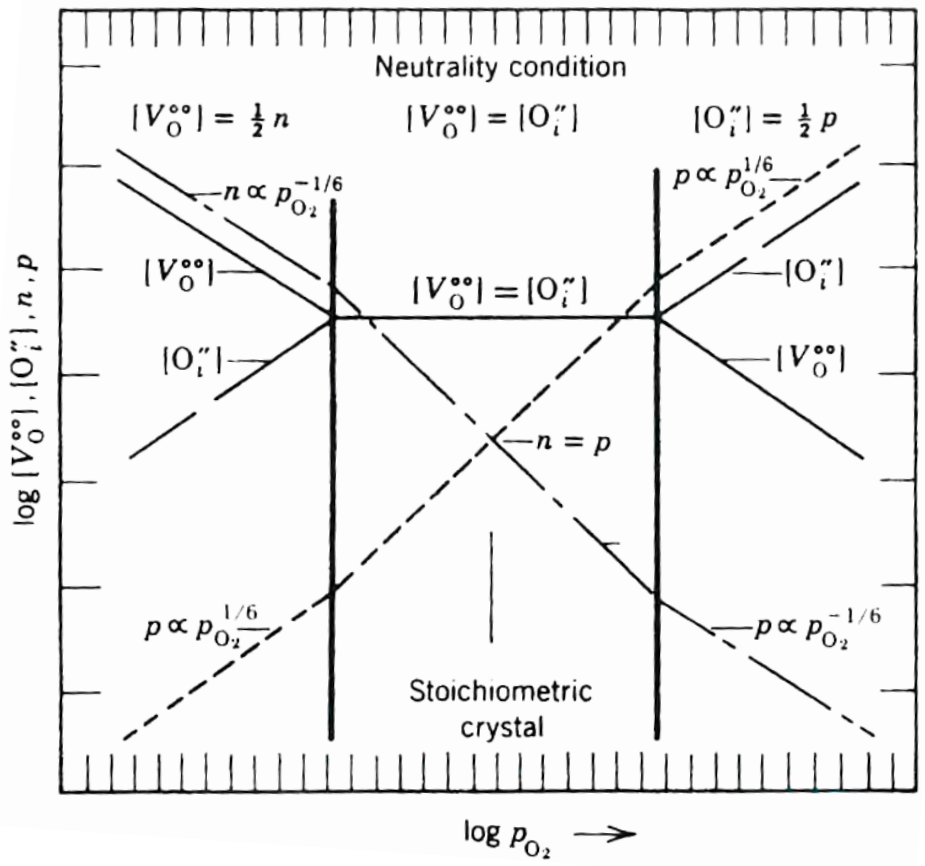
$$K = \exp\left(-\frac{\Delta g}{kT}\right) = \exp\left(\frac{\Delta s}{T}\right)\exp\left(-\frac{\Delta h}{kT}\right)$$

Brower diagram

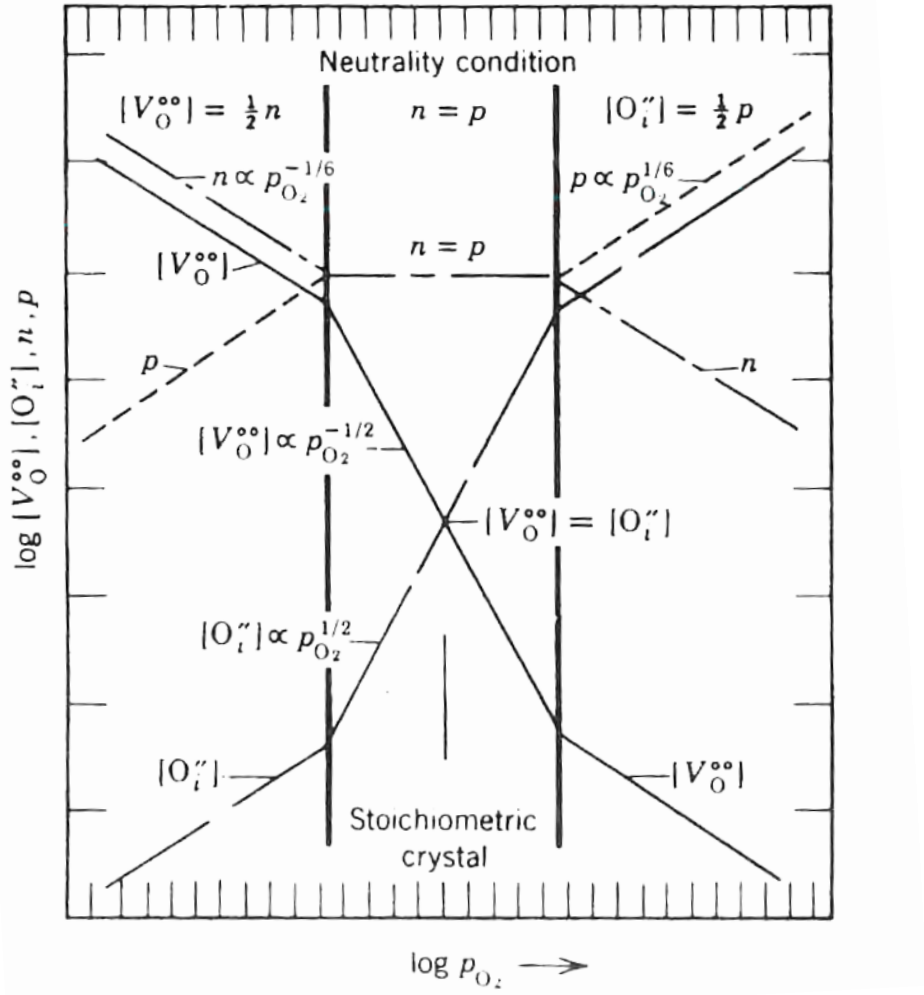


Brouwer diagrams for other systems

MO oxide
Anti-Frenkel disorder
$K_F > K_i$



MO oxide
Anti-Frenkel disorder
$K_i > K_F$



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Brouwer diagrams: General procedure

1. Decide how many defects are relevant
    1. Consider the crystal structure, bandgap, impurity concentration

2. Equilibrium constant for each independent defect reaction according to mass action
    1. Should have (N-1) equations for N defect species

3. From the overall electroneutrality: Brouwer approximations of one positive and one negative defect species.

4. Each Brouwer approximation defines a region of P_{O_2}. The Brouwer diagram will usually have 3 or 4 regions

5. Insert the Brouwer approximations into equilibrium constants to calculate the defect concentrations for a region of P_{O_2}. Often start at stoichiometric point.

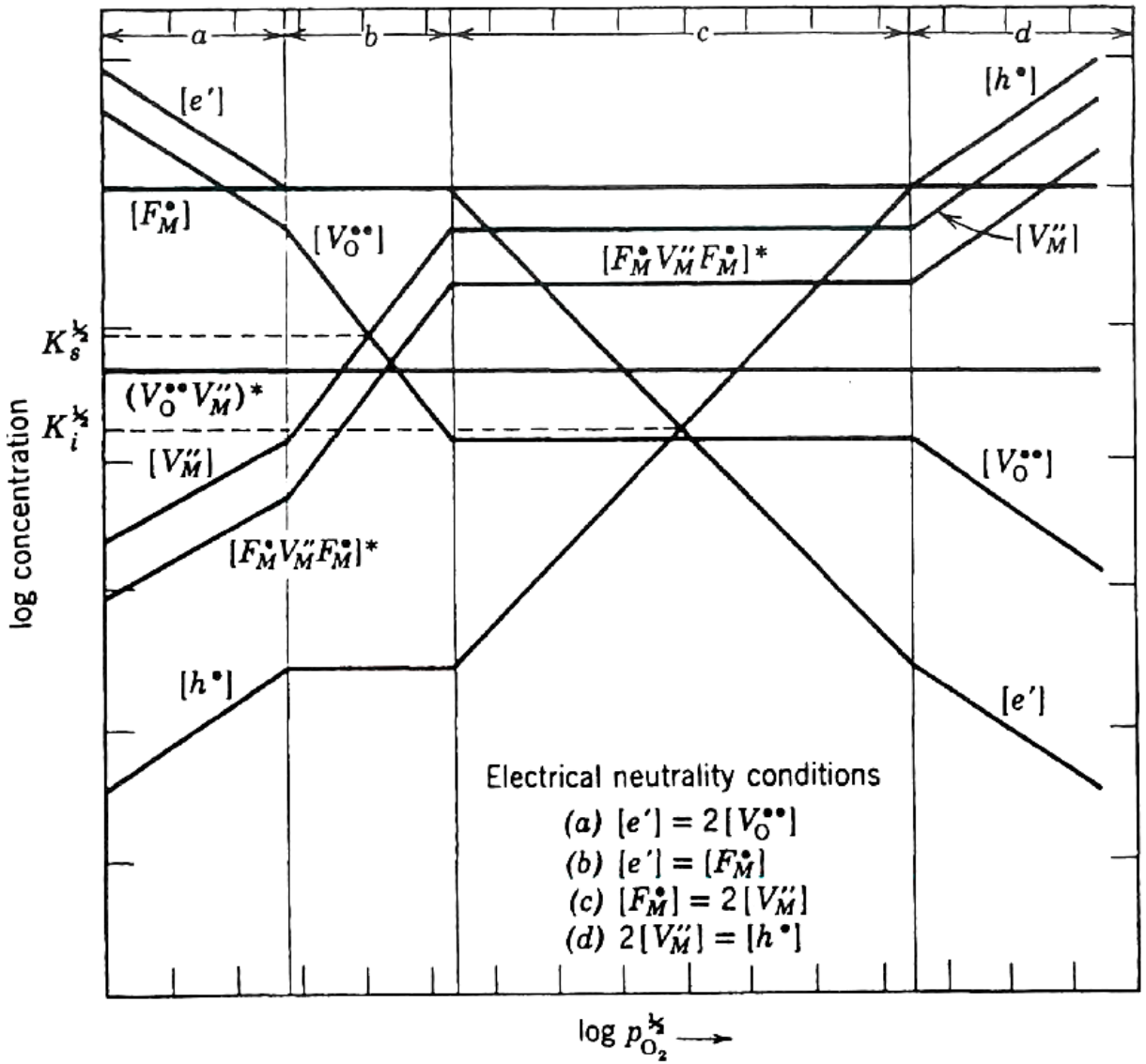
6. By extrapolating the defect concentrations along P_{O_2} to see which minority defect will take over. Repeat in both directions.

Brouwer diagrams: with solutes

Doner doped MO oxide

$$2[\mathrm{v_O^{\cdot\cdot}}] + [\mathrm{D_M^{\cdot}}] + \mathrm{p} = [\mathrm{v_M''}] + \mathrm{n}$$

1. $\mathrm{n} = 2[\mathrm{v_O^{\cdot\cdot}}]$
2. $\mathrm{n} = [\mathrm{D_M^{\cdot}}]$
3. $[\mathrm{D_M^{\cdot}}] = 2[\mathrm{v_M''}]$
4. $2[\mathrm{v_M''}] = \mathrm{p}$
5. $[\mathrm{v_O^{\cdot\cdot}}] = [\mathrm{v_M''}]$
6. $\mathrm{n} = \mathrm{p}$



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Summary

- Defect = real – ideal
- Defining defects is extremely useful
- Kröger-Vink notation
  - Do not mix up species and site
  - Use small v's and i's
  - Always use relative charge and never ever mix up real and relative charge

- Brouwer diagrams can be readily constructed and are instrumental in understanding defect concentrations in non-stoichiometric systems.