Defects in Materials

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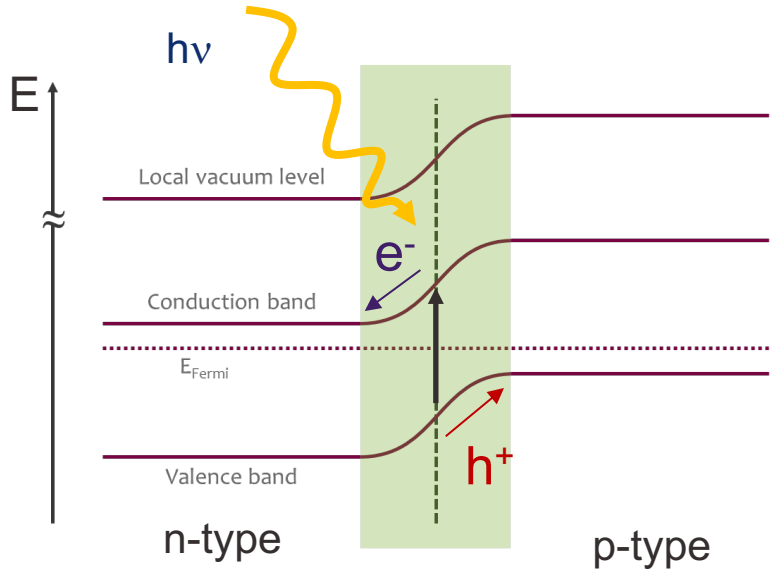
Northwestern | McCORMICK SCHOOL OF ENGINEERING

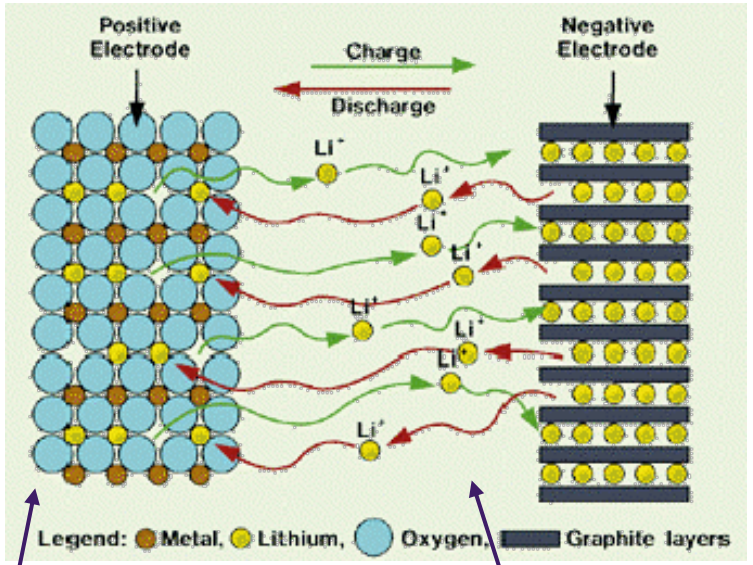
Point Defects in Non-metals

Photovoltaics



Semiconductors

Batteries



Electrolyte (ionic conductor)

Mixed ionic and electronic conductor (MIEC)

Lecture Outline

Thermodynamics of defect formation

- Macroscopic thermodynamic approach
  - Gas and solid state in equilibrium
  - Experimental methods
- Microscopic thermodynamics
  - Reduction/oxidation reaction
- Microscopic point defects
  - Energetics of defect formation
- Brouwer diagrams – Defect concentrations

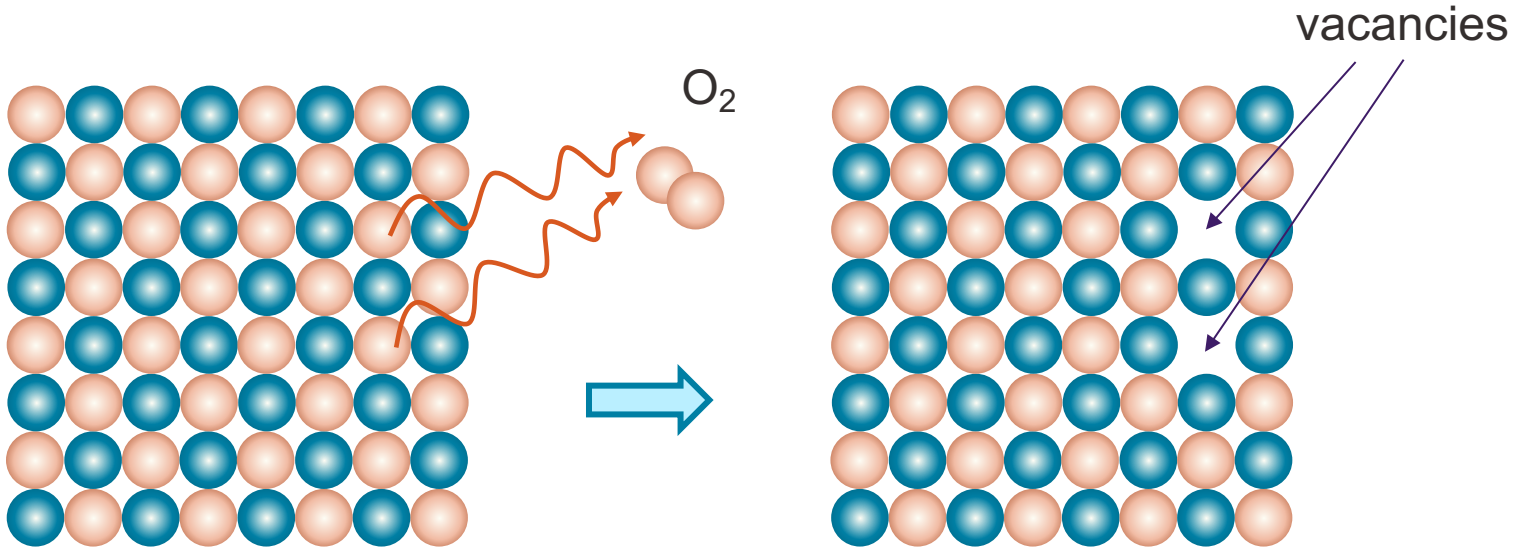
Point Defect Formation: a Chemical Reaction

Partial reduction of a variable valence oxide

$$MO \rightarrow MO_{1-d} + \frac{d}{2}O_2$$

$$\frac{2}{d}MO \rightarrow \frac{2}{d}MO_{1-d} + O_2$$

$$\frac{1}{d}MO \rightarrow \frac{1}{d}MO_{1-d} + \Omega O_2$$

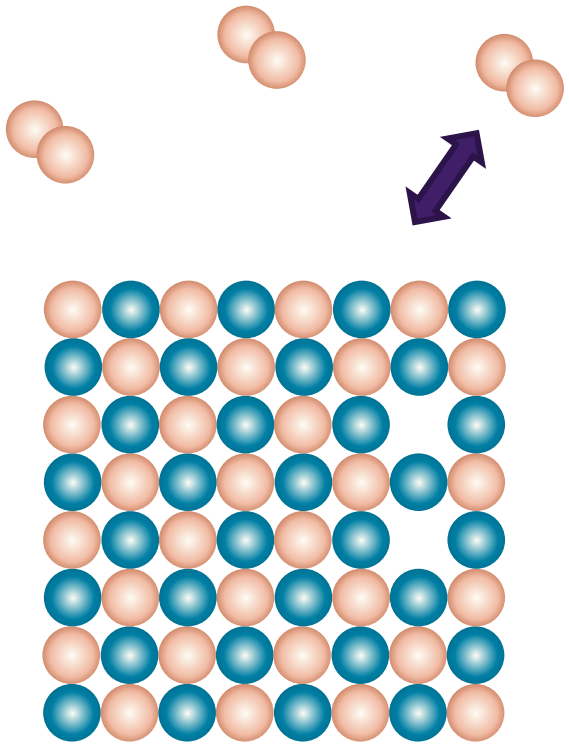


δ = oxygen nonstoichiometry

1. What is the nature of the defects that result from oxygen loss?
2. In fact, we don't need to know the answer in order to measure the thermodynamics.

Macroscopic Thermodynamic Description

oxygen in the gas phase



oxygen in the solid phase

Equilibrium:

$$\mu_O(sol) = \mu_O(gas)$$ chemical potential of oxygen

$\mu_O(gas)$ is directly given by oxygen partial pressure in the gas phase

Ideal gas:

at reference pressure

$$\mu_O(T) = \mu_O^0(T) + RT \ln\left(\hat{p}_{O_2}^{1/2}\right)$$

$$\hat{p}_{O_2} = p_{O_2} / p_{O_2}^{ref}$$

Goal: measure δ at known $\hat{p}_{O_2}$

$\delta\ (T, \hat{p}_{O_2})$ reflects thermodynamics of defect formation

Macroscopic Thermodynamic Description

Gibbs (free) energy

$$G\left(T,P,\{n_j\}\right) = H - TS$$

enthalpy entropy

chemical potential

$$\left.\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \mu_i \equiv \bar{G}_i$$

partial molar Gibbs energy

$$\Rightarrow \mu_i = \bar{H}_i - T\bar{S}_i$$

partial molar enthalpy partial molar entropy

or use lower case

$$\mu_i = h_i - Ts_i$$

$$\mu_{\mathrm{O}}(T) = \mu_{\mathrm{O}}^0(T) + RT\ln\left(\hat{p}_{\mathrm{O}_2}^{1/2}\right)$$

relative chemical potential

$$\mu_{\mathrm{O}}(T) - \mu_{\mathrm{O}}^0(T) = \Delta\bar{G}_{\mathrm{O}}^0 = RT\ln\left(\hat{p}_{\mathrm{O}_2}^{1/2}\right) = \Delta\bar{H}_{\mathrm{O}}^0 - T\Delta\bar{S}_{\mathrm{O}}^0$$

relative partial molar enthalpy and entropy

relative partial molar Gibbs energy

these *G*, *H* and *S* terms are functions of δ in $MO_{1-\delta}$

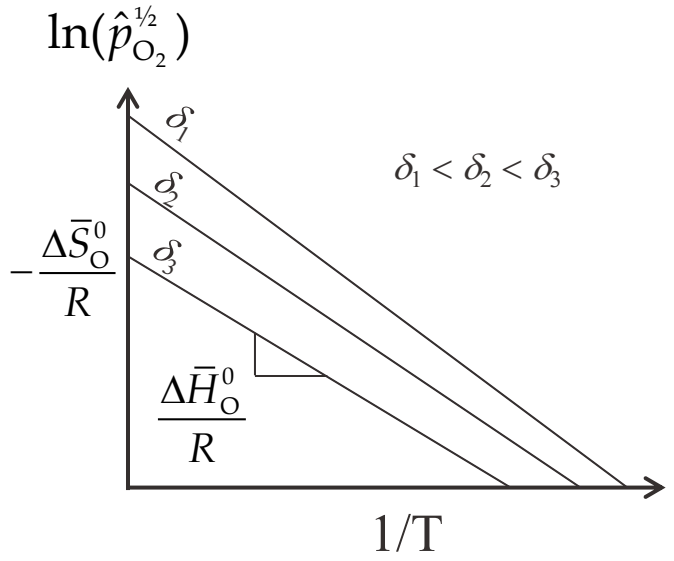
Macroscopic Thermodynamic Description

$$\Delta\mu_{O}^{0} = \Delta\bar{H}_{O}^{0} - T\Delta\bar{S}_{O}^{0} = RT\ln\left(\hat{p}_{O_2}^{1/2}\right)$$ ← terms depend on δ

Enthalpy $$\frac{\Delta\mu_{O}^{0}}{T} = \frac{\Delta\bar{H}_{O}^{0}}{T} - \Delta\bar{S}_{O}^{0} \qquad \frac{\partial\left(\Delta\mu_{O}^{0}/T\right)}{\partial(1/T)} = \Delta\bar{H}_{O}^{0} \qquad \Delta\bar{H}_{O}^{0} = \tfrac{1}{2}R\frac{\partial\ln\left(\hat{p}_{O_2}\right)}{\partial(1/T)}$$

Entropy $$\frac{\partial\Delta\mu_{O}^{0}}{\partial T} = -\Delta\bar{S}_{O}^{0} \qquad \Delta\bar{S}_{O}^{0} = -\tfrac{1}{2}R\frac{\partial T\ln\left(\hat{p}_{O_2}\right)}{\partial T}$$

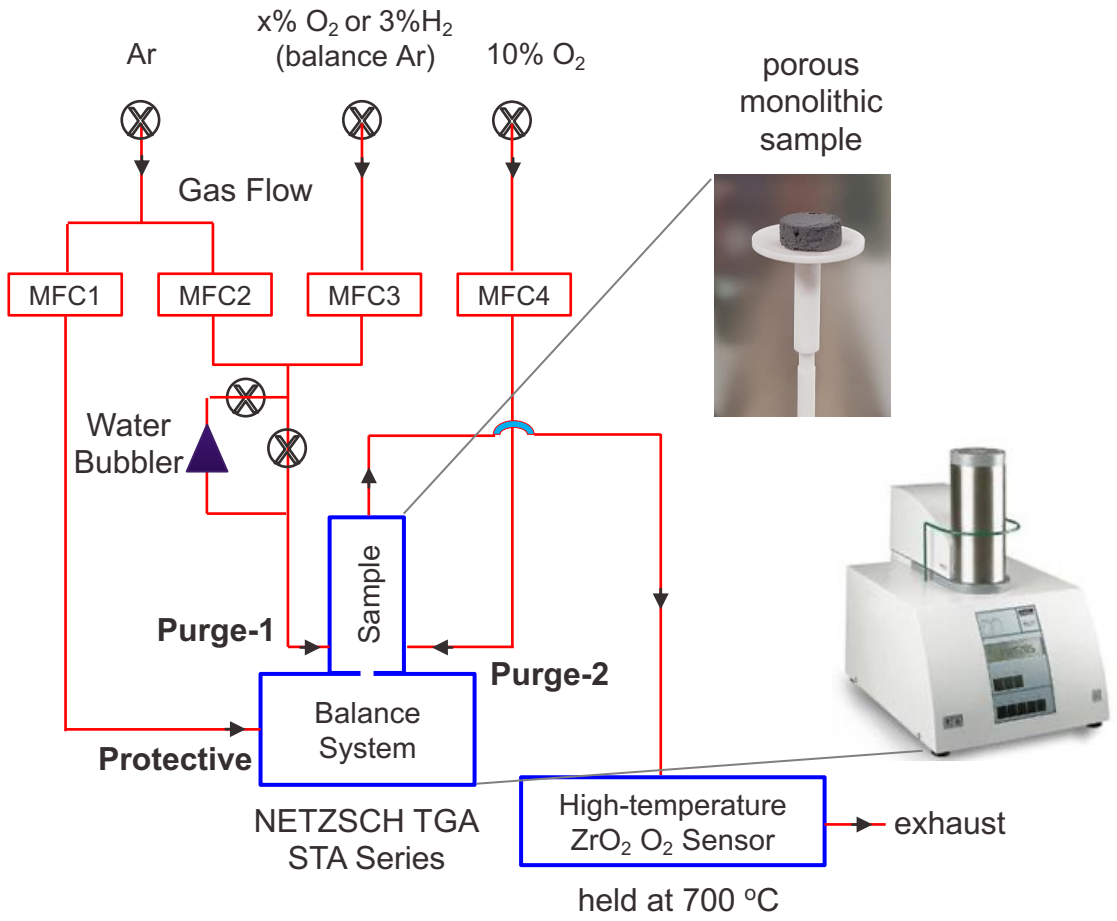
Both from one plot $$\ln\left(\hat{p}_{O_2}^{1/2}\right) = \frac{\Delta\bar{H}_{O}^{0}}{RT} - \frac{\Delta\bar{S}_{O}^{0}}{R}$$



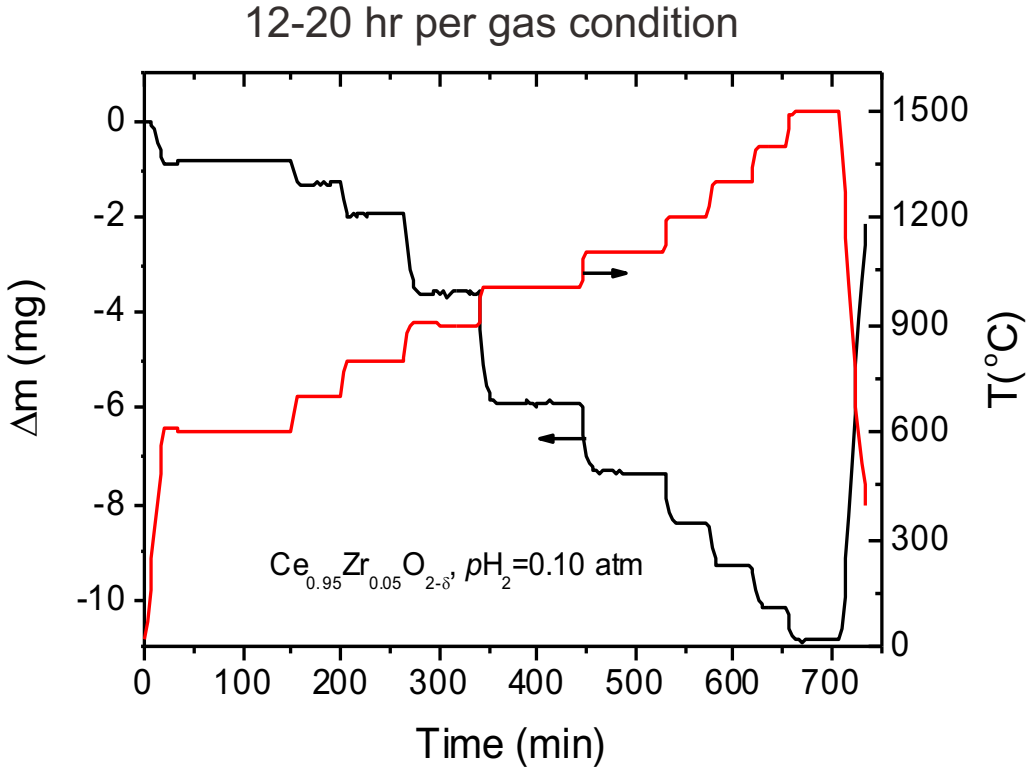
Nonlinearity from heat capacity effects, or temperature induced change in defect chemistry

Measuring Thermodynamics of Defect Formation

Goal: measure δ at known $\hat{p}_{O_2}$



Mass as a function of *T* under various gases

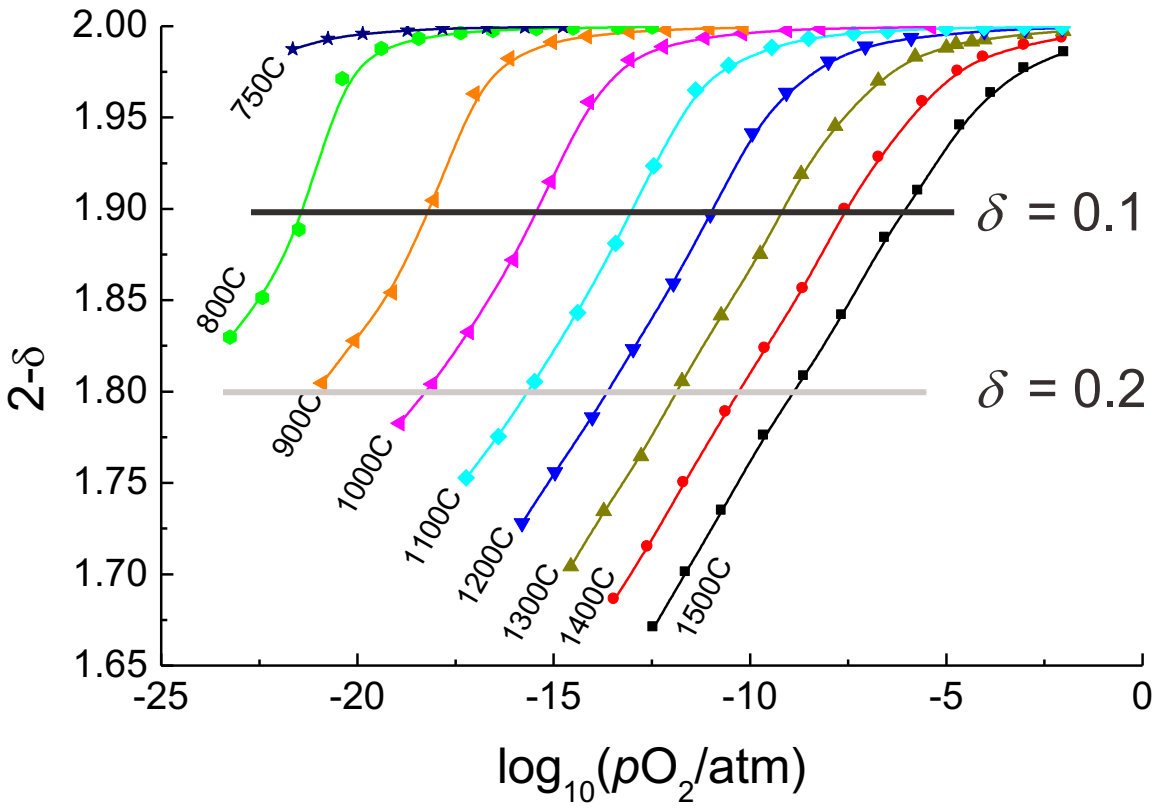


- Moderate pO_2: O_2/Ar mixtures
- Low pO_2: H_2O/H_2/Ar mixtures

Establishing Thermodynamic Functions

$$\mu_O(T) - \mu_O^0(T) = \Delta\bar{G}_O^0 = RT\ln\left(\hat{p}_{O_2}^{1/2}(\delta)\right) = \Delta\bar{H}(\delta)_O^0 - T\Delta\bar{S}(\delta)_O^0$$

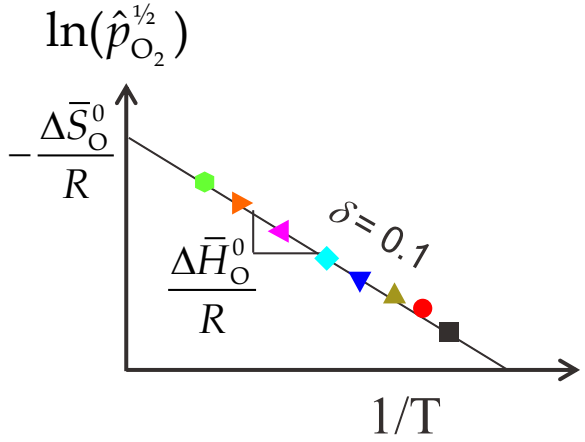
Example: $CeO_{2-\delta}$



$$\ln\left(\hat{p}_{O_2}^{1/2}\right) = \frac{\Delta\bar{H}_O^0}{RT} - \frac{\Delta\bar{S}_O^0}{R}$$

T, °C	pO_2, atm
800	10^{-23}
900	10^{-19}
1000	10^{-16}
1100	etc.

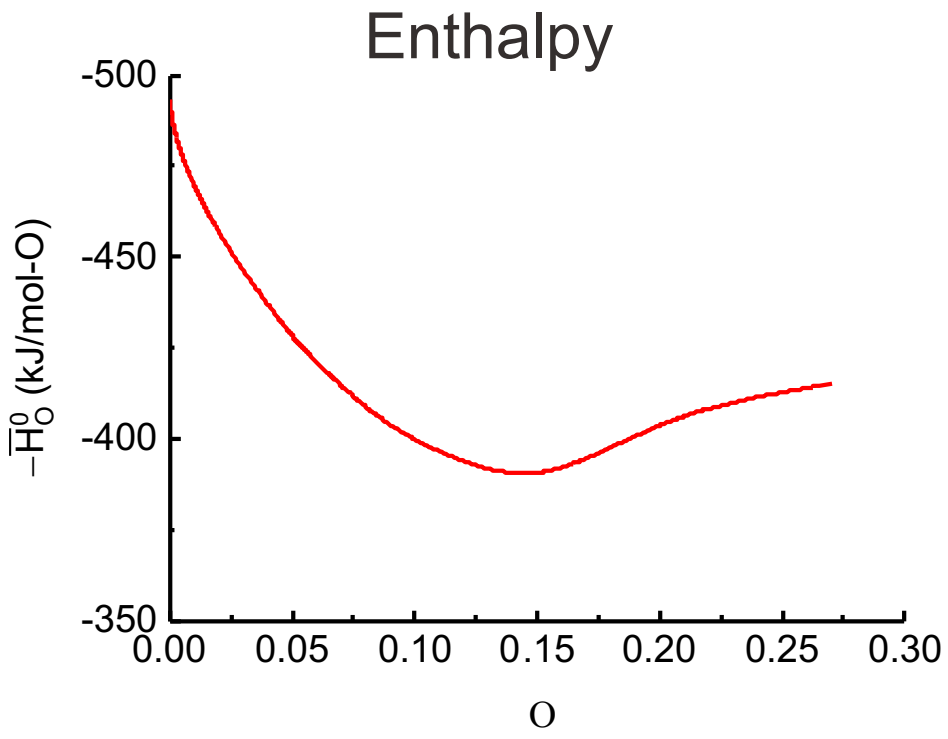
conditions for $CeO_{1.9}$

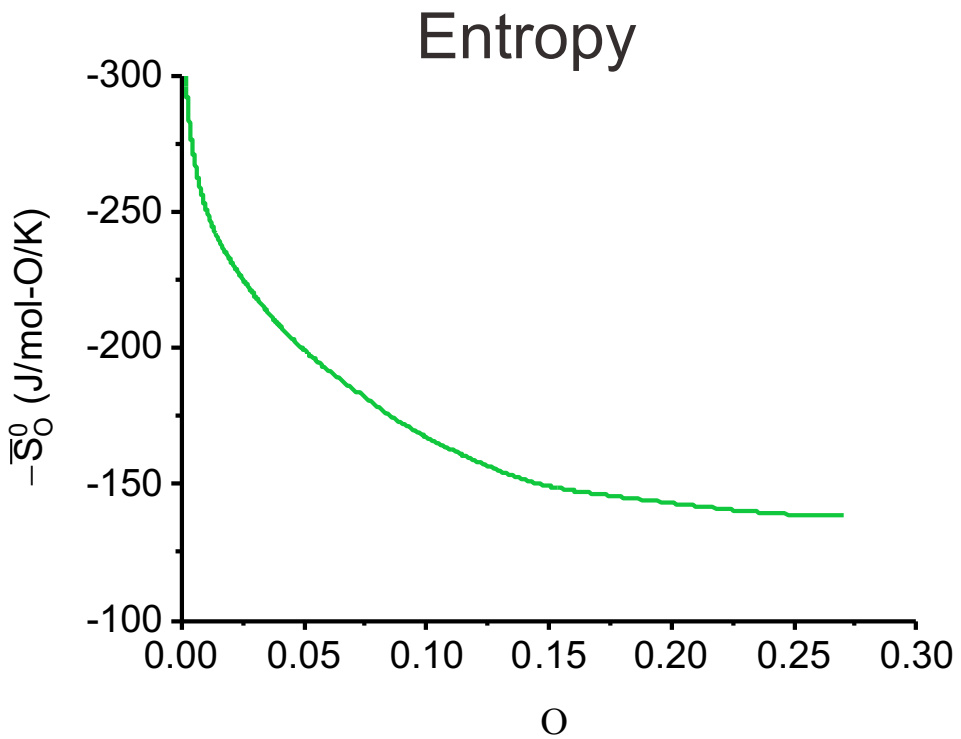


another set for $CeO_{1.8}$, etc.

Panlener et al., *J Phys. Chem. Solids*, (1975).

Thermodynamic Functions





Value? Invert $\ln\left(\hat{p}_{O_2}^{1/2}\right) = \frac{\Delta\bar{H}_O^0}{RT} - \frac{\Delta\bar{S}_O^0}{R}$ to solve for δ at given T and $\hat{p}_{O_2}$

Insight into chemical and physical nature of defects from functional forms of H and S

Panlener et al., *J Phys. Chem. Solids*, (1975).

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- Microscopic thermodynamics
  - Reduction/oxidation reaction
- Microscopic point defects
  - Energetics of defect formation
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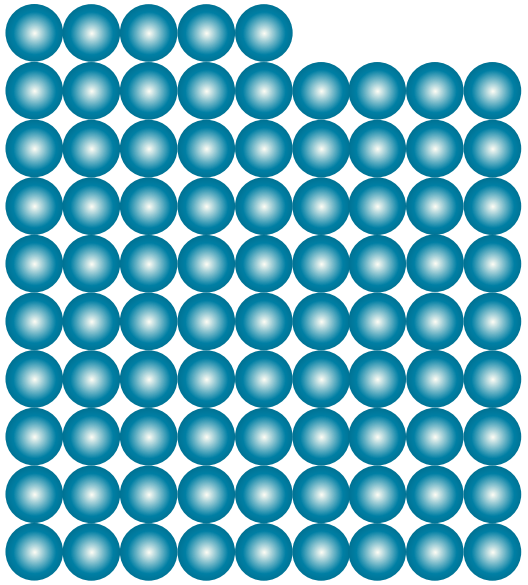
Microscopic Thermodynamic Description



Vacancies in metals

Equilibrium: minimize G of the system

$$G - G_0 = \Delta G = \Delta H_{vac} - T\Delta S_{vac}$$

N_{vac} = moles of vacancies

G: with vacancies; G_0: no vacancies

non-interacting (dilute limit)

$$\Delta G = N_{vac}(\Delta h_{f,vac} - T\Delta s_{f,vac}^{non-config}) - TS_{vac}^{config}$$

"excess" entropy

$$S_{vac}^{config} = R\ln\Omega$$

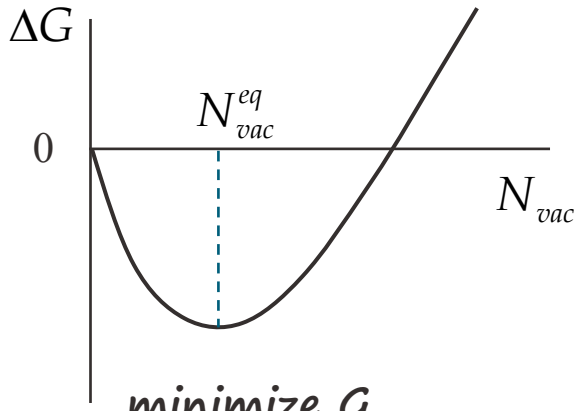
not directly proportional to N_{vac}

$$\Delta G = N_{vac}(\Delta h_{f,vac} - T\Delta s_{f,vac}^{non-config}) + RT\left[N_{vac}\ln\left(\frac{N_{vac}}{N_A + N_{vac}}\right) + N_A\ln\left(\frac{N_A}{N_A + N_{vac}}\right)\right]$$

non-interacting, randomly distributed vacancies

Point Defect Concentration in Metals

$$\Delta G = N_{vac}(\Delta h_{f,vac} - T\Delta s_{f,vac}^{non-config}) + RT\left[N_{vac}\ln\left(\frac{N_{vac}}{N_A + N_{vac}}\right) + N_A \ln\left(\frac{N_A}{N_A + N_{vac}}\right)\right]$$



minimize G
wrt N_{vac}

$$\Rightarrow \mu_{vac} = 0$$

$$\frac{\partial \Delta G}{\partial N_{vac}} = \frac{\partial G}{\partial N_{vac}} = \Delta h_{f,vac} - T\Delta s_{f,vac}^{non-config} + RT\ln\left(\frac{N_{vac}}{N_A + N_{vac}}\right) = 0$$

fractional concentration χ_{vac}

$$\Rightarrow \chi_{vac} = \exp\left(\frac{-\left(\Delta h_{f,vac} - T\Delta s_{f,vac}^{non-config}\right)}{RT}\right) = \exp\left(\frac{-\left(\Delta g'_{f,vac}\right)}{RT}\right)$$

$\Delta g'_{f,vac}$

Defect Formation as a Chemical Reaction

Generic reaction $bB + cC \rightarrow dD + eE$

Equilibrium: $\sum_i^{prod} \nu_i \mu_i = \sum_j^{react} \nu_j \mu_j$

in the state of interest

$$\mu_i = \mu_i^0 + RT \ln a_i$$

in the reference state

ideal gas $\hat{p}_i$

$$\mu(T) = \overbrace{\mu(T, p^0)}^{\mu^0(T)} + RT \ln \left(\frac{p}{p^0} \right)$$

standard pressure

dilute component χ_i

$$\mu(T) = \overbrace{\mu(T, pure)}^{\mu^0(T)} + RT \ln \left(\frac{n}{n_{pure}} \right)$$

standard concentration

Equilibrium:

$$\underbrace{\sum_i^{prod} \nu_i \mu_i^0 - \sum_j^{react} \nu_j \mu_j^0}_{\Delta_{rxn} g^0} = -RT \ln \left(\frac{a_{p1}^{\nu_{p1}} a_{p2}^{\nu_{p2}} a_{p3}^{\nu_{p3}} \ldots}{a_{r1}^{\nu_{r1}} a_{r2}^{\nu_{r2}} a_{r3}^{\nu_{r3}} \ldots} \right)$$

products / reactants

$$Q = \left(\frac{a_{p1}^{\nu_{p1}} a_{p2}^{\nu_{p2}} a_{p3}^{\nu_{p3}} \ldots}{a_{r1}^{\nu_{r1}} a_{r2}^{\nu_{r2}} a_{r3}^{\nu_{r3}} \ldots} \right)$$

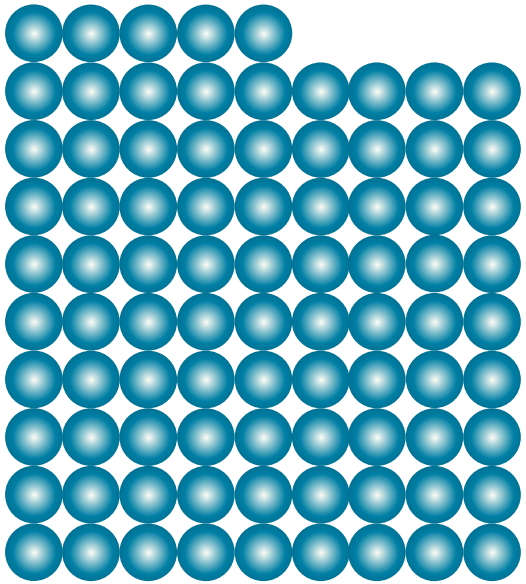
Equilibrium:

$$\left(\frac{a_{p1}^{\nu_{p1}} a_{p2}^{\nu_{p2}} a_{p3}^{\nu_{p3}} \ldots}{a_{r1}^{\nu_{r1}} a_{r2}^{\nu_{r2}} a_{r3}^{\nu_{r3}} \ldots} \right) = \exp \left(\frac{-\Delta_{rxn} g^0}{RT} \right) = K_{eq}$$

Vacancy Formation Reaction in Metals

Minization of G, considering configurational entropy gave

$$\chi_{vac} = \exp\left(\frac{-\left(\Delta h_{f,vac} - T\Delta s_{f,vac}^{non-config}\right)}{RT}\right) = \exp\left(\frac{-\left(\Delta g'_{f,vac}\right)}{RT}\right)$$



Treat as defect reaction

$$M_M \rightarrow V_M + M_S \qquad K_{eq,vac} = \frac{a_{vac}a_{M,surf}}{a_{M,bulk}} = \chi_{vac}$$

$$K_{eq,vac} \equiv \exp\left(\frac{-\left(\Delta_{rxn}g^0\right)}{RT}\right) \quad \Rightarrow \quad \Delta_{rxn}g^0 = \Delta h_{f,vac} - T\Delta s_{f,vac}^{non-config}$$

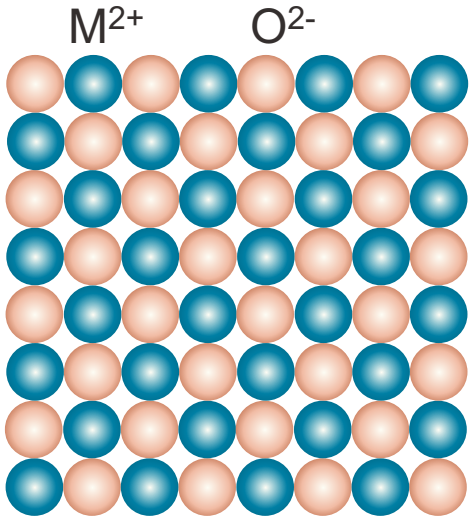
$$\Delta_{rxn}g^0 = \Delta_{rxn}h^0 - T\Delta_{rxn}s^0$$

$$\Delta_{rxn}g^0 = \sum_i^{prod} \nu_i \mu_i^0 - \sum_j^{react} \nu_j \mu_j^0 = \mu_{vac}^0$$

Note that the standard Gibbs energy of reaction **does not include solid state configurational entropy**

Microscopic Defect formation in Metal Oxide

Define the point defects involved in the reaction $\frac{1}{d}MO \text{ Æ } \frac{1}{d}MO_{1-d} + \Omega O_2$



O_2

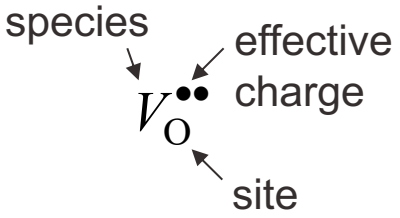
Vacancies created at oxygen ion sites

O^{2-} ions must be removed as neutral species

Electrons have to be 'placed' somewhere:

1. Electrons trapped at vacancies
2. M^{2+} reduced to M^{+}, electrons trapped at metal sites
3. Electrons added to the conduction band, itinerant electrons

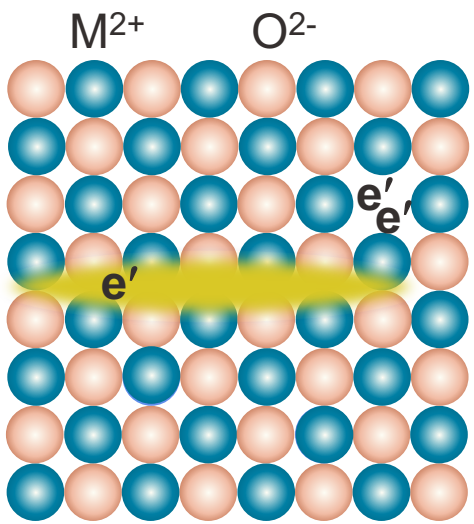
Describe using formal defect notation:



′ negative
• positive
× neutral

Microscopic Defect formation in Metal Oxide

Define the point defects involved in the reaction $\frac{1}{d}\mathrm{MO} \text{ Æ } \frac{1}{d}\mathrm{MO}_{1-d} + \Omega\mathrm{O}_2$



charged defects

1. Electrons trapped at vacancies

$$\mathrm{O}_\mathrm{O}^\times \leftrightarrow \tfrac{1}{2}\mathrm{O}_2 + V_\mathrm{O}^\times$$

2. M^{2+} reduced to M^+, electrons trapped at metal sites

$$\mathrm{O}_\mathrm{O}^\times + 2\,\mathrm{M}_\mathrm{M}^\times \leftrightarrow \tfrac{1}{2}\mathrm{O}_2 + V_\mathrm{O}^{\bullet\bullet} + 2\,\mathrm{M}'_\mathrm{M}$$

3. Electrons added to the conduction band, itinerant electrons

$$\mathrm{O}_\mathrm{O}^\times \leftrightarrow \tfrac{1}{2}\mathrm{O}_2 + V_\mathrm{O}^{\bullet\bullet} + 2\mathrm{e}'$$

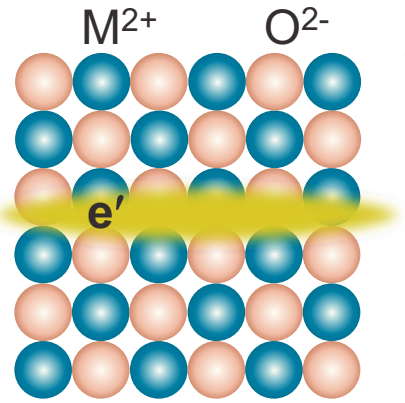
Reactions obey charge, site, and mass balance

'Isolated' charged defect formation impacts electron count: $\mathrm{M}_\mathrm{M}^\times + \mathrm{e}' \leftrightarrow \mathrm{M}'_\mathrm{M}$

Consider Electrons in Conduction Band

$$O_O^{\times} \rightarrow \tfrac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e^- \qquad \Delta_{rxn}g^0 = \sum_i^{prod} \nu_i \mu_i^0 - \sum_j^{react} \nu_j \mu_j^0$$

$$\Delta_{red}g^0 = \tfrac{1}{2}\mu_{O_2}^0 + \mu_{V_O^{\bullet\bullet}}^0 + 2\mu_{e^-}^0 - \mu_{O_O^{\times}}^0 = -RT\ln\left(\frac{a_{O_2}^{1/2} a_{V_O^{\bullet\bullet}} a_{e^-}^2}{a_{O_O^{\times}}}\right) \approx -RT\ln\left(\hat{p}_{O_2}^{1/2} \chi_{V_O^{\bullet\bullet}} \chi_{e^-}^2\right)$$



$$-\Delta_{red}g^0 = RT\ln(\hat{p}_{O_2}^{1/2}) + RT\ln(\chi_{V_O^{\bullet\bullet}}\chi_{e^-}^2)$$

relative partial molar quantities

Recall: $\mu_O = \mu_O^0 + RT\ln\left(\hat{p}_{O_2}^{1/2}\right) \Rightarrow RT\ln\left(\hat{p}_{O_2}^{1/2}\right) = \mu_O - \mu_O^0 = h_O - h_O^0 - T(s_O - s_O^0) = \Delta\bar{H}_O^0 - T\Delta\bar{S}_O^0$

partial molar configurational entropy on removing O

$$-\Delta_{red}g^0 = \Delta\bar{H}_O^0 - T\Delta\bar{S}_O^0 + RT\ln(\chi_{V_O^{\bullet\bullet}}\chi_{e^-}^2) = \underbrace{\Delta\bar{H}_O^0}_{-\Delta_{red}h^0} - T\left(\underbrace{\Delta\bar{S}_O^0 - R\ln(\chi_{V_O^{\bullet\bullet}}\chi_{e^-}^2)}_{-\Delta_{red}s^0}\right)$$

for ***reduction*** reaction

oxidation has opposite sign

Contributions to Thermodynamic Terms

Treat **oxidation** for sanity's sake $\tfrac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e^- \rightarrow O_O^{\times}$

$$\Delta_{rxn} g^0 = \sum_i^{prod} \nu_i \mu_i^0 - \sum_j^{react} \nu_j \mu_j^0$$

$$\Delta_{oxd} g^0 = \mu_{O_O^{\times}}^0 - \mu_{V_O^{\bullet\bullet}}^0 - 2\mu_{e^-}^0 - \tfrac{1}{2}\mu_{O_2}^0$$

$$\Delta_{oxd} h^0 = \Delta \bar{H}_O^0$$

$$\Delta_{oxd} s^0 = \Delta \bar{S}_O^0 - R \ln(\chi_{V_O^{\bullet\bullet}} \chi_{e^-}^2)$$

configurational entropy change

$$\bar{S}_{oxd,config} < 0$$

$$\Delta_{oxd} h^0 = h_{O_O^{\times}}^0 - h_{V_O^{\bullet\bullet}}^0 - 2h_{e^-}^0 - \tfrac{1}{2}h_{O_2}^0$$

$$\Delta_{oxd} s^0 = s_{O_O^{\times}}^0 - s_{V_O^{\bullet\bullet}}^0 - 2s_{e^-}^0 - \tfrac{1}{2}s_{O_2}^0$$

← entropy of gas phase oxygen (large)

"excess" entropy in the solid (vibrational, electronic, magnetic)

$$\Delta_{oxd} \bar{S}_{non-config}^0$$

Recall, we measure

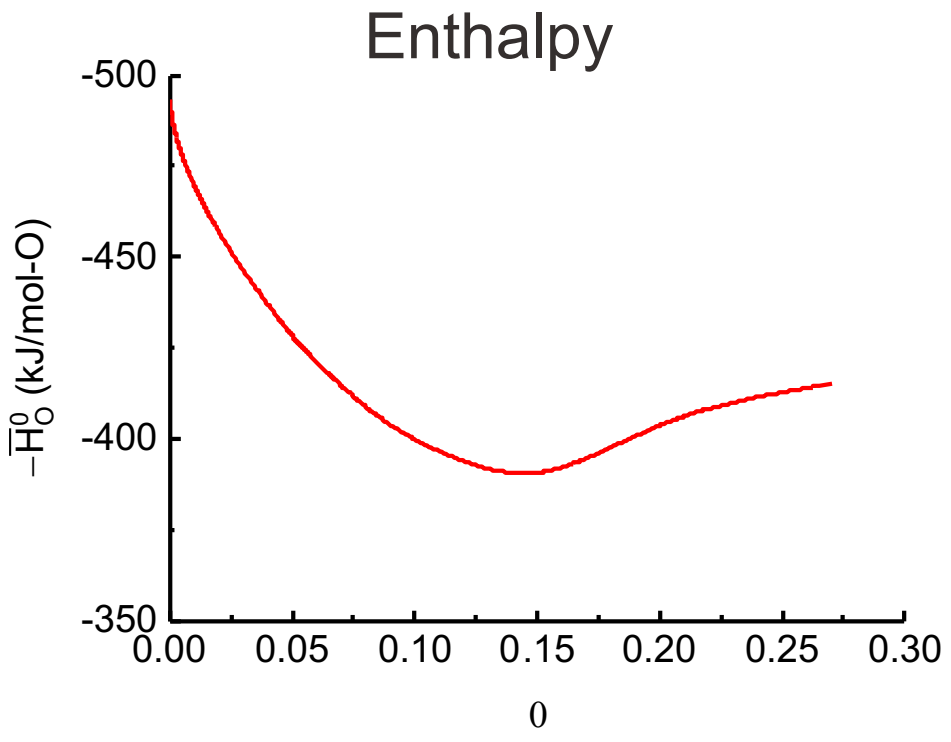
Partial molar enthalpy of oxygen

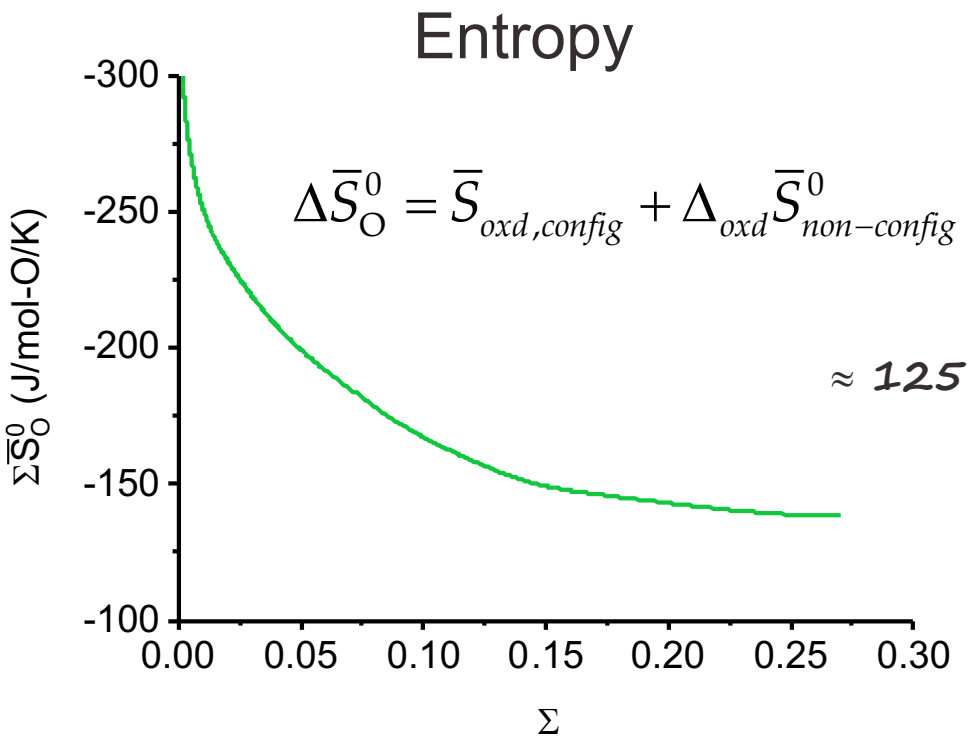
$$\Delta \bar{H}_O^0 = h_{O_O^{\times}}^0 - h_{V_O^{\bullet\bullet}}^0 - 2h_{e^-}^0 - \tfrac{1}{2}h_{O_2}^0$$

Partial molar entropy of oxygen

$$\Delta \bar{S}_O^0 = \Delta_{oxd} \bar{S}_{non-config}^0 - \tfrac{1}{2}s_{O_2}^0 + \bar{S}_{oxd,config}$$

Thermodynamic Functions





$$\Delta\bar{S}_O^0 = \bar{S}_{oxd,config} + \Delta_{oxd}\bar{S}^0_{non-config} - \tfrac{1}{2}s^0_{O_2}$$

≈ 125 J/mol-O/K

Lowest δ $2Ce^{\times}_{Ce} + O^{\times}_{O} \leftrightarrow 2Ce'_{Ce} + V^{\bullet\bullet}_{O} + \tfrac{1}{2}O_2$

Increasing δ $2Ce^{\times}_{Ce} + O^{\times}_{O} \leftrightarrow (Ce'_{Ce}\, V^{\bullet\bullet}_{O}\, Ce'_{Ce})^{\times} + \tfrac{1}{2}O_2$

Dominated by large S of gas phase oxygen

Report: $\Delta\bar{S}_O^0 + \tfrac{1}{2}s^0_{O_2} = \bar{S}_{oxd,config} + \Delta_{oxd}\bar{S}^0_{non-config}$

Panlener et al., *J Phys. Chem. Solids*, (1975).

Configurational Entropy*

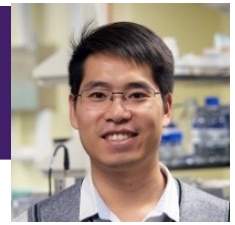
Depends on nature of reaction $\bar{S}_{config} = -R\ln\left(\frac{\chi_{p1}^{\nu_{p1}}\chi_{p2}^{\nu_{p2}}\chi_{p3}^{\nu_{p3}}\cdots}{\chi_{r1}^{\nu_{r1}}\chi_{r2}^{\nu_{r2}}\chi_{r3}^{\nu_{r3}}\cdots}\right)$ tends to -∞ as $\rightarrow 0$

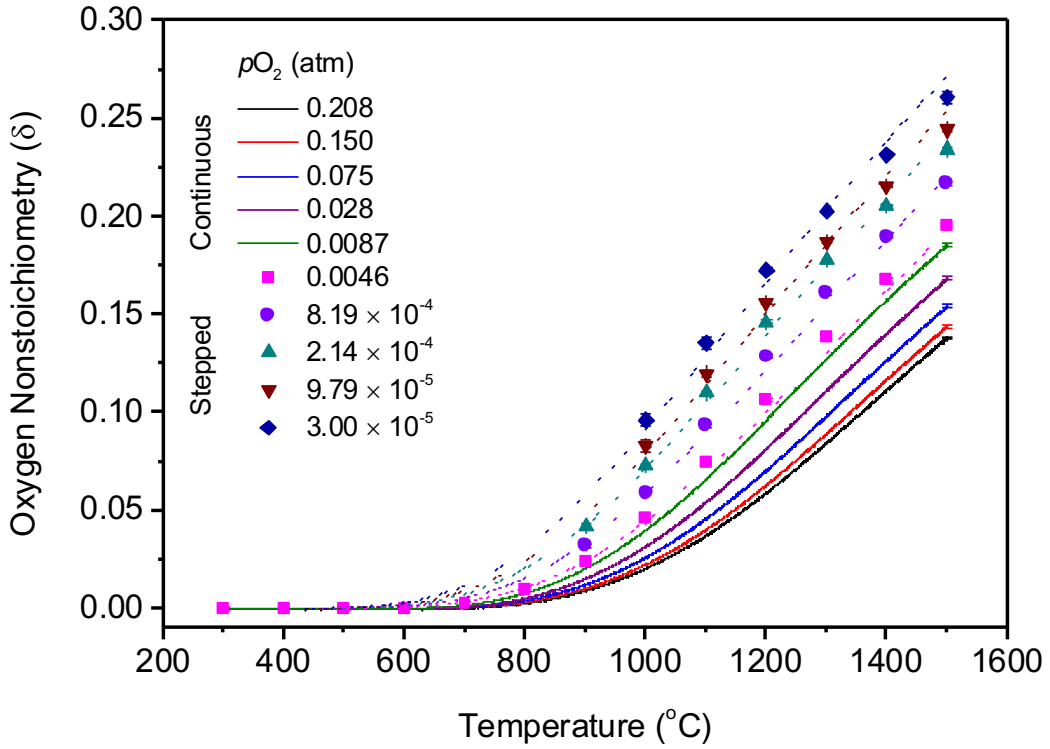
	$\bar{S}_{config}$	neutrality constraint	$\bar{S}_{config}$
1. Electrons trapped at vacancies $\frac{1}{2}O_2 + V_O^{\times} \leftrightarrow O_O^{\times}$	$R\ln(\chi_{V_O^{\times}})$	N/A	$\sim R\ln(\delta)$ ↳ $R\ln\left(\frac{\delta}{2-\delta}\right)$
2. M^{2+} reduced to M^{+}, electrons trapped at metal sites $\frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2M'_M \leftrightarrow O_O^{\times} + 2M_M^{\times}$	$R\ln(\chi_{V_O^{\bullet\bullet}}\chi^2_{M'_M})$	$\chi_{V_O^{\bullet\bullet}} \propto \chi_{e^-}$	$\sim 3R\ln(\delta)$
3. Electrons added to the conduction band, itinerant electrons $\frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e' \leftrightarrow O_O^{\times}$	$R\ln(\chi_{V_O^{\bullet\bullet}}\chi^2_{e^-})$	$\chi_{V_O^{\bullet\bullet}} \propto \chi_{e^-}$	$\sim 3R\ln(\delta)$

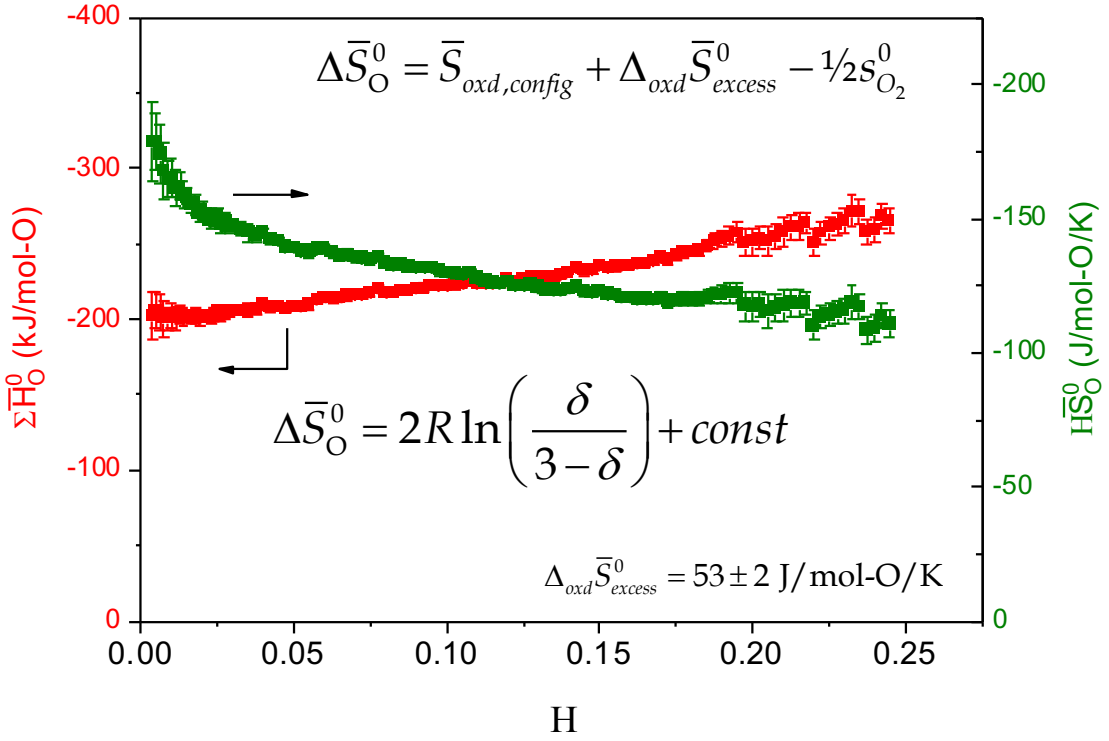
At large δ, need to include concentration of product in the quotient

*partial molar change in solid state configurational entropy

Example: $Sr(Ti_{0.5}Mn_{0.5})O_{3-\delta}$







$$Mn^{//}_{Mn} + V^{\bullet\bullet}_{O} + \tfrac{1}{2}O_2 \leftrightarrow Mn^{\times}_{Mn} + O^{\times}_{O}$$

2+ 4+

negligible Mn^{3+} (!)

X. Qian, J. He, E. Mastronardo, B. Baldassarri, C. Wolverton, S. M. Haile, *Chem. Mater.* **32** 9335−9346 (2020).

Lecture Outline

Thermodynamics of defect formation

- Macroscopic thermodynamic approach
  - Gas and solid state in equilibrium
  - Experimental methods
- Microscopic thermodynamics
  - Reduction/oxidation reaction
- Microscopic point defects
  - Energetics of defect formation
- Brouwer diagrams – Defect concentrations

Energetics

$MO \rightarrow MO_{1-d} + \frac{d}{2}O_2$ presume an oxygen vacancy is created, defect state agnostic

We wish to **define** the oxygen vacancy and **calculate** its energy of formation

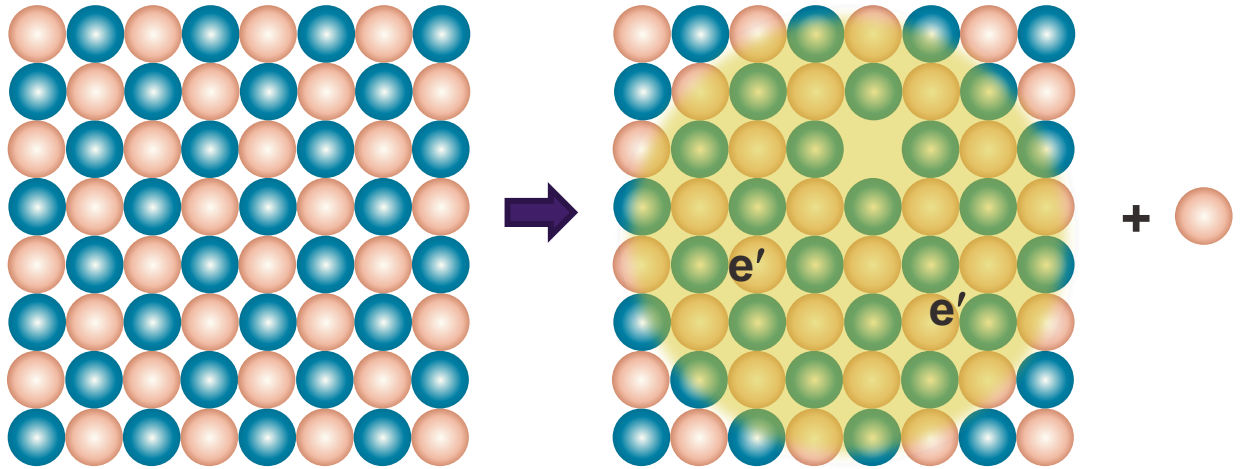
$$O_O^{\times} \rightarrow \tfrac{1}{2}O_2 + V_O^{\times} \qquad O_O^{\times} + 2M_M^{\times} \rightarrow \tfrac{1}{2}O_2 + V_O^{\bullet\bullet} + 2M'_M \qquad \boxed{O_O^{\times} \rightarrow \tfrac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e'}$$

$$MO \rightarrow \underbrace{(MO_{1-d})^{2d+} + 2de^-}_{\text{solid}} + \underbrace{\frac{d}{2}O_2}_{\text{gas}}$$

$$\frac{1}{d}MO \rightarrow \frac{1}{d}(MO_{1-d})^{2+} + 2e^- + \frac{1}{2}O_2$$

$$\Delta_{red}G = \frac{1}{\delta}\left[\mu_{MO_{1-\delta}} - \mu_{MO}\right] + \mu_O + 2E_F$$

$$\mu_O = \tfrac{1}{2}\mu_{O_2} \qquad \mu_{e^-} = E_F$$



From Energetics to Concentration

$$\Delta_{red}G = \frac{1}{\delta}\left[\mu_{MO_{1-\delta}} - \mu_{MO}\right] + \mu_O + 2E_F \qquad \mu_{MO_{1-\delta}} = h_{MO_{1-\delta}} - Ts^{non-config}_{MO_{1-\delta}} - Ts^{config}_{MO_{1-\delta}}$$

$$\equiv \mu^*_{MO_{1-\delta}} - Ts^{config}_{MO_{1-\delta}}$$

$$\Delta_{red}G = \frac{1}{\delta}\left[\mu^*_{MO_{1-\delta}} - \mu_{MO}\right] + \mu_O + 2E_F - \frac{1}{\delta}Ts^{config}_{MO_{1-\delta}}$$

$$\equiv \Delta G_{V_O^{\bullet\bullet}}$$

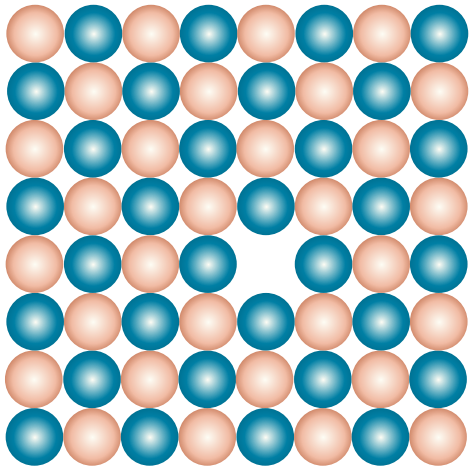
at equilibrium

$$\Delta_{red}G = 0 \quad \Rightarrow \Delta G_{V_O^{\bullet\bullet}} = \frac{1}{\delta}Ts^{config}_{MO_{1-\delta}}$$

$$S = R\ln\Omega$$

$$\Omega_{MO_{1-\delta}} \approx (\chi_{V_O^{\bullet\bullet}})^{-\delta}$$

1/δ moles of MO



$$\Omega = \exp\left(\frac{S}{R}\right) \qquad (\chi_{V_O^{\bullet\bullet}})^{-\delta} = \exp\left(\frac{\delta\Delta G_{V_O^{\bullet\bullet}}}{RT}\right)$$

$$\chi_{V_O^{\bullet\bullet}} = \exp\left(\frac{-\Delta G_{V_O^{\bullet\bullet}}}{RT}\right)$$

From Energetics to Concentrations

$$\chi_{V_O^{\bullet\bullet}} = \exp\left(\frac{-\Delta G_{V_O^{\bullet\bullet}}}{RT}\right)$$

$$\Delta G_{V_O^{\bullet\bullet}} \equiv \frac{1}{\delta}\left[\mu^*_{\mathrm{MO}_{1-\delta}} - \mu_{\mathrm{MO}}\right] + \mu_{\mathrm{O}} + 2E_{\mathrm{F}}$$

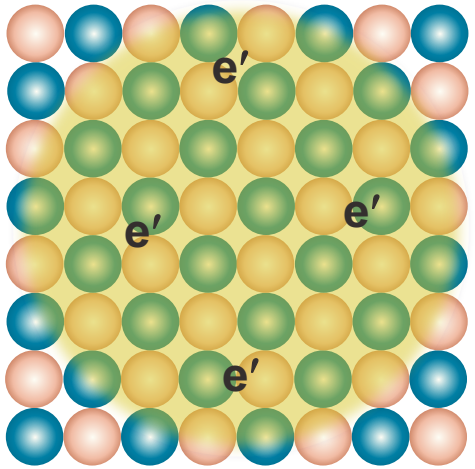
Vacancy concentration depends on Fermi energy, as well as on oxygen chemical potential

Express $\Delta G_{V_O^{\bullet\bullet}}$ relative to a reference state

$$\Delta G^0_{V_O^{\bullet\bullet}} \equiv \frac{1}{\delta}\left[\mu^*_{\mathrm{MO}_{1-\delta}} - \mu_{\mathrm{MO}}\right] + \mu^0_{\mathrm{O}} + 2E^0_{\mathrm{F}}$$

$$\mu^*_{\mathrm{MO}_{1-\delta}} \approx \mu^{*,0}_{\mathrm{MO}_{1-\delta}} \qquad \mu_{\mathrm{MO}} \approx \mu^0_{\mathrm{MO}}$$

$$\Delta G_{V_O^{\bullet\bullet}} = \Delta G^0_{V_O^{\bullet\bullet}} + (\mu_{\mathrm{O}} - \mu^0_{\mathrm{O}}) + 2(E_{\mathrm{F}} - E^0_{\mathrm{F}})$$



Connect to Defect Chemical Reaction

$$O_O^{\times} \rightarrow \tfrac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e^-$$

$\mu_O = \tfrac{1}{2}\mu_{O_2}$ $\quad$ $\mu_{e^-} = E_F$

complete entropy

$$\Delta_{red}g^0 = \mu_{V_O^{\bullet\bullet}}^0 - \mu_{O_O^{\times}}^0 + \mu_O^0 + 2E_F^0 = -\left[\Delta\bar{H}_O^0 - T\left(\Delta\bar{S}_O^0 - R\ln(\chi_{V_O^{\bullet\bullet}}\chi_{e^-}^2)\right)\right]$$

excludes configurational entropy

$$\frac{1}{d}MO \text{ Æ } \frac{1}{d}\left(MO_{1-d}\right)^{2+} + 2e^- + \frac{1}{2}O_2$$

$$\Delta G_{V_O^{\bullet\bullet}}^0 = \frac{1}{\delta}\left[\mu_{MO_{1-\delta}}^{*,0} - \mu_{MO}^0\right] + \mu_O^0 + 2E_F^0$$

also excludes configurational entropy

Recognize $\quad \frac{1}{\delta}\left[\mu_{MO_{1-\delta}}^{*,0}\right] = \mu_{V_O^{\bullet\bullet}}^0 \qquad \frac{1}{\delta}\left[\mu_{MO}^0\right] = \mu_{O_O^{\times}}^0 \quad \Rightarrow \quad \Delta G_{V_O^{\bullet\bullet}}^0 = \Delta_{red}g^0$

by extension

$$\Delta G_{V_O^{\bullet\bullet}} = \Delta_{red}g$$

$\Delta G_{V_O^{\bullet\bullet}}$, $\Delta_{red}g$ depend on E_F, pO_2 $\qquad$ $\Delta G_{V_O^{\bullet\bullet}}^0$, $\Delta_{red}g^0$ are fixed

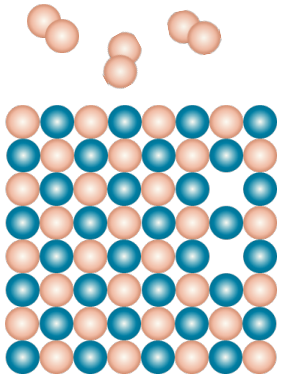
Comparing Approaches

Macroscopic thermodynamics

$$\mu_O(sol) = \mu_O(gas)$$

$$\mu_O(T) - \mu_O^0(T) = \Delta\bar{G}_O^0 = RT\ln\left(\hat{p}_{O_2}^{1/2}(\delta)\right) = \Delta\bar{H}(\delta)_O^0 - T\Delta\bar{S}(\delta)_O^0$$

invert to solve for δ (*T*, pO_2)



Point defect chemical reaction

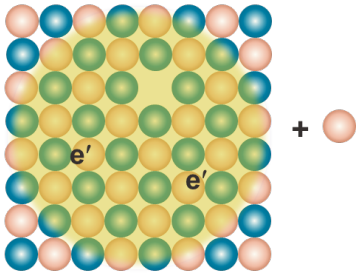
$$O_O^{\times} \rightarrow \tfrac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e^- \qquad \Delta_{red}h^0 = -\Delta\bar{H}_O^0 \qquad \Delta_{red}s^0 = -\Delta\bar{S}_O^0 - \bar{S}_{red,config}$$

$$\Delta_{red}g^0 = \tfrac{1}{2}\mu_{O_2}^0 + \mu_{V_O^{\bullet\bullet}}^0 + 2\mu_{e^-}^0 - \mu_{O_O^{\times}}^0 \qquad \Delta\bar{S}_O^0 = \bar{S}_{oxd,config} + \Delta_{oxd}\bar{S}_{non-config}^0 - \tfrac{1}{2}s_{O_2}^0$$

Point defect formation

$$MO \rightarrow (MO_{1-d})^{2d+} + 2de^- + \frac{d}{2}O_2 \qquad \Delta G_{V_O^{\bullet\bullet}} \equiv \frac{1}{\delta}\left[\mu^*_{MO_{1-\delta}} - \mu_{MO}\right] + \mu_O + 2E_F$$

$$\Delta_{red}G = \frac{1}{\delta}\left[\mu_{MO_{1-\delta}} - \mu_{MO}\right] + \mu_O + 2E_F \qquad \Delta G_{V_O^{\bullet\bullet}} = \Delta_{red}g \qquad \chi_{V_O^{\bullet\bullet}} = \exp\left(\frac{-\Delta G_{V_O^{\bullet\bullet}}}{RT}\right)$$



entropy argument

Lecture Outline

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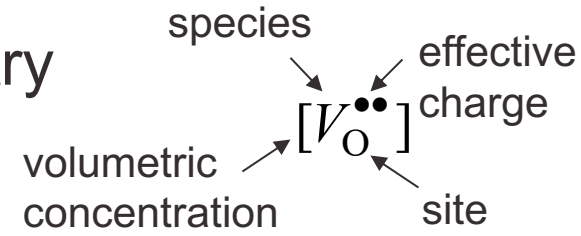
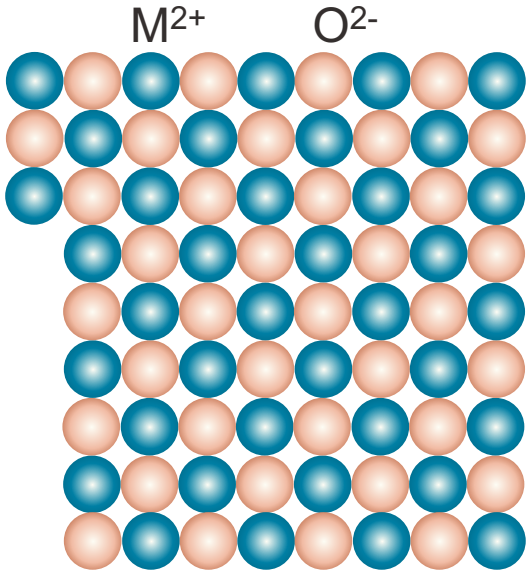
Treatment of Defect Concentrations

Formal Defect Chemistry



′ negative, • positive, × neutral

$$\exp\left(\frac{-\Delta_{rxn}g^0}{RT}\right) = K_{eq} = \left(\frac{a_{p1}^{\nu_{p1}} a_{p2}^{\nu_{p2}} a_{p3}^{\nu_{p3}} \cdots}{a_{r1}^{\nu_{r1}} a_{r2}^{\nu_{r2}} a_{r3}^{\nu_{r3}} \cdots}\right)$$



Energetics independent of E_F and pO_2

Typically one dominates

Reduction $\quad O_O^{\times} \leftrightarrow \tfrac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e'$

$$K_{red} = \left(\frac{\hat{p}_{O_2}^{1/2} \chi_{V_O^{\bullet\bullet}} \chi_{e^-}^2}{\chi_{O_O^{\times}}}\right) \approx \hat{p}_{O_2}^{1/2} \chi_{V_O^{\bullet\bullet}} \chi_{e^-}^2$$

Schottky defect formation

$$M_M^{\times} + O_O^{\times} \leftrightarrow V_M'' + V_O^{\bullet\bullet} + M_{M,surf}^{\times} + O_{O,surf}^{\times}$$

$$K_{Sch} = \left(\frac{\chi_{V_M''} \chi_{V_O^{\bullet\bullet}}}{\chi_{M_M^{\times}} \chi_{O_O^{\times}}}\right) \approx \chi_{V_M''} \chi_{V_O^{\bullet\bullet}}$$

Frenkel cation defect $\quad M_M^{\times} \leftrightarrow V_M'' + M_i^{\bullet\bullet}$

$$K_{F,C} = \left(\frac{\chi_{V_M''} \chi_{M_i^{\bullet\bullet}}}{\chi_{M_M^{\times}}}\right) \approx \chi_{V_M''} \chi_{M_i^{\bullet\bullet}}$$

Frenkel anion defect $\quad O_O^{\times} \leftrightarrow O_i'' + V_O^{\bullet\bullet}$

$$K_{F,A} = \left(\frac{\chi_{O_i''} \chi_{V_O^{\bullet\bullet}}}{\chi_{O_O^{\times}}}\right) \approx \chi_{O_i''} \chi_{V_O^{\bullet\bullet}}$$

Treatment of Defect Concentrations

Reduction $\mathrm{O_O^\times} \leftrightarrow \tfrac{1}{2}\mathrm{O_2} + V_\mathrm{O}^{\bullet\bullet} + 2\mathrm{e}'$ $K_{red} = \hat{p}_{O_2}^{1/2} \chi_{V_\mathrm{O}^{\bullet\bullet}} \chi_{\mathrm{e}^-}^2 = \exp\left(\frac{-\Delta_{red} g^0}{RT}\right)$

Frenkel anion defect $\mathrm{O_O^\times} \leftrightarrow \mathrm{O_i''} + V_\mathrm{O}^{\bullet\bullet}$ $K_{F,A} = \chi_{\mathrm{O_i''}} \chi_{V_\mathrm{O}^{\bullet\bullet}} = \exp\left(\frac{-\Delta_{F,A} g^0}{RT}\right)$ $\tilde{K}_{F,A} = [V_\mathrm{O}^{\bullet\bullet}][\mathrm{O_i''}]$ has units

Electronic defects $\mathrm{nul} \leftrightarrow e^- + \mathrm{h}^\bullet$ $K_{eh} = \chi_{\mathrm{e}^-} \chi_{h^\bullet} = \exp\left(\frac{-E_g^{\,0}}{RT}\right)$ $\tilde{K}_{np} = np = N_c N_v \exp\left(\frac{-E_g^{\,0}}{RT}\right)$

4 unknowns: $\chi_{\mathrm{O_i''}}$ $\chi_{V_\mathrm{O}^{\bullet\bullet}}$ χ_{e^-} $\chi_{\mathrm{h}^\bullet}$ fractional concentrations volumetric concentrations, [ ], n, p

Additional equation from electroneutrality constraint: $\sum_i q_i c_i = 0$ $2[V_\mathrm{O}^{\bullet\bullet}] + p = 2[\mathrm{O_i''}] + n$

Wide band gap ionic material (electrolyte) at moderate pO_2: n, p are low $2[V_\mathrm{O}^{\bullet\bullet}] = 2[\mathrm{O_i''}]$

Brouwer Diagram of Defect Concentrations

Take equilibrium constants to be known, evaluate defect concentrations as f(pO_2) at a given temperature

$$2[V_O^{\bullet\bullet}] + p = 2[O_i''] + n$$

$$\tilde{K}_{red} = \hat{p}_{O_2}^{1/2}[V_O^{\bullet\bullet}]n^2 \qquad \tilde{K}_{F,A} = [V_O^{\bullet\bullet}][O_i''] \qquad \tilde{K}_{np} = np$$

Moderate pO_2 $\quad [V_O^{\bullet\bullet}] = [O_i'']$

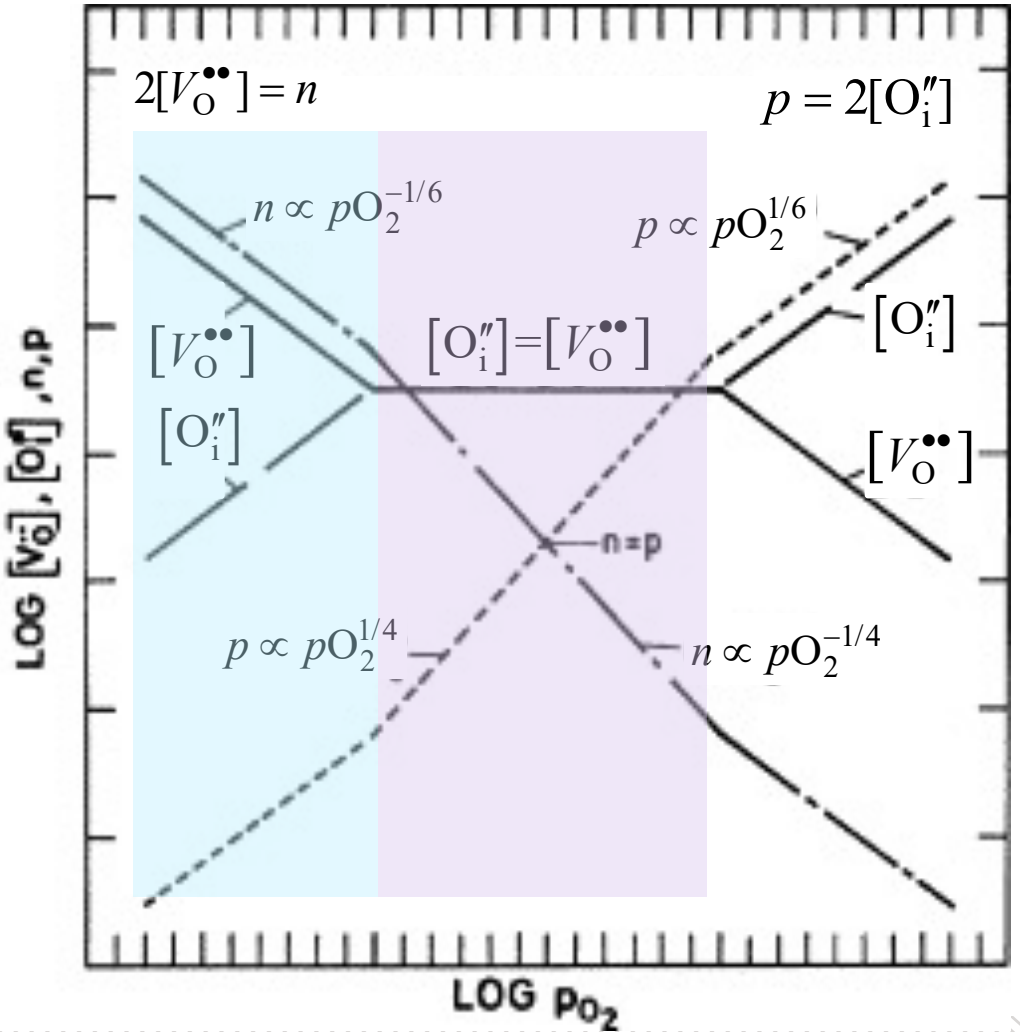
$$\Rightarrow \tilde{K}_{F,A} = [V_O^{\bullet\bullet}]^2 \quad \Rightarrow [V_O^{\bullet\bullet}] = (\tilde{K}_{F,A})^{1/2} = const$$

$$\Rightarrow \tilde{K}_{red} / const = \hat{p}_{O_2}^{1/2} n^2 \quad \Rightarrow \; n \propto \hat{p}_{O_2}^{-1/4}$$

$$p = \tilde{K}_{np} / n \quad \Rightarrow \; p \propto \hat{p}_{O_2}^{1/4}$$

Low pO_2 $\quad 2[V_O^{\bullet\bullet}] = n \quad \Rightarrow \; \tilde{K}_{red} = \hat{p}_{O_2}^{1/2} 4[V_O^{\bullet\bullet}]^3$

$$\Rightarrow [V_O^{\bullet\bullet}],\; n \propto \hat{p}_{O_2}^{-1/6} \quad \tilde{K}_{F,A} \Rightarrow [O_i''] \propto \hat{p}_{O_2}^{1/6} \quad \tilde{K}_{np} \Rightarrow p \propto \hat{p}_{O_2}^{1/6}$$



Small Band-gap Semiconductor

$$2[V_O^{\bullet\bullet}] + p = 2[O_i''] + n$$

$$\tilde{K}_{red} = \hat{p}_{O_2}^{1/2}[V_O^{\bullet\bullet}]n^2 \qquad \tilde{K}_{F,A} = [V_O^{\bullet\bullet}][O_i''] \qquad \tilde{K}_{np} = np$$

Moderate pO_2 $\quad p = n$

$$\Rightarrow \tilde{K}_{np} = n^2 \Rightarrow n = (\tilde{K}_{np})^{1/2} = const$$

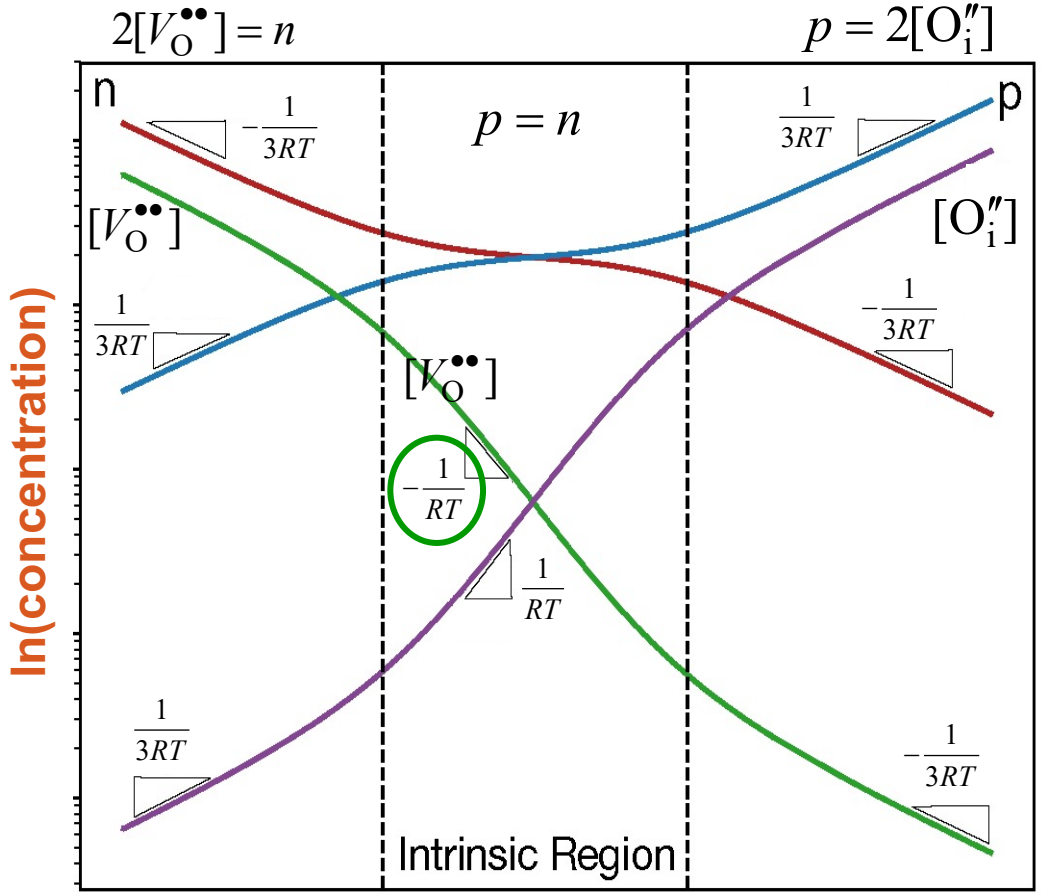
$$\Rightarrow \tilde{K}_{red} / \tilde{K}_{np} = \hat{p}_{O_2}^{1/2}[V_O^{\bullet\bullet}] = const \qquad \ln[V_O^{\bullet\bullet}] = \ln(\hat{p}_{O_2}^{-1/2}) + const$$

$$\ln[V_O^{\bullet\bullet}] = \frac{-1}{RT}\left(RT \ln \hat{p}_{O_2}^{1/2}\right) + const$$

Low pO_2 $\quad 2[V_O^{\bullet\bullet}] = n \Rightarrow \tilde{K}_{red} = \hat{p}_{O_2}^{1/2} 4[V_O^{\bullet\bullet}]^3$

$$\Rightarrow [V_O^{\bullet\bullet}],\ n \propto \hat{p}_{O_2}^{-1/6} \Rightarrow \ln[\,] = \frac{-1}{3RT}\left(RT \ln \hat{p}_{O_2}^{1/2}\right) + const$$

Courtesy G. J. Snyder and S. Anand

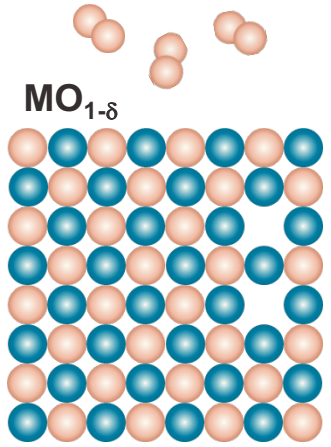


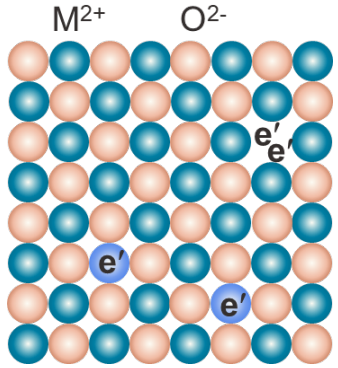
chemical potential

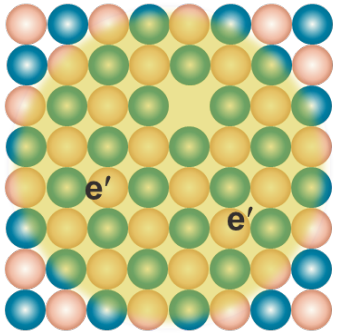
$$\mu_O(T) = \mu_O^0(T) + RT \ln\left(\hat{p}_{O_2}^{1/2}\right)$$

Summary

- Defect formation in ionic solids and in compound semiconductors are analogous processes
- Language used to describe them is distinct
  - You now have the Rosetta stone for translating
- Macroscopic chemical view
  - Completely defect agnostic
- Point defect chemical reactions
  - Require site, mass and charge balance
- Defect formation energies
  - Assume charged defect, with electrons released/consumed
- With energetics known & form of entropy assumed
  - Can compute defect concentrations as f(μ,T)







CONGRATULATIONS!!

You've made it through a tough lecture at the end of a long day!

I wish you all the success in the world as you navitage these challenging times!

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