

DFT and beyond

Hands-on Tutorial Workshop 2011

Ab Initio Atomistic Thermodynamics

(Elizabeth C. Beret)

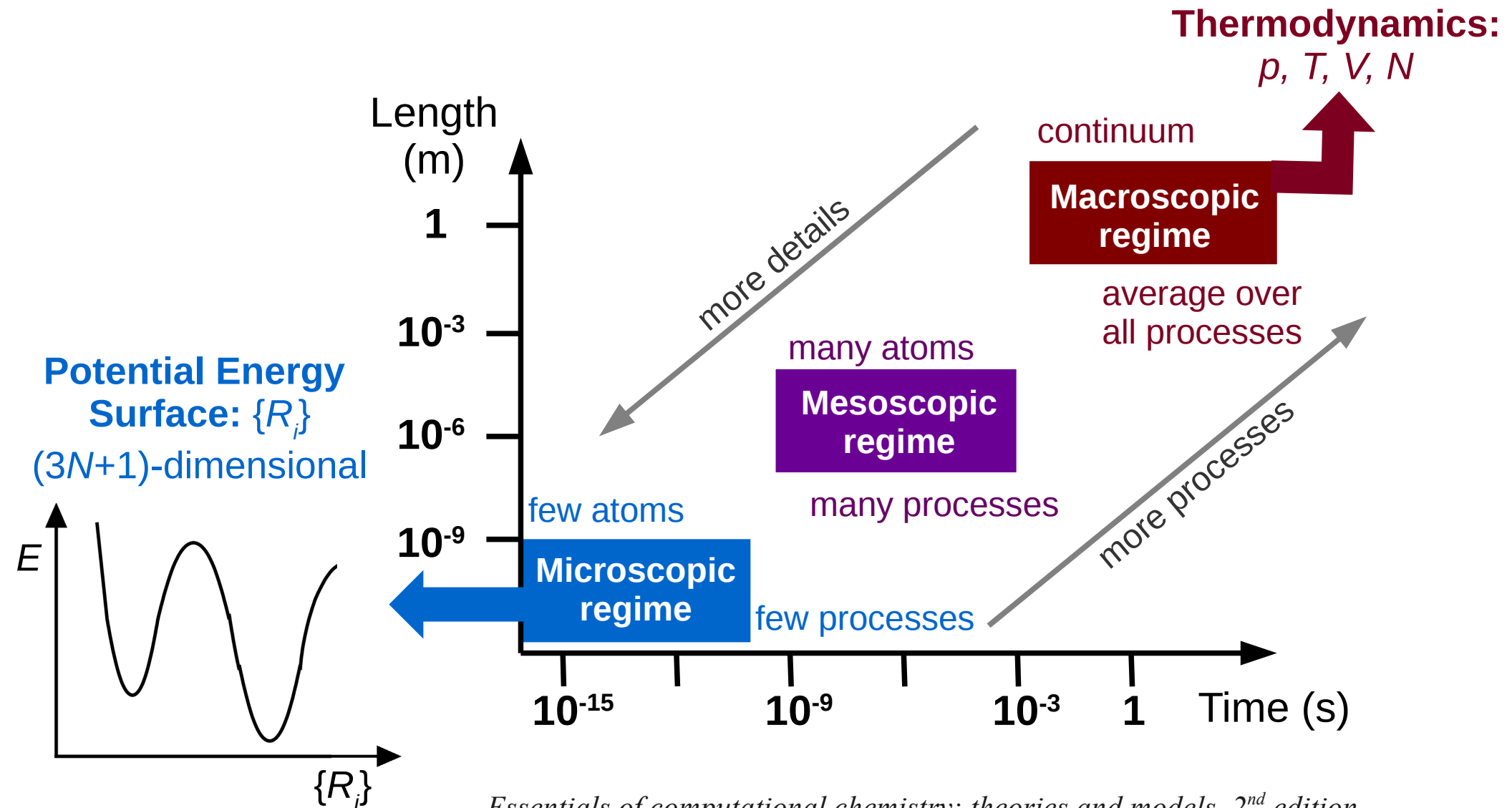
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MAX-PLANCK-GESELLSCHAFT

Extending the scale



Essentials of computational chemistry: theories and models. 2nd edition.
C. J. Cramer, John Wiley and Sons Ltd (West Sussex, 2004).

*Ab initio atomistic thermodynamics and statistical mechanics
of surface properties and functions*

K. Reuter, C. Stampfl, and M. Scheffler, in: *Handbook of Materials Modeling Vol. 1,*
(Ed.) S. Yip, Springer (Berlin, 2005). <http://www.fhi-berlin.mpg.de/th/paper.html>

Equilibrium concentration of point defects

On entropic grounds there will always be a finite concentration of defects at finite temperature, even though the creation of a defect costs energy ($E^{def} > 0$).

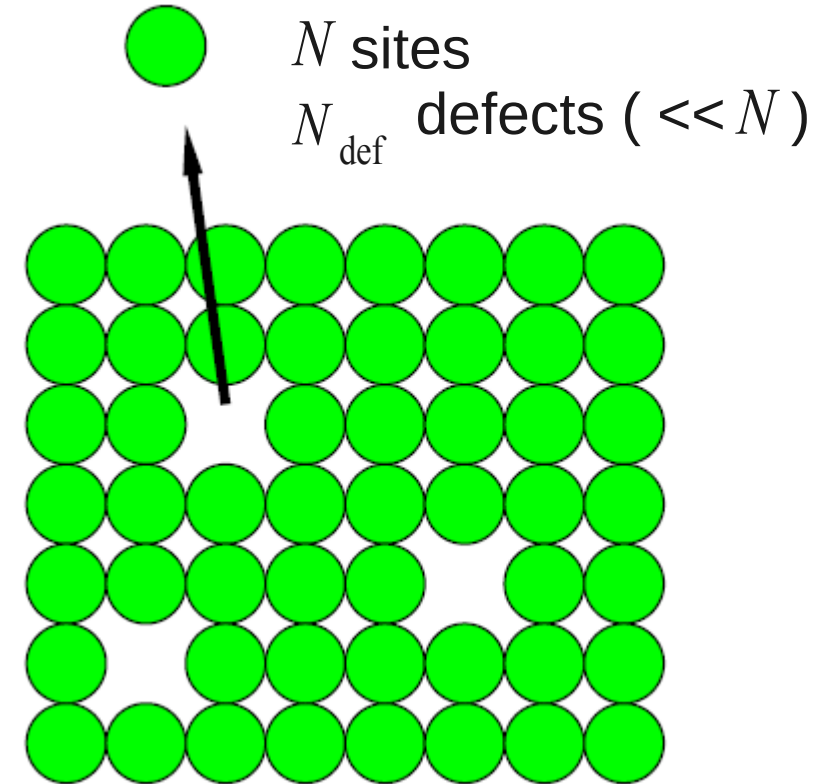
$$S^{conf} = k_B \ln(Z(n)) = k_B \ln\left(\frac{N!}{(N - N_{def})! N_{def}!}\right)$$

(assumes no interaction between defects)

In equilibrium:

$$\frac{dG^{def}}{dN_{def}} = \frac{d}{dN_{def}} \left[G^{perf} + N_{def} \Delta G^{def} - TS^{conf} + pV \right] = 0$$

$$\frac{N_{def}}{N} \approx \frac{1}{\exp(\Delta G^{def} / k_B T) + 1} \approx \exp(-E^{def} / k_B T)$$



Ab initio atomistic thermodynamics: General concepts

Oxide formation on a metal surface

Adsorption of O₂ and CO on a metal oxide

Formation of defects in semiconductors

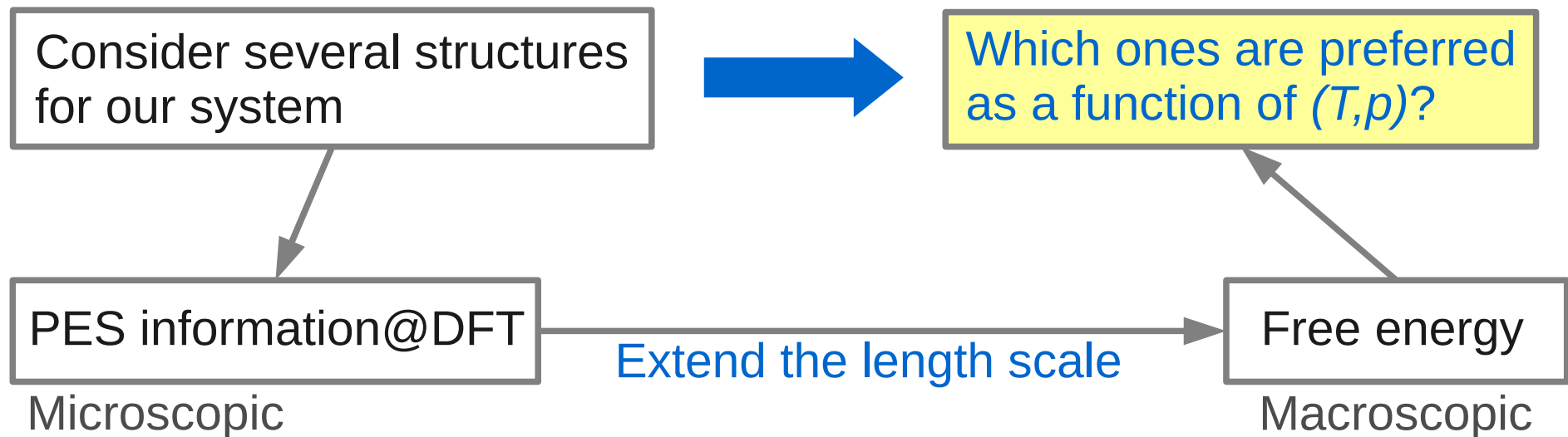
Ab initio atomistic thermodynamics: General concepts

Oxide formation on a metal surface

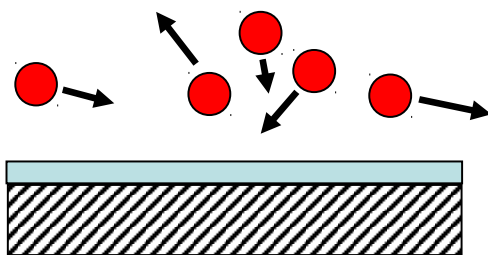
Adsorption of O_2 and CO on a metal oxide

Formation of defects in semiconductors

Ab initio atomistic thermodynamics



A surface cannot be separated from a gas (or liquid) above it



$$v = \frac{p}{\sqrt{2\pi mkT}}$$

For $T = 300$ K, $p = 1$ atm
 $\Rightarrow v \sim 10^8 \text{ site}^{-1} \text{ s}^{-1}$

Requires $p \leq 10^{-12}$ atm to keep a "clean" surface clean; surface can also lose atoms

(DFT) internal versus free energy

At constant T a system minimizes its free energy, not internal energy U

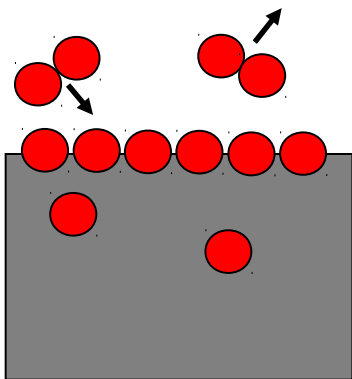
If also volume V is constant, the energy minimized is Helmholtz free energy F

$$F = U - TS$$

If (T, p) are constant, the energy minimized is Gibbs free energy G

$$G = U + pV - TS = \sum_i \mu_i N_i$$

Chemical potential μ_i of the i -th atom type is the change in free energy as the number of atoms of that type in the system increases by one



In thermodynamic equilibrium, μ_i is the same in the whole system (surface, bulk, gas)

Statistics plays a crucial role due to a macroscopically large number of particles in the system

$$Q = \frac{1}{N!} q^N$$

$$q = q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} q^{\text{el}} q^{\text{conf}} \cancel{q^{\text{nucl}}}$$

Translational: $q^{\text{trans}} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} V$

➔ Need: particle mass m

Use the ideal gas law to relate V and p

Rotational:
$$\left\{ \begin{array}{l} q^{\text{rot}} = \frac{8\pi^2 I_A k T}{h^2} \\ q^{\text{rot}} = 8\pi^2 \left(\frac{2\pi k T}{h^2} \right)^{\frac{3}{2}} (I_A I_B I_C)^{\frac{1}{2}} \end{array} \right.$$

Linear molecules

Non-linear molecules

Rigid rotor

➔ Need: moments of inertia

$$I_A, I_B, I_C$$

$$Q = \frac{1}{N!} q^N$$

$$q = q^{trans} q^{rot} q^{vib} q^{el} q^{conf} \cancel{q^{nucl}}$$

Vibrational: $q^{vib} = \prod \left[\exp\left(-\frac{h\nu_i}{2kT}\right) \left(1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right)^{-1} \right]$ → Need: vibrational modes

Harmonic oscillator

Electronic: $q^{el} = \sum v_i e^{-\frac{E_i}{kT}} \approx v_0 e^{-\frac{E_0}{kT}}$ → Need: total (DFT) energy of the ground state and its degeneration

$$v_i = 2S_i + 1$$

Assuming that the first excited state is energetically inaccessible

Conformational $q^{conf} = \frac{1}{\sigma}$ → Need: symmetry number (N. equivalent orientations)

Diatomic molecules:

$$\sigma = 1$$

(heteroatomic)

$$\sigma = 2 \text{ (homoatomic)}$$

Polyatomic molecules:

$\sigma = N.$ symmetry operations according to the symmetry point group

From the partition function Q :

Helmholtz free energy: $F = -kT \ln Q$

Canonical ensemble
(NVT)

Gibbs free energy: $G = -kT \ln Q + pV$

Isothermal-isobaric ensemble
(NpT)

Chemical
potential:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} = \left(\frac{\partial G}{\partial N} \right)_{p,T} \left\{ \begin{array}{ll} \mu = kT \ln N - kT \ln q & (NVT) \\ \mu = kT [\ln N + 1 - \ln q] & (NpT) \end{array} \right.$$

Computation of free energies: solids

$$G(T, p) = E^{tot} + F^{trans} + F^{rot} + F^{vib} + F^{conf} + pV$$

E^{tot} Total electronic energy → DFT

F^{trans} Translational free energy }
 F^{rot} Rotational free energy } → Discarded (consider fixed solids)

F^{vib} Vibrational free energy

$$\left\{ \begin{array}{l} F^{vib} = \int d\omega F^{vib}(T, \omega) \sigma(\omega) \\ F^{vib}(T, \omega) \approx \frac{h\omega}{2} + kT \ln \left[1 - \exp\left(-\frac{h\omega}{kT}\right) \right] \end{array} \right.$$

F^{conf} Conformational free energy → Needs more advanced methods
(Ex: cluster expansion)

pV Expansion term → Usually small, often neglected

$$G(T, p) \approx E^{tot} + F^{vib}$$

Ab initio atomistic thermodynamics: General concepts

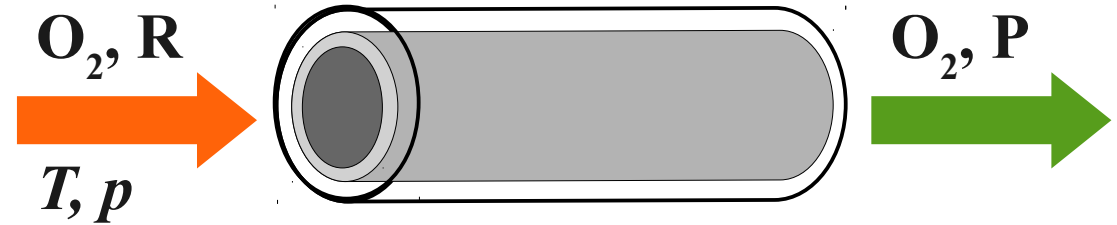
Oxide formation on a metal surface

Adsorption of O_2 and CO on a metal oxide

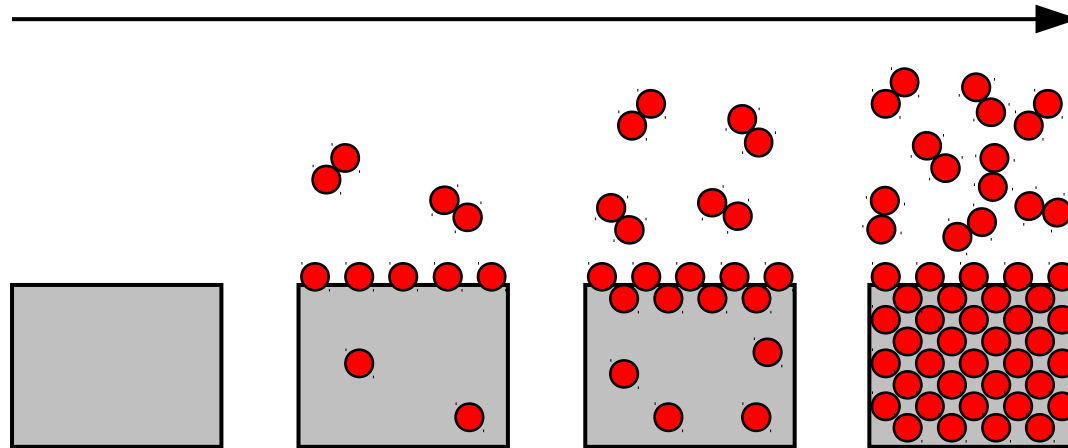
Formation of defects in semiconductors

Oxide formation on Pd(100)

Heterogeneous catalysis:



$p(O_2)$



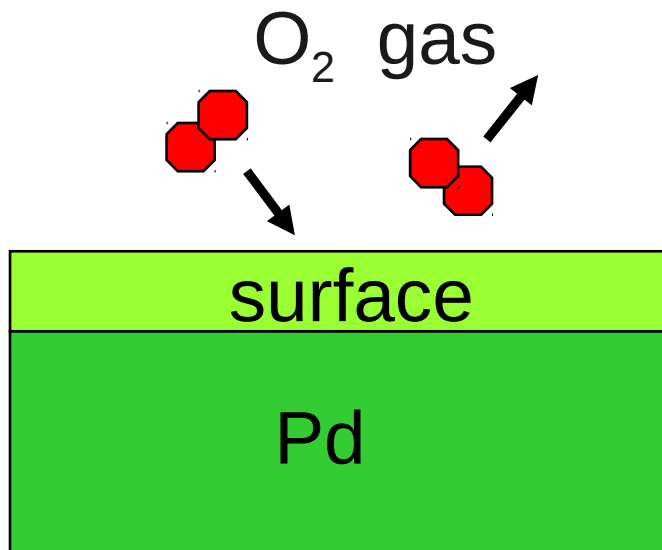
Which oxide forms at given experimental conditions (T, p)?

Reuter and Scheffler, Appl. Phys. A, 78, 793-798, 2004

J. Rogal and K. Reuter, Ab initio atomistic thermodynamics for surfaces: A primer.

In: Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Hypersonic Flights. Educational Notes RTO-EN-AVT-142, Neuilly-sur-Seine (2007)

Oxide formation on Pd(100)



$$\Delta G^{ad} = \frac{1}{A} (G_{\text{Pd} \cdot \text{O}_x} - G_{\text{Pd}(100)} - x \mu_{\text{O}})$$

$$G(T, p) \approx E^{total} + F^{vib} \approx E^{total}$$

$$\Delta F^{vib} \approx \pm 5 \text{ meV/\AA}^2 \text{ up to } T = 600 \text{ K}$$

$$\mu_{\text{O}}(T, p) = \frac{1}{2} \mu_{\text{O}_2}(T, p)$$

$$\mu_{\text{O}_2}(T, p) = E_{\text{O}_2}^{DFT} + E_{\text{O}_2}^{ZPE} + \Delta \mu_{\text{O}_2}(T, p)$$

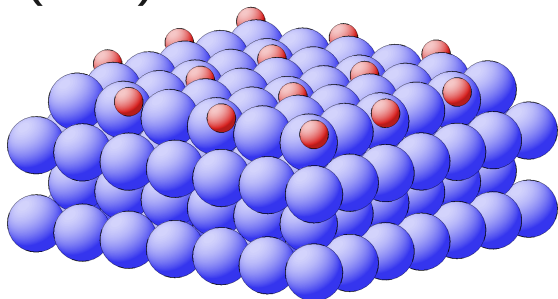
$$\mu_{\text{O}}(T, p) = \frac{1}{2} E_{\text{O}_2}^{DFT} + \frac{1}{2} E_{\text{O}_2}^{ZPE} + \Delta \mu_{\text{O}}(T, p)$$

$$\Delta G^{ad} \approx \frac{1}{A} \left[E_{\text{Pd} \cdot \text{O}_x} - E_{\text{Pd}(100)} - x \left(\frac{1}{2} E_{\text{O}_2}^{DFT} + \frac{1}{2} E_{\text{O}_2}^{ZPE} + \Delta \mu_{\text{O}}(T, p) \right) \right]$$

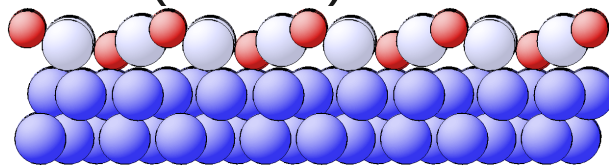
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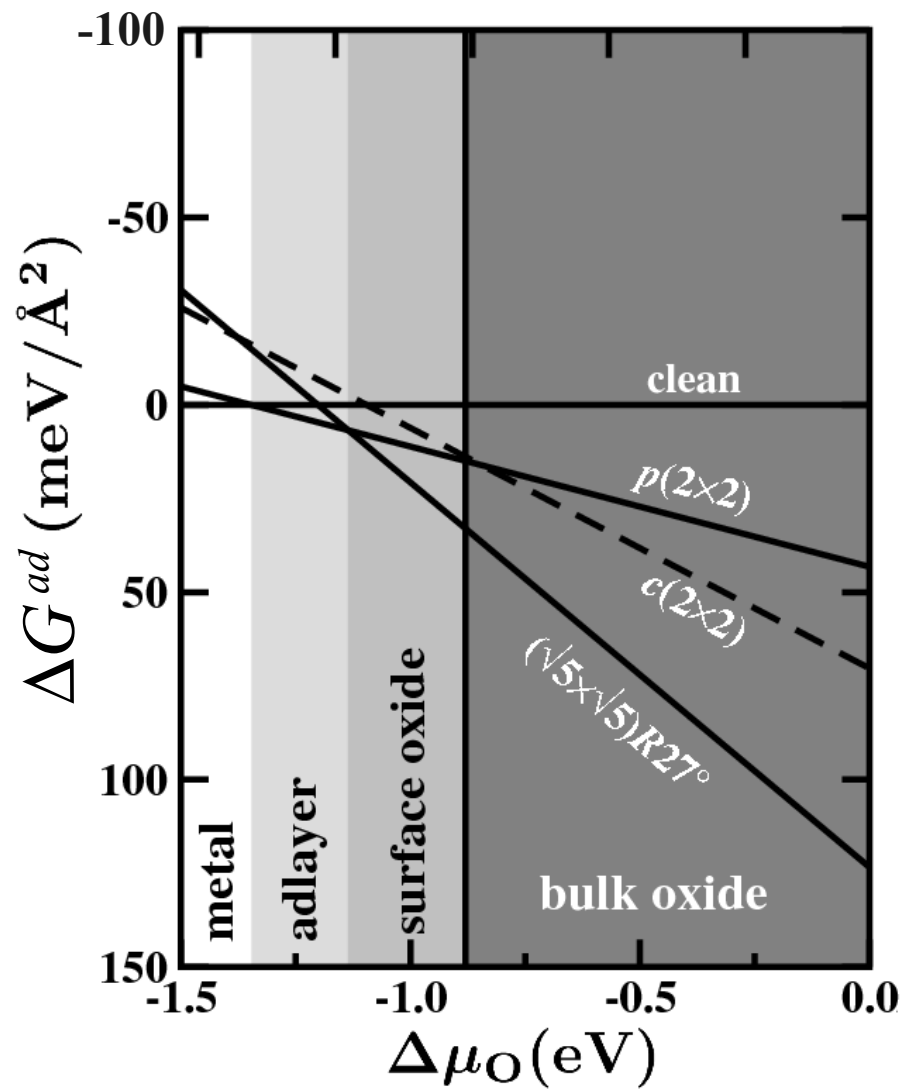
- Clean Pd(100) surface
- O/Pd(100) adlayers:
 $p(2 \times 2)$: 0.25 ML
 $c(2 \times 2)$: 0.50 ML



- PdO(101)/Pd(100) surface oxide:
 $(\sqrt{5} \times \sqrt{5})R27^\circ$: 0.80 ML



- Bulk PdO



Relation between chemical potential and (T, p)

$$\mu_{O_2}(T, p) = E_{O_2}^{DFT} + E_{O_2}^{ZPE} + \Delta \mu_{O_2}(T, p)$$

From the O_2 partition function:

$$\mu(T, p) = -kT \ln \left[\left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} (kT)^{\frac{5}{2}} \right] + kT \ln p - kT \ln \left(\frac{8\pi^2 I_A kT}{\sigma h^2} \right) + \frac{1}{2} h\nu + kT \ln \left(1 - e^{-\frac{h\nu}{kT}} \right) + E^{DFT} - kT \ln v_0$$

$\Delta \mu(T, p)$

From thermochemical tables:

$$\Delta \mu(T, p) = \mu(T, p^\circ) - \mu(T^\circ, p^\circ) + kT \ln(p/p^\circ)$$

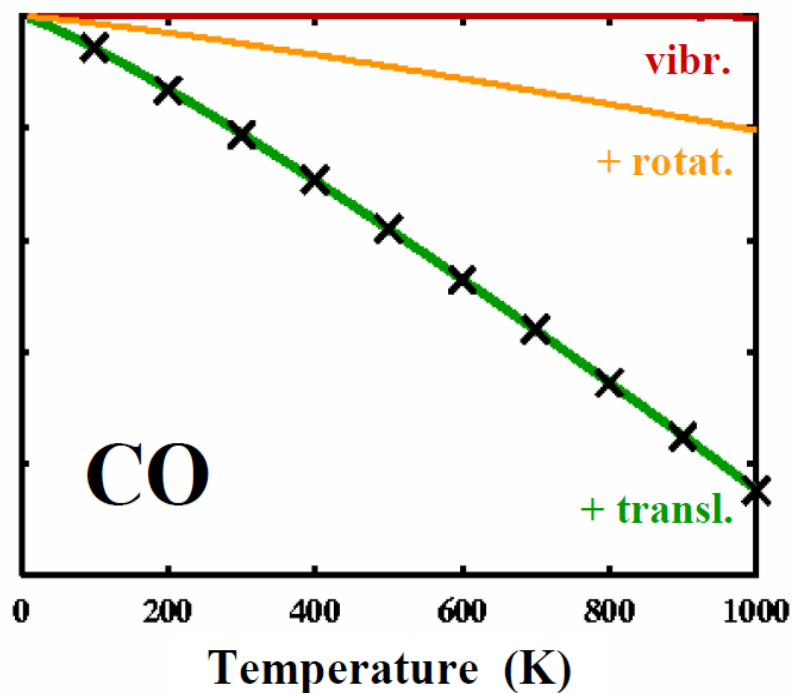
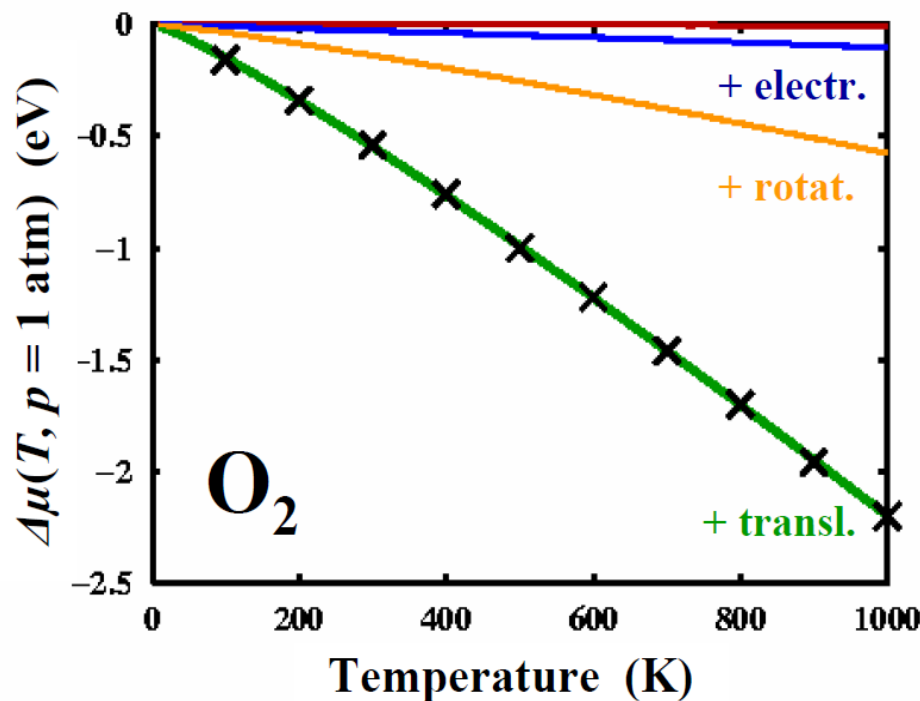
Tables

Example: JANAF Thermochemical tables, D.R. Stull, H. Prophet.
US National Bureau of Standards, Washington DC, 1971

→ $S^\circ(T), H^\circ(T)$

Relation between chemical potential and (T, p)

$$\mu_{O_2}(T, p) = E_{O_2}^{DFT} + E_{O_2}^{ZPE} + \Delta\mu_{O_2}(T, p)$$



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↑ ↑
Tables

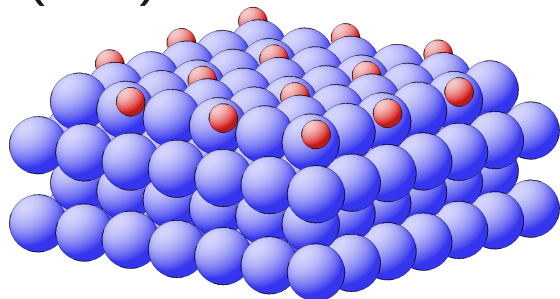
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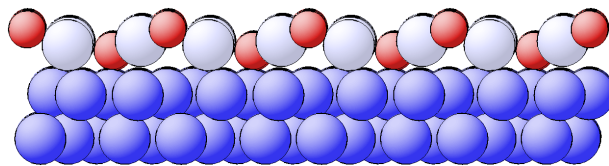
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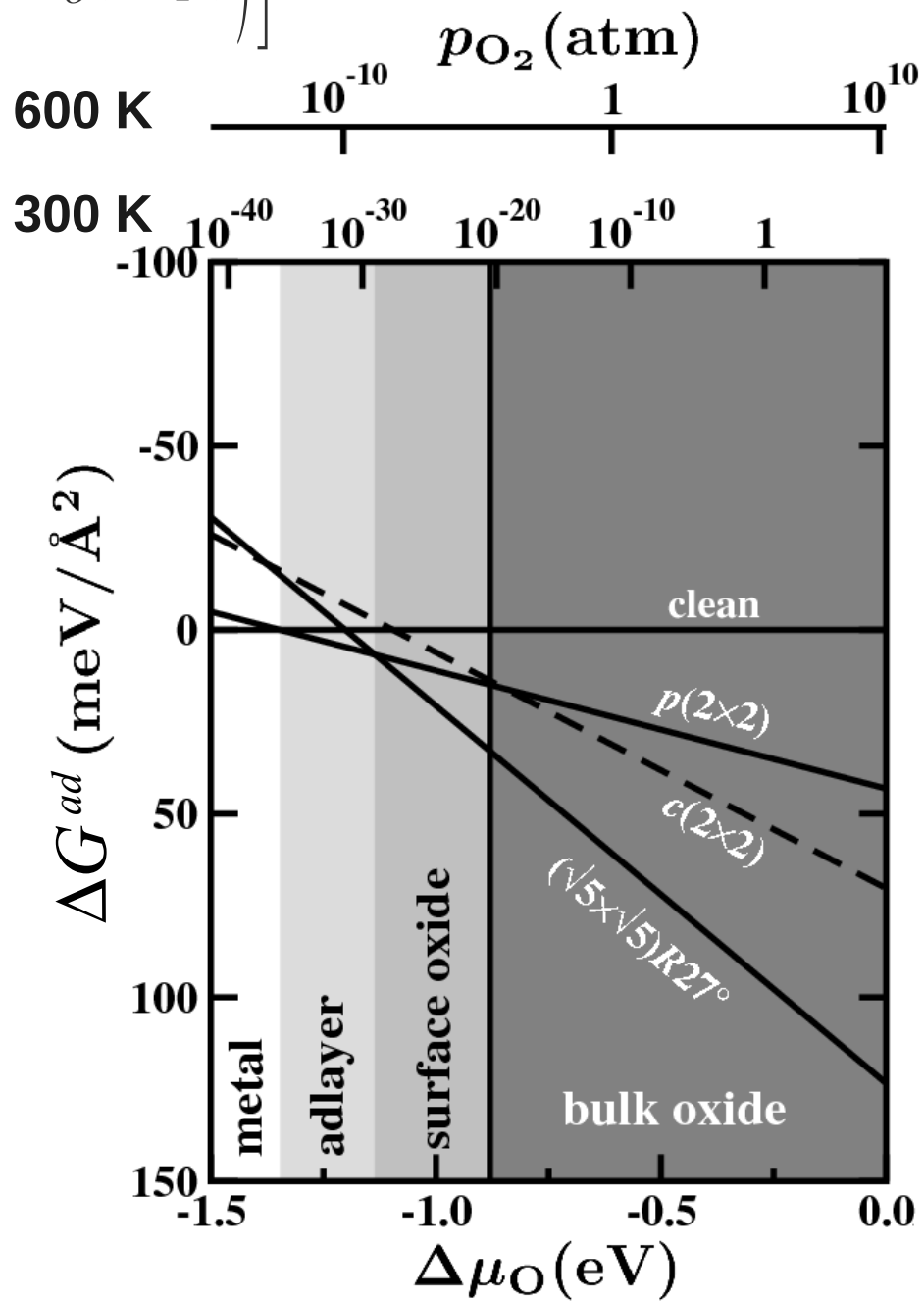
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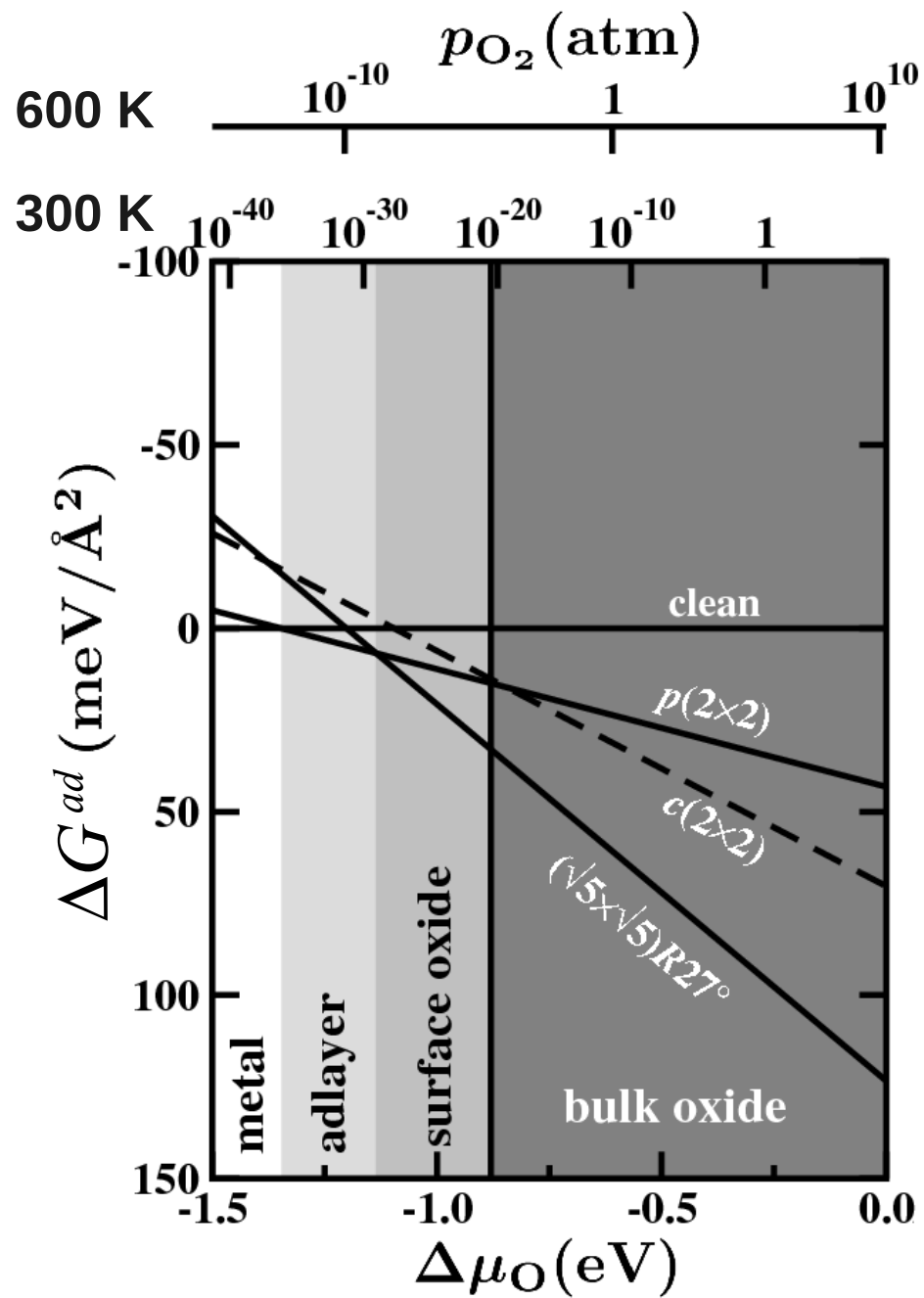


- Bulk PdO

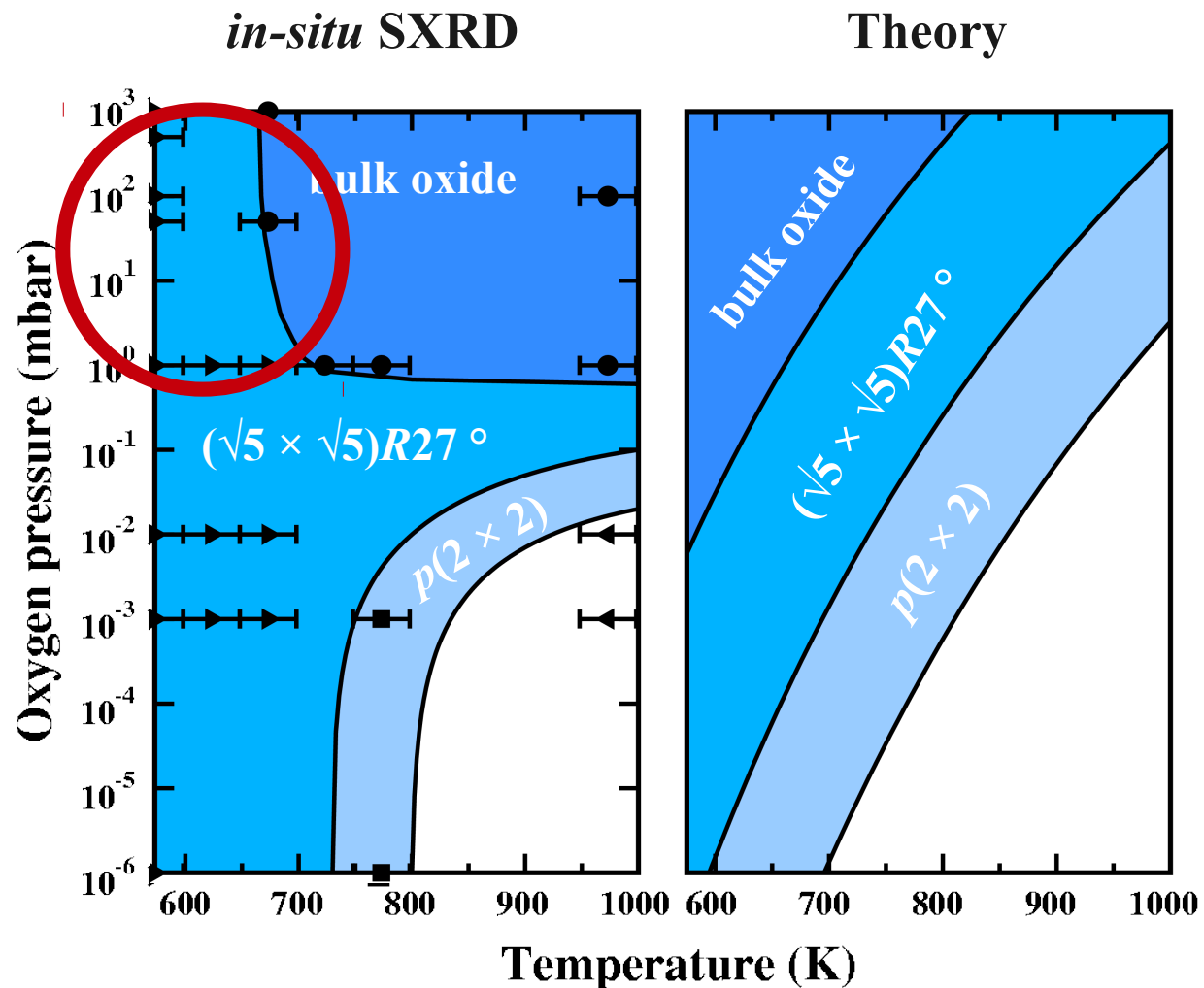


Limitations

- Number of screened structures: structures not considered cannot be predicted
- Neglecting F^{vib} : (slight) horizontal shift of lines
- Neglecting F^{conf} : smearing of phase transitions
- Systems in equilibrium: possible kinetic effects in experiment



Comparing with experiment: kinetic effect



Ab initio atomistic thermodynamics: General concepts

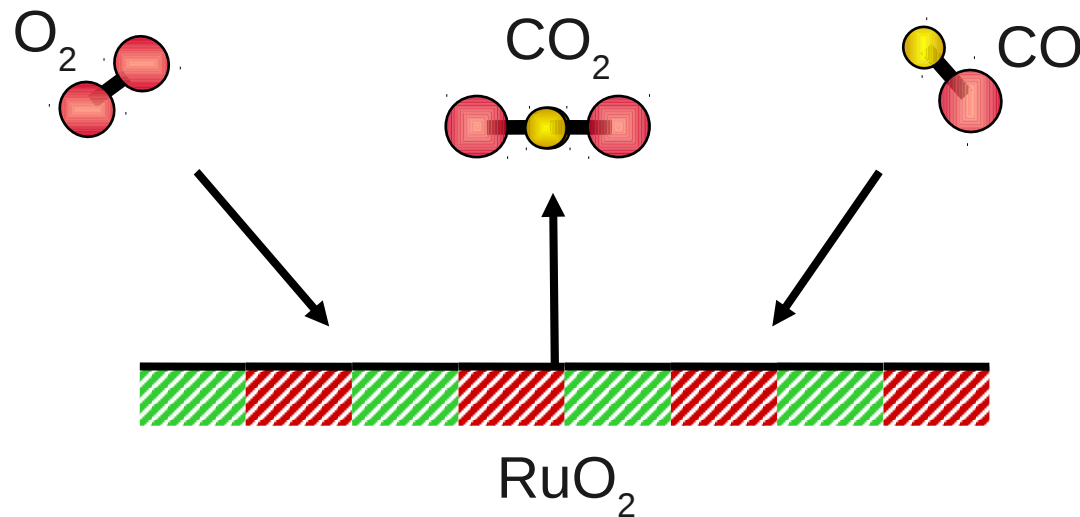
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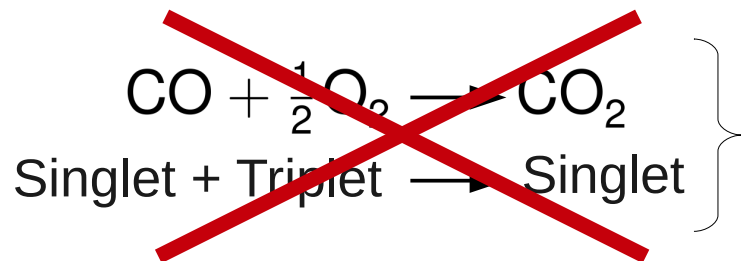
Adsorption of O₂ and CO on RuO₂(110)

CO oxidation over a Ru catalyst:



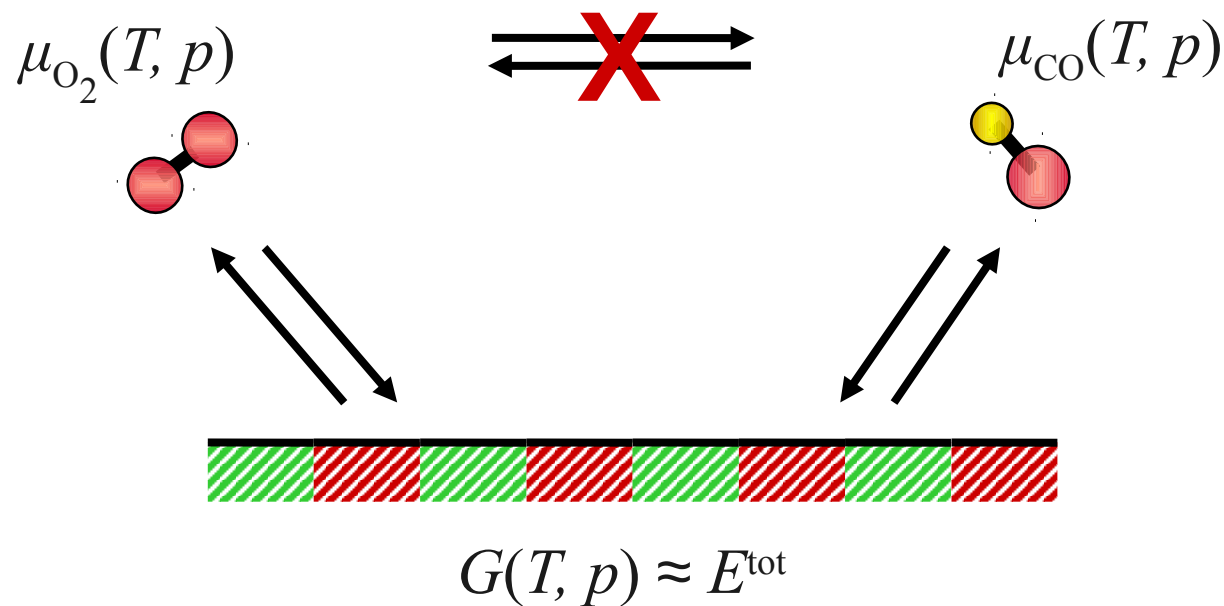
What are the preferred structures for
RuO₂·(O)_x·(CO)_y?

This reaction does not take place in the gas phase:



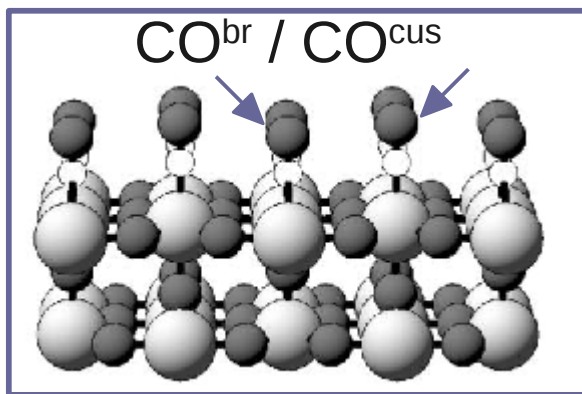
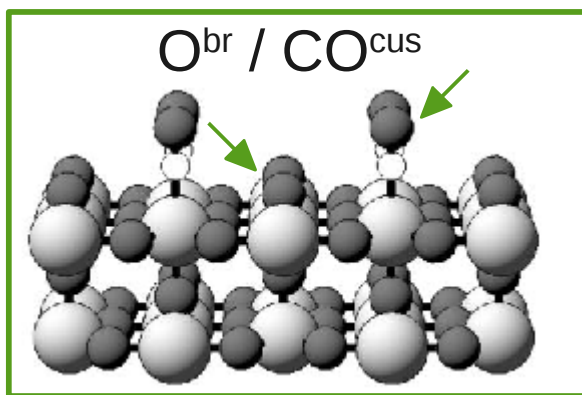
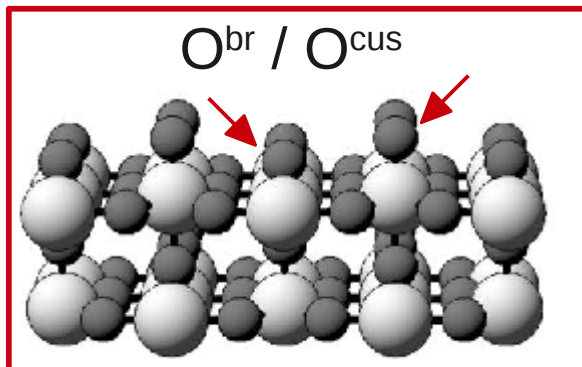
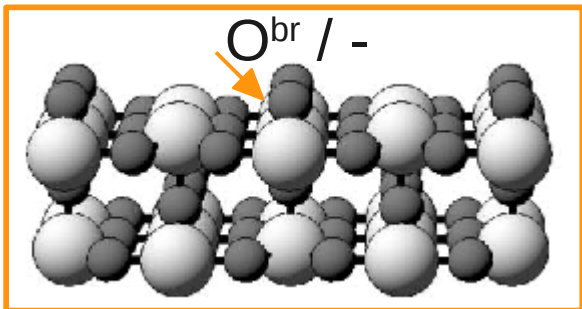
$\Delta E = -3.27$ eV (DFT-PBE+vdW)
Spin forbidden!

Constrained equilibrium

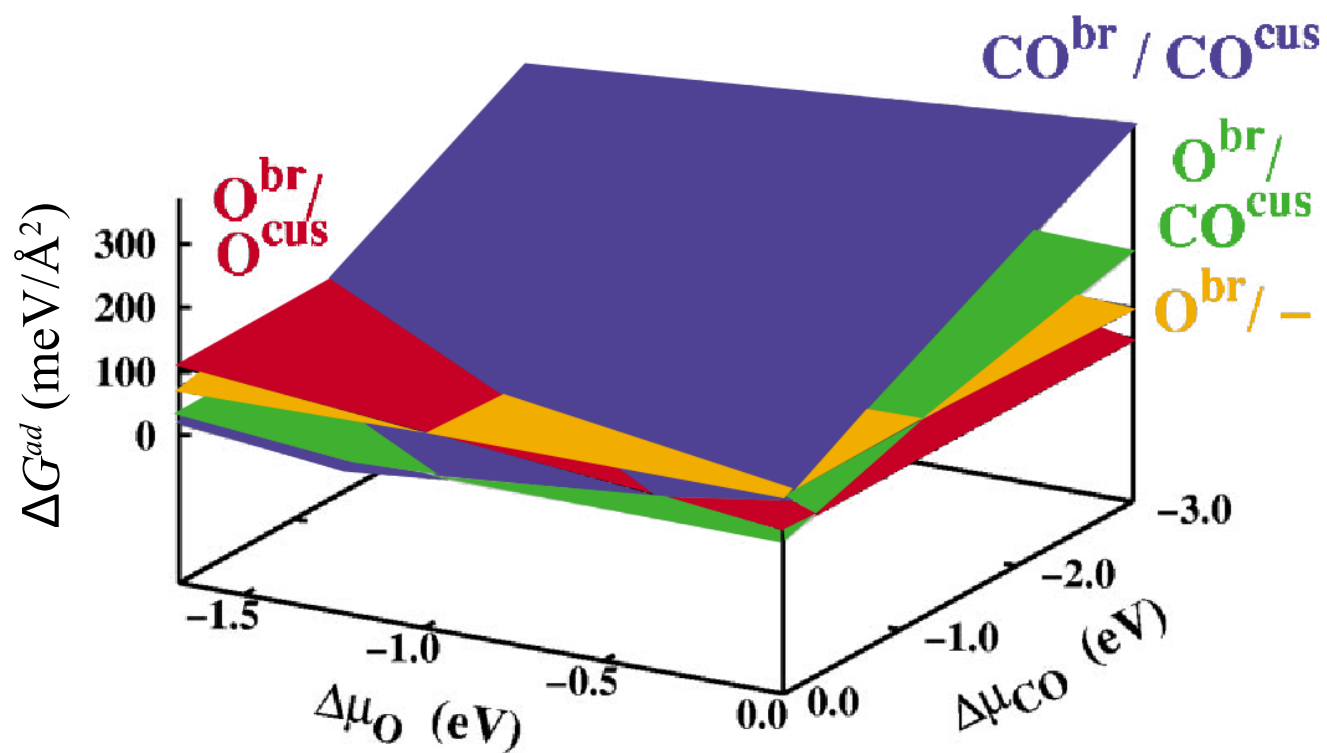


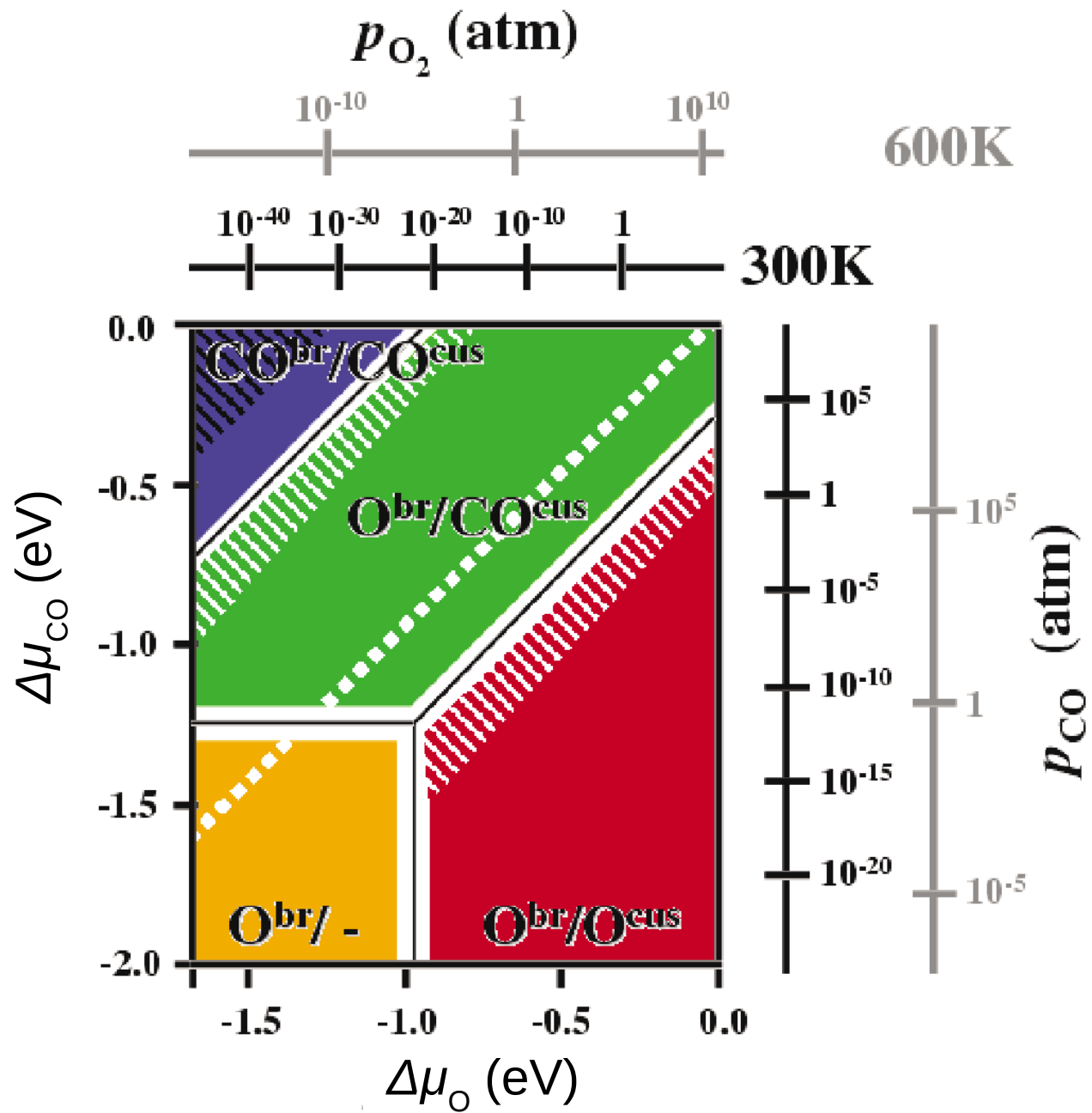
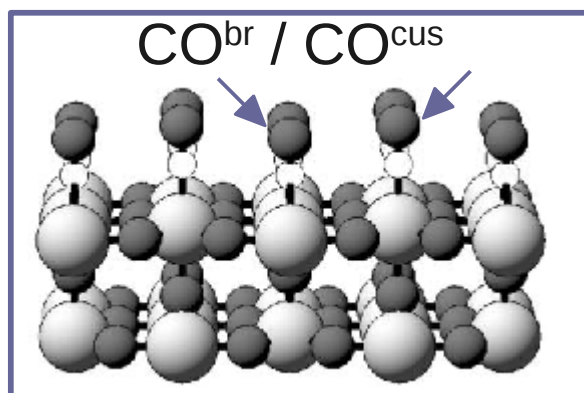
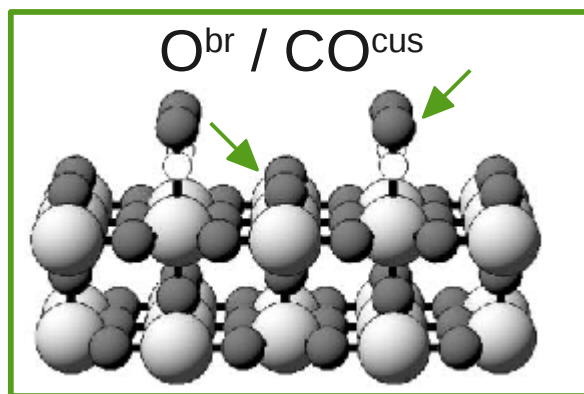
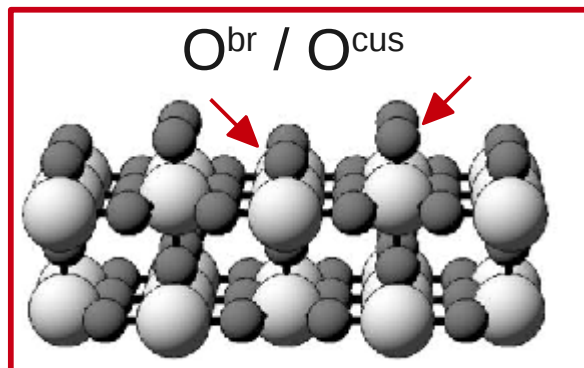
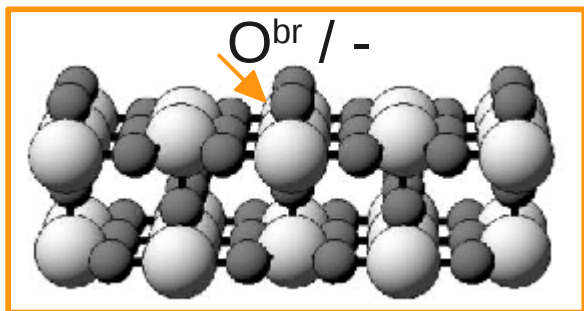
$$\Delta G^{\text{ad}} = \frac{1}{A} \left[G_{\text{RuO}_2 \cdot (\text{O})_x \cdot (\text{CO})_y} - G_{\text{RuO}_2(110)} - x \mu_{\text{O}} - y \mu_{\text{CO}} \right]$$

$$\Delta G^{\text{ad}} \approx \frac{1}{A} \left[E_{\text{RuO}_2 \cdot (\text{O})_x \cdot (\text{CO})_y} - E_{\text{RuO}_2(110)} - x \left(\frac{1}{2} E_{\text{O}_2}^{\text{DFT}} + \frac{1}{2} E_{\text{O}_2}^{\text{ZPE}} + \Delta \mu_{\text{O}} \right) - y \left(E_{\text{CO}}^{\text{DFT}} + E_{\text{CO}}^{\text{ZPE}} + \Delta \mu_{\text{CO}} \right) \right]$$

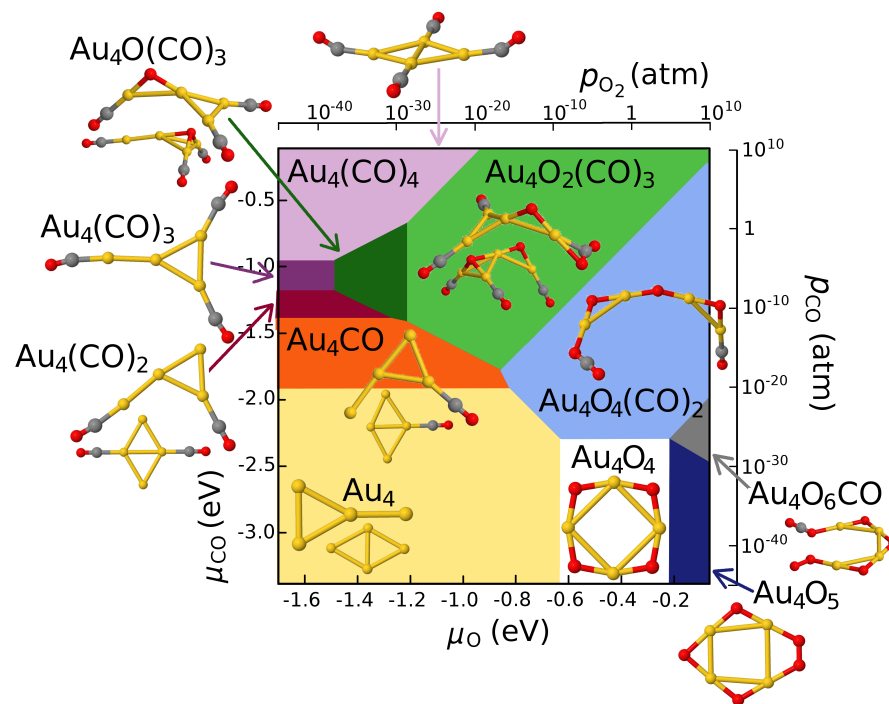
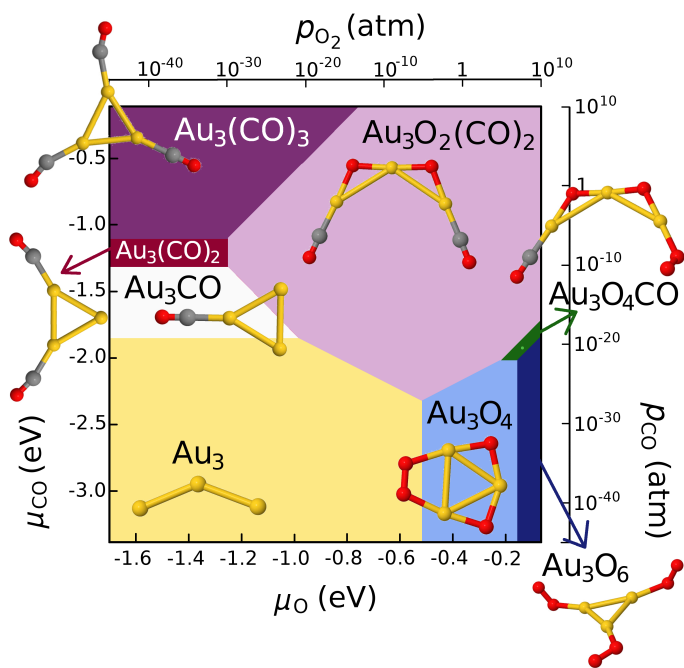
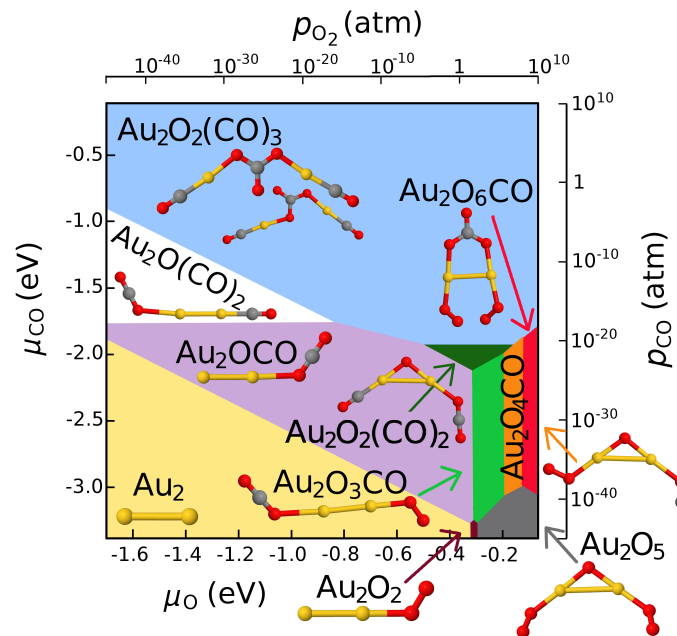
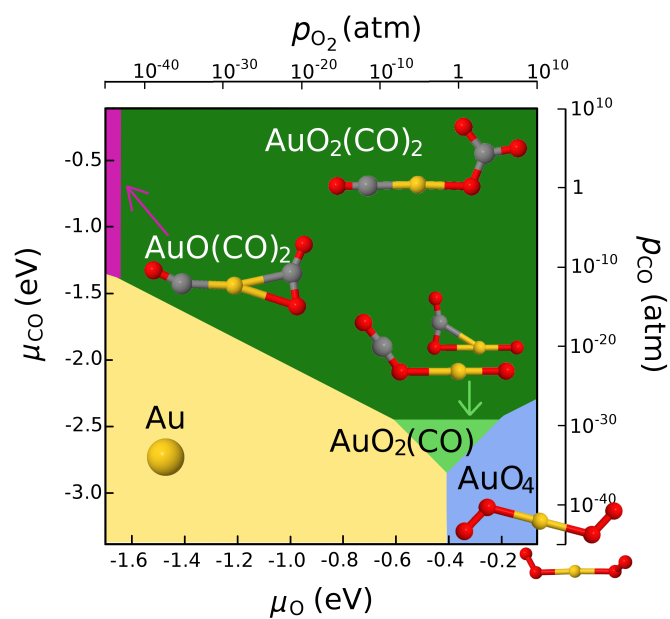


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Adsorption of O₂ and CO on gold clusters



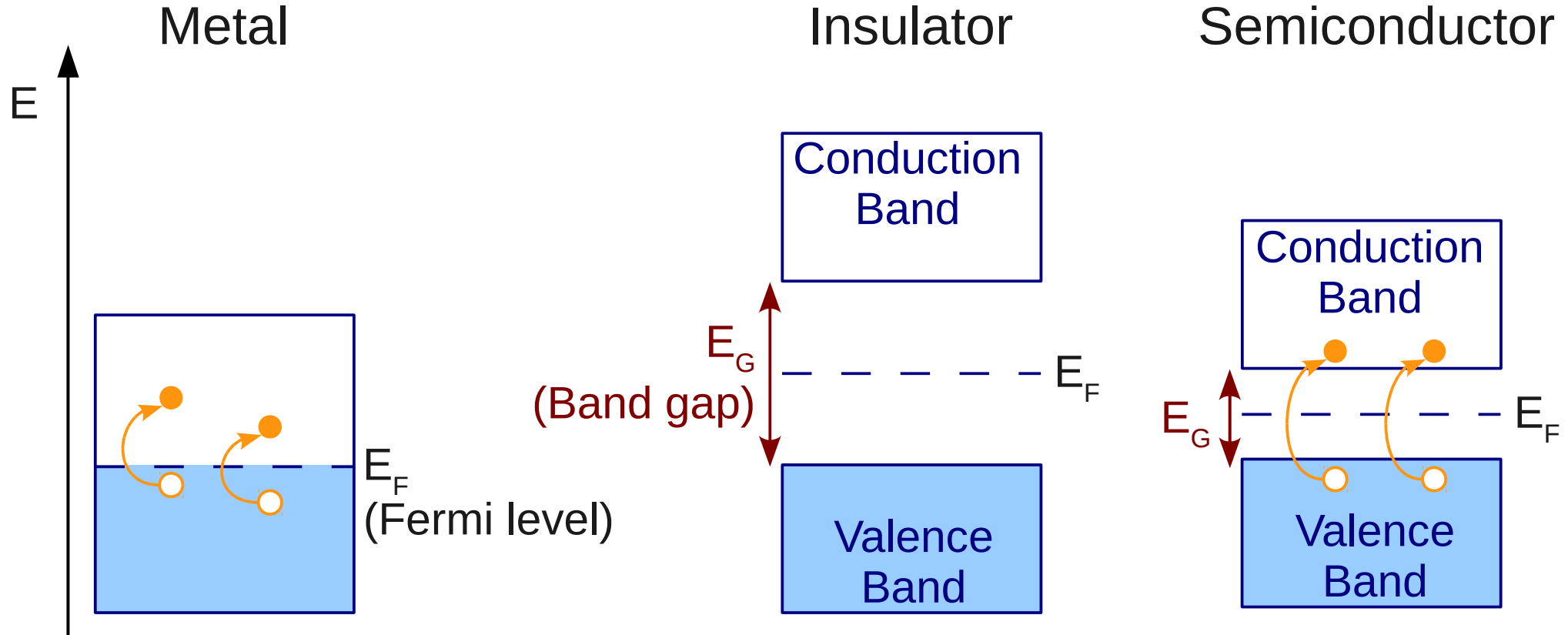
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Electronic structure of solids



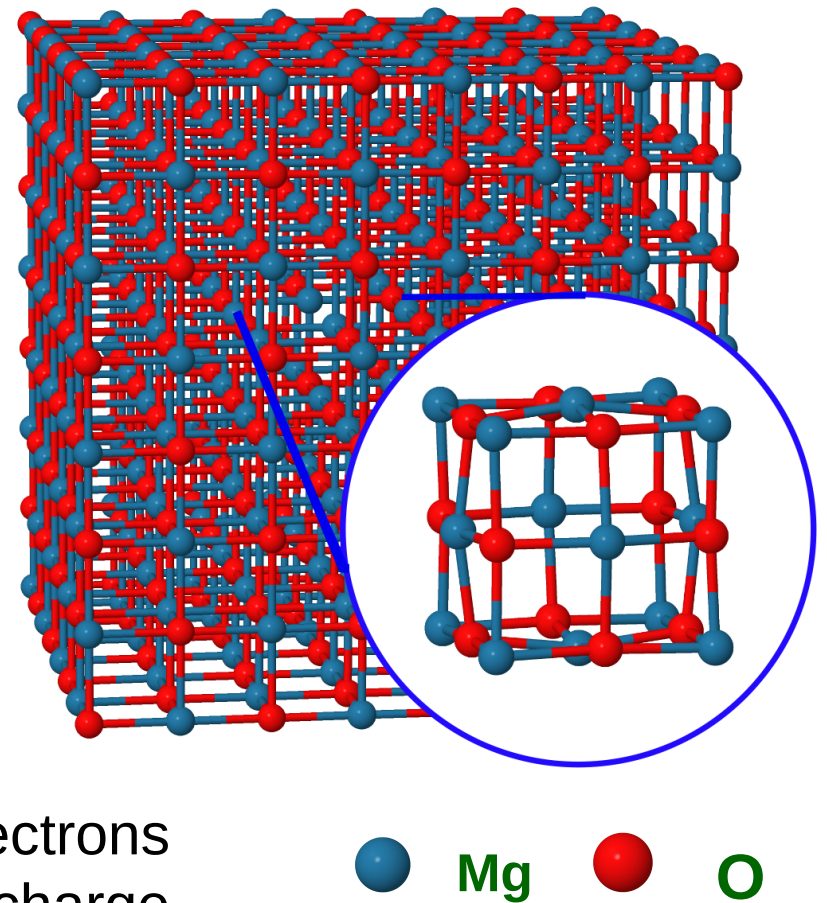
The electrical conductivity of semiconductors can be enhanced by the presence of defects (vacancies, interstitials, impurities...) which can contribute:

- electrons to the CB: donors, n-type conductivity
- holes to the VB: acceptors, p-type conductivity

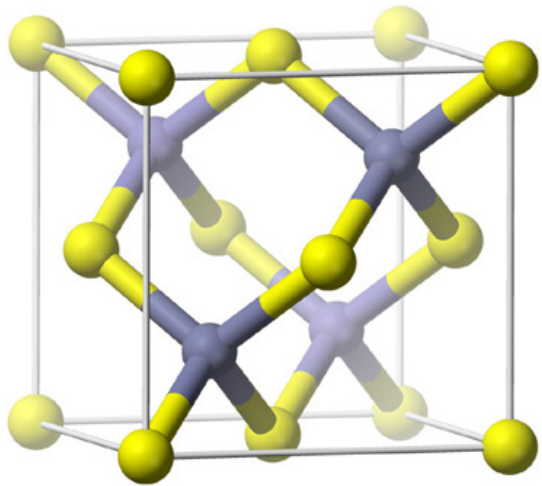
The presence of defects can affect the position of the Fermi level

Defects and material properties

- Defects can transform insulator into a semiconductor or a metal (doping)
- Defects can determine optical properties (color)
- At surfaces, defects have unique chemical properties
- Defects can have different number of electrons associated with them (charge), and each charge state can have very different chemical properties
- Measuring concentration of defects, especially at temperatures and pressures relevant for practical applications, is very difficult



Defect thermodynamics in GaAs



Perfect crystal

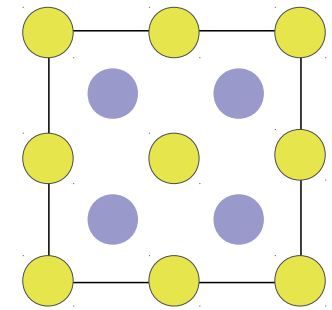
Zincblende structure:

Each Ga binds 4 As

Each As binds 4 Ga

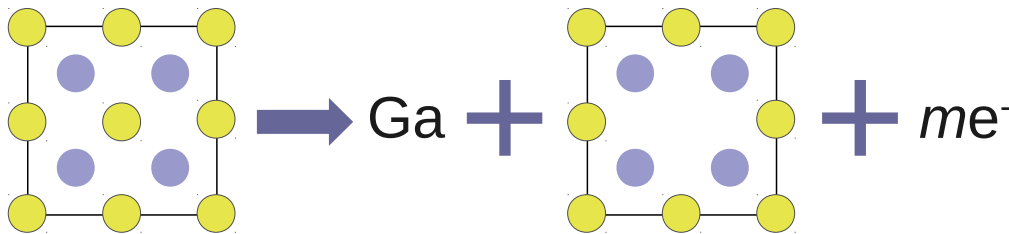
in a tetrahedral environment

Ga: s^2p^1
As: s^2p^3



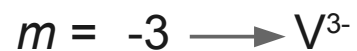
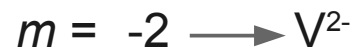
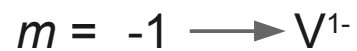
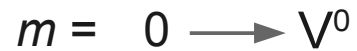
Ga: ●
As: ●

a) Ga vacancy

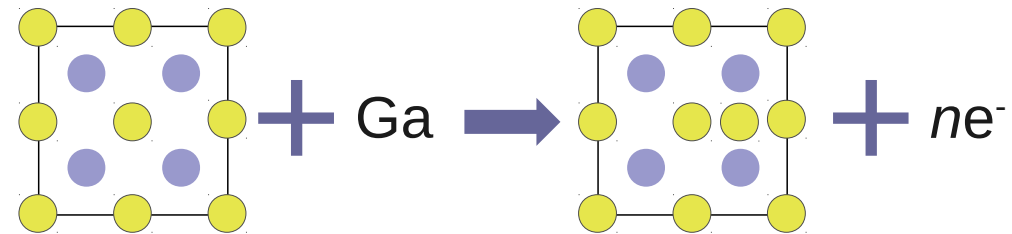


$5e^-$ remain in the vacancy

Acceptor: $m \leq 0$

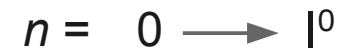


b) Ga interstitial



Ga can donate up to $3e^-$

Donor: $n \geq 0$



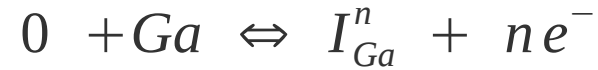
Defect thermodynamics in GaAs

a) Ga vacancy



$$\Delta G = \mu_{Ga} + G_V + m \mu - G_0$$

b) Ga interstitial



$$\Delta G = G_I + n \mu - G_0 - \mu_{Ga}$$

Need to know: G_0 , G_V , G_I , μ , μ_{Ga}

$$\left. \begin{array}{l} G_0 \approx E_0 \\ G_V \approx E_V \\ G_I \approx E_I \end{array} \right\}$$

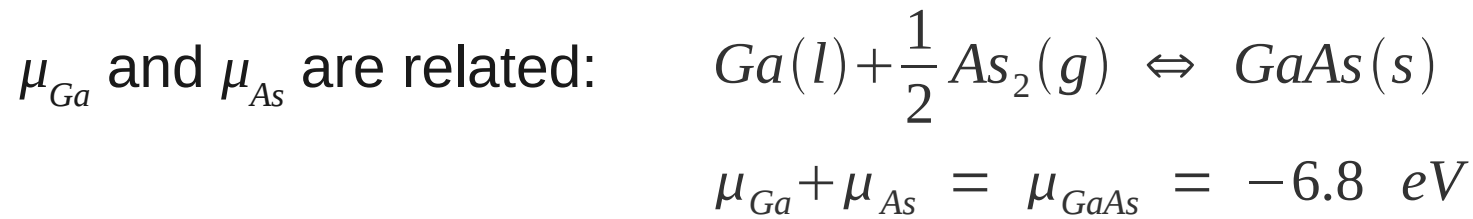
From DFT calculations (use the same cell size)
Discard vibrational contributions (very small here)

$$\mu = E_F - E_{VB}$$

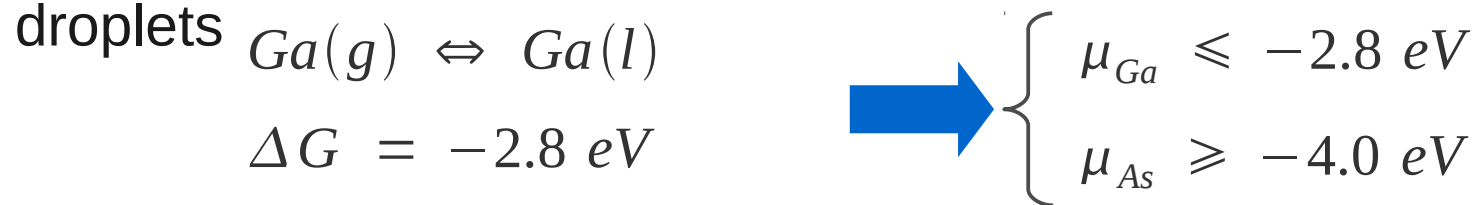
Energy of Fermi level, wrt the maximum of the valence band
Varies from E_{VB} to E_{CB}

μ_{Ga} Depends on the environmental conditions:
define upper and lower limiting values

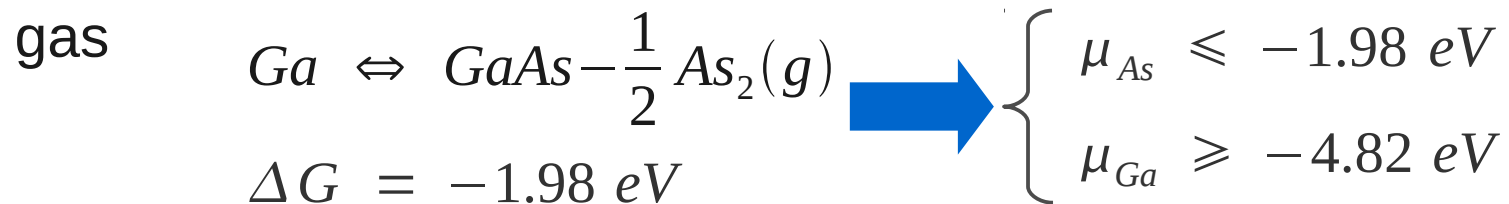
Limiting values for μ_{Ga}



Ga-rich (As-poor) conditions: formation of Ga droplets



As-rich (Ga-poor) conditions: formation of As_2 gas



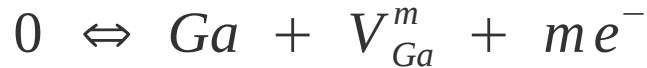
Energies taken from:

R. Hultgren et al, *Selected values of the Thermodynamic Properties of the Elements*, American Society for Metals, Ohio (1973).

R. C. Weast, *Handbook of Chemistry and Physics*. 60th edition, CRC Press (1980).

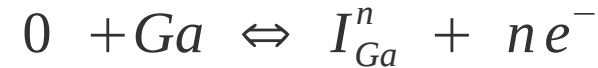
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From DFT calculations (use the same cell size)
Discard vibrational contributions (very small here)

$$\mu = E_F - E_{VB}$$

Energy of Fermi level, wrt the maximum of the valence band
Varies from E_{VB} to E_{CB}

μ_{Ga} Depends on the environmental conditions:
define upper and lower limiting values

$$-4.82 \text{ eV} \leq \mu_{Ga} \leq -2.80 \text{ eV}$$

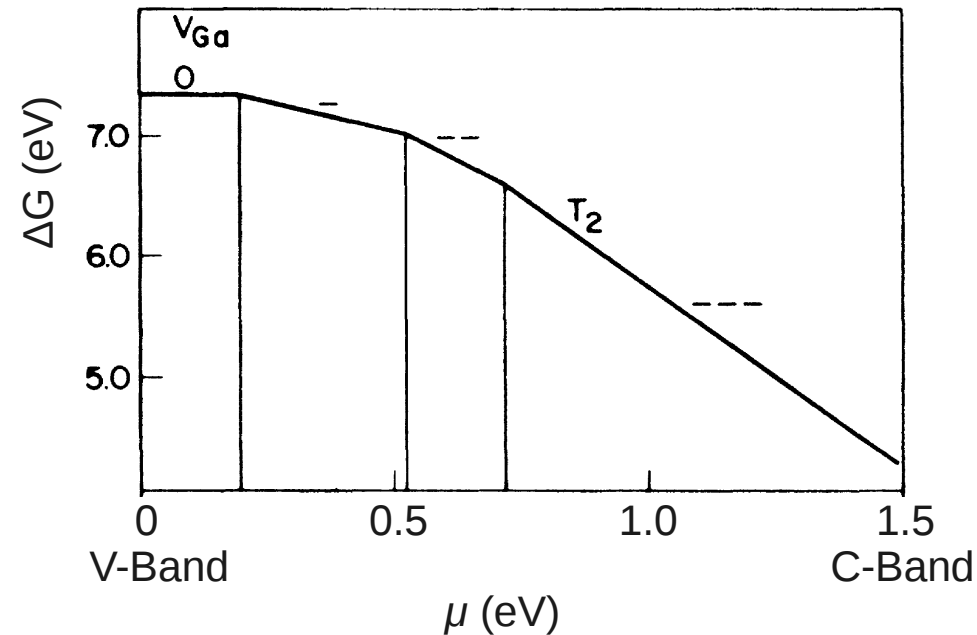
Defect thermodynamics in GaAs

a) Ga vacancy



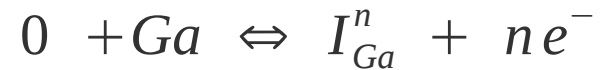
$$\Delta G = \mu_{Ga} + G_V + m\mu - G_0$$

As-rich limit ($\mu_{Ga} = -4.82 \text{ eV}$)



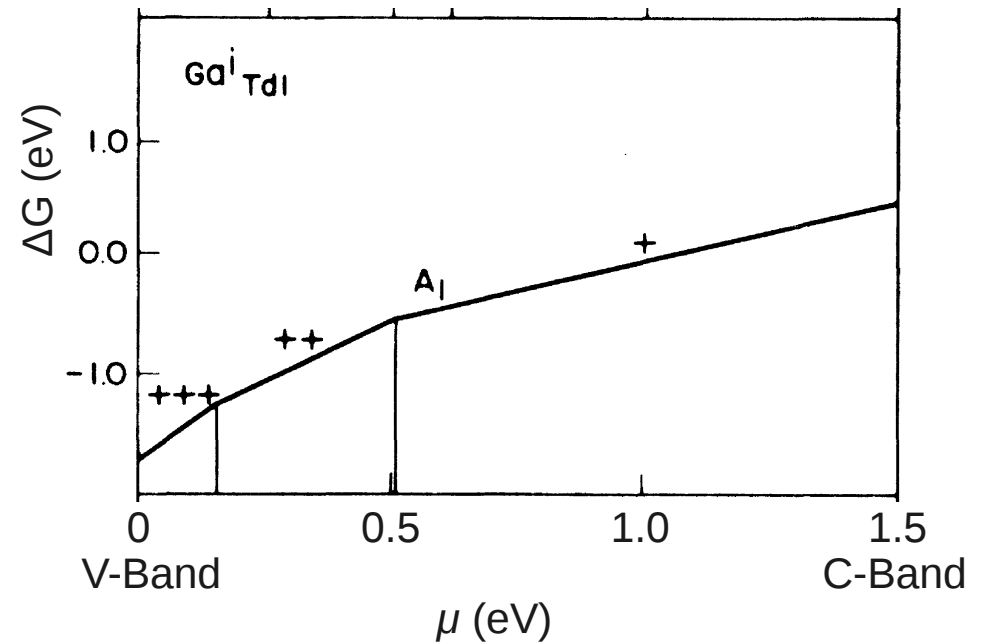
High formation energy
Reasonable good acceptor

b) Ga interstitial



$$\Delta G = G_I + n\mu - G_0 - \mu_{Ga}$$

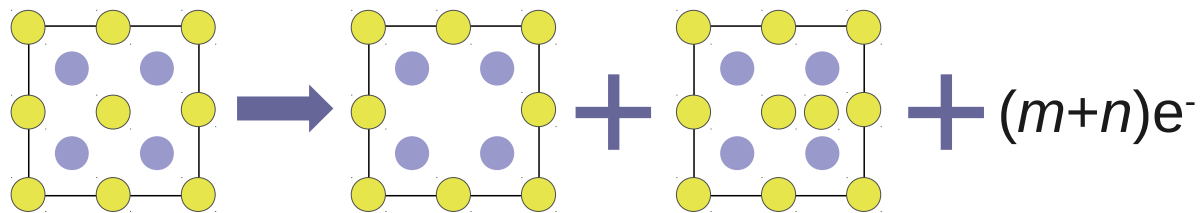
Ga-rich limit ($\mu_{Ga} = -2.80 \text{ eV}$)



Energetically favored
Good donor

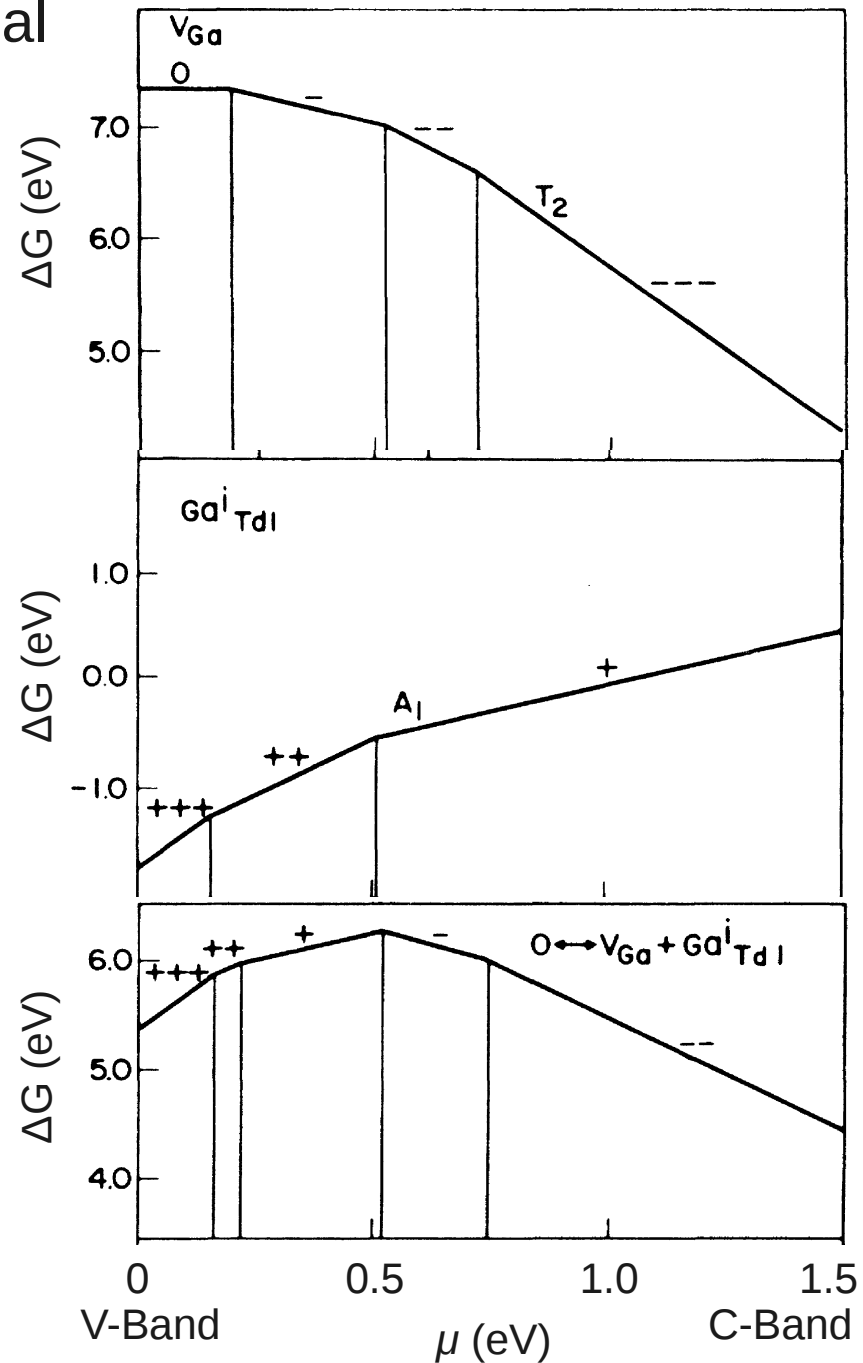
Defect thermodynamics in GaAs

c) (Independent) Ga vacancy and Ga interstitial



$$\Delta G = G_V + G_I + (m+n)\mu - G_0$$

V_{Ga} and I_{Ga} have opposite charges:
 Partial compensation of effects
 Possibly annihilate



Summary

Ab initio atomistic thermodynamics provides a connection between the microscopic and macroscopic regimes

With *ab initio* atomistic thermodynamics one can predict

- the preferred structure of a material as a function of environmental conditions
- the regions of enhanced catalytic activity

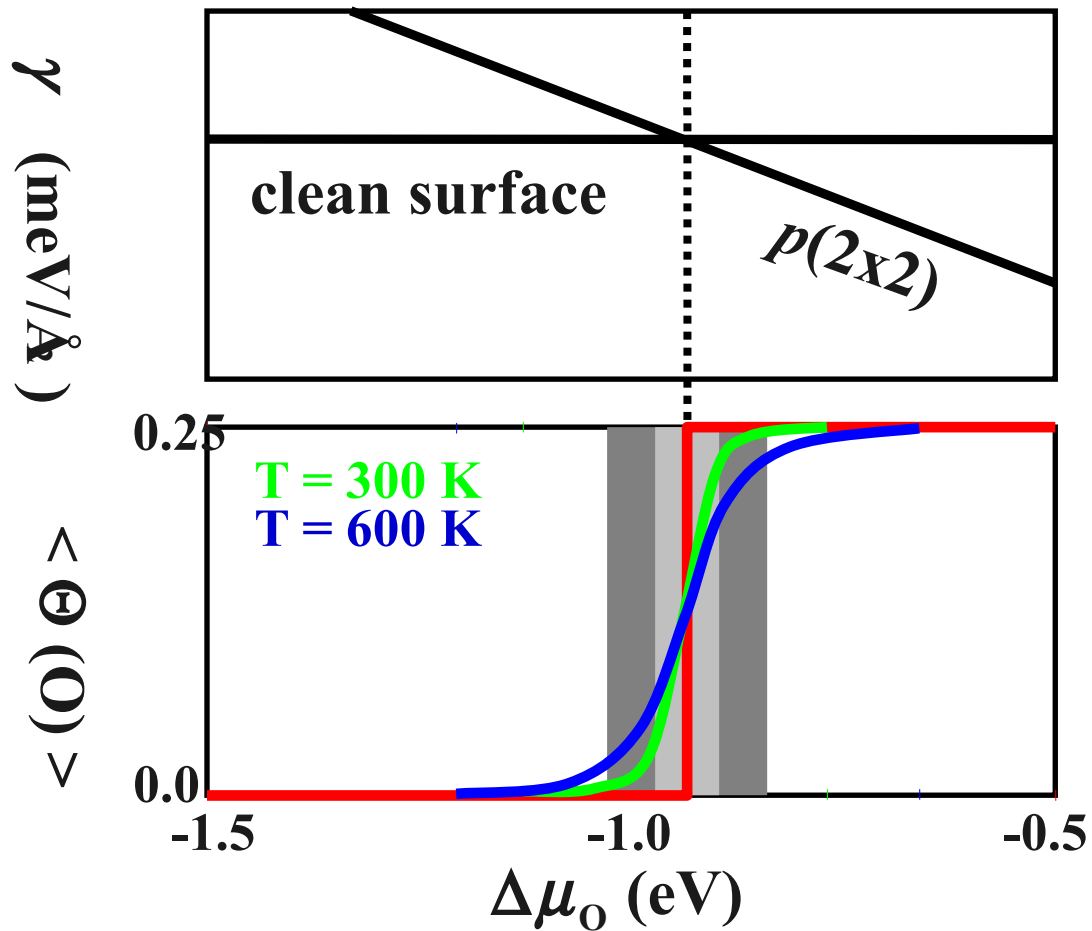
Limitations:

- Only actually sampled structures enter the free energy contest:
- Need for an exhaustive structural sampling
- Equilibrium assumption: possible kinetic hindrance in experiment

Acknowledgements

Sergey Levchenko

Appendix: configurational entropy and phase transitions



No lateral interactions:

$$F^{\text{conf}} = k_B T \ln \frac{(N+n)!}{(N!n!)}$$

Langmuir adsorption-isotherm

$$\langle \theta(\text{O}^{\text{cus}}) \rangle =$$

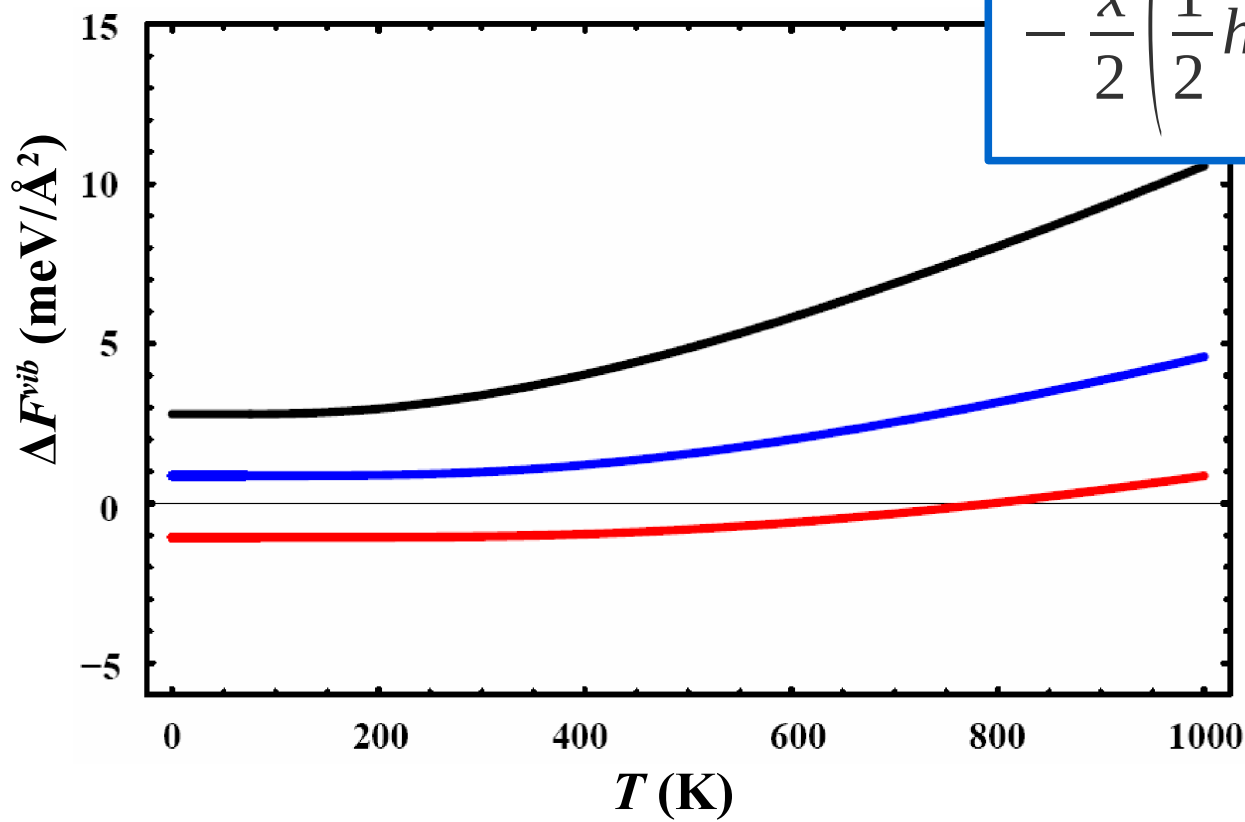
$$\frac{1}{1 + \exp((E^{\text{bind}} - \Delta\mu_0)/k_B T)}$$

Configurational entropy smears out phase transitions

Appendix: estimation of ΔF^{vib}

$$\Delta F^{vib} = \frac{1}{A} \left[F_{Pd \cdot O}^{vib} - F_{Pd(100)}^{vib} - \frac{x}{2} \mu_{O_2}^{vib} \right]$$

$$\Delta F^{vib} \approx \frac{1}{A} \int d\omega F^{vib}(T, \omega) \sigma_{Pd \cdot O}(\omega) - \int d\omega F^{vib}(T, \omega) \sigma_{Pd(100)}(\omega) - \frac{x}{2} \left(\frac{1}{2} h \nu_{O_2} + kT \ln \left(1 - \exp \left(- \frac{h \nu_{O_2}}{kT} \right) \right) \right)$$



$\nu_o = 196$ meV gas phase
 120 meV } Pd·O
 80 meV }
 40 meV }

J. Rogal and K. Reuter, Ab initio atomistic thermodynamics for surfaces: A primer. In: Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Hypersonic Flights. Educational Notes RTO-EN-AVT-142, Neuilly-sur-Seine (2007)

Appendix: chemical potential from tables

$$\begin{aligned}\mu(T, p) = & -kT \ln \left[\left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} (kT)^{\frac{5}{2}} \right] + kT \ln p - kT \ln \left(\frac{8\pi^2 I_A kT}{\sigma h^2} \right) \\ & + \frac{1}{2} h\nu + kT \ln \left(1 - e^{-\frac{h\nu}{kT}} \right) + E^{DFT} - kT \ln \nu_0\end{aligned}$$


$$\mu(T, p) = kT \ln p + E^{DFT} + E^{ZPE} + f(T)$$


$$\mu(T, p^\circ) = E^{DFT} + E^{ZPE} + f(T)$$

$$\mu(0, p^\circ) = E^{DFT} + E^{ZPE}$$

$$\Delta\mu(T, p) = \mu(T, p) - \mu(0, p^\circ) = kT \ln p + f(T)$$

$$\Delta\mu(T, p^\circ) = \mu(T, p^\circ) - \mu(0, p^\circ) = f(T)$$


$$\Delta\mu(T, p) = \mu(T, p^\circ) - \mu(0, p^\circ) + kT \ln p$$



Tables