Computational Materials Design
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Electrochemical Pourbaix phase diagrams from ab initio calcualtions

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Motivation

- ZnO is a wide band gap semiconductor of interest to diverse areas of application: passivation layers on steel surfaces, catalysis, corrosion, adhesion, gas sensing, and micro- or optoelectronics

- Its surface structure and stoichiometry is of high practical interest and essential to all of them

  Aim: Achieve an ab initio based understanding of how the environment influences the stability of polar ZnO(0001) surface and oxidised Zn phases

Formation energies

Bulk phase
$$G^f(\mathbf{X_b})(\{\mu_i\}) = G_0^f(\mathbf{X_b}) - \sum_i N_i \mu_i$$

Defect
$$G^f(\mathbf{X}^q)(\{\mu_i\}, \mu_e) = G_0^f(\mathbf{X}^q(\mathrm{aq})) - \sum_i N_i \mu_i + q\,\mu_e$$

Gibbs free energy: $G = E^{tot} + F^{vib} + F^{conf} + pV$; $F(T,V) = E - TS$

Atomistic thermodynamics

Construct surface phase diagrams based on the computed excess surface energy[5]

$$G^f = G_{ad/sub} - G_{sub} - \sum_i N_i \mu_i(T,p)$$
$$= G_0^f - \sum_i N_i \mu_i(T,p)$$

Chemical potential of the gas phase
$$\mu_i(T,p) = \mu_i(T,p^0) + \tfrac{1}{2} k_B T \ln(p_i/p^0)$$

I. Common approximation: Temperature independent surface phase diagrams

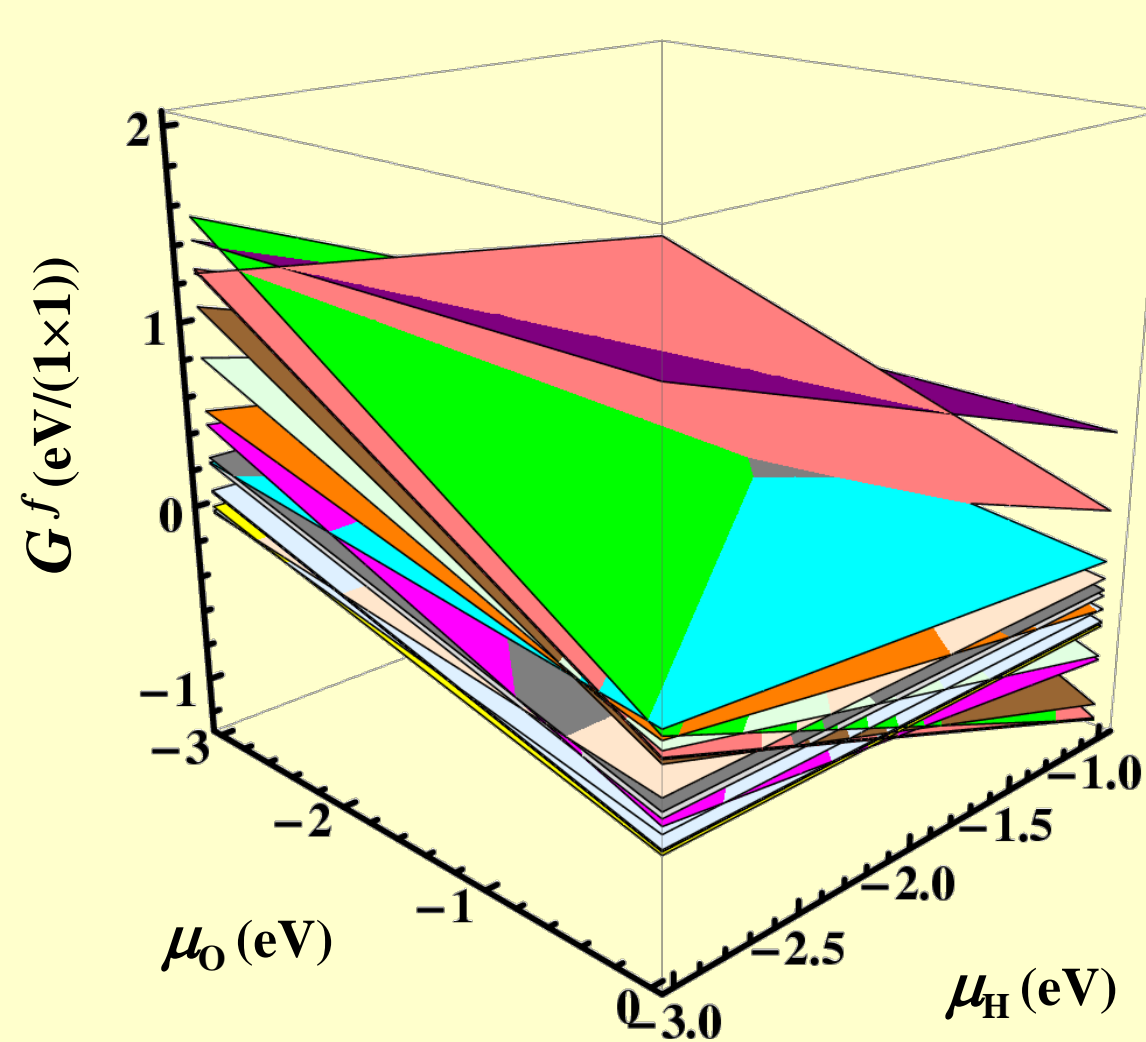T-effect (vibrations): tens of **meV** $<<$ T-effect (chem. Potential): several **eV**

$$\Rightarrow \quad G^f(\mu_i(T,p)) \approx \Delta E^\sigma_{tot} - \sum N_i \mu_i(T,p)$$

Temperature effects are restricted to the T-dependence of the gas phase chemical potentials

II. When the approximation $G(T, \mu_i(T,p)) \approx G(\mu_i(T,p))$ is not justified
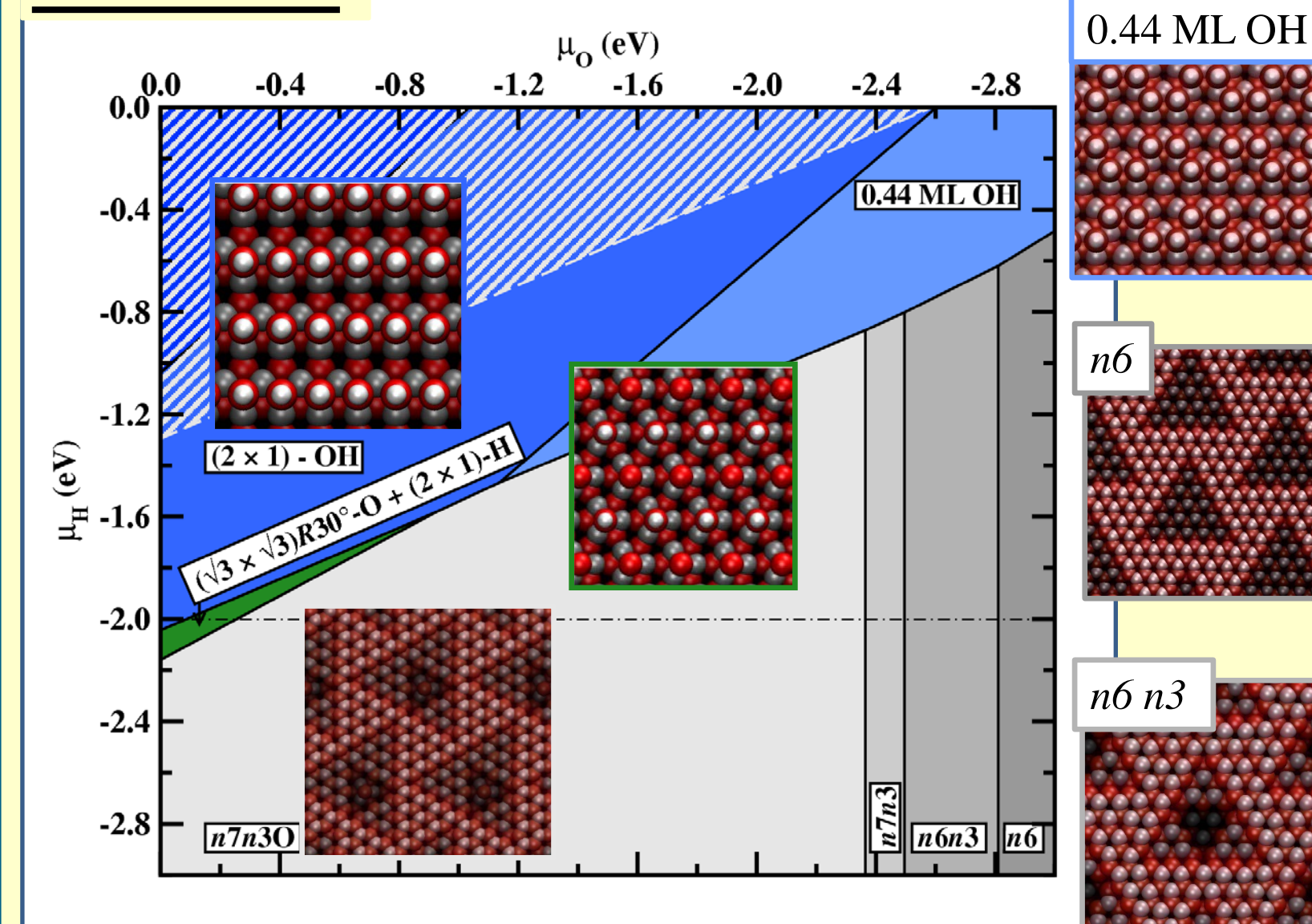
$$\Rightarrow \quad G^f(T, \mu_i(T,p)) = \Delta E^\sigma_{tot} - T\Delta S^{vib} - \sum N_i \mu_i(T,p)$$

The excess Gibbs free energy becomes explicitly temperature dependent → Temperature dependent surface phase diagrams

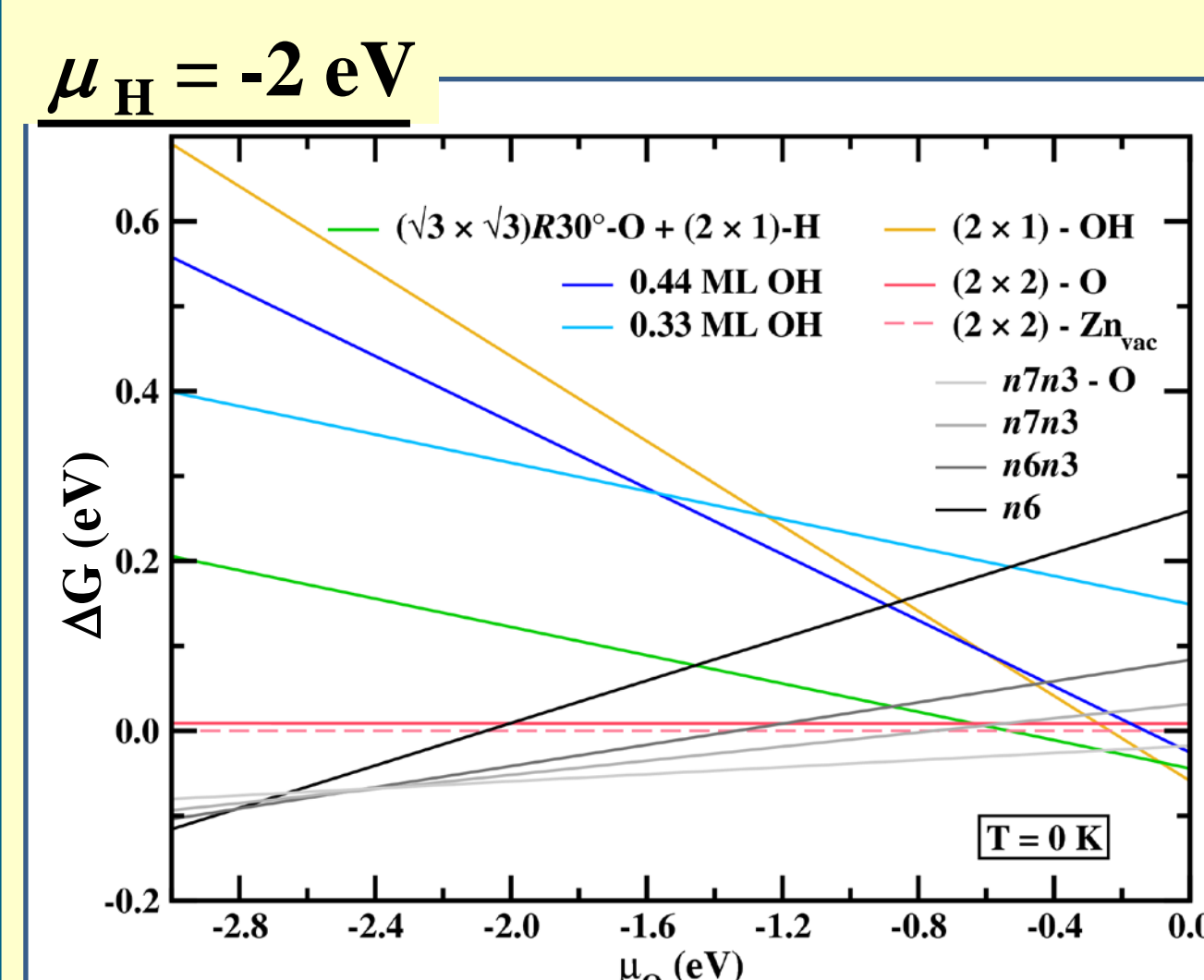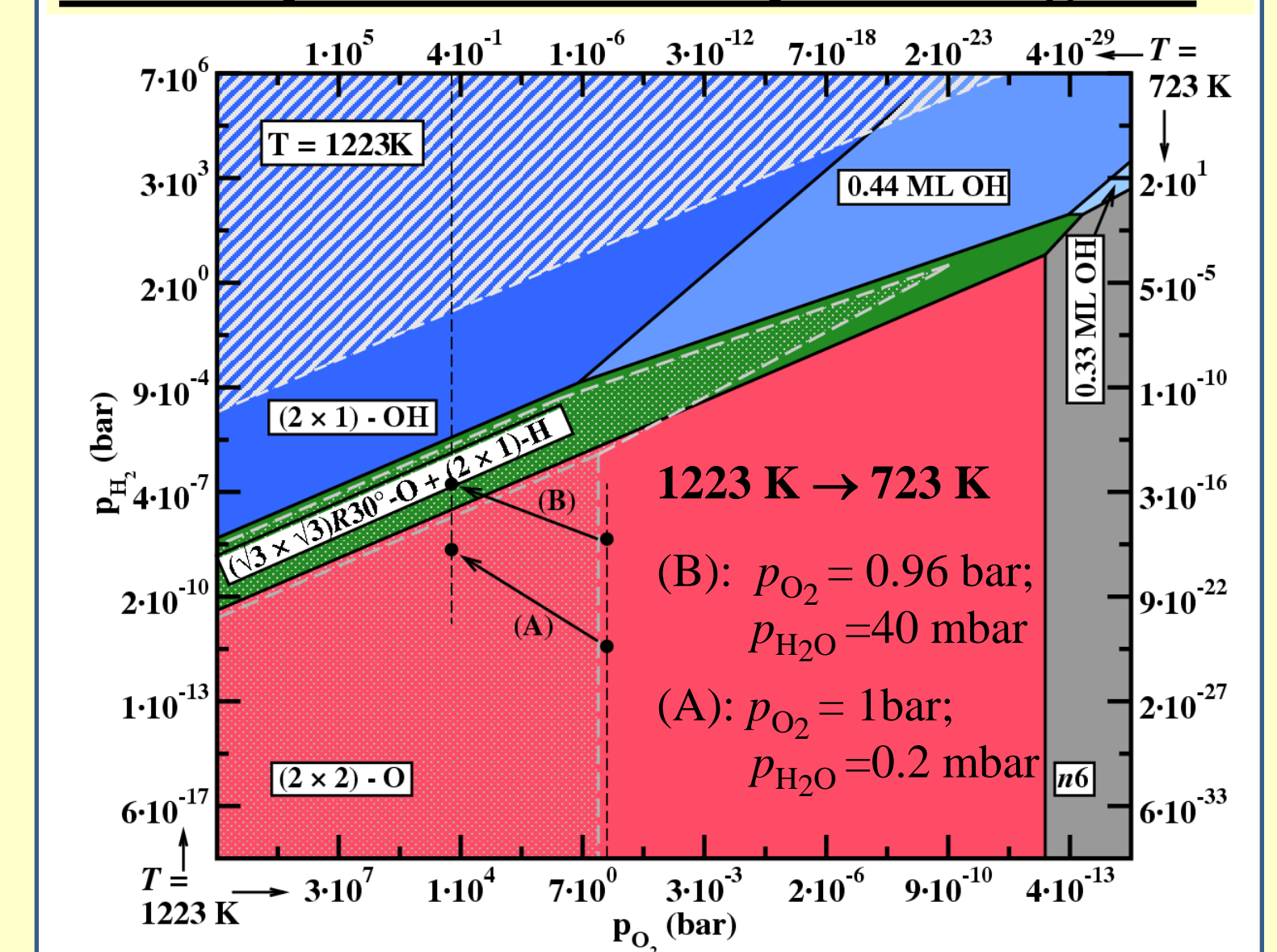## Experimental observations

Early 1970's UHV studies [1]:

controversial discussion about the observation of a (2×2) vs. (1×1) vs. ($\sqrt{3}\times\sqrt{3}$)$R30°$

UHV STM studies [2]:

Formation of ¼-ML Zn^{2+} vacancies

Ambient conditions/ in electrolytes [3]:

Adsorption of OH or O on the surface

(2 × 2) - O   ($\sqrt{3} \times \sqrt{3}$)R30° - OH

He-scattering experiments [4]:

He-TDS: unusually broad peaks; cannot be reconciled with the few in-equivalent adsorption sites found on ZnO(0001)

XPS: *both* Zn-H and Zn-O bonds present

Prolonged H exposure: loss of lateral order of the top substrate layer

Stable surface phases on ZnO(0001) [6]

I. T = 0 K

0.44 ML OH

II. T dependent surface phase diagrams

T = 1223K   0.44 ML OH

1223 K → 723 K
(B): $p_{O_2} = 0.96$ bar; $p_{H_2O} = 40$ mbar
(A): $p_{O_2} = 1$ bar; $p_{H_2O} = 0.2$ mbar

$\mu_H = -2$ eV

($\sqrt{3} \times \sqrt{3}$)R30°-O + (2 × 1)-H
0.44 ML OH
0.33 ML OH
(2 × 1) - OH
(2 × 2) - O
(2 × 2) - Zn_{vac}
n7n3 - O
n7n3
n6n3
n6

T = 0 K

- Surface phase diagram for 1223K with superimposed stability regions for (2×2)O and ($\sqrt{3} \times \sqrt{3}$) $R30°$-O + (2 × 1) H at T = 723K

- Initial and final experimental conditions indicated

O-rich conditions: The excess Gibbs free energy G^f for structures with similar stoichiometry but very different geometry changes by 20 - 30 meV

The (2×2)-O phase becomes increasingly more stable with increasing T
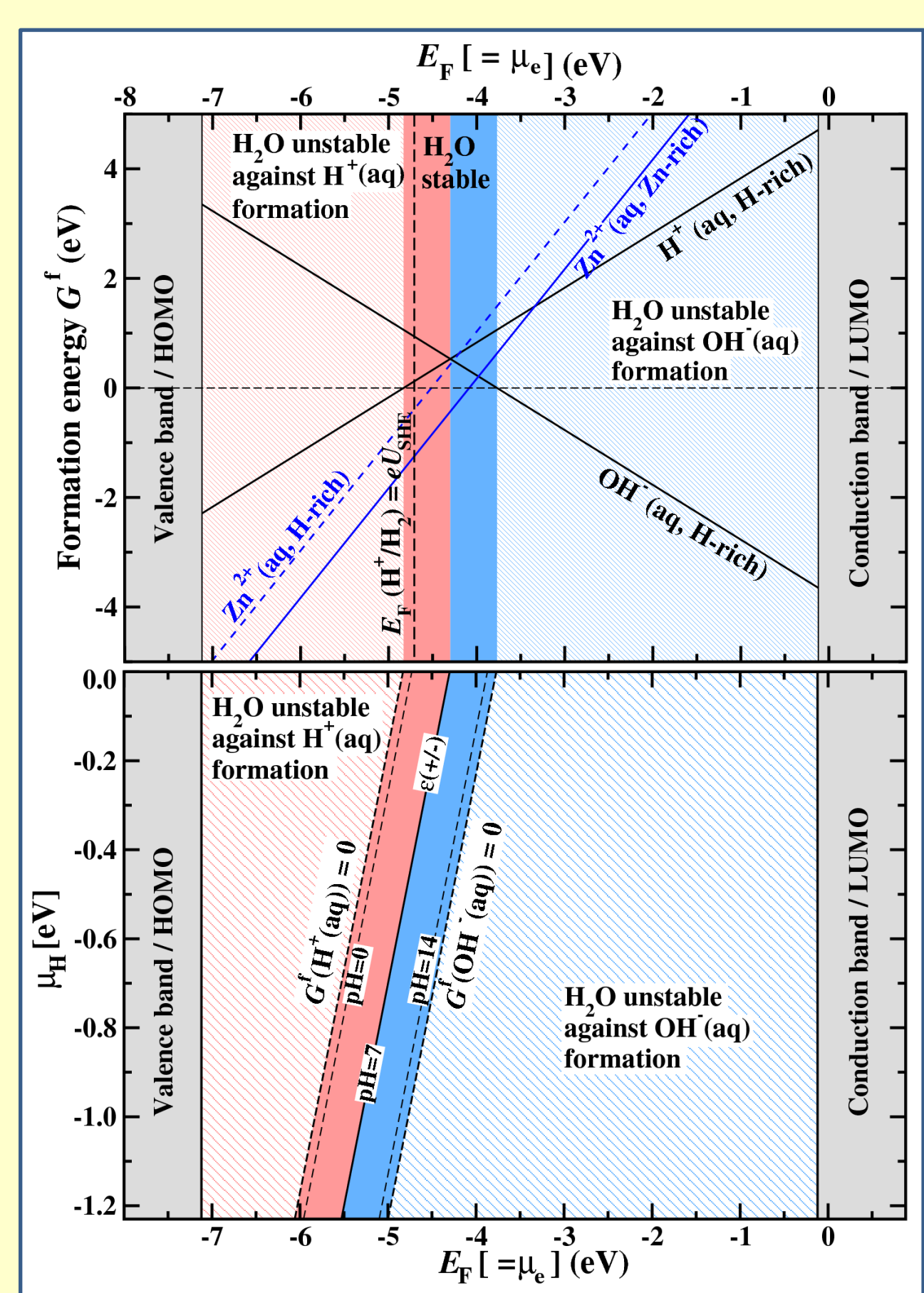
Water stability

Ion formation energies

$$H(g) \xrightarrow{IE} H^+(g) + e^-(g)$$
$$\tfrac{1}{2} H_2(g) \rightarrow H^+(aq) + e^-(aq)$$

$\Delta_f G°$ $\Delta_{hyd} G°$ alignment
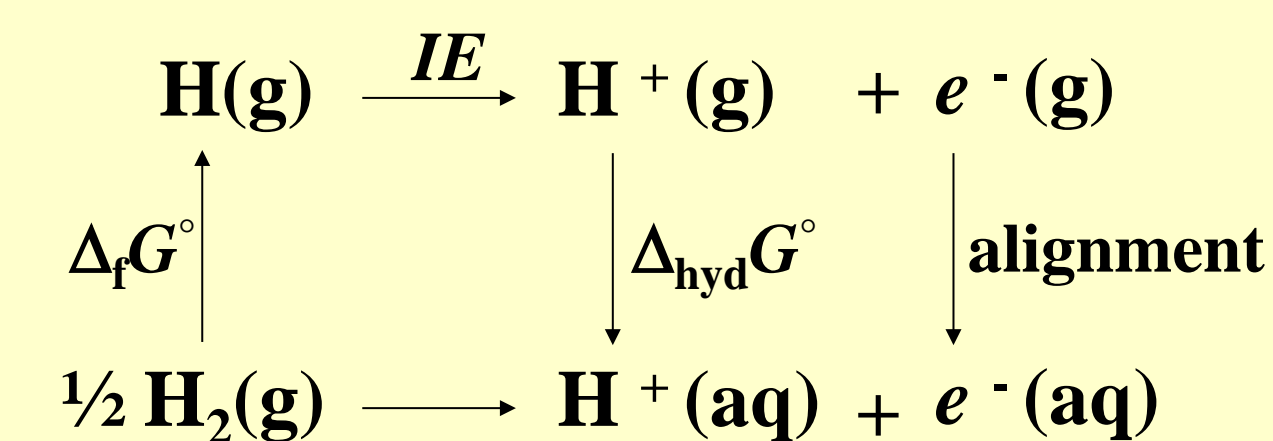
$$G^f(H^+(aq)) = 4.83 - \mu_H + \mu_e$$
$$G^f(OH^-(aq)) = -3.77 + \mu_H - \mu_e$$

The water stability region is narrow, shift with respect to μ_e as the chemical potential conditions change, but remains otherwise unperturbed

@ $pH = 0$: $G^f(H^+(aq)) = 0.10$ eV
@ $pH = 14$: $G^f(H^+(aq)) = 0.91$ eV

Electrochemical phase diagrmas

Ion concentrations (typical unit: *mole/l*): $c(\mathbf{X}^q) = 55.55\,[mole/l] \cdot \exp[-G^f(\mathbf{X}^q)/(k_B T)]$

$$10^{-pH} = 55.55 \cdot \exp\left[-\frac{G^f(H^+(aq))}{k_B T}\right]\ in\ (mole/l)$$
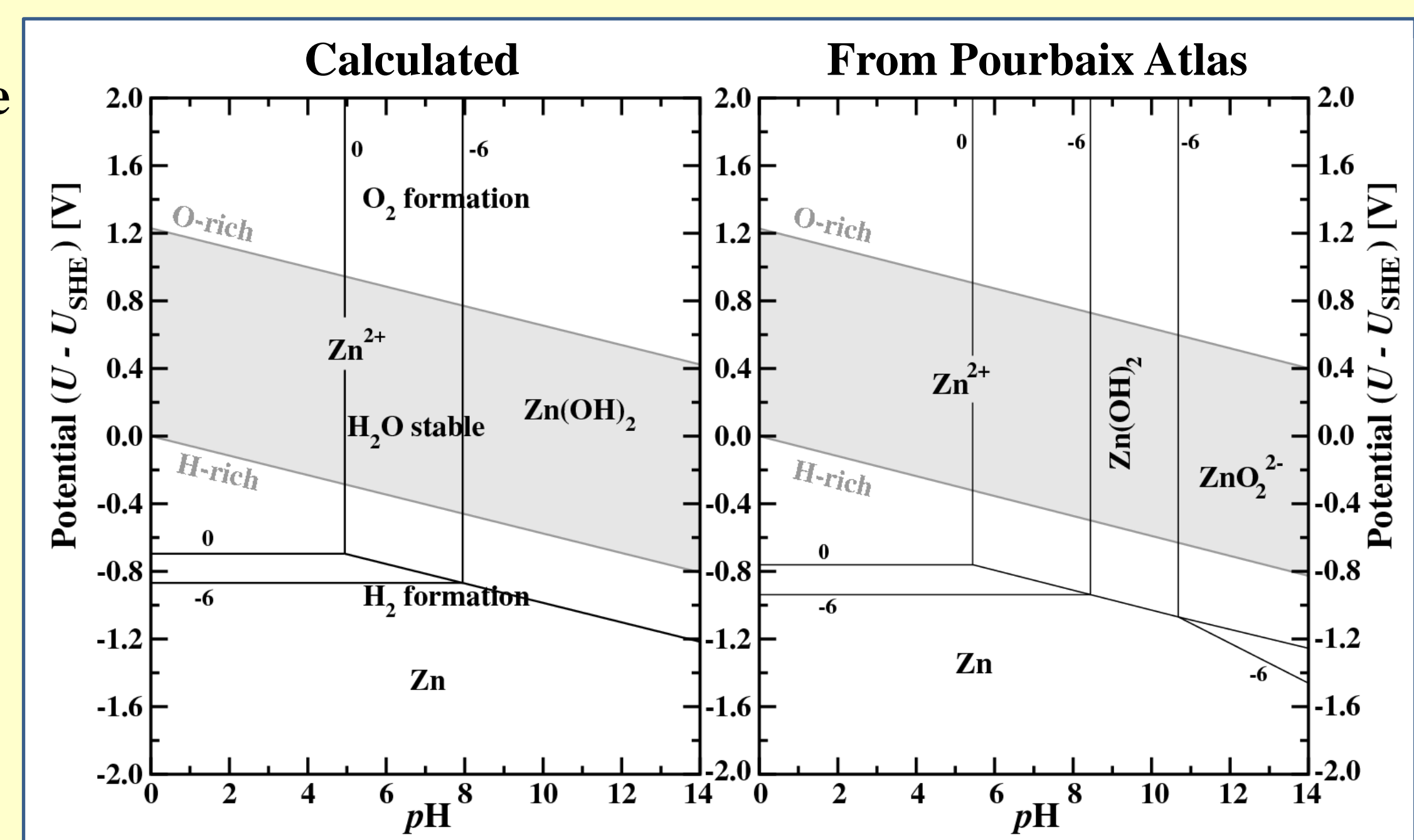
Standard Hydrogen Electrode ($U_{SHE} = 0$ V)

$pH = 0$ & H-rich conditions

$$\mu_e^{SHE} = eU_{SHE} = -[G_0^f(H^+(aq)) - k_B T \cdot ln(55,55)]$$

Possible to identify a Fermi Energy corresponding to the SHE and obtain the pH-scale from the Gibbs free energy of formation of ions in solution

Calculated   **From Pourbaix Atlas**

O-rich O_2 formation Zn^{2+} H_2O stable $Zn(OH)_2$ H-rich H_2 formation   Zn

O-rich Zn^{2+} $Zn(OH)_2$ ZnO_2^{2-} H-rich   Zn

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Summary and Conclusions

➤ The type of reconstruction observed on ZnO(0001) depends on
  - preparation conditions;
  - is largely affected by finite temperature effects: the vibrational entropy of the surface plays a decisive role in the competition between different phases to gain thermodynamic stability;

➤ The common approximation $G(T, \mu_i(T,p)) \approx G(\mu_i(T,p))$ is not always justified.

➤ Quantities accessible by first-principles calculations and measurable quantities, which influence the electrochemical behaviour of a system, can be linked via the developed thermodynamic approach

➤ The approach can be easily extended to incorporate any number of species which may become relevant within a system; it is general and can be applied to various electrochemical problems or questions involving ions in solution