Non-electricity based renewable fuels: Theory and computation for solar thermochemical hydrogen

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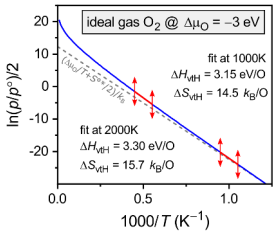
Chemical potential analysis vs van't Hoff



$$\frac{k_B}{2}\ln\frac{p}{p^\circ} = -\frac{1}{T}\delta H^r + \delta S^r + \frac{1}{2}\left[S^{\circ\kappa} + c_p\left(\ln\frac{T}{T^*} - 1\right)\right]$$

Solid state enthalpy and entropy (δH^r, δS^r)

$$\Delta G^{tot} = [\Delta G(M_qO_{1-\delta}) - \Delta G(M_qO)] + \delta\Delta\mu_O$$
$$= [\Delta H^r - T\Delta S^r] + \delta\Delta\mu_O$$
$$\frac{\partial}{\partial\delta}\Delta G^{tot} \equiv \delta G^{tot} = 0 \quad \Rightarrow \quad \delta H^r - T\delta S^r + \Delta\mu_O = 0$$

Shortcomings of van't Hoff $\frac{1}{2}\ln\frac{p}{p^\circ} = -\frac{1}{T}\frac{\Delta H_{vtH}}{k_B} + \frac{\Delta S_{vtH}}{k_B}$

- Convolution of solid state and gas phase properties
- Non-linearity due to gas phase term
- No analysis of T-dependence, $\delta H^r(T)$ and $\delta S^r(T)$

Chemical potential method

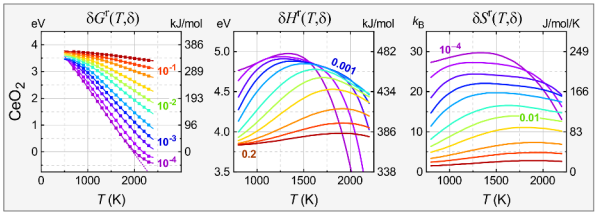
$$-\Delta\mu_O(T)\big|_\delta = \delta H^r(T,\delta) - T\delta S^r(T,\delta)$$
$$\equiv \delta G^r(T,\delta) = g_0 + g_1 T + g_2 T^2 + \ldots$$

polynomial expansion in T

$$\delta S^r(T) = -\frac{d}{dT}\delta G^r(T)$$
$$\delta H^r(T) = \delta G^r(T) + T\delta S^r(T)$$

decomposition of δG^r into δH^r and δS^r

Chemical potential analysis of simulated (pO_2,T) data (validated CeO_2 defect model)



- Strong T-dependence of δH^r and δS^r
- Physical origin: Defect ionization
- Large electronic entropy due to charged V_O^{+2}

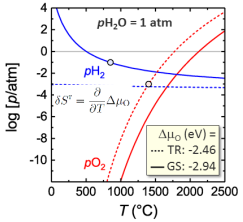
SL, JACS 146, 14114 (2024)

Impact of defect mechanism on STCH performance

$M_xO \rightarrow M_xO_{1-\delta} + \frac{\delta}{2}\cdot O_2$ Reduction (solar heat)

$M_xO_{1-\delta} + \delta\cdot H_2O \rightarrow M_xO + \delta\cdot H_2$ Oxidation (H_2 production)

$H_2 + ½\,O_2 \leftrightarrow H_2O$ Ideal gas law (H_2, O_2, H_2O)



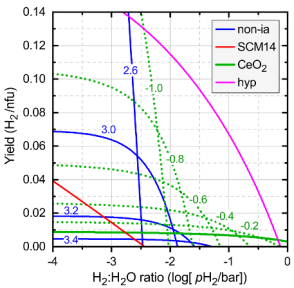
SL, J Chem Phys, 148, 071101 (2018)

Capacity – yield tradeoff

- higher $\delta_{red} \Rightarrow$ lower pH_2
- defect interactions bad
- charged defects good

Hypothetical systems

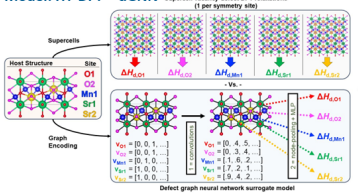
- limited gains via ΔH_D in CeO_2
- high capacity and yield via defect ionization energies



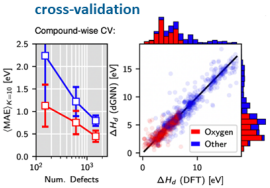
SL, JACS 146, 14114 (2024)

Defect Graph Neural Network

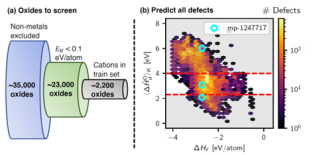
Model: HT-DFT + dGNN



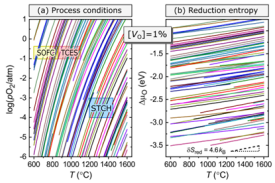
cross-validation



database screening

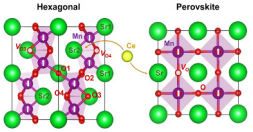


HT-thermodynamics



M.D. Witman, A. Goyal, T. Ogitsu, A.H. McDaniel, SL, Nature Comp Sci 3, 675 (2023).

Equilibria with interacting (neutral) defects



A. Goyal, M.D. Sanders, R.P. O'Hayre, SL, PRX Energy 3, 013008 (2024)

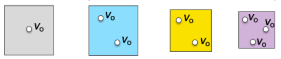
$\Delta H_D = \Delta H_D^{ref} + \Delta\mu_O$

VASP
(SCAN+U)
$U_{Mn\text{-}d}$ = 2 eV
$U_{Ce\text{-}f}$ = 1 eV

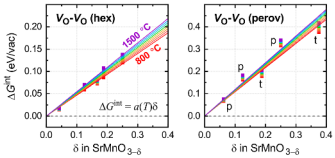
$$\Delta G^{tot} = f_d\left(x_V\left(\Delta H_D + \Delta G_D^{int}\right) + k_B T\left(x_V \ln(x_V) + (1-x_V)\ln(1-x_V)\right)\right)$$

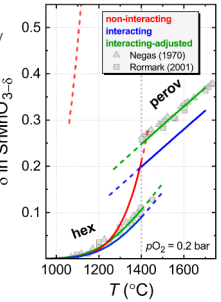
Free energy of defect interaction

Non-interacting | Interacting defects



$$\Delta E_i^{int} = \Delta H_{D,i}(nV_O) - n\times\Delta H_D(V_O)$$
$$\Delta G^{int} = -\frac{k_B T}{n}\ln\sum_i\left(g_i \exp\left(-\Delta E_i^{int}/k_B T\right)\right)$$
$$\Delta G^{int}(T) = (a_0 + a_1 T)\delta$$ parameterization



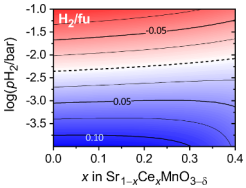


- Non-interacting:

$$3\delta = \frac{\exp(-\Delta H_D/k_B T)}{1+\exp(-\Delta H_D/k_B T)}$$

too large at high conc

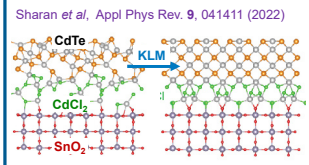
- Interacting: slightly too low
- Adjusted ΔH_D (by < 0.2 eV): essentially perfect
- T-dependence correct
- Phase transition from ΔG^{tot}

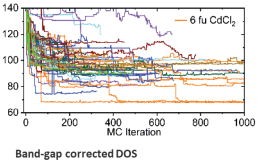


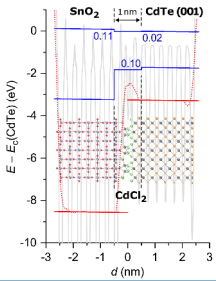
- SCM splits water, but only at low H_2:H_2O
- little benefit of Ce
- Enthalpy/entropy tradeoff

Interface atomic structure prediction

Sharan *et al*, Appl Phys Rev. **9**, 041411 (2022)







- Interface structure prediction from first principles
- Statistical structure sampling (no assumptions)
- Incommensurate heterostructural interface
- Discovery of atomic $CdCl_2$ interlayer phase
- Near-perfect electronic structure and band offsets

Band-gap corrected DOS

- DFT relaxation: SCAN meta-GGA
- Electronic structure: Single-shot hybrid with onsite-potential (SSH+V)

E_g(eV)	SCAN	GW	SSH+V
SnO_2	1.69	3.33	3.32
CdTe	0.99	1.69	1.71

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