|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **CO2RR** | | | | | | |
|  | | | |  | Systems (Metal) | |
|  | | | |  |  |  |
| System | Energy | ZPE | T\*S | G |  |  |
| GN-Ni | -649.61906 |  |  |  |  |  |
|  |  |  |  |  |  |  |
| GN4-Ni-COOH | -674.98431 | 0.612945 | 0.224709 | -674.596074 | H2 | -6.7592772 |
| GN4-Ni-CO | -664.55435 | 0.147962 | 0.283352 | -664.689740 | H2O | -14.219472 |
| GN4-Ni-H | -651.60953 | 0.167515 | 0.016964 |  | CO | -14.795910 |
|  |  |  |  |  | CO2 | -22.988805 |
|  |  |  |  |  | 1/2H | -3.3796386 |

GasPhase – molecule data

Reff: O2= G(298.15 K) = E DFT + ZPE + TS(T) = -9.863 + 0.09714-298.15x(205.147 x 0.0000103642723) = -10.3097 eV

=-9.863+0.09714-0.633926342024803015‬ = -10.309

H2 = G(298.15 K) = E DFT + ZPE + TS(T)

H2: Freq: 4401 cm–1 (Harmonic)

= -6.7592772+0.2728285‬-298.15\*(130.680\*0.0000103642723)

-6.7592772+0.2728285-0.4038152855064966‬ = -6.89026 eV

1/2H = -3.44513

CO2 = G(298.15 K) = E DFT + ZPE + TS(T)

<https://cccbdb.nist.gov/exp2x.asp>

vibrational zero-point energy: 2508.0 cm-1 (from fundamental vibrations)

-22.988805+0.31095-298.15\*(213.795\*0.0000103642723)

-22.988805+0.31095-0.66058311927235842 = -23.33843 eV

CO = G(298.15 K) = E DFT + ZPE + TS(T)

vibrational zero-point energy: 1071.6 cm-1 (from fundamental vibrations)

-14.795910+0.13286-298.15\*(197.66\*0.0000103642723)

-14.795910+0.13286-0.6107907050291867 = -15.27384 eV

H2O = G(298.15 K) = E DFT + ZPE + TS(T)

vibrational zero-point energy: 4504.0 cm-1 (from fundamental vibrations)

-14.219472+0.55843-298.15\*(188.84\*0.0000103642723)

-14.219472+0.55843-0.5835359543545058 = -14.24457 eV

CO2-RR-Mech-Ni-SAC

Step 1: \*COOH Formation

\*COOH = (\*COOH)-(\* + CO2 + ½ H2)

(-674.596074)-(-676.40262) = 1.81 eV

Step 2: \*CO Formation

\*CO = (\*CO+ H2O)-(\* + CO2 + H2)

= (-678.93431)-(-679.84775) = 0.91 eV

**HER-Ni-SAC**

STEP 1

Ni-H

ΔE = (\*H)-(\*+1/2H2)

= (-651.60953)-(-652.9986986)

ΔE = 1.39 eV

STEP 2

Experimental ZPE for H2 = 0.27 eV

Calculated ZPE for H atom = 0.167515 eV

ZPE = [ZPE(H\*)-1/2ZPE(H2)]

= (0.167515-0.135)

= + 0.032515 eV

Entropy (TΔS) of Adsorbed H\* is almost zero

Experimental T\*S for H2 = -0.40 eV

Entropy (TΔS) of Adsorbed 1/2H is = -0.200 eV

= (ZPE)-(-TΔS) = (0.032515)-(-0.200) = 0.232515 eV

ΔGH\* = ΔEH\*+ΔEZPE -TΔSH

ΔGH\* = (1.39)+(0.232515) = 1.62 eV