

龙讯教程

Calculating Pourbaix Diagram

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support@pwmatt.com

What is Pourbaix diagram?

The Pourbaix diagram is a phase stability diagram for material A under water at different electrode potential U and pH value. At different (U , pH) point, the most stable form of A could be A_1 , A_2 , ...

References:

(1) K.A. Persson, B. Walldwick, P. Lazic, G. Ceder, “Prediction of solid-aqueous equilibria: Scheme to combine first principle calculations of solids with experimental aqueous states”, Phys. Rev. B 85, 235438 (2012).

The basic concepts of calculation Pourbaix Diagram

(1) One should consider all the products of A: Ax^q made from A and water (q: charge)

(2) The stability of Ax^q is represented by its formation energy $H(Ax^q)$, which is defined as:

$$H(Ax^q) = G(Ax^q) - G(A) - n_1 * G(H_2O)_L - n_2 * (G(H^+) - U) - qU$$

Here, q is the charge state of q, and we assume, in terms of chemical formula:



Note, Ax only has one original A formula, and n_1 , n_2 can be negative. Ax is any specie which can be made out of A, water, H^+ (or alternatively, any thing which can be made of A, OH^- and H^+) and electron q. Note, if Ax^q is dissolved specie, it is usually assume $G(Ax^q)$ will not depend on U and pH. So, its value can be obtained from $\Delta G(Ax^q)$ at SHE.

(3) One subtle issue: in calculating $H(Ax^q)$, we should not use O_2 and H_2 as references. In other words, in considering all the possible reactions, we prevent the generation of O_2 and H_2 (assuming their energies are extremely high). Otherwise, in some (U,pH) point, the system is unstable, and the Pourbaix diagram is not well defined.

The calculation of $H(Ax^q)$

(1) $H(Ax^q) = G(Ax^q) - G(A) - n_1 * G(H_2O)_l - n_2 * (G(H^+) - U) - qU$

(2) Since $G_{H^+} + \mu_e(SHE) = 0.5H_2(g)$ at $pH=0$, and we define $\mu_e(SHE)=0$, so:

$$\begin{aligned} G(H^+) &= 0.5 G(H_2)_{gas} (298.15K, 1bar) - kT * \ln(10) * pH \\ &= 0.5 [E_{H_2} + ZPE_{H_2} - TS_{H_2}] - kT * \ln(10) * pH \\ &= 0.5 [E_{H_2} + 0.26 - 0.41 \text{ eV}] - kT * \ln(10) * pH \\ &= 0.5 E_{H_2} - 0.075 - 0.059 pH \quad (G(H^+) \text{ is independent of } U). \end{aligned}$$

Here, E_{H_2} , ZPE_{H_2} are the energy and zero phonon mode energy of isolated H_2 molecule.

(3) $G(H_2O)_l = E_{H_2O} + ZPE_{H_2O} - TS_{H_2O} = E_{H_2O} + 0.56 - 0.67 \text{ eV} = E_{H_2O} - 0.11 \text{ eV}$

Here, the subscript l means liquid, E_{H_2O} , ZPE_{H_2O} are the energy and zero phonon mode energy of isolated H_2O molecule

(4) If Ax^q is a dissolved specie (e.g, Zn^{2+}) in the liquid water, then we cannot calculate $G(Ax^q)$ directly (the calculated result is not very reliable). Check experiment.

The calculation of $G(\text{Ax}^q)$ for ion dissolved in water

(1) For dissolved cation and anion, we cannot directly calculate its free energy. We have to rely on experimental values.

(2) There are several good sources.

(a) CRC, Handbook of Chemistry and Physics

(b) NIST Chemistry Webbook: <https://webbook.nist.gov/chemistry>

(c) O. Kubaschewskii, C.B. Alcock, P.J. Spencer, “Materials thermochemistry”, 6th ed (Pergamon, New York, 1992).

(d) J. W. Johnson, O.E.H, and H.H. C. ,Comput. Geosci. 18, 899 (1992).

(e) M. Pourbaix, “Atlas of electrochemical equilibria in Aqueous solutions (National Association of Corrosion Engineers, Houston, Texasm 1974).

(3) They give $\Delta G(\text{Ax}^q)$ at $U=0$ (SHE).

For example, from Ref.(e), we can have:

$$\Delta G(\text{Zn}^{2+}) = -1.525 \text{ eV (independent of } U)$$

$$\Delta G(\text{ZnOH}^+) = -3.518 \text{ eV}$$

$$\Delta G(\text{ZnO}_2^{2-}) = -4.042 \text{ eV}$$

$$\Delta G(\text{HZnO}_2^-) = -4.810 \text{ eV}$$

The calculation of $G(\text{Ax}^q)$ for ion dissolved in water

(3) They give $\Delta G(\text{Ax}^q)$ at $U=0$ (SHE).

The definition of these formation energies is the energy difference between the ionic specie and the standard elemental phase (neutral) of each element.

$$\Delta G(\text{Zn}^{2+}) = -1.525 \text{ eV}$$

$$\Delta G(\text{ZnOH}^+) = -3.518 \text{ eV}$$

$$\Delta G(\text{ZnO}_2^{2-}) = -4.042 \text{ eV}$$

$$\Delta G(\text{HZnO}_2^-) = -4.810 \text{ eV}$$

The standard elemental phase for metal is the metal bulk, for H is H_2 gas, for O is O_2 gas.

Note, the definition of $\Delta G(\text{Ax}^q)$ is different from $H(\text{Ax}^q)$. $\Delta G(\text{Ax}^q)$ is the energy decomposed to standard neutral elemental phase (gas phase for H and O), and $H(\text{Ax}^q)$ is the energy decomposed to aqueous species (H^+ , OH^- , or H_2O).

We can calculate the Gibbs free energies of these elemental phases, then using ΔG , we can get the Gibbs free energy of the dissolved ionic specie (note, the Gibbs energy of the dissolved ion does not depend on pH values).

For example: $\Delta G(\text{Zn}^{2+}) = G(\text{Zn}^{2+}) - G(\text{Zn, bulk})$.

We can calculate $G(\text{Zn, bulk})$, then we can get $G(\text{Zn}^{2+})$ [Note $G(\text{Zn}^{2+})$ itself does not depend on U and pH]

Another example: $\Delta G(\text{ZnOH}^+) = G(\text{ZnOH}^+) - G(\text{Zn, bulk}) - 0.5 G(\text{O}_2)_g - 0.5 G(\text{H}_2)_g$

So, if we calculate $G(\text{Zn, bulk})$, $G(\text{O}_2)_g$ and $G(\text{H}_2)_g$, we can get $G(\text{ZnOH}^+)$.

The calculation of $G(\text{O}_2)_g$

$$\Delta G(\text{ZnOH}^+) = G(\text{ZnOH}^+) - G(\text{Zn, bulk}) - 0.5 G(\text{O}_2)_g - 0.5 G(\text{H}_2)_g$$

So, in order to get $G(\text{ZnOH}^+)$, with experimental, $\Delta G(\text{ZnOH}^+)$, we need to calculate $G(\text{O}_2)_g$

Previously, we have stated that, in the calculation of Pourbaix diagram, in the calculation of formation energy $H(\text{Axq})$, We do not use O_2 as the reference state. That is still correct in concept. However, here we just use $G(\text{O}_2)_g$ to get $G(\text{ZnOH}^+)$, It does not involve the definition of Pourbaix diagram, so it is okay.

In practice, the directly DFT calculated $G(\text{O}_2)_g$ is not good. We need to correct it.

There are two ways to correct it:

(1) Use water formation energy to get $G(\text{O}_2)_g$. We use this approach first

$$\Delta G(\text{H}_2\text{O}) = G(\text{H}_2\text{O})_l - 0.5 G(\text{O}_2)_g - G(\text{H}_2)_g = -2 \times 1.23 = -2.46 \text{ eV}$$

$$\begin{aligned} \text{Thus: } G(\text{O}_2)_g (1) &= 2 G(\text{H}_2\text{O})_l - 2 G(\text{H}_2)_g + 4.92 \text{ eV} \\ &= 2 E_{\text{H}_2\text{O}} + 2 \text{ZPE}_{\text{H}_2\text{O}} - 2 \text{TS}_{\text{H}_2\text{O}} - 2 E_{\text{H}_2} - 2 \text{ZPE}_{\text{H}_2} + 2 \text{TS}_{\text{H}_2} + 4.92 \text{ eV} \\ &= 2 E_{\text{H}_2\text{O}} - 2 E_{\text{H}_2} + 5.00 \text{ eV} \end{aligned}$$

Note, $\text{ZPE}_{\text{H}_2\text{O}} = 0.56 \text{ eV}$, $\text{ZPE}_{\text{H}_2} = 0.26 \text{ eV}$, $\text{TS}_{\text{H}_2\text{O}} = 0.67 \text{ eV}$, $\text{TS}_{\text{H}_2} = 0.41 \text{ eV}$

So, for the first method, we have: $G(\text{O}_2)_g (1) = -865.44 \text{ eV}$

PWmat calc. E (X) (eV)

H2O	-466.96
H2	-31.74

The calculation of $G(\text{O}_2)_g$

(2) For the second method, we choose an related experimental formation energy, e.g., ZnO, calculate $G(\text{ZnO})$ and $G(\text{Zn,bulk})$, then use the experiment $\Delta G(\text{ZnO})$ to obtain $G(\text{O}_2)_g$. This has the advantage of cancelling the ZnO bond energy in ZnOH^+ and ZnO, thus might lead to smaller error.

$$\Delta G(\text{ZnO}) = G(\text{ZnO}) - G(\text{Zn}) - 0.5 G(\text{O}_2)_g$$

The experimental $\Delta G(\text{ZnO})$ is -3.67 eV (e.g., from Ref.(e), or NIST Chemistry webbook)

$$G(\text{O}_2)_g(2) = -863.82 \text{ eV}$$

phase	E (ev)
Zn	-5430.28
ZnO	-5865.86

This is 1.6 eV higher than the one obtained from water consideration!

Unfortunately, this is the current status of DFT calculations. They do not really agree with each other.

As we discussed before, it might be better to use this $G(\text{O}_2)_g(2)$, since it can offer some error cancellation.

The Pourbaix Diagram

Taking the above calculations together, we can calculate the formation energy

$H(Ax^q)$ as a function of U and pH .

Note, unlike the ΔG , which is the formation energy at $U=0$ from the standard neutral elemental phase, $H(Ax^q)$ is the formation energy from specie A , and aqueous species OH^- and H^+ (or say H_2O and H^+).

$H(Ax^q)(U,pH)$ is a function of U and pH (has a form of $a + b*U + c*pH$)

Now, for each (U,pH) point, we just need to compare $H(Ax^q)(U,pH)$ for all potential phase: Ax^q .

Whoever has the lowest formation energy, it will be the most stable phase at this (U,pH) .

We can have a $A(1000 \times 1000)$ grid for (U,pH) , scan all $H(Ax^q)(U,pH)$, assign this point to the lowest specie Ax^q (say, from 1 to 10 phases). Then, we can plot this $A(1000 \times 1000)$ array (e.g., from Matlab), we will have the Pourbaix Diagram).

The Pourbaix Diagram of ZnO

In the following, we use ZnO as one example to calculate its Pourbaix diagram

We first need to know all the possible phases:

This can be obtained by checking the data base for all possible Zn, O, H combined phases, and cation, anion solutions.

For the Zn related system, we found: Zn, ZnO₂, ZnO, Zn²⁺, ZnOH⁺, HZnO₂⁻, ZnO₂²⁻

For the ionic species, from the reference book, we found:

$$\Delta G(\text{Zn}^{2+}) = -1.525 \text{ eV (independent of U)}$$

$$\Delta G(\text{ZnOH}^+) = -3.518 \text{ eV}$$

$$\Delta G(\text{ZnO}_2^{2-}) = -4.042 \text{ eV}$$

$$\Delta G(\text{HZnO}_2^-) = -4.810 \text{ eV}$$

The Pourbaix Diagram of ZnO

The basic formation energy equations:

$$H(\text{Zn}) = G(\text{Zn}) - G(\text{Zn}) = 0.$$

$$H(\text{ZnO}_2) = G(\text{ZnO}_2) - G(\text{Zn}) - 2 G(\text{H}_2\text{O})_l + 4 G(\text{H}^+) - 4U$$

$$H(\text{ZnO}) = G(\text{ZnO}) - G(\text{Zn}) - G(\text{H}_2\text{O})_l + 2 G(\text{H}^+) - 2U$$

$$H(\text{Zn}^{2+}) = G(\text{Zn}^{2+}) - G(\text{Zn}) - 2 U = \Delta G(\text{Zn}^{2+}) - 2U$$

$$H(\text{ZnOH}^+) = G(\text{ZnOH}^+) - G(\text{Zn}) - G(\text{H}_2\text{O})_l + G(\text{H}^+) - 2 U = \Delta G(\text{ZnOH}^+) + 0.5G(\text{O}_2) + 0.5G(\text{H}_2) - G(\text{H}_2\text{O})_l + G(\text{H}^+) - 2U$$

$$H(\text{HZnO}_2^-) = G(\text{HZnO}_2^-) - G(\text{Zn}) - 2 G(\text{H}_2\text{O})_l + 3 G(\text{H}^+) - 2 U = \Delta G(\text{HZnO}_2^-) + 0.5G(\text{H}_2) + G(\text{O}_2) - 2G(\text{H}_2\text{O})_l + 3G(\text{H}^+) - 2U$$

$$H(\text{ZnO}_2^{2-}) = G(\text{ZnO}_2^{2-}) - G(\text{Zn}) - 2 G(\text{H}_2\text{O})_l + 4 G(\text{H}^+) - 2 U = \Delta G(\text{ZnO}_2^{2-}) + G(\text{O}_2) - 2 G(\text{H}_2\text{O})_l + 4G(\text{H}^+) - 2U$$

-----General formula -----

$$G(\text{H}_2) = E(\text{H}_2) - 0.15 \text{ eV}$$

$$G(\text{H}^+) = 0.5 E(\text{H}_2) - 0.075 - 0.059 \text{ pH (eV)}$$

$$G(\text{H}_2\text{O})_l = E(\text{H}_2\text{O}) - 0.11 \text{ eV}$$

----- PWmat calc. result from the table -----

$$G(\text{H}_2) = -31.89 \text{ eV}$$

$$G(\text{H}^+) = -15.795 - 0.059 \text{ pH (eV)}$$

$$G(\text{H}_2\text{O})_l = -467.07 \text{ eV}$$

$$G(\text{O}_2) = -865.44 \text{ (method1)} = -863.82 \text{ (method2) eV}$$

$$\Delta G(\text{Zn}^{2+}) = -1.525 \text{ eV}$$

$$\Delta G(\text{ZnOH}^+) = -3.518 \text{ eV}$$

$$\Delta G(\text{ZnO}_2^{2-}) = -4.042 \text{ eV}$$

$$\Delta G(\text{HZnO}_2^-) = -4.810 \text{ eV}$$

phase	E (ev)	zpe	TS
Zn	-5430.28	0	0
ZnO	-5865.86	0	0
ZnO2	-6297.86	0	0
H2O	-466.96	0.56	0.21
H2	-31.74	0.26	0.63

PWmat
Calculated
(depending on
Pseudopotential
And Ecut. Need
to be consistent).

Plug everything in, we have:

Using $G(\text{O}_2)_g$ method1

$$H(\text{Zn}) = 0.$$

$$H(\text{ZnO}_2) = 3.38 - 0.236 \text{ pH} - 4\text{U}$$

$$H(\text{ZnO}) = -0.100 - 0.118 \text{ pH} - 2\text{U}$$

$$H(\text{Zn}^{2+}) = -1.525 - 2\text{U}$$

$$H(\text{ZnOH}^+) = -0.908 - 0.059 \text{ pH} - 2\text{U}$$

$$H(\text{HZnO}_2^-) = 0.56 - 0.177 \text{ pH} - 2\text{U}$$

$$H(\text{ZnO}_2^{2-}) = 1.28 - 0.236 \text{ pH} - 2\text{U}$$

Using $G(\text{O}_2)_g$ method2

$$H(\text{Zn}) = 0.$$

$$H(\text{ZnO}_2) = 3.38 - 0.236 \text{ pH} - 4\text{U}$$

$$H(\text{ZnO}) = -0.100 - 0.118 \text{ pH} - 2\text{U}$$

$$H(\text{Zn}^{2+}) = -1.525 - 2\text{U}$$

$$H(\text{ZnOH}^+) = -0.098 - 0.059 \text{ pH} - 2\text{U}$$

$$H(\text{HZnO}_2^-) = 2.18 - 0.177 \text{ pH} - 2\text{U}$$

$$H(\text{ZnO}_2^{2-}) = 2.90 - 0.236 \text{ pH} - 2\text{U}$$

Plot the Pourbaix Diagram

Modify the included python code using the number in the last slide: Pourbaix_plot.py:

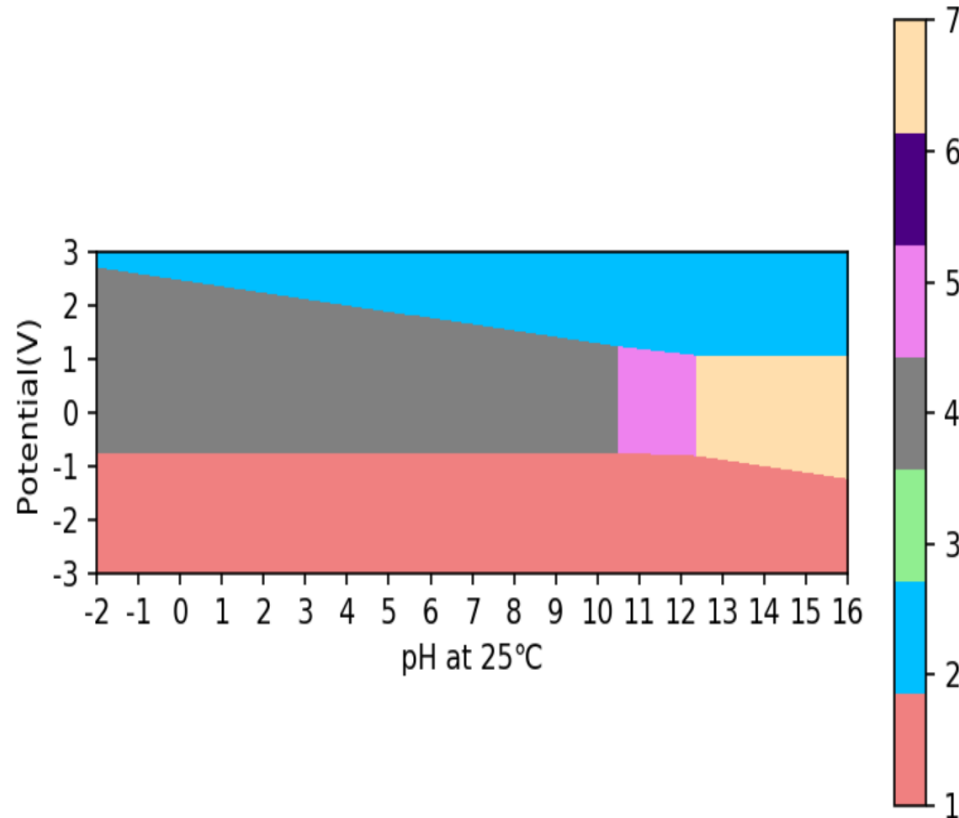
```
8 import numpy as np
9 import matplotlib.pyplot as plt
10 from matplotlib.colors import ListedColormap
11 #from mpl_toolkits.mplot3d import Axes3D
12
13
14
15 DPI = 150    ##~Y个~X~[~I~G大~O~L~\~Y~G~L~[~N~T就~O以
16
17 ##~[~T~\~I~L~L~I1-7~Z~D顺~O
18 colors = ('lightcoral', 'deepskyblue', 'lightgreen', 'gray', 'violet', 'Indigo', 'navajowhite')
19
20 def select(x,y):
21 # =====
22 # ~\~此~[~T~G~U~O~B~U~P~N~L~L~I F5 ~P~L~M~O
23 # =====
24
25     z1 = 0 + 0 * x - 0 * y
26     z2 = 3.38 - 0.236* x - 4 * y
27     z3 = -0.100 - 0.118 * x - 2 * y
28     z4 = -1.525 - 2 * y
29     z5 = -0.908 - 0.059 * x - 2 * y
30     z6 = 0.56 - 0.177 * x - 2 * y
31     z7 = 1.28 - 0.236 * x - 2 * y
32
33     return z1,z2,z3,z4,z5,z6,z7
34
```

Here is X is pH value, and Y is the U.

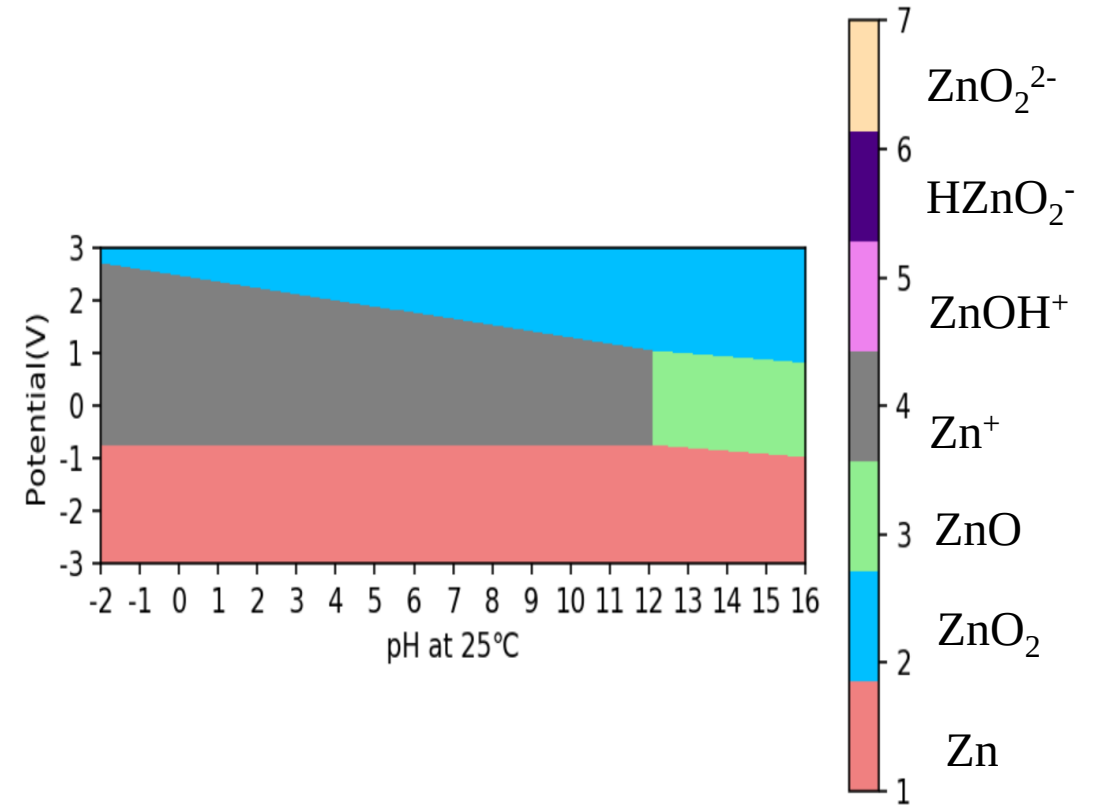
Then run it: >python3 ./pourbaix_plot.py, you will get the Pourbaix diagram figure.

The Pourbaix Diagram

Using method1 for $G(\text{O}_2)_g$



Using method2 for $G(\text{O}_2)_g$



Note, we get slightly different Pourbaix diagram result compared with that in P.R.B 85, 235438 (2012), due to slight different procedure and numbers used.