An universal method to plot Pourbaix diagram

Yecheng Zhou* and Nuria Lopez*

Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Av.Paisos Catalans, 16,43007 Tarragona, Spain

E-mail: yzhou@iciq.es; nlopez@iciq.es

Pourbaix diagram is a phase diagram used in electrochemical analysis, which shows the most stable phase under certain pH and applied potential. In a Pourbaix diagram each boundary line is determined by a chemical reaction between two phases. In principle, to plot a Pourbaix diagram, one has to consider all possible chemical reactions between each two phases. Usually, one kind of metal may have several phases, the number of reactions may excess 30, which has to pay large mount of labor. The considered reaction is about proportional to n^2, where n the number of phases. Here, I show a simple method by only considering n reactions. The most meaningful advantage is that all phases are referenced to one reference, which can be used to determined possible meta-stable phases.

In 2012, Persson et al. developed a computational method to predict the Pourbaix diagram by comparing the defining enthalpy of each phase, which can be calculated from first-principles calculations.[1] This method has been widely used,[2–6] including the phase diagram in the Materials Project. Shortly, Huang and Zeng et al. corrected this method with zero point energy(ZPE),[3–5] as some materials may have large ZPE contribution in the scale of 1 eV, especially for the compound include hydrogen ions. In this method, the Gibbs free energy change of all possible chemical reactions between each two phases has to be calculated. For a metal element with phase number of n, the number of reaction is C_n^2. For example, for Ni-water system, possible phases include NiO, NiO_2, Ni_2O_3, Ni_3O_4, $Ni(OH)_2$, NiOOH, Ni^{2+},

$Ni(OH)_4{}^{2-}$, $Ni(OH)_3{}^{1-}$, $Ni(OH)^+$, and Ni. The number of phase is 11, then more than 100 reactions have to be calculated. Although we can ignore some unreasonable reactions based on our experience, we still have to calculate about 30 chemical reactions. The reaction with negative free energy change ($\Delta G = G_{right} - G_{left}$) goes to the right side. The compound at right is more stable. Otherwise, the compound at left is more stable. After checked all reactions, we can get the most stable phase. If we want to find metal-stable phases, we then needs to assume that all compounds react with the most stable phase, and evaluate the free energy differences of those reactions. Phases with small free energy difference are considered as meta-stable.

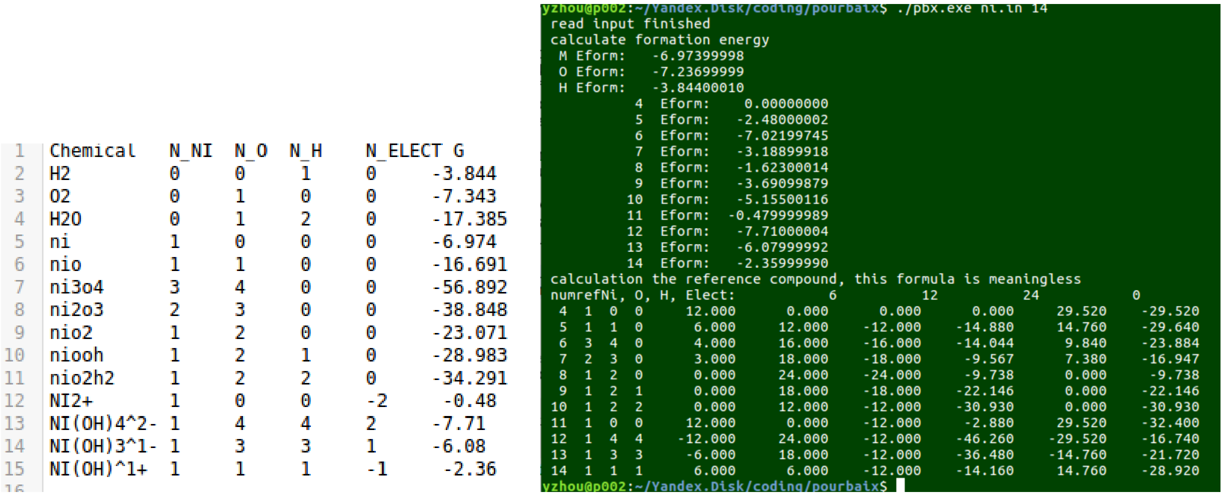
Here, I give a simple method, which is less elaborative and more convenient to analyze meta-stable phases. The method is based on the Hess' law, also called the law of additivity of reaction heat, the reversible reaction of $H_2O \longleftrightarrow OH^- + H^+$ at U=0 and pH=0. The first step is to define a reference compound, which should include all elements, for example, $M_xO_yH_z$. But this compound is just a imaginary compound, it may not exist in natural. Then we calculate the free energy change of reactions between this reference compound and all other possible phases. We assume A goes to B with reaction heat of ΔG_{AB}. If $\Delta G_{AB} > 0$, that means A is more stable, otherwise, B is more stable. Here, if we add a reference compound C, and the reaction heat of A to C, and B to C are ΔG_{AC} and ΔG_{BC}, respectively. According to Hess' law, ΔG_{AB} can be calculated by ΔG_{AC}-ΔG_{BC}. Then $\Delta G_{AB} > 0$ is equivalent to $\Delta G_{AC} > \Delta G_{BC}$. Hence, A is more stable. For the same reason, the compound with highest reaction heat should be the most stable.

In the calculation, we assume $M_xO_yH_z$ is the product, and other phases are reactants. Take $M_aO_bH_c$ as an example.

$$x\ M_aO_bH_c^q + (ay - xb)\ (OH^- - e^-) + [az - xc - (ay - xb)]\ (H^+ + e^-) + q\ e^- \longleftrightarrow a\ M_xO_yH_z; \Delta G$$

Where, ^{q} is the oxidation state of the compound and ΔG_{abc} is the free energy change (reaction heat) of $M_aO_bH_c^q$ reacts to $M_xO_yH_z$, defined by $\sum G_{products} - \sum G_{reactants}$. The Gibbs free energy of the reactants is calculated by $G_{reactants} = xG_{M_aO_bH_c^q} + (ay - xb)G_{OH^-} - ln10RTpH - \{q + [az - xc - (ay - xb)] - (ay - xb))U_{SHE}\}$, where $G_{M_aO_bH_c^q}$ is the formation energy of $M_aO_bH_c^q$. For a solid, it is calculated by $E_{M_aO_bH_c} + ZPE_{M_aO_bH_c} - (S - C_p)T$. ST is the entropy contribution and C_p is the heat capacity at constant pressure. C_p is usually ignored or replaced by C_v as its contribution is relative small. $G_{OH^-} = G_{H_2O} - G_{H+}$ as $H_2O \longleftrightarrow OH^- + H^+$, $\Delta G = 0$ at pH=0 and U=0. There is an alternative method, which uses H_2O rather than OH^-. Due to the chemical potential of Oxygen is very difficult to obtain a correct value.[1] Here, we use an experiment fact that G(H_2O)=2.46eV, then the chemical potential of Oxygen can be calculated by $\mu_O = (E + ZPE - ST)_{H_2O} + 2.46\ eV - 2\mu_H$. This chemical potential must be used to calculate the formation energy of compounds. Please keep in mind that the coefficient of reactants may be very large, a small error in the calculation of μ_O may introduce a significant error. The balance of charge has to take the charges of OH^- and H^- into consideration. If we divide the equation by a, then we can get the reaction heat per formula. The compound, which produces the highest reaction heat per formula is the most stable phase. We also can sort the meta-stable phase by their energies.

Let's take the Ni-H_2O system as an example. The reference compound is defined as $Ni_6O_{12}H_{24}$. 6, 12 and 24 are the least common multiples of the coefficients of Ni, O and H in all phases. The product of all reactions is $Ni_6O_{12}H_{24}$, then the reaction heat can be directly compared. I wrote a small program to plot the Pourbaix diagram. It require the input of Gibbs free energy of H,H_2O, and compounds. See the attached ni.in. The first row is a comment line, The 2nd-4th row must be information of H_2, O_2, and H_2O. You may change the sequence. The 5th line must be the metal element data. After that, are profiles of other compounds. The first column is the name of compounds, its length is limited by 9 characters. It just a name, you may use number 1-9 to replace it. Columns from 2nd to 5th are the number of metal, Oxygen, Hydrogen, and electrons per formula. The last column is the chemical potential of elements, or Gibbs free energies(E+ZPE-ST) of water and compounds. Please note that, last column is not the formation energy of compounds.



```
Chemical    N_NI  N_O  N_H    N_ELECT G
H2          0     0     1     0       -3.844
O2          0     1     0     0       -7.343
H2O         0     1     2     0       -17.385
ni          1     0     0     0       -6.974
nio         1     1     0     0       -16.691
ni3o4       3     4     0     0       -56.892
ni2o3       2     3     0     0       -38.848
nio2        1     2     0     0       -23.071
niooh       1     2     1     0       -28.983
nio2h2      1     2     2     0       -34.291
NI2+        1     0     0     -2       -0.48
NI(OH)4^2- 1     4     4     2       -7.71
NI(OH)3^1- 1     3     3     1       -6.08
NI(OH)^1+  1     1     1     -1       -2.36
```

```
yzhou@p002:~/Yandex.Disk/coding/pourbaix$ ./pbx.exe ni.in 14
 read input finished
 calculate formation energy
  M Eform:   -6.97399998
  O Eform:   -7.23699999
  H Eform:   -3.84400010
          4  Eform:    0.00000000
          5  Eform:   -2.48000002
          6  Eform:   -7.02199745
          7  Eform:   -3.18899918
          8  Eform:   -1.62300014
          9  Eform:   -3.69099879
         10  Eform:   -5.15500116
         11  Eform:  -0.479999989
         12  Eform:   -7.71000004
         13  Eform:   -6.07999992
         14  Eform:   -2.35999990
 calculation the reference compound, this formula is meaningless
 numrefNi, O, H, Elect:           6          12          24           0
  4  1  0  0     12.000      0.000      0.000      0.000     29.520    -29.520
  5  1  1  0      6.000     12.000    -12.000    -14.880     14.760    -29.640
  6  3  4  0      4.000     16.000    -16.000    -14.044      9.840    -23.884
  7  2  3  0      3.000     18.000    -18.000     -9.567      7.380    -16.947
  8  1  2  0      0.000     24.000    -24.000     -9.738      0.000     -9.738
  9  1  2  1      0.000     18.000    -18.000    -22.146      0.000    -22.146
 10  1  2  2      0.000     12.000    -12.000    -30.930      0.000    -30.930
 11  1  0  0     12.000      0.000    -12.000     -2.880     29.520    -32.400
 12  1  4  4    -12.000     24.000    -12.000    -46.260    -29.520    -16.740
 13  1  3  3     -6.000     18.000    -12.000    -36.480    -14.760    -21.720
 14  1  1  1      6.000      6.000    -12.000    -14.160     14.760    -28.920
yzhou@p002:~/Yandex.Disk/coding/pourbaix$ 
```

Figure 1: Input file and screen output.

Run it with command “pbx.exe ni.ni 14”, where, “ni.in” is the name of input file, and 14 is the number of data in the input file. It gives the formation energies of compounds after “Eform”, number of element in the reference compound, and their difference between this compound and the reference compound and the reaction heat at pH=0 and Ushe=0. The code will outputs three files: “ni.out” and “nil.dat”. The 3D or Contour plot data is written in “ni.out”. “nil.dat” is data of phase boundary lines.“ni.gnuplot” and “nil.gnuplot”, are gunplot scripts, which plot the Contour Pourbaix diagram and the boundary of phases. You can plot the Pourbaix diagram use the command “gnuplot ni.gnulopt”.

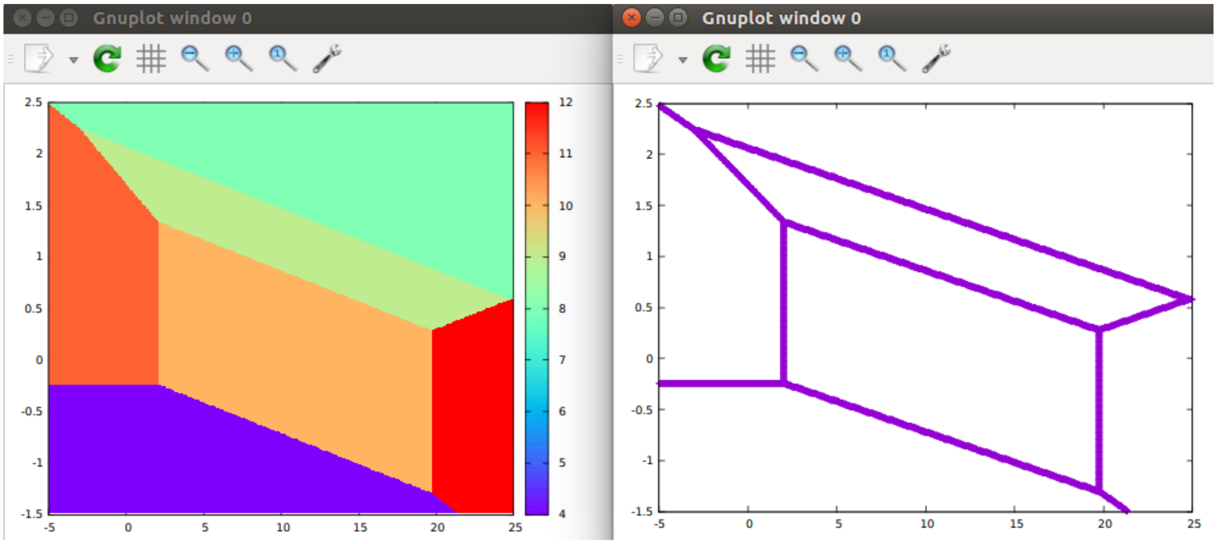


Figure 2: Left and right are figures produced by “gnuplot ni.gnulopt” and “gnuplot nil.gnulopt”, respectively.

References

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