

An universal method to plot Pourbaix diagram

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Pourbaix diagram is the phase diagram in electrochemical analysis, which shows the most stable phase under certain pH and applied potential. In a Pourbaix diagram each boundary line is a chemical reaction between different 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 have to pay large mount of labor. The considered reaction is propotional to n^2 , where n the number of phases. Here, I show a simple method by consider 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.

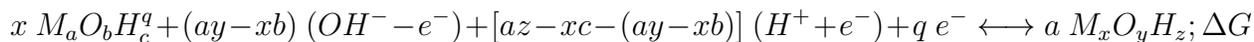
In 2012, Persson et al. developed a computational method to predict the Pourbaix diagram by comparing the defining enthalpy of each phase, which can be calculated from first-principles calculations.¹ This method has been widely used,²⁻⁶ including the Materials Project. Shortly, Huang and Zeng et al. corrected this method with zero point energy(ZPE),³⁻⁵ as in 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 energy change of all possible chemical reactions between each two phases has to be calculated. For a metal with phases number of n , the number of reaction is C_n^2 . For example, for Ni-water system, possible phases include NiO, NiO₂, Ni₂O₃,

Ni_3O_4 , $\text{Ni}(\text{OH})_2$, NiOOH , Ni^{2+} , $\text{Ni}(\text{OH})_4^{2-}$, $\text{Ni}(\text{OH})_3^{1-}$, $\text{Ni}(\text{OH})^+$, and Ni . The number of phase is 11, then more than 100 reaction have to be calculated. Although we can ignore some unreasonable reactions base on our experience, we still have to calculate about 30 chemical reactions. By 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 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 simpler method, which is less elaborative and 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 $\text{H}_2\text{O} \longleftrightarrow \text{OH}^- + \text{H}^+$ at $U=0$ and $\text{pH}=0$. The first step is to define a reference compound, which should include all elements, for example, $\text{M}_x\text{O}_y\text{H}_z$. But this compound is just a imaginary compound, it may not exist. Then we calculate the free energy change of the reactions between this reference compound and all 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, it is B. This is the definition used to make a Pourbaix diagram. 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 $\Delta G_{AC} - \Delta G_{BC}$. 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 $\text{M}_x\text{O}_y\text{H}_z$ is the product, and other phases are reactants. Take $\text{M}_a\text{O}_b\text{H}_c$ as an example.



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 $\sum G_{right} - \sum G_{left}$. The Gibbs free energy of the left side is calculated by $G_{left} = xG_{M_aO_bH_c^q} + (ay - xb)G_{OH^-} - \ln 10 RT pH - \{q + [az - xc - (ay - xb)] - (ay - xb)U_{SHE}\}$, 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 $H_2O \leftrightarrow OH^- + H^+$, $\Delta G = 0$ at $pH=0$ and $U=0$. There is an alternative method, which uses H_2O rather than OH^- . But due to the chemical potential of O is very difficult obtain a correct value.¹ Here, we use an experiment fact that $G(H_2O)=2.46eV$, then the chemical potential of O 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 compound. Please keep in mind that the coefficient of reactants may be very large, a small error in the calculation of μ_O may induce significant error. The balance of charge has to take the electrons of the 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. The products of all reaction is $Ni_6O_{12}H_{24}$, 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. After that, are profiles of 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.

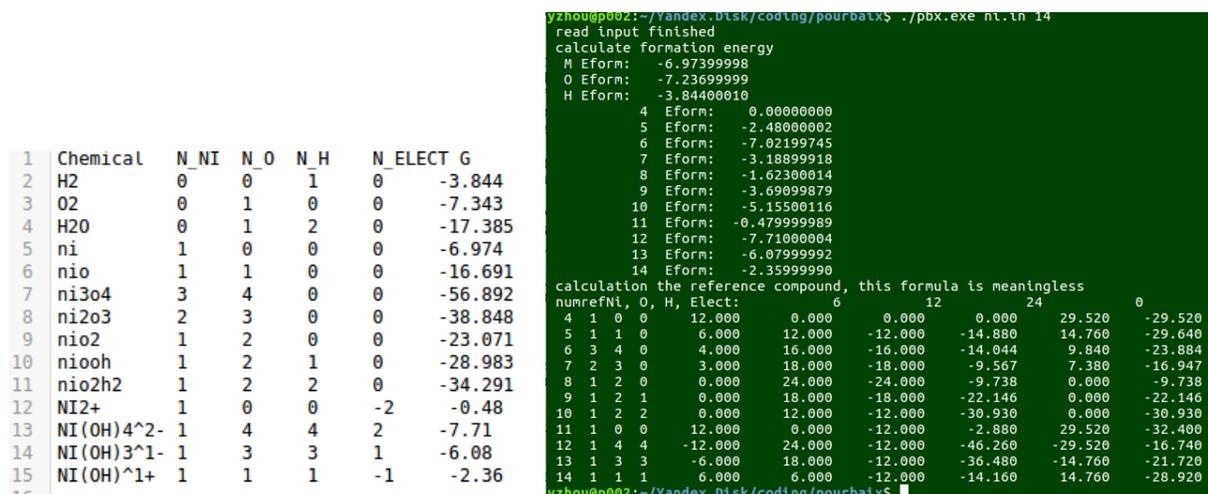


Figure 1: Input file and screen output.

Run it with command “pbx.exe ni.in 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 $U_{she}=0$. 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 gnuplot scripts, which plot the Contour Pourbaix diagram and the boundary of phases. You can plot the Pourbaix diagram use the command “gnuplot ni.gnuplot”.

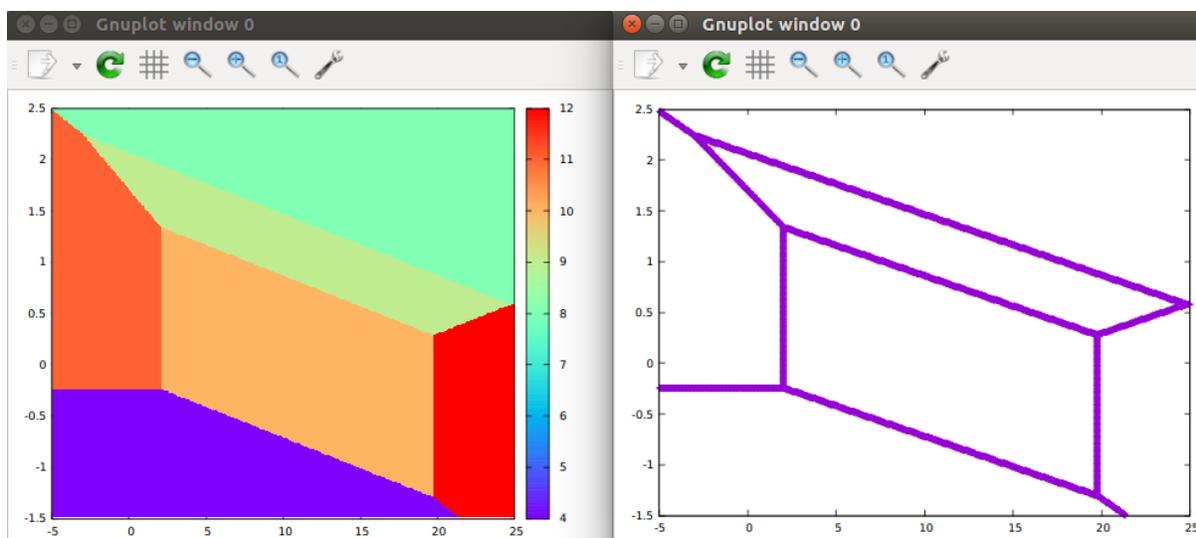


Figure 2: Left and right are figures produced by “gnuplot ni.gnulopt” and “gnuplot nil.gnulopt”, respectively.

References

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