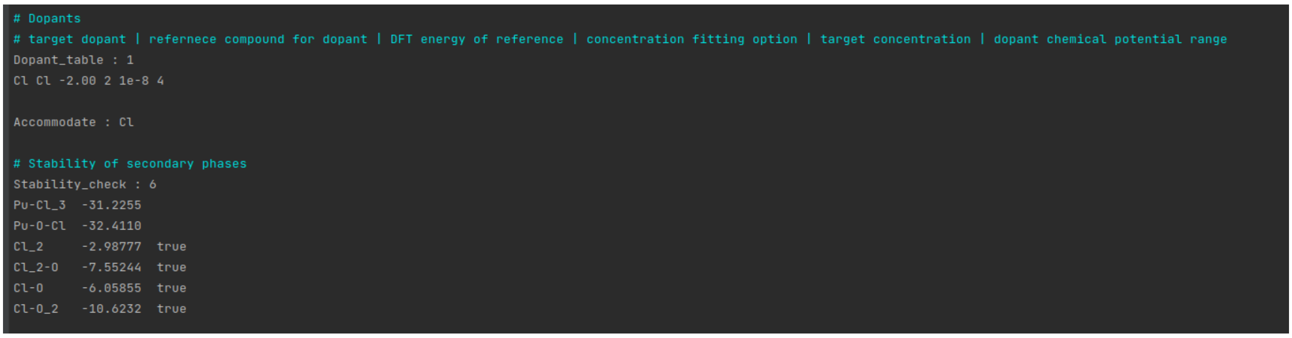
DefAP Change-log

PyroMat Thermodynamic Library

- PyroMat is a python thermodynamic library. This library can calculate the temperature contributions to gas chemical potentials

- For the chemical potential methods “volatile” and “volatile-rich-poor”, PyroMat can be called with real_gas = 3

- For secondary phases under “stability_check” , PyroMat can be called by adding the tag “true” after the energy supplied. Default is “false” if no tag is specified



```
# Dopants
# target dopant | refernece compound for dopant | DFT energy of reference | concentration fitting option | target concentration | dopant chemical potential range
Dopant_table : 1
Cl Cl -2.00 2 1e-8 4

Accommodate : Cl

# Stability of secondary phases
Stability_check : 6
Pu-Cl_3   -31.2255
Pu-O-Cl   -32.4110
Cl_2      -2.98777  true
Cl_2-O    -7.55244  true
Cl-O      -6.05855  true
Cl-O_2    -10.6232  true
```

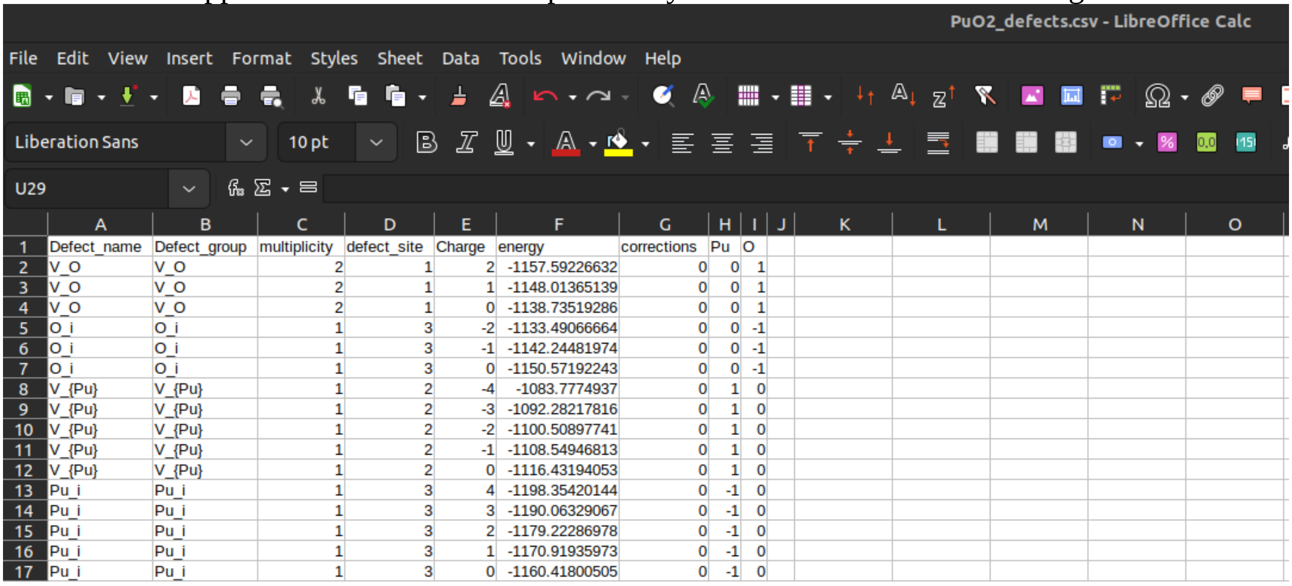
- Note: Setting “true” to include temperature contributions on any secondary phase will set real_gas=3 automatically

Input files

- Added ability to input .defects, .gibbs and .entropy files as csv files. These are named as _defects.csv, _gibbs.csv and _entropy.csv, respectively. Old file formats are still supported.

- _gibbs.csv and _entropy.csv are inputted in the same format as before

- _defects.csv requires a header row before inputting defect data. Header names are arbitrary but the columns must appear in the same order as previously. .defects file format is unchanged



	A	B	C	D	E	F	G	H	I
1	Defect_name	Defect_group	multiplicity	defect_site	Charge	energy	corrections	Pu	O
2	V_O	V_O	2	1	2	-1157.59226632	0	0	1
3	V_O	V_O	2	1	1	-1148.01365139	0	0	1
4	V_O	V_O	2	1	0	-1138.73519286	0	0	1
5	O_i	O_i	1	3	-2	-1133.49066664	0	0	-1
6	O_i	O_i	1	3	-1	-1142.24481974	0	0	-1
7	O_i	O_i	1	3	0	-1150.57192243	0	0	-1
8	V_{Pu}	V_{Pu}	1	2	-4	-1083.7774937	0	1	0
9	V_{Pu}	V_{Pu}	1	2	-3	-1092.28217816	0	1	0
10	V_{Pu}	V_{Pu}	1	2	-2	-1100.50897741	0	1	0
11	V_{Pu}	V_{Pu}	1	2	-1	-1108.54946813	0	1	0
12	V_{Pu}	V_{Pu}	1	2	0	-1116.43194053	0	1	0
13	Pu_i	Pu_i	1	3	4	-1198.35420144	0	-1	0
14	Pu_i	Pu_i	1	3	3	-1190.06329067	0	-1	0
15	Pu_i	Pu_i	1	3	2	-1179.22286978	0	-1	0
16	Pu_i	Pu_i	1	3	1	-1170.91935973	0	-1	0
17	Pu_i	Pu_i	1	3	0	-1160.41800505	0	-1	0

chem_pot_method: volatile

- There are 4 methods for calculating the standard chemical potential of a volatile species in a binary host compound:

- **“volatile”**:
- Classic formulation in DefAP using the method of Finnis et al. The method uses the standard formation energy of the compound, and the DFT energies of the compound and the metal element

$$\Delta G_{\mathrm{f}}^{\mathrm{M}_\alpha \mathrm{V}_\beta}(P^{\circ}_{\mathrm{V}_2}, T^{\circ}) = \mu^{\mathrm{DFT}}_{\mathrm{M}_\alpha \mathrm{V}_{\beta(\mathrm{s})}} - \alpha \mu^{\mathrm{DFT}}_{\mathrm{M}_{(\mathrm{s})}} - \beta \mu_{\mathrm{V}}(P^{\circ}_{\mathrm{V}_2}, T^{\circ})$$

- **“volatile-stoic”**:
- New method that fits the chemical potential of the volatile species to the reaction energy of two volatile-containing compounds in different stoichiometric ratios.
- For the reaction:

$$x\,\mathrm{M}_\alpha \mathrm{V}_\beta + \frac{1}{2}\mathrm{V}_2 \rightarrow y\,\mathrm{M}_\delta \mathrm{V}_\omega$$

where the stoichiometry balances by:

$$x\alpha = y\delta$$
$$x\beta + 1 = y\omega$$

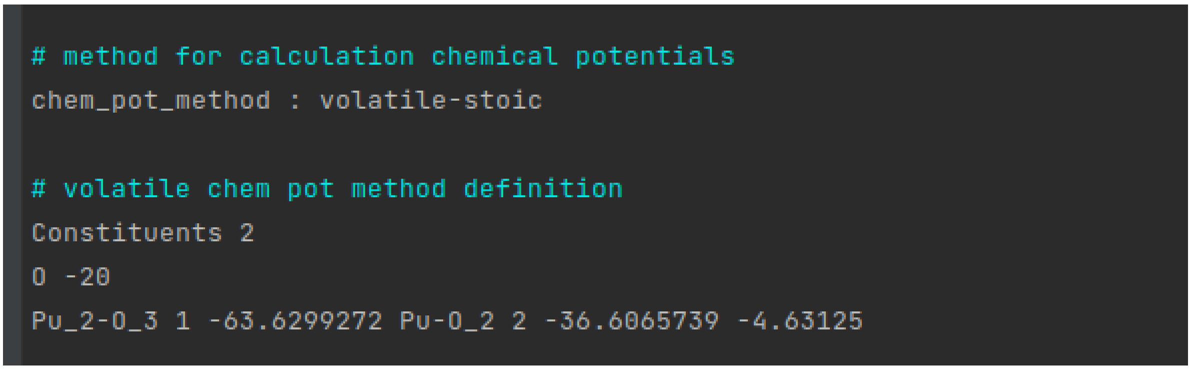
As DFT and experimental formation energies should be approximately equal, we can fit the standard chemical potential of the volatile to the following equation:

$$\Delta G^{\mathrm{exp}}_{\mathrm{r}} = y\,\mu^{\mathrm{DFT}}_{\mathrm{M}_\delta \mathrm{V}_\omega} - x\,\mu^{\mathrm{DFT}}_{\mathrm{M}_\alpha \mathrm{V}_\beta} - \frac{1}{2}\mu^{o}_{\mathrm{V}_2}$$

- This method is recommended for materials studied with DFT+*U*, where the classic method may incur errors due to differing *U* parameters between the compound and the metal element.

- In DefAP, this method can be called for the following example reaction:

$$\mathrm{Pu}_2\mathrm{O}_3 + \frac{1}{2}\mathrm{O}_2 \rightarrow 2\,\mathrm{Pu}\mathrm{O}_2$$



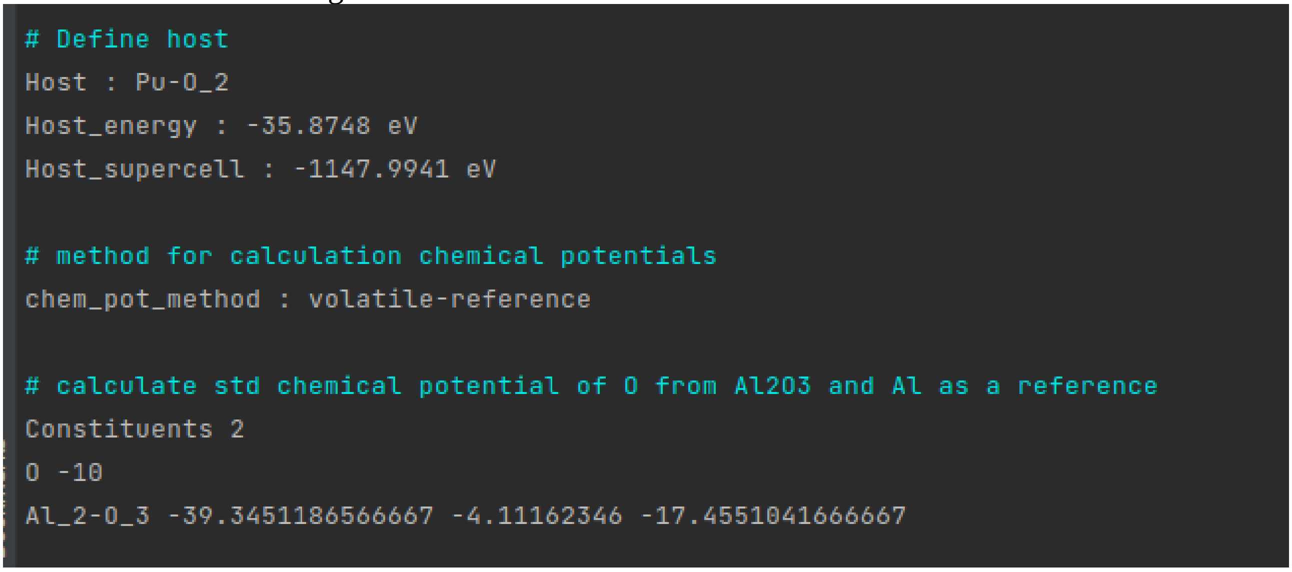
```
# method for calculation chemical potentials
chem_pot_method : volatile-stoic

# volatile chem pot method definition
Constituents 2
O -20
Pu_2-O_3 1 -63.6299272 Pu-O_2 2 -36.6065739 -4.63125
```

- Row 2 in the constituents is defined with seven elements as:

$$\mathrm{M}_\alpha \mathrm{V}_\beta \quad x \quad \mu^{\mathrm{DFT}}_{\mathrm{M}_\alpha \mathrm{V}_\beta} \quad \mathrm{M}_\delta \mathrm{V}_\omega \quad y \quad \mu^{\mathrm{DFT}}_{\mathrm{M}_\delta \mathrm{V}_\omega} \quad \Delta G^{\mathrm{exp}}_{\mathrm{r}}$$

- The chemical potential of the metal element in the host can then calculated from the host DFT energy and the volatile chemical potential under desired conditions

- **“volatile-reference”**:
- The same method as the classic formulation, however, the standard chemical potential of the volatile is calculated using another reference material



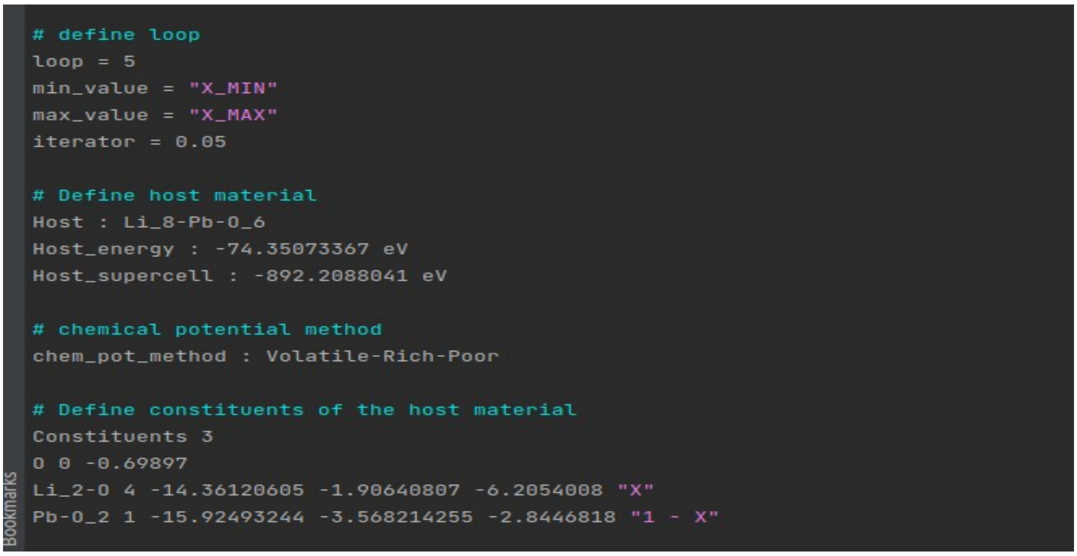
```
# Define host
Host : Pu-O_2
Host_energy : -35.8748 eV
Host_supercell : -1147.9941 eV

# method for calculation chemical potentials
chem_pot_method : volatile-reference

# calculate std chemical potential of O from Al2O3 and Al as a reference
Constituents 2
O -10
Al_2-O_3 -39.3451186566667 -4.11162346 -17.4551041666667
```

- The chemical potential of the metal element in the host can then calculated from the host DFT energy and the volatile chemical potential under desired conditions
- This method is recommended for materials studied with DFT+*U* but also do not have many well-defined compounds with different stoichiometric ratios of the volatile component
- Recommended reference materials for GGA are: Li_2O, MgO and Al_2O_3

- “volatile-rich-poor” chem_pot_method only has the classic implementation at present

<u>loop = 5</u>

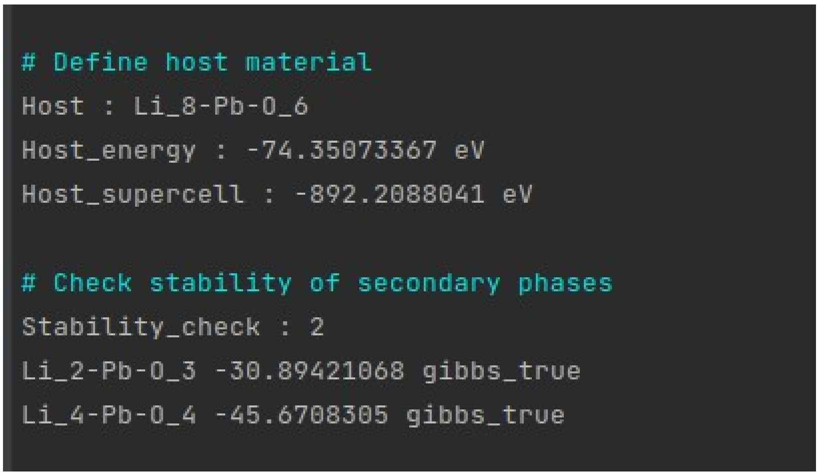
- New function to loop over the rich-poor fraction of the constituents in the host
- Only available for “rich-poor” and “volatile-rich-poor” chem_pot_methods
- Only available when there are two constituents that make up the host
- Loop = 5 loops over the rich-poor fraction of the first constituent defined, as shown below:



```
# define loop
loop = 5
min_value = "X_MIN"
max_value = "X_MAX"
iterator = 0.05

# Define host material
Host : Li_8-Pb-O_6
Host_energy : -74.35073367 eV
Host_supercell : -892.2088041 eV

# chemical potential method
chem_pot_method : Volatile-Rich-Poor

# Define constituents of the host material
Constituents 3
O 0 -0.69897
Li_2-O 4 -14.36120605 -1.90640807 -6.2054008 "X"
Pb-O_2 1 -15.92493244 -3.568214255 -2.8446818 "1 - X"
```

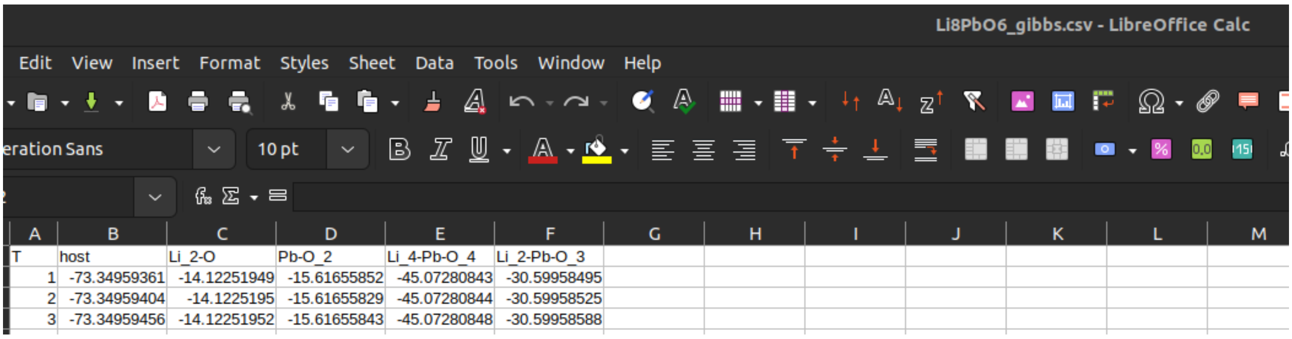
Stability_check and Gibbs functions

- The energies of secondary phases can also be provided by the gibbs energy functions
- This is called by adding the “gibbs_true” tag in the stability_check input



```
# Define host material
Host : Li_8-Pb-O_6
Host_energy : -74.35073367 eV
Host_supercell : -892.2088041 eV

# Check stability of secondary phases
Stability_check : 2
Li_2-Pb-O_3 -30.89421068 gibbs_true
Li_4-Pb-O_4 -45.6708305 gibbs_true
```

- Remember to add a column for each secondary phase in the _gibbs.csv or .gibbs file



Li8PbO6_gibbs.csv - LibreOffice Calc
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eration Sans
10 pt

A	B	C	D	E	F
T	host	Li_2-O	Pb-O_2	Li_4-Pb-O_4	Li_2-Pb-O_3
1	-73.34959361	-14.12251949	-15.61655852	-45.07280843	-30.59958495
2	-73.34959404	-14.1225195	-15.61655829	-45.07280844	-30.59958525
3	-73.34959456	-14.12251952	-15.61655843	-45.07280848	-30.59958588

Performance

- Improved the performance of the linear bisection solver when determining chemical potentials with a single dopant by removing redundant for-loops

- Improved the performance when calculating the concentrations of electrons and/or holes with the “fermi-dirac” method, by reading the .dos file once before executing any task rather than during every loop cycle

- Rewritten “calc_chemical_volatile”, “calc_chemical_volatile_rich_poor” and “defect_energies” to reduce the number of loops

Miscellaneous

- .input file parameters are no longer case sensitive (except element symbols)

- Added more error messages for improper defined input parameters

- Converted exit() calls on error messages to “raise Exception”. Aids user self-diagnostics on error messages by pointing to the exact line the program failed

- Fixed the Gibbs energy function for calculating chemical potentials

- Split the “temperature_cont” function into 3 functions to reduce repeated code and improve clarity

- Added “pressure_contribution” function to calculate pressure contribution to volatile chemical potentials (reduces repeated code)

- Added ability to plot defect_phase task as a function of two dopant concentrations

- Added a progress bar for the y-axis loop in the defect_phase tasks

- Output files from defect_phase and dopant tasks are now stored in separate directories

- Removed the redundant “phases” task from the code

- Moved the main body of the code into a main() function and call it with “if __name__==’__main__’”

- Added a warning for using real_gas = 2 (Johnston et al) due to refitting of the parameters used since publication

- Modified the print out of “stability_check” to improve clarity on when secondary phases are indicated to be thermodynamically stable