

# SOP4chem – simplex optimization procedure for chemistry

[Matthew.Lewis@gmail.com](mailto:Matthew.Lewis@gmail.com)



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# Simplex optimization of chemical systems

C. L. Shavers, M. L. Parsons, and S. N. Deming

**Cite this:** *J. Chem. Educ.* 1979, 56, 5, 307

Publication Date: May 1, 1979 ▾

<https://doi.org/10.1021/ed056p307>

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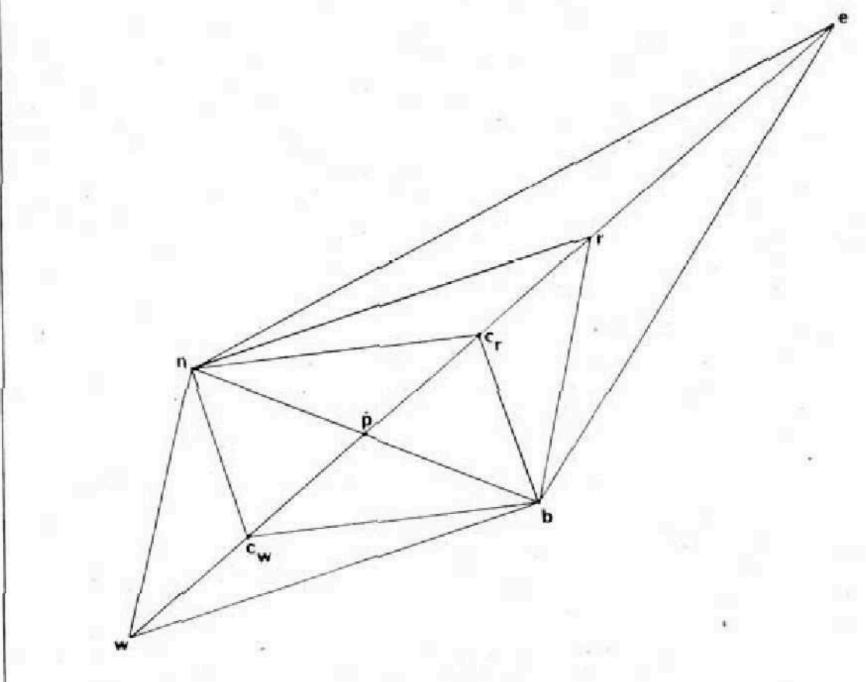


Figure 1. Possible moves in a modified simplex method.

by varying all factors (variables) simultaneously. The rules of the simplex algorithm are presented here for completeness. More detailed discussions may be found in the literature (1-4, 6, 9, 10).

#### Simplex Rules

The variable size simplex method of Nelder and Mead (2) is a logical algorithm consisting of reflection, expansion, and contraction rules. These rules can be understood by referring to the two-dimensional example shown in Figure 1. The algorithm can be used with any number of dimensions.

A simplex is a geometric figure defined by a number of points ( $n + 1$ ) equal to one more than the number of variables (dimensions). In the initial simplex  $BNW$  shown in Figure 1, Vertex  $B$  was measured and found to have the best response,  $W$  the worst response, and  $N$  the next-to-the-worst response.  $\bar{P}$  is the centroid of the face remaining when the worst vertex is eliminated (6).

Reflection is accomplished by extending the line segment  $WP$  beyond  $P$  to generate the new vertex  $R$  (i.e., a new set of experimental conditions)

$$R = \bar{P} + (\bar{P} - W) \quad (1)$$

Three possibilities exist for the measured response at  $R$ .

- 1) The response at  $R$  is more desirable than the response at  $B$ . An attempted expansion is indicated and the new vertex  $E$  is generated:

$$E = \bar{P} + 2(\bar{P} - W) \quad (2)$$

If the response at  $E$  is better than the response at  $B$ ,  $E$  is retained and the new simplex is  $NBE$ . If the response at  $E$  is not better than at  $B$ , the expansion is said to have failed and  $BNR$  is taken as the new simplex. The algorithm is restarted using the new simplex.

- 2) If the response at  $R$  is between that of  $B$  and  $N$ , neither ex-

pansion nor contraction is recommended and the process is restarted with the new simplex  $BNR$ .

- 3) If the response at  $R$  is less desirable than the response at  $N$ , a step in the wrong direction has been made and the simplex should be contracted. One of two possible vertices must be generated:

- a) If the response at  $R$  is worse than the response at  $N$  but not worse than that at  $W$ , the new vertex should lie closer to  $R$  than to  $W$ :

$$C_r = \bar{P} + 0.5(\bar{P} - W) \quad (3)$$

The process is restarted with the new simplex  $BNR$ .

- b) If the response at  $R$  is worse than the response at  $W$ , then the new vertex should lie closer to  $W$  than to  $R$ :

$$C_w = \bar{P} - 0.5(\bar{P} - W) \quad (4)$$

The process is restarted with the new simplex  $BNR$ .

False high results caused by experimental error which might mislead the simplex can be detected and corrected if the response of a vertex appearing in  $n + 1$  successive simplexes is reevaluated (1). The average response can be taken as the response of reevaluated vertices.

If a vertex lies outside the boundaries of one or more of the factors (variables), a very undesirable response is assigned to that vertex. The simplex will then be forced back inside the boundaries.

Calculations are simplified if a worksheet such as the one shown in Figure 2 is used (22).

#### Experimental

A simple method for introducing the application of simplex optimization to chemical systems is a modification of a vanadium spot test (23). The procedure involves the addition of varying amounts (number of drops) of hydrogen peroxide solution and sulfuric acid solution to a standard amount (number of drops) of a sample of fixed vanadium concentration. After a sufficient time has elapsed, absorbance is

These rules are implemented. Additionally, if boundary constraints are employed and a pivot vertex is outside the allowable range, rule 3a is applied repeatedly until pivot vertex is valid.

# Input files

- CSV file with initial experiments and ‘scores’/utility values
- First column must be labeled ‘iteration’
- Followed by 2 or more columns with experimental parameters and arbitrary labels
- Last column must be labeled ‘score’

```
iteration,KeV,center,width,score
1.0,40.0,50.0,380.0,4.2
2.0,50.0,100.0,250.0,3.4
3.0,60.0,290.0,570.0,1.3
4.0,70.0,150.0,350.0,2.1
26.02.23.csv (END)
```

Additional number of rows should be one greater than number of experimental variables to properly define simplex. If there are additional rows, extra rows at the top will be ignored.

# Input files

- All experimental parameters can be optionally constrained using a second CSV file
- First column must be labeled ‘bound’ and rows must be labeled ‘U’ and ‘L’ for upper and lower bounds.
- Experimental parameters must be in same order as data input CSV.

```
<U+FEFF>bound,KeV,center,width  
U,100.,999999.,999999.  
L,30.,0.,0.  
bounds.csv (END)
```

Unicode encoding character at start of file can be safely ignored. Partial constraints are not supported. Use large magnitude numbers to simulate one-sided bounds.

```
[bash-3.2$ python SOP4chem.py --help  
usage: SOP4chem.py [OPTION] [FILE]
```

Generate next experimental parameters via simplex optimization procedure. CSV file is updated each time. Note: iterations will become sorted due to simplex progression. <https://pubs.acs.org/doi/10.1021/ed056p307>

**positional arguments:**

**file** CSV file containing history of experimental parameters.  
Format of column labels should be: iteration, 2 or more experimental parameter labels, score.

**optional arguments:**

**-h, --help** show this help message and exit  
**-v, --version** show program's version number and exit  
**-bounds BOUNDS** Optional CSV file with bounds for experimental parameters.  
Format of column labels should be: bound, same experimental parameter labels as ordered in data CSV file. Row labels should be: U, L for upper and lower bounds respectively.  
Defaults to NoneType.

```
bash-3.2$ █
```

```
[bash-3.2$ python SOP4chem.py 26.02.23.csv -bounds=bounds.csv
    bound      KeV     center      width
0       U   100.0  999999.0  999999.0
1       L    30.0      0.0      0.0
    iteration      KeV     center      width      score
2            3.0    60.0    290.0    570.0      1.3
3            4.0    70.0    150.0    350.0      2.1
1            2.0    50.0    100.0    250.0      3.4
0            1.0    40.0      50.0    380.0      4.2
4            5.0    50.0      5.0    205.0 -99999.0
Please perform the experiment in the latest iteration above.
Then re-run this program and enter new score.
```

```
bash-3.2$
```

```
[bash-3.2$ python SOP4chem.py 26.02.23.csv -bounds=bounds.csv
```

	bound	KeV	center	width	
0	U	100.0	999999.0	999999.0	
1	L	30.0	0.0	0.0	
	iteration	KeV	center	width	score
0	3.0	60.0	290.0	570.0	1.3
1	4.0	70.0	150.0	350.0	2.1
2	2.0	50.0	100.0	250.0	3.4
3	1.0	40.0	50.0	380.0	4.2
4	5.0	50.0	5.0	205.0	-99999.0

If you have performed last experiment in table above, please enter new positive score (negative value will exit program): 3.555555

	iteration	KeV	center	width	score
0	3.0	60.0	290.0	570.0	1.300000
1	4.0	70.0	150.0	350.0	2.100000
2	2.0	50.0	100.0	250.0	3.400000
4	5.0	50.0	5.0	205.0	3.555555
3	1.0	40.0	50.0	380.0	4.200000
5	6.0	35.0	2.5	242.5	-99999.000000

Please perform the experiment in the latest iteration above.

Then re-run this program and enter new score.

```
bash-3.2$ █
```

```
bash-3.2$ python SOP4chem.py 26.02.23.csv -bounds=bounds.csv
```

	bound	KeV	center	width
0	U	100.0	999999.0	999999.0
1	L	30.0	0.0	0.0

	iteration	KeV	center	width	score
0	3.0	60.0	290.0	570.0	1.300000
1	4.0	70.0	150.0	350.0	2.100000
2	2.0	50.0	100.0	250.0	3.400000
3	5.0	50.0	5.0	205.0	3.555555
4	1.0	40.0	50.0	380.0	4.200000
5	6.0	35.0	2.5	242.5	-99999.000000

If you have performed last experiment in table above, please enter new positive score (negative value will exit program): 4.3

	iteration	KeV	center	width	score
0	3.0	60.000	290.0000	570.0000	1.300000
1	4.0	70.000	150.0000	350.0000	2.100000
2	2.0	50.000	100.0000	250.0000	3.400000
3	5.0	50.000	5.0000	205.0000	3.555555
4	1.0	40.000	50.0000	380.0000	4.200000
5	6.0	35.000	2.5000	242.5000	4.300000
6	7.0	40.625	9.0625	279.0625	-99999.000000

Please perform the experiment in the latest iteration above.  
Then re-run this program and enter new score.

```
bash-3.2$
```

# Notes

- The iteration dataframe table stores the simplex values that were used in calculations.
- In some cases, the experimental parameters that you used in additional experiments will be changed in the CSV file according to the simplex rules.
- It should be easy to a create separate log file that records all experimental results if truly needed. Contact the author.