Sources of Properties and Empirical Estimation Methods

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Sources of Properties

- Literature - 1st place to look
- Experiment - Hard to do
- Ab Initio Calculations - Hard to do but not impossible
- Empirical Estimation Methods - Often good for first approximation

Literature Sources of Properties

Recall that we can always construct the fundamental relation from experimental data. There is a large body of data in the literature and much of it available in NIST data bases.

Atoms:

http://physics.nist.gov/PhysRefData/Handbook/index.html

Molecules

http://webbook.nist.gov/chemistry/

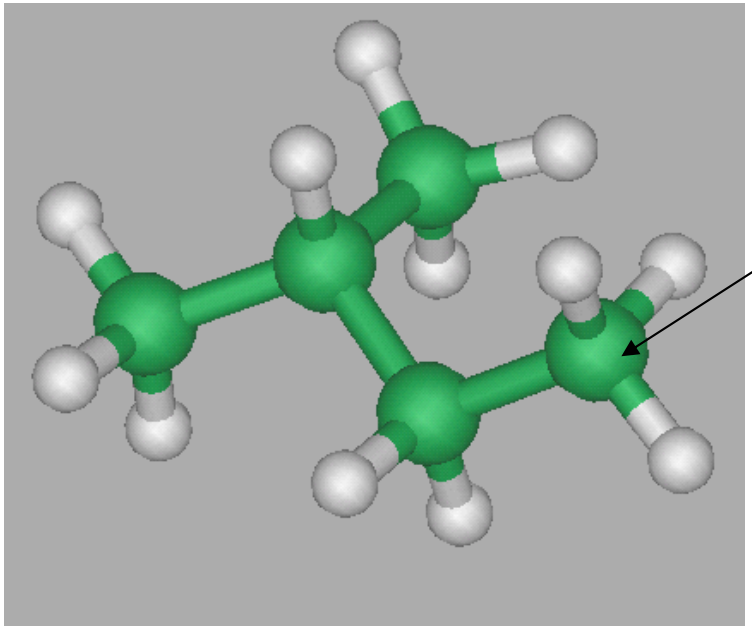
https://atct.anl.gov

Group Additivity

- What to do if no data or ab initio calculations are available.
- Based on the concept that functional groups behave similarly.
- Developed by Professor Sydney Benson of UCLA.

Method

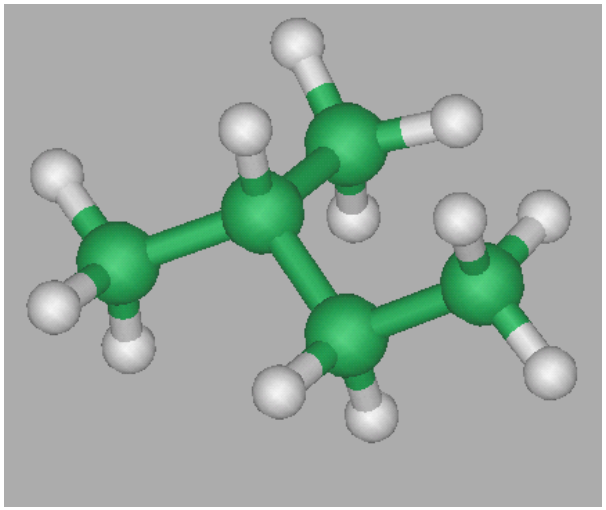
The molecule is considered to be made up of several groups. Example iso-pentane



Center is C,
Attachments are
3 H's and 1 C:
C-$(H)_3$(C)

Each heavy atom is a group. Groups are identified by the atoms they are attached to.

Isopentane also called methylbutane or 2-methylbutane is made up of:



3 C-$(H)_3(C)$
1 C-$(H)_2(C)_2$
1 C-$(H)(C)_3$

There are tables of group properties:

Group	$\Delta H_f^\circ(298)$	$S^\circ(298)$	$C_p^\circ(T)$ cal mol^{-1} K^{-1}						
	kcal mol^{-1}	cal mol^{-1} K^{-1}	300	400	500	600	800	1000	1500
C-$(H)_3(C)$	-10.08	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C-$(H)_2(C)_2$	-4.95	9.42	5.50	6.95	8.25	9.35	11.07	12.34	14.25
C-$(H)(C)_3$	-1.90	-12.07	4.54	6.00	7.17	8.05	9.31	10.05	11.17

So, we estimate the thermochemical properties of isopentane as

$\Delta H_f^\circ(298) = 3(-10.08) + (-4.95) + -1.90 = -37.1$ kcal/mol

$S^\circ(298) = 3(30.41) + 9.42 - 12.07 = 88.6$ cal/(mol K)

$C_p^\circ(300) = 3(6.19) + 5.50 + 4.54 = 28.6$ cal/(mol K), etc.

It is almost that simple. There are corrections for special situations, and for some groups there isn't any data and so the method cannot be applied.

However, there is a web based resource provided by NIST located at:

http://webbook.nist.gov/chemistry/grp-add/ga-file.html

You will need to provide a structure file (.mol). These can be drawn using special chemical drawing software (i.e. ChemDraw) or downloaded from the NIST chemistry webbook.

http://webbook.nist.gov/chemistry/

Marching Orders

1. Look for data, i.e. NIST Chemistry webbook, search literature.
2. Try group additivity.
3. Call a chemist!