New Directions in HSP Part 1 Splitting δ_D

HSPiP
Dr. Hiroshi Yamamoto

2017.4.5

H. Yamamoto, personal History

HSP Birth 1967 Elementary School first year

My first programmable electric calculator. (High school 2nd grade) 1977

MO calculation 1987 My second PC (16bit)

G3 Mac

Neural Network research 1997 I married

1St Generation of iPhone 2007 Took Dr. degree

Chemo-Informatics

2008

↓

HSPiP

HSP50 2017 :

Prime Number

Can you divide Prime Number, 2017 ?

My answer is always "depend on".

$2017 = (44 - 9i)*(44 + 9i)$

Properties Estimation depend on **Dataset**.
Hydrocarbons' Equation **applicability** for XX.

How we can serve 2017 version of Hansen Solubility Parameters?

TABLE 1.1
Group Contributions to Partial Solubility Parameters

Functional Group	Molar Volume,[a] ΔV (cm³/mol)		London Parameter, $\Delta V\,\delta_D^2$ (cal/mol)			Polar Parameter, $\Delta V\,\delta_P^2$ (cal/mol)			Electron Transfer Parameter, $\Delta V\,\delta_H^2$ (cal/mol)		Total Parameter,[a] $\Delta V\,\delta^2$ (cal/mol)	
	Aliphatic	Aromatic[b]	Alkane	Cyclo	Aromatic	Alkane	Cyclo	Aromatic	Aliphatic	Aromatic	Aliphatic	Aromatic
CH_3	33.5	Same	1,125	Same	Same	0	0	0	0	0	1,125	Same
CH_2<	16.1	Same	1,180	Same	Same	0	0	0	0	0	1,180	Same
–CH<	–1.0	Same	820	Same	Same	0	0	0	0	0	820	Same
>C<	–19.2	Same	350	Same	Same	0	0	0	0	0	350	Same
CH_2 = olefin	28.5	Same	850 ± 100	?	?	25 ± 10	?	?	180 ± 75	?	1,030	Same
–CH = olefin	13.5	Same	875 ± 100	?	?	18 ± 5	?	?	180 ± 75	?	1,030	Same
>C = olefin	–5.5	Same	800 ± 100	?	?	60 ± 10	?	?	180 ± 75	?	1,030	Same
Phenyl-	—	71.4	—	—	7,530	—	—	50 ± 25	—	50 ± 50[c]	—	7630
C-5 ring (saturated)	16	—	—	250	—	0	0	—	0	—	250	—
C-6 ring	16	Same	—	250	250	0	0	0	0	0	250	250
–F	18.0	22.0	0	0	0	1,000 ± 150	?	700 ± 100	0	0	1,000	800[b]
=F_2 twin[f]	40.0	48.0	0	0	0	700 ± 250[c]	?	500 ± 250[c]	0	0	1,700	1,360[b]
≡F_3 triplet[f]	66.0	78.0	0	0	0	?	?	?	0	0	1,650	1,315[b]
–Cl	24.0	28.0	1,400 ± 100	?	1,300 ± 100	1,250 ± 100	1,450 ± 100	800 ± 100	100 ± 20[c]	Same	2,760	2,200[b]
=Cl_2 twin[f]	52.0	60.0	3,650 ± 160	?	3,100 ± 175[c]	800 ± 150	?	400 ± 150[c]	165 ± 10[c]	180 ± 10[c]	4,600	3,670[b]
≡Cl_3 triplet[f]	81.9	73.9	4,750 ± 300[c]	?	?	300 ± 100	?	?	350 ± 250[c]	?	5,400	4,300[b]
–Br	30.0	34.0	1,950 ± 300[c]	1,500 ± 175	1,650 ± 140	1,250 ± 100	1,700 ± 150	800 ± 100	500 ± 100	500 ± 100	3,700	2,960[b]
=Br_2 twin[f]	62.0	70.0	4,300 ± 300[c]	?	3,500 ± 300[c]	800 ± 250[c]	?	400 ± 150[c]	825 ± 200[c]	800 ± 250[c]	5,900	4,700[b]
≡Br_3 triplet[f]	97.2	109.2	5,800 ± 400[c]	?	?	350 ± 150[c]	?	?	1,500 ± 300[c]	?	7,650	6,100[b]
–I	31.5	35.5	2,350 ± 250[c]	2,200 ± 250[c]	2,000 ± 250[c]	1,250 ± 100	1,350 ± 100	575 ± 100	1,000 ± 200[c]	1,000 ± 200[c]	4,550	3,600[b]
=I_2 twin[e]	66.6	74.6	5,500 ± 300[c]	?	4,200 ± 300[c]	800 ± 250[c]	?	400 ± 150[c]	1,650 ± 250[c]	1,800 ± 250[c]	8,000	6,400[b]
≡I_3 triplet[e]	111.0	123.0	?	?	?	?	?	?	?	?	11,700	9,350[b]
–O– ether	3.8	Same	0	0	0	500 ± 150	600 ± 150	450 ± 150	450 ± 25	1,200 ± 100	800	(1,650 ± 150)
>CO ketone	10.8	Same	—[e]	2,350 ± 400	2,800 ± 325	(15, 000 ± 7%)/V	1,000 ± 300	950 ± 300	800 ± 250[f]	400 ± 125[c]	4,150	Same
–CHO	(23.2)	(31.4)	950 ± 300	?	550 ± 275	2,100 ± 200	3,000 ± 500	2,750 ± 200	1,000 ± 200	750 ± 150	(4,050)	Same
–COO-ester	18.0	Same	—[f]	?	—[f]	(56,000 ± 12%)/V	?	(338,000 ± 10%)/V	1,250 ± 150	475 ± 100[c]	4,300	Same
–COOH	28.5	Same	3,350 ± 300	3,550 ± 250	3,600 ± 400	500 ± 150	300 ± 50	750 ± 350	2,750 ± 250	2,250 ± 250[c]	6,600	Same

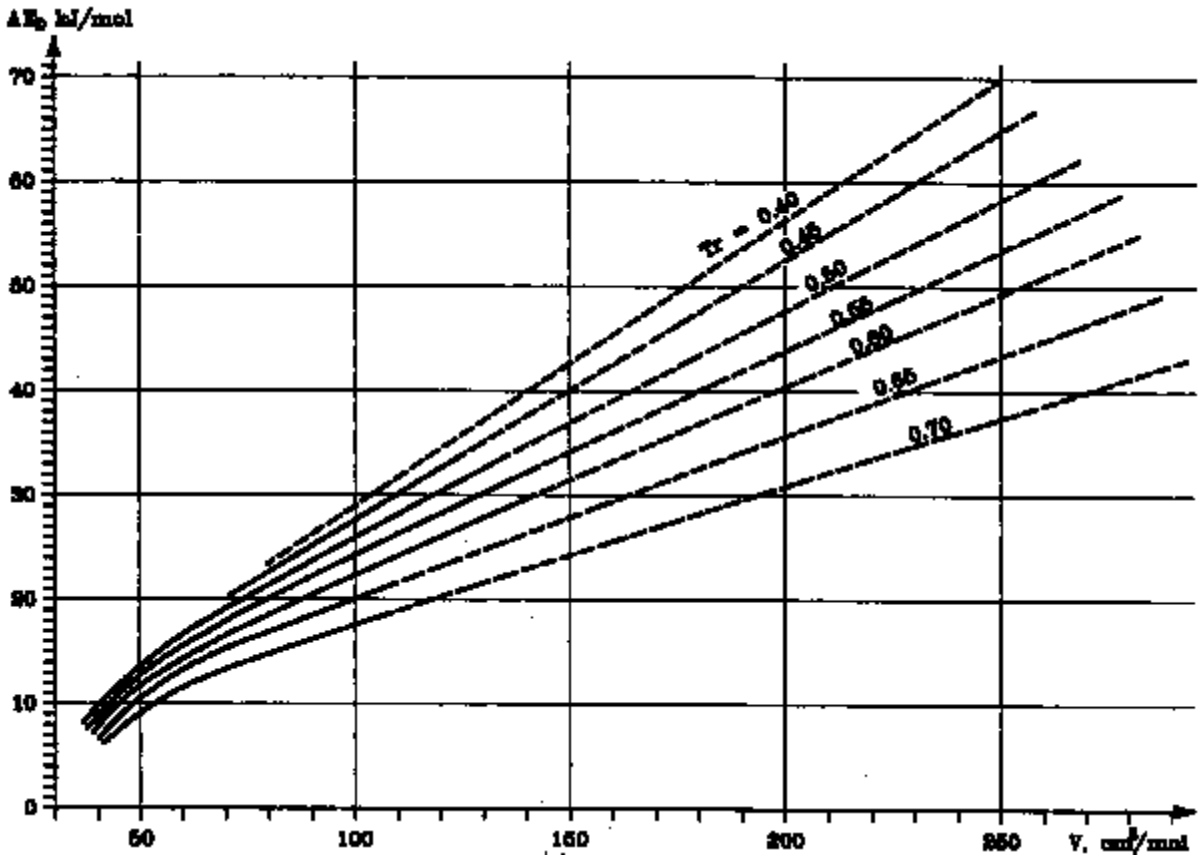
Depend on what?

CALCULATING δ_D

- HOMOMORPH CONCEPT (**E_D** = **E** FOR SIMILAR HYDROCARBON
- CORRESPONDING STATE THEORY (CST)
- CST FIGURE FOR **E_D** FOR EACH OF ALIPHATIC, CYCLOALIPHATIC, OR AROMATIC STRUCTURE

E_D versus V for $T_r = T_{298.15.}/T_{CRITICAL}$

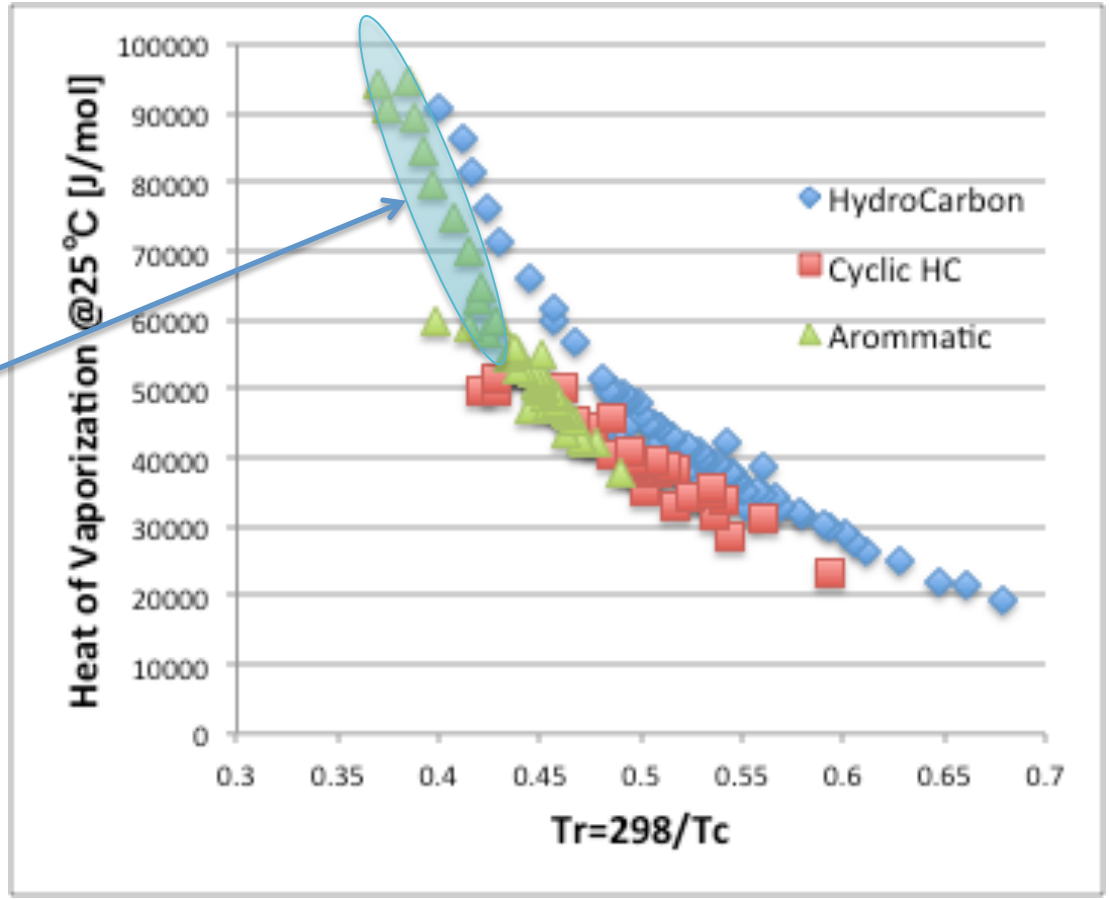
FIGURE FOR E_D FOR ALIPHATIC HYDROCARBONS



2 other charts exist for Cycloalkanes and Aromatics.

The reason why 3 charts exist

Aromatic
+
long Alkyl chain



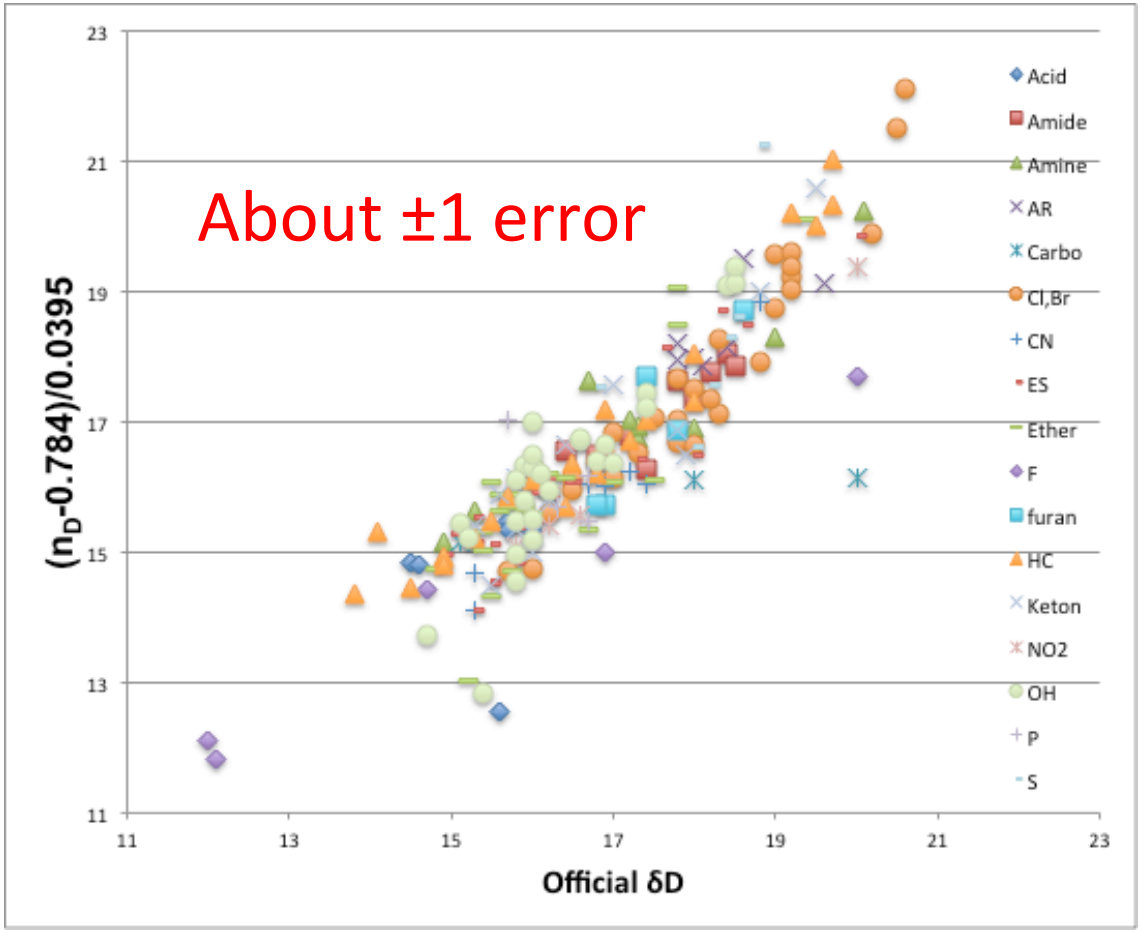
Different curves between Tr and H_V

We can't apply Chart Method for more complicated molecules.

CALCULATING δ_D in HSPiP

$$\delta_D = (n_D - 0.784)/0.0395$$

n_D: Refractive Index



δ_P - Final Result

Adjusted from Trial and Error Values

Böttcher Equation, cal/cm^3

$$\delta_P^2 = \frac{12108}{V^2}\frac{\varepsilon - 1}{2\varepsilon + n_D^2}\left(n_D^2 + 2\right)\mu^2$$

When constants not available

Beerbower Equation, MPa^{½}

$$\delta_P = 37.4(\mu)/V^{½}$$

Later Functional Group Contributions

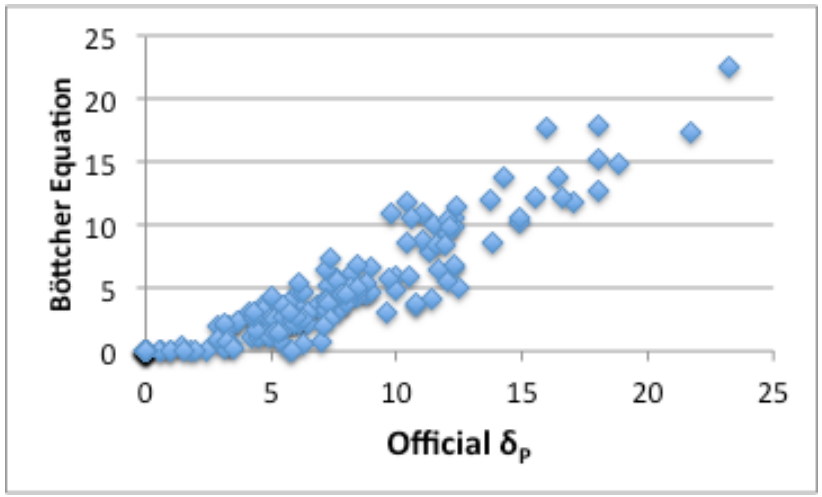
Evaluation of δ_P

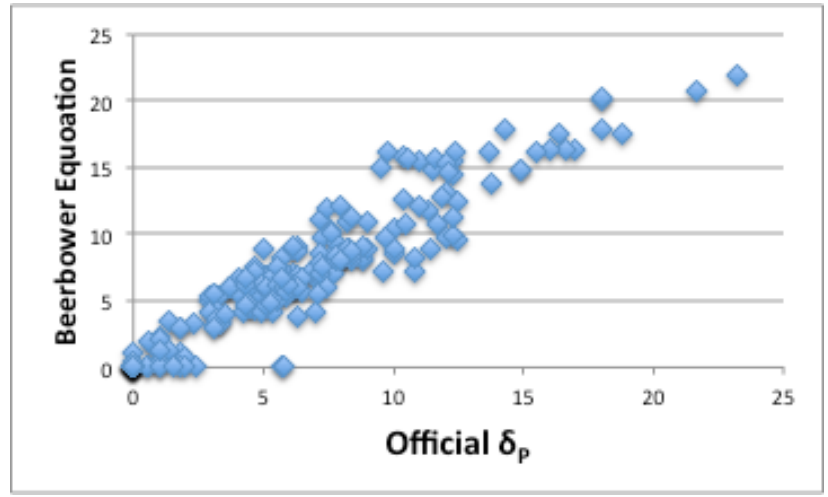
Böttcher Equation

$$\delta_P^2 = \frac{12108}{V^2}\frac{\varepsilon - 1}{2\varepsilon + n_D^2}\left(n_D^2 + 2\right)\mu^2$$

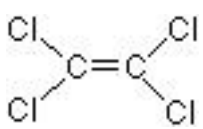
Beerbower Equation

$$\delta_P = 37.4(\mu)/V^{1/2}$$





If the Dipole Moment (μ) is very small δ_P become 0

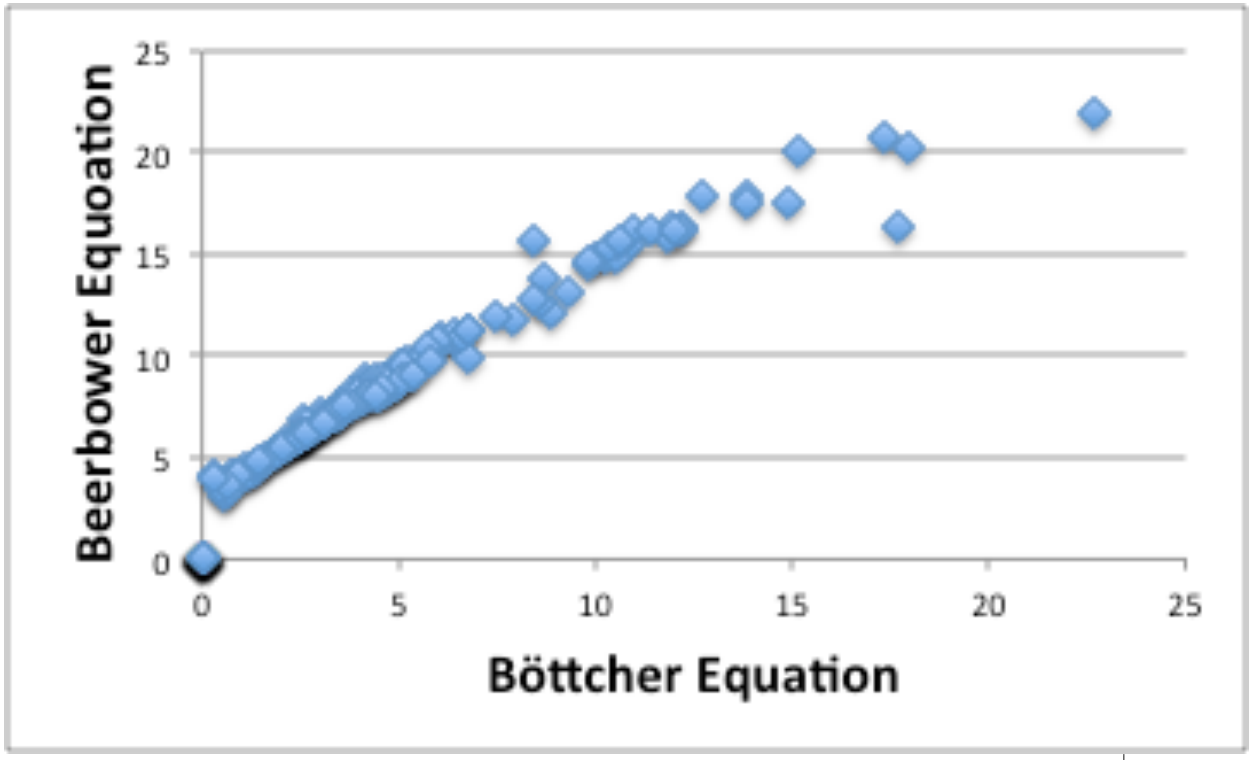


$\mu=0$ $\varepsilon=2.52$ $\delta_P=11.8$

$\mu=0$ $\varepsilon=2.3$ $\delta_P=5.7$

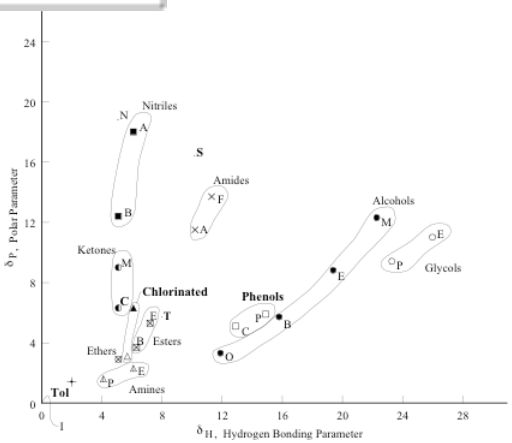
symmetrical molecules Problem

Comparison of 2 Equations



δ_P(Beerbower) = δ_P(Böttcher) + 3.5

For symmetrical molecules, Hansen determined them by hand via analogy.



δ_H – Final Result (What was left over)

$$E_H = E_T - E_D - E_P$$

$$\delta_H = (E_H/V)^{1/2}$$

CHECK where possible that:

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

Later Functional Group Contributions for E_H

We need Heat of Vaporization @25°C(E_T) before calculating δ_H

CORRESPONDING STATE THEORY (CST)

Pitzer-Carruth-Kobayashi Method

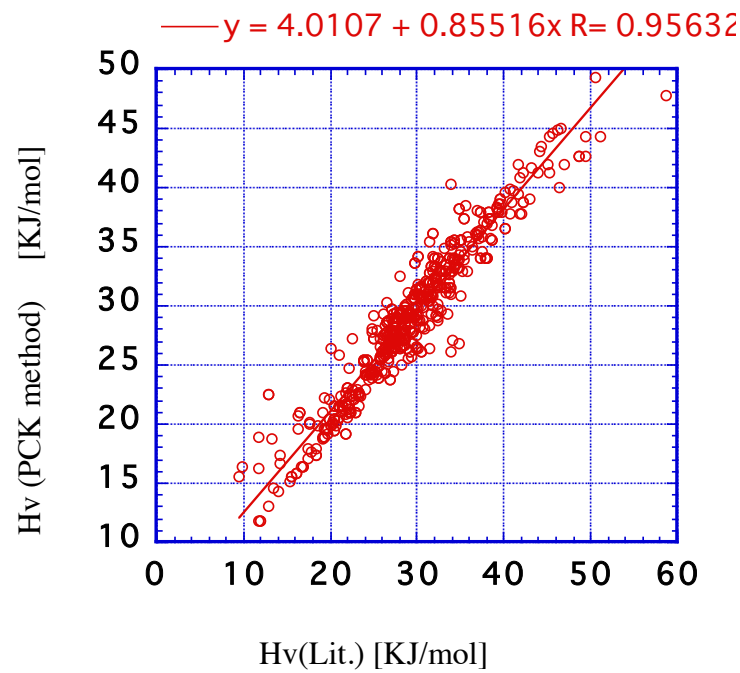
$$\frac{\Delta Hv}{RTc} = 7.08(1 - Tr)^{0.354} + 10.95\,\omega\,(1 - Tr)^{0.456}$$

ΔHv : Heat of Vaporization

Tr : Reduced Temperature (T / Tc)

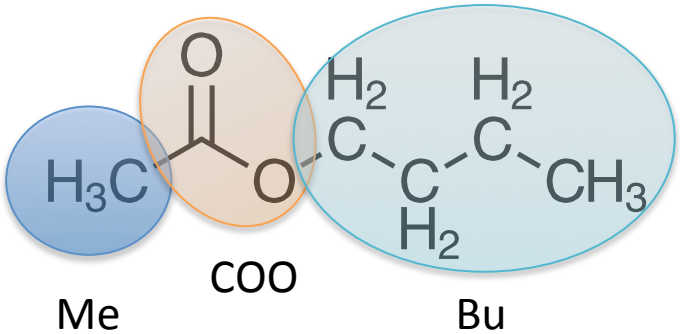
ω : Acentric factor

R : Gas constant



If we have Tc and ω, we can calculate H_v @25℃ with PCK method

Functional Group Contribution Method



$$\text{Property} = \sum_{i=1}^{172} \text{factor}_i * \text{FG}_i$$

Properties:

δ_D, δ_P, δ_H, Antoine A, B, C

BP, MP, Tc, Pc, Vc, n_D, MVol

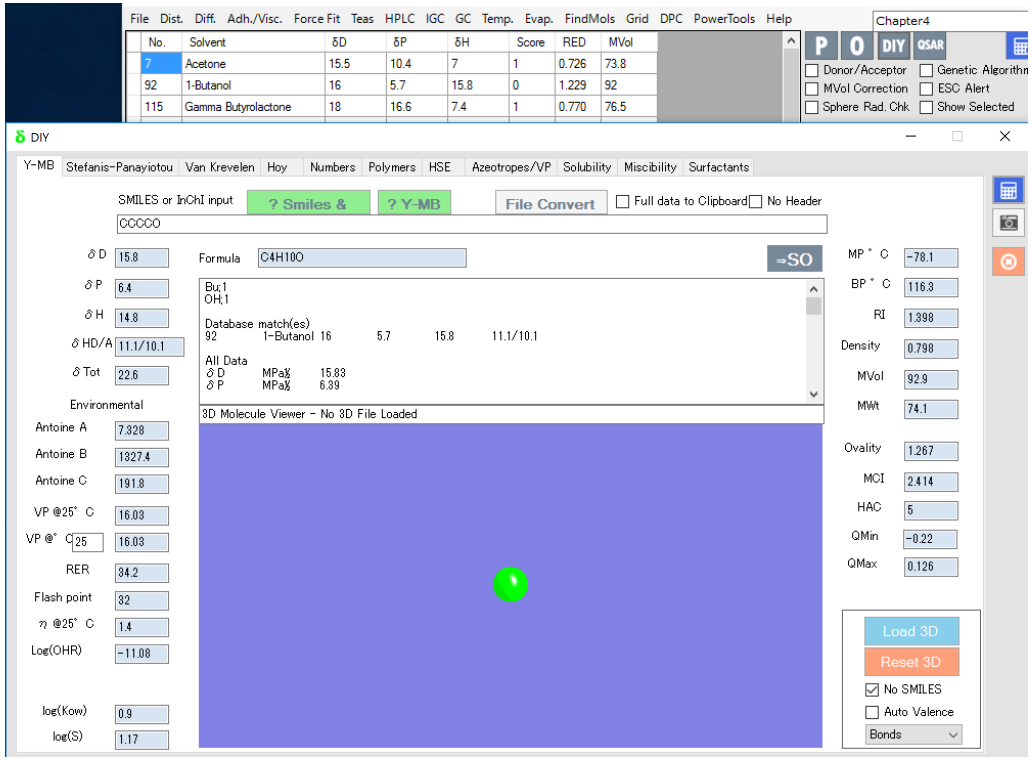
H_v, logKow, logS

so on.

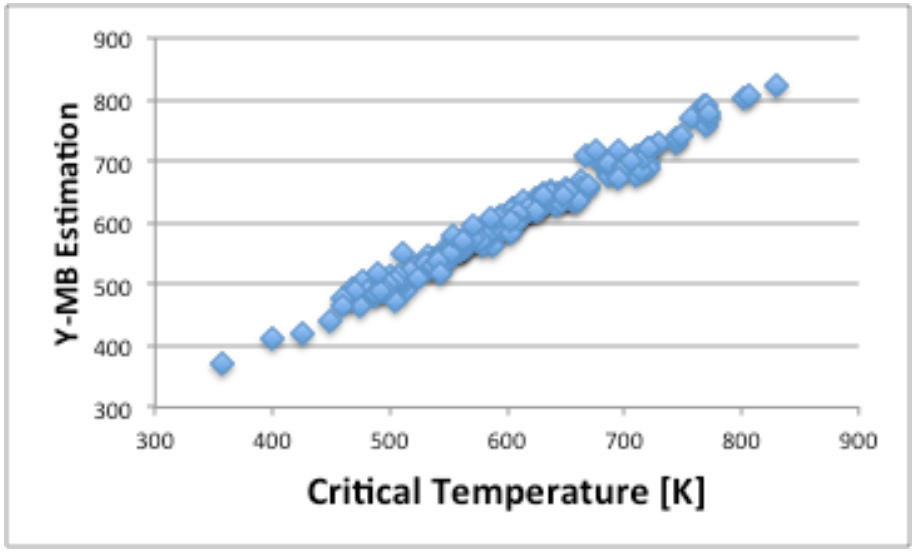
Yamamoto

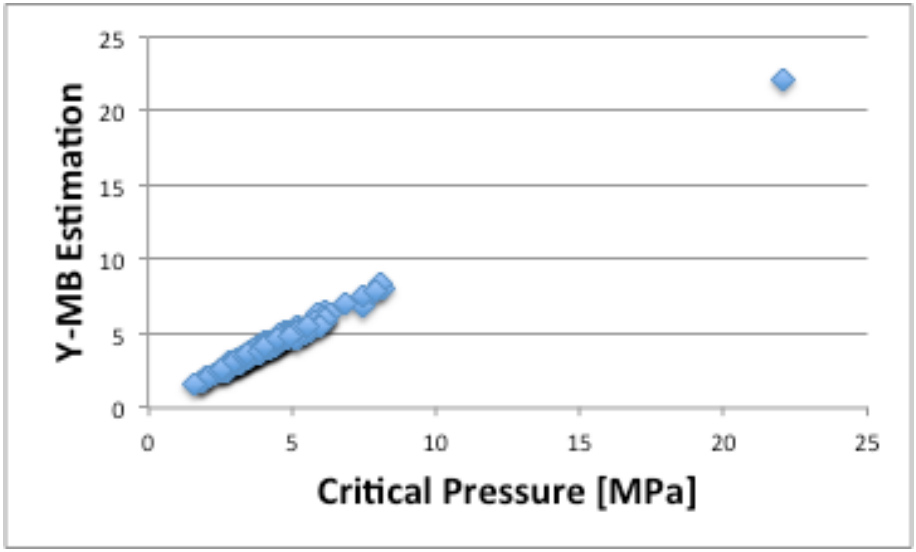
Molecular Break to Functional Group Algorithm

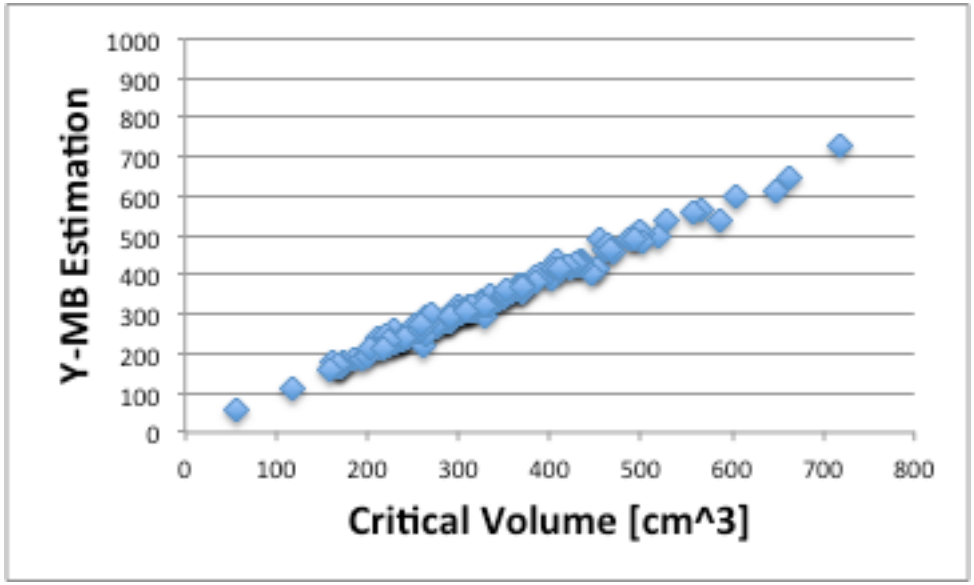
Y-MB is implemented in HSPiP



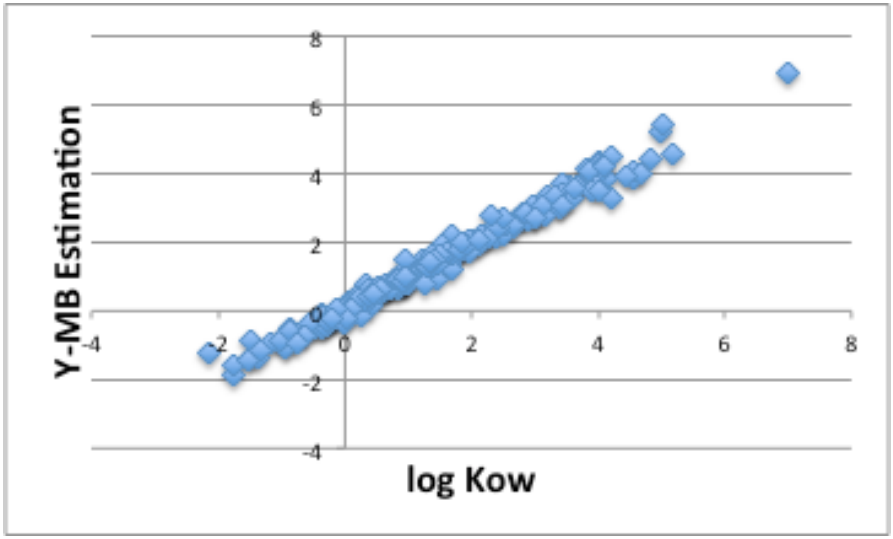
Y-MB Estimation(Critical Properties)

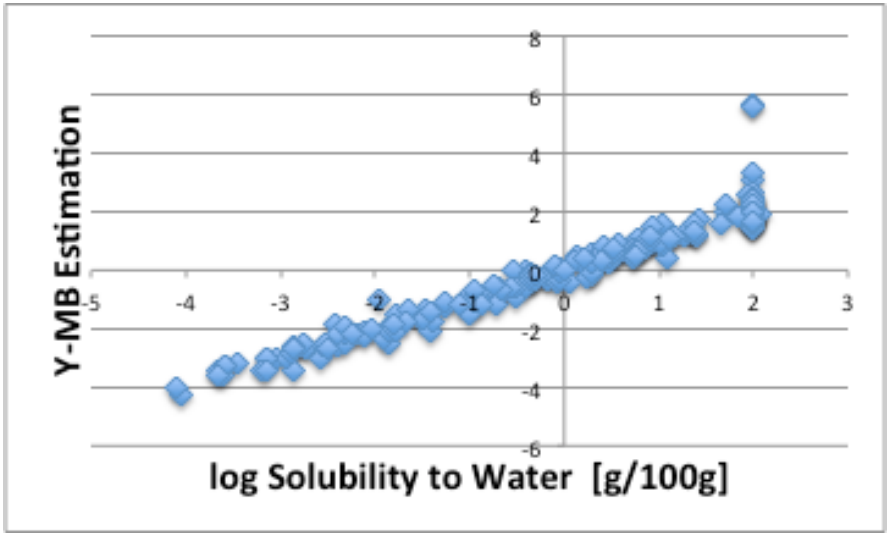


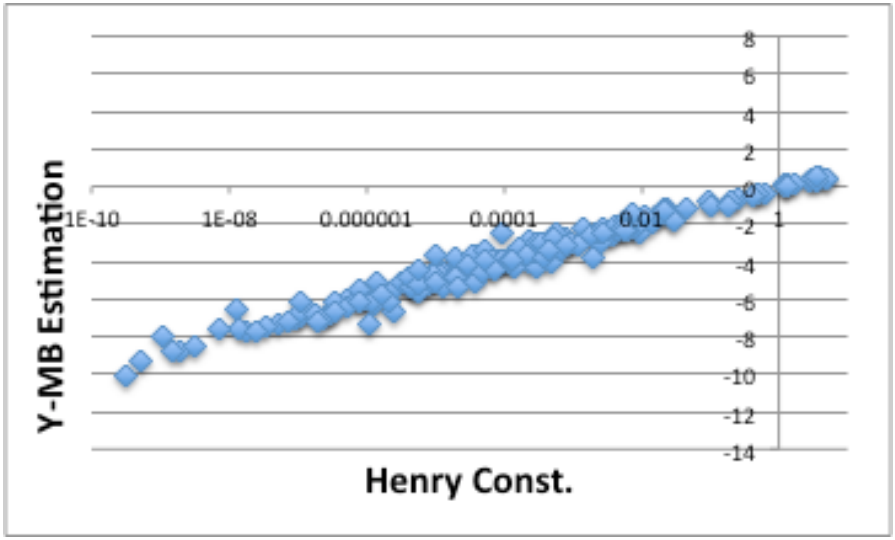


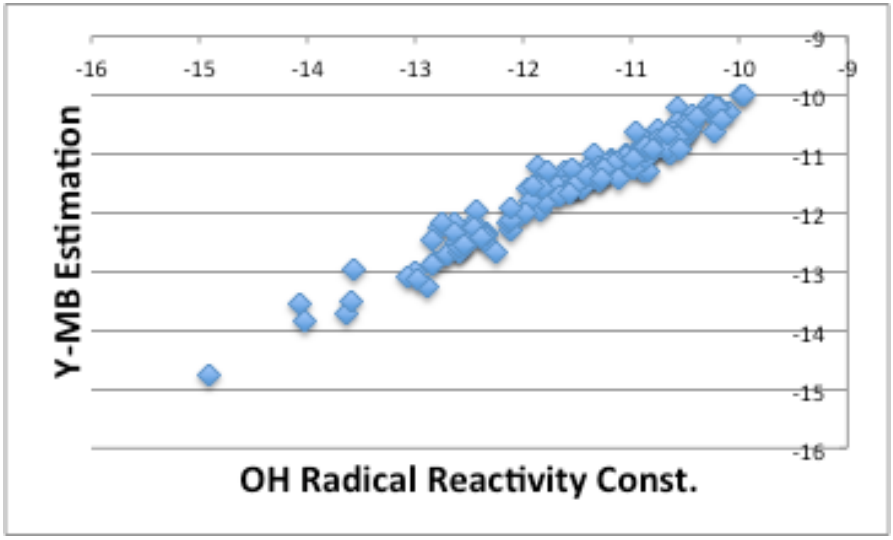


Y-MB Estimation (Environmental Properties)

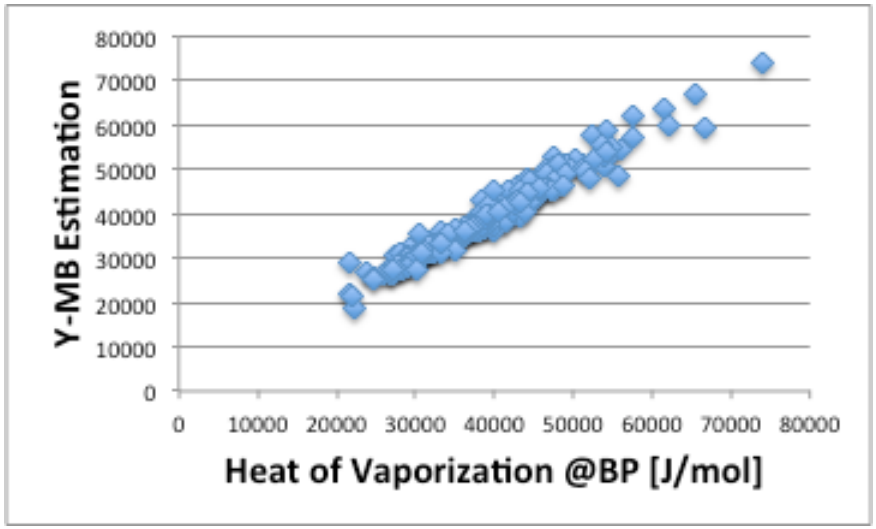


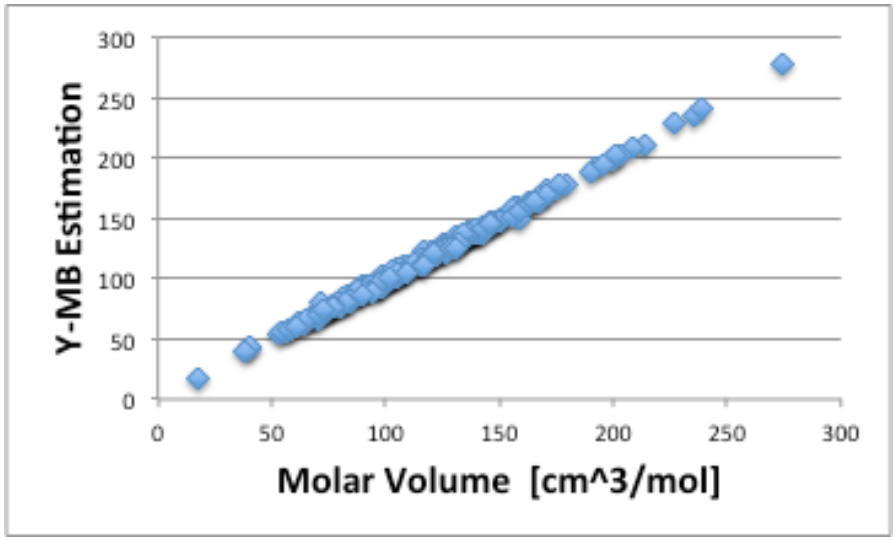


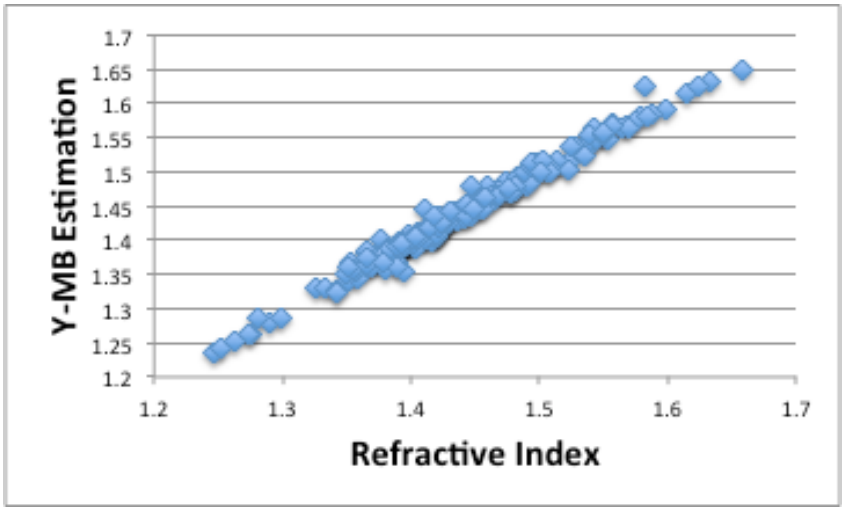




Y-MB Estimation (Other properties)





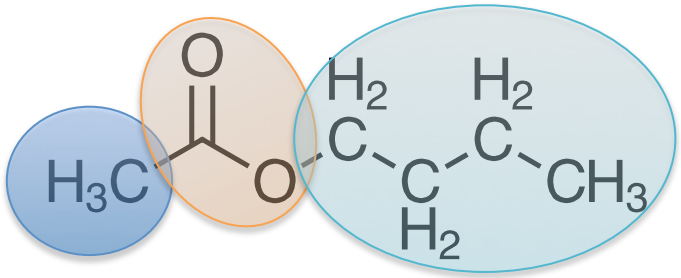


Developing 2017 version of Functional Group Contribution for HSP.

FG[δ_D, δ_P, δ_H] Vol

[19.0, 8.1, 10.8] 37.02

COO



Me

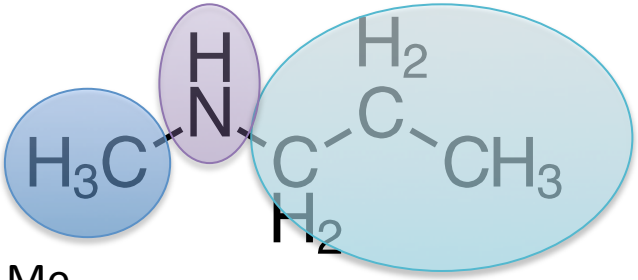
[12.9, 0.7, 0.1] 28.85

Bu

[15.2, 0, 0] 94.25

[20.7, 9.7, 14.9] 16.53

NH



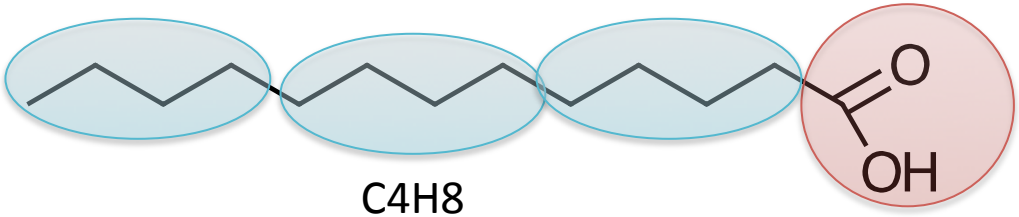
Me

Pr

[14.7, 0, 0] 72.2

Bu

C4H8



C4H8

[16.2, 0, 0] 88.04

COOH

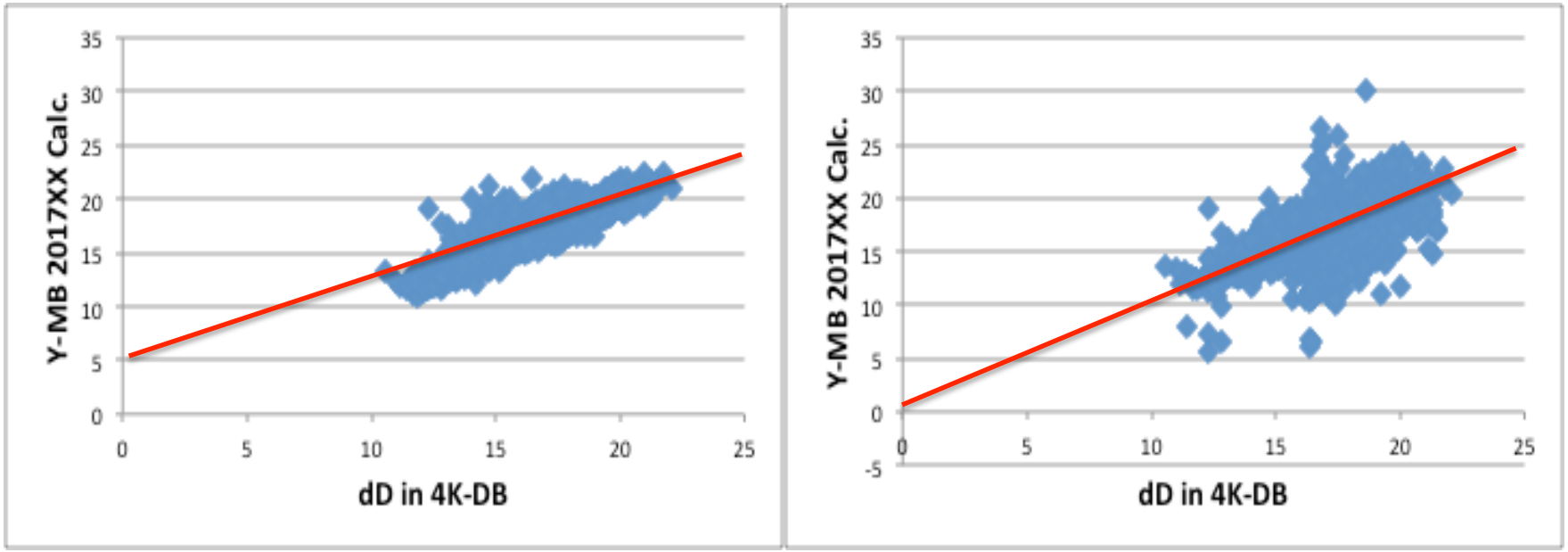
[17.9, 11.8, 22.1] 44.37

Volume weighted HSP mixture

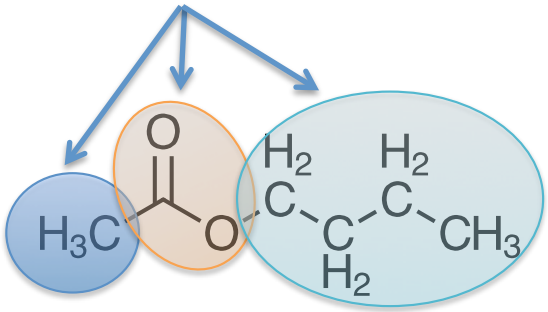
$$HSPmix = \frac{HSP1*\phi 1 + HSP2*\phi 2}{\phi 1 + \phi 2}$$

ϕ: Volume Fraction

Can't determine δ_D coefficients for each Functional Group!



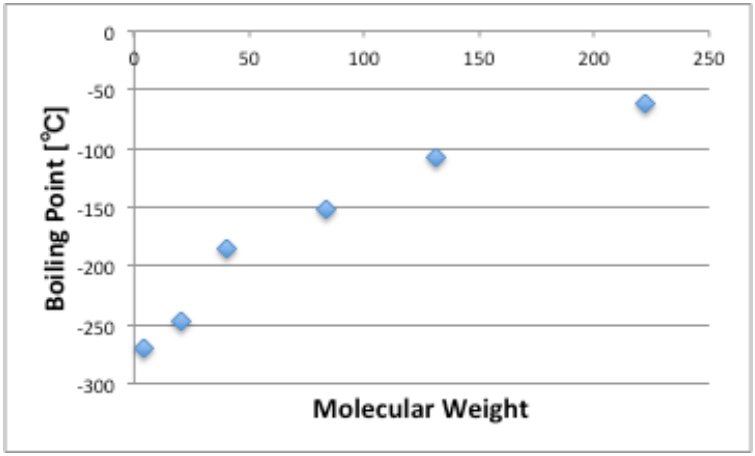
$\sum$ FGsFactor*FGsNumber+Const.



?

Rare Gases (Noble Gases)

- **Helium** $1s^2$
- **Neon** [He] $2s^2\ 2p^6$
- **Argon** [Ne] $3s^2\ 3p^6$
- **Krypton** [Ar] $3d^{10}\ 4s^2\ 4p^6$
- **Xenon** [Kr] $4d^{10}\ 5s^2\ 5p^6$
- **Radon** [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$



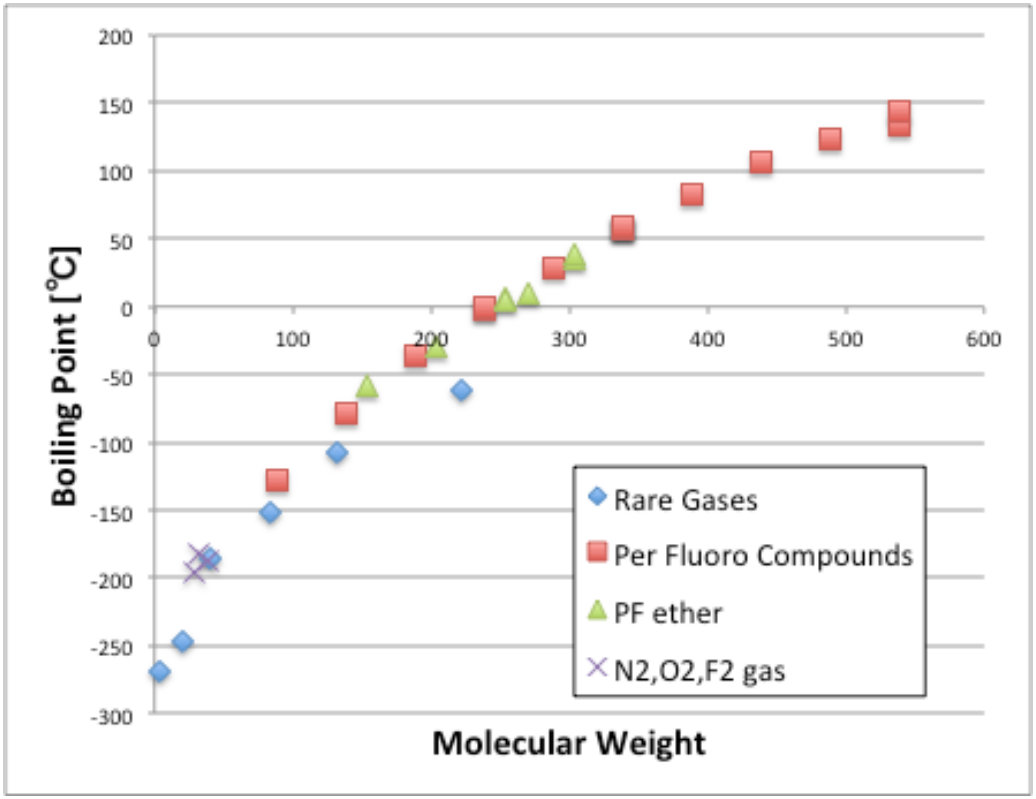
There is very good correlation between Molecular Weight and BP

Table 1: Trends within Group 18

	Atomic #	Atomic mass	Boiling point (K)	Melting point (K)	1st Ionization (E/kJ mol^{-1})	Density (g/dm^3)	Atomic radius (pm)
He	2	4.003	4.216	0.95	2372.3	0.1786	31
Ne	10	20.18	27.1	24.7	2080.6	0.9002	38
Ar	18	39.948	87.29	83.6	1520.4	1.7818	71
Kr	36	83.3	120.85	115.8	1350.7	3.708	88
Xe	54	131.29	166.1	161.7	1170.4	5.851	108
Rn	86	222.1	211.5	202.2	1037.1	9.97	120

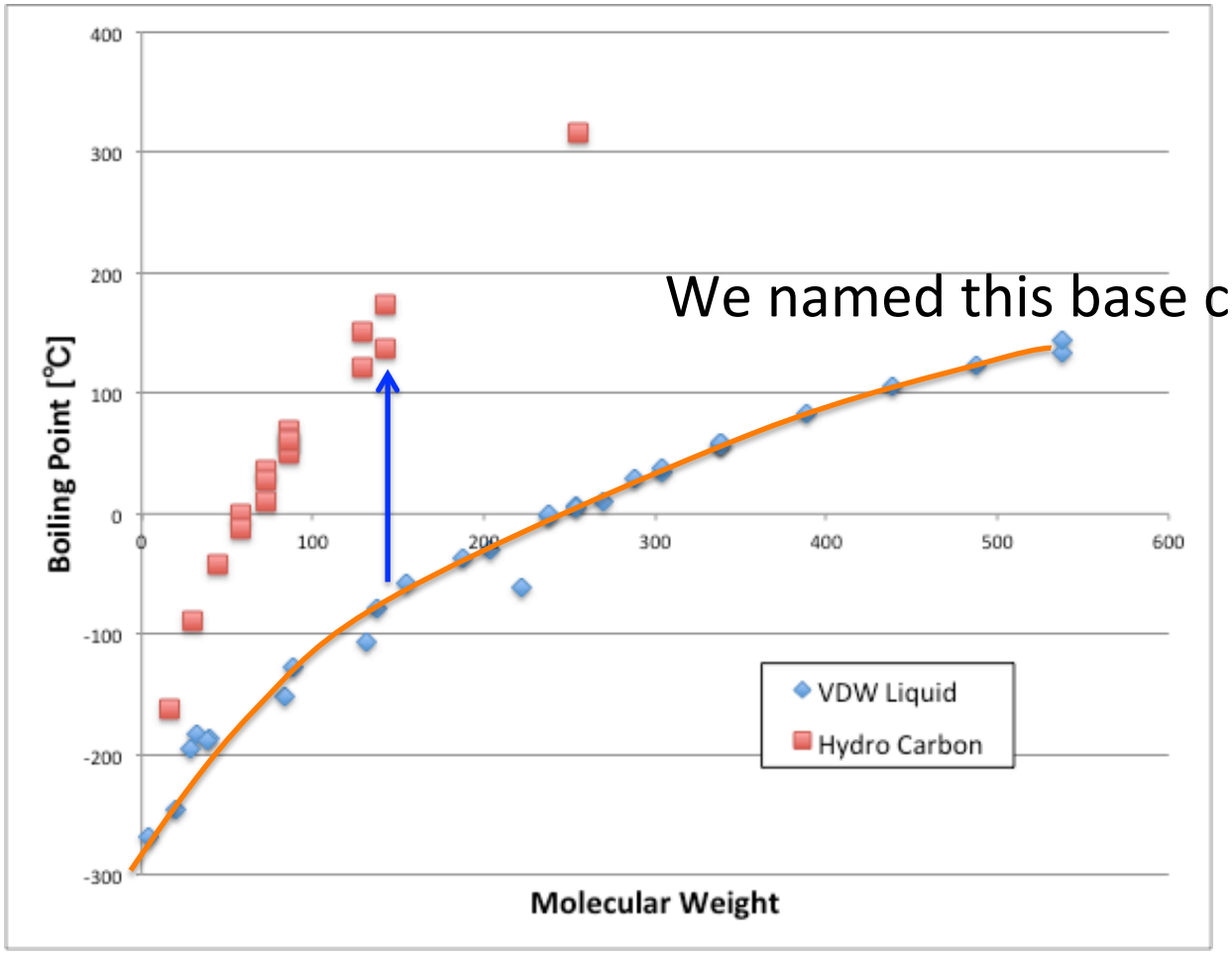
We know that Rare Gases become liquid only with the Weak Van Del Waals(VDW) Force.

Rare Gases & Fluorinated Compounds



The perfluoro compounds become liquid with only weak VDW force.

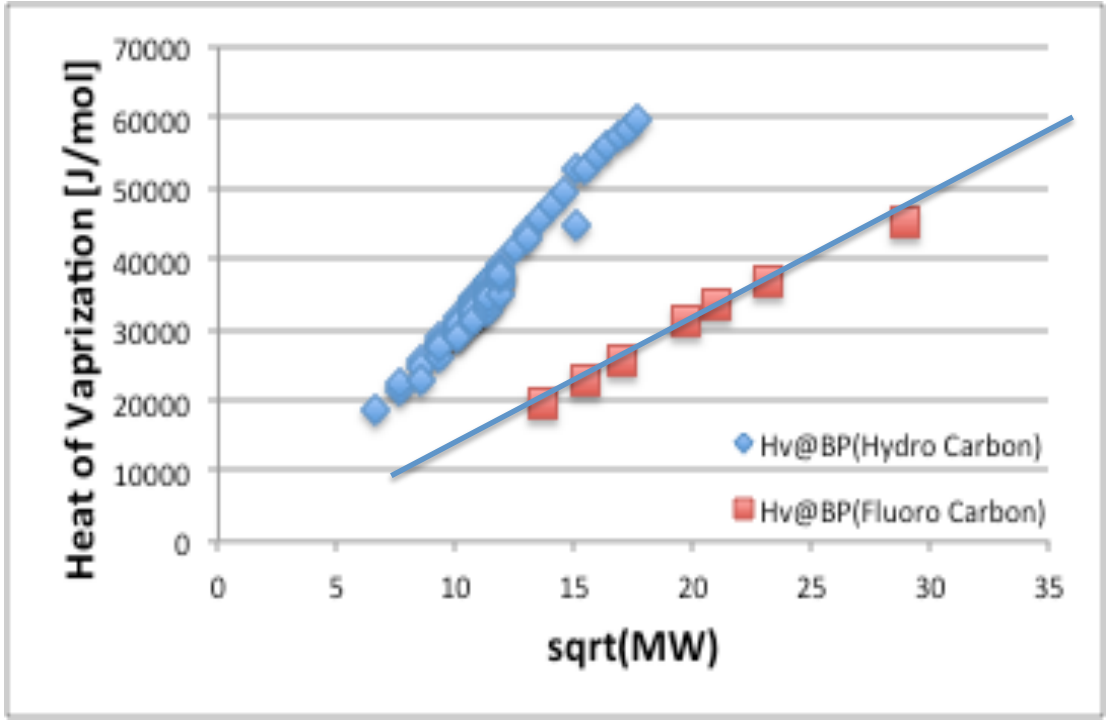
+Hydrocarbons



We named this base curve as δ_{Dvdw}

Even same molecular weight, hydrocarbons need much higher boiling point.

Change Axes

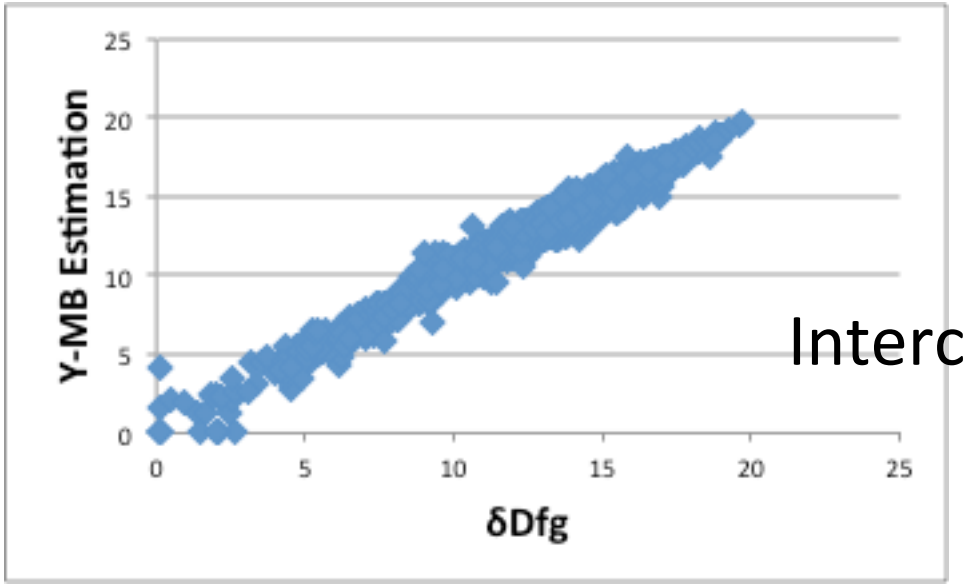


$$\delta_{Dvdw} = (9.0463 * MW^{0.5} + 28.512)/(MVol)^{0.5}$$

New definition $\delta_D^2 = \delta_{Dvdw}^2 + \delta_{Dfg}^2$

δ_D for Functional Group

Split δD to δ_{Dvdw} and δ_{Dfg}



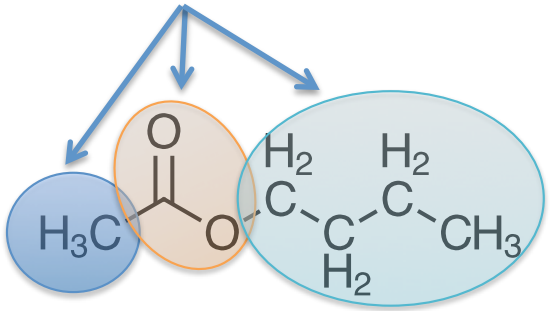
Intercept for $\delta_{Dfg}=0$

δ_D → δ_{Dvdw} + δ_{DFg}

MVol

MW

$\sum$ FGsFactor*FGsNumber



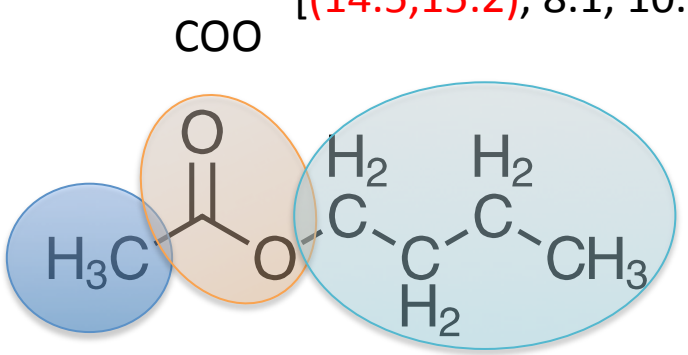
2017 version of Functional Group Contribution for HSP.

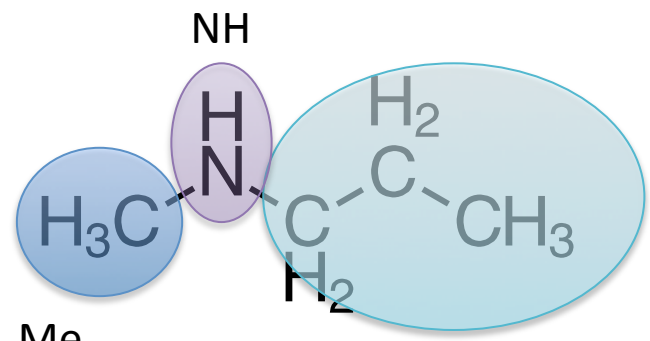
$d_D = (d_{Dvdw}^2 + d_{Dfg}^2)^{0.5}$

FG[(δ_{Dvdw}, δ_{Dfg}) ,δ_P, δ_H] Vol

[(14.5,15.2), 8.1, 10.8] 37.02

[(15.6,17.8), 9.7, 14.9] 16.53





Me

Bu

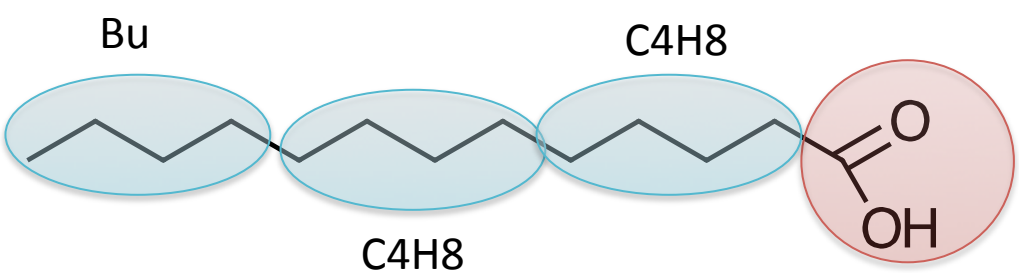
Me

Pr

[(11.8, 7.5), 0.7, 0.1] 28.85

[(10.0,12.3), 0, 0] 94.25

[(10.7,14.0), 0, 0] 72.2



COOH

[(10.3,14.0), 0, 0] 88.04

[(13.4,13.2), 11.8, 22.1] 44.37

Volume weighted HSP mixture

$$HSPmix = \frac{HSP1*\phi 1 + HSP2*\phi 2}{\phi 1 + \phi 2}$$

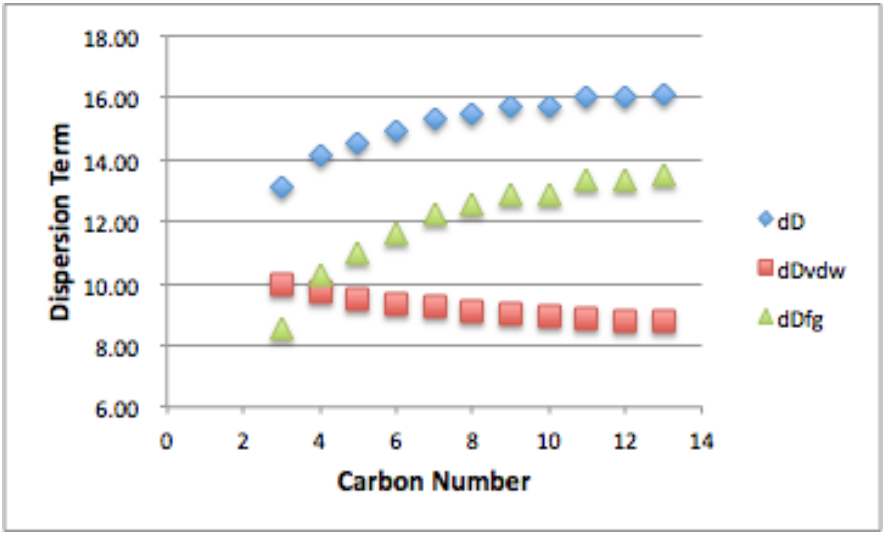
ϕ: Volume Fraction

HSP FG parameters

Label	dD	dDfg	dP	dH	CosVol	MW	Label	dD	dDfg	dP	dH	CosVol	MW
CH3	12.9	7.5	0.7	0.1	28.85	15.034	NH	20.7	17.8	9.7	14.9	16.53	15.018
CH2	16.4	14.3	1.5	0.9	22.05	14.026	NH_R	19.0	15.5	14.1	18.3	16.41	15.018
CH2_R	17.0	13.7	1.7	1.9	21.65	14.026	NH@Ar	30.7	28.7	16.6	23.6	15.08	15.018
CH2:	11.0	0.0	3.2	4.2	26.50	14.026	N	25.2	24.7	9.3	11.9	10.27	14.01
CH	21.2	21.6	0.1	0.0	14.67	13.018	N_R	25.0	22.2	7.6	19.5	9.26	14.01
CH_R	19.1	18.0	0.0	0.0	14.57	13.018	N@Ar	30.3	31.3	0.0	16.4	12.07	14.01
CH:	19.0	16.8	0.1	0.1	18.26	13.018	C#N	17.0	12.5	21.8	9.6	34.12	26.02
CH:_R	17.3	14.0	2.3	5.3	17.95	13.018	C#N@Ar	18.9	14.8	20.8	4.4	34.00	26.02
CH:_reso	18.3	14.9	0.1	4.8	17.84	13.018	NO2	17.9	12.4	20.6	6.9	40.26	46.01
#CH	14.2	9.2	3.6	4.1	24.50	13.018	NO2@Ar	19.3	14.0	15.7	7.6	38.78	46.01
C	33.3	37.2	0.1	5.3	5.48	12.01	SH	19.1	15.0	9.0	9.7	36.40	33.078
C_R	31.7	32.5	0.1	0.0	6.58	12.01	SH@Ar	22.6	19.0	3.1	9.1	37.17	33.078
C:	26.0	26.6	0.0	0.0	10.42	12.01	S	23.4	20.6	7.0	6.9	28.33	32.07
C:_R	25.4	25.3	0.1	4.7	10.64	12.01	S_R	23.1	19.2	11.4	11.6	28.15	32.07
C:_reso	24.5	24.0	1.0	0.1	10.12	12.01	S@Ar	27.2	24.9	9.7	0.0	28.20	32.07
C:_rrr	25.3	24.1	0.1	1.1	10.92	12.01	S:O	23.8	20.5	21.0	9.4	38.82	48.07
#C	19.6	16.7	7.7	6.6	14.87	12.01	NHCO	21.3	17.2	23.1	17.5	42.13	43.028
OH	18.4	11.3	16.6	36.6	18.05	17.008	NHCO_R	23.7	20.6	24.0	13.1	42.67	43.028
2_OH	18.6	12.6	15.0	32.2	18.29	17.008	NCO	24.4	21.8	22.3	13.6	34.89	42.02
3_OH	19.8	15.7	12.4	25.3	18.58	17.008	NCO_R	22.6	19.7	19.2	12.5	36.30	42.02
OH@Ar	17.3	10.7	13.5	28.8	18.84	17.008	OCOO	17.6	13.5	10.9	9.6	47.85	60.01
O	17.8	12.1	12.2	10.9	11.97	16	OCOO_R	19.5	14.5	29.0	10.3	50.20	60.01
O_R	18.0	11.7	13.1	12.4	12.06	16	CF3	10.7	0.0	1.8	0.0	52.73	69.01
O@Ar	22.0	18.0	16.1	16.7	11.30	16	CCl3	17.9	13.2	0.0	0.0	94.36	118.36
C:O	20.8	17.4	14.0	9.6	25.69	28.01	CF2	13.4	3.5	0.0	1.1	36.24	50.01
C:O_R	22.4	18.9	15.1	8.9	26.16	28.01	CCl2	18.8	13.6	6.6	4.3	62.76	82.91
C:O@Ar	23.3	19.9	16.8	7.7	25.54	28.01	CF	15.9	7.8	0.0	0.0	21.27	31.01
HCO	17.1	12.4	14.5	10.4	34.57	29.018	CCl	20.6	18.2	6.7	3.9	36.98	47.46
CHO@Ar	18.2	14.0	18.4	12.4	33.72	29.018	F	0.1	0.1	0.0	4.6	14.84	19
COOH	17.9	13.2	11.8	22.1	44.37	45.018	Cl	16.4	8.7	0.0	0.0	27.46	35.45
COOH@A	19.4	15.1	11.4	19.4	43.99	45.018	Br	19.8	10.2	7.1	6.3	36.43	79.9
COO	19.0	15.2	8.1	10.8	37.02	44.01	I	21.0	11.4	5.6	5.2	47.22	126.9
COO_R	19.3	14.2	25.9	11.6	38.47	44.01	Si	10.7	11.3	0.0	0.0	29.98	28.09
COO@Ar	17.6	14.3	13.6	6.3	37.69	44.01	P	17.7	13.7	6.5	0.0	30.30	30.97
NH2	17.7	12.1	10.2	17.1	22.95	16.026	B	20.5	18.8	0.1	0.0	13.34	10.81
NH2@Ar	20.6	16.2	13.7	24.2	22.30	16.026							

Solvent Size Effect

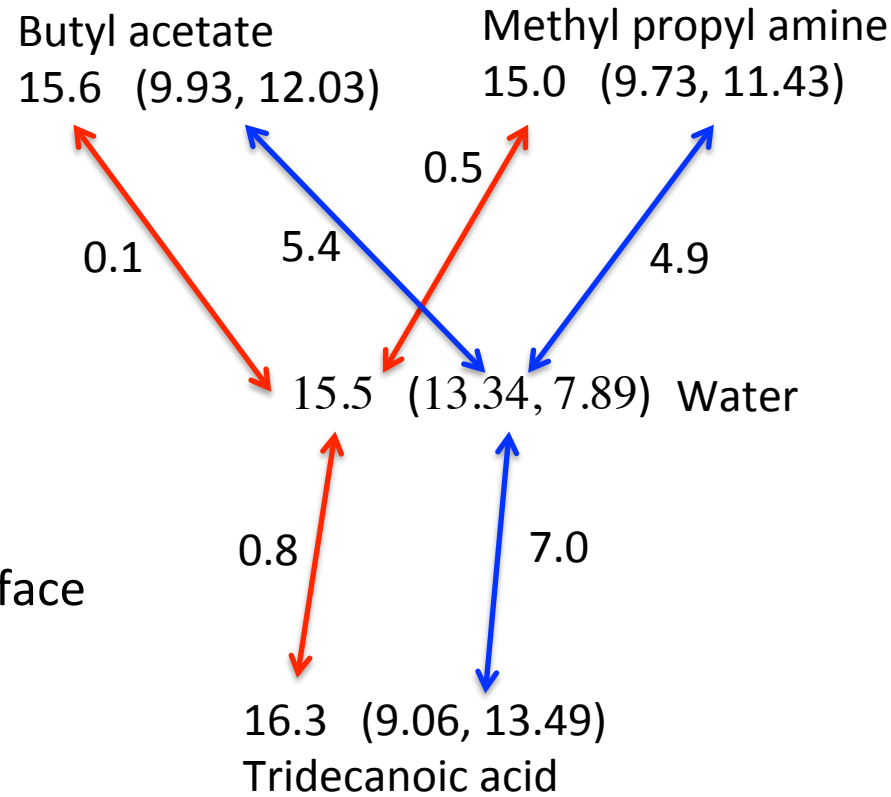
n-Alkane's Dispersion Term



As the molecule becomes larger, the surface area decreases.

δ_{Dvdw} decreases as the size becomes larger

δ_D (δ_{Dvdw} , δ_{Dfg})

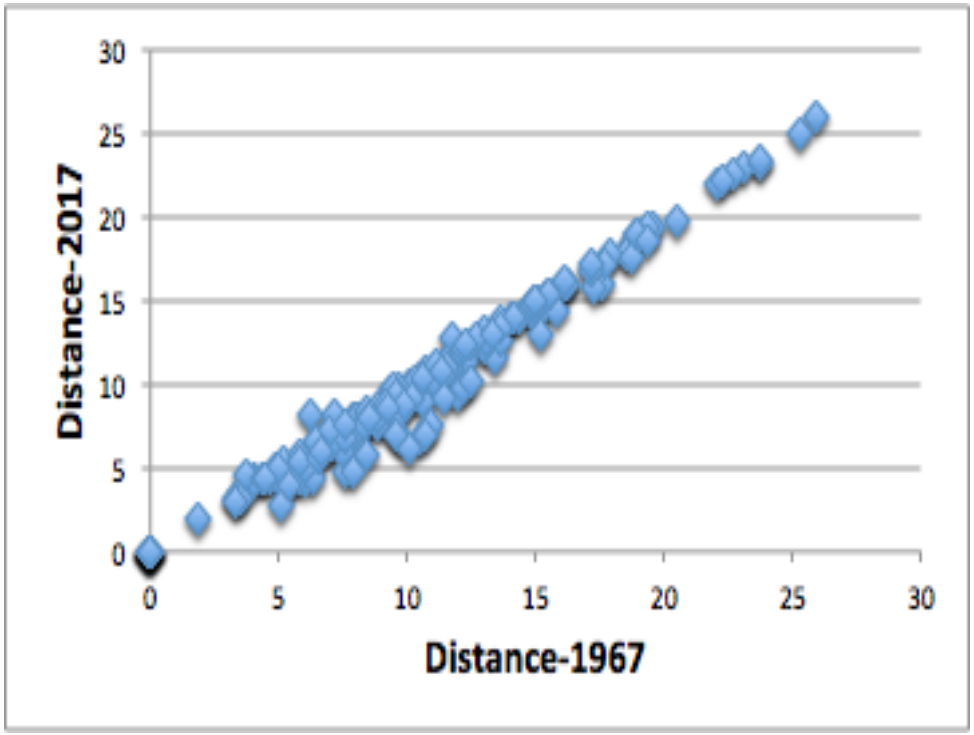


Small Solvent's specific Nature

New HSP Distance

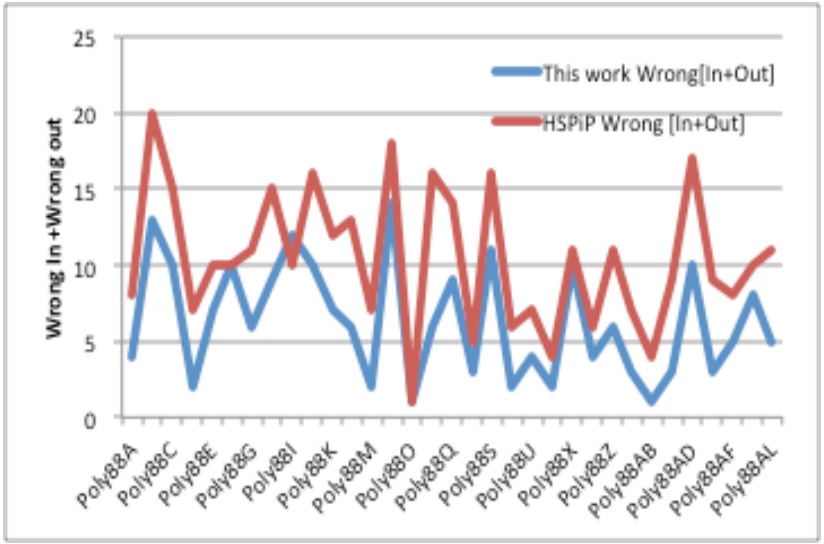
$$\text{Distance}_{1967}=\{4.0*(\delta_{D1}-\delta_{D2})^2+(\delta_{P1}-\delta_{P2})^2+(\delta_{H1}-\delta_{H2})^2\}^{0.5}$$

$$\text{Distance}_{2017}=\{(\delta_{Dvdw1}-\delta_{Dvdw2})^2+(\delta_{Dfg1}-\delta_{Dfg2})^2+(\delta_{P1}-\delta_{P2})^2+(\delta_{H1}-\delta_{H2})^2\}^{0.5}$$



Polymer 88 solvents

Polymer 88 examples

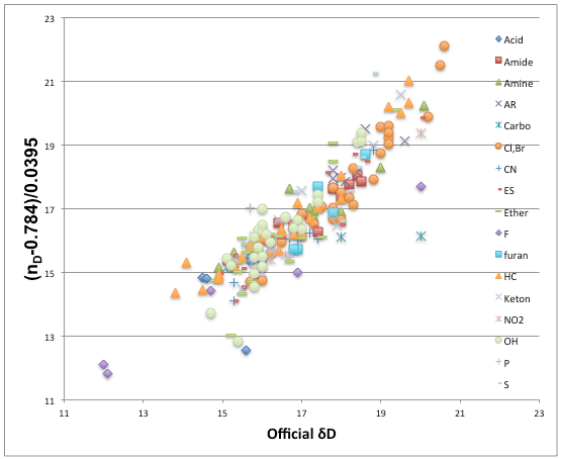


δ_D determination

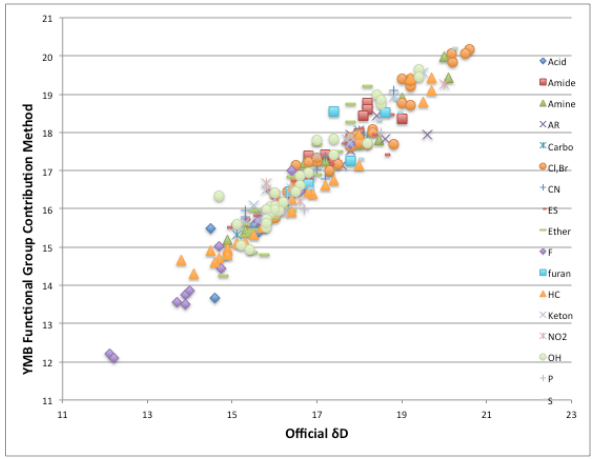
Official δ_D is not always "Correct Answer".

Cross Check with independent method.

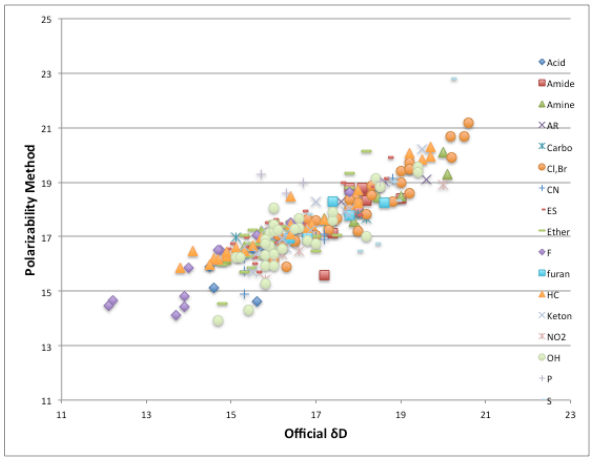
Refractive Index method



YMB method

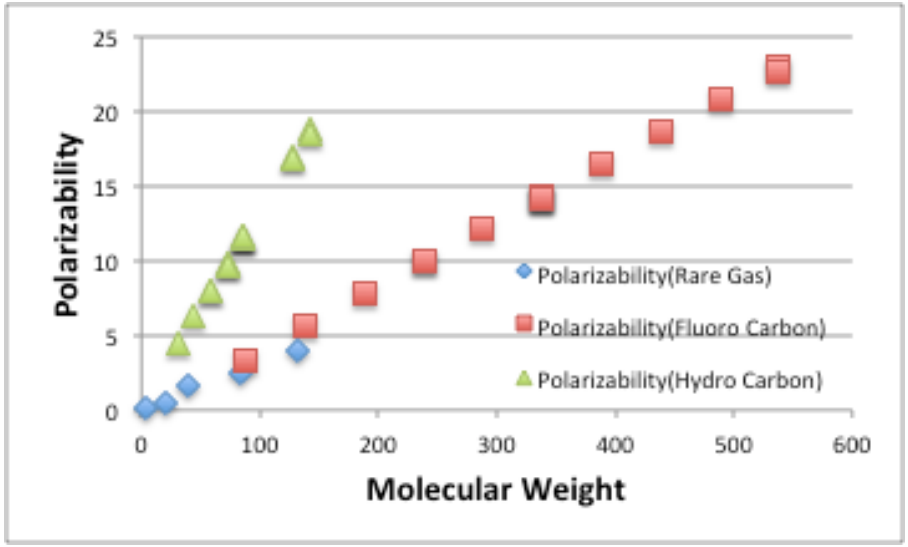


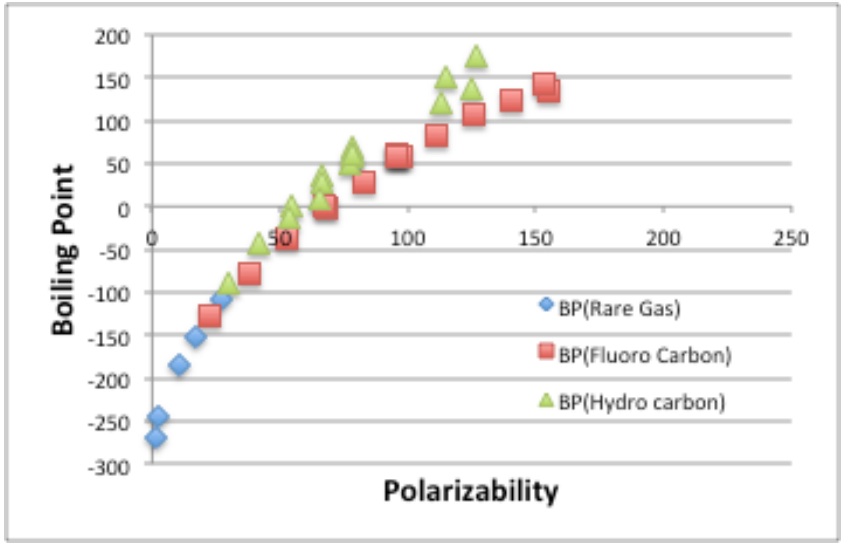
Polarizability Method

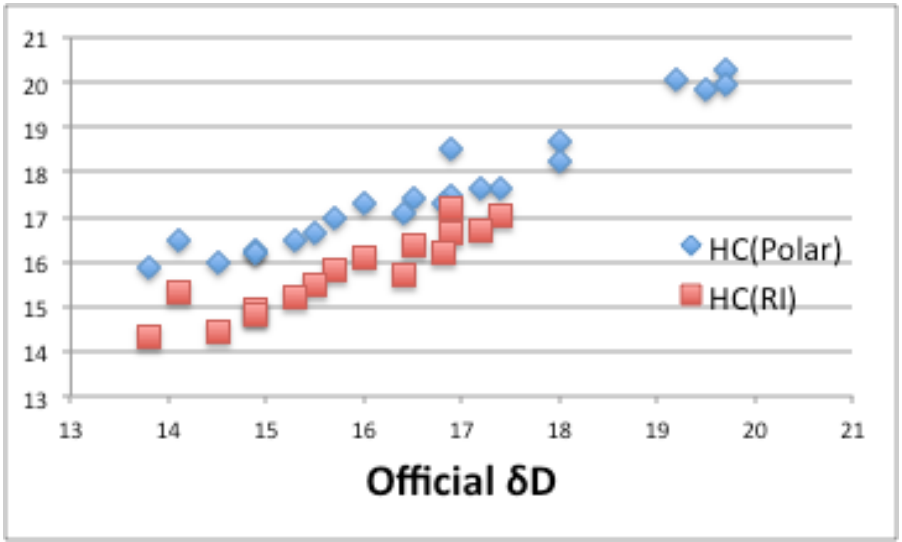


Polarizability Method

Calculated 4,000+ molecules with MOPAC 2012 and obtained Polarizability values.







δ_D= ((Polarizability*1000−719.94)/(0.3231*MVol))$^{0.5}$

Polarizability Method

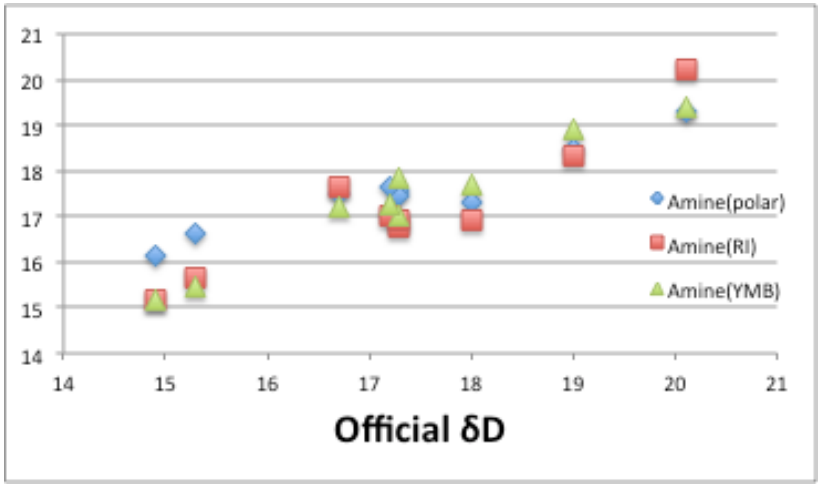
Refractive Index method

Almost parallel

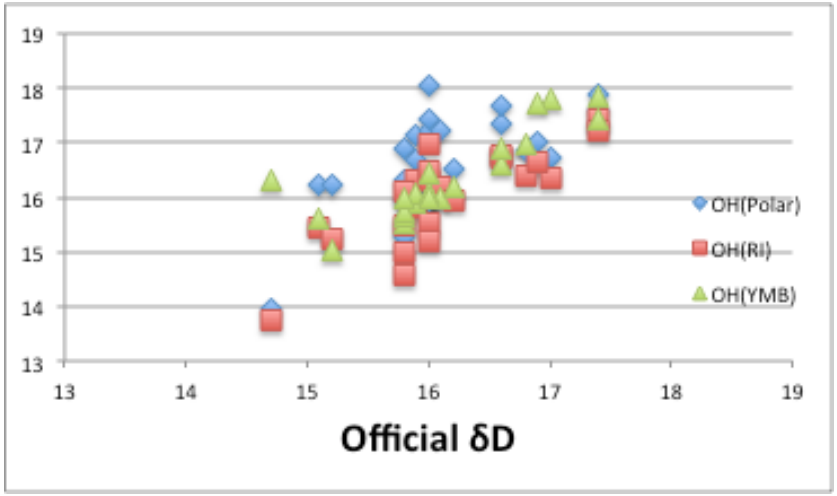
Cross Checking for δ_D

Polarizability
Refractive
Y-MB

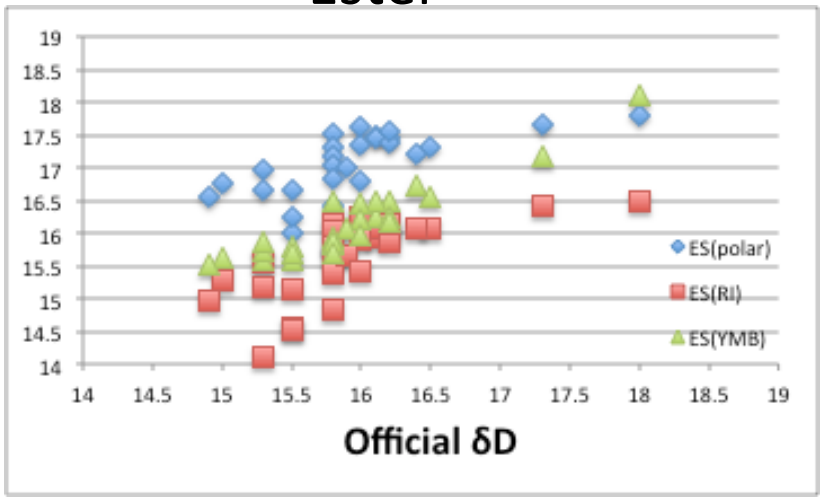
Amine



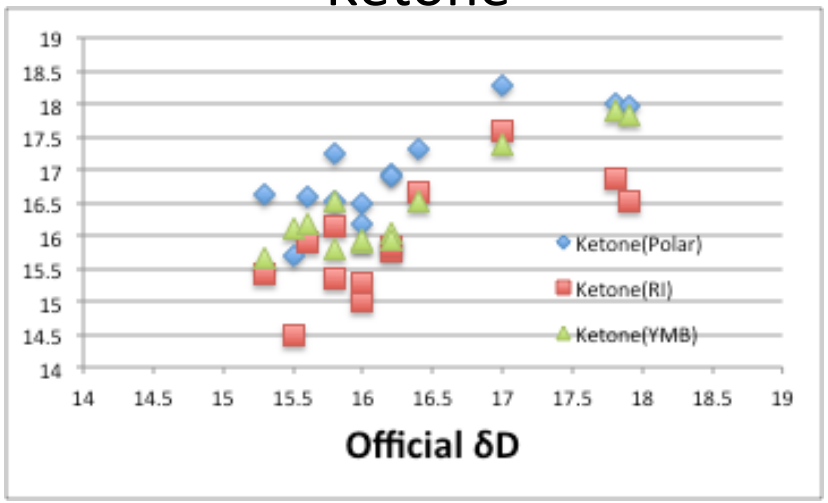
Alcohol



Ester



Ketone



δ_P determination

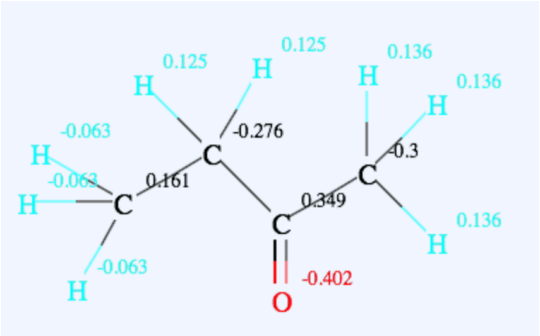
Official δ_P is not always “Correct Answer”.

Cross Check with independent method.

Dipole moment method

YMB method

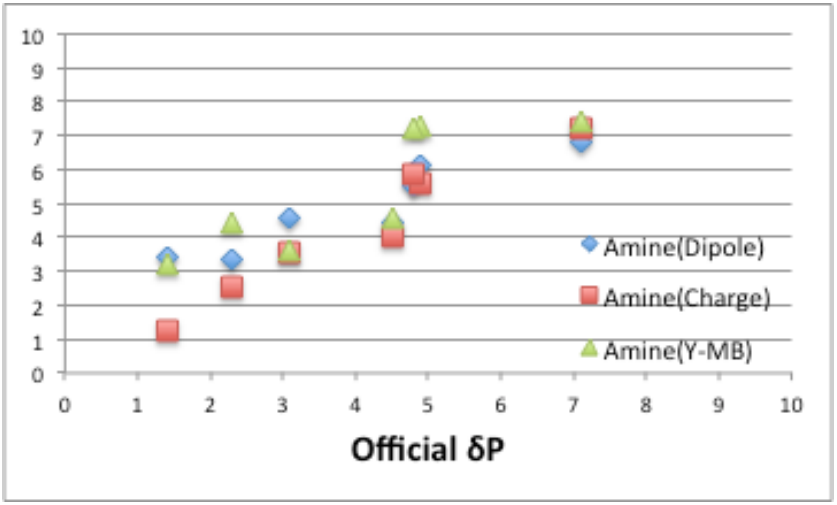
qEQ Charge Calculation Method



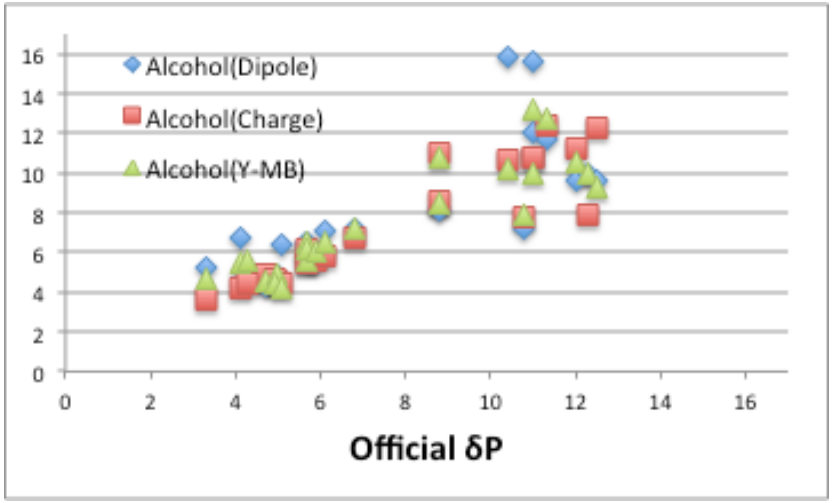
Cross Checking for δ_P

Dipole
Charge
Y−MB

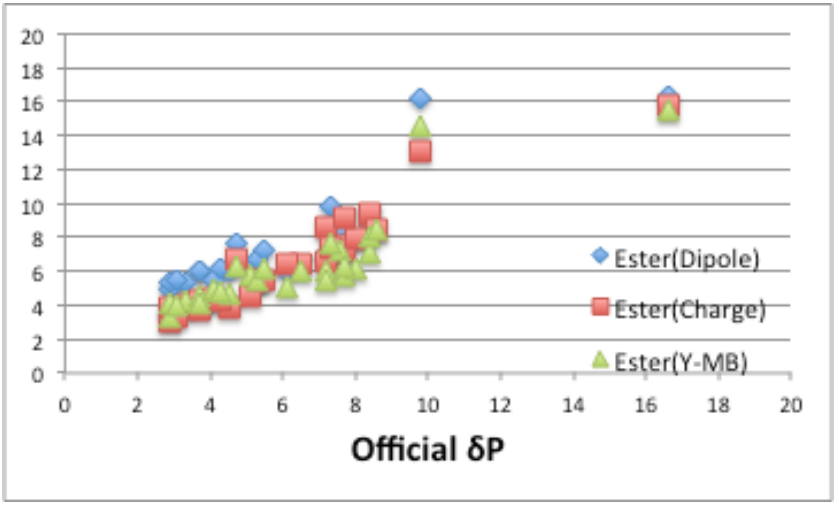
Amine



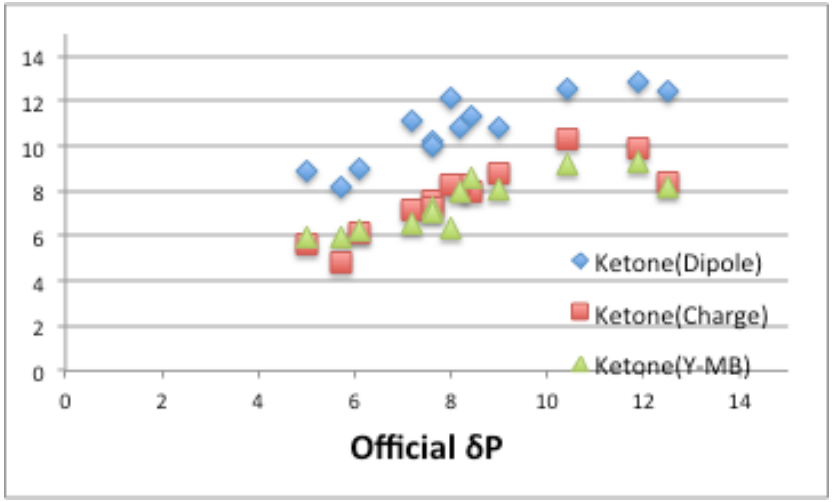
Alcohol



Ester



Ketone



Temperature Dependency of HSP

Original Scheme

$$d\delta_D/dT = -1.25\alpha\delta_D$$

$$d\delta_P/dT = -0.5\alpha\delta_P$$

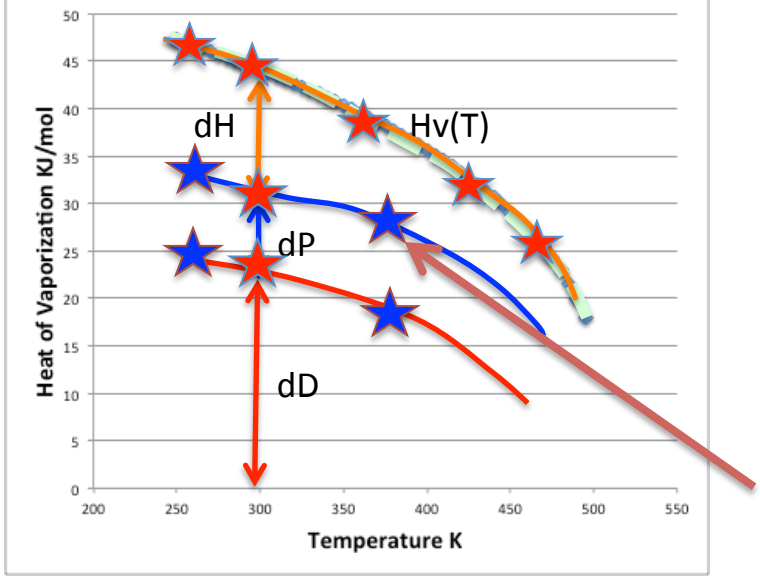
$$d\delta_H/dT = -\delta_H(1.22 \times 10^{-3} + 0.5\alpha)$$

α: Coefficient of thermal expansion

New Scheme

CST

$Hv(T) = F_{dD}(T) + F_{dP}(T) + F_{dH}(T)$

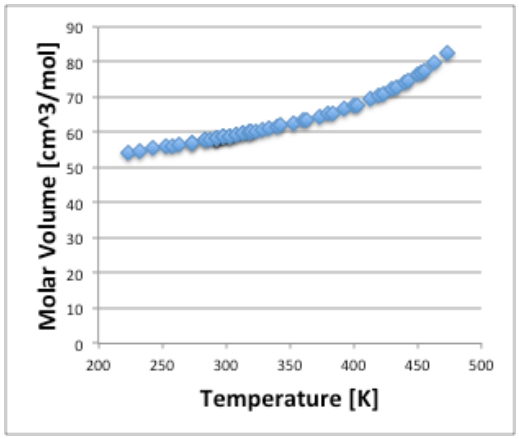


$\delta_D(T) = (F_{dD}(T)/Mvol(T))^{0.5}$

$\delta_P(T) = (F_{dP}(T)/Mvol(T))^{0.5}$

$\delta_H(T) = (F_{dH}(T)/Mvol(T))^{0.5}$

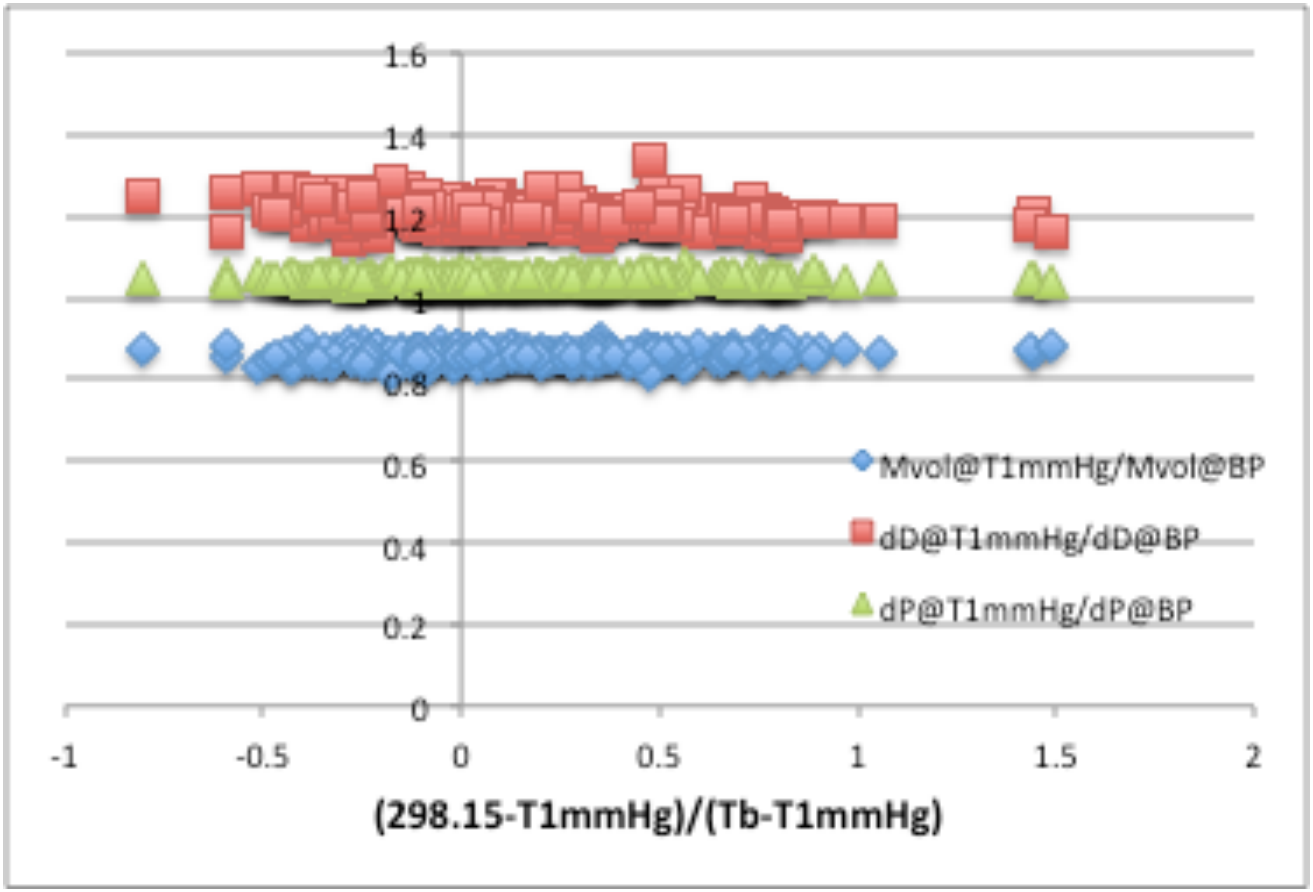
CST



How can we determine $F_{dD}(T)$, $F_{dP}(T)$, $F_{dH}(T)$?

Need other data at different temperature .

Corresponding State Theory(CST)



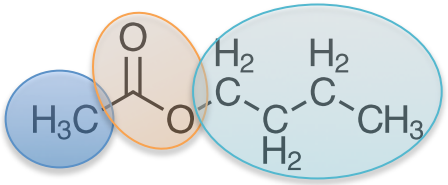
Properties@T_{1mmHg} / Properties @ T_b → Identical

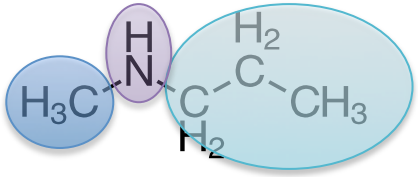
Verification of Temperature dependency

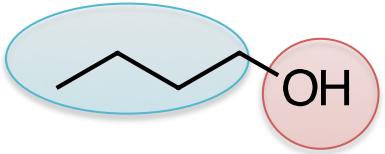
$$\log P(\text{mmHg}) = A - B/(T^{\circ}C + C)$$

Antoine Parameters
A, B, C

$$\log 1(\text{mmHg}) = 0 = A - B/(T_{1\text{mmHg}} + C)$$
$$\log 760(\text{mmHg}) = A - B/(T_B + C)$$







MVol @T_{1mmHg}		MVol @T_b			δD @T_{1mmHg}		δD @T_b		
128.2	/	150.3	=	0.85	16.6	/	13.6	=	1.22
94.1	/	110.8	=	0.85	17.1	/	14.1	=	1.22
90.3	/	105.0	=	0.86	16.5	/	13.6	=	1.21

identical

Conclusion

Built Functional Group Contribution Method 2017

Need to split δ_D term to δ_{Dvdw} and δ_{Dfg}

Small Solvent's specific Nature

Built new HSP Distance Scheme 2017

$$\{(\delta_{Dvdw1}-\delta_{Dvdw2})^2+(\delta_{Dfg1}-\delta_{Dfg2})^2+(\delta_{P1}-\delta_{P2})^2+(\delta_{H1}-\delta_{H2})^2\}^{0.5}$$

Without factor 4

Building new HSP Official Values 2017

Cross Checking

Temperature dependent HSP

The new name?

Please think of new name of HSP!

In Japan, I used HSP^2

Hansen-Hiroshi-Steven Solubility Parameters for Prediction

Keep brand identity of "HSP"
Network searchable.
Image of new and powerfulness.

Expanded HSP

EHSP: English for High School Preparation, Enhanced High Speed Processor
Equine Health Studies Program

HSP^2

Y-Solvent2017

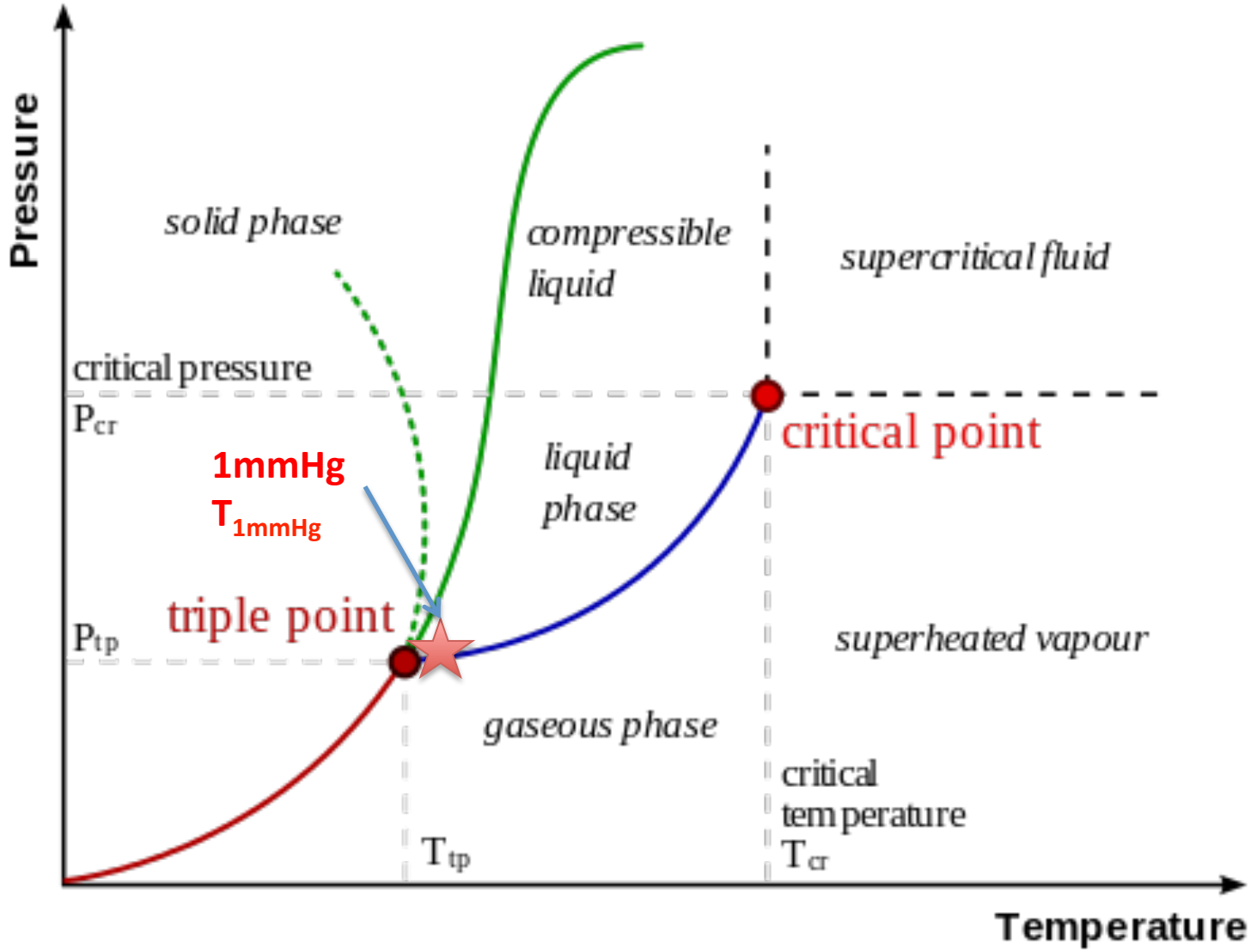
Y-Fit2017

Specific Japanese users are using now

Their feed back, revise.

Will release within this year (?)

CST base point



Revise policy

1. For 14K compounds, I ranked each molecule.

Category 1: I checked Barton's Book "CRC, Hand Book of of Solubility Parameters and other cohesion Parameters" and select 206 solvents.
Category 2: I checked HSPiP examples and select 83 solvents

Category 1-2 solvents HSP are widely used and I do not revise these HSP.

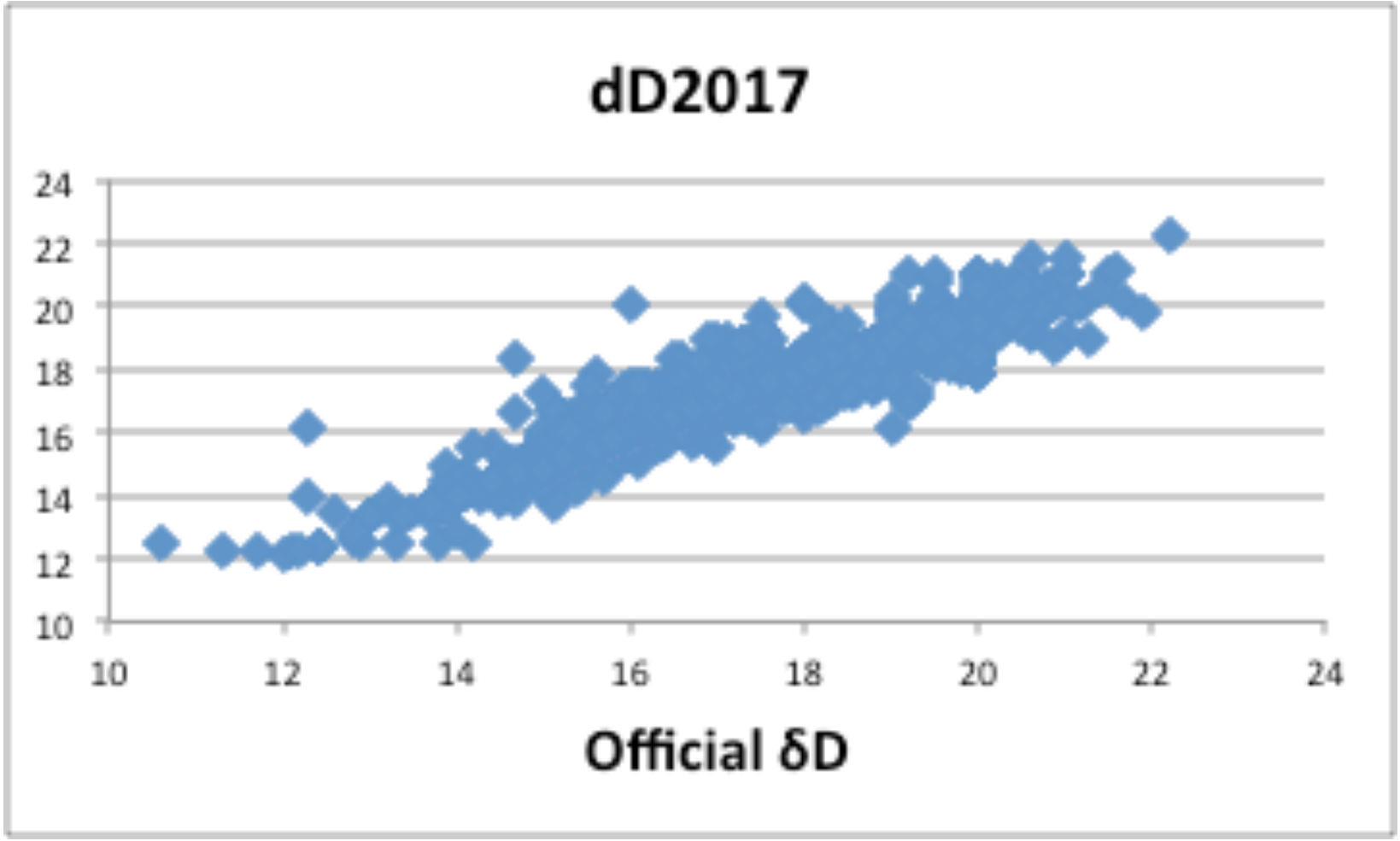
Category 3: I checked Dipper801 database and extract SP values and Heat of vaporization at 25℃.

For category 3, If Official totHSP in HSPiP are good agreement (415 solvents)

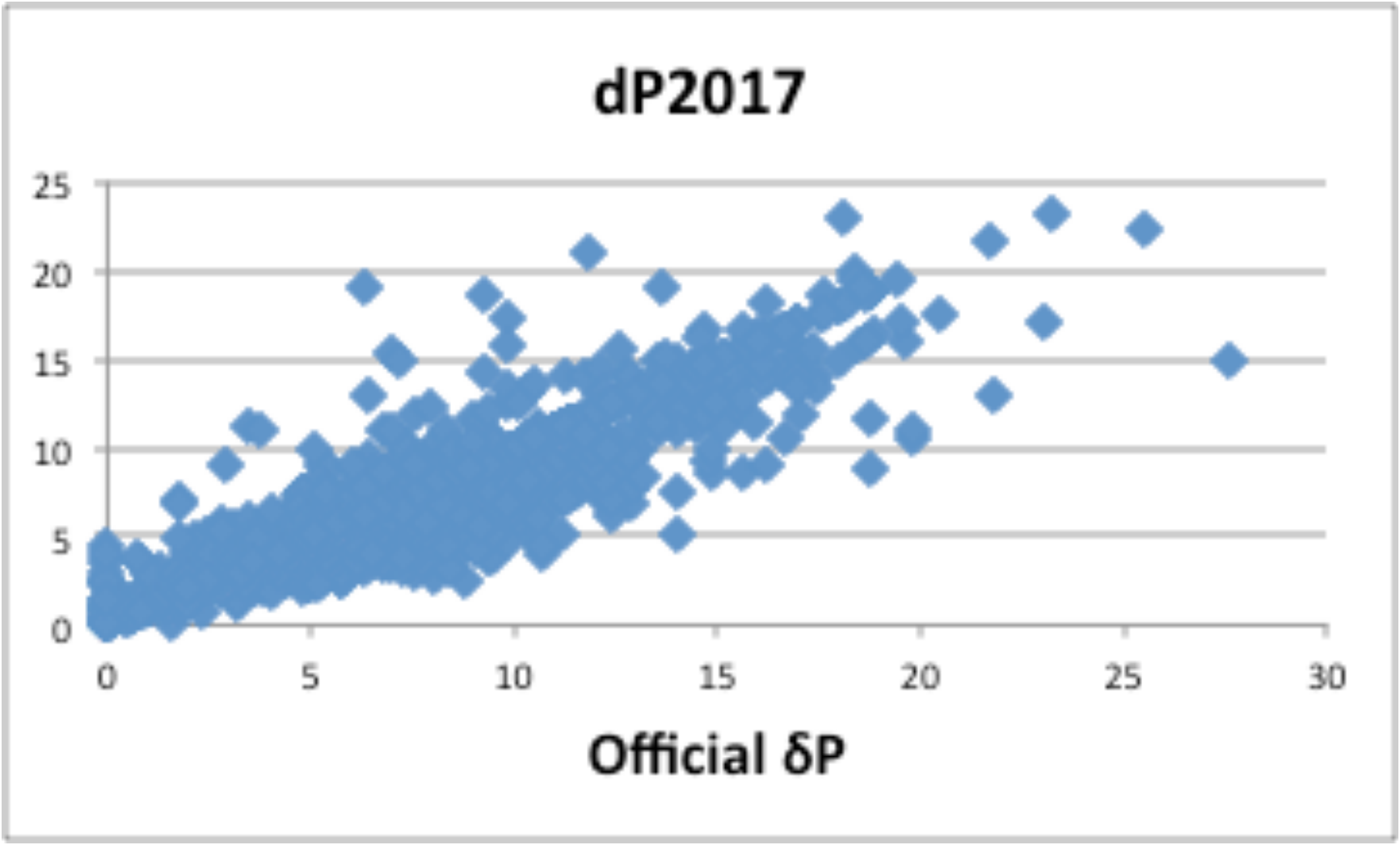
Category 4: YMB calculation result of totHSP and Dipper values are good agreement, I import YMB result. (1325 solvents)
Category 5: Very simple mono-functional solvents. (1572 solvents)
Category 6: Halogenated solvents or other important 378 solvents
Category 7: Important flavor 561 compounds
Category 8: Not above.

1-2 I never change. Others I revised.

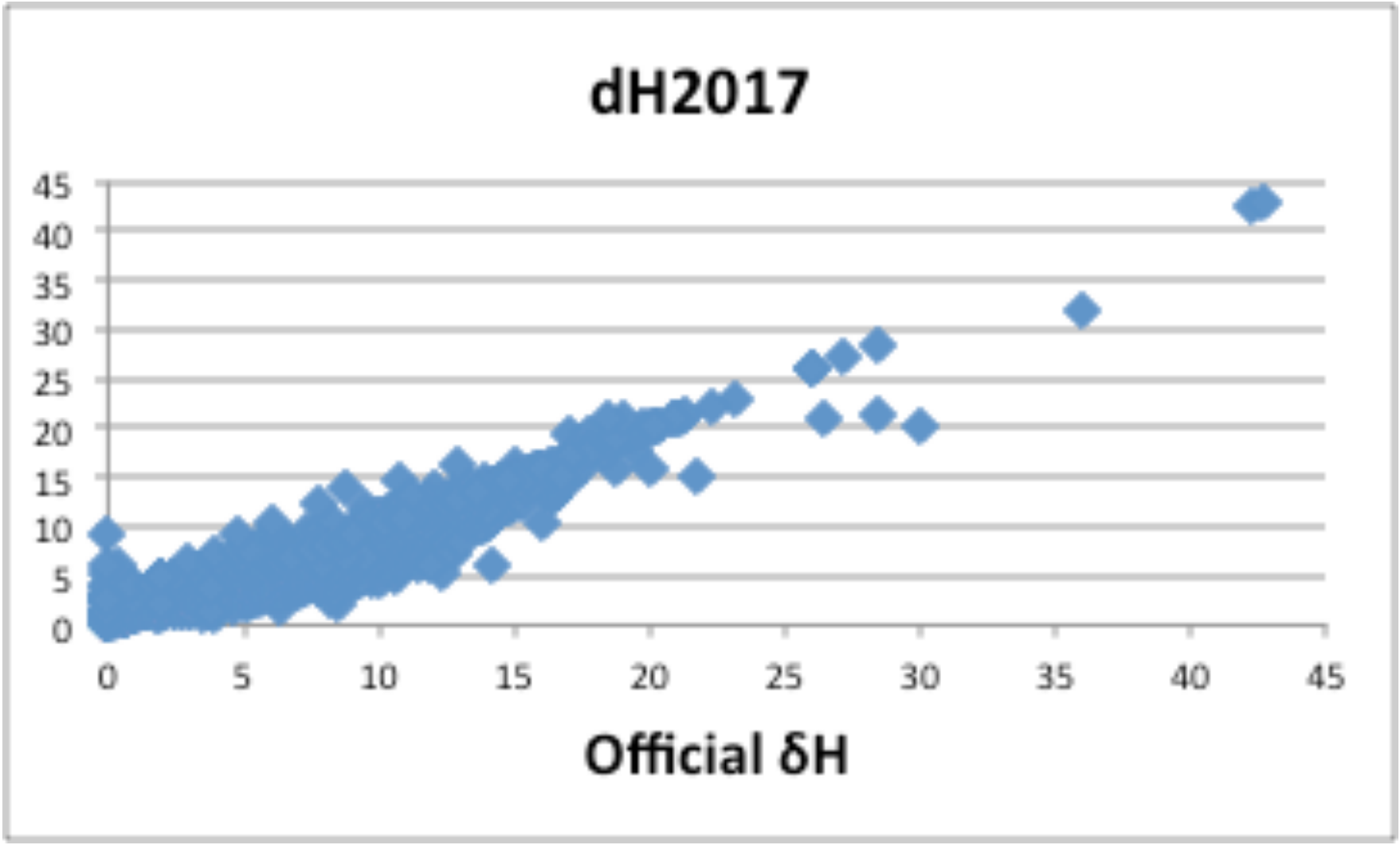
HSP to HSP^2 δ_D



HSP to HSP^2 δ_P



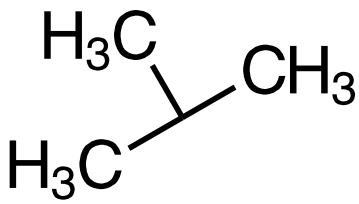
HSP to HSP^2 δ_H



In HSPiP

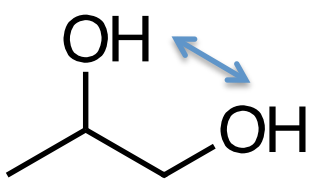
version 5.1 ?
6.0 ?

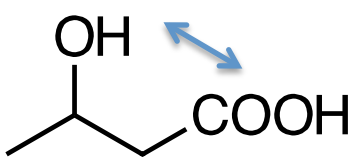
More Large FG

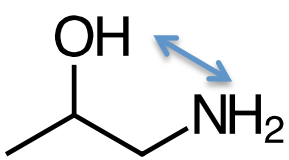


≠ 3*CH3 + C

FG interactions

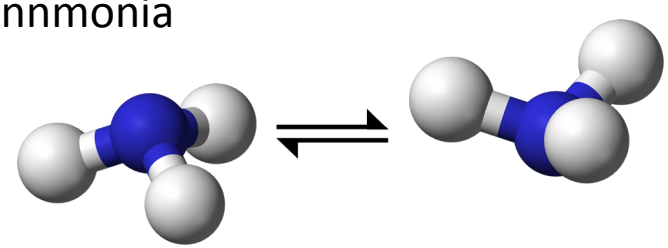




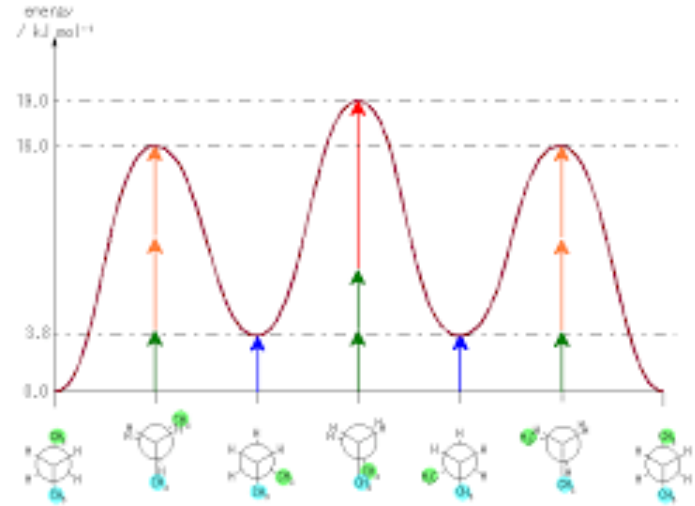


More Dynamic feature of Molecule

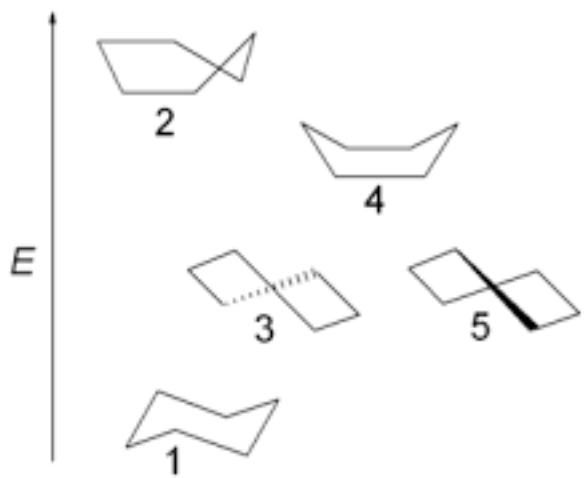
Annmonia



30GHz



Cyclohexane Boat-Chair Conformation change



Change Volume → $\Delta\delta_T$

Induced Charge → $\Delta\delta_P$

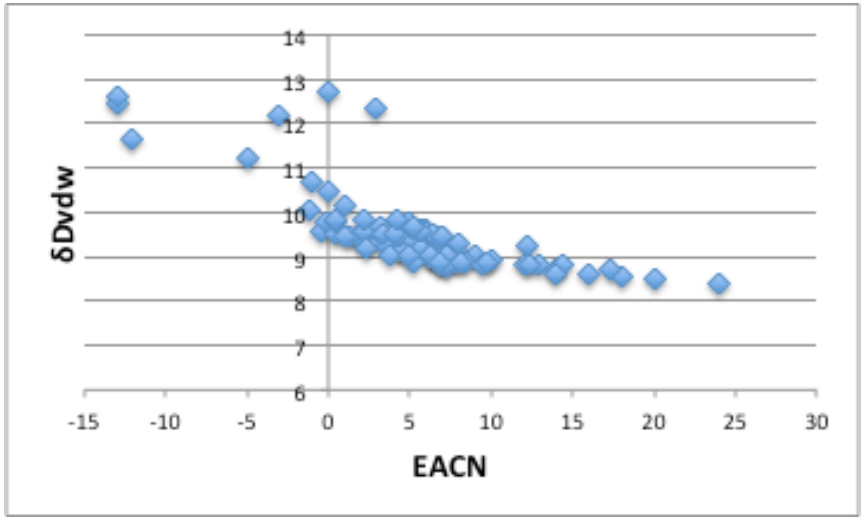
Kill Hydrogen Bond → $\Delta\delta_H$

Even Hydrocarbons have δ_{Dfg}

Fluorocarbons have little δ_{Dfg}

100,000 times per second at room temp.

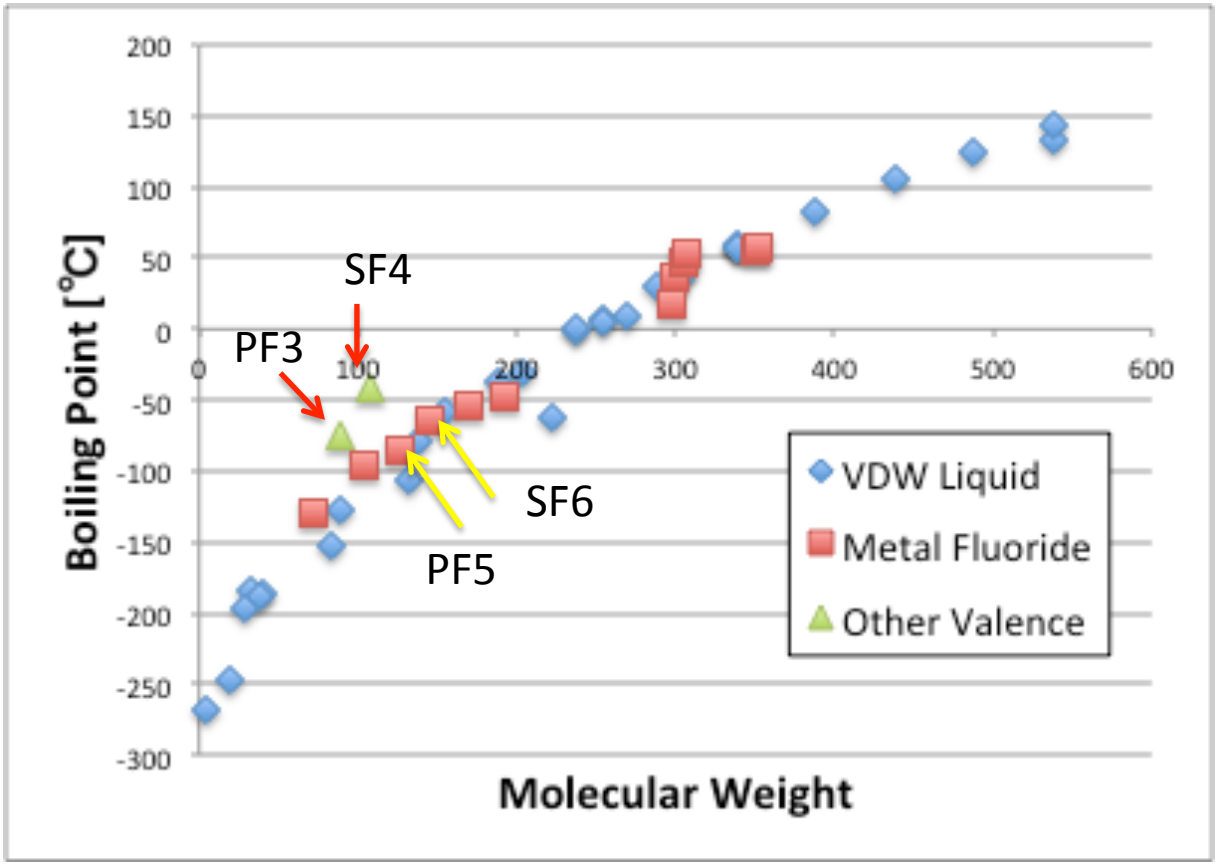
Equivalent Alkane Carbon Number (EACN)



EACN=7.9 δDvdw=8.9

EACN=8.0 δDvdw=9.1

Some of the Metal Fluorides become Liquid with only VDW force



From left NF3, SiF4, PF5, SF6, AsF5, SeF6, WF6, ReF6, OsF6, IrF6, NpF6, UF6

These Metal Fluorides may have no Catalytic activity