Health and Safety Session

Solvents, Scents and Sensibility

Part II

Swapping: Solvent Substitution Strategies

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Please Note: This slideshow was originally presented in the Health & Safety Committee Session, *Sustaining the Conservator,* at the American Institute for Conservation's 42nd Annual Meeting on May 31st, 2014.

Questions or comments, please contact: HealthandSafety@conservation-us.org

Yesterday – Sustainability Session

- Yesterday’s talk focused on minimizing the use of solvents by mixing solvent based systems in very small quantities and replacing solvents, where possible, with Pemulen emulsions.
- Today I’ll talk about strategies for substituting safer solvents for less-safe solvents.
- (Sorry about the title mix-up)

The very bad boys
(very sexist, I know)

- Benzene - known human carcinogen
  - Really bad – don’t use
  - Replace with xylene or toluene (pick your poison)
- n-Hexane – neurotoxin that causes peripheral nerve damage
  - To make it water soluble so it can be excreted from the body, it’s metabolized into a really nasty chemical
  - Pretty bad and no reason to use
  - Replace with n-heptane – nearly same behavior and doesn’t react in the body the same way because it’s a 7 carbon chain rather than 6

More bad boys
(also sexist)

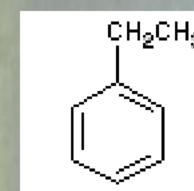
- DMF (N, N-dimethylformamide)- likely carcinogenic and teratogenic
  - Readily passes through skin
  - Replace with N-Methyl-2-pyrrolidone (NMP) – perhaps – not much safer
- Methanol – toxic – 10mL can cause blindness
  - Readily passes through skin
  - Replace with ethanol – close enough

Even more bad boys
(still sexist)

- Cellosolve® and Cellosolve® acetate (2-ethoxyethanol and 2-ethoxyethyl acetate)
  - Blood changes, teratogenic
  - Replace with butyl Cellosolve® (?) (2-butoxyethanol)
- Chlorinated solvents
  - Really bad for people (except 1,1,1 trichloroethane) and all are really bad for environment (ozone depletion)
  - Banned, don't use

The problem with the xylene

- Properly **xylenes**
  - Mixture of the ortho- meta- and para- isomers
  - That’s fine and dandy, but…
- Also contains ethyl benzene
  - Bad guy
  - Possible human carcinogen
  - Can be present at 10% – 30%!!!



Can’t really know anything about xylenes’ or xylene’s H&S because of the variable amount of ethyl benzene

- That’s why epidemiological studies of xylene are all over the map in terms of hazard to humans
- Use single isomer of xylene?
  - Perhaps better/safer
  - Never really studied because it’s much more expensive and it’s not used industrially
  - Fisher: o-xylene 4L = $294
same grade xylenes 4L = $242
conservation supplier 4L = $ 44

Safe solvents vs. Untested solvents

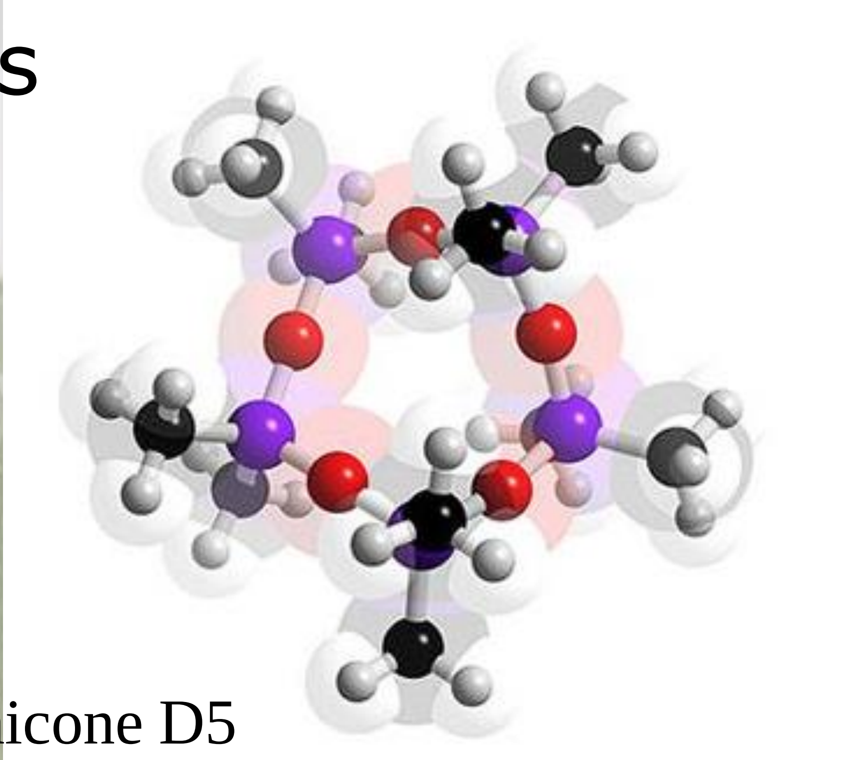
- Many solvents, particularly newer solvents seem safe because they haven't been thoroughly tested and haven't been around long enough for epidemiological studies
- e.g. d-limonene and NMP marketed as "safe solvents" until usage and testing demonstrated not as safe as thought to have been

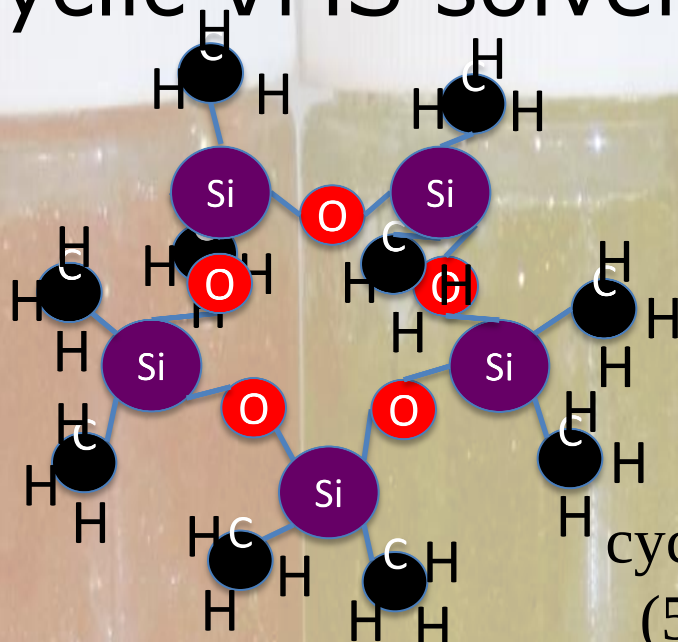
Lots of new solvents

- Ask Alan Phenix about the exotic ones

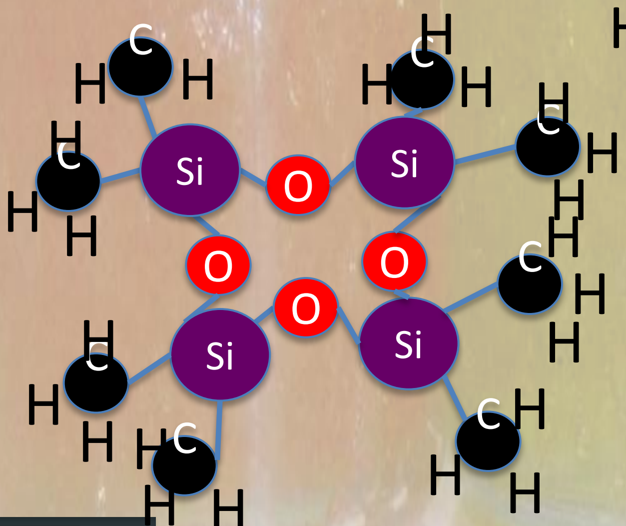
- Silicone solvents
  - Often referred to as VMS - Volatile MethylSiloxanes
    - Cyclic or linear
    - Part of family that include non-volatile silicone oils, gels and rubbers
  - Used in:
    - Antiperspirants
    - Skin care products
    - Sunscreen products
    - Hair conditioners
    - Facial make-up
  - Add new meaning to low polarity.

Cyclomethicone Solvents (cyclic VMS solvents)



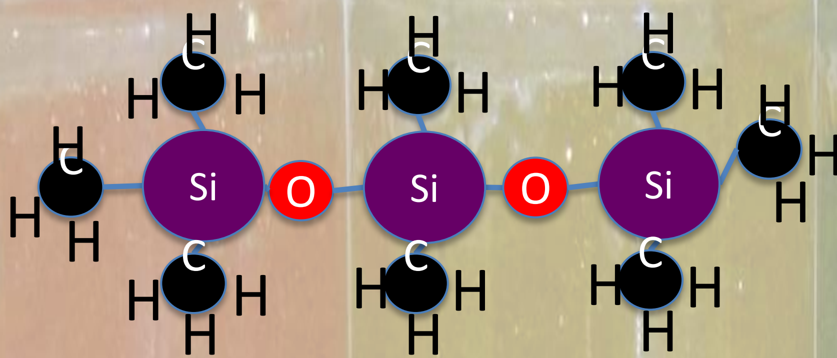


cyclomethicone D5
(5 silicon atoms)
bp. 210° C

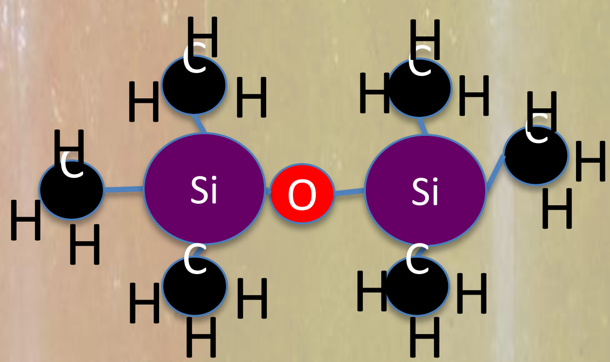


cyclomethicone D4
(4 silicon atoms)
bp. 172° C

Linear VMS Solvents



Octamethyltrisiloxane
(3 silicon atoms)
bp. 152° C



Hexamethyldisiloxane
(2 silicon atoms)
bp. 100° C

Silicone solvents

- Practically odorless – not necessarily a good thing, but nice
- Probably safe
  - Some studies are showing potential health hazards
  - Daily exposure (particularly for women) is quite high
  - Body burden – particularly problematic for people with silicone breast implants

Environmental

- Bad in wastewater stream (where hair conditioner goes)
- Decomposes quickly in atmosphere to silicon dioxide and methane (yes, a greenhouse gas)
- One of the chemicals used for cloud seeding (clouds nucleate on silica)
- Solvent waste can be burned in cement manufacture to add micro-silica

Really mean

When added to a car's gasoline supply:

- Converts to silica during combustion
- Literally grinds down cylinder and destroys engine
- Unlike sugar, which every mechanic knows the symptoms of, source of damage would be unrecognized

The good guys

- Benzyl alcohol
  - Aromatic and alcoholic functionality
  - Generally very safe
    - Used in cosmetics
    - Preservative (bacteriostatic preservative in low concentrations in IV medications)
  - Toxic to eyes – pure benzyl alcohol produces corneal necrosis (thank you Google and Wikipedia)
  - Toxic to neonates

More good guys

- Ethyl alcohol
  - MSDS looks pretty bad, but heck, we drink the stuff
  - Yes, it’s a fetotoxin when consumed by pregnant women
  - Yes, you can die of alcohol poisoning, but you have to drink a lot.
  - Problem of denatured alcohol – methanol, isopropanol, jet fuel added to make it non-drinkable

Yet more good guys

- Isopropyl alcohol – rubbing alcohol
- Acetone – had been demoted lately, but still used in nail polish remover
- Ethyl acetate – not used much in conservation, but relatively safe (also in nail polish remover)

What you really came here for:

- Is there a perfect, safe substitute for xylene?

Nope

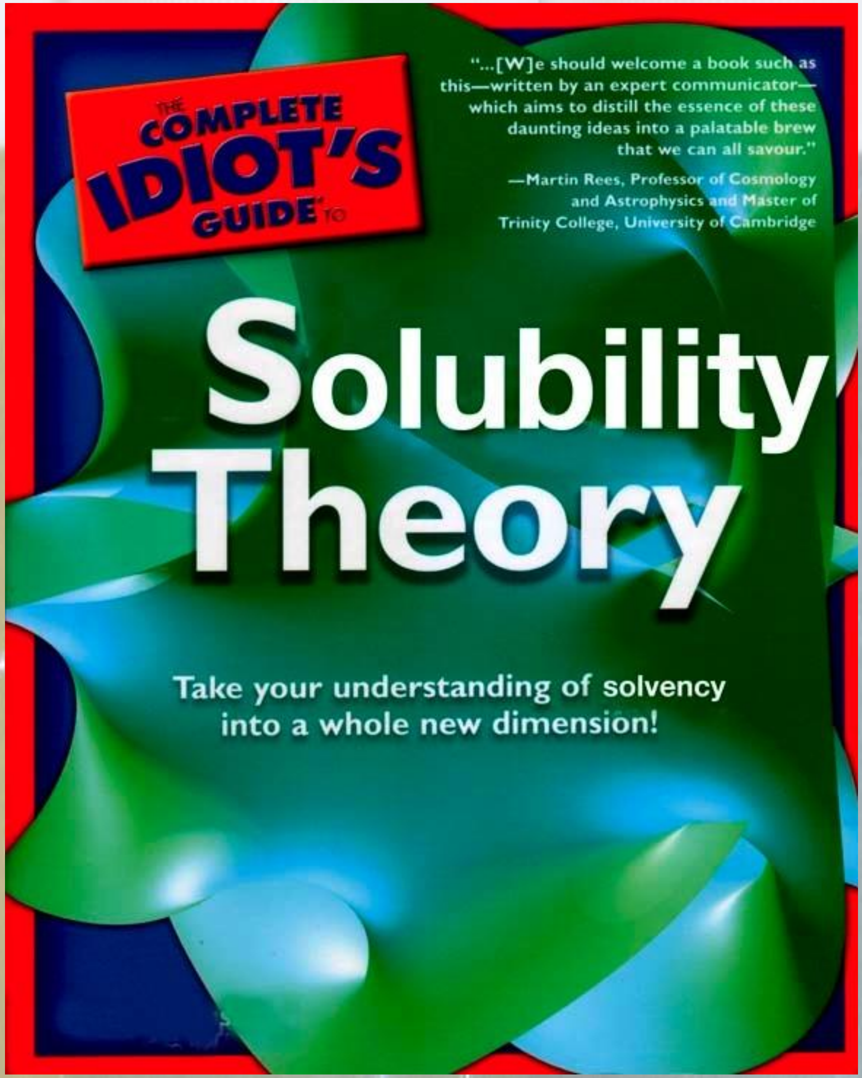
(Damn)

And now for a word or two about solubility theory

(damn)

- Tool for understanding why solvents work the way they do
- Basis for combining solvents to work better - tailoring solvent cleaning systems
- Basis for finding solvents or solvent combinations to replace less healthy solvents on a case-by-case basis

A Simplified View of Solubility Theory



(not a real book)

Like Dissolves Like

Intermolecular Forces:

- If there were no intermolecular forces, organic molecules would all be gasses.

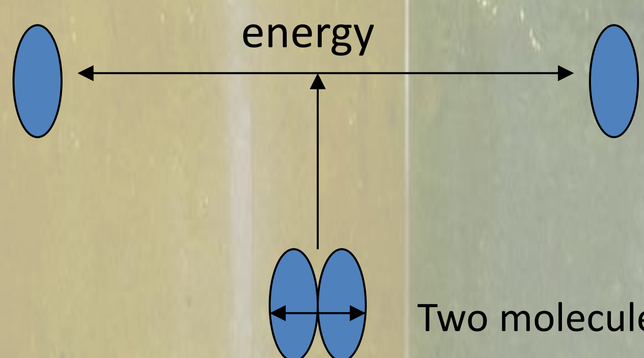
"Like dissolves like"

- "Like" must be evaluated in a decidedly chemical way.
- The more one molecule of a material is "like" another material, the greater is the chance for them to be mutually attracted.
- An interesting special case of mutual attraction is when the molecules are identical as in a solvent.

The basic thought experiment:

Consider a pure solvent.

- it's a liquid
- there is some attractive force holding the molecules together
- let's try to quantify it



Two molecules in a liquid

The energy to separate molecules of a solvent:

Energy to separate a mole of solvent molecules: -U

$-U = \Delta H_V - RT$ (at room temperature).

The Molar Vaporization Enthalpy at 25°C: ΔH_V

Solvent	-U (kJ/mole)	ΔH_V @ 25° (kJ/mole)
Ethanol	39.84	42.32
Acetone	28.51	30.99
Toluene	35.62	38.10
n-Heptane	34.09	36.57

Not very revealing

More practical: work in volume not moles:

Molar Volume: V_M = MW/density

[density = g/ml • MW (molecular weight) = grams/mole]

Solvent	V_M (ml/mole)
Ethanol	58.5
Acetone	74.0
Toluene	106.8
n-Heptane	147.4

Cohesive Energy Density (CED)

Cohesive energy divided by molar Volume - Cohesive energy per volume.

Solvent	CED
Ethanol	681
Acetone	385
Toluene	333
n-Heptane	231

Hildebrand Solubility Parameter (δ)

Square root of CED - solubility parameter, total solubility parameter, Hildebrand solubility parameter or cohesion parameter.

Solvent	CED	δ
Ethanol	681	26.5
Acetone	385	20.0
Toluene	333	18.3
n-Heptane	231	15.3

Hildebrand Solubility Parameter (δ)

$$\delta = \sqrt{(\Delta H_V - RT)/V_M}$$

Hildebrand Scott Equation:

- an <u>estimate</u> of the molar enthalpy of vaporization based only on the boiling point of the solvent!

- $\Delta H = -12340 + 99.2(T_b) + 0.084(T_b)^2$

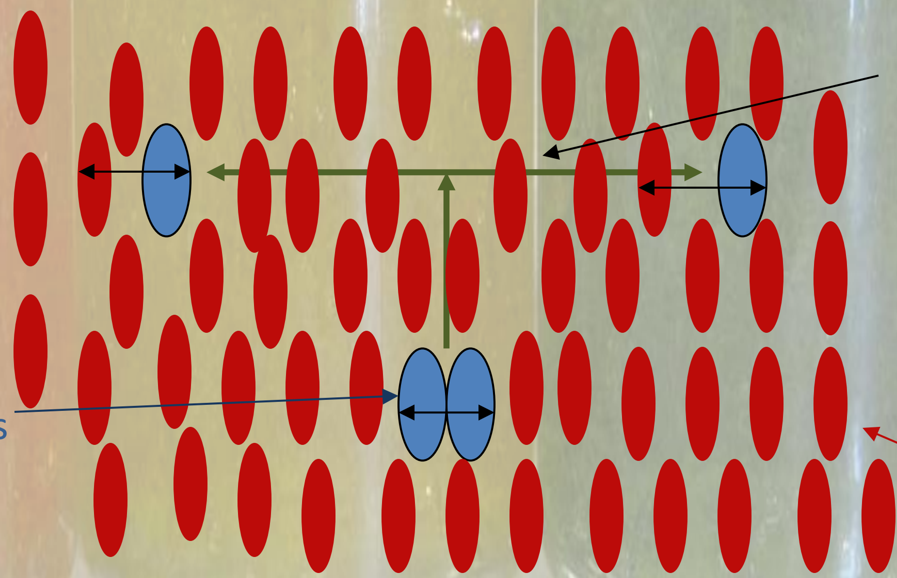
so

$$\delta = \sqrt{(12340 + 99.2(T_b) + 0.084(T_b)^2 - RT)/V_M}$$

The concept with solvents and solutes:

Really the same thing

- solute is being dissolved into solvent
- the more alike solvent is to solute the more likely it is that the solute can be dispersed into the solvent
- obvious case, when solvent and solute are the same, the solution is well dispersed (into itself)



A problem with Hildebrand solubility parameters:

n-propanol: $\delta = 24.5$

dimethylformamide (DMF): $\delta = 24.8$

- solvents are very different
- total solubility parameter is an aggregate value
    - combines many different types of intermolecular interactions

Component intermolecular forces:

- dispersion forces
- dipolar forces
- hydrogen bonding forces

Dispersion forces

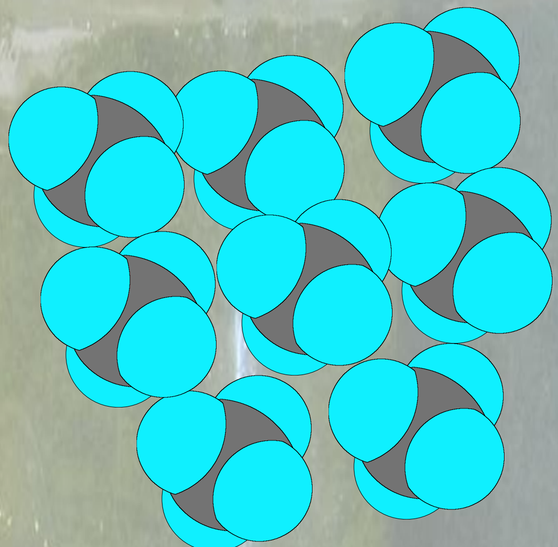
- weakest
- present between all molecules
- van der Waals or London
- based on quantum mechanics
- like attracted to like
- alkanes

Dispersion forces I

- alkanes

- Methane - CH_4

gas
mp -182.4° C (-296.3° F)
bp -161.6° C (-258.9° F)



Gas because

- Very little area of overlap and contact between molecules
- lower force

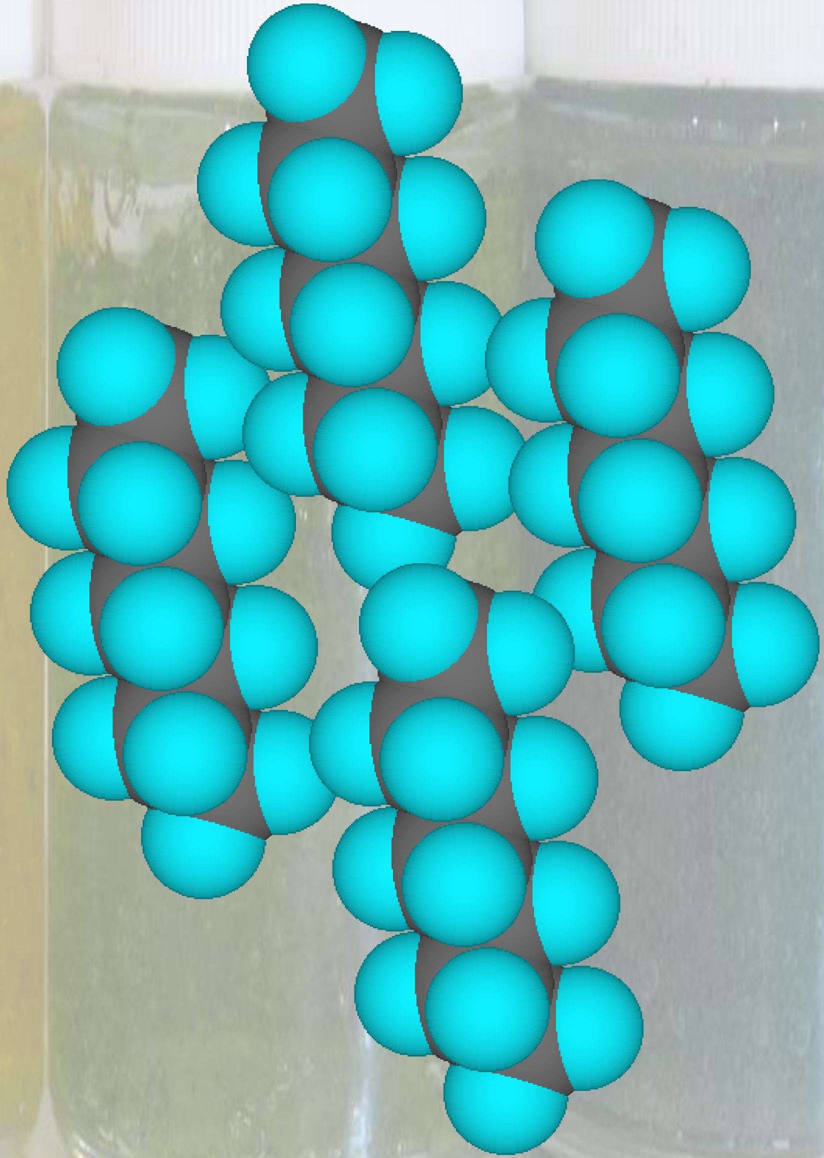
Dispersion forces II

- alkanes
  - n-heptane - C_7H_{16}

liquid

mp -90.6° C (-131.1° F)

bp 98.5° C (209.3° F)



Liquid because

- lower area of overlap and contact between molecules
- lower force

Dispersion forces III

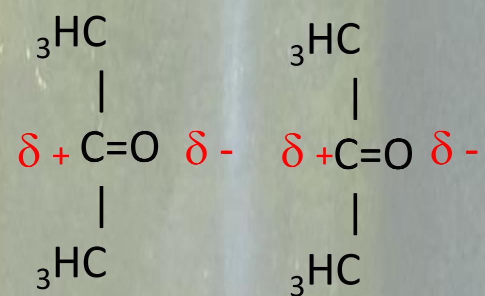
- alkanes
  - octadecane - $C_{18}H_{38}$
    a waxy solid (on a cold day)
    mp 28° C (82° F)
    bp 316° C (600° F)

solid because

- greater area of overlap and contact between molecules
- higher attractive force

Dipolar forces

- often called Polar forces (confusing…)
- electrostatic attraction between dipoles (both permanent and induced)
- ketones



Hydrogen bonding forces

- strongest intermolecular forces
- form weak bonds between hydrogen attached to a strongly electronegative atom and another strongly electronegative atom
- alcohols

R-O - - - H O-R
    H

Hydrogen bonding - Problems

- need a H-bond donor and an H-bond acceptor to form bonds
- some solvents have both donor and acceptor functionality - alcohols & water

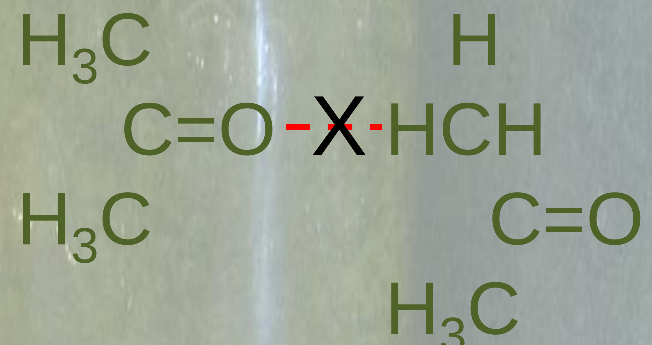
R-O - - - HO-R
H

H-O - - - H-O
H H

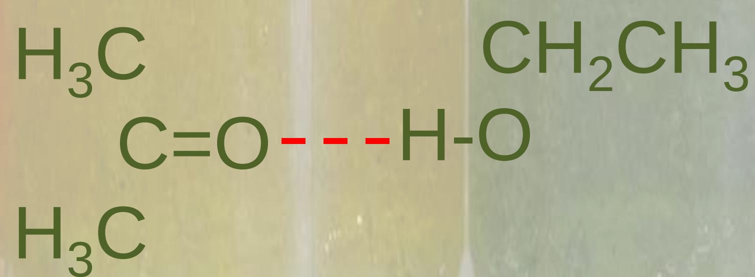
- why water is a liquid at room temperature and why it expands on freezing

Hydrogen bonding - Problems II

- but, a ketone has only an acceptor site
- by itself, a ketone has no capacity for hydrogen bonding (but it still has strong dipolar attraction)



- but, add an alcohol….



Hydrogen bonding - Problems III

H_3C CH_2CH_3

$C{=}O$---$H\text{-}O$

H_3C

- This is why acetone seemed to be misplaced in those calculations for the amount of energy it took to separate the molecules and it's Hildebrand solubility parameter
- Also why it can absorb water so strongly

H_3C

$C{=}O$---$H\text{-}O$

H_3C H

Hansen Solubility Parameters

Separate Hildebrand into three component forces

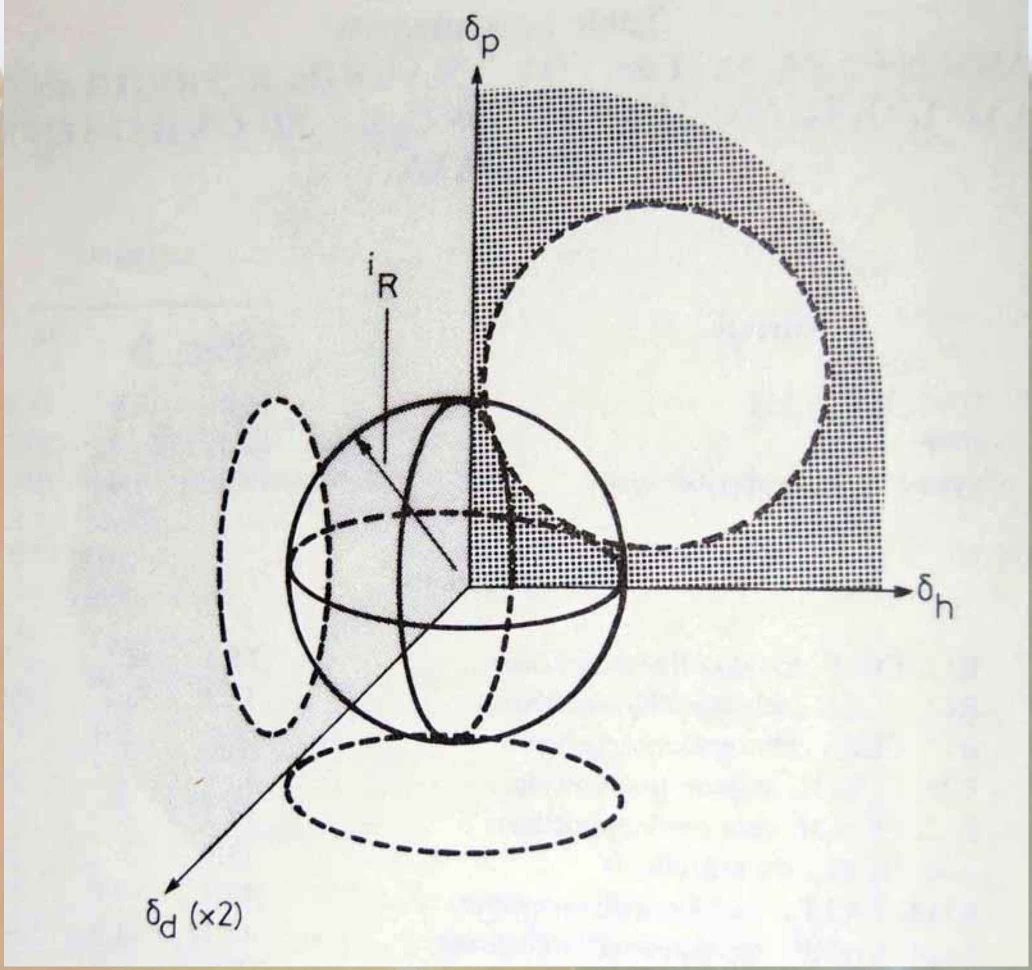
- dispersion δ_d
- dipolar δ_p
- hydrogen bonding δ_h

$$\delta^2 = \delta^2_d + \delta^2_p + \delta^2_h$$

Hansen Solubility Space

- Requires three dimensions
- Solvents are represented as points in three dimensional space
- Solutes are represented as a sphere in three dimensional space
- Specified by the point at the center of the sphere and a radius
- The center of the sphere is the point of optimum solubility
- Any solvent inside the sphere will dissolve the solute
- Any solvent outside the sphere will not dissolve the solute

Hansen Solubility Space II

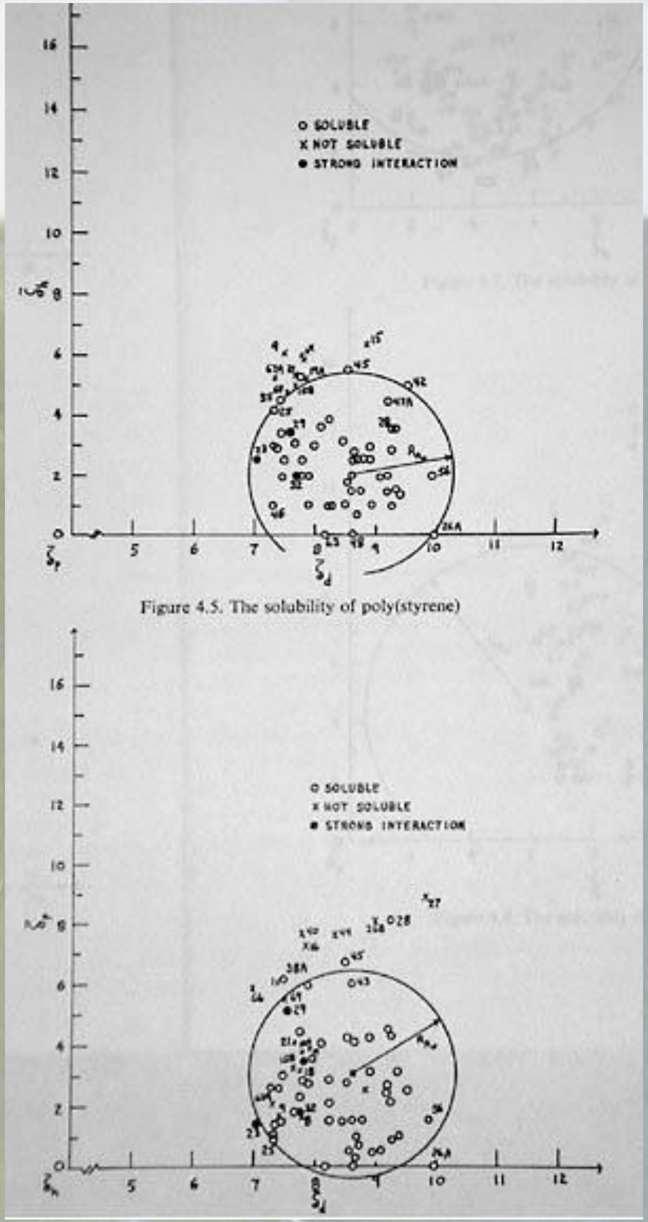


from “CRC Handbook of Solubility Parameters and Other Coghesion Parameters” by Allan F. M. Barton, 1983, p 163

Hansen Solubility Space III

The solubility of poly(styrene) projected on:

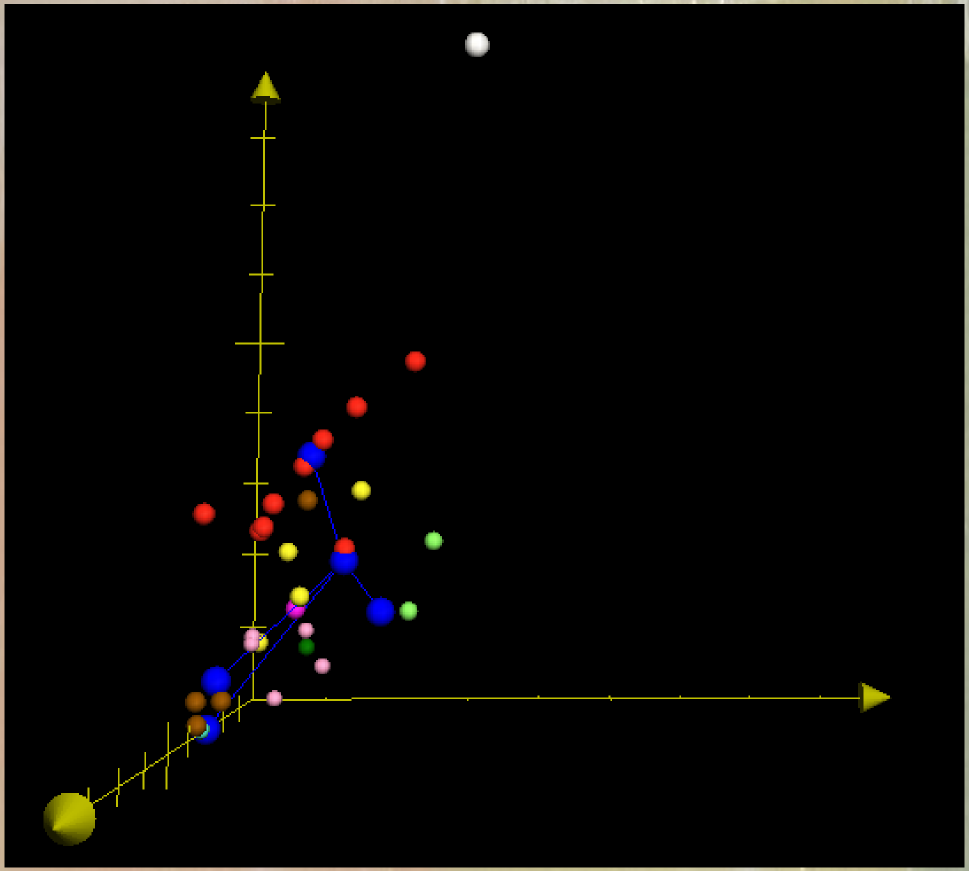
- δ_d and δ_h plane
- δ_p and δ_d plane

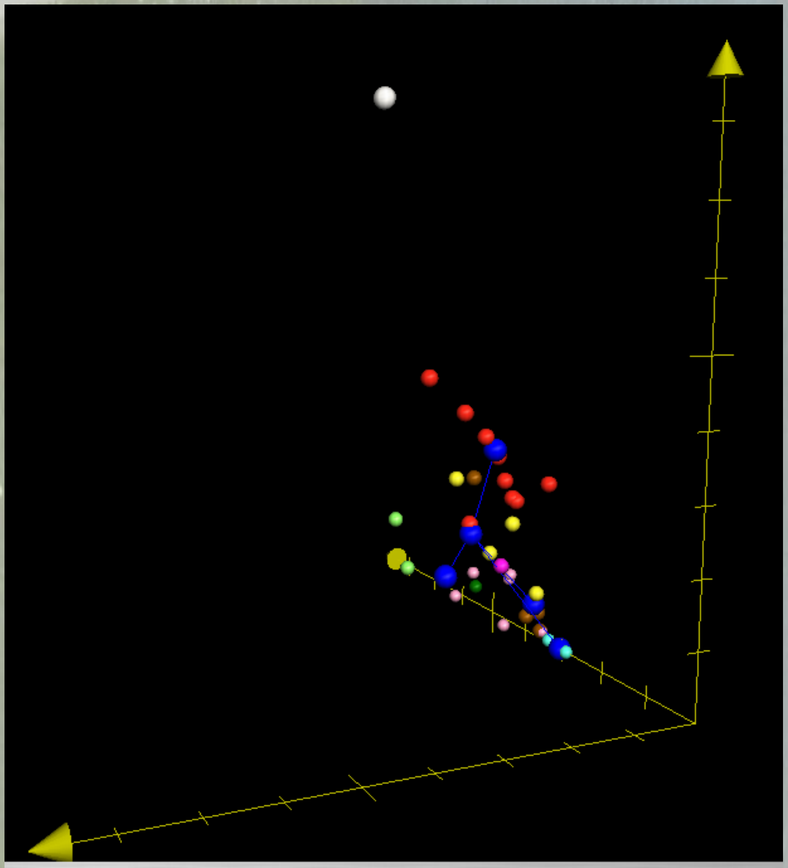


from “The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient” by Charles H. Hansen, 1967, p 36.

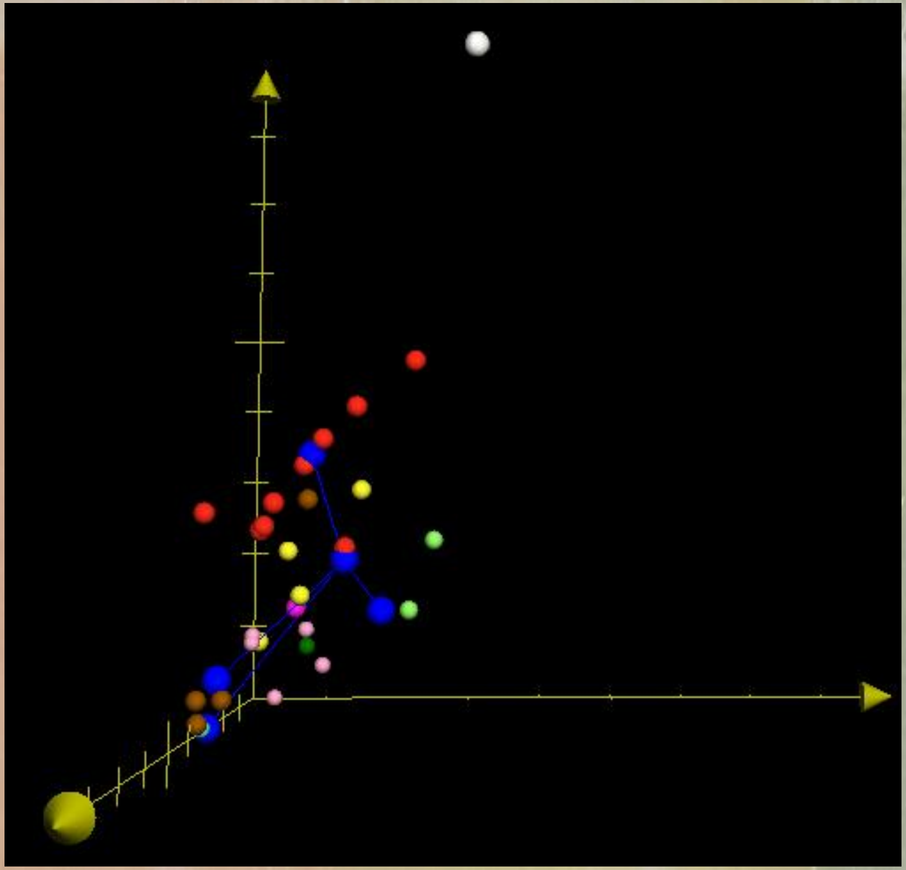
Hansen Solubility Space

- three dimensional - Macs can view with Grapher





Hansen Solubility Space



Indices:

- dispersion
- dipolar
- H-bonding

Data points

red - alcohols

blue - four solvents mixed

white - water

Hydrogen bonding - Problems redux

Hansen

- assumes all molecules capable of hydrogen bonding will form bonds
- assumes that there is no distinction between H-bond donors and acceptors
- assumes “like dissolves like”

The Teas Diagram

In 1968, J. P. Teas normalized Hansen solubility parameters and graphed the fractional solubility parameters on a triangular graph.

- An excellent visualization tool.
- shorthand when you can't work in three dimensional space (either graphically or computationally).

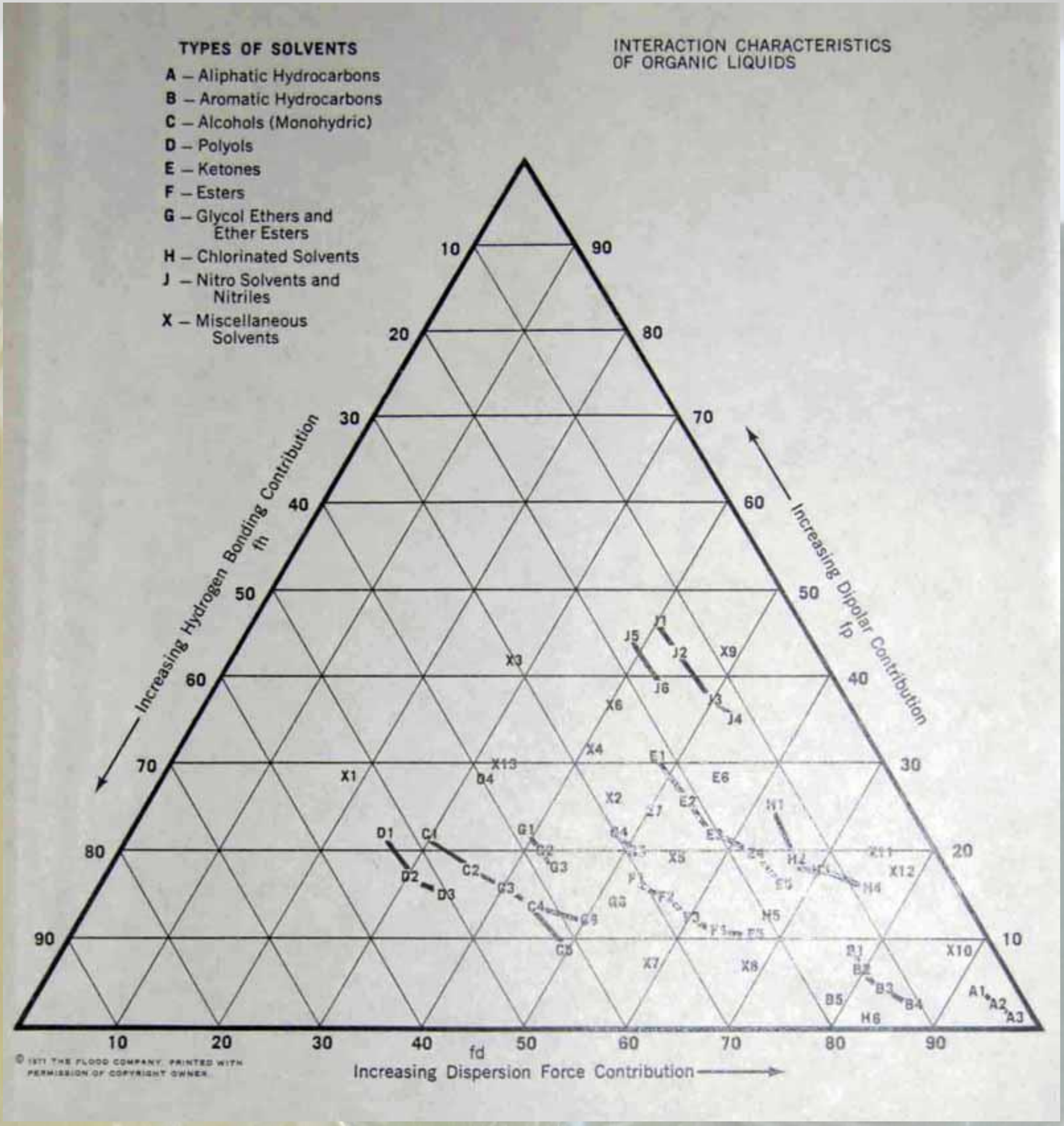
The Teas Fractional Solubility Parameters

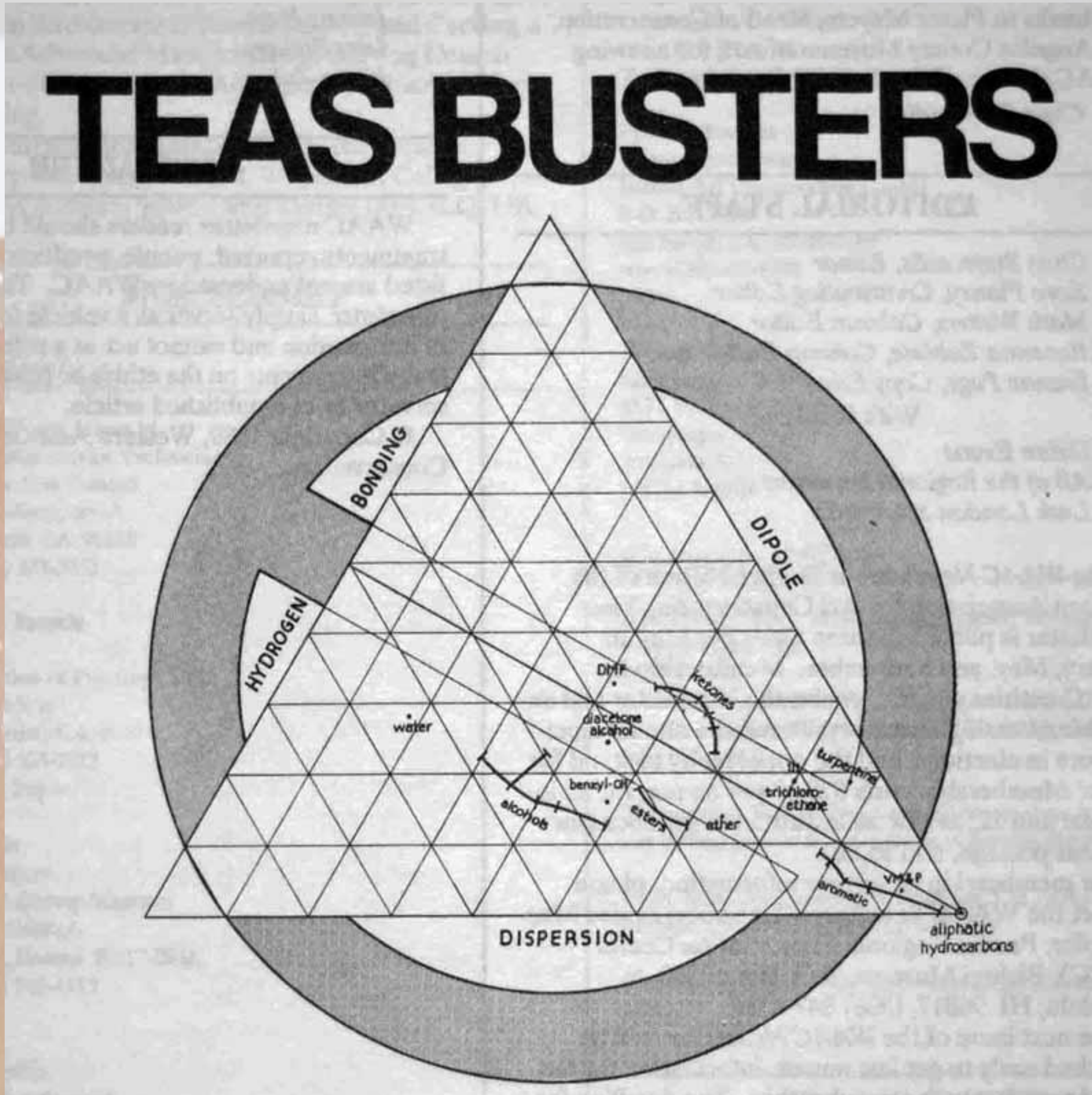
$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h} \times 100$$

$$f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h} \times 100$$

$$f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \times 100$$

The Teas Diagram




TEAS BUSTERS
HYDROGEN
BONDING
DIPOLE
DISPERSION
DMF
ketones
diacetone alcohol
water
turpentine
benzyl-OH
trichloro-ethane
alcohols
esters
ether
aromatic
VM&P
aliphatic hydrocarbons

For more information on Hansen and other solubility theories, see:

Alan Phenix: "Solubility Parameters and the Cleaning of Paintings: an update and review." *Kunsttechnologie Konservierung*, Heft 2, Jargang 12. 1998. pp 387-409.

John Burke: "Solubility Parameters: Theory and Application." AIC Book and Paper Annual, Volume 3. 1984. Pp 13-58. Also available online.
http://sul-server-2.stanford.edu/byauth/burke/solpar/

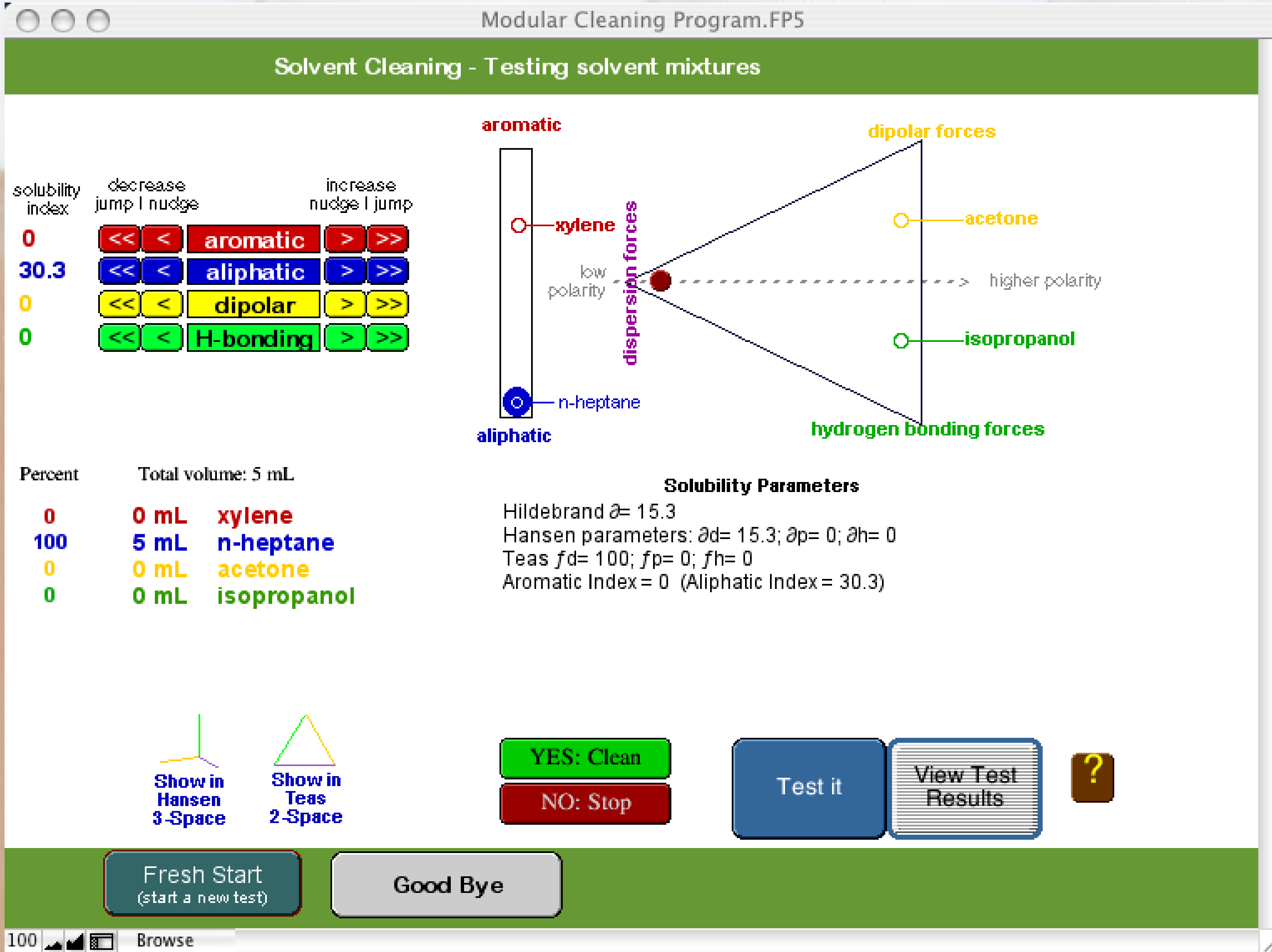
Working with Solvents in the MCP

A solution set is a selection of four solvents.

Each solvent represents one of four solubility indexes:

aromatic
aliphatic
dipolar
hydrogen bonding

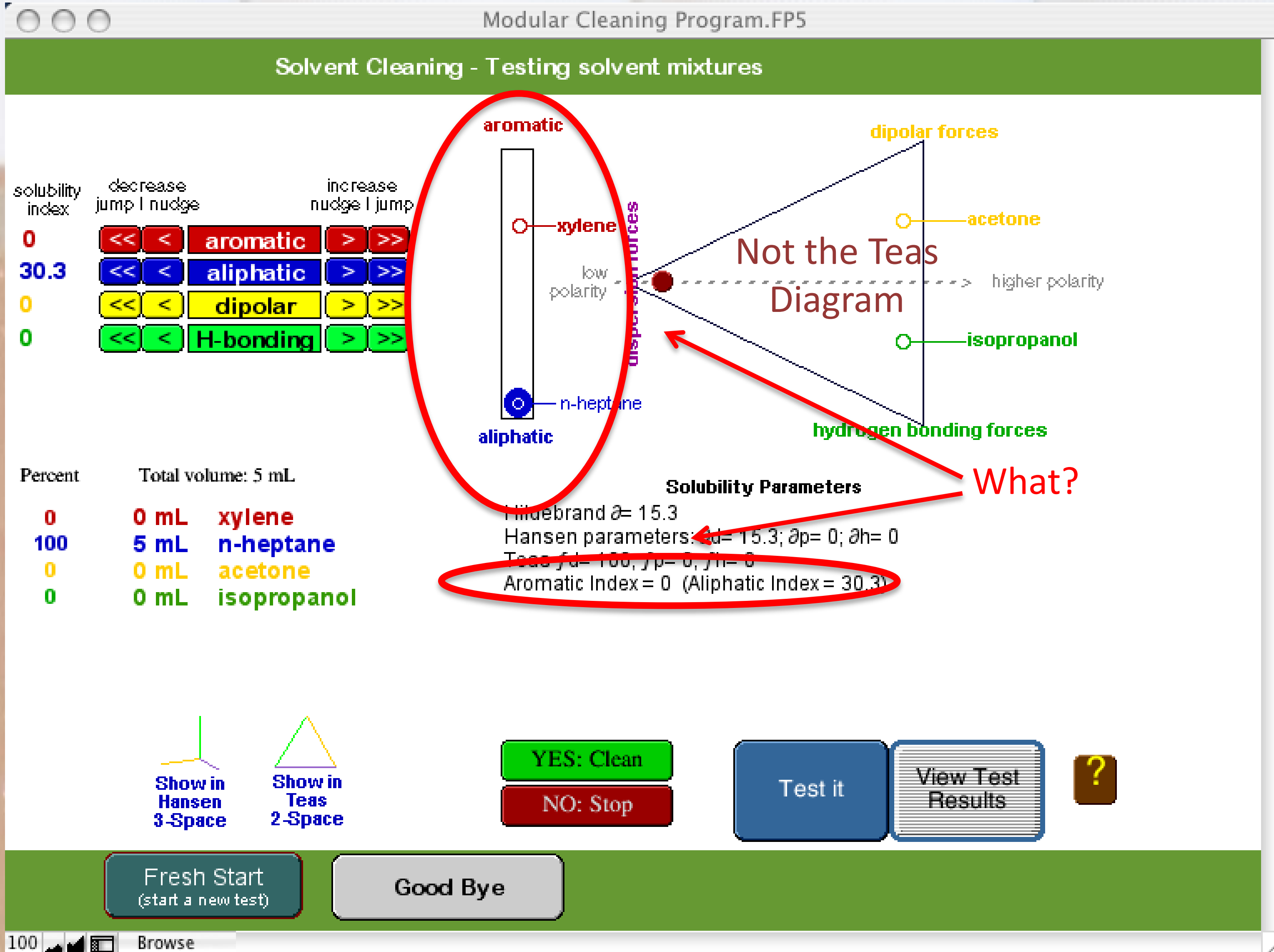

Modular Cleaning Program.FP5
Solvent Cleaning - Step One, Setting Up
aromatic solvent / solution
xylene
change
aliphatic solvent / solution
n-heptane
change
dipolar solvent / solution
acetone
change
hydrogen bonding solvent / solution
isopropanol
change
50.4% n-heptane
% isopropanol
volume of test solution: 5 mL
resolution of mixing proportions: 1 mL drop(s)
Continue with Solvent Cleaning



Modular Cleaning Program.FP5
Solvent Cleaning - Testing solvent mixtures
solubility index
decrease jump I nudge
increase nudge I jump
0
30.3
0
0
<< < aromatic > >>
<< < aliphatic > >>
<< < dipolar > >>
<< < H-bonding > >>
aromatic
xylene
dispersion forces
low polarity
higher polarity
n-heptane
aliphatic
dipolar forces
acetone
isopropanol
hydrogen bonding forces
Percent
Total volume: 5 mL
0 0 mL xylene
100 5 mL n-heptane
0 0 mL acetone
0 0 mL isopropanol
Solubility Parameters
Hildebrand ∂= 15.3
Hansen parameters: ∂d= 15.3; ∂p= 0; ∂h= 0
Teas ƒd= 100; ƒp= 0; ƒh= 0
Aromatic Index = 0 (Aliphatic Index = 30.3)
Show in Hansen 3-Space
Show in Teas 2-Space
YES: Clean
NO: Stop
Test it
View Test Results
?
Fresh Start (start a new test)
Good Bye
100
Browse

Also note:

- **Hildebrand solubility parameter**
- **Hansen fractional solubility parameters**
- **Teas fractional solubility parameters**


Modular Cleaning Program.FP5
Solvent Cleaning - Testing solvent mixtures
solubility index
decrease jump | nudge
increase nudge | jump
0
30.3
0
0
aromatic
aliphatic
dipolar
H-bonding
aromatic
xylene
low polarity
n-heptane
aliphatic
dipolar forces
acetone
higher polarity
isopropanol
hydrogen bonding forces
Not the Teas Diagram
What?
Percent
Total volume: 5 mL
0 0 mL xylene
100 5 mL n-heptane
0 0 mL acetone
0 0 mL isopropanol
Solubility Parameters
Hansen parameters: ∂d= 15.3; ∂p= 0; ∂h= 0
Aromatic Index = 0 (Aliphatic Index = 30.3)
Show in Hansen 3-Space
Show in Teas 2-Space
YES: Clean
NO: Stop
Test it
View Test Results
?
Fresh Start (start a new test)
Good Bye
100
Browse

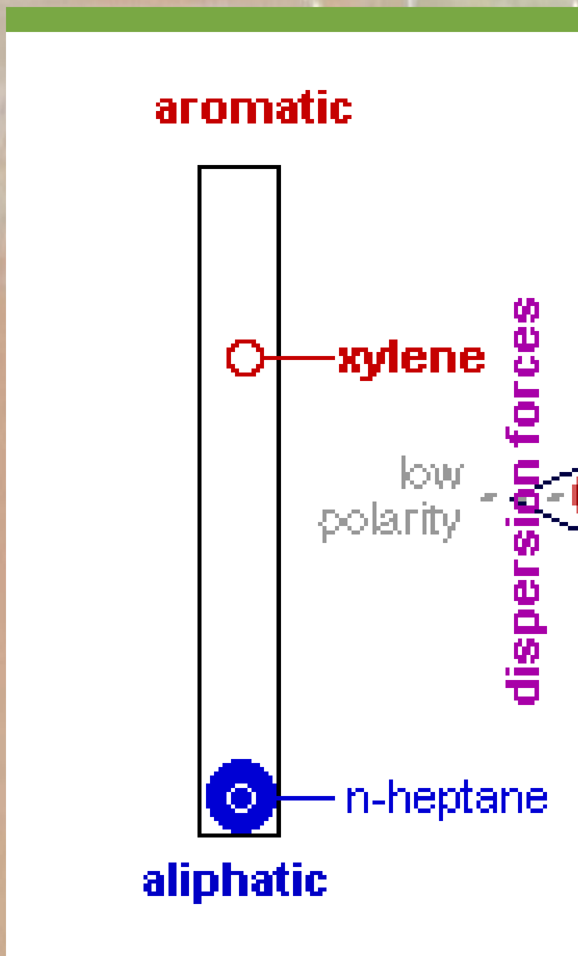
And, What you may ask is the aromatic aliphatic index

- Experience with cleaning tests
    - The aromaticity is critically important in conservation
- Cleaning an acrylic medium “varnish” that had gone off
    - In 5mL of 0% aromatic Shell Sol
    - 15 drops of Shell A-100 did nothing
    - 16 drops swelled “varnish” with minimal effect on paint below
    - 17 drops picked up paint below

Right or wrong – aromatic aliphatic index is mine

- Copied original Hansen calculation for hydrogen bonding parameter of alcohols
- Used energy difference between cyclohexane and benzene and divided by 6 (number of carbon atoms in each)

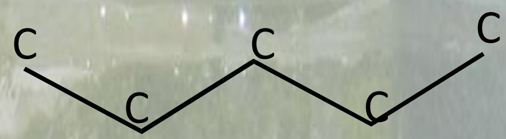
Aromatic aliphatic index



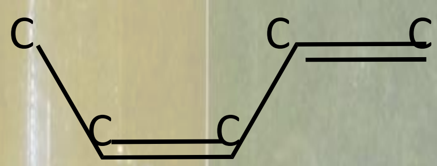
Kind of a "zoom in" on dispersion force more accurately reflecting our needs

Why? – Simplified model of ageing of organic molecule – light and oxidation

-C-C-C-C-C-



C-C=C-C=C



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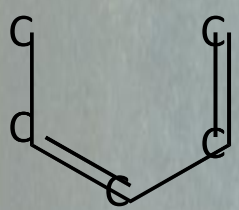
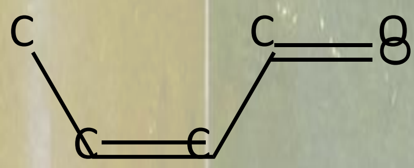


-C-C=C-C=O



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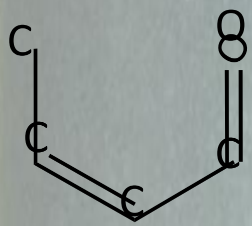
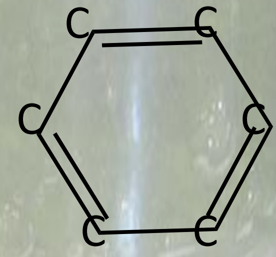


Aromatic ring:



What you really came here for Again?

- Is there a perfect, safe substitute for xylene?

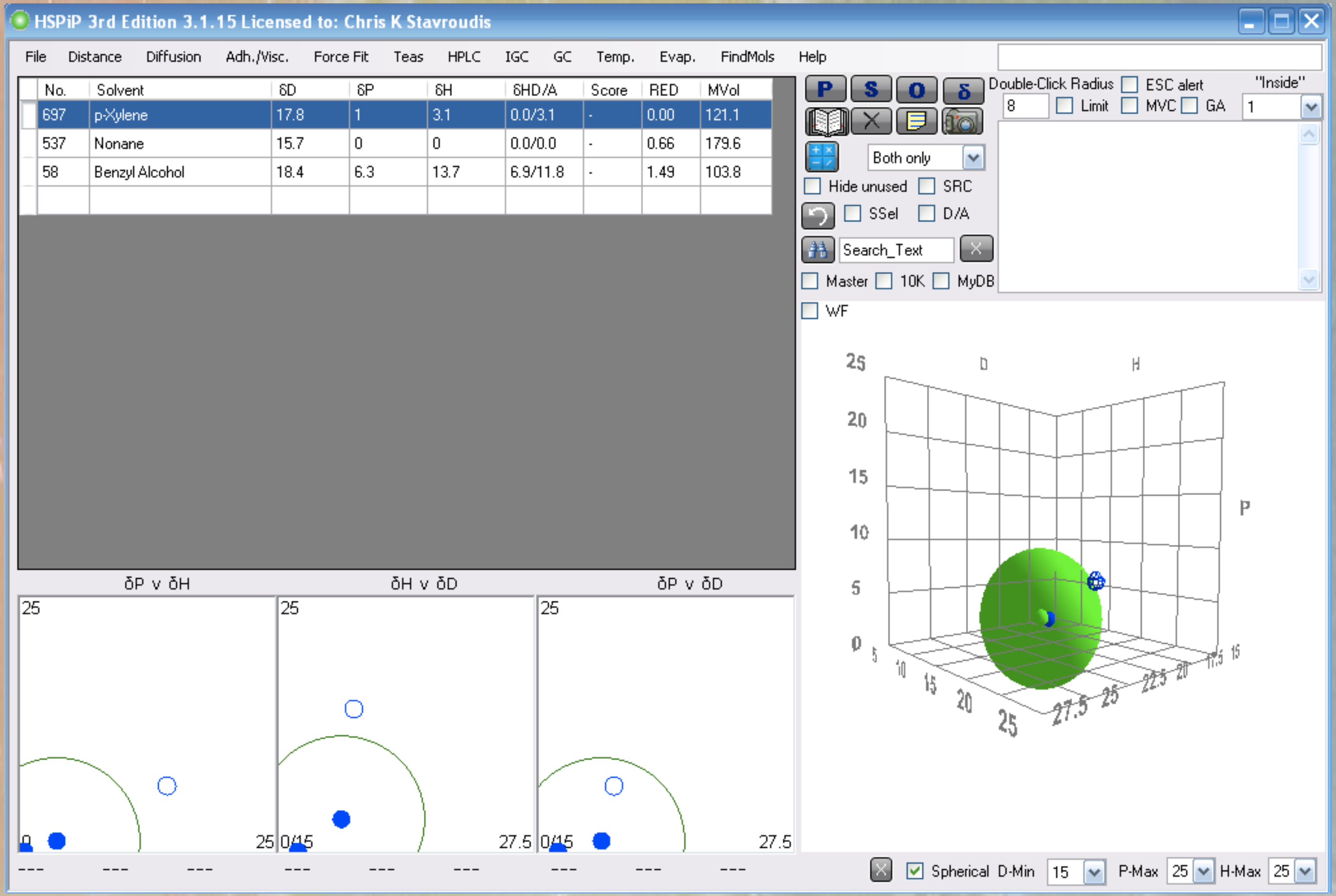
Nope

(Damn, again)

Let's try

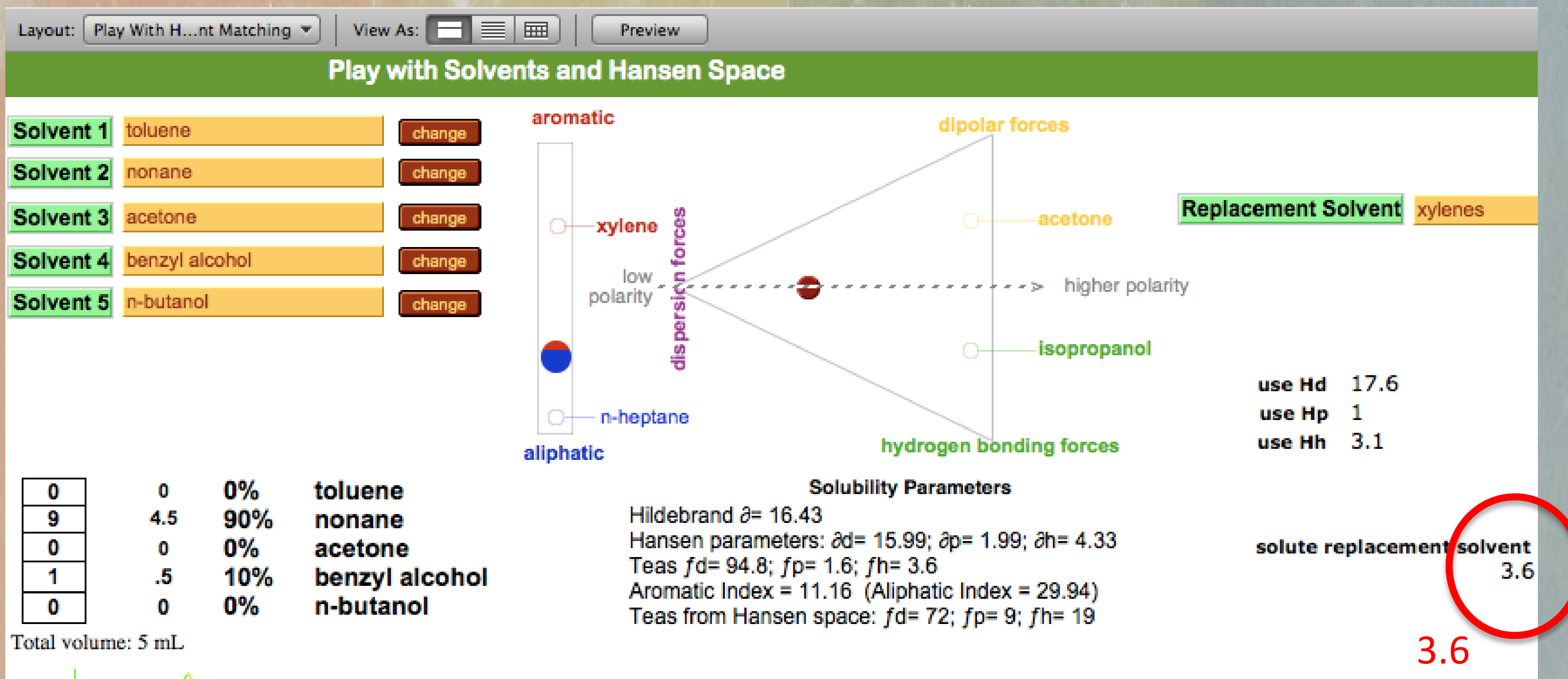
- Hansen's HSPiP (Hansen Solubility Parameters in Practice)
    - Windows Program that calculates everything Hansen (and I'm a Mac guy)
    - Expensive
    - Frustrating as all get-out
    - Damned if I can really get it to do what it's supposed to do

Here's a diagram of a Hansen sphere around xylene showing nonane and benzyl alcohol



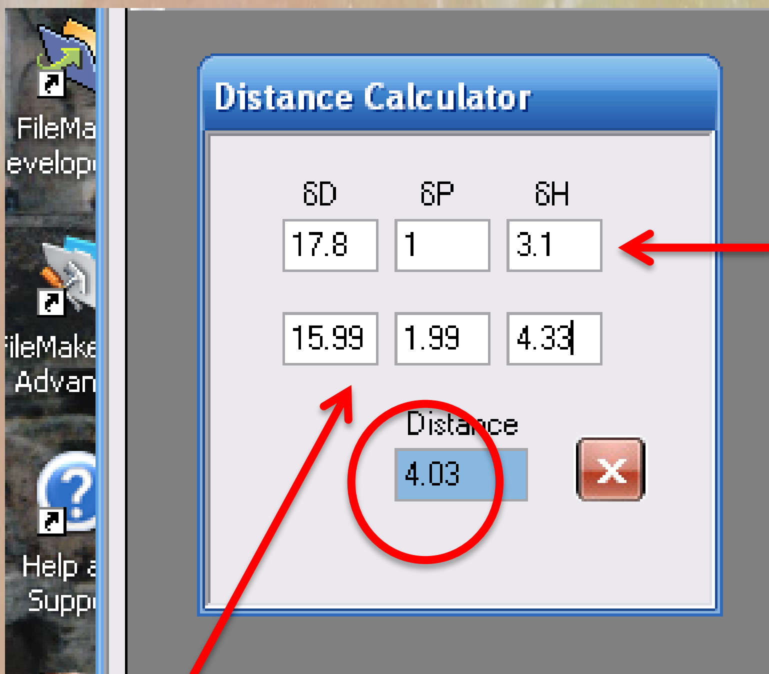
A 9:1 mixture of nonane and benzyl alcohol

(a new – as in not working entirely – feature of the MCP)



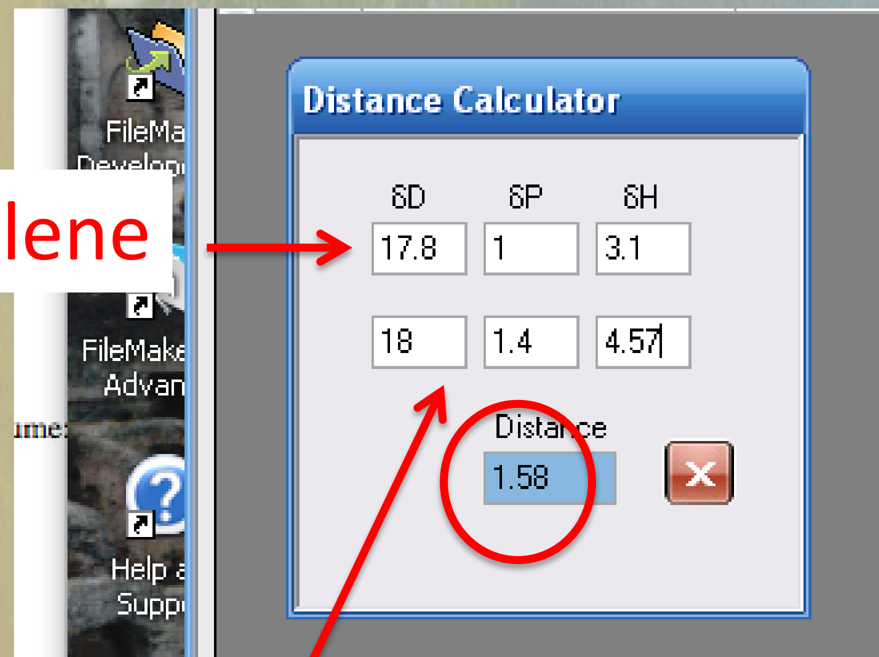
Same thing in HSPiP caluclator

For reference:



xylene

9 nonane : 1 benzOH



toluene

But do we really want a substitute for xylene?

- I would argue – No
- What we want is a safer solvent that dissolves a substrate as effectively as (or more effectively than) xylene
- Need to consider:
  - Solubility parameters
  - Evaporation rates
  - Toxicity

Examples

- Replace xylene for dissolving Gamblin Conservation Colors with
  - Isopropyl alcohol – evaporates rather quickly
  - Mixtures of mineral spirits and alcohol
  - Shell Sol A-100 (probably just as bad as xylene)

Examples

- Replace turpentine or xylene for dissolving dammar to make varnish
  - "National Gallery" formula – mixture of Shell Sols (aromatic and aliphatic –see what did I tell you about the importance of the aromatic aliphatic index?) with similar evaporation rates

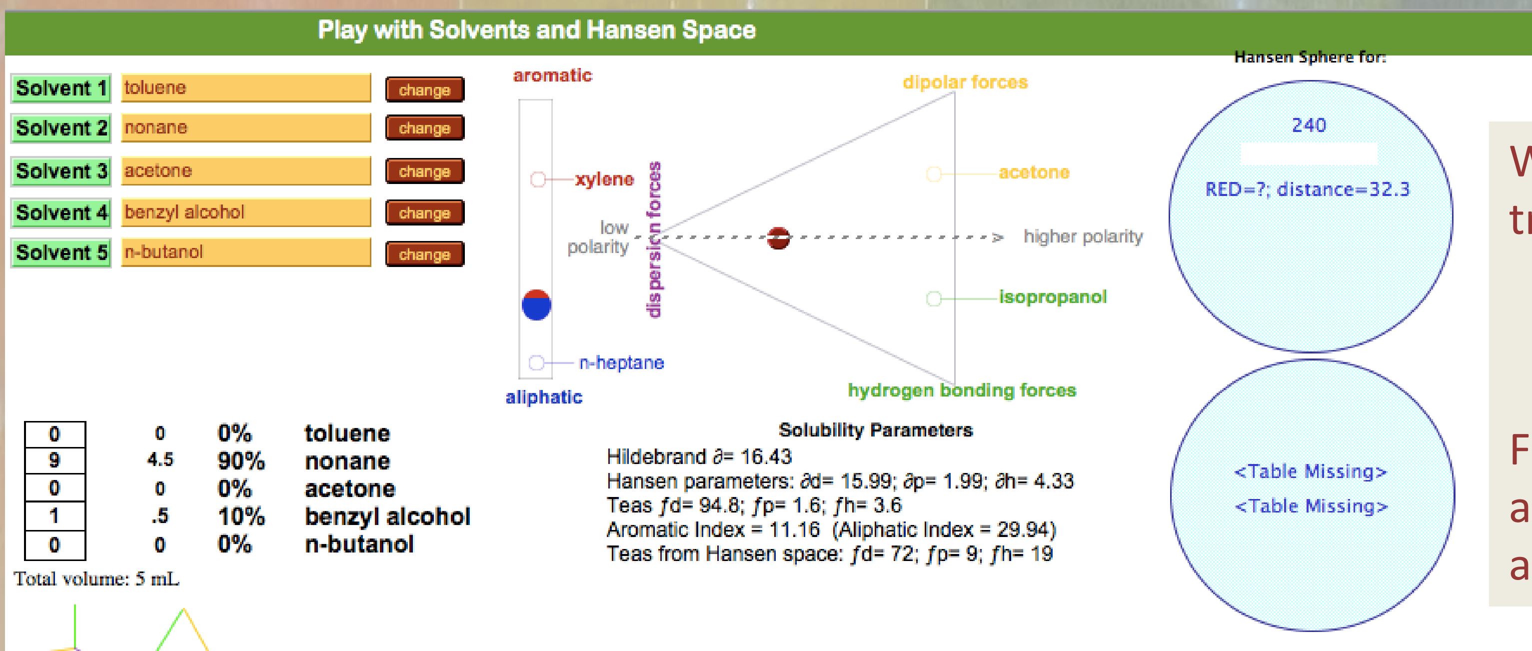
HSPiP should be able to do this

- Input Horie’s and Greg Smith’s (Buffalo students’) Teas solubility data
- Calculate Hansen sphere and radius
- Calculate best combination of safe solvents
- Calculate evaporation rate

(Damned if I can figure out how, but hope springs eternal)

Next version of MCP

- Due in the "next couple of months" …for the last two years



What we are trying to remove

From what we are trying not to affect