

Material (Chemical) Substitution for Pollution Prevention

**Dr. Kevin G. Joback
Molecular Knowledge Systems, Inc.
<http://www.molknow.com>
kevin@molknow.com
Phone: 603-472-5315**

Chemical Substitution

Thinking: Chemicals, Molecules, Properties Drivers for Pollution Prevention

- Chemical Substitution Concepts**
- Substitution Methodology**
- Strategies and Homework**

Why Substitute ?

Are you using ...

- Methylene Chloride as a Reaction Solvent ?
- Toluene as an Extraction Solvent ?
- Perfluorocarbons for Cleaning ?
- Brominated Flame Retardant Additives ?
- HCFCs as Foam Blowing Agents ?

Should I Switch To ...

Process Design / Product Design

- Ethyl Lactate as a Reaction Solvent ?
- H₂O₂ as a Cleaning Solvent ?
- Vegetable Oil as a Lubricant ?
- Ozone as a Bleaching Agent ?

Key Concept

Same Performance but Better Environmental

Property	Units	Toluene	N-Ethylmorpholine
Density	g / cc	0.86	0.91
Sol Param - P		8.00	7.60
Sol Param - H		1.60	0.70
Boiling Point	C	110.61	139.00
Flash Point	C	4.85	27.77
Daphnid 48hr LC50	ppm	15.86	28.44
Oral Rat LD 50	mg / kg	636.0	1780
Pvp at 20C	mmHg	21.80	5.80
ThOD	mg / mg	3.13	2.76

Methodology

Step 1: Specify Properties

- Solubility, BOD, Volatility, Reactivity

Step 2: Match and Design

- Closest match, Tradeoffs, Additives

Step 3: Simulate and Experiment

- Multiple Case Studies, Evaluation

Step 1: Specify Properties

**Why
are you using/making
your current chemical ?**

Step 1: Specify Properties

Gas Absorption



Pump Specs:
Flow: 1200 GPM
Head: 65 ft
Mat: Zirconium

Solvent Specs:
Solubility: ??
Volatility: ??
Reactivity: ??

Step 1: Specify Properties

- Aquatic Toxicity
- Biodegradation Rate
- Biological Oxygen Demand
- Boiling Point
- Carcinogenicity
- Compressibility
- Corrosivity
- Density
- Enthalpy of Combustion
- Enthalpy of Vaporization
- Flammability
- Freezing Point
- Global Warming
- Heat Capacity
- Ozone Degradation
- Permeability
- Reactivity
- Solubility
- Surface Tension
- Thermal Conductivity
- Vapor Pressure
- Viscosity

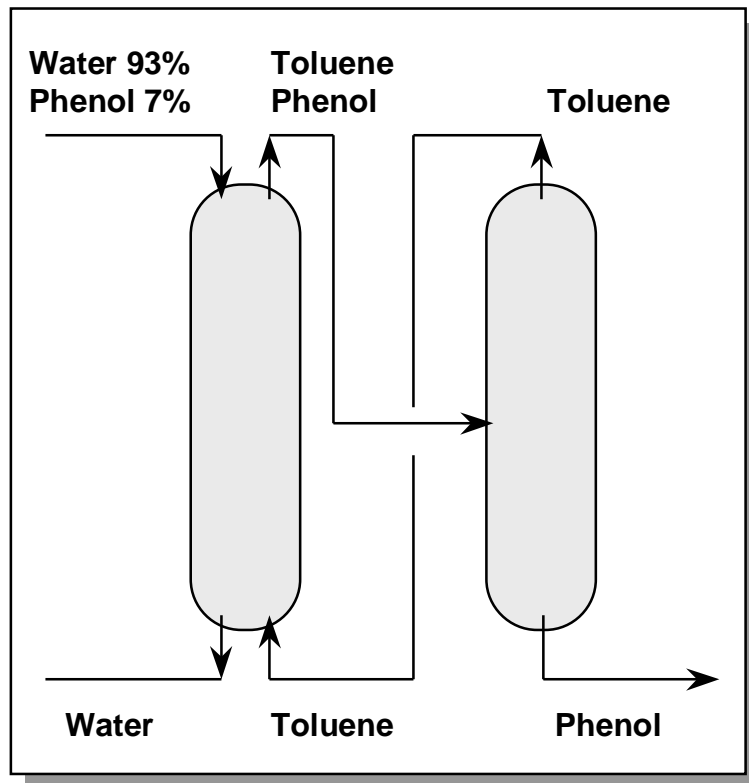
Step 1: Specify Properties

Examine Material's Life Cycle for Sources of Property Specifications

- Synthesis and Production**
- Use and Performance**
- Design and Retrofit**
- Disposal and Reuse**

Step 1: Specify Properties

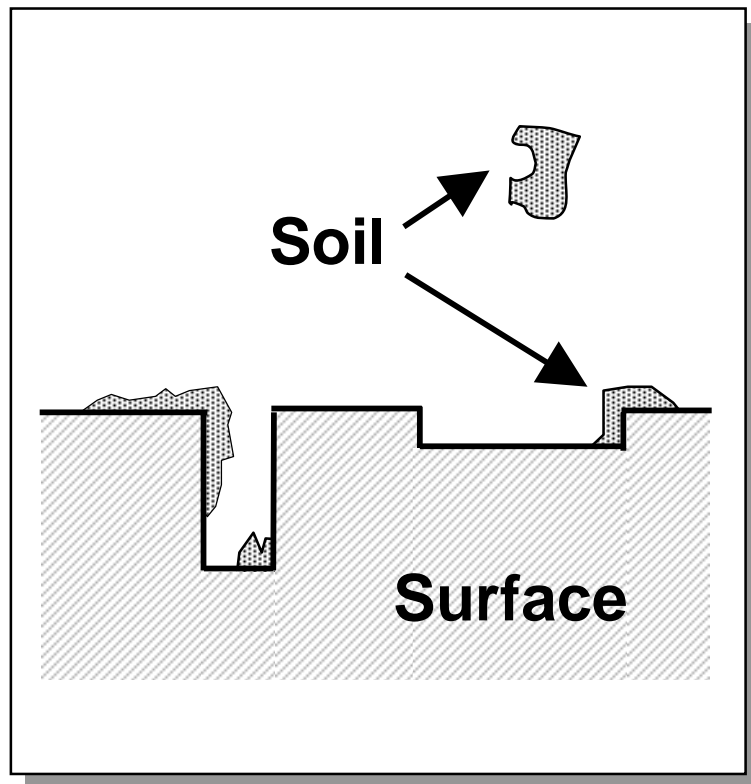
Liquid Extraction



- ✓ Aquatic Toxicity
- ✓ Biodegradation Rate
- ✓ Biological Oxygen Demand
- ✓ Corrosivity
- ✓ Density
- ✓ Enthalpy of Vaporization
- ✓ Solubility
- ✓ Surface Tension
- ✓ Vapor Pressure

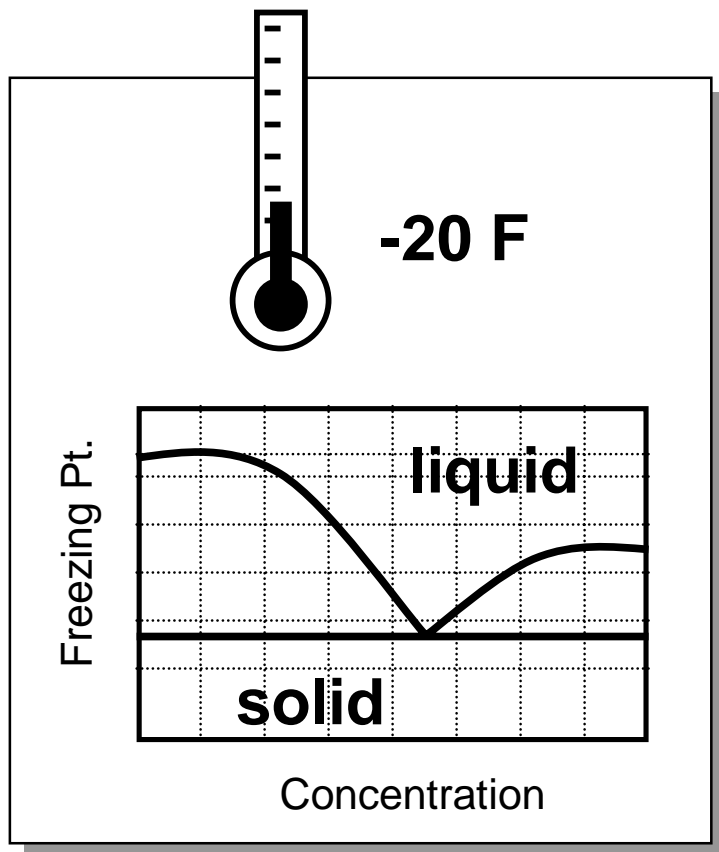
Step 1: Specify Properties

Cleaning Solvent



- ✓ Biological Oxygen Demand
- ✓ Boiling Point
- ✓ Corrosivity
- ✓ Enthalpy of Vaporization
- ✓ Flammability
- ✓ Global Warming
- ✓ Ozone Degradation
- ✓ Solubility
- ✓ Surface Tension

Step 1: Specify Properties

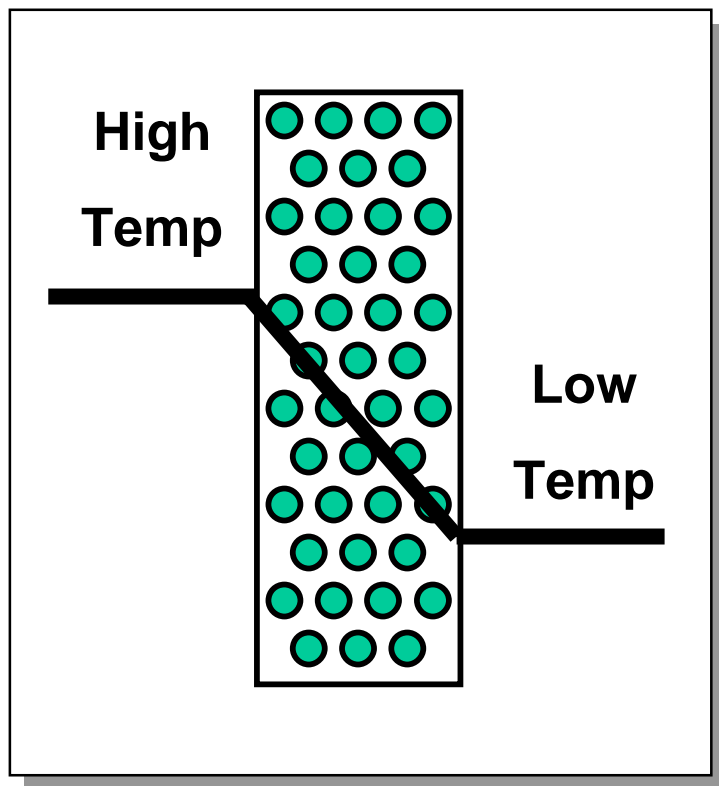


Antifreeze

- ✓ Aquatic Toxicity
- ✓ Biodegradation Rate
- ✓ Biological Oxygen Demand
- ✓ Boiling Point
- ✓ Carcinogenicity
- ✓ Corrosivity
- ✓ Flammability
- ✓ Freezing Point
- ✓ Heat Capacity

Step 1: Specify Properties

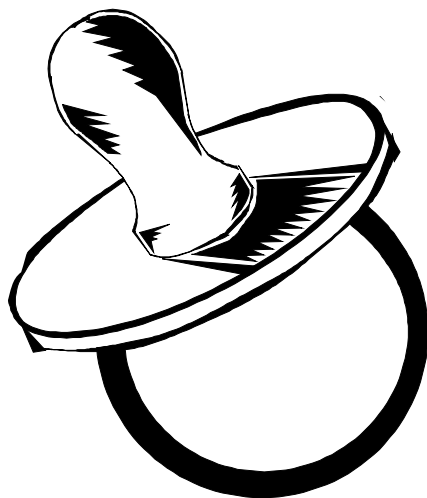
Blowing Agents



- ✓ Boiling Point
- ✓ Density
- ✓ Flammability
- ✓ Global Warming
- ✓ Heat Capacity
- ✓ Ozone Degradation
- ✓ Permeability
- ✓ Solubility
- ✓ Thermal Conductivity

Toxicity

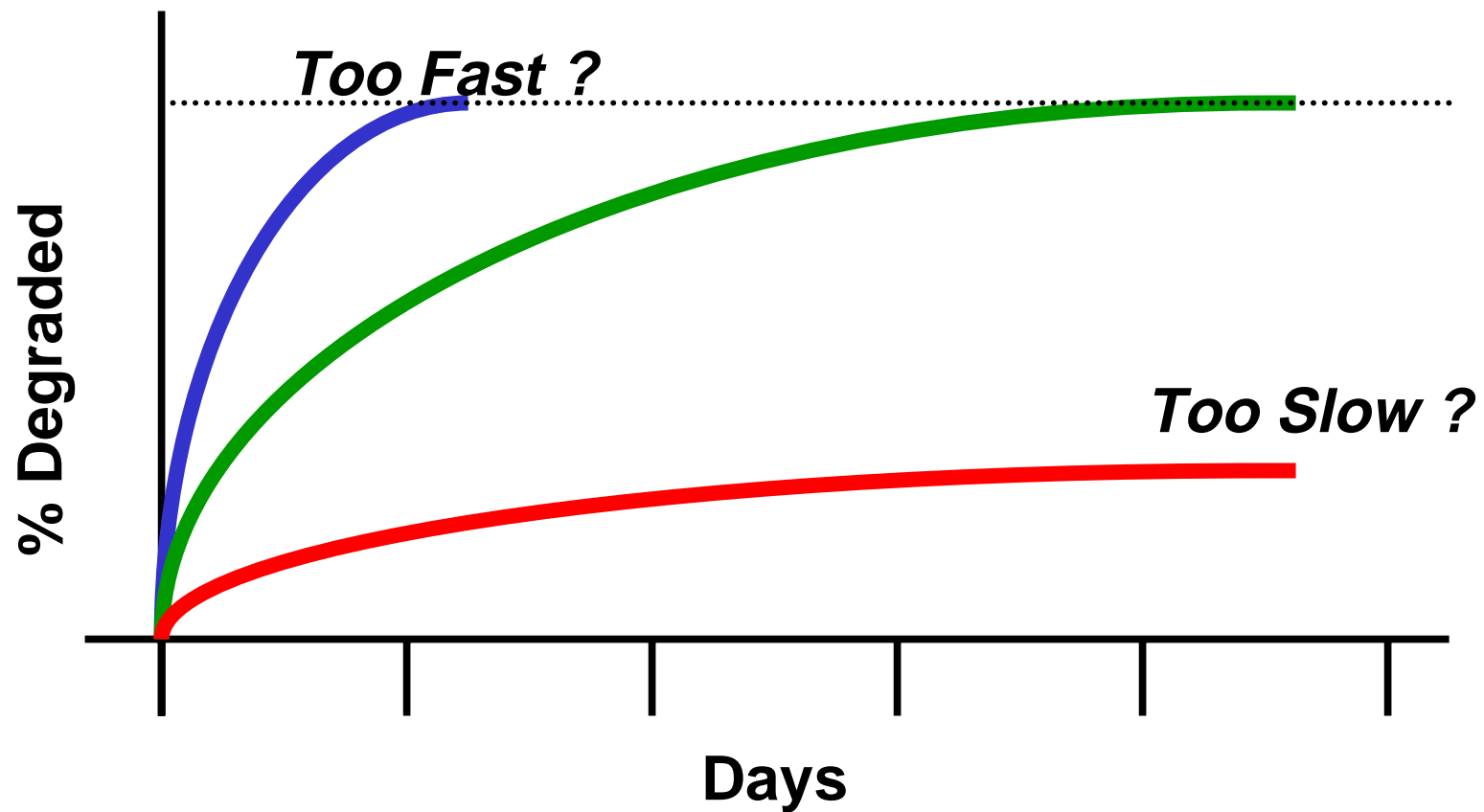
**Toxicity is a Level
Not a Chemical**



- Needed Amount**
- Solubility**
- Diffusivity**
- Toxic Level**

BOD

Too Biodegradable ??



Step 1: Specify Properties

Chemical Properties Especially Reactivity

-CH₃

-COOH

-S-

=CH-

-COO-

-NH₂

-Cl

>C=O

>N-

-F

-O-

-CN

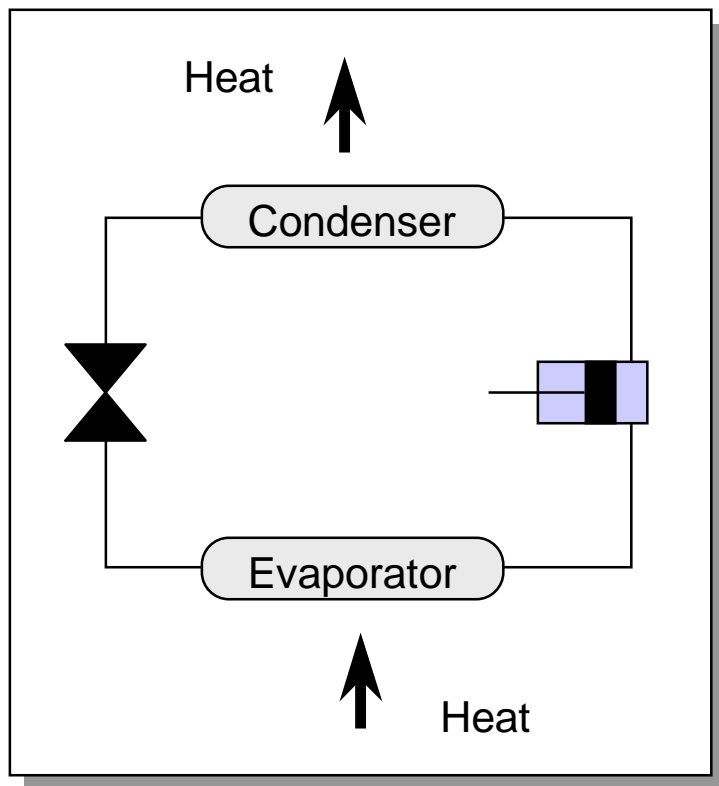
-Br

-NO₂

-CH=O

Step 1: Specify Properties

Lubricant Additive



✓ -CH₃

✓ =CH-

X -Cl

✓ -F

X -Br

X -COOH

✓ -COO-

✓ >C=O

✓ -O-

✓ -NO₂

X -S-

X -NH₂

✓ -CN

✓ -CH=O

Step 2: Matching Properties

Use an Appropriate Objective Function

Property	Toluene	Substitute	Distance
Density	0.86	0.91	0.05
Sol Param - P	8.00	7.60	-0.4
Sol Param - H	1.60	0.70	-0.9
Boiling Point	110.61	139.00	28.39
Flash Point	4.85	27.77	22.92
Daphnid 48hr LC50	15.86	28.44	12.58
Oral Rat LD 50	636.0	1780	1144
Pvp at 20C	21.80	5.80	-16
ThOD	3.13	2.76	-0.37

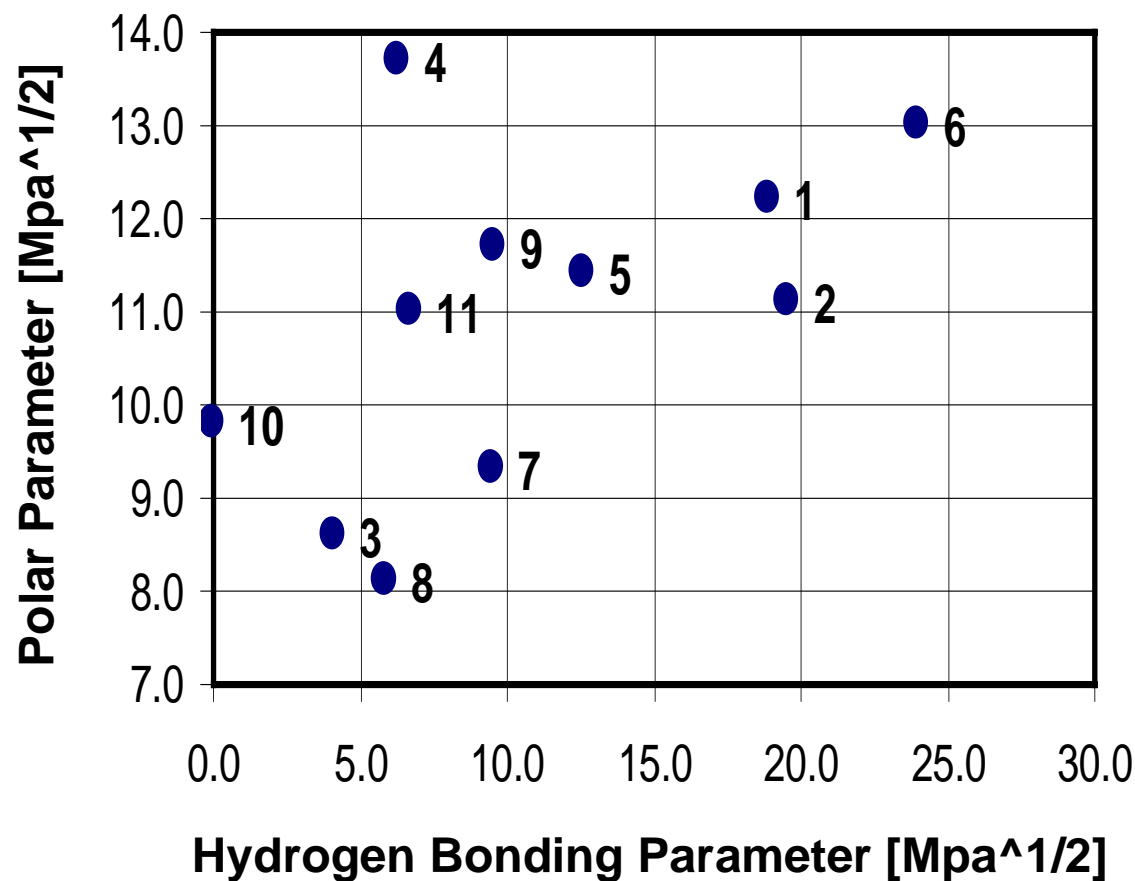
Step 2: Matching Properties

Matching Solvent Power

Solvent	Dispersive	Polar	H-Bonding
Acetic acid	13.9	12.2	18.9
Acetonitrile	10.3	11.1	19.6
Benzene	16.1	8.6	4.1
Chloroform	11.0	13.7	6.3
Diacetone alcohol	10.7	11.4	12.6
Methanol	11.6	13.0	24.0
Methyl ethyl ketone	14.1	9.3	9.5
Methyl isobutyl ketone	14.4	8.1	5.9
Methylene chloride	13.4	11.7	9.6
Tetrahydrofuran	13.3	11.0	6.7

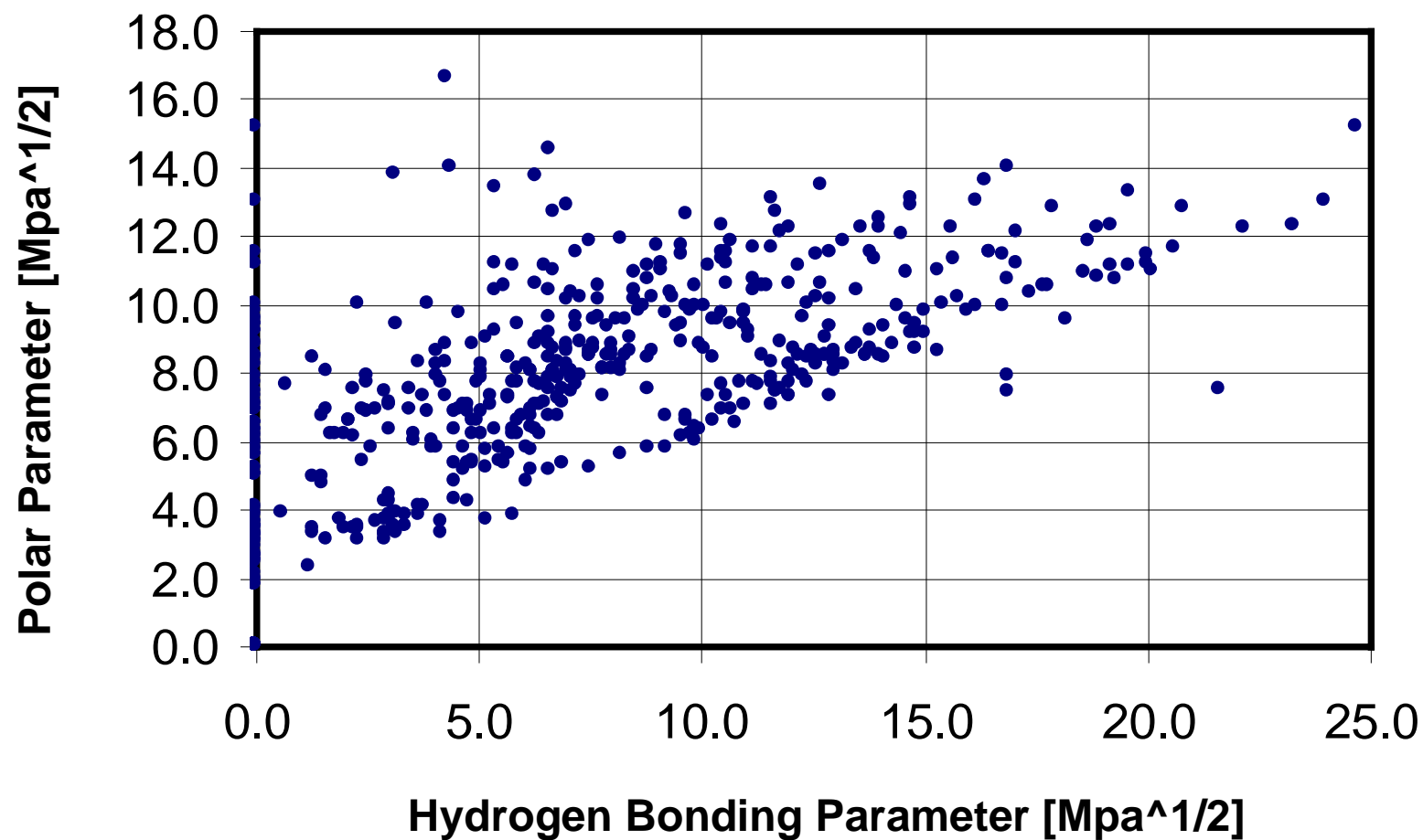
Reference: "CRC Handbook of Solubility Parameters"

Step 2: Matching Properties

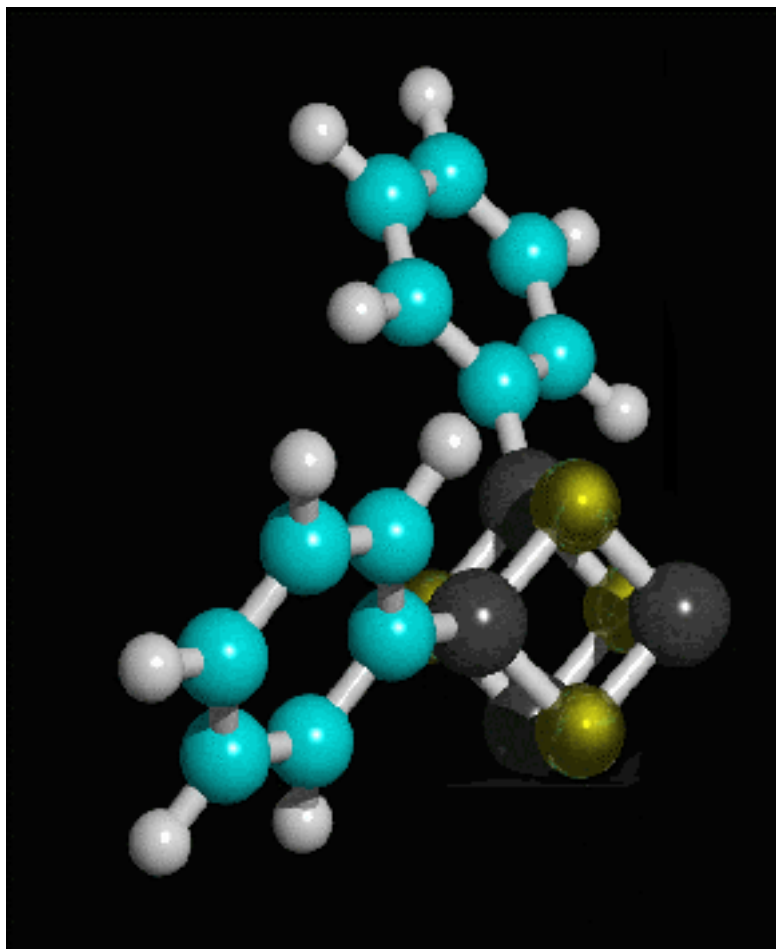


- 1) Acetic acid
- 2) Acetonitrile
- 3) Benzene
- 4) Chloroform
- 5) Diacetone alcohol
- 6) Methanol
- 7) Methyl ethyl ketone
- 8) Methyl i-butyl ketone
- 9) Methylene chloride
- 10) o-Dichlorobenzene
- 11) Tetrahydrofuran

Step 2: Matching Properties



Step 2: Matching Properties



Molecular Modeling

- Force Fields
- Canonical Ensemble
- Monte Carlo Method
- Receptor Matching
- Simple is Okay

Step 3: Simulate & Experiment

- Multiple Case Studies**
 - Different solvents, products, chemicals
- Retrofitting Concerns**
 - Densities, viscosities, volatilities
- Estimating Properties**
 - Pure, mixtures, product simulation
- Establish Standard Screening Tests**
 - “20 Common solvents”

Strategies and Homework

Establish Chemical Specifications During Design

- What properties were found important ?
- What chemical classes were tested ?
- Why were candidates eliminated ?
- What are the top 5 candidates ?

Strategies and Homework

Use Life Cycle Analysis to Establish Specification Team

- Synthetic chemists
- Process chemists and engineers
- Environmental engineers
- Maintenance engineers
- Safety engineers

Strategies and Homework

What About Water ?

- Very Polar and Hydrogen Bonding**
- Very Large Heat of Vaporization**
- Very Large Surface Tension**
- Promotes Corrosion (Salts)**

Strategies and Homework

Consolidate Solvents Used Plant-wide

- 35 Solvents reduced to 7**
- Less documentation**
- Economies of Scale**
 - Research & Disposal**

Summary

Chemical Substitution

- Chemical Specifications**
- Physical and Chemical Properties**
- Matching Properties Graphically**
- Chemicals, Properties, Molecules**

Cranium: Chemical Substitution

Material Search Dialog

Target Constraints

	Property ---	Temp C	Pres bar	Target ---	Units ---	Weight ---
1	Boiling Point	---	---	3.83E+02	K	1.00E+00
2	---	---	---	---	---	---
3	---	---	---	---	---	---
4	---	---	---	---	---	---

Clear Edit Remove Enable Disable Match

Search Results

	Distance	Valid	Material
1	7.80E-01	Yes	Toluene
2	2.15E+00	Yes	sec-Butyl acetate
3	6.65E+00	Yes	Methyl isobutyl ketone
4	7.81E+00	Yes	Butanol
5	8.05E+00	Yes	Acetic acid
6	8.92E+00	Yes	Methylcyclohexane
7	9.85E+00	Yes	Water

Done Search Sort Go To Update KB Print

Synapse: Chemical Design

Combinatorial Design1

Design Techniques Groups Elements

Design Groups

	Group	Min	Max
1	-CH3	---	---
2	-CH2-	---	---
3	>CH-	---	---
4	>C<	---	---
5	-OH	---	2
6	-COO-	---	1

Design Parameters

	Parameter	Value
1	Minimum Total Groups	2
2	Maximum Total Groups	10
3	Number of Rings	0

Constraints

	Constraint
1	Match Solubility Param
2	Vapor Pressure Constr
3	Boiling Point Constrai

Candidates

	Candidate Molecule
1	3[-CH3] 1[-CH2-] 2[=C<] 1[-CN]
2	1[-CH3] 5[-CH2-] 1[=CH2] 1[=CH-]
3	2[-CH3] 2[-CH2-] 1[>CH-] 1[NO2]
4	3[-CH3] 1[>CH-] 2[-O-]
5	2[-CH3] 4[-CH2-] 1[>CH-] 1[-CH=O]
6	2[-CH3] 3[-CH2-] 1[-COO-]

Web Site

<http://www.molknow.com>

- Software Demonstrations**
- Copies of Presentations**
- Technical Papers**