Designing Chemical Products

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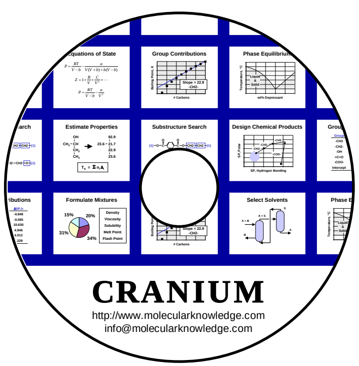
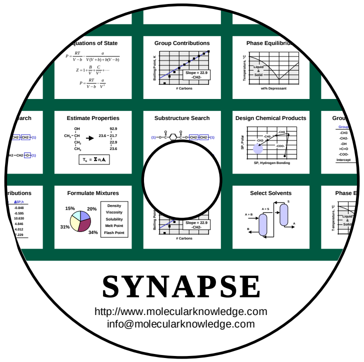
Molecular Knowledge Systems, Inc.

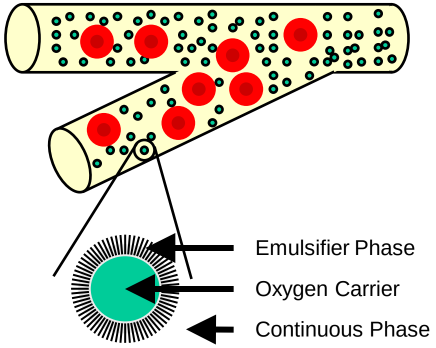
http://www.molecularknowledge.com

Molecular Knowledge Systems

- Located in New Hampshire, USA
- Company Started in 1989
- Computer Software
- Consulting







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Designing Chemical Products

Some example projects we have worked on

- Artificial Blood
- Refrigeration Lubes
- Degreasing Solvents
- Non-MMH Rocket Fuels
- Aircraft Deicing Fluids
- Soil Consolidants
- Sonar Fill Fluids
- Phase Change Materials
- CO_2 Absorption Solvents
- Hydraulic Energy Storage
- Windshield Washer Fluid
- Pour Point Depressant

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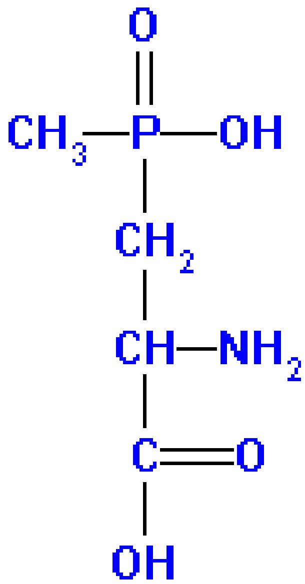
Our Core Knowledge



Thermal Conductivity

Liquid Viscosity

Surface Tension

Heat Capacities

Vapor Pressure

Liquid Density

Flash Point

Structure Property Relationships

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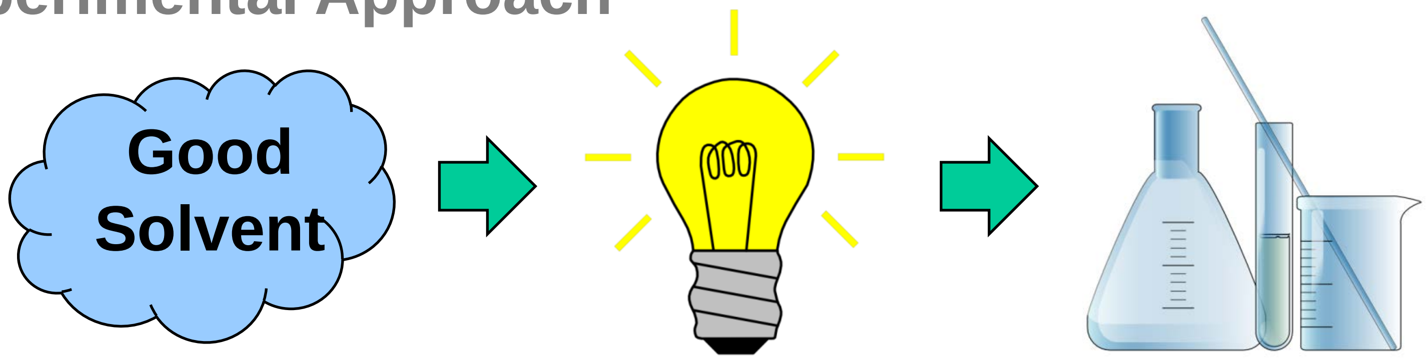
Designing Chemical Products

Three Main Steps

1) **Identifying physical property constraints**
2) **Generating candidate structures and mixtures**
3) **Testing if candidates satisfy constraints**

Experimental Approach



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Designing Chemical Products

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Computational Approach

$T_b > 100$ °C
$T_m < -40$ °C
$\rho > 1000$ kg/m^3

→

CH_3-O-CH_2-CH_3
CH_3-S-CH_2-CH_3
CH_3-NH_2-CH_2-CH_3
CH_3-CO-CH_2-CH_3

→

$\sum n_i \Delta_{i,Tb}$
$\sum n_i \Delta_{i,Tm}$

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→

$\sum n_i \Delta_{i,Tb}$
$\sum n_i \Delta_{i,Tm}$

Step 1: Identify Constraints

Do not focus on chemicals or ingredients. Focus on physical properties.

"People don't need drills. People need holes."

- Basic Marketing

"People don't need chemicals. People need the properties those chemicals possess."

- Kevin G. Joback

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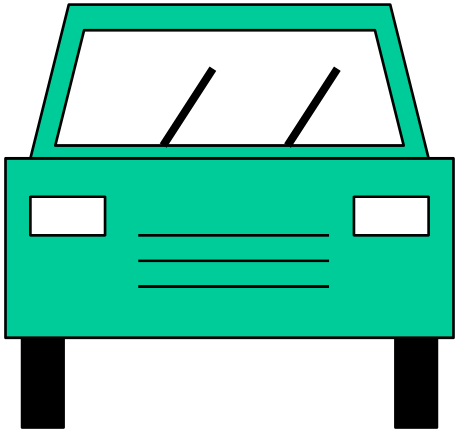
Example: Windshield Washer Fluid



US Patent 07,585,828
Example Formulation

Why are these ingredients in this product?

Ingredient	Weight %
1. Methanol (solvent)	34.750
2. Chromatech Yellow	0.005
3. XD-56 Antifoam	0.020
4. Formasil 593	0.200
5. Water	65.025

Example: Windshield Washer Fluid

Focus on physical properties

Surface Tension – Wetting

Phase Equilibria – Solubility

Phase Equilibria – Evaporation

Viscosity – Fluid Flow

Density – Fluid Flow

Phase Equilibria – Non-solubility

Reactivity – Corrosion

Phase Equilibria – Low Freezing Point

Light Absorption – Color

Safety – Low Flammability

Safety – Toxicity

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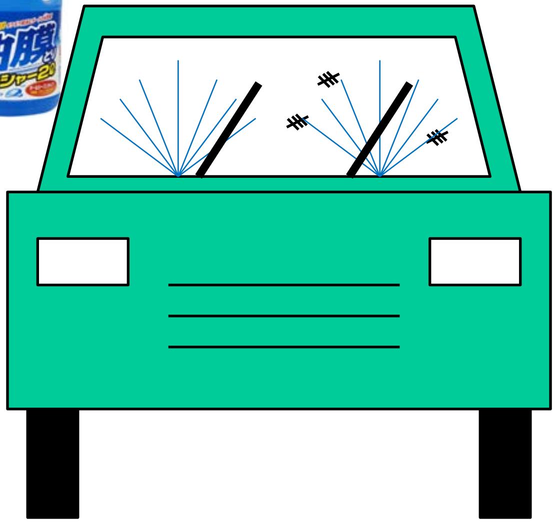
Step 1: Identify Constraints

The required physical properties place constraints on the molecular structure of the solvent



1. Non-reactive with metal – no -COOH group
2. Environmentally friendly – no –Cl, -F, -Br
3. Must wet glass surface – hydrocarbon
4. Rapid evaporation rate – low Mw
5. Low freezing point – -OH group
6. Low flammability – -OH, -Cl, -F
7. Low toxicity – water soluble
8. Low viscosity – low Mw

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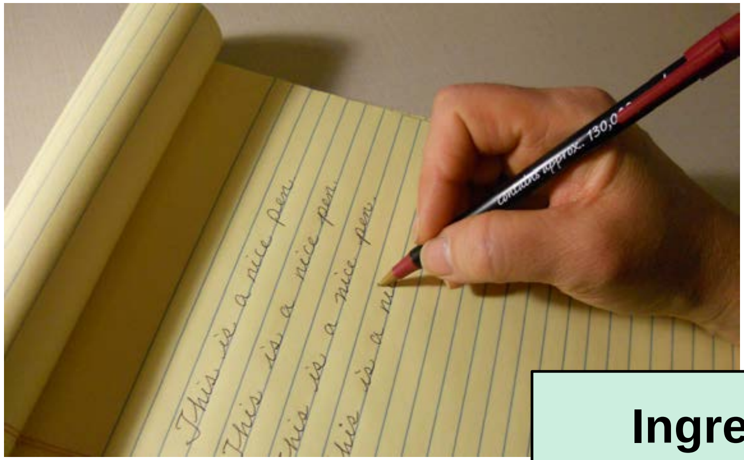
Example: Ball Point Pen Ink



US Patent 05,466,281 Example Formulation

Why are these ingredients in this product?

Ingredient	Weight %
1. Sunsperse black LHD-9303	20.00
2. Ammonia as 20% NH3	0.10
3. Cobratec TT-25-EG	0.25
4. Ethylene glycol	74.12
5. Surfynol 104E	0.18
6. Xanthan gum	0.20
7. Proxel GXL	0.15
8. Joncryl 58	5.00

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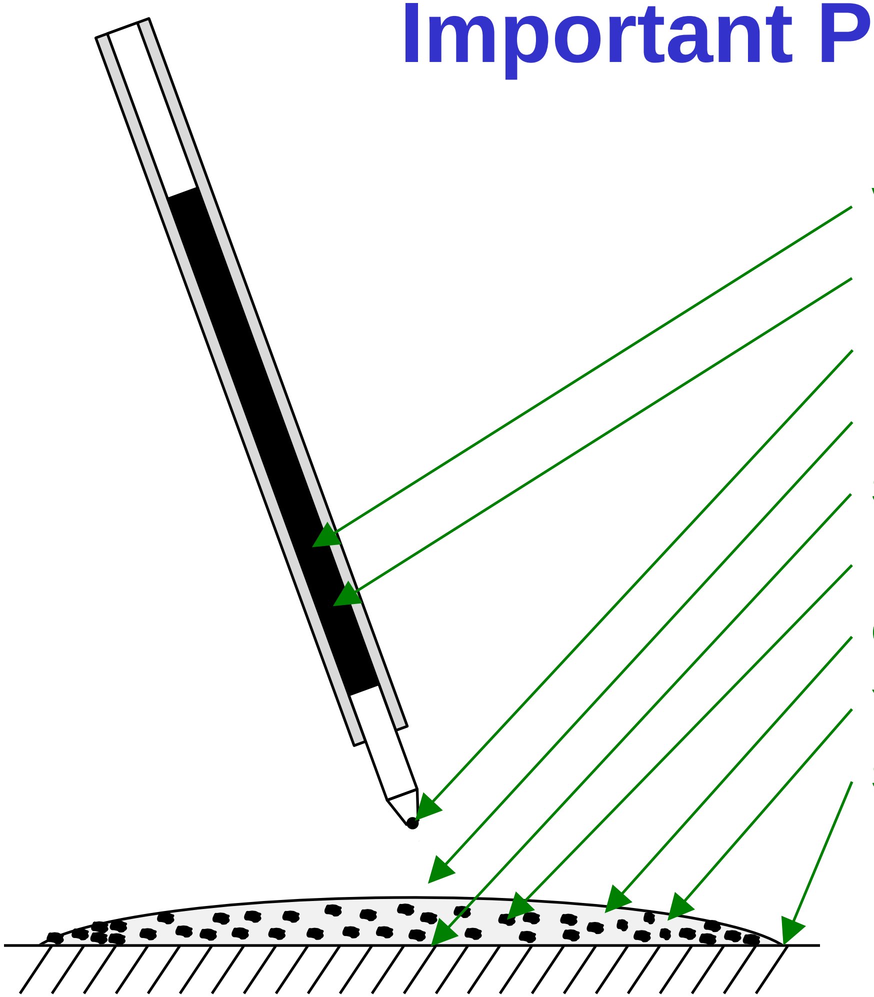
Example: Ball Point Pen Ink

Important Physical Properties



Viscosity - **Suspension**

Density – **Fluid Flow**

Reactivity – **Corrosion**

Phase Equilibria – **Drying**

Surface Tension – **Adhesion**

Light Absorption – **Color**

Glass Transition Temp – **Film Forming**

Young's Modulus – **Stress Strain**

Surface Tension – **Wetting**

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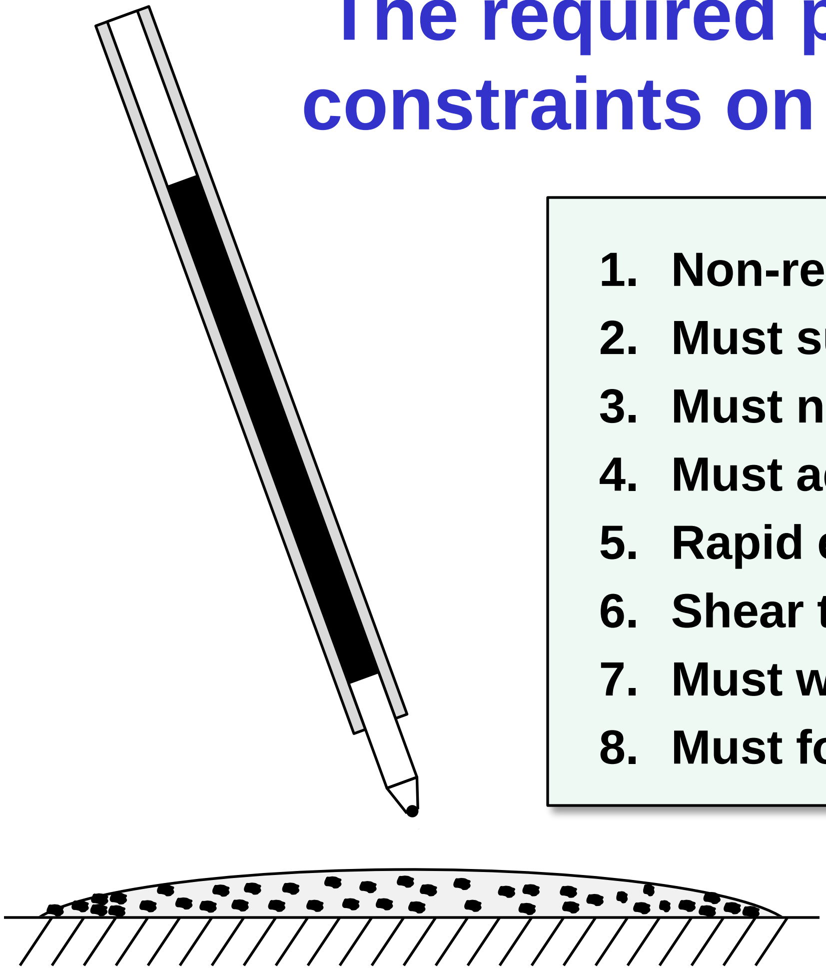
Step 1: Identify Constraints

The required physical properties place constraints on the mixture's ingredients



1. Non-reactive with metal – corrosion inhibitor
2. Must suspend pigment particles – thickener
3. Must not degrade for many years – biocide
4. Must adhere particles to paper – polymer
5. Rapid evaporation rate – low Mw solvent
6. Shear thinning viscosity – thickener
7. Must wet paper surface – surfactant
8. Must form a tough film – polymer

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Designing Chemical Products

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CH_3-CO-CH_2-CH_3

→

$\sum n_i \Delta_{i,Tb}$
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$\sum n_i \Delta_{i,Tb}$
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Generating Candidates
Pure Components and Mixtures

1) Generating Structures: the molecular structure of pure component candidates
2) Generating Mixtures: the components and concentration of mixture candidates

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Pure Components and Mixtures

1) **Generating Structures: the molecular structure of pure component candidates**
2) Generating Mixtures: the components and concentration of mixture candidates

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Step 2: Generating Structures

Groups are small pieces of molecular structure. Begin by compiling groups.

$–CH_3$	$–CH_2–$	>CH–
–COO–	–OH	–CO–
$–NH_2$	–NH–	>N–
–O–	-Br	–F
–Cl	–COOH	–SH

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Step 2: Generating Structures

Eliminate groups based on reactivity, corrosivity, odor, safety, ...

–CH_3	–CH_2–	>CH–
–COO–	–OH	–CO–
–NH_2	–NH–	>N–
~~–O–~~	~~-Br~~	–F
~~–Cl~~	~~–COOH~~	~~–SH~~

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Step 2: Generating Structures

Exhaustively generate all combinations.
Combinations of 2 groups, 3 groups, …

2 Groups

$-CH_3$	$-CH_3$
$-CH_3$	$-CH_2-$
$-CH_3$	>CH-
$-CH_3$	-OH
$-CH_3$	-NH-
$-CH_3$	>N-
⋮	

3 Groups

$-CH_3$	$-CH_3$	$-CH_3$
$-CH_3$	$-CH_3$	$-CH_2-$
$-CH_3$	$-CH_3$	>CH-
$-CH_3$	$-CH_3$	-OH
$-CH_3$	$-CH_3$	-NH-
$-CH_3$	$-CH_3$	>N-
⋮		

4 Groups

$-CH_3$	$-CH_3$	$-CH_3$	$-CH_3$
$-CH_3$	$-CH_3$	$-CH_3$	-CH2-
$-CH_3$	$-CH_3$	$-CH_3$	>CH-
$-CH_3$	$-CH_3$	$-CH_3$	-OH
$-CH_3$	$-CH_3$	$-CH_3$	-NH-
$-CH_3$	$-CH_3$	$-CH_3$	>N-
⋮			

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Step 2: Generating Structures

Delete infeasible combinations.
Feasible combinations must satisfy:

$$\frac{b}{2} = n - 1 + r$$

b = number of bonds
n = number of groups
r = number of rings

$-CH_3$ $-CH_3$ $-CH_3$ -CH3

b = 4 n = 4 r = 0

$$\frac{4}{2} = 4 - 1 + 0$$

✗

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Step 2: Generating Structures

Delete infeasible combinations.
Feasible combinations must satisfy:

$$\frac{b}{2} = n - 1 + r$$

b = number of bonds
n = number of groups
r = number of rings

$-CH_3$ $-CH_3$ $-CH_3$ >N-

b = 6 n = 4 r = 0

$$\frac{6}{2} = 4 - 1 + 0$$ ✓

CH_3-N-CH_3
$\quad\quad\;\; |$
$\quad\quad CH_3$

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Step 2: Generating Structures

Delete infeasible combinations.

$$b/2 \neq n - 1 + r$$

2 Groups

$-CH_3$	$-CH_3$
$-CH_3$	$-CH_2-$
$-CH_3$	>CH-
$-CH_3$	-OH
$-CH_3$	-NH-
$-CH_3$	>N-
⋮	

3 Groups

$-CH_3$	$-CH_3$	$-CH_3$
$-CH_3$	$-CH_3$	$-CH_2-$
$-CH_3$	$-CH_3$	>CH-
$-CH_3$	$-CH_3$	-OH
$-CH_3$	$-CH_3$	-NH-
$-CH_3$	$-CH_3$	>N-
⋮		

4 Groups

$-CH_3$	$-CH_3$	$-CH_3$	$-CH_3$
$-CH_3$	$-CH_3$	$-CH_3$	-CH2-
$-CH_3$	$-CH_3$	$-CH_3$	>CH-
$-CH_3$	$-CH_3$	$-CH_3$	-OH
$-CH_3$	$-CH_3$	$-CH_3$	-NH-
$-CH_3$	$-CH_3$	$-CH_3$	>N-
⋮			

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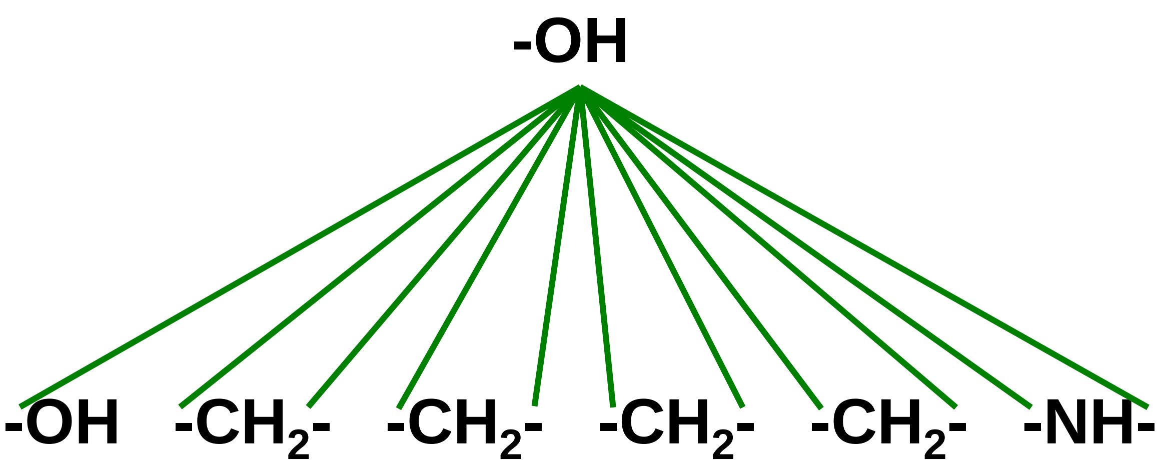
Step 2: Generating Structures

Groups must now be connected.
Enumeration of all bonds

-OH	-OH	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	-NH-



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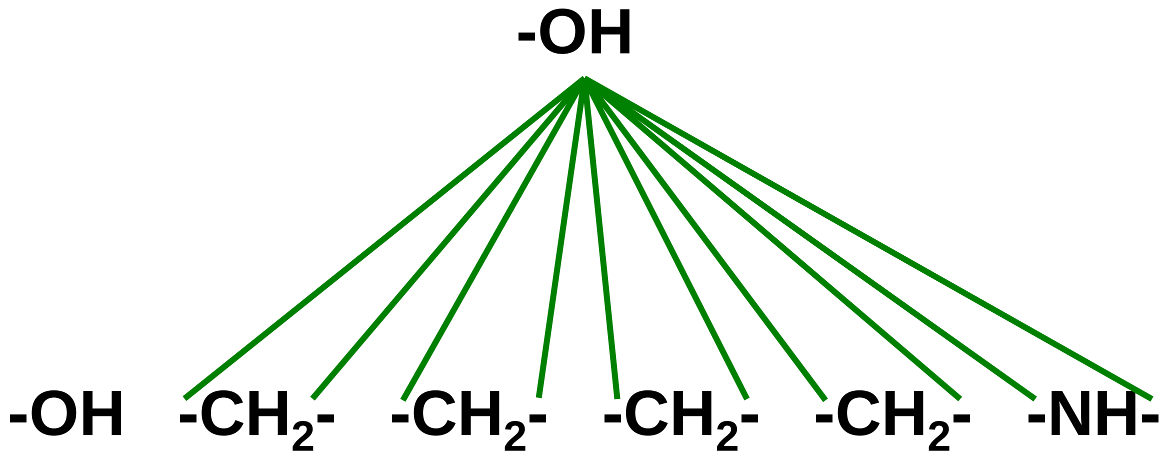
Step 2: Generating Structures

Eliminate infeasible bonds
Eliminate duplicate structures

-OH	-OH	-CH_2-	-CH_2-	-CH_2-	-CH_2-	-NH-



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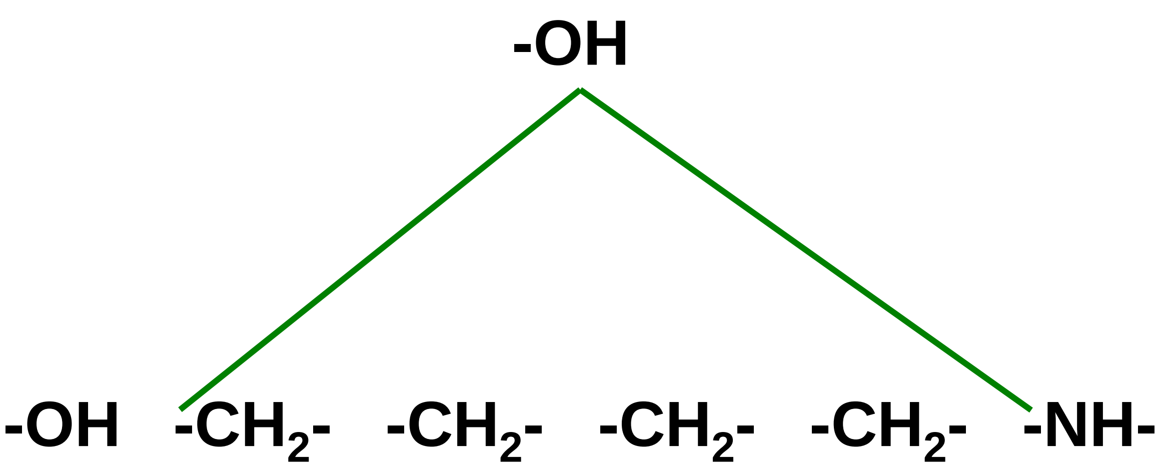
Step 2: Generating Structures

Eliminate infeasible bonds
Eliminate duplicate structures

-OH -OH $-CH_2-$ $-CH_2-$ $-CH_2-$ $-CH_2-$ -NH-



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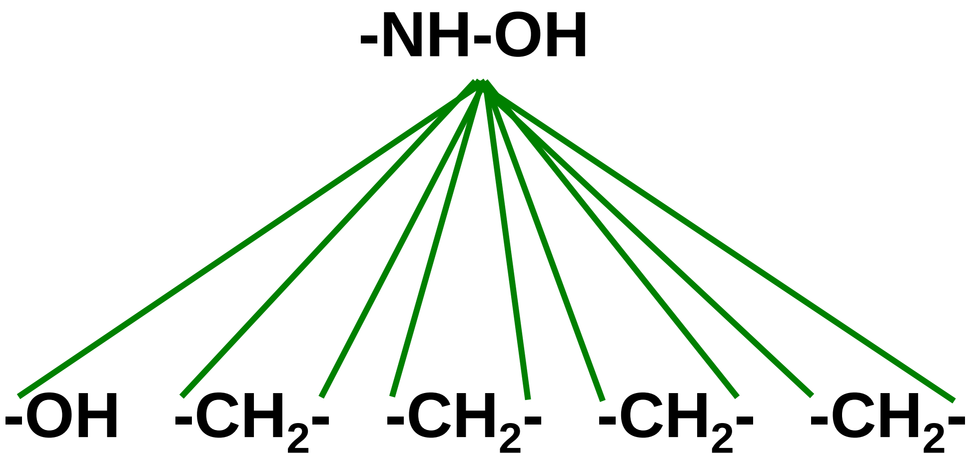
Step 2: Generating Structures

Repeat the procedure for each bonded substructure

-OH   -OH $-CH_2-$ $-CH_2-$ $-CH_2-$ $-CH_2-$ -NH-



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Step 2: Generating Structures

Finally we have enumerated all candidate molecular structures

-OH	**-OH**	**$-CH_2-$**	**$-CH_2-$**	**$-CH_2-$**	**$-CH_2-$**	**-NH-**

$HO-CH_2-CH_2-CH_2-CH_2-NH-OH$

$HO-CH_2-CH_2-CH_2-NH-CH_2-OH$

$HO-CH_2-CH_2-NH-CH_2-CH_2-OH$

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Generating Candidates
Pure Components and Mixtures

1) Generating Structures: the molecular structure of pure component candidates

2) **Generating Mixtures: the components and concentration of mixture candidates**

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Step 2: Generating Mixtures

Begin by collecting chemicals into component categories

Category: Solvent 1	Category: Solvent 2	Category: Water
Propylene glycol	Propylene glycol	Water
Isopropanol	Isopropanol	
Methanol	Methanol	
Glycerol	Glycerol	
Ethanol	Ethanol	

Step 2: Generating Mixtures

Specify each category's concentration: minimum, maximum and increment

Category	Min, wt%	Max, wt%	Increment
Solvent 1	0	60	10
Solvent 2	0	60	10
Surfactant	0.001	0.010	0.001
Colorant	0.05	0.10	0.05
Water	20	70	q.s.

q.s. = quantum sufficit (amount needed)

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Step 2: Generating Mixtures

First all concentrations are generated for the component categories

Candidate 0001		Candidate 0002		...	Candidate 0253	
Solvent 1	30.000	Solvent 1	40.000		Solvent 1	50.000
Solvent 2	0.000	Solvent 2	0.000		Solvent 2	30.000
Surfactant	0.001	Surfactant	0.001	•••	Surfactant	0.004
Colorant	0.050	Colorant	0.050		Colorant	0.100
Water	69.949	Water	59.949		Water	19.899

Constraint: concentration must total 100%

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Three Main Steps

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Step 3: Evaluating Candidates

Three Main Categories of Property Estimation Techniques

- ❑ **Group Contribution Techniques**
- ❑ **Equation Oriented Techniques**
- ❑ **Mixture Estimation Techniques**

Step 3: Evaluating Candidates

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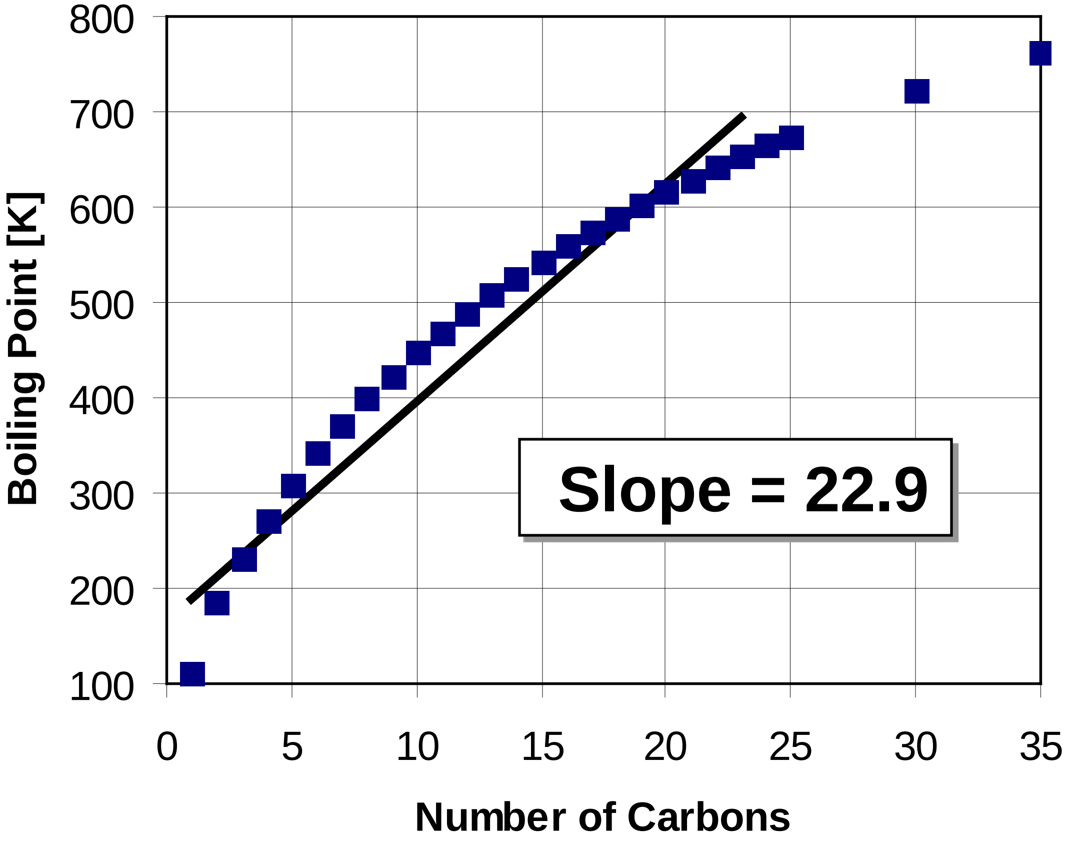
Group Contribution Techniques

Normal Paraffins Homologous Series



Contribution

-CH2- = 22.9

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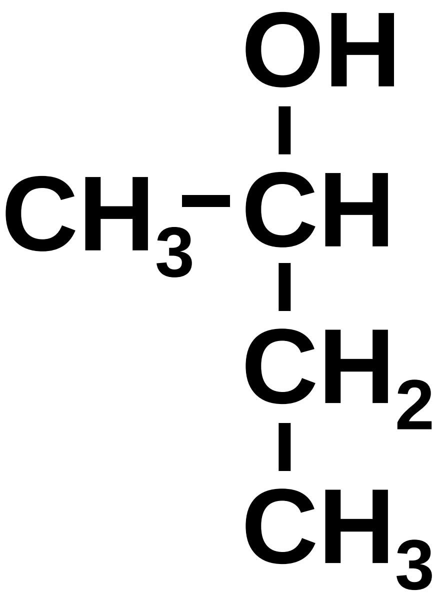
Group Contribution Techniques



1) Select Technique
2) Dissect Structure
3) Get Contributions
4) Insert into Model

Group	ΔTb
-CH3	23.6
-CH3	23.6
-CH2-	22.9
>CH-	21.7
-OH	92.9
Tb (est)	382.8 K
Tb (lit)	372.7 K

$$Tb = 198.1 + \Sigma\Delta_i$$

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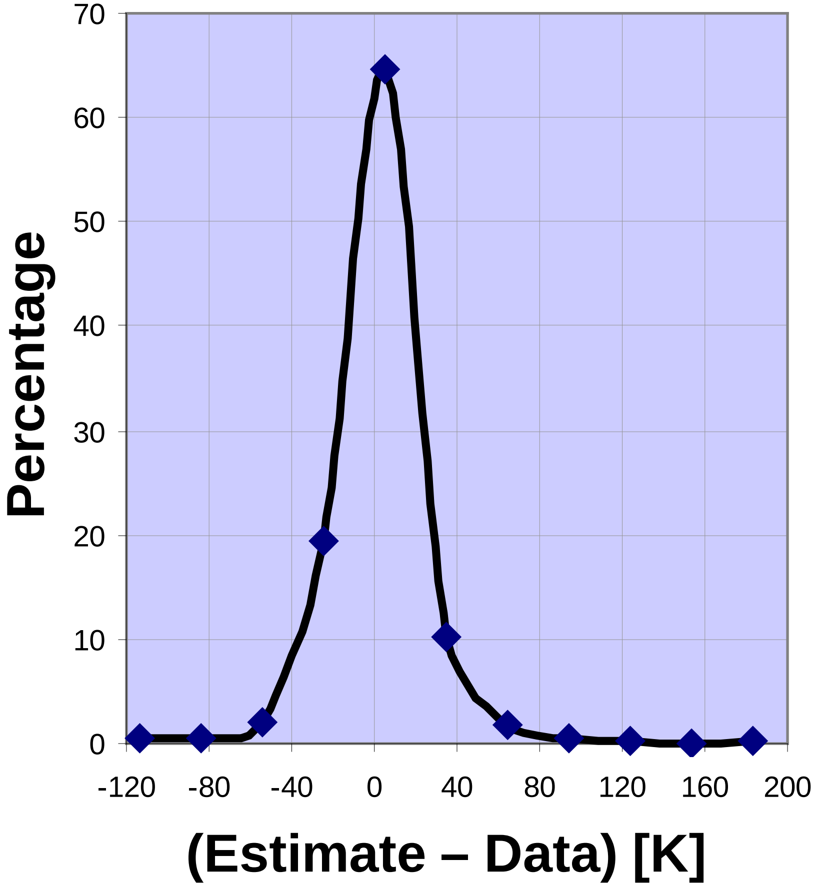
Boiling Point, Estimation Errors



Estimates generated using Joback's method

Statistics

Observations	559
Avg Error	0.97 K
Avg Abs Err	15.1 K
Avg % Error	4.8 %
Max Error	197.4 K

Outliers, Errors

N-Methylformamide	-128.5 K
Acetamide	-122.6 K
Fluorine	113.1 K
Cyanogen	197.4 K

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Step 3: Evaluating Candidates

Three Main Categories of Property Estimation Techniques

- ❑ Group Contribution Techniques
- ❑ **Equation Oriented Techniques**
- ❑ Mixture Estimation Techniques

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Equation Oriented Techniques

$$\ln\left(\frac{P_{vp}}{P_c}\right) = T_{br}\,\frac{\ln(P_c)}{1-T_{br}}\left(1-\frac{1}{T_r}\right)$$

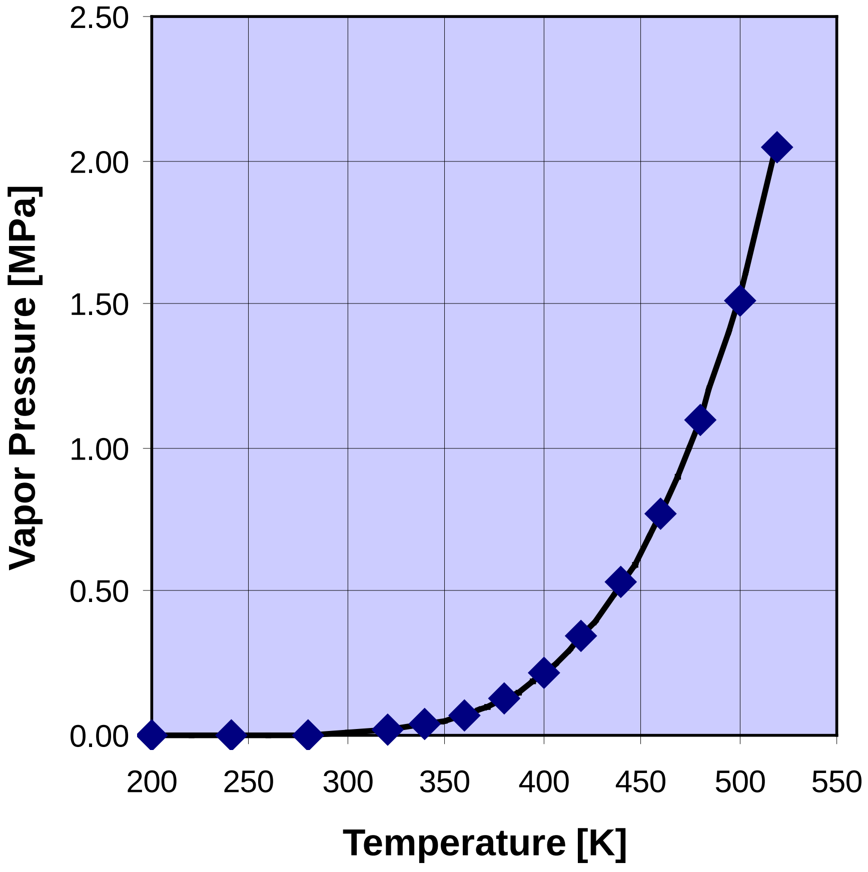
Required Properties

Tc – Critical Temperature

Pc – Critical Pressure

Tb – Boiling point

Vapor Pressure - Heptane



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Step 3: Evaluating Candidates

Three Main Categories of Property Estimation Techniques

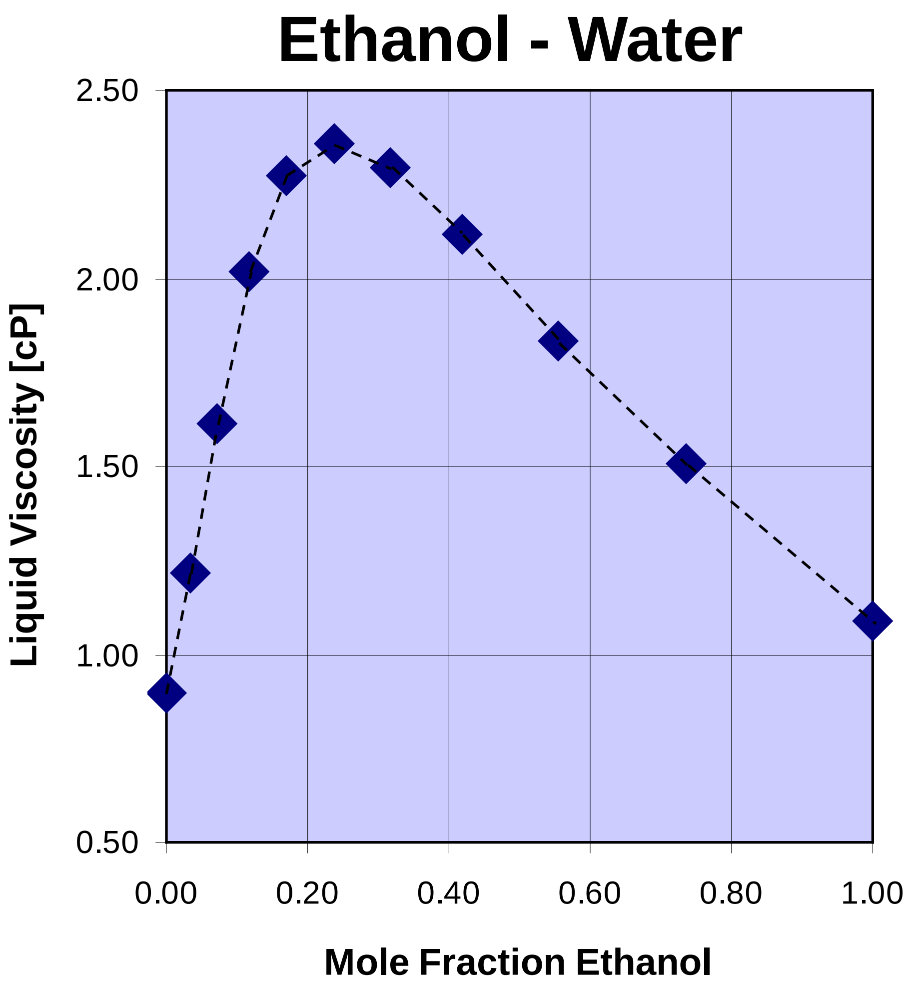
- ❑ Group Contribution Techniques
- ❑ Equation Oriented Techniques
- ❑ **Mixture Estimation Techniques**

Mixture Techniques

$$\ln(\eta_m) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + x_1 x_2 G$$

Mixture Functions

- ❑ Pure Data Inputs
- ❑ Reduces to Pure
- ❑ Molecular Forces
- ❑ Characteristics



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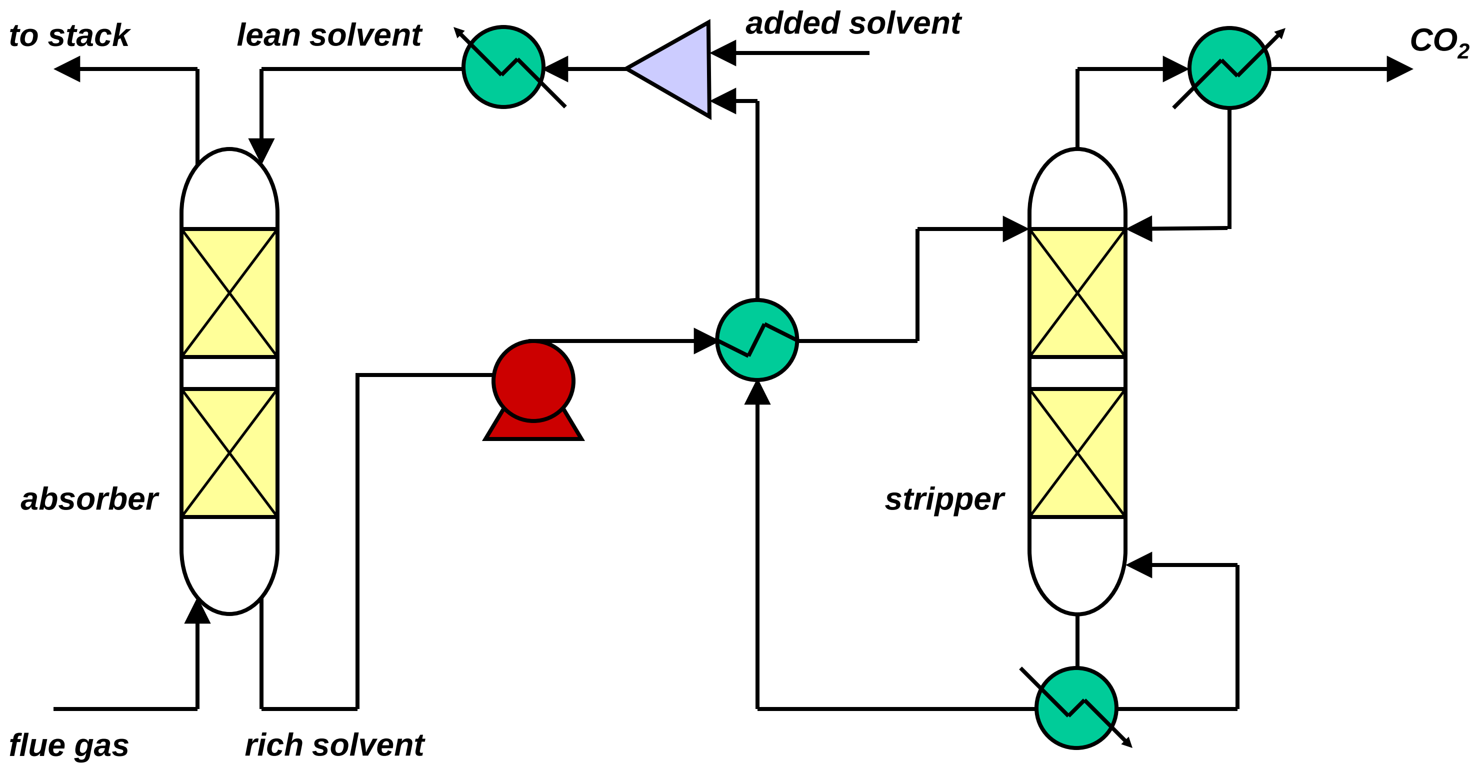
Example: CO_2 Absorption Solvent

Absorption, Heat Exchange, Distillation



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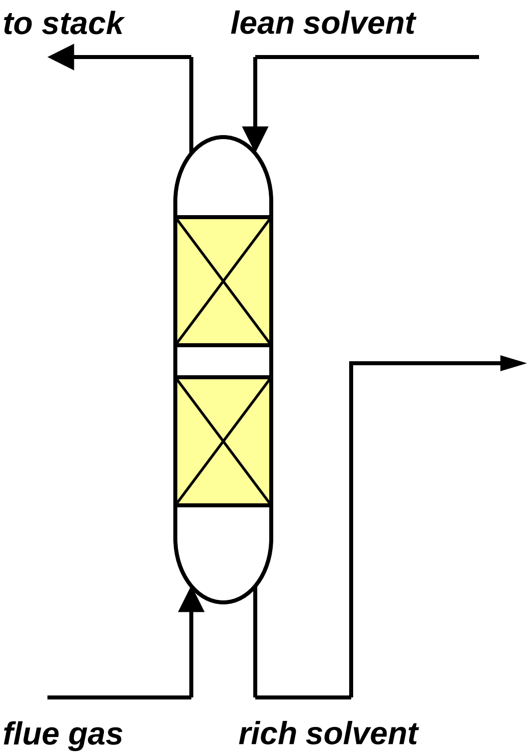
Example: CO_2 Absorption Solvent

Absorber



Packed Column: Percentage of packing wetted by the solvent is important

Wilcox, Rochana, Kirchofer, Glatz and He. Energy and Environmental Science, volume 7, page 1769, 2014.

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Example: CO_2 Absorption Solvent

Percentage of packing wetted by the solvent

$$\frac{a_w}{a_t} = 1 - \exp\left\{-1.45\left(\frac{\sigma_c}{\sigma}\right)^{0.75}\left(\frac{\rho L}{a_t \mu}\right)^{0.1}\left(\frac{L^2 a_t}{g}\right)^{-0.05}\left(\frac{\rho L^2}{\sigma a_t}\right)^{0.2}\right\}$$

a_t = total area
a_w = wetted area
L = liquid velocity
ρ = solvent density

σ_c = critical surface tension
σ = solvent surface tension
g = gravitational constant
μ = solvent viscosity

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Example: CO_2 Absorption Solvent

For 30 wt% Monoethanolamine (MEA) in Water

$$\frac{a_w}{a_t} = 1 - \exp\left\{-1.45\left(\frac{\sigma_c}{\sigma}\right)^{0.75}\left(\frac{\rho L}{a_t \mu}\right)^{0.1}\left(\frac{L^2 a_t}{g}\right)^{-0.05}\left(\frac{\rho L^2}{\sigma a_t}\right)^{0.2}\right\}$$

Temp = 313.5 K

σ_c = 0.061 N/m

a_t = 500 m^2/m^3

L = 0.006 m/s

g = 9.81 m/s^2

μ = 0.00091 Pa·s

ρ = 953.6 kg/m^3

σ = 0.065 N/m

Estimated values

$$\frac{a_w}{a_t} = 0.462$$

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Step 1: Identify Constraints

A more extensive design would have constraints on the percentage of wetted surface area, the potential for flooding, the energy usage, and many more. For this example we simply create a constraint on the percentage of wetted surface area.

$$\frac{a_w}{a_t} > 0.462$$

Constraint:

Better than MEA

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Step 2: Generate Candidates

We chose the following design groups

-CH3 -CH2- >CH- >C< -OH

-NH2 >NH >N-

We chose a fixed amount of solvent in water:

30% Water Mixtures

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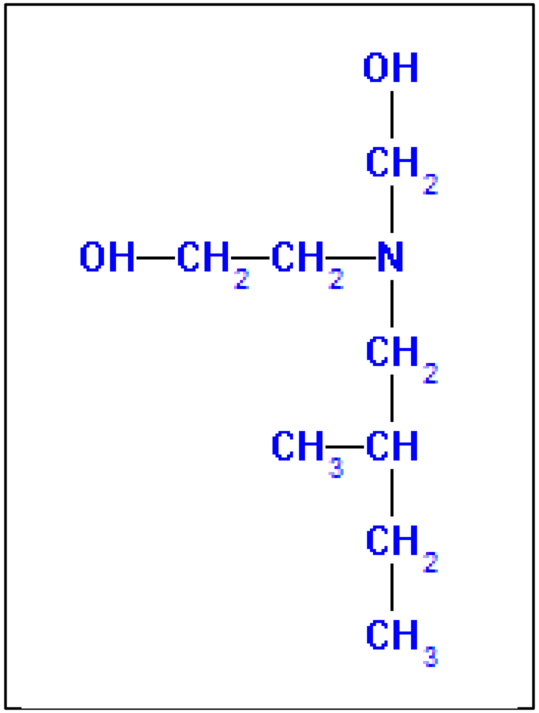
Step 3: Evaluate Candidates

$$\frac{a_w}{a_t} = 1 - \exp\left\{-1.45\left(\frac{\sigma_c}{\sigma}\right)^{0.75}\left(\frac{\rho L}{a_t \mu}\right)^{0.1}\left(\frac{L^2 a_t}{g}\right)^{-0.05}\left(\frac{\rho L^2}{\sigma a_t}\right)^{0.2}\right\}$$



T_b = Joback's Technique (GCT)
T_c = Joback's Technique (GCT)
P_c = Joback's Technique (GCT)

σ = Sastri + Rao Technique (EOT)
μ = Joback's Technique (GCT)
ρ = Rackett Equation (EOT)

First estimates are generated. Estimates are then inserted into the wetting equation.

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Step 3: Evaluate Candidates

Mixtures: 30 wt% Candidate + 70 % Water

$$\frac{a_w}{a_t} = 1 - \exp\left\{-1.45\left(\frac{\sigma_c}{\sigma}\right)^{0.75}\left(\frac{\rho L}{a_t \mu}\right)^{0.1}\left(\frac{L^2 a_t}{g}\right)^{-0.05}\left(\frac{\rho L^2}{\sigma a_t}\right)^{0.2}\right\}$$

μ = Arrhenius Equation (Mix)

ρ = Weight Fraction Average (Mix)

σ = Weight Fraction Average (Mix)

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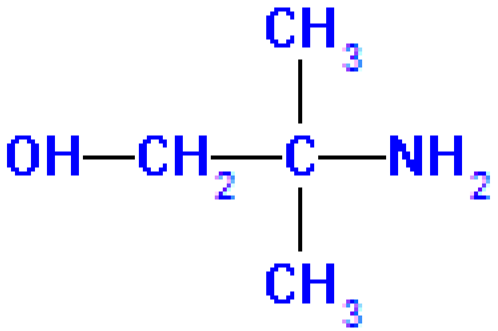
Step 3: Evaluate Candidates

2-Amino-2-methylpropanol



Pure Component Ests

μ = 0.04760 Pa·s
ρ = 844.2 kg/m^3
σ = 0.043 N/m

Mixture Estimates

μ = 0.00092 Pa·s
ρ = 947.5 kg/m^3
σ = 0.062 N/m

$$\frac{a_w}{a_t} = 0.476$$

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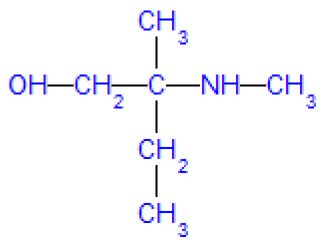
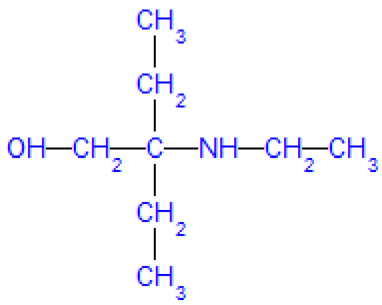
Interesting Candidates

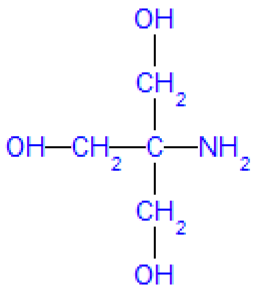
Some designed candidates and their a_w/a_t values



0.490



0.492



0.399

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Three Main Steps

1) Identifying physical property constraints
2) Generating candidate structures and mixtures
3) Testing if candidates satisfy constraints

Computational Approach

$T_b > 100\ °C$
$T_m < -40\ °C$
$\rho > 1000\ kg/m^3$

→

CH_3-O-CH_2-CH_3
CH_3-S-CH_2-CH_3
CH_3-NH_2-CH_2-CH_3
CH_3-CO-CH_2-CH_3

→

$\sum n_i \Delta_{i,Tb}$
$\sum n_i \Delta_{i,Tm}$

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Designing Chemical Products

Applicable to many types of chemical products

- ❑ Artificial Blood
- ❑ Refrigeration Lubes
- ❑ Degreasing Solvents
- ❑ Non-MMH Rocket Fuels
- ❑ Aircraft Deicing Fluids
- ❑ Soil Consolidants
- ❑ Sonar Fill Fluids
- ❑ Phase Change Materials
- ❑ CO2 Absorption Solvents
- ❑ Hydraulic Energy Storage
- ❑ Windshield Washer Fluid
- ❑ Pour Point Depressant

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Thank You

Thank you again for the opportunity to speak to you today.

Questions ?

2000-11-15-01