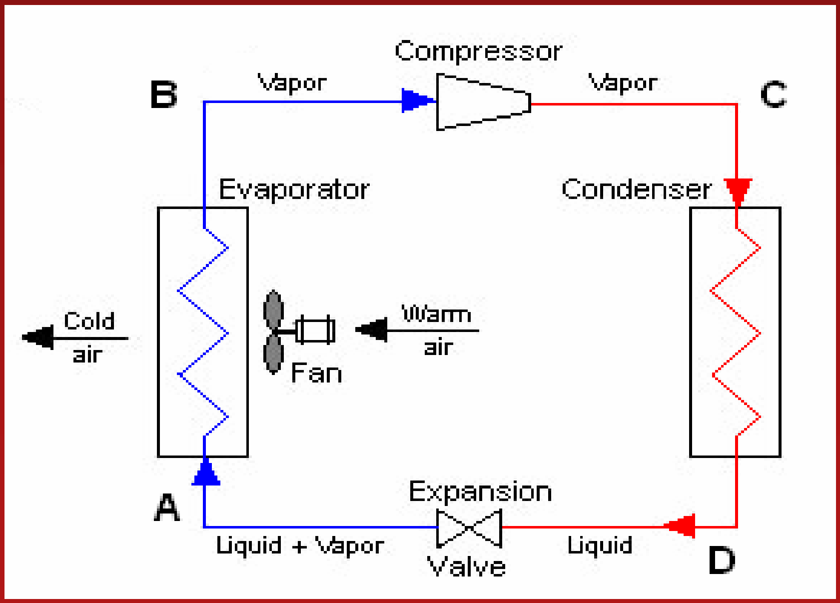
Incorporating Product Design into the Development of New Refrigerants

By: Isaac Anderson and Christopher DiGiulio



[1] *Vapor-Compression Refrigeration*. Answers.com. 4/27/2007
<http://www.answers.com/topic/vapor-compression-refrigeration>.

chemical, biological & materials engineering
university of oklahoma

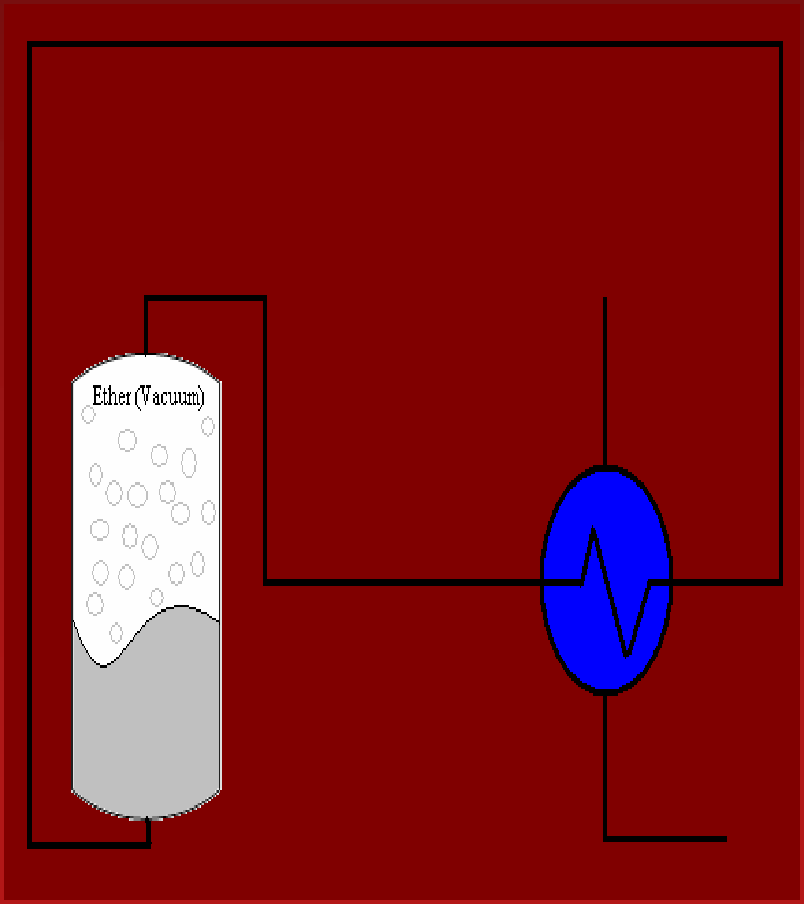
Presentation Outline

1. Background
2. The Use of Consumer Preference Functions in Refrigerant Design
3. Design of New Refrigerants Based on Consumer Preference Functions and the Chosen Market
   - A. Discussion of Group Contribution Theory
   - B. Enumeration Modeling in Excel using Group Contribution Theory
4. Conclusions
5. Recommendations

BACKGROUND

History of Refrigeration

- Refrigeration goes back to ancient times
  - Stored Ice
  - Evaporative Processes
- In 1805, Oliver Evans proposed the use of a volatile fluid in a closed cycle to freeze water into ice



chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

HISTORY OF REFRIGERATION

- **Evan's theories most likely influenced Jacob Perkins and Richard Trevithick**
- **They proposed an air-cycle system in 1828, but it wasn't built either**
- **Actual refrigerants were introduced in the 1830s with the invention of the vapor compression system by Perkins**

Table 1: Historical introduction of refrigerants

year	refrigerant (/absorbent)	chemical formula or makeup
1830s	caoutchoucine	distillate of india rubber
	sulfuric (ethyl) ether	CH_3-CH_2-O-CH_2-CH_3
1840s	methyl ether (R-E170)	CH_3-O-CH_3
1850	water / sulfuric acid	H_2O / H_2SO_4
1856	ethyl alcohol	CH_3-CH_2-OH
1859	ammonia / water	NH_3 / H_2O
1866	chymogene	petrol ether and naphtha (hydrocarbons)
	carbon dioxide	CO_2
1860s	ammonia (R-717)	NH_3
	methyl amine (R-630)	$CH_3(NH_2)$
	ethyl amine (R-631)	CH_3-$CH_2(NH_2)$
1870	methyl formate (R-611)	$HCOOCH_3$
1875	sulfur dioxide (R-764)	SO_2
1878	methyl chloride (R-40)	CH_3Cl
1870s	ethyl chloride (R-160)	CH_3-CH_2Cl
1891	blends of sulfuric acid with hydrocarbons	H_2SO_4, C_4H_{10}, C_5H_{12}, $(CH_3)_2CH$-CH_3
1900s	ethyl bromide (R-160B1)	CH_3-CH_2Br
1912	carbon tetrachloride	CCl_4
	water vapor (R-718)	H_2O
1920s	isobutane (R-600a)	$(CH_3)_2CH$-CH_3
	propane (R-290)	CH_3-CH_2-CH_3
1922	dielene (R-1130) [a]	$CHCl=CHCl$
1923	gasoline	hydrocarbons
1925	trielene (R-1120)	$CHCl=CCl_2$
1926	methylene chloride (R-30)	CH_2Cl_2

[a] blend of *cis*- and *trans*-1,2-dichloroethene isomers

[2] Calm, James M. and David A. Didion. "Trade-Offs in Refrigerant Selections: Past, Present and Future." *Int. J. Refrig., 21, 308 (1998).*

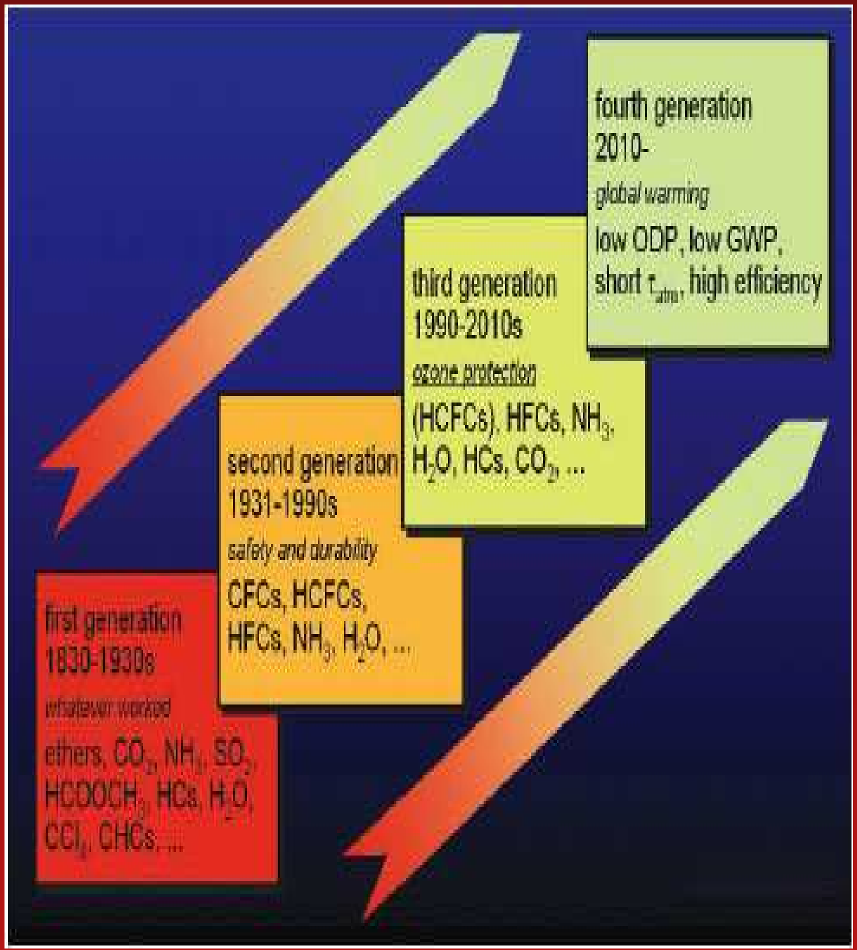
History of Refrigeration

- In 1928, Midgely, Henne, and McNary of GM pioneered work to obtain molecules with desirable properties using systematic design
  - They synthesized all 15 combinations of one carbon with various combinations of chlorine, fluorine, and hydrogen.
  - They finally chose dichlorodifluoromethane (Freon) as having the most desirable characteristics, thus introducing the first chlorofluorocarbons

chemical, biological & materials
chemical, biological and materials engineering university of oklahoma

Refrigerants from 1830-Present

- **First Generation**
  - **Generally solvents, fuels or volatile components (whatever worked)**
- **Second Generation**
  - **CFCs were introduced**
- **Third Generation**
  - **Shift to HCFCs**
- **Fourth Generation**
  - **Focused on refrigerants that do no contribute to global warming**



[3] Calm, James M. and Glenn C. Hourahan. *Refrigerant Data Update*. January 2007. Heating/Piping/Air Conditioning Engineering. Feb. 7, 2007 <http://www.hpac.com/Issue/Article/44475/Refrigerant Data Update>.

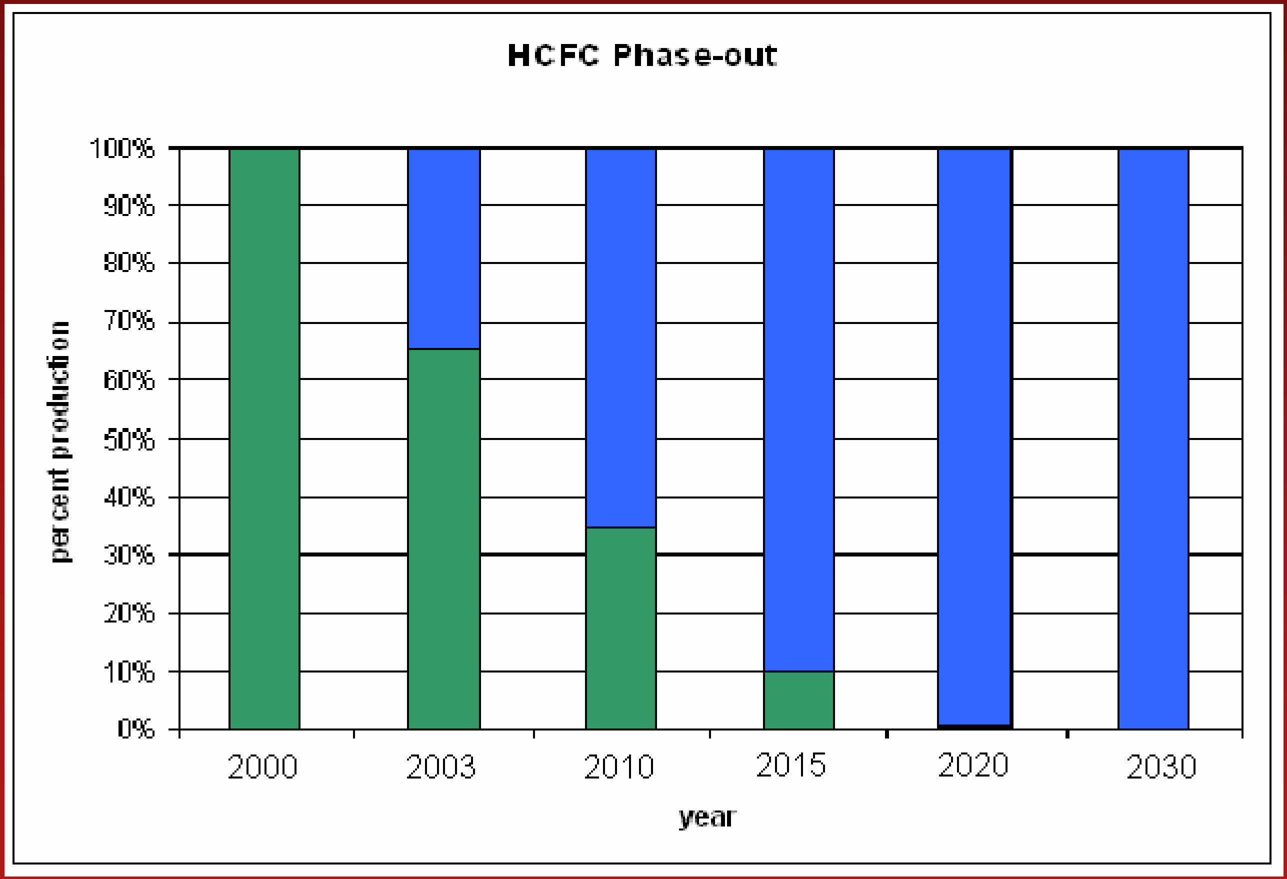
Refrigerant Phase-Out

- 1987
  - Montreal Protocol established requirements that began the world wide phase-out of CFCs
- 1992
  - Montreal Protocol established phase-out for HCFCs

Phase-out Schedule for HCFCs

- **2003**
  - **The amount of all HCFCs that can be produced nationwide must be reduced by 35.0%**
- **2010**
  - **The amount of all HCFCs that can be produced nationwide must be reduced by 65.0%**
- **2015**
  - **The amount of all HCFCs that can be produced nationwide must be reduced by 90.0%**
- **2020**
  - **The amount of all HCFCs that can be produced nationwide must be reduced by 99.5%**
- **2030**
  - **No HCFCs can be produced**

Phase-out Schedule for HCFCs



The Use of Consumer Preference Functions in Refrigerant Design

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Consumer Preference Functions and Demand

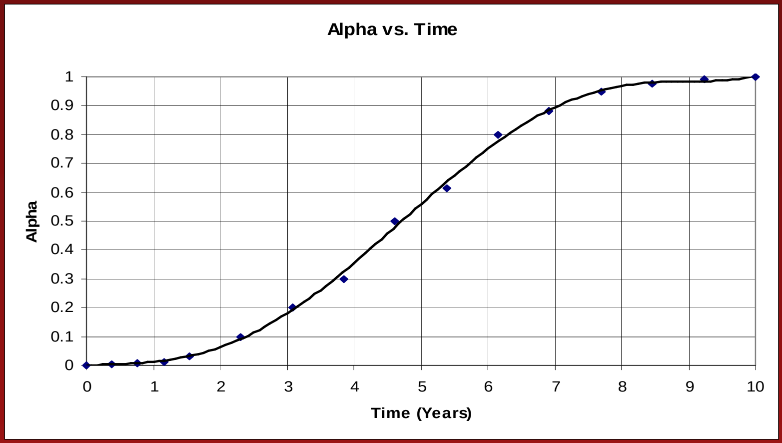
- In the design of the potential refrigerants, consumer preference functions were used to evaluate refrigerant properties
- Consumer preference functions can also be used to solve for the demand (d_1) of a new refrigerant when it is in competition with an existing refrigerant
- In the following equation, β is the only variable dependent on consumer preference functions

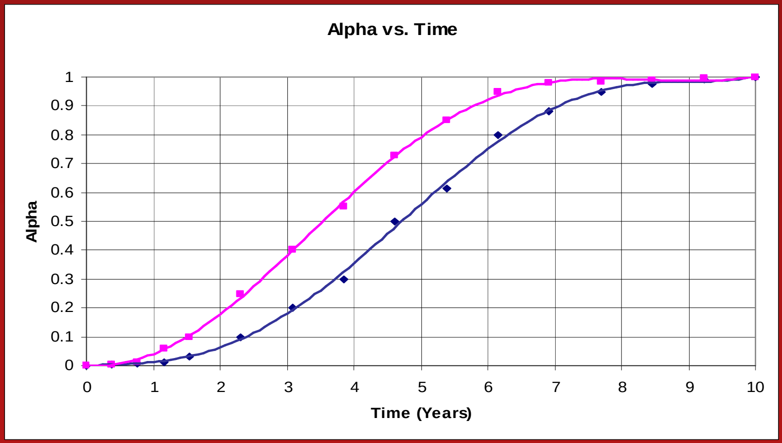
$$\phi(d_1) = p_1 d_1 - \left(\frac{\alpha}{\beta}\right)^{\rho} p_2 \left[\frac{Y - p_1 d_1}{p_2}\right]^{1-\rho} d_1^{\rho} = 0$$

Where:
Y is the market potential
P is the price
D is the demand
ρ was set to a constant value of 0.76
α is the consumer awareness of our product
β relative consumer preference
The subscript 1 refers to the new product
The subscript 2 refers to the existing comparison product

DEVELOPMENT OF α

- Alpha is the consumer awareness of the new refrigerant as a function of time.
- The plots on the right show the values of alpha that were used when calculating the demand
- The bottom figure illustrates the effect of increases advertising





chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

DEVELOPMENT OF β

- **The equation used to derive β is as follows**

$$\beta = \frac{H_2(\text{competition preference})}{H_1}$$

- **Where H_i is the respective consumer preference of each product**

$$H_i = \sum \omega_i y_i$$

Where : ω_i is the weight of refrigerant property

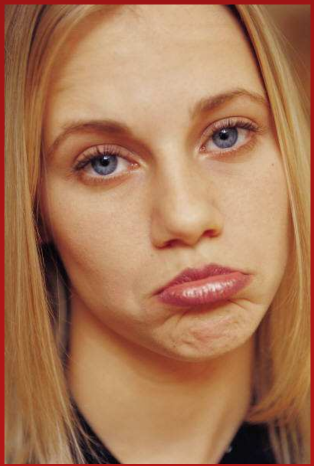
y_i is the property score of each refrigerant property

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Consumer Preference Functions

- **Consumer preference functions predict consumer reactions to different refrigerant design properties**

- **The consumer preference functions were estimated using expected consumer reactions to refrigerant properties**



chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

What makes a good refrigerant?

- Safe: non-toxic, nonflammable, and nonexplosive
- Environmentally friendly: low ODP, low GWP
- Compatible with existing refrigeration materials
- Desirable thermodynamic characteristics: high latent heat, low compression ratio, low specific heat of liquid
- Stable at operating temperatures

Consumer Preference Functions

- Based on 6 characteristics
  - Flammability
  - Explosiveness
  - Toxicity
  - Global Warming Potential
  - Ozone Depletion Potential
  - Coefficient of Performance
- The outlook for discovery or synthesis of ideal refrigerants is extremely unlikely. Trade-offs among desired objectives are necessary to achieve balanced solutions[4]

[4] Calm, James M. and David A. Didion. "Trade-Offs in Refrigerant Selections: Past, Present and Future." *Int. J. Refrig., 21, 308 (1998).*

chemical, biological & materials
chemical, biological and materials engineering university of oklahoma

SURVEY 1

Survey 1 – Refrigerant Design

Please Rank each of these issues on a scale of 1 to 10 (**10** is very important and **1** is not important)	
Refrigerant Property / Refrigeration Cycle Properties	**Rank**
Is a refrigerant with a **low toxicity** important to you	7
Is a refrigerant that doesn't contribute to **global warming** important to you	8
The potential for **ozone depletion** is something that concerns you	8
The **efficiency** of the system should be as **high** as possible	9
The **flammability** of the refrigerant should be as **low** as possible	10
The system should have the lowest possible **explosion potential**	10

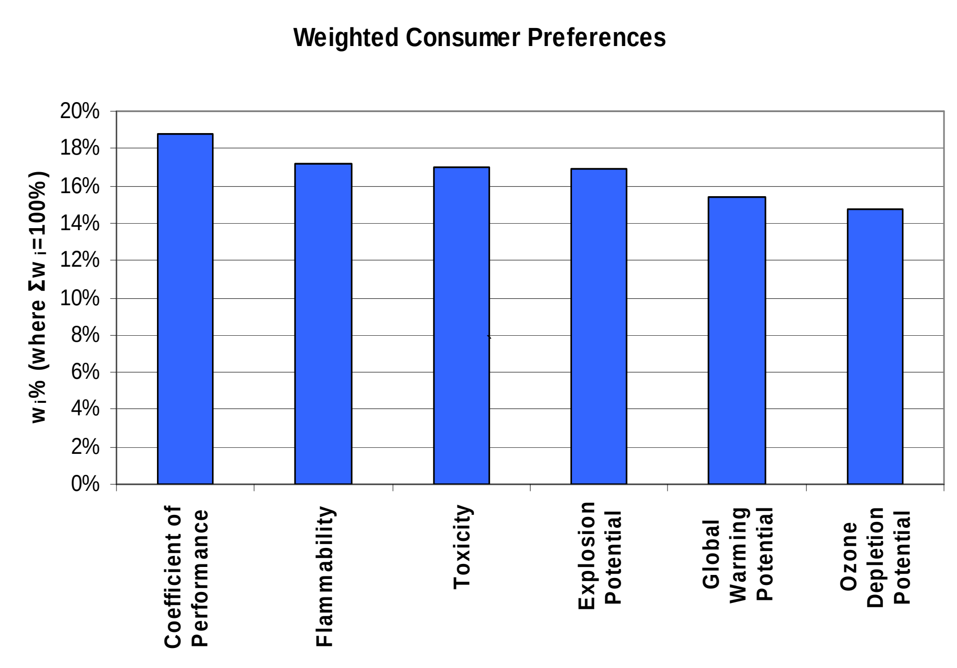
REMEMBER … COST IS NOT AN ISSUE!!!

Expected consumer response

ESTIMATING ω_i

- This figure represents the expected weights of the refrigerant properties

- It can be seen that efficiency is the most important property to consumers



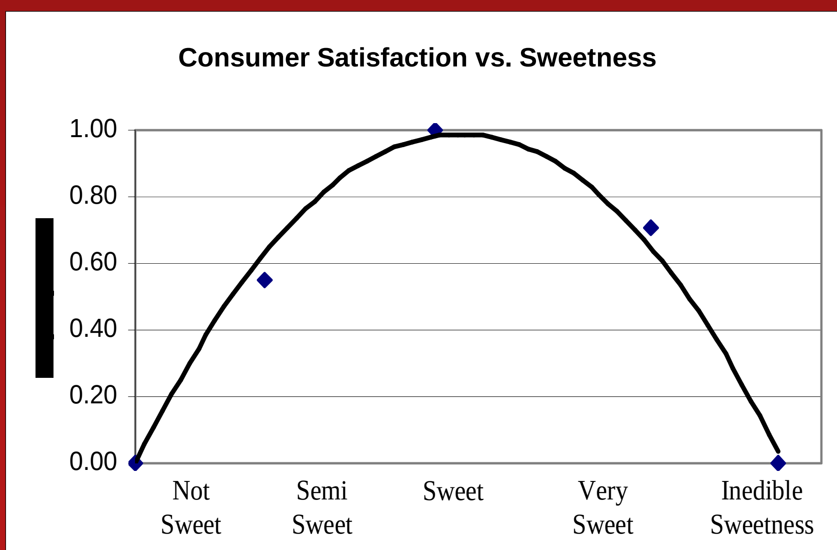
chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

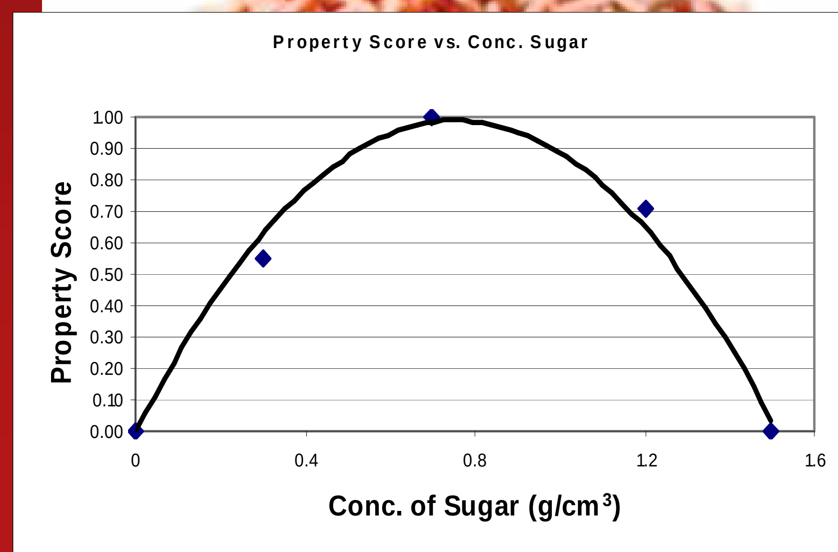
SURVEY 2

Example – Donut Design (Sweetness)

The following options are meant to gauge consumer preferences when concerning the sweetness of donuts. In the following options, a sweet rating would be equivalent to the sweetness of a chocolate bar. Based on this information, please assign percentage values indicating how happy you would be with each option.

PERSON	Not Sweet	Semi Sweet	Sweet	Very Sweet	Inedible Sweetness
1	0%	75%	50%	25%	0%
2	0%	100%	50%	0%	0%
3	0%	0%	100%	75%	0%



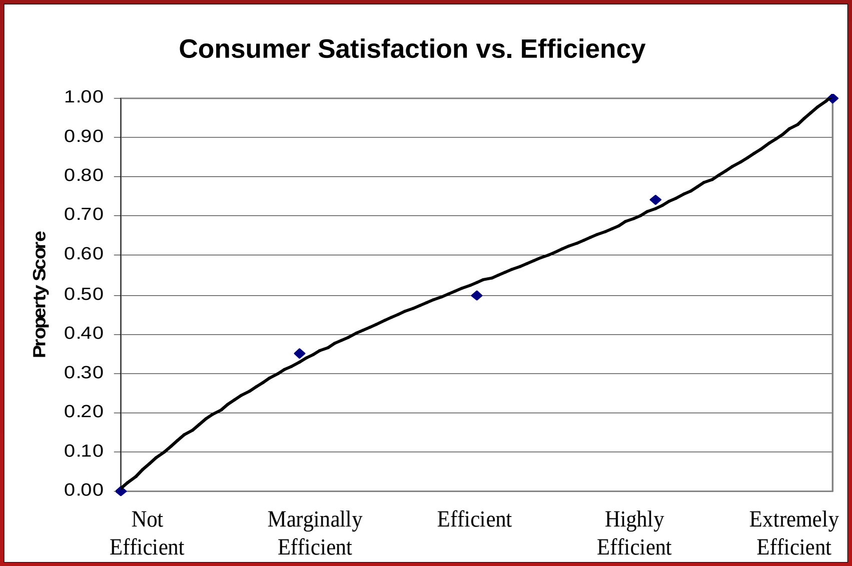


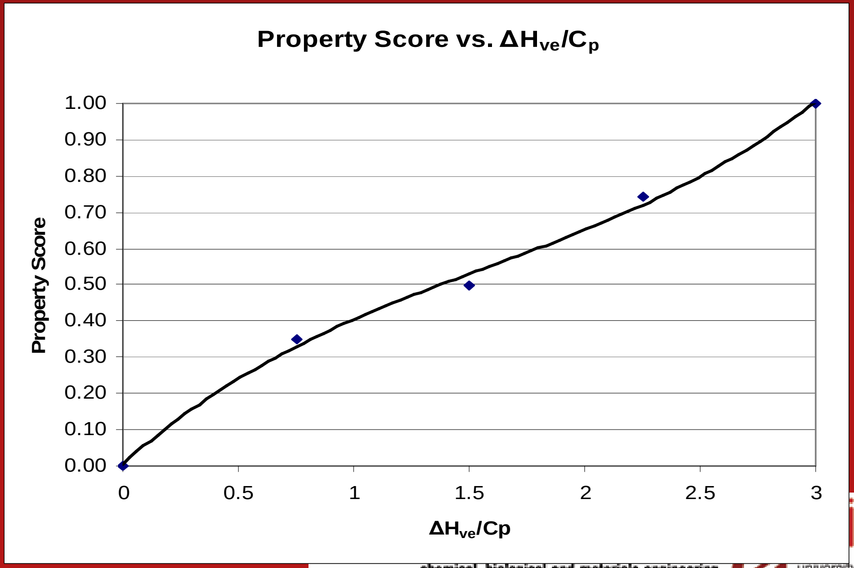
SURVEY 2 – EFFICIENCY

Coefficient of Performance (Efficiency)

In the following options, R-12 (Freon) would be considered an efficient refrigerant.
Based on this information, please assign percentage values indicating how happy you would be with each option.

The system is **not efficient**	The system is **marginally efficient**	The system is **efficient**	The system is **highly efficient**	The system is **extremely efficient**





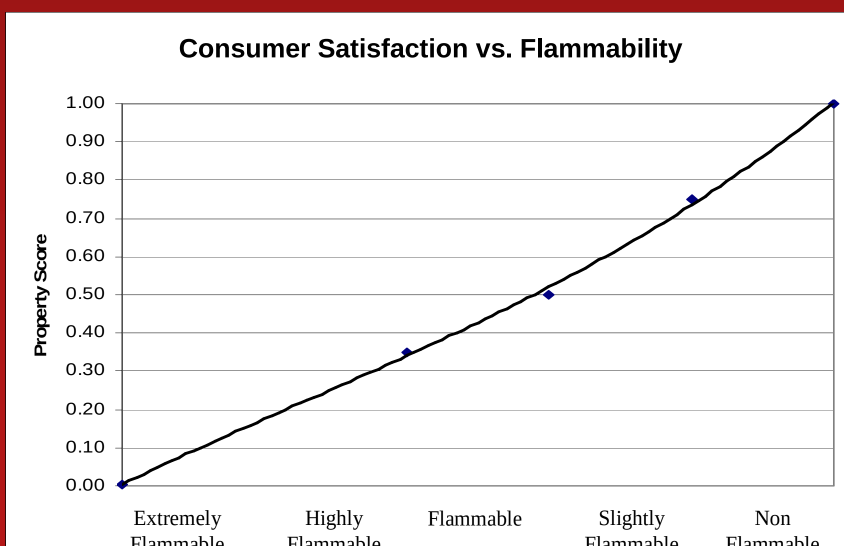
SURVEY 2 – FLAMMABILIT

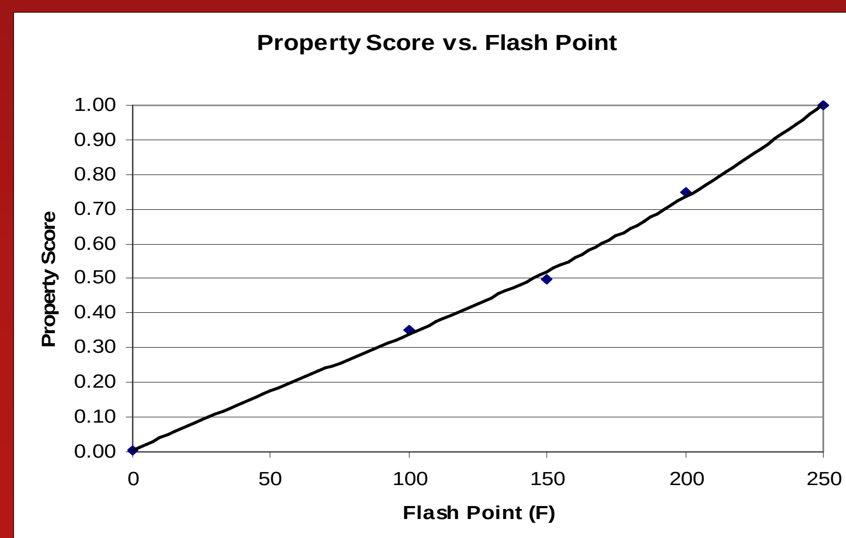
FLAMMABLE MATERIALS

Flammability

Ethanol (200 proof), or more commonly know as consumable liquor, would have a ranking of extremely flammable on the following scale. Based on this information, please assign percentage values indicating how happy you would be with each option.

The refrigerant is **non flammable**	The refrigerant is **slightly flammable**	The refrigerant is **flammable**	The refrigerant is **highly flammable**	The refrigerant is **extremely flammable**



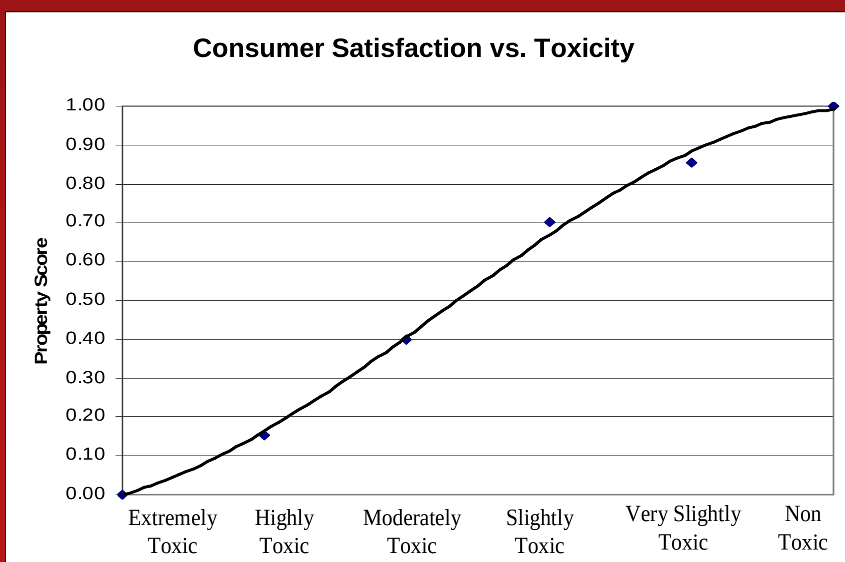


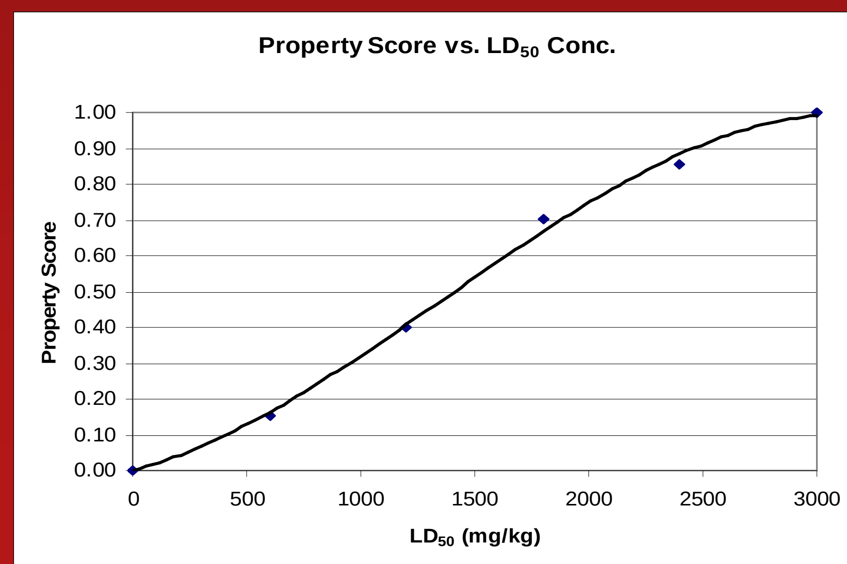
SURVEY 2 – TOXICITY

Toxicity

The following options are meant to gauge the consumer's preference to toxicity. Phenol would be considered highly toxic and water would be considered non toxic out of the list of options. To present the dangers associated with different levels of toxicity, the precautions associated with phenol are listed. Exposure to phenol can result in acute poisoning by ingestion, and inhalation or skin contact may lead to death. Phenol is readily absorbed through the skin. It is highly toxic by inhalation, corrosive and is a severe irritant. **Based on this information, please assign percentage values indicating how happy you would be with each option.**

The refrigerant is **non toxic**	The refrigerant is **very slightly toxic**	The refrigerant is **slightly toxic**	The refrigerant is **moderately toxic**	The refrigerant is **highly toxic**	The refrigerant is **extremely toxic**



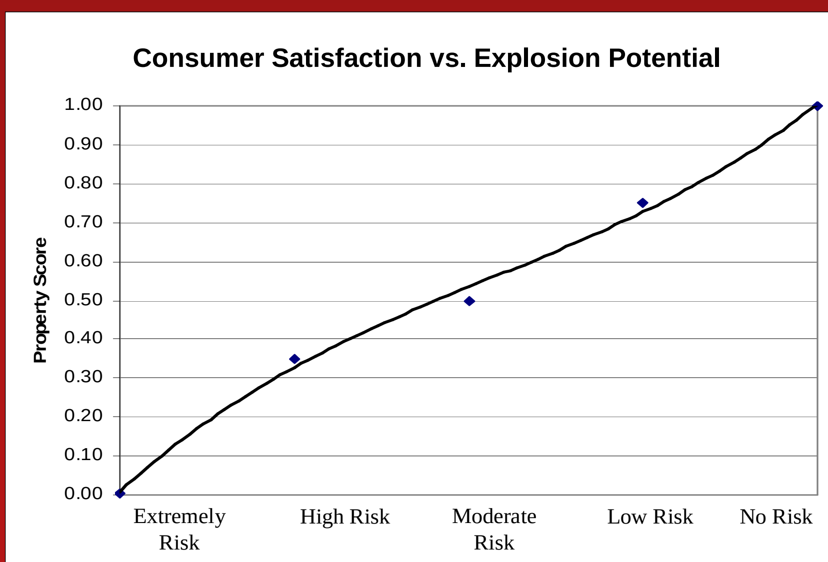


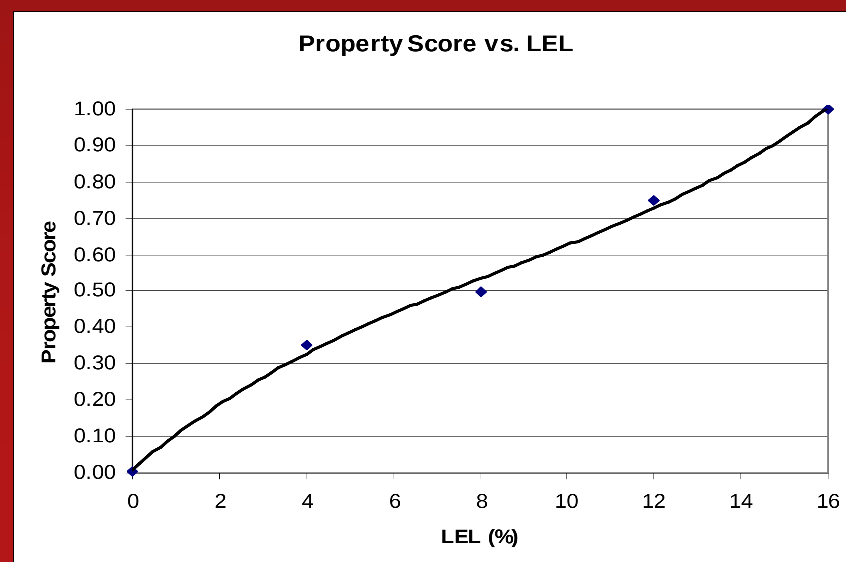
SURVEY 2 – EXPLOSION POTENTIAL

Explosion Potential

Ethanol, used in the preceding example, would pose a moderate risk for explosions because it can form explosive mixtures with air. **Based on this information, please assign percentage values indicating how happy you would be with each option.**

The refrigerant has **no risk** for explosions	The refrigerant has a **low risk** for explosions	The refrigerant has a **moderate risk** of explosions	The refrigerant has a **high risk** of explosions	The refrigerant has a **extremely high risk** of explosions



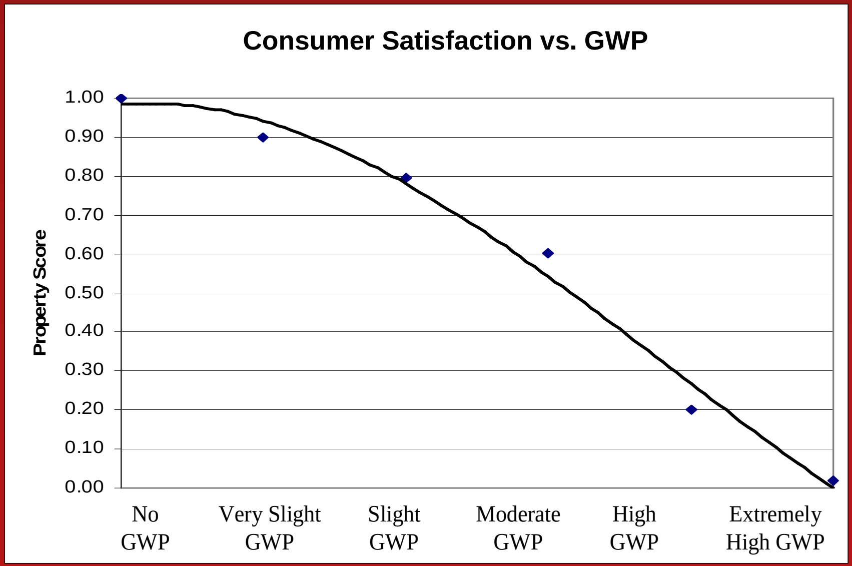


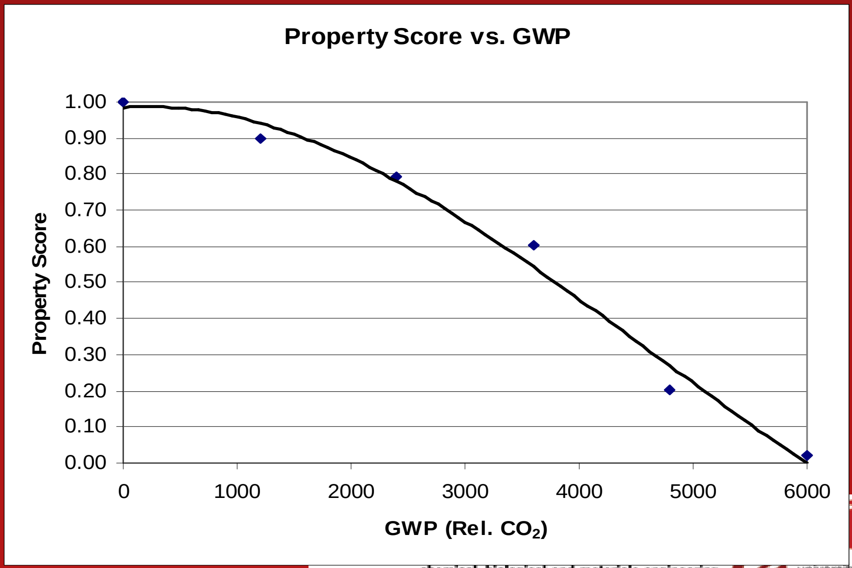
Survey 2 – Global Warming Potential

Global Warming Potential

Global warming potential (GWP) is evaluated on a scale that uses CO_2 as the benchmark. Meaning, CO_2 is assigned a value and other components are compared to CO_2. Sulfur hexafluoride has one of the highest GWP's on this scale and would be ranked as having an extremely high GWP on this survey. Oxygen has no GWP and would be ranked as having no GWP on this survey. **Based on this information, please assign percentage values indicating how happy you would be with each option.**

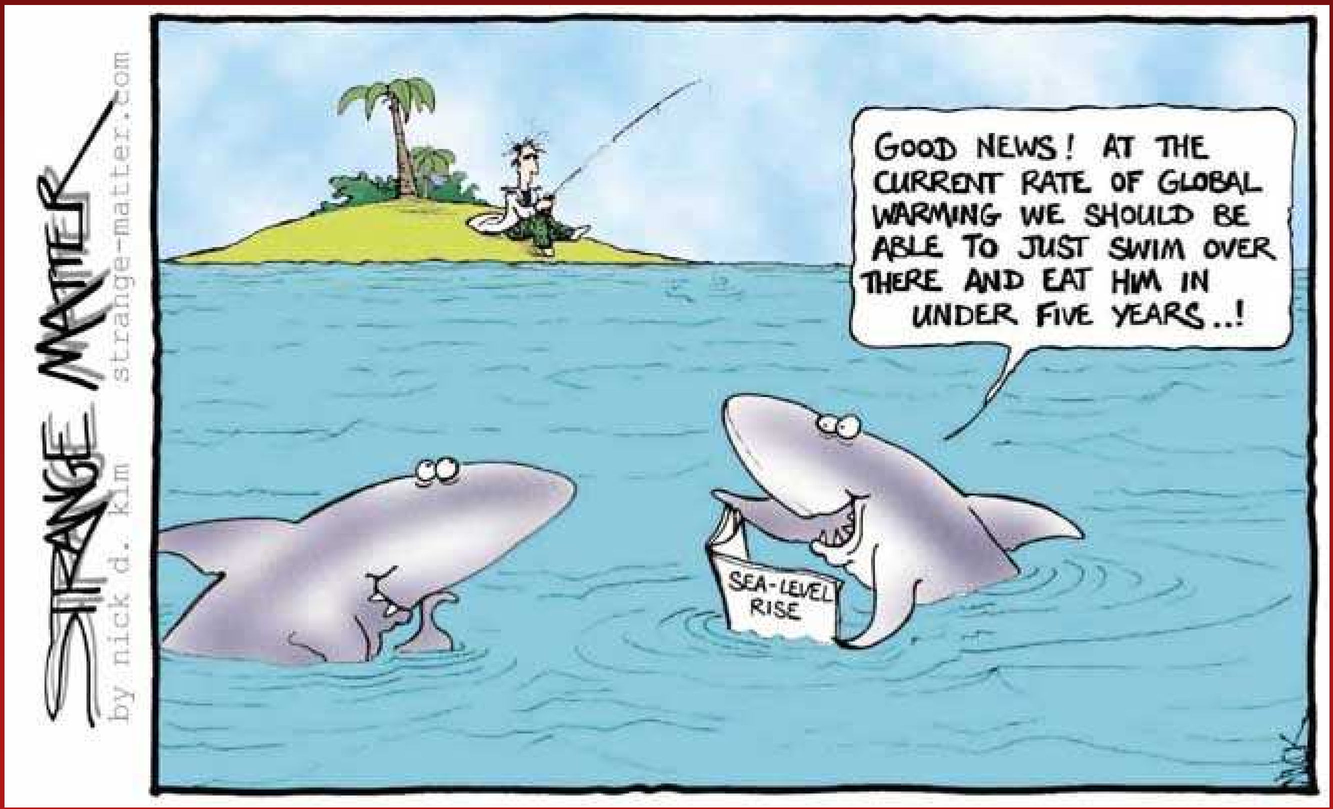
The refrigerant has **no** GWP	The refrigerant has a **very slight** GWP	The refrigerant has a **slight** GWP	The refrigerant has a **moderate** GWP	The refrigerant has a **high** GWP	The refrigerant has an **extremely high** GWP





chemical, biological and materials engineering
university of oklahoma

Survey 2 – Global Warming Potential



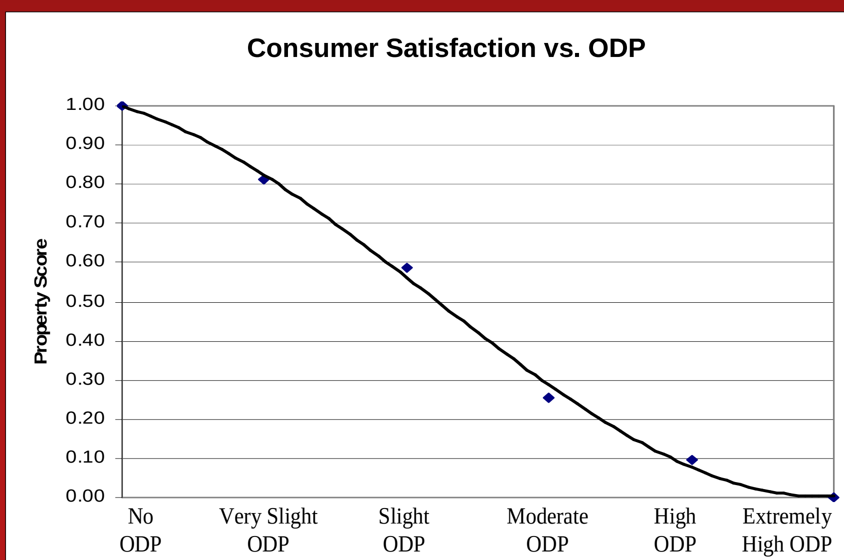
chemical, biological & materials
chemical, biological and materials engineering university of oklahoma

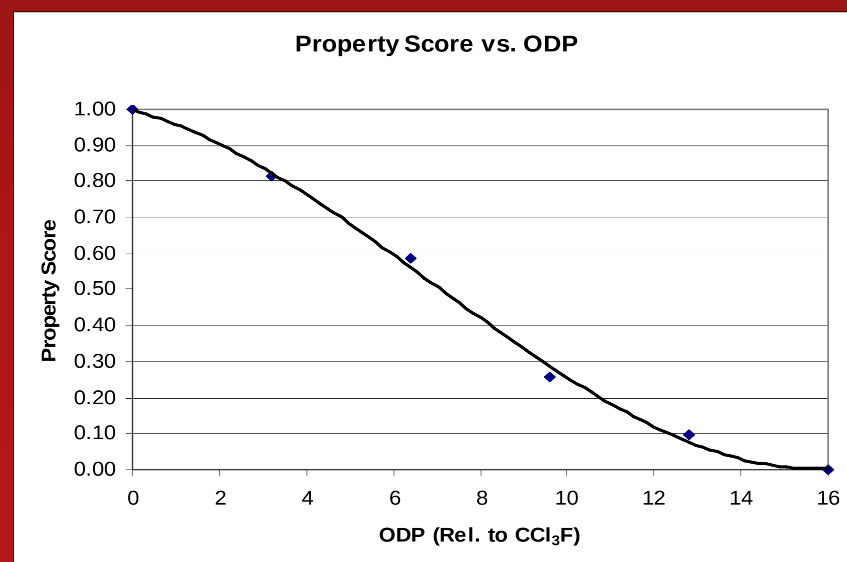
Survey 2 – Ozone Depletion Potential

Ozone Depletion Potential

Ozone depletion potential (ODP) is evaluated on a scale that uses CFC-11 as a benchmark. All other components are based on how damaging to the ozone they are in relation to CFC-11. On this scale, CFC-12 (Freon) would be considered to have a moderate ODP. **Based on this information, please assign percentage values indicating how happy you would be with each option.**

The refrigerant **has no ODP**	The refrigerant has a **very slight ODP**	The refrigerant has a **slight ODP**	The refrigerant has a **moderate ODP**	The refrigerant **has a high ODP**	The refrigerant **has an extremely high ODP**

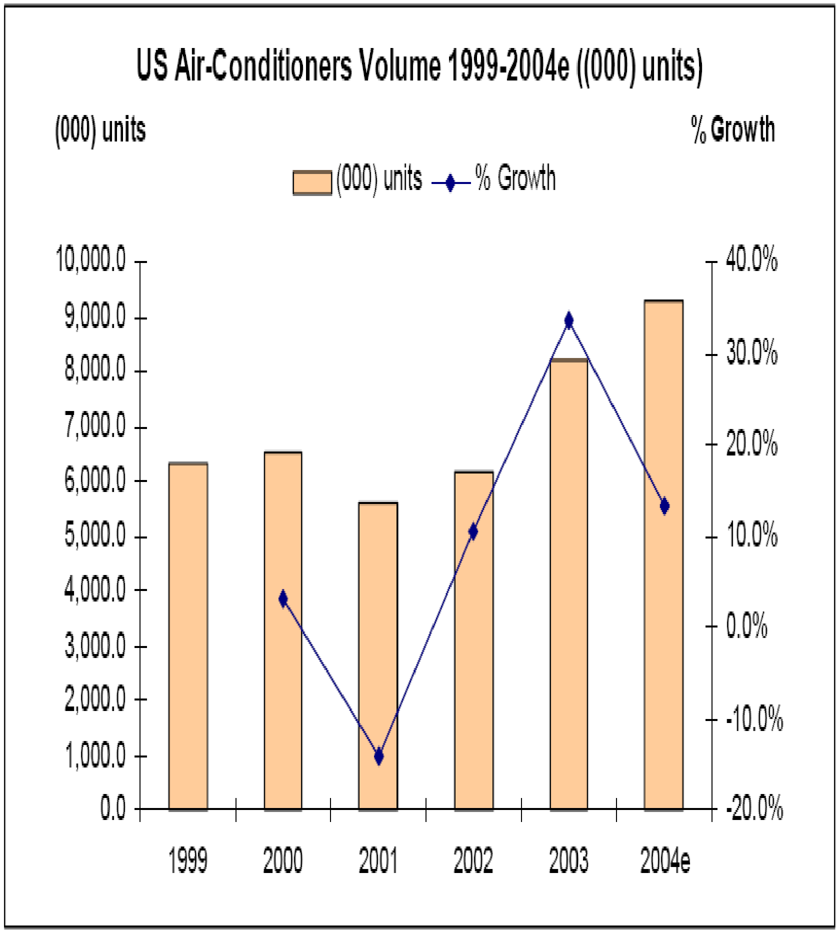




Solving for the Market Potential (Y)

- Before the market potential can be solved for, a market must be defined
- Possible Markets for New Refrigerants include:
  - Air conditioning for homes and commercial buildings
  - Air conditioning of personal cars, trucks and sport utility vehicles
  - Refrigerated transportation (food, animals, beer, medical supplies etc.)
  - Refrigerators and freezers
  - Industrial operations

CENTRAL AIR/HOUSEHOLD UNITS

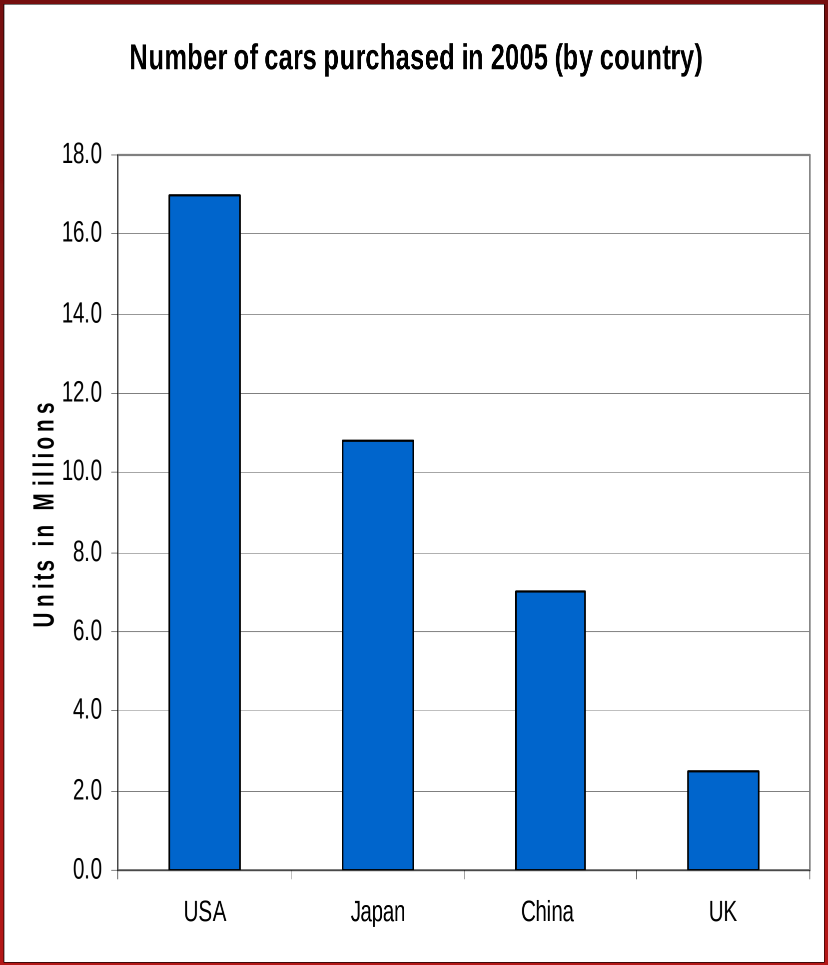


Source: AHAM, Appliance Magazine, Appliance Manufacturer, Snapdata Research

- **In 2006, the number of total housing units in the US was 124.4 Million Units**
- **The number of air conditioners sold in the US is estimated to reach 10.7 million units in 2008**

[5] *US Air Conditioners 2004.*

AUTOMOBILES SOLD IN 2005



- The automotive industry offers higher numbers of units sold per year
- Advantage of the automotive market
  - Higher Volume

Estimating the Market Potential of the Auto Market

- In this study, the automotive market was chosen because it offers higher volume in sales
- The market potential was estimated by multiplying automotive sales by an average refrigerant volume required of 24oz.
- The answer obtained was approximately 14.2 thousand metric tons per year

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Comparing This Value to Data Provided by the UNFCCC

- **The market potential was then compared to information obtained from United Nations Framework Convention on Climate Change (UNFCCC). The table is on the following slide**
- **The UNFCCC provides the amounts of varying refrigerants produced by the participating countries**
  - **These countries are Australia, Colombia, the European Union and its member states, Japan, Switzerland and the USA.**
- **Using the aforementioned estimation, it was calculated that the US accounts for 1/10th R-134a production cited by UNFCCC**
- **This value seems reasonable given the volume of automobile purchased each year**

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

PRODUCTION & RELEASE DATA PROVIDED BY THE UNFCCC

Table 10 Production and Atmospheric Release — Expanded Data — Reporting Companies only

HFC-134a (thousand metric tonnes) — (thousand metric tonnes)

	Annual		Cumulative Total			Short Banking Times			Medium Banking Times			Long Banking Times		
	Production	Released	Production	Released	Unreleased	Sales	Released	Unreleased	Sales	Released	Unreleased	Sales	Released	Unreleased
1990	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0
1991	2.2	0.2	2.4	0.3	2.1	0.2	0.1	0.0	2.2	0.2	2.0	0.0	0.0	0.0
1992	6.4	0.8	8.8	1.1	7.7	0.5	0.3	0.2	8.2	0.8	7.4	0.1	0.0	0.1
1993	26.5	3.6	35.3	4.7	30.6	2.2	1.4	0.9	32.7	3.2	29.4	0.4	0.1	0.3
1994	50.4	9.1	85.7	13.8	71.9	5.1	3.6	1.4	78.7	9.5	69.2	1.9	0.6	1.3
1995	73.8	19.8	159.5	33.6	125.9	15.5	10.3	5.2	140.0	21.9	118.0	4.0	1.4	2.6
1996	83.7	32.0	243.2	65.6	177.6	25.5	20.5	5.0	210.9	42.7	168.2	6.7	2.3	4.4
1997	101.9	41.9	345.1	107.4	237.7	32.9	29.2	3.7	301.8	74.5	227.3	10.4	3.7	6.6
1998	112.2	53.9	457.3	161.3	296.0	39.5	36.2	3.3	398.3	118.1	280.2	19.6	7.0	12.5
1999	133.7	69.8	591.0	231.1	359.9	53.8	46.7	7.2	509.4	174.2	335.2	27.8	10.3	17.5
2000	132.0	85.3	723.0	316.4	406.6	69.4	61.6	7.8	620.0	241.8	378.2	33.6	13.0	20.6

Notes

Emissions are calculated from production and categorised sales using "emission functions".

The emission function for "Long" banking times has been changed in view of the results of a survey commissioned by AFEAS:

(Ashford P., 1999, Development of a global emission function for blowing agents used in closed cell foam, Final Report to AFEAS)

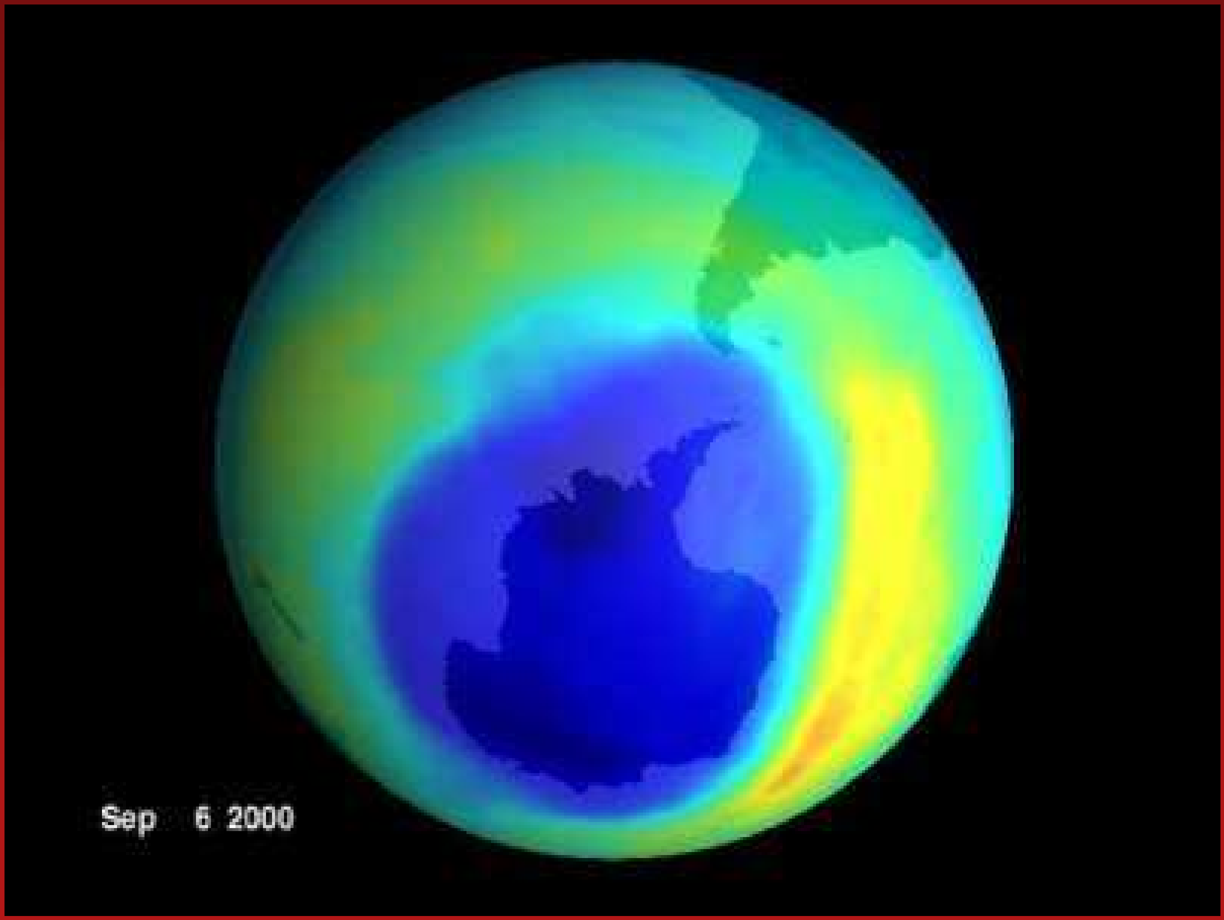
This showed that most (99%) of the HFC-134a in closed cell foams was used to blow expanded polystyrene, the emission function for which comprises 32.5% loss in the year of manufacture and 3%/yr thereafter.

Columns affected by this change are shaded pale green/blue.

The emission function for "Short" banking time (e.g. aerosols) is the same as in previous reports (50% emitted in the year of manufacture and 100% the year after).

The emission function for "Medium" banking time (predominantly refrigeration) is the same as in previous reports (normally distributed about a mean 4.5 year service lifetime).

HOLE IN THE OZONE



chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Design of New Refrigerants Based on Consumer Preference Functions and the Chosen Market

chemical, biological & materials

chemical, biological and materials engineering university of oklahoma

Methods for Examining Refrigerants

Analysis from a list

- Only known molecules can be considered
- Extensive database is necessary for complete analysis
- Limited to molecules already identified as refrigerants

Group contribution theory

- Allows for the consideration of unknown molecules
- No need for extensive databases
- Generalized approach

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

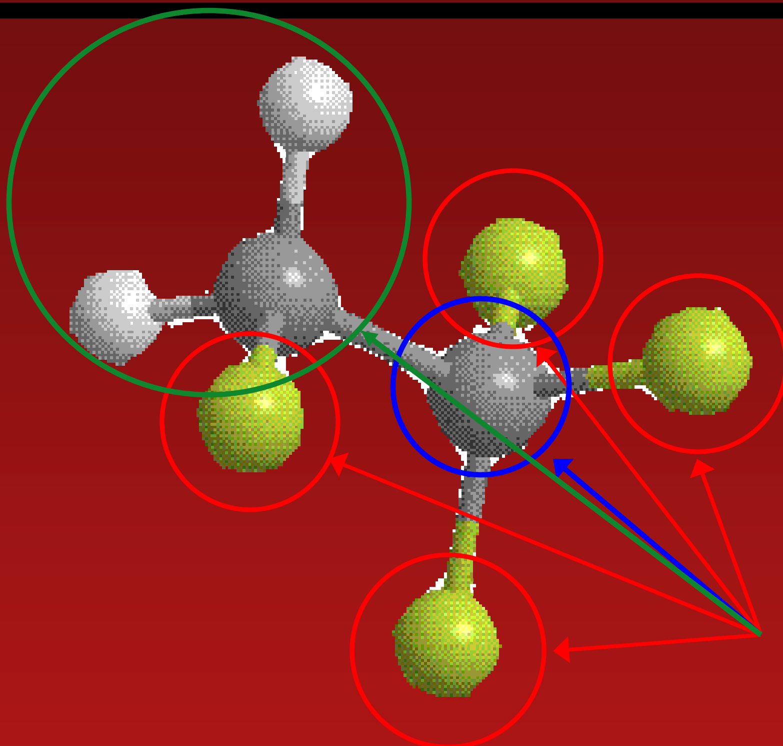
Discussion of Group Contribution Theory

Group Contribution Theory

- Developed by observation of existing molecules as a way to predict the basic characteristics of ANY molecule

- Uses characteristics of each functional group to estimate the characteristics of a molecule formed from the functional groups

Molecule Made of Functional Groups



1,1,1,2-Tetrafluoroethane

- Specific groups of atoms within a molecule
- Responsible for the chemical make-up of the molecule
- Example:
  - 3 different functional group types
  - 6 total groups

FUNCTIONAL GROUPS

Acyclic Groups	Cyclic Groups	Halogen Groups	Oxygen Groups	Nitrogen Groups	Sulfur Groups
-CH3	R-CH2-R	-F	-OH	-NH2	-SH
-CH2-	2R>CH-R	-Cl	-O-	>NH	-S-
>CH-	2R>C<2R	-Br	R-O-R	2R>NH	R-S-R
>C<	R=CH-R	-I	>CO	>N-	
=CH2	R=C<2R		2R>CO	R=N-	
=CH-			-CHO	-CN	
=C<			-COOH	-NO2	
=C=			-COO-		
			=O		

= represents a double bond, bonding site

-- represents a single bond, bonding site

R represents a ring bonding site

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Enumeration Modeling in Excel Using Group Contribution Theory

chemical, biological & materials
chemical, biological and materials engineering university of oklahoma

Enumeration vs. Optimization

Enumeration

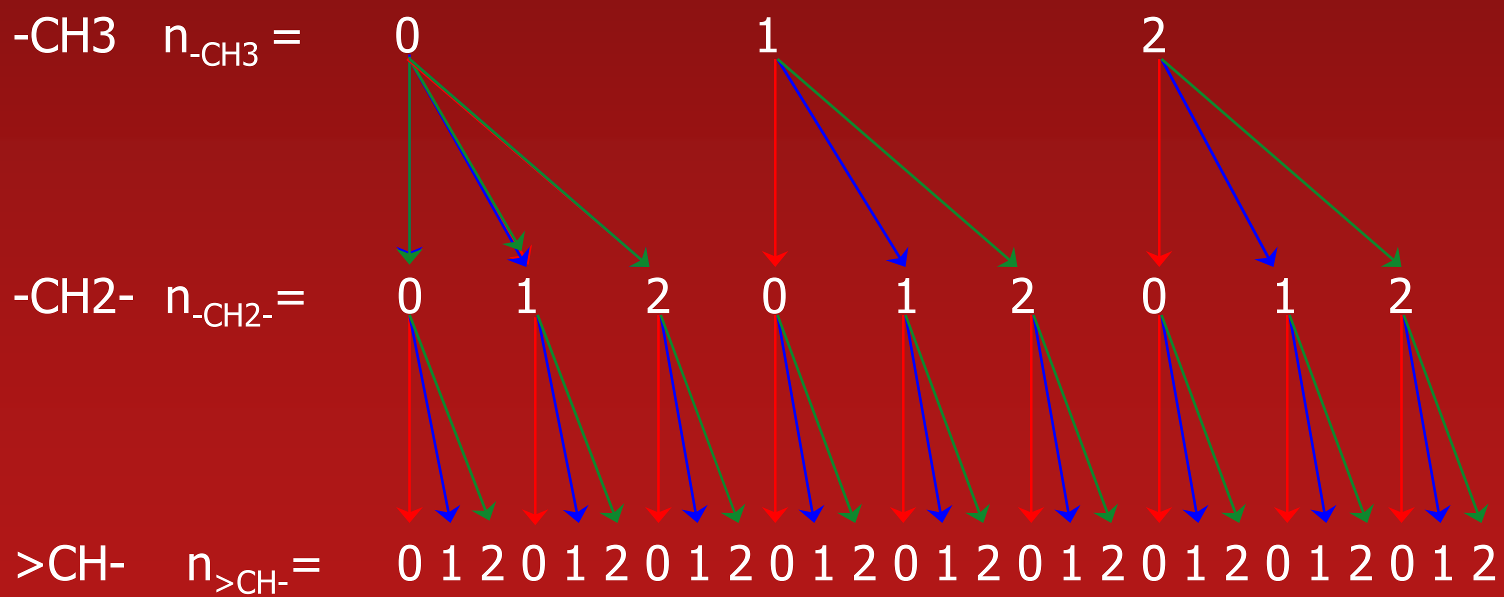
- No initial guess required
- Calculates every possible option
- Complete confidence in solution
- Very time consuming – requires hours or days for processing

Optimization Model

- Requires a good initial guess
- Calculates only options which lead to a more likely solution
- Almost complete confidence in solution
- Less time consuming – requires a few hours for processing

What is the Enumeration Method?

- **Also known as the exhaustive method or brute force method**
- **Take into account every possible combination of functional groups**



Iterations for 3x3 = 27

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

VBA CODE

```
Module2 - 1

Sub enumerator()
counter1 = 0
counter2 = 0
Nmax = 10
Tbmax = 310
For i = 0 To 7
Cells(4, 5) = i
For j = 0 To 8
Cells(5, 5) = j
If i < Nmax Then
If i * 23.58 + 198 < Tbmax Then
For k = 0 To 3
Cells(6, 5) = k
If i + j < Nmax Then
If i * 23.58 + j * 22.88 + 198 < Tbmax Then
For l = 0 To 2
Cells(7, 5) = l
If i + j + k < Nmax Then
If i * 23.58 + j * 22.88 + k * 21.74 + 198 < Tbmax Then
For m = 0 To 7
Cells(8, 5) = m
If i + j + k + l < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 < Tbmax Then
For n = 0 To 4
Cells(9, 5) = n
If i + j + k + l + m < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 < Tbmax Then
For o = 0 To 3
Cells(10, 5) = o
If i + j + k + l + m + n < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 < Tbmax Then
For p = 0 To 4
Cells(11, 5) = p
If i + j + k + l + m + n + o < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 < Tbmax The
n
For q = 0 To 6
Cells(12, 5) = q
If i + j + k + l + m + n + o + p < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 < Tbmax Then
For r = 0 To 3
Cells(13, 5) = r
If i + j + k + l + m + n + o + p + q < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 < Tbmax Then
For s = 0 To 2
Cells(14, 5) = s
If i + j + k + l + m + n + o + p + q + r < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 < Tbmax Then
For t = 0 To 6
Cells(15, 5) = t
If i + j + k + l + m + n + o + p + q + r + s < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 < Tbmax Then
For u = 0 To 2
Cells(16, 5) = u
If i + j + k + l + m + n + o + p + q + r + s + t < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 < Tbmax Then
For v = 0 To 7
Cells(17, 5) = v
If i + j + k + l + m + n + o + p + q + r + s + t + u < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 < Tbmax Then
For w = 0 To 7
Cells(18, 5) = w
If i + j + k + l + m + n + o + p + q + r + s + t + u + v < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) < Tbmax Then
For x = 0 To 4
Cells(19, 5) = x
```

```
Module2 - 2

If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 < Tbmax Then
For y = 0 To 3
Cells(20, 5) = y
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 < T
bmax Then
For z = 0 To 1
Cells(21, 5) = z
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 < Tbmax Then
For aa = 0 To 4
Cells(22, 5) = aa
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 < Tbmax Then
For bb = 0 To 2
Cells(23, 5) = bb
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 < Tbmax Then
For cc = 0 To 2
Cells(24, 5) = cc
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 < Tbmax Then
For dd = 0 To 1
Cells(25, 5) = dd
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 < Tbmax Then
For ee = 0 To 1
Cells(26, 5) = ee
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd < Nmax Th
en
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 < Tbmax Then
For ff = 0 To 1
Cells(27, 5) = ff
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee < Nm
ax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 < Tbmax Then
For gg = 0 To 1
Cells(28, 5) = gg
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 < T
bmax Then
For hh = 0 To 2
Cells(29, 5) = hh
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 < Tbmax Then
For ii = 0 To 4
Cells(30, 5) = ii
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh < Nmax Then
```

VBA Code

```
Module2 - 3

If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) < Tbmax Then
For jj = 0 To 5
Cells(31, 5) = jj
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 < Tbmax Then
For kk = 0 To 5
Cells(32, 5) = kk
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 < Tbmax Then
For ll = 0 To 3
Cells(33, 5) = ll
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 < Tbmax Then
For mm = 0 To 5
Cells(34, 5) = mm
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 < Tbmax Then
For nn = 0 To 2
Cells(35, 5) = nn
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 < Tbmax Then
For oo = 0 To 2
Cells(36, 5) = oo
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 < Tbmax Then
For pp = 0 To 4
Cells(37, 5) = pp
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn + oo < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 + oo * 152.54 < Tbmax Then
For qq = 0 To 4
Cells(38, 5) = qq
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn + oo + pp < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 + oo * 152.54 + pp * 63.56 < Tbmax Then
For rr = 0 To 5
Cells(39, 5) = rr
```

```
Module2 - 4

If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn + oo + pp + qq < Nmax Then
Cells(45, 2) = counter2
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 + oo * 152.54 + pp * 63.56 + qq * 68.78 < Tbmax Then
If Cells(86, 13).Value > 0 Then
e = 2
d = 134 + counter1
Cells(d, e) = Cells(93, 13).Value
Cells(d, e + 1) = Cells(86, 13).Value
Cells(d, e + 2) = Cells(4, 5).Value
Cells(d, e + 3) = Cells(5, 5).Value
Cells(d, e + 4) = Cells(6, 5).Value
Cells(d, e + 5) = Cells(7, 5).Value
Cells(d, e + 6) = Cells(8, 5).Value
Cells(d, e + 7) = Cells(9, 5).Value
Cells(d, e + 8) = Cells(10, 5).Value
Cells(d, e + 9) = Cells(11, 5).Value
Cells(d, e + 10) = Cells(12, 5).Value
Cells(d, e + 11) = Cells(13, 5).Value
Cells(d, e + 12) = Cells(14, 5).Value
Cells(d, e + 13) = Cells(15, 5).Value
Cells(d, e + 14) = Cells(16, 5).Value
Cells(d, e + 15) = Cells(17, 5).Value
Cells(d, e + 16) = Cells(18, 5).Value
Cells(d, e + 17) = Cells(19, 5).Value
Cells(d, e + 18) = Cells(20, 5).Value
Cells(d, e + 19) = Cells(21, 5).Value
Cells(d, e + 20) = Cells(22, 5).Value
Cells(d, e + 21) = Cells(23, 5).Value
Cells(d, e + 22) = Cells(24, 5).Value
Cells(d, e + 23) = Cells(25, 5).Value
Cells(d, e + 24) = Cells(26, 5).Value
Cells(d, e + 25) = Cells(27, 5).Value
Cells(d, e + 26) = Cells(28, 5).Value
Cells(d, e + 27) = Cells(29, 5).Value
Cells(d, e + 28) = Cells(30, 5).Value
Cells(d, e + 29) = Cells(31, 5).Value
Cells(d, e + 30) = Cells(32, 5).Value
Cells(d, e + 31) = Cells(33, 5).Value
Cells(d, e + 32) = Cells(34, 5).Value
Cells(d, e + 33) = Cells(35, 5).Value
Cells(d, e + 34) = Cells(36, 5).Value
Cells(d, e + 35) = Cells(37, 5).Value
Cells(d, e + 36) = Cells(38, 5).Value
Cells(d, e + 37) = Cells(39, 5).Value
Cells(d, e + 38) = Cells(40, 5).Value

Cells(d, e + 40) = Cells(65, 13).Value
Cells(d, e + 41) = Cells(66, 13).Value
Cells(d, e + 42) = Cells(67, 13).Value
Cells(d, e + 43) = Cells(68, 13).Value
Cells(d, e + 44) = Cells(69, 13).Value
Cells(d, e + 45) = Cells(70, 13).Value
Cells(d, e + 46) = Cells(71, 13).Value
Cells(d, e + 47) = Cells(72, 13).Value
Cells(d, e + 48) = Cells(73, 13).Value
Cells(d, e + 49) = Cells(74, 13).Value
Cells(d, e + 50) = Cells(75, 13).Value
Cells(d, e + 51) = Cells(76, 13).Value
Cells(d, e + 52) = Cells(77, 13).Value
Cells(d, e + 53) = Cells(78, 13).Value
Cells(d, e + 54) = Cells(79, 13).Value
Cells(d, e + 55) = Cells(80, 13).Value
Cells(d, e + 56) = Cells(81, 13).Value
Cells(d, e + 57) = Cells(82, 13).Value
Cells(d, e + 58) = Cells(83, 13).Value
Cells(d, e + 59) = Cells(84, 13).Value
Cells(d, e + 60) = Cells(85, 13).Value
Cells(d, e + 61) = Cells(86, 13).Value
```

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

VBA CODE

Module2 - 5

```
counter1 = counter1 + 1
End If
End If
counter2 = counter2 + 1
End If
Next rr
End If
End If
Next qq
End If
End If
Next pp
End If
End If
Next oo
End If
End If
Next nn
End If
End If
Next mm
End If
End If
Next ll
End If
End If
Next kk
End If
End If
Next jj
End If
End If
Next ii
End If
End If
Next hh
End If
End If
Next gg
End If
End If
Next ff
End If
End If
Next ee
End If
End If
Next dd
End If
End If
Next cc
End If
End If
Next bb
End If
End If
Next aa
End If
End If
Next z
End If
End If
Next y
End If
End If
Next x
End If
End If
Next w
End If
End If
Next v
End If
```

Module2 - 6

```
End If
Next u
End If
End If
Next t
End If
End If
Next s
End If
End If
Next r
End If
End If
Next q
End If
End If
Next p
End If
End If
Next o
End If
End If
Next n
End If
End If
Next m
End If
End If
Next l
End If
End If
Next k
End If
End If
Next j
Next i
End Sub
```

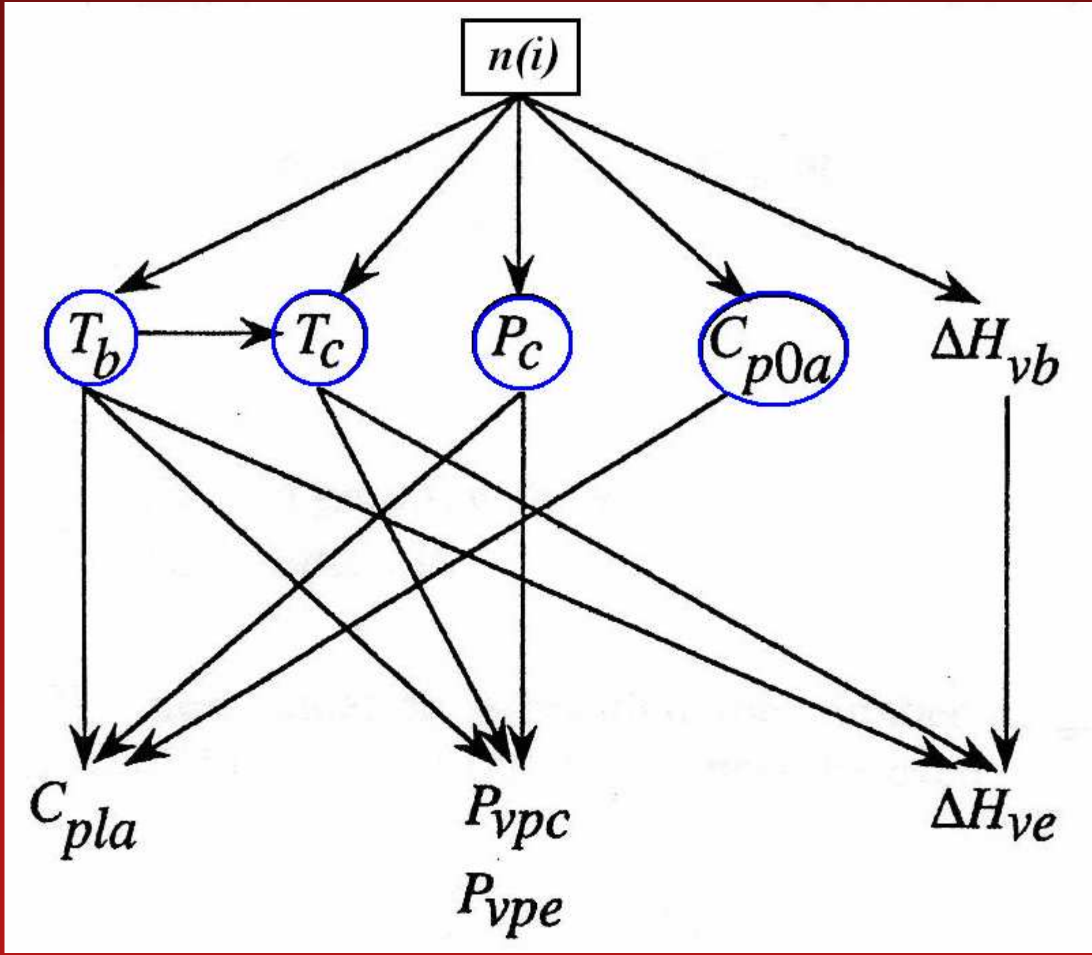
chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Refrigerant Modeling

Our design

1. Design Basic Thermodynamic Optimization
2. Include structural constraints
3. Include physical constraints
4. Find information on existing molecules
5. Select molecules for further research

Flow of Variables from Group Contribution Theory



chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

HOW TO USE GROUP CONTRIBUTION THEORY

$$T_b = 198.21 + \sum_{i=1}^{N} n_i * T_{bi}$$

$$T_c = \frac{T_b}{(0.584 + 0.965 * \sum_{i=1}^{N} n_i * T_{ci} - \left(\sum_{i=1}^{N} n_i * T_{ci}\right)^2}$$

$$P_c = \frac{1}{\left(0.113 + 0.0032 * \sum_{i=1}^{N} n_i * a_i - \sum_{i=1}^{N} n_i * P_{ci}\right)^2}$$

$$C_{p0a} = \sum_{i=1}^{N} n_i * C_{p0ai} - 37.93 + \left(\sum_{i=1}^{N} n_i * C_{p0bi} - 0.21\right) * T_{avg}$$
$$+ \left(\sum_{i=1}^{N} n_i * C_{p0ci} - 3.91*10^{-4}\right) * T_{avg}^2$$
$$+ \left(\sum_{i=1}^{N} n_i * C_{p0di} - 2.06*10^{-7}\right) * T_{avg}^3$$

Tb=Boiling temperature

Tbi=contribution of group i to boiling temperature

Tc=critical temperature

Tci= contribution of group i to critical temperature

ai=number of atoms in group i

Pci= contribution of group i to critical pressure

Tavg= average temperature (user defined)

Cp0ai=*a* contribution to heat capacity

Cp0bi=*b* contribution to heat capacity

Cp0ci=*c* contribution to heat capacity

Cp0di=*d* contribution to heat capacity at average temperature

***** Equations 1-4 are the only ones dependent upon values of ni**

chemical, biological & materials

chemical, biological and materials engineering

university of oklahoma

Thermodynamic Equations

- **Liquid Heat Capacity at T_{avg}**

$$C_{pla} = \frac{1}{4.1868} * \left\{ C_{p0a} + 8.314 * \left[1.45 + \frac{0.45}{1 - T_{avgr}} + 0.25 * \omega * \left(17.11 + 25.2 * \frac{\left(1 - T_{avgr}\right)^{1/3}}{T_{avgr}} + \frac{1.742}{\left(1 - T_{avgr}\right)} \right) \right] \right\}$$

- **Heat of vaporization at boiling temperature (Riedel Method)**

$$\Delta H_{vb} = 1.093 * R * T_c * T_{br} * \left(\frac{\ln\left(P_c\right) - 1.013}{0.930 - T_{br}} \right)$$

- **Heat of vaporization at evaporation temperature**

$$\Delta H_{ve} = \Delta H_{vb} * \left(\frac{1 - T_{evp} / T_c}{1 - T_b / T_c} \right)^{0.38}$$

Pressure Equations

- **Vapor pressure at condensing**

$$\ln\left(P_{vpcr}\right) = \frac{-G}{T_{cndr}} * \left[1 - T_{cndr}^{2} + k * \left(3 + T_{cndr}\right)\left(1 - T_{cndr}\right)^{3}\right]$$

$$P_{vpc} = P_{vpcr} * P_{c}$$

- **Vapor pressure at evaporation**

$$\ln\left(P_{vper}\right) = \frac{-G}{T_{evpr}} * \left[1 - T_{evpr}^{2} + k * \left(3 + T_{evpr}\right)\left(1 - T_{evpr}\right)^{3}\right]$$

$$P_{vpe} = P_{vper} * P_{c}$$

Group Combination Constraints

1. Structural feasibility
2. Size and molecular weight
3. Vapor pressure

Structural Feasibility

- **Even number of groups with odd number of bonding sites**
  - **2 "-CH3" groups or 1 "-CH3" group and 1 ">CH-" group**
- **Groups must be able to connect to form ONE molecule**
  - **2 "-CH3" groups cannot connect with 2 "-F" groups to make ONE molecule**
- **Total number of bonding sites should be even**
  - **2 bonding sites make 1 bond**

Structural Feasibility Con'd

- **Number of each bonding type should be even**
  - **2 "=CH2" groups, 2 "=O" groups, or 1 "=CH2" with 1 "=C=" with 1 "=O" group**
- **Mixed bonding types should have a transition group**
  - **1 "=CH2" and 1 "-F" requires 1 "=CH-" group**
- **Every branch should have an edge (end cap)**
  - **Example: 1 ">C<" group have 4 branches which will require 4 groups with only 1 bonding site such as "-F"**

Molecular Size

- Minimum number of groups is 2
- Maximum number of groups is 10
  - Max groups by type:

    one bond = 7 – $C\text{-}CH\text{-}C(F)_7$=10

    two bonds = 8 – $CH_3\text{-}(CH_2)_8\text{-}CH_3$=10

    three bonds = 4 – $(CH)_4(F)_6$=10

    four bonds = 2 – $(C)_3(F)_8$=11
- Our results show that the maximum number of groups used is 9
- Typically larger molecules have higher boiling points making them unfit for refrigeration

Vapor Pressure

- Minimum vapor pressure at evaporation temperature of 1 bar
  - Atmospheric pressure
- Maximum vapor pressure at condensation of 10 bar
  - Mechanical compressibility factor
  - Multi-stage compressor (cost prohibitive)
- Heat capacity must be positive
  - Negative heat capacity is not possible physically

"MAKING" A MOLECULE

- $n_{-F} = 2$
- $n_{-Cl} = 2$
- $n_{>C<} = 1$
- Freon

- $n_{-CH3} = 2$
- $n_{-CH2-} = 2$
- Butane

- $n_{-CH3} = 3$
- $n_{>CH-} = 1$
- iso-butane

- $n_{-CH3} = 2$
- $n_{>CH-} = 1$
- $n_{-CH2-} = 1$
- $n_{-OH} = 1$
- iso-butanol

- $n_{=CH2} = 1$
- $n_{=C<} = 1$
- $n_{-O-} = 1$
- $n_{-F} = 2$
- ??

MOLECULE MAKER

	n=
sCH3	2
sCH2s	2
ssCHs	2
ssCss	0
dCH2	0
dCHs	0
dCss	0
dCd	0
rCH2r	0
rrCHr	0
rrCrr	0
drCHr	0
drCrr	0
sF	0
sCl	0
sBr	0
sI	0
sOH	0
sOs	0
rOr	0
ssCO	0
rrCO	0
sCHO	0
sCOOH	0
sCOOs	0
doO	0
sNH2	0
ssNH	0
rrNH	0
ssNs	0
drNs	0
sCN	0
sNO2	0
sSH	0
sSs	0
rSr	0
	6

Physical Constraints		
Pvpe	FALSE	0
Pvpc	FALSE	0
heatcap	TRUE	1
		0
Structural Constraints		
Ynt	true	1
oddfree	true	1
connected	true	1
nofree	true	1
bond type	true	1
singlefree	true	1
double free	true	1
triple free	true	1
single cyclic fre	true	1
double cyclic fr	true	1
mixed	true	1
end cap	false	0
real structure		0
Binary Variables		
Yss		1
Ydd		0
Ytt		0
Ysr		0
Ydr		0
Yr		0
Ysd		0
Yst		0
Yssr		0
Ysdr		0
Ydsr		0
Y0m		1
Ym5		0
Ym1		1
Ym6		0
Ym2		1
Ym7		0
Ym3		1
Ym8		0
Ym4		1
Ym9		0

Thermodynamic Properties		
Tavg	K	294
Tevp	K	272
Tcnd	K	317
N groups		6
Tboil	K	334.61
Tcrit	K	499.73
Pcrit	bar	35.01
heatcap	J/molK	0.131
Tb reduced		0.670
Tavg reduced	K	0.588
Tcnd reduced		0.633
Tevp reduced		0.544
alpha		-0.942
beta		-2.734
omega		0.345
heat capacity	J/molK	45.325
enthalpy of vaporiza	kJ/mol	29.502
enthalpy of vaporiza	kJ/mol	33.335
h		7.179
G		3.790
ka		0.561
Pvpcr		0.015
Pvper		0.002
Pvpc	bar	0.533
Pvpe	bar	0.070
t=		0.000

iterations
27

Results from Excel

- 3,692,945 possible solutions (16 hours)
- 649 solutions
- 566 structurally feasible solutions (passed the filter, but not feasible)
- Since each solution was evaluated by referencing online databases the process for finding molecules was extremely tedious
- are included in optimization function calculations for comparison

β VALUES

Chemical Formula	$H = \Sigma x_i y_{ij}$	$\beta = H_2/H_1$	Rank
CH2=CH-F	0.61	1.39	2
CH3 -CH=CH2	0.61	1.39	4
CH2=CF2	0.51	1.68	8
CH2=CH-Cl	0.50	1.69	1
CH2=CFCl	0.49	1.75	3
CH2=C=CH-F	0.40	2.13	5
CH2=CH-O-F	0.40	2.14	6
CH2=CH-C(=O)-F	0.40	2.14	20
Cl2	0.40	2.15	7
F-Br	0.39	2.17	9
CH2=CCH3F	0.39	2.17	10
CH2=CH-CH2-F	0.39	2.18	11
CH2=C=CF2	0.39	2.18	12
CH2=C=C=C=O	0.39	2.19	13
FSH	0.39	2.19	14
CH2=C(-F)-O-F	0.39	2.19	15
FNH2	0.39	2.19	16
cyc(CH=CH-CH2)	0.39	2.19	17
cyc(CH=CH-O)	0.39	2.20	18
O=CH-Br	0.38	2.22	19
R134a	0.85	1.00	-

- Using the preceding six quantitative plots, a value for β for each possible refrigerant can be defined

LIMITATIONS OF GROUP CONTRIBUTION THEORY

- **Actual data compared with data found using functional group theory**

  $$\mathrm{abs}(T_{b(theory)} - T_{b(act)}) = \Delta T_b$$

- **Average ΔT_b = 39.7K**
- **Examples:**

  3-fluoro-1-propene, min ΔT_b=1.2K

  1-fluoro-2-propanone, max ΔT_b=89.9K

ERROR	T_{boil}	T_{crit}	P_{crit}
max	47%	32%	36%
min	0.4%	1.1%	0.5%
average	16%	14%	12%

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Limitations of Functional Group Theory

- **Errors reveal inconsistencies with functional group theory**
- **Possibly good refrigerants were likely excluded from our findings**

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Recommendations

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Recommendations

1. Develop correlations to relate data obtained from models to consumer preference functions. Relationships could be developed to relate properties that can be found from the empirical data to those exclusive to an individual molecule.
2. Link spreadsheets to databases to quickly search through molecules. Not all properties can be examined from a molecule's empirical formula or structure. Many databases, in periodicals, for potential refrigerant molecules are available for possible refrigerants. These databases could eliminate error caused by property estimation.
3. A large scale survey needs to be performed. A large scale random survey is needed to find actual consumer preferences to refrigerant properties.

Recommendations

3. More structural constraints need to be developed. Some molecular structures pass the filters in the iterative method, but do not exist in reality.
4. Considering refrigerant blends would create many more options for refrigerant solutions.
5. Laboratory study - The laboratory setting offers the benefit of being able to measure properties for synthesized refrigerants. In this way, more accurate correlations for group contributions or efficiency could be developed.

Questions?

Works Cited

1. *History of the Refrigerator*. History.com. 2/7/2007 <http://www.history.com/exhibits/modern/fridge.html>.
2. *Refrigerant Data Update*. January 2007. Heating/Piping/Air Conditioning Engineering. Feb. 7, 2007 <http://www.hpac.com/Issue/Article/44475/Refrigerant_Data_Update>.
3. *What you Should Know about Refrigerants when Purchasing or Repairing a Residential A/C System or Heat Pump*. Jan. 29, 2007. Environmental Protection Agency. Jan. 29th, 2007 <http://www.epa.gov/ozone/title6/phaseout/22phaseout.html>.
4. *HCFC Phaseout Schedule*. April 16th, 2006. Environmental Protection Agency. Feb. 5th, 2007 <http://www.epa.gov/ozone/title6/phaseout/hcfc.html>.
5. *Air Conditioners 2004*. July 2004. Snapshot International. Feb. 11th, 2007 <http://dx.doi.org/10.1337/us080034>.
6. *American Housing Survey for the United States: 2005*. August 2006. U.S. Department of Housing and Urban Development and the US Department of Commerce. Feb 11th, 2007 <http://www.census.gov/prod/2006pubs/h150-05.pdf>.
7. *Trends in Residential Air-Conditioning Usage from 1978 to 1997*. July 24, 2000. US Department of Energy. Feb 11th, 2007 <http://www.eia.doe.gov/emeu/consumptionbriefs/recs/actrends/recs_ac_trends.html>.
8. *The Properties of Gases and Liquids 5th Edition*. O'Connell, J., B. Poling and J. Pransnite.McGraw-Hill, New York, 2001. Chapter 2 (78-89).

APPENDIX

Creating More Accurate Consumer Preference Functions

- To accurately predict the refrigerant market, a large scale survey needs to be performed
- The large scale survey will eliminate inaccuracies present in the survey prepared and presented previously
- These inaccuracies stem from the inherent bias in a small survey

More Thermodynamic Equations

$$\alpha = -5.97214 - \ln\left(\frac{P_c}{1.013}\right) + \frac{6.09648}{T_{br}} + 1.28862 * \ln(T_{br}) - 0.169347 * T_{br}^6$$

$$\beta = 15.2518 - \frac{15.6875}{T_{br}} - 13.4721 * \ln(T_{br}) + 0.43577 * T_{br}^6$$

$$\omega = \frac{\alpha}{\beta}$$

$$h = \frac{T_{br} * \ln(P_c / 1.013)}{1 - T_{br}}$$

$$G = 0.4835 + 0.4605 * h$$

$$k = \frac{h/G - (1 + T_{br})}{(3 + T_{br})(1 - T_{br})^2}$$

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Thermodynamics

- Functional group theory can be used to determine many important characteristics
- Temperature-Entropy data are needed to accurately determine efficiency, but cannot be determined from functional group theory
- $\Delta H/C_p$ is used to estimate efficiency

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

GAMS CODE

```
                              gamstext.txt
sets
         i all possible groups / sCH3,sCH2s,ssCHs,ssCss,dCH2,dCHs,dCss,
dCd,rCH2r,rrCHr,rrCrr,drCHr,drCrr,sF,sCl,sBr,sI,sOH,sOs,rOr,ssCO,
rrCO,sCHO,sCOOH,sCOOs,doO,sNH2,ssNH,rrNH,ssNs,dNs,drNs,sCN,sNO2,sSH,sSs,rSr/
         k thermodynamic labels / Tbi , Tci, Pci/
         l heat capacity contribution / Cp0Ai, Cp0Bi, Cp0Ci, Cp0Di/
         j bond types / SS, DD, TT, SR, DR/;
table c(i,k) group contribution to molecular thermodynamics
              Tbi           Tci           Pci
sCH3         23.58        0.0141       -0.0012
sCH2s        22.88        0.0189        0.0000
ssCHs        21.74        0.0164        0.0020
ssCss        18.25        0.0067        0.0043
dCH2         18.18        0.0113       -0.0028
dCHs         24.96        0.0129       -0.0006
dCss         24.14        0.0117        0.0011
dCd          26.15        0.0026        0.0028
rCH2r        27.15        0.0100        0.0025
rrCHr        21.78        0.0122        0.0004
rrCrr        21.32        0.0042        0.0061
drCHr        26.73        0.0082        0.0011
drCrr        31.01        0.0143        0.0008
sF           -0.03        0.0111       -0.0057
sCl          38.13        0.0105       -0.0049
sBr          66.86        0.0133        0.0057
sI           93.84        0.0068       -0.0034
sOH          92.88        0.0741        0.0112
sOs          22.42        0.0168        0.0015
rOr          31.22        0.0098        0.0048
ssCO         76.75        0.0380        0.0031
rrCO         94.97        0.0284        0.0028
sCHO         72.20        0.0379        0.0030
sCOOH       169.09        0.0791        0.0077
sCOOs        81.10        0.0481        0.0005
doO         -10.50        0.0143        0.0101
sNH2         73.23        0.0243        0.0109
ssNH         50.17        0.0295        0.0077
rrNH         52.82        0.0130        0.0114
ssNs         11.74        0.0169        0.0074
dNs          74.60        0.0255       -0.0099
drNs         57.55        0.0085        0.0076
sCN         125.66        0.0496       -0.0101
sNO2        152.54        0.0437        0.0064
sSH          63.56        0.0031        0.0084
sSs          68.78        0.0119        0.0049
rSr          52.10        0.0019        0.0051


table d(i,l) heat capacity contribution
             Cp0Ai          Cp0Bi          Cp0Ci           Cp0Di
sCH3        19.500      -8.08E-03       1.53E-04       -9.67E-08
sCH2s       -0.909       9.50E-02      -5.44E-05        1.19E-08
ssCHs      -23.000       2.04E-01      -2.65E-04        1.20E-07
ssCss      -66.200       4.27E-01      -6.41E-04        3.01E-07
dCH2       -23.600      -3.81E-02       1.72E-04       -1.03E-07
dCHs        -8.000       1.05E-01      -9.63E-05        3.56E-08
dCss       -28.100       2.08E-01      -3.06E-04        1.46E-07
dCd         27.400      -5.57E-02       1.01E-04       -5.02E-08
rCH2r       -6.030       8.54E-02      -8.00E-06       -1.80E-08
rrCHr        8.670       1.62E-01      -1.60E-04        6.24E-08
rrCrr      -90.900       5.57E-01      -9.00E-04        4.69E-07
drCHr       -2.140       5.74E-02      -1.64E-06       -1.59E-08
drCrr       -8.250       1.01E-01      -1.42E-04        6.78E-08
                                Page 1
```

```
                              gamstext.txt
sF          26.500      -9.13E-02       1.91E-04       -1.03E-07
sCl         33.300      -9.63E-02       1.87E-04       -9.96E-08
sBr         28.600      -6.49E-02       1.36E-04       -7.45E-08
sI          32.100      -6.41E-02       1.26E-04       -6.87E-08
sOH         25.700      -6.91E-02       1.77E-04       -9.88E-08
sOs         25.500      -6.32E-02       1.11E-04       -5.48E-08
rOr         12.200      -1.26E-02       6.03E-05       -3.86E-08
ssCO         6.450       6.70E-02      -3.57E-05        2.86E-09
rrCO        30.400      -8.29E-02       2.36E-04       -1.31E-07
sCHO        30.900      -3.36E-02       1.60E-04       -9.88E-08
sCOOH       24.100       4.27E-02       8.04E-05       -6.87E-08
sCOOs       24.500       4.02E-02       4.02E-05       -4.52E-08
doO          6.820       1.96E-02       1.27E-05       -1.78E-08
sNH2        26.900      -4.12E-02       1.64E-04       -9.76E-08
ssNH        -1.210       7.62E-02      -4.86E-05        1.05E-08
rrNH        11.800      -2.30E-02       1.07E-04       -6.28E-08
ssNs       -31.100       2.27E-01      -3.20E-04        1.46E-07
dNs
drNs        8.830       -3.84E-03       4.35E-05       -2.60E-08
sCN        36.500       -7.33E-02       1.84E-04       -1.03E-07
sNO2       25.900       -3.74E-03       1.29E-04       -8.88E-08
sSH        35.300       -7.58E-02       1.85E-04       -1.03E-07
sSs        19.600       -5.61E-03       4.02E-05       -2.76E-08
rSr        16.700        4.81E-03       2.77E-05       -2.11E-08


table gr(i,j) heat capacity contribution
            SS        DD        TT        SR        DR
sCH3        1         0         0         0         0
sCH2s       2         0         0         0         0
ssCHs       3         0         0         0         0
ssCss       4         0         0         0         0
dCH2        0         1         0         0         0
dCHs        1         1         0         0         0
dCss        2         1         0         0         0
dCd         0         2         0         0         0
tCH         0         0         1         0         0
tCs         1         0         1         0         0
rCH2r       0         0         0         2         0
rrCHr       0         0         0         3         0
srCHr       1         0         0         2         0
rrCrr       0         0         0         4         0
srCHrr      1         0         0         3         0
ssCHrr      2         0         0         2         0
drCHr       0         0         0         1         1
drCrr       0         0         0         2         1
drCsr       1         0         0         1         1
dCHrr       0         1         0         2         0
sF          1         0         0         0         0
sCl         1         0         0         0         0
sBr         1         0         0         0         0
sI          1         0         0         0         0
sOH         1         0         0         0         0
sOs         2         0         0         0         0
rOr         0         0         0         2         0
ssCO        2         0         0         0         0
rrCO        0         0         0         2         0
sCHO        1         0         0         0         0
sCOOH       1         0         0         0         0
sCOOs       2         0         0         0         0
doO         0         1         0         0         0
sNH2        1         0         0         0         0
                                Page 2
```

GAMS CODE

gamstext.txt

```
ssNH       2       0       0       0       0
rrNH       0       0       0       2       0
ssNs       3       0       0       0       0
dNs        1       1       0       0       0
drNs       1       0       0       0       1
sCN        1       0       0       0       0
sNO2       1       0       0       0       0
sSH        1       0       0       0       0
sSs        2       0       0       0       0
rSr        0       0       0       2       0

Parameter a(i) number of atoms in group i
/sCH3 4,sCH2s 3,ssCHs 2,ssCss 1,dCH2 3,dCHs 2,dCss 1,dCd 1,
rCH2r 3,rrCHr 2,rrCrr 1,drCHr 2,drCrr 1,sF 1,sCl 1,sBr 1,
sI 1,sOH 2,sOs 1,rOr 1,ssCO 2,rrCO 2,sCHO 3,sCOOH 4,sCOOs 3,doO 1,
sNH2 3,ssNH 2,rrNH 2,ssNs 1,drNs 1,sCN 2,sNO2 3,sSH 2,sSs 1,rSr 1/
b(i) number of bonds in each group i
/sCH3 1,sCH2s 2,ssCHs 3,ssCss 4,dCH2 1,dCHs 2,dCss 3,dCd 2,
rCH2r 2,rrCHr 3,rrCrr 4,drCHr 2,drCrr 3,sF 1,sCl 1,sBr 1,
sI 1,sOH 1,sOs 2,rOr 2,ssCO 2,rrCO 2,sCHO 1,sCOOH 1,sCOOs 2,doO 1,
sNH2 1,ssNH 2,rrNH 2,ssNs 3,drNs 2,sCN 1,sNO2 1,sSH 1,sSs 2,rSr 2/
Tavg avergage temperature of coolant
/294/
Tevp temperature at evaporation
/272/
Tcnd temperature at condensation
/316.5/
Nmax largest possible ring
/16/
*n(i) number of atoms in group i
*/sCH3 0,sF 2,sCl 1,sSH 0,sOs 0,doO 0,dCd 0, dCHs 0,ssNs 1/;
*/drCHr 6/;
Variables
n(i)      number of groups of type i
Nt
Tb        boiling temperature
Tc        critical temperture
Pc        critical pressure
Tbr       reduced temperature
Cp0a      heat capacity at standard temperature
Tavgr     reduced average temperature
Tcndr     reduced condensing temperature
Tevpr     reduced evaporating temperature
alpha
beta
omega
Cpla      liquid heat capacity
dHvb      heat of vaporization at boiling
dHve      heat of vaporization at evaporation
h
G
ka
Pvpcr     reduced vapor pressure at condensing
Pvper     reduced vapor pressure at evaporating
Pvpc      vapor pressure at condensing
Pvpe      vapor pressure at evaporating
t1        opitmization variable
t2
t3
Ya
Yc
Ym
Yr
```

Page 3

gamstext.txt

```
Yss
Ydd
Ytt
Ysr
Ydr
Ysd
Yst
Yssr
Ysdr
Ydsr
aux0
aux1
aux2
aux3
aux4
aux5;
Positive variables Nt,omega,Tbr,Tavgr,Pc,Tb,Tc,Cp0a,Tcndr,Tevpr,Cpla;
Binary variables Ya, Yc,Ym,Yss,Ydd,Ytt,Ysr,Ydr,Ysd,Yst,Yssr,Ysdr,Ydsr;
integer variable n,aux0,aux1,aux2,aux3,aux4,aux5;

*********starting molecule***************
n.l('sF')=1;
n.l('sSH')=1;
n.l('dCH2')=0;
NT.l=3;
***************thermodynamics for initial molecule*******************
Tb.l= 198.21 + sum(i, n.l(i)*c(i,'Tbi'))    ;
Tc.l = Tb.l/(0.584+0.965*sum(i, n.l(i)*c(i,'Tci'))
                   -(sum(i,n.l(i)*c(i,'Tci')))**2);
Tbr.l= Tb.l/Tc.l;
Pc.l= (0.113+0.0032*sum(i, n.l(i)*a(i))-sum(i, n.l(i)*c(i,'Pci')))**(-2);
alpha.l=(-5.97214-log(Pc.l/1.013)
         +6.09648/Tbr.l+1.28862*log(Tbr.l)
         -0.1693477*Tbr.l**(6));
beta.l=(15.2518-15.6875/Tbr.l
         -13.4721*log(Tbr.l)+0.43577*Tbr.l**6);
omega.l=alpha.l/beta.l;
Cp0a.l= (sum(i,n.l(i)*d(i,'Cp0Ai'))-37.93
        +(sum(i,n.l(i)*d(i,'Cp0Bi'))+0.21)*Tavg
        +(sum(i,n.l(i)*d(i,'Cp0Ci'))-0.000391)*Tavg**2
        +(sum(i,n.l(i)*d(i,'Cp0Di'))+0.000000206)*Tavg**3)/1000;
Tavgr.l=Tavg/Tc.l;
Tevpr.l=Tevp/Tc.l;
Cpla.l=(1/4.1868)*((Cp0a.l*1000)+8.314*(1.45
                      +0.45/(1-Tavgr.l)+0.25*omega.l*(17.11
                      +25.2*((1-Tavgr.l)**(1/3)/Tavgr.l)
                      +1.742/(1-Tavgr.l)))) ;
Tcndr.l=Tcnd/Tc.l;
dHvb.l = ((1.093*8.314*Tc.l*Tbr.l)*log(Pc.l)-1.013)/(0.93-Tbr.l) ;
h.l=Tbr.l*log(Pc.l/1.013)/(1-Tbr.l);
G.l=0.4835+0.4605*h.l;
ka.l=(h.l/G.l-(1+Tbr.l))/((3+Tbr.l)*(1-Tbr.l)**2);
Pvpcr.l=EXP(-G.l/Tcndr.l*(1-Tcndr.l**2+ka.l*(3+Tcndr.l)*(1-Tcndr.l)**3));
Pvper.l=EXP(-G.l/Tevpr.l*(1-Tevpr.l**2+ka.l*(3+Tevpr.l)*(1-Tevpr.l)**3));
Pvpc.l=Pvpcr.l*Pc.l;
Pvpe.l=Pvper.l*Pc.l;
***binary***
*$ontext
Yr.l=0;
Ya.l=1;
Yc.l=0;
Ysd.l=1;
Ydr.l=0;
```

Page 4

GAMS CODE

gamstext.txt

```
Yss.l=1;
*$offtext
******************************limits*************************************
Nt.lo=2;
Nt.up=7;
Tbr.lo=0.01;
Tbr.up=0.99;
Pc.lo=0.1;
Tavgr.lo=0.01;
Tavgr.up=0.99;
Tevpr.lo=0.01;
Tevpr.up=0.99;
Tcndr.lo=.01;
Tcndr.up=0.99;
Tc.lo=0.01;
Pvpcr.lo=0.000001;
Pvpcr.up=0.99;
Pvper.lo=0.000001;
Pvper.up=0.99;
Pvpe.lo=1.1;
Pvpc.lo=1.1;

Equations
Groups1     total number of groups in molecule
*Yaeq       finds the binary value for acyclic molecules
*Yceq       finds the binary value for cyclic molecules
*Ymeq1a     checks for existance of transition group acyclic
*Ymeq1b     checks for existance of transition group cyclic
*Ymeq2      checks for that a cyclic and acyclic group are in the molecule
*Yreq1      finds the binary value for cyclic molecules
*Yreq2      makes sure the ring has at least 3 groups
*Yreq3
oddfree     checks for even # of bonds (everything has something to bond with)
connect     checks for connectivity (no lone groups)
nofree      check for free bonds
Ysseq       single acyclic bond ? binary
Yddeq       double acyclic bond ? binary
*Ytteq      triple acyclic bond ? binary
Ysreq       single cyclic bond ? binary
Ydreq       double cyclic bond ? binary
Ysda        single&double transition
Ysdb        single&double transition
Ysdc
*Ysta       single&triple transition
*Ystb       single&triple transition
*Yssra      single&single cyclic transition
*Yssrb      single&single cyclic transition
*Ysdra      single&double cyclic transition
*Ysdrb      single&double cyclic transition
Ydsra       double&single cyclic transition
Ydsrb       double&single cyclic transition
Ydsrc
*nodangle
typefree1   even # of single bonds
typefree2   even # of double bonds
*typefree3  even # of triple bonds
*typefree4  even # of single cyclic bonds
*typefree5  even # of double cyclic bonds

Tboil       equation to find boiling Temperature
Tcrit       equation to find critical Temperature
Pcrit       Critical Pressure
Tbrud       Reduced boiling temperature
```


gamstext.txt

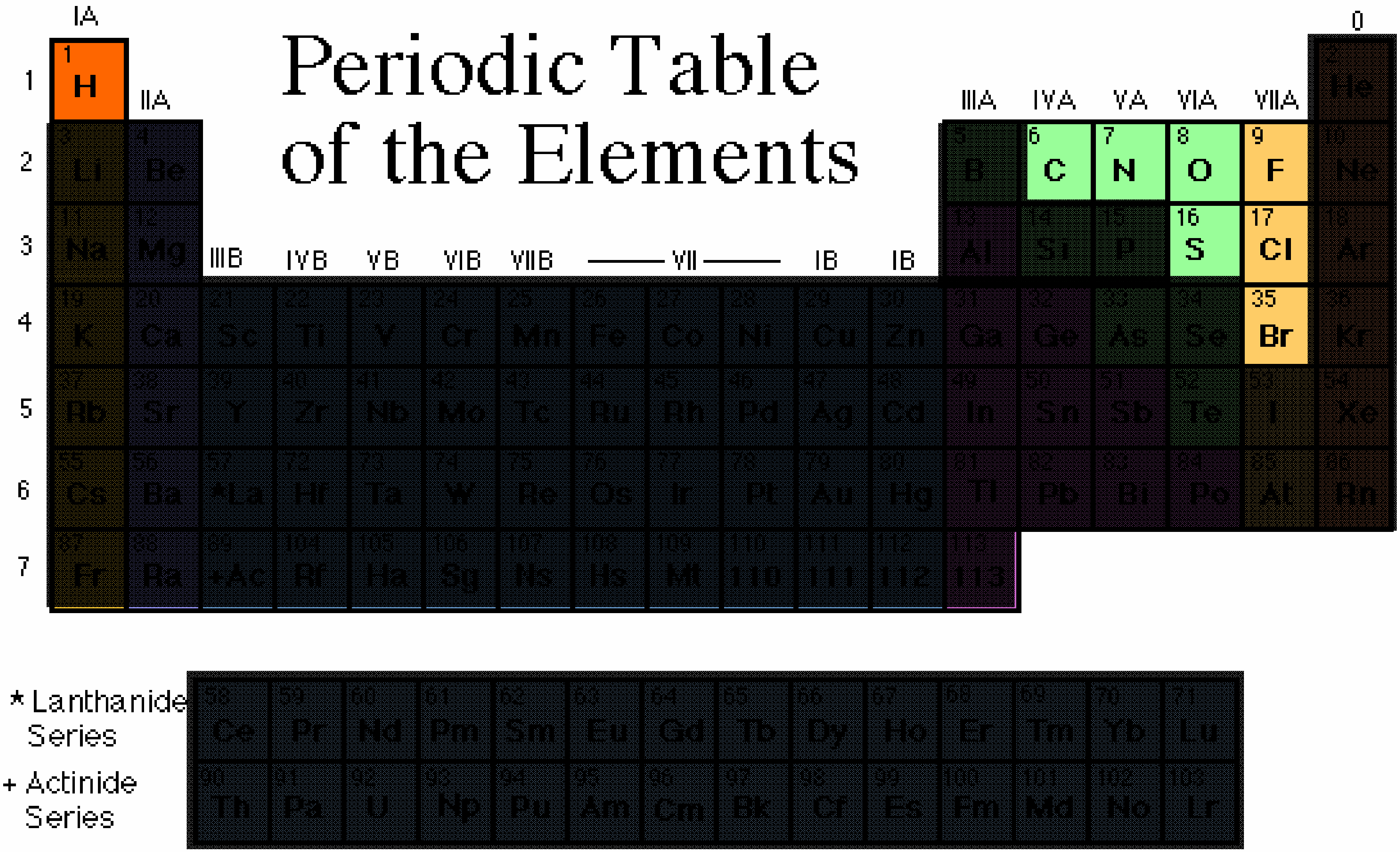
```
Heatcap     Heat capacity
Tavgrud     finds reduced temperature average
Tcndrud     finds reduced temperature of condensation
Tevprud     finds reduced temperature of evaporation
alphae
betae
omegae
Cpliq       finds liquid heat capacity
delHvb      finds heat of vaporization at boiling temperature
delHve      finds heat of vaporization at evaporation temperature
heq
Geq
kaeq
Pvpcreq     finds reduced pressure of condensation
Pvpereq     finds reduced pressure of evaporation
Pvpceq      finds pressure of condensation
Pvpeeq      finds pressure of evaporation
optimize1   optimization formula
optimize2
optimize3;
*********************Structural Constraints***************************
*********requirement 1
groups1 ..        Nt=e= sum(i, n(i));

*********requirement 2
*Yaeq ..          sign(sum(i,n(i)*gr(i,'SS'))+sum(i,n(i)*gr(i,'DD')))=e=Ya;
*Yceq ..          sign(sum(i,n(i)*gr(i,'SR'))+sum(i,n(i)*gr(i,'DR')))=e=Yc;
*Ymeq1a ..        Ym=L=Ya;
*Ymeq1b ..        Ym=L=Yc;
********requirement 3
*Ymeq2 ..         Ym=l=Ya+Yc;
********requirement 4
*Yreq1 ..         sign(sum(i,n(i)*gr(i,'SR'))+sum(i,n(i)*gr(i,'DR')))=e=Yr;
*Yreq2..          3*Yr=l=sum(i$(ord(i)>3),n(i));
*Yreq3..          sum(i,n(i)*gr(i,'SR'))+sum(i,n(i)*gr(i,'DR'))=l=Nmax*Yr;
********requirement 5
oddfree ..        sum(i,n(i)*b(i))=e=2*aux0;
********requirement 6
connect ..        sum(i,n(i)*b(i))=g=2*(Nt-1);
********requirement 7
nofree..          sum(i, n(i)*b(i))=l=Nt*(Nt-1);
********requirement 8
Ysseq ..          sign(sum(i,n(i)*gr(i,'SS')))=e=Yss;
Yddeq ..          sign(sum(i,n(i)*gr(i,'DD')))=e=Ydd;
*Ytteq ..         sign(sum(i,n(i)*gr(i,'TT')))=e=Ytt;
Ysreq ..          sign(sum(i,n(i)*gr(i,'SR')))=e=Ysr;
Ydreq ..          sign(sum(i,n(i)*gr(i,'DR')))=e=Ydr;
********requirement 8.1
Ysda ..           Ysd=e=sign(sum(i,n(i)*gr(i,'SS')*gr(i,'DD')));
Ysdb ..           Ysd=L=Ydd;
Ysdc ..           Ysd=l=Yss;
********requirement 8.2
*Ysta ..          Yst=L=Yss;
*Ystb ..          Yst=L=Ytt;
********requirement 8.3
*Yssra ..         Yssr=L=Yss;
*Yssrb ..         Yssr=L=Ysr;
********requirement 8.4
*Ysdra ..         Ysdr=L=Yss;
*Ysdrb ..         Ysdr=L=Ydr;
********requirement 8.5
Ydsra ..          Ydsr=e=sign(sum(i,n(i)*gr(i,'SR')*gr(i,'DD')));
Ydsrb ..          Ydsr=L=Ydd;
```

GAMS CODE

gamstext.txt

```
Ydsrc ..         Ydsr=L=Ysr;

********requirement 9

********requirement 10
*nodangle ..     sum(i,b(i)*n(i))=e= 2*(Nt-1);

********requirement 11
typefree1 ..     2*aux1=e=sum(i,n(i)*gr(i,'SS'));
typefree2 ..     2*aux2=e=sum(i,n(i)*gr(i,'DD'));
*typefree3 ..    2*aux3=e=sum(i,n(i)*gr(i,'TT'));
*typefree4 ..    2*aux4=e=sum(i,n(i)*gr(i,'SR'));
*typefree5 ..    2*aux5=e=sum(i,n(i)*gr(i,'DR'));

*********************Thermodynamic Equations***************************
Tboil ..         Tb    =e= 198.21 + sum(i, n(i)*c(i,'Tbi'))    ;
Tcrit ..         Tb    =e= Tc*(0.584+0.965*sum(i, n(i)*c(i,'Tci'))
                      -(sum(i,n(i)*c(i,'Tci')))**2);
Pcrit ..         Pc    =e= (0.113+0.0032*sum(i, n(i)*a(i))
                      -sum(i, n(i)*c(i,'Pci')))**(-2);
Tbrud ..         Tbr*Tc =e= Tb;
Heatcap ..       Cp0a  =e= (sum(i,n(i)*d(i,'Cp0Ai'))-37.93
                   +(sum(i,n(i)*d(i,'Cp0Bi'))+0.21)*Tavg
                   +(sum(i,n(i)*d(i,'Cp0Ci'))-0.000391)*Tavg**2
                   +(sum(i,n(i)*d(i,'Cp0Di'))+0.000000206)*Tavg**3)/1000;
Tavgrud ..       Tavgr*Tc =e= Tavg;
Tcndrud ..       Tcndr*Tc =e= Tcnd;
Tevprud ..       Tevpr*Tc =e= Tevp;

alphae ..        alpha =e= (-5.97214-log(Pc/1.013)
                    +(6.09648/Tbr)+1.28862*log(Tbr)
                    -0.1693477*(Tbr**6));
betae ..         beta =e= (15.2518-(15.6875/Tbr)
                    -13.4721*log(Tbr)+0.43577*(Tbr**6));
omegae ..        omega*beta =e= alpha ;
Cpliq ..         Cpla=e=(1/4.1868)*((Cp0a*1000)+8.314*(1.45
                    +0.45/(1-Tavgr)+0.25*omega*(17.11
                    +25.2*((1-Tavgr)**(1/3)/Tavgr)
                    +1.742/(1-Tavgr)))) ;
delHvb ..        dHvb =e=(8.3145*Tc*Tbr*(0.4343*Log(Pc)
                    -0.69431+0.89584*Tbr)/(0.37691
                    -0.37306*Tbr+0.15075/(Pc*Tbr**2)))/1000;
delHve ..        dHve =e=dHvb*((1-Tevp/Tc)/(1-Tb/Tc))**0.38;
heq ..           h=e=Tbr*log(Pc/1.013)/(1-Tbr);
Geq ..           G=e=0.4835+0.4605*h;
kaeq ..          ka=e=(h/G-(1+Tbr))/((3+Tbr)*(1-Tbr)**2);
Pvpcreq ..       Pvpcr=e=EXP(-G/Tcndr*(1-Tcndr**2+ka*(3+Tcndr)*(1-Tcndr)**3));
Pvpereq ..       Pvper=e=EXP(-G/Tevpr*(1-Tevpr**2+ka*(3+Tevpr)*(1-Tevpr)**3));
Pvpceq ..        Pvpc=e=Pvpcr*Pc;
Pvpeeq ..        Pvpe=e=Pvper*Pc;
optimize1 ..     t1*Cpla=e=dHve;
optimize2 ..     t2*Pvpc=e=Pvpe;
optimize3 ..     t2*t1=e=t3;
Model refrigdesign /all/ ;
refrigdesign.optfile=1;
options iterlim=10000000;
Solve refrigdesign using minlp manimizing t3 ;
Display Tbr.l,Cp0a.l,Tb.l,Tc.l,Pc.l,Tbr.l,Tavgr.l,
        Tcndr.l,Tevpr.l,alpha.l,beta.l,omega.l,Cpla.l,
        dHvb.l,dHve.l,h.l,G.l,ka.l,Pvpcr.l,Pvper.l,Pvpc.l,Pvpe.l,t1.l,t3.l
        Yss.l,Ydd.l,Ysd.l,n.l;
```

SYSTEMATIC DESIGN



Environmental Effects

- **Ozone depletion potential**
  - **Only heavy halogens are known to contribute**

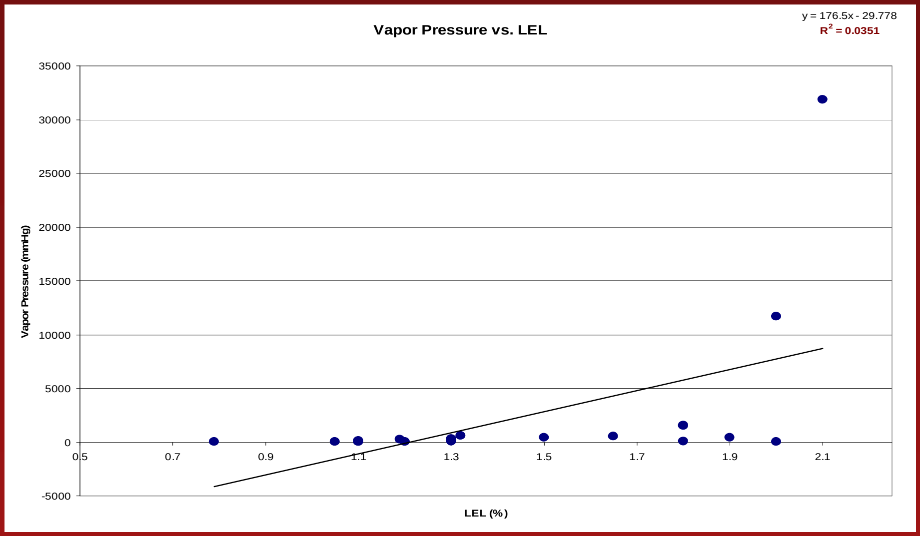
$$ODP = 0.05013\,(n_{Cl})^{1.510} * \exp(-3.858 / \tau)$$

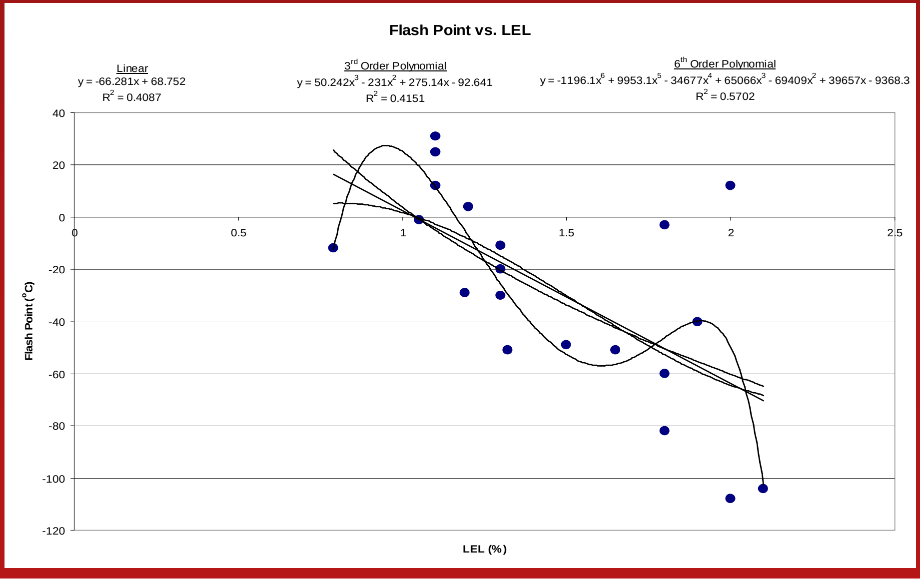
- **Global warming potential**
  - **Requires experiments to find radiative efficiency and time dependent decay**

$$GWP(x) = \frac{\int_0^{TH} a_x \cdot [x(t)]\, dt}{\int_0^{TH} a_r \cdot [r(t)]\, dt}$$

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

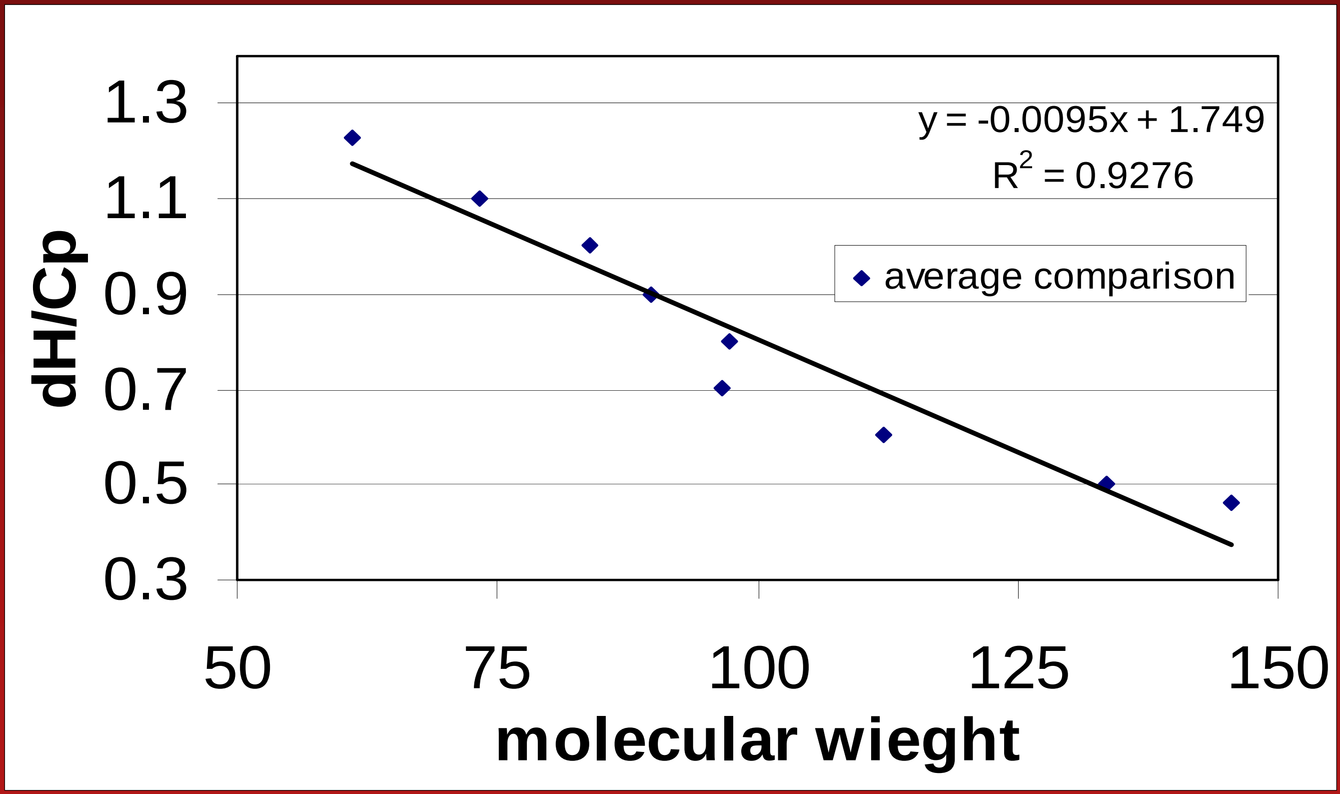
OBTAINING VALUES FOR THE OBJECTIVE FUNCTION





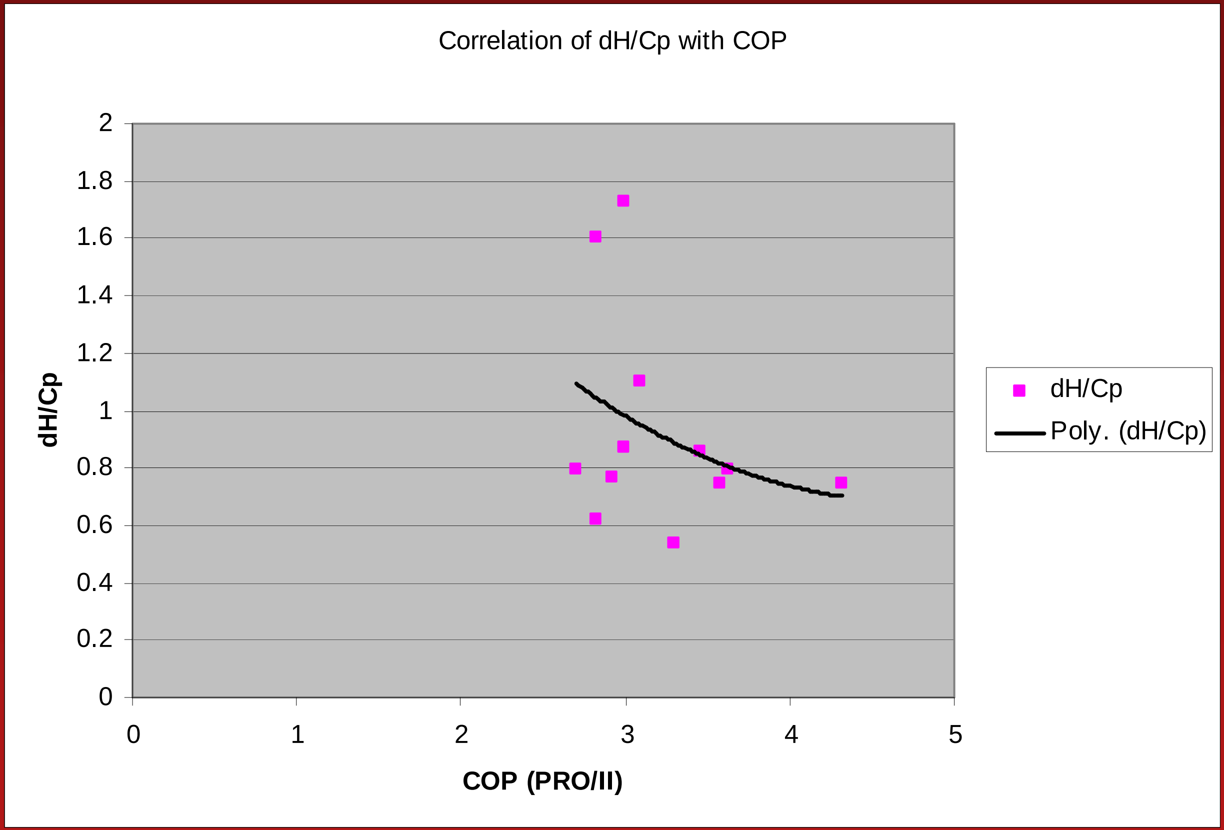
- **Flammability and explosiveness**
  - **Based on lower explosive limit**
  - **Based on vapor pressure**
  - **No strong correlation**
- **Toxicity**
  - **Based on experimental results**
  - **Found only for existing molecules**

Correlation with Molecular Weight



chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

$\Delta H/C_p$ Correlation with COP



chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Evaluating the COP for New Refrigerants

- **The following journal publications describe in detail how the COP for new refrigerants can be evaluated**

1. **Fleming, John S., Alex C. Bwalya and William Dempster. "The testing and evaluation of trial refrigerants: Part 1. System description." *International Journal of Energy Research* 24.14 (2000): 1217-1241.**
2. **Fleming, John S., Alex C. Bwalya and William Dempster. "The testing and evaluation of trial refrigerants: Part 2. The practical use of measured data." *International Journal of Energy Research* 24.14 (2000): 1243-1256.**

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma

Evaluating the COP for New Refrigerants

- Following a similar procedure, outlined in these two articles, would provide the COP for the tested refrigerants
- Then a correlation could be developed to relate the COP to functional group contributions
- This correlation would allow for a more rigorous analysis of all the possible refrigerants
- The refrigerants could then be ranked and analyzed using more accurate consumer preference functions

chemical, biological & materials
chemical, biological and materials engineering
university of oklahoma