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ASHRAE Chapter Visits

Update on Refrigerants: Past, Present and Future

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Update on Refrigerants: Past, Present and Future

by Eckhard A. Groll

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Course Description

- Update on Refrigerants: Past, Present and Future
  - » In recent decades, the refrigeration and air conditioning industries have been in a state of flux primarily because of the phase-out of ozone-depleting CFC and HCFC refrigerants, and secondarily because of environmental concerns related to the direct global warming impacts of some of the replacement refrigerants. Due to these concerns, there is significant worldwide interest in using substances that are naturally occurring in the biosphere as refrigerants, which are considered benign to the environment and are termed "natural working fluids". Surprisingly, many of these substances were already used as refrigerants at the dawn of the refrigeration technology in the late 1800's. Thus, when looking at the refrigerants of the future, it is essential to understand which substances have been used in past. This presentation provides a detailed review of the past and present refrigerants, and proposes refrigerants and their respective technologies that could be used in the future. An assessment of their characteristics related to choice of one versus another, and an identification of trends set by these choices will be made.

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Learning Objectives

1. Distinguish between the refrigerants that have been in used in vapor compression systems up to now
2. Describe the basic chemical compositions of refrigerants and the numbering system used to classify refrigerants
3. Explain the concepts of ozone depletion and global warming and the contribution of CFC/HCFC/HFC refrigerants to both issues
4. Identify refrigerants that are available for use in the future and the technical issues associated with them

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Today's Refrigeration

- Refrigeration of Food
- Cooling in Medical Applications
- Air Conditioning
- Cooling of Manufacturing Processes
- Chemical Engineering (Pharmaceutical and Petrochemical)
- Environmental Engineering
- Liquid Fuels for Space Applications
- Cryo Engineering
- …
  - → Refrigeration is present in all aspects of engineering and the daily life

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Refrigeration of the past

- How did it all start?
- At the beginning ….

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"Refrigeration" from about 1600 until 1920

Harvest and transport of natural ice, e.g., from New York to Charleston starting in 1799, or up to 500,000 tons/year imported to England (1899)

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Harvesting Natural Ice in 1838

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Industrial Revolution in the 1800's

1834: Jacob Perkins (London) invented and patented the compression refrigeration machine, using ethyl ether. The first machine was built by John Hague in London.

1850: A.C. Twinning constructed an ether compression refrigeration system in Cleveland, Ohio (1 ton of ice per day).

1873: David Boyle (US). First ammonia compressor.

1874: Raoul Pictet (Switzerland). First sulfur-dioxide compressor.

1876: F. Windhausen (Germany). First industrial water vapor refrigerating machine.

1887: J. & E. Hall (Great Britain). Industrial manufacture of carbon-dioxide compressors.

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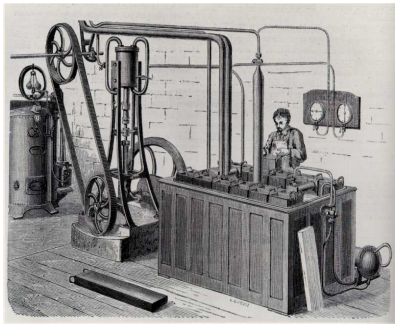
First Mechanical Ice Production
(Raoul Pictet 1877)



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Further Developments in the early 1900's

1905: Audriffren (France). First hermetic refrigerating unit (SO_2).

1911: W. Carrier. First studies on centrifugal compressors.

1912: Maurice Leblanc (France). Prototype water vapor centrifugal compressor.

1913: W.S.E. Rolaff (US). Rolling piston compressor.

1926: General Electric (US). Hermetic compressors in domestic refrigerators.

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Refrigerants up to 1930:

Substance	Refrigerant Number	Chemical Formula	NBP °C	CT °C	Rel vol	COP -15/30°C
Air [1]	R-729	-	-	-221.0	83.0	1.1
Water	R-718	H_2O	100.0	375.0	477	4.1 [3]
Carbon Dioxide	R-744	CO_2	-55.6[2]	31.0	1.0	2.56
Ammonia	R-717	NH_3	-33.3	135.0	3.44	4.76
Sulphur Dioxide	R-764	SO_2	-10.0	157.0	9.09	4.87
Diethylether	R-610	$C_2H_5.O.C_2H_5$	34.6	214.0	55.0	4.9
Dimethylether	E-170	$CH_3.O.CH_3$	-24.8	128.8	34.0	4.5
Methyl Chloride	R-40	CH_3Cl	-24.2	143.0	5.95	4.9

1. Reversed Brayton Cycle
2. Triple point
3. +5/30°C

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Refrigerants up to 1930 continued:

Refrigerant	Engineering Challenges
Air	Inefficient; reversed Brayton cycle operation
Water	Low pressures; operation above freezing
Carbon dioxide	High pressure; transcritical operation
Ammonia	Toxic, somewhat flammable
Sulphur Dioxide	Toxic, aggressive
Ethers	Toxic, aggressive
Hydrocarbons, e.g., propane, butane, etc.	Highly flammable

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Chlorofluorocarbons (CFCs)

Introduced as "Miracle Substances"

- In 1930, T. Midgley, A.L. Henne and McNary developed halogenated hydrocarbons ("Freons") as refrigerants at the General Motors Labs for Frigidaire (Dayton, Ohio)
- Excellent thermodynamic properties
- Inexpensive, non-flammable and non-toxic
- Used as: refrigerants, solvents, propellants, blowing agents
- Stable - *perhaps too stable*

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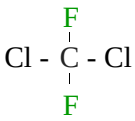
Refrigerant Designations (~~Freons~~)

R-xyz

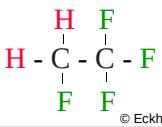
- x: # fluorine atoms
- y: # hydrogen atoms + 1
- z: # carbon atoms - 1

(remaining atoms are chlorine)

R-12



R-134a



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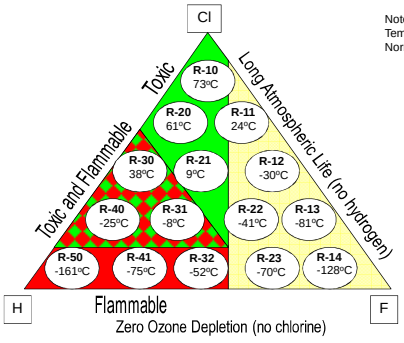
The Methane (CH_4) Family



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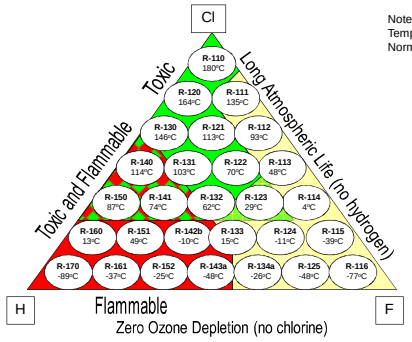
The Ethane (C_2H_6) Family



Note:
Temperatures indicate
Normal Boiling Point

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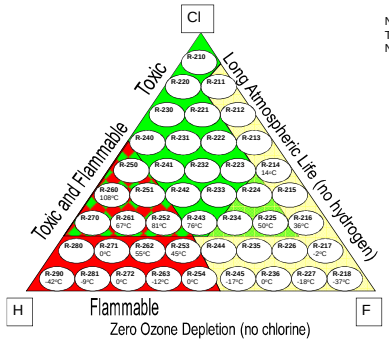
The Propane (C_3H_8) Family



Note:
Temperatures indicate
Normal Boiling Point

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Refrigerant Designations continued

Inorganic Refrigerants: R-700+M

R-717: ammonia
R-744: carbon dioxide

Azeotropic Refrigerant Mixtures: R-5XX

R-500: R-12/R-152a (73.8/26.2) mass %
R-501: R-22/R-12 (75.0/25.0)
R-502: R-22/R-115 (48.8/51.2)

Zeotropic Refrigerant Blends: R-4XX

R-401A: R-22/R-152a/R-124 (53/13/34)
R-407B: R-32/R-125/R-134a (10/70/20)
R-407C: R-32/R-125/R-134a (23/25/52)

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Refrigerants around 1970

Household Refrigerators & Freezers | Automotive Air-Cond'g | Window Air Conditioners | Residential Air Conditioners & Heat Pumps | Commercial & Industrial Refrigeration & Air Cond'g | Large Air Conditioning

R-12 (CCl_2F_2)

R-22 ($CHClF_2$)

R-11 (CCl_3F)

R-502 (48.8% R-22 & 51.2% R-115)

Ammonia (NH_3)

Engineering Challenges: None!

… Until …

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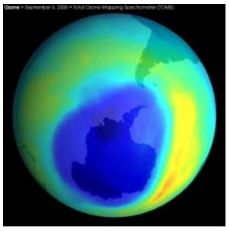
Ozone Depletion



(Image courtesy the TOMS science team and the Scientific Visualization Studio, NASA GSFC)

- **1974 Molina and Rowland propose ozone depletion hypothesis by CFCs**
- **1978 CFCs banned in aerosols in USA**
- **1984 First ozone hole over Antarctica**
- **1985 Vienna Convention**
  - » **Formalized international cooperation**
- **1987 Montreal Protocol**
  - » **Reduce CFC production by 50% by 1998**
- **1988 Documented losses of ozone over the Northern Hemisphere**
- **Amendments:**
  - » **1990 London**
  - » **1992 Copenhagen**
  - » **1997 Montreal**

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What is Ozone Depletion?

7% of extraterrestrial solar radiation is UV (λ < 380 nm)
but less than 1% reaches earth's surface

dynamic equilibrium

$$O_2 \xrightarrow{h\nu\ \lambda<245\text{ nm (UV-C)}} 2\,O\cdot$$

$$O\cdot + O_2 \longrightarrow O_3$$

$$O_3 \xrightarrow{h\nu\ \lambda<320\text{ nm (UV-B)}} O\cdot + O_2$$

Concern: Reduced O_3 allows more UV-B (280 - 320 nm)

Results:
- increase in skin cancer and cataracts
- damage to human immunity systems
- reduced crop yields
- altered terrestrial and aquatic ecosystems

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Atmospheric Chemistry of CFCs
Simplified – Many Pathways

CFC diffuses to stratosphere or is driven by wind

$$CFC + O_3 \xrightarrow{h\nu\ (UV\text{-}C)} O_2 + ClO\cdot + ...$$

chain

$$2\ ClO\cdot \longrightarrow Cl_2 + O_2$$

$$Cl_2 \xrightarrow{h\nu\ (UV\text{-}A)} 2\ Cl\cdot$$

$$Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$$

$$2\ O_3 \xrightarrow{h\nu\ (UV\text{-}A)} 3\ O_2$$ Net effect

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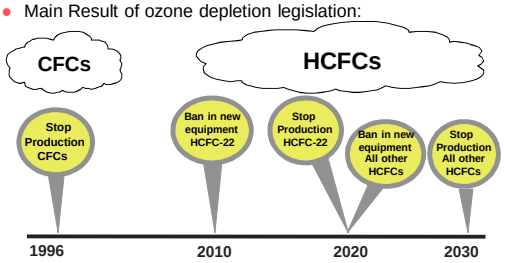
Current Phaseout Schedule

- Main Result of ozone depletion legislation:



20 years later → Ozone Depletion Continues !
2005 "Ozone Hole" was one of largest and deepest ever !
Latest NASA predictions delays recovery until 2068
→nearly 20 years later than previously believed …

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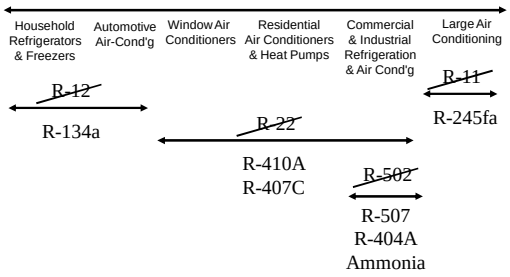
HFC's to the rescue!



However, ozone depletion is not the whole story!

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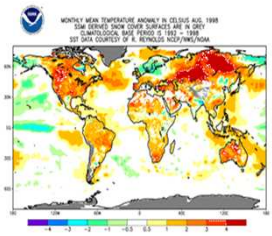
Global Warming



1827 Fourier describes theory of the naturally occurring global warming effect (the earth is about 30 K warmer due to the natural global warming effect, i.e., average temp is +15°C instead of -15°C)

1896 Arrhenius predicts the increase in CO_2 emissions due to human related processes

1900 Mankind welcomes the additional global warming effect

1970 Researchers issue warnings regarding human induced global warming

1988 Founding of the "Intergovernmental Panel on Climate Change" (IPCC)

1992 United Nations Framework Convention on Climate Change (FCCC)

1997 Kyoto Protocol: drastic reduction of global warming gases emissions (CO_2, N_2O, CH_4, HFC, PFC, SF_6)

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What is Global Warming?

- The earth radiates heat to the universe at various wavelengths.
- Global warming gases in the upper stratosphere "close windows" of certain wavelengths.
- Thus, some of the earth's heat is not radiated to the universe, but instead reflected to the earth surface (trapped inside the atmosphere).
- The results is an average increase of the earth's temperature.
- How is the global warming impact of different substances measured?
  - » Relative to the global warming impact of the same mass of CO_2

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Global Warming Impact of HFC Refrigerants

Refrigerant Number	Chemical Formula	NBP °C	Glide K	CT °C	GWP	Safety Group
R-134a	**$CH_2F.CF_3$**	**-26**	**0.0**	**101**	**1300**	**A1**
R-413A	**R-134a/218/600a**	**-35**	**6.9**	**101**	**1770**	**A1/A2**
R-404A	**R-143a/125/134a**	**-47**	**0.7**	**73**	**3260**	**A1/A1**
R-507	**R-143a/125**	**-47**	**0.0**	**71**	**3300**	**A1**
R-407C	**R-32/125/134a**	**-44**	**7.4**	**87**	**1520**	**A1/A1**
R-417A	**R-125/134a/600**	**-43**	**5.6**	**90**	**1950**	**A1/A1**
R-410A	**R-32/125**	**-51**	**0.2**	**72**	**1720**	**A1/A1**
R-508	**R-23/116**	**-86**	**0.0**	**13**	**11860**	**A1**

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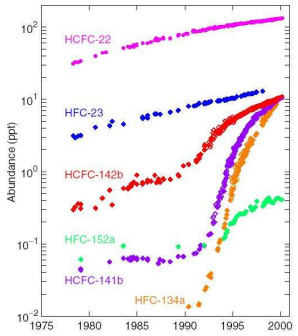
HFC Refrigerants in the Atmosphere



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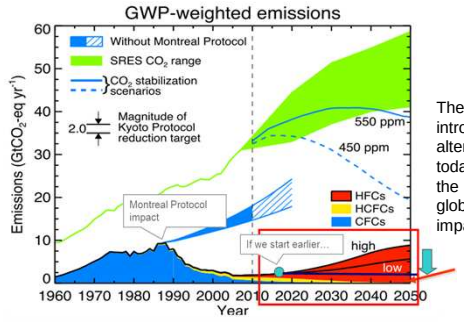
Global Warming: We need to Act Now



The sooner we introduce better alternatives for today's HFCs, the lower the global warming impact will be!

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Source: "The large contribution of projected HFC emissions to future climate forcing" by Guus J.M.Velders et.al.

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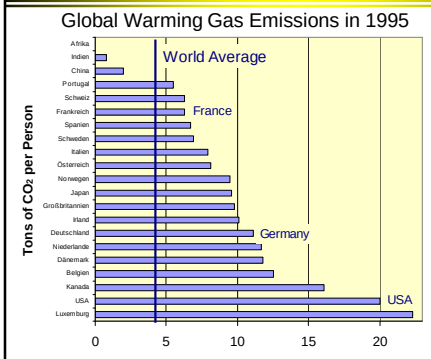
Reduction of Global Warming Gas Emissions basend on Kyoto-Protokol



Country	Reduction of global warming gas emissions
Portugal	+ 27%
Ireland	+ 13%
Sweden	+ 4%
Norway	+ 1%
USA	- 6%
Switzerland	- 8%
EU (Total)	- 8%
Denmark	- 21%
Germany	- 25%
Luxemburg	- 28%

Status June 1998

CO_2 + CH_4 + NO_2 + + HFC + PFC + SF_6

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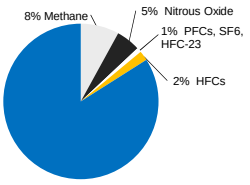
Kyoto Protocol

- International Climate Change Treaty
- Signed in 1997 by 187 countries
- United States of American is not currently a signatory
  - » Significant reduction commitments without a defined verification mechanism
  - » Funding for developing nations to conform
  - » Technology transfer requirements
- CO_2 from automotive and power plant emissions is the leading greenhouse gas
- HFCs are only 2% of total GHG production but seen as the most easily addressed

The Green House Gases (GHG)

Total gas emissions – assumes all gases vented to atmosphere (100% leakage)



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HFC regulations in various countries

Austria :	Discussion of HFC-taxes
Denmark :	HFC tax of 0.1 DKK/kg CO_2-eqivalent (e.g. R-134a = $20) HFC ban in certain applications starting 2002 and 2006
Germany :	Federal Ministry of Environment issued HFC Regulations
Great Britain :	Discussion of possible actions
Iceland :	HFC usage other than refrigeration prohibited since 1998
Japan :	Relying on voluntary leakage reduction agreements with industry
Netherlands :	Max. leakage permitted by law
Norway :	HFC-tax 0.18 NOK/kg CO_2-equivalent effective since 1.1.2003
Sweden :	Reduction of leakage Prohibition of HFC systems with more than 25 kg charge Sweden discusses HFC-taxes 4 times higher than Denmark
Switzerland :	Discussion of measures to reduce HFC emissions
USA:	HFC recovery required by legislation

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What is the Alternative?

Natural Refrigerants

Donella Meadows, American writer:

”The eighty thousand different chemicals now manufactured end up everywhere, from our stratosphere to our body. They were created to accomplish functions that can now be carried out far more efficiently with biodegradable and naturally occurring compounds.”

Ammonia, carbon dioxide, hydro carbons, water, air, helium ...

R-717, R-744, R-290, R-600a, R-718, R-729, R-704 ...

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Natural Refrigerants, continued

Refrigerant Number	Chemical Formula	NBP °C	Glide K	CT °C	GWP	Safety Group
R-717	**NH_3**	**-33**	**0.0**	**133**	**0**	**B2**
R-600a	**$CH.(CH_3)_3$**	**-12**	**0.0**	**135**	**3**	**A3**
R-290	**C_3H_8**	**-42**	**0.0**	**97**	**3**	**A3**
R-1270	**C_3H_6**	**-48**	**0.0**	**92**	**3**	**A3**
R-744	**CO_2**	**-57**	**0.0**	**31**	**1**	**A1**

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Already, some Consumer are Trendsetters

- McDonalds goes for natural refrigerants, first HFC-free restaurant opened in Denmark in 2003
- The Coca-Cola Company will only use HFC-free technology in bottle coolers from 2004
- Unilever wants to use HFC-free technology
- Nestlé wants to use natural refrigerants wherever possible
- Scandinavians value natural refrigerant supermarkets higher than conventional supermarkets
- British insurance companies are said to reduce investments in greenhouse warming industry
- Carlsberg brewing company is looking at HFC-free beer coolers

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Also, Suppliers & Manufacturers are Trendsetters

- AEG (D), Bosch-Siemens (D), Electrolux (S), Liebherr (D), Vestfrost (DK) etc.: iso-butane in household refrigerator / freezers
- Earth Care Technology (GB): hydrocarbon air conditioners: unitary, split and central
- Airned (NL): hydrocarbon air conditioners, split + central
- Axima (D), York Refrigeration (DK, D, NL): carbon dioxide in industrial refrigeration
- Gea, Linde, York: ammonia water chillers for air conditioning
- York Refrigeration (DK): hydrocarbons in chillers
- DeLonghi (I): hydrocarbon plug-in air conditioners
- ILK Dresden (D): water as refrigerant
- A, DK, D, NL, S, CH … heat pumps with hydrocarbons
- German car manufacturers wanted to use CO_2 in mobile AC

… and others …

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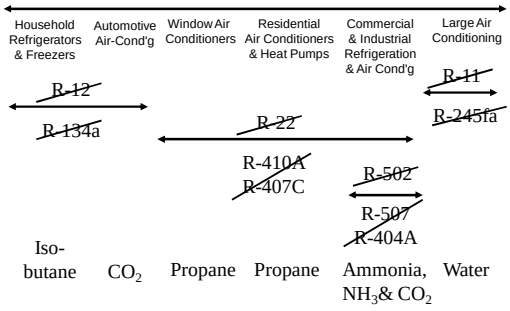
Refrigeration of tomorrow



Have we come "full circle"?

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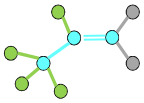
Not so fast, what about HFO?

- Hydro-Fluoro-Olefin (2,3,3,3-tetrafluoropropene)
- HFO – 1 2 3 4 y f



# of fluorine atoms

# of hydrogen atoms +1

# of carbon atoms -1

# of unsaturated bonds

Substitution on terminal methylene carbon:
a = CCl_2 ; b = CClF ;
c = CF_2 ; d = CHCl
e = CHF ; f = CH_2

Substitution on central carbon
x = Cl ; y = F ; z = H

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HFO Consideration

- R-1234yf, R-1234ze
  - » Classified as Mildly Flammable (A2L) by ASHRAE 34 and ISO817
  - » Use of A2L refrigerants should be discussed for wider application
- HFO-1234yf:
  - » Leading candidate to replace R-134a in mobile applications
  - » GWP of 4, no Toxicity, slightly flammable
  - » Possible applications: stationary HVAC equipment, will require significant engineering and safety code changes
- HFO-1234ze:
  - » Ideal application: Foam Blowing, not necessarily HVAC&R
  - » GWP of 4
- HFO/HFC/? Blends:
  - » Better Performance at the cost of higher GWP

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If "Mildly" Flammable becomes Acceptable?

- What about R-32?
  - » GWP: 675
  - » Suitable for all R-410A products
  - » Better performance than R-410A in cooling and heating
  - » Better performance for high ambient temp. than R-410A
  - » Classified as Mildly Flammable (A2L) by ASHRAE 34 and ISO817
  - » Refrigerant charge volume can be reduced
  - » Use of A2L refrigerants should be discussed for wider application
  - » Upper charge volume should be decided by taking into consideration safe use of multi system
  - » Continuous refrigerant containment measures are necessary

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Summary

- An "Unprecedented" Situation:
  - » Natural refrigerants can *not* be used in existing equipment without significant modifications
  - » Nearly all refrigeration equipment must be redesigned
  - » Alternative technologies need to improve performance, or they are not "feasible"
  - » Incentives to improve performance by better design

  → *Many Opportunities Unfold*

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An "Unprecedented" Situation

- However, not this one:

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Thank you!

I would be happy to answer any questions
you may have!

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