The Problem of Counterfeit Refrigerants

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Outline

- Refrigerants over the years
- Montreal and Kyoto protocols
- European F-gas regulations
- Refrigerant counterfeiting

What do we desire of our refrigerant?

- Chemical stablity
- Non-toxicity
- Non-flammability
- Low molecular weight
- High ‘energy carrying capability’
- Miscibility with lubricating oil
- Suitable operating pressure range

What do we desire of our refrigerant?

- Good electrical insulation properties
- Low index of compression (compressor efficiency)
- Non-ozone depleting
- Low or zero global warming potential
- Others…

History of refrigerant development

- BC to 19^{th} century – cold air and ice
  - 1100 BC – Chinese poem mentions ice stored specifically for domestic use.
  - 5th Century BC – Protagoras reported Egyptians producing ice by placing water on their roofs when there was a clear night sky
  - 37 AD - 68 AD – Roman Emperor Nero Claudius is reported to have sent slaves to the mountains to fetch snow to be used specifically for cooling fruit drinks

History of refrigerant development

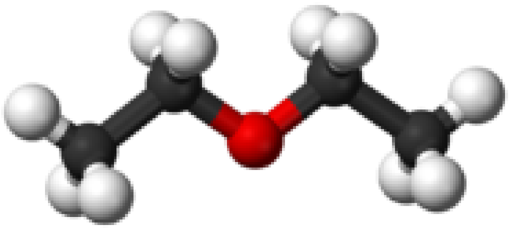
- Latter half of 19th century – international ice trade, e.g. from USA and Norway to England

History of refrigerant development

- 1755 – William Cullen of Glasgow produces ice by evaporating water at low pressure

History of refrigerant development

- 1834 – Jacob Perkins patents a vapour compression (VC) system using ethyl-ether

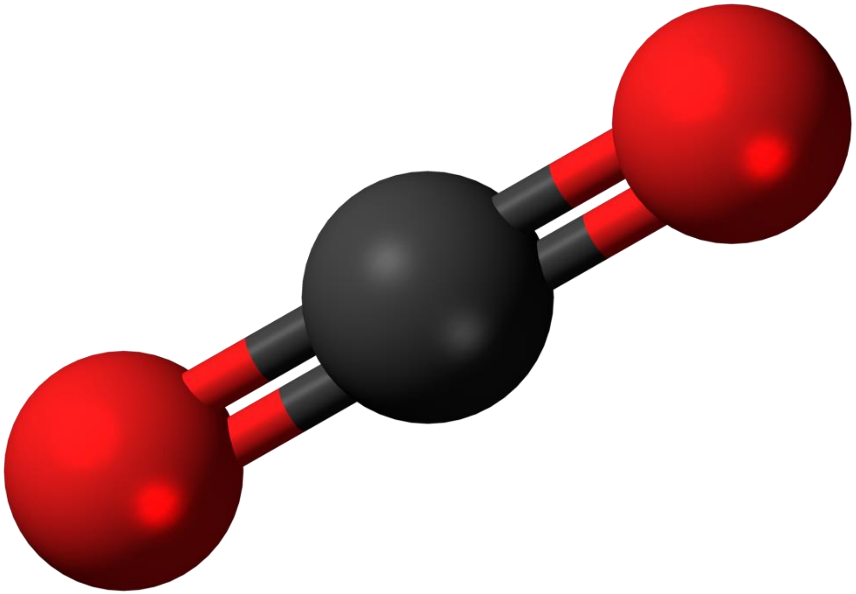


- Flammable
- Anaesthetic

- 1863 – Charles Tellier patents a VC cycle running on methyl-ether

History of refrigerant development

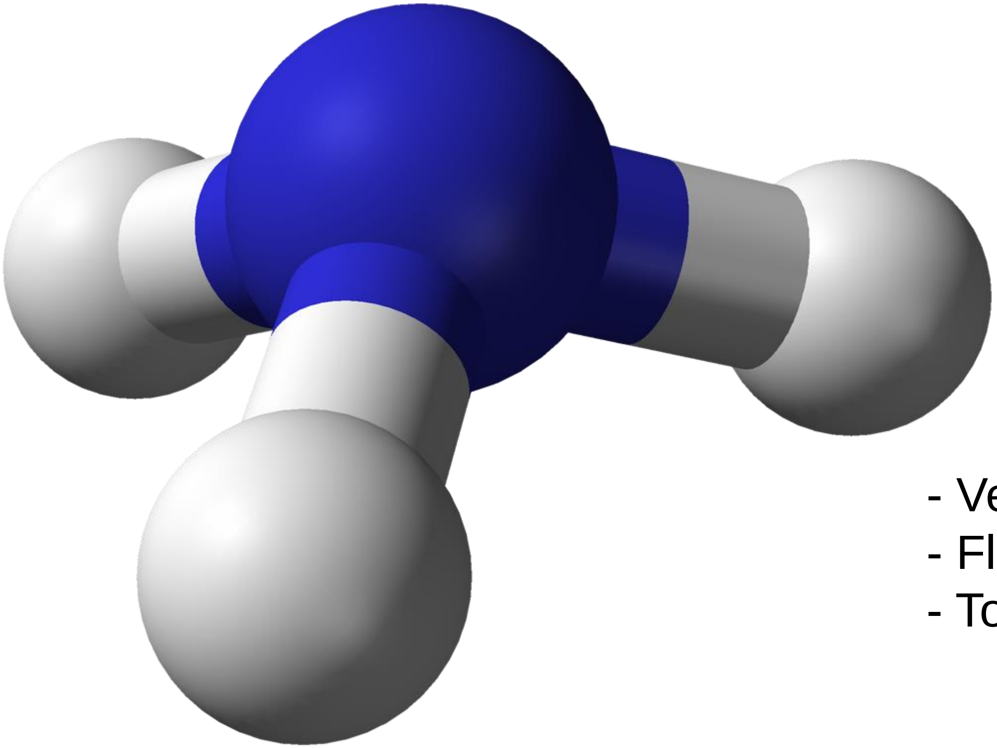
- 1862 – Thaddeus Lowe uses carbon dioxide in a VC system



- Non-flammable
- Low-critical point
- Toxic
- Requires high pressure machinery

History of refrigerant development

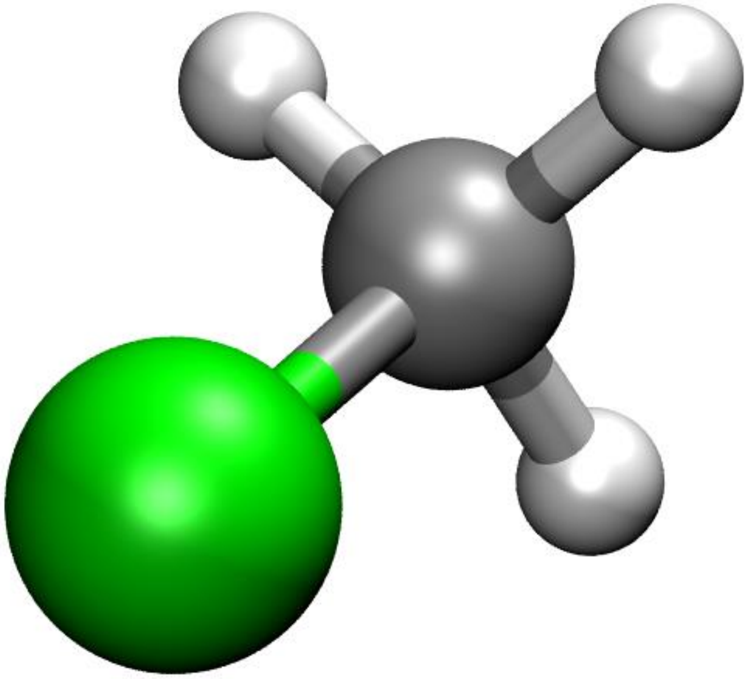
- 1872 – David Boyle uses ammonia in a VC cycle, and subsequently Carl von Linde employed ammonia as a refrigerant



- Very efficient
- Flammable
- Toxic

History of refrigerant development

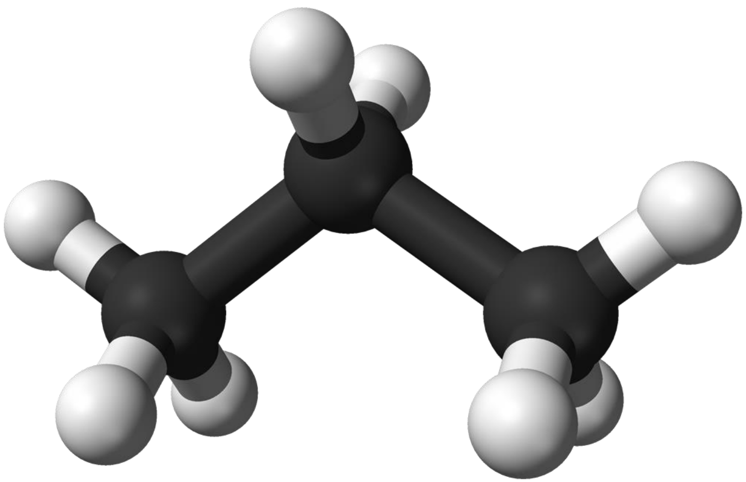
- 1878 – methyl chloride is used as a VC refrigerant in France

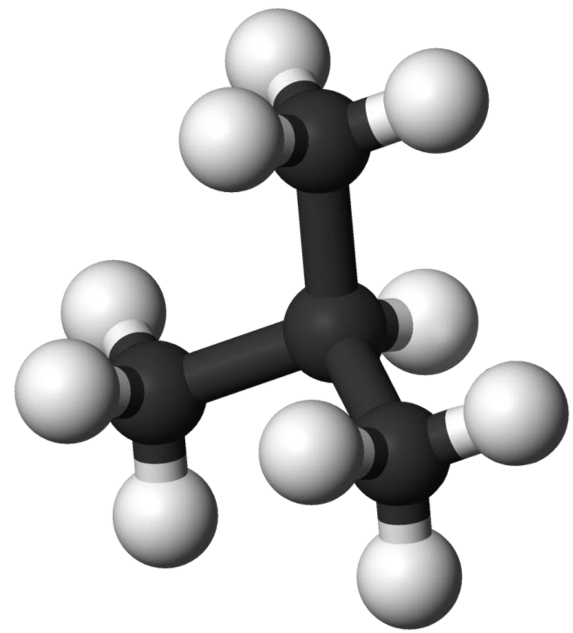


- Flammable
- Toxic

History of refrigerant development

- Early 20th Century – hydrocarbons (propane, iso-butane) began to be experimented with for use in domestic-scale refrigeration in the United States



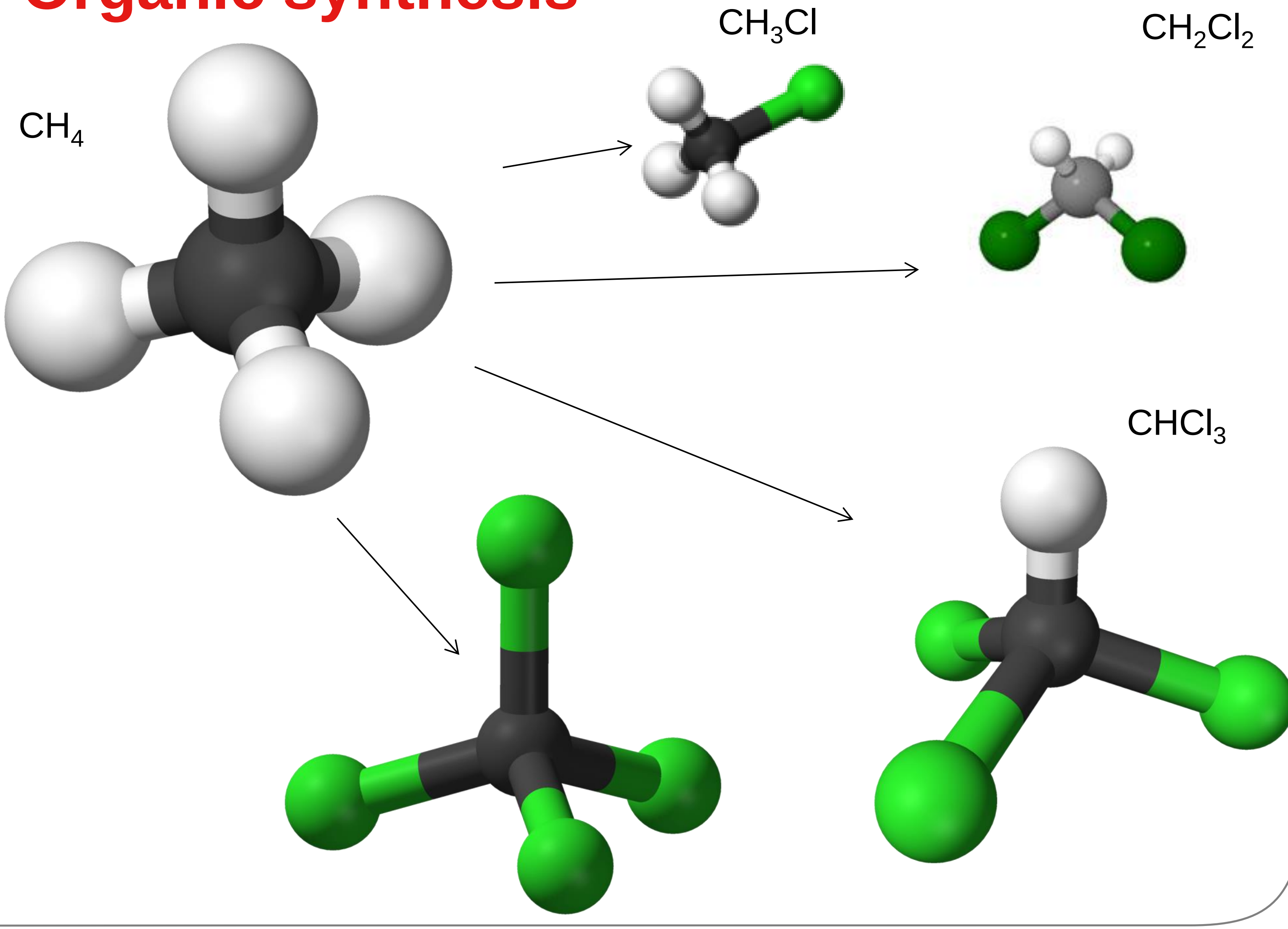


- Flammable

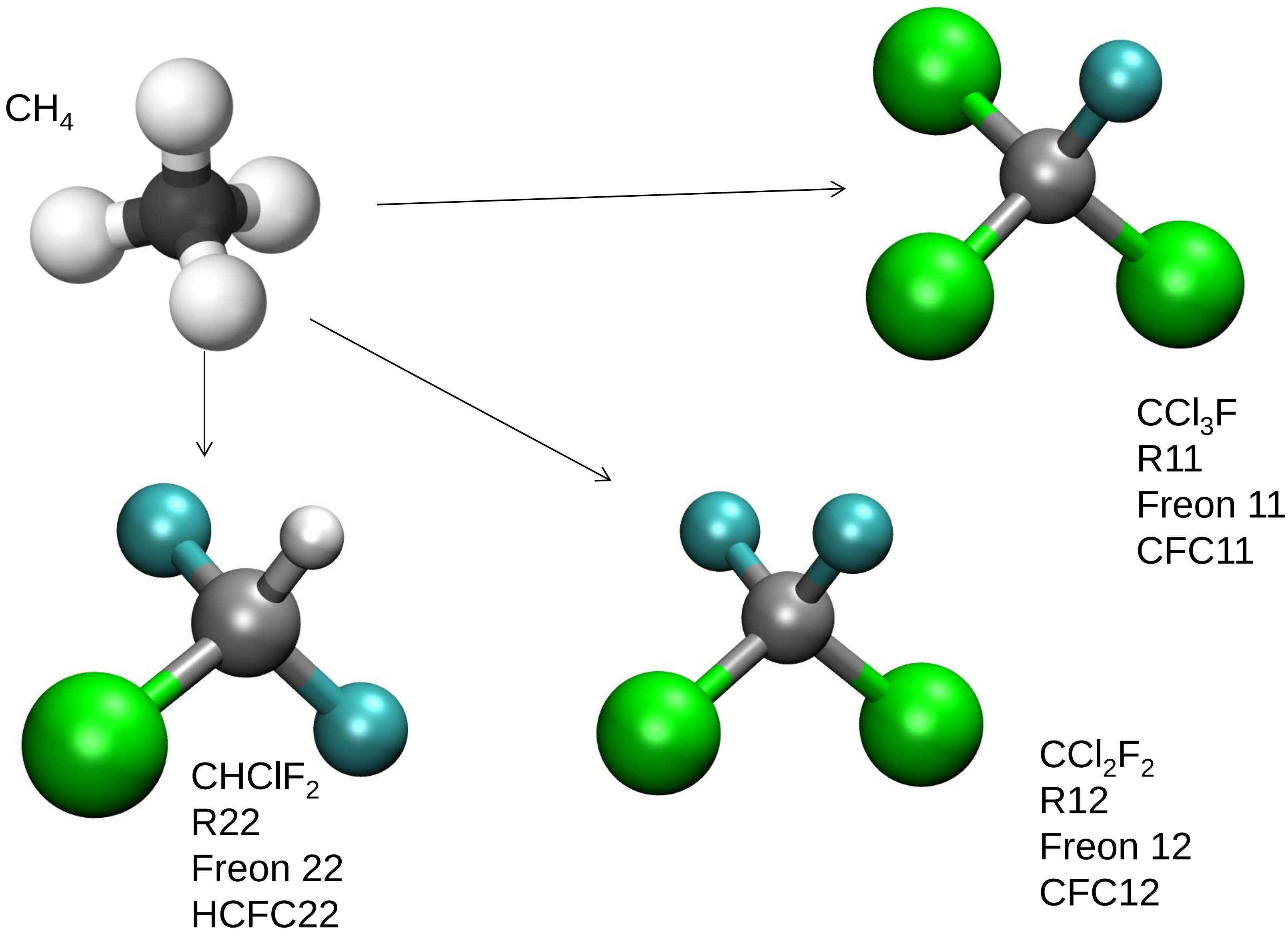
History of refrigerant development

- Late 1920s Charles Kettering of General Motors tasks Thomas Midgley with finding or synthesising the ideal refrigerant as an alternative to methyl chloride, propane and ammonia
- To reduce flammability, Midgley experimented with the family of *halo-carbons*; molecules based on carbon with halogens (fluorine and chlorine) instead of hydrogen atoms

Organic synthesis

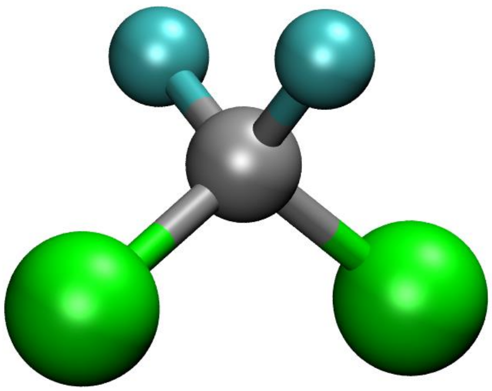


Development of CFCs and HCFCs

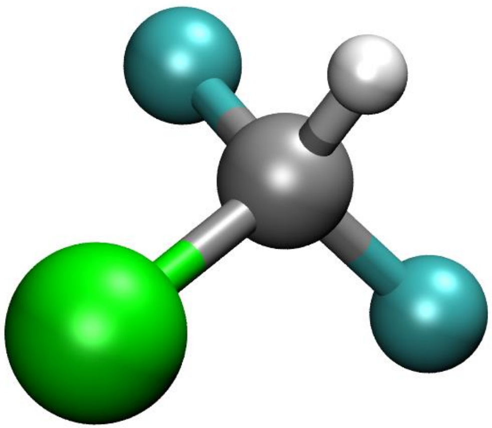


R12 – close to being the ideal refrigerant

- Thermodynamically efficient
- Chemically stable
- Non-toxic
- Non-flammable,
- Miscible with lubricating oil
- Capable of operating in a domestic refrigerator without going below atmospheric pressure
- Good electrical insulator
- Low index of compression so that the compressor would run cool



R22 – another excellent refrigerant



- Thermodynamically efficient
- Non-toxic
- Non-flammable,
- Miscible with lubricating oil
- Less stable than R12
- Requires less swept volume than R12
- Viewed as a safer alternative to ammonia

Domination of CFCs and HCFCs

- CFCs and HCFCs were able to meet the full range of refrigerant needs from domestic to industrial – seemed destined to entirely dominate the refrigerant market
- In addition to refrigerants, they were also used as propellants and blowing agents for polymer foam manufacture – applications where the gases were simply released to the atmosphere

Chlorine and the ozone layer

- 1974 – researchers Roland and Molina proposed that chlorine-containing molecules in the stratosphere were destroying the ozone layer
- After initial skepticism, mounting evidence, particularly in the atmosphere over Antarctica, leads to an international agreement to phase-out chloro-flouro-carbons (CFCs)

Montreal protocol

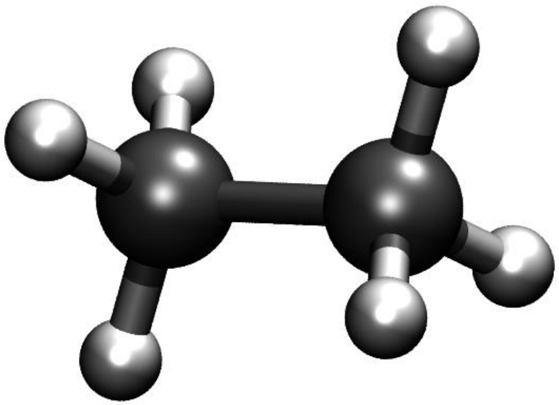
- 1987 – 46 countries meet in Montreal to sign the *Montreal Protocol on Substances that Deplete the Ozone Layer*, with the initial target of reducing CFC consumption by 50 % over 10 years
- The following year Du Pont, producer of the *Freon*™ brand of refrigerants, agrees to reduce production
- Subsequent protocol meetings were attended by more and more signatory nations, and eventually it was agreed to completely* phase out CFC production and usage

Replacing the CFCs

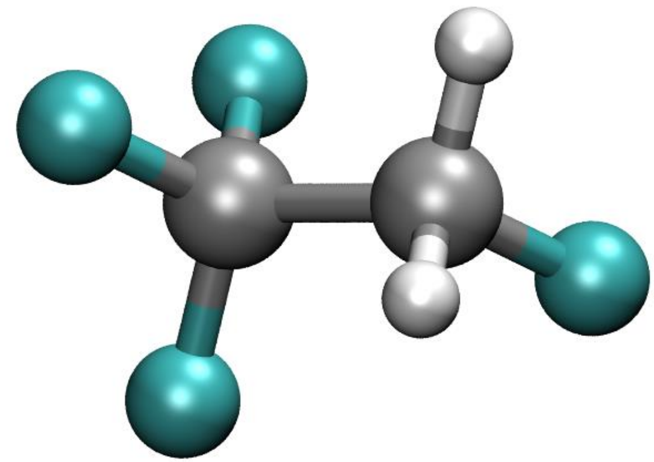
- With chlorine no longer an option for refrigerants, the search began for replacements for R11 and R12
- Ideally the replacements would be physically and thermodynamically similar to the CFCs in order that they could be used in the same equipment (‘drop-in’ replacements)

R134a – the drop-in replacement for R12

- By far the most successful CFC replacement has been R134a – a hydrofluorocarbon (HFC)



CH_3CH_3
Ethane



CH_2FCF_3
R134a

R134a – the drop-in replacement for R12

- R134a has very similar properties to R12, although it is slightly less chemically stable and has a lower critical point
- It was also originally not miscible with commonly used lubricants, but that problem was soon overcome
- R134a remains in high usage worldwide today

Kyoto Protocol

- 1997 – United Nations Framework Convention on Climate Change holds a meeting of UN countries in Japan with the aim of reducing greenhouse gas emissions (which include HFCs)
- As a result of this and subsequent meetings signatory countries agree to different targets and different time frames for emissions reductions through better handling and storage practices and, in some cases, reducing the usage or completely phasing out some refrigerants

GWP data (taken from IRHACE refrigerant code of practice, 2001)

APPENDIX 2

FLUOROCARBON REFRIGERANTS

Environmental properties: A long term replacement refrigerant should have a zero Ozone Depletion Potential, a low Global Warming Potential and a short Estimated Atmospheric Life.

NUMBER	NAME	CHEMICAL FORMULA	O.D.P.	G.W.P.	E.A.L.
CFCs					
R11	Trichlorofluoromethane	CCl_3F	1.0	4000	50
R12	Dichlorodifluoromethane	CCl_2F_2	1.0	8500	102
R13	Chlorotrifluoromethane	$CClF_3$	1.0	11700	640
R113	Trichlorotrifluoroethane	CCl_2FCClF_2	0.8	5000	85
R114	Dichlorotetrafluoroethane	$CClF_2CClF_2$	1.0	9300	300
R500	CFC/HFC Blend	CFC-12 (74%) HFC-152a(26%)	0.5	5210	102*
R502	CFC/HCFC Blend	CFC-115 (51%) HCFC-22 (49%)	0.33	4510	1700*
R503	CFC/HFC Blend	CFC-13 (40%) HFC-23 (60%)	0.5	11900	640*
R717	ammonia	NH_3	0	0	
R744	Carbon dioxide	CO_2	0	1.0	

GWP data (taken from IRHACE refrigerant code of practice, 2001)

NUMBER	NAME	CHEMICAL FORMULA	O.D.P.	G.W.P.	E.A.L.
HCFCs & HFCs					
R22	Chlorodifluoromethane	$CHClF_2$	0.055	1700	13.3
R123	Dichlorotrifluoroethane	$CHCl_2F_3$	0.02	93	1.4
R124	Chlorotetrafluoroethane	$CHFClCF_3$	0.022	480	5.9
R401A	HCFC/HFC Blend	HCFC-22 (53%) HFC-152a(13%) HCFC-124 (34%)	0.04	1120	13.3*
R401B	HCFC/HFC Blend	HCFC-22(61%) HFC152a(11%) HCFC-124(28%)	0.04	1230	13.3*
R401C	HCFC/HFC Blend	HCFC-22 (33%) HFC-152a(15%) HCFC -124 (52%)	0.03	870	13.3*
R402A	HCFC/HFC/HC Blend	HCFC-22 (38%) HFC-125(60%) HC290(Propane) (2%)	0.02	2380	36*

GWP data (taken from IRHACE refrigerant code of practice, 2001)

NUMBER	NAME	CHEMICAL FORMULA	O.D.P.	G.W.P.	E.A.L.
HCFCs and HFCs					
R402B	HCFC/HFC/HC Blend	HCFC-22(60%) HFC-125(38%) HC-290(2%)	0.03	2080	36*
R403B	HCFC/PFC/HC Blend	PFC-218(39%) HC-290(Propane) (5%) HCFC-22 (56%)	0.03	2640	2600*
R406A	HCFC/HC Blend	HCFC-22 (55%) HCFC-142b (42%) HC-600a (4%)	0.05	1700	19*
R408A	HCFC/HFC Blend	HFC-143a(46%) HFC-125(7%) HCFC-22(47%)	0.023	3060	55*
R409A	HCFC Blend	HCFC-124(25%) HCFC-142b(15%) HCFC-22(60%)	0.05	1530	19*
R409B	HCFC Blend	HCFC-124(25%) HCFC-142b(10%) HCFC-22(65%)	0.05	1510	19*
R134a	Tetrafluoroethane	CF_3CH_2F	0.0	1300	14
R125	Pentafluoroethane	C_2HF_5	0.0	3200	36
R404A	HFC Blend	HFC-125 (44%) HFC-134a (4%) HFC-143a (52%)	0.0	3850	55*
R407B	HFC Blend	HFC-32 (10%) HFC-125 (70%) HFC-134a (20%)	0.0	2300	36*

Phase-out of F-gases in Europe

- The European Union has been particularly aggressive at phasing out refrigerants containing fluorine (“F-gases”)
- 2006 – EU government releases Regulation (EC) No 842/2006 covering the containment and recovery of F-gases along with storage labelling, and training requirements

Refrigerant counterfeiting

- Scheduled phase-out of HFCs causes their price to rise as supply becomes restricted
- Refrigerants being sold under false labelling
  - e.g. Times of India reported a businessman was caught selling R22 as R134a
- Refrigerants being contaminated with cheaper refrigerants
  - e.g. R134a is diluted by cheaper refrigerants

Contaminated R134a a particular concern

- Product advertised as R134a may have varying amounts of R22, R30, R40 and R142b
- The IIR reported an estimated 10 – 15 % of reefer containers worldwide had contaminated refrigerant

Explosion of a reefer in Vietnam

Hazards associated with R40

- Of the R134a contaminants, R40 (methyl chloride) is particularly hazardous
  - Anaesthetic
  - Flammable
  - Reacts with aluminium producing compounds more flammable and toxic than methyl chloride itself

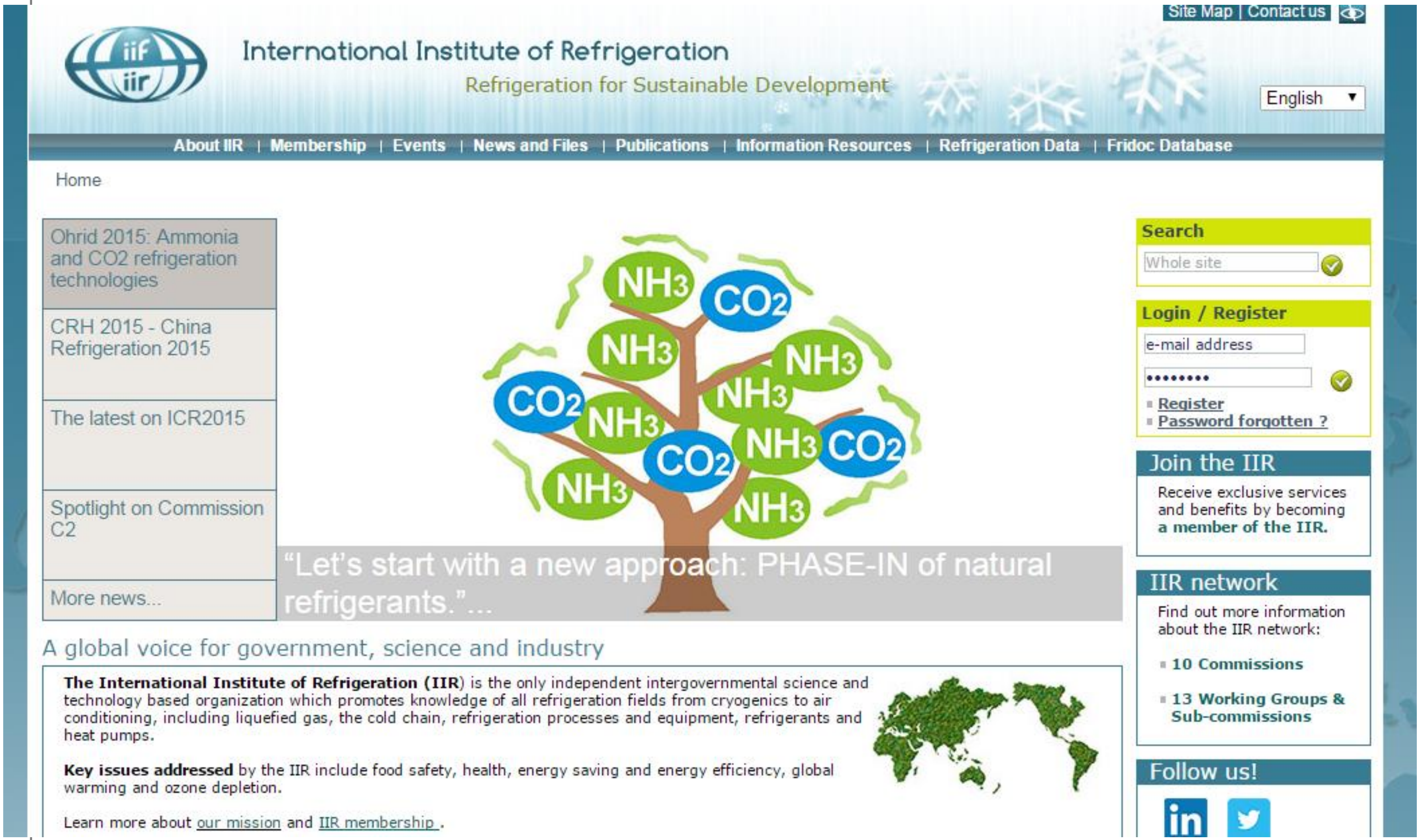
Potential consequences of charging with counterfeit refrigerants

- Contravention of government regulations
- Poor refrigeration performance
- Equipment damage
  - Corrosion
  - Explosions
  - Fires
- Loss of product/cargo
- Injury and death
  - Several explosions have caused deaths

Checking for, and dealing with contaminated refrigerant

- Reputable refrigerant suppliers provide guidelines for establishing whether refrigerant is authentic
  - e.g. http://www2.dupont.com/Refrigerants/en_US/brand_assurance/index.html
- The presence of R40 can be determined with a halide flame test (should be done in a well-ventilated area)
- Modern refrigerant analysers are capable of identifying R40
- R40 can be removed from a system in gaseous form; however, the liquid reaction products will collect at the lowest point in the system, making removal more difficult

Into the future?



Conclusions

- Due to environmental concerns, fluorine-containing refrigerants (HFCs) have been scheduled for phase-out (i.e. mandatory reduction of production and usage)
- This has resulted in a price rise in HFC refrigerants, particularly R134a
- The high price of some refrigerants has lead to counterfeiting, either by diluting them with cheaper refrigerant(s), or by replacing the advertised refrigerant by a completely different one
- Vigilance is required when dealing with refrigerant systems, particularly when the origin of system, or the reputability of the refrigerant supplier is unknown