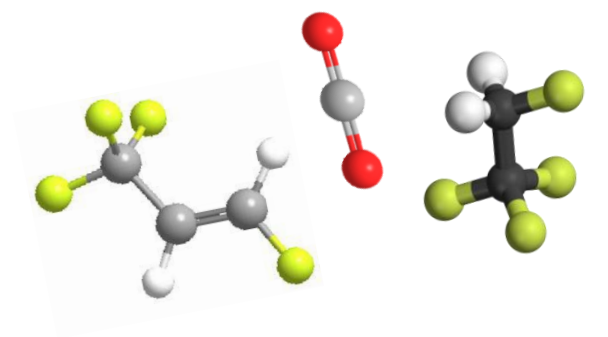


# From the Beginnings of Artificial Cold to Climate-Friendly Fluids; Evolution of Refrigerants Application



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Acknowledgement

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# Background

## ○ Refrigeration is used everywhere

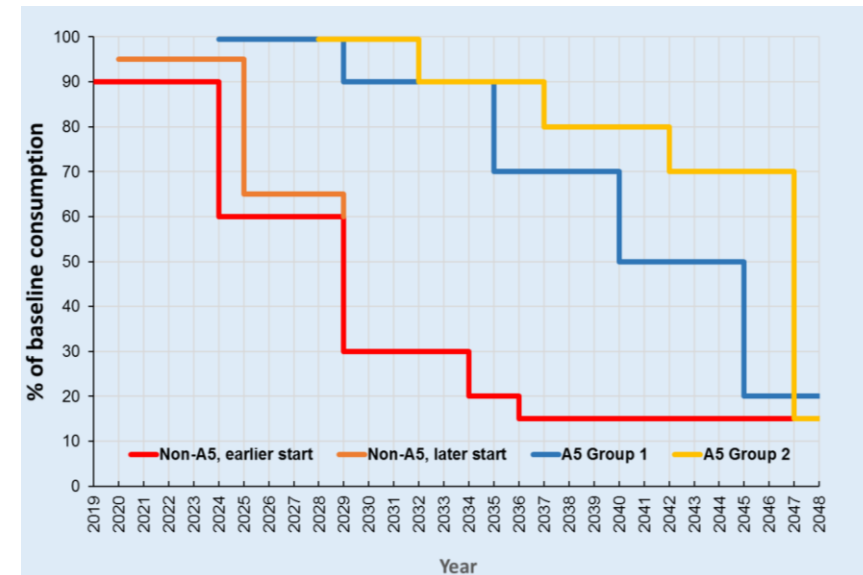
Food industry, air conditioning, cryogenics, medicine and health products, energy, etc.

## ○ Use of refrigeration will increase, particularly in developing countries

## ○ Use of refrigeration has environmental consequences

- Current refrigerants (HFCs) are greenhouse gases; **need for low-GWP refrigerants**
- Emissions of CO<sub>2</sub> from fossil fuel power plants; **need for high efficiency**
- Kigali amendment to the Montreal Protocol (2016); **production & consumption of HFCs to be cut by more than 80 % over the next 30 years.**

Weighed GWP across all sectors ≈ 300



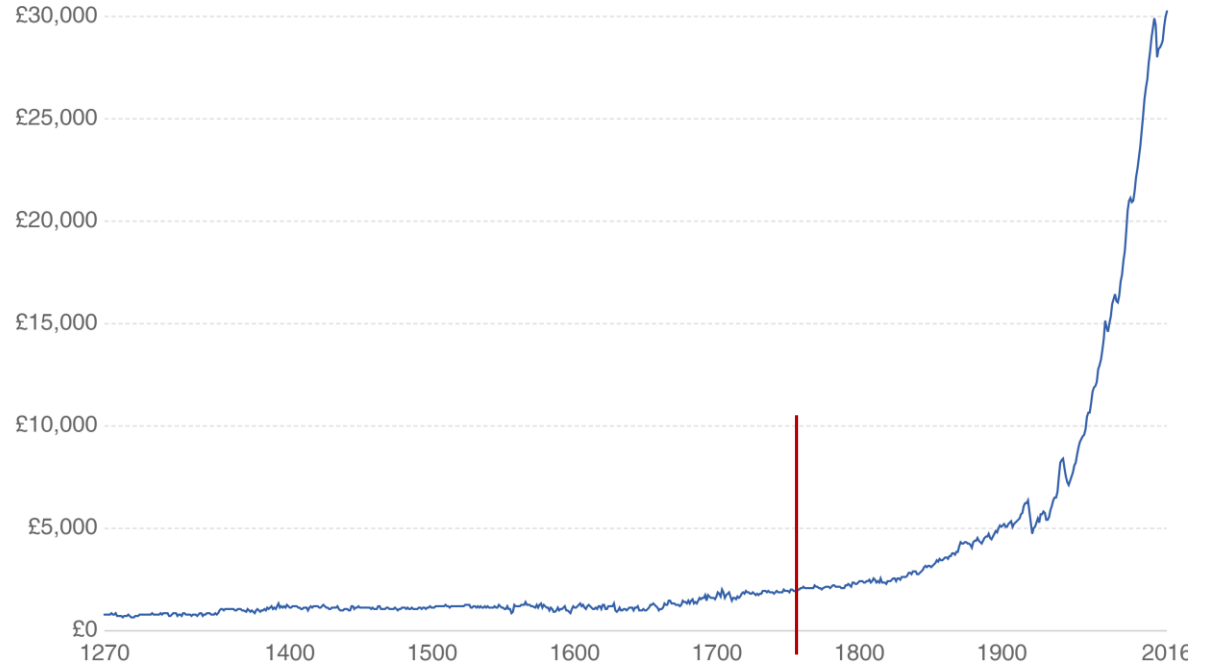
# Industrial revolution (1760~1840)



## GDP per capita in England since 1270

Adjusted for inflation and measured in British Pounds in 2013 prices

OurWorld  
in Data



Source: GDP in England (using BoE (2017))

Note: Data refers to England until 1700 and the UK from then onwards.

OurWorldInData.org/economic-growth • CC BY-SA

OurWorldInData (2018)

- Improved productivity through inventions and new production methods  
(Watt's steam engine; iron production; textile industry)
- Sustained growth of income and population
- The most important event since the domestication of animals and plants (10 000 years ago)

# Beginnings of artificial cold

1755 – apparatus to make ice by evaporation of water at reduced pressure; W. Cullen

1824 – genesis of thermodynamics; Carnot

1834 – refrigeration machine using compression of a liquefiable gas; Perkins

1834 – demonstration of the Peltier effect

– reliable compressor; Harrison

– absorption machine; F. Carre

– **air** cycle machine; Gorrie

– machine relying on evaporation of **water (R-718)** at reduced pressure; E. Carre

– refrigerants: **ethyl ether, methyl ether (R-E170), petrol ether + naphtha (chemogene), CO<sub>2</sub> (R-744), ammonia (R-717), SO<sub>2</sub> (R-764), methyl chloride (R-40)**

1876 – ammonia compressors by Linde; application of thermodynamics

**Main applications: ice making, transport of meat by sea, and brewing**

1890 -> 1900 – collapse of ice harvesting

1918 – dominant refrigerants: **ammonia, CO<sub>2</sub>, SO<sub>2</sub>**

1920s – introduction of HCs

1931 – introduction of CFC refrigerants

## Ice harvesting



# Application of refrigerants

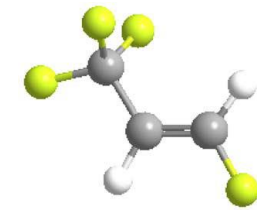
<span style="color: blue;">■</span>	No flame propagation
<span style="color: orange;">■</span>	Lower flammability
<span style="color: red;">■</span>	Higher flammability

## Natural fluids

<b>H<sub>2</sub>O</b>	<b>100.0</b>	<b>R-717</b>	<b>-33.3</b>	<b>R-600a</b>	<b>-11.7</b>
<b>CO<sub>2</sub></b>	<b>-78.4</b>			<b>R-290</b>	<b>-42.1</b>
<b>air</b>	<b>-194.2</b>			<b>R-1270</b>	<b>-47.7</b>

Ammonia (points to R-717)

Normal boiling point (°C) (points to the boiling point column)



HFO-1234ze(E)

- # of fluorine atoms
- # of hydrogen atoms +1
- # of carbon atoms -1
- # C=C double bounds

## Fluorinated fluids

**Whatever worked**

**1<sup>st</sup> Generation**

1830 – 1930

*safety & durability*

**Water chillers**  
(centrifugal)

**Domestic refrigeration**

**Air conditioners**

**Industrial refrigeration**

**CFCs & HCFCs**

**2<sup>nd</sup> Generation**

1931 – 1990s

<b>R-11</b>	<b>23.7</b>
<b>R-12</b>	<b>-29.8</b>
<b>R-22</b>	<b>-40.8</b>
<b>R-502</b> (R-115/22)	<b>-45.3</b>

*ozone protection*

**HFCs & HCFC**

**3<sup>rd</sup> Generation**

1990 – 2010s

<b>R-123</b> (HCFC)	<b>27.8</b>
<b>R-134a</b>	<b>-26.1</b>
<b>R-407C</b>	<b>-43.6</b>
(R-32/125/134a)	
<b>R-410A</b>	<b>-51.4</b>
(R-32/125)	
<b>R-404A</b>	<b>-45.7</b>
(R-125/143a/134a)	

*global warming mitigation*

**HFOs (Hydrofluoroolefins)**

**4<sup>th</sup> Generation**

2010s –

<b>R-1336mzz(Z)</b>	<b>33.4</b>
<b>R-1233zd(E)</b>	<b>18.3</b>
<b>R-1224yd(Z)</b>	<b>14.6</b>
<b>R-1234ze(E)</b>	<b>-19.0</b>
<b>R-1234yf</b>	<b>-29.5</b>

**GWP ≤ 2**

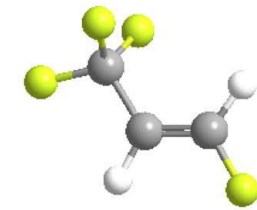
# Application of refrigerants

<span style="color: blue;">■</span>	No flame propagation
<span style="color: orange;">■</span>	Lower flammability
<span style="color: red;">■</span>	Higher flammability

## Natural fluids

H <sub>2</sub> O	100.0	R-717	-33.3	R-600a	-11.7
CO <sub>2</sub>	-78.4			R-290	-42.1
air	-194.2			R-1270	-47.7

Ammonia ← Normal boiling point (°C)



HFO-1234ze(E)

— # of fluorine atoms  
— # of hydrogen atoms +1  
— # of carbon atoms -1  
— # C=C double bounds

## Fluorinated fluids

**Whatever worked**

**1<sup>st</sup> Generation**  
1830 – 1930

*safety & durability* →

Water chillers (centrifugal)

Domestic refrigeration

Air conditioners

Industrial refrigeration

### CFCs & HCFCs

**2<sup>nd</sup> Generation**  
1931 – 1990s

R-11	23.7
R-12	-29.8
R-22	-40.8
R-502 (R-115/22)	-45.3

*ozone protection* →

### HFCs & HCFC

**3<sup>rd</sup> Generation**  
1990 – 2010s

R-123 (HCFC)	27.8
R-134a	-26.1
R-407C (R-32/125/134a)	-43.6
R-410A (R-32/125)	-51.4
R-404A (R-125/143a/134a)	-45.7

*global warming mitigation* →

### HFOs (Hydrofluoroolefins)

**4<sup>th</sup> Generation**  
2010s –

R-1336mzz(Z)	33.4	} <b>GWP ≤ 2</b>
R-1233zd(E)	18.3	
R-1224yd(Z)	14.6	
R-1234ze(E)	-19.0	
R-1234yf	-29.5	
R-32	-51.7	
R-32/HFC/HFO		} <b>GWP = 677</b>
R-32/HFC/HFO		

# NIST search for low-GWP fluids (2012 – 2017)

**Objective:** Identify molecules that might be good replacements for R-410A and R-22

Air-conditioning and refrigeration applications

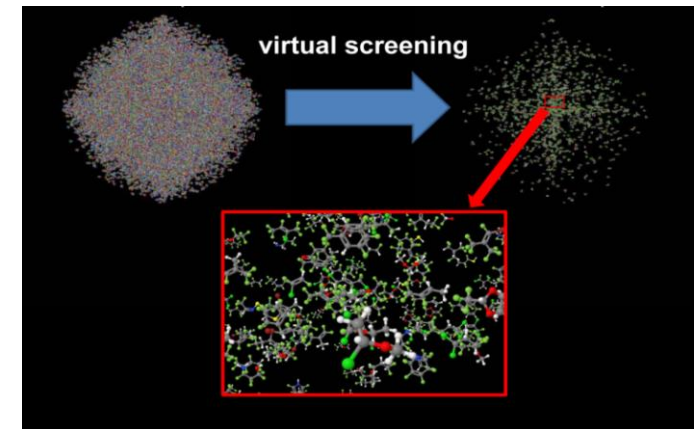
- positive displacement compressors
- forced-convection air-to-refrigerant heat exchangers

**Approach:** Perform screening using comprehensive database

(PubChem lists over 60 million unique chemical structures)

**Important attributes/filters:**

- Performance: COP, volumetric capacity ( $Q_{vol}$ )
- Environmental: ODP, GWP
- Safety: toxicity, flammability
- Materials: stability, compatibility (lubricant, seals, metals, etc.)
- Cost



# NIST search for low-GWP fluids (cont.)

## PubChem database

- Component atoms: C, H, N, O, S, F, Cl, Br
- Maximum number of atoms: 18
- $GWP_{100} < 1000$
- Critical temperature:  $46\text{ °C} < T_{crit} < 146\text{ °C}$
- Toxicity (MSDS, RCL, TLV, =CF<sub>2</sub>)
- Stability
- Volumetric capacity  $> 0.33 Q_{vol,R-410A}$   
(Basic cycle simulations)

Evaluated manually

Molecule count

60 000 000

184 000

138

21

15 - at least mildly flammable  
6 - unknown hazards

Nonmetallic					
				H	
B	C	N	O	F	Noble gases
	Si	P	S	Cl	
		As	Se	Br	
Metals			Te	I	
				At	

- 21 (primary interest) + 3 (commercial interest) + 3 (low  $T_{crit}$ ) → 27 fluids
- New toxicity data on R-1132a; 27 + 1 (low  $T_{crit}$ ) → 28 fluids

Performed detailed simulations with optimized heat exchangers for 24 fluids

Air conditioning (McLinden et al., 2017)

Refrigeration and heating (Domanski et al., 2017)



# 28 candidate fluids

Basic cycle; air conditioning;  
optimized heat exchangers

## 21 fluids of primary interest:

$$46\text{ °C} < T_{cr} < 146\text{ °C}$$

$$Q_{vol} > 0.33 Q_{vol,R-410A}$$

15 - at least mildly flammable

6 - unknown hazards

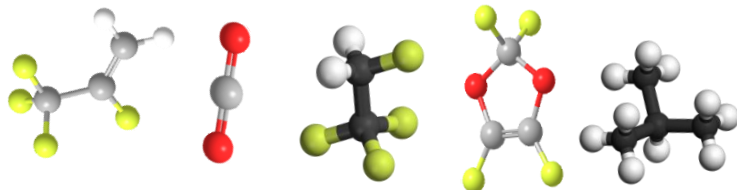
## 7 additional fluids:

- subcritical operation; 3 fluids

[R-134, R-1123, R-1225ye(Z)]

- supercritical or near-critical operation; 4 fluids

[R-170, R-41, R-1132a, R-744]



### Hydrocarbons and dimethylether

ethane	CH <sub>3</sub> -CH <sub>3</sub>	● R-170
propene (propylene)	CH <sub>2</sub> =CH-CH <sub>3</sub>	R-1270
propane	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	R-290
methoxymethane (dimethylether)	CH <sub>3</sub> -O-CH <sub>3</sub>	R-E170
cyclopropane	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	R-C270

### Fluorinated alkanes (HFCs)

fluoromethane	CH <sub>3</sub> F	● R-41
difluoromethane	CH <sub>2</sub> F <sub>2</sub>	R-32
fluoroethane	CH <sub>2</sub> F-CH <sub>3</sub>	R-161
1,1-difluoroethane	CHF <sub>2</sub> -CH <sub>3</sub>	R-152a
1,1,2,2-tetrafluoroethane	CHF <sub>2</sub> -CHF <sub>2</sub>	● R-134

### Fluorinated alkenes (HFOs) and alkynes

1-1-difluoroethene	CF <sub>2</sub> =CH <sub>2</sub>	● R-1132a
fluoroethene	CHF=CH <sub>2</sub>	R-1141
1,1,2-trifluoroethene	CF <sub>2</sub> =CHF	● R-1123
3,3,3-trifluoroprop-1-yne	CF <sub>3</sub> -C≡CH	n.a.
2,3,3,3-tetrafluoroprop-1-ene	CH <sub>2</sub> =CF-CF <sub>3</sub>	R-1234yf
(E)-1,2-difluoroethene	CHF=CHF	R-1132(E)
3,3,3-trifluoroprop-1-ene	CH <sub>2</sub> =CH-CF <sub>3</sub>	R-1243zf
1,2-difluoroprop-1-ene‡	CHF=CF-CH <sub>3</sub>	R-1252ye‡
(E)-1,3,3,3-tetrafluoroprop-1-ene	CHF=CH-CF <sub>3</sub>	R-1234ze(E)
(Z)-1,2,3,3,3-pentafluoro-1-propene	CHF=CF-CF <sub>3</sub>	● R-1225ye(Z)
1-fluoroprop-1-ene‡	CHF=CH-CH <sub>3</sub>	R-1261ze‡

### Fluorinated oxygenates

trifluoro(methoxy)methane	CF <sub>3</sub> -O-CH <sub>3</sub>	R-E143a
2,2,4,5-tetrafluoro-1,3-dioxole	-O-CF <sub>2</sub> -O-CF=CF-	n.a.

### Fluorinated nitrogen and sulfur compounds

N,N,1,1-tetrafluormethaneamine	CHF <sub>2</sub> -NF <sub>2</sub>	n.a.
difluoromethanethiol	CHF <sub>2</sub> -SH	n.a.
trifluoromethanethiol	CF <sub>3</sub> -SH	n.a.

### Inorganic compounds

carbon dioxide	CO <sub>2</sub>	● R-744
ammonia	NH <sub>3</sub>	R-717

GWP

$T_{cr}$   
(K)

$\frac{COP}{COP_{R410A}}$

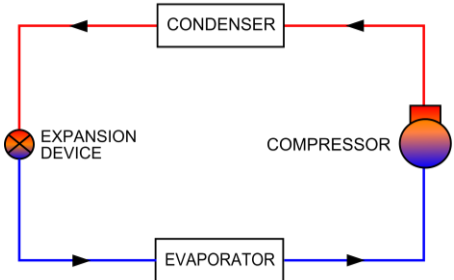
$\frac{Q_{vol}}{Q_{vol,R410A}}$

6	305.3		
2	364.2	1.033	0.689
3	369.9	1.014	0.571
1	400.4	0.996	0.392
86	398.3	1.018	0.472
116	317.3		
677	351.3	1.038	1.084
4	375.3	1.026	0.601
138	386.4	0.981	0.399
1120	391.8	0.967	0.348
<1	324.2		
<1	327.1	0.968	1.346
3	343.0	0.956	1.054
1.4	363.3	0.988	0.545
<1	367.9	0.954	0.414
1	370.5	1.016	0.591
<1	376.9	0.964	0.372
2	380.7	0.973	0.355
<1	382.5	0.939	0.320
<1	384.0	0.922	0.273
1	390.7	0.975	0.353
523	377.9	0.957	0.366
1	400.0	0.936	0.337
20	341.6	0.965	0.807
1	373.0	1.010	0.582
1	376.2	0.977	0.418
1.00	304.1		
<1	405.4	1.055	0.746

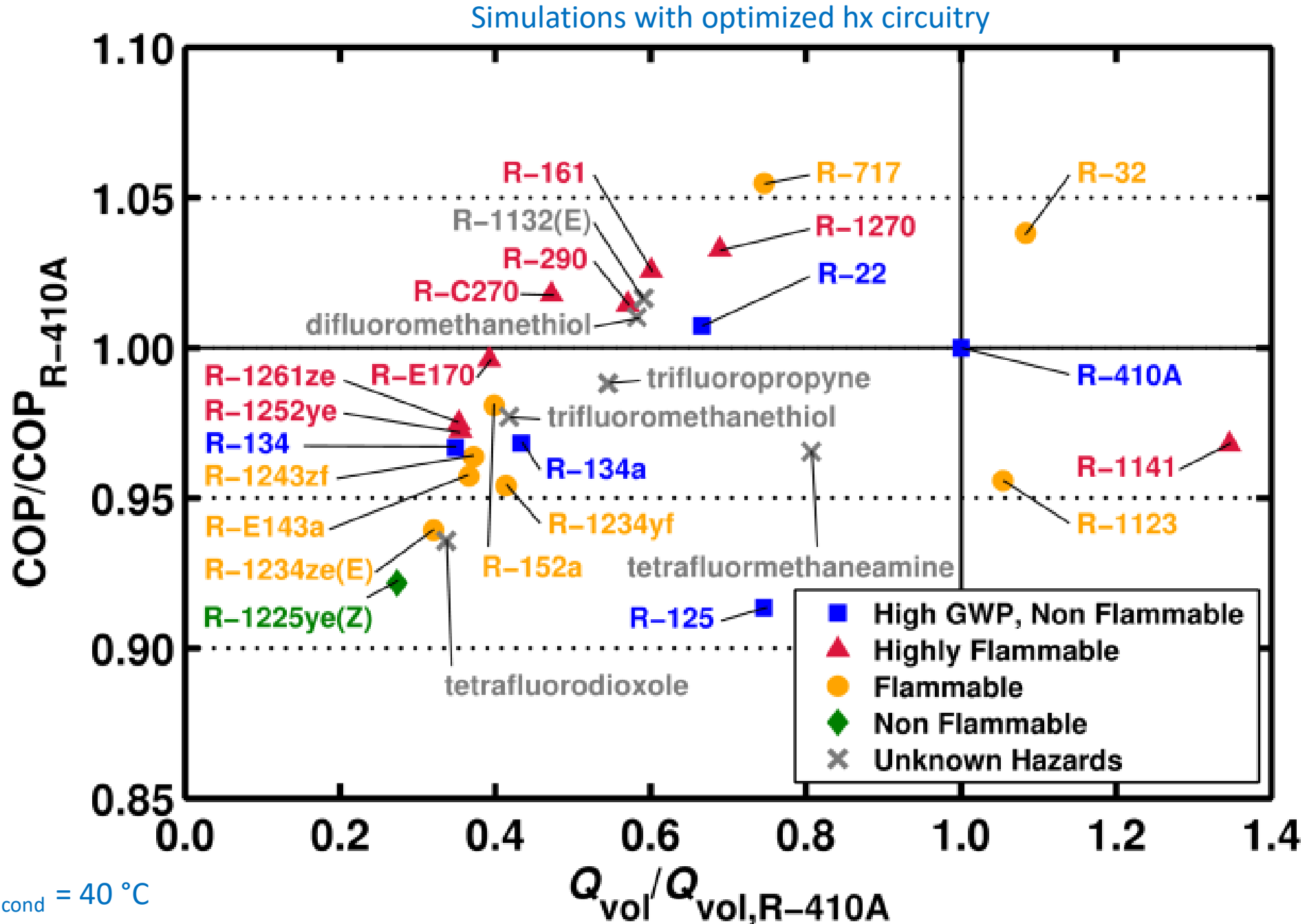
# COP and $Q_{vol}$

## Air conditioning

Basic cycle

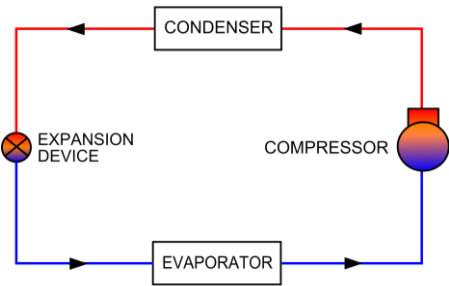


R-410A:  $T_{sat, evap} = 10\text{ }^{\circ}\text{C}$ ;  $T_{sat, cond} = 40\text{ }^{\circ}\text{C}$

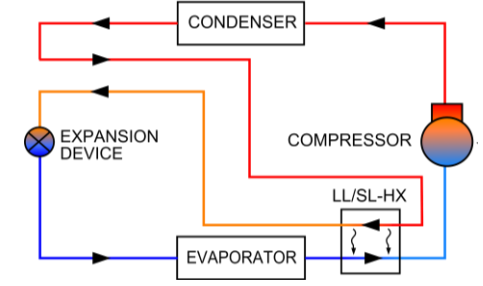


# COP and $Q_{vol}$ ; air conditioning

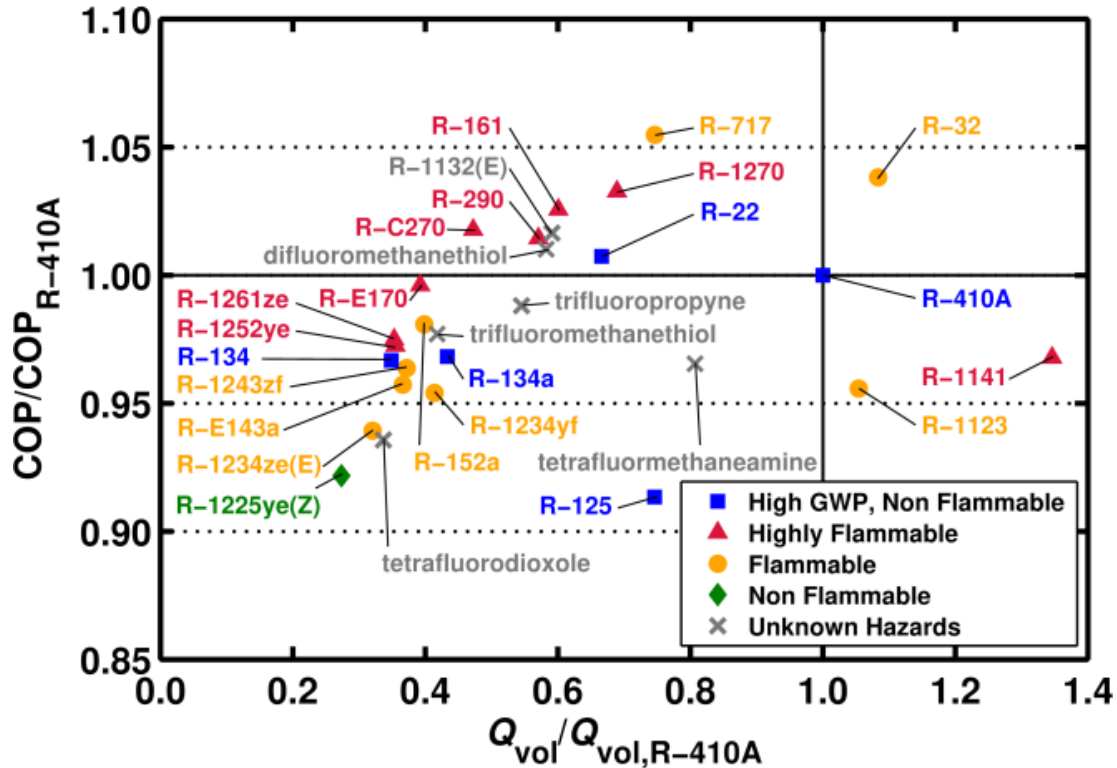
Basic cycle



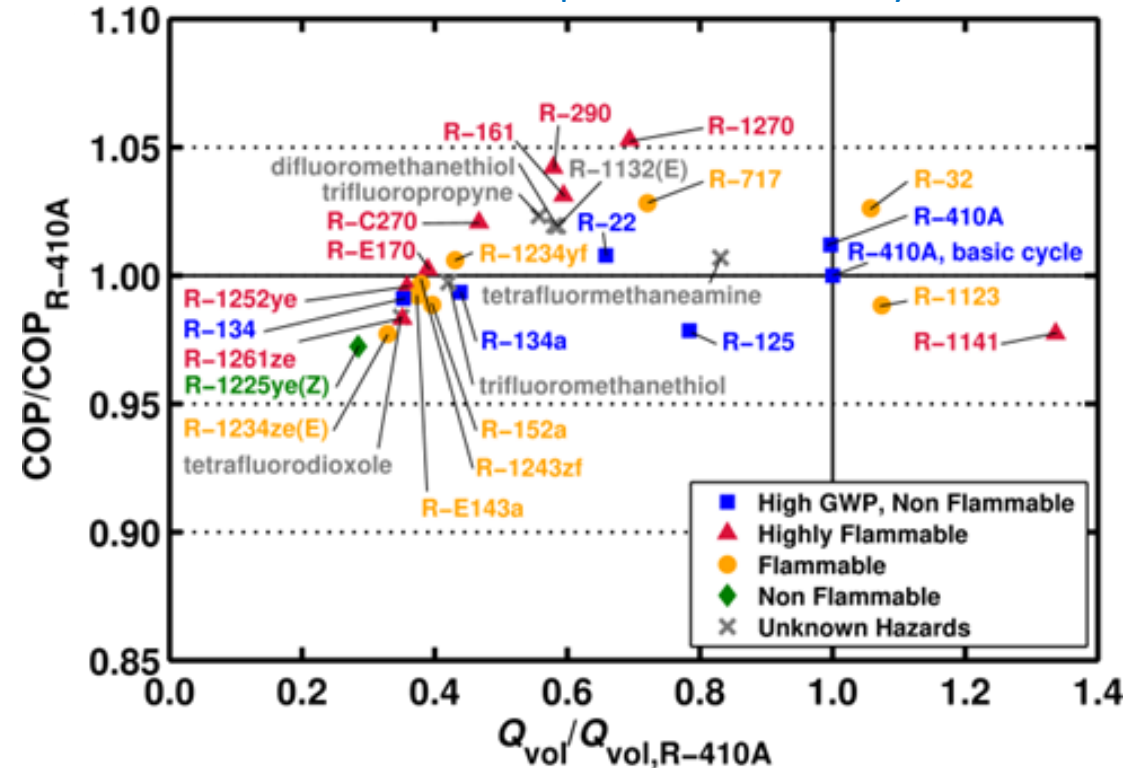
Cycle with LL/SL-HX



Simulations with optimized hx circuitry

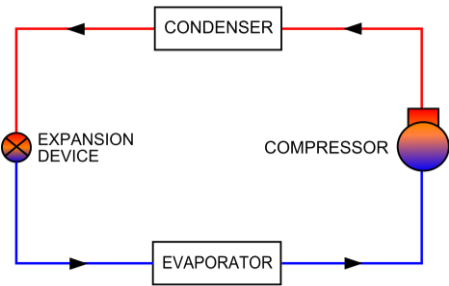


Simulations with optimized hx circuitry

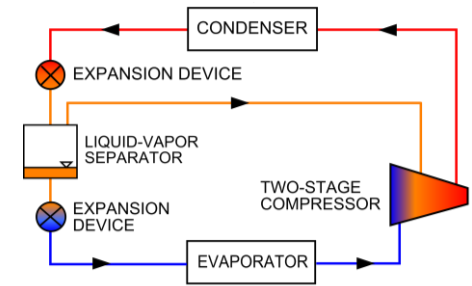


# COP and $Q_{vol}$ ; air conditioning

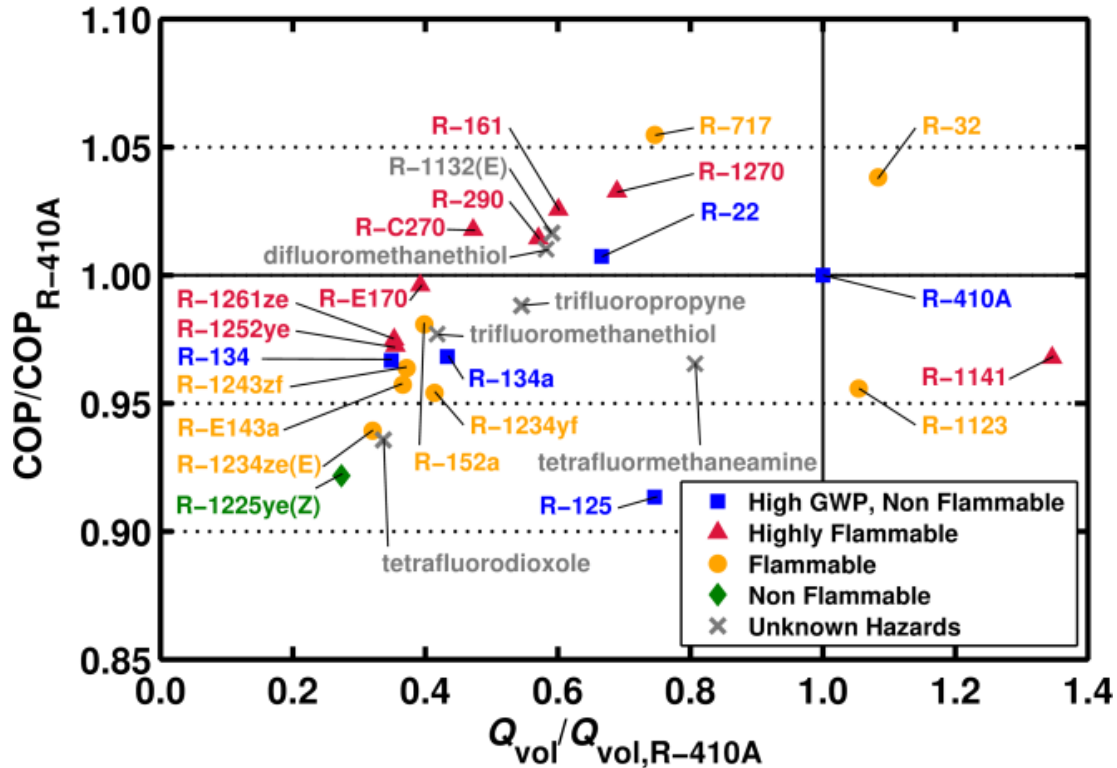
Basic cycle



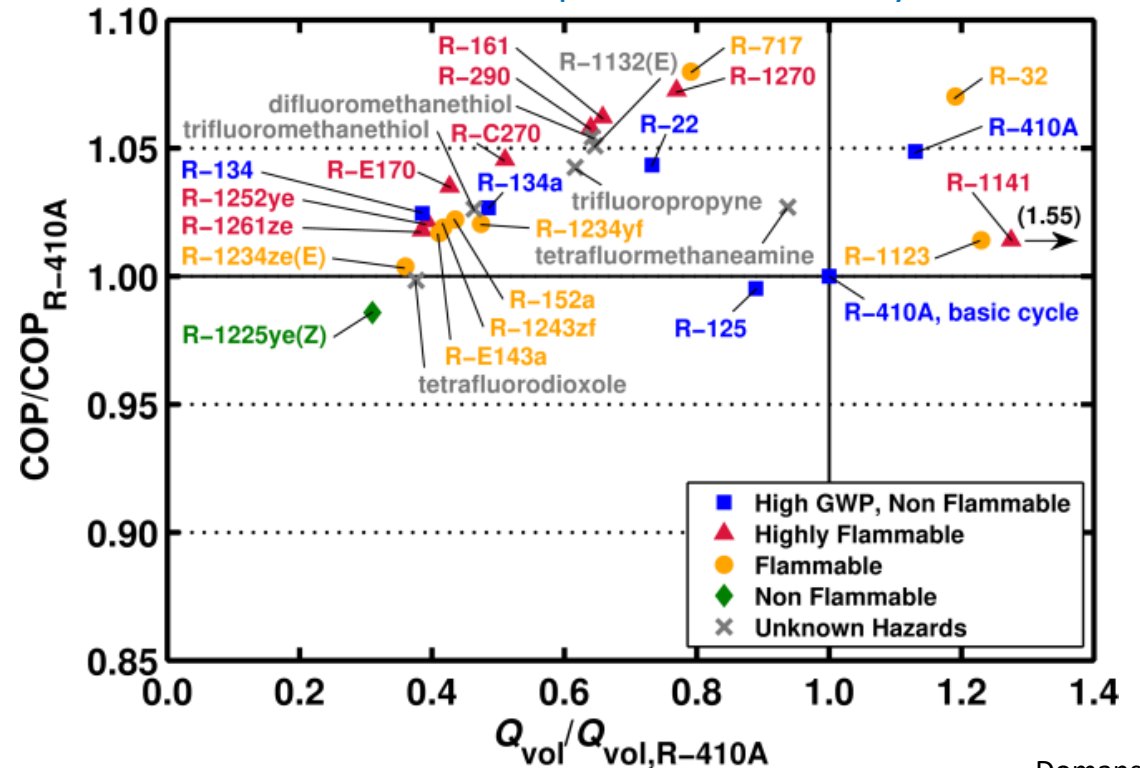
Economizer cycle



Simulations with optimized hx circuitry

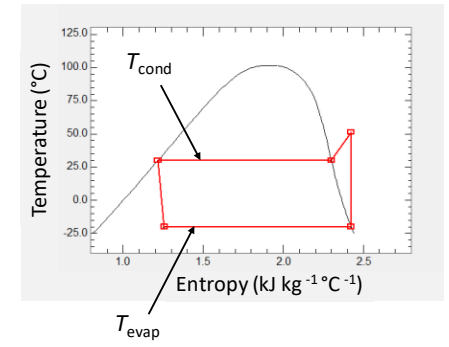
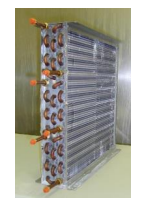
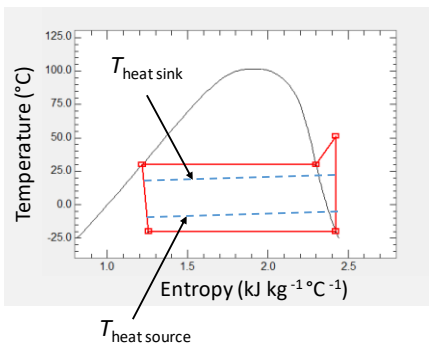
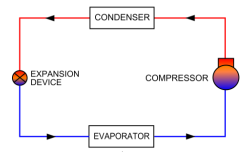


Simulations with optimized hx circuitry

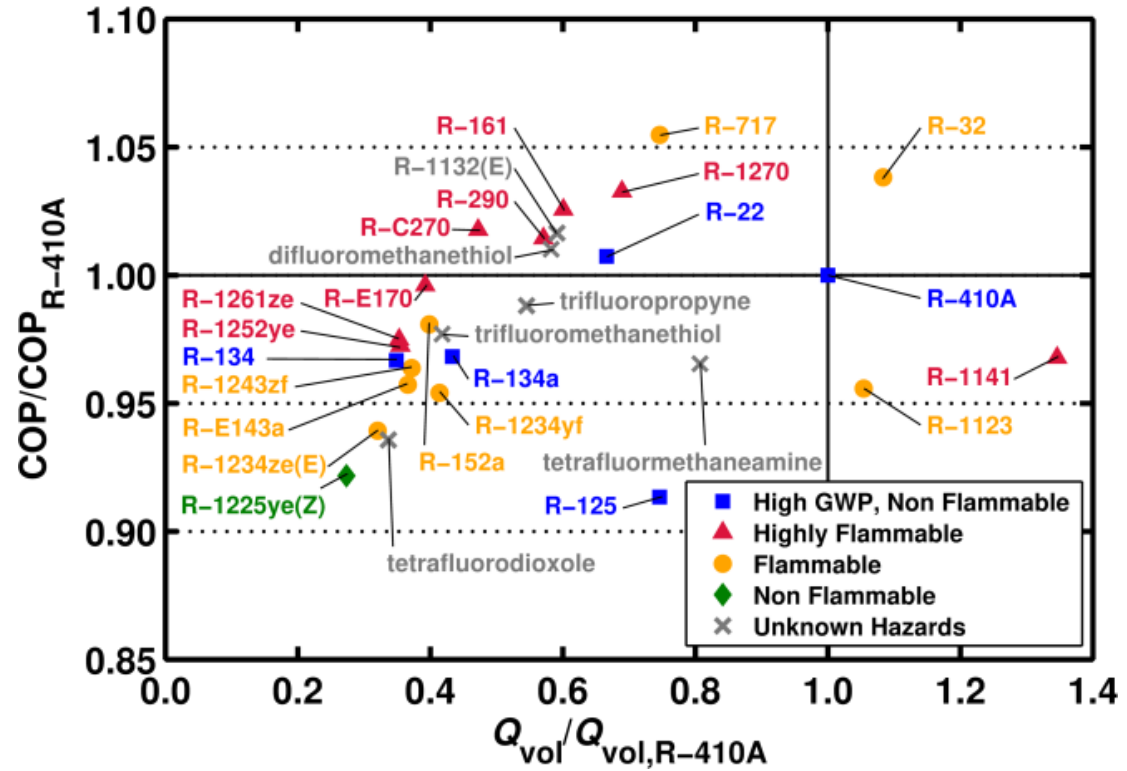


# COP and $Q_{vol}$ ; air conditioning

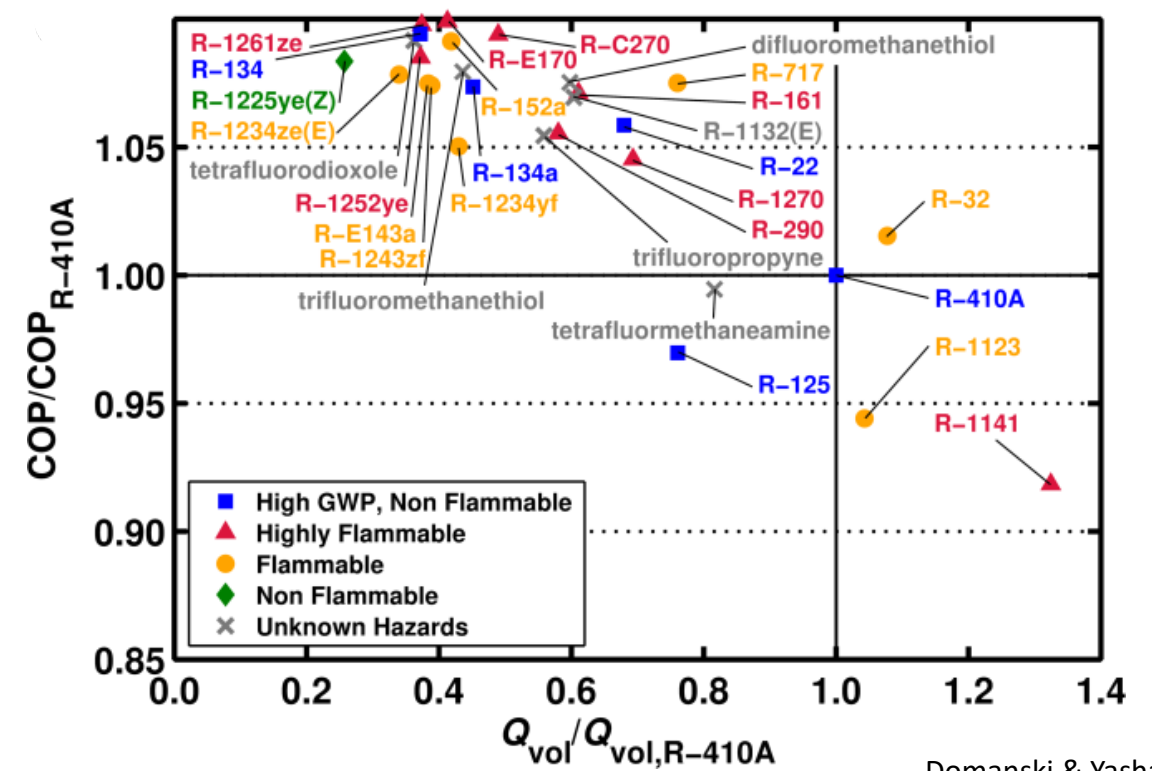
## Basic cycle



## Simulations with optimized hx circuitry



## Ideal cycle simulations

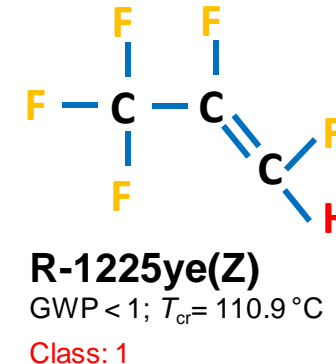
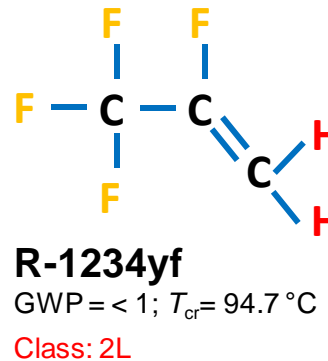
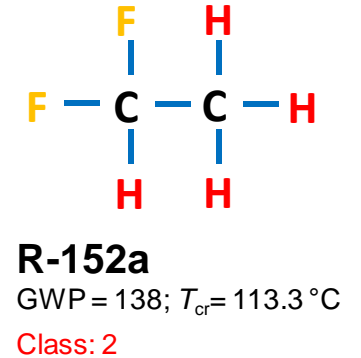
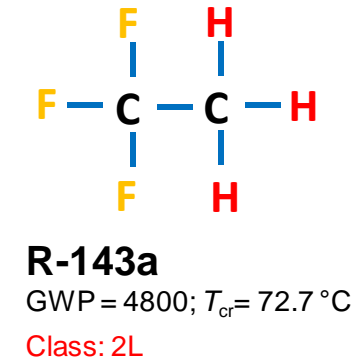
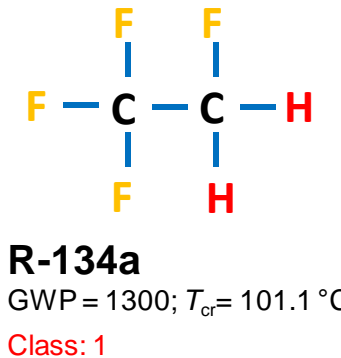
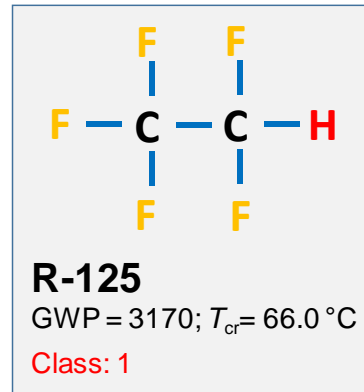


# Why there are no low-GWP fluids that are nonflammable and have high $Q_{vol}$ ?

## Trade-off between low GWP and flammability

GWP can be lowered by:

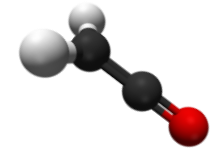
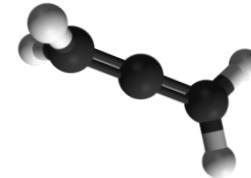
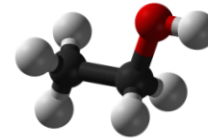
- **Replacing F or Cl with H.**  
It shortens the atmospheric life but leads to flammability.
- **Adding a C=C double bond.**  
Contributes to the reaction with oxygen.



# Is it all ?

## Why some other fluids did not make it ?

- Peroxides [-O-O-]: unstable, one dropped
- Alkynes [-C≡C-]: ≡ generally less stable than =, one retained
- Ketenes [ $\text{>C=C=O}$ ]: generally very reactive, three dropped
- Allenes [ $\text{>C=C=C<}$ ]: very reactive
- Alcohols [-OH]: high  $T_{cr}$
- = CF<sub>2</sub> group: high reactivity often associated with toxic effects; some exceptions
- = OF group: not stable, may lead to hydrofluoric acid



# How reliable was the screening process?

Did we miss good fluids?

- PubChem database is complete (?)

PubChem lists 30 three-carbon HFOs out of 31 possible. It is unlikely that the missing molecule would possess significantly different properties than those already listed.

- Component atoms: only C, H, N, O, S, F, Cl, Br (?) Maximum number of atoms: 18 (?)

Additional screening of a different database with 2000 industrial fluids yielded small molecules with the above eight elements only.

- $GWP_{100} < 1000$  (?)

- Critical temperature:  $46\text{ °C} < T_{cr} < 146\text{ °C}$  (?)

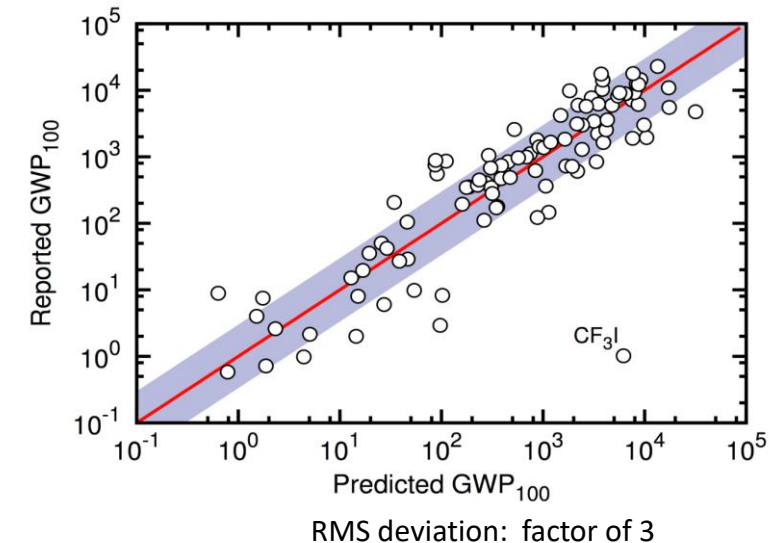
Estimated with standard deviation of 16.5 K (4.5 %).  $T_{cr, R-410A} = 71.3\text{ °C}$

- Stability and toxicity (?)

Published data, which may be erroneous. E.g., toxicity of R-1132a

Unstable fluid may be stabilized and used in the system. E.g., R-1123, R-1311 (CF<sub>3</sub>I)

Nonmetallic					
				H	
B	C	N	O	F	Noble gases
	Si	P	S	Cl	
		As	Se	Br	
			Te	I	
				At	





# CF<sub>3</sub>I - ASHRAE Standard 34 proposed addenda 't' and 's'

## Addendum 't'

R-13I1

Chemical name = trifluoroiodomethane

Chemical formula **CF<sub>3</sub>I**

OEL = 500 ppm v/v

Safety Group = A1

GPW = 0.4

## Addendum 's'

R-466A

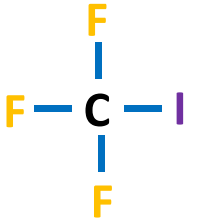
Composition (mass %) = R-32/125/13I1  
(49/11.5/39.5)

OEL = 860 ppm v/v

Safety Group = A1

GWP = 733

- ODP = 0.008
- Good thermodynamic properties
- Fire suppression properties
- **Toxicity** of **CF<sub>3</sub>I** was studied in the 1990s (McCain and Macko, 1999). **CF<sub>3</sub>I** is SNAP-approved fire suppressing agent replacing halon 1301 (total flooding) and halon 1211 (streaming), with restrictions to unoccupied and non-residential uses, respectively.
- R-1234yf/**CF<sub>3</sub>I** (70/30) was studied in the 2000s for automotive ACs, within the Cooperative Research Program CRP150 (SAE). Dropped over concerns related to the **non-zero ODP** and **reactivity** of **CF<sub>3</sub>I**. (Brown, 2012)



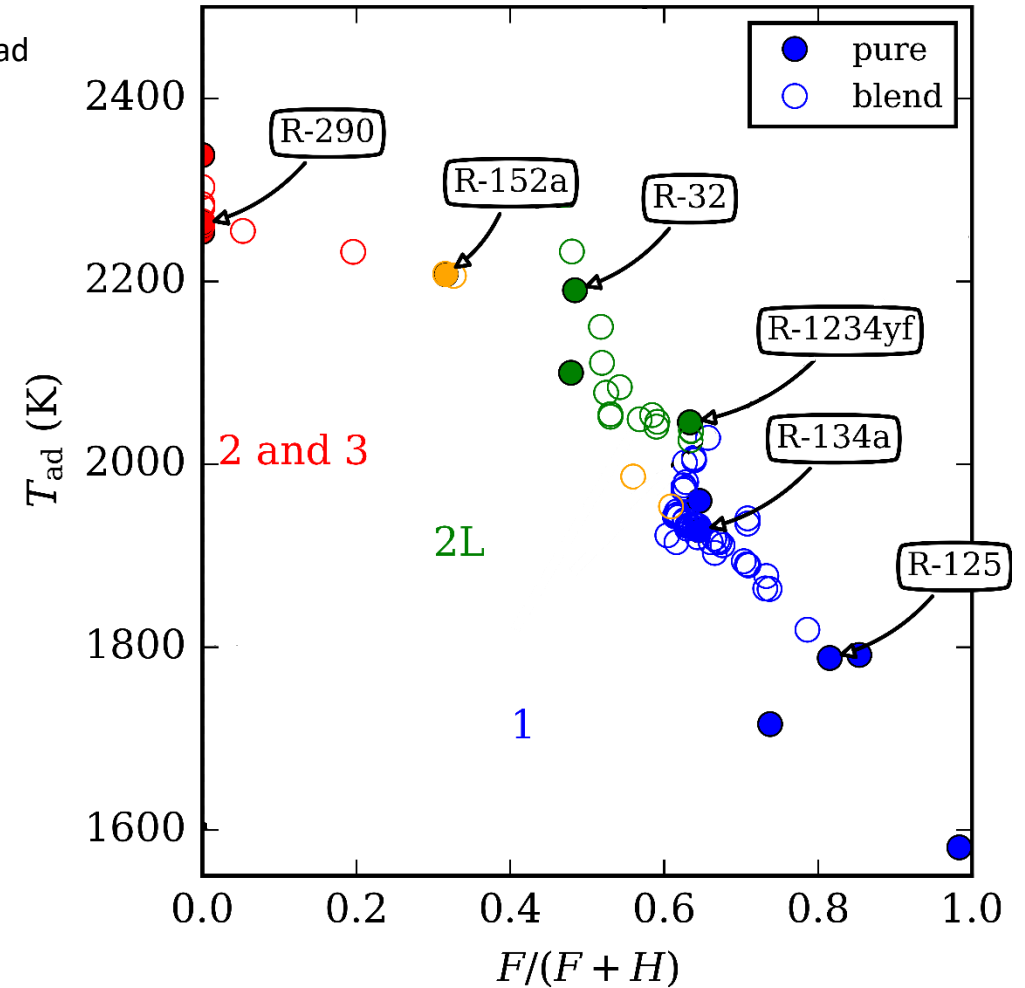
**CF<sub>3</sub>I is expected to see future application as a component of nonflammable blends.**

**Application challenge: reactivity**

# Normalized Flammability Index $\bar{\Pi}$

## Novel empirical flammability estimate

- Uses  $F/(F+H)$  in reactants and adiabatic flame temperature  $T_{ad}$
- Effects of humidity are included
- Based on the ASHRAE Std. 34 experimental database of refrigerant flammability



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## Flammability index

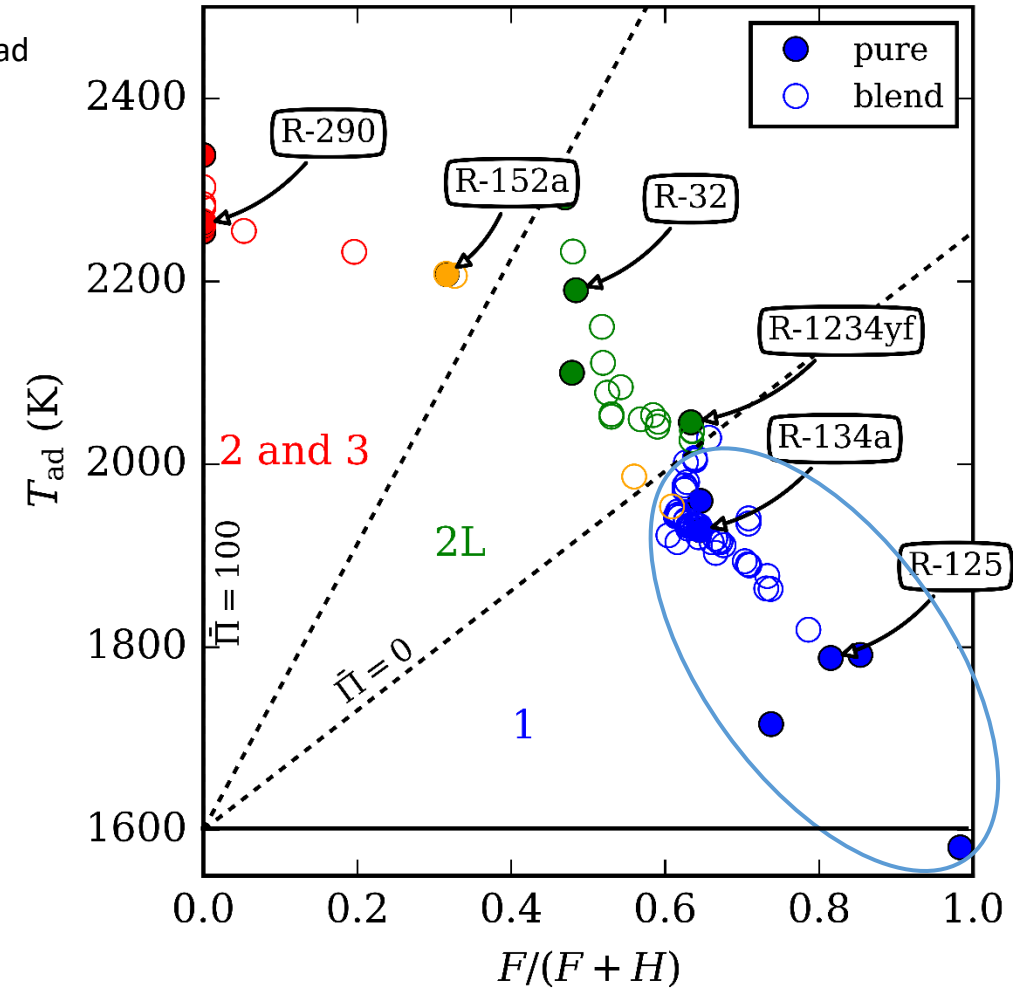
$$\Pi = \arctan2\left(\frac{T_{ad} - 1600}{2500 - 1600}, \frac{F}{F+H}\right) \cdot \left(\frac{180}{\pi}\right)$$

$\Pi_{1,2L} = 36$ ; flammability boundary between classes 1 and 2L

## Normalized flammability index

$$\bar{\Pi} = \frac{\Pi - \Pi_{1,2L}}{90 - \Pi_{1,2L}} \cdot 100$$

$\bar{\Pi} < 0$  No flame propagation



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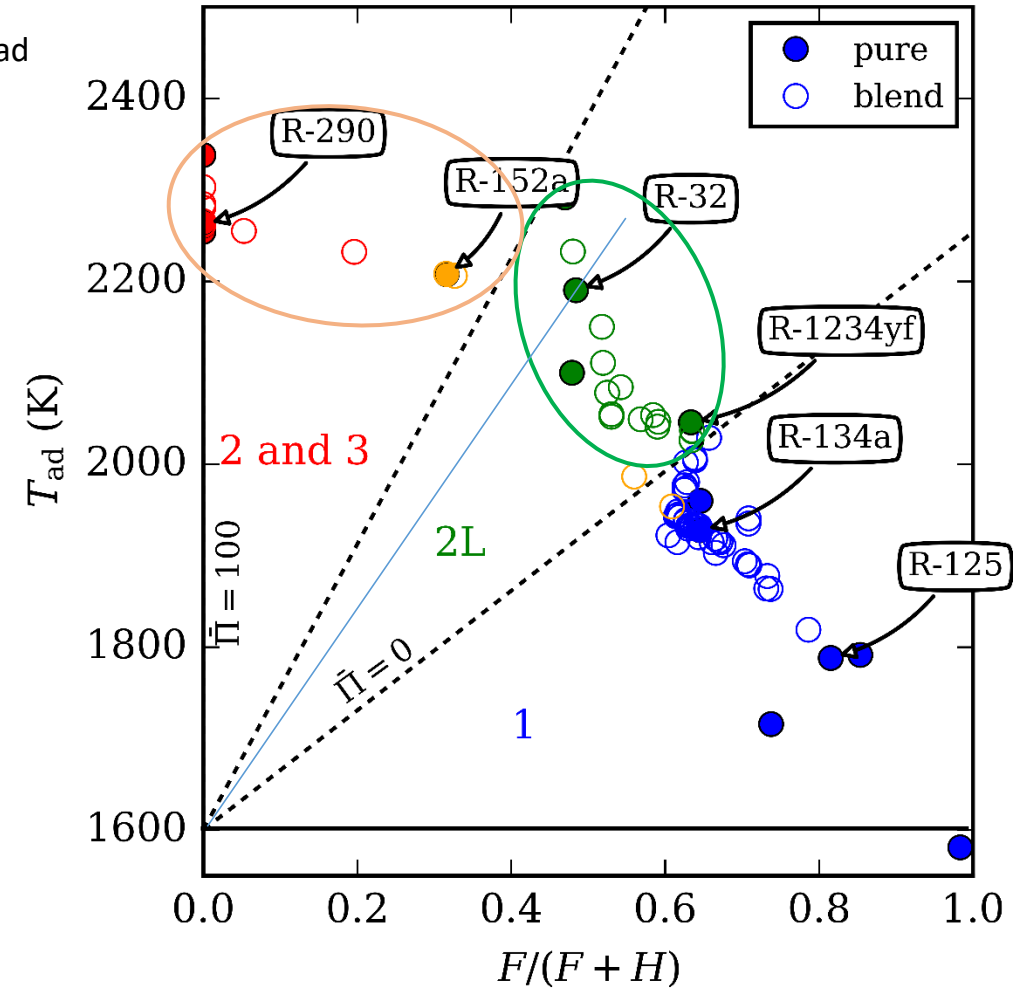
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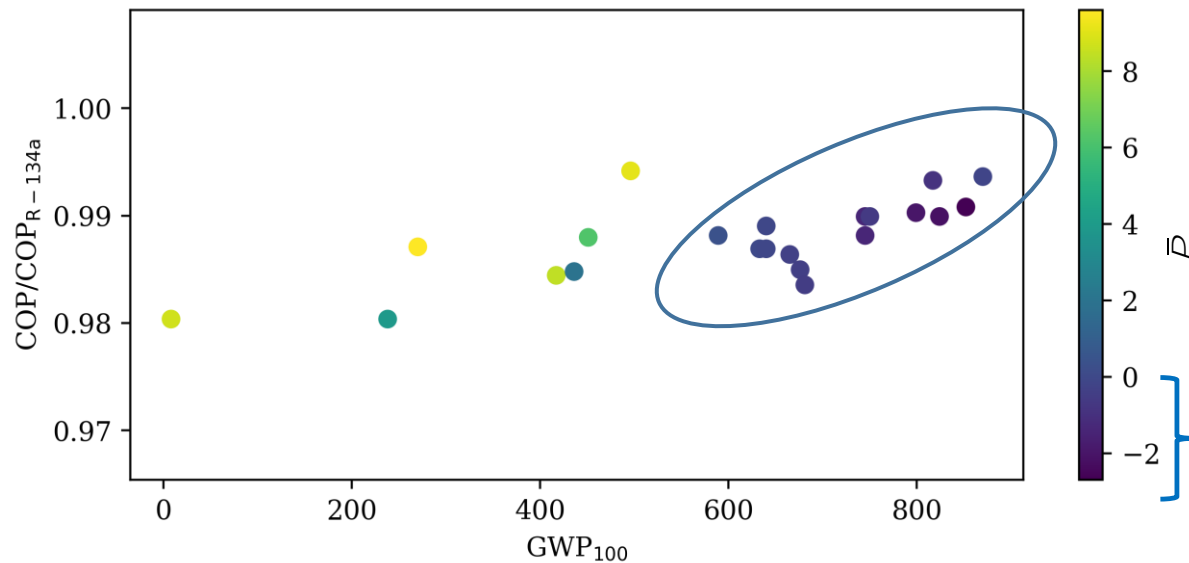
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# Search for nonflammable replacements for R-134a

- Comprehensive evaluation binary, ternary and four-component blends (13 compounds considered)
- Selection criteria:
  - Minimize flammability
  - Minimize GWP
  - Maximize COP
  - Match volumetric capacity to that of R-134a



Blend components	Composition (molar)	GWP	COP		$\bar{P}$
			$\frac{COP}{COP_{R-134a}}$	$\frac{Q}{Q_{R-134a}}$	
R-152a/1234yf	0.08/0.92	8	0.980	0.957	7.7
R-134a/1234yf	0.20/0.80	238	0.980	0.996	2.8
R-134a/152a/1234yf	0.20/0.16/0.64	270	0.987	0.984	8.7
R-152a/1234yf/134	0.16/0.48/0.36	417	0.984	0.900	7.5
R-134a/1234yf	0.36/0.64	436	0.985	1.018	1.0
R-134a/1234yf/1243zf	0.36/0.44/0.20	451	0.988	1.004	5.2
R-134a/152a/1234yf	0.36/0.20/0.44	496	0.994	0.994	8.3
R-134a/1234yf	0.44/0.56	537	0.987	1.025	-0.1
R-134a/1234yf	0.468/0.532 <sup>†</sup>	573	0.988	1.027	-0.4
R-134a/1234yf/134	0.48/0.48/0.04	633	0.987	0.975	-1.1
R-134a/1234yf/1234ze(E)	0.52/0.32/0.16	640	0.987	0.989	-1.2
R-134a/1234yf	0.52/0.48	640	0.989	1.029	-1.2
R-134a/1234yf/134	0.4/0.44/0.16	665	0.986	0.958	-1.3
R-134a/125/1234yf	0.44/0.04/0.52	676	0.985	1.049	-1.5
R-134a/227ea/1234yf	0.40/0.04/0.56	681	0.984	1.007	-1.5
R-134a/1234ze(E)	0.60/0.40	745	0.988	0.908	-2.4
R-134a/1234yf	0.60/0.40	745	0.990	1.031	-2.4
R-134a/1234ze(E)/1243zf	0.60/0.36/0.04	750	0.990	0.966	-1.5
R-134a/1234yf/1234ze(E)	0.64/0.2/0.16	799	0.990	0.986	-3.0
R-134a/152a/1234yf	0.64/0.04/0.32	817	0.993	1.023	-1.8
R-134a/1234yf/134	0.52/0.32/0.16	824	0.990	0.966	-3.2
R-134a/1234ze(E)	0.68/0.32	852	0.991	0.929	-3.7
R-134a/1234yf/1243zf	0.68/0.2/0.12	870	0.994	1.020	-1.1

<sup>†</sup> R-513A

# Low-GWP refrigerant options

<span style="color: blue;">■</span>	No flame propagation
<span style="color: orange;">■</span>	Lower flammability
<span style="color: red;">■</span>	Higher flammability

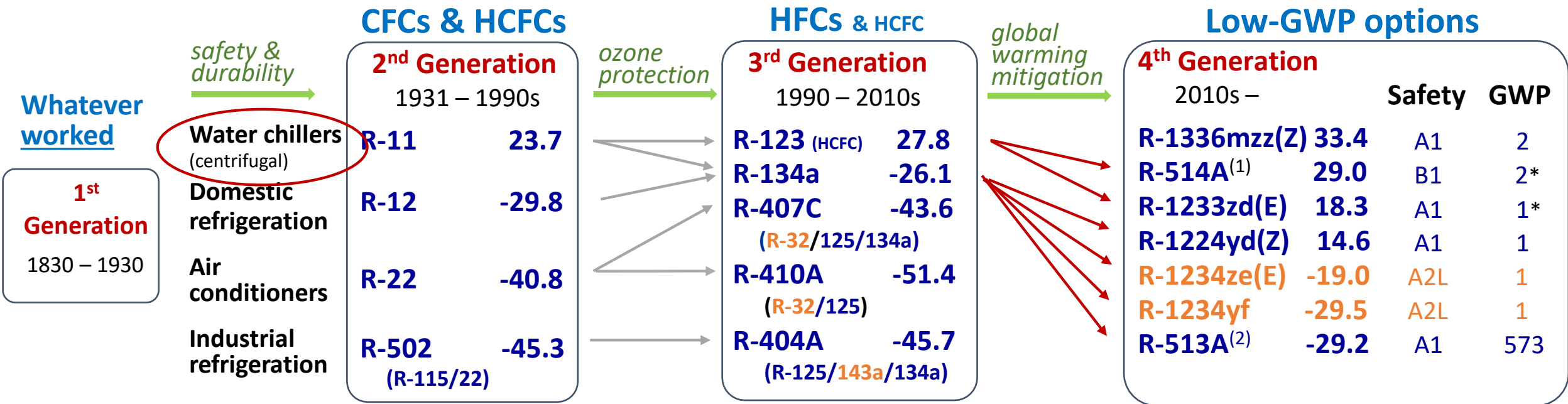
## Natural fluids

H <sub>2</sub> O	100.0	R-717	-33.3	R-600a	-11.7
CO <sub>2</sub>	-78.4			R-290	-42.1
air	-194.2			R-1270	-47.7

Ammonia (points to R-717)

Normal boiling point (°C)

## Fluorinated fluids



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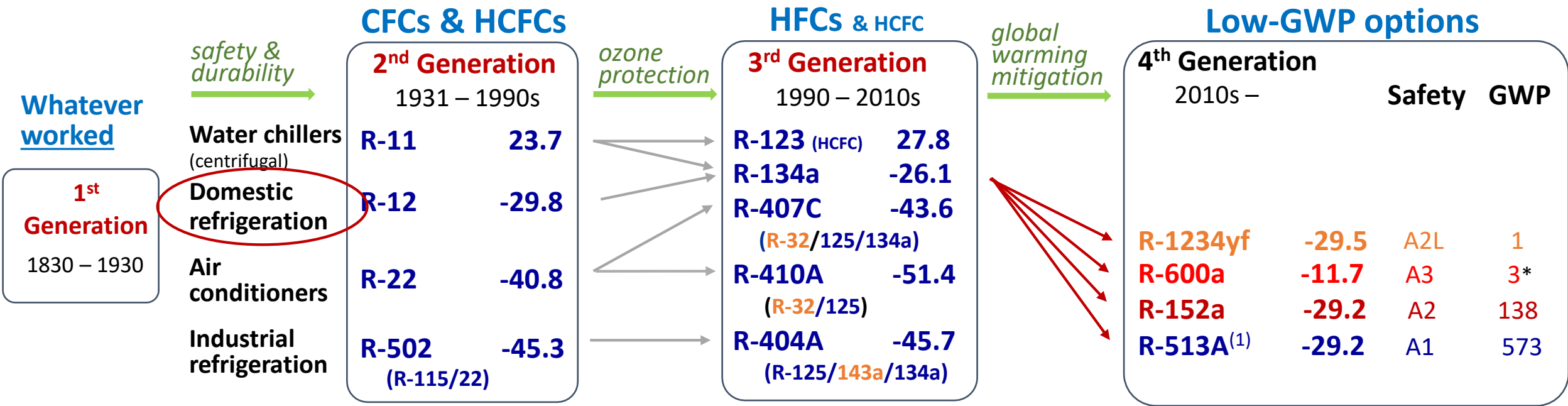
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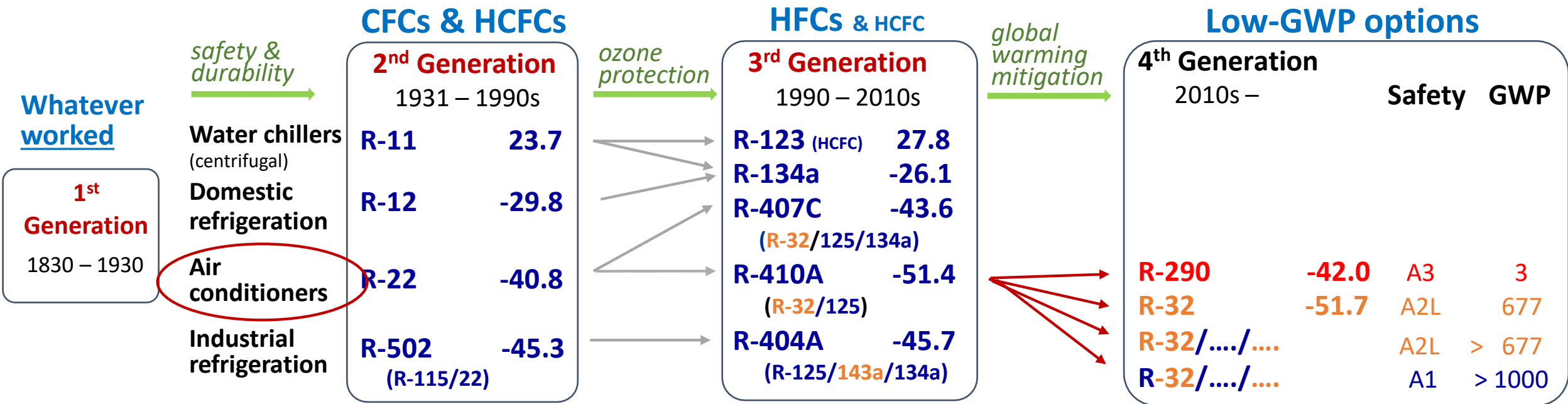
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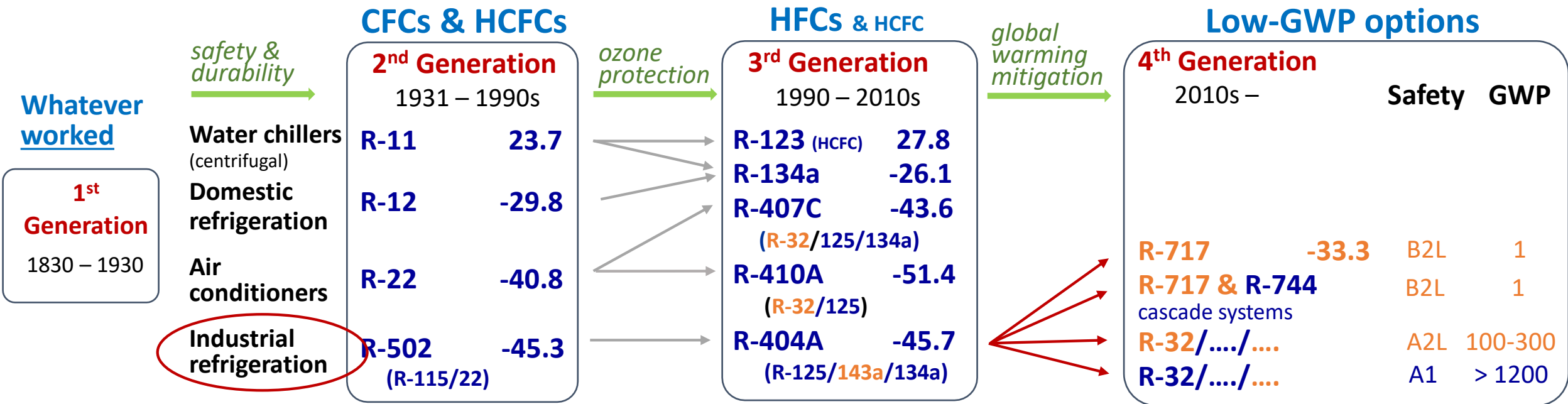
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# Cooling technologies

sorted by primary energy input

## Acceptance criteria

- Coefficient of Performance
- Environmental
- Safety
- Cost
- Reliability
- Serviceability
- Physical size, weight

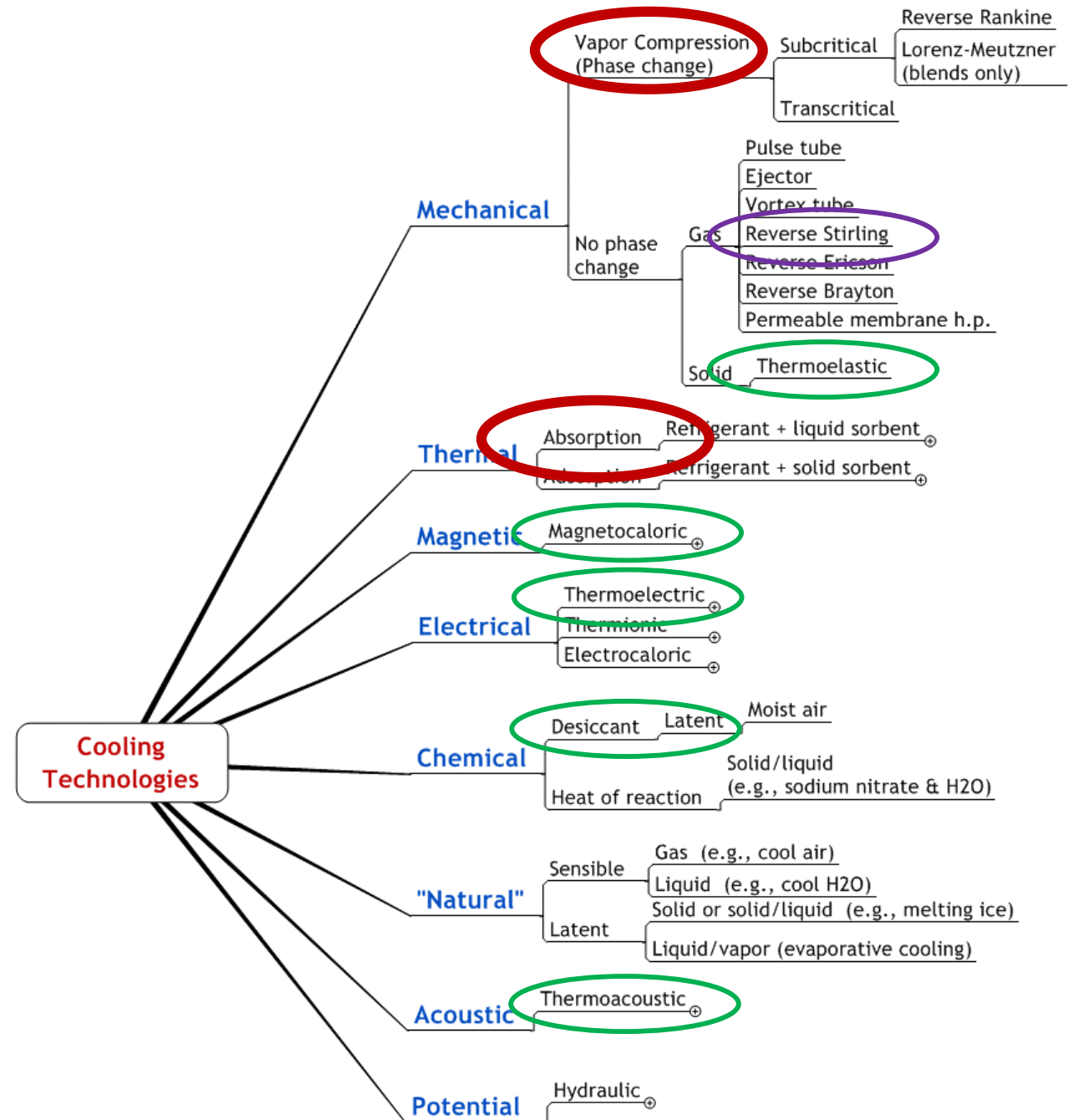
## Best prospects for competing with vapor compression



Space conditioning



Food refrigeration



# Concluding comments

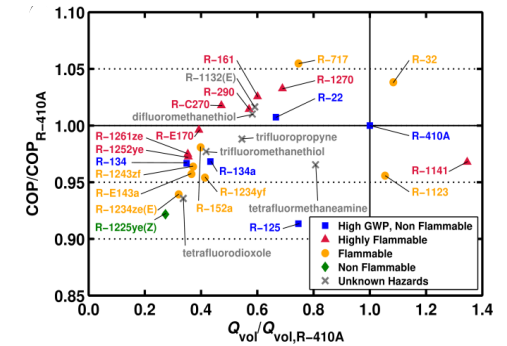
- Availability of low-GWP refrigerants varies between applications

- Good availability of low-pressure fluids (low GWP, nonflammable)
- No direct HFO replacement candidate for R-22 or R-410A  
Single-component medium- and high-pressure replacement fluids are at least mildly flammable

- Prospects for finding new viable refrigerants are minimal.

New equipment will have to be designed using the fluids we know already and their blends.

- Trade off between GWP ↓ and flammability ↑



# Concluding comments

## ○ Alternative cooling technologies?

Alternative technologies will gain entry in niche applications

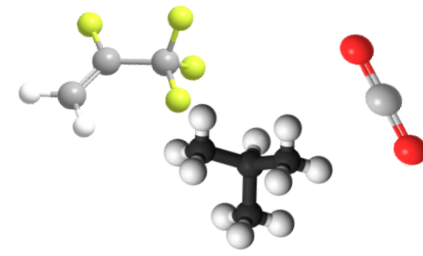
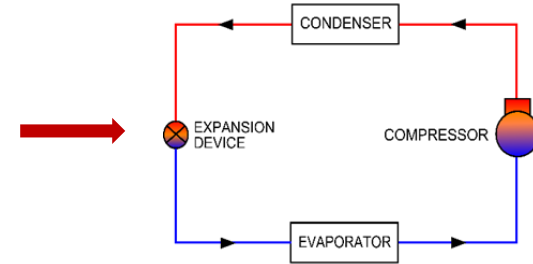
but

will need significant development effort and material breakthroughs to be competitive and enter the main stream.

Ice harvesting



Vapor compression



## ○ We will have to use refrigerants judiciously, which includes:

- Selection of refrigerant for each application recognizing environmental and safety considerations
- High-efficiency, leak-free equipment
- Improved refrigerant handling practices (equipment commissioning, servicing, and decommissioning).



**Thank you for your attention.**

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