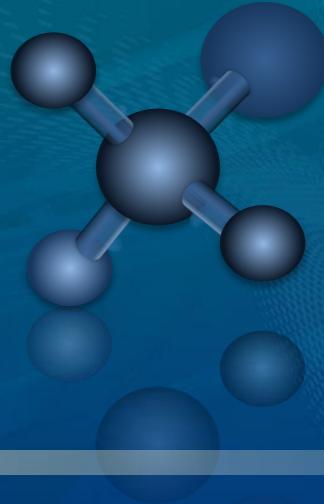


Transition to Low-GWP Refrigerants: Options and Tradeoffs



Piotr A. Domanski

Leader, HVAC&R Equipment Performance Group
Engineering Laboratory
National Institute of Standards and Technology
Gaithersburg, MD

Mark O. McLinden and Andrei Kazakov; NIST, Boulder, CO

J. Steven Brown; The Catholic University of America, Washington, DC
Jaehyeok Heo; Solar Thermal Laboratory, Daejeon, S. Korea
Janusz Wojtusiak; George Mason University, Fairfax, VA

Study sponsored by the DOE/BTP; Project Manager: Antonio Bouza

Florida International University, April 1, 2016

Outline

- **Background**
 - Introduction to vapor compression systems
 - Refrigerant selection
- **NIST study / search for low-GWP fluids**
 - Exploration of the thermodynamic space
 - Database screening
- **Conclusions**



Background

□ Refrigeration is used everywhere

Cryogenics, medicine and health products, air conditioning, food industry, etc.

Examples of health benefits:

- Mortality during hot days decreased in U.S. by 80 % (MIT study).
- Refrigeration and improved hygiene have reduced stomach cancer in U.S. by 90 % since 1930 (WHO study).

□ Use of refrigeration will increase (developing countries)

□ Refrigeration is implicated in the climate change

- Current refrigerants (HFCs) are greenhouse gases; **need for low-GWP refrigerants**
- Emissions of CO₂ from fossil fuel power plants; **need for high efficiency**

□ Phase-down of refrigerants with high GWP is imminent

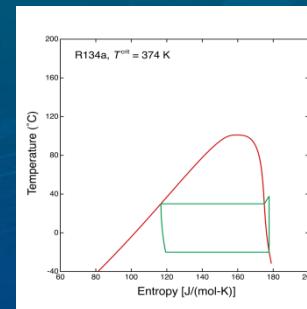
- North American proposal to Montreal Protocol calls for 85 % phase-down by 2035

Refrigerant selection criteria

What properties are important?

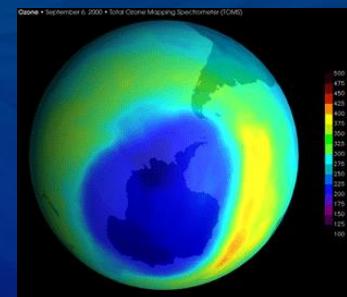
□ Performance; COP, capacity

- thermodynamic properties
- transport properties



□ Environmental

- global warming potential (GWP)
- ozone depletion potential (ODP)



□ Safety

- toxicity (acute and chronic)
- flammability

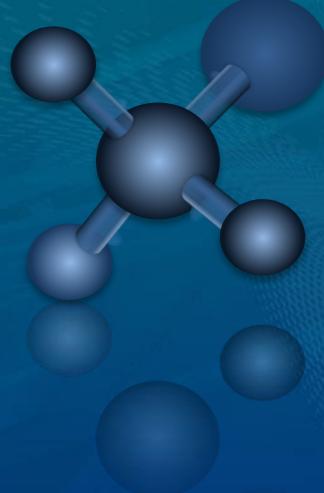


□ Materials

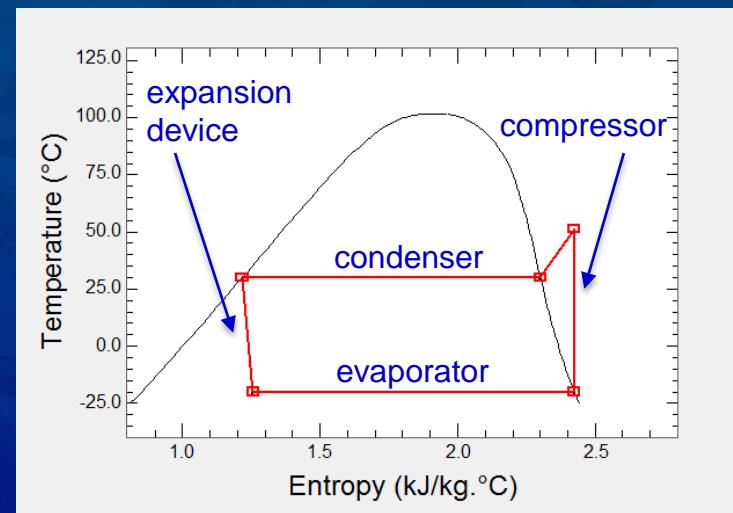
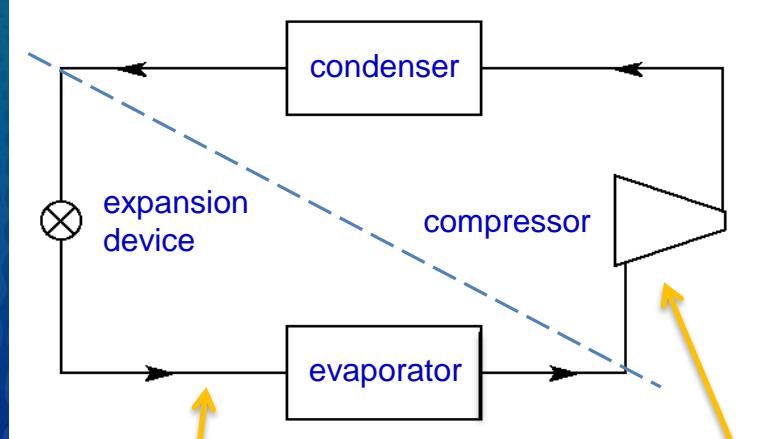
- stability (hydrolysis, polymerization, etc.)
- compatibility with metals, seals, etc.
- lubricant



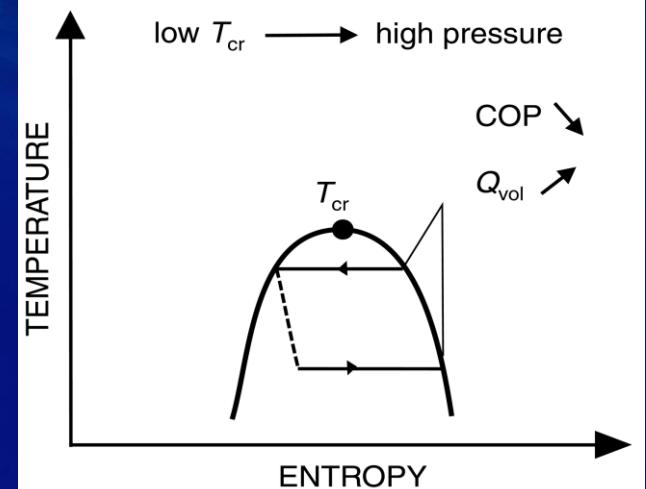
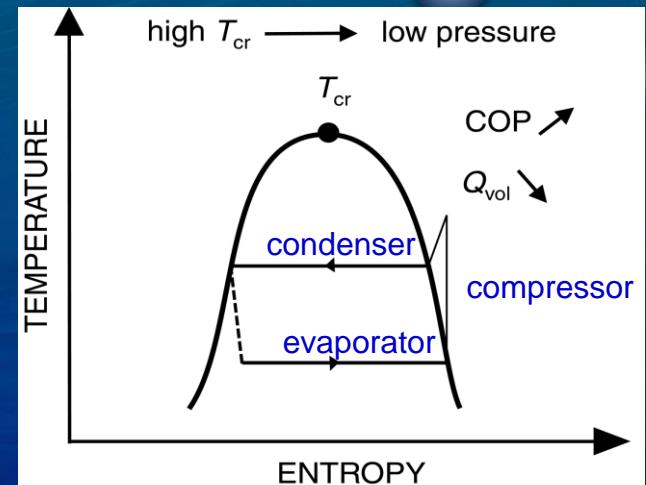
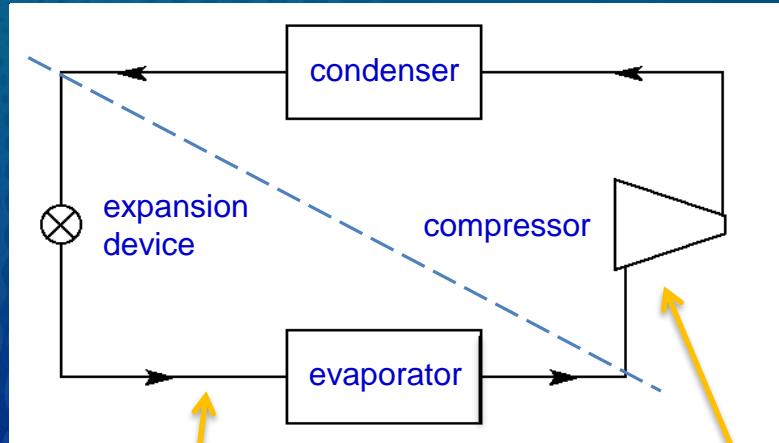
□ Cost



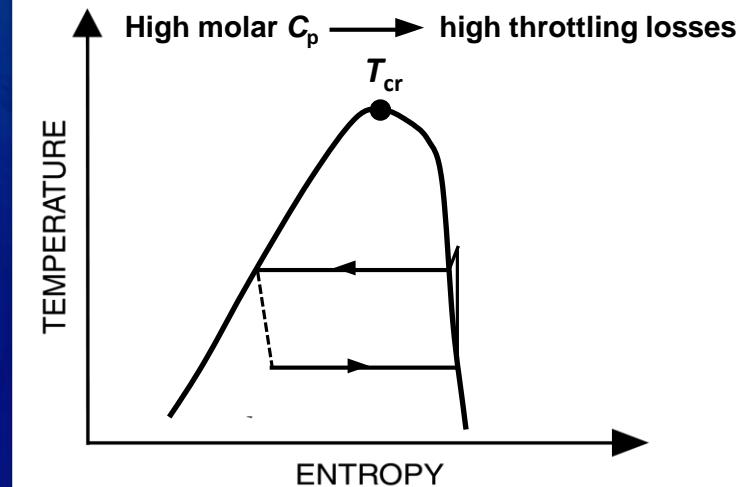
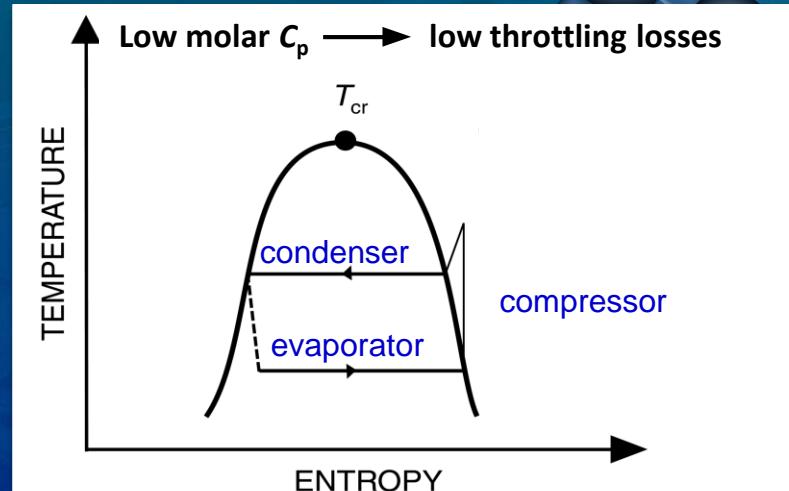
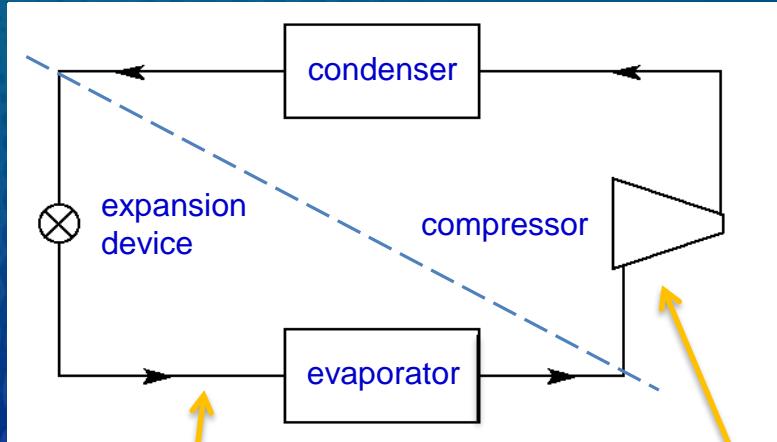
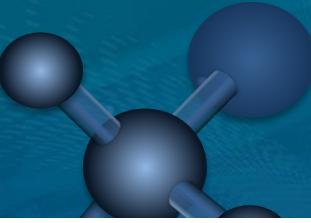
Introduction to vapor compression cycle



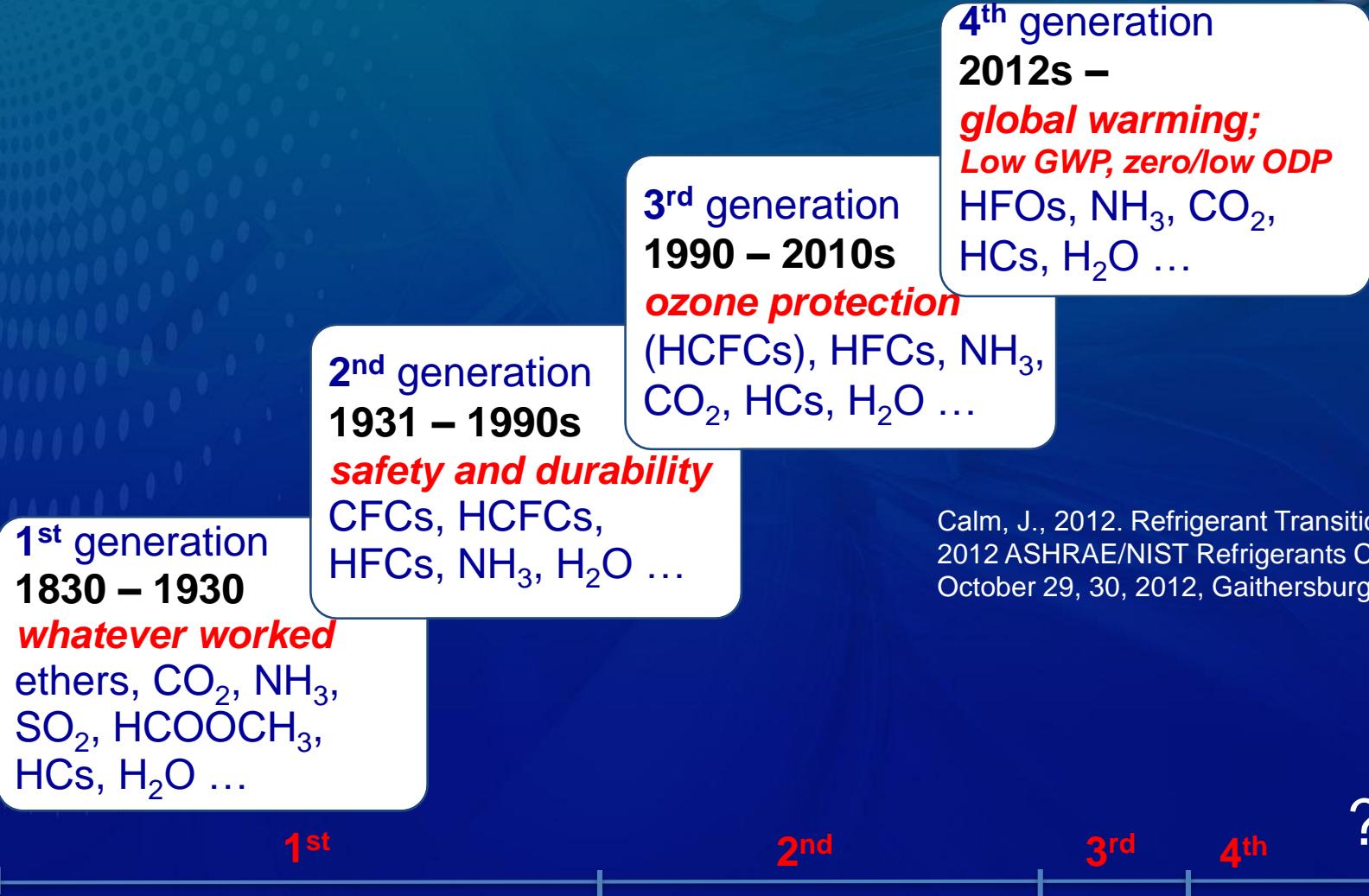
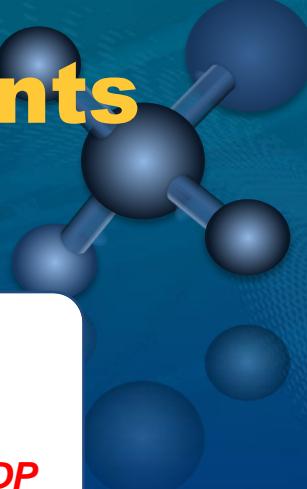
Effect of T_{crit}



Effect of molar heat capacity

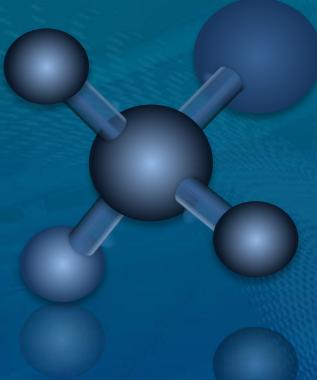


Historic application of refrigerants



Calm, J., 2012. Refrigerant Transitions ... Again, 2012 ASHRAE/NIST Refrigerants Conference, October 29, 30, 2012, Gaithersburg, MD.

Fluids for air conditioning and domestic refrigeration



Fluorinated fluids

2nd generation

1931 – 1990s

safety and durability

	NBP (°C)
R-11	23.7
R-12	-29.8
R-22	-40.8

3rd generation

1990 – 2010s

ozone protection

	NBP (°C)
R-123 (HCFC)	27.8
R-134a	-26.1
R-407C (R32/125/134a)	-43.6
R-410A (R-32/125)	-51.4 -51.7/-48.1

3th generation

GWP_s

1300

1600

677/3170/1300

1900

677/3170

“Natural” fluids

H₂O 100.0

CO₂ -78.4

air -194.2

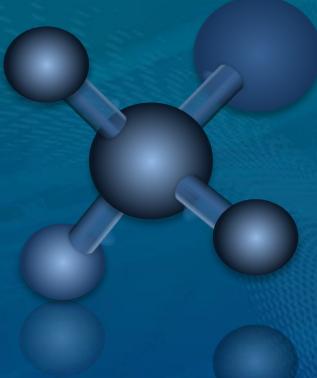
R-600a -11.7

R-290 -42.1

R-1270 -47.7

NH₃ -33.3

Fluids for air conditioning and domestic refrigeration



Fluorinated fluids

2nd generation

1931 – 1990s

safety and durability

	NBP (°C)
R-11	23.7
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R-407C (R32/125/134a)	-43.6
R-410A (R-32/125)	-51.4 -51.7/-48.1)

4th generation

2012s –

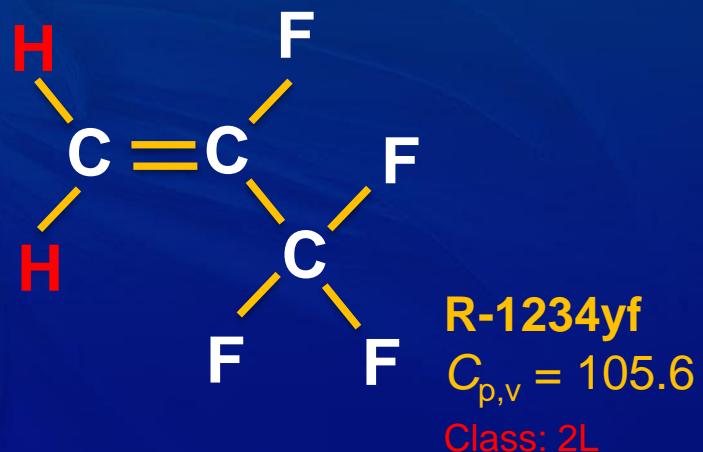
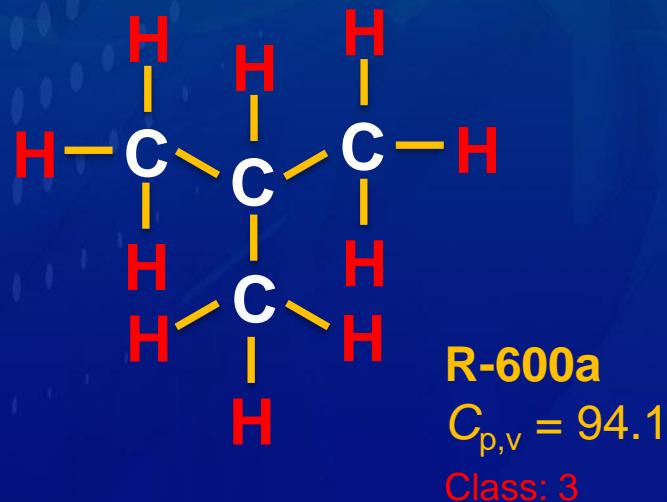
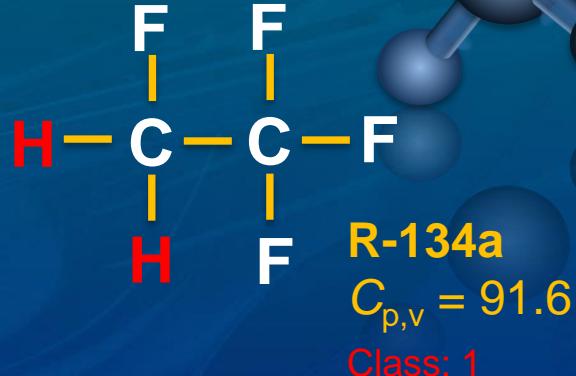
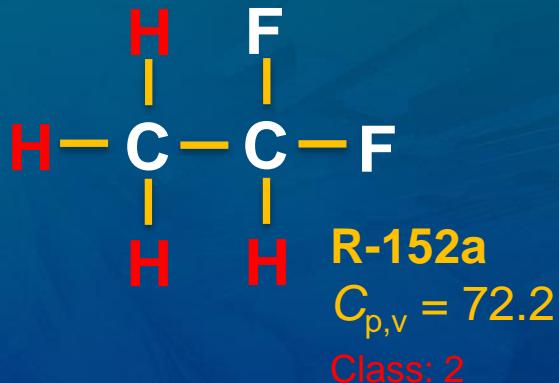
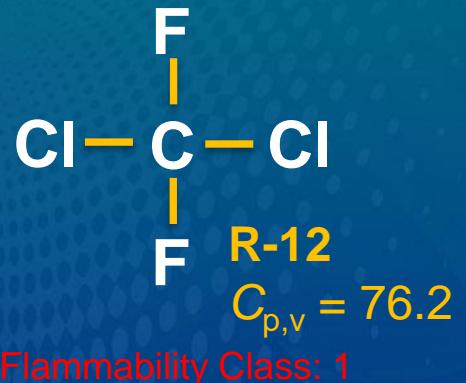
global warming

	NBP (°C)
R-1336mzz	33.4
R-1233zd(E)	18.3
R-1234ze(E)	-19.0
R-1234yf	-29.5

“Natural” fluids

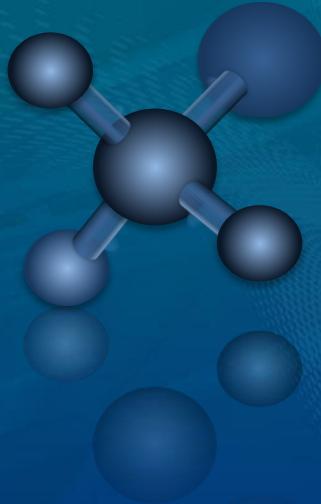
H ₂ O	100.0	R-600a	-11.7	NH ₃	-33.3
CO ₂	-78.4	R-290	-42.1		
air	-194.2	R-1270	-47.7		

Low-pressure refrigerants



$C_{p,v}$ – molar heat capacity of saturated vapor at 0 ° C (kJ/(kmol.K))

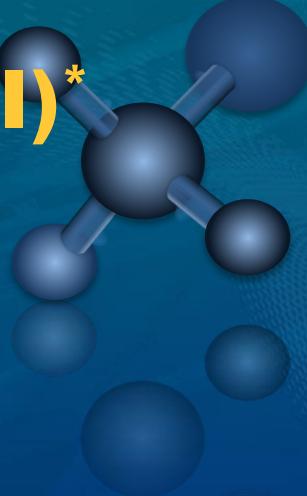
Proposed low-GWP HFOs have at least 3 carbons



Large molecules:

- Tend to be of low volatility
- Tend to have high molar heat capacity
- Are expensive to synthesize
- Tend to be unstable (long chains)

Fluids studied in Low-GWP AREP (I)*



Nine R22 and R407C replacements:

- R-717 (ASHRAE B2L)
- R-1270 (A3)
- R-290 (A3)
- Six mixtures of R-744, R-32, R-125, R-134a, R-152a, R-1234ze(E), R-1234yf (3 A1 fluids, 3 A2L fluids)

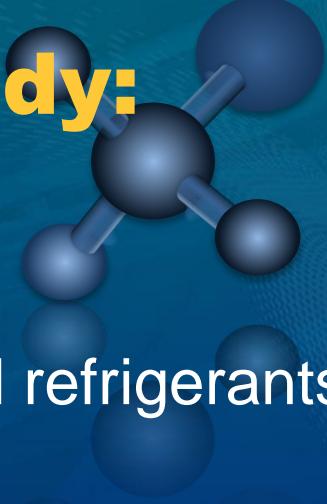
Ten R410A replacements:

- R-744 (A1)
- R-32
- Six mixtures of R-744, R-32, R-125, R-134a, R-152a, R-1234ze(E), R-1234yf (A2L fluids)

Mixture development involves a trade-off between GWP, flammability, COP, volumetric capacity, and glide.

* Johnson, P.A., Wang, X., Amrane, K., 2012. AHRI Low-GWP Alternative Refrigerant Evaluation Program., 2012 ASHRAE/NIST Refrigerants Conference

NIST Refrigerant Screening Study: Thermodynamic Analysis of Refrigerants



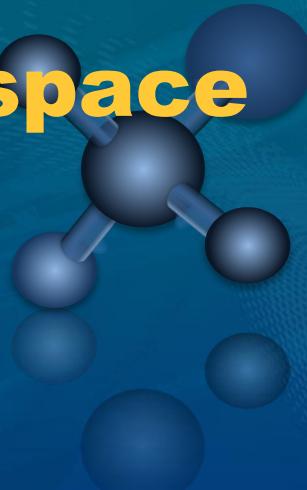
Objective: To identify molecules that might be good refrigerants for AC and refrigeration applications

Approach: Perform refrigerant screening using comprehensive database (over 100 million entries)

Important properties/filters:

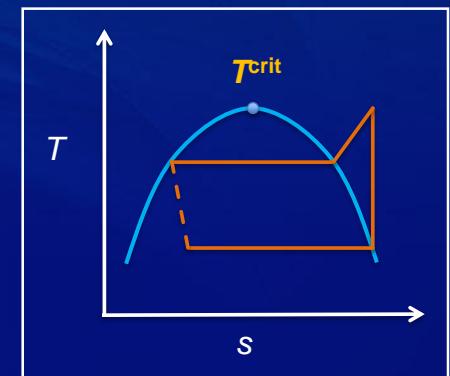
- Performance: COP, volumetric capacity (Q_{vol})
- Environmental: ODP, GWP
- Safety: toxicity, flammability
- Materials: stability, compatibility (lubricant, seals, metals, etc.)
- Cost

Exploration of thermodynamic space by cycle analysis*



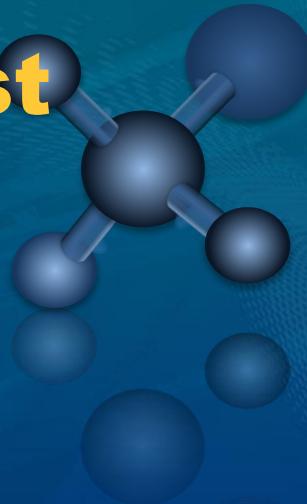
Questions:

- What are thermodynamic limits of performance?
COP & Q_{vol}
- Which refrigerant thermodynamic parameters are the most important?
What are their optimal values?

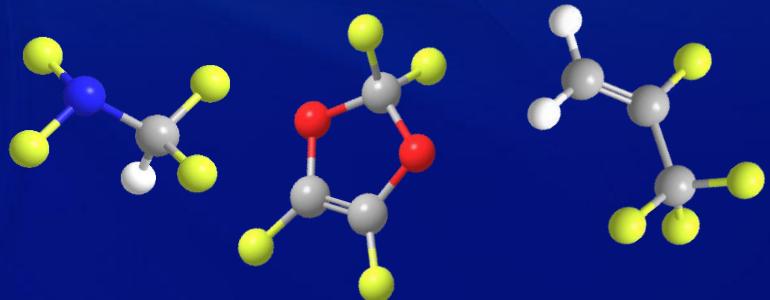


* Domanski, P.A., Brown, J.S., Heo, J., Wojtusiak, J., McLinden, M.O., 2014. A Thermodynamic Analysis of Refrigerants: Performance Limits of the Vapor Compression Cycle, Int. J. Refrigeration, 38:71-79.

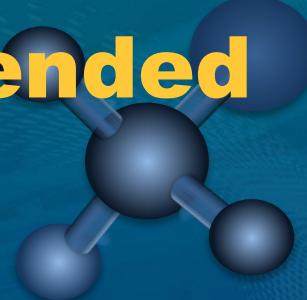
Search for refrigerants with best COP and Q_{vol}



- Vapor compression cycle model
- Extended Corresponding States (ECS) model for representation of refrigerant properties; 9 parameters
- Vary values for each ECS parameter in search of the best performance



Refrigerant parameters for Extended Corresponding States model



*Critical
parameters*

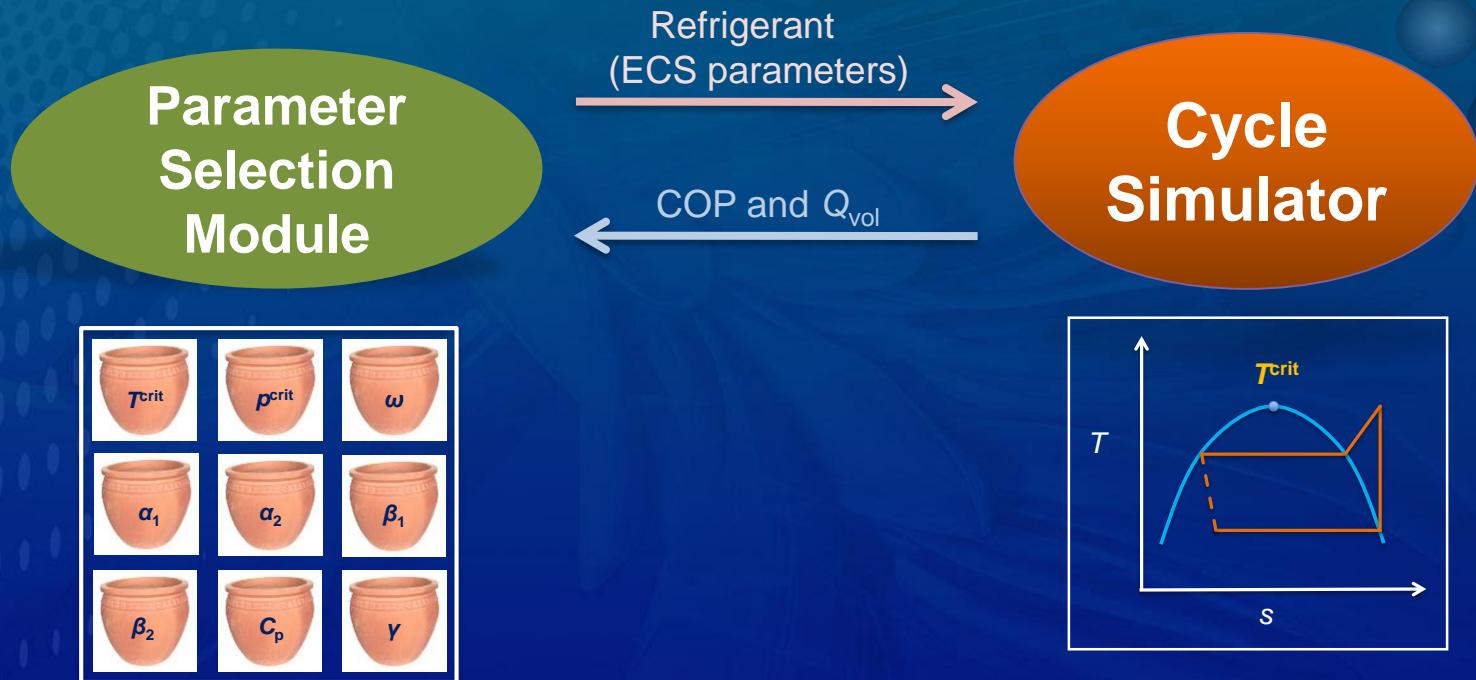
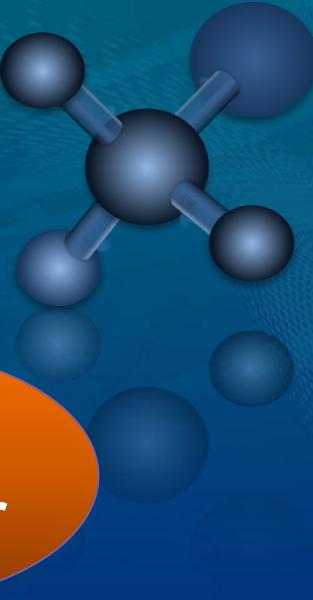
Acentric factor

Shape factors

*Vapor heat
capacity*

Parameter	Units	Range	Granularity
T^{crit}	K	305 ~ 650	0.5
p^{crit}	MPa	2.0 ~ 12.0	0.05
ω	-	0.0 ~ +0.6	0.005
α_1	-	-0.3 ~ +0.3	0.01
α_2	-	-0.8 ~ 0.0	0.1
β_1	-	-1.0 ~ +1.0	0.01
β_2	-	-0.8 ~ +0.8	0.1
$C_p^{\circ}(300 \text{ K})$	J·mol ⁻¹ ·K ⁻¹	20.8 ~ 300	0.2
γ	K ⁻¹	0.0 ~ 0.0025	0.0001

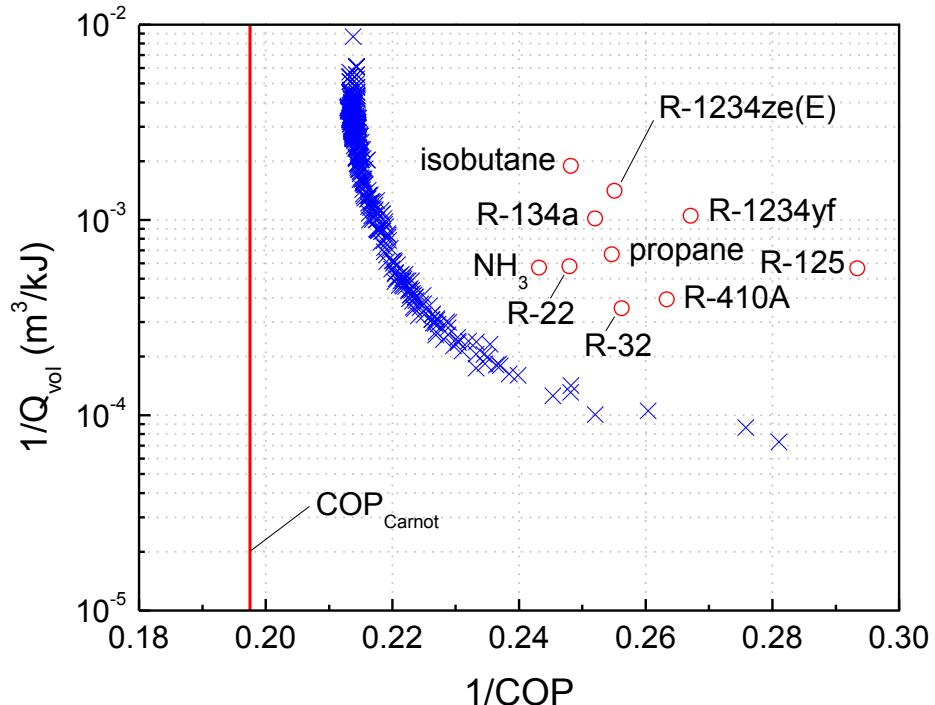
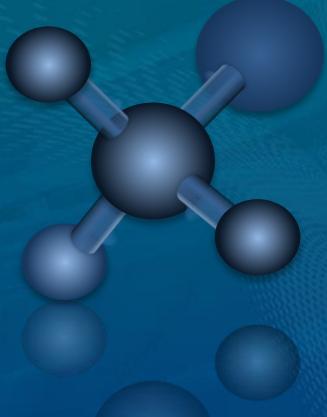
Search for optimal refrigerants parameters



- Bi-objective optimization: COP & Q_{vol} ; Pareto optimality
- Evolutionary approach: Population size: 100
Number of populations: 200
Number of runs: 5

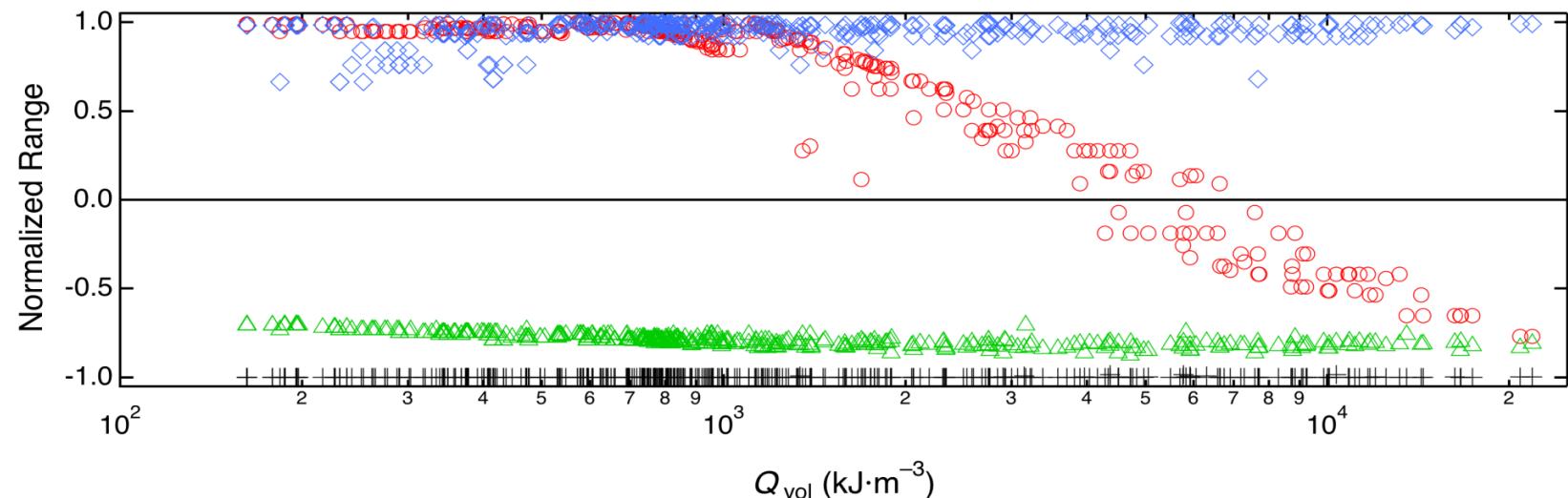
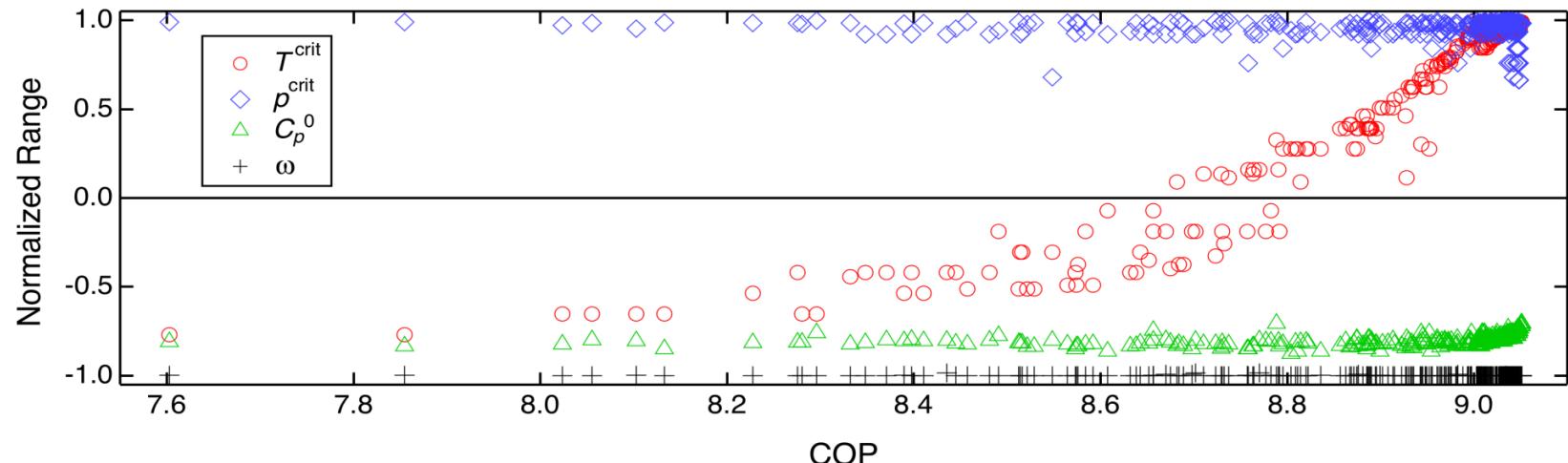
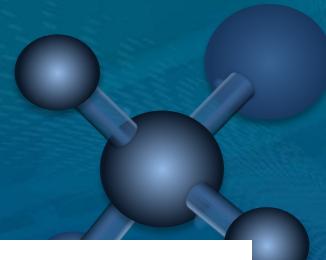
Pareto front – basic cycle

Commercial Refrigeration



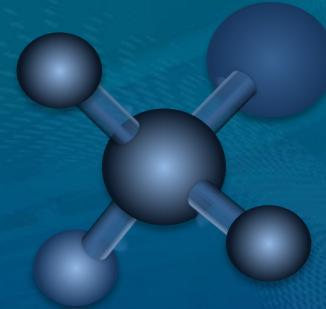
$$COP = \frac{T_{evap}}{T_{cond} - T_{evap}}$$

Refrigerant parameters along Pareto front – basic cycle



Fluid screening

Use PubChem database;
over 100 million compounds



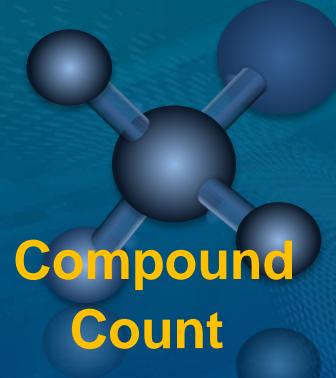
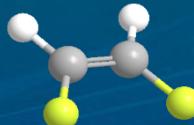
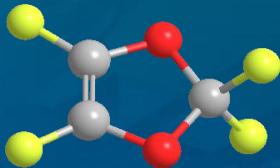
Nonmetallic						
					H	
B	C	N	O	F		
Si	P	S	Cl			
		As	Se	Br		
Metals			Te	I		
				At		
					Noble gases	

First screening filters*

- Component atoms: C, H, N, O, S, F, Cl, Br ← PubChem
- Max. number of atoms in the molecule ← PubChem
- Global Warming Potential (GWP) ← NIST estimation method (Kazakov, *et al.*, 2012)
- Toxicity ← Markers/groups (Lagorce, *et al.*, 2008)
- Flammability ← NIST estimation method (Kazakov, *et al.*, 2012)
- Critical temperature (T^{crit}) ← NIST estimation method (Kazakov, *et al.*, 2010)
- Stability ← E.g., peroxides (O-O), 3-member rings

* McLinden, M.O., Kazakov, A.F., Brown, J.S., Domanski, P.A., 2014. A Thermodynamic Analysis of Refrigerants: Possibilities and Tradeoffs for Low-GWP Refrigerants, Int. J. Refrigeration, 38:80-92

First screening filters



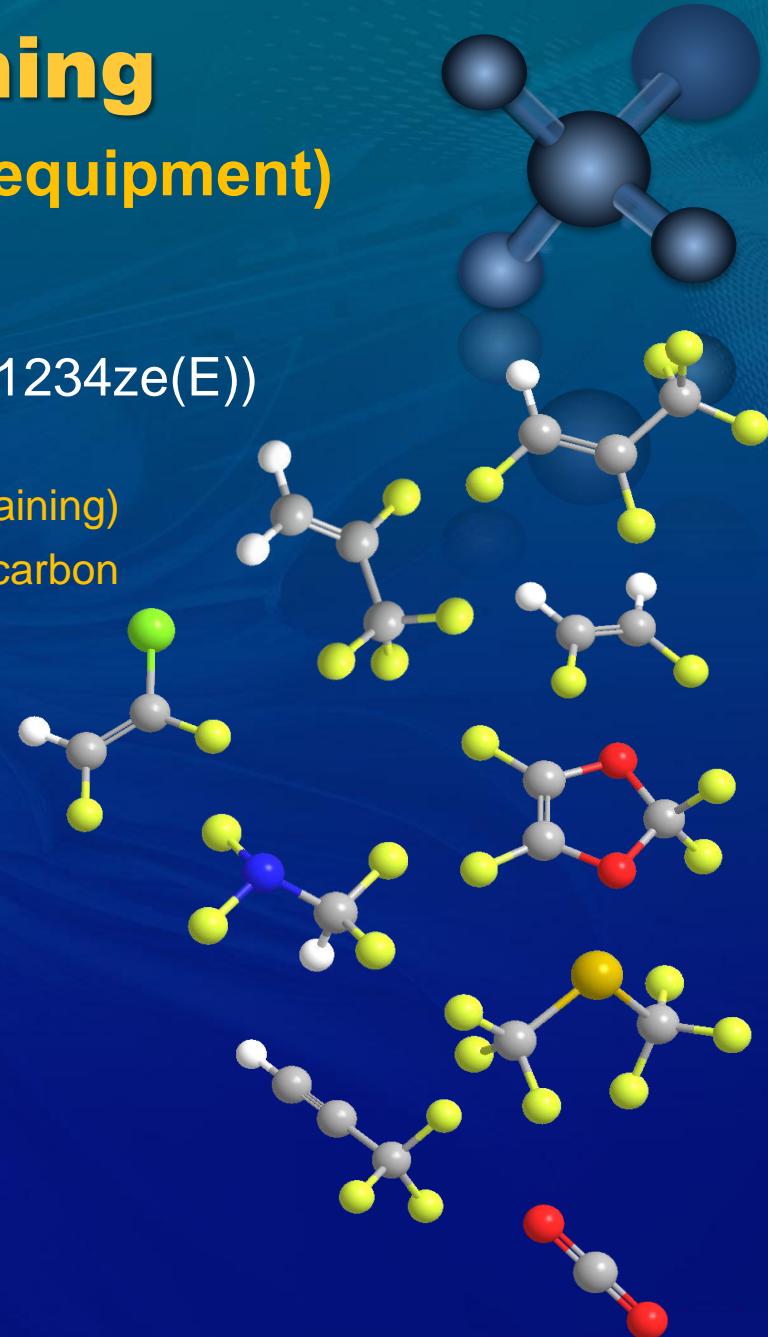
• PubChem database	100 000 000
• Component atoms: only C, H, N, O, S, F, Cl, Br Maximum number of atoms: 15	56203
• GWP ₁₀₀ < 200	52265
• Toxicity	30135
• Flammability: Lower flammability limit LFL > 0.1 kg/m ³	20277
• Critical temperature: 300 K < T ^{crit} < 550 K (80 °F - 530 °F)	1728
• Stability: screen out problematic groups	1234
• Critical temperature: 300 K < T ^{crit} < 400 K (80 °F - 260 °F)	62

Results of first screening

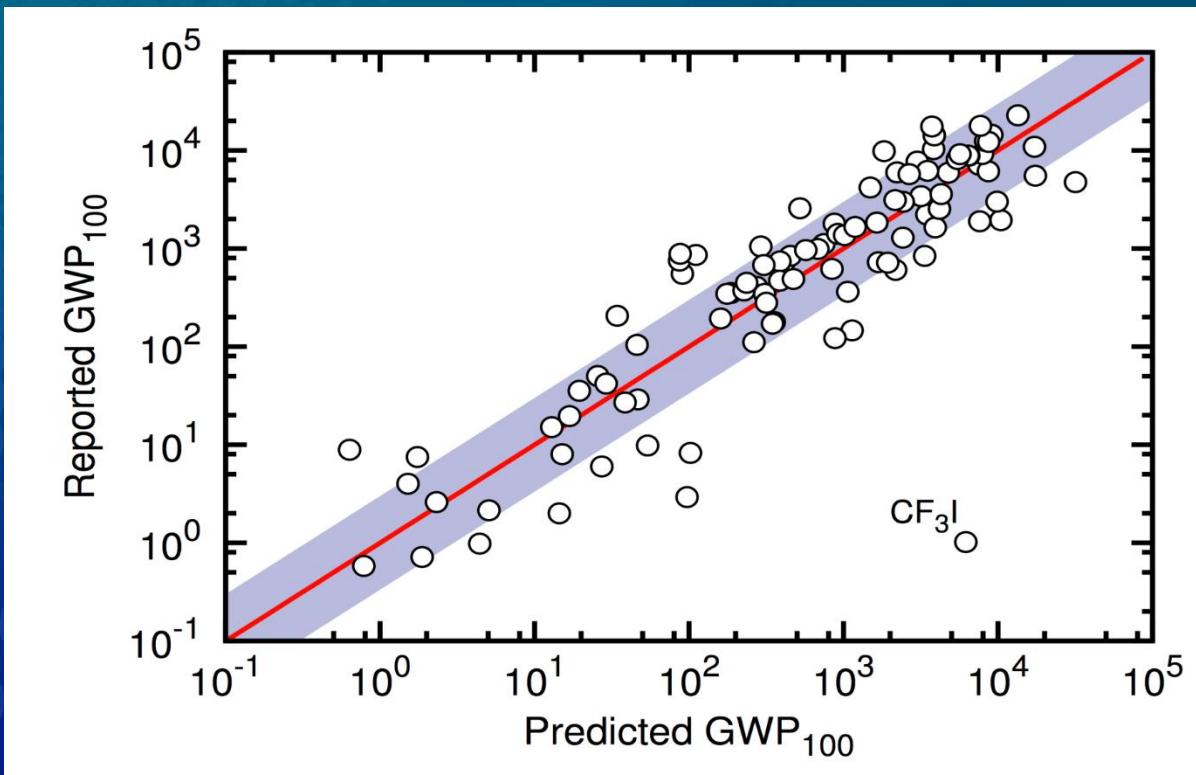
$300 \text{ K} \leq T^{\text{crit}} \leq 400 \text{ K}$ (majority of equipment)

62 compounds passed

- 39 halogenated olefins (e.g., R1234yf, R1234ze(E))
23 HFOs; 8 FOs (fully fluorinated)
7 HCFOs (Cl-containing); 1 HBFO (Br-containing)
7 2-carbon; 20 3-carbon; 10 4-carbon; 2 5-carbon
- 11 halogenated ethers (C-O-C)
all contain a C-C double bond
2 cyclic ethers
- 4 halogenated amines
+ ammonia, $T^{\text{crit}} = 405 \text{ K}$
- 3 sulfur-containing compounds
2 thioethers; 1 thiol
- 3 halogenated alkynes (C-C triple bond)
- CO₂
- 1 halogenated alkane (HFC-152a)



Estimation of GWP

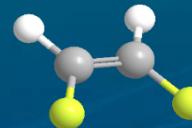


RMS deviation:
factor of 3

Concern: Some fluids may have been passed over due to overly restrictive screens

Decision: Repeat the screening with modified screens

Second screening with modified filters*

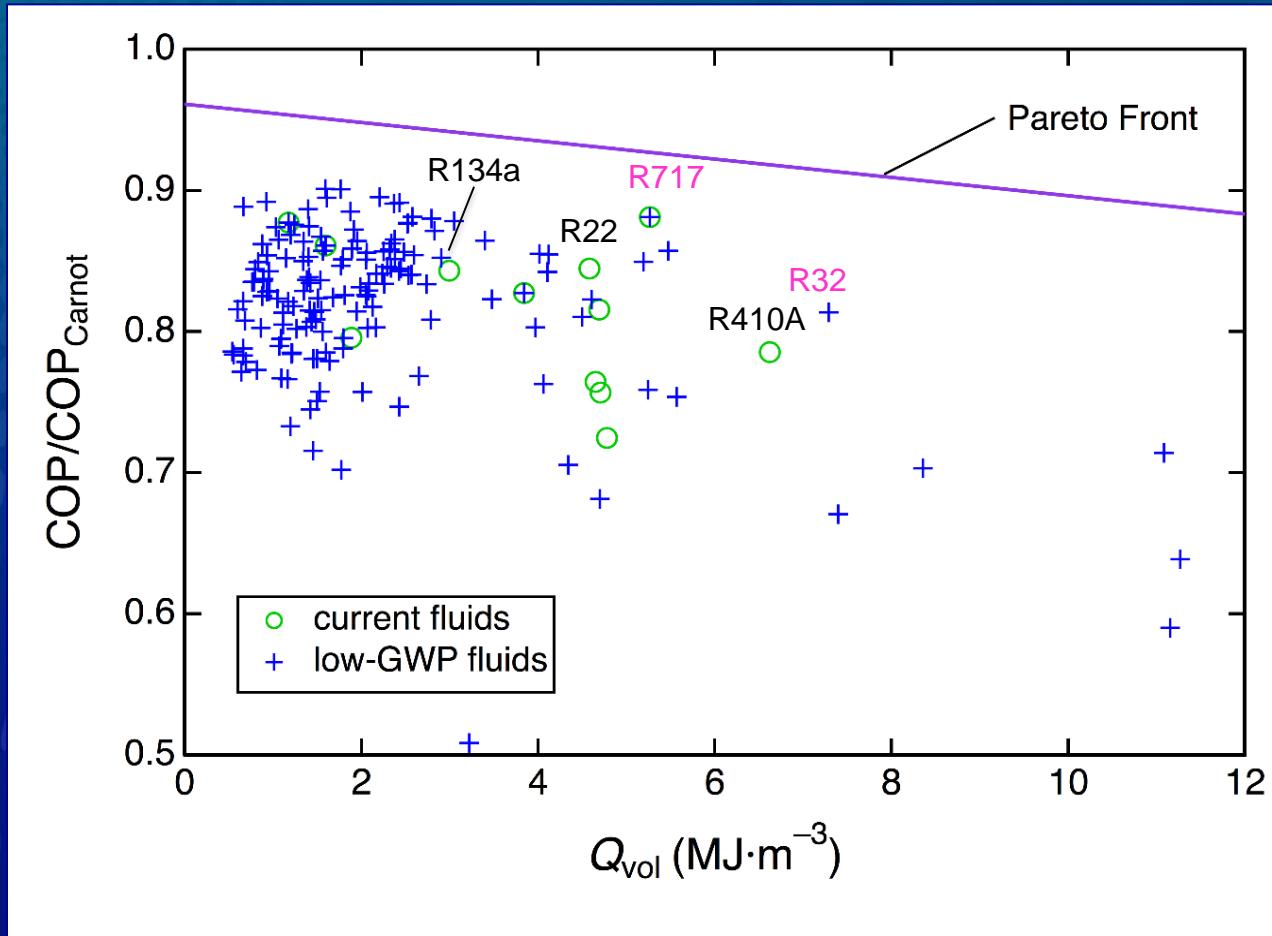
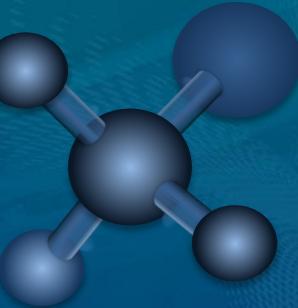


Compound count

- PubChem database 100 000 000
- Component atoms: only C, H, N, O, S, F, Cl, Br }
Maximum number of atoms: 18 184 000
- GWP₁₀₀ < 1000 172 000
- Flammability: dropped
- Critical temperature: $320 \text{ K} < T^{\text{crit}} < 420 \text{ K}$ 144
20 new additional fluids were found in the $320 \text{ K} < T^{\text{crit}} < 385 \text{ K}$ range
- Toxicity: evaluated manually (MSDS, REL, TLV, =CF2)
- Stability: evaluated manually
- Cycle performance / Volumetric capacity: $> 2.4 \text{ MJ}\cdot\text{m}^{-3}$

* McLinden, M.O., Brown, J.S., Kazakov, A., Domanski, P.A., 2015. Hitting the Bounds of Chemistry: Limits and Tradeoffs for Low-GWP Refrigerants. Keynote, 24th IIR International Congress of Refrigeration, 16-22 August, Yokohama, Japan

Cycle simulations – basic cycle

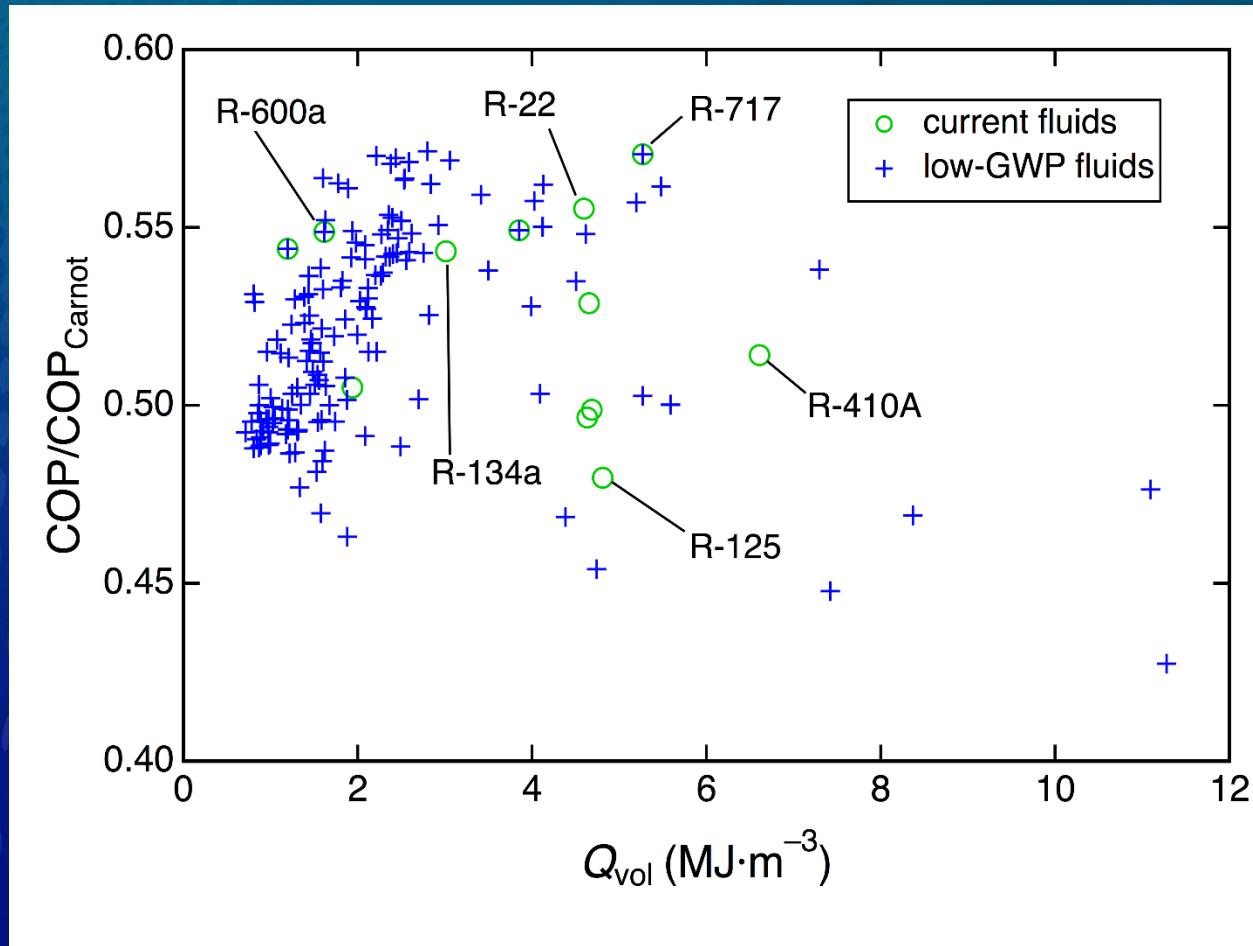


AC application, ideal cycle
(100 % compressor
efficiency,
zero pressure drop)

- Most low-GWP refrigerants have low Q_{vol}

Cycle simulations – basic cycle

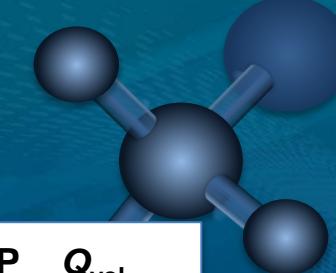
with compressor and heat exchanger irreversibilities



AC application.
Effects of compressor
efficiency and
pressure drop included

Best 22 candidate fluids

$Q_{vol} \geq 2.4 \text{ MJ/m}^3$, AC applications



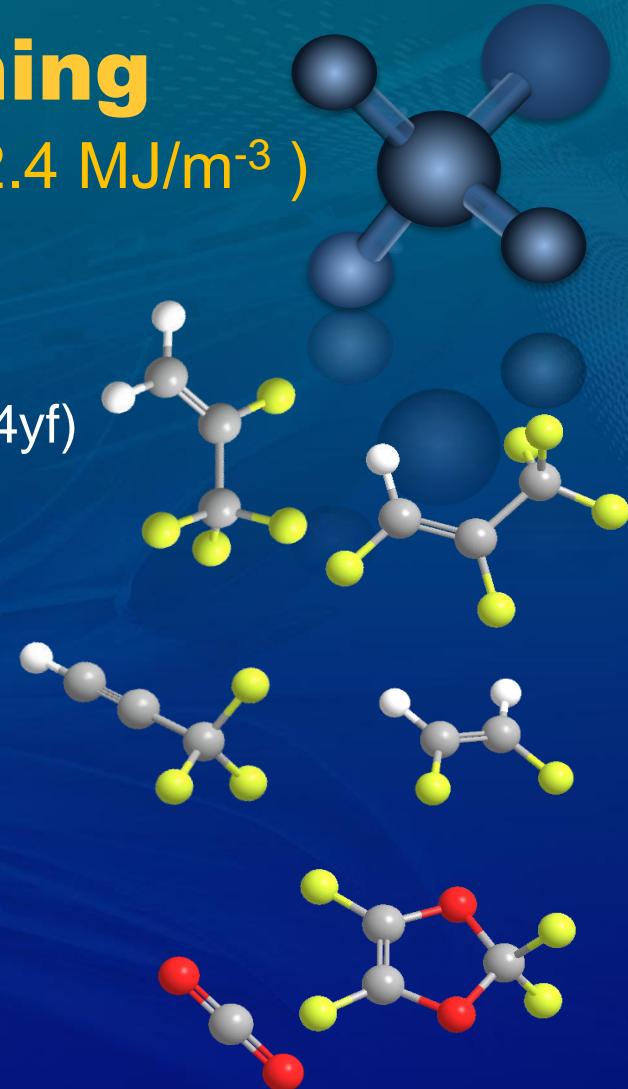
			GWP	LFL (kg/m ³)	T _{crit} (K)	COP	Q _{vol} (MJ/m ³)
Hydrocarbons and Dimethylether							
propene (propylene)	CH ₂ =CH-CH ₃	R-1270	1	0.037	364.2	0.548	4.61
propane	CH ₃ -CH ₂ -CH ₃	R-290	9	0.038	369.9	0.549	3.85
methoxymethane (dimethylether)	CH ₃ -O-CH ₃	R-E170	0.3	0.064	400.4	0.571	2.80
Halogenated Alkanes (HFCs)							
fluoromethane	CH ₃ F	R-41	116	0.099	317.3	0.397	11.18
difluoromethane	CH ₂ F ₂	R-32	677	0.307	351.3	0.538	7.29
fluoroethane	CH ₂ F-CH ₃	R-161	4	0.062	375.3	0.562	4.13
1,1-difluoroethane	CHF ₂ -CH ₃	R-152a	138	0.130	386.4	0.562	2.84
Halogenated Alkenes (HFOs)							
fluoroethene	CHF=CH ₂	R-1141	<1	0.064	327.1	0.535	4.50
1,1,2-trifluoroethene	CF ₂ =CHF	R-1123	3	0.214	343.0	0.500	5.59
2,3,3,3-tetrafluoroprop-1-ene	CH ₂ =CF-CF ₃	R-1234yf	<1	0.289	367.9	0.525	2.82
(E)-1,2-difluoroethene	CHF=CHF	R-1132(E)	1	0.124	370.5	0.543	2.75
3,3,3-trifluoroprop-1-ene	CH ₂ =CH-CF ₃	R-1243zf	1	0.185	376.9	0.543	2.59
1,2-difluoroprop-1-ene	CHF=CF-CH ₃	R-1252ye	2	0.093	380.7	0.552	2.50
1-fluoroprop-1-ene	CHF=CH-CH ₃	R-1261ze	1	0.212	390.7	0.564	2.54
(Z)-1,2-difluoroethene	CHF=CHF	R-1132(Z)	1	0.124	405.8	0.547	2.46
Halogenated Oxygenates							
trifluoro(methoxy)methane	CF ₃ -O-CH ₃	R-E143a	523	0.350	377.9	0.541	2.55
2,2,4,5-tetrafluoro-1,3-dioxole	-CF ₂ -O-CF=CF-O-	n.a.	1	0.515	400.0	0.543	2.40
Halogenated Nitrogen and Sulfur Compounds							
N,N,1,1-tetrafluormethaneamine	CHF ₂ -NF ₂	n.a.	20	0.383	341.6	0.503	5.27
difluoromethanethiol	CHF ₂ -SH	n.a.	1	0.250	373.0	0.557	4.03
trifluoromethanethiol	CF ₃ -SH	n.a.	1	0.517	376.2	0.551	2.92
Inorganic Compounds							
carbon dioxide	CO ₂	R-744	1.00	n.a.	304.1		
ammonia	NH ₃	R-717	<1	0.105	405.4	0.571	5.27

Results of second screening

(includes performance screening, $Q_{vol} \geq 2.4 \text{ MJ/m}^{-3}$)

22 compounds passed

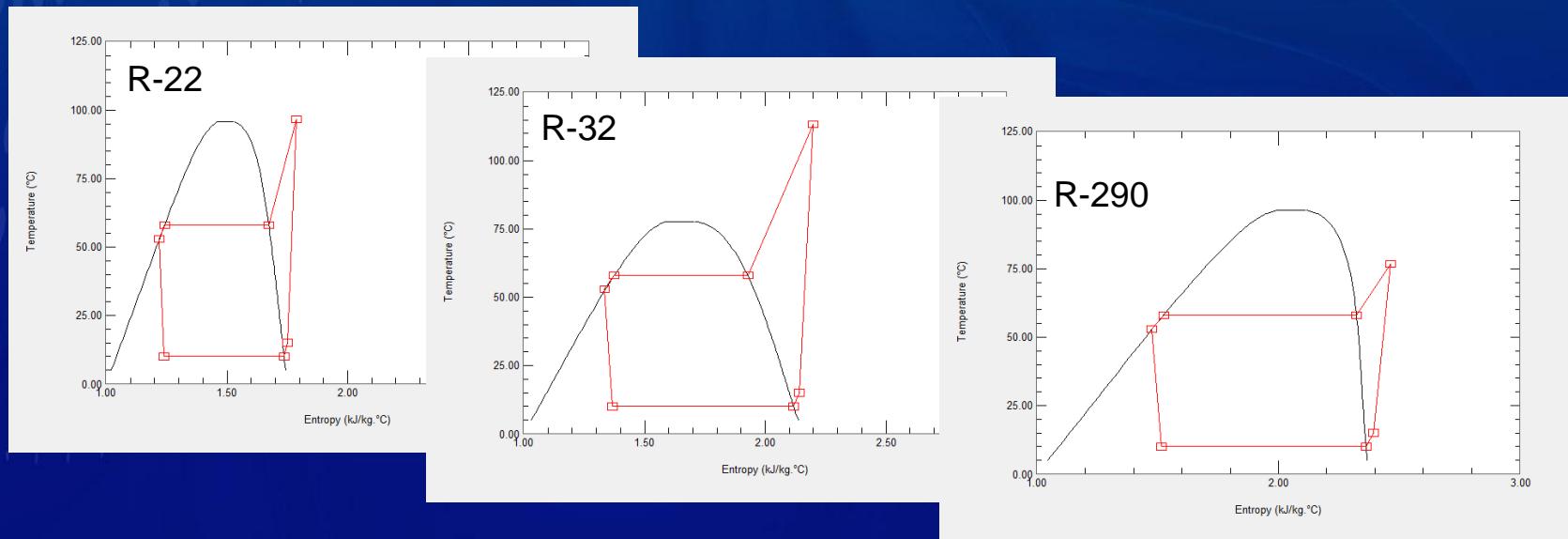
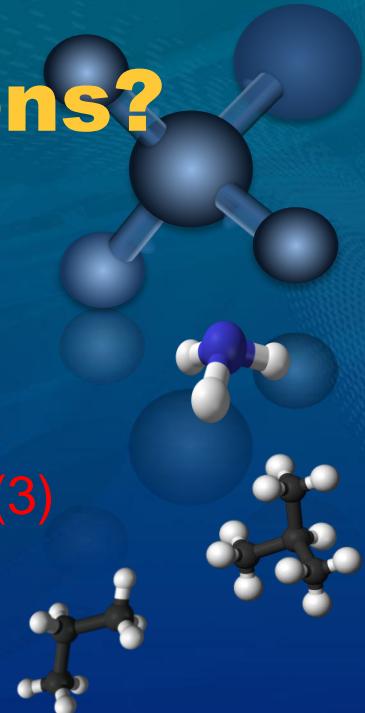
- 8 halogenated olefins (e.g., R1234ze(E), R1234yf)
4 2-carbon; 4 3-carbon
- 4 halogenated alkane (HFCs)
- 3 halogenated nitrogen and sulfur compounds
- 2 hydrocarbons and dimethylether
- 2 halogenated oxygenates (C-O-C)
- 2 inorganic compounds (ammonia & CO₂)



Except CO₂, all fluids are at least mildly flammable

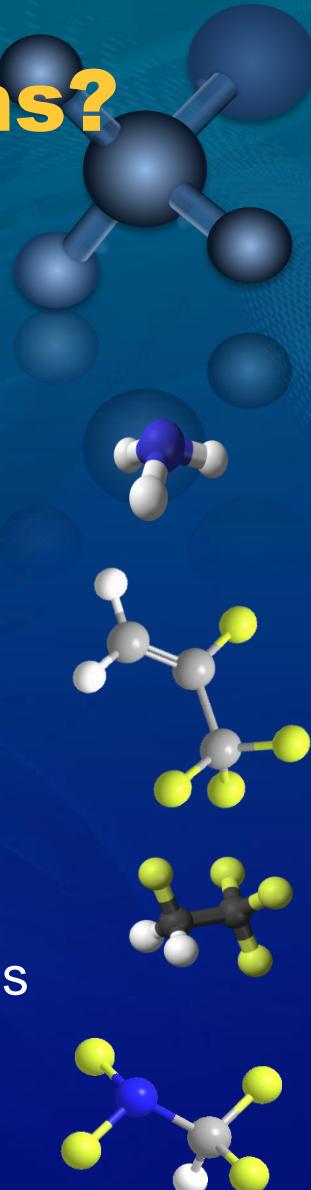
So what are low-GWP AC options?

- Single-component refrigerants
 - NH_3 (ammonia); GWP < 1, mildly flammable (2L), toxic
 - HFOs; GWP \approx 1, mildly flammable (2L), low Q_{vol}
 - hydrocarbons: R-290, R-1270; GWP = 20, **flammable (3)**
 - R-152a; GWP = 140; **flammable (2)**, low Q_{vol}
 - R-32; GWP = 675; mildly flammable (2L)



So what are low-GWP AC options?

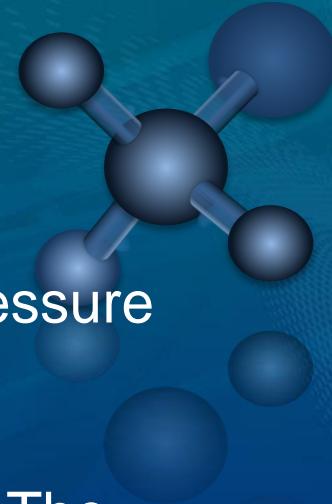
- Mixtures
 - R-32 and HFOs
mildly flammable (2L), GWP << 675
 - R-32 and HFCs (and HFOs)
non-flammable, GWP > 675
or
mildly flammable (2L), GWP < 675
- New fluids
 - Not fully characterized
 - Do not offer improved performance above the known fluids
 - ??



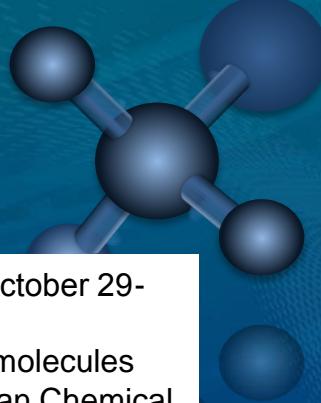
Concluding remarks

(AC applications)

- New low-GWP fluids (HFO) have markedly lower pressure than R-22 and R-410A and are mildly flammable.
- Viable refrigerants are restricted to small molecules. The prospects of discovering new refrigerants that would offer better performance over the known fluids is minimal.
- R-32 is a dominant component in most mixtures proposed as a replacement of R-22 and R-410A.
- There is a tradeoff between GWP and flammability of low-GWP mixtures. The lower-GWP mixtures have a higher flame velocity.
- The choices are limited. Tradeoffs are inevitable.



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