NIST

Hitting the Bounds of Chemistry: Limits and Tradeoffs for Low-GWP Refrigerants

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Outline/Motivation

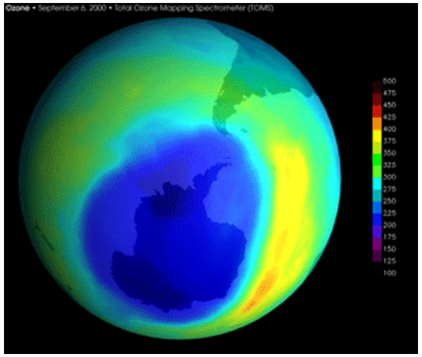
- Industry needs low-GWP refrigerants
- What properties do we want in a refrigerant?
- What is the best that we can do?
  - what are the thermodynamic limits to performance?
  - how do current fluids compare?
- What other molecules are out there?
  - properties from molecular structure
  - simulation of candidate fluids & tradeoffs
- Is that all there is, really?

➔ Can We Do Better? ➔

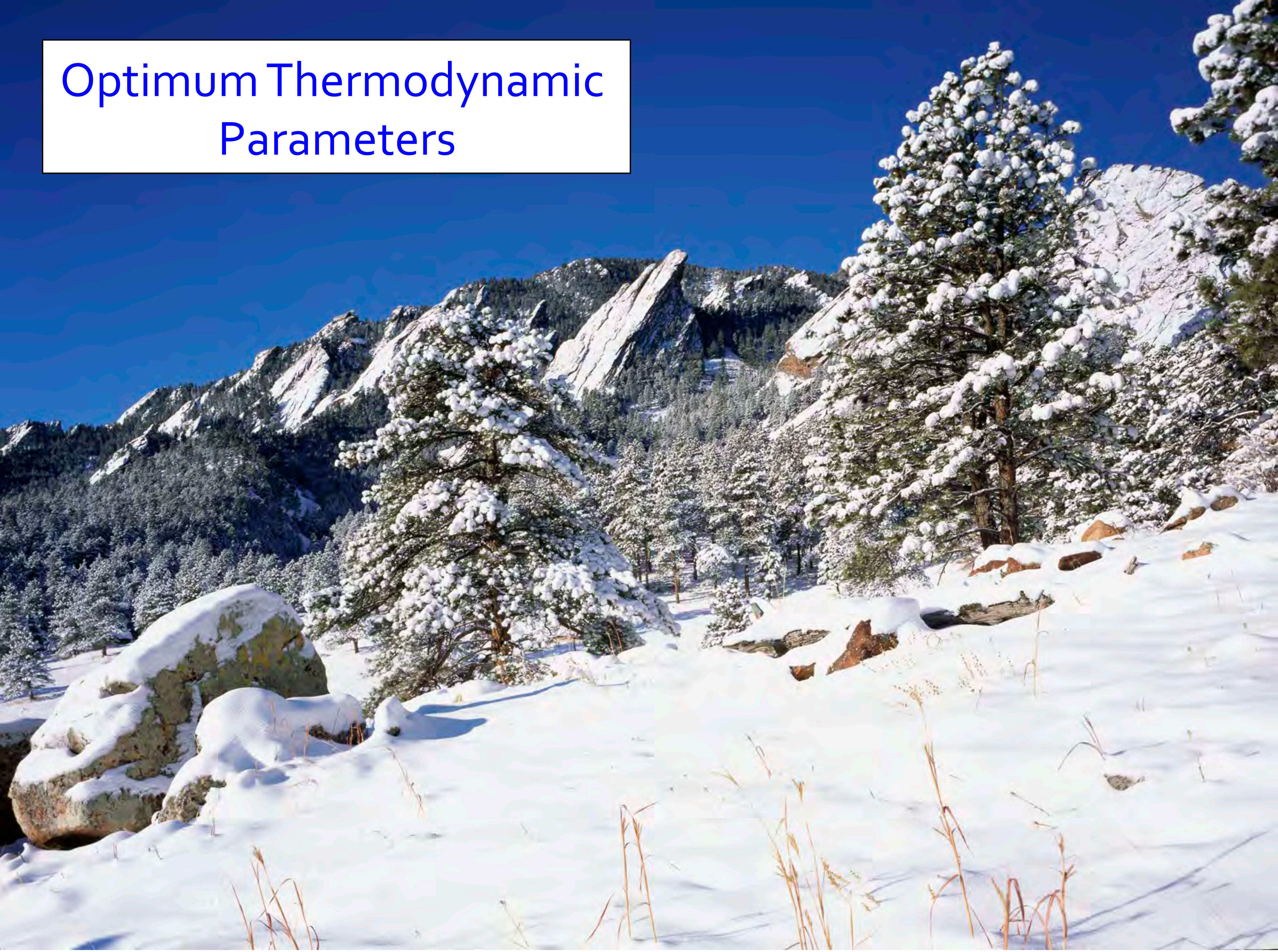
What Properties are Important?

- Safety
  - ➥toxicity (acute and chronic)
  - ➥flammability*
- Environmental
  - ➥ozone depletion potential (ODP)
  - ➥green house warming potential (GWP)*
  - ➥atmospheric life (impacts ODP & GWP)*
- Materials
  - ➥compatibility with metals, seals, etc.
  - ➥lubricant
  - ➥stability (hydrolysis, polymerization, etc.)
- Performance
  - ➥thermodynamic properties**
  - ➥transport properties

**focus of this project
*secondary objective



Optimum Thermodynamic Parameters



Optimal Thermodynamic Parameters

Optimize for what application?

→medium & high pressure refrig. in positive-displacement compress.

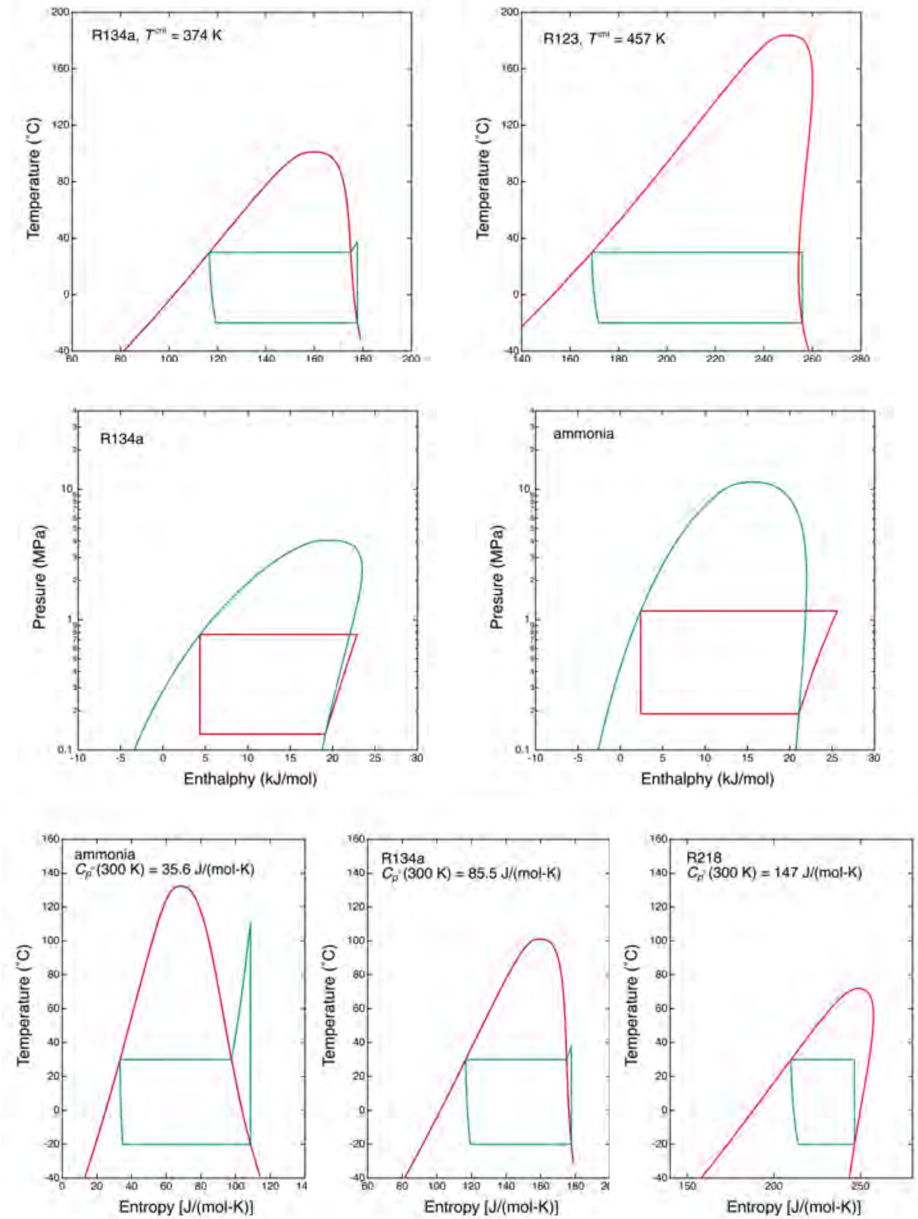
Optimize: COP? Capacity?

How to determine?

- Simulate known fluids, infer optimal parameters
  BUT:
  - limited number of fluids
  - what are we missing?
  - could we do better?

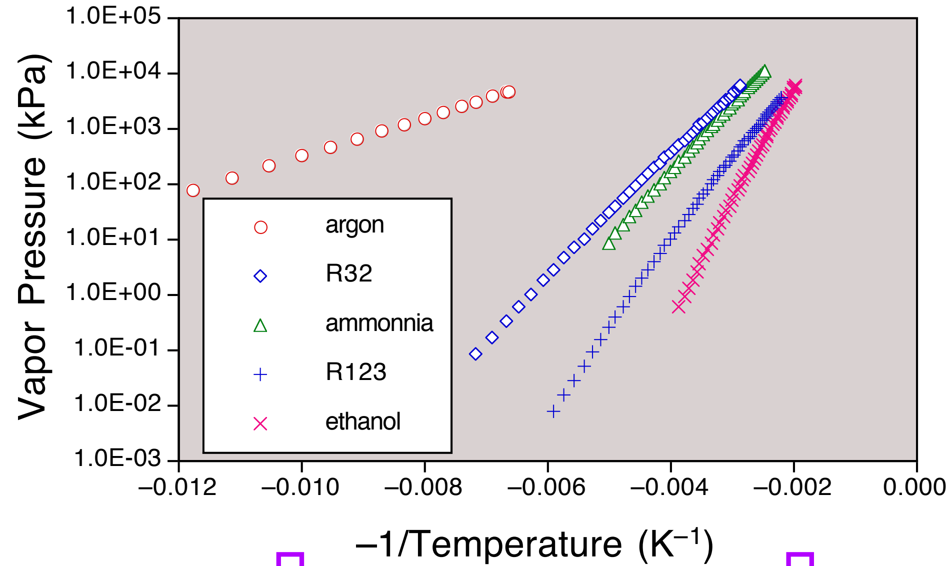
—OR—

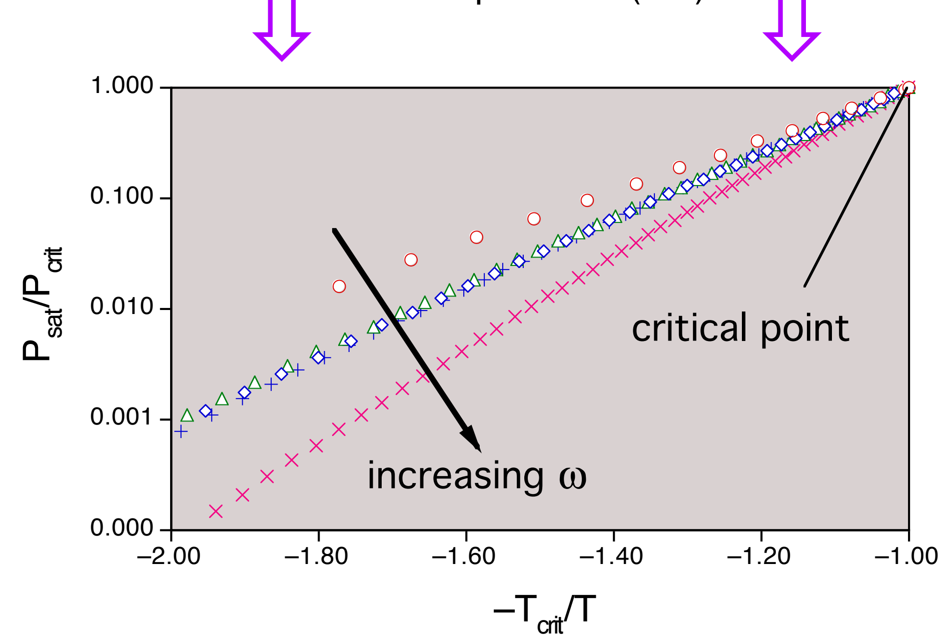
- Model directly in terms of fundamental parameters



Thermo Properties by Extended Corresponding States

Concept: Thermodynamic properties are similar when scaled by critical parameters T_{crit}, p_{crit}



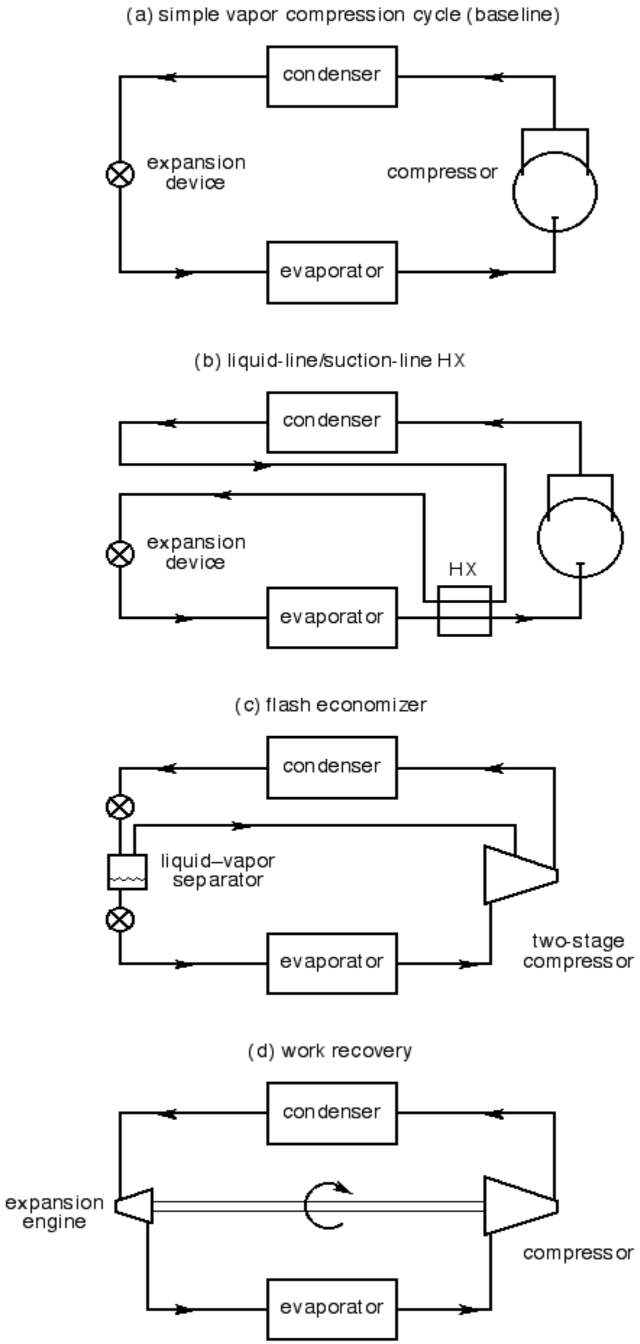


- Combine with heat capacity in limit of zero pressure C_p°
- Refine with additional parameters
- All possible fluids expressed in term of ~10 parameters

➔Amenable to optimization🡐

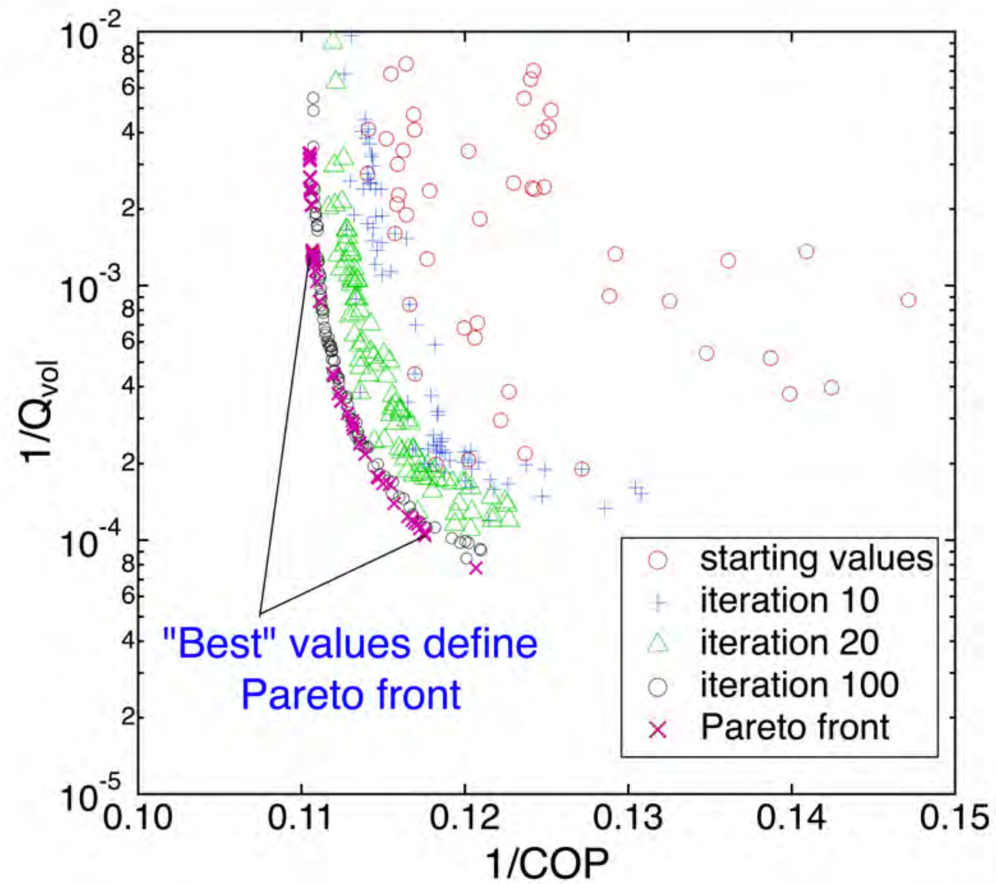
Cycle Analysis

- Modify NIST CYLE-D model
- Investigate variety of cycles:
  - ideal vapor compression cycle
  - internal LL/SL heat exchanger
  - single-stage flash economizer
  - work recovery device
- Define what is possible
  - explore "thermodynamic space" with evolutionary algorithms in terms of ECS parameters
- Define optimum thermodynamic parameters for the applications:
  - cooling (T_{evap} = 10 ˚C, T_{cond} = 40 ˚C)
  - heating (T_{evap} = –10 ˚C, T_{cond} = 30 ˚C)
  - refrigeration (T_{evap} = –20 ˚C, T_{cond} = 30 ˚C)



Optimization (Exploration of Thermodynamic Space)

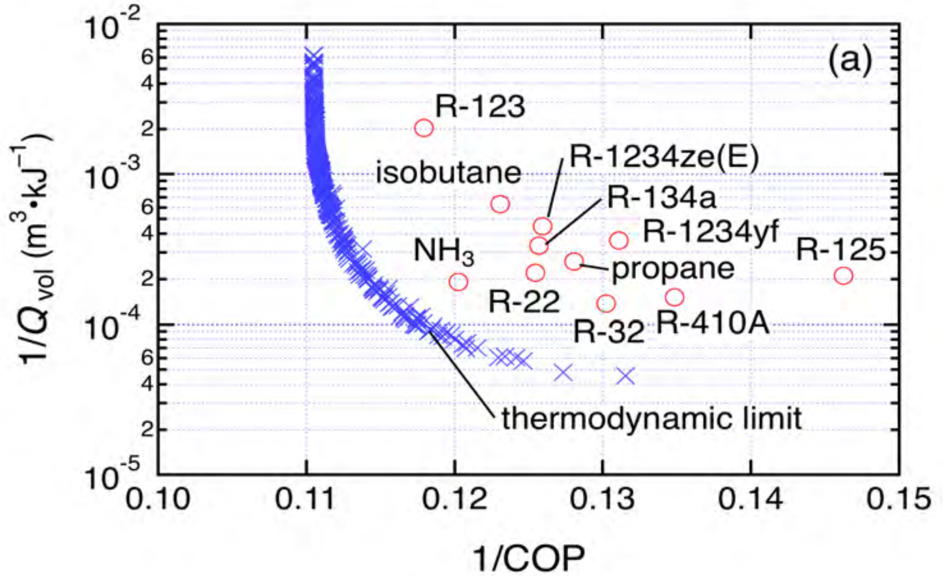
- Hypothetical fluids defined by sets of ECS parameters
- Starting "generation" of fluids randomly selected
- Compute COP and Q_{vol}
- Evolutionary algorithm selects "children" for next generation (*i.e.*, iteration)
- Random parameters also used
- 100,000 hypothetical fluids for each cycle/application
- "Best" COP/Q_{vol} pairs define the Pareto front



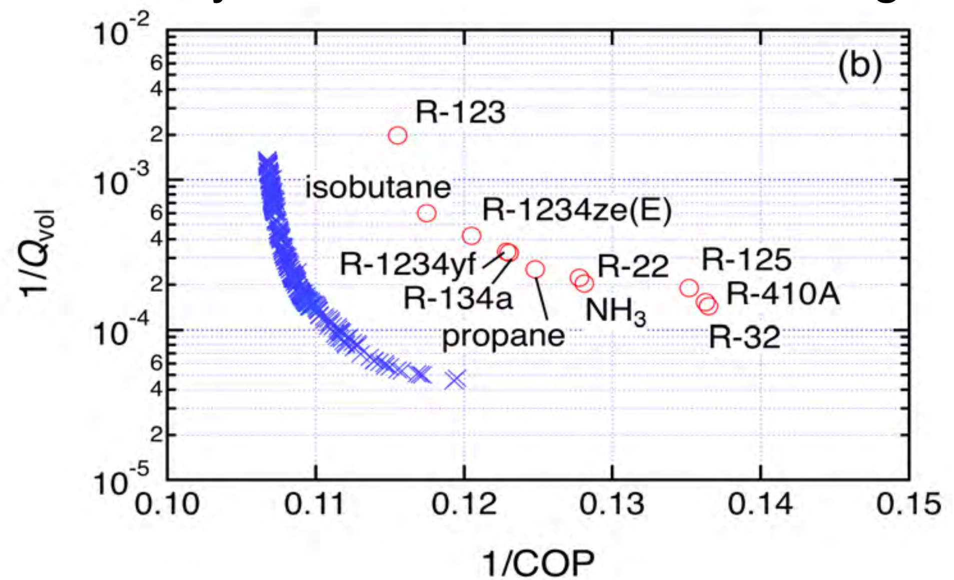
Cycle Simulations—Results

- Simulations yield clear Pareto front
- Current fluids well away from Pareto front
  - ➥ better fluids at least *allowed* by thermodynamics
- Cycle with internal HX:
  - ➥ Pareto front (thermo limit) shows better performance
  - ➥ effect for real fluids varies

Baseline cycle



Cycle with LL/SL heat exchange



Results—Parameters Along Pareto Front

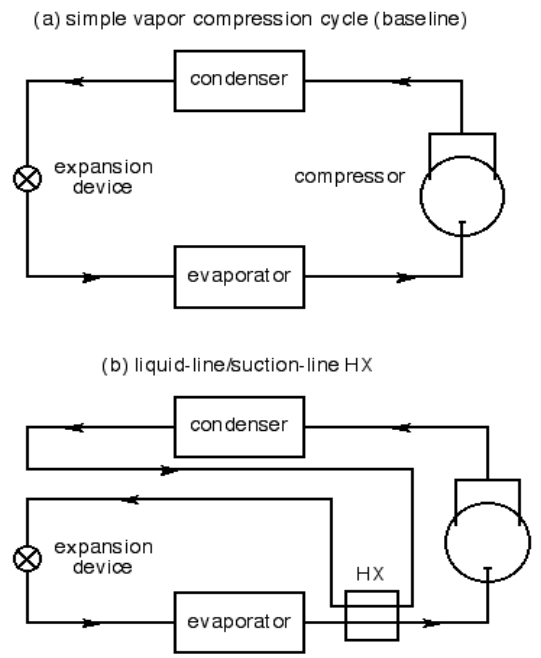
Simple cycle (& economizer cycle):

- Critical temperature:
  efficiency/capacity tradeoff
- Critical pressure: high values optimal
- Vapor heat capacity (molar basis):
  low values optimal
- Acentric factor
  (slope of vapor pressure curve):
  low values optimal

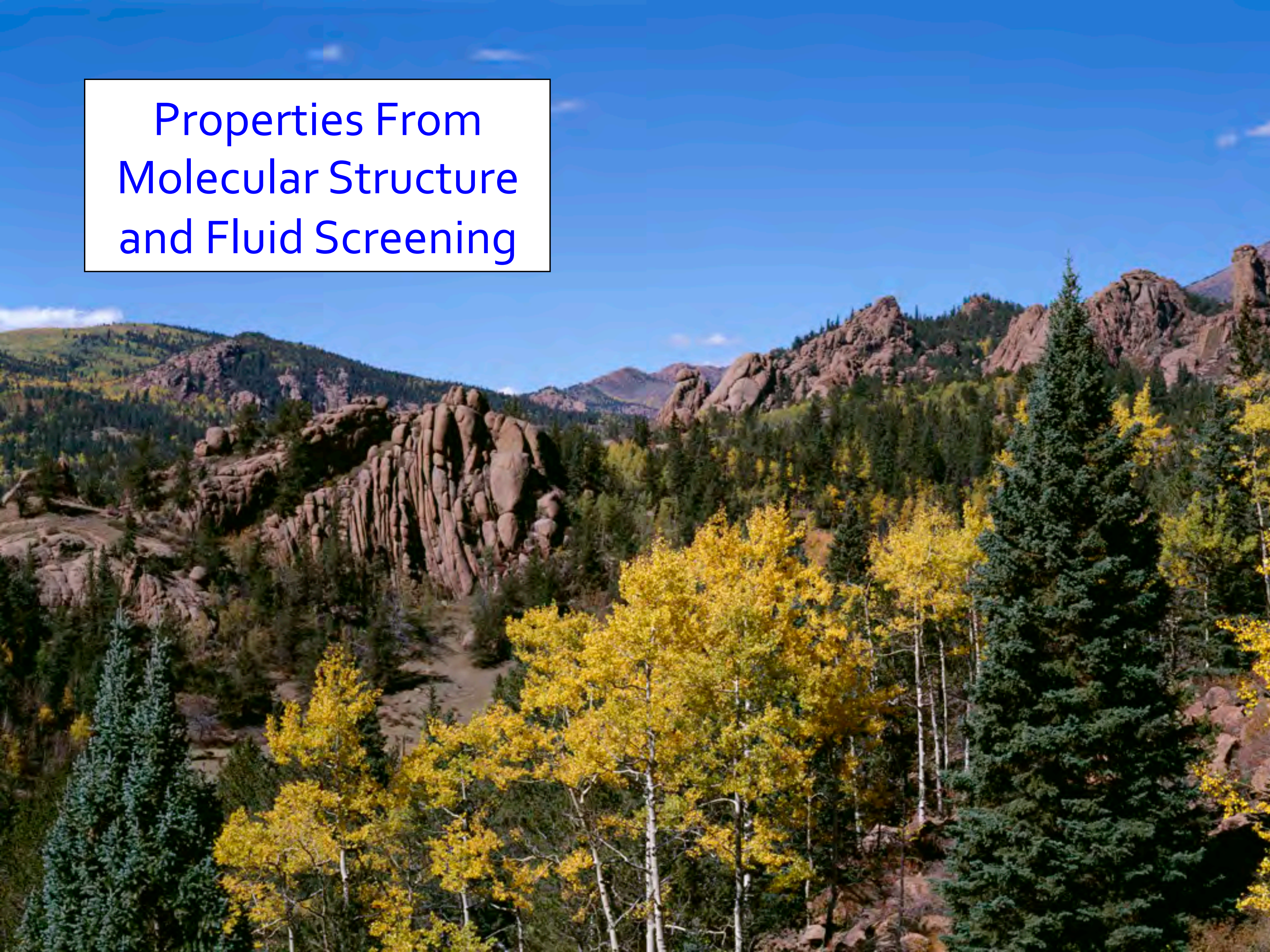
Cycle w/ LL-SL HX (or work recovery):

Same as above, except:

- Vapor heat capacity:
  moderate to high values optimal

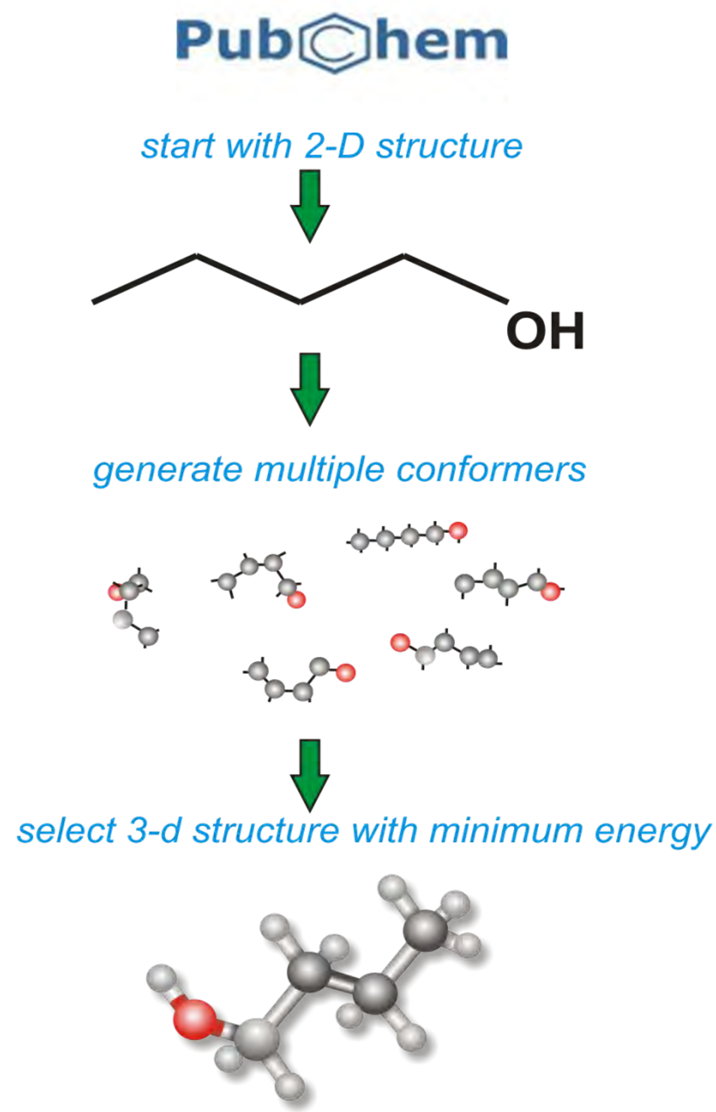


Properties From Molecular Structure and Fluid Screening



Fluid Screening

- Starting list: 100,000,000 compounds in PubChem data base (U.S. NIH)
- ≤15 atoms in molecule
  only C, H, N, O, S, F, Cl, Br
- Generate 3-D structure using quantum-mechanical methods
- All other properties follow from structure
- T^{crit}, T^{crit}/p^{crit}, ω correlated with "descriptors"
  (*e.g.*, molecular volume,
  charge surface density,
  "carbon types,"
  "molecular distance edges")



(First) Fluid Screening (2012)

	Remaining Fluid Count
• Starting list: 100,000,000 compounds in PubChem	
• ≤15 atoms in molecule only C, H, N, O, S, F, Cl, Br	56,203
• $GWP_{100} < 200$ ↪ NIST estimation method of Kazakov, *et al.* (2012)	52,265
• Toxicity screen ↪ markers/groups compiled by Lagorce, *et al.* (2008)	30,135
• Flammability: LFL > 0.1 kg/m^3 ↪ NIST estimation method of Kazakov, *et al.* (2012)	20,277
• Critical temperature: 300 K $< T^{crit} <$ 550 K ↪ NIST estimation method of Kazakov, *et al.* (2010)	1728
• Stability: screen out problematic groups (*e.g.*, peroxides, 3-member rings)	1234

(2nd) Fluid Screening (2015)

- Starting list: 198,000,000 compounds in PubChem
- ≤18 atoms in molecule
  only C, H, N, O, S, F, Cl, Br
- GWP_{100} < 1000
  ↪ NIST estimation method of Kazakov, *et al.* (2012)
- Flammability screen ↪ dropped
- Critical temperature: 320 K < T^{crit} < 420 K
  ↪ NIST estimation method of Kazakov, *et al.* (2015)
- Toxicity screen ↪ examine "manually"
- Stability screen ↪ examine "manually"

↪ Ensure that we did not eliminate viable candidates (flammable or moderate GWP might be acceptable)

Remaining Fluid Count

184,000

172,000

163

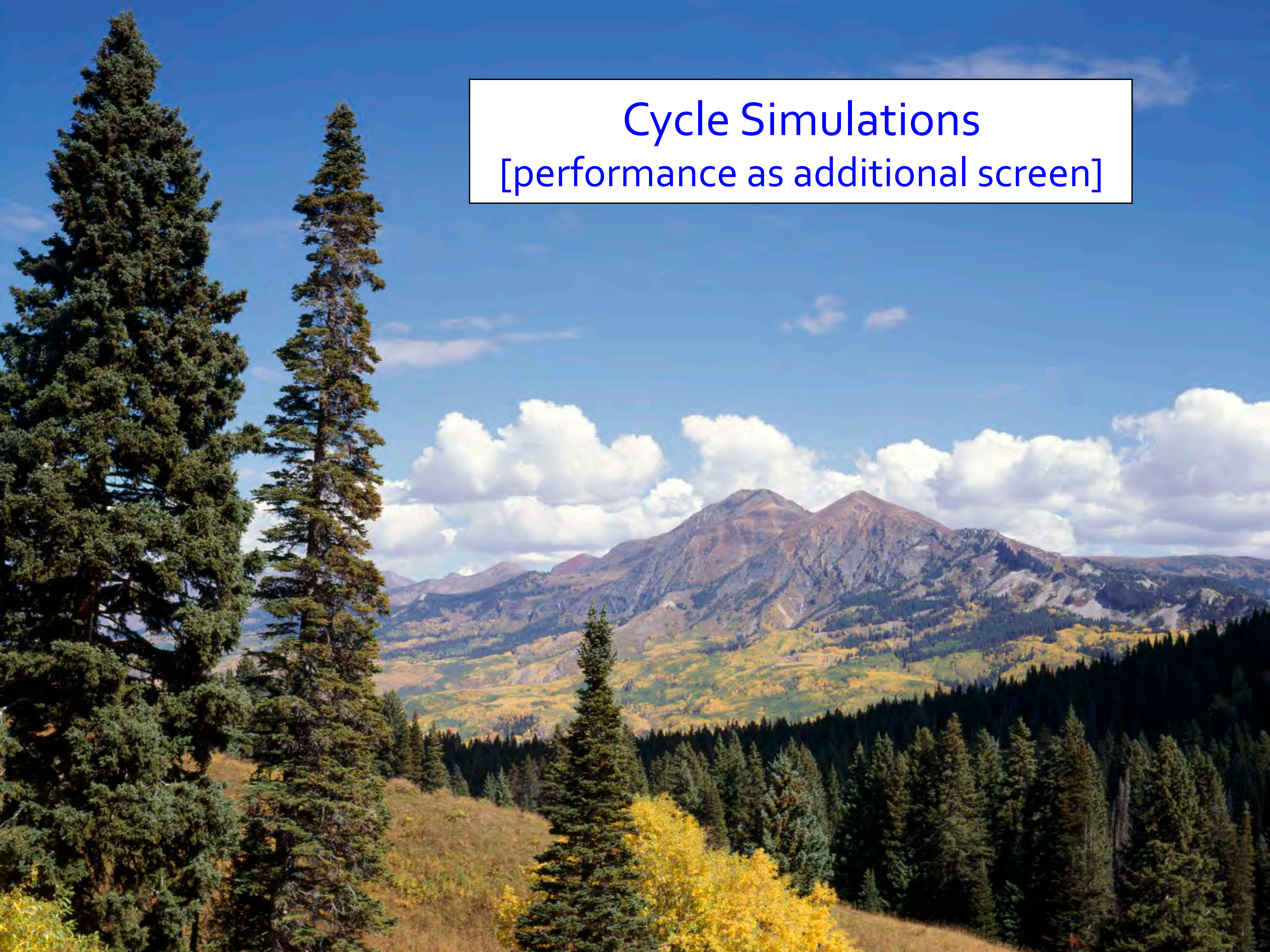
Screening of the DIPPR Database

DIPPR
Design Institute for Physical Properties
An AIChE Technology Alliance

- Starting list: 2,278 compounds
  - industrial fluids (*i.e.*, available)
  - wide range of properties included (T^{crit}, p^{crit}, etc.)
- Screen on critical temperature (no other filters applied)
- 59 fluids with 300 K < T^{crit} < 400 K
  - 26 also in PubChem screen, of the 33 remaining:
  - 17 CFCs and HCFCs (ODP and high GWP)
  - 8 HCl, HBr, etc. eliminated in 1st PubChem screen
- 8 fluids with elements other than C, H, N, O, S, F, Cl, Br, including: radon (radioactive); arsine (AsH_3, toxic & pyrophoric) phosphine (PF_5, toxic); silanes (flammable & toxic)

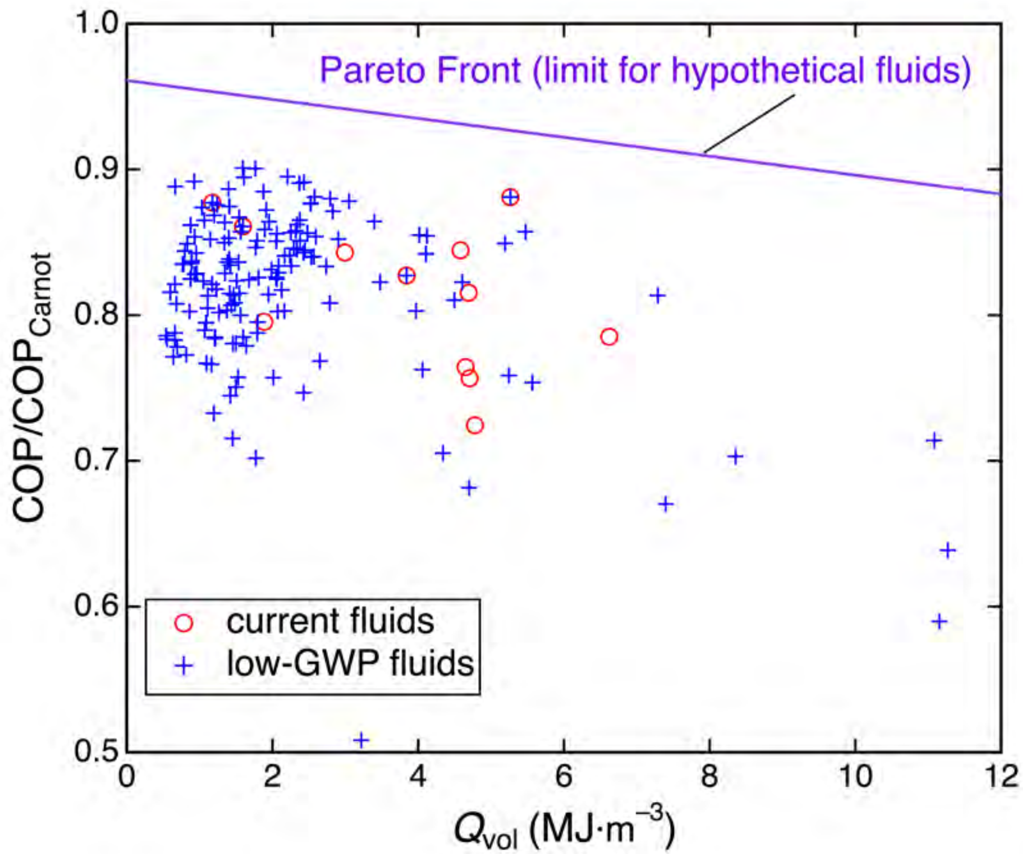
⤷ Original list of elements valid

Cycle Simulations
[performance as additional screen]



Cycle Simulations—Ideal Cycle

- Simple cycle
- Air-conditioning application: T_{evap} = 10˚C, T_{cond} = 40 ˚C
- 100 % compressor efficiency
- Zero pressure drops
- Plot COP/COP_{Carnot} for 163 candidates
- Low-GWP slightly lower COP
- Few candidates w/ high Q_{vol}



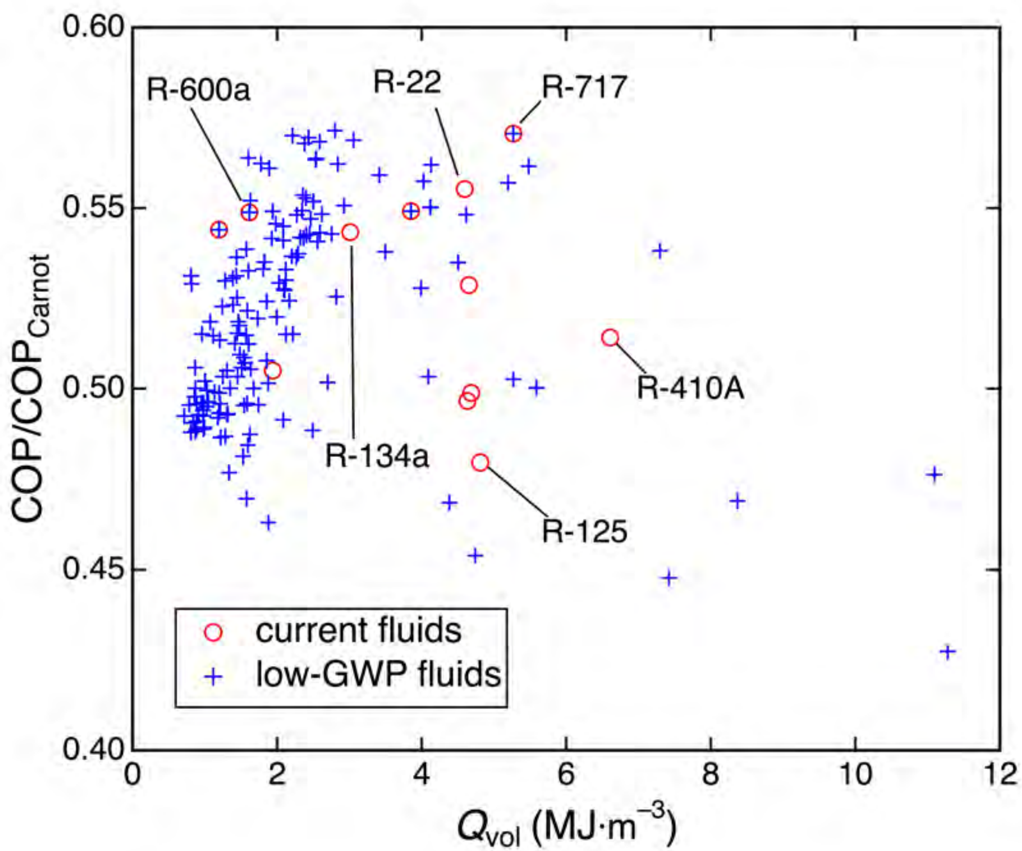
Cooling: T_{evap} = 10 ˚C, T_{cond} = 40 ˚C

Cycle Simulations—Compressor Efficiency & Pressure Drop

- Simple cycle
- Compressor efficiency ≈ 70 %
  $f\,(p_{cond}/p_{evap})$
- Pressure drops = f (fluid)
- Slightly larger penalty for low-capacity fluids
- COP vs. Q_{vol} tradeoff:
  ➔ Not! ⬅

↳Pareto optimization:
high p^{crit}, low C_p^o

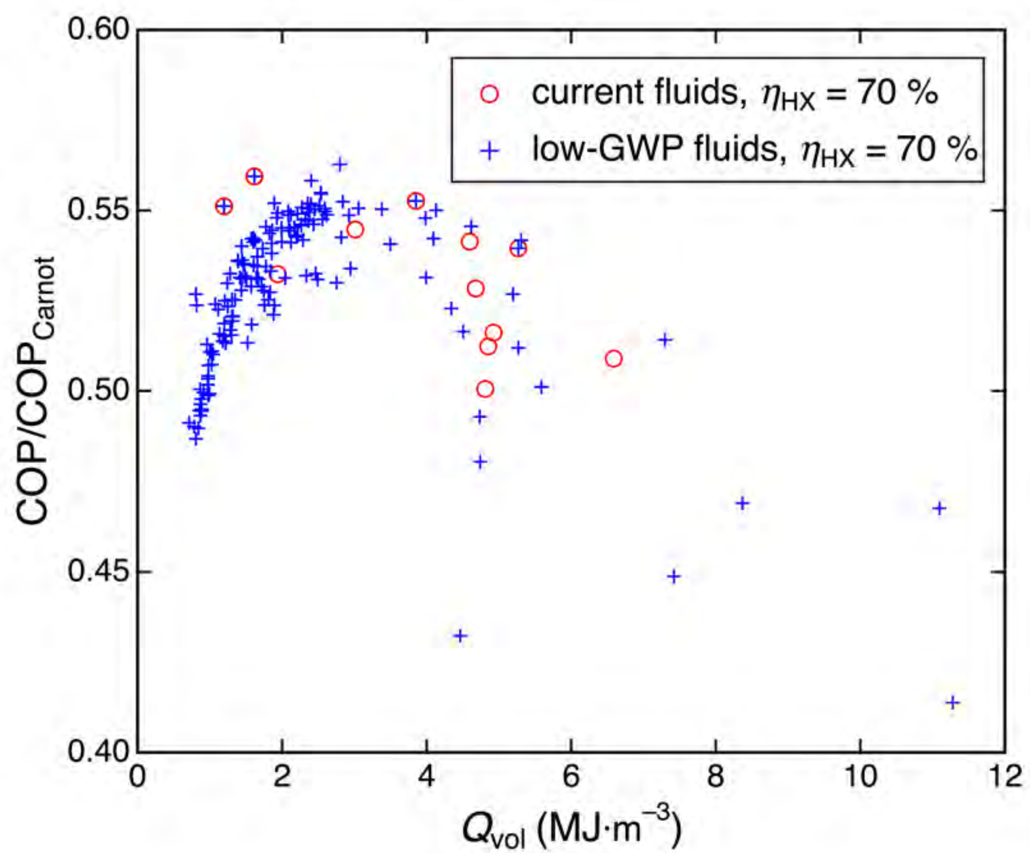
↳real fluids:
as molecular complexity ↑
T^{crit} ↑, p^{crit} ↓, C_p^o ↑



Cooling: T_{evap} = 10 ˚C, T_{cond} = 40 ˚C

Cycle Simulations—LL/SL HX (70 %)

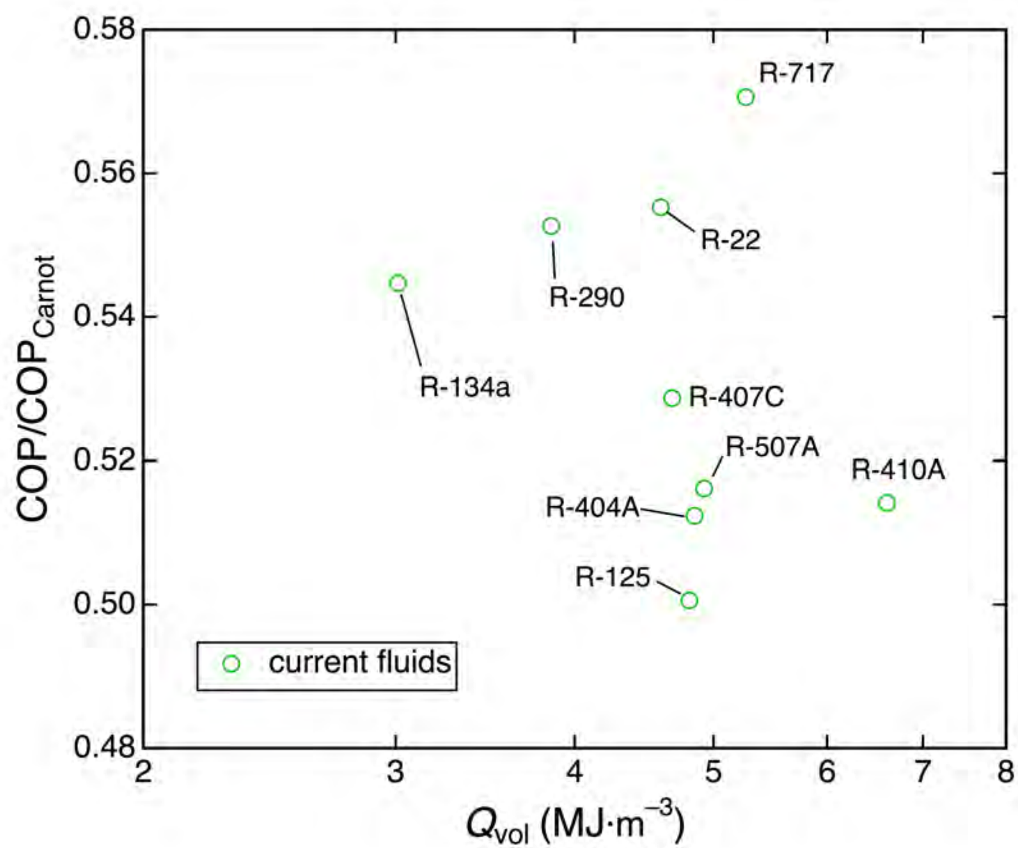
- Cycle with liquid-line/ suction-line heat exchanger with 70 % effectiveness
- Compressor efficiency ≈ 70 %
  $f\,(p_{cond}/p_{evap})$
- Pressure drops = f (fluid)
- Most fluids benefit
  ↳but effect varies
- Significantly less scatter
- Max in Q_{vol} at ~ 2.5 MJ/m^3



Cooling: T_{evap} = 10 ˚C, T_{cond} = 40 ˚C

Cycle Simulations—"Current" Fluids

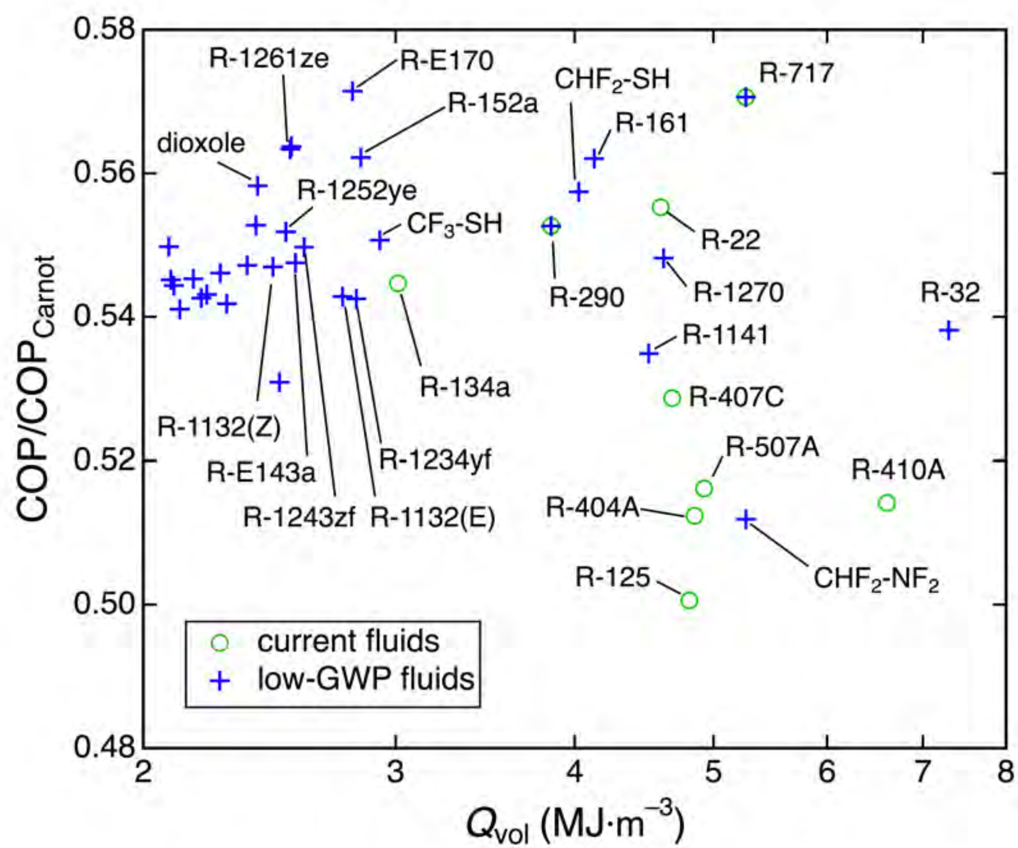
- As above except:
  - only higher-COP fluids
  - log-scale for Q_{vol}
  - limit range of Q_{vol}
- LL/SL-HX *if* COP improved (otherwise simple cycle)
- Current fluids for comparison



Cooling: T_{evap} = 10 ˚C, T_{cond} = 40 ˚C

Cycle Simulations—"Best" Low-GWP Fluids

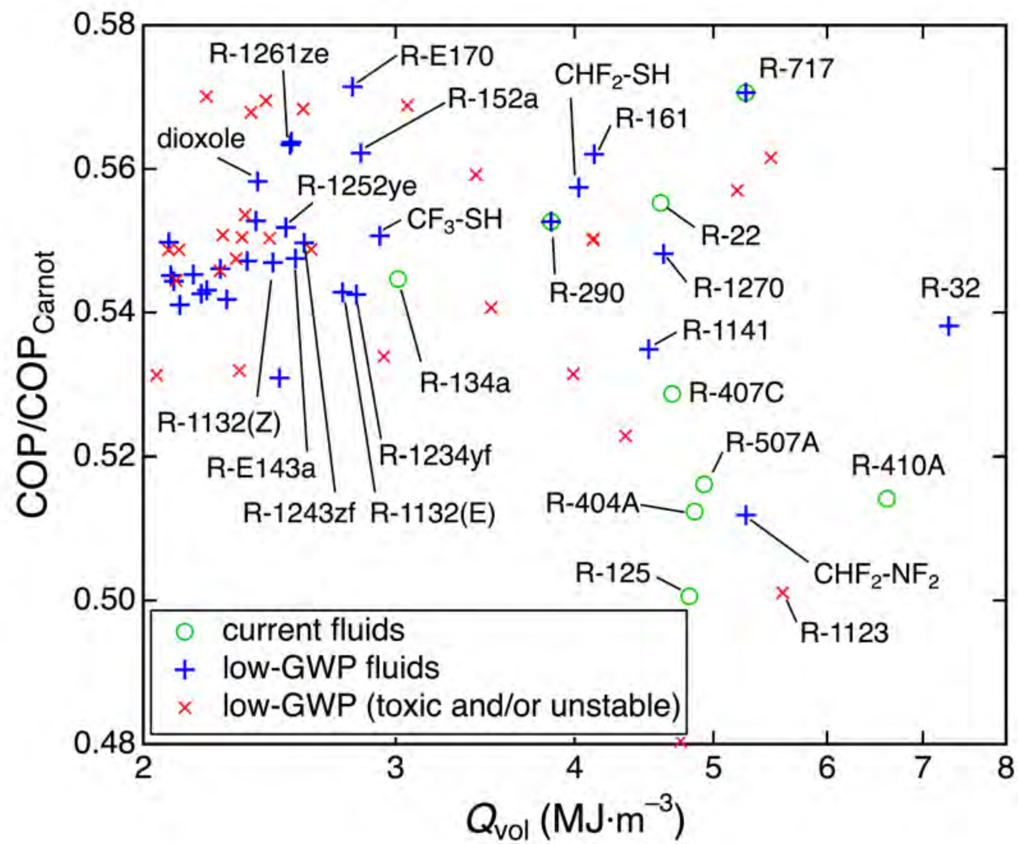
- R-717 (ammonia) and R-E170 (dimethylether): highest COPs
- Few candidates with $Q_{vol} \sim Q_{vol}$ (R410A or R22)
  ↳all flammable or slightly flam.
- 4 with $Q_{vol} > 8$ MJ/m^3
  ↳but low COP, flammable: R-41, acetylene, O=N-OF, 1,2-difluoroethyne [unstable]
- More with $(4 < Q_{vol} < 5)$ MJ/m^3:
  - R-717 (ammonia)
  - R-1270 (propylene)
  - R-290 (propane)
- And $(2.4 < Q_{vol} < 2.7)$ MJ/m^3:
  - R-152a, several HFOs



Cooling: T_{evap} = 10 ˚C, T_{cond} = 40 ˚C

Cycle Simulations—Also Toxic/Unstable Fluids

- As above except:
  - only higher-COP fluids
  - log-scale for Q_{vol}
  - limit range of Q_{vol}
- LL/SL-HX *if* COP improved (otherwise simple cycle)
- Distribution of toxic/unstable fluids similar to “viable” candidates

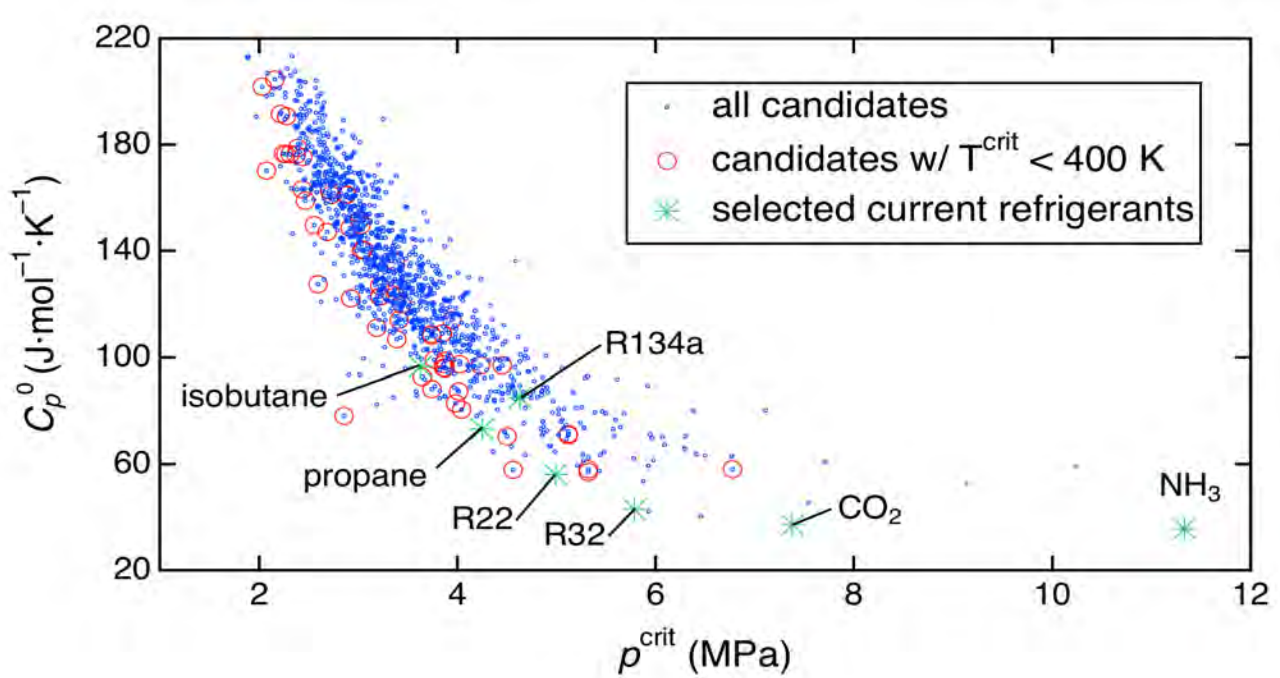


Cooling: T_{evap} = 10 ˚C, T_{cond} = 40 ˚C

Is that all there is, Really?

Tradeoffs—Chemical Reality

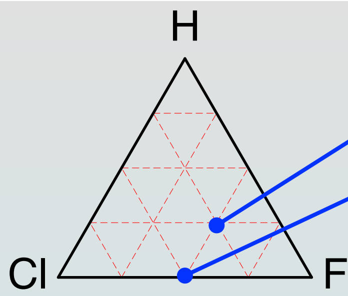
- Cycle analysis:
  ↪high p^{crit}, low $C_p{}^0$ optimal for simple cycle
- High p^{crit}, low $C_p{}^0$ sparsely populated by real fluids
- Thermodynamics *allows* better fluids,
  but chemistry does not cooperate!



Constraints on Molecular Structure (1)

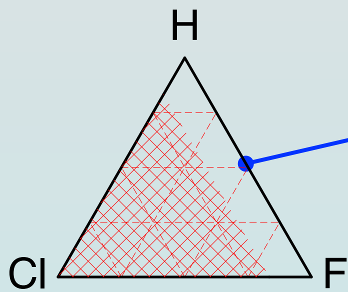
Why are the low-GWP fluids more complex?

- "Anything goes":
  1 carbon:



R22 (T_{NBP} = –41 ˚C, GWP = 1760)
R12 (T_{NBP} = –30 ˚C, GWP = 10200)
↳also ozone-depleting

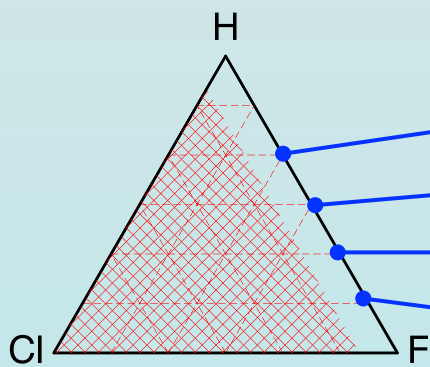
- ODP constraint:
  1 carbon:



R32* (T_{NBP} = –52 ˚C, GWP = 677)

* flammable

2 carbons:



R152a* (T_{NBP} = –24 ˚C, GWP = 138)
R143a* (T_{NBP} = –47 ˚C, GWP = 4800)
R134a (T_{NBP} = –26 ˚C, GWP = 1300)
R125 (T_{NBP} = –48 ˚C, GWP = 3170)

Constraints on Molecular Structure (2)

Low-GWP further constrains choices

- HFCs R32 & R152a
  - ⤷ flammable, moderate GWP
- Carbon-carbon double bond (HFOs):
  - ⤷ reactive with OH, low GWP

    2 carbons:

    low boiling point for most

    R1132(E), R1132(Z) ???

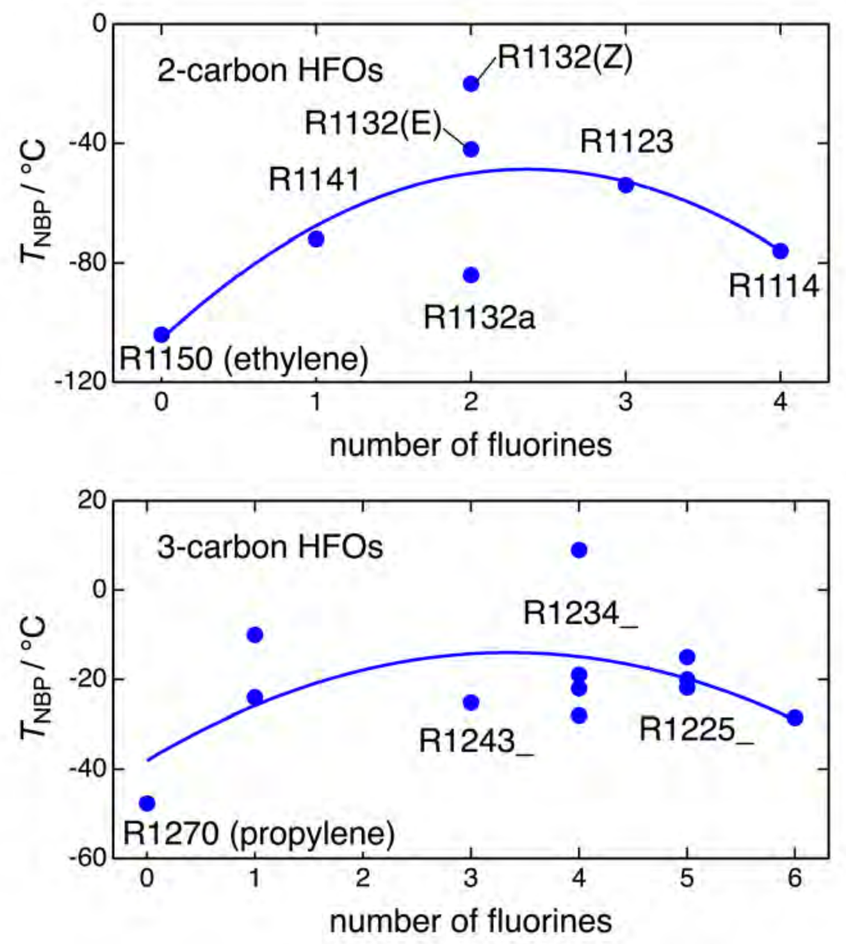
    others toxic or unstable

    3 carbons:

    boiling point in good range

    R1234yf, other R1234 isomers with higher boiling points

    others are somewhat toxic or flammable

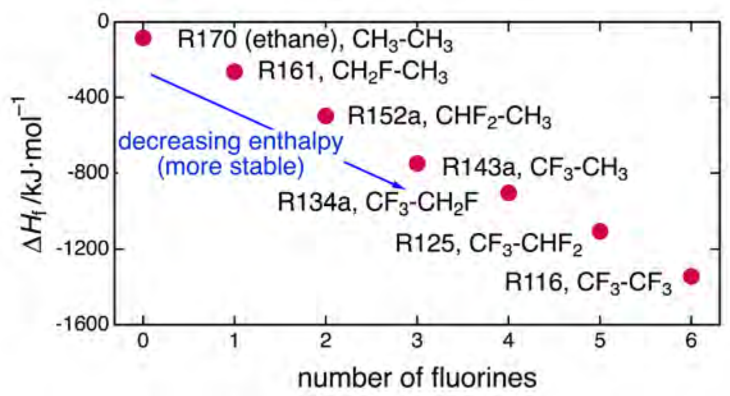


Why Fluorine?

Replacing H with F reduces flammability
But how?

- Combustion is reaction with oxygen, with release of heat
- Reactions proceed if Gibbs energy is reduced
  (*i.e.*, products have lower energy [are more stable] than reactants)
  $G = H - TS$;
  if: $[(H - TS)_{products} - (H - TS)_{reactants}] < 0$ ➥ reaction is favored
  enthalpy term is (usually) dominant
  ➥ reaction proceeds if heat is released (ignoring kinetics)
- Carbon–fluorine bond is strongest (most stable) single bond

Enthalpy of formation for ethane-series (2-carbon) HFCs

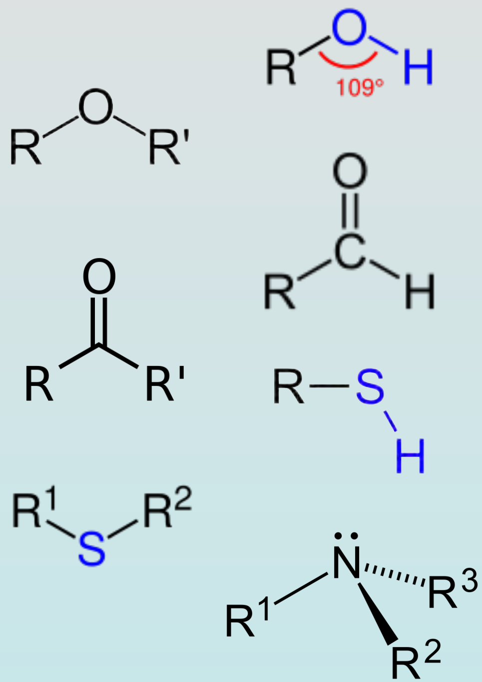


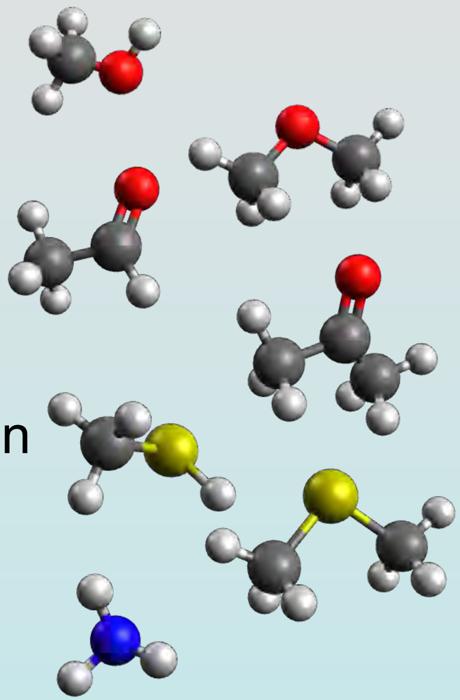
Other Functional Groups?

Why the focus on simple fluorocarbons? (HFCs, HFOs)

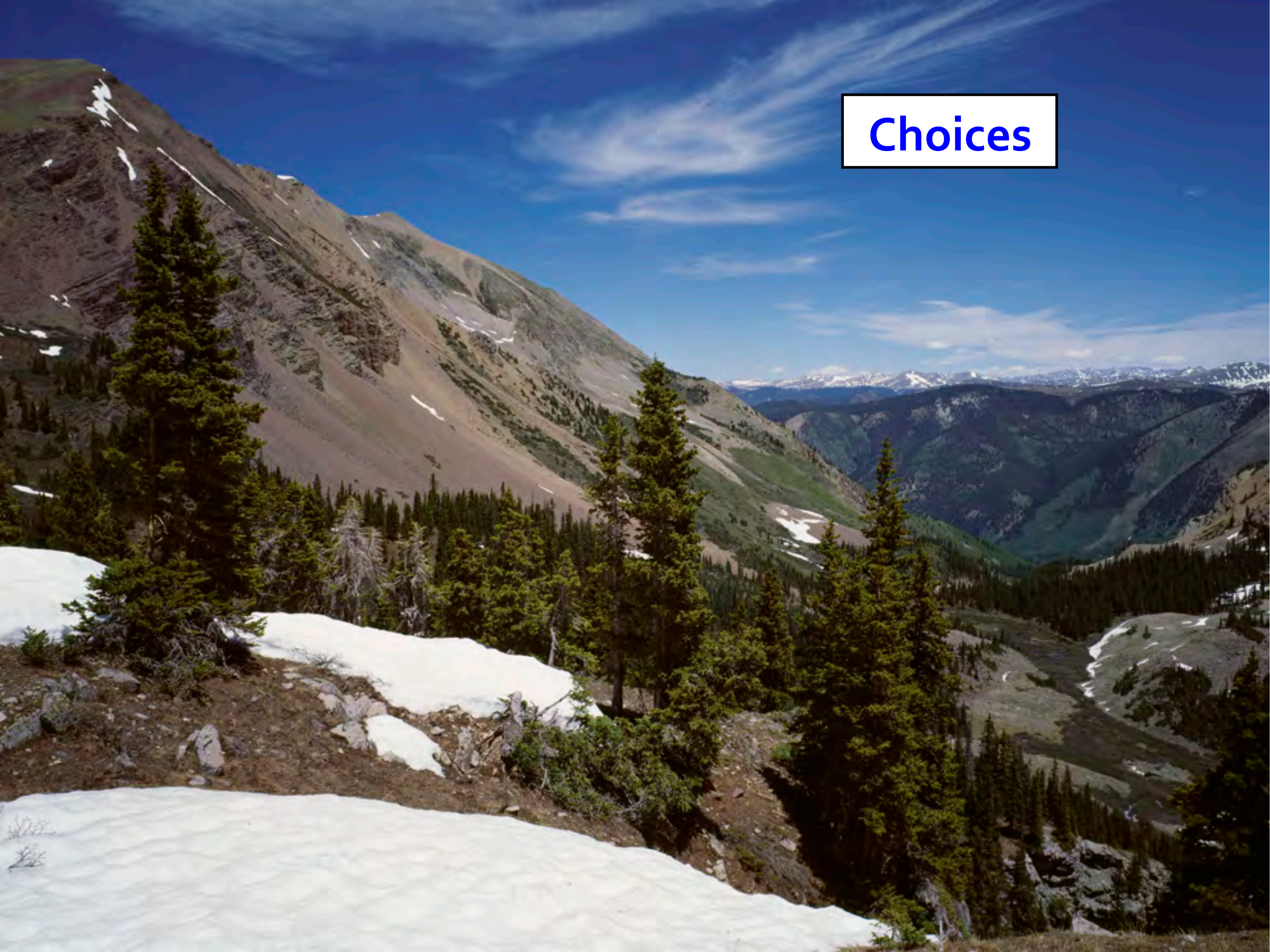
Name	Simplest Example	T_{NBP}/°C
alcohol	methanol	65
ether	dimethylether	–25
aldehyde	acetaldehyde	20
ketone	acetone	56
thiol	methylmercaptan	6
thioether	dimethylsulfide	38
amine	ammonia	–33

Functional Group





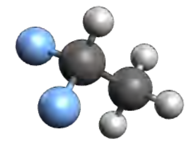
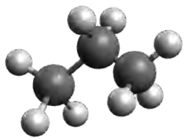
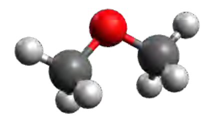
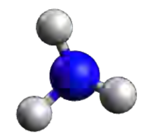
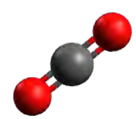
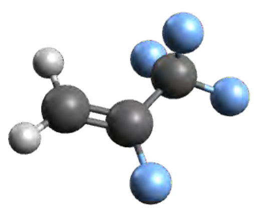
- Included in PubChem screening


Choices

So What are the Choices (1)?

Medium & high pressure refrigerants in positive-displacement compressors:
21 candidates identified in paper

- HFCs: R-32, R-152a, R-41, R-161
  - ↳familiar, but low-GWP are flammable
- HCs (hydrocarbons) & dimethylether
  - ↳flammable, ASHRAE class A3
- NH_3 (ammonia)
  - ↳excellent thermodynamics, ASHRAE B2L
- CO_2 (carbon dioxide)
  - ↳ASHRAE A1
  - ↳high operating pressures, supercritical cycle (not simulated here)
- HFOs (hydrofluoroolefins)
  - ↳*e.g.*, R-1234yf (ASHRAE A2L)
  - ↳but others more flammable or somewhat toxic

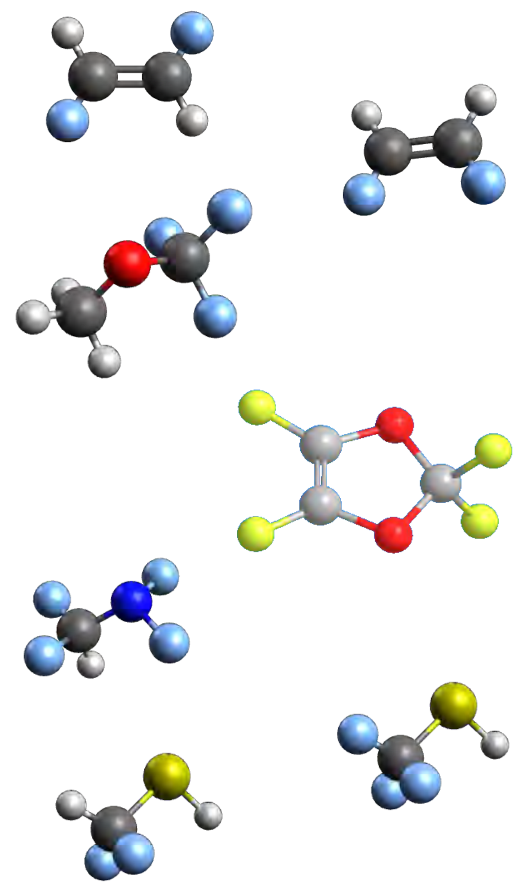
So What are the Choices (2)?

"Novel" compounds identified

- HFOs:
  - R-1132(E) & R-1132(Z): flammable
- Fluorinated oxygenates
  - R-E143a: GWP = 523
  - 2,2,4,5-tetrafluoro-1,3-dioxole

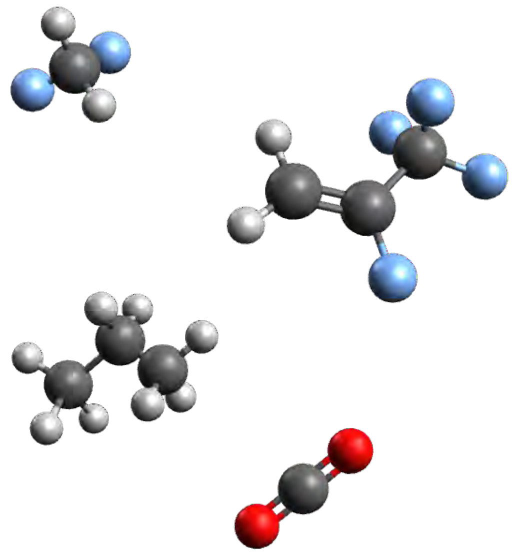
    cyclic ether with C-C double bond

    unknown hazards, could it be made?
- Nitrogen or sulfur containing:
  - long shots (toxicity, corrosivity, odor)



So What are the Choices (3)?—Blends

- Use blends to:
  - ➥adjust properties
  - ➥azeotropes can give higher Q_{vol} than pures
  - ➥allow use of additional components (flammable or moderately toxic?)
- HFO + HFC:
  - ➥proposed and currently under test
- HFO + HFO
- Blends with hydrocarbons:
  - ➥likely to be flammable if HC > 5 %
- Blends with CO_2:
  - ➥adjust properties (raise pressure & Q_{vol})



Discussion

Refrigerant "Generations"
[J. Calm, *Int. J. Refrig.* **31**:1123 (2008)]

- 1st: "whatever worked" (CO_2, SO_2, NH_3, HC …)
- 2nd: "safety & durability" (CFCs, HCFCs)
- 3rd: "ozone protection" (HFCs,
  resurgence of CO_2, NH_3, HC)
- 4th: "global warming concerns" (HFOs …)

Will there be a fifth Generation?

→ No! ←

- All of the candidates are on the table
- We have hit the bounds allowed by chemistry

Discussion

A Paradigm Change in Refrigerant Selection?

- No longer just: thermodynamics,
  engineering,
  economics
- But also: public acceptance & public relations
- Not: find the fluid that fits your cycle/application
- But: select a fluid based on your comfort with GWP, flammability, “natural vs. synthetic” …

— and —

Design the cycle accordingly

In Conclusion

- Thermodynamics *allows* better fluids
  - optimum parameters: simple molecules
  - possibilities limited by chemistry
- Tradeoffs are inevitable
  - low-GWP options comparable to current fluids
- That's all there is—*really*!
  - pick your fluid and design cycle accordingly

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Thank You!
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