The Future of Refrigerants

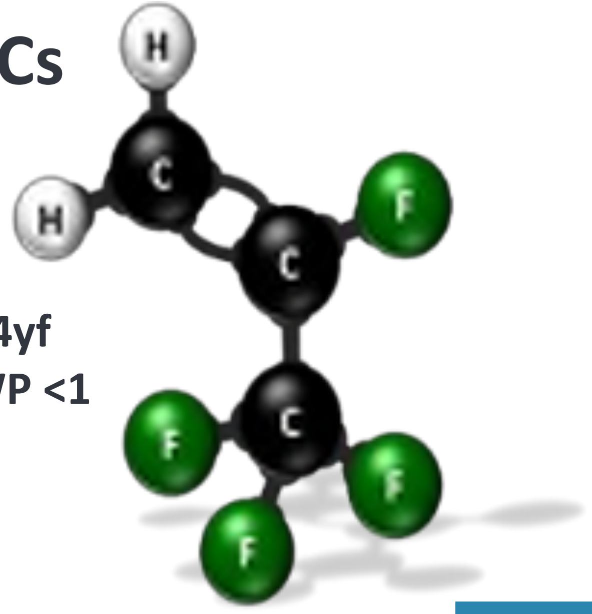
Steve Kujak
Director
Next Generation Refrigerant Research
TRANE TECHNOLOGIES

Distinguish Lecturer Series
Version 091223

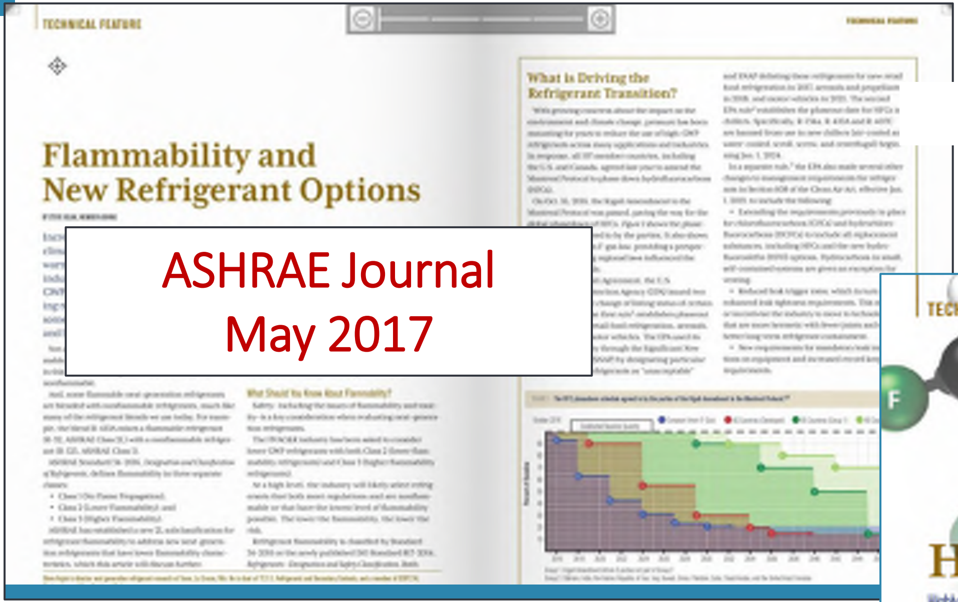
Agenda - Outline

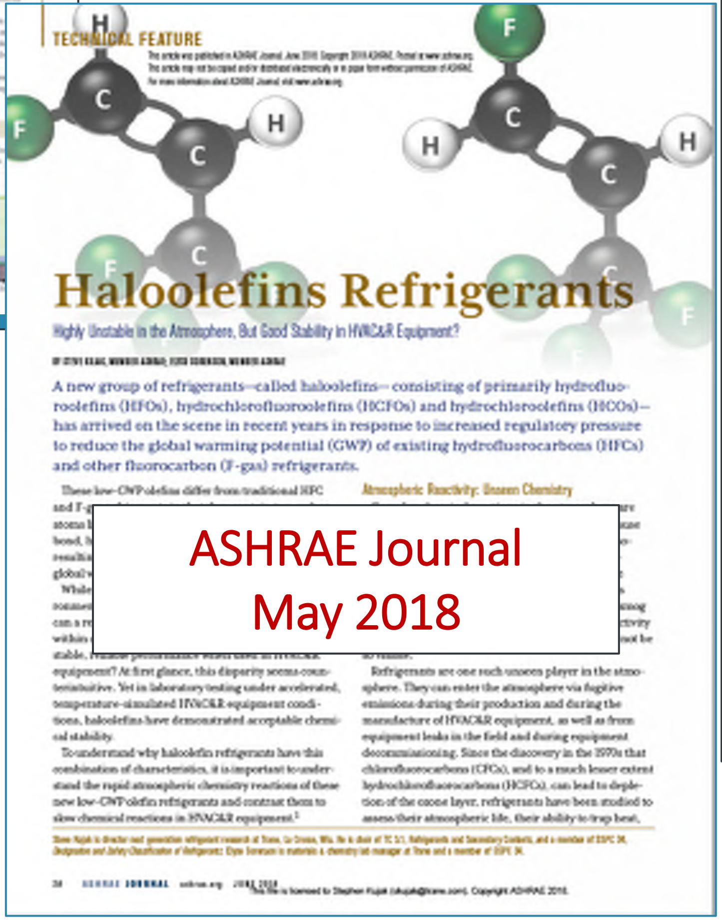
- Brief History of Refrigerant
- Global Warming Potential of Refrigerants and Their Impacts
- Review of HFC Refrigerant Regulations & Regulatory Mechanisms
- Sustainable Refrigerant Selection & Challenges
- Review of Lower GWP Refrigerant Options For Various HFCs
- Summary & Conclusions
- Q&A

R1234yf
A2L GWP <1



Background – Articles on Regulatory, Basics & Flammability

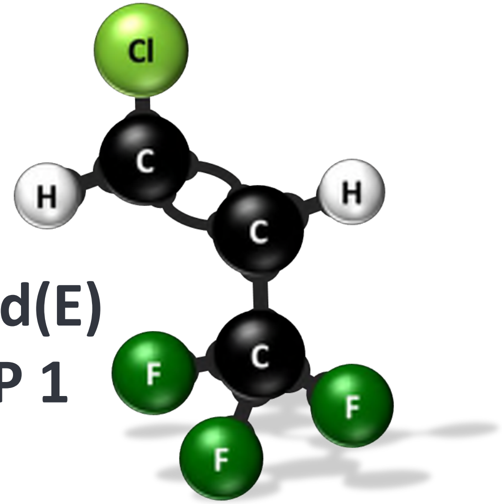




Learning Objectives

1. Describe HFC regulations, regulatory mechanisms and timelines.
2. Explain the challenges when selecting new refrigerants.
3. Provide an update on new lower GWP alternatives and highlight some important considerations, particularly flammability, that engineers, designers, and building owners should keep in mind regarding next-generation refrigerants.

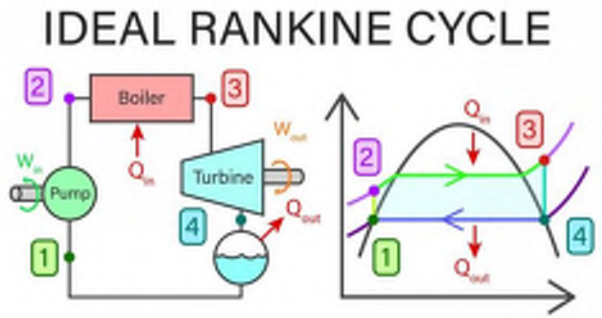
Putting the focus on the "R" in ASHRAE



R-1233zd(E)
A1, GWP 1

Four Generational Search for “Perfect” Reverse Rankine Refrigerants

William Rankine
Theory of Heat Engines
“Rankine Cycles”



Thomas Midgley

Albert Henne

1st Generation *“What Ever Worked”*	2nd Generation *“Safety and Stability”*	Environmental Sustainability Generations (Direct & Indirect) Refrigerant GWP & Energy Efficiency	
1830’s – 1930’s	1930’s – 1990’s	1990’s – 2030	2010 - 2050
• Limited applications mainly industrial • “Poor safety & cost”	• Innovation enabled exponential societal improvements	Preserved 2nd gen. innovations, safety, stability and efficiency	• Fewer choices • Safety and design challenges
• NH_3 • CO_2 • Various Hydrocarbons • H_2O • **Sulfur Dioxide** • Methyl Chloride (R40)	• NH_3 • CFCs and HCFCs o R11 o R12 o R22 o R502	• NH_3 • HCFCs & HFCs o R22 o R123 o R134a o R410A o R404A o Many Blends	• NH_3 • Low GWP HFCs & HFOs o R1233zd(E) o R1234yf & R1234ze(E) o HFC/HFO blends • Renewed “Natural” interest o CO_2 o Hydrocarbons

Societal Demands for Higher Standard of Living Drove Refrigerant Innovations

Why Synthetic Refrigerants?
Optimizing for Safety – Efficiency - Design – Applications

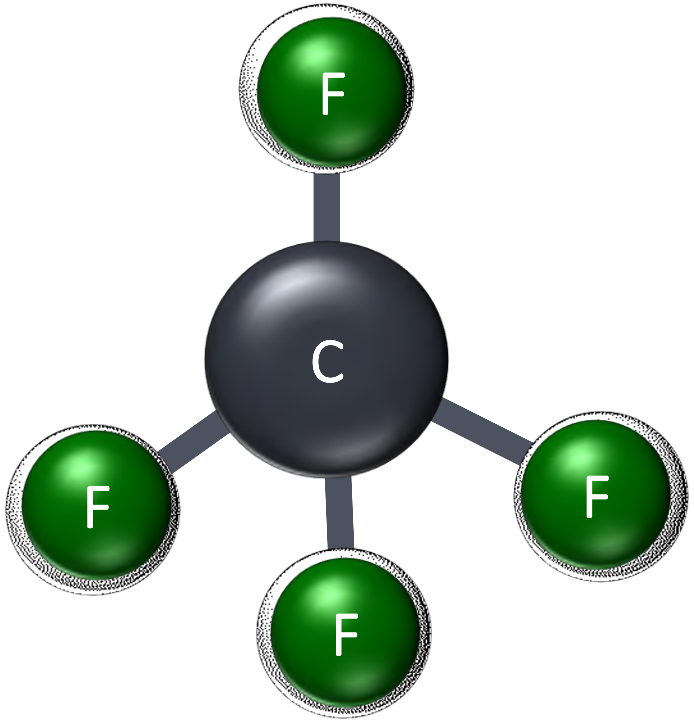
Thomas Midgley Albert Henne

2nd Generation
"Safety and Stability"

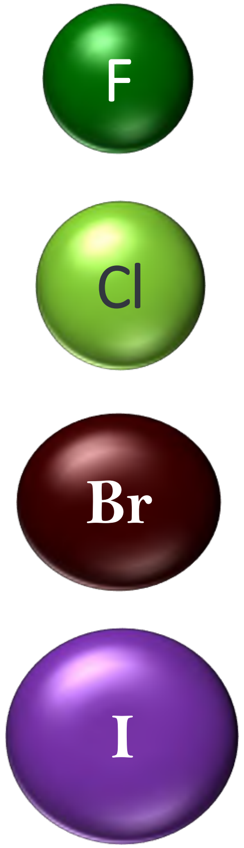
1930's – 1990's

- Innovation enabled exponential societal improvements

- NH_3
- CFCs and HCFCs
  - R11
  - R12
  - R22
  - R502



R-14
ASHRAE Flammability Class 1
GWP - 6630



Halogens

Why Synthetic Refrigerants?
More Potential Rankine Fluid Options

Thomas Midgley

Albert Henne

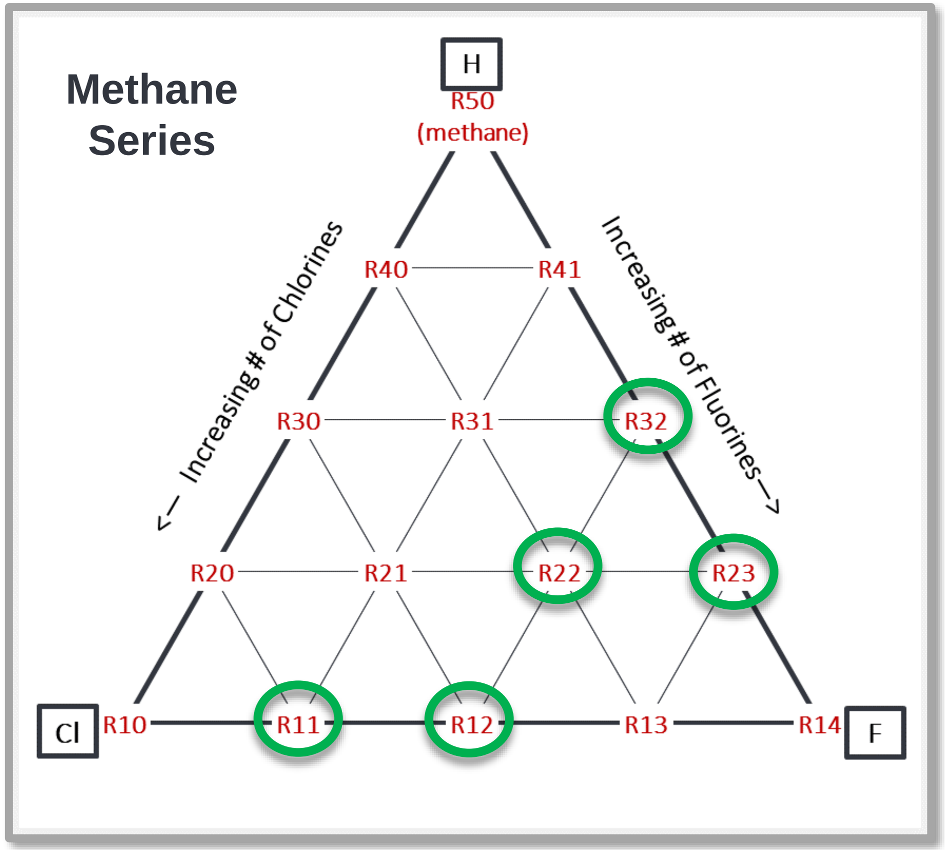
2nd Generation
"Safety and Stability"

1930's – 1990's

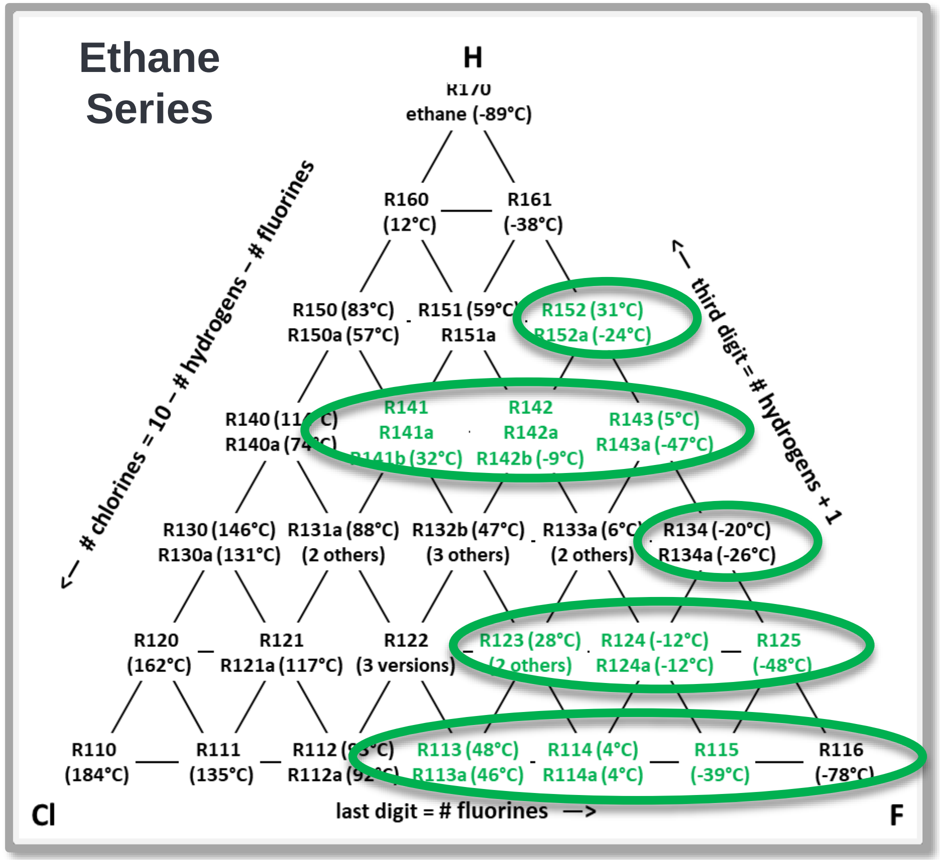
- Innovation enabled exponential societal improvements

- NH_3
- CFCs and HCFCs
  - R11
  - R12
  - R22
  - R502

CFCs, HCFCs, HFCs



14 New Molecules from 1 Methane



55 New Molecules from 1 Ethane

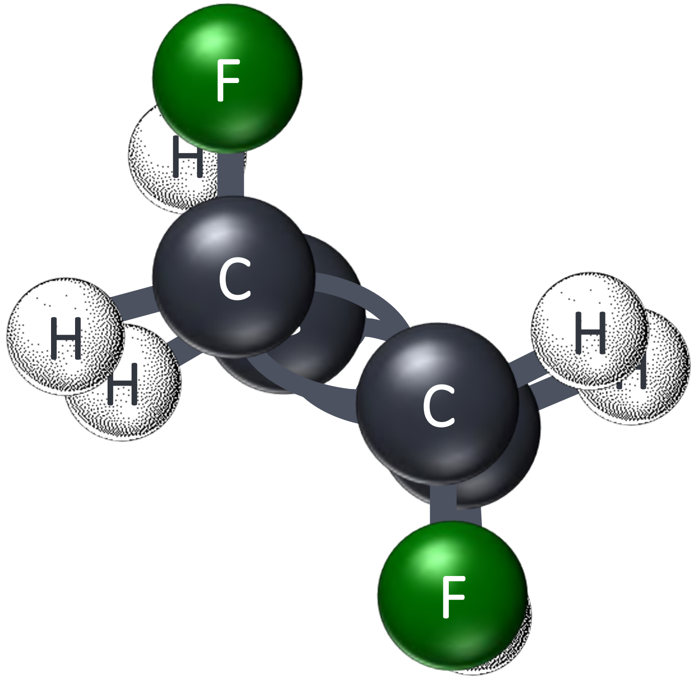
Designing Synthetic Refrigerants for Low GWP?
Optimizing for Safety – Efficiency - Design – Applications

4th Generation
"Global Warming"

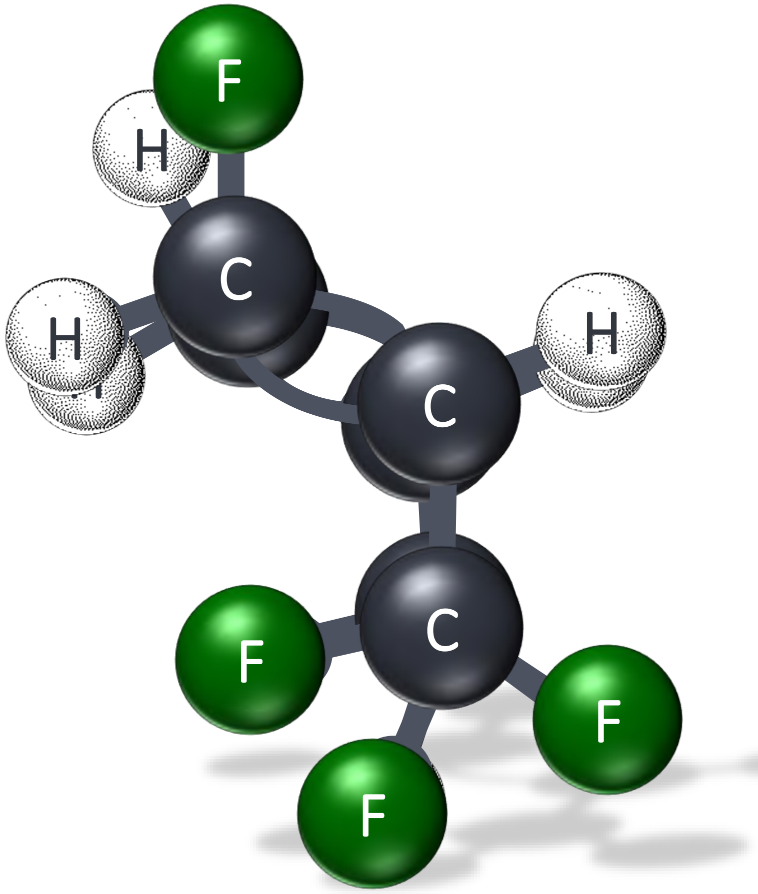
2010's – 2050's

- Fewer choices
- Safety and design challenges

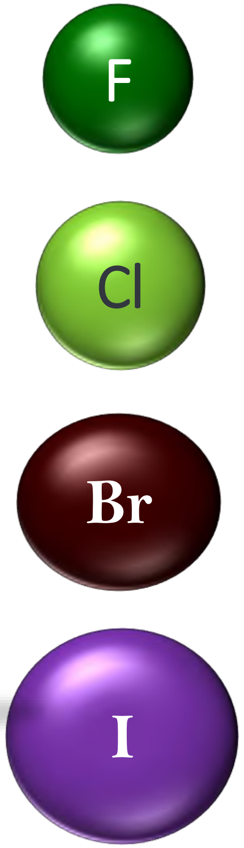
- NH_3
- Low GWP HFCs & HFOs
  - R1233zd(E)
  - R1234yf & R1234ze(E)
  - HFC/HFO blends
- Renewed "Natural" interest
  - CO_2
  - Hydrocarbons



Ethene R-1150 / R-1132(E)
ASHRAE Class A3 / A2
GWP – 20 / 1



Propene R-1270 / R-1234ze(E)
ASHRAE Class A3 / A2L
GWP – 2 / 6



Halogens

Global Warming Potential of Refrigerants and Their Impacts

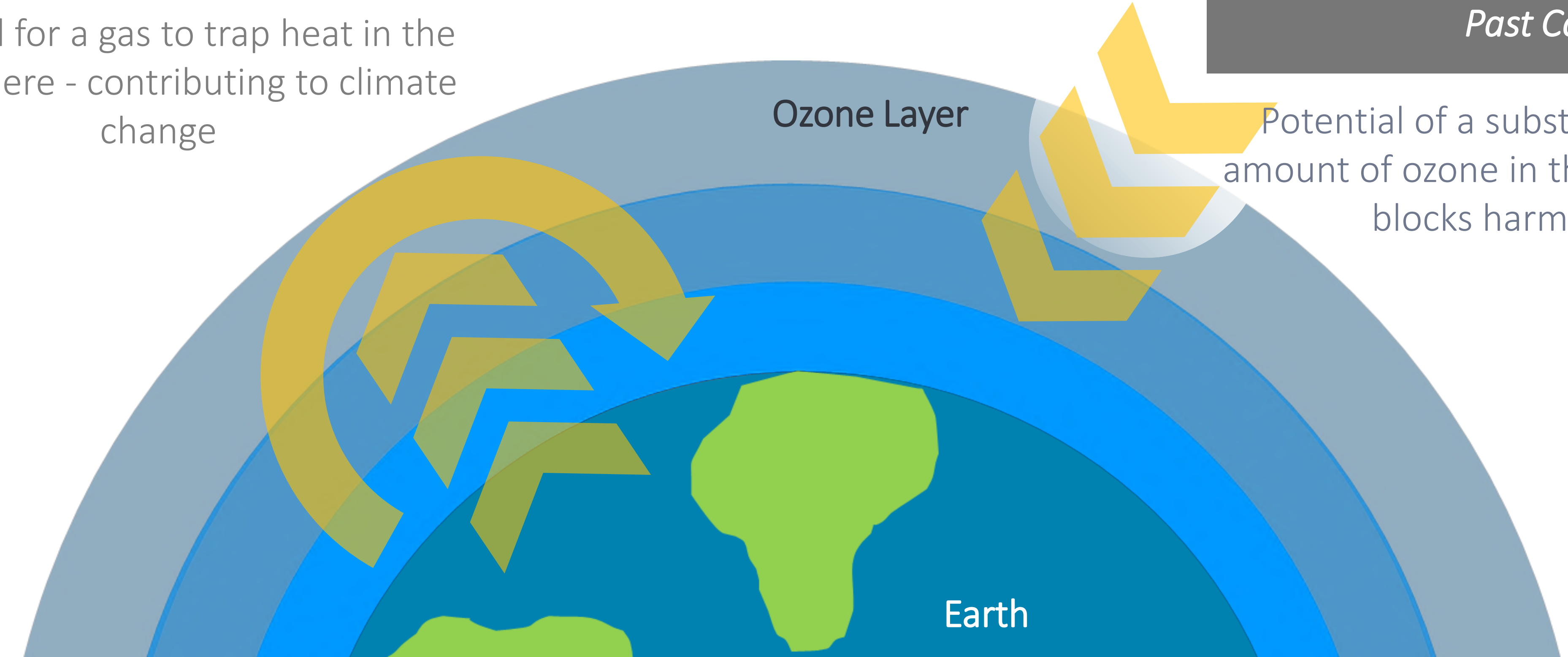
Why Are Refrigerants Transitioning?

Global Warming Potential (GWP)
Current Concern

Potential for a gas to trap heat in the atmosphere - contributing to climate change

Ozone Depletion Potential (ODP)
Past Concern

Potential of a substance to reduce the amount of ozone in the atmosphere which blocks harmful radiation



How is GWP of a Gas Calculated?

Global warming potential (GWP) is the heat absorbed by any gas in the atmosphere, as a multiple of the heat that would be absorbed by the same mass of CO_2 over a specified time, e.g., 20 or 100 years. All effects beyond 20 or 100 years are disregarded. The GWP value depends on how the gas concentration and CO_2 concentration decays over time in the atmosphere.

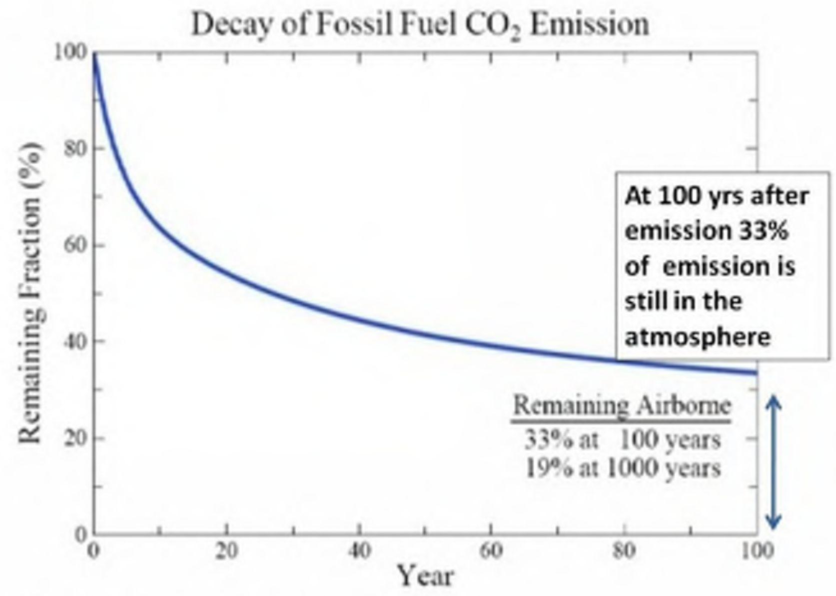
$$GWP(x) = \frac{a_x}{a_r} \frac{\int_0^{TH} [x](t)\, dt}{\int_0^{TH} [r](t)\, dt}$$

Gas / CO_2

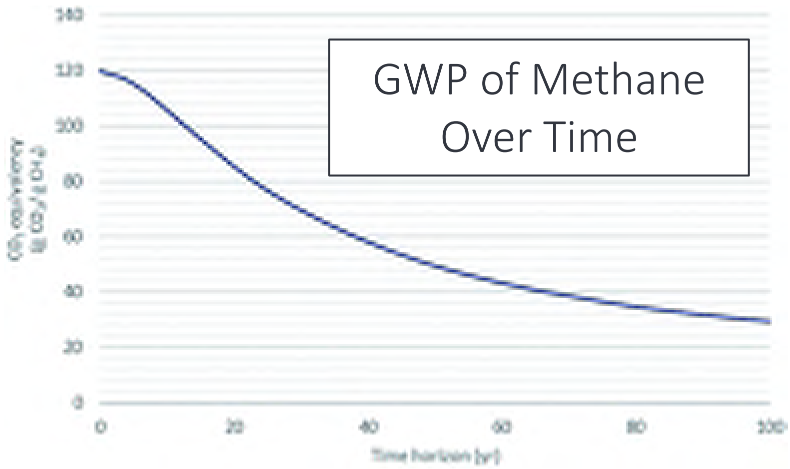
Time Horizon

Radiative Efficiency
*Not necessarily
Linear over time

Concentration
Decay Rate

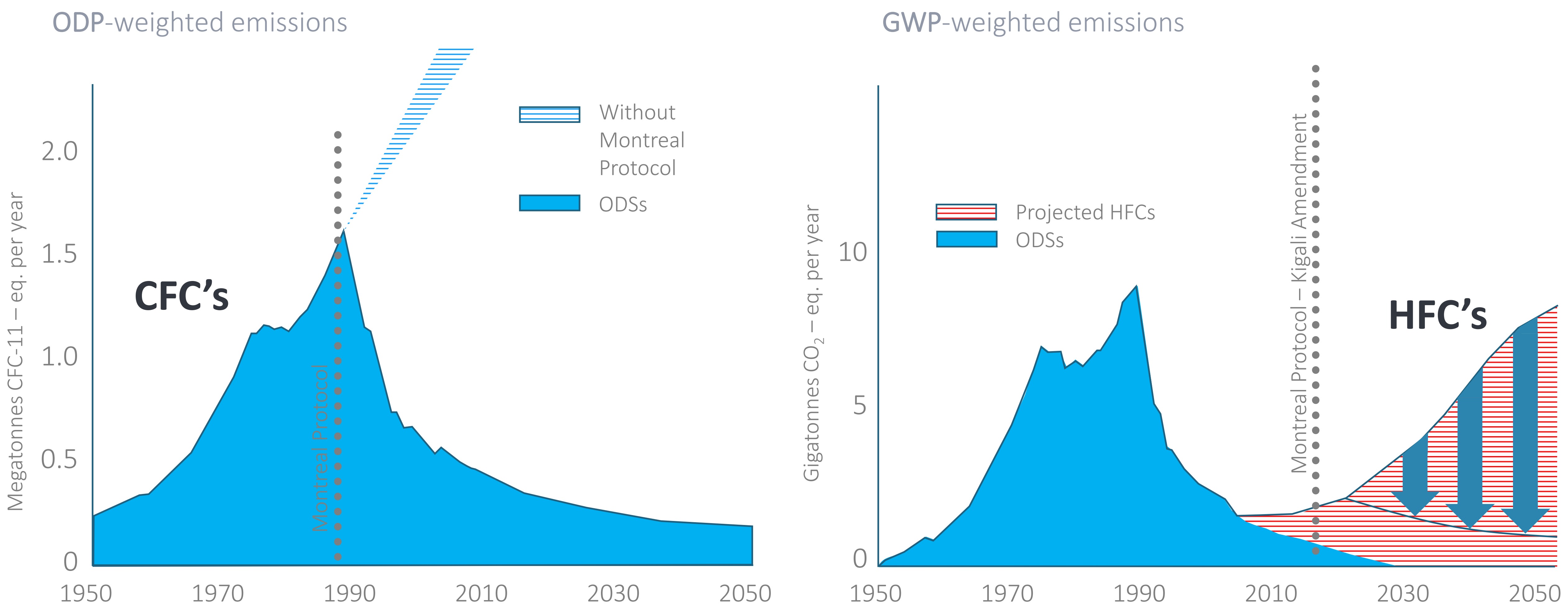


IPCC 2007 Science Technical



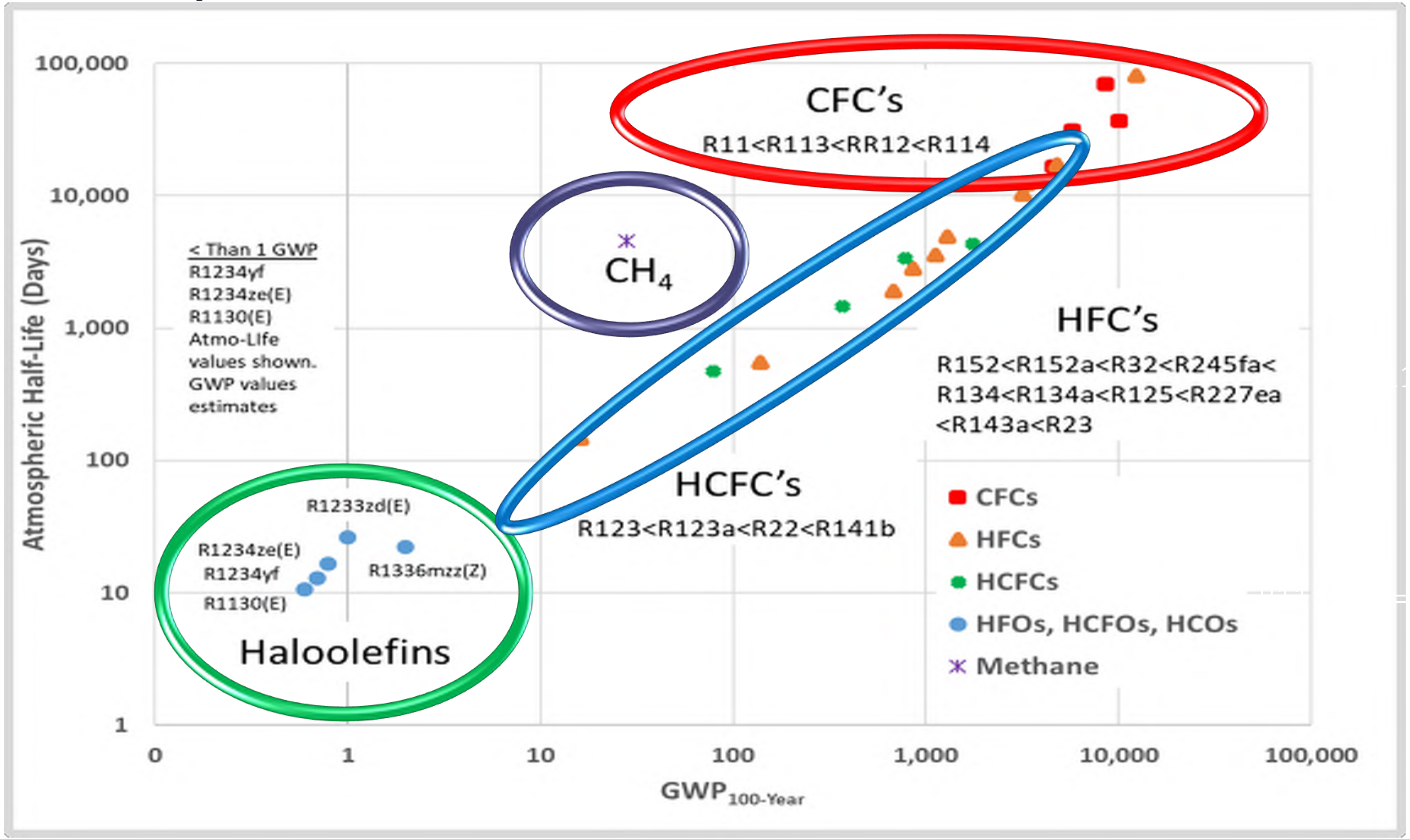
UNEP Climate Assessment Reports Determine and Publish GWP Values (AR1-AR6)
Regulators Using AR4 100 Year Time Horizon for Gases

Refrigerant Global Warming Impacts



Source: Velders et al., PNAS (2009)

F-Gases Atmospheric Life vs GWP

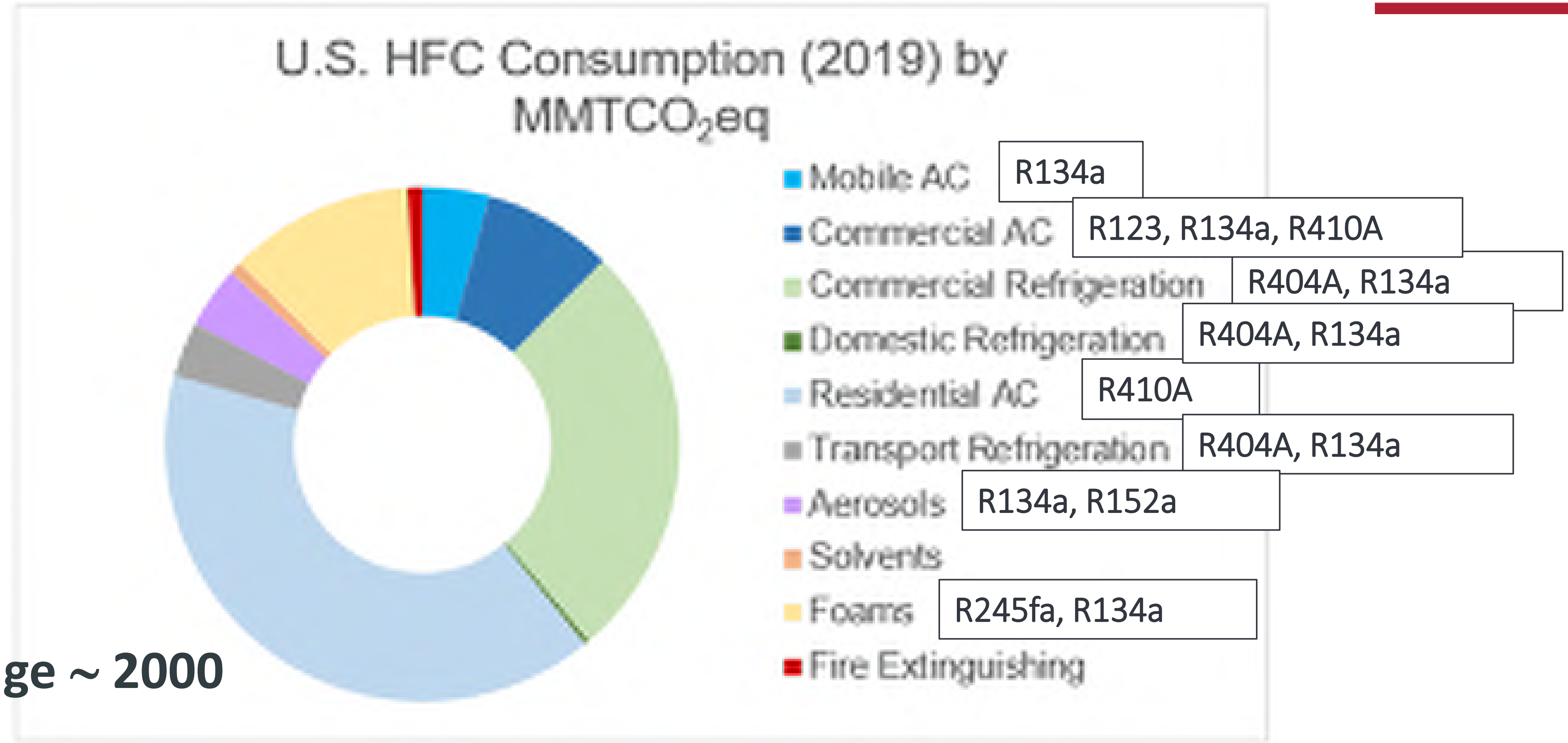


Two Choices

Possible Actions: Reduce Emissions Or Shorter Atmospheric Life or Both

HFC Regulations & Regulatory Mechanisms

Today - HFCs Used by Category (GWP Based Consumption)



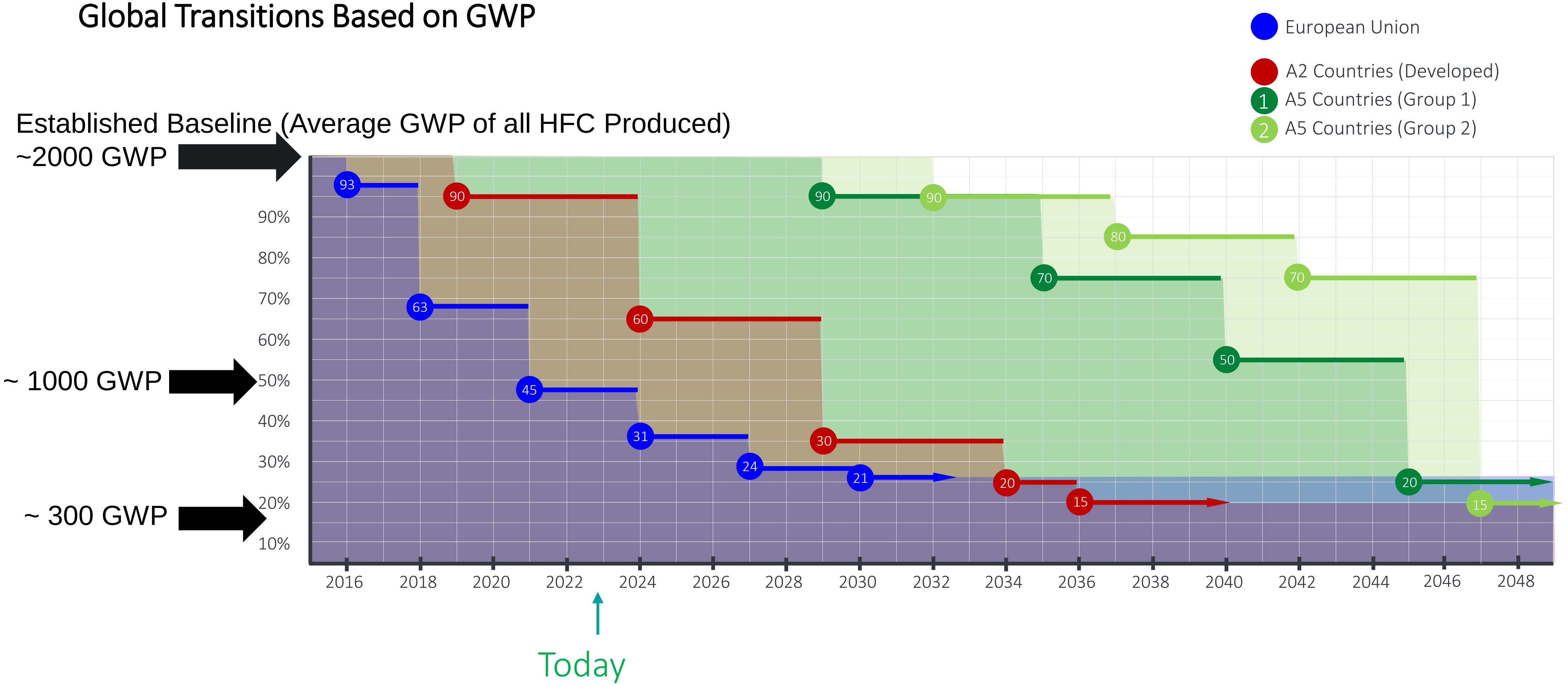
GWP Average ~ 2000

Source: U.S. EPA, April 2016. EPA Report EPA-430-R-16-002.

>60% HFC GHG Consumption Used for Commercial Refrigeration (R404A) & Residential ACs (R410A)

Summary of Global HFC Phase Downs Agreement

Kigali Amendment + EU F-Gas
Global Transitions Based on GWP



This is a Phase Down, Not Phase Out (All Refrigerants Available for Use)
Kigali Phase-Down of HFCs Started in 2019 for Developed Nations

The U.S. is Regulating the HFC Transition Now

Comprehensive Federal U.S. HFC phase down

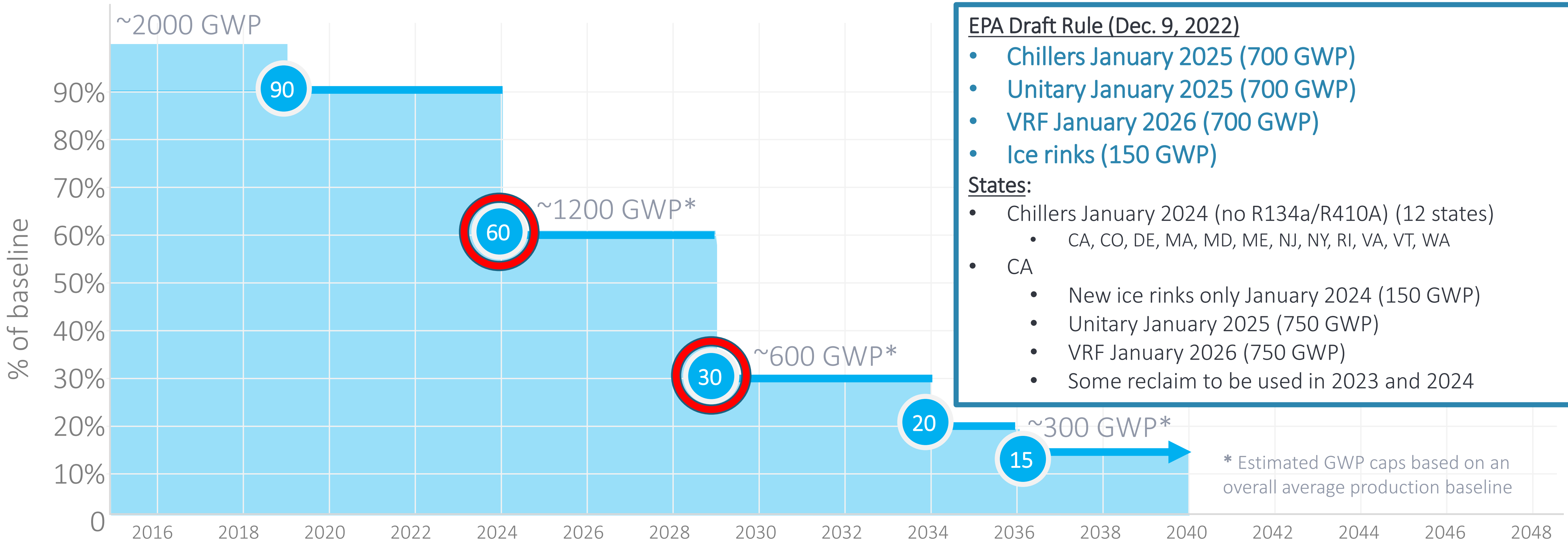
- [x] U.S. AIM Act requires EPA to regulate HFC phase down in the same time frame as the Kigali Amendment (Senate Ratified Oct 22)
- [x] EPA allocation regulation (Sept. 2021) reduces refrigerant supply by 10 percent (GWP) in 2022 to align with legislation
- [x] EPA sets equipment sector bans with GWP limits by **Oct 2023** per AIM Act – Draft rule out Dec. 9, 2022
- [ ] EPA to add HFCs to refrigerant management regulation (CAA 608)
- [x] Federal regulation reduces refrigerant supply by 40 percent (GWP) in 2024

The Future is Known… the How and When is becoming Clearer
Final Technology Transition Rule – Due Oct 6, 2023

AIM (American Innovation and Manufacturing) Act – Enacted Dec 2020

The U.S. HFC Transition

AIM Act Requires Production/Consumption Reductions through Allocations Following the Montreal Protocol Kigali Schedule for Developed Countries



EPA Draft Rule (Dec. 9, 2022)

- Chillers January 2025 (700 GWP)
- Unitary January 2025 (700 GWP)
- VRF January 2026 (700 GWP)
- Ice rinks (150 GWP)

States:

- Chillers January 2024 (no R134a/R410A) (12 states)
  - CA, CO, DE, MA, MD, ME, NJ, NY, RI, VA, VT, WA
- CA
  - New ice rinks only January 2024 (150 GWP)
  - Unitary January 2025 (750 GWP)
  - VRF January 2026 (750 GWP)
  - Some reclaim to be used in 2023 and 2024

Transition Date: Date of manufacture - The date the label is put on equipment unless it is field assembled then it is the date the system is filled with refrigerant for startup.

New Equipment – Does not include modifications, servicing, or repairs to equipment in existence prior to December 27, 2020. (Beyond EPA's regulatory authority)

Significant GWP Reductions in 2024 and 2029 and Overlapping Product Bans
GWP Target: <700 GWP by 2024 to 2026

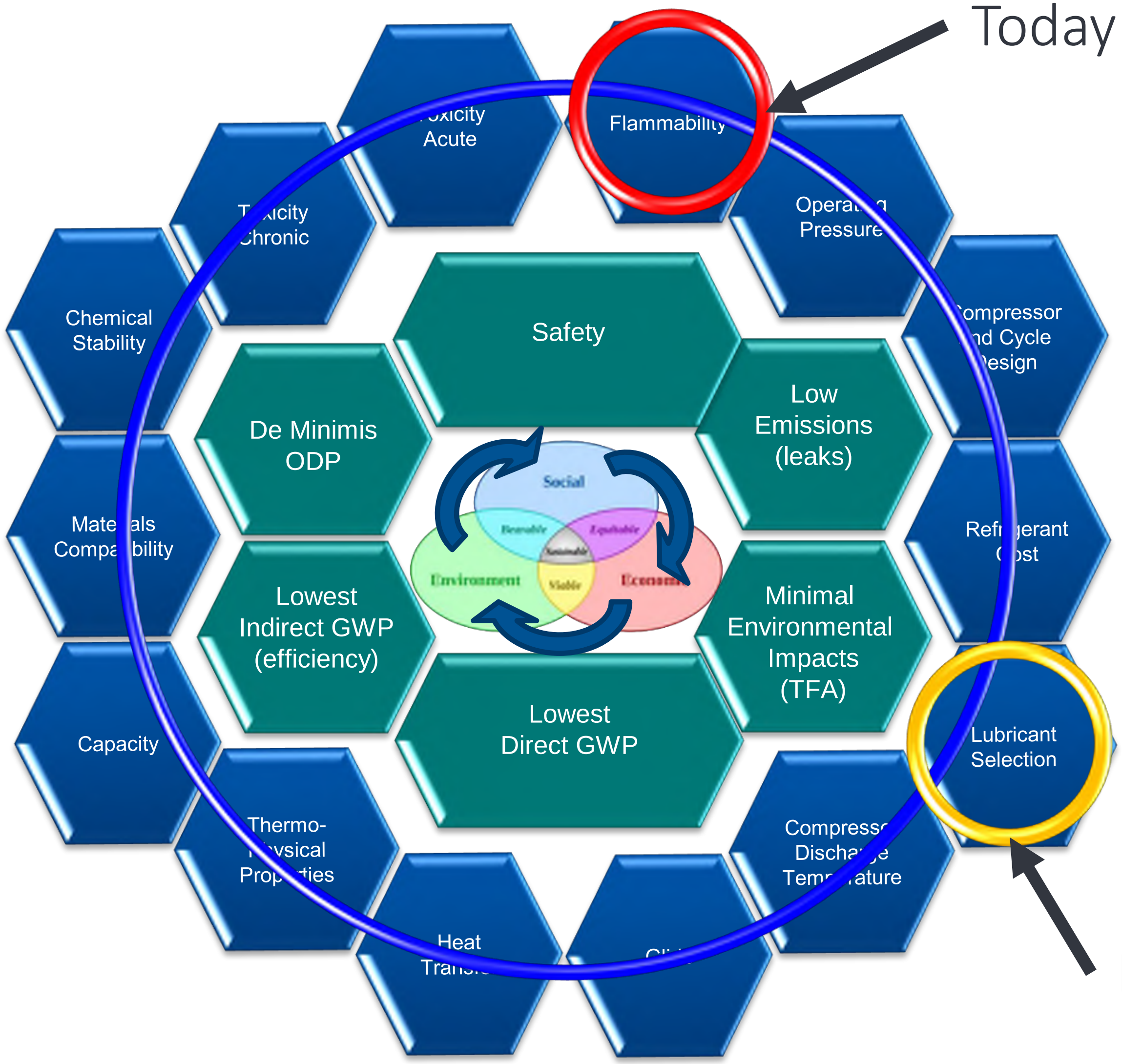
The U.S. HFC Transition – Refrigeration

	Refrigeration Equipment (Proposed Compliance Date 1/1/25)	GWP
Industrial Process Refrigeration	Systems with refrigerant charge capacities of 200 pounds or greater	150
	Systems with refrigerant charge capacities less than 200 pounds	300
	High temperature side of cascade systems	300
	Chillers	700
Retail Food Refrigeration	Stand-alone units	150
	Refrigerated food processing and dispensing equipment	150
	Supermarket systems with refrigerant charge capacities of 200 pounds or greater	150
	Supermarket systems with refrigerant charge capacities less than 200 pounds charge	300
	Supermarket systems, high temperature side of cascade system	300
	Remote condensing units with refrigerant charge capacities of 200 pounds or greater	150
	Remote condensing units with refrigerant charge capacities less than 200 pounds	300
	Remote condensing units, high temperature side of cascade system	300
	Vending machines	150
Cold Storage Warehouse	Systems with refrigerant charge capacities of 200 pounds or greater	150
	Systems with refrigerant charge capacities less than 200 pounds	300
	High temperature side of cascade system	300
	Ice rinks	150
	Automatic commercial ice machines – selfcontained with refrigerant charge capacities of 500 grams or lower (Note: Does not align with petition)	150
	Transport refrigeration – intermodal containers	700
	Residential refrigeration	150

Refrigeration - More Complex Based On Available Technology by Application

Sustainable Refrigerant Selection & Challenges

Refrigerant Replacement Challenge



Today Primary Challenge

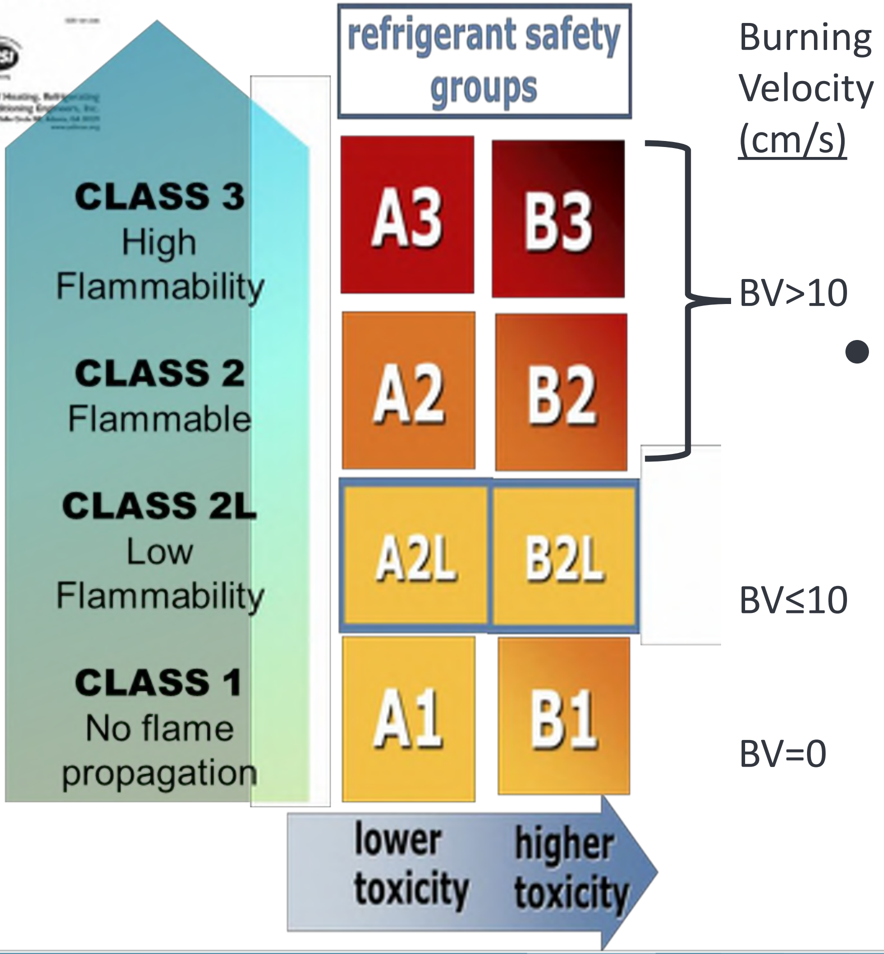
Last Trar

Balancing Key Factors for;

- Direct Refrigerant GWP
- Efficiency (Indirect GWP)
- Safety
- Transition Costs
- Intellectual Property
- Product Sustainability

Challenge: Selecting Refrigerants with Best Balance (Sustainability)
Flammability Greatest Challenge for this Transition – Not in All Cases

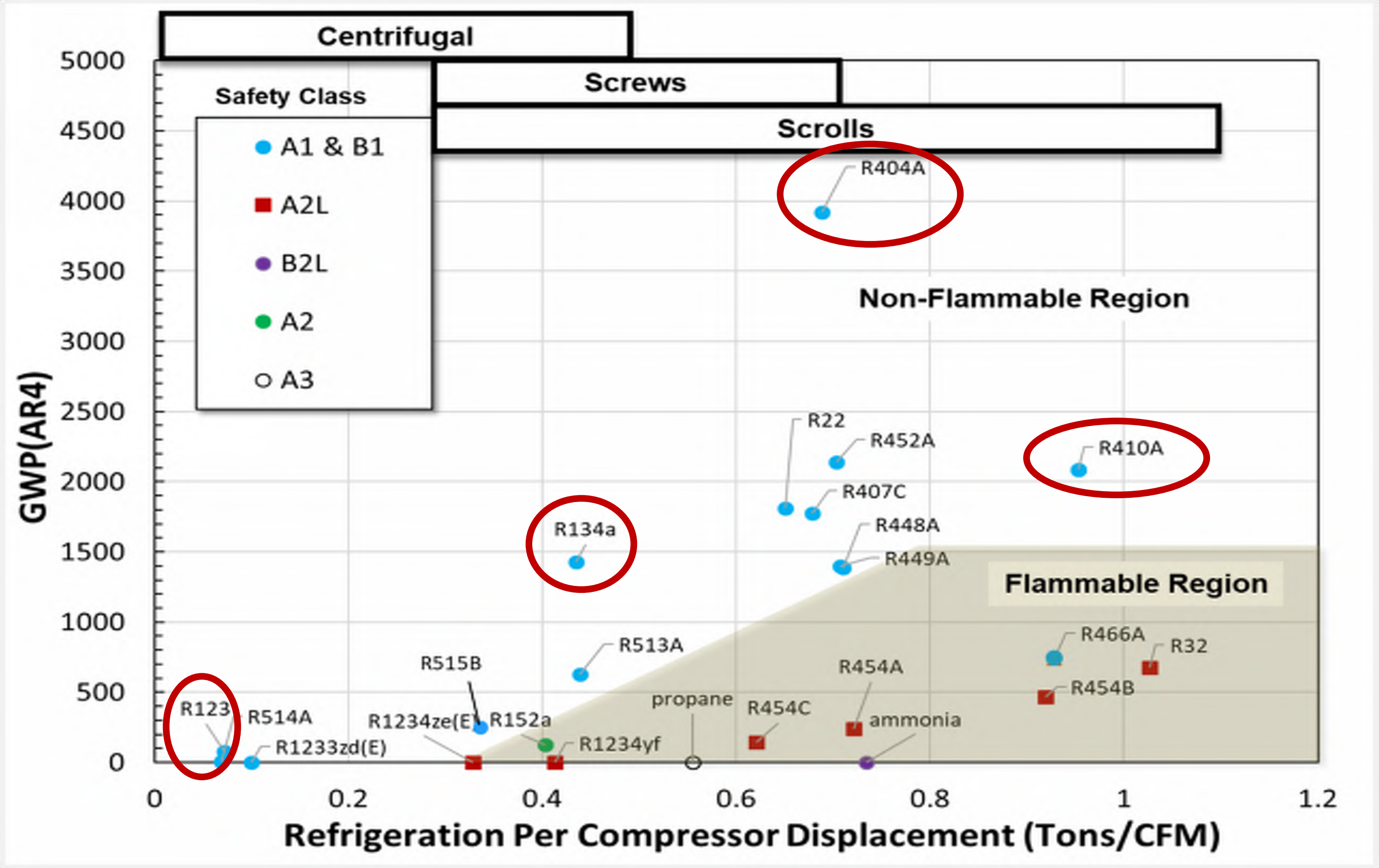
ASHRAE Standard 34
Safety Classification of Refrigerants



- Toxicity
  - A or B Based > or = to 400 ppm Occupational Exposure Limit (OEL) Dividing Line
  - **Class A**, most refrigerants, like R134a
  - **Class B**, R123 and ammonia are examples
- Flammability
  - **Class 1**, Non-flame propagating most refrigerants used today, like R123, R134a, R404A, R410A, etc., called nonflammable
  - **Class 2L**, Lower Flammable Class 2's <10 cm/sec burning velocity, most new HFO's, R32, R1234yf
  - **Class 2**, more flammable, R152a
  - **Class 3**, explosive, like propane (R290), Isobutane (R600a)

Flammability is a Continuum without Specific Limits
"Flammables are Flammable"

Viable Lower GWP & Ultra Low GWP Alternatives

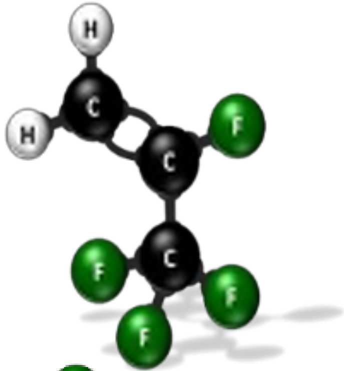


Flammable Refrigerants Required For Some Applications to Achieve a Low GWP Refrigerant Future

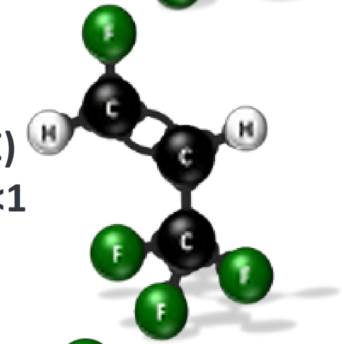
Review of Lower GWP Refrigerant Option for Various HFCs

Toolbox of <10 GWP Next Generation Refrigerants

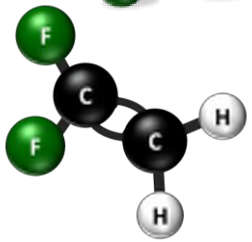
R1234yf
A2L GWP <1



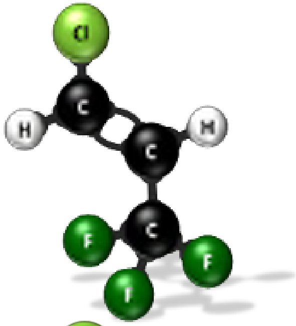
R1234ze(E)
A2L GWP <1



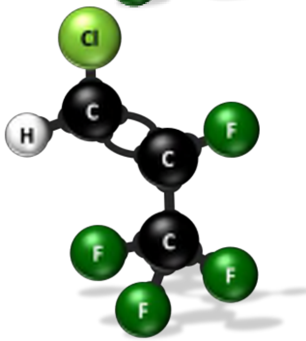
R1132a
A2 GWP <1



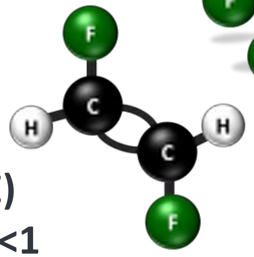
R1233zd(E)
A1 GWP 1



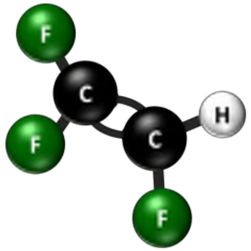
R1224yd(Z)
A1 GWP 1

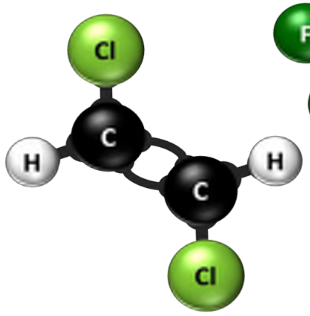


R1132(E)
B2 GWP <1

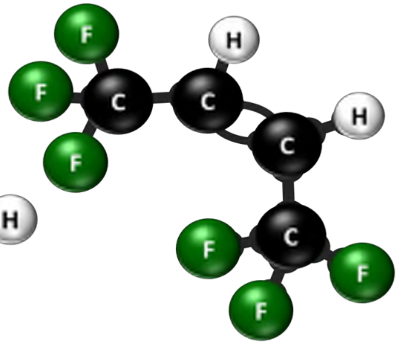


R1123
?2L GWP <1





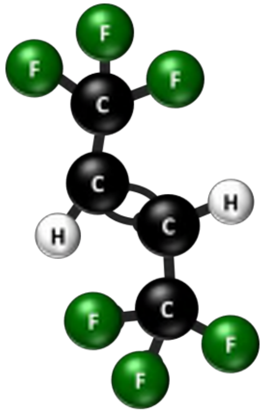
R1130(E)
B2L GWP <1



R1336mzz(Z)
A1 GWP <2

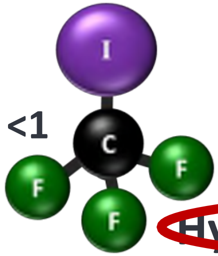
Azeotropic

R514A
B1 GWP<2



R1336mzz(E)
A1 GWP <6

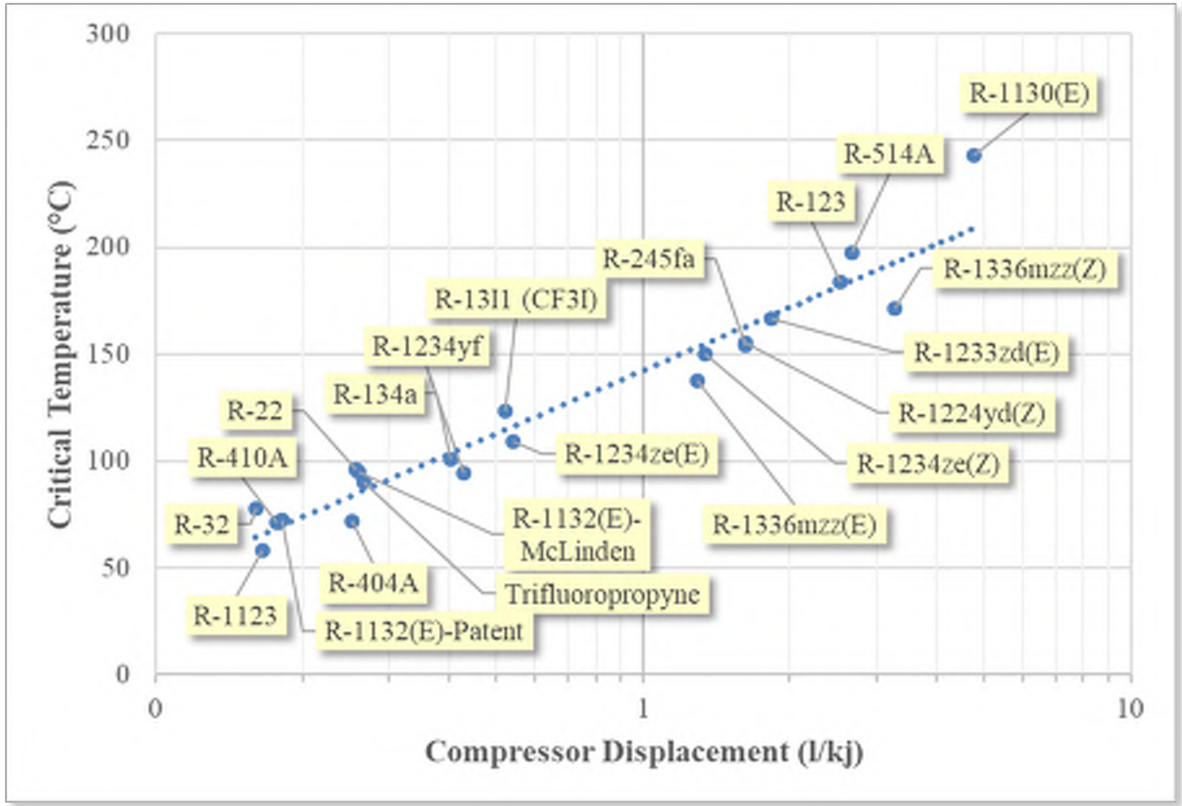
R13I1
A1 GWP <1

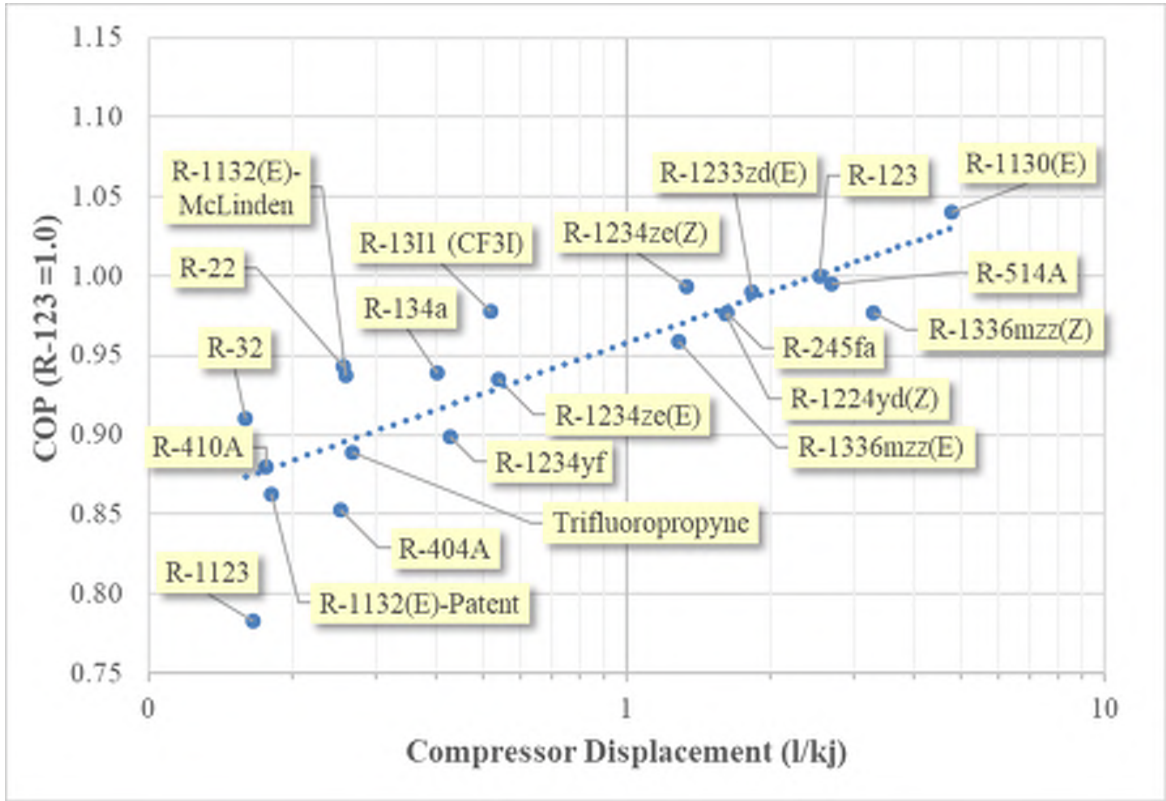


Along with
Carbon Dioxide (R744) – A1
Ammonia (R717) – B2L
Hydrocarbons (R290, R600, R600a) – A3

8 New Molecules/9 Older Molecules - HFOs, HCFOs, HCOs, IFC, CO2, NH3, HCs
Many of Which are Flammable

Summary of <10 GWP Refrigerants in the Toolbox





The Same or Better Efficiency Over HFCs - Still Less Than CFCs
Many of these are Zeotropic (R-400) Blends to Optimize Properties
Some R-500 Series Refrigerants are Azeotrope – No Change in Blend Composition if Leaked

Low Pressure Alternatives R123 Replacements

Alternatives Attributes

- Most Low GWP (<10)
- Non-flammable
- Good efficiency
- Near design compatible alternatives available
- Near R123 and R245fa capacities
- All with no glide
- Issues: none

		Baseline	Ultra-Low GWP	
		R-123	R-514A	R-1233zd(E)
Flammability	ASHRAE Class	1	1	1
Toxicity[1]	ASHRAE Class	Higher (B)	Higher (B)	Lower (A)
	OEL (ppm)	50	320	800
Efficiency (COP)		8.95	8.91	8.87
Capacity Change		baseline	~5% loss	~35% gain
GWP[2]		77	1.7	1
Atmospheric Life		1.3 years	22 days	26 days

*Modeling Conditions: 100% isentropic compressor efficiency, 95°F/44°F, 0 superheat, 0 subcooling

R1233zd(E) and R514A – Good Choices Nonflammable, GWP <2, High Efficiency
All These Candidates Considered "Long Term Solutions"
R514A & R1233zd(E) Products Available in Market Place

Medium Pressure Alternatives - R134a Replacements

Alternatives Attributes

- Flammability
  - GWP 300-600 nonflammable
  - GWP <150 flammable
- Good to ok efficiency
- All with no glide (azeotropes)
- Near design compatible alternatives available
  - Near R134a capacity (R513A)
  - R1234ze(E) = -25% capacity
- Issues: Lower superheat than R134a

		Baseline	Lower GWP		Ultra-Low GWP	
		R-134a	R-513A	R-515B	R-1234yf	R-1234ze(E)
Flammability	ASHRAE Class	1	1	1	2L ⚠	2L ⚠
Toxicity[1]	ASHRAE Class	Lower (A)	Lower (A)	Lower (A)	Lower (A)	Lower (A)
	OEL (ppm)	1000	650	810	500	800
Efficiency (COP)		8.47	8.27	8.32	8.17	8.45
Capacity Change		baseline	similar	~25% loss	~5% loss	~25% loss
GWP[2]		1430	630	298	6	4
Atmospheric Life		13.4 years	5.9 years	3.1 years	11 days	18 days

*Modeling Conditions: 100% isentropic compressor efficiency, 95°F/44°F, 0 superheat, 0 subcooling
*R-513A introduced for ice rinks applications in 2019

R513A & R515B (Nonflammable) and R1234ze(E) Good Choices
R513A & R515B Products Available In Market Place (USA) – ZE & YF in EU

High Pressure Alternatives - R404A Replacements

		R-404A	R448A	R449A	R407H	R454A	R454C
Flammability	ASHRAE Class	1	1	1	1	2L	2L
Toxicity[1]	ASHRAE Class	Lower (A)	Lower (A)	Lower (A)	Lower (A)	Lower (A)	Lower (A)
	OEL (ppm)	1000	860	840	1000	690	620
Efficiency (COP)		2.65	2.70	2.70	2.71	2.69	2.72
Capacity Change		baseline	~4% loss	~5% loss	~8% loss	~3% gain	~13% loss
Glide (R) Condenser		0.8	9.7	9.0	10.4	9.9	13.5
GWP AR4		3922	1397	1387	1494	239	148
Atmospheric Life		36 years	11.5 years	11.6 years	13 years	1.84 years	1.14 years

Conditions: 65% Isentropic compressor efficiency, 35% SLHX, -25F Evap, 60F Cond, 5R SC, 10R SH

- Flammability
  - R448A, R449A, R407's (Nonflams)
  - R454A, R454C leading flammables
  - R600a, R290, leading hydrocarbons
- Issues: High glide, high CDT, <150 GWP lower capacity, all flammable
- No low glide blends for low temperature refrigeration flooded evaporator chillers

R448A, R449A, R452A Good Interim Candidates (Nonflammables)
Innovation Still Needed and Underway <150 GWP Possible - Tradeoffs

High Pressure Alternatives R410A Replacements

Alternatives Attributes

- Flammability
  - R454B & R32 leading candidates are both 2L
- Efficiency - equal or greater
- R454B Near design compatible
- Low glide
  - R454B-R410A like with low glide (0 to <2K)
- Issues: No <300 GWP "R410A Like"
- Issues: <300 GWP "R404A Like", but with high glide/CDT

		Baseline	Lower GWP	
		R-410A	R-454B	R-32
Flammability	ASHRAE Class	1	2L	2L
Toxicity[1]	ASHRAE Class	Lower (A)	Lower (A)	Lower (A)
	OEL (ppm)	1000	850	1000
Efficiency (COP)		7.99	8.16	8.22
Capacity Change		baseline	~3% loss	~8% gain
GWP[2]		2088	467	675
Atmospheric Life		17 years	3.6 years	5.2 years

*Modeling Conditions: 100% isentropic compressor efficiency, 95°F/44°F, 0 superheat, 0 subcooling

R454B & R32 Primary "Interim" GWP Phasedown Refrigerants
Innovation Still Needed and Underway to Achieve <300 for All Products

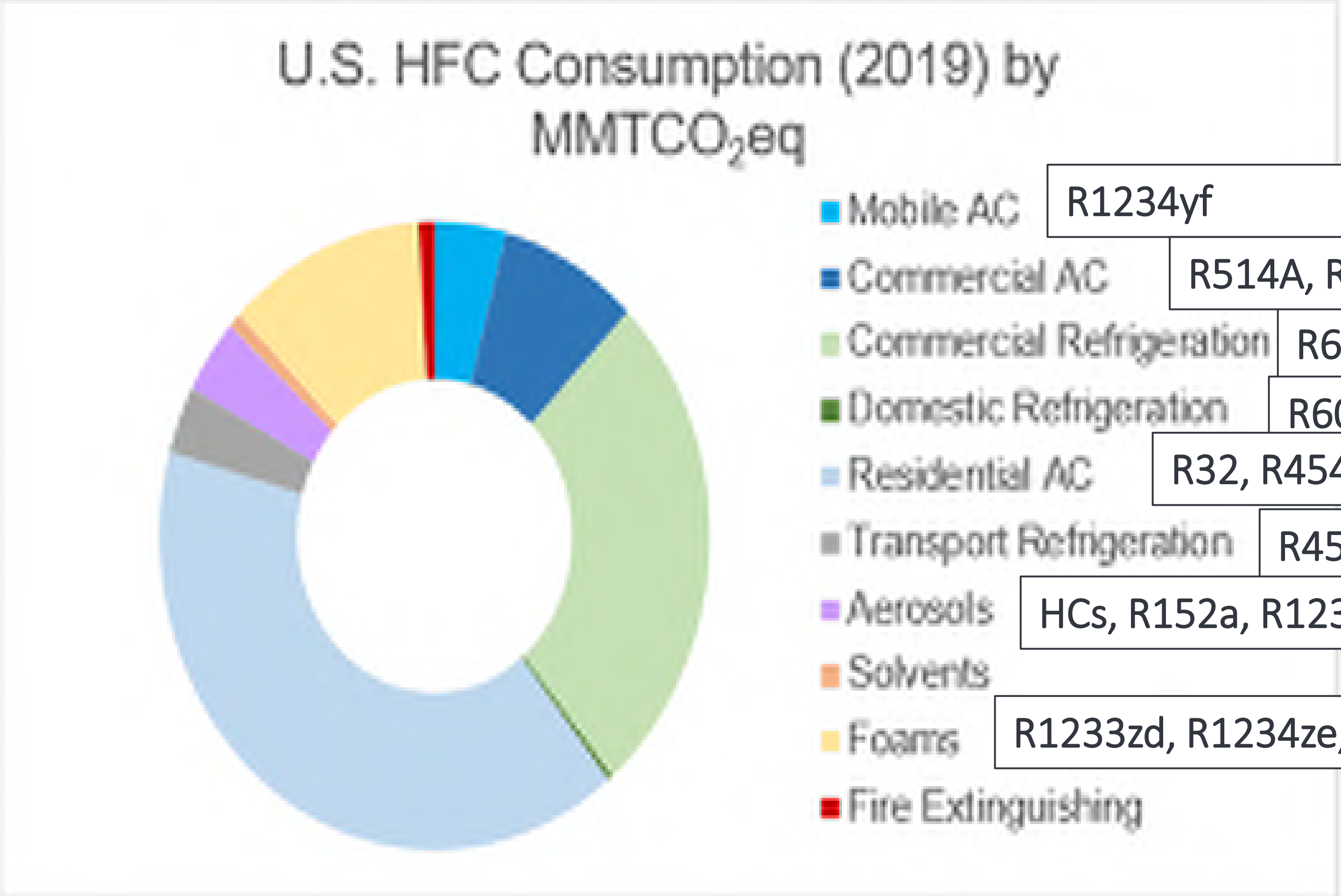
Summary & Conclusions

Summary & Conclusions

- Single Refrigerants or Blends will not be used from small to large capacity products
- Lack of low glide
- There is no Perfect Refrigerant! A balanced approach is required
  - *Safety, Environmental Impact, Efficiency*
  - *Reaching final GWP goals requires more refrigerant technology innovation (Interim Adoptions)*
  - *Widespread Use of Flammable Refrigerants Required to Achieve Final Phasedown Goals*
    **Remember – Flammables are Flammable No Matter the ASHRAE Classification (Class 2L, 2 and 3)*
  - *Leak tightness is key!*
- Low or ultra low alternatives are available today/will be shortly for many products
- Use of Natural Refrigerant expanding
  - *Ammonia (R717) continues in US. Carbon dioxide (R744) trials accelerating/maturing in specific applications. Hydrocarbons common in small portable appliances*
- Expect more product fragmentation by refrigerant. A single refrigerant may not be used from small to large capacity products

Use the Facts to Plan for Tomorrow

Tomorrow - HFCs Used by Category



R1234yf

R514A, R1233zd, R513A, R515B, R1234yf, R1234ze, R32, R454B

R600a, R290, CO2, Ammonia, R454A, R454C, R515B, R1234yf

R600a, R290

R32, R454B

R452A, R454A, R454C, R513A, R1234yf

HCs, R152a, R1234ze

R1233zd, R1234ze, R1336mzz, HCs, Water

GWP Average < 300

Low GWP Goals Achievable – But with Increased Market Fragmentation

People Continue to Argue…
Nature Acts

Sunrise over the Mississippi River at my House – Brownsville, MN – July 2020