Introduction to Refrigerants – Part I

Sameer Khandekar
Sir M. Visvesvaraya Chair Professor
Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur (UP) 208016 INDIA
Webpage: home.iitk.ac.in/-samkhan/

ME340A: Refrigeration and Air Conditioning
Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur 208016 India

In this lecture…

- Importance of selection of suitable refrigerant.
- Classification of refrigerants into primary and secondary.
- Important differences between primary and secondary refrigerants.
- Refrigerant selection criteria based on thermodynamic, thermophysical, environmental and economic properties.
- Numbering system used for designating refrigerants.
- Comparison between different refrigerants.

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Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

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1 Introduction

What are refrigerants?

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Kanpur 208016 India

Introduction

- Refrigerant : is the primary working fluid used for absorbing and transmitting heat in a refrigeration system.
- In principle, any fluid can be used as a refrigerant.
- Refrigerants absorb heat at low temperature and low pressure and release heat at a higher temperature and pressure
- Typically, refrigerants undergo phase-changes during heat absorption (evaporation) and heat releasing (condensation)
- Air used in an air-cycle refrigeration system can also be considered as a refrigerant (no phase-change).
- We will focus on those fluids that can be used as refrigerants in VCR systems only.

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Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

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Introduction

- The thermodynamic efficiency of a refrigeration system depends mainly on its operating temperatures.
- However, important practical issues such as the system design, size, initial and operating costs, safety, reliability, and serviceability etc. depend very much on the type of refrigerant selected for a given application.
- Due to several environmental issues such as ozone layer depletion, global warming and their relation to the various refrigerants used, the selection of suitable refrigerant has become one of the most important issues in recent times.

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Introduction

- Replacement of an existing refrigerant by a completely new refrigerant, for whatever reason, is an expensive proposition as it may call for several changes in the design and manufacturing of refrigeration systems.
- Hence, it is very important to understand the issues related to the selection and use of refrigerants.

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2 Primary and Secondary Refrigerants

Importance, use, differences…

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Primary and secondary refrigerants

- Primary refrigerants are those fluids, which are used directly as working fluids, for example in VCR and absorption based systems.
- These fluids provide the necessary refrigeration by undergoing a phase-change process in the evaporator, absorbing latent heat.
- As the name implies, secondary refrigerants are those liquids, which are used for transporting thermal energy from one location to other.
- Secondary refrigerants are also known referred to as brines or anti-freezes.

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Primary and secondary refrigerants

- If the operating temperatures are above 0°C, then pure water can also be used as secondary refrigerant, for example in large air conditioning systems (like we have in IIT Kanpur).
- Antifreezes or brines are used when refrigeration is required at sub-zero temperatures.
- Unlike primary refrigerants, secondary refrigerants do not undergo phase change as they transport energy from one location to other.

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Primary and secondary refrigerants/ Cooling Medium

- Secondary refrigerants are also called as Cooling medium.
- Cooling Medium: is a working fluid cooled by the refrigerant to transport the cooling effect between a central plant and remote cooling units and terminals
- Chilled water, brine, and glycol are used as cooling media in many refrigeration systems.
- It reduces the extensive circulation of the primary refrigerant.

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Tel: 7038; e-mail: samkhan@iitk.ac.in

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Primary and secondary refrigerants

- An important property of a secondary refrigerant is its freezing point. Generally, the freezing point of a brine will be lower than the freezing point of its constituents (i.e. mixture components).
- The temperature at which freezing of a brine takes place depends on its concentration. The concentration at which a lowest temperature can be reached without solidification is called as eutectic point.
- The commonly used secondary refrigerants are the solutions of water and ethylene glycol, propylene glycol or calcium chloride. These solutions are known under the general name of brines.

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History of refrigeration

- 1830s - Jacob Perkins - Vapor Compression (ether)
- 1851 - John Gorrie - Patent for Air Cycle
- 1859 - R-717 / R-718 (Ammonia / Water)
- 1866 - CO_2 - Marine Applications
- 1873 - R-717 (Ammonia) Commercial Refrigeration
- 1875 - R-764 (Sulfur dioxide)
- 1920s -R-600a (Isobutane) & R-290 (Propane)
- 1922 - Willis Carrier - R-1130 (Dielene)
- 1926 - R-30 (Methylene Chloride)

Main challenges

- Low Toxicity
- Non-flammable
- Good Stability
- Atmospheric Boiling Point between -40°C and 0°C

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Common refrigerants in 1920-30

- Ammonia (R-717) NH_3
- Carbon Dioxide CO_2
- Sulfur Dioxide SO_2
- Hydrocarbons C_nH_m
- Methyl Choride CH_3Cl
- Water H_2O

Use of Synthetic Refrigerants:
(Stability, non-toxicity and efficiency)

- 1930: R11, R12
- 1936: R22
- 1961: R507

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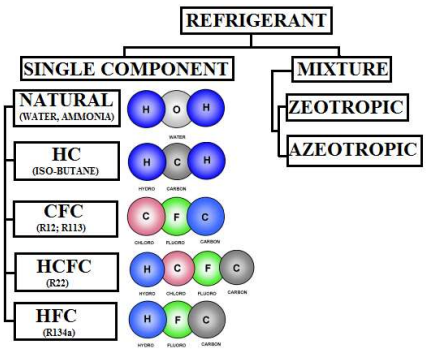
Classes of refrigerants

Organic: Some examples

- Hydro-carbons HC (natural starting molecules from which most refrigerants are synthesized)
  - Methane (R-50) and Ethane (R-170)
- Chloro-Flouro Carbons (CFC)
- Hydro Chloro-Flouro Carbons (HCFC)
- Hydro-Fluoro Carbons (HFC)

In-organic: Some examples

- Water
- Ammonia
- CO_2



Refrigerants can also be mixed with each other

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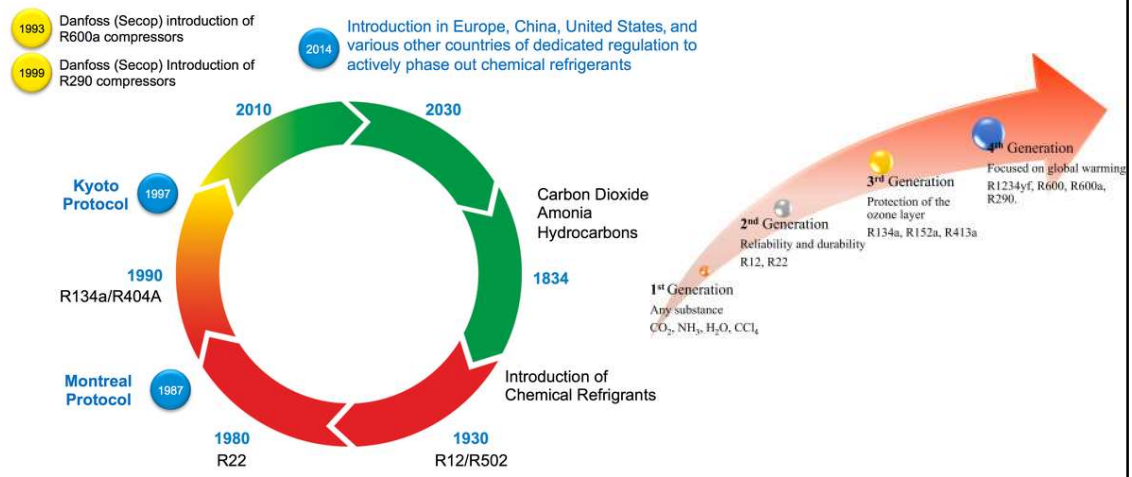
Historical perspective



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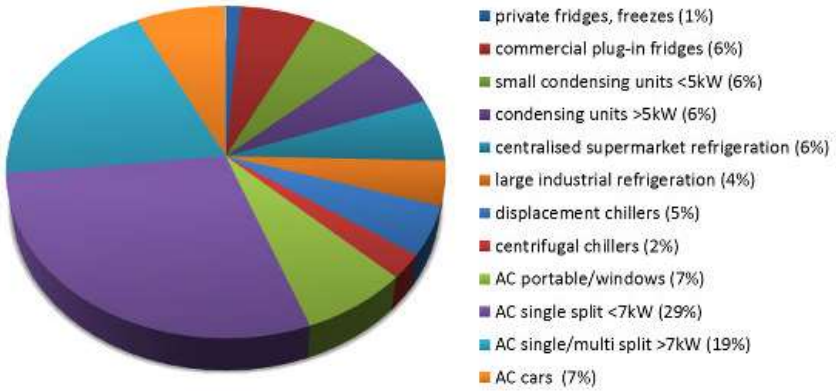
Refrigerant consumption in developing countries (2015)



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Hydrocarbon refrigerants

- Many hydrocarbon gases have successfully been used as refrigerants in industrial, commercial and domestic applications.
- Examples:
  - R170, Ethane, C_2H_6
  - R290 , Propane C_3H_3
  - R600, Butane, C_4H_{10}
  - R600a, Isobutane, C_4H_{10}
  - Blends of the above gases

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Halocarbons

- Halocarbon refrigerants are all synthetically produced and were developed as the FREON family of refrigerants.
- Examples :
  - CFC's : R11, R12, R113, R114, R115
  - HCFC's : R22, R123
  - HFC's : R134a, R404a, R407c, R410a

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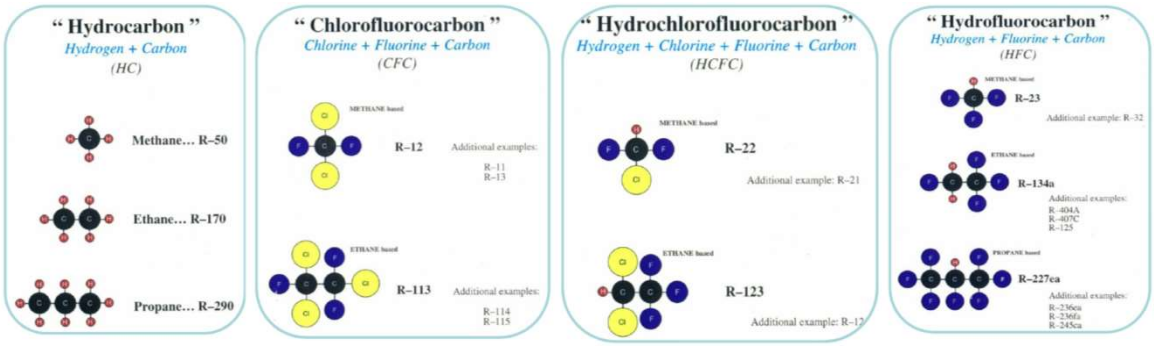
Molecular structures of common refrigerants



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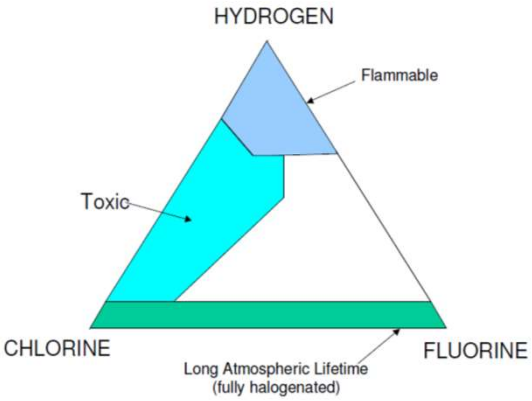
Property trends/ H-Cl-F

- CFCs, HCFCs, HFCs & HFOs
- Limited Combinations
  - Adding Chlorine Or Bromine Increases ODP
  - Adding Fluorine Increases GWP
  - Adding Hydrogen Increases Flammability And Lowers Atmospheric Lifetime



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Blending of refrigerants

- Two or more refrigerants can be suitably blended to achieve the required/desired properties
  - Flammability
  - Volumetric Capacity
  - Limit discharge superheating for lower discharge Temp
- Two Basic Types
  - Zeotropes
  - Azeotropes

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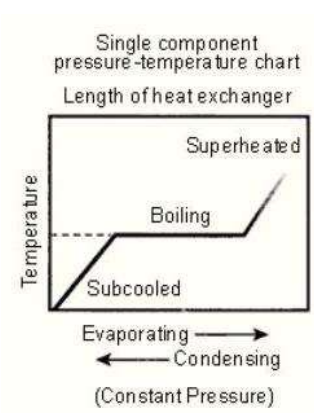
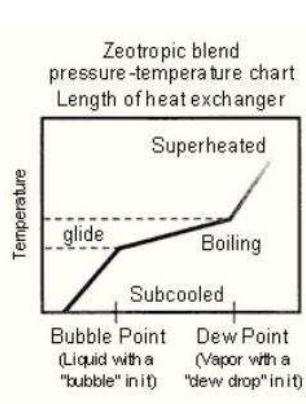
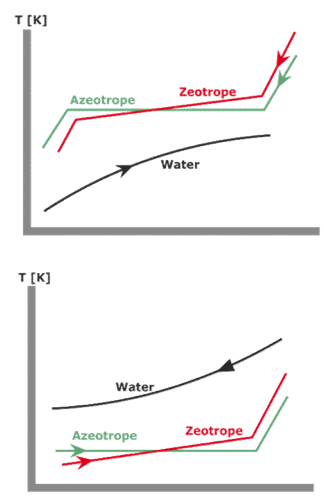
Thermodynamics of mixtures







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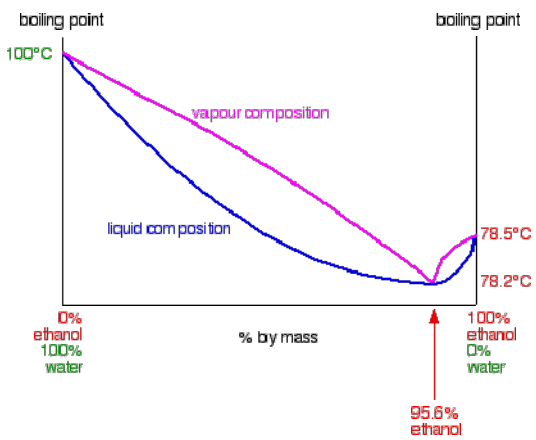
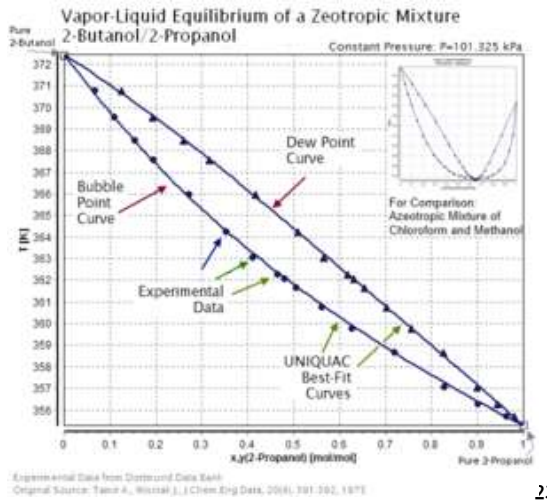
Thermodynamics of mixtures





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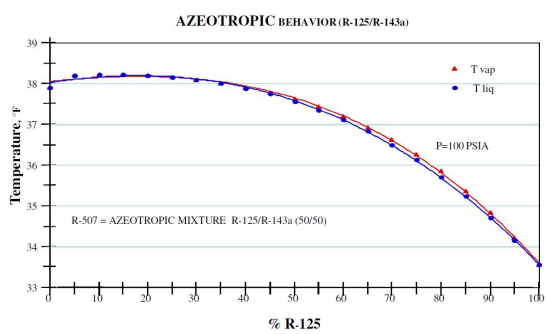
Azeotropic refrigerants

- A stable mixture of two or several refrigerants whose vapor and liquid phases retain identical compositions over a wide range of temperatures.
- Examples:
  - R-500: 73.8% R12 and 26.2% R152
  - R-502: 8.8% R22 and 51.2% R115
  - R-503: 40.1% R23 and 59.9% R13



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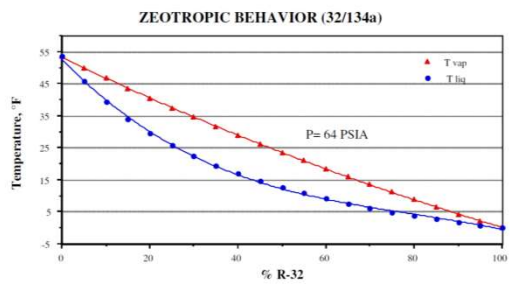
Zeotropic refrigerants

- A zeotropic mixture is one whose composition in liquid phase differs to that in vapor phase. Zeotropic refrigerants therefore do not boil at constant temperatures unlike azeotropic refrigerants.
- Examples:
  - R404a : R125/143a/134a (44%,52%,4%)
  - R407c : R32/125/134a (23%, 25%, 52%)
  - R410a : R32/125 (50%, 50%)
  - R413a : R600a/218/134a (3%, 9%, 88%)



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3 Properties of Refrigerants

Desirable thermophysical properties…

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Essential properties of refrigerants

- Latent heat of vaporization is one of the most important properties.
- Chemical stability under conditions of use is another equally important characteristics.
- Safety codes may require a non-flammable refrigerant of low toxicity for most applications.
- Cost, availability, efficiency, and compatibility with compressor lubricants and materials with which the equipment is constructed.

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Physical properties

- The refrigerants are arranged in increasing order of atmospheric boiling point, from air at -194.3°C to water at 100°C
- Normal boiling point is most important because it is a direct indicator of the temperature level at which a refrigerant can be used.

Refrigerant		Chemical Formula	Molecular Mass	Boiling Point at 100.325 kPa [°C]	Freezing Point [°C]
No	Chemical Name				
729	Air	-	28.97	-194.3	-
23	Trifluoromethane	CHF_3	70.02	-82.1	-155
13	Chlorotrifluoromethane	$CClF_3$	104.47	-81.4	-181
744	Carbon dioxide	CO_2	44.01	-78.4	-56.6
22	Chlorodifluoromethane	$CHClF_2$	86.48	-40.76	-160
717	Ammonia	NH_3	17.03	-33.3	-77.7
12	Dichlorodifluoromethane	CCl_2F_2	120.93	-29.79	-158
11	Trichlorofluoromethane	CCl_3F	137.38	23.82	-111
113	Trichlorotrifluoromethane	CCl_2FCClF_2	187.39	47.57	-35
718	Water	H_2O	18.02	100	0

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Refrigerant selection criteria

- Selection of refrigerant for a particular application is based on the following requirements:
  - Thermodynamic and thermo-physical properties.
  - Environmental and safety properties, like:
    - Ozone depletion potential (ODP), global warming potential (GWP), and combustibility
    - Economics of production/maintenance/etc.

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Thermodynamic and thermo-physical properties

- Suction pressure: At a given evaporator temperature, the saturation pressure should be above atmospheric for prevention of air or moisture and non-condensable gases ingress into the system and ease of leak detection. Higher suction pressure is better as it leads to smaller compressor displacement
- Discharge pressure: At a given condenser temperature, the discharge pressure should be as small as possible to allow light-weight construction of compressor, condenser, pipe, etc.

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Thermodynamic and thermo-physical properties

- Pressure ratio or Compression ratio: Should be as small as possible for high volumetric efficiency and low power consumption
- Latent heat of vaporization: Should be as large as possible so that the required mass flow rate per unit cooling capacity will be small

$$\ln(P_{sat}) = -\frac{h_{fg}}{RT} + \frac{s_{fg}}{R} \qquad \frac{P_c}{P_e} = \exp\left[\frac{h_{fg}}{R}\left(\frac{1}{T_e} - \frac{1}{T_c}\right)\right]$$

- From the above equation, it can be seen that for given condenser and evaporator temperatures, as the latent heat of vaporization increases, the pressure ratio also increases.
- Hence a trade-off is required between the latent heat of vaporization and pressure ratio.

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Thermodynamic and thermo-physical properties

- Isentropic index of compression: Should be as small as possible so that the temperature rise during compression will be small.
- Liquid specific heat: Should be small so that degree of subcooling will be large leading to smaller amount of flash at evaporator inlet.
- Vapor specific heat: Should be large so that the degree of superheating will be small.
- Thermal conductivity: Thermal conductivity in both liquid as well as vapor phase should be high for higher heat transfer coefficients.
- Viscosity: Viscosity should be small in both liquid and vapor phases for smaller frictional pressure drops.

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Environmental and safety properties

- In contemporary times, environment friendliness of the refrigerant is a major factor in deciding its usage.
- Ozone Depletion Potential (ODP): According to the Montreal protocol, the ODP of refrigerants should be zero, i.e., they should be non-ozone depleting substances.
- Refrigerants having non-zero ODP have either already been phased-out (e.g. R11, R12) or will be in near-future (e.g. R22).
- Since ODP depends mainly on the presence of chlorine or bromine in the molecules, refrigerants having either chlorine (i.e., CFCs and HCFCs) or bromine cannot be used under the new regulations.

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Environmental and safety properties

- Global Warming Potential (GWP): Refrigerants should have as low a GWP value as possible to minimize global warming.
- Refrigerants with zero ODP but a high value of GWP (e.g. R134a) are likely to be regulated in future.
- Total Equivalent Warming Index (TEWI): The factor TEWI considers both direct (due to release into atmosphere) and indirect (through energy consumption) contributions of refrigerants to global warming.
- Naturally, refrigerants with as a low a value of TEWI are preferable from global warming point of view.

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Environmental and safety properties

- Toxicity: Ideally, refrigerants used in a refrigeration system should be non-toxic. However, all fluids other than air can be called as toxic as they will cause suffocation when their concentration is large enough.
- Hence, toxicity is a relative term, which becomes meaningful only when the degree of concentration and time of exposure required to produce harmful effects are specified.
- Some fluids are toxic even in small concentrations. Some fluids are mildly toxic, i.e., they are dangerous only when the concentration is large and duration of exposure is long.

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Environmental and safety properties

- Some refrigerants such as CFCs and HCFCs are non-toxic when mixed with air in normal condition. However, when they come in contact with an open flame or an electrical heating element, they decompose forming highly toxic elements (e.g. phosgene-$COCl_2$).
- In general the degree of hazard depends on:
  - Amount of refrigerant used vs total space
  - Type of occupancy
  - Presence of open flames
  - Odor of refrigerant, and
  - Maintenance condition

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Environmental and safety properties

- Flammability: The refrigerants should preferably be non-flammable and non-explosive. For flammable refrigerants special precautions should be taken to avoid accidents.
- Based on the above criteria, ASHRAE has divided refrigerants into six safety groups (A1 to A3 and B1 to B3).
- Refrigerants belonging to Group A1 (e.g. R11, R12, R22, R134a, R744, R718) are least hazardous, while refrigerants belonging to Group B3 (e.g. R1140) are most hazardous.
- Finally, economic properties: The refrigerant used should preferably be inexpensive and easily available.

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37

ME340A: Refrigeration and Air Conditioning
Instructor: Prof. Sameer Khandekar
Tel: 7038; e-mail: samkhan@iitk.ac.in

Department of Mechanical Engineering
Indian Institute of Technology Kanpur
Kanpur 208016 India

Comparison/ Issues

Refrigerant Type	Example(s)	Remarks
HCs	HC-290 (Propane), CH_4 (Methane)	Not typically used in commercial A/C products, flammable.
CFCs	CFC-11, 12, 113, 114, 115	Contains ozone depleting chlorine, most harmful, phased out in '95, High GWP.
HCFCs	HCFC-22, HCFC-123	Contains ozone depleting chlorine, Short term replacements, phased out in '10 from new equipment, High GWP.
HFCs	HFC-134a, HFC-407C, HFC-410A,	Contains ZERO ozone depleting chlorine, ZERO ODP, Long term replacements, High GWP.

Sameer Khandekar

38

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4

Nomenclature of Refrigerants

How to name them?

Sameer Khandekar

39

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Designation of refrigerants/ Nomenclature

- Since a large number of refrigerants have been developed over the years for a wide variety of applications, a numbering system has been adopted to designate various refrigerants.
- From the number one can get some useful information about the type of refrigerant, its chemical composition, molecular weight etc.
- All the refrigerants are designated by R followed by a unique number.

Sameer Khandekar

40

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ASHRAE Standards (Number 34)

- The number assigned to each refrigerant is related to its chemical composition and the system has been formalized as ASHRAE Standard 34. Broadly, the numbering system is as follows:

000 Series	Methane Based
100 Series	Ethane Based
200 Series	Propane Based
300 Series	Cyclic Organic Compounds
400 Series	Zeotropes
500 Series	Azeotropes
600 Series	Organic Compounds
700 Series	Inorganic Compounds
1000 Series	Unsaturated Organic Compounds

Sameer Khandekar

41

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Designation of refrigerants/ Nomenclature

1. Fully saturated, halogenated compounds:

- These refrigerants are derivatives of alkanes (C_nH_{2n+2}) such as methane (CH_4), ethane (C_2H_6) and propane (C_2H_8).
- These refrigerants are designated by R-XYZ, where:
  - X+1 indicates the number of Carbon (C) atoms
  - Y-1 indicates number of Hydrogen (H) atoms, and
  - Z indicates number of Fluorine (F) atoms
  - The balance indicates the number of Chlorine atoms.
- Only 2 digits indicates that the value of X is zero.

Sameer Khandekar

42

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Kanpur 208016 India

Nomenclature: Example

Example: R 22

- X = 0 ⇒ No. of Carbon atoms = 0 + 1 = 1 ⇒ derivative of methane (CH_4)
- Y = 2 ⇒ No. of Hydrogen atoms = 2-1 = 1
- Z = 2 ⇒ No. of Fluorine atoms = 2
- The balance = 4 – no. of (H+F) atoms = 4-1-2 = 1 ⇒ No. of Chlorine atoms = 1

∴ The chemical formula of R 22 = $CHClF_2$

- Similarly it can be shown that the chemical formula of:

- R12 = CCl_2F_2
- R134a = $C_2H_2F_4$ (derivative of ethane)

- (letter a stands for isomer, e.g. molecules having same chemical composition but different atomic arrangement, e.g. R134 and R134a)

Sameer Khandekar

43

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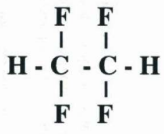
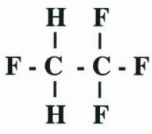
Isomeric refrigerants

The Two Isomers of Tetrafluorethane

1, 1, 2, 2–Tetrafluoroethane R–134	1, 1, 1, 2–Tetrafluoroethane R–134a
	
$CHF_2–CHF_2$	$CH_2F–CF_3$
Attached mass delta 39 - 39 = 0	Attached mass delta 57 - 21 = 36

Chemical name… Tetrafluoroethane

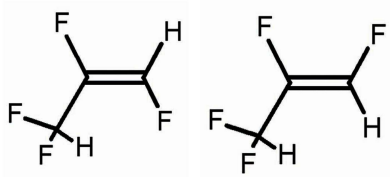
ANSI/ ASHRAE	Chemical Structural Name	Structural Molecular Formula
R–134	1, 1, 2, 2-Tetrafluoroethane	CHF_2-CHF_2
R–134a	1, 1, 1, 2-Tetrafluoroethane	CH_2F-CF_3

Molecular Weight
C… 12.0
H… 1.0
Cl…35.5
F… 19.0

2,3,3,3-Tetrafluoropropene, HFO-1234yf, is a hydro-fluoro-olefin (HFO) with the formula CH_2=$CFCF_3$.

This molecule can have several isomers

NEW CLASS OF REFRIGERANT



Sameer Khandekar

44

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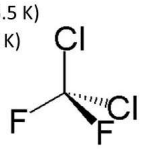
Examples

R12

- **R12 (1bar = -30°C)**
- Molecular formula CCl_2F_2
- Molar mass 120.91 g/mol
- Appearance – colorless gas with ether-like odor
- Density 1.486 g/cm³ (−29.8 °C)
- Melting point −157.7 °C (115.5 K)
- Boiling point −29.8 °C (243.3 K)

- ODP = 0.82
- GWP = 8100

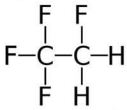


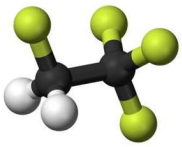
R134a

- **R134a (1bar = -26°C)**
- Molecular formula $C_2H_2F_4$
- Molar mass 102.03 g/mol
- Appearance Colorless gas
- Density 4.25 kg/m³, gas
- Melting point -103.3°C (169.85 K)
- Boiling point -26.3°C (246.85 K)

- ODP = 0
- GWP = 1430

- Replacement for R11 & R12 (not a drop-in)





Sameer Khandekar

45

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Nomenclature

2. Inorganic refrigerants:

These are designated by number 7 followed by the molecular weight of the refrigerant (rounded-off).

- Ex.: Ammonia: Molecular weight is 17, ∴ the designation is R-717
- Carbon dioxide: Molecular weight is 44, ∴ the designation is R-744
- Water: Molecular weight is 18, ∴ the designation is R-718ide
- Sulpher dioxide:
- Air

Sameer Khandekar

46

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Complete Nomenclature explained

- The first digit on the right is the number of fluorine (F) atoms.
- The second digit from the right is one more than the number of hydrogen (H) atoms.
- The third digit from the right is one less than the number of carbon (C) atoms. When this digit is zero it is omitted from the number.
- The fourth digit from the right is equal to the number of unsaturated carbon-carbon bonds in the compound. When this digit is zero, it is omitted from the number.

Sameer Khandekar

47

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Complete nomenclature explained

- The number of chlorine (Cl) atoms is found by subtracting the sum of the flourine (F), bromine (Br - if present) and hydrogen (H) atoms from the total number that can be attached to carbon. With one carbon, the total number of attached atoms is four. With two carbons, the total number is six and with three carbons, the total number is eight.
- In some cases, part or all of the chlorine atoms are replaced with bromine and the letter B is used in the number. The number following the letter B shows the number of bromine atoms present.

Sameer Khandekar

48

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Complete nomenclature explained

- Blends are designated by their respective refrigerant numbers and weight proportions. rest of text okay, add this. To differentiate among blends having same components with different proportions, an uppercase letter shall be added to designation. For example, R-402A and R-402B.
- Zeotropic blends that have been commercialized shall be assigned an identifying number in the 400 series. This number designates which components are in the mixture but not the amount of each. The amount of each component is designated as described in 7 above. For example the 60/40 weight % mixture of R-12 and R-114 would be R-400 (60/40).

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49

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Complete nomenclature explained

- Azeotropic compounds that have been commercialized shall be assigned an identifying number in the 500 series. It is not necessary to cite the percentages parenthetically once a 500 series is assigned.
- The 600 series has been assigned to miscellaneous organic compounds. Within the organic 600 series, the assignments are serial.
- The 700 series has been assigned to inorganic compounds with relative molecular masses less than 100. Within the 700 series, the relative molecular mass of the compounds is added to 700 to arrive at the identifying refrigerant numbers. When two or more inorganic refrigerants have the same relative molecular masses, uppercase letters (i.e., A, B, C, etc.) are added to distinguish among them.
- The 1000 series has been assigned to unsaturated organic compounds.

Sameer Khandekar

50

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Department of Mechanical Engineering
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Thanks!

Any questions ?

You can write to me

- samkhan@iitk.ac.in

Sameer Khandekar

51