REFRIGERANT GASES MANIPULATION CERTIFICATION & REEFERMAN TRAINING

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1. **Refrigeration basics**
   1.1. Thermodynamic basics
   1.2. Change of phase and two phase flow
   1.3. Refrigeration cycles (p-T, T-s, p-h)
   1.4. Coefficient of performance (COP)
   1.5. Refrigerants and lubricating oils properties
   1.6. Simple substance and mixture change of phase
   1.7. Zeotropic and azeotropic mixtures
   1.8. Ecology and international rules and regulations

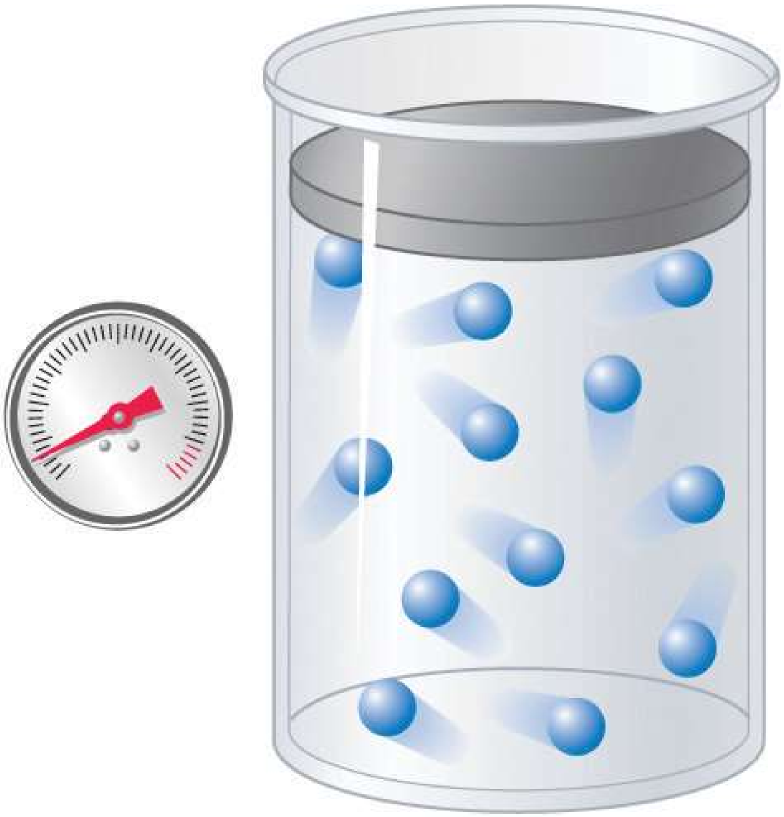
1.1. Thermodynamic basics

Basic topics

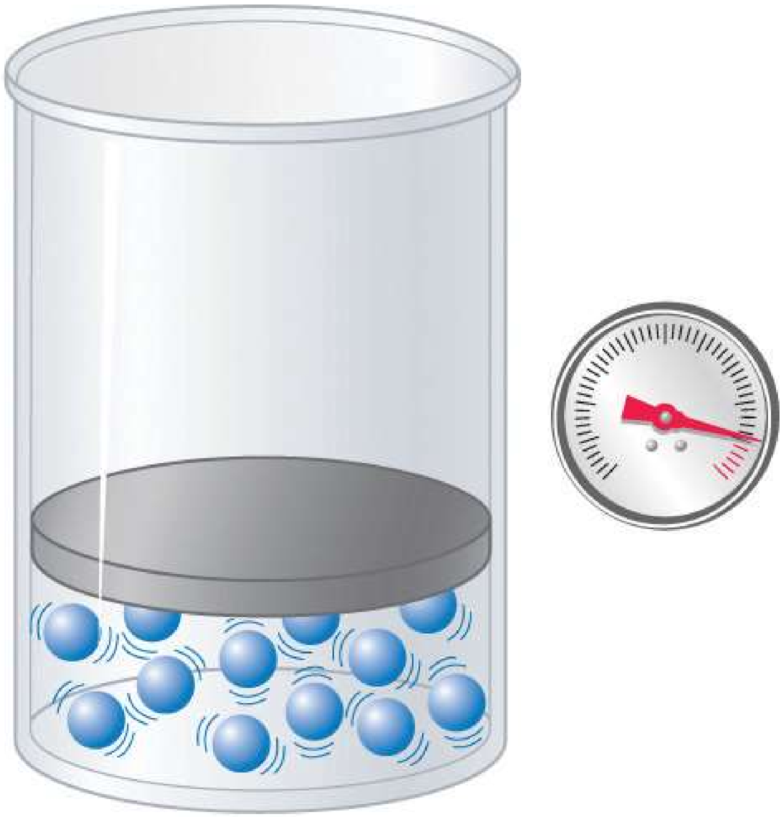
- pressure
- heat and temperature
- phases
- saturation temperature and pressure
- characteristic states (saturated liquid, dry saturated vapor)
- superheated vapor
- subcooled condensate

Pressure

THE PRESSURE IS A CONSEQUENSE OF MOLECULES HITTING WITH EACHOTHER AND WITH THE VESSEL. AS SHOWN ON THE PICTURE b THE SAME AMOUNT OF SUBSTANCE IS PLACED IN A SMALLER VOLUME THUS THE MOLECULES MORE OFTEN HITS EACHOTHER AND THE VESSEL.



(a) LOW PRESSURE

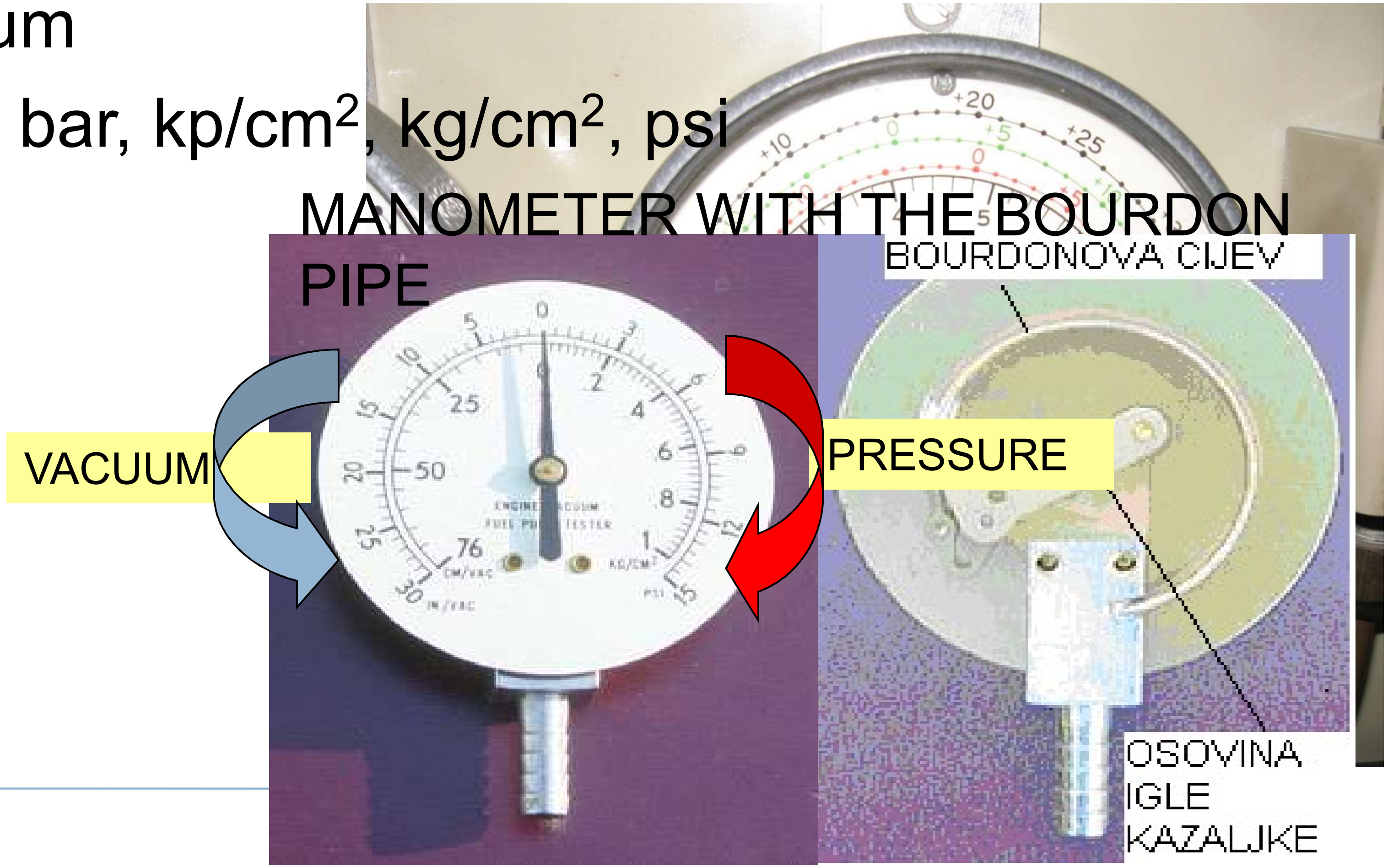


(b) HIGH PRESSURE

Pressure measuring units

- manometer pressure
- vacuum
- units: bar, kp/cm^2, kg/cm^2, psi

MANOMETER WITH THE BOURDON PIPE



Heat and temperature

Temperature can be defined as a relative warmth of substance, compared with certain fixed condition on a measuring scale. Celsius scale region between two characteristic conditions, icing point and saturation point of fresh water at atmospheric pressure, divides in 100 parts (˚), where the icing point is given value of 0˚C, and the saturation point of 100 ˚C. Fahrenheit scale divides the region in 180 grades, setting the icing point as 32˚F, and saturation as 212˚F. Measuring instruments used in refrigeration can have anyone of those two scales or even both of them.

Fahrenheit and Celsius temperature relation is given with the expression

$$t_{\circ C} = \frac{5}{9}\left(t_{\circ F} - 32\right)$$

The temperature is a concequence of kinetic energy of atoms and molecules of substance. If a movement of particles is faster temperature is higher and vice versa. At absolute zero (T=0K ili t=-273,15˚C) all movement is stopped.

Temperature measuring instruments types: with liquids (mercury, alcohol), with bimetal, pneumatic, thermoelectric, optical…

Sensible and latent heat

Molecules in a solid have limited freedom and they only vibrate around fixed position.

Molecules in a liquid have greater freedom, while the freedom of molecules of a gaseous matter is absolute.

As heat is being added to the matter consequence can be:

- Increase in temperature
- Melting or evaporation
- Change of volume and color
- Increase of pressure

Opposite happens as heat is being removed.

Sensible heat when added or removed causes a change in temperature of matter but not in state.

Latent heat when given or absorbed by a substance causes a change of state. There is no change in temperature. There are latent heat of melting and evaporation, reversed processes – latent heat of solidification and condensation.

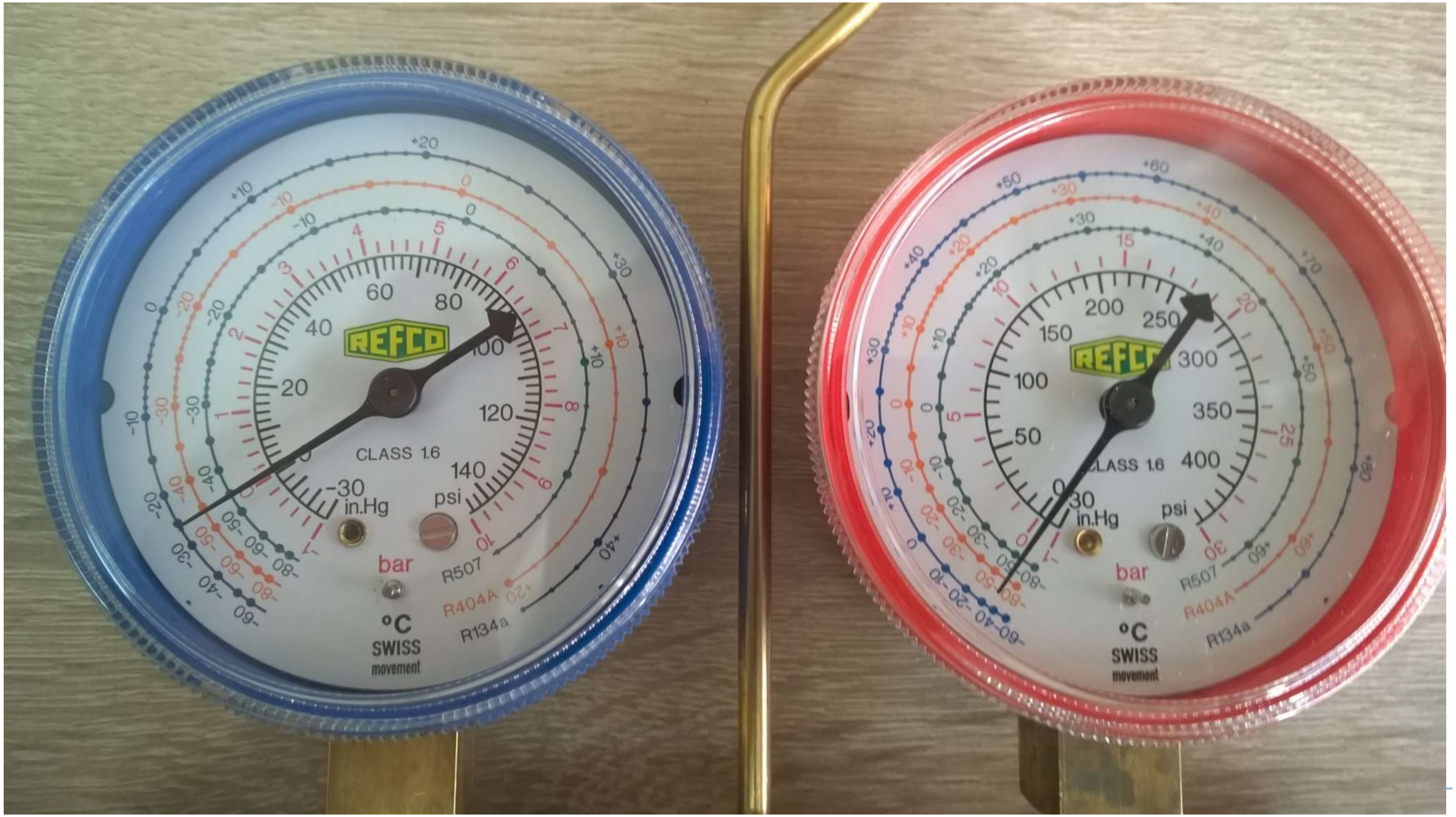
Saturation temperature and pressure

Saturation temperature, known also as temperature of evaporation and temperature of condensation is the temperature at which the substance will change state from liquid to vapor or vice versa. It depends on pressure and there are data tables or diagrams with saturation temperature and saturation pressure relation for practically every technical fluid on the market.

Saturation temperature and pressure are determined by each other.

Pressure measuring instruments (manometers) often have temperature scales which can be used instead of thermodynamic tables.

Saturation temperature and pressure



Superheating and subcooling

A state after vapor has absorbed total amount of latent heat of evaporation (it evaporates completely) is called dry saturated vapor. If more heat is being added to that kind of vapor (which would happen in refrigerating equipment for several reasons) we say it's being superheated. Vapor temperature rises.

When vapor is being cooled in the condenser there is first decrease in temperature, than condensation occurs. There is the state of saturated liquid after total amount of latent heat of condensation is removed. If more heat is being removed, in the condenser itself or in the supplement cooler (sub cooler or economizer), subcooling occurs. The condensate is cooled below saturated pressure-temperature. Bigger refrigerators have condensate sub cooler to increase efficiency.

Phase diagram T-Q

A - B sensible heat, solid
temperature rises

B – melting point

B - C latent heat of melting,
temperature is constant

C – finish point of melting

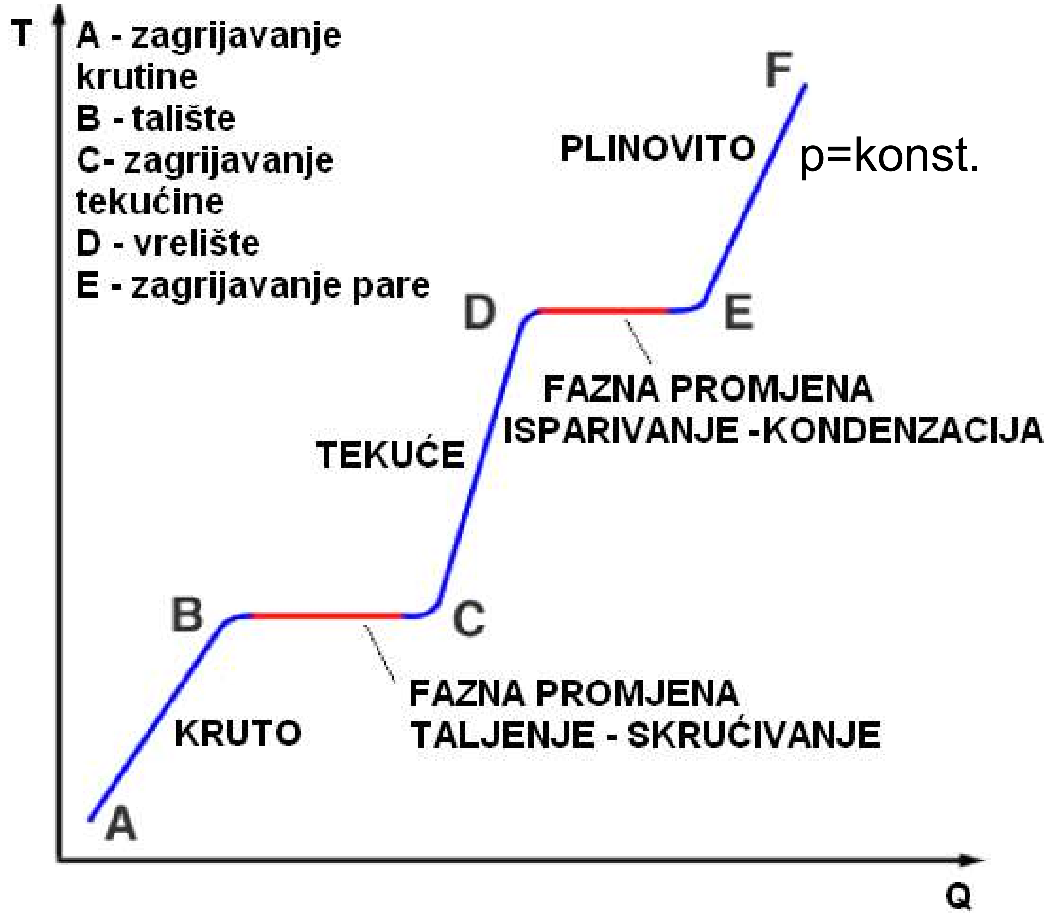
C – D sensible heat, temperature
rises

D – saturation point

D – E latent heat of evaporation,
temperature is constant

E – finish point of evaporation,
superheating

F – superheated vapor



Entropy and enthalpy

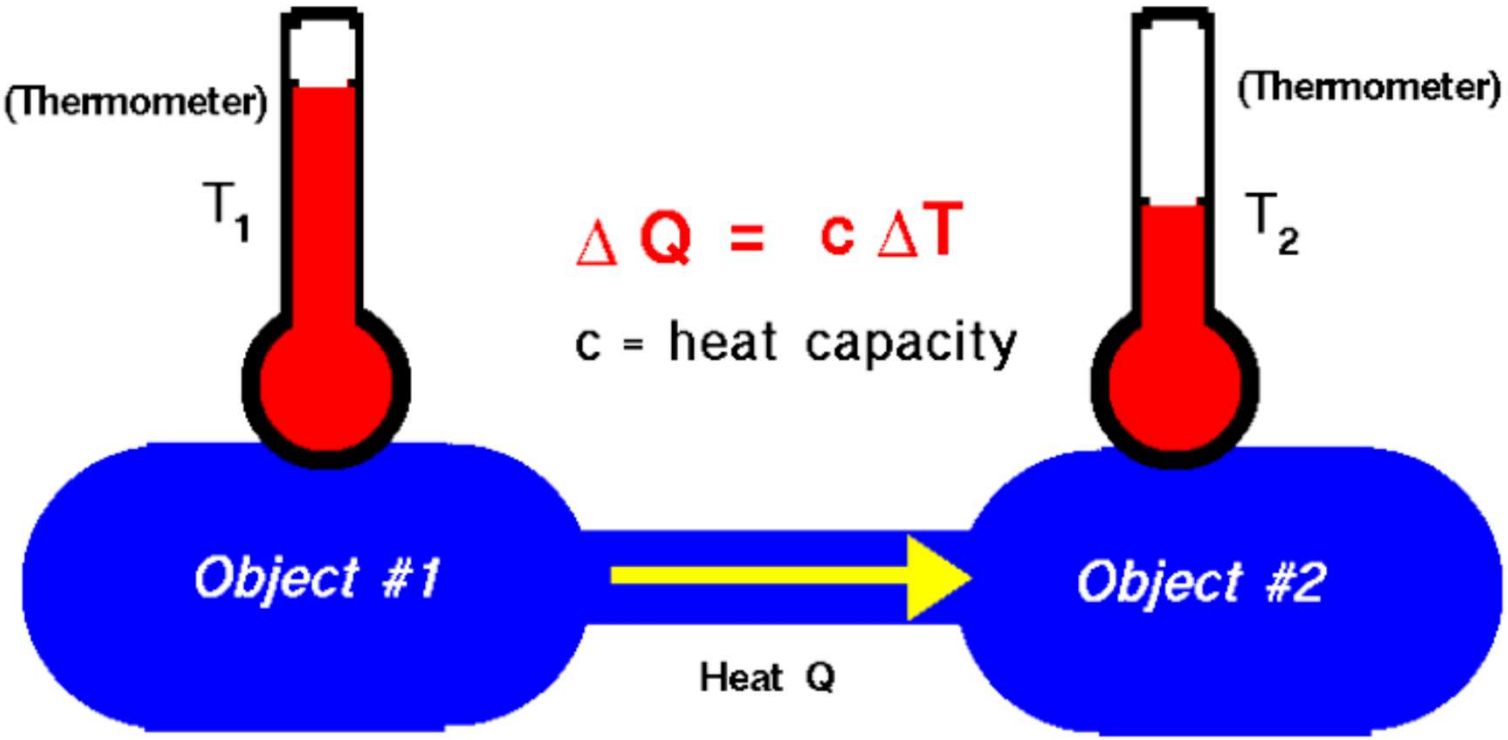
Entropy is a thermodynamic quantity that helps to account for the flow of energy through a thermodynamic process. It is a measure of a reversibility of a process. A compression is theoretically a reversible process, because by an expansion we get the same condition. Thus the entropy of that process is a constant. Opposite to that a process in a metering device is an irreversible process so the entropy rises.

Enthalpy or heat content shows total heat energy of the matter. It includes the energy of work (p, V) and it shows capability of substance to perform work and substance internal energy. It's increased with heat being added to the matter, and decreased by heat being removed.

Natural (thermodynamic) laws

- Heat exchange exists if there is a temperature difference: $q \sim \Delta T$
- heat flows from higher temperature towards lower
- Heat flow exists until temperature equilibrium
- Purpose of refrigeration: to extract heat from a space, fluid in a space or flowing through...until its temperature is lower than surrounding one and to maintain that temperature
- There is a collision with the natural low
- A <u>process</u> should be included

Exchange of heat and temperature

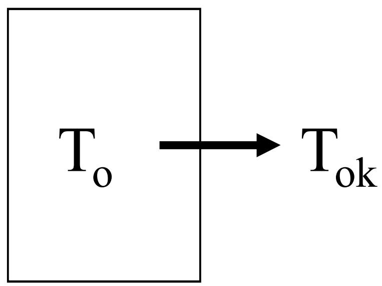


HEAT FLUX EXISTS IF THERE IS A TEMPERATURE DIFFERENCE. HEAT FLOWS FROM THE OBJECT HAVING HIGHER TEMPERATURE TO THE OBJECT HAVING LOWER TEMPERATURE.

Heat flow in the nature

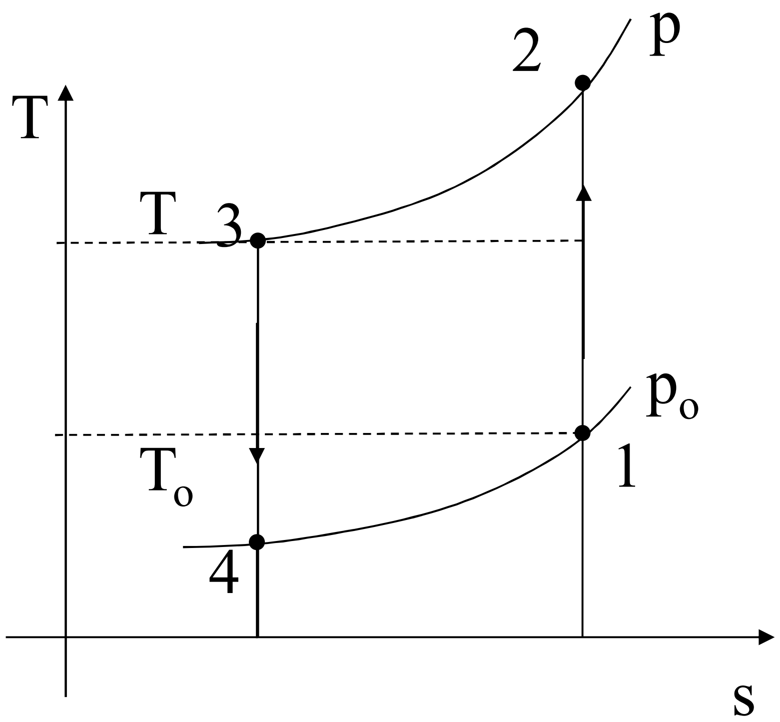
If there is $T_o<T_{sur}$ heat flows from the surroundings to the isolated space, until there is a temperature difference.

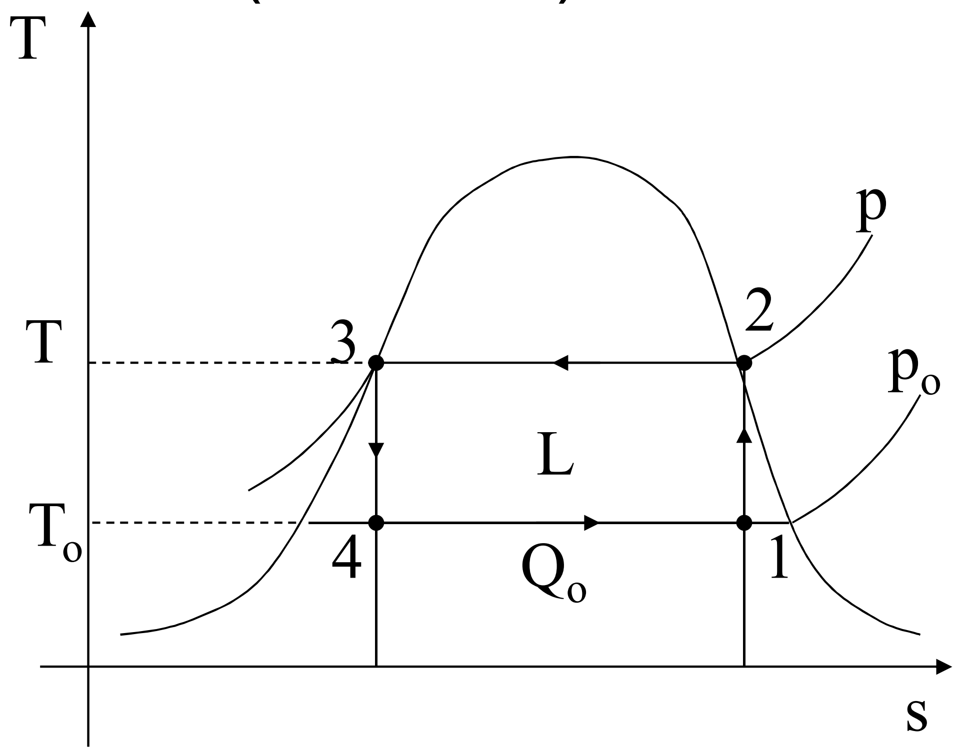
The purpose of refrigeration is to achieve temperature lower than the surrounding temperature and to maintain that temperature, so a technological process is needed.



Simple refrigeration processes

- Air compression vs. Carnot (reversed)





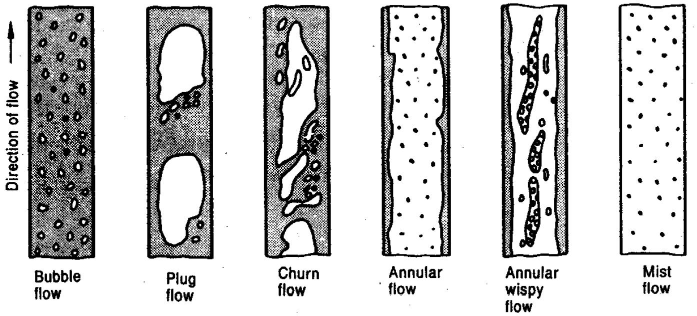
Heat exchange

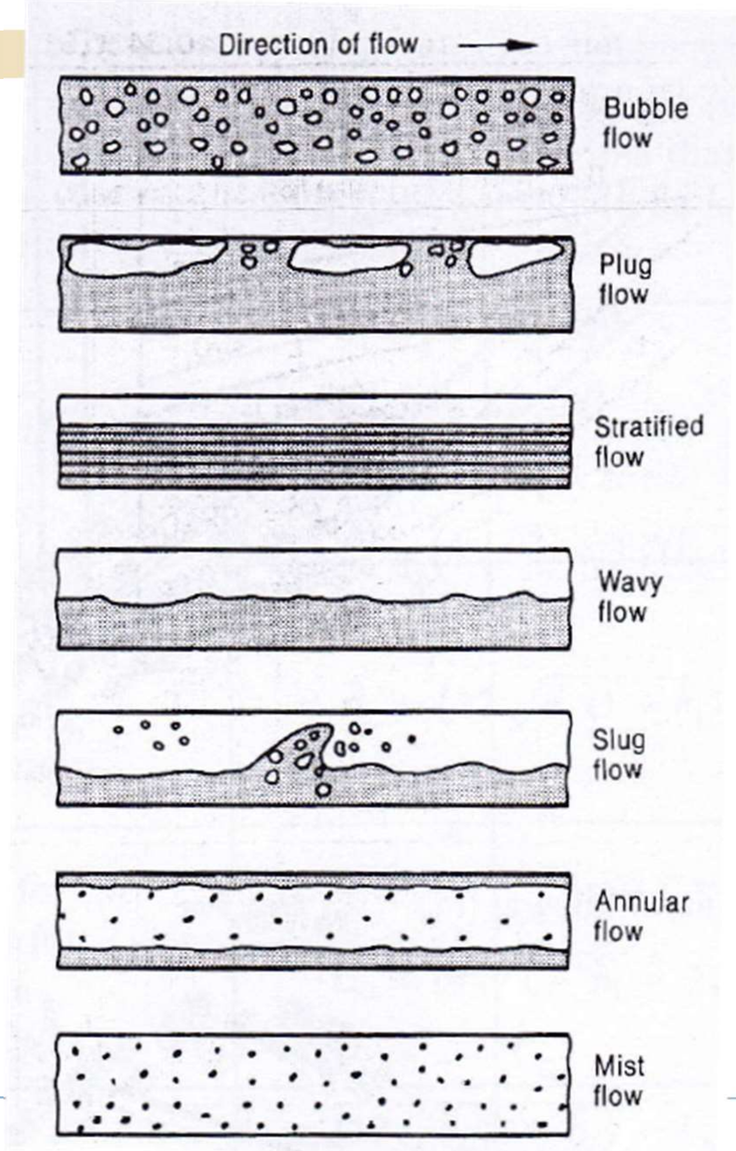
- Heat exchangers
- Heat exchange coefficient
  - Construction
  - Conditions vary during exploitation
- Sensible and latent heat
- Condensation – evaporation
- Channel shape, properties of fluids and of tubbing, fluids velocities...

1.2. Phase change and two phase flow

Phase change in the heat exchanger's pipes

- Evaporation – condensation
- Flow through pipes, pipe type heat exchangers
- **horizontal** and vertical pipes
- Oil and other substances



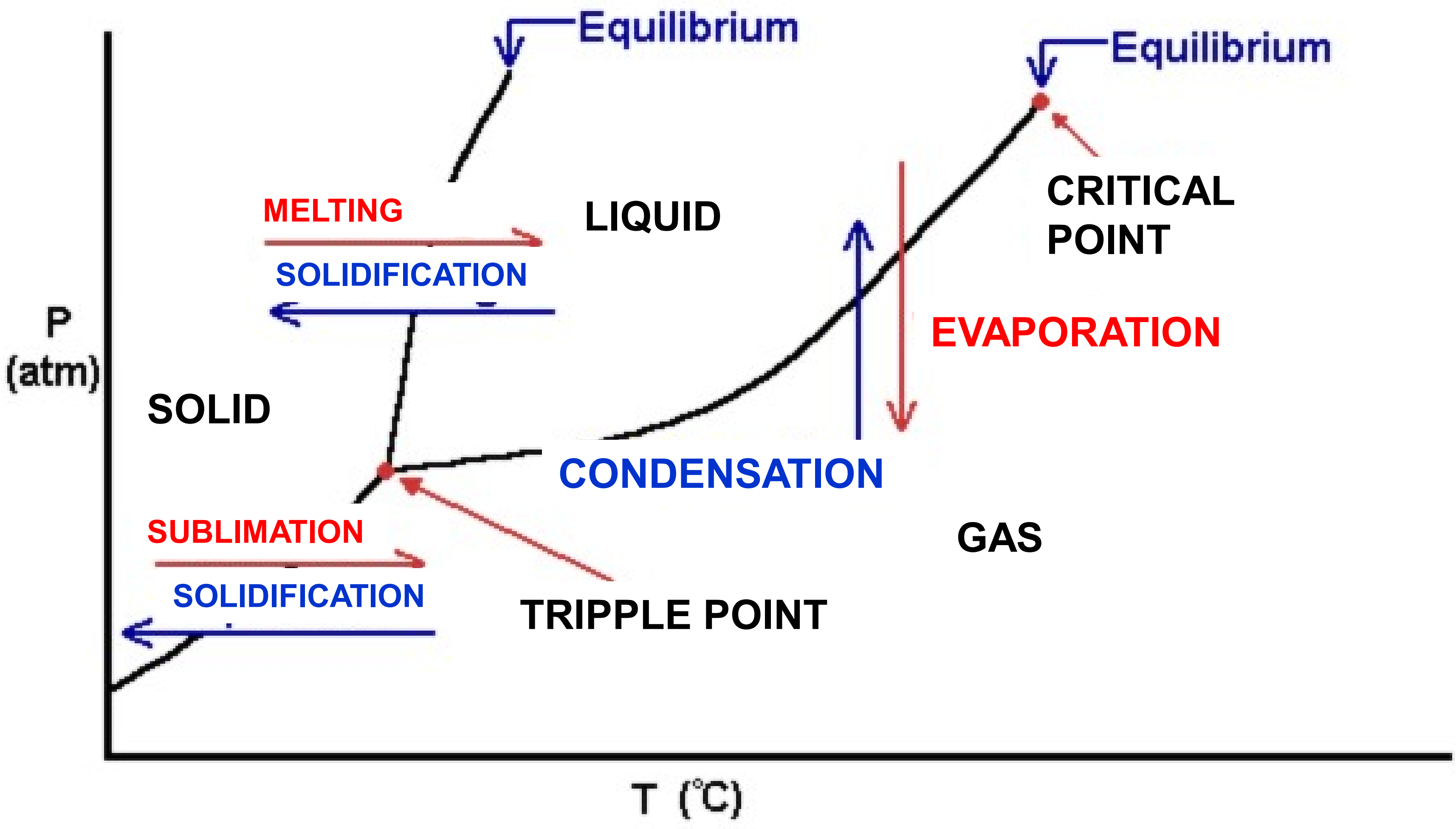


1.3. Refrigeration cycles (processes)

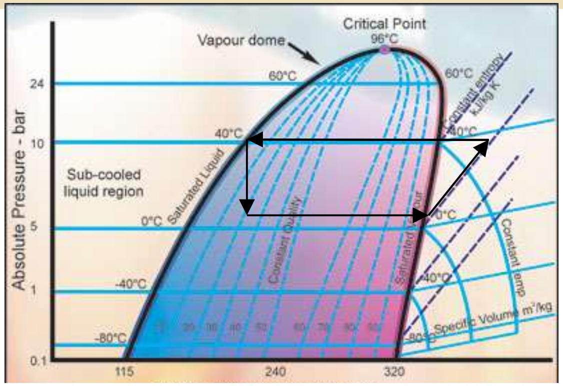
Compression (vapor) - absorption

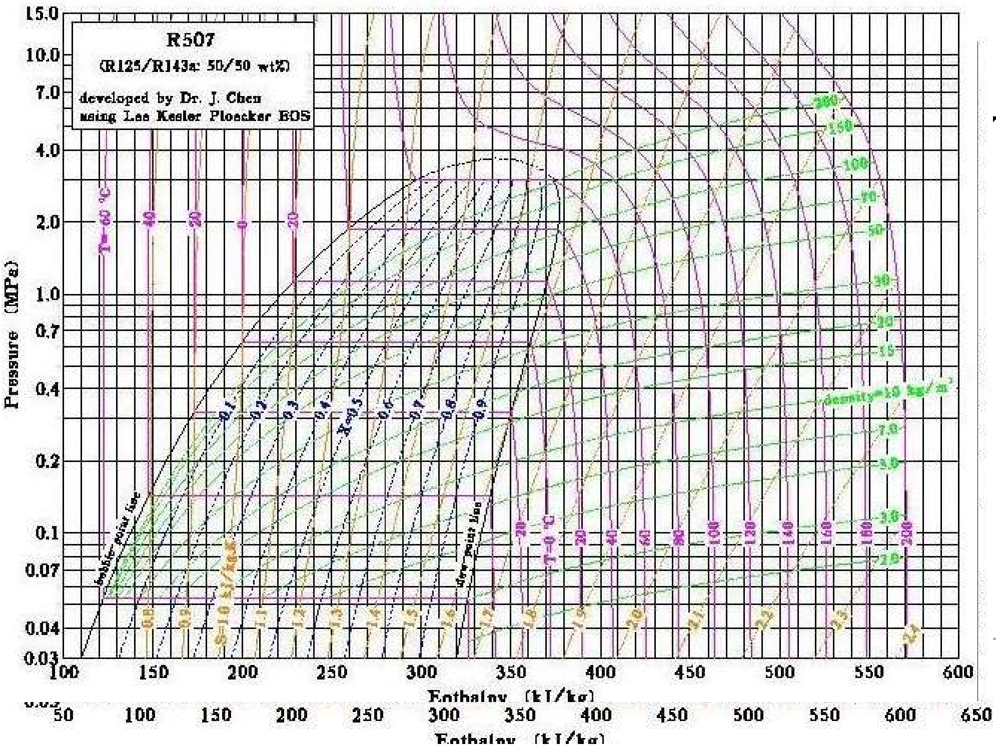
- Compression – air: sensible heat, low heat capacity, massive, low efficiency
- Vapor- Compression since XIX cent.: ethyl ether $\Rightarrow$dimethyl ether $\Rightarrow$ NH_3 $\Rightarrow$ CO_2 $\Rightarrow$$SO_2$ $\Rightarrow$ N_2O $\Rightarrow$ ethana (ethylene, propane, isobutene) $\Rightarrow$ chloromethane, marine equipment - CO_2 i NH_3 $\Rightarrow$ FREONs (R-12, R-22) $\Rightarrow$ R-134a, R-143a, R-410A, R-507...
- absorption equipment need mainly heat and are rarely used on board ships

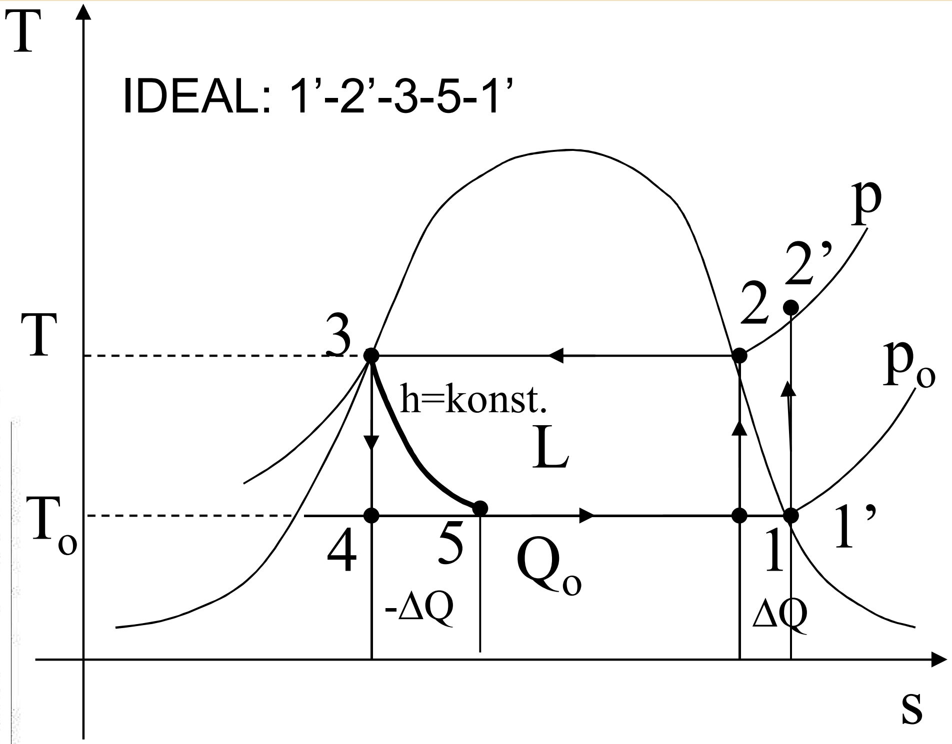
Phase diagram p-T



Refrigeration processes







A real process – difference from the theory

- TEV is applied and the vapor on evaporator exit is superheated
- Vapor is heated up even in the pipe between the evaporator and the compressor, and there is a small pressure drop too
- Pressure drop exists in the compressor suction valves
- Fluid heats up during suction
- Compression is a polytrophic with variable coefficient
- Pressure and temperature drop occurs during exit through compressor pressure valve
- Pressure drop occurs in the pipe between compressor and the condenser and in the condenser too
- Sub cooling can occur in the condenser, and if there is a sub cooler vapor is superheated before compressor suction
- Pressure drop in the evaporator tubes

- confirmation: SIMULATOR

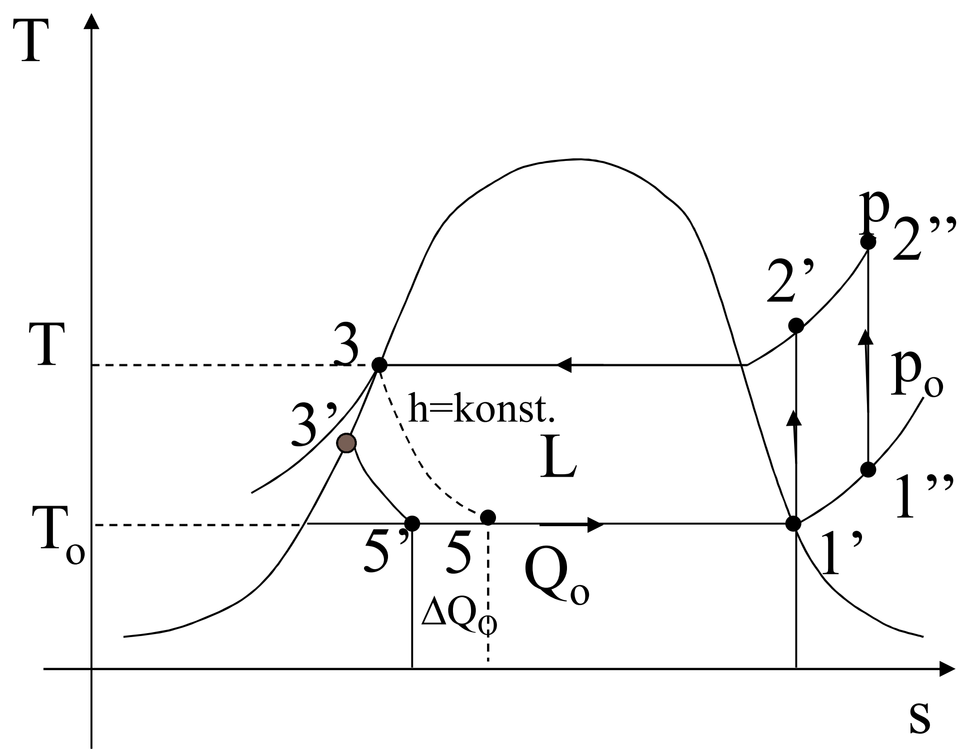
1.4. Coefficient of performance (COP)

Efficiency of a vapor-compression refrigerator

- Coefficient of performance shows the quality of vapor-compression equipment
- $COP(\varepsilon) = Q_o / L$
- It is not comparable with the heat coefficient η_t
- improvements
  - Sub cooling of the condensate
  - Two stage or multi stage compression
- Refrigerant properties

Improvements

- Two stage compression is used only if necessary
- Condensate sub cooling
- Cooler vapor sub cools the condensate
- Cooling effect and COP increased

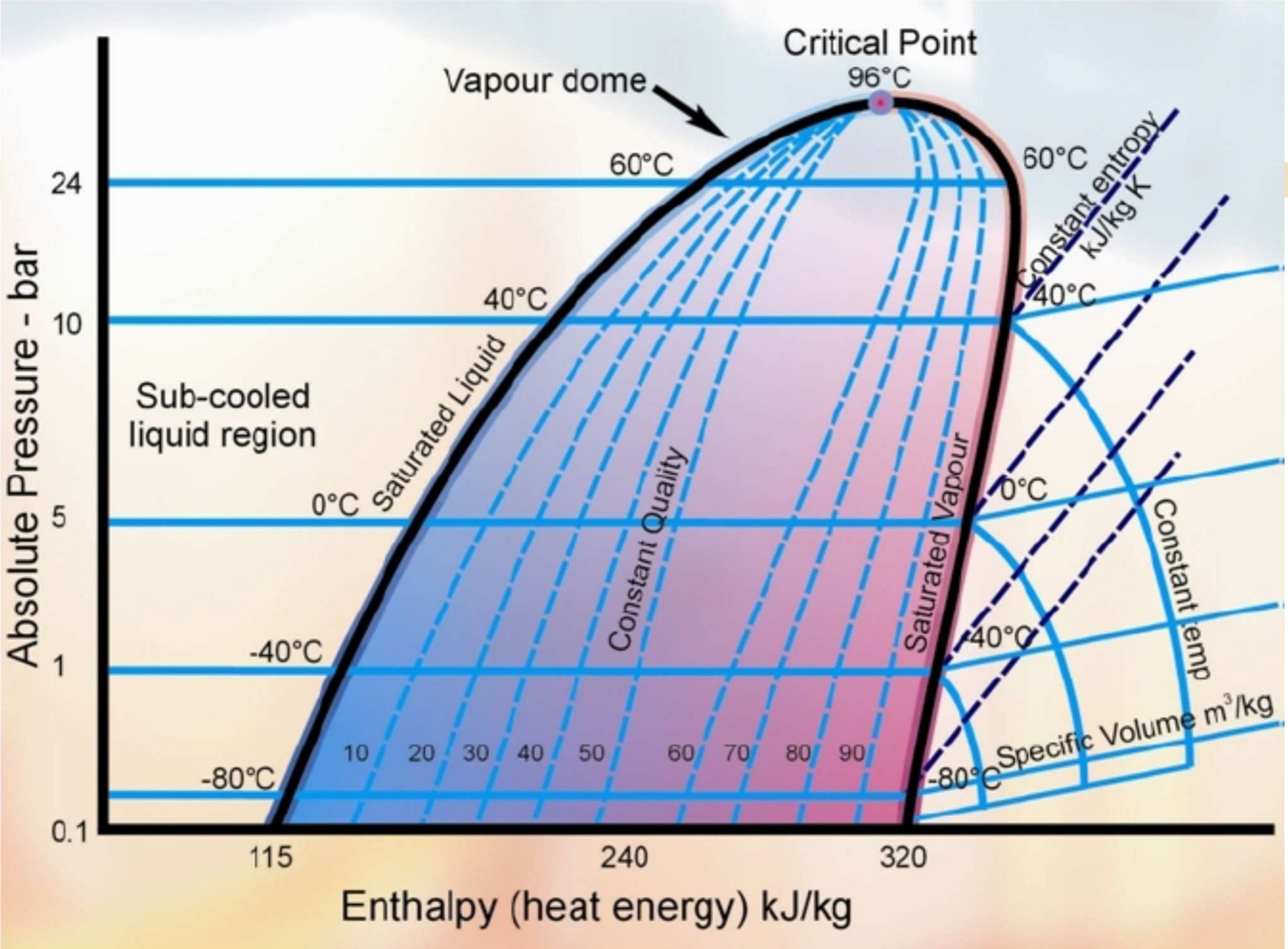


1.5. Refrigerants and lubricating oils properties

What is a refrigerant?

A refrigerant (fluid, substance) is the working agent that absorbs, carries and releases heat from the space to be cooled. This heat transfer generally takes place through a phase change of the refrigerant.

A more complete definition of a refrigerant could be: refrigerant is the fluid used for heat transfer in a refrigerating system that absorbs heat during evaporation from the region of low pressure and temperature, and releases heat during condensation at a region of higher pressure and temperature.



Critical Point
96°C
Vapour dome
60°C
60°C
Constant entropy kJ/kg K
40°C
40°C
Sub-cooled liquid region
Saturated Liquid
0°C
0°C
Constant Quality
Saturated Vapour
Constant temp
-40°C
-40°C
Specific Volume m³/kg
-80°C
-80°C
10
20
30
40
50
60
70
80
90
24
10
5
1
0.1
Absolute Pressure - bar
115
240
320
Enthalpy (heat energy) kJ/kg

Primary and secondary refrigerants

The primary refrigerants are those that pass through the processes of compression, cooling or condensation, expansion and evaporation or warming up during cyclic processes. Ammonia, R12, R22, carbon dioxide come under this class of refrigerants.

Secondary refrigerants are those fluids used to transfer heat between primary refrigerant system and what's being cooled (cargo, air in central acclimatization units etc.). It can be water, brine solutions of sodium chloride and calcium chloride etc.

Properties of primary refrigerants

- Thermodynamic properties
  - Large cooling capacity
  - Moderate working pressures, but above atmospheric
- Physical properties
- Chemical properties
  - Non corrosive, chemically inert
  - Not harmful to the environment
- Safety properties
  - Flammability and toxicity
- Economic criteria

Thermodynamic properties

Critical temperature should be as high as possible above the condensing temperature (which depends on the condenser's cooling agent temperature) in order to have a greater heat transfer at a constant temperature.

Critical pressure should be moderate, above the working pressure, but not very high.

Specific heat of the liquid phase should be as small as possible (better effect of condensation, better sub cooling, smaller losses in the metering device), but specific heat of vapor as high as possible.

Enthalpy of vaporization should be as large as posible to increase heat efficiency of the equipment – because for the same cooling effect lowers the required flow rate of the refrigerant.

Conductivity of the refrigerant should be as high as possible to increase heat exchange coefficient in the condenser and evaporator.

Thermodynamic properties

Evaporator and condenser pressures need to be above atmospheric otherwise there is a possibility of air leaking into the system. On the other hand it is not desirable to have to high pressures in the system which is related to the safety aspects.

Volumetric heat capacity should be as high as possible to decrease flow of refrigerant in the system for the same cooling effect. For refrigerants having higher volumetric heat capacities piston compressors are used, while for those having lower capacities turbo (centrifugal) compressors are used.

Density should be as large as possible to reduce cylinder dimensions and to enable pressure rise in the compressor.

Compression temperature should be lowest possible. Whenever a refrigerant gets compressed, there is a rise in the temperature of the refrigerant resulting in the heating of the cylinder walls. This necessitates external cooling of the cylinder walls, two or multi stage compression and more expensive oils.

Physical properties

It is desirable that the refrigerant has a smell or some other property to enable detection of leakage. Leakage detectors are used.

Refrigerants should not be miscible with the oils because this would reduce the oil lubricating property. Although, some miscibility could be desirable.

Viscosity should be as small as possible to reduce pressure drop in the system and driving power of the compressor.

Chemical properties

Refrigerants should be chemically stable, i.e. inert under all pressures and temperatures. They should not chemically react with any of the substances in the system: metal that system is built of, rubbers or various plastic seals, drying agents, water, air, and lubricating oils.

Refrigerants should not be toxic, especially if used in food preservation.

Refrigerants should not be flammable. Carbon dioxide is very good solution in that respect, while ammonium is a very bad solution.

Safety properties

Under safety criteria toxicity, flammability, action on perishable food and formation of explosive compound on exposure to air are considered. An ideal refrigerant should be non-toxic, non-flammable, have no effect on food products and should not react with atmospheric air.

Refrigerants are grouped according to their flammability and toxicity levels.

Safety marks

VERY FLAMMABLE	A3	B3
LOW FLAMMABILITY	A2	B2
NOT FLAMMABLE	A1	B1
	LOW TOXICITY	HIGH TOXICITY

Oznaka	Naziv	Sastav ili kemijska formula	Sigurnosna oznaka
		(maseni udjeli)	
Anorganske tvari			
R-717	amonijak	NH_3	B2
R-718	voda	H_2O	A1
R-744	ugljični dioksid	CO_2	A1
Organske tvari			
Ugljikovodici			
R-290	propan	$CH_3CH_2CH_3$	A3
R-600	butan	$CH_3CH_2CH_2CH_3$	A3
R-600a	izobutan	$CH(CH_3)_2CH_3$	A3
R-1270	propilen	$CH_3CH{=}CH_2$	A3
Fluorougljikovodici (HFC)			
R-32	difluormetan	CH_2F_2	A2
R-125	pentafluoretan	$CHF_2\,CF_3$	A1
R-134a	1,1,1,2-tetrafluoroetan	$CH_2\,FCF_3$	A1
R-143a	1,1,1-trifluoroetan	$CH_3\,CF_3$	A2
R-152a	1,1-difluoroetan	$CH_3\,CHF_2$	A2
Azeotropne smjese			
R-502		R22/R115 (48.8/51.2)	A1
R-507		R125/R143a (50/50)	A1
Zeotropne smjese			
R-404A		R125/R143a/R134a (44/52/4)	A1
R-407C		R32/R125/R134a (23/25/52)	A1
R-410A		R32/R125 (50/50)	A1

Mixture safety mark

It is defined according to the mark of the worse component, i.e. it is assumed the worse scenario when that component remained in the system.

Economic criteria

Naturally, the lowest possible cost of refrigerant is desirable. The refrigerating equipment total cost is affected by refrigerant availability on the market and its mode of preserving. Refrigerants that could be transported in small receivers having low pressures, being non-flammable and non-toxic and that could be placed in rooms with no special ventilation system are better.

Chemical composition of refrigerants

- Halogenated hydrocarbons
- Hydrocarbons
- Inorganic substances (nitrogen, oxygen, helium, hydrogen...)
- Zeotropic and azeotropic mixtures
- Secondary: water solutions (brines)

Refrigerants identification - numbering

- xx + 90 = XYZ, where X – is a number of C atoms, Y – number of H atoms, Z – number of F atoms, 2X-Y-Z+2 – number of Cl atoms; if Cl=0 it is a HFC compound
- Little letter after the numeric mark is used for isomers (having the same number of atoms, but with a different structure)
- Example R-134a: 134+90=224; C=2; H=2; F=4; Cl=0 => C H_2F – $CF_{3;}$ tetrafluoroethane (HFC 134a)
- Cyclic hydrocarbons have letter C (RC316, RC317 and RC318)
- Various hydrocarbons (serial 600, ex. isobuthane is R-600a)
- The fourth digit on the right stands for unsaturated carbon-carbon bonds (ethylene, propylene etc.(serial from 1000)

Other fluids

- ASHRAE standard 34 -2004 and ISO 817: zeotropic mixtures - serial 400; azeotropic mixtures - serial 500
- Numbers assigned by chronological order after approval of ASHRAE
- Capital letters means the same composition, but with different mass proportions (R-407A R32/125/134a (20/40/40), R-407B R32/125/134a (10/70/20), R-407C R32/125/134a (23/25/52), R-407D R32/125/134a (15/15/70), R-407E R32/125/134a (25/15/60)
- inorganic substances
- mark=700+molecular mass
- m_{NH3}=17 (R-717), m_{CO2} (R-744), m_{H2O} (R-718)
- Some indirect refrigerators use water or brines as secondary fluid

Market (container systems)

- R134a
- R404A
- R407C, R407D
- R410A
- R413A
- R507A

Compressor lubricating oils

- In accordance with compressor manufacturers specification
- properties:
  - Low wax content – it can cause plug in refrigerant control orifices
  - Good thermal stability so they should not form hard carbon deposits on hot surfaces of the compressor (discharge valves)
  - Good chemical stability
  - Low pour point – ability to remain liquid even at the lowest temperature in the system
  - Good miscibility and solubility so it could return to the compressor
  - High viscosity index means that viscosity doesn't change much with the temperature

On the market

- mineral oils – used with CFC fluids
- alkyl benzene oils (AB)
- polyol ester oils (POE)
- Poly alpha olefin oils (PAO)
- Poly alkyl glycol oils (PAG)
- HFC compound need synthetic oils

Today

Refrigerant	Appropriate Lubricant				
	Mineral Oil (MO)	Alkyl benzene (AB)	Polyol Ester (POE)	Poly alpha oelfin (PAO)	Poly alkyl glycol (PAG)
CFC-11	✓	✗	□	□	✗
CFC-12	✓	✓	□	□	✗
R-502	✓	✓	□	□	✗
HCFC-22	✓	✓	□	□	✗
HCFC-123	✓	✓	□	□	✗
HFC-134a	✗	✗	✓	✗	□
HFC-404A	✗	✗	✓	✗	□
HFC-407C	✗	✗	✓	✗	□
HFC-410A	✗	✗	✓	✗	□
HFC-507A	✗	✗	✓	✗	□
HC-600a	✓	□	✓	✓	□
HC 290	✓	□	✓	✓	□
R 717 (NH_3)	✓	□	✗	✓	□
R 744 (CO_2)	□	□	✓	✓	✓

✓: Good Suitability □: Application with limitations ✗: Not Suitable

1.6. Chage of state of simple substance and of a mixture

Heat exchange with the change of state

- Simple substance: evaporates with pressure and temperature being constant
- Mixture: evaporates with temperature and composition of both the liquid and gaseous phase change
- Influence: if there is a leakage in the system composition changes (engl. composition shift) and performance of the refrigerator drops (engl. temperature shift)
- With refilling of the system condition improves, but not completely

1.7. Mixtures

Mixture vs. simple substance

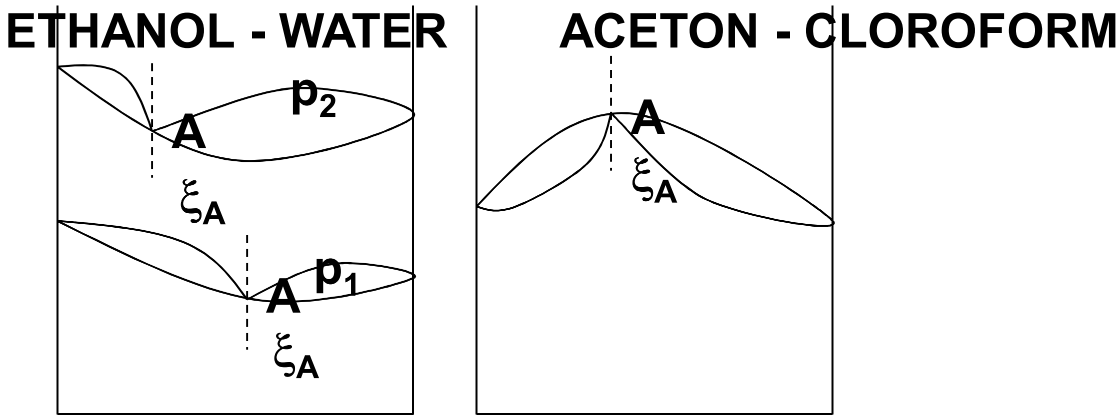
Simple substance changes phase with constant pressure and temperature.

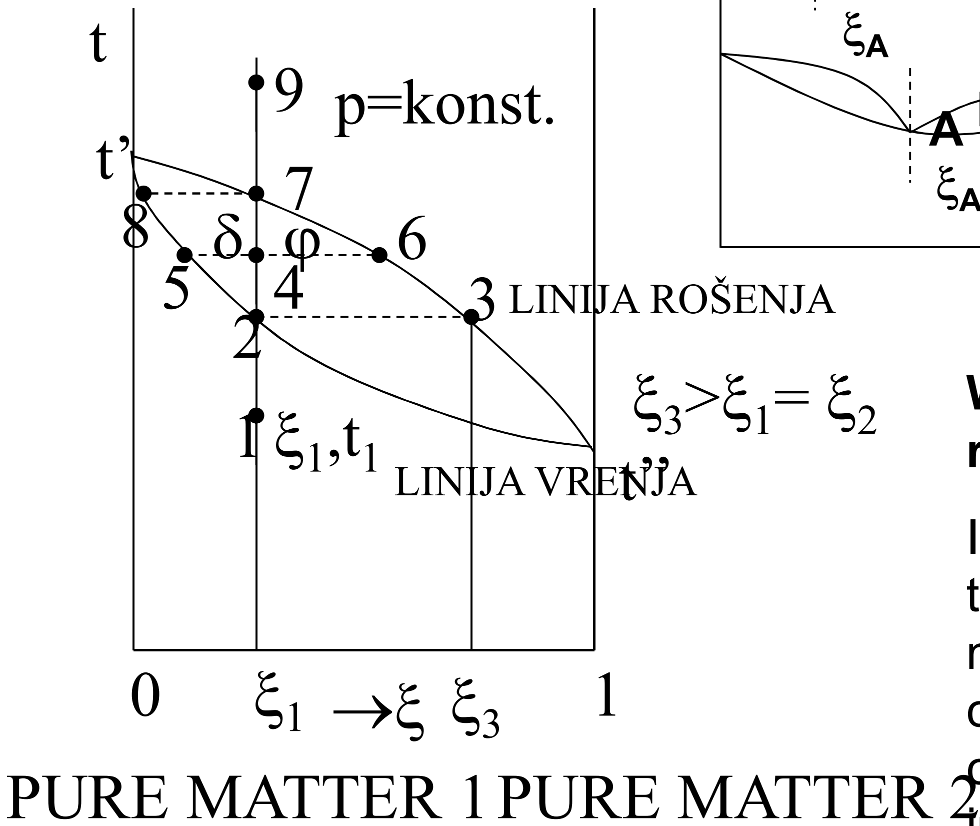
Mixtures could be homogenous and heterogeneous.

During change of phase process mixture changes composition of both phases and the temperature changes also.

Zeotropic and azeotropice mixtures are different because the second ones have a concentration (point) at which they act as a simple matter.

Zeotropic and azeotropic mixtures





What exploitation problem occurs in refrigerators working with mixtures?

If there is a leakage in the system some of the refrigerant gets lost, but since it's a mixture, not equal mass proportion of the components is lost. Mainly the lighter component is lost. By refilling condition improves but not completely!

1.8. Ecology and international rules and regulations

Harmfull influence on the environment

- ozone layer + global warming of atmosphere
- halogenated hydrocarbons (CFC and HCFC substances), CO_2, CH_4, N_2O...
- Montreal protocol
  - 1987, as amended in London 1990, Copenhagen 1992, Vienna 1995, Montreal 1997 and Beijing 1999
- Kyoto protocol adopted 1997 came into force 2005
- European conventions
- Amendment VI of MARPOL convention
- refrigerating equipment operator’s duty is to take care to release in to the atmosphere as low quantities as possible
- HFC’s are using today (no chlorine)

Practical exercises on the Carrier simulator

- system elements
- normal operation with TEV
- TEV superheat determination
- lack of working fluid in the system operation
- TEV
  - oversized
  - sensing bulb detached
- filthy condenser
- ice on the evaporator

THANK YOU!