Refrigeration

Dr. Zana János

Antecedents

- Ice creation experiments
William Cullen XVIII. century
- Heat engines, practice
James Watt XVIII. century
- Heat engines, theory
John Dalton, Lord Kelvin XIX. century

Antecedents

- Claim for increase the coefficient of performance
- Planning, building machines cylinder, piston, control parts

Antecedents

- Nicole Léonard Sadi Carnot
  no better heat engine exists than consists of

1. Isothermic heat addition
2. adiabatic compression
3. Isothermic heat removal
4. adiabatic expansion

$$\eta = \frac{W}{Q}, W \leq Q$$

Antecedents

Carl Paul Gottfried von Linde

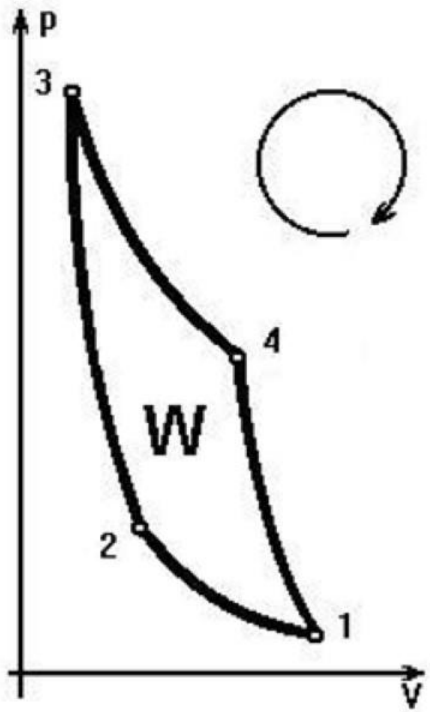
✓If the Carnot cycle gives the best efficiency than reversing it gives the best coefficiency of performance

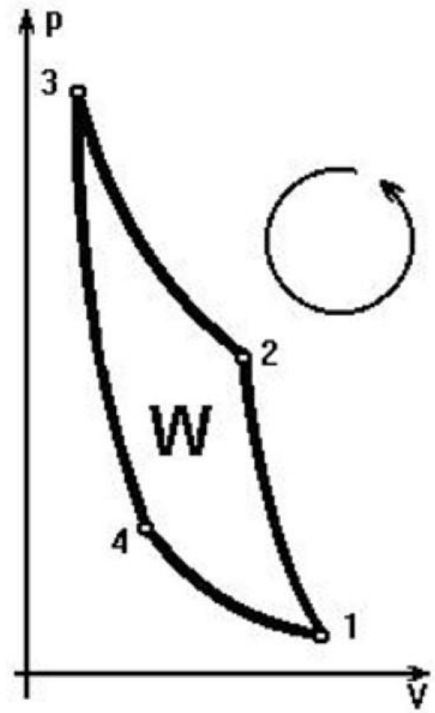
✓If a Carnot (Joule, Rankine) cycle tranfers heat from high temperature to a low tmperature resulting mechanical work, than *reversing* it

- Transfers heat from low temperature to a high temperature place, and needs for it
- Gets mechanical work

Antecedents

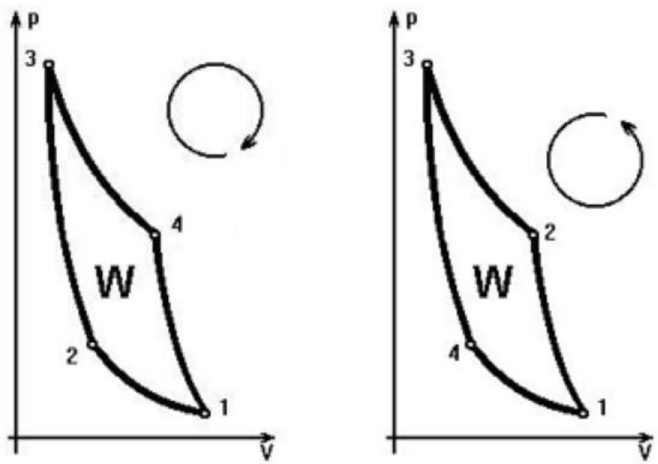
Carl Paul Gottfried von Linde





Antecedents

Carl Paul Gottfried von Linde



The integral over the closed line is the sum of areas on pV diagram

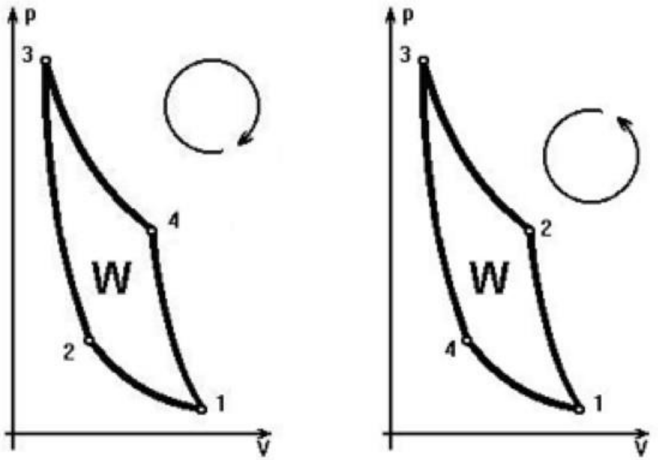
When changing the direction for counter clockwise causes the sign of work

$$W = \oint p \cdot dV$$

The integral over the closed curve gives the sum of the areas below the chart. The real refrigeration is suspended only the adiabatic compression signed 1–2

Antecedents

Carl Paul Gottfried von Linde



Sum of four change of states. Really the 1–2 adiabatic compression suspends the cycle

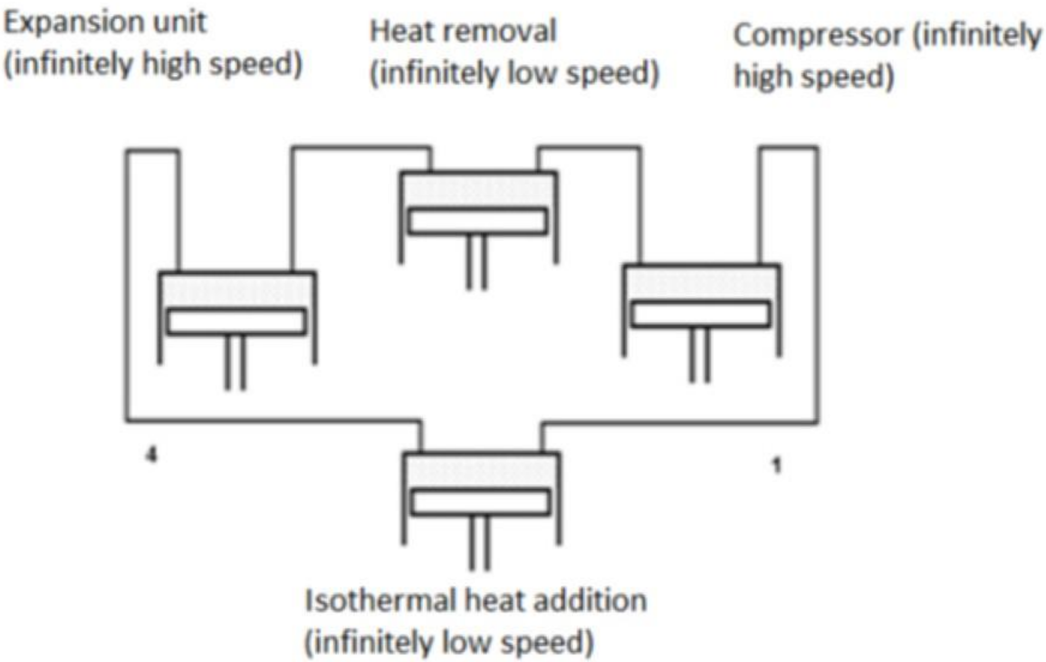
$$W_{12} = \frac{1}{\kappa - 1}(p_1 V_1 - p_2 V_2)$$

The equations are valid for proper gases only.. E.g. for the 2–3 isothermal compression the heat transfer and the work are equal

$$W_{23} = Q_{23} = RT \cdot \ln \frac{V_3}{V_2}$$

Realisation

Carl Paul Gottfried von Linde



The

- Ideal cycle
- Ideal gas

only theoretically can be realised

E.g. the 2–3 isothermal compression would have realised a piston moving infinitely slow. Its power would be zero

Realisation

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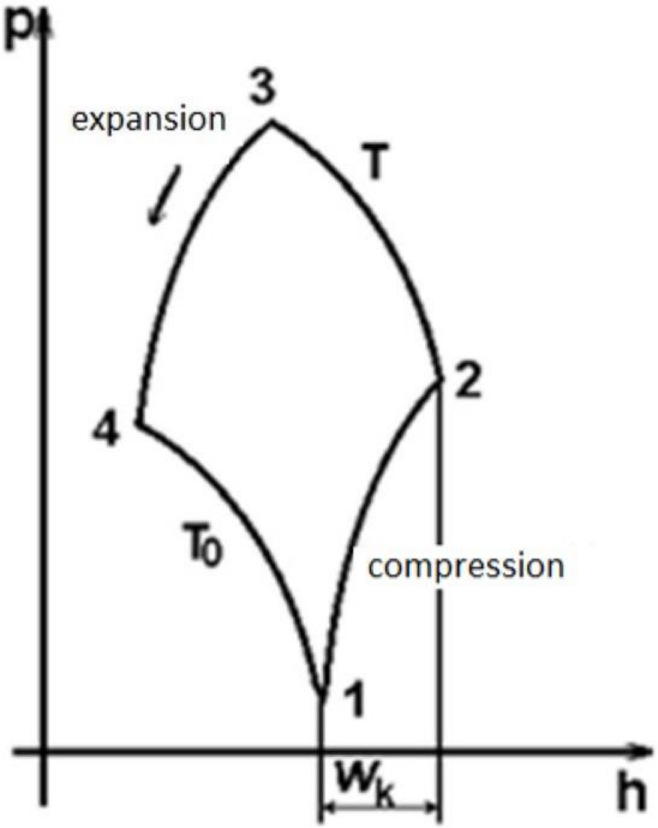


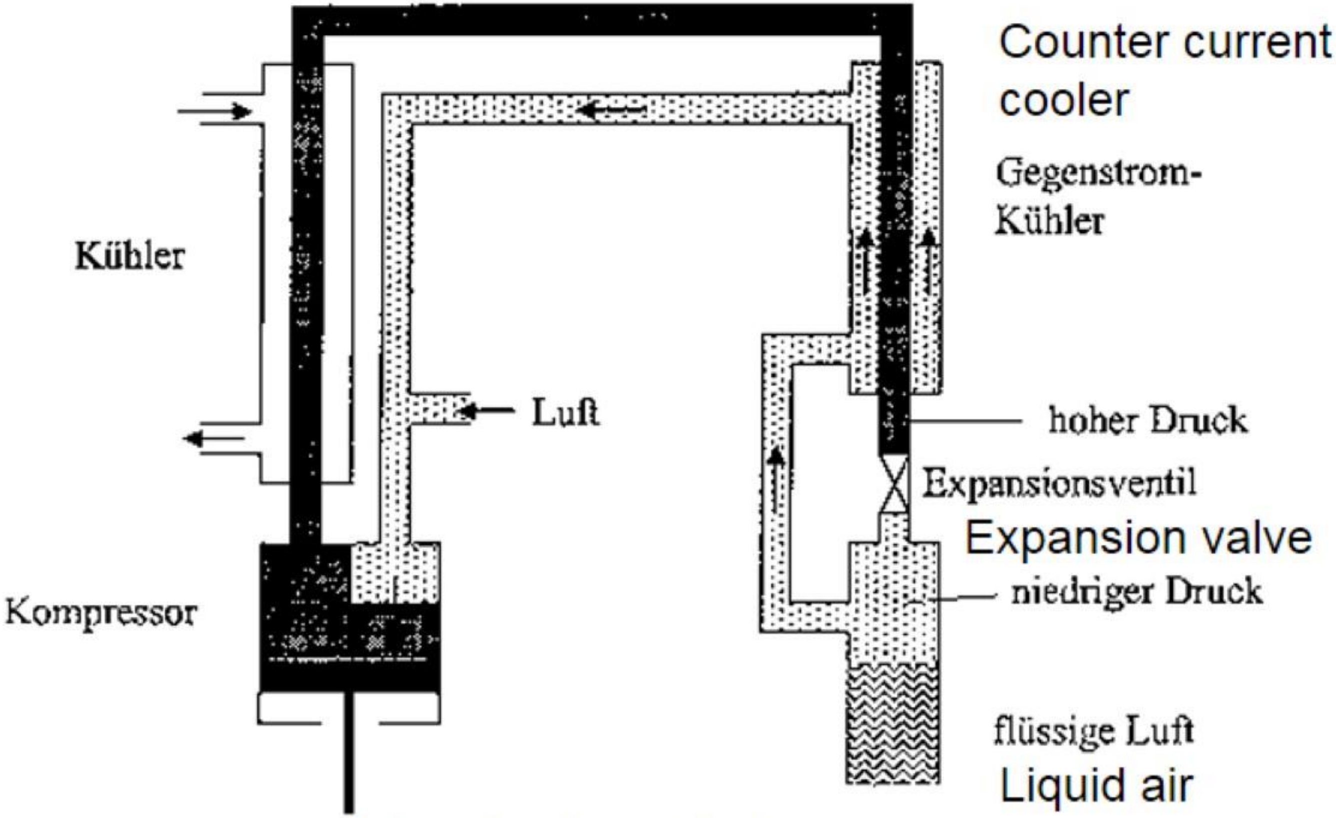
Thermodynamic diagram for refrigerator cycle. The work of compressor can be read from the change of the enthalpy. For unit mass we calculate the specific enthalpy

$$\mathrm{d}h = \delta q + v \cdot \mathrm{d}p$$

There is no heat exchange. So the change of enthalpy is equal to the isentropic work input.

Original realisation

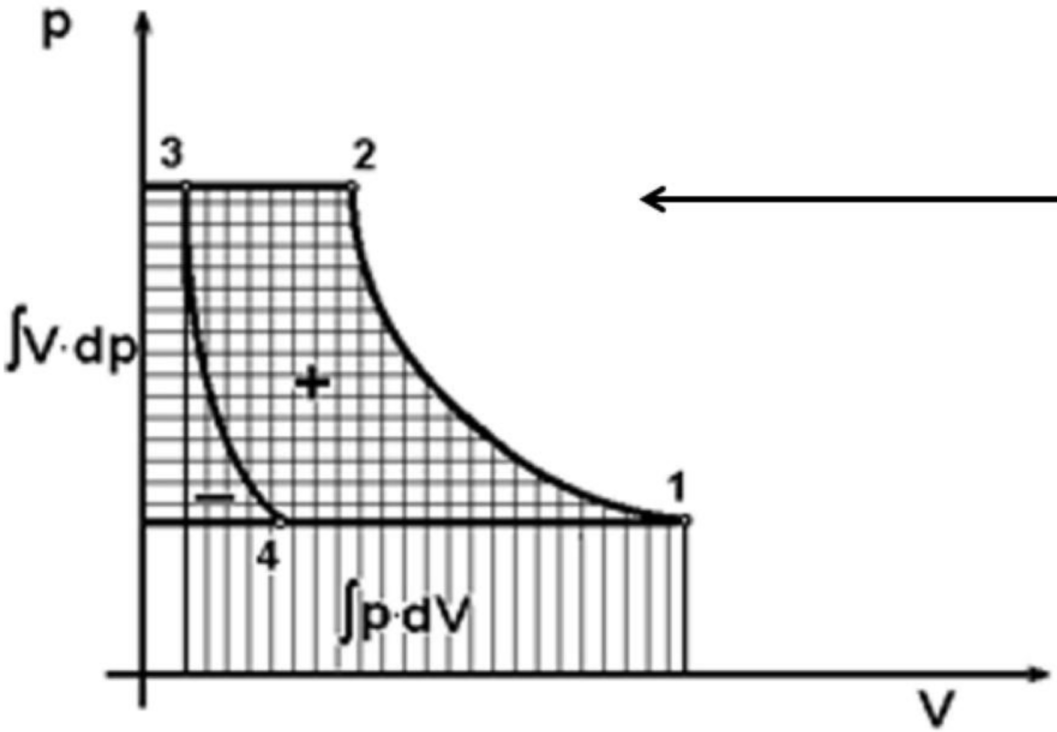
Carl Paul Gottfried von Linde



Liquefaction of air.
A historical experiment

Compression

Indicator diagram

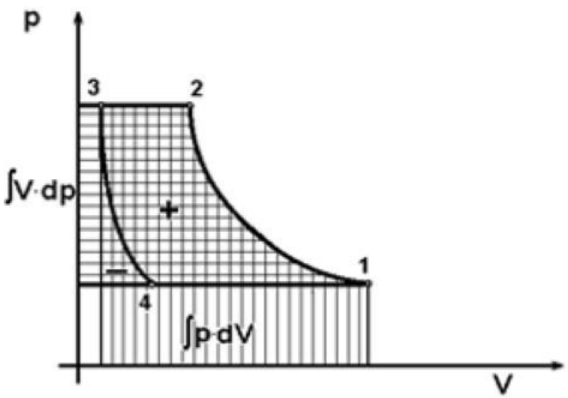


$$W_t = \int_{p_1}^{p_2} V \cdot \mathrm{d}p$$

$$W = \int_{V_1}^{V_2} p \cdot dV$$

Compression

Indicator diagram



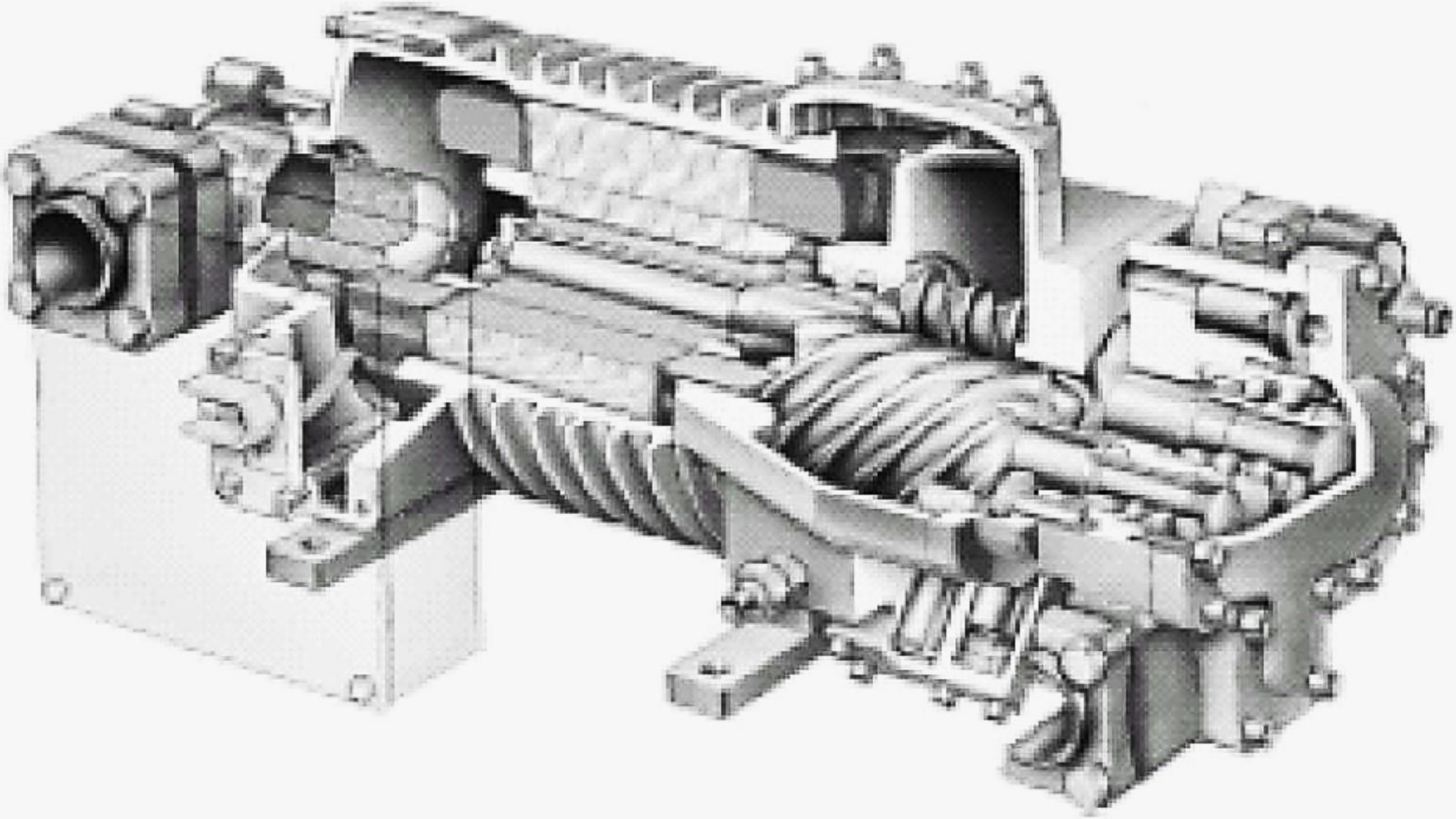
Steps of the real working compressor:

1. Sucking up to the point 1 (full volume of cylinder)
2. Adiabatic compression, 1–2
3. Removing the gas from the cylinder. 2–3
   We can not decease its volume down to zero.; V_3 is the clearance volume (minimal volume of cylinder)
4. The remainder gas undergoes an adiabatic expansion, 3–4

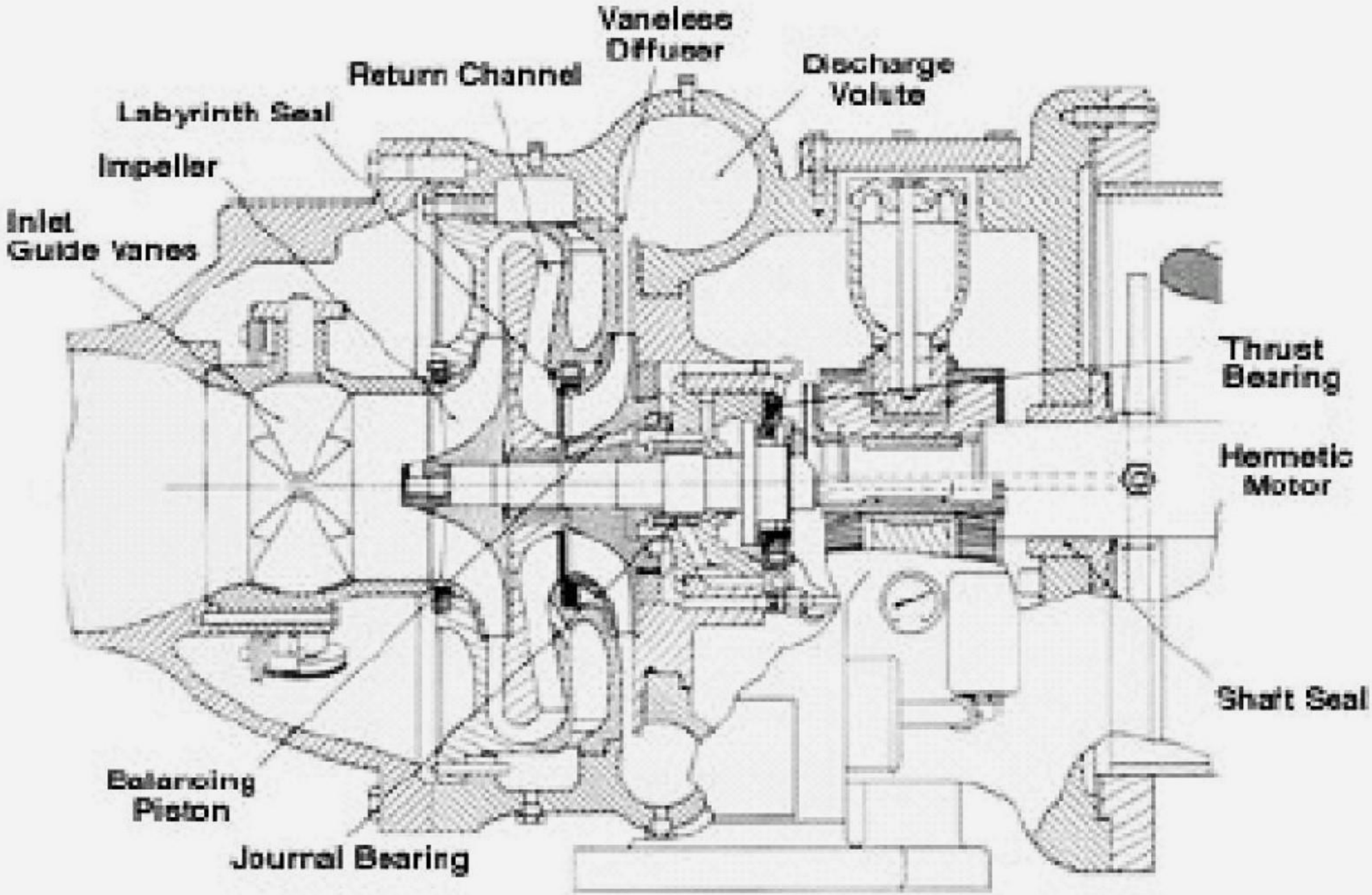
V_3 theoretically zero. The sum of four works ***p·dv*** results the area of line integral of ***v·dp***

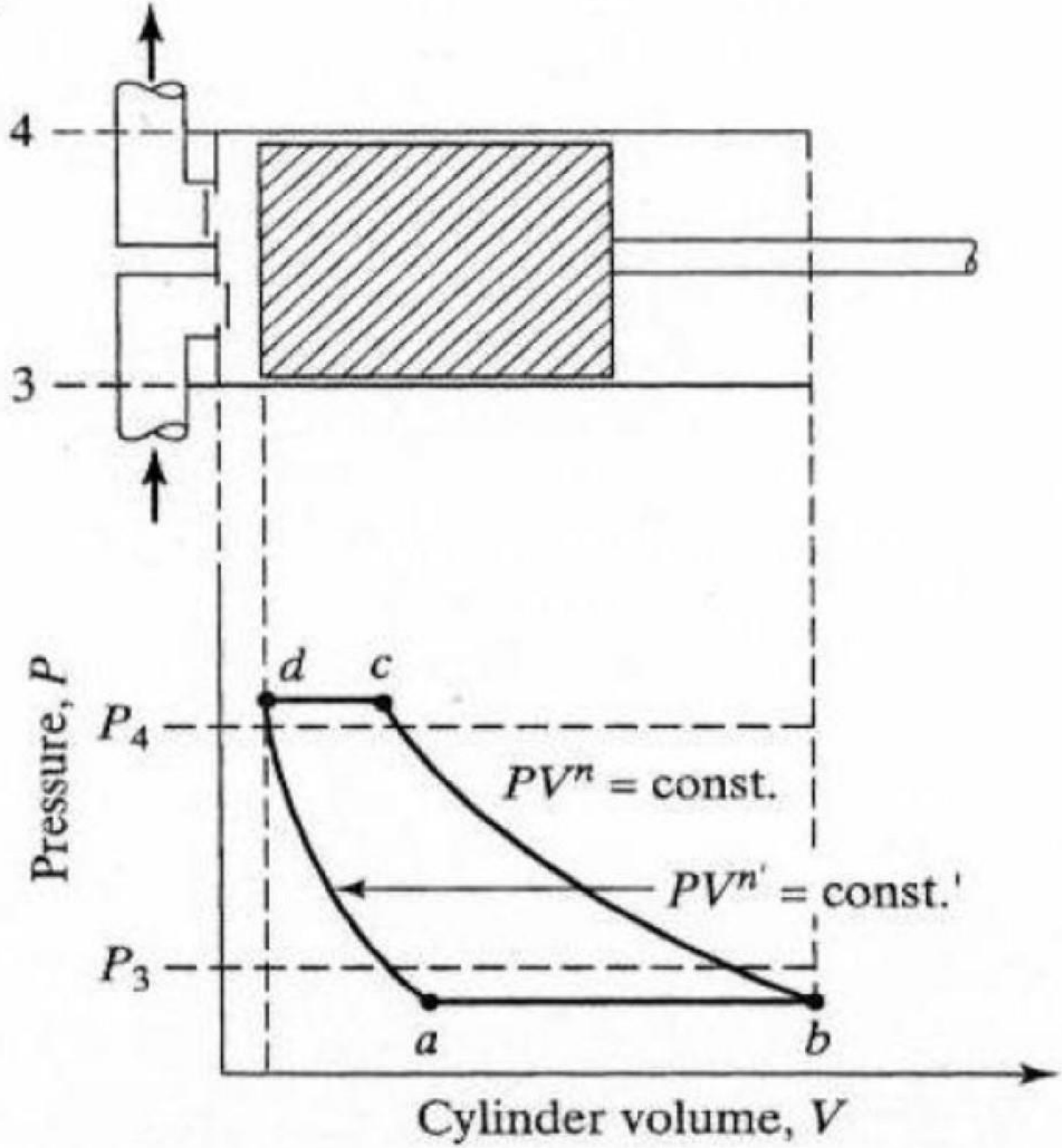
The mass inside the cylinder is constant so the shape of graphs related to ***v*** (specific volume) the same that related to the ***V*** (full volume)

Rotary screw compressor



centrifugal compressor





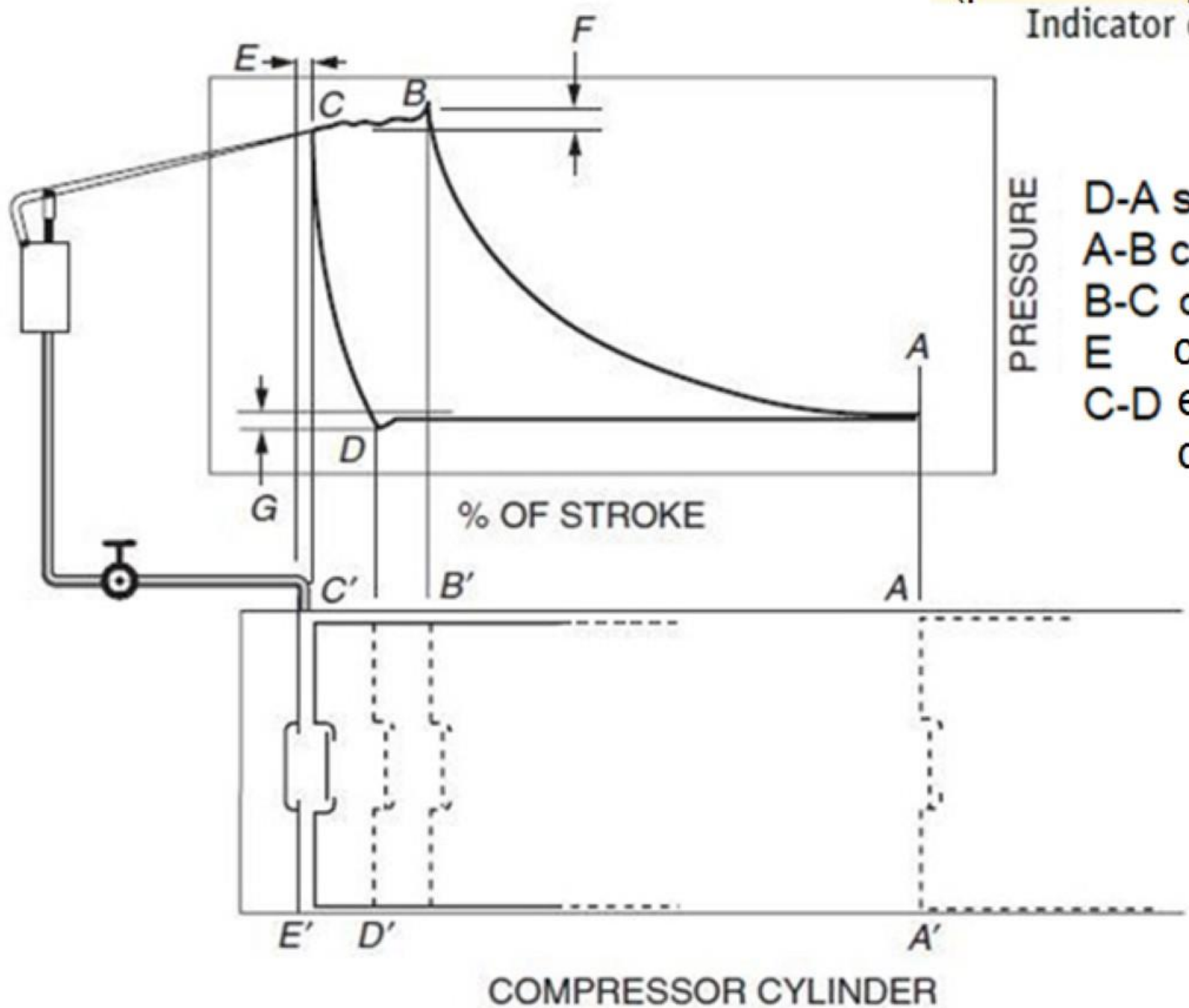
reciprocating compressor

The compression is not adiabatic but, in many cases polytropic

The construction have the suction and discharge valves on the cylinder head

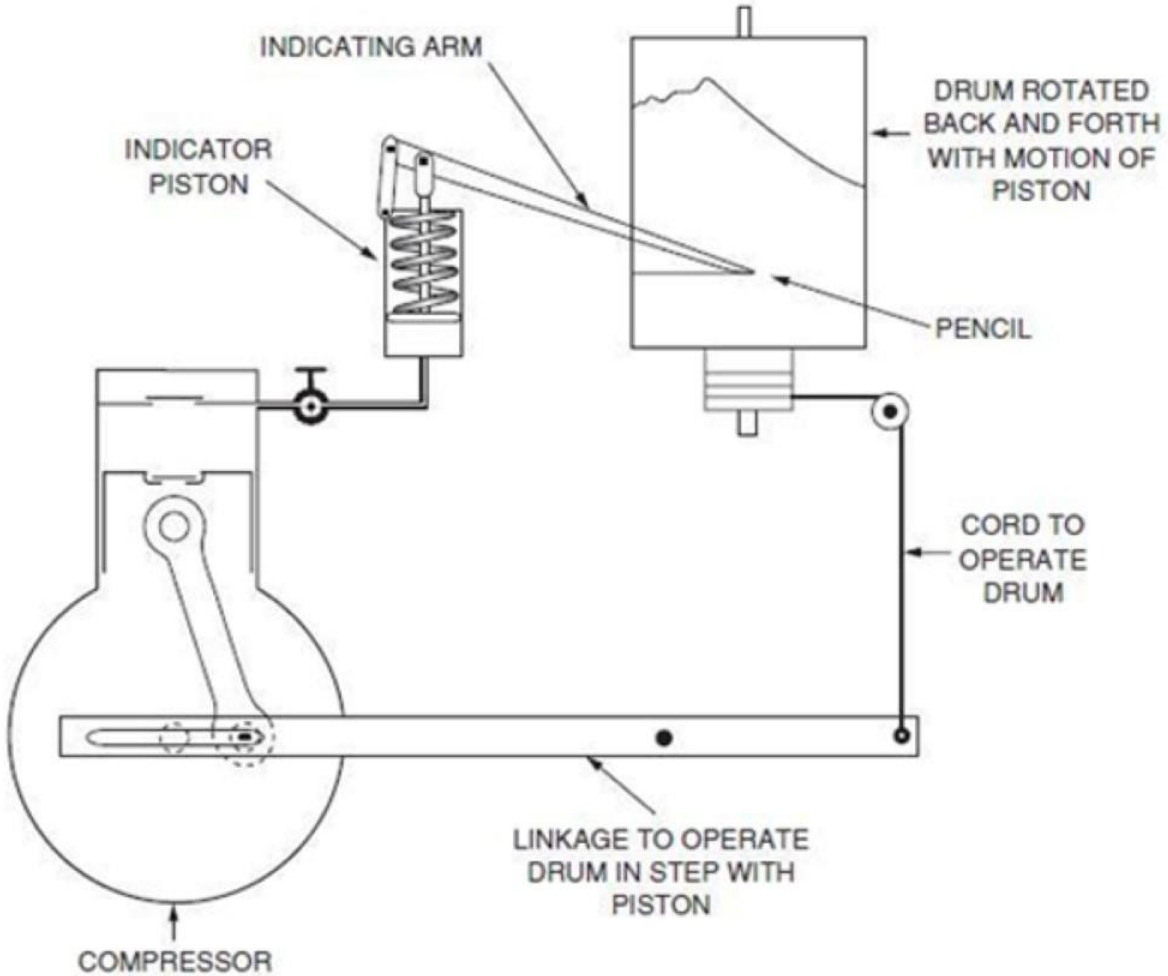
Compression

Not to learn: engine indicators
(pressure speed 10^9 Pa/s)



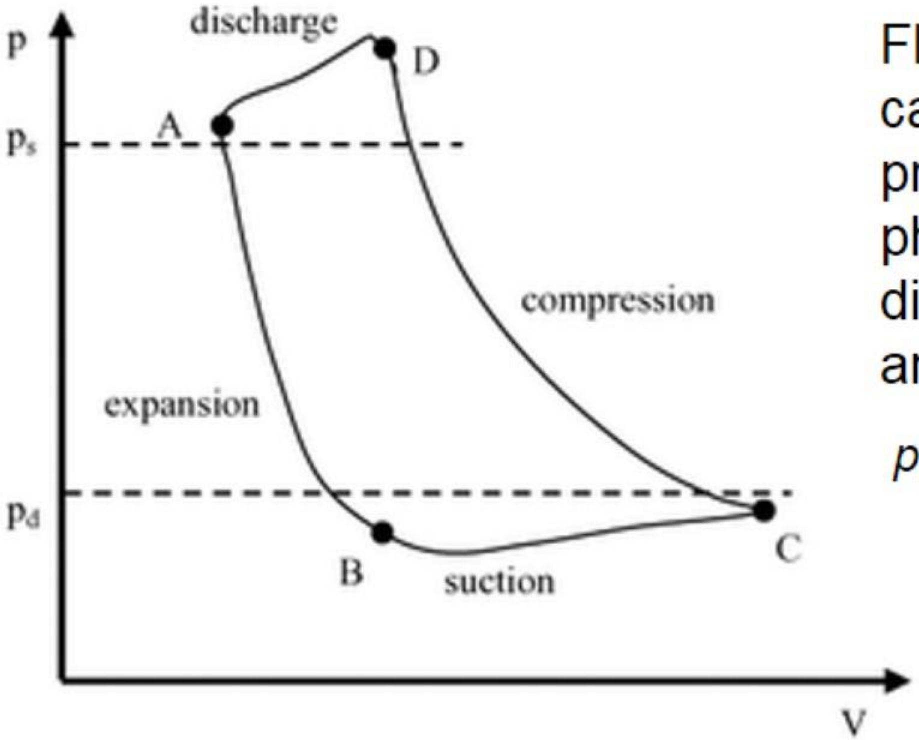
D-A suction
A-B compression
B-C discharge
E clearance volume
C-D expension from clearance volume

Compression



Compression

(a)



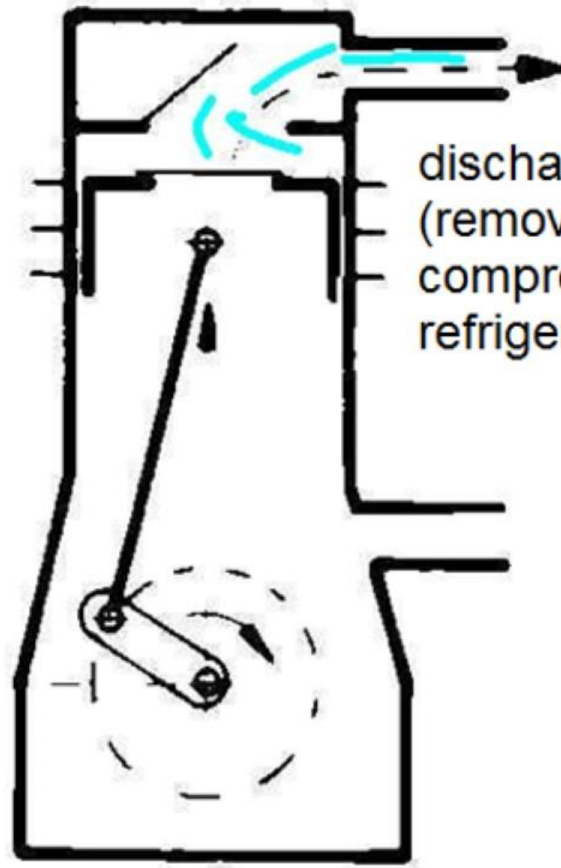
(b)

Flow friction loss causes some pressure drop in the phase of suction and discharge (valves and pipelines)

$p_D > p_A$ and $p_C > p_B$

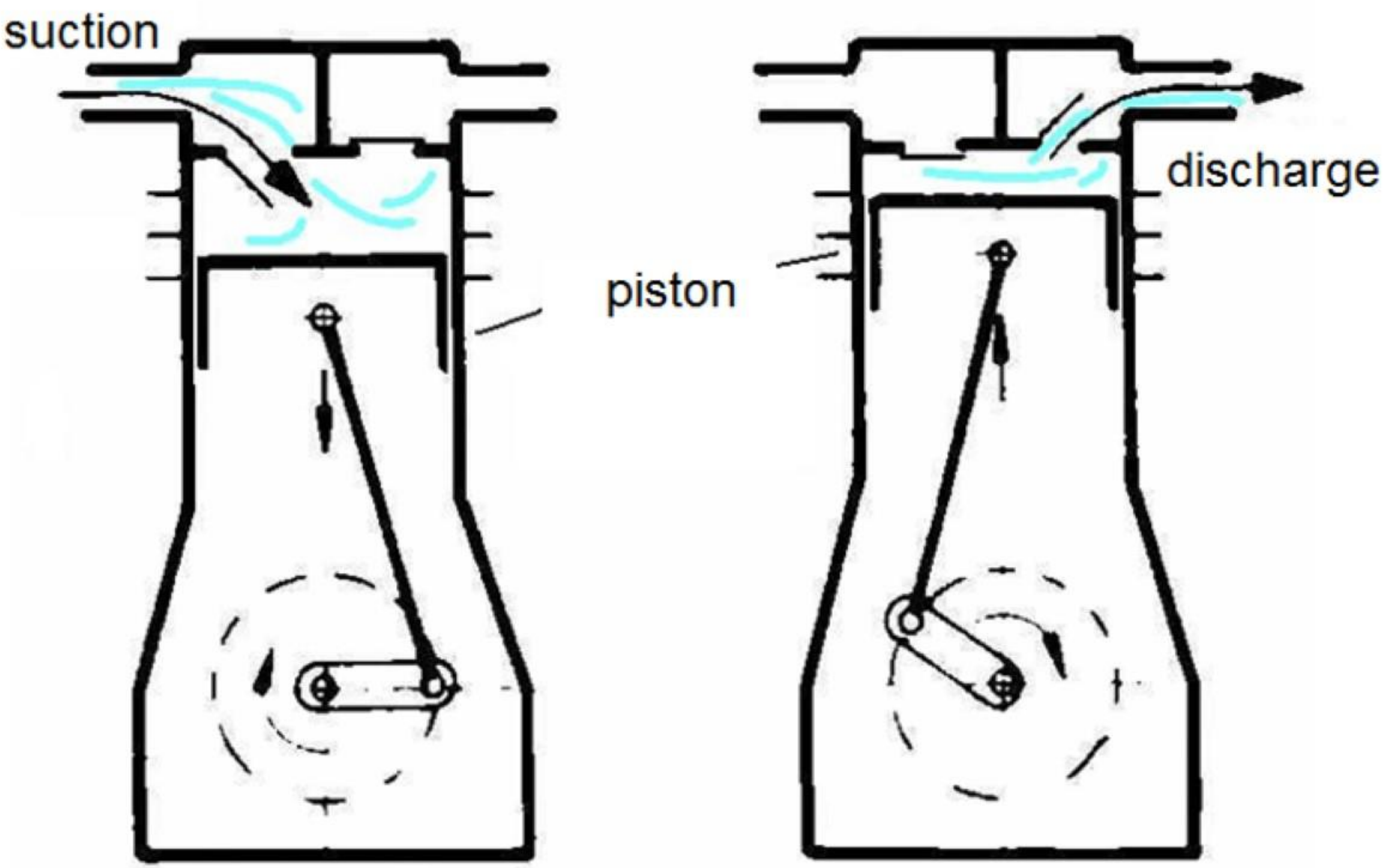
Compression

Unidirection compressor.
Suction from the crankcase



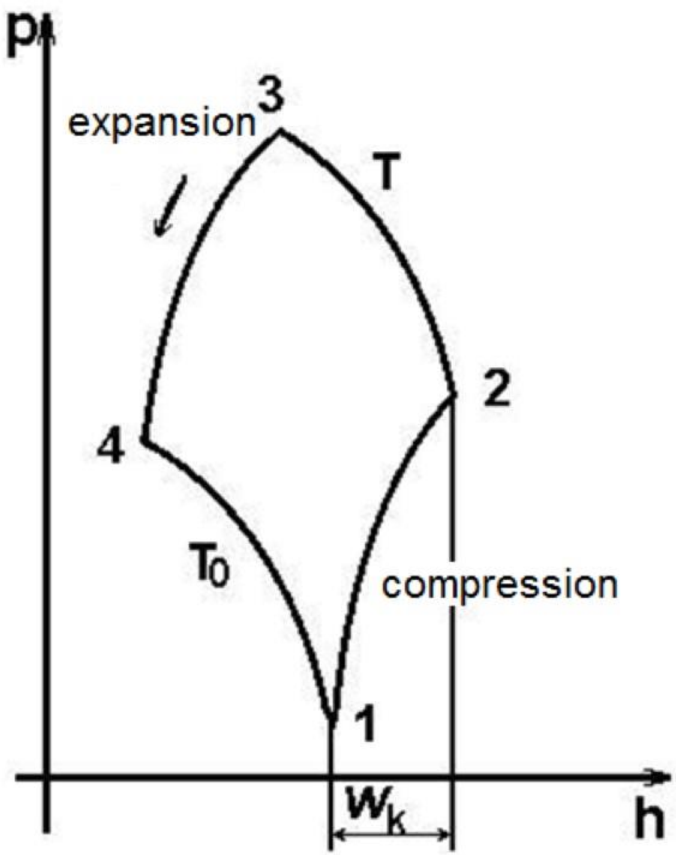
discharge
(removal of the
compressed
refrigerant)

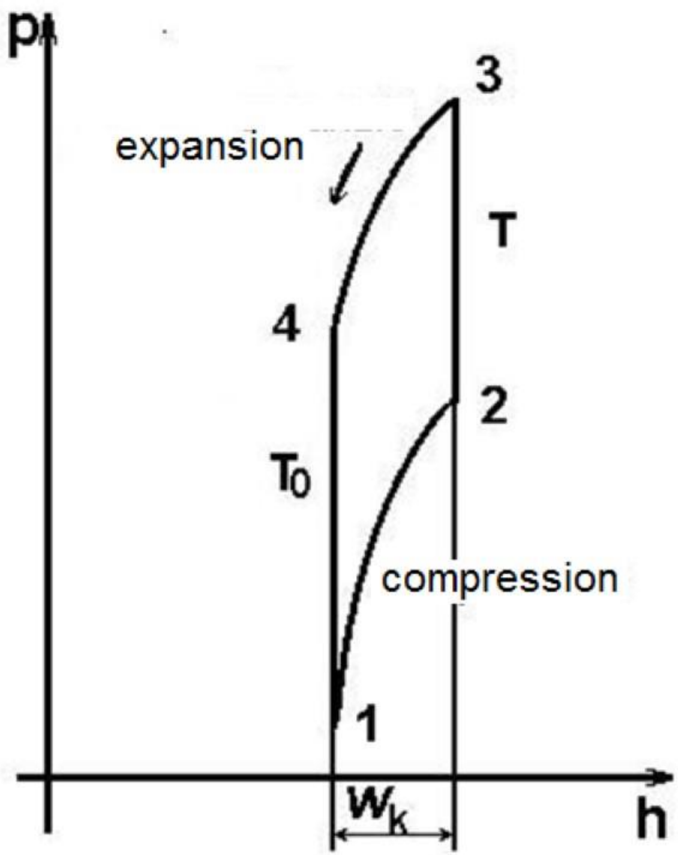
Compression



Reciprocating compressor.
Both valves placed on the cylinder head

Diagrams

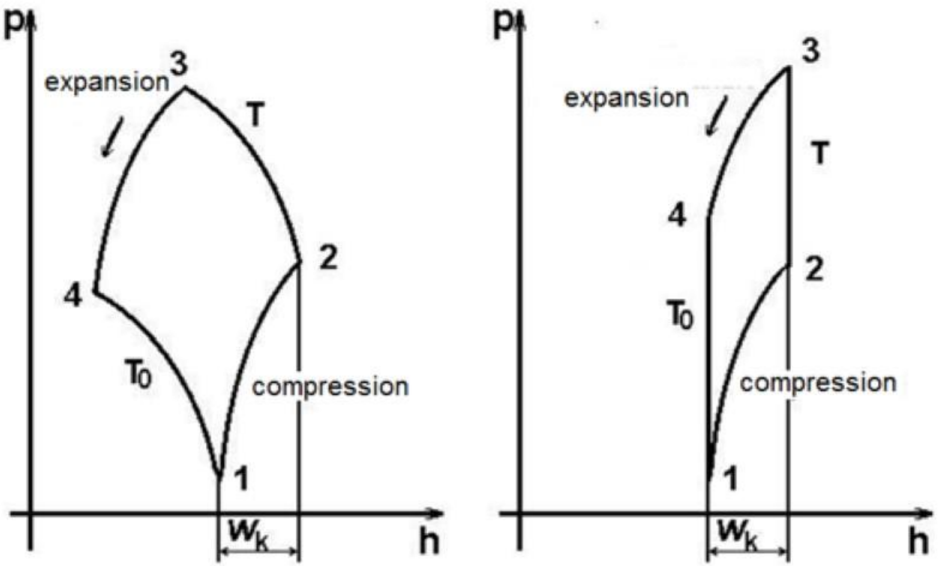




Left: real gas

right: proper gas

Diagrams



$$\mathrm{d}h = \mathrm{d}u + p\mathrm{d}v + v\mathrm{d}p$$

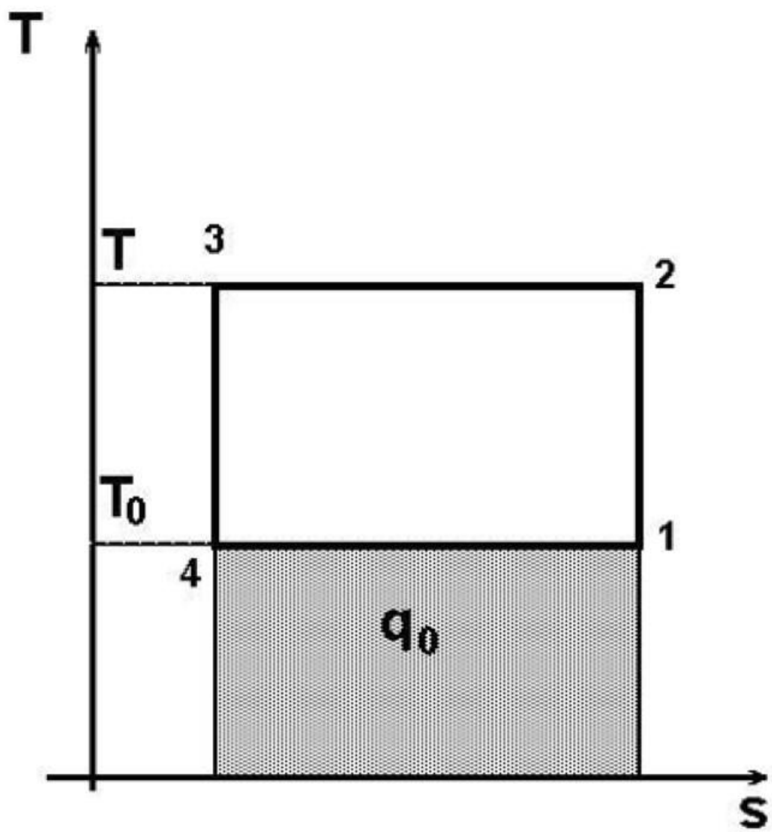
For isothermal thermodynamic processes pv=constant. Therefore the enthalpy contains only the internal energy

$$\mathrm{d}u = c_v \mathrm{d}T$$

We can see on the left-hand side the isothermal process of a real gas when it is close to the saturated state (overheated vapor).

We must calculate using the van der Waals equation.
The shape of the process differ from the ideal vertical line

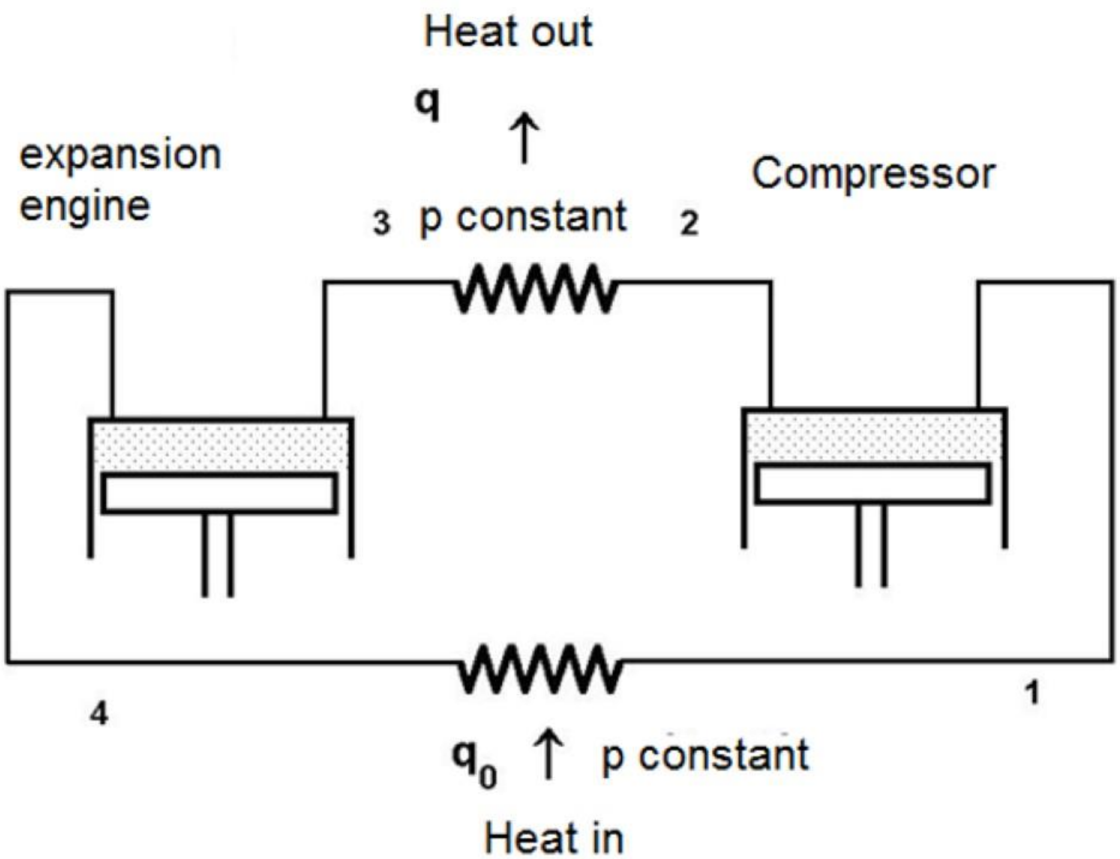
Diagrams



So simple the refrigeration cycle drawn on the T-s diagram:
it consists of isothermal and adiabatic lines only.

q_0 is the heat get away in the cooler divided by the mass of refrigerant

Realisation

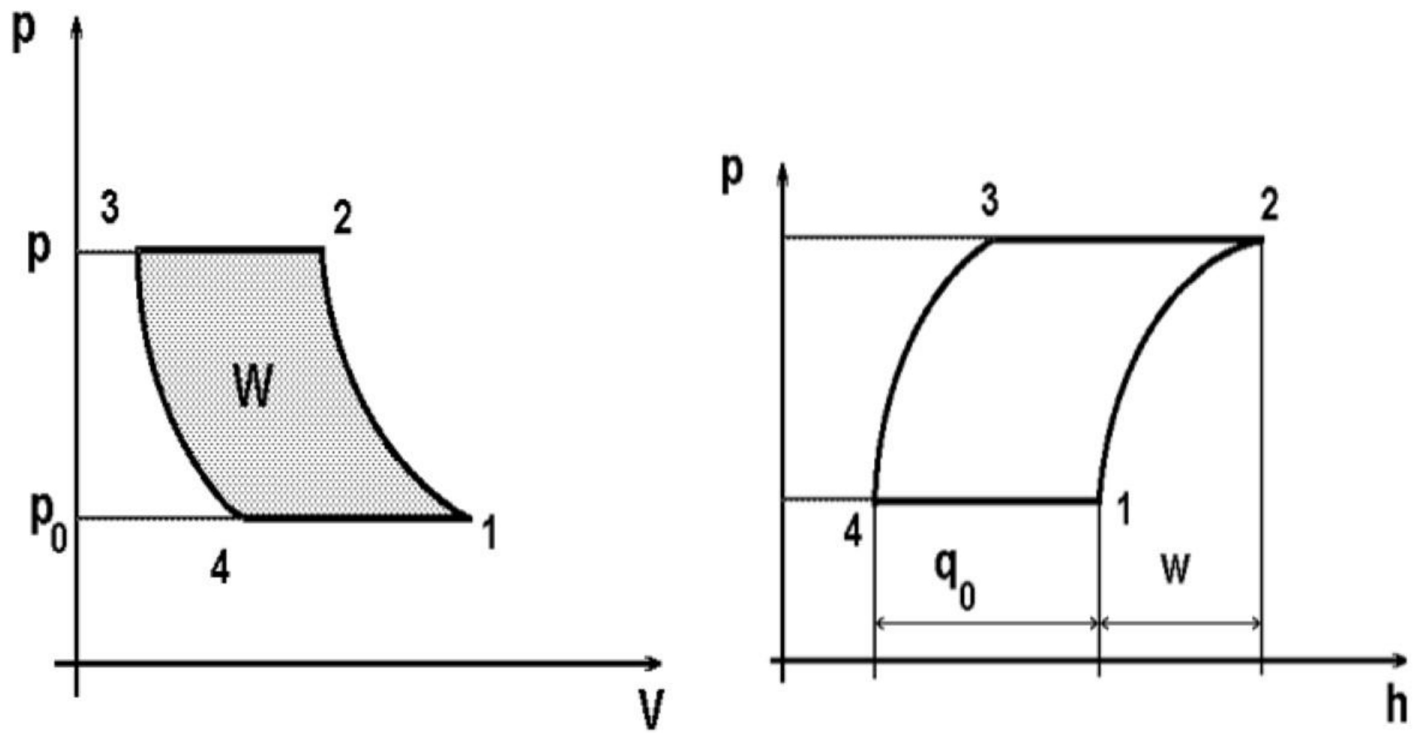


Isobaric process instead of isothermal

Benefit: *realisable, simple*

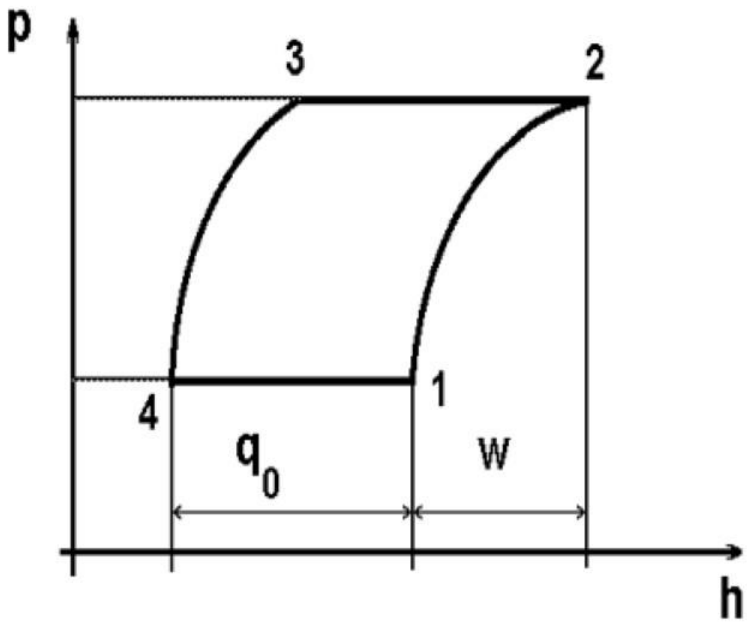
Inconvenience: lower efficiency because of the machines work is not Carnot cycle at all

Realisation



Heat exchange is isobaric process.
Its shape on pv and ph diagram

Realisation



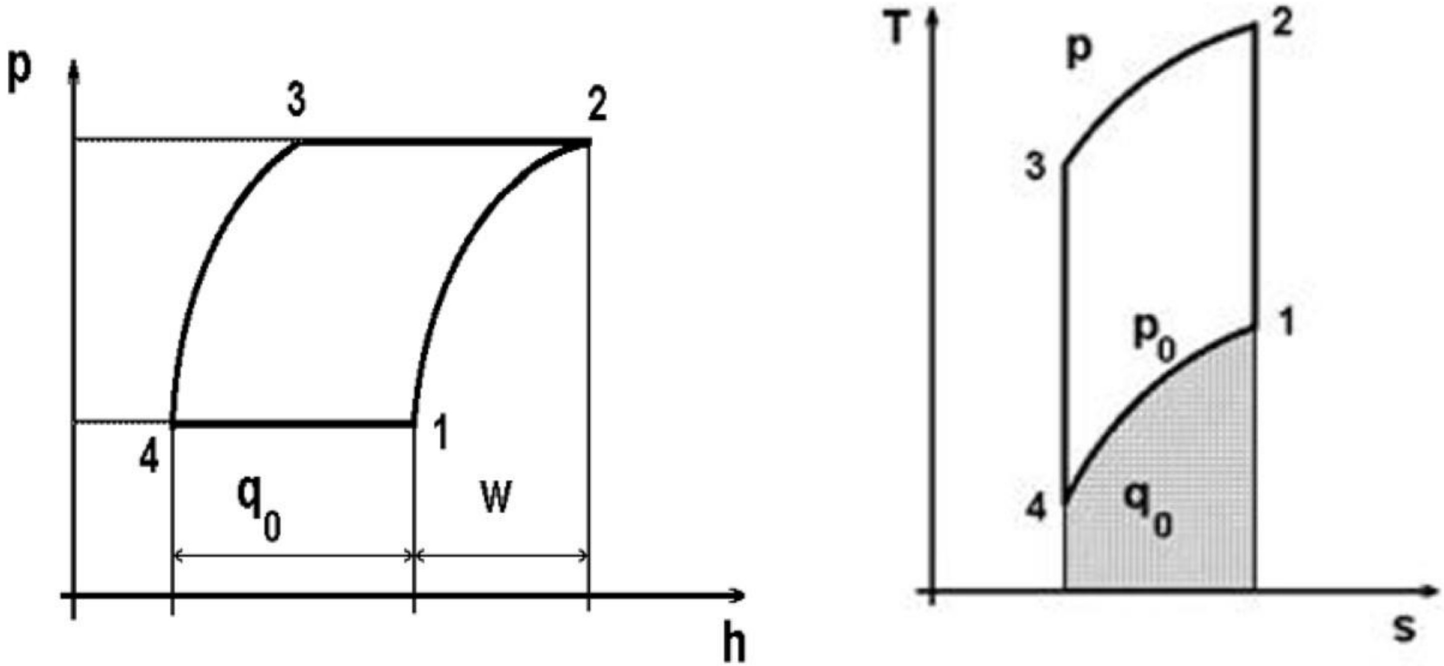
$$\mathrm{d}h = \mathrm{d}u + p\mathrm{d}v + v\mathrm{d}p$$

The last member of equation is zero at isobaric process. Therefore the heat is equal to the change of enthalpy

Benefits of this diagram:

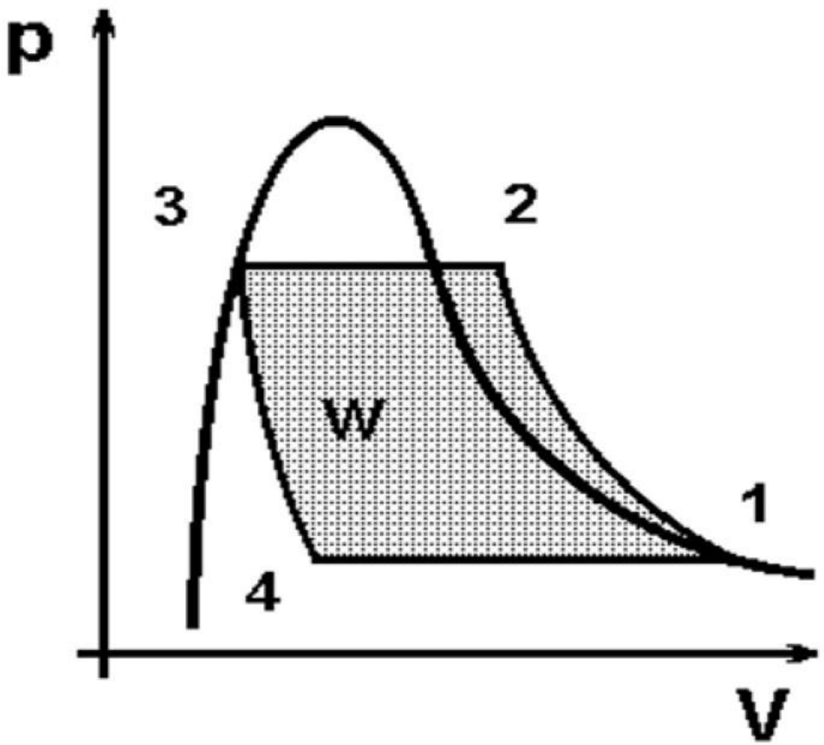
1. The compression work is equal to the increase of enthalpy
2. The heat input and output can be calculated the difference of (specific) enthalpies

Realisation



There is no simple the shape the process that happens in the cooler on the T-s diagram. The heat uptake q_0 is henceforward the area below the curve of the process

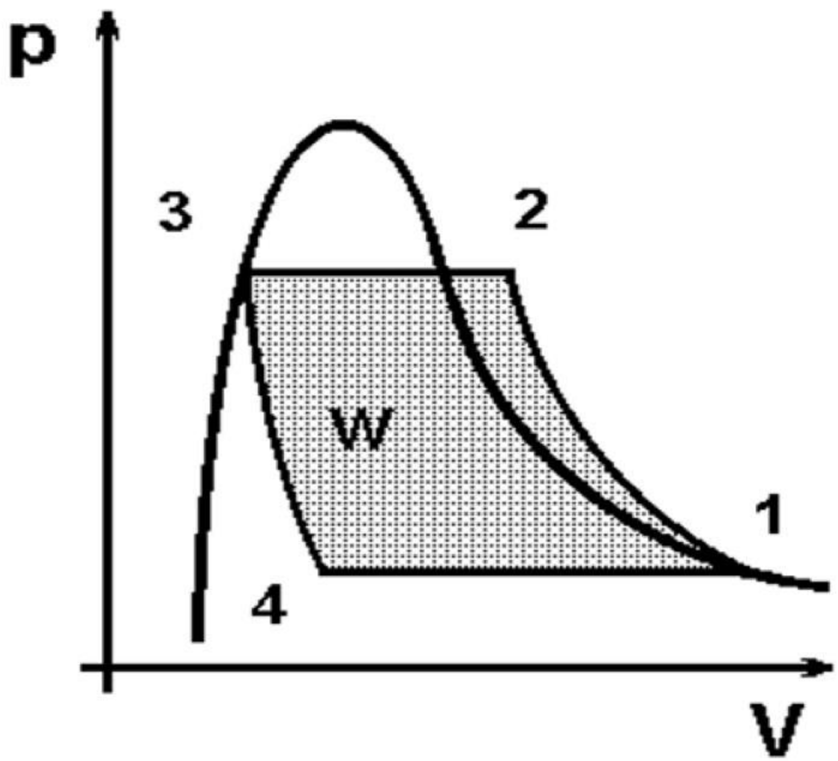
Applying refrigerant that undergo on phase change



We have talked up to this point using the equations of proper gases. Now we move on the diagram from right to left (or downward) reaching the limit where the refrigerant start to condensate. Here we can see the phase limits and the refrigeration cycle together

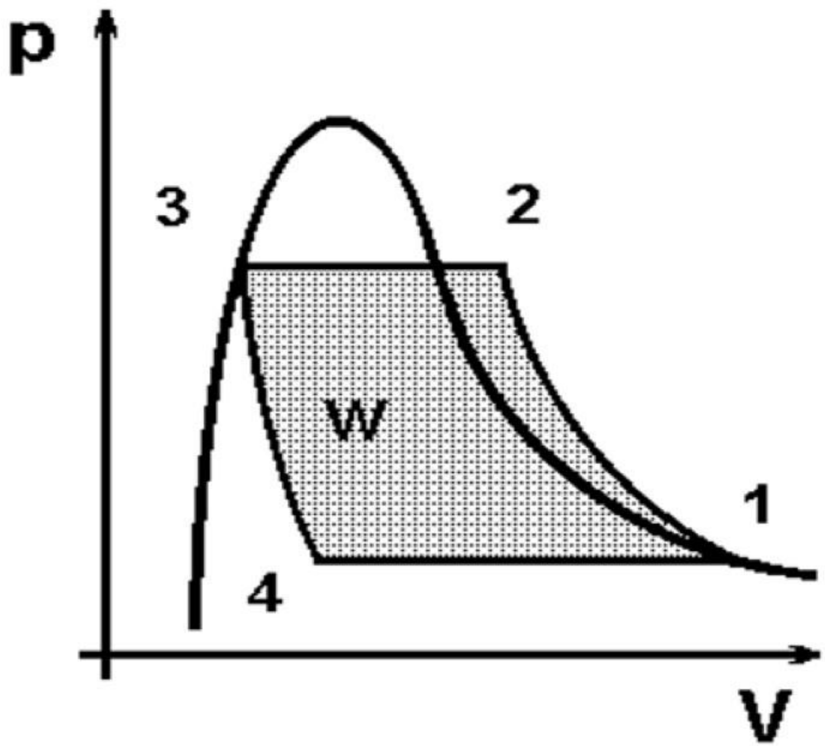
We can see the saturation limit right hand side which is the limit of saturated vapor (signed 1). Left hand side (signed 3) is the liquid state limit. Between the two lines the refrigerant liquid and vapor are in coexistent phases.

Applying refrigerant that undergo in phase change



Right to the point 1. the material is in overheated state. At the point 3, and the osculate line means that the refrigerant is at the limit of the liquid state. Left of this curve the refrigerant is liquid. The liquid and saturated state meets (above of the diagram) a significant point. This is *the critical point*. E.g. on the p-v diagram the length of a horizontal line analogous to the volume change belonging to the condensation (evaporation, too, reversing it)

Applying refrigerant that undego in phase change



Let's see what is the difference what we have stated on the proper gas previously:

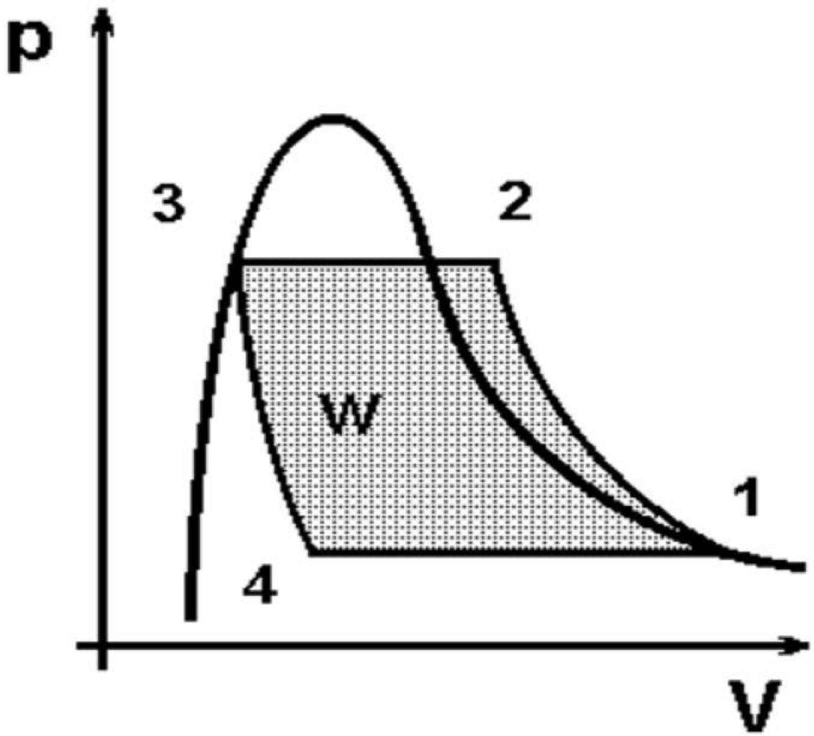
1–2 adiabatic compression

2–3 isobaric heat output

3–4 adiabatic expansion

4–1 isobaric heat intake in the cooler

Applying refrigerant that undergo in phase change



What happen in contrast of the proper gas cycle:

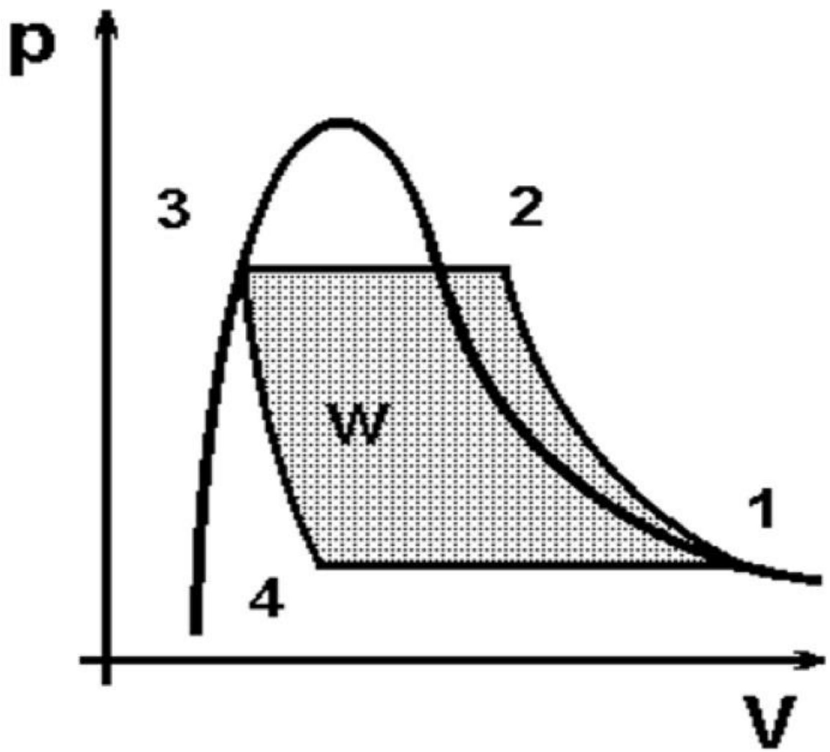
1–2 the process starts with saturated vapor that overheated while the compression

2–3 the overheated vapor gets cooler and reaching the saturated vapor line starts condensing to the liquid state

3–4 while expanding the liquid its small part starts to evaporate

4–1 all the refrigerant evaporates

Applying refrigerant that undergo in phase change



In this situation we change the name of the parts of the refrigeration cycle.

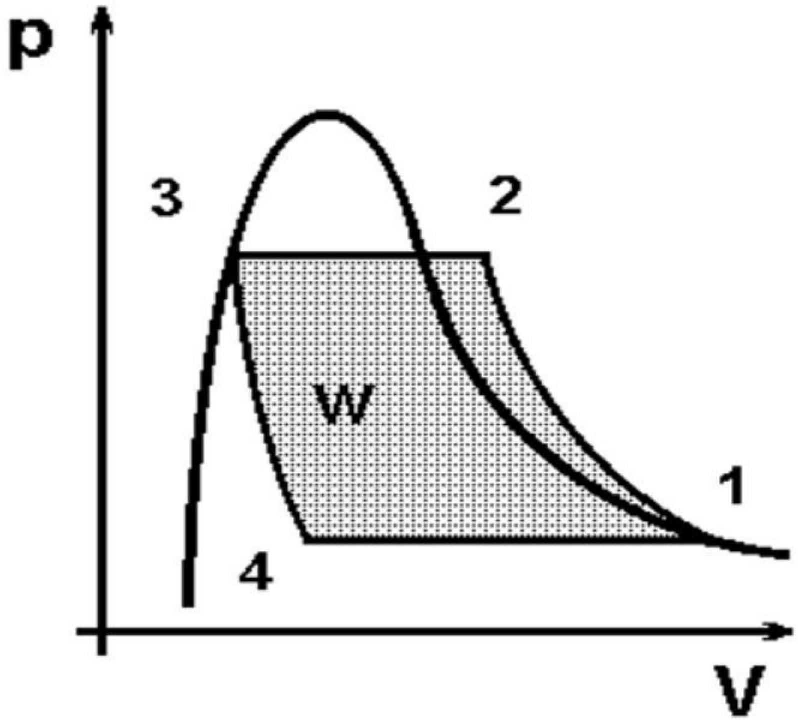
1–2 compression in the compressor

2–3 condensation in the **condenser**

3–4 expansion in the expansion engine

4–1 evaporation in the **evaporator**

Applying refrigerant undergo in phase change

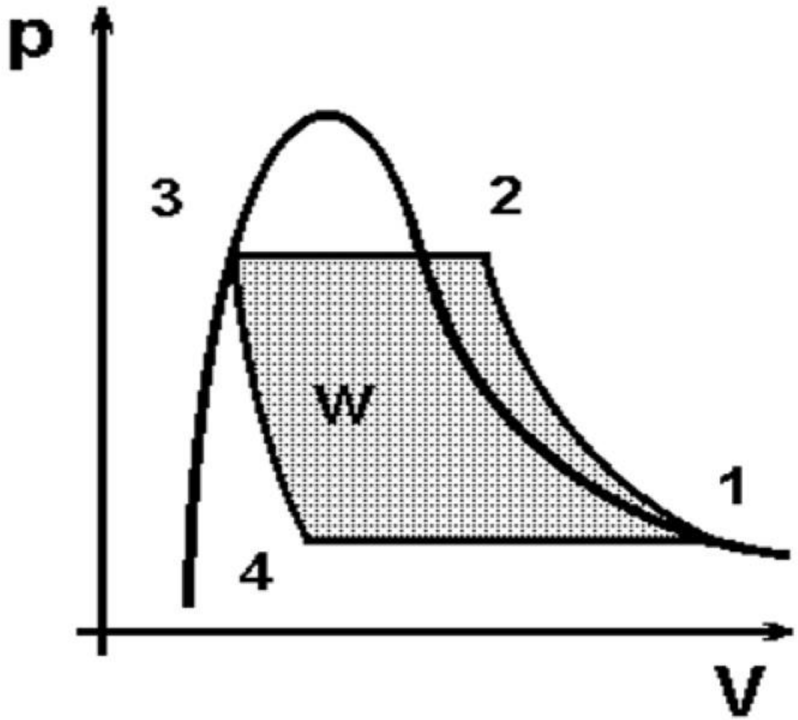


According the Gibbs phase rule the degree of freedom of a system decreases in coexistence of two phase of the same component. In this case we can not change independently the pressure and the temperature. So

- an isobaric process is isothermal
- an isothermal process is isobaric

between the two saturation curves

Applying refrigerant undergo in phase change

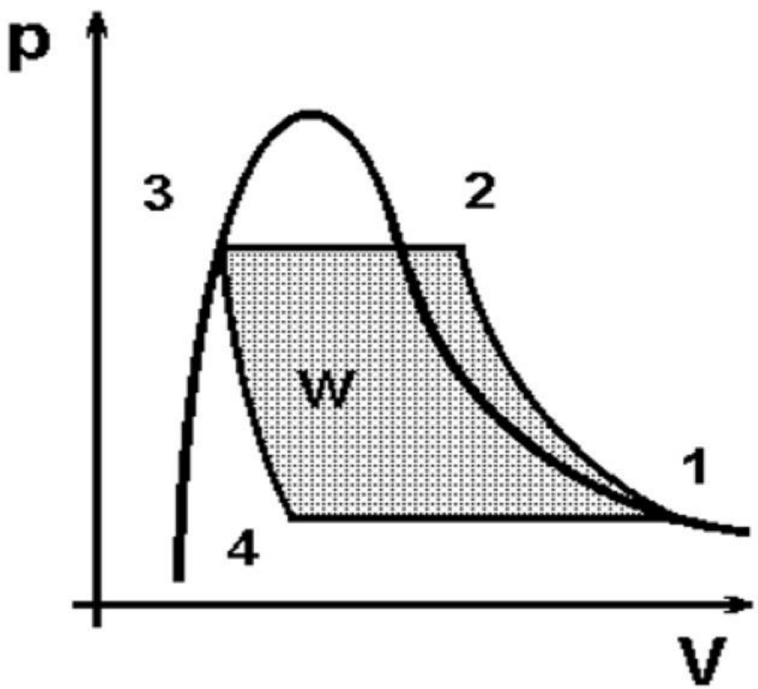


The benefits of the Gibbs phase rule

The coefficient of performance theoretically as the same as the Carnot cycle, consequently it is maximal

Both heat intake and heat output are isobaric, consequently technically realizable; using simple heat exchanger

Applying refrigerant undergo in phase change



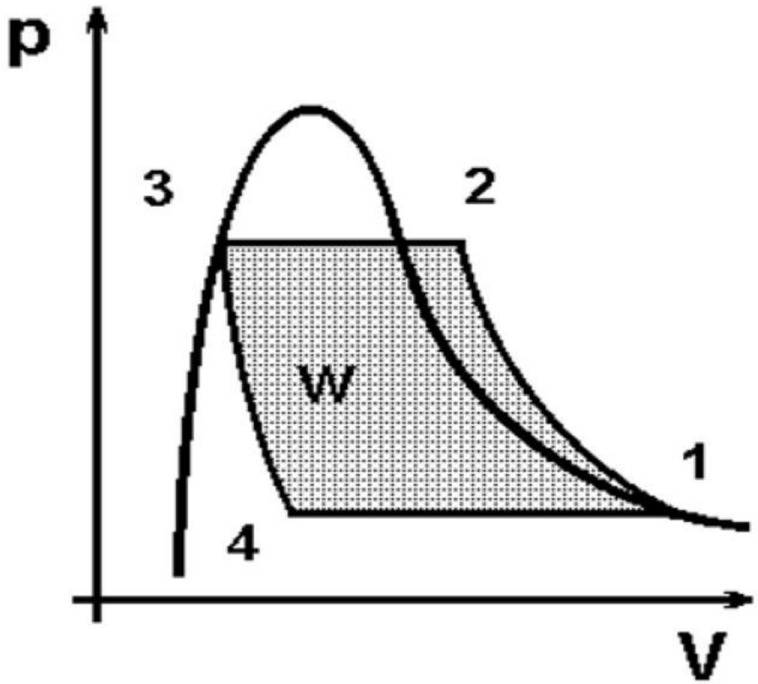
The coefficient of performance is a reverse form of the efficiency

$$j = \frac{q_0}{w} = \frac{T_0}{T - T_0}$$

- q_0 is the heat input taken up in the cooler (specific for mass)
- w the work that suspends the full process (specific for mass)

q_0 > w, e.g. 100 kJ/kg mechanical work gains circa 200 kJ/kg heat transfer (even if the cycle is not lossless)

Applying refrigerant undergo in phase change



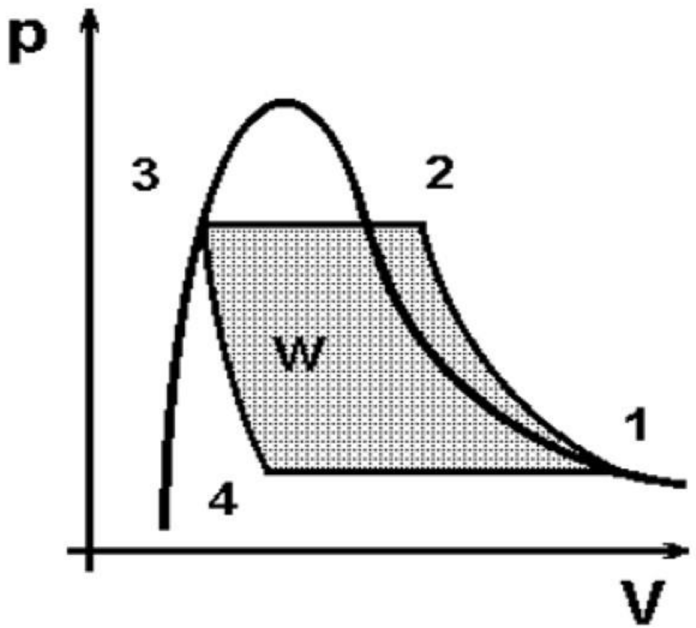
Other benefits:

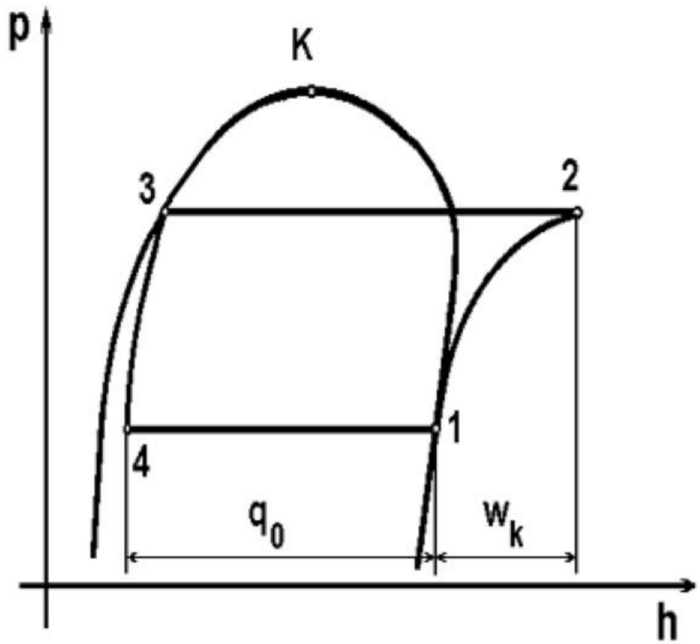
The flow in the condenser 2–3 is strongly turbulent. Consequently the heat transfer on the same area is maximal

There is turbulence in the evaporator 4–1, consequently the heat transfer is maximal

Both phenomena causes loss of energy because of hydrodynamics, however this loss is negligible against of the benefits

Applying refrigerant undergo in phase change

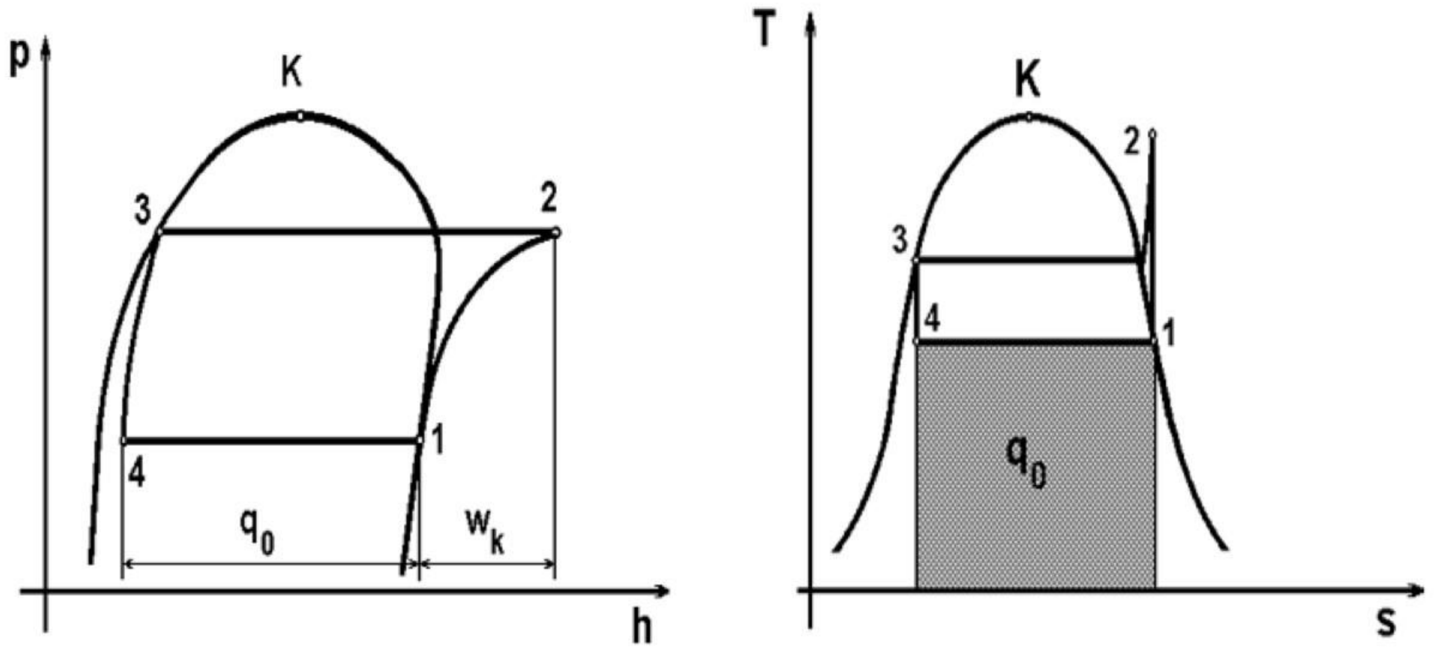




q_0 heat intake in the cooler, w_k work of compression

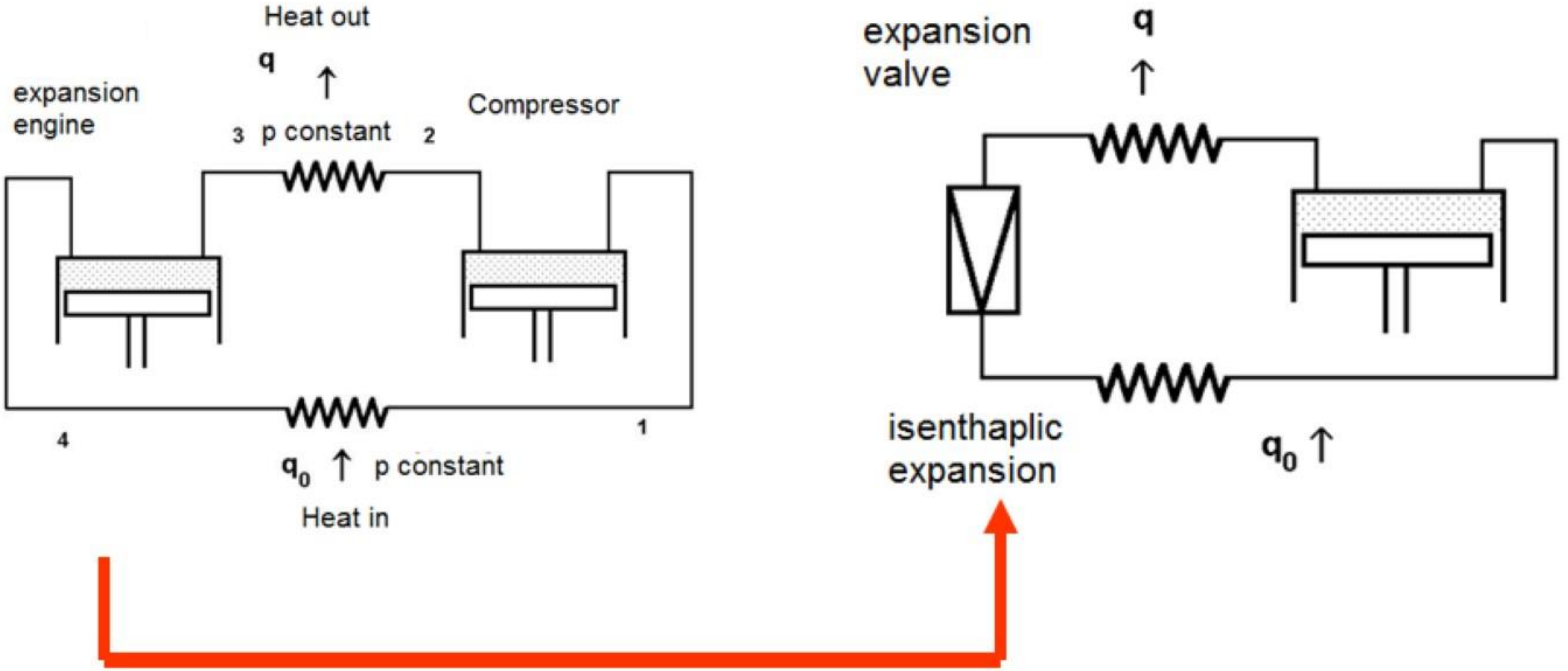
We calculate the work of the compressor only

Applying refrigerant undergo in phase change



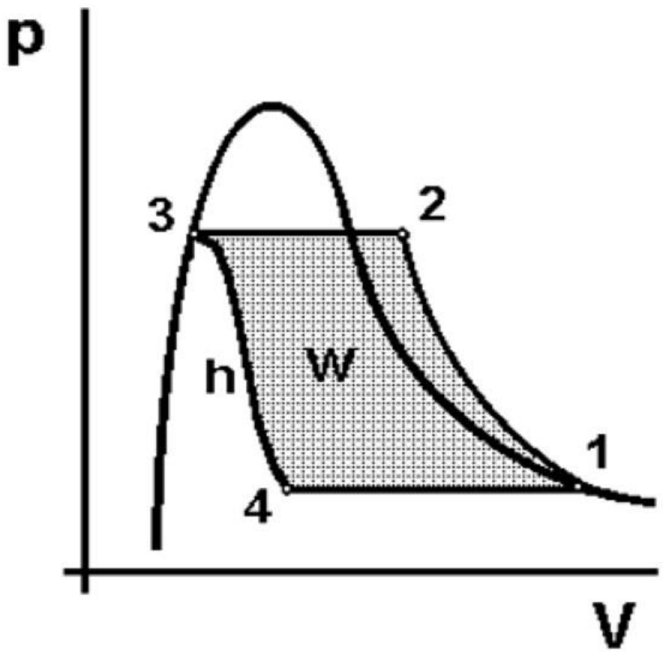
While using a T-s diagram we can realise the very high endpoint temperature of the compression. Consequently the start of process 2–3 we have to cool the refrigerant to the saturation temperature before the real condensation came off. We can observe the small area below this process so it does not bring down the coefficient of performance

Applying refrigerant undergo in phase change



We use expansion valve instead of piston engine. There is a loss of energy but it is more simple according to construction. There is no more loss than ten percent but we can forget the O-ring, the piston, the crankshaft, the lubrication, etc.

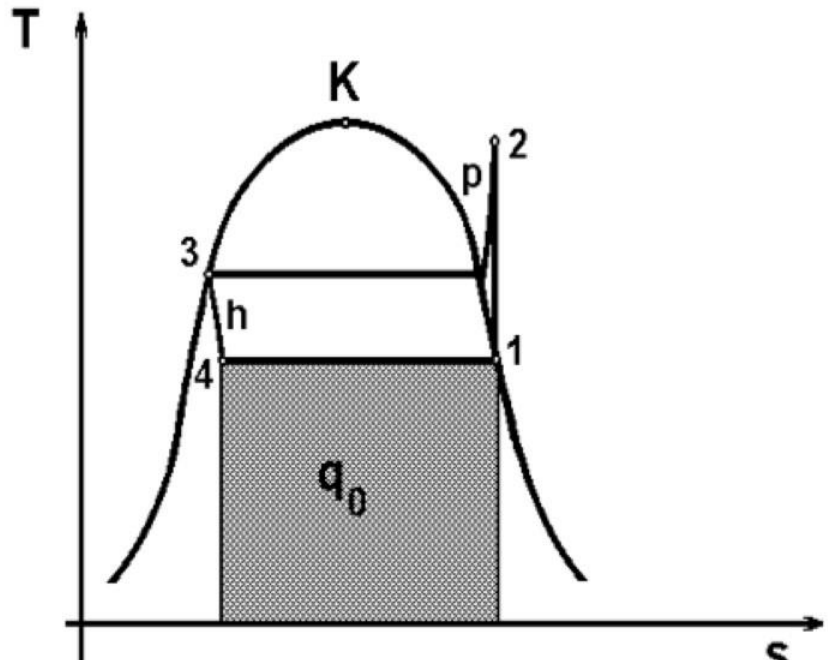
Refrigeration cycle on diagrams



The cycle closes to the adiabatic process if the expansions speed fast enough. Similar examplele is well known at the steam turbine. The really highest value is the speed of sound.

If we decease the speed the expansion, we get a process more and more to the **isenthalpic process.** We can see the result on the *p-v* diagram

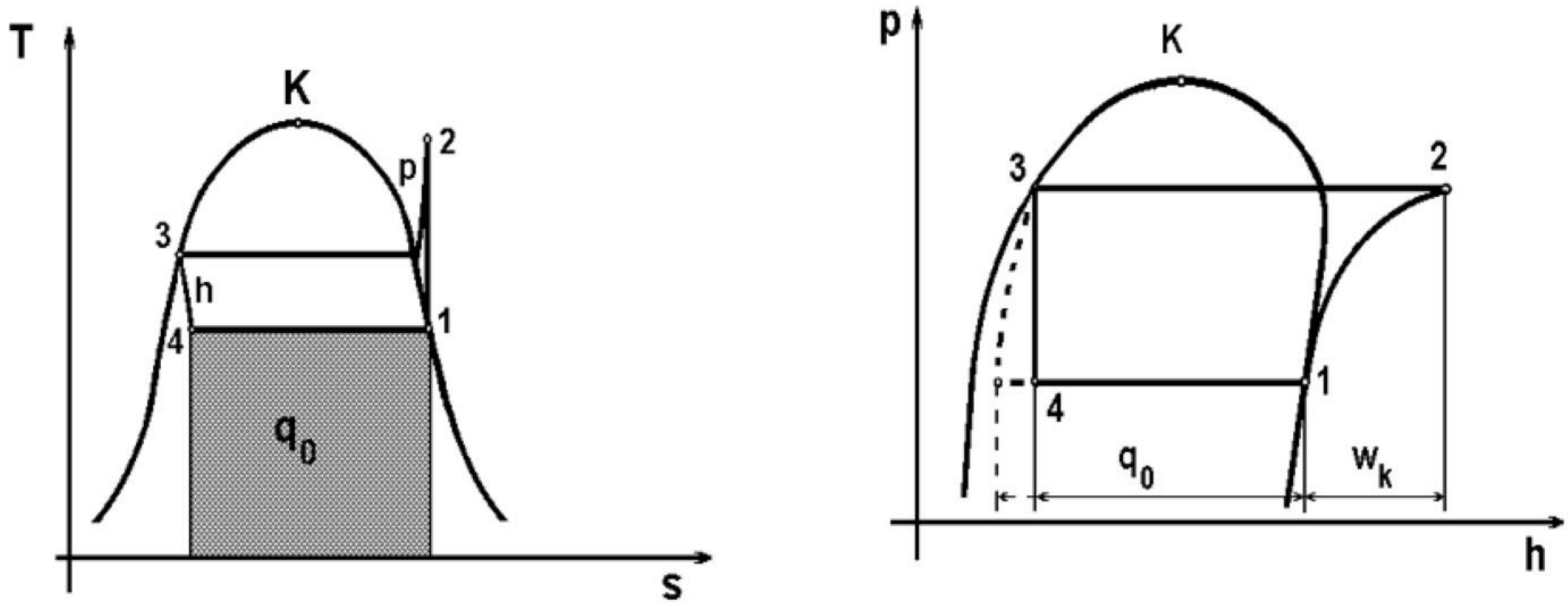
Refrigeration cycle on diagrams



We can see the result, applying expansion valve: the area below the curve 4–1 became less. This means that the same amount of refrigerant can transfer less heat

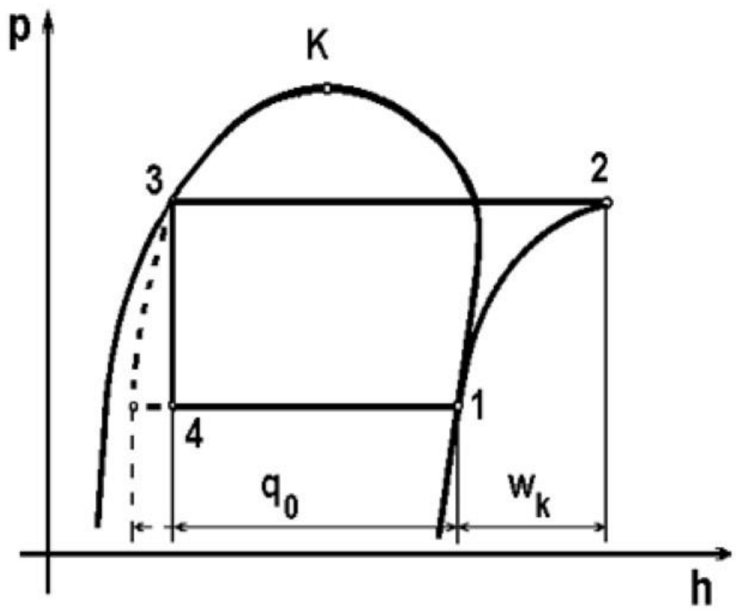
(If we say performance this means the heat flow. In industrial circumstances we use the unit kW for heat flow. We can calculate its value knowing the mass flow circulating in the refrigerant and use the unit of kg/s, or kg/h)

Refrigeration cycle on diagrams



Now proved why we use the pressure-enthalpy diagram

Refrigeration cycle on diagrams



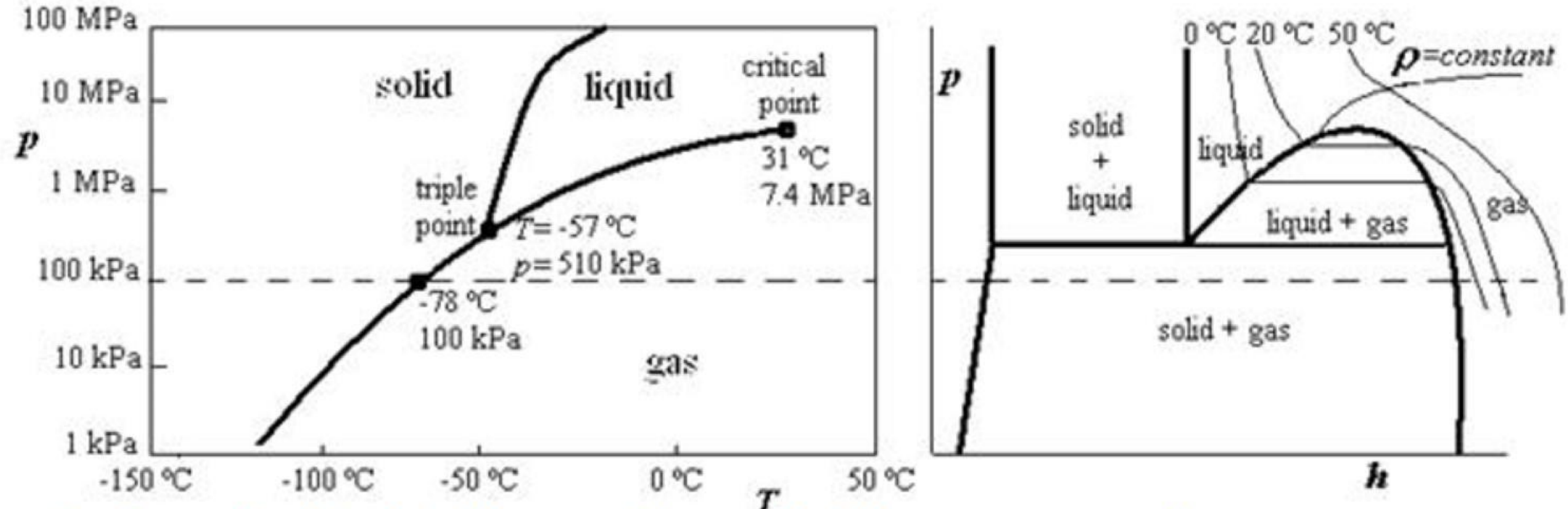
$$\mathrm{d}h = \mathrm{d}u + p\mathrm{d}v + v\mathrm{d}p$$

We can not build a diagram showing the work. In this case the adiabatic work equal to the enthalpy change $w_k = h_2 - h_1$ readable on the diagram

The heat transfer is isotherm and isobaric too, so is readable from enthalpy difference: $q_0 = h_1 - h_4$

We show the difference of the adiabatic and the isenthalpic expansion: the heat input in cooler q_0 decreases

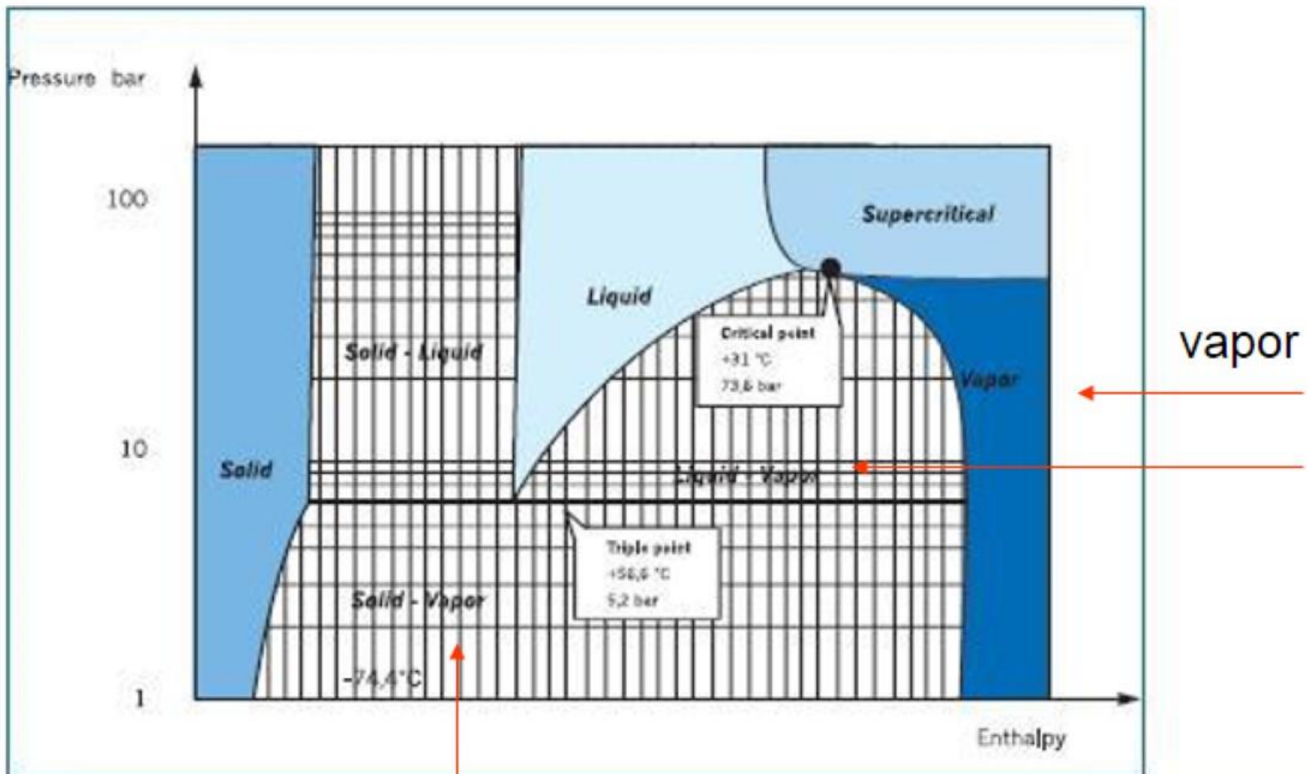
Diagrams in thermodynamics



Carbon dioxide (R744 as refrigerant). We can see on the pressure-enthalpy diagram the solid state too. The slope of the freezing curves are not vertical but the difference between them hardly depends the pressure (it is the freezing heat). There is a frequently misuse of the word „gas". This compound only above the critical point (+31°C) can be gas. It is vapor at lower temperatures. (Even the +50 °C temperature line is curved). Close to it we can see a constant density line (ρ) whre the carbon dioxide is in supercritical state.

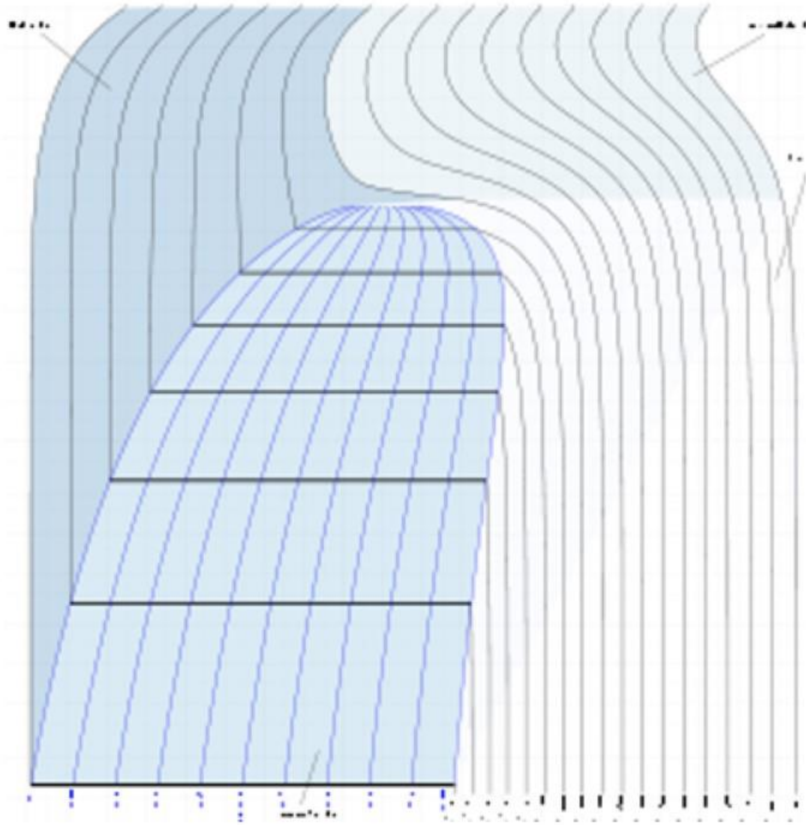
Diagrams in thermodynamics

CO_2 Phase diagram

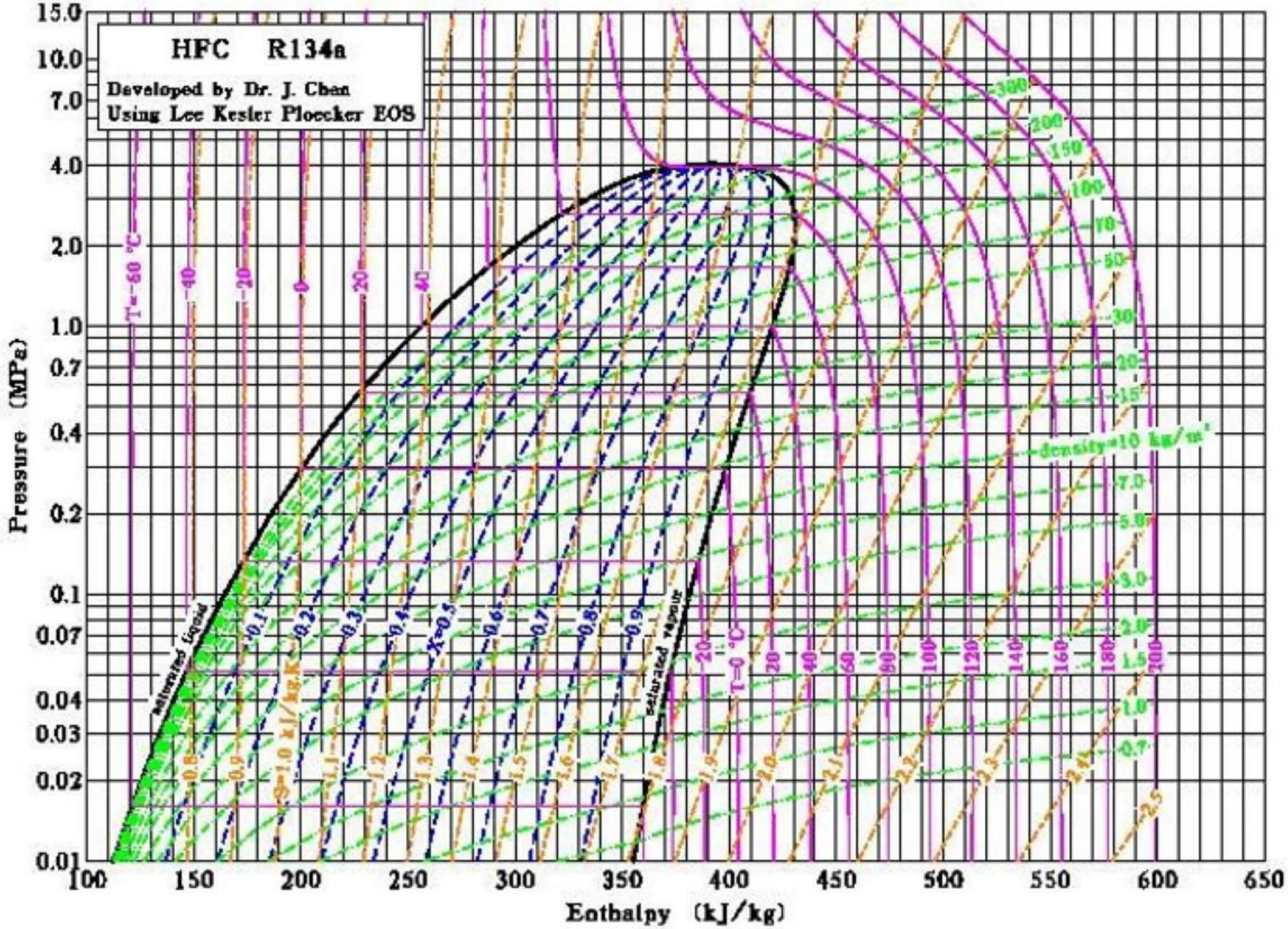


The correct expression in this case is „vapor". Please observe the unfrequently mentioned state: *supercritical liquid below the critical temperature*

Diagrams in thermodynamics

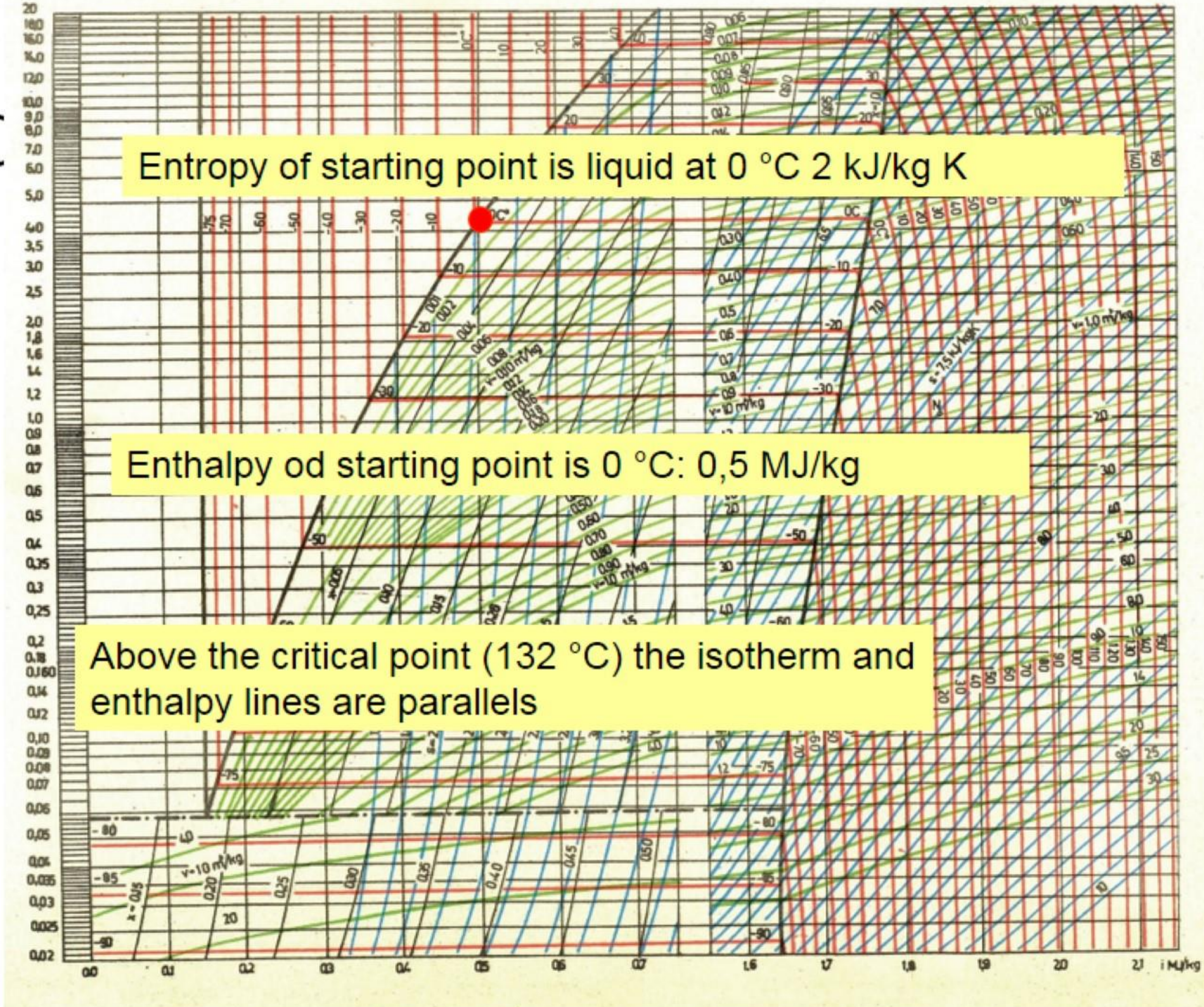


Pressure-enthaply diagram of water (R718 refrigerant). The isothermal lines are S-shape. At the critical point the inflexion has a horizontal tangent line (not drawn).



The isotherms are violet-coloured, the constant density lines are green; the constant entropy lines are orange (the adiabat lines). Blue coloured lines drawn where the liquid-vapor ratio are the same

The tangent of the critical temperature (100 °C) is horizontal ammonia

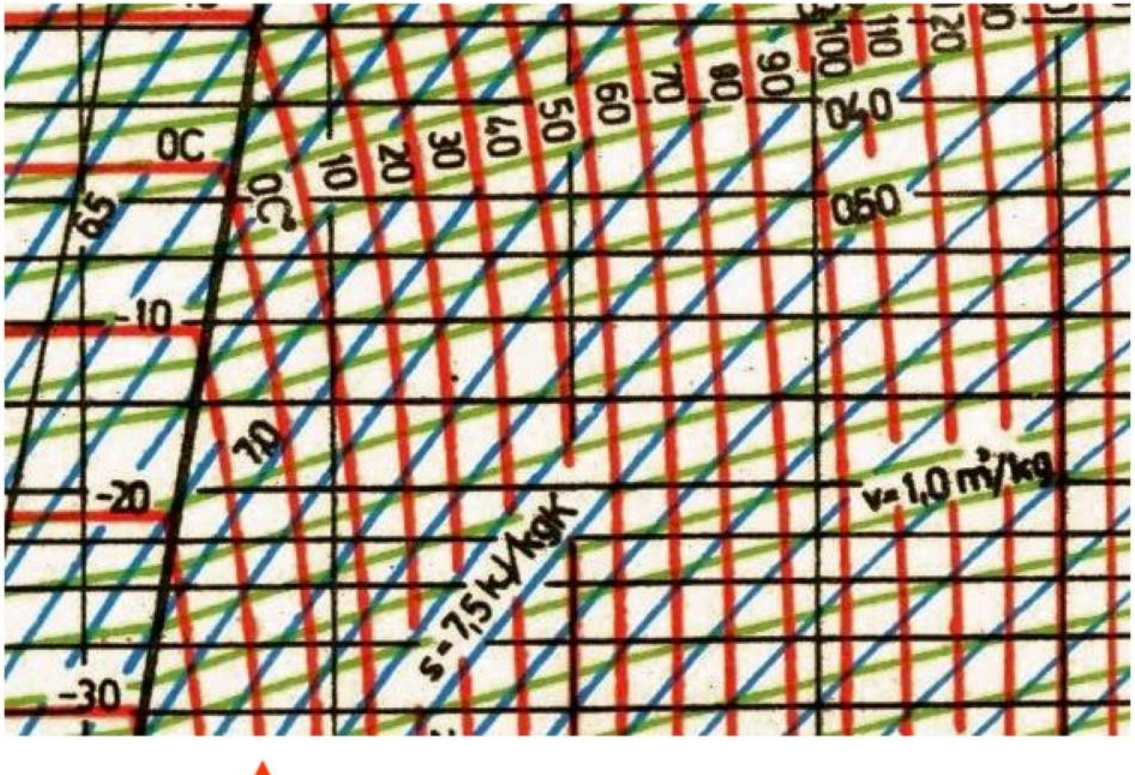


Entropy of starting point is liquid at 0 °C 2 kJ/kg K

Enthalpy od starting point is 0 °C: 0,5 MJ/kg

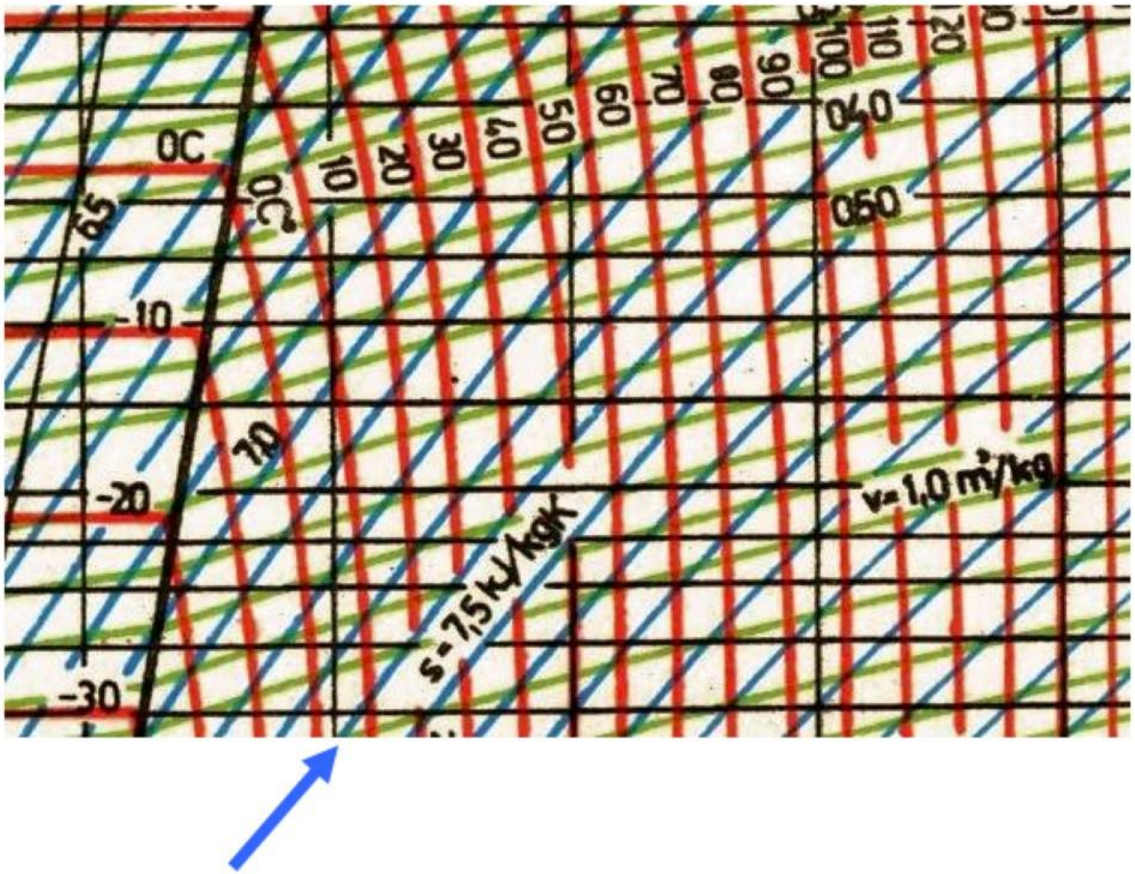
Above the critical point (132 °C) the isotherm and enthalpy lines are parallels

Using diagrams



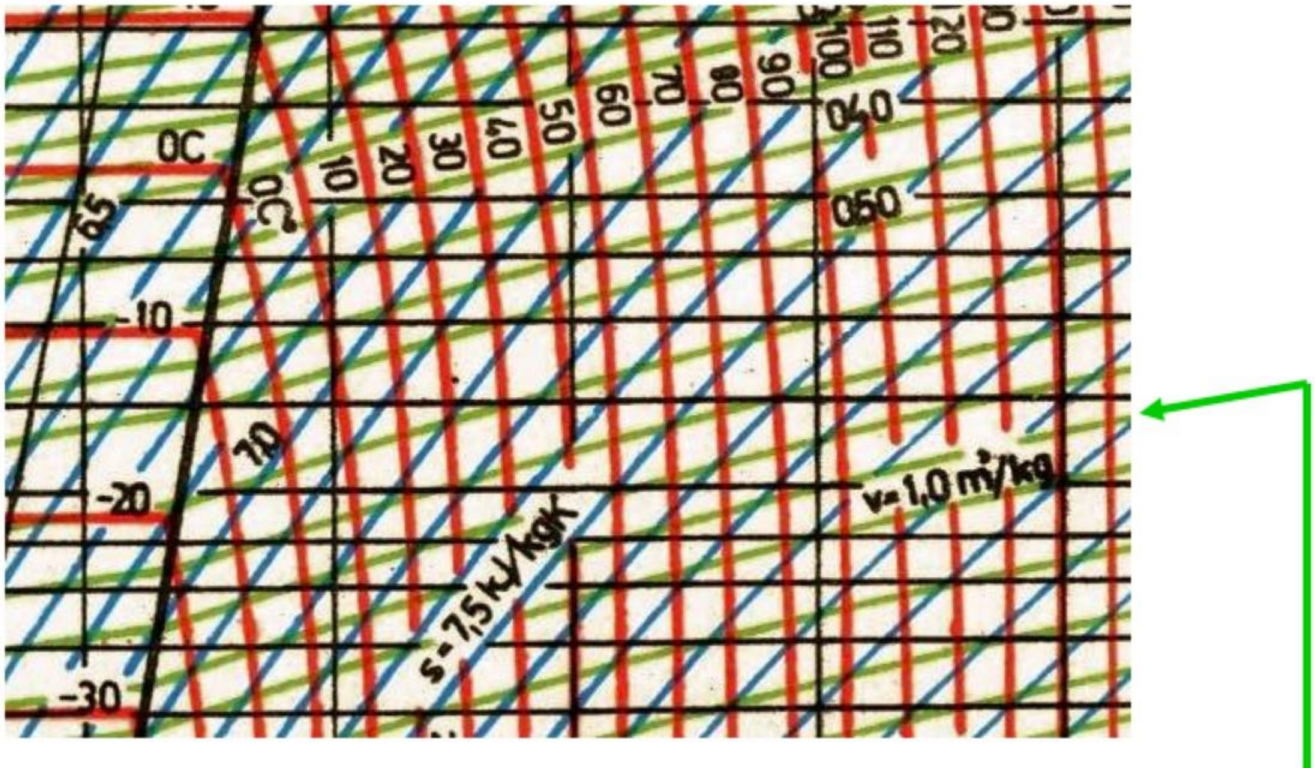
The temperature here is -10 °C

Using diagrams



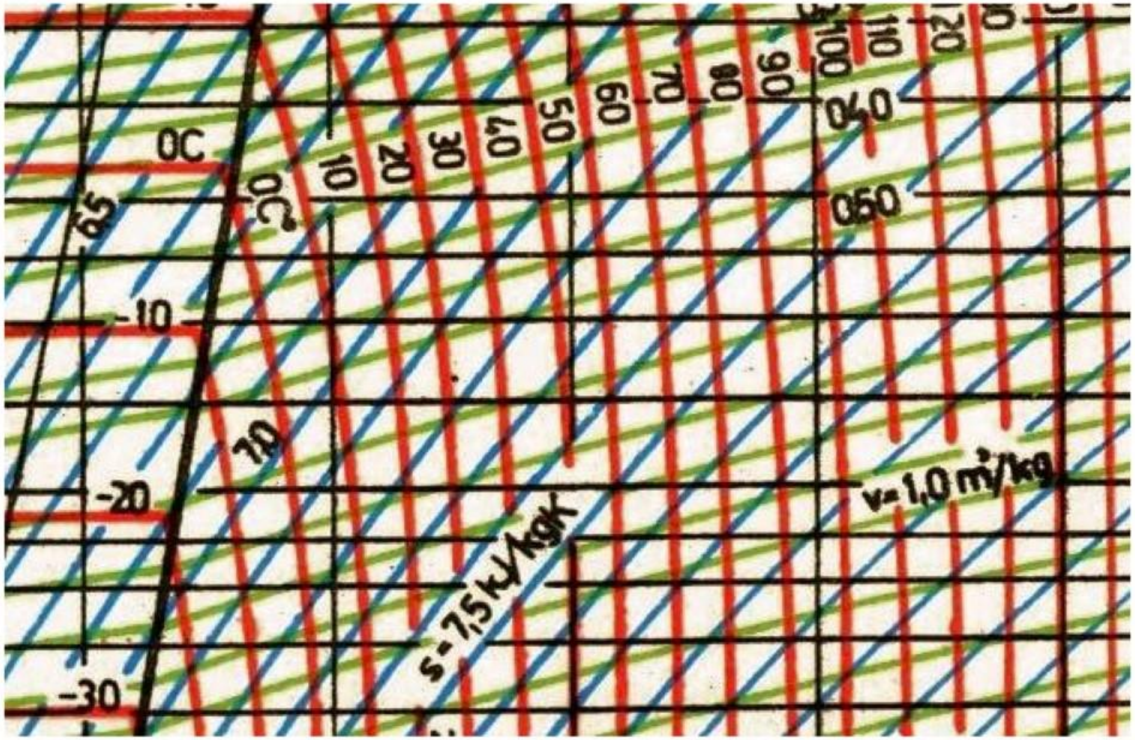
The specific enthalpy here is 7,4 kJ/(kg·K)

Using diagrams



The specific volume here is 0,9 m³/kg

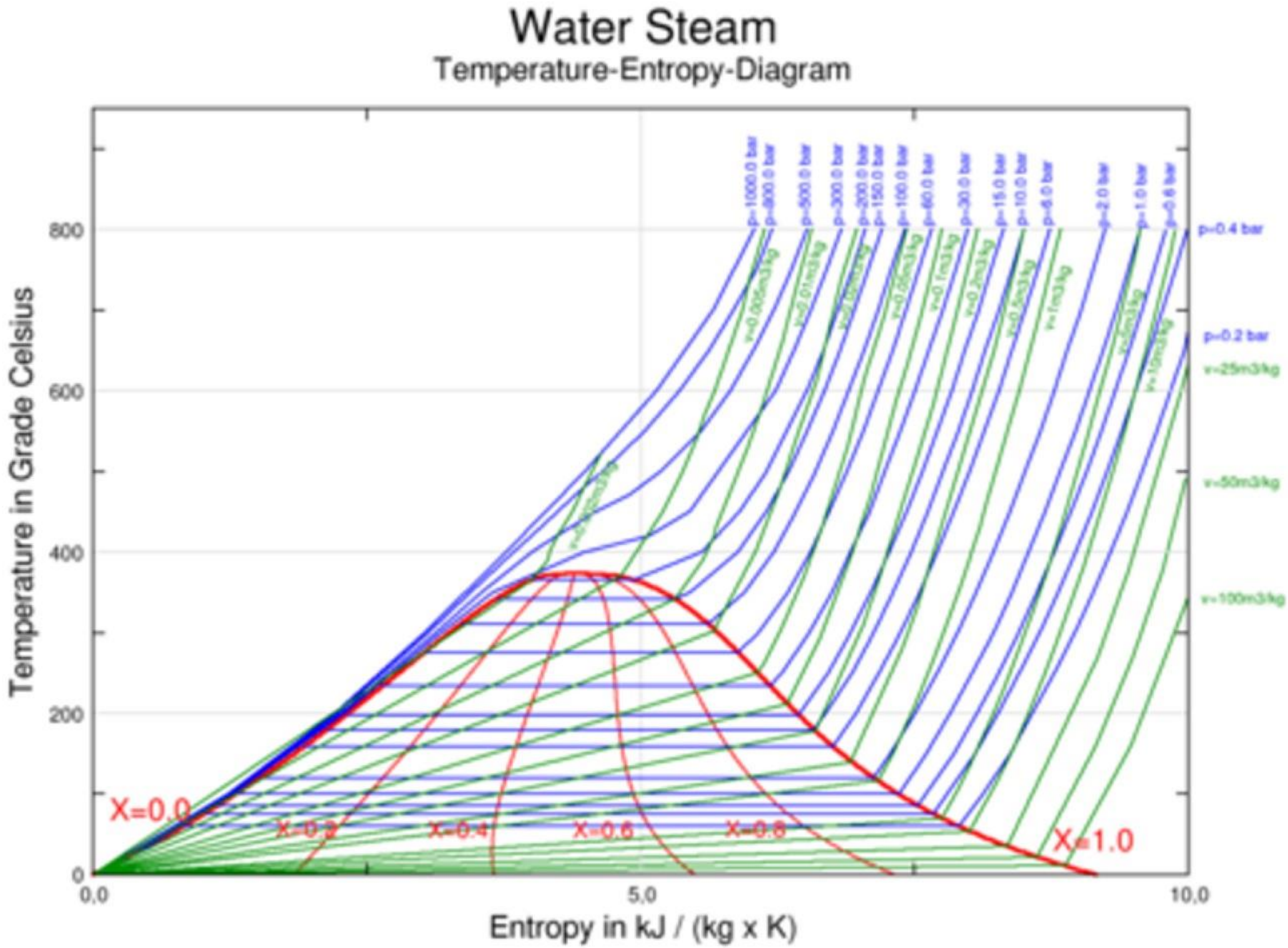
Using diagrams



Overheated vapor

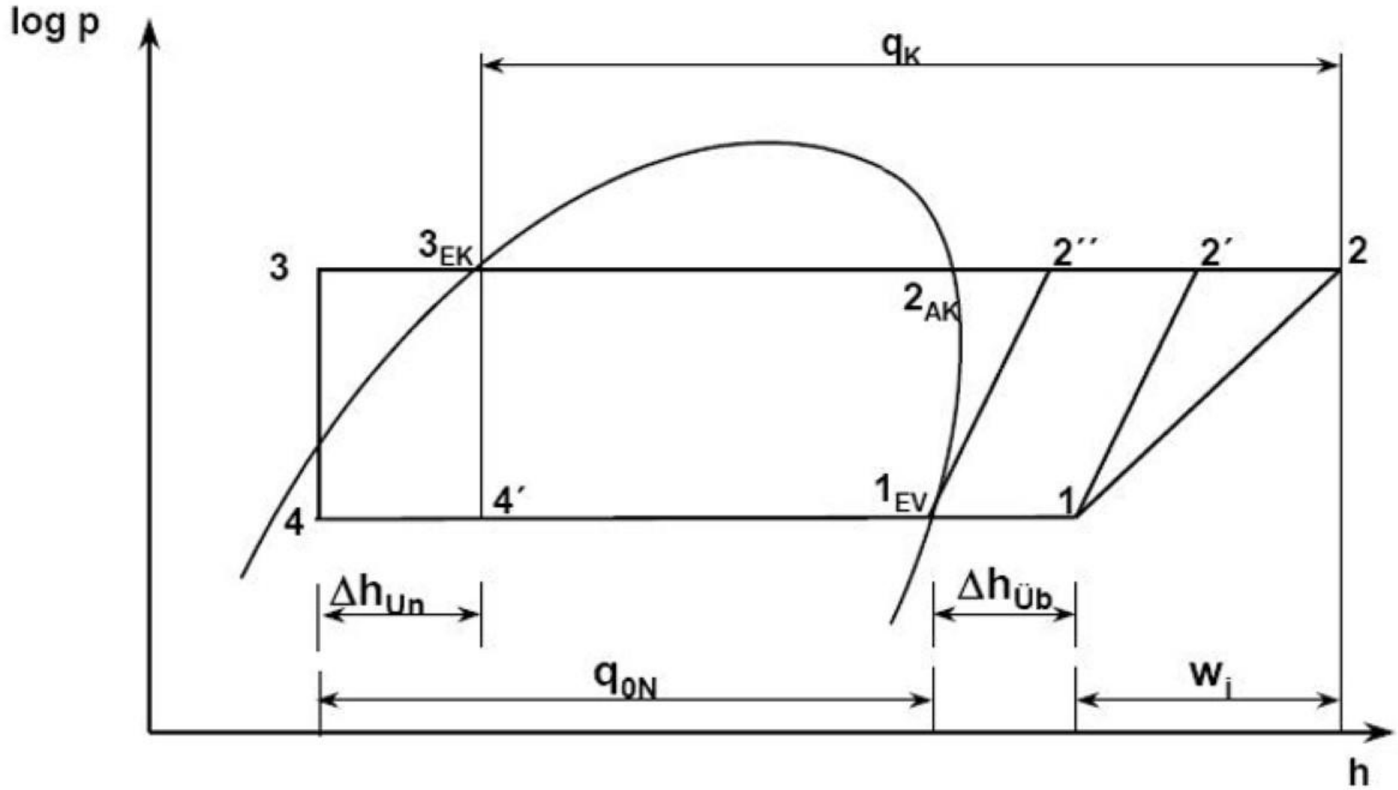
Saturated vapor at -30 °C

Critical temperature is +132 °C



Blue: constant pressure, green: constant specific volume

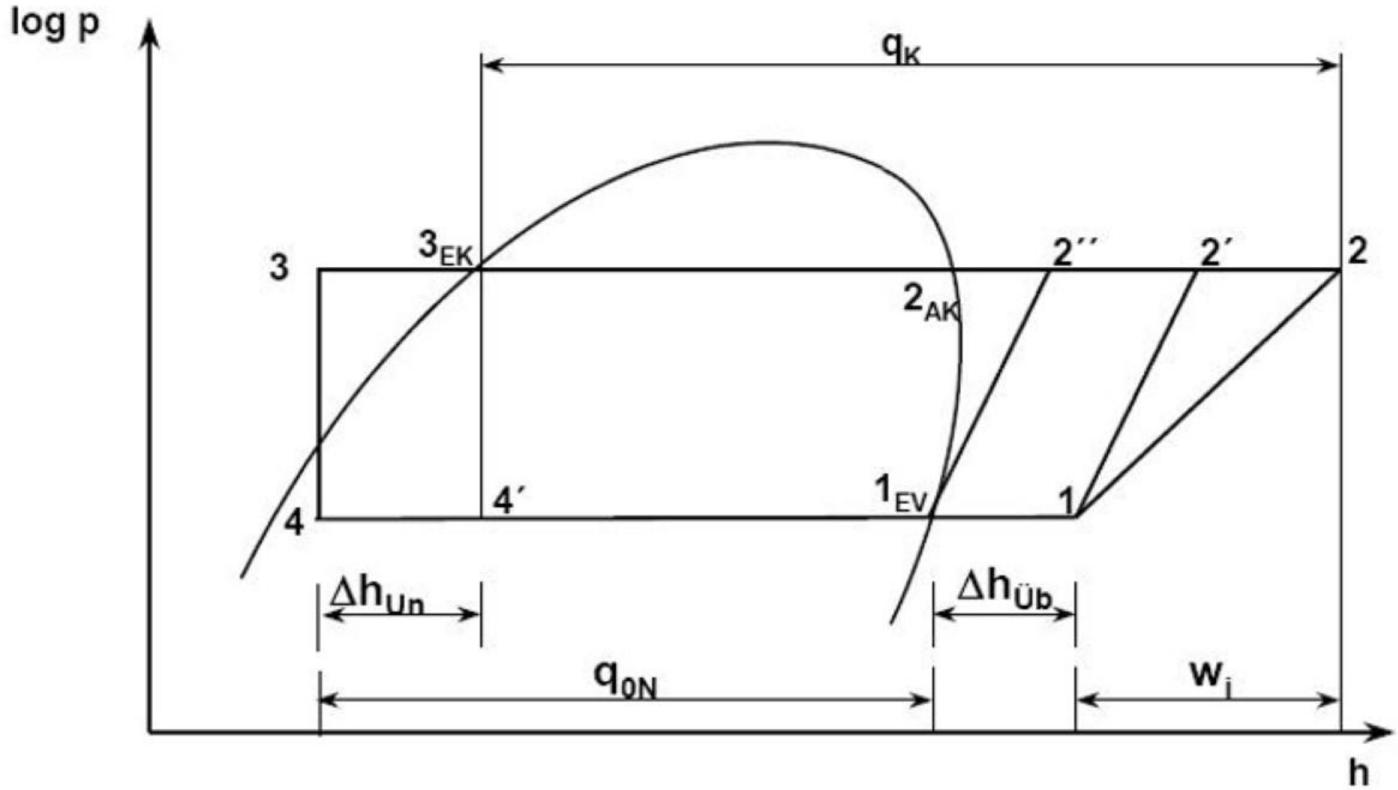
The real refrigeration cycle



Δh_u (unterkühlung) subcooling rises the efficiency

$\Delta h_{üb}$ overheating (überhitzung) rises the performance (q_{0N} get bigger)

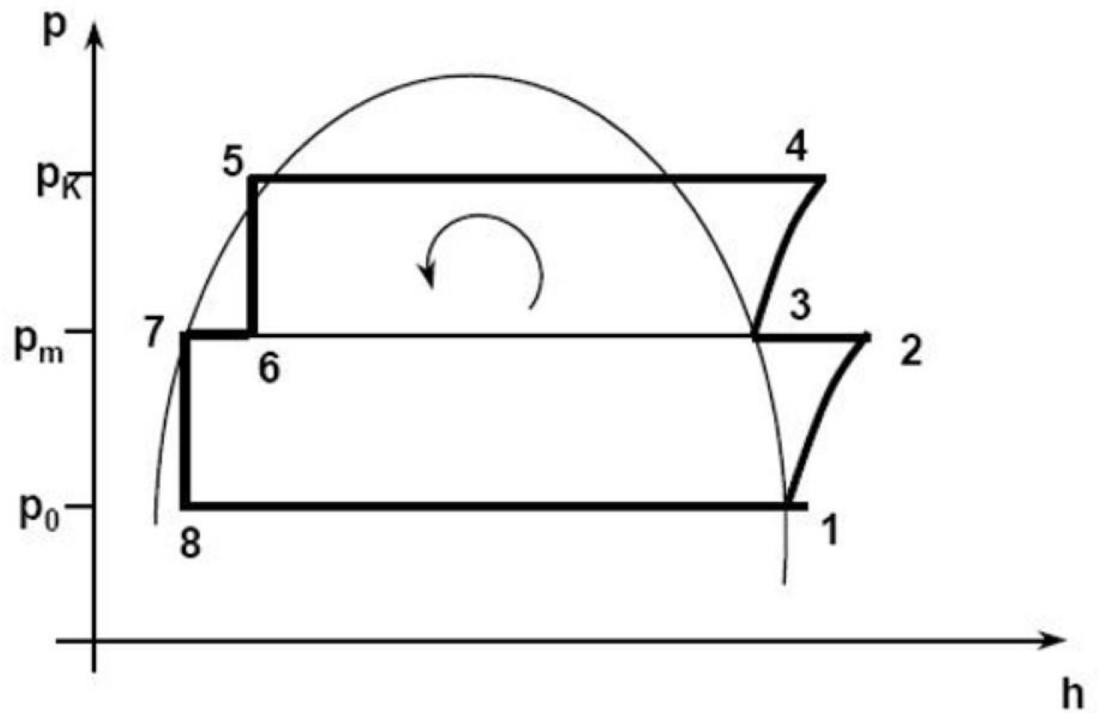
The real refrigeration cycle



1_{EV} *the compression starts at saturated vapor (dry vapor compression cycle)*

1–2 *the work requires by compressor get bigger at superheating (see the slope of 1-2 instead of 1-2')*

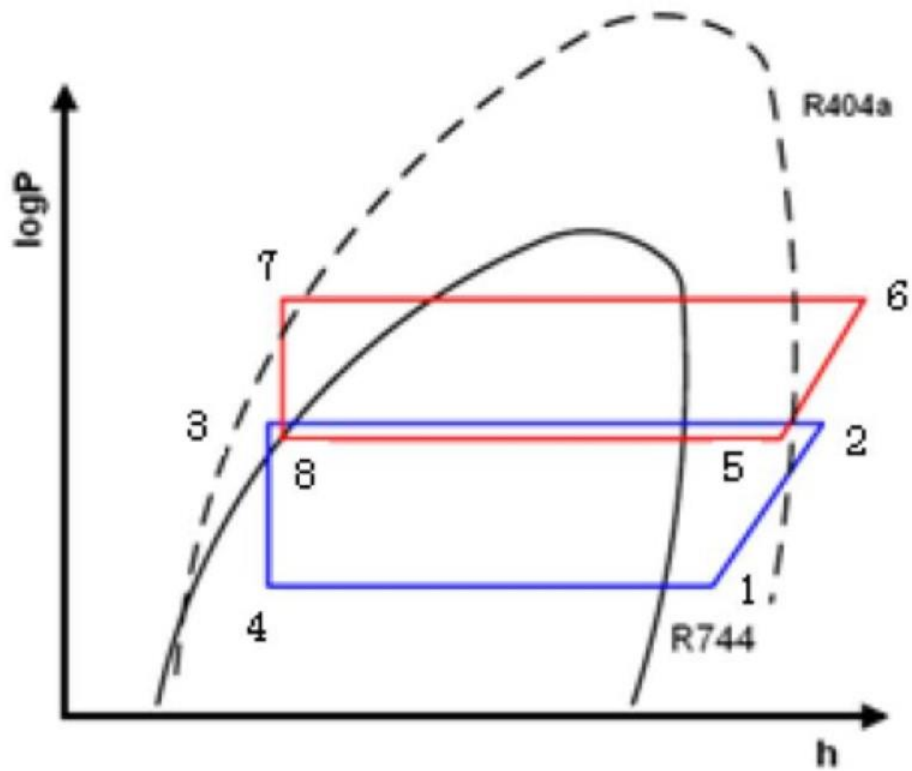
The real refrigeration cycle



Fließbild einer zweistufigen Verdichter-Kältemaschine

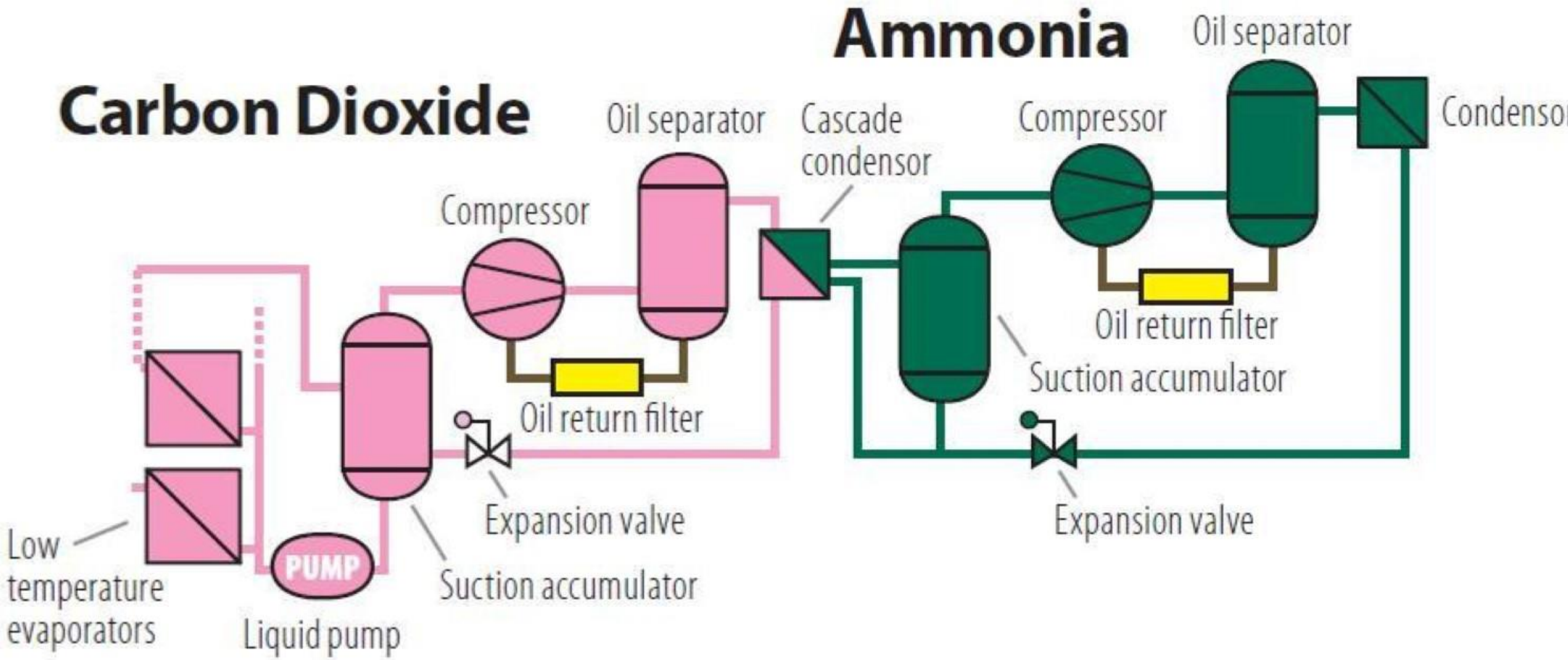
Two level refrigeration cycle. The lower cycle transfers heat (h_2-h_7) to the upper level (h_3-h_6). There are two compressors that need work: h_2-h_1 and h_4-h_3). *Internal heat exchanger flooded by liquid.*

The real refrigeration cycle



Two level refrigerator. The refrigerant is different in the lower and the upper cycle. This is why a continuous and a dotted line shows the saturation lines of the two refrigerants

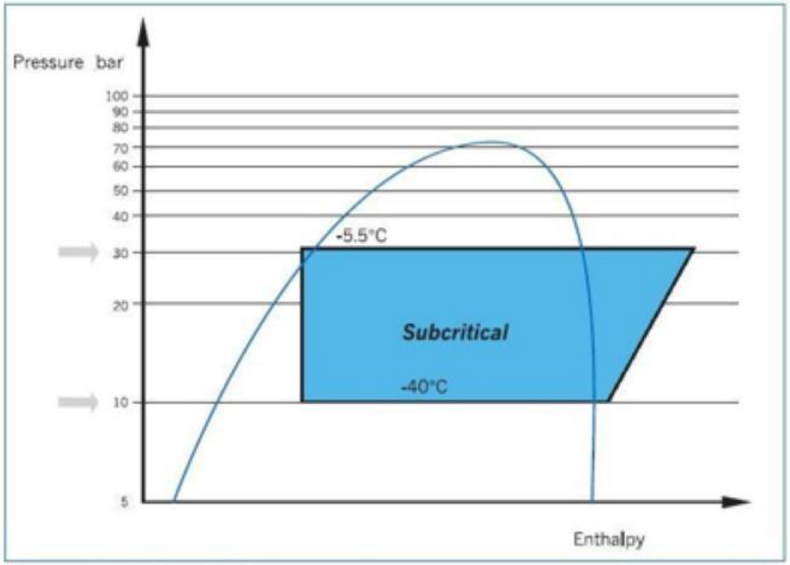
The real refrigeration cycle



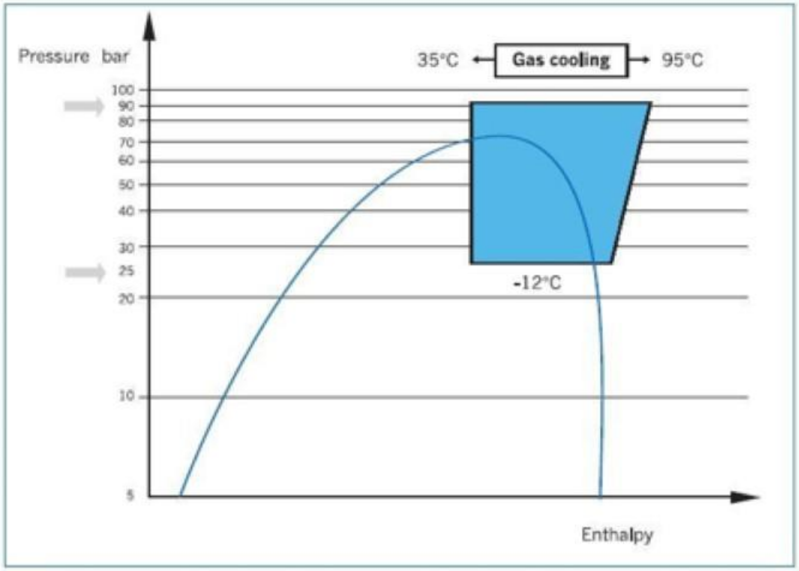
Schematic of a carbon dioxide – ammonia cascade system (courtesy of Grasso)

Two level refrigeration system with two refrigerants. *Cascade condenser transfers the heat from the lower cycle to the upper cycle*

The real refrigeration cycle



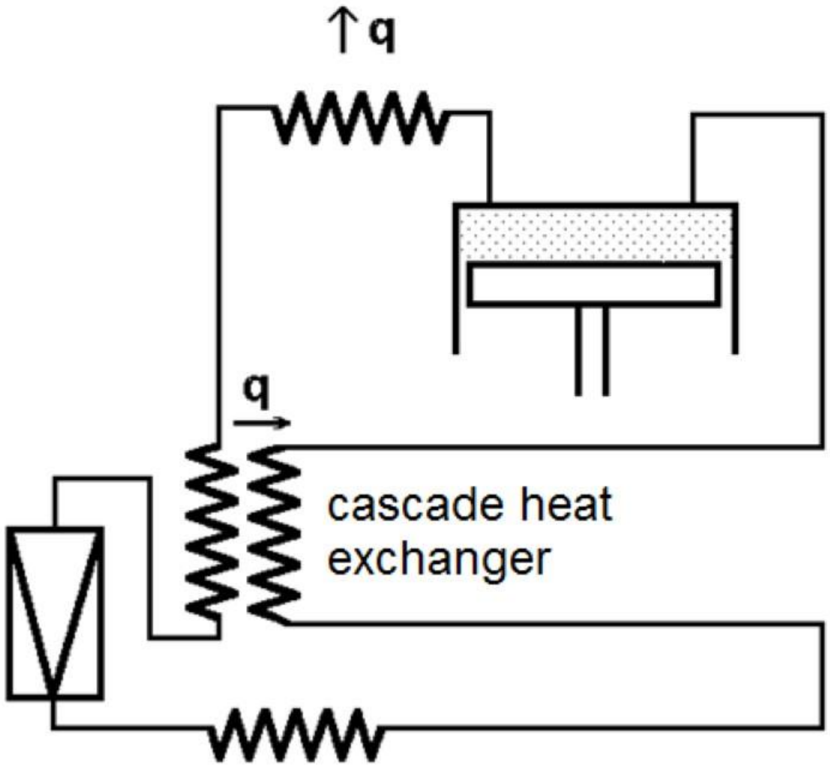
Subcritical CO_2 Refrigeration Circuit



Transcritical CO_2 Refrigeration Circuit

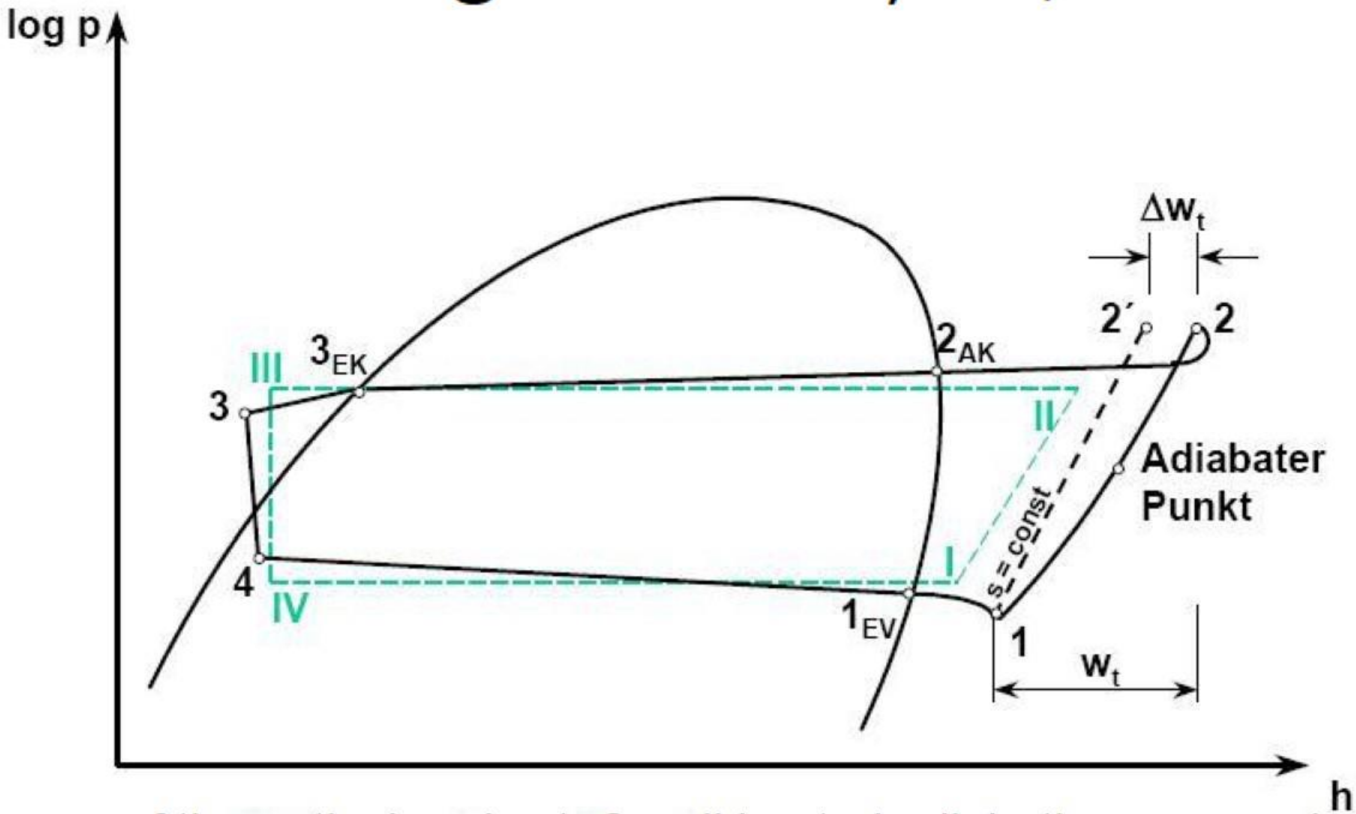
Trans critical version. Right: the CO_2 goes round of the critical point. The **expansion** starts with gas (35°C), its line crosses the saturated liquid line downward and ends as mixture of liquid and vapor (-12°C)

The real refrigeration cycle



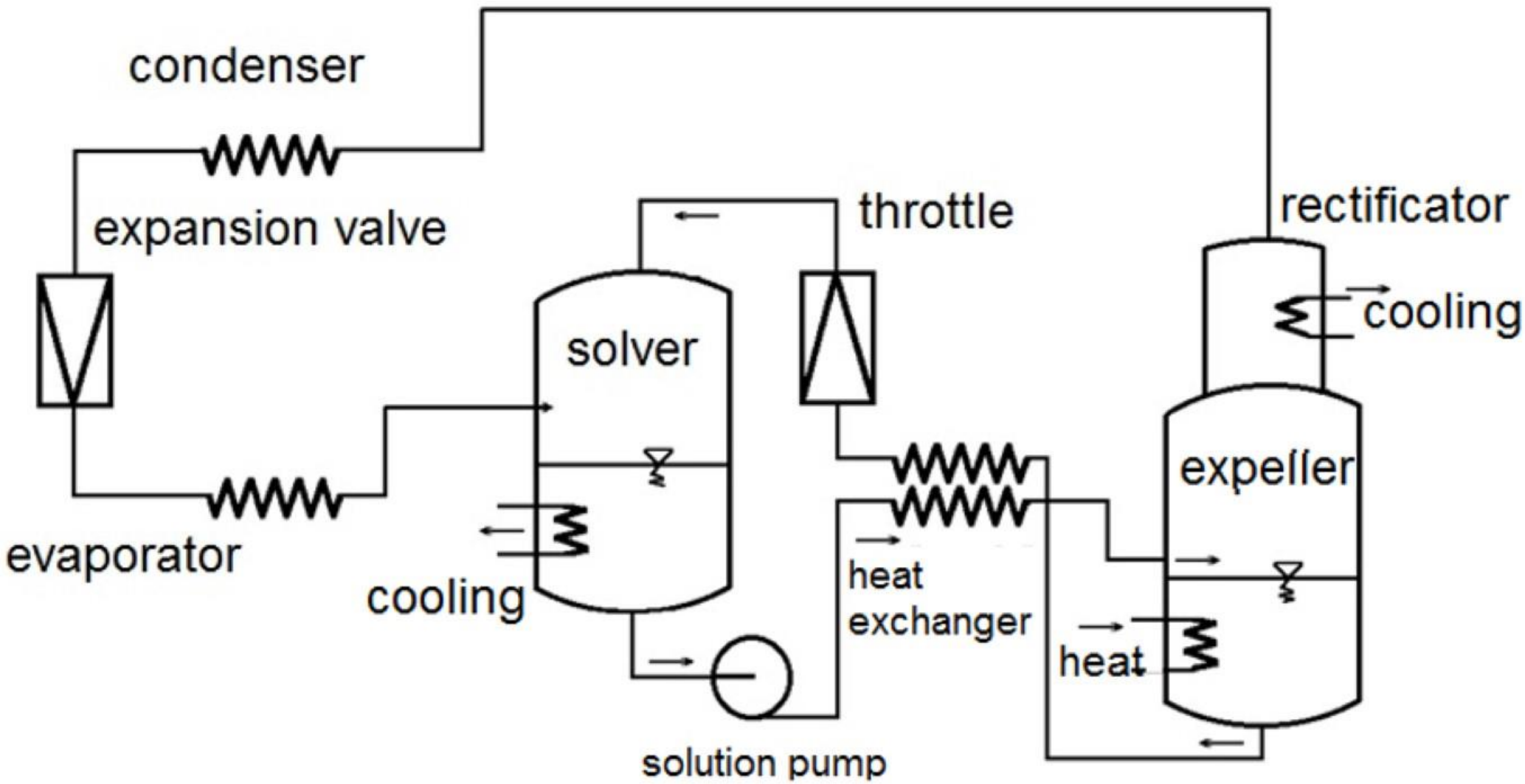
The cascade heat exchanger generates overcooling (left). Its other side overheated vapor created (right). This version prevent the compressor from hitting by liquid droplets destructing the cylinder inside wall

The real refrigeration cycle, differences



Differences of theoretical cycle: 1–2 wall heated adiabatic compression, 2–2' pressure drop at the discharge valve, 2–3 hydrodynamic loss in the condenser, 3–4 expansion heated by the valve and pipeline, 4–1 $_{EV}$ hydrodynamic loss in the evaporator, 1_{EV}–1 pressure drop at the suction valve

Absorption refrigerator



Solvent: water, solute: ammonia, transport gas: hydrogen

Solvation and absorption have the same meaning in this sense

Composition-enthalpy diagram

exhausting ammonia 7-8

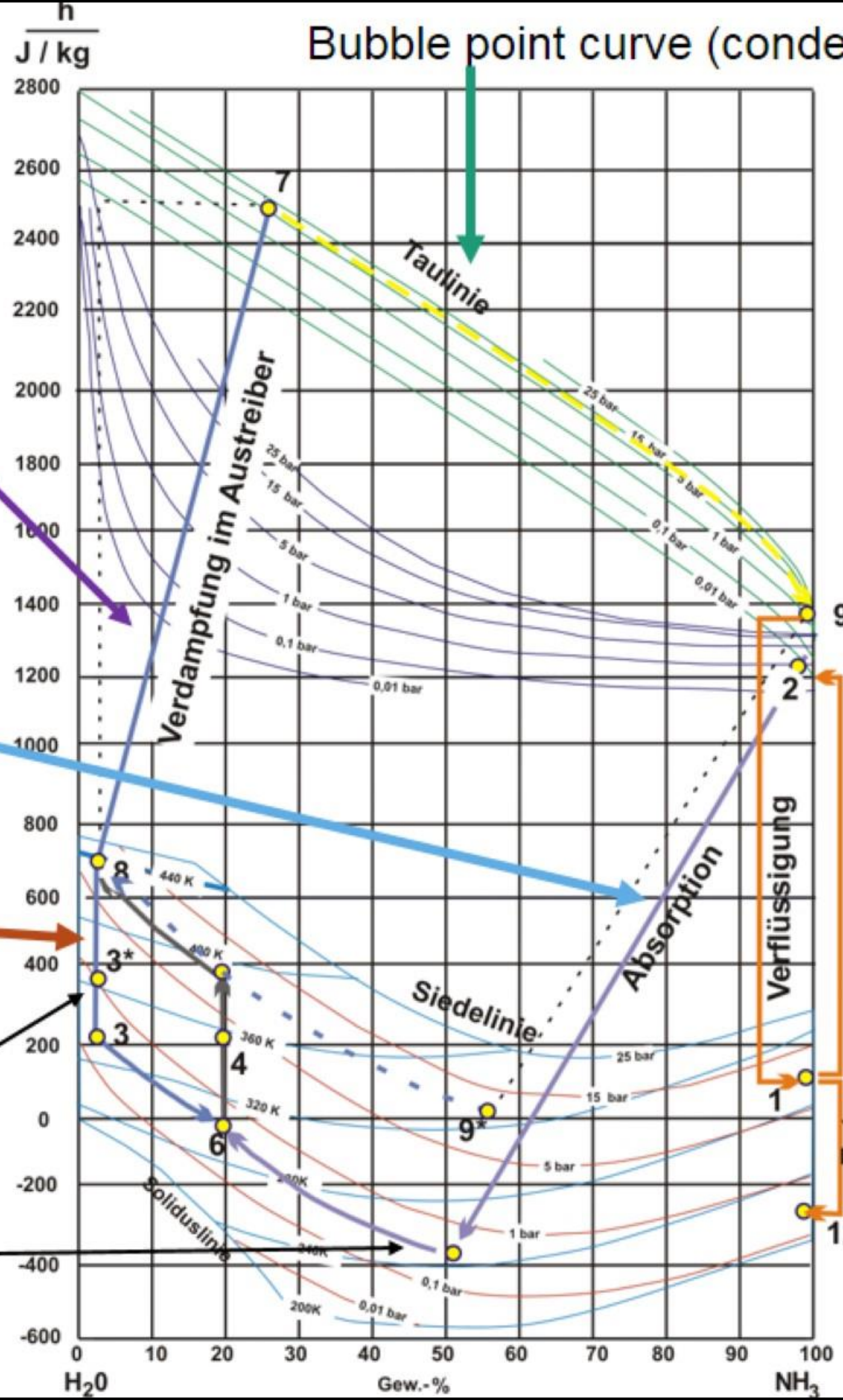
absorbing ammonia 1-2 (solution)

Heat exchanger

Solution weak in ammonia (kb. 3%)

Solution rich in ammonia (50%)

Bubble point curve (condenser pressure)

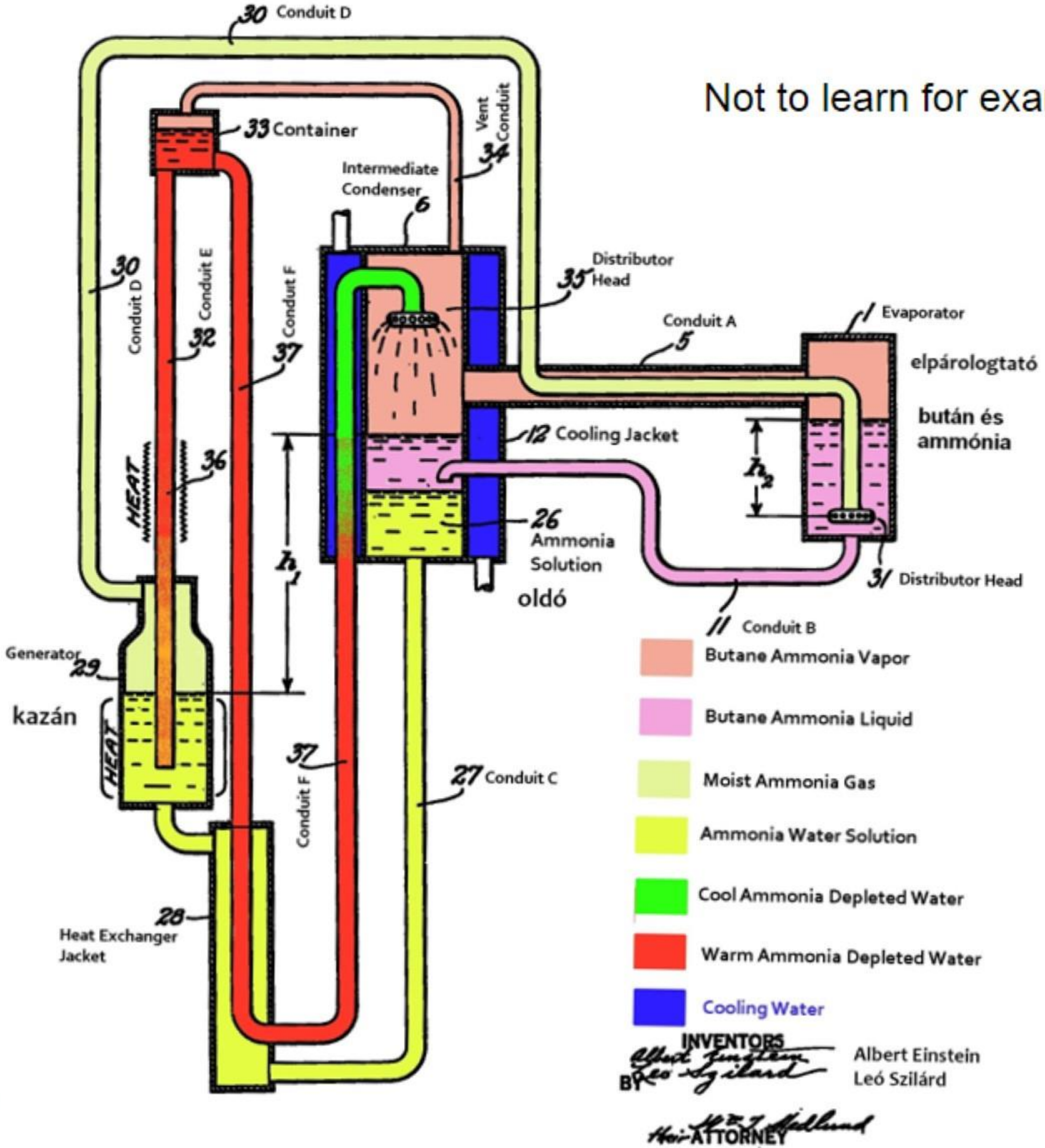


Only the vapor go into the condenser from the state 7 solution (Taulinie = dew point curve 7-9)

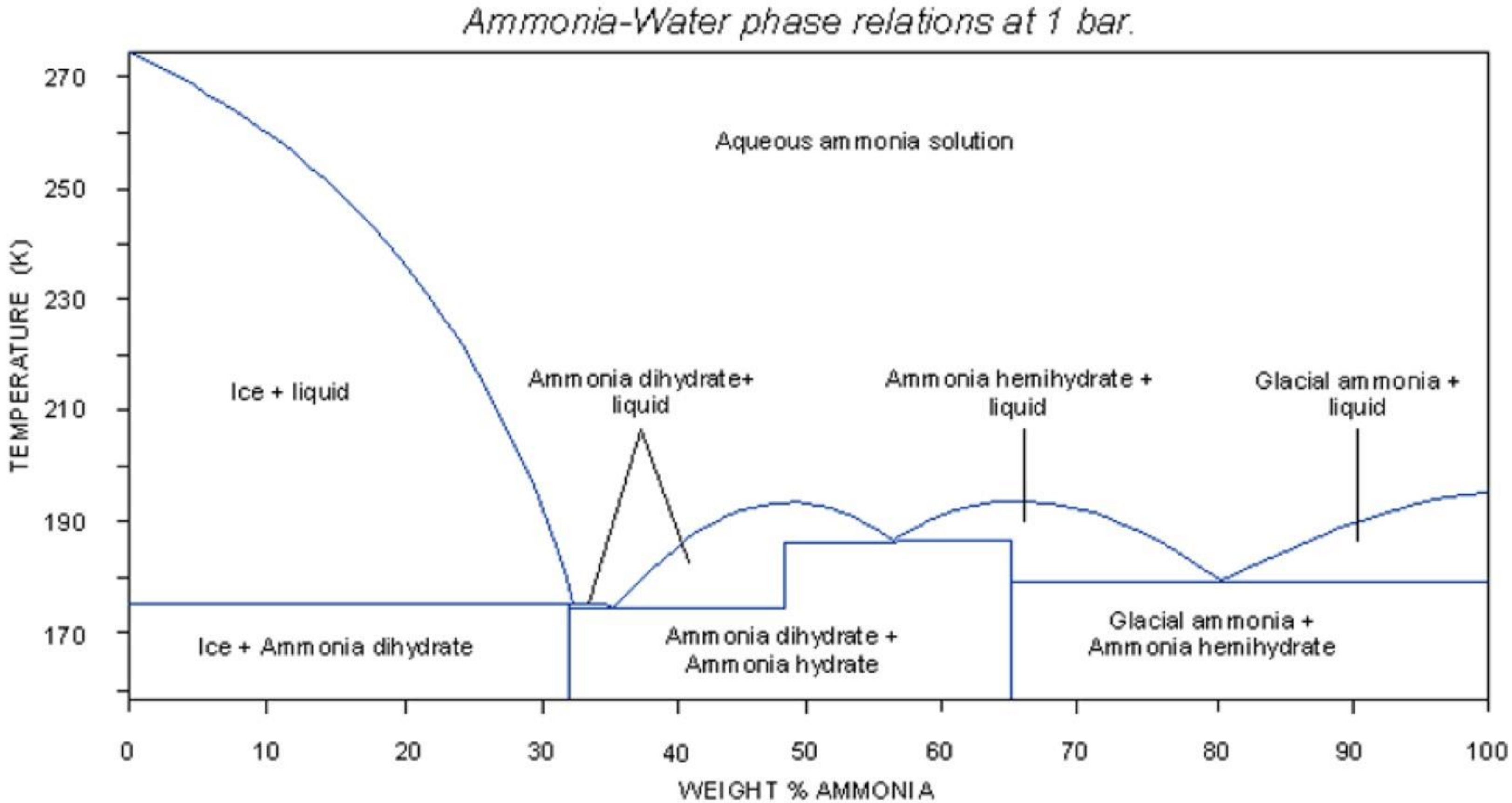
condensation 9-1, expansion 1-2, evaporation 12-2; the other part of the refrigeration cycle

Einstein–Szilárd absorption refrigerator

Not to learn for exam



Absorption refrigerator; ammonia in water



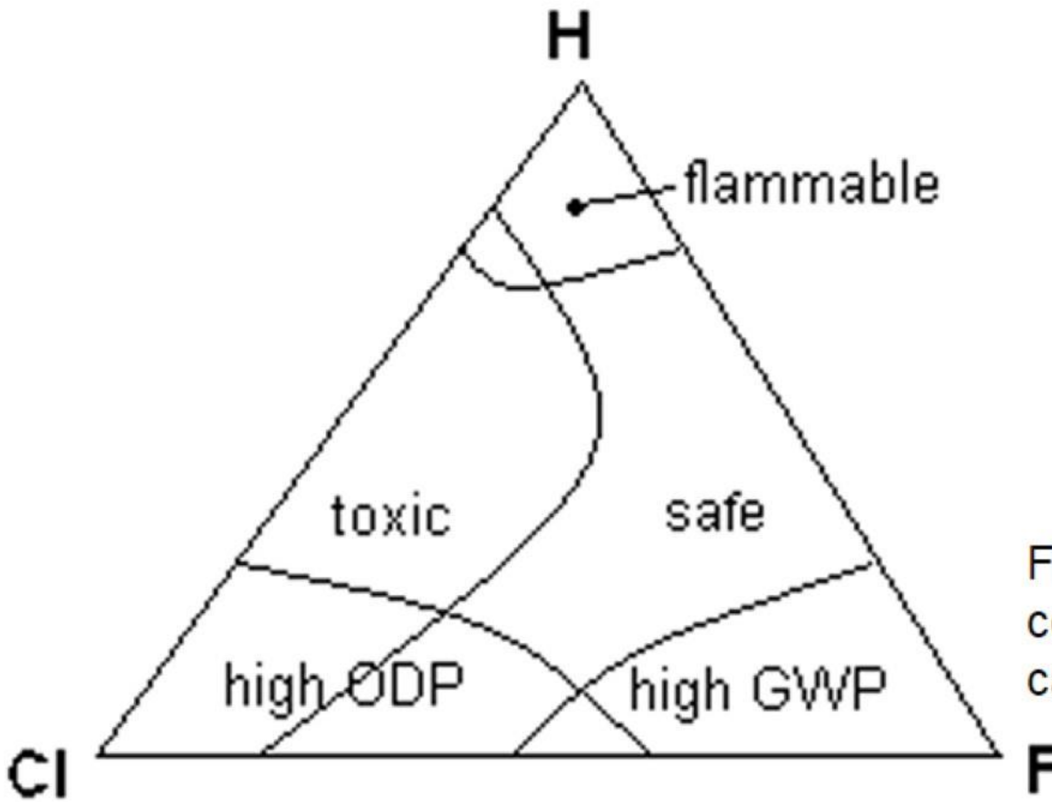
Glacial ammonia: frozen ammonia

Hemyhidrate: two ammonia molecule connected by on water molecule

This system contains three eutectic points depending on mass fraction

Refrigerants

Chlorinated carbohydrates



Fluor containing carbohydrates

Ozone Depletion Potential

Global Warming Potential

This picture is related to carbohydrates used in refrigerators and doesn't contains more than five carbon atoms

Refrigerants used in trade names

Corporation	Tarade name
Imperial Chemicals	Arcton
Daikin Industries	Daiflon
Eskimo Refrigerating Edmonton Ltd.	Eskimon
Elf Atochem	Forane
DuPont	Freon
Hoechst	Frigen
Allied Signal	Genetron
ASP International	Halon
Rhone-Poulenc	Isceon
Pennsylvania Salt	Isotron
Jefferson Chemical	Jeffcool
Johann Adam Benckiser	Kaltron
Union Carbide	Ucon

Refrigerants in trade names

CFC Chlorofluorocarbon	CCl_2F_2
HCFC Hydrochlorofluorocarbon	$CHClF_2$
HFC Hydrofluorocarbon	CHF_3
PFC Perfluorocarbon	C_2F_6

ASHRAE

American Society of Heating, Refrigerating and Air Conditioning Engineers

R = refrigerant, e.g.: R12, R22, R23, R116

B = Containing Bromine: CH_3Br = R40B1, CF_2ClBr = R12B1

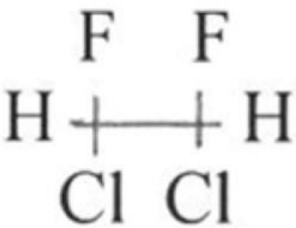
Isomeric's of compounds

ASHRAE

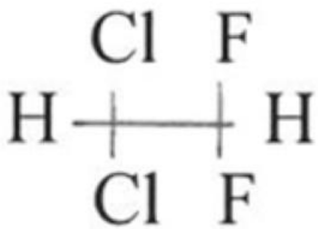
American Society of Heating, Refrigerating and Air Conditioning Engineers

Derivatives of ethane (first: HCFC dichlorodifuoroethane)

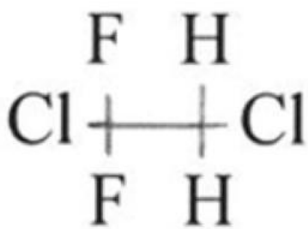
Lowercase letter identifyes the isomer a compound



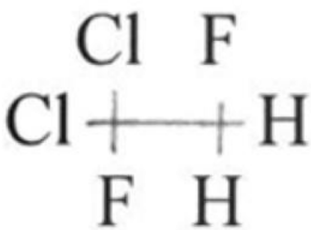
R132



R132a



R132b



R132c

Isometric's of compounds

CH_4
(R-50)

CH_3Cl (R-40) | *CH_3F (R-41)*

CH_2Cl (R-30) | CH_2ClF (R-31) | *CH_2F_2 (R-32)*

$CHCl_3$ (R-20) | $CHCl_2F$ (R-21) | $CHClF_2$ (R-22) | *CHF_3 (R-23)*

CCl_4 (R-10) | <u>CCl_3F (R-11)</u> | <u>CCl_2F_2 (R-12)</u> | <u>$CClF_3$ (R-13)</u> | CF_4 (R-14)

Chlorofluorocarbon compounds derived from methane (CH_4)

Isomeric's of compounds

C_2H_6 (R-170)						
C_2H_5Cl (R-160)	C_2H_5F (R-161)					
$C_2H_4Cl_2$ (R-150)	C_2H_4ClF (R-151)	$C_2H_4F_2$ (R-152)				
$C_2H_3Cl_3$ (R-140)	C_2H_3Cl2F (R-141)	$C_2H_3ClF_2$ (R-142)	$C_2H_3F_3$ (R-143)			
$C_2H_2Cl_4$ (R-130)	$C_2H_2Cl_3F$ (R-131)	$C_2H_2Cl_2F_2$ (R-132)	$C_2H_2ClF_3$ (R-133)	$C_2H_2F_4$ (R-134)		
C_2HCl_5 (R-120)	C_2HCl_4F (R-121)	$C_2HCl_3F_2$ (R-122)	$C_2HCl_2F_3$ (R-123)	C_2HClF_4 (R-124)	C_2HF_5 (R-125)	
C_2Cl_6 (R-110)	C_2Cl_5F (R-111)	$C_2Cl_4F_2$ (R-112)	$C_2Cl_3F_3$ (R-113)	$C_2Cl_2F_4$ (R-114)	C_2ClF_5 (R-115)	CF_6 (R-116)

Chlorofluorocarbon compounds derived from ethane (C_2H_6)

Using different refrigerants

High pressure Medium pressure Low pressure

See their evaporation temperature at atmospheric pressure

Chlorotrifluoromethane	R13	-81,0	CClF3
carbon-dioxide	R744	-57,0	CO2
Chlorodifluoromethane	R22	-40,8	CHClF2
1-Chloro-1,1,2,2,2-pentafluoroethane	R115	-38,0	ClF2C-CF3
Ammonia	R717	-33,3	NH3
Dichlorodifluoromethane	R12	-29,8	CCl2F2
2-Chloro-1,1,1,2-tetrafluoroethane	R124	-12,0	CHFClCF3
sulfur-dioxide	R764	-10,0	SO2
1-Chloro-1,1-difluoroethane	R142b	-9,2	ClF2C-CH3
Bromochlorodifluoromethane	R12B1	3,7	CBrClF2
1,2-Dichloro-1,1,2,2-tetrafluoroethane	R114	3,8	ClF2C-CClF2
Dichlorofluoromethane	R21	8,9	CHCl2F
Chlorofluoromethane	R31	9,1	CH2ClF
Dibromodifluoromethane	R12B2	22,8	CBr2F2
Trichlorofluoromethane	R11	23,0	CCl3F
Chloromethane	R40	24,2	CH3Cl
1,1-Dichloro-1-fluoroethane	R141b	32,0	Cl2FC-CH3

Chlorine free refrigerants

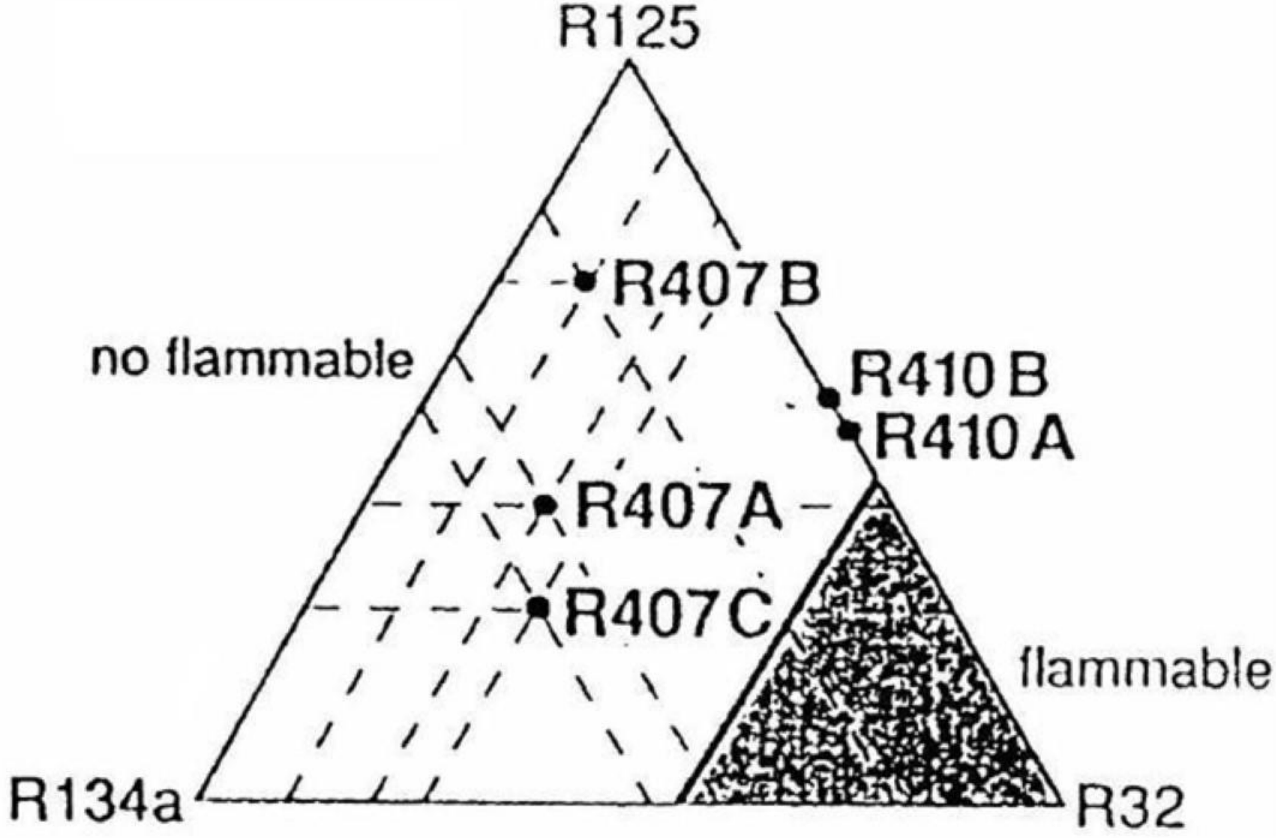
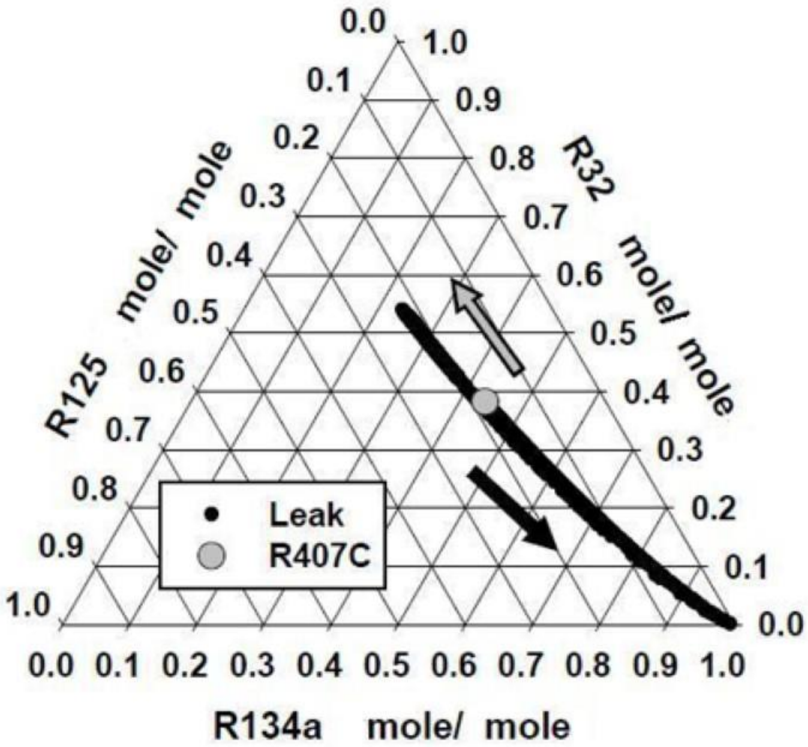


Figure 2-1 Various mixture combinations of the Chlorine free R125-R32-R134a

Zeotropic and azeotrope mixtures



leak = easy evaporating mixture

Three component mixtures

From R400 zeotropic mixtures: while isobaric boiling temperature changes

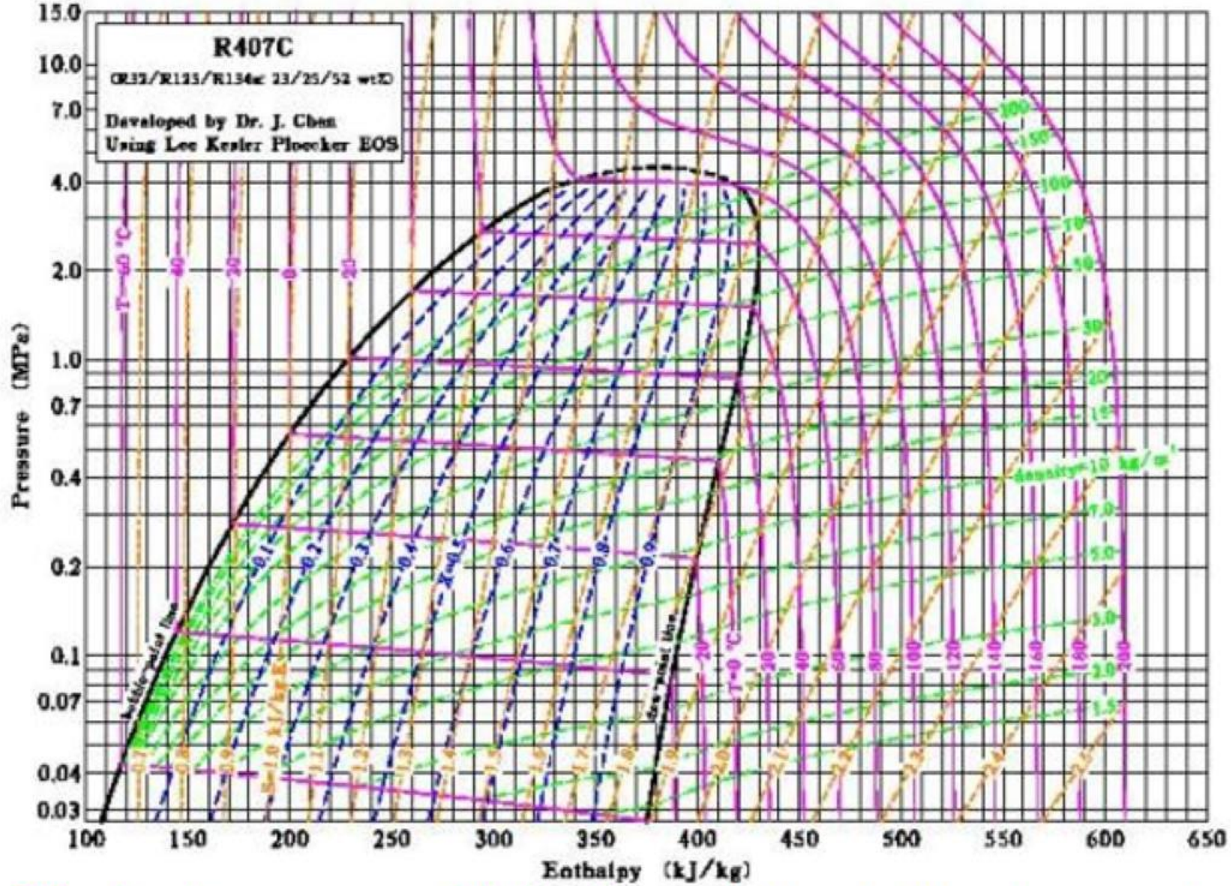
R407C air conditioners (low pressure refrigerants)

glide = change of boiling temperature

From R500 azeotrope mixture: while isobaric boiling temperature is constant

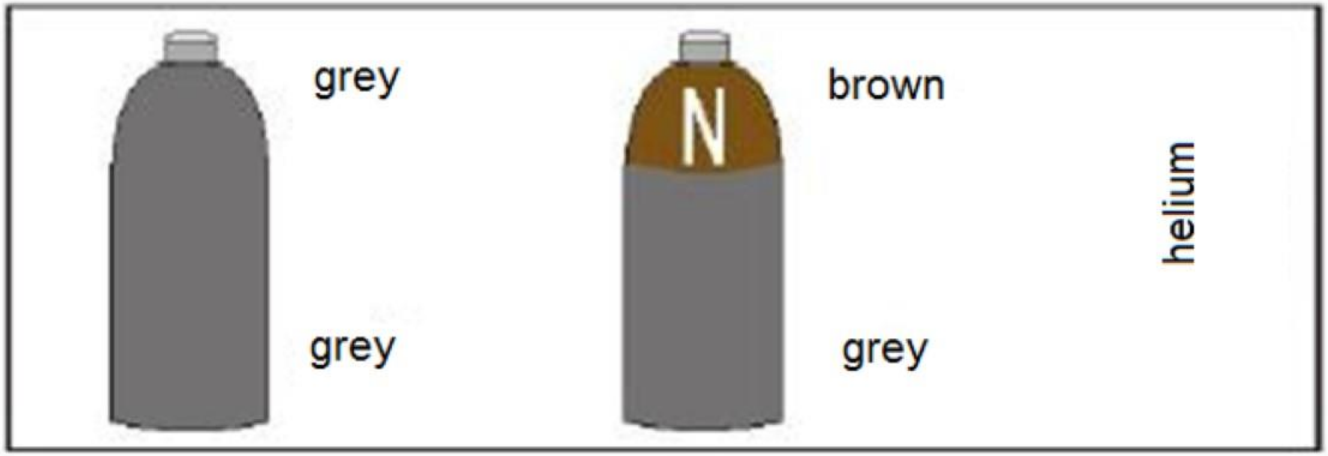
R508b air conditioners (low pressure refrigerants)

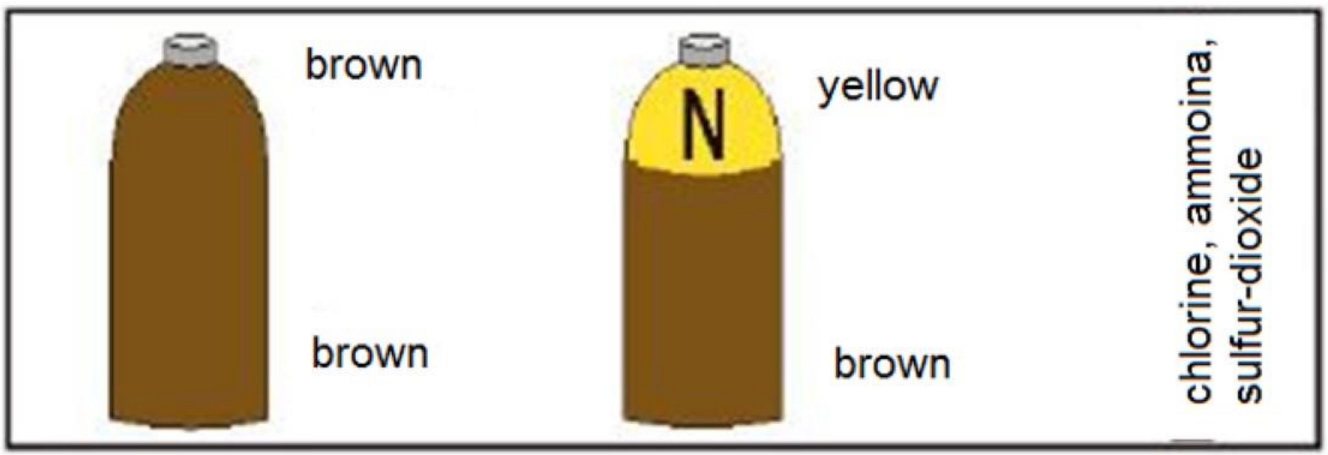
Example: zeotropic refrigerant



The isotherms are violet coloured. The boiling temperature for R407C refrigerant increases by 7 °C at constant pressure. Its critical temperature is 86,2 °C

Transport and storage

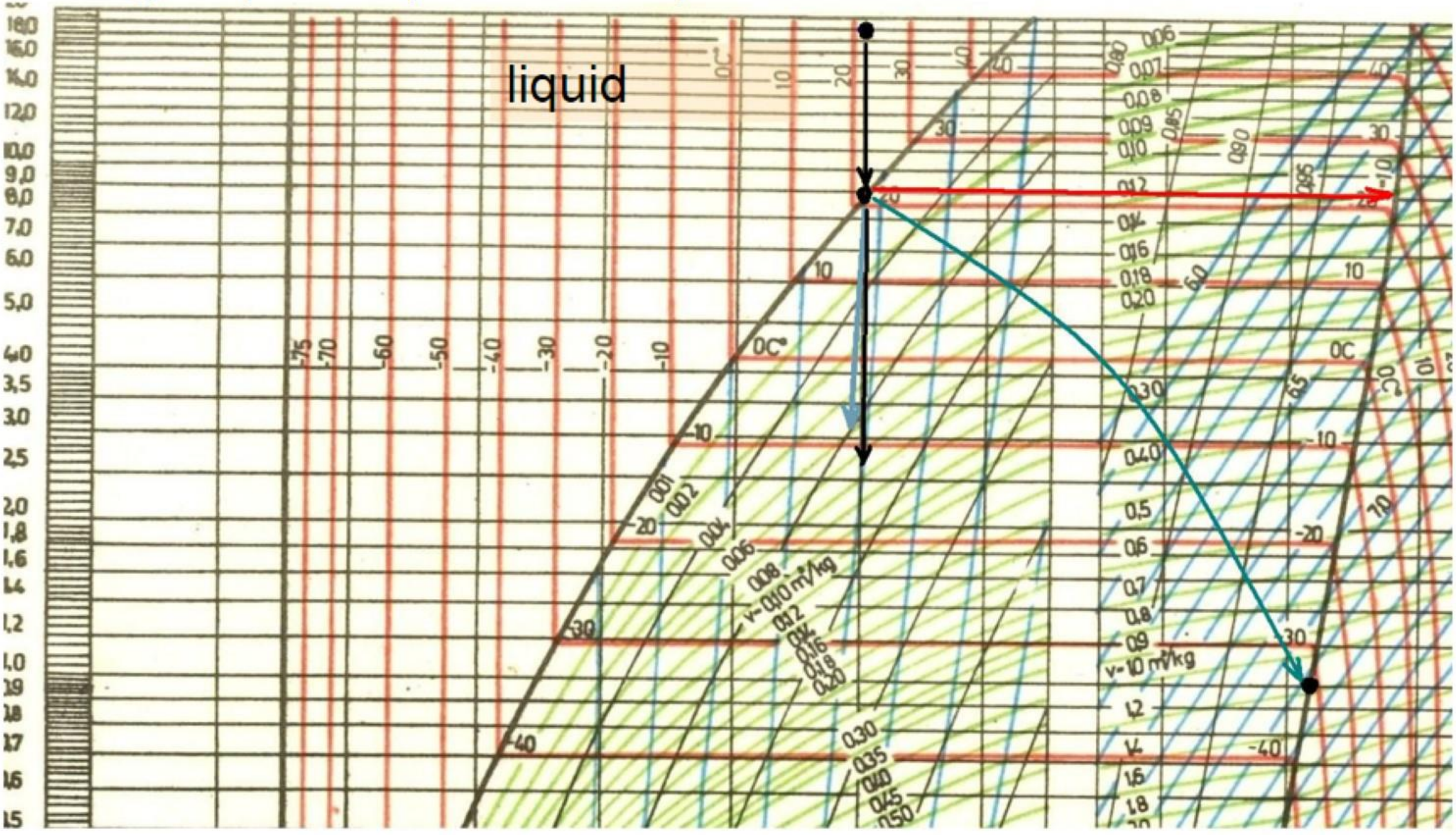




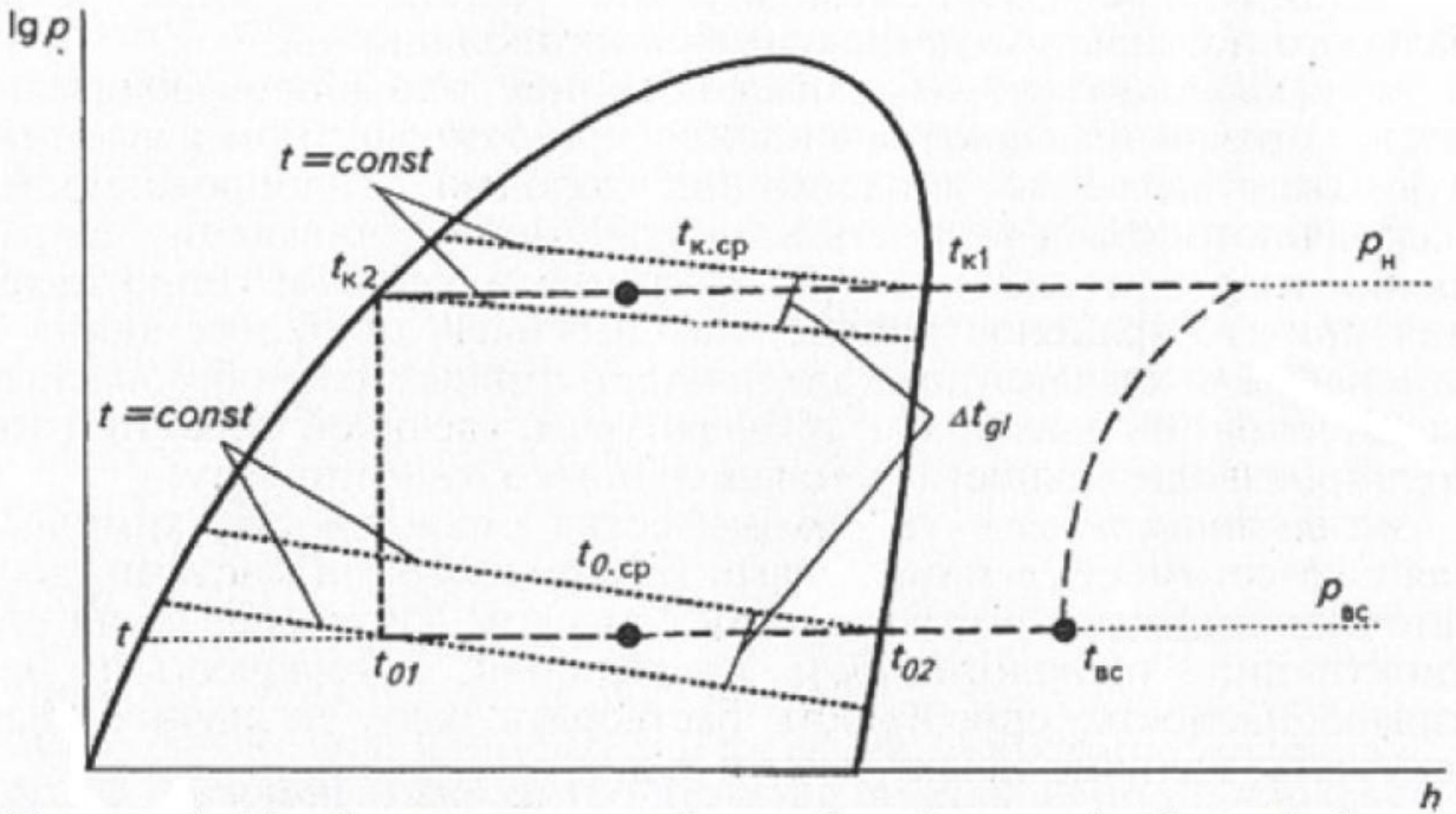
Refrigerant transport and storage

hazard type	cap colour	example
poisonous	yellow (RAL 1018) 	ammonia, chlorine, nitrogen-monoxide
flammable	red (RAL 3000) 	hydrogen, methane, ethylene
oxidant	light blue (RAL 5012) 	oxygen
neutral	vivid green (RAL 3018) 	krypton, xenon, air

Expansion. Black: start from liquid state, red: slow (isotherm), green: medium speed, blue: high speed (adiabatic)

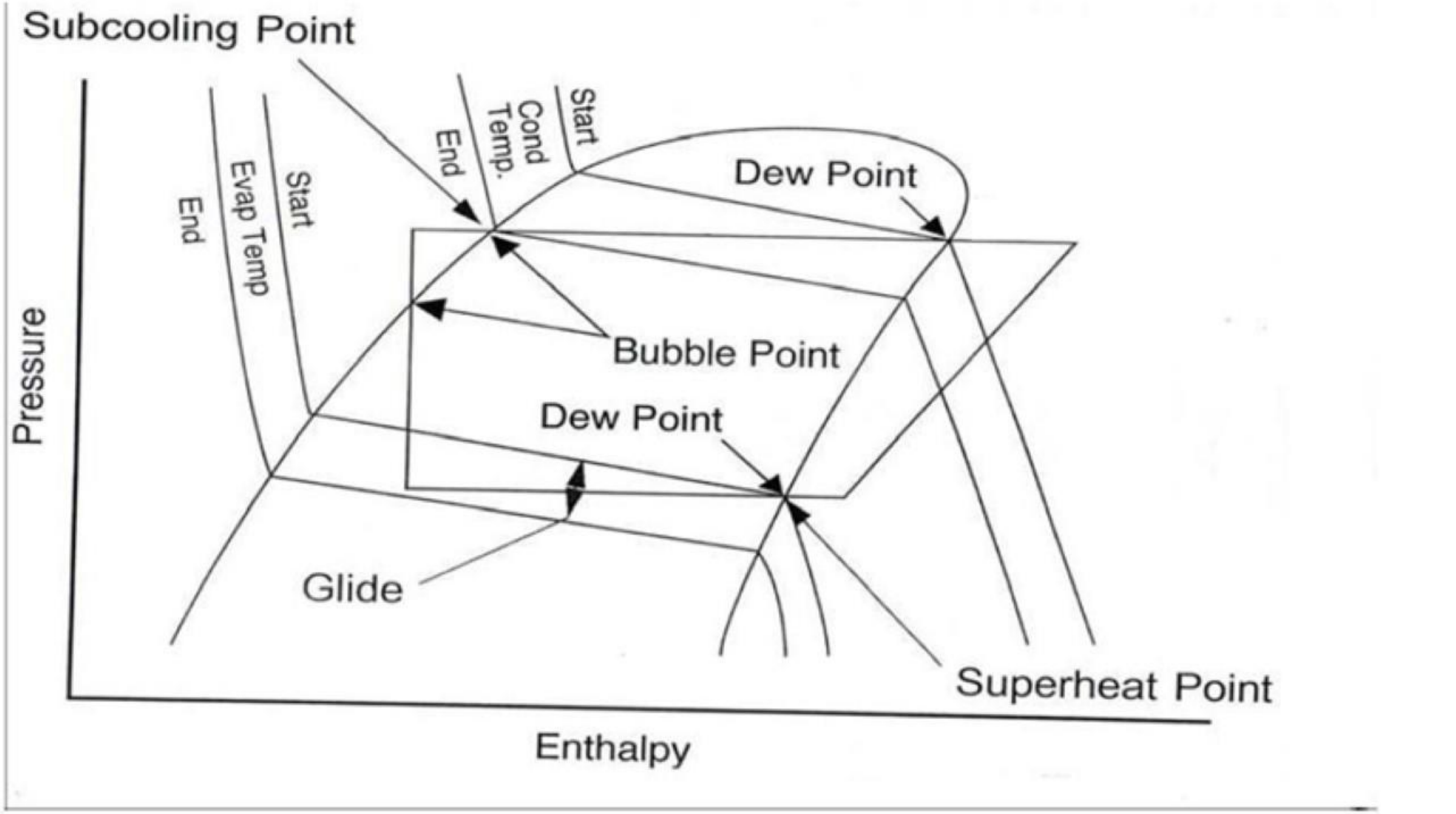


Refrigeration at zeotropic mixture



Zeoptropic blend vapor compression cycle using non-isothermal phase change

Refrigeration at zeotropic mixture



Graph illustration of a vapor compression cycle using zeotropic blend with specific composition

Refrigeration technics

end