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## Evaluation of Cyclopropane as Working Agent in Small Refrigeration Systems

Jörgen Rogstam

Sekretariatet för  
ALTERNATIVA  
KÖLDMEDIER

CIT

Chalmers Teknikpark  
S-412 88 Göteborg.

Tel 031-772 36 91

031-772 36 96

Fax 031-41 80 56

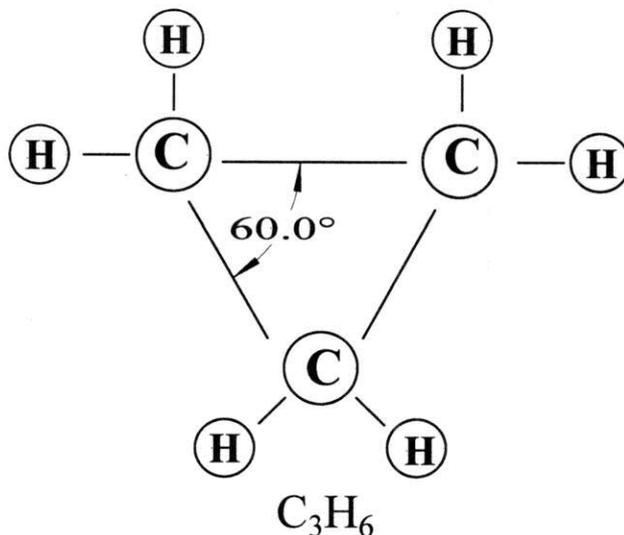
e-mail:

[lil@cit.chalmers.se](mailto:lil@cit.chalmers.se)

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KTH



## Evaluation of Cyclopropane as Working Agent in Small Refrigerating Systems

Delrapport 1

Jörgen Rogstam

Stockholm 1995

**Projekt B3.1 - Ren cyklopropan och blandningar av propan och isobutan  
som köldmedium**

PROJEKTET INGÅR I NUTEKPROGRAMMET: ERSÄTTNING AV  
MILJÖFARLIGA MEDIER I KYLANLÄGGNINGAR OCH VÄRMEPUMPAR

Institutionen för Energiteknik  
Avd för Tillämpad termodynamik  
och kylteknik

Department of Energy Technology  
Div. of Applied Thermodynamics  
and Refrigeration

Kungl Tekniska Högskolan  
Stockholm

The Royal Institute of Technology,  
Stockholm, Sweden

## SAMMANFATTNING

Detta arbete redovisar första fasen i ett projekt som syftar till att klarlägga om cyklopropan kan vara ett alternativ som köldmedium i kyl- och frysapplikationer för hushållsbruk. Utredningen har koncentrerats runt några viktiga frågor avseende införandet av nya köldmedia. De områden som studerats har varit kemisk stabilitet, termodynamiska egenskaper, medicinska biverkningar samt tillgänglighet.

Historiskt patenterades cyklopropan (RC270) 1927 som köldmedium men kom aldrig att användas i någon större utsträckning p.g.a. dess brännbarhet och narkotiska egenskaper. Under tidsperioden från trettio- och fram till sextioalet användes den främst som narkosgas. Dess användning minskade successivt då det infördes mer elektrisk utrustning i sjukvården varvid olyckstillbud uppstod p.g.a. explosiviteten.

RC270 anses kemiskt vara "mindre" stabil och detta till följd av sin ringstruktur som dessutom bidrar till att skapa en inre spänning i molekylerna. Sönderfall till följd av termisk upphettning startar vid 400-500°C vilket knappast är vanligt förekommande temperaturer i kylsystem. Denna sk barriär gäller förutsatt att inga föroreningar, såsom olja eller metallrester, är närvarande vilket skulle kunna sänka sönderfallstemperaturen. Teoretiskt har det inte framkommit någonting som skulle kunna omöjliggöra användandet av RC270 som köldmedium.

De teoretiska utvärderingarna av de termodynamiska egenskaperna visar att RC270 är mer effektivt än R12, R134a, propan (R290) samt isobutan (R600a). Den volymetriska köldalstringen är mellan 20 och 35 % högre, beroende på driftfall, än R12. Denna egenskap skulle kunna medföra en minskning av kompressorns dimensioner vilket även kan spara vikt. Den teoretiska köldfaktorn är mellan 1.5 och 8 % högre än R12 vilket innebär ett bättre energiutnyttjande med RC270. Ett problem föreligger dock, RC270 ger klart högre hetgastemperaturer än de övriga köldmedierna. Detta kan dock avhjälpas med ett lämpligt systemutförande. Dagens system kan sannolikt inte användas med cyklopropan som köldmedium.

Cyklopropan har inga allvarliga medicinska biverkningar. Förgiftning ger sig uttryck som nedsövning och medvetslöshet vilket inträder vid volymkoncentrationer av 7 till 10 %. Om koncentrationen blir kritiskt hög kan kvävningsrisk föreligga, men detta gäller för alla gaser utan fritt syre.

Cyklopropan har en lugnande inverkan på hjärtat och kan därför vara farligt för personer med hjärtproblem. Det kan också leda till att bronker och luftvägar dras samman något vilket gör att astmatiker kan få problem vid förgiftning. Det måste dock betonas att dessa effekter uppträder först vid allvarlig förgiftning dvs vid djup nedsövning.

Tillgängligheten är i dagsläget inte stor. I Sverige kunde endast en leverantör av gasen uppbringas och det var AGA Gas AB. En kvantitet kunde uppbringas och det var 2 kg till priset 5795:- vilket innebär ett kiloprpris av 2898:-. I ett läge där större kvantiteter är aktuella kan det dock antas att priset minskar betydligt.

Studien har visat att det finns anledning att gå vidare med undersökningen där då praktiska prov blir nästa steg. I första läget är det stabilitetstester samt applikationsprov som kommer att vara aktuella.

## ABSTRACT

This investigation was carried out in order to evaluate cyclopropane as working agent in household refrigerator and freezer applications. The evaluation has been focused on some key subjects which are considered as critical when it comes to a new refrigerant. Among those subjects the most important were stability, thermodynamics, medical aspects and availability.

Cyclopropane (RC270) was patented as refrigerant 1927. It never came in to use, though, because of its flammability and anaesthetic properties. The latter property brought it into use as a general anaesthetic in the medical service, where it was used until the 60's when more electrical equipment was introduced. Some explosions caused by cyclopropane made it more or less disappear as a general anaesthetic during the 60's.

RC270 is considered as a "less" stable compound because of its ring structure and the fact that it is a strained molecule. However, its barrier for thermal destruction is given to 400-500°C, which is a temperature rarely reached in a refrigeration circuit. Contamination such as oil and traces of metals can lower barrier for decomposition. This is a matter of further evaluation which will be carried out with stability tests. Theoretically there is nothing that with respect to stability data prevents the use of RC270 as refrigerant.

When it comes to thermodynamics RC270 shows a theoretically superior efficiency compared to R12, R134a, propane (R290) and isobutane (R600a). The volumetric cooling capacity is between 20 and 35 % higher than the one of R12, depending on the operation conditions. This property can decrease the size of the compressor dimensions and consequently also the weight. The coefficient of performance is between 1.5 and 8 % higher than R12, which leads to an improved energy efficiency. One problem exists though, the discharge temperatures are high, but can be brought down with proper system design. The present system design can most likely not be used with RC270 as refrigerant.

The health influence by cyclopropane is very low. Severe poisoning which leads to unconsciousness is obtained when the concentration in the air reaches 7 to 10 %. If the concentration goes very high it may lead to suffocation, but this is the same for all gases without free oxygen.

Cyclopropane has a depressing influence of the heart and can therefore be harmful to persons with cardiac problems. It also tends to constrict the bronchi and the bronchioles which may cause problems for persons with asthma. It has to be emphasised, though, that this is only in case of severe poisoning, i.e. in deep anaesthesia.

The availability is not too good for the moment. Only one supplier was found in Sweden that could provide a quantity and it was AGA Gas AB. The delivered quantity was 2 kg and the price was 5795 SEK, which makes 2898 SEK per kg. In a future perspective, when larger quantities might be ordered, the price should decrease considerably.

This investigation has, however, revealed that cyclopropane should be further investigated as refrigerant. The coming actions will be tests related to the stability matter and application tests in a commercial refrigerator/freezer.

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# 1. INTRODUCTION

## 1.1 Background

In the beginning of 1994 a major project, called Alternative Refrigerants, was initiated as a co-operation between The Swedish National Board for Technical Development (NUTEK) and parts of the industry. The aim of this project was to find replacements for refrigerants with environmental influence. The way to gather the knowledge was to make the industry and the universities to co-operate.

Companies involved are mainly ones with production or servicing within the field of refrigeration or heat pump technology. The universities involved are The Royal Institute of Technology in Stockholm (KTH) and The Chalmers University of Technology in Gothenburg (CTH). A number of sub-projects have been initiated during 1994 within this above mentioned project. The main objective has been replacement of working agents with environmental influence in refrigerating and heat pump installations and also improvement of components related to these processes. The subjects of the projects are for instance heat exchanger and compressor design for optimisation of natural refrigerant use, conversion from CFC to HFC in existing installations. These are just examples among many others.

The financing of the different projects are split between NUTEK and the involved companies with the shares 40 to 60 %. The total budget for the overall project is about 28 million SEK.

One of the above mentioned projects is this one, which is a co-operation between the KTH and the company Electrolux. Electrolux is one of the major compressor, refrigerator and freezer manufacturer for household applications in the world.

Since the early 1930's the freon R12 is the most commonly used in the above mentioned applications. After the discovery of the so called ozone depletion, which was assumed to be caused by the Chloro Fluoro Carbons (CFC), a debate started. The result of this debate was that the CFCs are to be abolished in new production from January 1st 1995 and the Hydro Chloro Fluoro Carbons (HCFC) are to be abolished from January 1st 1998. These regulations concern Europe but the US have similar regulations. The replacement for R12, this far, has been the Hydro Fluoro Carbon (HFC) R134a, which has no ozone depletion potential (ODP) but a considerable global warming potential (GWP). The market now demands so called natural refrigerants which, this far, are limited to ammonia (R717) and different kinds of hydrocarbons. Among the hydrocarbons there are only a few that are thermodynamically suitable. One of these is cyclopropane (RC270). The reason why this one was specifically chosen is that its thermodynamical characteristics are very similar to those of R12. If RC270 would be possible to use in existing R12 systems, as a so called drop-in, it could lead to a major saving, since redesign of systems and components could be avoided.

## 1.2 The Objective of The Study

In order to investigate whether or not cyclopropane is suitable as a refrigerant in the present applications, it has to be investigated with respect to:

- Stability
- Commercial availability
- Toxicity

These criteria are only three among an endless row of *desired* characteristics that are concerned in an evaluation of a *new* refrigerant. However, if any of these three criteria would be considered as critical, the use of the medium would probably not be possible. Many technical or other general aspects can be solved with the right technique or to *some* price, but these matters are not *negotiable*. Exactly what is critical or not will be treated in the subsequent sections. Each criterion will be divided into a manifold of subdivisions in order to evaluate each matter as thoroughly as possible.

## 1.3 Substitutes

Many studies have been focused on the application of environmentally more acceptable refrigerants in refrigerating and heat pump applications. The same requirements for the properties of a refrigerant apply to both small and large systems. When the formerly used R12 is replaced, the alternatives should be substances with properties equal to those of refrigerants belonging to the CFC range. However, the following properties are usually considered:

- Environmental influence
- Stability
- Flammability
- Thermodynamic properties
- Thermodynamic efficiency
- Toxicity
- Cost

Some of these criteria are not "negotiable" like for instance the stability. Others are a matter of "give and take" like the flammability. Already today a great number of household refrigerators are manufactured with flammable refrigerants. This is possible due to an acceptance from the market which on other markets is completely out of the question. When it comes to the cost the amount of refrigerant used in the present application has to be considered. In this study for example, small systems is the objective of the investigated refrigerant. Even though a small amount is charged to each system the cost issue still is an important factor, since the number of manufactured products is considerable. In case of a large refrigerating or heat pump application the cost becomes even more critical.

The acceptance of environmental influences from almost all of the modern society's equipment becomes lower and lower. This fact makes it more difficult to motivate an introduction of a replacement to the former refrigerants if it is not fully free from environmental influence. For instance this is the situation now when a lot of installations are about to be converted from R12

to R134a. Is the latter really a choice for the future? Or does the installation have to be converted again?

One way to find safer refrigerants has been to investigate blends of some less *dangerous* HFCs. Less, in this context, refers to the CFC's. The reason why blends were considered, is once again that similar properties as those of the previously used freons were desired. Now it is also common with blends of flammable refrigerants, for instance propane/isobutane as replacement for R12. Unfortunately there are some complications related to the use of blends. One example is that there is seldom the same ratio of the compounds running in the system as desired. It is also common that one of the components is accumulated somewhere in the system. This phenomenon introduces incorrectness compared to what was theoretically calculated and will result in a capacity different from that was expected. The above mentioned phenomena are not fully under control yet but major research efforts are dedicated to the field.

Another characteristic related to "non-azeotropic" blends is the so called temperature glide. During evaporation and condensation there will be a gliding temperature, due to different boiling temperatures of the components. This doesn't have to be disadvantageous but it depends on system design and type of application. Proper design can help to avoid some of the problems mentioned but this also illustrates some of the difficulties involved with the use of blends.

## 2. METHOD

The following section deals with the methods used for the literature search and the results that the search generated. The number of items found is presented and also from which database or corresponding source they were found. The discussion gives a clue of the extent of the search and hopefully the width and reliability of the facts collected in this paper.

As a first step all possible handbooks, conference papers and such collections, inside the walls of the Department of Applied Thermodynamics and Refrigeration, were searched. The next step was to contact external sources such as the library of The Royal Institute of Technology (KTHB), in order to find articles and papers that treated the technical (chemical and thermodynamic) aspects of the media. Medical aspects of the media were also desired but references that dealt with that subject were only represented to a very limited extent in the above mentioned library. There is also a major school of medicine (The Karolinska Institute) situated in Stockholm. In the library of that school it was possible to obtain some further information about medical and toxicological aspects.

### 2.1 Introductory Search

The first items found were some selected conference papers from the International Conference: New Applications of Natural Working Fluids in Refrigeration and Air Conditioning, Hannover 1994. Since this conference dealt with natural refrigerants, a considerable number of items also treated hydrocarbons. Specifically cyclopropane was treated in two items only<sup>10,11</sup> and those were computational assessments of theoretical behaviour in an idealised refrigeration cycle. However, everything was interesting initially and these evaluations gave a hint of what there was to expect. Furthermore two other conference reports have been searched and those were the 1994 International Refrigeration Conference at Purdue and the International Conference, "CFCs, The Day After", in Padoa 1994. The first gave none (!) useful references and the latter gave two<sup>2,3</sup>.

Handbooks was another way to collect at least general information about the medium. The major problem with this medium is that it has not been used for such a long time, which implies that modern handbooks does not contain any information about this at all. Fortunately there were still old handbooks left and ref.6 gave some general information. It also contained some references which for instance gave the information that cyclopropane was patented as refrigerant 1927<sup>7</sup>. Furthermore a number of chemical handbooks<sup>21</sup> were read in order to find data about the stability. Generally the handbooks had very little information to add, mainly because of the rareness of the medium.

One database with references mostly related to refrigeration is the Fridoc database. This database is the *data version* of the International Journal of Refrigeration (IJR, Institute International du Froid). Surprisingly this database did not contain any reference of interest. However, these introductory searches generated quite many interesting items since once one interesting paper is found, it often has interesting references itself.

## 2.2 Search at KTHB

For this search an informatician was consulted. She was specialised in chemistry which was convenient since the major points, such as stability, flammability and toxicity, concerned the chemical field. Two databases were chosen as especially interesting with respect to the desired information. Searches for information in such databases can be considerably expensive and that was one more reason for consulting a professional. However, the main reason was of course to obtain the best competence, in order to find the desired information.

The first database to be searched was Biosis. It provides a preview of the bibliographic and Chemical Abstracts (CA) chemical section data and documents that appears in printed CAS and in the CA files. The latter covers journals, patents, technical reports, books, conference proceedings and dissertations from all areas of chemistry and chemical engineering world wide. First of all, when a search concerning a medium like this is carried out, the so called CAS number has to be known. The number is a sort of identification number that every existing substance is given. Cyclopropane has the number 75-19-4.

When first the CAS number was given in the search 2146 files (!) that dealt with cyclopropane was found. In combination with the *search operators* "Stability or Safety" 18 files were distinguished. Furthermore it was combined with "Refrigeration" which gave 11 more files and finally it was combined with "Flammability or Fire or Explosivity" which gave 15 additional files. It turned out to be 45 interesting files in Biosis. However, from these 45 files only 11 were considered as interesting when the abstracts were read. Out of those 11 chosen ones, 5 were related to the stability matter, 2 to thermodynamic properties and the remaining 4 were related to the matters flammability and explosivity.

A search was also made in the database Chemsafe. This base mostly contains information about safety, handling and general regulations concerning flammable gases. During the search 20 items were found, only four of these seemed to be of interest. Most of the references found were out of date and thereby hard to find. Finally, out of those four items none were available to a reasonable effort or resource input.

## 2.3 Search at The Library of The Karolinska Institute

This search resulted in eight items containing general information about cyclopropane as anaesthetic and also something about the risks related to the use of this medium in the mentioned application. A reference<sup>30</sup> with a list of all institutes and organisations that dealt with classification and investigation of dangerous substances was found. It was a very useful publication as it listed all treated chemical substances vs. all the organisations that carried out the investigations. Thereby it was possible to get a good view over which organisations that were worth to contact in order to receive a more detailed information concerning the health aspects.

### 3. STABILITY

The objective of the following section is to present the structure and some aspects of the chemical behaviour of cyclopropane in a way that is comprehensive even for a "non-chemist". The structure of the discussion is mainly based on reference 31. Key issues in the discussion are stability and factors related to stability such as heat of combustion, heat of formation and ring strain. In order to quantify the figures obtained a comparison is made between the studied cyclopropane, R12, propane and isobutane. The two latter ones are also, as earlier mentioned, of current interest as replacements in various refrigeration applications.

#### 3.1 Survey of Alkanes

The family of organic compounds called hydrocarbons can be divided into several groups based on the type of bond between the individual carbon atoms. Those hydrocarbons in which all of the carbon-carbon bonds are single bonds are called alkanes. Those hydrocarbons that contain at least one double bond are called alkenes and eventually those with a triple bond are called alkynes.

Generally it can be concluded that the more branched the alkane is, the lower is the normal boiling point (n.b.p.). For example, n-butane has a n.b.p. of  $-0.5^{\circ}\text{C}$ , whereas the branched isomer isobutane has a n.b.p. of  $-11.7^{\circ}\text{C}$ .

Cycloalkanes are alkanes in which the carbon atoms are arranged in a ring. Alkanes have the general formula  $\text{C}_n\text{H}_{2n+2}$ , such as propane  $\text{C}_3\text{H}_8$  and butane  $\text{C}_4\text{H}_{10}$ . Monocyclic cycloalkanes have two fewer hydrogen atoms and thus the formula  $\text{C}_n\text{H}_{2n}$ , like cyclopropane  $\text{C}_3\text{H}_6$ . For a comparison of the structures, see fig. 3.1.

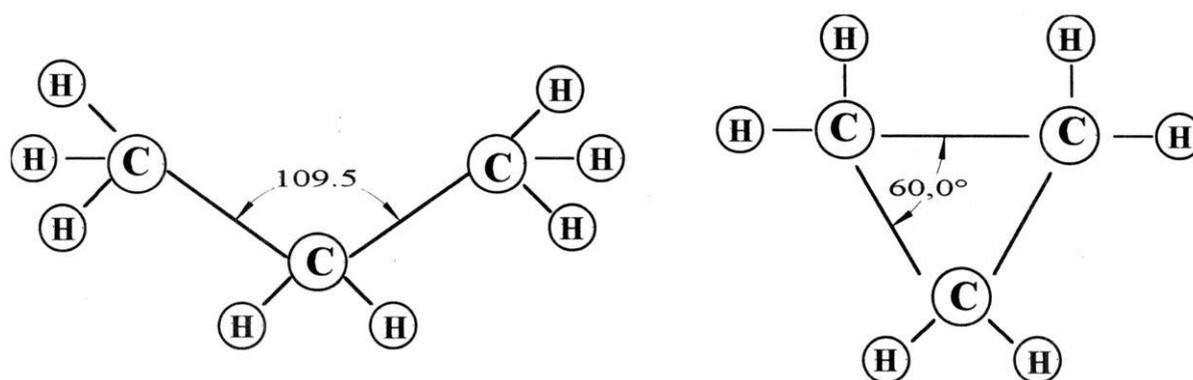


Figure 3.1 Structure of Propane and Cyclopropane.

Alkanes and cycloalkanes are so similar that many of their basic properties can be considered side by side. Some differences remain, however, and certain structural features arise from the ring of cycloalkanes that are more conveniently studied separately.

### 3.2 General Aspects of Cycloalkanes

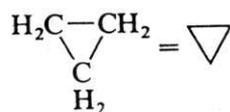
The first four cycloalkanes in the cycloalkane series are gases at normal room temperature while the heavier ones are in a liquid state. All members of the group are saturated hydrocarbons or derivatives from those. The term saturated means that there are no double bonds and that all *connections* on the carbon atoms are occupied with another carbon or a hydrogen atom. A derivative is some parent alkane where one or more hydrogen atoms are substituted for another atom, for instance fluorine or chlorine. Derivatives are not of great interest in this evaluation but derivatives of cyclopropane and their behaviour are treated in<sup>14,15</sup>.

The most interesting cycloalkanes for the present study are those with three to eight carbon atoms. Cycloalkanes, however, have higher boiling points than unbranched alkanes with the same number of carbon atoms (tab. 3.1).

Number of carbon atoms	Alkanes	Normal boiling point (°C)	Cycloalkanes	Normal boiling point (°C)
3	Propane	-42.1	Cyclopropane	-32.9
4	Butane	-0.5	Cyclobutane	13
5	Pentane	36.1	Cyclopentane	49
6	Hexane	68.7	Cyclohexane	81

**Table 3.1** A comparison of normal boiling point between alkanes and cycloalkanes.

The general formula for this group is, as mentioned,  $C_nH_{2n}$  as long as there are no double bonds involved. Independent of the size of the rings they are all flammable or extremely flammable which has brought, at least the larger ones, into use as fuels.



Cyclopropane

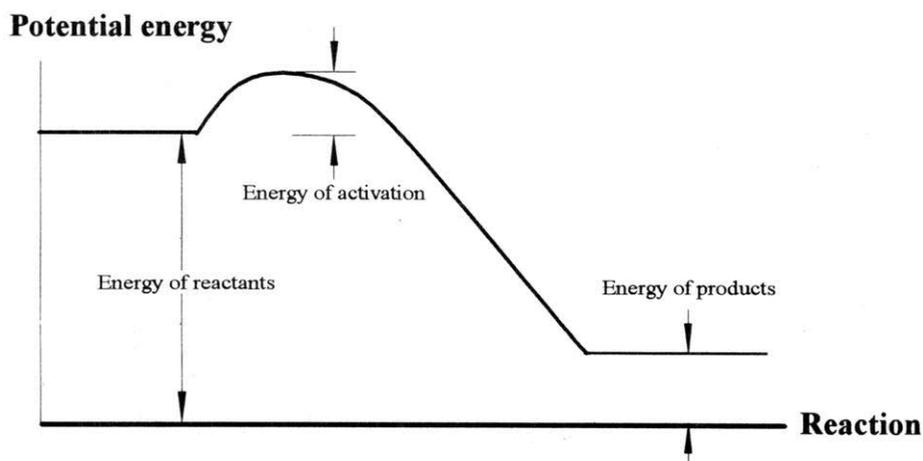
**Figure 3.2** The structure of cyclopropane.

Cyclopropane (trimethylene) is the smallest member of the group of cycloalkanes. From the formula of cyclopropane,  $C_3H_6$ , it can be seen that the synonym trimethylene comes from the structural construction of three methylene ( $CH_2$ ) groups (fig.3.2).

### 3.3 Energies and Stability

Before the different energy concepts are further evaluated it has to be emphasised what the two fundamental types of energy (kinetic and potential) means to a system. Kinetic energy in its macroscopic means is mainly left out in this discussion, but the potential energy is of a more central meaning here. The most central point in this context is the term stability or relative stability. **The relative stability of a system is inversely related to its relative potential energy.** The *higher* potential energy a system has, the *less* stable it is. Consider, as an example, the relative potential energy of a pile of stapled cans. As long as the pile is standing it has, due to the gravity, a high potential energy and it can actually develop a considerable work. As soon as the pile has fallen down and all the cans lie on the ground it has a low potential energy. The great stability makes it incapable of releasing such an energy.

All organic compounds have potential energy. If there would not exist barriers for chemical reactions they would all be transformed into carbon dioxide and water. These barriers are of great interest, since they determine the stability of the compound. It works the way that a higher barrier makes it more difficult for a reaction to take place, and consequently the compound is more stable.



**Figure 3.3** A potential energy diagram for an exothermic reaction.

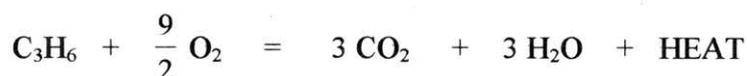
The energy of activation is the so called barrier mentioned above. The height of the barrier is the interesting fact that will be evaluated in this study. The way that the top is reached is normally by increasing the temperature which consequently increases the energy. How high the increase will be before decomposition takes place will depend on which other compounds that are present. Some compounds work as catalysts in reactions like these. They can considerably lower the energy of activation necessary to initiate the reaction. Oils and traces of metals could be such factors that influence the stability.

The energy factor accounts for another important observation: There is a relation between the reaction rate and the magnitude of the energy of activation for different reactions occurring at the same temperature. A reaction with a lower energy of activation will occur much faster than one with a higher energy of activation. Consequently it is desirable to keep as big margin as possible to the energy of activation. In other words: if the energy of activation is low. Keep the temperature as low as possible.

### 3.4 Heat of Combustion

Cycloalkanes do not all have the same relative stability. Data from heats of combustion show that cyclohexane is the most stable one and cyclopropane and cyclobutane are much less stable. The relative instability of the latter ones is a direct consequence of their cyclic structures and the ring strain. This can further be demonstrated experimentally if their relative heats of combustion's are examined.

The heat of combustion of a compound is the enthalpy change for the complete oxidation of the compound. This can be seen in fig. 3.3 as the difference between the level of potential energy for the reactants and the products. Such a reaction is called exothermic since it evolves energy. A corresponding reaction that demands energy to take place is called endothermic. Complete oxidation for a hydrocarbon means that it is converted to carbon dioxide and water. This can be accomplished experimentally, and the amount of heat evolved can be accurately measured. For cyclopropane, for example, the heat of combustion is 499.8 kcal/mole. The stoichiometric reaction is as follows:



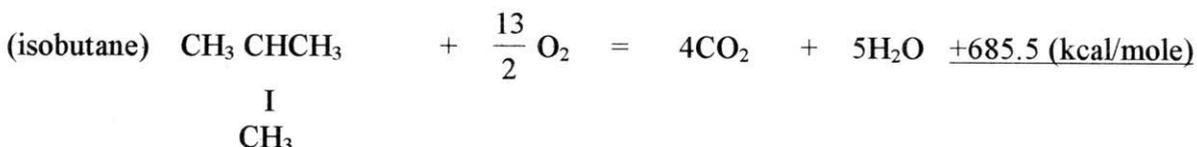
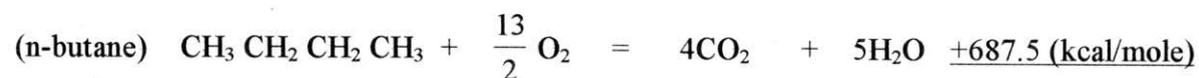
The heat is, as mentioned, called heat of combustion and is represented  $\Delta H$  (kcal/mole or kJ/mole). The value *per mole* is based on the fuel, in this case per mole cyclopropane.  $\Delta H$  is more clearly spoken the difference between the enthalpy per mole of the incoming reactants and the exiting combustion products:

$$\Delta H = \sum_P n_c h_p - \sum_R n_i h_R$$

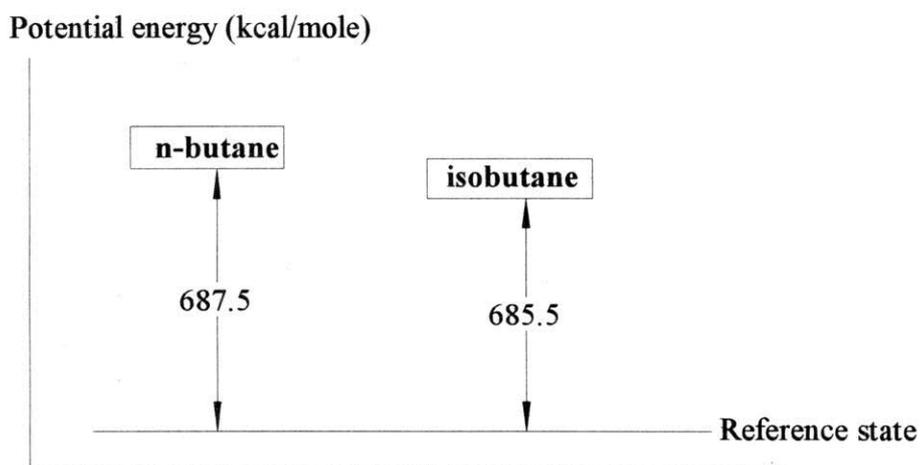
where

- $h_p$  and  $h_R$  are the enthalpy per mole of the reactants and products respectively
- $n_i$  and  $n_c$  are the number of moles of the incoming and exiting media *per mole of fuel*

In order to exemplify that this could be used as a measurement of the stability, an example is presented here. Consider the combustion of butane and isobutane, which are two isomers with the same formula but different structure:



Since n-butane liberates more heat on combustion than isobutane, it must contain relatively more potential energy. Isobutane must therefore be the more stable one, since it liberates two kcal per mole less. In fig. 3.4 this discussion is visualised with a reference state for the reaction products set to zero.



**Figure 3.4** Heats of combustion show that isobutane is more stable than butane.

Because the cycloalkanes are not isomeric, their heats of combustion cannot be compared directly. However, the amount of heat evolved per  $\text{CH}_2$  can be calculated. On this basis, the stabilities of cycloalkanes become directly comparable. The results from such an investigation are shown in tab. 3.2.

Cycloalkane	Heat of Combustion(kcal/mole)	Heat of Combustion per $\text{CH}_2$ (kcal/mole)
Cyclopropane	499.8	166.6
Cyclobutane	655.9	164.0
Cyclopentane	793.5	158.7
Cyclohexane	944.5	157.4
Cycloheptane	1108.2	158.3
Unbranched		157.4

**Table 3.2** Heat of combustion of cycloalkanes.

From the results in the table it can be concluded that cyclohexane has the lowest heat of combustion per  $\text{CH}_2$  group. In the comparison is also seen that a  $\text{CH}_2$  group from an unbranched alkane has the same value. This indicates that cyclohexane has no ring strain. The fact that cyclohexane has no ring strain is actually what the ring strain comparison in table 3.2 is based on.

The combustion of cyclopropane evolves the greatest amount of heat per  $\text{CH}_2$  group. Therefore, molecules of cyclopropane must have the greatest ring strain. Since the molecules evolve the greatest amount of energy per  $\text{CH}_2$  group on combustion, they must also contain the greatest potential energy per  $\text{CH}_2$  group. Thus what is called ring strain is a form of potential energy that the cyclic molecules contain. The more ring strain a molecule possesses, the more potential energy it has and the less stable it is compared to its cyclic homologues.

### 3.5 Heat of Formation

Every substance is given a so called heat of formation value, which is the enthalpy of the chemical elements in their most stable states. By international agreement, the standard state of all substances for the purpose of recording thermodynamic data is their state at a pressure of  $P^\circ = 101.32 \text{ kPa}$ . Furthermore if the substance is a gas, its standard state is that of the ideal gas. The superscript  $^\circ$  on a symbol denotes a value taken at the standard pressure  $P^\circ$  and (for gases) the ideal-gas condition.

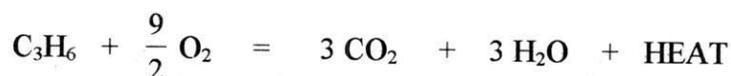
When it comes to enthalpy data the reference standard state is  $P^\circ = 101.32 \text{ kPa}$  and  $298.15 \text{ K}$  ( $25^\circ\text{C}$ ). For basic elements such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{C}$  and so on the reference state is given the value  $0 \text{ kcal/mole}$ . Thus, other chemical compounds could have positive or negative values of the enthalpy of formation, depending on whether their value is higher or lower than that for the basic elements.

The standard enthalpy of formation,  $\Delta h_f^\circ$ , of any compound is the enthalpy of the reaction,  $\Delta h_r^\circ$ , from which it is formed from its elements. All the reactants and products are at  $P^\circ = 101.32 \text{ kPa}$ . We can, however, have standard enthalpies of formation at different temperatures, so that the temperature of the reaction of formation must be separately specified. Thermochemical data are conveniently tabulated as standard enthalpies of formation and are obtainable from ordinary chemical handbooks.

In order to investigate what influence  $\Delta h_f^\circ$  has on the stability, or if the figure can say something in comparison with other compounds, it is here exemplified with the oxidation of cyclopropane. From tables  $\Delta h_f^\circ$  values are found for the reactants concerned:

- $\text{CO}_2 = -94.1 \text{ kcal/mole}$
- $\text{H}_2\text{O} = -68.4 \text{ kcal/mole}$
- $\text{C}_3\text{H}_6 = 12.7 \text{ kcal/mole}$

For cyclopropane the stoichiometric reaction is:



which with the heat of formation values gives:

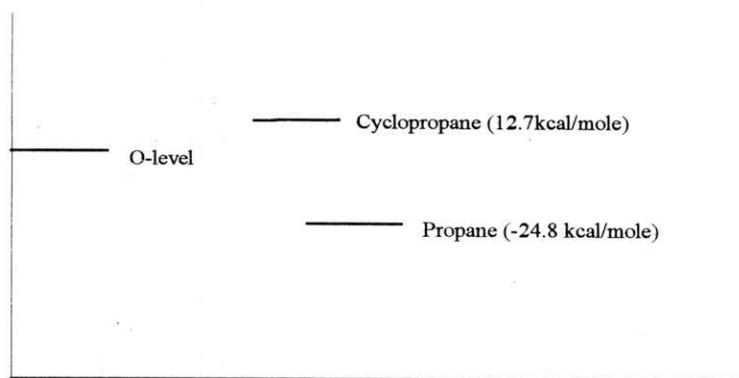
$$\text{The left term: } 12.7 + \frac{9}{2} \cdot 0 = 12.7$$

$$\text{The right term: } -3 \cdot 94.1 - 3 \cdot 68.4 + 499.8 = 12.3$$

The left and right term is "almost" in accordance. The difference depends on the fact that the figures comes from different sources and small deviations are always present. If the heats of formation of all combustion products are known, the heat of formation of a compound can be calculated. The "heat" value above is measured and out of that the heat of formation is obtained. Many thermochemical data have been obtained from heat of combustion. This is exactly what is exemplified above. However, the heat of formation value of cyclopropane is

positive and most comparable compounds have negative heats of formation. This means that cyclopropane has a smaller margin to the reference state and will consequently be more likely to decompose (fig. 3.5).

### Heat of formation



**Figure 3.5** *Heats of formation for cyclopropane and propane.*

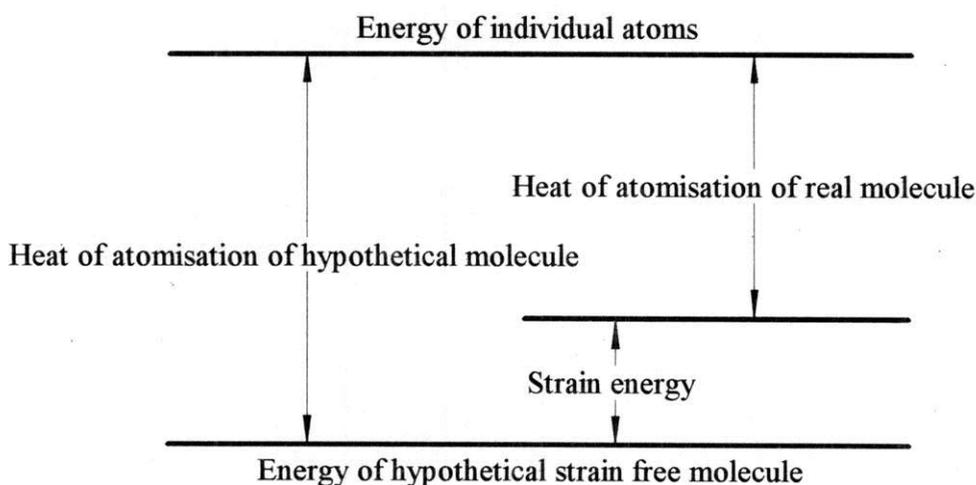
In fig. 3.5 the heats of formation for cyclopropane and propane are shown. The fact that cyclopropane has a higher value indicates that it is less stable. If a reaction takes place it is a "downhill" reaction which means that heat would be evolved.

Finally, as a conclusion of this section it could be stated that the value of the heat of formation is one measure of the stability. Namely, the higher value of heat of formation the compound has the less stable it is. In section 3.10 a comparison is made between some interesting compounds.

### 3.6 Strain

The discussions in the sections concerning strain are mainly based on reference 28. Strain exists in a molecule when bonds are forced to make abnormal angles. This results in higher energy than would be the case in the absence of angle distortions. There are, in general, two kinds of structural features that result in sterically caused abnormal bond angles. One of these is found in small-ring compounds, where the angles must be less than those resulting from normal orbital overlap. Such strain is called small-angle strain. The other arises when non-bonded atoms are forced into close proximity by the geometry of the molecule. These are called non-bonded interactions.

Strained molecules possess strain energy. This means that their potential energies are higher than they would be in the absence of strain. The strain energy could be estimated from heat of atomisation or heat of combustion data. A strained molecule has a lower heat of atomisation than it would have if it was free of strain (fig. 3.5).



**Figure 3.5** Strain energy calculation.

Strain energies can not be known exactly, because the energy of a real molecule can be measured, but not the energy of a hypothetical unstrained model. It is possible to calculate strain energies by molecular mechanics, not only for real molecules, but also for those that can not be made. Since this calculation is based on a simplified model, the result would not be exactly correct though.

### 3.7 Strain in Small Rings

Three-membered rings have a great deal of angle strain, since  $60^\circ$  angles represent a large departure from the tetrahedral angles ( $109.5^\circ$ ).



**Figure 3.6** Representation of angle distortion (a) and orbital overlap that leads to bent bonds and angle strain (b).

The compression of the internal bond is the so called angle-strain. Angle strain exists because the  $sp^3$  orbitals of the carbon atoms cannot overlap as effectively as they do in alkanes. The bonds of cyclopropane are often described as being *bent*<sup>16</sup>. The carbon-carbon bonds of cyclopropane are weaker, and as a result of that, the molecule has a higher potential energy. While angle strain accounts for most of the strain energy in cyclopropane, it does not account for it all, there is some torsional strain as well. From table 3.3 where ring strain values for some cycloalkanes are compared<sup>17</sup>, it can be concluded that cyclohexane is the most stable cycloalkane.

Cycloalkane	Ring strain (kcal/mole)
Cyclopropane	27.6
Cyclobutane	26.4
Cyclopentane	6.5
Cyclohexane	0
Cycloheptane	6.4

**Table 3.3** Ring strain of cycloalkanes.

Cyclopropane is cleaved more easily than would be expected for an alkane. Thus, thermal isomerisation converts it into propene at 406 to 492 °C. The same reaction can take place already at 310-400 °C in the presence of platina or asbestos<sup>35</sup>. Propene, which has the same formula as cyclopropane ( $C_3H_6$ ) but a different structure, is a non-cyclic molecule with one double-bond. From a refrigeration system point of view it would not be desirable that this reaction took place, since propene has a lower normal-boiling-point, namely  $-47.72^\circ C$ , compared to  $-32.9^\circ C$  for cyclopropane. If parts of the working agent would turn towards propene the pressure would most likely increase in the system which also could damage the system. A decomposition like this is less likely since the above mentioned temperatures are *normally* not reached in a refrigeration system.

### 3.8 Final Comparison of Some Compounds with Respect to Stability Data

In this section a comparison is made between the *former* refrigerant R12 and the *new* refrigerants propane, isobutane and cyclopropane. This is made in order to have some sort of reference for the stability data for cyclopropane. In table 3.4 a couple of interesting thermodynamic and chemical stability parameters are tabulated for the above mentioned compounds.

<u>Substance</u>	<u>R12</u>	<u>Cyclopropane</u>	<u>Propane</u>	<u>Isobutane</u>
<b>Molecular formula</b>	<b>CCl<sub>2</sub>F<sub>2</sub></b>	<b>C<sub>3</sub>H<sub>6</sub></b>	<b>C<sub>3</sub>H<sub>8</sub></b>	<b>CH(CH<sub>3</sub>)<sub>3</sub></b>
<b>Molecular weight (kg/kmol)</b>	<b>120.91</b>	<b>42.08</b>	<b>44.09</b>	<b>58.13</b>
<b>Normal boiling point (°C, 101.3 kPa)</b>	<b>-29.8</b>	<b>-32.9</b>	<b>-42.1</b>	<b>-11.7</b>
<b>Heat of formation (25°C, kcal/mole)</b>	<b>-114.0</b>	<b>12.7</b>	<b>-24.8</b>	<b>-31.5</b>
<b>Heat of combustion (25°C, kcal/mole)</b>	<b>–</b>	<b>499.8</b>	<b>530.6</b>	<b>686.3</b>
<b>Free energy of formation (25°C, kcal/mole)</b>	<b>-105.0</b>	<b>-5.3</b>	<b>-5.6</b>	<b>-4.3</b>
<b>Heat of fusion (cal./g)</b>	<b>–</b>	<b>30.9</b>	<b>19.1</b>	<b>18.7</b>

**Table 3.4** Comparison of R12, cyclopropane, propane and isobutane in terms of thermodynamical and chemical stability data.

The three first rows are more of general interest and especially the normal boiling point which will be treated further in the section "Thermodynamic properties". R12 is without competition the heaviest of the media while the others are comparable.

In the fourth row an interesting difference can be seen. There is actually a big difference in the heat of formation and if we recall what was mentioned in the previous section about potential energies and stability, it could be concluded that R12 seems to be extremely stable. This is hardly any news. That is, as a matter of fact, the reason why R12 was abolished. The more stable a medium is, the further up in the atmosphere it can go before it decomposes. If it furthermore is chlorinated, it will create a *mean* combination.

However, it can be seen that cyclopropane is the least stable compound of those compared here but it can hardly be concluded that it would be critical in some way. As mentioned in section 3.9, it does not start to decompose until the temperature reaches 400-500 °C which it rarely does in a refrigeration circuit. The latter is on the condition that the medium is pure and does not take into account any contamination of oil or metals for example.

As far as it concerns oil contamination and stability there are hardly any investigations found, at least not with cyclopropane. One reference was found where a stability test according to ASHRAE standard 97-1983 was performed with cyclopropane. This test calls for 14-day period in OP-oil at 175 °C and in the presence of metals. No decomposition was detected.

Since this is the only test found, further tests will be carried out during 1995. In these tests contamination of R12 will be added in order to see if that will influence the stability.

Heat of combustion is also worth to be looked at a little closer since it could be the case that cyclopropane was considerably more flammable than for instance propane or isobutane. R12 is not flammable at all, that is why the square in the heat of combustion row is empty for R12. However, let us take an example in order to compare cyclopropane with isobutane, since it is already used in refrigeration applications. Propane is also included since it is used as a reference in the other comparisons. Pretend that a refrigeration system contains 100 grams refrigerant, which corresponds to a number of moles according to:

$$n = \frac{m}{M}$$

where

- n is the number of moles
- m is the mass in the system (g)
- M is the mole mass (g/mole)

The mole mass according to table 3.4 is:

- |                  |              |
|------------------|--------------|
| 1. Isobutane:    | 58.13 g/mole |
| 2. Cyclopropane: | 42.08 g/mole |
| 3. Propane:      | 44.09 g/mole |

This gives the number of moles of the working media inside the system:

$$n_1 = \frac{m}{M_1} = \frac{100}{58.13} = 1.72$$

$$n_2 = \frac{m}{M_2} = \frac{100}{42.08} = 2.37$$

$$n_3 = \frac{m}{M_3} = \frac{100}{44.09} = 2.26$$

It is now possible to calculate the maximum energy evolved ( $Q_f$ ) if the total contents of refrigerant would be oxidised. The heat of combustion per mole *fuel* is also given in table 3.4.

- |                  |   |
|------------------|---|
| 1. Isobutane:    | $Q_{f1} = n_1 \cdot \Delta H_1 = 1.72 \cdot 686.3 = 1180.6 \text{ kcal (282.4 kJ)}$ |
| 2. Cyclopropane: | $Q_{f2} = n_2 \cdot \Delta H_2 = 2.37 \cdot 499.8 = 1187.7 \text{ kcal (284.1 kJ)}$ |
| 3. Propane       | $Q_{f3} = n_3 \cdot \Delta H_3 = 2.26 \cdot 530.6 = 1199.2 \text{ kcal (286.9 kJ)}$ |

This estimation is a little rough but gives at least the clue that there should not be a big difference in the flammability or the consequences of a *hypothetical* fire, since there is just a slight difference in the evolved energy. Hypothetical in this context means that if the entire quantity of refrigerant in the system is oxidised, this heat will be evolved. This scenario is less likely to happen, though, since parts of the refrigerant is solved in the oil. It is also very unlikely that the entire filling leaks out at once and creates a flammable mixture with the air.

## 4. THERMODYNAMICS

In this section some of the thermodynamical properties of the chosen media will be presented and compared. All properties are obtained from the refrigerant properties computer program, Refprop 4.0<sup>36</sup> and from different handbooks<sup>8,21</sup>. The discussion and the theoretical background in this section is mainly based on reference 37. Theoretical assessments are presented in diagrams in order to visualise the results. In the last section cycle studies based on a basic refrigeration cycle are carried out. The refrigeration cycle is adjusted, in terms of temperature levels, to simulate a household refrigerator/freezer application.

### 4.1 Properties

Some thermodynamical properties of the agents of interest are listed below (tab. 4.1). These are the most fundamental in order to choose a suitable working agent. The meaning and importance of the different properties will be further discussed in this section.

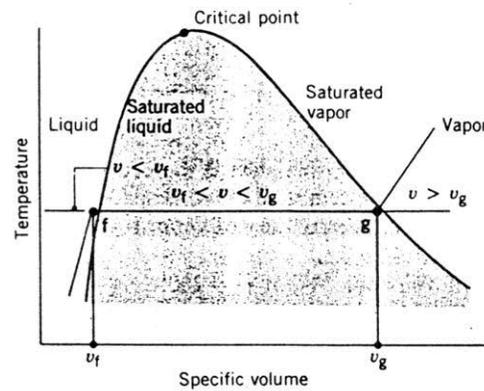
Refrigerant	R12	RC270	R134a	R600a	R290
Molecular Formula	CCl <sub>2</sub> F <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	CH(CH <sub>3</sub> ) <sub>3</sub>	C <sub>3</sub> H <sub>8</sub>
Molecular Weight (g)	120.91	42.08	120.0	58.13	44.09
*Normal Boiling Point (°C)	-29.8	-32.9	-26.5	-11.7	-42.1
Critical Pressure (bar)	41.1	55.4	40.7	36.5	42.5
Critical Temperature (°C)	112.0	124.8	101.2	135.0	96.8
*Latent Heat of Vaporisation (kJ/kg)	165.4	475.2	216.8	366.2	425.6

\*Atmospheric pressure (101.3 kPa)

**Table 4.1** The fundamental thermodynamical properties.

The normal boiling point (n.b.p.) is of great interest. This is the temperature at which the agent starts to boil at atmospheric pressure. This characteristic determines the pressure in the different parts of the system. If an agent has a low n.b.p. it will result in high pressures at high temperatures and the other way around. High n.b.p. could consequently cause system pressures below the atmospheric pressure at low temperatures which is not desirable. This is the case with isobutane when it is used in freezer applications. Pressures below the atmospheric pressure could cause air leakage into the system, which may lead to severe damage and extensive service need.

The critical pressure and temperature determines the so called *critical point* of the agent. Temperatures above the critical temperature are not possible in a refrigerating system of this type. Above this point the two phase area does not exist anymore, consequently no evaporation or condensation is possible see fig. 4.1.



**Figure 4.1** An example of a temperature-specific volume diagram.

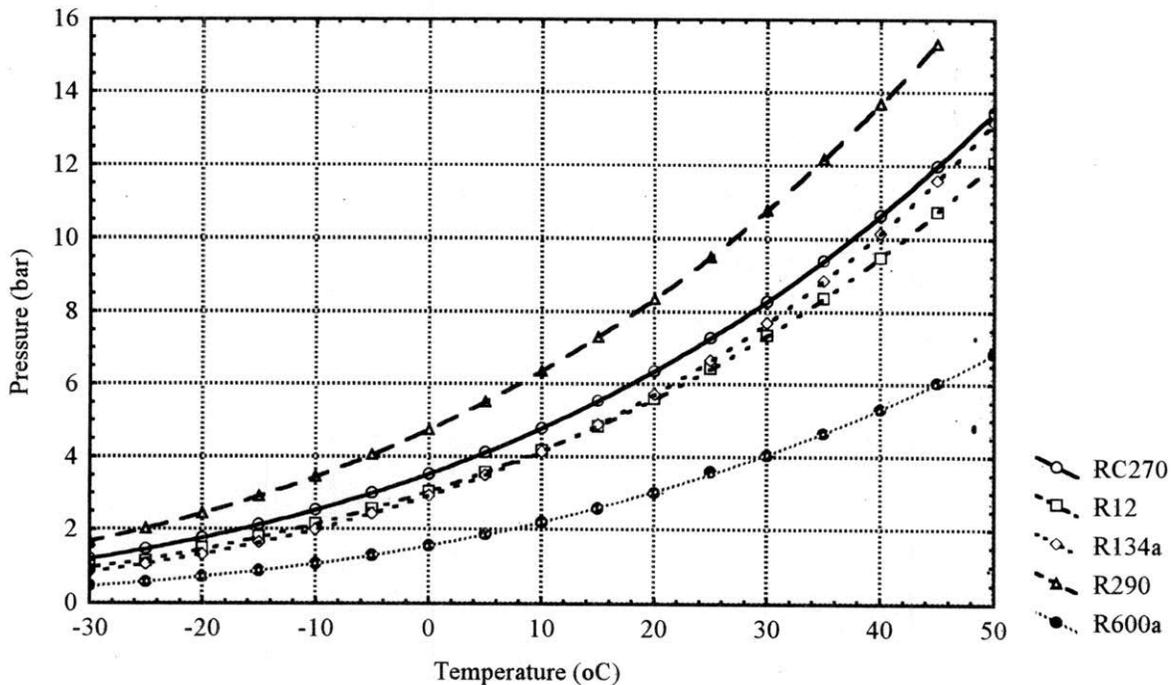
The latent heat of vaporisation is the difference in enthalpy between the saturated liquid and saturated vapour line at the prevailing pressure. This determines the maximum available heat of condensation or evaporation per kg agent at a certain pressure/temperature.

In order to carry out the theoretical assessments some basic operating conditions had to be chosen. Based on experiences from prevailing system conditions in a commercial refrigerator/freezer the temperature and pressure ranges were chosen in order to simulate these conditions as close as possible. The conditions were obtained with ambient air temperature 25 °C and a refrigerator temperature of about 5 °C. The freezer temperature was about -18 °C, where this is the temperature of the warmest piece of goods in the freezer. These temperatures are chosen in order to follow the iso-standard ISO/DIS 8561, which is one of the common standards for tests of refrigerator/freezers.

Due to the transient operation conditions in this kind of applications, it is hard to tell the exact evaporation or condensation temperature. The chosen temperatures are in the same range as the prevailing ones and they are based on the average values during the compressor operating period. However, the condensing temperature was approximately 40 °C and the evaporating temperatures for the refrigerator and freezer were -15 °C and -28 °C respectively. The subcooling was 2-4 °C and the superheat around 30 °C.

These kind of systems are equipped with a suction gas heat exchanger where the capillary tube is placed inside or attached to the suction tube. This is not taken into consideration in this study but it should not influence the general conclusions of the results to any wider extent.

The first parameter to be showed is the saturation pressure of the media at different temperatures (fig. 4.2).

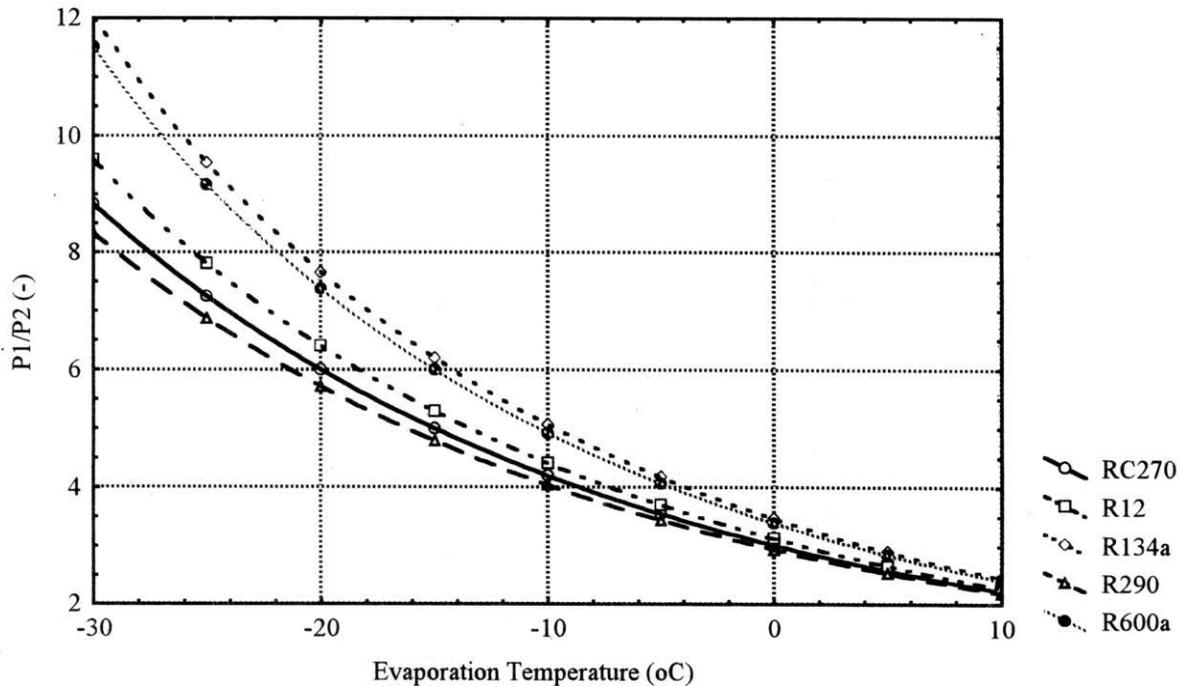


**Figure 4.2** Saturation pressure at different temperatures.

The saturation pressure shows the pressure that would exist at a certain temperature in the system. From figure 4.2 it can be seen that isobutane gives the lowest system pressure due to its, in this comparison, high normal boiling point. Consequently propane has the highest pressures due to its relatively low normal boiling point. The conclusion from this is that propane would not be convenient in high temperature applications. As far as it concerns isobutane it is less convenient in low temperature applications, where the low pressures will cause high specific volume. High specific volumes of the working agent demands compressors with big swept volume, which increases the dimensions and the weight.

However, as expected the curves of R12 and R134a are quite similar which is the reason that R134a became the predominant successor and substitute of R12. The most interesting result is of course that RC270 follows the above mentioned agents very close. RC270 diverges slightly more from R12 at higher pressures. The pressure difference at 40 °C corresponds to an increase in pressure of 12% compared to R12 and 4.8% to R134a. Neither of these pressure increases should be considered as critical if RC270 was used as a drop-in substitute.

An other important factor when it comes to the pressures is the ratio between the evaporating and condensing pressure. The energy demand of the compressor is very dependent on this ratio. The lower pressure ratio an agent has between evaporating and condensing pressure, the better it is. In fig. 4.3 this relation is represented at the fixed condensing temperature 40 °C and varying evaporation temperatures.



**Figure 4.3** The ratio between condensing and evaporating pressures with fixed condensing temperature 40°C.

In order to illustrate the influence of the pressure ratio on the compressor energy demand, it could be mentioned that the theoretical energy demand per m<sup>3</sup> refrigerant ( $\epsilon_v$ ) is given by the expression:

$$\epsilon_v = \frac{\kappa}{\kappa - 1} p_2 \left[ \left( \frac{p_1}{p_2} \right)^{(\kappa-1)/\kappa} - 1 \right]$$

where  $\kappa$  is the specific heat ratio  $c_p/c_v$ .

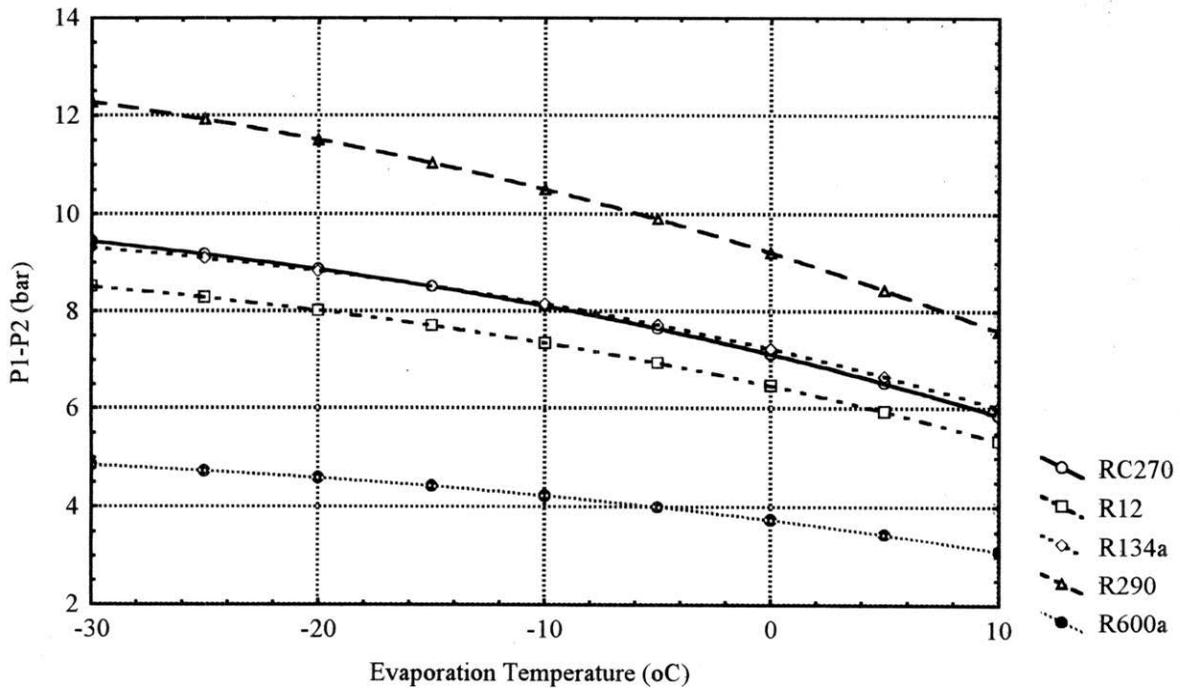
The theoretical volumetric efficiency ( $\eta_{s,theo.}$ ) of the compressor is also affected by the pressure ratio:

$$\eta_{s,theo} = 1 - \frac{V_0}{V_s} \left[ \left( \frac{p_1}{p_2} \right)^{1/\kappa} - 1 \right]$$

where  $V_0$  and  $V_s$  are volumes given by the compressor design.

However, from fig. 4.3 it could be established that except for propane, RC270 is the agent with the lowest pressure ratio. The difference seems to increase, in favour of RC270, the lower the evaporation temperature is compared to the other agents. A property like that should make RC270 even more profitable in freezer applications compared to the other agents.

A second way to compare these media, in terms of pressures, is to look at the differences in pressures between, once again, condensing pressure at 40 °C and different evaporation temperatures.



**Figure 4.4** Pressure difference with constant condensing pressure (40 °C) vs. evaporation temperature.

Once again it can be seen that RC270 has properties very similar to those of R12 and R134a. Propane which has the highest pressure level within this interval, also receives the greatest, in absolute terms, pressure difference.

## 4.2 Volumetric Cooling Capacity and Energy Demand

The so called volumetric cooling capacity is a measure of the cooling capacity per volume unit refrigerant transported in the system. This property is of great interest since it governs the expected cooling capacity in a system which is converted from one refrigerant to another. The capacity is possible to predict since the compressor has a given volumetric flow and consequently the capacity will be governed by the properties of the refrigerant. The factors with the major influence of the volumetric cooling capacity is the heat of vaporisation and the specific volume at the suction point in the system. The specific volume is governed by the evaporating pressure and the degree of superheat. The expression looks like:

$$q_v = \frac{h_{2k} - h_s}{v_{2k}}$$

Where

- $q_v$  is the volumetric cooling capacity ( $\text{kJ}/\text{m}^3$ )
- $h_{2k}$  is the enthalpy at the suction point ( $\text{kJ}/\text{kg}$ )
- $h_s$  is the enthalpy at the evaporator inlet ( $\text{kJ}/\text{kg}$ )
- $v_{2k}$  is the specific volume at the suction point ( $\text{m}^3/\text{kg}$ )

The basic refrigerating cycle can be seen in fig. 4.5 where the properties of interest can be found in order calculate the volumetric cooling capacity. As mentioned, all properties used in this study are obtained from Refprop<sup>36</sup>.

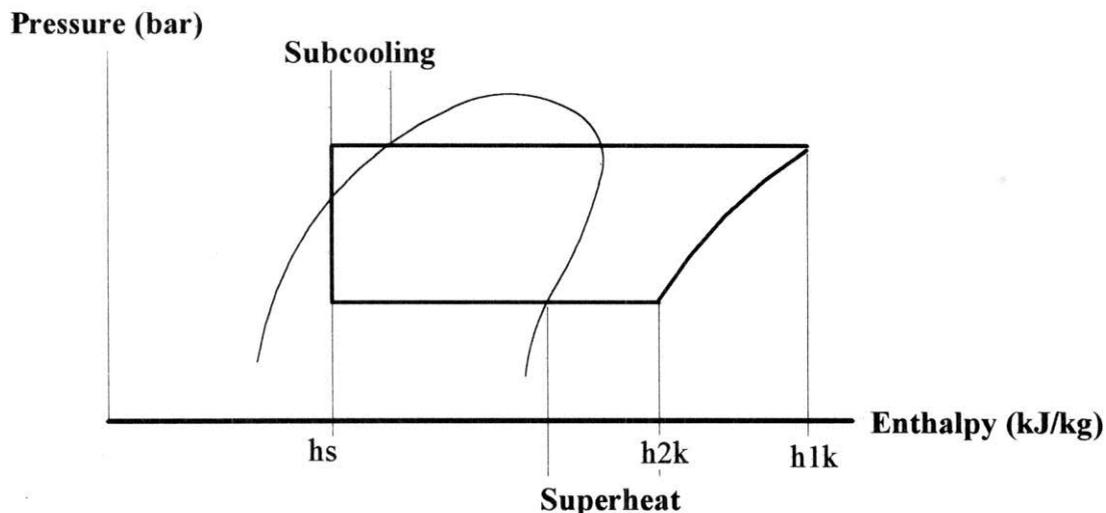


Figure 4.5 The basic refrigeration cycle.

In fig. 4.6, the volumetric cooling capacity is displayed versus the evaporation temperature for the five chosen media. The assumptions related to the refrigerating cycle are that the condensing temperature is  $40^\circ\text{C}$ , the subcooling is  $0^\circ\text{C}$  and the superheat is  $30^\circ\text{C}$ . In order to establish the point  $h_{1k}$  the total isentropic efficiency was chosen to 65%. These assumptions unequivocally gives the required properties necessary to calculate the volumetric cooling capacity.

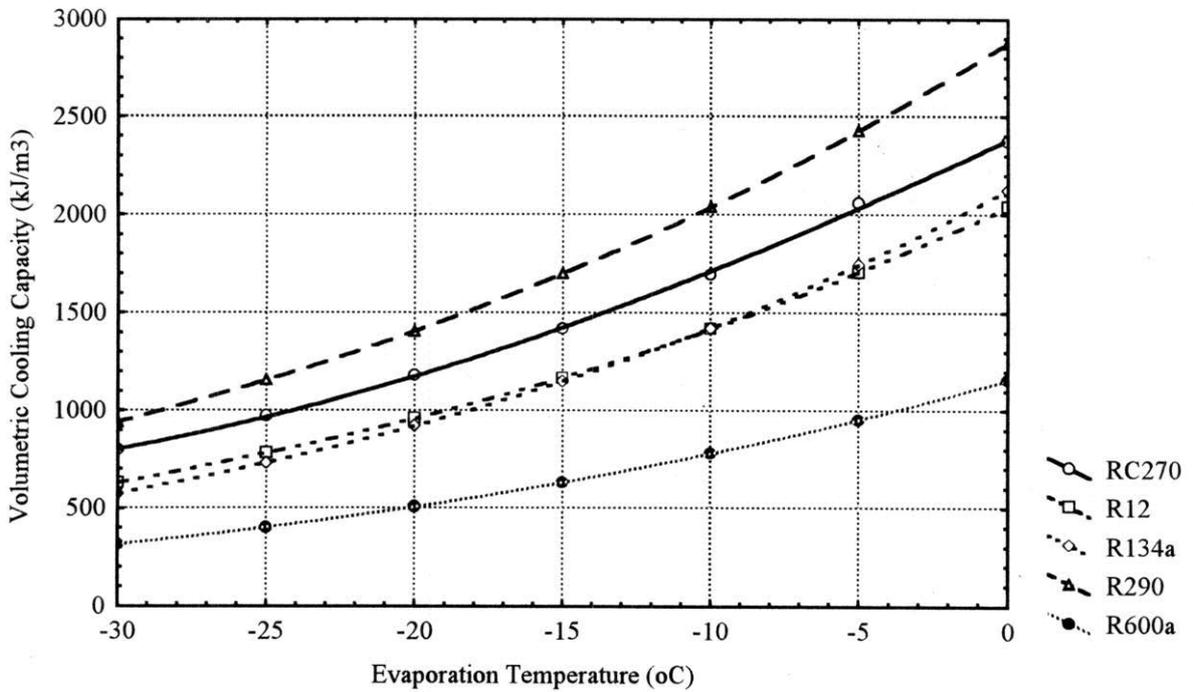


Figure 4.7 Volumetric cooling capacity vs. evaporation temperature.

In order to visualise the differences better, the volumetric cooling capacity of the different media are displayed relatively R12 in fig. 4.8.

$$\text{Volumetric cooling capacity relatively R12} = \frac{q_v}{q_{v,R12}} (-)$$

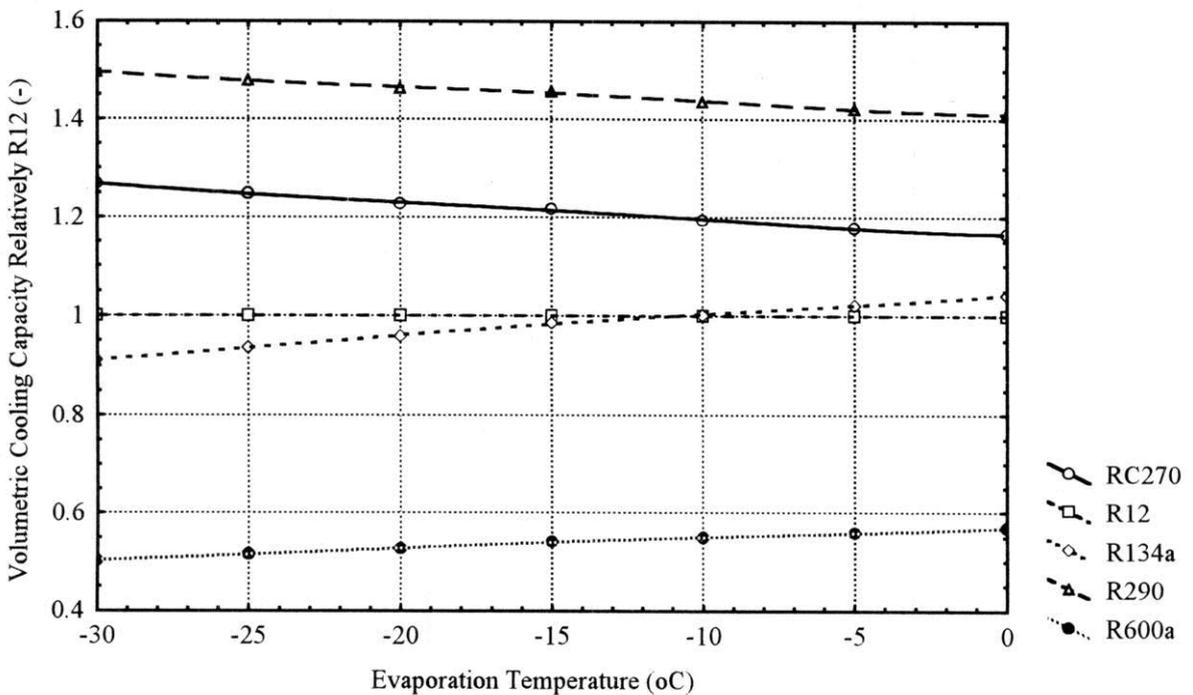
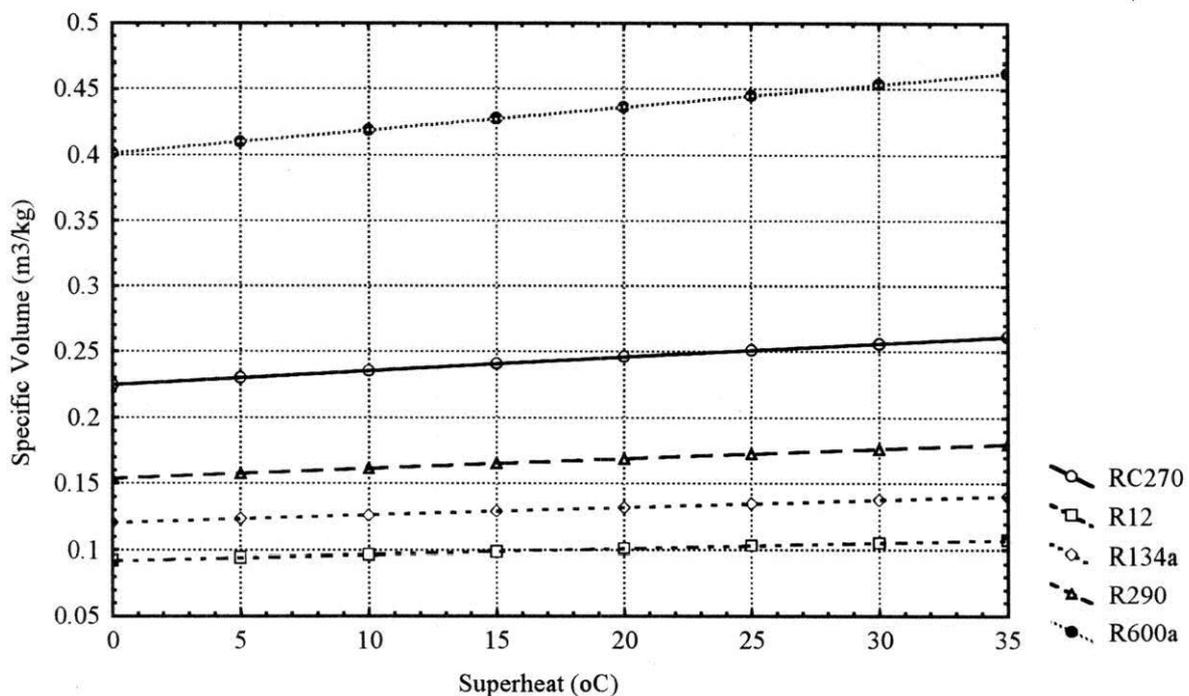


Figure 4.8 Volumetric cooling capacity relatively R12.

In fig. 4.8 it can be seen that cyclopropane has a considerably higher volumetric cooling capacity, compared to R12 and R134a, over the entire evaporation temperature range. At the "normal" operating point for a refrigerator (-15°C) the increase corresponds to approximately 20%, and as the evaporating temperature decreases the difference only increases. The consequences from this fact is that if a given refrigerating system is converted from R12 to RC270, the relative compressor running time would be shorter. This is due to the fact that RC270 would give increased cooling capacity and thereby reduce the necessary running time.

The relative running time is a matter of optimisation, but it is without the scope of this investigation. If the relative running time is perfectly optimised today, a conversion to RC270 would actually detoriate the energy consumption. The relative running time is only one of several factors that have influence on the energy consumption, though.

As earlier mentioned, the specific volume at the suction point is a very important factor when it comes to the volumetric cooling capacity. The specific volume is mainly influenced by two factors. Those two are the suction pressure and the superheat where the latter governs the actual temperature. In fig. 4.9 the specific volume for the media is shown. If the ideal gas equation of state was completely valid, the inclination of the lines should be a straight lines. This is not the case but it can still be used as an approximation, which gives a clue of the differences in inclination of the lines.



**Figure 4.9** *The specific volume vs. superheat.*

According to the ideal gas equation of state, the inclination will be governed by the ideal gas constant and the pressure:

$$pv = RT$$

Where

- $p$  is the pressure (kPa)
- $R$  is the ideal gas constant (kJ/kg·K)
- $T$  is the temperature (K)

$R$  depends on the molecule weight according to:

$$R = \frac{\bar{R}}{M}$$

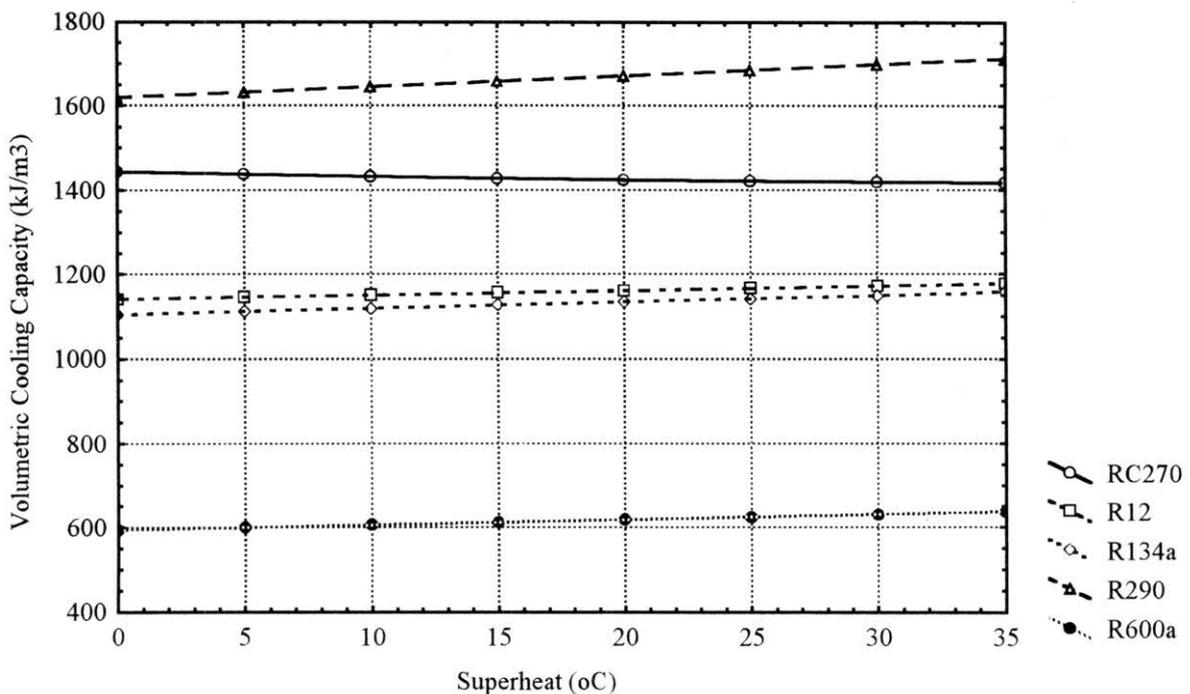
Where

- $\bar{R}$  is the ideal gas constant per mole = 8.314 kJ/kmole·K
- $M$  is the molecule weight of the media (kg/kmole)

If the expression for the ideal gas equation of state is remodelled, this expression is obtained:

$$v = \frac{\bar{R}}{pM} T$$

where it can be seen that the expression describes a straight line if the temperature is the only variable. The media dependent characteristics, pressure (at the desired temperature) and  $M$ , will govern the inclination of the line. However, the more the specific volume increases the less favourable it is, since it will decrease the refrigerant mass circulated by the compressor. The compressor can just produce a given volume flow. At the same time the enthalpy difference on the cold side increases with the superheat. For some media the increase in the enthalpy difference compensates the increased specific volume. This is the reason why the volumetric cooling capacity is intact even with a considerably high superheat (fig. 4.10).



**Figure 4.10** Volumetric cooling capacity vs. superheat.

From fig. 4.10 it can be established that RC270 does not take favour from high superheat, it should rather be used with as low superheat as possible.

The other factor of interest treated in this section is the so called volumetric energy demand  $\varepsilon_v$ , which similarly to the volumetric cooling capacity can be calculated with properties obtained from fig. 4.5.

$$\varepsilon_v = \frac{h_{1k} - h_{2k}}{v_{2k}} = \frac{1}{\eta_{is}} \cdot \frac{h_{1k, is} - h_{2k}}{v_{2k}}$$

Where

- $\varepsilon_v$  is the volumetric energy demand (kJ/m<sup>3</sup>)
- $h_{2k}$  is the enthalpy at the suction point (kJ/kg)
- $h_{1k}$  is the enthalpy at the compressor outlet (kJ/kg)
- $h_{1k, is}$  is the enthalpy at the compressor outlet, if isentropic compression was prevailing (kJ/kg)
- $v_{2k}$  is the specific volume at the suction point (m<sup>3</sup>/kg)
- $\eta_{is}$  is the isentropic efficiency (see next section)

The relations between the different refrigerants are very similar to those of the comparison of the volumetric cooling capacity. The only difference is the shape of the curves.

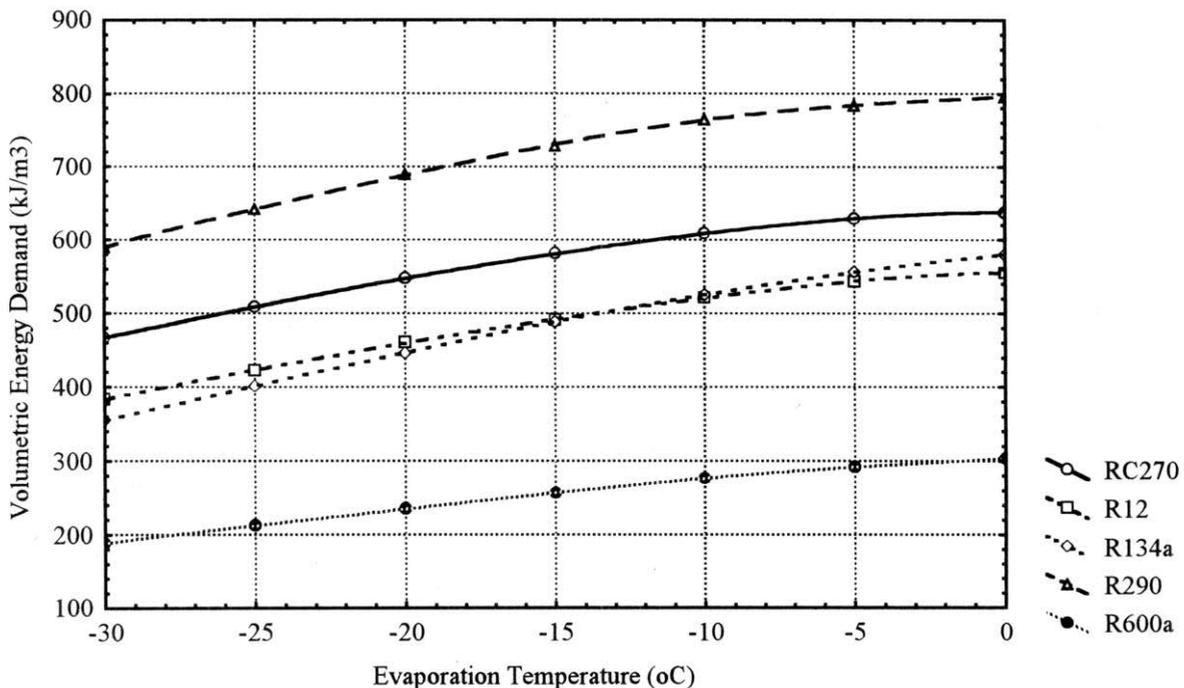


Figure 4.11 Volumetric energy demand vs. evaporation temperature.

Also for this case an evaluation of the influence of the superheat was made. The result showed that only small differences, or non at all, could be detected over the entire range of superheat.

### 4.3 Discharge Temperature

The discharge temperature is of great interest, since it is the warmest temperature in the system and that might be critical. If the temperature is above 120°C, which normally is considered as critical, a considerable risk for damage of the compressor valves exists. The damage is normally related to the thermal destruction of the lubricating oil which can form coke on the valves. The discharge temperature is found as the temperature on the isobar where the condensing pressure is equal to the desired 40°C. The second parameter which is necessary to know in order to establish the point is the enthalpy after the compressor ( $h_{1k}$ ).

With the assumptions made in the previous section, the point  $h_{1k}$  (fig. 4.5), can be established. One parameter which has to be assumed is the total isentropic efficiency ( $\eta_{is}$ ), which is a measure of how much the compression diverges from the theoretically ideal isentropic compression. It is calculated from the expression:

$$\eta_{is} = \frac{h_{1k, is} - h_{2k}}{h_{1k} - h_{2k}}$$

where

- $\eta_{is}$  is the total isentropic efficiency (-)
- $h_{1k}$  is the enthalpy at the discharge (kJ/kg)
- $h_{2k}$  is the enthalpy at the suction point (kJ/kg)
- $h_{1k, is}$  is the enthalpy at the discharge with isentropic compression (kJ/kg)

The efficiency was assumed to be 65%, which is the efficiency of a "good" reciprocating compressor. In this case the figure 65% was probably a little "optimistic", since compressors in this type applications seldom are that good. However, it will still give a clue about what the enthalpy will turn out to be.

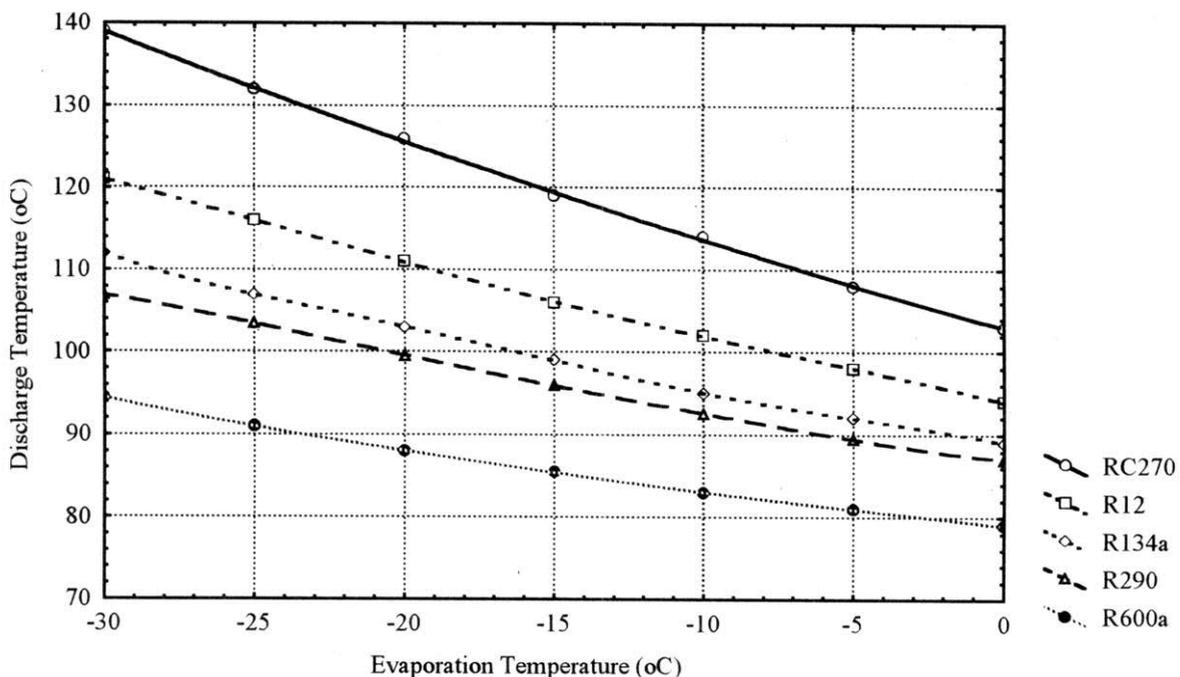


Figure 4.12 Discharge temperature vs. evaporation temperature.

As could be seen in fig. 4.12 there exists a major problem with cyclopropane. The discharge temperature is close to 140°C at the lowest evaporating temperatures. This is far above what is considered as critical. On the other hand one must not forget that this is calculated for a superheat of 30°C, which is "high". Every degree that can be cut on the superheat will decrease the discharge temperature with approximately the same number of degrees. If the superheat is brought down to the "normal" range of 5-10°C, the discharge temperature would come down to 115-120°C, which is more reasonable. In order to obtain this, the design with heat exchange in the suction line must probably be given up. An other option is to use compressors with higher isentropic efficiency, which also brings down the discharge temperatures. If there are other types of oils on the market which are more resistant to formation of coke it could also be a good option to use.

It should be emphasised, though, that these results must first be experimentally validated. There are still too big uncertainties in these results since no experimental data have been found on cyclopropane.

#### 4.4 Coefficient Of Performance

In this section the cycle studies are focused on the comparison of the Coefficient Of Performance (COP). The COP in this case is related to the evaporator side, since the entity of interest in this study is the refrigeration capacity, and thereby the index 2 is connected to the COP (COP<sub>2</sub>). Index 2 is normally used to indicate that the entity is referred to the cold side.

The COP<sub>2</sub> is based on the assumptions made in section 4.1 which could be recalled as:

- condensing temperature: 40°C
- evaporation temperature: -15°C
- superheat: 30°C
- subcooling: 0°C
- total isentropic efficiency: 65%

The evaporation temperature, the superheat and the subcooling will be varied in order to estimate its influence on the COP<sub>2</sub>. The COP<sub>2</sub> is based on the refrigerant diagram sketched in fig. 4.13, where it is defined as the relation between the refrigerating capacity ( $Q_2$ ) and the energy demand of the compressor ( $E_k$ ):

$$\text{COP}_2 = \frac{Q_2}{E_k} = \frac{h_{2k} - h_s}{h_{1k} - h_{2k}}$$

where

- $h_{2k}$  is the enthalpy at the suction point (kJ/kg)
- $h_s$  is the enthalpy at the evaporator inlet (kJ/kg)
- $h_{1k}$  is the enthalpy at the discharge point (kJ/kg)

Pressure (bar)

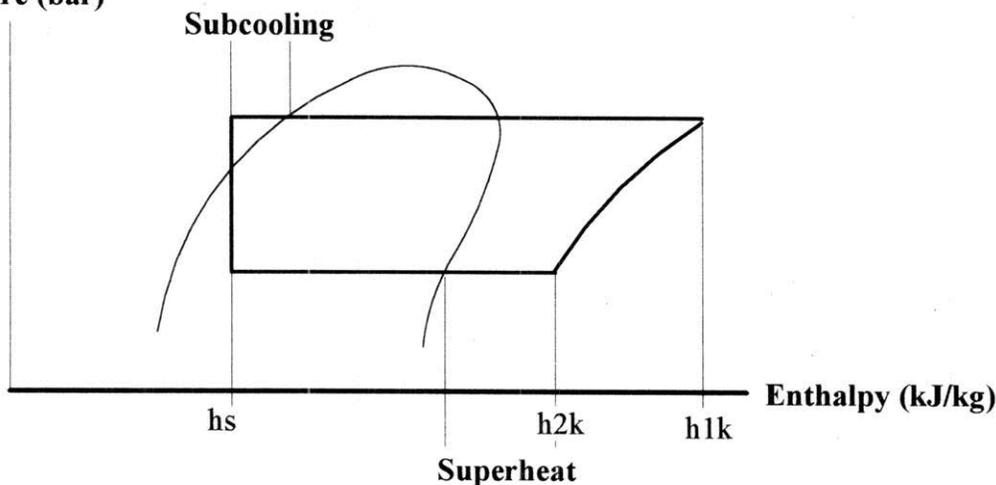


Figure 4.13 Sketched refrigerant diagram.

In the first diagram (fig. 4.14) the evaporation temperature is varied with other conditions fixed in accordance to what was mentioned above.

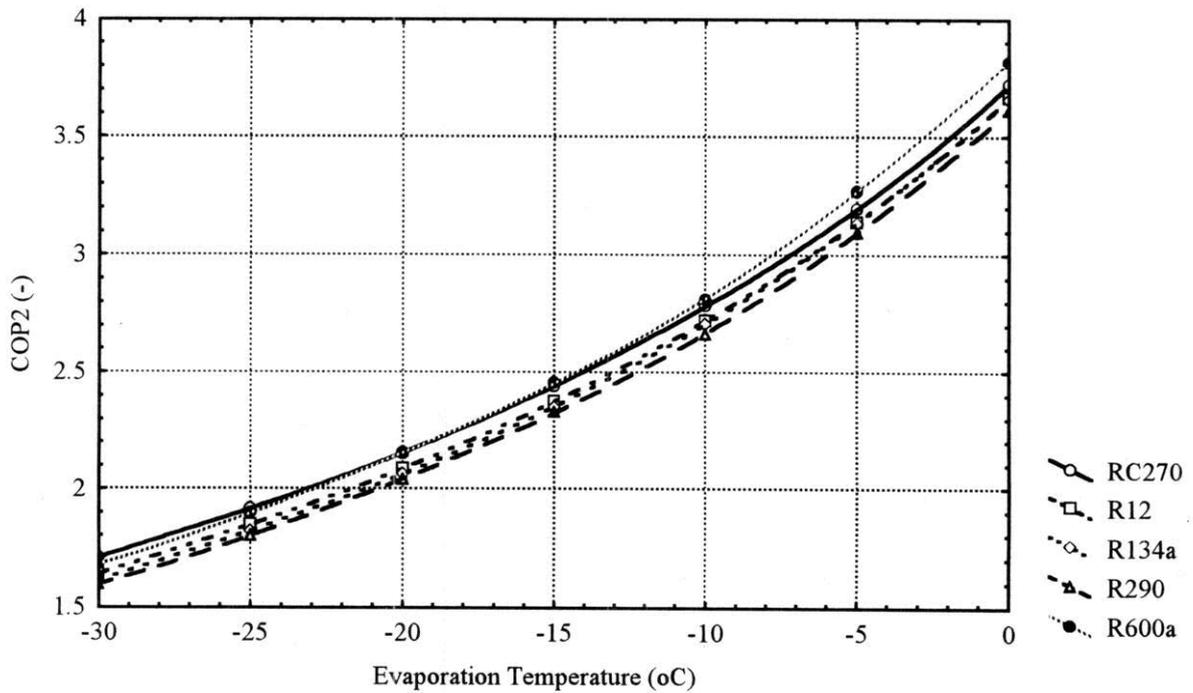


Figure 4.14 COP2 vs. evaporation temperature.

From this diagram it is hard to tell something about the results since the differences between the media are quite small. In the next figure the COP2 is shown relative to R12 in accordance to what was made with the volumetric cooling capacity in section 4.2.

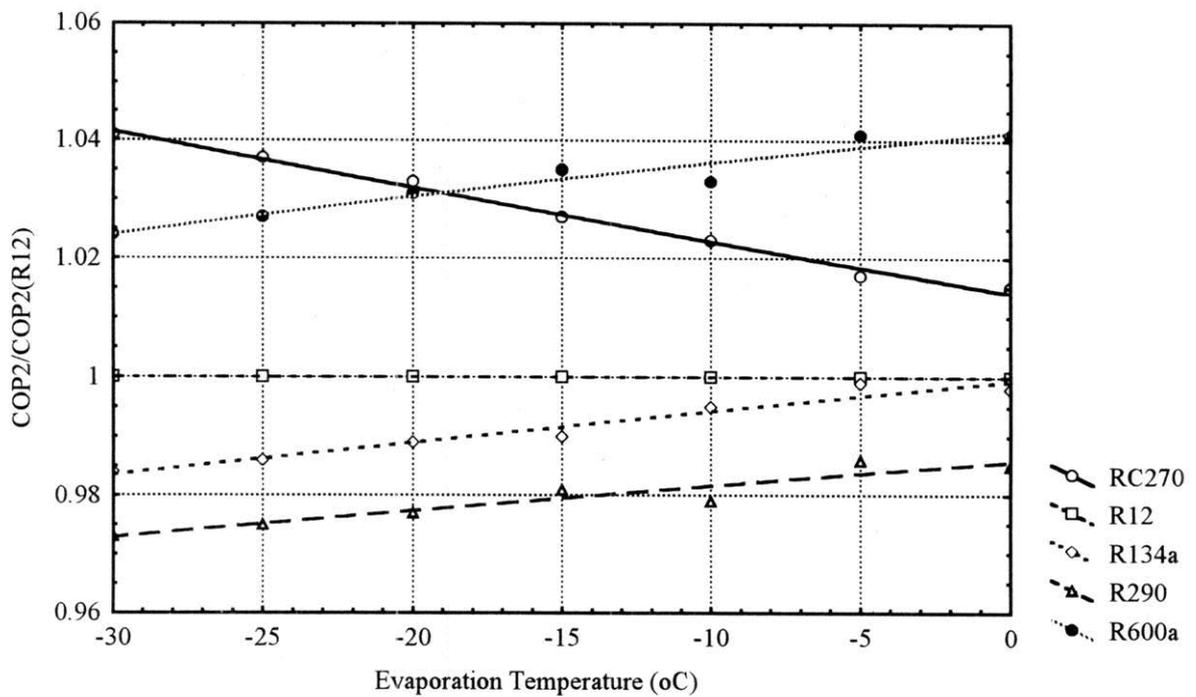


Figure 4.15 COP2 relatively R12 vs. evaporation temperature.

From fig. 4.15 it can be seen that RC270 seems to be most favourable media at low

evaporation temperatures of the other refrigerants in this investigation. With a quick look the differences may look dramatic. A closer look at the scale reveals that compared to R12, RC270 is approximately 4.2% more effective at the lowest evaporation temperature. The higher the evaporation temperature gets the less favourable RC270 is compared to R12. Still the efficiency at 0°C evaporation temperature is higher than R12 by approximately 1.5%.

The second parameter to be varied is the superheat. As could be seen in section 4.3, it would be desirable to keep the superheat as low as possible due to high discharge temperatures. In fig. 4.16 the influence of the superheat on the COP2 can be seen.

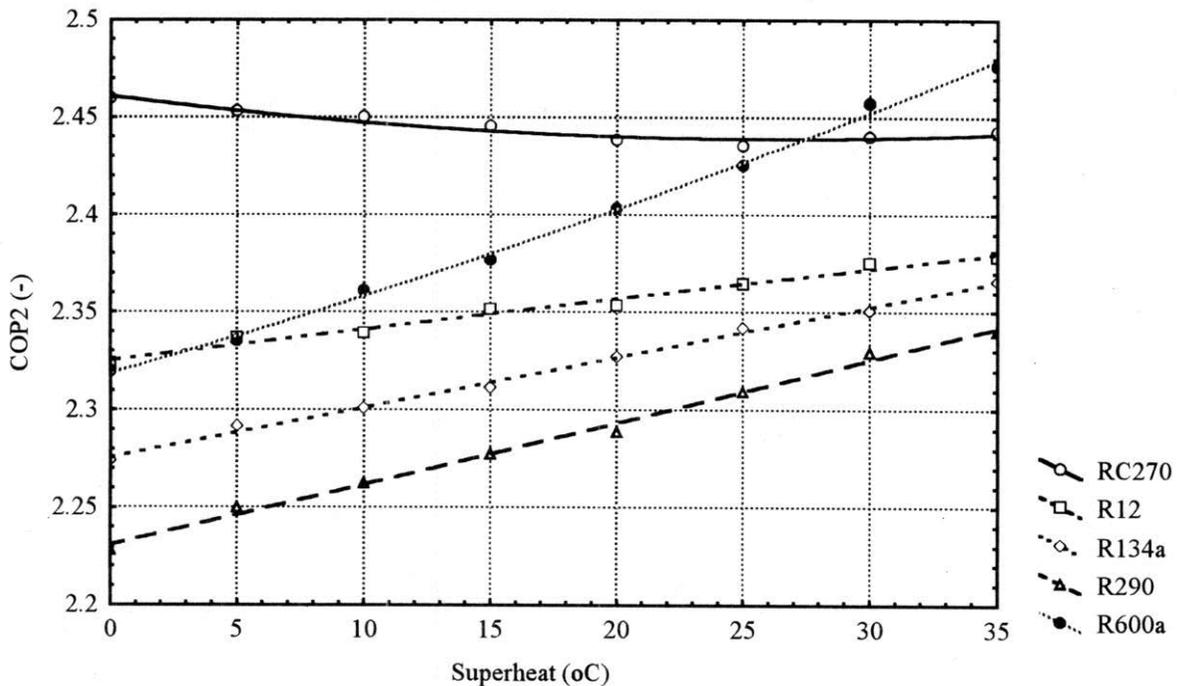


Figure 4.15 COP2 vs. superheat.

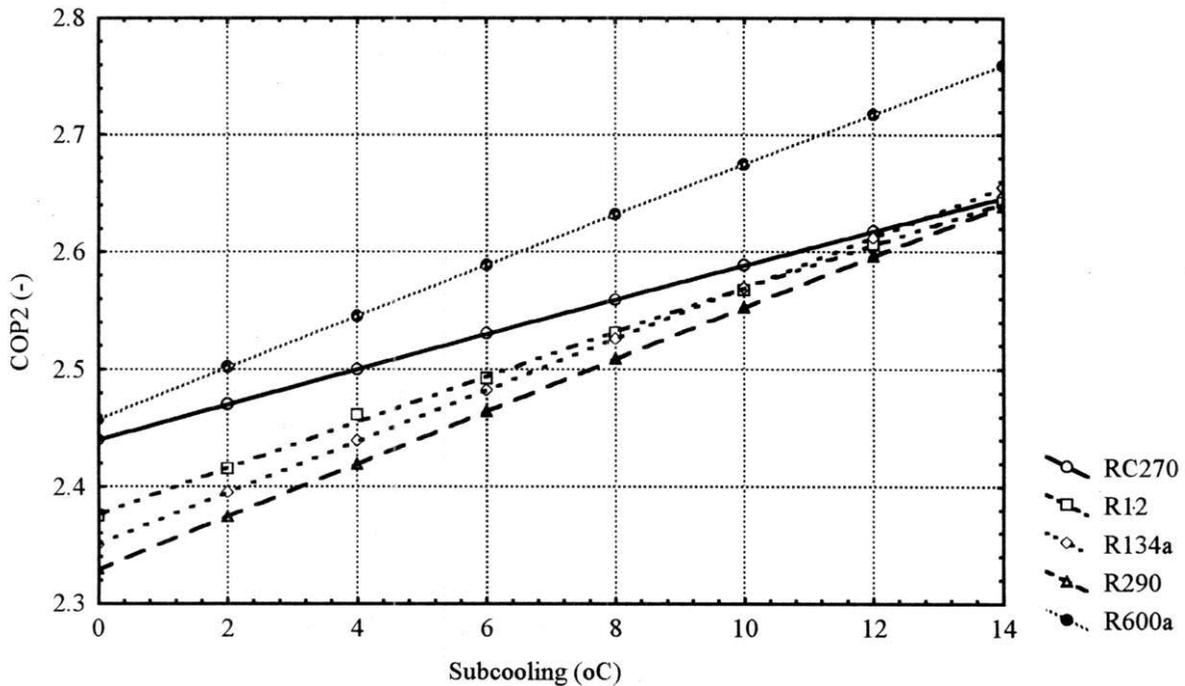
There is a major difference in behaviour between RC270 and the other media. With the other four, an increased superheat leads to an increased COP2. With RC270 the COP2 decreases slightly the higher the superheat gets.

In this simplified model for the COP2, it is assumed that the entire superheat comes to use in the evaporator. This is not the case in most "real" applications, since a superheat of about 30°C would take a considerable temperature difference in the evaporator. This is mentioned in order not to give the impression that the higher the superheat gets, the better the COP2 will be. It is more important to bring down the temperature differences in order to minimise the ratio  $p_1/p_2$ . If the superheat in the evaporator is brought down, a greater part of it can be used for evaporation. This will increase the evaporation temperature and consequently the ratio  $p_1/p_2$  will decrease.

It has to be emphasised that this model is based on the actual prevailing conditions where the suction gas is used for heat exchange with the capillary tube and as coolant for the compressor motor. However, these two ways to heat the gas are quite complex to analyse and to take in to consideration in a cycle study like this.

The conclusion of the results in fig. 4.15 is, once again, that high superheat should be avoided with RC270.

The last factor to be investigated is the influence of subcooling on the COP<sub>2</sub>. Generally subcooling has a favourable influence on the COP<sub>2</sub>. Here it will just be concluded whether there are any differences in the positive influence.



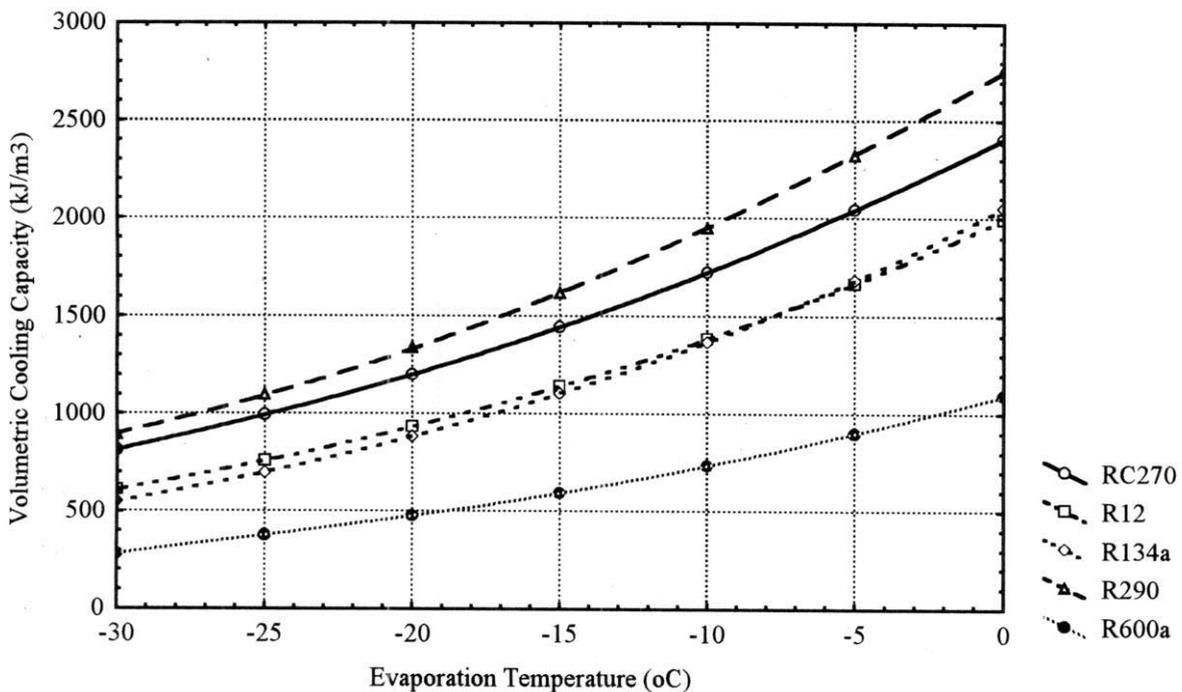
**Figure 4.15** COP<sub>2</sub> vs. subcooling.

As expected all media show positive influence of subcooling. RC270 shows a little less positive influence from subcooling, since its inclination in the diagram is less than for the other media.

#### 4.5 Evaluation of Low Superheat Conditions

As have been concluded in the previous sections, high superheat is a problem with cyclopropane. Therefore it would be interesting to see how much influence low superheat actually has. In this section the superheat therefore is set to 0°C. The condensing temperature is as before 40°C, the subcooling is 0°C and the isentropic efficiency is 65%.

The evaluation in this section will not be as fundamental as it was in the previous ones, since the scope of that is assumed to be known now. This is only a comparison with the previous sections. When it comes to definitions, the reader is referred to the corresponding discussions in the previous sections. However, first the volumetric cooling capacity is evaluated when the superheat is assumed to be 0°C.



**Figure 4.16** Volumetric cooling capacity vs. evaporation temperature.

The general pattern is the same as it was in fig. 4.7 where the volumetric cooling capacity is displayed with 30°C superheat. The difference that can be seen is that cyclopropane has taken a considerable "step up". This is partly explained by the greater increase of the specific volume for cyclopropane when the superheat is increased. The definition of the volumetric cooling capacity ( $q_v$ ) is recalled as:

$$q_v = \frac{h_{2k} - h_s}{v_{2k}}$$

The expression above shows that if the specific volume increases, the value of the expression will decrease. In the case of cyclopropane the increase in specific volume is relatively higher than the increase in the enthalpy difference when the superheat is brought up. However, the

volumetric cooling capacity is also calculated relatively R12 (fig. 4.17).

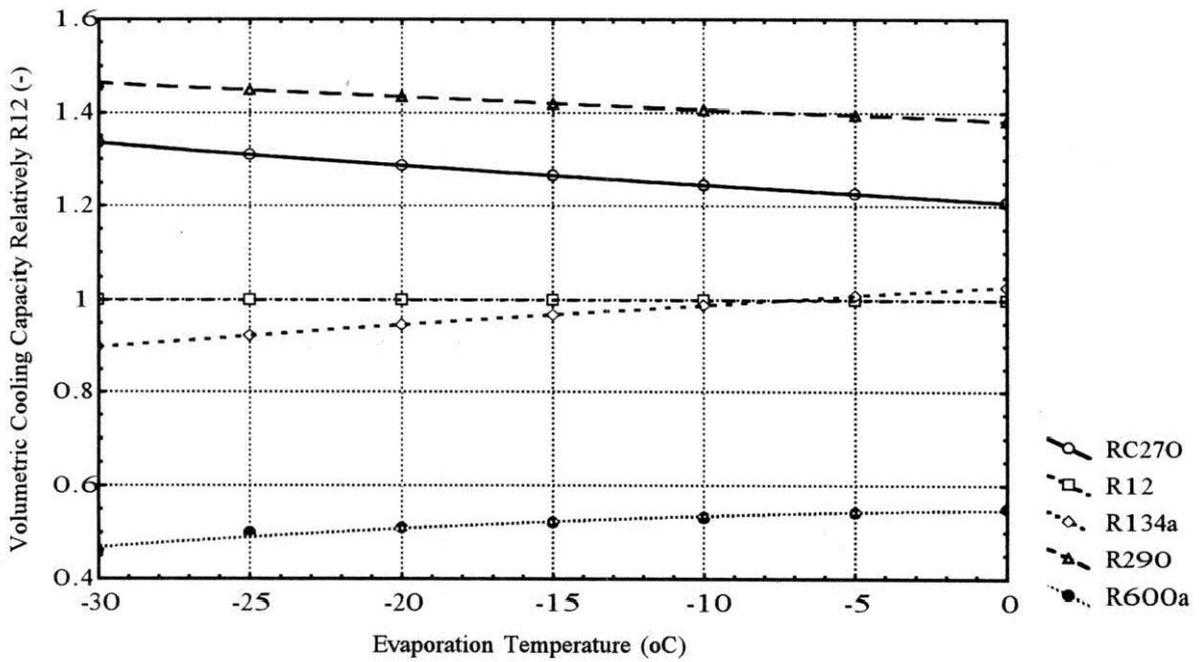


Figure 4.17 Volumetric cooling capacity relatively R12.

Compared to the results in fig. 4.8 it can be concluded that cyclopropane gained some volumetric cooling capacity and propane lost some on the lowered superheat. The rest look about the same.

The next interesting parameter is the coefficient of performance, which is defined according to section 4.4 but with the superheat set to 0°C.

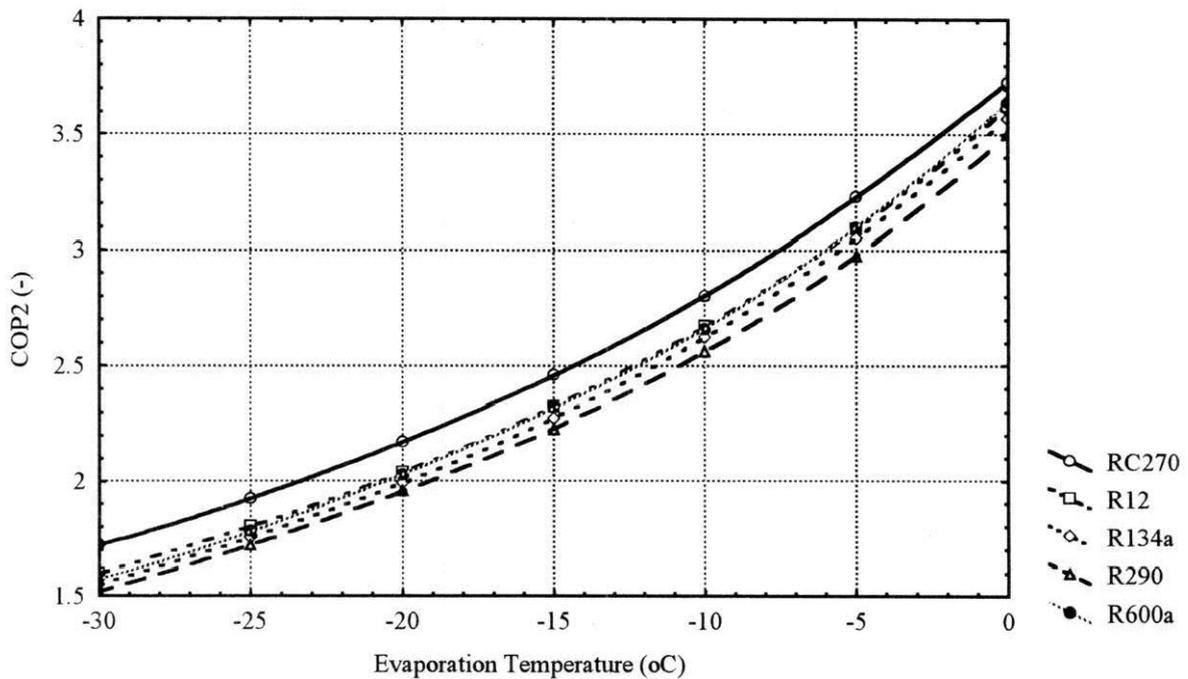
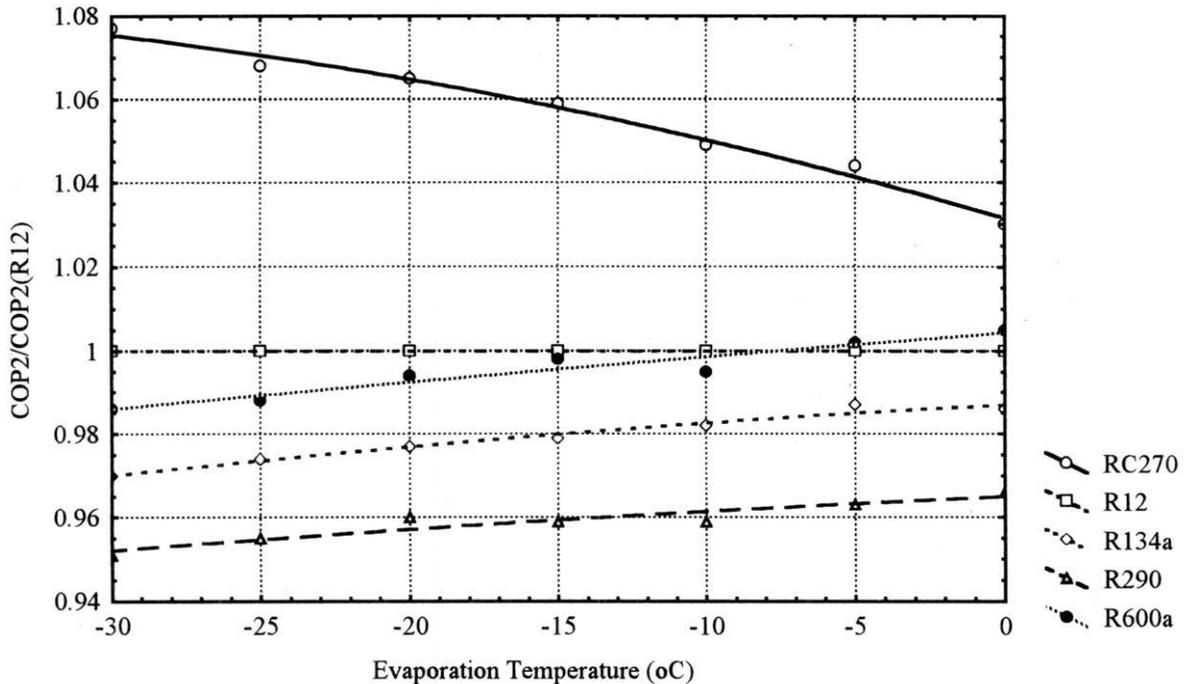


Figure 4.18 COP2 vs. evaporation temperature.

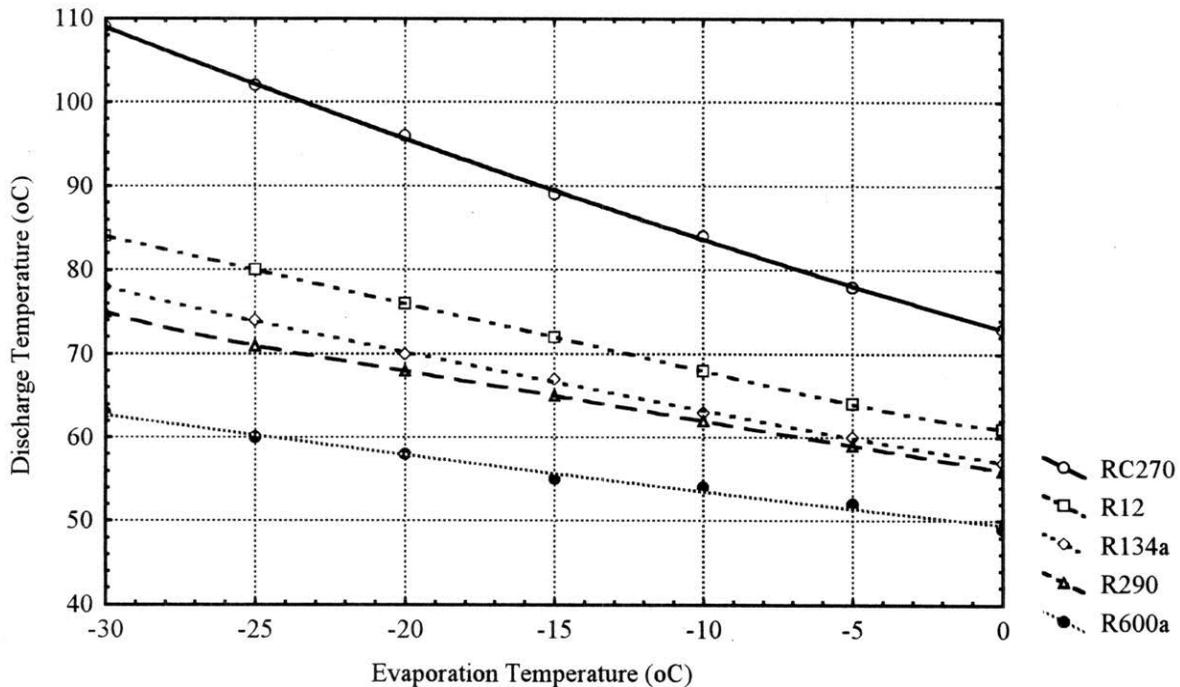
The relations between the media are much like the previous evaluation of the COP<sub>2</sub> in terms of small deviations, but with one exception. Cyclopropane seems to have improved considerably compared to the case with high superheat. As could be anticipated from the previous section cyclopropane would improve if the superheat was brought down, but this is a major improvement.



**Figure 4.19** COP<sub>2</sub> relatively R12 vs. evaporation temperature.

This diagram reveals several interesting results. First of all it can be seen that cyclopropane seems to be almost 8 % more efficient than R12 at the lowest evaporation temperature and around 3 % more efficient at 0°C. The improvement is between 2 and 4 percent units compared to the case with 30°C superheat. Another interesting result is that isobutane dropped from having been more efficient than R12 over the entire range to a position where it only reaches R12 at high evaporation temperatures. R134a also dropped from a position in the very same range as R12 to a deterioration of between 1 and 3 % compared to R12.

The last and maybe the most critical point was the discharge temperature, which also decreased considerably. As can be seen in fig. 4.20 the critically high discharge temperature of cyclopropane sunk from close to 140°C to slightly less than 110°C. This corresponds almost exactly to the decrease of the superheat.



**Figure 4.20** Discharge temperature vs. evaporation temperature.

Compared to fig. 4.12 it can be seen that the discharge temperatures of the other four agents decreased with more than 30°C. Unfortunately it seems like cyclopropane is a little less sensitive to a lowering of the suction gas temperature, with respect to the discharge temperature, than the other agents.

With a proper system design it should be possible to take advantage of the properties of cyclopropane. As have been concluded already the suction gas heat exchange has to be given up. Possibly also the suction gas cooling of the compressor motor. All these actions are in order to bring down the superheat to a minimum. Other types of compressors are perhaps also necessary to obtain a higher total isentropic efficiency, which also contributes to bring down the discharge temperature. An increased efficiency also brings down the energy demand of the compressor which is a factor that comes more and more in focus. In other terms, a low total energy demand is not only a sales argument, it might also be a necessity in order to follow the coming regulations. Consequently the demands of "tomorrow" might force the manufacturers to take rotation and scroll compressors into consideration, since they can obtain a superior efficiency.

## 5. MEDICAL ASPECTS

The aim of this section is to give an outlook of the possible medical side-effects of cyclopropane. Due to "difficulties" with the medical terms the medical phenomenon are tried to be described in a more comprehensive way. As already known cyclopropane was used as anaesthetic, because of this the medical descriptions are mainly related to anaesthetics applications.

### 5.1 Background

Cyclopropane was first prepared 1882 by von Freund, but its anaesthetic properties were not appreciated. Years later, propylene, an isomer of cyclopropane was studied extensively for its usefulness as general anaesthetic but was found too depressant to the heart. In searching for the cause of this depression, Lucas and Henderson (1929) tested cyclopropane as a possible impurity. Cyclopropane not only was exonerated but also was found in itself to be a safe and potent anaesthetic agent. After a 3-year period of study at the University of Wisconsin General Hospital, Waters and Smith (1934) published the first clinical report on the use of cyclopropane as a general anaesthetic.

Cyclopropane was widely used as anaesthetic between 1930-60. When more electrical equipment was introduced in the surgery during the 60's the use of the agent decreased because of its severe flammability. It is used also today because of its favourable anaesthetic properties but only to a minor extent with consideration to flammability and price.

Flammable concentrations are obtained within the range 2.4 to 10.3% in air, and 2.5 to 60% in oxygen. It is a colourless gas with a sweet, not unpleasant, characteristic odour, resembling that of petroleum ether. It is stored in metal cylinders as liquid under pressure. At room temperature the pressure is about 5 atmospheres and the aggregation form is a clear, water like, liquid.

### 5.2 Anaesthetic Properties

Cyclopropane is a relatively insoluble and extremely potent anaesthetic gas. Unlike nitrogen oxide, it can produce any desired level of anaesthesia, and the deeper planes are accompanied by sufficient muscular relaxation to obviate the need for neuromuscular blocking agents. The induction of surgical anaesthesia with cyclopropane-oxygen requires only 2-3 minutes and is not unpleasant. It is minimally irritating to the respiratory tract, and, therefore respiratory alterations such as breath-holding and coughing are less frequent than with some anaesthetics such as ether. Salivation is not prominent. Delirium is not uncommon during induction but can be avoided by administering a sleep inducing dose of an additional agent before cyclopropane inhalation is begun.

The signs of anaesthesia are similar to those of other general anaesthetic agents, with certain differences. Arterial pressure is well maintained at all levels of anaesthesia. Cardiac rate is typically normal, although it may slow gradually with the induction of anaesthesia. Cardiac irregularities may arise from excessive anaesthetic depth. Cyclopropane causes analgesia without unconsciousness if continuously inhaled in concentrations as low as 1%.

Consciousness is lost when the alveolar concentration reaches 7 to 10% (volume). 20 to 25% cyclopropane in the inhaled air gives so called surgical anaesthesia. Due to this can cyclopropane always be used with a satisfactory excess of oxygen. The waking up procedure is very quick just like the induction. Effects after the anaesthesia can be vomiting which are quite frequent but less severe than after ether and headache.

### 5.3 Toxicity And Health Influence

There is no evidence that this agent is hepatotoxic, and unexplained hepatic necrosis has not been a problem. It does not affect the kidneys but cyclopropane tends to enhance intestinal tone due to its direct action on the intestinal smooth muscle. Smooth muscles of blood vessels, as well as that of the bronchi and bronchioles, tends to constrict when exposed to cyclopropane. For this reason patients with a history of bronchial asthma may be poor choices for cyclopropane anaesthesia.

Cyclopropane is rapidly absorbed and almost entirely eliminated by way of the lungs. A small amount diffuses through the skin and an additional small amount (roughly 0.5%) is metabolised in the body and excreted as carbondioxide and water. By the time of return of consciousness after anaesthesia, the concentration of the agent in the expired gases fallen to approximately 1%, and after 3 hours are only traces left.

Due to cyclopropane's ability to cause irregular cardiac rhythm, it should be avoided as anaesthesia for patients with any form of cardiac decease. The irregularities tends to increase in conjunction with adrenaline, why adrenaline injection should be avoided together with cyclopropane as anaesthetic.

Post anaesthetic problems can also be so called "cyclopropane-chock". This has symptoms which makes the patient pale, cold and feeling sick.

### 5.4 Conclusions

The health influence by cyclopropane is very low. Severe poisoning which leads to unconsciousness is obtained when the concentration reaches 7 to 10 %. If the concentration goes very high it may lead to suffocation. But this is same for all gases without any free oxygen.

Cyclopropane has a depressing influence of the heart and can therefore be harmful to persons with cardiac problems. It also tends to constrict the bronchi and the bronchioles which may cause problems for persons with asthma. It has to be emphasised, though, that this is only in case of severe poisoning, i.e. in deep anaesthesia.

## 6. AVAILABILITY

It was a known fact that cyclopropane could be both difficult to find and expensive. This assumption turned out to be quite true. Initial rumours told that prices up several 10 000 SEK per kg could be prevailing.

After have sent a request to more or less all gas suppliers in Sweden, there were only three left which had any form of contacts that could provide the gas. Those three were AGA Gas AB, Air Liquide Gas AB (former Alfax) and a company called Halterman with origin in Germany. The two first mentioned told that they could provide some cyclopropane while the third could "possibly" obtain some. However, finally it was only AGA left which could provide a quantity.

They managed to provide a bottle of two kg of gas. The price turned out to be 5795 SEK which makes 2898 SEK per kg. The quality of the gas was 1.8, which means it is guaranteed to contain at least 98% cyclopropane. In the light of the prices of the conventional refrigerants, this seems terribly expensive. On the other hand this agent is very rare and the total production on a year basis is probably not too high. A comparison of prices is therefore of no sense for the moment.

Just as a comparison it could be mentioned that cyclopropane was found in a catalogue containing media for chemical experiment applications. It was sold in laboratory quantities of 25 g and the price was 216 DM. This would make a price of 42 340 SEK per kg! Maybe this example shows that it is quite irrelevant to make a comparison of the prices today.

From Statoils laboratory it was learnt that cyclopropane is obtained as a side-product when propene and ethene is manufactured from butane and propane. During the process butane and propane is cracked. Cyclopropane is obtained as a side-product in concentrations of about 200 PPM. Obviously it is not a rest product that is found in any larger quantities!

## 7. DISCUSSION

It can be concluded that cyclopropane is the least stable compound of those compared in this investigation, but it can hardly be concluded that it would be critical in some way. It does not start to decompose until the temperature reaches 400-500 °C, which are temperatures rarely reached in a refrigeration circuit. The latter is on the condition that the medium is pure and does not take into account any contamination of oil or metals for example.

The heat of combustion for the three flammable compounds in this investigation is analysed. The result shows that there are only small differences in the heat evolved, if 100 g refrigerant is completely oxidised.

When it comes to thermodynamics the saturation curve of cyclopropane is very similar to those of R12 and R134a. The pressure is slightly higher over the entire temperature range and at 40°C the pressure is 12 % higher compared to that of R12 and 4.8 % to R134a. Cyclopropane has the lowest pressure ratio of the examined media except for propane. This ratio influences both the compressor energy demand and the volumetric efficiency (the less the better).

The volumetric cooling capacity for cyclopropane is considerably better than for both R12 and R134a. The difference is around 20 % in the investigated range. In the same way the volumetric energy demand for the compressor can be found to be approximately 20 % higher. The coefficient of performance (COP) is found to be around 4.2 % higher than for R12 at the lowest investigated evaporation temperature (-30°C). The difference decreases towards higher evaporation temperatures but still at 0°C it is 1.5%.

Superheat is not favourable to cyclopropane in contrast to the other investigated media. When it comes to COP it shows a negative influence of increasing superheat. This is the same phenomenon that could be seen with the volumetric cooling capacity. An other disadvantage with high superheat is that the discharge temperature increases. With cyclopropane the discharge temperature seems to become critical. At the lowest evaporation temperature the discharge temperature reaches 140°C.

The above obtained results are critical but they are obtained with an assumed superheat of 30°C. If the superheat is brought down to 0°C the situation changes dramatically. The COP2 increases and turns out to be between 3 and 8 % better than R12 over the investigated range. The discharge temperature drops down to slightly below 110°C at the most critical operation point.

The health influence by cyclopropane is very low. Severe poisoning which leads to unconsciousness is obtained when the concentration in the air reaches 7 to 10 %. If the concentration goes very high it may lead to suffocation, but this is same for all gases without free oxygen though.

Cyclopropane has a depressing influence of the heart and can therefore be harmful to persons with cardiac problems. It also tends to constrict the bronchi and the bronchioles which may cause problems for persons with asthma. It has to be emphasised, though, that this is only in case of severe poisoning, i.e. in deep anaesthesia.

The availability is a problem for the moment. Only one supplier was found in Sweden that could provide a quantity and it was AGA Gas AB. They delivered a quantity of 2 kg to a price of 5795 SEK, which makes 2898 SEK per kg. In a future perspective when larger quantities might be ordered the price should decrease considerably.

With a proper system design it is possible to take advantage of the properties of cyclopropane. The suction gas heat exchange has to be given up and also the suction gas cooling of the compressor motor. These actions are carried out in order to bring down the superheat to a minimum. Other types of compressors are, however, necessary in order to obtain a higher total isentropic efficiency, which both brings down the discharge temperature and also decreases the energy demand of the compressor. A low total energy demand is not only a sales argument, it is also a necessity in order to follow the coming regulations. Consequently the demands of "tomorrow" might force the manufacturers to take rotation and scroll compressors into consideration, since these compressors generally can obtain a superior efficiency. However, the main point is that efficient compressors has be used and it doesn't matter whether it is a reciprocating, scroll or rotation compressor. It would be an advantage, though, if it was not suction gas cooled, in order to keep the superheat as low as possible.

This investigation has, however, revealed that cyclopropane should be further investigated as refrigerant. The coming actions will be tests related to the stability matter and application tests in a commercial refrigerator/freezer.

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