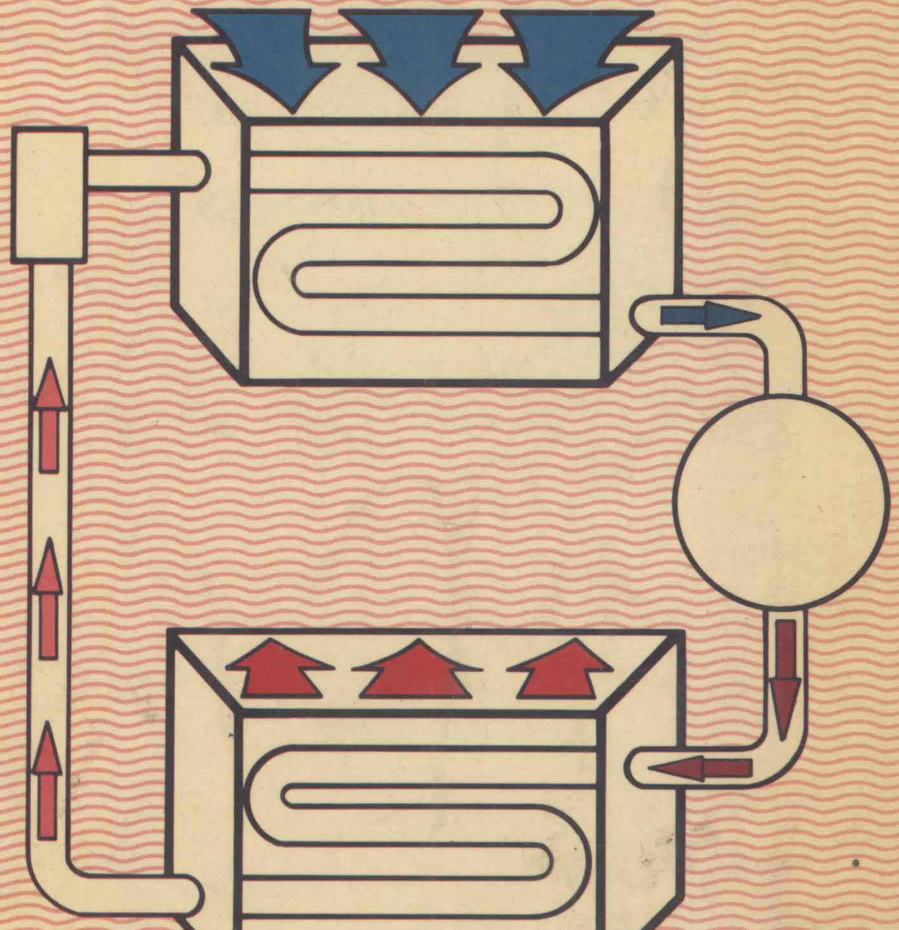
Papers presented at the
2nd BHRA International Symposium on

THE LARGE SCALE APPLICATIONS OF HEAT PUMPS

York, England.

25th-27th September 1984



BHRA
THE FLUID ENGINEERING CENTRE

PAPERS PRESENTED AT THE
SECOND INTERNATIONAL SYMPOSIUM ON

THE LARGE SCALE APPLICATIONS OF HEAT PUMPS

YORK, ENGLAND
25-27 SEPTEMBER 1984

Organised and sponsored by
BHRA, THE FLUID ENGINEERING CENTRE

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Editor: G.A. Watts and J.E.A. Stanbury

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Title, Author(s), Paper No., Pages, 2nd International Symposium on the Large Scale Applications of Heat Pumps, York England. Organised and sponsored by BHRA,
The Fluid Engineering Centre, Cranfield, Bedford MK43 0AJ, England
(25-27 September, 1984).

British Library Cataloguing in Publication Data

BHRA.*International Symposium on the Large Scale Applications of Heat Pumps (2nd : 1984 : York)*
2nd International Symposium on the Large Scale Application of Heat Pumps.——(Symposium on the industrial application of heat pumps ISSN 0263-4333 ; 2)
1. Heat Pumps
I. Title II. Watts, G.A. III. Stanbury, J.
IV. Series
621.402'5 TJ262

ISBN 0-906085-97-7

The complete volume may be purchased from BHRA, The Fluid Engineering Centre at a cost of £38.00 (UK & EEC) £40.00 (Elsewhere).

Printed and published by
BHRA, The Fluid Engineering Centre
Cranfield, Bedford MK43 0AJ, England.

ISBN 0 906085 97 7

ACKNOWLEDGEMENTS

The valuable assistance of the Organising Committee and Panel of Referees is gratefully acknowledged.

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2nd BHRA International Conference on

The Large Scale Applications of Heat Pumps

York, England: 25-27 September, 1984

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2nd International Symposium on

THE LARGE SCALE APPLICATIONS OF HEAT PUMPS

York, England: 25-27 September, 1984

PAPER A1

SOME TECHNICAL ASPECTS ON NONAZEOTROPIC MIXTURES AS WORKING FLUIDS

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Summary

In heat pumps with a pure refrigerant as working fluid both the condensation and the evaporation take place at constant temperature, if the pressure drop is neglected. With a nonazeotropic mixture of refrigerants as working fluid, however, the temperature will decrease during the condensation and increase during the evaporation. Although the discussions in the literature in most cases concentrate on the possibilities of improving the COP with the aid of a mixture, there are several other parameters in the heat pump cycle that can be improved, which may prove to be at least as important as the COP one. Such parameters are: The heating capacity, variations of the heating capacity with the load, adjustment of pressure levels and compressor discharge temperature, adjustment of series-manufactured equipment to various heating capacity needs, and allowment of higher temperature gradients in the heat sink and the heat source.

There are several ways of making comparisons between heat pumps with mixtures and with pure working fluids. Of special importance is the size of the heat exchangers. An example from calculations with a computer program shows, that the influence on the COP when the working fluid is changed from a pure one to a mixture is to a high extent depending on the way of comparison and the absolute sizes of the heat transfer areas.

The heating capacity may in many applications be increased considerably compared with the pure working fluids normally used today. Calculations of the "ideal relative capacity" with eight mixtures and several pure working fluids have been carried out in six applications. From these calculations it can be concluded that from a heating capacity point of view the mixtures R12/R11, R12/R113, R12/R114, R22/R114, and R13B1/R152a are of special interest.

Aspects on COP will be discussed in another paper at this conference given by the same authors.

Held at York, England.
Organised and sponsored by BHRA, The Fluid Engineering Centre, Cranfield Bedford MK43 0AJ, England.

1. INTRODUCTION

In heat pumps with a pure refrigerant as working fluid both the condensation and the evaporation take place at constant temperature, if the pressure drop is neglected. With a nonazeotropic mixture of refrigerants as working fluid, however, the temperature will decrease during the condensation and increase during the evaporation. As will be shown in this paper, such mixtures can improve the heat pump performance in several aspects and in many types of applications, especially those with high temperature gradients of both the heat sink and the heat source. Applications of interest are both in space heating systems and in industrial processes.

In the conference two papers will be given by the same authors. In this paper a general introduction to the technique will be given, possibilities of improving main parameters in a heat pump system will be discussed, and a discussion about how to compare the performance with a mixture and with a pure working fluid will be made. Finally, possibilities to improve the heating capacity with the aid of a mixture will be discussed. In a second paper possible influences on the COP will be presented.

2. THERMODYNAMICAL BACKGROUND

One important thermodynamical consequence for a heat pump when a binary nonazeotropic mixture is used instead of a pure working fluid is shown schematically in Fig. 1. In the figure the temperature variations of the working fluid, the heat source, and the heat sink along the heat exchanger are shown for the condenser and the evaporator. In the case of a pure working fluid, the temperature is constant in the condenser and the evaporator, respectively, if the pressure drop is neglected. For a nonazeotropic mixture of two working fluids, on the other hand, the temperature will decrease along the condenser and increase along the evaporator, as is shown with the dotted lines. (For simplicity, the parts of the evaporator and the condenser used for superheating and for cooling the superheated vapour, respectively, are excluded in the figure.) The reason for these temperature variations is the following:

For a given pressure a nonazeotropic mixture will have bubble-point and dew-point curves as shown in principle in the T,x-diagram, Fig. 2. When a liquid is vapourized, the more volatile component will be enriched in the vapour phase, thus successively increasing the mole fraction for the less volatile component in the liquid phase (see Fig. 2). This means that the bubble point of the liquid also is increased successively. If equilibrium between the liquid and vapour phases is assumed along the whole heat exchanger, the temperature continues to increase until it reaches the dew point of the vapour phase with the same mole fractions as the initial liquid phase. A corresponding discussion for the condenser would explain the temperature decrease in this heat exchanger.

The resulting smaller difference between the condensing and evaporating temperatures at the compressor end of the heat pump when a mixture is used indicates that the ratio between the compression work and the heating capacity can be decreased considerably, and hence that the COP can be increased compared to a pure working fluid. However, the magnitude of such an increase depends on how the heat transfer coefficients and the heating capacity of the heat pump are influenced when a pure working fluid is replaced by a mixture. The figure indicates that the possibilities of increasing the COP are greatest for the types of heat pumps in which the temperature decrease of the heat source and the temperature increase of the heat sink are considerable and where the heat exchangers can be arranged as counter-current ones. Due to the temperature variation of the refrigerant along the heat exchangers when a mixture is used, the COP is more influenced by the size of the heat transfer areas in this case than for the case of a pure refrigerant.

3. POSSIBLE IMPROVEMENTS WITH NONAZEOTROPIC MIXTURES

Although the discussions in the literature in most cases concentrate on the possibilities of improving the COP, there are several other aspects of the heat pump cycle that may be improved, which may prove to be at least as important as the COP one. The main parameters, in addition to the COP, that may be influenced by the use of mixtures, are:

The heating capacity can in many cases be increased. The reason is that the upper limit for the condensing temperature of a normally used fluid can be moved upwards when a proper second fluid is introduced to it. By such an introduction the condensing pressure and/or the compressor outlet temperature can be decreased to such a level, that the condensing temperature may be increased considerably compared with the pure working fluid. The influence on the heating capacity will be discussed later in this paper. Mixtures, which at certain conditions are able to increase both the heating capacity and the COP will in the future probably be strong competitors to the working fluids normally used today.

Variations of the heating capacity with the load. By varying the composition of a nonazeotropic mixture, the heat output from a heat pump can be controlled. With the aid of a distillation column, connected to a heat pump, this control can be made continuously. Such a distillation can be made in one stage or multi-stage columns according to Schwind (Ref. 1) and Cooper (Ref. 2).

The pressure levels in the condenser and the evaporator can be adjusted to appropriate values. The condenser pressure can be decreased, thereby allowing for higher condensing temperatures, and the evaporator pressure can be adjusted to be slightly above 1 bar. A decreased condenser pressure would lead to a decrease in the bearing loads in the compressor and hence to an increased life length.

The compressor discharge temperature can be decreased for a given condensing temperature by the proper choice of mixture. This would lead to an increased chemical stability of the working fluid and increased compressor life length.

Adjustment of series-manufactured equipment to various heating capacity needs. Small- and medium-sized heat pumps, normally manufactured in discrete sizes, can be better adjusted to a given heat demand by the use of a mixture. This would lead to a smaller number of annual starts for the compressor and hence a longer life length.

Allowment of higher temperature gradients in the heat sink and the heat source. Due to the gliding temperatures with mixtures, the temperature gradients in the heat sink and the heat source can be allowed to be somewhat higher without decreasing the COP. This may lead to smaller investment costs of the heat exchangers, lower noise levels in air-to-refrigerant evaporators, etc.

From the discussion above it is obvious that mixtures can improve the performance in many ways. The advantages of using mixtures over pure working fluids must therefore be examined individually for each type of heat pump application.

4. VARIOUS WAYS OF COMPARING MIXTURES AND PURE WORKING FLUIDS

As there are many parameters influenced by the use of mixtures, the question arises how to compare heat pumps using mixtures with conventional heat pump systems. As mixtures influence the COP, the heating capacity, investment costs, compressor life length, etc., this is a difficult question. The discussion below will be restricted to one of the most important parameters, the COP. Aspects on comparisons concerning the heating capacity will be discussed later in part I.

In addition to the thermodynamic data of the working fluid or mixture, the COP is influenced by the performances of the compressor and the heat exchangers. The knowledge about compressor efficiencies for mixtures is today very limited and must be increased considerably before fair comparisons in this respect can be made.

The sizes of the heat exchangers influence the COP to a great extent. Two different ways for comparison are shown in Fig. 3, which can be considered as the extreme ones. In the upper part of the figure, the conditions are the same as in Fig. 1, i.e. the initial condensing and evaporating temperatures, respectively, for the mixture are the same as the corresponding constant ones for the pure working fluid. This means that the heat transfer areas must be enlarged considerably when a mixture is used compared with a pure working fluid. The reasons for this are that the logarithmic mean temperature difference in each heat exchanger decreases and that the heat transfer coefficients on the refrigerant side most probably decreases due to an additional mass transfer resistance.

A comparison can also be made at essentially the same investment cost, i.e. with the same size of each heat exchanger in the two cases, as shown in the lower part of the figure. This case would of course result in a smaller increase of the COP compared with the first one.

In future heat pumps with mixtures, the components in the heat pump should of course be optimized for the actual mixture used. Due to the temperature variation along the heat exchangers, the COP is more influenced by the size of the heat transfer areas in the mixture case than for a pure working fluid. Therefore, optimal values from a technical-economical point of view of the heat transfer areas will probably be increased when a mixture is used. Such optimized areas will probably lead to a COP somewhere between the two extreme cases shown in Fig. 3.

To illustrate the importance of the heat exchanger sizes, one example from theoretical calculations of the COP will be presented. The calculations have been made with a computer program for system simulations of heat pumps, developed at Chalmers University of Technology. A description of the program can be found in (Ref. 3).

The conditions for the example shown here are the following: Pure R12 is compared with the mixture 70 % R12/30 % R114. The mixture is considered to be an ideal solution. The comparison is made at a given size of the heat source. The temperature gradients have been chosen to be 10 K both in the heat source and the heat sink in the pure R12 case. In the mixture case the heat sink gradient is marginally smaller, due to the increase of the COP. In order to get the same cooling capacity, the compressor must be approx. 30 % larger in the mixture case than in the pure R12 case. The initial heat sink temperature is in all cases 45 ^{o}C and the incoming temperature of the heat source is 10 ^{o}C.

The heat pump cycle is a one-stage one with an internal heat exchanger, which subcools the condensate and superheats the suction gas. The superheating is in all cases 10 ^{o}C. There is no external subcooling. Due to the complex variation of the specific heat with the temperature for the mixture, the conditions in the heat exchangers must be simulated by stepwise calculations instead of the normally used way with logarithmic mean temperature differences. Some experimental experience indicates that the decrease in the heat transfer coefficient in the evaporator is typically approx. 30 % when a mixture is used instead of a pure working fluid, see e.g. Radermacher et al. (Ref. 4). This has been taken into account in the calculations. For the condensing heat transfer coefficient no such information exists. In the calculations a decrease of 20 % has been assumed. The evaporator has been designed for an in all cases constant inlet liquid Re number and influence of the pressure drop has been taken into account. The compressor isentropic efficiency has been set to 80 % in all cases.

The result from the calculations is shown in Fig. 4. The COP is shown versus three relative values of the heat exchanger sizes of the evaporator and condenser, 100 %, 200 %, and 300 %. 100 % means heat exchanger sizes, which give "normal" minimum temperature differences in the R12 case, 5 K in the evaporator and 3 K in the condenser. As can be seen in the figure, there is a substantial influence of the heat exchanger size. The absolute value of this size also influences the result even when the comparison is made at the same size. An increase of the size gives a higher influence on the COP for a mixture than for a pure working fluid. When discussing various heat exchanger sizes, it shall be borne in mind that the cost for the whole uninstalled heat pump equipment is always small compared with the whole cost for the system, heat source, installation, building, etc., for large heat pumps, normally 40 % or smaller. It shall also be pointed out that the results shown are from one example only. The increase of the COP can be both much higher and lower in other applications, depending on the application and the conditions.

5. POSSIBLE IMPROVEMENTS OF THE HEATING CAPACITY

At Chalmers University of Technology, Sweden, calculations of the heating capacity for eight different mixtures in various applications have been carried out. The general aim of the calculations was to identify mixtures of special interest in this respect for further, more thorough, calculations and for experiments.

Due to the lack of data for many mixtures, and in order not to complicate the calculations too much, each capacity was calculated as the "ideal relative capacity" according to the following:

The condenser heat per kilogram of working fluid has been set equal to the heat of condensation at the condensing pressure, Δh_{cond}. Thereby the superheat of the vapour has been neglected. The relative flow by weight has been set to the density of the saturated vapour at the evaporating pressure, $1/v''_{evap}$, thereby neglecting any superheating after the evaporator. Hence, the relative capacity has been calculated as $\Delta h_{cond}(1/v''_{evap})$. This also means that the variation in the volumetric efficiency of the compressor with the pressure ratio is neglected. This method of calculating relative capacities, although simple and approximative, has often been used previously in the refrigeration and heat pump field for identification of pure working fluids of interest for various applications.

As was discussed above, mixtures and pure working fluids can be compared in several different ways. For the comparisons made in the study presented here, the situation shown in the lower part (method II) in Fig. 3 was selected. (This method is more disadvantageous for mixtures than method I in the same figure, as it gives somewhat smaller heating capacities due to a higher v''_{evap} and a smaller Δh_{cond}.) The condensing and evaporating temperatures, respectively, of the pure working fluids have therefore been set to the linear mean value of the incoming and outgoing temperature of the mixture in each heat exchanger.

Due to the many calculations involved and lack of data for mixtures, simple methods were used for calculation of the heat of condensation and the specific volume for mixtures according to the following:

The Δh_{cond} was calculated as the difference between the enthalpy of the saturated vapour and the corresponding enthalpy for the saturated liquid. These two enthalpies, in turn, were calculated as the weighted mean value of the two vapour enthalpies and the two liquid enthalpies, respectively, at the given temperature and pressure. As one of the components cannot exist as vapour at these conditions and the other component cannot exist as liquid, these enthalpies had to be calculated by a small extrapolation into the part vapour/part liquid area, assuming the same specific heat as at the saturated condition.

The specific volume was calculated with the aid of generalized compressibility charts. The pseudo-critical pressures, temperatures and acentric factors were calculated according to recommendations by Reid et al. (Ref. 5).

5.1 Types of mixtures and applications investigated

Eight mixtures, R12/R11, R12/R113, R12/R114, R22/R11, R22/R113, R22/R114, R114/R113, and R13B1/R152a, have been investigated. These have been selected because they are most frequently discussed in the literature. The heating capacities have been calculated for a number of applications, i.e., given temperature levels and temperature gradients in the heat exchanger (with the same gradients in the evaporator and the condenser). Comparisons were then made between the mixtures and with pure working fluids.

The applications investigated were:

1. T_{cond} = 100 °C, T_{evap} = 20 °C, ΔT = 10 °C and 20 °C
2. " = 70 °C, " = 0 °C, " = 10 °C and 20 °C
3. " = 90 °C, " = 10 °C, " = 10 °C
4. " = 120 °C, " = 30 °C, " = 10 °C
5. " = 50 °C, " = 0 °C, " = 10 °C
6. " = 50 °C, " = -10 °C, " = 10 °C

The condensing and evaporating temperatures given above are values at the compressor end of each heat exchanger.

For each mixture 22 bar has been assumed to be the highest acceptable pressure for both practical and chemical stability reasons. (Hence, such problems as known or suspected problems with chemical stability with oil, e.g. for R11, have not been taken into account.) This assumption must, of course, be checked for each mixture. 1 bar has been assumed to be the lowest acceptable pressure in the evaporator.

5.2 Results

Some results of the calculations are shown in the enclosed tables. The mixtures giving the highest capacity for each application are shown in Table 1. Values for the corresponding "normal" working fluid in each application are also included. From this table it can be concluded that each of the investigated mixtures is of interest in at least one application.

A comparison of the results between mixtures and pure working fluids shows that in several cases one or more mixtures have higher capacities than the pure working fluids used today in each temperature range. This is true in the following cases:

Appl. 1, $\Delta T = 10\ ^{o}C$: R12/R11, R12/R113, and R12/R114 have higher capacities than R114.

Appl. 2, $\Delta T = 10\ ^{o}C$: R22/R114 has higher capacity than R12.

Appl. 2, $\Delta T = 20\ ^{o}C$: R22/R113 and R22/R11 have higher capacities than R12.

Appl. 3: R12/R114 has higher capacity than R114.

Appl. 4: No mixture has higher capacity than R114.

Appl. 5: No mixture has higher capacity than R22.

Appl. 6: R13B1/R152a has approximately the same capacity as R22.

From the discussion above it can be concluded that from a heating capacity point of view R12/R11, R12/R113, R12/R114, R22/R114, and R13B1/R152a are of interest for further investigations, the last one above all for the possibilities of boosting at low evaporator temperatures. It should in some cases be possible to achieve considerable increases of the capacity when mixtures are used instead of pure working fluids.

6. ACKNOWLEDGEMENTS

Great thanks are due to the participants in the IEA group "Advanced heat pumps. Annex VI" for numerous valuable discussions, especially

Prof. Kruse and Dipl. Ing. Schröder, Hannover University, Germany

Univ. Lect. Knudsen, Denmark Technical University

Prof. Moser, Graz Technical University, Austria

Tekn. Dr. Ljungkvist and Chem. Eng. Svensson, Chalmers University of Technology, Sweden

Mr. Levins, Oak Ridge, USA

Prof. Stoecker, University of Illinois, USA

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Table 1.

T_k (°C)	T_f (°C)	ΔT_k (°C)	Mixture/ refrigerant	Capacity (kJ/m^3)	P_k/P_f (bar)
100	20	10	R12/R114	1834	19.0/3.00
			R114	1062	12.7/1.53
100	20	20	R12/R11	1344	19.0/2.05
			R114	931	11.5/1.28
70	0	10	R22/R114	1989	22.1/3.20
			R12	1679	17.0/2.61
70	0	20	R22/R113	1511	18.5/2.35
			R22/R11	1494	17.0/2.20
			R12	1481	15.3/2.19
90	10	10	R12/R114	1405	16.4/2.10
			R114	809	10.3/1.06
120	30	10	R114/R113	1131	14.9/1.60
			R114	1214	18.8/2.14
50	0	10	R13B1/R152a	2583	16.85/4.00
			R22/R113	2465	15.1/3.50
			R22	2908	17.3/4.21
50	-10	10	R13B1/R152a	2090	16.85/3.20
			R22	2073	17.3/2.96

Table 2.

Comparison, Mixtures of working fluids

T_k = 100 °C $\Delta T \sim 10^o$

T_f = 20 °C

Indices:

k = condensing conditions
f = evaporating conditions

Mixture ①/②	y_1 (mol-%)	ξ_1 (weight-%)	P_k (bar)	P_f. (bar)	Capacity (kJ/m^3)	Remarks
R12/R11	92	91	25,8	3,90	1846	T_k = 98,5 °C, ΔT_k = 9^o OBS! P_k > 22 bar
R12/R113	96	94	27,0	4,10	1849	T_f = 21,5 °C, ΔT_f = 12^o OBS! P_k > 22 bar
R12/R114	50	41	19,0	3,00	1834	T_k = 98 °C, T_f = 23 °C
R114/R113	82	81	10,0	1,15	913	T_f = 23 °C, ΔT_f = 11^o

Pure working fluids

T_k = 95 °C

T_f = 15 °C

Working fluid	P_k (bar)	P_f (bar)	Capacity (kJ/m^3)	Remarks
R11	7,336	0,7343	204	OBS! P_f < 1 bar
R12	30,57	4,914	2025	OBS! P_k > 22 bar
R114	12,73	1,527	1062	
R113	3,897	0,2937	299	OBS! P_f < 1 bar

Table 3.

Mixtures

T_k = 50 °C $\Delta T \sim 10^o$

T_f = -10 °C

Indices:

k = condensing conditions
f = evaporating conditions

Mixture ①/②	y_1 (mol-%)	ξ_1 (weight-%)	P_k (°C)	P_f (°C)	Capacity (kJ/m^3)	Remarks
R22/R11	96	94	14,8	2,35	1702	
R22/R113	98	96	15,1	2,40	1727	
R22/R114	88	79	13,9	2,20	1637	
R13B1/R152a	55	73	16,85	3,20	2090	T_k = 48 °C, ΔT_k = 8^o T_f = -9 °C

Pure working fluids

T_k = 45 °C

T_f = -15 °C

Working fluid	P_k (bar)	P_f (bar)	Capacity (kJ/m^3)	Remarks
R11	2,023	0,2027	226	OBS! P_f < 1 bar
R12	10,84	1,826	1375	
R13B1	25,44	5,379	2647	OBS! P_k > 22 bar
R22	17,29	2,957	2073	
R113	0,9253	0,06798	87	OBS! P_f < 1 bar, P_k > 22 bar
R114	3,885	0,4654	454	OBS! P_f < 1 bar
R152a	10,58	1,547	1254	

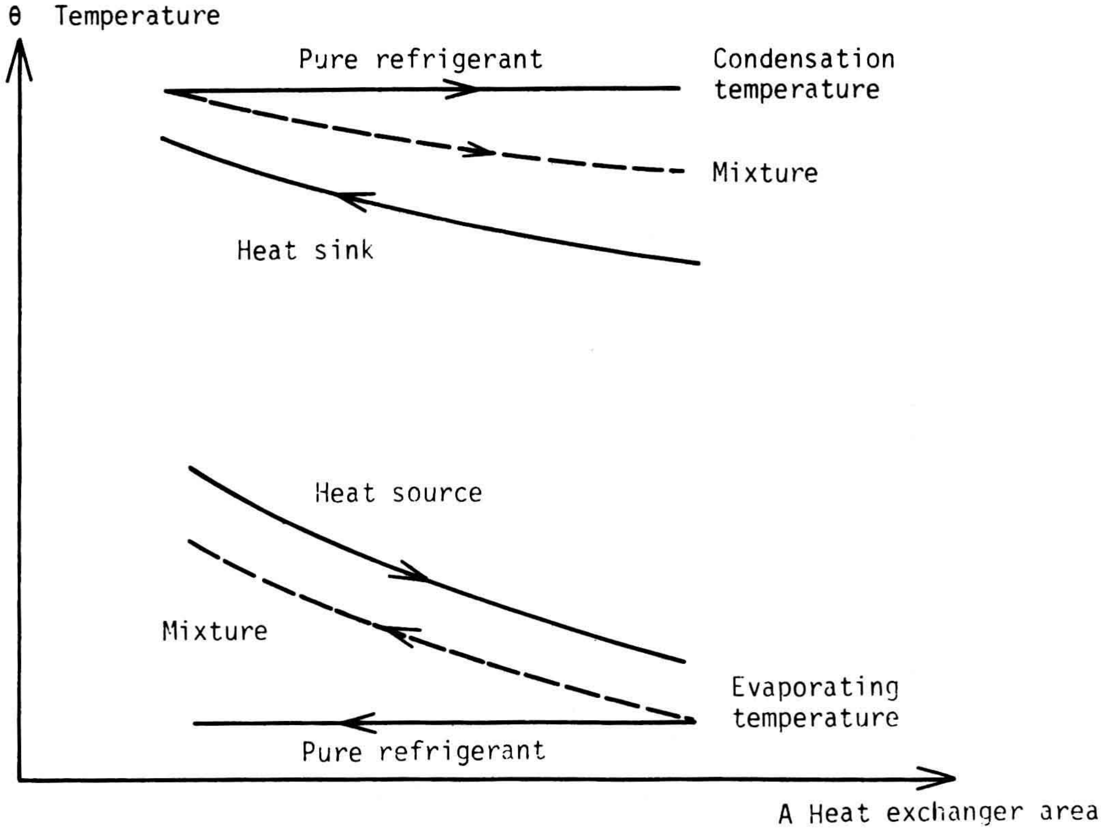

Fig. 1 Temperature variations in the condenser and evaporator for a pure refrigerant and for a nonazeotropic mixture.

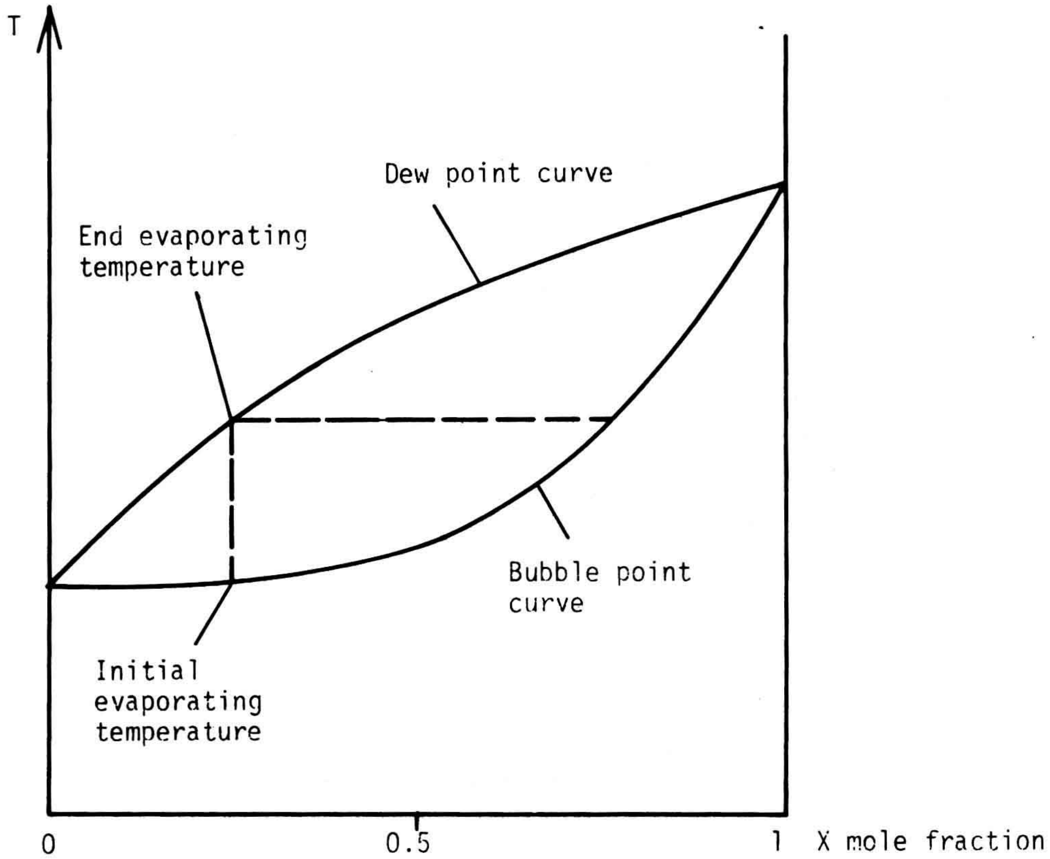

Fig. 2 T,x-diagram for a nonazeotropic mixture. Temperature variation during evaporation is shown.

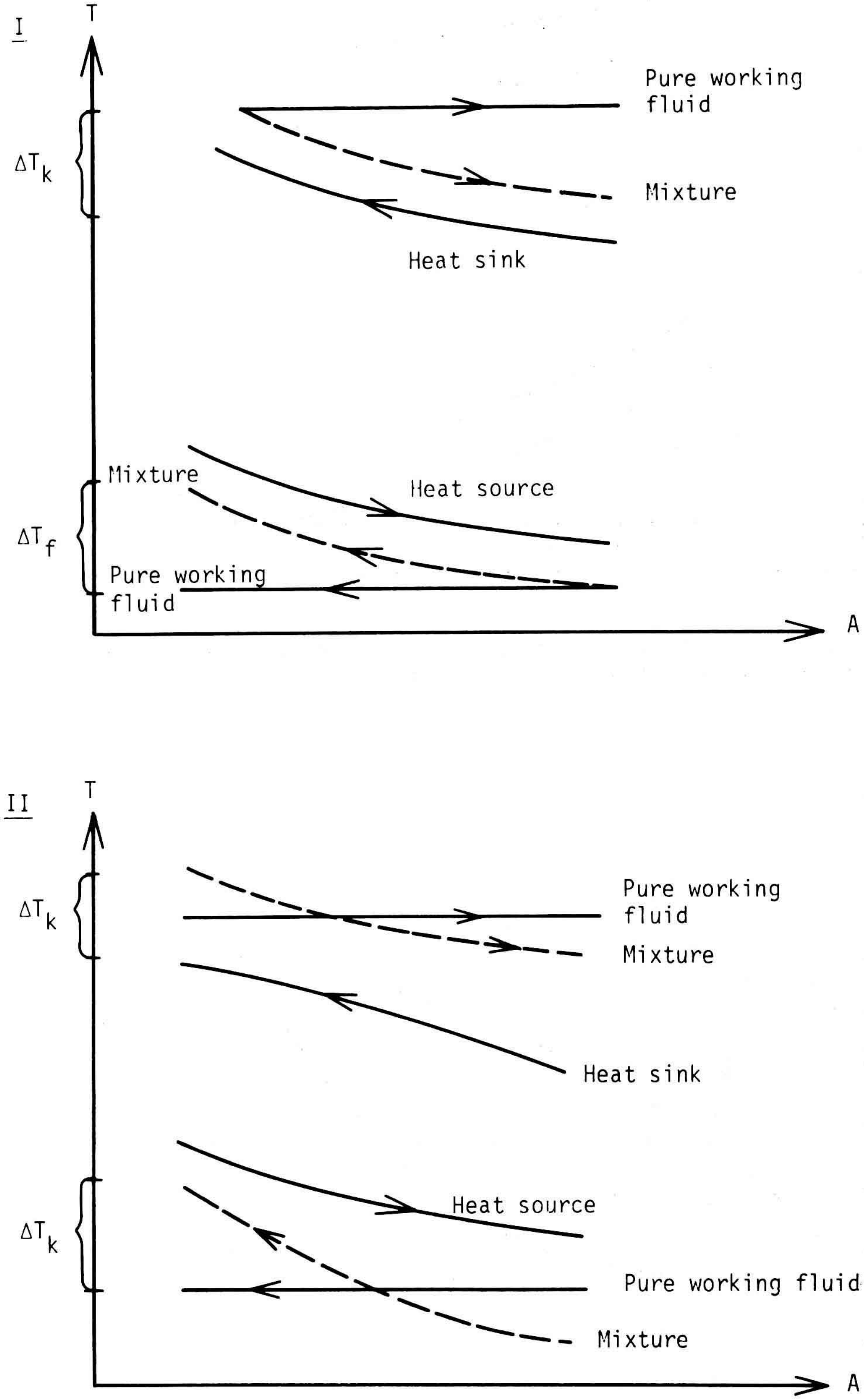

Fig. 3 Two ways of comparing a mixture and a pure working fluid (A = heat transfer area).

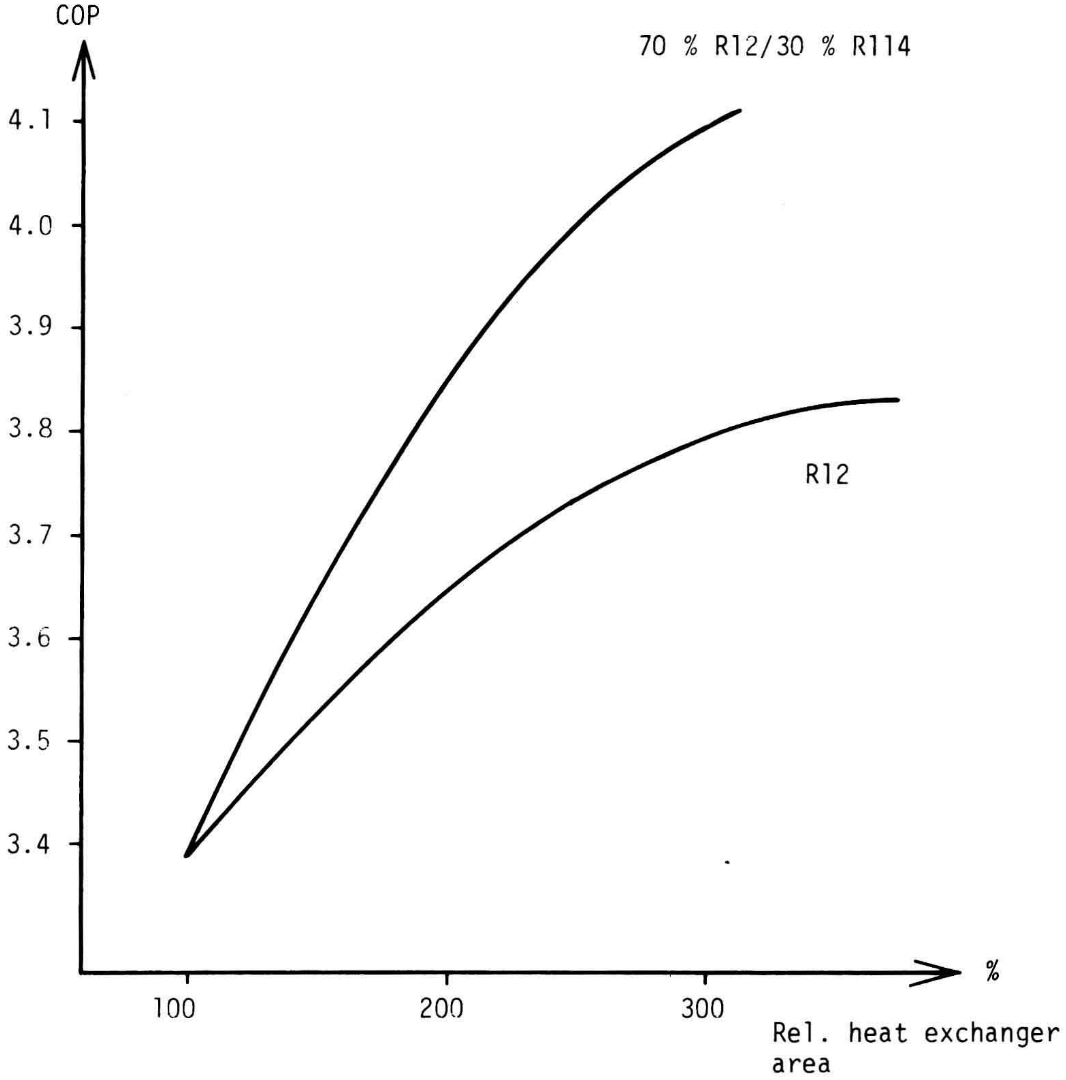

Fig. 4 COP versus heat exchanger areas for R12 and 70 % R12/30 % R114.