

# ADVANCED VERSIONS OF HEAT PUMPS WITH ZEOTROPIC REFRIGERANT MIXTURES

R. Radermacher, Ph.D.

ASHRAE Associate Member

## ABSTRACT

Two heat pump cycles operating with halogenated hydrocarbon mixtures are considered. Each cycle promotes vastly extended ranges of capacity control by composition shift. Further the Coefficient of Performance (COP) increases up to 50% under extreme temperature lifts when reciprocating compressors are employed. This is due to a reduction of the pressure ratio by a factor of more than two.

## INTRODUCTION

Currently the application of nonazeotropic mixtures (or better: zeotropic mixtures) in heat pumps and air conditioners is being studied in several laboratories (Stoecker 1981). Zeotropic mixtures offer two advantages compared to the usual single refrigerant systems: (1) capacity control due to adjustment of composition, and (2) performance improvement due to gliding temperatures in the evaporator and condenser.

Despite the advantages of these two features, they limit each other so that neither can be exploited to the fullest extent. Capacity control, which means control of the suction side pressure, independent of evaporator temperature, calls for a refrigerant mixture of components with boiling points as far apart as possible. On the other hand, the gliding temperature interval should not exceed a range of approximately 30 F (16 K) for practical reasons. For a mixture of components with very different boiling points, this limit will be exceeded due to the inherent requirement that all liquid must evaporate. These mutual restrictions are overcome by so called "heat pump cycles with solution circuit".

## Heat Pumps with Solution Circuit: Single-Stage Version

If capacity control is to be achieved by adjustment of composition to any significant extent, then the boiling points of the two refrigerant components have to be as far apart in temperature as possible. As outlined above, this would result in excessively large gliding temperature intervals. However, these temperature intervals can be deliberately reduced to an acceptable size (or eliminated almost completely) when we eliminate the requirement that all liquid in the evaporator must evaporate. The remaining liquid portion is then circulated into the condenser by means of a circulation pump. Figure 1 shows the schematic of such a heat pump cycle. (Superimposed is a pressure-temperature diagram, so that the relative location of such main heat exchangers which include a phase change of the working fluid is indicative of the prevailing temperature and pressure levels.) As in a conventional heat pump, there are four main components: evaporator, compressor, condenser, and expansion device. In addition, a second liquid line with a pump is provided, circulating the liquid remaining in the evaporator into the condenser. With two liquid streams available (one from the condenser to the evaporator and one from the evaporator to the condenser), it is advisable to bring them into heat exchange for better performance of the cycle. In order to achieve the gliding temperature

Reinhard Radermacher is assistant professor, Department of Mechanical Engineering, University of Maryland, College Park, MD, and affiliated with the Thermal Machinery Group of the National Bureau of Standards.

THIS PREPRINT IS FOR DISCUSSION PURPOSES ONLY. FOR INCLUSION IN ASHRAE TRANSACTIONS 1986, V. 92, Pt. 2. Not to be reprinted in whole or in part without written permission of the American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., 1791 Tullie Circle, NE, Atlanta, GA 30329. Opinions, findings, conclusions, or recommendations expressed in this paper are those of the author(s) and do not necessarily reflect the views of ASHRAE.

interval to the fullest extent thermodynamically possible, the solution stream entering the condenser has to be in heat exchange with the condensing fluid first, and then it is released into the condenser to undergo the phase change. The analogous could be provided in the evaporator as well. This is not included in the consideration here, since for a heating application the temperature interval in the evaporator is not crucial. A more detailed consideration of this cycle reveals that the evaporator is converted into a desorber and the condenser into an absorber, components that are commonly thought of as being reserved for absorption heat pumps only. In contrast to absorption heat pumps the input of availability is in the form of work not heat.

The cycle described was originally proposed about 30 years ago (Altenkirch 1950) and is now realized in a district heating system (Mucic 1983). It is under investigation in a laboratory in Switzerland (Stocker 1985). That work focused on ammonia-water as the working fluid pair because the thermophysical properties are very favorable. Of course any mixture is a possible candidate.

### Heat Pump Cycle with Two Stage Solution Circuit

The boiling points of the two components may be far apart. The resulting large range in boiling temperatures can be covered at constant pressure by varying composition (solution field), and can accommodate two loops built by an absorber, desorber, pump, and liquid heat exchanger, both of them simultaneously served by the same compressor. A possible configuration is shown in Figure 2. The heat released by the first stage absorber is supplied to the desorber of the second stage: the desorber of the first stage extracts heat from an outside source and the absorber of the second stage rejects heat to an outside sink. This configuration is especially useful when large temperature lifts are required at very low pressure ratios. These cycles are discussed in more detail by Alefeld (1982).

In this paper the potential of halogenated hydrocarbon mixtures is explored as working fluid for the described cycles, their performance is evaluated, and compared to the performance of a cycle using a conventional zeotropic mixture of the same constituents.

### Calculation Procedure

All calculations are based on an equation of state that has been adapted to accommodate refrigerant mixtures Morrison (1985). The equation allows for the calculation of all thermodynamic and caloric properties in the liquid, vapor, and two-phase region, fitting only one parameter to account for mixture effects. For each state point (numbered in Figure 1), the compositions of the liquid and vapor phase, the pressures, temperatures, enthalpies and flow rates have been calculated, assuming saturated conditions at desorber and absorber outlets. The flow rates are based on one mole of vapor passing through the compressor. A set of values is given in Table 1 as an example. The numbers assigned to the state points in Table 1 refer to those shown in Figure 1. Based on these data enthalpy and mass balances are performed for each heat exchanger and the amount of heat exchanged is calculated.

It is assumed that the liquid-liquid heat exchanger has an infinite area. The efficiency of the pump is set to 0.7 and the volumetric efficiency  $\eta$  of the compressor is calculated according to:

$$\eta = 1 - m \left( \frac{V_s}{V_d} - 1 \right) \quad (1)$$

where  $m$  is the fraction of clearance volume/total volume for the cylinder, and  $V_s$  and  $V_d$  are the specific volumes at the suction and discharge side of the compressor, respectively.

Table 2 shows a set of thermodynamic data for the two-stage cycle. The numbers assigned to the state points in table 2 refer to those in Figure 2. Here the calculation is based on one mole of vapor generated in each evaporator. Then the requirement is introduced that the amount of heat released by the low temperature absorber has to match the heat required by the high temperature desorber. The flowrates in the high temperature cycle are adjusted accordingly. This requires a somewhat lengthy iterative process since the vapor mixture entering the compressor changes as well. Once the iteration converged the amounts of heat released or absorbed by each component is calculated under consideration of the changed mass flow rates.

## Results and Discussions

The calculations conducted here were performed for a rather conventional mixture, R114/R22. This mixture was selected because sufficient data are known, and the equation of state therefore produces reasonably accurate values. Another reason for selection of R22/R114 is that its performance can be evaluated as a conventional zeotropic mixture for comparison. Three cases are considered: a zeotropic refrigerant mixture, the single-stage heat pump with one solution circuit, and the two-stage version with two solution circuits.

In the case of the single-stage heat pump, the gliding temperature in the condenser was required not to exceed 18 F (10 K). In the two-stage heat pump, the composition shift,  $\Delta X$ , was fixed at  $\Delta X = 0.1$  in order to limit the required iterations. All calculations were performed for a lowest desorber temperature of 122 F (50°C) and for the two highest evaporator temperatures of 47 F (8°C) and -4 F (-20°C).

Figure 3 shows the available gliding temperature intervals for all cases. At intermediate R114 concentrations the conventional zeotropic mixture cycle (denoted by circles in Figure 3) produces an excessively large temperature interval (up to about 35 F (19 K)). Therefore, this mixture can hardly be used over the entire composition range in conventional heat pump cycles. Accordingly, the wide range in potential capacity adjustment cannot be utilized. In case of the single-stage cycles (open triangles), the gliding temperature range for compositions high in R22 or R114 is the same as for the conventional cycle. For intermediate compositions the gliding temperature range is 18 F (10 K) as chosen. The two-stage cycle (black triangles) has a gliding temperature range grouped around 18 F (10 K). The composition indicated on the graph is the one of the strong absorbent of the low temperature stage.

Figure 4 shows the heating COP for all three heat pump cycles. Also the performance for pure R114 and pure R22 is calculated twice assuming saturated fluid leaving the evaporator and condenser. (This causes the COP of R114 to drop below the expected value which would be close to the one of pure R22 [ASHRAE 1981] if the R114 would be superheated at the evaporator outlet.) The first calculation accounts for the fact, that for a meaningful comparison, the pure components should achieve the same highest and lowest temperatures as the cycle with single stage solution circuits (open squares). The second calculation does not account for this fact ( $\Delta T = 0$  always, full squares in all figures). These two sets of results for the pure components show two facts: firstly, the degradation of the COP due to increased temperature lift, and secondly the benefit gliding temperatures, especially in conjunction with solution circuits, do provide. The cycles with solution circuits exhibit a consistently higher COP than the pure components for the same temperatures. The COP does hardly depend on composition, while for the zeotropic mixtures a significant dependence on composition is found.

For the higher evaporator temperature, the single and two-stage cycles show an increase in COP of up to 17% compared to R22 (open squares). The reason for this performance increase is mainly due to the gliding temperature interval. This allows to achieve higher condenser temperatures without increasing the pressure ratio as much as it is the case for pure components.

At the lower evaporator temperature the two-stage cycle is superior to any other case, and achieves a performance increase of up to 50% compared to R22 (open square). The Carnot COP in this case would be 4.2, when accounting for the gliding temperatures (Lorentz Cycle). This increase in performance is mainly due to the very low pressure ratio of this cycle.

Figure 5 shows that the pressure ratio for all three cycles depends on composition. The pressure ratio of any solution circuit cycle is lower than the one for either pure component. While the pressure ratio for the conventional zeotropic mixture shows a peak in much the same way as its gliding temperature interval, exhibits the single-stage version an almost constant pressure ratio. In contrast the pressure ratio of the two-stage cycle is extremely low. Although heat is pumped from -4 F (-20°C) to 122 F (50°C) plus the  $\Delta T$  of about 18 F (10 K) the pressure ratio to be overcome by the compressor and pumps is never higher than 3.5. This low pressure ratio allows the two-stage cycle to achieve a reasonable volumetric efficiency in reciprocating compressors, even under extreme conditions. Thermodynamically the low pressure ratio can be explained in the following way. If a heat pump works with a fluid having a vapor pressure curve of an extremely flat slope, the required pressure ratio is low, and due to Clapeyron's relation the latent heat, and therefore the capacity are low too. Applied to this case, for each mole evaporated from the first-stage desorber, the compressor has to compress a second mole evaporated from the second-stage desorber. Figure 6 shows the capacities achieved by each cycle. The capacity of the two-stage cycle is at least 50% lower than the one of the pure R22.

**ACKNOWLEDGMENT**

The work reported here is part of a larger Refrigerant Mixture Program at the National Bureau of Standards which is supported by the Electric Power Research Institute, U.S. Department of Energy through Oak Ridge National Laboratory and the National Bureau of Standards.

**TABLE 1**  
**Properties of Fluid Streams for the Cycle with Single-Stage Solution Circuit.**  
 (The numbers of the first column are the same as in Figure 1.)

No	T(K)	P(kPa)	liq. comp. (mole fract. R 114)	vap. com (mole fact. R 114)	liq. enthalpy (kJ/Kmol)	vap. enthalpy (kJ/Kmol)	vap. entropy (kJ/Kmol K)	liquid flow rate <u>mole liq.</u> mole vap.
1	253.15	169.2	.500	.132	3512	21965	91.282	0.78
2	349.93	1556.4	--	.132	--	26942	91.283	--
3	333.17	1556.4	.500	--	14569	--	--	0.78
4	323.15	1556.4	.293	--	11791	--	--	1.78
6	249.68	169.2	.362	.091	7676	--	--	--
7	--	1556.4	.293	--	7676	--	--	1.78
8	323.15	1556.4	.500	--	13071	--	--	0.78

**TABLE 2**  
**Properties of Fluid Streams for the Cycle with Two-Stage Solution Circuit**  
 (The numbers of the first column indicate the statepoints of Figure 2)

No	T(K)	P(kPa)	liq. comp. (mole fract. R 114)	vap. com (mole fact. R 114)	liq. enthalpy (kJ/Kmol)	vap. enthalpy (kJ/Kmol)	vap. entropy (kJ/Kmol K)	liquid flow rate <u>mole liq.</u> mole vap.
1	288.90	202.8	.948	.750	9335	22372	114.42	0.99
2	319.90	705.9	--	.484	--	29117	103.99	--
3	334.48	705.9	.948	--	17182	--	--	0.99
4	323.15	705.9	.848	--	14763	--	--	1.99
6	283.44	202.8	.905	.598	11890	--	--	--
7	--	705.9	.848	--	11890	--	--	1.99
8	323.15	705.9	.948	--	15181	--	--	0.99
11	253.15	202.8	.300	.079	3198	21570	88.13	1.21
13	291.70	705.9	.300	--	7781	--	--	1.21
14	288.90	705.9	.200	--	6909	--	--	2.21
16	251.36	202.8	.215	.060	4612	--	--	--
17	--	705.9	.200	--	4612	--	--	2.21
18	288.90	705.9	.300	--	7436	--	--	1.21

The total vapor flow rate through the compressor is 2.52 moles due to the coupling of the two solution circuits by heat exchange. One mole of vapor is supplied by the low temperature loop, 1.52 moles by the high temperature loop.

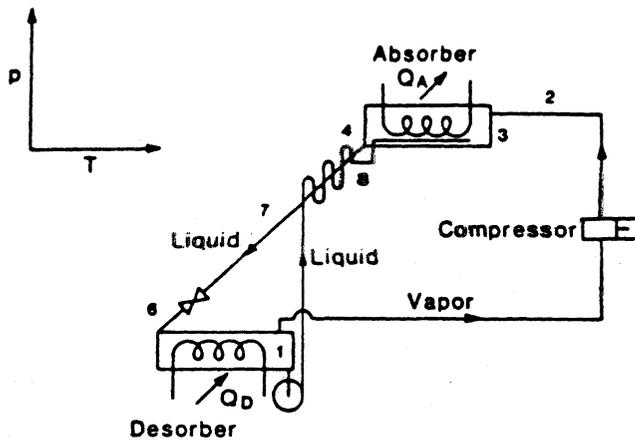


Figure 1. Schematic of single-stage heat pump cycle with solution circuit

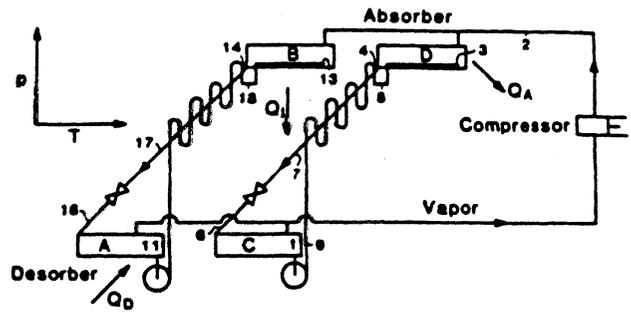


Figure 2. Schematic of two-stage heat pump cycle with solution circuits

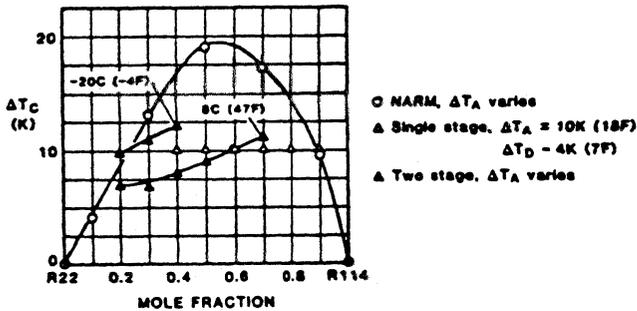


Figure 3. Gliding temperature differences,  $\Delta T_c$ , available at absorber for heat rejection to external heat sink vs. composition at low temperature desorber outlet for a conventional vapor compression cycle operating with pure and mixed refrigerants, and single- and two-stage cycles employing solution circuit(s) operating with refrigerant mixtures

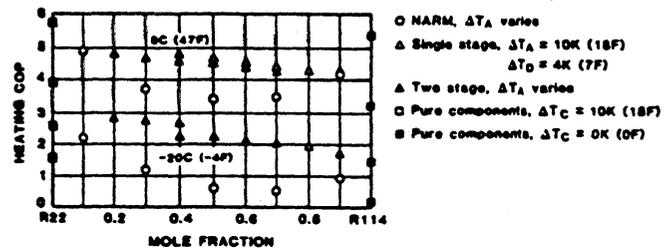


Figure 4. Coefficient of performance vs. composition for a conventional vapor compression cycle operating with pure and mixed refrigerants, and single- and two-stage cycles employing solution circuit(s) operating with refrigerant mixtures

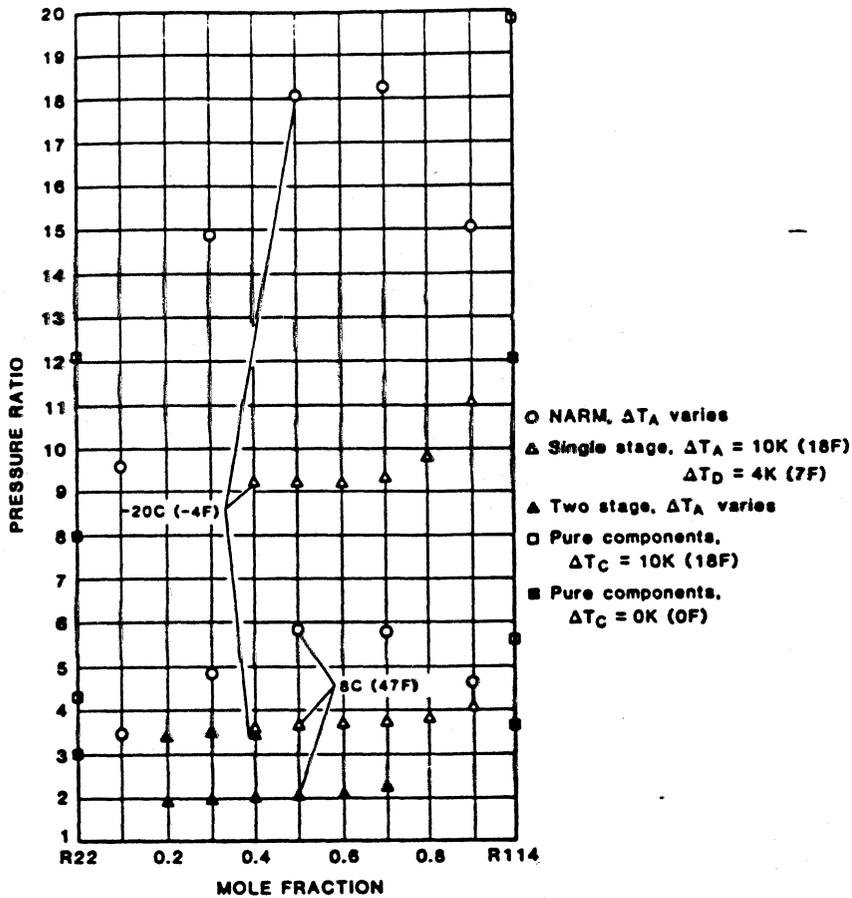


Figure 5. Pressure ratio vs. composition for a conventional vapor compression cycle operating with pure and mixed refrigerants, and single- and two-stage cycles employing solution circuit(s) operating with refrigerant mixtures

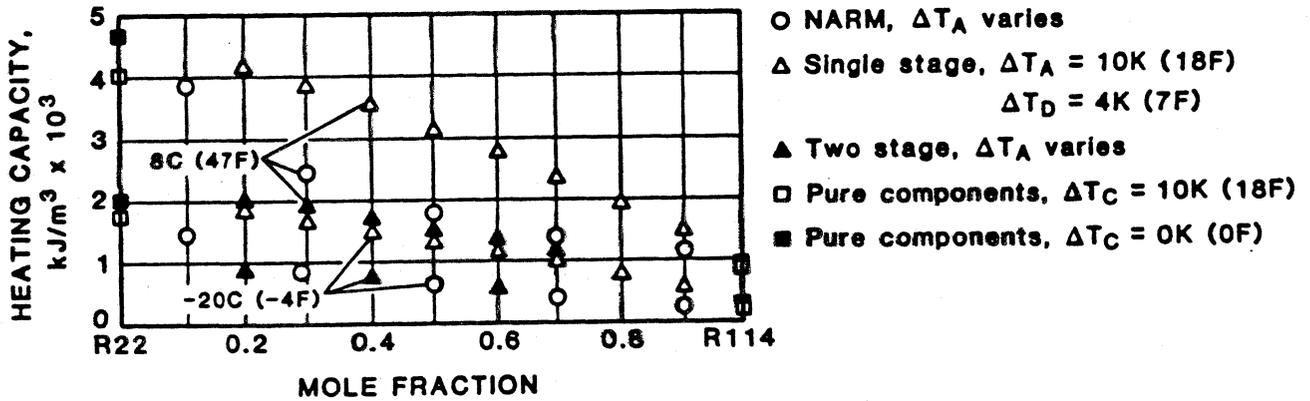


Figure 6. Heating capacity vs. composition for a conventional vapor compression cycle operating with pure and mixed refrigerants, and single- and two-stage cycles employing solution circuit(s) operating with refrigerant mixtures