

# Design considerations for refrigeration cycles

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Received 13 March 1991; revised 28 September 1991

The Carnot COP, which assumes a thermodynamically ideal cycle in which no irreversibilities exist, is often considered to be a design goal for actual cycles. However, the Carnot COP does not consider heat transfer mechanisms. Heat transfer at a finite rate is necessarily an irreversible process and unavoidable in a refrigeration cycle. The lack of consideration of rate processes reduces the usefulness of the Carnot COP as a realistic design goal. In this paper, the limitations of both thermodynamics and heat transfer are considered to identify a more realistic design goal for the COP of refrigeration cycles. The consideration of heat transfer limitations leads to a design rule for the optimum distribution of heat exchange area between the low- and high-temperature heat exchangers.

(Keywords: Carnot COP; heat transfer; refrigeration cycle)

## Considérations sur la conception de cycles frigorifiques

*On considère souvent que le COP de Carnot, qui suppose un cycle thermodynamiquement idéal sans irréversibilité, doit être atteint dans la conception des cycles réels. Cependant, le COP de Carnot ne tient pas compte des mécanismes de transfert de chaleur. Le transfert de chaleur à un taux fini est nécessairement un processus irréversible et inévitable dans un cycle frigorifique. Si l'on ne prend pas en considération ces processus, l'utilité du COP de Carnot, comme conception réaliste, est moins évidente. Dans l'article, on utilise les limites de la thermodynamique et du transfert de chaleur pour identifier un objectif de conception plus réaliste pour le COP des cycles frigorifiques. Si l'on considère les limites du transfert de chaleur, on est conduit à formuler une loi pour la configuration optimale de la zone d'échange de chaleur entre les échangeurs de chaleur à basse température et à haute température.*

(Mots clés: COP de Carnot; transfert de chaleur; cycle frigorifique)

The coefficient of performance (COP) for a refrigeration cycle is defined as the ratio of the rate of heat transfer from the refrigerated space to the power supplied to the refrigeration cycle. The second law of thermodynamics places an upper limit on the COP which is often called the Carnot COP.

$$\text{COP}_{\text{Carnot}} = \dot{Q}_L / \dot{W} = T_L / (T_H - T_L) \quad (1)$$

where  $\dot{Q}_L$  is the rate at which thermal energy is transferred from the refrigerated space,  $\dot{W}$  is the power supplied to the refrigeration cycle,  $T_L$  is the temperature of the refrigerated space and  $T_H$  is the sink temperature.

The Carnot COP, which assumes a thermodynamically ideal cycle in which no irreversibilities exist, is often considered to be a design goal for actual cycles. However, the Carnot COP does not consider heat transfer mechanisms. Heat transfer at a finite rate is necessarily an irreversible process and unavoidable in a refrigeration cycle. The lack of consideration of rate processes reduces the usefulness of the Carnot COP as a realistic design goal. In this paper, the limitations of both thermodynamics and heat transfer are considered to identify a more realistic design goal for the COP of refrigeration cycles. The consideration of heat transfer limitations leads to a design rule for the optimum distribution of heat exchange area between the low- and high-temperature heat exchangers.

## Maximum COP for a refrigeration cycle providing a specified cooling capacity

The criterion of reversible heat transfer requires infinitesimal temperature differences between the machine and external streams. For finite heat exchange areas, the infinitesimal temperature differences result in zero heat transfer rates. As a consequence, the cooling capacity supplied by a finite-sized machine operating at the Carnot COP is zero.

The heat transfer processes occurring in a refrigeration cycle are major sources of thermodynamic irreversibility. In the following analysis, a refrigeration cycle is considered in which the heat transfer processes are the only irreversibilities. The results of this analysis provide a relation between the maximum COP of a refrigeration cycle and its cooling capacity for specified heat exchange conditions.

Consider the internally reversible refrigeration cycle shown in *Figure 1*, which is designed to provide a specified cooling capacity  $\dot{Q}_L$  to a flowing stream that enters at temperature  $T_L$  and flowrate  $\dot{m}_L$ . In this process, heat is rejected to a second fluid entering at temperature  $T_H$  and flowrate  $\dot{m}_H$ . In order to provide a finite cooling capacity, heat must be transferred to the refrigeration cycle at temperature  $T_1$ , which is lower than  $T_L$ . The difference between  $T_L$  and  $T_1$  is dependent upon characteristics (e.g. surface area, external fluid flowrate) of the low-temperature heat exchanger. Similarly, the cycle must reject heat at temperature  $T_h$ , which is higher than  $T_H$  by an amount dependent on characteristics of the high-temperature

Nomenclature			
$C$	Sum of effectiveness-capacitance-rate products for both heat exchangers, defined in Equation (9) ( $\text{kW K}^{-1}$ )	$T_j$	Temperature of refrigerant at state point $j$ (K)
$\dot{C}_H$	Capacitance rate (mass-flowrate-specific-heat product) for the external high-temperature heat transfer fluid ( $\text{kW K}^{-1}$ )	$T_h$	Temperature at which heat is transferred from the internally reversible refrigeration cycle to the sink (K)
$\dot{C}_L$	Capacitance rate (mass-flowrate-specific-heat product) for the external low-temperature heat transfer fluid ( $\text{kW K}^{-1}$ )	$T_1$	Temperature at which heat is transferred to the internally reversible refrigeration cycle from the refrigerated space (K)
COP	Coefficient of performance for a refrigeration cycle	$T_H$	Entry temperature of the high-temperature external fluid (K)
$f_H$	Ratio of the condenser effectiveness-capacitance-rate product to the sum of the effectiveness-capacitance-rate products for the condenser and evaporator	$T_L$	Entry temperature of the low-temperature external fluid (K)
$h_j$	Specific enthalpy of refrigerant at state point $j$ ( $\text{kJ kg}^{-1}$ )	$(UA)_H$	Overall heat transfer coefficients for the condenser ( $\text{kW K}^{-1}$ )
$\dot{m}$	Refrigerant mass flowrate ( $\text{kg s}^{-1}$ )	$(UA)_L$	Overall heat transfer coefficients for the evaporator ( $\text{kW K}^{-1}$ )
$\dot{Q}_L$	Rate of heat transfer from the refrigerated space at temperature $T_L$ to the refrigeration cycle (kW)	$\dot{W}$	Power required to operate refrigerant cycle (excluding fan power) (kW)
$\dot{Q}_H$	Rate of heat transfer from the refrigeration cycle to the thermal sink at temperature $T_H$ (kW)	$\dot{W}_s$	Power required for isentropic compression (kW)
		$\Delta T$	Temperature difference defined in Equation (7) (K)
		$\varepsilon_L$	Effectiveness of the low-temperature (evaporator) heat exchanger
		$\varepsilon_H$	Effectiveness of the high-temperature (condenser) heat exchanger
		$\eta$	Compressor isentropic efficiency

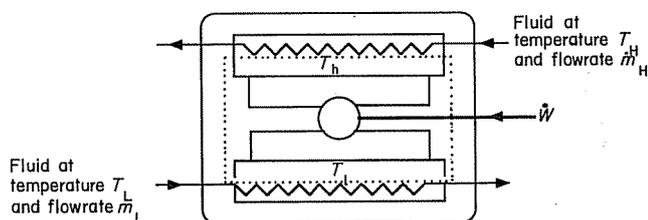


Figure 1 Schematic of an internally reversible refrigeration cycle that irreversibly transfers heat to external streams  
 Figure 1 Schéma d'un cycle frigorifique réversible, qui transfère irrégulièrement de la chaleur à des courants externes

heat exchanger. The effects of irreversibilities resulting from heat transfer to and from the cycle are considered in this section. The refrigeration cycle itself is assumed to be internally reversible, operating between uniform temperatures  $T_1$  and  $T_h$ , as in the Carnot cycle, and, approximately, in actual vapour compression cycles in which heat transfer occurs during constant-temperature vapour-liquid phase changes. The system shown within the dotted-line box in Figure 1 is essentially a Carnot cycle.

The heat transfers to and from the cycle occur by convection to flowing fluid streams having finite mass flowrates and specific heats. The rate of heat transfer to the cycle at the low temperature is

$$\dot{Q}_L = \varepsilon_L \dot{C}_L (T_L - T_1) \quad (2)$$

where  $\varepsilon_L$  is the low-temperature heat exchanger effectiveness defined by Kays and London<sup>1</sup> and  $C_L$  is the capaci-

rate (mass-flowrate-specific-heat product) of the external low-temperature heat transfer fluid.

Similarly, the rate of heat transfer between the refrigeration cycle and the sink is

$$\dot{Q}_H = \varepsilon_H \dot{C}_H (T_h - T_H) \quad (3)$$

where  $\varepsilon_H$  is the high-temperature heat exchanger effectiveness and  $C_H$  is the capacitance rate of the external high-temperature heat transfer fluid.

The coefficient of performance of the refrigeration cycle is defined by

$$\text{COP} = \frac{\dot{Q}_L}{\dot{W}} = \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L} \quad (4)$$

Because the refrigeration cycle is assumed to have no internal irreversibilities, it operates as a Carnot refrigeration cycle so that

$$\text{COP} = \frac{T_1}{T_h - T_1} \quad (5)$$

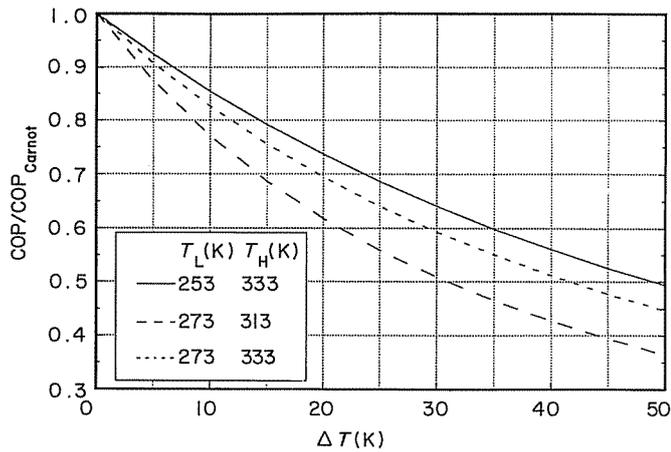
Equations (2)–(5) can be algebraically manipulated to eliminate  $T_h$  and  $T_1$ , resulting in

$$\text{COP} = \frac{(T_L - \Delta T)}{T_H - (T_L - \Delta T)} \quad (6)$$

where

$$\Delta T = \dot{Q}_L \frac{(\varepsilon_L \dot{C}_L + \varepsilon_H \dot{C}_H)}{\varepsilon_L \dot{C}_L \varepsilon_H \dot{C}_H} \quad (7)$$

The significance of  $\Delta T$  is that it is a measure of the



**Figure 2**  $COP/COP_{Carnot}$  as a function of  $\Delta T$  (defined in Equation (7))  
 Figure 2  $COP/COP$  de Carnot en fonction de  $\Delta T$  (défini dans l'équation (7))

differences between the external fluid inlet and refrigeration cycle heat exchange temperatures. This significance can easily be observed for the case in which the thermal resistance of the high-temperature heat exchanger is eliminated by allowing its capacitance rate and surface area to be very large. In this case,  $\Delta T$  in Equation (7) reduces to

$$\lim_{\varepsilon_H \dot{C}_H \rightarrow \infty} \Delta T = \frac{\dot{Q}_L}{\varepsilon_L \dot{C}_L} = (T_L - T_1)$$

If instead, the thermal resistance of the low-temperature heat exchanger is eliminated, then

$$\lim_{\varepsilon_L \dot{C}_L \rightarrow \infty} \Delta T = \frac{\dot{Q}_L}{\varepsilon_H \dot{C}_H} = \frac{COP}{COP + 1} (T_h - T_H)$$

Equations (6) and (7) provide a relation between the maximum COP of a refrigeration cycle and its cooling capacity for specified capacitance rates and inlet temperatures of the external streams. The COP in Equation (6) is a maximum COP in that there are no irreversibilities other than those resulting from the unavoidable heat transfers to and from the cycle. A plot of  $COP/COP_{Carnot}$  versus  $\Delta T$  is shown in Figure 2 for several combinations of  $T_L$  and  $T_H$ . The major point of Figure 2 is that as  $\Delta T$  (and thus  $\dot{Q}_L$  for fixed external stream conditions and heat exchanger sizes) is increased, the maximum COP must decrease. The Carnot COP can be achieved only when  $\Delta T$  is zero, which occurs only if  $\dot{Q}_L$  is zero when external flowrates are finite.

### Optimum distribution of heat exchange area

The heat exchanger effectiveness factors appearing in Equations (2) and (3) are, in general, functions of the heat exchanger design and surface area, as described by Kays and London<sup>1</sup>. When one fluid undergoes heat exchange isothermally, as for example during phase change, the effectiveness is independent of the flow arrangement. In this case:

$$\varepsilon_L = 1 - \exp(-(UA)_L / \dot{C}_L) \quad (8a)$$

$$\varepsilon_H = 1 - \exp(-(UA)_H / \dot{C}_H) \quad (8b)$$

where  $(UA)_L$  and  $(UA)_H$  are the overall heat transfer

coefficients for the low- and high-temperature heat exchangers, respectively.

The design of a refrigeration cycle requires a selection of the external stream capacitance rates and heat exchanger parameters which determine the physical size and cost of the heat exchangers. Increasing the effectiveness-capacitance-rate product of a heat exchanger generally increases its size and cost, but not in a linear manner. However, increasing the effectiveness-capacitance-rate product also decreases parameter  $\Delta T$  in Equation (7), which means the refrigeration cycle can operate at a higher COP in providing a specified cooling capacity. An engineering compromise must be reached between the first cost of the refrigeration equipment and its operating costs. A problem involved in this optimization is how to allocate the total heat exchanger area between the two heat exchangers so as to minimize the power required to provide a specified cooling capacity for a fixed first cost. A reasonable postulate is that a larger fraction of the total heat exchanger  $UA$  should be allocated to the high-temperature heat exchanger since it must transfer more energy than the low-temperature heat exchanger. However, this is not the case.

Consider a situation in which a refrigeration cycle is to supply a specified cooling capacity,  $\dot{Q}_L$ , operating with external streams which enter at specified temperatures  $T_L$  and  $T_H$ . Equations (2)–(5) and (8) provide six equations involving 10 undetermined variables, namely  $T_1$ ,  $T_h$ , COP,  $\dot{Q}_H$ ,  $\varepsilon_L$ ,  $\dot{C}_L$ ,  $\varepsilon_H$ ,  $\dot{C}_H$ ,  $(UA)_L$ , and  $(UA)_H$ , resulting in four degrees of freedom. Equations (2) and (3) demonstrate that only the products of the effectiveness and capacitance rates, not their individual values, enter into the refrigeration cycle performance calculations. As a result, it is possible to reduce the number of degrees of freedom from four to two in the following optimization study by considering the effectiveness-capacitance-rate product for each heat exchanger to be a single variable. In this case, Equations (8a) and (8b) and  $(UA)_L$  and  $(UA)_H$  are eliminated, resulting in four equations with six unspecified variables. (The  $UA$  and capacitance rate values that result in the optimum effectiveness-capacitance-rate product can be determined in separate optimizations for each heat exchanger in which Equations (8a) and (8b), in addition to pumping power, duct noise and comfort considerations are considered.) Two additional relations between the remaining six variables are required in order to fix the design. One relation results by placing a limit on the total heat exchanger investment such that

$$\varepsilon_L \dot{C}_L + \varepsilon_H \dot{C}_H = C \quad (9)$$

where  $C$  is a specified constant. Equation (9) produces an effect similar to setting the sum of  $(UA)_H$  and  $(UA)_L$  to a fixed constant, but it is algebraically simpler and more general in that it directly considers the effects of changes in the external fluid capacitance rates. A second relation is obtained by setting the derivative of the COP with respect to any one of the five other undetermined variables (such as  $\varepsilon_L \dot{C}_L$ ) to zero so as to maximise the COP.

Although the algebra is somewhat complicated, this set of six equations can be solved analytically. A remarkable conclusion obtained from the solution is that, when the COP is at a maximum,

$$\varepsilon_L \dot{C}_L = \varepsilon_H \dot{C}_H \quad (10)$$

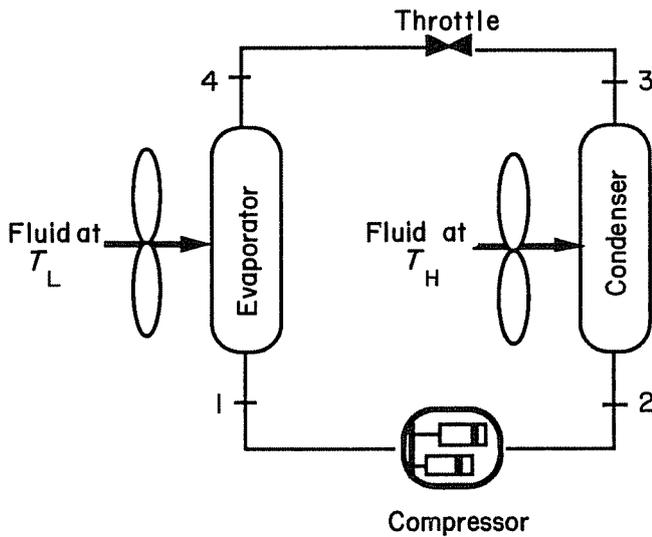


Figure 3 Schematic of a vapour-compression refrigeration cycle showing state point locations  
 Figure 3 Schéma d'un cycle frigorifique à compression de vapeur montrant les localisations des points d'état significatifs

Equation (10) is valid for any specified values of  $C$ ,  $\dot{Q}_L$ ,  $T_L$  and  $T_H$ . If the capacitance rates of the external streams are equal, Equation (10) indicates that the optimum COP will be attained when  $(UA)_H = (UA)_L$ .

**Actual vapour compression cycle performance**

Equation (10) indicates that the heat exchangers in a refrigeration cycle should be treated equally in order to achieve optimum performance, even though the high-temperature heat exchanger must transfer energy at a larger rate. However, Equation (10) was derived for a refrigeration cycle with no irreversibilities other than those due to heat transfers to and from the cycle. In this section, the validity of this result is investigated for vapour compression machines that have additional irreversibilities due to vapour compression and expansion and perform in a manner dependent on the thermodynamic properties of the refrigerant.

The standard vapour-compression cycle shown in Figure 3 is investigated with R12 as the refrigerant. Control of the cycle is assumed such that, during steady operation, saturated vapour enters the compressor at state 1 and saturated liquid exits the condenser at state 3. The compressor operation is described in terms of an isentropic efficiency,  $\eta$ , so that its power requirement is given by

$$\dot{W} = \dot{m} (h_2 - h_1) = \dot{W}_s / \eta \tag{11}$$

where  $\dot{m}$  is the mass flowrate of the refrigerant,  $h_1$  and  $h_2$  are the specific enthalpies of the refrigerant at state points 1 and 2, and  $\dot{W}_s$  is the power required for isentropic compression. The refrigerant enters the condenser at state 2 in a superheated state. However, the majority of the heat transfer takes place while the refrigerant is condensing. This heat transfer process can be described, approximately, in terms of a heat exchanger effectiveness based on the condensation temperature,  $T_3$ , as suggested by Stoecker and Jones<sup>2</sup>.

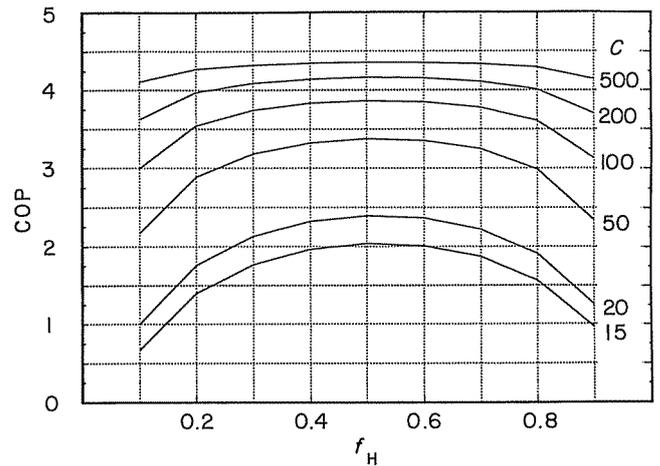


Figure 4 COP versus the heat transfer factor  $f_H$  (Equation (16)) for a range of values of  $C$  (Equation (9)) with  $\eta = 0.60$ ,  $T_L = 0^\circ\text{C}$ ,  $T_H = 40^\circ\text{C}$  and refrigerant R12  
 Figure 4 COP par rapport au facteur de transfert de chaleur  $f_H$  (équation (16)) pour une série de valeurs de  $C$  (équation (9)) avec  $\eta = 0.60$ ,  $T_L = 0^\circ\text{C}$ ,  $T_H = 40^\circ\text{C}$  et du R12 comme frigorigène

$$\dot{Q}_H = \dot{m} (h_2 - h_3) = \varepsilon_H \dot{C}_H (T_3 - T_H) \tag{12}$$

The throttling process is assumed isenthalpic:

$$h_4 = h_3 \tag{13}$$

The low-temperature heat transfer occurs while the refrigerant vaporizes at temperature  $T_1$ :

$$\dot{Q}_L = \dot{m} (h_1 - h_4) = \varepsilon_L \dot{C}_L (T_L - T_1) \tag{14}$$

The COP of the cycle (neglecting the power required to move the external fluids) is

$$\text{COP} = \frac{\dot{Q}_L}{\dot{W}} \tag{15}$$

To investigate the effect of relative heat exchanger size, a factor  $f_H$  is defined as

$$f_H = \frac{\varepsilon_H \dot{C}_H}{C} \tag{16}$$

where  $C$  is defined by Equation (9). The factor  $f_H$  is related to the fraction of the total heat exchanger area (for the condenser and evaporator) that is used by the condenser, but the relation between heat exchanger area and  $f_H$  is not linear.

Equations (11)–(16) have been solved numerically for a range of values of  $C$ ,  $\eta$ ,  $T_L$  and  $T_H$  by using thermodynamic property data for several different refrigerants. The equation-solving program<sup>3</sup> EES, which incorporates refrigerant property data algorithms, was used for this purpose. Representative results are shown in the following figures.

Figure 4 shows how the COP varies with  $f_H$  for a range of values of  $C$  with  $\dot{Q}_L = 10 \text{ kW}$ ,  $T_L = 0^\circ\text{C}$ ,  $T_H = 40^\circ\text{C}$  and  $\eta = 0.60$  with R12 as the refrigerant. The refrigerant mass flowrate varies as necessary to achieve the specified capacity. Increasing  $C$  increases the total (condenser and evaporator) heat exchange capability and, as a result, the COP increases. The COP approaches an asymptotic

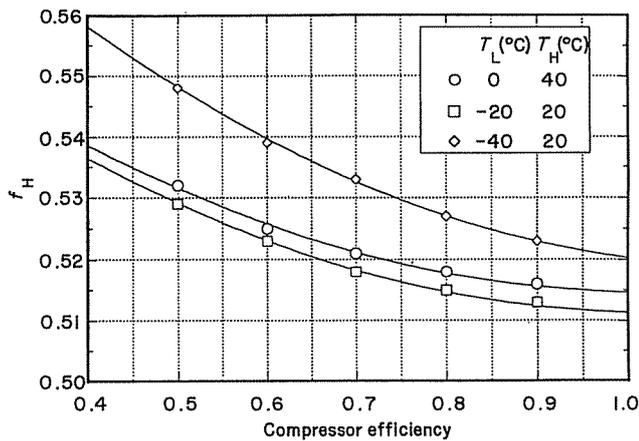


Figure 5 Optimum values of  $f_H$  versus compressor isentropic efficiency for various values of  $T_L$  and  $T_H$  and refrigerant R12

Figure 5 Valeurs optimales de  $f_H$  par rapport au rendement isentropique du compresseur pour plusieurs valeurs de  $T_L$  et  $T_H$  et pour le frigorigène R12

value for values of  $C$  greater than about 500. At any specified value of  $C$ , the COP is at a maximum when  $f_H$  is approximately (but not exactly) 0.5. The results in Figure 4 can be scaled for any cooling capacity since they depend on the ratio of  $Q_L/C$ . Similar results to those in Figure 4 were obtained for other values of  $T_L$  and  $T_H$  and for other refrigerants.

In Figure 5 the value of  $f_H$  that maximizes the COP of the cycle is plotted as a function of compressor isentropic efficiency. The results in this figure are nearly independent of the value of  $Q_L/C$ . Figure 5 shows that, as the compressor efficiency decreases, the fraction of total heat exchange area needed by the condenser to achieve a maximum COP increases. This additional compressor area is needed to dissipate the additional compressor power required. The optimum value of  $f_H$  is slightly affected by the values of  $T_L$  and  $T_H$ . However, the opti-

imum value of  $f_H$  is still quite close to 0.5. Results similar to those in Figure 5 were found for other refrigerants.

### Conclusions

The Carnot analysis provides an upper bound on the COP of a refrigeration cycle, but this upper bound can only be attained as the cooling capacity approaches zero. A more useful design goal for the COP is provided by Equation (6) for a refrigeration cycle that provides a specified cooling capacity with no irreversibilities other than those resulting from heat exchange between the cycle and external streams. The analysis presented here assumes that the heat transfers occur to and from the refrigeration cycle isothermally, as in the Carnot and the ideal vapour-compression cycles. The COP given in Equation (6) could be exceeded by a refrigeration cycle that reduces heat transfer irreversibilities by transferring heat over a temperature range, as in a cycle using a non-azeotropic refrigerant.

Analysis of the internally reversible refrigeration cycle indicates that its COP is maximized for a specified cooling capacity when the product of the heat transfer effectiveness and external fluid capacitance rate is the same for both heat exchangers. The result is found to be true, approximately, for actual vapour-compression cycles as well, despite the irreversibilities of throttling and non-isentropic compression and the effects of refrigerant thermodynamic properties. This result is directly useful in identifying economic optimum refrigeration cycle designs.

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# Bubble pressures and saturated liquid molar volumes of the propane (1)–dichlorotetrafluoroethane(2)–trichlorotrifluoroethane(3) ternary system and of the three corresponding binaries

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Received May 1989; revised 4 September 1991

An apparatus described previously has been used for the present measurements. It is based on a synthetic static method with a variable-volume cell. Results are given at different temperatures between 343 and 423 K for three binary mixtures: propane–dichlorotetrafluoroethane ( $C_3H_8$ –R114), propane–trichlorotrifluoroethane ( $C_3H_8$ –R113), dichlorotetrafluoroethane–trichlorotrifluoroethane (R114–R113), and the corresponding ternary propane–dichlorotetrafluoroethane–trichlorotrifluoroethane ( $C_3H_8$ –R114–R113). The two binaries with propane are well represented by a one-parameter  $\delta_{ij}$  Peng–Robinson equation of state to within less than 1% for pressures and 6%, without volume translation, for saturated liquid molar volumes. By using a volume translation, an improved volume representation, 2%, for the propane–dichlorotetrafluoroethane system is achieved. For the third binary system,  $\delta_{ij} = 0$  is the best choice (representation is within 0.6% for pressure and 2% for molar volumes through a volume translation). Use of values of the binary interaction parameters  $\delta_{ij}$  established for binary systems enables good prediction of ternary data (representation to within 1% for pressures and 3.8% for saturated molar volumes). Volume translation does not improve the representation of the ternary saturated liquid molar volumes because it does not do it for the propane–trichlorotrifluoroethane system.

(Keywords: bubble pressure; saturated liquid molar volume;  $C_3H_8$ –R114–R113)

## Pressions de bulle et volumes molaires de liquides saturés pour le mélange ternaire propane(1)-dichlorotétrafluoroéthane(2)-trichlorotrifluoroéthane(3) et les trois binaires correspondants

Les mesures présentées ici ont été réalisées à l'aide d'un appareil décrit précédemment. Ce dernier est basé sur le principe d'une méthode synthétique avec utilisation d'une cellule à volume variable. Les résultats sont donnés à des températures comprises entre 343 et 423 K pour les trois systèmes binaires suivants: propane–dichlorotétrafluoroéthane ( $C_3H_8$ –R114), propane–trichlorotrifluoroéthane ( $C_3H_8$ –R113), dichlorotétrafluoroéthane–trichlorotrifluoroéthane (R114–R113) et pour le ternaire correspondant: propane–dichlorotétrafluoroéthane–trichlorotrifluoroéthane ( $C_3H_8$ –R114–R113). Les deux binaires contenant du propane sont bien représentés avec l'équation de Peng–Robinson à un paramètre, et ce, à mieux que 1% pour les pressions et 6% pour les volumes molaires de liquides saturés (sans translation de volume). La méthode de translation de volume permet une amélioration sensible de la représentation du mélange propane–dichlorotétrafluoroéthane:  $\sigma^s = 2,1\%$ . Pour le troisième binaire,  $\delta_{ij} = 0$  est le meilleur choix (la représentation est à 0.6% pour les pressions et à 2% pour les volumes molaires de liquides saturés moyennant une translation de volume). L'utilisation des paramètres d'interaction binaire  $\delta_{ij}$ , ajustés sur les systèmes binaires, permet une bonne prédiction des données ternaires (représentation à 1% sur les pressions et à 3.8% sur les volumes molaires de liquides saturés). Une translation de volume n'améliore pas la représentation des volumes molaires à saturation du ternaire en raison de la mauvaise représentation des volumes du système propane–trichlorotrifluoroéthane.

(Mots clés: pression de bulle; volume molaire de liquide saturé;  $C_3H_8$ –R114–R113)

This work is part of a project for constructing a large database on refrigerant mixtures. A synthetic method was developed to obtain very accurate determinations of mixture compositions (e.g. masses of components in the range 1–30g are obtained from weighing to within  $10^{-4}$  g on an analytical balance). By working with a variable-volume cell it is possible to record pressure against volume and to determine bubble pressures and saturated liquid molar volumes from the break points displayed by such records at temperatures below the critical temperature. At the break point, the whole system is in a liquid

state, and the mole fraction composition of the mixture is known from the weight of its components.

### Experimental

#### Apparatus

Details of the equipment are given in a paper by Fontalba *et al.*<sup>1</sup>, but this equipment was used in a simplified form, as described in another paper<sup>2</sup>.