

## **R-407C: PRACTICAL CONSEQUENCES OF COMPOSITION SHIFT**

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### **Abstract:**

The widespread use of R-407C as a replacement for R-22 in air-conditioning applications is the first general use of a refrigerant mixture with a significant temperature glide. This paper discusses the causes of temperature glide (as being a consequence of the difference in composition between the liquid and vapour phases in equilibrium), and the consequential effects on system operation. System performance anomalies, in terms of what can and cannot be attributable to composition shift, are discussed.

### **Background:**

The refrigeration industry is well accustomed to handling and working with volatile (liquids which change to a vapour phase, and back, readily) fluids. The original, purpose developed, fluorocarbon refrigerants, introduced from the 1930s, were single substances: R-11, R-12 and R-22.

With the increasing sophistication air conditioning equipment, the use of mixed refrigerant working fluids has become accepted practice.

The phase-out of CFCs, and later of HCFCs, spurred an intense development effort in the late 1980s and 1990s to find safe refrigerant fluids that could be used as replacements for these Ozone Depleting Substances (ODSs). Attention quickly focussed on selected HFCs which would provide the necessary safety and non-ozone-depleting properties.

In the case of R-22 a single substance replacement HFC with adequate safety and physical property characteristics was not available and a 3 component mixture, R-407C, which has similar properties to R-22 was adopted for new air-conditioning systems in Europe.

### **Thermophysical Properties of Fluids:**

Mechanical refrigeration is a process by which heat is transferred from a lower to a higher temperature. The most commonly used refrigeration technology uses the evaporation of a working fluid to extract heat from the medium to be cooled, thus lowering its temperature. In general, refrigeration systems (with the exception of water evaporation cooling systems) use the working fluid in a closed circuit with the heat being absorbed in a heat exchanger known as the evaporator, and rejected at another heat exchanger: the condenser. Heat absorption – cooling (evaporation), and heat rejection, are, in most refrigeration systems, physical processes involving a phase change between vapour and liquid phases of the working fluid. These processes occur at different temperatures. Control of the evaporation and condensation temperatures is effected by controlling the pressures of the working fluid at evaporation and condensation. Compressors and expansion devices are used for this purpose.

The working refrigerant fluid is a critical part of the refrigeration system. Its thermophysical properties are important in defining its application, and the energy efficiency of the refrigeration system itself.

In this paper we will discuss the vapour/liquid equilibrium Pressure, Temperature and Composition properties of mixed refrigerants and the impact of changes in refrigerant composition on system operation.

### **Refrigerant fluid mixtures – Ideal fluids**

Refrigerant mixtures can be considered as exhibiting solvent-solute behaviour in which the components of the mixture are both solvent and solute simultaneously. The mixture will obey Dalton's Law of Partial Pressures [Ref. 1] (which states the pressure exerted by each component of the mixture will be additive to the pressures of each of the other components, the total pressure of the mixture being the sum of the individual pressures of all the components):

$$P = p_1 + p_2 + p_3 + \dots + p_n \quad \text{Equation 1}$$

For a mixture exhibiting ideal behaviour the equilibrium vapour pressure of each component (the saturation pressure at a given temperature),  $p_i$  (etc.) in the above equation, is given by Raoult's Law [Ref. 2]:

$$p_i = p_i^0 \cdot \tilde{n}_i \quad \text{Equation 2}$$

Thus for a mixture of two or more components, where the mixture exhibits ideal behaviour, the equilibrium (saturation) pressure of the mixture at any given temperature can be calculated easily from Raoult's and Dalton's Laws.

### **Refrigerant fluid mixtures – Real fluid systems**

In the case of refrigerant mixtures Raoult's Law is obeyed, in reality, only over a narrow range of composition, and only for the component of the mixture which has its mole fraction close to 1 (that is to say the equivalent of the solvent in a dilute solution). Those components which are present as solutes in dilute solution, i.e. which have their mole fractions in the mixture close to zero, will obey Henry's law [Ref. 3] over a limited composition range:

$$P_i = K_i \cdot \tilde{n}_i \quad \text{Equation 3}$$

As the concentration of the dilute component (the solute) is increased in a mixture, the mixture ceases to follow Raoult's Law for the major component and Henry's Law for the minor component and the mixture deviates from ideality. The deviation can be either positive (in which the partial pressures of the two components are higher than predicted) or negative.

### **The implications of composition difference between liquid and vapour phases**

Arising from the fact that most fluid mixtures contain component fluids with different saturation pressures (at a given temperature), the concentration of the individual components in the vapour phase, when in equilibrium with the liquid phase, is different from the liquid phase composition (azeotropic mixtures being the exception).

The immediate consequence of this composition difference between the two phases in equilibrium is that the vapour phase of a standard refrigerant mixture stored in a container is not necessarily within the allowed (specification) composition range for that refrigerant. To ensure that any product removed from the refrigerant container is indeed within specifications, it must be removed from the container from the liquid phase.

A second, also important, consequence of the difference in equilibrium composition between the liquid and vapour phases relates to the changes in composition as the mixture evaporates (changes from a liquid to a vapour) or condenses from the vapour phase to become liquid.

As the liquid phase of a fluid mixture evaporates (passes from the liquid to the vapour phase at a constant pressure) its composition will change. Because the proportion of the more volatile component is higher in the vapour phase than in the liquid phase, it will deplete from the liquid phase more rapidly than the less volatile component, as the liquid evaporates. Both the more volatile and the less volatile components will evaporate together (however in different proportions) **and the last drop of the liquid phase to evaporate will still contain both components, albeit in different proportions than at the start of evaporation.**

Many commercial refrigerants are mixtures of 3 or more components. Such mixtures will exhibit similar behaviour to binary mixtures including exhibiting non-ideality (deviations from Raoult's Law). Equations of State have been developed to describe the thermodynamic properties for standard (commercial) multi- component refrigerant blends. [ References 4, 5 and 6]

Multi-component refrigerant blends exhibit similar characteristics to those of binary mixtures, having different liquid and vapour saturation compositions and consequently different equilibrium Pressure-Temperature relationships for the saturated liquid and saturated vapour (Bubble Point and Dew Point) conditions. The saturated liquid and vapour phases will contain, at any given pressure (or temperature), all the components of the mixture, but in different proportions. Using R-407C (R-32/R-125/R-134a in the mass proportions 23/25/52%) as an example, at the Bubble Point pressure equivalent to 10°C, the equilibrium compositions are given in table 2:

**Table 2**  
**Bubble Point and Dew Point Compositions**  
**R-407C (776 kPa Pressure)**

|               | Bubble Point |        | Dew Point |        |
|---------------|--------------|--------|-----------|--------|
|               | Liquid       | Vapour | Liquid    | Vapour |
| <b>R-32</b>   | 23%          | 33.9%  | 13.7%     | 23%    |
| <b>R-125</b>  | 25%          | 32.6%  | 17.0%     | 25%    |
| <b>R-134a</b> | 52%          | 33.5%  | 69.3%     | 52%    |

At this pressure (776 kPa) the Dew Point temperature of R-407C is 15.9°C, thus R-407C can have a temperature Glide in an evaporator of up to 5.9K.

## Change in Composition

Because many refrigerant blends do have a significant composition difference between their liquid and vapour phases (when at equilibrium) a transfer of a significant mass of either phase to the other phase can result in a change in the composition of each individual refrigerant phase in the system. Such a composition change is known as a Composition Shift. There are several situations where composition shift can be important. Such situations fall into two groups:

- a) **Closed systems.** In which the overall mass of refrigerant in a system (with a fixed total volume) does not change. The proportion of the refrigerant charge in the liquid phase might change as a result of changing operating conditions.
- b) **Non-closed (or variable volume) systems.** These situations include transfer between refrigerant containers (or containers and refrigeration systems) and, importantly, leaking systems (or containers).

We will discuss the second group first.

The first consideration (which has been discussed above) for scenario (b) is that of intentional transfer of refrigerant. Because the vapour phase in equilibrium with a liquid refrigerant mixture will generally have a different composition from that of the liquid phase, transferring the vapour phase will result in a refrigerant of the wrong composition being transferred. (The transferred refrigerant will be rich in the more volatile component(s) of the blend.) This is the reason for the recommended practice of transferring a refrigerant “blend” only from the liquid phase.

If a refrigeration system (or a container) leaks in such a way that only the vapour phase leaks, the remaining refrigerant in the system will become progressively richer in the less volatile component(s) of the refrigerant mixture. The pressure, at a given reference temperature, of the residual refrigerant will decrease.

In practice for an operating refrigeration system such composition-shifting leaks are relatively rare: In most leak scenarios the liquid phase leaks (or is expelled) together with the vapour phase and there is only a very slight composition change, if any, of the residual charge. Such composition shifting leaks can occur, however, during system shut-down. For many refrigerant mixtures (this has been demonstrated with R-407C, which has a relatively high composition shift. [Ref. 7]) topping up the refrigeration system with the correct refrigerant after a leak will restore the system performance parameters (pressures, operating duty, power draw) to levels which are not noticeably different from normal.

For closed refrigeration systems (scenario (a) above) there are circumstances in which the proportion of the refrigerant charge as liquid or vapour within the system can change, and the mass of either phase at a specific location in the system can vary. These changes are often a consequence of transient conditions during system start-up (or stopping), or of changes in cooling (or heating) load.

One equipment configuration where significant composition shifts are possible for mixed refrigerants is that of pumped refrigerant systems where a low pressure receiver or a “flooded evaporator” is used. As the cooling load changes considerable changes in the relative mass of liquid:vapour refrigerant can occur.

For a refrigerant such as R-407C in which there is a very large composition difference between the Bubble Point and Dew Point conditions, large composition swings during operation of such systems are possible. Significant vapour composition swings are particularly undesirable when centrifugal compressors are used, and, as a consequence, R-407C cannot be used satisfactorily in a centrifugal compressor chiller. Positive displacement compressors are recommended for such equipment configurations. (It should be noted that pool boiling Heat Transfer coefficients are also adversely affected by wide composition differences between liquid and vapour phases. As a consequence shell-side refrigerant evaporators and condensers are also not recommended for use in R-407C water chillers. Further discussion of this aspect is beyond the scope of this paper. See[Ref. 8])

Because the vapour in equilibrium with the liquid refrigerant will have a different composition from that of the liquid, in refrigeration systems where there is the possibility for liquid phase refrigerant to become static, or “stagnant” (albeit in contact with the refrigerant vapour), the circulating (or working) refrigerant composition can be different from that of the standard composition. A significant fraction of the overall refrigerant charge would have to be “stagnant” to have a significant effect on the composition of the refrigerant involved in the working refrigeration cycle. For the case of R-407C if some 30% of the mass of the original charge in a DX system becomes “stagnant” the new composition of the circulating refrigerant (richer in R-32 and R-125 than standard R-407C) will result in a higher condensing pressure (by approx. 5%) and a greater cooling capacity for the system of around 5% also. [Ref. 9]

### **The Effect of Composition Changes in closed (non-leaking) R-407C Systems**

As discussed refrigerant mixtures such as R-407C have, in a closed system at a given temperature or pressure, two composition extremes: The vapour in equilibrium with Saturated Liquid (at the Bubble Point) and the liquid in equilibrium with Saturated Vapour (at the Dew Point). The Bubble Point and Dew Point have different Pressure/Temperature conditions. At any point between the two Pressure/Temperature curves the R-407C in a closed system will exist as the two phases in equilibrium, with the relative masses of liquid and vapour (or Vapour Quality) dependent on the pressure and temperature of the system. As an example at a temperature of 10°C and 709 kPa (see Table 3) the vapour quality of the system will be approximately 50% - the temperature being mid-way between the Bubble Point and Dew Point temperatures. (At a constant 10°C the Bubble Point and Dew Point Pressures are substantially different also, 709 kPa being almost at the mid point.) Outside the pressure and temperature ranges defined by Bubble Point and Dew Point conditions the refrigerant mixture will exist as either a sub-cooled liquid, or as a superheated vapour.

At each of the extremes represented by the Bubble and Dew Points the composition of the refrigerant in equilibrium with the bulk mass (at its nominal composition) will be different. These compositions represent the composition boundaries to which R-407C can composition shift. These boundary compositions occur when there is zero mass in that specific phase.

Table 3 gives one such set of equilibrium conditions for R-407C. (The numbers in parentheses identify the condition. E.g. (1) is the Bubble Point Temperature at 709 kPa, etc.)

Table 4 gives the compositions at the conditions given in Table 3. These compositions are not the composition of a bulk phase, but are the compositions in equilibrium with the bulk phase at the very start (or end) of phase change.

**Table 3**  
**R-407C at 10°C and 709 kPa**

|                    | <b>Bubble Point</b> | <b>Dew Point</b> | <b>At</b> |
|--------------------|---------------------|------------------|-----------|
| <b>Temperature</b> | 7°C (1)             | 13°C (2)         | 709 kPa   |
| <b>Pressure</b>    | 776 kPa (3)         | 644 kPa (4)      | 10°C      |

**Table 4**  
**R-407C “Last Drop” Compositions at**  
**Conditions given in Table 3**  
(Bulk Composition: 23/25/52% mass basis)

| <b>Point</b> | <b>State</b>  | <b>R-32%</b> | <b>R-125%</b> | <b>R-134a%</b> |
|--------------|---------------|--------------|---------------|----------------|
| <b>1</b>     | <b>Vapour</b> | 34.1         | 32.8          | 33.1           |
| <b>2</b>     | <b>Liquid</b> | 13.5         | 16.8          | 69.7           |
| <b>3</b>     | <b>Vapour</b> | 33.9         | 32.6          | 33.5           |
| <b>4</b>     | <b>Liquid</b> | 13.3         | 16.5          | 70.2           |

These compositions represent the extreme limits for the conditions of pressure and temperature given. As significant mass of the “minority” phase forms so its composition moves towards that of the standard mixture (in the case of R-407C: 23% R-32, 25% R-125 and 52% R-134a).

Table 3 shows that, for R-407C, the maximum pressure change due to a change in composition in a closed system will be of the order of 1.3 bar (when at 10°C). This maximum pressure change range does depend on the temperature/pressure also. For example, for R-407C again, this time at 45°C, the maximum pressure range is 2.2bar. In a real operating refrigeration circuit, if there is a composition shift due to product “segregation” in the system, the pressure changes will be substantially lower than these values because there will be a finite mass of refrigerant with changed composition and thus the actual composition of the shifted part will be closer to the standard refrigerant composition, i.e. the pressure will be closer to that of the standard mixture.

Separation of the components further than the boundaries set by the Bubble and Dew Point compositions can only occur through a process of fractional distillation. Fractional distillation is a process in which (usually on a continuous basis) a fraction of the original mass of the mixture is evaporated, condensed to liquid phase and partially evaporated again. This new vapour phase is condensed and again partially vaporised, the process being repeated to obtain the separation needed. Each new condensed liquid fraction does not mix with its precursor liquid fraction, but is in a separate equilibrium with the vapour phase. The various stages of evaporation and condensation occur at what are called theoretical plates in the distillation process.

Each theoretical plate in a distillation process will operate at different temperatures and/or pressures.

As the distillation process involves the transfer of mass, it requires energy input (usually in the form of heat) at the high boiling end of the process and recovery of heat of condensation of the low boiling component(s).

### **Can fractional distillation occur in a refrigeration system??**

It is possible to visualise that conditions, in say a DX evaporator, might allow distillation to occur: there is a process of vapourisation (evaporation) of the refrigerant along a tube (or tubes) with the possibility of liquid and vapour phases moving in counter-flow. The evaporation is driven by the input of heat. The comparison with an fractional distillation process ends here, however. In a fractional distillation process the theoretical plates operate at either substantially different pressures, or, if at equivalent pressures, a negative temperature gradient (from liquid inlet to vapour outlet). Neither of these two situations (nor a combination of either) is feasible in a standard normal refrigeration system. Also, in the closed loop of a refrigeration system, the working fluid is continually re-mixed. No component is added or removed from the system. The total overall refrigerant composition does not change. In an operating refrigeration system the pressure and/or temperature changes are limited to the extreme conditions set by the Bubble and Dew Point conditions of the specific refrigerant mixture. Transient changes in composition within the system will be to within the limits defined by the Bubble and Dew Point compositions.

### **Conclusions**

Refrigerant blends do have different saturated compositions at any given temperature or pressure. These composition differences give rise to the phenomenon called Temperature Glide.

While a large value for the Temperature Glide does indicate a large composition difference between saturated vapour and liquid phases, a small temperature glide does not imply that the composition difference is insignificant. Composition shifting in a closed refrigeration circuit using R-407C is unlikely to result in large (>>1bar) pressure changes from expected values.

### **Symbols used in this Paper:**

|               |   |
|---------------|---|
| $K_i$         | - Henry's Law constant for component "i"                                  |
| $n_i$         | - mass of component "i" in molar units                                    |
| $\tilde{n}_i$ | - the mole fraction of component "i"                                      |
| $P$           | - the absolute pressure   |
| $P_i$         | - the partial pressure of component "i"                                   |
| $p_i^0$       | - the saturated vapour pressure of component "i" at a defined temperature |
| $R$           | - The Gas Constant  |
| $T$           | - Temperature   |
| $V$           | - Volume  |

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