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ASHRAE RP-923

WATER SOLUBILITY AND CLATHRATE HYDRATES IN HFC REFRIGERANTS AND REFRIGERANT BLENDS

by

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ABSTRACT

This research project determined the solubility of water in HFC refrigerants R-134a, R-32, R-143a, R-125, and R-152a and HFC refrigerant blends R410A, R407C, R507A, and R404A from -100°F (-73°C) to 160°F (71°C) (or within 15°F (8.3°C) of critical temperature) in liquid refrigerant and in the presence of refrigerant clathrate hydrate below 60°F (16°C). Water solubility curves were constructed for each refrigerant and blend by measuring water content at 20°F (11°C) increments over the entire temperature range. In this study, all refrigerants in the presence of 1% w/w water were confirmed to form stable solid clathrate hydrates between 50°F (10°C) and 60°F (16°C), with R-32 and blends containing R-32 demonstrating stable clathrate hydrates up to 80°F (27°C).

Evaluation of water solubility in HFC refrigerants and blends was performed using a small, bench-top unit constructed of type 316 stainless steel that was temperature controlled, inexpensive to build, and easy to operate. The test cell/unit controlled the temperature of both the liquid and vapor refrigerant phases. This instrument and a Karl Fischer coulometer were used to measure the water equilibrium in solution of the aforementioned HFC refrigerants and blends at the specified temperatures, as well as water equilibrium between clathrate hydrate and liquid refrigerant. This project determined the maximum amount of water permissible for operating systems down to -40°F (-40°C).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

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INTRODUCTION

One of the universal contaminants in hermetic systems is water, which can enter the system through manufacturing and other means. HVAC sealed systems are manufactured, evacuated, and nitrogen purged with heat to remove moisture before refrigerant is added. The solubility of water in refrigerant is important nonetheless. Knowing the solubility properties of water in refrigerant is necessary to help manufacturers in the production of sealed systems, the calculation of desiccant quantity, the determination of water distribution ratios, and the prevention of freeze-up conditions. Normally, a properly desiccated system has a water content below 50 ppm, which generally does not pose a problem.

Desiccants play the vital role of maintaining refrigerant systems in an acceptably dry state and free of circulating inorganic acid contaminants (Cavestri and Schooley 1998). Historically, refrigerant systems were CFC and HCFC chemicals with mineral or alkylbenzene lubricants. However, the latest systems are quite different; HFC refrigerants generally use polyolesters, which are more polar oxygen bearing lubricants. The equilibrium water solubility in HFCs may be different and requires measurement. Since the circulating water equilibrium conditions are desiccant/temperature dependent, knowledge of water equilibrium with desiccant at various temperatures is a necessity (Cavestri and Schafer 1999a and 1999b).

Unlike CFC refrigerants, HFC and HCFC refrigerants carry hydrogen atoms that create a polarized portion of the molecule, increasing the solubility of water. Refrigerants that are fully substituted, such as R-12, carry the least amount of water in solution (ASHRAE 1994 and DuPont 1982a). One or two hydrogen-substituted carbon refrigerants such as R-22 and R-134a provide the best solubility for water.

Regardless of which refrigerant or lubricant is used, moisture can cause problems in refrigerating and air-conditioning systems. These problems are avoidable when loose and solid filter driers are used with new and/or field-serviced equipment, or with refrigerant reclaim and recycle equipment. For maximum life and reliability, it is essential for a system to be maintained at a minimum circulating water content.

BACKGROUND

No measured data is available regarding the solubility of water in HFC refrigerants R-32, R-143a, R-125, and R-152a and blends of these refrigerants, R410A, R407C, R507A, and R404A. While data for R-123, R-134a, and R-22 is available (ASHRAE 1994), literature on simple, cost-effective test methods that provide unequivocal analytical data is not. Thrasher *et al*. (1993), using an NMR to measure dissolved water, reported measurement difficulties at low temperatures.

The temperature range of this research study was -100°F (-73°C) to 160°F (71°C), or within 15°F (8.3°C) of critical temperature. The formation of clathrate hydrates was a serious point of concern, since their constraints on this project were unknown. However, an abundance of information on clathrate hydrates has been published by such researchers as Chinworth and Katz (1947), Akiya *et al*. (1997), Holder *et al*. (1988), Walker *et al*. (1960), and Sloan (1990). The main objective of this research was to determine the solubility of water in liquid refrigerants; this is simple in theory, but difficult in practice. Logic dictated the development of a test device and method that was insensitive to temperature, refrigerant changes, and solid suspensions. The method was actualized with a device custom-built from readily available components.

ANALYTICAL PROTOCOL

The initial protocol was to load an apparatus that circulated a quantity of degassed refrigerant and dissolved water. Dissolved air was reported to reduce water solubility at the specified temperature and pressure in an excess of 2.7% deionized, degassed water (w/w) (Thrasher *et al*. 1993).

Test Unit 1

The first test device (Figure 1), designed for safety and high pressure, was intended to promote slow agitation of the water and liquid refrigerant and to incorporate the vapor space in a temperature controlled environment. This was similar in concept and design to a device used by

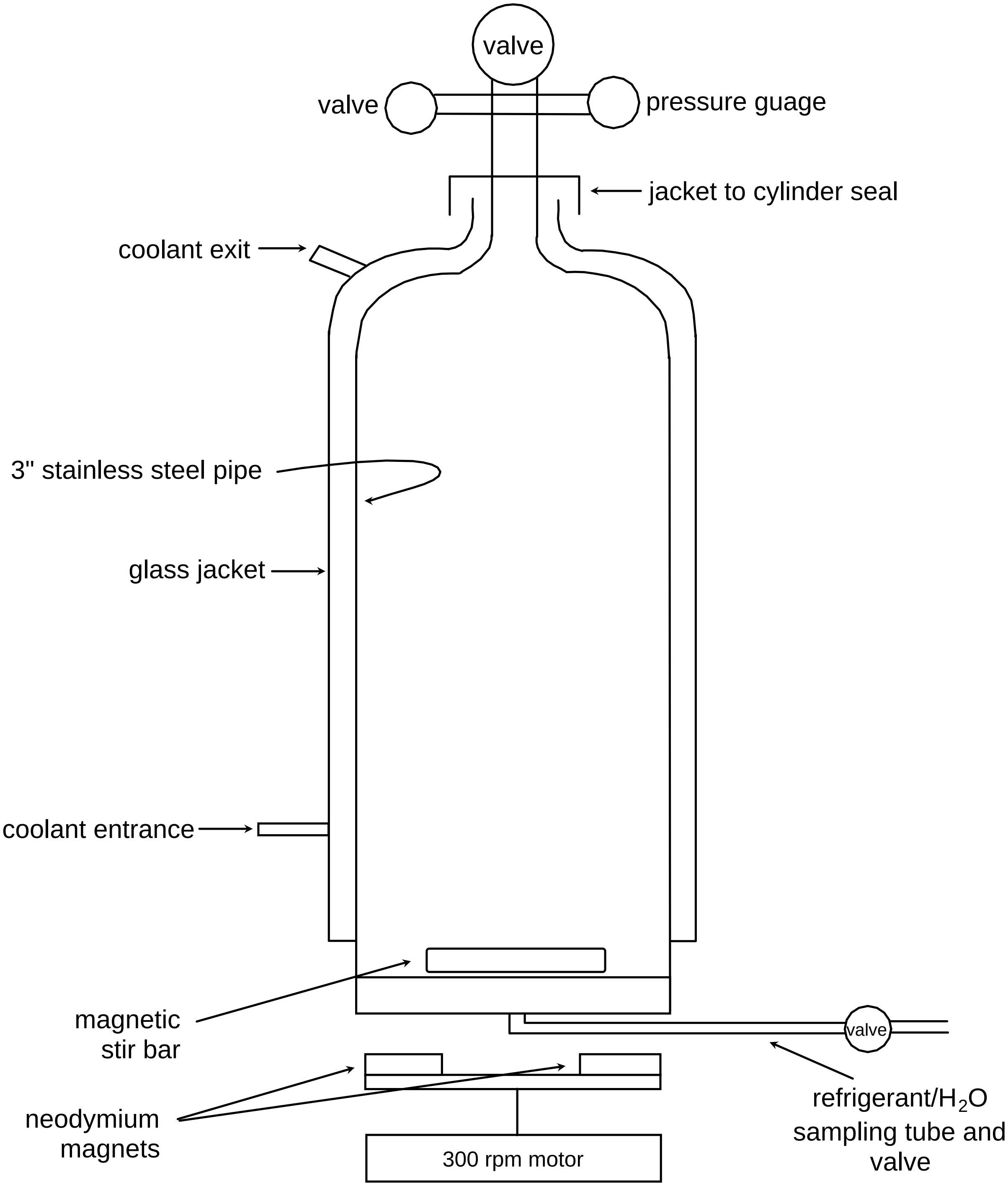
DuPont (Sturgis 1996). Test Unit 1 consisted of an inverted 3.5” OD x 14” stainless steel tube fitted at the top with a weld cap and pipe fitting assembly. The bottom was configured with a type C flange, drilled, and tapped to accept 5/16 x 18 studs. The bottom plate was stainless steel configured with a sampling tube and tap. The test cylinder was enclosed in an insulated glass jacket for temperature control. Temperature was regulated by circulating refrigerated methanol, with the aid of solid dry ice for temperatures below -40°F (-40°C), from a microprocessor-controlled cryostat between the test cylinder and the glass jacket. For temperatures of 80°F (27°C) and above, a microprocessor-controlled heating bath was used to circulate a water/ethylene glycol mixture. This system was used to test R-134a, R-143a, R-125, R410A, R407C, and R507A. Temperature test points were taken from 80°F (27°C) to 160°F (71°C) (or within 15°F (8.3°C) of critical temperature) and then from 60°F (16°C) to -100°F (-73°C).

Test Unit 2

The second test system (Figure 2), simply a modification of Test Unit 1, was designed and built to provide additional slow stirring of the entire mixture and to minimize clathrate hydrate formation near the sampling port. In the second test unit, the magnetic stirring bar was replaced with a ¼” diameter, stainless steel tube equipped with two stirring arms, two opposing neodymium magnets, and three holes to permit sample flow to the sampling port. The mixing device, which sat on the base of the enclosed cylinder, was rotated by a 300 rpm stirring motor. Water and refrigerant were introduced in the usual manner, but the principal difference was that the sampling orifice was placed 2½” up from the bottom. The sample was stirred by both a 1/16” diameter pin that held the internal tube plug and the bottom magnet armature. This system was used to test R-32, R-152a, and R404A. It was also used in the attempt to collect R-22 and R-23 data. The temperature test points were taken in order from lowest to highest (-40°F (-40°C) through 160°F (71°C)) (or within 15°F (8.3°C) of critical temperature) per the committee’s suggestion. The lowest temperature at which data points were collected changed from -100°F (-73°C) to -40°F (-40°C) because data collected below -40°F (-40°C) was not reproducible.

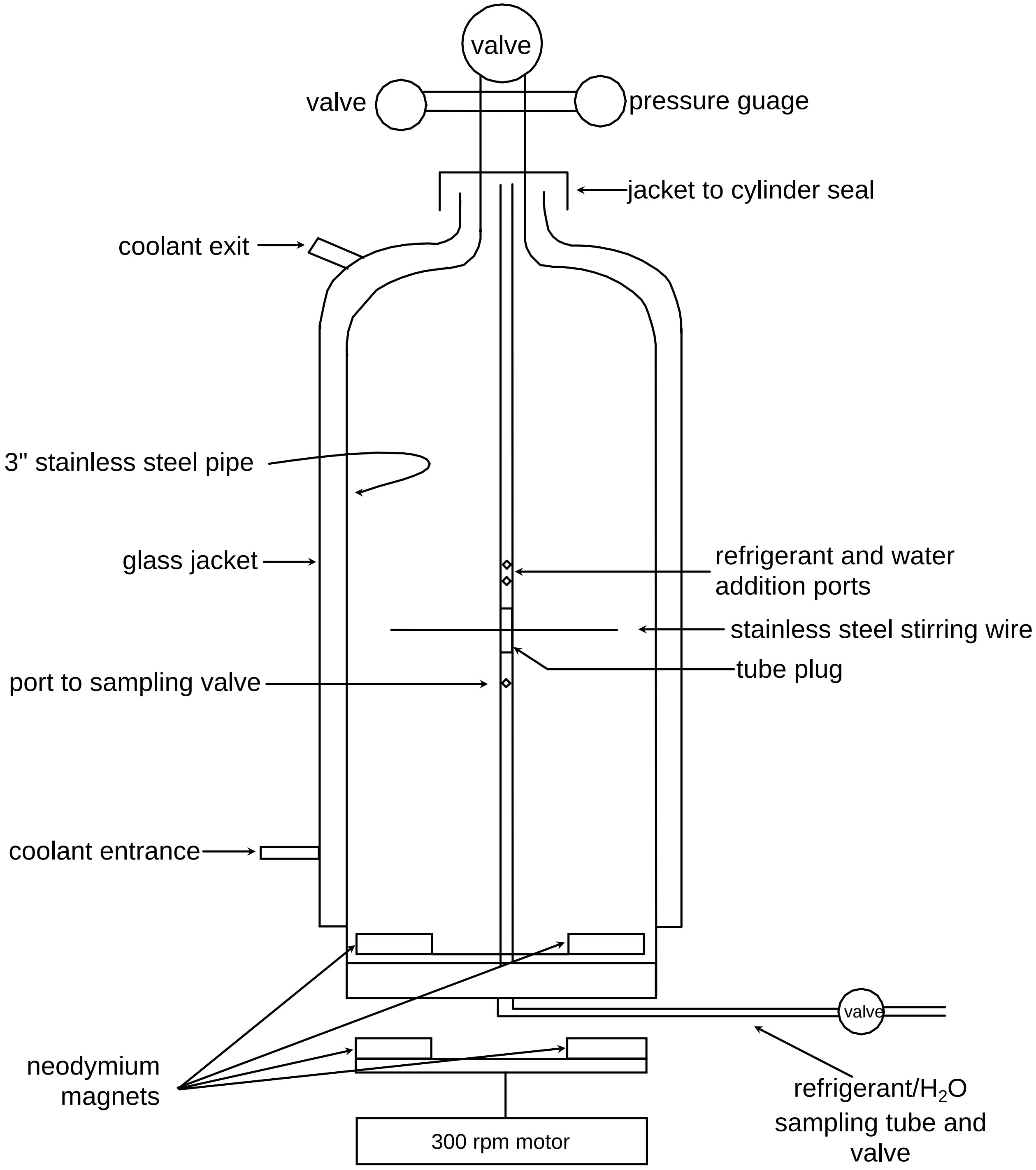
Test Unit 1

Figure 1



Test Unit 2

Figure 2



The redesign of Test Unit 1 resulted from examining the water equilibrium test points plotted as log refrigerant water content (ppm) vs. temperature (1000/°K). In particular, R-143a clearly demonstrated two distinct slopes (see *Discussion*). At this point in the project, clathrate hydrates were assumed less dense than the refrigerant; therefore, it was presumed, they would float. Additional experimentation became necessary to learn more about the characteristics of clathrate hydrates.

Unlike previous investigations (Akiya *et al*. 1997 and Lederhos *et al*. 1992), this study showed clathrate hydrate formation in excess refrigerant. In order to characterize the physical properties of the clathrate hydrates formed, sealed tubes were made with 1% and 5% water (w/w) (Appendix C), which was outside the scope of the work statement, but necessary for this investigation. Observation of the sealed tubes containing water and refrigerant confirmed clathrate hydrate formation and disappearance as temperatures increased and decreased between 0°F (-18°C) and 80°F (27°C) (Appendix C). The amount of clathrate hydrates formed and the temperature at which they appeared depended on the amount of water in the system, the refrigerant being tested, and whether measurements were taken as the temperature was decreasing or increasing (Figures 3 and 4).

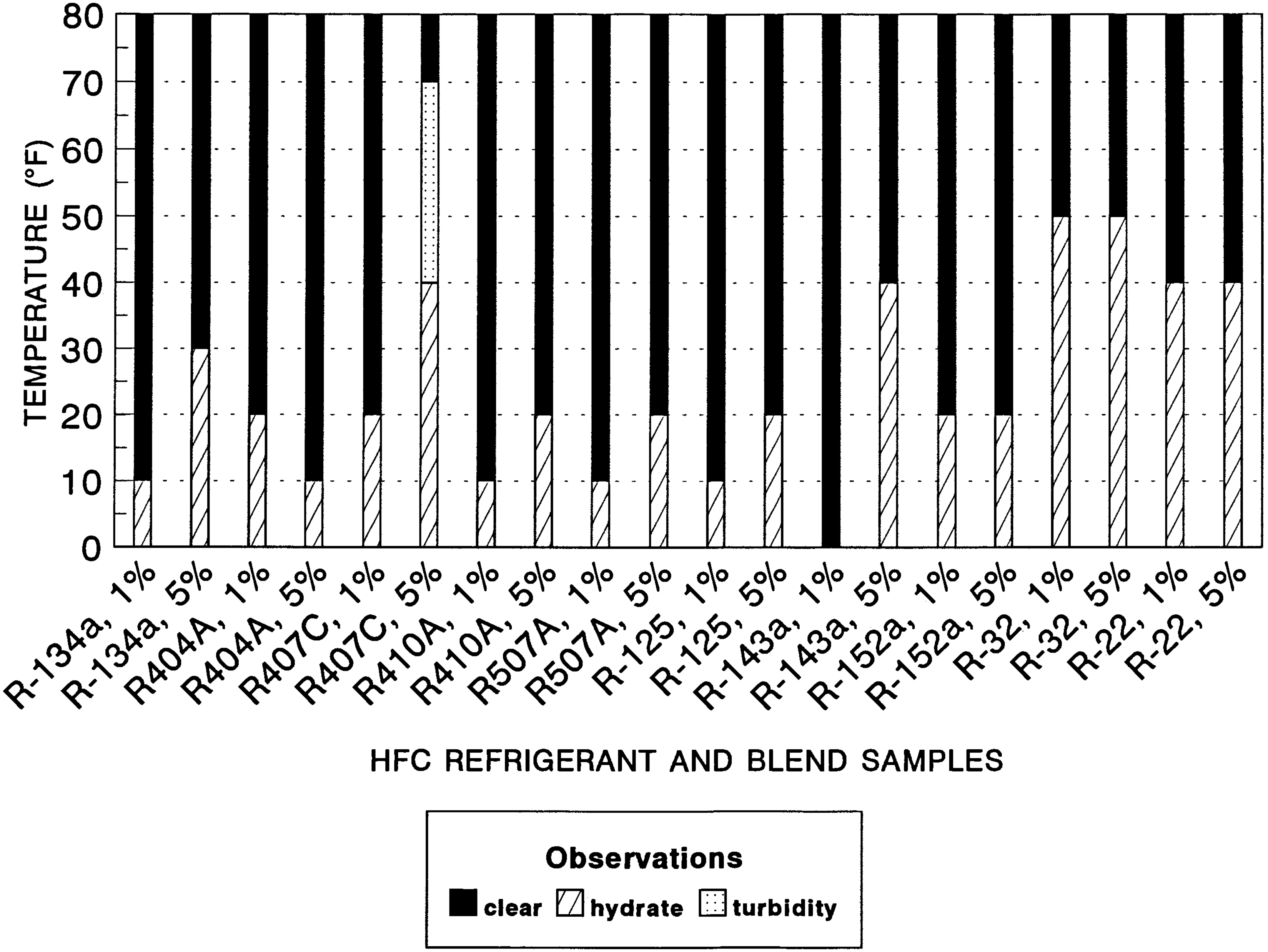
Test Unit 3

Test Unit 3 (Figure 5) is a modification of Test Unit 2. It was suggested that free water should not be used in water solubility equilibrium studies with liquid refrigerant and that the available water be retained in a saturated desiccant in an effort to minimize clathrate hydrate crystal formation (Parrish *et al.* 1982 and Walker *et al.* 1960). A small can was fabricated that could hold up to 75g of desiccant by using 30 gauge stainless steel sheet metal and 80 mesh screens. The top was removable, but spring loaded in compression to retain the desiccant. The top, sides, and bottom of the can had slots allowing free flow of the liquid refrigerant. The set up of the system was otherwise the same as Test Unit 2. This system was used only with R-32 (see *Discussion*).

Observations of HFC Refrigerants and Blends with 1 % and 5% Water (w/w) Added

Observations made at ten degree intervals starting at 80°F(27°C) down through 0°F(-18°C)

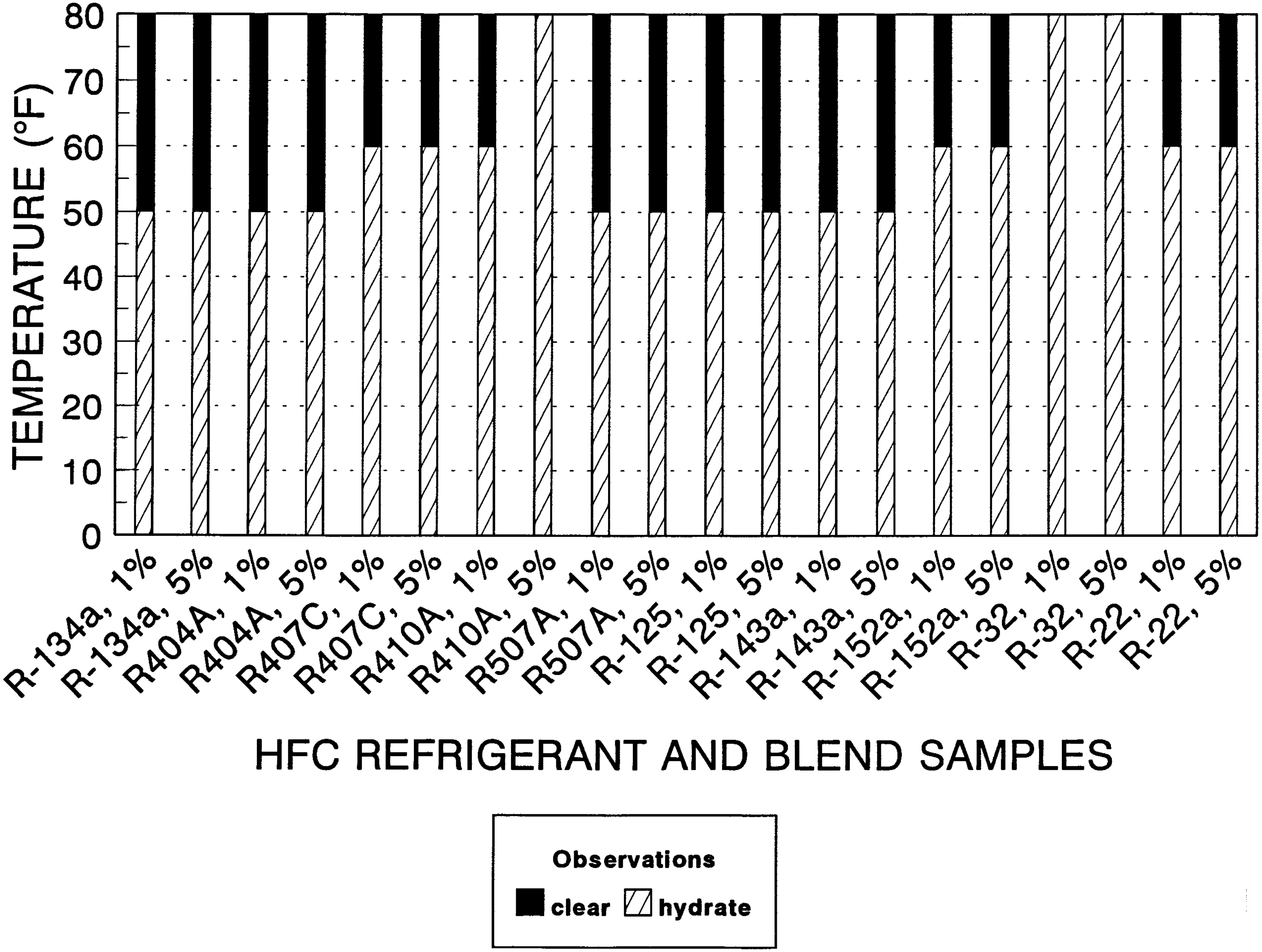
Figure 3



Observations of HFC Refrigerants and Blends with 1 % and 5% Water (w/w) Added

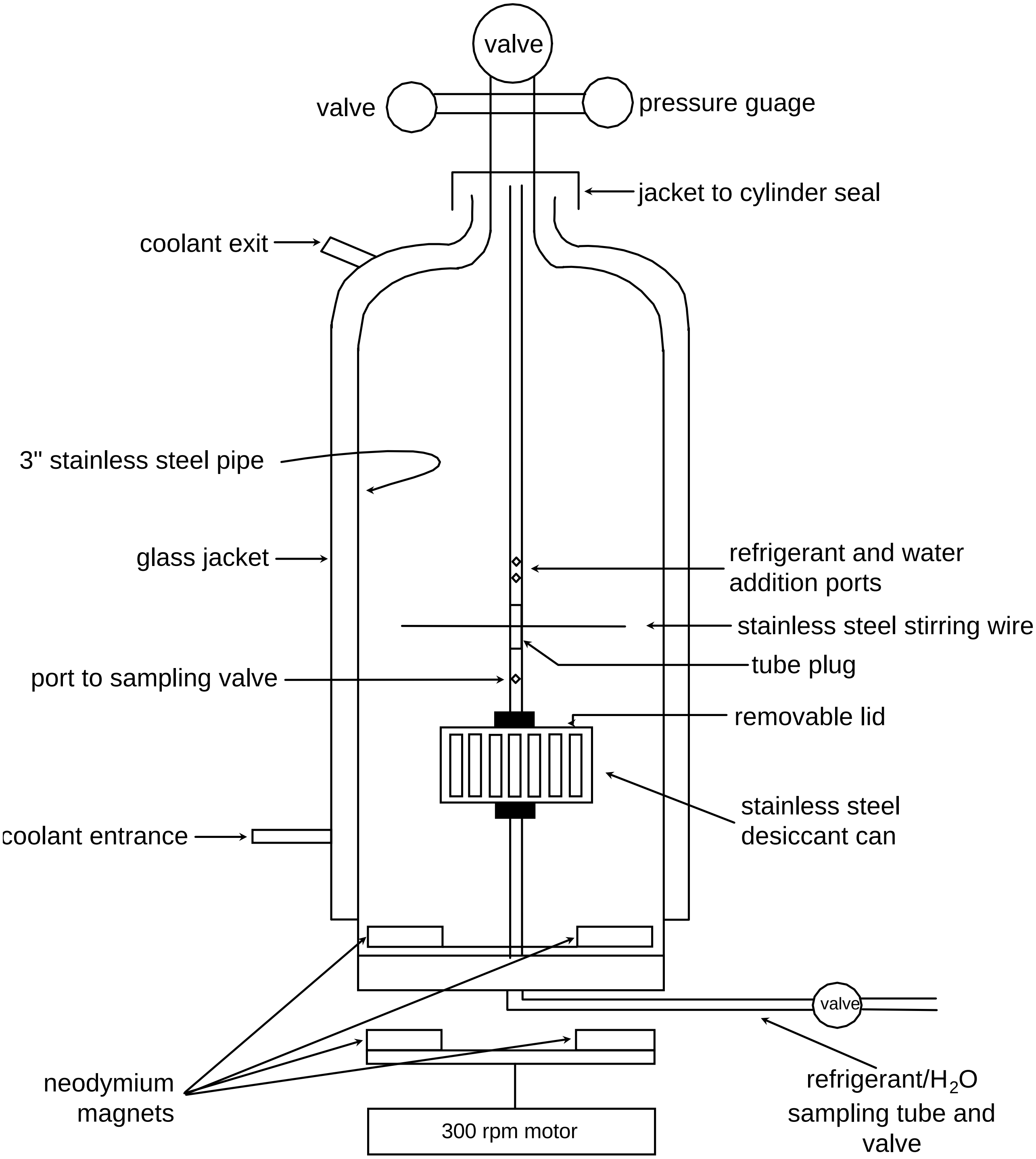
Observations made at ten degree intervals starting at 0°F(-18°C) up through 80°F(27°C)

Figure 4



Test Unit 3

Figure 5



Clathrate Hydrates

A brief discussion of clathrate hydrates, commonly referred to as gas hydrates, is necessary given the impact these crystalline molecular complexes have on the findings of this study. A hydrate is a complex containing water that belongs to the class of compounds known as clathrates. Clathrate refers to an open crystalline structure of one compound, in this case water, which encloses molecules of another compound, which are usually gas molecules typically referred to as the guest molecule. The guest molecule or gas molecule (refrigerant) is referred to as such even when it is not in the gas phase. There is no chemical tie between the gas and water molecules; instead, they interact through van der Waals type dispersion forces (Holder *et al*. 1988). These forces between molecules reflect the momentary and induced dipoles from electrons normally moving about; the net result is attraction between the two molecules. van der Waals forces are short range and act between portions of different molecules that are in close contact (Morrison and Boyd 1973). The crystalline lattice entrapping the gas molecules is formed by strong hydrogen bonds between water molecules. Examination of clathrate hydrates reveals that they may have two different structural forms, referred to as Structures I and II. Formation of either structure is dependent on their stability and both can coexist under certain conditions. Structure I is comprised of 46 water molecules configured to provide two small and six large cavities for gas molecules to occupy. Structure II's arrangement of 136 water molecules hosts 16 small and eight large cavities in which gas molecules can reside (Holder *et al*. 1988).

A discussion of clathrate hydrates centers around three concepts: solubility, metastability, and the establishment of critical nuclei as they relate to water clustering (Sloan 1990). The water in refrigerant, as temperature decreases, becomes a short-lived liquid cluster of irregular and broken hydrogen-bonded water molecules (metastability) surrounding a dissolved hydrocarbon. This metastability develops into well-formed hydrogen bonds fixed in position to form a solid clathrate cage around a guest molecule (refrigerant) defining the critical nuclei or nucleation phase (Sloan 1990). Therefore, water measurements above the metastable temperature represent water solubility/equilibrium in liquid refrigerant. Water measured at metastability or nucleation temperatures is likely decomposed clathrate hydrate in liquid refrigerant.

While the subject of gas hydrates is well documented, most of the research has focused on the plugging of natural gas lines and naturally formed hydrates found beneath the earth's surface that are an attractive source of natural gasses (Holder *et al*. 1988). Clathrate hydrates are formed in a variety of conditions with a variety of gasses and their existence must be acknowledged when interpreting the results of this study.

The presence of clathrate hydrates in liquid refrigerant poses problems in interpreting water solubility measurements in HFC refrigerants and blends below 80°F (27°C). For instance, it is known that clathrate hydrates separate from refrigerant at temperatures above the freezing point of water (ASHRAE 1994, Chinworth and Katz 1947, and Downing 1988). Other investigators show clathrate hydrate formation by several refrigerants, but do not report water solubility measurements in those refrigerants or in HFCs (Chinworth and Katz 1947). Studies focused primarily on clathrate hydrate formation were conducted by Lederhos *et al*. (1992), Akiya *et al*. (1997), Sugaya *et al*. (1996), and Mori *et al*. (1989), all of whom used a water rich phase, as opposed to the refrigerant rich phase used in this study. The *Fluorocarbon Refrigerants Handbook* (Downing 1988) briefly discusses clathrate hydrates, but discusses the solubility of water in liquid refrigerant separately. With regard to clathrate hydrates, the handbook states that there is not a sufficiently large amount of water present in refrigeration systems to present a clathrate hydrate formation problem. The information on solubility of water in liquid refrigerant does not address clathrate hydrates, nor does it provide a test method (ASHRAE 1994). Like many of the other references, it provides an abundance of information, discussion, and graphs on the solubility of refrigerant in water.

In summary, there is a short supply of documented research addressing the impact of clathrate hydrates on measuring water solubility in refrigerants. The test procedures used to compile the data for the small number of published solubility charts and graphs are equally difficult to find.

All of the refrigerants examined clearly form clathrate hydrates. Once formed at lower temperatures, clathrate hydrates with R-32 and blends containing R-32 are stable up to 80°F (27°C). More importantly, in this study, some clathrate hydrates were denser than the refrigerant under test, which necessitated a redesign of Test Unit 1.

Method

Hydrofluorocarbon refrigerants are known to form clathrate hydrates at substantially lower temperatures (Chinworth and Katz 1947) than their decomposition temperatures (Akiya *et al*. 1997). Therefore, the following method was devised. This method was based on the concept that the metastable period of water solubility exists and then ends just before the onset of the secondary nucleation of the clathrate hydrate crystals (Sloan 1990). The temperature profile protocol was designed based on these reported observations and on those that described the decomposition temperature of HFC refrigerant gas hydrates in water rich systems. Akiya *et al*. (1997) reports the critical decomposition temperature for R-134a (70°F/21°C), R-125 (52°F/11°C), R-32 (50°F/10°C), R407C (68°F/20°C), and R410A (57°F/14°C); these correlate well with our sealed tube observations of a refrigerant rich system. In order to prolong the metastable period of liquid water equilibrium solubility, the temperature was lowered in 20°F increments starting from 80°F (27°C).

The water solubility data for R-134a, R-143a, R-125, R410A, R407C, and R507A was measured by thermostatting the test cell at 80°F (27°C) and then proceeding upward to 160°F (71°C) (or within 15°F (8.3°C) of critical temperature) in 20°F (11°C) increments, as previously mentioned. This provided the liquid water solubility equilibria with liquid refrigerant in the absence of any solid clathrate. After the upper temperature scan was complete, the cell was cooled to the lower temperatures. The starting point was 60°F (16°C). The temperature was then lowered to -100°F (-73°C) in 20°F (11°C) increments. Based on data in the progress reports submitted during this study, the project monitoring committee decided that water solubility determinations be accomplished by starting at -40°F (-40°C) and proceeding upwards in 20°F (11°C) increments to 160°F (71°C) (or within 15°F (8.3°C) of critical temperature). Refrigerants R-32, R-152a, and R404A were processed in this manner.

Refrigerant and Water Introduction

To guarantee that a sufficient amount of water was present to ensure saturation of liquid refrigerant, the initial target was approximately 10,000 ppm or 1% water (w/w). To introduce refrigerant and water into any of the test systems, the apparatus was first placed under vacuum by the top sampling port valve for approximately 15-30 minutes. After isolating the system with the top valve, the appropriate amount of water was aspirated into the apparatus through the bottom sampling port valve (Test Units 1 and 2) and then the system was cooled to 0°F (-18°C). Test Unit 3 required disassembly for wetted silica gel addition for each refrigerant test. Then, a second vacuum was pulled from the top cell valve for approximately one minute and the appropriate amount of refrigerant was added through the bottom port.

The amount of water in the test system was also critical to data collection at lower temperatures (<80°F (27°C)). Ideally, water should be present in slight excess of saturation at each temperature measurement to insure maximum water saturation (Daniels *et al*. 1962). Clathrate hydrate formation is compounded by the addition of too much water (see Appendix C).

Data Collection

To obtain a measurement of water solubility in wet refrigerant, the test system was allowed to stir for a minimum of four hours at the desired temperature to attain equilibrium. Stirring was discontinued 15-30 minutes prior to sampling. A 5-10g sample was introduced into a pre-weighed sampling device under vacuum and cooled with either ice water or liquid nitrogen if necessary. After the sampling device was weighed, it was placed in a 220°F (104°C) sand bath and the sample was slowly discharged into a coulometer for moisture determination. Finally, a dry nitrogen gas purge of the sampling device insured that all sample moisture was extracted. Each data point is the average of multiple raw data determinations (see Appendices A and B). Error, represented by error bars on the graphs, was calculated as standard deviation of the measurements (see Figures 6-15). This sampling method was utilized with all test units.

DISCUSSION OF RESULTS

Water solubility in liquid refrigerant data was graphed as temperature (1000/°K) vs. log refrigerant water content (ppm), with most refrigerants clearly showing two distinct water solubility slopes (see Figures 6-15). Figure 16 shows water solubility comparisons of all pure refrigerants used in this study and figures 17-20 show water solubility data for the blends, azeotropes, and their components. Some refrigerants tested have data points at -60°F (-51°C), -80°F (-62°C), and -100°F (-73°C), but these low temperature data points were excluded from the water solubility graphs because the percent error calculations called their validity into question.

R-134a

The water (w/w) content of 0.8% produced curves that began to closely resemble the data presented previously by ASHRAE (1994) (see Figure 6). R-134a measurements, taken with Test Unit 1, followed the initial sampling protocol of raising the temperature from 80°F (27°C) to 160°F (71°C) and then lowering it from 60°F (16°C) to -100°F (-73°C). Figure 6 illustrates a small change in solubility in the temperature region where clathrate hydrates are known to form (see Figure 3). This suggests a maximum allowable water content of 70 ppm or less in liquid refrigerant for the low-pressure region of a system that operates below -20°F (-29°C) to prevent clathrate hydrate formation. (See also Appendix D, Picture 1)

R-32

R-32 measurements used Test Unit 2. The cell was loaded with 1% water (w/w) and data recorded from 20°F (-6.7°C) to 100°F (38°C). No samples were attempted above 140°F (60°C) because of safety concerns due to high pressure; attempts below 20°F (-6.7°C) resulted in clogging of the sampling valve. Figure 7 shows a dramatic change in the water solubility at 60°F (16°C). Referring to Gibbs Phase Rule,

$$F = 2 + C - P$$

where F = number of degrees of freedom (system variance),
C = number of components, and
P = number of phases,

and allowing one degree of freedom to set the system temperature, it is possible to have three phases using a pure refrigerant. At 60°F (16°C), there was a phase change from clathrate hydrate to liquid water, thereby affecting water solubility. The other two phases are liquid and vapor refrigerant. Figure 7 shows that a water level below 125 ppm at 20°F (-6.7°C) will reduce clathrate hydrate formation in the evaporator region of an operating system.

R-32 was also tested using Test Unit 3 (Figure 5) with wetted 14-20 mesh silica gel as the source of water (25 g H_2O/50 g silica gel) (see Figure 8). No data was taken between -40°F (-40°C) and 60°F (16°C) due to clogging of the sampling valve. In this work, solubility results obtained using a solid adsorbent (silica gel) as the water source differed from results using straight water addition. The adsorbent method of water reported by Walker *et al*. (1960) was limited to one data point for R-22 at 86°F (30°C) in their study of the stability of fluorocarbon refrigerants and refrigerating oil mixtures. Here, the adsorbent-generated data form a straight line while the water-addition data form two intersecting lines (see Figures 7 and 8). Since both data sets are limited, it is difficult to draw a conclusion about which method of water addition is better. (See also Appendix D, Picture 2)

R-143a

R-143a measurements used the same temperature, sampling protocol, amount of water, and test unit used with R-134a. Figure 9 clearly demonstrates the difference of solubility between liquid water in refrigerant and clathrate hydrate in refrigerant when plotted using the log profile. Again, a marked change in the slope is apparent at 60°F (16°C), signifying a phase change from liquid water to clathrate hydrate, adhering to Gibbs Phase Rule. Water levels below 15 ppm at -40°F (-40°C) are advisable to avoid clathrate hydrate formation in the evaporating low-pressure region of an operational system. (See also Appendix D, Picture 3)

R-125

R-125 measurements used the same temperature, sampling protocol, and test unit (loaded with 1% water (w/w)) used with R-134a. This data is graphed in Figure 10. Water solubility in R-125 is affected by a phase change from liquid water in R-125 to the solubility of clathrate hydrate in R-125 at 40°F (4.4°C). In order to minimize clathrate hydrate formation on the low-pressure side of a system, water levels should be below 125 ppm at -20°F (-29°C). (See also Appendix D, Picture 4)

R-152a

Based on occurrences within the test cell during R-143a experimentation and sealed tube observations, R-152a measurements used Test Unit 2. The cell was loaded with 1% water (w/w) and the temperature scanned from 0°F (-18°C) to 140°F (60°C). This data is shown in Figure 11. The log plot clearly shows that two water solubility slopes could be plotted, indicating the phase change of liquid water to clathrate hydrate at 60°F (16°C) and the results of liquid water and clathrate hydrate solubility in R-152a. The phase change temperature of 60°F (16°C) was predicted with the sealed tube observations (see Figure 4). The sampling valve was clogged at lower temperatures. The maximum allowable water content of an operating system should be less than or equal to 350 ppm at 0°F (-18°C) to prevent clathrate hydrate formation in the low-pressure region of the system. (See also Appendix D, Picture 5)

R410A

R410A measurements used the same temperature, sampling protocol, and test unit as R-134a with 1% water (w/w). This data is shown by itself in Figure 12 and with components R-32 and R-125 in Figure 17. The R410A results are a good example of complications caused by clathrate hydrates. It appears as if two lines intersect at 0°F (-18°C). The solubility is less below 0°F (-18°C) because of clathrate hydrate formation. Figure 12 indicates that a water level less than 15 ppm at -40°F (-40°C) will prevent clathrate hydrate formation in the low-pressure region of an operational system. Sealed tube observations confirm clathrate hydrate formation at 10°F (-12°C) (see Figure 3). Figure 12 illustrates a change in water solubility at 0°F (-18°C). Considering Gibbs Rule (F = 2 + C – P) and the fact that this azeotrope has two components, the number of components is three (R-32, R-125, and water), thereby permitting the existence of four phases so that one degree of freedom remains in tact for setting the temperature of the system.

Therefore, the phase changes affecting water solubility in R410A at 0°F (-18°C) through 10°F (-12°C) might be from the presence of V, L_1, and L_2 to one of the following combinations:

1) V, L_1, L_2, and H_I *or* H_{II},
2) V, L_2, I, and H_I *or* H_{II}, or
3) V, L_2, H_I, *and* H_{II},

where: V = refrigerant vapor,

L_1 = liquid water,
L_2 = liquid refrigerant,
I = solid water (ice),
H_I = clathrate hydrate structure I, and
H_{II} = clathrate hydrate structure II.

The sealed tube observations show clathrate hydrate appearance at 10°F (-12°C) for R410A and R-125 and at 50°F (10°C) for R-32 (see Figure 3). This is interesting because the existence of a hydrate azeotrope has been reported with a lower dissociation pressure than that of either of the components of the mixture (Holder *et al*. 1988). (See also Appendix D, Picture 6)

R407C

R407C measurements used the same temperature, sampling protocol, and test unit as R-134a with 1% water (w/w). This data is shown in Figures 13 and 18. The R407C figures illustrate a more subtle change in water equilibrium below 20°F (-6.7°C) with respect to temperature points taken at 20°F (-6.7°C) and above. This can be explained by the temperature at which clathrate hydrate is formed and dissolved (see Figure 3, R407C with 1% water (w/w)). This is not surprising since clathrate hydrate observance for R407C and its components, except R-32, is below 20°F (-6.7°C). A change in water solubility is noted below 20°F (-6.7°C), reflecting a change in water equilibrium in R407C to clathrate hydrate equilibrium in R407C. Operating levels of 15 ppm water at -40°F (-40°C) prevent clathrate hydrate formation in the evaporator. (See also Appendix D, Picture 7)

R507A

R507A measurements used the same temperature, sampling protocol, and test unit as R-134a. 1% water (w/w) was added. This data is displayed in Figures 14 and 19. R507A is a blend of R-125 and R-143a and below 40°F (4.4°C) the water/clathrate hydrate solubility in R507A falls between that of its two component refrigerants. All three refrigerants' water/clathrate hydrate solubility lines on Figure 19 show two changes in the slope, one at either 40°F (4.4°C), 60°F (16°C), or 80°F (27°C) and one at 20°F (-6.7°C). The slope changes for R507A and its components correspond with a phase change from liquid water to liquid water and hydrate, liquid water to ice and hydrate, or liquid water to hydrate. This data confirms the sealed tube observations in Figure 3. In addition, examination of Figure 14 predicts that water levels should be lower than 30 ppm at -40°F (-40°C) to prevent clathrate hydrates from forming in the evaporator. (See also Appendix D, Picture 8)

R404A

R404A measurements used Test Unit 2. The cell was loaded with 1% water (w/w) and data acquired successfully from -40°F (-40°C) to 100°F (38°C). This data is shown in Figures 15 and 20. Clearly, two slopes exist, one for data above 40°F (4.4°C) and another for data below 40°F (4.4°C). Keeping water levels below 30 ppm at -40°F (-40°C) will reduce clathrate hydrates in an operating systems' evaporator region. Comparing R404A with its components (see Figure 20), each refrigerant goes through a phase change near 20°F (-6.7°C). (See also Appendix D, Picture 9)

R-22

Although published R-22 water solubility data was intended to be an analytical control along with R-134a in this study, at the time the proposal was written it was unknown that R-22 formed significant amounts of clathrate hydrates. The results of this project predict clathrate hydrate formation at or below 60°F (16°C); Chinworth and Katz (1947) reported that wet R-22 formed a solid hydrate at 64°F (18°C). Nevertheless, R-22 water solubility measurements were attempted for comparison with published ASHRAE data (1994). The water solubility of R-22 was comparable to the reported ASHRAE value, 950 ppm vs. 970 ppm respectively, at 60°F (16°C), but was vastly different at 80°F (27°C). Because R-22 forms flocculant clathrate hydrates as readily as R-32 (see Appendix D, Pictures 2 and 10) and based on the difficulty experienced during R-32 testing at lower temperatures, further R-22 testing was terminated.

R-23

Although liquid R-23 was to be tested in this project, no data points were attempted. Raising the test unit to 80°F (27°C) and above with R-23 would have resulted in pressures greater than 600psig, which exceeded safe limitations of the test apparatus. In addition, based on previous testing, water solubility information obtained at temperatures of 60°F (16°C) or below would have been misleading because of clathrate hydrate existence/interference. Because no meaningful data could have been obtained without extensive reconstruction of the test cell, R-23 was eliminated from the project.

CONCLUSION

At lower temperatures, the amount of water in the test assembly is related to the amount of clathrate hydrates formed, which interferes with the measurement of water and/or clathrate hydrate solubility. The straight addition of water to the test system gives the analyst the most precise method of controlling how much water is introduced. It is not advisable to exceed 2% water (w/w) or to use less than 1% water (w/w). These amounts of water are in slight excess of saturation so that maximum solubility is achieved at each temperature while the amount of clathrate hydrate production is minimized at the lower temperatures (see Appendix D, 1% v. 5% water (w/w) added).

The water solubility data reported by ASHRAE (1994) in Table 1, *Solubility of Water in the Liquid Phase of Certain Refrigerants*, matches the data (excluding R-134a and R-123) reported by DuPont in Bulletins B-43 (1982a) and M-5 (1982b) up to 100°F (38°C). More importantly, Chinworth and Katz (1947) reported the formation of refrigerant clathrate hydrates for R-11 (47°F/8.3°C), R-12 (52°F/11°C), and R-22 (62°F/17°C). This is further confirmed by Briggs and Barduhn (1962). Some data supplied to the industry was correlated to experimental data and may represent water solubility measured in the presence of clathrate hydrates. It is questionable to conclude that straight-line water solubility exists based on the results of this research. The more recent data for R-134a seems to have been partially obtained from an ASHRAE research project (RP-602) using an NMR technique. The data reported in the ASHRAE handbook was taken from a temperature range of -9.7°F (-23°C) to 98°F (37°C), which is within the range of clathrate hydrate formation. Examining the water solubility range below 0°F (-18°C) is pointless due to NMR crystal broad banding. Downing (1988) reports the solubility of R-152a and R-23 at temperatures where both clathrate hydrates and liquid conditions exist. However, he reports straight-line solubility curves in regions where clathrate hydrates may exist.

The solubility of water is the concentration of water in solution in the immiscible refrigerant-rich liquid phase in equilibrium with 1) a water rich liquid phase or 2) at or below metastable temperatures, the solid clathrate hydrate phase. The solubility of water plotted as log refrigerant water content (ppm) vs. temperature (1000/°K) may show a different slope in the clathrate hydrate temperature region than in the non-clathrate hydrate temperature region because of a phase change affecting water solubility. The solubility of liquid water in liquid refrigerant above the clathrate hydrate formation temperature is independent of the overall water concentration in the test cell. However, water content does indeed have a noticeable effect at the lower temperatures when clathrate hydrates are formed. This is due to the varying amounts of liquid water and/or clathrate hydrate formation. It is difficult to determine the impact blends and azeotropes have on clathrate hydrate formation. By itself, one component of a blend may form clathrate hydrates at an observed temperature. However, the presence of other components in a blend or azeotrope may change the clathrate hydrate formation temperature.

When interpreting the results of this study on water and/or clathrate hydrate equilibrium/solubility in a liquid refrigerant rich environment under isothermal conditions, the impact of clathrate hydrates cannot be ignored. Although clathrate hydrates were not the focal point of this research, their presence affected the level of equilibrium water solubility. The fact that water was measured in temperature regions where clathrate hydrates exist is significant. The water level measured can be attributed to clathrate hydrates since, recalling Gibbs Phase Rule (F=2+C-P) for a pure refrigerant rich environment at a temperature supporting metastability and nucleation, only three phases can exist: liquid and vapor refrigerant and clathrate hydrate. This means that some clathrate hydrate was expelled with refrigerant during the sampling procedure, representing the solubility of clathrate in refrigerant at that sampling temperature and theoretically accounting for all the water in that sample's result.

This research provides ASHRAE with data and relevant information regarding liquid refrigerant properties in the presence of water. It also contributes a firm foundation for further research to understand water solubility in refrigerants. The use of liquid water in a water equilibrium isothermal situation with liquid refrigerant is a sound approach at a temperature above clathrate hydrate formation. The water solubility data generated in this research compares favorably with R-134a data taken by an NMR method (Thrasher *et al*. 1993) and data taken using near infrared spectroscopy (Jackson *et al*. 1995).

Finally, based on this research the authors recommend the maximum tolerable amount of water in liquid refrigerant for system operation below -40°F (-40°C). Typically, in mineral oil and R-22 systems, desiccants routinely maintain water concentration below 30 ppm. It is unknown, however, the effect typical amounts of synthetic lubricant may have on solubility and clathrate formation at these lower temperatures. In conclusion, for each refrigerant tested, the maximum amount (ppm) of water that should be tolerated for operations at -40°F (-40°C) is:

Maximum Amount of Water Tolerable in Systems at -40°F (-40°C)
Based on Clathrate Formation
Table 1

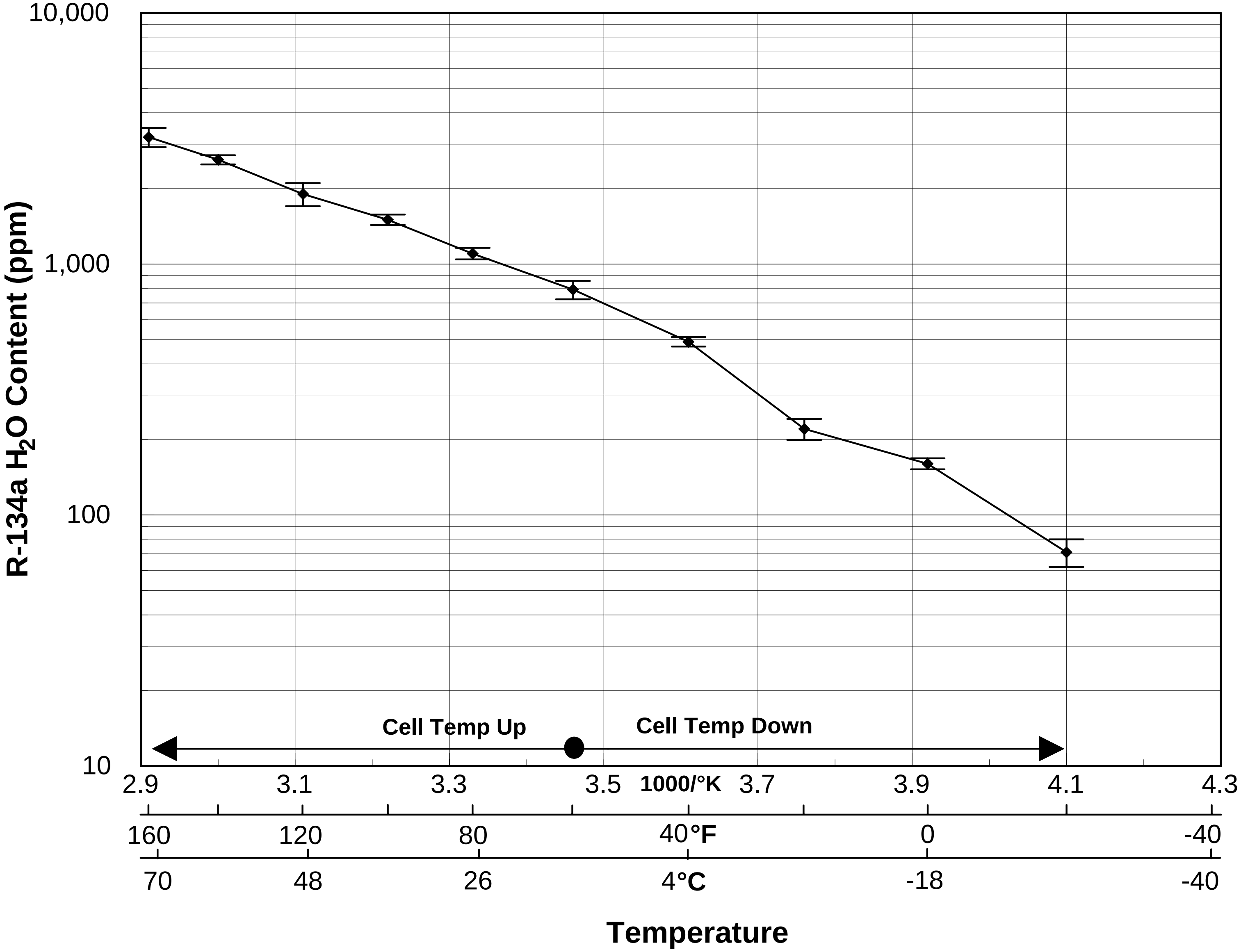
Refrigerant	Water (ppm)
R-134a	30*
R-32	<10*
R-143a	15
R-125	200*
R-152a	150*
R410A	15
R407C	15
R507A	40
R404A	40

*extrapolated

Water Solubility in R-134a

8.0g H_2O and 1.0Kg R-134a

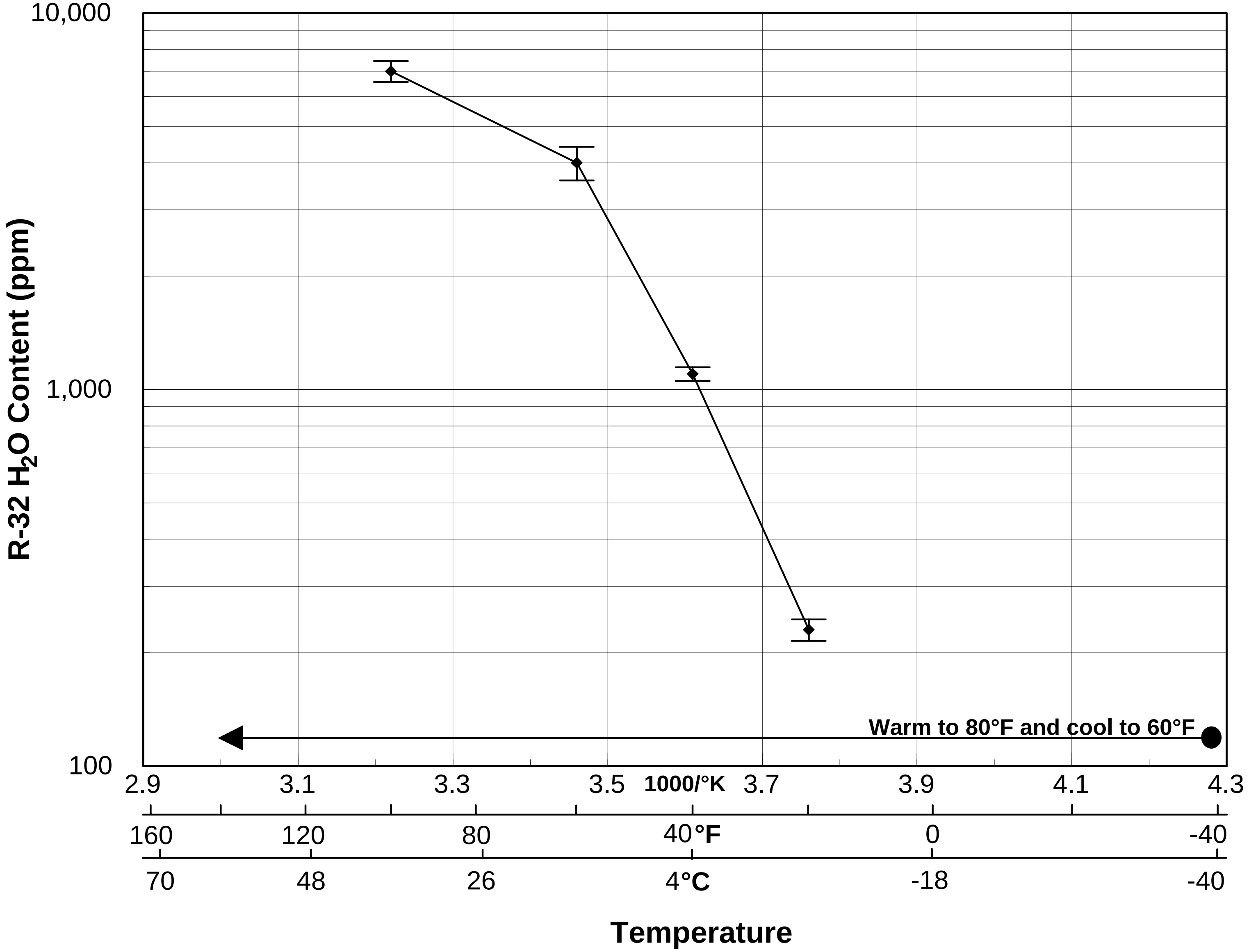
Figure 6



Water Solubility in R-32

15g H_2O and 1.5Kg R-32

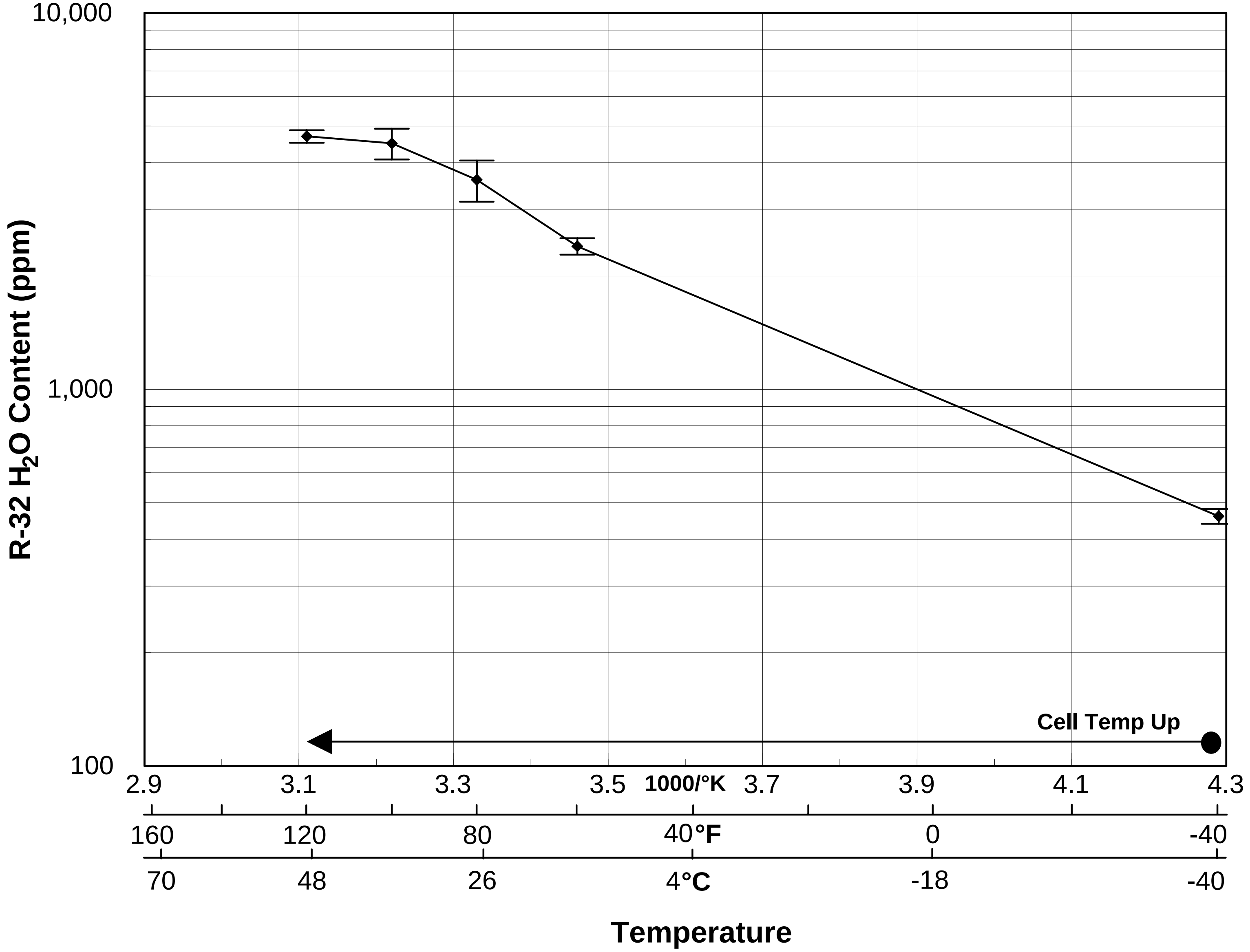
Figure 7



Water Solubility in R-32

25g H_2O in 50g 14-20 mesh Silica Gel and 1.5Kg R-32

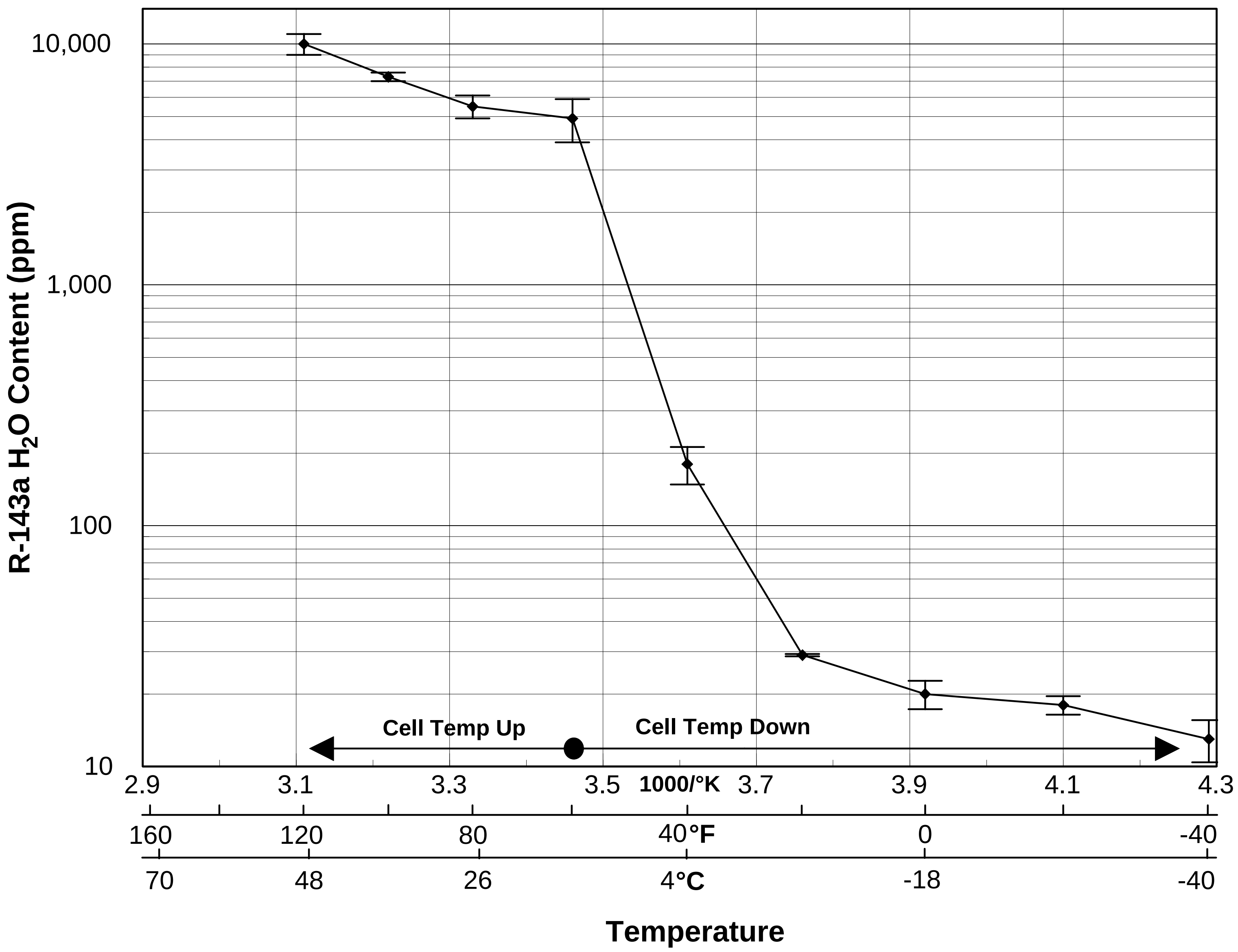
Figure 8



Water Solubility in R-143a

15g H_2O and 1.5Kg R-143a

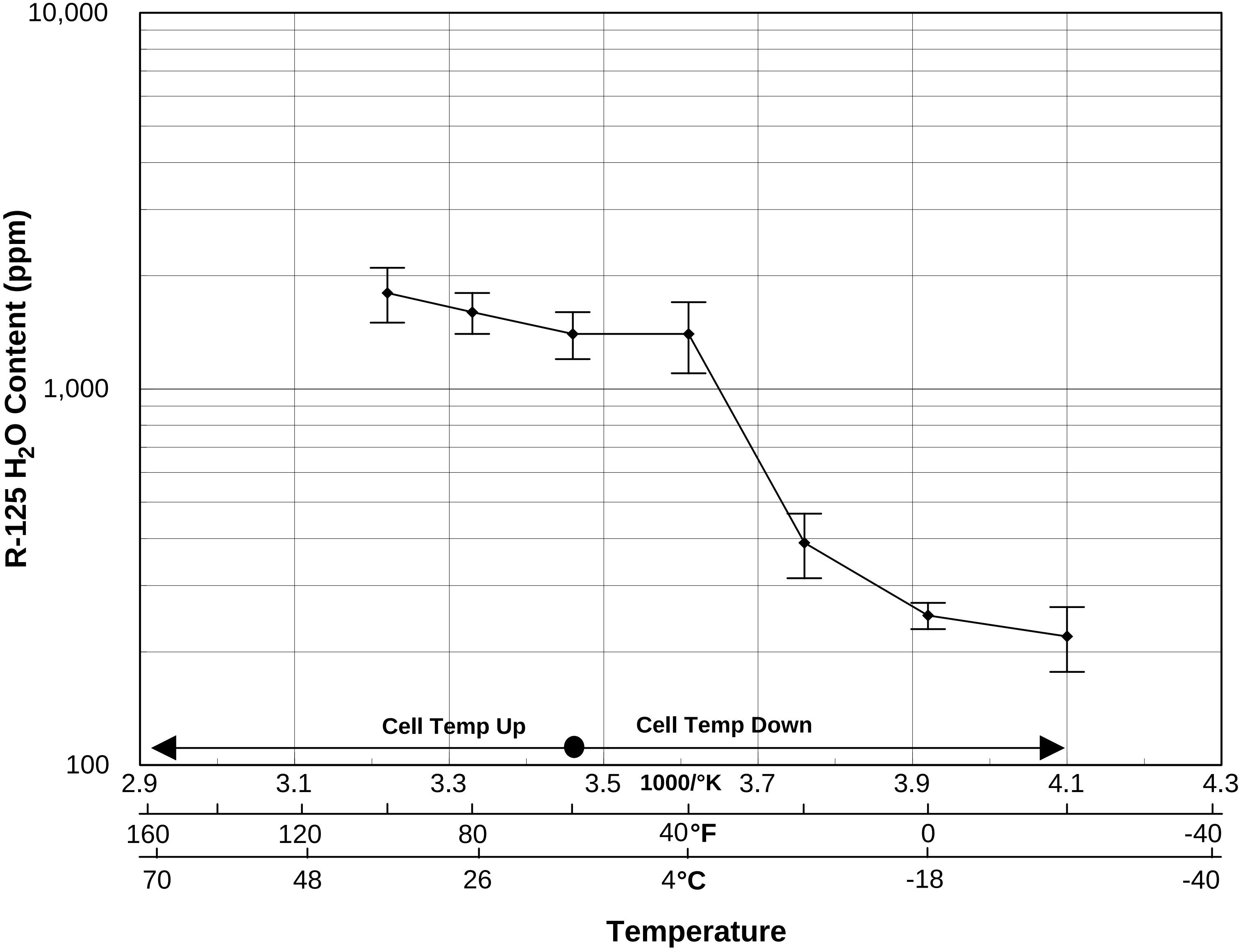
Figure 9



Water Solubility in R-125

10g H_2O and 1.0Kg R-125

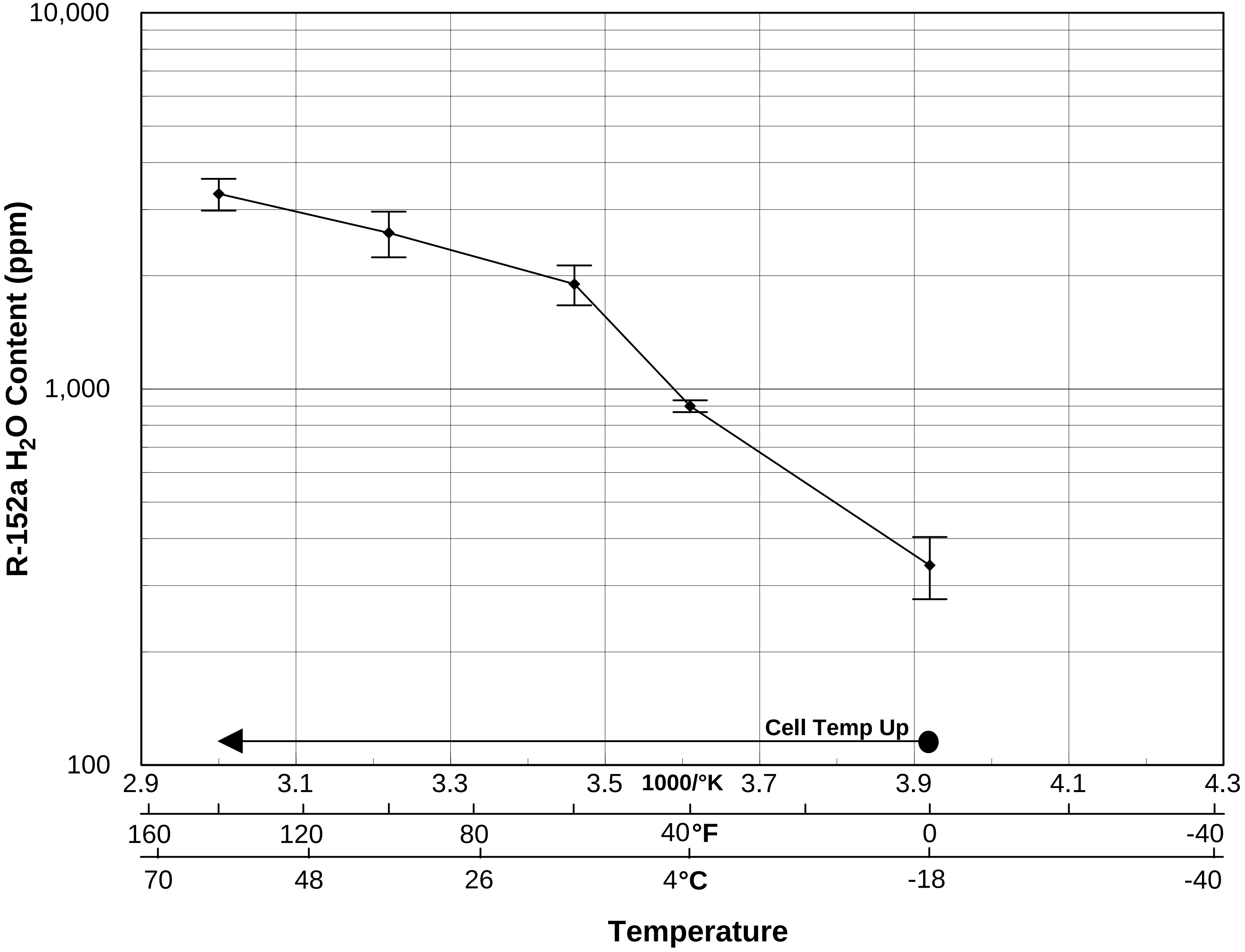
Figure 10



Water Solubility in R-152a

15g H_2O and 1.5Kg R-152a

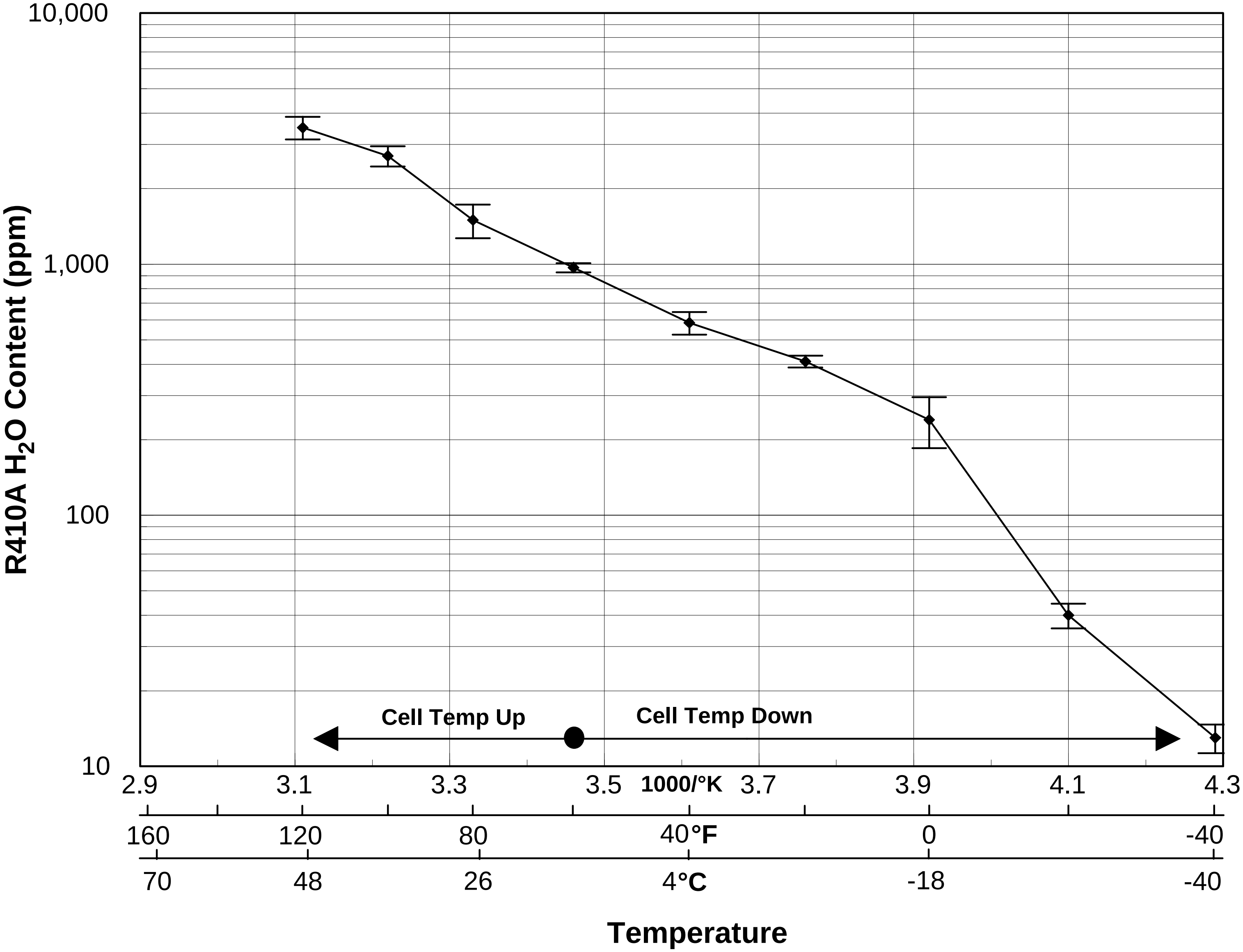
Figure 11



Water Solubility in R410A

10g H_2O and 1.0Kg R410A

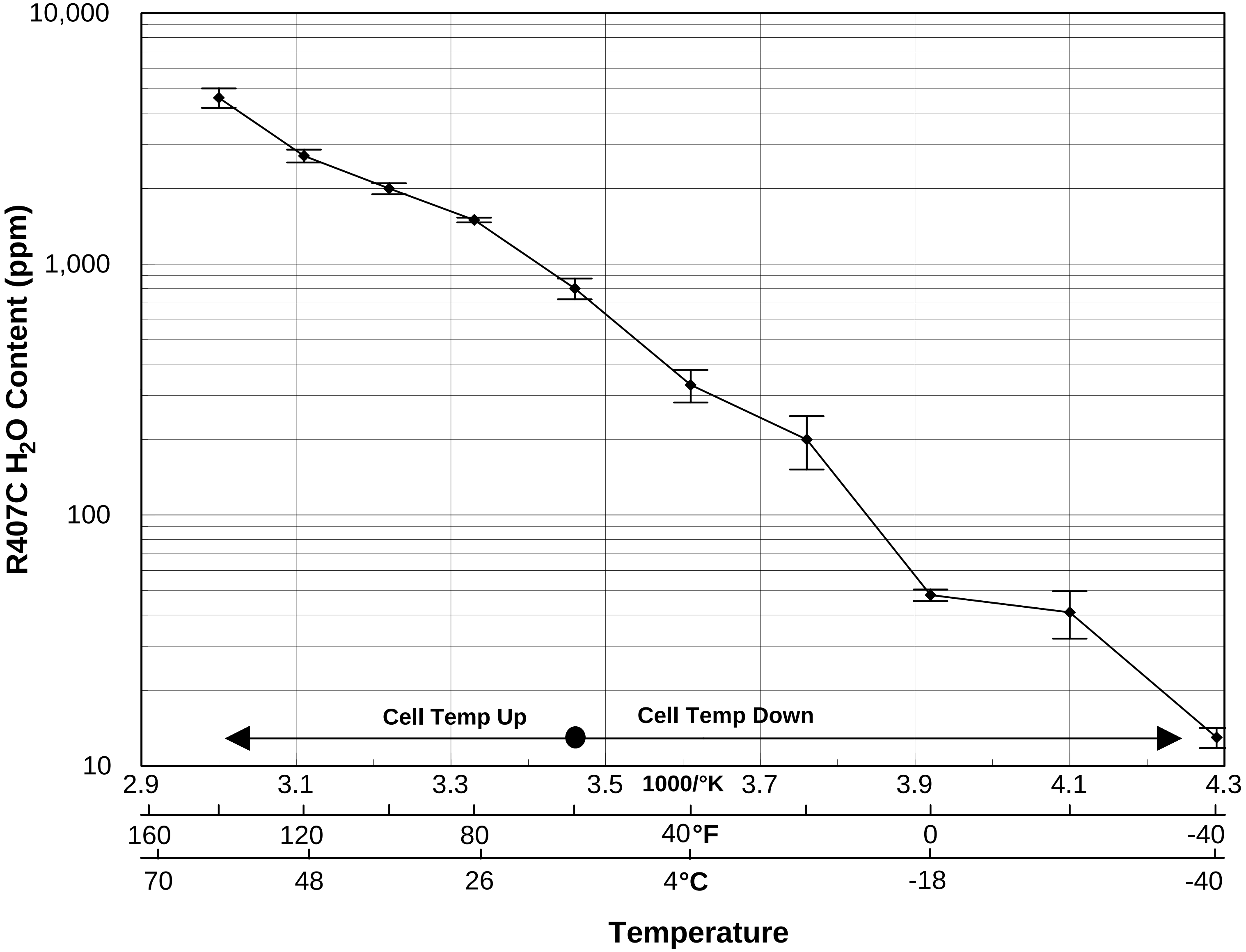
Figure 12



Water Solubility in R407C

10g H_2O and 1.0Kg R407C

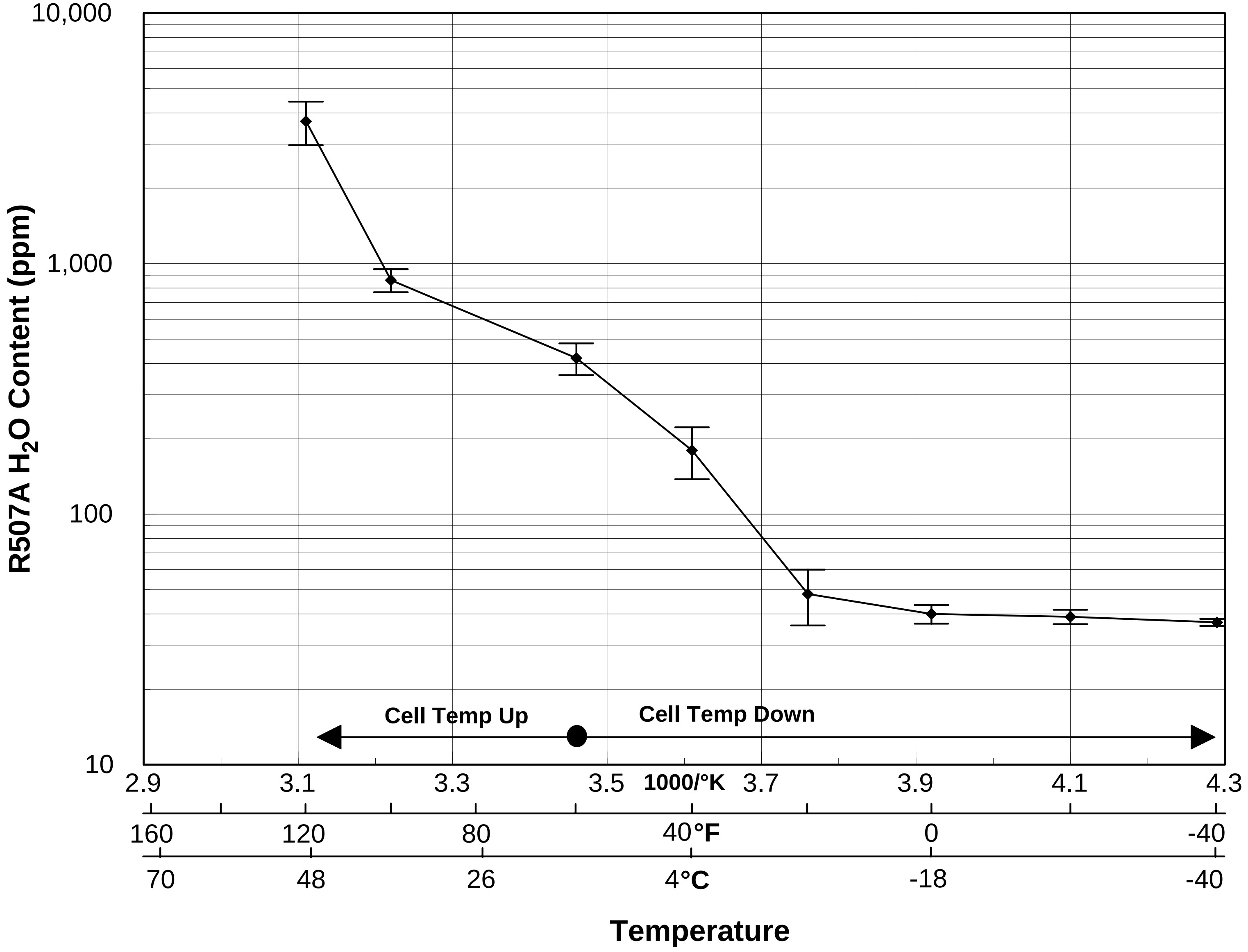
Figure 13



Water Solubility in R507A

10g H_2O and 1.0Kg R507A

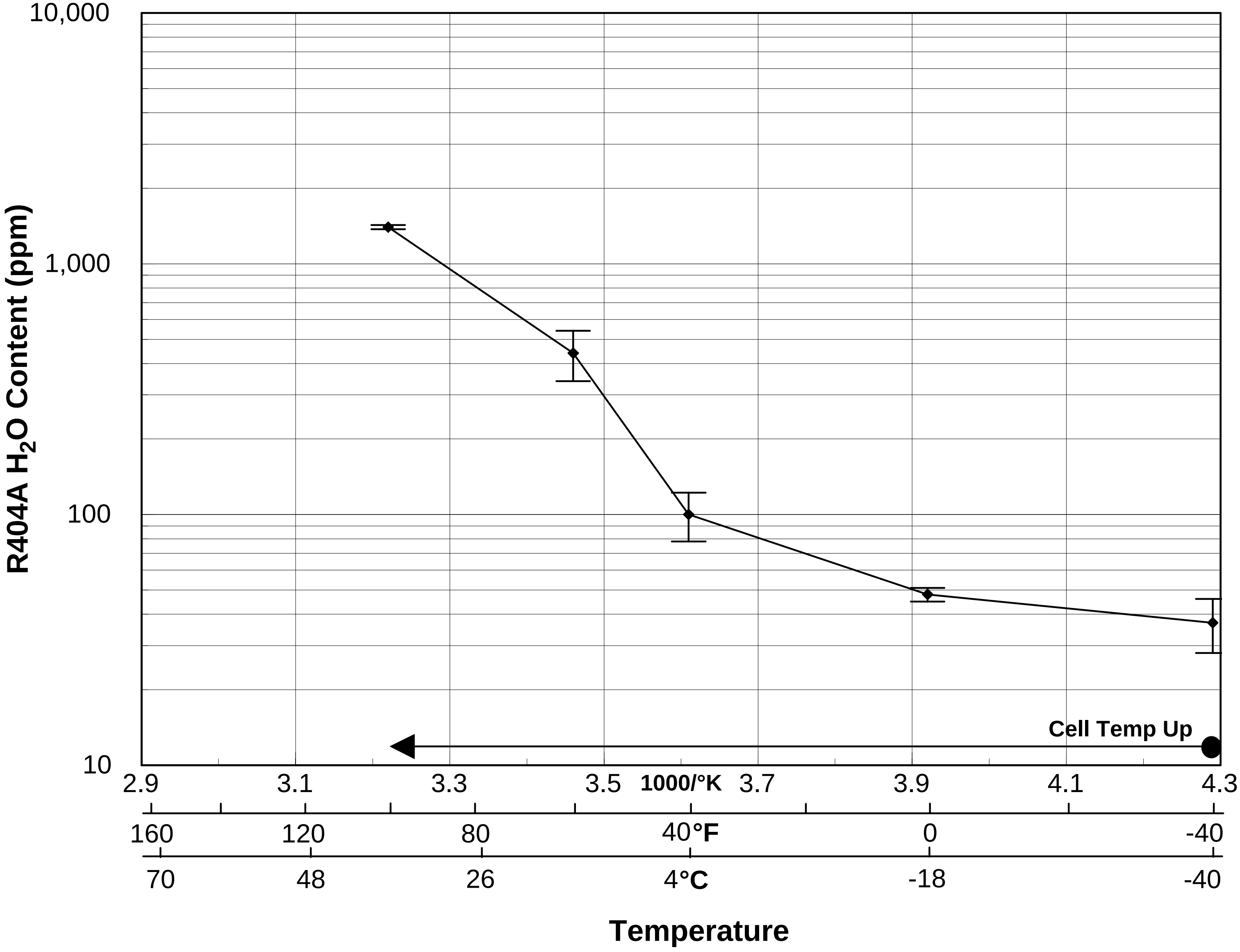
Figure 14



Water Solubility in R404A

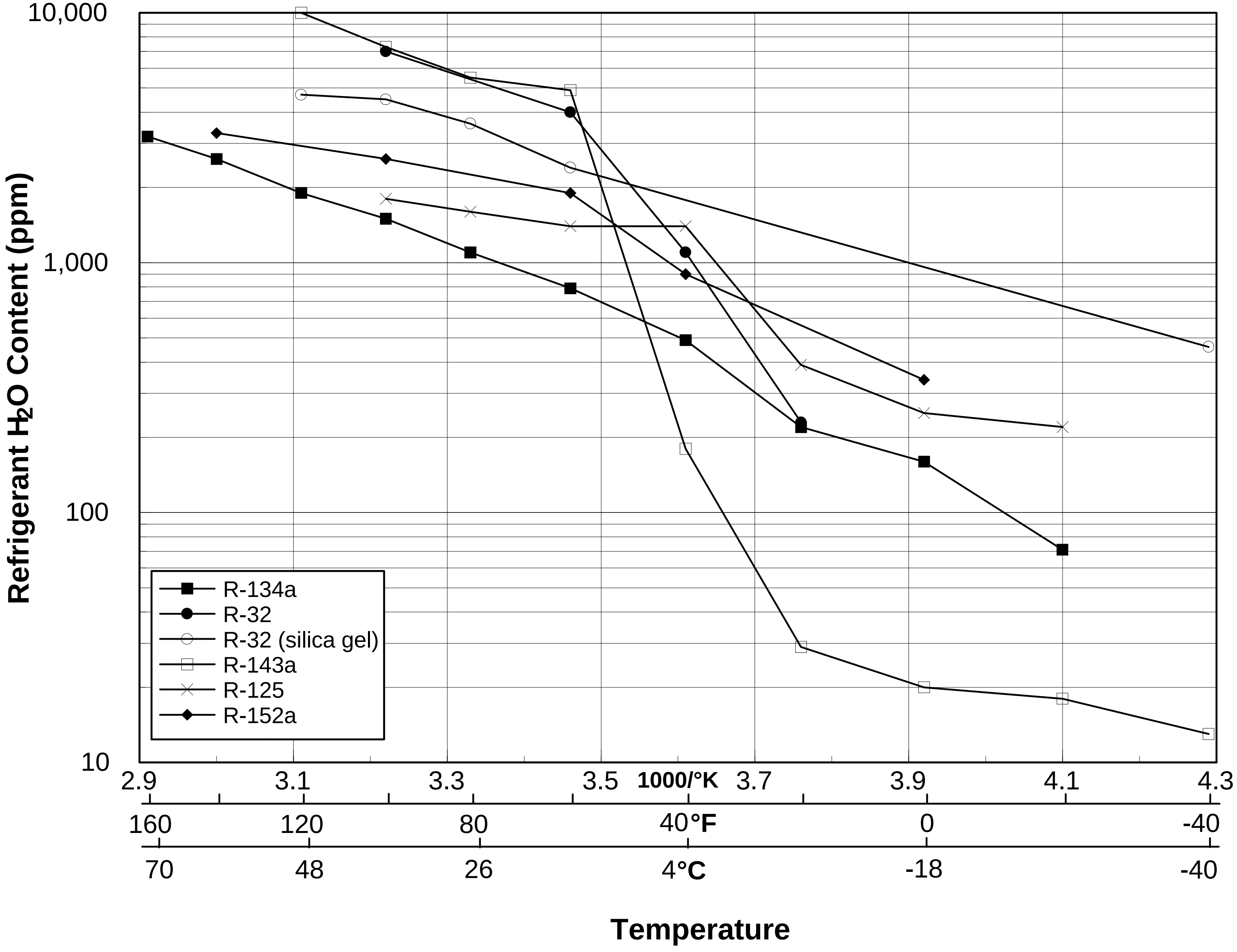
15g H_2O and 1.5Kg R404A

Figure 15



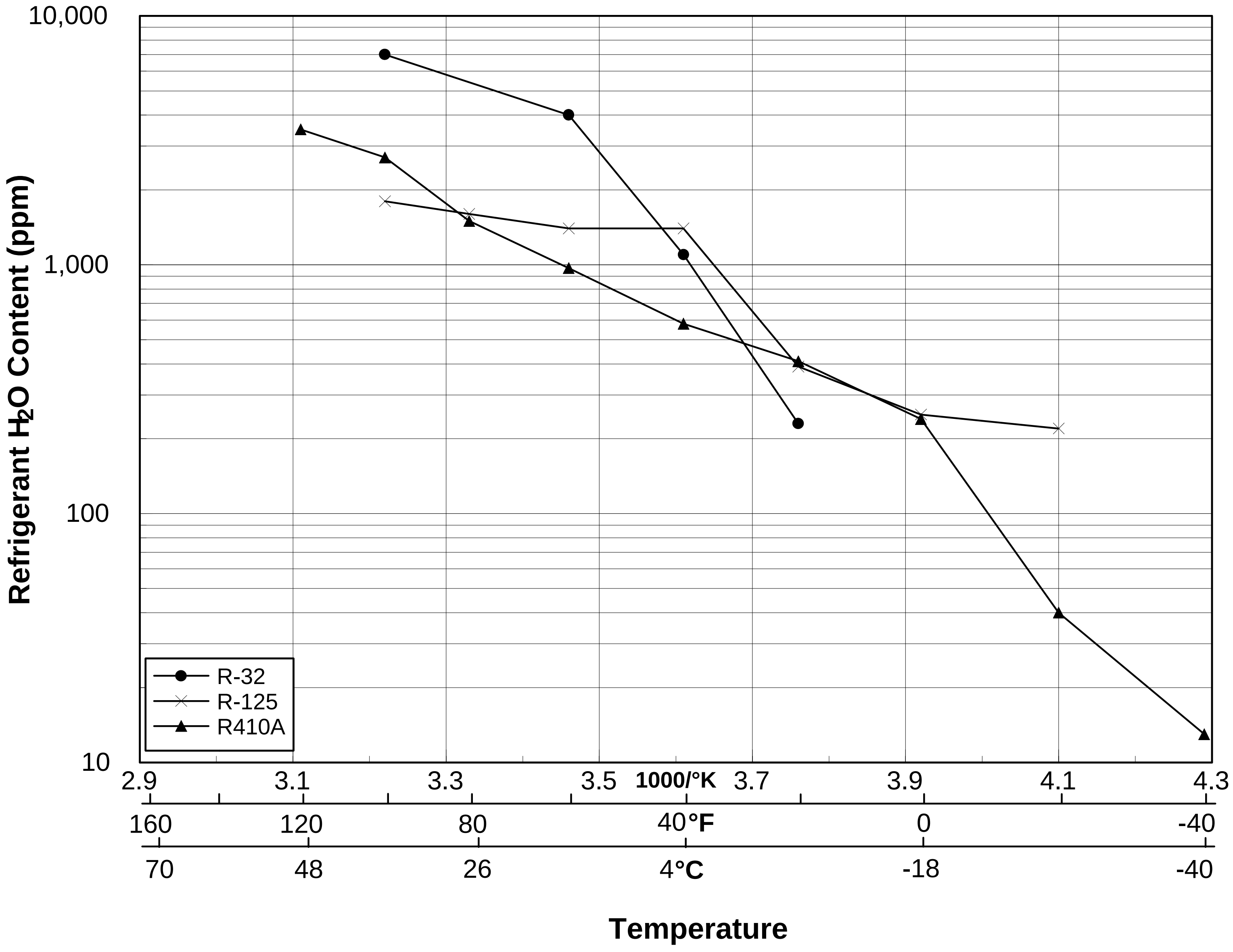
Water Solubility Comparison of R-134a, R-32, R-143a, R-125, and R-152a

Figure 16



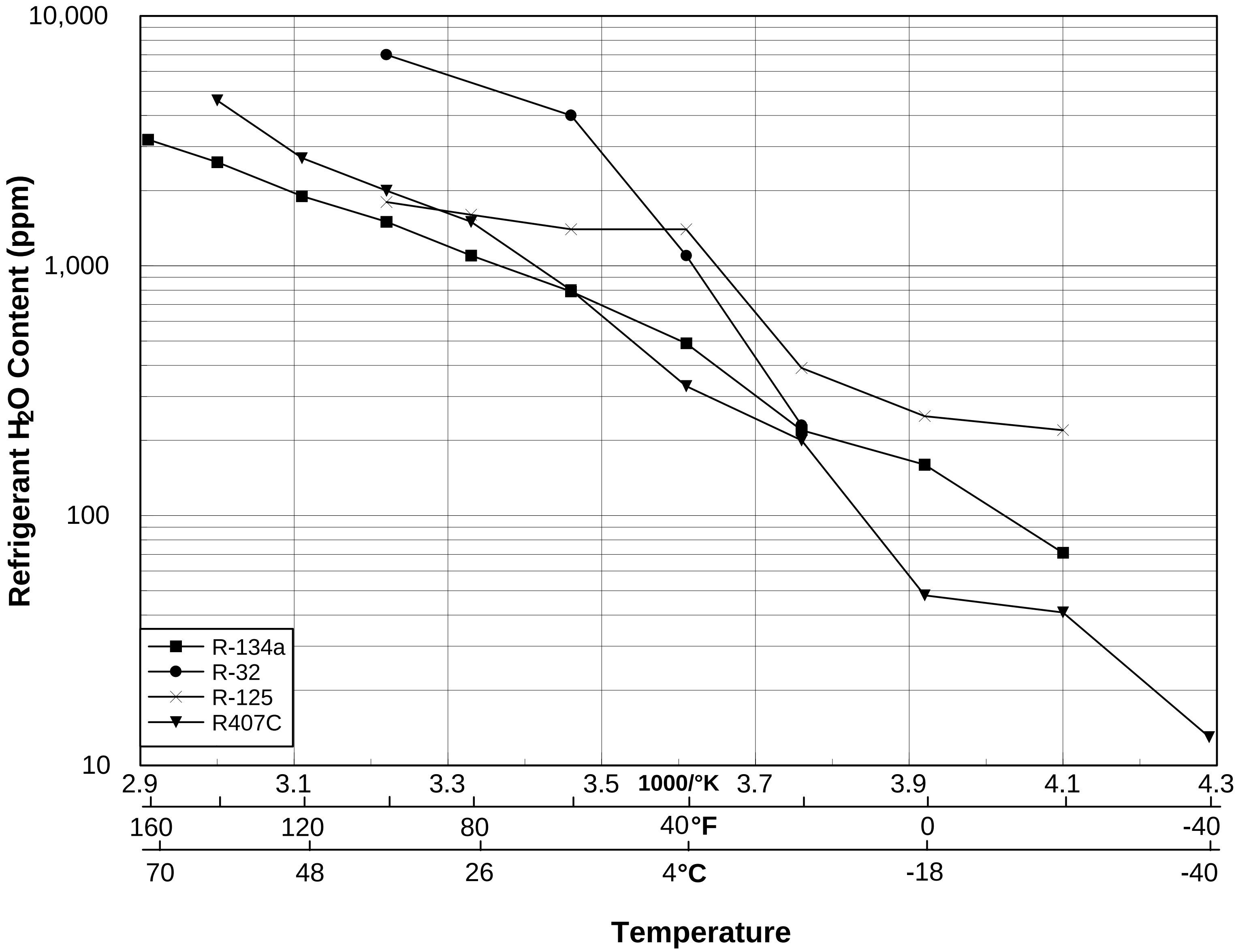
Water Solubility Comparison of R-32, R-125, and R410A

Figure 17



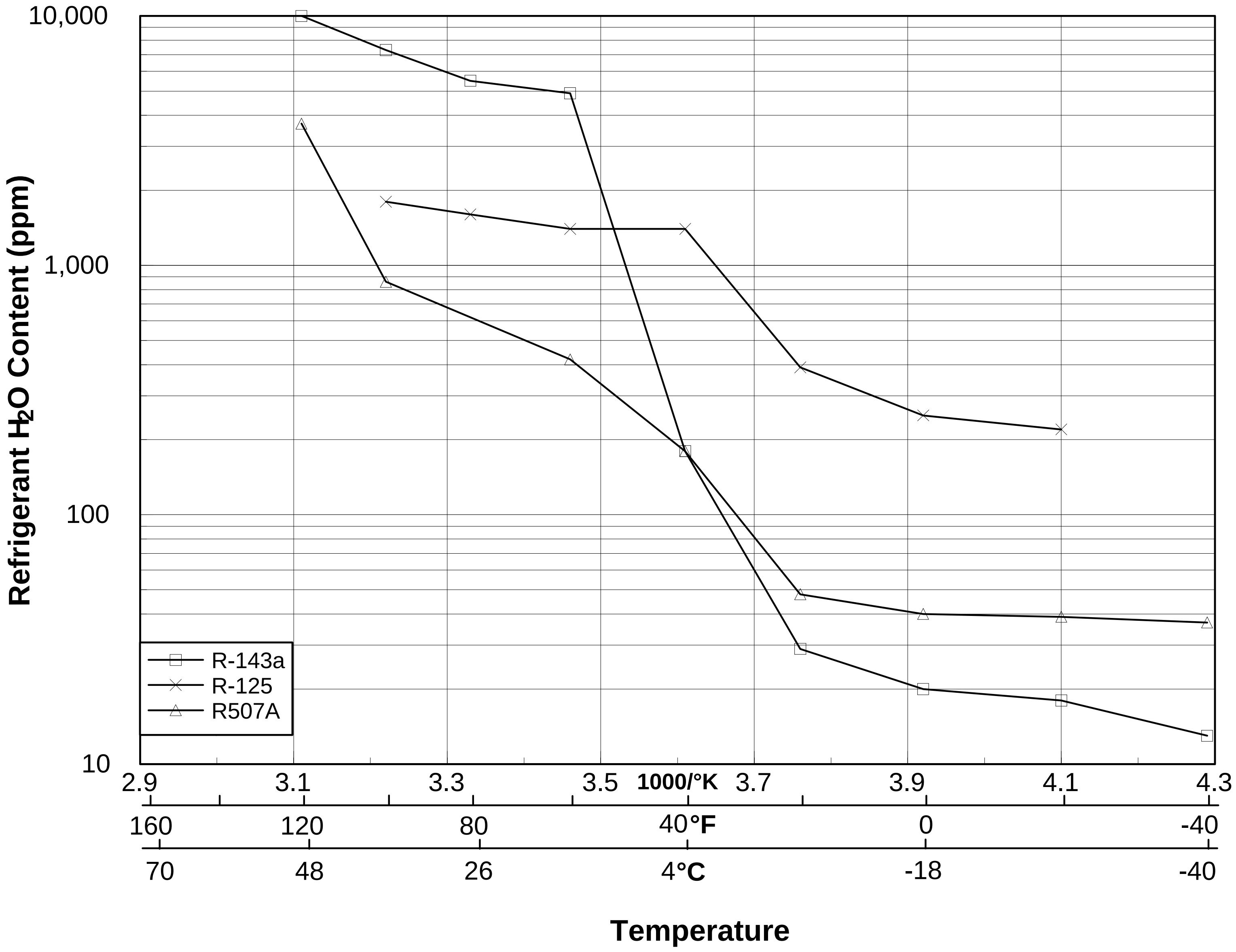
Water Solubility Comparison of R-134a, R-32, R-125, and R407C

Figure 18



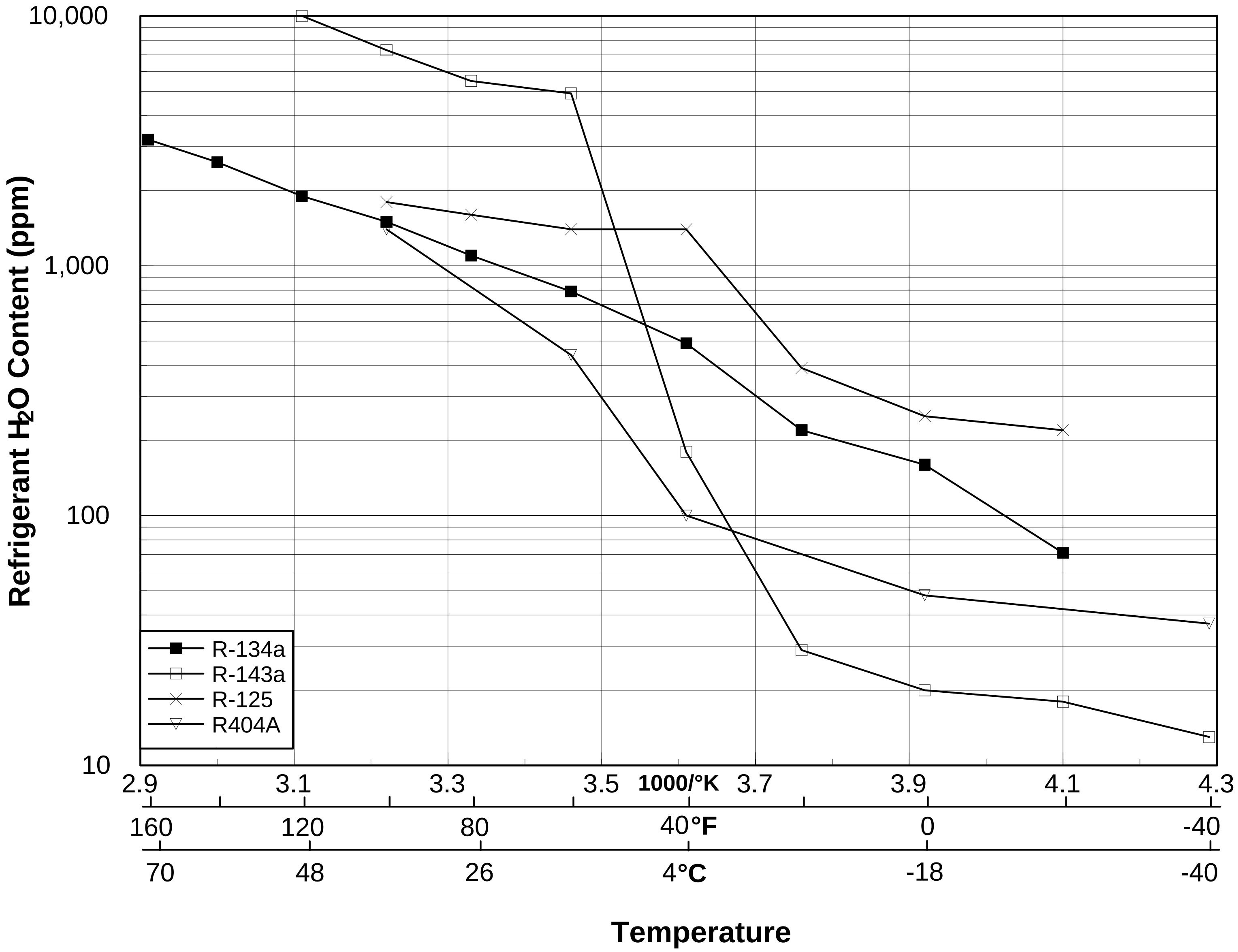
Water Solubility Comparison of R-143a, R-125, and R507A

Figure 19



Water Solubility Comparison of R-134a, R-143a, R-125, and R404A

Figure 20



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Appendix A
Raw Data

Raw Data Points: Solubility of H_2O in R-134a with 8.0g H_2O and 1.0Kg R-134a

Table A.1

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-100/-73	5.00	0	5.7
		0	
		0	
		22.8	
-80/-62	4.74	32.3	12
		0	
		0	
		15.7	
-60/-51	4.50	16.1	23
		0	
		52.3	
		23.6	
-20/-29	4.10	64.7	71
		79.9	
		63.5	
		76.9	
0/-18	3.92	168	160
		162	
		158	
20/-6.7	3.76	225	220
		199	
		227	
		237	
40/4.4	3.61	478	490
		469	
		511	
		509	
		483	
60/16	3.46	763	790
		730	
		810	
		856	
80/27	3.33	1,067	1,100
		1,094	
		1,088	
		1,092	
		1,042	
100/38	3.22	1,546	1,500
		1,552	
		1,428	
		1,488	
		1,529	

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
120/49	3.11	2,057	1,900
		1,929	
		1,823	
		1,754	
		2,097	
		1,837	
140/60	3.00	2,488	2,600
		2,667	
		2,687	
		2,511	
160/71	2.91	3,040	3,200
		3,018	
		3,482	
		3,481	
		2,936	
		3,008	

Raw Data Points: Solubility of H_2O in R-32 with 15g H_2O and 1.5Kg R-32
Table A.2

Temperature		H_2O (ppm)	
(°F/°C)	**(1000/°K)**	**Raw Data Points**	**Average**
20/-6.7	3.76	243	230
		215	
40/4.4	3.61	1,054	1,100
		1,108	
60/16	3.46	4,411	4,000
		3,601	
100/38	3.22	7,108	7,000
		7,367	
		6,548	

Raw Data Points: Solubility of H_2O in R-32 with 25g H_2O in 50g 14-20 mesh Silica Gel and 1.5Kg R-32

Table A.3

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-40/-40	4.29	479	460
		439	
		462	
60/16	3.46	2,520	2,400
		2,393	
		2,303	
80/27	3.33	3,883	3,600
		3,152	
		3,870	
100/38	3.22	4,271	4,500
		4,289	
		4,919	
120/49	3.11	4,519	4,700
		4,567	
		4,645	
		4,720	
		4,804	

Raw Data Points: Solubility of H_2O in R-143a with 15g H_2O and 1.5Kg R-143a

Table A.4

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-100/-73	5.00	1.20	2.5
		3.80	
-80/-62	4.74	0	4.1
		0	
		12.2	
-60/-51	4.50	3.51	6.9
		0	
		17.2	
-40/-40	4.29	15.6	13
		10.9	
		11.8	
-20/-29	4.10	17.6	18
		16.9	
		19.6	
0/-18	3.92	21.9	20
		17.3	
20/-6.7	3.76	29.3	29
		29.3	
40/4.4	3.61	148	180
		194	
		189	
60/16	3.46	5,170	4,900
		3,899	
		5,563	
80/27	3.33	5,800	5,500
		4,900	
		5,800	
100/38	3.22	7,600	7,300
		7,000	
120/49	3.11	11,100	10,000
		9,000	

Raw Data Points: Solubility of H_2O in R-125 with 10g H_2O and 1.0Kg R-125
Table A.5

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-100/-73	5.00	71.1	52
		32.9	
-80/-62	4.74	0	72
		144	
-60/-51	4.50	28.0	100
		172	
-20/-29	4.10	249	220
		177	
		214	
		225	
0/-18	3.92	267	250
		230	
20/-6.7	3.76	350	390
		404	
		466	
		336	
40/4.4	3.61	1,500	1,400
		1,500	
		1,100	
60/16	3.46	1,400	1,400
		1,200	
		1,600	
80/27	3.33	1,700	1,600
		1,400	
100/38	3.22	2,000	1,800
		1,900	
		1,500	

Raw Data Points: Solubility of H_2O in R-152a with 15g H_2O and 1.5Kg R-152a

Table A.6

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
0/-18	3.92	375	340
		357	
		276	
40/4.4	3.61	868	900
		922	
60/16	3.46	2,062	1,900
		1,674	
100/38	3.22	2,816	2,600
		2,240	
		2,669	
140/60	3.00	3,622	3,300
		3,202	
		3,058	

Raw Data Points: Solubility of H_2O in R410A with 10g H_2O and 1.0Kg R410A
Table A.7

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-100/-73	5.00	0.114	0.06
		0	
-80/-62	4.74	0.200	0.31
		0.630	
		0	
		0.410	
-60/-51	4.50	0	1.7
		5.07	
		0	
		1.67	
-40/-40	4.29	11.6	13
		14.7	
		12.7	
		11.7	
-20/-29	4.10	39.2	40
		44.5	
		39.5	
		36.0	
0/-18	3.92	253	240
		295	
		222	
		193	
20/-6.7	3.76	407	410
		395	
		432	
40/4.4	3.61	645	580
		550	
		545	
		585	
60/16	3.46	953	970
		937	
		1,011	
		983	
80/27	3.33	1,420	1,500
		1,293	
		1,731	
100/38	3.22	2,759	2,700
		2,466	
		2,952	
120/49	3.11	3,252	3,500
		3,356	
		3,862	

Raw Data Points: Solubility of H_2O in R407C with 10g H_2O and 1.0Kg R407C
Table A.8

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-100/-73	5.00	0	1.2
		2.36	
-80/-62	4.74	5.10	2.6
		0	
-60/-51	4.50	0	5.5
		16.5	
		0	
-40/-40	4.29	14.2	13
		12.3	
-20/-29	4.10	48.8	41
		41.4	
		32.2	
0/-18	3.92	48.3	48
		50.5	
		46.3	
20/-6.7	3.76	162	200
		227	
		213	
		237	
		152	
40/4.4	3.61	320	330
		379	
		297	
60/16	3.46	777	800
		876	
		729	
		804	
		792	
80/27	3.33	1,513	1,500
		1,533	
		1,511	
		1,532	
100/38	3.22	1,908	2,000
		2,078	
		2,055	
		1,897	
120/49	3.11	2,861	2,700
		2,643	
		2,745	
		2,569	
140/60	3.00	4,188	4,600
		4,935	

Raw Data Points: Solubility of H_2O in R507A with 10g H_2O and 1.0Kg R507A
Table A.9

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-100/-73	5.00	0	3.8
		7.50	
-80/-62	4.74	3.20	7.3
		11.4	
-60/-51	4.50	6.90	14
		20.6	
-40/-40	4.29	37.8	37
		35.8	
-20/-29	4.10	40.9	39
		36.4	
0/-18	3.92	37.5	40
		43.4	
		37.6	
		38.1	
20/-6.7	3.76	41.5	48
		59.6	
		42.3	
40/4.4	3.61	154	180
		148	
		210	
		154	
		222	
60/16	3.46	481	420
		409	
		406	
		375	
100/38	3.22	934	860
		897	
		773	
		769	
		946	
120/49	3.11	3,711	3,700
		4,355	
		2,974	

Raw Data Points: Solubility of H_2O in R404A with 15g H_2O and 1.5Kg R404A

Table A.10

Temperature		H_2O (ppm)	
(°F/°C)	(1000/°K)	Raw Data Points	Average
-40/-40	4.29	45	37
		28	
0/-18	3.92	50	48
		45	
40/4.4	3.61	122	100
		82	
60/16	3.46	338	440
		535	
		453	
100/38	3.22	1,426	1,400
		1,384	
		1,421	

Appendix B
Data Points (averaged)

Data Points (averaged): Solubility of H_2O in R-134a with 8.0g H_2O and 1.0Kg R-134a

Table B.1

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-100/-73	5.00	5.7	±17	300
-80/-62	4.74	12	±20	170
-60/-51	4.50	23	±29	130
-20/-29	4.10	71	±8.9	13
0/-18	3.92	160	±8.0	5.0
20/-6.7	3.76	220	±21	10
40/4.4	3.61	490	±21	4.3
60/16	3.46	790	±66	8.4
80/27	3.33	1,100	±58	5.3
100/38	3.22	1,500	±72	4.8
120/49	3.11	1,900	±200	11
140/60	3.00	2,600	±110	4.2
160/71	2.91	3,200	±280	8.8

Data Points (averaged): Solubility of H_2O in R-32 with 15g H_2O and 1.5Kg R-32

Table B.2

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
20/-6.7	3.76	230	±15	6.5
40/4.4	3.61	1,100	±46	4.2
60/16	3.46	4,000	±410	9.8
100/38	3.22	7,000	±450	6.4

Data Points (averaged): Solubility of H_2O in R-32 with 25g H_2O in 50g 14-20 mesh Silica Gel and 1.5Kg R-32

Table B.3

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-40/-40	4.29	460	±21	4.6
60/16	3.46	2,400	±120	5.0
80/27	3.33	3,600	±450	13
100/38	3.22	4,500	±420	9.3
120/49	3.11	4,700	±180	3.8

Data Points (averaged): Solubility of H_2O in R-143a with 15g H_2O and 1.5Kg R-143a
Table B.4

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-100/-73	5.00	2.5	±1.3	52
-80/-62	4.74	4.1	±8.1	200
-60/-51	4.50	6.9	±10	140
-40/-40	4.29	13	±2.6	20
-20/-29	4.10	18	±1.6	8.9
0/-18	3.92	20	±2.7	14
20/-6.7	3.76	29	±0.3	1.0
40/4.4	3.61	180	±32	18
60/16	3.46	4,900	±1,000	20
80/27	3.33	5,500	±600	11
100/38	3.22	7,300	±300	4.1
120/49	3.11	10,000	±1,000	10

Data Points (averaged): Solubility of H_2O in R-125 with 10g H_2O and 1.0Kg R-125
Table B.5

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-100/-73	5.00	52	±19	37
-80/-62	4.74	72	±72	100
-60/-51	4.50	100	±72	72
-20/-29	4.10	220	±43	20
0/-18	3.92	250	±20	8.0
20/-6.7	3.76	390	±76	19
40/4.4	3.61	1,400	±300	21
60/16	3.46	1,400	±200	14
80/27	3.33	1,600	±200	13
100/38	3.22	1,800	±300	17

Data Points (averaged): Solubility of H_2O in R-152a with 15g H_2O and 1.5Kg R-152a
Table B.6

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
0/-18	3.92	340	±64	19
40/4.4	3.61	900	±32	3.6
60/16	3.46	1,900	±230	12
100/38	3.22	2,600	±360	14
140/60	3.00	3,300	±320	9.7

Data Points (averaged): Solubility of H_2O in R410A with 10g H_2O and 1.0Kg R410A
Table B.7

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-100/-73	5.00	0.06	±0.06	100
-80/-62	4.74	0.31	±0.32	97
-60/-51	4.50	1.7	±3.4	170
-40/-40	4.29	13	±1.7	13
-20/-29	4.10	40	±4.5	11
0/-18	3.92	240	±55	23
20/-6.7	3.76	410	±22	5.4
40/4.4	3.61	580	±65	11
60/16	3.46	970	±41	4.2
80/27	3.33	1,500	±230	15
100/38	3.22	2,700	±250	9.3
120/49	3.11	3,500	±360	10

Data Points (averaged): Solubility of H_2O in R407C with 10g H_2O and 1.0Kg R407C
Table B.8

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-100/-73	5.00	1.2	±1.2	100
-80/-62	4.74	2.6	±2.6	100
-60/-51	4.50	5.5	±11	200
-40/-40	4.29	13	±1.2	9.2
-20/-29	4.10	41	±8.8	21
0/-18	3.92	48	±2.5	5.2
20/-6.7	3.76	200	±48	24
40/4.4	3.61	330	±49	15
60/16	3.46	800	±76	9.5
80/27	3.33	1,500	±33	2.2
100/38	3.22	2,000	±100	5.0
120/49	3.11	2,700	±160	5.9
140/60	3.00	4,600	±410	8.9

Data Points (averaged): Solubility of H_2O in R507A with 10g H_2O and 1.0Kg R507A
Table B.9

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-100/-73	5.00	3.8	±3.8	100
-80/-62	4.74	7.3	±4.1	56
-60/-51	4.50	14	±7.1	51
-40/-40	4.29	37	±1.2	3.2
-20/-29	4.10	39	±2.6	6.7
0/-18	3.92	40	±3.4	8.5
20/-6.7	3.76	48	±12	25
40/4.4	3.61	180	±42	23
60/16	3.46	420	±61	15
100/38	3.22	860	±91	11
120/49	3.11	3,700	±730	20

Data Points (averaged): Solubility of H_2O in R404A with 15g H_2O and 1.5Kg R404A

Table B.10

Temperature		H_2O (ppm)	Error (ppm)	Error (ppm)/H_2O (ppm) (%)
(°F/°C)	(1000/°K)			
-40/-40	4.29	37	±9	24
0/-18	3.92	48	±3	6.3
40/4.4	3.61	100	±22	22
60/16	3.46	440	±100	23
100/38	3.22	1,400	±26	1.9

Appendix C
Sealed Tube Analysis Method

Sealed tubes were prepared to observe the formation and disappearance of clathrate hydrates in water and refrigerant as temperatures decreased from 80°F (27°C) to 0°F (-18°C) and increased from 0°F (-18°C) to 80°F (27°C). Specific ratios of water and refrigerant were sealed in heavy walled glass tubes labeled with ceramic marking ink on both ends. When labeling tubes, the ink turns red as it is burned into the glass with a propane torch, then a cooler flame is used to smooth the stress lines in the glass around the burned area.

The total weight of water and refrigerant in the specified ratio in the macro tubes should be approximately 10g. The amount of water needed in each tube is calculated and added to the tube using a 10µl syringe or a long Pasteur pipette. A four-place electronic balance is used for weighing and the weights are recorded before and after water addition.

Oxygen and a MAPP gas torch form a thick-walled capillary in the glass above the water in each tube, about 2½" from the top. A uniform glass wall thickness should be maintained while constricting the tube. Didymium eye glasses assist in seeing the glass during this manipulation.

To add refrigerant, first attach the constricted tube to the gas manifold. Submerge the tube in liquid nitrogen in a thermos dewar. Evacuate the sample to <40mTorr and then close the valve to the sample. Attach the refrigerant gas to the manifold with a charging hose and evacuate the hose. Purge the manifold three times by adding refrigerant and evacuating it. The third evacuation should be <60mTorr. Add refrigerant to the manifold so that the internal pressure is 800-900 mm Hg. Slowly open the tube valve to the manifold and allow the refrigerant gas to condense as it contacts the cold tube. Control the amount of added refrigerant by observing the manometer Hg fall. The difference in Hg levels can be related to the weight of condensed refrigerant. Since the specific gravities of all refrigerants are different, a refrigerant constant, which relates Hg pressure drop to refrigerant gas weight, must be determined before sample tubes are charged with refrigerant. After sufficient refrigerant has been added, fill the dewar with liquid nitrogen and evacuate the manifold to <40mTorr. Open the tube valve to eliminate non-condensable gases (such as air) from the tube and evacuate to <40mTorr.

To determine the aforementioned refrigerant constant, first prepare empty glass tubes. Accurately record their weight and constrict the tubes. Attach them to the manifold and precisely add varying amounts of refrigerant from 150-300 mm Hg. Seal and allow the tubes to warm to room temperature. Re-weigh matched tops and bottoms of each tube. Calculate the constant for each of the samples by the formula below and obtain an average.

$$C = \frac{b - a}{H} = \text{grams} / \text{mm Hg}$$

where C = refrigerant constant

a = initial weight of the tube (g)

b = final weight of refrigerant + tube (g)

H = mm of Hg pressure difference in manifold

Once the water is accurately weighed into the tube, the proper weight of refrigerant to be added based on the specified ratio can be calculated by the formula:

$$R = \frac{L(1 - P)}{P}$$

where R = refrigerant weight (g)

L = water weight (g)

P = percent water [expressed as a decimal (i.e. 40% = .40)]

The mm of Hg manometer pressure drop needed to deliver a certain weight of refrigerant can be calculated from the above equation and the refrigerant constant.

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

where M = mm Hg manometer pressure drop

R = refrigerant weight (g)

C = refrigerant constant (g/mm Hg)

After refrigerant has been added to the tube, proceed to seal the tube. Adjust the oxygen and MAPP gases to give a 3-4" flame. With the tube still evacuated and in liquid nitrogen, warm the constriction uniformly until it is drawn inward by the vacuum. Heat the fused portion strongly and lower the tube to produce a molten thread. Cut the thread with the flame. The tube can be annealed while in liquid nitrogen using a cooler carbon-rich flame. The annealing process deposits carbon on the glass that must be wiped off later. Remove the tube from the liquid nitrogen.

SAFETY NOTE: Once the tube has been sealed and brought to room temperature, it is under high internal pressure and could explode at any time. When possible, keep it behind a safety shield and wear safety glasses, heavy gloves, and a face shield.

Prior to heating in the oven, the two parts of the tube are matched and re-weighed so that the actual weight of refrigerant added can be determined. Thus, the actual weight ratio of water:refrigerant in the sealed tube can be calculated.

Carefully insert the sealed tube into a protective metal sleeve and cap it. Put it into a 122ºF (50ºC) oven for 2-3 hours as a safety check. Taking appropriate safety precautions inspect the tube for hydrate formation going up and down in temperature from 0°F (-18°C) to 80°F (27°C).

The photographs in Appendix D were taken with a blue filter, 200 speed film, and a 1/30 second shutter speed and developed by subtracting 2 densities and 1 cyan to compensate for low light.

Appendix D
Photographic Evidence of Clathrate Hydrate Formation

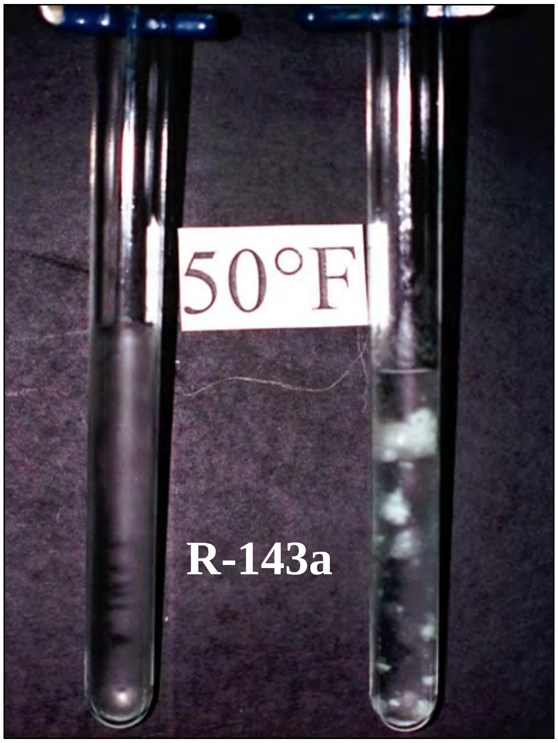
Picture 1

1% water 5% water

Picture 2

1% water 5% water

Picture 3

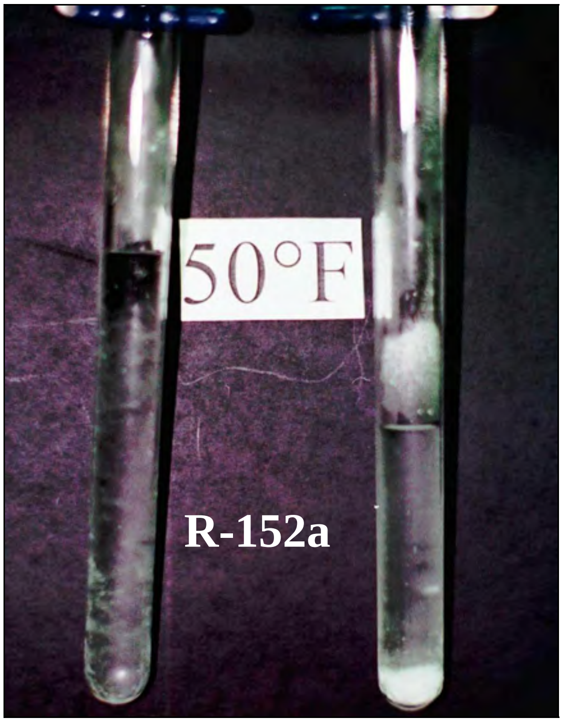


1% water 5% water

Picture 4

1% water 5% water

Picture 5

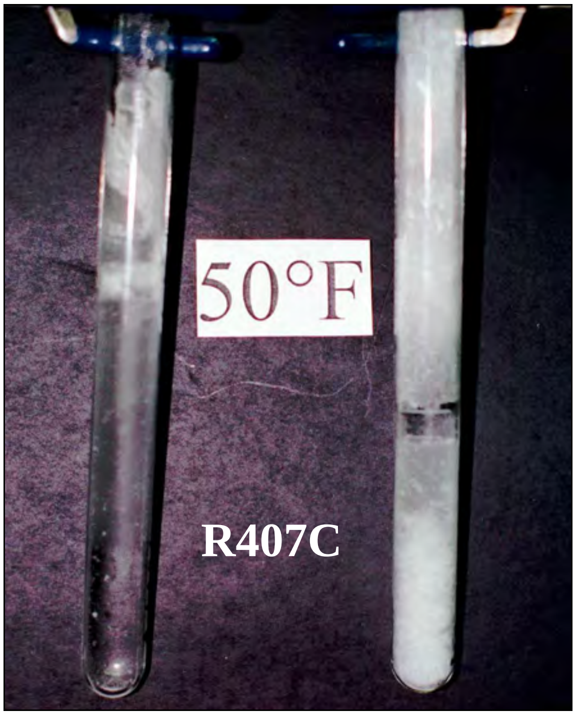


1% water 5% water

Picture 6

1% water 5% water

Picture 7



1% water 5% water

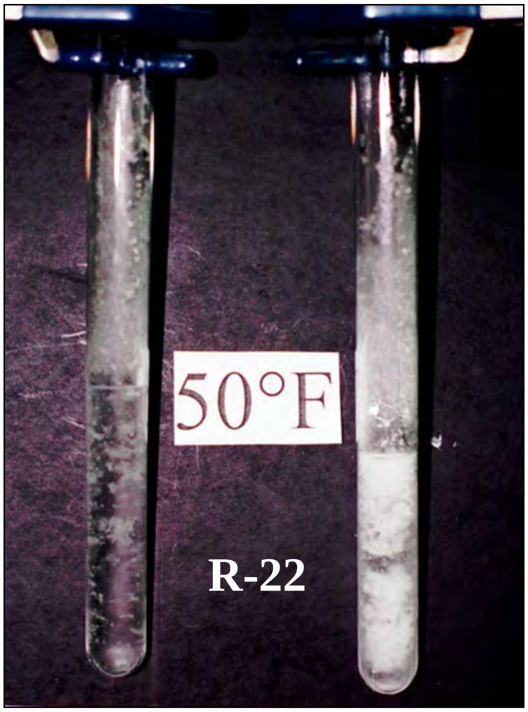
Picture 8

1% water 5% water

Picture 9

1% water 5% water

Picture 10



1% water 5% water