INVITATION TO SUBMIT A RESEARCH PROPOSAL ON AN ASHRAE RESEARCH PROJECT

1886-TRP, Kinetic and Mechanistic Study of the Breakdown and Interactions of HFO Refrigerants

Attached is a Request-for-Proposal (RFP) for a project dealing with a subject in which you, or your institution have expressed interest. Should you decide not to submit a proposal, please circulate it to any colleague who might have interest in this subject.

Sponsoring Committee: TC 3.2 Refrigerant System Chemistry and Contaminant Control
Co-sponsored by: N/A

Budget Range: $120,000 may be more or less as determined by value of proposal and competing proposals.

Scheduled Project Start Date: **April 1st, 2026,** or later.

All proposals must be received at ASHRAE Headquarters by 8:00 AM, EDT, December 15th, 2025. NO EXCEPTIONS, NO EXTENSIONS. Electronic copies must be sent to rpbids@ashrae.org. Electronic signatures must be scanned and added to the file before submitting. The submission title line should read: 1886-TRP, Kinetic and Mechanistic Study of the Breakdown and Interactions of HFO Refrigerants, and *"Bidding Institutions Name"* (electronic pdf format, ASHRAE's server will accept up to 10MB)

If you have questions concerning the Project, we suggest you contact one of the individuals listed below:

For Technical Matters
Technical Contact
Morgan Leehey
E-Mail: Morgan.Herried@tranetechnologies.com

For Administrative or Procedural Matters:
Manager of Research & Technical Services (MORTS)
Steve Hammerling
ASHRAE, Inc.
180 Technology Parkway, NW
Peachtree Corners, GA 30092
Phone: 404-636-8400
Fax: 678-539-2111
E-Mail: MORTS@ashrae.net

Contractors who plan to submit a proposal must notify the Manager of Research and Technical Services (MORTS) via email by December 1st. This will ensure that they receive any late or additional information regarding the RFP before the bid due date. Monday, December 1st, 2025, is the deadline for submitting technical inquiries.

All proposals must be submitted electronically. Electronic submissions require a PDF file containing the complete proposal preceded by signed copies of the two forms listed below in the order listed below. **ALL electronic proposals are to be sent to rpbids@ashrae.org.**

All other correspondence must be sent to ddaniel@ashrae.org and shammerling@ashrae.org. In all cases, the proposal must be submitted to ASHRAE by 8:00 AM, EDT, Monday, December 15th 2025.
NO EXCEPTIONS, NO EXTENSIONS.

The following forms (Application for Grant of Funds and the Additional Information form have been combined) must accompany the proposal:

(1) ASHRAE Application for Grant of Funds (electronic signature required) and
(2) Additional Information for Contractors (electronic signature required) ASHRAE Application for Grant of Funds (signed) and

ASHRAE reserves the right to reject any or all bids.

State of the Art (Background)

Over recent years the industry has moved to support the adoption of hydrofluoroolefin (HFO) refrigerants. While a great deal of work was performed to support the adoption of these fluids – with basic material compatibility and chemical stability performed – there still exist knowledge gaps related to the underlying mechanisms and rates driving the reactivity of this new class of refrigerant.

HFO refrigerants, unlike CFC, HCFC, and HFC refrigerants, have a unique chemical link to drive their low global warming potential (GWP). This uniqueness, characterized by a carbon-carbon double bond, presents different reaction mechanisms compared to prior fluids. During initial chemical stability tests for these fluids, screening tests were performed to understand the thermal stability of these fluids relative to current HFC fluids. Two key studies were supported by the industry [Rosine, Majurin] however, while results pointed to the liberation of fluoride from the HFO molecule, no follow up work has yet been proposed to verify reaction mechanisms associated with these observations to date.

As the degradation and use of HFCs did not lead to fluoride production, this observation merits continued investigation, to improve understanding of the chemical stability, and potential contamination formation from HFO refrigerants, including identification of decomposition products not yet identified to balance a reaction yielding fluoride.

Justification and Value to ASHRAE

This work will support ASHRAE in the facilitation of the adoption low GWP synthetic refrigerants for cooling and more importantly electrification of heating application (heat pumps to very high temperature heat pumps) by fully understanding these reactions mechanism pathways and potential impacts on systems and lead to potential mitigation practices. The proposed mechanistic study will aim to provide the ability to better comprehend interactions concerning chemical breakdown while using HFO refrigerants in AC&R systems. In doing so we will be learning information to help the industry optimize choices in lubricants, additives, and materials. This will lead to better reliability and efficiency that can extend the effective life of the system. A reduction in maintenance through optimization could bring down the cost of owning the system as well as reducing need of servicing equipment leading to less refrigerant used through the life of the system.

Through the alignment with ASHRAE's efforts in implementing low GWP refrigerants we are fully confident ASHRAE's members will certainly benefit from and be respected for partly or fully funding this initiative.

Potential Co-Funding: Co-funding this via its DOE/MCLR study (Xudong Wang).

Objectives

The primary objective of this work is to better understand the reaction mechanisms at play as related to the stability and reactivity of HFO refrigerants, specifically for R-1234yf. The better understanding of these fundamental aspects can drive better approaches to future research as well as will immediately impact technology development and implementation surrounding HFO refrigerants and blends in areas such as lubricant formulation (stabilizer additives), selection of materials and chemicals of construction, and contaminant control.

Additionally, findings as part of this study with R-1234yf could be applied to other HFO/HCFO chemistries to enable better understanding of refrigerant chemistry in systems using these fluids or blends containing these fluids.

Optionally: Based on research findings and methods used to follow reaction rates and kinetics, could lead to proposals for new standard method development.

Scope:

This evaluation and testing shall be phased (gated with milestones) in terms of both money and efforts, as follows. The project may be halted at any point if the PMS deems it necessary based on the results.

Task; Duration; Task/Milestone; Payment

1; 1 month; White paper review of past studies, reaction mechanisms and proposal of reaction products for R-1234yf refrigerant molecules (with and without lubricants) with documentation of testing time, temperature and findings.

2; 5 months; ASHRAE '97 Aging Study [Qualitative Study - Evaluation of proposed mechanisms]

3; 5 months; ASHRAE '97 Aging Study [Quantitative/Arrhenius Study – leverage Task 2 learning]

4; 1 month; Proposal of future work to enable continued understanding

1 - To investigate prior publications related to reaction mechanisms of HFO/HCFO/HCO molecules [and related olefin and fluorinated/chlorinated olefins reaction mechanisms] and to apply fundamental reaction mechanisms to R-1234yf, to develop a proposal of potential system reaction products for HFO refrigerants (with and without lubricants [POE, PVE, PAG] & common system contaminants such as air and water).

Background:

The scope of work of AHRTI-Rpt-09004-01 (Rohatgi 2012) was to evaluate thermal and chemical stability of HFO refrigerants with different lubricants. The following are the refrigerant/lubricant blends:

R1234yf/ Mixed Acid POE	R1234yf/ Branched Acid POE	R1234yf/ PVE Oil
R1234ze(E)/ Mixed Acid POE	R1234ze(E)/ Branched Acid POE	R1234ze(E)/ PVE Oil
R1234yf/R32(50:50)/ Mixed Acid POE	R1234yf/R32(50:50)/ Branched Acid POE	R1234yf/R32(50:50)/ PVE Oil

*All Lubricants used were ISO 32 viscosities.

For the scope of work for WS 1886, refrigerant R1234YF has been selected for the Kinetic and Mechanistic study of the breakdown and interaction.

Air and moisture were the independent variables that were manipulated to determine if a certain combination of refrigerant and lubricant would exhibit elevated reactivity levels in test conditions. The refrigerant/lubricant mixtures were exposed to the following conditions:

Low Moisture(~50ppm)	No Air
	High Air(~2000ppm)
High Moisture(~500ppm)	No Air
	High Air(~2000ppm)

- Refrigerant and Lubricant Decomposition was evaluated as a function of the concentration of air, moisture, and with both air and moisture. TAN and Fluoride ion concentration values were collected and analyzed after testing.
- R1234yf with an ISO 32 mixed acid demonstrated the highest number of test conditions with refrigerant decomposition. With high levels of air present in both high and low moisture concentrations illustrated almost no refrigerant decomposition, despite having high fluoride ion concentrations.
- R1234yf with an ISO 32 Branched acid with high levels of air present in both high and low moisture concentrations illustrated almost no refrigerant decomposition, despite having high fluoride ion concentrations.

- R1234yf with a PVE 32-A exhibited high levels of fluoride ion concentration regardless of the amount of air or moisture present independently of each other or in conjunction. One test condition showed the highest amount of refrigerant decomposition of 1.41%.

Conclusion:

The research demonstrates that by varying the amount of air and moisture no strong correlations can be made as to the potential kinematic mechanism of reactivity of R1234yf with an ISO 32 mixed or branched acid and or a PVE 32-A.

2 – Based on findings from step 1, determine scope for design of aging studies to enable the understanding of proposed mechanisms for HFO refrigerants. Follow ASHRAE Standard 97 testing method to expose Lubricant, metals and refrigerants to HVAC&R Conditions using the following:

Refrigerants to be Used: R-1234yf
Lubricants to be used: POE, PAG, PVE
Lubricant to Refrigerant Ratio: 50:50

Additional Experimental Variables
- <50 ppm Water
- 1000 ppm Water

Temperatures and exposure times listed below are typically used to simulate accelerated HVAC&R conditions.
- 2 weeks at 200°C
- 2 weeks at 175°C
- 8 weeks at 150°C

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EXAMPLE TEST MATRIX

	X Weeks @ XXX°C					
REFRIGERANT	50	50	50	50	50	50
POE	50	50				
PAG			50	50		
PVE					50	50
WATER <50ppm	x		x		x	
WATER 500ppm		x		x		x

After exposure, perform characterization of post-test fluids and materials to either validate or negate proposed mechanisms from task one. Testing should consider reaction products that could form in the vapor or liquid phase.

3 – With knowledge of the specific reaction/decomposition products gained from tasks 1 and 2, design experiments that will allow for determination of the rates of formation of the products and/or rate of disappearance of the subject refrigerant. Conduct kinetic studies, varying the concentrations/amounts of the refrigerant, contaminants and material of construction. Use the rate data as function of concentrations to determine the order of reaction for each of the components (refrigerant, oil, materials of construction, and any contaminants). An understanding of the order of the reaction with respect to each component provides a first insight into the mechanism of the reaction.

Conduct reactions at various temperatures, measuring rates of disappearance and formation of various components. Use this rate as a function of temperature data to generate the activation energy (E_a) and frequency factor (A) of the reaction using the Arrhenius Equation. Activation energy, frequency factors as well as entropy changes provide more in-depth knowledge of the transition states of the reaction and can provide additional details on the reaction mechanism.

<u>Analytical Techniques</u>

Potential analytical techniques for quantifying the reaction products, as well as for measuring the rates of reaction are:

1) GC/MS

2) Fluorine, proton and carbon Nuclear Magnetic Spectroscopy

3) LC/MS

4 – Propose future research necessary to understand reaction mechanisms or interactions with HVAC&R materials and chemicals.

<u>Deliverables</u>:

1. Contractor will meet with the Project Monitoring Subcommittee (PMS) to kick-off the project and confirm understanding of the goals and the details of the work statement. This may be done via teleconference.
2. The contractor will prepare a project plan with a timeline. This may be in the form of a presentation. The PMS will review this and discuss any other remaining issues with the contractor. This may be done via teleconference.
3. Intermediate report 1: The contractor shall prepare a presentation relating to Task 1.
4. Intermediate report 2: The contractor shall prepare a presentation relating to Task 2.

5. Intermediate report 3: The contractor shall prepare a presentation relating to Task 3.
6. The contractor shall prepare a presentation relating to Task 4.

Progress, Financial and Final Reports, Technical Paper(s), and Data shall constitute the deliverables ("Deliverables") under this Agreement and shall be provided as follows:

a. Progress and Financial Reports

Progress and Financial Reports, in a form approved by the Society, shall be made to the Society through its Manager of Research and Technical Services at quarterly intervals; specifically on or before each January 1, April 1, June 10, and October 1 of the contract period.

The following deliverables shall be provided to the Project Monitoring Subcommittee (PMS) as described in the Scope/Technical Approach section above, as they are available:

Furthermore, the Institution's Principal Investigator, subject to the Society's approval, shall, during the period of performance and after the Final Report has been submitted, report in person to the sponsoring Technical Committee/Task Group (TC/TG) at the annual and winter meetings, and be available to answer such questions regarding the research as may arise.

b. Final Report

A written report, design guide, or manual, (collectively, "Final Report"), in a form approved by the Society, shall be prepared by the Institution and submitted to the Society's Manager of Research and Technical Services by the end of the Agreement term, containing complete details of all research carried out under this Agreement, including a summary of the control strategy and savings guidelines. Unless otherwise specified, the final draft report shall be furnished, electronically for review by the Society's Project Monitoring Subcommittee (PMS).

Tabulated values for all measurements shall be provided as an appendix to the final report (for measurements which are adjusted by correction factors, also tabulate the corrected results and clearly show the method used for correction).

Following approval by the PMS and the TC/TG, in their sole discretion, final copies of the Final Report will be furnished by the Institution as follows:

-An executive summary in a form suitable for wide distribution to the industry and to the public.
-Two copies; one in PDF format and one in Microsoft Word.

c. *Science & Technology for the Built Environment*

One or more papers shall be submitted first to the ASHRAE Manager of Research and Technical Services (MORTS) and then to the "ASHRAE Manuscript Central" website-based manuscript review system in a form and containing such information as designated by the Society suitable for publication. Papers specified as deliverables should be submitted to Research Papers for HVAC&R Research for ASHRAE Transactions. Research papers contain generalized results of long-term archival value, whereas technical papers are appropriate for applied research of shorter-term value, ASHRAE Conference papers are not acceptable as deliverables from ASHRAE research projects. The paper(s) shall conform to the instructions posted in "Manuscript Central" for HVAC&R Research papers. The paper title shall contain the research project number 1886-RP) at the end of the title in parentheses, e.g., (1886-RP).

All papers or articles prepared in connection with an ASHRAE research project, which are being submitted for inclusion in any ASHRAE publication, shall be submitted through the Manager of Research and Technical Services first and not to the publication's editor or Program Committee.

d. Data

Data is defined in General Condition VI, "DATA"

e. Project Synopsis

A written synopsis totaling approximately 100 words in length and written for a broad technical audience, which documents 1. Main findings of research project, 2. Why findings are significant, and 3. How the findings benefit ASHRAE membership and/or society in general shall be submitted to the Manager of Research and Technical Services by the end of the Agreement term for publication in ASHRAE Insights

The Society may request the Institution submit a technical article suitable for publication in the Society's ASHRAE JOURNAL. This is considered a voluntary submission and not a Deliverable. Technical articles shall be prepared using dual units; e.g., rational inch-pound with equivalent SI units shown parenthetically. SI usage shall be in accordance with IEEE/ASTM Standard SI-10.

Level of Effort
Approx. Funding amount: $120,000/ Duration: 12 months

Project Milestones:

No.	Major Project Completion Milestone	Deadline Month
1	Quarterly progress and financial report to the Society's Manager of Research and Technical Services (MORTS)	3, 6, 12
2	Review of findings from literature review and proposed test plan (Phase I). Review Phase 2 scope based on findings from Phase 1	1
3	Review results and conclusions from Phase 2. Review proposed test plan for Phase 3.	6
4	Review results and conclusions from Phase 3.	11
5	Final Report, including recommendations for potential future work (Phase 4)	12

Proposal Evaluation Criteria
Proposals submitted to ASHRAE for this project should include the following minimum information:

No.	Proposal Review Criterion	Weighting Factor
1	Contractor's understanding of Work Statement as revealed in proposal. a) Logistical problems associated b) Technical problems associated	10
2	Quality of methodology proposed for conducting research. a) Organization of project b) Management plan	20
3	Contractor's capability in terms of facilities. a) Managerial support b) Analytical testing capabilities c) Technical expertise	20
4	Qualifications of personnel for this project. a) Project team 'well rounded' in terms of qualifications and experience in related work b) Project manager person directly responsible; experience and corporate position c) Team members' qualifications and experience d) Time commitment of Principal Investigator	30

5	Probability of contractor's research plan meeting the objectives of the Work Statement. a) Detailed and logical work plan with major tasks and key milestones b) All technical and logistic factors considered c) Reasonableness of project schedule	15
6	Performance of contractor on prior ASHRAE or other projects	5

References

1. 2022 ASHRAE Handbook: Refrigeration, Chapter 6: Refrigerant System Chemistry, ASHRAE, Inc., Atlanta, GA 30329: p. 6.1-6.16.
2. AHRI Standard 700-2019, Specifications for Refrigerants, Air-Conditioning, Heating and Refrigeration Institute, Arlington, VA.
3. ASHRAE Guideline 38, Guideline for Using Metal Pressure Vessels to Test Materials used in Refrigeration Systems, ASHRAE, Inc., Atlanta, GA 30329.
4. ASHRAE Standard 97-2017, Sealed Glass Tube Method to Test the Chemical Stability of Materials for use within Refrigerant Systems, ASHRAE, Inc., Atlanta, GA 30329.
5. ASHRAE Standard 34-2022, Designation and Safety Classification of Refrigerants, ASRHAE, Inc., Atlanta GA 30329.
6. Fujitaka, A., et al. Application of Low Global Warming Potential Refrigerants for Room Air Conditioner. 2010 International Symposium on Next-Generation Air Conditioning and Refrigeration Technology, 17-19 Feb 2010, Tokyo
7. Kujak, S., Sorenson, E. (2018). Haloolefin Refrigerants. ASHRAE Journal, June 2018: p 28-35
8. Majurin, J., Sorenson, E. (2014). Material Compatibility and Lubricant Research for Low GWP Refrigerants – Phase II: Chemical and Material Compatibility of Low GWP Refrigerants with HVACR Materials of Construction. Air-Conditioning, Heating and Refrigeration Institute. AHRI Report 08007.
9. Rohatgi, R. (2012). Material Compatibility & Lubricants Research for Low GWP Refrigerants – Phase I: Thermal and Chemical Stability of Low GWP Refrigerants with Lubricants. Air-Conditioning, Heating and Refrigeration Institute. AHRI Report 09004-01.
10. Sasaki, Tatsuya; Nakao, Hideto; Maeyama, Hideaki; and Mizuno, Kota, "Tribology Characteristics of HFO and HC Refrigerants with Immiscible Oils - Effect of Refrigerant with Unsaturated Bond -" (2010). International Compressor Engineering Conference. Paper 1946
11. Sorenson, E., Kujak, S., Leehey, M., Robaczewski, C., Stellpflug, T. (2021). Material Compatibility and Lubricants Research for Low GWP Refrigerants – Chemical Stability of Low GWP Refrigerants with Lubricants. Report AHRI 09016. Arlington, VA: Air Conditioning, Heating, and Refrigeration Technology Institute, Inc.