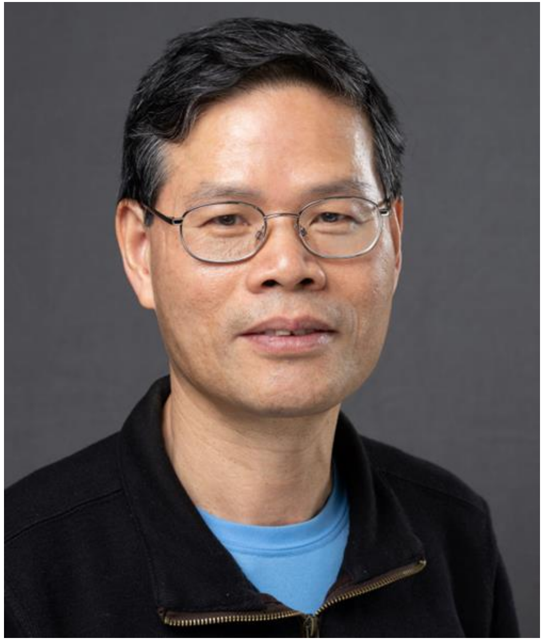
Dr. Jiliang He



- Senior Process Safety Specialist, DEKRA Services.
- Responsible for chemical hazard evaluation using techniques, such as, ARC, VSP2, RC1, DSC, and GC-MS. Work also includes kinetic modeling, SADT calculation, and incident investigation.
- Ph.D. in Chemistry, McGill University.
- 50+ peer-reviewed journal papers.

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Utilizing Accelerating Rate Calorimetry (ARC) for Thermal Hazard Evaluation of Gaseous Reactions and Derivation of Physical Properties

Jiliang He

DEKRA Process Safety, 113 Campus Drive, Princeton, New Jersey 08540

Contents

ARC APPLICATION IN EVALUATING GASEOUS CHEMICAL HAZARD

Gas phase ARC testing - essential but some difficulties

- Handling reactive gas without leaks (toxic/pyrophoric/corrosive/odorous)
- Quantitative gas charging
- Safe disposal of gaseous products and unreacted sample

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HANDLING HAZARDOUS GAS

Chlorine Trifluoride (ClF_3) – Initial Motivation

- Hypergolic (ignites many materials without an ignition source).

- Extremely reactive with most inorganic and organic materials (very violent or explosive).

- An incident: burnt 1 ft concrete & 3 ft gravel underneath the spill. (The concrete was on fire!)

- Compatible with steel, copper, and nickel (but not Pt, Au, etc).

Air Products, *Safetygram 39: Chlorine Trifluoride.*

(Guess three most scary chemicals?
-- ClF_3, C_2N_{14}, $S{=}C(CH_3)_2$)

→ Gas Vacuum System/Schlenk Line

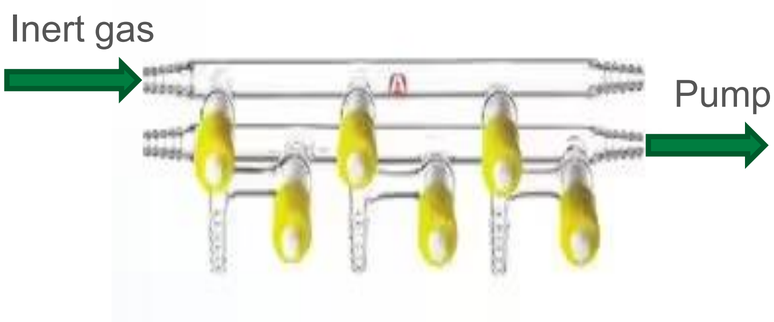
PE tube

Exposure to ClF_3

TRADITIONAL SCHLENK LINE - VACUUM GAS MANIFOLD

- Transferring air/moisture-sensitive chemicals (gas/liquid/solid)
- Removing residual solvent without exposure to air (drying chemicals)

(developed by Wilhelm Schlenk in early 1900's)

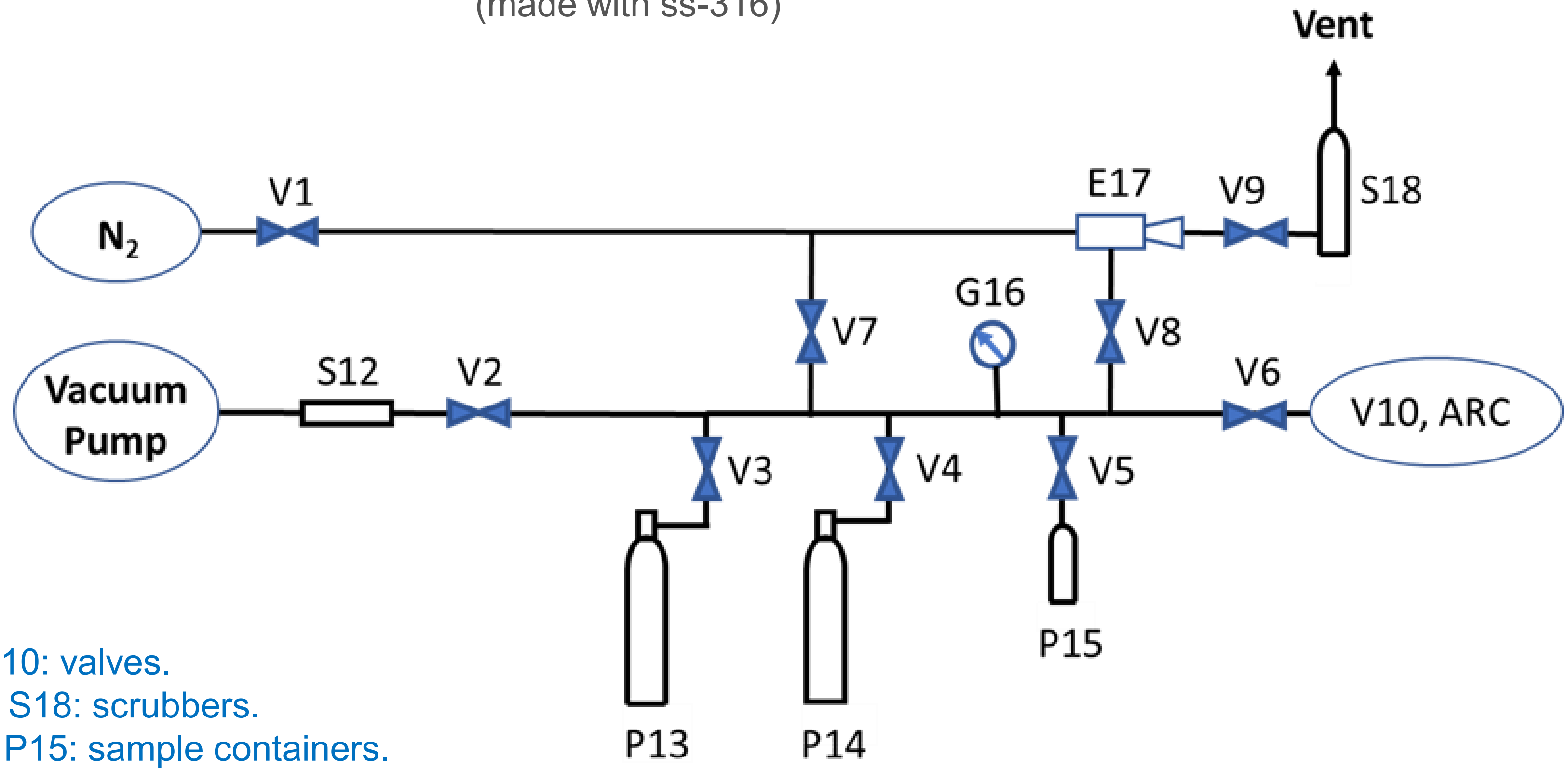


1. *Tidwell T. Wilhelm Schlenk: The Man Behind the Flask. Angew. Chem. Int. Ed. Engl. 2001, **40**: 331–337.*

2. *Chandra T, Zebrowski JP. Reactivity control using a Schlenk line. J Chem Health Saf. **2014**, 21 (3), 22-28.*

MODIFIED SCHLENK LINE

(made with ss-316)



V1 - V10: valves.
S12 & S18: scrubbers.
P13 – P15: sample containers.
G16: digital pressure/vacuum gauge.
E17: eductor.

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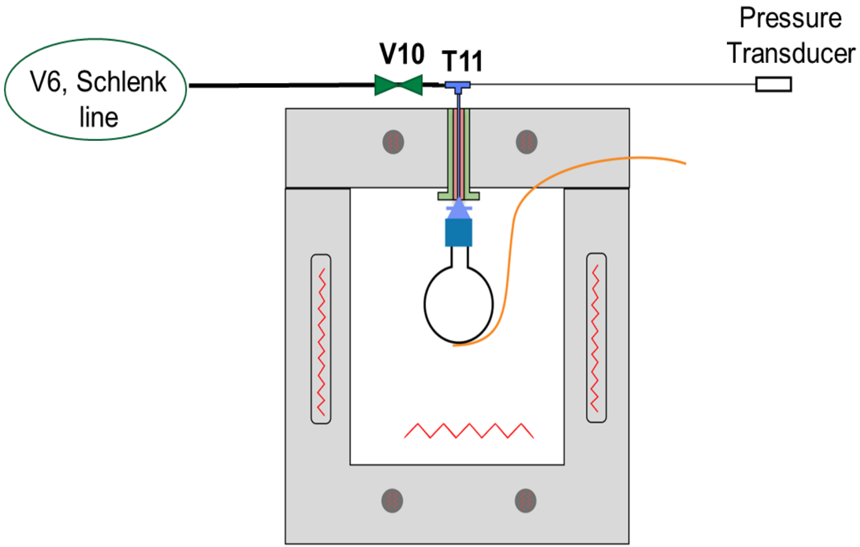
CONNECTION BETWEEN SCHLENK LINE AND ARC



To minimize the condensation of vapors in headspace,

the feedthrough tube connection is kept as short as possible

MODIFIED SCHLENK LINE

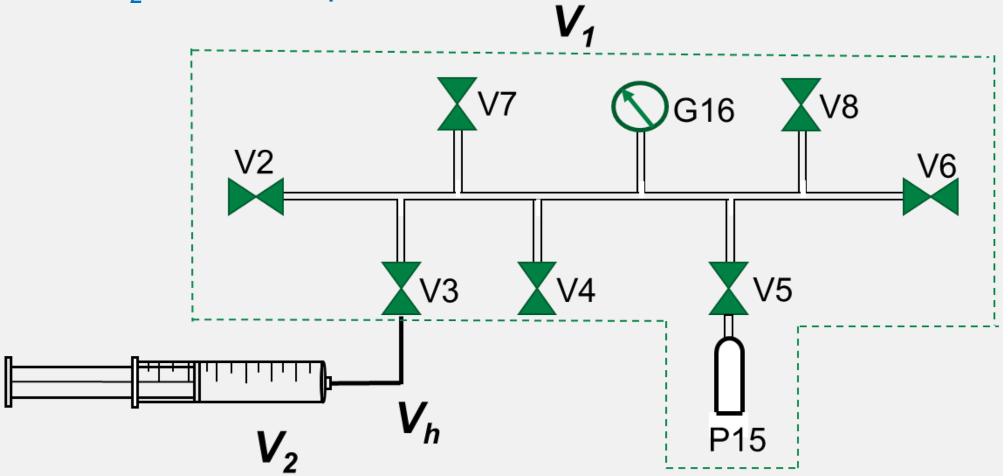
A simplified stand-alone gas vacuum manifold for gas phase ARC testing

- Quantitative sample charging
- Safe disposal of reactive gases
- Shot addition of gas sample
- Quick system leak check
- Removing residual air from the headspace

THE MEASUREMENT OF FEEDLINE VOLUME

$$P_1(V_1 + V_h) = P_2(V_2 + V_h)$$

V_1 – feedline volume (enclosed by dot line)
V_2 – syringe volume
V_h – void volume
(between syringe tip and valve V3)
P_1 – pressure in feedline after air injection by syringe
P_2 – ambient pressure



QUANTITATIVE GAS LOADING

Ideal Gas Law

$$Wt = \Delta P \left(\frac{V_1}{RT}\right) Mw$$

Equation of State

$$Wt = \left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right)\frac{V_1 Mw}{RT}$$

Wt: loaded sample weight

Mw: sample molecular weight

ΔP: the difference in P_1 and P_2

(the pressures before and after the feedline was pressurized)

V_1: the volume of feedline

T: ambient temperature at which gas sample is loaded

R: gas constant

Z_1, Z_2: the compressibility factors

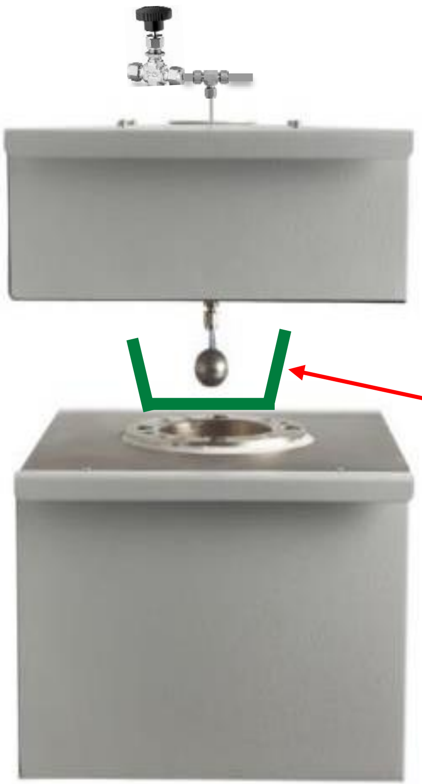
For liquefied gas that vapor-liquid equilibrium (VLE) is present, the gas pressure in the feedline must be kept less than the VLE pressure.

GAS TRANSFER USING COLD BATH

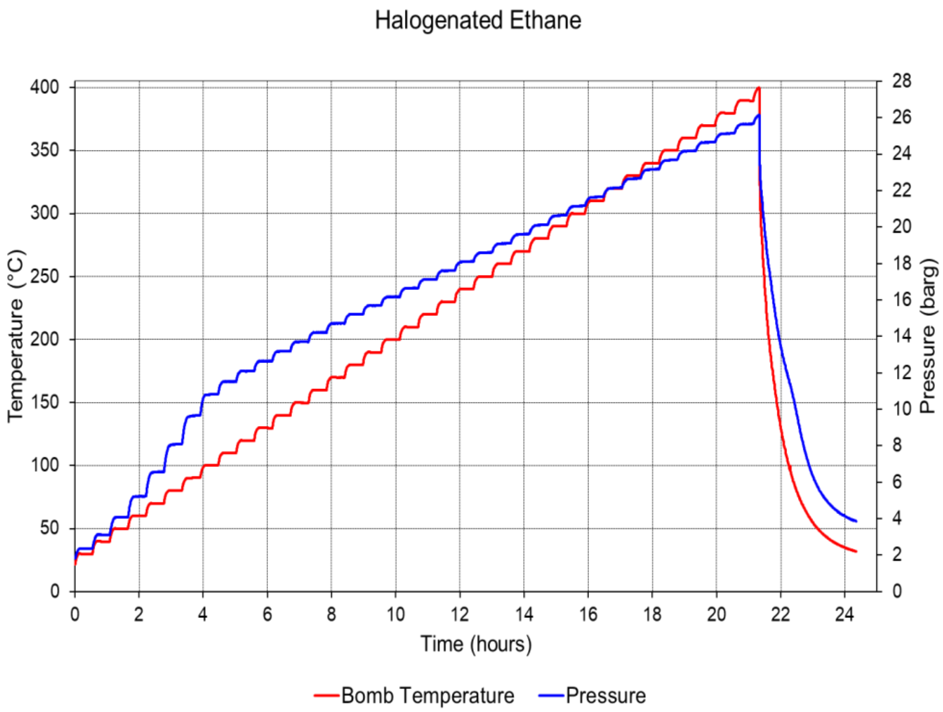
Cold bath, L-N_2 or dryice/IPA, is used to aid the transfer.

If source pressure is not enough for one-step gas transfer, repetitive transfers are needed to achieve a desired quantity.

Dryice can be directly placed in the radiant heater cavity.



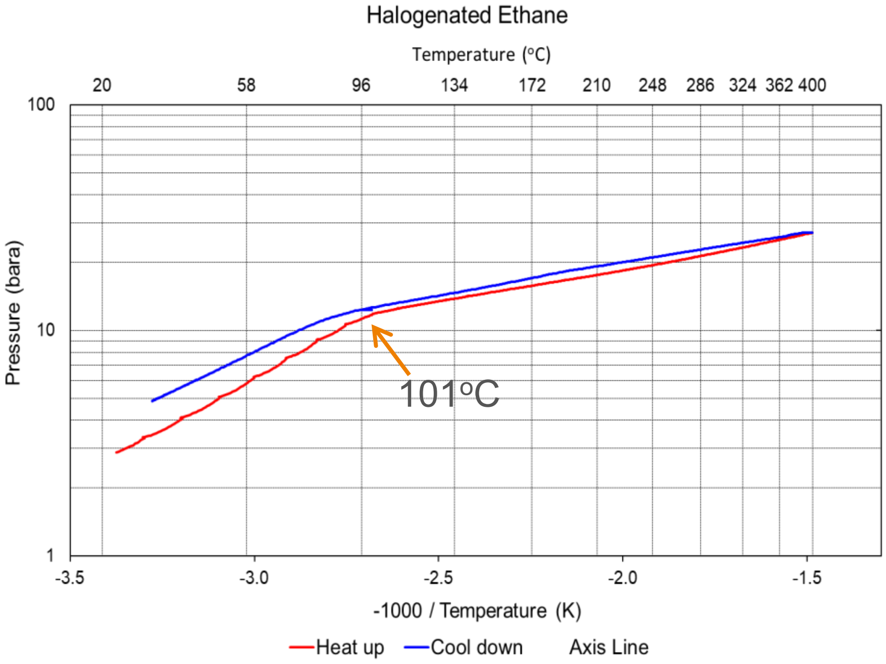
THERMAL STABILITY OF HALOGENATED ETHANE, A VERIFICATION TEST



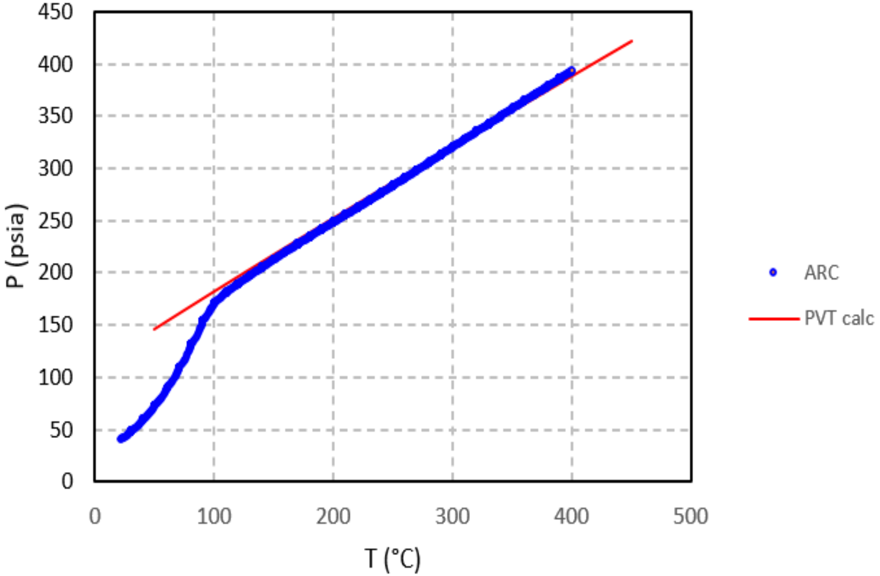
- Quantitative gas charging for single gas using Schlenk line gas transfer technique.
- Same technique can be applied for multiple-gas loadings.

Temperature and pressure vs. time for ARC run of halogenated ethane

THERMAL STABILITY STUDIES OF HALOGENATED ETHANE



Antoine plot for ARC run of halogenated ethane



Brandes T, Smith D, Dupre G. Some Best Practices with Calorimetric Testing. *DIERS Fall 2021 Virtual Meeting*, 2021, October.

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CHLORINATION OF TOLUENE

$C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$ (1)

$2C_6H_5CH_3 + 2Cl_2 \rightarrow o\text{-}C_6H_4ClCH_3 + p\text{-}C_6H_4ClCH_3 + 2HCl$ (2)

Experiments

1. Co-loading Cl_2 and toluene at dry ice temperature.
2. Shot addition of Cl_2 to toluene at ambient temperature.

Jiliang He, *Process Safety Progress*, 2023, 42, 701-711.

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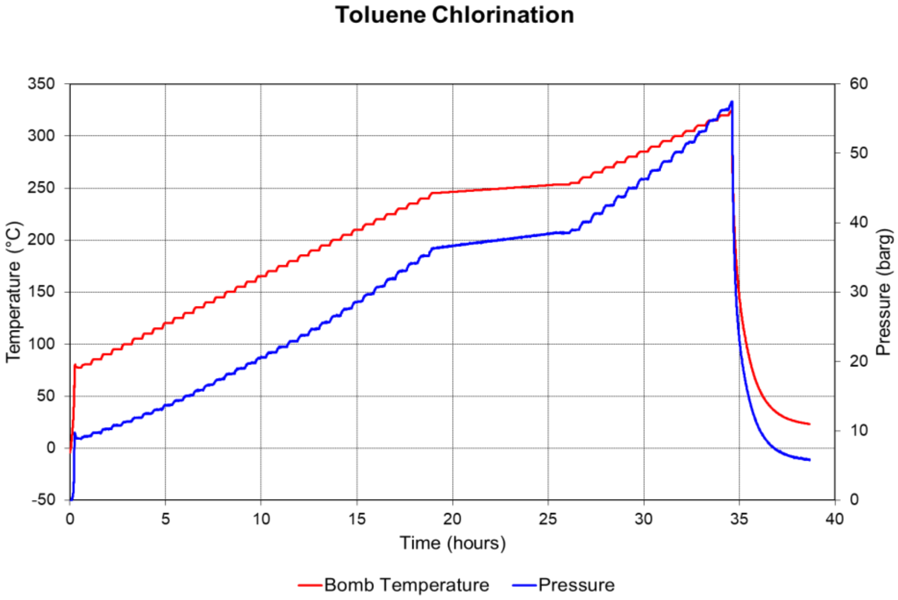
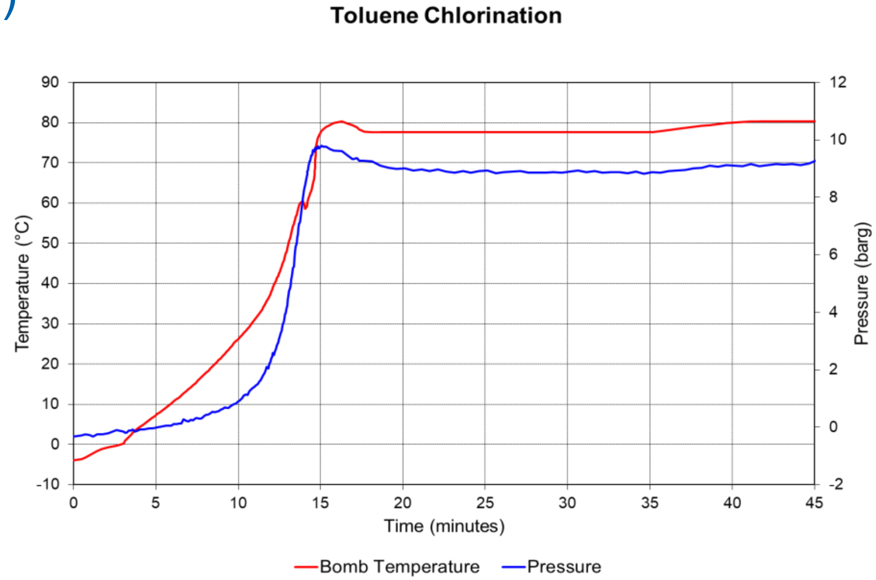
CHLORINATION OF TOLUENE

Co-loading Cl_2 and toluene at dry ice temperature
($2.09g\ C_6H_5CH_3 + 0.53g\ Cl_2$, no pad gas)



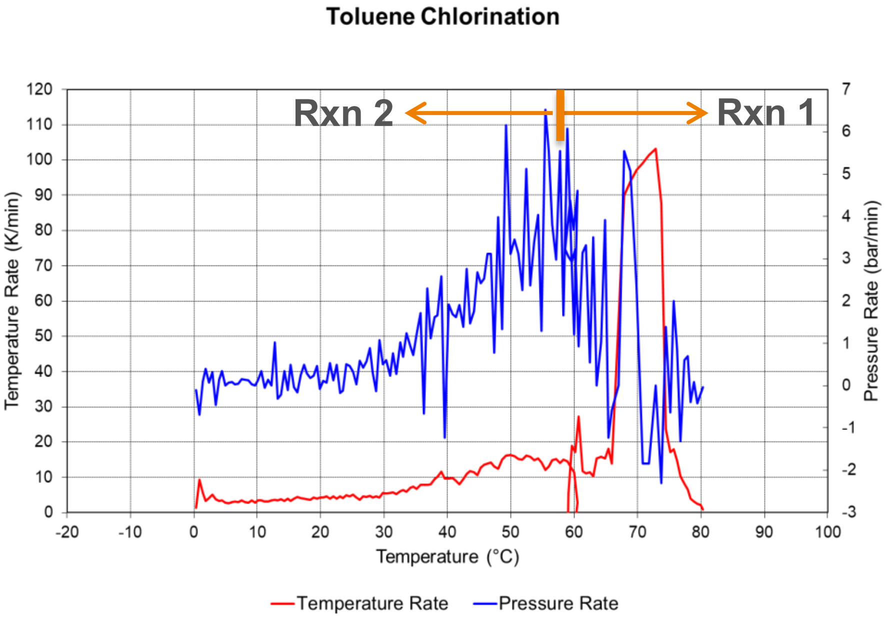
Temperature and pressure vs. time for ARC run of chlorination of toluene with chlorine (cold loading).



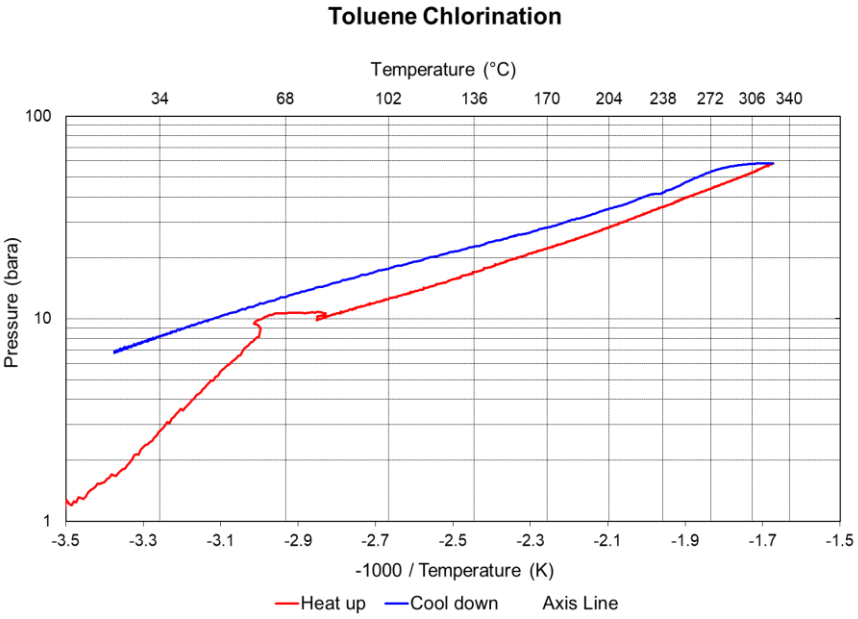
Temperature and pressure vs. time for ARC run of chlorination of toluene with chlorine (cold loading) during first exotherm

CHLORINATION OF TOLUENE

Co-loading Cl_2 and toluene at dry ice temperature



Temperature rate and pressure rate for ARC run of chlorination of toluene with chlorine (cold loading) during first exotherm



Antoine plot for ARC run of chlorination of toluene with chlorine (cold loading)

GAS DOSING/SHOT ADDITION

If sample gas is too reactive to be co-loaded before ARC run

1. A valve to the ARC bomb is installed at the outer enclosure of containment vessel so that sample gas can be manually added.
2. Pressurize sample gas in feedline (V_1)
3. ARC is programed with HWS mode. When the ARC is in the middle of "search" mode at a desired temperature step, the valve is open to add sample gas.
4. Pressure difference (ΔP) before and after the addition is gas pressure added.
5. Gas compression may increase the cell temperature by 1-3°C and needs to be corrected.

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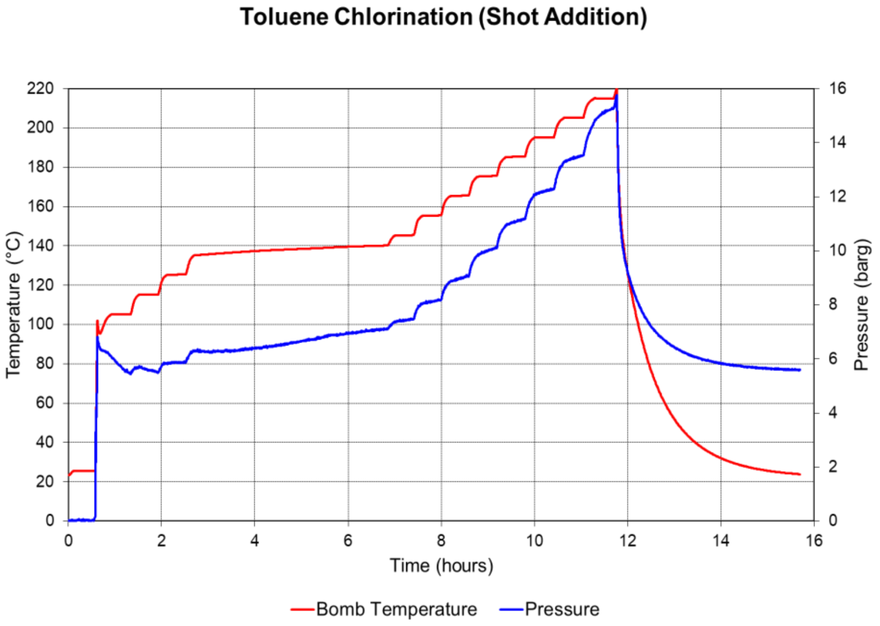
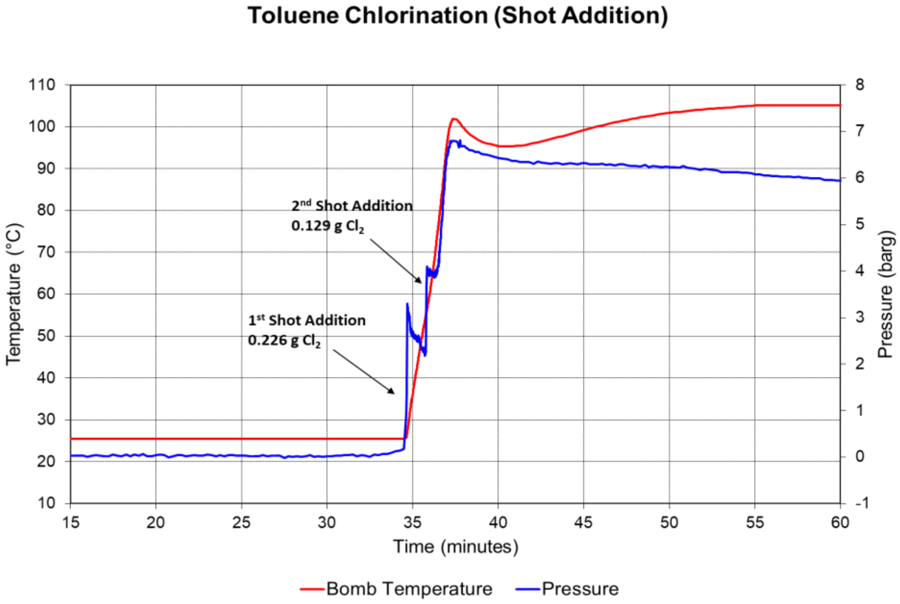
CHLORINATION OF TOLUENE

Shot addition of Cl_2 to toluene at ambient temperature

Air in the headspace of bomb was removed; then 1 bara N_2 pad gas was added.



Temperature and pressure vs. time for ARC run of chlorination of toluene with chlorine (shot addition)



Temperature and pressure vs. time for ARC run of chlorination of toluene with chlorine (shot addition) during first exotherm

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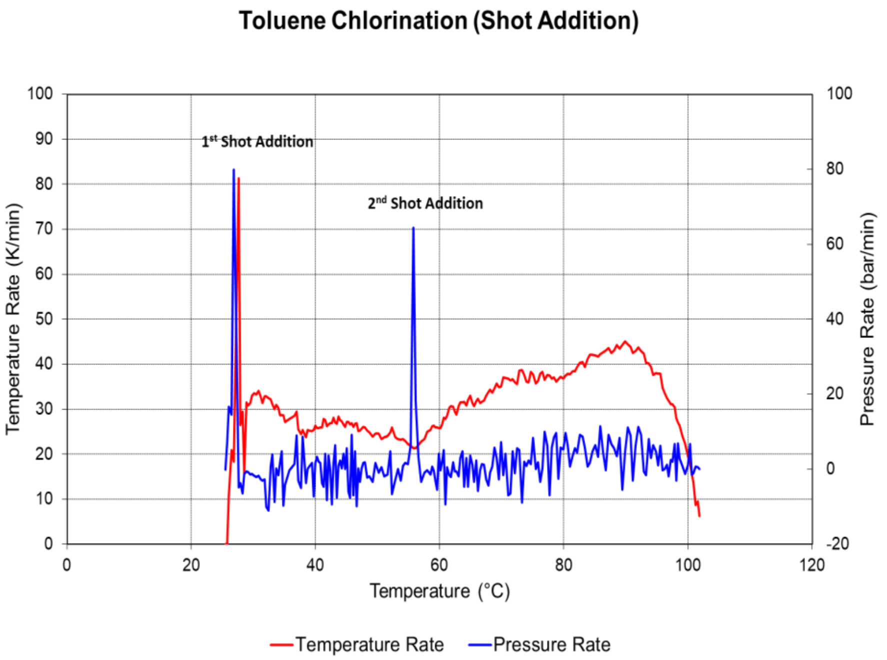
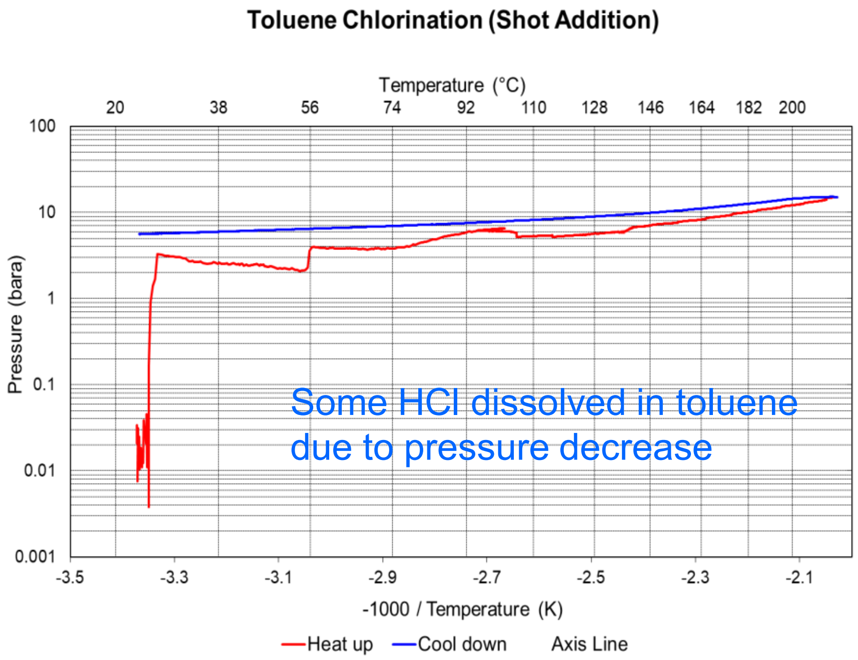
CHLORINATION OF TOLUENE

Shot addition of Cl_2 to toluene



Temperature rate and pressure rate for ARC run of chlorination of toluene with chlorine (shot addition) during first exotherm



Antoine plot for ARC run of chlorination of toluene with chlorine (shot addition)

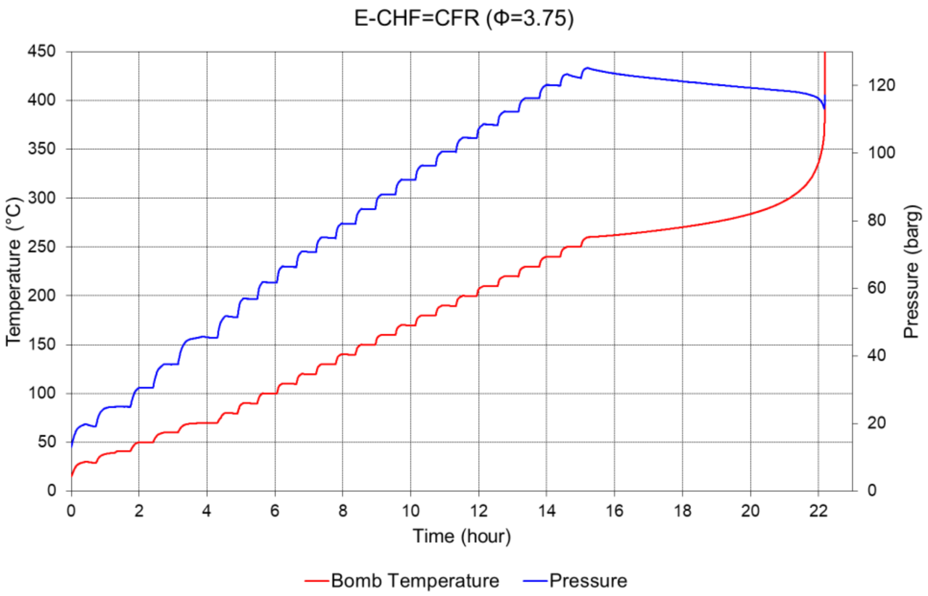
THERMAL STABILITY STUDY OF REFRIGERANTS

- **Ensure Safety**: Assess risk of thermal runaway or decomposition under heat.
- **Realistic Conditions**: ARC simulates adiabatic conditions, mimicking worst-case scenarios.
- **Critical Data**: Provides onset temperature, pressure rise, and heat release info.
- **Process Design & Compliance**: Informs safer system design and supports regulatory requirements.
- **Material Selection**: Helps compare refrigerants for stability and performance.

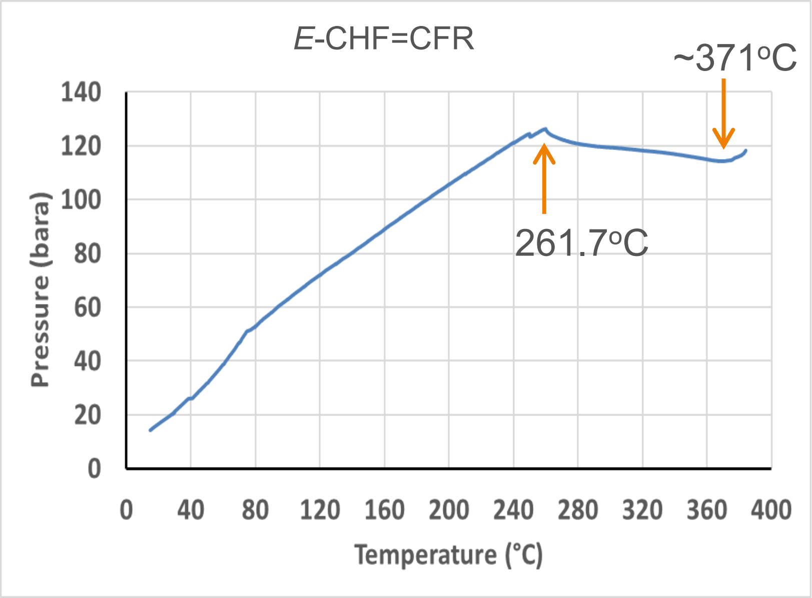
THERMAL STABILITY STUDY OF HYDROFLUOROOLEFINS (HFOs)

Trans-Difluoroalkene Derivative (*E*-CHF=CFR)

(Test Example, loading via Schlenk technique)



Temperature and Pressure vs Time



Pressure vs Temperature

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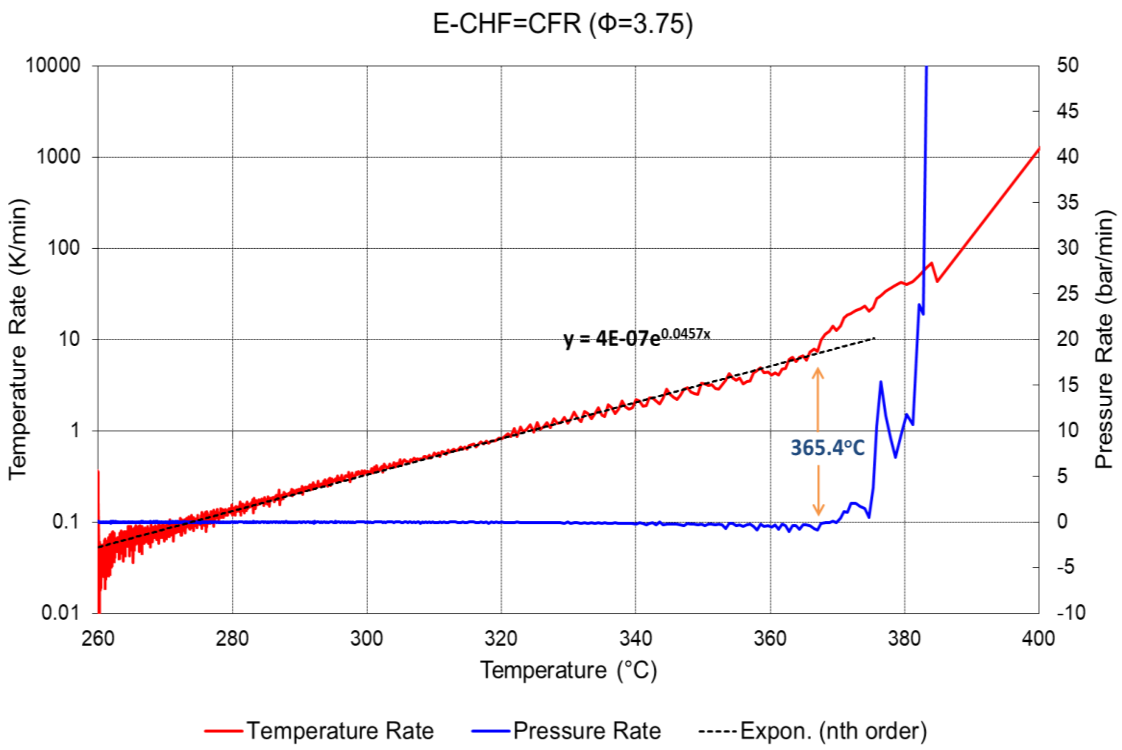
KINETIC MODELING



$$ln\left[\frac{\frac{dT}{dt}\cdot\frac{\phi}{\Delta T_{ad}}}{C_{A_0}^{n-1}\left(1-\frac{T-T_0}{\Delta T_{ad}/\phi}\right)^n}\right] = ln[A] - \frac{E}{RT}$$

C_0: initial concentration (mole/L)
Φ: thermal inertia (3.75)
T: temperature (K)
T_f: exothermic final temperature
ΔT: T_f - T_0
R: 8.314 J/(mol.K)

$$E_a = 255.53\ (\frac{\text{kJ}}{\text{mole}})$$

$$A = 4.91095\ E18\ (\text{S}^{-1})$$

$$n = 0$$

(Zero-order reaction before runaway)

Self-heat Rate & Pressurization Rate *vs.* Temperature

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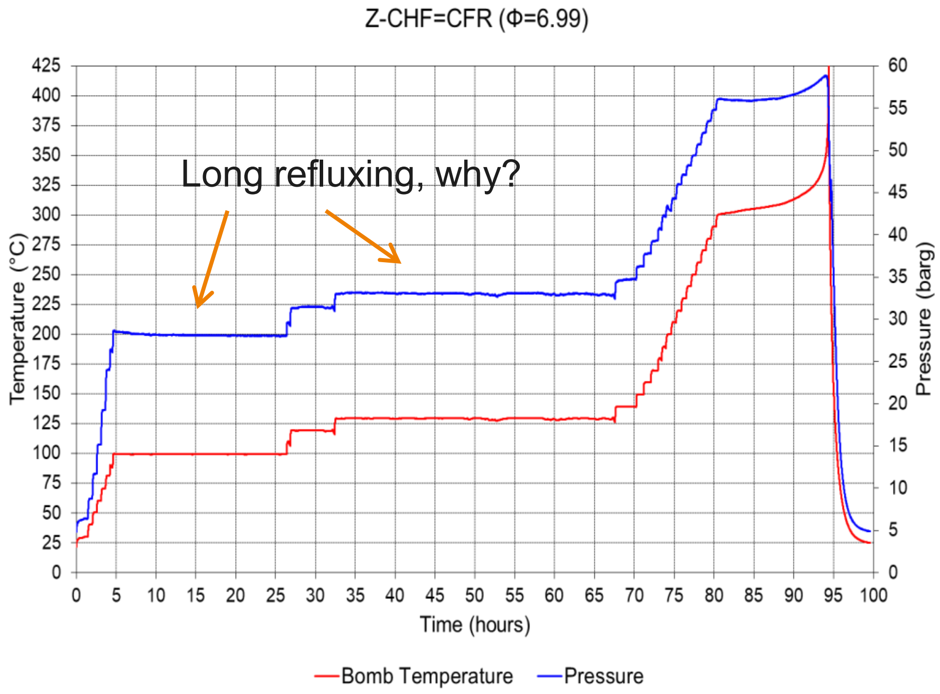
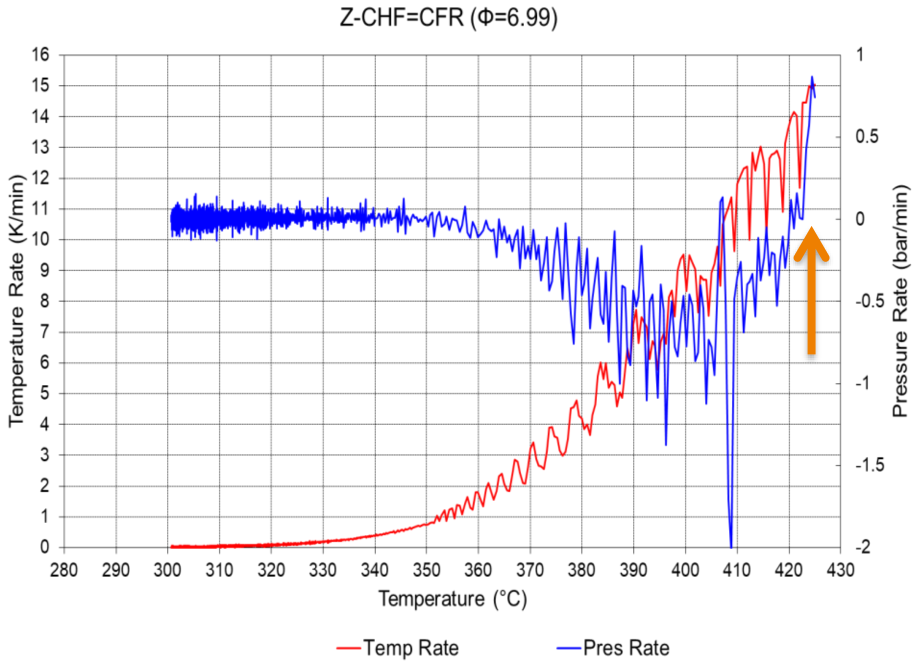
Cis-Difluoroalkene Derivative (Z-CHF=CFR)

(Test Example)



Temperature and Pressure vs Time



Self-Heat Rate (SHR) and Pressurization Rate vs Temperature

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Minimizing Condensation & Long Reflexing

Hardware Modifications

1. Minimize the headspace
2. Add insulation
3. Use side-arm bomb

Software Controls

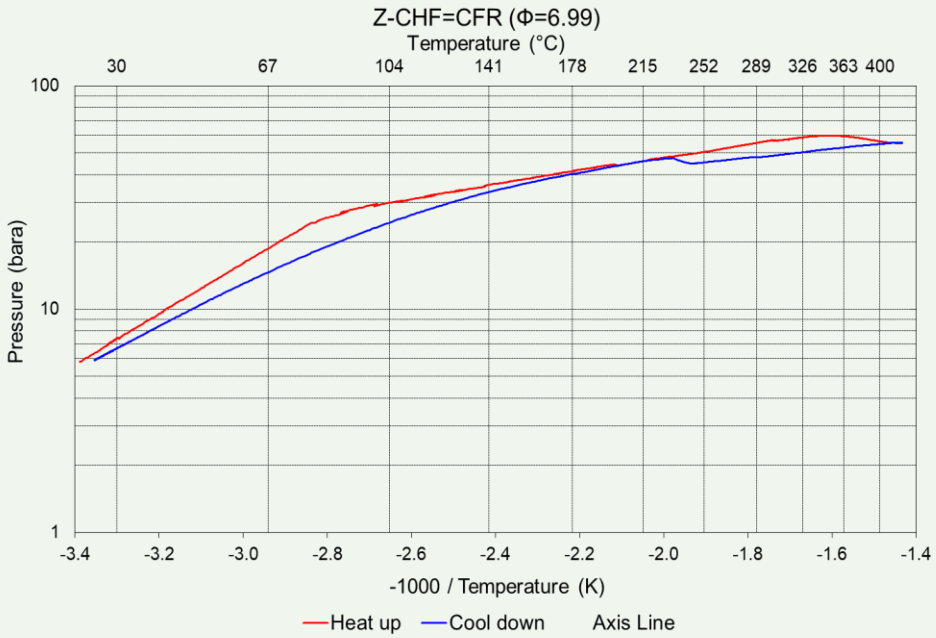
Increase the radian heater power (e.g., from initial 30% to 60%).

Or reset the current temperature (e.g. 200ºC) to the next target temperature (210ºC).

Cis-Difluoroalkene Derivative

1. Antoine plot

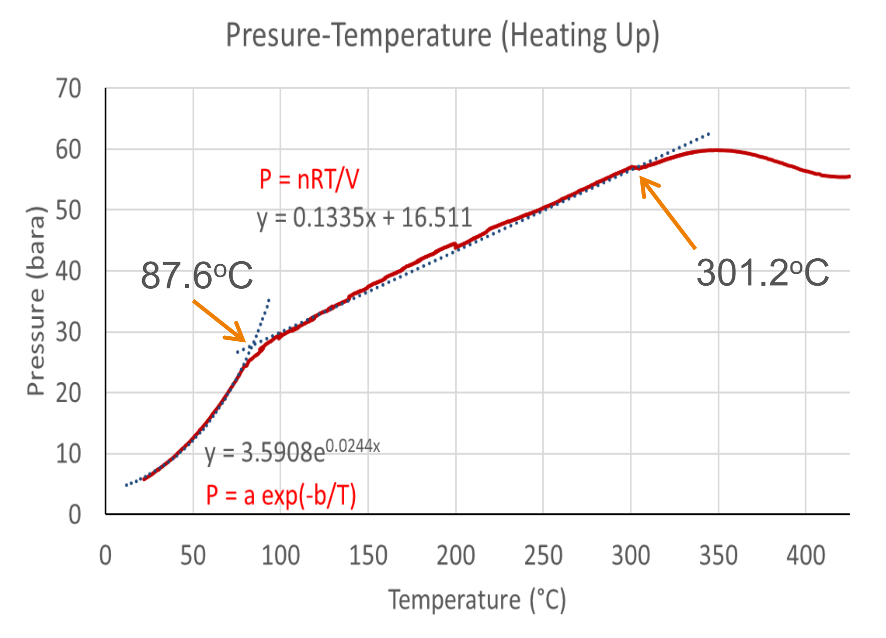
$\log_{10}$P vs 1/T (T in K).



Small pressure variations at low temperatures are magnified, while larger changes are compressed, making it easier to fit the Antoine equation and extract its coefficients.

2. Direct P–T plot

P vs T (in °C) on linear scales.



Both axes use uniform scaling, so exponential or linear trends in the data are immediately obvious.

THERMAL SAFETY ASSESSMENT

Severity of Thermal Runaway

High if $\Delta T_{ad} \geq 200K$

Medium if $50K < \Delta T_{ad} < 200K$

Low if $\Delta T_{ad} < 50K$ and no pressure

$(\Delta T_{ad} = \Phi(T_{peak} - T_{oset}))$

Time to Maximum Rate – Probability

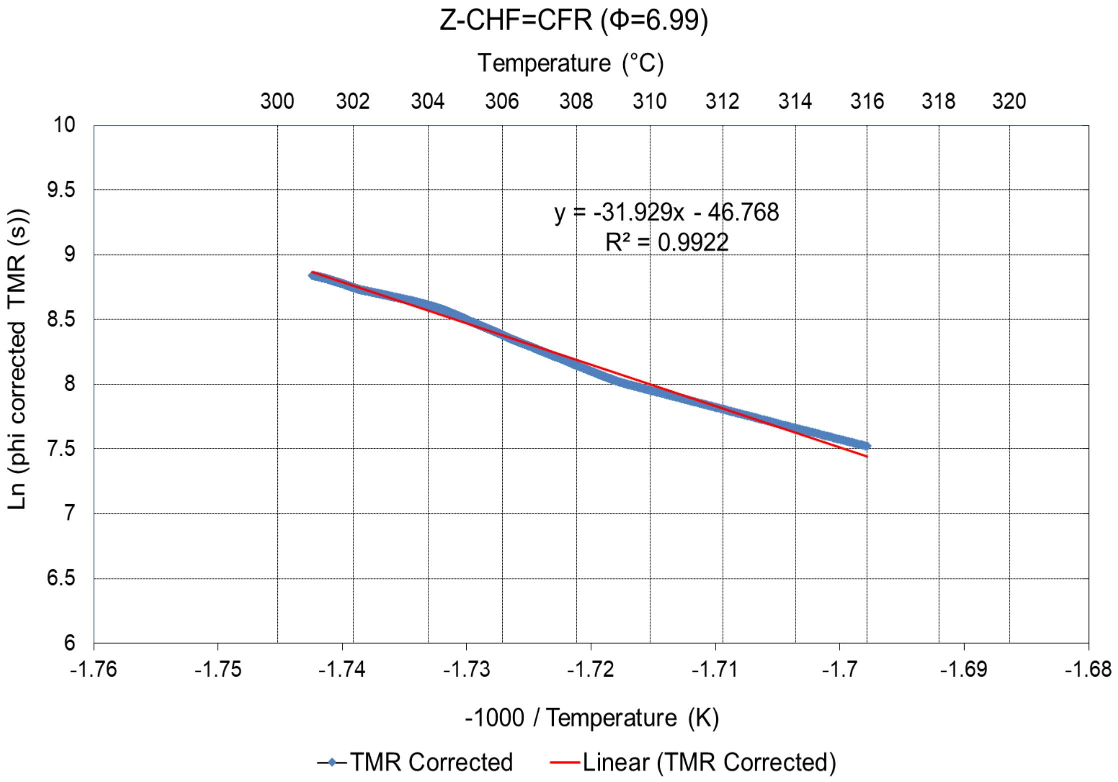
Low if $TMR_{ad} \geq 24h$

Medium if $8h < TMR_{ad} < 24h$

High if $TMR_{ad} \leq 8h$

Stoessel F., 2020, Thermal Safety of Chemical Processes: Risk Assessment and Process Design.

Time to Maximum Rate (TMR_{ad})



Arrhenius Plot of TMR - ln(TMR) vs -1000/T

TMR_{ad} data can be extracted directly from the phi -corrected ARC data.

For zero-order reaction:

$$ln[TMR_{ad}] = \frac{E_a}{RT} - ln(A)$$

Low probability of TR if TMR > 24h

High probability of TR if TMR < 8h

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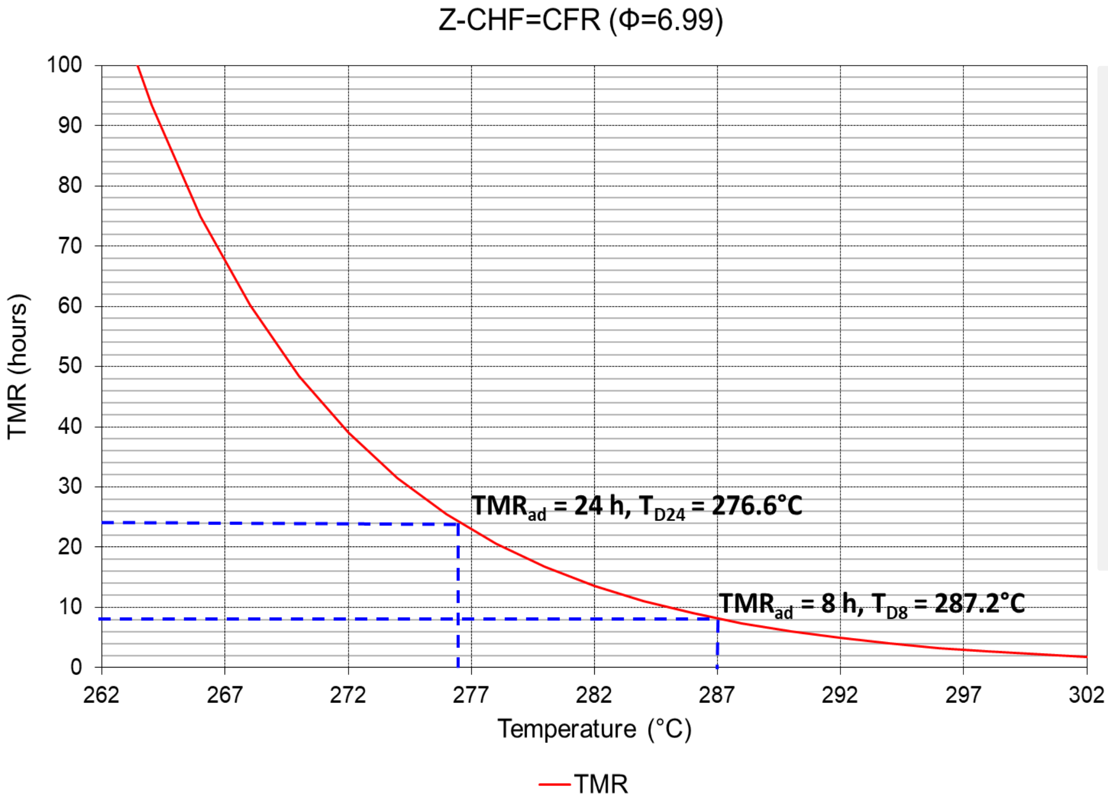
THERMAL SAFETY DIAGRAM (T_{D24}, T_{D8})



Thermal Safety Diagram - TMR vs Temperature

Time to Maximum Rate (TMR_{ad})

$$TMR_{ad} = \frac{C_p R T^2}{q E_a}$$

Operation is safe if $T_{proc} \leq T_{D24}$

Operation is at risk if $T_{proc} \geq T_{D8}$

Jiliang He, *et al.*, Thermal Hazard Evaluation and Safety Assessment for 1-Hydroxybenzotriazole Hydrate. *20th Global Congress on Process Safety*, New Orleans, LA, March 24-28, 2024.

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Summary of ARC Test Results for Several HFOs

	Z-CHF=CFR	*E*-CHF=CFR	F_2C=CFR	F_2C=CFR'
Onset temperature (°C)	301.70	261.70	281.90	221.60
Peak temperature (°C)	426.10	402.40	332.20	273.48
Adiabatic temperature rise (K)	869.56	527.25	594.90	280.67
Heat of reaction (J/g)	-891.96	-1048.74	-447.67	-375.68
Activation energy (kJ/mol)	265.46	117.13	218.53	107.04
Pre-exponential factor (S^{-1})	1.97447E+20	4.60851E+07	5.73767E+17	3.47260E+07
T_{D24} (°C)	276.56	212.6	241.8	184.7
Severity	High	High	High	High
T_{D8} (°C)	287.2	230.3	252.3	202.9

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HYDROCRACKING OF LONG CHAIN ALKANES

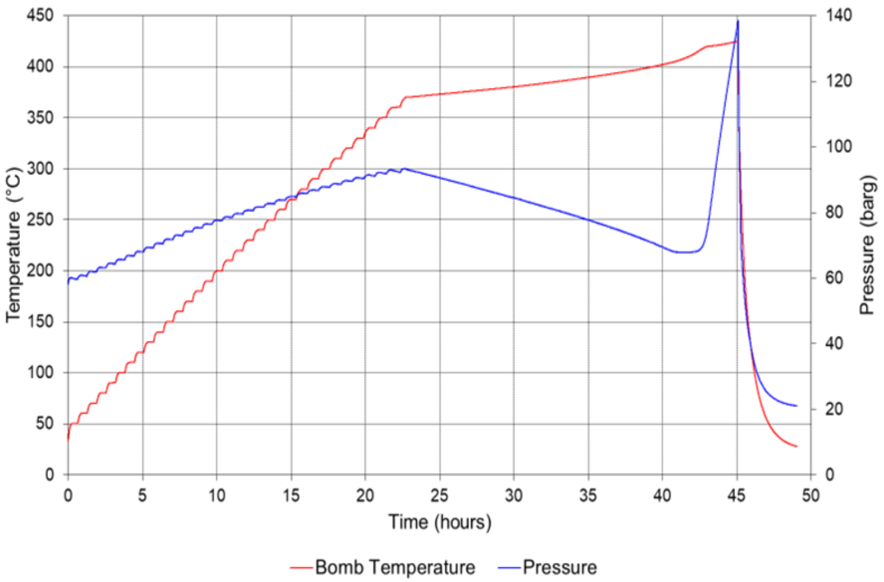
(Example)

Reaction	ΔH_f (J/g-C_{16})
$C_{16}H_{34} + H_2 \rightarrow 2\ C_8H_{18}$	-208
…	…
$C_{16}H_{34} + 5\ H_2 \rightarrow 5\ C_3H_8 + CH_4$	-1040
$C_{16}H_{34} + 7\ H_2 \rightarrow 8\ C_2H_6$	-1456
$C_{16}H_{34} + 15\ H_2 \rightarrow 16\ CH_4$	-3120

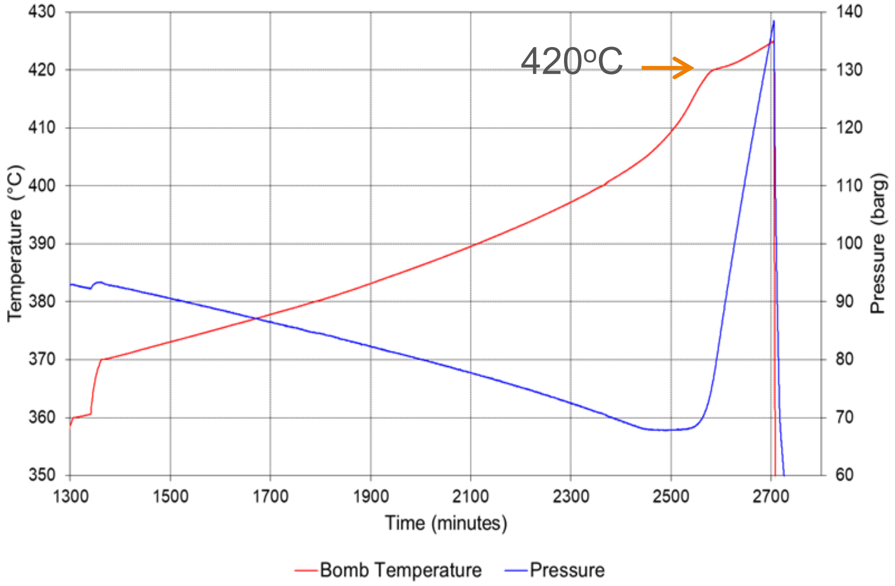
The reactions are exothermic. The more hydrogen is consumed, the more heat is generated.

Long Chain Alkane Hydrocracking

(Test Example)

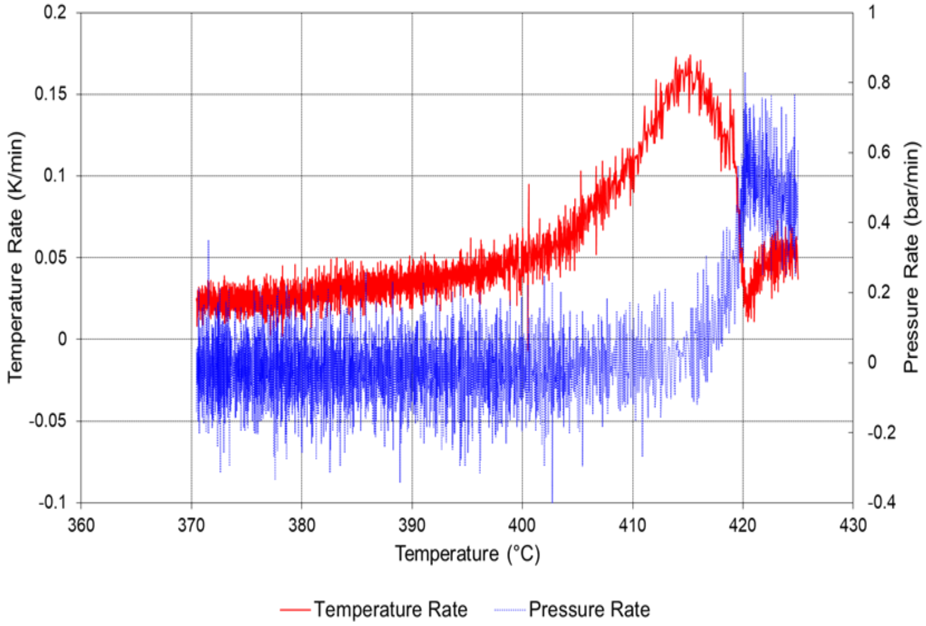


Temperature and Pressure vs Time

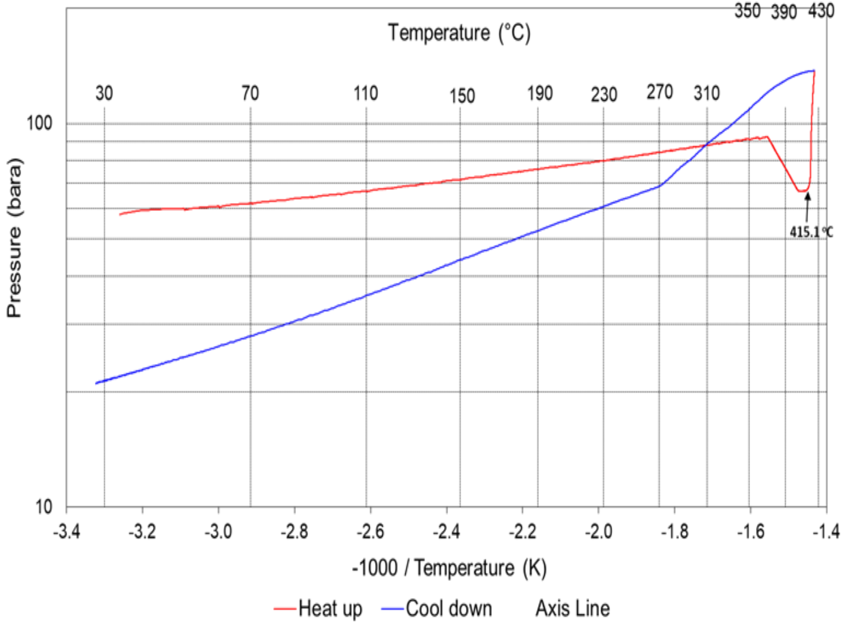


Temperature and Pressure vs Time (Exotherm)

Hydrocracking



Self-Heat Rate (SHR) and Pressurization Rate vs Temperature



Pressure vs -1000/Temperature (Antoine Plot)

SHR and pressurization rate were tracked until 425°C only, although the exotherm appeared to extend beyond this temperature. Pressure increased dramatically due to thermal decomposition starting at 415°C.

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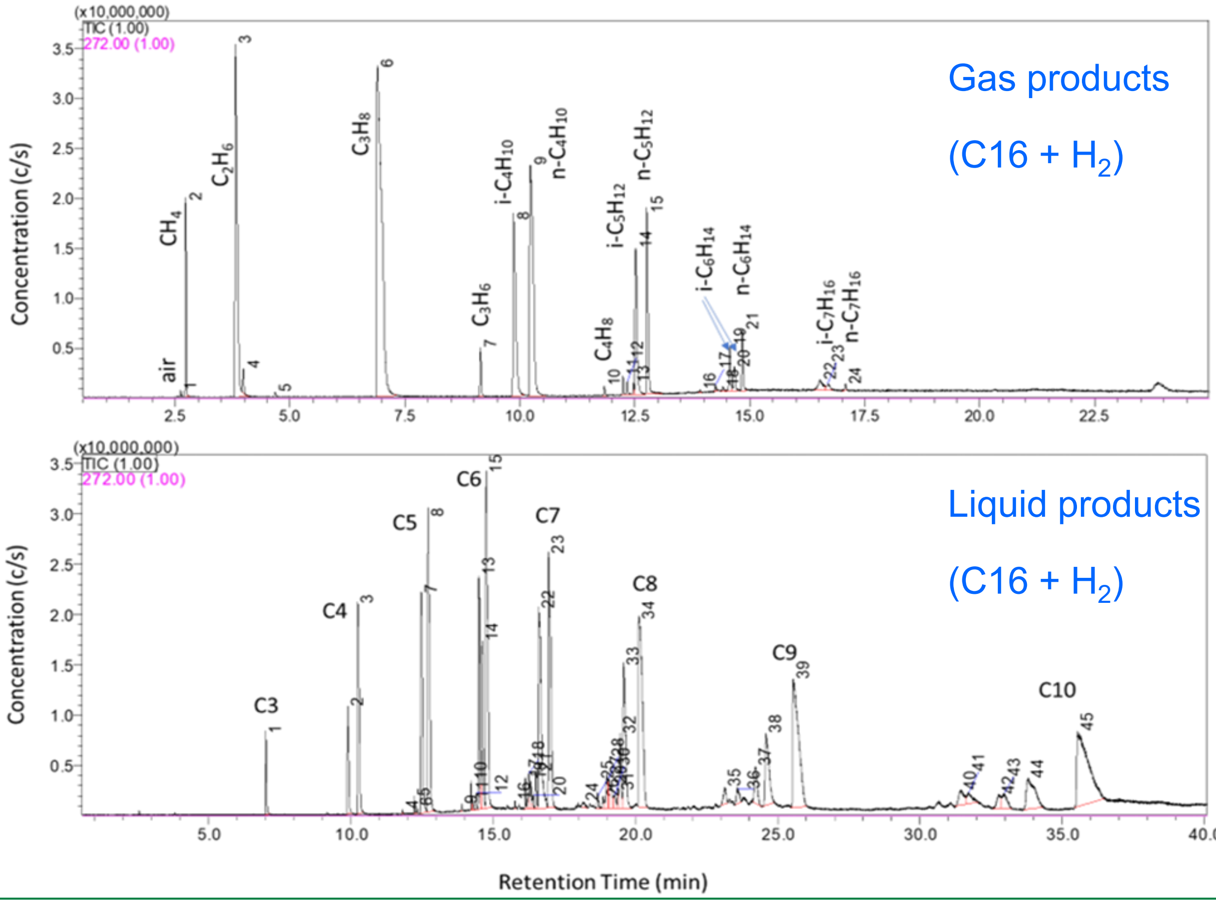
Product Analysis of Hexadecane Hydrocracking by GC-MS



Major:

C_1-C_{10} alkanes

Minor:

C_2-C_4 alkenes

Summary for Hexadecane Hydrocracking	
Onset temperature (°C)	370.5
Peak temperature (°C)*	425
Max self-heat rate (K/min)	0.174
Max pressurization rate (bar/min)	0.83
Adiabatic temperature rise (K)*	107.8
Heat of reaction (J/g)*	-175.6
Quantity of gas changed (mL/g-C16 at STP)	182.4
Activation energy (kJ/mol)	80.15
Pre-exponential factor (S^{-1})	2.0346E+8
T_{D24} (°C)	355.7
Severity*	Medium
T_{D8} (°C)	379.2

*Exotherm was not fully recorded as the test ended at the pre-set temperature at 425°C, the values of temperature and heat would be higher if the full exotherm was obtained.

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ARC FOR PHYSICAL PROPERTY DETERMINATIONS

Normal Boiling Point

Vapor Pressure

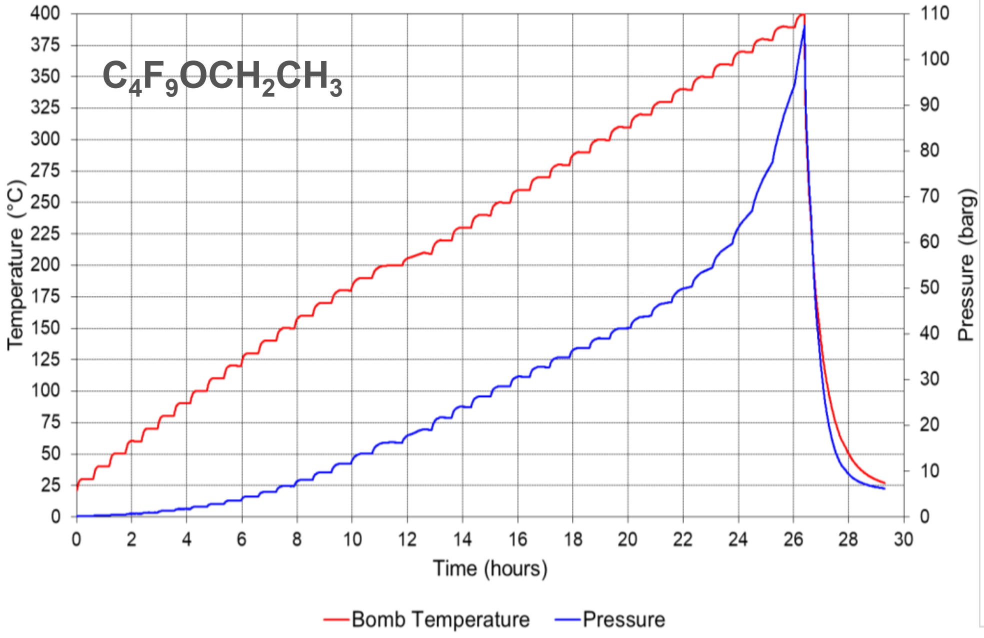
Heat of Vaporization

Critical Temperature

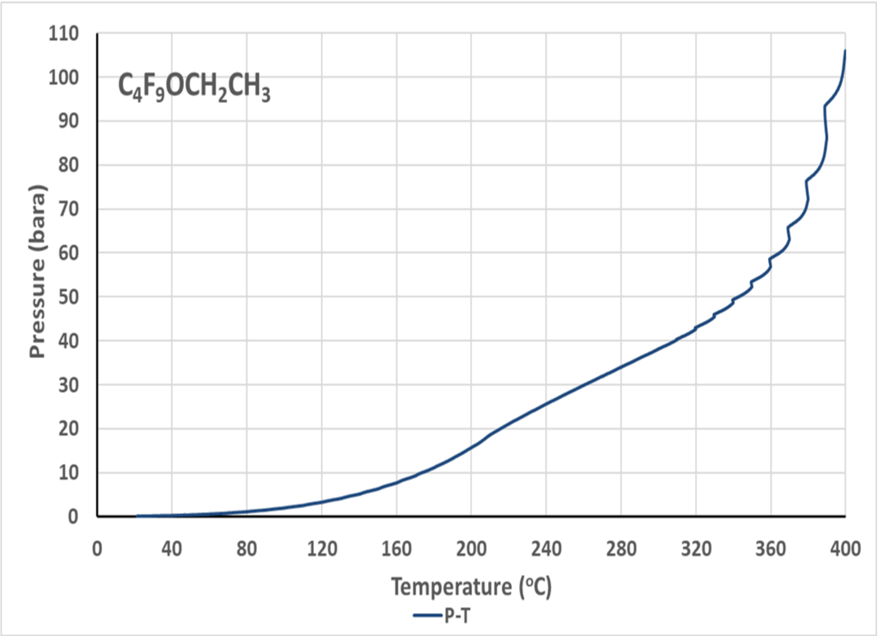
The ARC approach is especially useful when a substance is prone to decomposition or other hazards in conventional instruments during testing.

PRESSURE - TEMPERATURE DATA FROM ARC

Test Example: Thermal Decomposition without a Detectable Exotherm

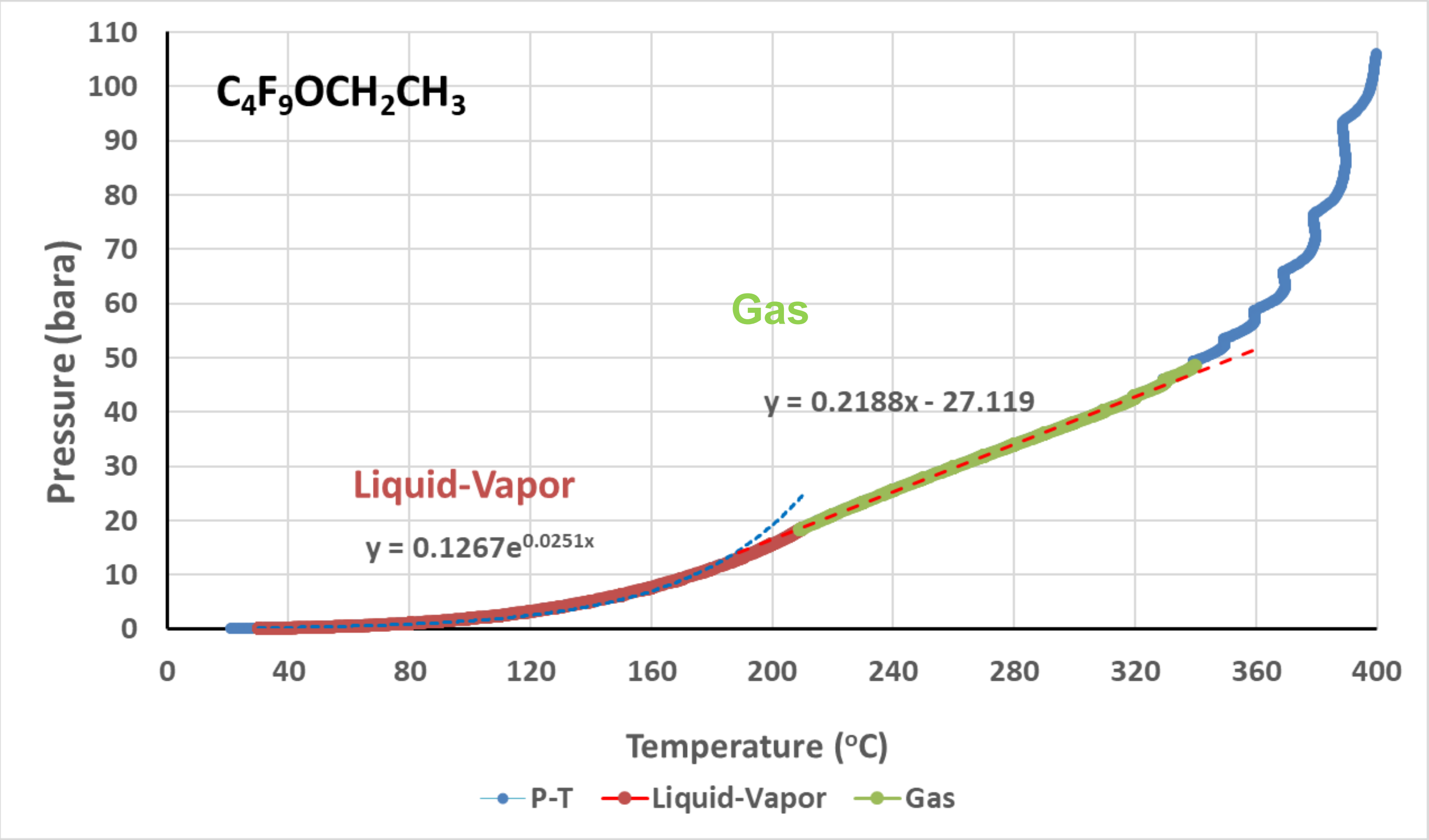


Temperature and Pressure vs Time



Pressure as Function of Temperature

Direct P-T Diagram



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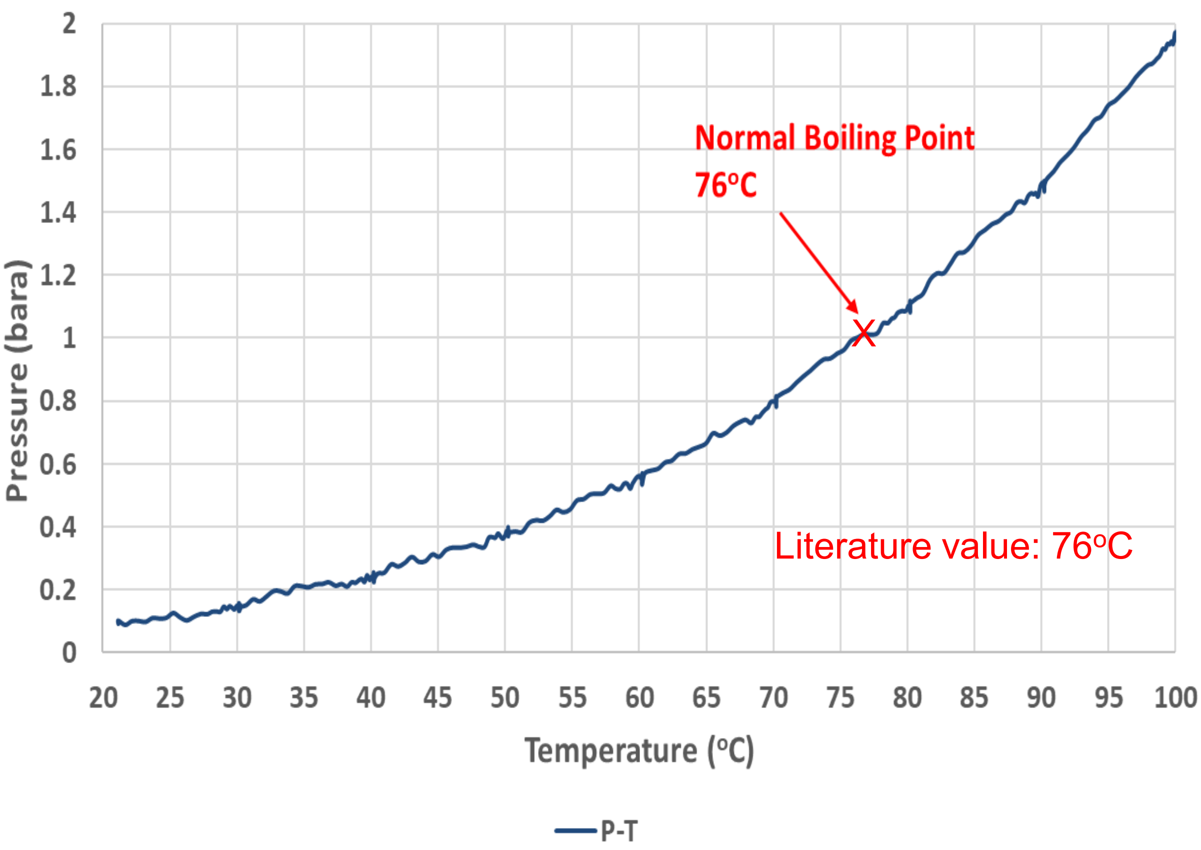
Boiling Point

Testing Conditions:

1. Evacuate the cell before test starts.
2. Keep headspace within the calorimeter.
3. Recommend cell type:



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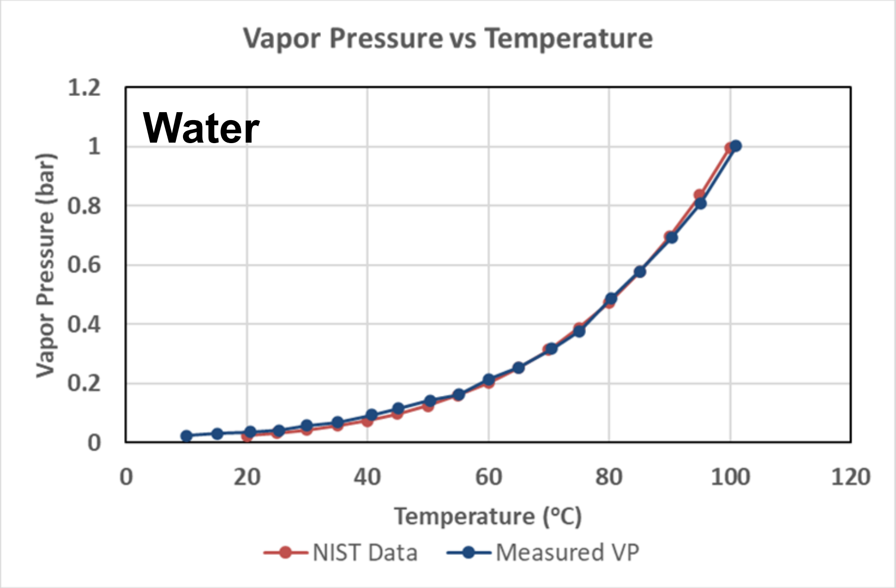
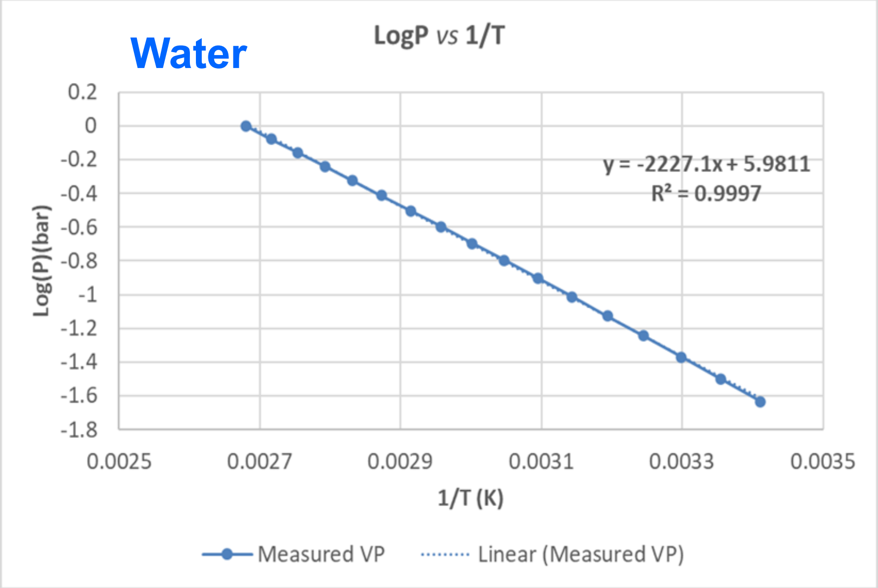
Measurement of Vapor Pressure & Enthalpy of Vaporization

Clausius-Clapeyron equation

$$\ln(P) = -\frac{\Delta H vap}{RT} + C$$

This method is equivalent to ASTM D2879, "Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope".





Same testing conditions as boiling point test

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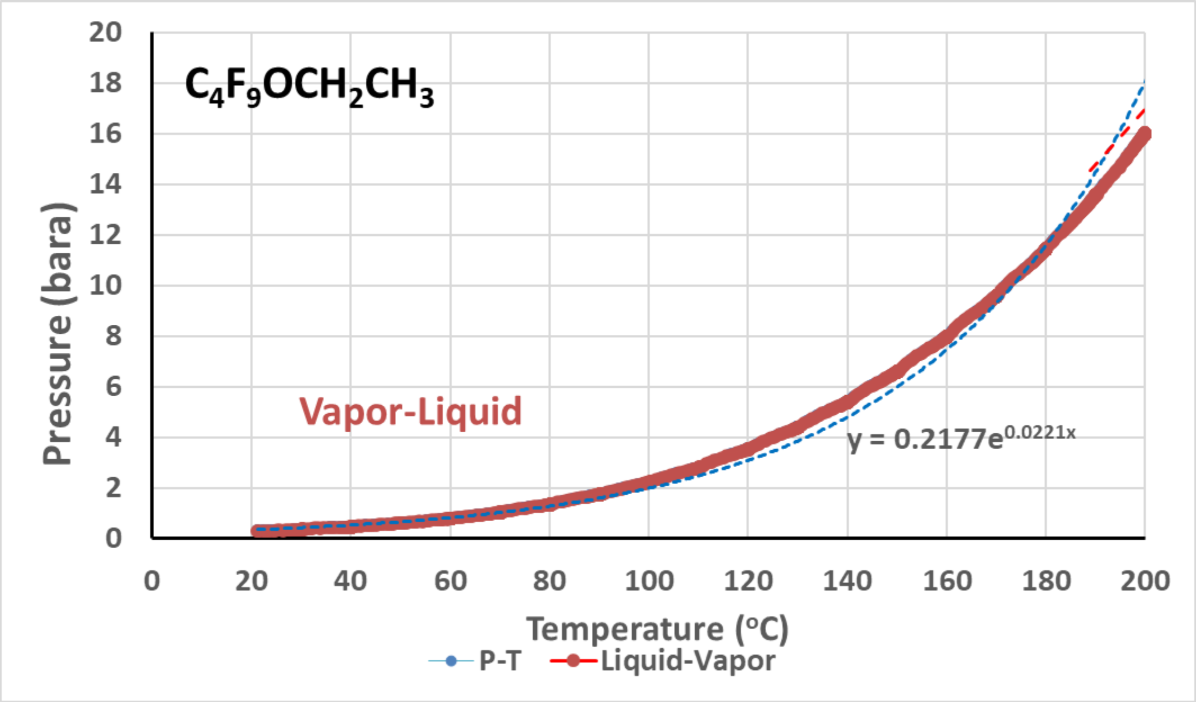
Vapor Pressure



Vapor pressures follow Clausius–Clapeyron equation closely below the boiling point.

Deviation occurs above the boiling point, indicating that more advanced thermodynamic models are required for accurate curve fitting.

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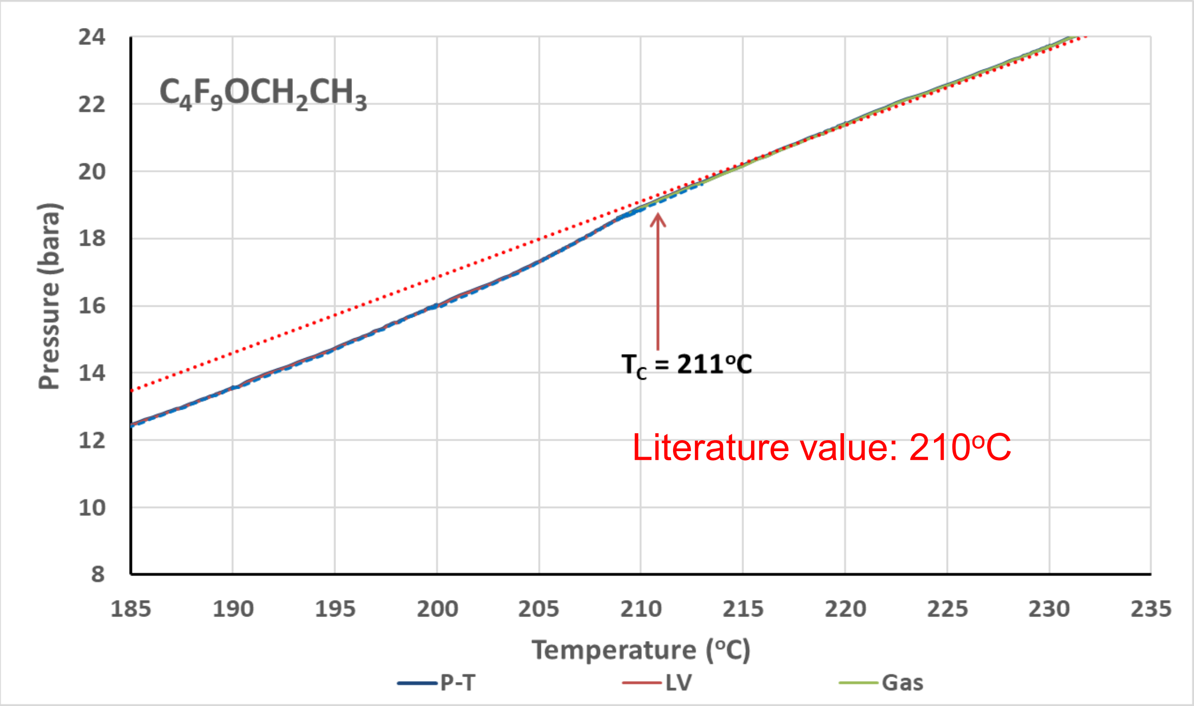
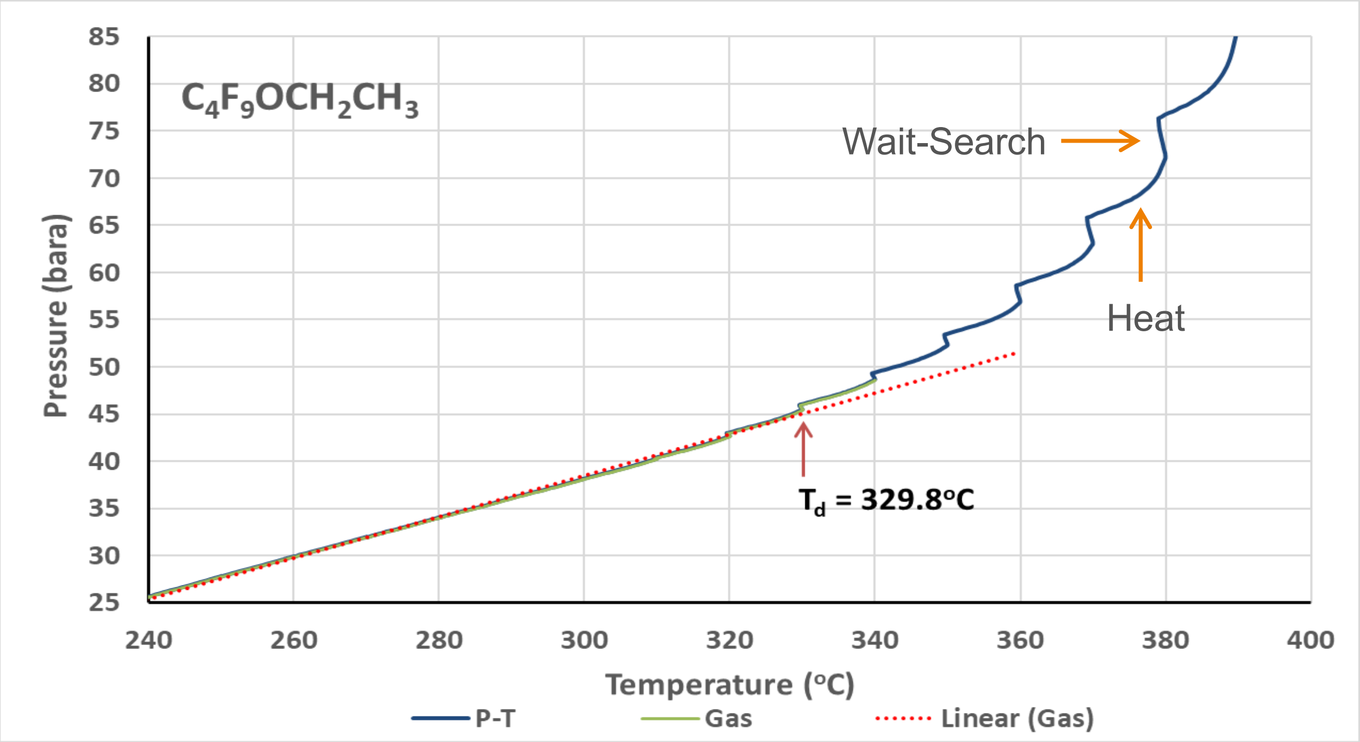
Critical Temperature (T_c)



T_c corresponds to the point where the vapor–liquid equilibrium curve meets (or is extrapolated to meet) the single-phase gas line.

Decomposition Onset Temperature



A mild endotherm with decomposition onset at 329.8°C.

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Concluding Remarks

- **Modified Schlenk Line Performance**
  The Schlenk line reliably measures the mass of gases charged to the ARC bomb, while also providing safe handling—collection, dosing, and disposal—of toxic or highly reactive gaseous reagents.

- **Demonstrated Case Studies**
  Toluene Chlorination, *HFO Refrigerants*, *Hexadecane Hydrocracking*

- **Fundamentals of ARC**
  We reviewed key ARC metrics—adiabatic temperature rise (ΔT_{ad}), Time to Maximum Rate (TMR), and related indices (T_{D24}, T_{D8})—and demonstrated how they translate into severity and controllability criteria for thermal-runaway hazards.
  We also discussed kinetic parameters—activation energy (E_a), pre-exponential factor (A) and reaction order (n).

- **Beyond Hazard Evaluation**
  ARC can also be employed to extract physical properties such as normal boiling points, vapor pressures, heats of vaporization, and critical temperature data, offering a versatile, one-stop approach, especially valuable for thermally sensitive or hazardous substances.

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Questions and Comments

Thank you!

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