

Ignition and Explosion



"The past is never dead. It's not even past."

Joe Shepherd

California Institute of Technology

Pasadena, CA USA

UKELG 65th Meeting, Sunbury, UK, November 27, 2025

Roadmap

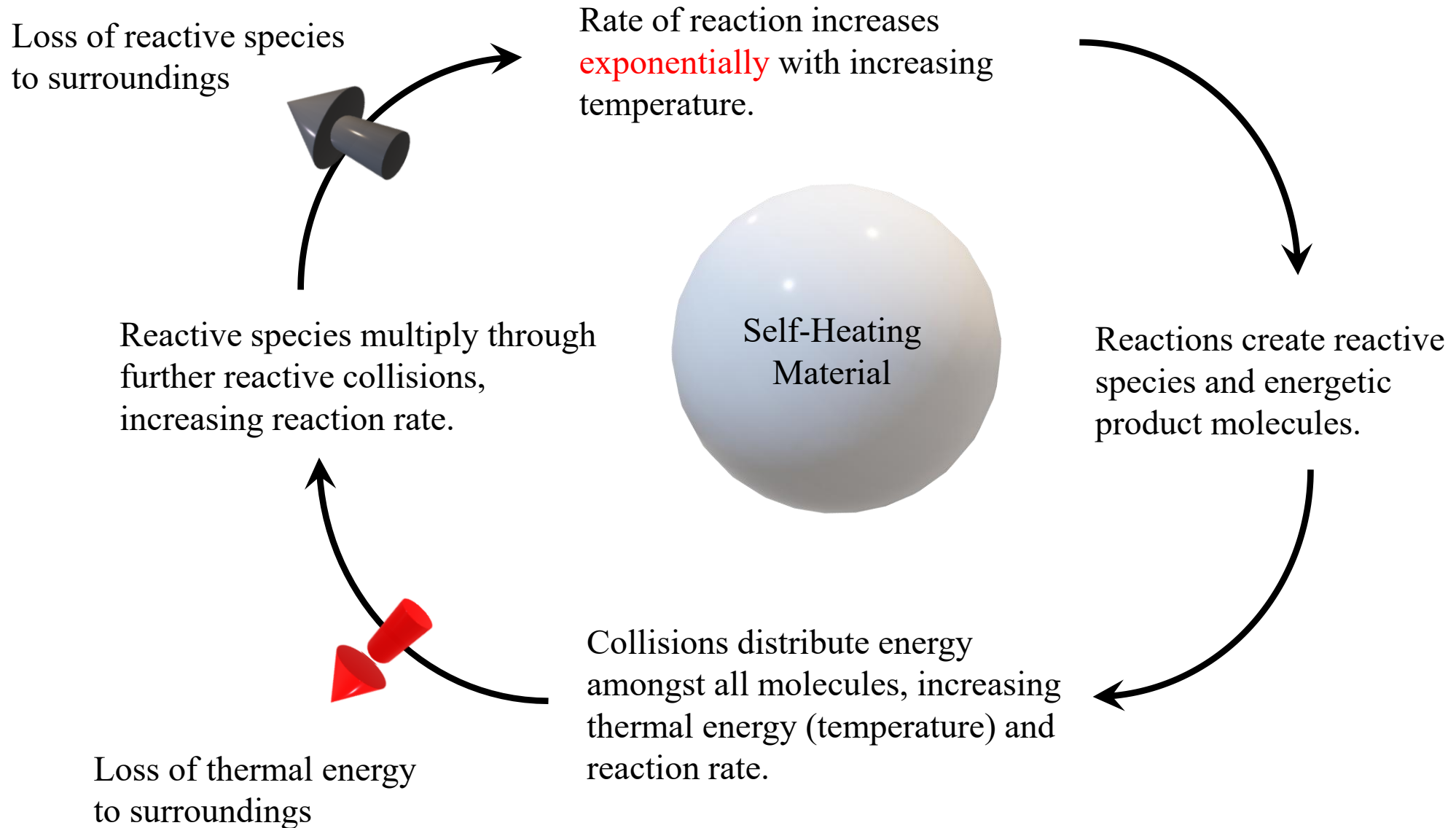
- Context
- History
- Current status of autoignition studies
- Current status of hot surface ignition

Self-Heating



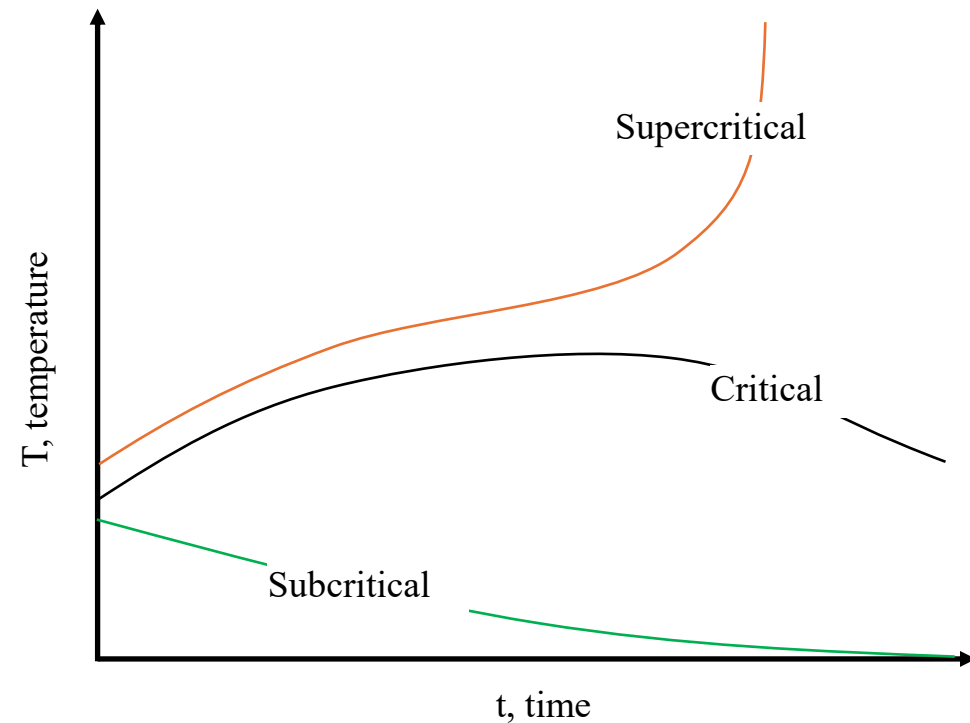
When the grass is cut it should be turned towards the sun and must never be stacked until it is quite dry. If this last precaution is not carefully taken, a kind of vapor will be seen arising from the rick in the morning, and as soon as the sun is up it will ignite to a certainty and so be consumed. Pliny the Elder, *Natural Philosophy*, 77 CE.

Self-heating due to positive feedback cycle

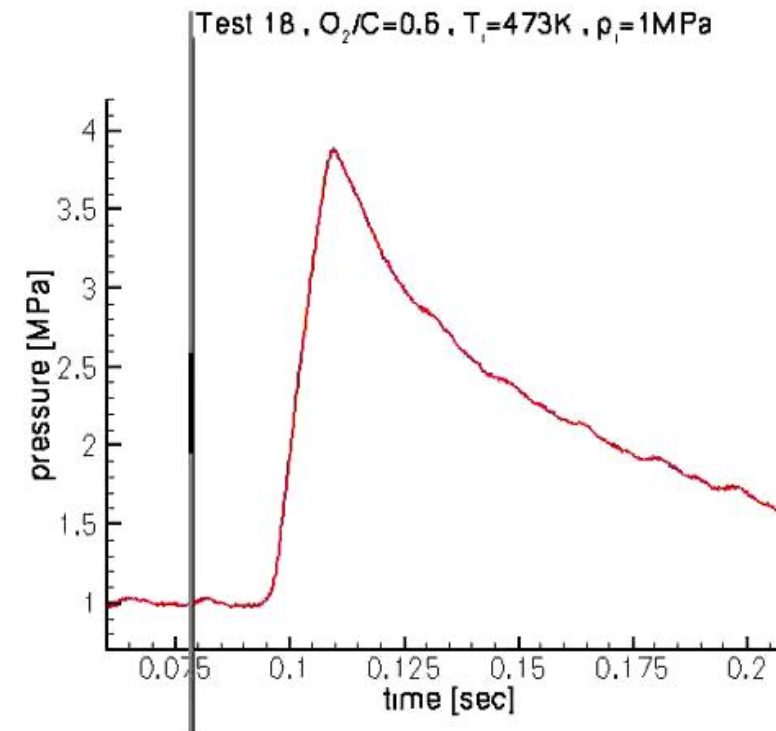


Critical Conditions

- Self-heating leads to ignition, flame propagation and explosive event when critical conditions are exceeded:
 - Critical mass or size (volume, thickness)
 - Temperature of material or surroundings
 - Reactivity
 - Rate of reaction
 - Energy release
 - Losses of species or energy to surroundings



Explosion



D. Lieberman 2002

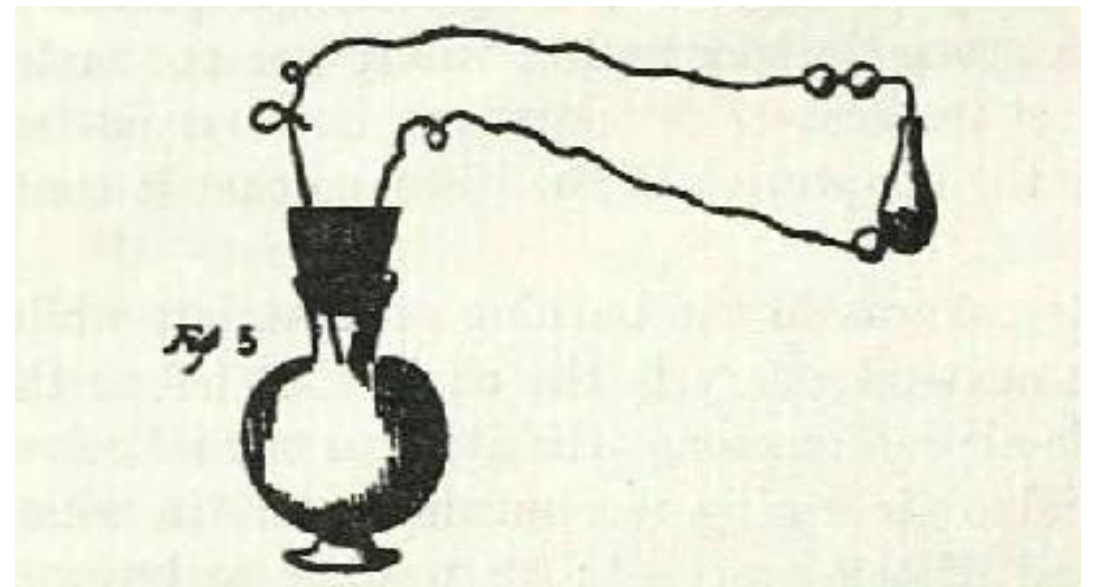
Rapid energy release and species transformation generates pressure and temperature transient.

Some History

Motivation provided by nature and early technology such as mining, smelting, charcoal production

“Marsh” gas

- Primarily methane due to bacterial anaerobic decomposition of cellulose and proteins.
- May be responsible for legends of “ignis fatuus” or foolish fire reported near swamps, stagnant water, and cemeteries.
- Volta 1776 - Demonstrated that electric sparks could ignite the “inflammable air” of the marshes, developed first quantitative tool for combustion gas analysis “the inflammable air eudiometer”.
- Basis of “gasometry” studies by Lavoisier, Cavendish, Bunsen, Kirchhoff, Haber, ... that let to modern concepts of combustion thermochemistry.



Firedamp

“The accidents arising from the explosion of the fire-damp or inflammable gas of coal mines, mixed with atmospherical air, are annually becoming more frequent and more destructive in the collieries in the North of England. A committee has been for some time formed at Sunderland for the benevolent purpose of investigating the causes of these accidents, and of searching for means of preventing them....

It is evident, then, that the opinion formed by other chemists respecting the fire damp is perfectly correct; and that it is the same substance as the inflammable gas of marshes, the exact chemical nature of which was first demonstrated by Mr. Dalton. ..

It was very important to ascertain the degree of heat required to explode the fire-damp mixed with its proper proportion of air...

An iron rod at the highest degree of red heat, and at the common degree of white heat, did not inflame explosive mixtures of the fire-damp; but, when in brilliant combustion, it produced the effect.”

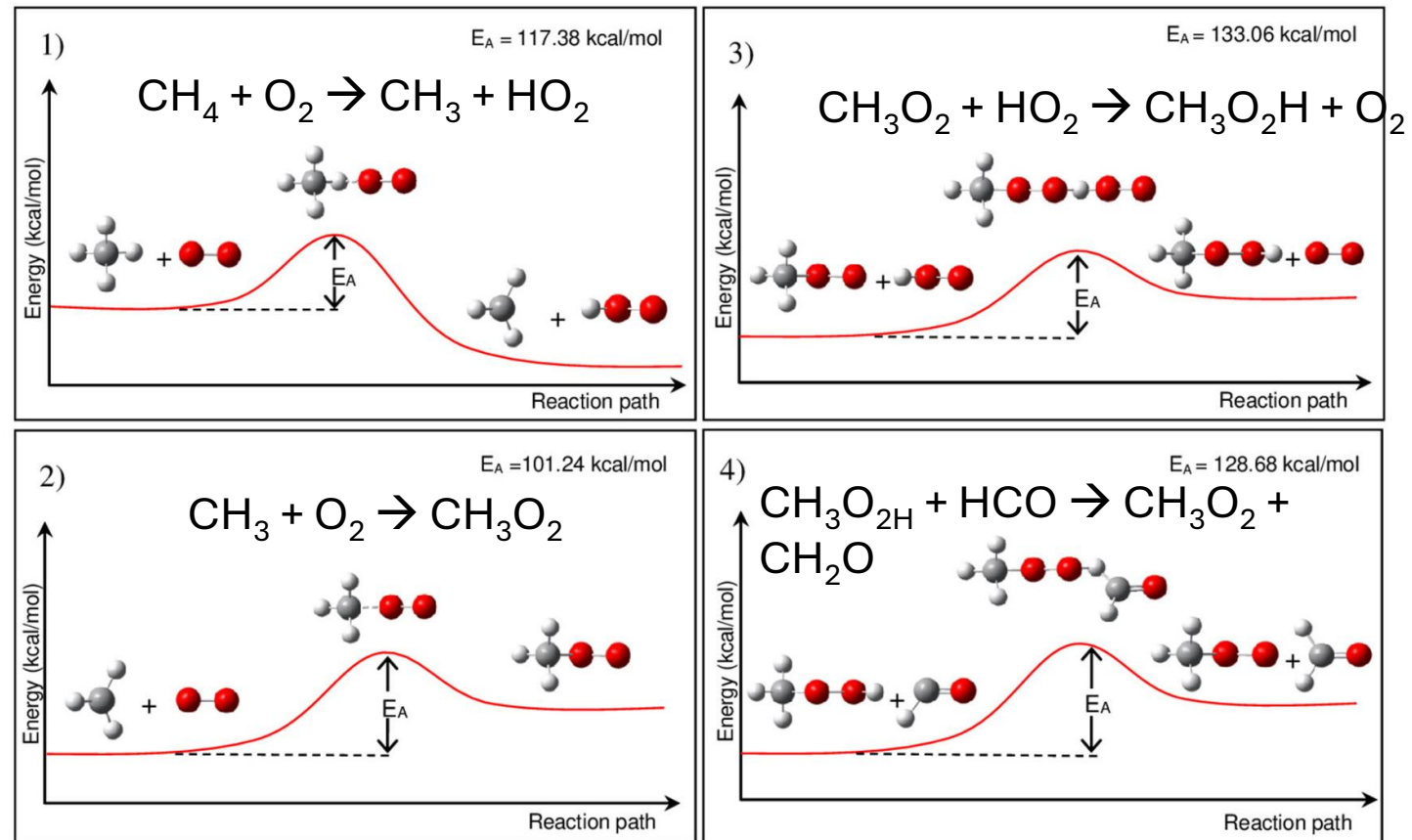
Davy, Phil. Trans., 106, 1-22, 1816.



Miners' Safety Lamp

Cool Flames

- Sir Humphry Davy 1817
“When the experiment on the slow combustion of ether is made in the dark, a pale phosphorescent light is perceived above the wire...”
- First observations of “cool flames”, the blue glow is now known to be due to electronically excited formaldehyde(CH_2O^*) chemiluminescence.



Pavao et al. 2023

Robert Bunsen

G A S O M E T R Y ;

COMPRISING THE LEADING

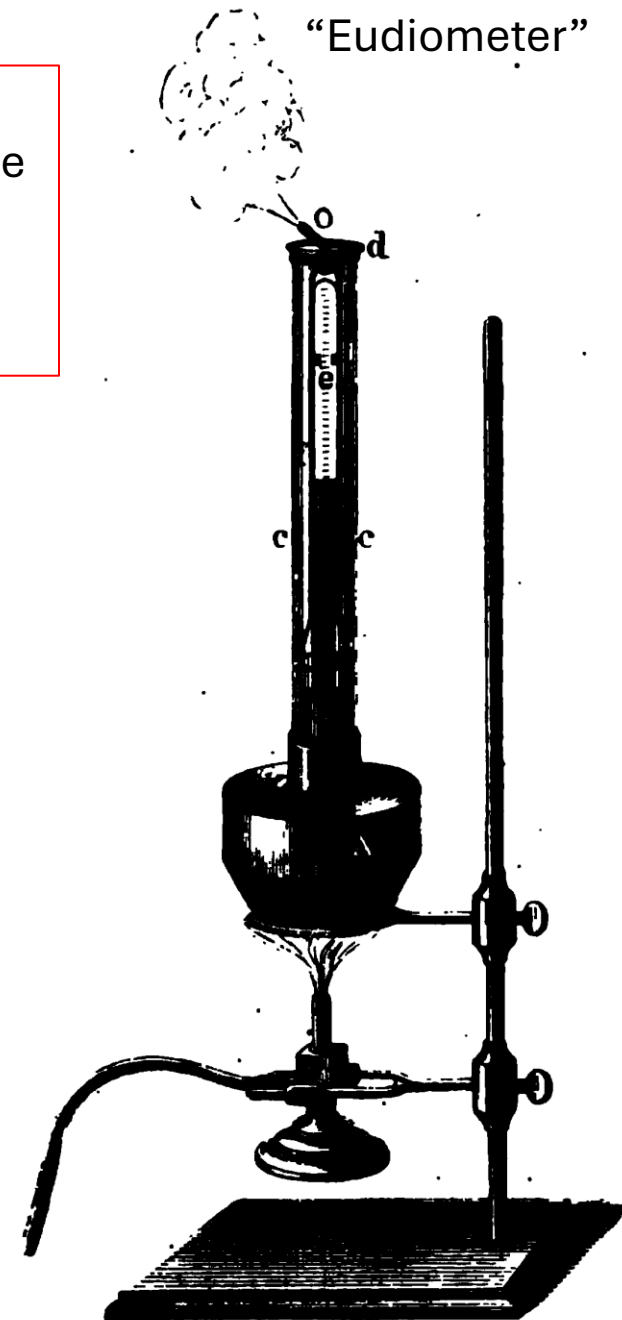
PHYSICAL AND CHEMICAL PROPERTIES OF GASES.

“One of the most important problems in gasometry consists in the determination of the nature, volume, and condensation of the elementary constituents of a single combustible gas of unknown composition.”



“Temperature of ignition of gases. If an explosive mixture of gases is diluted with a large quantity of a non-combustible gas, a limit is reached, beyond which the mixture ceases to be capable of ignition. This limit can be so closely approached that the smallest addition of a non-combustible gas is sufficient to cause a gaseous mixture which was before perfectly inflammable to become as perfectly non-combustible.

A gas which has thus become non-inflammable regains its combustibility if it is prevented from expanding freely during the ignition, or when its temperature has been increased. The limit of dilution at which this sudden check is given to the inflammability is essentially dependent upon the nature of the gases used as diluents.” - Bunsen 1854



RECHERCHES

EXPÉRIMENTALES ET THÉORIQUES

SUR

LA COMBUSTION

DES

MÉLANGES GAZEUX EXPLOSIFS

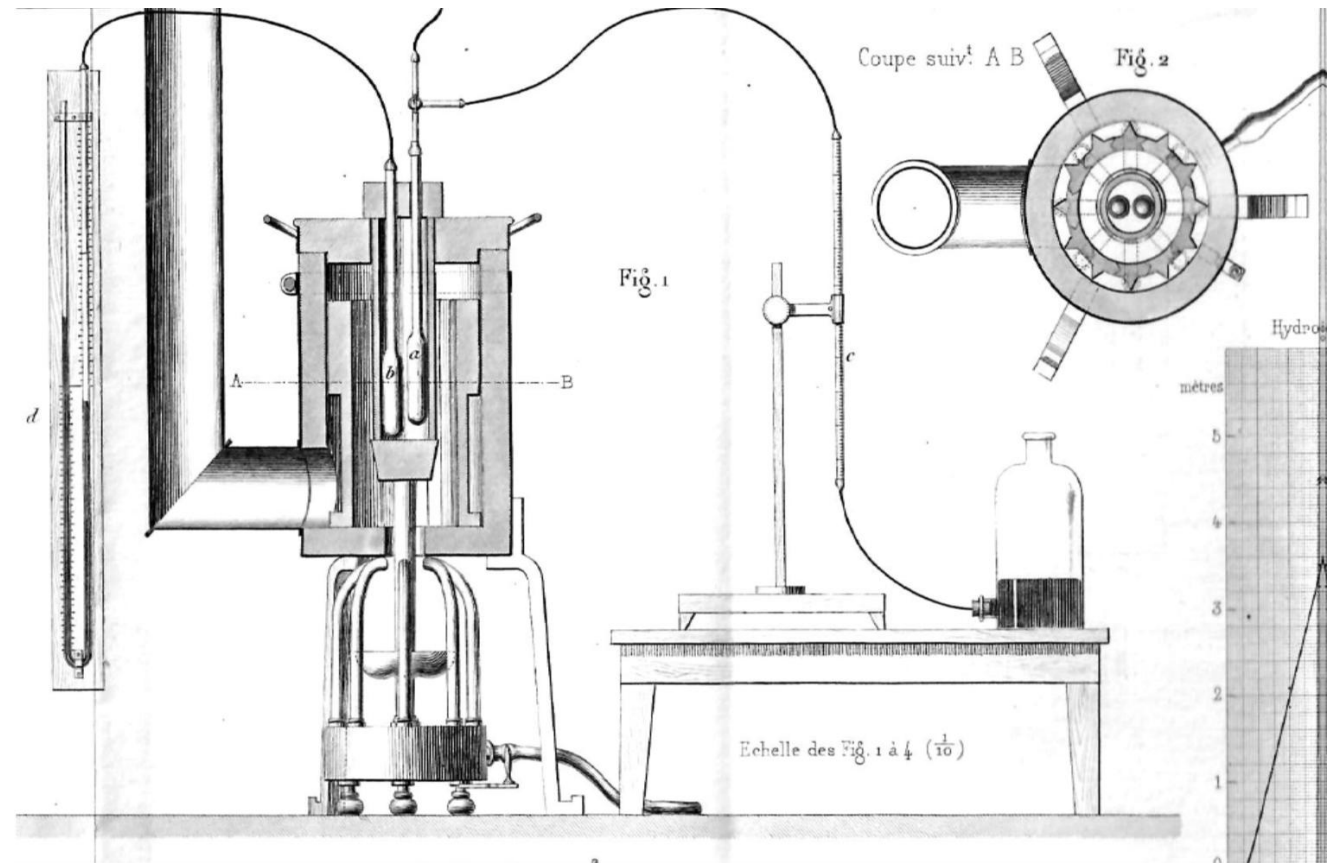
PAR

MM. MALLARD ET LE CHATELIER

Ingénieurs au corps des Mines.

“The Firedamp Commission, of which we were a member, had entrusted us with the task of seeking to elucidate, through appropriate experimental research, the conditions for producing firedamp explosions and the various phenomena that accompany them.”

1883



Determined ignition temperatures for three mixtures:

555°C for the flammable mixture of hydrogen and oxygen;
655°C carbon monoxide and oxygen;
650°C formene (methane) and oxygen.

Mallard and Le Chatelier (1883)

Moving film strip ~ 1 m/s, 3 m long tube

CS₂ + 6NO
20 mm dia

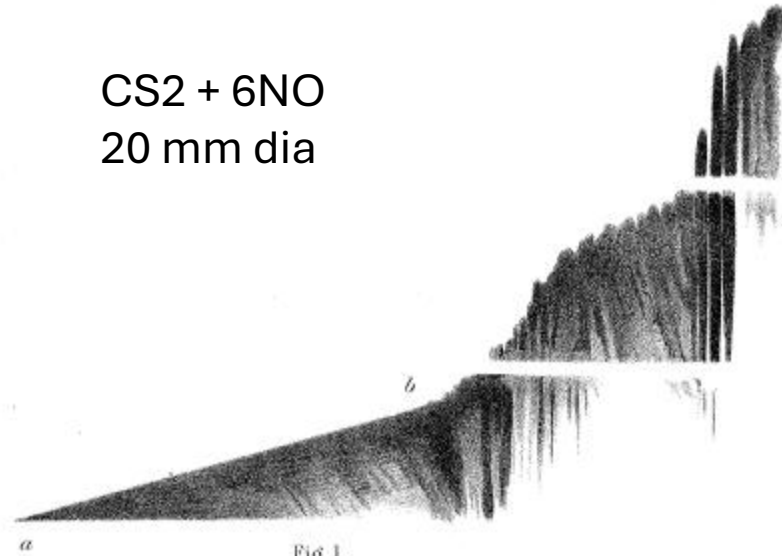


Fig. 1.

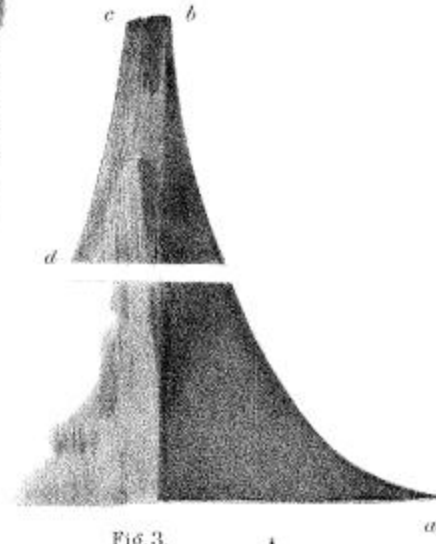


Fig. 3.

CS₂ + 6NO
10 mm dia

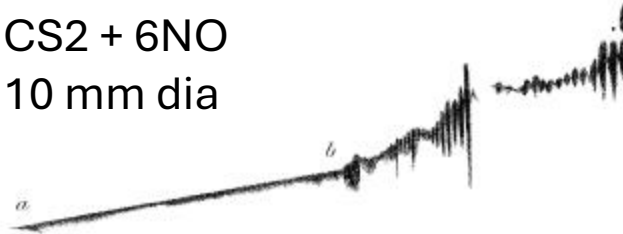


Fig. 2.

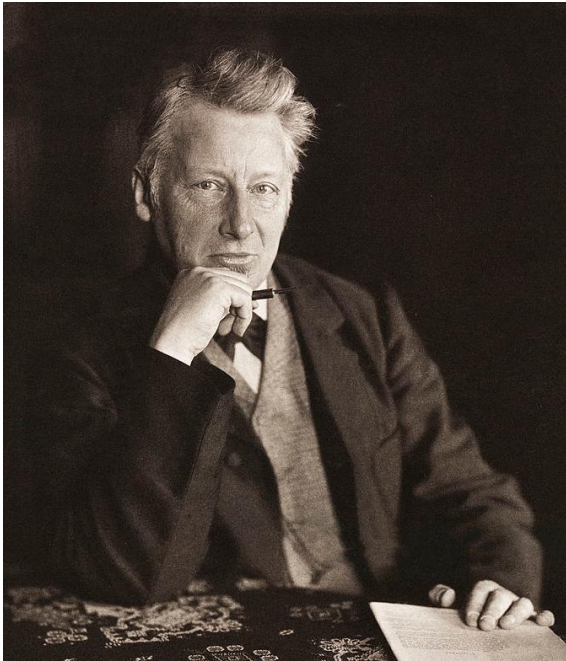
CS₂ + 3O₂



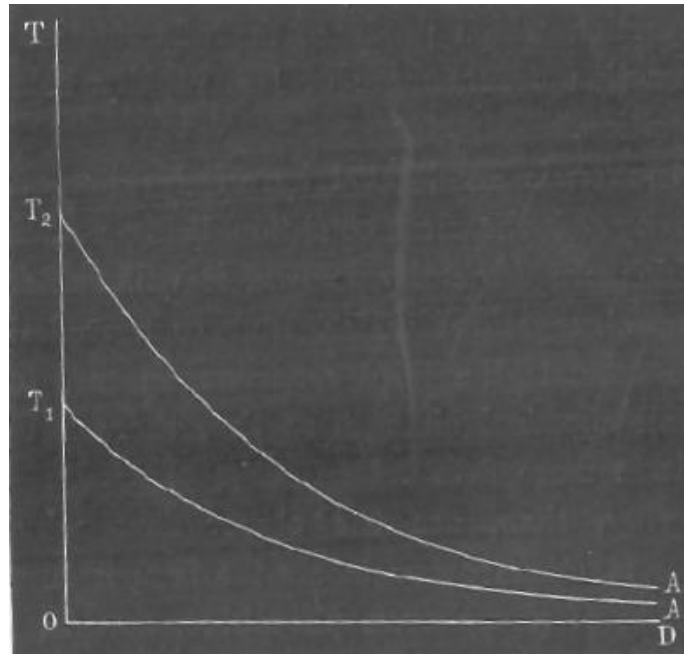
Fig. 4.

Mallard and Le Chatelier's Photographs.

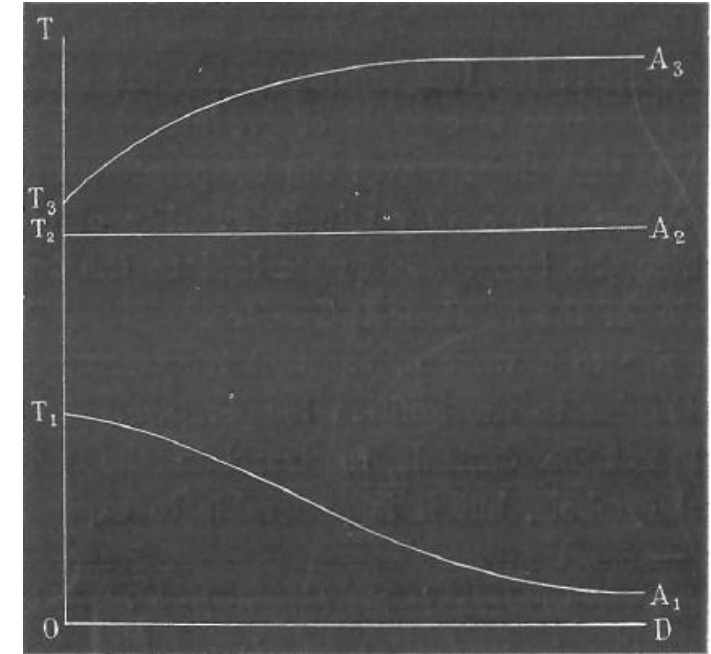
Jacobus Henricus van 't Hoff *Études de Dynamique chimique*, 1884



Inert gas

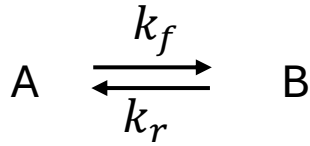


Flammable gas



The ignition temperature is the temperature at which the initial loss of heat, due to conduction, etc, is equal to the heat of evolved in the same time by the chemical reaction. – van't Hoff 1896

van't Hoff to Arrhenius



van't Hoff 1884

Thermodynamics:

$$\frac{[B]}{[A]} = K_p$$

$$\boxed{\frac{dK_p}{dT} = K_p \frac{\Delta H}{RT^2}}$$

Arrhenius 1889

Chemical dynamics

$$\frac{d}{dt} [B] = k_f [A] - k_r [B]$$

$$K_p = \frac{k_f}{k_r} \Rightarrow \frac{d \ln K_p}{dT} = \frac{d \ln k_f}{dT} - \frac{d \ln k_r}{dT}$$

$$\frac{dk_{f,r}}{dT} \propto \frac{E_{f,r}}{RT^2} \rightarrow k_{f,r} \propto \exp\left(-\frac{E_{f,r}}{RT}\right)$$

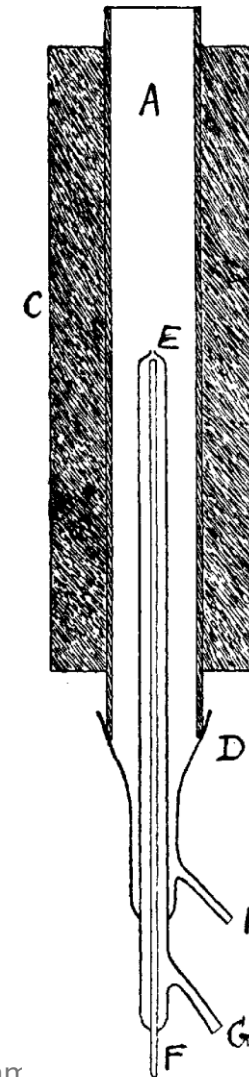
Town or Coal Gas

(coal \rightarrow H₂, CO, CH₄, CO₂)

Harold Baily Dixon (1852-1930)



Report By Mr. A.G. *Vernon Harcourt*, . . . Gas Referee to the Board of Trade, of the Circumstances Attending the Explosion of Gas in the *Tottenham Court Road* in 1880



Rate of flow of
ethylene,
c.c. per min.

Ignition-
temperature.

Crackling ignition

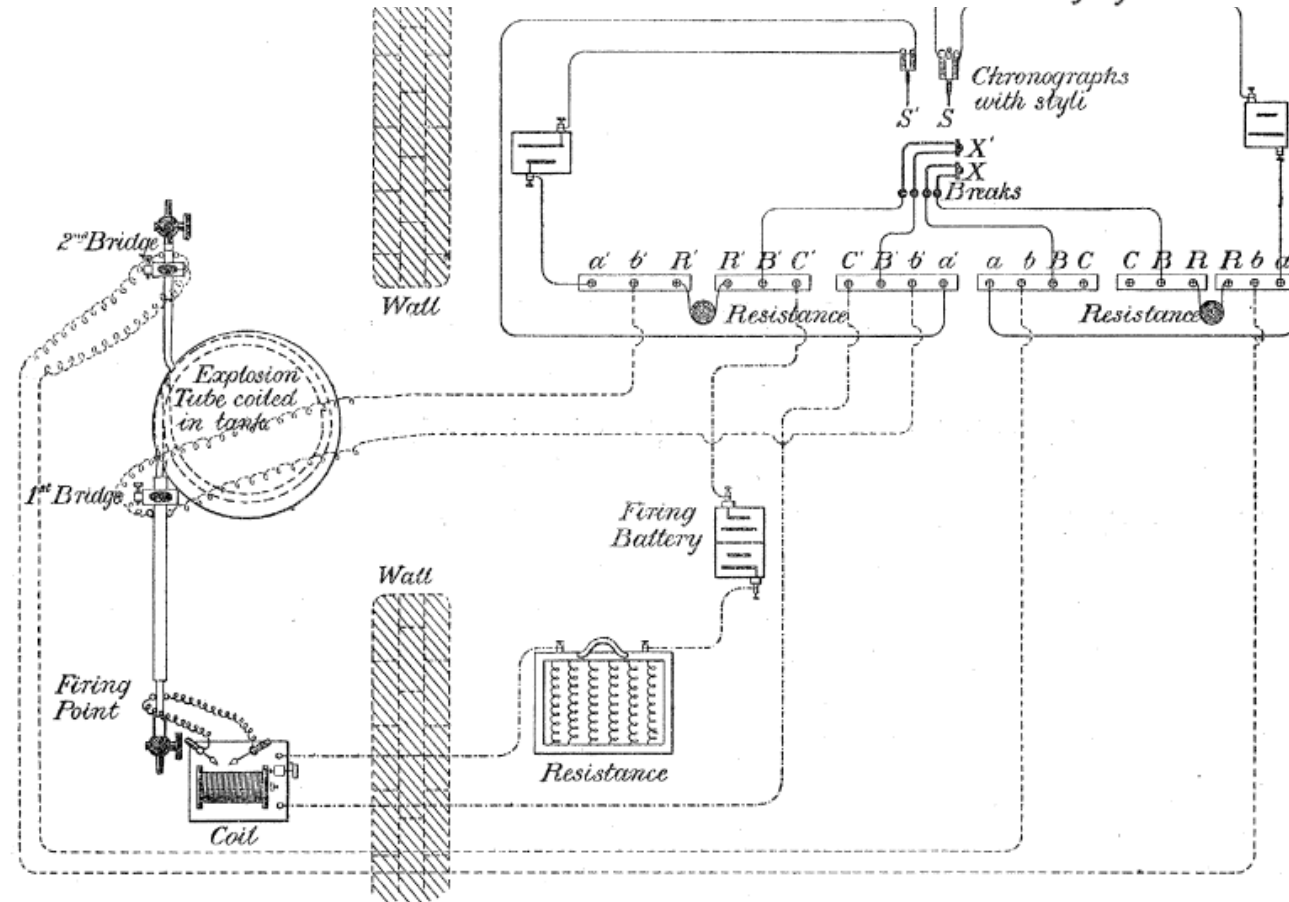
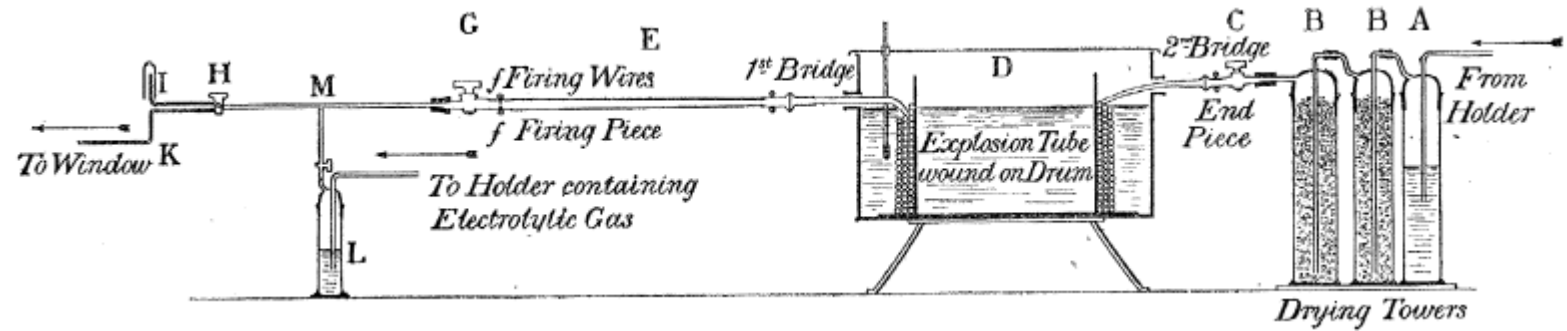
0.5
1.4
1.4
1.7
2.2
2.4
2.7
3.6
3.6
4.8
6.5
6.7
6.7
9.5

666°
616
627
626
610
595
591
575
539
537
536
559
555
532

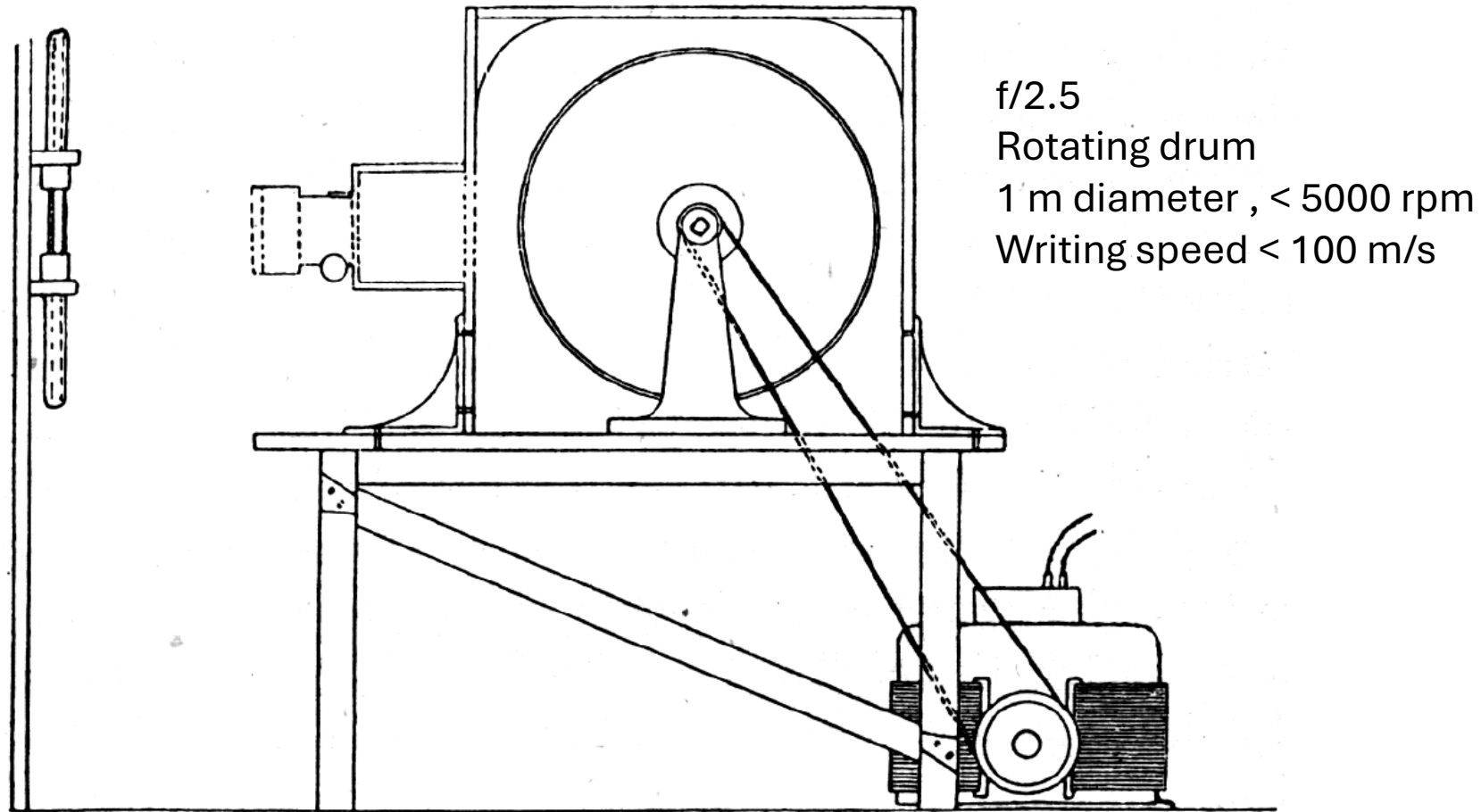
“ ”
“ ”
“ ”
“ ”
“ ”
“ ”
“ ”
“ ”
“ ”
Moderate explosion
“ ”
“ ”
“ ”
Loud explosion

Dixon, Harold Baily, and Hubert Frank Coward. “LXVII.—The Ignition-Temperatures of Gases.” *J. Chem. Soc., Trans.* 95, no. 0 (1909): 514–43.

Dixon 1893



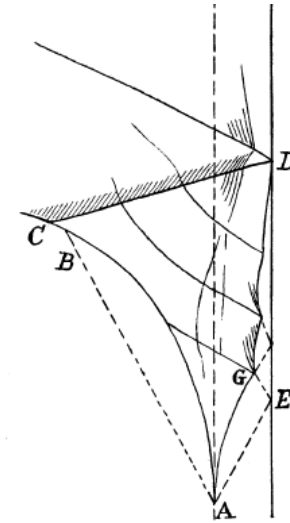
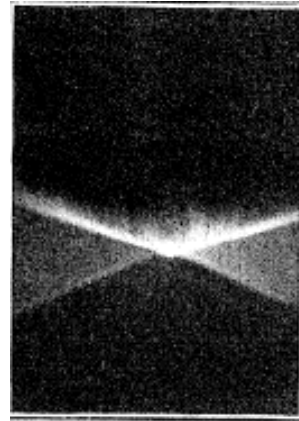
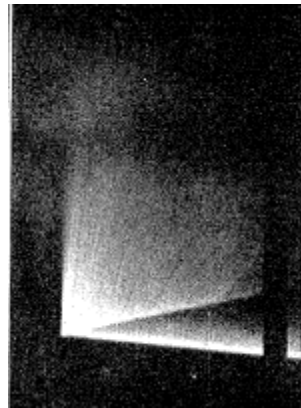
Dixon, Graham, Strange 1896



H. B. Dixon, E.H. Strange, E. Graham “The explosion of Cyanogen”, Journal Chem Soc (1896)

Dixon 1903

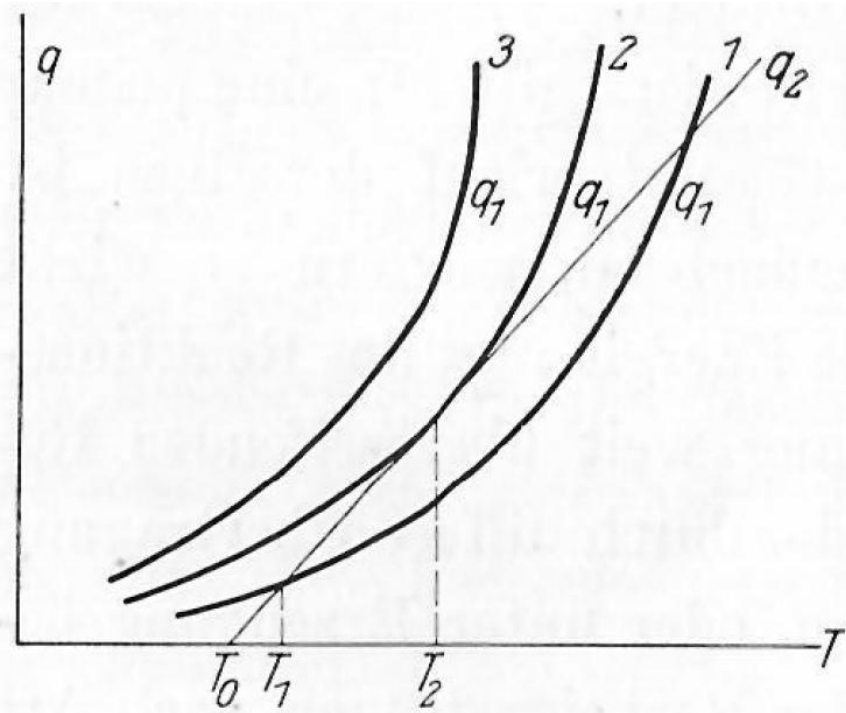
- (1) It starts suddenly, throwing back a strongly luminous wave through the burning gases and leaving a dark space where it started ;
- (2) It travels with constant velocity, unless it traverses a junction not rigidly attached ; after being damped down by such an obstacle, it recoups itself and again starts with abruptness ;
- (3) On collision with a similar detonation-wave moving in the opposite direction, or with a rigid diaphragm, it sends back a reflected wave not so rapid as itself, and as a rule not so luminous.



Self-Heating

Le Chatelier 1908, Semenov 1928

Frank-Kamenetskii 1939



$$\Delta_z \theta = -\delta \cdot e^{\theta}$$

$$\theta = \frac{E}{RT_0^2} (T - T_0)$$

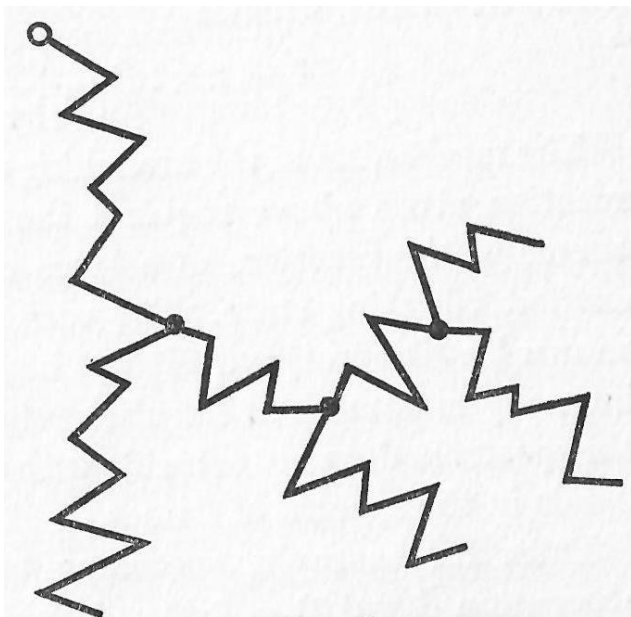
$$\delta = \frac{Q}{\lambda} \cdot \frac{E}{RT_0^2} \cdot r^2 z e^{-\frac{E}{RT_0}}$$

“Assuming that the walls of the vessel have a constant temperature T_0 , we shall find the stationary distribution of temperature within the vessel which satisfies equation (1). The values of the parameters, at which such a solution becomes impossible, give the condition of inflammation.” - Frank-Kamenetskii 1939

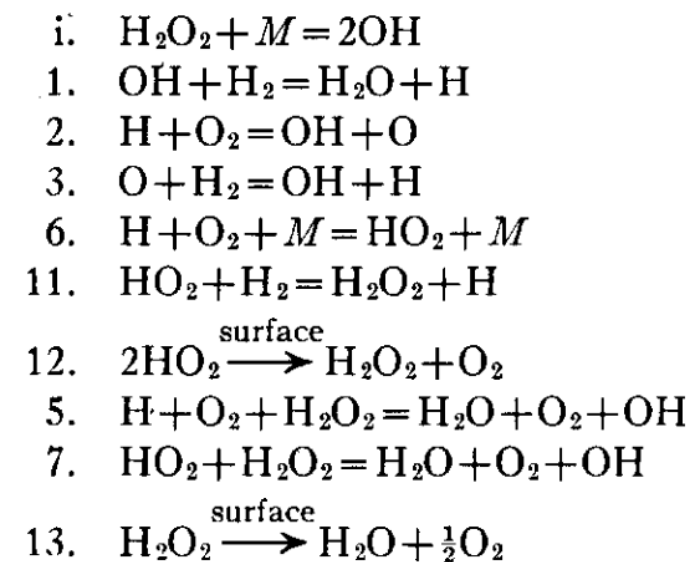
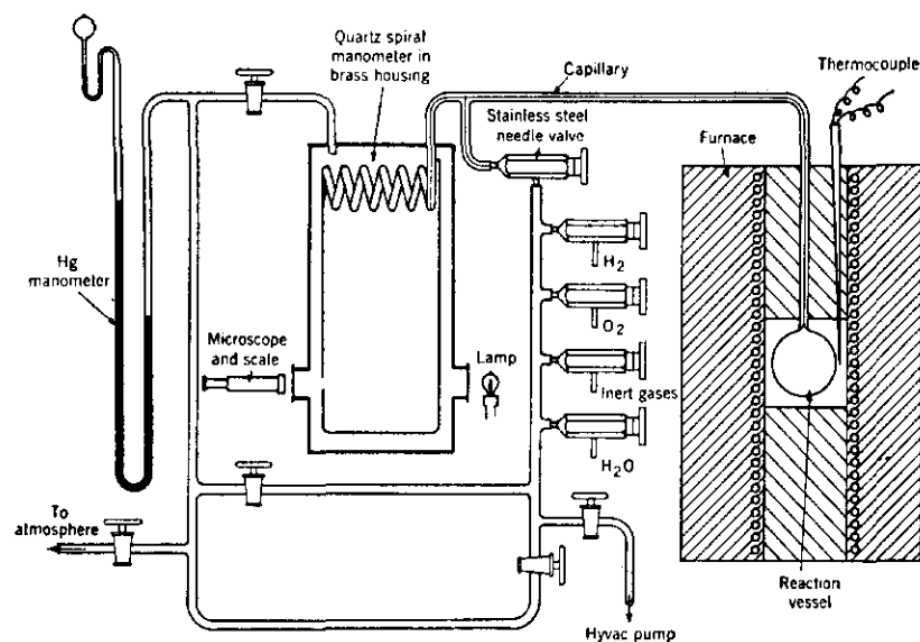
Chain Reactions

Bodenstein, Nernst, Semenov, Hinshelwood, ...

“The most widespread type of explosion is forwarded, however, by the combined chain-thermal explosion.” Semenov 1935



The Reaction between Hydrogen and Oxygen by C. N. Hinshelwood and A. T. Williamson (Oxford, Clarendon Press, 1934)

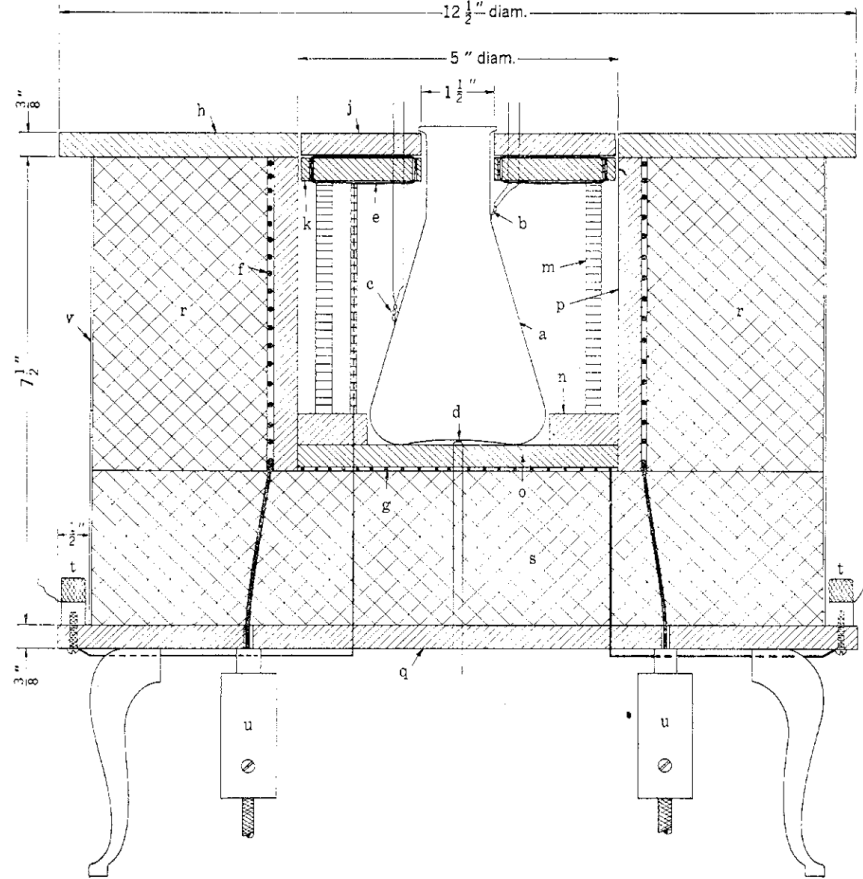


Von Elbe, Guenther, and Bernard Lewis. “Mechanism of the Thermal Reaction Between Hydrogen and Oxygen.” *The Journal of Chemical Physics* 10, no. 6 (1942): 366–93.

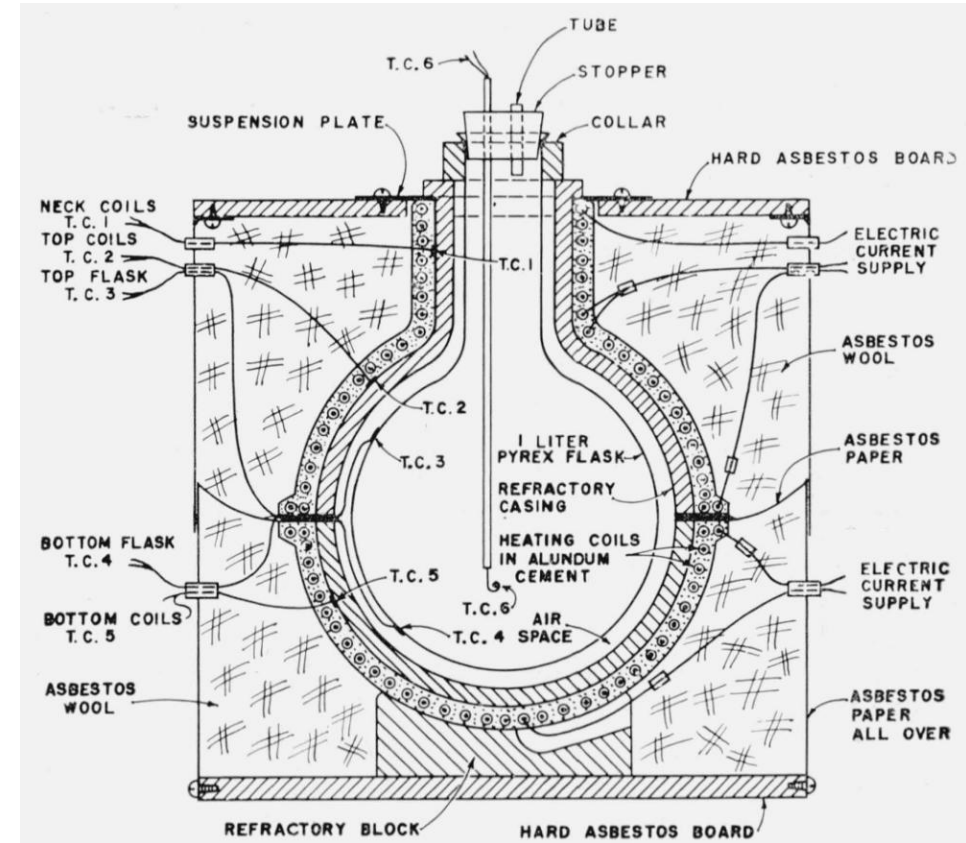
Autoignition in gases

Automation and improved instrumentation enables quantification and uncertainty analysis.

Development of Standardized Testing



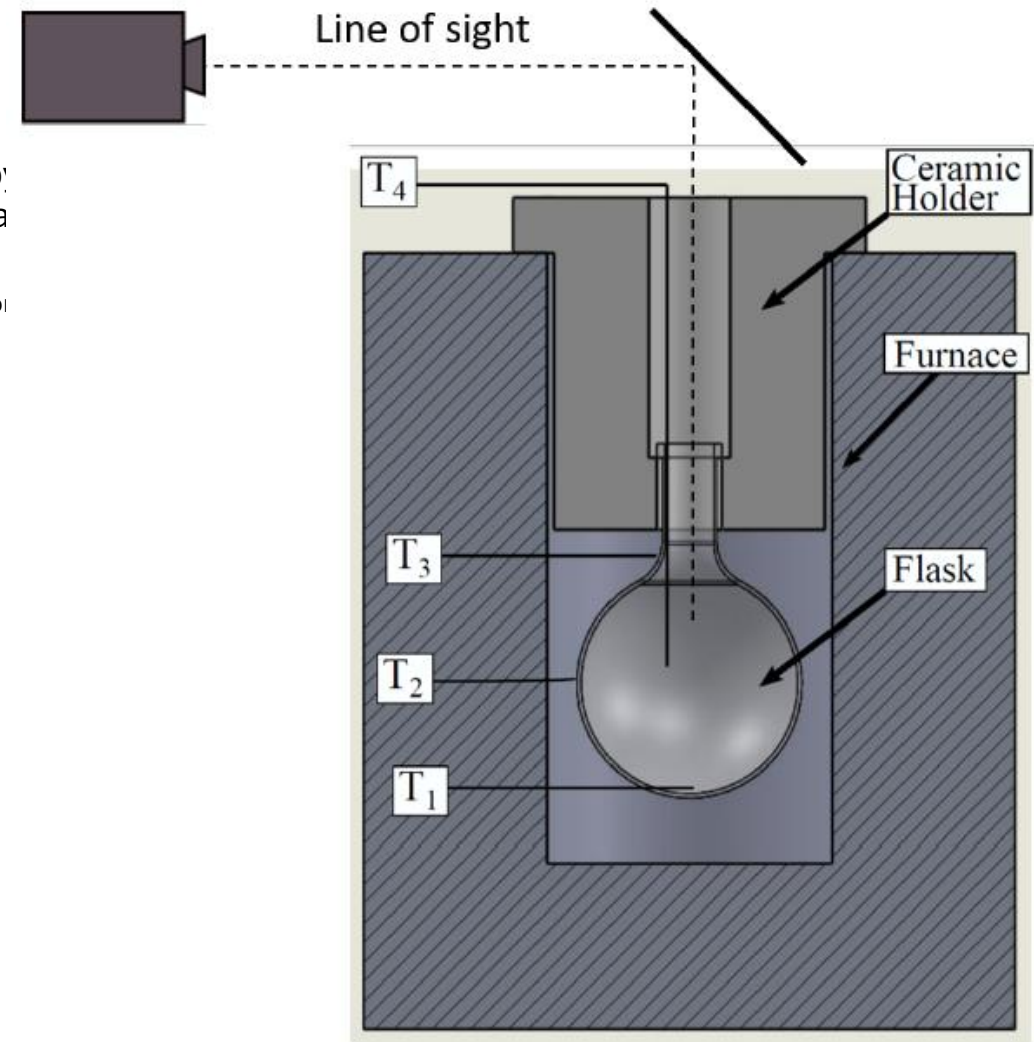
Zabetakis, M. G., A. L. Furno, and G. W. Jones. "Minimum Spontaneous Ignition Temperatures of Combustibles in Air." *Industrial & Engineering Chemistry* 46, no. 10 (October 1954): 2173–78.



Setchkin, N.P. "Self-Ignition Temperatures of Combustible Liquids." *Journal of Research of the National Bureau of Standards* 53, no. 1 (July 1954): 49.

Standardized Testing for Self-Heating in Gases

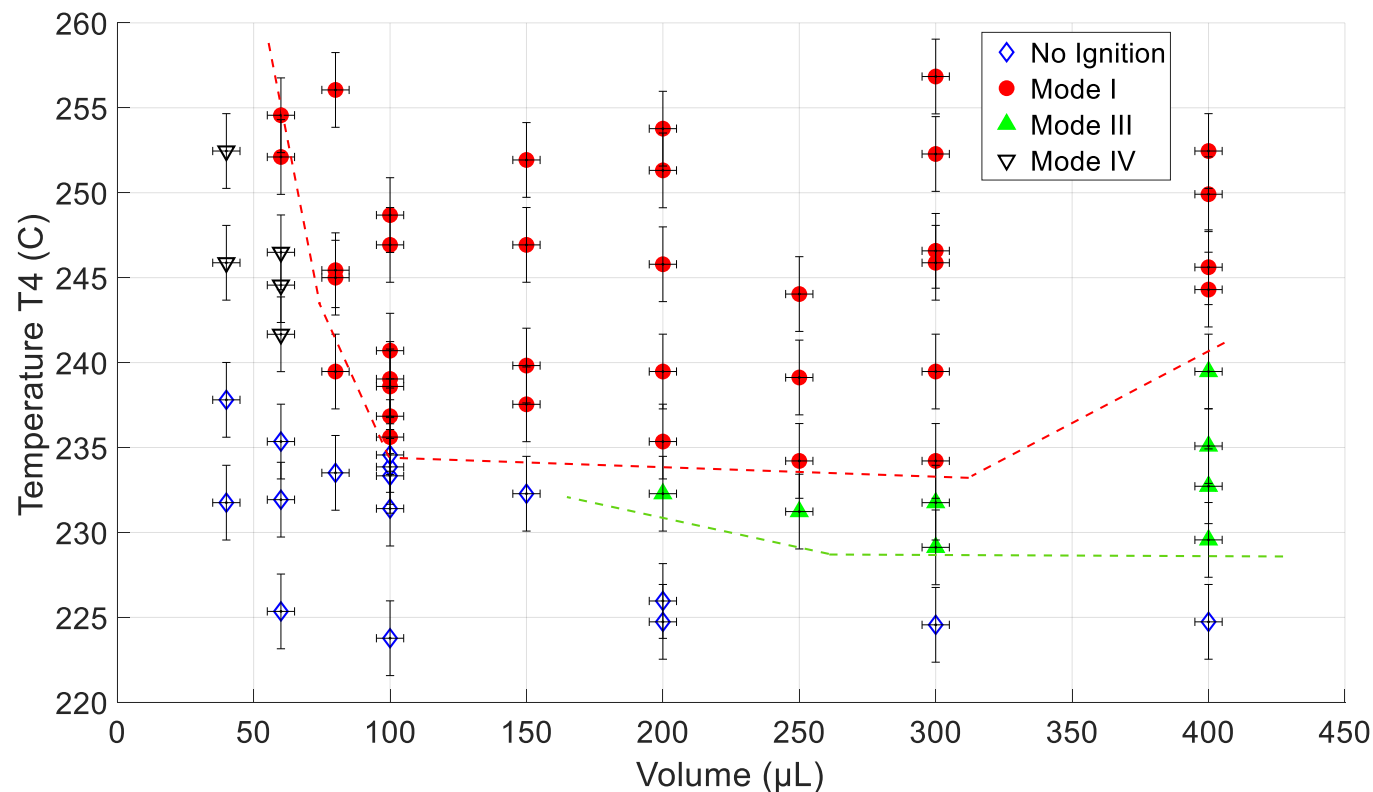
- ASTM E659, EN 14522 and DIN 51794 (ISO/IEC 80079-20-1, 2017) widely used by hazards analysts for process safety evaluation and regulation of transportation and handling of reactive materials.
 - ASTM-E659 Standard test method for autoignition temperature of liquid chemicals. American Society for Testing and Materials
- 500 mL spherical flask heated to specified temperature (T)
- 0.1 mL liquid sample injected through open top
- Wait up to 10 min for flash of light (by eye)
 - If no flash: repeat steps 1-3 at higher T
 - If flash: repeat steps 1-3 at lower T
- Iterate until T between ignition and non-ignition reached
- Repeat for range of sample volumes
- Results:
 - Subjective evaluation based on visual results and operator judgement
 - Single Auto ignition temperature (AIT) reported (lowest T from any of the tested samples) based on arbitrary ignition criteria.



Event classification

- Ignition depends on the tested volume
- Ignition can occur without a visible flame
- Overlap of no ignition / ignition cases around the AIT

Both considered as ignition event



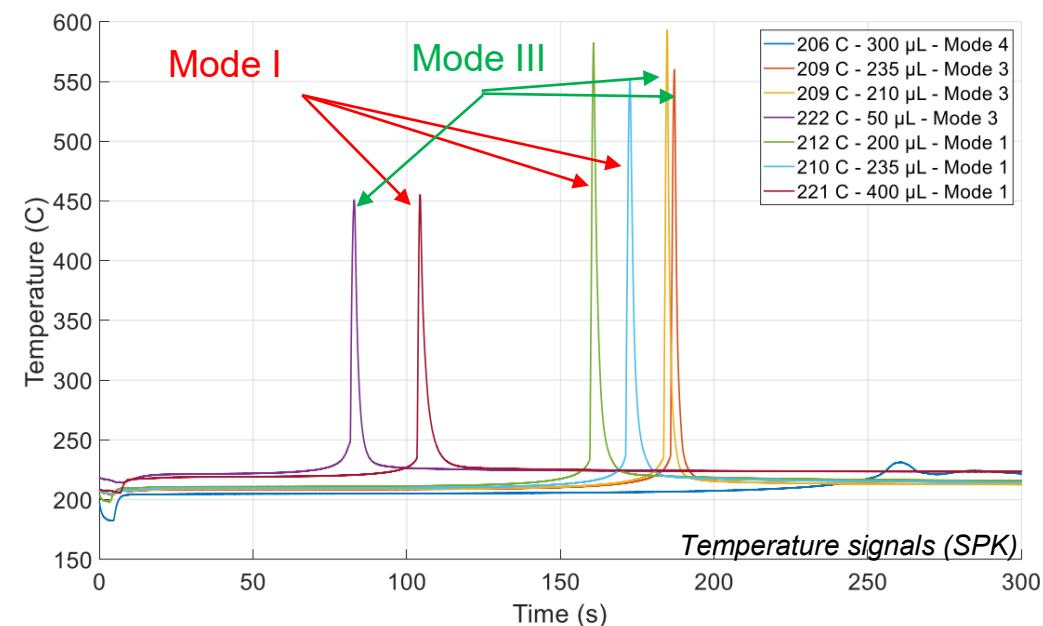
Ignition Map - Jet A POSF4658

Conor Martin, Experiments in Thermal Ignition: Influence of Natural Convection on Properties of Gaseous Explosions, Caltech, 2023

Ignition Mode	Name	Luminosity	Temperature Rise
I	Ignition	Large ^a	Large
II	Cool Flame	Small	Small
III	Non-Luminous Cool Flame	None ^b	Large
IV	Rapid Reaction	None	Small
-	Non-Ignition	None	< 15°C

^a Associated with a weak to intense explosion sound

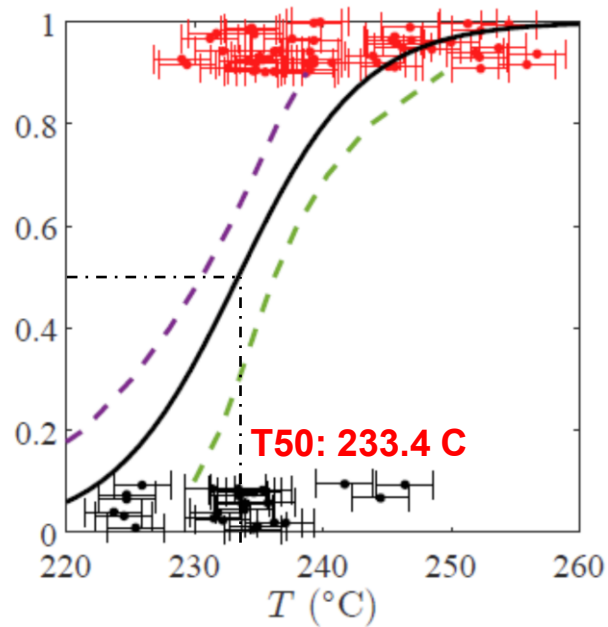
^b None or faint glow only visible to the naked eye, and small puff of smoke



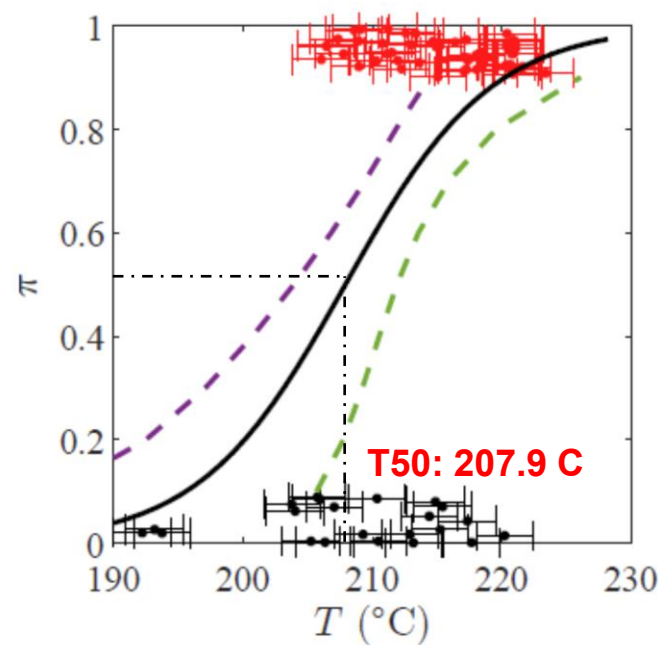
Statistical Analysis

- Categorical outcomes treated as Bernoulli trials
 - 1 = ignition (mode I and III)
 - 0 = non-ignition (Modes IV, and None)
 - Assume fuel volume is secondary and use measured (T4) gas temperature as stimulus x

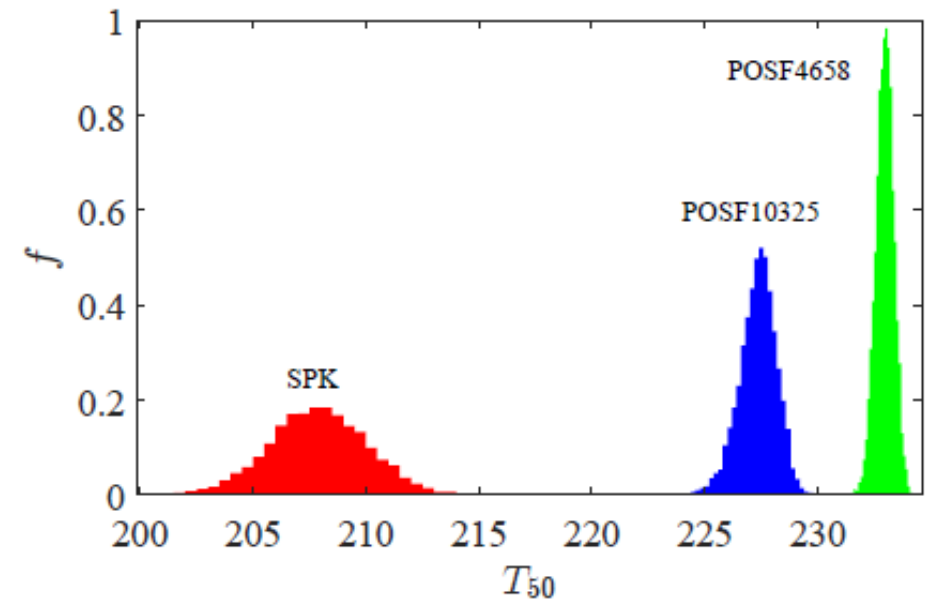
- Maximum likelihood estimation of probability π based on logistic model
$$\pi(\beta; x) = \frac{1}{1 + e^{-\beta_0 - \beta_1 x}}$$



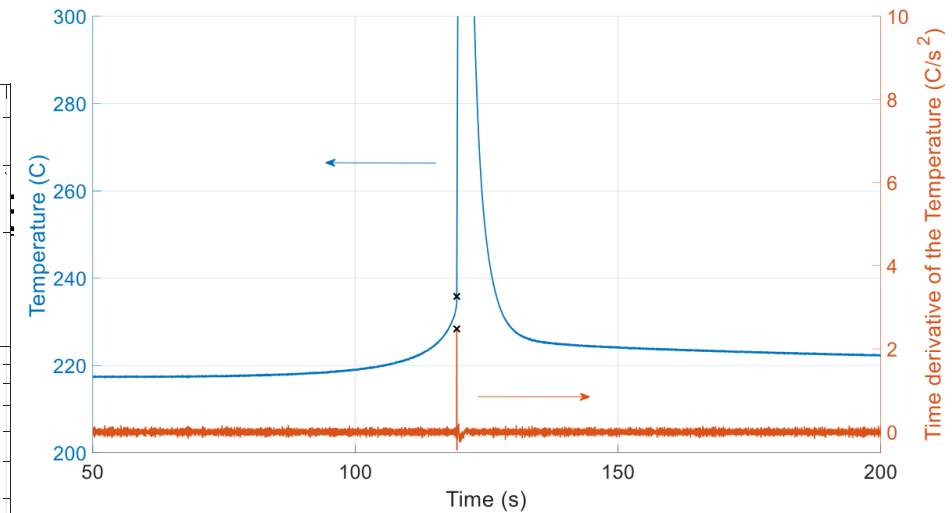
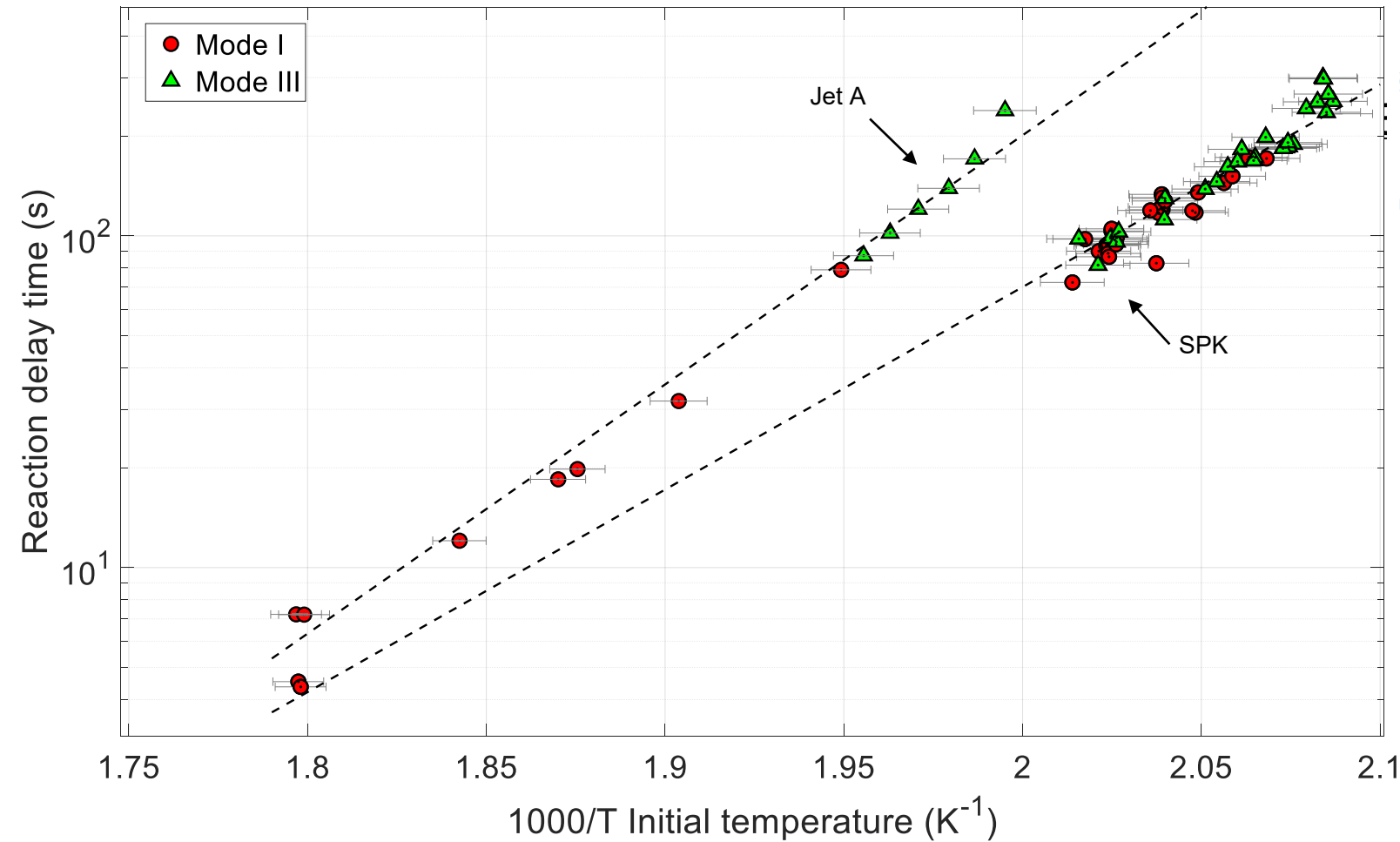
POSF4658



SPK



Ignition delay time



Effective activation energy

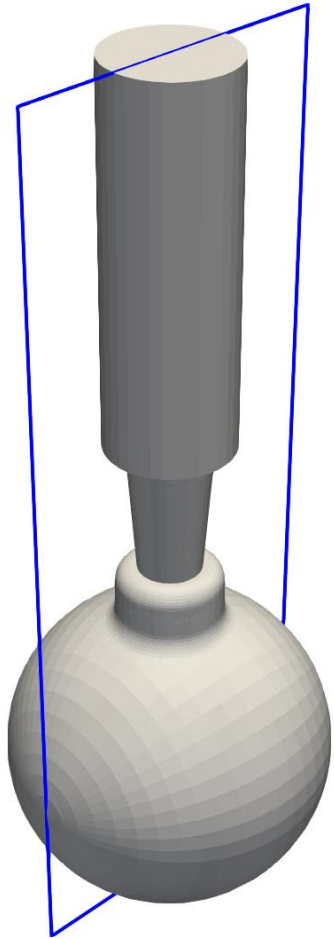
Jet A	SPK
141 $\text{kJ}\cdot\text{mol}^{-1}$	116 $\text{kJ}\cdot\text{mol}^{-1}$

Estimation of the effective activation energy using the simple Arrhenius form of a one-step model reaction and the Semenov/FrankKamenetskii model for the ignition delay time:

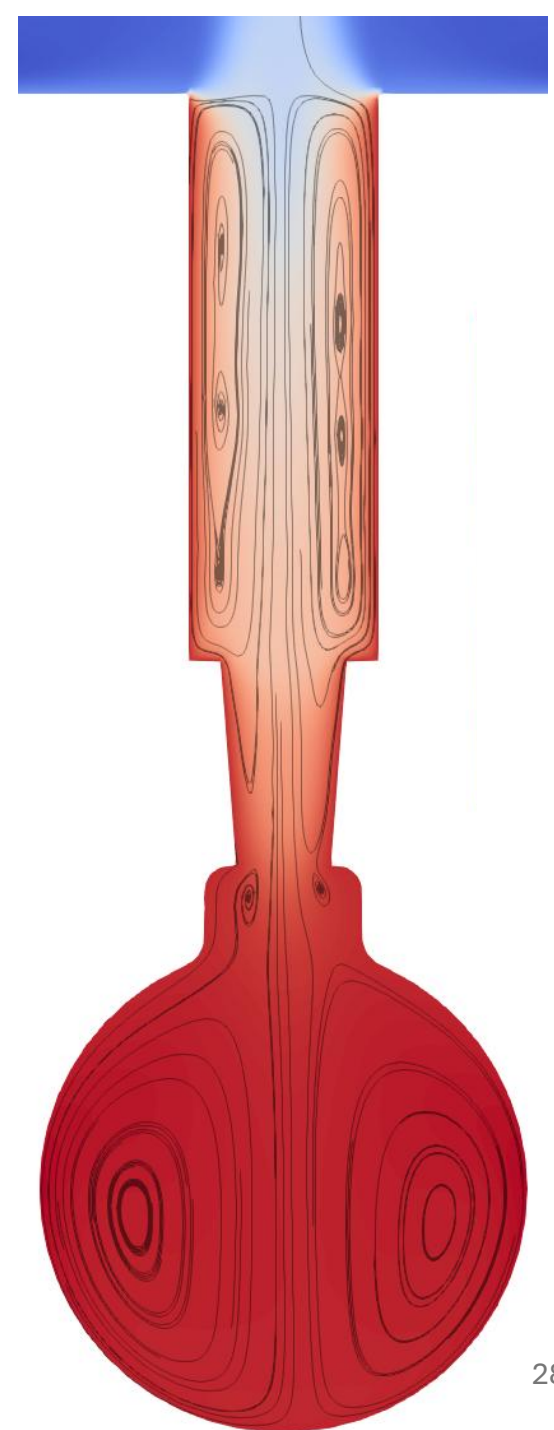
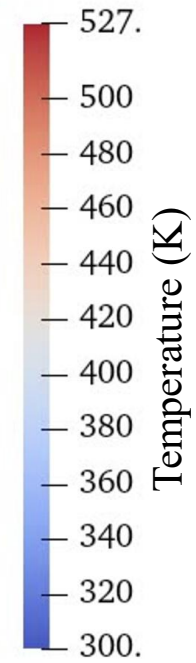
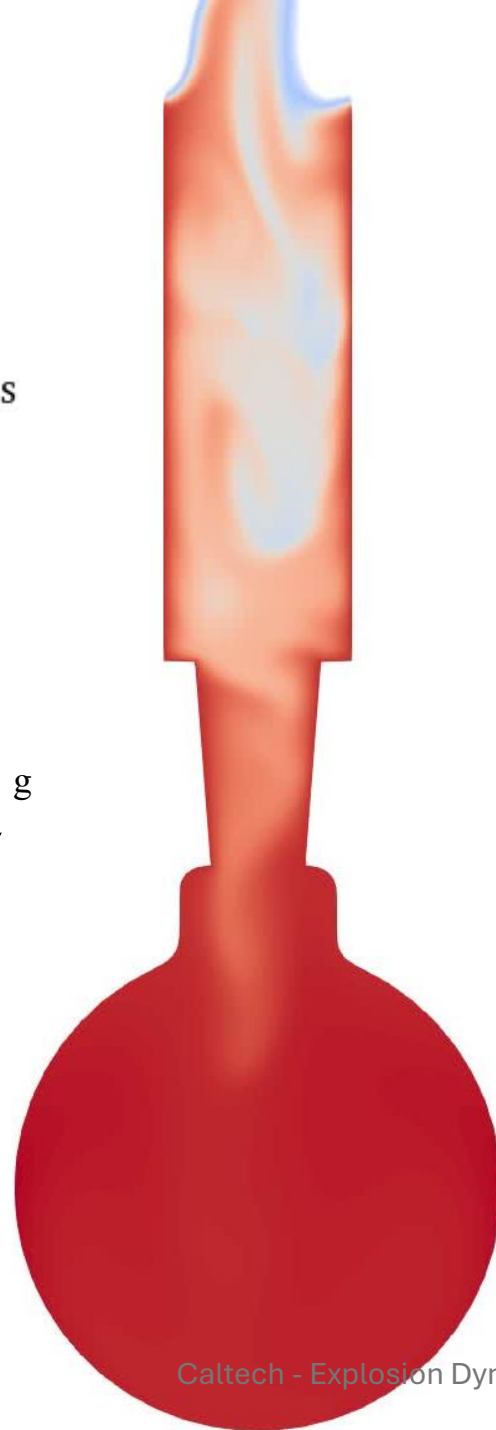
$$\tau_i \propto e^{E_a/(RT^*)}$$

Mixing Simulation

Davis et al 2025

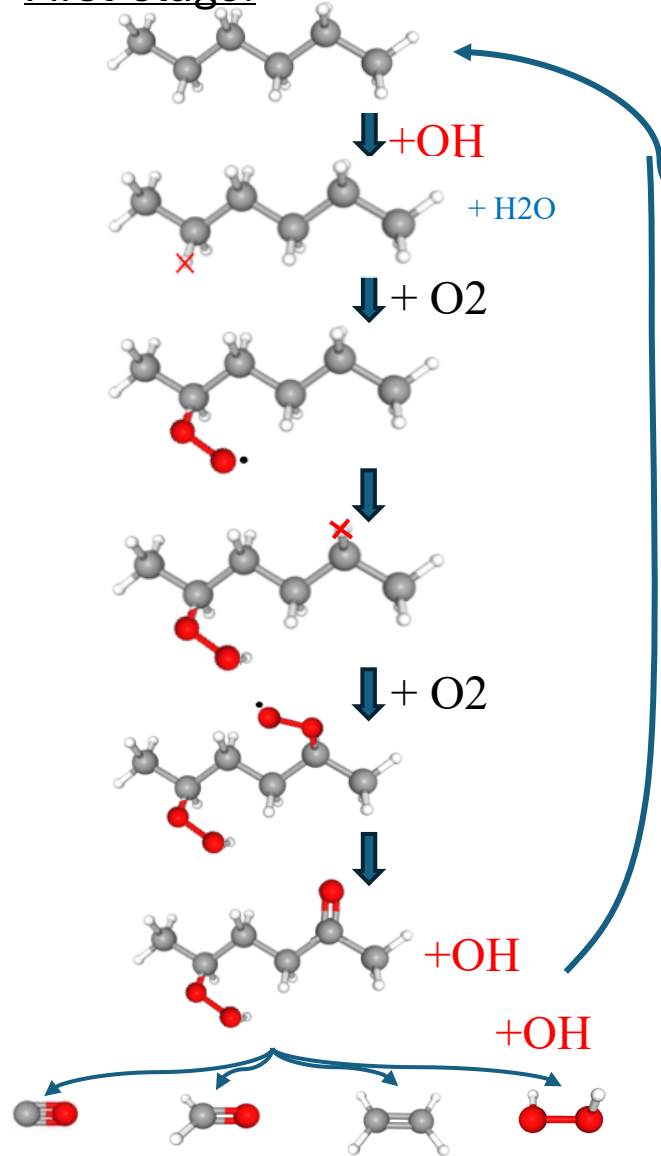


Time: 0 s



Ignition Reaction Pathways

First-stage:



First-stage:

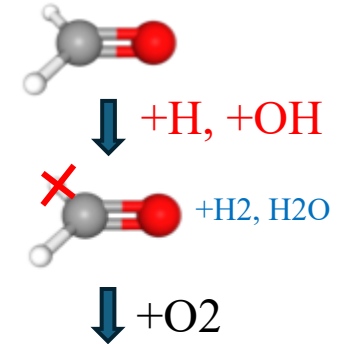
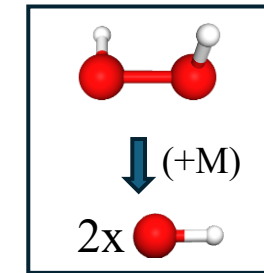
- Formation of larger, oxygenated hydrocarbons that then break apart into stable intermediates: CO, CH₂O, C₂H₄, H₂O₂
- Sequence is exothermic on the aggregate
- Net-positive production of chain carrier, OH

Second-stage:

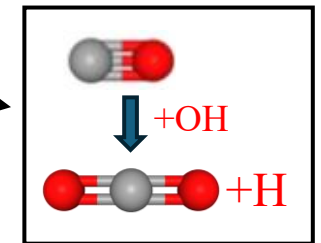
- Generation of OH radicals by breaking H₂O₂ from the first stage
- OH oxidize CH₂O to form more CO
- Primary heat release converting CO → CO₂
 - Consistent with high temperature pathways described in other studies [1–2]
- Secondary heat release due to lack of O₂
 - C₂H₄ → CH₂CHO → CH₂CO → CH₃
 - Exothermic CH₃ + H(+M) → CH₄(+M)
 - Feedback to produce H₂ products

Second-stage:

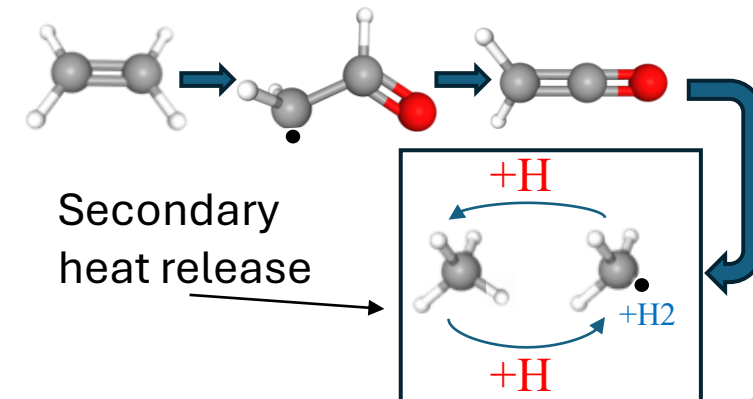
OH generation



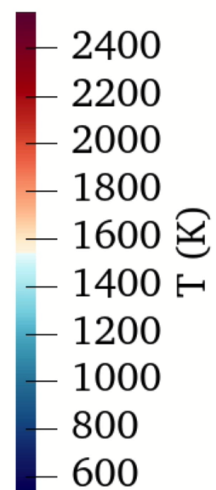
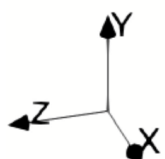
Primary heat release



Secondary heat release (fuel rich):



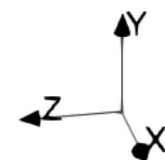
Time: 0 s



Time: 16.33885 s

Davis 2025

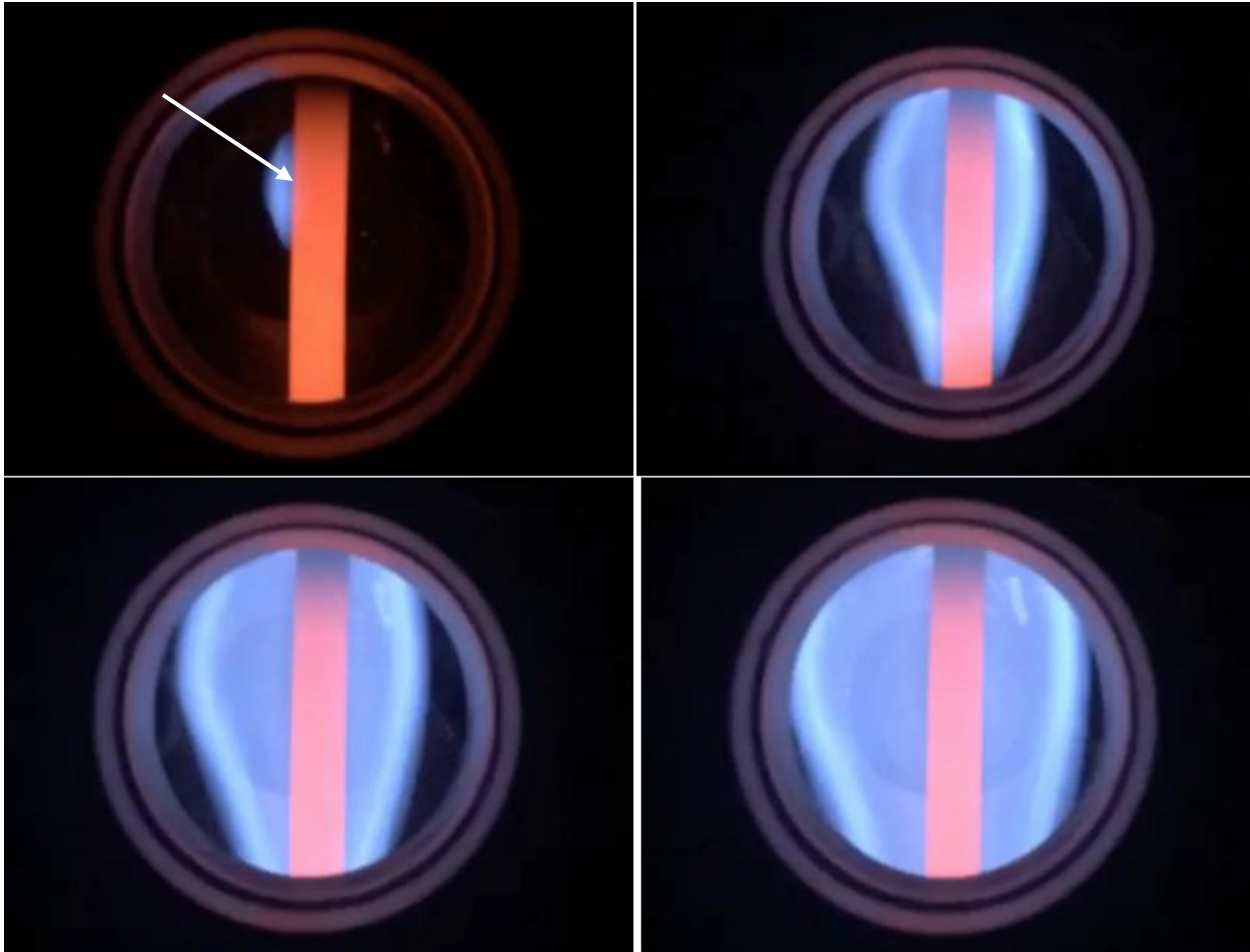
$T = 1200$ K
isosurface



Hot Surface Ignition

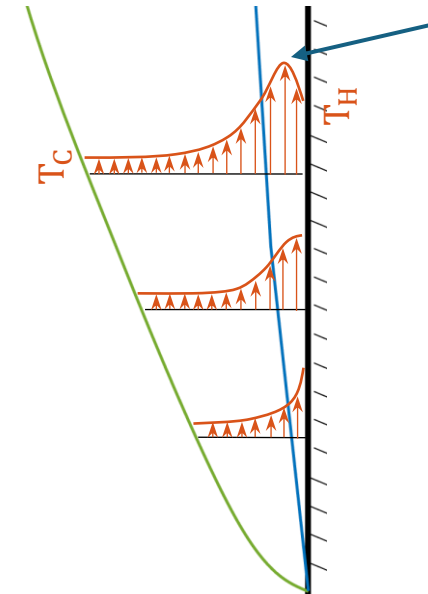
Hot surfaces in cold flammable atmospheres require completely different approach to analysis than self-heating (autoignition) testing

Thermal Ignition in Flammable Gases



S. Jones, 2021, C. Martin 2023

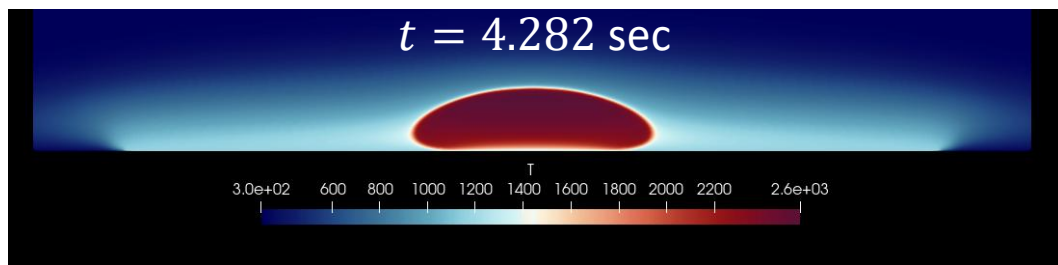
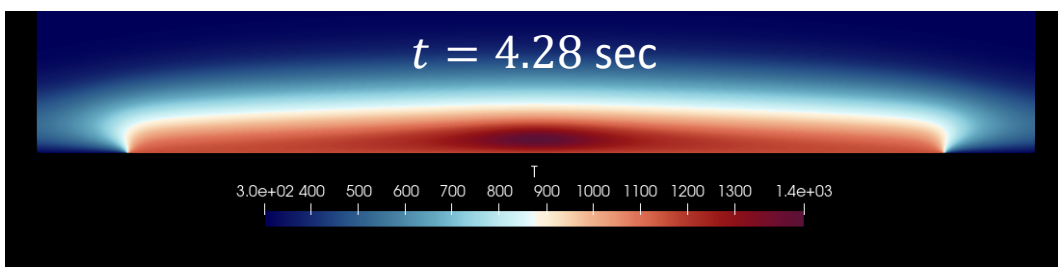
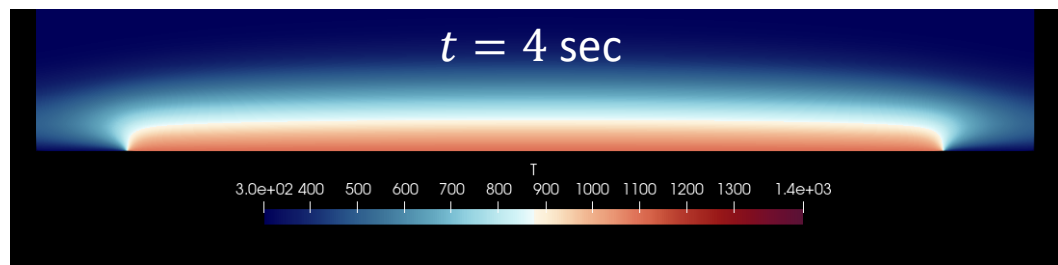
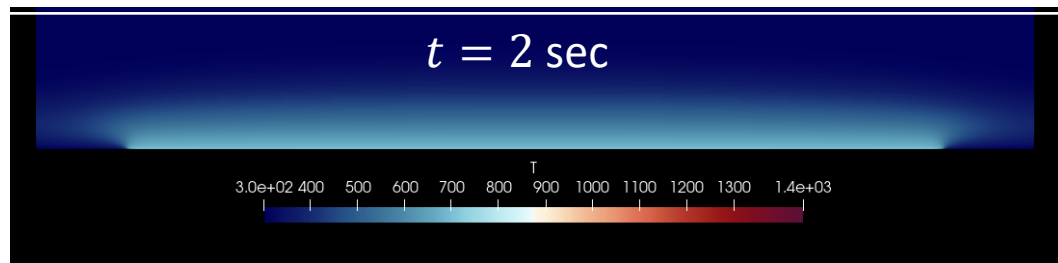
- Momentum, thermal, and species boundary layer near hot surface
- Buoyancy driven flow
- Transport of energy and species in wall normal direction, convection along wall
- Chemical reaction and energy release near wall drives localized self-heating
- Ignition event spreads as flame



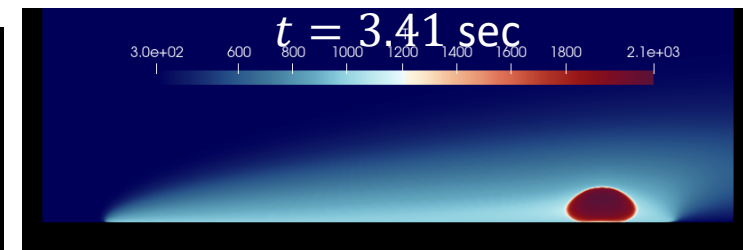
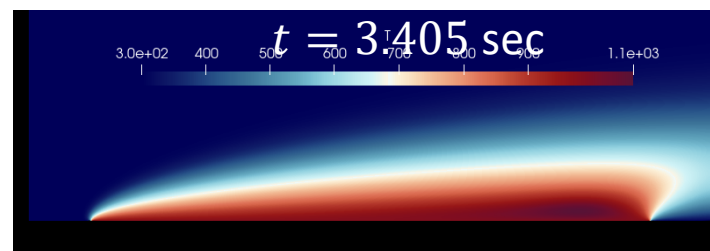
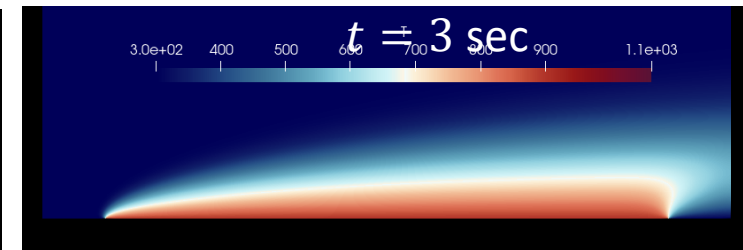
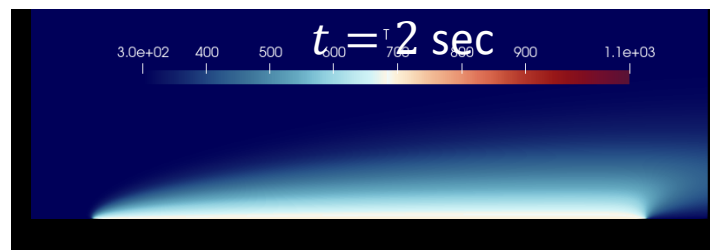
Hot surfaces and cold flammable gas?

- Isolated hot surface with cool flammable atmosphere, no recirculation or significant heating of atmosphere outside thermal layer near surface
- Experiments
 - Diesel engine glow plugs
 - Stainless steel cylinders
 - Small 10 mm
 - Large 100-1000 mm
 - Titanium and ceramic spheres (2-6 mm)
 - Heated wires
 - Hot spots ($< 10 \text{ mm}^2$) – laser and electrical heating
- Numerical simulation
 - Reactive, Navier-Stokes, variable density, low-Mach-number, finite-volume
 - Detailed chemical kinetics for range of fuels including both high and low temperature pathways

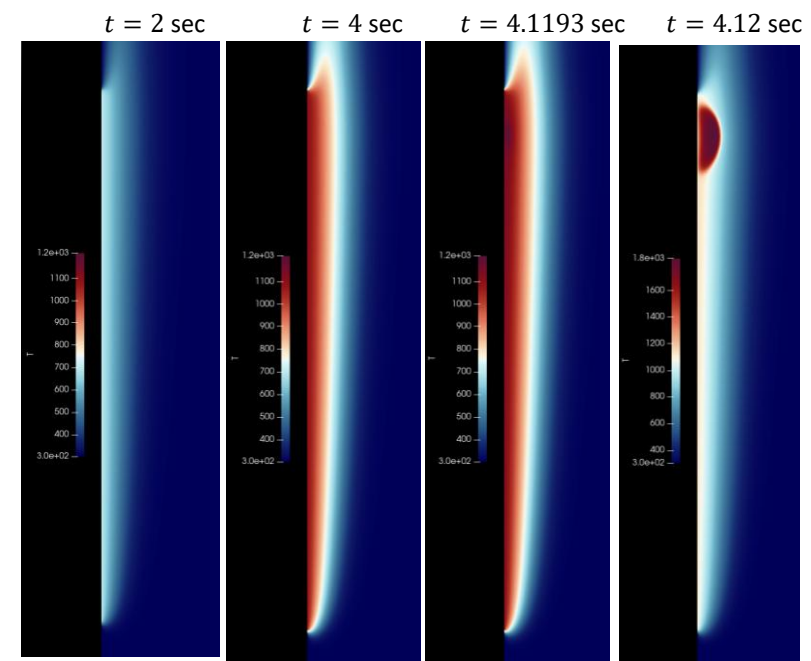
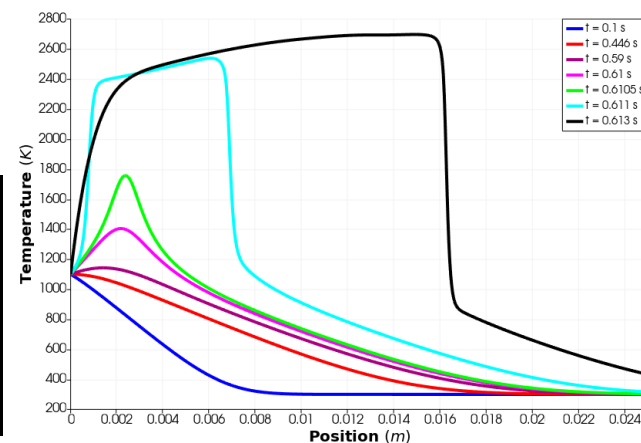
Stagnation Point



Forced Convection

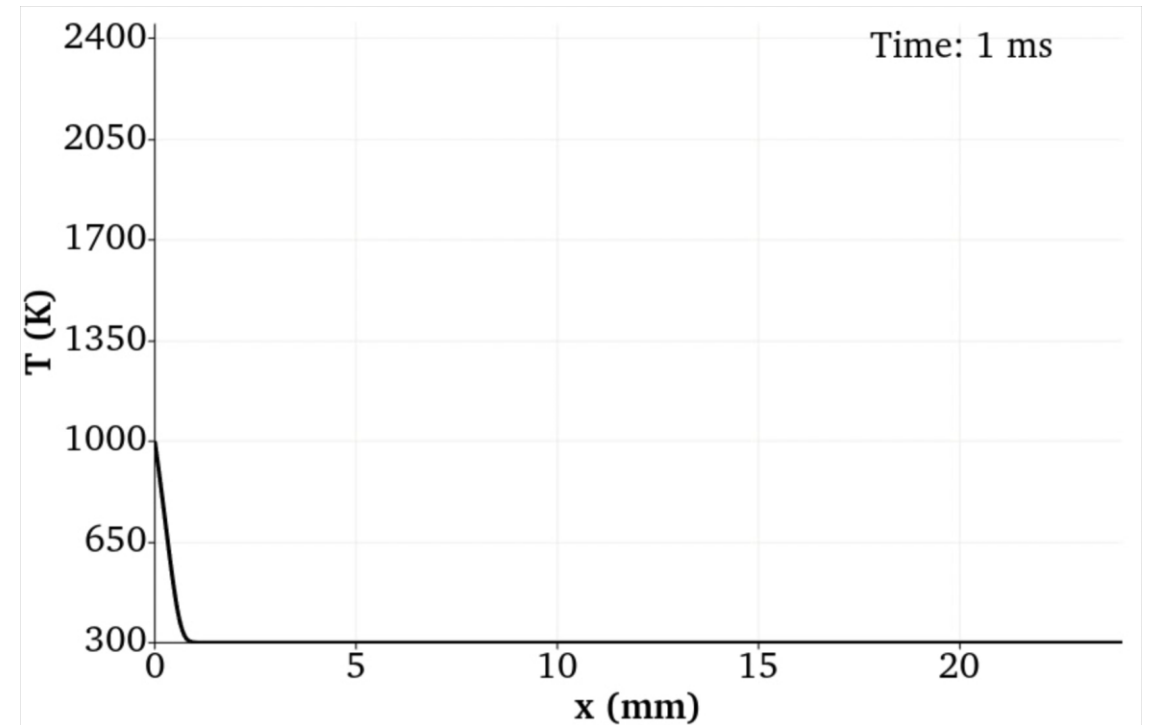
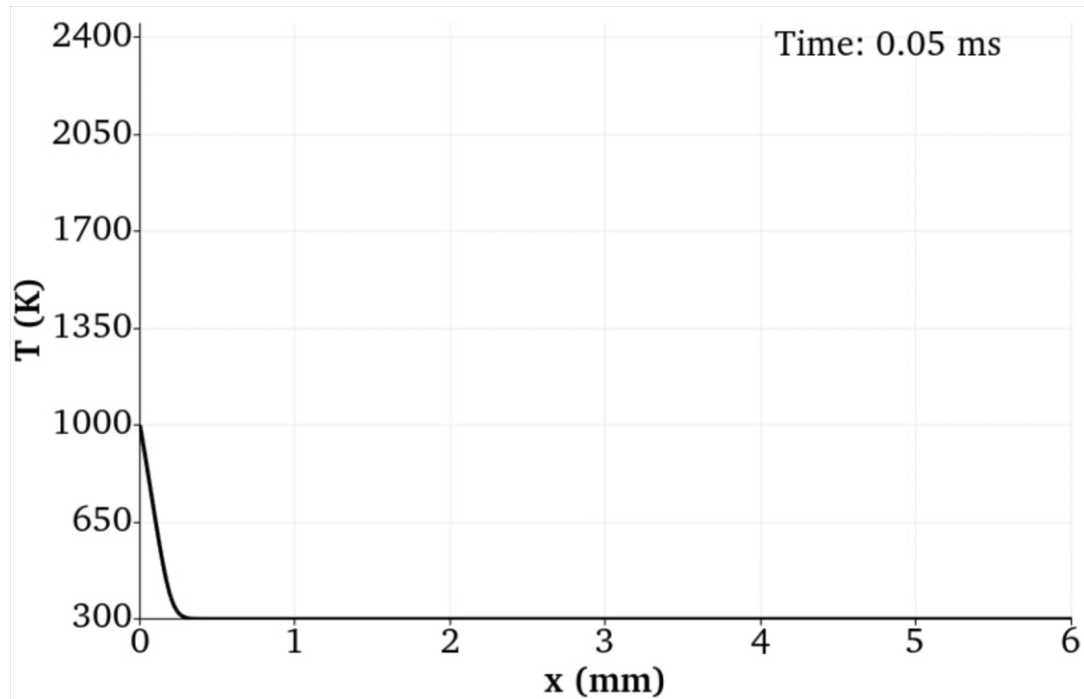


1D Diffusing Thermal Layer



Natural Convection

Common Feature – Ignition in a Thermal Layer



Ratio of Length Scales Determines Outcome

Heat transfer length scale:

$$\Lambda = \frac{T_H}{\partial T / \partial y \big|_{c, y^- \rightarrow \infty}}$$

- **Solution** - Approximate the critical gradient immediately at the hot wall using chemically frozen flow

$$\Lambda \approx \frac{T_H}{\partial T / \partial y \big|_{w, \text{frozen}}}$$

Chemical length scale:

$$\ell_k = \left[\frac{1}{2} \frac{E_a}{RT_H} \frac{c_p T_H}{q_c} \frac{\kappa}{A} \exp \left(\frac{E_a}{RT_H} \right) \right]^{\frac{1}{2}}$$

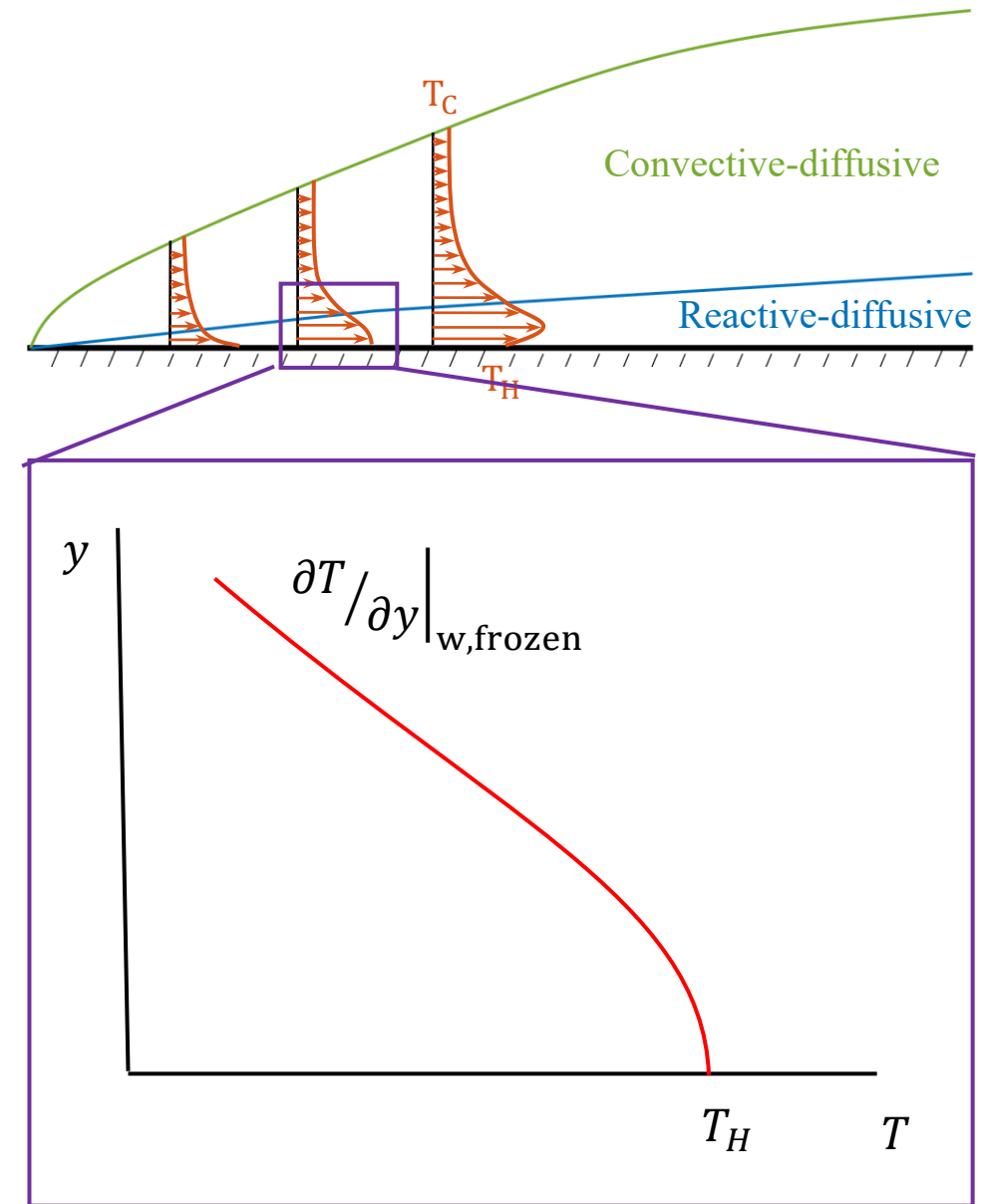
- **Solution** - Adiabatic thermal explosion theory

$$\rho c_p \frac{dT}{dt} = q_c \rho A (1 - Y) \exp \left(-\frac{E_a}{RT} \right)$$

Asymptotic time-to-explosion:

$$t^* = \frac{RT_0}{E_a} \frac{c_p T_0}{q_c} \frac{1}{A} \exp \left(\frac{E_a}{RT_0} \right)$$

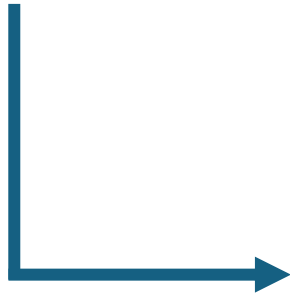
$$\ell_k = \Theta \cdot \left[\frac{\kappa t^*}{2} \right]^{\frac{1}{2}} \quad \Theta = \frac{E_a}{RT_H}$$



Procedure for application to simulation data

1. Determine the ignition temperature from a reacting simulation

$$T_{IGN}$$



2. Use equivalent *chemically-frozen simulation* to compute wall normal temperature gradient at ignition temperature to formulate the characteristic heat transfer length scale:

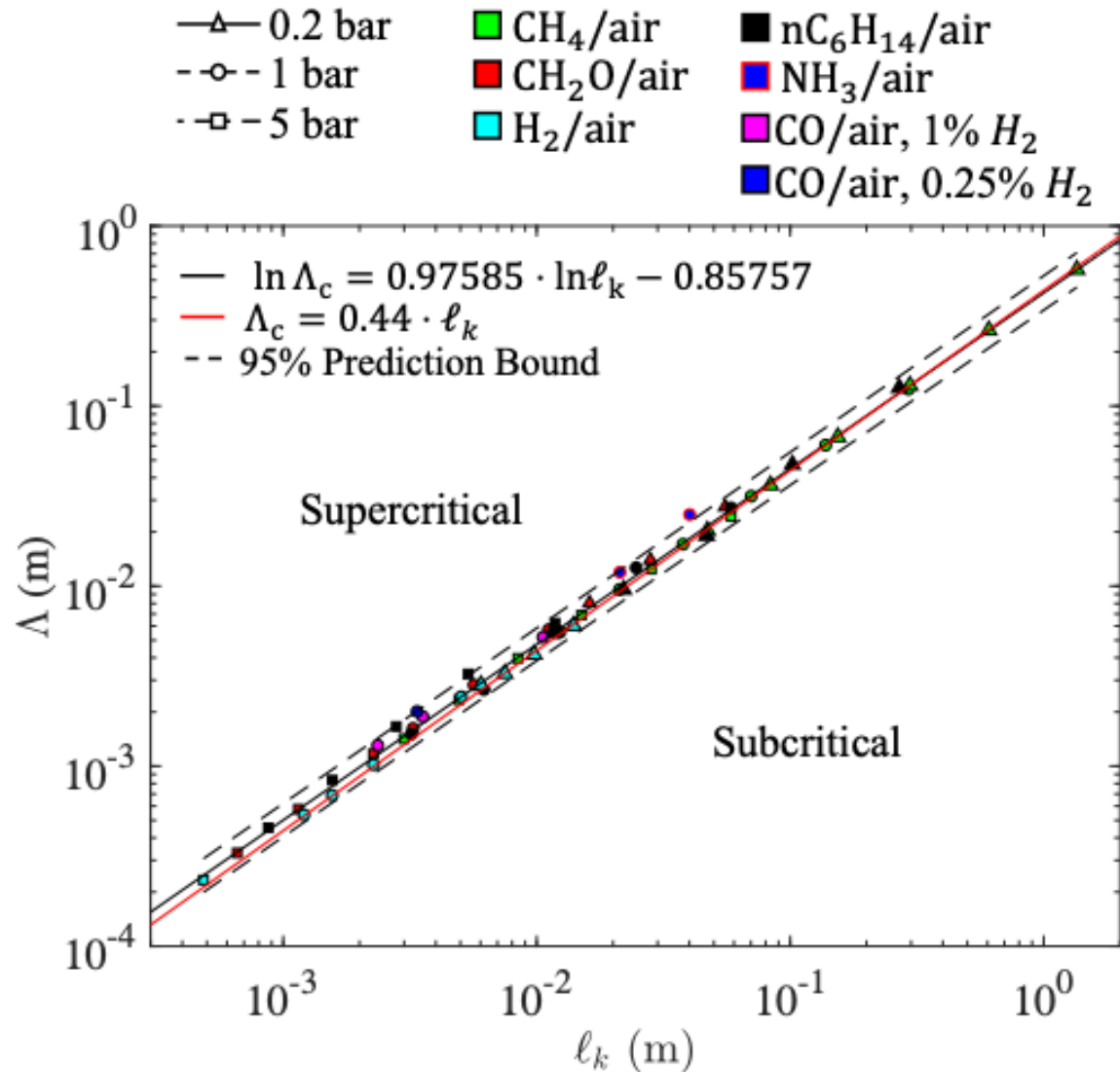
$$\Lambda \approx \frac{T_{IGN}}{\left| \partial T / \partial y \right|_{\text{wall, frozen}}}$$



3. Simulate 0D adiabatic thermal explosion to formulate the characteristic chemical length scale:

$$\ell_k = \Theta \cdot \left[\frac{\kappa t^*}{2} \right]^{\frac{1}{2}}$$

The line of criticality

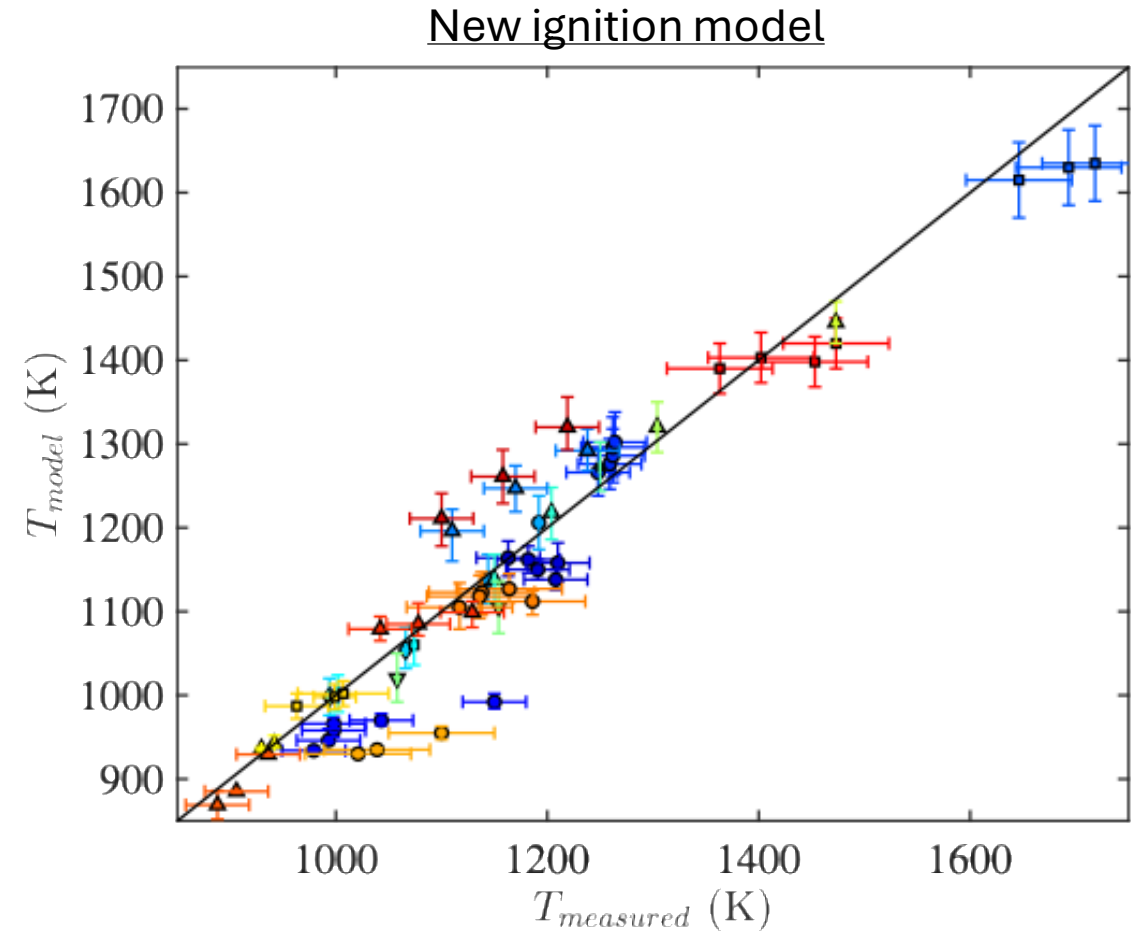
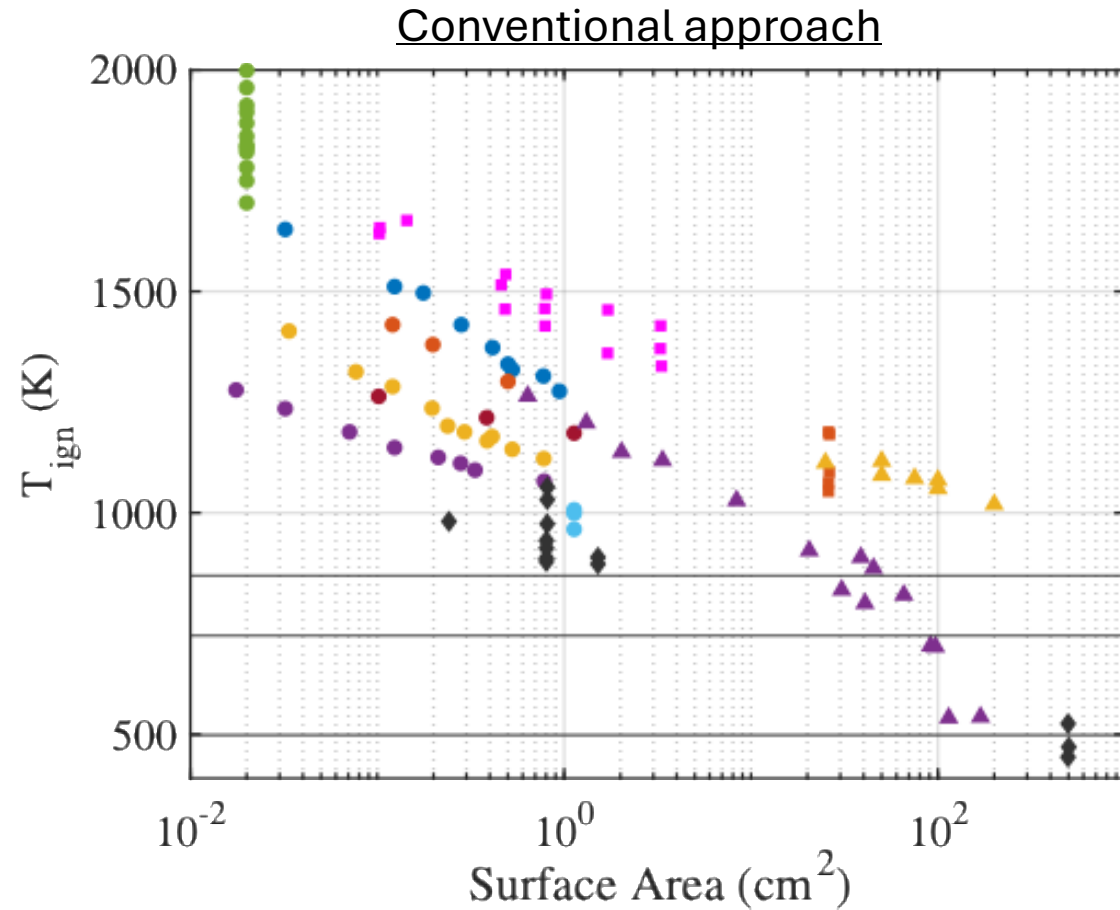


- Simulation data collapse to a single line of criticality over **four orders of magnitude**
- The ratio defines a critical Damköhler number for hot surface ignition problems

$$Da_c = \Lambda_c / \ell_k$$
- Slight nonlinearity suggest additional relevant scaling is not captured by the model
 - Near wall convection or unsteadiness
 - Depletion of fuel/oxidizer
 - Production of intermediates before ignition
- The theory is correct!
 (At least for this one-dimensional system)

Question: does this model work for predicting experimental ignition thresholds in real systems?

Validation for all configurations

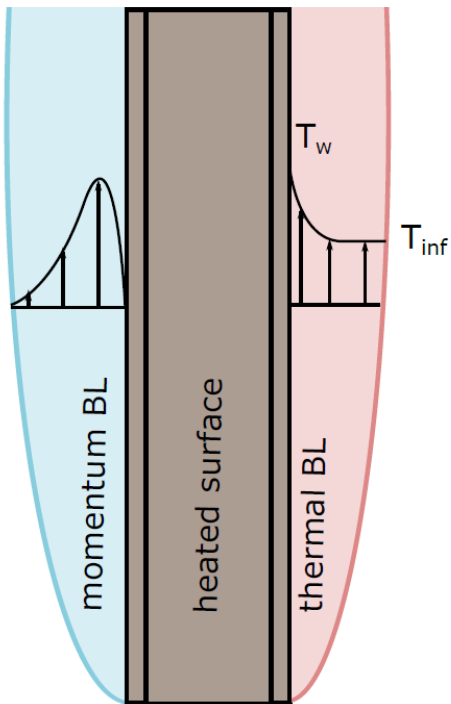


Unification of hot surface ignition theory with detailed simulation and experiments

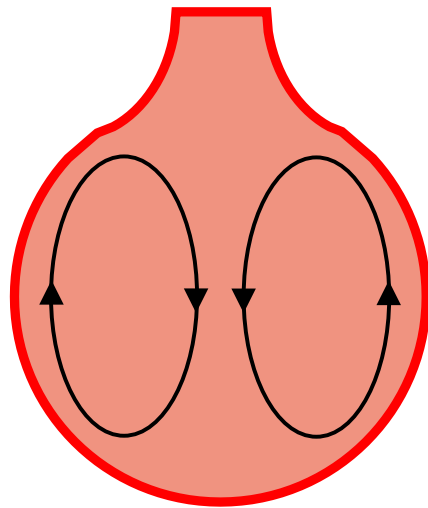
Can be applied to complex engineering system using standard heat transfer and 0D chemical models

Hot Surface Ignition vs. Autoignition

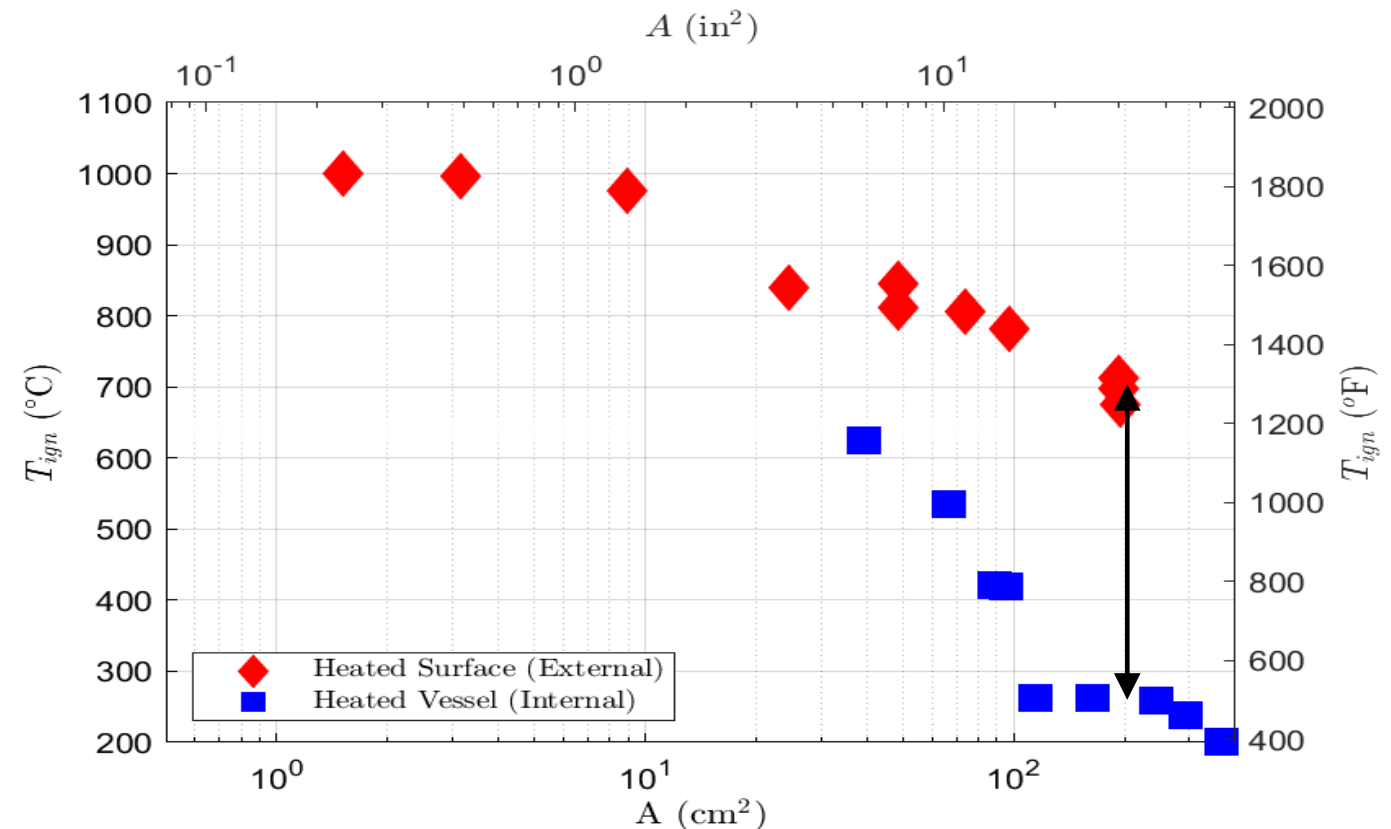
Unconfined flow, cold atmosphere external to heated surface



Confined flow, hot atmosphere internal to heated surface



Ignition threshold temperature **450°C (700°F) higher** for unconfined vs confined flammable atmospheres at largest sizes. Ignition threshold temperature **increases significantly with decreasing size.**



Acknowledgements

- **Caltech studies supported by the Boeing Company through a Strategic Research and Development Relationship Agreement CT-BA-GTA-1.**
- Recent researchers contributing (2019- present)
 - Dr. Charline Fouchier
 - Dr. Branson Davis
 - Dr. Conor Martin
 - Dr. Silken Jones
 - Dr. Remy Mevel
 - Mr. Colin Gary
 - Ms. Hannah Ramsperger
 - Mr. Lucas Favretto
 - Ms. Isabella Pagano
 - Mr. Noel Esparza-Duran

Selected References from <https://shepherd.caltech.edu/EDL/>

- P. A. Boettcher, R. Mével, V. Thomas, and J. E. Shepherd. The effect of heating rates on low temperature hexane air combustion. *Fuel*, 96:392–403, 2012.
- P.A. Boettcher, S. K. Menon, B.L. Ventura, G. Blanquart, and J. E. Shepherd. Cyclic flame propagation in premixed combustion. *Journal of Fluid Mechanics*, 735:176–202, 2013.
- Boeck, L., M. Meijers, A. Kink, R. Mével, and J.E. Shepherd. “Ignition of Fuel-Air Mixtures from a Hot Circular Cylinder.” *Combustion and Flame* 185 (2017): 265–77.
- Coronel, S., J. Melguizo-Gavilanes, R. Mével, and J.E. Shepherd. “Experimental and Numerical Study on Moving Hot Particle Ignition.” *Combustion and Flame* 192 (2018): 495–506.
- Mével, R., F. Rostand, D. Lamrié, L. Breyton, and J.E. Shepherd. “Oxidation of N-Hexane in the Vicinity of the Auto-Ignition Temperature.” *Fuel* 236 (2019): 373–81.
- L.R. Boeck, J. Melguizo-Gavilanes, and J.E. Shepherd. Hot surface ignition dynamics in premixed hydrogen-air near the lean flammability limit. *Combustion and Flame*, 210:467–478, 2019.
- Jones, S M, and J E Shepherd. “Thermal Ignition by Vertical Cylinders.” *Combustion and Flame* 232 (2021): 111499.
- C. D. Martin and J. E. Shepherd. Low temperature autoignition of Jet A and surrogate jet fuel. *Journal of Loss Prevention in the Process Industries*, 71:104454, July 2021.
- B. Davis, C. Fouchier, and J. E. Shepherd. Fluid motion and heat transfer in an ASTM E659 apparatus. *Journal of Loss Prevention in the Process Industries*, 94:105558, April 2025.
- C. Fouchier and J. E. Shepherd. ASTM E659 standardized test analysis and results for synthetic paraffinic kerosene. *Journal of Loss Prevention in the Process Industries*, 94:105568, April 2025.
- B. Davis, J. E. Shepherd, and R. Mével. Numerical modeling of gaseous n-hexane autoignition in an ASTM-E659 apparatus. *Fuel*, 405:136691, 2026.