

# Ignition and Explosion



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

Joe Shepherd  
California Institute of Technology  
Pasadena, CA USA

UKELG 65<sup>th</sup> Meeting, Sunbury, UK, November 27, 2025

# Roadmap

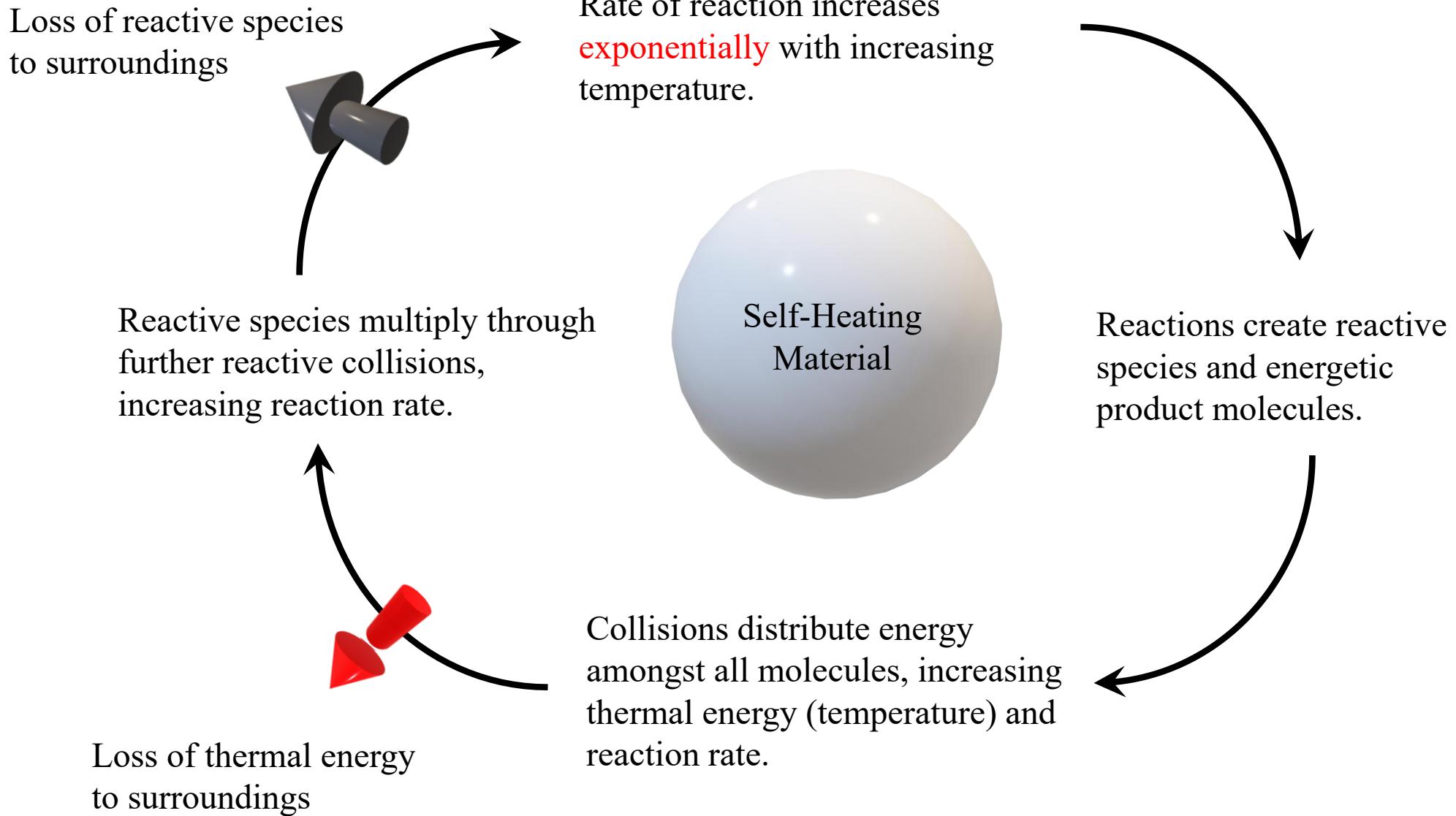
- Context
- History
- Current status of autoignition studies
- Current status of hot surface ignition

# Self-Heating



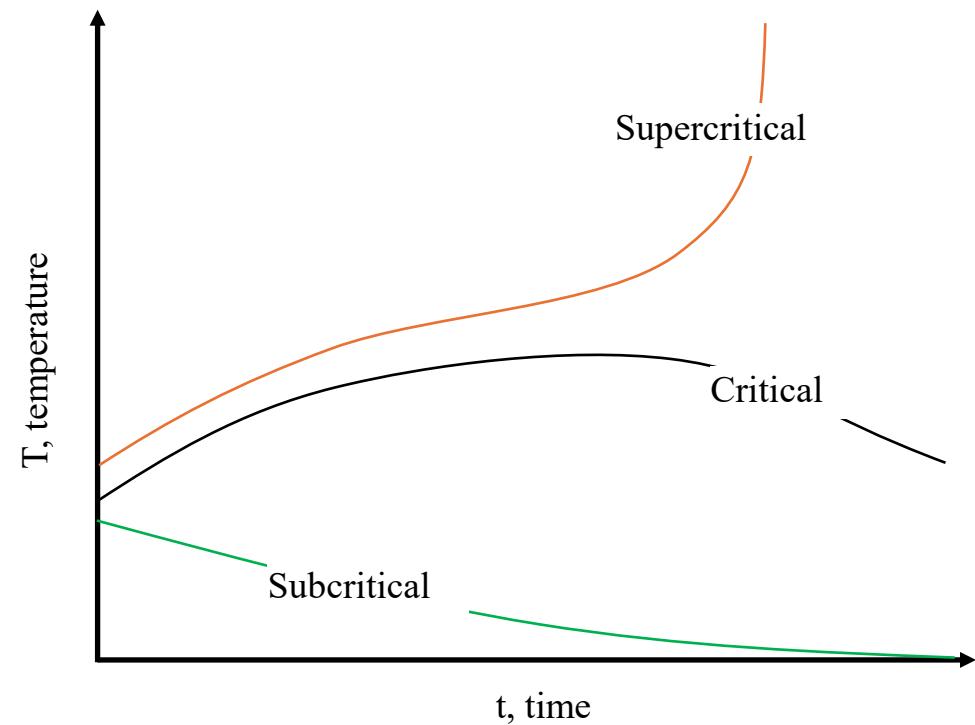
When the grass is cut it should be turned towards the sun and must never be stacked until it is quite dry. If this last precaution is not carefully taken, a kind of vapor will be seen arising from the rick in the morning, and as soon as the sun is up it will ignite to a certainty and so be consumed.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

# Self-heating due to positive feedback cycle

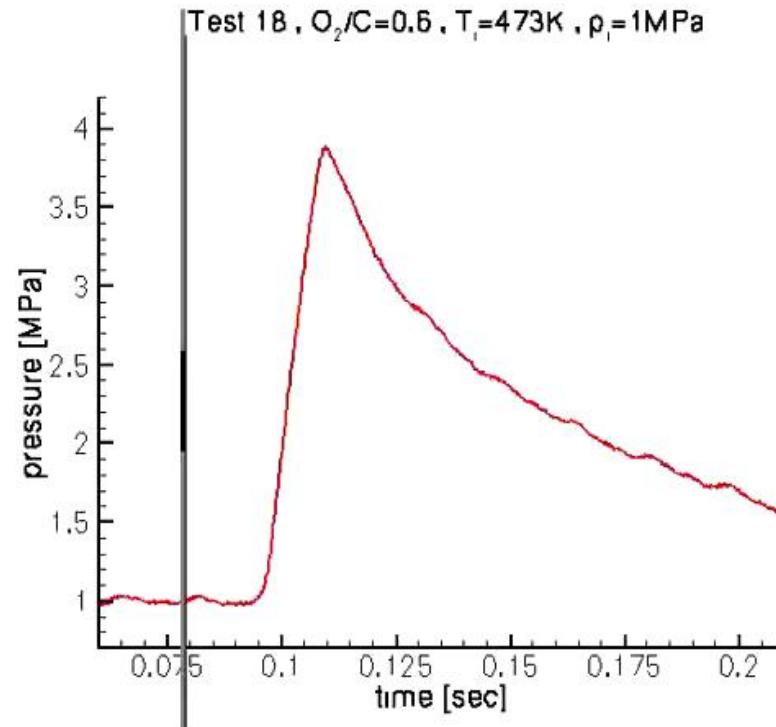
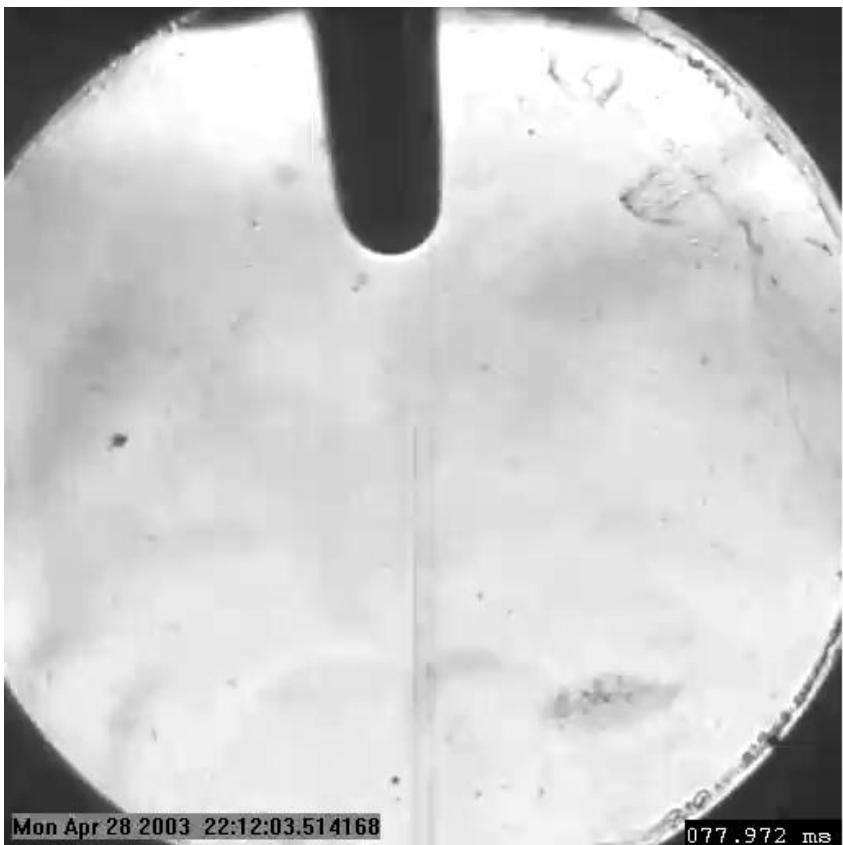


# Critical Conditions

- 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

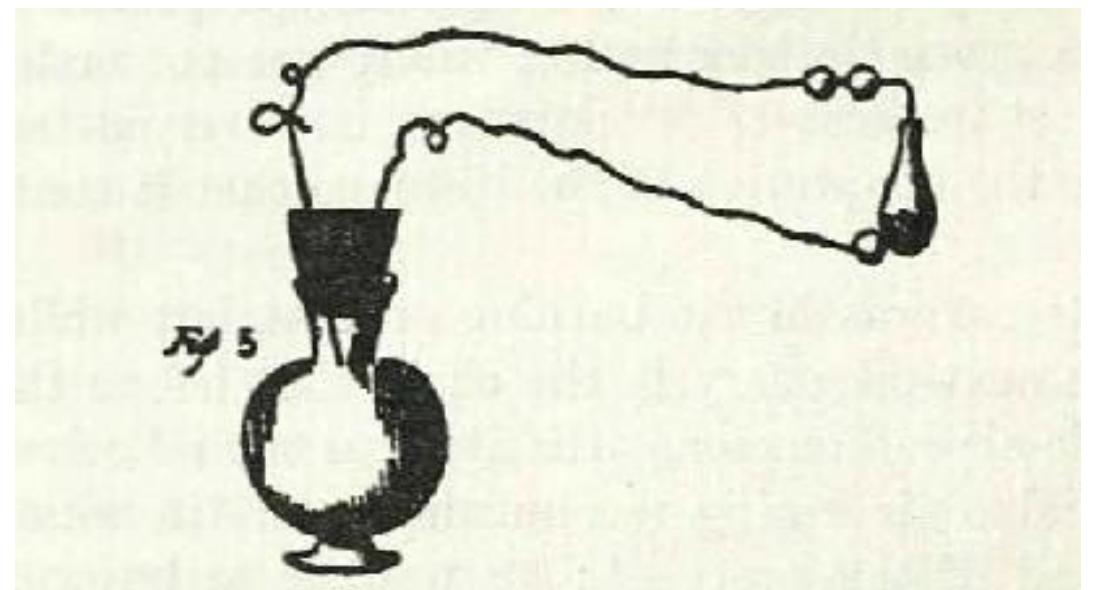
Rapid energy release and species transformation generates pressure and temperature transient.

# 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 led 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.”**

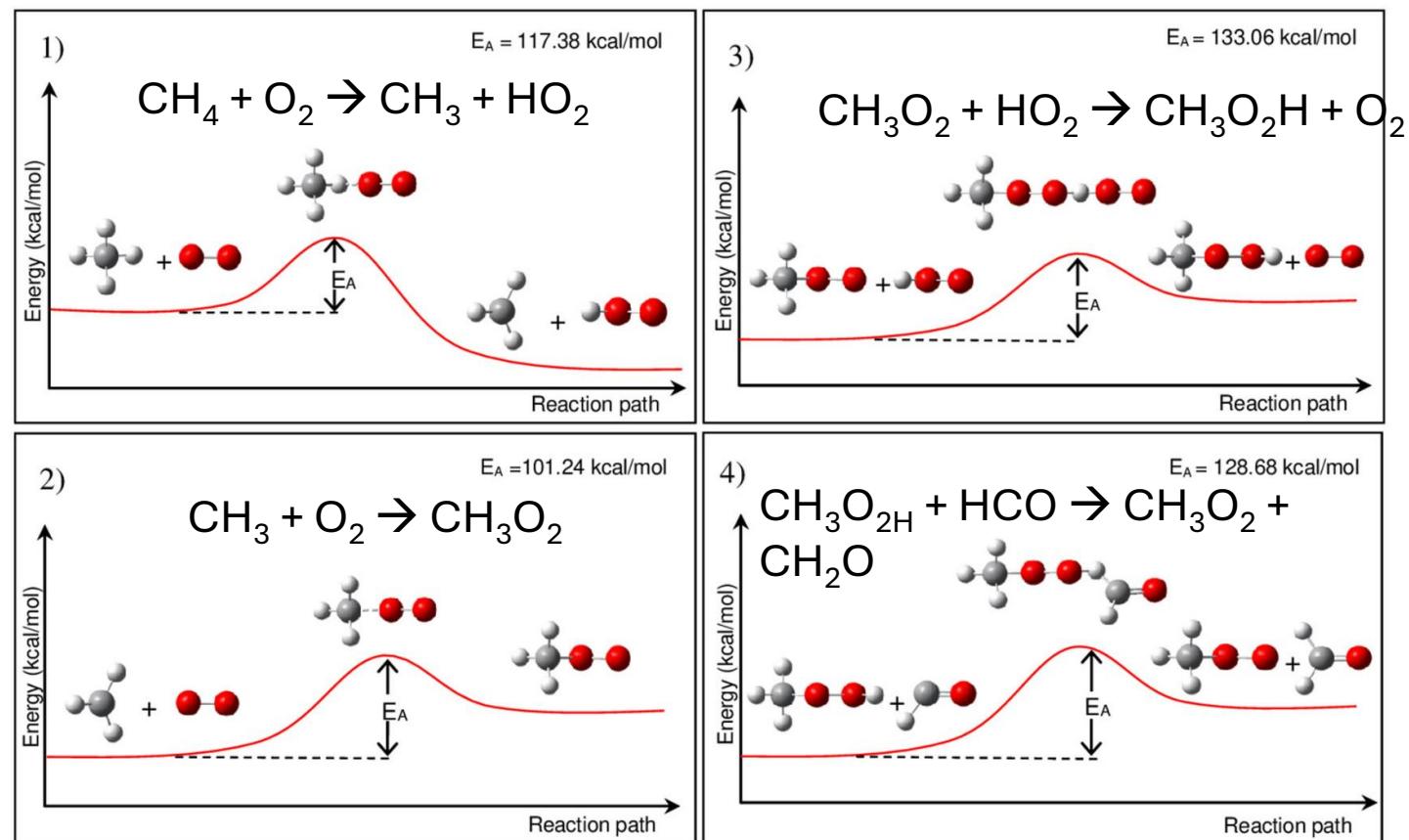
Davy, Phil. Trans., 106, 1-22, 1816.



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 formally excited formaldehyde( $\text{CH}_2\text{O}^*$ ) chemiluminescence.



Pavao et al. 2023

# Robert Bunsen

## GASOMETRY;

COMPRISING THE LEADING

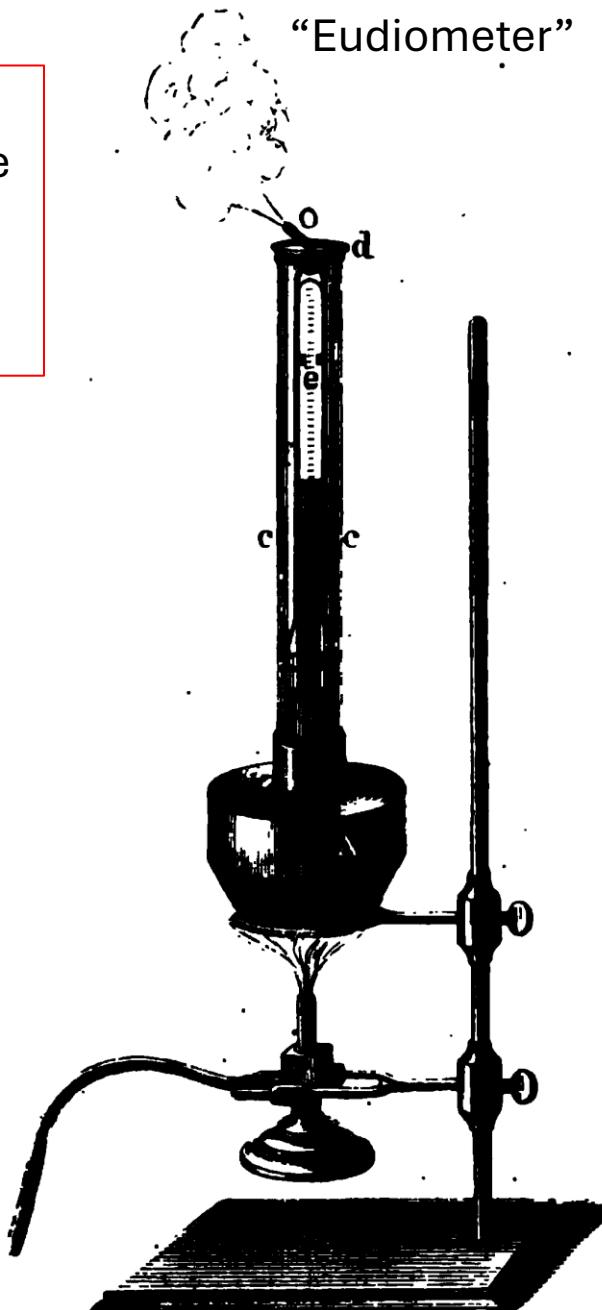
### PHYSICAL AND CHEMICAL PROPERTIES OF GASES.

“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.

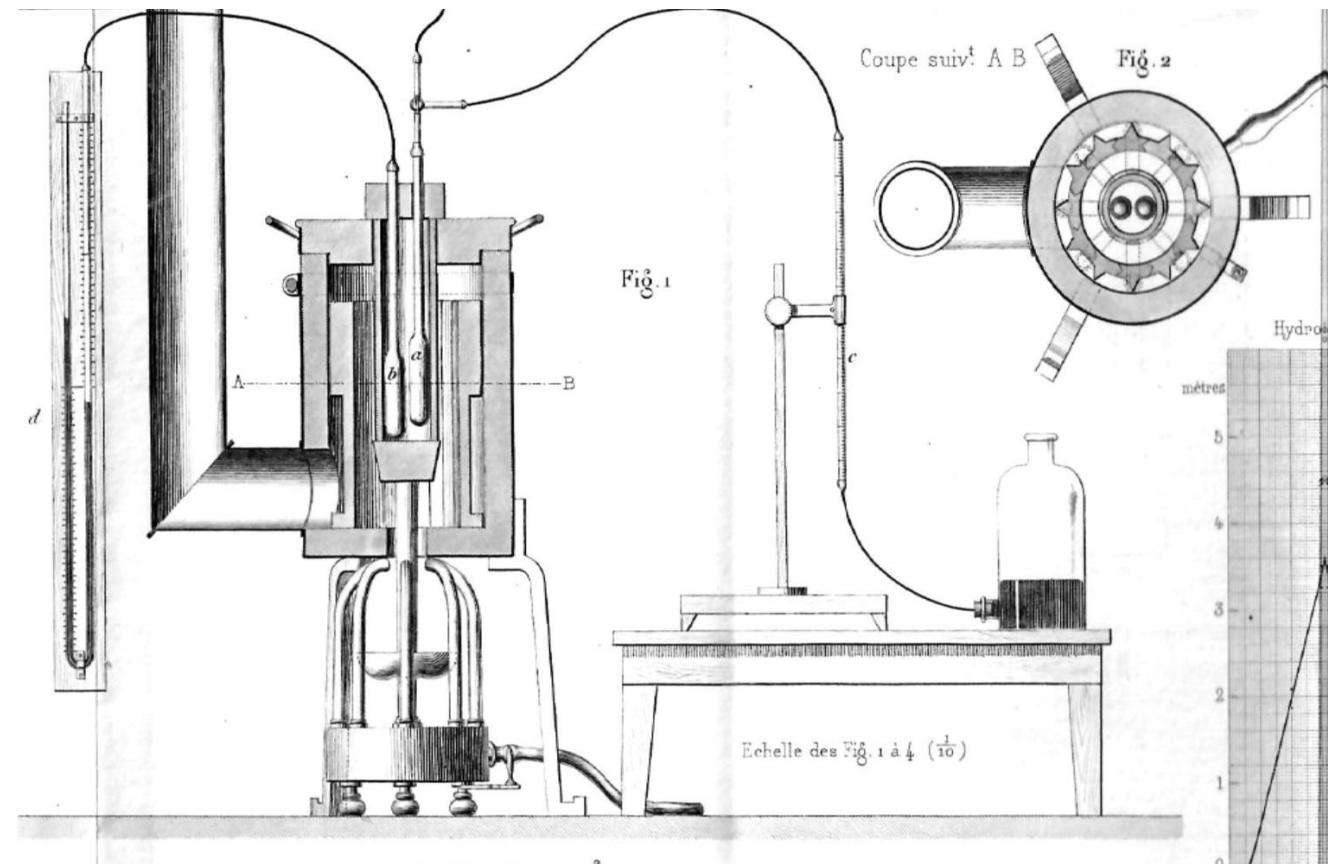
A gas which has thus become non-inflammable regains its combustibility if it is prevented from expanding freely during the ignition, or when its temperature has been increased. The limit of dilution at which this sudden check is given to the inflammability is essentially dependent upon the nature of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



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.

1883

# Mallard and Le Chatelier (1883)

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

CS<sub>2</sub> + 6NO  
20 mm dia

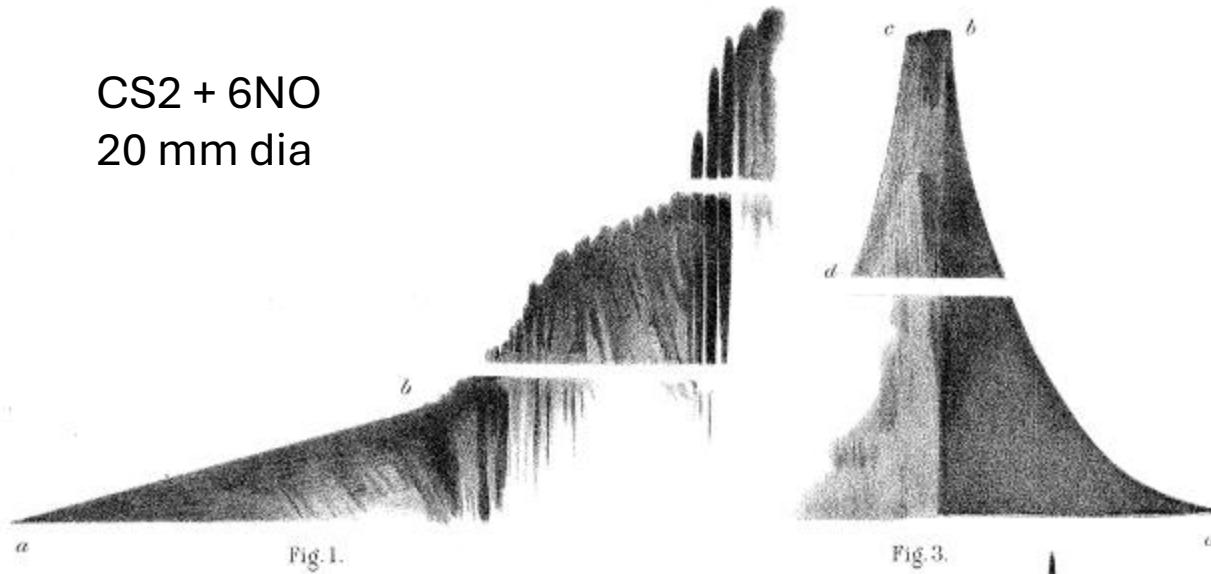


Fig. 1.

Fig. 3.

CS<sub>2</sub> + 6NO  
10 mm dia

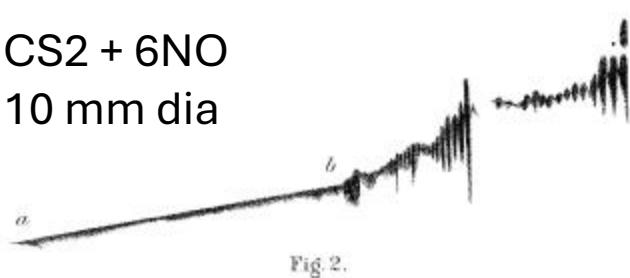


Fig. 2.

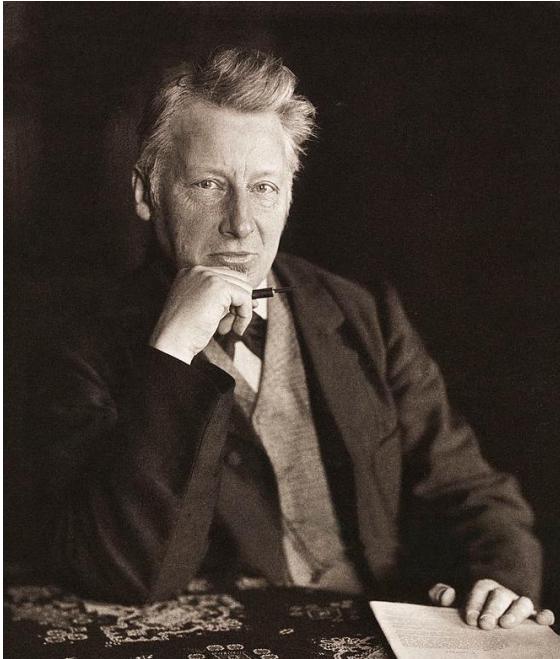
CS<sub>2</sub> + 3O<sub>2</sub>



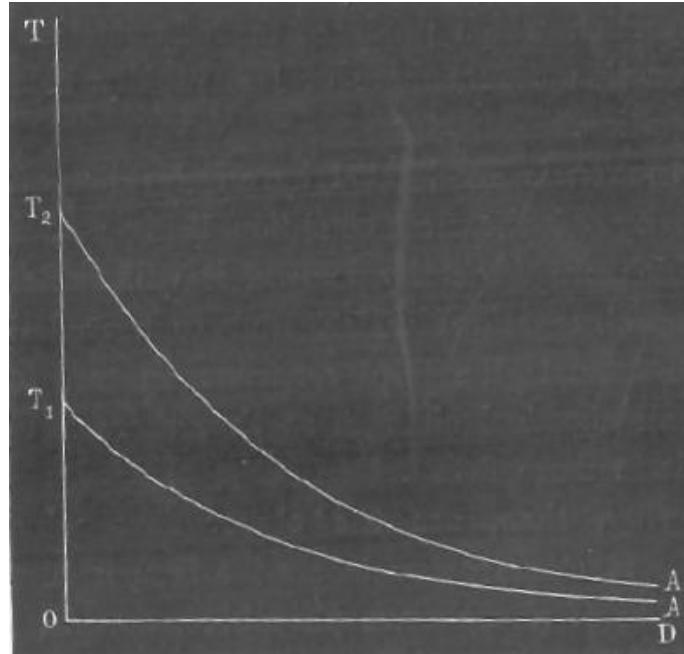
Fig. 4.

*Mallard and Le Chatelier's Photographs.*

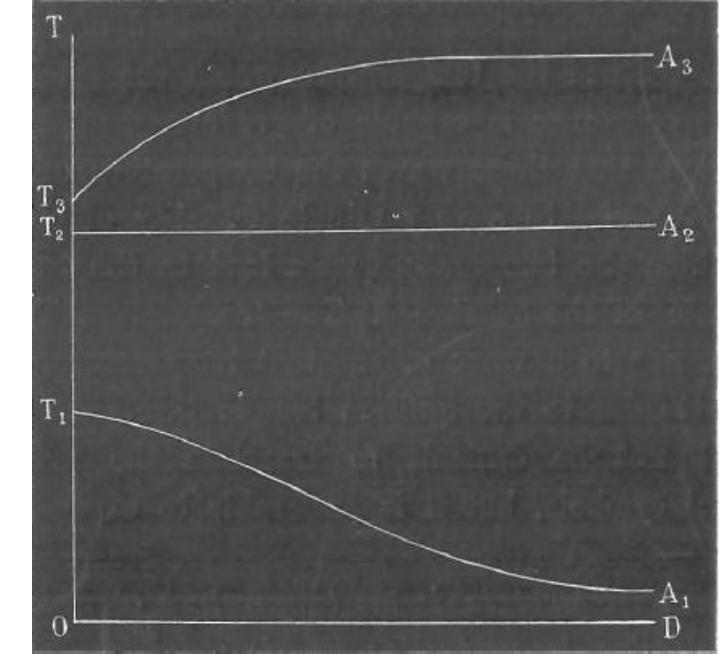
# Jacobus Henricus van 't Hoff *Études de Dynamique chimique*, 1884



Inert gas

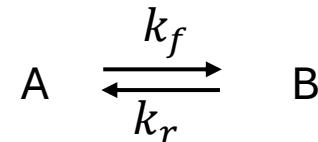


Flammable gas



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:

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

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

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

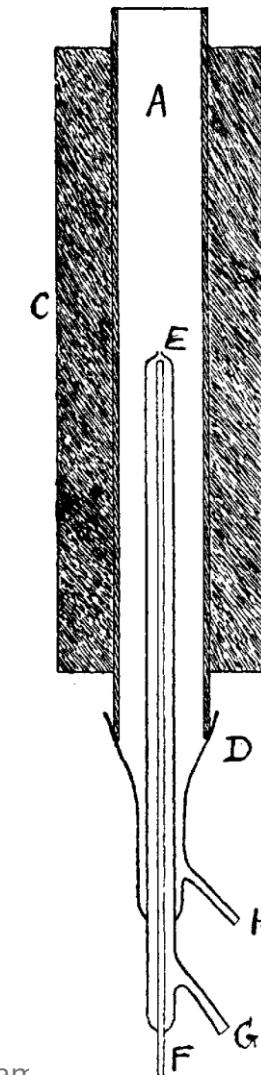
(coal → H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>)



THE GAS MAIN EXPLOSION: SCENE IN CHARLOTTE-STREET, TOTTENHAM-COURT-ROAD, ON MONDAY EVENING.—SEE NEXT PAGE.

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

Harold Baily Dixon (1852-1930)



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

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

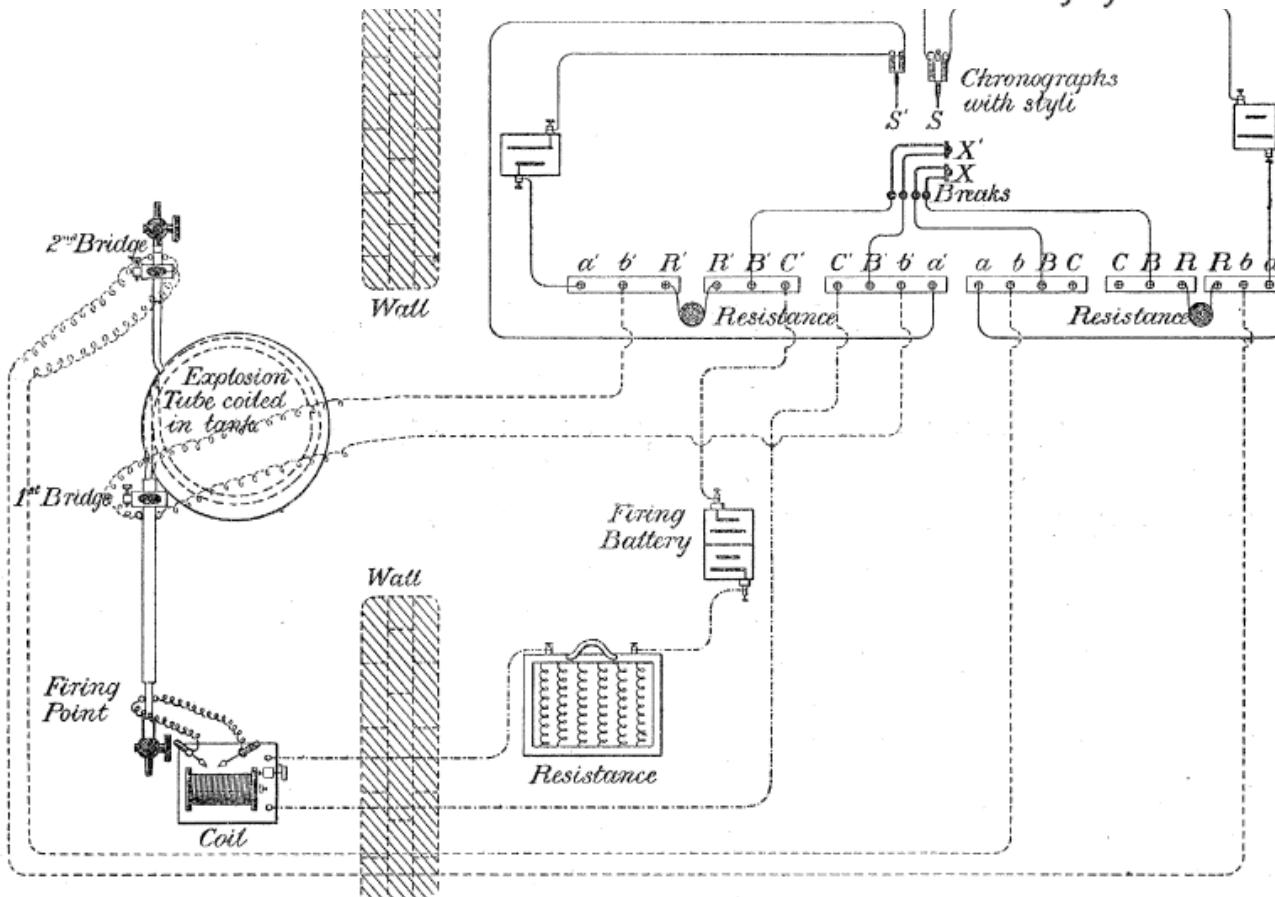
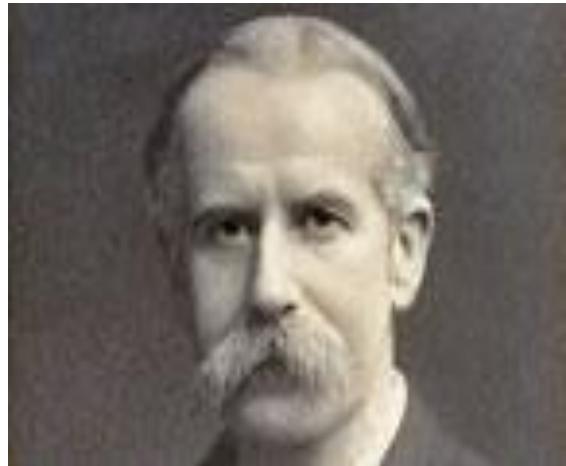
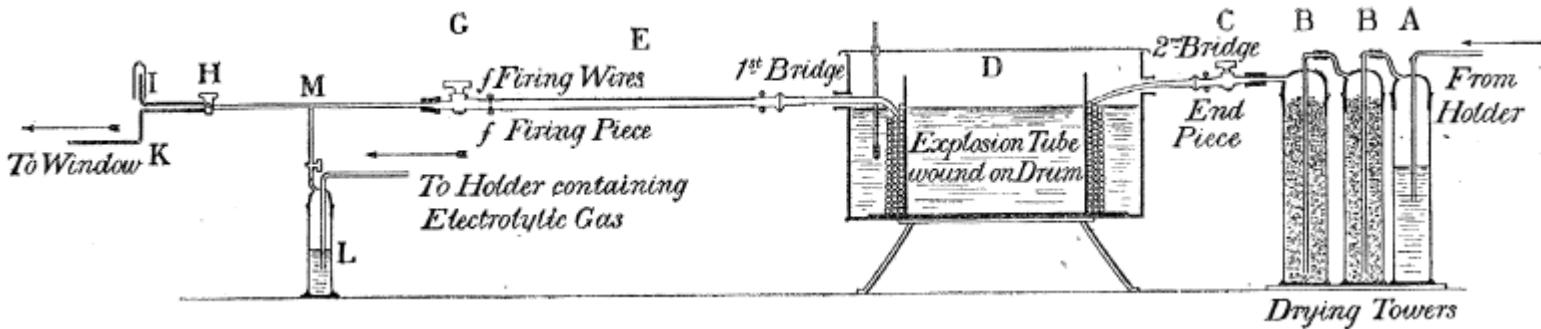
Ignition-  
temperature.

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

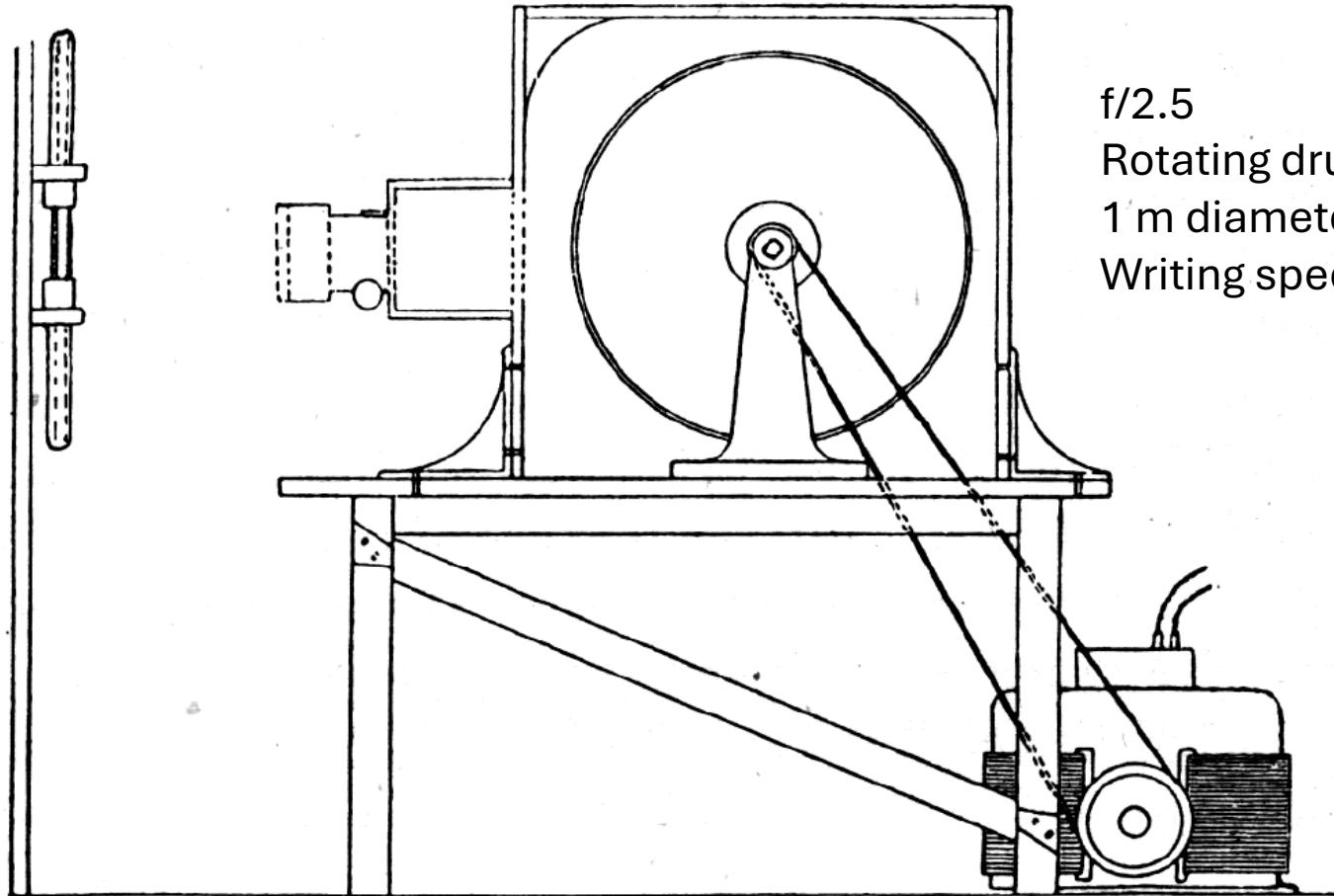
Crackling ignition  
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Moderate explosion  
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" "  
" "  
Loud explosion  
" "

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

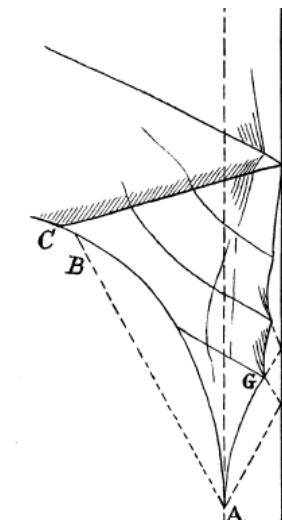
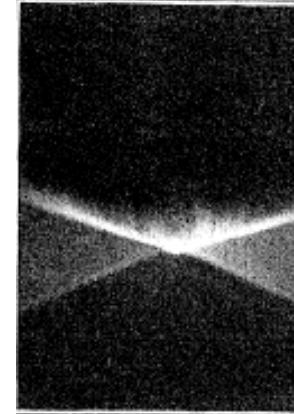


f/2.5  
Rotating drum  
1 m diameter , < 5000 rpm  
Writing speed < 100 m/s

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

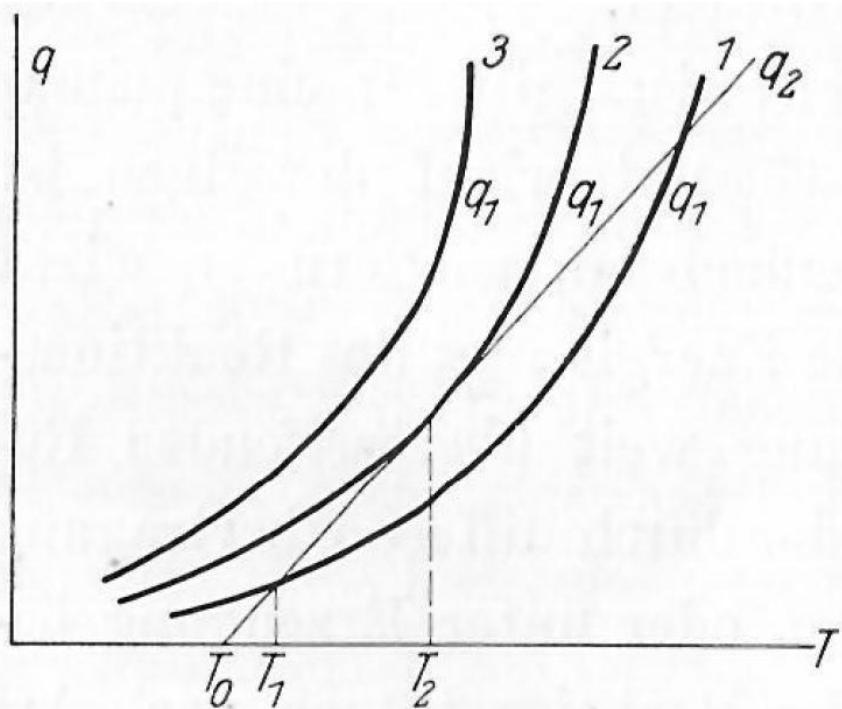
# Dixon 1903

- (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

$$\Delta \zeta \theta = -\delta \cdot e^\theta$$

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

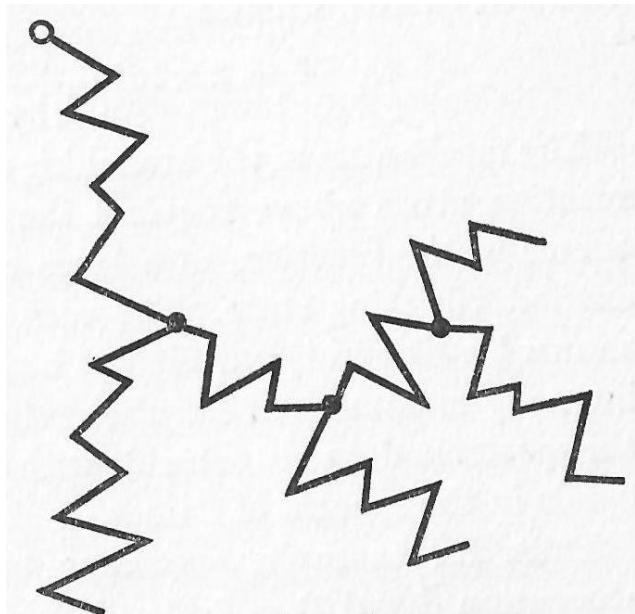
$$\delta = \frac{Q}{\lambda} \cdot \frac{E}{RT^2} \cdot r^2 z e^{-\frac{E}{RT_0}}.$$

“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

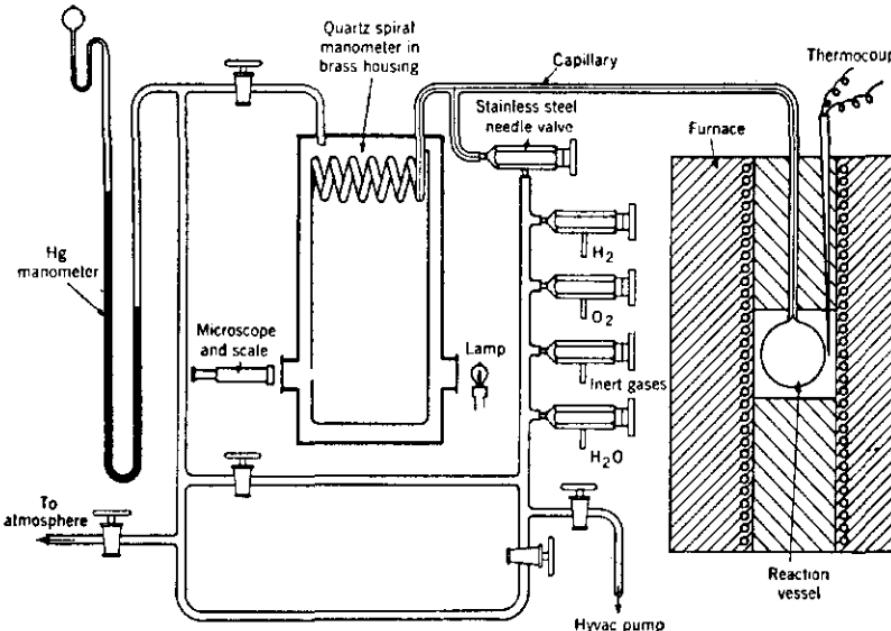
# Chain Reactions

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)



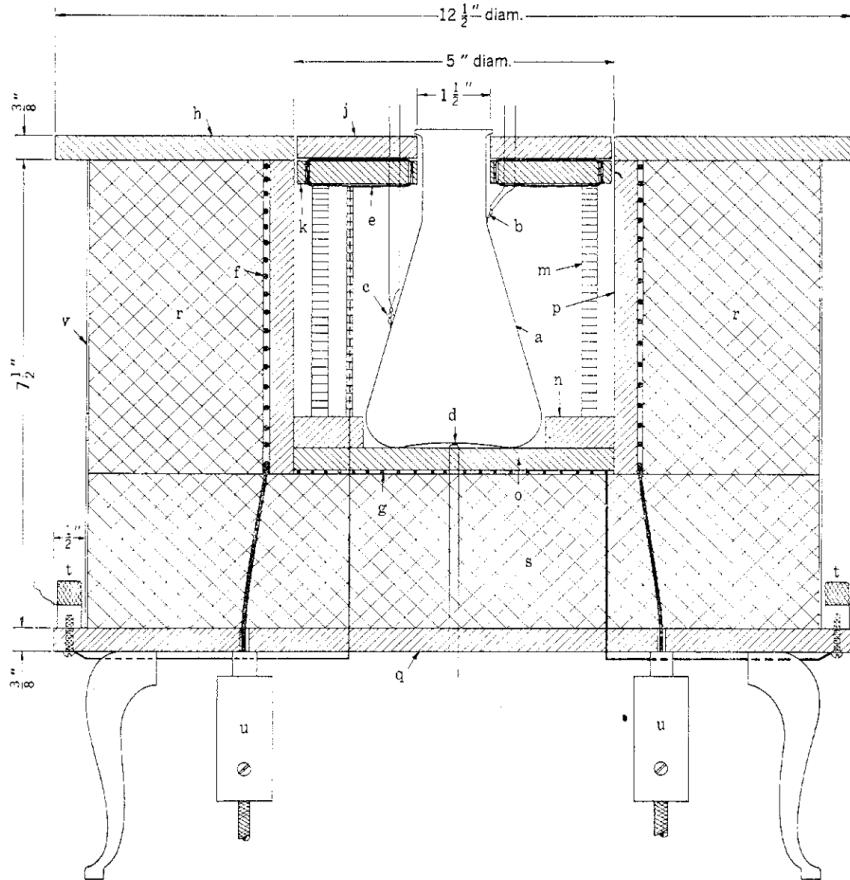
- i.  $\text{H}_2\text{O}_2 + M = 2\text{OH}$
1.  $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$
2.  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$
3.  $\text{O} + \text{H}_2 = \text{OH} + \text{H}$
6.  $\text{H} + \text{O}_2 + M = \text{HO}_2 + M$
11.  $\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
12.  $2\text{HO}_2 \xrightarrow{\text{surface}} \text{H}_2\text{O}_2 + \text{O}_2$
5.  $\text{H} + \text{O}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}_2 + \text{OH}$
7.  $\text{HO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}_2 + \text{OH}$
13.  $\text{H}_2\text{O}_2 \xrightarrow{\text{surface}} \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$

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.

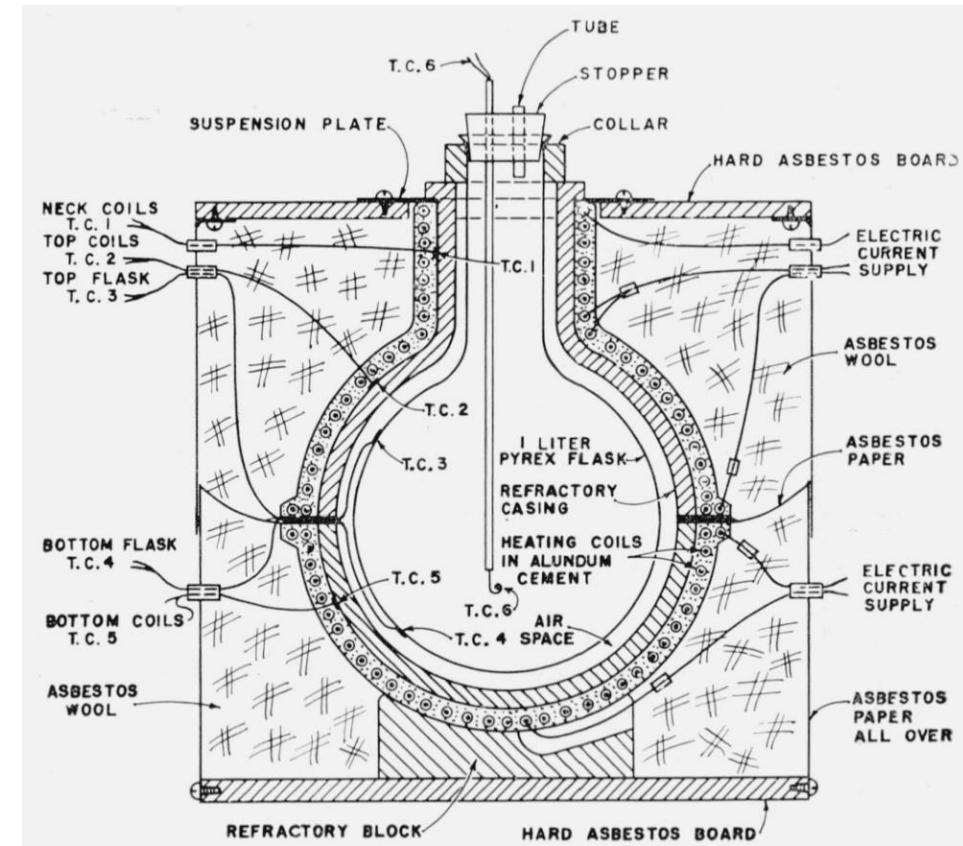
# Autoignition in gases

Automation and improved instrumentation enables quantification and uncertainty analysis.

# Development of Standardized Testing



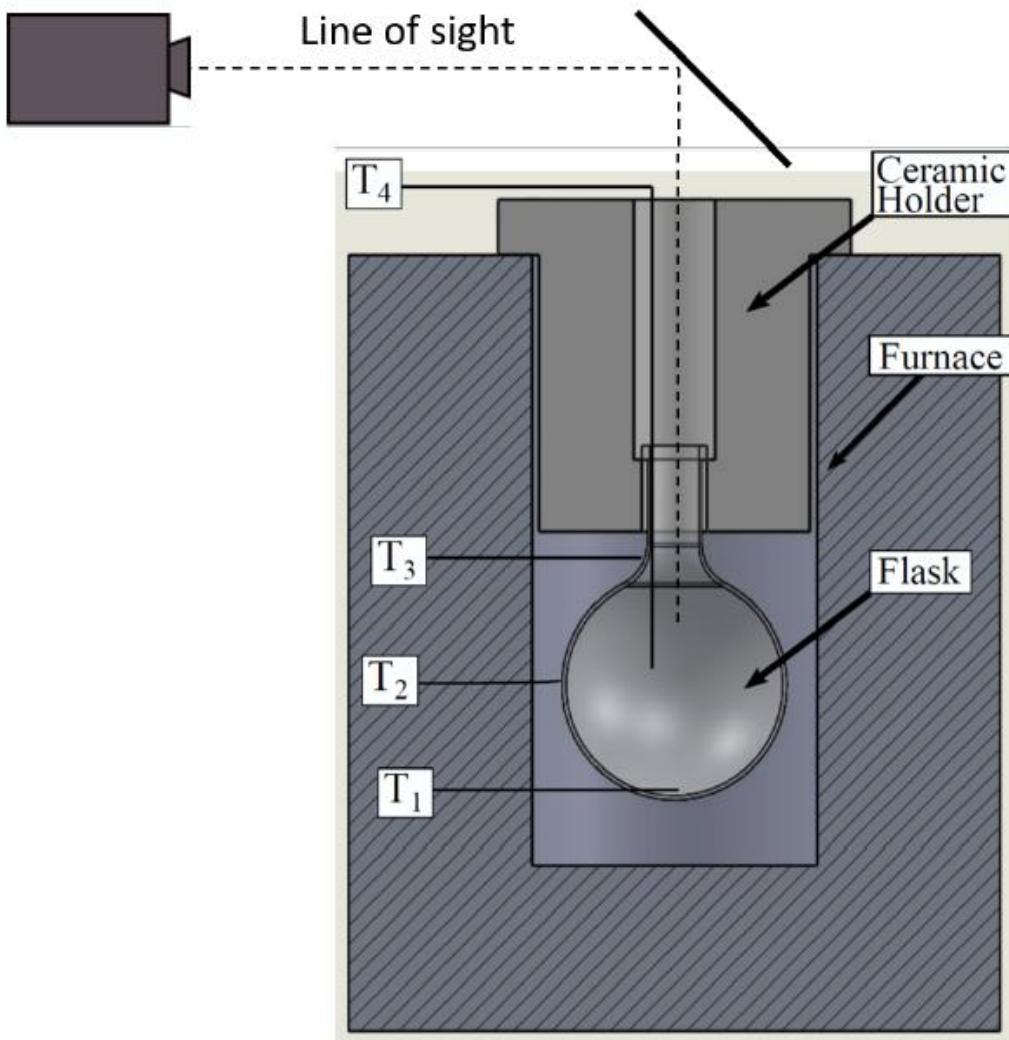
Zabetakis, M. G., A. L. Furno, and G. W. Jones. "Minimum Spontaneous Ignition Temperatures of Combustibles in Air." *Industrial & Engineering Chemistry* 46, no. 10 (October 1954): 2173-78.



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

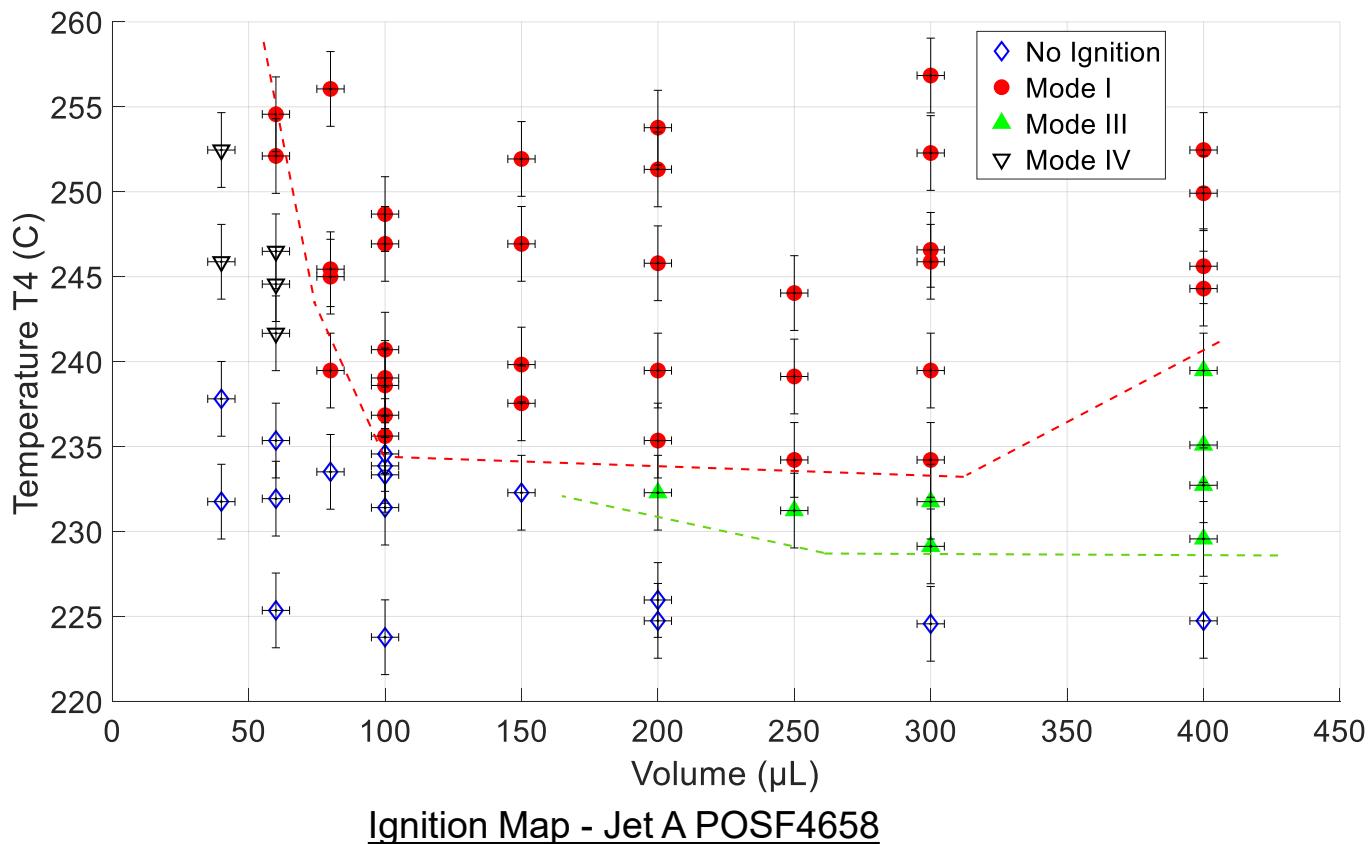
# Standardized Testing for Self-Heating in Gases

- 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

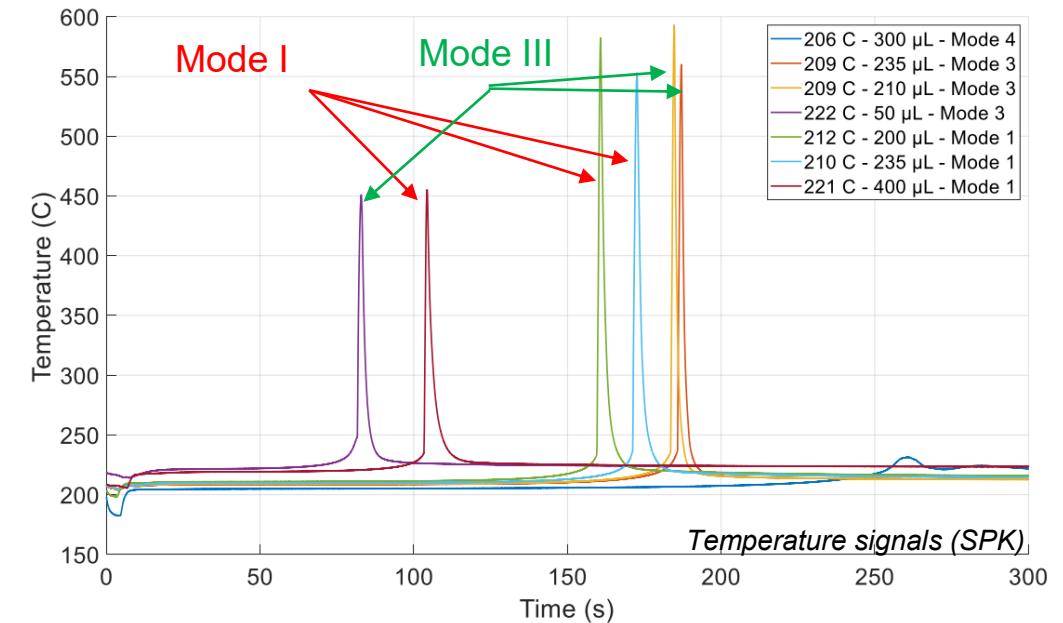


Both considered as  
ignition event

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

<sup>a</sup> Associated with a weak to intense explosion sound

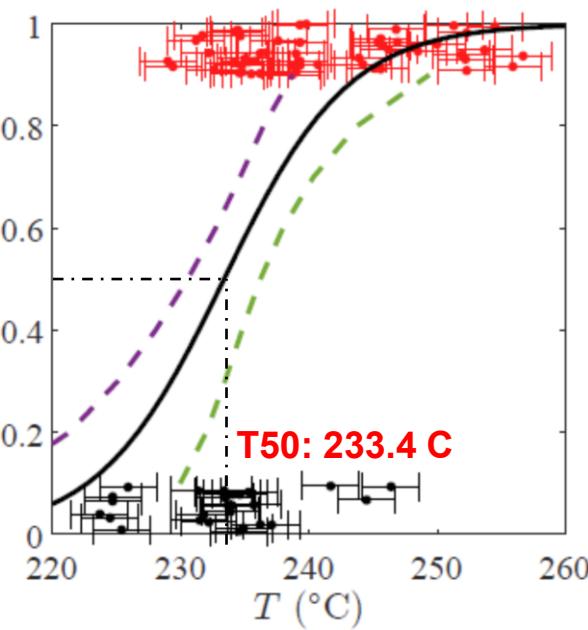
<sup>b</sup> None or faint glow only visible to the naked eye, and small puff of smoke



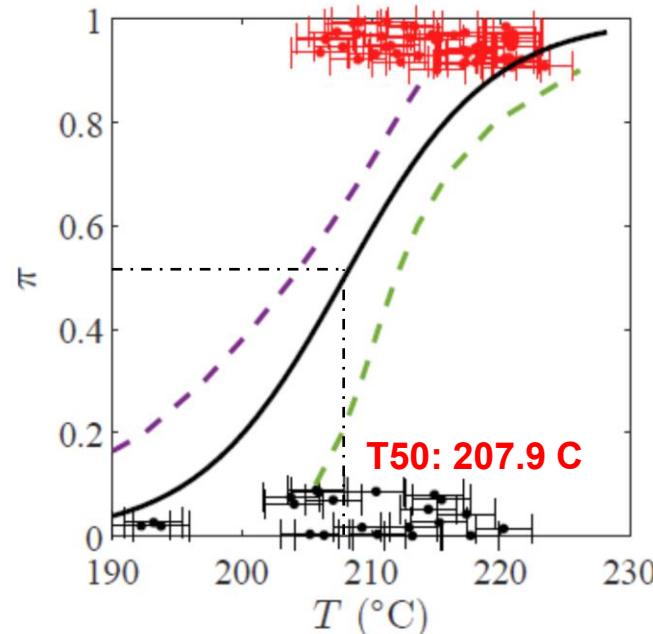
# Statistical Analysis

- 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  $\pi$  based on logistic model

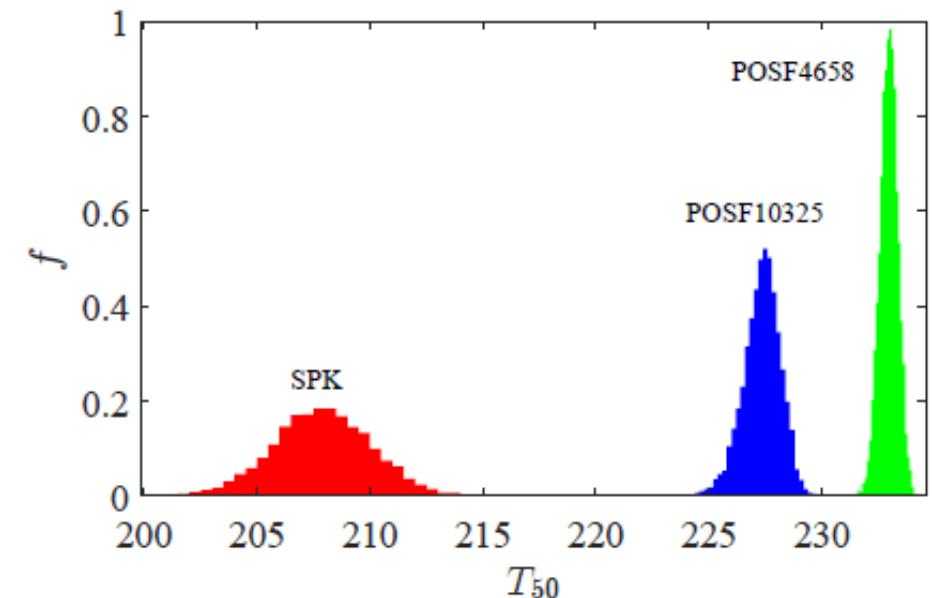
$$\pi(\beta; x) = \frac{1}{1 + e^{-\beta_0 - \beta_1 x}}$$



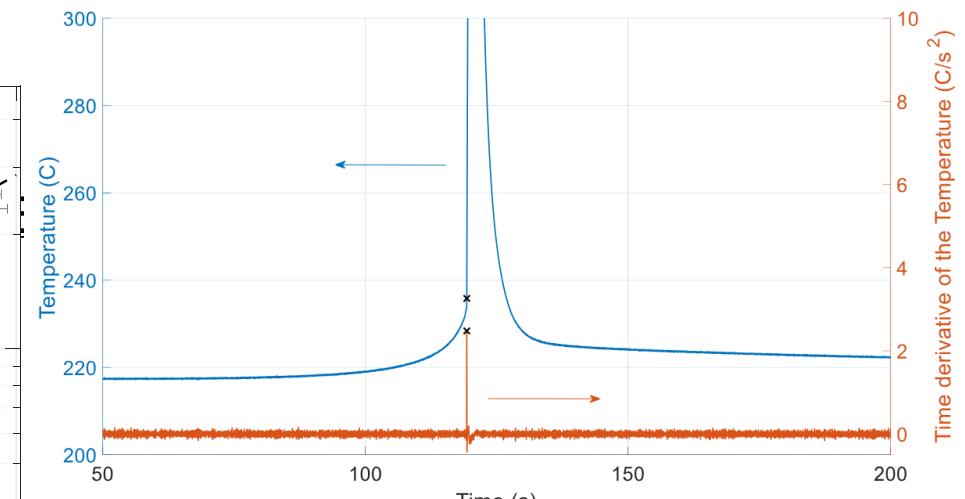
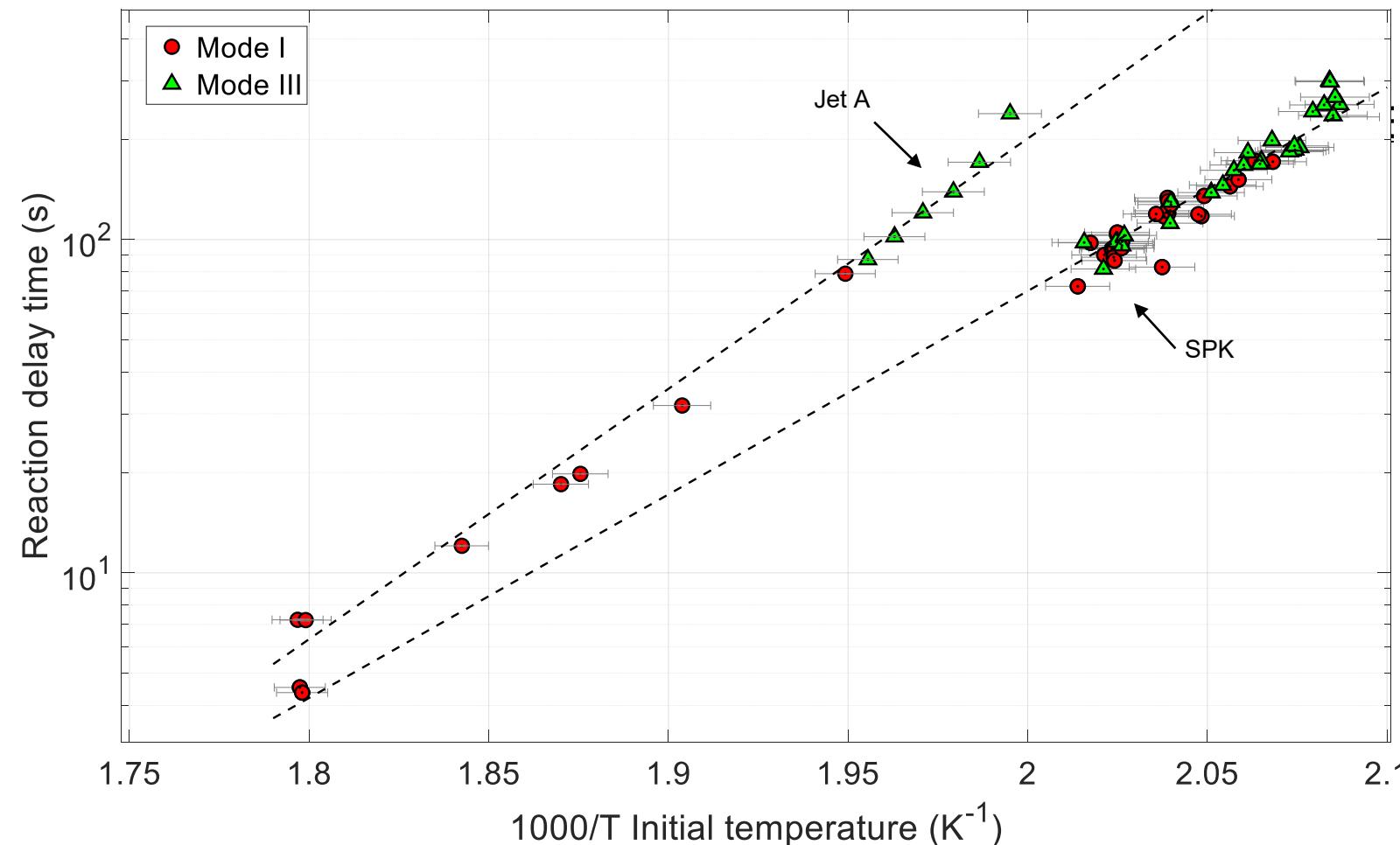
POSF4658



SPK



# Ignition delay time



## Effective activation energy

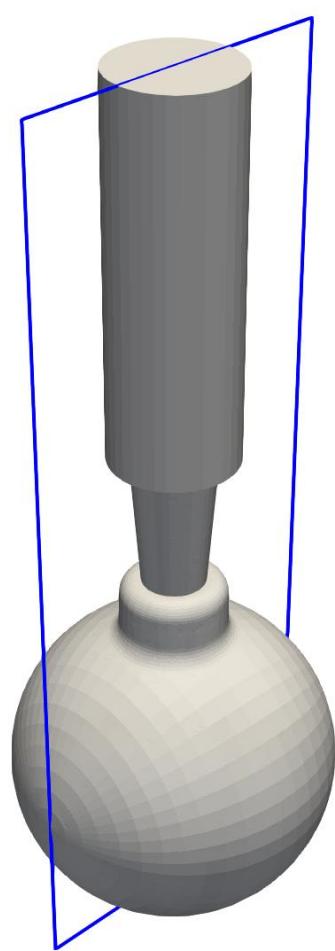
Jet A	SPK
$141 \text{ kJ}\cdot\text{mol}^{-1}$	$116 \text{ kJ}\cdot\text{mol}^{-1}$

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:

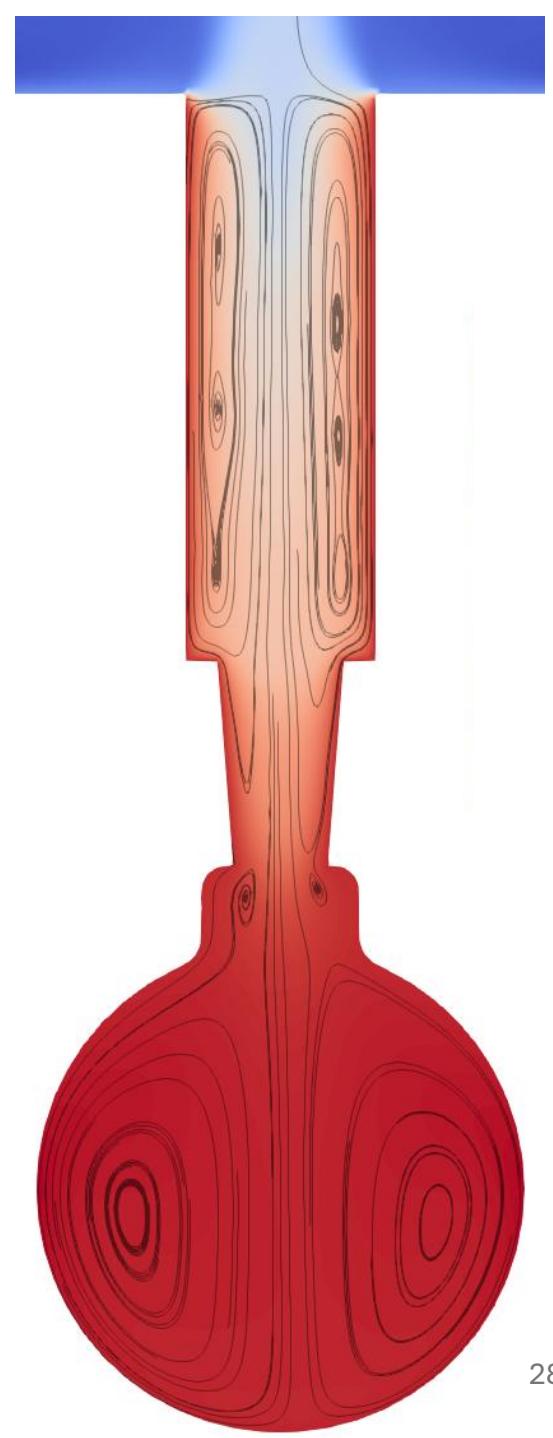
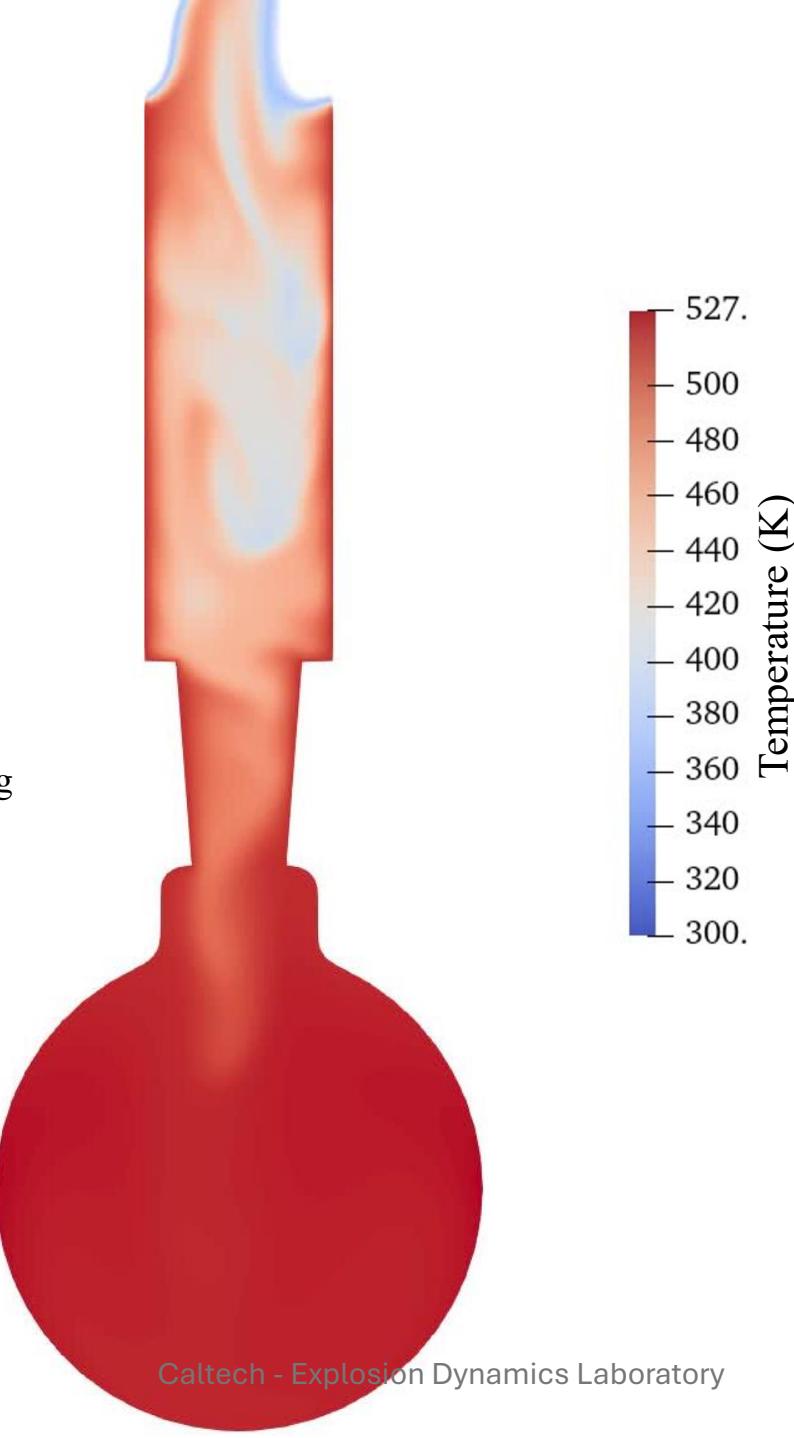
$$\tau_i \propto e^{-E_a/(RT)}$$

# Mixing Simulation

Davis et al 2025

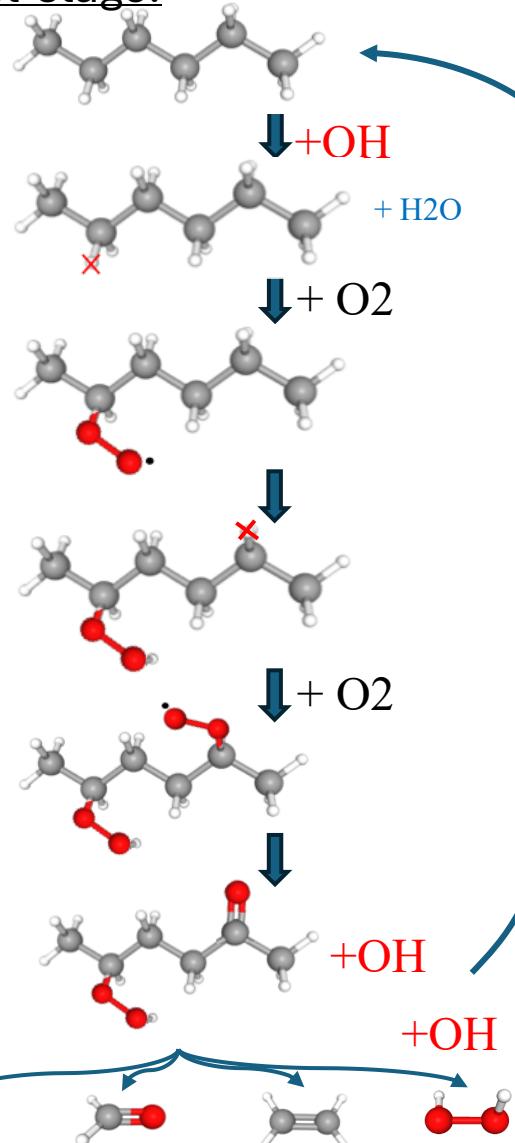


Time: 0 s



# Ignition Reaction Pathways

## First-stage:



## First-stage:

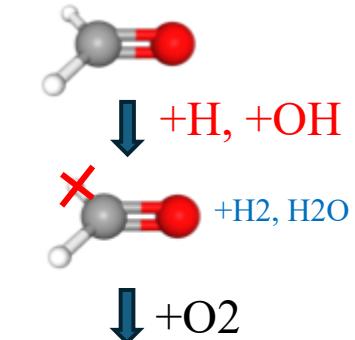
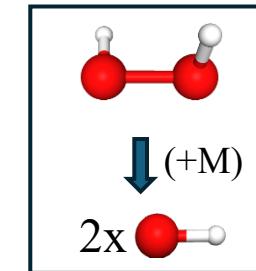
- Formation of larger, oxygenated hydrocarbons that then break apart into stable intermediates: CO, CH<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>
- Sequence is exothermic on the aggregate
- Net-positive production of chain carrier, OH

## Second-stage:

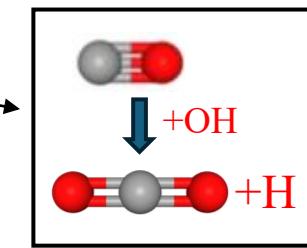
- Generation of OH radicals by breaking H<sub>2</sub>O<sub>2</sub> from the first stage
- OH oxidize CH<sub>2</sub>O to form more CO
- Primary heat release converting CO → CO<sub>2</sub>
  - Consistent with high temperature pathways described in other studies [1–2]
- Secondary heat release due to lack of O<sub>2</sub>
  - C<sub>2</sub>H<sub>4</sub> → CH<sub>2</sub>CHO → CH<sub>2</sub>CO → CH<sub>3</sub>
  - Exothermic CH<sub>3</sub> + H(+M) → CH<sub>4</sub>(+M)
  - Feedback to produce H<sub>2</sub> products

## Second-stage:

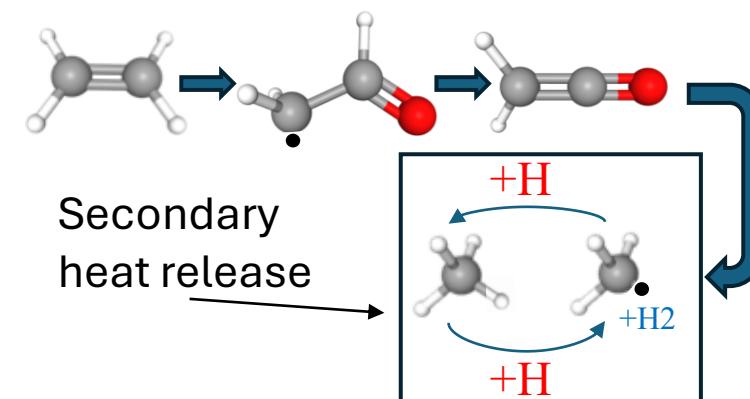
### OH generation



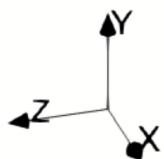
### Primary heat release



### Secondary heat release (fuel rich):



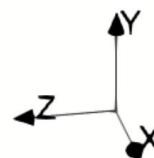
Time: 0 s



11/27/2025

Time: 16.33885 s

$T = 1200 \text{ K}$   
isosurface



Caltech - Explosion Dynamics Laboratory

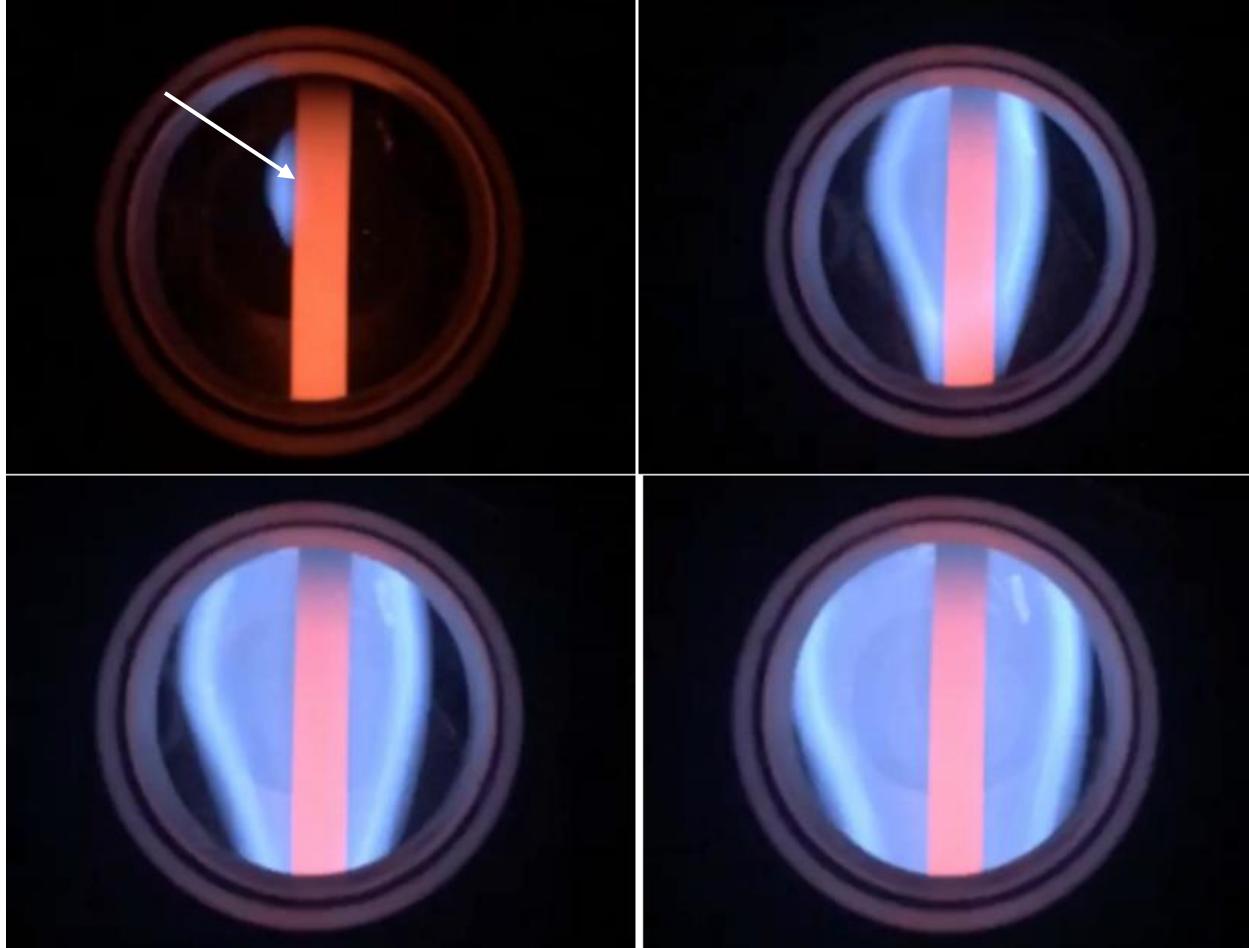
Davis 2025

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# Hot Surface Ignition

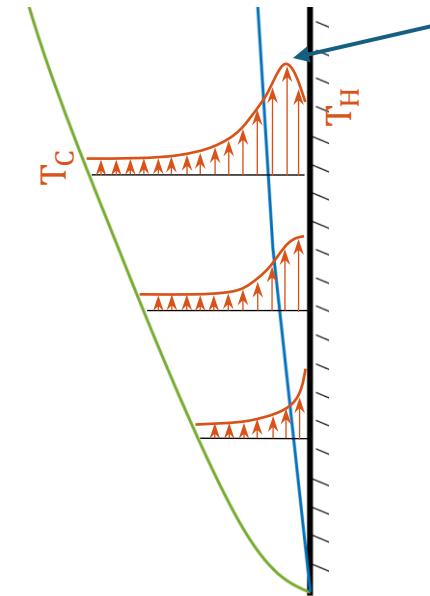
Hot surfaces in cold flammable atmospheres require completely different approach to analysis than self-heating (autoignition) testing

# 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

$t = 2 \text{ sec}$

3.0e+02 400 500 600 700 800 900 1000 1100 1200 1300 1.4e+03

$t = 4 \text{ sec}$

3.0e+02 400 500 600 700 800 900 1000 1100 1200 1300 1.4e+03

$t = 4.28 \text{ sec}$

3.0e+02 400 500 600 700 800 900 1000 1100 1200 1300 1.4e+03

$t = 4.282 \text{ sec}$

3.0e+02 600 800 1000 1200 1400 1600 1800 2000 2200 2.6e+03

## Forced Convection

$t = 2 \text{ sec}$

3.0e+02 400 500 600 700 800 900 1.1e+03

$t = 3 \text{ sec}$

3.0e+02 400 500 600 700 800 900 1.1e+03

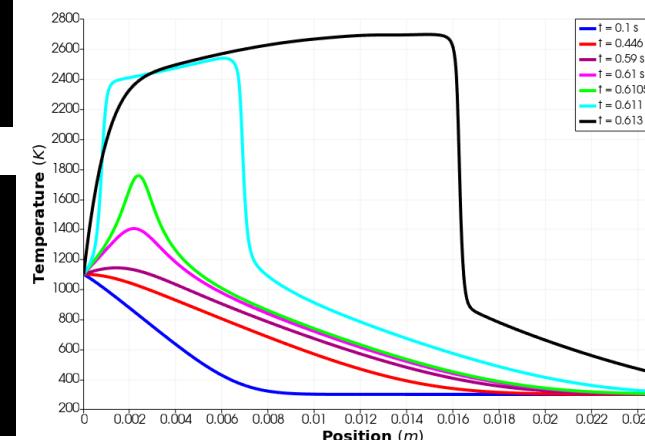
$t = 3.405 \text{ sec}$

3.0e+02 400 500 600 700 800 900 1.1e+03

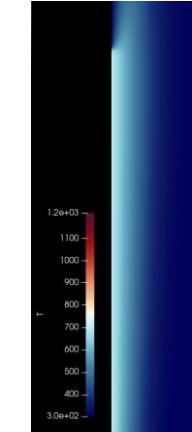
$t = 3.41 \text{ sec}$

3.0e+02 600 800 1000 1200 1400 1600 1800 2.1e+03

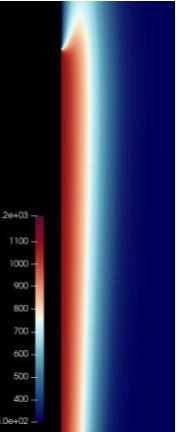
## 1D Diffusing Thermal Layer



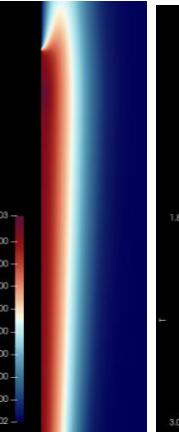
$t = 2 \text{ sec}$



$t = 4 \text{ sec}$



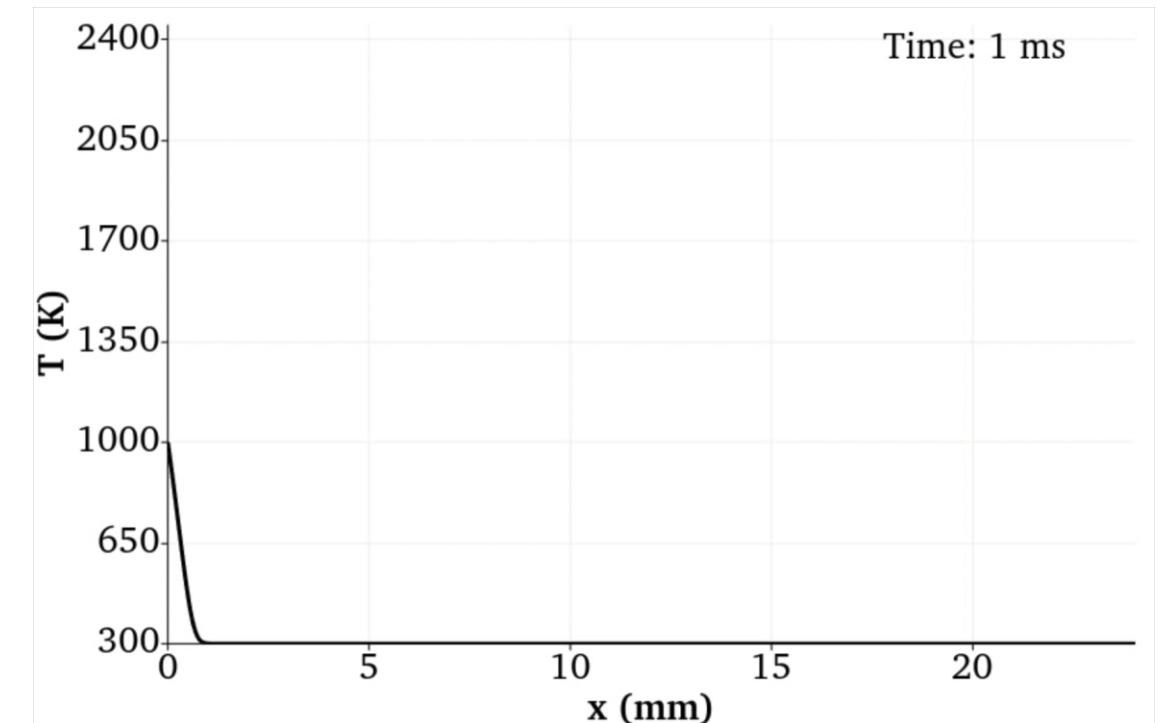
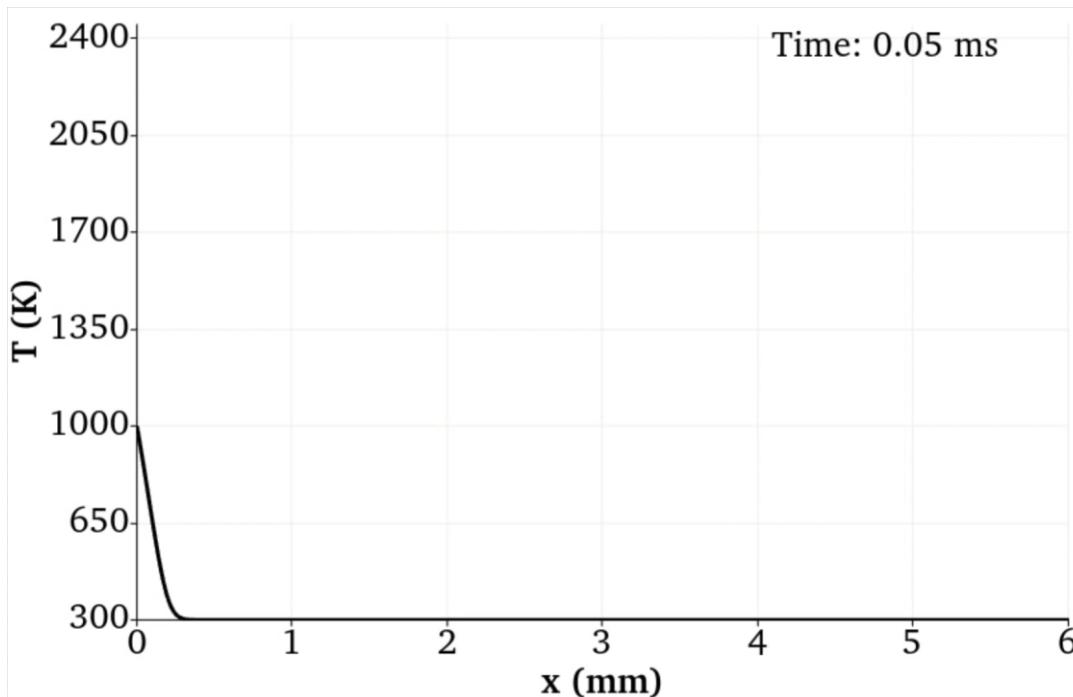
$t = 4.1193 \text{ sec}$



$t = 4.12 \text{ sec}$



# Common Feature – Ignition in a Thermal Layer



# Ratio of Length Scales Determines Outcome

Heat transfer length scale:

$$\Lambda = \frac{T_H}{\left. \frac{\partial T}{\partial y} \right|_{c,y \rightarrow \infty}}$$

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

$$\Lambda \approx \left. \frac{T_H}{\frac{\partial T}{\partial y}} \right|_{w,frozen}$$

Chemical length scale:

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

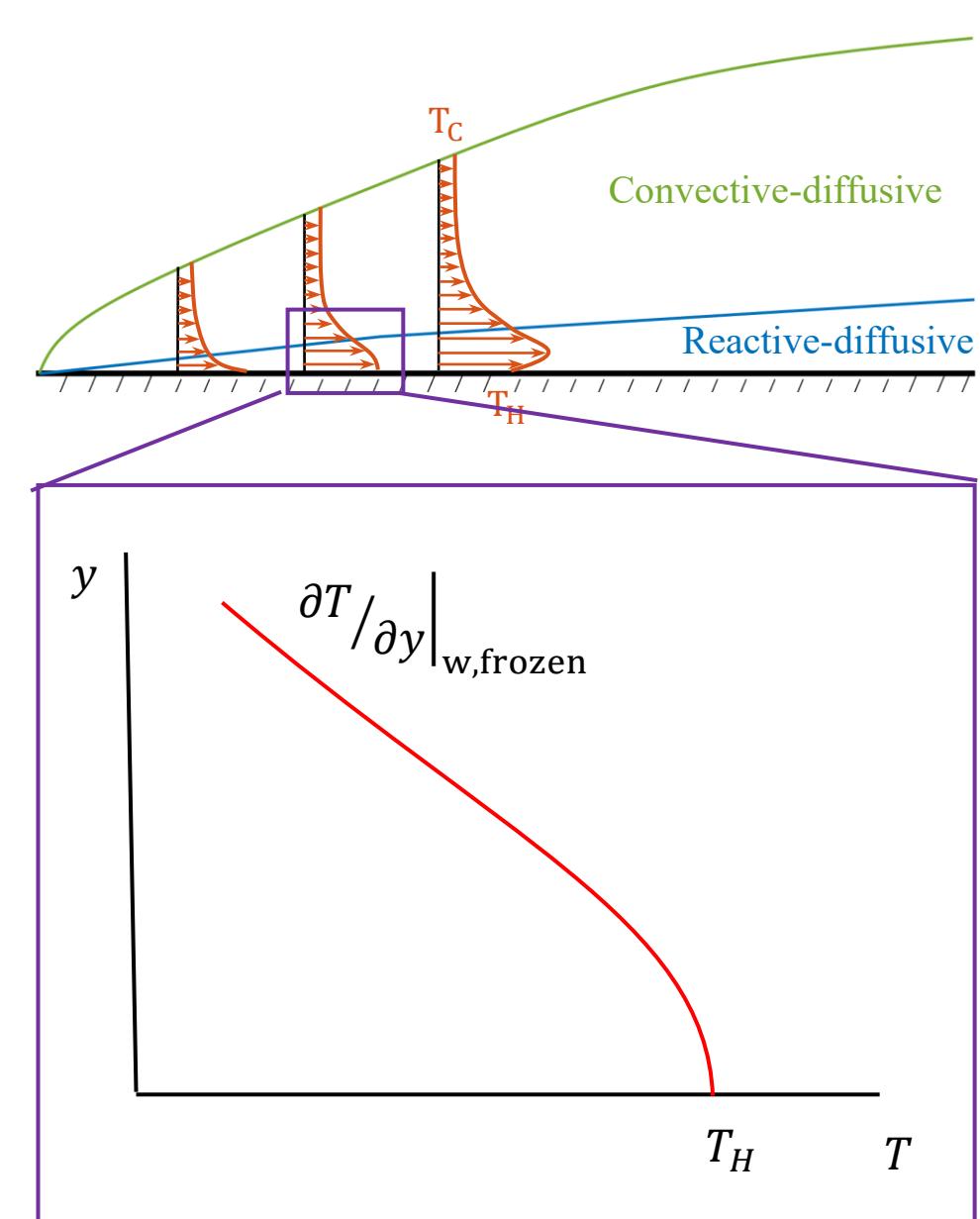
- Solution** - Adiabatic thermal explosion theory

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

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

$$T_{IGN}$$

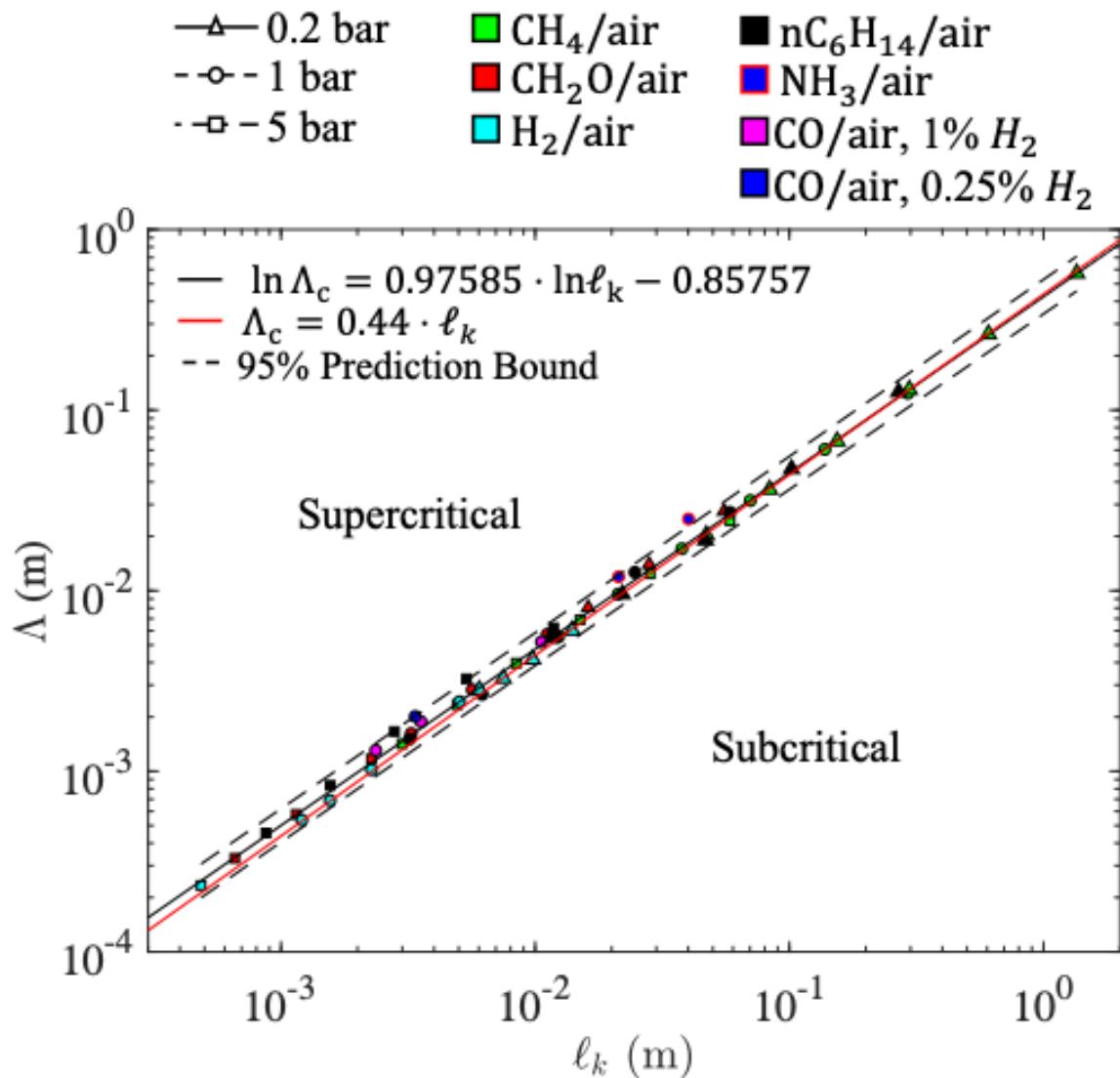
2. Use equivalent *chemically-frozen simulation* to compute wall normal temperature gradient at ignition temperature to formulate the characteristic heat transfer length scale:

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

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

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

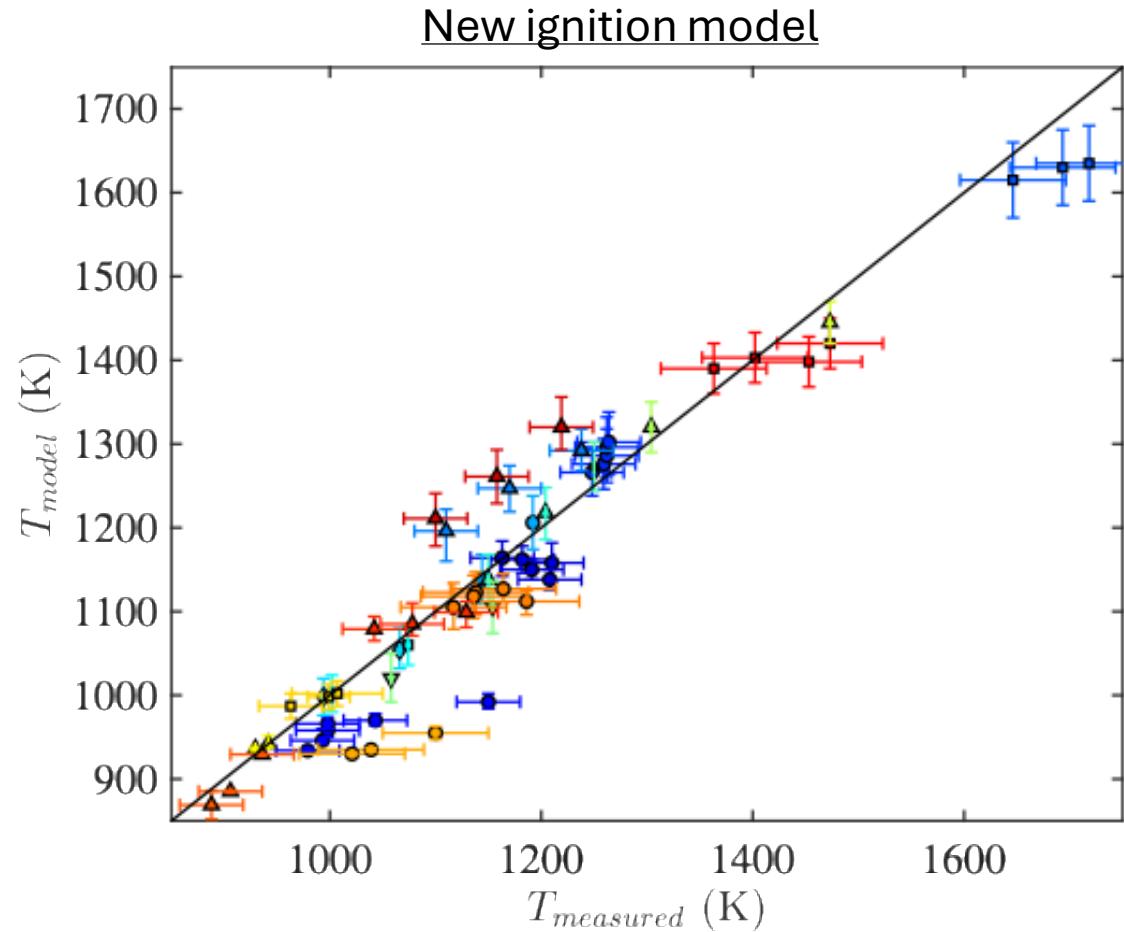
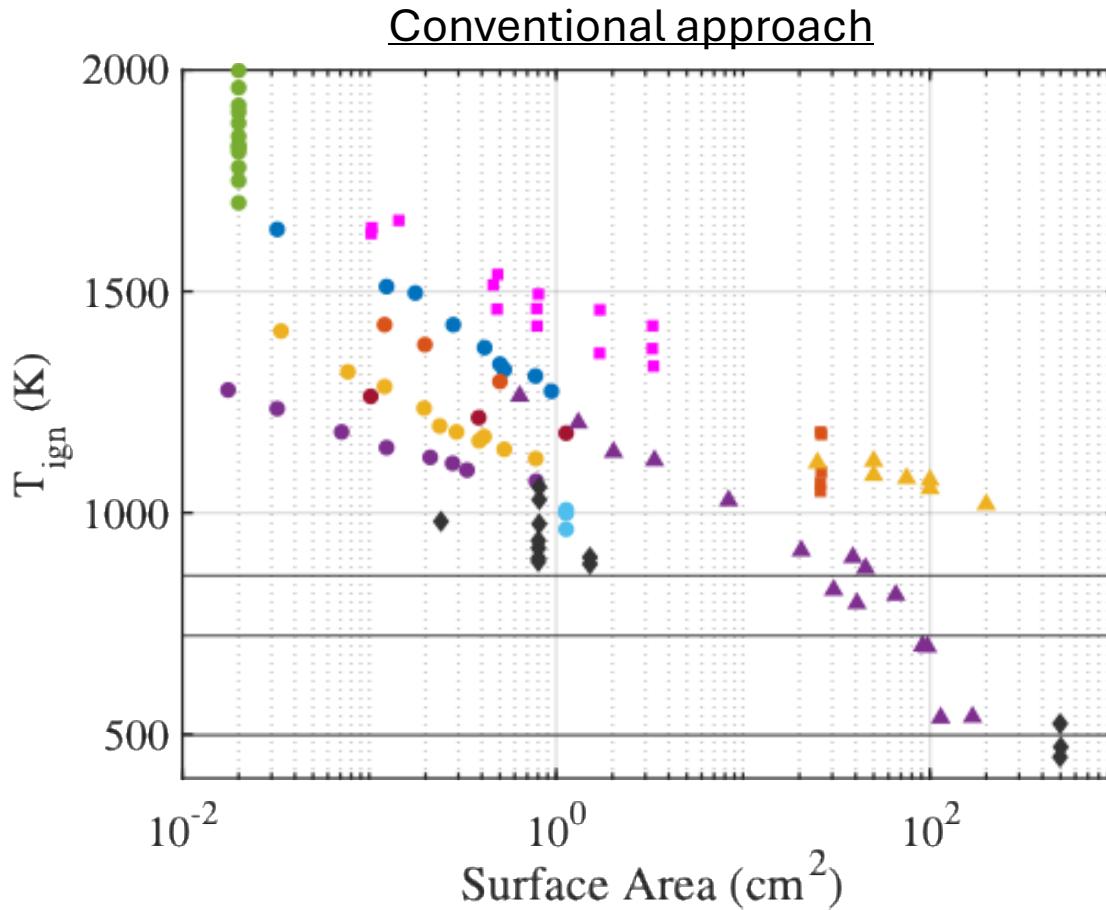
# The line of criticality



- 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?

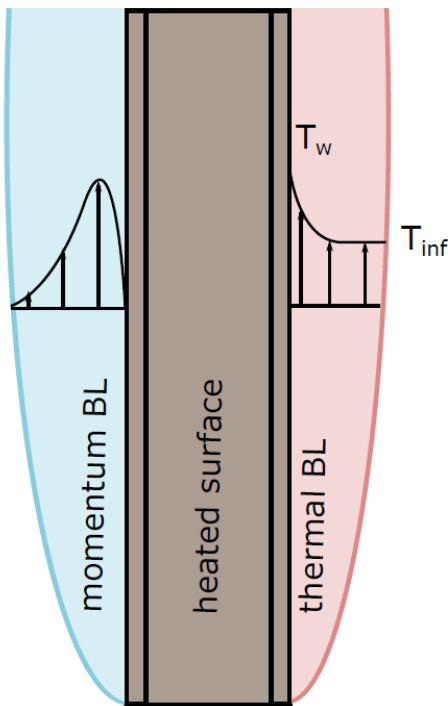
# Validation for all configurations



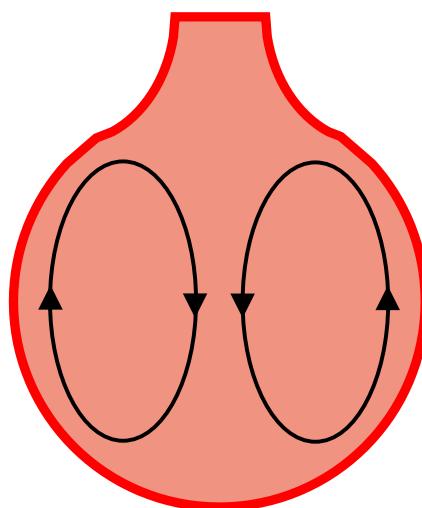
**Unification of hot surface ignition theory with detailed simulation and experiments**  
**Can be applied to complex engineering system using standard heat transfer and 0D chemical models**

# Hot Surface Ignition vs. Autoignition

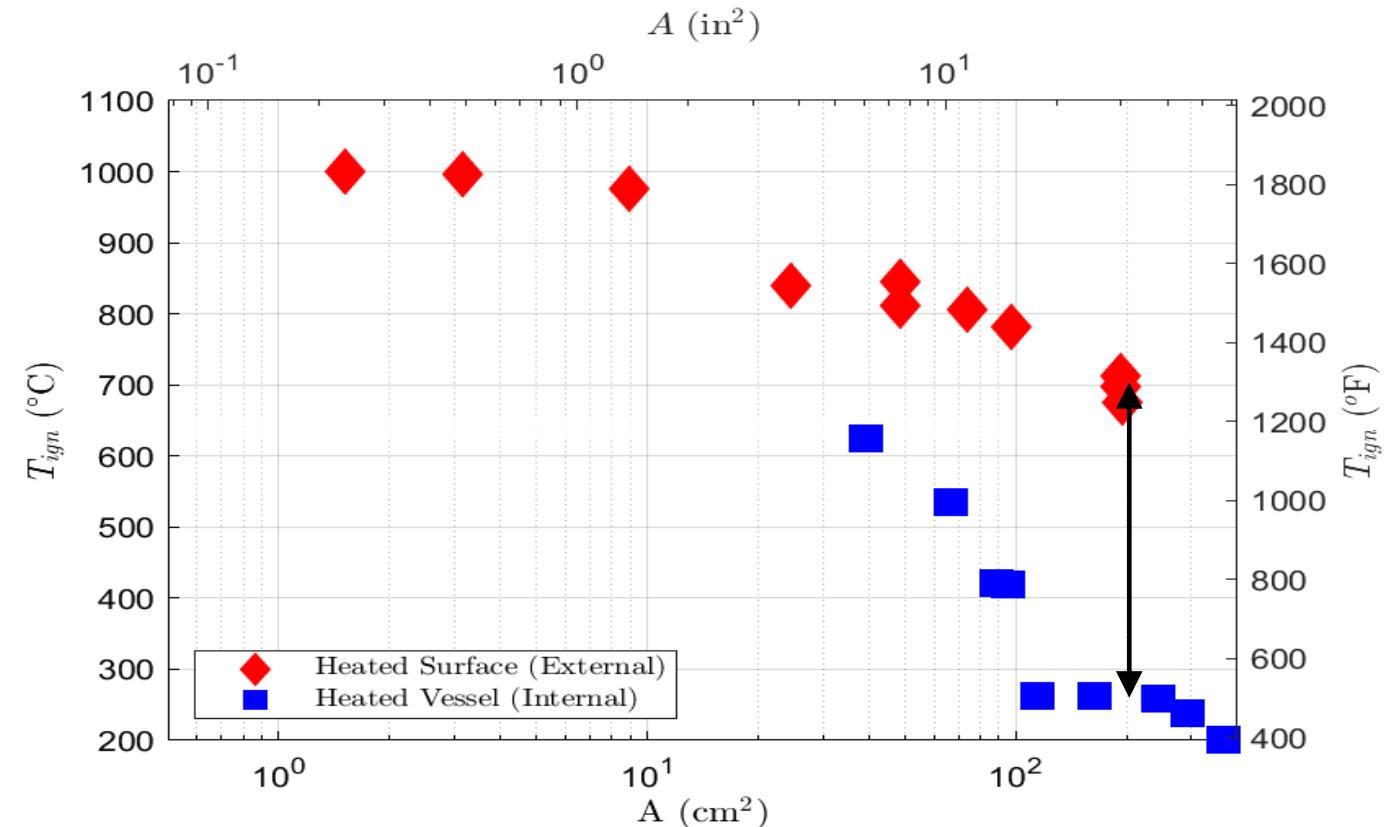
Unconfined flow, cold atmosphere external to heated surface



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**.



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  - Ms. Hannah Ramsperger
  - Mr. Lucas Favretto
  - Ms. Isabella Pagano
  - Mr. Noel Esparza-Duran

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