Australian Government
Department of Defence
Guided Weapons and
Explosive Ordnance Group

# A Case for Chemical Kinetics in Explosives Ordnance Engineering

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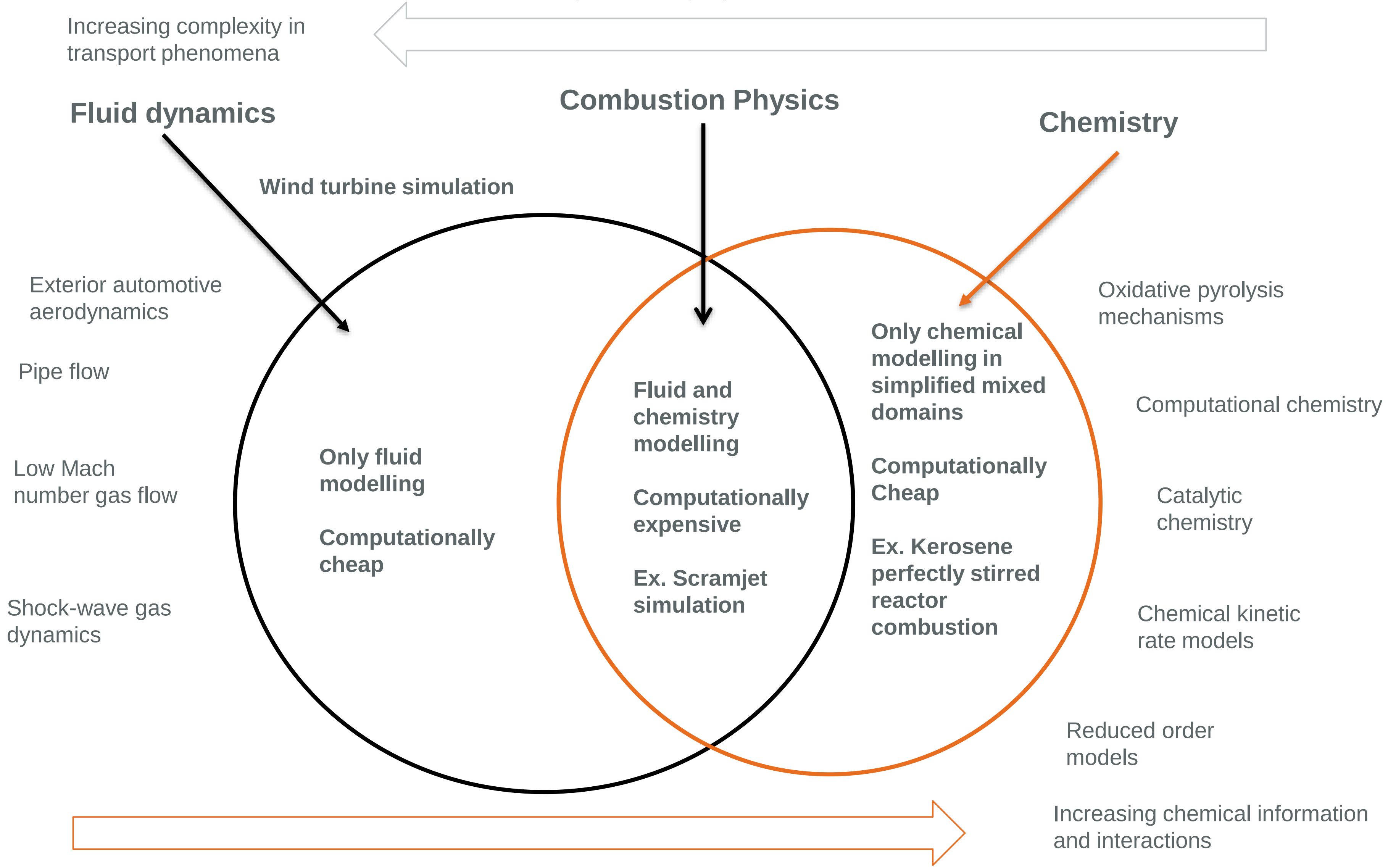
# What is the need?

- Working with limited data sets to inform stabiliser depletion in single and double base munitions.
  - Small data-sets of stabiliser testing
  - Resource constrained for experimental testing
- Understanding the toxicity aspect of functioning propellants
  - Sovereign capability leading to increased domestic manufacture and proof testing.
  - Growing awareness of toxicity and impact on biological organisms.
- Developing processes to assist the performance difference between different potential propellant blends, or propellant substitution.
  - Agile munition base, substitution of suppliers
  - Accelerate engineering capacity for comparison

**How can we bridge the knowledge gap?**

# Chemical Kinetics - General

- Can chemical kinetics bridge the gap?



Increasing complexity in transport phenomena

**Fluid dynamics**

**Combustion Physics**

**Chemistry**

**Wind turbine simulation**

Exterior automotive aerodynamics

Pipe flow

Low Mach number gas flow

Shock-wave gas dynamics

**Only fluid modelling**

**Computationally cheap**

**Fluid and chemistry modelling**

**Computationally expensive**

**Ex. Scramjet simulation**

**Only chemical modelling in simplified mixed domains**

**Computationally Cheap**

**Ex. Kerosene perfectly stirred reactor combustion**

Oxidative pyrolysis mechanisms

Computational chemistry

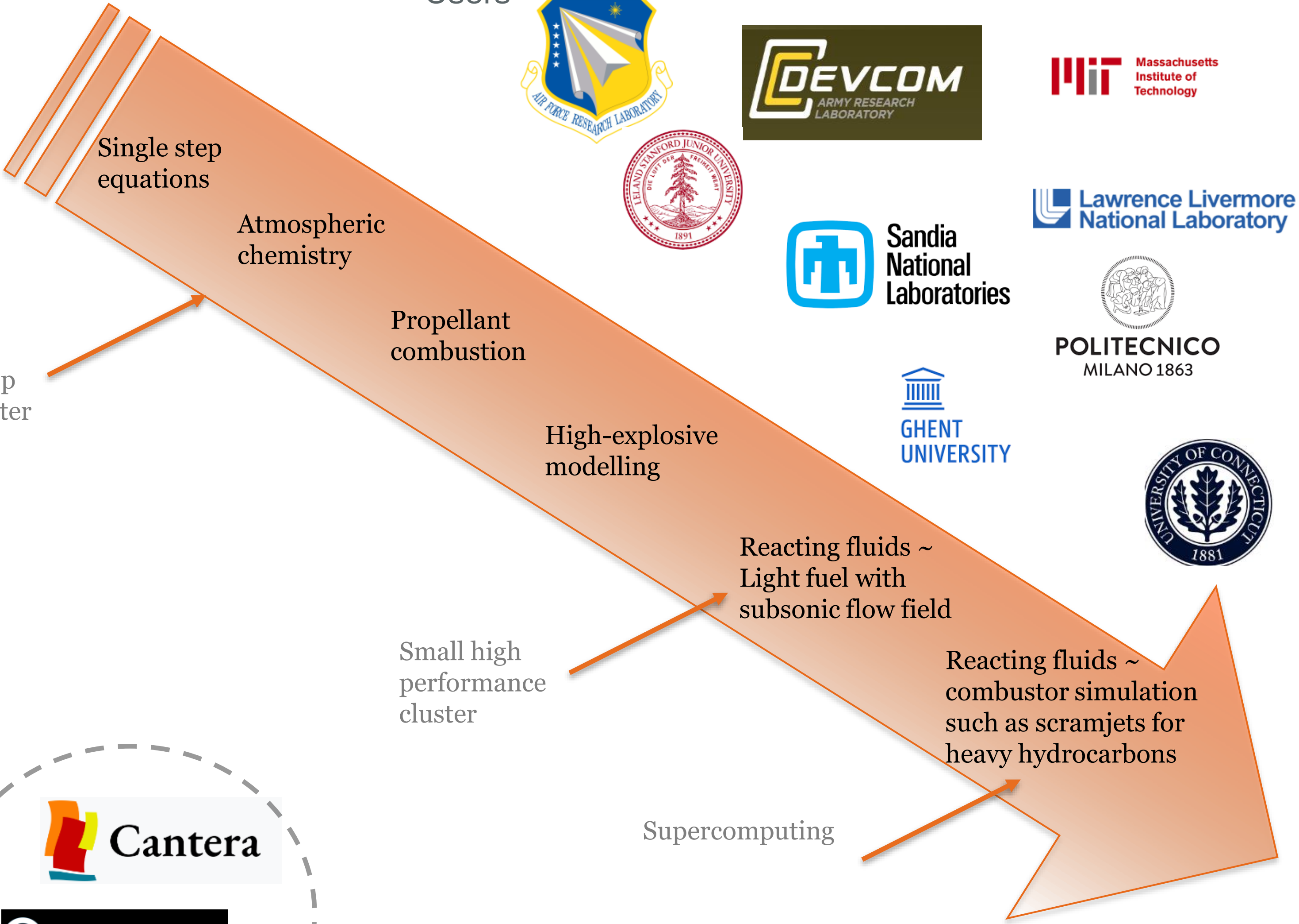
Catalytic chemistry

Chemical kinetic rate models

Reduced order models

Increasing chemical information and interactions

## Chemical Kinetics - General



Applications

Single step equations

Atmospheric chemistry

Propellant combustion

High-explosive modelling

Reacting fluids ~ Light fuel with subsonic flow field

Reacting fluids ~ combustor simulation such as scramjets for heavy hydrocarbons

Hardware requirements

Desktop computer

Small high performance cluster

Supercomputing

Users

Air Force Research Laboratory

DEVCOM Army Research Laboratory

Massachusetts Institute of Technology

Leland Stanford Junior University

Sandia National Laboratories

Lawrence Livermore National Laboratory

Politecnico Milano 1863

Ghent University

University of Connecticut

Commercial solution

**Ansys Chemkin-Pro**

Software packages

Cantera

OpenSMOKE++

Open source packages

# Chemical Kinetics Background: Reaction Types

Unimolecular reaction

$$[A] \rightarrow [B] + [C] \tag{1}$$

Bimolecular reaction

$$[A] + [B] \rightarrow [C] + [D] \tag{2}$$

Re-combination reaction

$$[A] + [B] + [M] \rightarrow [AB] + [M] \tag{3}$$

Elementary reactions used to describe various chemical pathways in a energetic material or fuel. These elementary reactions can then be expressed as some form or chemical rate equation, where k is the rate constant.

Unimolecular rate of consumption

$$\frac{dA}{dt} = -k[A_0] \tag{4}$$

The rate constant is then expressed by variety of different mathematical relationships. These tend to have an exponential component, signifying the exponential relationship to increased temperature in driving forward reactions. There are a variety of other forms including fall-off reactions which allow for pressure dependence etc.

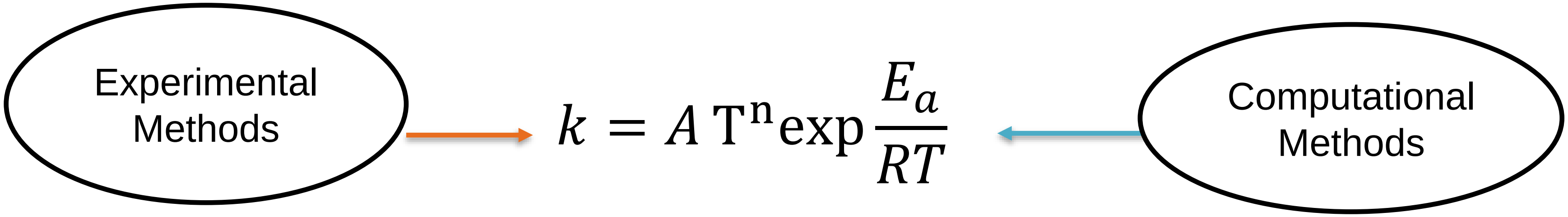
Arrhenius rate equation

$$k = A \exp \frac{E_a}{RT} \tag{5}$$

$$k = A\,\mathrm{T}^{\mathrm{n}} \exp \frac{E_a}{RT} \tag{6}$$

# Chemical Kinetics Background: Rate Formulation

How do we get these rate values for the kinetic equation?



Experimental Methods

$$k = A\,\mathrm{T}^{\mathrm{n}} \exp \frac{E_a}{RT}$$

Computational Methods

- Shock-tube studies for high temperature rates
- Spectrophotometry
- Plug flow reactors
- Laminar flame speeds
- Mass spectrometry
- Gas chromatography

- Density functional theory

Do I need to worry about the rate values?

# Chemical Kinetics Background: Mechanism Development

**Table 1. Chemical Kinetic Mechanisms**

| No. | Document Title | Date | Mechanism Type | Composition | Application |
|---|---|---|---|---|---|
| 1 | Modeling of smokeless powders shelf life using results of multi-temperature study on stabilizer consumption | 2021 | One-Step Reaction Scheme | Single base | Stabiliser depletion |
| 2 | Prediction of In-Service Time Period of Three Differently Stabilized Single Base Propellants | 2009 | One-Step Reaction Scheme | Single base | Stabiliser depletion |
| 3 | Detailed Combustion Modeling as an Aid to Propellant Formulation: Two New Strategies | 2000 | 177- Reactions | Nitro-glycerine | Gas-Phase Combustion |
| 4 | A Chemically Specific Burning Rate Predictor Model for Energetic Materials | 2001 | 35-Species, 178-Reactions | RDX and Nitroglycerine | Gas-Phase Combustion |
| 5 | CYCLOPS, A Breakthrough Code to Predict Solid-Propellant Burning Rates | 2003 | 59-Species, 365-Reactions | Nitrocellulose and Nitroglycerine (double base) | Gas-Phase Combustion |
| 6 | A skeletal, gas-phase, finite-rate, chemical kinetics mechanism for modeling the deflagration of ammonium perchlorate—hydroxyl terminated polybutadiene composite propellants | 2016 | 81-Species, 100-Reactions | AP-HTPB | Gas-Phase Combustion |
| 7 | A kinetic model for the premixed combustion of a fine AP/HTPB composite propellant | 1998 | 39-Species, 72-Reactions | AP-HTPB | Condensed phase and Gas-Phase Combustion |
| 8 | Modeling of HMX/GAP pseudo-propellant combustion | 2002 | 19-Species, 10-Reactions | HMX | Condensed phase pyrolysis |
| 9 | An eigenvalue method for computing the burning rates of HMX propellants | 1998 | 3-Global Reactions | HMX | Liquid phase pyrolysis |
| 10 | RDX/GAP Pseudo-Propellant Combustion Modelling |  | 4-Global Reactions,<br>83-Species, 534-Reactions | RDX-GAP | Condensed phase and Gas-Phase Combustion |
| 11 | A detailed chemical kinetic model for gas phase combustion of TNT | 2007 |  | TNT | Gas-Phase Combustion |
| 12 | Detailed kinetic mechanism for nitrocellulose low temperature decomposition | 2023 | 62-Species, 803-Reactions | Nitrocellulose (NC) | Gas-Phase Combustion |
| 13 | High-Temperature Combustion Reaction Model of H 2/CO/C 1–C 4 Compounds | 2007 | 111-Species, 784-Reactions | C2H4 | Gas-Phase Combustion |
| 14 | Low-and intermediate-temperature ammonia/hydrogen oxidation in a flow reactor: Experiments and a wide-range kinetic modeling | 2023 | 31-Species, 203-Reactions | NH3 | Gas-Phase Combustion |
| 15 | High-temperature chemistry of HCl and Cl2 | 2015 | 25-Species, 103-Reactions | HCl and Cl2 | Gas-Phase Combustion |

# Chemical Kinetics Background: Mechanism Development

## What if the mechanism still does not exist?

Chemical products of interest

Fuel molecule of interest

Radical chemistry of interest

Reaction Mechanism Generator*

Comprehensive chemical mechanism

Utilising some knowledge of our chemical system of interest, the reaction mechanism generator can take all published reactions of interest to form a detailed chemical mechanism. Implementing chemical species which may be necessary to represent the reactant or sub-component chemistry.

*Liu, M., Grinberg Dana, A., Johnson, M. S., Goldman, M. J., Jocher, A., Payne, A. M., ... & Green, W. H. (2021). Reaction mechanism generator v3. 0: advances in automatic mechanism generation. *Journal of Chemical Information and Modeling*, *61*(6), 2686-2696.

# Application 1: Stabiliser depletion Modelling

- Autocatalytic degradation of nitrocellulose (NC) has in part led to or contributed to a number of accidents,
  - 1981, ammunition magazine explodes in Zimbabwe [1].
  - 1994, an Indian magazine explodes [1].
  - 1996, 25 tonnes of ammunition functions in the Brazilian naval storage [1].
  - 1996, Red River in the united states has an ammunition storage function [1].
  - 1999, Finish bunker functions with 65 tonnes of ammunition [1].
  - 2000, Japanese propellant storage functions [1].
  - 2001, Indian munitions handling accident with nitrocellulose [1].
  - 2015, a large mass of nitrocellulose exploded in the Tianjin port in China. The cited mechanism for said explosion was the loss of the storage medium for which the nitrocellulose would have been handled and storied under [2].

[1]de Klerk, W. P. (2015). Assessment of stability of propellants and safe lifetimes. *Propellants, Explosives, Pyrotechnics*, *40*(3), 388-393.

[2] Liu, C., Zhu, S., Wu, J., Tao, L., & Wang, W. (2020, September). Study on the spontaneous combustion risk and thermal decomposition characteristics of nitrocellulose. In *IOP Conference Series: Earth and Environmental Science* (Vol. 565, No. 1, p. 012110). IOP Publishing.

# Application 1: Stabiliser Depletion Modelling

Nitrate-ester (NE) initial pyrolysis

$$NE \rightarrow P + R \qquad (1)$$

Nitrate-ester autocatalytic reaction

$$NE + P \rightarrow 2P + R \qquad (2)$$

Stabiliser reaction

$$S + P \rightarrow P - S \qquad (3)$$

Stabiliser reaction rate equations

$$\frac{dS}{dt} = -k \qquad (10)$$

Zero-order

$$\frac{dS}{dt} = -k.S(t) \qquad (12)$$

First-order

$$\frac{dS}{dt} = -k.S(t)^n \qquad (13)$$

nth-order

$$\frac{dS}{dt} = -k_1.S(t)^n - k_0 \qquad (14)$$

Linear + exponential

# Application 1: Stabiliser Depletion Modelling

- N-th order

$$S = \left[1-(1-n)Ae^{-\frac{E_a}{RT}}\right]^{\frac{1}{1-n}}$$

- Linear + exponential

$$S = \left(S_o + \frac{k_o}{k_1}\right).\mathrm{e}^{-\mathrm{k}_1\mathrm{t}} - \frac{k_o}{k_1}$$

$$k_o = A_o e^{-\frac{E_o}{RT}}$$

$$k_1 = A_1 e^{-\frac{E_1}{RT}}$$

Table 2. Values fitted for DPA consumption only for varying propellant blends

* A in units of 1/s, time in secondas

** Values for *ko*, A in units of 1/days, time in days

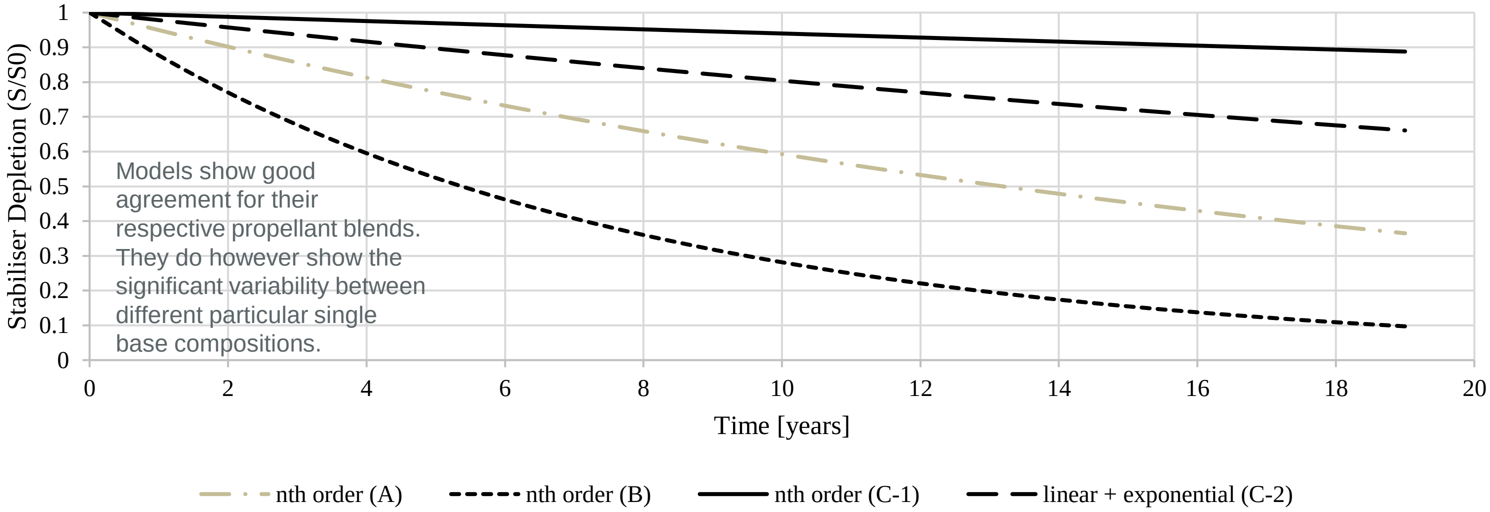
| Sample | Model order | Propellant | Ea (kJ/mol) | N (-) | A | Ref |
|---|---|---|---|---|---|---|
| A | Nth-order | Single base 7.62 x 54R propellant with 9.32% DPA and 0.45% NO-DPA | 131.6 | 0.94 | $1.91\,.\,10^{14*}$ | [1] |
| B | Nth-order | Single base 12.7 x 107 propellant with 0.93% DPA and 0.37% NO-DPA | 92.8 | 1.06 | $7.72\,.\,10^{7}$ | [1] |
| C-1 | Nth-order | Single base with 0.74% DPA and 0.48% DPa. | 135.5 | 0.656 | $9.49\,.\,10^{18}$ | [2] |
| C-2 | Linear + exponential | Single base with 0.74% DPA and 0.48% DPa. | 210.8** | - | $1.24\,.\,10^{29**}$ | [2] |
| | | | 114.2*** | - | $6.22\,.\,10^{15***}$ | |

[1] Krejčíř, F., Adam, J., & Buldra, R. (2021, June). Modeling of smokeless powders shelf life using results of multi-temperature study on stabilizer consumption. In *2021 International Conference on Military Technologies (ICMT)* (pp. 1-6). IEEE.

[2] Bohn, M. A. (2009). Prediction of In-Service Time Period of Three Differently Stabilized Single Base Propellants. *Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials*, *34*(3), 252-266.

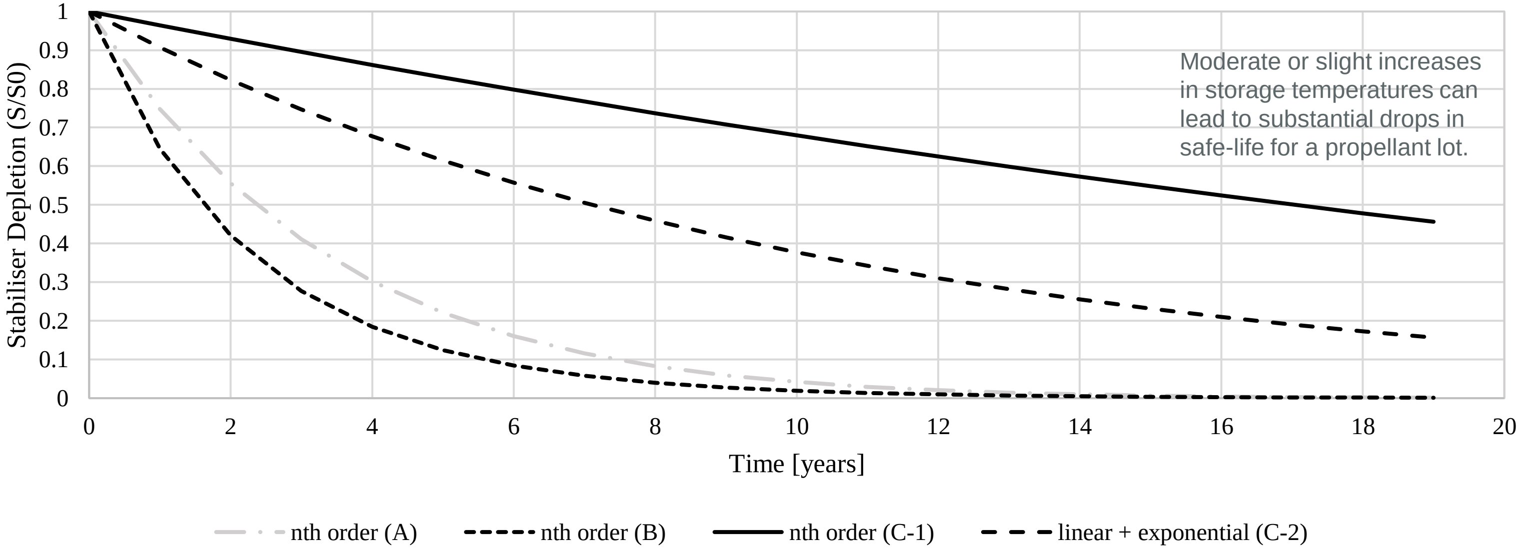
# Application 1: Stabiliser Depletion Modelling

**Figure 1** DPA stabiliser depletion models for different single base propellants at 25 degrees' Celsius storage



Models show good agreement for their respective propellant blends. They do however show the significant variability between different particular single base compositions.

**Figure 2** DPA stabiliser depletion models for different single base propellants at 35 degrees' Celsius storage



Moderate or slight increases in storage temperatures can lead to substantial drops in safe-life for a propellant lot.

# Application 2: Propellant Toxicity

- Reasons for environmental and personnel exposure
  - Increased domestic testing, proof testing and surveillance activities
  - New gun system design and inclusion of muzzle breaks
  - Operating in enclosed environments
  - Increasing or sustained usage of a product with personnel, such as increased training and duration
- Examples of different toxic products

| | | | |
|---|---|---|---|
| Ashpyxiants | Carbon Dioxide<br>$CO_2$ | Chlorine<br>$Cl_2$ | Hydrogen Cyanide<br>HCN |
| Irritant Gases | Hydrogen Chloride<br>HCL | Sulphur Dioxide<br>$SO_2$ | Nitrogen Dioxide<br>$NO_2$ |
| Inorganic irritants | Ammonia<br>$NH_3$ | Hydrogen Chloride<br>HCL | Phosgene<br>$COCl_2$ |
| Isocyanates | Methyl isocyanate<br>$C_2H_3NO$ | | |

# Application 2: Propellant Toxicity

- Toxicity

Table 3. Toxicity Products [1]

STEL – Short term exposure limit defined at 15 minutes duration
STID – Short term irreversible damage at 10 minutes duration

| Chemical component | STEL [ppm] | STID [ppm] | Normalised risk coefficient |
|---|---|---|---|
| Chemical Asphyxiant | | | |
| HCN | 10 | 17 | 24.71 |
| $CO_2$ | 15000 | - | |
| $CO$ | 200 | 420 | 1 |
| Irritant Gases | | | |
| HCL | ▨ | 100 | 4.2 |
| HBr | ▨ | 100 | 4.2 |
| HF | ▨ | 95 | 4.42 |
| $SO_2$ | ▨ | 0.75 | 560 |
| $NO_2$ | ▨ | 20 | 21 |
| Inorganic irritants | | | |
| Ammonia, $NH_3$ | 35 | 220 | 1.91 |
| Chlorine, $Cl_2$ | 1 | 2.8 | 150 |
| Phosgene, $COCl_2$ | 0.06 | 0.6 | 700 |
| Isocyanates | | | |
| Methyl isocyanate | ▨ | 0.4 | 1050 |

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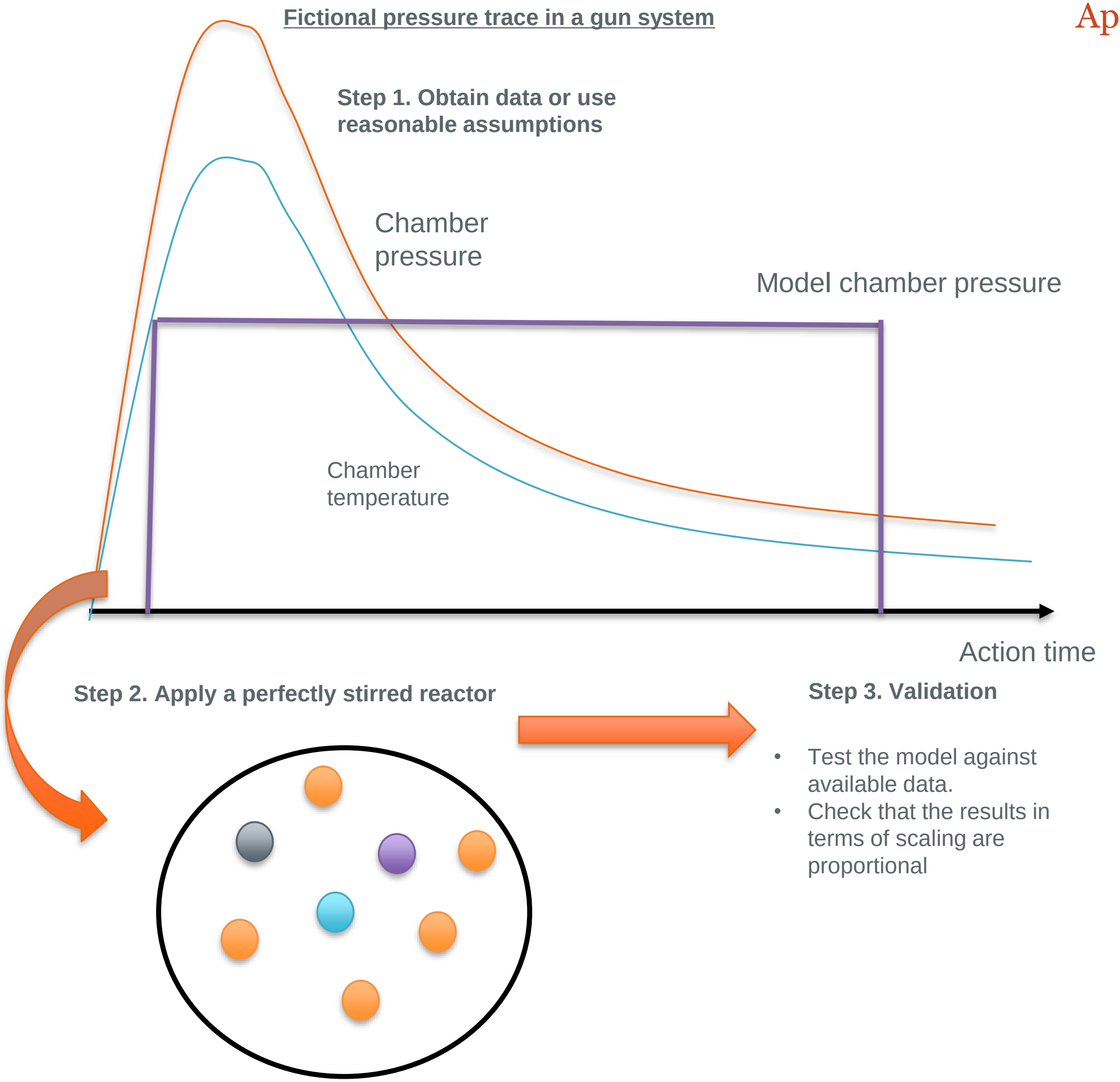
[1] Wakefield, J. C. (2010). *A toxicological review of the products of combustion*. Chilton, UK: Health Protection Agency, Centre for Radiation, Chemical and Environmental Hazards, Chemical Hazards and Poisons Division.

# Application 2: Propellant Toxicity



Fictional pressure trace in a gun system

**Step 1. Obtain data or use reasonable assumptions**

**Step 2. Apply a perfectly stirred reactor**

**Step 3. Validation**

- Test the model against available data.
- Check that the results in terms of scaling are proportional

Assumptions:

- Assume 80% goes to gaseous species for example.
- Internal chamber temperature is reasonably close to theoretical flame temperature.
- Frozen flow for expansion of gas products out of the chamber barrel or system enclosure.

**What do we need?**

Step 1

- Captured barrel pressure or calculated average barrel pressure.
- Captured peak chamber temperature or design temperature.

Step 2

- All energetic components in the composition and fractional weights
  (i.e NC-NG content)

Step 3

- More data the better, this allows us to test the validity of the model.

# Application 2: Propellant Toxicity

- What do we do with this initial data from a chemical kinetic model or benchtop study?
  - Use initial modelling data to focus in on potentially hazardous culprits in the experimental validation.
  - Modelling helps identify specific key species of interest.
  - Chemical mechanisms for single and double base gas phase combustion exist.
  - Computationally speaking this could all be conducted on a desktop computer.

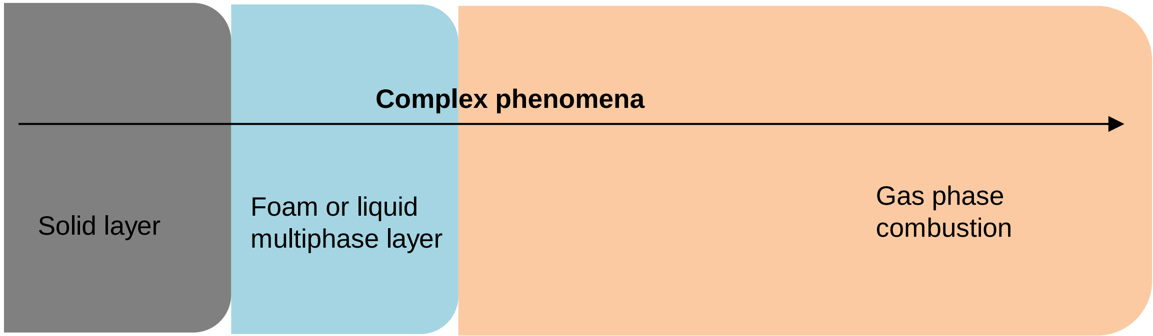
# Application 3: Solid motor and propellant internal modelling

- Changing suppliers – how does the performance compare? What are the changes in burn rates?

- Chemical kinetics could be used to:
  - Model different compositions in idealised environments to compare theoretical burn rates. Such as RDX-HTPB vs HMX-HTPB solid motors.
  - Tolerance or defect modelling for items which may yield higher burning surface area.
  - Provide early scoping of general technical requirements, and ascertaining theoretical compositional requirements for end product use.

# Application 3: Solid motor internal modelling

Combustion of our spherical propellant, cast-composite rocket



We can simply the problem itself by using the following approach

To bridge the gap, an appropriate model for describing pyrolysis and proliferation of the condensed or gas phase chemical species must be implemented.

$$\dot{m} = f(A_b, T_s, P_c)$$

$$\dot{m} = A_s \exp - \frac{E_a}{RT_s}$$

Complex and more difficult process to solve, and is system dependant

AP-HTPB

NC-NG

RDX-HTPB

Semi-empirical global kinetic equations which connect liquid-condensed phase to a more robust gas phase.

$$RDX \rightarrow 3H_2CN + 3NO_2$$

$$C_2H_4$$

Intermediate C-C chemistry

Detailed hydrocarbon or base gas-phase mechanism

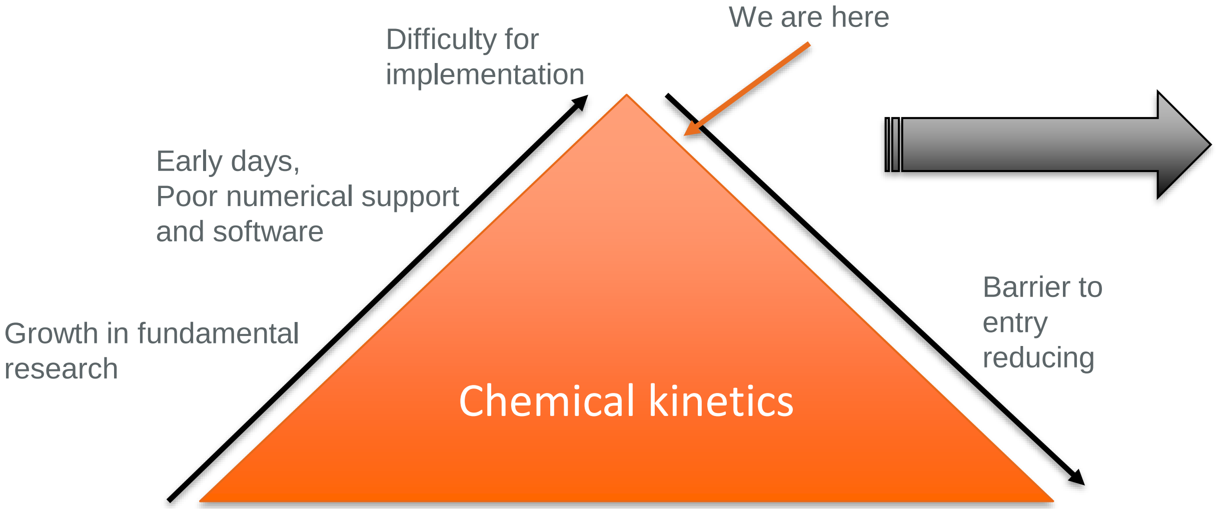
$$CH_3^* \; OH^* \; H^*$$

Radical chemistry

# Summary

Chemical kinetics:

- Developing internal tools can maximise engineering outputs, new capabilities.
- Progress in the direction of a smart consumer and user of energetics.
- The tools are readily available, mechanisms generated, and the hardware is easily accessible.



We are here

Difficulty for implementation

Early days,
Poor numerical support and software

Growth in fundamental research

Chemical kinetics

Barrier to entry reducing

Areas of interest:

- Emission modelling
- Fleet leader analysis
- Lifing digital twin for stabiliser depletion with environmental conditions.

- Questions ?