Anna final presentation (references not up to date due to file size)

by Anna Williams

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Pyrotechnics: from design to implementation

Anna Williams, Joshua Evans, and Will Noakes


“The art of fire is indeed the supreme art; for fire is at once the universal slave, the universal master” [1] –
Marvin Dana

Presentation Contents

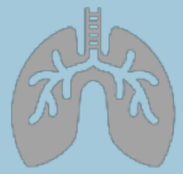
- What is a Pyrotechnic
- History
- Chemistry of Pyros
- Hazards
- Effects of Pyrotechnics:
  - Colour/smoke
  - Sound
  - Gas
- Air Countermeasures
- Alternatives and Future
- References



What is a pyrotechnic?



"Pyrotechnic" comes from the Greek for an art (*techne)* of fire *(pyr)*.



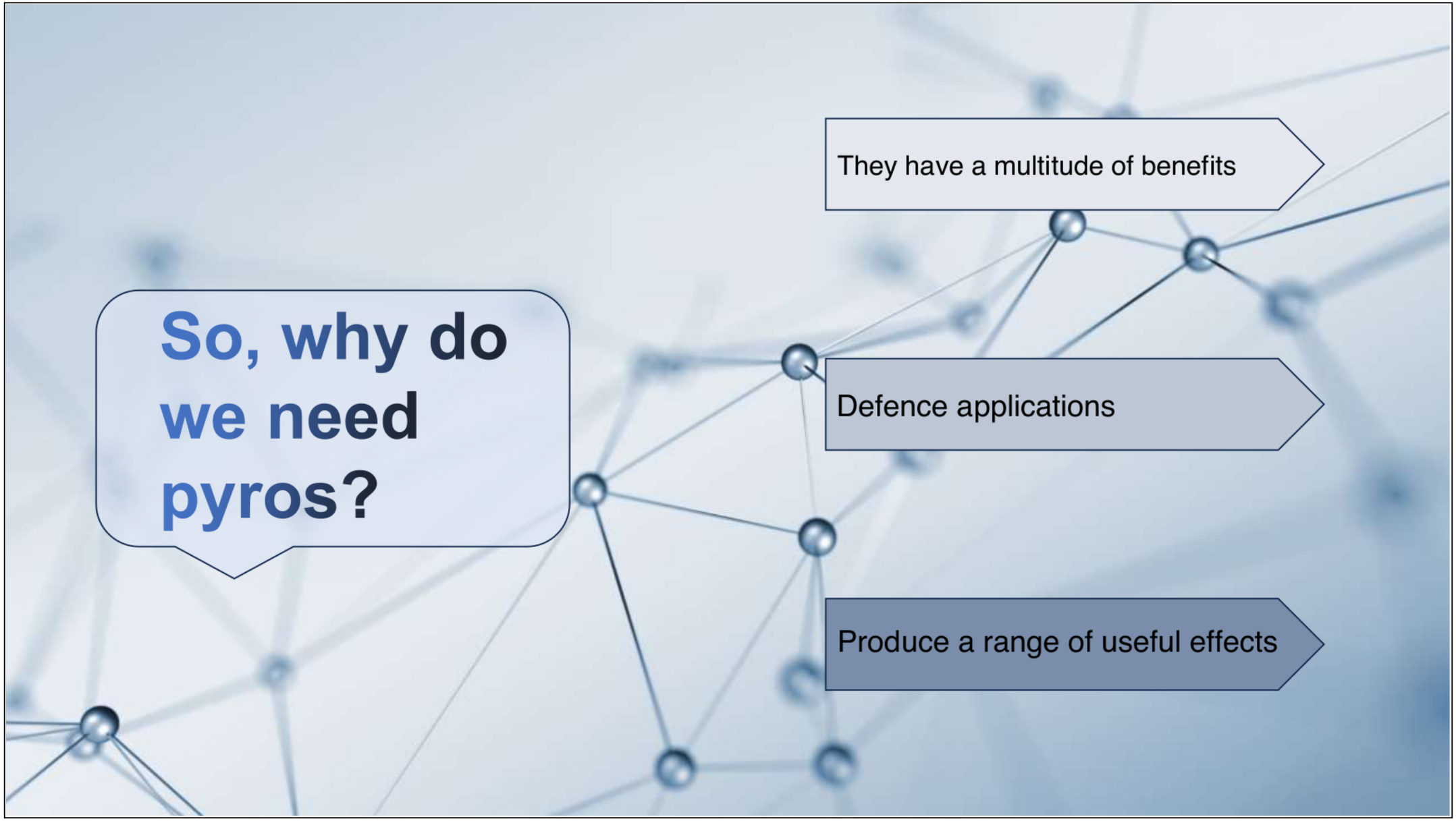
No external source of oxygen required!



They can perform on land and in water, air and space.

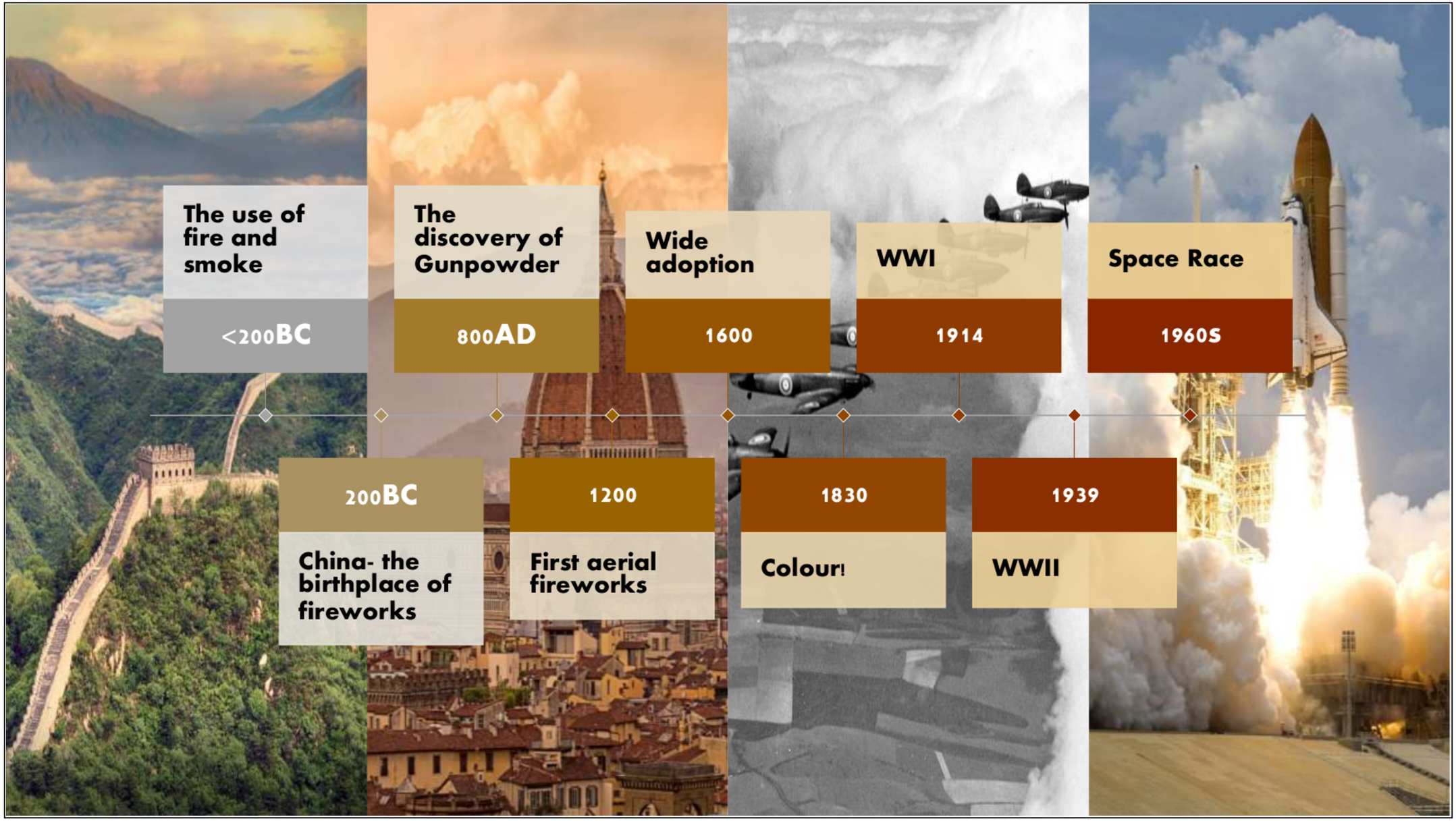


They can combust slowly (smoulder – mm/s), moderately (fast burn), or quickly (deflagration - m/s)


So, why do we need pyros?
They have a multitude of benefits
Defence applications
Produce a range of useful effects



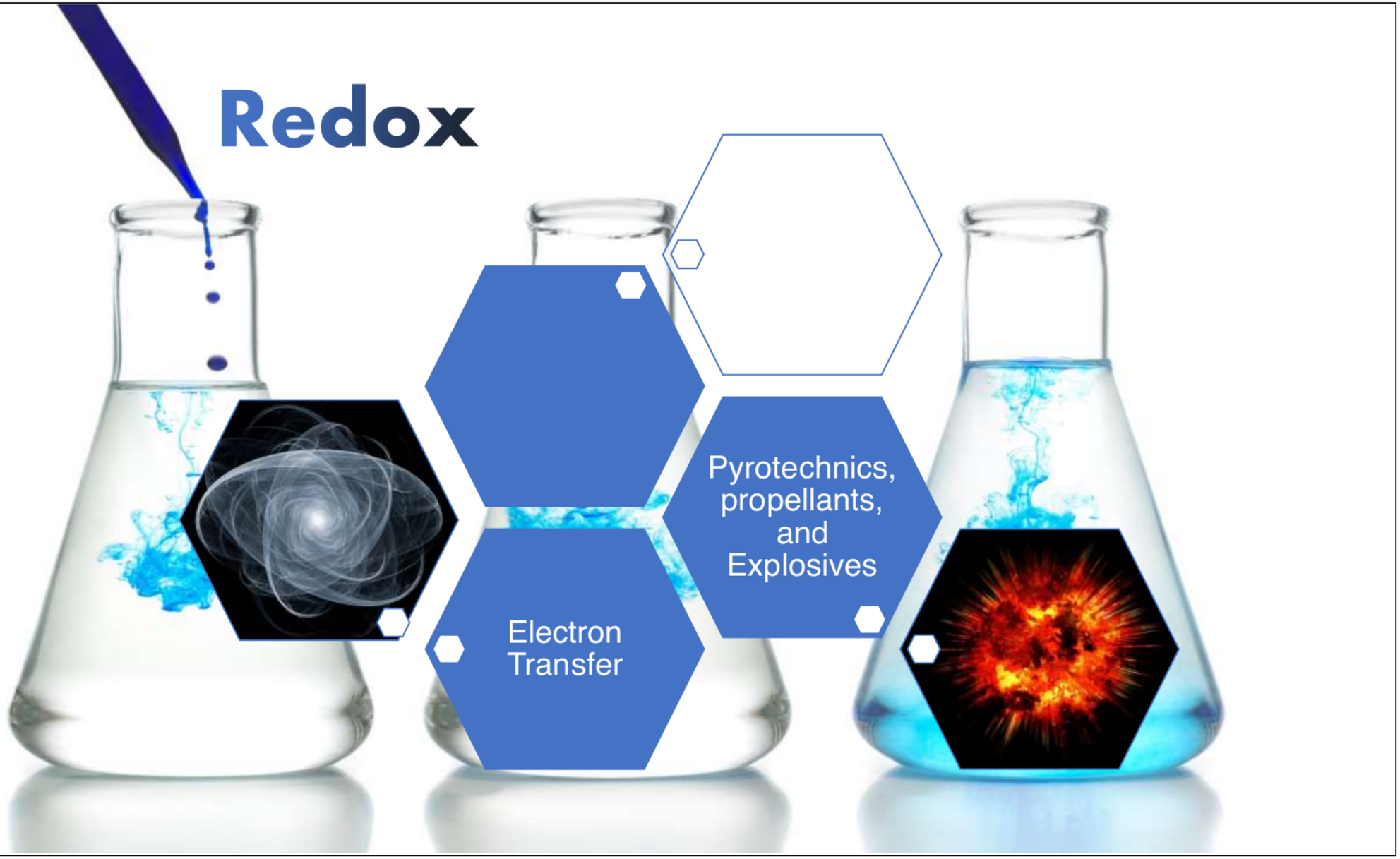
History of pyrotechnics


The use of fire and smoke
<200BC
The discovery of Gunpowder
800AD
Wide adoption
1600
WWI
1914
Space Race
1960S
200BC
China- the birthplace of fireworks
1200
First aerial fireworks
1830
Colour!
1939
WWII

Chemistry of Pyrotechnics



Redox


Electron Transfer
Pyrotechnics, propellants, and Explosives

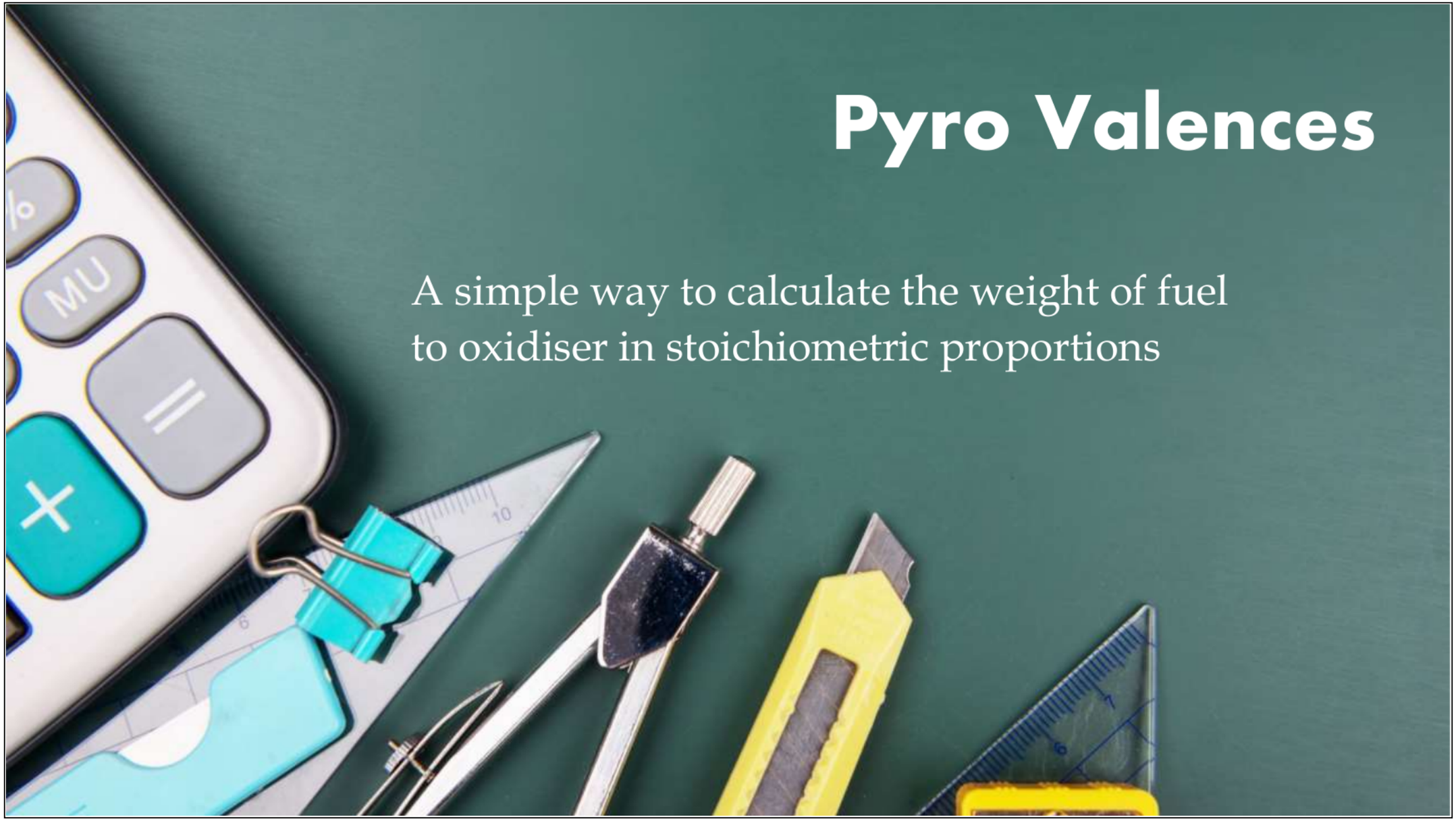
Electronegativity



Battery reactions are similar to pyrotechnic reactions



Electron donors and acceptors


Pyro Valences
A simple way to calculate the weight of fuel
to oxidiser in stoichiometric proportions

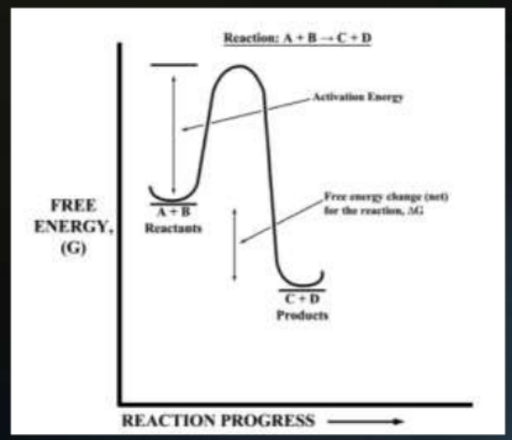
Thermodynamics

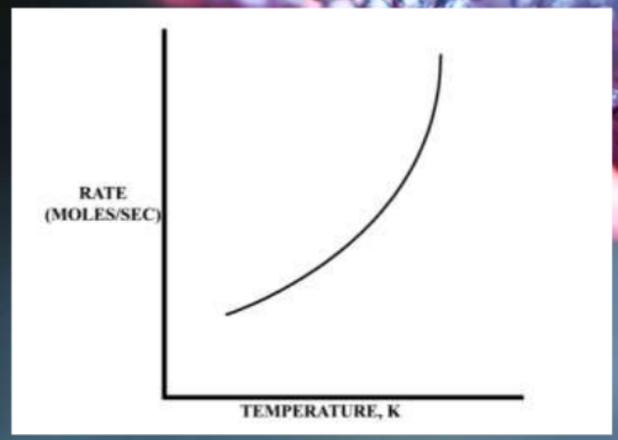
- Two major factors that dictate whether a desired reaction will occur:
  - Is the reaction spontaneous?
  - The reaction rate
- Negative enthalpy = exothermic reaction
  - Fe_2O_3 + Al = -0.96 kcal/g – used for Thermite
- Positive entropy corresponds with an increase in the randomness or disorder of the system when the reaction occurs.

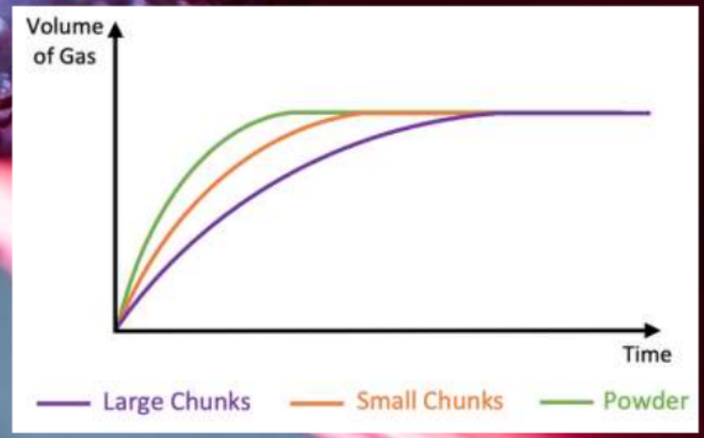
$$\Delta H(\text{reaction}) = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

- Also requires the energy of activation to be achieved.

Rate of Reaction







$$k = Ae^{-E_a/RT}$$

Oxidising agents





OXIDIZING AGENT

- Oxygen rich: oxygen donating, electron accepting
- Decompose at moderate to high temperatures
- Readily available in a reasonably pure form, in the correct particle size and at reasonable cost.
- Neutral reaction when wet
- Be stable over a wide temperature range (-55 C, up to 100 degrees C)
- Acceptable species include a range of anions, containing high-energy Cl-O or N-O bonds
- Must be low hygroscopicity. Water can cause problems in pyro mixtures, and materials that readily pick up water are usually avoided.
- The oxidiser's cation must not adversely affect the desired flame colour. Sodium for instance is an intense emitter of yellow-orange light, and its presence can ruin attempts to generate red, green, and blue flames.
- The alkali metals and alkaline earth metals are preferred for the positive ion.
- The compound must have an acceptable heat of decomposition
- Toxicity

TABLE 2.8
Standard Reduction Potentials

Half-Reaction	Standard Potential @25°C, in Volts[a]
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$CO_3^+ + e^- \rightarrow CO_2^+$	1.8
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4(s) + 2H_2O$	1.69
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.49
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H_+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96
$Hg^{2+} + 2e^- \rightarrow Hg$	0.85
$Ag^+ + e^- \rightarrow Ag$	0.8
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + e^- \rightarrow Cu$	0.52
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Cu^{2+} + e^- \rightarrow Cu^+$	0.15
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15

Fuels

- Needs to be good electron donor (high negative reduction potential)
- Forms an oxidised product and heat
- This heat allows for production of colour, motion, light, smoke, noise based upon the specific mixture
- **Fuel choice depends upon the requirements...**
- Heat required and rate of heat release
- Gas volume required
- Stability with the respective oxidiser in mixture
- **Fuel Types...**
- Metal fuels (aluminium, magnesium)
- Non-metallics (sulphur, boron)
- Carbohydrates (lactose, dextrin)

Standard Reduction Potentials

Half-Reaction	Standard Potential @25°C, in Volts (West 1994)
$2H^+ + 2e^- \rightarrow H_2$	0
$Fe^{3+} + 3e^- \rightarrow Fe$	–0.04
$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25
$CO^{2+} + 2e^- \rightarrow CO$	–0.29
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	–0.359
$PbI_2 + 2e^- \rightarrow Pb + 2I^-$	–0.365
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	–0.4
$Cd^{2+} + 2e^- \rightarrow Cd$	–0.4
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.41
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$	–0.83
$V^{2+} + 2e^- \rightarrow V$	–1.18
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18
$Al^{3+} + 3e^- \rightarrow Al$	–1.66
$Mg^{2+} + 2e^- \rightarrow Mg$	–2.37

[a] West (1994).

TABLE 3.7
Fuel Capacity/Pyro Valence of Some Common Binders

Binder	Monomer Unit	Grams/ Unit	Pyro Valence/Unit	Pyro Valence/ Gram
Paraffin	C_2H_4	28	+12	+0.429
Polybutadiene	C_4H_6	54	+22	+0.407
Waxes	$\sim C_{36}H_{72}O_2$	536	+212	+0.396
Linseed oil	$\sim C_{17}H_{30}O_2$	272	+100	+0.368
Polyvinyl alcohol (PVA)	C_2H_4O	44	+10	+0.227
VAAR (vinyl alcohol-acetate resin)	$C_6H_{10}O_5$	130	+28	+0.215
Polyvinyl acetate	$C_4H_6O_2$	86	+18	+0.209
Laminac®	$\sim C_{20}H_{30}O_9$	400	+78	+0.195
Polyvinyl chloride (PVC)	C_2H_3Cl	62.5	+10	+0.160
Dextrine, starch, and gums	$C_6H_{10}O_5$	162	+24	+0.148
Viton®	$C_2H_2F_2$	64	+8	+0.125
Alloprene (Parlon®)	$C_{10}H_{11}Cl_7$	380	+44	+0.116
Nitrocellulose	$C_{12}H_{15}N_3O_{10}$	389	+43	+0.111 (12.5% N)
Teflon®	C_2F_4	100	−4 (→C)	−0.040

Binders

- Contain a small percentage of binder (2-6% by weight)
- Homogenous blend
- Provides mechanical strength
- Also serve as an additional fuel.
- Generate gaseous products
- Can have separate reactions with fuel and oxidiser materials
- Reduce dust generation

Burn Rate Modifiers

Calcium carbonate

Magnesium carbonate

Guanidine nitrates and carbonates
(but in quantities low enough so as to avoid the risk of these causing detonation)

Design Considerations

- What is the requirement?
- Once the initial composition has been prepared and its reaction rate measured, the oxidiser/fuel ratio is varied in small increments to observe the effect on the reaction rate. This will give you both an insight into the effect of small changes in composition on the reactivity of the composition as well as an indication of whether you are close to the actual stoichiometric point for the primary reaction.
- Chemical analysis of the reaction products can be performed to verify that the primary reaction is the only that is actually taking place.
- Analysing a mixture by the pyro valence method consists of calculating the valence for a given mass (typically 100g for easier calculation) of the mixed composition.
    - Calculate the number of moles of each component in 100g mixture
    - Multiple the moles of each species by its pyro valence, to calculate the fractional valence for each component.
    - The individual valences are summed up to give the net valence for 100g of composition.
    - If the sum is negative, the mixture is oxygen rich; if it is positive, the composition is fuel rich; and if the net valence is 0, the mixture is stoichiometric.
- This method is scalable for systems with more than two components.
- There are computer models that can perform detailed calculations on energetic mixtures, but the pyro valence method gives you a quick insight into the fundamental nature of an energetic system and suggests the effect that various chemical additives might have on the system.

How to prep a pyrotechnic



Prep Ingredients



Prep composition



Mixing



Granulation



Drying



Pressing/Loading

Testing


Proof of function and proof of design
Static testing
Dynamic testing- test track
Platform trials

Hazards of pyrotechnics



High friction and impact sensitivities

Often high ESD and spark sensitivities

Sometimes harmful gaseous products

Toxicity of reactants

Deflagration to detonation transition

Notable Examples:

Potassium perchlorate

Lead tetroxide


Effects

Light

Sodium

$$E = h\left(\frac{c}{\lambda}\right)$$

E= 3.38 x 10^{-19} J

h = 6.63 X 10^{-34} J s

c = 3 x 10^{8} m/s

$$\lambda = \mathrm{h}\left(\frac{c}{E}\right)$$

$$\lambda = \frac{(6.63 \times 10^{-34})(3 \times 10^{8})}{3.38 \times 10^{-19}}$$

=5.89 x 10^{-7}m

=589 nm

Coloured Smokes



Pyrotechnic compositions mixed with solvent dye

Used for signaling, screening and also widely in the commercial/entertainment sector

Traditionally made from pyrotechnic fuel-oxidiser composition with solvent dyes

- Potassium chlorate or perchlorate
- Lactose or other sugars
- Solvent Dyes

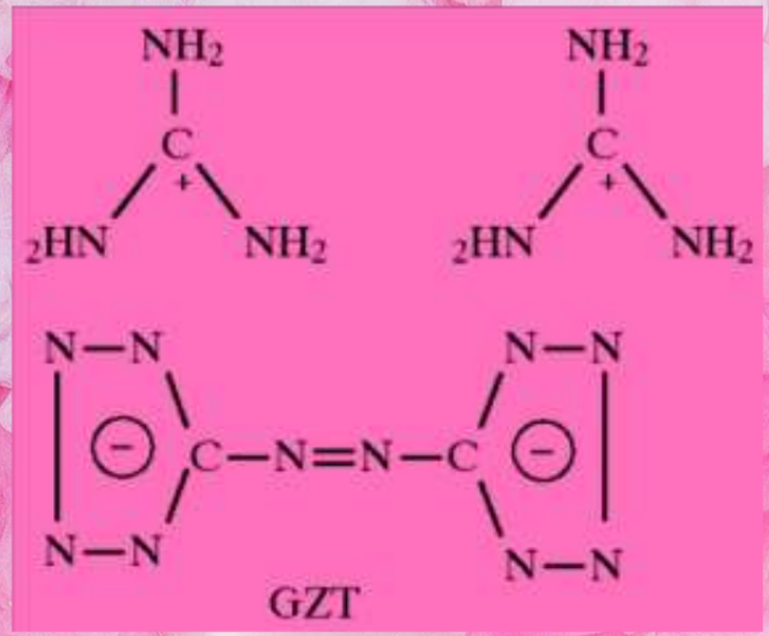
Problems with chlorate & lactose

- Toxic and environmentally harmful
- Can spontaneously and unpredictably react
- May produce carcinogenic chlorinated organic compounds
- Mixture has high sensitivity to impact and friction

Coloured Smokes - Future

Guanidinium 5,5, azotetrazolate or GZT

- **Produces similar visual effects to traditional smokes**
- **Single ingredient mixed with solvent dyes**
- **More stable mixture, with lower impact and friction sensitivity**
- **Reactant and products are non-toxic and don't harm the environment**



GZT

Paper link:
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7383485/

Pyrotechnics for sound

A variety of sounds can be produced using pyrotechnic mixtures...

Whistles

Crackles

Salutes



Gas Generating Pyrotechnics

- Ammonium perchlorate
- Air bag compositions

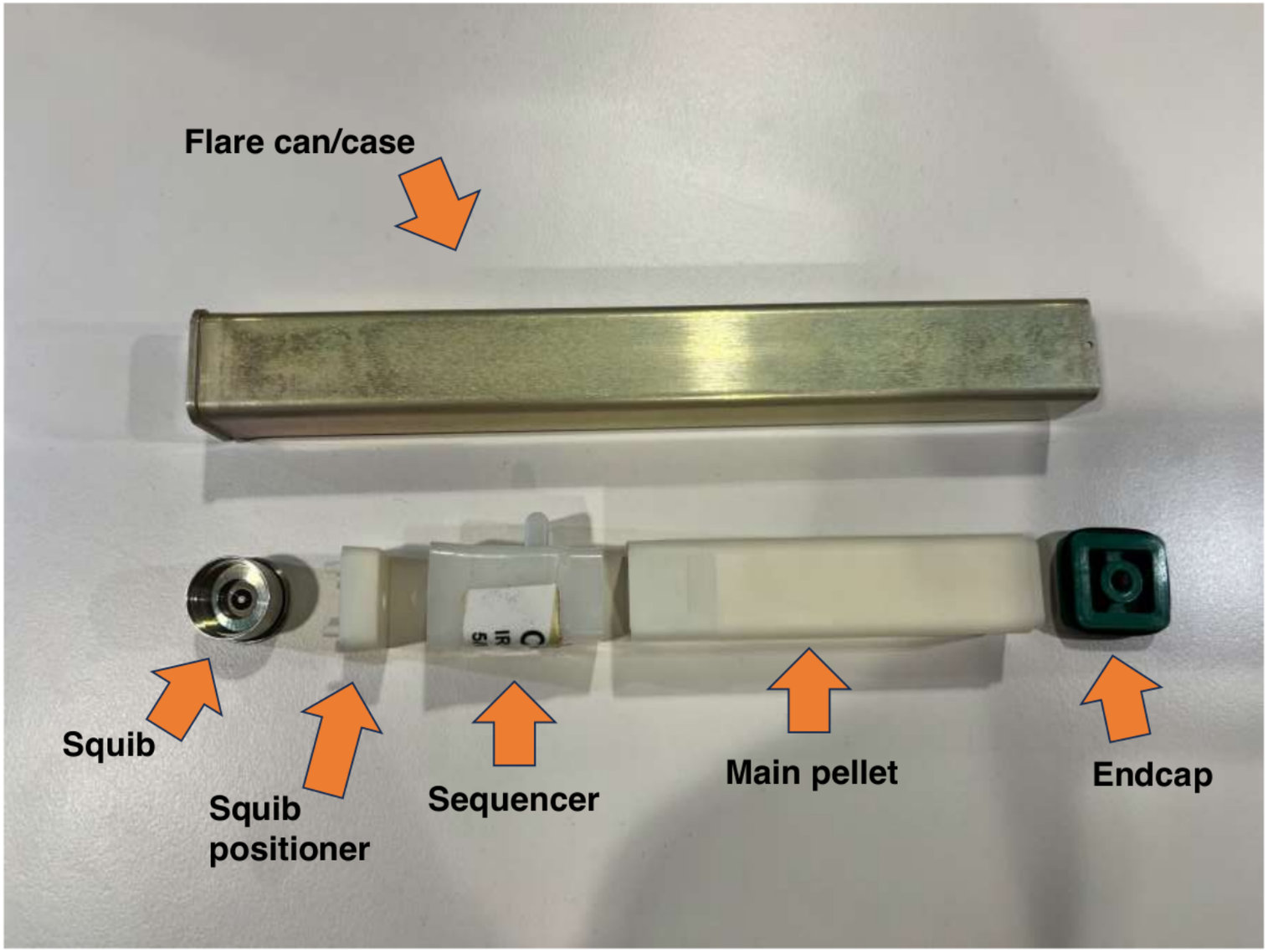


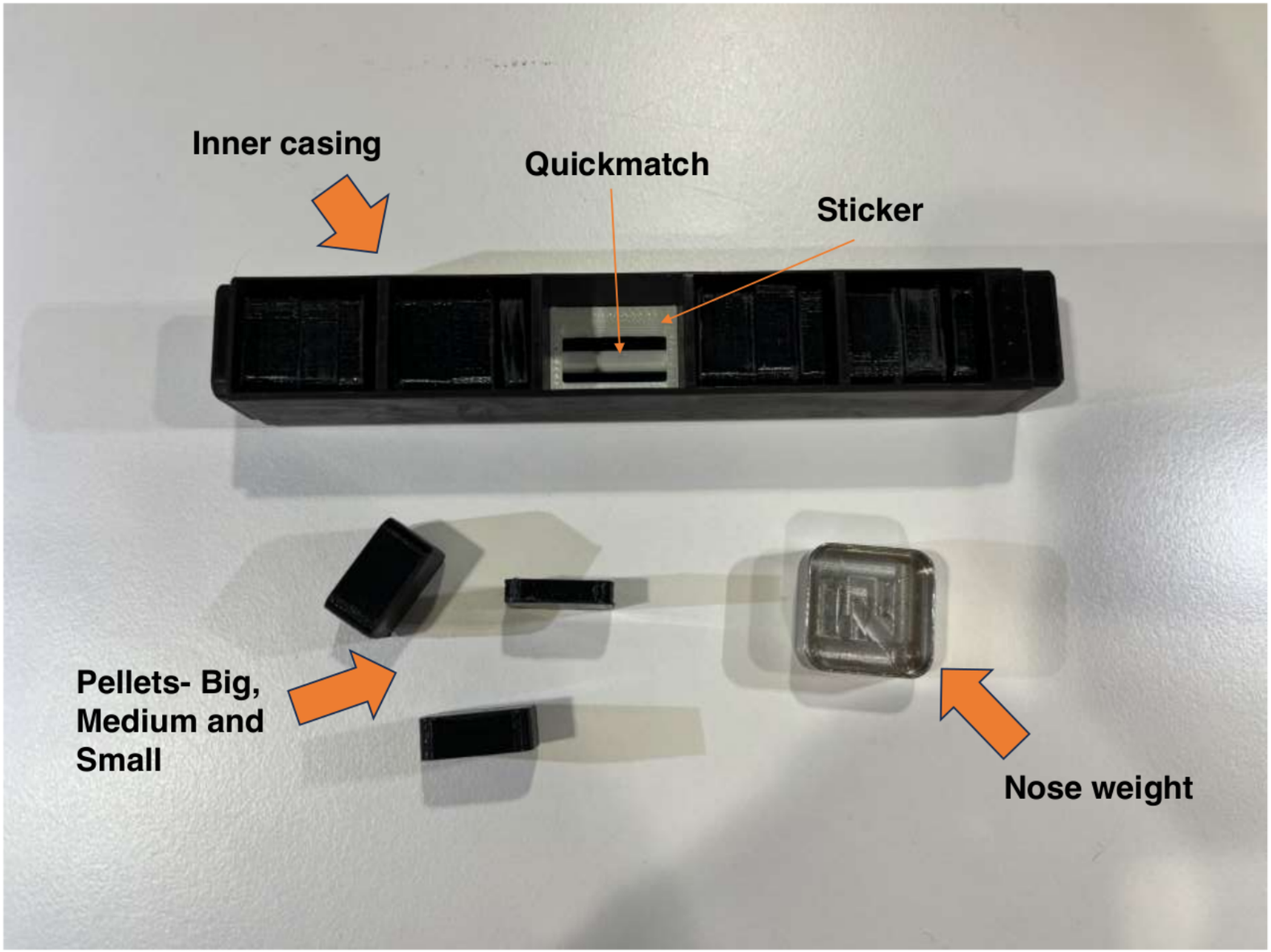
Pyros in Defence: Air Countermeasures

- Used to defeat IR missile threats
- Aim is to distract the missile from the aircraft to enable getaway for aircraft
- Mainly MTV, spectral compositions and smoke/obscurants
- Range of effects depending on threat and aircraft
- Tested at a range of speeds, temperatures and condition (i.e. Vibration)
- Usually in 118 or 218 formats





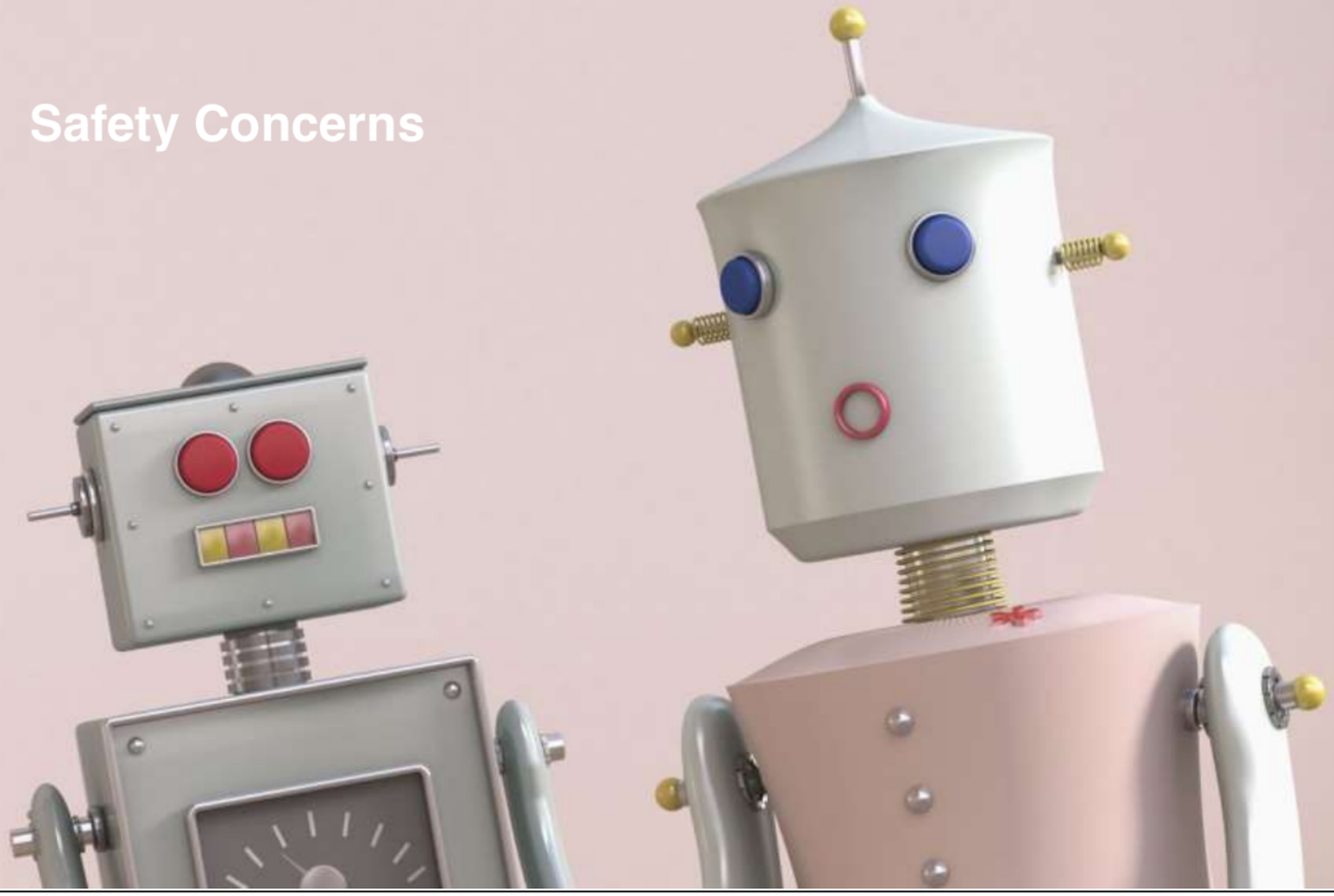

Flare can/case
Squib
Squib positioner
Sequencer
Main pellet
Endcap


Inner casing
Quickmatch
Sticker
Pellets- Big, Medium and Small
Nose weight

Future Developments

Threat dependant

Safety Concerns




The End.
Questions?

References

- https://ssec.si.edu/stemvisions-blog/evolution-fireworks
- https://www.todayifoundout.com/index.php/2013/10/explosive-history-fireworks/
- https://www.bulletpicker.com/pdf/Military%20Pyrotechnics,%20Vol%201.pdf
- Chemistry of Pyrotechnics, Basic Principles and Theory, 3rd Edition (2019) – John A. Conkling; Christopher J. Mocella
- GZT for smokes https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7383485/

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GRADEMARK REPORT

FINAL GRADE

65 /100

GENERAL COMMENTS

Engagement with literature (8/10)

You demonstrated excellent engagement with literature by selecting variety of relevant and credible sources.

IEEE format applied to all references.

In your future presentations/reports/etc use recent (within 5 years) sources and choose more books/journal articles than websites.

Knowledge and understanding skills (18/30)

Your knowledge and understanding of various chemistry areas relevant to pyrotechnic compositions was very good.

The logical progression of your ideas was evident.

For your next presentation consider delving deeper in the key aspects to show more comprehension.

Cognitive and intellectual skills (17/30)

You showed excellent ability to connect different ideas and synthesise information (redox, thermochemistry, kinetics vs preparation and testing of pyrotechnics) but this part of your presentation is rather descriptive and lacks deeper discussion. Next time try to be more analytical.

Practical skills (15/20)

The props you showed were well-chosen and effectively supported the key points of your presentation.

In your future presentations avoid reading from your notes. Use prompt cards (sparingly)

Transferable skills (7/10)

Fantastic team work and not most common (but very effective) way of sharing and delivering the content.

Very good time management.

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