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Do you know of someone in the chemical industry that is a dynamic speaker? Recommend them to be featured on ACS Webinars! For more information and to nominate please visit

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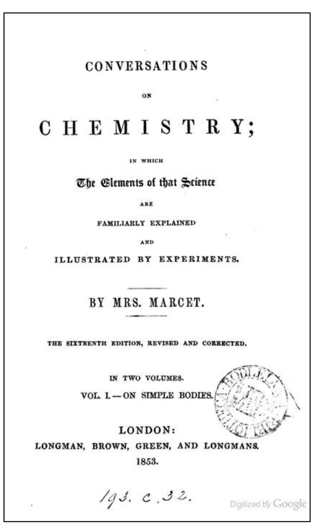
Today in Chemical History


CONVERSATIONS

ON

CHEMISTRY;

IN WHICH

The Elements of that Science

ARE

FAMILIARLY EXPLAINED

AND

ILLUSTRATED BY EXPERIMENTS.

BY MRS. MARCET.

THE SIXTEENTH EDITION, REVISED AND CORRECTED.

IN TWO VOLUMES.

VOL. I.—ON SIMPLE BODIES.

LONDON:

LONGMAN, BROWN, GREEN, AND LONGMANS.

1853.

Title Page to Conversations on Chemistry 1853

Jane Marcet passes away 1858

Jane Marcet Published Conversations on Chemistry in 1805 which was one of the first elementary science textbooks. It had16 editions in England, and was an early inspiration for the young Michael Faraday. The book was widely plagiarized in America.

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Upcoming ACS Webinars™
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Thursday, July 12, 2012

Chemicals and the Economy – Mid Year Review

Paul Hodges, International eChem
Bill Carroll, Occidental Chemical Corporation

Thursday, July 19, 2012

How Green Is Your Company…and How Do You Tell Your Story?

Dr. Karen Buechler Colorado Nanotechnology Alliance

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ACS WEBINARS™
June 28, 2012

Flash, Sound, and Smoke – Advanced Fireworks – The Sequel

Chris Mocella
Summer Pyrotechnic Seminars

Darren Griffin
University of Kent

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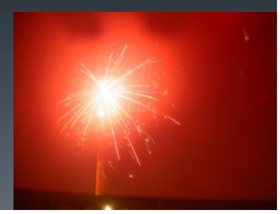
Advanced Pyrotechnics: Flash, Sound, and Smoke (oh my!)

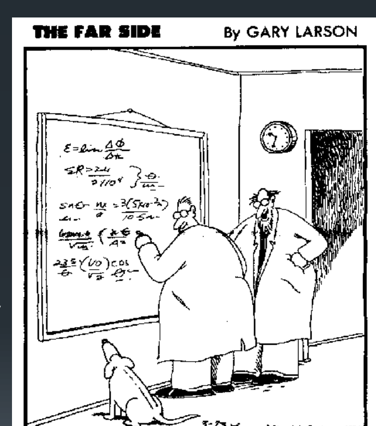
Chris Mocella (with many thanks to Dr. John Conkling)

ACS Webinar - June 2012



Review: The Chem 101 of Fireworks

- Redox Reactions
- Thermochemistry
- Stoichiometry
- States of matter
- Emission spectroscopy
- Surface chemistry



"Ohhhhhhh . . . Look at that, Schuster . . . Dogs are so cute when they try to comprehend quantum mechanics."

Review: Basics of Pyrotechnics

- Oxygen source (oxidizer) + electron source (fuel)
  → Products + Energy
- Energy Output =
  - Light (color)
  - Sound
  - Pressure
  - Motion
  - "The effect"

Ingredients for Pyrotechnic Mixes

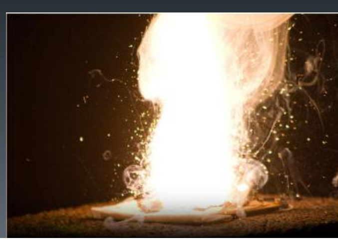
- Oxidizing Agents (oxygen rich, occasionally fluorine)
- Fuels (organic, metallic, other)
- Color ingredient
- Intensifier
- Binder (small %, can also act as a fuel)

- Charcoal + KNO_3 + Sulfur = Black Powder
- Light a match → CO_2, H_2O, K_2O, N_2, SO_2, "soot", and

ENERGY!

Flash Powder (Photoflash)

- Very hot + very fast = **very bright**
- Al (fine) + $KClO_4$
- Mg + Teflon + Viton (“MagTef” or “MTV”) – fluorine is the oxidant
- Zr + $KClO_4$ (“ZPP”) – V<u>ery</u> sensitive to heat/spark/friction ignition
- Mg + $Sr(NO_3)_2$ – Lower toxicity than perchlorates, red color of Sr is washed out by brightness



Photoflash Brightness

- Boiling points of the products (oxidized fuel) are the typical limiting factor in flame temperature (and overall brightness)
- Al_2O_3 b.p. = 2,980 ^oC
- MgO b.p. = ~3,600 ^oC
- ZrO_2 b.p. = ~5,000 ^oC!!
- Lose compositions: flash!
- Confined compositions: BOOM! → “flash bang”

Sound Production

- "Salutes" are produced through the rapid expansion of gas and generation of pressure waves:

1. Rapid heating of the ambient air by a confined composition
2. Rapid gas generation by the composition itself

- Sound can be in the form of a pop/boom/ crackle or "whistle"

Sound Production

The venerable M-80

- $KClO_4$ + Al + Sulfur + Antimony Sulfide (Sb_2S_3)
- Oxidizer + Fuel + Accelerants = a true explosive

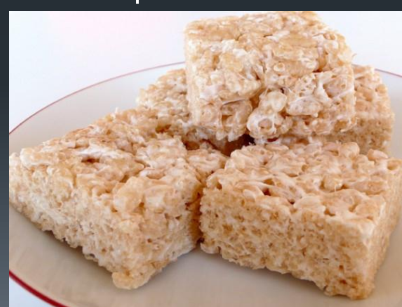
"Dragon Eggs" – Old formula

- Mg/Al + CuO + PbO_4 + Sulfur
- Fuel + Oxidizers + Accelerant (low melting/ignition point for sulfur)
- Flame temp ~3,600 ^{o}C
- SNAP! / POP! sound

Poll: What's that sound?

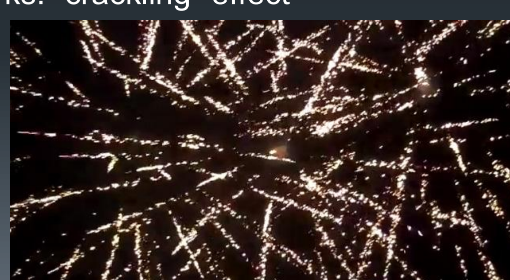
- Dragon Eggs: What makes the sound?

1. Rapid heating of the surrounding air
2. Confined gasses rapidly expand
3. Immediate generation and boiling of products
4. Small % Rice Krispies included for effects



Dragon Eggs:

- Mg/Al is oxidized, Pb is reduced to elemental state
- Flame temperature is ~3,600 ^{o}C, but b.p. of lead is ~1,750 ^{o}C
- "CRACK!" as lead vapor is produced rapidly
- New formula uses BiO_3, less toxic
- Commercial fireworks: "crackling" effect

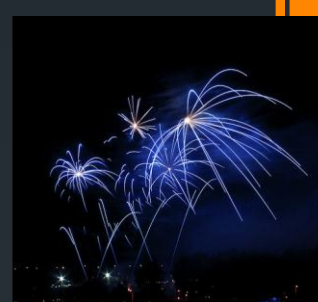


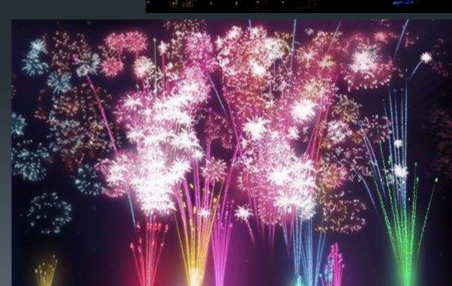
Whistles!

- Just like when a person whistles, forced air through a small opening generates a whistle sound
- Potassium beznozate + $KClO_4$ → lots of CO_2 and H_2O generated rapidly (but not too rapidly)
- Composition is pressed into a suitably sized tube (larger diameter tubes tend to deflagrate/detonate)
- Whistle reactions are prepared to be on the verge of, but not actually, explode – very careful!
- A whistle composition is actually burning intermittently from layer to layer in a pressed composition, and the pitch will drop as the composition burns down and a “longer” tube is left
- Other fuels: Gallic acid, sodium salicylate, potassium hydrogen phthalate

Color Production

- Produced through emission of vapor-state species in the flame
- Red - strontium compounds
- Orange - calcium compounds
- Blue - copper compounds
- Green - barium or boron compounds
- Yellow - sodium atoms (strong “d-line”)
- Violet - strontium and copper





Blue Flare Composition

- NH_4ClO_4 – Oxidizer/chlorine donor
- $KClO_4$ – Oxidizer/chlorine donor
- Copper carbonate – oxidizer and copper source for blue color
- Red Gum – organic fuel
- Dextrin – fuel and binder
- Fleeting CuCl- radical species emit blue color.
- Flame can't get too hot (wash out or decompose CuCl- species)

Old Green Flame Composition

- Mg – fuel
- $Ba(NO_3)_2$ – Oxidizer and barium source
- $Ba(C_2O_4)$ – Oxidizer and barium source
- Wonderful green color!

- But…
- Barium can be toxic and cost prohibitive in bulk quantities
- Alternative: boron

New Green Flame Composition

- Sabatini et al., Angew. Chem. Int. Ed. 2011, 50, 4624-4626
- Substitution of boron compounds for barium
- KNO_3 + Boron carbide (B4C) + Binder
- Comparable burn times, luminescence, color purity:

Barum-based

B_4C-based

Smoke Production

- Most pyrotechnic reactions produce some amount of smoke, although it is avoided so it does not obscure color/flame.
- Smoke production may be desirable in certain situations
- Smoke can be produced through two common methods:

1. Generate smoke through combustion products
2. Vaporize and re-condense a material in the air - fog

Combustion Smokes

- $KClO_3$ + Sulfur + Naphthalene – **Black Smoke**

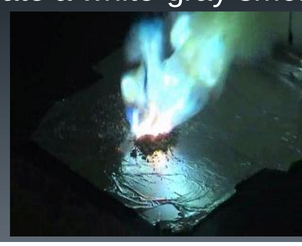
→ Incomplete combustion of naphthalene leads to "cracking" and sooty particles, a very thick black smoke

- KNO_3 + Sulfur + Sb_2S_3 – **White** Smoke

→Sublimation of sulfur

- Zn + Sulfur – **Gray** Smoke

→ Formation of ZnS_2, which condenses in the air and attracts water to create a white-gray smoke



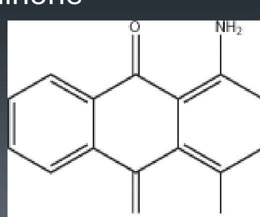
Vaporization Smokes

- Need to burn hot enough to vaporize the material, but not so hot to burn (destroy) it – tricky balance!
- Often use $MgCO_3$ to "cool" the mixture → CO_2 + MgO
- Sugar + $KClO_3$ + $MgCO_3$ + Synthetic Wax

→ White Smoke from wax "fog"

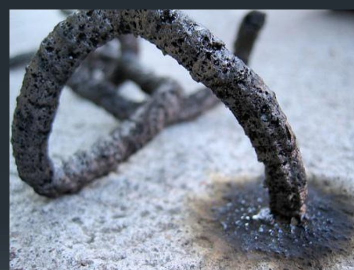
- Sugar + $KClO_3$ + $MgCO_3$ + Violet Dye

→ Violet smoke from dye 1,4-diamino-2,3-dihydro-anthraquinone



Other Effects: Snakes!

- Snakes: Generation of sticky ash, pressed into a pellet to burn in one direction:



- KNO_3 + Dextrine + $NH_4Cr_2O_7$

→Cr_2O_3 ash has a high volume (but is also hexavalent chromium ☹)

Other Effects: Strobes

- Essentially a flash powder with additives pressed into a pellet
- Mg/Al + NH_4ClO_4 + Ca_2SO_4

→The Mg/Al and NH_4ClO_4 will react to "flash"

→The Mg/Al and calcium sulfate will react and "smolder", covering the top later

→The fuel and oxidizer will react and break through the layer to "flash"

→Repeat, repeat, repeat

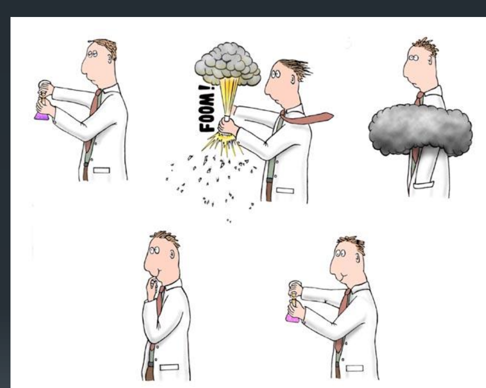
- Color additives can be included
- Fireworks shows: gives the "twinkling" effect

"Green" Fireworks – The Perchlorate Problem

- Perchlorates, ClO_4^-, make <u>excellent</u> oxidizers: high oxygen amount, good stability, low cost, good reactivity with fuels, great for producing red and green colors
- Problem: high stability of perchlorates means that they persist in the environment and are linked to thyroid disorders, replacing iodide (I^-) in the body
- Alternatives are being explored, such as nitrates for commercial fireworks and periodates (IO_4^-) for military applications
- Research is ongoing…

Safety!

- All pyrotechnic compositions are sensitive to some form of stimulus: heat/flame, spark, shot, friction, shock
- Every effort needs to be made to handle materials safely
- Do not experiment with chemicals that you do not understand!



Other Resources

- A.A. Shidlovskiy, Principles of Pyrotechnics
- T. Shimizu, Fireworks, The Art, Science, and Technique
- J.A. Conkling, C.J. Mocella, Chemistry of Pyrotechnics
- Journal of Pyrotechnics, Pyrotechnic Chemistry
- American Pyrotechnics Association
- **Local hobbyist clubs and groups**

Thanks For Attending!

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