Possible Applications for Computer Codes in the Development of Pyrotechnic Compositions

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The following letter contains some comments on the possible applications for computer codes in the development of pyrotechnic compositions. It is hoped to stimulate more discussion on the practical applications of thermodynamic computer codes in the development of pyrotechnic compositions. (For example, for modeling colored compositions).

In brief, if one has the possibility to choose from various fuels and oxidizers, and wants to predict possible pyrotechnic reactions, simple balanced stoichiometric equations may, in some cases, be reasonably fine. But in other situations, one wishes to have more information, such as the reaction products that can be formed, and at what temperature. Certain thermodynamic computer codes can calculate these for you. (They give you reaction products and temperatures—and more—from given compositions. Most modern PC's require a very short runtime, and it is often possible to feed large numbers of compositions to them in one run.) These codes were originally developed for rocket propellants.[1,2] There are a number of different codes; two are listed in the Table. The idea of using the output from a thermodynamic code for theoretical modeling of pyrotechnic illumination compositions was apparently first described by Dr. Bernard Douda.[3] Theoretical modeling of pyrotechnic color compositions has also been described by Arno Hahma.[4] Ramohalli[5] described modeling gas generators. Vladimiroff[6] calculated flame temperatures of propellants.

Name	Comments
NASA Lewis CEA	Computer code from NASA Lewis[1]
PROPEP	A version of the NWC Propellant Evaluation Program (PEP) that was provided by the NSWC during 1988. This program is basically the PEP program written by D. R. Cruise at NWC described in NWC TP 6037 titled "Theoretical Computations of Equilibrium Compositions, Thermodynamic Properties, and Performance Characteristics of Propellant Systems".[2]

CEA = Chemical Equilibrium with Application
NWC = Naval Weapons Center
NSWC = Naval Surface Weapons Center

It is important, for this application, to use the results of such a 'tool' with proper care, before attempting to derive conclusions from it. One has to be aware of various limitations. Some examples of limitations are:

- The output often does not tell anything about kinetics (rate at which the chemical reactions take place).
- Calculations are based on minimization of free energy; equilibrium is assumed.
- Programs have difficulty converging when many solids are present.
- Flames have many different shapes, which are not modeled, influencing their radiative performance.[7]
- Accurate input data for fireworks binders/fuels may not always be available.

The 'useful' output, for this situation, is the predicted reaction products and temperatures. In case one is interested in modeling a colored-fire composition, the output can be used to calculate a ratio between 'desired emitters' and 'undesired emitters' of a color composition. Arno Hahma named this a 'quality factor' (Q). For example, for an imaginary barium magnesium flare, a simple Q could be calculated by:

$$Q = \frac{a[\mathrm{BaCl}]}{b[\mathrm{BaO}] + c[\mathrm{MgO}]}$$

in units of mole per mole.

Calculating less simplified Q's would seem more appropriate, but it is beyond the scope of this letter. Gradual changes in composition lead to new values of Q, which allows one to optimize it. If the trend of Q as a function of composition does not correlate with what one sees in real life, one has to go back to the 'drawing table' on how to calculate more accurate Q's. At the moment work on this is ongoing.

The effort to predict radiated spectra from combustion of energetic materials appears to overlap with more than just one military application. For example, the radiation emitted from exhaust plumes of solid rocket propellants has been modeled since the 1960's and probably earlier.[8,9,10] Also other related combustion phenomena have been modeled.[11,12]

In conclusion, I would like to emphasize that this approach is not new, and that it is not my idea. These codes have advantages and disadvantages. Interested readers are encouraged to react.* (This letter has been kept short and, needless to say, there is much more to it.) I am greatly indebted to Arno Hahma, Dr. Bernie Douda, and Bonnie McBride for providing their help.

* Arno Hahma added to this "the codes are still much better than back of the envelope calculations. You can get close to the optimum quickly and do the fine tuning with traditional methods (i.e., experimentation)."

References

1) S. Gordon and B. J. McBride, "Computer Program for Calculating Complex Chemical Equilibrium Compositions and Applications. I. Analysis", NASA Reference Publication 1311, October 1994.

2) E. D. Brown, "An Introduction to PROPEP, A Propellant Evaluation Program for Personal Computers", *Journal of Pyrotechnics*, Issue 1, 1995.

3) B. E. Douda, "Radiative Transfer Model of a Pyrotechnic Flame", AD-769237, NAD/RDTR-258, September 1973, pp 14-15.

4) A. Hahma, "Theoretical Modeling of Some Pyrotechnic Mixtures", *International Symposium on Energetic Material Technology, ADPA Proceedings*, September 24-27, 1995, Phoenix, Arizona, USA.

5) T. Vladimiroff et al., "Flame Temperature Calculations at High Temperature and Pressure", *Propellants, Explosives, Pyrotechnics*, Vol. 19, 1994, pp 281–285.

6) K. Ramohalli, "Combustion Modeling of Explosive Pyrotechnics", paper 12, *Proceedings of the International Annual Conference ICT 1988*, "Combustion and Detonation Phenomena", Karlsruhe, Germany, 1988.

7) A.G. Gaydon and H.G. Wolfhard, *Flames, Their Structure, Radiation and Temperature*, Chapman and Hall, 4th ed., 1979.

8) E. J. Beiting, "Predicted Optical Characteristics of Solid Rocket Motor Exhaust in Stratosphere", *Journal of Spacecraft and Rockets*, Vol. 34, No. 3, May-June 1997.

9) L. Deimling et al., "Radiation Emitted from Rocket Plumes", *Propellants, Explosives, Pyrotechnics*, Vol. 22, 1997, pp 152–155.

10) Victor Technology's page on the Internet http://members.aol.com/victec

11) Chang Eun Choi et al., "Numerical Analysis of a Gray Combustion with Nongray Radiation Using Weighted Sum of Gray Gases Model", *Combustion Science and Technology*, Vol. 115, 1996, pp 297–315.

12) W. Eckl et al., "Spectroscopic Investigation of Nitromethane Flames", *Propellants, Explosives, Pyrotechnics*, Vol. 22, 1997, pp 180–183.