Comment on:


Having read Clive Jennings-White's excellent article on glitter chemistry, I have revisited the writings of M. Stanbridge on this topic.

The following refers to material published in Stanbridge’s letter in *Pyrotechnica* XII, June 1988, p 3 ff.

1. On page 4, there is a table of thermodynamic quantities associated with various “flash reactions”, calculated for a temperature of 3800 K. These are not consistent. If the $\Delta G$ values are calculated from the listed $\Delta H$ and $\Delta S$ values using $\Delta G = \Delta H - T \cdot \Delta S$, the results are very close to the listed values for 4 of the 5 reactions. The calculated $\Delta G$ value for the $\text{Al}_4\text{C}_3/\text{K}_2\text{SO}_4$ reaction, however, differs from the published one by over a factor of 2.

2. A temperature of 3800 K was used by Stanbridge because this is the “limiting temperature” reached in the flash. It would be more appropriate to use the temperature at which the flash initiates, which, according to Stanbridge, is around 1100 °C (1373 K). When his numbers are recalculated using this temperature, however, they do not change the arguments that follow, which apply equally well in either case.

3. Stanbridge appears to have been confused about the significance of $\Delta G$ and $\Delta H$. $\Delta G$ indicates the “driving force” behind a chemical reaction. Fundamentally, it is derived from the change in entropy of the Universe that would result if the reaction occurred. If $\Delta G$ is negative, the entropy of the universe will increase when the reaction proceeds to equilibrium, and the reaction will be thermodynamically spontaneous. Once initiated, the reaction will spontaneously proceed to equilibrium. If $\Delta G$ is large and negative, the equilibrium position will overwhelmingly favor the products. This is the case for all the reactions he lists. That means that if all
that Al$_2$S$_3$ is the fuel in the flash reaction. I have calculated the $\Delta H$ value independently, using data from the *CRC Handbook of Chemistry and Physics* and confirmed that $\Delta H$ is indeed large and positive as Stanbridge’s figures indicate.

4. Of the reactions between a fuel and K$_2$SO$_4$, the one having the most negative $\Delta H$ (i.e., the greatest heat output) is the Al/K$_2$SO$_4$ reaction. This is so whether one calculates the heat per gram of Al (relevant if K$_2$SO$_4$ is present in excess) or the heat per gram of K$_2$SO$_4$ (relevant if Al is in excess).

5. My calculations indicate that if all the Al were to be converted to Al$_4$C$_3$ before the flash reaction, the effect would be to *lower* the heat output of the flash reaction by about 38%. This is assuming excess K$_2$SO$_4$ and calculating the heat evolved *per gram of Al*. Alternatively, the reaction could be assumed to be limited by the availability of K$_2$SO$_4$. Calculation of the heat evolved *per gram of K$_2$SO$_4* then indicates that the heat output of the flash reaction is reduced by 59% if all the Al is converted to Al$_4$C$_3$ before the flash reaction. This is consistent with the observations of Clive Jennings-White on the reaction of Al$_4$C$_3$ with K$_2$SO$_4$, compared to that of Al and K$_2$SO$_4$.

6. Stanbridge wrote “… the rate at which the reaction proceeds is not indicated by the free energy magnitude”. This is absolutely correct. The kinetics will be at least as important as the thermodynamics in determining what actually happens. He then writes, “An initial examination of the rate equations for these reactions does, however, suggest that the Al$_4$C$_3$/K$_2$SO$_4$ reaction should be faster than the others.” This almost throw-away line actually implies a great deal. The “rate

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Published $\Delta H$ (kJ/mol)</th>
<th>Published $\Delta S$ (kJ/K)</th>
<th>Published $\Delta G_{3800}$ (kJ/mol)</th>
<th>Calculated $\Delta G_{3800}$ (kJ/mol)</th>
<th>Ratio Pub./Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_4$C$_3$/K$_2$SO$_4$</td>
<td>-1274</td>
<td>0.269</td>
<td>-5074</td>
<td>-2372</td>
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<tr>
<td>Al$_4$C$_3$/O$_2$</td>
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<td>-0.575</td>
<td>-2141</td>
<td>-2137</td>
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<tr>
<td>Al/O$_2$</td>
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<td>-980</td>
<td>-977</td>
<td>1.00</td>
</tr>
<tr>
<td>Al/K$_2$SO$_4$</td>
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<td>-0.386</td>
<td>-2190</td>
<td>-2189</td>
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<td>+1772</td>
<td>1.698</td>
<td>-4545</td>
<td>-4680</td>
<td>0.97</td>
</tr>
</tbody>
</table>
equations” could only be derived if one knew the detailed mechanism for these reactions. If Stanbridge has indeed worked out the mechanisms and figured out the rate equations, it was very modest of him not to have provided more details. Even today, the kinetics of much simpler high-temperature solid state or heterogeneous reactions than these is controversial. See, for example, “Forty years of electrothermal atomic absorption spectrometry. Advances and problems in theory”, Boris V. L’vov, Spectrochimica Acta Part B, 52, (1997) 1239-1245 and references therein.

7. Setting aside the question of whether or not the rate equations for these reactions are known, it has to be said that Stanbridge’s claim that “the Al₄C₃/K₂SO₄ reaction should be faster than the others” does not really support his case. If the reaction were indeed faster than the others, the Al₄C₃ would be consumed quickly. How, then, could enough accumulate to cause the flash? Whatever the flash reaction is, it must have a sufficiently high activation energy to allow the reactants to persist unreacted to quite a high temperature.

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