Communications

Brief technical articles, comments on prior articles and book reviews

Comment on:

Glitter Chemistry, Issue 8.

Having read Clive Jennings-White's excellent article on glitter chemistry, I have re-visited 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 ΔG values are calculated from the listed ΔH and ΔS 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 ΔG value for the Al_4C_3/K_2SO_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 ºC (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 ΔG and ΔH. ΔG 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 ΔG 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 ΔG 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

the reactants were present at the temperature being considered, the reactions would *all* be thermodynamically spontaneous. Stanbridge writes "The Al_4C_3/K_2SO_4 reaction increases its output with temperature, exceeding all the others in its output". Here he clearly is using 'output' to mean ΔG. Curiously enough, the values of ΔG calculated from his ΔH and ΔS values do *not* give the most negative ΔG to the Al_4C_3/K_2SO_4 reaction. That honor belongs to the Al_2S_3/K_2SO_4 reaction. See the Table.

that Al_2S_3 is the fuel in the flash reaction. I have calculated the ΔH value independently, using data from the *CRC Handbook of Chemistry and Physics* and confirmed that ΔH is indeed large and positive as Stanbridge's figures indicate.

4. Of the reactions between a fuel and K_2SO_4, the one having the most negative ΔH (i.e., the greatest heat output) is the Al/K_2SO_4 reaction. This is so whether one calculates the heat per gram of Al (relevant if K_2SO_4 is present in excess) or the heat per gram of K_2SO_4 (relevant if Al is in excess).

T = 3800 K Reaction	Published			Calculated	Ratio
	ΔH (kJ/mol)	ΔS (kJ/K)	ΔG_{3800} (kJ/mol)	ΔG_{3800} (kJ/mol)	Pub./Calc.
Al_4C_3/K_2SO_4	–1274	0.289	–5074	–2372	2.14
Al_4C_3/O_2	–4322	–0.575	–2141	–2137	1.00
Al/O_2	–3352	–0.625	–980	–977	1.00
Al/K_2SO_4	–3656	–0.386	–2190	–2189	1.00
Al_2S_3/K_2SO_4	+1772	1.698	–4545	–4680	0.97

Obviously the flash reaction must be spontaneous, and once initiated must proceed to completion (the equilibrium position must overwhelmingly favor the products), so its ΔG must be large and negative. The magnitude of ΔG, however, has *no relevance* to the "energy" of the flash reaction as perceived by an observer. The relevant quantity is ΔH. The released enthalpy of reaction, indicated by ΔH, increases the temperature of the reaction products and causes them to emit light. The flash reaction must be highly exothermic, so its ΔH must be large and negative.

There are many examples of processes having a large negative ΔG (i.e., they are thermodynamically spontaneous, and the equilibrium overwhelmingly favors the products) but which absorb heat from the surroundings (i.e., they have a positive ΔH). The melting of ice is one example; the dissolving of ammonium nitrate in water is another. For a third example, we need only look at Stanbridge's figures for the Al_2S_3/K_2SO_4 reaction. This reaction is thermodynamically spontaneous, but it has a positive ΔH. That is to say, when this reaction takes place, it soaks up heat from the surroundings. This, by the way, refutes the Troy Fish theory

5. My calculations indicate that if all the Al were to be converted to Al_4C_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_2SO_4 and calculating the heat evolved *per gram of Al*. Alternatively, the reaction could be assumed to be limited by the availability of K_2SO_4. Calculation of the heat evolved *per gram of* K_2SO_4 then indicates that the heat output of the flash reaction is reduced by 59% if all the Al is converted to Al_4C_3 before the flash reaction. This is consistent with the observations of Clive Jennings-White on the reaction of Al_4C_3 with K_2SO_4, compared to that of Al and K_2SO_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_4C_3/K_2SO_4 reaction should be faster than the others." This almost throw-away line actually implies a great deal. The "rate

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 Al_4C_3/K_2SO_4 reaction should be faster than the others" does not really support his case. If the reaction were indeed faster than the others, the Al_4C_3 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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