Apparent Anomalies in Correlations for Theoretical Rocket Thrust with Shifting Equilibrium

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PREVIOUSLY mentioned[1] were empirical correlations between 1) the theoretical enthalpy drop in the combustion products of rocket propellants on equilibrium expansion from 1000 psia to 1 atm, and 2) the propellant heat of reaction at 298°K. These applied when the heat values were the average per mole of major (i.e., "effective") species regardless of their degrees of dissociation at rocket conditions, and with the systems grouped with respect to the average number of atoms per mole of effective species. In this note, apparent anomalies in the correlations are mentioned.

When a system includes monatomics from the noble gases, the correlations do not hold. This is exemplified by the theoretical data computed for the $(BF_3)(He)$ formulation, which does not fit the (appropriate) 2.5 atoms/mole locus curve taken from Fig. 4 of Ref. 1, as shown in Fig. 1 of this note. On the other hand, the system $(BF_3)(F)$, which comprises similar proportions and types of species but has a reactable monatomic instead of a noble gas, provides theoretical data that fit the proper locus curve. Apparently, then, interreactions between effective species are required to achieve the compensatory changes that underlie the correlations.

When a system is formulated so that carbon dioxide should be an effective species, the correlations do not hold. This is exemplified in Fig. 2, where the system (CO_2) does not fit the 3.0 atoms/mole locus. Carbon dioxide is the only multiatomic product uncovered so far which 1) apparently can be unambiguously predicted to be an effective species from the system formulation, but 2) does not fit the correlations. Its uniquely anomalous character apparently results from the extraordinary stability of CO, whose atoms do not enter into the over-all CO_2 equilibrium to the free extent required.

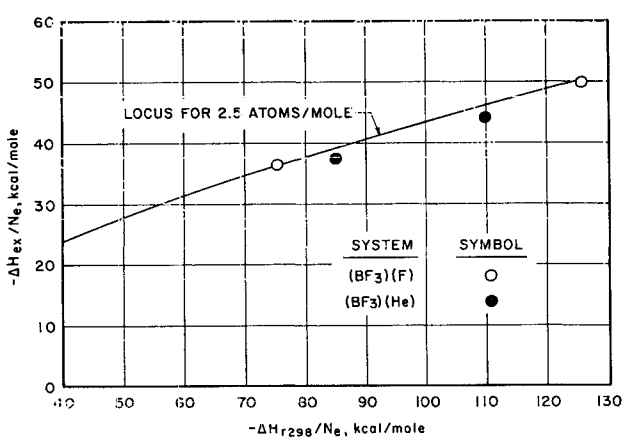

Fig. 1 Theoretical energy conversions of $(BF_3)(F)$ and $(BF_3)(He)$ systems (1000 psia/1 atm, shifting expansion).

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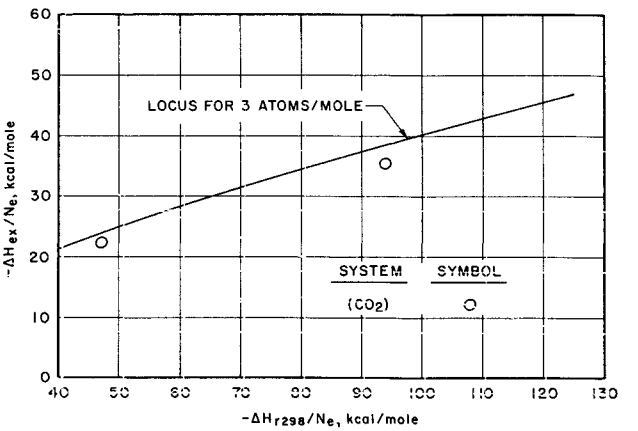

Fig. 2 Theoretical energy conversions for (CO_2) system (1000 psia/1 atm, shifting expansion).

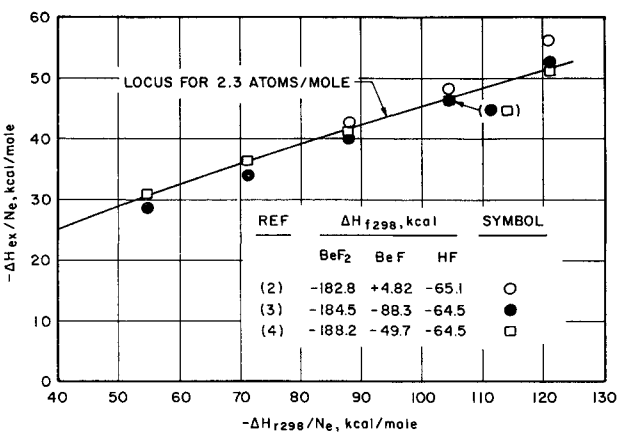

Fig. 3 Theoretical energy conversions for $(BeF_2)(HF)_2$ system with diverse ΔH_{f298} of its products (1000 psia/1 atm, shifting expansion).

When the thermodynamic data used in computation of theoretical thrust are inconsistent, the correlations do not hold. This is exemplified in Fig. 3 for $(BeF_2)(HF)_2$, with sets of points computed for the three heats-of-formation series given on the figure. The latter include the "accepted" values from the recent past, as given in Refs. 2–4, and have notable changes for BeF. The latest set, from Ref. 4, is considered very reliable and provides theoretical data that, alone, fit the appropriate 2.3 atoms/mole curve.

To summarize, the empirical rocket thrust correlations mentioned in Ref. 1 appear invalid when the constituent species are incapable of chemical interreaction, when an assumed effective species is derived from constituents of extraordinary stability, and when inconsistent thermodynamic data are used.

References

[1] Greiner, L., "Correlations for theoretical rocket thrust with shifting expansion," J. Spacecraft Rockets **1**, 339–340 (1964).

[2] Stull, D. R., *JANAF Thermochemical Tables* (The Dow Chemical Co., Midland, Mich., December 31, 1960).

[3] Stull, D. R., *JANAF Thermochemical Tables* (The Dow Chemical Co., Midland, Mich., September 30, 1961).

[4] Stull, D. R., *JANAF Thermochemical Tables* (The Dow Chemical Co., Midland, Mich., March 31, 1963).