

# The Paradox of Thermodynamic Instability

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## Abstract

The constraints on the Gibbs free energy equation required to intercompare the stabilities of chemical species are reviewed, and the concept of thermodynamically unstable but kinetically stable compounds is defined. A method for synthesizing these compounds is then discussed based on a rule first stated by the French chemist, Pierre Macquer, in 1749, and its modern application illustrated using several concrete examples. A simple graphical method for visualizing trends in thermodynamically stable versus thermodynamically unstable compounds is then introduced and illustrated with example plots. The paper concludes with a brief note on terminology.

**Keywords:** kinetic stability, thermodynamic stability, synthesis, terminology

## 1. Introduction

Most introductory chemistry textbooks intended for the use of science and engineering students contain a discussion of the Gibbs free energy equation (Moore & Stanitski, 2015; Silberberg & Amateis, 2021; Gillespie et al., 1986):

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta H^\circ - T\Delta S^\circ + RT \ln Q \quad [1]$$

where  $\Delta G$  is the Gibbs free energy change,  $\Delta H^\circ$  is the standard enthalpy change,  $T$  is the absolute temperature,  $\Delta S^\circ$  is the standard entropy change, and  $Q$  is the activity quotient, which in introductory texts is usually approximated either as a concentration or partial pressure quotient.

Application of this equation to the question of whether a given chemical species – be it a nonmolecular solid, a discrete molecule, or an ion – is or is not thermodynamically stable requires that one first answer the question “stable with respect to what?” In other words, one must first specify a particular mode of formation or decomposition for the species in question in the form of a balanced chemical reaction before applying equation 1. Furthermore, one must also specify the temperature and pressure, as well as the value of  $Q$ . All of these constraints mean that, if one wishes to intercompare the thermodynamic stabilities of a wide variety of different species, then all of these factors must be kept constant.

## 2. Standard Gibbs Free Energy of Formation

This intercomparison is usually accomplished using a concept known as “the standard Gibbs free energy of formation.” This sets the values of  $T$  and  $P$  at the “standard state” values of 298.15 K and 1 bar (approximately 1 atm.), respectively, and the value of  $Q$  at 1 – thus eliminating the  $RT \ln Q$  term in equation 1. As for the particular mode of formation, this is defined as the Gibbs free energy for the formation of one mole of a given species from its constituent simple substances when all of the reactants and products are in their standard states. Under these constraints equation 1 reduces to:

$$\Delta G_{std. st.} = \Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ \quad [2]$$

where the superscripted  $^\circ$  sign indicates that the equation is restricted to standard state conditions and the subscripted  $f$  sign indicates that it applies only to the formation of a mole of a given species from its constituent simple substances in their standard states. It is the resulting standard state of formation values for  $\Delta G_f^\circ$  and  $\Delta H_f^\circ$  that are listed in compilations of thermodynamic data (Wagman, 1982; Stull et al., 1969; Karapet'yants & Karapet'yants, 1970; Lide, 2005). However, by way of contrast, these tables list only the absolute standard state entropy values,  $S^\circ$ , for each species, and these must, in turn, be used to calculate the corresponding  $\Delta S_f^\circ$  values. (Alternatively,  $\Delta S_f^\circ$  values can be calculated from the equation  $\Delta S_f^\circ = (\Delta H_f^\circ - \Delta G_f^\circ)/T$ ). Since the reactants and products for the formation of mole of a simple substance from itself are identical, the corresponding values of  $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$ , and  $\Delta S_f^\circ$  for the simple substances in their standard states are all zero by definition.

Many textbooks unintentionally leave the impression that  $\Delta G_f^\circ$  must be negative in sign if a given chemical species is to exist – a requirement shown in the Gibbs free energy - reaction coordinate diagram in Figure 1.

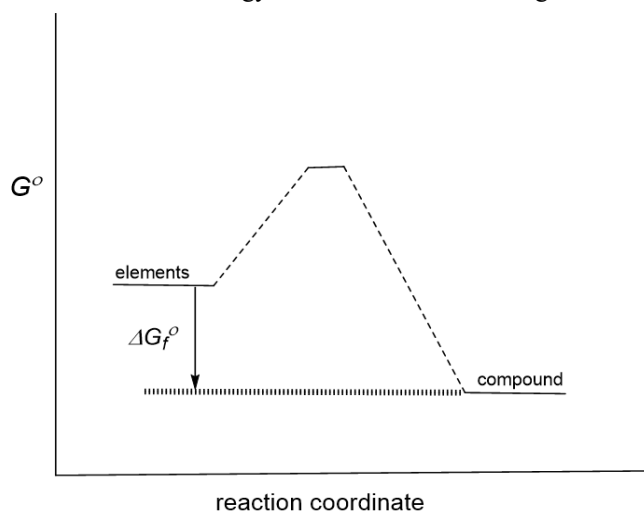


Figure 1.  $G^\circ$  versus reaction coordinate diagram for a compound for which  $\Delta G_f^\circ < 0$

This is equivalent to the assumption that only thermodynamically stable species exist. However, consultation of  $\Delta G_f^\circ$  tables quickly reveals that this is not true and that, in fact, many well-known chemical species have positive values for  $\Delta G_f^\circ$  – a situation shown in the corresponding diagram in Figure 2. In other words, many known chemical species are actually thermodynamically unstable relative to their constituent simple substances in the standard state.

The rationale for these apparent exceptions is also shown in Figure 2. Though such species have positive  $\Delta G_f^\circ$  values, they also have a large activation energy relative to their decomposition into their more thermodynamically stable constituent simple substances, and it is their resulting sluggish kinetics of decomposition once they are formed that accounts for their existence. For this reason, such species, though thermodynamically unstable, are said to be “kinetically stable.”

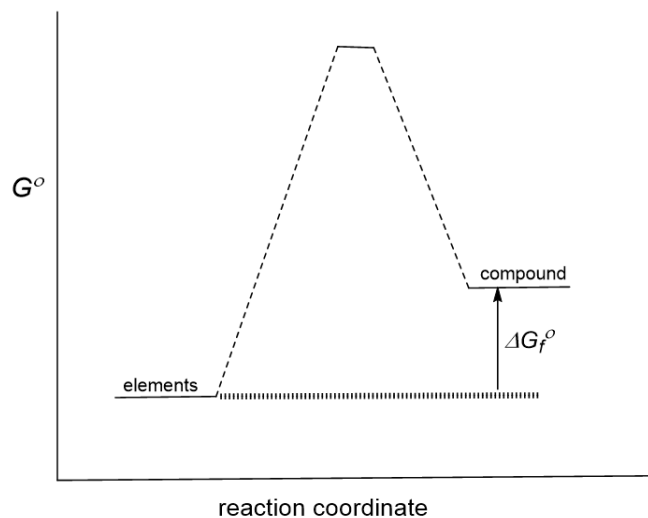


Figure 2.  $G^\circ$  versus reaction coordinate diagram for a compound for which  $\Delta G_f^\circ > 0$

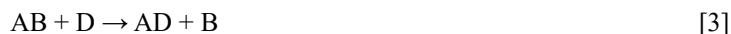
However, Figure 2 also reveals an inherent dilemma. If the activation energy for the decomposition of a species into its constituent simple substances is large, then the activation energy for its formation from those same simple substances must be even larger – so how can one directly synthesize such species? One approach is to pump in enough energy to ensure a practical rate of formation. Thus, thermodynamically unstable ozone gas is synthesized from thermodynamically stable dioxygen gas using a high voltage electrical discharge (Bauer, 1960), and even more extreme conditions of temperature and pressure are required to synthesize thermodynamically unstable diamonds from thermodynamically stable graphite (Hazen, 1999). But is there an easier, indirect route to the synthesis of thermodynamically unstable but kinetically stable species? The answer is yes, and surprisingly, it was first stated in the 18th century.

### 3. Macquer's Rule

In 1749 the French chemist, Pierre Macquer, published a textbook entitled *Elemens de chymie theoretique*, in which he listed seven laws of chemical affinity, the last of which read, in the somewhat awkward English of the 1764 British translation (Macquer, 1764):

*A body, which of itself cannot decompose a compound consisting of two substances, because ... they have a greater affinity with each other than it has with either of them, becomes nevertheless capable of separating the two by uniting with one of them, when it is itself combined with another body, having a degree of affinity ... sufficient to compensate for its own want thereof. In that case there are two affinities, and hence ensues a double decomposition and a double combination.*

What Macquer is saying here is that, if one has a compound AB and one is trying to decompose it to form a compound AD:

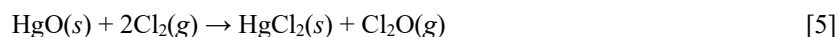


but the affinity between A and D is too weak to affect the decomposition, then one should react AB with compound CD to form compound AD with CB as a by-product in which C and B have a very strong mutual affinity:



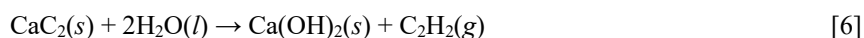
In short, one can make the weakly stable compound AD from AB if one makes the strongly stable compound CB at the same time.

Translating Macquer's rule into modern language, it is telling us that we can synthesize a thermodynamically unstable but kinetically stable compound with a positive  $\Delta G_f^\circ$  value if we use a reaction in which its by-product has a value of  $\Delta G_f^\circ$  sufficiently negative to offset this unfavorable value and so make the value of  $\Delta G_r^\circ$  for the overall reaction negative as well. As an example, take the synthesis of  $\text{Cl}_2\text{O}(\text{g})$ , which has a  $\Delta G_f^\circ$  value of +97.9 kJ/mol, using the reaction:



Here the value  $\Delta G_f^\circ$  for the  $\text{HgCl}_2$  by-product (-178.6 kJ/mol) is sufficiently negative to offset the unfavorable  $\Delta G_f^\circ$  value for  $\text{Cl}_2\text{O}$  and to give the overall reaction a favorable  $\Delta G_r^\circ$  value of -22.5 kJ/mol.

A more common example is the synthesis of acetylene ( $\Delta G_f^\circ = +209.2$  kJ/mol) from calcium carbide and water:



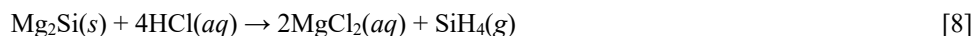
Here the value of  $\Delta G_f^\circ$  for the  $\text{Ca}(\text{OH})_2$  by-product (-898.49 kJ/mol) is sufficiently negative to offset the unfavorable  $\Delta G_f^\circ$  value for  $\text{C}_2\text{H}_2$  and to give the overall reaction a favorable  $\Delta G_r^\circ$  value of -105.23 kJ/mol.

Similarly, for the traditional preparation of laughing gas or dinitrogen oxide ( $\Delta G_f^\circ = +104.2$  kJ/mol) via the thermal decomposition of ammonium nitrate:

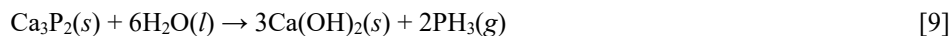


Here the value of  $\Delta G_f^\circ$  for the  $2\text{H}_2\text{O}$  by-product ( $2 \times -237.13$  kJ/mol) is sufficiently negative to offset the unfavorable  $\Delta G_f^\circ$  value for  $\text{N}_2\text{O}$  and to give the overall reaction a favorable  $\Delta G_r^\circ$  value of -186.2 kJ/mol.

Yet other examples of this approach to the synthesis of thermodynamically unstable compounds include the synthesis of silane ( $\Delta G_f^\circ = +56.9$  kJ/mol) from dimagnesium silicide and hydrogen chloride:



and the synthesis of phosphine ( $\Delta G_f^\circ = +13$  kJ/mol) from tricalcium diphosphide and water:



### 4. A Graphical Approach

Thermodynamic data are frequently presented in graphical form in order to make trends and intercomparisons more obvious. Examples include the use of Frost diagrams ( $zE_{\text{ox}}^\circ$  versus oxidation state) in the field of transition metal chemistry (Frost, 1951), Ellingham diagrams ( $\Delta G_r^\circ$  versus  $T$ ) in the field of metallurgy (Ellingham, 1944), and Pourbaix diagrams or Eh-pH diagrams ( $E_{\text{ox}}^\circ$  versus pH) in both the fields of geochemistry (Brookins, 1988) and corrosion science (Pourbaix, 1974). The same can be done when introducing students to the apparent paradox of thermodynamically unstable but kinetically stable compounds. Rather than looking for scattered examples by poring through boring tables of thermodynamic data, this concept can be visually summarized using a simple  $xy$  plot of the two parameters in equation 2 (i.e., of  $\Delta H_f^\circ$  versus  $-T\Delta S_f^\circ$ ) for the species of interest.

This plot has four quadrants, with the standard state values of  $\Delta H_f^\circ = 0$  and  $-T\Delta S_f^\circ = 0$  for the simple substances lying

at the origin in the center. In the lower left quadrant  $\Delta H_f^\circ$  and  $-T\Delta S_f^\circ$  are both negative so  $\Delta G_f^\circ$  is also negative and any species falling into this quadrant will automatically be thermodynamically stable with respect to its constituent simple substances. In the upper right quadrant, both  $\Delta H_f^\circ$  and  $-T\Delta S_f^\circ$  are positive so  $\Delta G_f^\circ$  is also positive and any known species falling into this quadrant will be automatically be thermodynamically unstable but kinetically stable with respect to its constituent simple substances. For both the upper left and lower right quadrants  $\Delta H_f^\circ$  and  $-T\Delta S_f^\circ$  have opposite signs and the question of whether  $\Delta G_f^\circ$  is negative or positive will depend on which term is larger. In these cases, we have drawn a diagonal parity line through these quadrants such that all known species lying above this diagonal fall into the thermodynamically unstable but kinetically stable region, whereas all those lying below the diagonal fall into the thermodynamically stable region. Though such plots can be made for any species for which the necessary thermodynamic data are available, in the following sample plots we will, for reasons of simplicity, restrict ourselves to neutral binary compounds.

Figure 3 shows such a plot for some selected binary compounds of carbon (for convenience, this will be called a stability plot). As may be seen, acetylene, benzene and ethene all fall within the thermodynamically unstable region, whereas carbon monoxide, carbon dioxide, carbon tetrachloride, methane, and ethane all fall within the thermodynamically stable region.

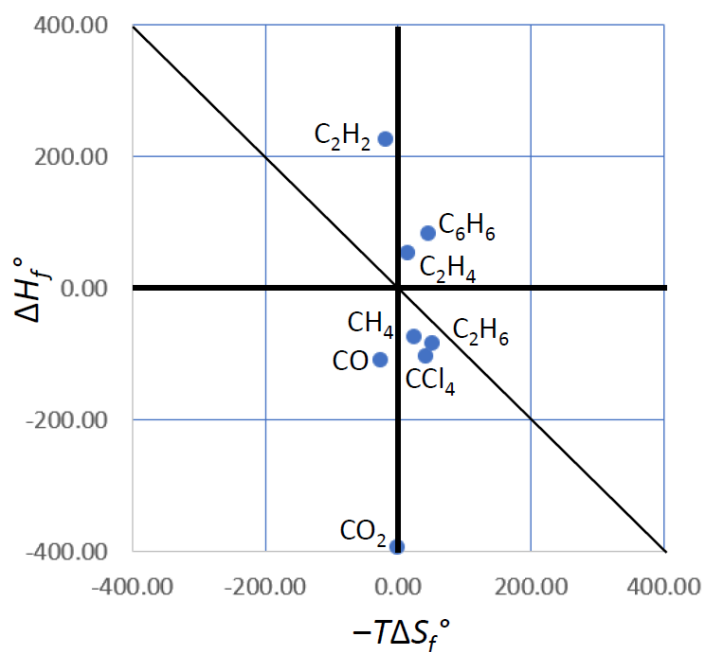


Figure 3. Stability plot ( $\Delta H_f^\circ$  vs.  $-T\Delta S_f^\circ$ ) for some binary carbon compounds

A more specialized result is illustrated in Figure 4, which shows the results for some linear  $C_nH_{2n+2}$  alkanes in the gas phase. Whereas the first six members of this series ( $CH_4$ - $C_6H_{14}$ ) all lie within the thermodynamically stable region, the higher alkanes ( $C_7H_{16}$ - $C_{20}H_{42}$ ) all lie in the thermodynamically unstable region. This is the result of the unfavorable  $-T\Delta S_f^\circ$  term and is an excellent example of Campbell's rule, which states that, to a first approximation, the entropy change for a reaction involving gases is determined by the net change in the moles of gas on going from the reactants to the products (Campbell, 1985; Craig, 2003; Jensen, 2004). If this change is negative, then the entropy of the reaction is negative, and thus,  $-T\Delta S_f^\circ$  is positive. If this change is positive, then the entropy of the reaction is positive, and thus,  $-T\Delta S_f^\circ$  is negative. If we write a generalized equation for the standard state of formation for our alkanes:



it is obvious that, the larger the value of  $n$ , the greater the decrease in the number of moles of  $H_2$  on going from the reactants to the products, the more negative  $\Delta S$ , and thus, the more positive the value of  $-T\Delta S_f^\circ$ .

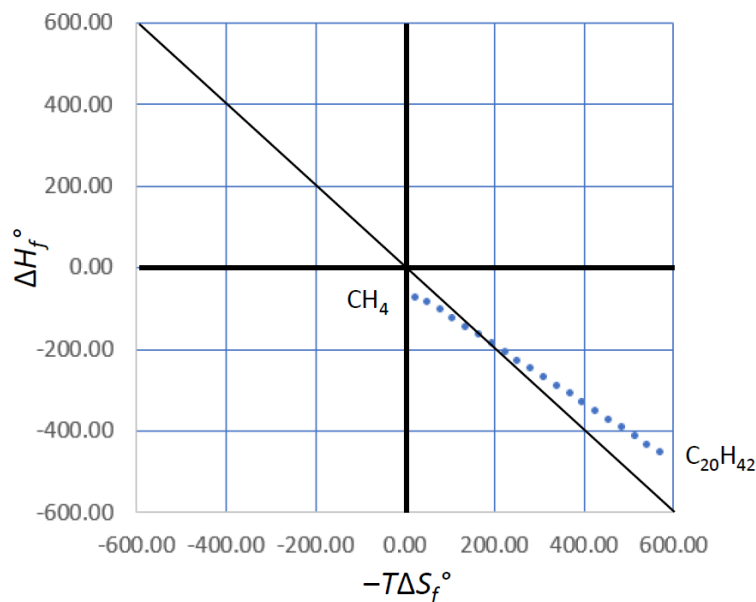


Figure 4. Stability plot ( $\Delta H_f^\circ$  vs.  $-T\Delta S_f^\circ$ ) for some linear alkanes

Figure 5 shows a similar plot for some typical cyclic hydrocarbons, where, in contrast to the simple alkanes, all of the examples fall within the thermodynamically unstable region, due not only to an unfavorable  $-T\Delta S_f^\circ$  term for the reasons given above, but also, in many cases, due to an unfavorable  $\Delta H_f^\circ$  term as well.

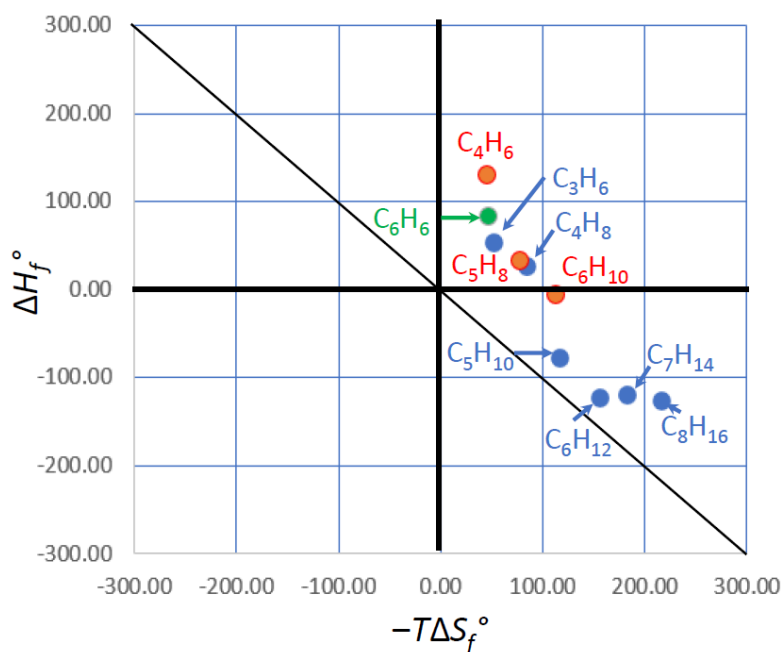


Figure 5. Stability plot ( $\Delta H_f^\circ$  vs.  $-T\Delta S_f^\circ$ ) for selected cyclic hydrocarbons

blue = cyclic alkanes, red = cyclic alkenes, and green = benzene

Figure 6 shows the plot for the binary oxides, halides, and hydrides of nitrogen. Except for ammonia and nitrogen trifluoride, all of the compounds fall within the thermodynamically unstable region. The standard rationale for those species having an unfavorable  $\Delta H_f^\circ$  term is the breaking of the very strong  $N_2$  triple bond required to make the compounds in question. The unfavorable  $-T\Delta S_f^\circ$  term is again explained by Campbell's rule, the sole exception being  $NO(g)$ , for which the change in the moles of gas on going from the reactants to the products is zero:



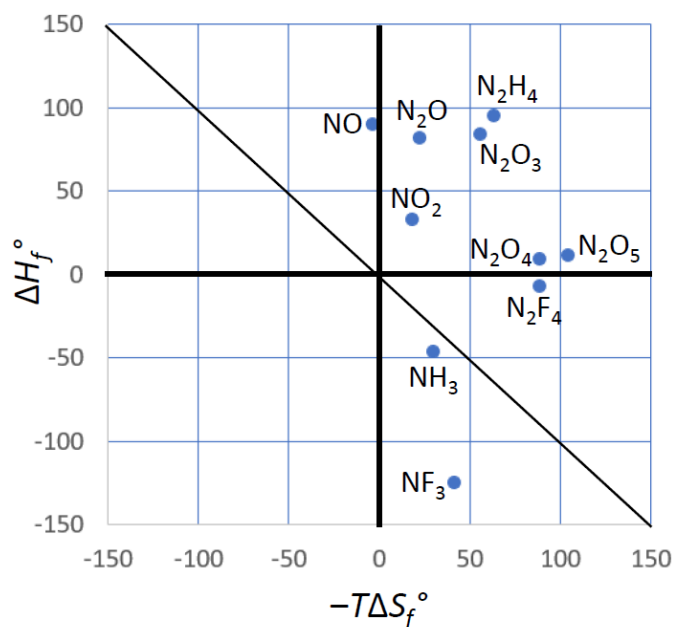


Figure 6. Stability plot ( $\Delta H_f^\circ$  vs.  $-T\Delta S_f^\circ$ ) for selected oxides, fluorides, and hydrides of nitrogen

Lastly, Figure 7 shows the plot for a random selection of compounds falling into the thermodynamically favorable region. Note the small values for the  $-T\Delta S_f^\circ$  terms in contrast to those for the  $\Delta H_f^\circ$  terms, due to the fact that the change in the moles of gas on going from the reactants to the products is zero for all of the examples except  $\text{CO}(\text{g})$  and  $\text{SO}_3(\text{g})$ . In the former case there is a net increase in the moles of gas on going from the reactants to the products:



thus, moving its point further to the left than the other points, where as in the latter case there is a decrease in the moles of gas on going from the reactants to the products:



which moves its point further to the right than the other points.

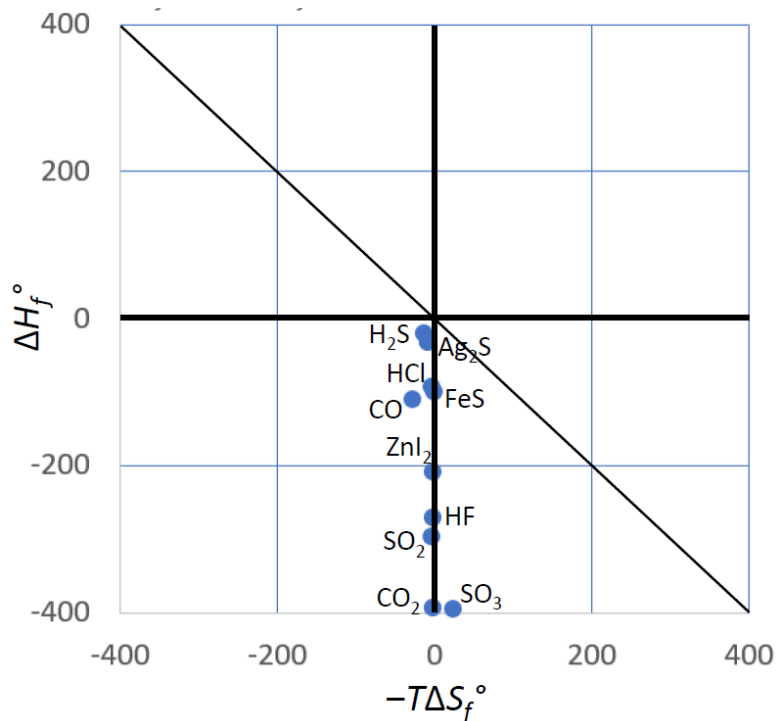


Figure 7. Stability plot ( $\Delta H_f^\circ$  vs.  $-T\Delta S_f^\circ$ ) for selected stable compounds

## 5. A Note on Terminology

There has been considerable debate in the chemical literature over the best term to use when describing what we have called “thermodynamically unstable, but kinetically stable” species (Jensen, 2015b and 2014). In most of the scientific literature the term “metastable” has been used to describe such species or states. This term originated in the field of mechanics but was applied to phase changes by Ostwald in the 1890s and later to chemical reactions as well. Other choices have included “states of instability,” “false equilibria,” “kinetically inhibited,” “suspended transformations,” and “kinetically labile versus kinetically inert.” In 1987, Hoffmann suggested the terms “thermodynamically stable versus kinetically stable” (Hoffmann, 1987) and, since these appear to be increasingly common in the chemical literature (Moore, 2015; Jensen, 2015a), we have chosen to use them in this paper, but with one further elaboration.

It has been known since the 19th century that thermodynamic stability and kinetic behavior are two separate and distinct aspects of chemical reactivity. This implies that two terms, rather than one, must be used in order to completely characterize a chemical species – one to describe its thermodynamic behavior and one to describe its kinetic behavior. We have done this when describing the species in the thermodynamically unstable but kinetically stable region of our plots but not for the species in the thermodynamically stable region. This is because we know that the species in the thermodynamically unstable region must be kinetically stable by definition or else they would not exist, but we have no way of knowing which species in the thermodynamically stable region are kinetically labile versus kinetically inert, since the necessary information is missing. As Dasent has shown, there are many simple compounds that, according to our rules of valence, should exist but which have never been prepared, some of which doubtlessly fall into the category of thermodynamically stable but kinetically unstable (Dasent, 1965).

## 6. Conclusion

This paper points out that a thermodynamically unstable compound can be synthesized if a very stable by-product is formed. It suggests a graphical way of presenting trends in thermodynamic stability and instability.

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### Authors contributions

All three authors contributed equally to all aspects of this publication.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Obtained.

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### Data availability statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

### Data sharing statement

No additional data are available.

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