

An Introduction to Chemical Thermodynamics

Part 3. Free Energy and Equilibrium

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ABSTRACT

This is the third article in a series presenting an introduction to chemical thermodynamics, emphasizing those aspects of particular relevance to pyrotechnics. It shows how the Gibbs free energy varies with temperature and pressure, and how this affects chemical equilibrium. It also shows how a number of useful facts about chemical systems can be predicted from the thermodynamic properties of the reactants and possible products. This is illustrated with examples from pyrotechnics.

Keywords: thermodynamics, free energy, equilibrium constant, thermodynamic modeling

Introduction

The previous article in this series^[1] introduced the Gibbs free energy, G , defined by

$$G = H - TS$$

where H is the enthalpy, T is the temperature and S is the entropy. It was shown that the change in the free energy, ΔG ,

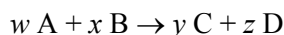
$$\Delta G = \Delta H - T\Delta S$$

is a measure of the change in the entropy of the universe. If ΔG is negative, the entropy of the universe will increase and the process will be thermodynamically spontaneous. In this article, the relationships between free energy and equilibrium will be explained, and the application of these concepts to pyrotechnic systems will be illustrated with some examples from the literature.

The Standard Free Energy of Formation

All pure substances have a Standard Free Energy of Formation, ΔG_f° . This is the free energy change when 1 mole of the compound is formed from its elements at some standard state, often a temperature of 298.15 K and a pressure of 1 bar. The bar is a unit of pressure (10^5 newtons per square metre) that is conveniently close to atmospheric pressure (standard atmospheric pressure is 1.013×10^5 newtons per square metre). The free energy of formation of the chemical elements at standard conditions is by definition zero; values for the free energies of formation of many compounds are available in tables of thermodynamic data. Standard free energy changes can be added and subtracted just like enthalpy changes, as described in the first article in this series.^[2]

For a chemical reaction



the standard free energy change ΔG° associated with the reaction is given by

$$\Delta G^\circ = [y\Delta G_{fC}^\circ + zG_{fD}^\circ] - [wG_{fA}^\circ + xG_{fB}^\circ]$$

where G_{fA}° is the Standard Free Energy of Formation of the species A, etc.

Like the enthalpy and the entropy, the Gibbs free energy is an *extensive* function; that is, it varies depending on the amount of substance in a system. The Gibbs free energy of formation of 1 mole of a substance is called the *molar free energy* of that substance. If a number of different substances are introduced into a system, with no chemical reactions, the total free energy change can be calculated by multiplying the

number of moles of each substance by its molar free energy and adding up the results. To reach chemical and thermodynamic equilibrium, substances undergo chemical reactions until the free energy is at a minimum. The reason for this, as discussed in the previous article in this series,^[2] is that minimizing the free energy in a system is the same as maximizing the entropy of the system and its surroundings.

Variation of the Gibbs Free Energy with Pressure, Temperature and Volume

Tabulated values of the molar free energy of various substances at specified conditions of temperature and pressure can be used to calculate the free energy changes involved in chemical reactions. To do this, it is necessary to know how free energy varies with temperature, pressure and volume.

By definition

$$G = H - TS$$

and

$$H = U + PV$$

Therefore

$$G = U + PV - TS$$

where U is the internal energy and V is the volume.

For the purposes of this discussion it can be assumed that the only work done by, or on, the system is the work involved in changing the volume of the system in response to pressure, or vice versa. That is, the only work to be taken into account is “pressure-volume” or “expansion” work. Electrochemical effects, for instance, are not considered. For very small (i.e., differential) changes in internal energy, pressure, volume, temperature and entropy, the corresponding change in Gibbs free energy is

$$dG = dU + PdV + VdP - TdS - SdT$$

But for a closed system, doing only “expansion” work,

$$dU = TdS - PdV$$

and these terms drop out of the equation, so

$$dG = VdP - SdT$$

At constant temperature, $dT = 0$, and consequently $dG = VdP$. At constant pressure, $dP = 0$, so $dG = -SdT$.

Variation of Gibbs Free Energy with Pressure, at Constant Temperature

At constant temperature

$$dG = VdP$$

and by integration

$$\Delta G = G_2 - G_1 = \int_1^2 VdP$$

For a perfect gas,

$$V = \frac{nRT}{P}$$

and for n moles at a constant temperature nRT is constant. For a pressure change from P_1 to P_2 ,

$$\begin{aligned} \Delta G = G_2 - G_1 &= \int_1^2 \left(\frac{nRT}{P} \right) dP \\ &= nRT \int_1^2 \frac{dP}{P} = nRT \ln \left(\frac{P_2}{P_1} \right) \end{aligned}$$

This gives the change in Gibbs free energy with pressure at constant temperature for a perfect gas.

For 1 mole of gas at standard temperature and pressure, $G_1 = G^\circ$, so the molar free energy G at some other pressure P is given by

$$G = G^\circ + RT \ln \left(\frac{P}{P^\circ} \right)$$

where G° is the free energy of one mole of the gas at standard conditions of temperature and pressure (P°).

What about a liquid or solid? As previously,

$$dG = VdP$$

and by integration

$$\Delta G = G_2 - G_1 = \int_1^2 VdP$$

In the pressure ranges of interest to pyrotechnics, the volume of a liquid or solid changes

very little with pressure. The volume can usually be treated as constant, and in this case

$$\Delta G = V\Delta P$$

This equation applies only for pressure ranges over which the substance can be considered incompressible.

The change in free energy with pressure for one mole of a solid or liquid is very much smaller than that for one mole of a gas, and it can usually be ignored. For example, suppose the pressure of one mole of a substance is increased from 1 to 10 atmospheres, at room temperature (298 K). If the substance is a gas, the free energy change is given by

$$\begin{aligned} \Delta G &= nRT \ln\left(\frac{P_2}{P_1}\right) \\ &= 1 \text{ mole} \times 8.3145 \text{ joules/K/mole} \times \\ &\quad 298 \text{ K} \times \ln(10/1) \\ &= 8.3145 \times 298 \times \ln 10 \text{ joules} \\ &= 5705.2 \text{ joules} \\ &= 5.71 \text{ kJ (3 significant figures)} \end{aligned}$$

On the other hand, taking water as an example of a liquid, the volume of one mole of water (18 grams) is around 18 cubic centimetres or 1.8×10^{-5} cubic metres. For a change in pressure from 1 to 10 atmospheres, the free energy change is

$$\begin{aligned} \Delta G &= V\Delta P \\ &= 1.8 \times 10^{-5} \text{ cubic metres} \times 9 \text{ atmospheres} \times \\ &\quad 1.013 \times 10^5 \text{ newtons/sq. metre/atmosphere} \\ &= 16.4 \text{ newton meters} \\ &= 16.4 \text{ joules} \\ &= 0.016 \text{ kJ (2 significant figures)} \end{aligned}$$

This is a bit less than 0.3% of the free energy change that the same pressure change would bring about in the same quantity of gas.

Variation of Gibbs Free Energy with Temperature, at Constant Pressure

At constant pressure

$$dG = -SdT$$

and so

$$\frac{dG}{dT} = -S$$

This is only true for constant pressure; to emphasize this, it is customary to write it in the form

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

where the symbol ∂ indicates partial differentiation and that the variable indicated by the subscript P (i.e., the pressure) must be held constant.

This simple equation is one version of the Gibbs-Helmholtz equation. There is another version that can be derived with the help of the differential calculus.

By definition,

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial T}\right)_P T - G = -H$$

Divide this equation by T^2

$$\frac{\left(\frac{\partial G}{\partial T}\right)_P}{T} - \frac{G}{T^2} = \frac{H}{T^2}$$

It can be shown that

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{\left(\frac{\partial G}{\partial T}\right)_P}{T} - \frac{G}{T^2}$$

The right hand side of this equation is the same as the left-hand side of the previous equation, therefore

$$\left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_P = \frac{H}{T^2}$$

This is the other form of the Gibbs-Helmholtz equation. Notice that it shows how G/T (rather than G) varies with temperature at constant pressure. Another variation of this equation is

$$\left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_P = \frac{\Delta H}{T^2}$$

Variation of Gibbs Free Energy with Chemical Composition, at Constant Temperature and Pressure

The free energy of a reacting mixture will change with pressure and temperature, and it will also change as the amount of each substance in the mixture changes. For a very small change in the number of moles of a substance in a mixture at constant temperature and pressure there will be a corresponding free energy change. The ratio of these changes, given by the partial derivative,

$$\left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j \neq i}} = \mu_i$$

is called the *chemical potential* of the substance i . The chemical potential is usually given the symbol μ (mu, the Greek equivalent of the letter ‘m’). It follows that *the chemical potential of a pure substance is numerically equal to the molar free energy of that substance*. The chemical potential of a substance has units of joules per mole. It is an *intensive* quantity – that is, it does not depend on the amount of substance.

In reaching equilibrium, systems move from conditions of high chemical potential to the lowest possible chemical potential. This is a bit like the tendency of objects in a gravitational field to move from a position of high potential energy to one of low potential energy, or of electric currents to flow from a high electrical potential to a low one. The reason for the movement from a state of high chemical potential to one of low chemical potential is simply

that such a movement corresponds to an increase in the total entropy of the system and its surroundings. In other words, it is nothing more (or less) than the natural tendency of molecules to get into a mess.

If n moles of a substance of chemical potential μ are added to a system, the change in Gibbs free energy is given by

$$\Delta G = n\mu$$

More generally, if substances $a, b, c \dots$ are added to a system, the change in Gibbs free energy is given by

$$\begin{aligned} \Delta G &= n_a \mu_a + n_b \mu_b + n_c \mu_c \dots \\ &= \sum n_i \mu_i \end{aligned}$$

where n_i is the number of moles of substance i , and μ_i is the chemical potential of substance i

Free Energy Changes and Chemical Reactions: Effect of Temperature

Recall that a process will be spontaneous (will continue to equilibrium once it has been started) if its Gibbs free energy change is negative. The equation for the Gibbs free energy change

$$\Delta G = \Delta H - T\Delta S$$

leads to some useful generalizations about chemical reactions. For example, if the entropy change is positive, there will *always* be a temperature at which $T\Delta S$ becomes greater than ΔH . Processes for which the entropy change is positive are those in which the molecular disorder increases. These include the melting of solids, the evaporation of liquids, and the decomposition of complex molecules into simpler ones and ultimately into atoms. The equation for the Gibbs free energy change indicates that as a solid is heated it will eventually melt, if it does not decompose first, and that a liquid will evaporate. Moreover, at a sufficiently high temperature every substance will be decomposed into its constituent atoms.

The temperature required to do this is around 5000 Kelvin. While such temperatures are routinely achieved in the plasma torches commonly

used for spectrochemical analysis, they are well above all pyrotechnic temperatures.

Free Energy Changes and Phase Changes: Freezing and Melting of Solids

If the enthalpy change (ΔH) is large and negative, the Gibbs free energy change is likely to be negative. Thus, exothermic processes are often spontaneous. The exceptions are those for which the change in the entropy is negative. The freezing of a liquid is always exothermic, but it also involves a decrease in entropy. The freezing of a liquid becomes spontaneous only when the temperature is low enough for $T\Delta S$ to be less than ΔH .

When $\Delta H = T\Delta S$, and there is no driving force for the change in either direction, the solid and the liquid are in equilibrium. At constant pressure, this occurs at just one temperature. This temperature is the freezing point (or melting point) of the substance. The Gibbs free energy change accounts for the fact that pure substances at constant pressure have fixed melting points.

Free Energy Changes and Phase Changes: Evaporation of Liquids

At the melting point, the solid and liquid are in equilibrium. The free energy change is zero. In other words, at the melting point the free energy of the liquid is exactly equal to the free energy of the solid. As long as both liquid and solid are present, the temperature remains precisely at the melting point, no matter how much heat is supplied to the system. At any given pressure there is one, and only one, temperature at which the two phases can exist in equilibrium.

Contrast this situation with that of a liquid and its vapor. As shown previously, at constant temperature, the free energy of a gas varies with pressure:

$$G = G^\circ + RT \ln \left(\frac{P}{P^\circ} \right)$$

At any temperature, a certain pressure of gas will have a free energy equal to that of the liquid at that temperature, so the gas and liquid will be in equilibrium. The corresponding gas pressure is called the *vapor pressure* of the substance at that temperature. When the vapor pressure becomes equal to the atmospheric pressure, the liquid and vapor are in equilibrium at atmospheric pressure. The corresponding temperature is the *boiling point* of the substance. The Gibbs free energy change predicts that a pure substance will have a fixed vapor pressure at any given temperature and a fixed boiling point at any given pressure, in accordance with experiment.

Free Energy and Chemical Reactions in Gases

If two gases undergo a *chemical reaction* to form two new gases, the reactants and products will be in equilibrium when the free energy of the products equals the free energy of the reactants. For each gas involved in the reaction, the free energy is given by

$$G_i = n_i \left(G_i^\circ + RT \ln \left(\frac{P_i}{P^\circ} \right) \right)$$

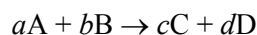
where n_i is the number of moles of that gas, P_i is the *partial pressure* of gas i and P° is the pressure to which the standard free energy G_i° corresponds. The term “partial pressure” simply means the pressure that each gas contributes to the total pressure.

For a constant pressure system, as in the present discussion, the partial pressure P_i of each gas is given by the total pressure multiplied by the *mole fraction* of the gas X_i .

$$P_i = PX_i$$

The mole fraction $X_i = n_i/n$ is the ratio of the number of moles n_i of the gas divided by the total number of moles of gas in the system.

Suppose the reaction is a moles of gas A reacting with b moles of gas B to form c moles of gas C and d moles of gas D:



The free energy of the reactants will be

$$a \left(G^\circ_A + RT \ln \left(\frac{P_A}{P^\circ} \right) \right) +$$

$$b \left(G^\circ_B + RT \ln \left(\frac{P_B}{P^\circ} \right) \right)$$

and the free energy of the products will be

$$c \left(G^\circ_C + RT \ln \left(\frac{P_C}{P^\circ} \right) \right) +$$

$$d \left(G^\circ_D + RT \ln \left(\frac{P_D}{P^\circ} \right) \right)$$

where P_A , P_B , P_C and P_D are the partial pressures of gases A, B, C and D.

The free energy change of the reaction will be the free energy of the products minus the free energy of the reactants.

$$\Delta G = c(G^\circ_C + RT \ln(P_C / P^\circ)) +$$

$$d(G^\circ_D + RT \ln(P_D / P^\circ)) -$$

$$a(G^\circ_A + RT \ln(P_A / P^\circ)) -$$

$$b(G^\circ_B + RT \ln(P_B / P^\circ))$$

$$= (cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B) +$$

$$cRT \ln(P_C / P^\circ) + dRT \ln(P_D / P^\circ) -$$

$$aRT \ln(P_A / P^\circ) - bRT \ln(P_B / P^\circ)$$

$$cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B =$$

$$(cG^\circ_C + dG^\circ_D) - (aG^\circ_A + bG^\circ_B) = \Delta G^\circ$$

Therefore

$$\Delta G = \Delta G^\circ + cRT \ln \left(\frac{P_C}{P^\circ} \right) + dRT \ln \left(\frac{P_D}{P^\circ} \right) -$$

$$aRT \ln \left(\frac{P_A}{P^\circ} \right) - bRT \ln \left(\frac{P_B}{P^\circ} \right)$$

Now, because $x \ln X = \ln X^x$

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C}{P^\circ} \right)^c + RT \ln \left(\frac{P_D}{P^\circ} \right)^d -$$

$$RT \ln \left(\frac{P_A}{P^\circ} \right)^a - RT \ln \left(\frac{P_B}{P^\circ} \right)^b$$

and, because $\ln X + \ln Y = \ln XY$

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C}{P^\circ} \right)^c \cdot \left(\frac{P_D}{P^\circ} \right)^d -$$

$$RT \ln \left(\frac{P_A}{P^\circ} \right)^a \cdot \left(\frac{P_B}{P^\circ} \right)^b$$

Finally, because $-\ln X = \ln(1/X)$:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{\left(\frac{P_C}{P^\circ} \right)^c \left(\frac{P_D}{P^\circ} \right)^d}{\left(\frac{P_A}{P^\circ} \right)^a \left(\frac{P_B}{P^\circ} \right)^b} \right)$$

This equation shows how the free energy change relates to the pressures of gaseous reactants and products at constant temperature. It is called the van't Hoff isotherm.

At equilibrium, the free energy of the reactants equals the free energy of the products, so $\Delta G = 0$ and

$$0 = \Delta G = \Delta G^\circ + RT \ln \left(\frac{\left(\frac{P_C}{P^\circ} \right)^c \left(\frac{P_D}{P^\circ} \right)^d}{\left(\frac{P_A}{P^\circ} \right)^a \left(\frac{P_B}{P^\circ} \right)^b} \right)$$

or

$$\Delta G^\circ = -RT \ln \left(\frac{\left(\frac{P_C}{P^\circ} \right)^c \left(\frac{P_D}{P^\circ} \right)^d}{\left(\frac{P_A}{P^\circ} \right)^a \left(\frac{P_B}{P^\circ} \right)^b} \right)$$

where P_A , P_B , P_C , and P_D are the pressures of gases A, B, C and D *at equilibrium*.

The right hand side of this equation can be written as $-RT \ln K$, where

$$K = \left(\frac{\left(\frac{P_C}{P^\circ} \right)^c \left(\frac{P_D}{P^\circ} \right)^d}{\left(\frac{P_A}{P^\circ} \right)^a \left(\frac{P_B}{P^\circ} \right)^b} \right)$$

K is called the *equilibrium constant* for the reaction, and therefore

$$\Delta G^\circ = -RT \ln K$$

Relative Activities

As shown previously, at constant temperature the free energy of a gas varies with pressure according to:

$$G = G^\circ + RT \ln\left(\frac{P}{P^\circ}\right)$$

where P is the partial pressure of the gas and G° is the free energy of one mole of the gas at pressure P° . This can be expressed in terms of chemical potentials:

$$\mu = \mu^\circ + RT \ln\left(\frac{P}{P^\circ}\right)$$

where $\mu^\circ = G^\circ$

This applies only to perfect gases. For other substances, it is useful to *define* a property called the *relative activity* such that the chemical potential is given by

$$\mu = \mu^\circ + RT \ln(a_A)$$

where a_A is the relative activity of the substance A. The equation requires the logarithm of the relative activity, a_A , which means that a_A must be a pure number—it cannot be some quantity requiring units. It has to be a ratio of some property of A, at the conditions of interest, to the value of that property at the standard state corresponding to μ° . The relative activity of a perfect gas is obviously P/P° . For a real gas (that is, a gas that does not conform exactly to the ideal relationship $PV = nRT$) the relative activity can be defined by assigning an “effective pressure” f to the gas such that

$$\mu = \mu^\circ + RT \ln\left(\frac{f}{P^\circ}\right)$$

This “effective pressure” f varies with temperature and has to be determined for each gas. It is called the *fugacity* of the gas. What is the relative activity for a pure solid or liquid?

For combustion problems, it is necessary only to take into account how the Gibbs free energy of a fixed amount of a substance (i.e., the chemical potential of that substance) varies with pressure. As discussed previously, the free energy per mole of a pure solid or liquid changes very little with pressure, and it is usually sufficiently

accurate to treat the chemical potential of a pure solid or liquid as constant. That simplifies matters greatly, because if the chemical potential is constant, then for 1 mole of a pure solid or liquid

$$\mu = \mu^\circ + RT \ln(a) = \mu^\circ$$

from which $RT \ln(a) = 0$ and thus $a = 1$. The relative activity of pure solids and liquids is 1.

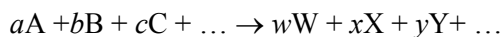
For perfect (or ideal) solutions, the chemical potential of a component i is given by

$$\mu_i = \mu_i^\circ + RT \ln X_i$$

where X_i is the mole fraction of i and μ_i° is the chemical potential of pure i in the same physical state as the solution.

Relative Activities and Equilibrium Constants

The definition of relative activity was chosen so that for *any* reaction



there is an equilibrium constant K of the form

$$K = \frac{(a_W)^w (a_X)^x (a_Y)^y \dots}{(a_A)^a (a_B)^b (a_C)^c \dots}$$

where a_W is the relative activity of W , etc.

The equilibrium constant is related to the standard free energy change for the reaction by

$$\Delta G^\circ = -RT \ln K$$

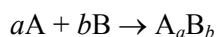
This equation can be rearranged to give

$$K = e^{-\Delta G^\circ / RT}$$

Equilibrium Constant, Free Energy and the Stability of Compounds

The relationship $K = e^{-\Delta G^\circ / RT}$ can be used to explain the stability of compounds in terms of their free energy of formation.

For the general reaction for the formation of a compound from its elements,



the equilibrium constant is given by

$$K = \frac{[A_a B_b]}{[A]^a [B]^b}$$

If the standard free energy of formation ΔG° is large and negative, then $-\Delta G^\circ/RT$ will be large and positive, so K will be large and the equilibrium concentration of the product will be large. As the temperature T increases, the value of $-\Delta G^\circ/RT$ will become smaller, K will decrease and the equilibrium concentration of the product will decrease. In general, the equilibrium will shift more and more towards the reactants as the temperature increases. Substances for which the standard free energy of formation is larger and more negative will withstand a higher temperature before the equilibrium lies in favor of the products. *The standard free energy of formation is thus a quantitative indicator of the thermal stability of a substance.*

Notice that if the reactants and products of a reaction are all solids, then the relative activity of each is 1, and the equilibrium constant is also 1. This means that $\Delta G^\circ = -RT \ln 1 = 0$. The solid reactants and products can be in equilibrium at one, and only one, temperature: that at which $\Delta G^\circ = 0$ (i.e., $T = \Delta H^\circ/\Delta S^\circ$). At all other temperatures, the system consists either *entirely* of reactants or *entirely* of products. This might seem odd, but it is no different from the familiar example of a pure solid being in equilibrium with its liquid at one and only one temperature.

Variation of Equilibrium Constants with Temperature

Recall

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\frac{\left(\frac{\Delta G^\circ}{T}\right)}{R}$$

The partial derivative of this equation with respect to temperature, assuming constant pressure, is

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_P = -\frac{\left(\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T}\right)_P}{R}$$

Then, by the Gibbs-Helmholtz equation:

$$\left(\frac{\partial(\ln K)}{\partial T}\right)_P = -\frac{\left(\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T}\right)_P}{R} = \frac{\Delta H^\circ}{RT^2}$$

It is not necessary to restrict this relationship to constant pressure, because neither ΔG° nor ΔH° vary with pressure. They are *defined* at a standard pressure, usually one bar. Therefore,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

This gives the relationship between the equilibrium constant and the temperature.

The equation can be rearranged to

$$d(\ln K) = \frac{\Delta H^\circ}{R} \left(\frac{dT}{T^2}\right)$$

Now, $dT/T^2 = -d(1/T)$, so

$$d(\ln K) = -\frac{\Delta H^\circ}{R} d\left(\frac{1}{T}\right)$$

This can now be integrated, assuming ΔH° to be constant with temperature, to give

$$\Delta(\ln K) = -\frac{\Delta H^\circ}{R} \Delta\left(\frac{1}{T}\right)$$

If the equilibrium constant is known at one temperature, this equation provides a way to calculate the equilibrium constant at any other temperature, provided that the relationship between ΔH° and temperature is known, and that the pressure is constant. As discussed previously,^[2] the effect of temperature on ΔH° can be calculated from the heat capacities of the reactants and products over the temperature range of interest. If the equilibrium constant at one temperature T_1 is K_1 , what can be said about the equilibrium constant (K_2) at a higher temperature T_2 ?

Rearrange the previous equation to obtain

$$\ln K_2 - \ln K_1 = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Since T_2 is greater than T_1 , $(1/T_2 - 1/T_1)$ will be negative. If ΔH° is also negative (that is, if the reaction is exothermic), $\ln K_2 - \ln K_1$ must be negative and K_1 must be greater than K_2 . Recall that a larger equilibrium constant corresponds to more products. Since the equilibrium constant is larger at the lower temperature, the equilibrium at the lower temperature favors the products. Thus, for an exothermic reaction, an increase in temperature results in the equilibrium shifting in favor of the reactants.

The same line of reasoning can also show that for an endothermic reaction an increase in temperature will result in the equilibrium shifting in favor of the products. This is the thermodynamic explanation of *Le Châtelier's Principle*, as applied to the effect of temperature on chemical equilibrium. *Le Châtelier's Principle* can be stated in various ways, for example: *if a system at equilibrium is subjected to a stress, it will respond in such a manner that tends to relieve the stress*. This is a useful guide to the behavior of chemical systems, and is often all that is needed for a qualitative explanation.

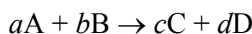
Variation of Equilibrium Constants with Pressure

The discussion of equilibrium constants so far has referred to conditions of constant pressure. The next step is to show how the composition of the equilibrium mixture can change with pressure. Recall that the composition can be expressed in mole fractions given by

$$X_i = \frac{P_i}{P}$$

where P is the total pressure and P_i is the partial pressure of the particular gas.

For the reaction of a moles of gas A reacting with b moles of gas B to form c moles of gas C and d moles of gas D



$$K = \frac{\left(\frac{P_C}{P^\circ}\right)^c \left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b}$$

Now,

$$P_i = X_i P$$

If the pressure P is expressed in atmospheres, and $P^\circ = 1$ then

$$K = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K = \frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b}$$

$$K = \frac{(X_C^c X_D^d) (P^c P^d)}{(X_A^a X_B^b) (P^a P^b)}$$

But

$$\frac{(P^c P^d)}{(P^a P^b)} = \frac{P^{(c+d)}}{P^{(a+b)}} = P^{(c+d)-(a+b)}$$

and $(c + d) - (a + b) = \Delta n$

where Δn is the change in the number of moles. So

$$K = \frac{(X_C^c X_D^d) P^{\Delta n}}{(X_A^a X_B^b)}$$

$$\frac{(X_C^c X_D^d)}{(X_A^a X_B^b)} = K P^{-\Delta n}$$

If Δn is positive, that is, if there are more moles of products than of reactants, the right-hand side of the equation becomes smaller as the pressure P increases. This means that the equilibrium must shift in favor of the reactants. Similarly, if Δn is negative, the equilibrium will shift in favor of the products as the pressure P increases. This is the thermodynamic explanation for *Le Châtelier's Principle*, as it applies to the effect of pressure on the equilibrium composition of a reacting mixture.

Application to Pyrotechnics

Two useful pieces of information about reacting pyrotechnic mixtures are the maximum temperature reached and the chemical species present at that temperature. In principle, both can be calculated from thermodynamics.

The process for calculating the temperature is conceptually very simple:

- 1) Calculate the enthalpy change ΔH° for the reaction at standard temperature and pressure.
- 2) Assume that all the released heat is available to raise the temperature of the products.
- 3) Calculate the final temperature from the relationship:

$$\Delta T = \frac{-\Delta H^\circ}{\sum n_i C_{p,i}}$$

where ΔT is the temperature rise in Kelvin, ΔH° is the enthalpy change in joules, n_i is the number of moles of product i , $C_{p,i}$ is the molar heat capacity (at constant pressure) of product i and the symbol Σ means "the sum of". Dolata^[3] has shown that this method can be used to predict the temperatures of the flames of burning pyrotechnic mixtures that burn at relatively low temperatures.

It has been known for a long time that such calculations work quite well for the flame temperatures of certain gas mixtures that burn at moderate temperatures. Examples of such mixtures include coal gas/air or hydrogen/air with either gas in excess.^[4a] In these calculations the "products" are the real end products of the reaction: carbon dioxide, water, nitrogen and argon in the case of an air/coal gas flame. There is no need to consider any intermediate products that might be formed along the way. For gas flames that burn at higher temperatures, however, these calculations yield flame temperatures that are much higher than the real flame temperatures.

This discrepancy can be understood if it is imagined that the energy released by the formation of the reaction's final products heats those products to such a high temperature that they start to break down again. This decomposition absorbs energy that would otherwise raise the temperature of the flame.

To calculate the temperatures of high-temperature flames one must consider not only the ultimate products (those that are stable at room temperature) but also those intermediate products that are stable at high temperatures. For example, ethylene (C_2H_4) burns in oxygen to form carbon dioxide and water. At the temperature of an ethylene-oxygen flame, however, the following species are in equilibrium: H_2O , O_2 , O , H_2 , H , OH , CO , and CO_2 . The enthalpies of formation of these are known, but the amount of each substance present is not. Nevertheless, the amount of each *element* is obviously constant, and the equilibrium constants of the various dissociation reactions can be calculated for any temperature. Consequently, the problem can be solved by trial and error. One makes a reasonable guess at the temperature and of the partial pressures of two of the substances. With the aid of the equilibrium constants, one can then calculate the partial pressures of all the other products. The sum of these partial pressures should be 1; if it is not, the calculation is repeated. After a few trials, the values for the next trial are chosen by carefully examining the results of the first few and choosing values that are likely to lead in the right direction. With care, the method can yield a result after five or six iterations. The method, which is explained in detail by Gaydon and Wolfhard,^[4a] can yield remarkably accurate results. For example, Snellenman^[5] measured the temperature of a carefully controlled, pre-mixed air-acetylene flame to be 2554 ± 3 K. The calculated temperature was 2600 ± 3 K. Energy losses from the flame were measured, and when these were taken into account, the calculated flame temperature was 2559 ± 4 K, in agreement with the measured value.

The calculation of flame temperatures of a burning pyrotechnic mixture is much more complicated. For a start, the reaction might never reach thermodynamic equilibrium. Certain reactions might take place at relatively low temperatures, and volatile products of those reactions might be lost before the system can come to equilibrium. Even if equilibrium is reached, unless the mixture is an unusually simple one, the exact composition of the products might not be known. Then, the enthalpies of formation of many common ingredients are not known, or if

they are known, they may be difficult to find. Examples of such ingredients are the natural products that are used as binders and fuels in fireworks. A compilation of *estimated* values for these has been published by Myerriecks.^[6-8]

Furthermore, the molar heat capacity of each product is not constant but varies with temperature. As a result, the products change with temperature: solids melt, liquids vaporize, and compounds decompose. The energy consumed in all these processes has to be taken into account. If all these problems can be overcome, eventually a combination of temperature and chemical composition is reached at which the enthalpy of the products exactly equals the enthalpy of the reactants. If the enthalpy of the products as a function of temperature is available, the maximum possible temperature reached in a reaction can be obtained graphically. One plots the enthalpy of the products versus temperature and then finds the temperature at which the graph intersects the line representing the enthalpy of the reactants.

For example, consider the formation of iron(II) sulfide from powdered iron and sulfur:



The reactants are pure elements, so their enthalpies of formation are (by definition) zero. Therefore, the enthalpy of the reaction is simply the enthalpy of formation of FeS. What is the maximum possible temperature that can be reached in this reaction?

Figure 1 is a graph of the molar enthalpy of formation of iron(II) sulfide as a function of temperature (data from reference 9). The graph cuts the zero line at 1463 K. This is the temperature at which the molar enthalpy of formation of iron(II) sulfide equals the room-temperature molar enthalpies of formation of iron and sulfur, and it is the maximum possible temperature that could be achieved in this reaction. The sharp rise in the curve at 1463 K corresponds to the melting of the solid. The maximum temperature reached is the temperature at which the solid product melts. This is consistent with experimental results. A stoichiometric mixture of powdered iron and sulfur glows bright red when heated to reaction, and the product is found to be partially melted. It is

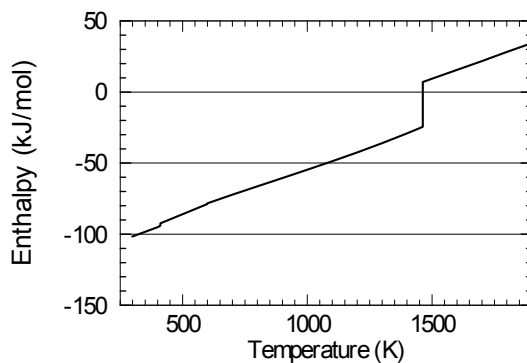


Figure 1. Molar enthalpy of iron(II) sulfide as a function of temperature.^[9]

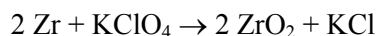
quite common for the maximum temperature of a pyrotechnic reaction to be determined by a phase change in the products. For example, the maximum temperature reached in the combustion of many metals in air corresponds to the boiling point of the metal oxide.^[4b]

The example just given was very simple because the possibility of some of the product decomposing at the maximum temperature of the reaction was ignored. In most cases, the decomposition of the product must be taken into account. As discussed previously, the increase in entropy associated with the formation of gases favors the decomposition of compounds at high temperatures. The problem is to find the equilibrium composition and the temperature, keeping the elemental composition and total energy constant.

Thermodynamic Modeling

Numerous computer programs have been developed to calculate high-temperature equilibria.^[10-12] As noted by Belov,^[10] the incentive for developing these programs came from the requirement for better rocket engines. The calculations are done iteratively; that is, an initial estimate is made, the calculation is run, and the results are used as a starting point for the next calculation. This is repeated until the results no longer change within pre-selected limits. Thermodynamic data have to be available, as functions of temperature, for all possible products.

The calculation most useful for pyrotechnics is the determination of the temperature and chemical composition at constant pressure. This is done by minimizing the Gibbs free energy, with the constraint that the total number of moles of each element remain unchanged. The details of these calculations are given by McBride and Gordon.^[12] The calculations are least complicated when the equilibrium products are all gases. If solids or liquids (condensed phases) are predicted, the calculations have to be revised to take into account the fact that the relative activity of a condensed phase of a pure substance is essentially constant and equal to 1. The results of thermodynamic modeling can be rather surprising. For example, a simple pyrotechnic mixture of a pure metal fuel with potassium perchlorate might be expected to produce nothing more than potassium chloride and the oxide of the metal. That is certainly what would be produced if the products were at room temperature, but at the high temperatures of the reaction the chemical composition will be very different. Powers and Gonthier^[13] analyzed the operation of a pyrotechnically actuated pin-puller device that used a burning mixture of zirconium and potassium perchlorate to move a piston. The mixture was fuel-deficient: Zr:KClO₄ = 1.4:1, compared to the 2:1 molar ratio required for the reaction



Presumably, this fuel-deficient composition was chosen to increase the amount of gas generated on combustion. On the basis of the properties of the products at room temperature, one would expect the reaction products to have been solid zirconium dioxide, solid potassium chloride and oxygen gas from the excess oxidizer. The calculations showed, however, that at the high temperature of the reaction even the highly refractory zirconium dioxide was partially vaporized. All the potassium chloride was vaporized, and the following species were calculated also to be present as gases: atomic oxygen (O), atomic chlorine (Cl), atomic potassium (K), atomic zirconium (Zr), diatomic oxygen (O₂), diatomic chlorine (Cl₂), diatomic potassium (K₂), potassium monoxide (KO), zirconium monoxide (ZrO), chlorine monoxide (ClO) and dipotassium dichloride (K₂Cl₂). As the hot products cooled to room temperature this diverse collection of

atoms and molecules would react to produce the three products (solid zirconium dioxide, solid potassium chloride and diatomic oxygen gas) that are thermodynamically stable at room temperature. The chemical nature of the products at the high temperatures prevailing during the very rapid operation of the device could not have been determined by conventional chemical analysis.

Farren et al.^[14] used thermodynamic modeling to simulate the combustion of pyrotechnic compositions including those used in US Navy colored flares. Their results showed that only about 18% of the strontium in the flame of the red flare was present as strontium monochloride (SrCl), the species that emits the desired red light. Most (~65%) was present as strontium dichloride (SrCl₂), while some (~15%) was there as strontium (Sr) vapor. Similarly, in the flame of the green flare less than 5% of the barium was present as the barium monochloride (BaCl) color emitter; most (~93%) was barium dichloride (BaCl₂), with a little (~1.5%) barium (Ba) vapor and the rest as barium monohydroxide (BaOH) (~0.7%) and barium dihydroxide (Ba(OH)₂) (~0.5%). The authors concluded that thermodynamic modeling “can be recommended as a useful tool to survey prospective pyrotechnic compositions as to their likely product distributions and their likely maximum achievable reaction temperature. However, those compositions showing potential usefulness should certainly be mixed, burned and analyzed in the laboratory before being recommended for use in any new or improved pyrotechnic device”.^[14] In other words, the predictions of modeling must be verified by practical experiments.

Thermodynamic modeling was used by Koch^[15] to support his analysis of the reasons why lithium compounds have so far been ineffective as color-producing agents in pyrotechnics. His calculations showed that very little atomic lithium was expected to be present in the flame of a published composition that gave a pink flame instead of the anticipated scarlet red. Furthermore, Koch showed—by thermodynamic modeling—that appropriately formulated compositions should be capable of generating much higher concentrations of atomic lithium, and ought to be effective emitters of red light. Recognizing that thermodynamic modeling always requires practical validation Koch

wrote, "it is hoped that an *experimental* proof will be found soon"^[15].

Successful efforts to produce the beautiful deep violet-blue atomic emission of indium in pyrotechnic flames have not yet been reported, although, like lithium, indium imparts an intense color to laboratory flames. Perhaps thermodynamic modeling can point the way to achieving a deep blue flame with indium. The cost of indium compounds would prohibit practical applications, but it would be an interesting exercise.

The basic requirements of an effective colored light composition are straightforward: a high concentration of the color-emitting species, minimum concentration of other light-emitting species and maximum temperature. Since these requirements can be in conflict, to achieve optimum results by formulating, manufacturing and testing can be time-consuming and expensive.

In general, the requirements of a pyrotechnic composition can be stated in terms of

- 1) the chemical composition of the products (either at room temperature or at the temperature of the reaction) and
- 2) the maximum temperature of the reaction.

Thermodynamic modeling provides the possibility of developing close-to-optimum compositions on the computer. This should greatly reduce the burden of formulation and testing.

Summary and Conclusion

Chemical systems can be described by a few properties called *state functions*. These include temperature T , pressure P , volume V , internal energy U , enthalpy H , entropy S and Gibbs free energy G .

A system is at *equilibrium* when the state functions have constant values throughout the system.

The change in any state function depends only on the initial and final states of the system, not on the intermediate steps.

Energy can be transferred between a system and its surroundings *mechanically*, as *work*, and *thermally*, as *heat*. The change in the *enthalpy*

of a system is the heat absorbed or emitted by the system at constant pressure.

Entropy is related to the degree of molecular disorder in a system. An increase in disorder corresponds to an increase in entropy.

A system plus its surroundings is called the *universe*.

- The energy of the universe is constant (First Law of Thermodynamics).
- The entropy of the universe increases (Second Law of Thermodynamics).

Consequently,

- For a spontaneous process, the Gibbs free energy change is negative. That is, $\Delta G = \Delta H - T\Delta S$ is negative for a spontaneous process.

Consequently:

- If ΔH is negative (heat is released) and ΔS is positive (molecular disorder increases), the process will *always* be spontaneous.
- If ΔH is negative (heat is released) and ΔS is negative (molecular disorder decreases), the process will be spontaneous at a sufficiently low temperature.
- If ΔH is positive (heat is absorbed) and ΔS is positive (molecular disorder increases), the process will be spontaneous at a sufficiently high temperature.
- If ΔH is positive (heat is absorbed) and ΔS is negative (molecular disorder decreases), the process will *never* be spontaneous.

The entropy change ΔS is positive for any process that results in an increase in the molecular disorder. Consequently, if the temperature is increased sufficiently

- Solids will melt.
- Liquids will vaporize.
- Compounds will decompose.
- Gases will ionize.

For a system in equilibrium, the Gibbs free energy change is zero. Consequently, at constant pressure

- Pure substances have fixed freezing (melting) points.

- Pure substances have fixed boiling points.
- There is an *equilibrium constant* K for chemical reactions, given by

$$\Delta G^\circ = -RT \ln K$$

The variation of the equilibrium constant with temperature and pressure can be calculated from thermodynamics. This accounts for Le Châtelier's Principle (*if a system at equilibrium is subjected to a stress, it will respond in such a manner that tends to relieve the stress*) as it applies to the effect of pressure and temperature on the equilibrium composition of a reacting mixture.

Thermodynamic modeling allows the maximum temperature and chemical composition of reacting pyrotechnic mixtures to be estimated from the thermodynamic properties of the reactants and possible products.

Table 1 (at the end of this article) shows, for illustrative purposes only, thermodynamic properties of some substances relevant to pyrotechnics. More complete data is available in Reference 9, for example. Table 1 is a continuation of the Table published in the first article in this series.^[2] Several typographical errors in the original Table have been corrected in this one.

Acknowledgement

I thank Professor Wesley Smith for constructive criticism and editorial assistance.

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Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics.

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]	ΔG_f° [b]	S° [b]	C_p° [b]
Aluminium	Al	26.98	0	0	0.028	0.024
carbide	Al ₄ C ₃	143.96	-209	-196	0.089	0.117
oxide	Al ₂ O ₃	101.96	-1676	-1582	0.051	0.079
sulfide	Al ₂ S ₃	150.16	-724	—	—	—
Ammonium						
chloride	NH ₄ Cl	53.49	-314	-203	0.095	0.084
nitrate	NH ₄ NO ₃	80.04	-366	-184	0.151	0.139
perchlorate	NH ₄ ClO ₄	117.49	-295	-89	0.186	—
Antimony	Sb	121.75	0	0	0.046	0.025
oxide	Sb ₂ O ₃	291.50	-720	-634	0.110	0.101
sulfide	Sb ₂ S ₃	339.69	-175	-174	0.182	0.120
Arsenic	As	74.92	0	0	0.035	0.025
oxide	As ₂ O ₃	197.84	-657	-576	0.107	0.096
sulfide	As ₂ S ₃	246.04	-169	-169	0.164	0.116
Barium	Ba	137.34	0	0	0.063	0.028
carbonate	BaCO ₃	197.35	-1216	-1138	0.112	0.085
chlorate	Ba(ClO ₃) ₂	304.24	-772	—	—	—
chloride	BaCl ₂	208.25	-859	-810	0.124	0.075
nitrate	Ba(NO ₃) ₂	261.35	-992	-797	0.214	0.151
oxide	BaO	153.34	-554	-525	0.070	0.048
peroxide	BaO ₂	169.34	-634	—	—	0.067
sulfate	BaSO ₄	233.40	-1473	-1362	0.132	0.102
sulfide	BaS	169.40	-460	-456	0.078	0.049
Boron	B	10.81	0	-141	0.200	0.122
oxide	B ₂ O ₃	69.62	-1273	-1194	0.054	0.063
Calcium	Ca	40.08	0	0	0.041	0.025
carbonate	CaCO ₃	100.09	-1207	-1129	0.093	0.082
oxide	CaO	56.08	-635	-604	0.040	0.043
sulfate	CaSO ₄	136.14	-1434	-1332	0.107	0.092
Carbon	C (graphite)	12.01	0	0	0.006	0.009
monoxide	CO(g)	28.01	-111	-137	0.198	0.029
dioxide	CO ₂ (g)	44.01	-394	-394	0.214	0.037
Chlorine	Cl ₂ (g)	70.91	0	0	0.223	0.034
atomic chlorine	Cl(g)	35.45	122	106	0.165	0.022
Copper	Cu	63.54	0	0	0.033	0.024
(I) chloride	CuCl	98.99	-137	-120	0.086	0.049
(II) chloride	CuCl ₂	134.45	-220	-176	0.108	0.072
(I) oxide	Cu ₂ O	143.08	-169	-146	0.093	0.064
(II) oxide	CuO	79.54	-157	-130	0.043	0.042
carbonate, basic	CuCO ₃ ·Cu(OH) ₂ ·H ₂ O	221.10	-1051	-894	0.186	—
Hydrogen	H ₂ (g)	2.02	0	0	0.131	0.029
chloride	HCl(g)	36.46	-92	-95	0.187	0.029
sulfide	H ₂ S(g)	34.08	-21	-34	0.206	0.034
(water)	H ₂ O(l)	18.02	-286	-237	0.070	0.075

Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics (Continued).

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]	ΔG_f° [b]	S° [b]	C_p° [b]
Iron	Fe	55.85	0	0	0.027	0.025
(III) oxide	Fe ₂ O ₃	159.69	-824	-742	0.087	0.104
(II,III) oxide	Fe ₃ O ₄	231.54	-1118	-1015	0.146	0.143
Lead	Pb	207.19	0	0	0.065	0.026
(II) oxide	PbO (yellow)	223.189	-215	-188	0.069	0.046
(IV) oxide	PbO ₂	239.19	-277	-217	0.069	0.065
(II,IV) oxide	Pb ₃ O ₄	685.57	-718	-601	0.211	0.147
Magnesium	Mg	24.31	0	0	0.033	0.025
carbonate	MgCO ₃	84.32	-1096	-1012	0.066	0.076
chloride	MgCl ₂	95.22	-641	-592	0.090	0.071
oxide	MgO	40.31	-602	-569	0.027	0.037
Manganese	Mn	54.94	0	0	0.032	0.026
dioxide	MnO ₂	86.94	-520	-465	0.053	0.054
Nitrogen	N ₂ (g)	28.01	0	0	0.192	0.029
(nitrous oxide)	N ₂ O(g)	44.01	82	104	0.220	0.038
(ammonia)	NH ₃ (g)	17.03	-46	-16	0.192	0.035
Oxygen	O ₂ (g)	32.00	0	0	0.205	0.029
atomic oxygen	O(g)	16.00	249	232	0.161	0.022
Phosphorus	P (red)	30.97	-18	-12	0.023	0.021
(V) oxide	P ₄ O ₁₀	283.89	-2984	-2698	0.227	0.212
Potassium	K	39.10	0	0	0.064	0.030
chlorate	KClO ₃	122.55	-398	-296	0.143	0.100
chloride	KCl	74.55	-437	-410	0.083	0.051
dichromate	K ₂ Cr ₂ O ₇	294.19	-2061	-1882	0.289	0.219
nitrate	KNO ₃	101.10	-495	-395	0.133	0.096
oxide	K ₂ O	94.20	-361	—	—	—
perchlorate	KClO ₄	138.55	-433	-303	0.151	0.112
permanganate	KMnO ₄	158.04	-837	-738	0.172	0.118
sulfide	K ₂ S	110.26	-381	—	—	—
Silicon	Si	28.09	0	0	0.019	0.020
dioxide	SiO ₂ (quartz)	60.08	-911	-857	0.042	0.044
Sodium	Na	22.99	0	0	0.051	0.028
bicarbonate	NaHCO ₃	84.01	-951	-851	0.102	0.088
carbonate	Na ₂ CO ₃	105.99	-1131	-1044	0.135	0.112
chlorate	NaClO ₃	106.44	-366	-262	0.123	—
chloride	NaCl	58.44	-411	-384	0.072	0.051
nitrate	NaNO ₃	84.99	-468	-367	0.117	0.093
oxalate	Na ₂ C ₂ O ₄	134.00	-1318	0	0.000	0.142
oxide	Na ₂ O	61.98	-418	-375	0.075	0.069
perchlorate	NaClO ₄	122.40	-383	-255	0.142	—

Table 1. Formula Weights and Thermodynamic Properties for Some Substances Relevant to Pyrotechnics (Continued).

Chemical Name	Chemical Formula [a]	Formula Weight	ΔH_f° [b]	ΔG_f° [b]	S° [b]	C_p° [b]
Strontium	Sr	87.62	0	0	0.052	0.026
carbonate	SrCO ₃	147.63	-1220	-1140	0.097	0.081
chloride	SrCl ₂	158.53	-829	-781	0.115	0.076
nitrate	Sr(NO ₃) ₂	211.63	-978	-780	0.195	0.150
oxalate	SrC ₂ O ₄	175.64	-1371	—	—	—
oxide	SrO	103.62	-592	-562	0.054	0.045
Sulfur	S (rhombic)	32.06	0	0	0.032	0.023
dioxide	SO ₂ (g)	64.06	-297	-299	0.248	0.040
trioxide	SO ₃ (g)	80.06	-396	-371	0.257	0.051
Titanium	Ti	47.4	0	0	0.031	0.025
dioxide	TiO ₂	239.19	-945	-890	0.050	0.055
Zinc	Zn	65.37	0	0	0.042	0.025
oxide	ZnO	81.36	-348	-318	0.044	0.040
sulfide	ZnS	97.43	-206	-201	0.058	0.046

[a] Unless otherwise indicated, these are crystalline solids. Gases are indicated as (g) and liquids as (l).

[b] Values are for 298.15 K, with units of kJ/mol.

Data are from references 9, 16 and 17. If data were inconsistent in the references, the most recent value is quoted. Data were rounded to the number of significant figures presented in the Table.