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Theory of Colored Flame Production

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ABSTRACT

The theories and attributes associated with the production of colored flames are presented. Particular attention is given to flames containing strontium (red), barium (green), sodium (yellow) and copper (green or blue). Thermal excitation of vaporized neutral atoms, molecules and ions is correlated with the emission of atomic, band and ionic spectra. These spectra are tabulated. The color contribution of C-type chemiluminescence, a non-thermal excitation, is described briefly.

The variability of emitters, emissions and color with the operating flame temperature is discussed in relation to the thermodynamic properties of the reactants and the products of combustion. These thermal properties are tabulated. Ionization is shown as a contributor to color degeneration. The use of an ionization buffer to reduce ionization is explained.

Depending on flame conditions and the metal being used, the influence of halogens on the production of color is discussed. The influence is not always beneficial. The flame equilibrium shift caused by the halogens is described for each of the metals. Metals and anions other than the halides are discussed in relation to their ability to intensify or suppress emission. The preferred emitters for each of the metals are listed, and idealistic postulates are presented which apply to the production of color in a flame.

Note added in proof by author:

At the time that these notes were written, some 35 years ago, I was quite naïve with respect to the combustion phenomenology and, as a consequence, I wrote an oversimplified explanation for what are very complicated events. In addition, I had not been introduced to such branches of learning as quantum mechanics, spectroscopy, combustion science, and related fields until much later in my career. That void of knowledge tends to explain why the presentation of these notes is approached qualitatively and in an unrefined manner. Finally, as a young scientist without a mentor, in retrospect, it seems quite presumptuous to have entitled these notes the "Theory of Colored Flame Production", when in fact, not much "theory" is included. Nevertheless, most of the recorded information is of value, even to this day. The reader's considerateness is appreciated.

Theory of Colored Flame Production

1. Purpose

a. The purpose of this presentation is to enumerate and discuss the theories and attributes associated with the production of colored flames.

2. Introduction

a. Ellern[16] states, "… colored flame production is beset with unusual problems. These problems are caused by the lack of choice in the available color-creating materials, the absorption of light by the atmosphere, the limits of discrimination by the human eye, and the chemistry and physics of the processes and substances involved." To overcome the "lack of choice" problem, additional color-creating materials can be made available by inorganic, organic and metal-organic chemical synthesis. In order to evaluate new materials, it is necessary to establish criteria by which the material may be judged.

b. If the chemistry and physics of the processes involved in colored flame production were known in detail, it would not be difficult to establish the criteria. Because, however, much information is not available, it is often necessary to judge materials by empirical methods. Ellern[15] summarized most of the problem when he stated, "With increased and fuller knowledge of the heats of formation, boiling points and dissociation temperatures of reaction products; and with greater insight into the emitting characteristics of gaseous flames and of solid particles, we should eventually be able to build formulas in a more rational manner. Even so, compromises are unavoidable. Maximum heat output per unit volume, highest stability, and lowest volatility of end products (lowest volatility for white light, highest volatility for colored light), and desirable behavior of original reactants, may not be attainable in one formula". One should not interpret this to mean that there is a complete void of knowledge of the chemical and physical processes related to colored light production. Certain facts and theories are available which can be used first to describe the process by which a colored flame is produced and secondly to evaluate and judge the value of new compounds intended for use in colored light formulations. It is for this purpose that the theories related to colored flame production were collected, formulated and discussed in this presentation.

3. Colored Flame Production

a. Mechanism

1. Only a few of the more than 100 elements are used to impart a color to a pyrotechnic flame. These are strontium (red), barium (green) copper (green or blue) and sodium (yellow). Ellern[13] states that lithium (red), boron (green), thallium (green), rubidium (red) and cesium (blue) are also strong color producers but that their use is not practical because of cost, toxicity or the nature of the compounds. All of these elements have certain properties and characteristics in common which contribute to colored light emission.

2. Colored flames are produced by excitation of metallic spectra. At the high temperature of the flame, the salt or metal is vaporized, and part or all of the gaseous molecules are progressively dissociated to give neutral atoms that are potentially emitting species. Some of the free metal atoms unite with other radicals or atoms present in the flame. The vapors of the neutral metal atoms, or of the molecules containing the metal atom, are then excited by
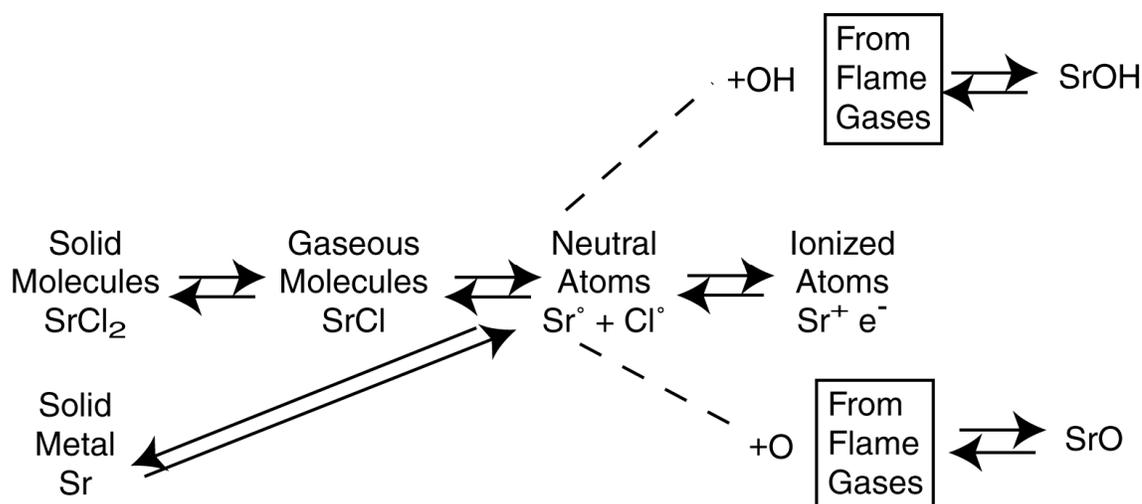
Figure 1.

the thermal energy of the flame. Ionization and excitation of the neutral atoms may occur to some degree. From the excited levels of the atom, or molecule, or ion, a reversion takes place to the ground state ‑ partly by impacts with other species, partly spontaneously by emission of light. The preceding sequence[2] of events occurs in rapid succession. Figure 1 may help to visualize the entire sequence if strontium chloride is used as the example.

b. Spectrum vs. Emitter

1. Different wavelengths of radiation are emitted whenever different events occur. No useful radiation (with respect to colored flames) results while the metal or metallic compound is a solid or liquid. As soon as it is vaporized, useful radiation may result. If the compound remains as an undissociated vaporized molecule, it produces a band spectrum. When the temperature is reached that causes the compound to dissociate to vaporized neutral atoms, a different spectrum results. Neutral atoms produce an atomic spectrum composed of atomic (arc) lines. When the temperature is increased further to the point that the electron is completely removed from the influence of the nucleus, the atom is ionized. Ionized atoms produce an ionic spectrum composed of ionic (spark) lines.

2. Now that a specific event has been described as being associated with a specific spectrum, the sequence of events shown in Figure 1 will be reviewed. The solid $Sr°$ metal or $SrCl_2$ molecule is vaporized. The $SrCl_2$ molecule dissociates to SrCl. The gaseous undissociated SrCl molecules emit a band spectrum. The gaseous neutral atoms of $Sr°$ emit an atomic spectrum. The gaseous neutral $Sr°$ atoms are obtained from the vaporization of the neutral $Sr°$ metal or the dissociation of the gaseous SrCl molecule. At this point, one of two things can happen to the neutral $Sr°$ atom. It can be heated until it ionizes, at which time it emits an ionic spectrum, or it can combine with an anion such as the hydroxide, OH, radical to form molecular SrOH. This new molecule will emit a band spectrum and will behave like the SrCl molecules. As long as it remains as an undissociated gaseous molecule, it will emit a band spectrum. When the temperature is raised, such that the SrOH dissociates into the neutral $Sr°$ atom and the OH radical, the $Sr°$ will once again emit an atomic spectrum. It should be obvious by now that the entire system is temperature dependent.

3. Up to this point, spectra were discussed in terms of radiation resulting from thermal excitation. When radiation results from non-thermal excitation it is described as one of three types of chemiluminescence. For purposes of colored pyrotechnic flames, the C-type

chemiluminescence[31,36] is most important. It results from the formation of an excited molecule directly in the excited state in amounts bearing little or no relation to the ground-state concentrations. This is a molecular, as opposed to an atomic, phenomenon. Colorful band systems for metallic-OH molecules, particularly for barium, strontium and copper, are probably due to molecules that have no independent[5] existence outside the flame. An equation representative of the C-type chemiluminescence is

$$Cu + OH + X \rightarrow CuOH + X$$
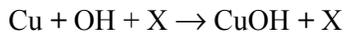
where X is a third body such as H_2O, H_2 or N_2 and CuOH is the directly formed excited molecule. Gaydon[20,22] discusses chemiluminescence in relation to flame reaction processes and equilibria.

4. There is a group of molecular emitters that do not provide desirable colors to pyrotechnic flames. Some of these emitters are OH, CO, O_2, CH, C_2 and H_2O. They make up the background radiation of the flame and will be present as long as organic binders or metal-organic compounds are used in colored flares. All of these radicals and molecules emit a band spectrum.

5. Another spectrum that exists in colored-flame pyrotechnics is due to continuous radiation and is called a continuous spectrum or continuum. No metal is free from a continuous spectrum, especially when present in large amounts. The continuous spectrum is normally a very wide, undifferentiated band.

6. For details concerning the theory of spectra, the reader is referred to books by Gaydon[18] and Pauling.[29]

7. Not only do different metals emit different spectra, but also any given metal may radiate several spectra simultaneously. To complicate the matter even more, all the lines and bands responsible for the colors in colored flare flames have not been assembled in composite form. Therefore, to fill this void and to make information readily available for reference in later discussion, data were assembled concerning the important lines, bands and continuum for strontium, barium, copper, sodium, lithium, boron, thallium, rubidium, cesium and potassium. These data are in Appendix I.

c. **Emitters vs. Temperature and Color**

1. Thus far, it has been established that gaseous metals or metallic compounds will emit various spectra when excited in a flame. The different types of spectra were introduced in relation to the degree or type of excitation involved. The elements that impart a strong red, green, yellow or blue color to a flame were listed. It was also stressed that the flame spectrum that results from the metal excitation is temperature dependent. If the composition of the flame is known to the extent that the emitters are identified, the flame spectrum corresponding to these emitters will be composed predominantly of energy radiating in wavelengths which the eye associates with a particular color. Thus, the apparent color of a pyrotechnic flame can be explained by relating the wavelengths of energy that correspond to that color with emitters that radiate in that wavelength. As mentioned previously, the existence in, or absence from, a flame of a given emitter species is related to the flame temperature. Therefore, in an effort to describe the color production mechanism, it is not only necessary to identify the emitting species but also it is necessary to specify the flame temperature.

d. Temperature

1. For purposes of this discussion, colored pyrotechnic flames will be described assuming a flame temperature of 2000 K. Most colored pyrotechnic flames will probably exceed that temperature. In comparison to other flames, the 2000 K reference temperature is equal to the temperature of an illuminating gas-air flame. The maximum theoretical temperature of an oxygen-hydrogen flame[1] is about 3050 K and that of an oxygen-acetylene flame is about 3325 K. Dean[6] gives 2450 K as the operating temperature of an oxygen-hydrogen flame and 2800 K for an oxygen-acetylene flame. The seemingly low reference temperature was selected primarily to later show that many molecular substances are decomposed below this temperature and, therefore, cannot be considered as emitters at or above this temperature. The reader is referred to Gaydon[23] for information concerning the measurement of flame temperature.

2. There are several temperature-energy relationships that will be used for estimating certain occurrences. For example, in an oxygen-acetylene flame (2800 K), emission is limited to lines[3] whose excitation potential is less than ~5.5 εv or 127 kcal/mole. One electron volt per molecule[21] is equivalent to 23.053 kilocalories per gram mole. At 2000 K, it is estimated that molecules with a dissociation energy of 75 kcal/mole (3.26 εv/molecule) or less will not be present in an appreciable amount and that molecules with a dissociation energy of 95 kcal/mole (4.13 εv/molecule) and larger can be formed and will be stable. Nominally, the 2000 K flame is equated to 3.7 εv/molecule or 30 kcal/mole. For diatomic molecules, the dissociation energy[30] is related to the heat of formation and to bond strength.

3. It is emphasized that the preceding relationships were presented for estimating purposes and must not be used quantitatively. The reason for this obvious lack of accuracy results from the lack of complete understanding of pyrotechnic flame mechanisms. The high temperature chemistry involved is not always predictable using room temperature theory. Brewer and Searcy[12] were quoted as having defined high temperature chemistry as the chemistry of systems at sufficiently high temperatures so that the oxidation states, compounds and general chemical behavior differ appreciably from those at room temperature. This definition emphasizes the probability that new and possibly unorthodox theories must be formulated to explain high temperature phenomena.

e. Energy Definitions and Relationships

1. Various energy terms have already been used in this presentation. To make certain their usage is understood, they are defined[39] as:

   a) Excitation Potential = Excitation Energy:

      1) The energy necessary to bring an atom, molecule, atomic nucleus, etc., from the ground state into an excited state. Example of use: In Appendix I the atomic spectrum strontium line λ4607.3 is shown with an excitation potential of 2.7 electron volts. Thus, 2.7 εv/molecule is necessary to excite this strontium line. From the preceding discussion of temperature, a 2000 K flame was approximated as 3.7 εv/molecule or 85 kcal/mole. A 2000 K flame, therefore, has sufficient energy to excite the λ4607.3 atomic spectrum strontium line but will not excite the 4.3 εv atomic spectrum strontium line λ4832.l. With knowledge of the flame temperature and its relationship to energy, the excitation potential is a measure used to determine whether or not a particular spectrum line will be emitted.

   b) Ionization Potential = Ionization Energy:

1) The energy per unit charge, for a particular kind of atom, necessary to remove an electron from the atom to infinite distance. Example of use: In Appendix I the ionic spectrum strontium line λ4077.7 is shown with an excitation potential of 8.7 εv. The ionization potential for strontium is shown as 5.69 εv. Thus, 5.69 εv is necessary to remove the first electron from the influence of the strontium nucleus and an additional 3.01 εv is necessary to excite the λ4077.7 ionic line for strontium. The previous discussion of temperature compared the oxygen-acetylene flame to 5.5 εv. Thus, the oxygen-acetylene flame cannot be expected to excite the λ4077.7 ionic line to any appreciable degree. Some ionization of strontium will, however, occur. The first ionization potentials[27] for the 10 elements being discussed are:

Element	kcal/mole	Electron volts
Lithium	124.3	5.39
Sodium	118.4	5.14
Potassium	100.0	4.34
Rubidium	96.3	4.18
Cesium	89.7	3.89
Thallium	140.8	6.11
Barium	120.1	5.21
Strontium	131.2	5.69
Boron	191.2	8.29
Copper	178.1	7.73

c) Dissociation Energy:

1) The energy necessary for the complete separation from each other of the two atoms forming a diatomic molecule, or for the removal of an atom or a group of atoms from a polyatomic molecule. More exactly, the dissociation energy is the difference between the energy of the molecule and its dissociation products in their respective ground states. If, therefore, the actual dissociation process leads to atoms (or radicals) in excited states the dissociation energy is the energy needed for their separation minus the excitation energy. Example of use: Dissociation energies for various diatomic and polyatomic molecules are listed in Appendix II. These values in conjunction with the heat of formation and free energy of formation are used to hypothesize the existence of molecules in a flame. Sodium hydride, for example, has a low dissociation energy and heat of formation and slightly negative free energy of formation. Conversely, these thermodynamic characteristics are numerically large for sodium fluoride. Thus, at high temperatures, sodium fluoride would be expected to be stable whereas sodium hydride would be expected to decompose.

d) Enthalpy = Heat Content, H.

1) Thermodynamic potential defined as

$$H = E + PV$$

where E is the internal energy of the system and PV is pressure-volume.

e) Heat of Formation

1) The increase of heat content of the system when one mole of a substance is formed from its elements. Example of use: Heats of Formation for various compounds are listed in Appendix II. In a manner similar to that described for disso-

ciation energy, heat of formation is used as a measure to estimate the existence of a compound in a flame at high temperature. This means is somewhat unreliable because of entropy changes.

f) Entropy, *S*.

1) The energy[33] per degree of absolute temperature that cannot be recovered as work. Entropy, *S*, is related to free energy and enthalpy by

$$H = F + TS$$

g) Free Energy of Formation, ΔF

1) The free energy[35] change accompanying the formation of the compound at unit activity from the elements also at unit activity. Free energy of formation is defined by the relationship

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

Example of use: The sign of the free energy[34] change of a process is very significant. A minus sign denotes that the reaction tends to proceed spontaneously. A positive sign indicates that the reaction is nonspontaneous and when $\Delta F = 0$, the system is at equilibrium. A negative free energy change for a process does not necessarily mean that the process will take place. It is merely an indication that the process can occur, provided the conditions are right. It is the sign of the free energy change that determines whether the potentiality to react exists, and it is the magnitude of the free energy change that tells how large that potentiality is. Thus, the free energy of formation of a compound may be used to hypothesize the existence of the compound in a flame. Free energies of formation at 2000 K are given for many compounds in Appendix II.

f. Ionization

1. Ten elements have been mentioned previously as being associated with the production of a colored flame. It is interesting to note that five of these are in Group I of the Periodic Table. They are lithium, sodium, potassium, rubidium and cesium. Two of the ten elements, barium and strontium, are in Group II of the Periodic Table. In addition, these seven also have ionization potentials of such magnitude that ionization in a flame can be expected. Table 1 gives the percent ionization[6] of the aforementioned seven elements in relation to various operating flame temperatures.

Table 1. Percent Ionization Relative to Various Operating Flame Temperatures.

Element	Ionization Potential εv	Air- Propane 2200 K	Hydrogen- Oxygen 2450 K	Acetylene- Oxygen 2800 K
Lithium	5.39	<0.01	0.9	16.1
Sodium	5.14	0.3	5.0	26.4
Potassium	4.34	2.5	31.9	82.1
Rubidium	4.18	13.5	44.4	89.6
Cesium	3.89	28.3	69.6	96.4
Strontium	5.69	<0.1	2.7	17.2
Barium	5.21	1.0	8.6	42.8

The Saha equation,

$$\log K = \frac{-5050E}{T} + \frac{5}{2}\log T - 6.50 + \log \frac{[g^+][g^-]}{[g]}$$

where E is the ionization potential in electron volts, T the absolute temperature and the g terms are the statistical weight of the ionized atom, the electron and the neutral atom, is used to determine the change in the degree of ionization with temperature. For alkali (Group I) metals the final term is zero; for the alkaline earth (Group II) metals the final term is 0.6.

2. At 2200 K, except for rubidium and cesium, Table 1 shows very little ionization. Thus, at the 2000 K reference temperature chosen for this presentation, even less ionization can be expected. An increase of relatively few degrees to 2450 K shows a significant increase in ionization. Therefore, unless the flare is operating near or below 2200 K, a significant amount of ionization must be anticipated.

3. For purposes of colored flame production, there are several flame characteristics associated with ionization that make ionization undesirable. This is, of course, why pyrotechnic formulators have always attempted to create "cool" burning compositions. The spectrum[4] of the ion is completely different from the spectrum of the neutral atom and resembles the spectrum emitted by the element of preceding atomic number. However, because of the additional positive charge on the nucleus, the zero energy level is higher than for the element of preceding atomic number, and consequently the emission lines are displaced toward the ultraviolet. Therefore, when appreciable ionization occurs a reduced quantity of the desired wavelength of energy is emitted and as a result, the flame color deteriorates. This occurs first because the ion is emitting an ionic spectrum which, for pyrotechnic purposes, is undesirable and secondly because of that ionization, a reduced number of neutral atoms are left to emit in the desired atomic spectrum or to form molecules that would emit the desired band spectrum.

4. If ionization occurs in a flame dependent on barium for its color, the deterioration in color becomes more noticeable than it would in a comparable sodium or strontium dependent flare because:

   a) Many emissions within the desirable atomic and band spectra are in the yellowish-green wavelength instead of deep green to blue-green and therefore do not, even under ideal conditions, provide a large contrast with yellow...and

   b) The intensity of the barium spectrum is less than that of strontium or sodium and therefore any reduction in emission due to ionization will be more noticeable...and

   c) Due to reduced luminous[40] efficiency and increased atmospheric attenuation in this wavelength, the visibility is reduced even further. By comparing the differences between the ionic and atomic spectrum for barium or strontium, as shown in Appendix I, the reader can readily visualize the color (wavelength) shift. No ionic spectrum was given in Appendix I for sodium or the other Group I alkali metals. These ionic spectra, as indicated earlier, would be expected to resemble the atomic spectra of the inert gases with a shift toward the ultraviolet. In any event, a strong, distinct, desirable color would not be expected from ionized alkali metals such as are emitted by their neutral atoms as atomic spectra.

5. Ionization in flames has been studied very extensively. The reader is referred to Gaydon,[24] Sugden[25,32,37] and others[26,38] for additional information concerning such ionization.

g. Ionization Buffer

1. Occurrence of ionization of metal vapors, especially the alkali metals, strontium and barium, has already been described. Ionization of barium has already been described. Ionization of barium in a barium-based flame has been described as being particularly detrimental to emission of the desired green color. One means for reducing ionization is to reduce the temperature. This relationship was previously described. From a practical standpoint, to reduce the operating temperature to the point that ionization of barium would be negligible may result in an unserviceable pyrotechnic for reasons other than color. It is, therefore, desirable to be able to suppress barium ionization by means other than temperature reduction. This can be accomplished[8] by the addition of an easily ionized metal to the flame. In Military Pyrotechnics, potassium, usually in the form of the perchlorate, is used to buffer the ionization. The selection of the perchlorate salt of potassium instead, for example, the nitrate salt, is to provide not only the buffer effect and oxygen supply but also a halogen supply. Halogen influences will be discussed separately.

2. Continuing with the ionization buffer discussion, the ionization of barium can be described as:

$$Ba^o \rightleftarrows Ba^+ + e^-$$

Potassium, which is even more readily ionizable than barium, can be described in a similar manner:

$$K^o \rightleftarrows K^+ + e^-$$

If conditions which approach equilibrium are assumed, then by Le Chatelier's Law of Mass Action, the electrons readily produced by the potassium ionization will bring stress to bear on the barium equilibrium, thereby displacing the barium reaction toward the neutral atom. In so doing, less barium is ionized leaving more barium to emit its atomic spectrum or to form a compound that will emit its band spectrum.

3. The effect of potassium on color should be noted. The ionized potassium will emit a spectrum that resembles the atomic spectrum for argon whose strongest lines are in the deep red and near infrared. As seen from the thermodynamic properties listed in Appendix II, except for the halogen salts, potassium will exist as the neutral atom in flames over 2000 K and, therefore, will emit the characteristic purplish-red and bluish-purple atomic lines listed in Appendix I. Flame emission spectra for the potassium-halogen salts could not be located. The ionic and atomic potassium spectra will not cause appreciable interference in a strontium-red flame. Somewhat more interference would be expected in a barium-green flame. Fortunately, however, the benefits of the ionic buffering action outweigh the disadvantage of the off-color ionic and atomic spectral emissions.

h. Halogen Influences and Color Production

1. Long ago, pyrotechnicians started to add halogens, in some form, to pyrotechnic compositions in order to intensify or enhance the color. Chlorine in the form of a perchlorate salt is frequently used for this purpose. In addition, non-oxidizing chlorinated additives such as hexachlorobenzene and polyvinyl chloride are also used. Although the effect is known, the mechanism is not completely understood.

a) Barium-Strontium

1) Ellern[14] credited Hart as referring to the red flame as due to molecular bands in the red region, caused by molecular strontium oxide and chloride, and diluted with other lines and bands from incandescent particles. Hart also referred to the green flame as being due to bright blue bands from copper and barium chloride in the 4000–5000 and 5000–5500 Å region. More recent information leads to a slightly different explanation.

2) Colored flame pyrotechnic compositions contain organic binders and chlorinated organic molecules. The combustion (oxidation) of these organic molecules provides the flame gases with a source of atomic and molecular hydrogen, neutral and negatively charged hydroxyl radicals, atomic and anionic chlorine and other materials. The low, 57 kcal/mole, dissociation energy of molecular chlorine as shown in Appendix II leads to the absence of molecular chlorine from the flame. Using barium as the example metal, several combinations can be expected.

$$Cl + H + OH \rightleftarrows HCl + OH$$
$$OH + Ba \rightleftarrows BaOH$$
$$Cl + Ba \rightleftarrows BaCl$$
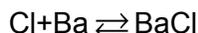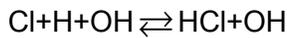
The combination of chlorine and hydrogen to form hydrochloric acid is spontaneous at 2000 K since the free energy of formation is –25.5 kcal/mole. Once formed, the HCl can be expected to be stable at temperatures in reasonable excess of 2000 K since the dissociation energy is about 103 kcal/mole. The high likelihood of HCl formation plus the stability after formation causes an excess of the OH radical. This excess, in turn, represses the diatomic metal chloride, BaCl formation and increases the triatomic metal hydroxide, BaOH, formation. Another consideration with respect to the suppression of the BaCl formation is the low, 51 kcal/mole, dissociation energy of the diatomic chloride. Enhancement, therefore, results by shifting the equilibrium toward the formation of BaOH that, as shown in Appendix II, emits in the green wavelength. Pyrotechnicians prefer BaOH formation to BaO formation because the BaO band spectrum encompasses many undesirable wavelengths. BaO would probably form in greater quantities if the BaOH formation were not promoted by the equilibrium shift caused by the chlorine addition. As a consequence, if BaOH formation is increased at the expense of BaO, this, in itself, will result in a more desirable or enhanced color.

3. Halogen enhancement of strontium is analogous to that described for barium. In both instances, because the pyrotechnic compositions are usually saturated with the metal and halogen, a very substantial amount of the metal halide will be present in the flame in addition to the hydroxide. The halide formation with barium and strontium is not objectionable because these molecules fortunately also emit energy as defined by their molecular band spectrum in the desired wavelength.

b) Alkali Metals

1) The halogen effect with respect to the alkali metals is different from that just described for barium and strontium. Generally, because the desirable emission from the alkali metals is the atomic spectrum of the neutral atoms, the addition of a halogen will not result in enhancement. The desired emission of the atomic spectrum will be substantially reduced because of salt formation.

2) All the alkali metals will not behave identically because of the stability differences in their hydroxide. Sugden[37] points out that at 2245 K, LiOH is very stable whereas NaOH is so unstable as to be effectively absent from the flame. Among the alkali metals, the stability in decreasing order is

$$LiOH > CsOH > RbOH > KOH > NaOH$$

In a manner similar to that used for barium and strontium, and using rubidium as the example metal, several combinations can be expected

$$Cl+H+OH \rightleftarrows HCl+OH$$
$$Cl+Rb \rightleftarrows RbCl$$
$$HCl+Rb \rightleftarrows RbCl+H$$
$$OH+Rb \rightleftarrows RbOH$$
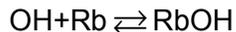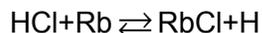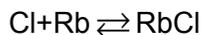
The equilibrium of the last equation will shift considerably for different alkali metals because of the previously mentioned stability differences. The variation in this equilibrium will affect the quantity of halogen salt formed. Sodium will form NaCl with little or no NaOH formation, whereas lithium will form LiOH and a significant amount of LiCl. In any event, whether it be hydroxide or halide formation, the formation of any alkali metal compound will reduce the amount of alkali metal neutral atoms available to radiate their atomic spectrum. Because halides stimulate alkali metal compound formation, the halogens must be classed as negative enhancement agents in flames containing alkali metals. In contrast, halogens are positive enhancement agents in flames containing the alkaline earth metals because, under those conditions, the hydroxide and halide band spectra are preferred over the atomic spectrum.

c) Boron

1) When boron is added to a flame, the green color that results is due predominantly to BO_2. Some BO is probably also formed which emits mostly in the blue to ultraviolet. From thermodynamic data listed in Appendix II, it is concluded that the boron oxides are not only very likely to form (ΔF_{High}) but also very stable (High dissociation energy). Except for iodine, the boron halides also are identified with high free energy of formation and dissociation energy. If the halide band spectrum were predominantly green in nature, the addition of a halide would be beneficial. On the contrary, however, BF has an undesirable yellow system and BBr and BCl emit primarily in near ultraviolet. If, therefore, a halogen other than iodine were introduced, a stable halide would form. This, in turn, would reduce the amount of the oxide present that was radiating in the beneficial green wavelengths. The net result would be a shift toward blue with a negative enhancement with respect to green.

d) Thallium

1) The great bulk of the thallium[11] in a flame is present as the free element. The green flame color is, therefore, due to the neutral atom atomic spectrum. Oxide and hydroxide formation do not occur in the flame to any appreciable degree. The more electronegative halogens will form reasonably stable halides in the flame. These can be expected to emit band spectra. Thallium fluoride, chloride and bromide emit in the deep blue to near ultraviolet wavelength. These emissions are of no particular value for green flame production. Thus, when a halogen is introduced, some stable halide forms. This in turn reduces the amount of the neutral atoms that are radiating in the desired green lines. The net result is a shift toward blue with a negative enhancement with respect to green.

e) Copper

1) The great bulk of the copper[36] in a flame is present as the free atom with not more than 10% as CuO. Appendix I shows an undesirable band spectrum for CuO in the orange region and weak bands in the green region. The free copper atoms emit a weak green line at ~5l05Å. The composite of these emissions would indicate a weak polluted greenish color. Contrary to this, copper, when introduced into a flame, exhibits a strong yellowish green color. This is attributed to CuOH

molecular emission. Note that CuOH formation is recognized even in the absence of halogens. In limited amounts, this is true also of barium, strontium and lithium.

2) During the discussion of the other metals, thermally stable salt formation was described as a result of halogen addition. Appendix II shows generally low dissociation energies for copper compounds. This accounts for the flame composition being predominantly free copper. When halogens are added to a copper flame, the color changes from green to blue. By the postulates laid down for barium and strontium, the addition of halogen to a copper flame would be expected to form the halide acid causing excess OH that, in turn, would combine with the metal to enhance the color emission by radiating the band spectrum. Because of the low dissociation energy, the halide salt would not be expected to form in large amounts. This explanation based on thermal considerations and room temperature theory does not appear to hold true for copper. This is obvious because blue color results instead of an enhanced green.

3) What appears to be a serious flaw in the argument is, in fact, support for the theory of chemiluminescence and is readily explained without deviation from the basic argument. When halogen is added to a flame containing copper, a small amount of the copper halide salt will form. A small amount (as contrasted to large) is formed because of the low dissociation energy. Thus the equilibrium favors dissociation. The small amount of halide salt formed emits a blue band spectrum. This emission dominates that of the CuOH emission that leads to the conclusion that CuOH is probably present in an extremely small quantity. As in the case of barium and strontium, the halogen combines with hydrogen to form the halide acid, thereby causing an OH excess which, in turn, contributes to formation of more CuOH. Also, as in the case of barium and strontium, although more metal hydroxide is formed, the metal halide is formed in even greater amounts. Because the strontium and barium metal halides emit in desirable wavelengths, the net result is a quantitative increase of emission in desirable wavelengths. In the case of copper, however, the increase in CuOH is outweighed by the increase in copper halide formation, thus resulting in a shift from CuOH green emission to blue copper halide emission.

4) The preceding discussion was based on thermal considerations. Gaydon,[19] in discussing carbon monoxide flames, suggested a catalytic effect that should be considered in addition to thermal possibilities. He stated, "Another persistent impurity in the spectra of CO flames is CuCl. These bands are strongest in the blue and blue-green and are degraded to the red. The reason why these bands occur so readily in CO but not other flames is something of a mystery; it is possible that CuCl acts as a catalyst in the oxidation and receives excitation energy from the process".

f) Metal Halide Molecule Excitation

1) Dean[5] states that the halide radical will tend to lessen the attraction of the electron to the nucleus and thus render easier the excitation process. This feature is of importance particularly in flames containing barium or strontium. In these flames a major part of the color is due to molecular excitation and a significant portion of the emitting molecules are the halide salt. The fact that the excitation process is made easier by the halide leads to a net increase in emission. This increase is also considered to be halide enhancement.

g) Halogen Selection

1) The color of pyrotechnic flames is dependent on the volatile material in the flame. This material may be the neutral atom, a diatomic or polyatomic molecule or ions. Color then is dependent on the ability to keep the material volatilized within the flame. The ability to keep material volatilized within the flame is, among other things, related to its boiling point and heat of fusion. It is logical to conclude that, for a flame with a given amount of energy, the amount of the material in the flame is a decreasing function of its boiling point. Thus a low boiling point favors a larger quantity of volatilized matter in the flame.

2) It has already been established that halogens are added to pyrotechnic colored flare compositions to benefit from their enhancement effect. When the metal halide is used as an emitter, it is desirable to keep it volatilized. Since the more electronegative halogens form salts with higher boiling points, the electronegativity of the halogen will be related to the quantity of halide salt which a flame can keep volatilized. The halogen electronegativity scale is:

$$F > Cl > Br > I$$
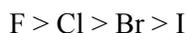
The complete electronegativity scale of the elements has been tabulated by Pauling.[28] Without considering other factors, iodine would be the best choice to provide a low boiling material. See Appendix II for a listing of melting and boiling points. Some iodides are, however, unstable at the flame temperature. A more electronegative halogen must, therefore, be selected. Another important consideration is the band spectrum that the metal halide will omit. These band spectra are described in Appendix I. Although, for example, a metal iodide is stable, its spectrum may not be beneficial to the desired color. In this instance, a compromise will probably result. A more electronegative halogen with a higher boiling point will probably be selected in order to obtain a preferred spectrum. The selection of the halogen, therefore, is not an arbitrary matter. Consideration must be given to such factors as stability, spectrum and boiling point of its salt.

3) Composite flame spectra for copper, barium and strontium are included in Appendix I. These hypothetical spectra would only exist if all of the halogens were present in the flame simultaneously. Such a condition would have no practical advantage. They were included, however, to illustrate wavelength shifts that can be expected by halogen variation.

i). Chemiluminescence

1) Chemiluminescence was discussed briefly in the Spectrum vs. Emitter Section. This phenomenon was also mentioned in the description of copper color production. The characteristic of C-Type chemiluminescence that is of particular importance is the ability of a small number of molecules to emit an abnormally large amount of radiation. The effect is remarkable. BaO has a dissociation energy of 124 kcal/mole and BaOH is estimated to have a dissociation energy (into Ba and OH) of less than 60 kcal/mole. Sugden[36] based on that data estimated the ratio of BaO:Ba:BaOH in a typical flame to be roughly $10^3:1:10^{-3}$. It, therefore, is remarkable that such a small quantity of BaOH will emit such an intense green color. C-Type chemiluminescence is, therefore, suggested.

2) It is emphasized that C-Type chemiluminescence results from the formation of an excited molecule directly in the excited state in amounts bearing little or no relation to the ground-state concentrations. The molecular emissions are probably due to molecules that have no independent existence outside the flame. The phenomenon is not a thermal type excitation and, therefore, must be considered as a radiation source in addition to thermal radiations. The strong strontium red, barium

green and copper green colors in a flame have been attributed primarily to C-Type chemiluminescence of SrOH, BaOH and CuOH.

j) Emission Suppression and Intensification

1) Pyrotechnicians empirically learned to avoid the use of various compounds in colored flame compositions. When used, serious degeneration of the color often results. Emission suppression of alkaline earth radiations is caused by elements[7] such as aluminum, boron, chromium, phosphorus, silicon, iron, beryllium and sulfur. The suppression appears to be based on the formation of molecular compounds with the alkaline earth metals which are either difficult to evaporate or difficult to dissociate. Many of the suppressors possess the ability to form anions such as the aluminates, borates, phosphates, chromates and sulfates. This phenomenon may be one of the reasons pyrotechnicians have been unable to color the flame from standard day-night type phosphorus compositions.

2) The red burning railroad "fusee" is shown by Ellern[17] to contain 10% sulfur. Sulfur is described along with other materials as having desirable properties from the viewpoint of being slow and cool burning. These references to successful commercial use in a colored flame composition and to its desirable properties emphasize that an element or its compound may be used to advantage when the suppression properties are outweighed by desirable thermodynamic, chemical and physical properties. When ultimate performance is required, the use of any of the listed suppressors should be considered very carefully.

3) Although the oxalate anion is reported[9] to seriously repress sodium emission, sodium oxalate is frequently used as a sodium donor in yellow flame formulations. From a practical standpoint, the suppression can frequently be tolerated because of the extremely high intensity of the sodium atomic lines. The oxalate ion does not appear to seriously suppress strontium or barium emission.

4.) Phosphates and sulfates strongly inhibit the emissions of most metals although sulfate has been reported[10] as an intensifier of boron emission. The acetate anion is generally considered to be an intensifier. This suggests that for yellow flames, sodium acetate may be better than sodium oxalate. For that matter, some benefits may be realized from using strontium or barium acetate instead of their oxalates.

k) Flame Equilibria

1) Throughout the discussions, molecule formations, dissociations, ionization and similar events were described by indicating whether or not the event would take place. Since most of the reactions in the flame are reversible, an equilibrium for each event must be considered. For example, because of incomplete combustion and turbulence, there is departure from equilibrium within the flame.

2) A quasi-equilibrium is probably established between the reactants and reaction products. In addition, there are temperature gradients within the flame which tend to upset established equilibria. It would be an advantage to describe each occurrence in a flame with an equilibrium constant. Under given and constant flame conditions, it would then be possible, for example, to calculate the quantity of a reactant or reaction product in the flame. Because, however, of departure from equilibrium, temperature gradients, turbulence, incomplete knowledge of existing reactions in the flame and other causes of variability, absolute statements of quantity were not used to describe events within the flame.

3) When it was stated that an event would or would not occur, the reader must recognize that these judgments are not absolute with respect to quantity. In addition,

many events were described using relative quantity descriptions. In most instances, the assessment was made based on thermodynamic properties of the materials involved. For example, it was stated that the low, 57 kcal/mole dissociation energy of molecular chlorine leads to its absence from the flame. This statement was made because of the relatively large separation between the 57 kcal/mole dissociation energy and the energy of a 2000 K flame that was nominally equated to 85 kcal/mole. If the dissociation energy of Cl_2 had been even lower, an even smaller amount of Cl_2 would form. Conversely, the more the dissociation energy is larger than the nominal flame energy, the more likely it is that the flame will not dissociate the material, thereby allowing more of the material to be present in the flame. It is in such a relative manner that each event's occurrence was described.

4. Postulates and Summary

a. An ideally formulated pyrotechnic colored flame composition is one which, when burned, produces combustion products all of which readily emit radiation in the wavelength of the desired color. The preferred emitters of various elements are:

Preferred Emitters of Various Elements.

Element	Combustion Product	Flame Color
Lithium	Li°	red
Sodium	Na°	yellow
Rubidium	Rb°	red
Cesium	Cs°	blue
Barium	BaX, BaOH	green
Strontium	SrX, SrOH	red
Boron	BO_2	green
Thallium	Tl°	green
Copper	Cu° and CuOH green	CuX blue

X = halogen

Ionized potassium, rubidium and cesium are useful ionization buffers. To prepare efficient formulations, pyrotechnics must be compounded to form the neutral atoms or molecules in large amounts. To do this, the approach will vary with the element used to produce the color. Certain postulates apply which disregard all practical material considerations, such as sensitivity, stability, hygroscopicity, combustion properties, cost and toxicity. Such postulates that apply only to the production of color in a flame are:

1. Formulate the composition so that a maximum amount of the preferred emitter is produced in the flame as a vapor.

2. Adjust the flame operating temperature in relation to the production of the maximum amount of excited emitter. This requires that the temperature be kept low to reduce ionization and that it be kept high enough to produce vaporization and excitation of preferred species and dissociation of unwanted molecules.

3. Use an ionization buffer to aid in ionization suppression. This is of particular advantage when the color is the result of the alkali or alkaline earth metals.

4. For elements whose color depends on the neutral atom, avoid the addition of materials whose elements can combine with the neutral atoms to form molecules. For the remaining elements, add materials whose elements will combine to form the preferred molecules.

5. Formulate to benefit from chemiluminescence and enhancement effects.

6. Select materials to reduce emission suppression that results from many anions and numerous metals.

7. Do not introduce material that is not essential to the production of color. This will reduce unwanted emissions and background radiation.

b. With consideration only to color production, it is concluded that simultaneous compliance with all the postulates is impossible. This reason alone makes compromise mandatory. When considerations related to practicality are introduced, additional concessions result. It is, therefore, fortunate for the author that the purpose of this presentation is to describe only the theory of colored flame production. Thus, it is not necessary to list flare formulae that will produce colored flames under all conceivable conditions and in fulfillment of all requirements. A better understanding of the chemical and physical processes involved in colored flame production will, however, enable the preparation of compositions in a more rational manner. It was for this purpose that the theories and attributes associated with colored flame production were discussed and enumerated.

References

1) J. A. Dean, *Flame Photometry*, McGraw Hill, New York (1960) p 17.

2) Ibid., p 31.

3) Ibid., p 33.

4) Ibid., p 36.

5) Ibid., p 37.

6) Ibid., p 42.

7) Ibid., pp 41 and 107.

8) Ibid., p 104.

9) Ibid., p 166.

10) Ibid., pp 229–230.

11) Ibid., p 236.

12) J. Drowart and P. Goldfinger, *Annual Review of Physical Chemistry*, Annual Reviews, Inc., Palo Alto, CA, Vol. 13 (1962) p 459.

13) H. Ellern, *Modern Pyrotechnics*, Chemical Publishing Co., Inc., New York (1961) p 78.

14) Ibid., p 81.

15) Ibid., p 90.

16) Ibid., p 96.

17) Ibid., pp 97 and 275.

18) A. G. Gaydon, *The Spectroscopy of Flames*, John Wiley, New York (1957) pp 48–72.

19) Ibid., p 92.

20) Ibid., p 195.

21) A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall, London (1953) p 3.

22) A. G. Gaydon and H. G. Wolfhard, *Flames; Their Structure, Radiation and Temperature*, Chapman and Hall, London (1960) p 226.

23) Ibid., pp 234–301.

24) Ibid., pp 302–323.

25) J. A. Green and T. M. Sugden, *Ninth Symposium (International) on Combustion*, Academic Press, New York (1963) pp 607–621.

26) S. A. Greene, *A Literature Survey of Ions in Flames*, Aerospace Corporation Report No. TDR-169 (S3153-0l)TN-5, Contract No. AF-04(695)-169, 15 June 1963. See NTIS AD410329.

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28) Ibid., p 93.

29) Ibid., pp 594–601.

30) Ibid., p 622.

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32) P. J. Padley and T. M. Sugden, *Eighth Symposium (International) on Combustion*, Williams and Wilkins, Baltimore (1962) pp 164–179.

33) C. F. Prutton and S. H. Maron, *Fundamental Principles of Physical Chemistry*, Macmillan, New York (1956) p 296.

34) C. F. Prutton and S. H. Maron, *Fundamental Principles of Physical Chemistry*, Macmillan Co., NY (1956) p 318.

35) Ibid., p 331.

36) T. M. Sugden, *Annual Review of Physical Chemistry*, Annual Reviews, Inc., Palo Alto, CA, Vol. 13 (1962) pp 381–382.

37) T. M. Sugden, *Fifth Symposium (International) on Combustion*, Reinhold Publishing, NY (1955) pp 406–408.

38) A. Van Tiggelen, *Ion Production and Concentration in Flames*, University of Louvain (Belgium), *Annual Summary Report No. 2,* Contract no. AF-61(052)-398, May 1962. See NTIS AD278417.

39) Unknown, *International Encyclopedia of Chemical Science*, D. Van Nostrand Co., Inc., NY (1964).

40) Unknown, *The Science of Color*, Thomas Y. Crowell Co., NY (1954) pp 227 and 308.

Appendix I

1. Contents

   a. Spectra

Lithium

Sodium

Potassium

Rubidium

Cesium

Thallium

Barium

Strontium

Boron

Copper

  b. Chromaticity Data Diagram

2. Symbols

λ = wavelength in Angstroms (Å)

I = relative intensity

εν = electron volts

Å = Angstrom

mμ = millimicron = l0 Å

3. References

a)   J. A. Dean, *Flame Photometry*, McGraw-Hill, New York, 1960.

b)   A. G. Gaydon, *The Spectroscopy of Flames*, John Wiley, New York, 1957.

c)   P. T. Gilbert, *Flame Spectra of the Elements*, Bulletin *753-A,* Beckman Instruments, Inc., Fullerton, CA, 1961.

d)   G. R. Harrison, *Massachusetts Institute of Technology Wavelength Tables*, John Wiley, New York, 1956.

e)   L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960.

f)   R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, John Wiley, New York, 1963.

4. Discussion of Contents

  a. The atomic and ionic spectra were selected from the MIT Wavelength Tables.[d] The elemental ionization potentials were calculated from the energies listed in Table 2–5 in Pauling.[e] The electron volt, εν, entry listed with the atomic and ionic spectra is the excitation potential or energy required to excite that particular line. These energy levels were selected from the MIT Tables. The band spectra were collected from Pearse,[f] Dean,[a] Gaydon[b] and Gilbert.[c] Data concerning continuum were selected from Gaydon and Dean.

  b. The intensities, I, are eye estimates based on a scale of 10 for the strongest line or band in the system. Because the values were collected from several sources, the values are very unreliable

and should not be used for any quantitative purposes. For that matter, they are even unreliable for qualitative purposes.

c. Composite flame spectra were prepared for barium, strontium and copper. Flames will probably never correspond to these composites since all halogens will undoubtedly never be present in one pyrotechnic composition. The information was, however, collected into its composite form so that by viewing one page, the reader can visualize the location of various molecules with respect to the wavelength and color that they emit and in relation to one another. These composite spectra do not include continuum or band emissions from molecular and free radical products of combustion from organic compounds.

d. All emissions for a specific element or molecule are not listed in this collection. Only the more intense and persistent lines and bands have been mentioned. For example, 175 lines are listed for sodium in the MIT Wavelength Tables whereas only six are listed herein. For extensive listings of emission data, the MIT Wavelength Tables and similar documents must be consulted.

e. A Chromaticity Data diagram that relates wavelength to color was included to aid the reader to visualize the color in relation to various radiation wavelengths.

Lithium

Elemental Lithium			Ionization Potential 5.39 εv
Atomic Spectrum			
λ	εv	I	Ionic Spectrum
6707.8	1.8	10	(None Located)
6103.6	3.9	5	
4603.0	4.5	4	Continuum 460 to 320 mµ
3232.6	3.8	3	

Sodium

Elemental Sodium			Ionization Potential 5.14 εv
Atomic Spectrum			
λ	εv	I	Ionic Spectrum
5895.9	2.1	9	(None Located)
5889.9	2.1	10	
5688.2	4.3	—	Continuum 602 to 360 mµ
5682.7	4.3	—	
3303.0	3.7	4	
3302.3	3.7	4	

Potassium

Elemental Potassium			Ionization Potential 4.34 $\varepsilon\nu$
Atomic Spectrum			
λ	$\varepsilon\nu$	I	Ionic Spectrum
7699.0	1.6	9	(None Located)
7664.9	1.6	10	
4047.2	3.0	4	Continuum 570 to 340 mμ
4044.1	3.1	5	

Rubidium

Elemental Rubidium			Ionization Potential 4.18 $\varepsilon\nu$
Atomic Spectrum			
λ	$\varepsilon\nu$	I	Ionic Spectrum
7947.6	1.6	10	(None Located)
7800.2	1.6	10	
6298.6	—	5	
4215.6	2.9	8	
4201.9	2.9	8	

Cesium

Elemental Cesium			Ionization Potential 3.89 $\varepsilon\nu$
Atomic Spectrum			
λ	$\varepsilon\nu$	I	Ionic Spectrum
8943.5	1.4	10	(None Located)
8521.1	1.4	10	
4593.2	2.7	7	
4555.4	2.7	8	

Thallium

Elemental Thallium			Ionization Potential 6.11 $\varepsilon\nu$
Atomic Spectrum			
λ	$\varepsilon\nu$	I	
5350.5	3.3	10	
3775.7	3.3	9	
3519.2	4.5	7	
3229.8	4.8		
2918.3	5.2	2	
2767.9	4.5	2	

Barium

1. Elemental Barium

Elemental Barium			Ionization Potential 5.21 εν		
Atomic Spectrum			Ionic Spectrum		
λ	εν	I	λ	εν	I
5777.7	3.8	9	4934.1	7.7	4
5535.6	2.2	10	4554.0	7.9	10
5519.1	3.8	6	4130.7	10.9	0.5
5424.6	3.8	1	3891.8	10.9	0.2
3071.6	4.0	1	2335.3	11.2	0.6

2. BaOH Band Spectrum

Green bands, maxima 487, 512, 515 and 527 mμ

3. BaO Band Spectrum

λ	I
7097.4	5
6782.8	8
6493.1	9
6291.0	8
6224.7	6
6165.1	6
6102.3	5

λ	I
6039.6	9
5976.3	3
5864.5	10
5805.1	6
5701.0	8
5644.1	9
5492.7	10

λ	I
5349.7	8
5214.7	7
5086.7	6
4965.4	3
4850.6	6
4680.3	5

4. Barium Oxide (emitter species uncertain)

Band groups at 4800, 5020 and 5500 Å. The 5500 group shows two main bands at 5445–5452 and 5482–5488. Band heads have been observed from 4730 to 4855 and from 5007 to 5018.

5. BaBr Band Spectrum

λ	I
5415.9	4
5360.1	10
5305.5	6

λ	I
5260.6	4
5208.2	10
5156.4	5

6. BaCl Band Spectrum

λ	I
5320.8	1
5240.5	10
5213	1
5167	2

λ	I
5139.2 \	10
5136 /	
5066	1

7. BaF Band Spectrum

Green System

λ	I
5000.6	8
4992.1	5
4950.8	10

Extreme Red System

λ	I
7430.8	7
7142.0	10
7119.2	10

λ	I
6958.7	6
6935.1	6

8. BaI Band Spectrum

λ	I
5609.5	10
5381.7	7
5260	—
5160	—

9. Barium Composite Flame Spectrum

λ	I	Species
7430.8	7	BaF
7142.0	10	BaF
7119.2	10	BaF
7097.4	5	BaO
6958.7	6	BaF
6935.1	6	BaF
6782.8	8	BaO
6493.1	9	BaO
6291.0	8	BaO
6224.7	6	BaO
6165.1	6	BaO
6102.3	5	BaO
6039.6	9	BaO
5976.3	3	BaO
5864.5	10	BaO
5805.1	6	BaO
5777.7	5	Ba
5701.0	8	BaO

λ	I	Species
5644.1	9	BaO
5609.5	10	BaI
5535.6	10	Ba
5519.1	2	Ba
5492.7	10	BaO
5424.6	1	Ba
5415.9	4	BaBr
5381.7	7	BaI
5360.1	10	BaBr
5349.7	5	BaO
5320.8	3	BaCl
5305.5	6	BaBr
5270	—	BaOH
5260.6	4	BaBr
5260	—	BaI
5240.5	1	BaCl
5214.7	7	BaO
5213	1	BaCl

λ	I	Species
5208.2	10	BaBr
5167	2	BaCl
5160	—	BaI
5156.4	5	BaBr
5150	—	BaOH
5139.2 \ 5136 /	10	BaCl
5120	—	BaOH
5086.7	6	BaO
5066	1	BaCl
5000.6	8	BaF
4992.1	5	BaF
4965.4	3	BaO
4950.8	10	BaF
4934.1	4	Ba$^+$
4870	—	BaOH
4850.6	6	BaO
4680.3	5	BaO
4554.0	10	Ba$^+$

Strontium

1. Elemental Strontium

Elemental Strontium			Ionization Potential 5.69 εν		
Atomic Spectrum			Ionic Spectrum		
λ	εν	I	λ	εν	I
4962.3	4.3	3	4305.5	11.6	0.4
4872.5	4.3	2	4215.5	8.6	3
4832.1	4.3	5	4077.7	8.7	4
4607.3	2.7	10	3474.9	12.2	0.8
			3464.6	12.2	2
			3380.7	12.2	1.5

2. SrBr Band Spectrum

λ	I
6666.7	10
6513.0	10

(Has a weak violet system)

3. SrCl Band Spectrum

λ	I
6755.6	3
6744.7	5
6619.9	5
6613.7	10

λ	I
6482.9	4
6362.4	5
6358.7	10
6239.3	2

4. SrF Band Spectrum

λ	I
6655.6	7
6632.7	10
6527.6	7
6512.0	10

λ	I
6419.0 \	8
6394.7 /	
6306.1 \	8
6283.1 /	

λ
5779.5
5772.0
5622 to 5670

5. SrI Band Spectrum

λ	I
7094.0	2
7011.0	10
6930.2	10
6847.7	10

λ	I
6767.8	10
6691.5	8
6662.3	8
6177.3	4

6. SrOH Band Spectrum

λ
6820
6675
6590
6460

λ
6114.2
6111.8
6109.8
6107.9
6107.5
6105.2

λ	I
6109.6	1
6101.1	3
6095.9	4
6089.9	6
6084.7	10
6076.6	8
6050	Strong

7. Sr$_2$O$_2$ Band Spectrum

λ
5950
5969

8. Strontium Composite Flame Spectrum

λ	I	Species
7094.0	2	SrI
7011.0	10	SrI
6930.2	10	SrI
6847.7	10	SrI
6820	—	SrOH
6767.8	10	SrI
6755.6	3	SrCl
6744.7	5	SrCl
6691.5	8	SrI
6675	—	SrOH
6666.7	10	SrBr
6662.3	8	SrI
6655.6	7	SrF
6632.7	10	SrF
6619.9	5	SrCl
6613.7	10	SrCl
6590	—	SrOH

λ	I	Species
6527.6	7	SrF
6513.0	10	SrBr
6512.0	10	SrF
6482.9	4	SrCl
6460	—	SrOH
6419.0\ 6394.7/	8	SrF
6362.4	5	SrCl
6358.7	10	SrCl
6306.1\ 6283.1/	8	SrF
6239.3	2	SrCl
6177.3	4	SrI
6114.2	—	SrOH
6111.8	—	SrOH
6109.8	—	SrOH
6109.6	1	SrOH

λ	I	Species
6107.9	—	SrOH
6107.5	—	SrOH
6105.2	—	SrOH
6095.9	4	SrOH
6089.9	6	SrOH
6084.7	10	SrOH
6076.6	8	SrOH
6050	—	SrOH
5779.5	—	SrF
5772.0	—	SrF
5622 \ 5670 /	—	SrF
4962.3	3	Sr
4872.5	2	Sr
4832.1	5	Sr
4607.3	10	Sr

Boron

1. Elemental Boron

Elemental Boron			Ionization Potential 8.29 εν		
Atomic Spectrum			Ionic Spectrum		
λ	εν	I	λ	εν	I
2497.7	4.9	5	3451.4	20.9	0.05
2496.8	4.9	4			

2. BF (may be BF$_2$ or BF$_3$) Band Spectrum

Yellow System

λ	I
5993.8	8
5984.4	6
5825.7	7

λ	I
5822.1	10
5815.1	8
5807.3	6

λ	I
5803.8	6
5664.0	6

Blue Green System

λ	I
5470.8	6
5460.1	4

λ	I
5456.8	8
4464.9	6

λ	I
4461.4	6
4443.5	6

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3. BO$_2$ Band Spectrum

λ	I
6200	5
6030	7
5800	7

λ	I
5450	9
5180	8
4930	5

λ	I
4710	3
4520	1

Copper

1. Elemental Copper

Elemental Copper			Ionization Potential 7.73 εν	
Atomic Spectrum			Ionic Spectrum εν	
λ	εν	I	λ	εν
5220.1	—	4		
5218.2	6.2	5	2247.0	15.9
5153.2	6.2	4	2192.3	16.2
5105.5	3.8	4	2136.0	16.2
3274.0	3.8	9		
3247.5	3.8	10		

2. CuBr Band Spectrum

λ	I
5032.2	3
4954.7	4

λ	I
4883.4	4
4879.3	8

λ	I
4810.4	2
4341.1	10
4288.6	7

3. CuCl Band Spectrum

λ	I
5262.3	6
5152	3
4982.2	2
4946.1	1

λ	I
4881.5	4
4846.9	3
4788.5	2
4755.7	1

λ	I
4515.9	5
4433.8	9
4353.9	10
4280.9	9

There are additional bands toward the ultraviolet.

4. CuI Band Spectrum

λ	I
5494.1	3
5477.1	4
5461.3	3
5402.2	5
5486.5	6
5371.5	5
5357.4	3
5328.5	3

λ	I
5312.4	5
5297.5	6
5283.8	4
5241.0	3
5226.1	5
5212.2	7
5155.8	3
5141.1	7

λ	I
5117.3	3
5101.9	3
5072.8	10
5034.6	3
5019.7	7
4983.9	4
4968.3	5
4919.1	3

Additional bands exist toward the ultraviolet.

5. **Orange Region:** CuO Band Spectrum

λ	I
6547	—
6530	—
6493.4	1
6430.0	3
6400.4	5

λ	I
6376.9	2
6294.0	5
6280.9	1
6161.5	9
6146.8	8

λ	I
6059.3	10
6045.1	9
5847.6	3
5832.7	2
5827.7	1

Green Region: Large number of weak bands, including a little group of heads between 5237 and 5228 Å, and heads at 5344, 5313, 5308, 5279 and 5274 Å. Emitter uncertain.

6. CuOH Band Spectrum

Strong diffuse band in green at 5350 to 5550 Å and a weaker band in the orange-red at 6150 to 6250 Å. Wide bands have also been reported at 505 and 524 mμ.

7. CuF Band Spectrum

λ	I
5694.3	6
5685.7	6
5677.2	5

λ	I
5086.4	2
5061.1	7
5052.3	6

λ	I
4932.0	8
4926.8	6
4901.3	5
4781.9	4

8. CuH Band System at 4280 Å.

9. Copper Composite Persistent Flame Spectrum

λ	I	Species
6400.4	5	CuO
6294.0	5	CuO
6250 \	—	CuOH
6150 /		
6161.5	9	CuO
6146.8	8	CuO
6059.3	10	CuO
6045.1	9	CuO
5694.3	6	CuF
5685.7	6	CuF
5677.2	5	CuF
5550 \	—	CuOH
5350 /		
5477.1	4	CuI
5402.2	5	CuI
5486.5	6	CuI
5371.5	5	CuI
5344	—	CuO
5313	—	CuO

λ	I	Species
5312.4	5	CuI
5308	—	CuO
5297.5	4	CuI
5283.8	6	CuI
5279	—	CuO
5274	—	CuO
5262.3	6	CuCl
5240	—	CuOH
5237 \	—	CuO
5228 /		
5226.1	5	CuI
5220.1	4	Cu
5218.2	4	Cu
5212.2	7	CuI
5153.2	4	Cu
5141.1	7	CuI
5105.5	4	Cu
5072.8	10	CuI
5061.1	7	CuF

λ	I	Species
5052.3	6	CuF
5050	—	CuOH
5019.7	7	CuI
4983.9	4	CuI
4968.3	5	CuI
4954.7	4	CuBr
4932.0	8	CuF
4926.8	6	CuF
4901.3	5	CuF
4883.4	4	CuBr
4881.5	4	CuCl
4879.3	8	CuBr
4781.9	4	CuF
4515.9	5	CuCl
4433.8	9	CuCl
4353.9	10	CuCl
4341.1	10	CuBr
4288.6	7	CuBr
4280.9	9	CuCl
4280.0	—	CuH

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Chromaticity Data
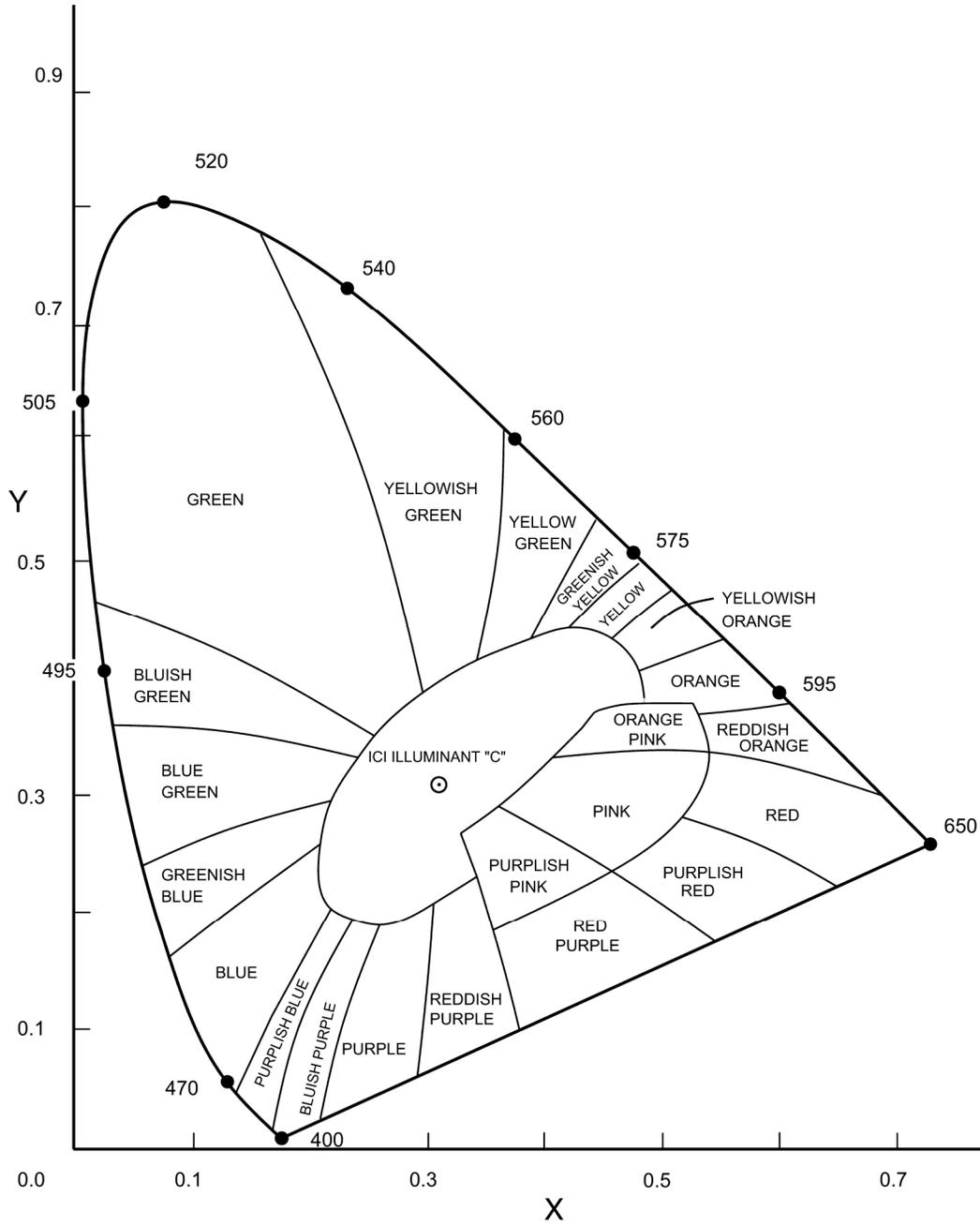
Appendix II

1. Contents

Thermodynamic and Physical Properties

2. Symbols

g = gas state

l = liquid state

c = crystalline state

K = Kelvin

d = decomposes

ΔH_f = heat of formation

ΔF = free energy of formation

D = dissociation energy

3. References cited in following tables.

gf   A. G. Gaydon and H. G Wolflard, *Flames, Their Structure, Radiation and Temperature*, Chapman and Hall, London, 1960.

g   A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall, London, 1953.

m   J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, John Wiley, New York, 16 Volumes, 1937–1961.

r   D. Rossini et al., *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Circular 500, Feb. 1952.

st   D. R. Stull and C. C. Sinke, *Thermodynamic Properties of the Elements*, American Chemical Society, Advances in Chemistry Series 18, 1956.

s   T. M. Sugden, *Fifth Symposium (International) on Combustion*, Reinhold Publishing, New York, 1955, p 406.

w   R. L. Wilkins, *Theoretical Evaluation of Chemical Propellants*, Prentice-Hall, Englewood Cliffs, NJ, 1963.

j   D. R. Stull et al., *JANAF Thermochemical Data*, Dow Chemical, Midland, MI, 1960–1963. Prepared under Advanced Research Projects Agency Program, U. S. Air Force Contract No. AF33(616)-6149.

Carbon, Hydrogen and Gases

Species	Free Energy[j] of Formation (kcal/mole) 2000 K	Heat of Formation (kcal/mole)		Dissociation Energy (kcal/mole)	
		0 K	298.15 K	0 K	298.15 K
H_2O	−32.4	−57.1	−57.8	219.3	221.5
H_2		0	0	103.2	104.2
OH	+2.16	+10.0	+9.3[j]	100.6	101.6
HF	−67.2	−64.2	−65.1[j]	134.2	134.6
HCl	−25.5	−22.0	−22.1	102.2	103.1
HBr			−8.6[r]	86.4[g]	
HI		+6.7[r]	+6.2[r]	70.4[g]	
F_2		0	0	36.7	36.7
Cl_2		0	0	57.1	57.9
Br_2		0	0	45.4[g]	
I_2		0	0	35.6[g]	
N_2		0	0	225.0	225.9
O_2		0	0	118.0	119.1
CO	-68.4	−27.2	−26.4	256.2	257.3
CO_2	−94.7	−94.0	−94.1	381.9	384.5

All gas state.

References: Wilkins except as noted by superscript.

Lithium

Species	State	Free Energy[j] of Formation (kcal/mole) 2000 K	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Li					1638[j]	454[j]
Li_2O	c	−64.2 ΔF changes sign from − to + at 3000 K	−l42.6[j]	276		1700[j]
LiO_2	g		−37.1.	170	2600[gf]	
LiH	c	+23.0 ΔF changes sign from − to + at 1200 K	-27.7[j]			959.6[j]
LiH	l	+15.6 ΔF changes sign from − to + at 1300 K	-15.1[j]		d1245[j]	
LiH	g	+10.7	+32.1[j]	56 (58[g])		
LiOH	c	−37.6	−116.6[j] −102[s]	263		744[j]
LiOH	l	−46.6 ΔF changes sign from − to + at 3100 K	−114.1[j]		~1850[j]	
LiOH	g	−50.0	−57.7[j]	215		
LiF	c	−93.9	−146 −140[s]	202 137[g]		1121[j]
LiF	l	−98.9	−140[j]		1966[j]	
LiF	g	−98.0	−80.5[j]	80.7		
LiCl	c	−50.1	−97.4[j] −116[s]	115[g]		880[j]
LiCl	l	−55.1 ΔF changes sign from − to + at 3700 K	−93.4[j]		1655[j]	
LiCl	g	−62.8	−43.8[j]			
LiBr	c		−83.7[r]	100[g]		823[r]
LiBr	g		−41[r]		1583[r]	
LiI	c		−64.8[r]	81[g]		722[r]
LiI	g		−16[r]		1444[r]	

References: Wilkins except as noted by superscript.

Sodium

Species	State	Free Energy[j] of Formation (kcal/mole) 2000 K	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Na					1177[j]	371
NaO_2	c		−61.9			d373[m]
Na_2O_2	c		−120.6		d	733
Na_2O	c	−1.67	−99.4		>1623[m]	1190[j]
Na_2O	l	−8.60	−93.2[j]			
		ΔF changes sign from – to + at 2200 K				
NaH	c		−13.5[j]	47[g]		d700[j]
		+21.1 at 1500 K				
		ΔF changes sign from – to + at 700 K				
NaH	g	+19.4	+29.8			
NaOH	c	−21.6	−102 −83[s]			593
NaOH	l	−24.9	−100[j]		~1450	
		ΔF changes sign from – to + at 2600 K				
NaOH	g	−38.0	−55.4[j]			
NaF	c	−72.7	−136 −122[s]	107[g]		1285[j] 1268[m]
NaF	l	−77.2	−131[j]		2100[j]	
NaF	g	−73.2	−67[j]			
NaCl	c	−41.1	−98.2 −96[s]	97.6[g]		1081[j] 1077[m]
NaCl	l	−46.8	−93.2[j]		1790[j]	
		ΔF changes sign from – to + at 3700 K				
NaCl	g	−52.0	−43.5		1738	
NaBr	c		−86	87.5[g]		1020[m]
NaBr	g		−36		1665	
NaI	c		−69	70.6[g]		935
NaI	g		−21		1577	

References: Rossini except as noted by superscript.

Potassium

Species	State	Free Energy[j] of Formation (kcal/mole) 2000 K	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
K					1039st	336
K_2O	c		−86.4	sublimes @ 600 mm	1154	
K_2O_2	c		−118		d1052[m]	763
K_2O_3	c		−125		d941[m]	703
KO_2	c		−134		d933[m]	653[m]
KH	c	+23.6 at 1500 K ΔF changes sign from − to + at 700 K	−13.8[j]	42.9[g]		d690[j]
KH	g	+21.7	+29.4			
KOH	c		−101.8 −86[s]			683[j]
KOH	l	−25.9	−98.7[j]		1600	
KF	c		−134.5 −126[s]	115[g]	1775	1129
KCl	g		−51.6		1680	
KCl	c		−104.2 −100[s]	101.4[g]		1043[m]
KBr	c		−93.7	90.6[g]	1656	1001[m]
KI	c		−78.3	76.4[g]	1597	958

References: Rossini except as noted by superscript.

Rubidium

Species	State	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Rb				974st	312
Rb_2O	c	−78.9			
Rb_2O_2	c	−101.7		d1284[m]	943[m]
Rb_2O_3	c	−116.7		d1111[m]	762[m]
Rb_2O_4	c	−126.2		d1430[m]	685[m]
RbH	g	+33	39[g]		
RbOH	c	−98.9 −88[s]			574
RbF	c	−131.3 −124[s]	123[g]	1681	1048
RbCl	c	−102.9 −104[s]	103[g]	1654	990
RbBr	c	−93.0	92[g]	1625	953
RbI	c	−78.5	77[g]	1577	913

References: Rossini except as noted by superscript.

Cesium

Species	State	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Cs	l			958st	302st
Cs_2O	c	−75.9			763
Cs_2O_2	c	−96.2		d1347[m]	867[m]
Cs_2O_3	c	−111.2		d1333[m]	775[m]
Cs_2O_4	c	−124.2		d1538[m]	705[m]
CsH	g	+29	41[g]		
CsOH	c	−97.2 −91[s]			545
CsF	c	−126.9 −128[s]	127[g]	1524[m]	955
CsCl	c	−103.5 −105[s]	106[g]	1573	918
CsBr	c	−94.3	95[g]	1573	909
CsI	c	−80.5	78[g]	1573	894

References: Rossini except as noted by superscript.

Strontium

Species	State	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Sr				1640st	1043
SrO	c	−141	106[g]	3273[m]	2688
SrO_2	c	−153			
Sr_2O	c	−154			
SrH	g	+52	38[g]		
SrH_2	c	−42			
$Sr(OH)_2$	c	−229			
SrF	g	−5	62[g]		
SrF_2	c	−290			1673
SrCl	g	+9	58[g]		
$SrCl_2$	c	−198			1148
$SrBr_2$	c	−171			916
SrI_2	c	−135			788
SrI			46[g]		

References: Rossini except as noted by superscript.

Barium

Species	State	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Ba				1910st	983st
BaO	c	−133	124[g]	2273[m]	2190
BaO_2	c	−150			
Ba_2O	c	−147			
BaH	g	+52	41[g]		
BaH_2	c	−41			
$Ba(OH)_2$	c	−226			681
BaF	g	−9	69[g]		
BaF_2	c	−287		1673[m]	1593
BaCl	g	+24			
BaCl	c	−111	51[g]		
$BaCl_2$	c	−205			1235
$BaBr_2$	c	−180			1123
BaI_2	c	−144			1013

References: Rossini except as noted by superscript.

Boron

Species	State	Free Energy[j] of Formation (kcal/mole) 2000 K	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
B					3949.9[j]	2313[m]
BO	g	−39.1	+3.74[j]	188 (175[g])		
		ΔF changes sign from + to − at 200 K				
(BO)$_2$	g	−119.8	−110.8[j]	491	Not isolated[m]	
		ΔF changes sign from − to + at 5800 K				
B$_2$O$_3$	c	−188.6	−305	749		723[gf]
B$_2$O$_3$	l	−194.0	−301[j]		2520[gf]	
		ΔF changes sign from − to + at 4800 K				
B$_2$O$_3$	g	−177.5	−208	652		
BH	g	+59.7	+06[j]	68 (69[g])		
BH$_2$	g	+41.0	+66.0[j]			
BH$_3$	g	+33.3	+18	270		
BF	g	−87.4	−45.5[j]	196		
BF$_2$	g	−149	−134[j]	327		
BF$_3$	g	−240	−270	458	174[r]	
BCl	g	−1.5	+42.5[j]	118[g]		
		ΔF changes sign from + to − at 2000 K				
BCl$_2$	g	−39.1	−20.7[j]			
BCl$_3$	g	−72.6	−97.1[j]		285.6[r]	
		ΔF changes sign from − to + at 4900 K				
BBr	g		+25[r]	97[g]		
BBr^3	l		−57.9[j]		364.4[j]	
		−32.5 at 1500 K				
BBr$_3$	g	−37.2	−49.7[j]			
		ΔF changes sign from − to + at 4200 K				
BI$_3$	g	+15.0	+15.0[j]			
		between 298 and 6000 K, ΔF is negative only in the 400 to 600 K range. In that range it reaches a maximum negative of −1.684.				
BN	c	−18.5	−60.3	306		
		ΔF changes sign from − to + at 2900 K				
BN	g		+154	92.5 (92[g])		

References: Wilkins except as noted by superscript.

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Thallium

Species	State	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Tl				1740st	577st
Tl_2O	c	−41.9		773	573
Tl_2O_3				−0 @ 1073[m]	990
TlH	g	+48	46[g]		
TlOH	c	−56.9			
$Tl(OH)_3$	c	−122			
TlF	g	−33	109[g]	923	600
TlCl	g	−16		1079	
TlCl	c	−49	87[g]		703[m]
$TlCl_3$	c	−83.9			
TlBr	g	−5		1089	
TlBr	c	−41	74[g]		732[m]
$TlBr_3$	c	−59			
TlI	g	+7		1098	
TlI	c	−30	60[g]		713[m]

References: Rossini except as noted by superscript.

Copper

Species	State	Heat of Formation (kcal/mole) 298.15 K	Dissociation Energy (kcal/mole) 0 K	Boiling Point K	Melting Point K
Cu				2855	1356
CuO	g	+35			
CuO	c	−37.1	113[g]	~2800[m]	1337[m]
Cu_2O	c	−39.8		d2073[m]	1502
CuH	g	+71	62[g]		
$Cu(OH)_2$	c	−107			
CuF	c	+44	69[g]	sublimes 1473[m]	1181[m]
CuF_2	c	−127		d733 to CuF[m]	
CuCl	g	+32			
CuCl	c	−32	85[g]	1227[m] to 1327	703
$CuCl_2$	c	−49		d	771[m]
CuBr	g	+38			
CuBr	c	−25	78[g]	1134[m] to 1227	761
$CuBr_2$	c	−33		d	771[m]
CuI	g	+62			
CuI	c	−16	46[g]	1032[m] to 1045	861
CuI_2	c	−1.7		Solid not isolated [m]	

References: Rossini except as noted by superscript.

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