

Thermodynamic and Spectroscopic Analysis of a Simple Lilac Flame Composition

B. T. Sturman^a and K. L. Kosanke^b

^a 6 Corowa Court, Mount Waverley, Victoria 3149, Australia

^b PyroLabs, Inc., Whitewater, CO, USA

Abstract: *A simple lilac flame composition consisting of 80% potassium nitrate and 20% shellac was investigated by emission spectroscopy and thermodynamic modeling. The flame from the burning composition had a reddish-pink core with a brighter pale lilac outer envelope. The core of the flame is presumably close to the equilibrium conditions predicted by thermodynamic modeling. The calculated equilibrium flame temperature is 1526 K; seven gases (CO, H₂O, N₂, CO₂, H₂, KOH, K) and one liquid (K₂CO₃) account for 99.7% of the molecules in the core of the flame. Of these, liquid potassium carbonate (mole fraction 9.6%) is expected to emit a continuous spectrum while atomic potassium (mole fraction 2.5%) imparts a red colour from the resonance doublet (766.491 and 769.897 nm), which is considerably broadened by self-absorption. The outer flame envelope is presumably a diffusion flame in which flammable gases from the core burn in entrained air. The maximum adiabatic temperature of such a flame was calculated as 1723 K; seven gases (N₂, CO₂, H₂O, KOH, K, Ar, K₂O₂H₂) account for 99.8% of the molecules in the outer flame envelope. The emission spectrum of atomic potassium superimposed on a continuous spectrum arising from the combining of atomic potassium with OH radicals to form gaseous KOH is responsible for the lilac colour of laboratory flames containing potassium and is the likely cause of the lilac colour of the outer regions of this pyrotechnic flame. The article includes a brief tutorial outline of some relevant aspects of the atomic spectroscopy of potassium.*

Keywords: *lilac flame colour, potassium nitrate, shellac, thermodynamic modeling, visible spectrum*

Introduction

Potassium nitrate, potassium perchlorate and potassium chlorate are very widely used in pyrotechnics as oxidizers. One of the advantages of potassium salts is that in most compositions they contribute little colour to the flame. It is well known, however, that potassium compounds emit visible light in laboratory flames¹ and it is to be expected that they would have some effect on the colour of pyrotechnic flames. Webster² studied the effect of potassium salts in magnesium-fueled flares and noted that visible emission from potassium may be part of the reason that high purity colours are not obtained from signal flares that incorporate a potassium salt as an oxidizer. Jennings-White³ noted that mixtures of potassium perchlorate or potassium chlorate with shellac burn with white or off-white flames respectively, but a mixture of potassium nitrate and shellac burns with a lilac flame and has been used as a composition for a coloured lance. In 1980 Winokur⁴ presented a comprehensive review of pyrotechnic mixtures for producing

purple fire and listed a very simple composition for a violet lance: 80% potassium nitrate and 20% shellac. The source was an Italian work⁵ published in 1845 (which the authors have not seen).

Recently Jennings-White⁶ observed for the potassium nitrate and shellac composition that

“...close examination of the flame shows the red is in the interior of the flame, with lilac on the outside. I had some observers look at this from a greater distance with a strontium pink comparison. The consensus was that the flames were clearly similar pink, but the potassium (nitrate) one had a bluish fringe.”

The authors decided to attempt to provide an explanation for these observations.

Background

1. Possible Sources of the Flame Colour

Flames emit light by several processes including:

1. Emission of continuous spectra by incandes-

- cent solids or liquids
2. Emission of line spectra by atoms
 3. Emission of band spectra by molecules
 4. Emission of continuous spectra by chemiluminescent recombination reactions.

Band emission from molecules is an extremely important source of pyrotechnic colour,⁷ but does not appear to be relevant in the case of the lilac flame being discussed.

It is well known that potassium salts impart a lilac colour to laboratory flames. The colour is attributable to the combination of the following:^{1a,8,9a}

1. Atomic emission from potassium. Possible lines include the pair of resonance lines at the far red extreme of the visible spectrum (at 766.491 and 769.897 nm) and another pair at the violet end of the spectrum (at 404.414 and 404.721 nm).
2. Continuum emission, extending from about 570 to 340 nm^{9a} and peaking in the violet around 400 nm,^{1a} arising from the chemiluminescent combination of atomic potassium with hydroxyl (OH) radicals to form gaseous potassium hydroxide.¹⁰

2. Tutorial Outline of Relevant Aspects of the Atomic Spectroscopy of Potassium^{1,11,12}

According to the quantum theory, electrons in an atom occupy regions of space around the atomic nucleus called *orbitals*. Different arrangements of electrons in orbitals correspond to different energy states of the atom. In atoms having more than one electron (such as the potassium atom) most of those electrons occupy very stable orbitals and do not participate in the electron rearrangements associated with chemical reactions or with interactions of atoms with light. Such changes involve rearrangements of only the outermost electrons, which are the most loosely bound. The potassium atom has only one electron that is not locked up in a highly stable inner orbital. That outer electron can occupy many different orbitals, but only the lowest energy one is stable. An electron in that orbital can stay there forever. If the atom gains energy, for example by colliding with another atom, the outer electron can move into another orbital that corresponds to a higher energy state, but it cannot remain there indefinitely. Most commonly, the atom will lose energy in the same way it gained it – in a collision with another atom. Even if the

atom were completely isolated, however, quantum theory predicts that the electron will eventually return to the stable orbital. The time that any one atom remains in a higher energy state is unpredictable, but the average time (referring to a large number of such atoms) is known and is called the *radiative lifetime* of the energy state. When an atom spontaneously changes from a higher energy state to a lower one, the excess energy is emitted as light. The energy difference (ΔE) between the two states corresponds to the energy of one photon of the emitted light (E_p). The wavelength of the emitted light (λ) is related to the photon energy by the Planck equation,

$$\Delta E = E_p = h\nu = hc/\lambda \quad (1)$$

where energy is expressed in joules (J), h is Planck's constant (6.626×10^{-34} J s), ν is the frequency (s^{-1}) of the emitted light, c is the velocity of light (2.998×10^8 m s^{-1}) and λ is the wavelength in metres. Similarly, the opposite process can take place, wherein the atom can absorb a light photon having an energy E_p that corresponds to the difference ΔE between two energy states of the outermost electron; in this process the electron temporarily moves from a lower energy state to a higher one.

Figure 1 shows some of the energy states of the potassium atom, together with some of the energy transitions giving rise to the emission lines discussed in this article. Not all lines are labeled, and not all possible lines are shown. Energy states above the lowest one are called *excited states* and atoms in such states are said to be *excited*. The lowest energy state is called the *ground state*. Emission lines that result from transitions from excited states to the ground state are called *resonance lines*. The four resonance lines indicated in Figure 1 are the most intense potassium emission lines in flames.^{1a}

Most potassium atoms in a flame will be in the ground state. Consequently, whenever potassium atoms are present in a flame, photons having energies corresponding to potassium resonance lines can be absorbed when they pass through the flame.

In Figure 1, the columns labeled 'S, P, D' indicate families of atomic energy states that differ from each other in the shape of the electronic orbitals.

According to quantum selection rules, electrons can participate in transitions where they move between S and P states, and between P and D states, but not between S and D states or between states having the same label (such as between S and S states). By convention, the superscript before the letter is one more than the number of unpaired electrons in an atom in that energy state. A potassium atom has one unpaired electron, so the superscript is 2. It is read as “doublet”, for the historical reason that spectral lines associated with atoms having one unpaired electron often occur in pairs that are called “doublets”. The subscript after the letter indicates the *total angular momentum* of the energy state, which depends on whether the angular momentum associated with the spin of the unpaired electron adds to, or subtracts from, the angular momentum associated with the motion of the electron around the nucleus of the atom (the electron’s *orbital angular momentum*). The electronic energy states in each family are labeled with lower case letters indicating the shape of the orbital preceded with a number (the *principal quantum*

number), which increases with increasing energy. In some cases, there are pairs of electronic energy states (e.g. $4p_{1/2}$, $4p_{3/2}$) that have the same principal quantum number and are labeled with the same letter, but have different angular momenta as a result of electron spin. The energy differences between the atomic energy states (e.g. $4^2P_{1/2}$, $4^2P_{3/2}$) are very small in the potassium atom. In Figure 1 these energy differences have been exaggerated for clarity – if shown to scale the difference would be lost in the thickness of the line. Electronic transitions from these energy states result in the characteristic “doublets” in the potassium spectrum (e.g. 766.491 and 769.897 nm). The energy state diagram, Figure 1, is based on data from the NIST *Handbook of Basic Atomic Spectroscopic Data*.⁸

The measurement of the intensity of resonance lines emitted from laboratory flames has long been used for the determination of potassium concentration in analytical samples by flame emission spectrometry.⁹ The success of this analytical method requires that the number of potassium atoms

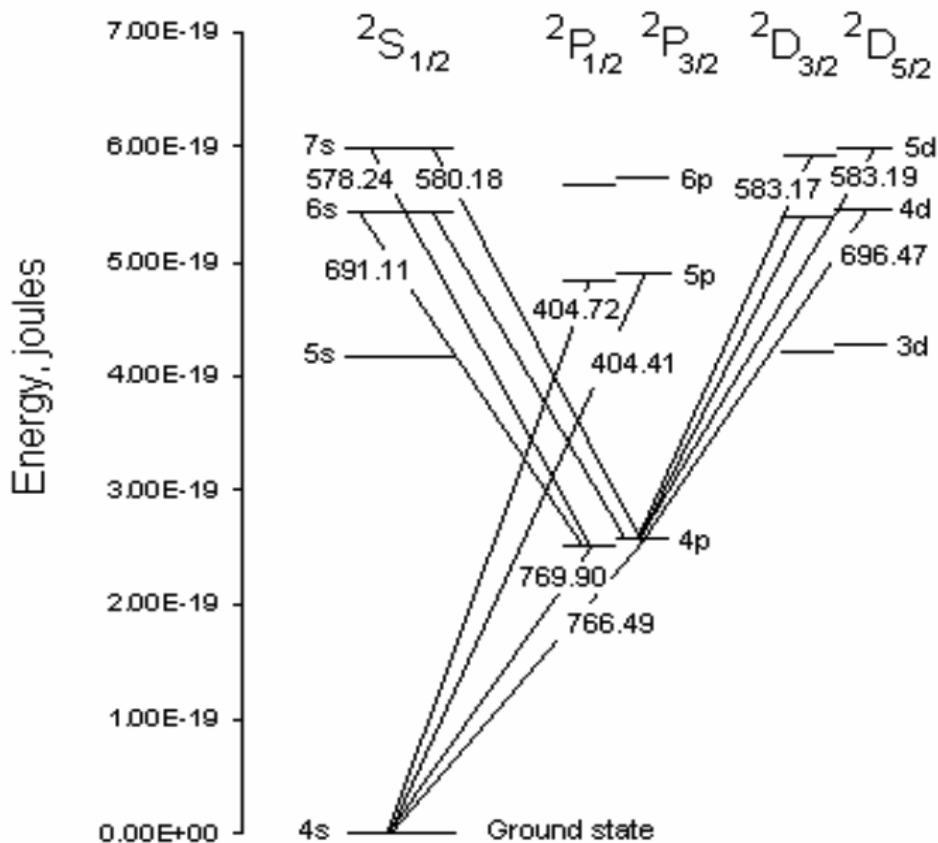


Figure 1. A simplified diagram of electronic states (energy levels) in the potassium atom.

in the path through the flame of the light being measured is so low that a photon emitted by one atom will have a high probability of escaping from the flame rather than being re-absorbed by another atom. Such a flame is described as being *optically thin*.

The gases in a flame can often be considered as being in *local thermodynamic equilibrium*. This means, amongst other things, that the number of potassium atoms in a particular excited state (n) is related to the total number of free potassium atoms (n_i) by the *Boltzmann equation*

$$n = n_i \frac{g}{Z} e^{-\Delta E/kT} \quad (2)$$

where g is the *statistical weight* of the excited state, Z is the *partition function* of the potassium atom (2 at the temperatures of interest), e is the base of natural logarithms (2.718...), ΔE is the *excitation energy* (the energy difference in joules between the excited state and the ground state), k is *Boltzmann's constant* (1.38×10^{-23} J atom⁻¹ K⁻¹) and T is the absolute temperature (K). If the number of excited atoms is consistent with the Boltzmann equation, the excitation process is described as *thermal* or *collisional* excitation.

In some flames, particularly in relatively cool flames or in the primary reaction zone of normal flames, the number of atoms in a particular high energy state sometimes greatly exceeds that predicted by the Boltzmann equation. In these circumstances the formation of excited atoms is attributed to *chemiluminescence*.^{13,14} Several different chemiluminescent processes have been described.^{13,14} In all of them a population of excited atoms or molecules arises as a result of energy released in the formation of chemical bonds being transferred directly to electrons in an atom or molecule, causing the most loosely-bound electron in

that atom or molecule to move to a higher energy state.

Irrespective of the mechanism that produces the excited species, the intensity of emission (I), expressed as photons per second, is simply

$$I = n/t \quad (3)$$

where n is the average number of excited atoms and t is the radiative lifetime. (To convert from photons per second to joules per second, one multiplies by the photon energy E_p ; see equation 1.)

The maximum temperature calculated for the air-propane flame by thermodynamic modeling is 2275 K. The expected thermally excited emissions from potassium atoms at this temperature are shown in Table 1. The intensity of the 766.49 nm line has been arbitrarily set to 100,000 and the intensities of the other lines have been normalized to this value.

As shown in Table 1 the two deep red lines are very intense and the two violet lines are much less so. Both pairs of lines lie in regions of the spectrum to which the human eye is not particularly sensitive, but they have been known for a long time and are shown in some of the very early drawings of flame spectra.¹⁵ Kirchhoff and Bunsen¹⁶ referred to the pair of deep red lines as “Ka α ” and the pair of violet lines as “Ka β ”. (The symbol “Ka” indicated potassium.) The prism spectroscope used by these researchers was evidently unable to resolve each pair of lines into their two components. Kirchhoff and Bunsen¹⁶ reported another very weak red line in the potassium flame. This line coincided with Fraunhofer line B. It was visible from a “highly intense flame” and described as “not very characteristic”. It can be identified with an unresolved group of five lines (696.47, 694.42, 693.88, 693.63, and 691.11 nm), arising from transitions

Table 1. *Spectroscopic Parameters of Potassium Resonance Lines and their Relative Intensities.*

Wavelength (nm)	Excitation Energy (J)	Statistical Weight of Excited State	Lifetime of Excited State (s)	Normalized Relative Intensity ^(a)
404.41	4.91×10^{-19}	4	1.16×10^{-6}	2.7
404.72	4.91×10^{-19}	2	1.07×10^{-6}	1.5
766.49	2.59×10^{-19}	4	2.67×10^{-8}	100000

^(a) Intensities were calculated in joules per second per unit atom concentration, assuming thermal excitation at 2275 K, and then normalized to 100,000.

between excited states.⁸ The coincidence of these red potassium lines with Fraunhofer line B is of no significance; Fraunhofer line B arises from absorption of sunlight by oxygen in the air.¹⁷ Two of the lines from this group of potassium lines are identified in Figure 1. These red lines are of comparable intensity to the other potassium lines at the high temperatures prevailing in the electric arc,⁸ but would be very weak in flames.

When Shimizu^{18a} described the flame spectrum of potassium he did not mention the deep red resonance lines and described the violet lines as “intense”. He wrote “The lines are very strong, but they are in the ultraviolet, at the outer edge of the eye’s visibility, and have no color influence”. Shimizu’s assessment of the intensity of the violet lines is certainly valid, given that he was comparing them to some faint yellow and green potassium lines arising from transitions between excited states that would be very sparsely populated at flame temperatures. Compared to the deep red lines, however, the violet lines are extremely weak. The literature suggests, however, that in some flames the violet lines are not always as weak as would be expected from calculations that assume thermal excitation. For example, referring to the use of these lines in flame photometry, Dean^{9a} states that “the sensitivity of the violet doublet is one tenth the sensitivity of the red doublet”. This is very different from the ratio of 2.8×10^{-5} calculated in Table 1. The issue is clouded by the fact that the detectors used in flame photometry vary greatly in sensitivity across the wavelength range,^{9b} but this variation is not sufficient to account for the difference in the ratios of the calculated and reported intensities of the two doublets. The implication is that the violet doublet can be excited by chemiluminescence in some laboratory flames. An example is given by Alkemade,¹⁹ but the enhancement over thermal excitation was not large. Whatever the excitation mechanism, the intensity of the violet doublet is always very much less than that of the red doublet. If the colour of the potassium flame were attributable solely to a combination of the deep red and violet lines, the flame would be red. Clearly there is another contributor to the colour of the potassium flame that changes the colour from red to lilac.

It has long been known that the distinctive lilac colour of the potassium flame is easily masked

by the yellow light from sodium and that this can be overcome by viewing the flame through blue cobalt glass. This glass transmits almost no light between about 500 and 700 nm but transmits quite efficiently at each of the extreme ends of the visible spectrum. The potassium flame, when seen through blue cobalt glass, is not lilac but purplish-red; when seen through green glass it is bluish-green.²⁰ Green glass transmits blue, green and yellow light but absorbs light at each of the ends of the visible spectrum. Accordingly the lilac colour of the potassium flame must result from a combination of the red light expected from the potassium resonance lines and light that is largely absorbed by blue cobalt glass but largely transmitted by green glass. That light is attributable to a continuum in the flame spectrum of potassium. This continuum has been known for a long time. It was described by Kirchhoff and Bunsen,¹⁶ who wrote “In the flame the volatile potassium compounds give a very long continuous spectrum with only two characteristic lines...”, and was subsequently studied by other spectroscopists.^{21,22a,10} It was once thought to originate from the recombination of electrons and potassium ions,^{22a} but in 1958 James and Sugden¹⁰ demonstrated that it was the result of the combination of hydroxyl radicals and potassium atoms to form gaseous potassium hydroxide. Shimizu^{18a} mentioned this continuum, attributing it to the potassium atom and noting that “it does tend to whiten the flame and interfere with other flame colors”.

The pale lilac colour of laboratory flames that are coloured by a vaporized potassium salt can thus be attributed to a combination of the deep red resonance lines from atomic potassium with the potassium hydroxide recombination continuum. The violet potassium resonance lines contribute very little to the colour, being much less intense than the red lines and the continuum. The fact that the continuum is a substantial contributor to the colour accounts for the pale, washed-out appearance of the lilac flame.

The observation of a lilac colour in a pyrotechnic flame containing potassium salts is consistent with observations of laboratory flames into which potassium has been introduced, and provides the explanation of the lilac colour of the outer regions of the flame from the potassium nitrate–shellac composition. The pink colour of the core, however,

was not so readily explained.

The discussion so far implies that each spectral line consists of photons having exactly the same energy, corresponding to exactly the difference between two atomic energy levels. In reality, the photons in each line have a range of energies and the emission “lines” might be better described as “peaks”. While each line (peak) has its maximum at the photon energy (or wavelength) predicted from the energy of the corresponding atomic transition, it tails away on either side. There are several factors that contribute to this *line broadening*.^{12a} In flames, the dominant effect operating at low concentrations of emitting/absorbing atoms is the collision of excited atoms with other atoms and molecules.^{12a} At higher atom concentrations emission lines can become extremely broad. When there is a relatively high concentration of emitting/absorbing atoms in the source, a photon emitted by one excited atom is very likely to be absorbed by another ground state atom. The chance of a photon being re-absorbed depends on its energy; a photon having an energy corresponding to the maximum of the emission line will have a much greater chance of being absorbed than a photon having energy that is slightly greater, or slightly less, than the maximum. The resulting excited state atom will then either transfer its extra energy to another atom or molecule in a collision or re-emit a photon. If the re-emission occurs after a collision, it is very likely that the energy of the emitted photon will be slightly different from that of the photon that was absorbed. Accordingly that emitted photon is likely not to correspond to the energy corresponding to the maximum of the emission line (peak). At these higher atom concentrations, this process occurs many times before a photon finally escapes from the flame. The result of these many emissions and re-absorptions before photons eventually manage to escape from the flame is greatly to broaden the energy distribution of those emitted photons. Such a flame is described as *optically thick*. The characteristics of spectral lines from atoms in optically thick sources are well documented in the literature.^{11a, 12a, 23}

The emission of light from an optically thick source can be thought of as intermediate between what happens in optically thin sources and in a *black body*. A black body is an object in which matter (atoms) and electromagnetic radiation (in-

cluding light) are in thermal equilibrium. The rate of emission of radiation by atoms exactly equals the rate of absorption by other atoms. For such perfect equilibrium, all emitted radiation is re-absorbed and no light leaves the object, which is why the object (“body”) is called “black”. An ideal black body can be approximated by the inside of a hollow object, so well insulated that there is no exchange of energy between the object and the outside world. The only way the spectrum of such an object can be viewed is to make a tiny hole in it, a hole so small that the effect on the equilibrium between atoms and radiation is not significantly disturbed by the slight loss of radiation through the hole. The spectrum of such an object is continuous, and the relationship between light intensity and wavelength at any given temperature can be calculated theoretically from the fact that radiation and matter are in thermal equilibrium.^{11b, 12b}

Recall that for an optically thin source a photon emitted by an atom in the source has a high probability of leaving the source without ever interacting with another atom. In contrast, a photon emitted by an atom in an optically thick source is highly likely to be absorbed by another atom as just described, but photons do eventually escape. Photons having energies corresponding to the theoretical maximum of the emission line are more likely to be absorbed than photons having energies away from the maximum. Eventually, if the concentration of emitting and absorbing atoms becomes sufficiently high, the rate of absorption at the peak’s maximum approaches the rate of emission. In other words, the photons having energy corresponding to the line’s maximum are close to being in equilibrium with the atoms. For photons of that energy, the source then behaves like a black body. The intensity of the emitted light at the line’s maximum approaches the intensity of light of that same wavelength that would be predicted for a black body at the same temperature as the source. Accordingly, at a given temperature, as the concentration of atoms of the emitting element increases, the intensity at the centre of the emission line only increases until it reaches the intensity that would be emitted at that wavelength by a black body at the same temperature. Thereafter, it is only the intensity of light having wavelengths on either side of the maximum that continues to increase with increasing concentration of emitting

atoms. The result is that as the concentration of emitting atoms increases, the radiation from the emission line is spread over an increasingly wide region of the spectrum on either side of the line's maximum. This line broadening process is described as *self-absorption*.

Douda^{24–28} has shown that the light from sodium nitrate–magnesium flares arises predominantly from sodium resonance lines that have been broadened by self-absorption. Such a substantially broadened line may be referred to as a *resonance line continuum*. Douda also demonstrated that in these flares, the light emitted by sodium atoms in the core of the flame is re-absorbed by sodium atoms in the cooler outer regions of the flame, resulting in a distinct dip in the centre of the broadened emission line where there would otherwise be a maximum. This is called *self-reversal* of the emission line. Of greater relevance to the discussion of lilac flame is the observation by Douda *et al.*²⁵ of broadened self-reversed potassium resonance lines in the spectra of potassium nitrate–magnesium flares.

The fact that self-absorption and self-reversal of sodium lines can transform the familiar amber-yellow sodium flame into the yellowish-white of the sodium nitrate–magnesium flare, coupled with the observation by Douda and his colleagues²⁵ of similar processes in potassium nitrate–magnesium flares, led the authors to consider whether the same mechanisms, applying to the deep red potassium lines, could account for the pink core of the potassium nitrate–shellac flame.

Experimental

The spectroscopic measurements were made using three slightly different configurations. However, each used an Ocean Optics CHEM-2000 spectrometer. The first configuration was one in which solutions are aspirated into a propane–air flame. This apparatus is sketched in Figure 2 and was previously described more completely.²⁹ The other two configurations were used to record spectra from burning pellets of pyrotechnic composition and tiny specially made tubes of lance composition. In these latter two configurations, the flame burner in Figure 2 is replaced with a holder for 6 mm (1/4 inch) diameter test pellets or 6 mm (1/4 inch) diameter lance. In one of these configura-

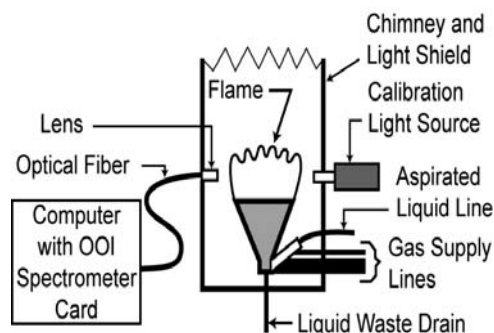


Figure 2. Illustration of the apparatus for taking spectral data from solutions of interest.

tions, a fish-eye lens was used so as to fully integrate the light emitted from the entire area of the flame. In the other configuration the lens was removed and a collimator used to limit light collection to a spot no more than approximately 5 mm in diameter. In this way, and by carefully positioning the flame source and by collecting data for only a fraction of a second, light could be collected from a relatively small portion of the flickering flame.

The potassium nitrate (KNO_3) used in this study (purchased from Service Chemical, USA) and the shellac (purchased from William Zinzer & Co., USA) were each of a grade normally used in the fireworks industry. The raw flame spectrum of potassium nitrate was obtained using the test configuration shown in Figure 2 with a 0.1 molar solution in distilled water. The spectrum was first corrected by subtracting a background flame spectrum (distilled water only) taken under the same measurement conditions as used for the potassium nitrate test solution. Then the background corrected spectrum was corrected for the wavelength dependent response function of the detector.²⁹ The final result is the potassium nitrate spectrum shown in Figure 3. For comparison purposes, the flame spectrum of a 0.1 M solution of analytical reagent grade potassium nitrate (Mallinckrodt, USA) is presented in Figure 4.

The 80% KNO_3 and 20% shellac lilac test composition was prepared by first thoroughly mixing the two components using a mortar and pestle. Then the composition was divided in two portions; one for use in making bound test pellets and the other for loading into the lance tubes. To make the bound

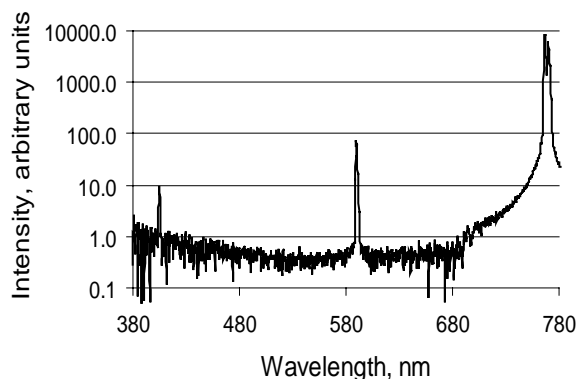


Figure 3. Spectrum of a solution of technical grade potassium nitrate aspirated into an air-propane flame, corrected for instrument background and detector response.

pellets, sufficient denatured ethanol was added to make a pliable mass. This dampened composition was then compacted into a series of 6 mm (0.25 inch) diameter and approximately 20 mm (0.8 inch) long test pellets. The test pellets were first allowed to air dry at approximately 20 °C (68 °F) for a day and were then raised to approximately 50 °C (122 °F) for approximately 1 hour. Figure 5 is a photograph of a burning test pellet, in which the brighter and lighter outer flame envelope is readily apparent.

The raw flame spectra of the test pellets were obtained by burning them in a darkened area using the test configuration described above using the fish-eye light collecting lens, which integrated the light from the entire flame. The raw spectra

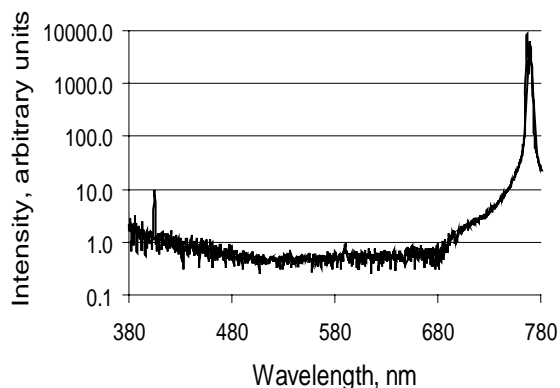


Figure 4. Spectrum of a solution of analytical reagent grade potassium nitrate aspirated into an air-propane flame, corrected for instrument background and detector response.



Figure 5. A photograph of a burning pellet of the lilac composition showing the brighter and lighter outer flame envelope.

were corrected for instrument background (dark current) and then corrected for the instrument response function.²⁹ The final result is the spectrum shown in Figure 6.

Using the un-dampened portion of the lilac flame composition, a series of lances was prepared. The lance tubes were specially made using just two wraps of thin tissue paper. This was done so as to limit the interfering effect of the burning lance tube. The lance tubes were 6 mm (1/4 inch) in diameter and approximately 25 mm (1 inch) long. The composition was carefully loaded using the traditional rod and funnel method. The spectra of the lances were recorded using the instrument

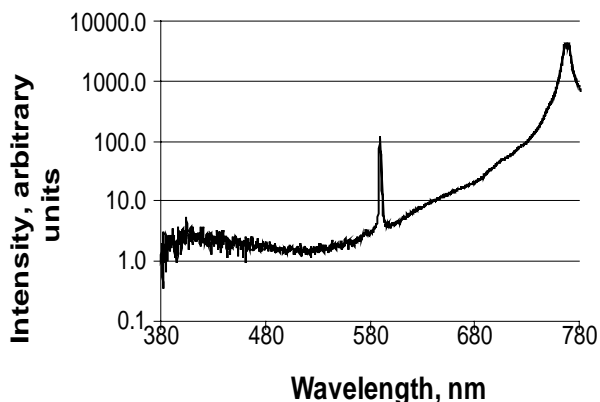


Figure 6. Spectrum of the flame of a burning pellet of 80% potassium nitrate and 20% shellac mixture, corrected for instrument background and detector response.

configuration described above using the collimator. By properly positioning the burning lance in front of the collimator, it was possible to collect spectra somewhat selectively concentrating on the emissions from either the inner or outer portions of the flame envelope. Lances were used for these measurements because they produced a more steady flame, which facilitated the collection of spectra from the two regions of interest within the flame. Nonetheless, the movement of the flame was still sufficient to require that the data collection intervals be kept to only 0.1 second to aid in limiting the light acquired from other portions of the flame. (The burning pellets of composition flickered greatly, which facilitated the taking of a photograph more clearly showing the difference between the inner and outer flame envelope, see Figure 5.)

The spectra collected from the inner and outer parts of the flame, corrected as described above, were smoothed with a 9-point moving average to remove some of the “noise” resulting from the low light intensity in this mode of measurement. Finally the intensity data points in each spectrum were normalized to the maximum value in that spectrum. The use of normalized intensities allows the different line widths in the spectra to be seen more clearly. Furthermore, the colour of the flame depends on the relative intensity of the various spectral features, not their absolute intensity.

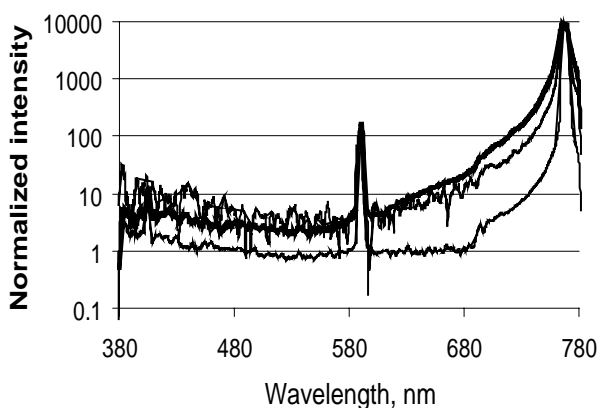


Figure 7. Spectra of the inner and outer parts of the flame of a burning lance made with 80% KNO_3 and 20% shellac. Bold trace: Inner part of the flame. Upper non-bold trace: Outer part of the flame. Lower non-bold trace: technical grade KNO_3 solution aspirated into the air–propane flame.

Results are presented in Figure 7. The data used to generate the spectrum of technical grade KNO_3 in the air–propane flame shown in Figure 3 were re-processed in the same way and the resulting spectrum is included in Figure 7 for comparison.

Additional spectra were derived from each of the test technical grade potassium nitrate and test composition spectra produced as described above. The purpose was an attempt to quantify the effect of the sodium impurities present in the raw chemical ingredients. This was accomplished by simply stripping out the sodium peaks from the two corrected test spectra. Finally, all spectra were converted to their CIE colour values using a program provided by Will Meyerriecks.³⁰ These results are presented and discussed below.

Results and Discussion

1. Flame Spectra

The visible spectrum of the technical grade KNO_3 solution aspirated into the air–propane flame is presented as Figure 3. Note that the intensity scale is logarithmic. The most prominent feature is the partially resolved pair of deep red potassium resonance lines. The yellow line (actually an unresolved pair of lines at 589.0 nm and 589.6 nm) from sodium impurities is also obvious. The (unresolved) pair of violet potassium resonance lines can be discerned, but, as expected, its intensity is very low. The continuous spectrum is evident by the offset of the spectrum from the 0.1 unit intensity line in Figure 3. Figure 4 presents the corresponding spectrum of analytical reagent grade KNO_3 solution aspirated into the air–propane flame. The obvious difference between this spectrum and that of the technical grade material is the very much lower intensity of the yellow sodium line.

Figure 6 presents the visible spectrum of the flame from the burning of a bound pellet of the 80% KNO_3 –20% shellac mixture. The spatial resolution of the apparatus used as configured and the dynamic flickering of the flame did not allow the separation of the spectrum of the reddish-pink core from that of the lilac outer regions of the flame. The pair of deep red potassium resonance lines is again the dominant feature of the spectrum. The extent to which these lines have broadened and extend well into the shorter wavelengths of the red

region of the spectrum to which the eye is more sensitive, can be seen by comparing Figure 6 with Figures 3 and 4. This broadening is attributed to self-absorption caused by a high concentration of potassium atoms in the flame. The sodium line is evident, as expected. The unresolved pair of weak violet potassium lines cannot be discerned above

the background noise. It is clear from Figure 6 that the continuum is greatly increased in intensity compared to that in Figure 3. This is attributable to two sources: (a) potassium–hydroxyl recombination, as expected for a flame containing potassium, hydrogen and oxygen, and (b) possibly from particles of solid or liquid suspended in the flame.

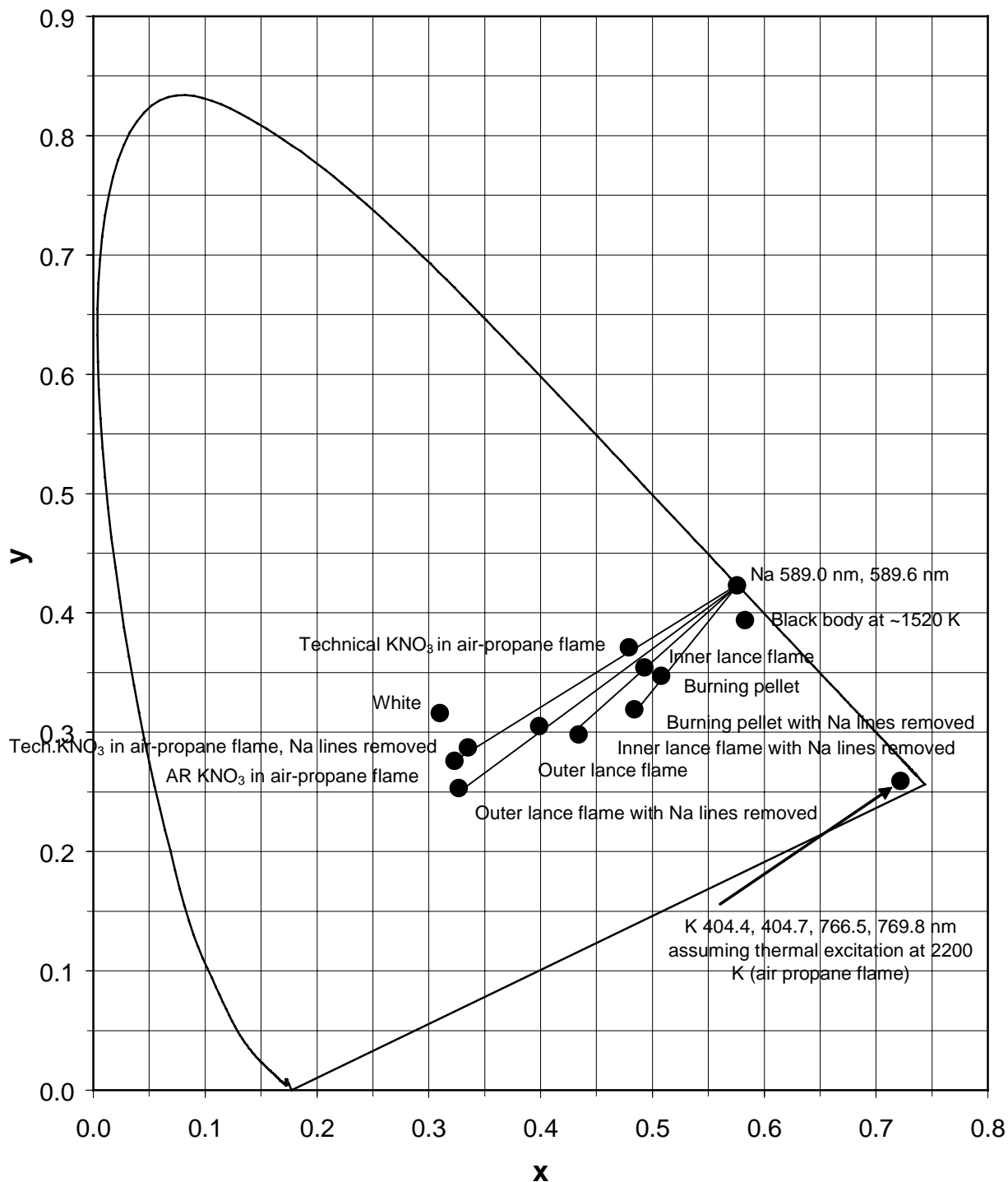


Figure 8. CIE chromaticity diagram showing the positions of the various flame colours, plotted from the coordinates in Table 2.

Table 2. CIE *x* and *y* Coordinates Calculated From the Spectra, and their Corresponding Colours.

Spectrum or Spectral Feature	CIE <i>x</i>	CIE <i>y</i>	Colour
Analytical reagent KNO ₃ in air–propane flame	0.323	0.276	Pale reddish-purple
Technical KNO ₃ in air–propane flame	0.479	0.371	Pink
Technical KNO ₃ in air–propane flame, Na resonance lines removed	0.335	0.287	Pale reddish-purple
Burning pellet of 80% KNO ₃ , 20% shellac	0.507	0.348	Pink
Burning pellet of 80% KNO ₃ , 20% shellac, Na resonance lines removed	0.484	0.319	Pink
Inner core of lilac lance flame	0.493	0.354	Orange-pink
Inner core of lilac lance flame, Na resonance lines removed	0.434	0.298	Pink
Outer envelope of lilac lance flame	0.399	0.305	Pink
Outer envelope of lilac lance flame, Na resonance lines removed	0.327	0.253	Pale reddish-purple
Potassium resonance lines from air–propane flame (calculated relative intensities, assuming thermal excitation at 2200 K)	0.722	0.259	Red
Sodium resonance lines	0.569	0.430	Yellowish-orange
Black body at ~1520 K ^{12b}	0.583	0.394	Orange

There was no attempt to calculate the contribution of the latter, but there would presumably be a considerable effect from the rather high concentration of molten potassium carbonate in the flame. The spectrum of a black body at ~1500 K would peak in the infrared, with sufficient “tailing” into the visible to make the body appear yellowish-orange. Flame particles are likely to be very small, with the result that the “black body” spectrum would be shifted to shorter wavelengths, making the emitted light whiter.³¹

Figure 7 presents spectra attempting to concentrate on the inner and outer parts of the lance flame, collected using the collimated light collection configuration. Because of the limited special resolution and the motion of the flame, it is likely that spectra of the edge of the flame included at least part of that from the inner flame. Further, the inner part of the flame had to be viewed through the outer part. Thus it must be expected that the both spectra are, to a significant extent, mixtures of the emissions from both the inner and outer regions of the flame, Nonetheless, there are distinct

differences in the spectra from the inner and outer parts of the flame. (As expected, most of the spectra collected were of intermediate character to the two presented in Figure 7.)

The spectrum of the inner part of the flame is similar to that of the burning pellet (Figure 6). The most notable difference is that the unresolved violet resonance line pair is clearly visible, but is still of low intensity. The spectrum of the outer part of the flame is different in several ways: the pair of red potassium lines is less broad, the continuum in the shorter wavelength region is relatively more intense and the pair of violet lines is not discernible above the background noise. The spectrum of potassium nitrate in the air–propane flame is different from either of the lance flame spectra, with the pair of red lines being less broad, the continuum much less intense and the unresolved violet lines distinctly more intense. The wavelength resolution of the spectrometer used in this work was not sufficient to show whether or not self-reversal of the potassium resonance lines was present.

2. CIE Chromaticity Diagram

Table 2 shows the CIE x and y coordinates (using the 1931 2° Chromaticity Diagram) of some relevant spectra and spectral features. Some of these colour coordinates are plotted on a CIE chromaticity diagram in Figure 8. The colours indicated on the diagram for the KNO_3 in the propane gas flame and for the lilac flame composition are consistent with observations, bearing in mind that the CIE descriptions cover quite a broad range of perceived hues. The CIE results and visual observations both find the inner part of the flame to be “redder” than the outer part. The results for the colours expected when the sodium lines were removed from the experimental spectra indicate that there would be a definite improvement in the colour of the lilac flame if there were less sodium present.

3. Thermodynamic Modeling

It seemed obvious that the colour of the flame from the potassium nitrate–shellac composition was attributable to potassium, but no data for the composition and temperature of the flame were available to support this. Thermodynamic modeling was used to obtain an indication of the potassium concentration in the flame and the flame temperature. It was assumed that at the core of the flame the temperature and composition were close to those expected at thermodynamic equilibrium. Moving

away from the core, the effects of entrained air would presumably be increasingly significant.

Thermodynamic modeling was done using the NASA-CEA program.^{32,33} The combustion was modeled at a pressure of 1 bar. The required inputs were the quantities of the reactants (relative weight), their chemical composition and their enthalpies of formation. The enthalpy of formation and chemical composition of potassium nitrate are included in the database that forms part of the NASA-CEA program. The data for shellac were taken from Meyerriecks.³⁴ The empirical formula was $\text{C}_6\text{H}_9.5\text{O}_{1.6}$ and the enthalpy of formation was -440 kilojoules per gram formula weight. As noted by Meyerriecks³⁴ this enthalpy value is subject to considerable uncertainty; the results of the modeling must therefore be regarded as semi-quantitative. Furthermore, no account of energy loss from the flame by radiation was considered. Despite these limitations it was thought that thermodynamic modeling would provide a useful basis for an explanation of the spectrum of the flame from the burning composition.

The output of the program included the equilibrium temperature and the mole fractions of the combustion products. The number of significant figures in the values reported in this paper does not indicate the uncertainty in the values, as no at-

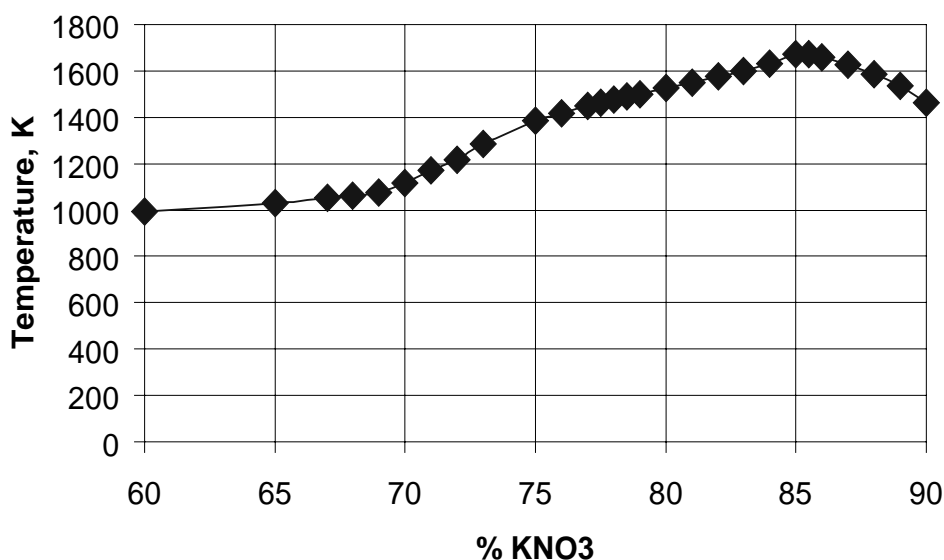


Figure 9. Equilibrium flame temperatures for the combustion of binary mixtures of potassium nitrate and shellac.

tempt was made to estimate the uncertainties. The aim was only to produce a plausible, consistent account of the flame colour. This certainly required an indication of the flame temperature and composition, but a fully detailed quantitative analysis was not necessary and probably not possible. The program took ionization effects into account but these turned out to be insignificant. No species are included in the output unless they are present at mole fractions greater than 5×10^{-6} ,²⁹ and no ions were reported in the output of the program.

A plot of equilibrium adiabatic temperature predicted for the combustion of a series binary mixtures of potassium nitrate and shellac is shown in Figure 9. For the 80% KNO₃ and 20% shellac mixture, the predicted flame temperature is 1526 K and the maximum temperature is predicted to be reached by a mixture of 85% KNO₃ and 15% shellac. The equilibrium composition of the

flame gases from these binary mixtures, each at their predicted flame temperature, is shown in Figure 10. The 80% KNO₃ and 20% shellac mixture is close to that producing the greatest concentration of atomic potassium in the flame. As indicated in Figure 10, the maximum atomic potassium concentration occurs at about 83% KNO₃.

Figure 11 shows the major components of the flame gases for the 80% KNO₃ and 20% shellac mixture. Of these, carbon monoxide (CO), hydrogen (H₂) and potassium (K) are expected to burn in the air, forming a diffusion flame around the flame core. Modeling such a flame is difficult because there are two competing factors operating: (a) the reaction of combustible gases with air, which tends to heat the flame, and (b) the cooling of the flame gases by the loss of heat into the surrounding cold air.

The maximum possible temperature of the diffu-

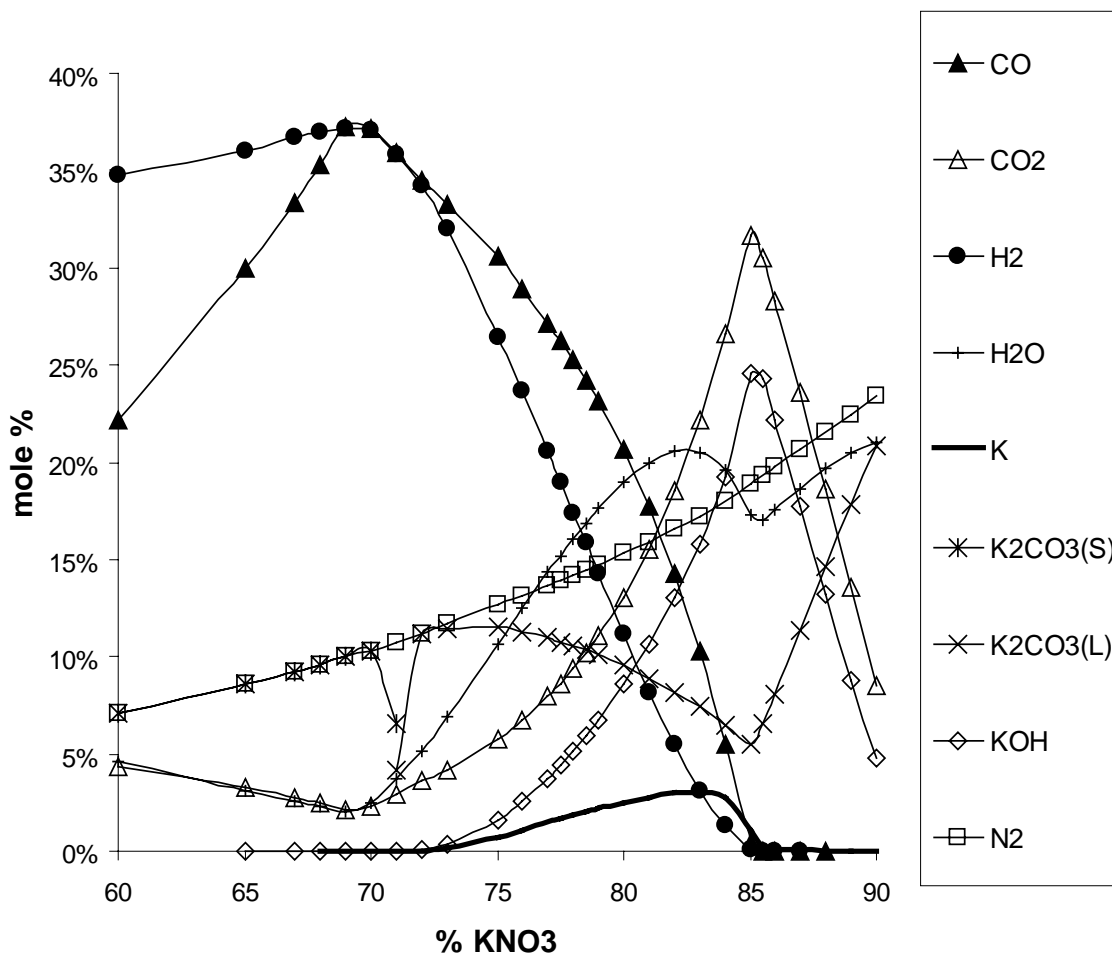


Figure 10. Equilibrium flame compositions for binary mixtures of potassium nitrate and shellac. Trace components (<1%) have been deleted for clarity.

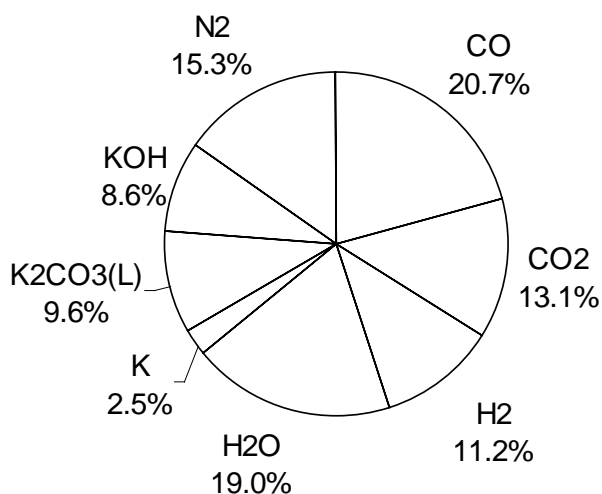


Figure 11. Equilibrium composition of the flame of 80% KNO_3 and 20% shellac mixture (1526 K).

sion flame was calculated by modeling the combustion of the 80% KNO_3 and 20% shellac mixture in varying amounts of air. The maximum temperature (1723 K) occurred with a mixture of 50.66% KNO_3 , 12.66% shellac and 36.68% air by mass and produced the products shown in Figure 12. As shown in Figure 12 there is still a significant concentration of atomic potassium in the diffusion flame, but the number of potassium atoms per unit volume (2.2×10^{16} atoms cm^{-3}) is only approximately 18% of that calculated to be present in the flame core (1.2×10^{17} atoms cm^{-3}). Concentrations of the various species in atoms or

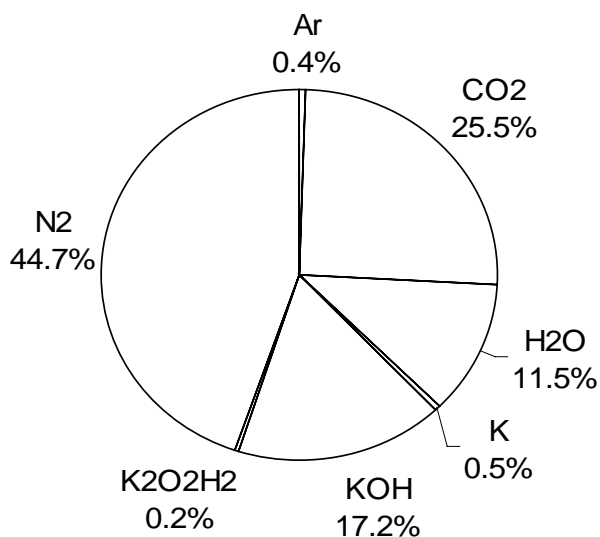


Figure 12. Equilibrium composition of the flame of 80% KNO_3 and 20% shellac mixture with sufficient entrained air to reach the maximum adiabatic flame temperature (1723 K).

molecules per cubic centimetre were calculated from the mole fractions and the molar volume at the flame temperature and a pressure of 1 bar, as found from the ideal gas law. The calculated concentrations of potassium atoms in the diffusion flame and in the flame core were of a similar magnitude to the concentration calculated by Doua and Bair²⁶ for sodium atoms in the flame of a sodium nitrate–magnesium (NaNO_3 –Mg) flare (4×10^{17} atoms cm^{-3}).

Despite the substantial decrease in the concentration of potassium atoms in the diffusion flame, the intensity of the deep red resonance lines is expected to be similar to (approximately 0.75 times) that from the core. This is because the diffusion flame is hotter, with the result that the fraction of potassium atoms excited to emit these lines is approximately 4.1 times greater in the diffusion flame than in the core. However, the lower concentration of ground state potassium atoms in the diffusion flame compared to the core would result in the deep red lines being less subject to broadening by self-absorption. Thus there would be less emission in the shorter wavelengths of the red region of the spectrum, making the diffusion flame appear less red than the core. The same considerations indicate that the violet potassium resonance lines would be approximately 2.7 times more intense in the diffusion flame than in the core, because the fraction of potassium atoms excited to emit these lines is approximately 14 times greater in the hotter diffusion flame.

It was not possible to test all of these predictions with the results of Figure 7, because the sampled volume of the flame was almost certainly not the same for each spectrum. Absolute intensity comparisons are meaningful only if the sampled volume is constant. The possibility of normalizing the intensities to that of the sodium line was rejected because this normalization would be valid only if the temperatures were the same in each part of the flame. Figure 7 does show, however, that the red lines are relatively less broadened, and the short-wavelength continuum relatively more intense, in the outer part of the flame than in the inner part, the standard of comparison being the maximum intensity of the red potassium line in each spectrum.

The calculated concentration of potassium hy-

droxide (KOH) in the diffusion flame (7.2×10^{17} molecules cm^{-3}) is greater than that in the flame core (4.1×10^{17} molecules cm^{-3}). Accordingly, assuming that the chemiluminescent potassium hydroxide emission is proportional to the equilibrium potassium hydroxide concentration, one can predict that the ratio of red potassium emission to the bluish-violet KOH continuum would be less in the diffusion flame than in the core. This would make the diffusion flame appear bluer than the core. Another source of blue light in the diffusion flame could be the blue emission associated with the combustion of carbon monoxide.^{22b} (This is the principal source of the familiar blue colour of the outer mantle of flames in which fuels containing carbon are burnt in air or oxygen).

Conclusions

The pink colour of the core of the flame from the 80% KNO_3 –20% shellac mixture is attributable to broadening of the deep red potassium resonance lines by self-absorption, which extends the emission into the region of the spectrum to which the eye is more sensitive. The potassium emission is superimposed on a continuum produced by a combination of thermal emission from droplets of molten potassium carbonate suspended in the flame and chemiluminescent emission from potassium–hydroxyl recombination. The lilac colour of the outer regions of the flame presumably arises from the same combination of emission lines from potassium atoms and the potassium–hydroxyl recombination continuum, with very much less thermal emission from liquid droplets. However, (1) the visible intensity of the red potassium emissions is reduced because of less self-absorption broadening of the 766.491 and 769.897 nm resonance lines; and (2) the intensity of the violet chemiluminescent emissions is increased. The result is the lilac colour of the outer (diffusion) flame envelope.

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