CHAPTER II

ATOMIC ABSORPTION AND FLAME PROPERTIES

Atomic Absorption Spectroscopy involves the absorption of radiant energy by atoms and the quantitative correlation of absorption with the concentration of metal atoms present in the absorbing medium serves as the basis of analytical atomic absorption spectroscopy.

The production of atoms requires a high temperature medium;which is most conveniently and inexpensively provided by flames. Although not available for the present work, high temperature ovens are also used effectively. A compound introduced into a flame is vaporized and partially or wholly dissociated into its elements in the gaseous form. The absorption process generally occurs between the ground state and the first excited state of atom ,with radiant energy of characteristic wavelength being absorbed. Atoms also can absorb energy from the flame directly becoming excited through collision with other species to higher energy states from which they can emit characterictic radiation on returning to either an excited state of lower energy or the ground state.

Assuming thermal equilibrium in the flame, the distribution of atoms in energy states is given by the Boltzman equation. The transition between ground state E_o and a excited state E_j is given by

$$N_o = cP_o \exp{-E_o/kT} \qquad (1)$$

$$N_j = cP_j \exp{-E_j/kT} \qquad (2)$$

where N_o, N_j = number density of atoms in the ground state and in the j^{th} state respectively

P_o, P_j = statistical weight

c = constant

T = absolute temperature

E_o, E_j = energy of ground state and excited state j, respectively

Combining equations (1) and (2) gives the equation

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} \exp - \frac{E}{kT} \qquad (3)$$

where $E = E_j - E_o$

For sodium at 2000^{o}K, resonance line at 5890^{o}A the ratio N_j/N_o calculated using equation (3) is 9.86×10^{-6}. This shows that the number of atoms in excited state is much smaller than the number of atoms in the ground state. This would appear that atomic absorption spectra would have important advantages over emission spectra as a means of chemical analysis.

At every point on the absorption line the absorption of radiation is related to concentration of absorbing atoms by the Beer-Lambert relationship.

$$I_\nu = I_{0\nu}\left[\exp - k_\nu l\right] \qquad (4)$$

The absorption coefficient k_ν is a function of frequency and varies continuously over the absorption line which has a finite width,dependent on the conditions of the absorbing medium.

The integrated absorption coefficient over the whole line is given by

$$\int_{\lambda}^{\lambda+d\lambda} k_\nu d_\nu = \left[\frac{\pi e^2}{mc}\right] N_\nu \ f \qquad (5)$$

where k_ν = absorption coefficient at frequency ν , e = electronic charge,m = mass of an electron, c = velocity of light, N_ν = number of atoms/c.c capable of absorbing radiation of frequency ν ,f = oscillater strength,i.e. the average number of electrons per atom capable of being excited by incident radiation. For a transition initiated from the ground state,for which N_ν is,for practical purposes, equal to N,it is seen that the integrated absorption coefficient is proportional to the total number of atoms and is essentially independent of temperature and wavelength.

There remains, however, a very difficult problem, how to determine k_ν at each point across the width of the line, i.e. to calculate the value $\int_{\lambda}^{\lambda+d\lambda} k_\nu \, d_\nu$ so that N_ν can be determined. At temperatures between 2000-3000°K, the width of an absorption line is of the order of 0.02°A, and is beyond the resolving capabilities of most spectrographs. Further four factors may influence the width and shape of the spectral line.

1. The natural width of the line.

2. Doppler broadening, due to movements of atoms relative to the observer.

3. Pressure broadening, due to the presence of neighbouring atoms. When broadening is due to the same kind of atoms as those absorbing radiation, this is known as resonance broadening. This type of broadening is generally known as collisional broadening.

4. Stark broadening, due to external electric fields or charged particles. Generally in flame environments the electrical forces are not sufficiently large for the Stark effect to be significant.

An alternative method for atomic absorption measurement is provided by using a sharp line source that emits a spectral line with a much smaller half-width than the absorption line. Using such a source, the absorption coefficient at the centre of the line can be measured. The most useful and common sharp line source is the hollow cathode lamp, the properties of which have been discussed by Tolansky (5)

Mitchell and Zemansky(6) have shown that if the shape of the absorption line is completely determined by Doppler broadening, then

$$k_{max} = \frac{2\lambda^2}{D_\lambda} \sqrt{\frac{\ln 2}{\pi}} \quad \frac{\pi e^2}{mc} \quad Nf \tag{6}$$

where k_{max} is the absorption coefficient at the centre of the line, D_λ = Doppler line width, e = electronic charge, m = mass of an electron, c = velocity of light, f = oscillater strength. N = number of atoms / c.c capable of absorbing radiation. The relationship between k_{max} and N is maintained only at low concentrations, where the Doppler effect predominates. At higher concentrations pressure and resonance broadening may make a significant contribution to line width.

Equation (6) may be combined with the Beer-Lambert equation (4) to give the following working equation.

$$\log \frac{I_0}{I} = \frac{1}{2.3} \cdot k'_{max} \cdot N.l \tag{7}$$

where $k'_{max} \times N = k_{max}$

Hence a graph of log I_0/I (absorbance) against concentration will be linear providing the concentration of absorbing atoms is relatively low and samples of unknown concentration will be interpolated from a standard graph. As the concentration increases, the graph will begin to show curvature due to the increasing magnitude of resonance broadening. Additional factors also may give rise to line curvature.

1. Instrumental factors.

The failure of some of the radiation to undergo absorption in the flame before being measured by the photocell can cause an error in the absorbance . If i_0 is the intensity of unabsorbed light, then the measured absorbance will be log $\frac{I_0 + i_0}{I + i_0}$ instead of log $\frac{I_0}{I}$. This will cause the calibration graph to be asymptotic to the value log $\frac{I_0 + i_0}{i_0}$ instead of to infinity. Generally, the effect is minimized by a proper design of the instrument.

In addition, sharp line sources must be used as sources emitting broader lines will fail to monitor only the centre of the absorption line and the absorption will be depressed.

2. Chemical factors.

This chemical factors can be divided into three catagories.

a. excitation where atoms are removed from the ground state to higher excited state, generally, this effect is almost negligible in flames.

b. ionization

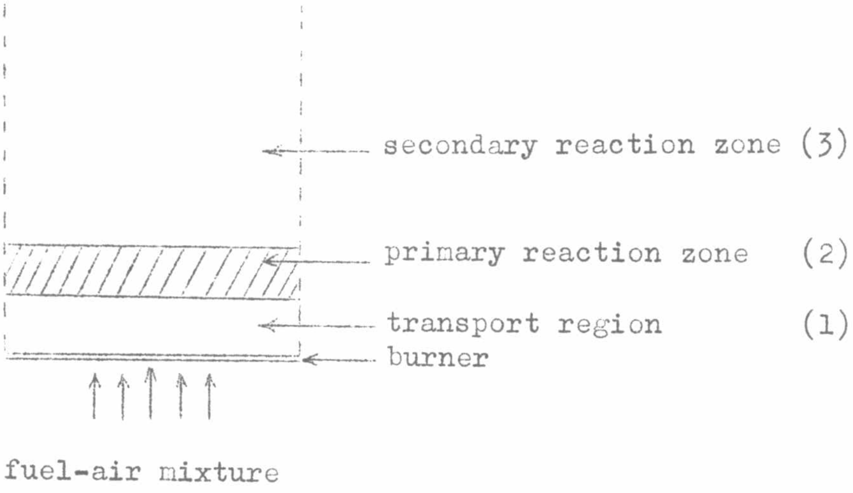
c. compound formation

In order to understand the chemistry of the last two factors clearly,the chemistry of flames shall be discussed.

The flames used in atomic absorption work are generally laminar pre-mixed long path-length flames. A variety of fuel-oxidizer mixtures is available and normally flames are operated at room temperature and atmospheric pressure. In this study an acetylene-air flame system was used.

Since the flame is an integral part of the atomic absorption system,it becomes important to consider its structure and chemistry,particularly in order to understand interference phenomena. Figure I, shows the general structure of a one-dimensional laminar flame which is the most simple flame system to consider

Fig.I (Diagram is not drawn to scale. Regions (1) and (2) are enlarged considerably)



Emerging from the burner tip is the transport region where diffusion and thermal conduction takes place. Above this region is a small region in space of primary reaction where rapid oxidation of acetylene occurs. This region is usually luminous. Following this primary reaction region is the secondary reaction region. In this region all radicals produced will reach the state of quasi-equilibrium i.e. steady state. Products in this region affect the primary reaction region because of molecular transport processes, specifically diffusion of radicals back to the reaction zone. In atomic absorption work the secondary reaction region is the region which is practical for atomic absorption and is a region where steady state conditions are likely to exist.

The chemical reactions of an acetylene flame have been investigated by several workers(7)-(12)and can be represented by the following set of equations:

Initiation reactions involve reactions of unburned fuel with radicals which diffuse into the primary reaction zone

$$C_2H_2 + \left\{\begin{array}{l} O \\ OH \\ H \end{array}\right. \rightsquigarrow \left\{\begin{array}{l} CH \\ CH_2 \\ CH_2O \end{array}\right. \quad \text{etc.} \qquad (8)$$

Radical concentrations are rapidly increased and maintained by a series of bimolecular exchange reactions,some of which are chain branching. Theseare represented as follows;

$$\mathrm{CH} + \mathrm{OH} \rightleftharpoons \mathrm{CO} + \mathrm{H_2} \tag{9}$$

$$\mathrm{C_2H} + \mathrm{O} \rightleftharpoons \mathrm{CH} + \mathrm{CO} \tag{10}$$

$$\mathrm{CH_2O} + \mathrm{OH} \rightleftharpoons \mathrm{HCO} + \mathrm{H_2O} \tag{11}$$

$$\mathrm{HCO} + \mathrm{OH} \rightleftharpoons \mathrm{CO} + \mathrm{H_2O} \tag{12}$$

$$\mathrm{O_2} + \mathrm{H} \rightleftharpoons \mathrm{OH} + \mathrm{O} \tag{13}$$

$$\mathrm{H_2} + \mathrm{O} \rightleftharpoons \mathrm{OH} + \mathrm{H} \tag{14}$$

$$\mathrm{H_2O} + \mathrm{O} \rightleftharpoons \mathrm{OH} + \mathrm{OH} \tag{15}$$

$$\mathrm{H_2O} + \mathrm{H} \rightleftharpoons \mathrm{H_2} + \mathrm{OH} \tag{16}$$

$$\mathrm{H_2} + \mathrm{OH} \rightleftharpoons \mathrm{H_2O} + \mathrm{H} \tag{17}$$

$$\mathrm{CO} + \mathrm{OH} \rightleftharpoons \mathrm{CO_2} + \mathrm{H} \tag{18}$$

The decay of radicals to equilibrium involves three body processes and is much slower than the bimolecular processes of radical production. They are generally written as follows

$$\mathrm{H} + \mathrm{H} + m \rightleftharpoons \mathrm{H_2} + m \tag{19}$$

$$\mathrm{O} + \mathrm{O} + m \rightleftharpoons \mathrm{O_2} + m \tag{20}$$

$$\mathrm{H} + \mathrm{O} + m \rightleftharpoons \mathrm{OH} + m \tag{21}$$

$$\mathrm{H} + \mathrm{OH} + m \rightleftharpoons \mathrm{H_2O} + m \tag{22}$$

where m is any third body molecule. Molecules such as H_2O or CO_2 which are stable products of the combustion process are likely to act as third bodies.

The rate of reactions (19)-(22) is much smaller than the rate of reactions (13)-(18), so that the radicals produced has a definite life time in the flame and can react with metal atoms to form compounds.

The equilibrium constants for these reactions are known and equilibrium values of OH, H and O can be calculated at various temperatures. The results of a typical calculation for flame systems are shown in Table I.

Table I

Partial pressures(atm) of minor constituents in flames.

Flame	ratio	T $^{\circ}$K	H	O	OH	O_2	H_2
H_2:N_2:O_2	2.0:3 : 1	2250	5.5(3)*	6.8(4)	1.2(2)	2.8(3)	3.2(2)
	2.0:4 : 1	2070	2.9(3)	5.5(4)	8.6(3)	4.0(3)	1.5(2)
	1.5:3 : 1	2040	6.7(4)	9.1(4)	9.7(3)	-	2.6(3)
	1.0:5 : 1	1300	2.6(5)	1.1(4)	5.2(4)	-	1.3(4)
H_2:air	stoi.	2373	-	-	0.01	-	0.02
C_2H_2:air	stoi.	2523	-	-	0.01	0.02	-
H_2:Cl_2	stoi.	2503	0.01	-	-	-	0.04

* 5.5(3) stands for 5.5 x 10^{-3} atm. etc.

As would be expected radical concentrations vary with the fuel oxygen ratio. In fuel rich flame [OH] and [H] are high and metal hydroxides would be expected (13) to form in greater concentration than the other more fuel lean flames.

Since there is a considerable amount of free metal atoms in the flame, they can readily react with flame radicals by the typical bimolecular reaction

$$MX \rightleftharpoons M + X \qquad (23)$$

where M is free metal atom

X is any flame radicals (OH, O or H)

The equilibrium constant can be written as

$$K_p = \frac{[M]\,[X]}{[MX]} \qquad (24)$$

This K_p is the temperature dependence quantity and the expression can be written

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H^{o}_{T}}{RT^{2}} \qquad (25)$$

where ΔH^{o}_{T} is the heat of dissociationat the standard state, D^{o}_{o}

R is the gas constant

T is the temperature in ^{o}K

It is clearly seen that K_p will increase with increasing in temperature. Assume ΔH^{o}_{T} is a constant at a small range of temperature, equation (25) can be integrated

$$\ln \frac{K_{p_1}}{K_{p_2}} = \frac{\Delta H^{o}_{T}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (26)$$

Generally, for alkali metal, D_0^0 is at the range of 80-110 kcal/mole, these values hold whether X in equation (23) is OH, H or O. In an air-acetylene flame at temperature 2200 °K, the K_{p_1} is of the order of 10^{-5} atm. Using these values and substituting in equation (26), the K_{p_2} at 2500 °K can be calculated.

The calculation gives

$$\text{using} \quad D_0^0 = 80 \text{ kcal/mole} \quad K_{p_2} = 9\times10^{-5} \text{ atm.}$$

$$D_0^0 = 110 \text{ kcal/mole} \quad K_{p_2} = 2\times10^{-4} \text{ atm.}$$

As it would be expected from the calculation that compound having D_0^0 of 80 kcal/mole would dissociate readily at the flame temperature while the one having D_0^0 of 110 kcal/mole is a stable compound.

In atomic-absorption study using an air-acetylene flame, from Table I. it is seen that for fuel-rich flame, compound formations other than the hydroxides seem unlikely. In all cases MH and M_2 are not sufficiently stable at flame temperature. Compounds such as MO, MO_2, M_2O are unlikely. Dimers and trimers of MOH were considered in the low temperature flames. Heat of dimerization of alkali metals has been measured using mass spectrometric techniques with a Knudsen cell. D_0^0 values for the reaction

$$(MOH)_2 \rightleftharpoons 2\ MOH$$

were reported to be of the order of 60 kcal/mole for LiOH at 1300°K (14) and for the other alkali metals ranged from 40 kcal/mole for Cs to 54 kcal/mole for NaOH at 900°K.(15) The magnitudes of the heats of dimerization suggest that dimer populations in both type of flames used are negligible and trimer even more so. The values of dissociation energy of alkali hydroxide and chloride are given in comparison in Table II.

Table II

All values are in kcal/mole

Element	MOH (a)	MOH (b)	MCl (c)
Li	96 ± 3	101 ± 3	111
Na	85 ± 2	77 ± 4	97
K	82 ± 2	81 ± 2	101
Rb	83 ± 2	83 ± 2	100
Cs	86 ± 3	91 ± 3	106
H	-	-	102

(a). Kronberg, J.E. and Wheeler, R. Unpublished work (1969)

(b). Jensen, D.E and Padley, P.J., Trans. Faraday Soc., 62, 2132 (1966)

(c). Brewer, L., and Brackett, E., Chem. Rev., 61, 425 (1961)

The heat of dissociation of the alkali metal hydroxides and those of the corresponding chlorides fall roughly into a similar pattern. RbOH and KOH are close in order of stability although RbOH is slightly more stable. D_0^0 for CsOH is of the right order, slightly more stable than RbOH and KOH but considerably less stable than LiOH. The D_0^0 value of sodium hydroxide is close to those of RbOH and KOH, but contrary to the chloride data is slightly more stable.

In atomic absorption, only atoms in ground state contribute to the absorption, therefore, any ionization that takes place will remove a number of atoms from the ground state and reduce the number of atoms in the flame which are capable of absorption. If another element is present that will increase or decrease this ionization, this will lead to an ionization interference.

Consider a neutral metal atom M, that can be split into a positive ion, M^+ and a free electron e^-. The ionization and reverse recombination process are formally described by

$$M \rightleftharpoons M^+ + e^- \qquad (27)$$

and the equilibrium constant is written

$$\frac{[M^+][e^-]}{[M]} = K_i(T)$$

where $K_i(T)$ is the ionization constant which depends only on temperature providing pressure is constant and specific for each element.

The dependence of the degree of ionization on temperature is given by Saha equation

$$\log K_1(T) = \frac{-5040}{T} E_i + \frac{5}{2} \log T - \log P - 6.18 \qquad (29)$$

where E_i is the ionization potential of the metal, in electron volts, T is the absolute temperature, P is the pressure.

It can be seen that the degree of ionization increases significantly with an increase in temperature and results in a decrease of concentration of ground state metal atom in the flame.

In the case of alkali metals which have rather low ionization potentials at a flame temperature of 2400-2500°K a significant percentage of the metal atoms can be ionized. Table III shows a calculation of partial pressure of alkali metals in the flame at temperatures of 2400-2500°K, the approximate temperatures of acetylene air flames used in this work.

Table III

T	Element	I.P in ev.	$K_i(T)$	α atm.
2400	Li	5.37	1.00(9)*	3.16(5)
	Na	5.17	2.99(9)	5.47(5)
	K	4.32	1.58(7)	3.97(4)
	Rb	4.16	3.42(7)	5.85(4)
	Cs	3.87	1.39(6)	1.18(3)
2500	Li	5.37	3.05(9)	5.52(5)
	Na	5.17	7.89(9)	8.88(5)
	K	4.32	4.07(7)	6.38(4)
	Rb	4.16	8.55(7)	9.25(4)
	Cs	3.87	3.28(6)	1.80(3)

* 1.00(9) stands for 1.00×10^{-9} atm. etc.

In this table the values $K_i(T)$ for the alkali metals are calculated at flame temperatures by using the Saha's equation. The partial pressure of ions, α, are computed by assuming that α is very small compare to 1 so $1-\alpha \simeq 1$. Then $K_i(T) = \alpha^2$ and α can be obtained. It is seen that in both flames the ionization of alkali metals is of the same order of magnitude but at 2500°K alkali metals ionize to a somewhat greater extent than the 2400°K flame. These partial pressures of ions in the flame are about an order of ten less than the partial pressure of free metal atoms. It should also be noted that caesium which has the lowest ionization potential has the highest percent ionization and the ionization is greater by an order of 1.9 in the hotter flame .