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STUDIES ON ATOMIZATION OF ELEMENTS
IN GRAPHITE FURNACE ATOMIC ABSORPTION
SPECTROMETRY

by

SHAMIL J. CATHUM, B. Sc., M. Sc., University of Baghdad

A thesis submitted to
the Faculty of Graduate Studies and Research,
in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy

Department of Chemistry
Carleton University
Ottawa, Ontario
March 15, 1991

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acceptance of the thesis,

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SHAMIL J. CATHUM, B. Sc., M. Sc., University of Baghdad
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Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

April 24, 1991

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Abstract

Theoretical and experimental studies on absorbance signal profiles in graphite furnace atomic absorption spectrometry (GFAAS) have been done with a view to understanding reactions involved in analyte atom formation and loss in a commercial, Massmann-type graphite furnace.

A computer simulation has been used to study the shape of the absorbance signal profiles. The simulation has been based on an equation derived from the rate of atom formation under non-isothermal conditions. The results of the computer simulation have been compared with the experimental results obtained with the graphite furnace to test the validity of the model. The model has been found satisfactory.

Arrhenius-type equations for atomization in GFAAS have been developed to determine activation energies for atomization of Cu, Co, Ga, Au, Ni, Fe, Ag and Al. Mechanisms of atomization have been proposed based on experimental activation energies, which have been correlated with the energies involved in a very limited set of possible reaction sequences. The order of reaction of the atom formation and the atomization efficiency of the graphite furnace for production and containment of atomic vapour have been determined by two different methods.

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I thank those who have contributed in so many ways to my life. First, I thank my mother, Ghaida, to whom this thesis is dedicated and my father, Jawad, who died when I was about two years old. I thank my elder brother, Hussein, for his encouragement and support since the very beginning of my life, my brothers Ferid and Abdulrasool, and my sisters, Dalla and Talee'a. May the Lord bless them all.

List of publication arising from this research

1. Investigation of the order of copper atomization at the absorbance maximum in graphite furnace atomic absorption spectrometry; S. J. Cathum, C. L. Chakrabarti and J. C. Hutton, *Spectrochim. Acta*, 1991, **46B** (35).
2. Arrhenius plots for activation energy of atomization in graphite furnace atomic absorption spectrometry; C. L. Chakrabarti and S. J. Cathum, *Talanta*, 1991, **38** (157).
3. Mechanism of cobalt atomization from different atomization surfaces in graphite furnace atomic absorption spectrometry; C. L. Chakrabarti and S. J. Cathum, *Talanta*, 1991, **37** (1111).
4. Atomization efficiency of a graphite furnace in atomic absorption spectrometry; C. L. Chakrabarti, D. Ferrarotto, S. J. Cathum and C. J. Rademeyer, *Can. J. Chem.*, 1987, **65** (1079).

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INTRODUCTION

A modern analytical laboratory determines trace elements which may be present at concentrations as low as sub-parts per billion or as major constituents of the sample. Graphite furnace atomic absorption spectrometry (GFAAS) has been widely used to perform these determinations. In comparison with flame atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry graphite furnace techniques are slow. If graphite furnaces are slow why does anyone bother with the technique ? In a pulse-heated graphite furnace (all commercially available graphite furnaces are of this type and are heated from room temperature to pre-determined atomization temperature at a heating rate in the range of 1000 to 2000 K/s) atom formation occurs in a confined space; thus the atom residence time is much longer than in a flame or in an inductively coupled plasma. This results in increased sensitivity and lower detection limits. Another advantage of graphite furnaces is that they can be used in the analysis of solid materials which is especially useful if the solid materials are difficult to dissolve. Hence, graphite furnaces play a very important role in trace element determinations. As a way of transferring an analyte from condensed state into atomic vapour, graphite furnaces have found wide applications not only in the field of atomic absorption spectrometry but also in emission, fluorescence, photoionization, and spectral analysis.

Several graphite furnaces have been developed and used for trace element analysis during the past few decades, e. g. L'vov furnace, Massmann furnace, and the later on modifications that have been done to the Massmann-type furnace, i.e., L'vov platform, and stabilized temperature platform furnace (STPF) concept. The

most widely used graphite furnace for both routine analysis and research is the Massmann-type furnace, which uses rapid heating of the furnace from the room temperature to a pre-determined atomization temperature. In the Massmann-type furnace, the sample is placed on the wall of the graphite furnace and the various materials present in the sample vaporize as the wall of the tube is heated. The rate of atom formation is dependent on the temperature and the composition of the sample.

For further improvement in GFAAS one has to know how the neutral gaseous atoms are formed and what parameters alter the reaction path of atomization; in other words, the mechanism of atom formation. The study of mechanisms of atom formation and loss in GFAAS is of prime importance in improving instrumentation and analytical methodology. Development of a better understanding of how atoms are formed and what can be done to alter atom formation and loss processes, will provide a better theoretical background framework.

In this thesis, mechanisms of atom formation and loss have been studied, both theoretically and experimentally. Also studied in this thesis is a related topic: efficiency of atomization of a commercial graphite furnace.

To simplify the mathematical formulation of processes of atom formation and loss the effect of change in temperature on the line width, and hence on the peak-height characteristic mass, has not been taken into account. The change in temperature involved would not significantly affect the slopes of the Arrhenius plots since the slopes were measured from the linear segments of the plots that encompassed temperature ranges of a few hundred degree—the line width did not significantly change over such narrow ranges of temperature.

Chapter 1

1.1. FORMULATION AND MEASUREMENTS OF ATOMIC ABSORPTION SIGNAL PROFILES

The kinetics of atom formation and dissipation in graphite furnace atomic absorption spectrometry (GFAAS) can be studied by measuring the absorbance which is proportional to the number density of analyte atoms. There are two convenient quantities that can be measured: the absorbance (or peak-height absorbance), A , and the integrated absorbance (sometimes peak area), $\int_0^{\infty} A \, dt$, taken over a defined time interval, which is proportional to the number density of analyte atoms in the atomizer [1, 2]. The shape of the absorbance signal profile for a given analyte element is determined by the physical and chemical properties of the element, and by experimental and instrumental parameters, such as, the heating rate and the response time of the overall measuring system.

1.1.1. *Theory of absorbance signal profile shape*

The study of absorbance signal profiles obtained in GFAAS is of fundamental importance as the signals contain essential kinetic information on the mechanisms of atomization. Mathematical models, used to describe the shape of an absorbance signal can shed light on proposed mechanisms for atom release. Such models, in combination with experimental results, have been used: (1) to assess the effect of changing experimental parameters e. g. heating rate, initial coverage of the atomization surface area by the sample aliquot on transient signals [3–9]; (2) to determine activation energies for atom formation [3, 7–14]; (3) to measure

atomization efficiencies [1, 15, 16]. Basically, the main goal of developing a mathematical model is to understand the processes involved in the rate of atom formation and the rate of atom removal. At the present time, two approaches have been used to analyze the absorbance signal profile. In one approach, the atomization of the element is done at a given constant temperature and is called the "isothermal model" [12, 13, 17–20]. In the other approach, the atom formation is considered as a function of the increasing temperature of the atomizer surface and is called the "non-isothermal model" [1–5, 10].

The problem of obtaining a good match between the simulated absorbance signal profile and the experimental one recorded under non-isothermal techniques can be solved by making the mathematical treatment reflect the real-life situations, which will result in a mathematical model that is too complicated to be of much practical use. A simplified mathematical model has been developed below. This simplified model has the advantage of allowing a direct comparison of the simulated and the experimentally recorded curve. Although the model is based on some approximations, good agreement between the model and the experiment is seen. This suggests the consistency of the assumptions used.

For the case of negligible condensation and loss of analyte atoms by any other means, the temperature-dependent flux of analyte atoms vaporizing from the graphite surface defines the rate of the atom formation and is an experimentally measurable parameter [21]. Recognizing that the absorbance signal from the graphite furnace is determined by two opposing processes which characterize the supply and removal of the analyte vapour, Paveri-Fontana et al. [3], van den Broek et al. [1] and Gilmutdinov et al. [22] have given an analytical expression for the number of atoms, N_g , present in the gas phase at time t , which is a convolution

integral of the form:

$$N_g = \int_0^t S(t') \mathcal{R}(t-t') dt' \quad (1-1)$$

where $S(t)$ is the supply rate of atoms and $\mathcal{R}(t)$ is the removal function linking the time-dependent source to the time-dependent number of analyte atoms in the analysis volume [3] and t' is a variable of integration. van den Broek and de Galan [1] have assumed that the rate of atom formation is slower than the rate of removal of atoms out of the graphite furnace and the shape of N_g , or the absorbance A , in this case, reflects the rate of atom formation (the supply function). Under these conditions N_g is given by the following equation:

$$N_g = S(t) \int_0^{\infty} \mathcal{R}(t) dt = S(t) \tau_R \quad (1-2)$$

where τ_R is the overall time constant of the removal function.

A number of authors [1-3, 10, 16, 17, 21, 23-25] have assumed that the rate of atom formation is proportional to the change in the number of analyte atoms remaining on the graphite surface. With this assumption the rate of atom formation, $S(t)$ is given by the following equation:

$$S(t) = -\frac{dN_w}{dt} = k_1 N_w \quad (1-3)$$

where, N_w is the number of unatomized analyte atoms at time t , k_1 is a first-order rate constant for the atom formation approximated by the Arrhenius law,

$$k_1 = k_{\infty} \exp \left(-\frac{E_a}{RT} \right) \quad (1-4)$$

where k_{∞} is the pre-exponential factor, E_a is the activation energy, and R and T are the gas constant and the absolute temperature, respectively. Considering the implicit time dependence of k_1 , through its dependence on the temperature as expressed by Eqn (1-4), the solution of Eqn (1-3) is straightforward,

$$N_w = N_0 \exp \left(-\int_0^t k_1 dt \right) \quad (1-5)$$

where N_0 is the number of analyte atoms initially deposited in the furnace. Because the number of unatomized atom N_w decreases with increase in time (temperature), and the rate constant k_1 increases with time, the rate of atom formation $S(t)$ should have a maximum. Therefore, the shape of the absorbance signal profile is approximated by the rate of atom formation, $S(t)$, vs time, t [1, 2, 14]. Before proceeding further, it should be made clear that Eqn (1-3) holds correctly in the Carbon Rod Atomizer (CRA), the strip heater [1, 14], and in vacuum conditions [2]; it is also valid for the Massmann-type graphite furnace if the latter is operated in the gas-flow mode of atomization [14], where the rate of analyte dissipation is much greater than that of analyte atom formation. This point will be discussed in greater detail in the Results and Discussion section.

1.1.2. Computer simulation of the absorbance signal profile

van den Broek and de Galan [1] have demonstrated that Eqn (1-3) offers the best description for the rate of atom formation in GFAAS, provided that the

atomization reaction follows first-order kinetics and the rate of atom removal is much faster than that of atom formation. The effect of the order of reaction on the shape of the absorbance signal profile will be considered in Chapter 5. Because of the integral in Eqn (1-5) which is unavoidable for non-isothermal atomizations occurring in commercially available atomizers, a number of authors [9, 20] have used graphite furnaces very rapidly heated (6000–60000 K/s) by discharge of a large bank of electrolytic capacitors to elucidate mechanisms of atomization. Others [1, 2] have used numerical calculations to simulate the absorbance signal profile. To avoid such procedures and to make Eqn (1-3) applicable for further mathematical treatment the integral in Eqn (1-5) has been solved [24, 25] to give the following expression, provided that high heating rates are excluded (Appendix A):

$$\int_0^t k_1 dt = T^2 \left(\frac{Rk_{\infty}}{\alpha E_a} \right) \exp \left(-\frac{E_a}{RT} \right); \quad T = \alpha t \quad (1-6)$$

where α is the heating rate. The above solution also requires that α is a constant during the entire duration of the absorbance signal. Substituting Eqn (1-6) into Eqn (1-3) and considering Eqn (1-4), one gets:

$$S(t) = N_0 \left\{ k_{\infty} \exp \left(-\frac{E_a}{RT} \right) \right\} \exp \left\{ -T^2 \left(\frac{Rk_{\infty}}{\alpha E_a} \right) \exp \left(-\frac{E_a}{RT} \right) \right\} \quad (1-7)$$

where $T = \alpha t$. Equation (1-7) will be used to simulate the absorbance signal profile. To cross-check the simulation performed by using Eqn (1-7) the following numerical solution for Eqn (1-3) is also used:

$$\begin{aligned}
 S(t) = N_0 \left\{ k_{\infty} \exp\left(-\frac{E_a}{RT}\right) \right\} \exp \left\{ - \left(\frac{k_1(t_0) + k_1(t_1)}{2} \right) (t_1 - t_0) \right. \\
 \left. - \left(\frac{k_1(t_1) + k_1(t_2)}{2} \right) (t_2 - t_1) - \dots - \left(\frac{k_1(t_{x-1}) + k_1(t_x)}{2} \right) (t_x - t_{x-1}) \right\}
 \end{aligned}
 \tag{1-8}$$

where $k_1(t_x)$ indicates the value of k_1 at t_x and the subscript in t refers to a certain value of t on the x -axis. In the above numerical solution, Eqns (1-4) and (1-5) have been taken into account. To obtain a smooth curve a small time interval ($t_x - t_{x-1}$) should be taken. The simulations curves obtained by Eqns (1-7) and (1-8) will be superimposed on one another for comparison. Also, a comparison between the simulated absorbance signal profile by Eqn (1-7) and that experimentally measured will be presented using the atomic absorption signal profile of copper.

1.2. EXPERIMENTAL

1.2.1. Apparatus

The Perkin-Elmer atomic absorption spectrophotometer, model 503, modified to allow recording of the absorbance signal with a 20 ms time constant and equipped with a D_2 -arc background corrector and the Perkin-Elmer Heated Graphite Atomizer (HGA), model 76B, was used. The graphite furnace was heated by a laboratory-made power supply capable of supplying variable heating rates. High temperatures of the atomizer surface were measured with an Ircon 1100 series automatic optical pyrometer (Ircon Inc. Skokie, IL); low temperatures were measured with an Ircon series 300 automatic optical pyrometer (Ircon Inc.). The

Perkin–Elmer pyrolytically–coated graphite tubes (part No. B0091–504) were used. The signals were recorded with a Nicolet digital oscilloscope, model 4094 (Nicolet Instrument Corporation, Madison, Wisconsin). The integrated absorbance was measured using a software package provided by Nicolet Instrument Corporation. A hollow–cathode lamp of copper (The Perkin–Elmer) was operated at the lamp current recommended by the manufacture.

1.2.2. *Standard solutions*

A stock solution of copper was prepared by dissolving the pure metal, with heating, in 50% (v/v) nitric acid (ULTREX, J. T. Baker Chemical Co., USA); the final solution was made up to make 1000 $\mu\text{g}/\text{ml}$ by dilution with ultrapure water.

The test solutions were prepared by serial dilution of the stock solution to the desired concentrations with ultrapure water immediately prior to use, and contained 1% (v/v) nitric acid (ULTREX). Ultrapure water of resistivity 18.3 megohm–cm was obtained direct from a Mill–Q2 water purification system (Millipore Corporation, Mississauga, Canada).

1.3. *Argon Gas*

Argon gas (99.995% pure) was used both as the sheath gas and as the purge gas for the graphite furnace.

1.2.4. *Procedure*

In all cases, 10 μl of the test solution was injected into the graphite furnace with an Eppendorf micropipet fitted with disposable plastic tips. The absorbance values were corrected for blanks.

1.3. RESULTS AND DISCUSSION

1.3.1. *Comparison of the simulated and the experimental absorbance signal profile*

A computer simulation was used to obtain absorbance signal profiles under isothermal and non-isothermal conditions. Table (1-1) summarizes the parameters used in the simulation. The simulation was done on an IBM compatible Turbo PC computer using the software package Lotus 1-2-3. Figure (1-1) shows the simulated absorbance signal profiles obtained by Eqns (1-7) and (1-8). As can be seen from Fig. (1-1), the simulated absorbance signal profile (Curve b) obtained by applying Eqn (1-8), is appreciably higher than that obtained by Eqn (1-7) indicating that either Eqn (1-7) or Eqn (1-8) is useful in the simulation. A close look at Fig. (1-1) indicates that the shapes of the two curves are very similar however, since they differ only in the amplitude and the position of the profile. The usefulness of the approximate solution given by Eqn (1-7) as an alternative to the numerical solution given by Eqn (1-8) has been tested by superimposing the theoretical absorbance signal profile obtained by the numerical solution on that obtained by the approximate solution. In order to make such superimposition clear and possible the heating rate α and the proportionality constant Q [given in Table (1-1)] were changed to 620 K/s and 1.8×10^{-18} , respectively. As it is concerned, at this stage, in illustrating the difference between shapes of the two simulated absorbance signal profiles, the change in α and Q values will not make a significant difference in the absorbance shape; they will affect only the position and the amplitude of the simulated curve. The result is presented in Fig. (1-2), which shows an excellent agreement between the shapes of the two curves, suggesting that Eqn (1-7) is better than Eqn (1-8) since the latter requires modification in the parameters (α and Q) to match with the experimental curve. Thus, one concludes

Table (1-1). Values of parameters used in simulations.

Time interval used in calculations, Δt (s)	0.020
Heating rate, α (K/s)	400.0
Initial temperature, T_0 (in K)	1450.0
Number of analyte atoms introduced, N_0	1.9×10^{15}
Activation energy, E_a (in kJ/mol)	338.0
Pre-exponential factor, k_{∞} (s^{-1})	2.0×10^7
Proportionality constant, Q (atom $^{-1}$)	3.3×10^{-17}
Gas combination factor, j	1.5
Tube length, l (cm)	2.8
Tube volume, V (cm 3)	0.79
Diffusion coefficient, D_0 (cm 2 /s) at $T = 273$ K	0.135
Proportionality factor, κ	90.0
Flow rate, F (ml/min)	625.0

Fig. (1-1). Absorbance signal profiles simulated for non-isothermal conditions. Curve a is obtained by applying Eqn (1-7) (approximate solution), Curve b by the numerical solution [Eqn (1-8)].

Fig. (1-2). Absorbance signal profile of numerical solution superimposed on that obtained by Eqn (1-7). Curve a is given by Eqn (1-7), parameters used in the simulation are shown in Table (1-1); Curve b is obtained by numerical solution [Eqn (1-8)], parameters are same as in Table (1-1), except that the values for α and Q are taken as 620 K/s and 1.8×10^{-18} , respectively.

that Eqn (1-7) represents a reasonable description for the atom formation and can be used to obtain useful kinetic information, provided that high α is excluded. Thus, from now on, Eqn (1-7) will be used to simulate the absorbance signal profile instead of the numerical solution given by Eqn (1-8).

Equation (1-3) is used to obtain the simulated absorbance signal, once each, under isothermal and under non-isothermal conditions (see Appendices A and B for the details of the mathematical treatment). Figure (1-3) shows the simulated absorbance signal profile obtained under non-isothermal condition superimposed on the experimentally measured absorbance signal profile with the HGA-76B operated in the gas-flow mode of atomization (Ar gas flow rate: 600 ml/min). The experimental absorbance signal profile obtained with the graphite furnace agrees well with the simulated absorbance signal profile. With these approximations in the mathematical treatment of the rate of atom formation, the leading edges of the two curves coincide. Also, the positions of the absorbance maxima agree very well. Obviously, however, the simulated curve falls off much more sharply than the experimental curve, whereas, the latter has a prolonged trailing edge [1]. This means, at this region of the experimental curve, that the experimental rate of atom formation cannot be fully described by first-order kinetics. Two reasons can be advanced to explain these differences. First, the experimental rate of atom formation is affected by gas phase-graphite tube wall interactions occurring after the initial atomization of the element from the graphite furnace wall by multiple adsorption and re-desorption of gaseous analyte atoms, especially for analyte atoms with a high sticking probability for the graphite tube wall surface. In other words, unequal sites energies which hold analyte atoms on (or in) the graphite surface cause this pronounced trailing in the experimental curve [14]. Secondly, the shape of the

Fig. (1-3). Simulated absorbance signal profile from Eqn (1-7) superimposed on experimental absorbance signal profile of 200 ng of copper atomized using a pyrolytically coated graphite tube in the gas-flow mode (flow rate of Ar = 625 ml/min). a: simulated; b: experimental.

experimental absorbance signal profile depends on the existence of temperature gradient in the longitudinal axis of the graphite tube, especially for the 28 mm-long tubes used in this study.

Figure (1-4), Curve a, presents the results of the simulation of the absorbance signal profile under isothermal conditions using Eqn (6B), Appendix B, compared with that experimentally measured with the cathodic sputtering in a glow discharge technique [26], shown as Curve b. The reason for comparing the simulated absorbance signal (under isothermal conditions) with that experimentally measured by the cathodic sputtering in a glow discharge for atomic absorption spectrometry is that the latter is a new technique used to produce neutral analyte atoms in isothermal conditions [26]. Good agreement between the theoretical model and the experimental results confirms the validity of the model. The shape of the simulated absorbance signal profile (under isothermal conditions) also should be comparable with that obtained using a graphite furnace, provided that a constant temperature is maintained during atom formation. Frech et al. [14] have reported an absorbance signal profiles for lead obtained under isothermal conditions (constant temperature) using the HGA-74 operated in the gas-flow mode (gas flow rate: 700 ml/min). Again, good matching between the shape of the simulated and the experimental absorbance signal is seen, which is another support for the above arguments. In contrast to the isothermal atomization, absorbance signal profile produced in non-isothermal conditions shows a maximum with an approximately bell-shaped absorbance signal profile, whereas only an exponential decay (with no maximum) is recorded under isothermal conditions. This can also be verified mathematically by differentiating Eqn (1-3) under both conditions (isothermal and non-isothermal conditions) and solving for the rate constant, k_1 , at the position of the absorbance

Fig. (1-4). Simulated absorbance signal profile under isothermal conditions superimposed on experimental absorbance signal profile measured with the cathodic sputtering in a glow discharge technique. **a**: simulated (parameters of simulation are: $k_1 = 13 \text{ s}^{-1}$, $N_0 = 1.9 \times 10^{15}$, $Q = 3.3 \times 10^{-17}$); **b**, experimental (data were taken from Ref. 26).

maximum where $dS(t)/dt = 0$, and then substituting the resulting solution for k_1 back into Eqn (1-3). It is quite clear that $S(t)$ has no maximum under isothermal conditions whereas under non-isothermal conditions it does have a maximum as illustrated in Appendix B.

Another good experimental support for the above conclusion can be drawn from Figs (1-3) and (1-4). From a comparison of the absorbance signal profile measured with the graphite furnace at the increasing tube wall temperature shown as Curve b, Fig. (1-3), and that recorded at a constant temperature with the cathodic sputtering in a glow discharge technique [26] shown as Curve b, Fig. (1-4), one can conclude as follows. The graphite furnace signal increases exponentially to a maximum and then falls exponentially back to the baseline, whereas, the signal obtained by the cathodic sputtering in a glow discharge has a very steep leading edge with t_m (defined as the time to reach the absorbance maximum) very close to the appearance time t_0 (defined as the time at which the initial absorbance is 0.0044), and also decays exponentially from a maximum back to the baseline. The maximum seen in the experimental absorbance signal profile recorded with the cathodic sputtering technique [26] (under the isothermal condition) is interpreted in terms of the initial value of a first-order exponential decay, $S(t) = N_0 k_1 \exp(-k_1 t)$, where $S(t) = N_0 k_1$ at $t = 0$, which is the maximum value for $S(t)$, and then decreases with time, t . In other words, there is no maximum for the isothermal curve [26] and the observed maximum, in fact, corresponds to the initial value of the exponential decay of the above equation. Both absorbance signal profiles (under isothermal and non-isothermal conditions) are represented by a distinct shape. This makes for a clearer interpretation of non-isothermal absorbance signals than for the case of isothermal atomic absorption measurements, allowing a possibility

for determination of the order of reaction at the absorbance maximum.

1.3.2. *Atom formation and atom removal in the gas-flow mode of operation*

Figure (1-5) presents the peak area and the peak-height of the absorbance signal for 200 ng of Cu measured with the Perkin-Elmer HGA-76B as a function of the flow rate of argon. As can be seen from Fig. (1-5), a rapid decrease in the signal is observed; the signal then levels off at higher flow rates. After the flow rate of about 600 ml/min, the absorbance signal attains a constant value which describes the rate of atom formation [1].

To verify the above experimental conclusion, the computer simulation is used which also considers the atom formation and loss of atoms in a graphite furnace operated in the gas-flow mode of atomization (similar to the above experimental conditions). In general, the removal of atoms out of a graphite furnace is the result of at least three different loss processes: diffusion, expansion and convection [1]. It is assumed that the atoms are formed according to Eqn (1-3) and the released atoms are transported to the analysis volume and removed from it by diffusion, expansion and convection only, with no other supply or loss sources, such as readsorption onto the graphite surface, gas phase reactions or diffusion into the graphite tube wall. To account for atom loss by the three processes an earlier expression which combines all of these processes will be used to simplify the simulation [1, 14, 27]. The following general equation which relates the number of analyte atoms leaving the graphite tube surface per unit time to the absorbance signal will be used in the computer simulation [1, 10, 14, 28, 29]:

$$\frac{dN_g}{dt} = S(t) - R(t) \quad (1-9)$$

Fig. (1-5). Peak area and peak-height absorbance of copper at a constant heating rate of the furnace as a function of the flow rate of argon gas, a: peak area; b: peak height.

where dN_g/dt is the change in number of analyte atoms within the atomizer, $S(t)$ is the rate of atom formation, as given by Eqn (1-7), and $R(t)$ is the rate of atom loss by diffusion, expansion and convection which is given by:

$$R(t) = k_2 N_g \quad (1-10)$$

where k_2 is the temperature-dependent, first-order rate constant for the rate of atom loss and is given by the following equation [1, 27, 29]:

$$k_2 = \left(\frac{8D_0 T^j}{l^2 T_0} \right)_{\text{dif}} + \left(\frac{\alpha}{4T} \right)_{\text{exp}} + \left(\frac{F T}{300 \kappa V} \right)_{\text{conv}} \quad (1-11)$$

where the three terms on the right side of Eqn (1-11) account for the atom loss by diffusion, expansion, and convection, respectively; T is the absolute temperature, D_0 is the concentration diffusion coefficient at T_0 (273 K); and l and j are the geometric length of the graphite tube and the gas combination factor, respectively; V is the graphite tube volume, F is the flow rate, and κ is a proportionality constant which depends on the flow pattern through the graphite furnace; its value is taken as 90.

Using a typical data set given in Table (1-1), the rate constant of atom formation k_1 and the rate constant of atom removal k_2 have been plotted vs time t . The result is presented in Fig. (1-6), which shows that k_1 (Curve a) is much smaller than k_2 (Curve b) within the time interval of the signal measurement. This is consistent with the assumption adopted in the theory. The difference between the two rate constants depends appreciably on experimental conditions, such as, the heating rate of the atomizer, and the flow rate of the purge gas.

Fig. (1-6). Rate constant for atom formation, k_1 , and rate constant for atom removal, k_2 , obtained under non-isothermal conditions; a: k_1 , b: k_2 . The simulated absorbance signal (broken line) is given for comparison.

From the results of the above computer simulations for the absorbance signal profiles one may draw the following conclusions. In GFAAS, an elementary reaction of atom formation may be satisfactorily represented by the simulated absorbance signal profile at linearly increasing temperature. This is demonstrated by the mathematical examination based on an approximated solution for the integral, $\int_0^t k_1 dt$, in Eqn (1-5), which is especially appropriate for low heating rates, and is transferable to complex processes. Although not generally applicable for accurate calculation of kinetic data, this method represents a satisfactory general path for visualizing the features for atom formation versus time curve. Also, from the asymmetry as well as from the width of the resulting curve useful information about the order of reaction of atom formation may be obtained, as demonstrated by Holcombe et al. [2, 30, 31] using Monte Carlo techniques.

SUMMARY

A simple mathematical treatment, based on the analysis of the rates of atom formation and dissipation is presented for the description of the atomic absorption pulse in graphite furnace atomic absorption spectrometry. The model is based on the approximate solution of the integral $\int_0^t k_1 dt$ which always arises in the mathematical expressions of the rate law of atom formation in graphite furnaces operated in normal experimental conditions, i. e. non-isothermal conditions.

Chapter 2

2.1. MECHANISMS OF ATOM FORMATION IN THE GRAPHITE FURNACE

The term "mechanism of atomization" means a description on a molecular level of the changes that analyte species undergo during atomization. It is a useful model to illustrate what occurs in atom release processes. The cornerstone upon which our understanding of what an atomization mechanism is based is reaction kinetics. The ultimate goal of reaction kinetics is the determination of the atomization mechanism in a reacting system. Reaction kinetics is best studied using a mathematical formulation of reaction rates [32]. In Chapter 1, it has been shown that an elementary reaction undergoing a linearly increasing temperature is accompanied by an absorbance signal profile that can be expressed mathematically. Recording of this profile using a suitable method of measurements offers the possibility of determination of the activation energy, which may be related to the processes occurring during atomization. The Arrhenius plot in which $\ln k$ is plotted vs $1/T$ proves to be very suitable for this purpose.

Reactions in the graphite furnace are extremely complex. Detailed knowledge of the nature of most of these reactions has so far eluded previous workers. Yet, no major advance in graphite furnace technology is possible without this detailed knowledge. Valuable kinetic information required to propose mechanisms for these complex reactions can be obtained from absorbance signal profiles. The atom release processes occurring in an electrothermal atomizer are dependent on many factors. This is reflected in the great variety of absorbance peak shapes recorded during atomization.

Since the introduction of graphite furnace atomic absorption spectrometry (GFAAS) various mathematical approaches to the physical interpretation of peak shapes have been made. These range from the simple kinetic model of Fuller [17] to the Monte Carlo techniques by Black et al. [31]. It has been shown in many instances that the shape of absorbance signal profiles is different for different graphite tube materials (atomization surfaces) depending on the topography and chemical reactivity of the graphite tube surface [33]. Smets [10] has mentioned the possibility of atom re-deposition on the graphite furnace, and Holcombe et al. [30] and Guerrieri et al. [11] have suggested that a series of adsorption and re-vaporization reactions may take place along the tube length during atomization, and that the shape of the absorbance signal profiles may therefore be largely determined by the degree of "stickiness" of the analyte atoms to the graphite tube surface. Existence of active sites on graphite substrate and catalytic activities of many metals ions lend support to the hypothesis that the rate-determining steps in the atomization of some analytes are kinetically controlled reactions occurring at the graphite surface-analyte interface.

A study of atom formation processes, both theoretically and experimentally, will be attempted in this chapter. The theoretical work will be to model sample vaporization from the graphite surface and to derive Arrhenius-type equations which are valid for any order of reaction and are capable of extending the linearity of the Arrhenius plot. The rate-determining steps will be identified by correlating experimental activation energies with the thermochemical values for probable reactions reported in the literature.

To investigate the mechanism of atom formation in GFAAS it is necessary to formulate a valid relationship between an absorbance signal and number of analyte

atoms in the sample. In the case of commercial electrothermal atomizers this relationship is found to be complicated since the sample to be atomized into the gas phase at a given rate may be distributed unevenly throughout the atomizer volume and atomizer surface because of the pronounced temperature gradients over most of the horizontal axis of the graphite tube-type atomizers.

In this thesis, the atomization phenomenon will be investigated in two ways as follows: (1) computer simulation of the absorbance signal profile (which is discussed in Chapter 1), and (2) experimental study of the relationship between the rate of atom formation and the recorded absorbance signal, which will allow valuable kinetic information to be determined from an absorbance signal profile. Since the shape of the absorbance signal profile is affected by the graphite tube material, as mentioned above, and since the graphite tube furnace is considered the heart of GFAAS, a brief description of the atomizer and some experimental parameters characterizing atom formation are presented first.

2.1.2. The function of the graphite furnace

The commercial graphite furnace (which has been used for this thesis) is a cylindrical, tube-type atomizer, which is resistively heated by an electrical power supply. The furnace is usually programmed to provide sequentially a low temperature (about 100 °C) for the drying cycle, followed by a higher temperature (about 1000 °C) for the charring cycle, followed by the atomization cycle, during which the furnace surface is heated at a heating rate up to 2000 K/s to a pre-determined atomization temperature. The terms "furnace" and "atomizer" will be synonymously used in this thesis to mean the above-described, pulse-heated, commercial, tube-type graphite furnace. It is crucial for every procedure in GFAAS

to convert the sample to be analyzed into neutral atoms. Generally, samples are introduced into the atomizer as aqueous solutions, liquids or solids, or as vapour (e.g., hydride or carbide vapour). Hence, atomization is an essential step in GFAAS. In fact, the atomization step consists of sequential steps of drying, charring, and atomization.

One trend in recent theoretical development in GFAAS is to decouple the processes involved in analytical measurements in order to obtain well-defined physical conditions for a single process [34]. Such a procedure offers the possibility that unwanted influences, such as matrix effects, can be minimized.

2.1.3. Description of the graphite furnace

Graphite tubes: Two types of graphite tube are commercially available; one is made of spectrally pure, high-density graphite, and is called electrographite tube; the other is made of the same material, but coated with a thin layer of pyrolytic graphite and is called a pyrolytically-coated tube. For special studies in GFAAS, a glassy carbon tube is also sometimes used. The graphite tube [Fig. (2-1)] has several small grooves in the inner surface near its ends to increase the temperature of the tube ends to decrease the temperature gradient along the horizontal axis of the graphite tube. The graphite tubes will typically have useful lifetimes of about 300 firings, dependent upon atomization time, temperature, the protective gas flow rate, and sample. As the tubes age, they may show different sensitivity. For maximum lifetime, low atomization temperature and short atomization time should be used.

Inert gas: An inert gas atmosphere for atomization is usual for any graphite furnace analysis. There are two functions for the inert gas: the protection of the hot

Fig. (2-1). Graphite tube furnace.

graphite parts from oxidation and wearing out, and sweeping away the vaporized sample matrix during drying and charring steps. In the Perkin–Elmer Heated Graphite Atomizer (HGA), Fig. (2–2), the inert gas is split into two separately controlled streams; the external protective gas stream around the graphite tube, and the internal purge gas stream which enters at the tube ends and leaves it through the central injection hole. During atomization, in contrast to the charring step, the analyte atoms should be kept in the analysis volume as long as possible to give highest absorbance. Therefore, the purge gas flow is usually interrupted during atomization, the so called "gas–interrupt mode".

2.1.4. *A schematic diagram of the graphite furnace*

A schematic cross–section of a typical Massmann–type (pulse–heated, commercial) electrothermal atomizer for atomic absorption measurements is shown in Fig. (2–2). The graphite tube is electrically heated. The sample is usually deposited on the graphite tube surface or it may be deposited on a graphite platform or a graphite probe. The atomization is the step by which the sample is brought from the condensed phase to the gas phase. The analyte may be atomized concurrently with its vaporization or the atomization may follow vaporization.

The atomization reactions are governed appreciably by the temperature program of the atomizer. As mentioned earlier, there are, basically, three temperature stages: drying, charring, and atomization. A typical program consisting of a succession of time intervals with constant (hold) and charring (ramp) temperature is shown in Fig. (2–3). Usually, the atomization stage is followed by a cleaning operation during which the atomizer is fired above the atomization temperature to get rid of any residual sample constituents. The cooling stage is

Fig. (2-2). A cross-section of a typical Massmann-type electrothermal atomizer (the Perkin-Elmer Corporation) for atomic absorption measurements.

Fig. (2-3). Schematic heating program of an electrothermal atomizer; a: drying; b: charring; c: atomization; and d: cleaning.

necessary before the next sample is introduced to allow the atomizer to cool down.

2.1.5. Parameters characterizing atom formation in GFAAS

The most important parameter of atom release process in GFAAS is the temperature of the graphite tube furnace. Because the furnace is heated at the middle part there can be severe temperature gradients [29]. Therefore, one has to define various temperatures: the tube wall temperature, T , which defines the temperature of the atomizer surface usually indicated by the surface where the sample is deposited; the temperature of the atomizer volume is described by the gas temperature, T_g , which is generally a function of time and space of the atomizer. The heating rate dT/dt in K/s usually means the change in the tube wall temperature in the middle part of the furnace. Another important parameter of atomization is the flow rate of the inert purge gas inside the atomizer. During atomization, very often, the internal gas flow is interrupted (the gas-interrupt mode of operation). The convective flow of the internal purge gas causes the rate of atom loss to be determined partly by the convection velocity.

2.1.6. Parameters characterizing the analyte element

The vaporization temperature, T_{vap} , is the temperature of the graphite tube surface at which the analyte begins to enter the vapour phase. T_{vap} depends on the chemical constituents of the sample, therefore, T_{vap} , may be influenced by adding chemicals, called chemical modifiers, which may undergo chemical reactions with the analyte, or with the matrix, or with both [35]. Chemical modifiers usually allow the analyte to be charred at high charring temperature, which will remove matrix components that may otherwise interfere.

2.1.7. Arrhenius plots for mechanisms of atomization

Arrhenius plots constructed using absorbance data have been widely used since their introduction by Tessari et al. [3–5], and the more extensive study by Sturgeon et al. [13] and later by Smets [10]. Frech et al. [14] have concluded from the results obtained by applying various Arrhenius plots reported in the literature [10, 13] which have used the rising part of the temperature to generate information about mechanisms of atom formation that several mechanisms are operative during atomization. Chung [36] has claimed a linear Arrhenius plot over the temperature range from the appearance of the absorbance signal profile to the absorbance maximum for all the cases studied. Recently, Yan Xiuping et al. [37] have reported an improvement of the Smets method and have discussed the effect of unjustified assumptions on the linearity of the Arrhenius plot. Holcombe [38] and Bass and Holcombe [39] have reported that the use of often non-linear Arrhenius-type plots to obtain energies characterizing the atom formation reaction in GFAAS is likely to be erroneous. Bass and Holcombe [39] have attributed the potential source for the non-linearity in Arrhenius plots obtained at the atmospheric pressure to the finite residence time of analyte atoms in GFAAS.

The majority of commercially available electrothermal atomizers has common features in that the atom formation in and the atom removal from the analysis volume are temperature-dependent. It may therefore be possible to study rates of atom formation due to the effect of temperature on the atom release in these atomizers. According to the Arrhenius law, the rate constant for atom formation, k_1 , can be expressed as, $k_1 = k_{\infty} \exp(-E_a/RT)$, where k_{∞} is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. To obtain kinetic information the rate constant of atom formation k_1

is very often related to an experimentally measurable parameter(s), such as, the absorbance, assuming simple first-order kinetics for the atom formation reaction. The activation energy, E_a , is determined by plotting the natural logarithm of the rate constant for atom formation versus the reciprocal of the absolute temperature; the slope of the straight-line plot ($-E_a/R$) yields the activation energy, E_a . Such procedures, however, do not yield a straight line if the Arrhenius-type plots are constructed using data points near the absorbance maximum. The methods for obtaining the Arrhenius plots reported in the literature [10, 13, 36, 40] do not satisfactorily account for the noticeable non-linearity in these plots. Furthermore, the problem of large uncertainties in the determination of activation energy [14, 38, 39], and the possibility that atomization reactions do not necessarily follow first-order kinetics [30] have hindered progress in the application of activation energy for elucidating atomization mechanisms. Most of the earlier studies on atomization mechanisms have been done by using data points near the very beginning of the absorbance signal profile, and have ignored the later part of the absorbance signal profile, which also contains useful information on atomization mechanisms. Also, the method of Smets [10], widely used by other workers to obtain the activation energy, does not provide reliable kinetic information on atomization reactions except near the appearance of the absorbance signal profile [10, 39]. This is probably attributed to the assumptions used in developing the equation by Smets [10], as recently pointed out by Yan Xiuping et al. [37]. It is also important to provide a method for obtaining activation energy that is valid for any order of reaction; to develop Arrhenius-type equations that are useful for extracting kinetic parameters, such as, activation energy; and to increase the range of data points usable for drawing Arrhenius plots, starting from the appearance of the

absorbance signal profile to the absorbance maximum.

2.2. THEORY

2.2.1. Arrhenius-type equations derived in the gas-flow mode of operation

To derive an Arrhenius-type equation which is useful in determining kinetic parameters for proposing mechanisms of atom formation in GFAAS it is important to seek a valid relationship between the rate of atom formation and the absorbance signal. The shape of the absorbance signal in GFAAS has been shown to be determined by the rate of release of analyte atoms from the surface of the graphite tube atomizer rather than by diffusive loss from the atomizer volume [41, 42]. For the sake of simplicity, the following assumptions will be made: (a) all unatomized analyte atoms are at the same temperature at the time of atomization; (b) the rate of atom removal in the gas-flow mode of atomization is much faster than the rate of atom supply; (c) there is no activation energy for the analyte atom-diffusion through the gas phase; (d) the rate constant for atom formation is approximated by the Arrhenius law and (e) atomization of the sample occurs at a constant, low heating rate.

With the above simplifying assumptions, the time-dependence of the analyte atom population in a graphite furnace can be described by consecutive reactions as follows [9]:

where n is the order of reaction (assumed constant), N_w is the number of analyte atoms left unatomized at time t , N_g is the number of analyte atoms that are in the

gas phase at time t (as distinct from the number of analyte atoms in the analysis volume), N_{lost} is the number of analyte atoms lost from the atomizer at time t ; k_1 and k_2 are temperature-dependent rate constants for the supply and the removal function, respectively. The time-dependent variation of N_g is expressed as a convolution integral given by Eqn (1-1), Chapter 1, i.e., $N_g = \int_0^t S(t') \mathcal{R}(t - t') dt'$, where $S(t)$ is the supply function defining the rate of atom formation, $\mathcal{R}(t)$ is the mass transport function which depends on the atom removal and t' is a variable of integration. If the removal rate is very rapid compared to the supply rate the above equation is reduced to: $N_g = S(t) \tau_R$ [see Chapter 1, Eqn (1-2)], where τ_R is the overall time constant of the removal function. The shape of the absorbance signal A will reflect the time-dependence of the supply function. Conversely, if the removal rate is very slow compared to the supply rate, the shape of the absorbance signal profile is determined by $\mathcal{R}(t)$ [1].

From reaction scheme (2-1), one may write the following differential equation for the release of analyte atoms N_g [24, 25]:

$$\frac{dN_g}{dt} = n k_1 N_w^n - k_2 N_g \quad (2-2)$$

Equation (2-2) has been reported earlier for $n = 1$ [10, 17]. With forced convection at low heating rates and no activation energy for the removal of analyte atoms, the loss by diffusion, expulsion and convection is fast and therefore cannot be the rate-determining step. This experimental observation has been reported in the literature [1, 14] and discussed in Chapter 1. Under these conditions, the supply function, $S(t)$, is approximated by the following equation: [1, 14, 24, 25]:

$$S(t) = - \frac{dN_w}{dt} = n k_1 N_w^n = \frac{A}{Q} \quad (2-3)$$

where Q is a proportionality constant which relates the absorbance A to the number of analyte atoms present in the analysis volume at time t under the proposed experimental conditions.

The next step in developing the Arrhenius-type equation is to find a mathematical relationship between the rate constant for atom formation and the absorbance. This can be done by integrating both sides of Eqn (2-3) to find an expression for N_w [which is then substituted back into Eqn (2-3)] subject to the boundary condition that the number of unatomized analyte atoms is N_0 at time $= 0$ and N_w at time $= t$,

$$-\int_{N_0}^{N_w} N_w^{-n} d N_w = \int_0^t n k_1 dt$$

which can be solved for $n \neq 0$ and $n \neq 1$ to yield [24] (see also Appendix C)

$$N_w^n = N_0^n \left(1 + (n-1) N_0^{n-1} \int_0^t n k_1 dt \right)^{n/(1-n)} \quad (2-4)$$

and for $n = 1$ to yield, Eqn (1-5) of Chapter 1, i. e. $N_w = N_0 \exp \left(-\int_0^t k_1 dt \right)$. Substituting Eqn (2-4) into (2-3) and rearranging terms one gets

$$A = Q n k_1 N_0^n \left(1 + (n-1) N_0^{n-1} \int_0^t n k_1 dt \right)^{n/(1-n)} \quad (2-5)$$

Taking the order of reaction n as equal to 1, in Eqn (2-3), and considering Eqn

(1-5) of Chapter 1, one gets

$$A = Q k_1 N_o \exp \left(- \int_0^t k_1 dt \right), \quad n = 1 \quad (2-6)$$

At the very beginning of the absorbance signal profile $\int_0^t k_1 dt \rightarrow 0$. Hence, upon applying the Arrhenius law to k_1 in Eqns (2-5) and (2-6) and taking natural logarithms of both sides of the resulting two equations one has the following expression (for $n \neq 0$):

$$\ln A = - \frac{E_a}{RT} + Z \quad (2-7)$$

where

$$Z = \ln \left(Q N_o k_o \right)$$

Equation (2-7) is valid for any order of reaction for atom release except for $n = 0$, whereas the other methods are valid only when atom formation follows a first-order reaction. Using the transition-state theory Sturgeon et al. [13] have derived Eqn (2-7) based on a general relationship between k_1 and $T^a \exp(-\Delta G^{o\#}/RT)$, where $\Delta G^{o\#}$ is standard free energy change of activation and a is a constant equal to 1.

L'vov [15] has reported that with the Massmann-type (pulse-heated) graphite furnace integrated absorbance has a much greater potential for giving absolute measurement of absorbance than peak-height absorbance. Use of integrated absorbance in an Arrhenius-type equation will increase the temperature range usable for collecting absorbance data for Arrhenius plots. To do this, Eqn (2-3) is

used to obtain the integrated absorbance. Various relationships between the integrated absorbance and the number of analyte atoms present in the atomizer can be developed using different time intervals. These useful mathematical expressions will facilitate the derivation of the relationship between the rate constant of atom formation and the absorbance signal are obtained. Thus, upon rearranging and integrating Eqn (2-3), subject to the boundary condition that $N_w = 0$ at time = ∞ and N_w at time = t , one gets

$$N_w = \frac{1}{Q} \int_t^{\infty} A \, dt \quad (2-8)$$

Similarly, Eqn (2-3) can be integrated, subject to the boundary condition that $N_w = N_0$ at $t = 0$ and N_w at time t to yield

$$N_g = \frac{1}{Q} \int_0^t A \, dt \quad (2-9)$$

Similar relationships between (N_g and N_w) and the integrated absorbance, as given by Eqns (2-8) and (2-9), were also derived by Smets [10] under different experimental conditions and used by Bass and Holcombe [39]. Substituting Eqn (2-8) into (2-3) one gets the following expression for k_1 :

$$k_1 = \frac{c \, A}{\left(\int_t^{\infty} A \, dt \right)^n} \quad (2-10)$$

where,

$$c = n^{-1} Q^{n-1}$$

It will be illustrated later in this chapter how Eqn (2-10) can be used to determine E_a from the absorbance signal profile by a method, to be called "the method of calculation" without recourse to Arrhenius plots, provided that $n = 1$. The value of n can be determined at the absorbance maximum by a method reported in the literature [24], and will be discussed in Chapter 5. For $n = 1$, and under the gas-flow mode of operation Eqn (2-10) reduces to:

$$k_1 = \frac{A}{\int_t^{\infty} A \, dt} \quad (2-11)$$

which is another form of Smets equation [10]. Other forms of Eqn (2-11) have been developed by Frech et al. [14], Bass and Holcombe [39], L'vov et al. [43], and Guerrieri et al. [11]. Applying the Arrhenius law to k_1 in Eqn (2-11) the E_a can be determined from a plot of $\ln(A / \int_t^{\infty} A \, dt)$ vs $1/T$; the slope equals $-E_a/R$, yielding the value of E_a .

2.2.2. Absorbance profile obtained at a constant heating rate of the atomizer

Mathematical treatment of atomization under non-isothermal conditions is simplified if the atom release process follows first-order kinetics and the temperature is increased at a constant heating rate, α , from an initial temperature T_i (Kelvin) to the final temperature T (Kelvin):

$$T = \alpha (t_0 + t'') = \alpha t \quad (2-12)$$

where t_0 is the time when the temperature of the tube wall is T_i , t'' is the time

required for the temperature to increase from T_i to T , and t is the time if the heating were started at the absolute zero of temperature. Thus, upon integrating Eqn (2-11) for the time interval, time = 0 to time = t , one gets,

$$\int_0^t \left(\frac{A}{\int_t^\infty A \, dt} \right) dt = \int_0^t k_1 \, dt \quad (2-13)$$

For the right-hand side of Eqn (2-13), it has been shown that the integral $\int_0^t k_1 \, dt$ is solvable and can be approximated by $T^2 \left(\frac{Rk_\infty}{\alpha E_a} \right) \exp(-E_a/RT)$ [see Chapter 1, Eqn (1-6), and the complete derivation in Appendix A]. The solution of the left-hand side of Eqn (2-13) is straightforward [25]; hence, Eqn (2-13) becomes,

$$-\ln \left(\frac{\int_t^\infty A \, dt}{\int_0^\infty A \, dt} \right) = T^2 \left(\frac{Rk_\infty}{\alpha E_a} \right) \exp \left(-\frac{E_a}{RT} \right) \quad (2-14)$$

which can be rearranged to give

$$y = \nu \exp \left(-\frac{E_a}{RT} \right) \quad (2-15)$$

where

$$y = -\ln \left(\frac{\int_t^{\infty} A \, dt}{\int_0^{\infty} A \, dt} \right) / T^2 \quad (2-16a)$$

and

$$\nu = \left(\frac{Rk_{\infty}}{\alpha E_a} \right) \quad (2-16b)$$

The value of y on the left-hand side of Eqn (2-15) is experimentally measurable.

Taking natural logarithm of both sides of Eqn (2-15) one gets

$$\ln y = -\frac{E_a}{RT} + \ln \nu \quad (2-17)$$

A plot of $\ln y$ vs $1/T$ should be linear with a slope $-E_a/R$ and an intercept $\ln \nu$.

2.2.3. Derivation of the Smets equation in the gas-flow mode of operation

There are several methods that have been developed to obtain kinetic parameters of atom formation in GFAAS [3, 10, 11, 17, 20, 36, 40, 44-48]. Among these methods is the Smets method [10], which relates the first-order rate constant of atom formation k_1 to experimentally measurable parameters as follows:

$$k_1 = \frac{1}{\beta} \frac{A}{\int_t^{\infty} A \, dt} \quad (2-18)$$

where β is the atomization efficiency of the atomizer defined by Smets as the fraction of the analyte atoms actually atomized, and A and $\int_t^{\infty} A \, dt$ are the peak-height and the integrated absorbance (over the indicated time interval), respectively. Equation (2-18) has been widely used in the literature to determine the activation energy of the rate-determining step by plotting $\ln (A / \int_t^{\infty} A \, dt)$ vs $1/T$; the curve is linear for the data points at the very beginning of the absorbance signal profile with a slope $(-E_a/R)$, yielding the E_a . It should be noted that the parameter β will not affect the determination of the activation energy by the Smets method as long as β remains constant since it can be combined, for instance, with the pre-exponential factor k_{∞} of the Arrhenius law, $k_1 = k_{\infty} \exp(-E_a/RT)$. However, it does matter in the determination of β , as illustrated in Chapter 7. Smets [10] has derived and used Eqn (2-18) for the strip heater, operated in the gas-interrupt mode of atomization, assuming that the rate of atom formation during the entire duration of the evaporation processes (for the strip heater) nearly equals the rate of atom disappearance. To make the derivation of the Smets equation valid for determination of E_a a number of authors [1, 14, 23] have suggested that the graphite furnace should be operated in the gas-flow mode of operation in order to shorten greatly the residence time of analyte atoms so as to make the rate of atom removal much faster than the rate of atom formation. Hence, if the Smets equation is to be chosen to investigate kinetic parameters, such as E_a and the order of reaction, it is very reasonable to address the following questions: Which gas-flow mode of operation should be used? Will the Smets equation be valid for both modes of operation (i. e. gas-flow and gas-interrupt mode of operation)? In this chapter, answer to the above questions has been

attempted by giving details of the derivation of the Smets equation under gas-flow and gas-interrupt mode of operation, and by presenting two sets of experimental values of E_a for copper, with one set of E_a values obtained by operating the atomizer in gas-flow mode and the other set in gas-interrupt mode of operation.

For the Heated Graphite Atomizers with forced convection of the analyte atomic vapour Eqn (2-6) can be used to describe the number of gaseous analyte atoms generated in the atomizer at a given time t . Integrating both sides of Eqn (2-6) subject to boundary conditions that at time t the integral $\int_0^t k_1 dt = \int_0^t k_1 dt$, and at time $t = \infty$, $\int_0^t k_1 dt = \int_0^\infty k_1 dt = T^2_{(t=\infty)} (Rk_\infty/\alpha E_a) \exp(-E_a/RT) = \infty$, [see Eqn (1-6), Chapter 1], yields

$$\int_t^\infty A dt = Q N_0 \exp \left(- \int_0^t k_1 dt \right) \quad (2-19)$$

Therefore, upon dividing Eqn (2-6) by (2-19) and cancelling identical terms one gets Eqn (2-11), which is the Smets equation obtained when the atomizer is operated in the gas-flow mode of atomization, and when the rate of atom formation follows first-order kinetics. Note that, under these experimental conditions, the Smets equation has been put in a general form for any order of reaction, except for $n = 0$ [see Eqn (2-10)].

2.2.4. Derivation of the Smets equation in the gas-interrupt mode of operation

Using the reaction scheme given by Eqn (2-1), and taking the order of reaction equal to 1, one may write the following first-order consecutive reactions for the atom formation [9]:

where k_1 and k_2 are first-order rate constants of atom formation and atom loss, respectively, N_w is the number of analyte atoms left unatomized, N_g is the number of analyte atoms in the gas phase, and N_{lost} is the number of analyte atoms that have been lost from the atomizer. To derive his well known equation Smets [10] has used the following general equation obtained from the above reaction scheme, which is in fact equivalent to Eqn (2-2) when n in the latter is equal to 1:

$$\frac{dN_g}{dt} = k_1 N_w - k_2 N_g \quad (2-21)$$

where $(k_1 N_w)$ and $(k_2 N_g)$ are the rate of atom formation, R_f , and the rate of disappearance, R_{dis} , respectively, in the Smets equation. Smets [10] has assumed that (a) the rate of atom formation during the entire duration of the evaporation process, for the strip heater, nearly equals the rate of atom disappearance; (b) atomization of the analyte is done in the gas-interrupt mode of operation; (c) atom loss is by diffusion only (no convection, expulsion, and re-deposition); and (d) the fraction of the total number of analyte atoms which will enter the analysis volume at a given time t defines the atomization efficiency, β , which is given by [10]

$$\beta = \frac{\int_0^t R_f dt}{N_g} \quad (2-22)$$

where $\int_0^t R_f dt$ is the actual number of analyte atoms that have entered the analysis

volume during the time interval $0 \rightarrow t$, and N_g is the total number of gaseous analyte atoms which are atomized at time t . Also

$$\beta = \frac{\int_0^{\infty} R_f dt}{N_0} \quad (2-23)$$

where N_0 is the total number of analyte atoms initially deposited in the graphite furnace [10]. Note that assumption (a) is in fact equivalent to saying that thermodynamic equilibrium (i.e., $dN_g/dt = 0$) between the atomic vapour and the condensed phase prevails at each instance of atom formation. Paveri Fontana et al. [49, 50] were the first to suggest that desorption of analyte from the surface of the graphite furnace could be considered a pseudo-equilibrium process, where the vapour flux desorbed from the surface is equal to that subsequently adsorbed. Based on the above assumptions (a-d), Smets has derived and used his equation to determine the E_a for atom formation. Guerrieri et al. [11] have derived another form of the Smets equation by introducing the condition of equilibrium during the entire duration of atom formation similar to a Langmuirian film between the solid-gas interface. However, with the assumption (a), Eqn (2-21) can be rewritten as follows:

$$k_1 N_w = k_2 N_g \quad (2-24)$$

At this stage one may address the following question: How can one account for the observed absorbance signal if equilibrium is established during each instance of atom formation? To answer this question one has to fall back on the expression of

the equilibrium constant K_p which may be written according to Eqn (2-24) as:

$$K_p = p_{N_g} \quad (2-25)$$

where p_{N_g} is the partial pressure of N_g and K_p is equal to k_1/k_2 . Realizing that, for an endothermic reaction, K_p increases with temperature [i.e., $K_p = \exp(-\Delta G^\circ/RT)$], the analyte atomic vapour will also increase with temperature causing the observed absorbance signal. Now, one proceeds with Eqn (2-24) as follows. Integrating both sides of Eqn (2-24) for the time interval, $0 \rightarrow t$, one gets the following equation [10]:

$$\int_0^t k_1 N_w dt = \langle k_2 \rangle \int_0^t N_g dt \quad (2-26)$$

where $\langle k_2 \rangle$ is the mean value of k_2 as expressed by [10, 37],

$$\langle k_2 \rangle = \frac{\int_0^t k_2 N_g dt}{\int_0^t N_g dt} \quad (2-27)$$

It has been assumed that the total number of analyte atoms atomized during the time period, $0 \rightarrow t$, is given by Eqn (2-28) [10],

$$N_g = \frac{\langle k_2 \rangle \int_0^t N_g dt}{\beta} \quad (2-28)$$

and that during the time period, $0 \rightarrow \infty$, is

$$N_0 = \frac{\langle k_2 \rangle \int_0^{\infty} N_g dt}{\beta} \quad (2-29)$$

where $\langle k_2 \rangle$ stands for the mean value of k_2 over the indicated time interval [10, 37],

$$\langle k_2 \rangle = \frac{\int_0^{\infty} k_2 N_g dt}{\int_0^{\infty} N_g dt} \quad (2-30)$$

Hence, upon substituting Eqns (2-28) and (2-29) into the general equation, $N_w = N_0 - N_g$, one gets

$$N_w = \frac{1}{\beta} \left(\langle k_2 \rangle \int_0^{\infty} N_g dt - \langle k_2 \rangle \int_0^t N_g dt \right) \quad (2-31)$$

Substituting Eqn (2-31) into Eqn (2-24) and rearranging terms, one gets

$$k_1 = k_2 \frac{N_g}{\frac{1}{\beta} \left(\langle k_2 \rangle \int_0^{\infty} N_g dt - \langle k_2 \rangle \int_0^t N_g dt \right)} \quad (2-32)$$

If, $k_2 = \langle k_2 \rangle = \langle k_2 \rangle$, then

$$k_1 = \beta \frac{A}{\int_t^{\infty} A \, dt} \quad (2-33)$$

which is the Smets equation derived under the conditions that the atomizer is operated in the gas-interrupt mode of atomization; note that β should be in the numerator instead of the denominator in Eqn (2-33). As mentioned earlier, β will have no effect on the determination of the E_a value if β remains constant.

2.2.5. An Arrhenius-type equation for the gas-interrupt mode of operation

Simplifying assumptions: The following approximations are used to simplify the mathematical treatment: (a) all unatomized analyte atoms are at the same temperature at the time of atomization; (b) atom formation and re-deposition of gaseous atoms on the graphite surface follow first-order kinetics; (c) the rate of release and the re-deposition of analyte atoms in the gas-interrupt mode of operation are equal [11]; (d) rate constants of both atom formation and re-deposition are approximated by the Arrhenius law; and (e) the atomization occurs under a constant, low heating rate.

With the above assumptions the following reaction scheme is proposed:

where N_w is the number of analyte atoms on the graphite surface at time t , and N_g is the number of gaseous analyte atoms, k_1 and k_{-1} are first-order rate constants for atom release from and re-deposition of atoms on the graphite surface, respectively; and N_{lost} is the number of analyte atoms lost from the analysis volume at time t ,

and k_2 is the first-order rate constant for analyte atom loss. In the gas-interrupt mode of operation it is assumed that the rate of transformation of the intermediate N_g to N_{lost} is much slower than the rate of formation of N_g and the rate of the reverse reaction (back to N_w). Hence, as a first approximation, k_2 may be ignored in the rate equation for N_g :

$$\frac{dN_g}{dt} = k_1 N_w - k_{-1} N_g \quad (2-35)$$

At equilibrium (assumption c) one can rewrite Eqn (2-35) as

$$0 = k_1 N_w - k_{-1} N_g$$

or,

$$\frac{k_1}{k_{-1}} = \frac{N_g}{N_w} \quad (2-36)$$

Under gas-interrupt mode of operation, it has been shown that N_g and N_w can be expressed by Eqn (2-31) and (2-28), respectively. Hence, upon substituting the latter two equations in Eqn (2-36), and taking into account the relationship between N_g and A (i.e., $N_g = A/Q$) one gets,

$$\frac{k_1}{k_{-1}} = \frac{\langle k_1 \rangle \int_0^t A \, dt}{> k_{-1} < \int_t^\infty A \, dt} \quad (2-37)$$

where $\langle k_{-1} \rangle$ and $\langle k_1 \rangle$ are the mean values of k_{-1} over the indicated time interval. Here it is assumed that $\langle k_{-1} \rangle = \langle k_1 \rangle$. Applying the Arrhenius law [Eqn (1-4)] to k_1 and k_{-1} in Eqn (2-37), and taking natural logarithm of both sides of the resulting equation one gets

$$\ln Y = - \frac{\Delta E_a}{RT} + y \quad (2-38)$$

where

$$Y = \frac{\int_0^t A \, dt}{\int_t^\infty A \, dt}$$

and

$$y = \ln \left(\frac{k_{1\infty}}{k_{-1\infty}} \right)$$

In Eqn (2-38), ΔE_a is the difference between the energy of activation for release of analyte atoms from the graphite surface and the energy of activation for redeposition of analyte atoms on the graphite surface and $k_{1\infty}$ and $k_{-1\infty}$ are pre-exponential factors in the Arrhenius law corresponding to the rate constants k_1 and k_{-1} , respectively. A plot of $\ln Y$ vs $1/T$ should be linear with a slope $-\Delta E_a/R$ and an intercept y .

2.2.6. *Steady-state approximation for atom formation*

The steady-state approximation has been applied to the study of mechanisms of atom formation in GFAAS to simplify the rate law expression. Sturgeon et al. [13] were the first to assume a steady-state approximation during atomization in a Massmann-type atomizer when the number density of the species no longer changes with time. Later on Chung [36] also assumed a steady-state approximation. However, nothing has been said about the experimental conditions that are required to justify a steady-state approximation, especially the inner purge gas flow rate. Since reactions in graphite furnaces are complex and the equation for the rates of change of analyte species becomes even more complicated, a steady-state approximation proves to be very useful. The question that may be asked, however, is when is this concept valid and under what conditions? Before answering the question it is useful to know what a kineticist [51] has said about it. For the purpose of illustration one takes the simplest consecutive reaction mechanism given by Eqn (2-20) as an example. The rate of change of the intermediate species, N_g , to a good approximation, can be set equal to zero "whenever the intermediate is formed slowly and disappears rapidly" [51]. Therefore, the first pre-requisite condition to justify the steady-state treatment is that the rate of atom removal must be made to be much faster than the rate of atom formation; in other words, $k_2 \gg k_1$. For the Massmann-type furnace, experimental conditions such as these can be achieved if the forced-convection mode of operation is used. The second condition is the existence of a transient species in the reaction mechanism; here, N_g is considered as an intermediate species. By operating the graphite furnace with a high inner purge gas flow rate of 625 ml/min, and assuming that, after a very short time relative to the duration of the atomization reaction, the intermediate species

N_g remains practically constant, so that to a good approximation $dN_g/dt = 0$. With such an approximation Eqn (2-36) can be immediately obtained. Next, N_g and N_w are related to the integrated absorbance using Eqn (2-3), yielding $\ln Y = -\Delta E_a/RT + y$ which is Eqn (2-38) mentioned above.

2.2.7. Activation energy by the "method of calculation"

As a by-product of the above mathematical formulation, the activation energy E_a , can be determined directly for any data point starting from the initial appearance of the absorbance signal to its maximum, using Eqn (2-14), and provided that atom formation follows first-order kinetics (see Chapter 5, for the determination of the order of reaction). This method allows one to cross-check the activation energy values that are obtained graphically from Arrhenius plots. Using Eqn (2-14), for a linear temperature program of the atomizer, the activation energy E_a can be expressed by the following equation (see Appendix D):

$$E_a = - \frac{A R T^2}{\alpha \int_t^{\infty} A dt \ln \left(\frac{\int_t^{\infty} A dt}{\int_0^{\infty} A dt} \right)} \quad (2-39)$$

The values of the parameters (except R which is the gas constant) on the right-hand side of Eqn (2-39) are experimentally measurable; hence, E_a can be obtained direct from the above equation.

2.3. EXPERIMENTAL

2.3.1. *Apparatus*

The Perkin–Elmer atomic absorption spectrophotometer, model 503, equipped with a D₂–arc background corrector and a Heated Graphite Atomizer (HGA), model 76B, was used. Pyrolytically–coated graphite tubes (The Perkin–Elmer part No. BOO91–504) were used. The details of the instrument and the experimental procedure have been given in Chapter 1.

2.3.2. *Standard solutions*

The stock solution of copper containing 1000 $\mu\text{g/ml}$ and the test solutions were prepared according to the procedure reported in Chapter 1.

2.3.3. *Argon gas*

Argon gas (99.995% pure) was used both as a sheath gas and a purge gas for the graphite furnace.

2.4. RESULTS AND DISCUSSION

To determine the E_a values by Eqns (2–7), (2–11), and (2–17), it is necessary that the graphite furnace is purged with Ar gas at a high flow rate of 625 ml/min. Hence, a relatively large amount of copper (200 ng) has been used to produce the absorbance signal under these experimental conditions. At the high flow rate of 625 ml/min of argon the convection velocity inside the atomizer is also high. The result is that the rate of atom removal is very rapid, and the rate of atom supply is slow; hence, the latter is considered to be the rate–determining step. This experimental

condition, regarding the use of forced convection has been reported to be reasonable by a number of authors [1, 14]; this is also supported by this work (see Chapter 1, for the details). For determination of E_a by Eqn (2-38) the graphite furnace is operated in the gas-interrupt mode. However, under these conditions, relatively small amount (5 ng) of copper is used to obtain the absorbance signal.

Figure (2-4) shows four Arrhenius plots, Curves a, b, c, and d prepared using Eqns (2-38), (2-17), (2-11), and (2-7), respectively. The four curves were drawn by normalizing data points of the above four equations for easy comparison. In Fig. (2-4), Curves a and b (of this work) are compared with those of Sturgeon et al. [13], Curve d, and Smets [10], Curve c. As can be seen from Fig. (2-4), Curves a and b give nearly longer linear range (from the beginning to the maximum of the absorbance signal profile) than Curves c and d. Obviously, the four curves bend towards the abscissa as they approach the absorbance maximum. Probably, this curvature may be attributed to the assumption used in developing these plots. In the theory the rate constant of atom formation k_1 is approximated by the Arrhenius law in which the pre-exponential factor k_∞ and the activation energy E_a are assumed temperature independent (i.e., do not change significantly with temperature at the very beginning of atom formation). This approximation is reasonable if the temperature range is relatively small.

If the logarithmic form of the Arrhenius law,

$$\ln k_1 = \ln k_\infty - E_a/RT$$

is examined term by term, it can be seen that it expresses much of what it has been learned about the rate of the atom release process. The above equation shows that

Fig. (2-4). Arrhenius-type plots from this work compared with those of Sturgeon et al. [13] and Smets [10]. The ordinate, $\ln X$, stands for: a: $\ln Y$ vs $1/T$, Eqn (2-38), b: $\ln y$ vs $1/T$, Eqn (2-17), c: $\ln (A / \int_t^{\infty} A \, dt)$ vs $1/T$, Eqn (2-11), d: $\ln A$ vs $1/T$, Eqn (2-7).

k_1 would increase if k_{∞} increases. In other words, the rate of atom formation increases as the pre-exponential factor k_{∞} increases.

The other term in the Arrhenius law, E_a/RT , gives a good deal of information about the factors that influence the rate of atom formation. For example, the value of this term depends on the value of E_a . The term usually has a positive value, because E_a for atom release is usually positive. Since this term is subtracted from $\ln k_{\infty}$ in the above equation, it can be seen that the value of k_1 decreases as the value of E_a increases. In other words, an increase in the value of E_a decreases the rate of the atom formation. Conversely, an increase in the temperature, T , which is in the denominator of the term E_a/RT in the logarithmic form of the Arrhenius law (i.e., $\ln k_1 = \ln k_{\infty} - E_a/RT$) reduces the value of E_a/RT and thus increases the value of k_1 . This is consistent with the experimental observation that the rate constant of atom formation increases with temperature.

From the above discussion one can conclude that the activation energy E_a may affect appreciably the linearity-range of the Arrhenius plot. If E_a increases with temperature the Arrhenius plot may bend towards the abscissa. However, the data points [near extreme right of Fig. (2-4)] taken at the beginning of the absorbance signal profile give linear curves for all of the four equations. Figure (2-5) shows the theoretical Arrhenius plots a, b, c, and d derived from Eqns (2-38), (2-17), (2-11) and (2-7), respectively. Good agreement between the theoretical and experimental curves is seen which again supports the validity of the model. However, deviation from the theory is observed as Arrhenius plots approach the absorbance maximum. This deviation between the theoretical and the experimental result may be explained by the atom formation reactions. At the very beginning of the absorbance signal profile atom formation is due to the release of analyte atom from the graphite

Fig. (2-5). Theoretical Arrhenius plots derived from the simulated absorbance signal profile for: a: $\ln Y$ vs $1/T$, Eqn (2-38), b: $\ln y$ vs $1/T$, Eqn (2-17), c: $\ln (A / \int_t^{\infty} A dt)$ vs $1/T$, Eqn (2-11), d: $\ln A$ vs $1/T$, Eqn (2-7). The data used in the calculation are summarized in Table (1-1) of Chapter 1.

surface top layer. As atomization proceeds, these atoms are depleted and release of other analyte atoms that are trapped in between graphite layers becomes effective. The atom release process continues until the last analyte species is atomized. Certainly, these later analyte atoms require high energy in order to reach and leave the graphite surface for the gas phase. This process will change the reaction mechanism and will result in significant curvature in the Arrhenius plots. Other reasons have been discussed in Chapter 1.

In Fig. (2-4), the plot of $\ln A$ vs $1/T$, Curve d, was drawn using data points from the very beginning of the absorbance signal profile to its maximum. In order to test the reproducibility three replicate determinations of the activation energy were made from Fig. (2-4) using the first few data points taken from the very beginning of the absorbance signal profile. The choice of these data points was based on the assumption that this plot (i.e., $\ln A$ vs $1/T$, Curve d) was valid only for the data points near the very beginning of the absorbance signal profile, as explained in the Theory [Eqn (2-7)]. Table (2-1) (second horizontal row from bottom) summarizes the E_a values for the three replicate determinations using the $\ln A$ vs $1/T$ plot, Curve d.

The activation energy values determined from the plot of $\ln(A / \int_t^\infty A dt)$ vs $1/T$, [Fig. (2-4)] Curve c, using data points taken from the very beginning of the absorbance signal profile are also shown in Table (2-1) (third horizontal row from top) for the three replicate determinations. It should be noted here that in Fig. (2-4), both methods i.e., $\ln A$ vs $1/T$ and $\ln(A / \int_t^\infty A dt)$ vs $1/T$ plots, Curves d and c, respectively, have been developed using the same mathematical treatment except for the order of reaction. In spite of the different assumptions for the order of reaction good agreement between the two plots is observed at the onset of the

Table (2-1). Activation energy values for atomization of copper obtained from different Arrhenius plots.

Equation used for Arrhenius plot	Fig. (2-4), curve	E _a , kJ/mol		
		Test Number		
		1	2	3
Eqn (2-38)	a	348 ^a , 274 ^b	339 ^a , 269 ^b	346 ^a , 286 ^b
Eqn (2-17)	b	346 ^a , 238 ^b	342 ^a , 224 ^b	339 ^a , 229 ^b
Eqn (2-11)	c	344 ^a	338 ^a	340 ^a
Eqn (2-7)	d	348 ^a	326 ^a	346 ^a
Ref. 36	—	329 ^a	316 ^a	323 ^a

^aCalculated using the data points from the initial segment, i.e. near the appearance temperature of the absorbance signal profile.

^bCalculated using the data points from the top segment of the absorbance signal profile, i.e.

long after the appearance temperature of the absorbance signal profile.

Arrhenius-type plot [see Curves c and d, Fig. (2-4)]. The activation energy values obtained by the above two methods lead to the following conclusion on the order of reaction for the atomization of copper. Since both plots give closely agreeing values for E_a , and since the order of reaction for one plot is assumed to be one, the order of reaction for the other plot must also be one. Further details regarding determination of the order of reaction at the absorbance maximum will be discussed in Chapter 5. Hence, one may conclude that the order of reaction has no effect on the determination of activation energy for atomization of copper by the above two equations under these experimental conditions, provided that the data points are taken from the very beginning of the absorbance signal profile. It should be noted that one of the serious limitations of using the $\ln A$ vs $1/T$ plots [Curve d, Fig. (2-4)] to obtain activation energy is that the condition that the integral $\int_0^t k_1 dt \rightarrow 0$ in Eqns (2-5) and (2-6) is fulfilled only by the data points near the very beginning of the absorbance signal profile where the value of the integral is extremely small and can be taken as equal to zero. Activation energy plots drawn using the data points corresponding to longer times do not fulfil the above condition, and hence, such plots bend towards the abscissa soon after the initial data points (the very beginning) of the absorbance signal profile. However, the method based on the $\ln A$ vs $1/T$ plot can be used to identify activation energy for an atomization reaction of any order of reaction provided that the data are taken near the very beginning of the absorbance signal profile. The method is also useful when the order of reaction for the atomization reaction is not known.

The activation energy values obtained from the three replicate determinations using a plot of $\ln y$ vs $1/T$, Curve b, Fig. (2-4), are also given in Table (2-1) (second horizontal row from top). The increase in the range of data points for linear

plots for activation energy obtained by using $\ln y$ vs $1/T$ (Curve b) results from using integrated absorbance in the method. The reliability of activation energy values obtained from Curve b can be tested using the proposed "method of calculation" by Eqn (2-39). The activation energy values from the two methods [Eqns (2-17) and (2-39)] should be comparable. Table (2-2) shows the reproducibility of activation energy values obtained from Eqn (2-39) of three replicate determinations; these values may be compared with those obtained graphically using Eqn (2-17), given in Table (2-1). The following conclusions can be drawn from Tables (2-1) and (2-2): the data points from the very beginning of the absorbance signal profile to the absorbance maximum used in the Arrhenius plots give activation energy values (superscripted *a*) in agreement with those obtained graphically; the results with superscript *b* (obtained from the data points from the high-temperature parts of the Arrhenius plots) agree among themselves. These results show the usefulness of Eqn (2-39) for obtaining activation energy using any data points from the beginning of the absorbance signal profile to its absorbance maximum without recourse to the Arrhenius plot.

The plot of $\ln Y$ vs $1/T$, Curve a, Fig. (2-4), shows a longer range of data points than those by the other Arrhenius plots. This improvement is probably the result of taking atom re-deposition into account. Analyte atoms initially generated from the sample are re-deposited onto the graphite surface, and are subsequently released at higher temperatures, as reported by Black et al. [31]. This may cause a curvature in the Arrhenius plot if the atom re-deposition is not taken into account. For the data points taken from the beginning of the absorbance signal profile, the above plot agrees very well with the other Arrhenius plots shown in Fig. (2-4). This agreement may be attributed to insignificant re-adsorption of copper, and

Table (2-2). Activation energy values for atomization of copper obtained using Eqn (2-39).

E _a , kJ/mol			Location of the data points on	
Test Number			Average	the absorbance signal profile
1	2	3	E _a , kJ/mol	used for calculation of E _a
355	325	344	341	At or immediately after the appearance temperature, i. e. at "low" temperatures.
349	343	325	339	
328	355	338	340	
337	343	343	341	
338	311	343	336	
304	284	321	303	At the "transition region" temperature, i.e. between the "low" and the "high" temperature.
271	254	296	274	At longer times after the appearance temperature i.e. when temperature is "high". The temperature increases as one descends the columns of Table (2-2).
242	230	268	247	
217	210	220	216	

hence, insignificant desorption of copper atoms near the appearance temperature. Table (2-1), first horizontal row from top shows that closely-agreeing values of activation energy are obtained from the data points taken at longer times, i.e. some time after the appearance of the absorbance signal profile.

Figure (2-6) shows a comparison between the plot of $\ln Y$ vs $1/T$ prepared using the data points taken from an absorbance signal profile recorded in the gas-flow mode of operation (Curve a), and that using the data points measured in the gas-interrupt mode (Curve b). As can be seen from Fig. (2-6) further improvement in extending the linear range of the Arrhenius plot is obtained when the atomic vapour is expelled by forced convection. Table (2-3) summarizes the activation energy values determined from the plot of $\ln Y$ vs $1/T$ under the two modes of operation; at the very beginning of the absorbance signal, these values are in good agreement with one another. The temperature range for the gas-flow mode of operation is better than that of the gas-interrupt mode of operation. One reason for this improvement in the linear range of the Arrhenius plot is that the steady-state approximation used in the formulation of the Arrhenius-type equation is a better approximation under forced convection than under the gas-interrupt mode of operation in which the inner purge gas is completely stopped. This lends support to the validity of the model. It should be pointed out that one of the serious causes for the bending of the Arrhenius plots are the assumptions which are used in developing the Arrhenius-type equation concerned. Limitations of these assumptions have recently been discussed in the literature [37]. For illustration, a plot of $\ln [A / (A_{\infty} - A)]$ vs $1/T$ is drawn and shown in Fig. (2-7). This kind of Arrhenius plot was used by Chung [36] for elucidating atomization mechanisms in GFAAS. Figure (2-7) shows that the slope increases asymptotically for the data

Fig. (2-6). Arrhenius plots prepared using the data points taken from two absorbance signal profiles, one recorded in gas-flow mode of operation (Ar gas flow-rate 625 ml/min) and the other in the gas-interrupt mode of operation, according to Eqn (2-38). a: gas flow; b: gas interrupt.

Table (2-3). Activation energy values for atomization of copper determined from the Arrhenius plot prepared under the gas-flow and the gas-interrupt mode of operation.

Gas-interrupt mode			Gas-flow mode		
E_a	T-range	Equation	E_a	T-range	Equation
kJ/mol	K		kJ/mol	K	
337	1300-1420	2-33	339	1300-1480	2-11
332	1310-1420	2-33	329	1300-1470	2-11
340	1300-1430	2-33	345	1300-1480	2-11
336	1300-1550	2-38	240	1300-1770	2-38
327	1310-1560	2-38	338	1310-1780	2-38
331	1300-1540	2-38	332	1300-1760	2-38

Fig. (2-7). A plot of $\ln [A / (A_m - A)]$ vs $1/T$ used by Chung [36].

points taken after the initial few data points of the absorbance signal profile, making kinetic information on the absorbance signal profile after the initial few data points questionable. Several researchers [10, 11, 13, 39] have reported that the Arrhenius plots bend towards the abscissa as the plots approach the absorbance maxima. However, the activation energy values obtained by using the data points near the very beginning of the absorbance signal profile is satisfactory and can be used to elucidate atomization mechanisms, which are valid for atomization reactions occurring near the beginning of an absorbance signal profile [Table (2-1)].

To generate experimental data points that will verify the validity of applying the Smets equation under both modes of operation, copper was atomized, once each, under the gas-flow and the gas-interrupt mode of operation, and the absorbance signal profiles were obtained. Arrhenius plots were drawn for each mode of operation using Eqns (2-11) and (2-33). The result is shown in Fig. (2-8), which clearly indicates that Arrhenius plots obtained using the two forms of the Smets equation give similar results for the value of the activation energy regardless to the mode of operation used, provided that measurements are taken at the very beginning of the absorbance signal profile. However, the two curves diverge as they approach the absorbance maximum (high temperature). A long linear range of the Arrhenius plot (Curve a) is obtained when the Smets equation is applied in the gas-flow mode of operation, and a short linear range is obtained when the plot is drawn using the gas-interrupt mode of operation (Curve b). As can be seen from Fig. (2-8), the Arrhenius plot prepared in the gas-interrupt mode of operation bends significantly towards the abscissa suggesting that if the Smets equation is to be used for determination of the activation energy from Arrhenius plots, the graphite furnace should be operated in the gas-flow mode of operation. The

Fig. (2-8). Arrhenius-plots prepared under gas-flow and gas-interrupt mode of operation; a: gas flow [Eqn (2-11)], b: gas interrupt [Eqn (2-33)]. $\ln S$ stands for $\ln (A / \int_t^\infty A dt)$.

difference in the curvature can be accounted for in terms of the convection velocity of the purge gas through the graphite tube furnace as follows. At the gas-interrupt mode of operation the purge gas flow is interrupted during the atomization step; the released analyte atoms diffuse into the atomizer volume freely. Such experimental conditions give more chance for the analyte atoms to "stick" to the graphite tube surface and be subsequently desorbed at high temperatures than in the gas-flow mode of operation. The result is that incomplete separation between the rate of atom formation and the rate of atom removal is obtained, which ultimately affects the linearity of the Arrhenius plot. In contrast to the gas-interrupt mode, the atomic vapour in the gas-flow mode of operation is expelled by forced convection, the high purge gas flow rate of 625 ml/min rapidly drives out the analyte atoms from the graphite surface, giving little chance for them to re-deposit on the graphite surface. Under these conditions, the possibility of getting incomplete separation of the rate of atom formation from the rate of atom removal may be ruled out. It is of interest to mention that one of the reasons for the different activation energy values reported for the same element by different researchers is the failure to achieve experimental conditions required to make the rate of atom loss much faster than the rate of atom formation [21]. Thus, one can conclude that it is possible to use the Smets equation in the gas-interrupt mode of operation to determine the activation energy of the rate-determining step of atom formation, provided that measurements are taken at the appearance of the absorbance signal profile, the atomization efficiency, β , has no effect on the slope ($-E_a/R$) of the Arrhenius plot. For a long linear range of the Arrhenius plot, the graphite furnace should be operated in the gas-flow mode.

2

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

2.4.1. *Mechanisms of copper atomization*

From the published reports [10, 13, 31, 36, 39, 44] on the activation energy of copper in GFAAS, it is clear that the reported activation energy values are widely different and the reason for this difference still remains unclear. The difference in the reported values of E_a for copper atomization is in many cases due to curvatures in the Arrhenius plots used by the researchers to obtain E_a values. Arthur and Cho [44] obtained an E_a value of 265 kJ/mol under vacuum conditions; Smets [10] 310 kJ/mol; Sturgeon et al. [10] 322 kJ/mol and 184 kJ/mol (for two atomization under two different experimental conditions, which resulted in two different atomization mechanisms) and Chung [36] 338 kJ/mol and 202 kJ/mol (for two different atomization mechanisms)—all under normal operating conditions. Using the Monte Carlo simulation technique Black et al. [31] reported 126 kJ/mol for a first-order release process for copper from a submonolayer coverage on the graphite tube surface.

The above E_a values range from the low value of 126 kJ/mol obtained from the Monte Carlo simulation technique to 202 kJ/mol obtained from a higher-temperature region to a still higher value, 338 kJ/mol, obtained from a lower-temperature region of Arrhenius plots. The highest value of E_a (338 kJ/mol) correlates with the heat of copper sublimation, $\Delta H_s = 338$ kJ/mol, whereas the lower values of E_a have been accounted for differently by different workers [10, 13, 31, 36, 44].

In this work, it has been attempted to eliminate some of the factors that cause curvatures in Arrhenius-type plots by deriving Arrhenius-type equations that are capable of using a longer range of temperatures for linear activation energy plots. Also, a method has been given which enables E_a value to be determined using any

data points from the beginning of the absorbance signal profile to its absorbance maximum; this also enables one to cross-check the E_a value obtained graphically.

The E_a values in Tables (2-1) and (2-2) obtained by using the data points corresponding to the appearance time (temperature) of the absorbance signal and some later times can be used to elucidate the mechanism of copper atomization reaction as follows. Copper nitrate (taken as an aqueous solution), on being heated in the graphite furnace, is reduced to free copper metal atoms [15, 31, 36, 44]. The energy required to release copper atoms from the graphite tube surface is not known for certain. Some authors [13] have assumed that this energy is the heat of vaporization of the pure copper metal, which can be equated with the energy of desorption of copper from the graphite tube surface. However, the energy of desorption of an analyte metal from rough surfaces, such as, graphite surfaces may have different values because the analyte atoms may be trapped inside the graphite surface at different depths and in tortuous channels, resulting in a multitude of different energies being required to release them. Even though the pyrolytically-coated graphite tube possesses a smooth surface on a macroscopic scale, the surface is rough on a microscopic scale, and it is reasonable to conclude that the energies required to release copper atoms from such a rough surface will have different values depending on the energy barrier encountered by the copper atoms to diffuse to the surface and to be released from it. If the surface is molecularly flat and there is no significant interaction between the copper atoms and the surface, the activation energy for release of copper atoms from that surface should have a single value.

2.4.2. Interpretation of activation energy values

Tables (2-1) and (2-2) show that the E_a values obtained in this work can be subdivided into two classes depending on the time (i.e., the temperature) at which the data for calculating the E_a values were collected from the absorbance signal profile. Regardless of the method for determining the activation energy, the activation energy values corresponding to the data points at or immediately after the appearance temperature of copper, i.e. at "low" temperatures, are consistently high and those corresponding to the data points at longer times after the appearance temperature, i.e. at "high" temperatures, are consistently low. There is also a set of E_a values in Table (2-2) that are shown as corresponding to the data points which are in between the "low" and the "high" temperature region (the so-called "transition region").

As can be seen from Table (2-2), the low-temperature value of the experimental activation energy [the median value calculated from Table (2-2) is 338 kJ/mol] correlates very well with the sublimation enthalpy of pure copper metal and also with the dissociation energy of $\text{CuO}_{(g)}$ [see Table (2-4)], whereas the high-temperature E_a values are quite different from any values in Table (2-4). In order to consider the possibility of the reaction, $\text{CuO}_{(g)} \rightarrow \text{Cu}_{(g)} + \text{O}$, as a pathway for $\text{Cu}_{(g)}$, one has to know the energy required to sublime $\text{CuO}_{(s)} \rightarrow \text{CuO}_{(g)}$ and thermal stability of $\text{CuO}_{(g)}$ at elevated temperatures (further discussion is given in Chapter 4). The high-temperature decrease in the experimental activation energy values may be attributed to the desorption of copper from the graphite tube surface which was initially clean. Copper has been reported [10, 30] to undergo short-range adsorption-desorption with increasing time (temperature) of atomization, which is particularly important in the long (28 mm), pyrolytically-coated graphite tubes

Table (2-4). Correlation of ΔH_{273}° (kJ/mol) for sublimation of copper, carbon reduction of copper oxide, and dissociation of copper oxide with the experimental activation energy, E_a , obtained from an Arrhenius plot [see Table (2-3)].

Reaction	ΔH_{273}° (kJ/mol) [10]
$\text{Cu}_{(s)} \rightarrow \text{Cu}_{(g)}$	338
$\text{CuO}_{(s)} + \text{C}_{(s)} \rightarrow \text{Cu}_{(s)} + \text{CO}_{(g)}$	46
$\text{CuO}_{(s)} + \text{C}_{(s)} \rightarrow \text{Cu}_{(g)} + \text{CO}_{(g)}$	389
$\text{CuO}_{(s)} \rightarrow \text{Cu}_{(g)} + \text{O}_{(g)}$	402
$\text{CuO}_{(g)} \rightarrow \text{Cu}_{(g)} + \text{O}_{(g)}$	343

used in this work. It should be noted that the low-temperature E_a values have been obtained using the data points near to the appearance time (i. e. appearance temperature) of copper when the loss of $\text{Cu}_{(g)}$ is assumed to be almost nil, whereas the high-temperature E_a values have been obtained using the data points corresponding to much longer times when the loss of $\text{Cu}_{(g)}$ by condensation onto the graphite tube surface is substantial. The E_a values shown in Table (2-2), which have been obtained using the data points from the "transition region", reflect the increasing contribution of the adsorbed Cu atoms to the $\text{Cu}_{(g)}$ as the atomization time (i. e. temperature) increases. As Holcombe [38, 39] has rightly pointed out there should be no single value for activation energy except within strictly defined limits.

SUMMARY

Activation energy plots for atomization reactions in graphite furnace atomic absorption spectrometry (GFAAS) drawn using various Arrhenius-type equations reported by other workers do not give reliable kinetic information on the atomization mechanism of elements beyond a few data points located near the very beginning of the absorbance signal profile. These plots are non-linear if they are drawn using data points near the maximum of the absorbance signal profile. This chapter presents two Arrhenius-type equations which give linear plots, and hence, reliable values for activation energy. Also, a simple method for calculating activation energy, E_a , using the data points anywhere from the initial appearance of the absorbance signal to the maximum of the absorbance signal profile is proposed. Activation energy values given by these two equations and by the method of calculation are compared with each other and with those given by the commonly used methods. The activation energy values obtained by the method of calculation can be used to verify those obtained experimentally from Arrhenius plots. The three proposed methods give linear activation energy plots over long range of data points of the signal profiles, and also provide reliable kinetic information on atom formation reactions in GFAAS. A mechanism for atomization of copper, based on the experimentally determined activation energy and the order of reaction is proposed.

Chapter 3

3.1. MECHANISM OF COBALT ATOMIZATION FROM DIFFERENT ATOMIZER SURFACES IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Mechanisms of atomization in graphite furnace atomic absorption spectrometry (GFAAS) have been studied by several authors using different theoretical models: the kinetic model [10, 17], the thermodynamic model [52–54], and the combined kinetic–thermodynamic model [13]. Investigation of the atomization mechanism requires both kinetics and thermodynamics to be taken into account [55, 56]. Atomization reactions occurring in graphite furnaces are generally complex and an insight to what is going on during atomization is almost impossible without consideration of kinetics and thermodynamics. In the thermodynamic approach it is very often postulated that atom formation is by the dissociation of metal oxides, and other molecular species, or by reduction of metal oxides. However, the predictions of thermodynamic models are sometimes different from experimental results. The kinetic approach seems to be better in predicting the order of reaction and the energy of activation. However, even though the kinetic approach is more useful in elucidating atomization mechanisms, it is sometimes difficult or impossible to interpret kinetic data unambiguously in terms of reaction mechanisms.

A common and easy method to elucidate a mechanism of atom formation reaction is to apply the Arrhenius law to the kinetic data. The Arrhenius law has been proven to be very useful for mechanism of atomization in GFAAS if the rate of atom formation is experimentally isolated from the rate of atom removal. By

plotting a graph of $\ln k_1$ vs $1/T$, a linear relationship, for a single process, should be obtained with a slope of the line equal to $-E_a/R$. Since the value of E_a represents the energy required in the rate-determining step to produce metal atoms in the gas phase, its value may be correlated to one of the thermochemical properties of the metal and its species that can exist under the experimental conditions prevailing during atomization [13, 56].

Earlier investigations [52] of mechanisms of atom formation in GFAAS showed the importance of the reduction of the metal oxide, MO, according to the following equation:

This simple equation for atom formation was considered to explain the observed activation energy and the appearance temperature in the graphite furnace for many elements including cobalt. Sturgeon et al. [13] found an activation energy of 406 kJ/mol for the atomization of cobalt (as the nitrate) and an appearance temperature of 1430 K for cobalt atom formation, and concluded that $\text{Co}(\text{NO}_3)_2$ was first converted into $\text{CoO}_{(s)}$, which was then reduced to $\text{Co}_{(s)}$, followed by sublimation of $\text{Co}_{(s)}$ to $\text{Co}_{(g)}$. Ham et al. [57] investigated the atomization of Co in a pyrolytically coated electrographite tube furnace operating in a vacuum with a rapid-scan mass spectrometric detection system, and by thermochemical calculation of the equilibrium in the furnace during atomization. Their calculation showed that the atomization reaction was $\text{Co}_{(s)} \rightarrow \text{Co}_{(g)}$ for both cobalt nitrate and cobalt chloride at the appearance temperature for cobalt. However, Grimley et al. [58] reported the dissociation energy of $\text{CoO}_{(g)}$ as 361 kJ/mol from mass spectrometry

of $\text{Co}_{(g)}$ and $\text{CoO}_{(g)}$ derived from $\text{CoO}_{(s)}$ in a Knudsen cell between 1578 and 1744 K. Thermochemical calculations by Ham et al. [57] demonstrated that if greater than 5×10^{-11} mole of cobalt was used as the sample, $\text{Co}_{(l)}$ would replace $\text{Co}_{(s)}$ at equilibrium above 1880 K, which would result in a heat of atomization of 309 kJ/mol for cobalt, as estimated by using Trouton's rule. Such conflicting reports have left the mechanism of cobalt atomization still unresolved and show a need for further investigation of the mechanism of cobalt atomization in GFAAS. Furthermore, mechanisms of cobalt atomization from different atomization surfaces in GFAAS need to be investigated.

One objective of this work has been to investigate the mechanisms of cobalt atomization from three different atomizers: pyrolytically coated electrographite, uncoated electrographite, and glassy carbon. The other objective has been to investigate how the linearity of Arrhenius plots is affected by different values for the constant m in Eqn (3-6).

3.2. THEORY

Paveri-Fontana et al. [3] and van den Broek et al. [1] have provided an analytical expression for the number of atoms present in the analysis volume at any instant t as a convolution integral of the following form, as mentioned in Chapter 1, Eqn (1-1):

$$N_g = \int_0^t S(t') \mathcal{R}(t-t') dt'$$

where $S(t)$ is the rate of atom formation, $\mathcal{R}(t)$ is a function that depends on atom removal and t' is a variable of integration. $S(t)$ is given by [14]:

$$S(t) = N_0 k_{\infty} \exp \left(-\frac{E_a}{RT} \right) \exp \left(-\int_0^t k_{\infty} \exp \left[-\frac{E_a}{RT} \right] dt \right)$$

where N_0 is the number of analyte atoms initially present, k_{∞} is the pre-exponential factor, E_a is the activation energy; R is the gas constant and T is the absolute temperature. The rate of atom removal, $R(t)$, is given by [1, 10]:

$$R(t) = k_2 N_g$$

where k_2 is the temperature-dependent, first-order rate constant for the combined rate of atom removal, i. e., by diffusion, expansion and convection; readsorption onto the atomizer surface is not considered. If it is assumed that the rate of atom removal is much faster than the rate of atom formation, another form of Smets equation [10] can be obtained from the rate of atom formation $S(t)$ as follows. Assuming that the first-order rate constant k_1 for the rate of atom formation is approximated by the Arrhenius law

$$k_1 = k_{\infty} \exp \left(-\frac{E_a}{RT} \right)$$

and that the amount of analyte $\int_t^{\infty} S(t) dt$, left unatomized at time t is, expressed as follows [14]:

$$\int_t^{\infty} S(t) dt = N_0 \exp \left(-\int_0^t k_{\infty} \exp \left[-\frac{E_a}{RT} \right] dt \right) \quad (3-2)$$

one gets,

$$k_1 = \frac{S(t)}{\int_t^{\infty} S(t) dt} = \frac{A}{\int_t^{\infty} A dt} \quad (3-3)$$

where A and $\int_t^{\infty} A dt$ are the absorbance and the integrated absorbance, respectively, at time t . Equation (3-3) is valid provided that the rate constant for atom removal, k_2 , is larger than the rate constant for atom formation, k_1 . This condition can be fulfilled in a graphite furnace by using forced convection of an inert purge gas during atomization [1, 14]. This point will be discussed again in the Results and Discussion section.

Using transition-state theory, Sturgeon et al. [13] formulated the following expression for the rate constant of atom formation, k_1 , and the change in free energy of activation, $\Delta G^{o\#}$:

$$k_1 = a T \exp \left(-\frac{\Delta G^{o\#}}{RT} \right) \quad (3-4)$$

where a is a constant; $\Delta G^{o\#} = \Delta H^{o\#} - T \Delta S^{o\#}$; $\Delta H^{o\#}$ and $\Delta S^{o\#}$ are the enthalpy and entropy of activation, respectively. Also, according to transition-state theory, the rate constant of atom formation, k_1 , may be formulated using statistical mechanics to yield the following expression:

$$k_1 = b T^{\frac{1}{2}} \exp \left(-\frac{E_o}{RT} \right) \quad (3-5)$$

where b and m are constants; the value of m may be deduced from partition functions which enter in the rate law expression, E_0 is the molar energy change at the absolute zero of temperature, and is assumed to be equal to the activation energy E_a in the Arrhenius law.

Rearranging terms and taking the natural logarithm of both sides of Eqn (3-5) one gets

$$\ln k = - \frac{E_a}{RT} + \ln b \quad (3-6)$$

where

$$k = \frac{k_1}{T^m}$$

Equation (3-6) shows that a plot of $\ln k$ vs $1/T$ should be linear with a slope = $-E_a/R$ and an intercept = $\ln b$.

The shape of the absorbance signal profile and the slope of the Arrhenius plot depend appreciably on the physico-chemical properties of the graphite surface interacting with the analyte [33], as well as thermochemical properties of the analyte element and the chemical species the analyte element forms during the release process, as mentioned earlier in previous chapters. Thus, it would be valuable in proposing a mechanism for atomization if accurate, quantitative information characterizing the activation energy for the release of analyte atoms is obtained. The modified form of the Smets equation, depicted by Eqn (3-6), will be used to determine the energy of activation from the initial rising edge of the

absorbance signal profile. The justification for using the above equation [i.e., Eqn (3-6)] is given as follows. The procedure of determining the activation energy from the Arrhenius plot requires that the pre-exponential factor in the Arrhenius law remain constant during atomization. However, this is not always the case as the pre-exponential factor may contain a variable, temperature-dependent parameter, which will result in a curvature in the Arrhenius plot [13, 59]. The currently used common procedure in obtaining kinetic information is to use the Arrhenius law when valid. However, if plots of $\ln k_1$ vs $1/T$ are not linear, plots of $\ln (k_1/T^m)$ vs $1/T$ can be used. There is a good theoretical basis for the latter, arising from the temperature dependence of partition functions which enter into the rate law expressions of atomization reactions. In some cases, the theory leads to a value of the exponent, m . When this is so, the applicability of the $\ln (k_1/T^m)$ vs $1/T$ plots can be tested [59].

3.3. EXPERIMENTAL

3.3.1. Apparatus

An atomic absorption spectrophotometer, the Perkin-Elmer model 503, equipped with a D_2 -arc background corrector and a Heated Graphite Atomizer (HGA), model 76B, was used. Details of the atomic absorption spectrophotometer have been given in previous chapters. A cobalt hollow-cathode lamp (Perkin-Elmer) was used and operated at a lamp current of 10 mA. The 240.7 nm line of cobalt was used as the analysis line together with a spectral band-pass of 0.7 nm.

The temperature of the inner graphite tube surface just below the sample injection hole was determined with an automatic optical pyrometer, model 1100

(Ircon Inc., Niles, Il., USA) from the measured voltage—the temperature was read off the calibration curve supplied by the manufacturer.

3.3.2. *Atomizer tubes*

Three different atomizer tubes were used: pyrolytically coated electrographite tubes (The Perkin–Elmer Corporation, part No. BOO91–504), uncoated electrographite tubes (The Perkin–Elmer Corporation, part No. 0290–1820), and glassy carbon tubes (Sigri Ringsdorff Werke, GmbH, West Germany). All these tubes had the same dimensions: length 28 mm, outside diameter 8 mm, and inside diameter 6 mm.

3.3.3. *Reagents*

A stock solution of 1000 $\mu\text{g}/\text{ml}$ cobalt was prepared by dissolving pure cobalt metal in pure nitric acid (ULTREX) and diluting the solution with ultrapure water obtained direct from a Milli–Q2 water purification system (Millipore Corporation). The test solutions were prepared immediately prior to their use by serial dilution of the stock solution with ultrapure water.

3.3.4. *Procedure*

10 μl aliquots of the cobalt solution (0.02 $\mu\text{g}/\text{ml}$) were used for determining the decomposition and atomization curves. The cobalt sample was atomized using a pyrolytically coated electrographite tube and the graphite furnace in the gas–interrupt mode of operation.

For determination of the activation energy for cobalt atomization from different atomizer surfaces the furnace was operated in the gas–flow mode, using an Ar gas

flow rate of 625 ml/min to ensure isolation of the source function [1] during the atomization stage. Samples were typically dried at 390 K with 20 seconds hold time and charred at 1070 K with 15 seconds hold time. Atomization temperature was set at 2700 K for the three atomizers. 10 μ l aliquots of the cobalt solution (0.02 μ g/ml) were deposited manually into the graphite furnace and atomized using the above heating program.

3.4. RESULTS AND DISCUSSION

3.4.1. *The decomposition and atomization curves*

Figure (3-1) shows the decomposition and atomization curves for cobalt (taken as the nitrate in aqueous solution) atomized in a pyrolytically coated electrographite tube. The decomposition curve is defined as the one obtained by atomizing the sample using a constant (optimum) atomization temperature as a function of the charring temperature. The atomization curve is defined as the one obtained by atomizing the sample using a constant (optimum) charring temperature as a function of the atomization temperature. Each datum point represents the arithmetic mean of three values which have been corrected for blanks. In Fig. (3-1), the left-hand side curve (Curve a) is the decomposition curve and the right-hand side curve (Curve b) is the atomization curve. For the decomposition curve, the sample was dried at 420 K and charred at various temperatures from 670 K to 2770 K. The atomization temperature was kept constant at the pre-determined optimum temperature of 2700 K. For the atomization curve, the charring temperature was kept constant at the pre-determined optimum charring temperature of 1070 K and the atomization temperature was varied from 1070 K to 3170 K. The graphite tube was cleaned after each run by firing at 3170 K. The

Fig. (3-1). Decomposition – atomization curves for 0.20 ng Co [taken as the nitrate in aqueous solution of 1% (v/v) HNO_3] by atomization from a pyrolytically coated electrographite tube. a: decomposition curve; b: atomization curve.

data for the decomposition curve show that the maximum charring temperature that can be used without a noticeable loss of cobalt is ~ 1100 K. The appearance temperature (defined as the temperature at which the analyte signal is just visible above the baseline) and the optimum atomization temperature (defined as the lowest temperature giving the maximum peak-height absorbance) are ~ 1400 K and ~ 2700 K, respectively. The decomposition curve (the left curve) can be interpreted as follows. As the charring temperature is increased, the cobalt nitrate is decomposed at about 970 K [not shown in Fig. (3-1)] to form $\text{CoO}_{(g)}$ [60], which is expelled from the graphite furnace. A noticeable loss of Co atoms occurs at a charring temperature about 1100 K. In Fig. (3-1), since there is no significant difference between the temperature in the decomposition curve at which the absorbance starts to decrease and the appearance temperature in the atomization curve it is reasonable to conclude that the decrease in the absorbance is due to loss of $\text{Co}_{(g)}$ as a consequence of the charring of the $\text{Co}(\text{NO}_3)_2$ at a temperature >1100 K in the pyrolytically coated electrographite tube. Any mechanism for the atomization of $\text{Co}(\text{NO}_3)_2$ must be consistent with these observations in order to be acceptable as satisfactory.

3.4.2. *The supply and removal functions*

Figure (3-2) shows a plot of the peak-height absorbance and the peak area (A.s) versus the internal inner purge gas flow rate for a constant amount (0.20 ng) of cobalt. The two signals decrease exponentially as the internal purge gas flow rate increases up to about 625 ml/min; after that the two curves become almost parallel to the abscissa. The constancy of the absorbance signals at high flow rates may be explained as follows. The high convection velocity of the internal purge gas sweeps

Fig. (3-2). Plots of the peak-height absorbance and peak area (A.s) vs the internal inner purge gas flow rate for a constant amount (0.20 ng) of cobalt. a: peak height, and b: peak area.

away quickly the atomic vapour from the analysis volume, preventing it from redepositing onto the surface of the graphite tube. The result is that the residence time decreases greatly, making the rate of the atom removal much faster than the rate of the atom formation. Such experimental conditions as above separate the two rates [1], thus validates the assumption made to develop the model.

3.4.2. *Rate constants for the supply and the removal function*

The time-dependence of the supply of analyte atoms into and their removal from the analysis volume has been reported in the literature. Fuller [17] has proposed a model consisting of a mathematical expression with two exponential terms to describe the release and removal of copper in The Perkin-Elmer graphite furnace, model HGA-70. He concluded from his study that the rate of atom removal exceeds the rate of atom formation by a factor of 3-20, depending on the atomization temperature. More rigorous studies of supply and removal of analyte atoms during the atomization were published later [1, 3-5, 13].

In order to verify that the value of the rate constant, k_1 , for atom formation is less than the value of the rate constant for atom removal, k_2 , [17] the k_1 and k_2 (which are proportional to the corresponding rates at specific temperature) will be calculated at each datum point and present the results graphically to show the difference between the two rate constants. It is assumed that k_1 is approximated by the Arrhenius law, and that k_2 is given by [1]:

$$k_2 = k_d + k_e + k_c \quad (3-7)$$

where k_d , k_e and k_c are assumed first-order rate constants for loss by diffusion,

expansion and convection, respectively. This assumption is approximately true for the system that one is investigating if one excludes (as has been done) other loss processes. For k_d one has the following [29]:

$$k_d = \frac{8 D_0}{l^2} \left(\frac{T}{T^0} \right)^j$$

where D_0 is the diffusion coefficient at STP, T^0 is the absolute temperature at 298 K, l is the tube length, and the value of j (to be called gas combination factor) varies from 1.5 to 2.0 for various combination of gases [61]. The value of k_e is given by [29]:

$$k_e = \frac{\alpha}{4 T}$$

where α is the heating rate of the atomizer in K/s. The value of k_c is expressed by the following equation [1]:

$$k_c = \frac{F T}{300 \kappa V}$$

where F is the flow rate of the internal purge gas in ml/min, κ is a proportionality constant which depends on the gas flow pattern through the furnace, and V is the analysis volume. The data used in the calculation are given in Table (3-1). The results are presented in Fig. (3-3), which shows that k_2 is greater than k_1 during the entire working temperature range. Under the experimental conditions shown as the input, our results agree with the experimental results reported by Fuller [17].

Table (3-1). Data used in the calculation of the rate constants, k_1 and k_2 ^{*}.

Time interval used in the calculation, Δt (s)	0.020
Number of analyte atoms initially deposited, N_0	4.1×10^{12}
Activation energy E_a , kJ/mol	387.0
Heating rate α , K/s	650.0
Pre-exponential factor k_0 , s ⁻¹	2.0×10^7
Gas constant R , J/mol K ⁻¹	8.314
Gas combination factor, j	1.89
Tube length l , cm	2.8
Tube volume V , cm ³	0.79
Diffusion coefficient D_0 , at $T = 273$ K	0.097
Proportionality factor, κ	90.0
Flow rate F , ml/min	625.0

^{*}The temperatures used are the same as in Fig. (3-6).

Fig. (3-3). Rate constants for the rate of atom formation and removal of Co as a function of the absolute temperature. a: rate constant k_2 for Co atom removal. b: rate constant k_1 for Co atom formation.

3.4.3. *Temperature profiles of the three tubes*

Figure (3-4) shows a plot of absolute temperature, T , vs time, t (in second), for the pyrolytically coated electrographite, uncoated electrographite and glassy carbon tubes (shown as Curves a, b, and c), respectively, used with the furnace, one tube at a time. The furnace was heated electrothermally, under the gas-interrupt mode of atomization, from a charring temperature of 1070 K to a final atomization temperature of 2700 K. Because of the different heating characteristics of the three furnace tubes certain adjustments in the voltage were made in order to bring the final atomization temperature of the furnace with each tube to 2700 K. These adjustments in the voltage were readily made with the modified power supply, described in earlier chapters. The tube wall temperature, at the center of the tube, was measured by focusing a pyrometer through the injection hole. As can be seen from Fig. (3-4), the heating rates of the three tubes are different. For the pyrolytically coated tube, the heating rate is 650 K/s, measured from the slope of the plot of T vs time curve. The uncoated electrographite tube heats up faster than the pyrolytically coated electrographite tube and has a heating rate of 800 K/s (measured at the beginning of the temperature vs time curve to a fixed atomization temperature of 2700 K). The glassy carbon tube heats up somewhat faster than the uncoated electrographite tube and has a heating rate of 850 K/s (taken from the beginning of the temperature vs time curve), which is higher than the heating rate of the pyrolytically coated electrographite tube. This difference in the heating rate of the three tubes is probably due to difference in the macro and micro structure of the tubes. Different graphite tube structure influences appreciably the bulk properties, such as electrical resistivity and heat conductivity [62]. It has been reported that the resistance of the glassy carbon tube decreases significantly as the

Fig. (3-4). Plot of absolute temperature, T , vs time, t (in second) for the three tubes. **a**: pyrolytically coated electrographite, **b**: uncoated electrographite tube, and **c**: glassy carbon tube.

temperature of the tube rises, hence allowing more electrical current to pass through the tube body [63], resulting in a high heating rate for the furnace. The resistance of the pyrolytically coated electrographite tube increases linearly with temperature [64] resulting in decreasing the electrical current passing the furnace body.

3.4.4. *Characteristic mass and peak shape*

Table (3-2) summarizes the characteristic mass values (m_0) of cobalt obtained by the peak-height and the peak-area method of evaluation using atomization from the tube wall and pyrolytically coated electrographite, uncoated electrographite and glassy carbon tubes. All absorbance signals were measured under the gas-interrupt mode of operation. It is clear from the experimental data given in Table (3-2), that the sensitivity of the pyrolytically coated electrographite tube is much better than those of the uncoated electrographite and glassy carbon tubes. A comparison between the uncoated electrographite and glassy carbon tubes, however, shows that the sensitivity of the uncoated electrographite tube is not better than that of the glassy carbon tube (peak-height basis). Also, the sensitivity of the latter two furnace tubes measured on the basis of the peak area are approximately the same; no appreciable difference is seen in Table (3-2). The uncoated and the glassy carbon tube give less sensitivity than the pyrolytically coated electrographite tube.

Figure (3-5) shows the absorbance signal profiles of 0.20 ng of cobalt atomized from pyrolytically coated electrographite, uncoated electrographite and glassy carbon tubes, superimposed on one another and shown as Curves a, b, and c, respectively. The difference in the shape of the absorbance signal profile of cobalt atomized from the pyrolytically coated electrographite tube and those from the other two tubes is obvious. The difference in the shapes of the three absorbance

Table (3-2). Characteristic mass values (m_o) of cobalt in peak-height absorbance and peak area (A.s) obtained by atomization from tube wall of pyrolytically coated graphite, uncoated electrographite and glassy carbon tubes operated under the gas-interrupt mode.

Tubes	Peak height	$m_o/0.0044 \text{ A}$	Peak area	$m_o/0.0044 \text{ A.s}$
		(pg)		(pg)
PG	0.160 ± 0.002	5.5 ± 0.1	0.219 ± 0.002	4.0 ± 0.0
UG	0.047 ± 0.001	18.6 ± 0.5	0.121 ± 0.017	7.3 ± 0.3
GC	0.060 ± 0.003	14.7 ± 0.7	0.125 ± 0.032	7.0 ± 0.5

PG: pyrolytically coated electrographite tube.

UG: uncoated electrographite tube.

GC: glassy carbon tube.

Values after $\pm$ represent % relative standard deviation of four replicate determinations.

Fig. (3-5). Absorbance signal profiles of 0.20 ng of cobalt atomized from three different tubes, a: pyrolytically coated electrographite tube, b: uncoated electrographite tube, and c: glassy carbon tube.

signal profiles is due to many factors, including reactivity of C, structure, resistivity, thermal conductivity, heating rate and temperature, porosity of the substrate, and to other properties of the analyte/substrate system, such as atomization mechanisms, sticking probability of the analyte species, rates of atom formation and dissipation.

3.4.5. *Activation energy for atomization of cobalt nitrate*

Table (3-3) summarizes the results for determination of the activation energies for the atomization of cobalt nitrate from the three different atomization surfaces: pyrolytically coated electrographite, uncoated electrographite and glassy carbon tubes. The values of E_a , have been calculated from the slopes of the Arrhenius plots, drawn using the data from the leading edge of the absorbance signal profile [Fig. (3-6)]. The slopes were calculated by the least-squares method. The initial linear portion of the slope covers a temperature range of about 340 K.

Figure (3-7) shows the effect of different values of m of Eqn (3-5) on the Arrhenius plots. It can be seen that the value of m does not have any discernible effect on the slope of the Arrhenius plots. The effect of the heating rate on E_a for cobalt atomization from a pyrolytically coated electrographite tube has been also studied, and the result is presented in Table (3-4). The heating rate α was determined graphically using the equation, $T = T_0 + \alpha t$, where T is the absolute temperature at time t . No significant effect on E_a is seen, which agrees with the experimental observation reported earlier by Sturgeon et al. [13].

3.5. MECHANISMS OF COBALT ATOMIZATION

The standard free energy change at the appearance temperature of 1400 K was

Table (3-3). Activation energy for atomization of cobalt from different atomizer surfaces.

Tube	Appearance	Atomization	Heating rate	E_a , kJ/mol
	temperature, K	temperature, K	K/s	
PG	1420	2700	650	$387 \pm 4\%$
UG	1450	2700	800	$375 \pm 5\%$
GC	1500	2700	850	$285 \pm 3\%$

PG: pyrolytically coated electrographite tube.

UG: uncoated electrographite tube.

GC: glassy carbon tube.

Values after $\pm$ represent % relative standard deviation of four replicate determinations.

Fig. (3-6). Arrhenius plots for atomization of 0.20 ng Co (taken as the nitrate in aqueous solution of 1% (v/v) HNO_3) in different atomizer tubes. a: pyrolytically coated electrographite; b: uncoated electrographite; c: glassy carbon.

Fig. (3-7). Arrhenius plots for the atomization of 0.20 ng Co (taken as the nitrate in aqueous solution of 1% (v/v) HNO_3 in a pyrolytically coated electrographite tube as a function of m [Eqn (3-6)]. a: $m = 1.5$; b: $m = 1.2$; c: $m = 1.0$.

Table (3—4). Activation energy of cobalt from a pyrolytically coated electrographite tube at different heating rates.

Appearance temperature, K	Heating rate [*] K/s	E _a , kJ/mol
1410	580	390 ± 3%
1440	1050	387 ± 3%
1420	2800	405 ± 4%

* At the appearance temperature.

Values after ± represent % relative standard deviation of four replicate determinations.

calculated by Sturgeon et al. [13] based on the assumption that $\text{CoO}_{(s)}$ is the precursor for $\text{Co}_{(g)}$, and was found to be equal to -100 kJ/mol , suggesting that the reduction of $\text{CoO}_{(s)}$ by $\text{C}_{(s)}$ at the appearance temperature is thermodynamically favourable. The activation energy for atomization of cobalt may be correlated with the dissociation energy of the oxide, or the heat of sublimation or the heat of vaporization of the pure cobalt metal. Table (3-3) presents a comparison of the activation energies of cobalt atomization from the three different atomization surfaces. Since the dimensions of the three furnace tubes are identical, and the appearance temperatures and the heating rate at the appearance temperatures are not very dissimilar, the activation energies can be compared and interpreted in terms of the mechanisms for cobalt atom formation from the different atomization surfaces.

Table (3-3) shows no significant difference in the activation energies obtained using the pyrolytically coated electrographite surface and that obtained using the uncoated electrographite surface, but these values are significantly different from the activation energy obtained using the glassy carbon tube. If surface spreading and penetration of the surface by the aqueous solution of the sample had played a role in the atomization, then all three E_a values should be appreciably different because significant spreading and penetration would be expected for the uncoated electrographite surface, but not for the pyrolytically coated electrographite surface and the glassy carbon surface. The pyrolytically coated surface is expected to show much less spreading than the uncoated electrographite surface, but no penetration as long as the pyrolytic graphite coating remains intact. The near identity of the E_a values for the pyrolytically coated electrographite surface and the uncoated electrographite surface rules out surface spreading and penetration as affecting the

observed difference in the E_a values in the present case. This means that surface spreading and penetration of the surface cannot explain the low E_a value for the glassy carbon tube. Perhaps, the cause for the observed low E_a value for the glassy carbon tube lies in a different atomization mechanism.

The E_a values [Table (3-3)] for the pyrolytically coated electrographite and the uncoated electrographite tube may be correlated with either the heat of sublimation of $\text{Co}_{(s)}$, 428.4 kJ/mol, or the heat of dissociation of $\text{CoO}_{(g)}$, 361 kJ/mol [Table (3-5)]. Since carbon reduction of $\text{CoO}_{(s)}$ is thermodynamically favourable at the appearance temperature of 1400 K, as mentioned above, the correlation of E_a with the heat of sublimation of $\text{Co}_{(s)}$ is not unreasonable. The above two mechanisms are shown below as Eqns (3-8) and (3-9).

The mechanism shown by Eqn (3-9) requires the prior formation of $\text{CoO}_{(g)}$ from $\text{CoO}_{(s)}$. Reaction (3-8) should be kinetically favourable because the $\text{CoO}_{(s)}$ formed by the decomposition of $\text{Co}(\text{NO}_3)_2$ in the charring cycle is in intimate contact with a very large excess of $\text{C}_{(s)}$ (present as the heated graphite tube). Reaction (3-9) is also kinetically favourable at the high temperature of atomization.

The other possibilities that any of the following reactions may be an effective pathway for the formation of $\text{Co}_{(g)}$ should also be examined:

Table (3-5). Physical and thermochemical properties of probable cobalt species.

Melting Point of Co	1768 K	[65]
Boiling Point of Co	3373 K	[60]
Melting Point of CoO	2208 K	[60]
Co ₂ O ₃ transformed to Co ₃ O ₄ at	1168 K	[60]
Co ₃ O ₄ transformed to CoO at	1223 K	[60]
Co _(s) $\longrightarrow$ Co _(g)	428.4 kJ/mol	[65]
Co _{2(g)} $\longrightarrow$ 2 Co _(g)	167 kJ/mol	[65]
Co _(l) $\longrightarrow$ Co _(g)	370 kJ/mol	[66]
CoO _(s) $\longrightarrow$ CoO _(g)	510.5 kJ/mol	[67]
CoO _(g) $\longrightarrow$ Co _(g) + O _(g)	361 kJ/mol	[68]

Although reaction (3-10) is thermodynamically favourable, it is kinetically less favourable than the other reactions considered earlier including reactions (3-11) and (3-12). This is because of the very low partial pressure of $\text{CO}_{(g)}$ [69]. In order for $\text{CO}_{(g)}$ to reduce $\text{CoO}_{(s)}$, $\text{CO}_{(g)}$ molecules must be adsorbed onto the condensed-phase $\text{CoO}_{(s)}$. The expected low surface coverage of $\text{CO}_{(g)}$ (because of the very low partial pressure of $\text{CO}_{(g)}$) will cause the reduction of $\text{CoO}_{(s)}$ to be kinetically unfavourable. Reactions (3-11) and (3-12) are coupled in the graphite furnace. The dissociation energy of $\text{CoO}_{(g)}$ is so much smaller than the heat of sublimation of $\text{CoO}_{(s)}$ that the sublimation of $\text{CoO}_{(s)}$ will occur with the attendant dissociation of $\text{CoO}_{(g)}$. It is possible that the small mass of the sample taken allows the sublimation of $\text{CoO}_{(s)}$ to deplete all $\text{CoO}_{(s)}$ by forming $\text{CoO}_{(g)}$, for which the dissociation energy is so much lower than the sublimation energy of $\text{CoO}_{(s)}$ that the sublimation of $\text{CoO}_{(s)}$ would result in the dissociation of $\text{CoO}_{(g)}$, which would be observed as the activation energy, E_a .

On the basis of the above discussion, it is reasonable to conclude that the more likely mechanism of atomization of $\text{Co}(\text{NO}_3)_2$ in the pyrolytically coated electrographite tube or the uncoated electrographite tube is the dissociation of $\text{CoO}_{(g)}$ concurrent with the sublimation of $\text{CoO}_{(s)}$.

The E_a value 380 kJ/mol [Table (3-3)] correlates better with the heat of dissociation of $\text{CoO}_{(g)}$ 361 kJ/mol [Table (3-5)] than the heat of sublimation of $\text{Co}_{(s)}$ 428.4 kJ/mol. However, both mechanisms [Eqns. (3-8) and (3-9)] are consistent with the experimental observations made earlier on the decomposition curve in Fig. (3-1).

The E_a value 285 kJ/mol for the glassy carbon tube is more difficult to account for as it does not correlate with any value of the thermochemical properties given in Table (3-5). By thermochemical calculations Ham et al. [57] have demonstrated that if greater than 5×10^{-11} mole (2.945 ng) of Co is taken, $\text{Co}_{(l)}$ should replace $\text{Co}_{(s)}$, for equilibria above 1880 K. Since the E_a values for Co atomization were obtained using 0.20 ng of Co, the Co atoms should be in the solid state rather than the liquid state. However, for a monolayer distribution of the analyte atoms on the atomization surface, the energy of interaction between the atomization surface and the analyte atoms may affect the activation energy. The chemical inertness of the glassy carbon [16, 69-71] may play an important role in determining the energy required to release cobalt atoms to the gas phase. If less chemical reactivity results in a weaker interaction between the glassy carbon surface and the Co atoms on it, and if the measured E_a corresponds to this interaction, then E_a would have a low value. The stronger interaction between $\text{Co}_{(s)}$ and the pyrolytically coated electrographite surface and between $\text{Co}_{(s)}$ and the uncoated electrographite surface accordingly should result in high E_a values. The experimental E_a values [Table (3-3)] are consistent with the above observation.

The E_a value 285 kJ/mol for the glassy carbon tube can be correlated with the

heat of vaporization, 309 kJ/mol, as estimated by Trouton's rule. However, such a correlation would require that the cobalt sample be converted into $\text{Co}_{(l)}$ near the appearance temperature 1500 K for atomization from the glassy carbon surface [Table (3-3)]. It is possible that cobalt exists as liquid on the tube surface even though its appearance temperature is lower than the melting point, since the latter can be lowered by the traces of impurities in the sample. However, according to thermochemical calculations, it is also possible that the small amount (0.20 ng) of $\text{Co}_{(s)}$ present can be totally sublimed at a temperature below the melting point of $\text{Co}_{(s)}$. Hence, the appearance temperature of cobalt may be well below the melting point or the sublimation point of cobalt.

SUMMARY

The mechanism of cobalt atomization from different atomization surfaces in graphite furnace atomic absorption spectrometry has been investigated. The atomization surfaces are: pyrolytically coated electrographite, uncoated electrographite, and glassy carbon. The activation energy of the rate-determining step in the atomization of cobalt (taken as the nitrate in aqueous solution) using a commercial graphite furnace has been determined from a plot of $\ln k_1$ vs $1/T$ (using T values immediately above the appearance temperature) where k_1 is a first order rate constant for atom release, and T is the absolute temperature. The activation energy, E_a , shows correlation either with the dissociation energy of $\text{CoO}_{(g)}$ or with the heat of sublimation of $\text{Co}_{(s)}$ formed by carbon reduction of $\text{CoO}_{(s)}$, the latter being the product of thermal decomposition of $\text{Co}(\text{NO}_3)_2$. The mechanism for Co atomization from the pyrolytically coated electrographite and the uncoated electrographite surface seems to be the same, whereas that from glassy carbon surface seems to be different from that for the other two surfaces. The suggested mechanisms are consistent with the chemical reactivity of the three atomization surfaces, and the physical and thermodynamic properties of cobalt and its chemical compounds in the temperature range involved in the charring and the atomization cycle of the graphite furnace.

Chapter 4

4.1. MECHANISMS OF ATOMIZATION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY USING BASIC PRINCIPLES OF THERMODYNAMICS

In graphite furnace atomic absorption spectrometry (GFAAS) researchers are concerned with the laws of analyte interactions. These laws are mainly divided into thermodynamic or kinetic. In thermodynamics, conclusions are reached on the basis of changes in the free energy of the system. From a value of the free energy change of a reaction, it is possible to predict the direction in which a chemical reaction will take place. Thermodynamics cannot, however, give any information about the rate of atom formation by which the analyte is converted into atoms. In many situations studied so far, much information can be obtained from thermodynamic and kinetic measurements. As illustrated in previous chapters, a complete picture about atom formation and loss cannot be obtained unless both approaches (thermodynamic and kinetic) are taken into account. In order to postulate a mechanism of atom formation it would be helpful to consider all thermodynamic and kinetic data that are available. To illustrate the relationship between the above two approaches one can consider that copper oxide (CuO) is the precursor for copper atom formation. When atomization of CuO occurs, two steps need to be considered, as follows:

and,

For the reduction of $\text{CuO}_{(s)}$ by $\text{C}_{(s)}$ to take place, at least 19.2 kJ/mol of energy must be acquired by collisions between copper oxide and carbon. Whereas sublimation of copper requires 337.6 kJ/mol of energy. The latter is, therefore, likely to be slow compared to the former, and hence is the rate-determining step.

The mechanism of atom formation in GFAAS has been the subject of several studies involving thermodynamic [52–54], kinetic [12, 17, 56, 72] and combined thermodynamic–kinetic approaches [13, 46]. Using a thermodynamic model, Campbell and Ottaway [52] concluded from their study of 27 elements that the reduction of the metal oxide by carbon was thermodynamically feasible. Sturgeon et al. [13, 46] used a combined thermodynamic and kinetic approach to obtain the activation energy of atom release from a plot of natural logarithm of the absorbance versus the reciprocal of the absolute temperature of the graphite tube wall at the beginning of the absorbance signal profile. Frech et al. [53] developed a thermodynamic model to study the distribution of solid, liquid and gaseous analyte species as a function of temperature for 16 analyte elements. Chakrabarti et al. [54] reported the importance of carbon in determining the partial pressure of CO gas as well as other gaseous species, such as, O and O_2 , in the graphite furnace during the heating cycle of the graphite tube atomizer.

Fuller presented a model [56] for atom formation process using a kinetic approach developed under isothermal conditions emphasizing the need for considering thermochemical properties of the element and its chemical compounds in order to propose a reasonable mechanism for atom formation.

By applying thermodynamics and by assuming that the change in pressure of

analyte atomic vapour in the gas phase varies directly as the rate of release of atoms from the graphite surface [30], one can formulate mathematical expressions to determine the heat of atom formation. The only assumptions required are a direct relationship between the absorbance and the number density of analyte atoms, the ideal gas behaviour for the analyte atomic vapour, and the equality of the activation energy with the enthalpy change of the reaction ΔH° . The latter assumption seems to be not unreasonable and has sufficient support from various authors [13, 46, 73, 74]. The experimental activation energy, E_a , is defined here as the energy required to produce gaseous free atoms [13, 75]. Several factors play an important role in determining the observed value of E_a . Among these factors are the energy required in the rate-determining step, to break existing bonds to release the analyte atoms. In the category of breaking bonds, one may include desorption and re-deposition on the graphite tube surface.

In previous chapters various methods have been reported to determine the activation E_a developed on the basis of a kinetic approach. In this chapter the enthalpy of atomization ΔH° is determined by a method derived from the basic principle of thermodynamics. A comparison between this method and others reported in the literature [10, 13] will be made to give support for the validity of this model.

Mechanisms of atomization for Cu, Co, Ga, Au, Ni, Fe Ag and Al using the enthalpy of atomization obtained by this method will be proposed.

4.2. THEORY

In this method, it is assumed that the release of atoms from the graphite surface is a desorption process [23, 30, 44, 76]. Once a desorption process is assumed for a

system thermodynamic relationships can be applied to experimental data to yield the heat of desorption [77]. A number of authors have assumed that thermodynamic equilibrium is established at each stage of atom formation between the solid phase and the analyte atomic vapour [3, 11, 49],

$$N_w \frac{k_1}{k_2} = N_g \quad (4-1)$$

where N_w is the number of analyte atoms left unatomized on the tube wall surface, N_g is the number of gaseous analyte atoms, k_1 and k_2 are rate constants for atom formation and for atom loss by re-deposition, respectively. The expression for the equilibrium constant K_p according to the above equation is given by,

$$K_p = P_{N_g} = \exp(-\Delta G^\circ/RT) \quad (4-2)$$

where P_{N_g} is the partial pressure of the element in the atomizer, R and T are the gas constant and the absolute temperature, respectively, and ΔG° is the standard free energy change given by,

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (4-3)$$

where ΔH° is the standard enthalpy change, ΔS° is the standard entropy change, and T is the absolute temperature. According to Eqn (4-2), K_p and hence P_{N_g} increases with increasing tube wall temperature. Thus, N_g will also increase as the temperature increases. Substituting Eqn (4-3) into Eqn (4-2) and taking natural logarithm of both sides of the resulting equation one gets,

$$\ln P_{N_g} = -\frac{\Delta H^0}{RT} + C' \quad (4-4)$$

where C' is a constant and ΔH^0 is the molar enthalpy of vaporization, sublimation or desorption. From Eqn (4-4), a plot of $\ln p$ vs the reciprocal of T should be linear with a slope $= -\Delta H^0/R$ and an intercept $= C'$. Sturgeon et al. [13, 23, 46] have assumed that the experimentally observed activation energy, E_a , may be equated to the enthalpy of atom formation ΔH^0 . Agreement between the experimentally determined E_a and the enthalpy of sublimation for several elements studied by Sturgeon et al. [13, 46, 23] indicates that the observed E_a can be correlated to only ΔH^0 for those elements. The Arrhenius plot then becomes in effect a van't Hoff plot [57] and one must conclude that the atomization of the analyte element at the appearance temperature is thermodynamically favourable.

In GFAAS it is difficult to measure the vapour pressure of trace elements as a function of time during atomization because of the extremely small value of this vapour pressure. For this reason it would be better to relate the atomic vapour pressure to other experimentally measurable parameters such as absorbance. Recognizing that in GFAAS the absorbance signal, A , is directly proportional to the number of gaseous analyte atoms in the furnace:

$$A = Q N_g \quad (4-5)$$

where Q is a proportionality constant. Assuming ideal gas behaviour for the analyte atomic vapour and using Eqn (4-4) and (4-5), one has,

$$\ln (A T) = -\frac{\Delta H^{\circ}}{RT} + C \quad (4-6)$$

with

$$C = C' + \ln (Q V L / R)$$

where V is the analysis volume, approximately equal to the volume of the graphite tube, and L is the Avogadro's number. The plot of $\ln (A T)$ vs $1/T$ is similar to the Arrhenius plots and can be used to obtain the ΔH° from the slope which is equal to $-\Delta H^{\circ}/R$; the intercept = C .

The following energy terms are involved in atom formation in a graphite tube furnace [13, 46, 56]: the enthalpy of vaporization (sublimation if there is no liquid phase) of the element, $\Delta H^{\circ} (M)$; the enthalpy of vaporization (or sublimation) of the metal oxide, $\Delta H^{\circ} (MO)$; the dissociation energy of the metal oxide, $D_o (M-O)$; and the dissociation energy of the metal carbide, $D_o (M-C)$.

Atomization mechanisms in GFAAS usually follow the reaction sequences shown in Table (4-1) [13, 46], where the subscripts s and g represent the phase of the subscripted term in the above reaction scheme.

The release of analyte atoms into the gas phase is determined to a large extent by both thermodynamic and kinetic factors. These factors should be considered in order to estimate the reduction of $MO_{(s)}$ by $C_{(s)}$ to form free analyte atoms. It is assumed that the production of $M_{(s)}$ can be expressed by the following chemical equations:

Table (4-1). Production of gaseous analyte atoms from the metal oxide.

From the point of view of thermodynamic equilibrium the reduction of $\text{MO}_{(s)}$ by $\text{C}_{(s)}$ [Eqn (4-7)] becomes increasingly favourable with the increasing temperature. The extent of the reaction in each of the above chemical equations for the formation of products i.e. $\text{M}_{(s)}$ depends on many factors. Of prime importance are the change in the free energy, ΔG , and the absolute temperature. The relative magnitude of the equilibrium constant involved in the reaction is of great help in predicting which reaction is thermodynamically more favourable at a given temperature.

The reduction of $\text{MO}_{(s)}$ by $\text{C}_{(s)}$ is well documented in the literature [12, 13, 17, 46, 52, 57]. The following three reactions determine the thermodynamic competitiveness of $\text{C}_{(s)}$ and $\text{CO}_{(g)}$ as reducing agents in the graphite furnace.

Assuming unit activities for all species a quantitative comparison of relative affinities of carbon or carbon monoxide for oxygen may be made on the basis of considering the free energy change of formation of the oxides under standard conditions. The particular advantage of carbon as a reducing agent over the other two reactions can be understood by reference to the change in ΔG° . As T increases ΔG° becomes more negative for reaction (4-12), remains almost the same for reaction (4-13), and becomes more positive for reaction (4-14). Because ΔS° for reaction (4-12) is positive, the greater the temperature is, the more negative ΔG° will be, and the greater will be the thermodynamic advantage of reaction (4-12) over reactions (4-13) and (4-14). With the unit activity assumption for all the species reaction (4-14) is more effective (as a reducing agent) than reactions (4-12) and (4-13) only at a temperature below 973 K. However, ΔG and not ΔG° is the measure of the actual drive of the reaction towards equilibrium. In the graphite furnace, the activity of carbon is one and the fugacity of carbon monoxide is much less than one [78, 79]. A careful study from this laboratory [79] showed that the partial pressure of CO in the graphite furnace at a heating rate of 1500 K/s is about 0.001 atm. At equilibrium, the decrease in ΔG° with increased temperature means K_p will increase and therefore products will be favoured over reactants to a greater extent. However, if the reduction of an oxide is not thermodynamically favourable at the appearance temperature the atom formation may be attributed to the thermal dissociation of the metal oxide [13].

Another important factor that has a profound effect on the mechanism of the atomization is the kinetics of the reaction. The rate of formation of $M_{(s)}$ from $MO_{(s)}$ depends on several factors: the energy barrier to be surmounted, the amounts of the species that appear in the rate law, and the pre-exponential factor in the

Arrhenius law. If the reduction of $\text{MO}_{(s)}$ by $\text{C}_{(s)}$ in Eqn (4-12) is kinetically controlled the rate of disappearance of $\text{MO}_{(s)}$ may sometimes be expressed by a pseudo first-order reaction. This is possible if $\text{C}_{(s)}$ is present in a large amount (as is the case in the graphite furnace—used in this study) and can be considered a constant. This is in contrast with the rate of reduction of $\text{MO}_{(s)}$ by $\text{CO}_{(g)}$, which is expressed by a second-order reaction. In order for the $\text{CO}_{(g)}$ to reduce the $\text{MO}_{(s)}$, a $\text{CO}_{(g)}$ molecule must become adsorbed onto the condensed-phase metal oxide. At a low surface coverage of CO (when a low partial pressure of $\text{CO}_{(g)}$ is present) the reduction of $\text{MO}_{(s)}$ occurs at a lower rate than the reduction of $\text{MO}_{(s)}$ by $\text{C}_{(s)}$. In the graphite furnace, after the charring step, the $\text{MO}_{(s)}$ is in intimate contact with the graphite surface which should kinetically favour reaction (4-7) relative to reaction (4-8). It is therefore reasonable to conclude that in the graphite furnace the reduction is by $\text{C}_{(s)}$ is the most predominant pathway.

4.3. EXPERIMENTAL

4.3.1. Apparatus

Absorbance measurements were made with The Perkin-Elmer atomic absorption spectrophotometer, model 503, equipped with a Deuterium Arc Background Corrector and a Heated Graphite Atomizer (HGA) model 400, operated in the internal purge gas-stop mode. The details of the equipment have been given in previous chapters. Argon gas of purity 99.997% and pyrolytically coated electrographite tubes (The Perkin-Elmer corporation, part No. B009-1504) were used.

Hollow cathode lamps of Al, Ga, Au, Ni, Ag and Fe (Westinghouse), Co (Varian Techtron) and Cu (Cathodeon) were used and operated at the lamp

currents recommended by the manufacturer.

4.3.2. *Standards and reagents*

Standards were prepared by using chemicals or elements of the highest purity commercially available. Stock solutions of cobalt, iron, nickel and gallium were prepared separately by dissolving the appropriate mass of pure metal in nitric acid (ULTREX, Baker Chemical Co.) and making up the solution to 1000 $\mu\text{g}/\text{ml}$ with ultrapure water. The stock solution of silver was prepared by dissolving an appropriate mass of silver nitrate in ultrapure water and diluting the solution to 1000 $\mu\text{g}/\text{ml}$ with ultrapure water. The stock solution of copper was prepared by dissolving copper metal in 50% (v/v) nitric acid (ULTREX) with heating; the final solution was made to 1000 $\mu\text{g}/\text{ml}$ in 1% (v/v) nitric acid by diluting with ultrapure water. The stock solution of aluminium was prepared by dissolving pure aluminum in 20% (v/v) nitric acid with heating and diluting the solution to 1000 $\mu\text{g}/\text{ml}$ with ultrapure water. The stock solution of gold was prepared by dissolving the appropriate mass of the gold metal in aqua regia and diluting the solution with ultrapure water to 1000 $\mu\text{g}/\text{ml}$. All test solutions were prepared daily by serial dilution of the stock solutions with ultrapure water to contain 1% (v/v) nitric acid. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 water purification system (Millipore Corporation).

4.3.3. *Procedure*

The experimental and instrumental conditions used in this work are listed in Table (4-2). The tube wall temperature was measured by automatic pyrometers series 1100 and 300 (Iacon Inc., Skokie IL.)—the former for high temperatures and

Table (4-2). Experimental and instrumental parameters.

Element	Mass taken ng	Analysis line nm
Al	0.10	309.3
Cu	0.02	240.7
Co	0.01	324.8
Ga	0.01	248.3
Au	0.01	232.0
Ni	0.30	287.4
Fe	0.10	242.8
Ag	0.01	328.1

the latter for low temperatures. The pyrometer was focussed through the injection hole of the graphite furnace on the inner surface of the graphite tube and the temperature of the sample area (a few mm²) was monitored. It seems most appropriate to use the tube wall temperature as, in fact, if the atomization is determined by a solid phase dissociation, the tube wall temperature is in any case the most relevant one. If the atomization is governed by gas phase dissociation this process will be predominant in the hottest zone, the zone at the middle part of the tube where the sample is deposited. Because of the large activation energies to be expected for the dissociation reaction, the number of atoms generated in the colder extreme ends of the graphite tube will be small.

In all cases 10 μ l aliquots were deposited manually in the graphite furnace with an Eppendorf micropipet fitted with disposable plastic tips. The signals were stored on floppy discs using a digital oscilloscope, model 4094 (Nicolet Corporation). The data were recalled later for evaluation.

4.4. RESULTS AND DISCUSSION

Plots of $\ln(A T)$ vs $1/T$ have been drawn for the eight elements and are shown in Fig. (4-1). Enthalpies of atomization were calculated from the slope of the linear region of the plots by the least-squares method using the data points at the beginning of the absorbance signal profile i.e. immediately after the appearance temperature, T_{app} . The appearance temperature of the element is defined as the temperature at which the analyte signal is just distinguishable from the baseline. Table (4-3) shows the enthalpy change, ΔH° , measured by this method which is compared with the activation energy, E_a , measured for this work by the method of Sturgeon et al. [13] and Smets method [10]. Figure (4-2) shows a typical plot for

Fig. (4-1). Plots of $\ln(AT)$ vs $1/T$.

Table (4-3). Comparison of the experimental enthalpy change, ΔH^0 , with the experimental activation energy, E_a , for the atomization reaction.

Element	ΔH^0 , kJ/mol this method	E_a , kJ/mol	E_a , kJ/mol
		by Sturgeon et al. [13] [*]	by Smets [10] [*]
Al	1340 ± 50	1350 ± 60	1370 ± 80
Cu	337 ± 10	340 ± 13	339 ± 17
Co	395 ± 17	421 ± 15	443 ± 16
Ga	261 ± 10	249 ± 10	248 ± 15
Au	371 ± 12	364 ± 15	364 ± 15
Ni	428 ± 15	432 ± 17	430 ± 16
Fe	409 ± 18	416 ± 15	416 ± 19
Ag	260 ± 8	284 ± 10	279 ± 12

^{*}—The graphite furnace was operated in the gas-flow mode (200 ml/min).

Values after ± represent relative standard deviation of 4 replicate determinations.

—Activation energy, E_a , was measured using the Sturgeon et al. [13] method and the Smets method [10].

Fig. (4-2). Plot of $\ln(AT)$ vs $1/T$ for copper compared with the results obtained by the method of Sturgeon et al. [13] and the Smets method [10]. a, this work; b, by the Smets method; c, by the method of Sturgeon et al.

copper by this method compared with those of Sturgeon et al. [13] and Smets [10]. The results obtained from Fig. (4-2) and those presented in Table (4-3) indicate that there is no significant difference between the results of the three methods, suggesting that for the elements under investigation, the ΔH° and E_a values are about the same. Over the initial part of the leading edge of the signal, a thermodynamic equilibrium may be established in a thin boundary or diffusion layer above the solid phase analyte wherein multiple release-adsorption processes occur resulting in equilibrium prior to transportation of the analyte vapour into the analysis volume. In such circumstances equilibrium exists and the Arrhenius plot yields ΔH° for the overall reaction [23]. Hence, one may conclude that at the very beginning of the absorbance signal profile, atom formation can be modelled by either the kinetic or the thermodynamic approach [21].

The bending of the plots of $\ln(A T)$ vs $1/T$ towards the abscissa for all the elements investigated in this work [Fig. (4-1)] was also observed by Sturgeon et al. [13, 46] and Smets [10]. It has been mentioned earlier that there are several explanations for this bending [21, 23, 30, 37, 51]. The explanation put forward by this thesis is the temperature dependence of the activation energy and of the pre-exponential factor in Arrhenius law cause deviation from the Arrhenius law which treats them as temperature-independent. Also, when the activation energy is dependent on temperature, the pre-exponential factor is also dependent on temperature [51]. The reaction order may be another cause for this nonlinearity [30], especially at higher temperatures where the surface coverage is continuously changing.

The experimental enthalpy of atomization can be correlated with the energies associated with a very limited set of possible primary steps in the atomization

sequences. These energies are mainly related to breaking bonds in molecular species. For a mechanism of atomization, one should also consider the heat of formation of the metal carbides and the metal oxides since these are the two chemical compounds that are most likely to be formed during the heating cycle of the graphite furnace. The heat of formation is of great help in explaining the thermal stability of a compound at a given temperature. For a given element, a chemical compound with a high negative heat of formation is thermally more stable than one having a less negative heat of formation. Table (4-4) presents the heat of formation of metal oxides and the metal carbides of the elements under investigation. The heat of formation has been assumed to be equal to the heat of atomization as reported by L'vov [80]. It can be seen from these data that metal oxides are thermally more stable than carbides. Assuming that values of ΔH° do not change appreciably with temperature, one concludes that the oxides are likely to be the precursors to atom formation for this group of metals (taken as nitrates). Good support for this conclusion is given in the literature [13, 60].

The experimental enthalpy of atomization ΔH° obtained by this method [Table (4-3)], and the mechanisms of atomization proposed in this thesis are reasonable and agree with those reported by others [10, 13, 30]. The main contribution of this work is that the results presented have been obtained by using an equation [Eqn (4-6)], which has been derived from basic principles of thermodynamics. The experimentally observed ΔH° values are in agreement with those obtained by applying the method of Sturgeon et al. [13] and the Smets method [10]. This confirms the experimental observation reported by Sturgeon et al. [13] that atom formation involves no energy barrier other than ΔH° and the experimentally measured E_a is equal to the enthalpy of atomization (ΔH°).

Table (4-4). Heat of formation, ΔH_f° , of the metal oxides and carbides.

Species	ΔH_f° , kJ/mol	Reference
$\text{Al}_2\text{O}_3(\text{s})$	-1673.6	65
$\text{Al}_2\text{O}_2(\text{g})$	-1527.1	82
$\text{AlO}(\text{g})$	83.7	93
$\text{Al}_4\text{C}_3(\text{s})$	-208.8	65
$\text{CuO}(\text{s})$	-157.3	65
$\text{CoO}(\text{s})$	-237.9	93
$\text{Ga}_2\text{O}_3(\text{s})$	-998.3	65
$\text{GaO}(\text{g})$	279.5	93
$\text{Ga}_2\text{C}_2(\text{s})$	560.7	93
$\text{NiO}(\text{s})$	-238.9	65
$\text{Ni}_3\text{C}(\text{s})$	67.4	65
$\text{FeO}(\text{s})$	-272.0	65
$\text{Fe}_3\text{C}(\text{s})$	25.1	93
$\text{Ag}_2\text{O}(\text{s})$	-31.0	65

The purpose of this study of atomization mechanism is understanding of the sequence of reactions in GFAAS. Before postulating a mechanism of atomization one has to consider the thermodynamic feasibility of the proposed series of elementary reactions and their relative rates. Enthalpy change of reaction is a useful concept [81]. An elementary reaction that requires higher energy (expressed as the enthalpy change of the reaction) relative to other steps is likely to be slow, hence may be considered as the rate-determining step. This approach is useful to generate data for studying the mechanism of atomization and has been mentioned in the literature [13, 81].

5.1. MECHANISMS OF ATOMIZATION

Aluminium. Upon heating, the aqueous solution of aluminium nitrate is converted into $\text{Al}_2\text{O}_3(\text{s})$ [46, 60] before the graphite furnace attains the appearance temperature for aluminium, 2070 K. The high heat of formation of $\text{Al}_2\text{O}_3(\text{s})$ compared to that of the simple carbide $\text{Al}_4\text{C}_3(\text{g})$ [Table (4-5)] rules out the formation of any significant amount of the carbide form.

The overall reaction for producing gaseous aluminium atoms from $\text{Al}_2\text{O}_3(\text{s})$ is:

The free energy change calculated assuming that the partial pressure of the carbon monoxide P_{CO} at the appearance temperature is equal to 0.001 atm [79] shows that the reaction is thermodynamically feasible ($\Delta G_{2070} = -129.7 \text{ kJ/mol}$). In the calculation of ΔG at the appearance temperature it has been assumed that ΔH° and ΔS° do not change appreciably with temperature which is a reasonable

Table (4-5). Change in free energy $\Delta G_{T_{app}}$ of reduction reactions at the appearance temperature^{*}.

Reaction	$\Delta G_{T_{app}}$, kJ/mol
$Al_2O_3(s) + 3 C(s) \rightarrow 2 Al(s) + 3 CO(g)$	-129.7
$CuO(s) + C(s) \rightarrow Cu(s) + CO(g)$	-288.7
$CoO(s) + C(s) \rightarrow Co(s) + CO(g)$	-172.0
$Ga_2O_3(s) + 2 C(s) \rightarrow 2 Ga(s) + 3 CO(g)$	-260.2
$NiO(s) + C(s) \rightarrow Ni(s) + CO(g)$	-295.8
$FeO(s) + C(s) \rightarrow Fe(s) + CO(g)$	-130.1

* Data were collected from Ref. 65 and 93.

T_{app} = Appearance temperature in Kelvin.

assumption. The following atomization mechanism is proposed:

The reactions (4-16) and (4-17) are coupled in the graphite furnace. For the former to proceed only 38.0 kJ/mol of energy is required, whereas the latter must acquire 1527.1 kJ/mol. Reaction (4-17) is likely to be slow and hence is considered the rate-determining step. Consideration of the experimentally determined ΔH° which is 1390 ± 50 kJ/mol and the heat of atomization of $\text{Al}_2\text{O}_2(\text{g})$ which is 1527 kJ/mol [82] suggests that the aluminum atomization is probably due to the dissociation of $\text{Al}_2\text{O}_2(\text{g})$. The transient species $\text{Al}_2\text{O}_2(\text{g})$ has been observed mass-spectrometrically in the graphite furnace by Styris [83].

Another possible mechanism for formation of gaseous aluminum atoms is by autocatalytic reduction of aluminum oxide by gaseous carbides, such as Al_4C_3 , that may form during the atomization step [84-88],

Gallium. Below the appearance temperature of gallium, 1500 K, Ga(III) nitrate or hydroxide in aqueous solutions are converted into $\text{Ga}_2\text{O}_3(\text{s})$ [89]. The latter is reduced to the metal by $\text{C}(\text{s})$ at the appearance temperature of 1500 K of gallium. There are no carbides of Ga which are stable at the room temperature [82], but formation of volatile carbides at low temperature cannot be ruled out. The calculated ΔG_{1500} which is -260.2 kJ/mol [Table (4-5)] suggests that the reduction of $\text{Ga}_2\text{O}_3(\text{s})$ by $\text{C}(\text{s})$ at the appearance temperature of 1500 K is thermodynamically favourable. The overall reduction-reaction is therefore:

which indicates that the reduction is not by one-step reaction as such a reaction would require the collisions of four molecules, the probability of which is very small. The following mechanism is, therefore, proposed:

followed by

The observed ΔH° value (261 ± 10) kJ/mol correlates with the heat of vaporization of $\text{Ga}_{(s)}$ (277.0 kJ/mol) rather than with the enthalpy of reaction (4-25) which is 245.1 kJ/mol. Formation of a volatile oxide $\text{GaO}_{(g)}$ may explain the relatively low atomization efficiency of gallium [16].

Copper. Upon heating, an aqueous solution of copper nitrate solution is converted into $\text{CuO}_{(s)}$ before the furnace attains the appearance temperature of 1450 K [13, 46, 65]. Upon further heating, $\text{CuO}_{(s)}$ is reduced by carbon to free Cu, which then sublimates yielding gaseous Cu atoms. The calculated $\Delta G_{1450} = -288.7$ kJ/mol [Table (4-5)]. The observed ΔH° (337 ± 10) kJ/mol correlates with the heat of sublimation of copper (337.6 kJ/mol). Because the heat of desorption of the copper from the graphite surface is approximately equal to the heat of sublimation of copper [21], the correlation between the experimentally observed ΔH° and the heat of sublimation is reasonable. The following atomization mechanism is therefore proposed:

Because reaction (4-28) requires only 46.8 kJ/mol of energy, whereas reaction (4-29) requires 337.6 kJ/mol of energy, the latter is the rate-determining step. The fair agreement between the heat of sublimation of copper and the experimentally determined enthalpy of atomization support the above mechanism. Although Cu is in liquid form at the appearance temperature [Table (4-6)], it seems that the

Table (4–6). Some properties of the elements.

Element	T_{app} in this work	Melting point K	State of aggregation of the metal at T_{app}
Al	2070	934	liquid
Cu	1450	1357	liquid
Co	1480	1768	solid
Ga	1500	303	liquid
Au	1450	1358	liquid
Ni	1960	1728	liquid
Fe	1500	1808	solid
Ag	960	1235	solid

T_{app} = Appearance temperature in Kelvin.

atomization of Cu occurs by sublimation. A case such as this is explained by using thermodynamic calculations mentioned earlier for cobalt (Chapter 3). According to these calculations the small amount of copper may vaporize totally at a temperature below the appearance temperature of 1450 K without passing through the liquid phase. Also, any impurities such as traces of carbon from graphite furnace are likely to lower the melting point of copper substantially.

Recently, Holcombe and co-workers [90] determined an activation energy of (130 ± 8) kJ/mol for copper (under vacuum) using higher temperature region of the Arrhenius plot and reported that, the initial absorbance signal is unusable for studying the atomization mechanism. Their mechanism for copper atom formation is that $\text{Cu}(\text{NO}_3)_2 \rightarrow \text{CuO}_{(\text{ads})} \rightarrow \text{Cu}_{(\text{ads})} \rightarrow \text{Cu}_{(\text{g})}$, suggesting the desorption of copper atoms from the graphite surface at individual active sites as the rate-determining step.

Cobalt. Upon heating, an aqueous solution of cobalt (as the nitrate or the chloride) is converted into $\text{CoO}_{(\text{s})}$ below the appearance temperature [13, 60]. At higher temperature $\text{CoO}_{(\text{s})}$ is reduced by $\text{C}_{(\text{s})}$ to $\text{Co}_{(\text{s})}$ as follows:

The above reaction is thermodynamically favourable with $\Delta G_{1480} = -172.0$ kJ/mol. The observed enthalpy of atomization (395 ± 17 kJ/mol) correlates with the heat of sublimation of the pure metal (428.4 kJ/mol). The formation of gaseous cobalt atoms is believed to be as follows:

For the reduction of $\text{CoO}_{(s)}$ one has to supply 127.4 kJ/mol of energy, whereas the sublimation of cobalt requires 428.4 kJ/mol of energy; hence, the latter considered the rate-determining step. The good agreement between the experimental enthalpy of atomization and the heat of sublimation of cobalt supports the above mechanism of atomization. Ham and McAllister [57] have also reported the above atomization mechanism based on thermochemical calculations using for their calculations small amounts of Co (as the nitrate or the chloride) normally taken for determination by GFAAS.

Nickel. Upon heating, an aqueous solution of nickel nitrate or chloride is thermally decomposed into $\text{NiO}_{(s)}$ [13, 46] below the appearance temperature of nickel, 1960 K. On further heating, $\text{NiO}_{(s)}$ is reduced by carbon to $\text{Ni}_{(s)}$, which then sublimes. The overall reaction is:

The calculated ΔG_{1960} at the appearance temperature of nickel 1960 K is -295.8 kJ/mol. The observed ΔH° (428 ± 15) kJ/mol correlates with the heat of sublimation (428.4 kJ/mol) of $\text{Ni}_{(s)}$. The following atomization mechanism is proposed:

In order for reaction (4-32) to proceed 129.2 kJ/mol of energy is required, whereas sublimation of Ni requires 430.1 kJ/mol. Hence, the latter is the rate-determining step. Good agreement between the experimentally determined enthalpy of atomization and the enthalpy of sublimation of pure nickel suggests that nickel atoms is formed by sublimation of nickel. Although nickel is liquid at the appearance temperature [Table (4-6)], the observed ΔH° correlates with the heat of sublimation and not with the heat of vaporization (375 kJ/mol) of the pure metal. Probably, the reason for this is similar to that given above for copper.

Iron. Upon heating an aqueous solution of ferric or ferrous nitrate to a temperature higher than 848 K at low O_2 partial pressure [91] it is converted into $\text{FeO}_{(s)}$, which is reduced by carbon to $\text{Fe}_{(s)}$ at a temperature ≤ 1500 K [Table (4-5)].

The calculated ΔG_{1500} for the above reaction is -130.1 kJ/mol. At the appearance temperature of iron, 1500 K, $\text{Fe}_{(s)}$ sublimates. The observed ΔH° (409 ± 18) kJ/mol correlates with the heat of sublimation (415.3 kJ/mol) of $\text{Fe}_{(s)}$.

The following atomization mechanism is therefore proposed for Fe:

The enthalpies of reactions (4-34) and (4-35) are 161.4 and 415.5 kJ/mol, respectively. The latter is likely to be slow and hence is the rate-determining step. The correlation of the measured enthalpy of atomization with the calculated enthalpy of sublimation of Fe gives sufficient support for the above mechanism.

Silver. When an aqueous solution of a soluble Ag salt is heated, $\text{Ag}_2\text{O}_{(s)}$ is formed below 523 K. When the concentration of the oxygen is extremely small (as in the graphite furnace), Ellingham diagram [92] predicts that even in the absence of carbon, Ag_2O decomposes when heated above 473 K. At the appearance temperature of silver, 960 K, the absorbance signal is attributed to the sublimation of $\text{Ag}_{(s)}$. The observed ΔH° (260 ± 8) kJ/mol correlates with the heat of sublimation (283.0 kJ/mol) for silver [65, 93].

Gold. Aqueous solutions of gold chloride upon heating produce, $\text{Au}_2\text{O}_3_{(s)}$ well below the appearance temperature of gold, 1450 K. On further heating $\text{Au}_2\text{O}_3_{(s)}$ decomposes to $\text{Au}_{(s)}$ below the appearance temperature of gold. Since Au is in a liquid state [Table (4-6)] at the appearance temperature, the correlation of the heat of formation of $\text{Au}_{(g)}$ with the heat of vaporization of $\text{Au}_{(l)}$ is reasonable. The observed ΔH° (371 ± 17) kJ/mol, however, correlates well with the heat of sublimation (368.2 kJ/mol) for gold [65, 93] and not with the heat of vaporization (343 kJ/mol), probably for reasons similar to those mentioned above for nickel and copper.

SUMMARY

Using thermodynamic relationships and the number density of analyte atoms in the atomizer volume, a method has been developed to determine the enthalpy of atom formation in graphite furnace atomic absorption spectrometry (GFAAS). The method is based on the equation, $\ln(A T) = -\Delta H^\circ/RT + C$, where A is the peak-height absorbance, T is the absolute temperature, ΔH° is the enthalpy of atom formation which for highly endothermic reactions may be considered to be equal to the activation energy, E_a , R and C are the gas constant and a constant of integration, respectively. The plot of $\ln(A T)$ vs $1/T$ is similar to the Arrhenius-type plot and should be linear with a slope $= -\Delta H^\circ/R$. Atomization mechanisms for eight elements, Cu, Co, Ga, Au, Ni, Fe, Ag and Al, are proposed by correlating the experimental enthalpy change of reaction ΔH° with a very limited set of possible primary reaction sequences. One significant result of this work is that the experimentally observed ΔH° correlates very well with the activation energy, E_a , determined by other methods which means no excess energy other than the enthalpy of atomization is involved in the rate-determining step of the elementary atomization reactions. This is in agreement with the results reported earlier in the literature.

Chapter 5

5.1. INVESTIGATION OF THE ORDER OF COPPER AND COBALT ATOMIZATION AT THE ABSORBANCE MAXIMUM IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

The order of reaction is important in mathematical formulation of the rate law of a chemical reaction. In graphite furnace atomic absorption spectrometry (GFAAS), the order of reaction is often assumed to be equal to one at low surface coverage [1, 10, 36, 40, 94]. On the basis of this assumption, different models [1, 10, 36, 40, 94] have been developed to obtain kinetic information about atomization reactions in GFAAS. For his investigation of the rate of desorption of metal in an evacuated chamber by "flash-filament", Redhead [95] has developed methods for determining the order of reaction. Arthur and Cho [44] have reported that the rate of thermal desorption has an order of one-half at low surface coverage under vacuum conditions, suggesting a two-dimensional nucleation of mobile adsorbed atoms. McNally and Holcombe [76] have used Monte Carlo simulation techniques to model the release of copper from a graphite furnace atomizer, and have concluded that the order of reaction of copper was equal to one. They have presented an explanation for the effect of the order of reaction on general shapes of absorbance signals, suggesting that the order of atom release can be obtained from the shapes of atomic absorption pulse signals. Recently using mass spectrometry in conjunction with GFAAS, Wang et al. [90] have shown that the order of copper atom formation can be determined from modified Arrhenius plots drawn with the mass intensity data (obtained under vacuum conditions) assuming a single release mechanism (i.e.,

single values of E_a and k_{∞}). The order of reaction by their method is the one that gives the best straight-line plot of the Arrhenius equation. However, such a procedure makes the evaluation of the order of reaction a difficult task if, for instance, the non-linearity in the Arrhenius plot is due to multiple release mechanism (i. e., variable values of E_a or k_{∞}); it would then be impossible to obtain a linear Arrhenius plot by fitting different values for the order of the reaction.

It would be useful to verify experimentally the validity of the first-order-reaction assumption of atom formation for a given sample before using the assumption for formulating a mathematical expression for determining activation energy for the atomization reaction since the order of reaction would affect the form of the mathematical equation.

This work was undertaken to devise a method for checking the validity of the first-order-reaction assumption frequently used to simplify mathematical treatment of atom formation in GFAAS and to determine the order of atom formation reaction of copper and cobalt at the absorbance maximum under non-isothermal conditions of atomization.

5.2. THEORY

All reactions are considered to occur under non-isothermal conditions under the normal operation of a pulse-heated (rapidly-heated) graphite furnace. Therefore, the mathematical treatment to be developed will take into account the temperature-dependence of the rate constant for atom release. It has been reported in the literature [1, 14, 21, 23-25] that in GFAAS the rate of atom formation is much slower than the rate of atom removal when the primary mechanism for atom removal is forced convection. Under such experimental conditions, the shape of

absorption signal profile observed in GFAAS can be expressed by the following equation [23–25, 39, 76] [see Eqn (2–3), Chapter 2]:

$$-\frac{d\sigma}{dt} = n \sigma^n k_{\infty} \exp \left(-\frac{E_a}{RT} \right) \quad (5-1)$$

where σ is the surface concentration of analyte (i.e. surface coverage), n is the kinetic order of atom formation, k_{∞} is the pre-exponential factor, E_a is the activation energy of the rate-determining step, and T and R are the absolute temperature at time t and the universal gas constant, respectively. The time-dependent decrease in the concentration of analyte species on the graphite tube surface is directly proportional to the increasing number of analyte atoms, N_g , leaving the surface per unit time; hence, Eqn (5–1) can be expressed as follows [39]:

$$\frac{dN_g}{dt} = S n \sigma^n k_{\infty} \exp \left(-\frac{E_a}{RT} \right) \quad (5-2)$$

where S is the surface area of the substrate. It has been assumed that the absorbance, A , is proportional to dN_g/dt (which is valid under the experimental conditions used) [39]. The following equation is obtained:

$$A = \beta Q n \sigma^n k_{\infty} \exp \left(-\frac{E_a}{RT} \right) \quad (5-3)$$

where Q is a proportionality constant which incorporates the necessary spectroscopic and geometric constants relating the absorbance, A , to the number of absorbing atoms, N_g , in the analysis volume, and β is the atomization efficiency,

defined as the fraction of the analyte atoms actually atomized. The parameters β and Q are sometimes lumped together in one term. Dividing Eqn (5-3) by Eqn (5-1) and rearranging terms one gets the following expression for the absorbance:

$$A = -\beta Q \frac{d\sigma}{dt} \quad (5-4)$$

This relationship between the absorbance and the decrease in the surface coverage (i.e. $-d\sigma/dt$) has been also reported by others [21, 24, 39, 94].

An important relationship between the rate constant, k_1 , of atom formation and the absorbance, A , which can be obtained by integrating both sides of Eqn (5-4) under the boundary conditions that $\sigma = 0$ at time = ∞ and σ at time = t

$$\int_t^{\infty} A \, dt = \int_{\sigma}^0 \left(-\beta Q \frac{d\sigma}{dt} \right) dt \quad (5-5)$$

which can be solved for σ to give

$$\sigma = \frac{1}{\beta Q} \int_t^{\infty} A \, dt \quad (5-6)$$

Equation (5-6) has been mentioned in Chapter 2. Substituting Eqn (5-6) into Eqn (5-3) one obtains the following expression for the rate constant of atom formation for $n \neq 0$:

$$k_1 = \frac{c A}{\left(\int_t^{\infty} A \, dt \right)^n} \quad (5-7)$$

where

$$c = n^{-1} (\beta Q)^{n-1}$$

and k_1 is defined by the Arrhenius equation as $k_1 = k_{\infty} \exp(-E_a/RT)$. Here, it should be mentioned that Eqn (5-7) is a modified form of the Smets equation [10] and has been derived earlier in Chapter 2. Bass and Holcombe [39] have derived another form of Eqn (5-7) for any value of n , and others [21, 24, 25, 43] for $n = 1$.

5.2.1. Graphical verification of the first-order-reaction assumption

The first-order-reaction assumption, which has been used by other researchers in the mathematical formulation of atom formation in GFAAS, can be verified graphically using Eqn (5-1). To do this, first, one has to find an expression for the surface coverage σ as a function of time. Such an expression may be obtained by integrating Eqn (5-1) from time = 0 to time t and solving for $n \neq 0$ and $n \neq 1$ to obtain the following equation for σ^n (see Appendix C)

$$\sigma^n = \sigma_0^n \left[1 + n(n-1) \sigma_0^{n-1} \int_0^t k_1 \, dt \right]^{n/(1-n)} \quad (5-8)$$

where σ_0 stands for the initial surface coverage (monolayer or multilayer coverage), which is then substituted into Eqn (5-3). Secondly, the derivative (dA/dt) of the

resulting equation is taken assuming a constant heating rate of the graphite tube i.e., $T = T_0 + \alpha t$, where α is the constant heating rate. By setting the derivative dA/dt equal to zero at the absorbance maximum, the rate constant for atom formation, k_1 , can be expressed as follows (see Appendix E):

$$k_m = \left(\frac{\alpha E_a}{RT_m^2} \right) \left(\frac{1 + n(n-1) \sigma_0^{n-1} \int_0^{t_m} k_1 dt}{n^2 \sigma_0^{n-1}} \right) \quad (5-9)$$

where k_m , T_m and t_m are, respectively the rate constant, the temperature, and the time corresponding to the absorbance maximum. The evaluation of the rate constant at the signal maximum has been published in the literature [24, 25, 32, 44, 94, 95]. Taking measurements of the T_m , the peak-height, and integrated absorbance at t_m Eqn (5-7) can be equated with Eqn (5-9), yielding the following expression:

$$\frac{c A_m}{\left(\int_{t_m}^{\infty} A dt \right)^n} = \left(\frac{\alpha E_a}{RT_m^2} \right) \left(\frac{1 + n(n-1) \sigma_0^{n-1} \int_0^{t_m} k_1 dt}{n^2 \sigma_0^{n-1}} \right) \quad (5-10)$$

Taking the logarithm of both sides of Eqn (5-10) and rearranging terms one gets

$$\log (A_m T_m^2) = n \log \int_{t_m}^{\infty} A dt + \log C \quad (5-11)$$

where A_m is the absorbance maximum, and

$$C = \left(\frac{\alpha E_a}{cR} \right) \left(\frac{1 + n(n-1) \sigma_0^{n-1} \int_0^{t_m} k_1 dt}{n^2 \sigma_0^{n-1}} \right) \quad (5-12)$$

In Eqn (5-12), the value of C is not a constant because it is dependent on the initial surface coverage σ_0 , and also on the integral $\int_0^{t_m} k_1 dt$, which is dependent on T_m . Hence, a plot of $\log(A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A dt$ of Eqn (5-11) is not linear under conditions where σ_0 and T_m are variable. The physical meaning of such plot is not clear. It is also difficult to determine the slope, n , because of the expected non-linearity under these conditions. However, for the special case where $n = 1$, the following equation is obtained (see Appendix F):

$$\log(A_m T_m^2) = \log \int_{t_m}^{\infty} A dt + \log \left(\frac{\alpha E_a}{R} \right) \quad (5-13)$$

The assumption of a first-order reaction can be verified graphically by atomizing different masses of analyte atoms in the graphite furnace and measuring the temperature, the peak-height and the integrated absorbance, measured from $t_m \rightarrow \infty$, as mentioned above. The plot of $\log(A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A dt$ should be linear with a slope equal to one and an intercept equal to $\log(\alpha E_a / R)$. It is interesting to mention here that one of the by-products of using such plot of Eqn (5-13) is that E_a can be calculated (at the absorbance maximum of the absorbance

signal profile) from the intercept, $\log (\alpha E_a/R)$, provided that α is known.

5.2.2. *Value of the order of atom formation at the absorbance maximum*

To begin with Eqn (5-7) will be used for the reason that this equation has been derived earlier and shown to be applicable to any order of atom formation [24, 25, 39], except for the case where $n = 0$. Difficulties in the direct calculation of the order of reaction from Eqn (5-7) arise from the uncertainties in the pre-exponential factor, k_w , in the Arrhenius equation, and in the constant (βQ) which is a composite of different physical, chemical and geometrical constants. If these uncertainties are eliminated, however, it would be possible to calculate the order of the atom formation reaction. As shown in Appendix D, these uncertain factors, k_w and (βQ) , in Eqn (5-7), disappear at the absorbance maximum. Hence, the order of atom formation reaction can be determined without recourse to the determination of the above two factors, and hence, possible uncertainties can be avoided. By rearranging terms and differentiating of both sides of Eqn (5-7) with respect to time and setting the derivative dA/dt to zero at the absorbance maximum one gets the following expression for the order of atom formation (Appendix G):

$$n_m = \left(\frac{\alpha E_a}{RT_m^2} \right) \left(\frac{\int_{t_m}^{\infty} A \, dt}{A_m} \right) \quad (5-14)$$

All parameters on the right-hand side of Eqn (5-14) can be experimentally measured except the activation energy, E_a , which can be determined from an Arrhenius plot [10, 13, 25], using the data points near the peak absorbance. The method used to calculate the activation energy at the absorbance maximum cannot

be based on the first-order-reaction assumption as this would necessarily lead to a value of $n = 1$ for the calculated order of atom formation. The method of Sturgeon et al. [13] does not invoke the first-order-reaction assumption; therefore, this method has been used to obtain the activation energy of copper and cobalt. Because of the possible uncertainties in the activation energy values (due to the limitation of the method of Sturgeon et al. [13] when applied to determine E_a near the absorbance maximum), the above calculation may produce uncertainties in the order of reaction.

5.3. EXPERIMENTAL

5.3.1. *Apparatus*

The Perkin–Elmer atomic absorption spectrophotometer, model 503, equipped with a D_2 -arc background corrector and an HGA–76B graphite furnace was used. The details of the instrument, temperature measurements, and analytical procedures have been given in previous chapters. The Perkin–Elmer hollow-cathode lamp of copper and cobalt were used and operated at the recommended lamp current. A Macintosh SE computer was used for processing data and drawing absorbance signal profiles.

5.3.2. *Graphite tubes*

Pyrolytically coated graphite tubes (The Perkin–Elmer catalog No. BOO9–1504) were used.

5.3.3. *Solutions*

A stock solution of copper containing 1000 $\mu\text{g/ml}$ was prepared by dissolving

0.5005 g of copper foil (Allied Chemical # 1620) of purity 99.90%, in 10 ml of 1:1 (v/v) HNO_3 (ULTREX). The solution was boiled and diluted to 500 ml. A stock solution of cobalt of 1000 $\mu\text{g}/\text{ml}$ was prepared by dissolving pure cobalt (99.99%) in pure nitric acid (ULTREX) and diluting the solution with ultrapure water to 1000 ml. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 water purification system (Millipore Corporation, Mississauga, Ontario, Canada). Test solutions containing 25.0, 50.0, 100.0, 150.0, 200.0 and 250.0 ng/ml copper; and that of cobalt containing 40.0, 80.0, 160.0, 320.0, 480.0 and 640.0 ng/ml were prepared by serial dilution of the above stock solutions immediately prior to determinations. In all cases 10 μl of the test solution was injected into the graphite furnace with an Eppendorf micropipet fitted with disposable plastic tips.

5.3.4. Gases

Argon gas (99.995% purity) was used both as sheath and purge gas (200 ml/min).

5.4. RESULTS AND DISCUSSION

Figures (5-1) and (5-2) show absorbance signal profiles obtained using various masses of copper (0.25–2.50 ng) and cobalt (0.40–6.40 ng) atomized from a pyrolytically coated graphite tube used for determination of the order of reactions. Figures (5-3) and (5-4) show the profiles of both the absorbance signal and the temperature for 2.00 ng of copper and 1.60 ng of cobalt. These figures were drawn by the computer using data points from the absorbance signal profiles drawn by the digital oscilloscope. The data set used for plotting $\log (A_m T_m^2)$ versus $\log \int_{t_m}^w A dt$ and for the calculation of n_m of copper by Eqn (5-14) is shown in Table (5-1); and

Fig. (5-1). Peak-height absorbance versus time for various amounts of copper taken as the nitrate in aqueous solution. Mass of Cu in ng: 0.25; 0.50; 1.00; 1.50; 2.00; 2.50.

Fig. (5-2). Peak-height absorbance versus time for various amounts of cobalt taken as the nitrate in aqueous solution. Mass of Co in ng: 0.40; 0.80; 1.60; 3.20; 4.80; 6.40.

Fig. (5-3). Peak-height absorbance and temperature versus time for 2.00 g of copper, taken as the nitrate in aqueous solution. a: absorbance; b: temperature.

Fig. (5-4). Peak-height absorbance and temperature versus time for 1.60 ng of cobalt, taken as the nitrate in aqueous solution. a: absorbance; b: temperature.

Table (5-1). The set of data used for drawing Fig. (5-2), taken from four experiments on copper.

Table (5-1). The set of data used for determination of the order of reaction of copper atomization.

Mass of Cu, ng	T_m , K	A_m	$\int_{t_m}^{\infty} A \, dt$
0.25	1730 ± 20	0.17 ± 0.00	0.12 ± 0.00
0.50	1750 ± 20	0.22 ± 0.02	0.14 ± 0.02
1.00	1750 ± 10	0.33 ± 0.01	0.22 ± 0.01
1.50	1740 ± 10	0.56 ± 0.04	0.39 ± 0.03
2.00	1740 ± 30	0.58 ± 0.02	0.42 ± 0.01
2.50	1740 ± 30	0.65 ± 0.03	0.44 ± 0.01

that for cobalt is shown in Table (5-2). Figure (5-5) shows a plot of $\log (A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A dt$ for copper, which is fairly linear within the range of the analyte mass investigated. Figure (5-6) presents a similar plot for cobalt, which also shows a fairly linear relationship between $\log (A_m T_m^2)$ and $\log \int_{t_m}^{\infty} A dt$. The slopes were calculated by the least-squares regression analysis, yielding the value for the kinetic order of copper atom formation equal to 0.95 ± 0.04 , and 0.96 ± 0.06 for cobalt. The E_a value for copper atomization calculated from the intercept $\log (\alpha E_a/R)$ was 177 kJ/mol, and that for cobalt was 150 kJ/mol.

Table (5-3) summarizes the values of the kinetic order of copper atom formation at the absorbance maxima of various analyte masses, 0.25–2.5 ng, calculated by Eqn (5-14). An activation energy value, 184 kJ/mol, was used in the calculation. The reason for using 184 kJ/mol as the activation energy value was that it was reported by Sturgeon et al. [13] for the higher temperature region of the Arrhenius plot. The kinetic order of copper atom formation averaged 1.01 with a standard deviation ± 0.04 .

For cobalt the activation energy of 180 kJ/mol obtained by applying the method of Sturgeon et al. [13] has been used. Table (5-4) summarizes the results for calculation of the order of reaction for cobalt. An average of 1.08 ± 0.11 has been obtained, indicating that the atom formation for cobalt follows first-order kinetics.

The method of calculation using Eqn (5-14) gave results for n_m consistent with those obtained graphically using the plot of $\log (A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A dt$. Wherever the graphical method is not applicable for the reason that $n \neq 1$, as mentioned in the theory section, Eqn (5-14) can be used to obtain the order of atom

Table (5-2). The set of data used for determination of the order of reaction of cobalt atomization.

Mass of Co, ng	T_m , K	A_m	$\int_{t_m}^{\infty} A \, dt$
0.40	1850 ± 20	0.06 ± 0.01	0.02 ± 0.00
0.80	1860 ± 10	0.11 ± 0.03	0.05 ± 0.01
1.60	1840 ± 20	0.18 ± 0.02	0.07 ± 0.00
3.20	1850 ± 10	0.27 ± 0.01	0.12 ± 0.01
4.80	1860 ± 10	0.39 ± 0.03	0.15 ± 0.01
6.40	1850 ± 20	0.54 ± 0.04	0.20 ± 0.01

Fig. (5-5). A plot of $\log (A_m T_m^2)$ vs $\log \int_{t_m}^{\infty} A \, dt$ for copper, where $\log H_m$ stands for $\log (A_m T_m^2)$ and $\log \Omega_m$ for $\log \int_{t_m}^{\infty} A \, dt$.

Fig. (5-6). A plot of $\log(A_m T_m^2)$ vs $\log \int_{t_m}^{\infty} A dt$ for cobalt, where $\log H_m$ stands for $\log(A_m T_m^2)$ and $\log \Omega_m$ for $\log \int_{t_m}^{\infty} A dt$.

Table (5-3). The order of reaction, n_m , for copper calculated for the absorbance maxima using Eqn (5-14).

Mass of Cu, ng	n_m
0.25	1.01 ± 0.04
0.50	0.97 ± 0.03
1.00	0.96 ± 0.05
1.50	1.02 ± 0.05
2.00	1.05 ± 0.05
2.50	1.05 ± 0.03
Average	1.01 ± 0.04

Table (5-4). The order of reaction, n_m , for cobalt calculated for the absorbance maximum using Eqn (5-14).

Mass of Co, ng	n_m
0.40	0.91 ± 0.07
0.80	1.19 ± 0.03
1.60	1.10 ± 0.08
3.20	1.23 ± 0.05
4.80	1.05 ± 0.04
6.40	1.01 ± 0.02
Average	1.01 ± 0.11

formation. The above experimental results for the order of copper atom formation agree with those obtained by Holcombe and co-workers [31, 76, 90].

The above two methods, i.e, the graphical method and that of using Eqn (5-14) can be used to verify the assumption of first-order atom formation in GFAAS. These methods have the advantage of being rapid and reproducible. Although the graphical method successfully generates data to verify a first-order release process in GFAAS using the slope of $\log (A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A \, dt$ plot, it is unable to give the order of atom formation if it is not one, simply because of the initial mass-dependence of σ_0 and the T_m -dependence of the $\int_0^{t_m} k_1 \, dt$ of the intercept, C , in Eqn (5-11), as mentioned earlier. If $n \neq 1$ the above plot will not be linear. Nevertheless, the graphical method may be used to investigate the order of atom formation of a given analyte by depositing a wide range of analyte masses in the graphite furnace and collecting a relatively large number of data points for T_m , A_m , and $\int_{t_m}^{\infty} A \, dt$. This will allow one to detect the non-linearity of the $\log (A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A \, dt$ plot since different orders of atom formation will affect the slope of the resulting curve to a different extent. The shape of the curve is characteristic of a given order of atom formation. Also, the shapes of absorbance signal profiles may be used to obtain useful information about the order of atom formation; for instance, a first-order release generates absorbance signal profiles with identical temperature at peak absorbance (A_m); a zero-order release for atom formation gives variable temperatures at peak absorbance [76, 90]. Hence, both the shapes of absorbance signal profiles and the shapes of the $\log (A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A \, dt$ plots may be used as possible indicators for the order of atom release in GFAAS.

SUMMARY

Two methods to determine the order of the atom formation reaction from the absorbance signal profile are proposed. In one method, the first-order-reaction assumption, which is often used to develop various Arrhenius-type plots in GFAAS, is graphically verified by plotting $\log(A_m T_m^2)$ versus $\log \int_{t_m}^{\infty} A \, dt$, where the subscript m indicates the value of the subscripted term at the absorbance maximum. The linearity of this plot confirms the first-order-reaction assumption. The other method allows one to determine the order of the atom formation reaction at the maximum of the absorbance signal using the equation,

$$n_m = \left(\frac{\alpha E_a}{RT_m^2} \right) \left(\frac{\int_{t_m}^{\infty} A \, dt}{A_m} \right).$$

The order of the atom formation reaction of copper from a pyrolytically coated graphite tube was found to be 0.95 ± 0.04 by the graphical method, and 1.01 ± 0.04 by the method of calculation. For cobalt 0.96 ± 0.06 and 1.01 ± 0.11 were determined by the graphical method and by the method of calculation, respectively. The results for the order of reaction of copper and cobalt atom formation indicate that the atomization of these two elements follows first-order kinetics.

Chapter 6

6.1. ATOMIZATION EFFICIENCY OF A GRAPHITE FURNACE IN ATOMIC ABSORPTION SPECTROMETRY AT HIGH HEATING RATES

Atomization efficiencies of some commercial graphite furnaces have been studied by several authors [1, 10, 16, 96]. However, the differences in the published results of different authors indicate that the problem of atomization efficiency still remains unresolved. Probably, part of the problem lies in the definition of atomization efficiency of graphite furnaces. Sturgeon and Berman [16] measured the absolute atomization efficiencies of the HGA-2200 for nine elements by determining electron concentrations using microwave attenuation techniques. Relative values of atomization efficiencies subsequently calculated by the authors [16] for several elements were, however, subject to uncertainties in the *gf* values (from the literature) used in the calculation [97]. van den Broek and de Galan [1] calculated the overall atomization efficiencies of two graphite furnaces (CRA-63 and HGA-72) for the atomization of Ag, Pb, Mn, and Cd. They concluded that, under common operating conditions, atomization efficiencies averaged less than 10% for the above elements. Smets [10] in his study of atom formation in and dissipation from an open strip atomizer made the following estimate of the atomization efficiency (taking into account the relative oscillator strengths of the atomic resonance lines): 1 for Au, Ag, Cu, Fe, Mn, and Mg, and less than 0.1 for Al. Kitagawa et al. [96] spectroscopically determined the atomization efficiency of a glassy carbon tube atomizer for Cu and calculated relative atomization efficiencies for Cr and Ag based on the absolute value established for Cu.

The objective of this research was to determine atomization efficiencies of The Perkin–Elmer HGA–400 for several elements at relatively high heating rates and to make a critical assessment of the atomization efficiencies.

6.2. THEORY

For simplicity, the analysis shall be confined to the passage of an atomic vapour through the analysis volume, without considering all other chemical reactions and physical processes that lead to formation of atomic vapour in and its loss from the graphite furnace. Also, any complicating processes that may accompany the transport of the material through the analysis volume shall be ignored and shall further assume that all of the element determined is in the atomic state while inside the analysis volume. The above assumptions are admittedly valid only for a limited number of elements which are completely atomized in graphite furnace and the ionization of which can be ignored at the atomization temperature used. These assumptions allow considerable simplification of the mathematical formulation of the model.

Assuming that consecutive, first–order reaction that occur during atom formation in and atom loss from the HGA–400 can be described by the following model [20]:

where [D] represents the concentration of the pre–atomization analyte species; [B] represents the concentration of the absorbing analyte atomic vapour formed; [C] represents the concentration of the analyte atomic vapour that is lost from the

analysis volume; and k_1 and k_2 are identified as the first-order rate constants for analyte atom formation and loss, respectively. At all times the concentrations are related by:

$$[D]_t + [B]_t + [C]_t = [D]_o \quad (6-1)$$

where the subscript t and o represent the time at which the concentration is considered. The above model yields the following differential equations:

$$-\frac{d[D]}{dt} = k_1 [D] \quad (6-2)$$

$$\frac{d[B]}{dt} = k_1 [D] - k_2 [B] \quad (6-3)$$

By solving Eqn (6-2) one gets Eqn (6-4),

$$[D] = [D]_o \exp(-k_1 t) \quad (6-4)$$

In the limit, $[D]$ in Eqn (6-3), tends to zero which is identified with the exhaustion of the supply of the pre-atomization species D at the trailing edge of the experimental trace. At this point, Eqn (6-3) simplifies to [98],

$$\frac{d[B]}{dt} = -k_2 [B] \quad (6-5)$$

Since the measured absorbance, A , is proportional to the concentration of the

absorbing species, B, the rate constant for the atom loss, k_2 , can be determined from this part of the absorbance signal profile. A plot of the logarithm of absorbance vs time should be linear, yielding the rate constant k_2 from the slope.

Extrapolation of this straight line plot to zero time (i.e., $t = 0$) will give the concentration of B (resulting from complete conversion of $[D]_0$ into $[B]$) necessary to produce the decay of the signal by diffusion process alone. However, Eqn (6-3) shows that the rate of atom formation of B is equal to the difference between the rate of conversion of species D into B and the rate of loss of species B by concentration diffusion. The difference between the extrapolated absorbance and the experimental absorbance at time t is equal to the concentration of the pre-atomization species D. Equation (6-4) suggests that a plot of the natural logarithm of this difference versus time should be linear, with a slope equal to the rate constant for atom formation, k_1 [98].

If the kinetic parameters are evaluated, the shape of the absorbance signal profile may then be determined by solving Eqn (6-3). Substituting Eqn (6-4) into Eqn (6-3) yields a first order differential equation which can be solved for $[B]$ to give the following expression:

$$[B]_t = \frac{[D]_0 k_1}{k_1 - k_2} \left(\exp(-k_2 t) - \exp(-k_1 t) \right) \quad (6-6)$$

where $[B]_t$ represents $[B]$ at time t . The concentration of B, which is initially zero, at first increases and reaches a maximum when $d[B]/dt$ is zero; the system is then said to have reached a stationary state.

$[B]_t$ can be related to the measured absorbance, A , by using a proportionality

factor Q:

$$A = \frac{Q[D]_0 k_1}{k_1 - k_2} \left(\exp(-k_2 t) - \exp(-k_1 t) \right) \quad (6-7)$$

where Q is a function of the oscillator strength (a constant) of the analysis line and the efficiency of formation of analyte atoms. The Q is therefore directly related to atomization efficiency, which can be increased by forming analyte species that are readily atomized, and by increasing the heating rate which increases k_1 and shifts the absorbance signal profile (at least the decay part) into the isothermal region of the tube wall temperature curve, thereby making analyte atoms loss by concentration diffusion only. Experimental conditions, such as these, make k_2 relatively small and constant at constant temperature.

On differentiating Equ (6-7) and setting $dA/dt = 0$, at the absorbance maximum, one obtains the following expression for t_m (the time required for the attainment of the stationary state):

$$t_m = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad (6-8)$$

The maximum concentration of B is seen to be [20, 98]:

$$[B]_{t=t_m} = [D]_0 \exp(-k_2 t_m) \quad (6-9)$$

where $[D]_0$ is the initial concentration of D. The efficiency of atomization, β_1 , is defined here as the fraction of analyte atoms present as atomic vapour at t_m (the

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time at which the absorbance reaches a maximum) and is given by

$$\beta_1 = \frac{[B]_m}{[D]_0} = \exp(-k_2 t_m) \quad (6-10)$$

It is important to note that this definition of atomization efficiency does not take into account those atoms which are lost by the process,

in going from 0 to t_m . It is a measure of those atoms that are present at t_m .

An alternative method of calculating the atomization efficiency can be derived from the above definition of β_1 . This atomization efficiency (to be called β_2) is defined as the number of atoms, N_m , present as atomic vapour at t_m over the total number of atoms initially deposited in the furnace, N_0 (i. e., at time = 0).

$$\beta_2 = \frac{N_m}{N_0} \quad (6-11)$$

However,

$$Q = \frac{A_m}{N_m} \quad (6-12)$$

where A_m is the peak-height absorbance at time = t_m .

As stated earlier, extrapolation of the straight line plot to zero will give the concentration of B necessary to produce the decay of the absorbance signal by

diffusion process alone. Therefore,

$$Q = \frac{A_o}{N_o} \quad (6-13)$$

where A_o is the peak-height absorbance at $t = 0$. A_m and A_o are defined in Fig. (6-1).

The final result is that the atomization efficiency, β_2 , can be obtained readily from the equation,

$$\beta_2 = \frac{A_m}{A_o} \quad (6-14)$$

Theoretically, having been derived from the same definition, β_1 should equal β_2 .

Because k_2 is weakly dependent on temperature, it is important for the calculation of β_1 that the descending part of the absorbance signal profile be located in the isothermal region of the tube wall temperature versus time curve. The k_2 values are calculated from the data points from the tail end of the experimental trace.

It can be seen from Eqn (6-10) that $\beta_1 \approx 1$ when $k_2 t_m \ll 1$. Hence, for the highest atomization efficiency, both k_2 and t_m must be made as small as possible. The time t_m is sensitive to heating rate; generally, high heating rates yield small t_m values. Although the rate constant k_2 for atom loss by concentration diffusion may increase with temperature it is reasonable to assume that k_2 does not change drastically since it is less sensitive to higher temperatures in comparison with k_1 [28]. This method employs relatively high heating rates coupled with moderately

Fig. (6-1). Plot of $\ln A$ vs time (in seconds). A_m and A_0 are peak-height absorbances at time $t = t_m$ and t_0 , respectively.

high atomization temperatures to keep both k_2 and t_m values small so as to approach the condition $k_2 t_m \ll 1$. As can be seen later, with the maximum heating rate available with the modified HGA-400 power supply (about 7000 K/s), this attempt has been only partly successful.

6.3. EXPERIMENTAL

6.3.1. *Apparatus*

The detailed description of the spectrophotometer, absorbance and temperature measurements have been given in earlier chapters. The Perkin-Elmer pyrolytically coated graphite tubes (part No. B009-1504) were used. Graphite tubes were replaced with new tubes after about 12 firings. Argon gas was used in the gas-stop mode of operation at the atomization step.

Hollow-cathode lamps of cobalt (Perkin-Elmer), aluminium (EEL), and copper, silver, iron, and gallium (the last four by Westinghouse) were operated at the lamp current recommended by the manufacturers.

6.3.2. *Reagents*

Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions of cobalt and iron were prepared separately by dissolving an appropriate mass of the metal in nitric acid (ULTREX, J. T. Baker Chemical Co.) and diluting the solution to 1000 $\mu\text{g}/\text{ml}$ with ultrapure water. The stock solution for silver was prepared by dissolving an appropriate mass of silver nitrate in ultrapure water. Stock solutions for gallium and copper were prepared separately by dissolving the metals in concentrated nitric acid (ULTREX) and 50% (v/v) nitric acid, respectively, with heating. The final solutions were made by dilution to

1000 $\mu\text{g}/\text{ml}$ with ultrapure water. The stock solution for aluminium was prepared by dissolving the metal in 20% HCl (ULTREX) with heating. The final solution was made by dilution to 1000 $\mu\text{g}/\text{ml}$ with ultrapure water. All stock solutions were made 1% (v/v) in HNO_3

All test solutions were prepared by diluting the stock solutions to desired concentrations with ultrapure water immediately prior to use. They contain 1% (v/v) HNO_3 (ULTREX). Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Mill-Q2 water purification system (Millipore Corporation).

6.3.3. Procedure

Sample solutions were injected into the atomizer using 10 μl Eppendorf pipette fitted with disposable plastic tips. High heating rates and moderately high atomization temperatures were used in order to shift the atomic absorption signal into the isothermal region of the tube wall temperature versus time curve as much as possible. The absorbance values were corrected for blanks.

6.3.4. Experimental and analytical parameters

Table (6-1) summarizes the experimental and analytical parameters used.

6.3. RESULTS AND DISCUSSION

Table (6-2) summarizes the atomization efficiency values of a selected group of elements at various heating rates and atomization temperatures. The heating rates listed were calculated from the tube wall temperature curve [such as the one shown in Fig. (6-2)] as follows, using its nearly-straight-line segment which encompasses the appearance temperature of Al of 2420 K:

Table (6-1). Experimental and analytical parameters^{*}.

Element	Wavelength (nm)	Mass of elements (pg)	Charring temperature (K)
Cu	324.8	50	1470
Co	240.7	100	1670
Al	309.3	50	1670
Ag	328.1	40	920
Ga	287.4	1000	1070

^{*} Spectral band width = 0.7 nm; test solution injected = 10 μ l; Ar gas in the gas-stop mode of operation during the atomization cycle.

Table (6-2). Atomization efficiencies at different heating rates and atomization temperatures.

Element	Atomization temperature	Heating rate at the appearance temperature	% of the absorbance signal under isothermal	β_1	β_2
	(K)	(K/s)	region		
Al	2800	3500	75	0.36	0.22
	2840	3900	74	0.33	0.20
	2910	4300	67	0.35	0.24
Cu	2560	5200	72	0.50	0.44
	2470	5400	76	0.49	0.43
	2420	5300	82	0.50	0.43
Co	2840	5600	92	0.50	0.40
	2710	5700	94	0.48	0.30
	2640	5800	95	0.48	0.35
Fe	2680	6200	72	0.44	0.30
	2710	6100	67	0.45	0.26
	2880	6000	72	0.49	0.35
Ag	2220	6000	56	0.44	0.31
	2190	6100	56	0.41	0.28
	2150	6000	62	0.46	0.33
Ga	2900	6600	58	0.23	0.17
	2760	6700	62	0.35	0.20
	2620	6800	75	0.33	0.17

Fig. (6-2). Absorbance profile of aluminium and the corresponding temperature profile of the graphite furnace; a is the tube wall temperature measured with the automatic optical pyrometer; b is the peak-height absorbance, A , obtained by atomizing 0.10 ng of Al in 1% (v/v) HNO_3 aqueous solution. Atomization temperature = 2800 K. Heating rate = 3500 K/s.

$$\text{Heating rate} = \frac{\Delta T}{\Delta t} = \frac{(2560 - 2420) \text{ K}}{(0.200 - 0.160) \text{ s}} = 3500 \text{ K/s}$$

Here ΔT is the change in the absolute temperature of the graphite tube wall and Δt is the time interval. The reason for using the above segment of the tube wall temperature curve was that the heating rate so calculated was what the analyte actually experienced at the appearance time of the signal and at times immediately following the the appearance time [98]. The above heating rate was greater than the average heating rate over the entire period of rise in the tube wall temperature shown in Fig. (6-2). The heating rate is one of the important factors that determine the rate of atom formation during the rising part of the atomic absorption profile, and hence, affects atomization efficiency strongly. The gas temperature, which like the tube wall temperature, was time and space-dependent, roughly followed the tube wall temperature in the immediate vicinity of the spot on the tube wall surface where the test solution was placed [99, 100]. The tube wall temperature of that spot and the gas temperature in its immediate vicinity determined the rate of atom formation at the appearance time (temperature) and at times immediately following the appearance time.

Most of absorbance signal profiles were located more than 70% within the isothermal region of the tube wall temperature versus time curves. This was achieved by using the highest possible heating rates and moderately high atomization temperatures.

Figure (6-3) shows a plot of $\ln A$ vs time for aluminium. The rate constant for aluminium atom loss, k_2 , was obtained by the least-squares method from the slope of line a, which was drawn from the experimental data points at the tail of the absorbance signal profile. The points of line b represent the "concentration" of the

Fig. (6-3). Plot of $\ln A$ vs time (in seconds) for aluminium shown in Fig. (6-2). The slope of Curve a shows the k_2 value (5.7 ± 0.2) s^{-1} ; the slope of Curve b, top linear segment, shows the k_1 value (12 ± 1) s^{-1} , and that on bottom linear portion of Curve b shows $(k_1 + k_3)$ which is 17.4 ± 0.3 s^{-1} . See the text for more details.

species D. The curve b has been plotted using the difference between the extrapolated absorbance, A_0 , and the experimental absorbance, A , plotted on the same axis (i.e., time), and shows two intersecting straight lines of different slope. These intersecting straight lines correspond to two different processes of atom formation of the species B. The first linear segment, top of line b, corresponding to the earlier times and having the lower slope gives a value of $(12 \pm 1) \text{ s}^{-1}$ for the rate constant, k_1 , for the reaction $D \xrightarrow{k_1} B$. The second linear portion, bottom of line b, corresponding to later times and having a slightly steeper slope $(17.4 \pm 0.3) \text{ s}^{-1}$ yields the other rate constant, k_3 , for vaporizing the species D, to produce B, as shown below:

where D' is another species that dissociates to yield species B. The mathematical treatment adopted above is admittedly a simplified treatment of a more complex process, but has the merit of showing two possible atomization mechanisms. However, where two straight-line segments are observed (as for aluminium) a more rigorous mathematical treatment is necessary if the mechanism is to be proposed as shown above.

Following the treatment described in Ref. 20 the following mechanism for aluminium atomization involving three first-order rate processes is proposed.

The above mechanism shows that a part of the $\text{Al}_{(g)}$ is formed from $\text{AlO}_{(g)}$ (with a rate constant k_3), and a part is formed from $\text{Al}_2\text{O}_{3(s)}$ (with a rate constant k_1); and the $\text{Al}_{(g)}$ is then lost (with a rate constant k_2) [98]. This mechanism is in agreement with what has been reported earlier in Chapter 5. Smets [10] has also reported that the mechanism of aluminium atomization is by dissociation of $\text{AlO}_{(g)}$.

Table (6-2) shows a summary of the β_1 and β_2 values. As can be seen from Table (6-2) the β_1 values are consistently larger than the β_2 values. Probably, the large extrapolations involved in obtaining the A_0 values result in their over-estimation and in lower β_2 values from Eqn (6-14).

Table (6-3) shows the values of k_1 , k_2 and the measured t_m at various final steady-state atomization temperatures. Precision values from the least-squares method of the rate constants are not shown since they depend on the number of points included, whereas the value of the rate constant itself does not. However, the precision of any rate constant value can be no better than 5% relative standard deviation, as the absorbance values used in the calculation of rate constants have this order of relative precision.

The t_m values used in calculating β_1 values in Table (6-2) were measured graphically from Fig. (6-1) since the measured t_m values had a smaller uncertainty than the t_m value calculated from Eqn (6-8). The uncertainty in the measured t_m arose from manually locating the appearance time and the time corresponding to A_m [Fig. (6-1)]. If t_m values were calculated from Eqn (6-8), it would have required

Table (6-3). First-order rate constants for atom formation and atom loss.

Element	Atomization temperature (K)	Experimental values of		
		k_1	k_2	t_m, s
Al	2800	12	5.7	0.180
	2840	12	6.7	0.166
	2910	13	6.4	0.164
Cu	2420	13	3.0	0.229
	2470	11	3.1	0.229
	2560	13	3.5	0.196
Co	2640	10	3.0	0.245
	2710	10	3.2	0.228
	2840	11	3.6	0.195
Fe	2680	11	4.2	0.195
	2710	11	4.0	0.197
	2880	15	4.8	0.148
Ag	2220	24	8.3	0.100
	2190	21	8.0	0.111
	2150	24	6.8	0.115
Ga	2620	16	7.3	0.151
	2720	16	7.3	0.135
	2900	18	8.8	0.169

use of the k_1 and k_2 values, each of which had an uncertainty of at least 5% relative standard deviation. The k_1 values were also subjected to unknown systematic error as they were calculated from the absorbance values from the rising part of the absorbance signal profile which was located to some degree in the non-isothermal region of the tube wall temperature curve [Fig. (6-2)]. Also, there are further complications in determining k_1 values in the case of an element such as Al in which there is an additional atom formation [identified as D' in the mechanism given by Eqns (6-15) and (6-16)] having a rate constant k_3 .

The measurement of t_m with the digital oscilloscope was preferred because it avoided the complications that would arise in the above mathematical formulations to obtain t_m in terms of the two rate constants involved in the loss of species D, and thereby simplified the task considerably. This was in addition to lower uncertainty in measuring t_m graphically from Fig. (6-1) than that in calculating t_m from Eqn (6-8). However, by using still high heating rates as used in Ref. 20, the location of the entire absorbance signal profile can be shifted to the isothermal region of the tube wall temperature curve; in that case t_m can be readily evaluated also from Eqn (6-8) since the uncertainty and error in measuring k_1 from the absorbance signal profile would then be comparable to those in measuring k_2 and t_m from the same absorbance signal profile.

6.4.1. *Comparison with the atomization efficiency values reported by other authors*

Sturgeon and Berman [16] used an HGA-2200 and van den Broek and de Galan [1] used an HGA-72 and a CRA-63, whereas this work was done with an HGA-400. Also, before comparison can be made, it must be noted that the efficiency values determined in this study were for the HGA-400, and were only applicable under the specific experimental conditions, especially the high heating rates used in this work. The most important difference between this work and those of the above authors was that the heating rates used (in this work) were much higher [Table (6-2)] than those used by the above authors [1, 16]. Regardless of whether atomization was isothermal or non-isothermal, high heating rates increases k_1 values much more than k_2 values, and hence decreased t_m values by Eqn (6-8). Equation (6-10), which shows $\beta_1 = \exp(-k_2 t_m)$, holds good as long as the decay of analyte atoms is by a first-order rate process with a rate constant k_2 . Fulfillment of the above condition required that the tail end of the absorbance signal profile from which the experimental data points for evaluating k_2 values were taken is located in the constant-temperature region of the temperature versus time curve. As Table (6-2) shows, this condition was certainly fulfilled by all the elements in this work. It can be predicted from Eqn (6-10) that much higher heating rates (used in this work) should produce higher β_1 values than those reported by the other workers [1, 16] who used much lower heating rates. The β_1 values reported in this work confirm the above prediction.

Sturgeon and Berman [16] defined the absolute atomization efficiency of the HGA-2200 for a particular point in time (conveniently at the time of maximum signal as the ratio of the sum of the number of neutral and ionized analyte atoms to the number of analyte atoms initially introduced in the furnace). Since all of the

elements in this work have ionization energies of about 6 eV or higher, loss of neutral atoms by ionization in the HGA-400 at the atomization temperatures used can be considered negligible. Table (6-4) shows that most of the atomization efficiencies reported by Sturgeon and Berman [16] are of the same order of magnitude as those of this work.

van den Broek and de Galan [1] reported that the theoretical atomization efficiency of the HGA-72 for Ag was 0.45 and that determined experimentally was 0.20. These authors [1] defined the atomization efficiency as N_m / N_o —the ratio of the maximum number of atoms, N_m (obtained from the measured peak absorbance), to the number of analyte atoms injected in the furnace, N_o . Table (6-4) shows that the atomization efficiency for Ag (reported by van den Broek and de Galan [1]) are similar to those obtained by this work.

It should be noted that not only were the atomizers of the above authors [1, 16] different from the HGA-400 used in this work, but also the experimental and analytical parameters, especially the heating rates used, were different.

6.4.2. *Critical appraisal of the atomization efficiency values, β_1 and β_2*

The atomization efficiency values, β_1 and β_2 , were obtained from the same theory and were subject to the assumptions made in developing the theory. However, as stated earlier, the method that has been used to obtain β_1 values had different sources of uncertainties in k_2 and in t_m values used in solving Eqn (6-10). The β_2 values were affected by uncertainties in measuring A_m and A_o used in solving Eqn (6-14).

Since all k_2 values were obtained from the last few experimental data points at the tail end of the absorbance signal profile which was located in the isothermal

Table (6-4). Comparison of mean atomization efficiency values of this work with those reported by other authors [1, 16].

Element	This work ^a		Sturgeon and Berman ^b [16]	van den Broek and de Galan ^c [1]	
	β_1	β_2	β	β_{theor}	β_{exp}
Al	0.35	0.22	0.10	—	—
Cu	0.50	0.43	0.19	—	—
Co	0.49	0.35	—	—	—
Fe	0.46	0.30	—	—	—
Ag	0.44	0.31	0.35	0.45	0.20
Ga	0.30	0.18	0.06	—	—

^aUsed HGA-400.

^bused HGA-2200.

^cused HGA-72. β = atomization efficiency.

region of the tube wall temperature curve, and since these experimental data points related to the time when atom loss by concentration diffusion was the only process occurring, it can be concluded that the k_2 values listed in Table (6-3) are fairly good. The line from which k_2 was calculated was reasonably straight [Fig. (6-3)], especially at the last few data points at the tail end of the absorbance signal. However, as explained earlier, k_2 values had an uncertainty of about 5% relative standard deviation, which added to the uncertainty in manually locating t_m , was transmitted to β_1 values. The uncertainty in β_2 was mainly due to the measurement of A_0 values since large extrapolation from the tail end of the absorbance signal profile were required for the determination of A_0 [Fig. (6-1)]. As can be seen from Table (6-2), β_2 is usually very close in magnitude to β_1 , but in each case β_2 is less than β_1 . As explained in the theory, it is reasonable to expect the β_1 and β_2 values to have approximately the same magnitude. The above difference was probably due to the sources of uncertainty mentioned above. Since the uncertainty in increasing k_2 and t_m was not nearly as large as that due to large extrapolations in calculating A_0 , the β_1 values seem to be a more reliable estimate of the fraction of analyte present as atomic vapour at t_m than the β_2 values.

The β_1 values were obtained by solving Eqn (6-10), i.e., by using the k_2 and t_m values, and were therefore not affected by uncertainty in the k_1 values. The k_1 values were, however, subject to larger uncertainty and errors than the k_2 values because some of the k_1 values were obtained from the experimental points [Fig. (6-3)] lying in the non-isothermal region of the tube wall temperature curve [Fig. (6-2)]. In contrast, the k_2 values were obtained from the last few experimental data points at the tail end of the absorbance signal profile [Fig. (6-3)] in order to make sure that the only process occurring at those times was loss of analyte atoms by

concentration diffusion at constant temperature. In view of the above discussion, the β_1 values are more reliable than the β_2 values. It is to be noted that the k_1 values were not used in calculating β_1 and β_2 values. However, from the k_1 and k_2 values in Table (6-3) and from Eqn (6-7), one finds that under the experimental and analytical parameters used in this work, elements such as Cu, Co, Fe, and Ag for which the condition $k_1 \gg k_2$ is more closely approached than elements such as Al, and Ga, yield greater β_1 values than the latter group of elements.

SUMMARY

The efficiency of the Perkin–Elmer HGA–400 for production and containment of atomic vapour was determined for several elements using relatively high heating rates. Two different atomization efficiencies β_1 and β_2 were experimentally determined by two variations of a method. Assuming that atomization in the HGA–400 can be described by consecutive, first–order reactions $D \xrightarrow{k_1} B \xrightarrow{k_2} C$, the method consisted of making the absorbance signal profile (at least the decay part of it) appear at constant tube wall (at the center) temperature and determining first–order rate constants for atom formation and atom loss, k_1 and k_2 , respectively. Two atomization efficiencies were calculated: β_1 and β_2 , which gave the fraction of analyte atoms which was present as atomic vapour at the peak of the absorbance signal profile. Experimental atomization efficiencies (β_1 and β_2) reported for Al, Cu, Co, Fe, Ag, and Ga average: 0.42 and 0.30, respectively, with a range from 0.30 to 0.50 for β_1 and from 0.18 to 0.43 for β_2 . Significance of the results and limitations of the two variations of the method in terms of validity of their underlying assumptions have been brought out in a critical assessment of the atomization efficiencies measured by the above two variations of the method. In both of the variations of the method, the heating rates used were much higher than those used by some other authors, with the result that in agreement with the prediction of the theory, the atomization efficiencies measured in this work were considerably higher than those reported by those authors.

Chapter 7

7.1. DETERMINATION OF THE ATOMIZATION EFFICIENCY OF A MASSMANN-TYPE GRAPHITE FURNACE UNDER NON-ISOTHERMAL CONDITIONS

The efficiency of the graphite furnace to produce and contain analyte atoms has been the subject of several studies [1, 16, 101–102]. Smets [10] has defined the atomization efficiency β_1 as the fraction of analyte atoms that are actually atomized. Using the above definition the atomization efficiency β_1 is expressed as follows:

$$\beta_1 = \frac{\int_0^{\infty} R_{\text{form}} dt}{N_0} \quad (7-1)$$

where R_{form} is the rate of atom formation, and N_0 is the total number of atoms introduced as sample. Note that $\int_0^{\infty} R_{\text{form}} dt$ is the number of vaporized atoms that enter the analysis volume during the time interval $0 \rightarrow \infty$.

Some other authors [1, 16, 101–102] have defined the atomization efficiency as the fraction of gaseous atoms present in the analysis volume at the time when the absorbance reaches its maximum value. Various methods have been reported in the literature to determine the number of analyte atoms at the absorbance maximum under various experimental conditions. Sturgeon and Berman [16] have defined the efficiency of atomization, ϵ_a , for an electrothermal atomizer at the time the signal has attained its maximum value, as the ratio of the number of neutral analyte atoms, N_a , plus ionized analyte atoms, N_i , to the total number of analyte atoms introduced as sample, N_0 , i. e.,

$$\epsilon_a = \left(\frac{N_a + N_i}{N_o} \right) \quad (7-2)$$

This method requires existence of thermodynamic equilibrium in the furnace during atomization. Falk and Tilch [101] have determined the atom number density within the atomizer using the following equation:

$$N_a = \left(\frac{(8.69 \times 10^7) A (T_a/M)^{0.5}}{l \gamma H(w,a) f \lambda_{21}} \right) \left(\frac{Z(T)}{\exp(-E_1/kT_a)} \right) \quad (7-3)$$

where N_a is the atom number density within the atomizer, A is the absorbance, $Z(T)$ is the partition function at temperature T , γ is a coefficient accounting for hyperfine splitting of the atomic line, $H(w,a)$ is the Voigt integral for the point of the absorption line contour at a distance of $w = 0.72a$ from the line center, f is the oscillator strength, λ_{21} is the wavelength of the absorption line, E_1 is the energy of the lower level involved, k is the Boltzmann constant and l and M are the atomizer tube length and the molar mass of the analyte atom, respectively. Determination of N_a by using Eqn (7-3) introduces uncertainties in the terms used in the equation [16]. van den Broek et al. [1] have reported that the number of analyte atoms at the absorbance maximum, N_m , is given by:

$$N_m = N_o \left(\tau_R / \tau_s \right) \quad (7-4)$$

where N_o is the total number of analyte atoms initially deposited and τ_R and τ_s are the overall time constants for the removal and the supply function, respectively.

Chakrabarti et al. [98] have reported that for isothermal atomization in a graphite furnace the number of analyte atoms at the absorbance maximum, N_m , is given by Eqn (7-5),

$$N_m = N_0 \exp \left(-k_2 t_m \right) \quad (7-5)$$

where k_2 is a first-order rate constant (s^{-1}) for atom loss and t_m is the time at which the absorbance reaches its maximum value. Recently, Frech and Baxter [102] have determined the atomization efficiency of the Perkin-Elmer HGA-600 operated under stabilized temperature platform furnace (STPF) conditions using the following equation:

$$\text{Atomization efficiency \%} = \frac{m_o(\text{calc})}{m_o(\text{exp})} \times 100 \quad (7-6)$$

where $m_o(\text{calc})$ and $m_o(\text{exp})$ are the calculated and the experimental characteristic mass, respectively.

The present work was undertaken in order to determine the atomization of the Perkin-Elmer HGA-400 by two methods which are different both in their definition of the efficiency and in the way the defined efficiency is determined. In Method 1, the atomization efficiency, β_1 , is defined as the fraction of the number of analyte atoms that are actually atomized. In Method 2, the atomization efficiency, β_2 , is defined as the fraction of the number of vaporized analyte atoms that are present at the maximum of the atomic absorption signal profile.

7.2. THEORY

7.2.1. Atomization efficiency, β_1

In the rapidly-heated graphite furnace used for this study, the number of analyte atoms present in the analysis volume at time t is determined by the release, and the transport of atoms into and their loss from the analysis volume [6]. The efficiency of the graphite furnace to produce and contain the analyte atomic vapour is governed by its ability to release neutral analyte atoms from the atomizer surface and to transport them into the analysis volume. Ideally, this process requires that the amount of analyte atoms released from the atomizer surface should enter the analysis volume. In reality, however, some of the analyte atomic vapour formed may be lost by various atom loss processes, for example, loss by diffusion to the cooler ends of the atomizer and through the injection hole, by re-adsorption, by expulsion and by convection.

The number of atomized analyte atoms N_g at time t is given by the difference between the number of analyte atoms initially deposited into the graphite furnace N_0 and the number of unatomized analyte atoms, N_w . Once atomization commences gaseous analyte atoms start to diffuse into the analysis volume. It should be pointed out that not all of the analyte atoms which are transported to the gas phase at time t necessarily enter the analysis volume; a fraction of them may be lost. The loss of analyte atomic vapour from a Massmann-type atomizer (The Perkin-Elmer HGA-72), operated under normal experimental conditions, has been estimated by van den Broek and de Galan [1] to be about 90%. In the gas-interrupt mode of operation, diffusion out of the analysis volume is assumed to be the major loss process for atoms [1, 10, 28, 103]. Various authors have used a correction factor to account for the atom loss at each stage of the atom formation

[10, 14–37]. Note that, according to Smets [10], the fraction of analyte atoms present in the analysis volume at a given instant t is $\beta_1 N_g$, where β_1 is the fraction of analyte atoms that are actually atomized, and N_g is the total number of analyte atoms vaporized from the atomizer surface at time t . In the gas-interrupt mode of operation, the number of analyte atoms which are left unatomized on the graphite tube surface, N_w , is given by the following equation [10] (see Appendix H for details of the assumptions and the mathematical treatment):

$$N_w = \frac{\langle k_2 \rangle}{Q \beta_1} \int_t^\infty A \, dt \quad (7-7)$$

where β_1 is as defined above, Q is a constant linking the number of gaseous analyte atoms in the atomizer with the measured absorbance signal, A , and $\langle k_2 \rangle$ is the mean value of k_2 taken over the indicated time interval, reported constant within 10% [10]. $\langle k_2 \rangle$ is assumed to be equal to k_2 ; hence, from now on k_2 will be used for $\langle k_2 \rangle$. In GFAAS, the absorbance A is related to the number of gaseous analyte atoms present in the analysis volume by the following expression:

$$A = Q N_g \quad (7-8)$$

Using of the general relationship between N_w and N_g [Eqn (H12), shown in the Appendix H] one gets,

$$A = Q N_0 - \frac{k_2}{\beta_1} \Omega \quad (7-9)$$

where, $\Omega \equiv \int_t^{\infty} A \, dt$. At the leading edge, Eqn (7-9) shows that as Ω decreases A increases. This relationship between A and Ω as given by Eqn (7-9) should hold starting from the leading edge of the absorbance signal profile up to the absorbance maximum, and a plot of A vs Ω should be linear with a slope $= -k_2 / \beta_1$, which will yield β_1 provided that k_2 is known. The value of k_2 can be estimated [10] from Eqn (7-10),

$$k_2 = \frac{8 D}{l^2} \quad (7-10)$$

where D is the concentration diffusion coefficient of the analyte element in Ar gas, which can be calculated by a formula given in the literature [29, 104], and l is the geometric length of the graphite tube (2.8 cm). The values of the parameters used for determining D can be found in the literature [105]. Since the length l used in Eqn (7-10) is greater than the "effective" length of the graphite tube because of the pronounced temperature gradient in the horizontal axis of the long tube (the Perkin-Elmer tube used in this study), the value of k_2 so obtained gives only an estimate of k_2 [100].

7.2.2. Atomization efficiency, β_2

The atomization efficiency β_2 is defined here as the fraction of the number of analyte atoms present as atomic vapour at the instant of absorbance maximum.

$$\beta_2 = \frac{N_m}{N_0} \quad (7-11)$$

where N_m is the number of analyte atoms at the absorbance maximum. Using the relationship between the absorbance maximum A_m and N_m (i.e., $A_m = Q N_m$, where Q is a proportionality constant), Eqn (7-11) may be re-written as:

$$\beta_2 = \frac{A_m}{Q N_o} \quad (7-12)$$

When the graphite furnace is operated in the gas-interrupt mode, the denominator of Eqn (7-12), may be expressed as follows [1, 10, 14, 37] (see also Appendix H):

$$Q N_o = \frac{k_2}{\beta_1} \int_0^{\infty} A \, dt \quad (7-13)$$

where β_1 is as defined earlier. Upon substituting Eqn (7-13) into Eqn (7-12), one gets,

$$\beta_2 = \frac{\beta_1 A_m}{k_2 \int_0^{\infty} A \, dt} \quad (7-14)$$

The β_2 is the atomization efficiency determined by operating the furnace under the gas-interrupt mode. Equation (7-14) shows a linear relationship between β_2 and β_1 . Hence, β_2 will increase when β_1 increases, i. e., if all the analyte atoms released from the atomizer surface are transported completely into the analysis volume and remain there for a relatively long time. Equation (7-14) also shows that β_2 is related to the rate constant of atom loss, k_2 (which is inversely proportional to the residence time of analyte atoms for a first-order loss process). Note that as k_2 is

increased, for instance by forced convection, a low absorbance peak will result because of appreciable decrease in the residence time, which will also mean that β_2 will decrease. In order to increase β_2 , the experiment should be conducted in the gas-interrupt mode and to use long graphite tubes (such as the Perkin–Elmer tubes) since these two factors will increase the residence time of analyte atoms which will result in a high absorbance peak (i. e., a high value of β_2).

7.3. EXPERIMENTAL

7.3.1. *Apparatus*

The Perkin–Elmer atomic absorption spectrophotometer model 503, modified to allow recording of the absorbance signal with a 20 ms time constant and equipped with a D₂–arc background corrector and the Perkin–Elmer Heated Graphite Atomizer (HGA) model 400, was used. The graphite furnace was heated with a laboratory–made power supply capable of supplying variable heating rates. The temperature of the atomizer surface was measured with two automatic optical pyrometers (Ircon Inc., Skokie, IL., USA); high temperatures with a 1100 series pyrometer and low temperatures with a 300 series pyrometer. The Perkin–Elmer pyrolytically–coated graphite tubes (part No. B0091–504) were used. Signals were recorded with a Nicolet digital oscilloscope model 4094 (Nicolet Instrument Corporation, Madison, Wisconsin, USA). Integrated absorbance was measured using a software package provided by Nicolet Instrument Corporation. Hollow–cathode lamps of cobalt (Perkin–Elmer), aluminium (EEL), copper, silver, iron, gold, nickel and gallium (the last six by Westinghouse) were operated at lamp currents recommended by the manufactures.

7.3.2. *Standard solutions*

Chemically pure metals or their salts were used to prepare stock solutions of standards. The stock solution of silver nitrate was prepared by dissolving an appropriate mass of silver nitrate in ultrapure water and diluting the solution to make the concentration 1000 $\mu\text{g}/\text{ml}$; the final solution contained 1% (v/v) nitric acid (ULTREX, J. T. Baker Chemical Co.). Stock solutions of cobalt and iron were prepared separately by dissolving each metal in nitric acid (ULTREX) by heating and then diluting the solution with ultrapure water to make the concentration 1000 $\mu\text{g}/\text{ml}$; the final solutions contained 1% (v/v) nitric acid. Stock solutions of gallium and copper were prepared separately by dissolving each metal in nitric acid (ULTREX) by heating and then diluting the solutions with ultrapure water to make the concentrations 1000 $\mu\text{g}/\text{ml}$; the final solutions contained 1% (v/v) nitric acid (ULTREX). The stock solution of aluminium was prepared by dissolving the metal in 20% (v/v) nitric acid (ULTREX) with heating; the solution was then diluted to 1000 $\mu\text{g}/\text{ml}$ with ultrapure water. The final solution contained 1% (v/v) nitric acid (ULTREX). The stock solution of gold was prepared by dissolving an appropriate mass of the metal in aqua regia and diluting the solution to 1000 $\mu\text{g}/\text{ml}$ with ultrapure water.

All test solutions were prepared daily by serial dilution of the stock solutions with ultrapure water just prior to determinations. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 water purification system (Millipore Co., Mississauga, Ontario, Canada).

7.3.3. *Argon gas*

Argon gas (99.995% pure) was used both as sheath gas and as purge gas for the

graphite furnace.

7.3.4. Procedure

In all cases, 10 μl of the test solution was injected into the graphite furnace with an Eppendorf micropipet fitted with disposable plastic tips. The absorbance values were corrected for blanks.

7.3.5. Experimental and instrumental parameters

Table (7-1) summarizes the experimental and instrumental parameters used.

7.4. RESULTS AND DISCUSSION

Table (7-2) summarizes the values of β_1 for eight elements, Al, Co, Au, Ni, Fe, Ag, Ga and Cu, determined using the gas-interrupt mode of operation of the graphite furnace. The values of β_1 ranged from 0.04 for Ga to 0.77 for Cu and had a precision of about 3% relative standard deviation. Figures (7-1) to (7-8) show the plots of A vs Ω for Al, Co, Au, Ni, Fe, Ag, Ga and Cu. Slopes of the plots were calculated from linear regions using the least-squares method. As Eqn (7-9) predicts, β_1 increases as the slope of the plot of A vs Ω decreases. Since the value of the slope is determined by the shape of the absorbance signal profile, the latter plays an important role in determining β_1 , as reported by van den Broek and de Galan [1]. To illustrate how the shape of the absorbance signal profile affects β_1 , two plots of A vs Ω for Ga and Cu are shown in Figs. (7-7) and (7-8). The reason for taking these two plots of A vs Ω as an example is that Ga and Cu have equal values of k_2 [Table (7-2)]. Thus, if the β_1 values of Ga and Cu differ from each other the only factor that should account for this difference is the slopes of the plot

Table (7-1). Experimental and instrumental parameters^{*}.

Wavelength (nm)	Mass in ng	Charring temperature, K	Atomization temperature, K
309.3, Al	1.4	1050	2700
240.7, Co	2.5	1090	2600
324.8, Cu	1.5	1000	2600
287.4, Ga	5.5	900	2600
328.1, Ag	0.7	800	2000
248.3, Fe	1.0	1080	2600
242.8, Au	1.3	1000	2400
232.0, Ni	1.2	1100	2600

^{*} Spectral band width = 0.7 nm.

Table (7-2). Atomization efficiency, β_1 , under the gas-interrupt mode of operation.

Element	D^* ($\text{cm}^2 \text{s}^{-1}$)	k_2 (s^{-1})	slope	
			$(-k_2/\beta_1)$	β_1
Al	8.7	8.9	-36.0	0.25
Co	6.4	6.5	-20.2	0.32
Cu	6.9	7.0	-9.1	0.77
Ga	6.9	7.0	-156.0	0.04
Ag	3.4	3.5	-17.8	0.20
Fe	6.5	6.6	-36.0	0.18
Au	4.5	4.6	-14.4	0.32
Ni	6.8	6.9	-10.2	0.68

* The values of the parameters used in the calculation of D have been taken from Ref. 105.

Fig. (7-1). Plot of peak-height absorbance, A , vs Ω for aluminium (taken as the nitrate).

Fig. (7-2). Plot of peak-height absorbance, A , vs Ω for cobalt (taken as the nitrate).

Fig. (7-3). Plot of peak-height absorbance, A , vs Ω for gold (taken as gold dissolved in aqua regia).

Fig. (7-4). Plot of peak-height absorbance, A , vs Ω for nickel (taken as the nitrate).

Fig. (7-5). Plot of peak-height absorbance, A , vs Ω for iron (taken as the nitrate).

Fig. (7-6). Plot of peak-height absorbance, A , vs Ω for silver (taken as the nitrate).

Fig. (7-7). Plot of peak-height absorbance, A , vs Ω for gallium (taken as the nitrate).

Fig. (7-8). Plot of peak-height absorbance, A , vs Ω for copper (taken as the nitrate).

of A vs Ω [Figs. (7-7) and (7-8)], which are significantly different (9.1 for Cu and 156 for Ga), and hence give different values of β_1 (for equal values of k_2). This difference in the slopes makes the value of β_1 for Cu (0.77) differ from that of Ga (0.04) by a factor of 19. For identical absorbance signal profiles (giving identical slopes of the plots of A vs Ω), the values of β_1 should be equal, provided that k_2 values are equal.

Table (7-3) summarizes the values of β_2 for Al, Co, Au, Ni, Fe, Ag, Ga and Cu determined by using Eqn (7-14). The precision is about 3% relative standard deviation, which reflects the combined reproducibility of the furnace thermal program and that of atom formation and loss.

Turning now to an important aspect of the atomization efficiency, β_2 , Eqn (7-14) shows the relationship between β_2 and the rate constant of atom loss, k_2 . Hence, β_2 can be increased by decreasing k_2 , for example, by operating the atomizer in the gas-interrupt mode. This is demonstrated by the effect of forced convection on the absorbance signal of Cu, as shown in Fig. (7-9). Curve a is the absorbance signal profile of 1.50 ng copper (taken as the nitrate) obtained by operating the graphite furnace in the gas-interrupt mode; Curve b is the absorbance signal profile of 2.50 ng copper (taken as the nitrate) by operating the graphite furnace using an argon flow rate of 625 ml/min. As can be seen from Fig. (7-9), the absorbance signal of copper is greatly increased when the graphite furnace is operated in the gas-interrupt mode.

From Eqns (7-14) the following observations on the values of β_1 and β_2 are made. Since the $A_m / k_2 \int_{t_m}^{\infty} A dt$ values given in Table (7-3) are < 1 , one would expect, according to Eqn (7-14), that the β_2 values to be less than the β_1 values. As mentioned earlier, the β_1 values have uncertainties originating from the use of Eqn

Table (7-3). Atomization efficiency, β_2 , under the gas-interrupt mode of operation.

Element	A_m	$\int_0^\infty A \, dt$	$A_m / k_2 \int_0^\infty A \, dt$	β_2
Al	0.230	1.769×10^{-1}	0.146	0.04
Co	0.520	5.608×10^{-1}	0.143	0.05
Cu	0.716	9.379×10^{-1}	0.109	0.08
Ga	0.530	1.868×10^{-1}	0.405	0.02
Ag	0.338	1.980×10^{-1}	0.488	0.10
Fe	0.401	3.259×10^{-1}	0.186	0.03
Au	0.350	9.649×10^{-2}	0.789	0.25
Ni	0.317	4.258×10^{-1}	0.108	0.07

Fig. (7-9). Atomic absorption signal profiles of copper (taken as the nitrate) obtained using two different experimental conditions. Curve a is the atomic absorption signal profile of 1.50 ng copper obtained by operating the graphite furnace in the gas-interrupt mode. Curve b is the atomic absorption signal profile of 2.50 ng copper obtained in an Ar purge gas flow rate of 625 ml/min.

(7-10) for estimating the first-order rate constant for atom dissipation, k_2 . It is therefore reasonable to conclude that the β_2 values which are obtained by using β_1 values have greater uncertainties than the β_1 values. Hence, the β_2 values given in Table (7-3) should be considered only as reasonable estimates of β_2 .

On the basis of the definition of β_1 and β_2 , one would expect that the β_1 values would be much larger than the β_2 values. This has indeed been experimentally observed. The β_1 values reflect peak areas, whereas β_2 values reflect peak heights. Since peak areas are more often used in practical applications of atomic absorption spectrometry, β_1 values are of greater practical utility. Also, since the β_1 values are generally much larger than the β_2 values, the sensitivity of measurement obtained by use of the peak area would seem to be much greater than that obtained by use of the peak height under the experimental and instrumental conditions used in this work. For the Perkin-Elmer HGA 400 (used in this work) the above observations mean that the geometry (length) of the furnace makes for relatively large residence times [which arise from small k_2 values—see Table (7-2)], resulting in high peak-area sensitivity. However, the graphite tube of the HGA 400 is relatively long and therefore has a relatively large mass, which results in slow heating and relatively low peak-height sensitivity.

SUMMARY

The efficiency of the Perkin–Elmer HGA–400 for the production and containment of atomic vapour has been determined for eight elements by two methods which are different both in their definition and the way the atomization efficiency is determined. In Method 1, the atomization efficiency, β_1 , is defined as the fraction of the number of analyte atoms that are actually atomized, and is determined graphically using data points from an atomic absorption signal profile and plotting absorbance A versus integrated absorbance, $\int_t^\infty A \, dt$; the slope $-k_2 / \beta_1$ of a straight–line plot yields the atomizer efficiency β_1 . This method has the advantage of being based on the entire absorption signal profile rather than on any particular part of it, but has the disadvantage of having a relatively large uncertainty arising from estimating the rate constant for atom loss k_2 from the geometric length l of the graphite tube, which has pronounced temperature gradient, making the "effective" length shorter than the geometric length l . In Method 2, the atomization efficiency, β_2 , is defined as the fraction of the number of analyte atoms that are present as atomic vapour at the maximum of the atomic absorption signal, and is determined using the equation:

$$\beta_2 = \frac{\beta_1 A_m}{k_2 \int_0^\infty A \, dt}$$

where β_1 is as defined above, and A_m is the absorbance at the maximum of the atomic absorption signal profile. The β_2 values have greater uncertainties than the β_1 values and should be considered only as reasonable estimates of β_2 values.

Appendices

(A) SOLVE THE INTEGRAL $\int_0^t k_1 dt$ IN EQN (1-6), CHAPTER 2

Considering Eqn (1-4) of Chapter 1 the above integral can be written as $\int_0^t k_w \exp(-E_a/RT) dt$. The solution of this integral is greatly simplified if the absolute temperature is increased at a constant heating rate α , from an initial temperature T_i to the final temperature T :

$$T = \alpha (t_0 + t'') = \alpha t \quad (1A)$$

where t_0 is the time when the temperature of the tube wall is T_i , t'' is the time required for the temperature to increase from T_i to T , and t is the time if the heating were started at the absolute zero. Thus, one gets

$$\int_0^t k_w \exp(-E_a/RT) dt = \int_0^t k_w \exp\left(-\frac{\epsilon}{t}\right) dt \quad (2A)$$

where $\epsilon = E_a / \alpha R$. Let

$$x = -\frac{\epsilon}{t} \quad (3A)$$

Then,

$$dx = -\frac{\epsilon}{t^2} dt \quad (4A)$$

Substitute Eqn (3A) in Eqn (4A) for t

$$dt = - \frac{\epsilon}{x^2} dx \quad (5A)$$

Taking into account Eqns (3A), and (5A), one gets the following expression:

$$\int_0^t k_{\infty} \exp\left(-\frac{\epsilon}{t}\right) dt = \epsilon k_{\infty} \int_x^{\infty} x^{-2} e^{-x} dx \quad (6A)$$

From Mathematical Tables one has

$$\int_x^{\infty} x^{\nu-1} e^{-\mu x} dx = \mu^{-\nu} \Gamma(\nu, \mu x) \quad (7A)$$

Therefore,

$$\int_0^t k_{\infty} \exp\left(-\frac{\epsilon}{t}\right) dt = \epsilon k_{\infty} \Gamma(-1, x) \quad (8A)$$

Again, from Mathematical Tables one has

$$\Gamma(-n, x) = \frac{(-1)^n}{n!} \left\{ E_1(x) - e^{-x} \left(\sum_{n=0}^{n-1} \frac{n! (-1)^n}{x^{n+1}} \right) \right\} \quad (9A)$$

where

$$E_1(x) = \Gamma(0, x) \quad (10A)$$

For $n = 1$, Eqn (9A) becomes

$$\Gamma(-1, x) = x^{-1} e^{-x} - E_1(x) \quad (11A)$$

The solution for $E_1(x)$ can be obtained from Mathematical Tables as follows:

$$E_1(x) = x^{-1} e^{-x} \left(\sum_{J=0}^{\infty} \frac{(-1)^J J!}{x^J} \right) \quad (12A)$$

Substituting Eqn (12A) into Eqn (11A) one gets

$$\Gamma(-1, x) = x^{-1} e^{-x} - x^{-1} e^{-x} \left(\sum_{J=0}^{\infty} \frac{(-1)^J J!}{x^J} \right) \quad (13A)$$

If $x \gg 1$

$$\Gamma(-1, x) = x^{-2} e^{-x} \quad (14A)$$

Substituting Eqn (14A) in Eqn (8A) and considering Eqn (2A) one gets

$$\int_0^t k_{\infty} \exp\left(-\frac{\epsilon}{t}\right) dt = T^2 \left(\frac{Rk_{\infty}}{\alpha E_a} \right) \exp\left(-\frac{E_a}{RT}\right) \quad (15A)$$

A similar treatment has been published in the literature [32].

(B) ATOM FORMATION UNDER NON-ISOTHERMAL AND ISOTHERMAL CONDITIONS

(a) *Atom formation under non-isothermal conditions.* Integrating both sides of Eqn (1-3), mentioned in Chapter 1, subject to the boundary conditions that $N_w = N_0$ at $t = 0$ and N_w at time t , one gets:

$$\int_{N_0}^{N_w} N_w^{-1} dN_w = - \int_0^t k_1 dt \quad (1B)$$

where k_1 is the rate constant assumed to be approximated by the Arrhenius law. Equation (1B) can be solved to yield:

$$N_w = N_0 \exp \left(- \int_0^t k_1 dt \right) \quad (2B)$$

Substituting Eqn (2B) in Eqn (1-3), Chapter 1, one gets the following expression for the rate of atom formation $S(t)$:

$$S(t) = k_1 N_0 \exp \left(- \int_0^t k_1 dt \right) \quad (3B)$$

After differentiating both sides of Eqn (3B) with respect to time at constant heating rate α , and considering that, $dS(t)/dt = 0$, one gets the following expression for k_1 ,

$$k_m = \left(\frac{\alpha E_a}{RT_m^2} \right) \quad (4B)$$

which upon substituting back into Eqn (3B) yields,

$$S_m = \left(\frac{\alpha E_a}{RT_m^2} \right) N_0 \exp \left(- \int_0^{t_m} k_1 dt \right) \quad (5B)$$

where the subscript m indicates a value at the maximum of $S(t)$. Equation (5B) shows that under non-isothermal conditions the supply function must *have a maximum*.

(b) *Atom formation under constant temperature (isothermal)*. For the atomization under a constant temperature, the rate constant in Eqn (1-3) remains constant during atom formation. Hence, upon performing similar treatments as mentioned above (for atomization under non-isothermal conditions) one gets the following equation for $S(t)$:

$$S(t) = k_1 N_0 \exp \left(-k_1 t \right) \quad (6B)$$

Differentiating Eqn (6B) with respect to time and setting the derivative equal to zero yields no solution for $S(t)$, i.e., $k_m = 0$. Hence, the shape of $S(t)$, i. e., the absorbance signal measured under isothermal conditions *has no maximum*.

(C) SOLUTION FOR N_w BY INTEGRATION OF EQN (2-3), CHAPTER 2

Insertion of the Arrhenius equation into Eqn (2-3) and integration from $t = 0$ to time t with the boundary condition that $N_w = N_0$ at $t = 0$ and N_w at time t yields:

$$- \int_{N_0}^{N_w} \frac{dN_w}{N_w^n} = \int_0^t n k_1 dt \quad (1C)$$

which can be solved for $n \neq 1$ and $n \neq 0$ to give

$$-\frac{1}{1-n} \left(N_w^{1-n} - N_o^{1-n} \right) = \int_0^t n k_1 dt \quad (2C)$$

Rearranging terms in Eqn (2C) one gets

$$N_w^{1-n} = N_o^{1-n} + n(n-1) \int_0^t k_1 dt \quad (3C)$$

Taking N_o^{1-n} as a common factor in the right hand side one gets

$$N_w^{1-n} = N_o^{1-n} \left(1 + n(n-1) N_o^{n-1} \int_0^t k_1 dt \right) \quad (4C)$$

Raising both sides of Eqn (4C) to the power $n/(1-n)$ yields the following equation:

$$N_w^n = N_o^n \left(1 + n(n-1) N_o^{n-1} \int_0^t k_1 dt \right)^{n/(1-n)} \quad (5C)$$

(D) DERIVATION OF EQN (2-39), CHAPTER 2

Starting with Eqn (2-14) of Chapter 2,

$$-\ln \left(\frac{\int_t^\infty A dt}{\int_0^\infty A dt} \right) = T^2 \left(\frac{Rk_\infty}{\alpha E_a} \right) \exp \left(-\frac{E_a}{RT} \right) \quad (1D)$$

Substituting k_1 given by the Arrhenius law,

$$k_1 = k_{\infty} \exp \left(-\frac{E_a}{RT} \right) \quad (2D)$$

into Eqn (1D) one gets

$$-\ln \left(\frac{\int_t^{\infty} A \, dt}{\int_0^{\infty} A \, dt} \right) = T^2 \left(\frac{R}{\alpha E_a} \right) k_1 \quad (3D)$$

Recognizing that, under the gas-flow mode of operation, the first order rate constant of atom formation, k_1 , can be expressed by the following equation [see Eqn (2-11), Chapter 2]:

$$k_1 = \frac{A}{\int_t^{\infty} A \, dt} \quad (4D)$$

which upon substituting into Eqn (3B) for k_1 one gets

$$-\ln \left(\frac{\int_t^{\infty} A \, dt}{\int_0^{\infty} A \, dt} \right) = T^2 \left(\frac{R}{\alpha E_a} \right) \left(\frac{A}{\int_t^{\infty} A \, dt} \right) \quad (5D)$$

Rearranging terms in Eqn (5D) one has the following expression for the activation energy, E_a :

$$E_a = - \frac{A R T^2}{\alpha \int_t^{\infty} A dt \ln \left(\frac{\int_t^{\infty} A dt}{\int_t^{\infty} A dt} \right)} \quad (6D)$$

(E) VALUE OF THE RATE CONSTANT AT THE ABSORBANCE MAXIMUM

The rate constant can be evaluated by substituting Eqn (5-8) into Eqn (5-3), both given in Chapter 5, and using the Arrhenius equation to yield the following equation:

$$A = \beta Q n k_1 \sigma_0^n \left(1 + n (n-1) \sigma_0^{n-1} \int_0^t k_1 dt \right)^{n/(1-n)} \quad (1E)$$

To simplify the differentiation we take the logarithm of both sides of Eqn (1E) to obtain:

$$\log A = \log (\beta Q n \sigma_0^n) + \log k_1 + \frac{n}{1-n} \log \left(1 + n (n-1) \sigma_0^{n-1} \int_0^t k_1 dt \right) \quad (2E)$$

On differentiating Eqn (2E) one gets:

$$\frac{1}{A} \frac{dA}{dt} = \frac{1}{k_1} \frac{dk_1}{dt} - \frac{n^2 \sigma_0^{n-1} k_1}{1 + n (n-1) \sigma_0^{n-1} \int_0^t k_1 dt} \quad (3E)$$

Realizing that at the absorbance maximum $dA/dt = 0$ and that dk_1/dt in Eqn (3E)

can be obtained from the Arrhenius equation at a constant heating rate, which is equal to $[\alpha E_a / (RT^2)] k_1$, one gets the following expression for the rate constant at the absorbance maximum:

$$k_m = \left(\frac{\alpha E_a}{RT_m^2} \right) \left(\frac{1 + n(n-1) \sigma_0^{n-1} \int_0^{t_m} k_1 dt}{n^2 \sigma_0^{n-1}} \right) \quad (4E)$$

where the subscript, m , indicates that the value corresponds to the peak absorbance.

(F) DERIVATION OF EQN (5-13), CHAPTER, 5

For $n = 1$, and using the Arrhenius equation, Eqn (5-1) of Chapter 5 can be simplified to Eqn (1F),

$$-\frac{d\sigma}{dt} = k_1 \sigma \quad (1F)$$

Integrating Eqn (1F), subject to the boundary conditions that $\sigma = \sigma_0$ at time $t = 0$ and σ at time t one has

$$-\int_{\sigma_0}^{\sigma} \frac{d\sigma}{\sigma} = \int_0^t k_1 dt \quad (2F)$$

which can be solved for σ to yield

$$\sigma = \sigma_0 \exp \left(- \int_0^t k_1 dt \right) \quad (3F)$$

Substituting Eqn (3F) into Eqn (1F)

$$-\frac{d\sigma}{dt} = \sigma_0 k_1 \exp \left(- \int_0^t k_1 dt \right) \quad (4F)$$

and then substituting Eqn (4F) into Eqn (5-3), Chapter 5, one has

$$A = \beta Q \sigma_0 k_1 \exp \left(- \int_0^t k_1 dt \right) \quad (5F)$$

Applying similar treatment as in Appendix E i.e. differentiating the logarithmic form of Eqn (5F) as follows:

$$\frac{dA}{dt} = \frac{1}{k_1} \frac{dk_1}{dt} - k_1 \quad (6F)$$

and setting $dA/dt = 0$ at the absorbance maximum to yield

$$k_m^2 = \frac{dk_m}{dt} \quad (7F)$$

where the subscript m indicates that the value corresponds to the absorbance maximum. The derivative dk_m/dt in Eqn (7F) can be obtained by differentiating the Arrhenius equation at a constant heating rate to yield:

$$\frac{dk_1}{dt} = \left(\frac{\alpha E_a}{RT^2} \right) k_1 \quad (8F)$$

Taking the value of $d k_1/dt$ at the absorbance maximum and combining with Eqn (7F), one obtains (for $n = 1$) the following expression for the rate constant k_m :

$$k_m = \left(\frac{\alpha E_a}{RT^2} \right) \quad (9F)$$

Equating Eqn (9F) with Eqn (5-6), Chapter 5, and rearranging terms one has Eqn (10F) for $n = 1$:

$$A_m T_m^2 = \left(\frac{\alpha E_a}{R} \right) \int_{t_m}^{\infty} A dt \quad (10F)$$

Taking logarithm of both sides of Eqn (10F) one gets the following expression:

$$\log (A_m T_m^2) = \log \int_{t_m}^{\infty} A dt + \log \left(\frac{\alpha E_a}{R} \right) \quad (11F)$$

where $\log (\alpha E_a / R)$ is a constant for a given set of experimental conditions.

(G) DERIVATION OF EQN (5-14), CHAPTER 5

Taking logarithm of both sides of Eqn (5-7), Chapter 5, and differentiating with respect to time one has

$$\frac{1}{k_1} \frac{dk_1}{dt} = \frac{1}{A} \frac{dA}{dt} - \left(\frac{n}{\int_t^{\infty} A dt} \right) \left(\frac{d}{dt} \int_t^{\infty} A dt \right) \quad (1G)$$

Using the boundary condition that $A = A$ at time t and $A = 0$ at $t = \infty$, Eqn (1G) becomes

$$\frac{1}{k_1} \frac{dk_1}{dt} = \frac{1}{A} \frac{dA}{dt} + \left(\frac{n A}{\int_t^\infty A dt} \right) \quad (2G)$$

At the absorbance maximum, $dA/dt = 0$, hence Eqn (2G) yields

$$n_m = \frac{1}{k_m} \frac{dk_m}{dt} \left(\frac{\int_{t_m}^\infty A dt}{A_m} \right) \quad (3G)$$

where the subscript m indicates that the values correspond to the absorbance maximum. The derivative dk_m/dt is obtained by differentiating the Arrhenius equation at a constant heating rate as follows:

$$\frac{dk_m}{dt} = \left(\frac{\alpha E_a}{RT_m^2} \right) k_m \quad (4G)$$

Substituting Eqn (4G) into Eqn (3G) one gets the following expression for the order of reaction:

$$n_m = \left(\frac{\alpha E_a}{RT_m^2} \right) \left(\frac{\int_{t_m}^\infty A dt}{A_m} \right) \quad (5G)$$

(H) DERIVATION OF SMETS EQUATION UNDER THE GAS-INTERRUPT MODE OF OPERATION

Smets [10] has derived his equation relating the rate constant of atom formation to the absorbance signal from the following general equation:

$$\frac{dN_g}{dt} = R_{\text{form}} - R_{\text{diss}} \quad (1H)$$

where dN_g / dt is the rate of change in the number of gaseous analyte atoms N_g in the atomizer, R_{form} is the rate of analyte atom formation and R_{diss} is the rate of analyte atom dissipation. Smets [10] has assumed that the two rates of atom formation and of atom dissipation follow first-order kinetics, and has rewritten Eqn (1H) as follows:

$$\frac{dN_g}{dt} = k_1 N_w - k_2 N_g \quad (2H)$$

where k_1 and k_2 are rate constants of atom formation and atom loss, respectively, N_w is the number of unatomized analyte atoms.

The integrated rate of atom formation has been assumed to be directly proportional to the number of analyte atoms initially deposited in the graphite furnace, N_0 , as given by the following expression:

$$\int_0^{\infty} R_{\text{form}} dt = \beta N_0 \quad (3H)$$

where β is atomization efficiency, defined as the fraction of analyte atoms which are

in fact atomized [10]. Similarly,

$$\int_0^t R_{\text{form}} dt = \beta (N_o - N_w) \quad (4H)$$

where $(N_o - N_w)$ represents the number of analyte atoms in the gas phase [10, 37].

Smets [10] has further assumed that, for the strip heater (used by him), during all stages of atom formation, the rate of disappearance is approximately equal to the rate of atom formation (i. e. $dN_g / dt = 0$). Other authors [11] have assumed that a local thermodynamic equilibrium between the analyte atomic vapour and the condensed phase prevails over the entire duration of the atom formation similar to that prevailing during vaporization from a Langmuirian film. Under these conditions one gets for Eqn (1H),

$$R_{\text{form}} = R_{\text{diss}} \quad (5H)$$

and for Eqn (2H),

$$k_1 N_w = k_2 N_g$$

or,

$$k_1 = k_2 \frac{N_g}{N_w} \quad (6H)$$

At this stage one may address the following question: How can one account for the

observed absorbance signal if an equilibrium is established during atom formation? To answer this question one has to fall back on the expression of the pressure equilibrium constant K_p which may be written according to Eqn (6H) as:

$$K_p = p_{N_g} \quad (7H)$$

where K_p is equal to k_1 / k_2 for elementary reactions. Since, K_p increases with temperature for endothermic reactions ($\ln K_p = -\Delta H^\circ/RT + \Delta S^\circ/R$), pressure of the analyte atomic vapour will increase resulting in increased absorbance. Upon integrating both sides of Eqn (5H) from $t = 0$ to t one gets the following equation [10, 37]:

$$\int_0^t R_{form} dt = \langle k_2 \rangle \int_0^t N_g dt \quad (8H)$$

Similarly, upon integrating Eqn (5H) from $t = 0$ to $t = 1$, one gets

$$\int_0^\infty R_{form} dt = \langle k_2 \rangle \int_0^\infty N_g dt \quad (9H)$$

where $\langle k_2 \rangle$ and $\langle k_2 \rangle$ are the mean values of k_2 over the indicated time intervals (assumed to be constant within 10% [10, 37]) as defined by the following two equations [10]:

$$\langle k_2 \rangle = \frac{\int_0^t k_2 N_g dt}{\int_0^t N_g dt} \quad (10H)$$

and

$$>k_2< = \frac{\int_0^\infty k_2 N_g dt}{\int_0^\infty N_g dt} \quad (11H)$$

The number of analyte atoms left unatomized on the graphite tube wall, N_w , is given by

$$N_w = N_o - N_g \quad (12H)$$

Substituting Eqns (8H) and (9H) into Eqn (12H) and taking into account Eqns (3H) and (4H) one gets,

$$N_w = \frac{1}{Q \beta_1} \left(>k_2< \int_0^\infty A dt - \langle k_2 \rangle \int_0^t A dt \right) \quad (13H)$$

where Q is a constant relating the absorbance A to the number of analyte atoms in the atomizer. If $k_2 = \langle k_2 \rangle = >k_2<$, then

$$N_w = \frac{k_2}{Q \beta_1} \int_t^\infty A dt \quad (14H)$$

The relationship between the number of unatomized analyte atoms N_w and the integrated absorbance signal $\int_t^{\infty} A \, dt$ expressed by Eqn (14H) has been published in the literature [10, 14, 37, 11]. It is of interest to note that the Smets equation [10] is obtained by substituting Eqn (14H) into Eqn (6H) for N_w and using the relationship between A and N_g (i. e., A / Q for N_g) to yield

$$k_1 = \frac{k_2 A / Q}{(k_2 / Q \beta_1) \int_t^{\infty} A \, dt} \quad (15H)$$

which, after rearrangement and cancellation of common terms in Eqn (15H), becomes

$$k_1 = \beta_1 \left(\frac{A}{\int_t^{\infty} A \, dt} \right) \quad (16H)$$

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