THERMODYNAMICS OF MAGNESIUM IN LIQUID NICKEL SOLUTIONS

by

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Abstract

A novel experimental method to determine the activity of alloy components in very dilute liquid metal solutions has been developed. The method is applied to the measurement of magnesium vapour pressure over nickel alloys to find the thermodynamic properties of magnesium in dilute liquid solutions at 1470°C. The experimental method employs a commercial Atomic Absorption Spectrophotometer to determine directly the vapour pressure of magnesium over the alloys. A radiatively heated Knudsen cell inside a vacuum system contains the metal.

Equilibrium constants are given for the reactions,

\[
\text{Mg(g)} + 2 \text{Al(\%)} + 4 \text{O(\%)} \rightleftharpoons \text{MgO} \cdot \text{Al}_2\text{O}_3(\text{s})
\]

and

\[
\text{Mg(g)} \rightleftharpoons \text{Mg(\%)},
\]

where Al, O and Mg are dissolved in liquid nickel. Further, values for the metal-oxygen interaction coefficients \(e_{\text{Mg}}^0\) and \(e_{\text{Al}}^0\) are determined. Finally, a value for the Raoultian activity coefficient at infinite dilution is suggested. A significant change in the activity of magnesium upon the addition of 20% chromium or iron to the dilute liquid nickel
alloys was not detected. This is believed due to overpowering magnesium-
oxygen interaction at these levels of chromium and iron.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>iv</td>
</tr>
<tr>
<td>List of Tables</td>
<td>viii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>x</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>xiv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>xvi</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Literature Review</td>
<td>4</td>
</tr>
<tr>
<td>2.1 Magnesium in Superalloys</td>
<td>4</td>
</tr>
<tr>
<td>2.1.1 Melting Practice</td>
<td>6</td>
</tr>
<tr>
<td>2.1.1.1 Vacuum Induction Melting</td>
<td>6</td>
</tr>
<tr>
<td>2.1.1.2 Vacuum Arc Remelting</td>
<td>8</td>
</tr>
<tr>
<td>2.1.1.3 Electro Slag Remelting</td>
<td>10</td>
</tr>
<tr>
<td>2.1.1.4 Electron Beam Melting</td>
<td>11</td>
</tr>
<tr>
<td>2.1.2 Alloy Properties</td>
<td>15</td>
</tr>
<tr>
<td>2.1.2.1 Hot Working</td>
<td>15</td>
</tr>
<tr>
<td>2.1.2.2 Weldability</td>
<td>20</td>
</tr>
<tr>
<td>2.1.2.3 Mechanical Properties</td>
<td>20</td>
</tr>
<tr>
<td>2.2 Atomic Absorption Studies of Vapour over Condensed Phases</td>
<td>23</td>
</tr>
<tr>
<td>2.2.1 Herbenar et al.</td>
<td>23</td>
</tr>
<tr>
<td>2.2.2 Scatchard et al.</td>
<td>26</td>
</tr>
<tr>
<td>2.2.3 Vidale</td>
<td>27</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>2.2.4</td>
<td>Brebrick and Strauss</td>
</tr>
<tr>
<td>2.2.5</td>
<td>Raperport and Pemsler</td>
</tr>
<tr>
<td>2.2.6</td>
<td>Masson et al.</td>
</tr>
<tr>
<td>2.2.7</td>
<td>Eliutin and Timofeev</td>
</tr>
<tr>
<td>2.3</td>
<td>High Temperature Experimental Methods</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Knudsen Cell Methods</td>
</tr>
<tr>
<td>2.3.1.1</td>
<td>Heating and Temperature Measurement</td>
</tr>
<tr>
<td>2.3.1.2</td>
<td>Detection Methods</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Pseudoisopiestic Method</td>
</tr>
<tr>
<td>2.4</td>
<td>Thermodynamic Data</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Background</td>
</tr>
<tr>
<td>2.4.2</td>
<td>The Pure Elements Ni, Mg, Ca and Al</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Magnesium and Calcium in Nickel and Iron Alloys</td>
</tr>
<tr>
<td>2.4.4</td>
<td>Deoxidation Equilibrium</td>
</tr>
<tr>
<td>2.4.4.1</td>
<td>Magnesium and Calcium</td>
</tr>
<tr>
<td>2.4.4.2</td>
<td>Aluminum</td>
</tr>
<tr>
<td>3.</td>
<td>Experimental Work</td>
</tr>
<tr>
<td>3.1</td>
<td>Equipment</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Atomic Absorption Spectrophotometer</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Vacuum System</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Furnace</td>
</tr>
<tr>
<td>3.1.4</td>
<td>Knudsen Cells</td>
</tr>
<tr>
<td>3.1.5</td>
<td>Temperature Determination</td>
</tr>
<tr>
<td>3.2</td>
<td>Materials</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Basic Alloys</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.2.2 Tin Alloys</td>
<td>89</td>
</tr>
<tr>
<td>3.2.3 Nickel Alloys</td>
<td>92</td>
</tr>
<tr>
<td>3.3 Experimental Procedure</td>
<td>93</td>
</tr>
<tr>
<td>3.4 Calibration</td>
<td>94</td>
</tr>
<tr>
<td>3.5 Test of the Method</td>
<td>95</td>
</tr>
<tr>
<td>3.6 Nickel Alloy Experiments</td>
<td>96</td>
</tr>
<tr>
<td>3.7 Chemical Analysis</td>
<td>96</td>
</tr>
<tr>
<td>4. Results and Discussion</td>
<td>98</td>
</tr>
<tr>
<td>4.1 Calibration</td>
<td>98</td>
</tr>
<tr>
<td>4.1.1 Cause of Discrepancies</td>
<td>103</td>
</tr>
<tr>
<td>4.2 Test of Method on Tin Alloys</td>
<td>107</td>
</tr>
<tr>
<td>4.3 Nickel Alloys</td>
<td>112</td>
</tr>
<tr>
<td>4.3.1 Preliminary Results</td>
<td>112</td>
</tr>
<tr>
<td>4.3.2 Applicable Equilibriums</td>
<td>112</td>
</tr>
<tr>
<td>4.3.3 Statistical Model</td>
<td>116</td>
</tr>
<tr>
<td>4.3.3.1 Equilibrium Constant</td>
<td>120</td>
</tr>
<tr>
<td>4.3.3.2 Interaction Coefficients</td>
<td>125</td>
</tr>
<tr>
<td>4.3.4 Energy of Solution</td>
<td>126</td>
</tr>
<tr>
<td>4.3.5 Raoultian Activity Coefficient</td>
<td>127</td>
</tr>
<tr>
<td>4.4 Alloys Containing Chromium and Iron</td>
<td>129</td>
</tr>
<tr>
<td>5. Conclusions</td>
<td>132</td>
</tr>
<tr>
<td>6. Suggestions for Further Work</td>
<td>134</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Chapter 2

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Examples of Nickel Base Superalloys and Their Applications</td>
</tr>
<tr>
<td>2.2</td>
<td>Summary of Atomic Absorption Studies of Vapour Pressure over Condensed Phases</td>
</tr>
<tr>
<td>2.3</td>
<td>Data for the Pure Elements</td>
</tr>
<tr>
<td>2.4</td>
<td>Behaviour of Deoxidizers and Oxygen at Infinite Dilution in Liquid Iron</td>
</tr>
<tr>
<td>2.5</td>
<td>Behaviour of Deoxidizers and Oxygen at Infinite Dilution in Liquid Nickel</td>
</tr>
<tr>
<td>2.6</td>
<td>First Order Interaction Coefficients, $e_j^f$, in Liquid Iron at 1600°C</td>
</tr>
<tr>
<td>2.7</td>
<td>First Order Interaction Coefficients, $e_i^f$ in Liquid Nickel at 1600°C</td>
</tr>
<tr>
<td>2.8</td>
<td>Deoxidation Equilibria in Iron Alloys</td>
</tr>
<tr>
<td>2.9</td>
<td>Deoxidation Equilibria in Nickel Alloys</td>
</tr>
</tbody>
</table>

Chapter 3

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Summary of Thermocouple Types used</td>
</tr>
<tr>
<td>3.2</td>
<td>Basic Alloys used in This Project</td>
</tr>
</tbody>
</table>

Chapter 4

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Results of Calibration Measurements with Pure Mg, using a Standard Knudsen Cell</td>
</tr>
<tr>
<td>4.2</td>
<td>Results of Calibration Measurements with Pure Mg, using an Isopiestic Cell. Orifice Temperature = 900°C</td>
</tr>
</tbody>
</table>
### Chapter 4 (Cont'd)

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3 Results of Calibration Measurements with Pure Mg, using and Isopiestic Cell Orifice Temperature = 1470°C.</td>
<td>101</td>
</tr>
<tr>
<td>4.4 Summary of Sn-Mg Experiments</td>
<td>109</td>
</tr>
<tr>
<td>4.5 Data from Nickel-Magnesium Experiments</td>
<td>117</td>
</tr>
<tr>
<td>4.6 $\gamma^o$ from Experimental Data</td>
<td>130</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Chapter 1

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Secondary Ion Mass Spectrometry (SIMS) dot maps of a polished nickel alloy (superalloy 718) surface showing the relative concentrations of the following ions: a) (^{24}\text{Mg}^+), b) (^{32}\text{S}^-), c) (^{16}\text{O}^-) and d) (^{27}\text{Al}^+).</td>
</tr>
</tbody>
</table>

Chapter 2

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Variation of oxygen activity (a_o) and total oxygen content (O_T) during vacuum induction melting of alloy 718 using virgin and revert charges; md, melt-down; r, end of refining period; other symbols on horizontal axis represent element additions to melt.</td>
</tr>
<tr>
<td>2.2</td>
<td>Reduction in melt sulphur content ([S]) over vacuum induction melting period.</td>
</tr>
<tr>
<td>2.3</td>
<td>Effect of MgO content in the ESR slag on Mg content in produced ESR ingots.</td>
</tr>
<tr>
<td>2.4</td>
<td>The hot ductility of Waspaloy billets with and without magnesium additions. RA% = Percent area reduction.</td>
</tr>
<tr>
<td>2.5</td>
<td>Effect of Ca and Mg additions and S content on hot ductility of Inconel 600.</td>
</tr>
<tr>
<td>2.6</td>
<td>Effect of Mg (a) or Ca (b) on hot tensile ductility of Ni-based alloys.</td>
</tr>
<tr>
<td>2.7</td>
<td>Variation of S/Ni intensity ratio as function of distance from intergranular fracture surface for various Inconel 600 alloys.</td>
</tr>
<tr>
<td>2.8</td>
<td>Inconel 718 microfissuring susceptibility versus magnesium content.</td>
</tr>
<tr>
<td>2.9</td>
<td>(a) Transparent quartz absorption vessel and (b) heating furnace.</td>
</tr>
</tbody>
</table>
Chapter 2  (Cont'd)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10</td>
<td>Optical path diagram</td>
<td>28</td>
</tr>
<tr>
<td>2.11</td>
<td>Cross sectional diagram of cell and furnace</td>
<td>29</td>
</tr>
<tr>
<td>2.12</td>
<td>Diagram showing the correlation between three sets of experiments, A, B and C presented by Vidale, according to equation 2.1</td>
<td>31</td>
</tr>
<tr>
<td>2.13</td>
<td>Typical Knudsen cells. (a) Tungsten cell. (b) Cell used with vacuum balance. (c) Cell with thermocouple and near-ideal orifice. (d) Knudsen's original apparatus for determining the vapour pressure of mercury</td>
<td>37</td>
</tr>
<tr>
<td>2.14</td>
<td>An apparatus for effusion studies by the collection technique</td>
<td>42</td>
</tr>
<tr>
<td>2.15</td>
<td>Some torsion-effusion cells. (a) Two-temperature cell made of fused alumina. The lower reservoir is made of Corning No. 7280 glass, fused directly to the alumina upper part. (b) Opposed-orifice cell for comparing vapour pressures of two systems. (c) Four-orifice cell machined from graphite. (d) Welded tantalum cell, showing removable yoke for suspending it from the torsion wire. (e) Demountable two-section cell, with 0.5 in. overlap to be suspended similarly to (d)</td>
<td>43</td>
</tr>
<tr>
<td>2.16</td>
<td>Twin crucible effusion source</td>
<td>46</td>
</tr>
<tr>
<td>2.17</td>
<td>Schematic of an &quot;isopiestic balance&quot;</td>
<td>48</td>
</tr>
<tr>
<td>2.18</td>
<td>Isopiestic equilibration tube</td>
<td>49</td>
</tr>
<tr>
<td>2.19</td>
<td>The magnesium-iron binary phase diagram</td>
<td>56</td>
</tr>
<tr>
<td>2.20</td>
<td>The magnesium-nickel binary phase diagram</td>
<td>57</td>
</tr>
<tr>
<td>2.21</td>
<td>Schematic calcium-iron binary phase diagram</td>
<td>58</td>
</tr>
<tr>
<td>2.22</td>
<td>The calcium-nickel binary phase diagram</td>
<td>59</td>
</tr>
</tbody>
</table>
## Chapter 2 (Cont'd)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.23</td>
<td>Activity of calcium in some Ni-Ca and Ni-Fe-Ca alloys as a function of the molar fraction of calcium</td>
<td>61</td>
</tr>
<tr>
<td>2.24</td>
<td>Activity of magnesium in nickel-magnesium binary alloys</td>
<td>62</td>
</tr>
<tr>
<td>2.25</td>
<td>Estimated liquidus surface in Fe-Ni-Mg system and range of magnesium-rich phases observed after solidification of Fe-Ni alloys</td>
<td>64</td>
</tr>
<tr>
<td>2.26</td>
<td>Estimated activity of magnesium in the Fe-Ni-Mg system</td>
<td>65</td>
</tr>
<tr>
<td>2.27</td>
<td>Estimated theoretical and effective solubility of magnesium in nickel alloys based on Figure 2.26 and experiments</td>
<td>66</td>
</tr>
<tr>
<td>2.28</td>
<td>Solubility of oxygen vs (a) aluminum, (b) titanium, and (c) vanadium contents. The curves are calculated on the basis of a first order interaction formalism with (a) $\epsilon_{\text{Al}} = -360$, (b) $\epsilon_{\text{Ti}} = -87$, (c) $\epsilon_{\text{V}} = -27.7$. The points are from experimental work</td>
<td>68</td>
</tr>
<tr>
<td>2.29</td>
<td>(a) Calculated equilibrium contents of oxygen and magnesium in iron. (b) Actual oxygen and magnesium contents in iron. 1- Mg introduced in a methane stream and 2- in an air stream</td>
<td>75</td>
</tr>
</tbody>
</table>

## Chapter 3

3.1 The experimental furnace and vacuum system in position in the Atomic Absorption Spectrophotometer | 77 |

3.2 Block diagram of an Atomic Absorption Spectrophotometer. Emission from the line source is split into sample and reference beams, then recombined and passed through monochromator. Signal from photo-detector is amplified and fed into circuitry which produces a manual electronic null. The sampling burner is replaced by the vacuum bell-jar in this study | 78 |

3.3 Schematic drawing of the vacuum bell-jar containing the molybdenum resistance furnace | 80 |
Chapter 3 (Cont'd)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4 Molybdenum Knudsen cell</td>
<td>83</td>
</tr>
<tr>
<td>3.5 Alumina Knudsen cell</td>
<td>84</td>
</tr>
<tr>
<td>3.6 Isopiestic Knudsen cell</td>
<td>85</td>
</tr>
<tr>
<td>3.7 Arrangement of thermocouples in the magnesium slug used for calibration. Measurements in mm.</td>
<td>90</td>
</tr>
</tbody>
</table>

Chapter 4

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Summary of calibration experiments</td>
<td>102</td>
</tr>
<tr>
<td>4.2 The relationship between oxygen partial pressures and compositions for the Ti-0 and Zr-0 systems at 1000°C</td>
<td>105</td>
</tr>
<tr>
<td>4.3 Results of the test experiments on tin alloys</td>
<td>108</td>
</tr>
<tr>
<td>4.4 Calculated vapour pressures using equation 4.14 versus experimental results</td>
<td>119</td>
</tr>
<tr>
<td>4.5 Surface plot from results calculated using equation 4.14, for Mg contents up to 100 ppm and Al contents up to 500 ppm. (Minor variations evident in the lower part of the plot are artificial and due to that a finite number of points were used to produce the plot)</td>
<td>121</td>
</tr>
<tr>
<td>4.6 Contour map showing the content of oxygen as a function of magnesium and aluminum content. Experimental points: x 17-19 ppm 0, o 20-25 ppm 0, * 26-30 ppm 0. Experiment numbers, see Table 4.5.</td>
<td>122</td>
</tr>
<tr>
<td>4.7 Area predominance diagram. Equations 1-5 are given in Appendix F. $P^Mg = 10^{-7}$, $P^Mg = 10^{-5}$ data from literature. $P^Mg = 10^{-6}$ suggested data.</td>
<td>124</td>
</tr>
<tr>
<td>4.8 Comparison between data for alloys containing no major additions and alloys containing 20% Fe or 20% Cr</td>
<td>131</td>
</tr>
</tbody>
</table>
NOMENCLATURE

A  Area
AAS  Atomic Absorption Spectrophotometry
a_i  Raoultian activity.
Al, O, Mg  Elements in liquid metal solution
B_0, B_1, B_2  Constants
c  Average molecular speed
C_1, C_2  Constants
d  Thickness of absorbing space, orifice diameter
d_0  Solid angle
EB  Electron Beam
EBCHR  Electron Beam Cold Hearth Refining
EDX  Energy Dispersive X-ray analysis
e_{j|i}  First order free energy interaction coefficient of j on i
         (Henrian)
ESR  Electro Slag Remelting
f_i  Henrian activity coefficient
h_i  Henrian activity
I_0, I  Intensity of AAS light beam before and after entering
         absorbing vapour
K  Absorption coefficient
K_{nn}  Equilibrium constant
MA      \text{MgO\cdotAl}_2\text{O}_3

M_i, M_j  \text{Molecular weight of i, j}

N/V      \text{Number of molecules per unit volume of the gas}

N(\theta)/Z_o \text{Probability}

p, p_i    \text{Vapour pressure, atm}

p_i^o     \text{Vapour pressure of pure element}

\%i, \%k  \text{Weight \% of i, k}

R         \text{Gas constant}

r_{j,k}^i \text{Second order interaction coefficient (Henrian)}

T         \text{Temperature, K, ^\circ C}

t         \text{time}

VAR      \text{Vacuum Arc Remelting}

VIM      \text{Vacuum Induction Melting}

w         \text{Weight loss}

X_i      \text{Molar fraction of component i}

a         \text{Evaporation or condensation coefficient}

\gamma_i, \gamma_i^o \text{Raoultian activity coefficient}

\varepsilon_j^i \text{First order free energy interaction coefficient of j on i, (Raoultian)}

\theta \text{Angle to normal}

\lambda \text{Mean free path}

\rho_{j,k}^i \text{Second order interaction coefficient (Raoultian)}

\sigma \text{Collision diameter of molecules}
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1. Introduction

Magnesium is an important alloying element in nickel base alloys for two major reasons. It is added to these alloys to improve the mechanical properties in the finished product. In addition, it enhances the hot ductility of the alloys, which is sometimes necessary for the fabrication process.

Nickel alloys with controlled additions of magnesium were patented in the early 1970's. One of these alloys exhibited an increased high temperature rupture life, and in the production of another alloy an expensive heat treatment cycle could be eliminated as a result of the magnesium content. Other benefits of magnesium additions, such as improved low cycle fatigue life, have since been suggested in the literature. Generally, the improvement of properties is achieved at a very low content of magnesium, less than 100 ppm and typically around 50 ppm.

The exact function of magnesium in the nickel alloys has not been established. It has been suggested that "the magnesium addition finishes any additional deoxidation of the superalloy, and then combines with residual sulphur to render the sulphur innocuous. Further, any remaining magnesium migrates to energy-lowering sites, such as grain boundaries and twin interfaces where it acts to prevent dislocation pileup and brittle behaviour by promoting dislocation tangling." The association of magnesium with oxygen and sulphur is clearly shown in Figure 1.1.
Figure 1.1 Secondary Ion Mass Spectrometry (SIMS) dot maps of a polished nickel alloy (superalloy 718) surface showing the relative concentrations of the following ions: a) $^{24}\text{Mg}^+$, b) $^{32}\text{S}^-$, c) $^{16}\text{O}^-$ and d) $^{27}\text{Al}^+$. 
Magnesium is added during primary melting, usually vacuum induction melting. The alloys are then subjected to secondary melting, most commonly Electro Slag (ESR) or Vacuum Arc (VAR) Remelting. Theoretical assessment of the magnesium content during melting has not been possible as thermodynamic data for magnesium in liquid nickel solutions have not been available. For instance, the distribution of magnesium between slag and metal during ESR melting has been difficult to calculate. With the introduction of Electron Beam Cold Hearth remelting of superalloys, the need to calculate evaporation rates of magnesium has become more urgent due to the large bath surface coupled with the low pressure utilized in the process. Such calculations require a knowledge of thermodynamic properties.

The objectives of this work are to develop an experimental method suitable for activity determinations for very dilute alloy components, such as magnesium in liquid nickel solutions, and to determine the basic thermodynamic properties of magnesium in liquid nickel alloys.

In this thesis, the pertinent literature is discussed in Chapter 2, a description of the experimental equipment and methods is given in Chapter 3, and the experimental results and mathematical treatment of the data are discussed in Chapter 4. Finally, the conclusions are presented in Chapter 5.
2. Literature Review

2.1 Magnesium in Superalloys

A superalloy has been defined by Sims and Hazel\(^1\) as "an alloy developed for elevated temperature service, usually based on group VIIIA elements, where relatively severe mechanical stressing is encountered and where high surface stability is frequently required". Hence, superalloys are mainly used in gas turbines, but also in space vehicles, nuclear reactors, petrochemical equipment and in other high temperature applications. Nickel-based superalloys are used, for instance, in many parts of aircraft gas turbines in both wrought and cast form. Some examples of nickel based superalloys and their applications are given in Table 2.1.

Magnesium is added to nickel-based superalloys to improve high temperature ductility. This property is important both from the manufacturing point of view, particularly in terms of open-die forgeability, and also from the in-service standpoint where rupture ductility is of primary importance. Further, it has been suggested that magnesium improves the low cycle fatigue strength\(^2\).
### TABLE 2.1. Examples of Nickel Base Superalloys and Their Applications

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Nb</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>B</th>
<th>Zr</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy Alloy X</td>
<td>47.3</td>
<td>22.0</td>
<td>1.5</td>
<td>9.0</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18.5</td>
<td>0.50</td>
<td>0.50</td>
<td>0.10</td>
<td>-</td>
<td>Wrought sheet alloy, used in combustion cans.</td>
<td></td>
</tr>
<tr>
<td>Inconel Alloy 718</td>
<td>53.0</td>
<td>18.6</td>
<td>-</td>
<td>3.1</td>
<td>-</td>
<td>5.0</td>
<td>0.4</td>
<td>0.9</td>
<td>18.5</td>
<td>0.20</td>
<td>0.30</td>
<td>0.04</td>
<td>-</td>
<td>Forged turbine discs</td>
<td></td>
</tr>
<tr>
<td>Waspalloy</td>
<td>58.3</td>
<td>19.5</td>
<td>13.5</td>
<td>4.3</td>
<td>-</td>
<td>1.3</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>0.006</td>
<td>0.06</td>
<td>Forged turbine discs</td>
</tr>
<tr>
<td>Udimet 500</td>
<td>52.0</td>
<td>18.0</td>
<td>19.0</td>
<td>4.2</td>
<td>-</td>
<td>3.0</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>0.007</td>
<td>0.05</td>
<td>Cast alloy used in turbine blades.</td>
</tr>
<tr>
<td>Rene 80</td>
<td>60.0</td>
<td>14.0</td>
<td>9.5</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.17</td>
<td>0.015</td>
<td>0.03</td>
<td>Cast alloy used in turbine blades.</td>
</tr>
</tbody>
</table>
1.1.1 Melting Practice

Melting of aerospace grade superalloys generally takes place in two or three steps. Cremisio has described the melting of superalloys in detail. The alloy is initially melted from scrap and/or virgin materials using Vacuum Induction Melting (VIM). The second step consists of either Vacuum Arc Remelting (VAR), Electro Slag Remelting (ESR) or Electron Beam (EB) Remelting. For some applications the metal is melted a third time, again utilizing either of the three remelting methods.

2.1.1.1 Vacuum Induction Melting

A typical VIM cycle starts with the charging of either virgin raw materials or scrap. Following the pumping down, the furnace contents are melted. When the metal is entirely molten and the bath stable, desulphurizing or deoxidizing additions are made. Finally, reactive elements are added, and when the bath composition is correct the melt is cast.

The change of oxygen and oxide content during a VIM melting sequence is illustrated by Figure 2.1. As can be seen, additions of aluminum and alkaline earth (AE) or rare earth (RE) metals decrease the activity and content of oxygen during the melting of a virgin heat. The
Figure 2.1 Variation of oxygen activity $a_0$ and total oxygen content $O_T$ during vacuum induction melting of alloy 718 using virgin and revert charges; md, melt-down; r, end of refining period; other symbols on horizontal axis represent element additions to melt.
increase of oxygen in the revert heat is probably due to pick-up from the refractories. In both cases however, the AE or RE additions help with the removal of oxygen-containing inclusions by the suggested mechanism of globurizing the alumina clusters.\(^4\)

Calcium, magnesium, and rare earth metals are also strong desulphurizing agents. Figure 2.2\(^4\) shows that the sulphur content can readily be reduced from ~150 ppm to ~10 ppm. The sulphide products deposit on the crucible walls. Hence, it is critical that the correct amount of desulphurizing agent can be predicted for each charge\(^4\).

Alexander\(^4\) suggests that the removal of magnesium from VIM melts is controlled by liquid mass transfer while Fu et al.\(^5\) suggest that the controlling steps are liquid mass transfer and the evaporation reaction. However, the latter were forced, for lack of better data, to assume that the activity of magnesium in nickel alloys is equal to the content. Clearly, additional data are required for more accurate analysis of the evaporation process during Vacuum Induction Melting.

2.1.1.2 Vacuum Arc Remelting

Aerospace grade superalloys are frequently produced via VIM and Vacuum Arc Remelting (VAR). VAR is basically consumable electrode melting under vacuum. Chemical interference from refractories is
Figure 2.2 Reduction in melt sulphur content [S] over vacuum induction melting period.
avoided as the solidification takes place in a water-cooled copper crucible. The sequence VIM-VAR combines the chemical control of the VIM process and the solidification control with low macro and micro-segregation of the VAR process.

Fu et al. investigated the evaporation of magnesium from a nickel-base superalloy during VAR. They found that magnesium evaporates mainly from the electrode tip. It was suggested that the evaporation rate is limited by the transport of magnesium through the melt to the surface. However, the analysis of the problem is limited by lack of fundamental data.

2.1.1.3 Electro Slag Remelting

The Electro Slag remelting process is similar to the VAR process in that both include consumable electrode melting into a water-cooled copper mould. In the ESR process the melting takes place through a resistance-heated slag. Thus, it is possible to control the ingot inclusion content and chemistry. The process is also an efficient desulphurizer. However, problems have been encountered in remelting titanium and aluminum-containing alloys as these elements tend to be lost in the slag during remelting.

Ichihashi et al. investigated the ability of the ESR process to
retain titanium, aluminum, and magnesium in the metal using different slag compositions. They show that increasing the contents of CaO and MgO will increase the content of magnesium in the ingot, as seen in Figure 2.3. They also suggest that titanium or aluminum can be lost to the slag through following reactions:

\[
3\text{MgO} + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Mg}
\]

\[
2\text{MgO} + \text{Ti} \rightarrow \text{TiO}_2 + 2\text{Mg}
\]

Simultaneously, these reactions would increase the magnesium content in the alloy. It may be noted that proper control of the reactive element content is dependent on a delicate balance between slag and metal chemistry. Ichihashi\textsuperscript{6} also found that magnesium can not be retained in the metal unless the slag is protected from air oxidation by an inert atmosphere, for instance argon. Generally, the conclusions of Chen et al\textsuperscript{7} agree with those of Ichihashi\textsuperscript{6}.

2.1.1.4 **Electron Beam Melting**

The Electron Beam melting process has recently emerged as another alternative for superalloy refining\textsuperscript{8}. The process, usually applied in the form of a Cold-Hearth Refining (EBCHR) furnace, offers more
Figure 2.3 Effect of MgO content in the ESR slag on Mg content in produced ESR ingots.
flexibility as to melting speed and ingot shape than the VAR process, since the heat source is independent of the charge material. However, the large area to volume ratio in the EBCHR process makes evaporation of alloying elements unavoidable. Hence, knowledge of the evaporation parameters of alloying elements is important if desired alloy compositions are to be produced.

Mitchell\textsuperscript{9} and Herbertson\textsuperscript{10} have discussed the evaporation of magnesium from superalloys during EBCHR refining. Mitchell\textsuperscript{9} suggests that the evaporation rate is controlled by the evaporation step and gives an evaporation rate constant of $2.5 \times 10^{-7} \text{ m s}^{-1}$ at 1700°C. On the other hand, Herbertson\textsuperscript{10} claims that the evaporation rate is controlled by bulk mass transfer and gives a Langmuir evaporation rate constant of $1.5 \times 10^{-1} \text{ m s}^{-1}$ at 1427°C. It appears that Herbertson\textsuperscript{10} has arrived at this value assuming an activity coefficient for magnesium in the liquid superalloy of unity. Using the suggested activity coefficient by Mitchell\textsuperscript{9} of $10^{-3}$ for magnesium in liquid nickel, one arrives at an evaporation rate constant of $1.2 \times 10^{-4} \text{ m s}^{-1}$ at 1427°C and $3.6 \times 10^{-4} \text{ m s}^{-1}$ at 1700°C\textsuperscript{11}. This would mean that magnesium evaporation is controlled by a combination of liquid mass transfer and evaporation. Hence, the activity coefficient is important in determining the rate-controlling step for evaporation during EBCHR refining.
Figure 2.4  The hot ductility of Waspaloy billets with and without magnesium additions. RA% = Percent area reduction.
2.1.2 **Alloy Properties**

In particular, small carefully controlled additions of magnesium greatly affect the hot workability of superalloys, as demonstrated for Waspalloy in Figure 2.4. It is suggested\(^3\) that "the magnesium addition finishes any additional deoxidation of the superalloy that can be achieved. In addition, magnesium combines with residual sulphur to render the sulphur innocuous. Finally, any remaining magnesium migrates to energy-lowering sites, such as grain boundaries and twin interfaces where it helps to prevent dislocation pileup and brittle behaviour by promoting dislocation tangling." Holt and Wallace\(^{12,13}\) have reviewed the influence of impurities and beneficial trace elements on the properties of nickel-base superalloys.

2.1.2.1 **Hot Working**

The ability of magnesium and calcium to counteract a relatively high content of sulphur is shown in Figure 2.5\(^{14}\). It also shows that excess alkaline earth metal indeed causes embrittlement of the alloy. This topic has been further investigated by deBarbadillo\(^{15}\). He shows that excess magnesium or calcium leads to the formation of intermetallic compounds, such as Ni\(_2\)Mg or Ni\(_5\)Ca. Particularly in the case of calcium these compounds occur as continuous intergranular films, causing severe hot and cold shortness. While equilibrium solubility is higher,
Figure 2.5  Effect of Ca and Mg additions and S content on hot ductility of Inconel 600. S, Ca, and Mg contents in ppm.
deBarbadillo\textsuperscript{15} found that due to severe segregation upon freezing the intergranular compounds occur already at solute concentrations of 0.05 weight percent. Turner\textsuperscript{16} points out that the malleability of nickel alloys is much more sensitive to excess Ca than excess Mg as seen in Figure 2.6. This is probably due to the ease of dissolution of Ni-Mg phases during heat treatment.

A marked increase in high temperature rupture life and ductility has been observed in magnesium treated nickel alloys\textsuperscript{17,18}. Schramm et al\textsuperscript{17} achieved increases in rupture life from 185 h to 1015 h and increases in area reduction from 32\% to 70\% for an addition of 350 ppm magnesium compared to an untreated alloy. The tests were done at 650°C (1200°F) and 4.8 \times 10^{8} \text{N/m}^{2} (70,000 \text{psi}). Muzyka and Whitney\textsuperscript{18} were able to eliminate an expensive heat treatment cycle to produce grains in the range of ASTM 6-8 by treating alloy 718 with magnesium. They found that alloys carefully treated with magnesium, calcium or neodymium attain roughly the same ductility for grain sizes coarser than ASTM 6 as untreated alloys for ASTM 6-8.

Yamaguchi et al\textsuperscript{19} suggest that optimum ductility can be achieved by keeping 0.003 > \Delta S > -0.004, where \Delta S = \%S - 0.8 \times \%Ca - 0.3 \times \%Mg - 0.5 \times \%Y - 0.1 \%Zr (\% = weight \%). They found that at \Delta S > 0.003 and a temperature of 950-1150°C fracture occurs intergranularly, and significant amounts of sulphur were segregated to the grain boundaries. Figure 2.7 also shows that no detectable segregation of sulphur occurs
Figure 2.6  Effect of Mg (a) or Ca (b) on hot tensile ductility of Ni-based alloys.  

- 18 -
Figure 2.7  Variation of S/Ni intensity ratio as function of distance from intergranular fracture surface for various Inconel 600 alloys."
in alloys treated with Mg or Ca. This is due to the formation of MgS and CaS which are present as inclusions in the nickel matrix.

2.1.2.2 **Weldability**

Morrison et al\textsuperscript{20} found that the tendency to microfissuring during welding of alloy 718 decreased with increasing magnesium content as shown in Figure 2.8. The decrease is suggested due to the formation of MgS, eliminating harmful effects of free sulphur. However, Gittos and Scott\textsuperscript{21} claim in a review paper that the effects of Mg on weld cracking are variable. This, they suggest, could be due to the existence of critical ranges within which an element is harmful.

2.1.2.3 **Mechanical Properties**

Moyer\textsuperscript{2} has shown that decreasing the carbon content of both laboratory and production line heats of alloy 718 to 0.01% does not lead to deteriorating tensile properties provided that the metal has been treated with magnesium. On the contrary, tensile properties appear to improve with lower carbon content. This finding, Moyer claims, offers the possibility to produce alloys with improved low cycle fatigue (LCF) properties, as LCF fracture may be initiated at carbides.

Chen et al\textsuperscript{22} found that magnesium additions to superalloys improve the creep properties. Further, they suggest that magnesium
Figure 2.8  Inconel 718 microfissuring susceptibility versus magnesium content.
defines the grain boundary carbides (mainly $M_6C$). As opposed to Yamaguchi et al.\textsuperscript{18}, Chen observed segregation of Mg to the grain boundaries. This segregation increased with treatment at 850°C for 1200 h suggesting that the segregated magnesium is in the metallic unbound state. Hence, if all magnesium in the Yamaguchi study is bound as sulphide or oxide the findings need not be contradictory.
2.2 Atomic Absorption Studies of Vapour over Condensed Phases

The technique of measuring vapour pressure over a condensed phase using atomic absorption spectrophotometry has been used in a number of investigations\textsuperscript{23-35}. All of these studies have been carried out at a temperature of less than 1100°C, as can be seen in the summary given in Table 2.2. Since these papers are important to this work, they will be given a relatively detailed discussion in chronological order.

2.2.1 Herbenar et al\textsuperscript{23}

Herbenar et al\textsuperscript{23} measured the vapour pressure of zinc over solid \textalpha-\textit{brasses} at temperatures up to 970°C. Their light source consisted of a spark produced by a high tension discharge between two electrodes of pure zinc. Further, a double prism type spectrograph was used in conjunction with photographic plates to measure the intensity. The absorption vessel was constructed from transparent quartz to fit inside a heating furnace as shown in Figure 2.9.

The cell was calibrated using pure zinc of known vapour pressure. The intensity was measured at the 3076 Å resonance line of the zinc spectrum and at 3035 Å where no tendency for absorption was detected. The absorption could then be represented by
<table>
<thead>
<tr>
<th>Investigators</th>
<th>Discussion in Section</th>
<th>Cell</th>
<th>Alloy System</th>
<th>Temperature</th>
<th>Standard</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herbenar et al</td>
<td>2.2.1</td>
<td>Quartz-Vacuum w. side-arm</td>
<td>Zn in Cu-Zn</td>
<td>642-970°C</td>
<td>Pure Zn(Jl)</td>
<td>22</td>
</tr>
<tr>
<td>Scatchard et al</td>
<td>2.2.2</td>
<td>As above</td>
<td>Zn in Ag-ZnCd in Ag-Cd</td>
<td>527-927°C350-600°C</td>
<td>Pure Zn(Jl)Pure Cd</td>
<td>23, 24</td>
</tr>
<tr>
<td>Vidale</td>
<td>2.2.3</td>
<td>Open cell in Ar-atm.</td>
<td>Na in glass</td>
<td>900-1020°C</td>
<td>None</td>
<td>25</td>
</tr>
<tr>
<td>Brebrick &amp; Strauss</td>
<td>2.2.4</td>
<td>Quartz-Vacuum w. side-arm</td>
<td>PbTe</td>
<td>725-924°C</td>
<td>Pure Te &amp; PbTe</td>
<td>26</td>
</tr>
<tr>
<td>Rapperport &amp; Pensler</td>
<td>2.2.5</td>
<td>Quartz-Vacuum cylinder</td>
<td>Ag &amp; Cd in Ag-CdZn in Cu-Zn</td>
<td>&lt; 800°C400-600°C</td>
<td>Pure Ag &amp; CdPure Zn</td>
<td>27, 28</td>
</tr>
<tr>
<td>Masson et al</td>
<td>2.2.6</td>
<td>Quartz-Vacuum w. side-arm</td>
<td>Zn in Au-ZnIn in Cu-InIn in Ag-InZn in Ni-Zn</td>
<td>478-738°C694-822°C758-863°C340-652°C</td>
<td>Pure ZnPure InPure InPure Zn</td>
<td>29, 30, 31, 32</td>
</tr>
<tr>
<td>Elintin &amp; Timofeev</td>
<td>2.2.7</td>
<td>Essentially open</td>
<td>Cr,Al,Fe, Si and Zr in binary melts</td>
<td>?</td>
<td>None</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure 2.9  (a) Transparent quartz absorption vessel and (b) heating furnace$^{23}$. 
\[ -\log \frac{I_{3076}}{I_{3035}} = K \frac{p}{T} d \]  

(2.1)

where \( K \) = absorption coefficient
\( p \) = pressure
\( T \) = absolute temperature
\( d \) = thickness of absorbing space

If Beer's absorption law is valid, as appears to be the case in the study of Herbenar, a plot of \( \log \frac{I_{3076}}{I_{3035}} \) versus \( p/T \) results in a straight line relationship. Experiments for solid Cu-Zn alloys were conducted in a similar fashion to the calibration.

2.2.2 Scatchard et al\textsuperscript{24,25}

Scatchard and Westlund\textsuperscript{24} applied the experimental technique of Herbenar et al\textsuperscript{23} to solid silver-zinc alloys. Later, Scatchard and Boyd\textsuperscript{25} replaced the spark source with a hollow cathode lamp and the photographic plates with an electronic system. This system was used to measure the vapour pressure of cadmium over solid silver-cadmium alloys. Scatchard and Boyd\textsuperscript{25} found a large deviation from linearity in Equation 2.1. They speculated that it may be due to the distribution in the emitting vapour not being Maxwellian.
2.2.3 Vidale

Vidale chose to employ an experimental system consisting of a tube furnace as shown in Figures 2.10 and 2.11. The cell is a cylinder with openings in both ends as a light path. By filling the tube furnace with argon the diffusion of measured atoms out of the cell is restricted. Thus, a cell length equal to that of the physical cell is assumed.

The system was tested by measurement of the pure sodium vapour pressure at temperatures from $120^\circ C$ (393 K) to $135^\circ C$ (408 K). The experimental procedure consisted of measuring the beam intensity ($I$) at the elevated temperatures, and then a maximum intensity ($I_0$) at a lower temperature when the furnace had been turned off.

The theoretical assumptions of Vidale differ significantly from the earlier papers. He states that it is never permissible to apply Beer's law to the absorption of unresolved lines. Instead, a relationship taking Doppler and pressure broadening as well as the effect of hyperfine structure of the line into account is developed. The relationship takes the form

$$\ln \frac{I}{I_0} = C_1 + C_2 \frac{P}{T^{3/2}}$$ (2.2)
Figure 2.10 Optical path diagram. 

26.
Figure 2.11 Cross sectional diagram of cell and furnace.26
where $C_1$ and $C_2$ are constants.

In fact, the three sets of experiments A, B and C each can be well represented by equation 2.1 as shown in Figure 2.12. Linear regression analysis gives a correlation coefficient of at least 0.99 for each experiment. The dashed line in Figure 2.12 occurs if $\ln \frac{I}{I_0}$ is calculated using equation 2.2 and literature values for $p_{Na}$ as a function of $T$. Hence, either of the relationships 2.1 or 2.2 describe well the data for sodium given by Vidale. One explanation for this may be that the temperature interval is very small, only 15°C. It is not clear why the relatively large discrepancy between experiments A and B/C occurred. Vidale\textsuperscript{26} also used the system to determine the vapour pressure of sodium over glasses. In these experiments he used a platinum cell to contain the vapours.

2.2.4 Brebrick and Strauss\textsuperscript{27}

Brebrick and Strauss used a closed silica cell, similar to earlier investigations\textsuperscript{22-24}, to measure the vapour pressure of $Te_2$ and $PbTe$ over solid $PbTe$ at temperatures of 725 to 924°C. They calibrated a system consisting of interference filters and electronic detectors using pure Te and PbTe. By switching filters they were able to measure the absorption of the two vapour species almost simultaneously.
Figure 2.12 Diagram showing the correlation between three sets of experiments, A, B and C presented by Vidale\textsuperscript{26}, according to equation 2.1.
2.2.5 *Rapperport and Pemsler*\textsuperscript{28,29}

Rapperport and Pemsler used closed cylindrical silica vacuum cells to measure the vapour pressure of silver or cadmium over solid silver–cadmium alloys\textsuperscript{28} and zinc over solid copper–zinc alloys\textsuperscript{29}. They used hollow cathode lamps as light sources and electronic equipment to record the absorption. As in earlier investigations\textsuperscript{23–25}, they assume and are able to use a linear relationship according to Beer's law. The authors originally intended to measure both the vapour pressure of zinc and copper over brasses using the same quartz cells\textsuperscript{29}. However, they found that different length cells were required due to the relationship of the absorption coefficients and vapour pressure variation with temperature\textsuperscript{29}.

2.2.6 *Masson et al*\textsuperscript{30–34}

Masson et al employed a system similar to that of earlier work\textsuperscript{23–25} as described by Lee\textsuperscript{31}. It consisted of a sealed quartz cell with a side arm containing the specimens. The cell was placed in a tube furnace which in turn was placed in the beam path of a commercial atomic absorption spectrophotometer. The following alloy systems were investigated: Au–Zn\textsuperscript{30} at 478–738°C, Cu–In\textsuperscript{31} at 694–822°C, Ag–In\textsuperscript{32,33} at 758–863°C, and Ni–Zn\textsuperscript{34} at 340–652°C. The vapour pressures measured were those of indium or zinc. Also in these investigations it was found that
Lambert-Beers law was obeyed, except occasionally at high absorption (> 0.7).

2.2.7 Eliutin and Timofeev

Eliutin and Timofeev attached atomic absorption equipment to an Electron Beam button melting furnace. They claim that the evaporation rate during melting can be continuously followed, although the electron beam had to be switched off during a measurement. The paper is rather sketchy and the notation poorly explained. However, a method of calculation similar to Vidale appears to be applied. Further, the cell consists of only part of the atomic beam over the melt as the light beam from the spectrophotometer has been "boxed in", with only a short segment open to the vapour.
2.3 High Temperature Experimental Methods

Excellent reviews of the literature covering most aspects of high temperature thermodynamic experimental methods have been published by Rapp and Kubaschewski and Alcock. This survey has been limited to Knudsen cell methods and isopiestic methods as they are of major importance to this investigation.

2.3.1 Knudsen Cell Methods

In addition to already mentioned reviews, a general literature survey and discussion of the Knudsen Cell or Effusion method is given by Cater, and the mass transfer aspect is discussed by Geiger and Poirier. The following paragraph discusses the fundamental assumptions applying to the Effusion method.

If a condensed phase is contained in a closed container it will develop a vapour pressure that is in equilibrium with the condensed phase. If the pressure is low enough to give molecular diffusion conditions the gas molecules will follow a Maxwellian distribution. This assumes molecular chaos, meaning that molecules strike the walls in random directions. The cosine law then gives the probability that a molecule strikes the wall at an angle $\theta$ to the normal,
\[ \frac{N(\theta)}{Z_0} = \frac{N}{V} c \cos \theta \frac{dw}{4\pi} \]  \hspace{1cm} (2.3)

where \( dw = 2\pi \sin \theta \, d\theta \), \( N/V \) = number of molecules per unit volume of the gas and \( c \) = average molecular speed. This is the cosine law. Assuming that an area, \( A \), small enough not to disturb the equilibrium, is removed from the container wall, the emerging molecules then will follow the distribution of the cosine law. Two additional restrictions apply to this concept, that the edge of the orifice is so thin that the chance of a molecular collision with the edge is negligible and that the pressure is low enough so that intra-molecular collisions are absent within the orifice. Under these conditions the Hertz-Knudsen equation applies,

\[ p = \frac{w}{\Delta t} \left( \frac{2 \pi RT}{M} \right)^{1/2} \]  \hspace{1cm} (2.4)

where \( p \) = pressure of gas, \( w \) = weight loss, \( t \) = time, \( R \) = gas constant, \( T \) = temperature and \( M \) = molecular weight.

In reality an infinitely thin orifice opening is difficult to construct, but so called Clausing factors are available to correct for cylindrical and conical openings. The upper limit for molecular effusion through an ideal orifice has been set at roughly \( \lambda/d = 10 \), where \( \lambda \) is the mean free path and \( d \) is the orifice diameter. The mean free path is given by
where $\sigma$ is the collision diameter of the molecules. Some typical Knudsen cells are depicted in Figure 2.13.

2.3.1.1 **Heating and Temperature Measurements**

For the cosine equation to be valid, uniform temperature distribution in the cell is important.

a. **Thermocouples**

Thermocouples constitute one alternative for temperature measurements. They can be either attached or situated adjacent to the cell if radiation heating is applied. It is generally recommended that either several thermocouples are attached to the cell, e.g. to the top and bottom, or that the temperature distribution be determined in dummy experiments. The major disadvantage with thermocouples is that electrical leads have to be fed through the vacuum wall.
Figure 2.13 Typical Knudsen cells. (a) Tungsten cell. (b) Cell used with vacuum balance. (c) Cell with thermocouple and near-ideal orifice. (d) Knudsen's original apparatus for determining the vapour pressure of mercury.
b. Optical Pyrometry

The other alternative for temperature measurements is optical pyrometry. The pyrometer is sighted through a window or prism either into the cell orifice or into a blackbody hole drilled elsewhere on the cell. The sighting window must be shuttered to prevent deposition of vapour which would change the transmissivity.

c. Radiation Shielding

Several alternatives for cell heating are available. Regardless of heating method, the cell is generally surrounded by several layers of radiation shielding. The shielding should fit as closely as possible to minimize heat loss by radiation. Annular shields are frequently laid on top of the effusion cell to maintain the temperature of the orifice. Shields around inductively heated containers have to be slotted or split to minimize direct heating in the high frequency field.

d. Resistance Heating

The cell is heated by passing an electrical current directly through it or through a band or filament wrapped around it. Thus, it
must be made from an electrically conducting material. Another disadvantage is that severe temperature gradients may occur where the electrical leads are attached.

e. Induction Heating

Induction heating of an electrically conducting cell has the advantage that no part of the heating system is inside the vacuum system. However, it has the serious disadvantage that the field may interfere with adjacent electronic equipment or thermocouple circuitry.

f. Electron Bombardment Heating

Effusion cells can be heated by electron bombardment by setting up a potential of 200-1000 V between the cell and a surrounding hot filament. This is an efficient, direct way of heating the container. However, for stable electron bombardment, a good vacuum (p < 5 x 10^{-5} torr) is required. This may be difficult to maintain during outgassing of the cell. Further, as with resistance heating, the cell must be made of an electrically conducting material.
g. Radiation Heating

Using radiation heating, the cell may be surrounded by a resistively or inductively heated sleeve. Among the advantages are that the cell can be made of any suitable material and that temperature measurements can be made by thermocouples which need not be attached to the cell. However, the hot sleeve or filament may result in a deteriorated vacuum due to outgassing.

2.3.1.2 Detection Methods

Knudsen in his landmark measurements of mercury vapour pressure simply condensed the effusate and measured the volume. Subsequently, a number of detection methods have been developed. However, only mass spectrometry has provided direct intensity measurements of specific vapour species.

a. Weight Loss Methods

The simplest approach to Knudsen experiments is to weigh the cell before and after heating to the experimental temperature. This of course assumes that significant evaporation of only one species occurs. The technique suffers from two major disadvantages. First, the vacuum has to be broken for each measurement. Secondly, weight loss during the heating and cooling cycle must be accounted for. Both of these problems
are resolved by suspending the cell from a vacuum balance.

b. Collection Techniques

If the effusate is condensible, it may be collected on targets coaxial with the orifice. An example of such a system is shown in Figure 2.14. This technique has two major advantages. First, Clausing correction factors are not needed. Secondly, as the target is exposed directly to the evaporating surface the collected effusate is more likely to be representative of the equilibrium pressure than if the molecules had first collided with the cell wall. However, sensitive analytical methods are needed to analyse the frequently small amounts of effusate.

c. Torsion Measurements

By measuring the deflection of a Knudsen cell, frequently with two or more orifices (see Figure 2.15) and suspended by a torsion wire, the vapour pressure of the contained substance can be determined. This technique can be applied for instance to alloys by placing one pure alloy component in one chamber and the alloy in the other. Further, a combination of vacuum balance and torsion techniques can be used to determine the molecular weight of the effusing species as the torsion technique is independent of the molecular weight.
Figure 2.14 An apparatus for effusion studies by the collection technique.
Figure 2.15 Some torsion-effusion cells. (a) Two-temperature cell made of fused alumina. The lower reservoir is made of Corning No. 7280 glass, fused directly to the alumina upper part. (b) Opposed-orifice cell for comparing vapour pressures of two systems. (c) Four-orifice cell machined from graphite. (d) Welded tantalum cell, showing removable yoke for suspending it from the torsion wire. (e) Demountable two-section cell, with 0.5 in. overlap to be suspended similarly to (d).
d. Mass Spectrometry

Mass spectrometry applied to high temperature experiments has been discussed by Drowart\textsuperscript{41} and Buchler\textsuperscript{42}. The method has the unique ability to analyse the composition of a complex vapour in the range of $10^{-3}$ to $10^{-8}$ torr. A mass spectrometer system consists of a vapour source, a region where ions are produced, a mass analyser and a detector. Two major types of mass spectrometers are used, magnetic deflection and time of flight (TOF) instruments.

Typically the metal vapour is ionized by bombardment with an electron beam. In the magnetic deflection instruments the ion beam is then accelerated by an electric field before entering the mass analyser. Mass analysis is performed by varying a magnetic field. In the time of flight instruments the ions are accelerated into a field-free space. Analysis is achieved by monitoring the time it takes for ions of different mass to pass through the field-free space. Generally, magnetic deflection instruments are more sensitive than TOF instruments.

Pressures are deduced from the detected mass to charge ratios. A practical problem in this respect arises as one ion species may be produced directly or through dissociation of more complex molecular species. Hence, the fundamental problems in data analysis consist in identification of species effusing from the Knudsen cell and establishment of the partial pressures of each species. Absolute
pressures can be determined by incorporating a substance of known vapour pressure in the cell. Direct determination of alloy vapour pressures can also be achieved by using a twin crucible arrangement as shown in Figure 2.16. Another obvious alternative to overcome problems caused by changes in the absolute sensitivity of the spectrometer is to measure the ratio of ion currents of the solution components.

2.3.2 Pseudoisopiestic Method

Literature surveys dealing with the isopiestic method have been presented by Norman and Lange. The isopiestic equilibration of two or several condensed phases is accomplished at isothermal conditions. This technique is not particularly applicable to high temperature systems as it requires very different volatilities of solute and solvent. Instead the nonisothermal equilibration in a closed system is more useful and has been given the name "pseudoisopiestic method".

One interesting application of this method is that of Milstead and co-workers. They determined the sorption of cesium on carbon by equilibrating cesium at the lowest temperature and carbon at a higher temperature in a glass-stainless steel system. By doping the cesium with radioactive tracer they were able to analyse the sorption directly at several consecutive temperatures.

Elliott et al. constructed a quartz system, shown in
Figure 2.16 Twin crucible effusion source.\cite{42}
Figure 2.17, attached to an analytical balance for direct measurements of cadmium vapour pressure over cerium and gallium alloys. By loading known amounts of the alloy components in the alloy leg, the alloy composition is known by the weight gain in the cadmium leg, and the vapour pressure is determined by the temperature of the cadmium leg.

Eldridge et al.\textsuperscript{48,49} developed a system where several specimens are located in a temperature gradient in a closed reaction tube. This system is depicted for the determination of magnesium activity in liquid tin alloys in Figure 2.18. Tin contained in covered graphite crucibles was equilibrated with pure magnesium. The resulting alloy compositions were simply determined by weighing the crucibles before and after the equilibration experiments.
Figure 2.17 Schematic of an "isopiestic balance".\textsuperscript{46,47}
Figure 2.18 Isopiestic equilibration tube.\textsuperscript{49}
2.4 Thermodynamic Data

2.4.1 Background

The thermodynamic activity of a component, i, in solution can be defined as

\[ a_i = \frac{p_i}{p_i^0} \]  \hspace{1cm} (2.6)

where \( p_i \) = pressure of component i and
\( p_i^0 \) = vapour pressure of the pure metal i at the same temperature.

The activity coefficient, which is based on Raoultian behaviour with the pure substance as standard and reference state, is defined as

\[ \gamma_i = \frac{a_i}{X_i} \]  \hspace{1cm} (2.7)

where \( X_i \) = molar fraction of component i.

For dilute metal solutions it is customary to apply a reference state of infinitely dilute solution with a hypothetical 1 weight % solution as standard state. Thus, the composition coordinate is also changed from
mole fraction to weight %. This standard state yields another definition of the activity coefficient,

\[ f_i = \frac{h_i}{(\%i)}. \]  (2.8)

As this standard state is frequently called Henrian, the activity is written \( h_i \).

To describe mathematically the variation of activity coefficient with composition, Wagner\(^{51}\) suggested a Taylor series expansion for the logarithm of the activity coefficient, written here in the notation of Elliot et al.\(^{50,52-53}\):

\[
\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{n} \varepsilon_j^i x_j + \sum_{j=2}^{n} \rho_j x_j^2 + \sum_{j=2}^{n} \sum_{k=2}^{n} \rho_j^i x_j x_k + \Theta(x^3) \tag{2.9}
\]

The first term on the right refers to the activity coefficient of \( i \) at infinite dilution, as the expansion is made for the limiting case of \( x_i \to 1 \). The first order terms are defined as

\[
\varepsilon_j^i = \left[ \frac{\partial \ln \gamma_i}{\partial x_j} \right]_{x_i \to 1} \tag{2.10}
\]

and called the first order free energy interaction coefficients. Similarly, the higher order coefficients are defined as
\[\rho_{i,j,k}^j = \frac{1}{n_j!n_k!} \left[ \frac{\partial^2 \ln \gamma_i}{\partial x_j \partial x_k} \right].\]  \hspace{1cm} (2.11)

where \(n_j\) and \(n_k\) are integers from 0 to 2, and the sum of \(n_j\) and \(n_k\) is equal to 2. For the weight percent coordinate equation 2.9 becomes

\[\log f = \sum_{j=2}^{n} e_j^j(\%j) + \sum_{j=2}^{n} r_j^j(\%j)^2 + \sum_{j=2}^{n} \sum_{k=2}^{n} r_j^j,k(\%j)(\%k) + o(\%)^3\]  \hspace{1cm} (2.12)

where the first order coefficients are defined

\[e_j^j = [\frac{\partial \log f_i}{\partial x_j}] \%i \rightarrow 100\]  \hspace{1cm} (2.13)

and the higher order terms defined

\[r_j^j,k = \frac{1}{n_j!n_k!} \left[ \frac{\partial^2 \log f_i}{\partial x_j \partial x_k} \right]\]  \hspace{1cm} (2.14)

similarly to expression 2.11. In equation 2.12 the zeroeth-order term disappears since the activity coefficient \(f_i^o\), is assigned the value of one at infinite dilution.
The most commonly used relationships between the different parameters are given by the following equations.

\[ e_i^j = e_j^i \] (2.15)

\[ e_i^j = 230 \frac{M_j}{M_i} e_i^j + \frac{M_1 - M_j}{M_i} \] (2.16)

\[ \rho_i^j = \frac{230}{(M_i)^2} [100M_j^2 r_i^j + M_j (M_1 - M_j) e_i^j] + \frac{1}{2} \left( \frac{M_1 - M_j}{M_i} \right)^2 \] (2.17)

First order interaction coefficients have been determined for a large number of solutes in iron. However, only in a few cases are the experimental data accurate enough to suggest second order interaction parameters of the type \( r_i^j \). In no case has the experimental accuracy permitted calculations of \( r_i^j \). Unfortunately the amount of data for nickel solutions is more limited than for iron solutions.

2.4.2 The Pure Elements Ni, Mg, Ca and Al

Basic data for the pure elements are well established. Pertinent equations are summarized in Table 2.3.
### TABLE 2.3 Data for the Pure Elements

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1455</td>
<td>2920</td>
<td>( \log p = \frac{-22500}{T} - 0.96 \log T + 13.6 )</td>
<td>( \log p = \frac{-22400}{T} - 3.02 \log T + 16.95 )</td>
<td>37</td>
</tr>
<tr>
<td>Mg</td>
<td>650</td>
<td>1105</td>
<td>( \log p = \frac{-7780}{T} - 0.855 \log T + 11.41 )</td>
<td>( \log p = \frac{-7550}{T} - 1.41 \log T + 12.79 )</td>
<td>37</td>
</tr>
<tr>
<td>Ca</td>
<td>843</td>
<td>1483</td>
<td>( \log p = \frac{-9350}{T} - 1.39 \log T + 12.82 )</td>
<td>( \log p = \frac{-8920}{T} - 1.39 \log T + 12.45 )</td>
<td>37</td>
</tr>
<tr>
<td>Al</td>
<td>659</td>
<td>2450</td>
<td>( \log p = \frac{-16380}{T} - 1.0 \log T + 12.32 )</td>
<td></td>
<td>37</td>
</tr>
</tbody>
</table>
2.4.3 Magnesium and Calcium in Nickel and Iron Alloys

As pointed out in Section 2.4.1 the thermodynamic data of dilute iron solutions are better known than those for nickel solutions\textsuperscript{55,56}. Because of that, when data for nickel alloys are lacking, many investigators apply those for iron as a best approximation. While this may be a valid approach for many systems, in the case of magnesium and calcium it is probably far from correct.

While the Mg-Fe phase diagram is incomplete, as can be seen in Figures 2.19 and 2.20 the binary systems Mg-Fe and Mg-Ni are essentially opposites\textsuperscript{57,58}. Nickel-magnesium exhibits complete solubility in the liquid phase and two intermetallic compounds in the solid phase, whereas iron-magnesium has an extensive miscibility gap in the liquid phase and no solid intermetallic phases. The situation is similar for the calcium-nickel and calcium-iron systems. The Ca-Fe phase diagram is even more tentative than the Mg-Fe diagram\textsuperscript{59}, Figure 2.21, but it is well known that the solubility of calcium in liquid iron is only 0.032 weight percent\textsuperscript{60}. As in the nickel-magnesium system, nickel-calcium exhibits several solid intermetallic compounds and complete solubility in the liquid\textsuperscript{61}, as can be seen in Figure 2.22.

In terms of activity data one can then expect that the Raoultian activity coefficients of Ca and Mg will be larger than one in iron, as in these systems the like atom attractions are stronger than the unlike
Figure 2.19 The magnesium-iron binary phase diagram.\textsuperscript{57}
Figure 2.20 The magnesium–nickel binary phase diagram.
Figure 2.21 Schematic calcium-iron binary phase diagram\textsuperscript{59}.
Figure 2.22 The calcium-nickel binary phase diagram. 

Figure 2.22 The calcium-nickel binary phase diagram.
atom attractions. In contrast, in nickel solutions the activity coefficients of Ca and Mg ought to be smaller than one as the intermetallic compounds indicate unlike atom attraction. This is also confirmed by Meysson and Rist\textsuperscript{62} for nickel and iron-rich solutions containing calcium as shown in Figure 2.23. This literature survey will therefore concentrate on magnesium/calcium in nickel solutions. deBarbadillo\textsuperscript{63} thoroughly surveyed published data for Mg and Ca in nickel-base alloys. Much of this review will be based on his paper.

The activity of calcium in nickel and iron alloys has been measured using a pseudo isopiestic technique at 1480°C\textsuperscript{62}. The results are shown in Figure 2.23. As can be seen, the resulting activity coefficient at infinite dilution, $\gamma_{\text{Ca}}^\circ$, is equal to 0.4. While activity data for solid nickel-magnesium alloys of all compositions are available\textsuperscript{64} little experimental work has been done on the liquid alloys. Schmahl and Sieben\textsuperscript{65} measured the vapour pressure of magnesium over eight nickel-magnesium alloys. Two of these alloys, at molar fractions of 0.95 and 0.89 of magnesium were in the liquid state at temperatures of 580 to 700°C. deBarbadillo\textsuperscript{63} extrapolated the data given by Schmahl and Sieben\textsuperscript{65} at 750°C to 100% nickel as shown in Figure 2.24. This treatment yields an estimate of $\gamma_{\text{Mg}}^\circ = 0.1$.

deBarbadillo\textsuperscript{63} also discusses the influence of other alloying
Figure 2.23 Activity of calcium in some Ni-Ca and Ni-Fe-Ca alloys as a function of the molar fraction of calcium.
Figure 2.24 Activity of magnesium in nickel-magnesium binary alloys.

Schmahl & Sieben 750°C

$\gamma_{mg}^o = 0.10$
elements on the solubility of magnesium in nickel alloys. For instance, iron and chromium decreases the magnesium solubility. While insufficient data are available deBarbadillo also proposes a tentative ternary liquid phase diagram for the Fe-Ni-Mg system. This diagram is reproduced in Figure 2.25. Figure 2.26 reproduces estimated activity data based on the limited data for the binary Ni-Mg system$^65$ and data for the system Si-Fe-Mg$^66$. deBarbadillo$^63$ added magnesium to binary nickel alloys in a furnace open to atmosphere. Essentially he found that high nickel (>50%) alloys retained all of the 3% additions seen in Figure 2.27. This indicates a very low activity coefficient in these alloys.

2.4.4 Deoxidation Equilibria

A deoxidation reaction in a liquid metal may be written$^67$

\[
x_{\text{M}} (\%) + y_{\text{O}} (\%) \rightarrow x_{\text{M}}y_{\text{O}}
\]

where \( \text{M} \) is the deoxidizing element added to the solution. Then

\[
K = \frac{a_{\text{M}O}}{x_{\text{M}}y_{\text{O}}} = \frac{a_{\text{M}O}}{x_{\text{M}}y_{\text{O}}} \left( \frac{[\%\text{M}]^x f_M^x [\%\text{O}]^y f_O^y}{h_M^x h_O^y} \right)
\]

(2.18)
Figure 2.25 Estimated liquidus surface in Fe-Ni-Mg system and range of magnesium-rich phases observed after solidification of Fe-Ni alloys.
Figure 2.26 Estimated activity of magnesium in the Fe-Ni-Mg system.
Figure 2.27 Estimated theoretical and effective solubility of magnesium in nickel alloys based on Figure 2.26 and experiments.
or

\[ \log K = \log a_{M}^{x y} - x(\log \%M + \log f_{M}) - y(\log \%O + \log f_{O}) \quad (2.19) \]

where \( K \) is the equilibrium constant. Deoxidizing elements have great affinity to oxygen. Hence, the oxygen metal interaction parameter, \( e_{O}^{M} \), is negative and large, in absolute terms generally much larger than the self-interaction parameter \( e_{M}^{M} \).

Contents of the deoxidizers Al, Ti, and V in iron solution are plotted versus oxygen content in Figure 2.28. As can be seen, the deoxidizing equilibria exhibit minima, which in terms of first order interaction coefficients can be expressed

\[ (\%M) = \frac{-0.434x}{ye_{O}^{M} + x e_{M}^{M}} \quad (2.20) \]

Deoxidation equilibria for the elements Mg, Ca and Al will be discussed. Published data for these elements in iron or nickel solution are summarized in Tables 2.4 to 2.9.
Figure 2.28 Solubility of oxygen vs (a) aluminum, (b) titanium, and (c) vanadium contents in iron at 1600°C. The curves are calculated on the basis of a first order interaction formalism with (a) $\epsilon_{\text{Al}}^O = -360$, (b) $\epsilon_{\text{Ti}}^O = -87$, (c) $\epsilon_{\text{V}}^O = -27.7$. The points are from experimental work. 
### TABLE 2.4 Behaviour of Deoxidisers and Oxygen at Infinite Dilution in Liquid Iron

<table>
<thead>
<tr>
<th>Element</th>
<th>$\gamma_1^o$ (1873 K)</th>
<th>$\Delta G^o$ (X), cal/mole</th>
<th>$\Delta G^o$(%), cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (l)</td>
<td>0.029</td>
<td>-1500 + 1.03 T</td>
<td>-15100 - 6.67 T</td>
</tr>
<tr>
<td>Ca (l)</td>
<td>2240</td>
<td>-9430 + 20.3T</td>
<td>-9430 + 11.8T</td>
</tr>
<tr>
<td>$1/2 O_2$ (g)</td>
<td>-</td>
<td>-</td>
<td>-28000 - 0.69 T</td>
</tr>
</tbody>
</table>

### TABLE 2.5 Behaviour of Deoxidizers and Oxygen at Infinite Dilution in Liquid Nickel

<table>
<thead>
<tr>
<th>Element</th>
<th>$\gamma_1^o$ (1873 K)</th>
<th>$\Delta G^o$ (X), cal/mole</th>
<th>$\Delta G^o$(%), cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (l)</td>
<td>0.0002</td>
<td>-37000 + 2.98 T</td>
<td>-37000 - 4.61 T</td>
</tr>
<tr>
<td>Ca (l)</td>
<td>0.6 (?)</td>
<td>-1920</td>
<td>-1920 - 8.37 T</td>
</tr>
<tr>
<td>Ca (g)</td>
<td>1.27</td>
<td>-44520 + 24.25 T</td>
<td>-44520 + 15.88 T</td>
</tr>
<tr>
<td>Mg (l)</td>
<td>0.32 (?)</td>
<td>-4200 (?)</td>
<td>-4200 - 7.38 T (?)</td>
</tr>
<tr>
<td>Mg (g)</td>
<td>2.2</td>
<td>-38910 + 22.34 T(?)</td>
<td>-38910 + 14.96 T (?)</td>
</tr>
<tr>
<td>$1/2 O_2$ (g)</td>
<td>-</td>
<td>-</td>
<td>-16970 + 0.336 T</td>
</tr>
</tbody>
</table>
### TABLE 2.6 First Order Interaction Coefficients, \( e^j_i \) in Liquid Iron at 1600°C
(References in Brackets)

<table>
<thead>
<tr>
<th>i j ( \rightarrow )</th>
<th>Al</th>
<th>Ca</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-0.0045(55)</td>
<td>-0.047 (55)</td>
<td>-6.6 (55)</td>
</tr>
<tr>
<td>Ca</td>
<td>-0.072 (55)</td>
<td>-0.002 (55)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-3.9 (55)</td>
<td>-62 (68)</td>
<td>-0.20 (55)</td>
</tr>
<tr>
<td></td>
<td>-3.9 (73)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-4.6 (72)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-5.2 (68)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1 (74)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2.7 First Order Interaction Coefficients, \( e^j_i \) in Liquid Nickel at 1600°C
(References in Brackets)

<table>
<thead>
<tr>
<th>i j ( \rightarrow )</th>
<th>Al</th>
<th>Ca</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.08 (56)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td>0.004 (56)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-1 (74)</td>
<td></td>
<td>0 (56)</td>
</tr>
</tbody>
</table>
### TABLE 2.8 Deoxidation Equilibria in Iron Alloys

<table>
<thead>
<tr>
<th>Deoxidation Reaction*</th>
<th>( K )</th>
<th>( T ) (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 \text{Al} + 3 \text{O} \rightarrow \text{Al}_2\text{O}_3 (s) )</td>
<td>( 1.8 \times 10^{13} )</td>
<td>1600</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>( 7.9 \times 10^{13} )</td>
<td>1600</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>( 1.7 \times 10^{13} )</td>
<td>1600</td>
<td>68</td>
</tr>
<tr>
<td>( \text{Ca} + \text{O} \rightarrow \text{CaO(s)} )</td>
<td>( 6.2 \times 10^{5} )</td>
<td>1600</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>( 1.1 \times 10^{6} )</td>
<td>1600</td>
<td>69,70</td>
</tr>
<tr>
<td>( \text{Mg} + \text{O} \rightarrow \text{MgO(s)} )</td>
<td>( 5 \times 10^{5} )</td>
<td>1600</td>
<td>69,70</td>
</tr>
</tbody>
</table>

### TABLE 2.9 Deoxidation Equilibria in Nickel Alloys

<table>
<thead>
<tr>
<th>Deoxidation Reaction*</th>
<th>( \log K )</th>
<th>( K )</th>
<th>( T ) (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 \text{Al} + 3 \text{O} \rightarrow \text{Al}_2\text{O}_3 (s) )</td>
<td>( -18.81 )</td>
<td>( 4.48 \times 10^{13} )</td>
<td>1600</td>
<td>56</td>
</tr>
<tr>
<td>( \text{Ca} + \text{O} \rightarrow \text{CaO(s)} )</td>
<td>( -6.59 )</td>
<td>( 2.16 \times 10^{8} )</td>
<td>1600</td>
<td>56</td>
</tr>
<tr>
<td>( \text{Mg} + \text{O} \rightarrow \text{MgO(s)} )</td>
<td>( -7.38 )</td>
<td>( 3.2 \times 10^{6} )</td>
<td>1600</td>
<td>56</td>
</tr>
</tbody>
</table>

* Henrian standard state on a weight % basis for the dissolved elements.
2.4.4.1 Magnesium and Calcium

No experimental study of the deoxidation equilibria of Mg and Ca in nickel-base alloys has been found in the literature. Some work has been done on these elements in various iron-based solutions. While these data may be useful in establishing deoxidation equilibria in nickel-base alloys the different solubility of Mg/Ca in the two solvents cannot be forgotten.

Gustafsson fitted solubility data for the calcium-oxygen system from several investigations using regression analysis. An interaction coefficient, \( e^0_{Ca} \) of -62 is suggested in conjunction with an equilibrium constant \( K_{Ca0} \) of \( 1.6 \times 10^{-6} \). This equilibrium constant is inconsistent with one deduced from the work of Sponseller of roughly \( 10^{-10} \), but fit the data better.

Gatellier et al. measured the activity of oxygen using an oxygen probe in iron solutions. The melts were pre-deoxidized with carbon and aluminum and then treated with either magnesium or calcium. Unfortunately the raw data, for instance, the contents of oxygen and alkaline earth metals, are not presented. Equilibrium constants \( K_{Mg0} = 2 \times 10^{-6} \) and \( K_{Ca0} = 9 \times 10^{-7} \) are given, but without oxygen interaction parameters.
Voronova discusses the treatment of hot metal with magnesium. A solubility product of $5 \times 10^{-7}$ at 1600°C can be deduced from equations given. Voronova presents a calculated graph along with plant data, both presumably at 1650 K as seen in Figure 2.29a and b. Clearly, the plant data do not fit the calculated graph.

2.4.4.2 Aluminum

Investigations of the deoxidation equilibrium with aluminum in liquid iron solutions are abundant and only a few examples are considered here. In contrast, little is published on the aluminum deoxidation equilibrium in nickel. Hence, most of the data have been taken from a compilation.

McLean equilibrated iron melts with $H_2/H_2O$ gas mixtures to determine the activity of aluminum-oxygen. The same equilibrium was investigated using an oxygen probe by Fruehan. Both McLean and Fruehan suggest values of the deoxidation equilibrium constant and interaction coefficient $e_0^{Al}$ that are not vastly different (see Tables 2.6 and 2.8). On the other hand, Gustafsson suggests that the older data are better represented by a second-order regression-fitted expression than by the traditional interaction coefficients. As a compromise he also gives values for the traditional equilibrium constant and interaction coefficient.
Vachet et al.\textsuperscript{74} compared activity coefficients of oxygen and aluminum in iron, nickel and cobalt solutions. They suggest that the same interaction parameter $\varepsilon_{Al}^0$ can be applied for all three solvents as differences in $\gamma_{Al}^0/\gamma_0^0$ tend to compensate.
Figure 2.29 (a) Calculated equilibrium contents of oxygen and magnesium in iron. (b) Actual oxygen and magnesium contents in iron. 1- Mg introduced in a methane stream and 2- in an air stream.
3. Experimental Work

3.1 Equipment

The major equipment used in this work consists of a vacuum system containing a molybdenum resistance furnace. The furnace and vacuum system were built to fit in the beam path of a commercial Atomic Absorption Spectrophotometer. Figure 3.1 shows an overview of the system in position in the Atomic Absorption Spectrophotometer.

3.1.1 Atomic Absorption Spectrophotometer

To generate the monochromatic light and measure the absorption, a Perkin Elmer model 306 Atomic Absorption Spectrophotometer was used. An earlier model of this instrument has been described by Kahn. The spectrophotometer is schematically shown in Figure 3.2, with the "sampling burner" replaced by the vacuum belljar in this study.

Briefly, features of this type of instrument include high stability and the ability to discriminate between emission from the vapour source and the hollow cathode lamp. This is accomplished by using a double beam system and by chopping the light from the lamp. For
Figure 3.1 The experimental furnace and vacuum system in position in the Atomic Absorption Spectrophotometer.
Figure 3.2 Block diagram of an Atomic Absorption Spectrophotometer. Emission from the line source is split into sample and reference beams, then recombined and passed through monochromator. Signal from photo-detector is amplified and fed into circuitry which produces a manual electronic null. The sampling burner is replaced by the vacuum bell-jar in this study.
the experiments in this work either the spectrophotometer digital meter or a separately connected Honeywell Electronic 196 recorder was used to read the output.

3.1.2 Vacuum System

A Pyrex belljar (Figure 3.3) with commercial-grade ground and polished quartz windows was made to fit in the beam path of the Atomic Absorption Spectrophotometer. The windows were attached to a short length of Pyrex tubing with epoxy glue. The window-pieces could in turn be attached to the belljar with a glass-O-ring-glass seal. The removable design was chosen to facilitate cleaning, and to make replacement of the windows possible. In the wavelength range of the strongest magnesium absorption line (285 nm) quartz windows transmit a minimum of 90% of the light. Thus, the absorption measurements are distributed minimally.

In this case a design where a complete cell is heated to the experimental temperature, as has been done before (see Chapter 2.2), cannot be used. This simpler design can only be used for temperatures up to about 870°C, which is the tridymite transition temperature for quartz. The belljar is sealed to a water-cooled brass bottom plate with a ground glass-O-ring type of seal. The brass plate is part of a conventional metal vacuum system (Figure 3.1) consisting of a CEC VMF-10
Figure 3.3 Schematic drawing of the vacuum bell-jar containing the molybdenum resistance furnace.
oil diffusion pump backed by an Edwards E2M8 double stage rotary pump. The pressure is monitored by an NRC thermocouple gage and ionization gage with corresponding meters. Vacuums of \(10^{-5}\) torr were achieved.

3.1.3 **Furnace**

The furnace part of the system can be seen in detail in Figure 3.3. As the furnace was to be used close to electronic equipment, a resistance heated furnace was chosen instead of an induction furnace. This caused some problems as the molybdenum heating coil is prone to break. The heating coil was made from 0.9 mm thick molybdenum wire and supported by three notched pure recrystallised alumina rods to prevent sagging. The rods were in turn held in place by two 0.25 mm thick molybdenum end plates. Two 6 mm diameter copper rods connect the furnace winding through the bottom plate using Kovar vacuum power feed-throughs. Power was supplied by a Metals Research Variac high current transformer.

Two to three layers of either molybdenum or zirconium radiation shields surrounded the furnace. The zirconium radiation shields served the additional purpose of oxygen (and nitrogen) getters. The zirconium radiation shields work as getters at temperatures of roughly 700°C to 1000°C. Thus, at the lower temperatures two Zr radiation shields would be used, while at the higher temperatures two inside molybdenum shields
and an outside Zr radiation shield is more suitable. The furnace was designed to make replacement of the radiation shields, as they broke or became oxidized, convenient. The complete assembly is supported by a threaded copper rod attached to the bottom plate. To protect the quartz windows during experiments, a strip of zirconium foil served as a window shutter. When an absorption reading was to be made, the shutter could be manipulated using magnets.

3.1.4 Knudsen Cells

A Knudsen cell used in the tin alloy experiments and some nickel alloy experiments is shown in Figure 3.4. These cells were machined from molybdenum. The top of each cell can hold an orifice plate securely by fitting a spring-loaded circular segment of 0.9 mm thick molybdenum wire into the top notch. The alloys were contained inside the cell in pure Al\text{$_2$O$_3$} crucibles. However, in alloy experiments at 1470°C these cells deteriorated rapidly, probably because of the direct contact with metal vapours. They were therefore replaced by an arrangement of an alumina tube, fitting the inside crucibles snugly, as shown in Figure 3.5.

An isopiestic type of Knudsen cell was used to calibrate the system. A schematic drawing of the cell can be seen in Figure 3.6. The cell was fabricated from a thin-walled tantalum tube with a molybdenum
Figure 3.4 Molybdenum Knudsen cell.
Figure 3.5 Alumina Knudsen cell.
Figure 3.6  Isopiestic Knudsen cell.
machined top. The dimensions of the tops of the two metal types of cells are identical. Thus, if desired, the same orifice plates could be used for both calibration and alloy experiments. The isopiestic cell was fitted with four baffle-type radiation shields designed not to impair the molecular flow of magnesium from the bottom part of the tube. The source of magnesium vapour for the calibration experiments was a piece of solid magnesium roughly fitting the cross-section of the tube and approximately 12 mm thick. Finally, to minimize back-streaming of vapour, the tube was fitted with a tight-fitting plug of either Inconel or copper below the magnesium slug.

The orifice plates were made of 0.04 mm thick molybdenum foil. To produce consistent orifices the plates were pierced with a machinist scribe on a surface of four layers of paper on top of a steel plate. The orifices obtained were not round, but the area was reproducible. The orifice areas were measured on a Leitz surface image analyser.

3.1.5 Temperature Determination

The furnace temperature was continuously measured with a thermocouple installed between the furnace coil and the inside radiation shield. The temperatures of the orifice plates were calibrated with a dummy plate with a separated thermocouple junction. Similarly, the temperature inside the crucible was calibrated to the stationary
thermocouple using a beaded thermocouple. All thermocouples were fed through the bottom plate using compressed rubber seals.

The types of thermocouples used are summarised in Table 3.1. At 1470°C platinum-based thermocouples were used where good mechanical ductility was needed. However, for the stationary thermocouple tungsten 32% rhenium versus tungsten 25% rhenium was more suitable as it gets poisoned at a slower rate. The hot junctions of all thermocouples were periodically renewed to ascertain that false temperature readings were not obtained by a poisoned thermocouple. In addition, the thermocouples were occasionally calibrated using the melting points of pure gold and nickel as reference points.\textsuperscript{78}

The furnace temperature was continuously monitored with a Honeywell Electronik 196 recorder, and the power input manually adjusted to obtain a steady temperature. For accurate measurements of the temperature during calibration or immediately before an absorption reading the thermocouples were switched to a PYE portable potentiometer.

Correct measurement of the temperature attained by the top of magnesium slug used in the calibration experiments is vital as it directly gives the vapour pressure. Measurement of the surface temperature by a thermocouple attached to the surface was rejected as
### TABLE 3.1

**SUMMARY OF THERMOCOUPLE TYPES USED**

<table>
<thead>
<tr>
<th>Position in System</th>
<th>Test Experiments at 900°C</th>
<th>Experiments at 1470°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary</td>
<td>Chromel-Alumel</td>
<td>W 3% Re – W 25% Re</td>
</tr>
<tr>
<td>Dummy Orifice Plate</td>
<td>Chromel-Alumel on Stainless Steel Plate</td>
<td>Pt 30%Rh – Pt 6%Rh on Pt plate</td>
</tr>
<tr>
<td>Beaded - inside</td>
<td>Chromel-Alumel</td>
<td>Pt 30%Rh – Pt 6%Rh</td>
</tr>
</tbody>
</table>
attaching a thermocouple to magnesium proved impossible. Furthermore, it was suspected that the presence of the thermocouple could alter the temperature reading. The arrangement finally arrived at can be seen in Figure 3.7. It consists of two butt-welded thermocouples running perpendicular to each other at different distances from the top surface. The holes containing the thermocouple junctions were drilled as narrow as practically possible (0.9 mm diameter) and thin (0.33 mm diameter) wires were used to prevent cooling of the junction by conduction along the wires. The temperature measurements were taken to represent the average temperature at the specific height in the magnesium slug.

3.2 Materials

3.2.1 Basic Alloys

The basic alloys used in this project are identified in Table 3.2. Impurity content in the magnesium containing alloys has not been analysed as these alloys are extremely dilute in the experimental alloys.

3.2.2 Tin Alloys

Master alloys containing up to 1000 ppm of magnesium were prepared by melting in the experimental vacuum furnace. For this purpose a 25 mm outside diameter alumina crucible covered by an alumina
Figure 3.7 Arrangement of thermocouples in the magnesium slug used for calibration. Measurements in mm.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg</td>
<td>Mg</td>
<td>&gt;99% Solid cast alloy used for Mg slug and Mg-Sn alloys.</td>
</tr>
<tr>
<td>Ni-Mg</td>
<td>Ni</td>
<td>83.7% Granular alloy used for Ni-Mg master alloy</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>14.8%</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.8%</td>
</tr>
<tr>
<td>Inco Nickel 270</td>
<td>Ni</td>
<td>99.98% Solid bar - major Ni source.</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.01%</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.003%</td>
</tr>
<tr>
<td></td>
<td>Mn, S, Si, Cu, Cr</td>
<td>0.001%</td>
</tr>
<tr>
<td></td>
<td>Ti and Co all</td>
<td></td>
</tr>
<tr>
<td>Glidden Electrolytic Iron</td>
<td>Fe</td>
<td>99.91%</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.0025%</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>0.005%</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.010%</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>0.005%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>0.060%</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.015%</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>&lt;0.005% ea</td>
</tr>
<tr>
<td>Fisher Chromium Metal</td>
<td>Cr</td>
<td>&gt; 99%</td>
</tr>
</tbody>
</table>
disc was used. The appropriate amounts of Mg and Sn were placed in the crucible and the system sealed. The vacuum system was pumped overnight to ensure a good vacuum and the contents of the crucible melted. The furnace was then held at temperature for a minimum of half an hour to ensure homogeneity of the alloy. The master alloy together with pure tin in different proportions was then melted in each vapour pressure experiment. Starting contents of magnesium varied from 500 to 1000 ppm.

3.2.3 **Nickel Alloys**

Master alloys containing about 2000 ppm magnesium were prepared by melting the granular nickel-magnesium alloy with appropriate amounts of nickel 270. The alloys were melted in alumina crucibles in a controlled atmosphere induction melting furnace. To ensure a clean, low oxygen atmosphere the furnace was evacuated and refilled with dried, hot titanium-treated argon several times before melting. The melt was held at approximately 1500°C for 15 minutes to ensure a homogenous alloy. The nickel master alloy was combined with suitable amounts of nickel, iron, chromium and aluminum to produce each experimental sample. Starting contents of magnesium varied from 1000 to 2000 ppm.
3.3 Experimental Procedure

The following procedure, with minor modifications, was used for both calibration and alloy experiments. The details pertaining to the specific type of experiments will be described in sections 3.4 to 3.6.

1. Clean the belljar and windows thoroughly and dry in drying oven.
2. If necessary, clean any radiation shields that will be reused, and the window shutter.
3. Position the Knudsen cell in the furnace.
4. Replace all radiation shields. Make sure that oxidized zirconium shields are replaced by new shields.
5. Assemble the belljar parts and put the shutter in position. Seal the system.
6. Pump the system for a minimum of an hour or until a vacuum of $10^{-4}$ torr or better is achieved.
7. While the vacuum system is pumping down, start the atomic absorption spectrophotometer. The standard procedure for starting the spectrophotometer can be used except no burner is installed and no flame lit. It is also important that the lamp current is kept constant (in these experiments it was kept at 6 mA) to make the calibration graph valid. The strongest magnesium line at 285 nm was used together with a slit width of 0.7 nm.
8. Put the belljar into the beam path, and adjust the position until the minimum absorption is observed. Zero the spectrophotometer.

9. When the spectrophotometer is stable, the window shutter is closed and the power turned on. The furnace is rapidly heated to the desired temperature.

10a. For calibration, the furnace is then left to run for 2-4 hours. Readings of temperature and absorption are then taken every half to full hour until the measurements stabilize.

10b. For an alloy experiment, the first measurement is taken after half an hour at temperature and additional readings taken every 15 minutes up to 1 hour.

11. Immediately after the last absorption reading the furnace is turned off. When the furnace has cooled down to 200-500°C a stable final absorption reading is made. The final low temperature reading plus a blank reading is deducted from the last absorption reading. This number then constitutes the result of a particular experiment.

3.4 **Calibration**

The isopiestic Knudsen cell used in the calibration experiments has been described in section 3.1.4. The calibration graph was produced by heating the orifice plate to the same temperature as the corresponding alloy experiments. Thus, a beam of magnesium atoms of the same shape and velocity was produced in both cases.
The slug of magnesium was heated only by radiation from the radiation shields and the tantalum tube. By varying the height of the magnesium piece in the tube, the temperature could also be varied. In this manner a calibration graph could be produced.

3.5 Test of the Method

To prove that the system employing both a novel atomic absorption application and a novel isopiestic Knudsen cell does indeed work, measurements were made on tin-magnesium alloys. This alloy system was selected as it is well documented. The experiments were conducted using the Knudsen cell previously described in 3.1.4. To prevent oxidation of magnesium in the cell, both the wall and the orifice plate were lined with zirconium foil. The experiments were conducted as described in 3.3 at an orifice plate temperature of 900°C.

At the conclusion of each experiment the 3 g samples were collected and later chemically analysed. Given the chemical composition and the activity coefficient, the activity and hence the vapour pressure of magnesium over the tin alloy can be calculated.
3.6 **Nickel Alloy Experiments**

Similar to the tin experiments, the nickel alloy experiments were conducted using the basic Knudsen cell, and the alumina "tube cell". The melts were also, as before, contained in pure alumina crucibles. For each experiment, desired amounts of the master nickel-magnesium alloy, pure nickel, and for the ternary alloy experiments some Fe or Cr, were weighed into the alumina crucible. The compositions of these alloys with regard to the major elements were taken to be determined by the weights.

The experiments were conducted at 1470°C. Generally, the time at temperature was shorter than for the test experiments. The first absorption reading was taken after 20 minutes and the second and usually final reading at no more than 40 minutes. The resulting samples, weighing roughly 5-12 grams, were collected for later chemical analysis.

3.7 **Chemical Analysis**

Analysis for magnesium and aluminum in all alloys followed the same basic procedure. The samples were digested in acid. The resulting concentrated solutions were treated in the standard manner to obtain dilute solutions suitable for flame atomic absorption chemical analysis. The accuracy in resulting metal alloy magnesium and aluminum content was ±3 and ±25 ppm. Oxygen analysis was performed using the inert carrier-
-gas method. The uncertainty of the this analysis was ±5 ppm. The procedures for chemical analysis are described in detail in Appendix B.
4. Results and Discussion

4.1 Calibration

Two methods of calibration were attempted. The first method entails heating pure magnesium to different temperatures in a standard Knudsen cell lined with an iron crucible resulting in varying magnesium vapour pressures. In this method the temperature of the orifice varies with the magnesium temperature. Results from these calibration experiments are given in Table 4.1.

The second method entails using the isopiestic Knudsen cell. Hence, the temperature of the magnesium slug is varied by moving the slug up and down while the orifice plate is kept at a constant temperature. Calibration experiments using this method were performed at orifice temperatures of 900 to 1470°C corresponding to the series of test experiments on tin alloys and the nickel experiments. The results of these experiments are summarized in Table 4.2 and 4.3.

The results of the three sets of calibration experiments are summarized in Figure 4.1. As can be seen, the results of experiments
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Absorbance (measured)</th>
<th>T[°C] (measured)</th>
<th>$p_{\text{Mg}}$ [atm.] (Eq. Table 2.3)</th>
<th>log $p_{\text{Mg}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.295</td>
<td>439</td>
<td>$1.46 \times 10^{-5}$</td>
<td>-4.84</td>
</tr>
<tr>
<td></td>
<td>0.315</td>
<td>446</td>
<td>$1.84 \times 10^{-5}$</td>
<td>-4.74</td>
</tr>
<tr>
<td></td>
<td>0.450</td>
<td>474</td>
<td>$4.54 \times 10^{-5}$</td>
<td>-4.34</td>
</tr>
<tr>
<td></td>
<td>0.476</td>
<td>478</td>
<td>$5.14 \times 10^{-5}$</td>
<td>-4.29</td>
</tr>
<tr>
<td></td>
<td>0.560</td>
<td>498</td>
<td>$9.33 \times 10^{-5}$</td>
<td>-4.03</td>
</tr>
<tr>
<td>B</td>
<td>0.075</td>
<td>369</td>
<td>$0.10 \times 10^{-5}$</td>
<td>-6.00</td>
</tr>
<tr>
<td></td>
<td>0.115</td>
<td>382</td>
<td>$0.18 \times 10^{-5}$</td>
<td>-5.74</td>
</tr>
<tr>
<td>C</td>
<td>0.140</td>
<td>388</td>
<td>$0.22 \times 10^{-5}$</td>
<td>-5.66</td>
</tr>
<tr>
<td></td>
<td>0.285</td>
<td>432</td>
<td>$1.14 \times 10^{-5}$</td>
<td>-4.94</td>
</tr>
<tr>
<td>D</td>
<td>0.320</td>
<td>450</td>
<td>$2.10 \times 10^{-5}$</td>
<td>-4.68</td>
</tr>
<tr>
<td></td>
<td>0.500</td>
<td>478</td>
<td>$5.14 \times 10^{-5}$</td>
<td>-4.29</td>
</tr>
<tr>
<td></td>
<td>0.500</td>
<td>485</td>
<td>$6.36 \times 10^{-5}$</td>
<td>-4.20</td>
</tr>
</tbody>
</table>
TABLE 4.2 Results of Calibration Measurements with Pure Mg, using an Isopiestic Cell. Orifice Temperature = 900°C

<table>
<thead>
<tr>
<th>Absorbance (measured)</th>
<th>T [°C] (measured)</th>
<th>p_Mg [atm.] (Eq. Table 2.3)</th>
<th>log p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>354</td>
<td>5.4 x 10^{-7}</td>
<td>-6.27</td>
</tr>
<tr>
<td>0.671</td>
<td>420</td>
<td>7.6 x 10^{-6}</td>
<td>-5.12</td>
</tr>
<tr>
<td>0.499</td>
<td>395</td>
<td>2.9 x 10^{-6}</td>
<td>-5.53</td>
</tr>
<tr>
<td>0.251</td>
<td>375</td>
<td>1.3 x 10^{-6}</td>
<td>-5.88</td>
</tr>
<tr>
<td>0.541</td>
<td>390</td>
<td>2.4 x 10^{-6}</td>
<td>-5.62</td>
</tr>
<tr>
<td>0.683</td>
<td>400</td>
<td>3.5 x 10^{-6}</td>
<td>-5.45</td>
</tr>
<tr>
<td>0.992</td>
<td>430</td>
<td>10.7 x 10^{-6}</td>
<td>-4.97</td>
</tr>
<tr>
<td>0.542</td>
<td>388</td>
<td>2.2 x 10^{-6}</td>
<td>-5.63</td>
</tr>
<tr>
<td>0.133</td>
<td>382</td>
<td>1.7 x 10^{-6}</td>
<td>-5.76</td>
</tr>
<tr>
<td>0.019</td>
<td>362</td>
<td>7.6 x 10^{-7}</td>
<td>-6.12</td>
</tr>
<tr>
<td>0.85</td>
<td>423</td>
<td>8.3 x 10^{-6}</td>
<td>-5.08</td>
</tr>
</tbody>
</table>
TABLE 4.3 Results of Calibration Measurements with Pure Mg, using an Isopiestic Cell. Orifice Temperature = 1470°C

<table>
<thead>
<tr>
<th>Absorbance (measured)</th>
<th>T[ °C] (measured)</th>
<th>$p_{Mg}$ [atm.] (Eq. Table 2.3)</th>
<th>log p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.94</td>
<td>431</td>
<td>$1.105 \times 10^{-6}$</td>
<td>-4.96</td>
</tr>
<tr>
<td>0.67</td>
<td>406</td>
<td>$4.46 \times 10^{-6}$</td>
<td>-5.35</td>
</tr>
<tr>
<td>0.20</td>
<td>368</td>
<td>$9.82 \times 10^{-7}$</td>
<td>-6.01</td>
</tr>
<tr>
<td>0.69</td>
<td>409</td>
<td>$5.00 \times 10^{-6}$</td>
<td>-5.30</td>
</tr>
<tr>
<td>0.23</td>
<td>371</td>
<td>$1.11 \times 10^{-6}$</td>
<td>-5.95</td>
</tr>
</tbody>
</table>
Figure 4.1 Summary of calibration experiments.
using the isopiestic cell yield almost identical graphs, which can be represented by the regression fitted equations,

\[
\text{Absorbance} = 4.82 + 0.778 \log p_{Mg} \text{[atm]} \quad (4.1)
\]

at 900°C and

\[
\text{Absorbance} = 4.46 + 0.710 \log p_{Mg} \text{[atm]} \quad (4.2)
\]

at 1470°C. Equations 4.1 and 4.2 are subsequently used for calibration of the tin test experiments and the nickel experiments.

Further, as can be seen in Figure 4.1 the calibration using a standard cell yields an entirely different relationship. The reasons for the discrepancies will be discussed in the following section.

4.1.1 **Cause of Discrepancies**

Possible explanations of the variation in calibration results may be found in the following areas:

- Doppler shift
- formation of dimers or oxides, and
- physical reasons
The Doppler shift\textsuperscript{81,82} occurs as the atoms are emitted from the Knudsen cell orifice in directions other than perpendicular to the light beam. As the speed of the atoms varies with the temperature, there is a possibility that different fractions of the atoms absorb at the different temperatures. Calculations (see Appendix C, p 152) show however, that the Doppler shift is very small in the range of interest. Thus it is unlikely that a Doppler shift causes the discrepancies between standard cell and isopiestic cell calibrations.

The likelihood of formation of dimers should also be considered. Dimers may form according to the equilibrium

\[ 2 \text{Mg(g)} \rightleftharpoons \text{Mg}_2(g) \quad (4.3) \]

which has an equilibrium constant of $10^{-3}$ or less\textsuperscript{83} for the considered temperatures. Hence, dimer formation is not likely to affect the absorption measurements.

Oxide formation in the gas phase can be assumed insignificant for the isopiestic experiments as zirconium at temperatures of roughly 600 to 800°C was present as an oxygen getter in the system. As demonstrated by Figure 4.2, solutions of oxygen in zirconium will form preferentially to MgO at 1000°C\textsuperscript{84}. Further, as the pressure of Mg is only $\sim 10^{-6}$ atm in the present system, the Mg – MgO line in Figure 4.2
Figure 4.2 The relationship between oxygen partial pressures and compositions for the Ti-O and Zr-O systems at 1000°C.
would move approximately 270 kJ up in the diagram, making MgO formation even more unlikely. The same situation applies to the isopiestic system although the temperature is slightly lower. However, the standard cell calibration was carried out at temperatures below 500°C. At this temperature the zirconium does not function well as an oxygen getter for kinetic reasons. There exists therefore a possibility that a portion of the magnesium vapour was oxidized in these experiments with the result that the absorption readings were decreased.

Another possible cause of the lower absorption when the standard cell was used is physical. After standard cell experiments, deposits of magnesium were observed on the radiation shields. Such deposits were not observed after the 'isopiestic cell' experiments. This should not affect the fraction of the atomic beam that intercepts the light path as no shields were placed directly in front of the orifice. It does however indicate that at these lower temperatures, sticking of atoms may occur also inside the Knudsen cell. Such sticking, which is particularly likely if the orifice plate is colder than the rest of the cell, would invalidate the Knudsen equation and cause fewer atoms to effuse. On the other hand, using the isopiestic cell, the magnesium slug is always the coldest surface, and subsequent sticking is much less likely.

The absorbance measures do not follow Lambert-Beer's law. The reasons for this are not well understood.
4.2 Test of Method on Tin Alloys

The results of the test experiments on tin alloys are presented in Table 4.4 and Figure 4.3. The solid line in Figure 4.3 represents the regression fitted graph from the isopiestic calibration at 900°C. The numbered points are the results of the tin experiments.

As can be seen in Figure 4.3 the points show a fair bit of experimental scatter. This is to be expected as the work was carried out at very low pressures of magnesium. It can also be seen in the figure that, on average, the tin results show a good fit with the calibration graph. This is taken as an indication that this novel method can be applied to determine the activity of magnesium in other alloys.

Figure 4.3 and Table 4.4 also show that the results are independent of the orifice area within the given limits. This is reasonable considering the equation

\[ p_{eq} = p_K \left(1 + \frac{A}{A_{s}}\right) \]  

(4.4)

where  
- \( p_{eq} \) = equilibrium vapour pressure,
- \( p_K \) = determined vapour pressure,
- \( A \) = orifice area,
Figure 4.3 Results of the test experiments on tin alloys.
<table>
<thead>
<tr>
<th>No</th>
<th>Absorbance</th>
<th>$X_{\text{Mg}}$ (Chemical analysis)</th>
<th>$P_{\text{Mg}}$ [atm.] (Chemical Analysis &amp; Literature Data)</th>
<th>log $P_{\text{Mg}}$</th>
<th>Area [mm$^2$]</th>
<th>Equivalent Diameter [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.951</td>
<td>0.0057</td>
<td>$1.97 \times 10^{-5}$</td>
<td>-4.70</td>
<td>0.063</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>0.955</td>
<td>0.0032</td>
<td>$1.10 \times 10^{-5}$</td>
<td>-4.96</td>
<td>0.063</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>0.624</td>
<td>0.0014</td>
<td>$5.00 \times 10^{-6}$</td>
<td>-5.30</td>
<td>0.063</td>
<td>0.28</td>
</tr>
<tr>
<td>4</td>
<td>0.954</td>
<td>0.0038</td>
<td>$1.32 \times 10^{-5}$</td>
<td>-4.88</td>
<td>0.063</td>
<td>0.28</td>
</tr>
<tr>
<td>5</td>
<td>0.992</td>
<td>0.0021</td>
<td>$7.37 \times 10^{-6}$</td>
<td>-5.13</td>
<td>0.52</td>
<td>0.82</td>
</tr>
<tr>
<td>6</td>
<td>0.807</td>
<td>0.0017</td>
<td>$5.79 \times 10^{-6}$</td>
<td>-5.24</td>
<td>0.52</td>
<td>0.82</td>
</tr>
<tr>
<td>7</td>
<td>0.941</td>
<td>0.0024</td>
<td>$8.16 \times 10^{-6}$</td>
<td>-5.09</td>
<td>0.022</td>
<td>0.18</td>
</tr>
<tr>
<td>8</td>
<td>0.720</td>
<td>0.0014</td>
<td>$4.74 \times 10^{-6}$</td>
<td>-5.32</td>
<td>0.022</td>
<td>0.18</td>
</tr>
</tbody>
</table>
A_s = area of evaporating surface, and,
\alpha = condensation coefficient

In this case A/A_s < 0.003 and any influence would be smaller than the
experimental scatter. The condensation coefficient is equal to one for
most metals, hence p_{eq} = p_K.

The pierced orifices are clearly not ideal. However, it has been
found that when collection techniques (see 2.3.1.2,b) are used Clausing
correction factors are not needed. As this technique measures the
absorption in a similar area directly over the cell it is assumed that
the effects of non-ideality may be neglected. It is possible that the
irregular shape produced when piercing the orifice may account for some
of the experimental scatter.

The limit for molecular effusion, \lambda/d \gg 10, is not approached at
either 900°C or 1470°C for magnesium. It is estimated to be larger than
10^3 in all cases. Both tin and nickel have lower vapour pressures at
the applied temperatures than the magnesium, and should not influence
the mean free path.

It should be noted that some of the restrictions of other Knudsen
methods may not be applicable here. The calibration and experiments
were run under conditions that were as similar as possible. For
instance, all orifices for both calibrations and experiments, with the exception of the tin experiments, were punched in a consistent manner to produce an orifice diameter of roughly 0.20 mm.
4.3 Nickel Alloys

4.3.1 Preliminary Results

Originally, chemical analysis of only magnesium in the alloys was performed. However, preliminary results indicated a strongly negative self interaction coefficient for magnesium. This is not reasonable as a negative coefficient would indicate attraction between like atoms. On the contrary, a positive coefficient is expected as several intermetallic Ni-Mg compounds form in the solid state. The results indicated that some other solute influenced the results. Oxygen is a prime candidate given that magnesium-oxygen should have a strongly negative interaction coefficient. Consequently, experiments were conducted where both magnesium, aluminum and oxygen were analysed.

4.3.2 Applicable Equilibriums

Given that the samples were contained in aluminum oxide crucibles, an equilibrium including some oxide phase was suggested. The oxide layers on the inside of several crucibles were therefore analysed using Energy Dispersive X-ray analysis. In addition, the outside layer of a nickel button was analysed. While the results from the crucibles occasionally showed higher than 50 molecular percent of $\text{Al}_2\text{O}_3$, the sample surfaces show almost exactly the composition of $\text{MgO} \cdot \text{Al}_2\text{O}_3$, a spinel. It is expected that the crucibles would show a higher than 50
percent Al₂O₃ because the electron beam penetrates the thin surface layer of spinel to the underlaying pure alumina. However, it may be concluded that the oxide phase in dynamic equilibrium with the elements in liquid nickel solution is most probably the spinel, MgO·Al₂O₃. (Original results of the EDX analysis are presented in Appendix D, page 157). It should be noted that no evidence of sulphur was detected during the analysis. Sulphur, given its high affinity to magnesium, could otherwise also take part in a magnesium containing equilibrium.

In view of the above discussion, the following reaction will be considered

\[ \text{Mg}(g) + 2\text{Al}(%) + 4\text{O}(%) \rightleftharpoons \text{MgO}·\text{Al₂O₃}(s). \] (4.5)

Further, the reaction subject to experimental investigation was

\[ \text{Mg}(g) \rightleftharpoons \text{Mg}(\%); \] (4.6)

It should be emphasised that these are dynamic equilibria and the chemical composition will change with time. However, by analysing for the content of magnesium at the time the pressure was measured the equilibrium 4.6 is "pinned down", as was also proven in the tin-magnesium alloy experiments.
The equilibrium equation for reaction 4.5 is

\[ K_1 = \frac{a_{\text{MgA}}}{p_{\text{Mg}} h_{\text{Al}}^2 h_0^4} \]  

(4.7)

where \( K_1 \) = equilibrium constant for reaction 4.5,

- \( a_{\text{MgA}} \) = activity of \( \text{MgO} \cdot \text{Al}_2\text{O}_3 \),
- \( p_{\text{Mg}} \) = vapour pressure of magnesium, atm,
- \( h_{\text{Al}} \) = Henrian activity of aluminum, and
- \( h_0 \) = Henrian activity of oxygen.

The Henrian activities can be expressed

\[ h_0 = (\%O) f_0, \text{ and} \]
\[ h_{\text{Al}} = (\%\text{Al}) f_{\text{Al}} \]

(4.8)

(4.9)

where \( f_x \) = the respective Henrian activity coefficients.

The activity coefficients can in turn be expressed

\[ \log f_0 = e_0^0 (\%O) + e_{\text{Al}}^\text{Al} (\%\text{Al}) + e_{\text{Mg}}^\text{Mg} (\%\text{Mg}) \]

(4.10)

\[ \log f_{\text{Al}} = e_{\text{Al}}^\text{Al} (\%\text{Al}) + e_{\text{Mg}}^\text{Mg} (\%\text{Mg}) + e_{\text{O}}^\text{O} (\%O) \]

(4.11)
As discussed in section 2.4.4, the oxygen interaction coefficient $e^M_0$ is generally in absolute terms much larger than the metal-metal, $e^M_M$, interaction parameters. For instance, for iron solutions, (see Table 2.6), the parameters $e^A_1$ and $e^C_a$ are at least two orders of magnitude smaller than $e^0_{Al}$ in absolute numbers. Similarly, the $e^0_Ca$ is an order of magnitude smaller than the $e^0_{Al}$ coefficient. This reasoning applies as well for calcium-oxygen interaction as $e^C_a$ has been given as $-62$, three order of magnitude larger than $e^C_a$. Although these are values for iron solutions, a similar relationship can be expected for nickel solutions. Hence, it will be assumed that $e^M_M$ and $e^0_0$ can be neglected. Equation 4.7 can then be rewritten in logarithmic form, incorporating relationships 4.8-4.11, to give

$$\log K = \log (a^M_{Ma}) - \log (p^M_{Mg}) - 2 \log (h^M_{Al}) - 4 \log (h^M_0) =$$

$$= \log (a^M_{Ma}) - \log (p^M_{Mg}) - 2 \log (\%Al) - 4 \log (\%0)$$

$$- 2 e^0_{Al} - 4 \left[ e^A_{Al} (\%Al) + e^M_{Mg} (\%Mg) \right] \quad (4.12)$$

Further, as

$$e^0_{Al} = \frac{M_{Ma}}{M_0} e^M_{Al} \quad (4.13)$$
and $a_{\text{MA}} = 1$, equation 4.12 can be reduced to

$$
\log K = -\log \left( p_{\text{Mg}} \right) - 2 \log \left( \%\text{Al} \right) - 4 \log \left( \%\text{O} \right)
- 4 \left( \%\text{Mg} \right) e_{0}^{\text{Mg}} - \left[ 3.37 \left( \%\text{O} \right) + 4 \left( \%\text{Al} \right) \right] e_{0}^{\text{Al}}
$$

(4.14)

Given the experimental data in Table 4.5 and literature values for $K$, equation 4.14 has two unknowns, $e_{0}^{\text{Mg}}$ and $e_{0}^{\text{Al}}$. However, the value for $K$ in available literature is probably erroneous and will also be treated as an unknown. The discrepancies between the literature value and the calculated value for $K$ will be discussed in section 4.3.3.1.

### 4.3.3 Statistical Model

To calculate $K_1$, $e_{0}^{\text{Mg}}$ and $e_{0}^{\text{Al}}$ multiple regression analysis with two predictors was applied. A program in the commercially available computer package "Minitab" was used to perform the statistical calculations. The program regresses to a graph of the form

$$
y = B_0 + B_1 x_1 + B_2 x_2
$$

(4.15)

on given data. In this case

$$
y = \log \left( p_{\text{Mg}} \right) + 2 \log \left( \%\text{Al} \right) + 4 \log \left( \%\text{O} \right),
$$
### TABLE 4.5 Data from Nickel-Magnesium Experiments

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>$P_{Mg}$ [atm]</th>
<th>Weight % Mg</th>
<th>Weight % Al</th>
<th>Weight % O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.8 \times 10^{-6}$</td>
<td>0.0035</td>
<td>0.0332</td>
<td>0.0026</td>
</tr>
<tr>
<td>2</td>
<td>$0.8 \times 10^{-6}$</td>
<td>0.0006</td>
<td>0.0257</td>
<td>0.0018</td>
</tr>
<tr>
<td>3</td>
<td>$0.6 \times 10^{-6}$</td>
<td>0.0002</td>
<td>0.0132</td>
<td>0.0020</td>
</tr>
<tr>
<td>4</td>
<td>$0.5 \times 10^{-6}$</td>
<td>0.0001</td>
<td>0.0130</td>
<td>0.0017</td>
</tr>
<tr>
<td>5</td>
<td>$1.0 \times 10^{-6}$</td>
<td>0.0001</td>
<td>0.0260</td>
<td>0.0019</td>
</tr>
<tr>
<td>6</td>
<td>$2.1 \times 10^{-6}$</td>
<td>0.0012</td>
<td>0.0513</td>
<td>0.0030</td>
</tr>
<tr>
<td>7</td>
<td>$2.0 \times 10^{-6}$</td>
<td>0.0083</td>
<td>0.0107</td>
<td>0.0021</td>
</tr>
<tr>
<td>8</td>
<td>$0.7 \times 10^{-6}$</td>
<td>0.0003</td>
<td>0.0255</td>
<td>0.0017</td>
</tr>
<tr>
<td>9</td>
<td>$1.8 \times 10^{-6}$</td>
<td>0.0022</td>
<td>0.0298</td>
<td>0.0019</td>
</tr>
</tbody>
</table>
The calculations yield the following results:

\[
\begin{align*}
B_0 &= \log K_1, \\
B_1 &= e^{A_1}, \\
x_1 &= [-3.37 (\%0) + 4 (\%A1)], \\
B_2 &= e^{Mg}, \\
x_2 &= -4 (\%Mg)
\end{align*}
\]

Sample computer output is given in Appendix E, page 162 together with explanations of the output.

While the standard deviation of \(e^e\) is large, the calculated parameters are all statistically significant.

Figure 4.4 shows the experimentally determined vapour pressures of magnesium plotted versus pressures calculated for each data point using equation 4.14 and the above parameters. The solid line is the ideal case, \(p_{\text{experimental}} = p_{\text{calculated}}\). The graph gives a visual
Figure 4.4 Calculated vapour pressures using equation 4.14 versus experimental results.
picture of the spread of experimental data in this work.

Equation 4.14 is plotted in three dimensions in Figure 4.5. The graph is reduced to two dimensions in Figure 4.6, where the data-points are also included. As can be seen, the experimental points do not always conform to the calculated oxygen content contours. However, it should be noted that oxygen analysis is only accurate to approximately ± 5 ppm.

4.3.3.1 Equilibrium Constant

The equilibrium constant as given by equation 4.7 can be calculated from the constants for the following reactions:

\[
\text{Mg(g) + 2Al(l) + } 2\text{O}_2(g) \rightleftharpoons \text{MgO•Al}_2\text{O}_3(s) \quad (4.16)
\]

\[
\log K_{16} = 46.367 \text{ (at 1743 K, ref. 83)}
\]

\[
\text{Al(l) } \rightleftharpoons \text{Al (%, Ni)} \quad (4.17)
\]

\[
\log K_{17} = 5.647 \text{ (at 1743 K, ref. 56)}
\]

\[
\frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{O (%, Ni)} \quad (4.18)
\]

\[
\log K_{18} = 2.054 \text{ (at 1743 K, ref. 56)}
\]
Figure 4.5 Surface plot from results calculated using equation 4.14, for Mg contents up to 100 ppm and Al contents up to 500 ppm. (Minor variations evident in the lower part of the plot are artificial and due to that a finite number of points were used to produce the plot).
Figure 4.6 Contour map showing the content of oxygen as a function of magnesium and aluminum content. Experimental points: x 17-19 ppm 0, o 20-25 ppm 0, * 26-30 ppm 0. Experiment numbers, see Table 4.5.
The value of $\log K_1$ for reaction 4.5 is then given by:

$$\log K_1 = \log K_{16} - 2 \log K_{17} - 4 \log K_{18} = 26.86$$

(4.19)

This value should be compared to the value of 22.0 determined in this work.

The discrepancy between the literature and the calculated equilibrium constant may have several explanations. It is quite unlikely that the free energy of solution of oxygen in liquid nickel is erroneous as this reaction has been well investigated$^{56,87-90}$. The free energy of solution of aluminum in liquid nickel is not nearly as well documented$^{56,74}$. Hence, it is quite possible that part of the discrepancy may be explained by an error in the free energy of dissolution of aluminum. In addition, the discrepancy between the literature and calculated value could be explained partly by an erroneous free energy of formation of $\text{MgO}^*\text{Al}_2\text{O}_3$. While the literature value is taken from a credible source$^{83}$, errors in the free energy of formation value for oxides have been discussed before$^{68,91-92}$.

The results are further illustrated by the area predominance diagram in Figure 4.7. The diagram provides a confirmation that $\text{MgO}^*\text{Al}_2\text{O}_3$ is the stable oxide phase in these experiments. The solid lines and dashed lines in the diagram are calculated from the literature.
Figure 4.7 Area predominance diagram. Equations 1-5 are given in Appendix F, p.168.

- $p_{Mg} = 10^{-6}$, $p_{Mg} = 10^{-5}$ data from literature.
- $p_{Mg} = 10^{-6}$ suggested data.
data for $p_{Mg} = 10^{-6}$ atm and $10^{-5}$, respectively. The dash-dotted line is calculated from equation 4.14 using the equilibrium constant suggested by this work. It is uncertain how this change in equilibrium constant would affect the other lines in this diagram.

4.3.3.2 Interaction Coefficients

Values of -17 and -28 for the interaction coefficients $e_{0}^{Al}$ and $e_{0}^{Mg}$ were found. They should be compared to values given in Tables 2.6 and 2.7. As can be seen, $e_{0}^{Al}$ has been suggested equal to -1 in previous work. This value was however not based on experimental data but rather on literature data for iron solutions. For iron solutions, values of $e_{0}^{Al}$ between -1 and -5.2 have been published with -3.9 as the most probable value. The magnesium-oxygen coefficient, $e_{0}^{Mg}$ could be compared to $e_{0}^{Ca}$ in iron which has been suggested to be -62.

For the case of the magnesium and aluminum interaction coefficients in nickel solution, the following facts should be considered. The free energies of formation of the oxides are almost identical at 1470°C for both aluminum and magnesium (Figure 4.2). The atoms of both elements are quite similar, and it may be expected that their behaviour in solution will not be widely different. It may
therefore be suggested that the metal-oxygen interaction coefficients for both magnesium and aluminum in nickel solution should be quite similar. In this light, the values of $-17$ for $e_{\text{A}1}^0$ and $-28$ for $e_{\text{M}g}^0$ calculated in this work seem reasonable. These values also fall within the literature values for similar parameters in iron solution.

### 4.3.4 Energy of Solution

The equilibrium constant for reaction 4.6

$$\text{Mg(g)} + \text{Mg (\%)}$$

may be calculated by subtracting

$$\text{Mg (\%)} + 2\text{A}1 (\%) + 4\text{O (\%)} \rightarrow \text{MgO·A}1_2\text{O}_3$$

from reaction 4.5. Doing this for the experiments given in Table 4.5 using calculated interaction coefficients yields an average log $K_{4.19} = 19.3$ and consequently log $K_{4.6} = 2.7$. This compares favourably with a literature value of 1.6 which was calculated assuming a regular solution using data for solid nickel at 650-850°C. The equilibrium constant for reaction 4.6 corresponds to a free energy of solution of $-21.5$ kcal at 1470°C.
4.3.5 **Raoultian Activity Coefficient**

The Raoultian activity coefficient for magnesium, $\gamma_{\text{Mg}}$, in nickel solution is given by

$$\gamma_{\text{Mg}} = \frac{p_{\text{Mg}}}{p_{\text{Mg}}^{e}X_{\text{Mg}}} \quad (4.20)$$

when the activity of magnesium is defined by

$$a_{\text{Mg}} = \gamma_{\text{Mg}} X_{\text{Mg}} = \frac{p_{\text{Mg}}}{p_{\text{Mg}}^{e}} \quad (4.21)$$

Further,

$$\ln \gamma_{\text{Mg}} = \ln \gamma_{\text{Mg}}^{e} + \varepsilon_{\text{Mg}}^{0} X_{0} \quad (4.22)$$

Hence, the activity coefficient at infinitely dilute solution is given by

$$\ln \gamma^{e} = \ln \left[ \frac{p_{\text{Mg}}}{p_{\text{Mg}}^{e}X_{\text{Mg}}} \right] - \varepsilon_{\text{Mg}}^{0} X_{0} \quad (4.23)$$

The values of $\gamma^{e}$ for experiments 1-9 (see Table 4.5) are given in
Table 4.6, using $e_0^{\text{Mg}} = -2667$ calculated from $e_0^\text{Mg} = -28$. The activity coefficient is also calculated for an additional four experiments, #10-13 for which oxygen was not analysed but calculated using equation 4.14.

As can be seen the values for $\log \gamma^\circ$ varies between -2.9 and -1.3. The average value is -2.1 ($\pm$ 0.4). This value falls between the literature values suggested by deBarbadillo $^6$ of -1 and by Mitchell $^9$ of -3.
TABLE 4.6 $\gamma^*$ from Experimental Data
*(Calculated using Equation 4.14)*

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>$P_{Mg}$ [atm.]</th>
<th>$X_{Mg}$</th>
<th>$X_0$</th>
<th>log $\gamma^*_{Mg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$8.5 \times 10^{-5}$</td>
<td>$9.5 \times 10^{-5}$</td>
<td>-2.6</td>
</tr>
<tr>
<td>2</td>
<td>$0.8 \times 10^{-6}$</td>
<td>$1.4 \times 10^{-5}$</td>
<td>$6.6 \times 10^{-5}$</td>
<td>-2.2</td>
</tr>
<tr>
<td>3</td>
<td>$0.6 \times 10^{-6}$</td>
<td>$0.5 \times 10^{-5}$</td>
<td>$7.3 \times 10^{-5}$</td>
<td>-1.8</td>
</tr>
<tr>
<td>4</td>
<td>$0.5 \times 10^{-6}$</td>
<td>$0.2 \times 10^{-5}$</td>
<td>$6.2 \times 10^{-5}$</td>
<td>-1.6</td>
</tr>
<tr>
<td>5</td>
<td>$1.0 \times 10^{-6}$</td>
<td>$0.2 \times 10^{-5}$</td>
<td>$7.0 \times 10^{-5}$</td>
<td>-1.3</td>
</tr>
<tr>
<td>6</td>
<td>$2.1 \times 10^{-6}$</td>
<td>$2.9 \times 10^{-5}$</td>
<td>$1.1 \times 10^{-4}$</td>
<td>-2.0</td>
</tr>
<tr>
<td>7</td>
<td>$2.0 \times 10^{-6}$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$7.7 \times 10^{-5}$</td>
<td>-2.9</td>
</tr>
<tr>
<td>8</td>
<td>$0.7 \times 10^{-6}$</td>
<td>$0.7 \times 10^{-5}$</td>
<td>$6.2 \times 10^{-5}$</td>
<td>-1.9</td>
</tr>
<tr>
<td>9</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$5.3 \times 10^{-5}$</td>
<td>$7.0 \times 10^{-5}$</td>
<td>-2.4</td>
</tr>
<tr>
<td>10</td>
<td>$0.4 \times 10^{-6}$</td>
<td>$1.9 \times 10^{-5}$</td>
<td>$*3.2 \times 10^{-4}$</td>
<td>-2.3</td>
</tr>
<tr>
<td>11</td>
<td>$4.4 \times 10^{-6}$</td>
<td>$3.2 \times 10^{-4}$</td>
<td>$*2.3 \times 10^{-4}$</td>
<td>-2.6</td>
</tr>
<tr>
<td>12</td>
<td>$11.7 \times 10^{-6}$</td>
<td>$2.8 \times 10^{-4}$</td>
<td>$*1.3 \times 10^{-4}$</td>
<td>-2.2</td>
</tr>
<tr>
<td>13</td>
<td>$13.3 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$*5.1 \times 10^{-4}$</td>
<td>-1.8</td>
</tr>
</tbody>
</table>
4.4 Alloys Containing Chromium and Iron

Raw data from experiments without any major alloy addition are compared to data from experiments with alloys containing 20% iron or chromium in Figure 4.8. As discussed earlier, interaction between metals in solution can be generally expected to be much smaller than the interaction between strong oxidizers, such as magnesium and aluminum, and oxygen. It is therefore not surprising, that no major differences are detectable between the alloys in Figure 4.8. deBarbadillo\textsuperscript{63} was also unable to detect a major change in magnesium solubility in nickel at less than 50% of the alloying element (see Figure 2.27).
Figure 4.8 Comparison between data for alloys containing no major additions and alloys containing 20% Fe or 20% Cr.
5. **Conclusions**

The following conclusions are presented in this investigation:

- A novel high temperature experimental method has been developed that employs Knudsen effusion in conjunction with Atomic Absorption Spectrophotometry.

- The experimental method was verified on liquid tin alloys, which have well known magnesium activities, for a calibration method employing a pseudoisopiestic Knudsen cell.

- The method was successfully applied to magnesium vapour pressure determinations for liquid nickel alloys at 1470°C.

Using the novel experimental method, the following thermodynamic data for dilute liquid nickel solutions at 1470°C were determined.

- The equilibrium constant, \( \log K = 22.0 \pm 0.2 \) for the reaction
  \[
  \text{Mg}(g) + 2 \text{Al}(%) + 4 \text{O}(%) \rightleftharpoons \text{MgO} \cdot \text{Al}_2\text{O}_3(s)
  \]
- The magnesium-oxygen interaction coefficient, $e_{0}^{Mg} = -27.7 \pm 6.2$, for magnesium and oxygen contents up to 100 ppm each.

- The aluminum-oxygen interaction coefficient, $e_{0}^{Al} = -16.7 \pm 1.3$ for aluminum contents up to 500 ppm and oxygen contents up to 100 ppm.

- The equilibrium constant, $\log K = 2.7 \pm 0.2$ for the reaction $\text{Mg}(g) \rightleftharpoons \text{Mg}(\%)$.

- The Raoultian activity coefficient for an infinitely dilute solution, $\log \gamma^{o} = -2.1 \pm 0.4$.

- A significant change in magnesium activity for 20 weight percent iron or chromium additions to the dilute nickel alloys could not be detected.
6. **Suggestions for Further Work**

This work suggests further development or refinement in the following areas:

1. The Atomic Absorption-Knudsen method may be extended to measure the vapour pressure of several elements simultaneously. Thus, the activity of several elements in a liquid metal solution could be determined.

2. Determination of the magnesium activity in MgO crucibles may yield $e_{\text{Mg}}$ values of greater certainty as interference from Al is eliminated.

3. It is suggested that any further work using the developed experimental method employs an AAS dedicated to this task. This would eliminate experimental scatter due to equipment changes.
REFERENCES


76. Quartz Scientific Inc.: Catalogue of Fused Quartz Laboratory Ware.


80. Perkin-Elmer: "Analytical Methods for Atomic Absorption Spectrophotometry"


94. "Instructions and Operation, # 589-600 Rapid Oxygen and Low Carbon Analyser," LECO Corporation manual # 176B.
APPENDICIES
APPENDIX A

Equations in the Literature Review

This appendix will describe the deduction of equation 2.2 as presented by Vidale and the deduction of the cosine law (Eq. 2.3) and the Hertz-Knudsen equation (2.4).

Vidale

a. Absorption equation

When a parallel beam of light of intensity \( I_0 \nu \) having a frequency \( \nu \) is passed through a homogeneous gas of thickness, \( l \), the absorption of this beam is given by:

\[
I_\nu = I_{0\nu} e^{-k_\nu l}
\]

(Nomenclature for Appendix A is given on page 147). If no broadening effect were present, \( k_\nu \) would be infinite at \( \nu = \nu_0 \) and would be zero elsewhere.
b. Doppler broadening

If Doppler broadening is the only form of broadening present,

\[ k_v = k_o \exp \left[ - \left( \frac{v - v_o}{v_o} \right) \frac{M_i}{2RT} \right] \]  
(A.2)

and

\[ k_o = \sqrt{\frac{\pi M}{2RT}} \frac{e^2}{mv_o^2} N_f \]  
(A.3)

For sodium, which was considered by Vidale \cite{26},

\[ v_o = 16 \, 973 \, \text{cm}^{-1}, \, M_i = 23, \, f = 0.65. \]

This yields,

\[ k_o = 1.563 \times 10^{12} \frac{P}{T^{3/2}} \]  
(A.4)

and hence

\[ \frac{I}{I_o} = \exp \left[ - 1.563 \times 10^{12} \frac{pl}{T^{3/2}} \right] \]  
(A.5)

and \( \Delta v_o = 0.0505 \) at 400 K.
c. **Natural broadening**

Natural broadening can generally be neglected in comparison with Doppler broadening.

d. **Pressure broadening**

According to the simple pressure broadening theory of Lorenz, the half width due to pressure broadening alone $\Delta v_L$ is given by:

$$\Delta v_L = \frac{Z_L}{\pi} = 0.359 \sigma_L^2 P_A \frac{P_A}{T^{1/2}} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \quad (A.6)$$

For sodium,

$\sigma_L = 9.0 \, \text{A}$, and $M_1 = 23$

For argon $M_2 = 40$, and the experimental conditions of Vidale were set at a temperature of 397 K and an argon pressure $P_A = 9.1 \, \text{cm Hg}$. This yields $\Delta v_L = 0.0457 \, \text{cm}^{-1}$.

When both Doppler and pressure broadening are present, the value of $k_v$ is given by
\[
\frac{k_v}{k_o} = \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-y^2}}{a^2 + (\omega-y)^2} dy
\]  
(A.7)

where

\[
a = \frac{\Delta v_L}{\Delta v_D} \sqrt{\ln 2} = 0.7534
\]  
(A.8)

\[
\omega = \frac{2(v-v_o)}{\Delta v_D} \sqrt{\ln 2} = 1.926 \text{ for } v=v_o + 0.0584
\]  
(A.9)

\[
0 \text{ for } v=v_o
\]

A numerical method was used by Vidale\textsuperscript{26} to determine the integral. The following results were obtained:

\[
\frac{k(v=v_o)}{k_o} = 0.5057 \quad \frac{k(v=v_o + 0.0584)}{k_o} = 0.1363.
\]  
(A.10)

e. **Hyperfine structure effect**

If the radiating atoms consist of a mixture of isotopes, or if they have a non-zero nuclear spin, the atomic line will contain more than one component both in the emission spectrum from the source and in the absorption spectrum in the furnace\textsuperscript{26}. The sodium line is a doublet and only the separation of the two components were considered by Vidale\textsuperscript{26} for the vapour pressure calculations. The intensity ratio of
the two components is 5:3 and the separation 0.0584 cm\(^{-1}\). Equation A.1 can then be written

\[
\ln \frac{I'}{I_0'} = -\frac{3}{8} k_o \lambda - \frac{5}{8} \ln (v - v_o + 0.0584)
\]

(A.11)

\[
\ln \frac{I''}{I_0''} = -\frac{5}{8} k_o \lambda - \frac{3}{8} \ln (v - v_o + 0.0584)
\]

The second term in each equation is present as there is an overlap between the two components. The monochromator of Vidale could not resolve the two components and therefore the measured intensities are \(I' + I''\) and \(I'_o + I''_o\). Also \(I'_o = \frac{3}{8} (I'_o + I''_o)\) and \(I''_o = \frac{5}{8} (I'_o + I''_o)\) so that

\[
(\frac{I'}{I_o'})_{\text{exp}} = \frac{I' + I''}{I_0'} = \frac{3}{8} \exp \left[-\frac{2}{8} k_o + \frac{5}{8} k_o (v - v_o + 0.0584)\right]
\]

(A.12)

The results presented in equation A.10 substituted into A.12 yields

\[
(\frac{I}{I_o'})_{\text{exp}} = \frac{3}{8} \exp (-0.2748 k_o \lambda) + \frac{5}{8} \exp (-0.3672 k_o \lambda),
\]

(A.13)

and if the result in equation A.4 is utilized and \(\lambda\) set at the cell length (10.16 cm)

\[
(\frac{I}{I_o'})_{\text{exp}} = \frac{3}{8} \exp (-4.347 \times 10^{12} \frac{P}{T^{3/2}}) + \frac{5}{8} \exp (-5.809 \times 10^{12} \frac{P}{T^{3/2}})
\]

(A.14)

This equation in simplified form is presented in the thesis as (2.2).
X. LIST OF SYMBOLS FOR THE WORK OF VIDALE

\begin{align*}
\begin{array}{ll}
c & = \text{velocity of light} \\
e & = \text{charge of the electron} \\
f & = \text{oscillator strength of the line in question} \\
\Delta F^0 & = \text{standard molar free energy of vaporization} \\
\Delta H & = \text{molar enthalpy of vaporization} \\
\Delta H^0 & = \text{standard molar enthalpy of vaporization} \\
I_\nu & = \text{intensity of the light beam of frequency } \nu \text{ after passing through absorbing path} \\
I_{0\nu} & = \text{original intensity of the light beam of frequency } \nu \text{ from the source} \\
\left( \frac{I}{I_0} \right)_{\text{exp}} & = \text{experimentally measured value of } \frac{I}{I_0}, \text{ when monochromator slit is much wider than the line under study} \\
k_\nu & = \text{absorption coefficient of the gas for light of frequency } \nu \\
k_0 & = \text{absorption coefficient of the gas at the center of the line when only Doppler broadening effects are present} \\
\lambda & = \text{length of the absorbing path} \\
m & = \text{mass of the electron} \\
M & = \text{molecular weight of the gaseous species} \\
M_1 & = \text{atomic weight of absorbing species} \\
M_2 & = \text{molecular weight of gas responsible for Lorentz broadening} \\
N & = \text{density of the species under consideration} \\
P & = \text{partial pressure of gas being analyzed} \\
P_A & = \text{pressure of gas responsible for Lorentz broadening} \\
R & = \text{gas constant}
\end{array}
\end{align*}
\[ \Delta S^0 \quad \text{standard molar entropy of vaporization} \]

\[ T \quad \text{temperature} \]

\[ Z_L \quad \text{number of collisions that the absorbing species makes with other molecules per second} \]

\[ \nu \quad \text{frequency of the light} \]

\[ \Delta \nu_D \quad \text{Doppler breadth of the line} \]

\[ \Delta \nu_L \quad \text{Lorentz half breadth of the line} \]

\[ \Delta \nu_S \quad \text{frequency shift of the center of the line due to pressure effects} \]

\[ \nu_o \quad \text{frequency of the center of the absorption line, when no shift is present} \]

\[ \sigma_L \quad \text{effective cross section for collisions between absorbing atoms and species responsible for the Lorentz broadening} \]

\[ \tau \quad \text{lifetime of the atom in the resonance state} \]

\[ \omega = \frac{2(\nu - \nu_o)}{\Delta \nu_D} \sqrt{\ln 2} \]
The Cosine law

The distribution of molecular velocities in a gas at low pressure obeys the Maxwell-Boltzmann distribution law which, expressed in terms of molecular speeds independent of direction is

\[
\frac{dN(c)}{N_0} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \exp\left(\frac{Mc^2}{RT}\right)
\]  

(A.15)

(Symbols are explained in "Nomenclature", p. xv).

The average molecular speed is,

\[
\bar{c} = (8RT/\pi M)^{1/2}
\]  

(A.16)

The rate of collision of molecules on unit area of the wall in unit time is,

\[
Z_0 = \frac{N}{V} \left(\frac{\bar{c}}{4}\right)
\]  

(A.17)

The assumption of molecular chaos leads to the probability that a molecule approaches the wall of an angle \(\theta\) to the normal within the element of solid angle \(d\omega\):

\[
\frac{N(\theta)}{Z_0} = \frac{N}{V} \bar{c} \cos \theta \frac{d\omega}{4\pi}
\]  

(A.18)
This is the cosine law, also presented as equation 2.3.

**The Hertz-Knudsen equation**

The molecular density $N/V$ is related to the pressure for an ideal gas by

$$p = \frac{(N/V) kT}{(N'/V)RT}$$  \hspace{1cm} (A.19)

Combining equations A.16 - A.19

$$p = \frac{Z_0}{A} \left(2\pi kTm\right)^{1/2}$$  \hspace{1cm} (A.20)

or in terms of the weight loss accompanying the effusion process

$$p = \frac{\omega}{At} \left(2\pi RT/M\right)^{1/2}$$  \hspace{1cm} (A.21)

Equations A.20 and A.21 (2.4) are different forms of the Hertz-Knudsen equation.
Procedures for Chemical Analysis

Each metal sample was either cut in half and analysed for magnesium/aluminum and oxygen or the entire sample was analysed for magnesium/aluminum only.

a. Magnesium Analysis

Mechanically cleaned solid metal samples (nickel-base or tin-base) were weighed. Generally, 3-6 g of metal was analysed. Each sample was digested in a 50% solution of either HNO₃ or HCl or a combination of the two acids and deionised H₂O. The proportions of acids varied, depending on alloy, e.g. it was found that the dilute nickel alloys dissolved well in nitric acid after ~ 10% hydrochloric acid was added. Care was taken to ensure that the alloy used as a standard was treated in the same manner as the sample solutions for each set of analysis. The solutions were heated in covered beakers until no metal remained. The solutions were then quantitatively transferred to either 100 ml or 200 ml volumetric flasks (depending on original amount of metal), cooled and diluted to volume with de-ionised water.
Portions (usually 5 ml) of concentrated solution were pipetted off into 50 ml volumetric flasks. 5 ml of a lanthanum chloride solution (29 g La\textsubscript{2}O\textsubscript{3} + 200 ml HCl diluted to 1000 ml) was added to each flask, and the solutions diluted to volume with de-ionised water. One sample of each set, which had a low magnesium content, was prepared for analysis according to the standard addition method. Thus, 0, 5, 10 and 20 ml of a 5 ppm magnesium stock solution was added to four solutions of the same concentrated solution prepared as above. This standard addition set of solutions was also used as standards for samples prepared in the same manner. All glassware used was thoroughly washed in laboratory detergent, rinsed in hot tap water, then soaked overnight in 5% nitric acid and finally rinsed repeatedly in de-ionised water.

Atomic Absorption Analysis was performed in the standard manner using an air-acetylene flame. Repeated analysis of the same metals showed a variation of ± 3 ppm.

b. Aluminum Analysis

Aluminum analysis solutions were prepared from the concentrated solutions described in section a, in the same manner as the magnesium solutions with the following exceptions. Generally, solutions of double
concentration were analysed. The AAS analysis was performed using a nitrous oxide - acetylene flame. The uncertainty is ± 25 ppm.

c. Oxygen Analysis

The inert carrier-gas method was applied for the oxygen analysis\(^9\). The equipment employed consisted of a LECO Corporation oxygen analyser (\#589-600) and induction furnace (\#537-100). The procedure described in the LECO manual\(^9\) for sample preparation and analysis was followed throughout. Oxygen calibration samples containing 89 ppm oxygen were utilised.

Three 1 g solid, clean samples of each nickel alloy were analysed. Generally, the difference between the highest and lowest results were less than 10 ppm. The average value from the three samples is taken as the oxygen content, except where one value differed widely from the other two, in which case the average of the closer two was taken as the oxygen content. The uncertainty is estimated to be ± 5 ppm.
Doppler Shift

The light emitted from a hollow cathode lamp is produced by a gas of Maxwellian distribution. Its peak wavelength, and hence peak absorption wavelength in these experiments is equal to $2852.13\AA = \lambda$. However, the atoms are emitted from the Knudsen cell in a directional manner, as schematically illustrated in Figure B.1. Thus, the peak absorption wavelength of the atoms emitted from the Knudsen cell may be shifted out of the "absorption window".

The following is a simple calculation to gain an understanding of how the Doppler effect may influence the absorption measurements in this investigation.

The distribution of atoms emitted from the orifice is determined by Lamberts cosine law, which in two dimensions is given by

$$I_\theta = I_0 \cos \theta$$  \hspace{1cm} (B.1)

where $I_0$ is the intensity of the beam perpendicular to the orifice plate and $I_\theta$ is the beam intensity at angle $\theta$. This equation is independent of the temperature and is not significant for these calculations.
The Doppler shift for electro-magnetic radiation is given by

\[ f = f' \left[ \frac{1 + \frac{v}{c}}{1 - \frac{v}{c}} \right]^{1/2} \]  

(B.2)

where \( f \) = frequency of shifted line;
\( f' \) = frequency of original line
\( v \) = speed of atoms
\( c \) = speed of light in vacuum

The frequency is given by

\[ f' = \frac{c}{\lambda} \]  

(B.3)

and the speed of atoms by

\[ E = \frac{1}{2} mv^2 = \frac{3}{2} kT \]
\[ v = \sqrt{\frac{3kT}{m}} \]  

(B.4)

Data: \( \lambda = 2852.13\text{Å}; \quad T = 900°C \)
\( c = 2.997925 \times 10^{10} \text{ cm/s} \)
\[ k = 1.38054 \times 10^{-23} \text{ J/K} = 1.38054 \times 10^{-20} \frac{\text{gm}^2}{\text{s}^2\text{K}} \]

\[ m_{\text{Mg}} = 24.312 \text{ g/mole} = 4.036848 \times 10^{-23} \text{ g/atom} \]

and

\[ f' = \frac{c}{\lambda} = 1.051118 \times 10^{15} \text{ s}^{-1} \]

\[ v = \sqrt{\frac{3kT}{m}} = 1.097016 \times 10^5 \text{ cm/s} \]

\[ f = f' \left[ \frac{1 + \frac{v}{c}}{1 - \frac{v}{c}} \right]^{1/2} = 1.051122 \times 10^{15} \text{ s}^{-1} \]

\[ \lambda = \frac{c}{f} = 2852.12 \text{ Å} \]

\[ \Delta \lambda = 0.01 \text{ Å} \]

Similarly for 1470°C:

\[ \lambda = 2852.12 \text{ Å} \]

\[ \Delta \lambda = 0.01 \text{ Å} \]

Hence, there is no difference in Doppler shift for 900°C and 1470°C. At lower temperatures the shift would be even smaller.

The half width of a hollow cathode lamp has been measured by L'Vov\textsuperscript{82} for the following conditions:
$p_{Ar} = 1.6 \text{ torr and}$

$I = 5 \text{ mA.}$

The width given is

$\Delta \nu = 0.17 \text{ cm}^{-1};$

$\Delta \lambda = 0.014 \text{ Å}$
EDX Analysis of Oxide Phase

Raw output of EDX analysis of the oxide phase is presented for the surface of a nickel sample in Figures D.1 and D.2 and for the inside of a crucible in Figures D.3 and D.4. The analysis was in both cases done at low magnification and covers areas large enough to be representative of the specimens. Both cases also show elemental nickel. In the case of the sample surface, the nickel content was picked up by the beam from the substrate. In the case of the crucible, the nickel was present as droplets on the surface.

The sample surface show a ratio of 1.03 molar percent MgO/Al₂O₃, and the crucible a ratio of 0.93 molar percent MgO/Al₂O₃.
Figure D.1
Mar. 9, 1987

SURFACE OF SAMPLE -

Accelerating voltage 20.0 KeV
Beam sample incidence angle 90.0 degrees
X-ray emergence angle 25.8 degrees
X-ray window incidence angle 25.8 degrees
Window thickness 20.0 microns

STANDARDLESS EDS ANALYSIS
(ZAF CORRECTIONS VIA MAGIC V)

<table>
<thead>
<tr>
<th>ELEMENT &amp; LINE</th>
<th>K-RATIO**</th>
<th>PERCENT</th>
<th>PRECISION</th>
<th>OXIDE FORMULA</th>
<th>OXIDE PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>O *</td>
<td>41.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg KA</td>
<td>0.1942</td>
<td>16.05</td>
<td>0.17</td>
<td>MgO</td>
<td>26.62</td>
</tr>
<tr>
<td>Al KA</td>
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<td>0.16</td>
<td>Al2O3</td>
<td>65.11</td>
</tr>
<tr>
<td>Ni KA</td>
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<td>8.28</td>
<td>0.09</td>
<td>Ni</td>
<td>8.28</td>
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<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

* DETERMINED BY STOICHIOMETRY

**NOTE: K-RATIO = K-RATIO x R
where R = reference(standard)/reference(sample)

NORMALIZATION FACTOR: 0.571

Figure D.2
Figure D.3
Accelerating voltage: 20.0 keV
Beam - sample incidence angle: 90.0 degrees
X-ray emergence angle: 25.8 degrees
X-ray - window incidence angle: 25.8 degrees
Window thickness: 20.0 microns

**STANDARDLESS EDS ANALYSIS (ZAF CORRECTIONS VIA MAGIC V)**

<table>
<thead>
<tr>
<th>ELEMENT &amp; LINE</th>
<th>K-RATIO**</th>
<th>WEIGHT PERCENT</th>
<th>PRECISION 2 SIGMA</th>
<th>OXIDE FORMULA</th>
<th>OXIDE PERCENT</th>
<th>NO. OF CATIONS IN FORMULA</th>
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</thead>
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<tr>
<td>O *</td>
<td>0.0952</td>
<td>0.0952</td>
<td>0.16</td>
<td>MoO</td>
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<td>0.7051</td>
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<tr>
<td>Na KA</td>
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<td>13.05</td>
<td>0.15</td>
<td>Al2O3</td>
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<td>1.5300</td>
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<tr>
<td>Ni KA</td>
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<td>0.10</td>
<td>Ni</td>
<td>18.98</td>
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<tr>
<td><strong>TOTAL</strong></td>
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<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>2.2350</td>
</tr>
</tbody>
</table>

**NUMBER OF CATIONS CALCULATED ON BASIS OF 3 OXYGEN ATOMS.**

* DETERMINED BY STOICHIOMETRY

**NOTE: K-RATIO = K-RATIO x R
where R = reference(standard)/reference(sample)**

NORMALIZATION FACTOR: 0.521

Figure D.4
APPENDIX E

Regression Analysis

The following are comments on the attached computer run of linear multiple regression analysis using "Minitab"\textsuperscript{85,86} (p. 166).

1) "VLP" (=y) is regressed on "CALO" (=X\textsubscript{1}) and "CMG" (=X\textsubscript{2}). Residuals for each experiment are saved in column C9.

2) The computer regressed equation.

3) Stdev = estimated standard deviation

\[ t\text{-ratio} = \frac{B - \text{(hypothesized value)}}{\text{estimated stdev of } B}, \]

where hypothesized value = 0. Should be \textgreater 2.

4) s = standard deviation of y (=VLP) about the regression line

\[ R\text{-sq} = \frac{\text{Regression SS}}{\text{Total ss}} \times 100, \text{ see also below.} \]
5) Analysis of Variance table:
Regression SS = regression sum of squared deviations, part of Total SS explained by the regression line.
Total SS = total sum of squared deviations.

The column of major interest is the "Residual" column. It shows the difference between the calculated y using the regressed equation and the given y (VLP).

Finally, page 167 gives the total table of experimental data as printed from the computer.
MTB > REGRESS 'VLP' on 2 predictors 'CALO', 'CMG';
SUBC> RESIDUALS into C9.

The regression equation is
\[ vlp = -22.0 - 16.7 \text{calo} - 27.7 \text{cmg} \]

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coef</th>
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<th>t-ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
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<td>-131.42</td>
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<tr>
<td>calo</td>
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<td>-12.94</td>
</tr>
<tr>
<td>cmg</td>
<td>-27.723</td>
<td>6.201</td>
<td>-4.47</td>
</tr>
</tbody>
</table>

\[ s = 0.1846 \quad R^{2} = 96.67 \% \quad R^{2}(adj) = 95.5\% \]

Analysis of Variance

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<th>SOURCE</th>
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<th>MS</th>
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</thead>
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<td>Error</td>
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<td>0.0341</td>
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<tr>
<td>Total</td>
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</table>

<table>
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<th>SEQ SS</th>
</tr>
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<tr>
<td>cmg</td>
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<td>0.6813</td>
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<table>
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<th>Stdev.Fit</th>
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<th>St.Resid</th>
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<tr>
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APPENDIX F

Equations for the area predominance diagram given in Figure 4.7.

1. \( \text{Mg}(g) + 2 \text{Al}(\%) + 4\text{O}(\%) \leftrightarrow \text{MgO}\cdot\text{Al}_2\text{O}_3(s) \)
   \[ \log K_1 = - \log p_{\text{Mg}} - 2 \log h_{\text{Al}} - 4 \log h_{\text{O}} \]

2. \( \text{MgO}(s) + 2\text{Al}(\%) + 3\text{O}(\%) \leftrightarrow \text{MgO}\cdot\text{Al}_2\text{O}_3(s) \)
   \[ \log K_2 = - 2 \log h_{\text{Al}} - 3 \log h_{\text{O}} \]

3. \( \text{Al}_2\text{O}_3(s) + \text{Mg}(g) + \text{O}(\%) \leftrightarrow \text{MgO}\cdot\text{Al}_2\text{O}_3(s) \)
   \[ \log K_3 = - \log p_{\text{Mg}} - \log h_{\text{O}} \]

4. \( \text{Mg}(g) + \text{O}(\%) \leftrightarrow \text{MgO}(s) \)
   \[ \log K_4 = - \log p_{\text{Mg}} - \log h_{\text{O}} \]

5. \( 2\text{Al}(\%) + 3\text{O}(\%) \leftrightarrow \text{Al}_2\text{O}_3(s) \)
   \[ \log K_5 = - 2 \log h_{\text{Al}} - 3 \log h_{\text{O}} \]