

KINETICS OF OXYGEN TRANSFER
BETWEEN GASES AND MOLTEN SILVER

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ABSTRACT

The kinetics of oxygen transfer between gases and liquid silver were studied in the oxygen partial pressure range of 0 - 1.0 atmosphere. Nitrogen and argon were used as the diluent gas. Three separate experimental systems were employed to alter the gas/liquid contacting configuration. The first involved gas jet impingement of the free surface of a 17 kg bath of liquid silver. The jet momentum and lance height were varied in the ranges 0 - 55,000 dynes and 5 - 15 cm respectively. The second was a thermogravimetric system in which 20 gm samples of silver were suspended in a gas stream of variable composition. In contrast to the jetting experiments, there was no convective stirring of the liquid silver by the gas stream. The total pressure was maintained at 1 atmosphere in both these experimental systems. The third system was also based on thermogravimetry, but could be operated at reduced total pressure. This permitted critical experiments to be carried out, which served to elucidate the kinetic mechanisms of oxygen transfer. For the conditions studied, the kinetics were controlled by mass transport in one or both of the gas and liquid phases. Under certain conditions, surface tension driven convection developed spontaneously in the liquid phase as a result of instabilities in the mass transfer process. These specific observations in a high temperature liquid metal system were consistent with the theoretical predictions of the Sternling-Scriven criterion, which has been supported previously by a body of experimental evidence from low temperature systems of interest to the chemical engineer.

To Marta, Nina and Jennie

CONTENTS

	Page
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 THEORETICAL BACKGROUND AND PREVIOUS WORK	3
2.1 Basic Mass Transfer Relationships	3
2.2 Gas Phase Considerations	7
2.2.1 Kinetic Influence of the Gas Phase Resistance	7
2.2.2 Bulk Flow	12
2.2.3 Jet Characteristics	13
2.3 Liquid Phase Mass Transfer	17
2.3.1 Molecular Diffusion	17
2.3.2 Forced Convection Induced by Gas Jet Impingement	18
2.4 Kinetic Studies in the Oxygen/Silver System	22
2.4.1 Diffusion in Quiescent Silver	22
(a) Absorption	22
(b) Desorption of Unstirred Silver	24
2.4.2 Oxygen Transfer with Inductively Stirred Liquid Silver	24
(a) Absorption	24
(b) Effusion	25
2.4.3 Oxygen Jetting of Silver	25
2.4.4 The Importance of Gas Composition	29
2.4.5 The Effect of Surface Movement	34
2.5 Marangoni Phenomena and Spontaneous Convection	36
2.5.1 Convective Instability during Mass Transfer	39
2.5.2 The Influence of an Existing Flow Field	45
2.5.3 Heat Transfer Effects	46
2.5.4 The Influence of Natural Convection	49
CHAPTER 3 EXPERIMENTAL INVESTIGATIONS AND RESULTS	51
3.1 Gas Jetting of Liquid Silver	51
3.1.1 Apparatus	51
3.1.2 Jet Temperature and Nozzle Characteristics	58

3.1.3	Procedure for Mass Transfer Runs	64
3.1.4	Results of Mass Transfer Experiments using Pure Oxygen Gas Jets	65
	(a) The Influence of Mechanical Stirring	68
	(b) The Influence of Jet Momentum and Lance Height	71
	(c) Comparison with Previous Work	72
3.1.5	Results of Mass Transfer Experiments using Dilute Oxygen Gas Jets	76
	(a) Calculations of the Overall Mass Transfer Coefficient	76
	(b) Calculations of the Gas Phase Mass Transfer Coefficient	81
3.2	Thermogravimetric Studies at Atmospheric Pressure	88
3.2.1	Apparatus	90
3.2.2	Procedure for Mass Transfer Runs	92
3.2.3	Results of Mass Transfer Experiments	92
3.3	Thermogravimetric Studies at Reduced Total Pressure (Effusion)	97
3.3.1	Apparatus	97
3.3.2	Procedure for Mass Transfer Runs	100
3.3.3	Results of Mass Transfer Experiments	101
CHAPTER 4	INTERPRETATION OF RESULTS	104
4.1	Thermogravimetric Studies	104
4.1.1	Analysis of the Mass Transfer Data	104
	(a) Absorption at Atmospheric Pressure	104
	(b) Desorption at Atmospheric Pressure	105
	(c) Effusion	108
4.1.2	Deduced Mechanism of Reaction	108
4.2	Marangoni Phenomena in the Gas Jetting Experiments	113
4.3	The Relevance of this Study to Previous Work	120
CHAPTER 5	CONCLUSIONS	125

APPENDIX A	Mass Transfer Data from Absorption Experiments using Pure Oxygen Jets	127
APPENDIX B	Mass Transfer Data from Absorption and Desorption Experiments using Dilute Gas Jets	134
APPENDIX C	Mass Transfer Data from Absorption and Desorption Thermogravimetric Experiments	140
	(a) Calibrations/Mass Balances	140
	(b) Mass Transfer Data	141
APPENDIX D	Dilute Gas Jetting Experiments – Calculations of the Gas Phase Mass Transfer Coefficient	145
LIST OF SYMBOLS		153
ACKNOWLEDGEMENTS		156
REFERENCES		157

LIST OF FIGURES

Figure 2.1	Composition Profiles During Mass Transfer (Absorption)	4
Figure 2.2	Relationship between λ , η and ϕ	10
Figure 2.3	Relationship between λ , ϕ and ϵ	11
Figure 2.4	Jet Velocity Profiles	15
Figure 2.5	Circulation Patterns in Water with CO ₂ Jets (Velocities in cm sec ⁻¹)	20
Figure 2.6	Liquid Phase Mass Transfer Data from Experiments with Pure Oxygen Jets (14)	27
Figure 2.7	Variation of Mass Transfer with Free Surface Area	28
Figure 2.8	Absorption and Desorption Data - Inductively Stirred Silver (40)	33
Figure 2.9	Surface Tension - Oxygen Activity Isotherms in the Ag-O System (51)	38
Figure 3.1	General Layout of Jetting Apparatus	52
Figure 3.2	Silver Furnace	54
Figure 3.3	Stirrer Assembly	56
Figure 3.4	Solid Electrolyte Probe Assembly	57
Figure 3.5	Arrangement for Jet Temperature Measurement	59
Figure 3.6	Sensitivity of Calculated Nozzle Discharge Coefficients to Variations in Assumed value of "r"	63
Figure 3.7	Summary of Liquid Phase Mass Transfer Data from Absorption and Desorption Experiments with Pure Oxygen Jets	69
Figure 3.8	The Effect of Lance Height on Liquid Phase Mass Transfer; 13,100 dynes	70
Figure 3.9	Comparisons of Previous and Present Work	73
Figure 3.10	Overall Mass Transfer Data from Absorption and Desorption Experiments at Low Momentum (about 6500 dynes) with Dilute Jets	78
Figure 3.11	Overall Mass Transfer Data from Absorption and Desorption Experiments at Medium Momentum (about 13,000 dynes) with Dilute Jets	79

Figure 3.12	Overall Mass Transfer Data from Absorption and Desorption Experiments at High Momentum (about 19,000 dynes) with Dilute Jets	80
Figure 3.13	Calculated Gas Phase Mass Transfer Coefficients at Low Jet Momentum (6500 dynes)	84
Figure 3.14	Calculated Gas Phase Mass Transfer Coefficients at Medium Momentum (13,000 dynes)	85
Figure 3.15	Calculated Gas Phase Mass Transfer Coefficients at High Momentum (19,000 dynes)	86
Figure 3.16	Gas/Liquid Contacting Configuration in Thermogravimetric Experiments	89
Figure 3.17	Apparatus for Thermogravimetric Experiments at Atmospheric Pressure	91
Figure 3.18	Mass Transfer Data from Preliminary Thermogravimetric Experiments	94
Figure 3.19	Summary of Overall Transfer Data from Thermogravimetric Experiments at Atmospheric Pressure	96
Figure 3.20	Apparatus for Thermogravimetric Experiments at Reduced Total Pressure	98
Figure 3.21	Mass Transfer Data from Desorption Experiments at Reduced Total Pressure	103
Figure 4.1	Interpretation of Thermogravimetric Data - Mass Transfer Control Model	107
Figure 4.2	Data Fitting Exercise for Gas Jetting Experiments at a Momentum of 6500 dynes	116
Figure 4.3	Data Fitting Exercise for Gas Jetting Experiments at a Momentum of 13,000 dynes	117
Figure 4.4	Data Fitting Exercise for Gas Jetting Experiments at a Momentum of 19,000 dynes	118
Figure 4.5	Reinterpretation of Data of Mori et al (40)	122
Figure A1-A6	lnR vs t; Pure Oxygen Jets	128 - 133
Figure B1-B5	lnR vs t; Dilute Oxygen Jets	135 - 139

Figure C 1	$\ln R$ vs $\frac{A}{V}t$, Absorption Data from Thermogravimetric Experiments	142
Figure C 2	$\ln R$ vs $\frac{A}{V}t$, Desorption Data from Thermogravimetric Experiments	143
Figure C 3	$\ln R$ vs $\frac{A}{V}t$, Mass Transfer Data from Desorption Runs at Reduced Pressure, $p_{O_2} = P_{TOT}$	144

LIST OF TABLES

Table 2.1	Oxygen Diffusivity in Liquid Silver at 1000°C	23
Table 2.2	Absorption and Desorption Data from Experiments using Dilute Oxygen Jets	31
Table 2.3	The Appearance of Marangoni Instabilities	43
Table 3.1	Experimental Data and Calculations of Jet Nozzle Characteristics	62
Table 3.2	Summary of Liquid Phase Mass Transfer Data with Pure Oxygen Gas Jets	66
Table 3.3	The Effects of Bulk Metal Mechanical Stirring on Free Surface Mass Transfer	67
Table 3.4	Summary of Mass Transfer Data with Dilute Gas Jets	77
Table 3.5	Regimes of Kinetic Control - The Effect of Hydrodynamic Conditions and Gas Composition	82
Table 3.6	Mass Transfer Data from Thermogravimetric Experiments at Atmospheric Pressure	95
Table 3.7	Mass Transfer Data from Thermogravimetric Experiments at Variable Total Pressure	102
Table 4.1	Results of Data Fitting Exercise : Dilute Gas Jetting Experiments	115
Table D1	Computer Programme	148
Table D2	Calculations of the Gas Phase Mass Transfer Coefficients	150

CHAPTER 1

INTRODUCTION

The present investigation was originally conceived as a study of the interaction between gas jets and liquid metals, following on from the work of Chatterjee (1) and Wakelin(2) in the John Percy Group. Process metallurgical research interest in jet/liquid systems is stimulated mainly by developments in oxygen steelmaking and various degassing processes. The previous studies covered aspects such as jet characteristics, geometry of the depression in the liquid bath, mass transfer at the free surface and so on. Room temperature analogue studies preceeded Wakelin's and Chatterjee's experiments with liquid silver. The high oxygen solubility and the absence of an oxide phase at normal pressures make silver attractive for preliminary gas/liquid metal kinetic studies. The general strategy was to proceed to jetting experiments with liquid copper, which would be of more direct commercial interest, and ultimately work with ferrous systems. The jetting programme as a whole has complemented other areas of process metallurgical research within the John Percy Group, particularly the work involving high temperature gas/metal and slag/metal reactions.

The previous workers (1,2) obtained some preliminary results which suggested that when the gas is not pure oxygen the gas phase mass transfer resistance plays a significant role in the overall kinetics of oxygen transfer between gases and liquid silver. The first objective of the present study was therefore to carry out more substantial experimentation with dilute jets. The oxygen partial pressures were selected purposefully to highlight the gas phase resistance effect. However, the results from these experiments showed that the kinetics were dependent on the direction of transfer

in a manner which could not be explained by the simple mass transfer model previously adopted.

Thermogravimetric experiments were therefore initiated in an attempt to elucidate the reaction mechanism. The small-scale thermogravimetric apparatus provided the flexibility to carry out critical tests which could not be readily conducted on the larger-scale jetting rig. Furthermore, the theoretical and experimental understanding of mass transfer between liquids and impinging gas jets is severely limited. In contrast, thermogravimetric studies were based on a simple, well defined gas/liquid contacting configuration.

In a recent review of interfacial turbulence in liquid metal systems, Brimacombe (80) has written : ... "our understanding is at an embryo stage : it is hoped that the present study will stimulate work on this fascinating subject". Interfacial phenomena from surface rippling to spontaneous emulsification are certainly important in numerous processes involving liquid metals, but direct evidence is unfortunately sparse to date. The thermogravimetric work described in this thesis resulted in well substantiated evidence for the emergence of spontaneous surface convection under certain conditions of oxygen transfer between gases and liquid silver. It was then possible to show that the mass transfer results from the jetting campaign were also influenced by such convection, which is driven by surface tension gradients within the gas/liquid interface. These observations of 'Marangoni' instabilities, which were consistent with the predictions of the Sternling-Scriven criterion (69), are believed to make a positive contribution to the subject of interfacial phenomena in metallurgical processes.

CHAPTER 2

THEORETICAL BACKGROUND AND PREVIOUS WORK

2.1 Basic Mass Transfer Relationships

In the present work, oxygen absorption and desorption experiments were carried out by contacting oxygen/nitrogen gas mixtures ($p_{O_2} = 0 - 1.0$ atm) with molten silver. Such exchange of oxygen between gas and liquid necessarily involves a gas phase mass transfer step, chemical reaction at the interface, and a liquid phase mass transfer step.

Figure (2.1) shows the concentration gradients of oxygen in the gas and the liquid in the general case. (Note: a list of symbols is given at the end of the thesis.) Unless the chemical reaction resistance is explicitly considered it is assumed throughout this thesis that chemical equilibrium exists at the interface. In other words, the chemical resistance is sufficiently less than the mass transport resistances to have no influence on the overall rate of oxygen transfer. The logic behind this assumption, given clear expression by Hills (20), is that chemical effects at high temperature should only be seriously considered when it is clear that transport phenomena can not explain the observed behaviour.

At equilibrium, oxygen dissolution in molten silver obeys Sievert's law (21,22) where :

$$C = q\sqrt{p} \quad (2.1)$$

At 1000°C , the Sievert's constant, q , is 1.76×10^{-3} gm atoms/cm³ atm ^{$\frac{1}{2}$} (1,22) such that at atmospheric pressure about 10 cc of oxygen dissolve in 1 gm of liquid silver. The high solubility and absence of an oxide at normal pressure make the oxygen/silver system attractive for gas/liquid kinetic studies.

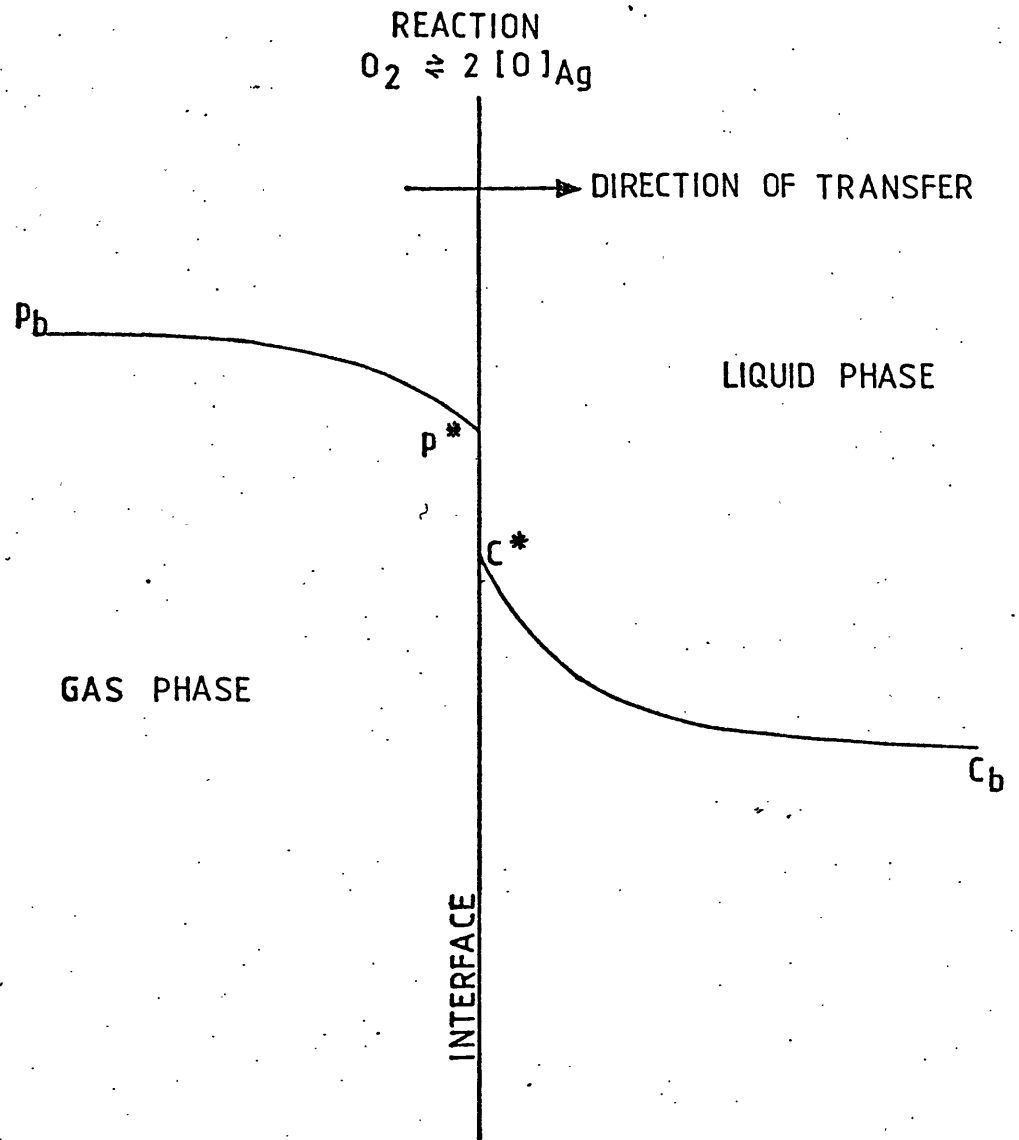


FIG. 2.1 COMPOSITION PROFILES DURING
MASS TRANSFER (ABSORPTION)

The diffusional flux equations for quasi-steady state transport in the gas and liquid phases are written in terms of mass transfer coefficients

$$\dot{n} = \frac{2 k_G A}{RT} (p_b - p^*) \quad (2.2)$$

$$\text{and } \dot{n} = k_L A (C^* - C_b) \quad (2.3)$$

The factor 2 in Equation (2.2) relates to the mass balance where one mole of gas yields two gram-atoms of dissolved oxygen in the silver.

The assumption of interfacial equilibrium allows C^* and p^* to be related :

$$C^* = q\sqrt{p^*} \quad (2.4)$$

In the particular case of using pure oxygen gas, at any total pressure, there can be no diffusional resistance in the gas phase. In the absence of a partial pressure gradient in the gas phase, $p_b = p^*$, the overall process becomes liquid phase controlled. The overall flux, from Equations (2.3) and (2.4) is :

$$\dot{n} = k_L A (q\sqrt{p_b} - C_b) \quad (2.5)$$

mass balance leads to

$$\dot{n} = \frac{V dC_b}{dt} \quad (2.6)$$

and combination and integration of the above equations yields the standard mass transfer relationship.

$$\ln \frac{q\sqrt{p_b} - C_b}{q\sqrt{p_b} - C_b(t=0)} = -k_L \frac{A}{V} t \quad (2.7)$$

The ratio $(q\sqrt{p_b} - C_b) / (q\sqrt{p_b} - C_b(t=0))$ will hitherto be designated R for convenience.

If the liquid phase mass transfer coefficient is constant throughout an experiment, then a plot of $\ln R$ vs $\frac{A}{V} t$ will be linear, with slope $-k_L$.

In the general situation of dilute gas mixtures being contacted with silver, the gas phase diffusional resistance can not be ignored. It can then be convenient to express the rate empirically in terms of the total driving force available for absorption or desorption, by defining an overall mass transfer coefficient, k_{OV} .

$$\dot{n} = k_{OV} A (q\sqrt{p_b} - C_b) \quad (2.8)$$

Combining Equations (2.6) and (2.8) gives

$$\ln R = -k_{OV} \frac{A}{V} t \quad (2.9)$$

This equation becomes identical to Equation (2.7) for the specific case of liquid phase control of the overall kinetics. In general k_{OV} will be less than k_L , depending on the relative influence of the gas phase resistance.

2.2 Gas Phase Considerations

2.2.1 Kinetic Influence of the Gas Phase Resistance

In any real situation of mixed kinetic control, the influence of the gas phase resistance can be estimated by solving the individual flux and equilibrium equations, provided the appropriate data are available. Well established chemical engineering theory (24) indicates the exact effect is dependent on the relative values of k_L and k_G , and the slope of the equilibrium line relating the gas and liquid phase concentrations of the transferred species. Since the oxygen/silver system obeys Sievert's law, the equilibrium relationship is not linear and the slope varies with concentration. Thus the degree to which the gas phase resistance influences the overall rate is not constant but a marked function of the concentration levels operative during an experiment.

Chatterjee and Bradshaw (10) have presented a mathematical treatment which gives a generalized appreciation of the interplay of the gas and liquid phase transport resistances. In combining the basic flux equations (2.2, 2.3, 2.8) and the equilibrium relationship (2.4), the unknown interfacial concentration terms, p^* and C^* , and the rate of transfer $\dot{n}$ are eliminated. The essential feature of these workers' solution is the definition of appropriate dimensionless parameters which reflect the degree of gas phase resistance, the driving force and the transport properties of the system. The solution is applicable to any Sievert's law system.

The dimensionless parameters are :

$$\lambda = \frac{k_{ov}}{k_L} \quad (2.10)$$

$$\eta = \frac{q\sqrt{p_b}}{C_b} \quad (2.11)$$

$$\phi = \frac{q \ k_L \ RT}{2 \sqrt{p_b} \ k_G} \quad (2.12)$$

$$\xi = \frac{q^2 \ k_L \ RT}{2 \ C_b \ k_G} \quad (2.13)$$

The term λ will have a value of 1.0 for liquid phase control, and will otherwise be less than 1.0 . Since Equations (2.8) and (2.10) combine to give

$$\dot{n} = \lambda \ k_L \ A \ (q \sqrt{p_b} - C_b) \quad (2.14)$$

it is clear that λ is the ratio of the rate per unit driving force in a mixed control situation to the maximum rate associated with liquid phase control. λ is therefore a dimensionless rate constant.

Reference to the equilibrium relationship, Equation (2.1) indicates that η is a dimensionless driving force that will be equal to 1.0 at equilibrium, less than 1.0 during desorption and greater than 1.0 in absorption. The parameters ϕ and ξ reflect the relative resistances of the gas and liquid phase mass transfer steps. ϕ is written in terms of p_b whereas ξ is written in terms of C_b .

The solution can be written as follows :

$$\lambda = \frac{\left(\frac{\phi^2}{4} + \frac{\phi}{\eta} + 1 \right)^{\frac{1}{2}} - \left(\frac{\phi}{2} + \frac{1}{\eta} \right)}{\left(1 - \frac{1}{\eta} \right)} \quad (2.15)$$

$$\lambda = \frac{\left(\frac{\xi^2}{4} + \xi + \frac{\eta^2}{1} \right)^{\frac{1}{2}} - \left(\frac{\xi}{2} + 1 \right)}{\eta - 1} \quad (2.16)$$

$$\lambda = \frac{\left(\frac{\xi^2}{4} + \xi + \frac{\xi^2}{\phi^2} \right)^{\frac{1}{2}} - \left(\frac{\xi}{2} + 1 \right)}{\left(\frac{\xi}{\phi} - 1 \right)} \quad (2.17)$$

Some interesting limiting cases can be derived ; for instance :

$$\text{Limit } \lambda_{\phi \rightarrow \infty} = 1 - \frac{\xi}{2} \left[\left(1 + \frac{4}{\xi} \right)^{\frac{1}{2}} - 1 \right] \quad (2.18)$$

which corresponds to desorption with an inert gas such as nitrogen or argon. At equilibrium,

$$\text{Limit } \lambda_{\eta \rightarrow 1.0} = \frac{2}{\xi + 2} \quad (2.19)$$

$$= \frac{2}{\phi + 2} \quad (2.20)$$

The most suitable form of the solution will be dictated by the information available and the experimental conditions. Equations (2.15) and (2.17) are of particular interest in the present work and are shown graphically in Figures (2.2) and (2.3).

A decrease in λ implies an increase in the kinetic influence of the gasphase mass transfer step. Figure (2.2) shows that the gas phase resistance is increased by

- (i) a reduction in p_b (which increases ϕ and η)
- (ii) a reduction in C_b (which increases η)
- (iii) a reduction in $\frac{k_G}{k_L}$ (which increases ϕ)

and (iv) an increase in the solubility, i.e. by q (which increases ϕ and η)

Furthermore, for a particular value of ϕ (representing experiments at constant hydrodynamic conditions and oxygen content

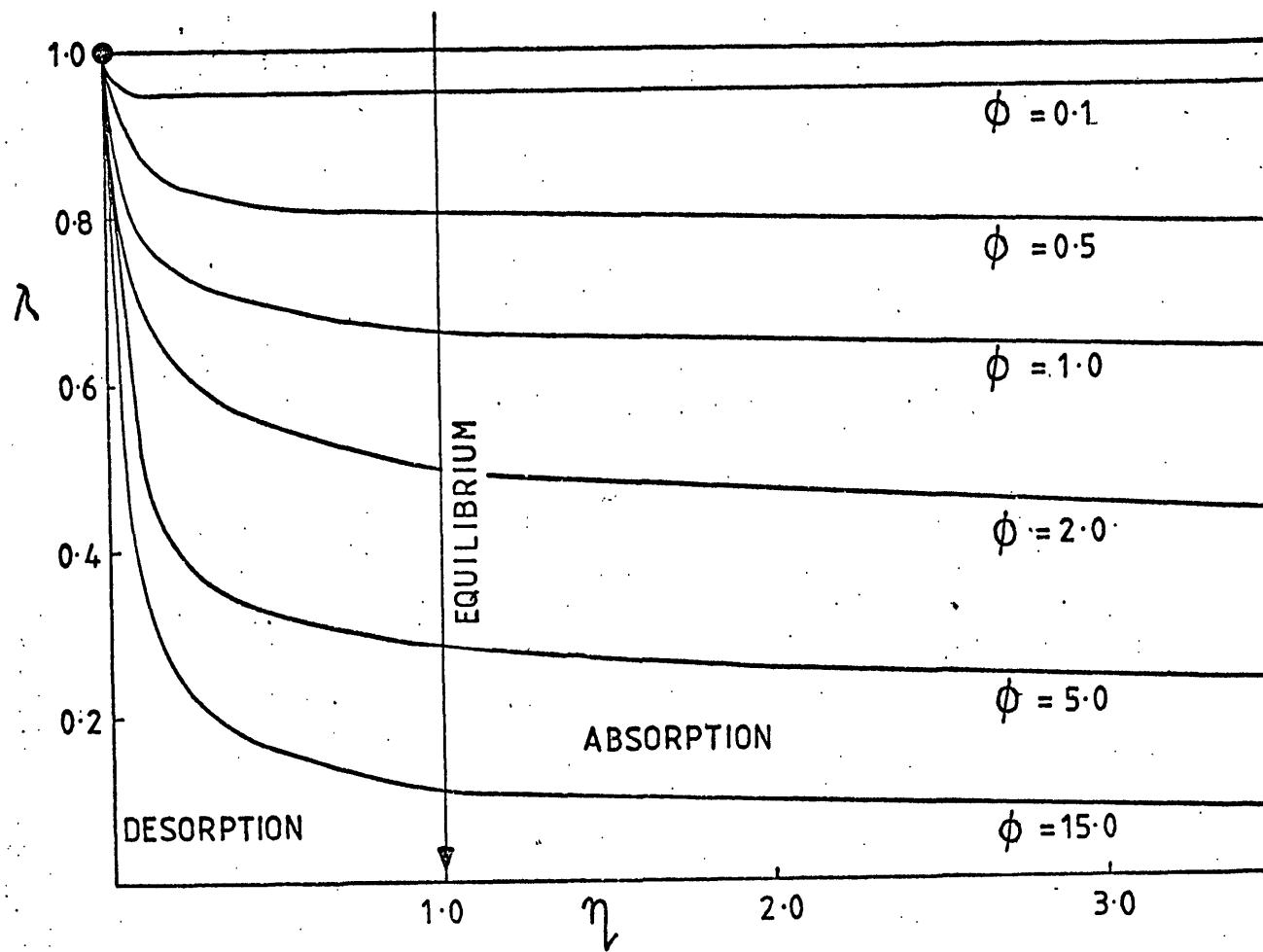


FIG.2.2 RELATIONSHIP BETWEEN λ , η AND ϕ

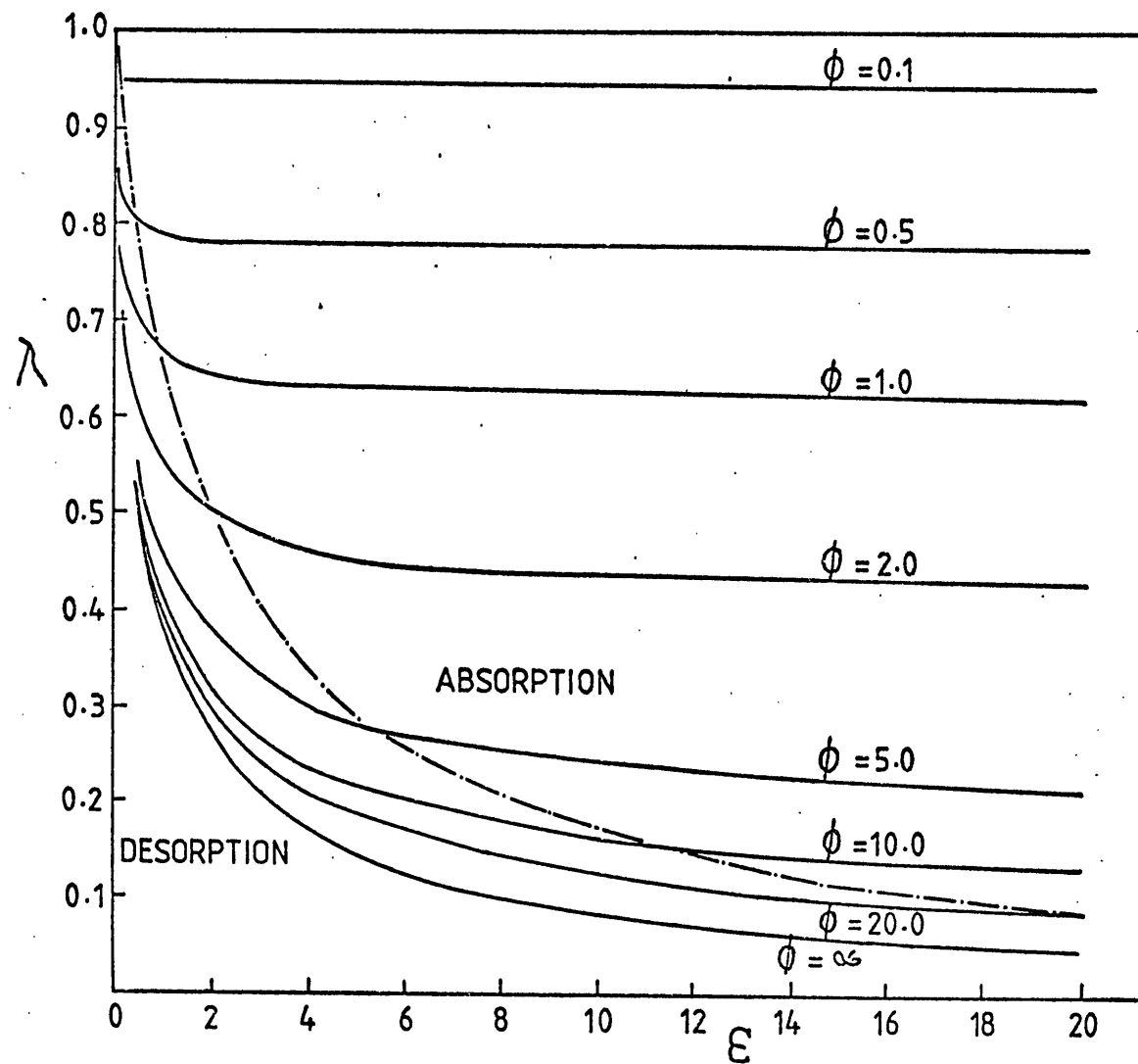


FIG. 2.3 RELATIONSHIP BETWEEN λ , ϕ AND ε

in the gas), λ will be greater in desorption ($\eta < 1$) than in absorption ($\eta > 1$). Thus a situation where the transport mechanism was independent of the direction of transfer would display an apparent asymmetry between absorption and desorption, if the results were viewed in terms of a plot of

$$k_{ov} \text{ vs } P_{O_2}.$$

A further point to note is that since λ is not constant at a particular value of ϕ , a plot of $\ln R$ vs $\frac{A}{\bar{V}} t$ (Equation 2.9) would not be linear despite the process being mass transfer controlled. This effect is likely to be more pronounced in desorption experiments. The slope ($-k_{ov}$) would decrease in desorption, but increase in absorption, the extent of the changes depending on the range of η . Clearly the linearity or otherwise of such plots is not a critical test of the influence of mass transfer or chemical kinetic effects.

2.2.2. Bulk Flow

The diffusional transport of oxygen through inert gas such as nitrogen induces a measure of convective bulk flow in addition to the diffusion mechanism. Thus the term k_G has a bulk flow component, which is dependent on the oxygen content of the gas and the rate of transfer. It is therefore convenient to define k_G^0 as the gas phase mass transfer coefficient in the absence of bulk flow. Since k_G^0 should be independent of concentration of transferring species it is a more fundamental reflection of the hydrodynamic condition of the gas. Bennett and Myers (24) give the following approximate relationship between k_G and k_G^0 :

$$k_G^0 = k_G (1 - x_A)_{lm} \quad (2.21)$$

where x_A is the mole fraction of the reactive species in the gas phase,

and the subscript lm implies the logarithmic mean of conditions in the bulk gas and at the interface. Since $x_A = \frac{p_A}{p_{tot}}$, for oxygen transport at 1 atmosphere

$$(1 - x_A)_{lm} = \frac{p^* - p_b}{\ln \frac{1 - p_b}{1 - p^*}} \quad (2.22)$$

The effect of bulk flow is negligible for very dilute gases, and very pronounced in concentrated gases such that there is no gas phase resistance in a pure solute gas.

The flux equation for gas phase transport must include the effect of bulk flow, but this can be separated from the diffusional component by rewriting Equation (2.2) in terms of k_G^o :

$$\dot{n} = \frac{2 \cdot k_G^o \cdot A}{RT (1 - p_{O_2})_{lm}} (p_b - p^*) \quad (2.23)$$

2.2.3. Jet Characteristics

The experimental work discussed in this thesis involved the use of subsonic gas jets, with Mach numbers up to 0.8, issuing from a quadrant shaped nozzle at temperature of approximately 1000°C. Gas expands in an essentially isentropic manner through such a nozzle, with the increase in velocity being accompanied by a drop in pressure and temperature. The temperature and pressure drops are linked as follows (24):

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2} \right)^{\frac{\gamma-1}{\gamma}} \quad (2.24)$$

Where γ is the ratio of the specific heats, and is 1.4 for ideal gases.

For isentropic flow the theoretical velocity reached at the nozzle exit plane is given by (24) :

$$u_2 = 2 \frac{\gamma - 1}{\gamma} RT_1 \left(1 - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} \right) \quad (2.25)$$

Where subscript 1 refers to a plane upstream of the nozzle and 2 represents exit plane. The nozzle discharge coefficient is the ratio of the actual jet velocity at the nozzle exit plane to the theoretically predicted one :

$$V_J = C_d u_2 \quad (2.26)$$

For nozzles identical in design to the one used in the current investigation, Wakelin (2) measured the discharge coefficient to be 0.92 - 0.95 for oxygen jets, and 0.97 for carbon dioxide jets, all at room temperature.

The jet structure is schematically depicted in Figure (2.4). Immediately beyond the nozzle exit, a region of intense shear exists at the boundary of the jet and the surrounding gas. The shearing action causes eddies to diffuse into the jet, thereby promoting mass entrainment of the surrounding gas. The conical shaped region below the nozzle exit, where the velocity is still unaffected by entrainment, is called the potential core, with the velocity equal to V_J . The length of the potential core has been reported to be between 3 - 7 times the exit diameter of the nozzle (4, 5, 6).

A feature of free gas jets is the momentum is conserved, making the momentum a suitable term to characterise the jet. The momentum at any plane, parallel to the nozzle exit plane, is given by (1) :

$$\dot{M} = 2 \pi \int_0^{\infty} \rho_G V^2 r dr \quad (2.27)$$

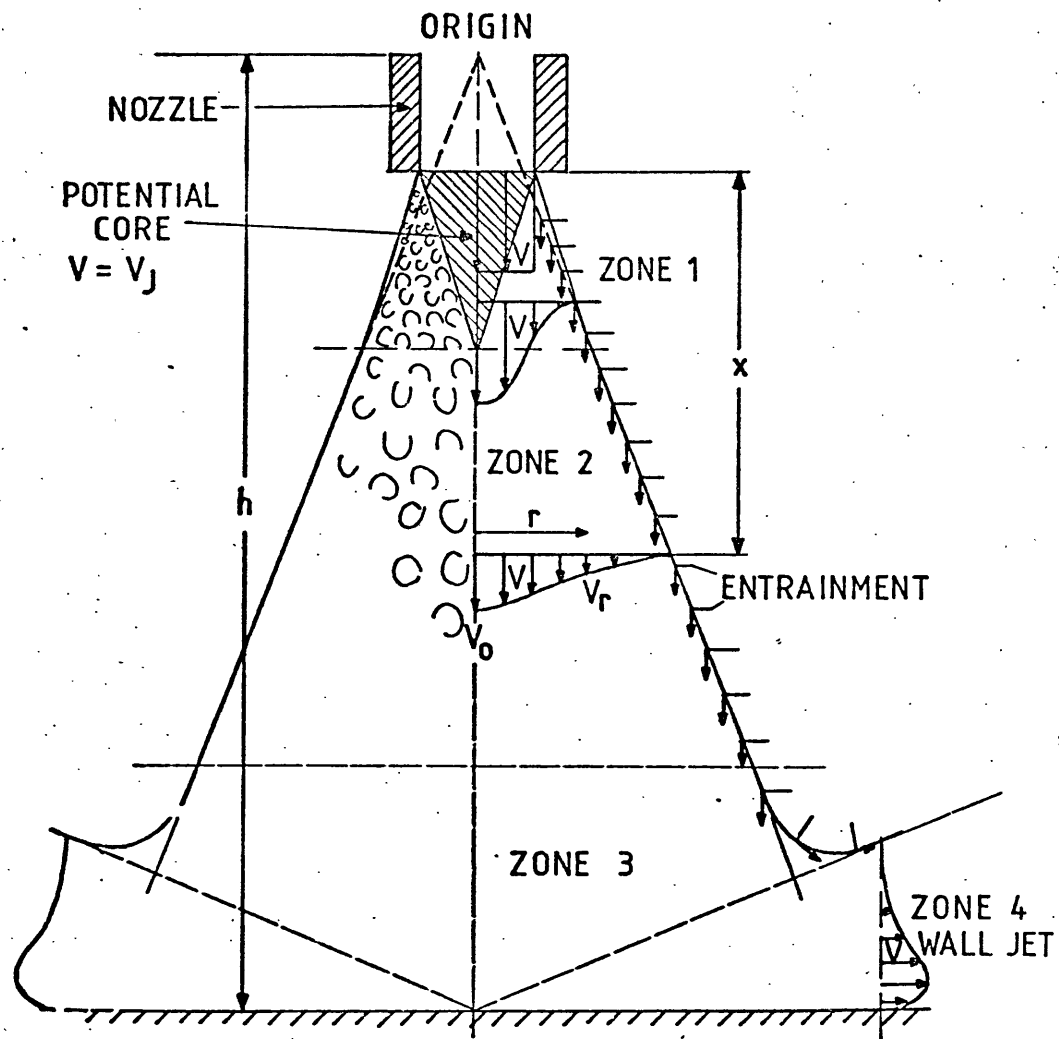


FIG. 2.4 JET VELOCITY PROFILES

which, for the nozzle exit plane is

$$\dot{M} = \dot{m}_J V_J \quad (2.28)$$

Where subscript J refers to the exit plane.

Mass balance and simple rearrangement yields :

$$\dot{M} = \frac{4 \dot{m}_J^2 RT}{\pi P_J MW d^2} \quad (2.29)$$

After a small transitional regime, downstream of the potential core, there is established a region of fully developed flow, where the decay in the centre line velocity due to mass entrainment is given by (23) :

$$\frac{V_o}{V_J} = K_1 \frac{d}{x} \quad (2.30)$$

and the corresponding increase in mass flow is (23) :

$$\frac{\dot{m}}{\dot{m}_J} = \frac{2}{K_1} \frac{x}{d} \quad (2.31)$$

The radial profile of the jet in established flow regime can be related to the centre line velocity at any distance from the jet origin (23,25) :

$$\frac{V}{V_J} = \exp -2 \left(K_1 \frac{r}{x} \right)^2 \quad (2.32)$$

Wakelin (13) found K_1 to vary from 6.2 - 8.6 in the Reynolds number range $8 - 51 \times 10^3$ indicating that it is not entirely satisfactory to assume kinematic similarity for all free jets.

2.3. Liquid Phase Mass Transfer

2.3.1 Molecular Diffusion

Molecular diffusion represents the lower limit of liquid phase mass transfer. Any forced or natural convection results in higher mass transfer rates. Unsteady state molecular diffusion is described by Fick's second law, which can be solved for the boundary conditions associated with the particular experimental procedure adopted.

Consider the case of oxygen transfer by diffusion into a pool of quiescent silver of depth 'l'. The oxygen is initially distributed evenly throughout the silver pool. At the start of an experiment the gas/liquid interface is brought instantaneously to equilibrium with gas of known oxygen partial pressure, and the interfacial concentration subsequently remains constant. No oxygen can diffuse through the base of the crucible. The solution of this problem is analagous to that for diffusion to the central-line of a sheet of thickness '2l' when both plane surfaces have been equilibrated with the vapour. For these boundary conditions, Crank (36) gives a solution in terms of the overall rate of solute uptake :

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \frac{-D_{AB} (2m+1)^2 \pi^2 t}{4l^2} \quad (2.33)$$

where M_t is the total weight of vapour absorbed after time t and M_{∞} is the amount corresponding to equilibrium, after infinite time.

It can be readily shown that :

$$1 - \frac{M_t}{M_{\infty}} = \frac{q \sqrt{p_b} - C_b}{q \sqrt{p_b} - C_b (t=0)} = R \quad (2.34)$$

Where C_b is the average oxygen concentration in the silver.

Equation (2.33) can therefore be written :

$$R = \frac{8}{\pi^2} \exp \frac{-D_{AB} \pi^2 t}{4l^2} \left[1 + \frac{1}{9} \exp \frac{-8 D_{AB} \pi^2 t}{4l^2} + \frac{1}{25} \exp \frac{-24 D_{AB} \pi^2 t}{4l^2} + \frac{1}{49} \exp \frac{-48 D_{AB} \pi^2 t}{4l^2} \dots \dots \right] \quad (2.35)$$

For sufficiently long times, for $\frac{D_{AB} t}{l^2} > .05$, the solution reduces to :

$$\ln R = \ln \frac{8}{\pi^2} - \frac{D_{AB} \pi^2 t}{4l^2} \quad (2.36)$$

2.3.2. Forced Convection Induced by Gas Jet Impingement

When a gas jet is directed onto the surface of a liquid, a depression is formed. The gas is deflected radially from the central impact region (stagnation point) and circulation in the liquid is induced by the drag between the radially flowing gas and the liquid surface. At sufficiently high jet velocities liquid droplets are sheared from the lip of the depression and splashing results. The depths and shapes of depressions have received theoretical and experimental attention from previous workers in the John Percy Research Group (1,2) who include detailed coverages of the relevant literature. On the basis of stagnation pressure analysis, the depth of depression is satisfactorily described by :

$$\frac{n_o}{h} \left(1 + \frac{n_o}{h} \right)^2 = \frac{115 \dot{M}}{\pi \rho_L g h^3} \quad (2.37)$$

There is a critical depth of depression, dependent mainly on liquid properties, at which splashing commences, and Chatterjee and Bradshaw (1,15) used dimensional analysis to determine the correlation :

$$\left(\frac{g \rho_L}{\gamma}\right)^{\frac{1}{2}} \bar{n}_c = 0.53 \log \frac{g \mu_L^4}{\rho_L \gamma^3} + 11.33 \quad (2.38)$$

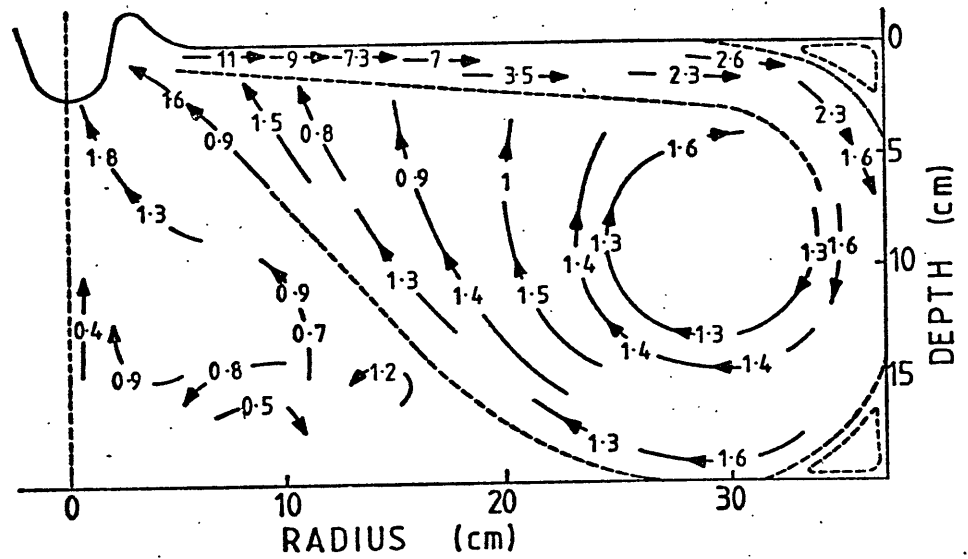
The forced convective mass transfer process at the free surface will depend on the fluid flow pattern induced in the liquid by the jet action. Water model studies by Wakelin (2,13) indicated a relatively fast stream of liquid moving radially outward close to the surface. The overall circulation pattern corresponds to a toroidal vortex, essentially occupying the bath volume, with small stagnant regions. Figure (2.5) depicts a typical circulation pattern in water (2,13).

Wakelin proposed a mass transfer mechanism of surface renewal based on the radial velocities at the free surface. Bradshaw and Chatterjee (16), using a Hot Wire Anemometer established that surface velocities were inversely proportional to radial position, i.e. $(U_r \times r) = \text{constant}$. Similar flow patterns were proposed by Machlin (18) for inductively stirred melts. Simple surface renewal theory for these conditions (2, 16, 18, 19) anticipates a liquid phase mass transfer coefficient of :

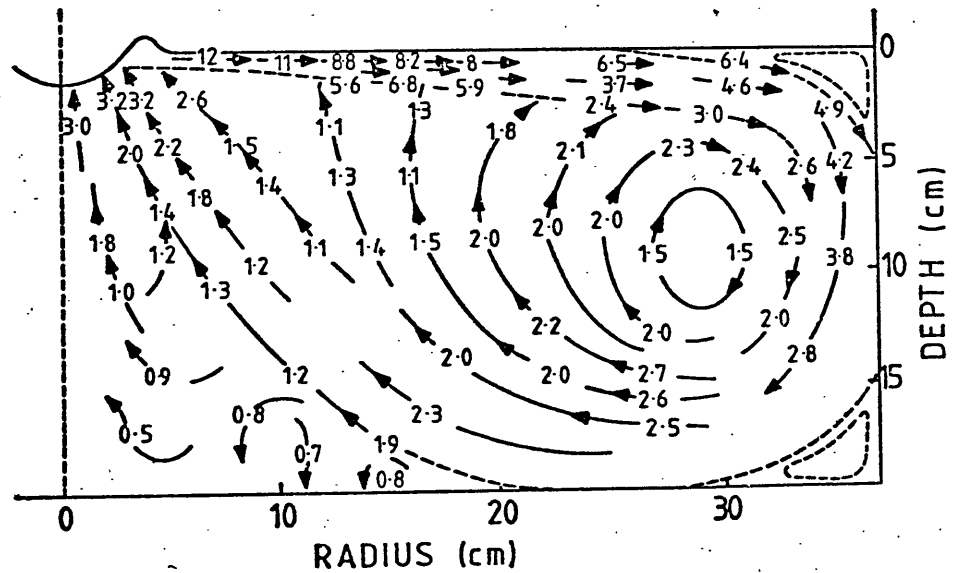
$$k_L = \left[\frac{8}{\pi} (U_r \times r) D_{AB} \right]^{\frac{1}{2}} \frac{1}{r_b} \quad (2.39)$$

where r_b is the bath radius.

Chatterjee and Bradshaw (16) conducted mass transfer experiments by absorbing CO_2 into water at various jetting intensities. Predictions ^{of} k_L based on the above model and measured values of $(U_r \times r)$ were in excellent agreement with practical results.



LANCE HEIGHT = 8 cm MOMENTUM = 8650 DYNES



LANCE HEIGHT = 17 cm MOMENTUM = 14,700 DYNES

FIG. 2.5 CIRCULATION PATTERNS IN WATER
WITH CO₂ JETS (VELOCITIES IN
cm sec⁻¹)

The model implies that there is no significant additional surface renewal by turbulent transport from the bulk of the bath to the free surface. Consistent with this, Szekely et al (63,64) theoretically determined that in such a system the turbulent energy is concentrated in the depression region, and that the bulk of the circulation could be regarded as laminar. These workers suggest that an impinging gas jet is inherently a poor means of agitating liquid pools. In fact, when jetting molten silver under similar conditions, it is found that the jet action at all but the highest momenta is insufficient to keep the bath evenly mixed (1,2).

The simple surface renewal model cannot be compared with mass transfer results from jetting experiments with liquid silver, since no information on surface velocities has been obtained. However, the model provides at least a conceptual frame of reference for considering forced convective mass transfer associated with jet action.

2.4 Kinetic Studies in the Oxygen/Silver System

2.4.1 Diffusion in Quiescent Silver

(a) Absorption

Molecular diffusion of oxygen into unstirred liquid silver has been the subject of considerable study. Mizikar, Grace and Parlee (26) employed a diffusion cell where a column of stagnant liquid silver was held in a quartz capillary (1.5 - 3.0 mm diameter) and the rate of oxygen absorption was monitored in the gas reservoir above the silver by buret and sensitive manometer. Parlee and Siebel (27) obtained results in agreement with the capillary work, when using cells as large as 17 mm diameter. Parlee and Shah (28) further consolidated the technique, with improved accuracy. An alternative approach has been to hold the silver inside a zirconia tube which serves both as a container and as a solid electrolyte. The oxygen concentration in the silver during absorption is measured by the electromotive force generated across the solid electrolyte. Values of oxygen diffusivity have been measured in this manner by Masson and Whiteway (30) and others (32,34) and refinements in the theoretical treatment of the electrolyte behaviour have been carried out by Oberg et al (29) and Sano et al (33). Besson et al (31) employed a thermogrametric method.

The results of all those workers showed oxygen absorption to be kinetically controlled by molecular diffusion in the liquid silver, which in the unsteady state region is described by Fick's second law (36). Vehlo (35) modified the gas reservoir diffusion cell of Parlee and co-workers (26, 27, 28) to enable steady state mass transfer of oxygen into silver to be studied.

The results of diffusivity data are summarized in Table 2.1 .

TABLE 2.1

Oxygen Diffusivity in Liquid Silver at 1000°C

Reference	Experimental Technique	$D_{O/Ag}$ ($\text{cm}^2/\text{sec} \times 10^5$)
26	gas reservoir diffusion cell	8.9
27	"	9.4
28	"	9.7
30	solid electrolyte cell	10.2
32	"	14.6
29	"	10.7
33	"	9.5
31	thermogravimetry	12.5

The value of $D_{O/Ag}$ reported in reference (32) is not in good agreement with the other results obtained using solid electrolyte cells and the single thermogrametric result appears high. Thus the average value of $D_{O/Ag}$ at 1000°C , ignoring the high values in reference (31) and (32), is found to be

$$D_{O/Ag} = (9.7 \pm 0.6 \text{ RMS}) \times 10^{-5} \text{ cm}^2/\text{sec}.$$

(b) Desorption of Unstirred Silver

The diffusion data with quiescent liquid silver relate to oxygen absorption experiments. Only Masson and Whiteway (30) include results for desorption experiments under otherwise identical conditions. Oxygen saturated silver was desorbed by passing argon gas through the reaction tube. They report that desorption rates per unit driving force were about five times faster than the corresponding absorption rates. This clearly implies the existence of convection in the liquid silver. Since the top of the silver column was maintained slightly hotter than the bottom, it was argued that such convection could not be driven by temperature gradients. Masson and Whiteway attributed the convection to variations in density associated with oxygen concentration gradients in the silver. There is no record in the literature of the effect of oxygen solution on the density of liquid silver, and Masson and Whiteway were unable to provide experimental evidence for their postulation. Desorption rates were not far below gas phase diffusion rates, which suggested that the enhanced liquid phase transport had thrown kinetic control into the gas phase.

2.4.2 Oxygen Transfer with Inductively Stirred Liquid Silver

(a) Absorption

The intense convective stirring associated with induction

heating gives rise to greatly accelerated liquid phase mass transfer. Zoellner and co-workers (37, 38, 81) studied the absorption of oxygen into inductively stirred liquid silver in the temperature range of 1060 - 1180°C with 10 - 20 gm silver samples. The reaction was monitored by sensitive manometer and burette. The mass transfer results extrapolate to a value of k_L at 1000°C of 0.9×10^{-2} cm/sec. With a similar experimental system, Utine and Parlee (39) obtained the slightly higher value of k_L of 1.58×10^{-2} cm/sec, but attributed this difference to alterations in induction 'coupling', which influences the degree of liquid stirring.

Mori et al (40) employed both resistance and induction heating. Oxygen gas was blown onto the surface of 210 gm silver samples and the absorption rate monitored with a solid-electrolyte probe. The value of k_L at 1000°C was 1.4×10^{-2} cm/sec when using induction alone, and 1.2×10^{-2} cm/sec when including some resistance heating.

(b) Effusion (desorption by reducing total pressure)

In addition to absorption data, Utine and Parlee (39) reported the results of effusion experiments with inductive heating. The liquid silver was brought to equilibrium with a particular oxygen total pressure, and then desorption was made to occur by reducing the total pressure. Pressures in the range 0.47 - 1.0 atm were investigated. During effusion the gas was always pure oxygen such that there could be no diffusional resistance in the gas phase. The values of k_L for effusion were equal to those for absorption, within experimental scatter.

2.4.3 Oxygen Jetting of Silver

Chatterjee, Wakelin and Bradshaw (1, 2, 13, 14, 17) studied the absorption of oxygen from pure oxygen gas jets directed

vertically onto the surface of liquid silver at a temperature of 1000°C . Subsonic jets were discharged through a converging nozzle (2.5 mm exit diameter) in the range of jet momentum of 3,000 - 56,000 dynes. The height of the lance above the silver surface was varied between 5 and 25 cm. These conditions were reported to be predominantly in the non-splashing region. The crucible contained approximately 20 kg of silver having a free surface area of 182 cm^2 . Oxygen concentrations were recorded continuously by a solid-electrolyte probe. A mechanical stirrer kept the bath homogeneous, but was shown not to alter absorption rates at the silver/oxygen interface. The results (14) are summarized in Figure 2.6, which show the average mass transfer coefficients, calculated on the basis of the total interfacial area of 182 cm^2 . The mass transfer coefficient was strongly dependent on jet momentum, and only mildly dependent on lance height. During some experiments the silver surface was disrupted by the jet, but this did not lead to a marked change in mass transfer coefficient. However, none of the experiments extended far into the splashing region.

The absorption data were obtained under essentially isothermal conditions, with both the jet and the silver temperature being about 1000°C . The mass transfer coefficient was not seriously altered when the jet temperature was reduced to 600°C , provided the momentum was maintained constant and serious thermal gradients were avoided in the liquid silver. The local mass transfer coefficient is likely to be far greater in the central regions of the bath, due to the action of the impinging gas stream. Wakelin (2, 14) was effectively able to blank off varying extents of the outer region of the free surface area, by placing "fiberfrax" annuli on the silver surface. For a jet momentum of 56,000 dynes and a lance height of 10.5 cm, 80% of the total absorption was found to take place in the central 25% of the surface area. The results, summarized in

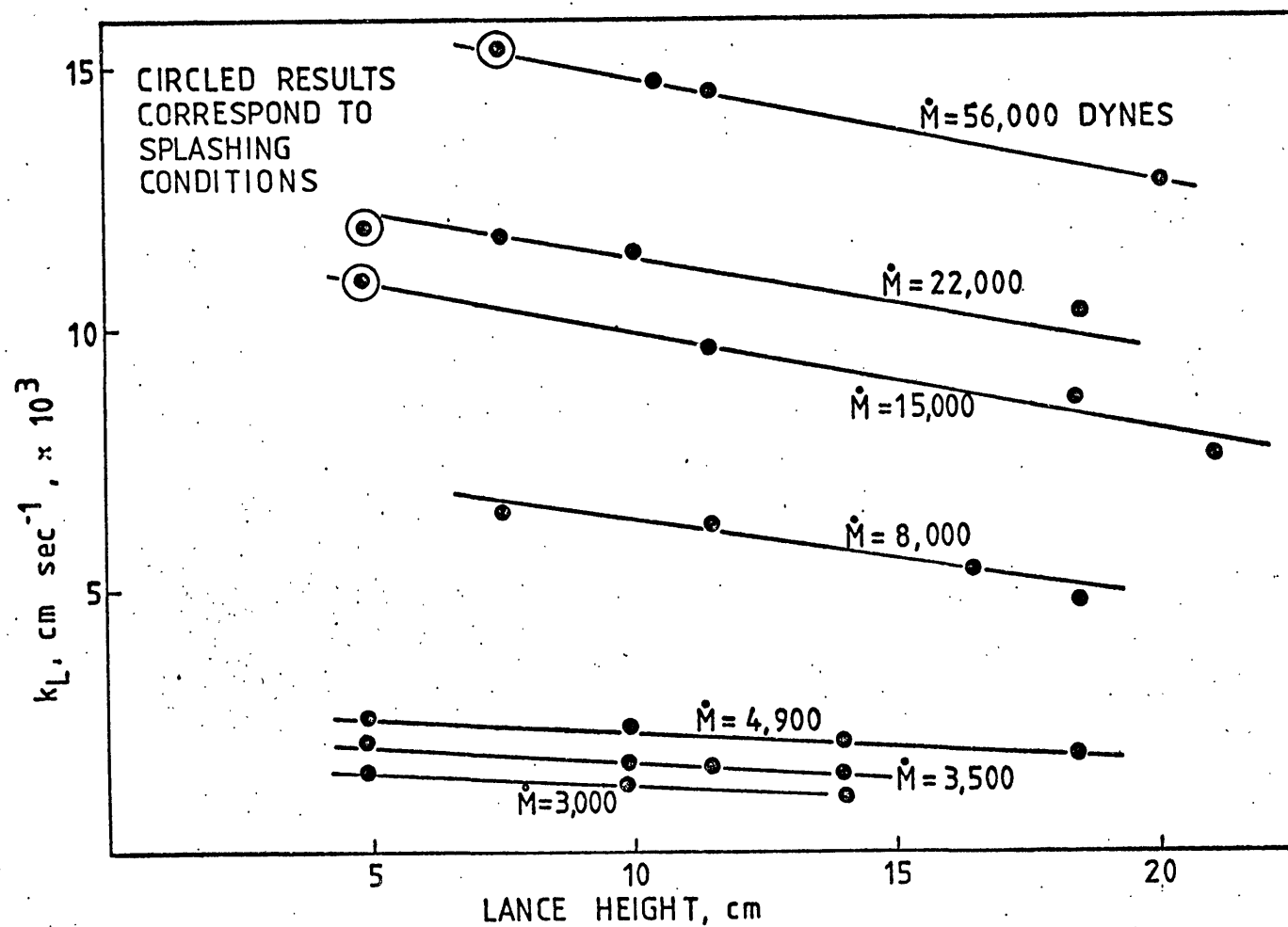


FIG.2.6 LIQUID PHASE MASS TRANSFER DATA FROM EXPERIMENTS WITH PURE OXYGEN JETS (14)

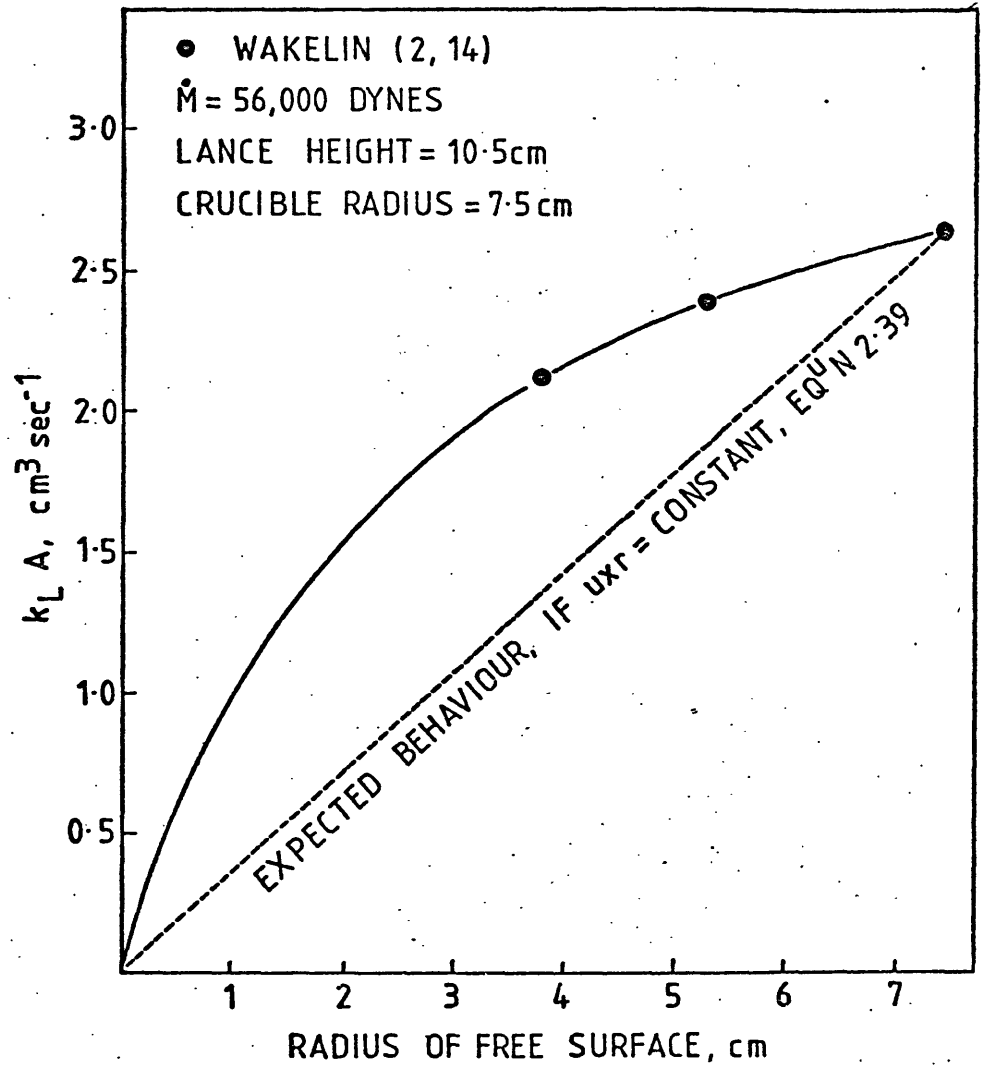


FIG. 2.7 VARIATION OF MASS TRANSFER WITH
FREE SURFACE AREA

Figure 2.7, anticipate sharper decline in radial surface velocity than would be expected for $U \times r = \text{constant}$, see Equation 2.39. This suggests that, in contrast to the water studies (16), the jet action probably induces a toroidal vortex which does not extend to the walls of a crucible of this size (15 cm diameter).

2.4.4 The Importance of Gas Composition

Chatterjee and Bradshaw (1, 10) and Mori and co-workers (40, 41) have studied the influence of gas composition on the kinetics of oxygen transfer between liquid silver and a gas phase containing oxygen and nitrogen or argon. The rates per unit of overall driving force decrease as p_{O_2} decreases, such that the kinetics can not be explained in terms of simple liquid phase control. Chatterjee and Bradshaw (10) attributed the effect to the gas phase mass transfer resistance, whereas Mori et al (40) assumed the chemical reaction at the interface was influencing the overall rate. Chatterjee (1, 10) carried out absorption and desorption experiments with gas jets in which the oxygen partial pressure was 0.1 and 0.2 atm and nitrogen was the diluent gas. The apparatus was the same as described in Section 2.4.3 for pure oxygen jetting experiments. Values of k_{OV} were measured for each run, see Equation (2.9). The value of k_L was assumed to be the same as previously determined at the particular jet momentum and lance height under conditions of liquid phase control, see Figure 2.6. The relationship developed between λ , η and ϕ , see Equations (2.15) to (2.17), was then used to calculate k_G for each run. The likely influence of bulk flow was also estimated, see Equation (2.21), to give values of k_G^o . The results are summarized in Table (2.2).

In absorption experiments, the average value of λ for air jets was 0.82, and for jets with $p_{O_2} = 0.1$ atm it was 0.71. These results are consistent with the mechanistic interpretation of a gas

$\dot{M}$ is in dynes $\times 10^{-3}$

h is the lance height in cm.

k_L is in cm/sec $\times 10^3$ and is obtained from previous data, see Figure (2.6)

k_{ov} is in cm/sec $\times 10^3$ and is measured from the experiments

k_G^0 is in cm/sec.

Series A : $p_{O_2} = 0.203$ atm, $\eta_{initial} = 3.98$, ABSORPTION

Series B : $p_{O_2} = 0.1$ atm, $\eta_{initial} = 2.78$, ABSORPTION

Series C : $p_{O_2} = 0.203$ atm, $\eta_{initial} = 0.405$, DESORPTION

Series D : $p_{O_2} = 0.1$ atm, $\eta_{initial} = 0.316$, DESORPTION

η values listed in Series A & B are final values

η values listed in Series C & D are average values

λ , ϕ and k_G^0 values are all average values

TABLE 2.2

Absorption and Desorption Data from
Experiments using Dilute Oxygen Jets (10)

Run	$\dot{M}$	h	k_L	k_{ov}	η	λ	ϕ	k_G^o
A1	8.0	11.5	6.15	4.67	1.45	0.78	0.52	1.97
A2	8.0	7.5	6.68	5.65	1.35	0.85	0.34	3.29
A3	8.0	5.0	7.20	5.85	1.33	0.81	0.44	2.85
A4	15.0	21.0	8.15	6.82	1.44	0.83	0.39	3.46
A5	22.0	11.5	11.16	9.10	1.33	0.82	0.44	4.78
B1	8.0	18.5	5.2	3.45	1.58	0.66	0.94	1.47
B2	8.0	7.5	6.68	4.71	1.47	0.70	0.74	2.30
B3	8.0	5.0	7.20	5.55	1.32	0.77	0.56	3.46
B4	15.0	7.5	10.35	7.47	1.23	0.72	0.71	4.02
B5	56.0	10.5	14.70	10.24	1.17	0.69	0.82	4.81
C1	15.0	21.0	8.15	7.23	0.51	0.89		
C2	22.0	11.5	11.16	12.57	0.58	1.12		
D1	8.0	18.5	5.20	3.46	0.38	0.67		
D2	8.0	7.5	6.68	4.89	0.39	0.73		
D3	15.0	7.5	10.35	10.48	0.44	1.01		

phase transport influence on the kinetics, since values of k_G^O in the range 1.47 - 4.81 cm/sec are physically realistic. However, with desorption, two of the five experiments suggest values of k_{OV} equal to, or greater than, k_L , i.e. $\lambda > 1.0$. Chatterjee and Bradshaw attribute this to experimental scatter, although it should be borne in mind that from an operational point of view, desorption runs are as accurate as absorption runs.

Mori et al (40) studied absorption and desorption rates with oxygen/argon mixtures ranging in oxygen partial pressure from 0 - 1.0 atm. Gas was blown at 1 Nl/min onto the surface of a 210 gm sample of inductively heated liquid silver. The gas emerged from a 1.0 cm diameter tube at a height of 1 cm above the silver. Calculation indicates this corresponds to a jet momentum of 1.55 dynes, compared to the 8,000 - 56,000 dynes employed by Chatterjee (1,10). Under these circumstances the gas is responsible only for supplying reactant, and all the liquid phase stirring would be due to the induction heating. Figure (2.8) shows the results of these workers in terms of the overall mass transfer coefficient as defined in the present study, see Equation (2.9). As the gas becomes less concentrated in oxygen k_{OV} tends to be reduced. Although the results show some scatter, there is no significant difference between absorption and desorption experiments. Within limits of experimental accuracy the kinetics can be explained mathematically by the combination of two rate equations proposed by Mori et al :

$$\dot{n} = k_1 A (C^* - C_b) \quad (2.40)$$

and
$$\dot{n} = k_2 A (C_{eq}^2 - C^{*2}) \quad (2.41)$$

Equation (2.40) corresponds to liquid phase mass transfer and is equivalent to Equation (2.3) above. From Sievert's law one can

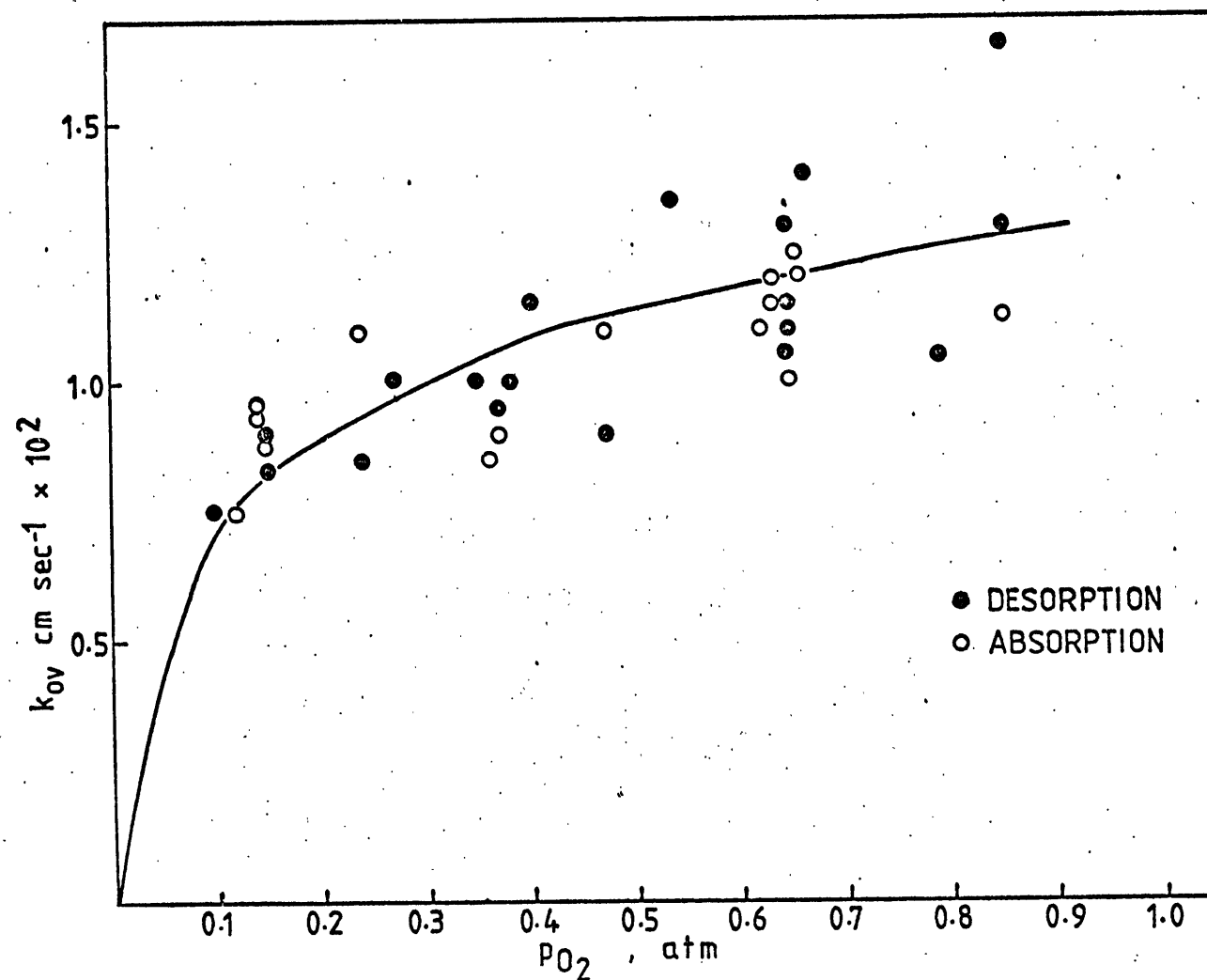


FIG. 2.8 ABSORPTION AND DESORPTION DATA - INDUCTIVELY
STIRRED SILVER (40)

write

$$C^2 = q^2 p \quad (2.42)$$

such that equation (2.41) can be rewritten as

$$\dot{n} = k_2 q^2 A (p_b - p^*) \quad (2.43)$$

which is mathematically equivalent to the equation for gasphase mass transfer, Equation (2.2), where

$$\frac{2k_G}{RT} = k_2 q^2 \quad (2.44)$$

Thus, the underlying mathematical treatment of results is similar for both Chatterjee and Bradshaw (10) and Mori et al (40). In contrast to Chatterjee's and Bradshaw's conclusions, Mori et al assumed that the gas flow rate was sufficient to preclude the possibility of a significant gas phase resistance and attributed the second order resistance to the chemical reaction at the interface. The alternative mechanistic interpretations lead to one additional difference between these workers. Because of bulk flow, the gas phase resistance concept of Bradshaw and Chatterjee indicates that absorption experiments with pure oxygen would correspond to simple liquid phase control. Mori et al assumed a constant value of k_2 and therefore postulated that even pure oxygen absorption experiments were controlled by a combination of the liquid phase mass transfer resistance and the chemical reaction step at the interface.

2.4.5 The Effect of Surface Movement

During their experimental campaign, Mori et al (40) claim to have observed that under certain conditions the surface movement of the molten silver was retarded, which resulted in lower mass transfer

rates. In subsequent investigations (42,44) these workers found that retardation occurred during desorption of silver of high oxygen concentration by pure argon gas streams. The surface movement recovered when the oxygen concentration of the melt became low. In absorption experiments with pure oxygen gas, no retardation was observed. The value of k_L for the 'mobile' surface was 4×10^{-2} cm/sec, and in the range $(0.6 - 2) \times 10^{-2}$ cm/sec for 'retarded' surfaces. Slightly different quantitative results were obtained when using alumina or sintered mullite crucibles.

Mori and Sano (42,44) postulated that an uneven distribution of oxygen concentration on the surface, leading to uneven distribution of surface tension, was responsible for the observed phenomena, and presented an analysis relating the interfacial shear stress to the surface tension gradients.

2.5 Marangoni Phenomena and Spontaneous Convection

During mass transfer between two fluid phases solute concentration or temperature gradients may produce surface tension or bouyancy instabilities which can result in interfacial movement. Convection driven by surface tension gradients is referred to as Marangoni Convection, named after a nineteenth-century Italian scientist who correctly interpreted such phenomena (82). Density driven movement is usually called natural convection. These forms of spontaneously developed convection can be important in inter-phase mass transfer even at high levels of forced convection, precisely because they are generated at the interface where the main resistance to transport lies. For instance, in previous work by the present author (75, 76, 77), density driven natural convection was shown to be the likely controlling mechanism of surface renewal for zinc mass transfer during vacuum distillation of the circulating lead of a zinc blast-furnace, despite the high Reynolds number of the flowing lead.

Marangoni phenomena are associated with fluid flow at a surface resulting from interfacial tension gradients within the interface itself. Surface flow produces traction on lower layers of fluid. If the depth of the fluid is much greater than the depth of penetration of the surface movement, then such surface flow can develop into surface renewal, which influences the mass transfer coefficient. If the depth of penetration is comparable to the fluid depth then surface movement can effect the interfacial area(48). Coalescence and dispersion of liquid surfaces are influenced by such Marangoni 'thin-film' behaviour. In fact a spectrum of phenomena, from gentle surface rippling to spontaneous emulsification, can be seen to be initiated by Marangoni effects (91,92,93). Sawistowski has published several excellent review papers on Marangoni phenomena (47, 48, 68).

In most gas/liquid and liquid/liquid systems the surface tension decreases with increases in solute concentration and temperature, and with surface density of electrical charge. Marangoni phenomena can therefore be associated with processes of mass, heat and electron transfer across an interface. The former is normally the more important since surface tension usually displays the greatest sensitivity to solute concentration. (It is well known that the internal circulation of bubbles can be inhibited by the opposing surface tension force produced by the compressed film of surfactants swept to the tail end of the bubble, but the present study is concerned with systems where the surface active solute is itself being transferred across the interface.)

A precondition for the emergence of spontaneous convection, namely a dependence of density or surface tension on solute concentration and/or temperature, is met in the oxygen/silver system. Eremenko and Naidich (52, 53 55) and Bernard and Lupis (51) have studied the effect of oxygen concentration on the surface tension of liquid silver and the results of the latter, which are more reliable, are presented in Figure 2.9 . Furthermore, the existence of surface phenomena under certain conditions of oxygen transfer between gases and molten silver is suggested by the experimental results of Masson and Whiteway (30) and Mori et al (42, 44), see Sections 2.4.1 and 2.4.5 above.

The appearance of convective instability should not be confused with its ultimate intensity. There is no satisfactory theory for predicting the intensity of Marangoni convection and thereby the effect on mass transfer rates. However, very considerable progress has been made in determining criteria for the appearance of instabilities (68).

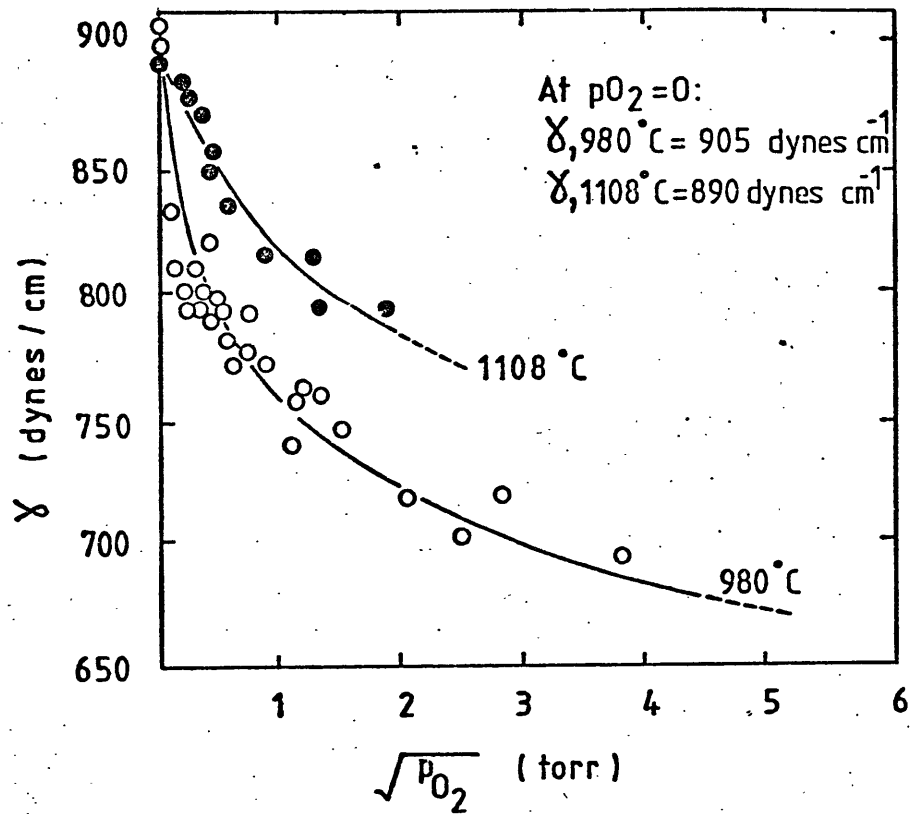


FIG. 2-9 SURFACE TENSION - OXYGEN ACTIVITY
ISOTHERMS IN THE Ag-O SYSTEM
(51)

The theoretical treatment of Marangoni convection is based upon hydrodynamic stability theory. Even in a quiescent system there always exist small perturbations in concentration and temperature, which can give rise to infinitesimal fluctuations of surface tension within the interface. These in turn can give rise to small flow disturbances, to which the system can react in three ways. The system will be hydrodynamically stable if the disturbances are damped by internal friction. The second possibility is that the flow will develop an interfacial tension gradients in the opposite direction to the original, in which case the system will be hydrodynamically stable. However, if the induced gradient is greater than the original the system can 'over react' in which case oscillatory instability results. The third possibility is that the system actually amplifies the initial perturbations and they grow into convective cells, ultimately capable of promoting surface renewal. Convective instability is also known as stationary, cellular or roll-cell instability. Surface tension induced cellular convection has frequently been observed experimentally in chemical engineering systems (68, 84, 85).

2.5.1 Convective Instability during Mass Transfer

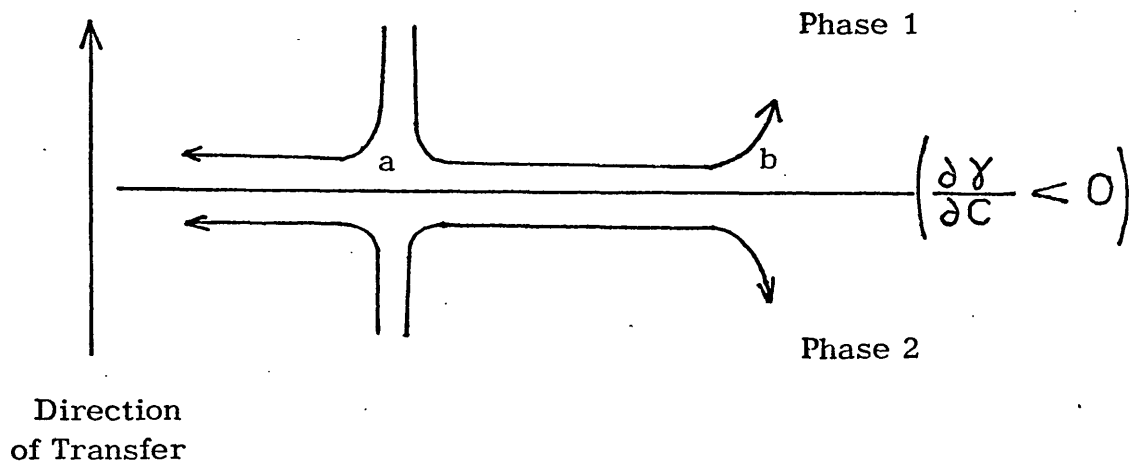
The question of whether small flow perturbations grow during mass transfer into roll cells and persist as such depends on the rate of supply of solute to and its removal from the region of the interfacial flow. This is a function of the relative diffusional transport rates in the two phases and will be affected by the relative depths of penetration of the surface flow into the two bulk phases. In fact the appearance of instabilities for initially quiescent fluids has been shown to be determined by four primary factors (47, 68)

(i) the sign of $\frac{\partial \gamma}{\partial C}$

- (ii) the direction of mass transfer,
- (iii) the ratio of the molecular diffusivities of the solute in the two phases, and
- (iv) the ratio of the kinematic viscosities of the two phases.

The absolute values of $\frac{\partial \gamma}{\partial C}$ and the transport properties are secondary factors, since they influence the ultimate magnitude of an instability, but not its appearance. Other secondary factors are the concentration levels of the solute in the two phases, the value of the distribution coefficient and any properties which effect the rheology of a surface. If the fluid phases are not initially quiescent, the nature of the existing field will be important, see Section 2.5.2 .

Consider the case below, in which a local reduction in surface tension (i.e. a local excess of solute if $\frac{\partial \gamma}{\partial C} < 0$) in the region marked 'a' in the interface has produced a flow perturbation from 'a' towards 'b'.



Certain intuitive predictions are possible regarding the influence of the primary factors on the fate of the surface flow perturbation (68). Consider steady state transfer of solute from phase 2 to phase 1, where the volumes of the two phases are equal or large, and $\frac{\partial \gamma}{\partial C} < 0$.

If the kinematic viscosities of the two phases are equal then the traction caused by the interfacial flow will tend to draw fluid from the same depth of penetration in each phase. From the direction of transfer it follows that fluid arriving at point 'a' from phase 2 will be richer in solute than the average for the interface, whereas fluid arriving from phase 1 will be of lower solute concentration. Since $\frac{\nu_1}{\nu_2} = 1$, the net result will depend on the relative diffusivities in the two phases since these dictate the steepness of the concentration gradients. If $D_2 < D_1$ the net effect will be to maintain a local enrichment of solute at region 'a'. As the fluid flows towards region 'b' the higher value of D_1 will ensure that this local surplus is reduced, with a corresponding increase in local surface tension. Thus the mass transfer process serves to develop a surface tension force in the interface causing flow which reinforces the original perturbation.

If, on the other hand, $D_1 < D_2$ the net effect will be to create a local deficiency in solute (relative to the average for the interface) which will be restored as the fluid moves towards 'b'. The ensuing surface tension gradient will induce flow towards 'a' and thereby oppose the original flow disturbance. The system will therefore be stable unless 'overreaction' leads to oscillatory instability.

If the kinematic viscosities are not equal then fluid from different depths of penetration will be brought to the surface by the

traction associated with the surface flow from 'a' to 'b'. If the diffusivities are equal then the net rate of supply and removal of solute from region 'a' will depend on the relative kinematic viscosities alone, provided the phases are initially quiescent. A net surplus of solute will exist if $\nu_2 > \nu_1$, since the flow field is deeper in phase 2, the phase of higher solute concentration. The excess solute concentration will be reduced with time at the interface as the fluid moves towards region 'b'. In these conditions the induced surface tension force will amplify the original flow disturbance and convective instability will result. The position would be reversed if $\nu_1 > \nu_2$ and the system would be stable.

The above arguments will be reversed for transport in the opposite direction ($1 \rightarrow 2$).

In a real situation it is unlikely that either the diffusivities or the kinematic viscosities would be equal. If the independent effects of the diffusivity and viscosity ratios suggest instability, then the combined effect will be one of convective instability. However, if the diffusivity and viscosity ratios are working in opposing tendencies, then no intuitive predictions can be made. Table 2.3 summarizes the qualitative considerations and is derived from a similar tabulation by Sawistowski (68).

It is apparent from the above considerations that for a system where $\frac{\partial \gamma}{\partial C} < 0$ (such as oxygen/silver), the system will be convectively unstable for solute transfer out of the phase of lower diffusivity and higher kinematic viscosity. This is known as the Sternling-Scriven criterion (50, 70). Since the diffusivities of solutes in gases are orders of magnitude greater than in liquids the criterion predicts stability for gas absorption and convective instability in desorption.

TABLE 2.3

The Appearance of Marangoni Instabilities

Relative Transport Properties $\frac{D_1}{D_2} \quad \frac{\nu_1}{\nu_2}$	Transfer $2 \rightarrow 1$ $\frac{\partial \gamma}{\partial C} > 0$ or Transfer $1 \rightarrow 2$ $\frac{\partial \gamma}{\partial C} < 0$	Transfer $2 \rightarrow 1$ $\frac{\partial \gamma}{\partial C} < 0$ or Transfer $1 \rightarrow 2$ $\frac{\partial \gamma}{\partial C} > 0$
1 1	Stable	Stable
< 1 1	Convective cells	Stable or oscillations
1 < 1	Stable	Convective cells
> 1 1	Stable or oscillations	Convective cells
1 > 1	Convective cells	Stable
< 1 > 1	Convective cells	Stable or oscillations
> 1 < 1	Stable or oscillations	Convective cells
< 1 < 1 > 1 > 1	No intuitive predictions; need mathematical analysis	

These general, intuitive arguments do not allow the influence of the secondary factors to be assessed, nor can the outcome be predicted for the situation where the primary transport factors (diffusivity and viscosity ratios) tend to work in opposition. Sophisticated, hydrodynamic instability models, such as that of Sternling and Scriven (50), have been developed to analyse these complex problems. The mathematical treatments, which are well reviewed by Sawistowski (68), support the intuitive predictions of criteria for the emergence of convection. But the detailed solution makes possible a further distinction between the diffusion-controlled mode of convective instability (where the diffusivity ratio is the determining factor) and the flow-controlled mode of convective instability (where the viscosity ratio is the significant one), and can predict the behaviour of the system when the diffusivity and viscosity effects oppose each other. It is seen that in such a case the system may be unstable in both directions of solute transfer, resulting in a diffusion-controlled convection in one direction and flow-controlled convection, which in most cases is oscillatory, in the other.

Since the pioneering work of Pearson (57) and Sternling and Scriven (50), several modifications have been published which overcome some of the limitations, and thereby extend the range of applicability of the theory (69, 73, 94). However, these models do not alter the generalised conclusions of the Sternling-Scriven criterion, namely that instabilities occur for transfer out of the phase of lower diffusivity and higher kinematic viscosity if $\frac{\partial \chi}{\partial C} < 0$.

No satisfactory theoretical basis has, as yet, been set up to predict the effect of surface phenomena on the mass transfer rates over the whole range of their existence. Bakker et al (95) have developed a model which applies to roll cell behaviour and

predicts that convection of this type increases the rate of mass transfer by a factor of 1.6 - 3.2 . This value is in reasonable agreement with experimental work (47).

2.5.2 The Influence of an Existing Flow Field

The stability theory discussed above is based on the assumption of small initial disturbances, and is therefore appropriate to an initially quiescent medium.. Small disturbances lead to the establishment of ordered cellular flow, or 'stationary' instability. (If the concentration difference between the phases is increased sufficiently, the intensity of the instability may increase and the ordered convection may degenerate into random instability, which can be called interfacial turbulence). If turbulence is present in the fluid, the interfacial disturbances are governed not by fluctuations in the mass transfer process but by the characteristics of the existing flow field(68).

If the turbulence in the bulk liquid gives rise to surface renewal by the random arrival of eddies, then during mass transfer solute can arrive at the interface in a discontinuous manner. Consider an eddy reaching the interface from the bulk of the solute rich phase. The excess concentration at this point in the interface will result in a local lowering of the interfacial tension (for the typical case where interfacial tension decreases with solute concentration). As the affected liquid expands under Marangoni forces it draws fresh liquid from the immediate vicinity of the interface, which is leaner in solute than the original eddy which arrived from the bulk of the fluid. Thus the local interfacial tension is raised and the direction of the initial motion is reversed. The reverse flow will produce an ejection of material normal to the interface into both phases. This phenomena is the best known form of disordered disturbances and is referred to as an 'eruption' (68).

This mechanism can occur in either direction of mass transfer, although the effect will ^{be} more intense in the naturally unstable direction.

If the intensity of the initial turbulence field is increased the individual eruptions lose their identity, and the interface will be in a state of intense agitation. This state is also referred to as interfacial turbulence, but this is not to be confused with the degeneration of intense convective instability in the absence of initial turbulence.

The flow field in the bulk fluid may not be sufficiently turbulent to lead to discontinuous supply of solute at the interface by random eddy renewal. For systems in which the existing flow field is ordered rather than random, it seems reasonable to argue that the Marangoni effects described in Section 2.5.1 would be superimposed on the existing cellular flow activity, and would accelerate the convective flow for transport in the naturally unstable direction of transfer. In the naturally stable direction of solute transfer, the stabilizing force of interfacial tension would be expected to retard the existing cellular convective flow.

2.5.3 Heat Transfer Effects

Since the surface tension of most liquids depends on temperature, the possibility exists for Marangoni convection to be initiated during heat transfer, in a manner analogous to that described above for mass transfer, see Section 2.5.1. In his pioneering work, Pearson (57) showed that cellular convection which hitherto had been attributed to buoyancy forces (i.e. density driven natural convection) could also be induced by surface tension gradients, and that such convective instability does arise in many

cases where the bouyancy forces would not in themselves promote instabilities.

Pearson (57) employed a small disturbance analysis of the type Sternling and Scriven (50) subsequently used for interpreting mass transfer effects. The details of Pearson's mathematical treatment, and the various modifications which have been presented in the literature (69, 71, 72), will not be discussed here. Consider in qualitative terms the simple case of a homogeneous liquid cooling by radiation from its upper free surface and heated at the lower fixed surface. Because of the direction of the temperature gradient within the liquid, the traction associated with a small flow fluctuation on the surface would bring liquid to the surface which is hotter than average for the surface. The liquid will cool as it flows across the interface. The decrease in surface temperature across the small flow perturbation will correspond to an increase in surface tension in the direction of the flow, which serves to amplify the original fluctuation. If the destabilizing surface tension forces overcome the stabilizing viscosity forces, the initial disturbances will grow and develop into ordered cellular convection.

The situation described here is one in which density driven natural convection could also develop, since the direction of heat transfer is opposite to gravity. However, the mechanism of surface tension driven convection does not depend on the relative directions of heat flow and gravity, and instability would be predicted whether the free surface was upward or downward facing.

The simple case considered by Pearson (57) assumes the environment exerts no mechanical forces on the liquid surface and serves only as a heat sink. In the case of unidirectional heat transfer by conduction between two fluid phases, such that a

temperature gradient exists adjacent to the interface in both phases, the relative thermal and transport properties of the two fluids would need to be taken into account when predicting the occurrence of convective instability.

In practice heat transfer often occurs simultaneously with mass transfer, for instance due to the heat of reaction. Cho and Jones (86) added heat of solution effects to the Sternling and Scriven analysis (50) and found that interfacial instabilities depend on the directions of both heat and mass transfer, and the relative magnitude of surface tension forces resulting from concentration and temperature gradients within the interface. Sawistowski and Perez de Ortiz (67) have developed a more sophisticated model which shows that when heat and mass transfer proceed simultaneously the concentration effects almost always predominate and form the controlling mechanism of instability except when the diffusivities of the solute are nearly equal in the two phases.

An interesting situation in which heat transfer effects may initiate convective instability during simultaneous heat and mass transfer is found in binary systems, in which one of the fluid pairs is a single component phase which has a positive solubility in the second. In the single component phase there can be no concentration gradient adjacent to the interface. If interfacial equilibrium is instantaneous and if heat effects are negligible, it follows that Marangoni convection could not develop. However, in practice, such systems are not always stable (87, 88). Perez de Ortiz and Sawistowski (49) studied the possibility that the mass transfer process could generate sufficient heat of solution at the interface to develop temperature gradients in the interface, and these workers used stability analysis to establish the criterion for instability. Even though the mass transfer effect could not in

itself cause instability, the very close interaction of heat and mass transfer can give rise to instability if $\frac{\partial \gamma}{\partial T}$ and the temperature gradient in the two component phase have the same sign.

2.5.4 The Influence of Natural Convection

Natural convection in a fluid is caused by bouyancy instability which can develop during heat and/or mass transfer. The pioneering theoretical work was carried out by Rayleigh (89) who used small-disturbance analysis to explain the convective cells observed by Bénard (90) when a horizontal layer of fluid is heated from below in terms of bouyancy instability. A detailed account of this well known phenomena is not necessary here; suffice it to say that if the temperature or concentration gradient associated with heat or mass transfer tends to increase the fluid density in the upward direction then the action of gravity will lead to instability. Cellular convection will result when this destabilizing force overcomes the stabilizing viscosity force, as reflected by the Rayleigh number exceeding a critical value. The effect of natural convection on the value of k_L has been predicted by Kraus (83) under conditions typical of high temperature liquid metal systems in which heat transfer occurs by radiation from the free surface.

$$k_L = D_{AB}^{\frac{1}{2}} (g B q / \nu \rho C_p)^{\frac{1}{4}} \quad (2.45)$$

Ironically, it is now almost certain that the Bénard cells were in fact controlled by surface tension forces (57, 69, 72). Pearson's(57) pioneering contribution in this area is discussed in the previous section, 2.5.3 . The rival theories have been combined by Nield (72) who found that the two agencies causing instability reinforce one another, thereby greatly increasing the range and

intensity of the resulting convective instability. The two mechanisms are very tightly coupled, presumably since the cells formed by surface tension are approximately the same size as those by bouyancy (72). Gumerman and Homsy (54, 74) have extended the study of the close interaction of bouyancy and surface tension instability to a situation of two-phase concurrent flow. Instabilities driven by shear are therefore included in the analysis, and the overall stability problem is described in terms of the Rayleigh, Marangoni and Reynolds numbers.

Sternling and Scriven (69) have proposed an interesting and simple criterion for distinguishing visually the dominant force in cellular convection in liquid pools. It follows from their detailed mathematical treatment that in steady state cellular convection driven by surface tension there is upflow beneath depressions and downflow beneath elevations of the free surface. The relationship is the converse in bouyancy-driven flows. One is intrigued whether with appropriate experimental techniques this simple criterion could be exploited in high temperature liquid metal systems.

EXPERIMENTAL INVESTIGATIONS AND RESULTS

3.1 Gas Jetting of Liquid Silver

The apparatus used by Wakelin (2) and Chatterjee (1) for high temperature experiments was reassembled, with modifications, for the study of oxygen transfer between gas jets and molten silver. The rig is represented in Figure 3.1 . The apparatus consisted of a metered gas supply capable of delivering gas of variable oxygen composition to a heated lance, from which the jet was directed vertically onto the surface of the molten silver. The silver was held in a resistance heated crucible with provisions for continuous oxygen concentration monitoring and bulk metal mixing.

3.1.1 Apparatus

The mass flux and composition of gas supplied from a bank of cylinders was monitored using Rotameter and MeTeRaTe flowmeters, manometer and thermometer. Preheating of the gas, such that experiments occurred at near isothermal conditions, was carried out in a "Nimonic" lance which incorporated "Crusilite" and "Kanthal" resistance heaters.

The heated gas discharged through a circular "Nimonic" nozzle, having a cross sectional area of 0.0519 cm^2 at 1000°C . Knowledge of the pressure drop across the nozzle, measured with a manometer, allowed calculation of the jet momentum. The lance was supported by a carriage which in turn was raised and lowered by a hydraulic ram, enabling the lance height to be varied. The

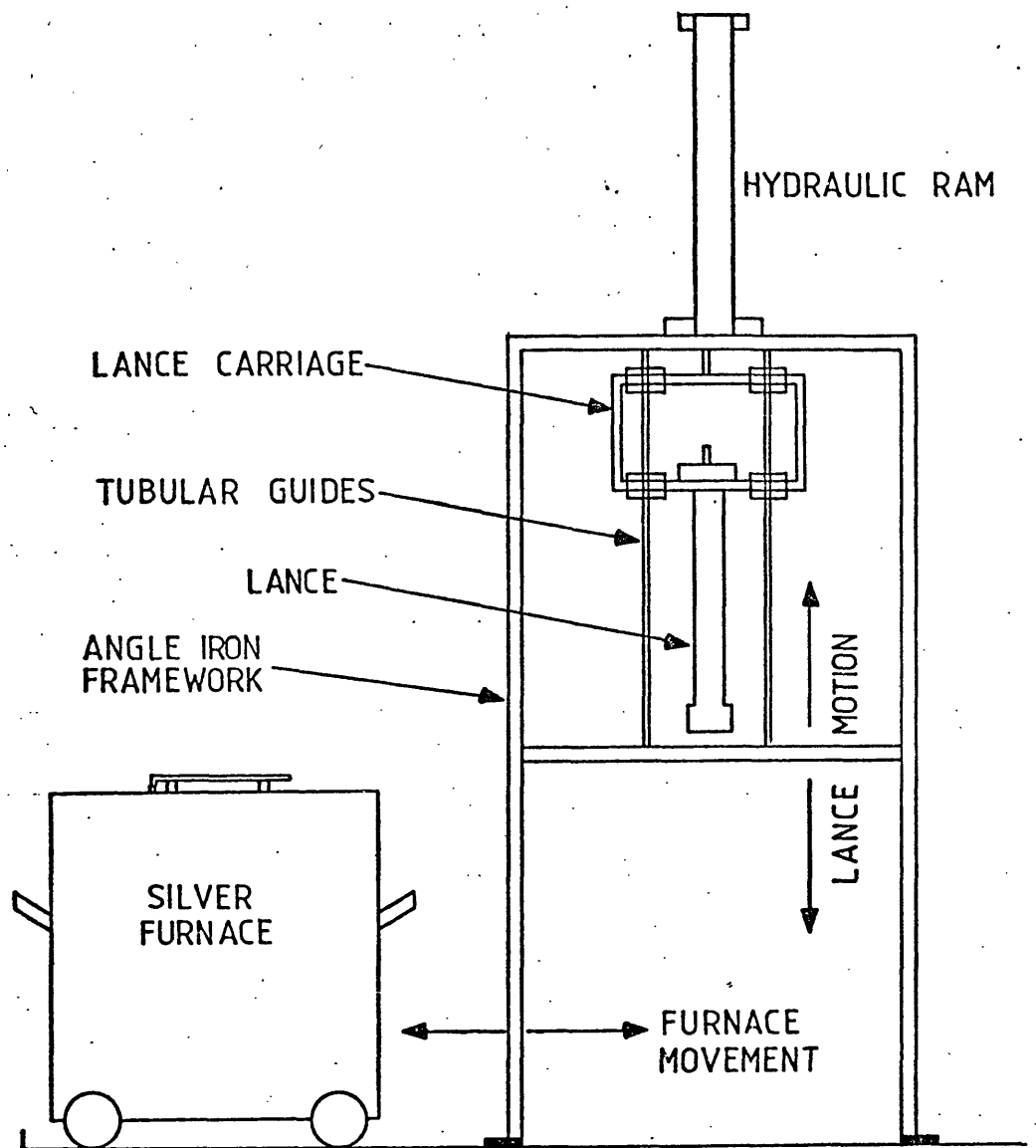


FIG.3-1 GENERAL LAYOUT OF JETTING
APPARATUS

lance height is defined as distance from the nozzle exit plane to the undisturbed surface of the molten silver. Further details of the lance, carriage and hydraulic system are given by Chatterjee (1).

Approximately 17 Kg of silver (99.9%, Johnson Matthey) was contained in a flat-bottomed 'Inconel' crucible, 15 cm internal diameter, 0.6 cm wall thickness. The general arrangement is indicated in Figure 3.2. Three 'Nimonic' lugs were welded at an inclined angle to the side of the crucible in order to provide access for a mechanical stirrer and solid electrolyte probes below the silver surface. "Nichrome" resistance heaters prevented silver solidifying in the lugs.

A considerable improvement in furnace life was achieved by winding "Kanthal" resistance wire, electrically insulated with fish-bone alumina insulators, directly around the metal crucible. A "Plicasto" refractory casting had separated the winding from the crucible in the earlier work, giving higher winding temperatures and power requirement.

The temperatures of both the main furnace winding and the lug heaters were controlled by 10 amp 'Eurotherm' controllers. The calibration of winding temperature against silver temperature was periodically checked using a dip thermocouple. The crucible was centrally located in a 60 cm square "Syndanyo" furnace box, with the lugs protruding through three of the side walls. 'Triton Kaowool' served as very efficient insulation, the total furnace power being about 1 KW (2 KW in the earlier work (1), using Vermiculite and alumina powder).

At all but the highest jet momenta the action of the jet on the silver surface was inadequate for thorough mixing of the bulk melt (1, 2). A mechanical stirrer similar to that used by Chatterjee (1) was therefore needed to give a homogeneous bath

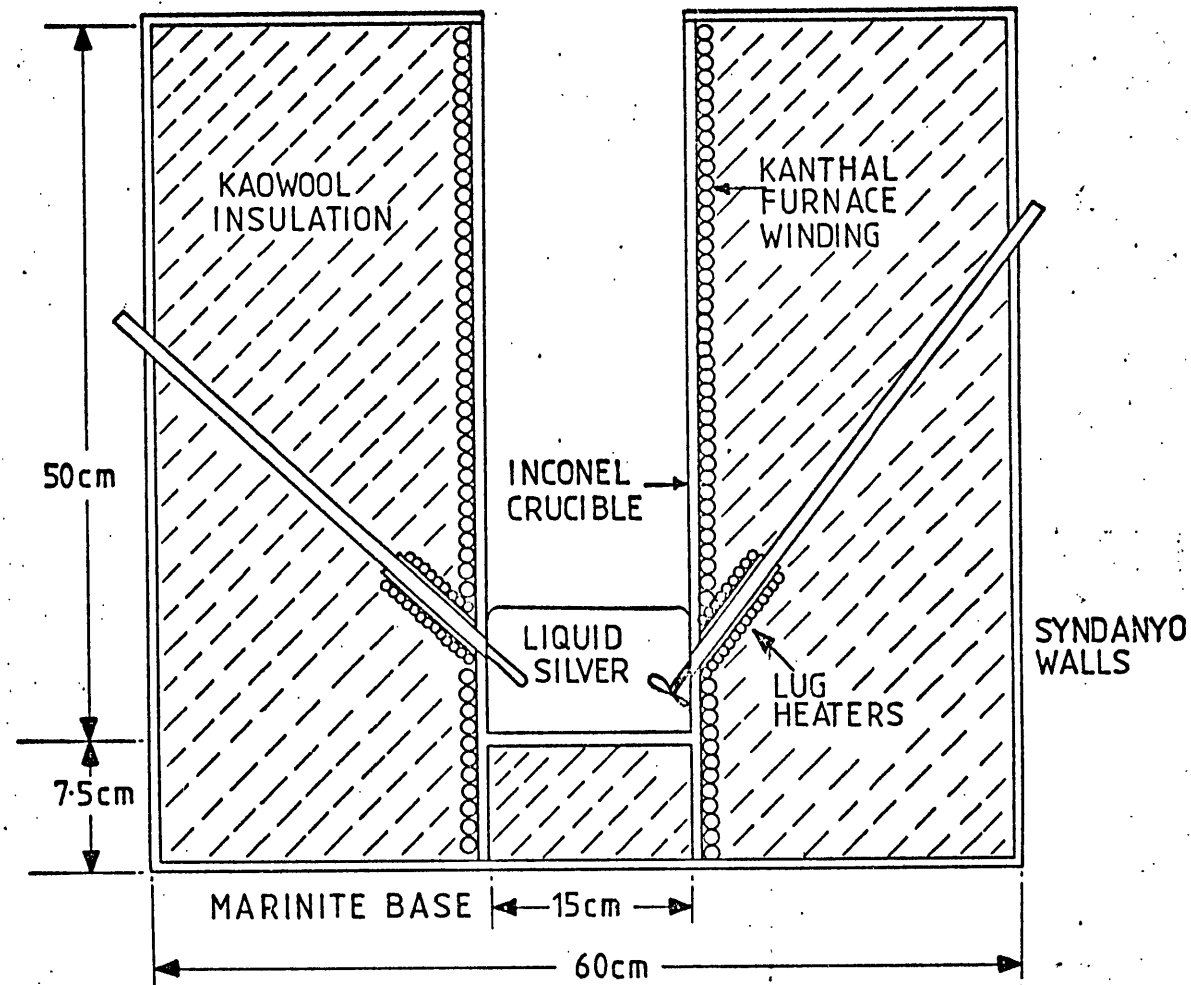


FIG. 3.2 SILVER FURNACE

and details are shown in Figure 3.3 . A "Nimonic" impeller, attached to a "Nimonic" shaft entering the crucible via one of the lugs, was turned by an electric motor. The stirring rate could be varied from 0 - 200 r.p.m. by thyristor control.

Lime stabilized (7.5 mole % CaO) and yttria stabilized (5 mole % Y₂O₃) zirconia probes were used to measure the oxygen concentration in the silver by comparison with a known reference oxygen potential. The electromotive force generated by a solid electrolyte probe (3) is given by

$$E = -2.303 \frac{RT}{4F} \log \frac{P_{O_2} \text{ (SILVER)}}{P_{O_2} \text{ (REFERENCE)}} \quad (3.1)$$

In the process of overcoming practical problems with probes in the earlier stage of the project a very simple design was evolved, as shown in Figure 3.4 . Closed-ended zirconia tubes, 15 cm long and 6.5 mm in diameter, served as the solid electrolyte. The open end was fixed with 'Autostic' high temperature cement to a stainless steel tube which acted as a probe holder. This arrangement, similar to that adopted by Mizoguchi (79), replaced the complex water-cooled brass holder soldered to zirconia tubes electro-plated with silver and copper (1). Reference gas (air or oxygen) was passed down the centre of the probe via an alumina tube. The same alumina tube carried a 0.3 mm diameter platinum wire, which was rolled into a small ball at the end, to enable electrical contact to be made with the inside (that is, reference side) of the solid electrolyte. The alumina tube was lightly spring loaded to ensure a sound contact.. The dry reference contact was found more reliable than the liquid silver contact used previously (1, 2, 79). Assembled probes were dipped into the molten silver bath through the side lugs in the crucible, and replaced as necessary. Cross checks with two probes were periodically carried out. Electrical contact with the silver was made with an earthed "Nimonic" rod entering via

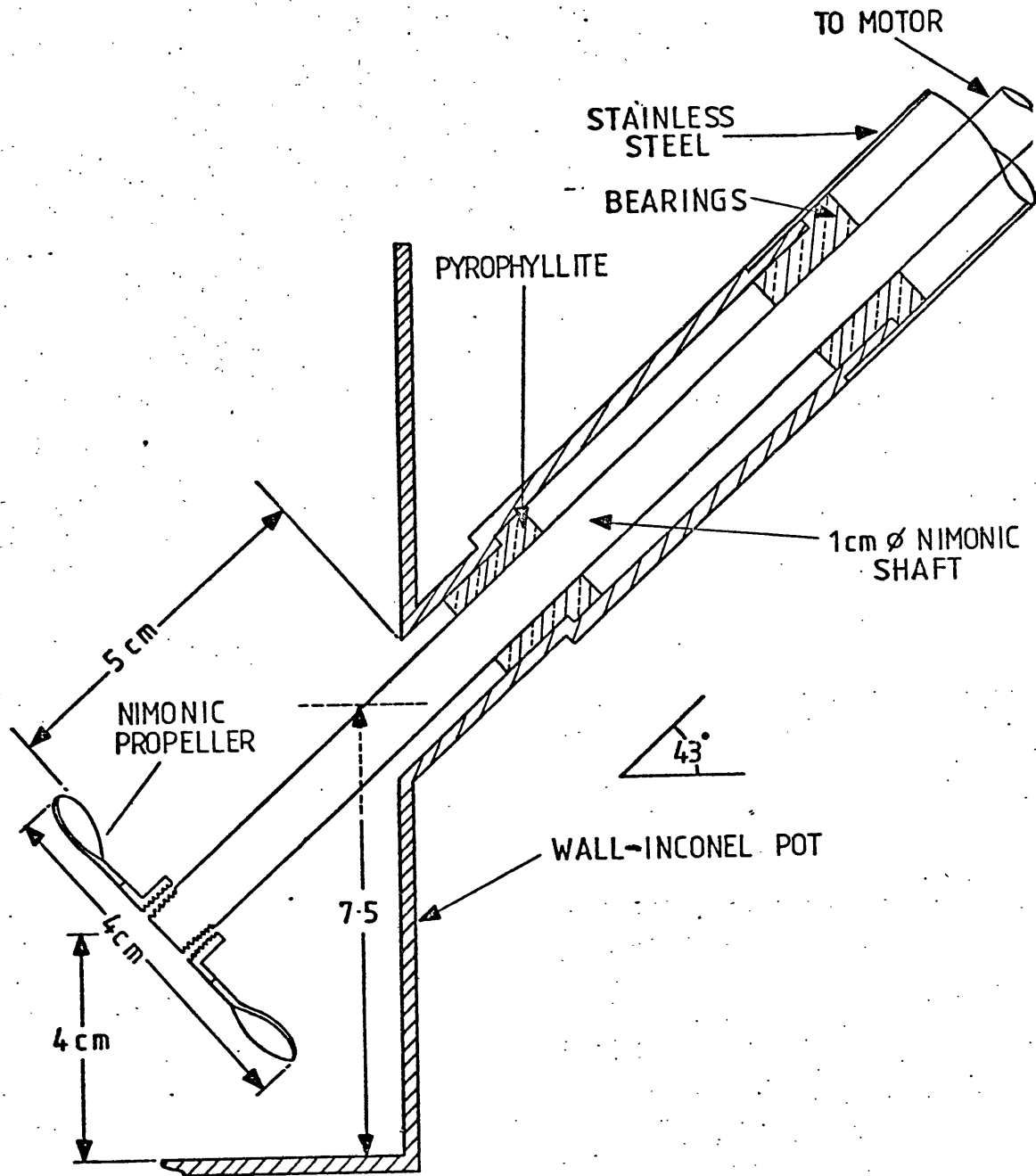


FIG. 3-3 STIRRER ASSEMBLY

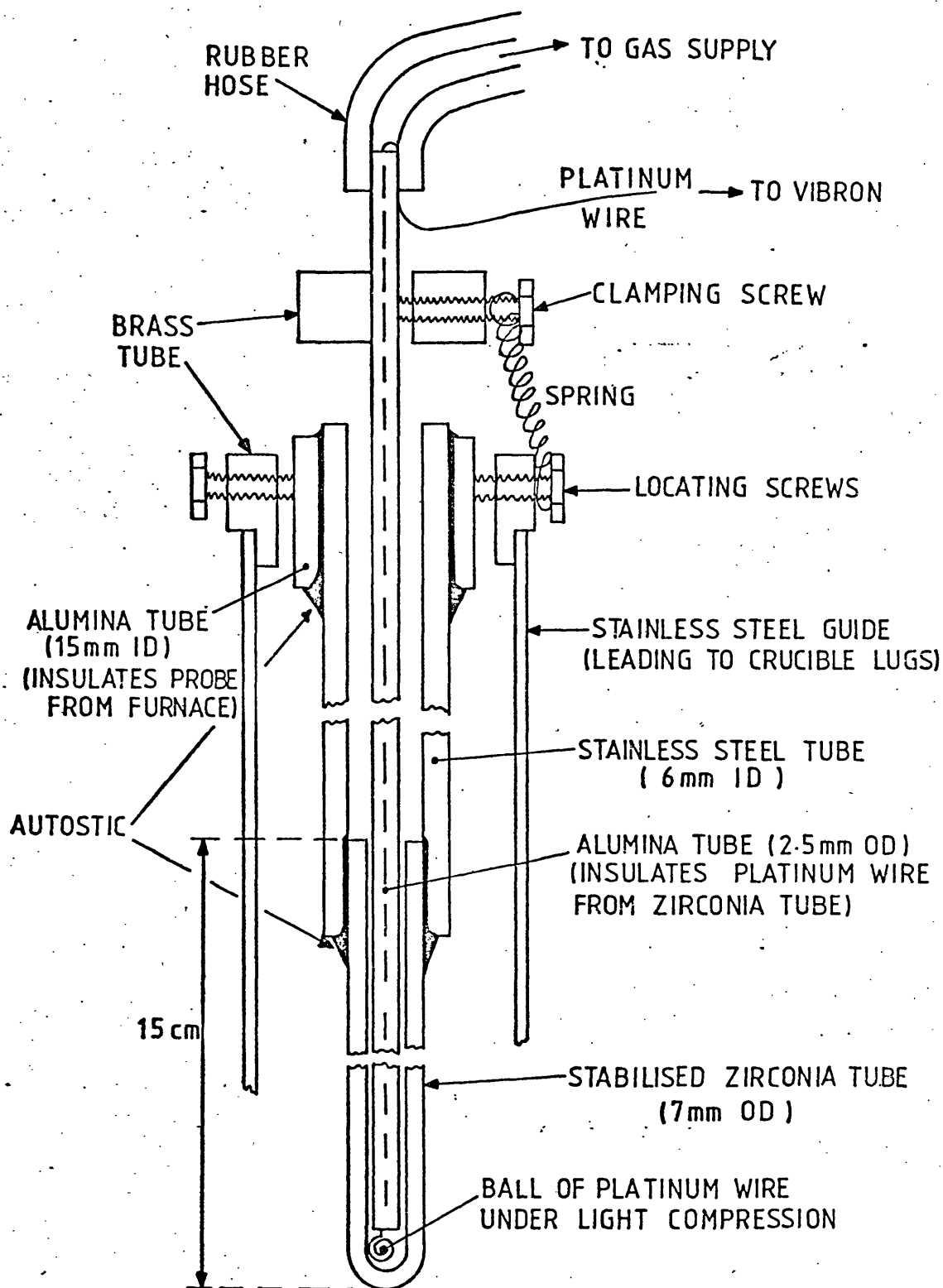


FIG.3.4 SOLID ELECTROLYTE PROBE ASSEMBLY

another lug, and the millivolt output between this and the reference platinum wire was measured by a Vibron Electrometer and recorded on a Servoscribe pen recorder.

3.1.2 Jet Temperature and Nozzle Characteristics

Since momentum is conserved in a free gas jet, the momentum has been used as a suitable parameter to define the jet (1, 2). Once the mass flux has been measured at room temperature, the momentum can be calculated if the jet temperature is known.

In the previous work (1, 2) the jet temperature was measured at a particular gas flow rate with the lance positioned in a preheating furnace. The lance was then transferred to the silver furnace and a mass transfer experiment carried out with the power to the lance adjusted to the value found to give a jet temperature of 1000°C in the preheating furnace. This technique is inevitably subject to considerable error and the transfer of furnaces involves delay as conditions are brought to steady state.

An alternative approach, developed in the present work, was to carry out a preliminary set of temperature measurement experiments which led to definition of the nozzle discharge coefficient. If the discharge coefficient is accurately known then the jet momentum can be calculated from the easily measured mass flux, and pressure drop across the nozzle. The jet exit temperature need not then be directly measured in subsequent experiments, but can be calculated.

A bare thermocouple bead was placed in the gas stream, as shown in Figure 3.5, 1 cm below the nozzle exit plane, and shielded from radiation. (Note : Pt/Pt (13% Rh) thermocouples

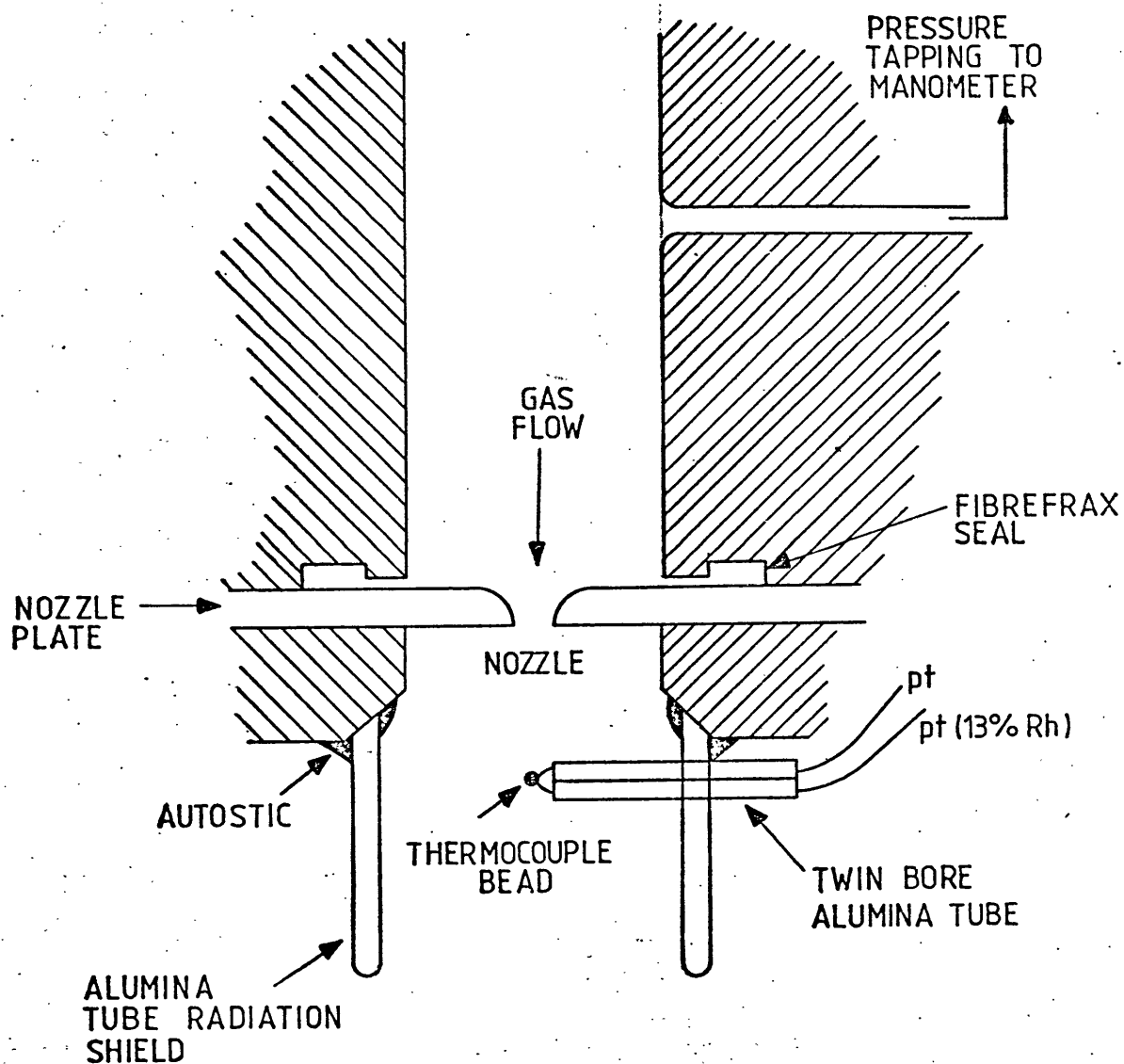


FIG.3.5 ARRANGEMENT FOR JET TEMPERATURE
MEASUREMENT

were used throughout the project.).

As the gas expands isentropically through the nozzle, the drop in pressure and increase in velocity are associated with a temperature drop, as described by Equation 2.24 . In the same but reverse fashion, as the gas impinges onto a stationary surface, its temperature and pressure are increased on the release of kinetic energy. This effect is significant above Mach Numbers of 0.2 and jet velocities in the present work corresponded to Mach Numbers up to 0.8 . The maximum temperature rise due to impingement onto a thermocouple bead in the potential core would be equal to the drop in temperature within the nozzle. The actual temperature rise for a bare thermocouple bead is about 70% of the theoretical maximum (8, 9). Assuming

$$T_{TC} - T_J = r \Delta T_N = 0.7 \Delta T_N \quad (3.2)$$

one can show, using Equation 2.24, that the real jet exit temperature is given by

$$T_J = \frac{T_{TC}}{0.3 + 0.7 \left(1 + \frac{\Delta P_N}{P_J} \right)^{\frac{\gamma-1}{\gamma}}} \quad (3.3)$$

Terms on the RHS of Equation 3.3 were experimentally measured, except for γ which can be taken to be equal to 1.4 since high temperature oxygen/nitrogen gas mixtures closely approximate to 'ideal' gases.

Experiments at various gas flow rates, gas compositions, and lance heights were carried out, and the lance power adjusted to give a jet temperature of approximately 1000°C . Table 3.1 summarizes the experimental data and calculated values of jet temperature.

A simple mass balance gives the jet velocity as

$$V_J = \frac{\dot{m} R T_J}{A_N P_J MW} \quad (3.4)$$

which, when compared to the theoretically calculated velocity, Equation 2.25, allows the nozzle discharge coefficient to be estimated from Equation 2.26. Table 3.1 includes the calculated values of the nozzle discharge coefficient. The average value of the discharge coefficient is 0.934 with of RMS deviation of $\pm 1.3\%$, which lies within experimental error.

The results in Table 2.1 display good internal consistency, and also agree well with previous work. The nozzle was identical in design to that used by Wakelin (2). Wakelin carried out determinations of the discharge coefficient at room temperature (where the practical problems connected with high temperatures are removed, and the expansion/contraction effects in the fluid are more easily monitored), and obtained values of $C_d = 0.92 - 0.95$ for oxygen jets and $C_d = 0.97$ for carbon dioxide jets.

In Figure 3.6, the nozzle discharge coefficients are recalculated for different values of 'r' and these results support the choice of $r = 0.7$. If the effect of isentropic compression of gas at the thermocouple bead had been ignored (i.e. $r = 0$), the internal consistency of the results would have disappeared, and theoretically impossible values of the discharge coefficient ($C_d > 1$) would have been obtained at the high jet velocities where the heat effects are more pronounced.

It is inherently difficult to measure the true temperature of high velocity gas streams at elevated temperatures. The approach adopted in this study, which is simpler in practice and more sophisticated in theory than previous methods (1, 2), gives

TABLE 3.1

Experimental Data and Calculations of Jet and Nozzle Characteristics

Run	P_{O_2} (atm)	Lance height (cm)	$\dot{m}$ (gm/sec)	ΔP_N (cm Hg)	T_{TC} (°C)	ΔT_N (°C) (calculated)	T_J (°C) (calculated)	$\dot{M}$ (dynes) (calculated)	Discharge Coefficient C_d (calculated)
T1	.05	15	0.351	7.8	1030	35	1005	8,809	0.926
T2	.10	5	0.489	15.3	1070	67	1023	16,788	0.921
T3	.02	5	0.507	17.0	1070	74	1018	18,411	0.923
T4	1.0	15	0.577	19.1	1070	83	1013	20,982	0.936
T5	1.0	5	0.573	19.3	1070	84	1012	21,102	0.930
T6	.20	5	0.551	19.3	1070	83	1013	21,051	0.927
T7	.05	15	0.763	40.3	1140	164	1025	41,574	0.938
T8	1.0	15	0.889	46.7	1140	185	1010	49,597	0.956
T9	1.0	5	0.892	47.7	1140	189	1008	49,982	0.952

(Note : Variations in atmospheric pressure and room temperature have been taken into account)

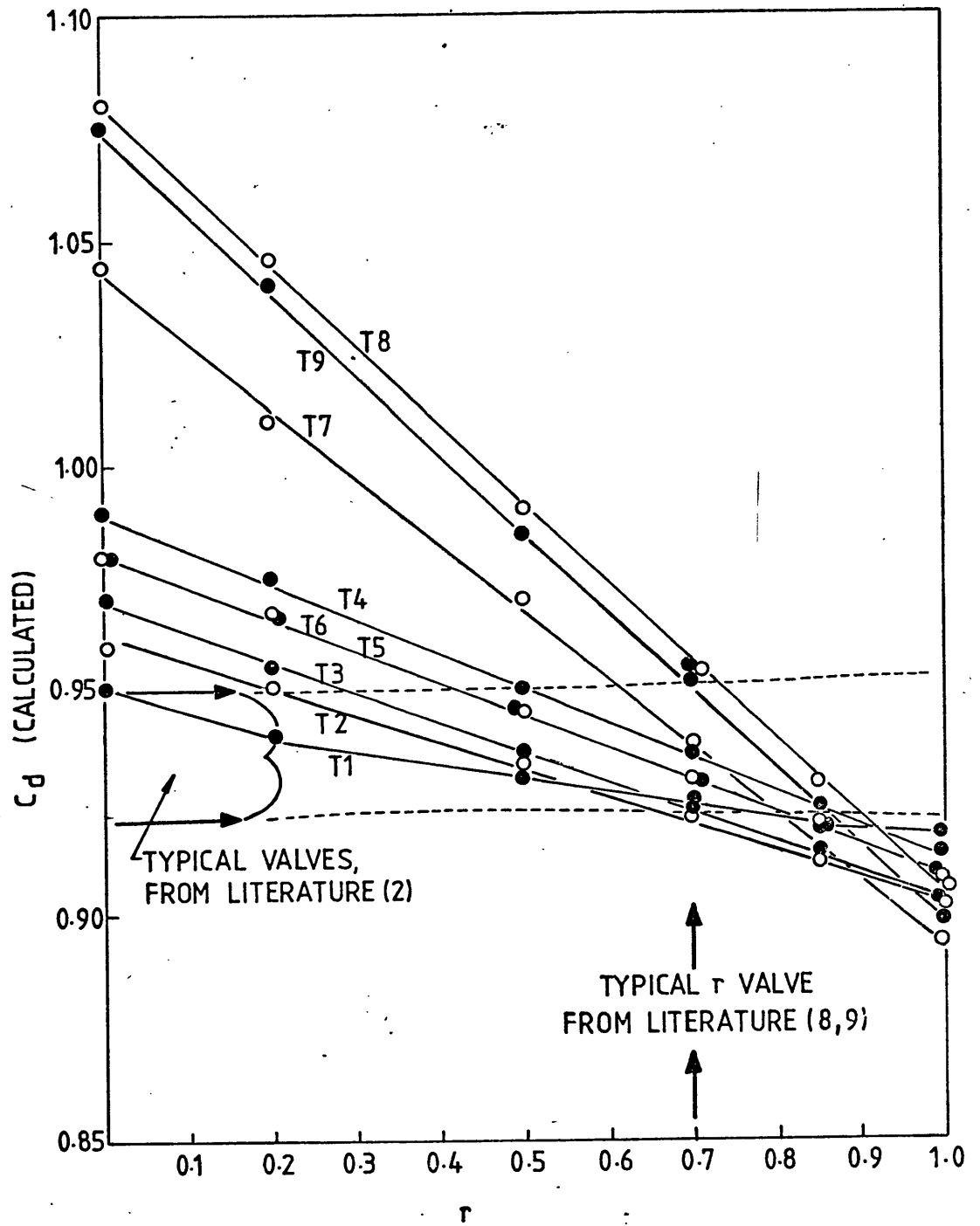


FIG. 3.6 SENSITIVITY OF CALCULATED NOZZLE DISCHARGE COEFFICIENTS TO VARIATIONS IN ASSUMED VALVE OF τ

reliable results. In all subsequent mass transfer experiments the momentum was calculated on the basis of a discharge coefficient of 0.934, simply by measuring the mass flow rate and the nozzle pressure drop.

3.1.3 Procedure for Mass Transfer Runs

Before each run the silver was thoroughly cleaned using 'Borax' as a flux. The lance nozzle was visually checked for blockages, and the lance lowered to the predetermined lance height in the silver furnace. The stirrer speed was set before the run and rechecked at intervals.

The reference gas to the probes was usually air. Prior to each run the reference gas was temporarily changed over to oxygen. This served as a check on the probes, since the resultant step change in probe reading (43.7 mV at 1000°C) is independent of oxygen concentration in the silver. The absolute reading of the probes included thermoelectric junction potentials arising from the various contacts in the measuring circuit. These were quantified by having equal oxygen potentials on both the reference and silver bath sides of the solid electrolyte. This was carried out regularly during a campaign as an additional check on the probes. That thermoelectric potentials were responsible for the non zero readings of probes, when bath and reference oxygen potentials were equal, was confirmed by comparing the readings of two probes : one incorporated a platinum reference wire, the other a platinum (13% rhodium) reference wire. The observed difference in probe readings corresponded exactly to the millivoltage expected from a simple Pt/Pt (13% Rh) thermocouple. Probes were immediately replaced whenever one of the routine tests suggested faulty performance. The typical life of a zirconia probe

at 1000°C was about one to two weeks, the stage when silver penetration into the electrolyte becomes significant (7).

Prior to a mass transfer experiment gas was passed through the heated lance at the desired flow rate until steady state thermal conditions were reached. The composition of the gas was then quickly altered to the predetermined value for the experiment, such that absorption or desorption could begin.

3.1.4 Results of Mass Transfer Experiments using Pure Oxygen Gas Jets

Absorption experiments using pure oxygen gas jets were carried out, prior to using dilute gas jets where the additional kinetic factor of gas phase diffusion is introduced. The effect of jet momentum up to 24000 dynes for two lance heights, 5 cm and 10 cm, was systematically studied, although experiments covered a momentum range of 0 - 50,000 dynes and a lance height range of 5 - 15 cm. Investigations on the stirrer were also carried out to establish the degree of stirring required to obtain a well mixed bath without significantly effecting the absorption rate at the free silver surface.

Since there can be no gas phase resistance with pure oxygen gas jets, the mass transfer data were interpreted on the basis of liquid phase transport control. Appendix A presents the raw data plotted according to the basic mass transfer relationship, Equation 2.7. The slope of these plots gives an average value of k_L for each experiment

Table 3.2 summarizes the mass transfer results and Table 3.3 gives details of experiments relevant to stirring investigations.

TABLE 3.2

Summary of Liquid Phase Mass
Transfer Data with Pure Oxygen Gas Jets

Run No.	Momentum (dynes)	Lance height (cms)	k_L (cm/sec) $\times 10^3$
P1	0	-	1.63
P2	3450	10	1.51
P3	7000	10	3.37
P4	8300	10	4.20
P5	11900	10	5.94
P6	12600	10	6.29
P7	15650	10	7.20
P8	21700	10	7.42
P9	21700	10	7.53
P10	13100	5	4.79
P11	13100	15	4.66
P12	13100	12.5	5.47
P13	13100	7.5	5.51
P14	13100	5	4.72
P15	47300	5	21.95
P16	21400	5	8.29
P17	45400	5	23.00
P18	6950	5	2.61
P19	8800	10.2	3.93
P20	18000	10	7.35
P21	23000	5	9.17
P22	23000	6.2	9.30
P23	24000	10.5	8.76
P24	11100	5	4.02
P25	18700	5	6.76

TABLE 3.3

The Effects of Bulk Metal Mechanical
Stirring on Free Surface Mass Transfer

Series	Run No.	Momentum (dynes)	Lance height (cm)	Stirring rate (revs/min)	k_L (cm/sec x 10^3)
51	P1A	0	-	0	1.00(NL)
	P1B			40	1.63
52	P5A	11900	10	0	5.94
	P5B			40	5.78
	P5C			85	6.14
53	P10A	13100	5	0	5.39
	P14A			0	4.86
	P14B			40	4.84
	P10B			40	4.72
	P10C			85	4.86
	P14C			85	4.45
	P10D			85	6.24
54	P11A	13100	15	40	3.12(NL)
	P11B			85	4.61
	P11C			85	4.71
	P11D			120	5.64
55	P12A	13100	12.5	0	5.38
	P12B			40	5.57
	P12C			85	5.47
56	P13A	13100	7.5	0	5.24
	P13B			40	5.78
	P13C			85	5.52
57	P18A	6950	5	0	2.57
	P18B			40	2.64
58	P9A	21700	10	0	6.30(NL)
	P9B			40	7.53
	P9C			85	7.87

Figure 3.7 shows the results in the form of liquid phase mass transfer coefficient versus jet momentum. The effect of lance height at a specific momentum of 13,100 dynes is shown in Figure 3.8.

(a) The Influence of Mechanical Stirring

The series of mass transfer experiments at different stirring speeds, see Table 3.3 and Appendix A, allow the influence of mechanical stirring to be assessed.

The solid electrolyte probe readings can only measure the required bulk oxygen concentration in the silver if the bath is homogeneous. Non linearity of the plots of $\ln R$ vs t (Appendix A) was taken to indicate inadequate mixing of the liquid silver bath. At high jet momenta or with additional mechanical stirring these plots tend to be linear, consistent with previous work (1, 2). Runs for which the plots of $\ln R$ vs t were non-linear are marked (NL) in Table 3.3. In these experiments the bath was thoroughly stirred at the end of the run and k_L was calculated on the basis of the total amount of absorption.

There are six results in Table 3.3 which could suggest some dependence of k_L on stirring speed, namely P1B, P10A, P10D, P11A, P11 D, and P9A. Two of these, P9A and P11A are runs in which there was inadequate mixing. The results from runs P10A and P10D were cross-checked by runs P14A and P14C, for which there appeared to be no dependence of k_L on stirring. Run P11D is the only one with the high stirring rate of 120 rpm.

Mechanical stirring would be expected to have its most pronounced influence at zero momentum, where in fact it lead to an increase in k_L from 1.0×10^{-3} to 1.6×10^{-3} cm/sec.

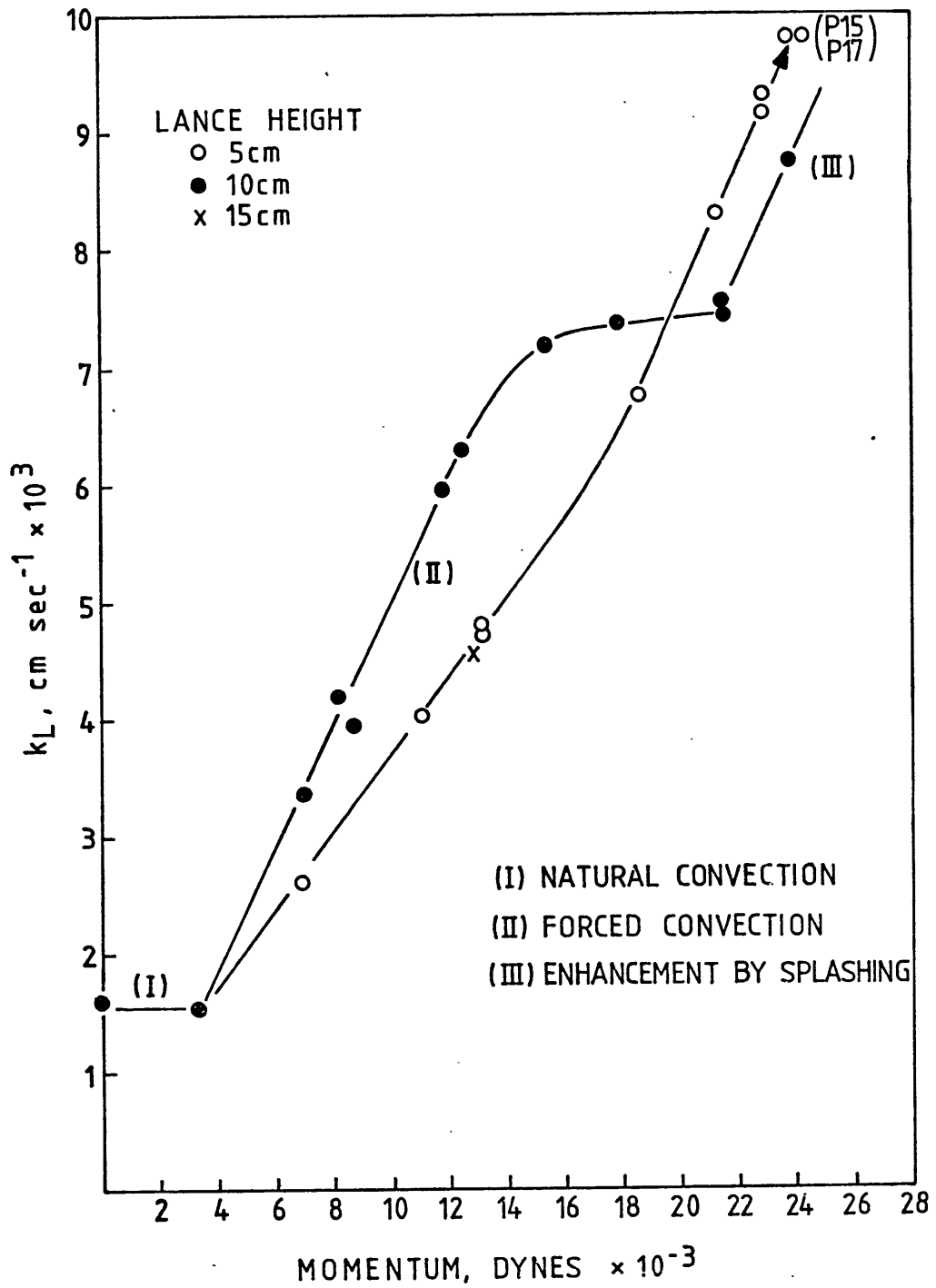


FIG. 3.7 SUMMARY OF LIQUID PHASE MASS TRANSFER DATA FROM ABSORPTION EXPERIMENTS WITH PURE OXYGEN JETS

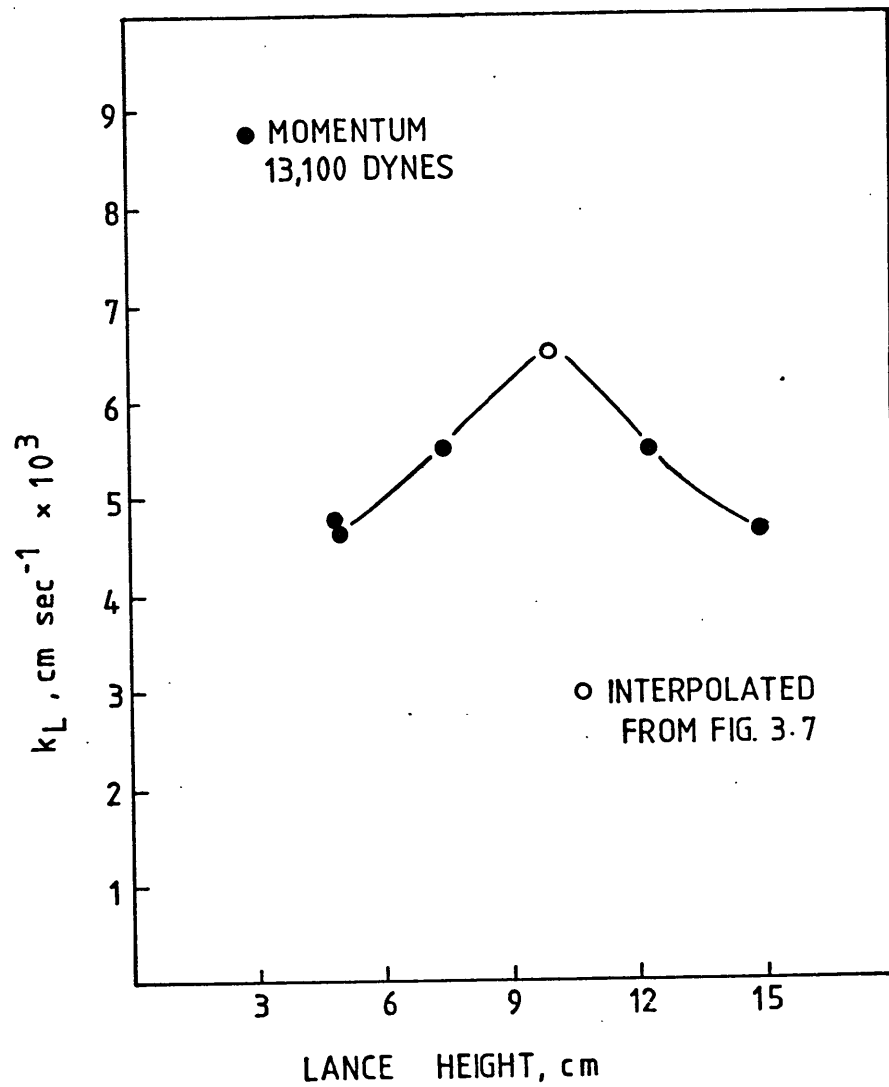


FIG. 3.8 THE EFFECT OF LANCE HEIGHT ON
LIQUID PHASE MASS TRANSFER ; 13,100 DYNES

Due to a failure in the lug heater surrounding the stirrer bearing, experiments P2, P3, P4, P6, P8 and P18 (see Table 3.2) were conducted with manual turning of the stirrer shaft, which necessitated a to-and-fro motion. The mass transfer data from these runs are fully consistent with the remainder of the runs, in which the stirrer was motor driven with full rotation. One can conclude that mechanical stirring is necessary to homogenise the bath, but it appears to have little or no effect on the actual rate of mass transfer at the free liquid surface for the conditions studied. This is inline with previous observations(1). In all subsequent mass transfer experiments a stirring speed of about 60 - 80 revs/min was therefore adopted, with no further tests on the effect of stirring on k_L .

(b) The Influence of Jet Momentum and Lance Height

The dependence of k_L on jet momentum, at constant lance height (5 and 10 cm), as shown in Figure 3.7, suggests three separate mass transfer regimes, marked on Figure 3.7 as I, II and III.

Regime I : For jet momenta less than about 4000 dynes, the impact of the jet induces insufficient forced convection to significantly increase the total mass transfer at the free surface. The predominant transport mechanism within this regime would be some form of natural convection, perhaps driven by the thermal gradients associated with radiation from the bath to the furnace top.

Regime II : Above about 4000 dynes, k_L increases linearly with jet momentum. In this regime, the predominant liquid phase transport mechanism would be the forced convection induced by

the jet action. The most striking feature of the results is that values of k_L are greater for a lance height of 10 cm than for one of 5 cm. The influence of lance height was subjected to closer attention, at a jet momentum of 13100 dynes, as shown in Figure 3.8 . There is a pronounced peak in the plot of k_L vs lance height, clearly suggesting optimum momentum transfer from jet to liquid at a lance height of about 10 cm at this momentum.

Regime III : Further increase in momentum leads to enhancement in mass transfer, possibly due to dispersion of silver droplets into the gas phase and agitation of the surface. Precise observation of the onset of splashing was not possible, but from the sound of droplets being caught by the jet and from the sight of silver covering the end of the lance after a run it was clear that dispersion of the surface was occurring in this regime. The plateau in the curve of k_L vs $\dot{M}$ for a lance height of 10 cm enables one to deduce on the assumption of the above argument, that splashing commences at 22,000 dynes. Despite the absence of an extended plateau with a lance height of 5 cm one would nevertheless deduce, on the same basis, that the splashing regime is established between 15,000 and 18,000 dynes.

(c) Comparison with Previous Work

Figure 3.9 provides a comparison of liquid phase data from the present and previous investigations into oxygen jetting of liquid silver. (The previous work (1, 2, 14) is discussed in Section 2.4.3). The detailed pattern of results in the present work differs quite significantly from that of the previous workers. In contrasting the results of Chatterjee et al (1, 14) with the present work, the following observations can be made :

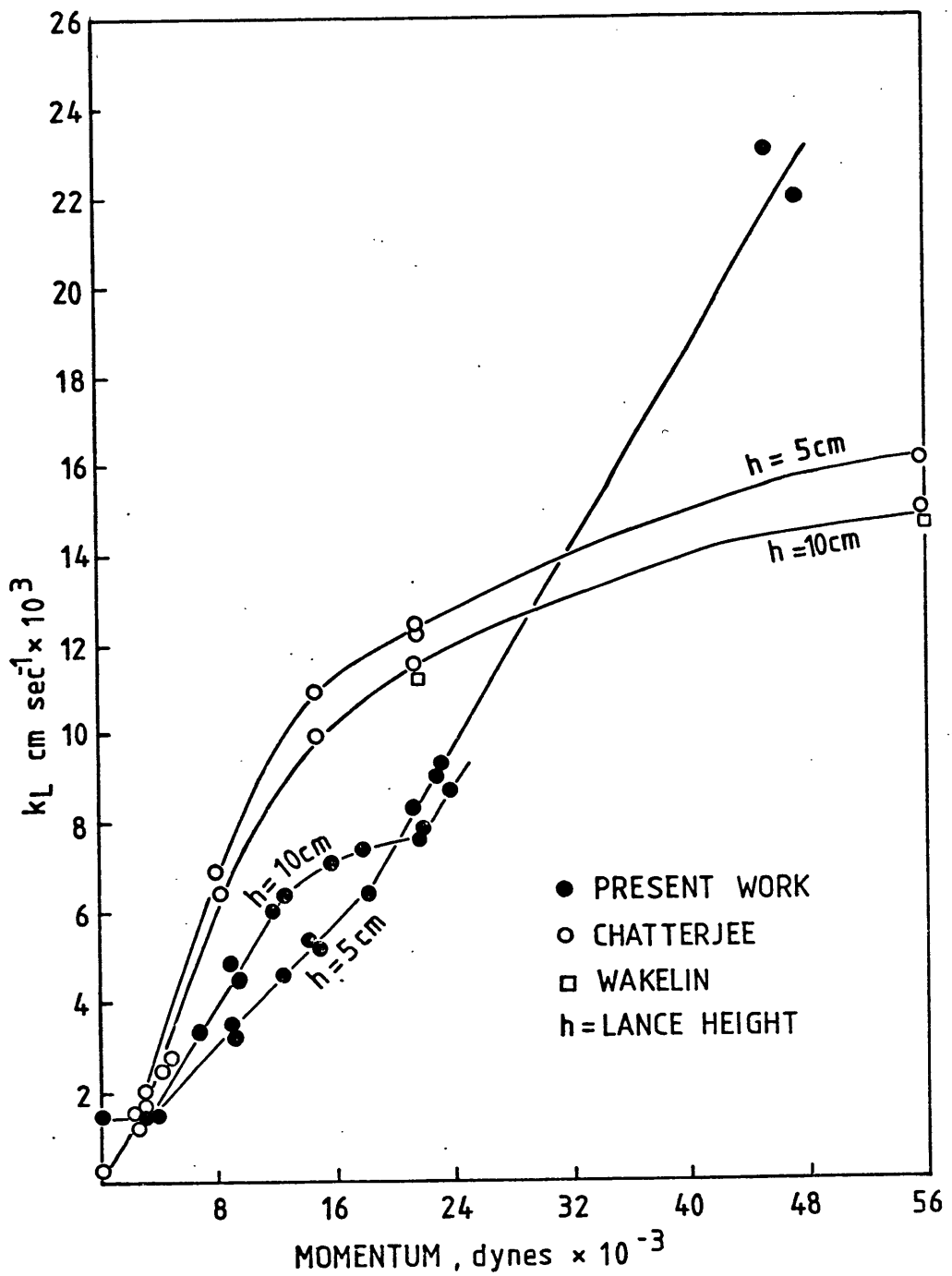


FIG. 3.9 COMPARISONS OF PREVIOUS AND PRESENT WORK

(i) In the forced convective regime (II), the absolute values of k_L reported by Chatterjee are roughly double the values presented in this investigation.

(ii) In regime (II), Chatterjee et al did not observe an optimum lance height for maximum mass transfer at a particular momentum as observed in the present work, see Figures 2.6, 3.8 and 3.9 . This is the most striking discrepancy in the results of the two investigations.

(iii) Chatterjee et al found no enhancement of k_L at momenta corresponding to the splashing regime. At high momenta, around 50,000 dynes, the values of k_L reported by Chatterjee et al are roughly half those measured with a lance height of 5 cm in the present work.

(iv) In the present investigation, splashing was deduced to commence at 15 - 18,000 dynes for a lance height of 5 cm. This is in excellent agreement with a momentum of 15,300 dynes calculated from Equations 2.37 and 2.38 which are based on Chatterjee's results. However, at 10 cm lance height the agreement is poor. The splashing regime was estimated to commence at 22,000 dynes in the present work, which can be compared to a value of 47,500 dynes calculated from Equations 2.37 and 2.38.

Obviously, the above discrepancies prompted extensive checking of all aspects of experimental procedure. No satisfactory explanations were found, even after the year's work which followed the discovery of these discrepancies. During this period there were several furnace re-builds, numerous probes had been used, jet temperature and momenta estimations were thoroughly investigated and the influence of mechanical stirring was studied.

In view of the results on their own merits, apart from the questions raised by the contradictions with the previous work, further experimental study of the effect of lance height and jet momentum on liquid phase mass transfer with silver would be interesting. However, the priority governing the pure oxygen jetting work was to obtain a reliable set of liquid phase mass transfer data under a limited variation of blowing conditions to serve as a basis for assessing the rate of the gas phase resistance in subsequent experiments with dilute gas jets. In this context, the liquid phase data at a lance height of 10 cm, in the momentum range of 4,000 - 21,000 dynes are wholly adequate. In view of the internal consistency established in the pure oxygen jetting work it was decided to proceed with the dilute gas jetting studies.

3.1.5 Results of Mass Transfer Experiments using Dilute Oxygen Gas Jets

Absorption and desorption experiments using oxygen/nitrogen gas jets were carried out in the same fashion as absorption experiments with pure oxygen jets. The lance height was maintained at 10 cm for all runs, and three levels of jet momentum were investigated : low (about 6,500 dynes), medium (about 13,000 dynes) and high (about 19,000 dynes). The splashing regime was avoided in this phase of the work. The controllable parameter of greatest interest, namely the oxygen composition of the jet, was varied in the 0 - 0.1 atm range, since this had been previously assessed to be the critical region from the point of view of studying the influence of the gas phase resistance. In addition to thirteen absorption and desorption experiments with oxygen/nitrogen mixtures, three desorption runs were carried out with pure argon gas jets. Pure nitrogen gas jets could not be used due to reaction with the 'Crusilite' heating elements within the lance.

(a) Calculations of the Overall Mass Transfer Coefficient

The mass transfer data were analysed on the basis of Equation 2.9 , so that the overall mass transfer coefficient could be calculated for each run. The data are presented in this form in Appendix B. The plots of $\ln R$ vs t are not strictly linear, and the average slope was taken which gives an average value of k_{OV} for each experiment.

Table 3.4 and Figures 3.10, 3.11 and 3.12 summarize the results of the mass transfer experiments with dilute oxygen gas jets.

TABLE 3.4

Summary of Mass Transfer Data with Dilute Gas Jets

Run	$\dot{M}$ (dynes)	Direction of Transfer	P_{O_2} (atm $\times 10^2$)	k_{ov} (cm sec ⁻¹ $\times 10^3$)
D1	6800	Absorption	3.13	0.776
D2	6450	"	6.38	0.881
D3	6700	"	9.96	1.06
D4	6450	"	9.99	0.891
D5	6450	Desorption	0.585	1.35
D6	6750	"	2.74	1.64
D7	13400	Absorption	0.435	0.785
D8	13700	"	4.83	1.12
D9	13750	"	4.80	0.897
D10	11300	"	6.94	1.68
D11	13750	"	9.24	1.1
D12	14500	"	16.95	1.38
D13	12800	Desorption	0.435	1.55
D14	12800	"	0.435	1.31
D15	12800	"	2.21	2.59
D16	11300	"	4.87	3.03
D17	13900	"	4.85	2.55
D18	12800	"	9.55	3.67
D19	19100	Absorption	1.66	1.70
D20	19100	"	4.96	1.81
D21	19100	"	10.06	2.35
D22	19000	Desorption	0.355	1.85
D23	19000	"	1.66	2.51
D24	19100	"	4.96	3.28
D25	18800	"	7.29	3.16
D26	18600	"	10.05	3.42
D27	7250	Desorption	0	1.24
D28	13640	with	0	1.23
D29	13640	Argon	0	1.20

(Notes : Lance Height = 10 cm; Nitrogen is diluent gas in D1-26)

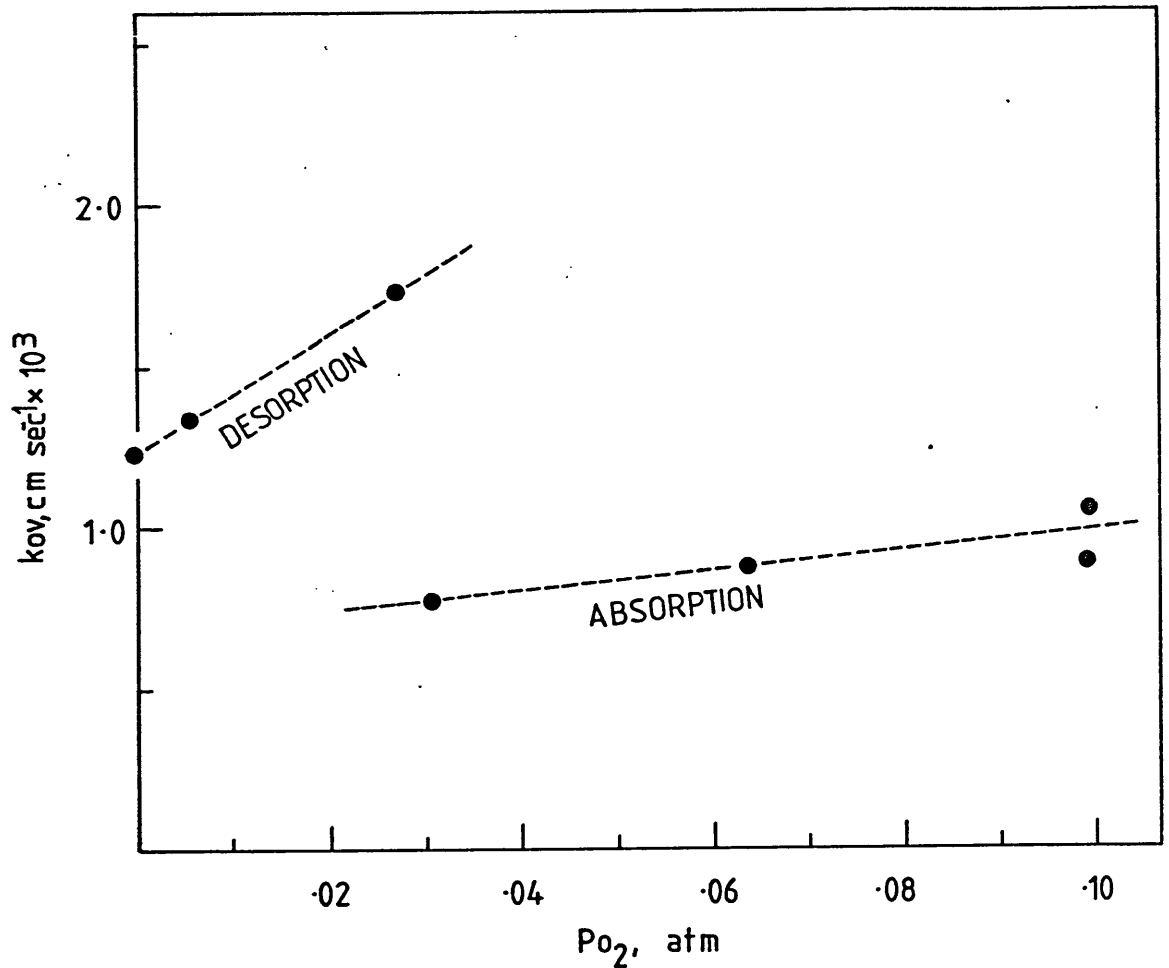


FIG. 3-10 OVERALL MASS TRANSFER DATA FROM
ABSORPTION AND DESORPTION EXPERIMENTS
AT LOW MOMENTUM (ABOUT 6500 DYNES)
WITH DILUTE JETS

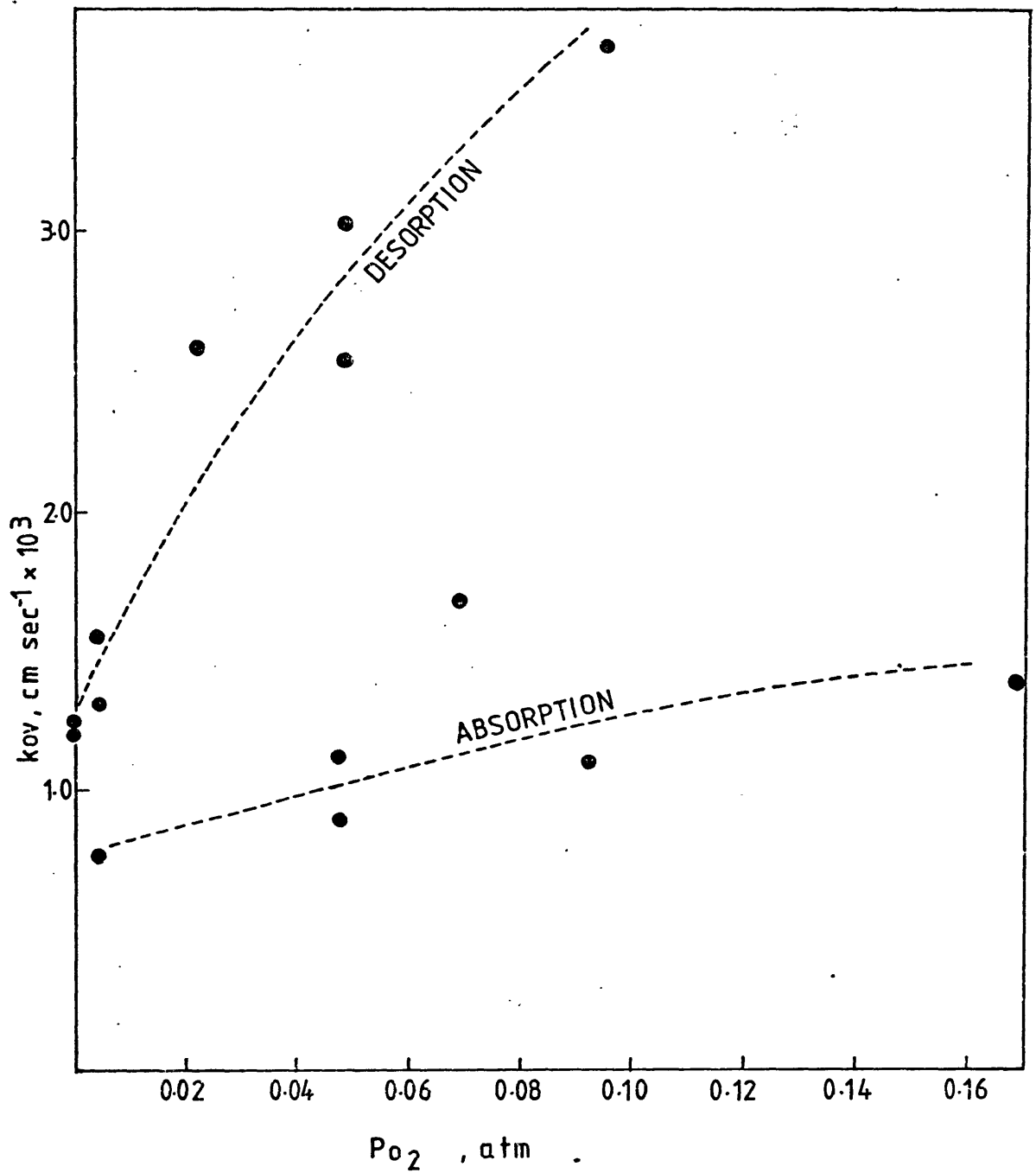


FIG. 3.11 OVERALL MASS TRANSFER FROM ABSORPTION AND DESORPTION EXPERIMENTS AT MEDIUM MOMENTUM (ABOUT 13,000 DYNES) WITH DILUTE JETS.

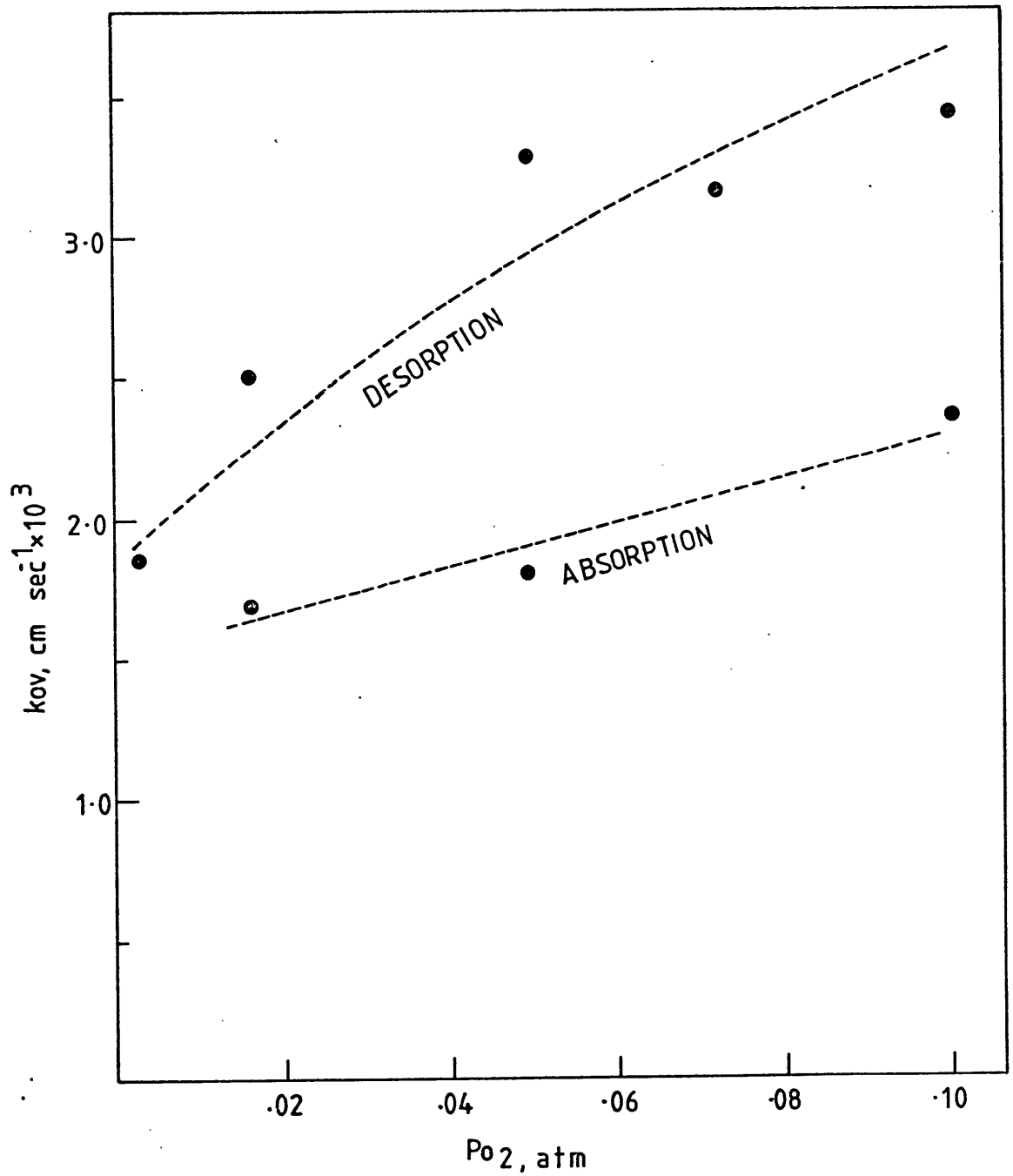


FIG.3-12 OVERALL MASS TRANSFER DATA FROM
ABSORPTION AND DESORPTION EXPERIMENTS
AT HIGH MOMENTUM (ABOUT 19000 DYNES)
WITH DILUTE JETS

(b) Calculations of the Gas Phase Mass

Transfer Coefficient

The dependence of k_{ov} on gas composition, see Figures 3.10, 3.11 and 3.12, indicates that the process kinetics are not simply controlled by mass transfer in the liquid phase. The additional resistance may be associated with gas phase mass transfer, as suggested by Chatterjee et al (10), or with the interfacial chemical reaction, as postulated by Mori et al (40).

From the discussion in Section 2.2.1, it can be seen that the relative importance of the gas phase mass transfer step will depend primarily on the value of ϕ . The process is controlled by liquid phase transfer when $\phi \rightarrow 0$, and actual rates of transfer will be within 10% of this limiting case if $\phi < 2$. On the other hand, the process will be controlled by gas phase transfer when $\phi \rightarrow \infty$, and real rates will be within 10% of this limiting case if $\phi > 20$, except for very low values of η . Thus the gas phase resistance would be significant for ϕ values greater than 0.2, and would essentially control the overall kinetics for ϕ values greater than 20.

There is inherently less scope for varying ϕ by altering the hydrodynamic conditions (i.e. k_G/k_L), than by changing the oxygen content of the gas. The ratio of the oxygen diffusion coefficients in nitrogen gas (45) and molten silver (see Table 2.1) is about 135. Thus it is unlikely that the value of k_G/k_L , for widely different fluid conditions, would extend outside the range 50 - 1000 (43). Table 3.5 sets out the likely regimes of kinetic control.

Mori et al's view (40) that "the gas flow rate was selected so that the mass transfer resistance in the gas phase could be

TABLE 3.5

Regimes of Kinetic Control - The Effect
of Hydrodynamic Conditions and Gas Composition

$\frac{k_G}{k_L}$	p_{O_2} (atm $\times 10^2$) for $\phi > 20$ (Gas Phase Control)	p_{O_2} (atm $\times 10^2$) for $\phi < 0.2$ (Liquid Phase Control)
50	< 8	> 90
200	$< .05$	> 65
1000	$< .002$	> 15

neglected" fails to recognise the central role of gas composition in determining the magnitude of this resistance in a Sievert's law system. For the present investigation with dilute jets, containing between 0 - 17% oxygen, Table 3.5 indicates that the gas phase resistance is bound to be significant. Only for oxygen contents greater than those listed in the final column of Table 3.5 could the gas phase resistance reasonably be ignored.

The approach adopted here is therefore to assume initially that the overall kinetics are controlled by a combination of the liquid phase and gas phase mass transfer resistances; in other words, to employ the simple mixed control model used by Chatterjee and Bradshaw (10). The details of the calculations are given in Appendix D. Corrections are made for bulk flow, as discussed in Section 2.2.2. Also, corrections are made for the effect of product gas entrainment. The shear action between the jet and the surrounding gas would reduce the driving force for interfacial reaction. An asterisk is used to identify gas phase mass transfer coefficients for which a correction has been made for product entrainment by the jet, viz $(k_G)^*$, $(k_G^O)^*$.

The values of $(k_G^O)^*$ should be inherently the best reflection of the hydrodynamic condition of the jet and should therefore be a function of jet momentum, but independent of oxygen composition of the jet or the direction of transfer. The calculated values of $(k_G^O)^*$ are shown in Figures 3.13, 3.14 and 3.15. As is immediately apparent from these figures the calculated values of $(k_G^O)^*$ do show a dependence on gas composition, and even more strikingly on the direction of transfer. These calculated values are therefore physically unrealistic.

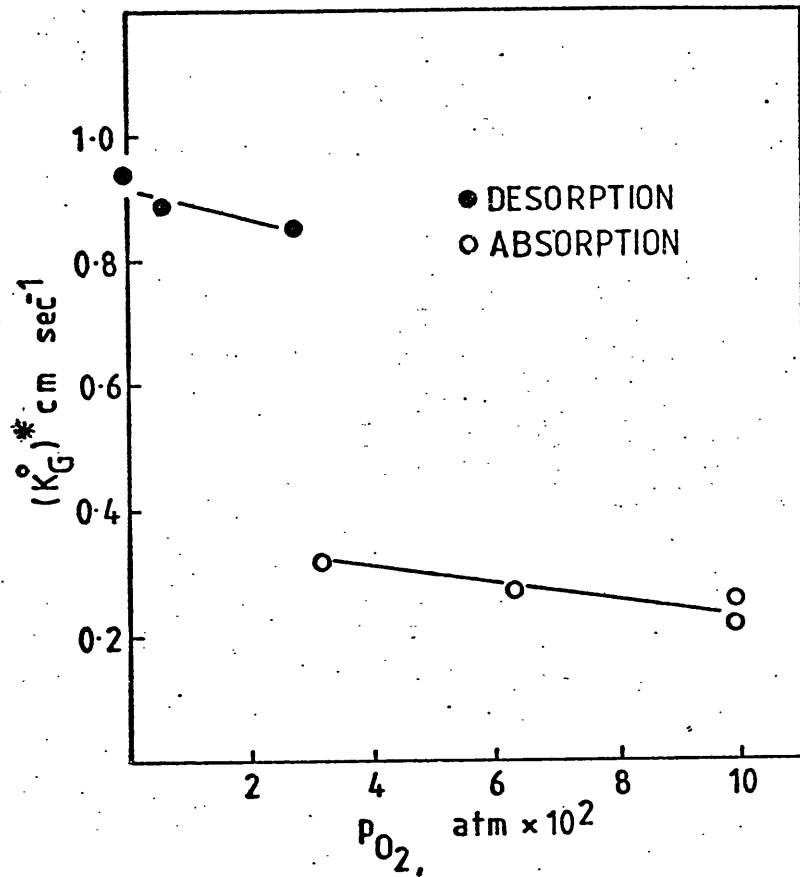


FIG. 3.13 CALCULATED GAS PHASE MASS
TRANSFER COEFFICIENTS, AT
LOW JET MOMENTUM (6500 DYNES)

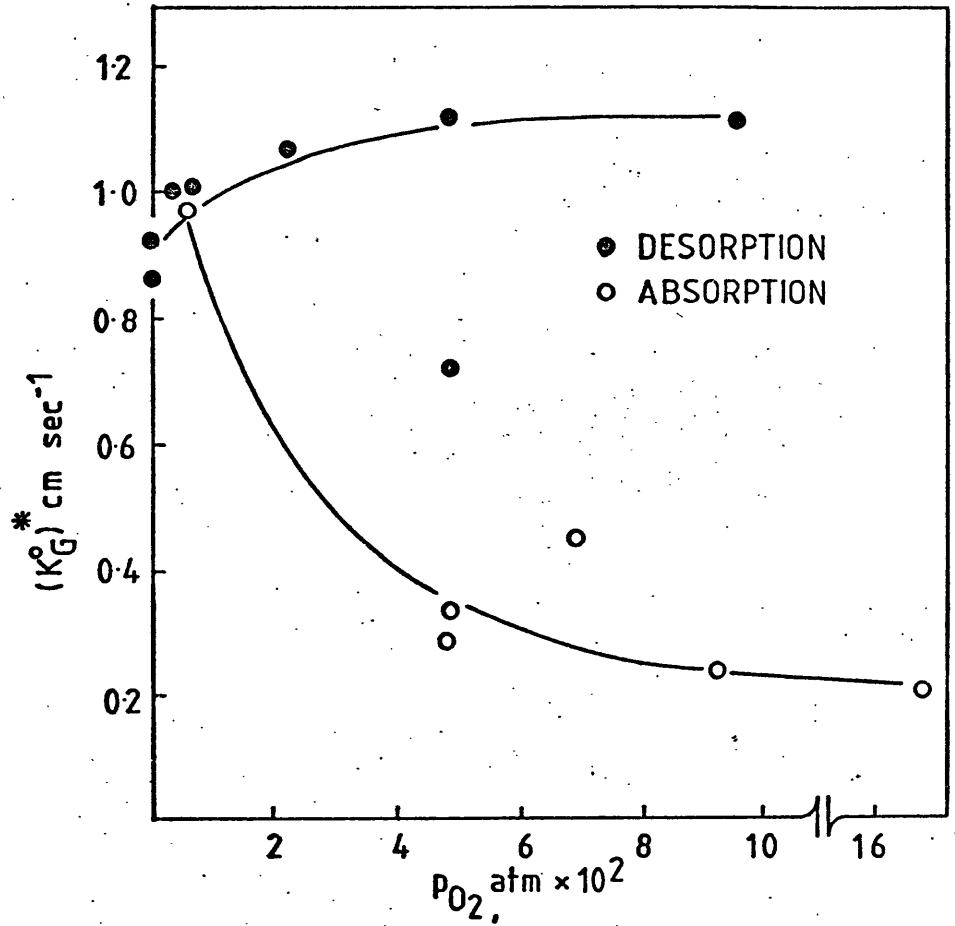


FIG. 3:14 CALCULATED GAS PHASE MASS
TRANSFER COEFFICIENTS, AT
MEDIUM MOMENTUM (13000 DYNES)

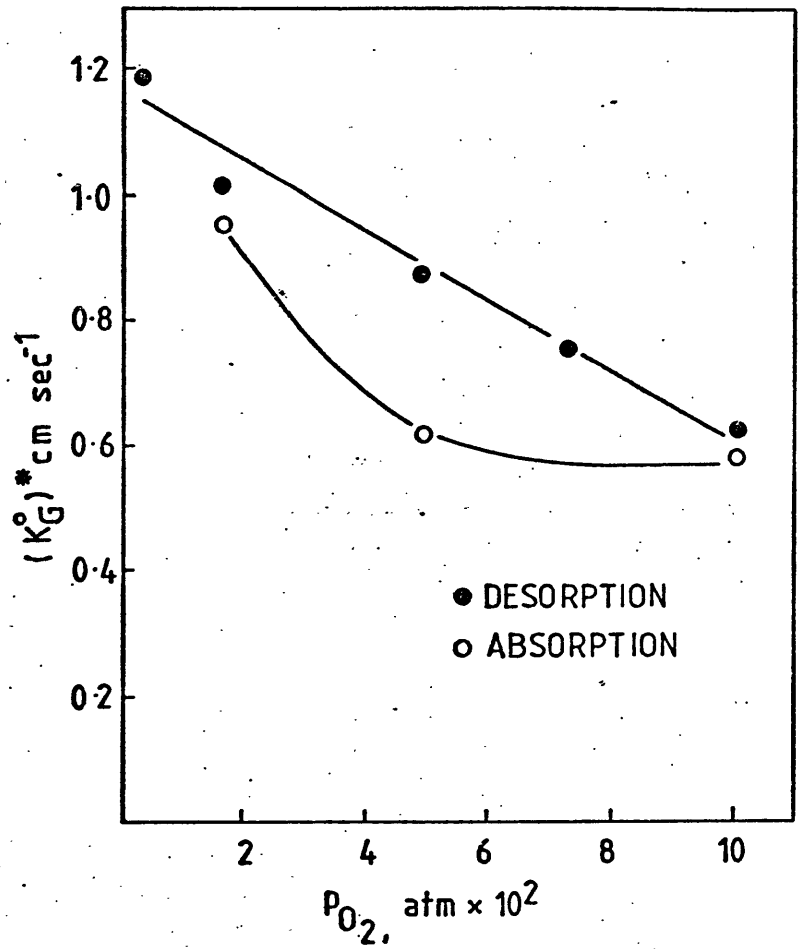


FIG. 3.15 CALCULATED GAS PHASE MASS
TRANSFER COEFFICIENTS, AT
HIGH MOMENTUM (19000 DYNES)

Considering the assumptions built into the analysis, the inability of the simple mixed control mass transfer model to account for the experimental results reflects two broad possibilities:

1. The process is not controlled simply by mass transfer, but is influenced by the kinetics of the interfacial chemical reaction. However, a simple second order reaction model, as proposed by Mori et al (40), could not explain the results, since their treatment is mathematically similar to the mixed control mass transfer model, see Section 2.4.4 . To account for the experimental results, the interfacial reaction would need to have a different mechanism in the forward and backward directions.
2. The overall kinetics are nevertheless mass transport controlled, but the assumption of k_L being independent of the direction of transfer may be invalid. This is a more plausible explanation, in view of the results of Masson and Whiteway (30), see Section 2.4.1 (b). The question of the development of density or surface tension driven convection in the liquid, acting in conjunction with the forced convection associated with jet impingement, would therefore deserve consideration.

3.2 Thermogravimetric Studies at Atmospheric Pressure

The mass transfer results obtained in the dilute gas jetting experiments reflect the underlying hydrodynamic features of Jet/liquid interactions on the one hand, and the specific properties of the O_2/Ag system on the other. To interpret the results satisfactorily the two aspects would need to be disentangled, and this poses a central difficulty. The effect of hydrodynamic behaviour on mass transfer in jet/liquid systems is poorly understood, certainly at elevated temperature. The local values of both k_L and k_G are sensitive to radial position, and the relative importance of the depression and the outer regions is not known quantitatively. Neither k_L nor k_G can be predicted. Apart from problems relating to limitations in present theory and experimental data, the large-scale jetting apparatus was not well suited for carrying out critical tests to elucidate the reaction mechanism.

Small-scale, non-jetting, thermogravimetric investigations of oxygen transfer between gases and molten silver were therefore initiated to complement the jetting experiments. The gas/liquid contacting configuration was well defined, and the small-scale nature of the work provided considerable flexibility.

Thermogravimetric studies involved the suspension of a crucible containing a quiescent pool of liquid silver in controlled gas streams of variable oxygen composition. The weight change associated with the oxygen absorption or desorption reaction was monitored continuously using a load cell device. The gas/liquid contacting configuration is shown in Figure 3.16. There was no forced convective stirring of the liquid by the gas.

- A MOLTEN SILVER
- B CRUCIBLE
- C SUPPORT WIRE TO LOAD CELL
- D FURNACE TUBE

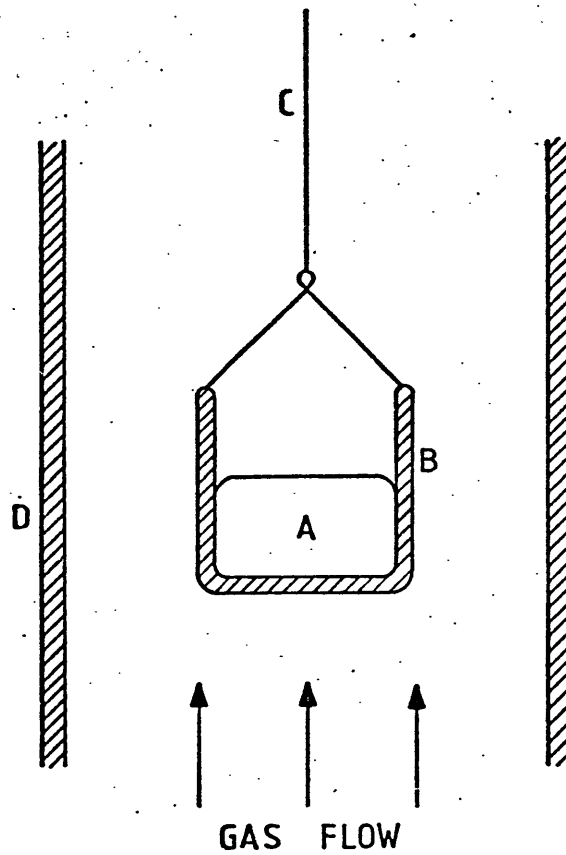


FIG. 3-16 GAS / LIQUID CONTACTING
CONFIGURATION IN THERMOGRAVIM-
ETRIC EXPERIMENTS

3.2.1 Apparatus

Apparatus incorporating a vertical tube furnace which could be raised around a sample suspended from a load cell had been constructed by Campbell (12) and Matyas(11) and is shown in Figure 3.17 . The 5 cm diameter alumina furnace tube was heated over its 45 cm length using 'Kanthal A1' wire of 21 ohms total resistance. A fast-cycling 'Eurotherm' controller controlled the furnace temperature to $\pm 0.5^{\circ}\text{C}$. Gas was introduced at the bottom end of the furnace, and passed through a bed of alumina chips to bring it to the reaction temperature before flowing past the suspended sample. Oxygen and oxygen-free nitrogen were metered by calibrated 'MeTaRaTe' and 'Rotameter' flowmeters.

The load cell, supplied by Statham Instruments Ltd., had a range of 60 gm but was equipped with a lever arm and counter-balance to increase the sensitivity by a factor of 10. The load cell calibration was determined to be 0.01175 mV per milligram (56). All electrical contacts to the load cell were made via gas tight seals in the load cell chamber base plate. Campbell (12) gives additional design details of the furnace and load cell assemblies.

Silver samples weighed about 19 gms and were held in flat-bottomed alumina crucibles with 1.9 cm internal diameter and approximately 2 cm height. Platinum (13% rhodium) wire was used to suspend the crucibles.

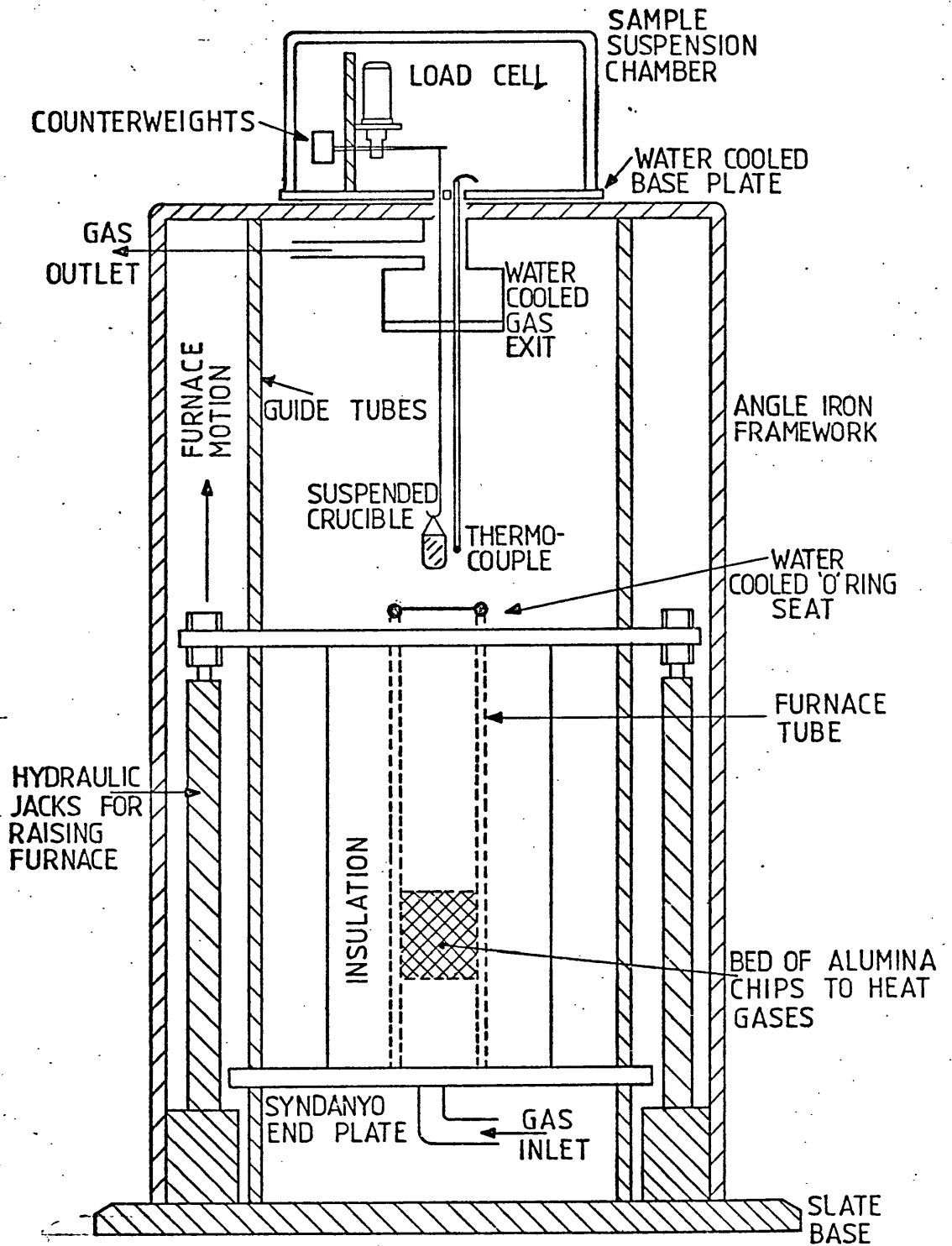


FIG. 3-17 APPARATUS FOR THERMOGRAVIMETRIC EXPERIMENTS AT ATMOSPHERIC PRESSURE

3.2.2 Procedure for Mass Transfer Runs

Having suspended the crucible containing the silver sample and adjusted the load cell counterbalance, the furnace was raised and sealed, and the power switched on. Melting of the silver was achieved within an hour and the temperature was subsequently controlled at 1000°C . Nitrogen was passed through the furnace during heating.

Absorption and subsequent desorption experiments were carried out by altering the gas composition to a predetermined level, through adjustment of the oxygen and nitrogen flow rates. Total gas flow rates were typically 2 litres/min at N.T.P. The millivolt output from the load cell was continuously recorded during the experiments on a Servoscribe chart recorder.

3.2.3 Results of Mass Transfer Experiments

The inherent accuracy of the technique and the validity of the load cell calibration were established during the commissioning period by examining the mass balances for oxygen absorption and subsequent desorption runs, see Appendix C. The difference in weight between oxygen-free silver and silver equilibrated with oxygen at 1 atmosphere and at 1000°C agreed with the value predicted by Sievert's law, see Equation 2.1, within 0.5%. Loss in weight in the subsequent desorption run with nitrogen gas was found to equal exactly the gain in weight by oxygen absorption. Mass balances were checked regularly in the subsequent experimental campaign.

Initial mass transfer experiments were carried out to prove whether or not there had been any contamination of the silver in the jetting campaign. A sample of silver which had been used in the jetting campaign was compared to silver fresh from the supplier (Johnson-Mathey) in its kinetic behaviour for both absorption with pure oxygen and desorption with nitrogen. The results are shown in Figure 3.18, plotted according to Equation 2.9 . These results establish clearly that the mass transfer data from the jetting campaign do not reflect any surface contamination effects.

The influence of oxygen partial pressure on both absorption and desorption kinetics was then studied systematically, using oxygen/nitrogen gas mixtures at 1 atmosphere total pressure. The raw data are presented in Appendix C. A value of k_{ov} for each run was calculated from the average slope of these plots. For desorption runs, where the plots display distinct non-linearity as equilibrium is approached towards the latter parts of each experiment, the slope for the first 80% of the reaction was taken as the basis for calculation of a value of k_{ov} . The results are shown in Table 3.6 and Figure 3.19 .

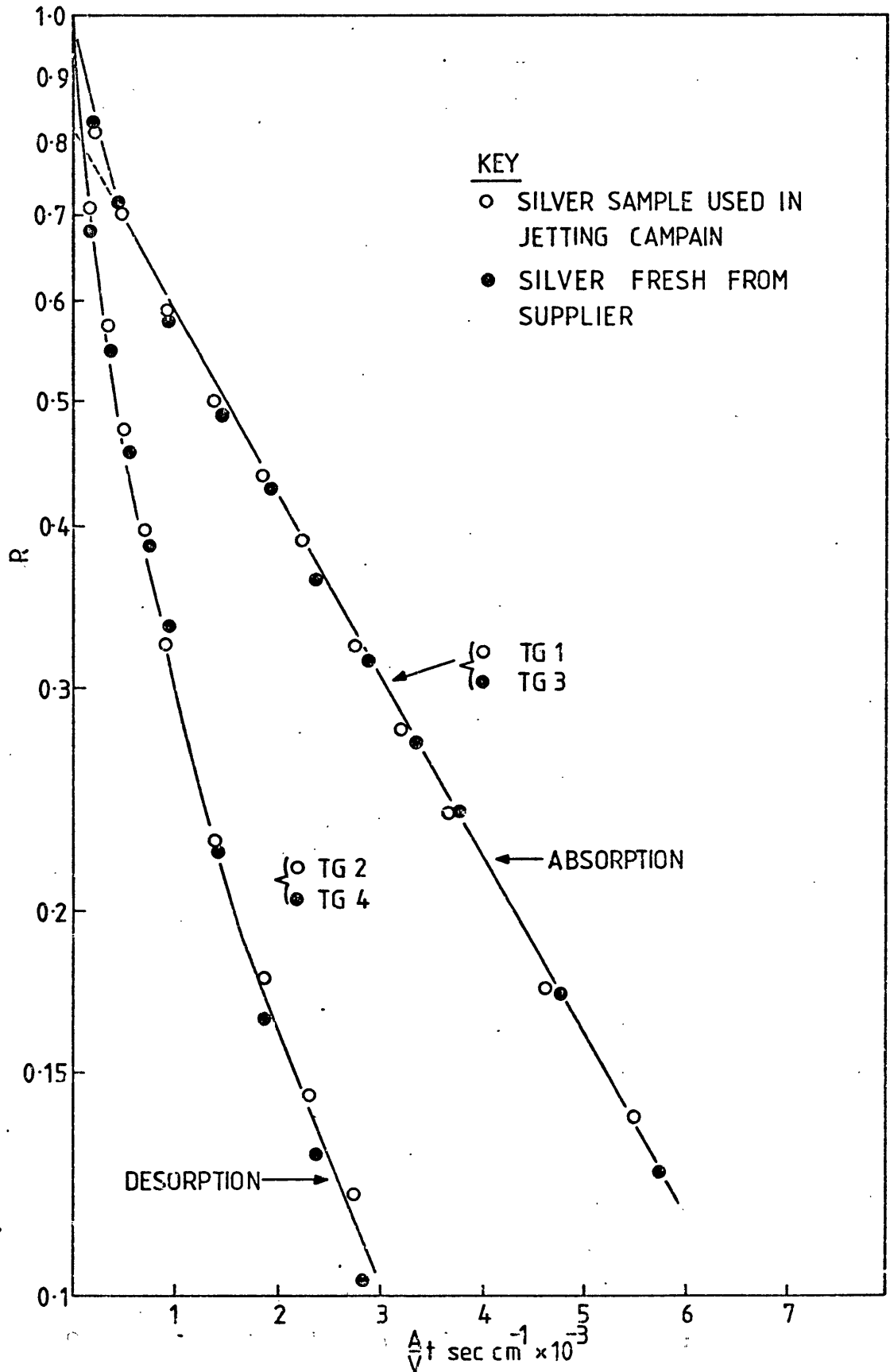


FIG. 3.18 MASS TRANSFER DATA FROM PRELIMINARY THERMOGRAVIMETRIC EXPERIMENTS

TABLE 3.6

Mass Transfer Data from Thermogravimetric
Experiments at Atmospheric Pressure

Run	Direction of Transfer	P _{O2} (atm x 10 ²)	k _{ov} (cm/sec x 10 ⁴)
TG1	Absorption	100	3.3
TG2	Desorption	0	9.9
TG3	Absorption	100	3.3
TG4	Desorption	0	9.2
TG5	Absorption	100	3.5
TG6	"	"	3.4
TG7	"	"	3.5
TG8	"	50	3.2
TG9	"	20.3	4.1
TG10	"	"	3.8
TG11	"	10	4.1
TG12	"	1	3.6
TG13	Desorption	50	24.5
TG14	"	20.3	21.3
TG15	"	"	21.5
TG16	"	10	18.4
TG17	"	1	13.8
TG18	"	0	11.5
TG19	"	"	11.0

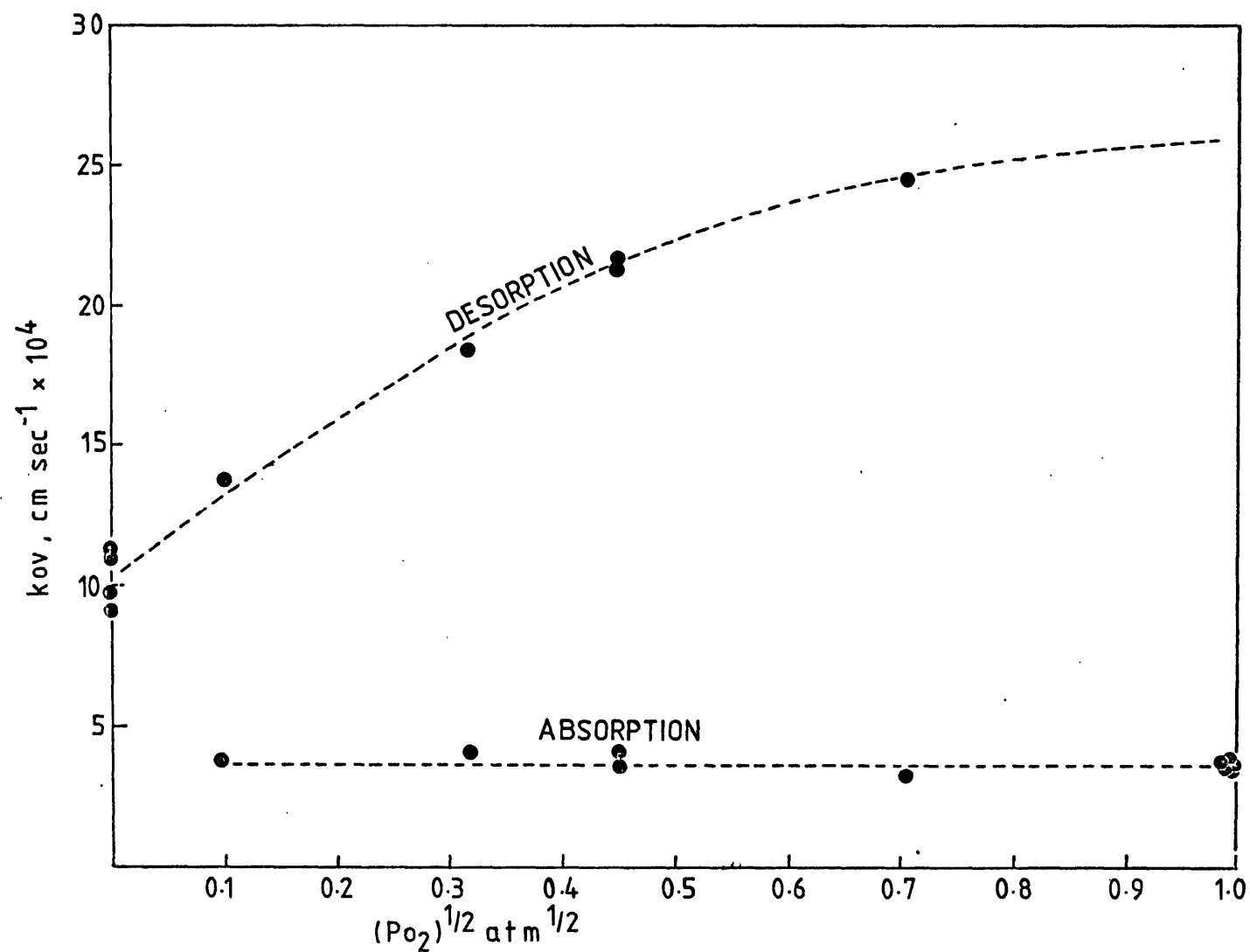


FIG. 3.19 SUMMARY OF OVERALL TRANSFER DATA FROM THERMOGAVIMETRIC EXPERIMENTS AT ATMOSPHERIC PRESSURE

3.3 Thermogravimetric Studies at Reduced Total Pressure (Effusion)

It was decided to carry out experiments under conditions such that the gas phase resistance was insignificant, since this should provide critical evidence regarding the mechanism of kinetic control. The diffusional resistance could most easily be removed by operating with pure oxygen gas streams. The driving force for reaction was controlled by adjusting the total gas pressure in the furnace chamber, rather than by varying the gas composition. Desorption accomplished by reducing the total pressure is known as effusion.

3.3.1 Apparatus

The apparatus used for the previous thermogravimetric studies, see Section 3.2.1, was not designed for operation at other than atmospheric pressure. A new piece of apparatus was therefore constructed for the purpose of carrying out experiments at reduced pressure.

The gas/liquid contacting configuration was the same as before, see Figure 3.16. The load cell was re-housed in the new equipment and the same type of alumina crucibles were employed to hold the silver samples.

The apparatus is shown in Figure 3.20. The reaction chamber consisted of a 5 cm diameter silica tube, 50 cm in length. A simple tube furnace wound with 'Nichrome' resistance wire and insulated with asbestos chord and 'Kaowool' was located around the silica reaction tube and provided the heating. This flexible arrangement would have allowed easy

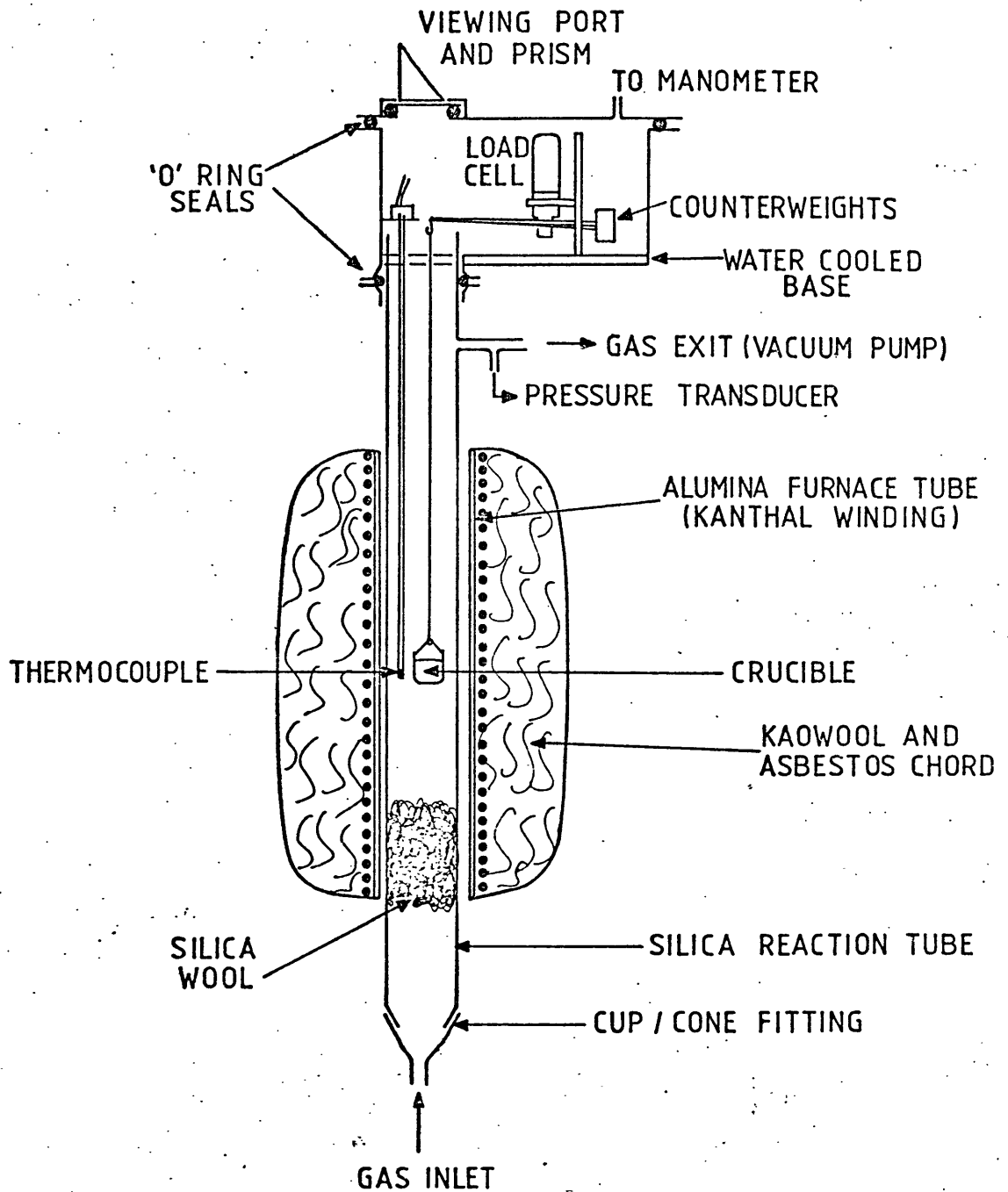


FIG. 3.20 APPARATUS FOR THERMOGRAVIMETRIC EXPERIMENTS AT REDUCED TOTAL PRESSURE

removal of the furnace for rewiring or in fact for replacement by an alternative heating source such as an induction coil.

A Pt/Pt (13% Rh) thermocouple was placed inside the silica tube at the level of the crucible and the furnace temperature was maintained constant at 1000⁰ C by a 'Eurotherm' controller. The gas inlet was in the bottom of the silica tube, which was sealed with a cup/cone fitting. The gas was passed through a layer of silica wool to allow it to reach the furnace temperature before flowing past the suspended crucible. Oxygen from cylinders was metered by calibrated 'MeTaRaTe' and 'Rotameter' flow-meters, and the flow rate was controlled by a needle valve.

The load cell was housed in a water cooled mild steel chamber which was sealed to the top of the silica reaction tube by an 'O' ring connection. A viewing port was incorporated into the top of the load cell chamber so that the free surface of the liquid silver could be observed.

Specpure silver was used to assure the cleanest possible surface. The alumina crucibles were thoroughly cleaned in aqua regia before use.

A mercury manometer was connected to the system via the load cell chamber, and a 'Bell and Howell' pressure transducer was fitted to the gas exit line. The manometer was used to calibrate the transducer. The gas exit line was attached to an 'Edwards' vacuum pump. The pressure in the system was controlled both by a needle valve on the gas exit line and also by adjusting the amount of air ballast to the vacuum pump. The load cell and pressure transducer millivolt outputs were simultaneously recorded on a 'Servoscribe' twin-pen chart recorder.

3.3.2 Procedures for Mass Transfer Runs

The crucible containing the silver was lowered into the silica reaction tube through the lid of the load-cell chamber and suspended from the lever arm of the load cell. The lid was then replaced and sealed with an 'O' ring.

Oxygen was passed through the system at atmospheric pressure and the silver was allowed to reach equilibrium with the gas at 1000°C. Desorption was made to occur by reducing the total pressure.

Nucleation of oxygen gas bubbles (i.e. boiling) occurred at very small levels of supersaturation, which made it impossible to carry out runs just below 1.0 atmosphere total pressure. However, after initial nucleation had occurred and the pressure had reached a level of about 0.3 - 0.5 atmosphere, considerable further reduction in total pressure was possible without additional boiling. It was therefore possible to carry out controlled effusion experiments in this pressure range.

Experiments were conducted for sufficient time (several hours) for the liquid silver to come to equilibrium with the oxygen pressure in the reaction chamber, as monitored by the pressure transducer. This allowed the load cell emf readings to be related to an absolute value of oxygen concentration in the liquid silver at the end of each run. It was more satisfactory to work back from the end of a run, due to the problems of obtaining meaningful load cell readings during the initial bubble nucleation period.

3.3.3 Results of Mass Transfer Experiments

Commissioning of the rig included an absorption experiment with pure oxygen (TG20) and a desorption run at $p_{O_2} = 0.34$ atmosphere (TG21), both at 1.0 atmosphere total pressure. The results of these experiments were reasonably consistent with the earlier thermogravimetric studies, see Section 3.2 .

Four desorption experiments at reduced total pressure (effusion) were carried out. The mass transfer data are plotted in Figure C3 in Appendix C according to Equation 2.9 .

Values of k_{OV} were calculated for each effusion run from the average slope of the near-linear, initial 70-80% of reaction, section of the plots, and these results are listed in Table 3.7 . In Figure 3.21 the effusion data are shown in a manner which allows direct comparison with the results of the mass transfer experiments at atmospheric pressure.

TABLE 3.7

Mass Transfer Data from Thermogravimetric
Experiments at Variable Total Pressure

Run	Direction of Transfer	P Total (atm)	P _{O₂} (atm)	k _{ov} (cm/sec x 10 ⁴)
TG20	Absorption	1.0	1.0	3.7
TG21	Desorption	1.0	0.34	29.0
TG22	Desorption	0.089	0.089	3.8
TG23	(Effusion)	0.16	0.16	4.1
TG24	"	0.116	0.116	3.0
TG25	"	0.137	0.137	3.7

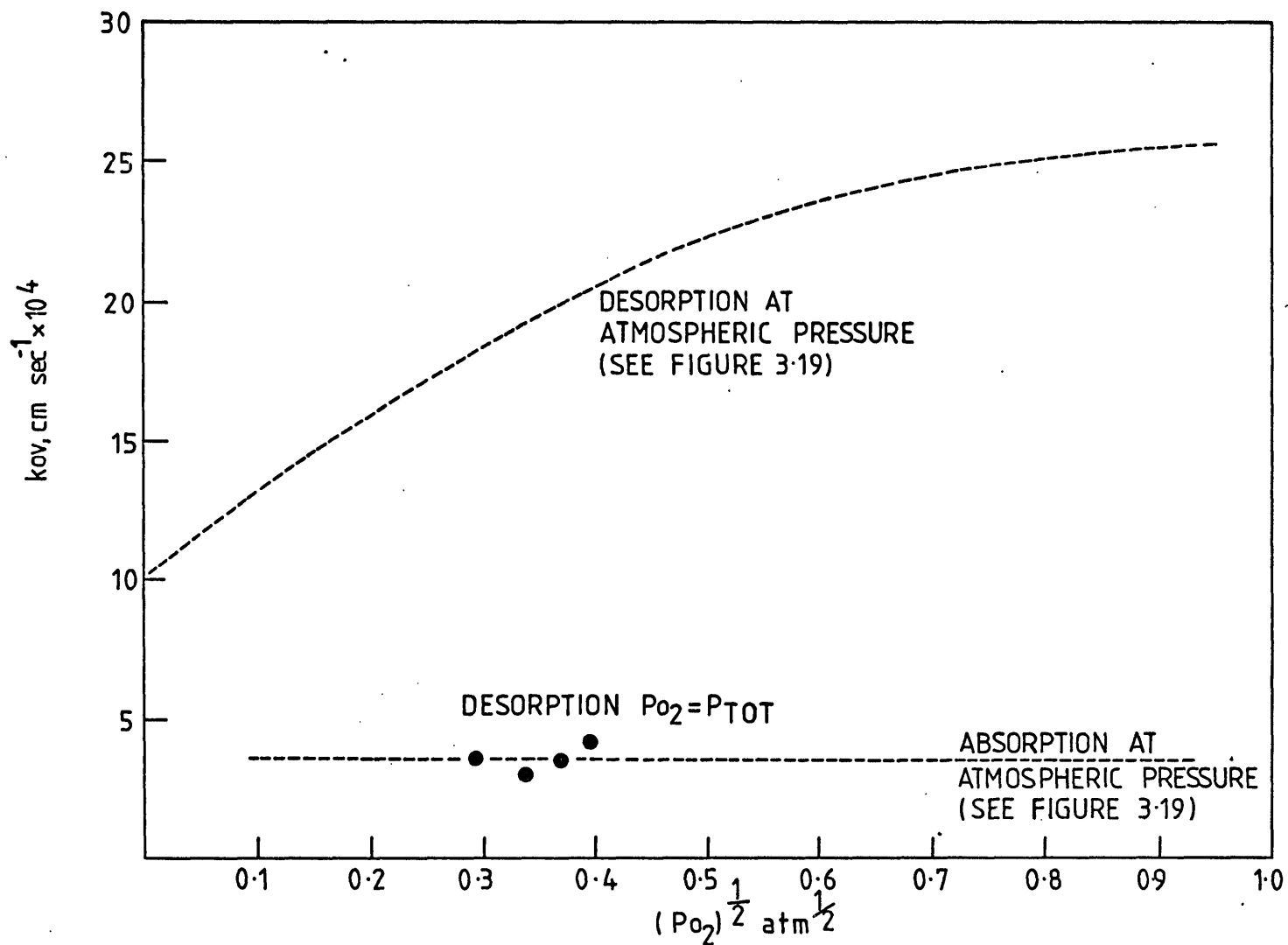


FIG. 3-21 MASS TRANSFER DATA FROM DESORPTION EXPERIMENTS AT
REDUCED TOTAL PRESSURE

CHAPTER 4

INTERPRETATION OF RESULTS AND DISCUSSION

4.1 Thermogravimetric Studies

4.1.1 Analysis of the Mass Transfer Data

One can predict the value of the liquid phase mass transfer coefficient for the limiting case of transport by molecular diffusion. This provides a useful frame of reference, since there was no forced convection applied to the liquid silver for the gas/liquid contacting configuration adopted in the thermogravimetric studies.

From Equation 2.36, the linear section of a plot of $\ln R$ vs $A/\sqrt{t}$ from a diffusion controlled experiment would have a slope of $(D_{AB} \pi^2 / 4l)$, and would have an extrapolated intercept at zero time of $R = 0.81$. The linear section could be expected for values of $A/\sqrt{t} > 350$. It follows from the definition of the mass transfer coefficient, Equation 2.7, that for diffusion control

$$k_L = \frac{D_{AB} \pi^2}{4l} \quad (4.1)$$

The depth of liquid silver was typically $l = 0.65$ cm, and the literature gives a value of $D_{O/Ag} = 9.7 \times 10^{-5}$ cm²/sec, see Section 2.4.1 (a). Thus for the particular geometry of the liquid pool in the thermogravimetric work (both rigs) one can predict that $k_L = 3.7 \times 10^{-4}$ cm/sec. for a diffusional transport mechanism.

(a) Absorption at Atmospheric Pressure

Throughout the gas composition range studied, namely

$p_{O_2} = 0.01 - 1.0$ atm, the mass transfer data from absorption experiments as presented in Figure 3.19, Table 3.6 and Figure C1, can be summarized by a value of $k_{ov} = (3.6 \pm 0.3 \text{ RMS}) \times 10^{-4}$ cm/sec. The plots of $\ln R$ vs $A/\sqrt{t}$ become linear for values of $A/\sqrt{t} > 350$ and extrapolation of the linear sections to zero time gives an intercept of $R_{t=0} = 0.81$.

One can conclude with confidence that the oxygen absorption experiments at atmospheric pressure were controlled kinetically by molecular diffusion in the quiescent liquid silver.

(b) Desorption at Atmospheric Pressure

The most striking feature of the mass transfer results from desorption experiments at atmospheric pressure with gas compositions in the range $p_{O_2} = 0 - 0.5$ atm is that values of k_{ov} are 3 - 7 times greater than for absorption experiments, see Figure 3.19. One can immediately conclude that the liquid phase mass transfer step is no longer limited to molecular diffusion. The increased value of k_L can be estimated by extrapolating the curve of k_{ov} vs p_{O_2} , see Figure 3.19, to the case of $p_{O_2} = 1.0$ atmosphere. This represents a situation of no gas phase resistance. On this basis one can assume that in the desorption experiments with O_2/N_2 gas mixtures the value of $k_L = 26 \times 10^{-4}$ cm/sec.

The second feature of the desorption results is that k_{ov} decreases as the gas becomes more dilute with respect to oxygen. This suggests the increasing influence of a second kinetic resistance, which from the discussion in Section 3.1.5 (b) could be expected to be the gas phase transport resistance. The mixed control model discussed above can be used to test this hypothesis.

The relationship between λ , η and ϕ , Equation 2.15, can be employed to predict the plot of k_{ov} vs p_{O_2} for a value of $k_L = 26 \times 10^{-4}$ cm/sec. The only unknown is k_G , and an iterative, curve-fitting procedure was adopted. Equation 2.21 was incorporated into the exercise to isolate the effect of bulk flow.

Figure 4.1 summarizes the results of these calculations, which show that the experimental data can be interpreted with the mixed control model if $k_L = 26 \times 10^{-4}$ cm/sec and $k_G^O = 0.7$ cm/sec.

The Reynolds number for the gas flow past the crucible can be estimated to be about 1.4, which indicates that the oxygen transfer process in the gas would be essentially by diffusion. The distance over which diffusion must take place between the crucible lip and the free surface of the silver was typically $\delta = 1.35$ cm. On the basis of the concepts of the 'film' theory

(24)

$$k_G^O = \frac{D_{AB}}{\delta} \quad (4.2)$$

and one would predict a value of $k_G^O = 1.2$ cm/sec. However, the actual value of k_G^O would in practice be less than this figure, due to the diffusional resistance within the boundary layer established by flow past the crucible. Thus a value of $k_G^O = 0.7$ cm/sec is, in absolute terms, an entirely reasonable figure.

One can conclude with confidence that the desorption experiments at atmospheric pressure are controlled kinetically by a simple combination of liquid phase and gas phase mass transport.

The mixed control model can be used to show that in absorption, where k_L is much lower than in desorption, the

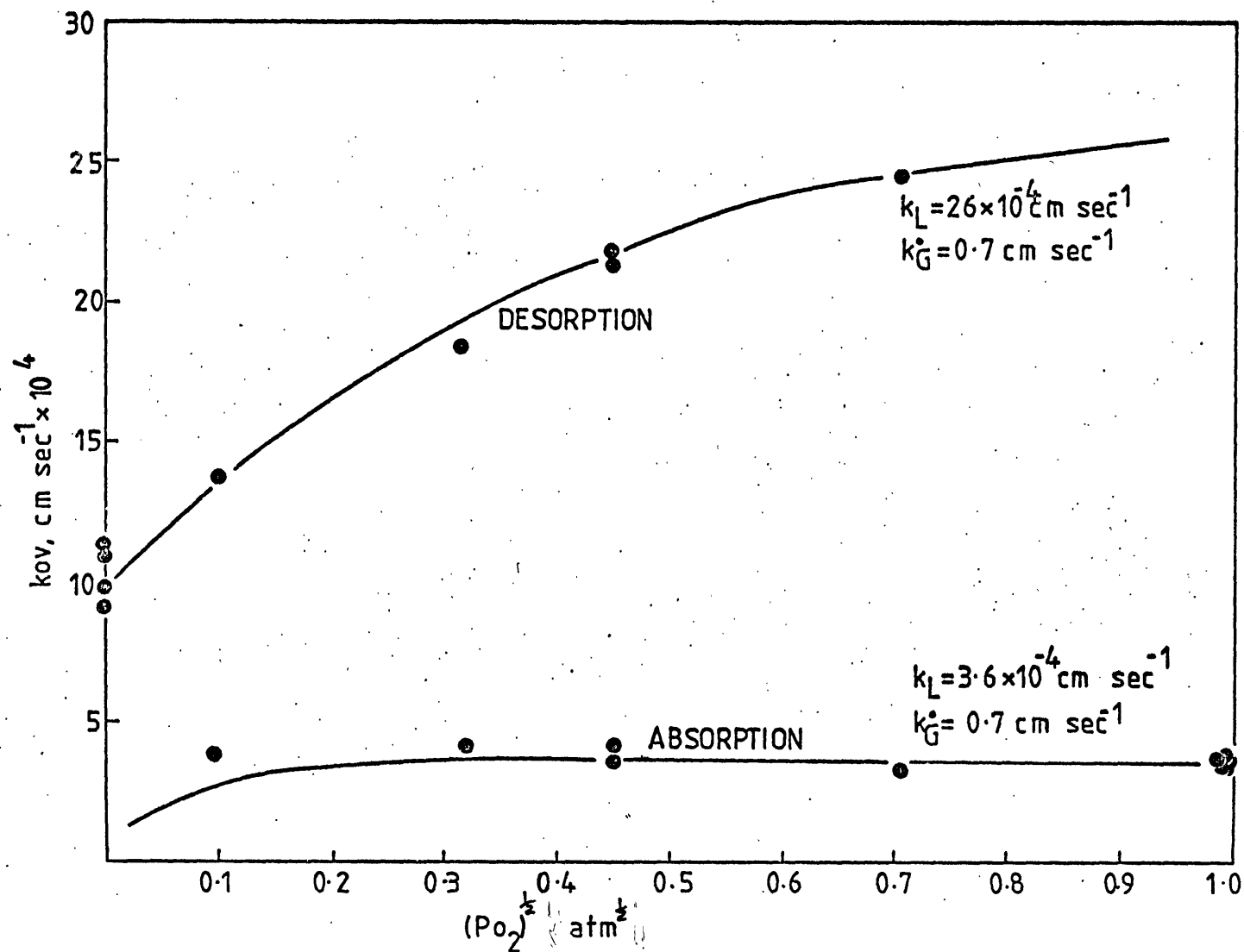


FIG. 4.1 INTERPRETATION OF THERMOGRAVIMETRIC DATA - MASS TRANSFER CONTROL MODEL

influence of the gas phase resistance only begins to be significant at very low oxygen composition, as shown in Figure 4.1 . This explains why, for the gas compositions studied, k_{OV} was essentially independent of p_{O_2} in absorption.

(c) Effusion

The results of the desorption mass transfer experiments at reduced total pressure (effusion) lead to a value of $k_{OV} = (3.7 \pm 0.4 \text{ RMS}) \times 10^{-4} \text{ cm/sec}$, see Figure 3.21, which is consistent with liquid phase control by a molecular diffusion mechanism. Thus, by removing the gas phase resistance, the mechanism of enhanced liquid phase transport in desorption disappears under otherwise similar conditions. Effusion and absorption are therefore both diffusion controlled.

4.1.2 Deduced Mechanism of Reaction

The analysis of the thermogravimetric data allows the regimes of kinetic control to be clearly, and confidently, identified. To briefly summarize :

(i) Absorption with oxygen/nitrogen mixtures ($p_{O_2} = 0.01 - 1.0 \text{ atm}$, $P_{TOTAL} = 1.0 \text{ atm}$) is controlled by molecular diffusion of oxygen in the liquid silver, with $D_{O/Ag} = 9.7 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $k_L = 3.7 \times 10^{-4} \text{ cm/sec}$.

(ii) Desorption with a pure oxygen gas phase at reduced pressure (effusion, $p_{O_2} = P_{TOTAL}$) is similarly controlled by

liquid phase molecular diffusion.

(iii) Desorption at atmospheric pressure with oxygen/nitrogen mixtures ($p_{O_2} = 0 - 0.5$ atm, $P_{TOT} = 1.0$ atm) is controlled by a combination of gas phase and liquid phase mass transfer, with $k_G^O = 0.7$ cm/sec and $k_L = 26 \times 10^{-4}$ cm/sec.

A value of $k_L = 26 \times 10^{-4}$ cm/sec in desorption with mixed gases reflects the existence of convection in the liquid silver. Since forced convection was absent the convection must have been generated spontaneously, by surface tension or bouyancy effects. The principal implication of the results is that the mechanism by which liquid phase transport is enhanced seems to depend on the existence of a gas phase resistance, and the attendant concentration gradients in the gas phase.

Absorption or desorption incorporates simultaneous mass and heat transfer, because of the heat of solution effect. Oxygen solution is exothermic, with $\Delta H = 4,000$ cal/mole (65). Temperature and oxygen concentration both influence the density and the surface tension of liquid silver. It follows from the discussion of spontaneous convection in Section 2.5 that one or a combination of the following four mechanisms could have been responsible for the enhanced desorption rates :

(A) Bouyancy instability associated with the transfer of the heat of solution to the interface in desorption. (Heat generated at the interface during absorption would stabilize the liquid.) For a heat flux typical of the desorption runs, Kraus' theory of natural convection (83), see Equation 2.45, predicts $k_L = 45 \times 10^{-4}$ cm/sec. Thus both the existence and the

intensity of convection in desorption could be explained in terms of temperature-linked bouyancy instability.

(B) Bouyancy instability associated with mass transfer. If the density of liquid silver decreases with oxygen solution (this is to be expected, but no experimental data has been published), then desorption would be the unstable direction of transfer, whereas absorption would be the stable direction. Masson and Whiteway(30) proposed this mechanism of natural convection to explain results which are similar to those presented in this study.

(C) Marangoni instability associated with the transfer of the heat of solution. For instability during desorption, this mechanism requires that $\partial\gamma/\partial T < 0$; see the discussion of Pearson's model in Section 2.5.3 . Although $\partial\gamma/\partial T$ is negative for pure liquid silver, Figure 2.9 shows that the situation is reversed in the presence of oxygen at partial pressures greater than about 0.01 torr.

Thus, for the levels of interfacial oxygen concentration in the desorption experiments, even with nitrogen or argon gas, this mechanism would become inoperative. In any case, the mass transfer effects would tend to be relatively more dominant.

(D) Marangoni instability associated with mass transfer. The oxygen/silver system is one in which $\partial\gamma/\partial C < 0$, see Figure 2.9, and therefore the Sternling-Scriven criterion, see Section 2.5.1, predicts instability for gas desorption. Instability develops for transfer out of the phase of lower solute diffusivity and higher

kinematic viscosity, see Table 2.3 . The oxygen diffusivity in liquid silver is some two orders of magnitude lower than in nitrogen gas. However, the kinematic viscosity of liquid silver at 1000°C , $\nu_{\text{Ag}} = 4.01 \times 10^{-3} \text{ cm}^2/\text{sec}$ (61, 62), is also less than the kinematic viscosity of O_2/N_2 gas mixtures at 1000°C , e.g. for air $\nu = 1.75 \text{ cm}^2/\text{sec}$ (45). Under these circumstances the diffusivity and viscosity effects tend to work in opposite ways, and simple intuitive predictions cannot be made. The detailed solution of Sternling and Scriven's model (50, 68), see Section 2.5.1, predicts 'diffusion - controlled' convective instability during desorption, and 'flow-controlled' oscillatory instability during absorption. The former can develop into ordered cellular convection capable of surface renewal, with a corresponding increase in k_L (as experimentally observed).

One or any combination of the three, equally plausible mechanisms, A, B and D, could account for the convection in the desorption experiments at atmospheric pressure. The need arises for critical evidence, and this is provided by the effusion results. The above mechanisms can be judged in light of the absence of convection during effusion.

The existence of temperature or concentration gradients between the bulk and the surface layers of the liquid silver depends on the rate of heat or mass transfer, and not on the presence or absence of a gas phase resistance. Mechanisms A and B would therefore be equally capable of promoting convection during effusion. The absence of convection in practice for effusion experiments thus rules out the possibility that either of these two natural convection mechanisms were responsible for the convection observed during desorption runs at atmospheric pressure.

The situation with mechanism D is fundamentally different. Surface tension driven Marangoni convection associated with mass transfer can only develop if concentration gradients can persist within the interface itself. If the gas phase is pure oxygen, then there exists no degree of freedom for concentration differences in the interface. The mechanism clearly depends on the existence of concentration gradients in both phases adjacent to the interface. (The additional degree of freedom could in principle be provided by the heat transfer process. As discussed in Section 2.5.3, close interaction of heat and mass transfer in binary systems can lead to instability when the sign of $\frac{\partial \gamma}{\partial T}$ is the same as the sign of the temperature gradient. For the oxygen/silver system this corresponds to instability in effusion and stability for absorption with pure oxygen gas. However, this mechanism was obviously not strong enough to generate significant convection during the effusion experiments.)

The thermogravimetric studies as a whole, both at atmospheric and reduced pressure, represent critical proof of the emergence of surface tension driven Marangoni convection in liquid silver during oxygen desorption with a mixed gas phase. The development of spontaneous convection stems fundamentally from two inherent properties of the oxygen/silver system; namely

$$\frac{\partial \gamma}{\partial c} < 0 \quad \text{and} \quad D_{O/Ag} < D_{O_2/N_2}.$$

4.2 Marangoni Phenomena in the Gas Jetting Experiments

The simple mixed control model could not explain the mass transfer data from jetting experiments with oxygen/nitrogen gas mixtures, see Section 3.1.5, since the kinetics displayed a marked dependence on the direction of transfer. Values of k_{ov} tended to be greater in desorption than in absorption, which are respectively the unstable and stable directions of transfer from a Marangoni convection point of view. The purpose of the section is to assess the likely influence of Marangoni convection on mass transfer in the presence of the forced convection induced by jet impingement. In view of the results of the thermogravimetric studies, only Marangoni convection associated with concentration gradients in the interface is considered.

The first assumption is that Marangoni phenomena were absent during experiments with pure oxygen gas jets, but that the liquid phase mass transfer process may have been influenced by surface tension forces in the experiments with dilute oxygen gas jets. The k_L values reported in Figure 3.7 therefore reflect forced convective transport without spontaneous convection.

Desorption is the naturally unstable direction of transfer, and in the presence of an existing flow field, see Section 2.5.2, the effect of Marangoni convection would be to increase k_L above the value found with pure oxygen jets under otherwise identical jetting conditions.

Absorption is the naturally stable direction of transfer, such that an initially quiescent liquid would remain quiescent. The influence of an existing flow field was discussed in Section 2.5.2. A distinction was drawn between situations in which the bulk phase turbulence is sufficiently intense to cause random, discontinuous eddy

renewal of the surface and situations in which the flow field is essentially ordered. Instabilities of the 'eruption' type could result from the discontinuous supply of solute to the interface, and even in absorption the effect would be to increase k_L . However, the available evidence on liquid phase fluid flow induced by gas jet impingement, see Sections 2.3.2 and 2.4.3, suggests that the surface flow field is ordered rather than random at the levels of jet momentum considered in this study. The effect of the Marangoni forces in absorption would therefore be to dampen the existing convection, with a corresponding reduction in k_L .

The intensity of the Marangoni convection would, in practice, depend on the distance from equilibrium and so on, but for the present purposes it is assumed simply that one constant value of k_L applies for all desorption runs at each momentum level, and another constant, but lower value of k_L applies for all absorption runs. These are respectively greater than and less than the value of k_L experimentally measured with pure oxygen gas at the particular momentum.

The final assumption is that k_G^O must be independent of the direction of transfer. It follows that the calculated values of k_G^O and $(k_G^O)^*$ presented in Section 3.1.5 (b) are overestimations in desorption and underestimations in absorption.

The mixed control mass transport model, Equations 2.15, 2.22 etc., can be used to predict the dependence of k_{ov} on p_{O_2} for different values of k_L and k_G^O , and such predictions can be compared with the experimental data shown in Figures 3.10, 3.11 and 3.12. The results of a trial-and-error data fitting exercise, which comply with the assumptions discussed above, are shown in Table 4.1 and Figures 4.2, 4.3 and 4.4. The computer programme mentioned in Appendix D was directly applicable to this trial-and-error exercise.

TABLE 4.1

Results of Data Fitting Exercise;

Dilute Gas Jetting Experiments.

$\dot{M}$ (dynes)	k_G^o (cm/sec)	DESORPTION k_L (cm/sec x 10^3)	ABSORPTION k_L (cm/sec x 10^3)	$\frac{k_L(DES)}{k_L(ABS)}$
6500	0.6	4.1	1.2	3.4
13000	0.7	8.0	2.1	3.8
19000	0.77	8.0	5.2	1.5

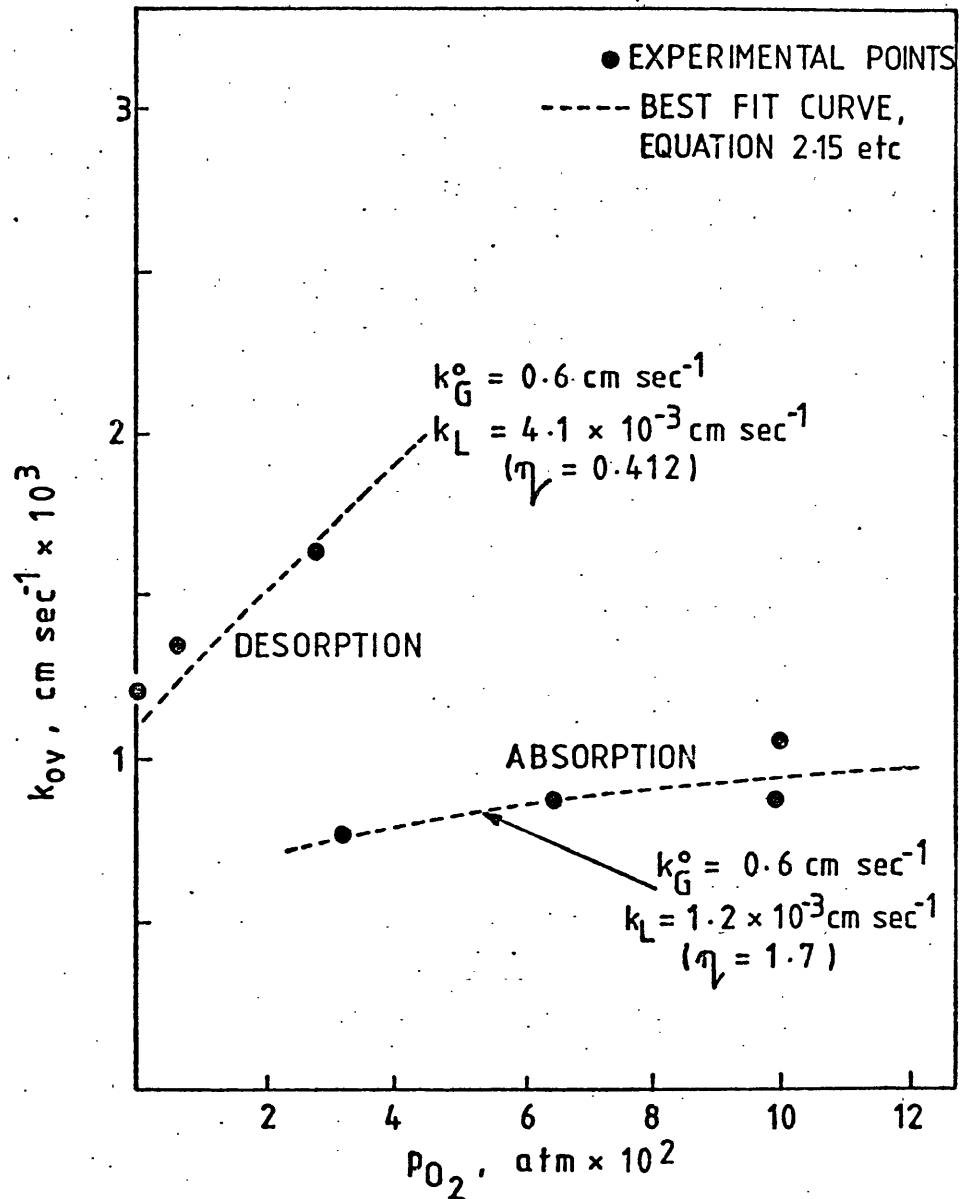


FIG. 4.2 DATA FITTING EXERCISE FOR GAS JETTING EXPERIMENTS AT A MOMENTUM OF 6,500 DYNES

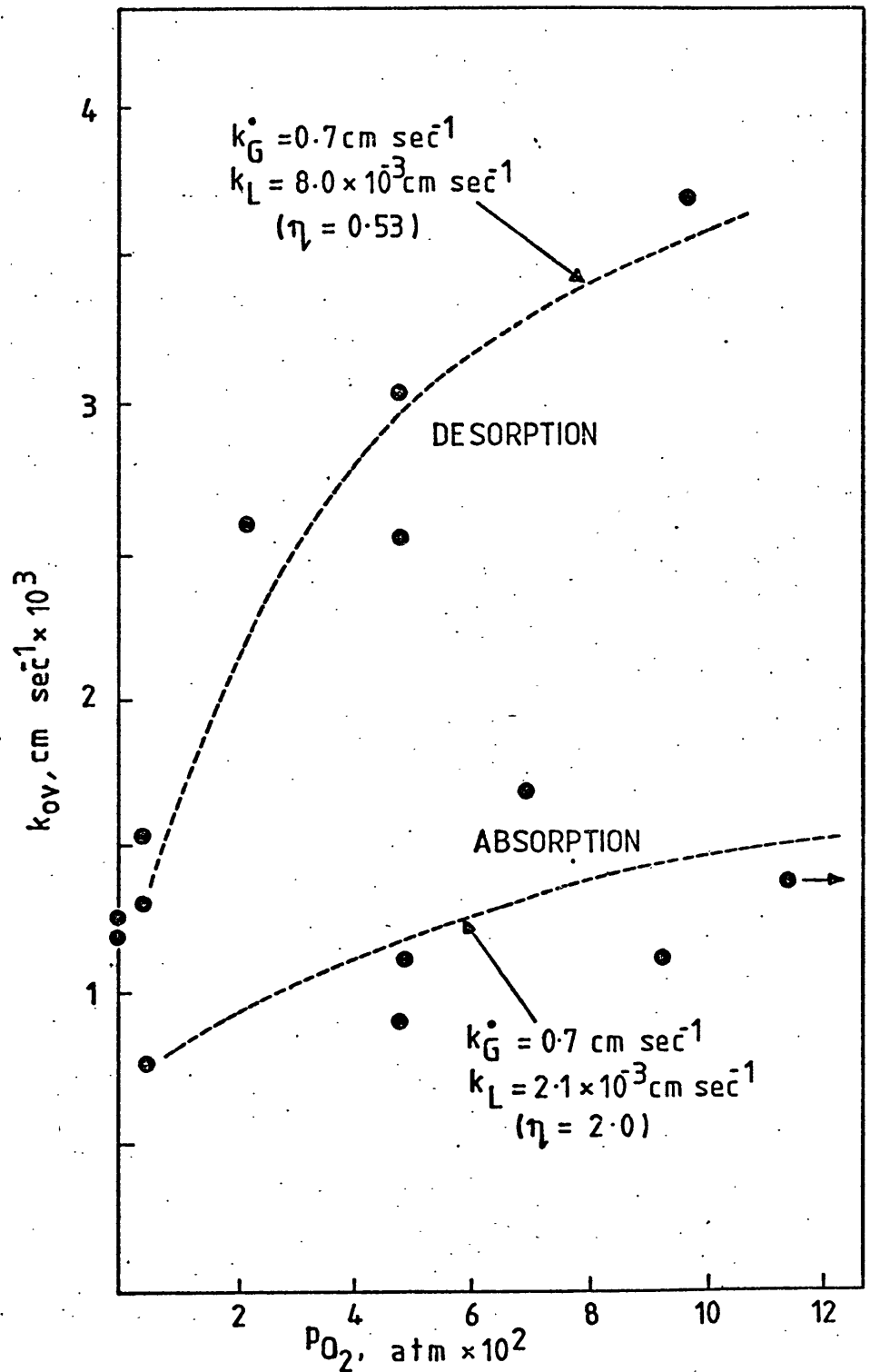


FIG. 4.3 DATA FITTING EXERCISE FOR GAS JETTING EXPERIMENTS AT A MOMENTUM OF 13,000 DYNES

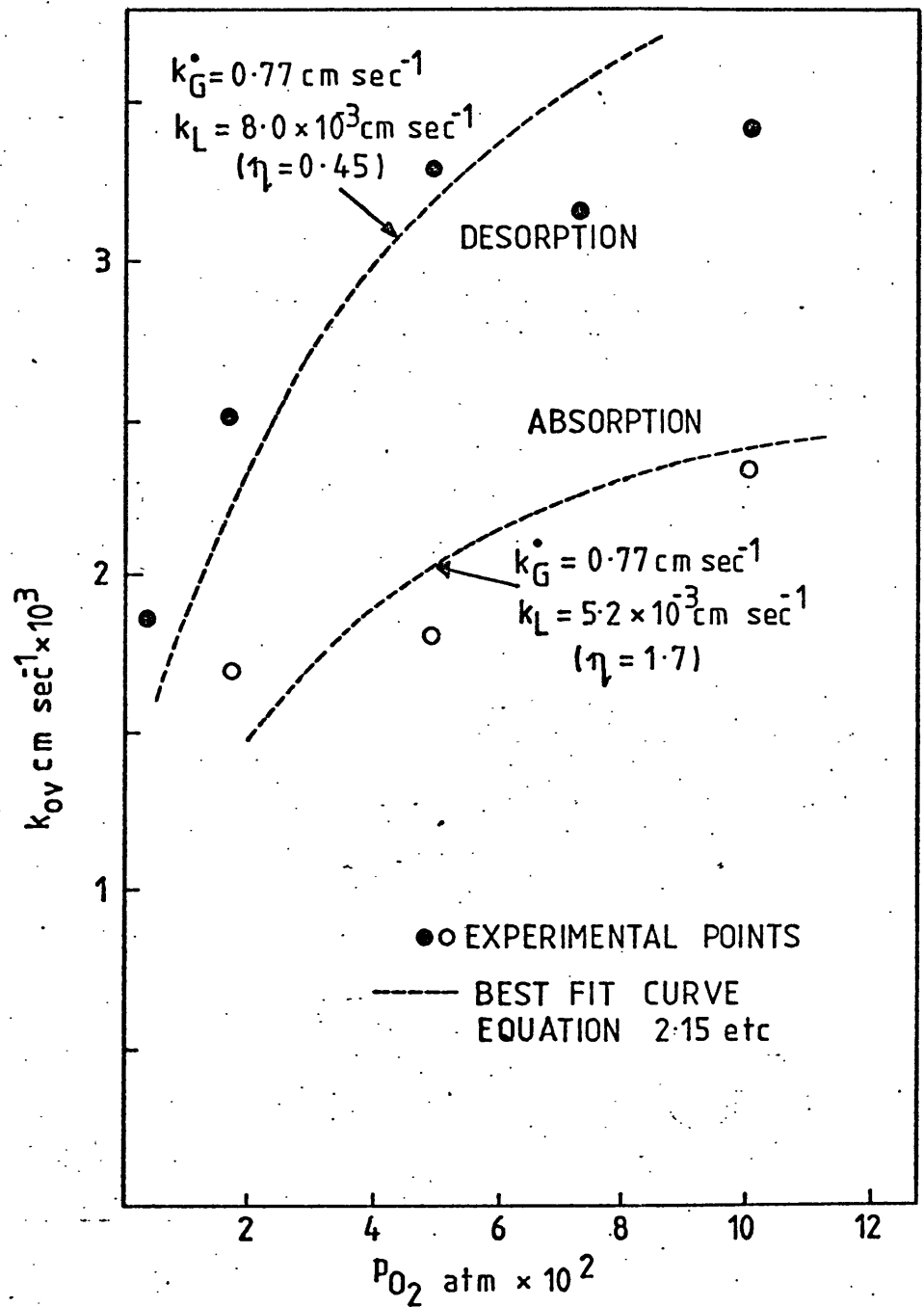


FIG.4.4 DATA FITTING EXERCISE FOR GAS JETTING EXPERIMENTS AT A MOMENTUM OF 19,000 DYNES

In view of the simplifications made to enable a quantitative solution to be reached, the agreement between the predicted curve and the experimental data is good. The numerical estimates of the ratio of k_L in desorption to that in absorption lie in the range 1.5 - 3.8, and these estimates would only marginally alter with sophistications in the mathematical treatment. The important point is that in absolute terms these results are wholly consistent with the likely influence of Marangoni convection. The only existing theory (95), predicts that for cellular convection Marangoni convection would increase the rate of mass transfer in the unstable direction of transfer by a factor of between 1.6 and 3.2. This has been supported by experimental evidence, see Section 2.5.1.

Although it was not possible with the jetting apparatus to carry out critical tests, such as the effusion experiments in the thermogravimetric investigations, it is reasonable to conclude with some confidence that Marangoni forces arising from oxygen concentration gradients within the interface were responsible for the enhanced rates of desorption relative to absorption in the experiments with dilute gas jets.

4.3 The Relevance of this Study to Previous Work

Masson and Whiteway(30), see Section 2.4.1 (b), recorded enhanced rates of oxygen desorption from initially quiescent liquid silver by argon. The liquid phase convection was attributed to density differences associated with oxygen concentration gradients within the bulk silver. No critical evidence for this mechanism was provided. The results of the present study suggest that the spontaneous convection observed by Masson and Whiteway was, in all probability, driven by surface tension gradients within the interface, that is a mass transfer linked Marangoni cellular convection mechanism.

Utine and Parlee(39), see Section 2.4.2 (b), carried out absorption and effusion experiments and found the kinetics were independent of the direction of transfer. This is predictable in view of the theory and data presented in the present investigation, since there was no degree of freedom for concentration gradients to develop within the silver surface. Utine and Parlee did not carry out desorption experiments with a two component gas phase.

The kinetics of oxygen transfer between a two component gas and liquid silver was discussed in terms of the similar mixed control models of Mori et al (40) and Chatterjee and Bradshaw (10) in Section 2.4.4 . In the present study the gas phase resistance has been shown clearly to influence the overall kinetics in a manner which is dependent on the oxygen partial pressure in the gas phase. Calculated values of k_G^O are physically realistic, and the role of the gas phase concentration gradients in the development of Marangoni convection has been demonstrated. In contradiction to Mori et al's postulation (40), the evidence in this work suggests that the interfacial chemical reaction ($O_2 \rightleftharpoons 2 [O]$) proceeds at equilibrium, and does not influence the

overall kinetics. It is therefore relevant to reinterpret the data of Mori et al (40) simply in terms of kinetic control by the liquid and gas phase mass transfer steps.

Employing Equations 2.40 and 2.41 , Mori et al obtained a value of $k_L = 22 \times 10^{-3}$ cm/sec and a value of $k_2 = 55 \times 10^{-3}$ cm/wt% sec. If their data are interpreted in terms of transport control, the effect of gas phase bulk flow must be taken into account, see Equation 2.23, and the gas phase resistance disappears for $p_{O_2} = 1.0$ atm. On this basis k_L should be 13.3×10^{-3} rather than 22×10^{-3} cm/sec. The data presented in Figure 2.8 relate to experiments which were carried out near to final equilibrium. Thus the dependence of k_{OV} on p_{O_2} can be readily calculated from Equations 2.20 and 2.23. For $k_L = 13.3 \times 10^{-3}$ cm/sec, the best fit of Mori et al's data is obtained when $k_G^O = 2.25$ cm/sec (or $k_2 = 79.8 \times 10^{-3}$ cm/wt% sec), which is physically realistic. The results of these calculations are shown in Figure 4.5 . It is immediately apparant that the mass transfer mixed control model describes Mori et al's data equally as well as their model of liquid phase transport combined with interfacial chemical reaction.

A feature of the results in Figure 4.5 is that there is no significant dependence of the kinetics on the direction of transfer. The liquid silver was inductively stirred, and this level of forced convection may have masked the effects of spontaneous Marangoni convection. However, no firm conclusions can be drawn since the experiments were carried out near to final equilibrium, under conditions where Marangoni convection would be expected to be very weak.

As discussed in Section 2.4.5 , under certain conditions of desorption with argon, Mori et al (40, 42, 44) found the value of k_L

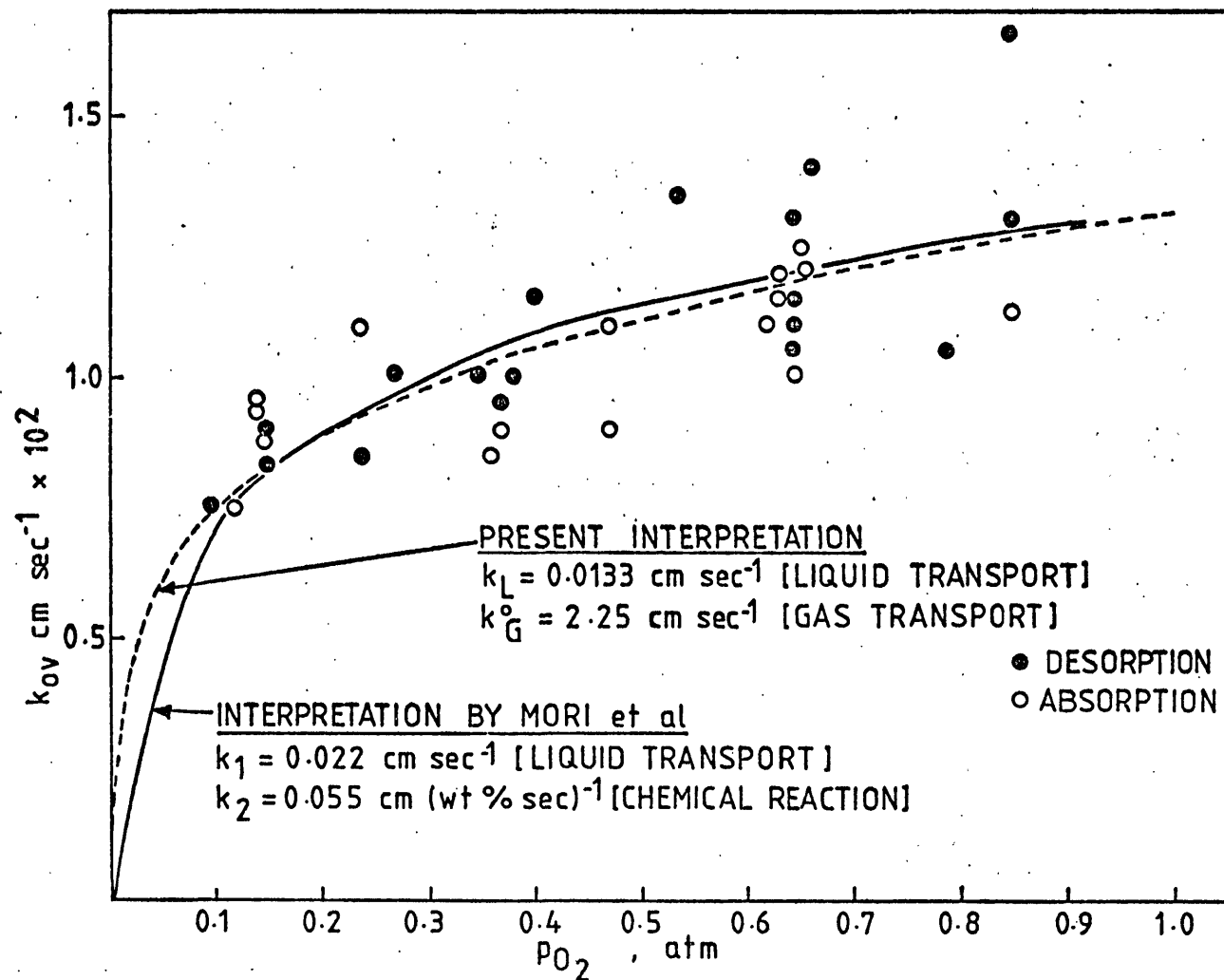


FIG. 4.5 REINTERPRETATION OF DATA OF MORI et al (40)

to be reduced due to 'surface retardation'. The phenomena was attributed to the development of surface tension gradients within the interface. This is very interesting since desorption is the naturally unstable direction of transfer from a Marangoni convection point of view. If the surface retardation effect was indeed real, the likely interpretation would be that the flow patterns in the gas jet and the inductively stirred liquid silver together dictated the type of concentration profile at the interface. Bakker et al (95) differentiate between the 'macro' effects of system geometry, flow patterns, etc. and the 'micro' effects described in Section 2.5.1 of this thesis. A similar distinction is drawn by Brückner (98) between forced instabilities and instabilities related to the system. This kind of distinction is probably relevant to the results of Mori et al (42, 44), since 'micro' effects could certainly not cause surface retardation during desorption, the naturally unstable direction of transfer.

In Chatterjee's preliminary work with dilute gas jets (1, 10), see Section 2.4.4 (a), two of the five desorption runs yielded value of $\lambda > 1$ which is physically impossible. This was attributed to experimental scatter, but a more plausible explanation is that Marangoni phenomena were causing some enhancement of the liquid phase transport step in desorption.

The main contribution of the present investigation is felt to be the substantiated evidence for mass transfer linked Marangoni convection under specific conditions of oxygen transfer between gases and liquid silver. The literature shows a growing interest in surface phenomena in high temperature liquid metal systems (46, 97), but to date there have been few direct observations (80). Most high temperature metallurgical reactions occur at interfaces between

liquid metals and gases or slags , and tend to be transport controlled. Furthermore, many solutes of obvious importance to metallurgical processes such as oxygen and sulphur are surface active with respect to iron, nickel, copper and so on (58, 59). There is no doubt that spontaneous interfacial phenomena play a significant role in many metallurgical processes (96, 98) and that further research work in the area is warranted.

Although Marangoni convection is a well established phenomena in various systems of interest to the chemical engineer, a search of the literature suggests that the present thermogravimetric study provides the first explicit evidence in a high temperature liquid metal system for the development of surface tension driven convection resulting from instabilities in the mass transfer process, as specifically defined by the Sternling-Scriven criterion (50).

CHAPTER 5

CONCLUSIONS

1. In the thermogravimetric and the jet impingement experiments carried out in this study, the kinetics of oxygen transfer between two component gases (nitrogen or argon diluent) and liquid silver were controlled by a combination of the gas and the liquid phase mass transfer steps. The chemical reaction at the interface exerted no kinetic influence. With a pure oxygen gas phase, the kinetics reflected simple liquid phase transport control.

2. In the thermogravimetric experiments, the liquid phase transport mechanism was molecular diffusion in absorption and effusion, but Marangoni convection in desorption. The Marangoni convection was driven by surface tension gradients within the interface, which arise from amplification of small instabilities in the mass transfer process. The appearance of this kind of spontaneous convection is described correctly by the Sternling-Scriven criterion; the surface tension of liquid silver decreases with oxygen content, and the diffusivity of oxygen in liquid silver is less than in gases. The mechanism depends on the existence of a solute concentration gradient adjacent to the interface in both of the phases.

3. The thermogravimetric investigations as a whole are thought to provide the first explicit, substantiated evidence in a high temperature, liquid metal system for the existence of mass transfer linked, surface tension driven, Marangoni convection, as specifically defined by the Sternling-Scriven criterion, in initially quiescent liquid.

4. In the experiments with dilute oxygen jets, where a flow field existed in the liquid due to the impingement of the gas jet, the effect of surface tension forces was to enhance the liquid phase mass transfer process during desorption and to retard it in absorption. The ratio of the liquid phase mass transfer coefficient in the naturally unstable direction of transfer to that in the naturally stable direction was deduced to be in the range of about 1.5 - 3.8 for the conditions of the jetting experiments, which is consistent with the proposed mechanism.

APPENDIX A

Mass Transfer Data from Absorption Experiments using Pure Oxygen Jets.

In order to plot the mass transfer data in terms of Equation 2.7 , the solid-electrolyte probe readings were converted to concentration units by using Equations 3.1 and 2.1 . The results of such calculations are presented graphically in the following figures : A1 - A6.

The bath volume was not constant for all experiments. Calculated values of bath volume, based on depth measurements, are given below :

Run	V (cm ³)	Run	V	Run	V
P1	1690	P10	1690	P18	1717
P2	1720	P11	1690	P19	1583
P3	1720	P12	1690	P20	1583
P4	1720	P13	1690	P21	1583
P5	1690	P14	1690	P22	1583
P6	1720	P15	1680	P23	1583
P7	1720	P16	1690	P24	1583
P8	1720	P17	1956	P25	1583
P9	1690				

The momentum figures quoted in Table 3.2 are calculated by using Equations 2.29, 2.24, 2.25 and 2.26 , with $C_d = 0.934$.

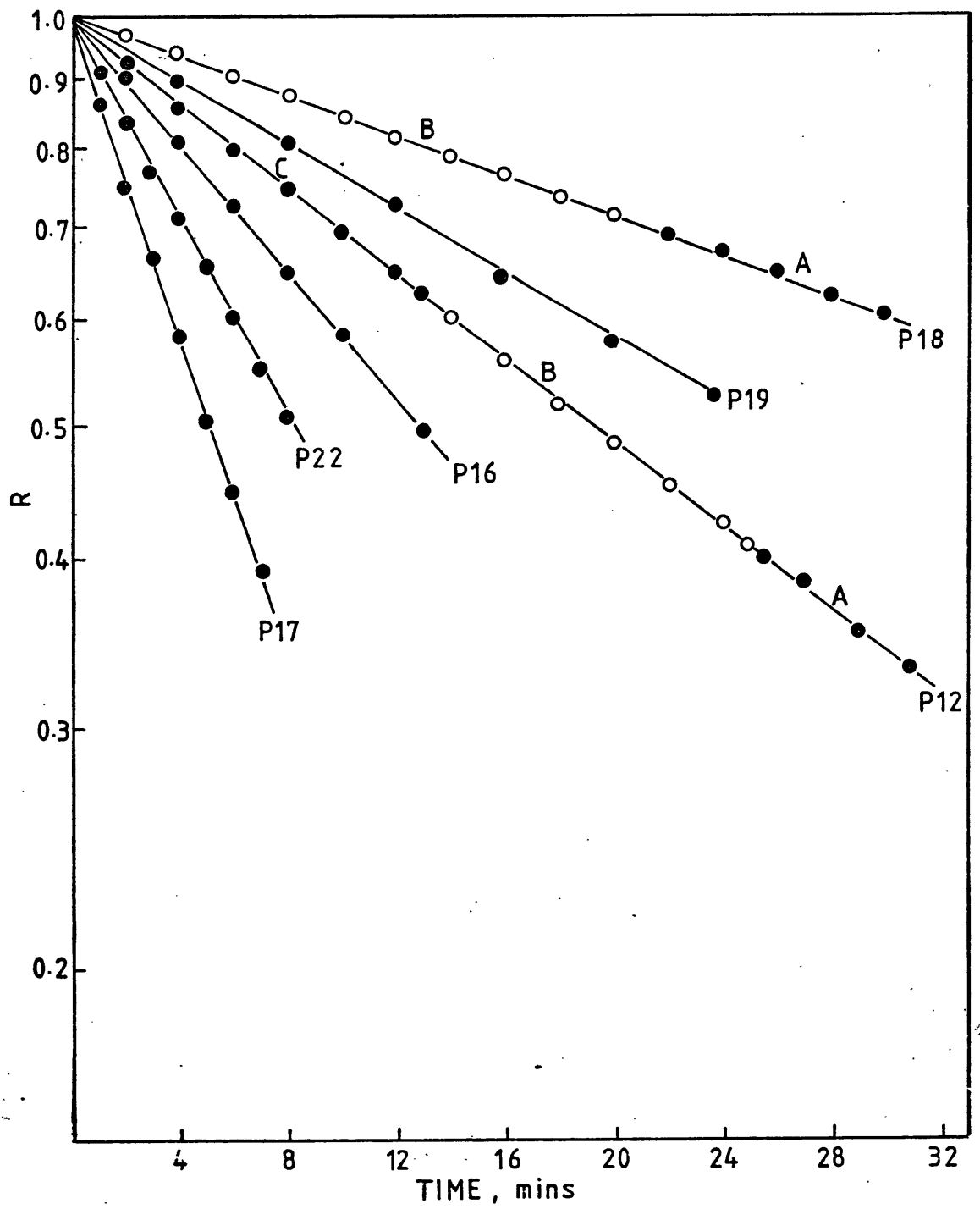


FIG. A1 : $\ln R$ vs t ; PURE OXYGEN JETS

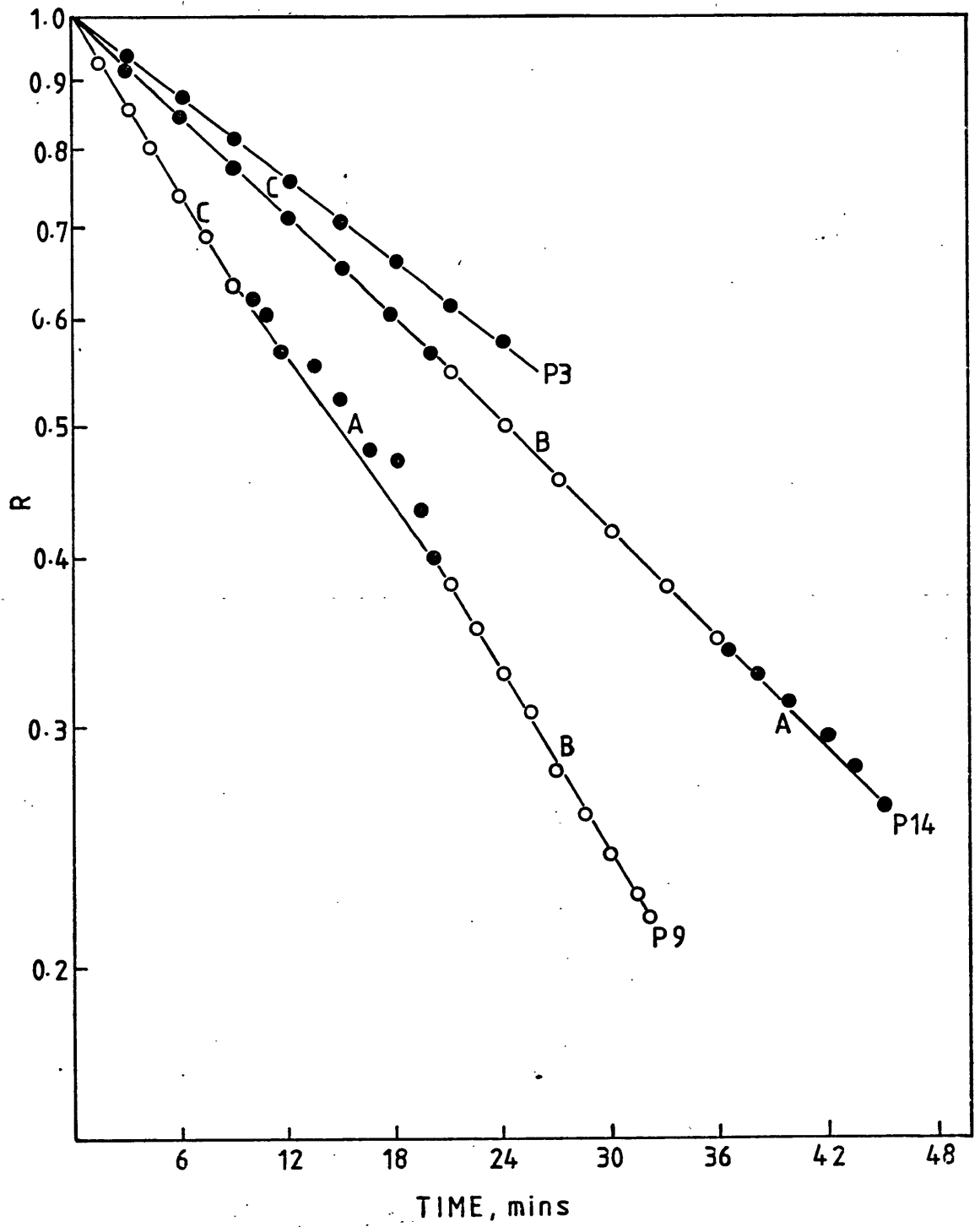


FIG.A2: $\ln R$ vs t ; PURE OXYGEN JETS

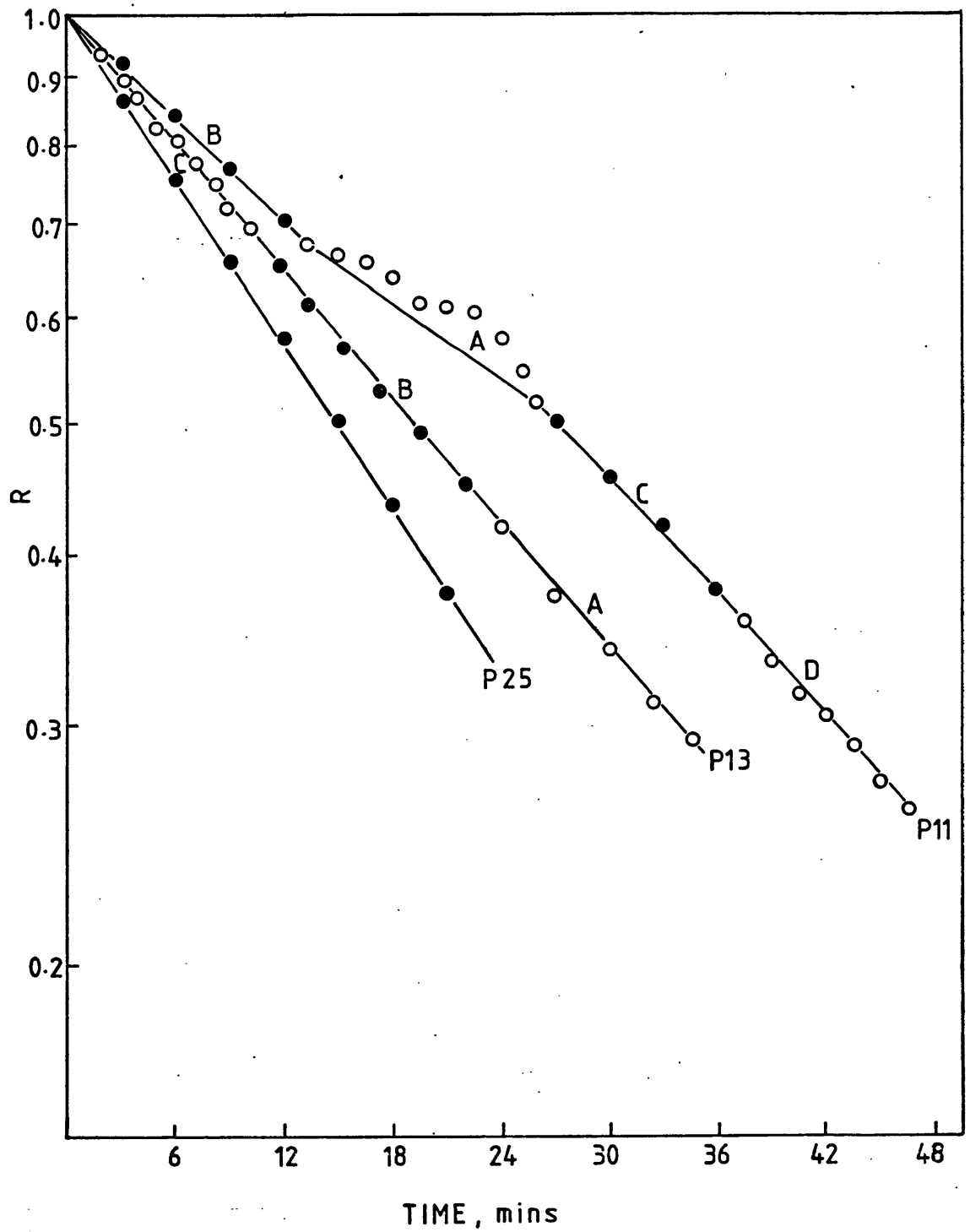


FIG. A3 : $\ln R$ vs t ; PURE OXYGEN JETS

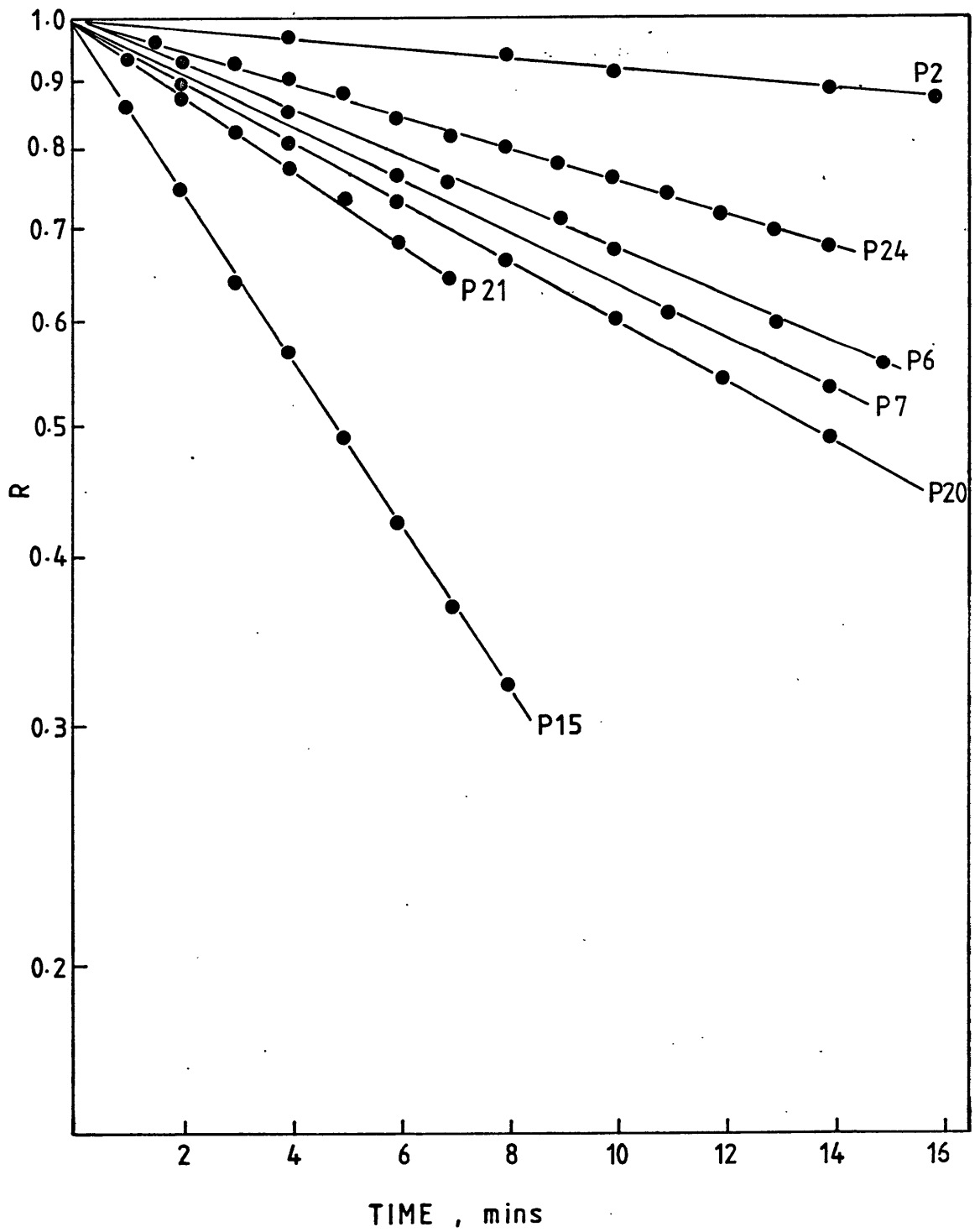


FIG. A4 : $\ln R$ vs t ; PURE OXYGEN JETS

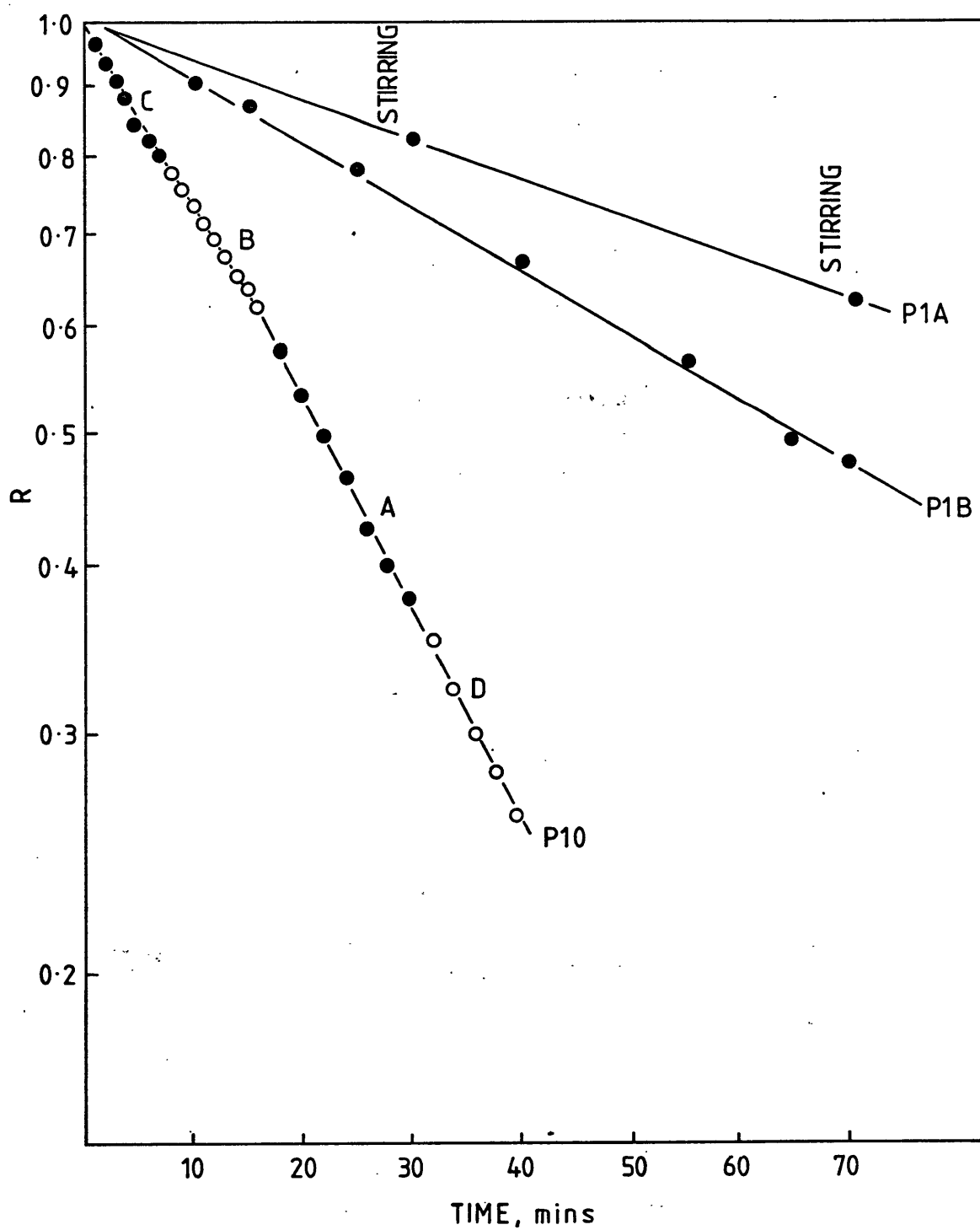


FIG. A5 $\ln R$ vs t ; PURE OXYGEN JETS

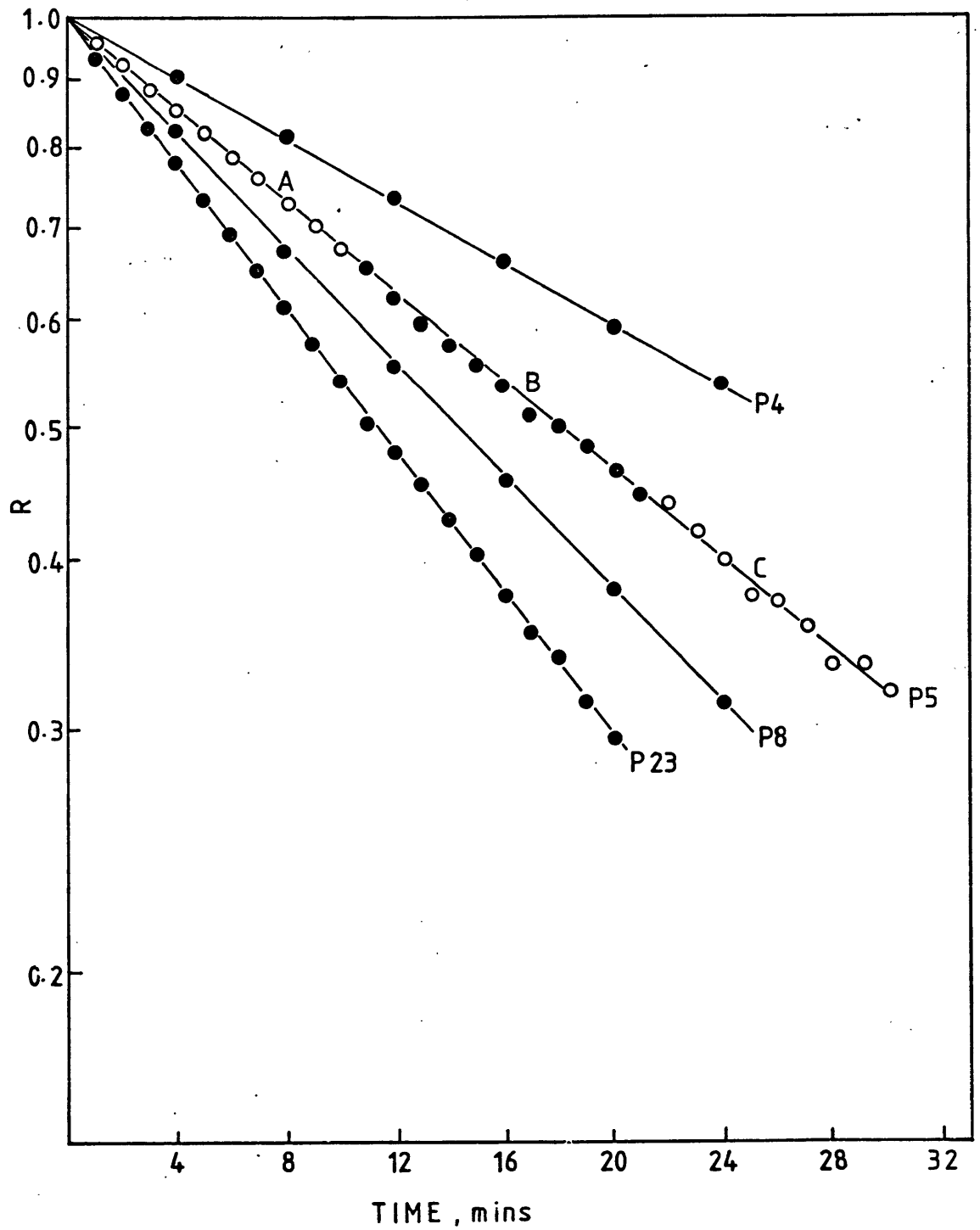


FIG. A6 : $\ln R$ vs t ; PURE OXYGEN JETS

APPENDIX B

Mass Transfer Data from Absorption and
Desorption Experiments using Dilute Gas Jets.

The mass transfer data are plotted in terms of Equation 2.9
in Figures B1 - B5.

Calculated values of bath volume, based on depth measurements,
are given below :

Run	V (cm ³)	Run	V	Run	V
D1	1530	D11	1530	D21	1583
D2	1625	D12	1625	D22	1583
D3	1530	D13	1625	D23	1583
D4	1625	D14	1690	D24	1583
D5	1530	D15	1690	D25	1583
D6	1530	D16	1690	D26	1583
D7	1530	D17	1530	D27	1625
D8	1625	D18	1625	D28	1625
D9	1625	D19	1690	D29	1625
D10	1625	D20	1583		

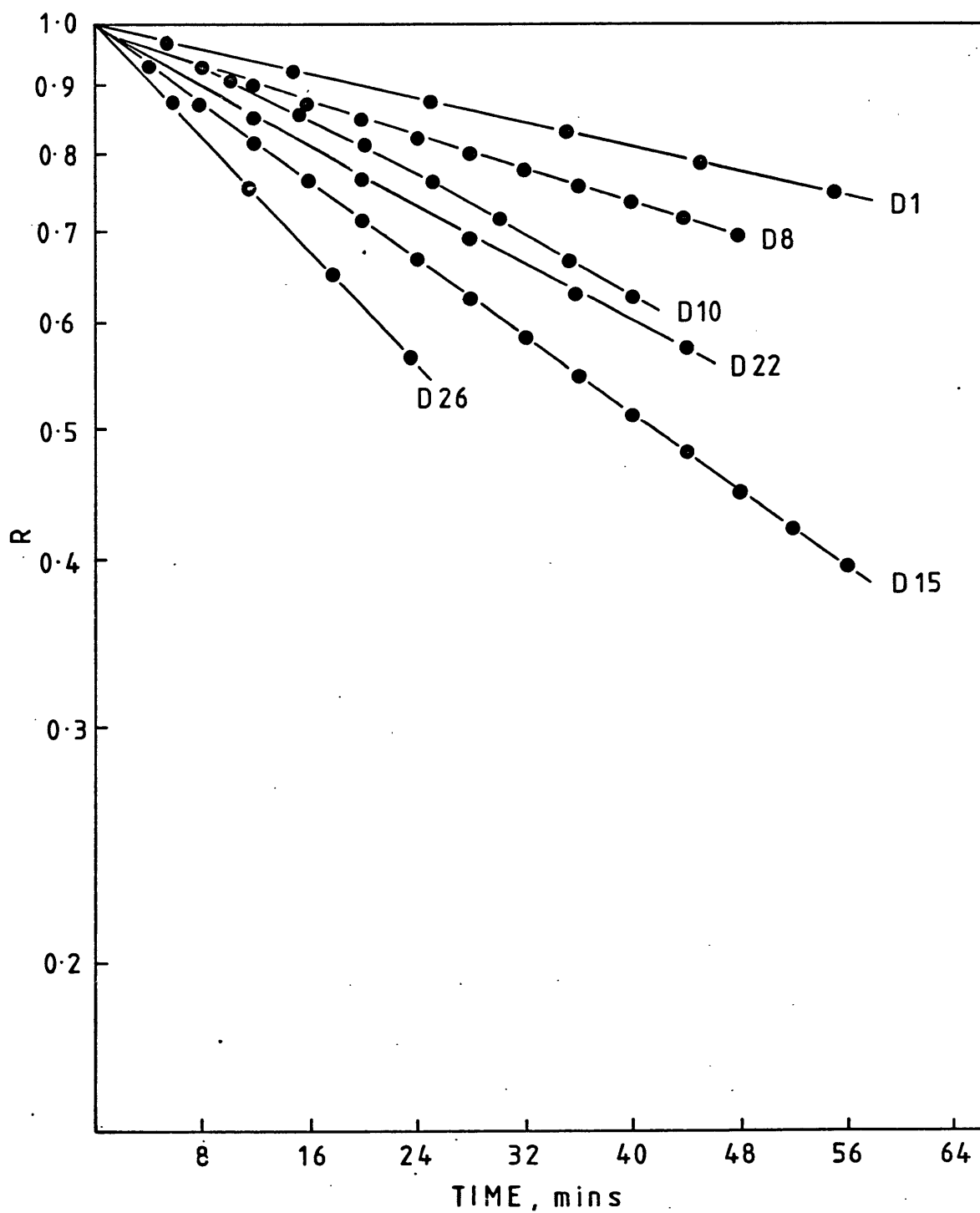


FIG. B1 $\ln R$ vs t ; DILUTE OXYGEN JETS

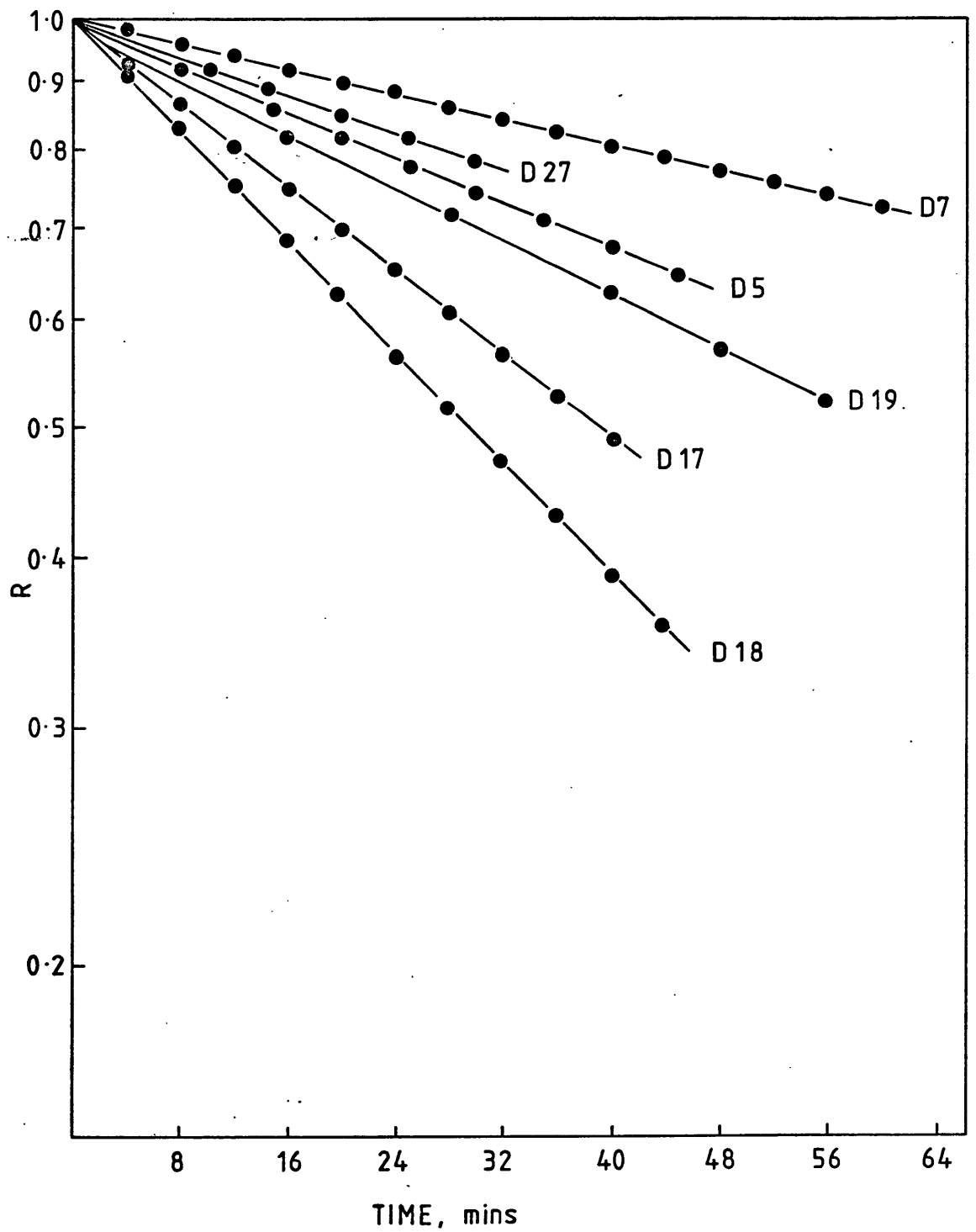


FIG. B2 $\ln R$ vs t ; DILUTE OXYGEN JETS

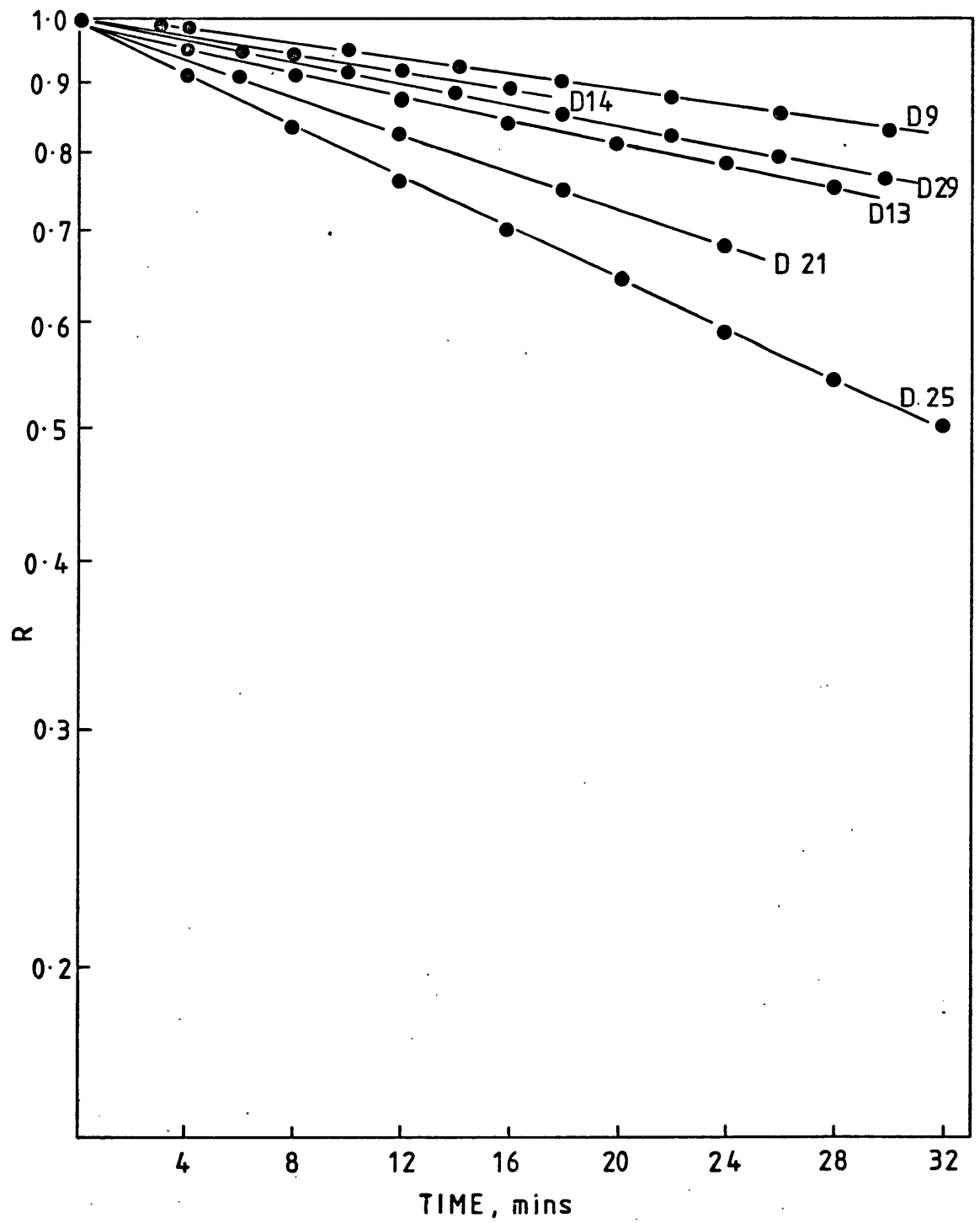


FIG. B3 $\ln R$ vs t ; DILUTE OXYGEN JETS

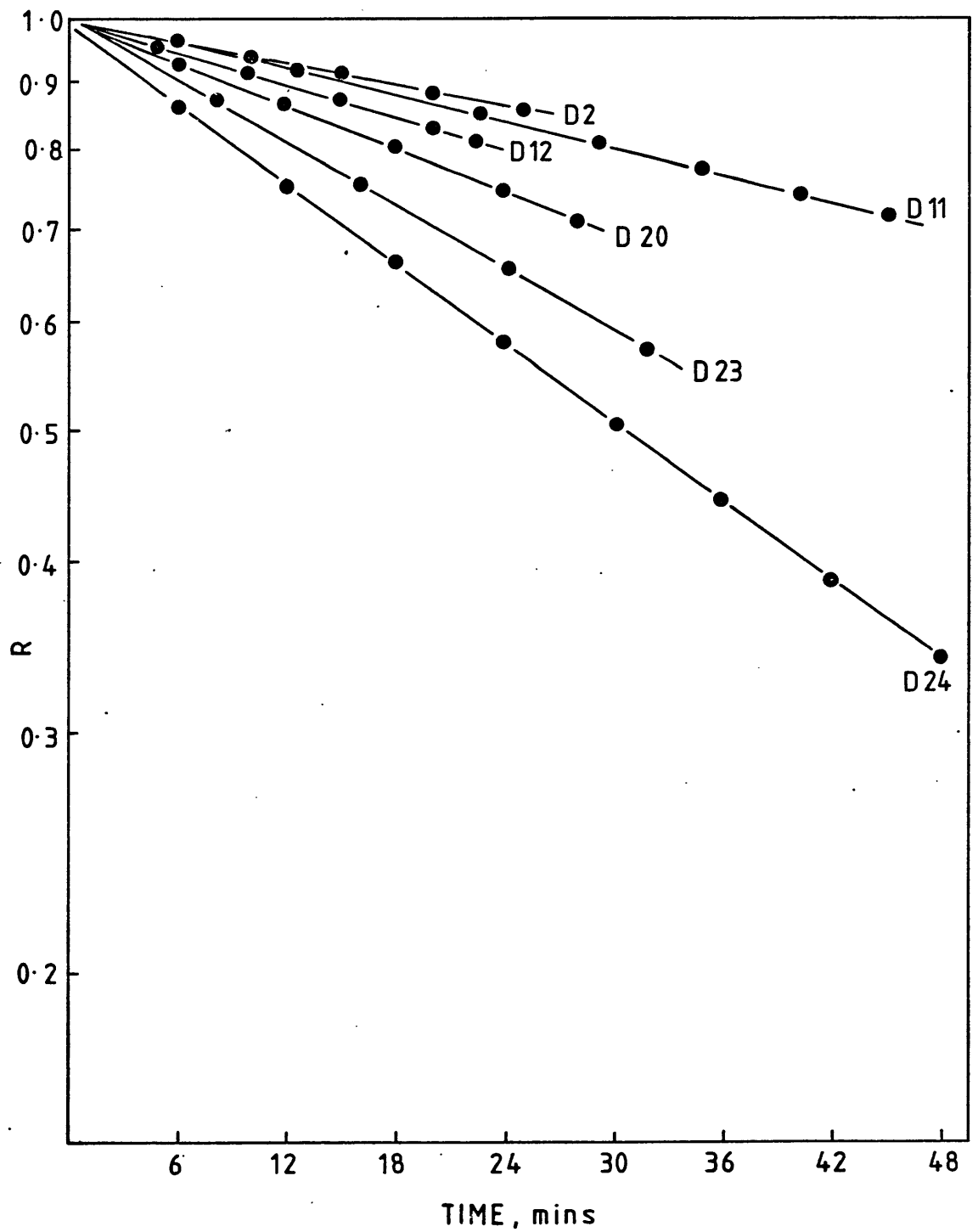


FIG. B4 $\ln R$ vs t ; DILUTE OXYGEN JETS

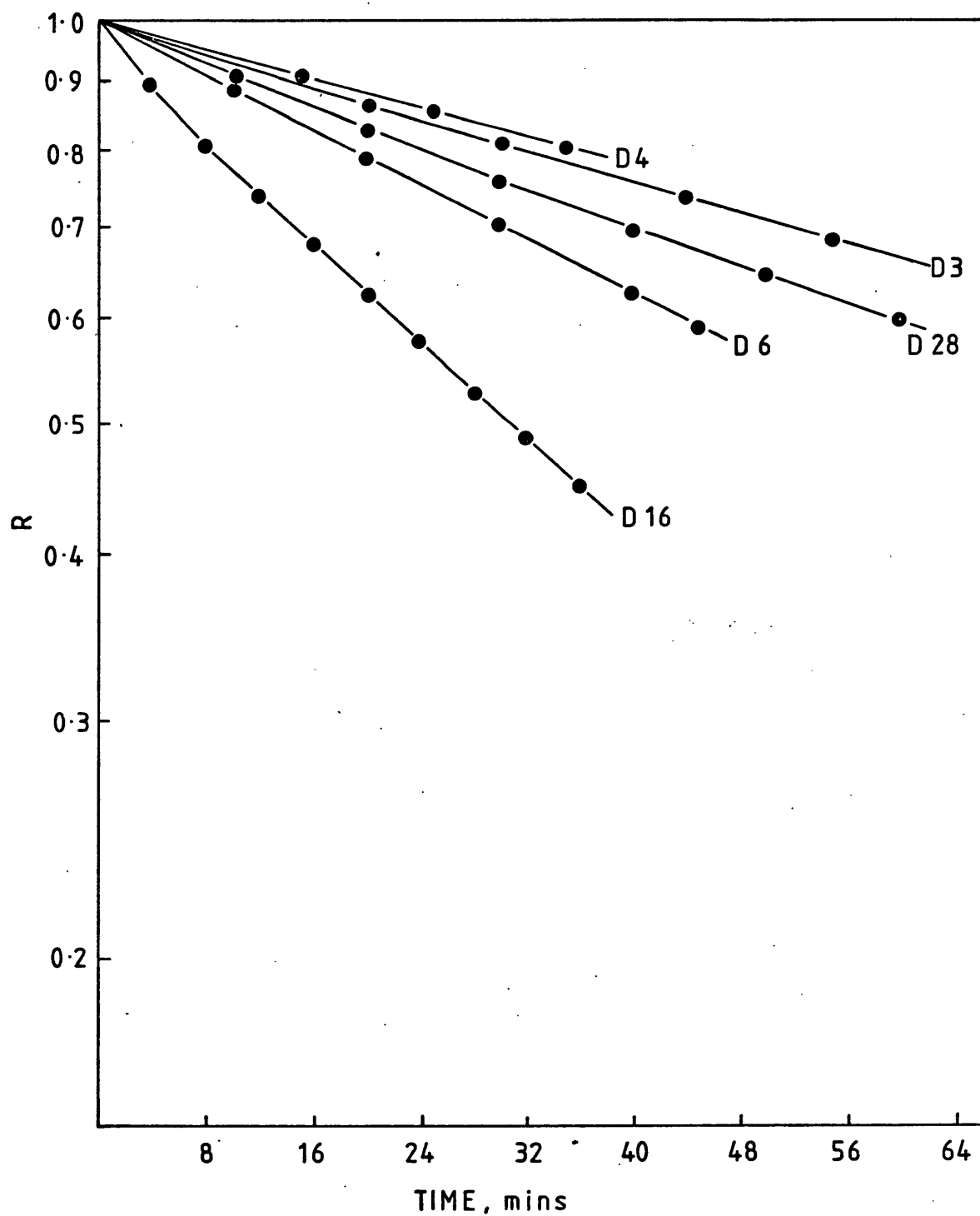


FIG. B5 $\ln R$ vs t ; DILUTE OXYGEN JETS

APPENDIX C

Mass Transfer Data from Absorption and Desorption Thermogravimetric Experiments

(a) Calibrations/Mass Balances

Since $C = q \cdot \sqrt{p}$ (Equation 2.1), $q = 1.76 \times 10^{-3}$ gm atoms/ $\text{cm}^3 \text{ atm}^{\frac{1}{2}}$, the atomic weight of oxygen = 16, the density of liquid silver at $1000^\circ\text{C} = 9.2 \text{ gm/cm}^3$, it follows that

$$W_O = 3.06 \times 10^{-3} W_{Ag} \sqrt{p_{O_2}} \quad (\text{C.1})$$

where W_O = the weight of oxygen dissolved in the silver
and W_{Ag} = the weight of the silver.

The load cell calibration was 0.01175 millivolts output per 1 milligram change in weight. At the beginning of the thermogravimetric investigations, several runs were allowed to proceed for very long times in an attempt to achieve equilibrium, and thereby check the calibration by mass balance. The results of these calculations are tabled below.

Run	W_{Ag} (gms)	Initial p_{O_2} , atm	Saturation p_{O_2} , atm	Predicted $\Delta mV \times 10^2$	Actual $\Delta mV \times 10^2$	Error %
A	20.23	0	1.0	72.8	71.5	-1.7
B	17.00	0	1.0	61.3	60.6	-1.2
C	19.05	0	.203	31.0	31.0	0
D	19.05	0	0.1	22.0	21.5	-2.3
E	17.00	1.0	0	61.3	61.5	+0.3
F	19.05	1.0	0	68.5	68.5	0
G	19.05	1.0	0.01	61.7	61.0	-1.1

(b) Mass Transfer Data

Equation 2.9 can be rewritten as

$$\ln R = \ln \frac{mV^* - mV}{mV^* - mV_{(t=0)}} = k_{ov} \frac{A}{V} t \quad (C.2)$$

The equilibrium value of the load cell millivolt output, mV^* , is calculated from the information in Section (a) above

$$mV^* = 0.01175 \times 3.06 W_{Ag} \sqrt{P_{O_2}} \quad (C.3)$$

provided W_{Ag} is in gms. The mass transfer data for both absorption and desorption experiments are presented in terms of Equation (C.2) in Figures C1 - C3. Values of A/V are listed below

Run	$\frac{A}{V} \text{ (cm}^{-1}\text{)}$	Run	$\frac{A}{V}$	Run	$\frac{A}{V}$
TG1	1.53	TG10	1.53	TG18	1.53
TG2	1.53	TG11	1.48	TG19	1.53
TG3	1.58	TG12	1.53	TG20	1.54
TG4	1.58	TG13	1.48	TG21	1.54
TG5	1.53	TG14	1.53	TG22	1.54
TG6	1.53	TG15	1.53	TG23	1.54
TG7	1.53	TG16	1.48	TG24	1.54
TG8	1.48	TG17	1.53	TG25	1.54
TG9	1.53				

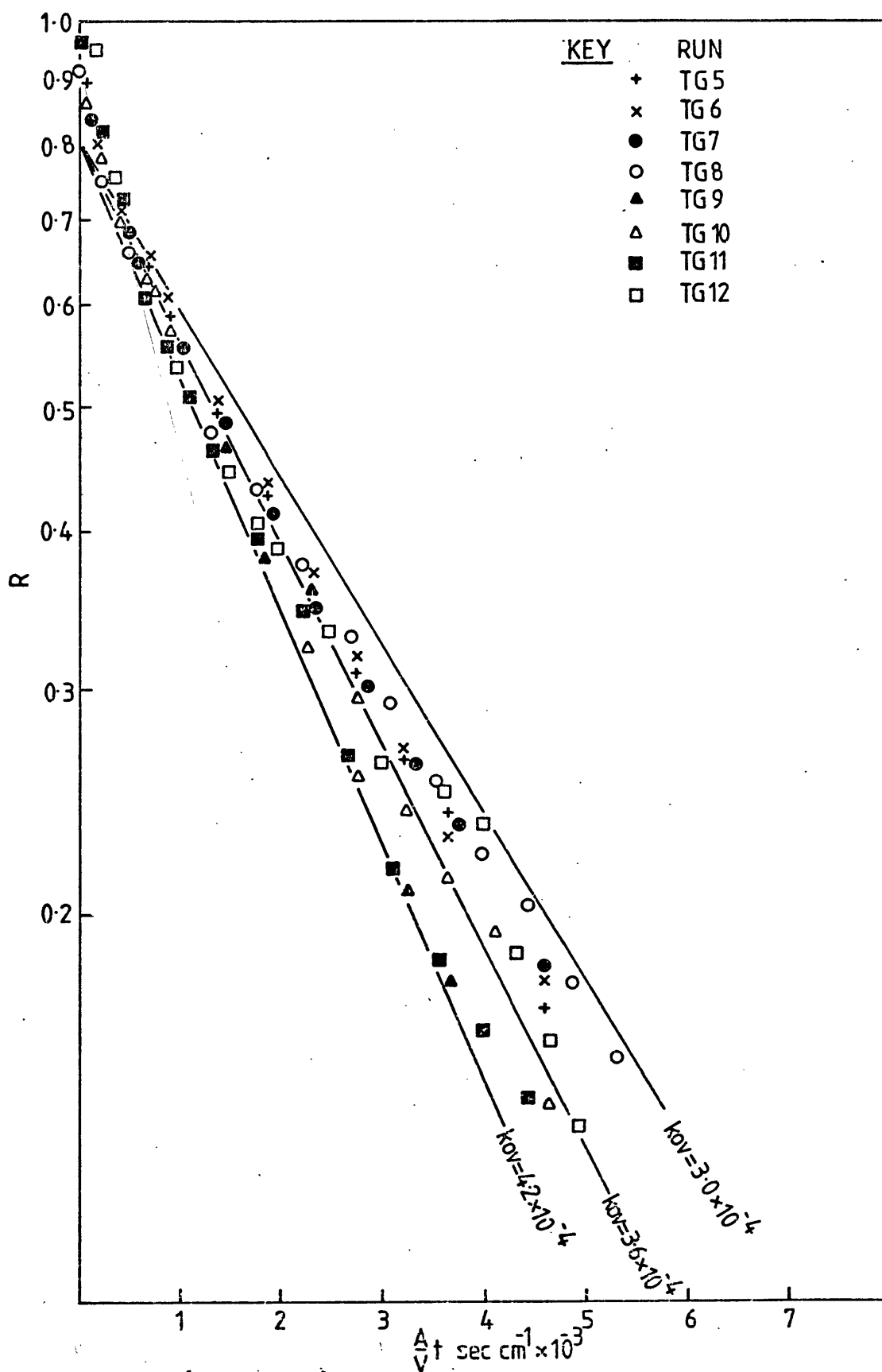


FIG.C1 $\ln R$ vs $\frac{A}{V} t$, ABSORPTION DATA FROM THERMOGRAVIMETRIC EXPERIMENTS

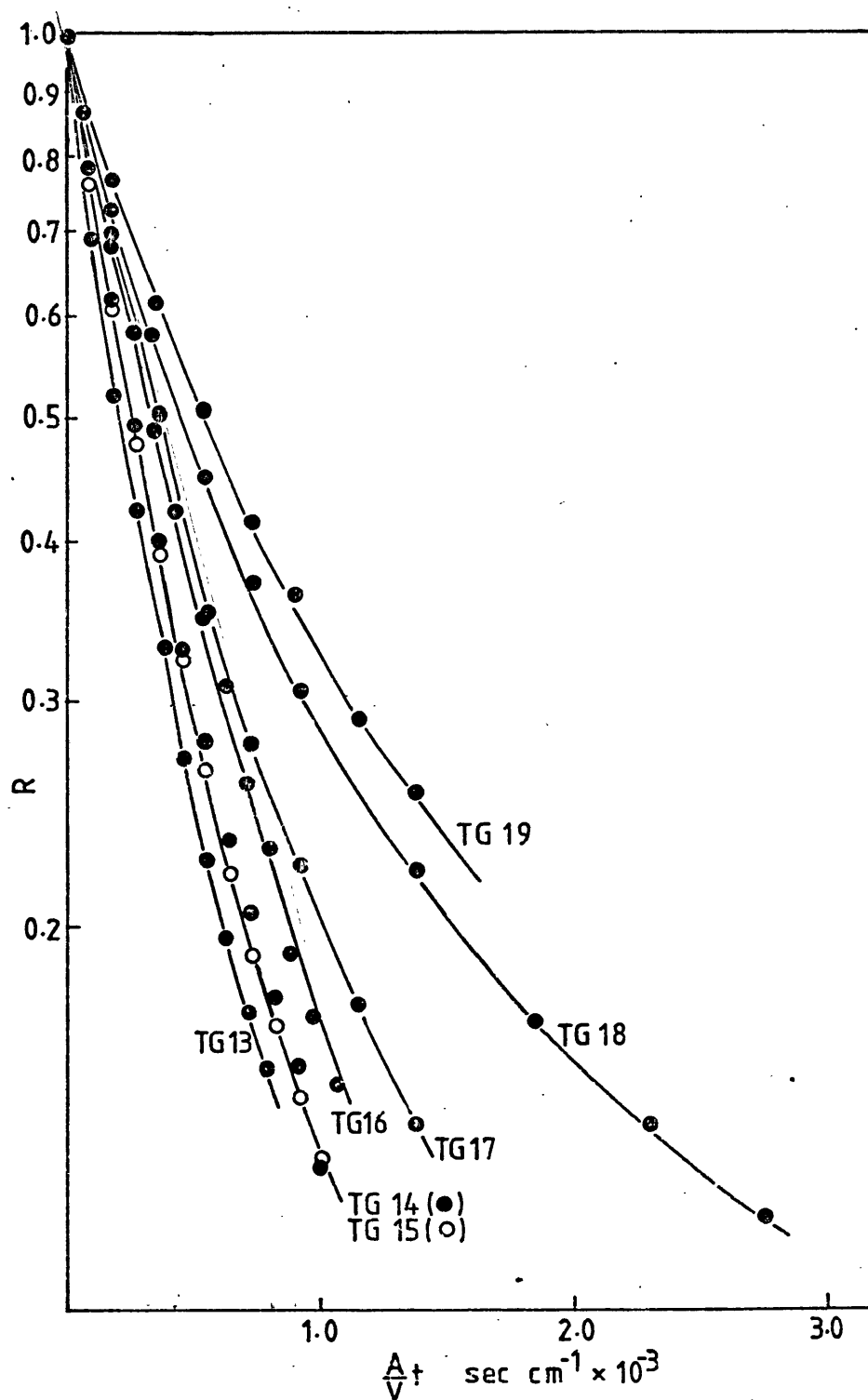


FIG. C2 $\ln R$ vs $\frac{A}{V}t$; DESORPTION DATA FROM THERMOGRAVIMETRIC EXPERIMENTS

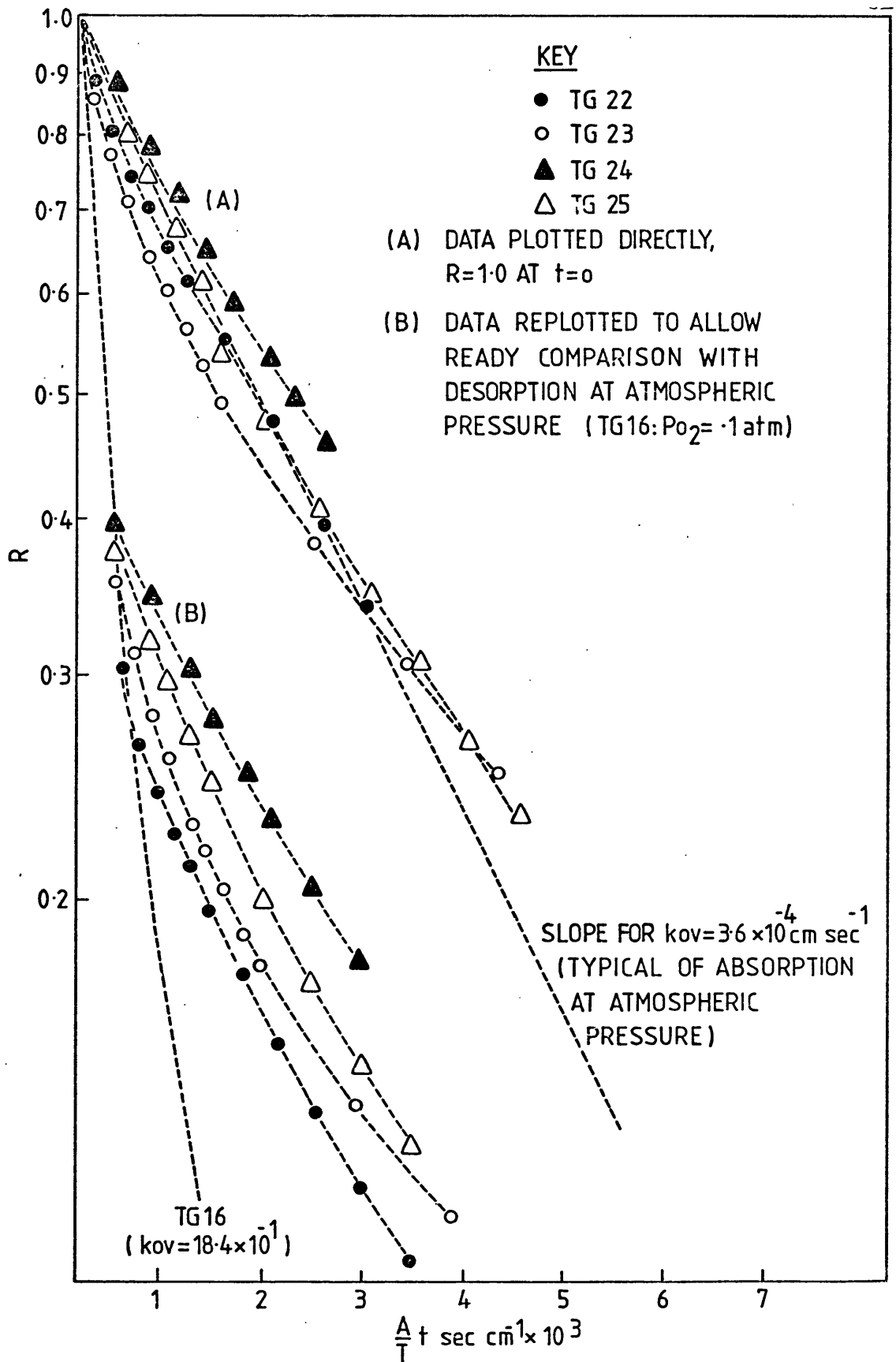


FIG.C3 $\ln R$ vs $\frac{A}{V} t$ MASS TRANSFER DATA FROM
DESORPTION RUNS AT REDUCED PRESSURE $P_{O_2} = P_{TOT}$

APPENDIX D

Dilute Gas Jetting Experiments - Calculation of the Gas Phase Mass Transfer Coefficient

The dilute gas jetting experiments are discussed in Section 3.1.5. The approach adopted initially was to analyse the results in terms of the mixed control model proposed by Chatterjee and Bradshaw (10), see Section 2.4.4 .

The value of k_L was assumed to be independent of gas composition and direction of transfer. Thus, a value of k_L was obtained from Figure 3.7 (representing pure oxygen jetting experiments) for the particular momentum of each dilute gas jetting experiment. The value of k_{OV} was then taken from Table 3.4 , and an average value of λ was calculated. An average value of the oxygen concentration in the silver was estimated from the solid electrolyte probe readings, and the jet composition was calculated from the rotameter readings. This allowed calculation of an average value of η . Equation 2.15 was then used to calculate ϕ . Once ϕ was known, a value of k_G was calculated for each run.

The effect of bulk flow is discussed in Section 2.2.2 . To solve Equation 2.22 and calculate k_G^O , the interfacial partial pressure must be known. To calculate p^* one must know the rate $\dot{n}$. The rate of absorption or desorption was estimated at selected instances during a run from the rate of change of oxygen concentration in the silver bath, Equation 2.6, which was derived from the slope of the C_b vs t curve. Equation 2.3 was then used to calculate C^* and the equilibrium relationship, Equation 2.4, lead to p^* .

A computer programme was written to enable speedy calculation of $\dot{n}$, p^* , k_G , k_G^O , etc. at set time intervals throughout each run. In

the computer calculations, $\dot{n}$ was related to the time averaged change in C_b for sufficiently small time increments such that, in reference to Equation 2.6 ,

$$V \frac{d C_b}{d t} \approx V \frac{\Delta C}{\Delta t} \quad (D.1)$$

In the above calculations it was assumed that $p_b = p_{JET}$. However, the entrainment of surrounding gas into the jet would alter the gas composition at the silver interface. Entrained gas would have a composition similar to the gas leaving the furnace, p_{EXIT} , and so in practice p_b would lie in between p_{JET} and p_{EXIT} . The exit gas composition is readily calculated from the overall oxygen mass balance for the furnace, which depends on the gas flow rate and composition, and the instantaneous rate of absorption or desorption, $\dot{n}$. The effect of product gas entrainment is to reduce the driving force for interfacial mass transfer in either direction of reaction. If radial concentration gradients in the jet are ignored, the effective partial pressure of oxygen immediately above the silver surface can be estimated from a mass balance to be

$$p_b = p_{JET} + \left(1 - \frac{\dot{m}_J}{\dot{m}_h}\right) (p_{EXIT} - p_{JET}) \quad (D.2)$$

where $\dot{m}_J$ is the total mass flow rate at the nozzle exit plane, and $\dot{m}_h$ is the total mass flow rate at a distance h from the nozzle corresponding to the lance height. From the discussion of jet theory presented in Section 2.2.3 , the degree of mass entrainment for a lance height of 10 cm would correspond to a value of $(1 - \dot{m}_J / \dot{m}_h) = 0.9$.

The computer calculations give values of $\dot{n}$ at intervals throughout each run, which allow p_{EXIT} to be estimated at specific times. Assuming, from Equation (D.2), that $p_b = 0.9 p_{EXIT} + 0.1 p_{JET}$, the value of the gas phase mass transfer coefficients in the calculations discussed above can be corrected for product gas entrainment effects.

An asterisk is used to identify gas transfer coefficients where such a correction has been made, viz $(k_G)^*$, $(k_G^O)^*$. Further refinement to account for radial concentration gradients would be complex, and not considered justified for lance heights as large as 10 cm.

The results of these calculations are presented in Figures 3.13, 3.14 and 3.15 . The computer programme and an example print-out are shown in Table D.1 . The calculations are summarized in Table D.2 . All figures in Table D.2, other than values of C_b ($t = 0$), are averages for each run.

COMPUTER PROGRAMME

TABLE D1

```

1*      DIMENSION FME(100), PLT(100), C(100), CB(100), RATE(100),
2*      CIF(100), PIF(100), ZKG(100), CF(100), ZKGO(100), ZKOV(100),
3*      XETA(100), XPHI(100), CHECK(100), XLAMDA(100)
4*      READ(5,1011) NE
5*      FORMAT(J3)
6*      DO 2002 N=1,NE
7*      DATA FOR THE RUN
8*      READ(5,1000) NRUN, PJET, MTUM, HEIGHT, ZKL, VOL, PREF, DT, J, A7
9*      WRITE(6,1001)NRUN, PJET, MTUM, HEIGHT, ZKL, VOL, PREF,J
10*
11*      1000 FORMAT(I4, F10.6, I10, F5.1, F10.5, F8.0, F7.3, F5.2, I5, F5.0)
12*      1001 FORMAT(1X,1H1, 7X, 6H RUN L, I3, 3X, F8.6, 4H PC2, 3X, I5, 6H DYNE
13*      1S, 3X, F4.1, 7H C/S LH, 3X, F6.5, 10H CM/SEC KL, 3X, F5
14*      2.0, 3X, F5.3, 3X, I3, 5H VALS )
15*
16*      IF(AD.GT.0.0) WRITE (6,1002)
17*      IF(AD.LT.0.0) WRITE (6,1003)
18*      1002 FORMAT(7X, 11H A=DESCRIPTION)
19*      1003 FORMAT(7X, 11H DESCRIPTION )
20*      OXYGEN PROBE READINGS FOR THE RUN
21*      READ(5,1004) (EMF(N), N=1,J )
22*      WRITE(6,1005) DT
23*      WRITE(6,1006) ( EMF(N), N=1,J )
24*      1004 FORMAT(6F10.2)
25*      1005 FORMAT(1X, 7X, 18H PROBE READINGS IN, F5.2, 17H MINUTE INTERVALS
26*      1 /)
27*      1006 FORMAT(7X, 15F7.2)
28*
29*      DO 2100 N=1,J
30*      PLT(N) = PREF-EXP(-0.01733*EMF(N)*2.303)
31*      C(N) = .00176*(PLT(N)**3.5)
32*      2000 CONTINUE
33*
34*      WRITE(6,1007)
35*      WRITE(6,1008) (PLT(N), N=1,J)
36*      1007 FORMAT(1X, 5H FLIG)
37*      1008 FORMAT(7X, 14F 9.6)
38*      INSTANTANEOUS CALCULATIONS OF KG
39*      WRITE(6,1009)
40*      1009 FORMAT(1X,1H1, 7X, 3H N, 11H CB, 11H CIF, 12H R
41*      1ATE, 10H PIF, 8H KG, 7H CF, 8H KGO, 10H KOV
42*      2, 8H ETA, 5H PHI, 7H LAMDA, 7H CHECK, / )
43*
44*      DO 2101 N=2,J
45*      CB(N-1) = (C(N) + C(N-1)) / 2.0
46*      RATE(N-1) = ( C(N-1) -C(N)) * VOL / (DT*60.0)
47*      CIF(N-1) = ( CB(N-1) - ( RATE(N-1) / (ZKL*131.0))
48*      PIF(N-1) = ( CIF(N-1) / 0.00176 )**2
49*      ZKG(N-1) = RATE(N-1) *82.05*1273.0 / (2.0*191.0*(PIF(N-1) - PJET))
50*      BULK FLOW CONTRICTION
51*      CF(N-1) = ( CIF(N-1) - PJET) / ALOG((1.0-PJET)/(1.0 -PIF(N-1)))
52*      ZKGO(N-1) = ZKG(N-1) * CF(N-1)
53*      RELATE TO BRASHAW/CHATTERJEE THEORY
54*      ZKOV(N-1) = RATE(N-1) / (161.0*(CB(N-1) - 0.00176* PJET**0.5))
55*      XLAMDA(N-1) = ZKOV(N-1) / ZKL
56*      XETA(N-1) = 0.00176 * ( PJET**0.5) / CB(N-1)
57*      XPHI(N-1) = 0.00176 * ZKL * 82.05 * 1273.0 / (2.0* (PJET -0.5)
58*      1 ZKG(N-1))
59*      CHECK THE ARITHMETIC
60*      CHECK(N-1) = (((XETA(N-1)*XPHI(N-1))**2 ) / 4.0 + XETA(N-1)*
61*      1 XPHI(N-1)+ XETA(N-1)**2 )**1.5 - 1.0 - XETA(N-1)*XPHI(N-1)/2.0)
62*      /
63*      (XETA(N-1) - 1.0)
64*
65*      WRITE(6,1010) N, CB(N-1), CIF(N-1), RATE(N-1), PIF(N-1), ZKG(N-1),
66*      1 CF(N-1), ZKGO(N-1), ZKOV(N-1), XETA(N-1), XPHI(N-1),
67*      2 XLAMDA(N-1), CHECK(N-1)
68*      1010 FORMAT(7X, I3, 2X, F9.7, 2X, F9.7, 2X, F10.9, 2X, F9.6, 2X, F6.3,
69*      1 2X, F5.3, 2X, F6.3, 2X, F3.6, 2X, F6.3, 2X, F7.3, 2X, F5.3, 2X,
70*      2 F6.3)
71*
72*      2001 CONTINUE
73*
74*      2002 CONTINUE
75*      STOP
76*      END

```

TABLE D1 (contd.)

(Sample Print-Out for Run D20)

DESORPTION .003550 P02 19000 DYNES 10.0 CMS LH .00740 CM/SEC KL 1583. .203 13 VALS

PROBE READINGS IN 4.00 MINUTE INTERVALS

37.50 39.80 41.90 44.00 46.00 48.00 49.90 51.80 53.70 55.40 56.90 58.50 60.00

.051733 .047572 .044066 .040818 .037548 .035279 .032918 .030715 .029660 .026937 .025514 .024059 .022778

N	CB	CIF	RATE	PIF	KG	BF	KGO	KOV	ETA	PHI	LAMDA	CHECK
2	.0003921	.0003112	.00010841	.031255	1.129	.983	1.109	.002035	.267	10.111	.262	.282
3	.0003767	.0003057	.00009509	.030163	1.031	.983	1.014	.001933	.273	11.073	.261	.286
4	.0003625	.0002942	.00008915	.027946	1.063	.984	1.066	.001962	.289	10.544	.265	.286
5	.0003492	.0002865	.00008336	.026504	1.055	.985	1.040	.001398	.300	10.816	.257	.285
6	.0003367	.0002763	.00008336	.024640	1.108	.986	1.092	.001929	.311	10.307	.251	.285
7	.0003230	.0002695	.00007422	.023453	1.076	.986	1.061	.001563	.323	10.609	.252	.285
8	.0003139	.0002604	.00007170	.021834	1.128	.987	1.114	.001895	.334	10.117	.256	.285
9	.0003031	.0002515	.00006632	.020410	1.135	.988	1.170	.001729	.346	9.637	.261	.285
10	.0002934	.0002456	.00005997	.019958	1.055	.988	1.042	.001757	.357	10.826	.237	.285
11	.0002850	.0002456	.00005513	.019537	.922	.983	.911	.001376	.368	12.381	.213	.285
12	.0002771	.0002372	.00005329	.018171	1.052	.989	1.040	.001710	.379	10.855	.231	.285
13	.0002693	.0002331	.00004357	.017534	1.002	.989	.992	.001632	.389	11.392	.228	.285

TABLE D2

Calculations of the Gas Phase Mass Transfer Coefficients

Run	Duration (mins)	$C_b(t=0)$ (gm.at/cm ³) x 10 ⁴	C_b (gm.at/cm ³) x 10 ⁴	C^* (gm.at/cm ³) x 10 ⁴	$\dot{n}$ (gm.at/sec) x 10 ⁵	p^* (atm) x 10 ²	P_{EXIT} (atm) x 10 ²
D13	28	3.13	2.92	2.49	4.96	2.00	0.58
D14	16	1.91	1.87	1.74	1.56	0.97	0.49
D15	60	6.88	5.59	4.34	14.19	6.23	2.47
D16	40	10.99	9.02	4.91	28.05	7.86	5.69
D17	40	7.01	6.29	5.38	11.24	9.37	5.25
D18	44	10.94	9.25	7.24	22.95	17.14	10.28
D7	65	0.24	0.37	0.46	1.12	0.073	0.39
D8	48	2.43	2.63	2.83	2.38	2.59	4.75
D9	50	1.74	1.99	2.24	3.00	1.62	4.70
D10	45	2.91	3.24	3.64	4.15	4.31	6.76
D11	60	2.41	2.90	2.76	4.47	3.49	9.04
D12	25	3.53	3.88	4.54	8.36	6.69	18.76
D5	50	6.35	5.48	3.64	10.33	4.30	1.05
D6	50	5.77	5.19	4.01	6.92	5.21	3.09
D1	65	1.65	1.83	2.11	1.65	1.44	3.04
D2	30	2.31	2.47	3.04	3.23	2.99	6.22
D3	100	2.97	3.60	4.32	4.19	6.05	9.81
D4	40	2.79	3.07	3.75	3.81	4.55	9.77

D22	48	3.92	3.31	2.72	7.83	2.44	0.61
D23	36	6.03	5.23	4.25	13.15	5.93	1.95
D24	52	12.53	9.70	6.77	39.10	15.23	6.09
D25	36	9.38	8.22	6.74	19.90	14.77	7.72
D26	26	14.22	12.36	9.47	23.89	29.64	10.85
D19	60	1.23	1.50	1.70	2.40	0.94	1.61
D20	32	1.92	1.21	2.68	6.18	2.33	4.81
D21	26	2.75	3.21	4.00	10.70	5.19	9.78

TABLE D2 (contd.)

Run	λ	η	ϕ	k_G (cm/sec)	k_G^o (cm/sec)	$(k_G^o)^*$ (cm/sec)
D13	.247	0.40	9.71	0.92	0.91	1.00
D14	.208	0.62	9.54	0.93	0.92	1.02
D15	.412	0.50	3.74	1.06	1.01	1.07
D16	.531	0.45	2.26	1.06	0.98	1.12
D17	.376	0.62	3.96	0.72	0.67	0.72
D18	.585	0.61	1.64	1.17	1.01	1.12
D7	.119	3.21	11.56	0.90	0.90	1.00
D8	.116	1.47	8.93	0.33	0.32	0.33
D9	.132	1.96	10.51	0.28	0.27	0.28
D10	.294	1.43	4.35	0.45	0.42	0.45
D11	.162	1.89	8.44	0.25	0.23	0.24
D12	.198	1.88	6.63	0.24	0.21	0.21
D5	.436	0.25	4.80	0.79	0.77	0.88
D6	.506	0.57	2.33	0.78	0.75	0.85
D1	.236	1.69	5.60	0.31	0.31	0.32
D2	.285	1.80	4.29	0.27	0.26	0.27
D3	.328	1.59	3.70	0.26	0.24	0.25
D4	.288	1.82	4.19	0.22	0.20	0.21
D22	.250	0.33	10.72	1.06	1.05	1.18
D23	.339	0.44	5.58	0.96	0.92	1.01
D24	.444	0.43	3.45	0.89	0.80	0.87
D25	.426	0.59	3.24	0.79	0.70	0.75
D26	.462	0.46	3.17	0.73	0.58	0.62
D19	.229	1.51	5.98	0.90	0.89	0.96
D20	.244	1.79	5.25	0.59	0.57	0.61
D21	.318	1.76	3.69	0.60	0.55	0.58

D13
 D14
 D15
 D16
 D17
 D18
 D7
 D8
 D9
 D10
 D11
 D12
 D5
 D6
 D1
 D2
 D3
 D4
 D22
 D23
 D24
 D25
 D26
 D19
 D20
 D21

0.74 at 19,000 rpm

LIST OF SYMBOLS

A	area	cm^2
B	coefficient of thermal expansion	$^{\circ}\text{C}^{-1}$
C	concentration	$\text{gm} \cdot \text{atom cm}^{-3}$
C_d	discharge coefficient	d'less
d	diameter	cm
D	diffusion coefficient	$\text{cm}^2 \text{sec}^{-1}$
E	electrolyte probe output	volts
F	Faraday constant (=96487)	coulomb per mole of electrons
g	gravity	cm sec^{-2}
h	lance height	cm
k	mass transfer coefficient	cm sec^{-1}
K_1	jet constant	d'less
l	bath depth	cm
$\dot{m}$	mass flux	gm sec^{-1}
$\dot{M}$	momentum flux	dynes
M	mass	gms
MW	molecular weight	gm mole^{-1}
mV	load cell output	millivolts
$\dot{n}$	rate of reaction	$\text{gm} \cdot \text{atom sec}^{-1}$
n_o	depth of depression	cm
p	partial pressure	atm
P	total pressure	atm
q	Sievert's constant	$\text{gm atm cm}^{-3} \text{atm}^{-\frac{1}{2}}$
q	heat flux density	$\text{cal cm}^{-2} \text{sec}^{-1}$
r	radius	cm
r	energy conversion factor	d'less
R	departure from equilibrium	d'less
R	gas constant (=1.987)	$\text{cal } ^{\circ}\text{K}^{-1} \text{mole}^{-1}$
t	time	secs
T	Temperature	$^{\circ}\text{K}$
u, U	velocity	cm sec^{-1}
V	velocity	cm sec^{-1}
V	volume	cm^3

W	weight	gm
x	mole fraction	d'less
x	distance	cm
λ	rate constant	d'less
η	driving force	d'less
ϕ	relative resistance	d'less
ϵ	relative resistance	d'less
γ	ratio of specific heats	d'less
γ	surface tension	dyne cm ⁻¹
ρ	density	gm cm ⁻³
μ	viscosity	poise
ν	kinematic viscosity	cm ² sec ⁻¹
δ	diffusion distance	cm

SUBSCRIPTS

A	species 'A'
Ag	silver
AB	two-component gas
b	bulk phase
eq	equilibrium
G	gas phase
h	distance equivalent to lance height
J	jet
L	liquid phase
lm	log mean
N	nozzle
ov	overall
O ₂ , 0	oxygen
o	jet origin
t	time
TC	thermocouple
TOT	total

SUPERSCRIPTS

- * interfacial (C^* etc)
- * corrected for product gas entrainment
 (k_G^* etc)
- o corrected for bulk flow (k_G^o)

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LIST OF REFERENCES

1. Chatterjee, A.,
Ph.D. Thesis, University of London, 1970.
2. Wakelin, D.H.,
Ph.D. Thesis, University of London, 1966.
3. Diaz, C.M. Masson, C.R., Richardson, F.D.,
Trans. I.M.M. (Sect. C), 75, p183-5, 1966.
4. Gauntner, J.W. Livingood, J.N.B. Hrycak, P.,
NASA T.N. D-5652, 1970.
5. Taylor, J.F., Grimmett, H.L. Cummings, E.W.,
Chem. Eng. Progress, 47 (4), p175-80, 1951.
6. Kuethe, A.M.,
Jl. Applied Mechanics, 2, p4-87, 1935.
7. Rogers, Dr. P.,
Imperial College, Private Communication.
8. Baulk, R.H.
"Progress in Gas Temperature Measurement"
Bull. Br. Coal Res. Ass., 1949.
9. Probert, R., Singham, J.R.,
J. Sci. Inst., 23, p72, 1946.
10. Chatterjee, A., Bradshaw, A.V.,
Met. Trans., 4, p1359-64, 1973.
11. Matyas, A.,
Ph.D. Thesis, University of London, 1972.
12. Campbell, F.R.,
Ph.D. Thesis, University of London, 1971.
13. Davenport, W.G., Wakelin, D.H., Bradshaw, A.V.,
"Heat and Mass Transfer in Process Metallurgy"
(Ed. A.W. Hills), I.M.M., London, p207-44, 1966.
14. Chatterjee, A., Wakelin, D.H., Bradshaw, A.V.,
Trans. AIME, 3, p3167-71, Dec. 1972.
15. Chatterjee, A., Bradshaw, A.V.,
Jl. I.S.I., p179-88, March 1972.

16. Bradshaw, A.V., Chatterjee, A.,
Chem. Eng. Sci., 26, p767-72, 1971.
17. Chatterjee, A., Bradshaw, A.V.,
"Kinetics of Metallurgical Processes in Steelmaking"
(Ed. W. Dahl et al), p314-42,
Verlag Stahleisen MBH, Düsseldorf, 1975.
18. Machlin, E.S.,
Trans. AIME, 218, p314, 1960.
19. Higbie, R.,
Trans. A.I.Ch.E., 31, p365, 1935.
20. Hills, A.W.,
"Heat and Mass Transfer in Process Metallurgy"
(Ed. A.W. Hills), p39-77,
I.M.M., London, 1966.
21. Sieverts, A., Hagenack, N.,
J. Physik. Chem., 68, p115, 1910.
22. Parlee, N.A.D., Sacris, E.M.
Trans. A.I.M.E. 233, p1918-9, 1965.
23. Albertson M.C. et al.
Trans. Am. Soc. Civil Engs., 115, p639.97,
(including discussion contribution by
Holdhusen, J. and Baines W.I.), 1950.
24. Bennett, G.O. Myers, J.E.
"Momentum, Heat and Mass Transfer"
McGraw Hill, 1962.
25. Abraham, G.,
Delft Hydraulics Lab. Publ., No. 29,
p183, 1963.
26. Mizkar, E.A., Grace, R.E. Parlee, N.A.D.
Trans. A.S.M., 56, p101-6, 1963.
27. Parlee, N.A.D. Siebel, H.,
Trans. A.I.M.E., 233, p1923-4, Oct. 1965.
28. Parlee, N.A.D. Shah, I.D.,
Trans. A.I.M.E. 239, p763-4, May 1967.
29. Oberg, K.E. Friedman, L.M., Boorstein, W.M.,
Rapp, R.A.,
Met. Trans, 4, p61-7, Jan. 1973.

30. Masson, C.R., Whiteway, S.G.,
Can. Met. Quart., 6, p199-217, No.3, 1967.
31. Besson, J., Deportes, C., Schmidt, R.,
Danger, G.,
Bull. Soc. Chim., France, 11, p3394-8, 1966.
32. Rickert, H., El-Miligy, A.,
J. Metallk, 59, p635-41, 1968.
33. Sano, N., Honma, S., Matsushita, Y.,
Met. Trans., 1, p301-3, 1970.
34. Otsuka, S., Katayama, I., Kozuka, Z.,
Trans. Jap. Inst. Metals, 12, p442-7, 1971.
35. Vehlo, L.R., El-Tayeb, N.M., Jani, J.,
Parlee, N.A.D.,
Trans, Met. Soc. A.I.M.E., 245, p184-6,
Jan. 1969.
36. Crank, J.,
"The Mathematics of Diffusion"
Oxford University Press, London, 1956.
37. Zoellner, C.,
M.S. Thesis, Department of Mineral Engineering,
Stanford University, 1965.
38. Parlee, N.A.D., Sacris, E.M.
Trans. A.I.M.E., 233, p1918-9, 1965.
39. Vtine, M.T., Parlee, N.A.D.,
Trans. A.I.M.E., 242, p1458-60, 1968.
40. Mori, K., Sano, M., Suzuki, K.,
Trans. I.S.I. Japan, 13, p63-70, 1973.
41. Mori, K., Sano, M., Matsushima, M.,
Tetsu-to-Hagané, 56, pS83, 1970.
42. Sano, M., Mori, K.,
Tetsu-to-Hagané, 60, p1432-42, Sept. 1974.
43. Robertson, D.G.C.,
Imperial College, Private Communication.
44. Mori, K., Sano, M.,
"Kinetics of Metallurgical Processes in Steelmaking"
(Ed. W. Dahl et al), p492-512,
Verlag Stahleisen MBH, Düsseldorf, 1975.

45. Perry, J.H.,
"Chemical Engineers' Handbook"
(4th Edn.), McGraw Hill, New York, 1963.
46. Richardson, F.D.,
Trans. I.S.I. Jap., 14, p1-8, 1974.
47. Sawistowski, H.,
Chem. Jng.-Techn., 45 (18), p1093-8, 1973.
48. Sawistowski, H.,
Chem. Ing.-Techn., 45 (18), p1114-7, 1973.
49. Pérez de Ortiz, E.S.,
Chem. Ing.-Techn., 45 (18), p1110-3, 1973.
50. Sternling, C.V. Scriven, L.E.,
A.I.Ch.E. Jl., 5 (4), p514-23, Dec. 1959.
51. Bernard, G., Lupis, C.H.P.,
Met. Trans., 2, p2991-8, Nov. 1971.
52. Eremenko, V.N., Naidich, Y.V.,
Inst. Metalloekhim i Spets. Splavov,
p100-4, 1961.
53. Eremenko, V.N., Naidich, Y.V.
"The Wetting of Refractory Compounds with
Liquid Metals"
Office Techn. Serv., U.S. Dept. Comm.,
p65-7, 1958.
54. Gumerman, R.J. Homsy, G.M.
A.I.Ch.E. Jl., 20 (5), p981-8, Sept. 1974.
55. Knox, B.E., Baker, E.H.,
J. Mat. Sci., 7, p476-9, 1972.
56. Rajakumar, V.,
Imperial College, Private Communication.
57. Pearson, J.R.A.,
J. Fluid Mech., 4, p489-500, 1958.
58. Monma, K., Suto, H.,
Trans. J.I.M., 2, p148, 1961.
59. Kozakevitch, P.,
"Surface Phenomena of Metals"
Society of Chemical Industry Monograph,
No. 28, p223, 1968.

60. Rosler, R.S., Stewart, G.H.,
J. Fluid Mech., 31 (1), p163-74, 1968.
61. Beyer, R.T., Ring, E.M.,
"Liquid Metals- Chemistry and Physics"
(Ed. S.Z. Beer), Marcel Dekker Inc.,
New York, 1972.
62. Wilson, J.,
Metall. Rev., 10, p381, 1965.
63. Szekely, J., Asai, S.,
Met. Trans., 5, p463-7, 1974.
64. Szekely, J., Asai, S., Chang, C.W.,
"Process Engineering of Pyrometallurgy"
(Ed. M.J. Jones), I.M.M., London
p60-70, 1974.
65. Lupis, C.H.P., Elliott, J.F.,
Trans. A.I.M.E., 242, p929-35, 1968.
66. Sutterfield, C.N.,
"Mass Transfer in Heterogeneous Catalysis"
Cambridge, Mass., p80, 1970.
67. Sawistowski, H.,
Imperial College, Private Communication.
68. Sawistowski, H.,
"Recent Advances in Liquid-Liquid Extraction"
(Ed. C. Hanson), Pergamon Press, Oxford,
p293-366, 1971.
69. Scriven L.E., Sternling, C.V.,
J. Fluid Mech., 19, p321-40, 1964.
70. Scriven, L.E., Sternling, C.V.,
Nature, London, 187, p186-8, 1960.
71. Smith, K.A.,
J. Fluid Mech., 24 (2), p401-14, 1966.
72. Nield, D.A.,
J. Fluid Mech., 19, p341-52, 1964.
73. Brian, P.L.T.,
A.I.Ch.E. Jl., 17 (4), p765-72, 1971.

74. Gumerman, R.J., Homsy, G.M.,
A.I.Ch.E. Jl., 20 (6), p1161-72, 1974.
75. Herbertson, J.G., Warner, N.A.,
Trans. I.M.M., 82, pC16-20, 1973.
76. Herbertson, J.G.,
Trans. I.M.M., 83, pC128-9, 1974.
77. Herbertson, J.G., Warner, N.A.,
Trans. I.M.M., 84, pC130, 1975.
78. Sherwood, T.K., Wei, J.C.,
Ind. Eng. Chem., 49, p1030, 1957.
79. Mizoguchi, S.,
Ph.D. Thesis, University of London, 1972.
80. Brimacombe, J.K.,
"The Physical Chemistry of Process Metallurgy -
The Richardson Conference"
(Ed. J.H.E. Jeffes, R.J. Tait), I.M.M.,
London, p175-85, 1974.
81. Parlee, N.A.D., Sacris, E.M., Zoellner, C.,
J. Metals, p120, Jan. 1966.
82. Marangoni, C.,
Ann. Phys. Chem., 143, p337-54, 1871.
83. Kraus, Th.,
Schweizer Arch. angew. Wiss Tech., 28,
p452-68, 1962.
84. Orell, A., Westwater, J.W.,
A.I.Ch.E. Jl., 8, p350, 1962.
85. Linde, H., Pfaff, S., Zirkel, C.,
Z. Phys. Chem., 225, p72, 1964.
86. Cho, S.H., Jones, M.A.,
Paper presented at the 21st Canadian Chemical
Engineering Conference, Montreal, 1971.
87. Merson, R.L., Quinn, J.A.,
A.I.Ch.E. Jl., 10, p804, 1964.
88. Austin, L.J., Ying, W.E. Sawistowski, H.,
Chem. Eng. Sci., in print.

89. Lord Rayleigh,
Phil. Mag., 32, p529-46, 1916.
90. Benard, H.,
Rev. Gen. Sci. pures et appl., 11,
p1261-71, 1900.
91. Berg, J.C.,
"Recent Advances in Separation Science"
(Ed. N. Li), Vol. 2, p1-31,
Chemical Rubber Co., Cleveland, Ohio, 1972.
92. Davies, J.T.,
Adv. Chem. Engng., 4, p1-50, 1963.
93. Davies, J.T., Rideal, E.K.,
"Interfacial Phenomena"
Academic Press, New York, 1961.
94. Marsh, B.D., Schleicher, C.A. Heideger, J.W.
Paper presented to the 57th Annual Meeting of
the A.I.Ch.E., Philadelphia, 1965.
95. Bakker, C.A.P., Van Buytenen, P.M.
Beek, W.J.,
Chem. Eng. Sci., 21, p1039, 1966.
96. Kozakevitch, P.,
"Kinetics of Metallurgical Processes in Steelmaking"
(Ed. W. Dahl et al), p513-34,
Verlag Stahleisen MBH, Düsseldorf, 1975.
97. Richardson, F.D.,
"Physical Chemistry of Melts in Metallurgy"
(2 vols), Academic Press, 1974.
98. Brückner, R.,
"Kinetics of Metallurgical Processes in Steelmaking"
p459-91, Verlag Stahleisen MBH, Düsseldorf,
1975.