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by B. A. Marples

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This introduction to stereochemistry starts with such basic concepts as chirality, symmetry and configurational nomenclature before moving on to conformation and the physical methods of conformational analysis. The final two chapters discuss cyclic and acyclic systems. Almost 300 chemical structures are displayed to illustrate the points made, and suggestions for further reading are included.

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by P. A. H. Wyatt

Approaching chemical thermodynamics by concentrating on $\log_{10} K$ values permits a good deal of chemistry to be discussed in quantitative terms before anything which passes for 'thermodynamics' is tackled. Professor Wyatt's book contains an appendix of $\log K$, H_f° , and S° values for a large number of elements and compounds; this table can be used in much the same way as tables of logarithms were used before the pocket calculator revolution.

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Brief Contents:

Principal Symbols Used; Equilibrium Constants; Fixing Variables in Solving Equilibrium Problems; Combining Equilibrium Constants; Some Worked Examples; Energy and Entropy; The Gibbs Function; Chemical Potentials and Activities in Chemical Equilibria; Perspective.

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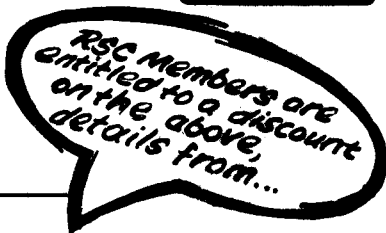
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THE CHEMISTRY OF BIOLOGICAL NITROGEN FIXATION

Raymond L Richards



CHEMISTRY CASSETTE

CHEMISTRY CASSETTES

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Please read this before you use the cassette.

This Chemistry Cassette learning programme consists of an audio-cassette and this workbook. The two are designed to be used together so always have the workbook with you as you work through the cassette.

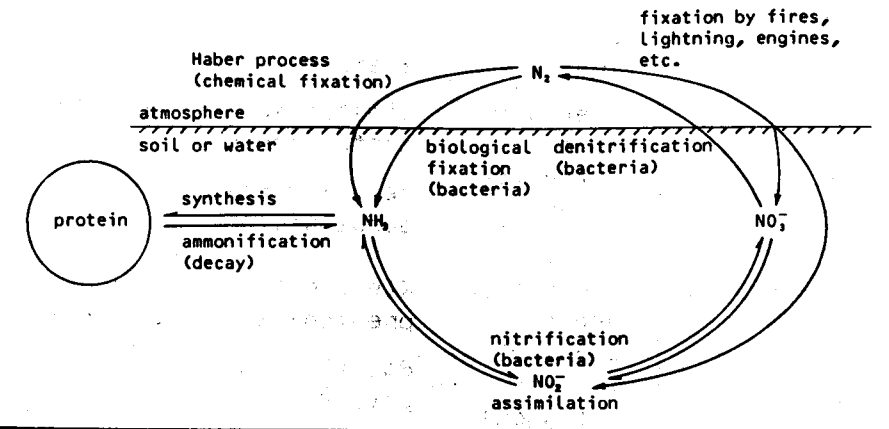
You will see that material in the workbook has been divided into numbered 'frames', each of which contains diagrams, tables, equations, etc. Whenever Dr Richards wants to refer you to any of this material he will give you the appropriate frame number.

The programme has been carefully designed for individual, self-paced learning, and you can work through it at a rate related to your own needs and understanding. Switch off the tape player whenever you want to think, to write some notes, or to answer a question. Use the rewind control to revise or repeat material that you may not fully understand on a first hearing. Always have pen and paper with you so that you can make notes to supplement or amplify the material contained in this workbook - this will enable you to build up a detailed set of personal notes which will serve as your own authoritative guide to the subject.

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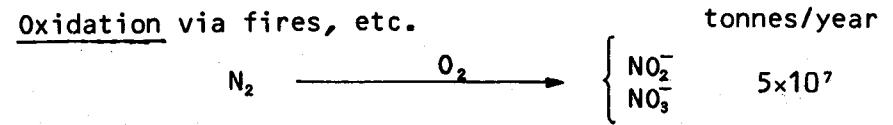
1

THE BIOLOGICAL NITROGEN CYCLE

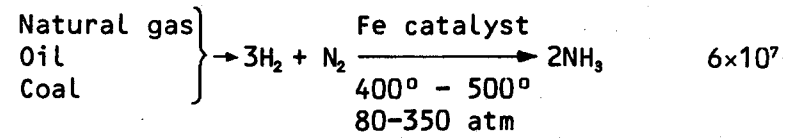


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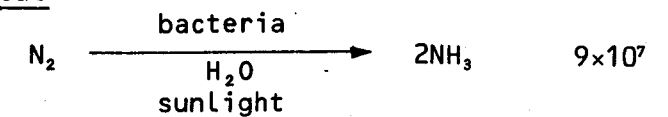
FIXATION PROCESSES



Industrial (Haber process)



Biological



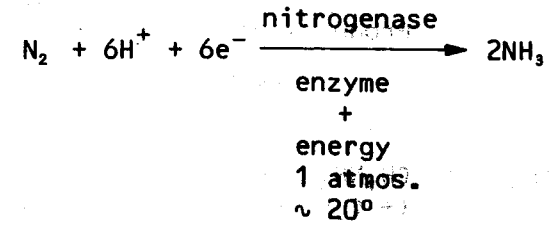
Total fixed N for agriculture 20 × 10⁷

3

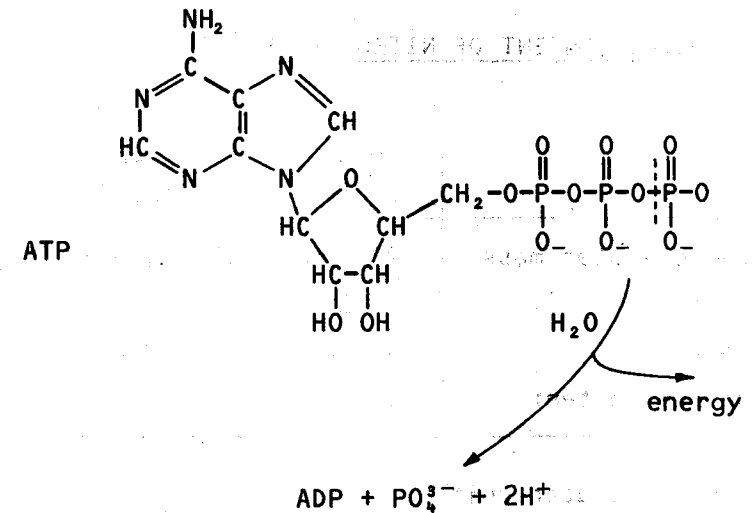
NITROGEN-FIXING BACTERIA

	Type	Example	Occurrence
Free-living	anaerobic (cannot metabolise oxygen)	Clostridium pasteurianum Desulfovibrio desulfuricans	anaerobic soils
	facultative (aerobic when not fixing nitrogen)	Klebsiella pneumoniae Bacillus polymyxa	aerobic and anaerobic soils, water
	aerobic (can metabolise oxygen)	Azotobacter chroococcum Derxia gummosa	aerobic soils
Symbiotic (legumes)		Rhizobium	root nodules of legumes, peas, beans, etc.

4

BIOLOGICAL REDUCTION OF DINITROGEN

In principle, adenosine triphosphate (ATP) hydrolysis provides the energy for the process.



5

SUBSTRATES OF NITROGENASE

Substrate	Products of reduction
dinitrogen (N_2)	$2NH_3$
proton (H^+)	$\frac{1}{2}H_2$
methyl isocyanide ($CH_3N\equiv C$)	$CH_3NH_2 + CH_4$ (+ C_2H_2 and C_2H_4 in low yield)
ethyne ($HC\equiv CH$)	$H_2C=CH_2$
cyanide ion ($C\equiv N^-$)	$CH_4 + NH_3$
carbon monoxide ($C\equiv O$)	not reduced

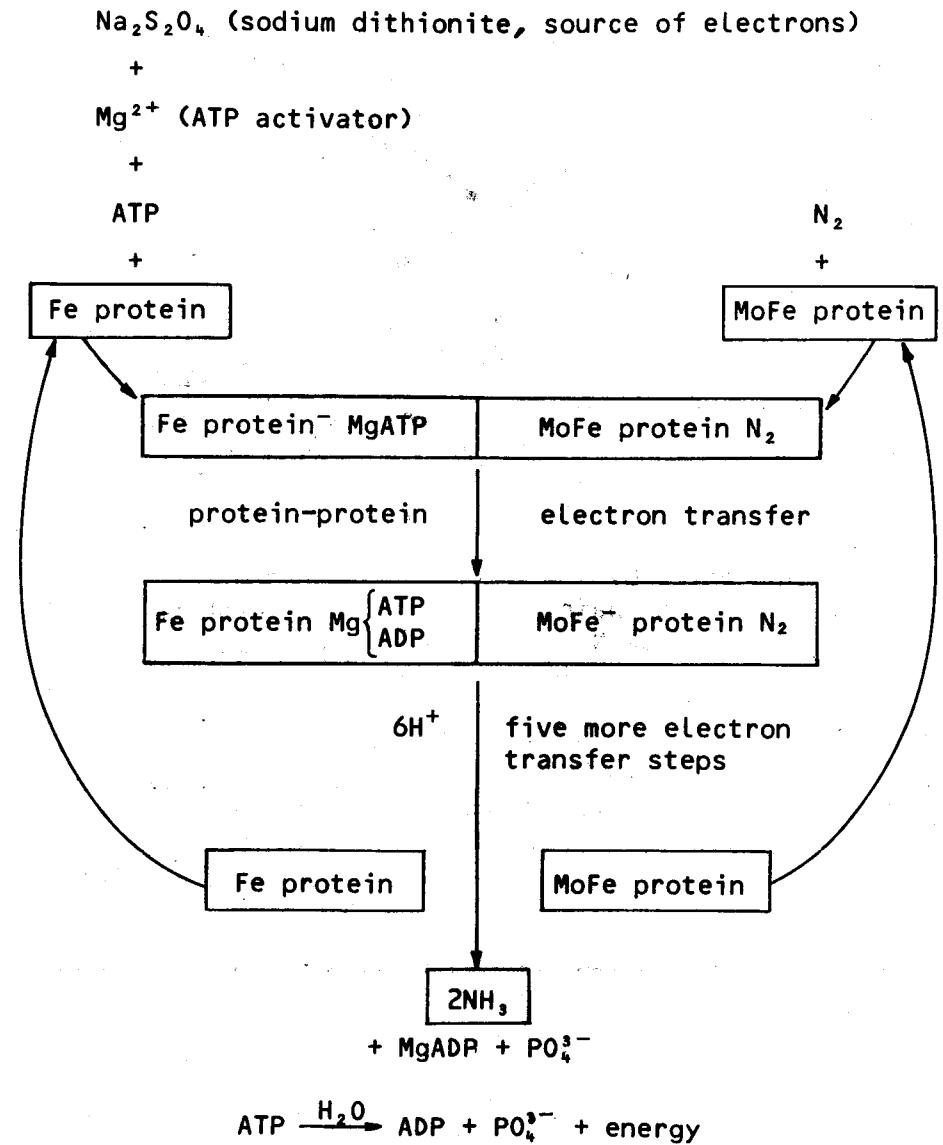
6

METAL CONTENT OF NITROGENASE PROTEINS

	Mo-Fe protein	Fe protein
relative molecular mass	220 000	55 000 - 70 000
Mo content [†]	2	0
Fe content [†]	18-32	4
sulphide ion content [†]	18-32	4

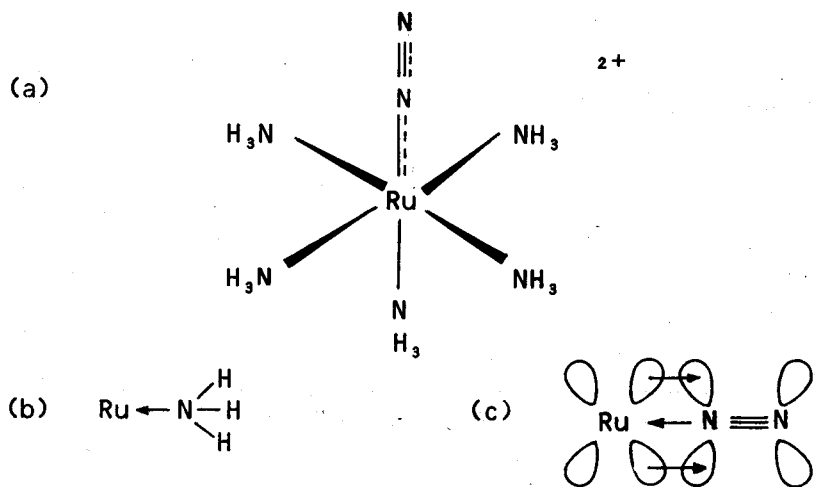
[†] atoms per molecular unit

7

SIMPLIFIED MECHANISM OF NITROGENASE ACTION

8

A DINITROGEN COMPLEX OF RUTHENIUM



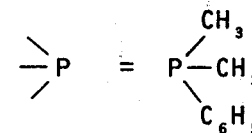
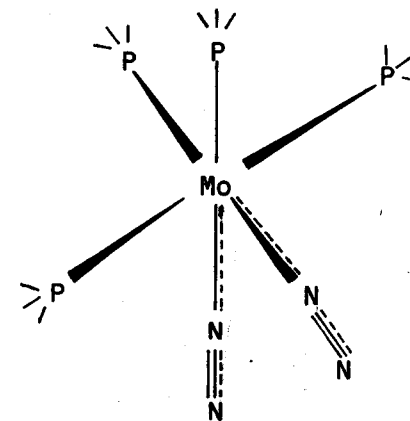
σ -bonding only, by donation of lone pair of electrons from N to Ru.

σ -bonding +
 π -bonding
Ru \equiv N \equiv N

Delocalised bonding. σ -lone pair donated from N to Ru, plus π -donation from filled d-orbitals of Ru to vacant π^* -orbitals on N_2

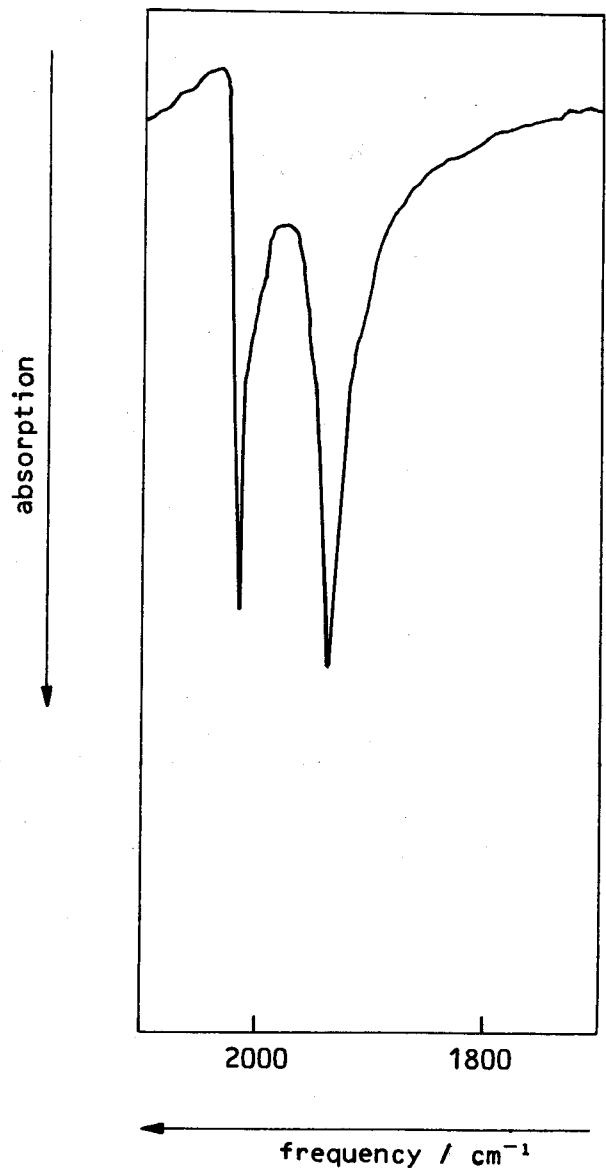
9

A DINITROGEN COMPLEX OF MOLYBDENUM



10

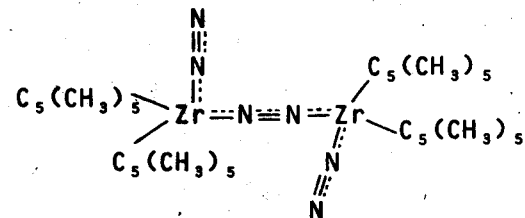
INFRA-RED ABSORPTION SPECTRUM OF $[\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_2]$
IN THE DINITROGEN REGION



12

11

STRUCTURE OF A BINUCLEAR DINITROGEN COMPLEX



12

SPECTROSCOPIC DATA AND BOND DISTANCES FOR DINITROGEN
AND ITS COMPLEXES

Compound	Frequency of N_2 vibration (cm^{-1})		N-N distance (\AA)
	IR	Raman	
N_2	-	2331	1.0976
$[\text{Mo}(\text{N}_2)_2\{(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\}_2]^\dagger$	1979	-	1.118
$[\text{Zr}(\text{C}_5(\text{CH}_3)_5)_2(\text{N}_2)]_2(\text{N}_2)$	2006 *	-	1.116 *
	2041 *	-	
	1556 [¶]		1.182 [¶]

† a very similar complex to that of frame 9.

* end-on

¶ bridging

¶ weak absorption

13

13

DINITROGEN REDUCING SYSTEMS

Complex	Redg. agent	P _{N₂} /atm	T /°C	Prod-uct	Yield [†]
(a) MoOCl ₃ [*]	TiCl ₃	100	85	N ₂ H ₄	2.0
VSO ₄ ·7H ₂ O [*]	-	100	20	N ₂ H ₄	0.22
VSO ₄ ·7H ₂ O [‡]	-	1	25	NH ₃	0.16
(b) Na ₂ [Mo ₂ O ₄ (cys) ₂] [¶]	NaBH ₄	1	27	NH ₃	0.04
K ₂ [MoO(CN) ₄ (H ₂ O)]	NaBH ₄	1	27	NH ₃ N ₂ H ₄	0.29 0.029

[†] yield expressed as mols NH₃ or N₂H₄ per metal atom.

^{*} with MgCl₂ and KOH in aqueous methanol.

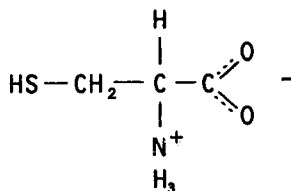
[‡] with added catechol at pH ~10.

[¶] cys = [SCH₂CH(NH₂)CO₂]²⁻ from cysteine (frame 14).

(a) = systems developed by Shilov.

(b) = systems developed by Schrauzer.

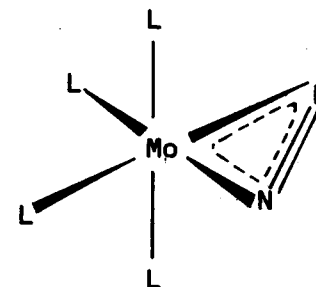
14

THE CYSTEINE MOLECULE

15

SIDEWAYS-BOUND DINITROGEN

A.



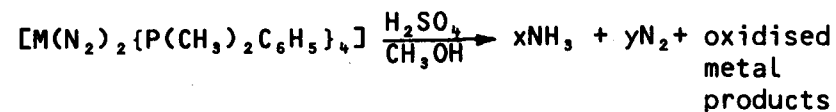
L = other ligands

B.



M_L = Mo or V atoms plus attached ligands, which bind to Mo and V via oxygen atoms.

16

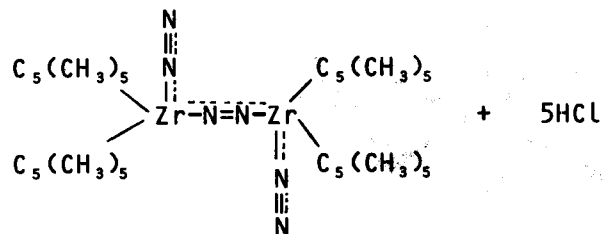
PRODUCTION OF AMMONIA FROM A MONONUCLEAR COMPLEX

$$M = W, x = 2, y = 1$$

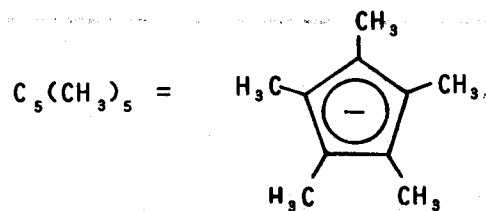
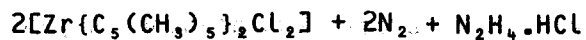
$$M = Mo, x = 1, y = 3/2$$

17

PRODUCTION OF HYDRAZINE FROM A BINUCLEAR COMPLEX

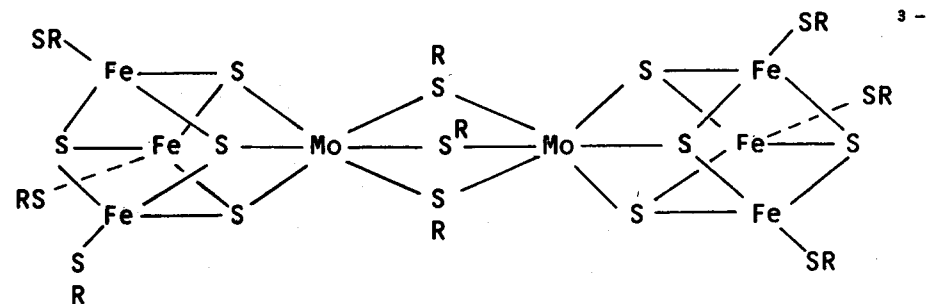


toluene -80°C



18

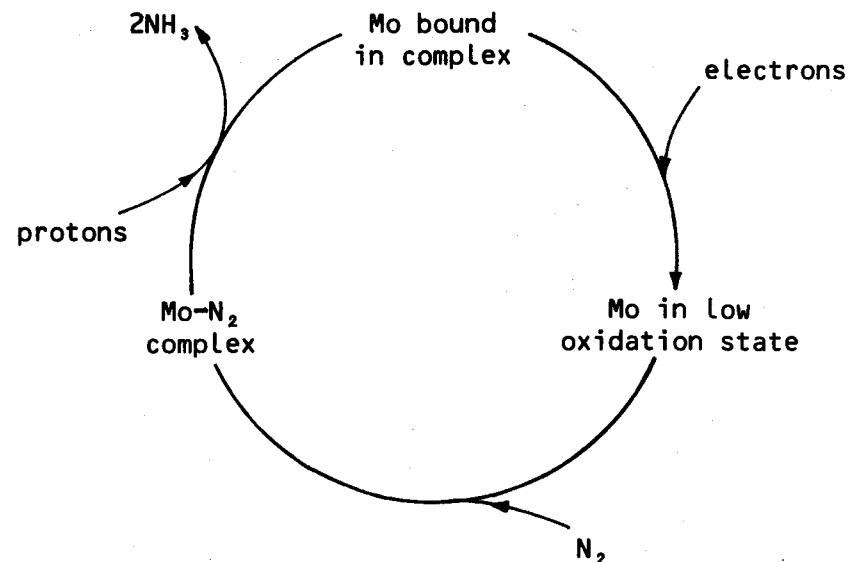
A COMPLEX CONTAINING MOLYBDENUM, IRON AND SULPHIDE IN A 'CLUSTER'

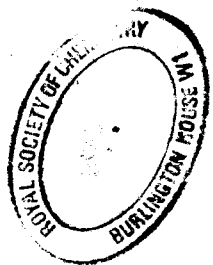


$\text{R} = \text{C}_6\text{H}_5 \text{ or } \text{C}_2\text{H}_5$

19

CYCLIC PROCESS FOR THE REDUCTION OF DINITROGEN





FURTHER READING

- J R Postgate: Nitrogen Fixation (Studies in Biology No. 92), Arnold, London, 1978
A general coverage of biological aspects.
- S P S Andrew: Haber Process, Education in Chemistry 1978, 15, 115.
A brief summary of the Haber process.
- R L Richards: Nitrogen Fixation, Education in Chemistry, 1979, 16, 66.
A brief summary of chemical aspects.
- J Chatt, L M Camara Pina and R L Richards (editors),
New Trends in the Chemistry of Nitrogen Fixation,
Academic Press, London, 1980.
A comprehensive account of chemical aspects.