

THE
TECHNOLOGY
OF THE
NEW SOUTH WALES TORBANITE
(INCLUDING AN INTRODUCTION ON OIL SHALE)

by
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P R E F A C E.

Although the nature of the products of thermal decomposition of oil shale has attracted the attention of both scientist and industrialist, oil shale possibly ranks as one of the least investigated substances which occur naturally and which yield valuable products on decomposition.

Scientists may approach the subject of oil shale from different aspects; for instance, the geologist may be interested in its rock structure and stratigraphy; the chemist may explore its fundamental character, or the nature of its decomposition; while the botanist may be required to explain its origin. The interest of the industrialist is aroused because the decomposition products of oil shale have extensive commercial value.

Unfortunately, most of the published work on oil shale has been based on geological observation or microscopical examination, and while these

investigations have produced interesting data, very little information is available on the properties of oil shale, per se, and of its reactions during decomposition.

As frequently observed in processes of similar nature, industry has progressed without obtaining full knowledge of the structure of its raw material and the types of reaction which occur during the commercial process. Especially is this so in the oil-shale industry where practically every operation is based on empirical knowledge. In order to achieve an effective and economic procedure, it is necessary to have a clear understanding of the nature of the raw substance and of the reactions which occur during its decomposition. In the present case, this knowledge should include as much information as can be made available on the chemical and physical properties of oil shale and a knowledge of the reactions which take place during the decomposition of oil shale to produce oil, gas and residue.

The results here presented are offered as an attempt at such a study of one oil shale - The New South Wales Torbanite - in the hope that the industrialist

and the scientist will progress together in the development of one of Australia's potentially rich resources - Oil Shale.

Reg. J. Cane.
23.2.45.

TABLE OF CONTENTS.

				<u>Page No.</u>
PREFACE	2
CONTENTS	5
ACKNOWLEDGEMENTS	8
FOREWORD	10
OUTLINE	11

SECTION IOIL SHALES AND THEIR DISTRIBUTION.

Definition	13
Distribution	13
Estonia	14
Scotland	15
America	17
Africa	18
Asia	18
France	19

OIL SHALES OF AUSTRALASIA.

Tasmania	20
Queensland	22
The Port Curtis Shales	22
The Torbanites of Alpha and Plevna	23
New South Wales	24
Coorongite	26
New Zealand	28

THE TORBANITE OF THE UPPER KAITIAROI BASIN

History	31
Distribution	32
Origin	34

SECTION IIPART A. THE PHYSICAL PROPERTIES OF TORBANITE.Page No.

Introduction	38
Specific Gravity	40
Specific Gravity and Oil Yield	47
Fracture	49
Structure	49
Microscopical Features	50

Thermal Properties.

Specific Heat	52
Thermal Expansion	58
Thermal Conductivity	62
Heat of Combustion	63
Heat of Wetting	68

Optical Properties

Colour	71
Refractive Index	73
Fluorescence	73
X-Ray Diagrams	75

<u>Electrical Properties</u>	78
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PART B. THE CHEMICAL PROPERTIES OF TORBANITE.

Introduction	79
Ultimate Analysis	80
Proximate Analysis	88

<u>The Constitution of Torbanite Kerogen</u>	97
Biological Background	97
The Nature of the Fatty Matter	101
The Polymerisation of Unsaturated Fatty Acids	103
Structure of Kerogen from Algal Origin	106
The Solubility in Organic Liquids...	110
Analysis of Torbanite Ash	120
The Oxidation of Torbanite	124
Structure of Kerogen from Analysis	127
Sulphur and Nitrogen in Kerogen, Role of	133

SECTION IIIPART A. THE PHYSICAL NATURE OF THE DECOMPOSITION

Minimum Temperature of Decomposition	137
Rate of Decomposition	143
Decomposition under Retorting Condi- tions ...	161
Heat Balance of the Decomposition reaction ...	167

PART B. THE CHEMICAL NATURE OF THE DECOMPOSITION 197

The Intermediate Products ...	199
Vacuum Distillation of "Bitumen"	208
Discussion and the Structure of Kerogen	210
Some Factors in the Thermal Decompo- sition ...	226

SECTION IV.CONCLUSIONS AND REFERENCES.

ACKNOWLEDGEMENTS.

The investigations contained in this thesis were carried out in troubled times (1939-1949) and for this reason, the writer was unable to obtain all the overseas information he desired, and certain pieces of equipment were not procurable in this country. Furthermore, as a combustion furnace and a refractometer were not available in the writer's laboratory and had to be obtained on loan, ultimate analyses and refractive indices are not given very frequently.

The writer wishes to thank those libraries and institutions, both in Australia and overseas, which placed Journals and Papers at his disposal, and also the Departments of Mines of New South Wales, South Australia, Queensland, New Zealand and South Africa for samples.

Finally, he would like to express his gratitude to National Oil Proprietary Limited, Sydney, for the facilities to enable him to carry out the research; to Mr. L. J. Rogers for his comments and encouragement, and to Professor W. E. Kurth for his interest, and for introducing the writer to the subject.

The work contained in this thesis represents entirely original work by the writer, and apart from results cited, very little specific information has been taken from the

work of others.

All references to literature have been quoted in the appropriate places, and any experimental work, other than that of the writer, has received due acknowledgement in the text.

A small portion of the investigation, together with other results not quoted herein, has been published in current scientific literature; reprints of these papers are enclosed inside the back cover of this thesis.

FOREWORD.

The broad outline of the investigations embodied in this thesis was envisaged while the writer was carrying out post-graduate work in the Department of Chemistry in the University of Tasmania. The major portion of the work was undertaken between the years 1939 and 1944, during which time the writer was a member of the technical staff of National Oil Proprietary Limited at Glen Davis, New South Wales. Certain portions, namely those dealing with X-ray diffraction, thermal conductivity, oxidation and certain electrical properties, were carried out in Melbourne in 1944 and 1945.

The writer was fortunate in that the nature of his duties and local conditions in Glen Davis allowed him to devote nearly "full-time research" to the subject, but because of company policy, the type of work varied considerably from time to time. However, the subject matter contained herein has been arranged to follow a logical sequence.

Section III Part A The Physical Nature of the Decomposition of Torbanite.

Part B The Chemical Nature of the Decomposition of Torbanite.

NOMENCLATURE.

To avoid later confusion it is desirable to point out that some doubt exists in regard to the classification of oil shale in general and cannel coal in particular.

A true cannel, although often having a high oil yield, consists mainly of plant macerals, whereas an oil shale, as the word 'shale' implies, contains a large amount of mineral matter. In Australia, on the other hand, the term 'cannel' usually designates an oil shale having a low oil yield, a black streak, and of which the ratio of volatile matter to Fixed Carbon is less than unity. For this reason it is preferable to give the term "Torbanite" to the rich Australian oil shale of the Kamilaroi Basin, as this substance closely resembles the "Boghead Cannel" of Torbanehill, (Scotland) commonly known as Torbanite, in fact many authorities consider that the 'kerosene shales' of New South Wales should not be described as oil shale, and therefore any distinct division is somewhat confusing.

If a definite demarcation, based on physical features, be made between an oil shale and a Torbanite, the important deposits of the latter are few and are limited to Australia, Scotland, South Africa, France and Kentucky.

SECTION I.

OIL SHALES AND THEIR DISTRIBUTION.

DEFINITION.

An oil shale may be defined as an argillaceous or arenaceous sedimentary rock, having an organic origin, the organic matter of which decomposes at elevated temperatures to yield substances of lower molecular weight, all three phases being represented, liquids, solids and gas. The liquid products are similar to petroleum and are not contained in the original shale. (The term 'oil shale' is used here in its widest sense.) A rich oil shale which resembles that discovered at Torbanehill, Scotland, may be referred to as a Torbanite.

DISTRIBUTION.

Oil shale occurs more frequently than is usually believed, having been found in widely scattered parts of the world, and in no particular geological age.

The main deposits of oil shale (including Torbanite) are found in:-

Estonia, Australia, South Africa, Scotland, America.

Other deposits occur in Manchukuo (49), France (62), Sweden (30), England (36b), Italy (9), Germany (64), Norway (3), Russia (37), Spain (24), and Czechoslovakia (61).

The following brief survey covers the main deposits mentioned above.

Estonia.

Probably the most extensively developed oil shale in the world is that of Estonia, and under Government control these deposits have received careful investigation, both from the economic and scientific point of view.

This oil shale has a calcareous skeleton and occurs in the Ordovician limestone of north-eastern Estonia. It is unnecessary to give any details here, as every aspect of this material has been treated by Iats in his monograph "Der Estlandische Brennschiefer - Kukersit, seine Chemie, Technologie und Analyse.", published in Estonia in 1934.

However, a few of the salient features may be mentioned and the following properties are taken from Iats (loc. cit.)

Colour:	Usually buff but may vary from reddish to a yellowish-green.
Specific Gravity:	1.3 to 1.8
Moisture:	10 - 14%
Carbon Dioxide:	8 - 13%
Ash:	30 - 40%
Oil Yield:	20 - 37% (of raw shale).

Ash Analysis:	SiO ₂	29 - 31%
	Fe ₂ O ₃	7 - 8%
	Al ₂ O ₃	7 - 11%
	CaO	43 - 40%
	SO ₃	9 - 8%
	MgO	2 - 1%
	K ₂ O + Na ₂ O	3 - 4%

(these figures have been rounded off for convenience.)

Literature.

- K. Luts:- Loc. cit.
- P.N.Kogerman:- On the chemistry of the Estonian Oil Shale "Kukersite". Oil Shale Research Laboratory Bull N° 3, May, 1932, Tartu, Estonia.
- P.N.Kogerman:- "Hundred Years of the Chemical Investigation of an Oil Shale?" "Oil Shale and Cannel Coal". The Institute of Petroleum, London, 1938.
- H. Gault:- "Etude préliminaire des schistes d'Estonie" Bull. lab. pétrole. Univ. de Strassbourg, Mar., 1922.

Scotland.

The oil shales of Scotland occur in juxtaposition to coal, with which material they are often confused. About twenty-two seams are found interspaced with other rocks, such as limestone, shale, and clay. The deposits are variable in composition and consequently a single description will not suffice to cover all types. The Scottish shale, as distinct from torbanite, is a dark grey, well-laminated rock, easily cut with a knife and slightly elastic. In macroscopic features it resembles that from Mt. Kembla in Australia, a description of which is given later.

Nevertheless as the Boghead Cannel closely resembles the torbanite of New South Wales, this is the only deposit which will be treated in any detail.

Although Boghead Cannel was known some years previous to 1853, it was not until this date that the mineral came

into public prominence, due to a lawsuit (Gillespie v. Russel) which ensued over a controversy regarding the exact nature of the material. The Cannel was found at Torbane Hill near Bathgate and has since become known as Torbanite; this name has now been extended to cover all oil shales resembling the above. Owing to its valuable nature the deposit at Torbane Hill is no longer in existence, having been entirely removed by extensive exploitation. This original Torbanite occurred in the Carboniferous stratum and is a fine-grained, massive rock, yielding on pyrolysis over one hundred gallons of oil per ton; it has a conchoidal fracture and it varies in colour from dark brown to black. Microscopical examination reveals a large amount of macerated plant debris, composed of minute bodies, the predominant entity of which being usually referred to as "yellow bodies," which have been shown to be algal remains. The yellow bodies, together with other organic macerals which are present, will be treated in some detail in the section dealing with the nature of the torbanite of New South Wales.

Literature.

- H.R.J. Conacher: "A Study of Oil Shales and Torbanites." Trans. Soc. Geol., Glasgow, 1917; 16, 164.
- R.G. Carruthers: "The Oil Shales of the Lothians". Mem. Geol. Survey 3rd Ed., 1927.
- J.B. Robinson: "A Chemical Examination of the Organic Matter in Oil Shale". Proc. Roy. Soc. Edin., 1914; 34, 190.
- W.J. Skilling: "The Nature of Scottish Cannels". "Oil Shale and Cannel Coal". Institute of Petroleum, London, 1938, p. 32.

America.

The occurrence and nature of the North American oil shales have been described more fully than any other deposits. The Bureau of Mines of the United States, in conjunction with different American Universities, has published several bulletins on the local deposits, the more informative of which are;-

"Oil Shale" by M. J. Gavin. Bull. N° 210.

"Studies of Certain Properties of Oil Shale and Shale Oil"
by E. Guthrie, Bulletin N° 415.

Another important contribution is the American Chemical Society Monograph "Oil Shale" by R. H. McKee. A.C.S. Monograph N° 25, 1925.

The American shales occur in about fifteen states of the United States of America and in about eight provinces of Canada. They are found in many different geological strata and vary in thickness from two feet to six thousand feet or more. However, their oil yield does not compare with that of the Australian torbanite and the present production of oil from them is practically nil. These deposits have been fully covered in previous publications and no useful purpose would be served in describing them in the present treatise.

In addition to the vast deposits mentioned above, a rich torbanite occurs at Beaver Dam (Kentucky) analyses of

which vary between:

Moisture:	0.40 - 0.77%
Volatile Matter:	53.70 - 63.52%
Fixed Carbon:	42.35 - 27.05%
Ash:	3.55 - 8.66%
Sulphur:	1.00%

Oil shale also occurs in most South American countries but mainly in Brazil, Peru and Chili. Unfortunately the available information is very meagre, and it appears that, with two exceptions, the shale is of poor quality. The two exceptions are the Marahuito found in Bahia, and the Olyoca in Espirito Santo, both in Brazil.

Africa.

Oil shales occur in the southern portion of Africa. Although the majority of deposits are of medium grade, the deposit of torbanite which occurs at Ermelo yields over a hundred gallons of oil per ton. From the available information it would appear that the South African torbanite closely resembles that of New South Wales.

Literature.

- S. L. Neppe: A Technical Study of Transvaal Torbanite.
Jour. Inst. Pet. 27, 31, 1941.
- H. Cunningham Craig: The Torbanites of South Africa.
Jour. Inst. Pet. Tech. 16, 620, 1930.
- du Toit: Oil Shale in South Africa.
South African Jour. Industries 4, 346, 1921.

Asia.

The only deposits in Asia which have received any

attention are those of Western Siberia and Manchukuo. Detailed reports on the former are not available but the latter has received extensive consideration in recent years.

The Fushun (Fuchun) deposits of Manchukuo are of very poor quality but as they overlie beds of good coal, the shale overburden has to be removed and therefore its exploitation is warranted. The shale is of a coaly nature and yields on an average about eleven gallons of oil per ton.

A small deposit of torbanite occurs at Hitachi (Kozuda Province) of which the following analysis is given by Godfrey (26):-

Moisture + Volatile Matter	= 72.34%
Fixed Carbon	= 18.80%
Ash	= 8.20%
Sulphur	= 0.66%

France.

Two outcrops occur at Autun and Buxiere-les-Mines and have been exploited for many years. There are two distinct seams, one in the Permian and the other in the Carboniferous stratum. The oil shale is of medium quality and oil yields up to fifty gallons per ton have been recorded.

OIL SHALES OF AUSTRALASIA.

The oil shales of Australia and New Zealand may be divided into different structural types, but will be treated under the following headings, from the point of view of their geographical distribution:

New South Wales.
Tasmania.
Queensland.
New South Wales (excluding the Upper
Kamilaroi Torbanites).
Elsewhere in Australia.
New Zealand.

New South Wales.

Very extensive and rich deposits of torbanite occur in the Kamilaroi Basin of New South Wales. Individual treatment will be given to these in a later section.

Tasmania.

The unique shale of Tasmania, termed Tasmanite ((11) and (24)), has been classified as a "spore shale" by Down and Himus (19b). The oil-producing substance when viewed under the microscope, appears as roundish discs, their diameter being given by Singh (63) as varying between 200-523 μ m. When not damaged the spores are circular in shape but it appears that during fossilisation they have been distorted and ruptured. The general opinion is that they are innumerable sporangia, and Johnson (32) suggests that they are closely allied to Lycopodiaceous macrospores. The shale itself is grey to brownish black in colour with

a well-laminated appearance. The specific gravity varies from 1.72 to 2.62, while the spore case material, which may be liberated by flotation, has a specific gravity of 1.1. Reid (57) gives the following average proximate analysis:-

Moisture:	0.80%
Volatile Matter:	30.84%
Fixed Carbon:	5.86%
Ash:	62.50%
Sulphur:	2.56%

The oil yield is low and the oil is particularly difficult to refine.

Two deposits of rich oil shale have been found in Tasmania and closely resemble the torbanite of New South Wales. These deposits occur as lenticular formations in the Greta series of the Coal Measures, at Mt. Pelion and Preclenna and Proximate Analyses of them have been given by Ward (76) as follows:

	<u>Preclenna</u>	<u>Mt. Pelion.</u>
Moisture:	1.2%	0.4%
Volatile Matter:	42.0%	51.1%
Fixed Carbon:	51.0%	44.3%
Ash:	5.8%	4.2%

Literature:

- A.McI.Reid: The Oil Shale Resources of Tasmania.
Tasm.Geol.Survey (Mineral Resources)
No. 8, Vol. 1, 1924.
- E.E.Kurth: The Oil Shales of Tasmania and New South
Wales.
Unpublished, D.Sc. thesis, University of
Tasmania, 1933.
- R.F.Cane: Studies in Tasmanite Shale Oil.
Pap. Proc.Roy.Soc. Tasm., 23, 1940.

E.E.Kurth and
L.J.Rogers.

"The Oil Shales of Australia"
"Oil Shale and Cannel Coal".
Inst. Pet. Tech. p.193, 1938.

Queensland.

The oil shales of Queensland may be divided into two distinct groups, (a) The Tertiary deposits occurring in the Port Curtis District, and at Strathpine near Brisbane.

(b) The torbanites of Alpha and Plevna.

The Port Curtis and Strathpine Shales; Macroscopically the shale has the appearance of a brown clay with a brown shiny streak, laminations are perceptible, but fracture irregular. There are many intrusions of hard material, formed from fossil sedges, although the shale itself is quite sectile. The highly fossiliferous nature of the shale is due to two entities, leaf impressions and innumerable rentiform bodies, the latter considered by Ball (1) to be the remains^{of} Ostracods, such as Cypris. The material is of very poor quality and the oil produced is dissimilar from that produced from Torbanite. Contrary to all shales so far examined, samples from these deposits showed a distinct porosity for, although the specific gravity in hand specimens varied between 1.3 and 1.5, the powdered shale was much heavier. This was illustrated by the fact that the whole mass of a finely powdered sample (100 mesh I.M.M.) sank in carbon tetrachloride (S.G. = 1.6), whereas hand samples did not. The result would indicate that the organic matter in this type of shale is totally different

or Tasmanite
from either that of Torbanite, or a most intimate binding
between the organic and inorganic constituents.

The results shown below were obtained by the writer
from samples kindly supplied by the Government of Queens-
land.

Proximate Analysis.

	<u>Sample Q4</u>	<u>Q7</u>	<u>Q8</u>
Moisture	5.8%	5.7%	6.4%
Ash	66.4	70.0	71.0
Volatile Matter	21.9	19.3	18.3
Fixed Carbon	5.9	5.0	4.3
Specific Gravity		1.37 - 1.46	
Sulphur		1.4 (avr. sample)	
Nitrogen		0.3 (avr. sample)	

Gray King Assay (18)

Weight Balance.

Wt. Shale	100%	Wt. Residue	76.0%
		Wt. Distillate	19.3
		Wt. Gas	4.7

Distillate: 10.9% Oil
8.4% water.

Oil Yield: 20.8 gallons per ton.

Literature.

- L.C. Ball: "Oil Shales of the Port Curtis District."
Qld. Gov. Min. Jour. 1915, 14, 73.
- L.C. Ball: "Tertiary Shales of Baffle Creek, Port Curtis
District."
Qld. Gov. Min. Jour. 1914, 15, 22.
- L.C. Ball: "Oil Shale at Strathpine".
Qld. Gov. Min. Jour., 1932, 33, 221.

(b) The Torbanites of Alpha and Plevna: In contrast
to the oil shales of Queensland mentioned above, the de-
posits at Alpha and Plevna may be classed as true torba-
nites.

The Plevna deposit is comparatively small and of poor quality, yielding between 20 to 50 gallons of oil per ton. The oil resembles that from the normal torbanite, except that sulphur and tar acids are high.

The Alpha torbanite and the oil produced therefrom cannot be classed apart from those of New South Wales. The oil yield is high and reaches nearly one hundred gallons per ton in some portions of the seam.

The sample supplied yielded the following assay results:

Moisture:	4.6%
Volatile Matter:	53.8%
Fixed Carbon:	14.3%
Ash:	27.3%
Oil Yield:	74 gallons/ton (Gray King).

Literature.

- H.I.Jensen: "Oil Shale"
Q'land. Gov. Mining Jour., 1921, p.92.
- J.H.Reid: "The Tertiary Oil Shales of Plevna-Eungella District".
Q'land. Gov. Min. Jour., 1942, V.43, p.2.
- A.Wade et. al: "A Note on the Plevna Deposit."
Q'land. Gov. Min. Jour. 1941. V.42, p.94.
- J.H.Reid: "Oil Shale Deposit of Drummond Range-Alpha".
Q'land. Gov. Mining Jour., 1940, 41, p.262.

New South Wales (excluding the Upper Kamilaroi Torbanite).

A peat-like deposit is found at Mt. Kembla on the South Coast and is the only material so far examined, resembling a true Scottish oil shale. The macroscopic

features of this oil-yielding substance are different from those of the normal torbanite associated with the coal measures of New South Wales.

The rock is a dull-black, argillaceous material, finely laminated, with indistinctive fracture and greasy to the touch. In structure it is very soft and noticeably flexible, the streak being dark black and shiny.

The oil yield is higher than would be expected from its appearance and the Gray-King assay yield was seventy-eight gallons per ton of a light gravity oil (S.G. = 0.831). The results of a Proximate Analysis of a sample were:

Moisture:	0.42%
Volatile Matter:	43.01%
Fixed Carbon:	19.97%
Ash:	36.53%
Specific Gravity:	1.463
Sulphur:	0.29

It is interesting to note that this deposit was one of the first to be discovered in Australia.

Four deposits are found in the LOWER Coal Measures at; Muswellbrook, Murrurundi and Greta in the North and at Clyde River in the extreme South. Their occurrence in the LOWER Coal Measures is exceptional and they may be classed apart from the Upper Kamilaroi Torbanite.

A sample of the Greta material was not available but the following analysis has been quoted by Carne (8):

Moisture:	1.47%
Volatile Matter:	53.80
Fixed Carbon:	27.95
Ash:	15.87
Specific Gravity:	1.30
Sulphur:	0.91

The Murrurundi deposit occurs at the extreme north-eastern base of the Coal Measures and is associated with volcanic agglomerates and basalt. In appearance it is more coal-like than the normal torbanite, and the streak is black and shiny; normally this fact would indicate a poor oil-yield, but the evidence is misleading as the material is comparatively rich; this feature may be explained by the peculiar conditions of deposition.

Only a small sample was available for investigation and the results obtained are shown below:

Moisture:	1.80%
Volatile Matter:	68.09
Fixed Carbon:	11.90
Ash:	18.21
Specific Gravity:	1.191
Sulphur:	0.93
Oil Yield:	153 gals./ton.
Sp. Gr. of Oil:	0.858

Elsewhere in Australia.

Isolated patches of oil-yielding material occur in the Northern Territory and Western Australia.

Although the occurrence of true oil shales has not had authentic verification in South Australia, a sapropelic deposit of a gummy nature occurs in the Coorong district, and also on Lake Martagallup in Western Australia.

Coorongite (79), as the South Australian deposit is

known, originates in an algal growth which has been identified by Blackburn (5) as *Botryococcus braunii* (Kutzing)). Coorongite decomposes on heating to yield an oil similar to certain shale oils, e.g. that from Strathpine, Queensland, but dissimilar from that produced from Torbanite. Specimens examined by the writer were yellow to brown in colour and varied in texture from a soft kelp-like nature to hard chips. Proximate Analysis of the sample of Coorongite gave the following results:

Moisture:	1.63%
Volatile Matter	82.13
Fixed Carbon:	6.91
Ash:	9.33%

(a small amount of sand grains are included in the ash).

Fuel Ratio: $\frac{VM}{F.C.} = 11.9$

On retorting in the Gray-King apparatus one sample yielded 106 gallons per ton of pungent oil, the specific gravity of which was 0.886.

A.S.T.M. distillation of the oil was as follows:

I.B.P.	37°C.
5%	71°C.
10%	112°C.
20%	178°C.
30%	220°C.
40%	247°C.
50%	275°C.
60%	298°C.
70%	341°C. with decomposition.

When quite fresh, Coorongite is soluble in aromatic solvents and in carbon bisulphide but its solubility decreases to a few percent after keeping for some time.

Some specimens of the aged material showed both a rubbery nature and a "swelling" in benzene, indicating thread-molecules, probably formed from the fatty acids present in the fresh material.

Literature.

A.C. Curming: "Coorongite - A South Australian Elastite".
Proc. Roy. Soc. Vic. 15, New Series, pt. I, 124,
1902.

L.K. Ward: Geological Survey of S.A.
Bull. No 2, 15, 1913.

H.R.J. Conacher: "Coorongite and its Occurrence."
Oil Shale and Cannel Coal, 42, 1938.

New Zealand.

The occurrence of oil shale of medium quality has been reported in several isolated places in New Zealand and comparatively large deposits are found in the Nevis Valley and at Orepuki. The writer obtained first-hand information on the Orepuki deposit and the results were published elsewhere, portion of which will be quoted herewith:-

"These deposits occur in the upper coal measures of the Permo-carboniferous age. The exact extent of the deposit is not known; it is of the order of one million tons, but systematic boring may reveal a greater extent. A few attempts have been made to exploit this seam but without success, partially on account of the nature of the oil itself. The seam is about 44" thick and has a thick seam of brown coal underlying it.

Physical Characteristics and Microscopic Structure. Macro-

scopically the rock is well laminated and of dark brown

colour, with conspicuous speckled appearance, due to the presence of numerous whitish minute crystals of micaceous habit, lying along the bedding plane. The gravity of a representative sample of the shale is 1.41, measured on a bulk sample. The streak is brown-black and is moderately shiny.

Proximate Analysis. A representative analysis would show:-

		<u>Ash-free Basis.</u>
Moisture:	3.1%	4.6%
Volatile Matter:	53.9%	80.2%
Ash:	32.7%	
Fixed Carbon:	10.3%	15.2%

Results of Gray-King Assay (20 gm. sample taken.)

Description	Weight %
Charge	100
Coke	52.8
Oil + Water	34.0
Oil	23.8
Water	10.2
Naphtha	6.9
Total Yield, gals./ton	<u>80.2</u>
Gas Mls. at 20°C. and 760 mm.	1180
Specific Gravity:	
Oil	0.900
Gas (air = 1)	0.892

Torbanite has been reported at Mongononui (69), the proximate analysis of which is given as:

Moisture:	0.51%
Volatile Matter:	87.33
Fixed Carbon:	7.92
Ash:	4.24

Literature.

- R.F.Cano: "Studies in Orepuki Oil Shale".
N.Z. Jour. Sci. and Tech., V.23, p.212B, 1942.
- P.G.Morgan: "Oil Shales at Waikato".
N.Z.Jour. Sci. V.2, p.119, 1919.
- R.W.Willet and
H.W.Wellman: "The Oil Shale Deposit at Orepuki, Southland".
N.Z.Jour. Sci. and Tech. V.21, 84B, 1940

THE TORBANITES OF THE UPPER HAMILTON BASIN.History.

The French exploratory expedition of 1802 made the first record of Australian shales in 1807 and further reports were given by Commander Duprey before the Royal Academy in 1825. The first company to exploit torbanite was formed in 1860 and the first retorting took place in 1866. Torbanite from Australia was exhibited in the Paris Exposition in 1854 and in the London International Exhibition in 1862.

In those times, as colonists and prospectors moved inwards, many reports of the occurrence of torbanites in the Blue Mountains country were forthcoming. Great blocks of torbanite were often found strewn down the gorges, having been carried along by the mountain torrents. This phenomenon has been explained in the following manner:-

"The overlying sandstone is very resistant to weathering but the coal measures, being less stable, erode away, causing the cliff face to collapse and liberate the underlying deposits of torbanite. It is well known that when the pressure on a torbanite stratum is relieved, as in mining, it shows great tendency to expand, often with explosive force and massive blocks are thrown off. When this occurs on an open face, the mass is carried down by water into

the valley below".

The present writer has had an opportunity to see a block of torbanite about one cubic yard in size, carried about two hundred yards in one heavy storm.

Distribution.

The great accumulation of Torbanite found in New South Wales is situated in the Kamilaroi Basin and covers an area of approximately three thousand square miles (see map opposite). This field is made up of a number of deposits which vary in size from about seven square miles to isolated small patches; as many as thirty-three deposits have been described in the literature and it seems probable that many more exist under the Hawkesbury sandstone. However, owing to the rough nature of the terrain, exploratory surveys are difficult. In some places the sheer rugged cliffs, with exposed faces over one thousand feet high makes a study of the geographical and stratigraphical distribution an easy task, but in other localities the arrangement is by no means easy to follow.

Charles Darwin, writing in 1890 (13) says:-

"These valleys which so long presented an insuperable barrier to the attempts of the most enterprising of colonists to reach the interior are most remarkable. Great armlike bays expand at their upper ends, other branch from the main valleys and even leave in them great almost isolated masses..... the most remarkable feature of this

structure is that although several miles wide at their head they generally contract towards their mouth to such a degree as to become impassible.....When cattle are driven into the Valley of the Wolgan by a path (which I descended) they cannot escape; for this valley is in every part surrounded by perpendicular cliffs and eight miles lower down it contracts from an average width of a half a mile to a mere chasm impassible to man and beast."

The torbanites of the Hamilaroi Basin appear close to the western margin of the Upper Coal Measures and extend for nearly 250 miles north and south. Roughly speaking they can be said to occupy an acute triangle with the deposits of Ulan and Baerami as the base line and Reedy Creek as the vertex (see map). From a stratigraphical viewpoint, the various deposits are widely dispersed, with nearly three hundred feet between the Ilford deposit, which is less than 30 feet below the Triassic Hawkesbury sandstone plateau, and the Mount Marsden deposit in the lowest coal horizon immediately above the Marangeroo Conglomerate. The majority of the known deposits, which are usually lenticular in shape, occur fairly close to the coal horizons, but there are isolated examples, such as those at Barigan and Katoomba (Mort's Upper Seam).

Origin of Torbanite.

There seems little doubt that torbanite is of vegetable origin, and that the aboriginal matter was of algal nature. Although this work is concerned with the present structure of torbanite, and not with its genesis, a discussion of its origin is important inasmuch as it helps to elucidate the present constitution of the substance.

Investigations into the mode of origin of torbanite, and of oil shale generally, began to receive serious consideration following the famous Torbane Hill case in 1853, and from this year onwards many theories have been put forward ascribing various origins to the material. These theories have resulted mainly from microscopical and geological investigation, and often led to greater confusion than before.

Although much has been done by the microscopist in explaining the origin of torbanite, insofar as the present problem is concerned, it provides practically no evidence at all of its present structure, and it is obvious that the original nature of the material has been so changed by metamorphism and geologic pressure as to render it nearly unrecognisable. It is justifiable, therefore, to assume that no useful purpose would be served by analysing the various theories that have been postulated.

When examined microscopically, torbanite is resolved into a heterogeneous structure in which yellow, orange and

red particles are seen distributed throughout a brownish-black, opaque matrix. The yellow particles, usually termed 'yellow bodies', are predominant, and the exact nature of these 'yellow bodies' and how they originated has led to the confusion above mentioned. They have been identified variously as spores, pollen grains, spore cases, partially bitumenised matter, resins, waxes and hydrocarbon material.

In 1892 Bertrand and Renault (4) published a paper which made the first important contribution to a knowledge of the origin of torbanite. Bertrand and Renault stated that the 'yellow bodies' were the remains of algae, and later papers have given further proof of their contention. In 1936, Temperley (71) gave very strong evidence that the algae were identical with, or very similar to, the now-living *Botryococcus braunii* found in Coorongite.

The general theory of the mode of origin of Torbanite, as held by the present writer, is as follows:-

Torbanite originated in a specific type of colonial microscopic algae which flourished in the transitional era between the Permian and Carboniferous ages. Along the western margin of the Coal Measures existed a series of lakes or lagoons in which algae flourished under excellent conditions but with more or less seasonal changes. The shallowness of these lakes is shown by fossils of *Glossopteris*, in which the plant is still in the living position.

Silt, clay and other finely divided material containing small amounts of humus were carried by streams into these lakes, and formed a muddy ooze on the bottom of the water in which the algae were growing.

After the death of the algal colonies, possibly caused by regular seasonal changes, the decaying matter sank through the water to produce a layer of sapropel on the bottom of the lake.

Owing to climatic changes, the lakes dried up and the algae, together with the inorganic material, caked together to give a thin layer. This cycle was repeated until an appreciable deposit was formed, consisting of a band of material of laminated structure.

Separating the laminated bands of oil shale were layers composed almost entirely of inorganic sediment (shales etc.) or vascular plant sapropel.

This phenomenon, as yet without the repeated cycles over long periods, occurs at the present time in South Australia (see Coorongite) and also in other isolated places in the world. These sapropelites are of algal genesis and *Botryococcus braunii* occurs in nearly all of them. Zalessky (78) gives the composition of the material from Lake Balkash (Siberia) as:-

Carbon	73.76%
Hydrogen	10.61
Sulphur	1.03
Nitrogen	0.56
Oxygen	13.74
Phosphorus	Trace

Specific Gravity: 0.995

Ash: 3 - 5%

Following the deposition stage, the decaying matter was covered with overburden and then, over geological times and with the pressure of the overlying strata, the gummy material polymerised to a hard massive rock. The subsided rock was brought to the surface in later Tertiary elevation and the fissures in the country exposed the material as it is found to-day.

There is little evidence that other than plant matter took part in the formation of torbanite, but animal remains have been identified in certain oil shales. The plant matter, includes minor amounts of spores and remains of higher plants in addition to the algae. In order to reduce the plant remains to a macerated mass and to explain the lack of cellulose derivatives in torbanite, it seems probable that the decaying algae were acted upon by some type of subaquatic bacteria.

SECTION IIPART A.THE PHYSICAL PROPERTIES OF TORBANITE.INTRODUCTION.

Torbanite contains two distinct and dissimilar types of matter, the proportions of which may vary greatly between any one sample and another; the organic portion which consists of small translucent particles, and the inorganic portion, composed of clays, sands and other adventitious mineral matter. Therefore, all physical properties and, to a less extent, chemical properties, are a function of the amount of each component, and these properties will vary between limits determined by the maximum permissible amount of either which can be present. When the properties of the organic portion are to be considered, and to obtain data which may be correlated on a common basis it is desirable that all properties be reduced to an 'ash-free' basis.

It may be said at the outset that, apart from intrinsic variations due to changes caused by the amount of mineral matter present, no single factor may be taken as sufficient criterion for the identification of any one deposit from another. Examination of the results obtained from the investigation of very many samples from over seventeen deposits, and the oil obtained therefrom, does not reveal

any particular property which would serve as a means of demarkation or identification. Certainly, torbanite which produces over one hundred and seventy gallons of oil per ton is not likely to be found in the Glen Davis deposit, but there are several localities from which samples may be obtained producing this amount of oil, e.g. at Coolaway, Joadja, or Wollar; on the other hand, it is impossible to differentiate between a poor sample from Coolaway (which is usually outstanding for its richness) and one from Glen Davis, if the latter were particularly rich.

Several attempts have been made to effect an identification by means of certain properties, but reported observations have been based on hand-specimens and not on the deposit as a whole. It may be stated, with the reservations above mentioned, that variations within one deposit may be, and often are, as great as the variations between any two deposits, which renders valueless any observation as a means to identification with regard to locality of origin.

The variations discussed here are caused, in the main, by differences in the ratio of organic to inorganic matter and not by changes in the constitution of the kerogen (the term applied to the organic matter in oil shales and torbanites) as a whole, the composition of which is remarkably uniform when considered as a separate entity. Although microscopic examination reveals that kerogen has a

heterogeneous structure, variations in the amounts of the different components seem to have little effect on macroscopic properties when these properties are reduced to an 'ash-free' basis, and in certain sections of this work the organic matter will be treated as a uniform chemical body. Although an explanation of the constitution of the organic matter of torbanite is an extremely complex problem, and as yet has not been elucidated, it is evident that one is dealing with the same underlying chemical structure in all deposits.

The removal of the inorganic matrix of torbanite, while leaving the organic portion unchanged, is no easy task; physical methods, based on the different densities of the two components will remove the large mineral fragments, but have no effect on the microscopic particles of clay etc. which are intimately bound up with the kerogen itself. Chemical attack is a little more satisfactory as frequent washings with hydrochloric and hydrofluoric acid will reduce the ash content to a few percent, but under these conditions it seems doubtful whether the organic matter would remain unchanged. Fortunately a small lens of extremely rich torbanite was discovered at Marangaroo (New South Wales) (10b), the ash content of which was less than that normally associated with the living algae, and this material was of great value in this investigation.

Specific Gravity of Torbanite.

The specific gravity of torbanite increases from an

Specific Gravity of Torbanite vs. Amount of Ash

Graph N° 1.

Specific Gravity

1.4

1.3

1.2

1.1

1.0

0.9

5

10

15

20

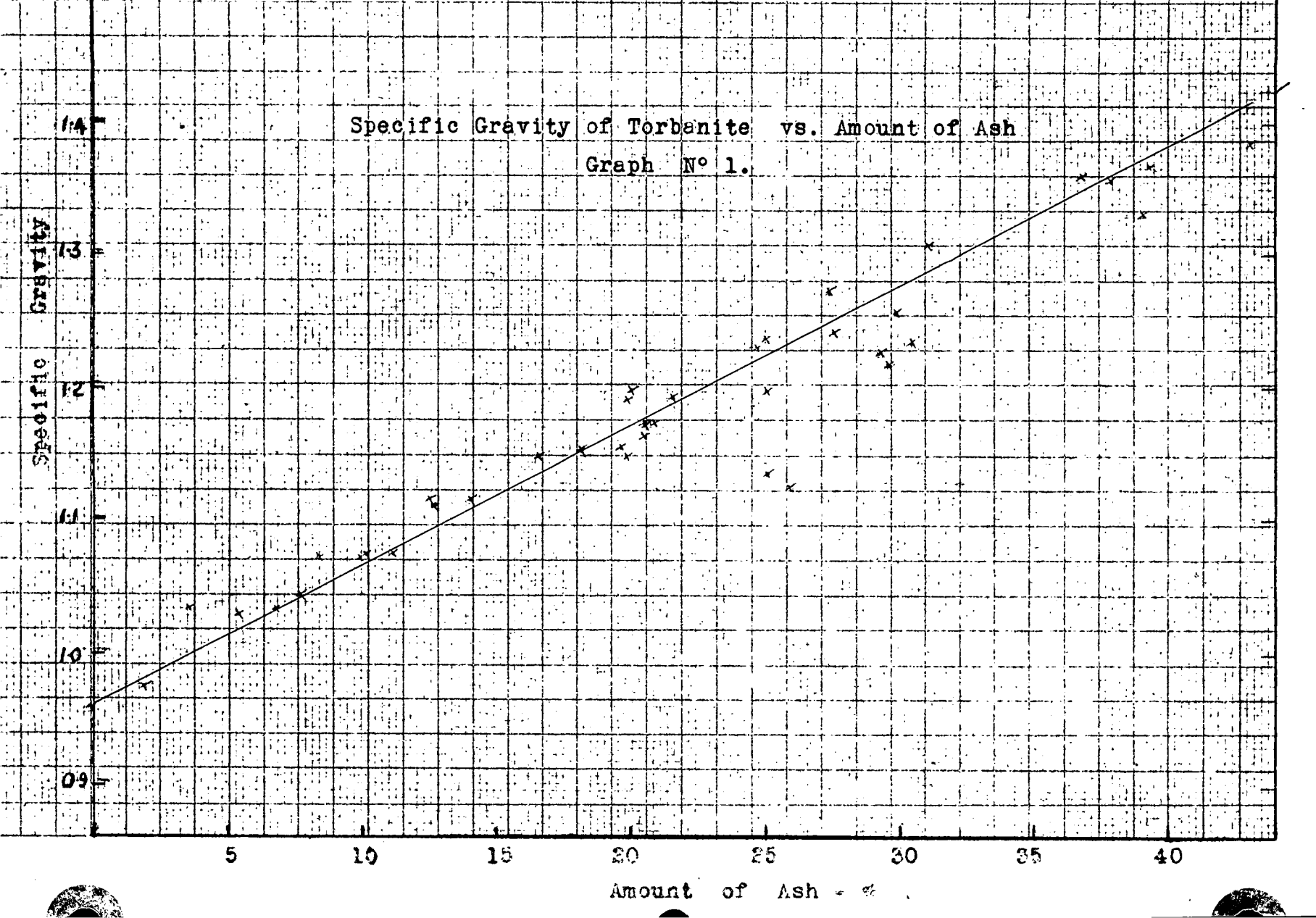
25

30

35

40

Amount of Ash - %



observed minimum of 0.973 to an indefinite maximum of 2, but most samples will vary between the limits of 1.1 and 1.4. It is difficult to designate a maximum specific gravity as this depends on the limitations of the definition of torbanite, as distinct from oil shale, but it is rare to find specific gravities in excess of 1.5 for a true torbanite, except in the case of silicified material when the specific gravity will sometimes reach 2, but rarely exceeds it.

Experimental.

Small test blocks were used to determine specific gravities, a Nicholson hydrometer being employed, and the determinations carried out at 20°C. or corrected thereto. A small amount of methanol was used as a wetting agent.

The ash determinations followed the method set out in the D.S.I.R. Bulletin "The Analysis of Coal" (18).

The results obtained, together with a few analyses from other sources are shown in Table 1 and in the graph opposite.

TABLE 1.

<u>Locality</u>	<u>Specific Gravity</u>	<u>Ash Content.</u>
Marangaroo	0.973	1.81
Coolaway	1.032	6.64
	1.075	10.01
	1.043	7.73
	1.154	18.06
Wollar	1.071	9.89 a
	1.032	3.52
	1.164	20.43
	1.074	11.05
	1.126	25.88
	1.334	38.99 a
Airly	1.115	14.03
	1.148	16.55
	1.136	25.07
	1.116	12.40 β
	1.359	36.67 β
Glen Davis	1.193	21.41
	1.228	29.32
	1.274	27.21
	1.308	31.09
	1.155	19.63
Barigan	1.217	29.45 a
	1.193	19.81
	1.231	24.61
	1.170	20.41 β
Newnes	1.173	20.81
	1.241	27.53
	1.148	19.80
Jpadja	1.028	5.45 β
	1.198	24.97 β
Baerami	1.237	24.91
	1.198	20.03
	1.170	20.41 β
	1.256	29.80 β
Tong Bong Mt.	1.384	43.05 a
	1.357	37.79
	1.368	39.21
Ulan	1.110	12.56 a
Ilford	1.235	30.37 a
Wondo	1.072	8.85 β

(a) data from Dulhenty (15)

(β) data from Carne (8).

Extrapolation of the plot to zero ash-content leads

to the conclusion that the specific gravity of pure kerogen is about 0.96.

Rich samples were chosen for the above correlation, as this choice tends to minimise any discrepancy caused by changes in the constitution of the mineral matter per se.

Statistical Analysis of Results.

A brief outline of the method used in analysing the results set out in Table 1 is given below.

If A is the quantity which, by means of many observations, is shown to be related to another quantity B, then the degree of correlation (m) is given by the expression:

$$m = \frac{\sum A'B'}{n \sigma_A \sigma_B}$$

where n = the number of observations.

σ_A = standard deviation of A

σ_B = standard deviation of B

A' = deviation of A from the mean.

B' = deviation of B from the mean.

If α and β are the deviation of A and B respectively from arbitrarily chosen mean values of the two,

then

$$\sum A'B' = \sum \alpha\beta - n\bar{\alpha}\bar{\beta}$$

$$\text{where } \bar{\alpha} = \frac{\sum \alpha}{n} \quad \text{and}$$

$$\bar{\beta} = \frac{\sum \beta}{n}$$

$$\text{also } \sigma_A^2 = \frac{\sum \alpha^2}{n} - \bar{\alpha}^2$$

$$\sigma_B^2 = \frac{\sum \beta^2}{n} - \bar{\beta}^2$$

therefore with respect to the arbitrary mean values;

$$m = \frac{\sum a\beta - n\bar{a}\bar{\beta}}{n\sqrt{(\frac{\sum a^2}{n} - \bar{a}^2)(\frac{\sum \beta^2}{n} - \bar{\beta}^2)}} = \frac{\sum A'B'}{n\sigma_A\sigma_B}$$

Properties of m

$$1 > m > -1$$

When $m = 1$ or -1 , the two variables are connected by a linear equation and all points would fall on that straight line. When $m = 0$, A and B are entirely independent of one another and no correlation is possible. It is necessary to apply a correction factor (p) to the coefficient of correlation (m) when the number of observations is small and this correction is given by:

$$p = \frac{1 - m^2}{\sqrt{n}} \quad \text{if } p > m \text{ there is no correlation.}$$

Let A denote specific gravity and B denote the ash content, and let the chosen arbitrary mean values of the two equal 1.20 and 20.00% respectively, then the first two columns given in Table 2 represent the deviation of A and B from 1.20 and 20.00%.

Then the following derivations may be obtained:

$$\bar{a} = \frac{\sum a}{n} = -0.0225 \text{ and } \bar{\beta} = \frac{\sum \beta}{n} = 1.166$$

$$\begin{aligned} \sigma_A^2 &= \frac{\sum a^2}{n} - (\bar{a})^2 = 0.0107 - 0.0005 \\ &= 0.0102 \end{aligned}$$

$$\begin{aligned} \sigma_B^2 &= \frac{\sum \beta^2}{n} - (\bar{\beta})^2 = 108.13 - 1.36 \\ &= 106.77 \end{aligned}$$

$$\begin{aligned}
 \Sigma AB &= \Sigma ap - n.\bar{a}\bar{p} \\
 &= 38.913 + 40(1.166)(0.0225) \\
 &= 39.952
 \end{aligned}$$

$$m = \frac{39.952}{40/\sqrt{0.0102} \times 106.77} = 0.957$$

$$p = \frac{1 - m^2}{\sqrt{n}} = 0.002$$

Coefficient of correlation equals 0.957 ± 0.002

This indicates a close relationship between specific gravity and ash content for the richer torbanites.

TABLE 2.

α	β	α^2	β^2	$\alpha\beta$
-.227	-18.19	.0515	330.09	+ 4.129
-.167	-13.26	.0279	178.50	+ 2.231
-.125	- 9.99	.0156	99.80	+ 1.249
-.157	-12.27	.0246	150.55	+ 1.926
-.045	- 1.94	.0020	3.76	+ .087
-.129	-10.11	.0166	102.22	+ 1.304
-.168	-16.48	.0282	271.59	+ 2.769
-.036	+ .43	.0013	0.18	+ 0.015
-.126	- 8.95	.0159	80.10	+ 1.128
-.074	+ 5.88	.0055	34.57	+ 0.435
+ .134	+18.99	.0180	360.62	+ 2.545
-.085	- 5.97	.0072	35.64	+ 0.507
-.052	- 3.45	.0027	11.90	+ 0.179
-.064	+ 5.07	.0041	25.70	- 0.324
-.084	- 7.60	.0072	57.76	+ 0.638
+ .159	+16.67	.0253	277.89	+ 2.650
-.007	+ 1.41	.0000	1.99	- 0.010
+ .028	+ 9.32	.0008	86.86	+ 0.261
+ .074	+ 7.21	.0055	51.98	+ 0.534
+ .108	+11.09	.0117	123.00	+ 1.198
-.045	- 0.37	.0020	0.14	+ 0.017
+ .017	+ 9.45	.0003	89.30	+ 0.161
-.007	- 0.19	.0000	0.04	+ 0.001
+ .031	+ 4.61	.0010	21.25	- 0.143
-.030	+ 0.41	.0009	0.17	- 0.012
-.027	+ 0.81	.0007	0.66	+ 0.022
+ .041	+ 7.53	.0017	56.70	+ 0.309
-.052	- 0.20	.0027	0.04	+ 0.010
-.172	-14.55	.0296	211.70	+ 2.503
-.002	+ 4.97	.0000	24.70	- 0.010
+ .039	+ 4.91	.0014	24.11	+ 0.182
-.002	- 0.03	.0000	0.00	+ 0.000
-.030	+ 0.41	.0009	0.16	- 0.012
+ .056	+ 9.80	.0031	96.04	+ 0.549
+ .184	+23.05	.0339	531.30	+ 4.241
+ .157	+17.79	.0246	316.48	+ 2.793
+ .168	+19.21	.0282	369.02	+ 3.227
-.090	- 7.44	.0081	55.35	+ 0.670
+ .035	+10.37	.0012	107.54	+ 0.363
-.128	-11.65	.0164	135.72	+ 1.491

 $\Sigma \alpha$ -0.900 $\Sigma \beta$ +46.65 $\Sigma \alpha^2$.4283 $\Sigma \beta^2$ 4325.01 $\Sigma \alpha\beta$ +38.913

Relation of Specific Gravity to Oil Yield.

General relationship of specific gravity: It has been shown in the preceding pages that in the case of rich material there is a distinct relationship between the ash content of a given sample and its specific gravity. As the oil yield, apart from retorting variables, depends on the amount of organic matter present, by deduction therefore, one can assume that the oil yield would vary with specific gravity. This is true although, on account of the greater complexity of the factors involved, to a lesser degree of correlation than in the previous case. If it were possible to define a standard retorting technique an even closer correlation might be expected. In order to make this statement clear it is first necessary to define what is meant by 'standard conditions' when applied to retorting technique.

Let the following conditions be assumed:-

- (1) Uniform and predefined time-temperature rise throughout the retort charge.
- (11) Constant size of torbanite particles.
- (111) Standard and reproducible retort and furnace.
- (1v) Predefined degree of packing of the sample into the retort.

thus, the possible variables in the treatment of any number of samples are minimised, but are not obviated. This is more readily realised if the nature of the thermal decomposition is examined in detail, for it will be seen that

$$\bar{a} = - 0.0106$$

$$\bar{b} = + 0.8635$$

$$\sigma A = 0.0428$$

$$\sigma B = 10.13 \quad m = -0.426$$

$$\text{Degree of correlation} = - 0.436 \pm 0.089$$

(These assays were not performed by the writer although carried out under his supervision.)

From the analysis it can be seen that, as might be expected, there is a fair degree of correlation between specific gravity and oil yield. Attempts were made to see whether any precise expression could be deduced to enable oil yield to be calculated from specific gravity, with a reasonable degree of accuracy but results were unsatisfactory.

Fracture.

When broken, rich torbanite exhibits a superb broad conchoidal fracture, whilst the fracture of a poorer specimen tends to be hackly. Cleavage along the bedding plane is quite common, and all torbanites show a greater break-resistance across the bedding plane than along it. Torbanite can be flaked with a knife but attempts to saw it, although successful, will always dull the blade because of the silica present in the mineral matter. Torbanite is extremely tough and is much more resistant to impact than coal. When struck with a hard object it emits a hollow wooden note, and a hammer rebounds from it with considerable force.

Structure.

Rich torbanite appears homogeneous to the sight and

gives no evidence of its laminated structure, although poor specimens show distinct laminations. When heated, rich torbanite tends to open up along the bedding plane, thus providing a means of ascertaining the plane of bedding of visually homogeneous specimens. In general, the texture is smooth, although very poor specimens are rough to the touch. Torbanite is brittle when cut into thin strips but demonstrates a certain amount of bending elasticity before fracture. The tensile strength is approximately 5000 Kg./sq.mm. (10% ash and parallel to bedding plane) and Rockwell M. hardness is between 70 and 76. It is interesting to note that the spherical indentations produced by the Rockwell penetrator gradually disappeared, and after eleven days no depression could be found when checked with a micrometer.

Microscopic Features.

When viewed in thin sections under a microscope, the dark mass of torbanite is resolved into an opaque matrix in which are embedded many translucent ellipsoidal bodies of more or less fibrous internal structure, ranging in colour from yellow to red. The organic bodies are not homogeneous but their variation is regarded as more of quality than of character. These entities are scattered throughout the material in no fixed manner except that their long axis is generally orientated towards the bedding

plane. The major portion of the organic matter is yellow in colour and is often so concentrated as to crowd out nearly all the other constituents.

The present chemical constitution of the organic bodies is still indefinite but, as will be shown later in this work, it seems likely that they are resins. The term 'resin' is here employed to designate highly polymerised compounds such as polystyrene, or the modern synthetic resins and does not refer to the gummy exudations from certain trees, such as that from the genus Pinus. Various writers have identified the 'yellow bodies' with bitumens, hydrocarbon globules and natural resins (rosin); however, their almost complete insolubility in both aliphatic and aromatic solvents shows that these premises are fallacious. Other writers have suggested that the 'yellow bodies' are fossilised pollen grains, spores, or remains of the higher plants, but it seems improbable that conditions were conducive and localised to such an extent as to produce the type of deposit we find at the present time. The lenticular nature of the deposits, their slight dip to the horizontal and their laminated structure, all suggest an aquatic form of plant life of algal origin.

Metamorphism has so altered the structure of the original substance that all investigations carried out on torbanite with the aid of the microscope must certainly be deductive, and as such, of little assistance in the

present problem, which is concerned with the actual composition and reactions of torbanite as it is found to-day.

THERMAL PROPERTIES.

The fact that torbanite consists of two very dissimilar components - organic and inorganic - and that the properties of the material as a whole are determined by the amount of each present, is well illustrated in the following pages dealing with the thermal properties.

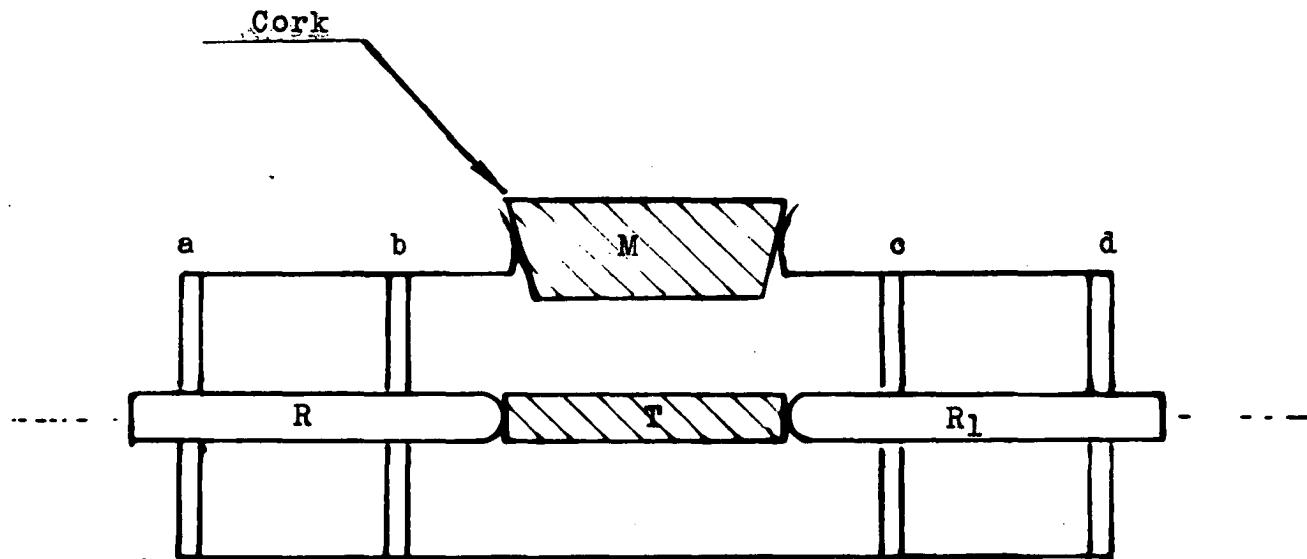
In some portions of this work, erroneous results were obtained, caused by decomposition of the sample under test at only moderate temperatures; for instance, in expansion tests, and this difficulty was only overcome by using sub-zero temperatures as one temperature limit.

SPECIFIC HEAT OF TORBANITE.

The specific heat of pure torbanite kerogen is 0.34 gram.cals./gram./°C. and decreases linearly with increasing ash content.

The experimental details of the work were as follows:-

The calorimeter was of the normal type containing a vacuum flask, accurate thermometer with telescope and stirring device, - the cooling constant of the apparatus was 0.00187 (Newtonian formulation). Weighed quantities of organic liquids such as carbon tetrachloride and nitrobenzene were used as heat media as they were good wetting agents and had low specific heats. This practice was the only deviation from the normal laboratory technique on



Apparatus for Expansion Experiments
Figure N° 1.

specific heat determinations.

Small sample blocks were cut from selected pieces of torbanite and maintained in an air-oven at constant temperature. At the end of two hours they were weighed and then replaced in the oven. When four hours had elapsed they were quickly transferred to the calorimeter (the calorimeter was placed close to the oven) and on reaching equilibrium the temperature was recorded. After the operation was concluded an ash determination was made on each sample. As a check on the above technique the following two variations were tested;

- (1) adding hot liquid to cold torbanite.
- (11) Adding cold liquid to hot torbanite immersed in hot liquid, the two liquids being identical.

Duplicates varied by a few percent but this could have been due to experimental error, as equilibrium temperatures were found with difficulty, owing to the low thermal conductivity of the torbanite. No correction was made for 'heat of wetting'.

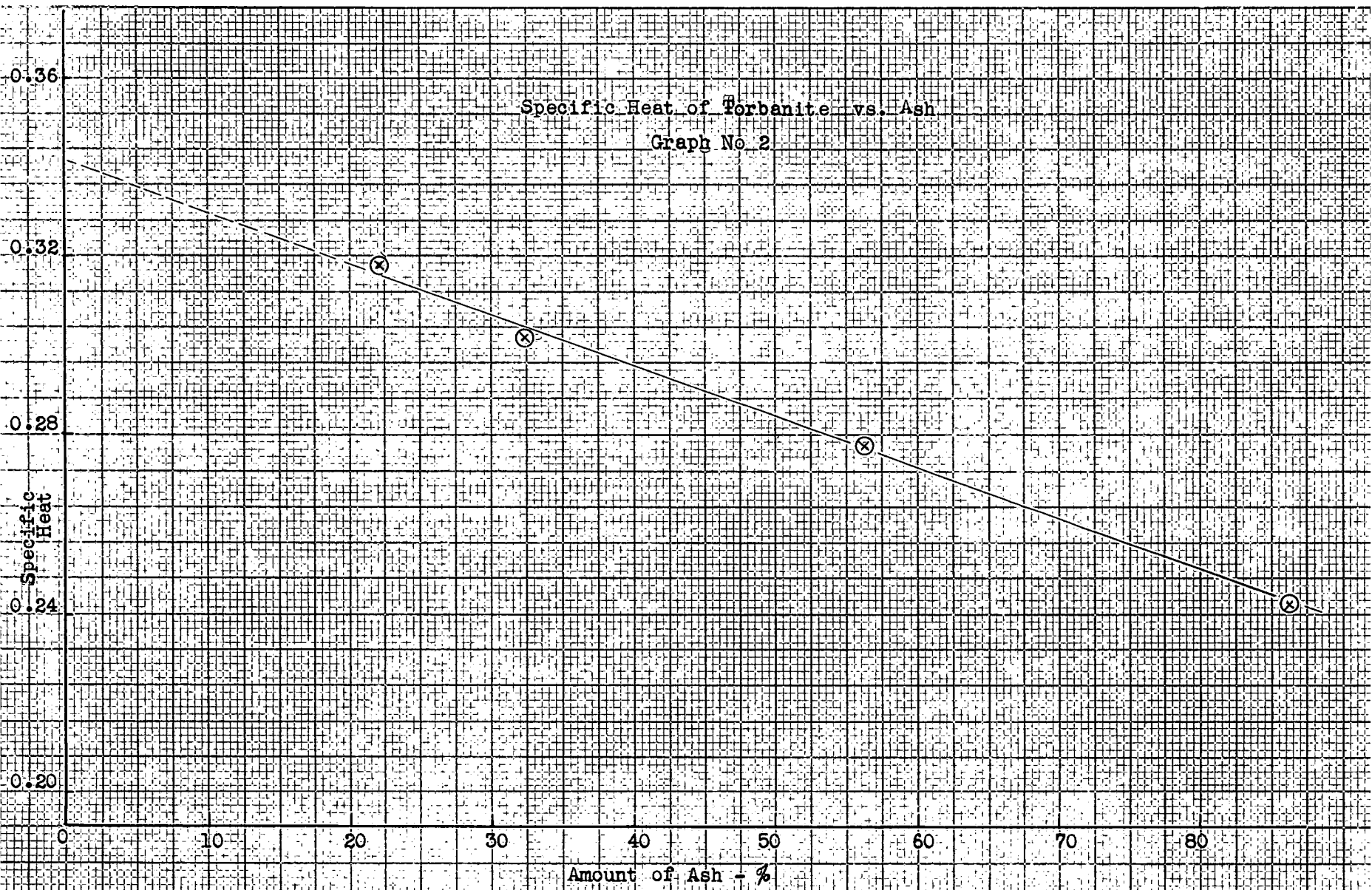


Table 4.The Specific Heat of Torbanite.

Sample No.	14	7	23	42
Ash %	22.2	32.3	56.4	86.2
Weight of Sample, grms.	40.21	45.45	28.33	38.62
Weight of Liquid, grms.	647	655	868	660
Sp. Heat of Liquid	0.342	0.367	0.203	0.342
Water Equivalent of:-				
* Calorimeter	57	57	57	57
Liquid	221	240	176	226
Total Cals.	278	297	233	283
<u>Temperatures °C. (Corr.)</u>				
Initial of Sample	49.8	80.1	51.4	50.8
Initial of Liquid	19.3	28.9	21.1	19.7
Equilibrium Temp.	22.6	31.2	22.1	20.7
Specific Heat	0.318	0.301	0.278	0.242
Temperature Range	20-30	30-80	20-50	20-50
Liquid employed	BzNO ₂	BzNO ₂	CCl ₄	BzNO ₂

* Water equivalent corresponding to a liquid level of 550 ml. in vacuum flask.

These results are illustrated in the graph 2 and extrapolation shows that pure kerogen has a specific heat of 0.54 cal./gm.

A theoretical approach to this subject may be made from the rule of Dulong and von Kopp on the additive character of specific heats and from this a check may be obtained on the experimental results given above.

Although the exact composition of the mineral matter in torbanite is not represented by an ash analysis, the results obtained from Table 5 are taken as sufficiently accurate to illustrate the application of this method.

The composition of a sample of ash from the Glen

Davis deposit is shown in Table 5 below:-

Table 5.

<u>Chemical Composition</u>	<u>Percentage</u>	<u>Specific Heat</u>	<u>Product (% x Sp.Ht.)</u>
SiO ₂	67.3	0.191	12.85
Fe ₂ O ₃	3.9	0.155	0.60
Al ₂ O ₃	22.0	0.184	4.05
CaO	0.9	0.181	0.16
MgO	0.5	0.220	0.11
SO ₂	2.6	0.18	0.47
Alkaline Oxides	2.8	0.2	0.56
			<u>18.80</u>

Specific Heat of shale ash: 0.19 cal./gram./°C.

The specific heat of the organic matter in oil shale may be approximated in the same manner, from the percentage composition of the kerogen and the atomic heats of the constituent atoms (see Table 6).

Table 6.

Percentage Composition (53).

C = 85.1%, H = 10.6%, S = 0.5%, N = 1.3%, O = 2.5%

<u>Analysis Percentage</u>	<u>Atomic Heat</u>	<u>Atomic Weight</u>	<u>Percentage x Atomic Heat Atomic Weight.</u>
C: 85.1	1.76	12	12.5
H: 10.6	2.3	1	24.38
S: 0.5	5.54	32	0.09
N: 1.3	3.42	14	0.32
O: 2.5	3.48	16	0.54
			<u>37.8</u>

Specific Heat: 0.38 cal./gram.

Thus, for dry shale containing 50% mineral matter, the specific heat may be calculated as:

$$\frac{0.38 + 0.19}{2} = 0.28 \text{ cal./gram.}$$

To this figure of 0.28 cal. per gram, a correction should be added for moisture and certain other inorganic volatile matter lost during the ashing process.

A graphical representation of the results obtained is shown in graph 2 and from the graph it can be seen that the calculated and observed values of the specific heat as given in Table 7, do not agree. In addition, the calculated values must be regarded as an approximation only, because of the many factors which must be considered.

Linear relationships between specific heat and ash content are found when dealing with substances of similar nature - coal and coke - showing the same correlation,

Table 7.

Sample Number	Ash Percentage	Specific Heat (obs.)	Specific Heat (calc.)
14	22.2	0.318	0.336
7	22.3	0.301	0.316
23	56.4	0.278	0.271
42	86.2	0.242	0.214

For purposes of comparison the specific heats of some American oil shales are given in Table 8 below:

Table 8

Source of Shale	Specific Heat	Authority.
De Beque	0.265	U.S. Bureau of Mines (75)
Parachute, Colorado	0.242	U.S. Bureau of Mines (75)
De Beque	0.273	McKee and Lyder (41)
Shale residue	0.223	U.S. Bureau of Mines (75)
De Beque	0.280	McKee and Lyder (41)
Gas Coal	0.314	Smithsonian Institute

Variation of Specific Heat with Temperature.

The general relationship between specific heat and temperature is given by:-

$$C_t = C_0 + at + bt^2$$

where C_t = specific heat at $t^\circ\text{C}$.

C_0 = specific heat at 0°C .

a and b are constants.

As torbanite decomposes when heated it is impossible to determine its specific heat at elevated temperatures, but an idea of the values involved may be obtained in the following manner.

Assuming the temperature coefficient of change of specific heat of the inorganic matter is similar to material such as silica brick or fire brick, a general equation for the specific heat of the mineral matter at any temperature ($t^\circ\text{C}$.) is given by:-

$$\text{Specific Heat} = 0.225 + 8 \times 10^{-4}t \dots\dots\dots(1)$$

Some difficulty is found in arriving at a figure for kerogen. However, when compared with semi-coke and coal, an increase in Specific Heat of 0.05 cal./gram. may be expected with a temperature rise of 400°C . and the following general equation is suggested:-

$$\text{Specific Heat} = 0.338 + 1.25 \times 10^{-4}t \dots\dots\dots(11)$$

As torbanite begins to decompose at measurable velocity over 250°C ., equation (11) is only applicable over a limited temperature range.

Combining equations (1) and (11), the following

equation gives the specific heat (C_t) in terms of ash content ($A\%$) and temperature:-

$$C_t = 0.338 - \frac{A}{100}(0.115) + 1.25 \times 10^{-4}t(1 - .003A) \dots (111)$$

For torbanite containing 20% ash;

Specific Heat = 0.32 cal./gram. from graph, observed between
20°C. and 50°C.

= 0.34 cal./gram. calculated from equation
(111) at 200°C.

Thermal Expansion.

At the outset it is necessary to differentiate between true thermal expansion and swelling. In order to make this statement clear, the behaviour of a strip of torbanite may be traced from subzero temperatures to the point of decomposition. As the temperature increases the torbanite expands in the normal manner, with a coefficient of expansion similar to most highly polymerised substances, e.g. Bakelite. When about 106°C. is reached there is usually a sudden change in the continuity of the expansion and this temperature possibly corresponds to the second order transition point. The second-order-transition-point is exhibited by most high polymers and is the temperature at which many physical properties show an abrupt change in continuity. This change is caused by the polymer ceasing to act as a rigid solid and tending to exhibit rubber-like characteristics. No allowance has been made for the second-order-transition-point in this work, as from the nature of torbanite it seems reasonable to assume that this temperature is outside the temperature limits of the determinations

(cp. second-order-transition-point of polystyrene = $82^{\circ}\text{C}.$)

At temperatures in excess of $200^{\circ}\text{C}.$ the term expansion loses its meaning when applied to torbanite, and it is preferable to give the term "swelling" to any further increase in dimensions. Between $20^{\circ}\text{C}.$ and the temperature of decomposition there is a more-or-less regular "swelling", until a point is reached where it is impossible to measure any further increase, owing to the softening of the material, caused by its decomposition.

Dulhunty (16) has recorded the fact that there is a permanent deformation of the torbanite when it has been heated at elevated temperatures, and then cooled to atmospheric conditions. He finds that there is an increase in dimension normal to the bedding plane and a decrease parallel to the bedding plane. Dulhunty introduces some confusion by giving the term "expansion" to any increase in length between atmospheric temperature and $500^{\circ}\text{C}.$, when it is obvious that at these high temperatures decomposition is taking place at a rapid rate, and true thermal expansion cannot be measured, - 'swelling' would be a better term in this case. However, it must be remembered that this swelling is a property of the organic portion only, and that poor specimens will show this phenomenon only to a small degree. In rich samples the swelling takes place with considerable force, being sufficient to open a small container, e.g. a

tobacco tin, if the charge is well packed before heating.

In order to determine accurately the true coefficient of thermal expansion of torbanite, it was decided to cool the torbanite from a given temperature, rather than to heat it. With this end in view an apparatus was constructed by which the dimensions of a standard block of torbanite could be measured at atmospheric conditions and also determined at the temperature of solid carbon dioxide ($-78^{\circ}\text{C}.$). The apparatus is shown diagrammatically in Figure 1. Thus it may be seen that the change in dimensions is measured over a temperature range where no chemical change would occur.

The apparatus was constructed of Pyrex glass and fibro-cement, all joints being made rigidly. The outer casing was of Pyrex glass and the four bearings, (a), (b), (c) and (d) were of $1/4$ " fibro-cement, turned on a lathe so as to fit tightly inside the glass tube. The mouth, (M), was blown in the side of the tube and was closed by a cork during determinations. This cork carried a toluene thermometer. Rods (R) and (R_1) were of $1/4$ " fused quartz, and were kept pressed against the test piece (T) by two rubber bands, (not shown) attached to hooks fused to the apparatus. The test piece was supported in the centre of the tube by a small platform. The whole apparatus was lagged with flannel cloth.

The experiment was commenced by placing the test piece in position and allowing it to stand at atmospheric temperature for as long as convenient. The distance between the

remote ends of the quartz rods was measured, by means of a 6" micrometer (Starrett No. 226), and the temperature of the thermometer noted. By placing a standard inch test-block in place of the test-piece, the dimensions of the torbanite could be obtained. Following this, the cork was removed from the mouth in the tube and powdered solid carbon dioxide ("dry ice"), was poured into the vessel through this mouth, and packed firmly in place. The contraction of the test block was measured and the final reading taken when equilibrium was obtained.

Any corrections to be applied to allow for contractions of the glass, quartz etc. were found by substituting a rod of pure silver for the test piece, and repeating the experiment under the same conditions.

Blocks of torbanite were cut from specimens of each of four deposits, the faces of the blocks being ground as nearly parallel as possible. A small mark was scratched on the centre of each face to show the plane of bedding.

The dimensions at two temperatures were obtained, as outlined above, and the coefficient of thermal expansion between temperature intervals of -78°C . and $+22^{\circ}\text{C}$. was obtained by this means, the results being shown in Table 9 below:

Table 9 .Thermal Expansion of TorbaniteParallel to Bedding Plane.

Locality	Dimensions (corr.) in inches at		Coefficient of Expansion $\times 10^6$
	-78°C.	+ 22°C.	
Wollar	1.166	1.176	85.8
Glen Davis	1.393	1.403	72.8
Coolaway	1.425	1.438	91.2
Marangaroo	0.387	0.391	103.3

Normal to Bedding Plane

Wollar	1.148	1.156	69.7
Glen Davis	1.028	1.036	77.8
Coolaway	1.158	1.167	77.7
Marangaroo	0.540	0.545	92.6

Thus it is seen that the coefficient of expansion varies with the richness of the sample and reaches a maximum of about 105×10^{-6} for pure kerogen, - a figure very similar to that shown by solid paraffins.

The difference between the coefficients of expansion/in a direction normal and parallel to the bedding plane is explained if one bears in mind the microscopic structure of the material.

Thermal Conductivity.

The experimental determination of the thermal conductivity of torbanite was unsuccessful and no reliable data were obtained. The main reason for the lack of information was the fact that samples decomposed on the heated face.

Experiments, using the radial heat flow method, were unsatisfactory but results indicated that the thermal conductivity of torbanite lies somewhere between 0.0004 and 0.0008 cal./cm.²/sec./°C./cm. thickness.

Heat of Combustion.

The heat of combustion of torbanite varies with its 'richness', as do other properties, and it will be shown that the gross heat of combustion of the pure organic matter is approximately 10,000 cal./gram. of kerogen.

The determinations were carried out in a Parr Oxygen Bomb Calorimeter, with simple jacket (contrast adiabatic jacket in later work.) The operating procedure was that given in the British Standard Specifications, as outlined in "Methods of Analysis of Coal and Coke - IX, Determination of Calorific Value", but with the following modifications:-

- (i) The bomb used was the two valve self-sealing Parr Oxygen Bomb.
- (ii) The platinum-cotton ignition system was replaced by a special Parr fuse wire of known heat of combustion (2.8 cal./cm. length).
- (iii) The cooling correction used was not that of Regnault-Pfaundler but that due to Dickinson.
- (iv) A smaller amount of water was used.

Corrections.

Calorimeters using the simple jacket, even though well

insulated, always need some corrections when accurate results are required. The following corrections were applied in the present work:-

(i) Scale Correction.

National Physical Laboratory correction factors for errors in Thermometer calibration, thermometer No. 36AW 3196 NPL37; standardised "immersed to reading". No correction was made for emergent stem.

(ii) Radiation correction.

To account for heat leakage from the contents of the calorimeter to the surrounding atmosphere. These were taken from the results of Dickinson, published under A.S.T.M. designation D271, and were read from nomographs published in Parr Bulletin No. 117.

Acid Correction; In the determination of heat of combustion the combustion of organic matter takes place in an atmosphere of oxygen under pressure, and under these conditions, appreciable amounts of the sulphur and nitrogen compounds are oxidised to the corresponding acids. Therefore, corrections have to be applied to take in this effect. The correction to be applied in the case of the nitrogen compounds is the heat of formation of aqueous nitric acid and corresponds to 1.43 calories per ml. of N/10 acid.

The sulphur correction is arrived at by deducting 22.5 cal./gm. for each 1 per cent of sulphur present in the sample, this representing the differences between the heat involved by oxidation of the sulphur to sulphur trioxide with formation of dilute sulphuric acid, and the oxidation of the sulphur to sulphur dioxide.

Correction for Fuse Wire; By deducting the amount of unburnt residual fuse wire from the original length, a correction of 2.8 cal./cm. length of burnt wire is applied.

Water Equivalent; The water equivalent of the calorimetric system was determined by the combustion of B.D.H. "Analar" Benzoic Acid.

Six determinations were carried out and the results obtained are given in Table 10 on the following page.

Table 10.Heat of Combustion of Torbanite.

Parr Bomb No. BB93
 Thermometer No. 3196
 Thermometer Range 0 - 50°C.
 Water Equivalent of Calorimeter 484 grm.cals.

Experimental Results.

Sample No.	16A	14	18A	23	20A	51
Wt. of Sample, grms.	1.5385	1.9654	1.3667	1.1894	2.0605	2.1000
Initial Temperature °C.	22.29	25.19	23.12	28.82	25.18	26.26
* True Initial Temperature °C.	22.29	25.20	23.11	28.85	25.19	26.28
Final Temperature °C.	27.14	31.17	26.25	30.64	27.80	28.24
* True Final Temperature, °C.	27.12	31.20	26.27	30.68	27.82	28.26
Corrected Temperature Rise °C.	4.83	6.00	2.96	1.83	2.63	1.98
Mass of Water, grms.	2000	2030	2173	2005	2005	2003
Total Water Equivalent grm.cals.	2484	2514	2657	2489	2489	2487
Total Heat Liberated, cal	12023	15084	7863	4555	6546	4924
Corrections: Sulphur	10.8	13.4	7.3	8.4	14.7	11.1
Fuse	3.5	19.6	10.1	3.9	37.0	39.2
Acid	1.4	11.8	2.4	1.6	3.0	7.5
Net Heat Liberated, Cals.	12007	15039	7843	4541	6491	4866
Heat of Combustion(gross)	7804	7652	5738	3819	3150	2317
Ash %	21.1	22.2	44.0	59.1	61.5	76.2

* True Initial (or Final) Temperature obtained from Initial (or Final) Temperature by adding scale correction and radiation correction.

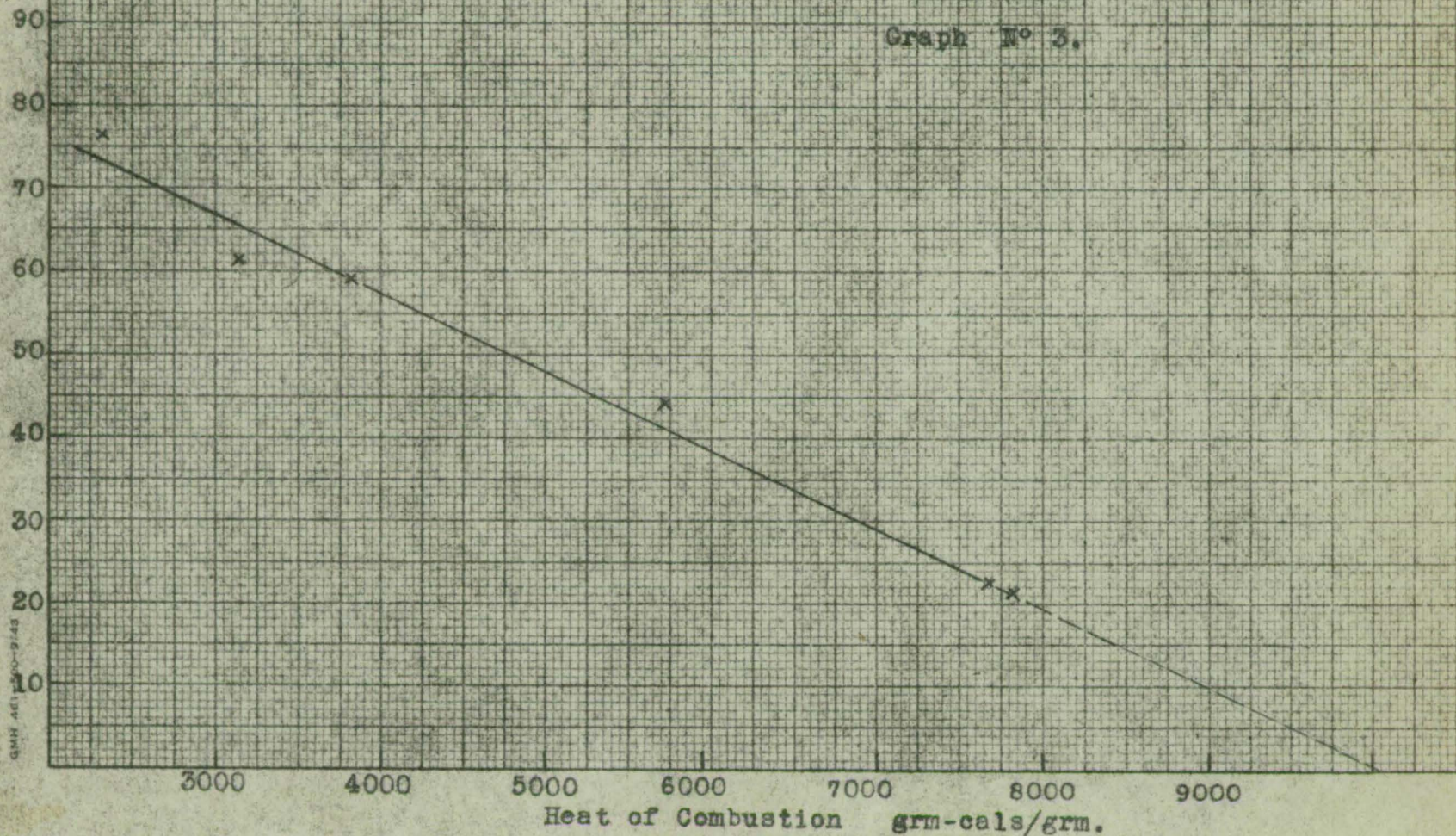
Heat of Combustion of Torbanite

Graph N° 3.

Ash of Sample %

QMS 451130-9/45

Heat of Combustion grm-cals/grm.



A graphical interpretation of these results is shown in graph No. 2; the dotted portion of the line indicates the extrapolation to zero ash content, and it can be seen that the value of the heat of combustion of pure kerogen is approximately 10,000 cal./gram.

If it is assumed that the ultimate analysis (from Table 13) of kerogen is given by:-

Carbon	=	84.2
Hydrogen	=	11.9
Sulphur	=	1.0
Nitrogen	=	0.3
Oxygen	=	2.6 (by diff.)

the calculated heat of combustion is 10,680 cal./gram., a figure very similar to that of crude oil.

"HEAT OF WETTING" OF TORBANITE.

The physical structure of torbanite and the nature of its origin would indicate that torbanite possesses a large internal pore surface, similar to that found in coal.

As in the case of coal, the internal surface manifests itself in an exothermic reaction when the solid is "wetted". The "Heat of Wetting" is, therefore, the energy change which occurs when the solid-vacuo interface in the pores is replaced by a solid-liquid interface, and the heat evolved is a measure of the surface area of the material. The exact translation of the amount of heat into terms of 'area wetted' is somewhat unsatisfactory, but the results give a good indication of the porosity of the material under investigation.

From the results of Huggs (81), it may be assumed that, for coal graphite and charcoal, 10.8 square metres of internal pore area is required to produce one calorie, and this figure will be taken in the study which follows.

Torbanite from Wollar was used in the experiment, the details of which are as follows:-

The calorimeter consisted of a small vacuum flask surrounded by a thermostatically-controlled water bath, the temperature of which could be maintained constant to within $\pm 0.05^{\circ}\text{F}$. The temperature rise was measured by a precision calorimeter thermometer and telescope capable of reading to 0.02°F .

The sample was finely powdered, dried and then outgassed

under a vacuum of 10^{-3} mm. Hg. The sample, before outgassing, was placed in a small glass bulb which was sealed during the final stages of the evacuation treatment.

The sample was placed in the vacuum flask which contained a stirrer, and methyl alcohol; the cork and thermometer were placed in position and the whole allowed to come to thermal equilibrium. After equilibrium had been attained, the bulb was broken in situ and any rise in temperature noted. Corrections were made for radiation losses, and the values obtained are shown below. Also included in Table 11 are the values of the "Heat of Wetting" calculated from the temperature rise and the water equivalent of the calorimeter (34 grm. cals.)

Table 11.

Heat of Wetting of Torbanite.

<u>Time(mins.)</u>	<u>Temperature °C. (corrected)</u>	<u>Cals./grm.</u>
0	19.05	-
3	19.07	0.7
6	19.16	3.4
8	19.18	4.4
10	19.21	5.4
12	19.22	5.8
14	19.23	6.1
18	19.23	6.1

The Heat of Wetting, determined by experiment is 6.1 cal./grm., from which a value of $66 \text{ m}^2/\text{grm.}$ is obtained for the internal surface of torbanite. The value of the Heat of Wetting of torbanite is very low when compared with similar substances (Table 12), and although repeated determinations gave no higher value, it is felt that the

experimental results are low; this may be caused by the fact that the vacuum treatment was not sufficiently rigorous. Some authorities state that a vacuum of at least 10^{-5} mm. is necessary for conclusive results, however, 10^{-3} mm. was the best vacuum that could be obtained with the available equipment.

Table 12.

Heat of Wetting of Various Substances.

<u>Substance.</u>	<u>Heat of Wetting.</u> cals./grm.
Sugar Charcoal	11.5
Animal Charcoal	17.6
Artificial Graphite	3.2
Coal	16.5 - 18.6

OPTICAL PROPERTIES.

Colour.

All torbanites so far examined vary from grey to black by reflected light, and from orange to red by transmitted light. Different shades of greenish grey, bluish black etc. have been described from time to time by various writers, but these vague terms are only arbitrary subdivisions which may be interpreted as the observer sees fit; although sometimes a brownish hue is definitely apparent. Generally speaking, poor torbanite is grey, and the colour deepens to glossy black in rich specimens. The extremely rich lens in the Marangaroo deposit is an exception to the above, the newly exposed surface being deep green by reflected light. From this observation one may infer that the colour of the pure organic matter, en masse, is dark green.

Powdered torbanite always shows a lighter colour than the bulk specimen, and the powdered sample (100MM) from the Marangaroo deposit mentioned above was a pale yellow.

By transmitted light, torbanite appears dark red in comparatively thick sections, but the colour progressively lightens to yellow as thinner sections are viewed.

Effect of Heat on Colour.

As the temperature of a piece of torbanite is raised the colour darkens, finally becoming black. This effect

is not due entirely to physical reactions, as samples heated in vacua showed less tendency to darken than samples heated in the atmosphere. If the powdered sample is heated in the presence of air, the upper portion becomes darker before the lower levels, and this reaction is accompanied by the absorption of oxygen, showing that some chemical change involving oxidation is occurring.

The present writer disagrees with Dalhanty's statement (16) that "In each deposit one colour predominates independently of variations of quality or texture", for the colour is so much a function of quality, and the personal error is so great in distinguishing minute variations of hue, that it is well nigh impossible to apply colour as a criterion for the separation of one deposit from another.

Lustre.

Lustre varies with the amount of organic matter in the torbanite, samples with a large amount of mineral matter possessing a dull, non-shiny lustre with a grained appearance; while a rich specimen shows a lustre which has been described variously as "silky", "resinous" or "satiny". As lustre depends on the nature of the reflecting surface this means, as might be expected, that poor samples break with a microscopically-irregular surface, and rich samples, when fractured, leave the exposed surfaces smooth.

Refractive Index.

The refractive index of rich torbanite is approximately 1.543 (measured with a Bausch and Lomb Refractometer - Abbe type and using white light). Dalhanty (10) records that the refractive index of gelosite (the principle constituent of Torbanite) varies between the limits 1.536 and 1.550, while other constituents have refractive indices between 1.625 and 1.545. Other optical phenomena such as optical activity have not been investigated, but Dalhanty, (loc. cit.), has reported that gelosite is anisotropic with regard to light.

The specific refraction equals 0.322, calculated from $n = 1.54$, specific gravity = 0.973 and Lorenz-Lorentz formula.

Fluorescence.

Torbanite is characterised by a distinct golden-yellow fluorescence, when examined under ultraviolet radiation. Coal and cannel, on the other hand, have no observable fluorescence and this serves as a useful means of separation of these materials. Examination of specimens under ultraviolet light enables one to distinguish clearly, veins of non-torbanite matter in samples, and it is interesting to note that even the richest material, which appears perfectly homogeneous under visible light, shows small streaks of canneloid or coal, when viewed in ultra-violet light.

The intensity of the emitted radiation decreases with

the weathering of the sample and newly fractured surfaces are noticeably more fluorescent than those which have been in contact with the atmosphere for even a few days. The distinction between the visible fluorescence of torbanite and the inactivity of cannel and coal must be connected with some fundamental difference in structure.

X-RAY DIFFRACTION PATTERN OF KEROGEN.

The X-ray diagram of kerogen, using the 'powder' technique is a halo-pattern, characteristic of nearly-amorphous substances and of many high polymers, both natural and synthetic.

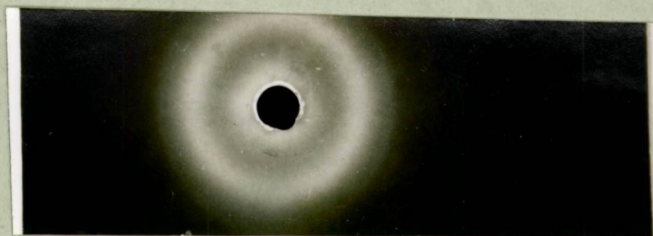
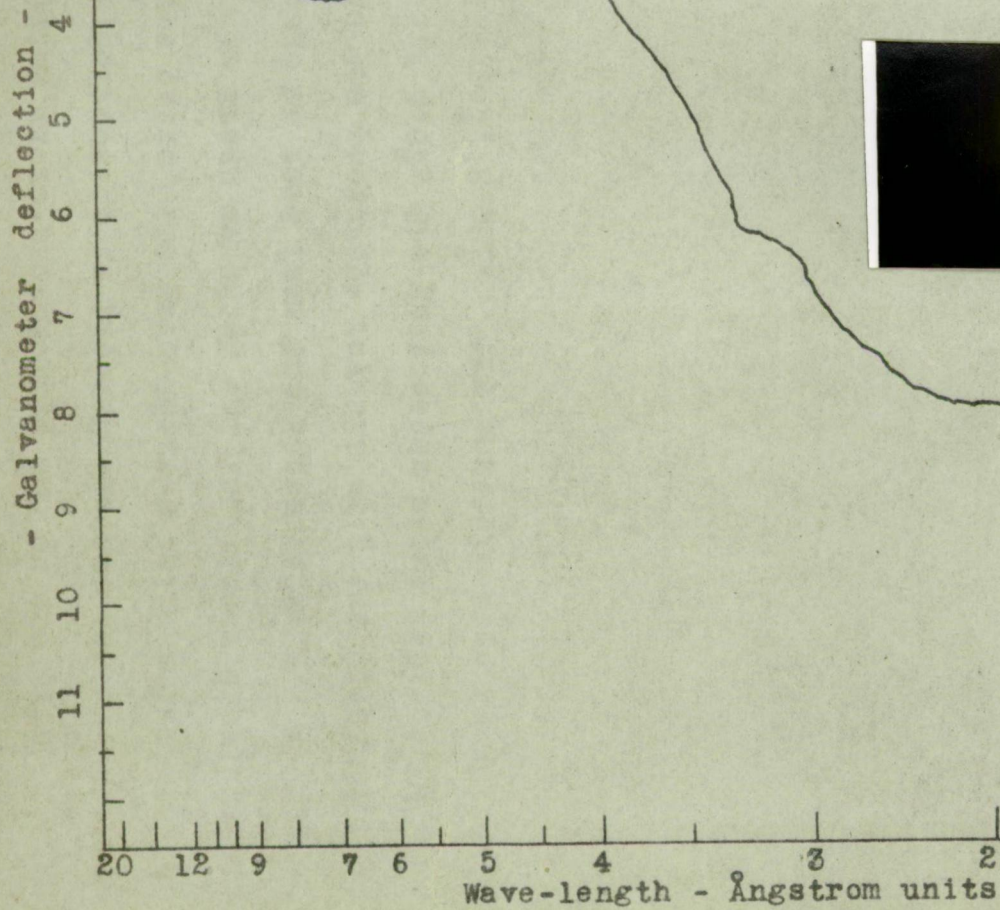
The diagrams were taken in collaboration with the P.M.G. Research Laboratory, Melbourne (to whom acknowledgement is made) and a reproduction of the pattern is given on the next page. Although X-ray methods of analysis of high polymers leave much to be desired, three important deductions may be made from the results of this method when applied to kerogen.

- (i) It excludes the conception that kerogen is composed of high molecular weight paraffin waxes. Waxes give sharp rings, especially one at 4.6\AA , which appears to be the mean effective diameter of the molecule.
- (ii) It places kerogen among polymers such as plastics and synthetic rubbers which give indistinct amorphous rings.
- (iii) It indicates a more-or-less random distribution of the particles, although it shows that most particles are about the same size.

In addition to the photograph, there appears a photometric curve. The pattern was measured with a Hilger

Photometric Curve of X-ray Diagram
of Torbanite

Graph N° 4.



non-recording micro-photometer, and on the graph the galvanometer deflection is plotted against the wave-lengths in Angstrom units, the wave-lengths being calculated by means of the Bragg equation and the linear displacement of the rings as read from the photometer.

While the photograph reveals only two distinct 'halos' at 15.8\AA and 5.0\AA , the photometer shows deflection steps at 3.06\AA , 2.54\AA , 2.09\AA . The particle size is 15\AA calculated from the Debye-Scherrer equation, viz.,

$$\beta_s = C \lambda / \epsilon \cos \theta$$

Where β_s = angular broadening (in radians) at half intensity.

ϵ = edge length of crystallite.

λ = wave-length = 1.787\AA
Cobalt K_α

θ = Bragg defraction angle.

C = Constant (0.94 (Scherrer))

Radius of camera = 28.5 mm.

As a detailed examination by means of X-rays is outside the scope of this work, no attempt was made to correct the calculations for background scattering, moreover, as a particle size estimation in the case of long-chain polymers is subject to many errors, no useful purpose would be served in extending the calculations.

The photometric 'peak' at 15.8\AA probably measures the average cross thickness of the molecule and this is supported

by the particle size estimation of 15\AA . The latter result is likely to be a unidirectional estimation because of the elongated shape of the molecule. The spacing at 5\AA would appear to be the distance between two long chains and is to be compared with the interplanar spacing at 4.6\AA found in paraffins.

ELECTRICAL PROPERTIES.

Torbanite acts as an insulator against electric currents, the electrical resistance of rich torbanite (6% ash) was 6.3×10^9 ohms/cm.³, measured with a resistance tester, employing an E.M.F. of 800 volts D.C.

The specific inductive capacity is approximately 8.8, determined with a General Radio Corporation Impedance Bridge. Because of the nature of the test, the value of the S.I.C. given above should be accepted as merely an indication of the figure involved.

CHEMICAL PROPERTIES.

INTRODUCTION.

The results of the preceding section have demonstrated the salient physical properties of the Australian Torbanite. The physical properties seem to indicate that the underlying structure of Torbanite kerogen is, or resembles, a highly polymerised hydrocarbon, with sulphur, oxygen and nitrogen playing small but important roles; in the present section this theory will be further substantiated.

The great difficulty encountered in the chemical treatment and analysis of torbanite is caused by its almost complete inertness to chemical reagents. It seems that torbanite is attacked only by those reagents which so destroy its chemical structure that very little of the original configuration is recognisable; however some hope of final elucidation of this problem comes with the use of alkaline potassium permanganate oxidation.

One inherent difficulty in the analysis of kerogen is the removal of the inorganic portion of the torbanite while leaving the organic matter in its original form. Up to the present, little success has been obtained by dissolving the mineral matter with successive treatments of hydrochloric and hydrofluoric acids; furthermore it seems doubtful whether this method is without criticism, inasmuch as some attack on the kerogen would be expected.

The actual structure of kerogen is still a matter

of enquiry and, up to the present, information on this subject has been very rare. Most of the available information appertains to oil shales, as distinct from torbanite, but there seems little reason to doubt that the fundamental structures of both are alike.

From the chemical point of view, torbanite may be classified as an asphaltic pyrobitumen. Asphaltic pyrobitumens may be defined as naturally occurring substances of dark colour, comparatively hard, nearly insoluble in organic solvents. They are composed mainly of hydrocarbons and are nearly free of oxygen. They are usually associated with mineral matter and the organic portion does not melt, but decomposes on heating.

ULTIMATE ANALYSIS.

Ultimate analyses of torbanite show a C/H ratio much lower than that of coal, but similar to that of crude petroleum. Several ultimate analyses are given in Table 13 following, and all results have been taken from the original literature and then calculated to a dry ash-free (D.A.F.) basis.

Table 13.

Ultimate Analysis of Torbanite Kerogen.

Source	Carbon %	Hydrogen %	Nitrogen %	Sulphur %	Oxygen (by Diff.)	C/H Ratio	Ash % on original	Authority.
<u>N.S.W.</u>								
Marangaroo	84.20	11.93	0.31	1.02	2.54	7.06	1.9	48
Joadja	80.60	12.90	0.33	0.30	5.87	6.25	6.55	14
Greta	78.21	8.95	0.32	1.10	9.53	8.74	16.11	14
<u>Scotland</u>								
Armadaile	80.52	10.13	0.77	0.34	8.24	7.95	18.38	59
Pumpherson	71.78	10.11	4.54	0.25	13.32	7.10	7 5.00	19a
<u>S. Africa</u>								
Transvaal	80.15	10.40	1.05	1.38	6.99	7.70	27.26	47
<u>"Australia"</u>								
not stated	82.53	10.13	1.05	0.56	5.73	8.14	22.96	59
not stated	81.85	10.28	0.81	0.66	6.40	7.87		27
<u>Other Substances.</u>								
Balkash Sapropelite	73.76	10.61	0.56	1.03	13.74	6.94	--	78
Scottish Shale	80.5	12.5	1.2	0.3	5.5	6.44	--	38
Kukersite	76.7	9.2	0.4	1.9	11.8 (+Cl ₂)	8.33	--	38
Bituminous coal	86.0	5.5	2.5 (+S)	-	6.0	15.64	4.9	65
Crude petroleum	84.00	12.70	1.70	0.75	1.20	6.61	--	52

One of the outstanding features of Table 13, is the uniformity of composition shown by the pure kerogen substance. It is granted that both sulphur and nitrogen (and therefore oxygen) show comparatively large ranges of variation, but sulphur and nitrogen are only present in such small quantities as to have little effect on the analysis as a whole, especially when it is remembered that these two elements have larger atomic weights than the other determined elements (oxygen found by difference). Converting the ultimate analyses to an atomic basis, it can be seen that,

taking the first analysis as an example, a molecule of sulphur occurs only once for about four hundred hydrogen atoms, or two hundred and thirty carbon atoms; nitrogen occurs even less, and the exact role of these two elements is somewhat problematical.

The presence of thiophenes and heterocyclic nitrogen compounds in the crude oil in no way proves that these two elements are present in ring structures in the original substance, for just as carbocyclic compounds may be formed by ring closure under severe cracking conditions, so heterocyclic compounds may be formed under similar conditions.

There seems to be one important difference between the combinations of sulphur and nitrogen; in that hydrogen sulphide is among the initial gases to be evolved during torbanite pyrolysis, whereas ammonia only appears during the final stages of decomposition. Thus it appears that some sulphur atoms, at least, are very loosely held, while the nitrogen (forming NH_3) is released only at high temperatures.

For the purpose of explaining its general chemical structure it may be assumed that the kerogen molecule is essentially hydrocarbon in composition and the nearest approach to the pure natural substance is that described by Cane (10⁴), the analysis of which appears at the top

of Table 13. The carbon/hydrogen ratio of this material is 7.66 and, neglecting the oxygen, nitrogen and sulphur, its empirical formula is approximately $(C_7H_{12})_n$ or more exactly $(CH_{1.71})_n$. The C/H ratio distinguishes the structure of kerogen from that of coal, the latter showing a more benzenoid character.

Previously it was supposed that; "The low hydrogen content in an oil shale has been stated as a reason for the unusually high percentage of unsaturates in shale oils. It is explained that the kerogen or oil-yielding material of the shale does not contain sufficient hydrogen to produce saturated compounds with a portion of the carbon in the hydrocarbon vaporised during the pyrolysis of the shale" (67)

Actually, it will be seen that this statement requires qualification, in view of results shown in this treatise (see Section III).

If the decomposition of torbanite is, as it must be, regarded as a cracking reaction from start to finish, then no matter how saturated the primordial substance, the product will always be less saturated. This statement may be followed from the point of view of the simplest splitting reaction.



Therefore, McKee is correct in stating that shale oil is comparatively unsaturated, but it does not necessarily follow that the reason for this is the low hydrogen content

of oil shale. To illustrate this point, an everyday example may be taken, e.g. in the commercial cracking of a pure paraffinic stock. The resulting cracked product is about 30% unsaturated, carbon is found in the heater tubes and reaction chamber, and a certain amount of free hydrogen in the stripped gases. This fact also explains why slow gentle retorting produces a more saturated oil than rapid treatment, for, in the former case, the cracking is less severe and consequently there is less tendency for cracking of paraffins to yield paraffins and olefins.

Thus the presence of free carbon in the retort residue does not prove that the kerogen must be regarded as unsaturated, as such, and in addition, it is obvious that for extremely complex substances, such as kerogen, simple nomenclature is not sufficiently specific for use without some qualification. An approximate determination of oil yield may be made from the C/H ratio and amount of ash contained in the shale, but as retorting technique plays such an important part in any oil assay, any information on oil yield, gleaned from C/H ratio, would have little practical application without further qualifying information.

One objection which might be raised against these remarks is that the specific gravity of a shale oil does not vary very much from start to finish of a retorting operation; this may be seen from Table 14 below. In this table specific gravities of oil samples collected over successive retorting

temperatures are tabulated against the temperature range as measured in the shale mass.

Table 14.

Temperature Range of retorting °C.	Specific Gravity of Oil at 20°C.
- 450	0.88
450 - 470	0.89
470 - 480	0.89
480 - 490	0.90
490 - 500	0.90
500 - 510	0.90
510 - 520	0.90
520 - 530	0.90
530 - 540	0.91
540 - 550	0.92
550 -	

This uniform gravity may be explained by the following facts:-

- (i) the oil is truly uniform with regard to density as the retorting progresses
- (ii) the effect of the increasing amount of lighter fractions (from the greater cracking) is counteracted by a corresponding increase in the amount of heavy residuum produced simultaneously.

By analysing the results obtained from distillations of the various oil samples it will be shown that both reasons are partially correct. It appears that the oil is fairly uniform in character as the pyrolysis proceeds but due to secondary cracking the distillation range increases, although the specific gravity does not alter very much. These statements have more detailed treatment in Section III B, under "Some Factors in the Thermal Decomposition

of Torbanite."

It must be remembered, nevertheless, that in a retort where the oil is liable to be refluxed over and over again, due to the retort design, the specific gravity will rise, as true distillation will be the controlling factor.

Regarding the decomposition purely from the point of view of ^{carbon/}hydrogen ratio, the percentage of carbon in the residue indicates that some portion of the molecule contains cyclic structures, for even though a study of the free energy equations of paraffins shows that they decompose into their elements at moderate temperatures, the reaction velocity at these temperatures is so very slow, that paraffins may be cracked at temperatures up to 550°C., without appreciable formation of carbon. On the other hand, torbanite may be almost entirely decomposed at temperatures not in excess of 400°C., giving oil, and a carbonaceous residue. From this one may infer that the free carbon indicates aromatic ring structures in a portion of the kerogen.

A variety of Carbon/Hydrogen ratios may be seen in Table 15, this table having been inserted for purposes of comparison.

Table 15.The C/H Ratios of Various Substances.
(from various Sources)

<u>Substance.</u>	<u>Ratio (mean)</u>
Anthracite	51.3 : 1
Coal (Semi-bituminous)	20.1 : 1
Coal (Bituminous)	15.6 : 1
Coal Tar (Paris)	10.8 : 1
Gilsonite	8.9 : 1
Cracked Residuum	8.7 : 1
Trinidad asphalt	7.8 : 1
Torbanite (average)	7.6 : 1
Torbanite (Marangaroo)	7.1 : 1
Shale Oil	6.9 : 1
Petroleum	6.6 : 1

Anthracene	16.8 : 1
Benzene	12.0 : 1
Isoprene	7.5 : 1
Heptadiene	6.9 : 1
Olefin	6.0 : 1
High Mol. Wt. Paraffin	6.0 : 1
Methane	3.0 : 1
Elaeostearic Acid	7.1 : 1
Linoleic Acid	6.7 : 1
Oleic Acid	6.3 : 1

An inspection of the above table shows that the structure of kerogen is less aromatic than that of coal, i.e. kerogen contains more aliphatic carbon-carbon linkages. Generally speaking, therefore, it may be said that the constitution of kerogen may be regarded as intermediate between coal and petroleum.

Proximate Analysis.

In addition to the Ultimate Analysis discussed in the previous section, there is another assay which may be used to classify torbanite, coal and allied substances. This assay is termed "Proximate Analysis" (the term appears to be a corruption of "approximate analysis"), and serves as a useful guide in determining the fuel value of coal, shale, torbanite etc. From the results of the Proximate Analysis, a derived index termed the "Fuel Ratio" is obtained, and equals the ratio of the percentage of volatile matter to the percentage of fixed carbon.

The analytical method for determining the Proximate Analysis is given in detail in "Methods in the Analysis of Coal and Coke" (18) and only an outline of the method will be given here;

Moisture, is determined as percent loss in weight of the sample when maintained at $108 \pm 2^{\circ}\text{C}$. in an inert atmosphere till the sample reaches constant weight.

Volatile Matter, is determined as percent loss in weight of the sample maintained for seven minutes at $925 \pm 25^{\circ}\text{C}$. The conditions of the furnace atmosphere are such that oxidation is reduced to a minimum.

Ash, the percent residue after oxidising the sample to constant weight in a muffle furnace.

Fixed Carbon, is the difference between one hundred and the sum of the results of the three

determined factors.

In the case of torbanite it is doubtful whether the volatile matter should be determined at such a high temperature, as this temperature is far in excess of that used in normal retorting practice. However, as 925°C. is widely employed in coal assays it is perhaps desirable to maintain a uniformity of technique. One of the widely used criteria for distinguishing torbanite from coal is that the fuel ratio of the former should be greater than unity.

Table 16.

Proximate Analysis of Torbanite and Allied Substances.

Sample	Moisture	Volatile Matter	Ash	Fixed Carbon (diff.)	Fuel Ratio	Authority.
Torbanite (max.)	0.3	93.0	2.0	4.7	19.8	R.F.C.
Torbanite (rich)	0.4	81.3	10.6	7.7	10.6	R.F.C.
Torbanite (medium)	0.9	67.3	22.6	9.2	7.3	R.F.C.
Torbanite (poor)	1.3	37.4	48.9	12.4	3.0	R.F.C.
Oil Shale	7.5	19.5	67.8	5.2	3.8	67
Cannel Coal	3.8	23.8	43.4	29.0	0.82	17
Wood (dry basis)	-	80	trace	20	4	65
Coal (Bituminous) (dry)	-	35	5	60	0.58	65
Anthracite (dry)	-	10	4	86	0.12	65

Visual analysis of the results given in Table 16 indicates the following points:-

- (1) The fuel ratio of torbanite is greater than unity and for coals the ratio is less than one. The fuel ratio of torbanite increases from unity to nearly twenty. Of sixty-one samples with volatile matter greater than 60%, examined by Carne (8) the fuel

ratio was greater than 4.9, while the eighty-three samples with volatile matter between 45 - 60%, had a fuel ratio in excess of 2.7.

- (ii) The amount of mineral matter does not appreciably influence the fuel ratio. This may be seen by comparing the Proximate Analysis of Scottish shale with that of torbanite. The Broxburn deposits show a general Proximate Analysis (moisture-free):

Volatile Matter	25%
Fixed Carbon	5%
Ash	70%
Fuel Ratio	5.0

and this analysis may be compared with the results given in Table 16.

- (iii) Examination of many analyses reveals the fact that there is a strong tendency for an increase of moisture with an increase in mineral matter. Extending this hypothesis, it does not seem impossible that pure kerogen would have practically zero moisture content.

Even in a single sample it can be shown that the finer particles contain the greater moisture, i.e. on powdering there is a tendency for the richer particles to resist crushing. This effect is shown in Table 17 below.

Table 17.Effect of Particle Size on Mineral Matter.

(a) Sample crushed in roll jaw crusher so that whole sample passed through 1/2" mesh screen.

Size: 1/2" - 1/4"	Yield: 91 gallons per ton.
1/4" - 1/8"	89 gallons per ton.
1/8" -	86 gallons per ton.

(b) Mines Department Sample 41/2597 (17)

Sieve Portion (Whole) -	30+60	-60+100	-100+150	-150+200	-200
Moisture %	1.94	1.79	1.90	1.96	2.03 2.07
Volatile Matter %	22.60	26.72	26.10	24.68	23.88 21.75
Fixed Carbon %	14.30	18.50	17.10	15.42	14.51 13.77
Ash %	61.16	52.99	54.90	57.94	59.58 62.41

It also appears that the ash from the richer torbanite has a lower fusion point and a higher iron content.

A Proximate Analysis cannot be correlated with oil yield nor will it identify any one deposit but it will serve to indicate possible sources, and the remarks made in the introduction to the section on physical properties are applicable to the results of Proximate Analyses. The following table shows the recorded variations in "Proximate Analyses" of Torbanite, from different sources.

Examination of this table reveals the fact that variations in Proximate Analyses are great enough to render useless any classification based on these results. However,

the table does indicate that certain deposits appear to have limiting values and so enables certain distinctions to be made; for example Wondo, Joadja and Hartley Vale have high "Volatile Matter" and this would differentiate these deposits from, say, the Ilford Deposit. It would be inadvisable to extend this hypothesis too far as no deposit has been fully examined, and further exploration may reveal richer or leaner, sections of any one deposit.

Graph No. 5, on the next page, illustrates the observed maximum and minimum ash values which have been recorded for Torbanite from various localities, and this graph further substantiates the above remarks.

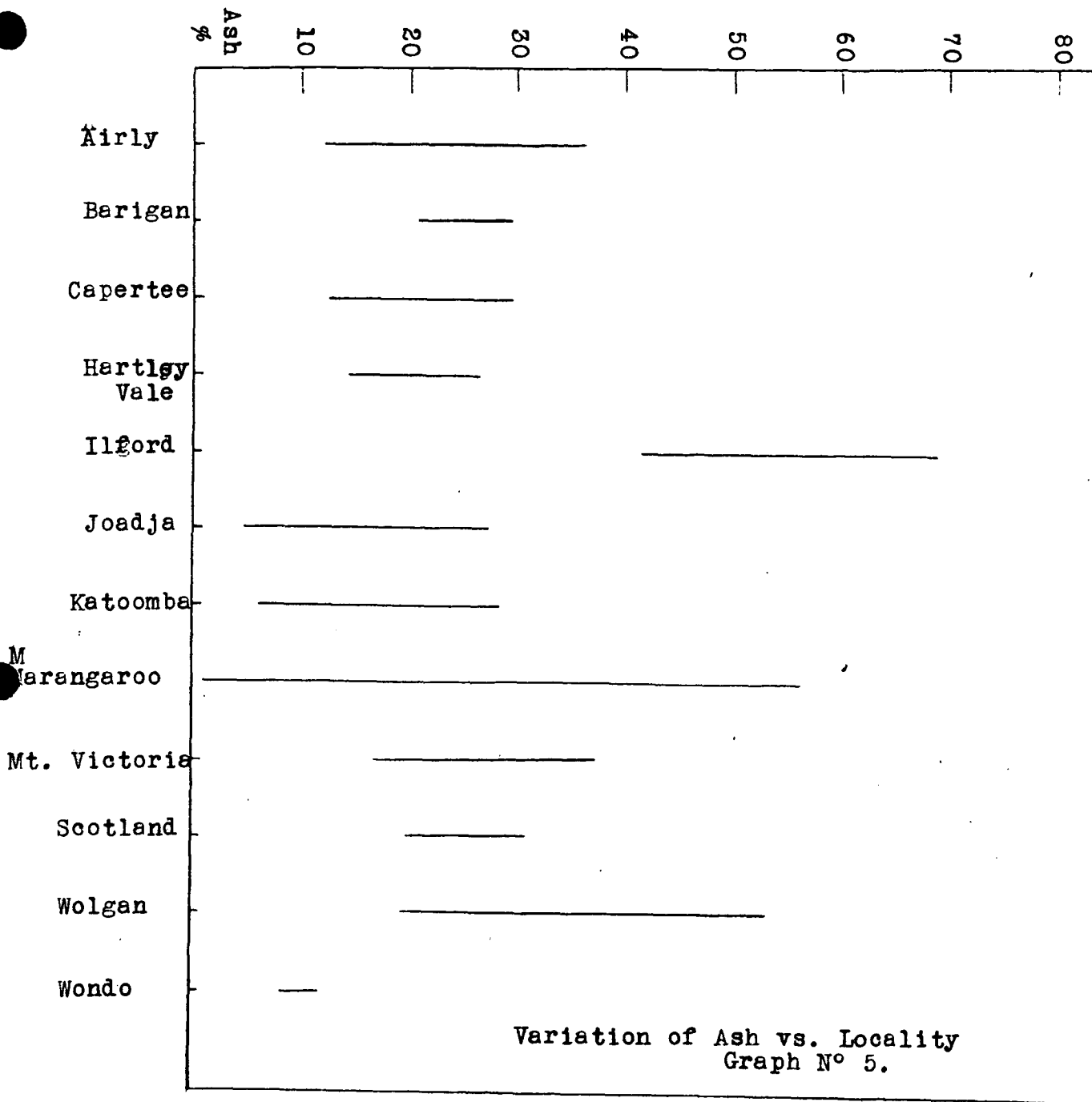


Table 18

Proximate Analyses of Various Torbanites from main seam (various sources and authorities)
About 230 assays taken.

Locality	Moisture		Volatile Matter		Fixed Carbon		Ash		Specific Gravity		Sulphur.	
	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
Airly	0.3	0.6	47.1	79.9	7.6	23.4	12.0	36.7	1.116	1.359	0.505	0.906
Capertee	0.3	0.9	52.3	70.7	7.6	16.1	12.8	29.9	1.129	1.348	0.164	0.549
Barigan	0.4	0.7	59.4	69.9	7.3	10.9	20.4	29.8	1.170	1.256	0.357	0.469
Wolgan	0.3	1.8	37.2	67.9	11.2	15.6	19.8	53.8	1.148	1.563	0.412	0.535
Wondo	0.1	0.7	70.2	75.6	15.6	18.9	8.5	12.0	1.072	1.111	0.453	0.642
Mt. Victoria	0.5	1.7	44.6	67.4	6.6	21.3	17.5	37.5	1.146	1.314	0.521	0.809
Joadja	0.1	1.8	52.8	89.6	5.3	25.0	4.6	27.6	1.008	1.198	0.384	0.837
Marangaroo	0.2	1.8	29.3	93.0	3.9	29.3	1.6	56.4	0.973	1.351	0.343	0.586
Ilford	0.9	1.7	19.0	36.6	8.9	19.5	41.8	69.7	1.231	1.613	0.381	0.601
Katoomba	0.3	1.1	51.3	79.8	12.6	29.8	6.4	28.5	1.050	1.290	0.524	0.837
Hartley Vale	0.2	0.6	41.0	78.1	6.1	10.3	14.9	26.5	1.097	1.245	0.398	0.466
Torbane	0.4	0.8	53.1	69.7	8.0	10.7	19.9	31.3	1.144	1.341	0.401	0.813
Scottish Shales	0.6	2.2	15.8	37.2	1.9	8.9	5.8	77	1.617	2.227	0.5	3.1

The amount of sulphur has also been shown in Table 18, although not strictly included in the "Proximate Analysis". This series of data also illustrates the variation which may be expected over a wide range of samples.

GENERAL DISCUSSION.

To clarify the discussion which follows, it is desirable to enumerate the special features of torbanite which the rich material has been shown to possess;-

Mechanical Properties: extremely tough and resilient.

Fracture: conchoidal.

Powder: very hard to powder and grind.

Colour: reflected; green.
transmitted; red to yellow.

Fluorescence; golden yellow.

Optical properties: refractive index, 1.54
 Specific Gravity: 0.973 min. (observed)
 Specific Heat: 0.34 cal./gm./°C.
 Heat of Combustion: 10,000 cal./gm.
 Coefficient of Expansion: 1.05×10^{-4}
 Electrical Resistance: High.

% Carbon: 84.20 Rounded average values.
 % Hydrogen: 11.93
 % Nitrogen: 0.31
 % Sulphur: 1.02
 % Oxygen: 2.54

Solubility in Organic Solvents: practically nil.

The facts leading to the presentation of a satisfactory chemical structure must agree with the above observations and with the extreme chemical stability of torbanite.

The high oil yield and low solubility of the pure substance indicate a high degree of polymerisation. That torbanite has no appreciable swelling in hydrocarbon solvents, whereas the first product of its decomposition does swell (see later), indicates initial large interatomic forces which are reduced during thermal breakdown. Assuming, then, that the structure of torbanite is that of an eucolloid of enormous molecular weight, it does not appear unlikely that the structure is that of a three-dimensional macromolecule with extensive cross-bridging. The cross-bridgings are not stable under the thermal conditions

of pyrolysis and a proportion of the linkages are destroyed in the initial stages. As no trace of terpenes has ever been found in the oil, it may be concluded that a terpenic structure does not exist inside the molecule.

Additional evidence to support the above hypothesis on the structure of torbanite, is shown in the mechanical properties of the material. One characteristic property of highly polymerised matter, whether natural or artificial, is its resistance to mechanical shock and powdering. This property is well-known in torbanite, and it is interesting to compare Ostromissleuski's (50) remarks on the general properties of polymerised α -metastyrene. Ostromissleuski records that α -metastyrene is "a substance which is tough and permanently transparent, and may be practically colourless. It shows a dull fracture and may be cut with a knife to form thin films or parings. It has a high refractive index, 1.5 - 1.75. Its specific gravity is approximately 1.05, hardness determined on the hardness scale for minerals, approximately 2 - 3. The product is substantially stable under the action of sunlight and weathering. It will withstand relatively strong blows with a hammer and is ground to a powder with great difficulty. In solution it does not decolorise a 3 per cent solution of bromine at 0°C. It shows substantially no change under prolonged action of hydrofluoric acid."

Comparing these observations with similar ones on torbanite it can be seen that the properties are very similar. The major contradiction between torbanite and highly polymerised synthetic hydrocarbon resins is specific gravity. The low specific gravity of torbanite, compared to other highly polymerised material, points to a nucleus

of low molecular weight, or small degree of polymerisation. For instance, the tetramer of polymethyl styrene has a specific gravity of 1.06 and the octamer, 1.07. In contradiction to this, the low solubility of tortanite indicates a high degree of polymerisation and at present the exact explanation is not at all clear.

THE CONSTITUTION OF TORBANITE KEROGEN.

Torbanite is a natural product and, therefore, the kerogen which it contains must have been produced by natural causes; these causes are:- living organisms, pressure caused by overburden and geological changes, time and temperature.

It must be assumed, a priori, that the original substance of kerogen was produced by the metabolic processes of living matter, and for this reason it would be as well to study what information can be gained from a discussion of the biological background.

Biological Background.

In 1936 Blackburn and Temperley (5,71) published a paper dealing with the algae *Botryococcus braunii*, and its relation to the origin of torbanite. In that paper the authors showed conclusively that the matter responsible for the occurrence of Coorongite and similar sapropelites was identical with the algae *B. braunii*. Furthermore, they suggested that the algae responsible for torbanite is the same as that responsible for Coorongite. This algae belongs to the Chlorophyceae and the authors state that it "is a polymorphic species and is a most striking example of an oil producing algae.....and that slight compression causes oily drops to exude from the colony matrix." The fatty matter is soluble in organic solvents and is unsaturated.

The algae contains carbohydrates including cellulose, a little starch, proteins, carotenes and an abnormal amount of fat. As mentioned under 'Corongite', the fresh algae is quite soluble but its solubility decreases with aging.

Under the conditions of deposition, as described in Section I - Origin of Torbanite - the sapropel would decompose due to bacterial action and this action would, presumably, cause breakdown of the carbohydrates and proteins to water-soluble compounds, and would hydrolyse the fats. Marcussen (45) has observed that the decomposition products of algae contain strongly hydrolysed glyceride fats, and that, in such decaying matter, there was slow formation of true waxes by decarboxylation of the free fatty acids. Following these reactions, the high pressure of the overburden, contact catalysis, time and temperature, would effect so great metamorphosis of the matter that very little of the original structure would remain unchanged.

The above hypothesis concerning the origin of kero-gen is similar to that propounded by Engler to explain the origin of flow oil. Engler, in his theory, assumed that all oil originated in fatty matter, these fats decomposed by hydrolysis or saponification to form free acids which gave rise to hydrocarbons, which then polymerised to an insoluble bitumen. The bitumen "depolymerised" to form oil. One of the main disadvantages of the Engler

theory is, that it supposes a thermal "depolymerisation" in the later stages of formation.

The two chief differences between the hypothesis herein put forward and that of Engler are that, in the formation of kerogen,

- (i) the acids have been polymerised to form a solid and not thermally decomposed to produce a liquid.
- (ii) no explanation is needed to cover gas formation, as gases are not found associated with torbanite.

The fatty acid theory seems the most acceptable in the present case.

This contention is supported by the waxy nature of the crude oil, which shows that the kerogen arose from hydrocarbons containing long chains of carbon atoms, for although various types of hydrocarbons may be produced from paraffins; waxes have never been produced by the thermal breakdown of other hydrocarbon types. Furthermore, as these long chains are still unruptured and the kerogen is insoluble, it shows conclusively that at no time could the temperature have exceeded 150°C.

In this section the following points are brought forward:

- (1) Kerogen had an algal genesis.
- (ii) The algae responsible for kerogen possesses an abundance of fats.
- (iii) From a study of the nature of the crude oil,

kerogen must contain long chain structures. Most plants contain appreciable amounts of fats in the form of triglycerides. These fats will hydrolyse to produce fatty acids possessing the required long chains.

- (iv) Decarboxylation of the acids will produce long chain aliphatic hydrocarbons. - Experimental evidence that polymerised unsaturated long-chain fatty acids may be decarboxylated to produce "paraffinic lubricating oils" is cited later.

The following additional points may be added:

- (v) No ethers or ketones have been reported in crude oil, indicating the absence of alkoxy or carbonyl groups in kerogen.
- (vi) Coorongite, which does produce an aliphatic oil on pyrolysis, is formed from algal remains.

Following these important points, it is necessary to postulate the exact nature of the fatty material which took part in the reactions; this is executed in the following pages.

THE NATURE OF THE FATTY MATTER.

The green algae (Chlorophyceae) of which *B. braunii* is a member, often contains large amounts of fatty matter and, as usual in nature, the acids present in these fats are mainly of the C_{16} and C_{18} series. The living algal tissues are very unsaturated, and this unsaturation decreases as the material ages. This would point to a polymerisation of the unsaturated compounds.

Apart from saturated acids, four C_{18} acids will be considered from the possibility of their occurrence, although doubtless C_{16} acids are also present;

Oleic Acid	$C_{17} H_{33}-COOH$
Linoleic Acid	$C_{17} H_{31}-COOH$
Linolenic Acid	$C_{17} H_{29}-COOH$
Elaeostearic Acid	$C_{17} H_{29}-COOH$

All these acids are unsaturated, possessing one or more double bonds. All are found in the vegetable kingdom and all possess the desired long-chain structure. Lovern (82), dealing with the fatty acids from green algae, states "The degrees of average unsaturation of the C_{16} and C_{18} acids are unusually high", and Takahashi (83) has isolated oleic and linoleic acids from marine algae possessing unsaturated acids, 14% of which contained two, three or four double bonds. Although saturated fatty acids occur in addition to unsaturated members, the former, because of their resistance

to polymerisation would presumably remain in their monomeric state.

Of the four acids above mentioned, the first and second named possess one and two double bonds respectively, and for this reason it is unlikely that they themselves would polymerise under the conditions of preservation, although they might act as copolymers.

Linolenic and Elaeostearic acids possess three double bonds each which, in the case of elaeostearic acid, are in the conjugated arrangement i.e. it possesses the resinophore group $-C=C-C=C-C=C-$. Linolenic Acid (9:12:15-octadecatrienoic acid) does not polymerise as readily as elaeostearic acid, but under suitable conditions the double bonds are rearranged into the conjugated position and polymerisation proceeds in the normal manner.

Elaeostearic Acid (9:11:13-octadecatrienoic acid) exists in two forms, α -Elaeostearic acid and β -Elaeostearic acid, the former is thought to be the trans-cis-cis isomer and the latter, the cis-cis-trans isomer. In this discussion, no differentiation will be made between the two isomerides.

THE POLYMERISATION OF UNSATURATED FATTY ACIDS.

During recent years much information has been made available on the polymerisation of unsaturated fatty acids (7a,7b,2). The results of these researches may be summed up as follows;

- (1) Acids possessing two or more double bonds in the conjugated position polymerise to viscous liquids or solids by means of a Diels-Alder reaction, to give derivatives of cyclohexene which then may be dehydrogenated to produce compounds possessing benzene rings.
This ring closure has received experimental confirmation by Petrov (54) who has observed cyclic compounds in the polymerisation products of fatty acids. In addition, Hurd states (31) that, by close vacuum fractionation, cyclic monomers containing six-carbon rings may be isolated from the polymer.
- (2) Non-conjugated systems are transformed into conjugated systems by bond migration, following which transference they polymerise in the manner described above (60).
- (3) During polymerisation, the unsaturation decreases, the Diene number and Bromine number may reach zero, and the specific gravity increases. These changes indicate a gradual transformation from

an unsaturated compound to a more saturated one containing ring structures, and it is interesting to note that when three double bonds are present, the increase in specific gravity is much greater than the corresponding increase in acids with only two double bonds. This effect is caused by the formation of dicyclic structures in the former case, whereas only monocyclic rings are produced from acids with two double bonds.

- (4) Polymerisation does not depend on the presence of oxygen, for Bauer and Liao (2) have formed a solid polymer from elaeostearic acid when the reaction was carried out in an atmosphere of carbon dioxide.
- (5) The carboxyl group retains its identity during polymerisation.
- (6) For acids, other than elaeostearic acid, the polymerisation is slow at ordinary temperatures. However, the reaction rate is increased by ultra-violet radiation, the presence of certain mineral acids (77), pressure and contact with infusorial earths.

On account of the fact that cyclic compounds have less molecular volume than the corresponding aliphatics, the effect of pressure is to promote ring formation.

In the light of the above findings, it is now possible

to postulate the formation of kerogen from unsaturated fatty acids produced by the original algae.

STRUCTURE OF KEROGEN FROM ALGAL ORIGIN.

Although, as will be shown later, certain analyses would indicate a specific acid taking part in the formation of kerogen, it seems unlikely that this is so owing to the complexity of natural processes.

In this portion of the work, kerogen is treated as a continuous solid, whereas, in actuality, it is composed of numerous small bodies, each of which is an individual particle. Each 'yellow body' is imagined as a droplet of oil which has reacted to produce the polymerised matter discussed herein.

The different types of particles probably vary in degree rather than character, and all are assumed to possess the same fundamental composition. The rich torbanite from Marangaroo (10b), on the other hand, was shown to contain practically only one type (microscopically homogeneous). The variations shown by the 'yellow bodies', however, do not affect the validity of this theory.

Notwithstanding this supposition, in the treatment which follows, only one acid will be discussed, as this acid provides sufficient information to account for the observed facts, and only small changes would make the theory tenable for similar unsaturated fatty acids.

In the previous sections the degradation of algal fats to free fatty acids was shown to be consistent with observed processes at the present day, and it is now possible

to trace the history of the process from the fatty acid to the solid kerogen.

The first stage in the process of polymerisation would be reached when the algal mass passed the decay period. The action of decay would raise the temperature in the sapropel and this would cause the polymerisation of the acid to a jelly-like, low-degree polymer. This polymer would correspond to the present-day Coprongite and the Balkash sapropelite.

At this juncture it is interesting to compare the ultimate analysis of elaeostearic acid with that of the sapropelite.

	Sapropelite (78)	Elaeostearic Acid
C	73.8	77.6
N + S + P	1.9	
H	10.6	10.9
O	13.7	11.5

Elaeostearic Acid = $C_{18} H_{30} O_2$

Sapropelite = $C_{18} H_{31} O_{2.5}$ - approx.

The next stage covers the transition of the soft polymer to a solid mass.

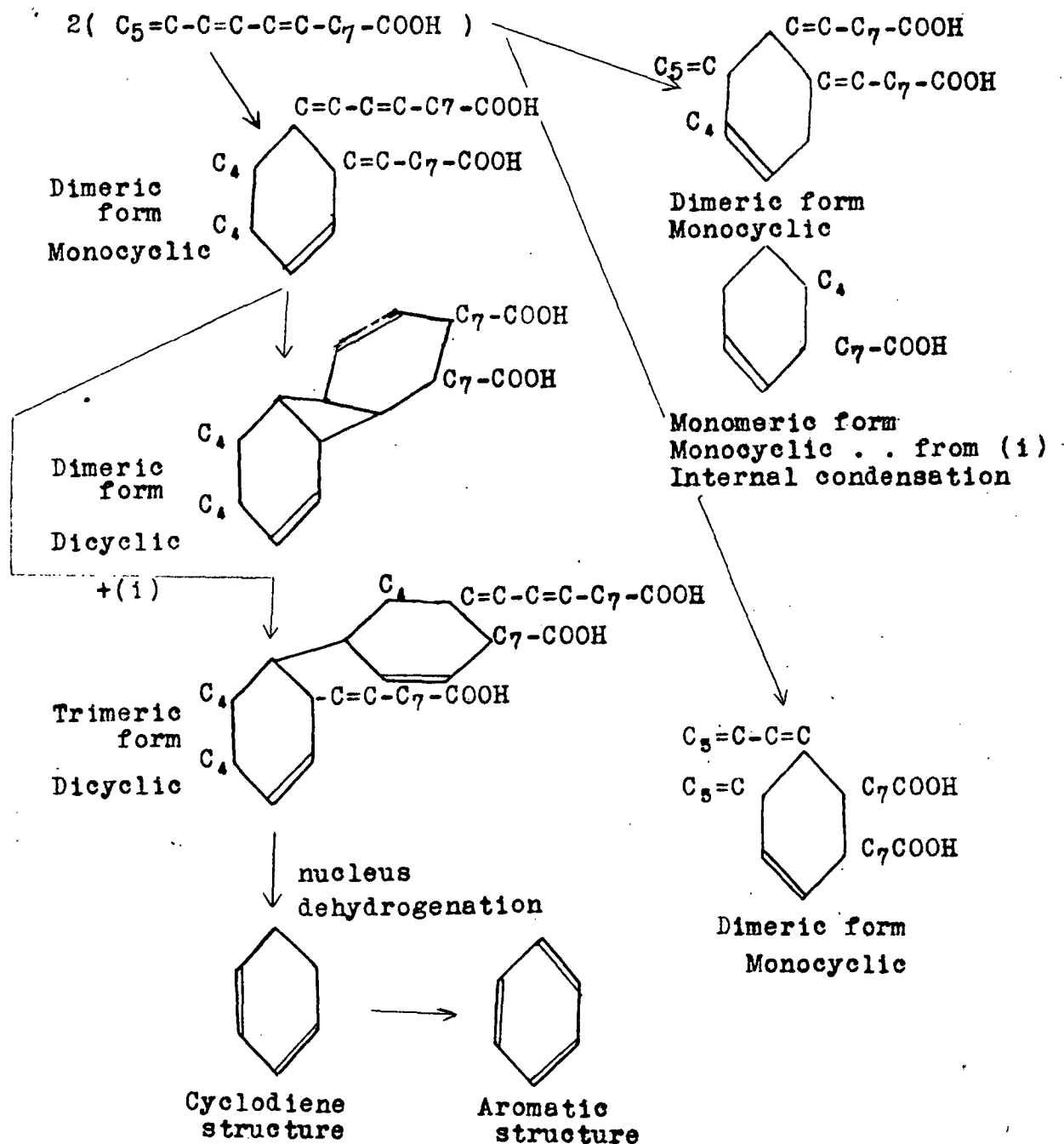
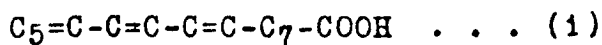
Following the first stage, the organic matter was covered with an overburden of sandstone and other rocks, causing a great pressure to be exerted on the rubbery mass, which further polymerised to a rigid solid. The effect of high pressure has been studied in relation to the polymerisation of diolefines, and recent research (12) has

demonstrated that under a pressure of 1800 atm., isoprene produces an insoluble non-plastic solid.

In the case of torbanite, it has been estimated that the pressure exerted by the covering rocks would approximate to 650 atms. Under these conditions, dimeric and higher forms of the acid would further polymerise to produce the rigid polymer which is termed Torbanite; a diagram of the early stages of such polymerisation is given on the following page. The diagram illustrates the polymerisation of eleostearic acid to the trimer by means of a Diels-Alder reaction; both dimer and trimer contain the reactive conjugated double bond system, and further polymerisation could then proceed at this point, either with other polymer molecules or with further quantities of eleostearic acid.

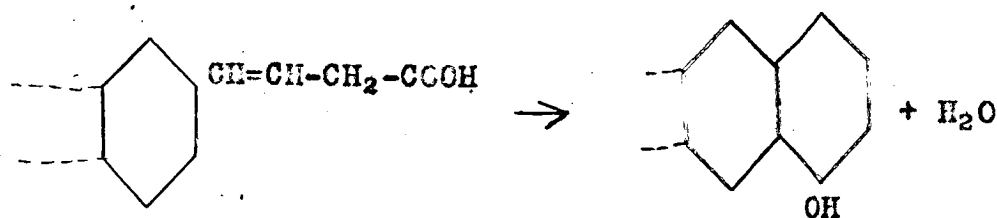
The diagram indicates only a few possibilities, and no doubt, under suitable conditions, other reactions would occur. In addition to the reactions given above, other oxygen, sulphur and nitrogen atoms take part in the polymerisation, but these elements occur in such small quantities compared with hydrogen and carbon, that it seems doubtful whether they should be included in a study of the polymer molecule. Possibly oxygen, and to a lesser degree sulphur, act as linking elements between two polymer molecules, as is thought to be the case in coal. Alternatively, oxygen may exist in the form of hydroxyl radicals produced by

THE POLYMERISATION OF ELAOSTEARIC ACID



(carbon skeleton only; strain angles neglected)

ring close of terminal carboxyls, as in the Fittig and Erdman (25) synthesis, thus;



Estimation of hydroxyl in the raw material gave zero result, but as phenols are present in the crude oil, the above reaction does not seem unlikely, although Carlson (84) suggests that free carboxyl groups are present in kerogen and that they give rise to portion of the carbon dioxide formed on pyrolysis. As mentioned in the earlier portion of this work, sulphur apparently occurs in two combinations, in one, the sulphur atom is loosely held and appears as hydrogen sulphide in the early stages of the decomposition, and in the other held in primary valencies which gives rise to thiophenes. It is probable that nitrogen originates from the protein material and occurs in complex formation; on thermal decomposition of the torbanite the nitrogen appears in combination in heterocyclic rings and as amines and ammonia.

The theory given above receives very strong support from the work of Chowdhury (85) and his co-workers, who decarboxylated the polymers of elaeostearic and linoleic acids by thermal treatment with metallic salts to produce viscous oils "resembling paraffinic lubricating oils" cp. shale oil.

Solubility of Torbanite in Organic Liquids.

One of the most characteristic features of torbanite is its stubborn resistance to dissolution in organic and inorganic liquids. This feature serves as one criterion in distinguishing torbanite from other products, similar in appearance, such as asphalts, bitumens and pitches.

Apart from those which actually attack it, and these are few, no solvent has yet been found which has any appreciable action on torbanite. The low solubility of torbanite, and of shales in general, has been a subject for discussion by various writers, and all are agreed that the solubility of kerogen is limited to a few percent. Some workers have reported increased solubility in certain high boiling solvents but it is doubtful whether this increased solubility is not due to some chemical effect.

The solvents which have been employed may be broadly divided into:

- (a) pure hydrocarbon solvents; these are not very effective.
- (b) others; such as heterocyclic nitrogen bases, oxygenated substances and halogenated solvents.

(a) Pure Hydrocarbon Solvents are probably the only liquids in which true solution is effected and for that reason the amount of material dissolved from the torbanite is negligible.

(b) All other solvents probably have certain chemical action.

It is well known that the high solvent activity of liquids such as pyridine, on coal, is due to its peptising action on the colloid, and Tideswell (70) thinks that the action of pyridine as a solvent should be regarded as that of 'loosening' the colloid mass. Furthermore, the great difficulty encountered in attempting to remove the last traces of pyridine from extracted torbanite, and the behaviour of the redispersed pyridine residue, gives evidence that pyridine exerts an action more than that of a pure solvent.

However, it is reasonably safe to assume that most low-boiling hydrocarbon solvents have very little chemical action on the torbanite. The question then arises whether the solute represents foreign material, such as resins which have been introduced in minute amounts into the kerogenous matrix, or a small portion of the kerogen which has been dissolved out in the normal manner. The problem has been solved, in the case of extracts of New Brunswick shale, by McKinney (43). McKinney extracted two hundred and seventeen kilograms of shale with acetone and then succeeded in demonstrating that most of the extracted material consisted of hydrocarbons belonging to the paraffin and cycloparaffin series, extending from a C_{12} fraction upwards. A small amount of non-hydrocarbon material was isolated but not examined. Similar results to the above were obtained

by Petrie (33) on the extracted products from New South Wales torbanite, who records that the extracted matter "consists of saturated hydrocarbons of high boiling point, together with a small quantity of other compounds of high specific gravity." The properties of the extract obtained by Petrie are given in Table 19 following:-

Table 19.

Chemical Properties of Extracted Oil
from N.S.W. Torbanite.

Specific Gravity ² _{4°}	= 0.9316
Refractive Index at 20°C.	= 1.5338
Setting Point, °C.	= 30
Carbon%	= 85.27
Hydrogen %	= 11.62
Not determined %	= 3.11

The limited amount of soluble material that can be obtained from the N.S.W. torbanite and overseas shales is shown in Table 20.

Table 20

Solubility of Torbanites and Shales.

% on dry weight of sample.

Solvent	Locality.			
	New Bruns- wick (43)	Colorado (40)	S.African Torbanite (47)	N.S.W. Tor- banite (this work)(ex Glen Davis)R.F.C.
Acetone	2.6	1.48	0.42	1.51
Chloroform	2.2	--	0.60	1.34
Benzene	3.2	--	0.50	1.00
Carbon Bi- sulphide	2.8	1.00	0.54	--
Ether	2.2	--	0.36	0.93
Carbon Tetra- chloride	2.6	--	0.47	1.04
Alcohol	1.5	1.43	--	1.40
Pyridine	2.6	2.04	--	2.05 *

* See special paragraph.

The solute in most cases consisted of a sticky semi-solid to solid tar which varied in colour from light orange to dark brown.

In order to ascertain whether any correlation existed between nature of solvent, the torbanite deposit, and the amount dissolved, a series of extractions were carried out on torbanite samples from different localities, using a variety of solvents. The following are the experimental details:-

Experimental.

The sample was usually a hand-picked one which was ground in a disc pulveriser to pass 60 IMV mesh. The powder was "cone-and-quartered" in the usual manner, and then dessicated in an air oven at 105°C. for a short time, usually about four days. A pre-extracted dried Soxhlet thimble of known weight was used to contain the sample, which was then extracted in the normal Soxhlet extraction apparatus; the apparatus used was of the ground-glass-joint type and made of Pyrex glass. After extraction, for a certain time interval (always in excess of that required to produce a colourless overflow in the extractor) the thimble was removed, dried to a constant weight and the loss in weight found. At a later stage in this section of the work a greater amount of extract was required and a larger extractor of the same type was used.

The following table shows that there appears to be no

correlation between the nature of the solvent, the amount of soluble material, or the source of the sample.

Table 21.

Locality of Sample	Solvent	Weight of Sample grms.	Loss in Weight grms.	Loss % w/w dry basis	Loss % w/w dry ash-free basis.
Coolaway	Benzene	7.5839	0.0624	0.82	0.88
Marangaroo	Benzene	3.2146	0.0322	1.00	1.04
Marangaroo	Ethanol	3.5618	0.0498	1.40	1.46
Mount Kembla (1)	Benzene	3.3816	0.1081	3.19	5.03
Glen Davis	Ether	4.9011	0.0338	0.69	1.03
Coolaway	Ether	4.4683	0.0416	0.93	1.00
Coolaway	Chloro- form	3.7177	0.0498	1.34	1.44
Coolaway	Acetone	5.0259	0.0759	1.51	1.62
Marangaroo	Carbon Tetra- chloride	6.0806	0.0632	1.04	1.09
Coolaway	Carbon Tetra- chloride	3.4536	0.0349	1.01	1.08
Plevna (2)	Benzene	4.0242	0.3367	8.36	27.23

(1) Mt. Kembla - A true laminated oil shale.

(2) Plevna - A tertiary shale from Queensland containing much moisture and foreign matter.

Attempts were made to extract the torbanite with higher-boiling solvents, such as phenol, α -phellandrene, furfural, cyclohexanone, with little success. Similar results have been reported with coal (86). Storch records that certain high-boiling solvents hold the extract tenaciously and are extremely difficult to remove, for instance aniline has a tendency to combine with the extract and it is impossible to remove it. In the case of phenol, the evolution of hydrogen sulphide from the exit of the extractor condenser showed decisively that

some decomposition was taking place, and after extracting for 18 hours, the thimble commenced to disintegrate. When a sample was extracted with α -phellandrene the residue showed a gain in weight, even after vacuum drying. Further extraction with benzene failed to convert this gain into a loss, as shown below;

Table 22.

Extraction of Glen Davis Torbanite with α -Phellandrene.

Weight of thimble	= 1.7400 grms.
Wt. of thimble and shale	= 6.0725 grms.
Weight of shale	= 4.3325 grms.
Weight after extraction	= 7.8015 (vac. dried)
Time of extraction	= 11.3 hours.
Weight increase	= 40.0%
Weight after re-extraction with benzene	= 6.1375 grms.
Weight increase	= 1.5% calc. on original.

Extraction with cyclohexanone.

Cyclo-hexanone has recently (23) been reported as being a good solvent for kerogen, but the present writer could not succeed in separating the solvent from the solute and the sample showed a gain in weight of 5.60%. The cyclo-hexanone extract was a hard orange solid which had to be clipped from its container, in appearance it was very much like shellac. This residue was soluble in benzene, from which solution it was precipitated as a brown powder by adding excess of petroleum ether.

Pyridine Extraction of Torbanite.

As mentioned in the beginning of this section, there

seems little doubt that the action of pyridine is more than that of a pure solvent, and it is probable that its action on torbanite resembles its action on coal, i.e. that of a peptising agent. Another point mentioned was that it is extremely difficult to remove the last traces of pyridine from both residue and extract. To illustrate this latter point, a sample of Glen Davis torbanite (powdered to pass a 100 IMM screen) was extracted with pyridine for 53 hours, and then dried in vacuo at 100°C. The residue was weighed at intervals and the observations below show this point conclusively:

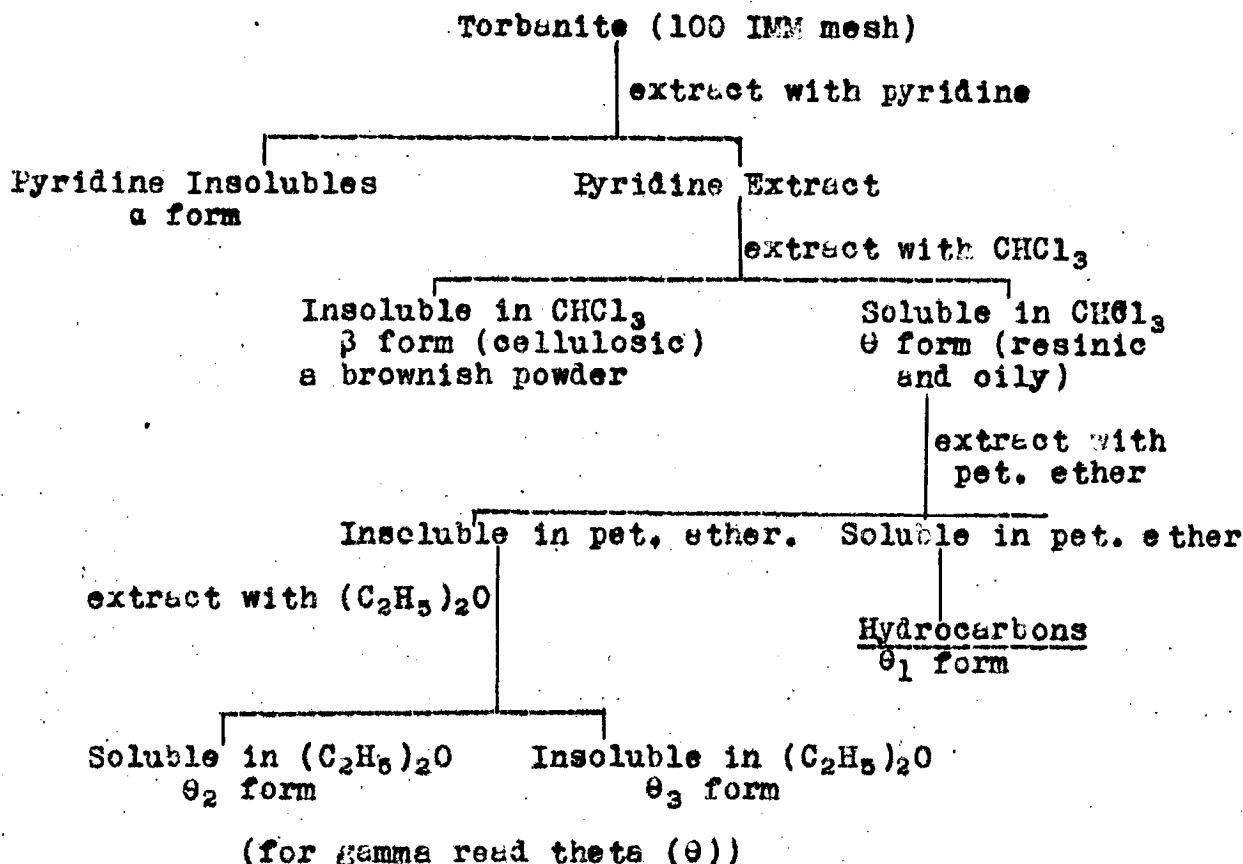
Table 23.

Time days.	Weight grms.	Loss %	Rate of Loss % per day.
0	6.9921	original weight	
1	6.9396	0.75	
3	6.9035	1.27	.21
5	6.8817	1.58	.15
6	6.8671	1.79	.13
8	6.8531	1.99	.07
12	6.8489	2.05	.01
16	6.8491	2.05	-

In order to demonstrate whether the pyridine extract had a uniform composition, a larger amount was prepared and treated along the lines of the Bone and Wheeler (80) technique, in which coal is extracted by a series of selective solvents and by this means the soluble portion is divided into resins, ulmins, cellulosic and other groups.

The actual technique employed in the present case was after Stopes and Wheeler (68) and is illustrated below

in the skeleton flow sheet;



The following observations were made during the extractions:-

α form; consisted of the main bulk of the powder (97.2% w/w) and was not examined further, except to note that whereas the original powdered sample had a dull appearance, after extraction by pyridine the residue (the α form) was strikingly shiny. This phenomenon is observed with some flake micas.

The Pyridine Extract (1.4% w/w on original) was a brown sticky solid, which could be moulded between the fingers.

The pyridine solution was deep-red in colour with an olive-green fluorescence.

β form (1.1% w/w on original) was a dark brown powder which swelled on heating, at the same time giving off acrid vapours. There was no perceptible melting point.

θ form - a dark brown waxy solid with a faint smell, which was separated into:-

- θ_1 form: orange waxy solid, m.p. $48^\circ\text{C}.$, no fluorescence, unsaturated.
- θ_2 form: a light brown powder.
- θ_3 form: a dark brown powder.

General Remarks.

Summing up these results, it may be said that the chemical structure of the pure kerogen of torbanite is such that its solubility is practically nil and there appears to be no correlation between the type of solvent and the small amount that it dissolves. In all cases the solute consists of orange to brown sticky semi-solid. It will be shown later in this work that although raw torbanite is nearly insoluble, its solubility increases greatly as it begins to decompose, and that this increase in solubility is not due to oil formation, but to the presence of an intermediate heavy tar which acts as the precursor to the crude oil.

It is unique to find a naturally occurring substance which will yield on pyrolysis over ninety percent of its weight of a petroleum-like oil, and yet is inert to

chemical reagents. However, if the underlying structure of kerogen is proved to be that of a highly polymerised hydrocarbon, many of the anomalies would disappear, for even certain low polymers are most insoluble, for instance the heptamer of polyoxymethylenedi-acetate, and the octamer of polyoxymethylenedimethyl ester have solubilities of only 42×10^{-5} and 4×10^{-5} grms./ml. respectively. Thus, when it is realised that artificial resins have been produced with a degree of polymerisation of over a hundred, and that ~~moderate~~ temperatures favour high polymerisation, the insolubility of torbanite may be readily understood.

Although torbanite itself shows no tendency to swell in organic solvents, the primary products of its decomposition has this power to a certain degree, and this fact indicates that at an early stage in the pyrolysis some of the cross-linkages have been ruptured, permitting a certain amount of solvation of the long-chain structures.

Analysis of Ash.

The inorganic matrix of torbanite contains silicon and aluminium in large amounts, but over twenty elements have been found. The mineral matter may be divided into two portions;

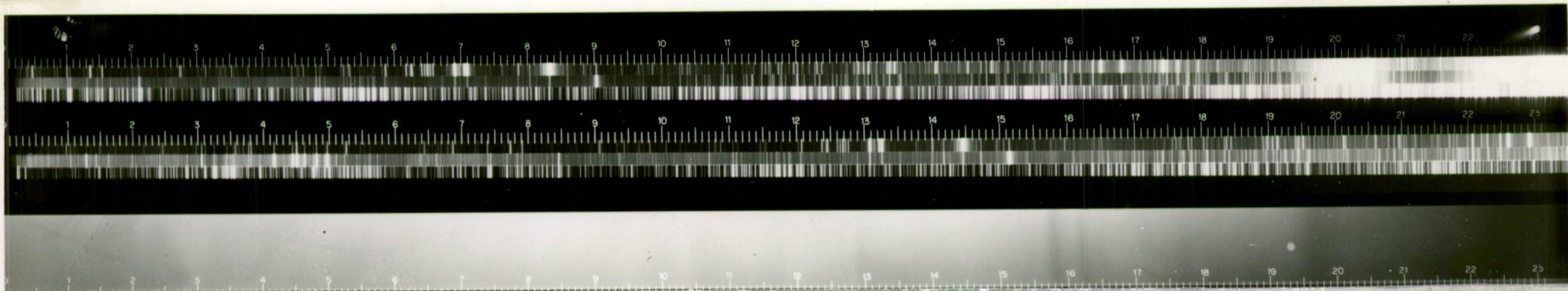
- (i) The adventitious, clayey matter introduced during, and subsequent to, deposition.
- (ii) The fundamental inorganic matter of the algae.

The adventitious argillaceous detritus consists of aluminium silicates, silica, iron compounds and the usual minerals associated with material of this nature. In addition to the above-mentioned compounds, comparatively large amounts of pyrites (FeS_2) and impure talc are found associated with torbanite in some localities of New South Wales. The relative concentrations of the various elements vary greatly from deposit to deposit and in different spots in the same seam. This variation will be especially noticed in exposed seams which have been burnt; localised patches of ash will have a bright red colour, denoting high amounts of ferric oxide, whereas patches, only a few inches away will be pure white in colour.

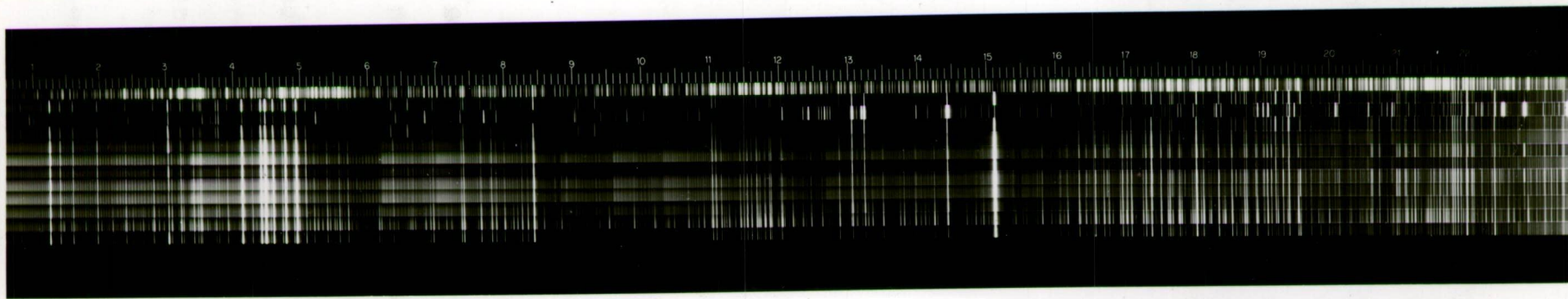
As a general rule, the fully ignited ash of torbanite is white, but variations from a dull red to a dirty yellow, may be expected (cp. ash from Strathpine (Queensland) shale which is brown, and ash from Crepuki (New Zealand) which is always pink).

A

B



I



II

The analyses which follow indicate the extreme variation to be found, rather than typical results, but nevertheless, alumina and silica constitute the main portion.

Table 24.

Analysis of Torbanite Ash.

Locality	Marangaroo	Wollar	Bong Tong Mt.	Newnes	Barigan.
Analysis					
SiO ₂	68.19	37.48	77.37	56.82	80.67
Al ₂ O ₃	15.24	54.15	16.30	35.09	13.36
Fe ₂ O ₃	11.53	3.92	4.04	2.88	5.11
CaO	1.89	1.42	1.04	2.56	0.37
MgO	1.11	0.31	0.18	0.92	0.25

Although the elements given in Table 24 constitute almost 98% of the total mineral matter, the residual two percent contains numerous other elements, both metallic and non-metallic. The spectrograms opposite were taken with a fully-automatic Hilger large quartz spectrograph with an exposure of thirty seconds, arcing between carbon electrodes (acknowledgement is made for the co-operation of Miss Blakney in taking these spectrograms).

Spectrogram 1 shows the spectra of (reading from the bottom of the triplet in each case);

(a) iron arc.

(b) ash from rich torbanite from Marangaroo.

(c) Raies Ultimes powder.

A and B are the same specimens taken over different ranges of wave-lengths.

Spectrogram 11 is the arc spectra of:- (reading from the bottom), the ash of:

- | | |
|-----------------------------------|--------|
| (1) Strathpine shale (Queensland) | |
| (2) Orepuki (New Zealand) shale. | |
| (3) Mt. Kembla shale. | E.S.W. |
| (4) Bong Tong Mountain torbanite. | " |
| (5) Ilford torbanite. | " |
| (6) Mudgee torbanite. | " |
| (7) Glen Davis torbanite. | " |
| (8) Airly Torbanite | " |
| (9) Coolaway Torbanite | " |
| (10) Raies Ultimes powder. | |
| (11) repeat of (9) | |
| (12) Iron | |

In Spectrogram I, the following elements were identified:

Magnesium +, Manganese; Zinc +; Lead +; Iron +; Calcium +, Tin; Silicon; Phosphorus, Iridium, Vanadium;+, Titanium +; Antimony; Bismuth; Molybdenum; Beryllium; Sodium +; Silver; Nickel +; Chromium +; Mercury; Aluminium +; Copper.

Those elements marked with the + sign have been found in the ash of Sapropelite (28), together with Arsenic, Barium, Boron and Strontium.

Although most of the above elements undoubtedly occur in the adventitious mineral matter, the occurrence of metallic ions in organo-metallic complexes must not be overlooked. When the origin of the organic matter is considered, the occurrence of chlorophyll, and other complexes must be taken into account. Porphyrin complexes in the form of iron and vanadium salts have been found in oil shales (73) and sterols have been reported to occur in bituminous shales (55). These results are interesting.

not only from the view-point of phyto-chemistry, but also from the fact that they prove that, at no time, has the temperature to which the shales has been subjected, risen much above 180°C.

THE OXIDATION OF TORBANITE.

Analyses by chemical methods are mainly degradative, in which the unknown material is broken down into simpler molecules which may be identified. From a knowledge of the simpler units a picture is obtained of the original material as a whole.

Unfortunately, torbanite is so inert, and the matter so unreactive, that the drastic treatment necessary for its complete decomposition provides little evidence of its entire structure.

The only method of chemical analysis which has provided appreciable information is that of alkaline permanganate oxidation. Down and Himus (19c) have published results of alkaline permanganate oxidation of various shales and found acetic, oxalic and various benzene carboxylic acids in the oxidation products. Alkaline permanganate oxidation of Balkash sapropelite (87) gives no benzene carboxylic acids but monobasic and dibasic aliphatic carboxylic acids, including formic, propionic, butyric and caproic acids, and oxalic succinic pimelic and adipic acids.

These acids can arise from the oxidation of fats and it is interesting to note that the last mentioned is easily formed from the oxidation of cyclohexane. These facts are to be contrasted with the oxidation of oil

shale from which aliphatic acids higher than acetic have not been reported. All the above facts are in accordance with the theory of the formation and structure of torbanite, put forward in this thesis.

Experimental.

A finely-powdered sample, weighing approximately eighty grams (79.68 grms.) was suspended in six litres of water to which had been added caustic potash, so that the mass-ratio of KOH/kerogen was 1.6, the suspension under reflux was kept at boiling point for 196 hours. During this period, solid potassium permanganate was added so as to maintain a permanent pink colour, and distilled water was added to maintain constant volume.

After the period of oxidation, the liquid was filtered to remove unreacted torbanite and oxides of manganese. The amount of torbanite which was oxidised by this treatment was 7.5%.

The filtrate was acidified and steam distilled. This procedure divided the organic acids into two portions;

(a) the steam-volatile acids.

(b) the non-steam-volatile acids.

A portion of the Steam-Volatile acids was converted into their ammonium salts and evaporated to dryness. Further heating of a portion of the residue produced the odour of crude acetamide. A further portion of the free acids was converted to the ethyl ester, from which the

anilide was produced. After recrystallisation, the melting point of the anilide was $110^{\circ}\text{C}.$, melting point of acetanilide = $114^{\circ}\text{C}.$

% nitrogen found = 10.0

calculated = 10.3

The non-Volatile acids were concentrated and the presence of oxalic acid confirmed by precipitation as calcium oxalate. Another portion of the non-volatile acids was converted to their potassium salts and the solution evaporated to dryness. The residual solids were dirty yellow in colour and showed only a slight tendency to crystallise. Owing to the small amount of benzenoid acids obtained, no further tests were undertaken on the bulk oxidation of torbanite.

A carbon-balance oxidation was carried out, the experimental details of which were taken from the work of Down and Himus (19c). After boiling for 93 hours, only 3.7% of the torbanite was converted into soluble material and only 7.2 ml. of 3% potassium permanganate was consumed.

In view of the stability of the sample and the small amount of oxidation which occurred, it was thought inadvisable to obtain quantitative data or to pursue further this line of investigation.

GENERAL DISCUSSION OF THE STRUCTURE OF KEROGEN.

The analyses which are to be discussed in relation to the general structure of kerogen may be grouped under the following two headings;

(i) Ultimate Analysis.

(ii) General Features.

For the purposes of the discussion which follows, the material found at Merangaroo in New South Wales and described by Cane (10b) will be accepted as pure kerogen, formed under ideal conditions.

Ultimate Analysis.

The ultimate analysis of kerogen given in Table 13 is:

Carbon	84.20
Hydrogen	11.93
Nitrogen	0.31
Sulphur	1.02
Oxygen	<u>2.54</u> (diff.)

100.00

In taking this analysis as typical kerogen, some criticism has been received because of the low oxygen figure, when compared with other analyses. The main reasons for assuming that pure kerogen would show a low oxygen figure are given in the two points which follow:-

(i) Although certain analyses have been performed on substantially pure kerogen, this material has been prepared by drastic chemical treatment, and it appears unlikely that no change has occurred in the substance. Furthermore, kerogen prepared in such manner is in a finely-divided state

and, in this condition, shows a strong tendency to oxidise. Kerogen prepared by the U.S. Bureau of Mines, containing less than 10% ash "will ignite spontaneously in an oven at 104°C., if not stirred thoroughly and frequently.... The kerogen seems to oxidise and generate heat to reach a temperature above that of the oven" (27b) (cp. high stability of torbanite from Marangaroo - 2% ash). Nevertheless, the U. S. Bureau of Mines results given in the Bulletin (27b) are based on samples dried in an air-oven (the emphasis is mine - R.F.C.) and for the kerogen of Australian torbanite they obtained;

Carbon	81.20
Hydrogen	10.20
Oxygen	6.35
Nitrogen	0.80
Sulphur	0.65
Ash	0.80

a result differing little from that taken in this work, with the exception of the higher oxygen content.

(ii) There seems a general tendency for the oxygen content to decrease with increasing oil yield. Whether this variation can be correlated with ash, or is an intrinsic quality of the organic matter, is a debatable question. It is the opinion of the writer that organic matter formed under favourable conditions (high oil yield) and allowed to polymerise undisturbed, would have a lower oxygen figure than material which, during the time of deposition, was disturbed by mixture with silt and argillaceous detritus.

In order to make a comparison of oxygen content with concentration of mineral matter in torbanite, the following

figures, taken from Table 13, have been arranged in decreasing oxygen percentage. These analyses have been performed on the raw material and calculated back to an "ash-free" basis.

Table 26.

<u>Source</u>	<u>Oxygen %</u>	<u>Ash %</u>
Marangaroo	2.54	1.9
Joadja	5.87	6.55
Transvaal	6.99	27.26
Greta	9.53	16.11
Armadale	8.24	18.38

op. Analysis on pure kerogen by chemical treatment
(27) 6.35 0.8

34.2 (on original)

On the other hand, a compensating factor for false high oxygen figures is obtained by calculating back to an "ash-free" basis, these analyses carried out on the raw material, for such analyses make no allowance for water given off from dehydration of the hydrated aluminium silicates, when the loss of water occurs at high temperatures. This is a source of two errors, first the ash content as given by ignition to constant weight does not represent a true figure for the mineral matter, secondly, evolved water of hydration is included in the water formed by oxidation of the hydrogen.

These points illustrate the difficulty encountered in arriving at a true oxygen figure for low quality torbanite.

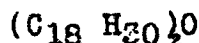
when this quantity is calculated "by difference", notwithstanding it is felt that the ultimate analysis given of the Marangaroo torbanite should be accepted as typical of nearly pure organic kerogen which has been formed by natural processes under ideal conditions.

Accepting the analysis given in Table 13, the following empirical formula may be calculated. In these calculations nitrogen and sulphur are neglected, as they aggregate only 1.3% of the whole.

	<u>% by Weight</u>	<u>Atomic proportions</u>	<u>Calc. to C₁₈</u>
Carbon	84.20	7.02	18
Hydrogen	11.93	11.84	30.26
Oxygen	<u>2.54</u>	0.16	0.41
	98.67		

i.e. C₁₈ H₃₀ O_{1/2}

which may be written:



cp. Elaeostearic Acid: C₁₈ H₃₀ O₂

and Balkash Sapropelite

calc. from Zallesky (78): (C₁₈ H₃₀ O₂)₂.H₂O *

(the grouping of hydrogen and oxygen in the place marked * is not to be taken as written - it is only a convenient means of making a comparison between the three formulae.)

The foregoing analysis and three others will be taken as constituting typical analyses for torbanite kerogen.

Table 27

Empirical Formulae of Kerogen.

Ultimate Analysis (from Table 13).

	Marangaroo	Joadja	"Australia"	Armadale	Elaeostearic Linolenic acids.	As comparison.	
	1	2	3	4		Pumpherston 5	Broxburn (19a) 6
Carbon	84.20	80.60	81.85	80.52		71.78	76.3
Hydrogen	11.93	12.90	10.28	10.13		10.11	10.9
Oxygen	2.54	5.87	6.40	8.24		13.32	10.3
N. and S.	<u>1.33</u>	<u>0.63</u>	<u>1.47</u>	<u>1.11</u>		<u>4.79</u>	<u>2.5</u>
	100.00	100.00	100.00	100.00		100.00	100.00

Ultimate Analysis (N. and S.-free)

Carbon	85.33	81.11	83.07	81.42	77.6	75.39	78.2
Hydrogen	12.10	12.98	10.44	10.25	10.90	10.62	11.2
Oxygen	<u>2.57</u>	<u>5.91</u>	<u>6.49</u>	<u>8.33</u>	<u>11.5</u>	<u>13.99</u>	<u>10.6</u>
	100.00	100.00	100.00	100.00	100.00	100.00	100.0

Ultimate Analysis (atomic %)

Carbon	7.10	6.75	6.92	6.78	18	6.28	6.5
Hydrogen	12.00	12.78	10.32	10.16	30	10.54	11.1
Oxygen	0.16	0.18	0.41	0.52	2	.87	0.66
C/H ratio	7.05	6.25	7.96	7.95	7.1	7.1	7.0

Empirical
Formula:(C₁₈ basis) C₁₈H₃₀O_{0.4} C₁₈H₃₄O_{0.5} C₁₈H₂₇O_{1.1} C₁₈H₂₇O_{1.4}C₁₈H₃₀O₂C₁₈H₃₀O_{2.5}C₁₈H₃₁O₂

The variation in empirical formulae shown in Table 27 is small when the mode of formation is considered, and may be caused by;

- (a) variation in the constitution of the monomer.
- (b) variation in the degree and/or type of polymerisation with subsequent side reactions.
- (c) addition of small amounts of other compounds.

High C/H ratios are usually accompanied by high oxygen figures and this may be caused by the oxidation of kerogen. As in the oxidation of linolenic acid, the reaction probably initially takes place with the formation of a peroxide at the double bonds, and as the divalence of oxygen corresponds to two atoms of hydrogen, any oxidation which occurs will correspond to a decrease in the 'potential' hydrogen content.

Bearing in mind the above facts, the third and fourth examples may be regarded as kerogen which, owing to specific conditions, has been slightly oxidised before complete polymerisation. As in the case of sulphur, it appears likely that oxygen occurs in two kinds of combinations, in the first place, intermolecular cross-bridging in which each oxygen atom has its valency bonds attached to different molecules. This type of oxygen-bridge occurs in some polymers, and coal, and gives rise to oil-resistant properties. Secondly, intra-molecular combinations of

oxygen, arising from partial oxidation of the monomer or dimer, - no alcohols or furans have been reported to occur in shale oil.

Although the preceding remarks have been based on the assumption that only one monomeric compound took part in the formation of kerogen, this is probably not true. In nature, the production of a single specific compound is a rare occurrence, and this rule would apply in the present case. Nevertheless, it seems likely that the C_{18} acids predominated, although the degree of unsaturation and subsequent polymerisation probably varied. The first analysis quoted exemplifies an ideal condition (extremely high oil yield) and the C/H ratio corresponds nearly exactly with the assumed monomer, whereas the second example would correspond to near-ideal conditions in which two (or more) monomers co-polymerised under nonoxidising conditions. The third and fourth examples correspond to mixed polymers formed under non-ideal conditions, with partial oxidation. All these remarks are applied to low-ash torbanite, and any oxygen arising from the mineral matter is neglected.

The Role of Sulphur and Nitrogen in Kerogen.

As a general rule, the amounts of sulphur and nitrogen in New South Wales torbanite are low, and when viewed from an atomic basis their concentration is insignificant. Nevertheless, although their concentrations are small, sulphur

and nitrogen have important effects on the oil produced.

From the chemical inertness of kerogen, it is improbable that nitrogen or sulphur occur in the end groups of the polymer, and the only satisfactory explanation for their presence is that they are "foreign elements", introduced into the kerogen mass, either within the polymer or in separate molecules. These elements probably originated in the protein matter of the algae and were "imprisoned" during polymerisation. Ammonia occurs in the gas formed during the decomposition but is not found in the initial stages of pyrolysis. The amount of ammonia present in the gas varies from about 0.02 - 0.1 grms. %, and the concentration varies with the rate of decomposition and also with the richness of the torbanite.

Actually, the effect of the richness of the material is an indirect one, inasmuch as more mineral matter necessitates "deeper" cracking and "deeper" cracking causes an increase in the amount of ammonia at the expense of other nitrogenous compounds.

The mode of occurrence of nitrogen and sulphur in the oil - acyclic and heterocyclic - suggests diverse forms of combination for both and, apart from their protein origin, no suggestions can be made.

General Features.

The extreme stability of kerogen indicates strong interatomic and intermolecular forces. This stability is

exhibited both with regard to natural weathering and in its resistance to chemical attack.

If the properties of kerogen are compared to similar properties of high molecular-weight synthetic resins, it is seen that there is a striking resemblance between them, and this resemblance is manifested in most chemical and physical properties. In order to illustrate the similarity which exists, the following table has been drawn up, giving the comparison between kerogen and polystyrene;

Table 28.

Property	Kerogen	Polystyrene.
Specific Gravity	0.97 - 1.05	1.054 - 1.070
Refractive Index	1.54 - 1.62	1.59 - 1.60
Specific Heat	0.38	0.23
Thermal Expansion/°C. (linear)	90×10^{-6}	$60 - 80 \times 10^{-6}$
Tensile Strength	3000 - 4000	5000 - 9000 lbs./in. ²
Hardness (Rockwell M)	70 - 75	85 - 93
Volume Resistivity (50% R.H. 70°F.)	10^{10}	$10^{15} - 10^{19}$ ohm.cm.
Effect of Water	none	none
Effect of alkalis	none	none
Effect of weak acids	none	none
Solution in Organic liquids;		
Aliphatic	insol.	slightly sol.
Aromatic	insol.	sol.
Aging	slight	slight
Moisture absorption	none	none
Fluorescence	yellow	blue
Impact Property	tough	tough.

Furthermore, the low temperature of formation would tend to create large molecules with high intermolecular forces; these forces are shown in the insolubility of the material. Staudinger has studied the solubility of polymerides in relation to the molecular configuration, and has found that unlimited swelling indicates thread molecules with little

or no cross-linkages, whereas molecules with a high netting index (many cross-linkages) have only limited swelling, and three-dimensional macromolecules scarcely swell at all. The property of swelling in organic liquids may be correlated with some mechanical properties, for instance, those polymers with unlimited swelling consist of thread molecules and often have high resilience (elastomers). As the netting index increases, the substance loses its rubbery properties, becomes harder, and its mechanical strength increases; finally when the cross-linkages are many, the material becomes brittle or "glassy". Three-dimensional polymers decompose at relatively high temperatures and the breakdown is accompanied by increased plasticity (cp. "Rubberoid" later). With kerogen the relatively high cross-linking is shown in the general toughness of the material, especially its resistance to pulverising.

If the properties of kerogen are viewed in the light of the above remarks, and those preceding them in this thesis, it is seen that the assumed constitution is consistent with the observed facts, and therefore kerogen may be accepted as a high polymer, formed by a natural process from natural products. The natural process was the degradation of fatty matter formed by the metabolism of certain algae, and the natural products consisted, in the first place, of glycerides of unsaturated, long-chain, fatty acids.

SECTION III PART A.THE PHYSICAL NATURE OF THE THERMAL DECOMPOSITION
OF TORBENTITE.

Although a relatively large amount of work has been performed on the decomposition of shale to oil, nearly all the available information has dealt with the relationship of oil yield to other variables, with the idea of utilising the results obtained in retort design.

Many hundreds of retorts have been patented, each incorporating devices based on the originators' ideas of the nature of the thermal break-down of shale, and although many ingenious devices have been suggested, little information has been made available on the fundamental changes which occur during the pyrolysis.

In order to investigate the nature of the decomposition, the following studies were carried out:-

- (i) A determination of the limiting minimum temperature at which the decomposition was noticeable.
- (ii) The chemical nature of the decomposition and of the products obtained during this decomposition.
- (iii) The rate of decomposition.
- (iv) The quantity of heat involved during the decomposition.

The Minimum Temperature of Decomposition.

Previous to 1920, it had been generally supposed that

the break-down of kerogen to oil occurred in one stage only, and that each molecule of kerogen yields, in itself, the whole range of products found on retorting.

Alternatively, it was held that the kerogen decomposed progressively, so that the first products of decomposition resembled gasoline, but as the retorting progressed, the products increased in gravity until tar and semi-solid matter was obtained. This latter hypothesis gave rise to the theory of "Fractional Eduction", which formulated that it would be possible to obtain different products according to the temperature of decomposition. The U. S. Bureau of Mines (27) showed that this theory was untenable and that, although the gravity did alter during retorting, the reason for this was not as postulated above. McKee and Lyder (42) were the first investigators to show conclusively that the break-down did not occur in one step, and they showed that the primary product of decomposition was not an oil but a semi-solid bitumen which, under the conditions of retorting, further decomposed to produce oil. These workers made an important step in elucidating the mechanism of the decomposition but, as will be shown later, their work was incomplete.

McKee and Lyder stated that "the kerogen has a decomposition temperature which is quite definite to within $10^{\circ}\text{C}.$, and they gave the lower limit of this temperature as $400^{\circ}\text{C}.$

Later work by Franks and Goodier (22) showed that McKee and Lyder were incorrect in their assumptions that

the primary decomposition of kerogen did not occur below 400°C. and Franks and Goodier demonstrated that the primary bitumen could be produced in quantity at temperatures as low as 300°C. While Luts (38) states that, in the case of Estonian shale, the decomposition becomes noticeable as low as 275°C.

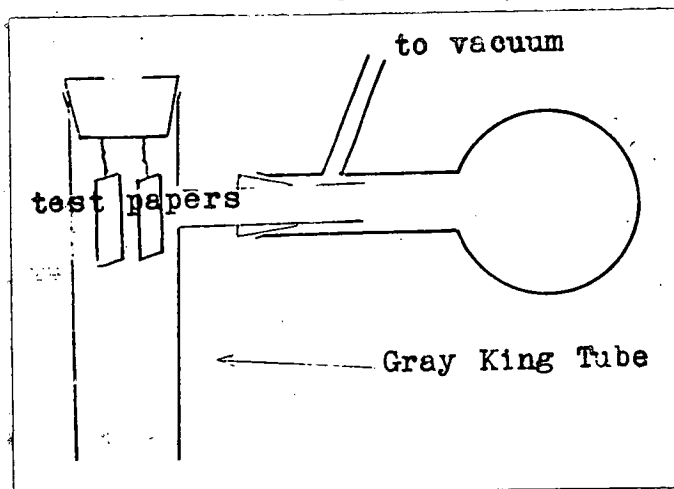
In order to ascertain conclusively, in the case of torbanite, the lowest temperature at which the decomposition becomes noticeable, a vacuum heating of torbanite was carried out. It was assumed, a priori, that any oil formed would tend to remain in the shale mass until the temperature was high enough to vaporise it, furthermore it seemed probable that this temperature (i.e. the boiling-point of the heavy oil) would be in excess of that required for the initial decomposition.

With this fact in mind, it was further reasoned that, while high vacuum would not have much effect on the decomposition temperature, low pressure would enable any oil and gas which were formed to be removed from the sphere of their formation and thus render their detection an easy matter.

Experimental.

The apparatus consisted of the standard Gray-King tube and furnace, which was placed in a vertical position. The side arm of the tube was connected to a small distilling flask and thence to a Cenco Hyvac Pump. A pH test paper

and a paper impregnated with lead acetate were suspended into the mouth of the retort tube. The scheme is shown in a diagrammatic form below.



Finely-powdered moisture-free torbanite (ash 6.64%) was introduced into the tube, the system was closed and the whole evacuated. The current in the furnace was turned on and the sample slowly heated. The observations made are shown in Table 29 below.

Table 29.

Vacuum Heating of Torbanite.

Weight of Torbanite Charge = 20.038 grm.

<u>Time</u> <u>mins.</u>	<u>Temperature</u> <u>°C.</u>	<u>Remarks.</u>
0	93	
15	131	Slight vapours.
30	200	pH = 2
45	275	pH = 2
55	311	H ₂ S ?
56	327	Oil? H ₂ S confirmed.
58	336	Oil confirmed.
60		Run finished.
Loss of weight of sample 1.2%		

This experiment shows conclusively that the decomposition commences at comparatively low temperatures and that oil formation occurs at temperatures less than $350^{\circ}\text{C}.$, but under normal conditions it is not noticed owing to the small amount produced.

The presence of hydrogen sulphide in the gas, evolved before the formation of oil, may arise from one or both of two causes;

(i) Reduction of sulphides.

(ii) Decomposition of the organic matter.

In order to determine whether the gas evolved at low temperatures was caused by (i) or (ii) mentioned above, a very rich sample was heated in vacuo under gentle conditions. In experiments such as these it is a difficult matter to measure small volumes of gas but it is a comparatively easy task to determine the pressure drop in the system and then calculate the volume of the gas by application of the Gas Laws.

The retorting was carried out in the normal Gray-King apparatus, with this modification, that the gas collecting system and condenser were replaced by a sensitive manometer in which could be measured differences in level corresponding to less than 0.5 cc. of gas.

Twenty grams of powdered vacuum-dried torbanite were placed in the tube and the system evacuated. The furnace was slowly heated and the volume of gas given off calculated

from the drop in pressure. The results are shown in Table 30.

Table 30.

Vacuum Heating of Torbanite.

Weight of Torbanite Charge = 20.536 grms.

<u>Time</u> <u>mins.</u>	<u>Temperature</u> <u>°C.</u>	<u>Volume (calc.)</u> <u>mls.</u>
0	159	0
40	212	0.6
55	245	1.3
60	261	3.1
65	275	5.3
70	292	34
75	308	48
80	322	54

The above results should be contrasted with those obtained when torbanite is heated in the presence of air for, in the latter case, oxidation of the material caused a diminution in volume of the ambient atmosphere which effectively masked any small amount of gas evolved at this temperature. (oxidation of heated torbanite will be discussed later). The volume of gas produced in the above run cannot be accounted for by the decomposition of the mineral matter which amounted to about 400 mg. Therefore, it can be taken that the gas produced arises from some chemical change within the kerogen molecule without the formation of oil. That this fact is true has been shown, and that the evolution of small amounts of gas indicates the first stage in the decomposition of kerogen, will be discussed later.

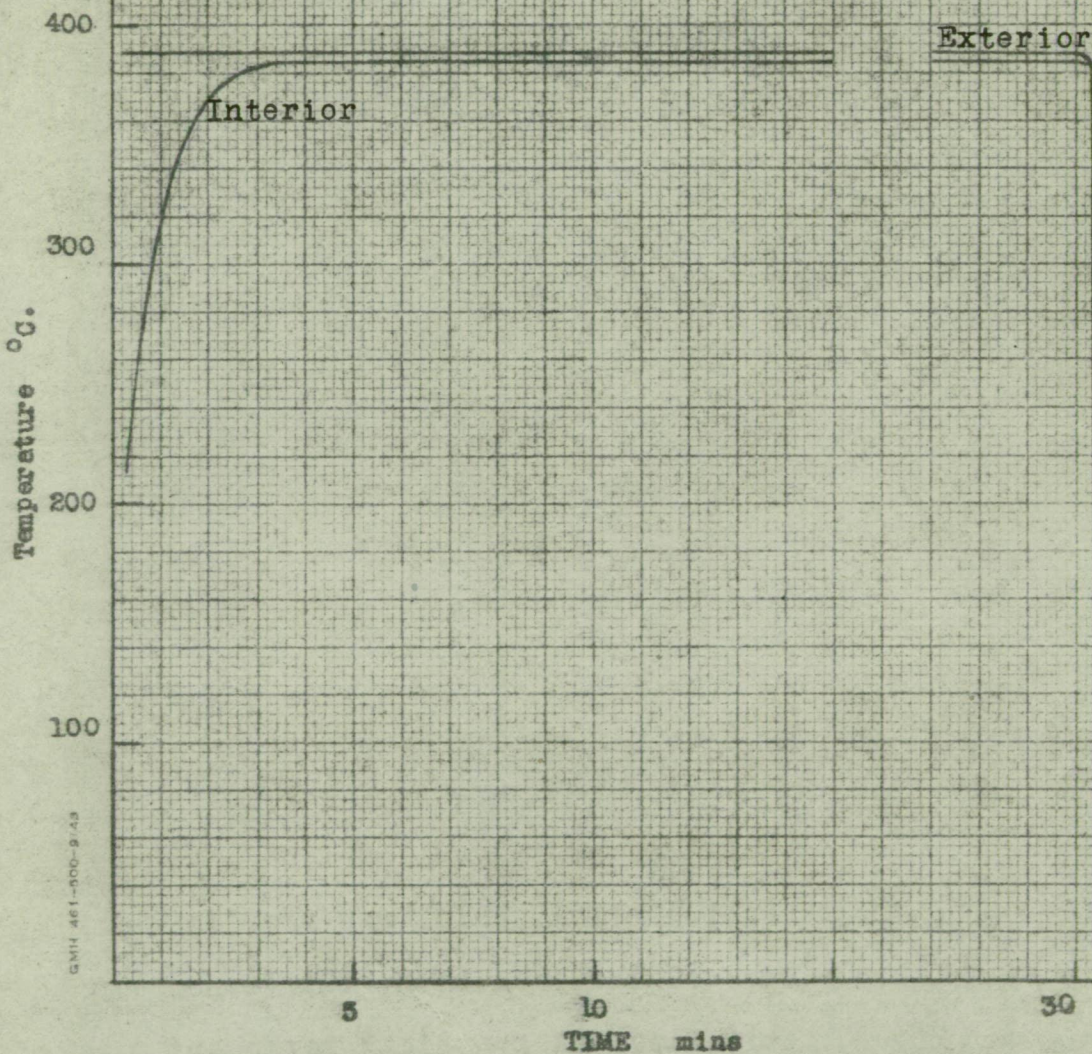
It has been proved that torbanite will decompose at

low temperatures, provided it is heated for a sufficient length of time, and it will be shown in the section entitled "Factors in Retorting", that over 25% of the available oil may be obtained at temperatures less than 300°C., provided the time of heating is sufficiently long. The question then arises, whether there is a lower limit to the temperature required for decomposition, or whether given sufficient time, the organic matter would decompose at normal temperatures.

The Rate of the Decomposition of Kerogen.

McKee and Lyder (42) have shown that the primary product in the break-down of kerogen is not an oil but a semi-solid bitumen which is soluble in benzene. The same phenomenon has been shown by Cane (10a) to occur in the New South Wales torbanite, and therefore it seemed desirable to determine whether the transformation of the kerogen into the benzene-soluble intermediate product, obeyed any law, and if so to get quantitative data on the amount of soluble product formed. Preliminary experiments on heating the torbanite in the presence of air indicated that oxidation occurred in the first instance and caused side reactions. The total amount of soluble material formed increased to reach a maximum and then decreased (this soluble material will be termed bitumen hereafter, although it is not a true bitumen, as will be shown in Section III B.) This is understandable, for as the bitumen is progressively decomposed to

Heating and Cooling Curves of Samples
Graph No 6



form oil, this oil will escape in the vapour phase and will not be included in the decomposition products. Eight runs were carried out in the presence of air, and the results obtained are given in Table 31.

The experimental details were as follows:-

The heating medium consisted of a gas-heated lead bath, thermostatically controlled for any given temperature. The bath was lagged on the outside and provided with a lid with the appropriate holes. The temperature was measured by an accurate A.S.T.M. thermometer immersed in the medium, close to the sample tube. Preliminary experiments indicated that there were two sources of error which could be approximately corrected by calculation and previous data.

- (1) The time lag before the sample reached thermal equilibrium with the lead bath, and a corresponding lag on removal from the bath. The heating-up time lag amounted to about 3-4 minutes and was compensated to a certain extent by immersing the hot tube in cold water after heating. This had the effect of rapidly cooling the peripheral portion of the sample while the central portion, which was slow in reaching the temperature of the lead bath, maintained its heat for a little time. A graphical representation of such heating and cooling is given in graph No.6 opposite. From experimental data and calculation (private communication from Dr. J.C.Jaeger) an additional 2-1/2 minutes was allowed to correct for the time lag i.e. Timing started 2-1/2 minutes after immersion of sample in lead bath.

(11) Differential Temperature across Sample. It was found that the central portion of the sample seldom reached the outside temperature; this temperature difference was a few degrees only and a correction was made by maintaining the lead bath one degree higher than the desired temperature.

The sample was powdered to 60 IWM mesh, dried, and placed in a small-diameter quartz tube, which was then placed in the molten lead bath. After a given period of time the sample was withdrawn, cooled, and the amount soluble in benzene determined by Soxhlet extraction. Benzene, and not carbon bisulphide, was used as the extracting medium as it has been shown (58) that the latter is particularly affected by small traces of water.

Table 31.

Heating of Torbanite in Air.

Temperature of Sample 400°C.

<u>Run No.</u>	<u>Time of Heating mins.</u>	<u>Amount Extracted.</u>
1	8	8.1%
2	16	16.3%
3	25	27.4%
4	30	33.5%
5	34	37.7%
6	40	41.0%
7	50	36.8%
8	60	28.1%

The above table shows that the results obtained by heating in air are of no value for determining reaction

rates, because the volatile matter formed during the decomposition escapes to the atmosphere, and no allowance can be made for this loss. There are two means of overcoming this error;

- (i) enclose the reactants in a sealed tube so that no loss can occur. This method is undesirable on account of the high gas pressure generated.
- (ii) measure the loss incurred by the escape of oil vapours and add to it the amount of product obtained by extraction.

Although no quantitative data were obtained from Table 31, several important observations were made.

In the first place, the residue after extraction was dissimilar from the original sample, for whereas the original sample was hard and brittle, the residue, after extraction, was a soft rubbery mass with appreciable elastic properties. When rubbed between the fingers it tended to disintegrate.

Secondly, when the powdered sample was heated, the uppermost portion rapidly darkened. This darkening was much less intense when the sample was protected against atmospheric oxygen, by carbon dioxide. By connecting the outlet of the sample tube to a water manometer it was shown that oxygen was being absorbed during the first period of heating. For example, the following observations were taken with the

manometer in position.

Table 32.

Oxidation of Torbanite on Heating.

<u>Time</u> <u>mins.</u>	<u>Temperature</u> <u>°C.</u>	<u>Manometer</u> <u>mm. H₂O</u>
0	339	0
11	339	-36
17	339	-37
27	340	-45
37	341	-40
40	338	-27
45	341	- 7
50	340	+ 2

These preliminary experiments indicate that the decomposition of kerogen to form oil occurs in a series of breakdown reactions, giving products of decreasing molecular complexity, the first of which is a semi-solid "bitumen". The cracking of oil to form gasoline occurs in the same manner with the formation of intermediate hydrocarbons.

In order to determine the true rate of formation of the bitumen it is, therefore, necessary to stop the escape of the volatile products or make a determination of the amount lost. With this in mind the following experimental procedure was found satisfactory.

Experimental.

The heating bath and controlling apparatus was the same as described previously, with the exception that the quartz containing-vessel was replaced by hard glass, narrow-diameter test tubes which were destroyed during the experiment.

The powdered torbanite sample was blanketed from atmospheric oxygen by carbon dioxide, generated by the sublimation of "Dry Ice".

The calculation of the experimental results are best illustrated by means of the following numbered operations;

(i) Weigh an empty dry test tube (w_1)

(ii) Add the sample and reweigh (w_2)

$$\text{Weight of sample} = w_2 - w_1$$

(iii) Heat in bath under the predefined conditions,

remove test tube, remove with razor blade traces of lead adhering to exterior, and follow by immersion in nitric acid, wash and dry tube. Weigh again (w_3) Loss in weight by loss of vapours = $w_3 - w_2$.

(iv) Place test tube in Soxhlet thimble, break tube in situ, remove any clean glass fragments (this explains why w_4 is less than w_3) and weigh.

Weight of decomposed torbanite and thimble and remainder of tube = w_4 .

(v) Extract thimble and contents with benzene, usually overnight, dry in air oven and weigh (w_5).

$$\text{Loss in weight by extraction} = w_4 - w_5$$

$$\text{Total loss in weight (W)} = (w_3 - w_2) + (w_4 - w_5)$$

$$\text{Percentage decomposed} = \frac{W100}{w_2 - w_1}$$

In all, twenty-five runs were carried out under the experimental conditions given above. The experimental

results of these determinations are given in Table 33.

The runs may be divided into two groups;

Table 34; Group I at constant temperature. Runs 2, 8, 20, 22, 24.

Table 35; Group II at various temperatures. Runs 7, 9, 11, 14, 15,
16, 17, 18, 18a,
19, 19a, 20.

The first feature to be noticed is that temperature alone on which is not sufficient criterion to state the amount of conversion, but that time must be taken into consideration. For purposes of analysis the results are arranged in their respective groups in the two tables following;-

Table 34.

Rate of Decomposition of Torbanite at Constant Temperature.

<u>Run No.</u>	<u>Temperature</u> °C.	<u>Time of Heating</u> mins.	<u>Loss</u> %
20	388	30	16.5
24	388	45	22.9
8	388	60	29.6
22	388	75	36.6
2	388	90	40.8

Table 35.

18	338	160	5.7
18a	340	370	11.7
19a	360	30	4.5
19	376	30	10.1
15	398	39	46.7
9	405	30	41.2
16	410	60	69.8
7	425	30	68.6
14	427	18	57.8
11	436	19	74.6

Table 33

Run No.	Weight of Test Tube w_1	Weight of Tube and Sample w_2	Weight of Sample $w_2 - w_1$	Weight after heating w_3	Loss of Volatiles $w_3 - w_2$	Loss %	w_4	w_4 after extraction = w_5	Loss on extraction	Loss %	Total Loss %	Time of Heating mins.	Temperature °C.
7	8.5193	10.5286	2.0093	10.2614	0.2672	13.3	9.2223	9.1112	0.1111	55.3	68.6	30	425
9	8.0194	9.2272	1.2078	9.1729	0.0543	4.5	6.2481	5.8048	0.4433	36.7	41.2	30	405
11	8.2972	10.0809	1.7836	9.8208	0.2601	14.6	9.4667	8.3976	1.0691	60.0	74.6	19	436
14	7.9137	9.7206	1.8069	9.5401	0.1805	10.0	9.8602	8.9958	0.8644	47.8	57.8	18	427
15	7.8923	9.8474	1.9551	9.7147	0.1327	6.8	9.9437	9.1624	0.7813	39.9	46.7	39	398
16	8.1677	10.2697	2.1020	10.0671	0.2026	9.6	9.1391	7.8731	1.2660	60.2	69.8	60	410
17	8.5097	11.3832	2.8735	11.4161	0.0329	Gain						630	207
18	8.0091	9.6741	1.6650	9.6559	0.0182	1.1	5.9116	5.8351	0.0765	4.6	5.7	160	338
18a	7.4793	8.7400	1.2607	8.7039	0.0361	2.9	8.4902	8.3788	0.1114	8.8	11.7	370	340
19	7.8410	9.1500	1.3090	9.1239	0.0261	2.0	9.2761	9.1693	0.1068	8.1	10.1	30	376
19a	8.1009	9.3477	1.2468	9.3327	0.0150	1.2	9.3861	9.3450	0.0411	3.3	4.5	30	360
20	7.9317	9.0308	1.0991	8.9835	0.0473	4.3	8.6110	8.4769	0.1341	12.2	16.5	30	388
24	8.2081	9.7825	1.5744	9.6943	0.0882	5.6	8.9907	8.7189	0.2718	17.3	22.9	45	388
8	7.8623	9.8634	2.0011	9.7335	0.1301	6.5	8.7273	8.2632	0.4621	23.1	29.6	60	388
22	7.9939	9.4571	1.4632	9.3518	0.1053	7.2	9.1420	8.7117	0.4303	29.4	36.6	75	388
2	8.1326	9.7484	1.6158	9.5820	0.1664	10.3	9.3352	8.8427	0.4925	30.5	40.8	90	388

Discussion.

Several factors and assumptions govern the accuracy with which the experiments may be performed, for although correction has been made for the amount of volatile material lost, no allowance is made for any polymerisation which might occur with the formation of benzene-insoluble products, or for any decomposition reactions accompanied by the formation of free carbon. In other words, one has to assume that the amount of material remaining after the extraction with benzene represents the undecomposed kero-gen. In addition, the method makes no allowance for any reaction which may occur without the formation of a soluble product.

In the case of the pyrolysis of a pure hydrocarbon, an analysis of experimental data is comparatively easy, for in this case the reactant is a pure compound and the evaluation of the quantity of product is not difficult. Tilicheyev (72b) has examined the decomposition rates of paraffins and has shown that the cracking velocity is nearly independent of the extent of conversion, and that the reaction is essentially a first order reaction. The cracking of naphthenes above certain temperatures is also a reaction of the first order.

The composition of paraffin-base flow oil is essentially that of a mixture of saturated hydrocarbons and it is not unreasonable to deduce that the overall cracking-

reaction-velocity will be of the first order, and this is found to be true. The cracking velocities of certain stocks are given in Plate II.

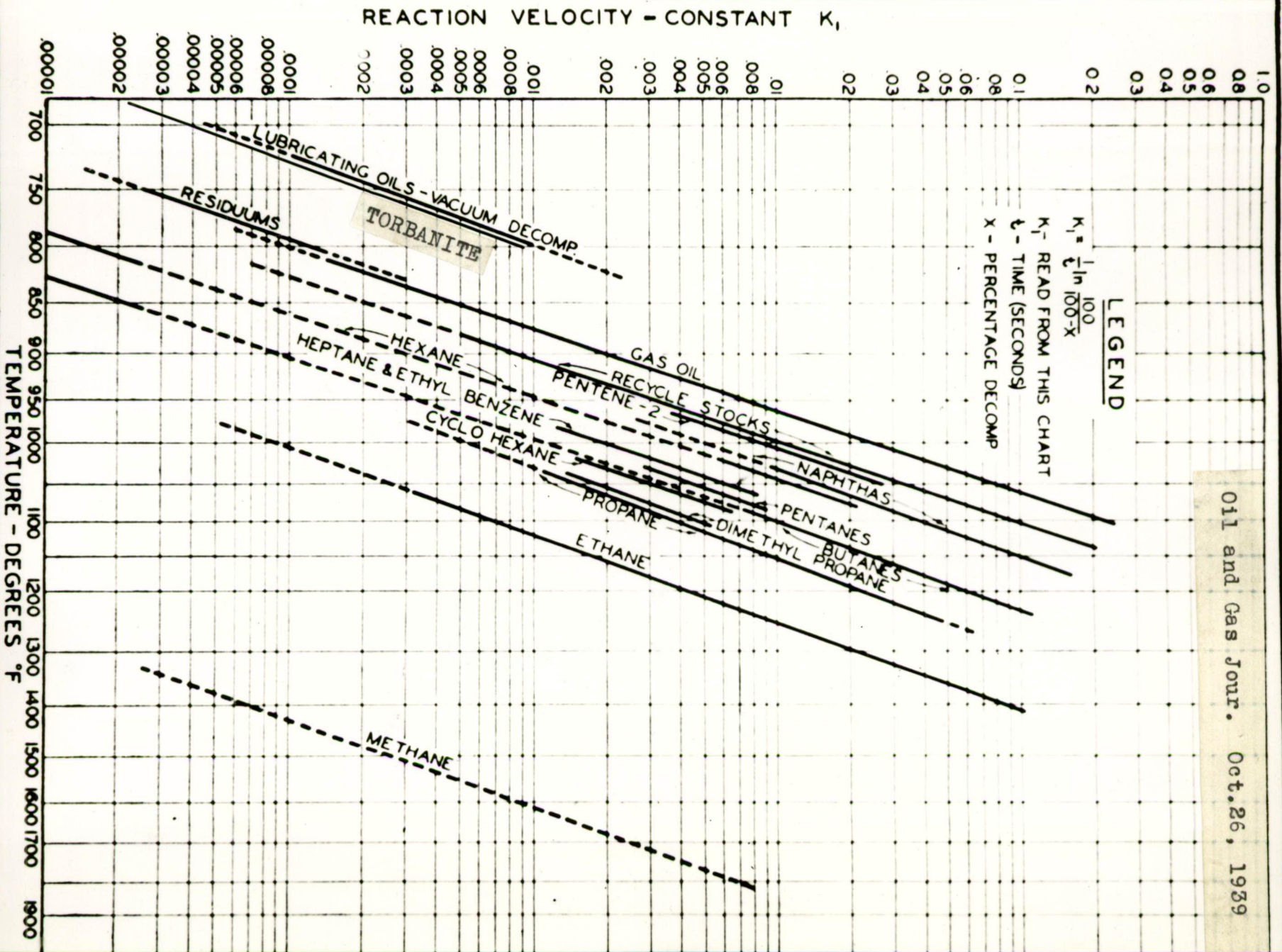
In the pyrolysis of kerogen, several factors have to be taken into account, namely;

- (1) In torbanite the reacting molecules may be of different weight and stability, but certainly less dissimilar than those of crude oil, so that the velocity constants found by experiment will be mean values.
- (2) When the reaction has been allowed to proceed for a considerable time it is found that, not only are the products dissimilar from those produced if the reaction is of shorter duration, but the reverse action becomes appreciable because of mass action.
- (3) Over long periods, polymerisation and side reactions give products which may or may not be soluble in benzene.

These difficulties may be minimised by keeping the reaction times reasonably short, choosing a suitable criterion for differentiating the reactant and product, and keeping the reactant in an inert atmosphere.

The amount of soluble product formed under different conditions has been found, and now an attempt may be made to determine whether the rate of reaction obeys any of the laws of chemical kinetics.

Oil and Gas Jour. Oct. 26, 1939



It will be shown later that the decomposition of torbanite to form oil occurs in a series of consecutive reactions which, although when taken as a whole are not step-wise but concurrent and continuous, may be separated into stages. The main stages are;

(i) Rigid Torbanite \rightarrow Rubbery Material \rightarrow Bitumen.

(ii) Bitumen to Heavy Oil.

(iii) Heavy Oil to Crude Oil, Gas and Naphtha.

Therefore, the reaction rate discussed in this work is either that of the fastest reaction or the effective mean velocity of the overall reaction. The free energy equations of the cracking of paraffins indicate that, as long as any torbanite (assumed paraffinic) remains in its original state, the experimental values represent the rate of reaction (i). In addition, it has been shown (72b) that the cracking reaction rates of paraffinic hydrocarbons is also of the first order and therefore it would be expected that reaction (ii) would be a first order reaction, although its velocity would be less than (i) at the same temperature.

From this discussion it is seen that the velocity constants given in Table 37 will be substantially those of the decomposition;

Rigid insoluble torbanite \rightarrow soluble bitumen.

but these data will be slightly low because they have been affected by further decomposition of the bitumen to oil.

However, as the reacting substance is practically homogeneous and, from the information at hand on the pyrolysis of high molecular weight hydrocarbons, the evidence would indicate that the reaction velocity would be of the first order. It is now necessary to determine whether this is so.

The integrated equation to a monomolecular reaction may be written;-

$$k = \frac{1}{t} \log_e \left(\frac{a}{a-x} \right)$$

where k = reaction velocity at T° ,

t = time (in seconds),

a = concentration of reactant,

x = decrease in concentration of reactant.

= concentration of product formed in time t
at temperature T° .

In the pyrolysis of hydrocarbons " a " and " x " are defined in concentration of grams % and usually " x " is measured as the amount of material boiling below a certain temperature. In the present case " a " is defined as the amount of kerogen in grms. % and " x " is defined as the amount of the benzene soluble material plus the amount of volatile matter in grms. %.

Rewriting Table 34 in a convenient form;

Temperature of Determination: 388°C .

Concentration of Reactant: 95.8%

<u>Time in mins.</u>	<u>Product %</u> <u>x%</u>	<u>a - x</u>	<u>k x 10⁶</u>
30	16.5	79.3	106
45	22.9	72.9	101
60	29.6	66.2	103
75	36.6	59.2	107
90	40.8	55.0	102

The reproducibility of the velocity constant is remarkable, and at the time of its determination (Feb. 1943) the writer believed that it was the first occasion on which this constant had been evaluated for the decomposition of kerogen; furthermore the experimental data were shown to be consistent with a first order reaction, before a survey was made on cracking kinetics. However, subsequent to this section of the research being completed, it was found that a similar investigation had been carried out on the American Shales (44), the results of which will be cited later.

As it has been shown that the pyrolysis of kerogen is monomolecular, it is now possible to evaluate the velocity constant over a series of different temperatures.

The details of the calculations are shown in Table 36, and the results set out in Table 37.

Table 36.

Velocity Constant of the Pyrolysis of Kerogen.

Run No.	Temp. ° C.	Loss (x)	a - x	$\frac{a}{a - x}$	$\log_e \frac{a}{a - x}$
18	338	5.7	90.1	1.063	0.061
18a	340	11.7	84.1	1.139	0.1302
19a	360	4.5	91.3	1.049	0.048
19	376	10.1	85.7	1.118	0.111
20	388	16.5	79.3	1.208	0.189
15	398	46.7	49.1	1.951	0.668
9	400	41.2	54.6	1.755	0.562
16	410	69.8	26.0	3.685	1.303
7	425	68.6	27.2	3.530	1.260
14	427	57.8	38.0	2.521	0.924
11	436	74.6	21.2	4.519	1.507

Run No.	Time (t) mins.	$\frac{1}{t} \times 10^3$ secs.	$k = \frac{1}{t} \log_e \frac{a}{a - x} \times 10^4$	Temp. °K
18	160	0.104	0.064	611
18a	370	0.045	0.059	613
19a	30	0.555	0.27	633
19	30	0.555	0.62	649
20	30	0.555	1.05	661
15	39	0.427	2.85	671
9	30	0.555	3.12	678
16	60	0.277	3.62	683
7	30	0.555	6.99	698
14	18	0.926	8.55	700
11	19	0.877	13.21	709

Velocity Constant of the Decomposition $\times 10^{-4}$

Rate of Decomposition of Torbanite
Graph N° 7.

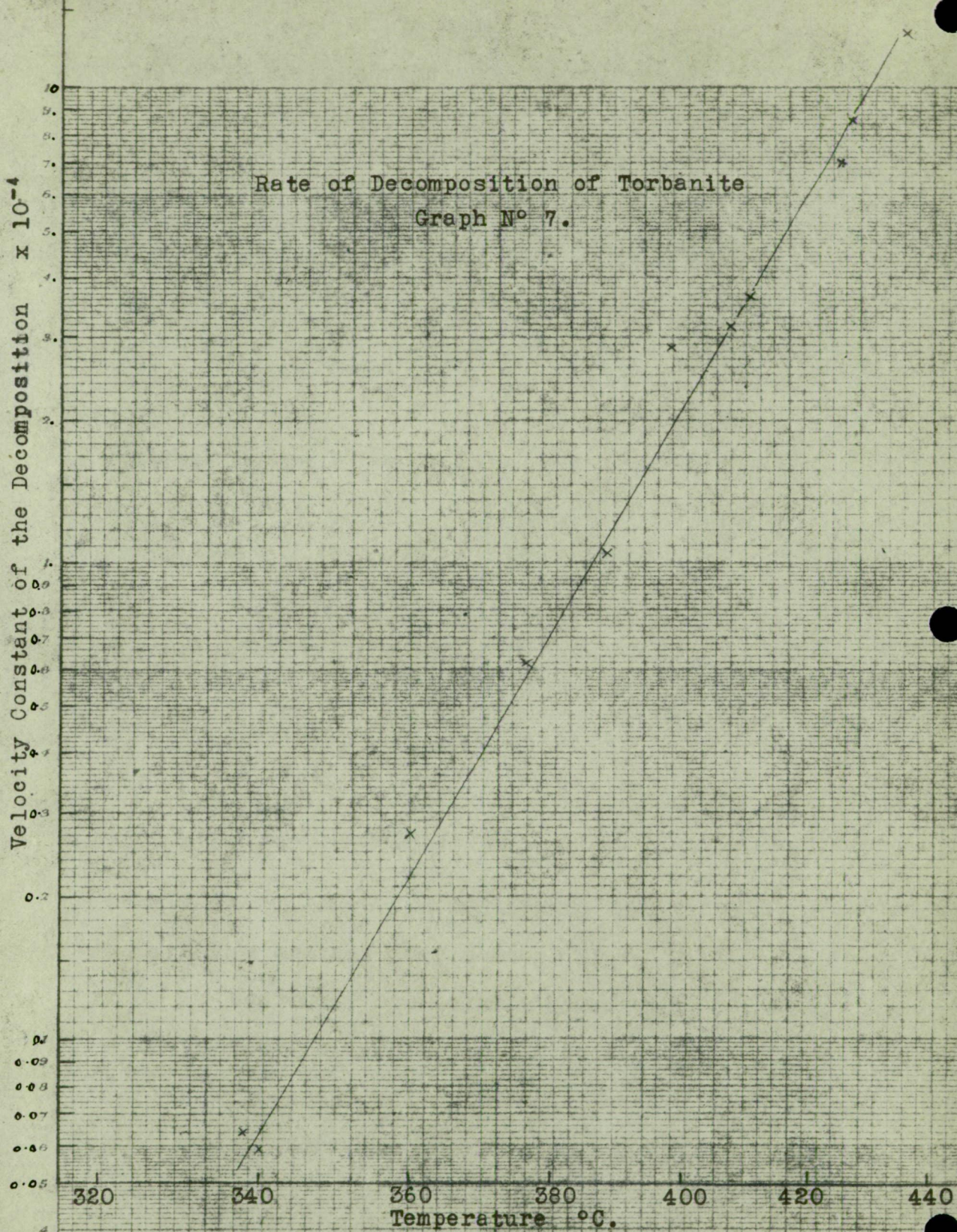


Table 37.Variation of Velocity Constant with Temperature.

<u>Temperature °C.</u>	<u>Velocity Constant (Sec⁻¹)</u>	<u>Value from Graph 7</u>
338	0.064 x 10 ⁻⁴	0.066 x 10 ⁻⁴
340	0.059	0.064
360	0.27	0.22
376	0.62	0.58
388	1.05	1.2
398	2.85	2.0
405	3.12	3.2
410	3.62	3.7
425	6.99	7.9
427	8.55	8.8
436	13.21	14.7

From these results a curve may be constructed, from which it is possible to find the Velocity Constant at any temperature. This is shown in Graph No. 7. The results of these experiments have several very important applications.

(1) They show that, in the primary and secondary stages at least, the decomposition of kerogen is similar to the cracking of flow oils, and the decomposition is essentially paraffinic in character (much less likely naphthenic).

(2) If it is assumed that benzene rings are stable at these temperatures and therefore the primary bitumen formation is essentially a paraffin C-C rupture, the figures indicate, using the results of Tilicheyev (72a), that some of the side chains contain more

than thirty carbon atoms

$$k_{425} = 5.3 \times 10^{-4} \text{ for } C_{30}H_{62}$$

This statement is supported by the waxy nature of the crude oil, and by the results of Bragg (6), who found that the cracking velocity of a mixture of paraffins of molecular weight 337 was 1.90×10^{-4} and 5.85×10^{-4} at 420°C . and 436°C . respectively; kerogen being more complex would have greater values.

- (3) It is now possible to calculate the temperature coefficient of the pyrolysis. The temperature coefficient is defined as the ratio $k_t + 10/k_t$, and it varies with t . In petroleum technology, the temperature coefficient is often defined as the temperature rise ($^{\circ}\text{C}$.) necessary to double the reaction rate e.g. in the cracking of oil the rate is doubled for a 14°C . rise at 450°C . and for a 21°C . rise at 600°C . For torbanite;

$^{\circ}\text{C}$.	$k_t + 10/k_t$	Temp. necessary to double reaction rate.
350	1.83	11°C .
400	1.68	14°C .

- (4) By the use of the Arrhenius equation;

$$(\log_e k = -\frac{E}{RT} + C) \dots \dots \dots (1)$$

it is possible to determine the energy of activation of the decomposition reaction.

The energy of activation over different temperature ranges has been calculated from the equation;

$$\log_e \frac{k_1}{k_2} = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \dots \dots \dots (11)$$

(C assumed constant)

and the results are given in Table 38 following.

Table 38.

Energy of Activation of the Decomposition of
Kerogen.

<u>Temperature Range</u> °C.	<u>Heat of Activation.</u> cals./grm.mol.
350 - 375	48,200
375 - 400	48,900
400 - 425	47,900
350 - 400	48,500

Taking the value of the energy of activation calculated from equation (11) and substituting it in equation (1), the value of the integration constant (C) may be obtained.

$$\begin{array}{lll} \text{Thus } k_{350} & = 0.12 \times 10^{-4} & \\ k_{400} & = 2.2 \times 10^{-4} & \text{from graph} \\ E & = 48,500 & \text{from equation (11)} \\ \underline{C} & = \underline{27.5} & \text{from equation (1)} \\ & & \text{mean value 350-400°C.} \end{array}$$

$$C_{350} = 27.9$$

$$C_{400} = 27.0$$

The value of C for torbanite should be compared with the values obtained for similar decompositions;

$$\begin{array}{ll} C = 28.8 & \text{Crude Oil (25)} \\ = 33.5 & \text{Estonian Shale (38)} \\ = 16.7 & \text{Paraffin wax (6)} \end{array}$$

The results obtained by Maier and Zimmerley (44) agree closely with the present work. These workers determined

the reaction velocity of the decomposition of American oil shale in a similar manner, with the exception that the experiments were carried out in sealed tubes, which prevented the loss of volatile material, (the pressure effect should be nil if the reaction is monomolecular). In the published results of Maier and Zimmerley (44), the velocity constant is given in terms of % per hour, but the following results taken from their paper have been converted into % per second.

Table 39.

Velocity constant of the Decomposition of Kerogen
from American Shales.

<u>Temperature</u> °C.	<u>Velocity Constant (sec.⁻¹)</u>
300	0.012×10^{-4}
325	0.057
365	0.269
400	1.3 (extrapolated from
425	3.15 their results).

Luts (38), in his monograph on the Estonian shales, quotes the work of Puksov concerning the decomposition of Kukersite. Puksov also determined the reaction rate by extraction of the soluble products. Although only one determination is given in detail it agrees closely with the results in the present work, and those of Maier and Zimmerley.

In order to show the comparison which exists between the results obtained from three very dissimilar shales, Table 40 has been drawn up, in which the velocity constants

have been calculated from the published experimental data.

Table 40.

Velocity Constants of Decomposition of Shale.

Temperature °C.	<u>$k \times 10^{-4}$</u>		
	Cane (this work)	Maier and Zimmerley (44)	Luts (38)
330	0.033	0.056	0.087
360	0.22	0.22	0.46
390	1.3	0.81	2.5
400	2.2	1.3 (interpolated)	4.4 (calc. from ex- perimental data).

These figures are similar to the cracking velocities of crude oil, and may be compared with the decomposition of the higher paraffins e.g. $C_{32}H_{66}$, of which the velocity constant of decomposition at 400°C . is 1.22×10^{-4} .

The cracking velocities of aromatics and olefins are of a different order, and this supports the earlier statement that the decomposition of kerogen is of the nature of a "paraffinic split".

The Energy of Activation given in Table 38 compares favourably with similar work published overseas. The two sources of information on reaction velocities of decomposition of oil shale mentioned earlier, give the energy of activation calculated from their respective experimental figures, and for purposes of comparison, the individual results are given in Table 41. Included in this table are figures for similar decompositions.

Table 41.Heat of Activation, from various sources.

<u>E. cal./grm.mol.</u>	<u>Material</u>	<u>Temperature Range °C.</u>	<u>Reference.</u>
48,500	Torbanite	350-400	this work.
41,500	U.S.A.shale	300-325	44
49,956	Kukersite	390-440	38
59,500	Paraffin Wax	425-450	72b
46,500	Heptane	625-650	51
53,400	Crude Oil	430-700	25

The foregoing results and the discussions arising from them have been based on a gentle pyrolysis of kerogen in the absence of oxygen. These conditions should be contrasted with the decomposition of kerogen under retorting conditions in the presence of oxygen.

In the decomposition of a rich torbanite at mild temperatures, and in the absence of air, it can be shown by a consideration of the free energy equations of the reactions which may occur, that C-C scission will predominate, especially towards the middle of the molecule, so that, assuming a paraffinic reactant, the product would contain olefins and paraffins in approximately equal proportions, and the olefins which are formed would be mainly mono-olefins, cp. composition of crude oil.

On the other hand, with a lean torbanite, and in the presence of air, not only has the effect of oxygen to be considered, but the presence of appreciable amounts of ash, (containing alumina and ferric oxide) may introduce a catalytic effect which may tend to cause paraffin dehydrogenation, and this is especially so in the presence of hydrogen sulphide.

In addition, as in the cracking of oil, three main factors, time, temperature and pressure, have to be considered; however, except for special conditions the last mentioned may be neglected.

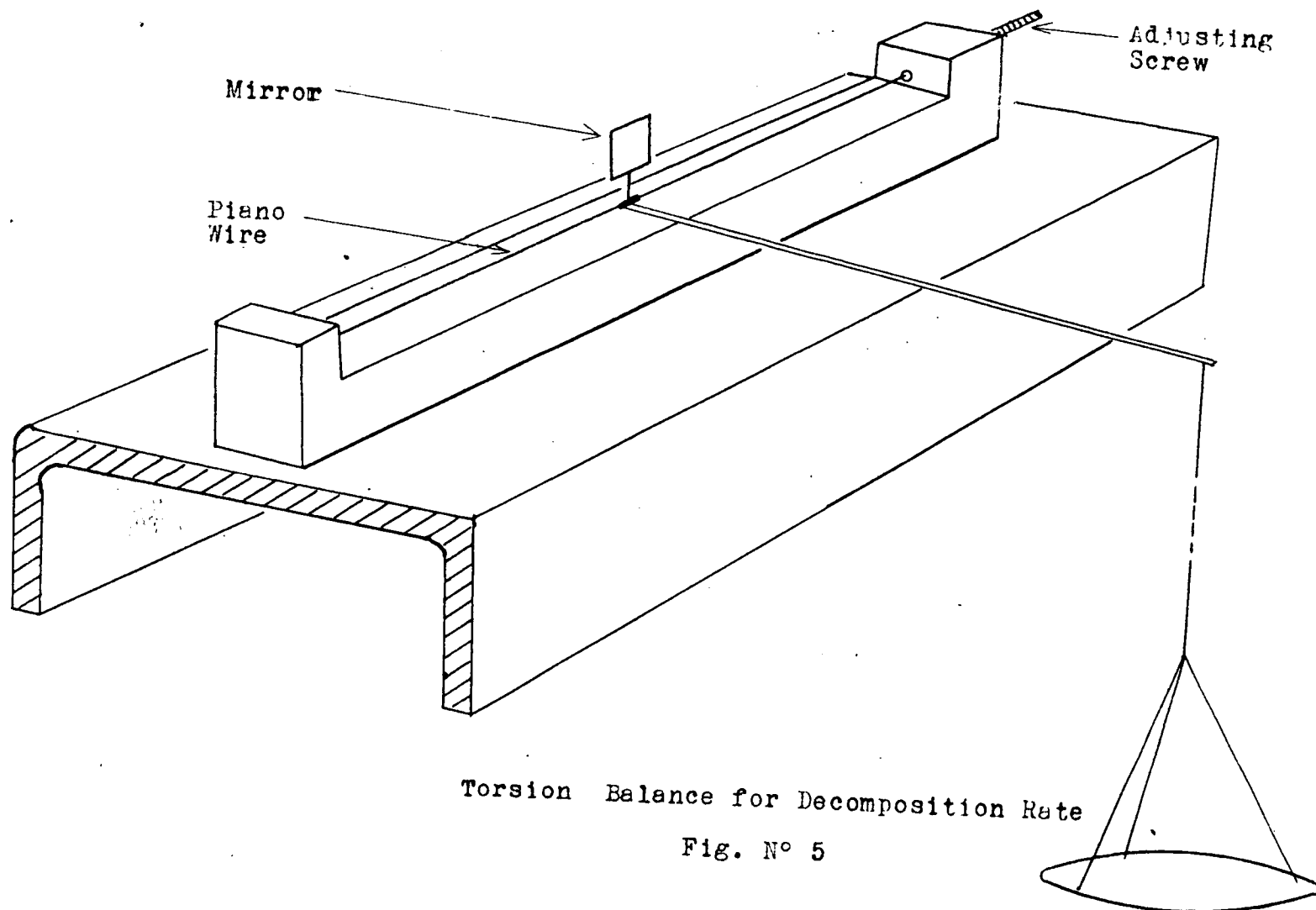
It is impossible to predict, a priori, the mechanism of the reactions which occur at retort operating temperatures, because the reactions will be so complex. The presence of free carbon produced from side reactions would weaken C-H bonds, and the presence of oxides from the mineral matter may have appreciable effect.

At temperatures approaching the end of the decomposition ($600^{\circ}\text{C}.$), polymerisation, carboid formation, and complete break-down of structures, have to be considered. The increasing amounts of hydrogen in the gas evolved as the temperature is increased, point to such decompositions; polymerisation would be extensive and the formation of complex polycyclic benzenoid compounds would be possible; doubling of simple aromatic structures would occur and, in all, no analysis of the problem would be possible.

Decomposition in the Atmosphere (Retorting Conditions)

In order to get some general idea of the rate of pyrolysis under retorting conditions, as compared with the academic approach described in the previous pages, a series of experiments were carried out under the following conditions;

Blocks of torbanite were heated under approximately



isothermal conditions, and the rate of evolution of volatile matter was measured.

The apparatus comprised a torsion balance, a furnace and an indicating device. The torsion balance resembled the normal laboratory model, with the exception that it was of very rugged construction. The balance was constructed from mild steel and consisted of a length of channel 18" x 7" x 3", this acting as a rigid base. On this base, running along the centre, a notched bar was welded; on this was stretched a piano wire. The layout can best be seen by examination of the figure. The piano wire carried two cross members at its mid-point.

One cross member was upright and carried a mirror, while the other, about 8" long, was horizontal and carried the sample. The sample was suspended from the end of the horizontal member.

Any alteration in the mass of the sample produced a corresponding movement of the mirror, which was indicated by the movement of an optical beam. The linear deflection of the beam was calibrated in terms of grams, by means of known masses on the sample pan.

The furnace was placed in an upright position, the ends were lightly closed, with the exception of a small hole in the upper blank, and the interior filled with carbon dioxide from "Dry Ice"; The conditions being similar to a retort with a lean air supply. The furnace was

brought up to temperature, the sample placed in the pan, and moved into position, in such a way that it hung down the centre of the muffle.

The deflection of the beam was noted over given time intervals. The experiment was repeated, using different sizes of sample and different temperatures. In all, eight runs were carried out, four at 400°C., and four at 450°C. The sample sizes were of definite measurements and were 1 cm., 2 cm., 3 cm., 4 cm. edge cubes in each run. The results obtained are shown in Tables 42 and 43 and graphs 8 and 9.

Table 42.Rate of Evolution of Volatile Matter.

Temperature 400°C.

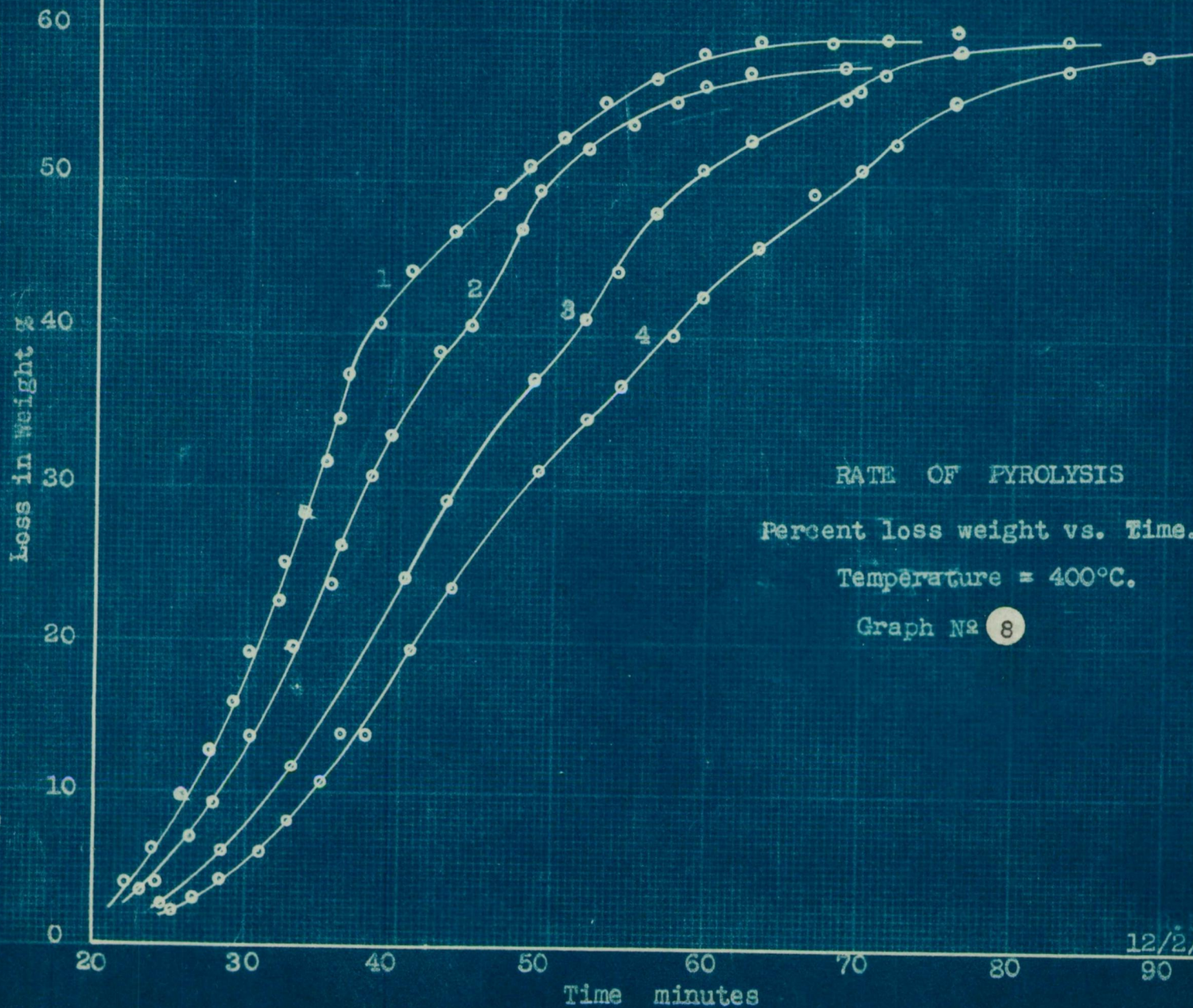
Results expressed as loss of weight %.

<u>Time</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>
22 mins.	4	3		
23	5	3.5		
24	6.5	4.5	3	
26	9	7	4	3
28	13	11	6	4
29	16	12	7	5
30	19	13	8	5
32	25	19	10	8
34	28	21	13	11
35	32	24	15	10.5
36	37	26	17	12
38	41	31	20	15
39	43	33	22	17
40	44	34	24	19
43	47	39	29	23
45	48	41	32	26
47	49	45	35	29
48	52	47	36	30
49	53	49	37	31
50	53	50	39	32
52	54	52	41	34
53	55	53	43	35
54	56	54	44	37
57	57	54	48	40
60	59	56	51	43
63	59	57	53	46
67	59.5	57	54	49
68	59.5	57.5	55.5	50
70	59.5	57.5	57	51
71	59.5		57.5	52.5
76			57.5	55
84			59.5	57.5
89				58.5

Run No.Size of Sample.

Run 1
Run 2
Run 3
Run 4

1 c.cm.
8 c.cm.
27 c.cm.
64 c.cm.



RATE OF PYROLYSIS

Percent loss weight vs. Time.

Temperature = 400°C.

Graph No. 8

12/2/42.

Table 43.Rate of Evolution of Volatile Matter.

Temperature 450°C.

Results expressed as loss of weight %.

Time	Run 1	Run 2	Run 3	Run 4
10 mins.	3		1	
12	4		1	
13	5		1	
14	6		1	3
15	9	5	1	4
16	15	7	2	4
17	21	9	3	5
18	26	13	4	7
19	32.5	17	6	8
20	45	23	7	10
21	51	24	8	13
23	54	29	12	15
24	56	32	14	20
25	57	37	16	22
26	58	38	18	24
27	59	40	20	26
28	60	42	25	28
29	60	44	30	30
30	60	45	34	31
31	61	47	36	32
32	61	50	37.5	34
33	62	51	39	36
34	62	52	42	37
35	62	54	45	39
36	62	55	47	40
37	62	56	49	41
38	63	57	50	43
40	63	58	52	46
41	63	58	53	46
42	63	58	54	47
43	63	59	54	49
45	63	60	56	50
47	63	60	57	52
49	63	61	57	54
51	63	61	58	56
54	63	62	58	58
56	63	62	58	60
58	63	62	58	61
60	63	62	58	61
63	63	63	58	63
67	63		58.5	63
69	63			63

Run No.

Run 1

Run 2

Run 3

Run 4

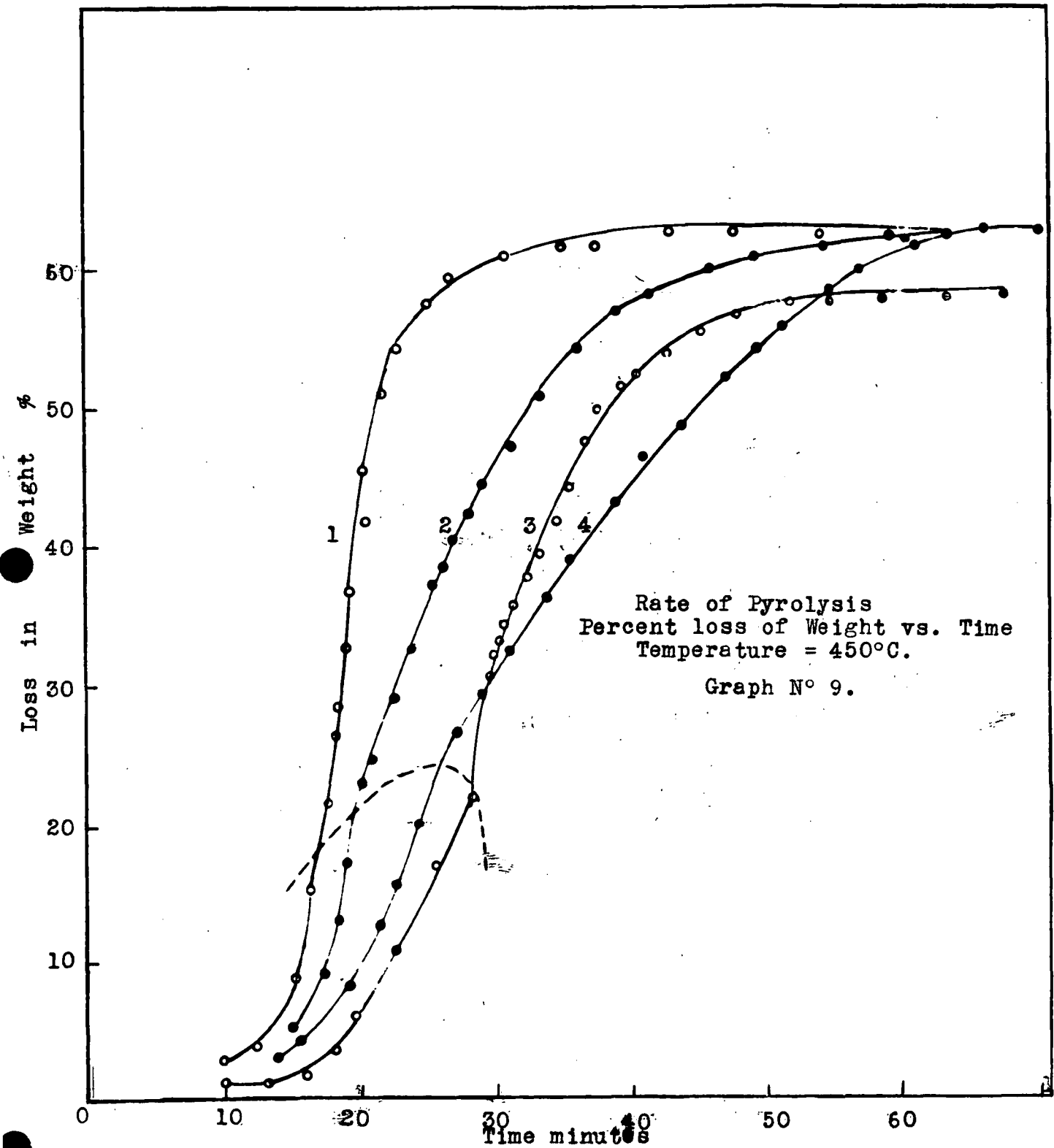
Size of Sample

1 c.cm.

8 c.cm.

27 c.cm.

64 c.cm.



The main feature of these determinations is to indicate how variations in retorting temperatures can affect the rate of oil formation.

HEAT BALANCE OF THE DECOMPOSITION REACTION.

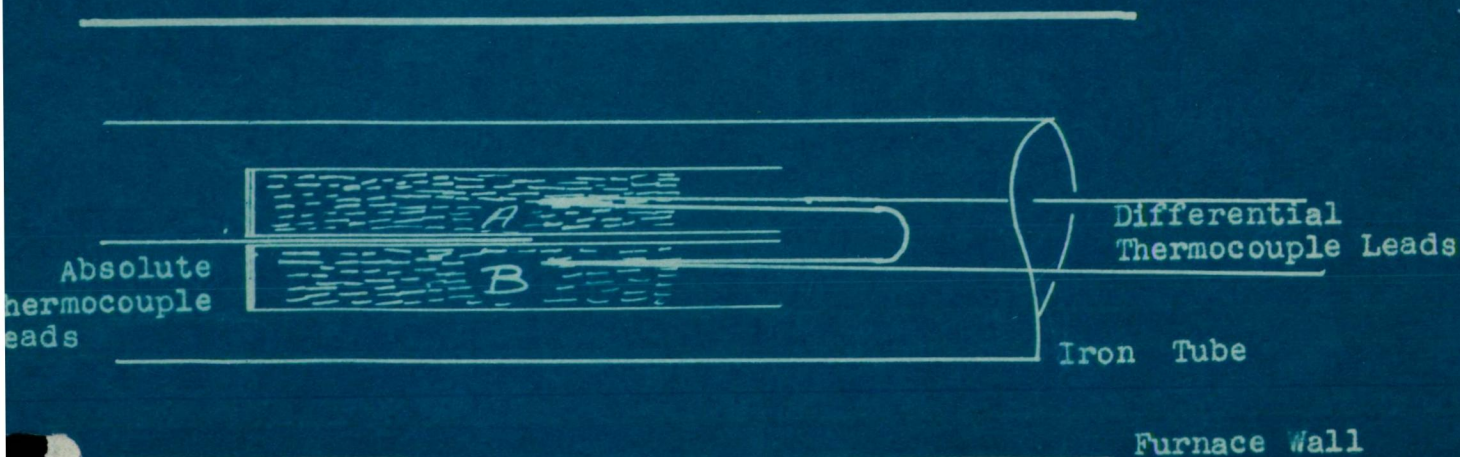
The Heat Balance of the pyrolysis of shale to produce oil (hereafter termed the Heat of Decomposition) is so fundamentally important that one would expect this subject to be fully covered in other investigations, but this is not the case. Only meagre information of doubtful value is available and no published results deal with the decomposition of torbanite. The data on the reaction velocity mentioned earlier show that the reaction is endothermic, but as the heat of activation is expressed in molar concentration, it gives no information on a mass basis.

As a preliminary to a quantitative estimation of the Heat of Decomposition an attempt was made to determine whether there was any definite thermal reaction over the whole retorting temperature. Hollings and Cobb (29) have shown that, in the decomposition of coal, no consistent thermal reaction occurs but during the decomposition the direction of the reaction varies from endothermal to exothermal and back again, over two cycles. In order to determine whether such was the case with torbanite, a similar series of tests were carried out.

The experiment consisted in slowly heating the torbanite in juxtaposition with a control sample and determining whether any temperature difference occurred between the two materials. The details were as follows:-

The heating medium was a tubular furnace, and in order to obtain even temperature conditions a 1" diameter iron tube was fixed in position coaxial with the furnace and the radial distance between two walls was about one and a half inches. This had the effect of producing a hot-air jacket around the inner metal tube, and by this means a very uniform temperature was obtained inside the inner tube.

The sample and control were packed in two short silica tubes which, side by side, just fitted into the metal tube. The temperature difference between the samples was measured by a differential base-metal thermocouple terminating inside the samples. In addition, another thermocouple was placed between the tubes to measure the actual temperature. The actual temperature was measured by a direct reading millivoltmeter and the differential temperature was measured by a sensitive Leeds and Northrup null-point bridge potentiometer. The layout of the tubes is shown in a diagrammatic form below.



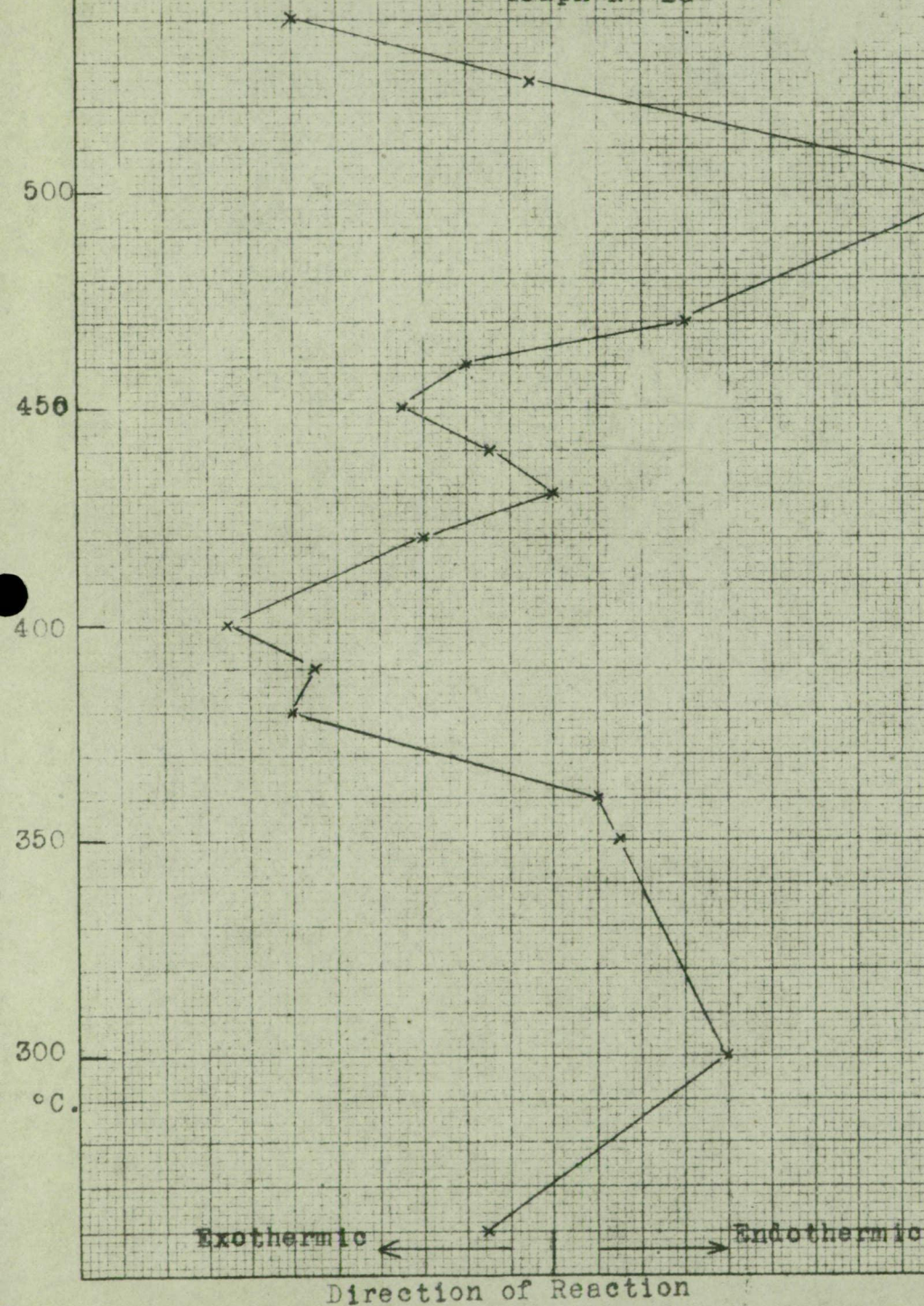
In order to check the effectiveness of the experimental arrangement, a preliminary run was carried out with ignited Fullers earth in both silica tubes, and within the limits of the instrument, no temperature differences were noticed on the potentiometer.

In the actual determination, one tube was packed with powdered torbanite and the other with ignited Fullers earth. The temperature of the furnace was raised at the rate of about 150°C. per hour, and the readings expressed in the form of a graph, where actual temperature is expressed as the ordinate and the thermal direction of the reaction expressed as the abscissa. As no quantitative expression may be derived from this experiment, the temperature-difference data are expressed in terms of the galvanometer deflections only.

The following table gives the galvanometer deflections (in scale units not mm.) obtained at the temperatures shown in the other column.

Temperature	Table 44. Galvanometer Deflection from zero.
260°C.	+3
300	-8
350	-3
360	-2
380	+12
390	+11
400	+15
420	+ 6
430	+ 0
440	+ 3
450	+ 7
460	+ 4
470	- 6
500	-20
525	+ 1
540	+12

Thermal Reactivity of Torbanite
Graph N° 10



From graph No. 10, it is seen that the reaction is by no means regular, and distinct endothermic and exothermic reactions occur.

The change in direction at about 300°C . is probably connected with some molecular rearrangement of the kerogen molecule before oil formation commences. The most important point, however, is the abrupt change in direction at 400°C ., a point where oil formation occurs at appreciable rates. As these experiments were carried out in the presence of air, it is possible that up to 400°C . oxidation gives rise to the exothermic reaction, but as the oil vapours progressively exclude the air, this oxidation is arrested.

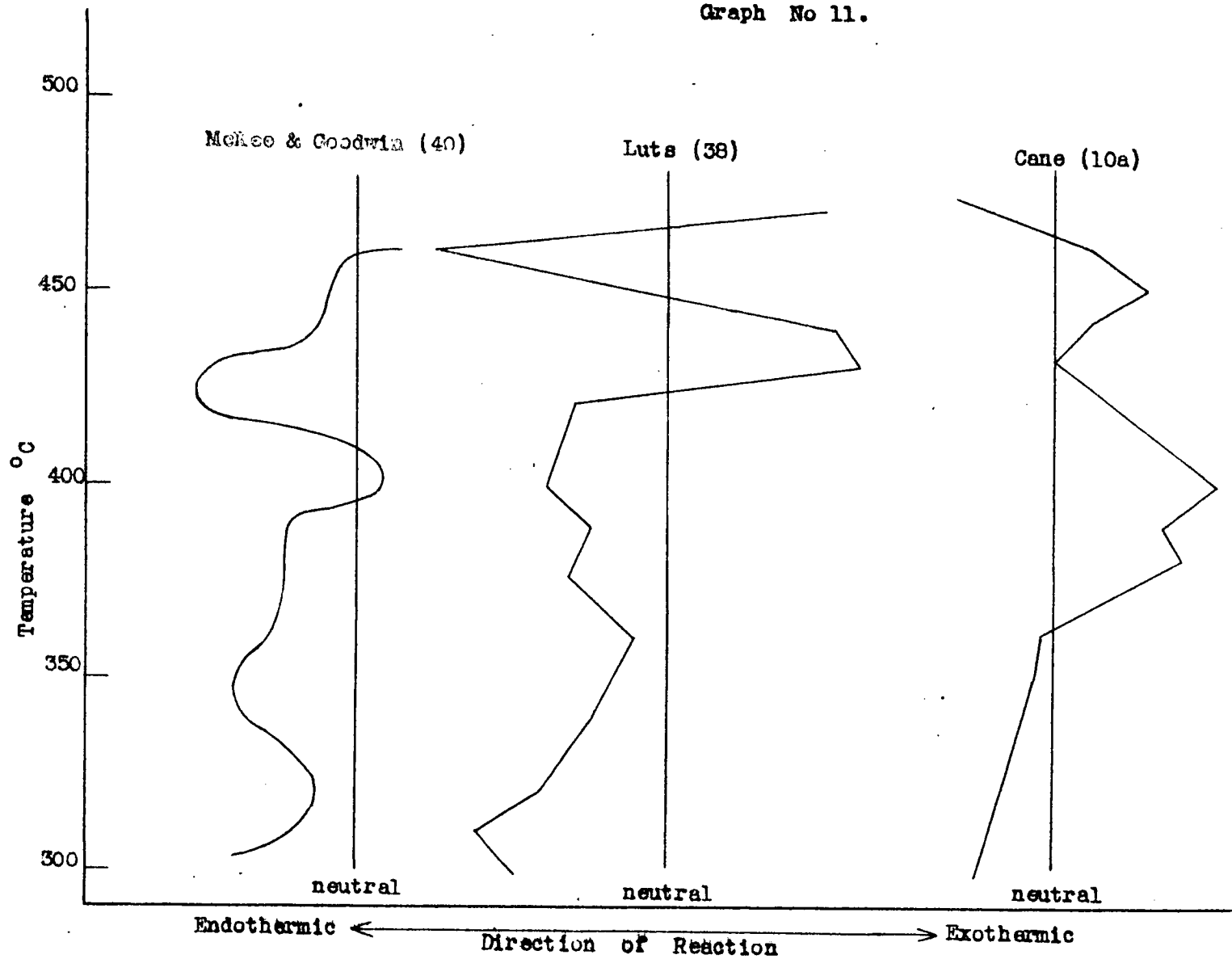
The thermal discontinuity of the reaction during oil formation from shale has received the attention of a few workers, and it is interesting to note that most shales show a reversal at about the same temperature.

The results of the present investigation, those of McKee and Goodwin (40) and those of Luts (38) are shown together in graph 11 on the following page.

Having shown that, in the presence of air, the continuity of the thermal decomposition of torbanite is by no means regular, the next step in the investigation is to attempt to measure the amount of heat involved during the transformation, in the absence of free air.

Cane (10a) has shown that in the Gray-King assay, the

Graph No 11.



overall heat balance is very small. The accuracy of the calculation is questionable, on account of the very many sources of error present. In the Gray-King assay the retort tube is initially filled with air and as it has been shown that in the decomposition of kerogen rapid oxidation occurs in the initial stages, this exothermic reaction would tend to produce very low results for the overall endothermic heat-balance.

Heat Balance of Pyrolysis of Torbanite.

The amount of heat required for the pyrolysis of kerogen has been a controversial subject for over twenty years and, as yet, no really satisfactory figure has been presented. As far as is known, only three reports of this determination have appeared in print, and none of these has been a thorough analysis. The first record is that of McKee and Lyder (42), presented in 1921. These investigators decomposed shale by means of the heat developed by an electric current. The apparatus consisted of a calorimeter in which was immersed a small, lagged brass cylinder containing the shale. The amount of added electrical energy was determined by measurement of the voltage and the current, and the excess heat by absorption in water. It is unfortunate that these investigators give no indication of the extent of the decomposition, nor the amount of charge in the 'retort'. The source of current was a battery of Edison cells, E.M.F. of which was measured by a voltmeter. Although the voltmeter was capable of reading to 0.01 of a volt, the published results show sudden changes greater than 200 times this value, in less than half a minute. This fluctuation, when considered with the fact that the current is practically constant, indicates some serious sudden increase in the electrical resistance of the circuit, the actual

change in resistance being over 18%. Thus it seems questionable whether their stated accuracy of 0.12 per cent is strictly correct.

Another important point which has not been made clear in their paper, is where the E.M.F. was measured; the comparatively large currents they used would cause an appreciable voltage drop along the leads and, to quote the authors, "The method was subject to several errors which could not be eliminated".

However, it must be said that theirs was the first method which indicated quantitatively any figure for the heat necessary for the decomposition, although it appears that they measured the heat necessary for only a certain degree of pyrolysis. The authors point out that the value published by them is only applicable for "the first stage of decomposition, from kerogen to shale oil". This value varied from 298 cal./gram. of product for Colorado shale, to 484 cal./gram. of product for Canadian shale.

The second investigators approached this problem from a different aspect. In 1924, Maier and Zimmerly (44) showed that the velocity constant of the decomposition of kerogen to the primary heavy oil followed a monomolecular reaction, and from this, with the aid of the Arrhenius equation, they showed that the primary decomposition to bitumen was endothermic, and 41,500 cal./gram. mol. was the heat necessary for the transformation. Actually, it

is impossible to so limit the decomposition that any one stage is produced to the exclusion of any other.

No confirming evidence was obtained to support Lyder's statement that it is possible to produce bitumen without the simultaneous production of oil. However, it is possible to produce bitumen without producing appreciable amounts of light material. The bitumen always contains some heavy oil; only, when the bitumen becomes sufficiently diluted with its own products of decomposition, does the oil phase predominate.

Therefore, the figure of 41,500 cal./grm. mol., obtained by Maier and Zimmerley, represents an average value taken over the decomposition and its products.

The important contributions of this paper were that it showed;-

- (i) the continuity and finality of the decomposition.
- (ii) that the decomposition obeyed definite chemical laws.
- (iii) the pyrolysis did not commence at a definite temperature as asserted by McKee and Lyder, but only became measurable at these elevated temperatures.
- (iv) the effect of air must be taken into consideration when arriving at a figure for the type and rate of decomposition (cp. remarks on page 171 and tables 31 and 32).

Maler and Zimmerley's paper is important inasmuch as the points enumerated above give some definite information. However, as the approach to the determination of the "Heat of Reaction" is an indirect one, and no correction has been made for secondary reactions, the figure arrived at cannot be regarded as accurate.

The third contribution came from Estonia, in 1938, in an article by Puksov, but unfortunately it is not available in the common European languages. Puksov's researches are alluded to by Kogerman (33) and he (Kogerman) quotes a value of 3850 cal. per Kg. of oil produced.

In addition to the work of Puksov, other workers, practically exclusively Russian and Estonian, have contributed short papers on this subject. Unfortunately all these have been published in their native language and, so far, are not available in this country.

This it can be seen that the available information on this pertinent subject is particularly meagre and furthermore, those results which have been published are of questionable accuracy.

In view of the above facts and the necessity for having reliable information on this topic, an attempt to determine this value is described herein.

Apparatus.

The design of apparatus suitable for this investigation was of primary importance and upon it depended the success

or failure of the determination.

The points to be kept in mind during the designing were;

- (i) The retort proper must be highly conductive on the outside shell, but well insulated on the internal surface of the interior.
- (ii) The water equivalent of retort, heat absorbing system and calorimeter must be kept at a minimum.
- (iii) The retort must be fairly substantial and capable of withstanding a maximum internal temperature of 600°C .
- (iv) The heat losses of the calorimeter must be very small and accurately known.

The final apparatus consisted of a silver decomposition vessel, heated by an a.c. electric current and suspended in a Dewar flask, the flask being kept under adiabatic conditions by means of a differential thermoregulator. The apparatus was an improved automatic form of the Parr Adiabatic Calorimeter.

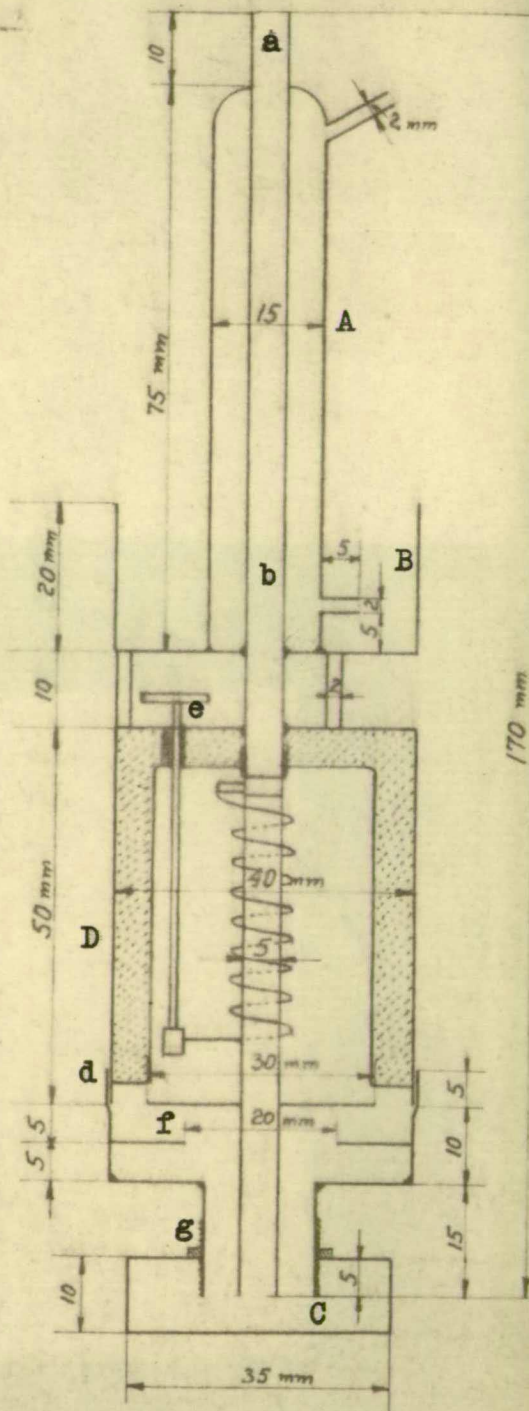
The Decomposition Vessel (fig. 7 and Plate III)

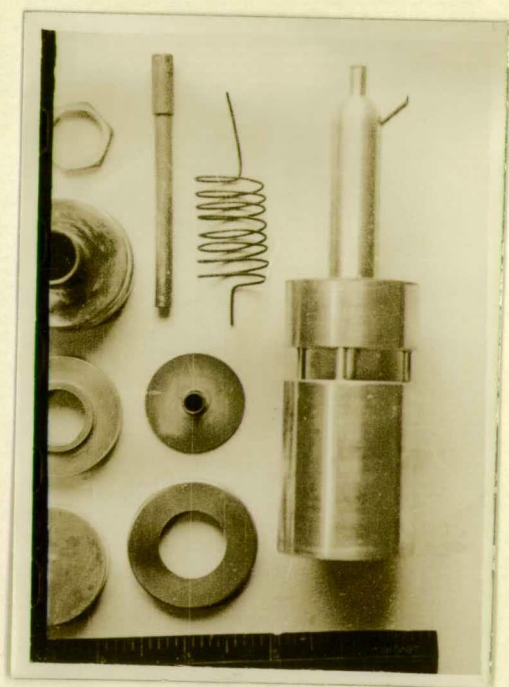
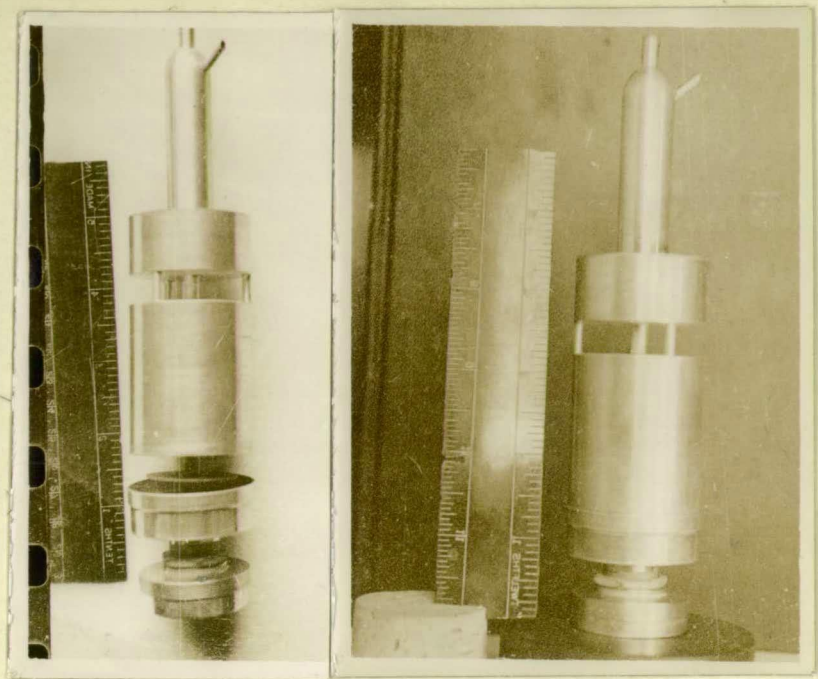
The decomposition vessel was made by Esdaile and Sons, Sydney, to a special design. The apparatus was of silver and the interior surfaces were chromium plated to resist sulphur corrosion.

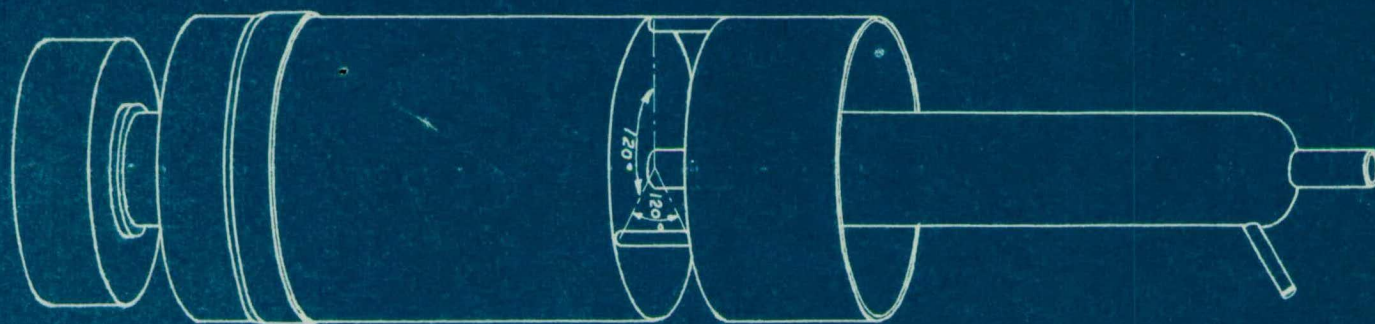
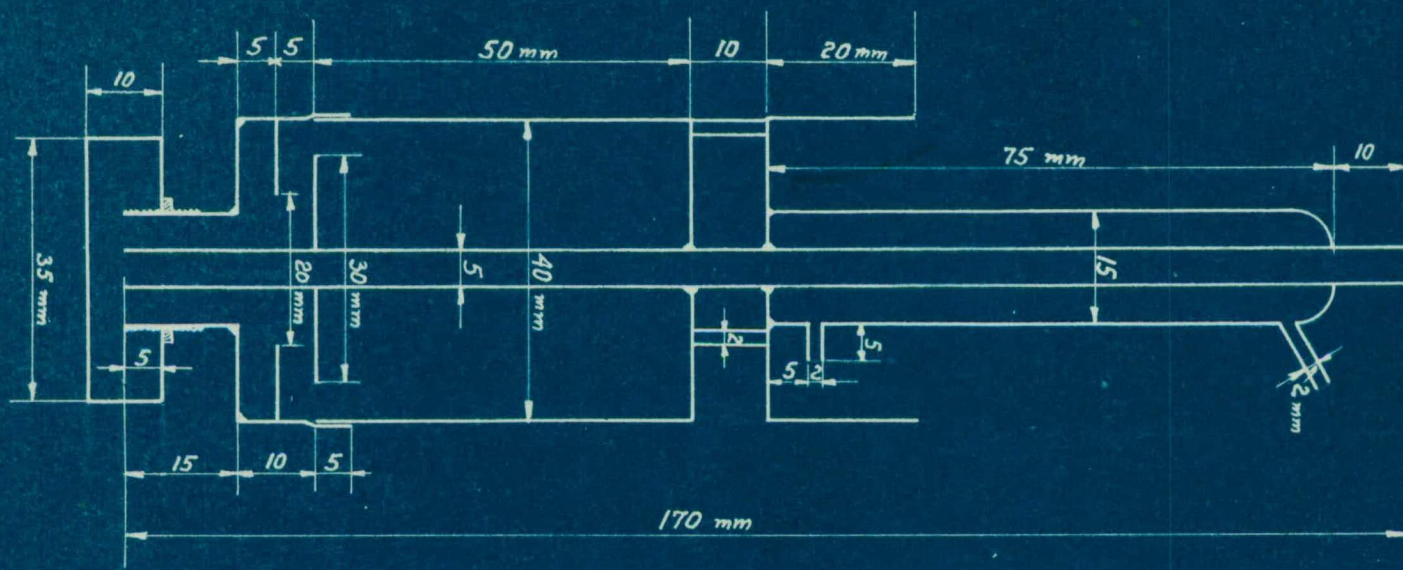
The vessel could be divided into three portions;

- (i) An upper portion which was a water condenser, A,

Figure N° 7.







whose outlet was at the top (a). The effluent water from the condenser collected in the circular trough (B). When the water reached a certain level the overflow siphoned over through a glass tube (not shown) and sprayed over the oil collecting pot (C); by this means the top and bottom portions were kept cool. The cooled gas from the decomposition passed through the central tube (b), through a metering device, thence to waste. The top portion was supported by three struts and the central gas offtake.

- (ii) The middle portion (D). This section was made in two parts, joining in a gas-tight fit at (d). The lower portion was removable and by this means the vessel was filled with the powdered shale charge. This portion was lagged on the inside and top walls with several layers of asbestos paper, leaving a cylindrical space about 27 mm. diameter, and 43 mm. high. This inner chamber contained a heating element of seven turns of 22 B. and S. gauge nichrome wire, wound so that five turns occupied a linear space of 2 cms. The upper end of the heating coil was 'earthed' to the vessel and the lower end was held by a light silver rod, taken through an insulated silver binding post to the exterior at (e) the top. A sliding-fit disc at (f) and a sliding-fit circular disc had the function of retaining the torbanite charge in position when the vessel was

upright. The oil produced during the pyrolysis ran down between the discs and finally collected in the oil-collecting pot (C). This pot screwed on to the base of the middle portion at (g).

The water equivalent of the whole apparatus may be calculated as follows;-

Table 45.

Water Equivalent of Apparatus.

		Water equivalent. (cals.)
Wt. of silver and shield, grms.	= 196.9 grms.	
Specific heat of Silver	= 0.056	= 11.0
Wt. of Heating Element	= 2.6 grms.	
Specific Heat of Nichrome, grms.	= 0.104	= 0.3
Wt. of Lagging.	= 27.5 grms.	
Specific Heat of Lagging	= 0.2	= 5.5
Wt. of Siphon Tube	= 2.01 grms.	
Specific Heat of Glass	= 0.121	= <u>0.2</u>
Water Equivalent of Decomposition Vessel		17.0 cals.
Water Equivalent of Stirrer and Thermometer		<u>2.4</u> cals.
	<u>Total</u>	<u>19</u> cals.

Calorimeter.

The calorimeter vessel was an efficient Dewar flask whose dimensions were as follows;-

Internal Diameter	= 9.7 cms.
Height	= 17.4 cms.
* Thickness of Inside Wall	= 0.2 cms.

In a glass vessel partially filled with liquid it will be found that there is a variation in water equivalent
* This dimension was measured some months later when the vessel was accidentally broken.

(depending on the liquid level inside the container) caused by the low conductivity of the glass. However, with constant level of liquid inside the flask, the water equivalent is relatively constant.

The calculated value of the water equivalent for the hemispherical bottom is 9.3 calories, to which is added an additional 1.9 cal. per cm. increase in liquid level in the cylindrical portion. With a liquid content of 500 ml., this gave a total water-equivalent of 16.5 cal. for the vessel, the "retort" being in place, and a further 2.5 calories increase per 100 ml. of cooling water in excess of 500 ml. Assuming that 600 grms. of condenser water were used for a run, and that seven grams of shale were used, the following addition shows the water equivalent of the whole apparatus;

Retort, stirrer, etc.	=	19.4 cal.
Vessel (600 ml. water)	=	19.0 "
Shale Charge	=	2.1 "
Water at 23°C.	=	<u>498.8</u> "
		639.3 cal.

Total water equivalent (for
600 ml. H₂O) = 639 cal.

Water equivalent of apparatus
(less water) = 40 cal.

In order to provide a check on the calculated magnitude, an experimental value was determined.

The standard method of mixtures was used, and the results obtained are shown below;

Water Equivalent of Calorimeter.

Weight of Water in Calorimeter = 300 grms.

Initial Temp. =	23.54	
Correction =	<u>-0.02</u>	23.52°C.

Final Temperature	36.44	
Correction	<u>+0.01</u>	36.45°C.

Weight of added water = 312 grms.

Temp. of added water	50.31	
Correction (inc. cooling)	<u>0.21</u>	50.52°C.

Water Equivalent (for 600 ml. H₂O level)=39 cal.

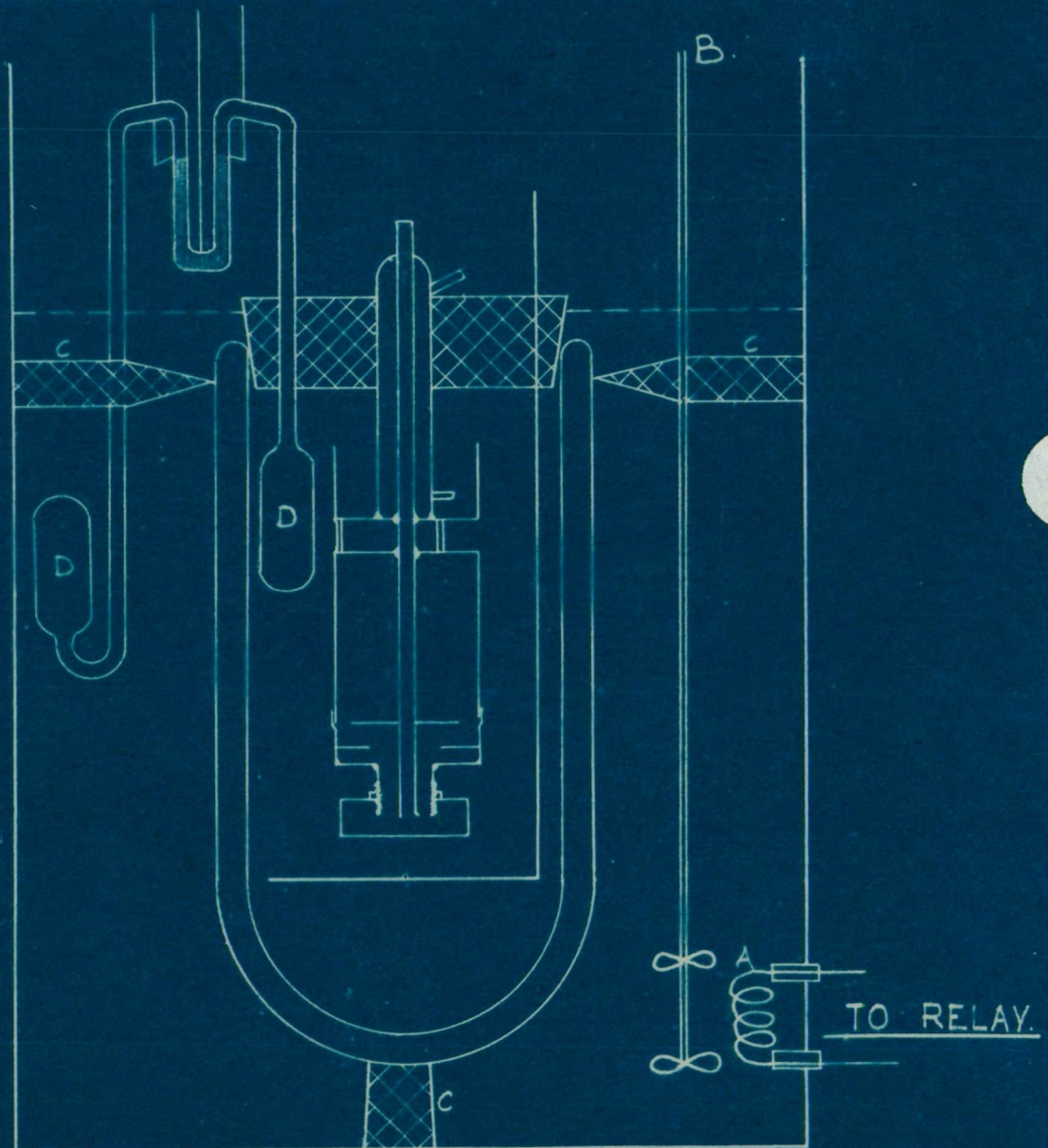
It is now necessary to indicate how the tedious task of applying corrections for radiation and other losses was obviated.

The initial idea originated from an examination of the Parr Adiabatic Calorimeter. The usual calorimeter consists of a central vessel, and a series of insulating media around it. With all calorimeters of this type a radiation correction is necessary and the application of this correction is rather complicated. It may, however, be overcome by one of two methods;

- (i) Complete thermal insulation of the calorimeter by suitable lagging. This is practically impossible, and at best it only reduces the heat losses to such a degree that they may be estimated with a reasonable degree of accuracy or neglected.
- (ii) Maintaining the ambient temperature of the

Figure N° 8.

TO DIFFERENTIAL
TEMPERATURE CONTROLLER RELAY



calorimeter equal to the internal temperature during the whole of the test.

It will be appreciated that the second method has many advantages to recommend it and it was adopted in the present investigation.

The general plan of the apparatus is shown in figure 8.

The thermos flask has been fully described under the heading of "calorimeter". This was supported in a polished copper jacket, by means of shaped corks (c) fixed to the sides. In the jacket was the heating element (A), the mechanical stirrer (B) and the thermoregulator bulb (D). The thermoregulator was designed expressly for this work and will be described in detail.

Two vapour capsules were employed, one in the surrounding liquid in the jacket, and the other in the atmosphere above the liquid inside the calorimeter. The two leads from these capsules terminated in two horizontally-opposed sensitive metal bellows (taken from a Micromax recorder). These two bellows were connected in opposition by a metal link, so that when there was equal pressure in both capsules the link rested in zero position, but when the pressures were unequal, the link moved from zero position and actuated a moving arm, which closed an electrical circuit. In later experiments the bellows were replaced by a differential manometer with contacts (see fig. 8). The circuit contained a sensitive relay (hot wire type with mercury

switch) whose output worked the heater (A) in the bath. At one stage, a two-way circuit was contemplated, including a reversing motor and valves carrying hot and cold water, so that cooling, as well as heating, could be effected, but provided sufficient care was taken with the cooling water to the condenser, this was found unnecessary. No provision was made for cooling the water in the bath, but owing to the slight time lag in the internal capsule, the temperature inside the calorimeter was always slightly hotter than that of the water in the bath. Actually there was nearly always a constant difference of 0.6°C . between the inner and outer liquids. This represents a maximum figure, as the temperature of the atmosphere at the inner top of the vacuum flask was slightly less than the contained water.

Therefore, assuming a constant temperature difference of 0.6°C . between the inside of the calorimeter and the ambient liquid, it was necessary to ascertain what losses were incurred by omitting to apply corrections for this temperature difference.

The rate of cooling was determined, then by application of Newton's law of cooling, an estimation of the required figure was obtained;

Cooling Rate of Dewar Flask.

Time mins.	Interior Temp. °C.	Ambient Temp.	Temperature Difference.	$K_1 \times 10^3$ (see equation following)
0	87.6	19.7	67.9	
10	86.4	20.1	66.3	2.38
20	85.0	20.0	65.0	2.18
30	83.7	19.9	63.8	2.07
60	80.9	20.0	60.9	1.81
79	76.8	19.7	57.1	2.19
99	74.8	19.9	54.9	2.14
121	72.6	19.8	52.8	2.08
165	67.5	20.0	47.5	2.16
380	63.0	20.1	32.9	1.91

Mean Value $K_1 = 0.0021$

Mean Value $K = 0.0021$ cals./°C./min./calorie water equivalent.

Maximum Loss from data = .8 calorie per minute.

Working loss = .6 cals. per minute.

It will be noticed that K is expressed per unit water equivalent, this being derived from the Newton formula;

$$\frac{d\theta}{dt} = -K(\theta_1 - \theta_2)$$

where K = cooling constant (Newton)

θ_1 = temperature at any time t

θ_2 = ambient temperature (atmospheric)

θ_0 = temperature at $t = 0$

$$\text{Then, } \frac{Wd\theta}{dt} = -K(\theta_1 - \theta_2) \quad \text{Let } K_1 = \frac{K}{W}$$

$$\text{By integration, } \log_e \frac{(\theta_1 - \theta_2)}{(\theta_0 - \theta_2)} = -K_1 t$$

$$\therefore -K_1 = t \cdot \log_e \frac{(\theta_1 - \theta_2)}{(\theta_0 - \theta_2)}$$

Therefore, assuming a constant temperature difference, the loss may be expressed as $0.6t$ where,

t = time in minutes for retorting procedure.

The Cooling Water FOR THE Condenser was fed from a constant level device, from a graduated container, a graduated screw clip on the tubing enabling the flow to be accurately controlled, or set to a predetermined rate. During the determinations, the flow was adjusted so that a slow temperature rise was maintained in the calorimeter.

The temperatures were taken by mercury-in-glass 0 - 50°C. thermometers placed in three positions to measure;

(i) the condenser cooling water temperature.

(ii) the temperature of the water in the calorimeter.

(iii) the temperature of the jacket water.

These thermometers were standardised against a N.P.L. standard, and the corrections to be applied are given in table 4B.

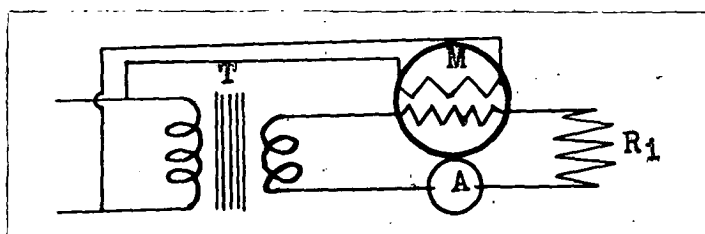
Table 45.

Thermometer Corrections.

Reading °C.	Thermometer Designation.			
	1	2	3	N.P.L.
10	-0.01	-0.03	+0.09	-0.005
15	-0.02	-0.03	+0.06	-0.020
20	-0.02	-0.01	+0.04	-0.035
25	-0.02	+0.02	+0.02	±0.000
30	-0.03	+0.03	±0.00	-0.035
35	-0.01	+0.02	-0.02	+0.015
40	+0.08	+0.04	-0.01	-0.010
45	+0.14	-0.01	+0.00	+0.145
50	+0.12	-0.05	-0.02	-0.195
55	+0.13	-0.04	-0.01	-0.230

The Electrical Circuit and Heating Element.

One of the main problems in this investigation was to provide a suitable source of current to generate the heat. Naturally the first question to be decided was whether a.c. or d.c. was to be used. Although some advantages of d.c. were obvious, for instance steady current over reasonable time intervals, and ease of accurate metering, there are some disadvantages in attempting to measure the quantity of heat when using direct current. After weighing both sides of the question, it was decided to use alternating current, taken from a stepdown transformer. In order to measure the quantity of electricity used in a determination, an accurate watthour meter was employed. The circuit used is shown in the figure herewith.



Examining this circuit it will be seen that the voltage coil of the meter is connected across the high tension mains, and the current coil is connected in the low tension circuit, so that the meter (M) reads a many times larger quantity than actually used. A factor (K_0) was determined so that the meter-reading divided by K_0 gave the quantity of electricity used by the retort (R).

The Transformer (T) was a 200 watt radio transmitter transformer with heavy-duty low-tension windings.

The Watthour meter (M) was a specially corrected type made by Emeco Meter Company of Sydney, No. 0162470, and calibrated to an accuracy of 0.1%. The calibration figures for different loadings and cycles are shown in the table 46.

Table 46.

Calibration of Watthour Meter (Power Factor 0.8)

Current Amperes	Rate + = fast	Frequency Cycles	Rate + = fast.
.5	+0.4%	48	-0.25%
1	±0.0%	49	-0.12%
5	-0.1%	50	±0.00%
10	+0.2%	51	+0.12%
20	+0.5%	52	+0.25%

The Resistance (R_1) was the retort wiring.

The Ammeter (A) was a commercial panel-mounted meter reading 0 - 20 amps. This was kept in the circuit to indicate any sudden changes of current (short circuits etc.), and in this way acted as a safety device. The potential difference across the ammeter was considered negligible.

Calculation of Reducing Factor (K_c)

This factor is perhaps the most important figure in the whole investigation, as on it depends the accuracy of all the succeeding determinations. In addition, by maintaining all conditions in the determination of this value as identical as possible to the actual retorting runs, it is possible to minimise any errors caused by meters, resistances and radiation.

In the table following, all figures have been corrected, using data from the previous two tables (Nos. 45 and 46). The first three runs represent conditions under which the current was switched off at a predetermined reading on the watthour meter, while the other three runs are taken at random. No corrections have been made for heat losses, as they amount to less than the required accuracy.

The calibration consisted of heating the decomposition vessel (filled with dried retort residue) for a given period, measuring the change in heat content of the system and the apparent electrical input, and determining the ratio of the two measurements.

Table 47.The Reducing Factor K_0 .

	Run 6	Run 8	Run 9	Run 4	Run 2	Run 5
Initial Temperature, °C.	31.83	30.96	31.24	31.66	32.95	31.82
Correction.	+0.03	+0.03	±0.00	-0.01	+0.01	-0.01
Corrected Initial Temp., °C.	31.86	30.99	31.24	31.65	32.94	31.81
Final Temperature °C.	41.21	40.27	40.58	41.92	44.93	48.42
Correction	+0.03	+0.03	-0.01	-0.01	±0.00	-0.01
Corrected Final Temp., °C.	41.24	40.30	40.57	41.91	44.93	48.42
Reading of Watthour meter: Initial	30469	30914	31317	29366	26807	29807
Final	30872	31317	31720	29807	27327	30469
Correction	+0.1	+0.1	+0.1	+0.1	+0.1	±0.0
Corrected Watt Hours	403	403	403	441	520	662
Apparent Input cals.	346,580	346,580	346,580	379280	447200	569320
Water Equivalent, Cals.	1097	1103	1099	1097	1102	1011
Actual Temp. Rise °C.	9.38	9.31	9.33	10.26	11.99	16.61
Actual Heat Input, cals.	10,290	10,269	10,254	11,298	13,219	16,791
Factor $K_0 = \frac{\text{Apparent}}{\text{Actual}}$	33.68	33.75	33.79	33.70	33.83	33.90

Mean Value = 33.78

Accuracy of Determination of K_0 .

The "Reducing Factor" may be written as an algebraic expression containing the three directly observable variables,

$$K_0 = \frac{860 W}{E\theta}$$

where W = watt hours.
 E = water equivalent.
 θ = temperature rise.

$$\begin{aligned} \text{for Run 4} &= \frac{860 \times 441(1 \pm 0.0011)}{1097 \times 10.26(1 \pm 0.0019)(1 \pm 0.0005)} \\ &= 33.70 \pm .12 \end{aligned}$$

Taking Run 4, the value of K_0 may then be expressed

as 33.70 ± 0.12 , and taking an average over the runs the mean value may be expressed as $33.78 \pm .05$, using the "root mean square of the mean" expression.

Torbanite Charge.

Selected samples of torbanite were ground to pass a 3 mm, mesh screen. These samples were "quartered and coned", bulked, dried in an air oven, and placed in a large airtight glass jar, for immediate use. This bulk sample constituted the standard charge for the retort. In order to obtain an idea of the ultimate oil yield which might be expected, a Gray-King assay was performed on the sample, in addition to a proximate analysis. These results are shown below;

Table 48.

Gray-King Assay (18).

Wt. of Shale Charge	17.16 grms.	100%
Wt. of Liquid Product	11.08 grms.	64.4%
Wt. of Shale Residue	5.38 grms.	31.4%
Wt. of Gas and Loss	0.78 grms.	4.2%

Proximate Analysis.

Moisture	= 0.03%
Volatile Matter	= 74.02%
Ash	= 14.43%
Fixed Carbon	= 11.52%

Experimental Procedure.

The different stages in the determination have been numbered below in chronological order;-

- (1) Place dry retort (with asbestos lining, weight β , in place) in air oven and weigh (W_1)
- (a) also weigh oil pot separately (W_2)

- (2) fill decomposition chamber with charge, replace oil pot and weigh (w_3).
- (3) Place retort in position in cork, make water and electrical connections (Let E = water equivalent of calorimeter with retort in position). adjust cooling water supply.
- (4) Fill external jacket and place all three thermometers in position.
- (5) Allow apparatus to come to thermal equilibrium (overnight if possible).

Read and record;

- (a) cooling water temperature (θ_1)
 - (b) calorimeter temperature (θ_2)
 - (c) jacket temperature (θ_3)
 - (d) watthour meter (e_2)
- (6) Switch on circuit and open cooling water valve, adjust water so that there is a steady rise in temperature of calorimeter, watching action of thermostat all the time.
 - (7) When sufficient time has elapsed to decompose torbanite, switch off current.
 - (8) Read and record;
 - (a) cooling water temperature (θ_1')
 - (b) maximum calorimeter temperature (θ_2')
 - (c) jacket temperature (θ_3')
 - (d) watthour meter (e_3)
 - (9) disconnect water and electrical connections.
 - (10) open up calorimeter, remove retort, making sure that no cooling water is spilt, and determine weight of cooling water used (W)
 - (11) place retort in air-oven to remove last traces of moisture.
 - (12) weigh retort (w_4)

(13) remove oil pot and weigh (w_3)

(14) open retort and remove asbestos paper and retort residue. Place paper and residue in a weighed Soxhlet thimble (m_1) and weigh (m_2). Extract thimble with benzene, weigh again (m_3).
 (15) Determine weight of Residue (R) in Soxhlet thimble.
 $= m_3 - (m_1 + \text{wt. of leaching}).$

Calculation of Results.

The following data may be obtained from the experiment:-

Weight of shale charge $= w_3 - w_1$

Weight of oil produced $= (w_4 - w_2) + (m_2 - m_3)$

Weight of Gas produced $= (w_3 - w_4)$

Weight of residue $= R = (m_3 - (m_1 + \beta))$

Heat input to calorimeter (H_1) $= \frac{860}{33.78} (e_3 - e_2)$

Heat given to calorimeter (H_2) $= \frac{W(e'_3 - e'_2 - e'_1 + e'_1)}{2} + E(e'_2 - e_2)$

Energy required for decomposition for charge $w_3 - w_1 =$

$$\frac{860}{33.78} (e_3 - e_2) - [W(e'_3 - e'_2 - e'_1 + e'_1)] + E(e'_2 - e_2)$$

Retorting Efficiency %
 (compared against Gray-King Assay)

$$= \frac{145.8(1 - \frac{w_3 - w_1}{R})}{H_1 + H_2}$$

Heat of Decomposition $= \frac{H_1 + H_2}{w_3 - w_1}$ per gram forbenite

$$= \frac{H_1 - H_2}{(w_3 - w_2) + (m_2 - m_3) + (w_3 - w_4)}$$

per gram. fluid product.

Table 50.

Run No.	3	4	6	7	8
Heat absorbed by Decomposition ($H_1 - H_2$)	3,479	1,676	3,074	2,074	2,703
Wt. of Shale Charged, grms.	5.569	3.878	5.767	4.076	6.132
Wt. of Shale decomposed grms. (calc.)	4.995	3.102	5.538	3.424	4.906
Wt. of Oil + gas, grms.	5.369	2.137	3.794	2.368	3.393
<u>Heat of Decomposition of Torbanite.</u>					
per gram decomposed	696	540	555	606	551
per gram of Oil + gas produced.	1033	784	810	869	797
Run No.	11	12	13	15	16
Heat absorbed by Decomposition ($H_1 - H_2$)	3,987	2,867	2,408	3,176	4,724
Wt. of Shale Charged, grms.	6.026	5.467	4.807	5.008	6.261
Wt. of Shale decomposed grms. (calc.)	5.604	4.319	4.326	4.457	5.823
Wt. of Oil + Gas, grms.	3.859	2.952	2.904	3.039	3.991
<u>Heat of Decomposition of Torbanite.</u>					
per gram. decomposed	696	664	557	713	811
per gram of Oil + Gas produced.	1033	971	829	1047	1184

Run No.	3	4	6	7	8	11	12	13	15	16
(5) Weight of Apparatus =	197.010	203.516	198.456	199.581	199.565	193.629	199.345	194.909	203.336	199.012
Weight of Lagging (β) =	27.740	27.416	25.243	27.601	24.734	24.885	24.685	26.628	25.242	17.501
Weight of Retort (w_1) =	224.750	230.932	223.699	227.182	224.299	218.514	224.030	221.537	228.578	216.513
Weight of Retort + Charge (w_3) =	230.319	234.810	229.466	231.258	230.431	224.540	229.497	226.344	233.586	222.774
Weight of Charge ($w_3 - w_1$) =	5.569	3.878	5.767	4.076	6.132	6.026	5.467	4.807	5.008	6.261
Weight of Oil Pot (w_2) =	23.691	23.609	23.704	24.003	23.692	23.757	23.835	23.671	23.786	23.711
Ditto + Oil (w_5) =	25.344	24.521	25.465	24.588	25.164	25.388	24.707	25.055	24.767	25.500
Weight of Oil ($w_5 - w_2$) =	1.653	0.912	1.761	0.585	1.472	1.631	0.872	1.384	0.981	1.789
Weight before Extraction (m_2) =	32.771	31.684	30.189	32.654	30.546	29.887	30.176	31.046	29.777	22.986
Ditto after Extraction (m_3) =	31.439	30.765	28.542	31.235	29.042	28.313	28.539	29.863	28.235	21.257
Weight of Oil (extracted) ($m_2 - m_3$) =	1.332	0.919	1.647	1.419	1.504	1.574	1.637	1.183	1.542	1.729
Total weight of Oil =	2.985	1.831	3.408	2.004	2.976	3.205	2.509	2.567	2.523	3.518
Weight of Retort + Charge (w_3) =	230.319	234.810	229.466	231.258	230.431	224.340	229.497	226.344	233.586	222.874
Ditto after Run (w_4) =	229.935	234.504	229.080	230.874	230.014	223.686	229.054	226.007	233.070	222.401
Weight of Gas ($w_3 - w_4$) =	0.384	0.306	0.386	0.384	0.417	0.654	0.443	0.337	0.516	0.473
Weight of Thimble (m_1) =	1.478	1.613	1.417	1.888	1.538	1.253	1.339	1.404	1.023	1.493
Weight of Thimble + Lagging ($m_1 + \beta$) =	29.218	29.029	26.560	29.489	26.272	26.138	26.024	28.032	26.265	18.994
(4) Ditto + Residue (m_3) =	31.439	30.765	28.542	31.235	29.042	28.313	28.539	29.863	28.235	21.257
Weight of Residue ($m_3 - (m_1 + \beta)$) =	2.221	1.736	1.982	1.746	2.770	2.175	2.515	1.831	1.970	2.263
WEIGHT BALANCE (Shale Charge = 100%)										
Weight percent of Oil =	53.7	47.3	59.1	49.2	48.5	53.3	45.9	53.4	50.4	56.2
Weight percent of Gas =	6.9	7.9	6.7	9.4	6.8	10.8	8.1	7.0	10.3	7.5
Weight percent of Residue =	40.0	44.8	34.3	42.8	45.2	36.1	46.0	38.1	39.3	36.2
Sum of Products =	100.6	100.0	100.1	101.4	100.5	100.2	100.0	98.5	100.0	99.9
Retorting Efficiency %	88	80	96	84	80	93	79	90	89	93

Notes: (1) Water Equivalent of Calorimeter (Dewar flask, retort etc.) will vary slightly with the shale charge, liquid level in flask, and accessories.

(4) Weight of Internal Lagging plus Residue plus partially decomposed shale charge.

(2) Temperature of inlet water to top of condenser.

(5) Weight of Decomposition Chamber varies slightly due to changes in heating element, shield etc.

(3) Temperature of cooling water in flask at end of run = temperature of retort at end of run.

Run No.	3	4	6	7	8	11	12	13	15	16
<u>CALORIMETER WATER.</u>										
Weight used, grms. (W)	721	681	631	602	618	396	602	498	514	451
(2)Cooling Water Temperature;										
Start °C. (θ_1)	29.00	23.52	26.46	29.53	29.35	23.28	24.78	23.42	25.81	24.91
Finish °C. (θ_1)	28.86	23.28	26.50	29.41	29.55	23.71	24.88	23.00	26.13	24.49
Average Initial Temperature °C.	28.93	23.40	26.48	29.47	29.40	23.50	24.83	23.21	25.97	24.70
Correction °C.	+0.03	+0.01	+0.02	+0.03	+0.03	+0.01	+0.02	+0.01	+0.02	+0.02
True Average Initial Temperature °C.	28.96	23.41	26.50	29.50	29.47	23.51	24.85	23.22	25.99	24.72
Final Temperature °C. (θ_2)	41.72	41.43	49.79	49.88	46.05	42.94	46.38	44.45	47.93	51.84
Correction	+0.11	+0.10	+0.12	+0.12	+0.14	+0.13	+0.14	+0.13	+0.12	+0.12
(3)True Final Temperature °C.	41.83	41.53	49.91	50.00	46.19	43.07	46.52	44.58	48.05	51.96
Corrected Temperature Rise °C.	12.87	18.12	23.41	20.50	16.72	19.56	21.67	21.36	22.06	27.24
Increase in Heat Content, cals.	9251	12303	14727	12304	10302	7723	13006	10605	11305	12249
<u>CALORIMETER.</u>										
(1)Water Equivalent, cals. (E)	43.5	42.0	40.8	40.1	40.5	35.0	39.9	37.6	37.7	35.1
Initial Temperature °C. (θ_2)	28.67	24.62	26.35	30.87	27.48	23.37	25.26	22.97	26.79	26.31
Correction	-0.03	-0.02	-0.02	-0.03	-0.03	-0.02	-0.02	-0.02	-0.02	-0.02
True Initial Temperature °C.	28.64	24.60	26.33	30.85	27.45	23.35	25.24	22.95	26.77	26.29
(3)True Final Temperature °C.	41.83	41.53	49.91	50.00	46.19	43.07	46.52	44.58	48.05	51.96
Corrected Temperature Rise, °C.	13.19	16.93	23.58	19.15	18.74	19.72	21.28	21.63	21.28	25.67
Increase in Heat Content, Cals.	534	711	962	770	759	690	849	813	802	901
Total Increase in Heat Content (H_2) Cals.	9785	13014	15689	13074	11061	8413	13885	11418	12107	13150
<u>ADIABATIC JACKET</u>										
Initial Temperature (cp. θ_2)	28.39	24.27	26.32	30.41	27.31	23.81	24.88	22.81	26.16	26.40
Final Temperature (cp. θ_2)	41.10	41.79	49.31	50.02	47.00	43.28	46.50	44.81	48.03	51.54
<u>WATT-HOUR METER.</u>										
Initial Reading (e_1)	32,612	33,133	33,730	34,948	32,065	35,604	36,181	38,081	38,559	39,043
Final Reading (e_2)	33,133	33,730	34,467	35,543	32,612	36,091	36,839	38,508	39,031	39,595
Watthours used	521	577	737	595	547	487	658	427	472	552
Total Heat Added (H_1) cals.	13,264	14,690	18,763	15,148	13,764	12,400	16,752	13,826	15,283	17,874
Heat absorbed by Torbanite Charge ($H_1 - H_2$)	3,479	1,676	3,074	2,074	2,703	3,987	2,867	2,408	3,176	4,724

The experimentally determined values of the Heat of Decomposition of Torbanite are given in Table 50 and vary between 540 cal./gram. and 810 cal./gram. of material decomposed, or between 780 cal./gram. and 1180 cal./gram. of fluid product. The variation obtained does not necessarily represent experimental inaccuracies (statistical analysis of the primary observations showed a maximum probable error of ± 3 per cent) but indicates variations in the degree of decomposition or 'depth of cracking'. For instance, in Runs 11 and 15 a high value was obtained for the heat of decomposition but this may be explained by severe cracking conditions with consequent high gas yields (10.8 per cent and 11.3 percent respectively). On the other hand, Runs 3 and 16 show figures with low gas yields. In no case was the gas yield as low as that obtained in the Gray-King analysis given in Table 48, from which it may be inferred that all values given in Table 50 are higher than would be obtained if the experiments were carried out under gentle conditions, similar to the Gray-King assay. However, the figures given in Table 50 may be compensated for excess oil-to-gas cracking by subtracting one calorie per milligram of excess gas; this figure being employed in cracking thermodynamics to calculate excess decomposition in the conversion of oil to gasoline. The adjusted values are given in Table 51.

The values for the Heat of Decomposition of torbanite

are noticeably higher than those obtained by McKee and Lyder (42), namely 228 to 484 cal. per gram of product, but as their experiments were confined to the first stage only of the decomposition, a comparison is not possible, nor is it with the energy of activation quoted earlier in this thesis, as this latter quantity is a measure of the reaction in which appreciable oil formation does not occur.

Table 51.

Heat of Decomposition of Torbanite.

Corrected for excess cracking to 5% gas yield.

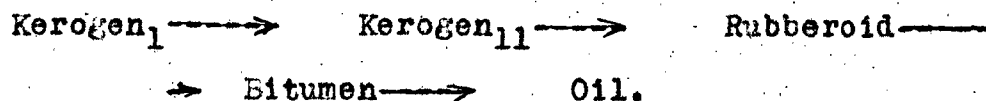
<u>Run No.</u>	<u>Heat of Decomposition per gram of oil + gas (corrected to 5% gas.)</u>
3	927
4	672
6	712
7	689
8	686
11	680
12	801
13	732
15	781
16	1024

An inspection of Table 51 shows a reasonably constant value for the Heat of Decomposition of Torbanite and, neglecting the first and last runs, the values of which are abnormally high, this value is approximately 700 cal./gram. of fluid product for 5% gas.

During the experimental work on the above section, many important observations were made on the chemical nature of the decomposition and of the intermediate products. The next section will describe these observations and discuss the nature of these products.

THE CHEMICAL NATURE OF THE THERMAL DECOMPOSITION
OF TORBANITE.

It may be stated at the outset that the production of oil from torbanite does not occur in a single stage, nor does it decompose in a two-stage reaction, as formerly supposed, but at least four stages may be observed. These stages may be represented as follows:-



Engler, in 1913, was the first worker to notice that oil was not formed by a direct decomposition of kerogen. He showed that the solubility of shale in organic solvents increased on heating, but made no mention of an attempt to isolate the intermediate material. In 1921, McKee and Lyder (42) proved the presence of an intermediate stage and stated that "The first product of decomposition was found to be a heavy semi-solid or solid bitumen, which is soluble in benzene and carbon bisulphide...."

That McKee and Lyder's statement is not true, in the case of the New South Wales Torbanite at any rate, will be shown in the proceeding pages. Furthermore, that the "Bitumen" is entirely soluble in paraffinic solvents, such as n-heptane, as well as aromatic solvents, shows that it is not a bitumen in the true sense of the word, but is a heavy aliphatic oil which acts as a precursor to true "crude oil".

In order to clarify the work which follows, a short description will be given of the nomenclature used in

describing the break-down products.

Kerogen₁ is the original raw kerogen as found. It is a rigid solid, mechanically tough, and orange in colour by transmitted light.

Kerogen₁₁ may be regarded as a subdivision which occurs before the formation of Rubberoid. It is not sharply defined from Kerogen₁. Kerogen₁₁ is soft but still solid, tends to crumble when rubbed, and is darker in colour than kerogen₁.

Kerogen₁ and Kerogen₁₁ are chemically inert and very insoluble in solvents, with which they give no measurable swelling on immersion.

Rubberoid is the next sharply defined stage in the decomposition and, in appearance, it resembles semi-vulcanised rubber. It is black in colour and on deformation by mechanical means, it returns to its original shape. Actually the reversion is slow and more or less incomplete. It possesses elasticity but is ruptured on slight elongation.

Rubberoid exhibits swelling characteristics similar to other elastomers possessing thread molecules.

Bitumen. although not a bitumen in the chemical sense of the word, resembles it in appearance. It is a very viscous or semi-solid sticky mass, which

on warm days is just free-flowing. It resembles cracked residuum except that it does not possess the aromatic nature of the latter.

Oil

is the crude oil in the normal sense of the word. The oil is an unsaturated waxy liquid, the properties of which vary somewhat with the manner of production.

THE INTERMEDIATE PRODUCTS.

Following along the lines of McKee and Lyder's work, on the isolation of bitumen, it was decided to prepare a large quantity of this material and perform a detailed examination of its properties. With this aim in view, many small portions of rich torbanite were heated for extended periods. Under these conditions, a minimum of oil formation occurred, and the bitumen produced was not subjected to appreciable thermal disintegration. The products from this treatment were extracted with benzene in a large Soxhlet extraction apparatus and the solutions were bulked.

The bulked solutions were concentrated on a steam bath, followed by vacuum drying at atmospheric temperature.

The black semi-solid residue was considered as bitumen.

The residue from the extraction consisted mostly of a rubbery mass but varied from a powdery solid to almost raw kerogen.

The bitumen obtained by the above procedure was a jet-black, semi-solid which, on warm days, was converted to a

very viscous liquid.

The properties of this bitumen were:-

Specific Gravity at 60°F.	= 0.931
Molecular Weight (Rast)	= 590
Aniline Point	= 74 - 77°C.
Solubility in H ₂ SO ₄	= 73.2%
Ultimate Analysis (48)	
C	= 86.5%
H	= 10.8%
N	= 0.9%
S	= 0.5%
Ash	= 0.1%
O	= 1.2% by diff.
Refractive Index N_D^{20}	= 1.517.

The Specific Gravity was determined by using a small specific gravity bottle in the normal manner.

The Aniline Point was carried out in the method prescribed under ASTM Designation D611-41T.

The Molecular Weight was determined by the method of Rast (56) using MAR camphor (supplied by the C.S.I.R.) The molecular depression of melting point was taken as 498, and the depression found in the experiment was 8.1°C. From this value a calculated molecular weight of 589.6 was obtained, or 590 to the nearest whole number. Actually, the molecular weight of the bitumen means very little as its magnitude depends entirely on the degree of decomposition of the kerogen which has preceded it.

DETERMINATION OF MOLECULAR WEIGHT.

i)	Weight of glass capsule	= 8.1348 grms.
ii)	ditto plus camphor	= 8.5989 grms.
	Weight of camphor (W)	= 0.4641 grms.
iii)	(ii) plus bitumen	= 8.6434 grms.
	Weight of bitumen (w)	= 0.0445

M.P. of Camphor = 173.5°C.

M.P. of Solution = 165.4°C.

T = 8.1°C.

K = 498.

$$\text{M.W.} = \frac{K \times 100w}{W \quad T} = 590.8$$

The determination of solubility in 87% sulphuric acid i.e. the amount of unsaturation, was no easy task, and several methods were tried until success was obtained. McKee and Lyder (42) stated that the bitumen they obtained was entirely soluble in sulphuric acid, but from the following discussion it appears that they were misled by the experimental difficulties and by the awkward nature of the material. Unless the bitumen is dispersed in some solvent it is impossible to separate the two layers formed on acid treatment, because of the tarry matter produced.

In the present investigation, about one and one half grams of bitumen were dissolved in normal heptane (previously washed with concentrated sulphuric acid). The solution was washed with equal volumes of 10% v/v, caustic soda and then 28% acetic acid, to remove phenols and tar bases respectively, but no tar acids or bases could be detected. The residue from this treatment was washed with successive ten percent volumes of 87% sulphuric acid until the acid layer remained clear.

The bulked acid solubles were hydrolysed with superheated steam, whereupon a dirty, greenish-gray oil was obtained. This oil was not further investigated.

The heptane layer was washed with dilute sodium carbonate solution, followed by a water wash. The resulting solution which had a superb blue fluorescence, was concentrated on a steam bath until a sticky, yellowish oil remained.

The residual oil was extracted with a propane-cresylic acid mixture as in the commercial DuoSol treatment of oils.

The propane layer containing the paraffinic portion was allowed to evaporate, and on evaporation a small amount of white wax remained.

The cresylic acid layer was neutralised with caustic soda, liberating an orange, sticky solid. This solid was, as would be expected, of aromatic nature, and gave rise to the blue fluorescence mentioned earlier.

Thus it can be seen that the bitumen produced was a mixture of several hydrocarbon groups and therefore the molecular weight obtained represents an average value of the compounds present.

Having shown that bitumen is a hydrocarbon mixture of high molecular weight, the next step in procedure is to determine whether this material acts as the progenitor of the crude oil, and that such is true is shown in the following experiments;

A Gray-King assay was carried out on Bitumen to determine what yield of oil could be obtained. Actually the results were not as high as expected when compared with the rich Torbanite described by Cane (10b).

The weight balance of the assay was;

Weight of oil	=	82.2%
Weight of Residue	=	12.6%
Weight of Gas	=	5.2%

The oil obtained was similar to crude oil produced in the normal manner.

GRAY-KING ASSAY ON BITUMEN.

Weight of Retort Tube	=	108.327 grms.
Weight of Retort Tube and Bitumen	=	119.017 grms.
Weight of Bitumen	=	10.690
Weight of Tube and Residue	=	109.677
Weight of Receiver	=	79.357
Weight of Oil and Receiver	=	88.156
Weight of Oil	=	8.779

Weight Balance of Retorting.

Weight of Bitumen	=	10.690	
Weight of Oil	=	8.779 grms.	82.2%
Weight of Residue	=	<u>1.390</u>	12.6%
Total	=	<u>10.129</u>	
Gas and Loss	=	<u>0.561</u>	5.2%

Thus, having shown that Bitumen will produce oil, the next step in the procedure is to determine by what means oil is produced. With this aim in view, two distillations were performed, one under atmospheric pressure, and the other under vacuum. The experimental details are given on pages 206 and 207. The distillations were carried out in A.S.T.M. distillation equipment, with the exception that the metal condenser was replaced by a glass one, also the charge was reduced from 100 ml. to 20 grms.

The distillates from these experiments were divided into two fractions;

Fraction I:	Temperature range	- 350°C.
Fraction II:	Temperature range	350 - 400°C.

A straight Engler distillation of the Bitumen is given in Table 52.

Table 52.

Distillation of Bitumen.

<u>Temperature Range</u>	<u>Distillate.</u>
- 250°C.	5.5% v/v
250- 275	5.0
275-300	8.9
300- 325	5.7
325- 350	15.4
350- 375	13.3
375- 400	7.2
400-	remainder.

Atmospheric Distillation.

The two fractions were examined, and the results obtained for each are given in Table 53.

ATMOSPHERIC DISTILLATION OF BITUMEN.

Weight of Bitumen and Flask	= 71.734 grms.
Weight of Flask alone	= 50.438
Weight of Bitumen	= 21.296
Weight of Flask and Residue	= 57.741

Fraction I

Weight of Receiver	= 30.266
Weight of Receiver plus Oil	= 39.343
Weight of Fraction I	= 9.077
% Fraction I	= 42.6

Fraction II

Weight of Receiver	= 30.267
Weight of Receiver plus Oil ₂	= 34.780
Weight of Fraction II	= 4.513
% Fraction II	= 21.2
Total Distillate	= 63.8%

Weight Balance of Distillation.

Weight of Bitumen		= 21.296 grms.
Weight of Fraction I	9.067 grms.	42.6%
Weight of Fraction II	4.513	21.2%
Weight of Residue	<u>7.393</u>	34.7%
Total	<u>20.973</u>	
Gas and Loss	<u>0.323</u>	1.5%

VACUUM DISTILLATION OF BITUMEN.

Weight of Bitumen and Flask	= 121.150 grms.
Weight of Flask alone	= 93.166

Weight of Bitumen	= 27.984
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Weight of Flask and Residue	= 110.900
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Fraction I

Weight of Receiver	= 23.240
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Weight of Receiver plus Oil	= 33.515
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Weight of Oil	= 5.275
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% Fraction I	= 18.9
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Fraction II

Weight of Receiver	= 32.703 grms.
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Weight of Receiver plus Oil	= 37.414
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Weight of Oil	= 4.711
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% Fraction II	= 16.8
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Total Distillate	= 35.7%
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Weight Balance of Distillation;

Weight of Bitumen	= 27.984 grms.
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Weight of Fraction I	= 5.275 grms.	18.9%
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Weight of Fraction II	= 4.711	16.8%
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Weight of Residue	<u>17.734</u>	63.4%
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Total	<u>27.720</u>
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Gas and Loss	<u>0.264</u>	0.9%
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Table 53.Properties of Atmospheric Distillations from Bitumen.

	<u>Fraction I</u>	<u>Fraction II</u>
Temperature Range	- 350°C.	350 - 400°C.
Weight % of cut	42.6	21.2
Specific Gravity (60°F.)	0.8523	0.8532
Aniline Point °C.	52.8	58.2
Colour	Dark red	red
Unsaturation	41	46
Refractive Index 20°	1.4800	1.4887
Nature	Non-waxy at 15°C.. Waxy at 15°C.	
Initial Boiling Point of		
Fraction when redistilled.	156°C.	259°C.

An analysis of these figures shows conclusively that Bitumen is unstable at temperatures below 400°C. and at these temperatures Bitumen decomposes to yield oils of lower molecular weight, and of varying chemical constitution. The general nature of the oil formed is the same as that produced by the retorting of torbanite.

Vacuum Distillation of Bitumen.

The effect of vacuum would be to lower the boiling point of those hydrocarbons present in a free state in the bitumen, while having little action on the cracking temperature. Thus, the net result of a vacuum distillation would be the removal of those hydrocarbons present, as such, in the mixture, while leaving the original matter unaffected by the thermal treatment. The apparatus used was essentially the same as that employed in the atmospheric distillation, plus a Cenco Hyvac pump maintaining the vacuum. As in the Atmospheric distillation, two fractions were collected, corresponding

to 350°C. and 400°C. at atmospheric pressure, and their properties examined.

Table 54.

Properties of Vacuum Distillation from Bitumen.

	<u>Fraction I</u>	<u>Fraction II</u>
Temperature Range	- 350°C. atm.	350-400°C. atm.
Weight % of Cut	18.9	16.8
Specific Gravity (60°F.)	0.8450	0.8987
Aniline Point °C.	52.4	64.8
Colour	Dark orange	Orange.
Unsaturation	23.9	-
Refractive Index at 20°C.	1.4678	1.5001
Nature	Clear liquid.	Solid.

By comparing Table 54 with the previous table, the extent of the bitumen decomposition may be judged. The points to be noticed in the comparison are;

- (i) the difference in the specific gravity between Fraction II (atm.) and Fraction II (vac.), indicating that the former contains much material of a cracked nature.
- (ii) the higher aniline point of Fraction II (vac.), showing greater paraffin content compared with Fraction II (atm.)
- (iii) The difference between the ratios of $\frac{\text{Fraction I}}{\text{Fraction II}}$ for the two distillations, being nearly two and one for the atmospheric and vacuum respectively.

Although strict quantitative estimations are not possible, it is interesting to note that, by difference in Tables 53 and 54, the two fractions may be split into;

0 - 350°C.	18.9 straight distillate. 23.7 cracked distillate.
350 - 400°C.	4.4 cracked distillate. 16.8 straight distillate.

(percentage on original).

These figures indicate that bitumen becomes very unstable with rise in temperature.

Discussion.

It has now been shown that Bitumen will decompose to produce oil, and that the oil produced during this decomposition may be regarded as a partially cracked product. The decomposition of the Bitumen is rapid at temperatures approaching 400°C. i.e. the temperature at which it (the Bitumen) is produced. In other words, it is impossible, or apparently so, to produce Bitumen and Bitumen alone without producing oil at the same time. Whether this statement is true at very low temperatures over hundreds of hours heating-time is not known, but from the work on reaction velocities described earlier, it seems unlikely.

Therefore, the bitumen must be regarded as an intermediate stage before oil formation. The oil produced by the mild cracking of the bitumen may be regarded as crude shale oil in all respects, with the exception that, whereas in normal crude oil light hydrocarbons are present, no light gasoline fraction was produced in the preceding experiments.

The question then arises whether the light fractions

are produced by severe cracking of the bitumen, or by a further pyrolysis of the crude oil.

To ascertain whether, given sufficient time, the bitumen will produce light ends at temperatures near $400^{\circ}\text{C}.$, the following experiment was carried out.

Decomposition under Reflux up to $400^{\circ}\text{C}.$

A Gray-King furnace was arranged in a vertical position and the retort tube (containing the Bitumen) clamped in such a way that any oil formed was refluxed back into the hot bitumen. The reflux condenser at the exit of the Gray-King tube was kept at $100^{\circ}\text{C}.$ and by this means any light hydrocarbons which were produced passed out and were collected in a receiver connected to the outlet of the condenser. This receiver was packed with "Dry Ice" to be quite sure of collecting any hydrocarbons from the C_3 fraction upwards. The temperature of the furnace was raised from $350^{\circ}\text{C}.$ to $400^{\circ}\text{C}.$ over a period of three hours, and on inspection of the chilled receiver, no light distillate could be found. After cooling, the furnace was tilted into an inclined position so that the crude oil condensate would not be returned to the retort tube. The temperature was raised to $300^{\circ}\text{C}.$, when 12.9% of cracked distillate was obtained.

It is evident from this experiment that gentle pyrolysis of Bitumen at temperatures up to $400^{\circ}\text{C}.$ will not produce hydrocarbons boiling below n-heptane (the initial boiling point of the distillate was $91^{\circ}\text{C}.$) although

DECOMPOSITION UNDER REFLEX UP TO
400°C.

Weight of Retort Tube	=	79.272 grms.
Weight of Retort Tube and Bitumen	=	92.294
Weight of Bitumen	=	13.022
Weight of Tube and Residue	=	90.138
Weight of Residue	=	10.863
Weight of Oil Receiver	=	53.300
Weight of Oil Receiver and Oil	=	54.995
Weight of Oil	=	1.695

Weight Balance.

Weight of Bitumen	=	13.022.
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Weight of Oil	1.695 grms.	13.0%
Weight of Residue	<u>10.863</u>	83.4%

Total	=	<u>12.558</u>
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Loss	=	<u>0.464</u>	3.6%
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DECOMPOSITION UNDER REFLEX UP TO 500°C.

Weight of Retort Tube	= 78.580 grms.
Weight of Retort Tube and Bitumen	= 95.510
Weight of Bitumen	= 16.930
Weight of Tube and Residue	= 83.870
Weight of Residue	= 5.290
Weight of Oil Receiver	= 53.311
Weight of Oil Receiver and Oil	= 63.950
Weight of Oil	= 10.639

Weight Balance.

Weight of Bitumen	= 16.930	
Weight of Oil	= 10.639	62.8%
Weight of Residue	= <u>5.290</u>	31.3%
Total	= <u>15.929</u>	
Gas and Loss	= <u>1.001</u>	5.9%

comparatively large quantities of middle oil were obtained. Another similar experiment was performed at 500°C., with no yield of light hydrocarbons, although the yield of oil was 81.7%. In this latter experiment the presence of ammonia was confirmed in the exit gas.

So far, all attempts to produce light hydrocarbons from bitumen have been without success. In contradiction to this, in the Gray-King Assay of raw torbanite, appreciable quantities of such hydrocarbons are formed and it is necessary to note where the conditions of pyrolysis of torbanite differ from the above experiments.

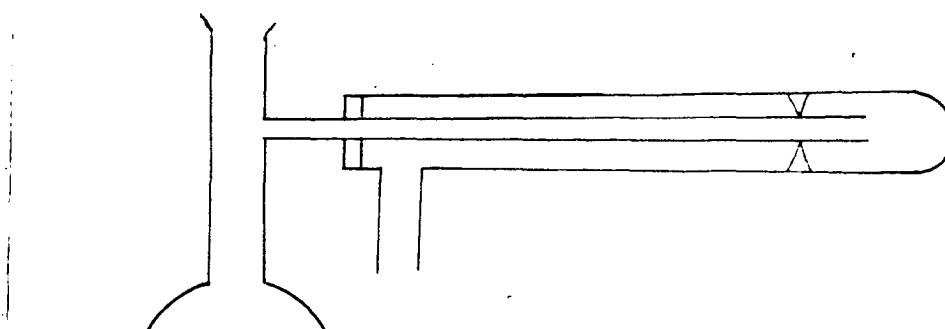
Using raw torbanite;

- I) The oil-producing substance is dispersed in an inorganic matrix with possible catalytic action.
- II) The oil vapours on formation have to pass through the mass of the shale particle which is at a higher temperature.
- III) The heated oil vapours are in motion, whereas it seems likely that under the present experiments a condition of equilibrium stratification may exist where the rate of vapour production may equal the rate of liquid reflux.
- IV) The bitumen stage is of very short duration and it may not have sufficient time to attain chemical equilibrium.

In order to reproduce to some extent the kinetic conditions of the oil vapour in the Gray-King pyrolysis and

to ensure that cracking occurs in the true vapour phase, an experiment was carried out, the details of which are as follows:-

The bitumen was placed in a distillation flask with thermometer. The side-arm of the distillation flask was sealed to a long piece of Pyrex tubing and this elongated side-arm was held coaxial with a Gray-King tube, by an asbestos plug (see figure below).



The outlet of the Gray-King tube was connected to two U-tubes in series. The first U-tube was maintained at cold water temperature and the second one was packed with "Dry Ice". The flask containing the bitumen was gradually heated with a gas burner and, as far as possible, the temperature of the Gray-King furnace was maintained about the same as the vapour temperature of the boiling bitumen. The maximum temperature reached was 500°C.

At the end of the run, both condensers were inspected and liquid was found in each.

Condenser 1 (at water temperature) contained 62.1% of oil and Condenser 2 (at -78°C.) contained 4.6% of light hydrocarbons. The Boilaway Temperature of the latter was +4°C.

THE VAPOUR PHASE CRACKING OF BITUMEN VAPOURS.

Weight of Flask	= 38.210 grms.
Weight of Flask and Bitumen	= 50.498
Weight of Bitumen	= 12.288
Weight of Flask and Residue	= 41.172
Weight of Residue	= 2.962
Weight of U-Tube 1	= 57.103
Weight of U-Tube 1 and Oil	= 64.728
Weight of Oil	= 7.625
Weight of U-Tube 2	= 55.735
Weight of U-Tube 2 and hydrocarbons	= 56.304
Weight of light hydrocarbons	= 0.569
Weight of G-K tube before experiment	= 92.108
Weight of G-K tube after experiment	= 92.448
Weight of Carbon	= 0.340

Weight Balance.

Weight of Bitumen	= 12.288
Weight of Oil	= 7.625 grms. 62.1%
Weight of Naphtha	= 0.569 4.6%
Weight of Residue	= 2.962 24.1%
Weight of Coke	= 0.340 2.8%
Gas and Loss	= 0.792 6.4%

It appears, then, that volatile hydrocarbons are produced only when the newly-formed oil is subjected to relatively high temperatures, and that Bitumen alone on gentle pyrolysis does not yield measurable quantities of light material. These findings are in accord with the free energy equations of the cracking of hydrocarbons and cracking kinetics.

Up to the present, no mention has been made of "Rubberoid", and the part it plays in the decomposition. "Rubberoid", as has been described earlier, occupies an intermediate position between the solid kerogen and the liquid Bitumen. The occurrence of "Rubberoid" was noticed during the investigation on the reaction velocity of the decomposition and, at the time, it was thought that "Rubberoid" was not a distinct entity but was composed of unreacted kerogen "stewed up" with polymerised bitumen. It was not until later, however, that it was realised that "Rubberoid" represented a distinct stage in the decomposition and that its properties were dissimilar from both the raw kerogen and the liquid bitumen. The presence of "Rubberoid" produces the pliable condition of heated torbanite noticed by many workers in this field.

It is interesting to note that no previous mention has been made, either here or overseas, of the occurrence of this intermediate substance, but this is understandable when one considers the amount of mineral matter present in

overseas shales. Many workers have noted the gradual softening of shale before decomposition but none has been fortunate enough to obtain either shale or torbanite of such richness that the reactions of the material as a whole may be considered as that of the pure organic material.

During the experiments on reaction velocities, it was observed that the residual material, after extraction of the soluble bitumen, was a soft black rubbery mass, which could be deformed by finger pressure, after which deformation it showed a strong tendency to revert to its original shape. This material (named "Rubberoid" in this work) represented a phase in the decomposing kerogen before the formation of bitumen, although some bitumen was always formed at the same time as the "Rubberoid".

During the decomposition of kerogen to "Rubberoid", a small amount of gas is given off, indicating that some chemical reaction is occurring. This gas contains relatively large amounts of hydrogen sulphide and olefins. Although no gas analyses are available on the decomposition Kerogen → "Rubberoid", the following figures give ^a gas analysis for the change Kerogen → Bitumen.

Table 35.

Gas Analyses of Various Stages.

	<u>A</u>	<u>B</u>	<u>C</u>
H ₂ S + CO ₂	9.1%	2.4%	3.1%
Olefins	10.8%	2.2%	7.9%

A Represents the gas given off in the change,

Kerogen \longrightarrow Bitumen.

B represents the gas given off towards the end
of oil production.

C represents a typical analysis of a Gray-King
assay.

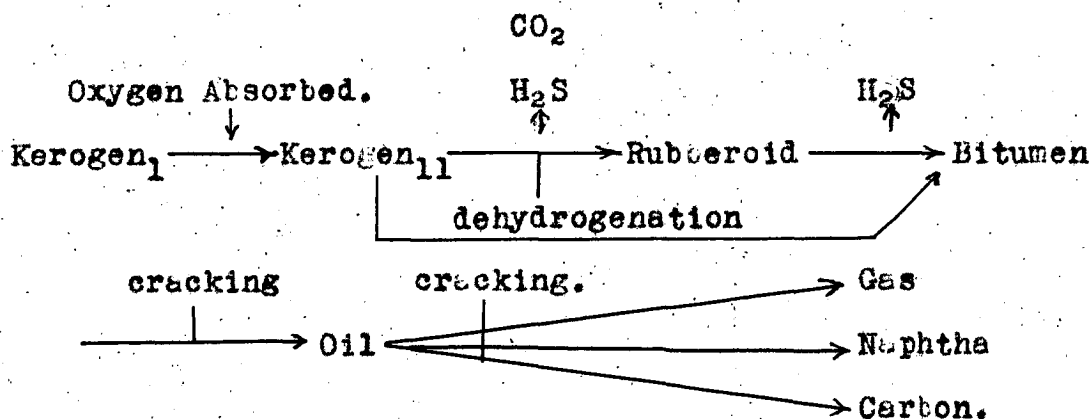
It is apparent that, in the early stages of the decomposition, dehydrogenation of the kerogen is occurring, and for this reason it is thought that sulphur takes an active part in the early reactions, and that sulphur atoms in the molecule may be combined in two ways. One type of sulphur atom is loosely held and gives rise to the hydrogen sulphide in the early stages of pyrolysis, and the other type occurs within the organic structure and breaks down to cyclic structures such as thiophenes.

In order to determine the general macroscopic properties of the "Rubberoid", a quantity of rich torbanite from Marangaroo (10b) was heated to incomplete decomposition and the resulting bitumen removed by extraction with 40° - 60° petroleum ether.

The residual "Rubberoid" was a dark, soft solid exhibiting the properties of semi-vulcanised rubber. Although it showed a certain amount of resilience to compression tests, it ruptured fairly easily under tension. When small cubical blocks were cut out by a razor blade and soaked in benzene,

"Rubberoid" exhibited "swelling" phenomena, characteristic of natural rubber, and certain other elastomers.

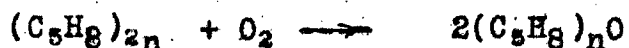
Having described the various stages which occur in the decomposition of kerogen to oil, and having indicated the order in which they occur, it is possible to show the decomposition in a diagrammatic form, which is as follows:-



There seems little doubt that the entire decomposition from the bitumen stage onwards is a cracking reaction, but the exact nature of the reactions preceding the formation of the bitumen, is still not clear. This change cannot be entirely one of depolymerisation, for some gas is evolved; this gas contains an appreciable amount of olefins. As unsaturates are easily formed in the first stages of cracking, this would indicate that the primary breakdown, in addition to those which follow, is one of cracking; furthermore, the presence of H_2S and H_2O will activate any catalytic action possessed by the metallic oxides in the inorganic matrix. If the structure of the kerogen is assumed to be essentially paraffinic in character, further evidence to support the

above hypothesis is provided by the presence of water vapour in the gas in the early stages of decomposition, the water being formed by the dehydrogenation of paraffins in the presence of air.

However, the initial softening of the material in the $\text{kerogen}_1 \rightarrow \text{Kerogen}_{11}$ reaction may be a partial depolymerisation, similar to that which is thought to take place in rubber. With rubber, a similar reaction occurs with gradual softening and absorption of oxygen.



The amount of combined oxygen is small but as it can be seen from the equation, the reaction will have a definite effect on physical properties.

If the decomposition of kerogen to bitumen were a true depolymerisation, the carbon/hydrogen ratio of the reactant and the product should remain unchanged; on the other hand, if the reaction were that of cracking, the carbon/hydrogen ratio of the product would be higher than that of the reactant. Referring back to Table 13 and the ultimate analysis of Bitumen on page 200, it can be seen that the data fulfil the second condition, being 7.06 in the case of kerogen, and 8.01 for bitumen.

A consideration of the above facts i.e. the evolution of hydrogen sulphide, carbon dioxide and water; the increase in C/H ratio and the physical changes occurring during the decomposition, leads to the conclusion that the break-down

Kerogen—→ Bitumen is not one of "depolymerisation" as postulated by Engler (21), but rather one of gentle cracking. This contention is supported by the known facts on the cracking of heavy oils, during which reaction, the heavy material does not decompose in one stage to form gasoline, but decomposes in a gradual manner by means of the formation of intermediate stages. These intermediate fractions further decompose with the formation of lighter oil and gasoline and the reaction would proceed in extremis with the production of hydrogen and free carbon only.

Investigations carried out overseas by Franks (22) and Luts (38) give further evidence that the reactions occurring during the thermal decomposition of kerogen are those of cracking. Franks, in his paper, says "The evidence from our work is all opposed to such a hypothesis, (i.e. Engler's depolymerisation theory) but indicates that the reaction which is identical with, or at least resembles a slow 'cracking'".

Luts, when referring to the decomposition, makes these remarks "What shall this phenomenon be called? Is it a depolymerisation? This conception is false."

The facts given in the preceding discussion must lead to the acceptance of the theory that the whole reaction from start to finish is one of thermal cracking. This being so, little information on the structure of kerogen would be gained by an analysis of the products of the decomposition,

and for this reason, no specific investigations were performed on the chemical constitution of the crude oil itself.

However, several general deductions may be made; The large amount of wax and the aromatic content of the crude oil indicate that the kerogen molecule must contain, in its structure, several long-chain paraffin radicles, and also aromatic rings. The aromatic compounds in the oil would not have been formed by ring closure from normal paraffins under normal temperatures, as no straight-chain paraffin (except $n\text{-C}_{16}\text{H}_{34}$) has been reported to yield aromatics in measurable quantities under normal cracking (20). On the other hand, the presence of polycyclic condensed benzene nuclei cannot be taken to indicate that these structures occur as such in the kerogen, for simple molecules such as benzene and toluene will yield diphenyl, stilbene, naphthalene and heavy solids, under temperature conditions commensurate with those of retorting.

The oil produced from the thermal decomposition of kerogen contains a diverse collection of hydrocarbons. All types are found, paraffins, mono-olefins, diolefins, naphthenes and aromatics. In addition to these hydrocarbons, sulphur, nitrogen and oxygen compounds are present.

The occurrence of paraffin waxes in the crude oil leaves no doubt that long chain paraffin structures are present, as such, in the kerogen molecule. Furthermore, as the number of carbon atoms in the wax may reach thirty, it

must be concluded that the kerogen molecule contains an equal or greater number of carbon atoms in straight chains. The aromatic hydrocarbons may arise from two sources;

(i) from aromatic ring structures in the kerogen.

(ii) formed by ring closure and dehydrogenation from other hydrocarbons (except n-paraffins).

A study of the optical properties of kerogen, leads to the conclusion that aromatic rings do exist and furthermore, it indicates that more than one ring exists in each molecule. As the pyrolysis of kerogen is a cracking reaction, the occurrence of naphthenes and olefins needs no explanation.

An interpretation of molecular structure from the products of decomposition has little value in this case because of the complexity of the original molecule. Apart from the complexity of the material itself, the many variables occurring during the decomposition must be considered. The rate of temperature rise, presence or absence of air, final temperature, and nature of retort, all have an effect on the oil produced.

Nevertheless, a general picture of the reactions which occur, and the main structure of kerogen, may be summed up as follows;

In the original kerogen, the molecule consists of many

units each containing one or more benzene nuclei possessing long side chains. These side chains are, in the main, saturated, but ethylene linkages are found in certain members. In addition to the long side chains, each benzene nucleus has a few short radicals.

As the kerogen is heated a slight oxidation takes place followed by the initial decomposition, causing loss of sulphur and oxygen corresponding to the disappearance of some cross linkages.

The result of these reactions is a general softening of the kerogen, accompanied by evolution of hydrogen sulphide and carbon dioxide.

As the reaction proceeds, cross linkages are progressively ruptured until a stage is reached where the macromolecule no longer exists. The three-dimensional structure has disappeared and most of the individual unit structures occur in the free state. To be sure, a few cross linkages still exist but they are not of sufficient number to give rigidity to the material as a whole.

The few remaining cross linkages disappear in the next stage and at the same time some side chains have received sufficient activation to break away from the parent ring.

The scission of the side chains may occur in several places, either individually, concurrently or consecutively. If the side chain is unsaturated it may decompose with

formation of methane and a diolefin, thus;



or if it is saturated it may form a paraffin or olefin,



or scission may occur at the centre of the chain. The deciding element depends largely on the electropositiveness (or negativeness) of the remainder of the molecule.

This stage would correspond to a semi-decomposed state in which small fragments of the original structure co-exist with long-chain paraffins from the side chains; olefins from the cracking of the paraffins, and cyclic structures from condensation, or ring closure, etc. This heterogeneous mixture constitutes the "Bitumen" discussed earlier.

From this stage onwards, no general plan is followed. Cracking would occur in the normal manner and those laws found to apply to the cracking of flow oil would be equally tenable from the Bitumen stage until the decomposition is complete; the final products being oil, gas and carbonaceous residue.

SOME FACTORS IN THE THERMAL DECOMPOSITION OF TORBANITE.

This section makes no attempt to be a discussion of the many factors affecting the oil yield during retorting. Only those factors which have a direct bearing on the previous discussion will be considered. Such variables as rate of temperature rise, particle size, effect of steam have been considered in detail elsewhere, and will be treated only in so far as they affect the present discussion.

Experimental

The experiments described in this section of the work were performed in a small stationary retort with a somewhat refined condensing apparatus. A description of the equipment follows.

The Heating Furnace was an electric tube furnace consisting of a two^{+1/2} inch diameter silica tube wound with nichrome wire, the winding being such as to give a maximum current of 3.0 amps. with no external resistance. The tube and windings were encased in a rectangular box, the dimensions of which were large enough to allow at least 3-1/2 inches of 85% magnesia lagging to be packed between the tube and the external casing. An ancillary resistance box allowed the current to be adjusted from 1.6 amps. to the maximum, in steps of about 0.2 amps.

The Retort was made from a short length of seamless boiler tubing, the external diameter of which was 2 inches and

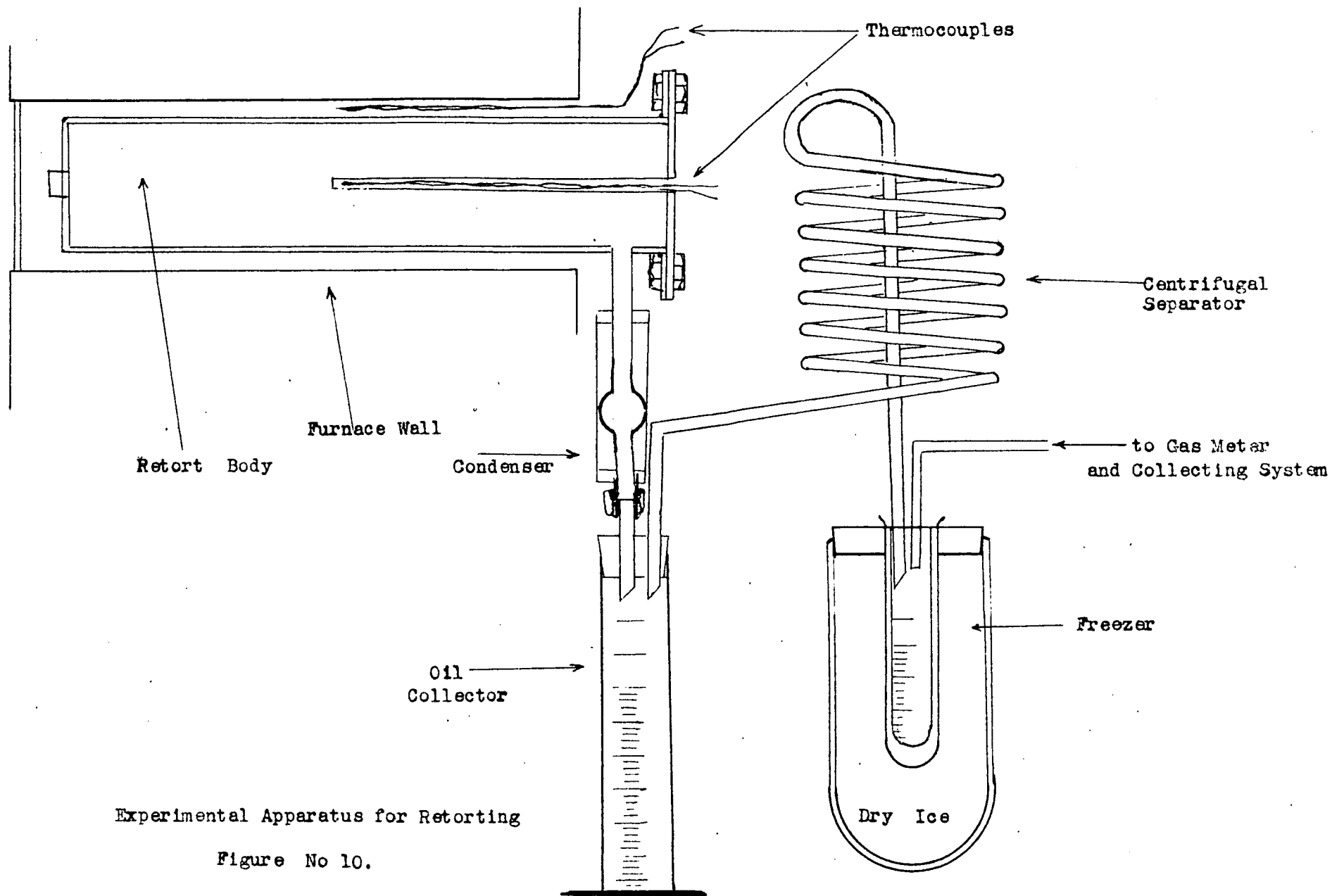
thickness $1/8$ inch. The steel tube was closed at one end except for a screwed plug, and at the other end it was flanged.

The sealing cap was a blank flange with six peripheral holes to allow $1/4$ inch bright steel bolts to hold the blank flange to the other flange. The blank flange contained a thermocouple-well so that the temperature at the centre of the retort could be measured. The oil escaped by a small $3/8$ inch pipe welded to the steel tube in a position close to the flanged end. In order to connect the exit tube to the condenser, this tube terminated in a $3/8$ inch hexagonal brass union.

The Condensing System may be divided into three portions;

- (i) the oil condenser.
- (ii) the centrifugal separator.
- (iii) the freezer.

The oil condenser was of the normal design and consisted of a bulbed central tube, 16 cms. long, surrounded by a water jacket. The condensed oil flowed down the central tube and collected in a graduated vessel (oil collector) attached at the remote end. This receiver was an ordinary 100 ml. graduate, the top of which had been cut off and the remaining edge ground and smoothed. The uncondensed vapours passed from the oil receiver into the centrifugal separator. This separator consisted of seven turns of 6 mm.



Experimental Apparatus for Retorting

Figure No 10.

Pyrex glass tubing wound to form a helix. The helix was 10 cms. in height and 8 cms. in diameter.

The three devices, oil condenser, oil collector and centrifugal separator, produced an efficient system for the removal of most of the oil from the gas. Any oil mist which escaped the oil collector, was removed by the centrifugal action of the separator.

After leaving the centrifugal separator the gas passed into the freezer. The freezer consisted of a 30 ml. cylindrical tube graduated from zero to 30 ml. in 0.2 ml. divisions. This tube - termed the butane receiver - fitted snugly into a test-tube, immersed in a vacuum flask containing "Dry Ice". This arrangement enabled a low temperature to be maintained for many hours and, in addition, no trouble was encountered in removing the butane receiver for other operations.

From the freezer the gas passed through a flow-meter to the gas holder. The flow meter was constructed on the orifice-meter pattern and was calibrated against a standardised wet gas-meter. The gas holder was portion of the standard Gray-King apparatus (18).

A diagram of the entire equipment is given in fig. 10.

All the retorting runs were performed on a carefully prepared sample of torbanite. The torbanite was crushed in a roll-jaw crusher and then screened in two stages. The first stage was through a 1/8 inch-mesh screen which removed

the "fines" and then through a second screen which removed any material larger than $3/8$ inch. The resulting sample consisted of particles between the sizes of $1/8$ inch and $3/8$ inch. The material was mixed repeatedly and finally placed in a bag. This sample constituted the "Bulk Sample", the properties of which are given in Table 56. Five retorting runs were carried out, the results of which are given on pages 231 to 234 and 236.

The results of previous investigations, and the results herein, are consistent with the hypothesis put forward in this work, namely that the decomposition of kerosen to oil is one of cracking. In the case of the New South Wales Torbanite, Guthrie (27) found that, with decreasing rates of retorting, the following effects were produced in the oil;

- (i) The specific gravity decreased.
- (ii) The carbon residue decreased.
- (iii) The setting point increased.
- (iv) The saturation of the "tops" increased.

Assuming a given boiling-range, points (i) to (iv) indicate an increasing paraffinicity of the oil, and this is what might be expected. Under gentle conditions of pyrolysis, there is a greater tendency for portions of the original straight-chain structures to exist, as such, in the oil than is the case in rapid retorting. Increased rates of retorting produce greater inter-particular (and intra-particular) gradients of temperature and

(continued on p. 235)

Table 56.Properties of the Bulk Sample.Proximate Analysis.

Moisture	0.17%
Volatile Matter	55.51%
Fixed Carbon	7.31%
Ash	<u>37.01%</u>
	<u>100.00</u>

Bulk Specific Gravity of Sample = 0.54

Mass Specific Gravity of Sample = 1.350

Gray-King Assay.

Torbanite Charge	= 20.80 grms.
Distillate Yield	= 9.79 grms.
Wt. of Water	0.18 grms.
Specific Gravity of Oil	= 0.859
Weight of Oil	= 9.61 grms.
Weight of Residue	= 9.94 grms.
Weight of Gas	= 1.07 grms. (by diff.)

Weight Balance of Operation.

Charge	100%	Residue	47.7%
		Oil	46.2%
		Water	0.9%
		Gas	5.2%

Run 1.

Shale Charge 180 grms.

Current 2.6 amps.

Time mins.	Temperature °C.		Distillate ml.		Manometer
	Outside	Inside.	Heavy	Light	Gas Flow ml/min.
0	26	28			
10	98	30			
20	169	41			
30	226	52			
40	281	70			
50	339	117			7
60	398	181	1		11
70	449	246	3	0.1	21
80	484	315	19	0.3	276
90	519	387	55	0.5	491
100	563	423	80	0.8	398
110	581	460	86	0.8	336
120	606	491	88	0.8	164
130	635	503	90	0.9	102
140	641	522	90.5	0.9	35
150	650	556	92	0.9	31
160	654	617	93	1.0	31

Weight of Shale = 180 grms.
 Weight of Residue = 81.0 grms.

Volume of Distillate = 93 ml.

Weight of Water = 1.8 grms.

Specific Gravity of Oil = 0.869

Weight of Oil = 79.1 grms.

Weight of 'Butane' = 0.7 grms.

Gas and Loss (by diff.) = 17.4 grms.

Weight Balance.

<u>Charge</u>	<u>Residue</u>	<u>Oil</u>	<u>Water</u>	<u>Gas.</u>
100%	45.0%	44.4%	1.0%	9.6%

Run 3.

Shale Charge

180 grms.

Current

1.2 - 1.5 amps.

Time Mins.	Temperature		Distillate	
	Centre	Outside	Heavy	Light
0	22	22		
25	27	74		
65	75	124		
85	116	191		
120	153	225		
180	227	281		
250	269	324	4	
278	276	343	18	
300	288	345	29	0.7
319	291	345	38	0.8
330	292	346	43	0.9
365	307	355	54	1.0
390	311	354	57	1.1
570	330	368	71	1.4
615	331	371	74	1.5
740	354	380	76	1.6
800	363	376	77	1.6

Weight of Shale

= 180 grms.

Weight of Residue

= 101.2 grms.

Volume of Distillate

= 77 ml.

Weight of Water

= 2.5 grms.

Specific Gravity of Oil

= 0.841

Weight of Oil

= 62.6 grms.

Weight of 'Butane'

= 1.1 grms.

Gas and Loss (by diff.)

= 12.6 grms.

Weight Balance.

<u>Charge</u>	<u>Residue</u>	<u>Oil</u>	<u>Water</u>	<u>Gas</u>
100%	56.2%	35.4%	1.4%	7.0%

Run 2.

Shale Charge 180 grms.

Current 2.2 amps.

Time Mins.	Temperature °C.		Distillate ml.		Manometer Gas Flow ml/min.
	Outside	Inside	Heavy	Light	
0	30	32			
20	181	40			
40	203	67			
60	237	144			
80	284	193			
100	330	242			2
120	394	297			3
140	427	353	1		16
160	459	390	6	0.3	37
180	482	420	14	0.5	73
220	541	471	68	0.9	85
240	564	509	79	1.0	65
260	598	542	84	1.0	44
280	603	578	87	1.2	30
300	621	605	89	1.3	22
320	635	621	90	1.4	18
340	641	625	90	1.4	15

Weight of Shale = 180 grms.

Weight of Residue = 89.6 grms.

Volume of Distillate = 90 mls.

Weight of Water = 2.5 grms.

Specific Gravity of Oil = 0.871

Weight of Oil = 76.2 grms.

Weight of 'Butane' = 1.0 grms.

Gas and Loss (by diff.) = 10.7 grms.

Weight Balance.

<u>Charge</u>	<u>Residue</u>	<u>Oil</u>	<u>Water</u>	<u>Gas</u>
100%	49.8%	42.8%	1.4%	6.0%

Run 4.

Catalytic Retorting with aluminium chloride.

Shale Charge 90 grms.

Weight of Anhyd. AlCl_3 9.5 grms.

Time Mins.	Temperature Outside.	Distillate.	
		Heavy	Light.
0	25		
30	205		
40	267	1	2
50	348	3	6
60	401	21	48 ml.
		Experiment stopped.	

During this run, much heavy red-coloured gas was produced. The torbanite charge swelled to a frothy mass, totally unlike that produced in the absence of catalyst. The heavy distillate consisted of a black tar on top of which floated 0.6 ml. of clear oil. The tar, on hydrolysis with hot water, produced a brown heavy oil. The two layers which were formed probably consisted of an upper layer of saturated hydrocarbons, and a lower one of an AlCl_3 -hydrocarbon complex. The residue from the experiment contained no free aluminium chloride. The light distillate was sweet-smelling and possessed a faint blue fluorescence.

The action of aluminium chloride on torbanite is so violent that little information may be obtained, however from the large amount of light hydrocarbons produced, it may be seen that the decomposition of torbanite is greatly affected by catalysts and, therefore, this fact opens a field for future enquiry.

consequently the "nascent" oil has to pass through a zone of relatively high temperature before escaping. In this passage, further cracking of the oil takes place, and still less of the original structure remains unchanged; further evidence of this contention being given in the section on the decomposition of bitumen.

Owing to the extreme complexity of the reacting substance and the high temperature at which these reactions take place, little information on the structure of kerogen may be deduced from the composition of the oil. However, a few important points may be made.

Point (1)

The general character of the oil does not alter very much during the process of gentle retorting, although the boiling-range of the oil does tend to increase progressively as the retorting temperature rises. This statement is not meant to apply to oil produced under abnormal conditions as in Run 3.

The relative constancy of the boiling-range of the oil is shown in Run 5, in which samples of oil were collected corresponding to different temperature intervals during the retorting process. The retort was placed in an inclined downward position so that any oil which was formed would tend to run out of the delivery tube and away from the hot zone.

Run 5.

Retort Centre Temp.	379	422	451	507	554
Retort Outside Temp.	450	475	500	550	600
Oil Yield	7	17	71	95	99
Distillation of Oil.					
I.B.P. °C.	82	87	85	92	91
10%	127	145	119	108	96
20	170	194	155	116	126
30	211	234	206	153	145
40	242	260	224	240	192
50	275	273	247	317	242
60	298	287	312	362	314
70	313	302	356	380	346
80	330	326	385	384	400
90	348	361	411	398	418

From the results of Run 5 it will be noticed that the amount of 'light ends' in the later fractions is actually greater than those in the early fractions; this no doubt being caused by the secondary cracking of the crude oil to lighter material. This secondary cracking of the crude oil is also shown up in the gradual increase in the amount of 'heavy ends', in other words, as the retorting temperature increases, there is a progressive tendency for the distillation characteristics of the oil to change from a smooth curve to a sigmoid curve, the latter denoting a preponderance of 'light and heavy ends' with less middle fraction.

In vertical retorts especially, and in all retorts in general, it is found on many occasions that the oil does increase in boiling-range as the decomposition progresses, but this fact should not be taken as a contradiction to the above; the explanation of which is as follows:-

In most retorts, there is a noticeable temperature difference between the hot central mass and the cooler extremities, and during the retorting process the oil-vapours partially condense as they leave the hot centre, and meet the 'cold ends' of the retort. Under these conditions, the condensed ^{oil} vaporises only when the retort as a whole reaches a temperature corresponding to the final boiling point of the oil. For this reason it often happens that oil formed during the retorting process has less 'heavy ends' than oil produced during the last stages of decomposition.

In a horizontal laboratory retort, as used for routine testing, the temperature gradient along the central axis of the cylinder was as follows:-

Table 57.

Temperature Gradient along Laboratory Retort.

<u>Distance along Central Axis.</u>	<u>Temperature</u>
centre	510 °C.
1" off centre	499
2" " "	459
3" " "	396
4" " " (exit cap)	301

Kurth (34) has shown that, as the boiling-point rises, successive fractions of oil contain gradually increasing amounts of aromatic and olefinic hydrocarbons, a more-or-less constant amount of naphthenes and a diminishing amount of paraffins. These facts are in accordance with the present hypothesis in which it is asserted that the

paraffins, being thermally unstable at the retorting temperatures, decompose to produce paraffins and olefins and, as monocyclic aromatics are the most stable hydrocarbons, under these conditions, the higherboiling fractions will contain appreciable amounts of this hydrocarbon type. It does not seem unlikely that some aromatics are formed in situ during the distillation test, as the temperature reached (350°C.) is quite sufficient to cause ring closure of certain unsaturated hydrocarbons.

Point 2.

The nature of the waxes present in the crude oil indicates long-chain structures in the original kerogen. As mentioned earlier, paraffin waxes cannot be produced by the thermal decomposition of any hydrocarbon other than higher waxes. From this statement it can be seen that some chains in the original material contain more than twenty carbon atoms. By repeated "sweating" of a sample of wax produced from the crude oil of torbanite, the melting-point of the wax was raised from 37°C. to 56°C.; as docosane ($C_{22}H_{46}$) has a melting point of 44°C. (74), the wax must have arisen from material possessing at least twenty-two straight-chain carbon atoms.

McKinney (43) has proved the presence of saturated hydrocarbons up to C_{26} in New Brunswick oil-shale.

Point 3.

Distillation characteristics of oil produced from

different torbanites under similar conditions are remarkably uniform and no information on source of oil may be deduced from distillation analyses.

Representative samples of torbanite from Barigan, Marangaroo, Glen Davis, Wollar, Coolaway and of the true oil shale at Mount Kembla, were retorted under controlled conditions (similar to Run 2), following which the oils were distilled under standard A.S.T.M. conditions. The results of these distillations are given in Table 58, from which it can be seen that there is no distinguishing feature between them. There is one exception to this uniformity, which is the specific gravity of the oil from Mt. Kembla Shale; although the distillation characteristics of this oil are similar to the others shown, the low specific gravity indicates a relatively small amount of closed ring structures, and confirms earlier statements that the oil-shale from Mt. Kembla must be regarded as distinct from the Kemilaroi torbanites.

Table 58.

Distillation Analyses of Various Oils.

Distillation Analysis	Source of Oil					
	Barigan	Marangaroo	Glen Davis	Wollar	Coolaway	Mt. Kembla
I.B.P.	83	78	80	85	81	80
5%	104	115	124	117	137	112
10%	138	158	138	151	181	139
20%	185	216	193	181	206	193
30%	233	246	235	242	234	250
40%	273	307	281	270	258	288
50%	320	337	305	310	306	325
60%	340	358	334	337	341	346
70%	353	360	360	358	354	356
80%	376	375	381	370	371	379
90%	382	400	397	388	387	395

	Barigan	Maran- garoo	Glen Davis	Wollar	Coolaway	Mt. Kembla
Specific Gravity $\frac{20}{4}$	0.873	0.876	0.871	0.875	0.872	0.842.

Point 4.Gas.

The analysis of the gas produced during the progressive stages of decomposition of torbanite gives important information on the mode of combination of some of the non-hydrocarbon atoms.

It has been pointed out earlier in this work that the three elements, oxygen, sulphur and nitrogen, are minor but important constituents of kerogen. Compounds of all three elements occur in the gas as well as in the oil. In the oil, nitrogen and sulphur occur in acyclic and cyclic organic structures, while oxygen appears only in the form of phenols, and naphthenic acids; in the gas they occur substantially as inorganic compounds.

If the gas evolved during the various stages of the decomposition is analysed for hydrogen sulphide and carbon dioxide it is seen that the concentration of these constituents exhibits regular variation, irrespective of the source of the kerogen. The figures which follow are taken from three sources (Guthrie (27), Neppe (47) and the present work).

Table 59.Analysis for H₂S and CO₂ in gases during retorting.

	<u>Hydrogen Sulphide %</u>	<u>Carbon Dioxide %</u>
<u>Guthrie</u> * I	17.0	17.0
II	33.5	7.5
III	34.0	5.5
IV	32.0	4.5
V	25.0	4.5
VI	1.0	4.0
<u>Neppe.</u>		
200 - 350°C.	5.0	15.1
350 - 400°C.	4.3	5.7
400 - 450°C.	3.5	8.6
450 - 525°C.	2.1	6.5
525 - 600°C.	0.4	1.8
600°C.	0.5	4.3
<u>Cane.</u>		
200 - 325°C.	6.8	2.2
325 - 375°C.	4.6	2.3
375 - 450°C.	3.4	2.4
450 - 500°C.	1.7	1.1
500 - 525°C.	0.8	1.0
525 -	0.6	1.4

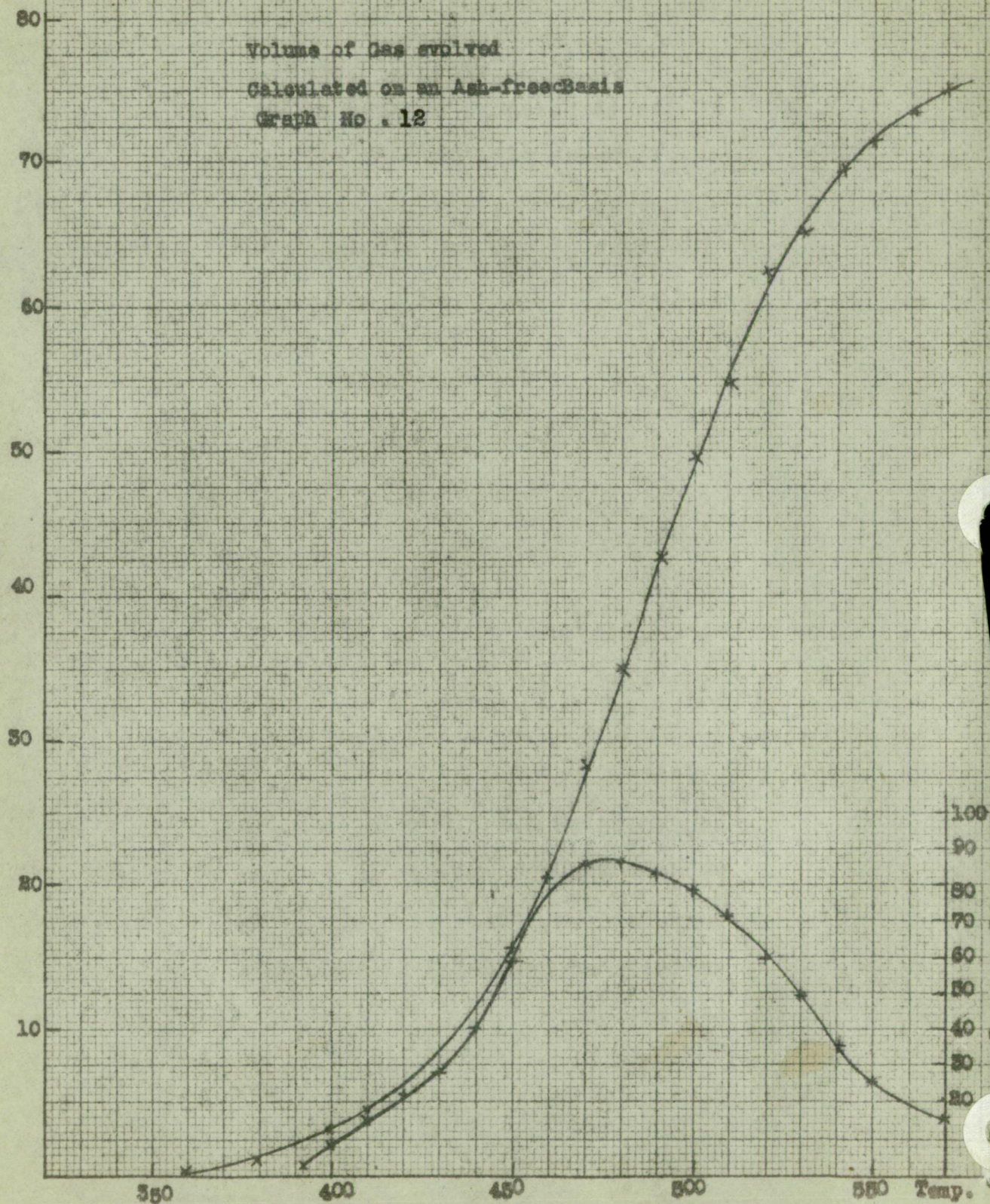
* No temperature mentioned

In the three examples quoted, the concentration of both gases decreases as the temperature rises, from which it may be deduced that the sulphur and oxygen atoms giving rise to these gases are in weak combination, and ⁱⁿ this way are dissimilar from those producing phenols and thiophenes.

The composition of gas produced appears to have no relationship to the source of the torbanite, but depends largely on the retorting procedure. However, the following general relationships are substantially true;

Total Volume of Gas. ml./g_m of Kerogen

Volume of Gas evolved
Calculated on an Ash-free Basis
Graph No. 12



- (1) The total volume of gas increases as the decomposition proceeds to completion, the rate of evolution of gas rises to a maximum and then decreases - see graph 12. The total volume increases greatly if the temperature exceeds 600°C.; for example, a sample which yielded 3623 ml. of gas per 100 grm. charge at 600°C. end-temperature, produced a further 2958 ml. of gas between 600°C. and 900°C. The weight balance of these operations is shown in Table 60 below.

Table 60.

Gas Produced During Decomposition (Gray-King Assay)

End temperature	yields given in %.	
	600°C.	900°C.
Residue	79.94	78.86
Distillate	15.49	15.53
Gas - grms. %	4.57	5.61
Gas - vol. ml.	3623	6581
S.G. gas (air = 1)	0.98	0.66

- (11) The specific gravity of the gas evolved at any temperature decreases sharply at retorting temperatures in excess of 500°C. This is caused by large amounts of hydrogen and methane in the gas produced at higher temperatures. The hydrogen may arise from the decomposition of condensed benzene nuclei formed by polymerisation.

Table 61.Specific Gravity of Gas.

<u>End temperature of Assay</u>	<u>Specific Gravity of Gas (Air = 1)</u>
550°C.	0.977
600	0.828
850	0.697

The specific gravities were measured by a Burrell diffusion apparatus which is a U.S. Bureau of Mines modification of the Schilling apparatus.

- (iii) The amount of gas calculated on an ash-free basis increases with the amount of ash in the torbanite; this probably being caused in the following manner. Large amounts of mineral matter necessitate high temperature gradients across the retort, also large temperature gradients across any one particle of torbanite. In rich material which has nearly completed its decomposition, very little matter remains in the retort and consequently the gas does not have to travel an appreciable intraparticular distance before it is removed from the zone of high temperatures. On the other hand, the gas produced from the interior of a particle of lean torbanite has an appreciable thickness of residue to pass through before being liberated, and this path is at a higher temperature than that at which the gas was formed. Ten consecutive analyses were

taken at random from the 1941 report of the New South Wales Department of Mines and the results arranged in logical sequence to illustrate the above facts.

Table 62.

Amounts of Gas Produced.

Gas figures calculated on an ash-free Basis.

Sample No. 1941/	Ash + Moisture %	Wt. of Gas % w/w	Vol. of Gas Litres per 100 grm.	Specific Gravity of Gas (Air = 1)
2589	14.7	5.8	5.2	0.88
2590	20.5	8.6	6.7	0.99
2588	22.0	8.0	6.4	0.96
2592	22.9	7.6	5.9	1.00
2587	26.3	8.2	6.5	0.97
2591	26.8	9.6	8.8	0.85
2586	39.8	7.8	6.1	0.99
2583	40.4	9.0	10.4	0.67
2584	68.4	9.3	7.9	0.91
2585	85.7	16.2	12.3	1.02

Table 63.

Typical Gas Analysis.

(Gray-King Assay)

	I	II	III
Acid Gases	4.5	4.0	3.6
Carbon Monoxide	6.3	10.7	6.6
Hydrogen	11.0	13.8	10.3
Methane	28.5	32.9	33.1
Ethane and Higher Paraffins	32.4	26.7	24.2
Ethene	3.9	3.5	5.5
Higher Olefins	9.2	6.3	12.0
Air by difference	4.2	2.1	4.7
Oil Yield of Shale, gals./ton	83	97	73

(1V) The concentration of ammonia in the gas is not measurable in the initial stages of decomposition but rises sharply as the temperature reaches 550°C., and then

diminishes at temperatures in excess of 700°C. The overall amount of ammonia varies between 0.01 to 0.1 grams % of torbanite and, in general, larger yields (on ash-free basis) are to be expected from leaner torbanite; and as mentioned under (iii) this is caused indirectly by the large amounts of ash.

Table 64.

Amount of Ammonia in Gas.

in grms. gas per 100 grms. Torbanite.

Temperature °C.	-500	500-600	600-800	800-900	900 -
Ammonia %	0.03	0.08	0.07	0.05	0.02

CONCLUSIONS.

The results contained in this thesis represent an investigation into the composition and reactions of a substance on which research has hitherto been extremely limited.

The important features including chemical and physical properties of the New South Wales torbanite have been described in detail. In addition the decomposition reactions of torbanite have received extensive consideration.

From a study of the properties and reactions of torbanite, a theory of its origin and formation has been put forward, and it has been shown that this theory is consistent with the observed facts.

Finally, it is hoped that the information contained in this thesis will suggest further lines of investigation to other research workers, and that the application of results contained herein will prove of interest to investigators in this field, and will prove of benefit to the oil shale industry as a whole.

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STUDIES IN TASMANITE SHALE OIL

By

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Studies in Tasmanite Shale Oil

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INTRODUCTION

Although the chemical composition of petroleum has received much attention in recent years, there is a surprising lack of information from the systematic study of any one shale oil, with perhaps the exception of the work of Kogerman (1931) in Estonia, Hellsing (1921) in Sweden, and Horie (1935) in Japan, together with the various articles which have been published on the Scottish shales. However, practically no work has been published on the chemistry of Tasmanite oil and very little more on any Australian mineral oil.

The oil-producing substance of Tasmanite, seen under the microscope, consists of roundish discs that can be just discerned by the naked eye, although, as Singh (1932) has pointed out, during fossilization these spore cases have been distorted and ruptured. The general consensus of opinion is that they are innumerable sporangia which are allied to Lycopodaceous macrospores. This spore case material is the true kerogen of Tasmanite, and, in common with all shales, its pyrolysis takes place in two stages. A primary decomposition occurs, causing the kerogen to change into a gummy semi-solid bitumen of highly unsaturated nature; this bitumen is unstable at the temperature of the retort, and immediately decomposes into compounds of greater stability and saturation.

The oil taken for this research was produced by a gentle and approximate isothermal distillation of the shale, the temperature never rising above 400°C. There is little or no hydrogen sulphide produced during this pyrolysis, whereas in commercial retorting large quantities of this gas are produced. Assuming that the production of hydrogen sulphide is the result of the secondary decomposition mentioned above, the type of oil chosen for this research should give valuable information on the chemical structure of Tasmanite kerogen.

Research on shale oil presents a more difficult problem than might at first be expected; this is caused by the relatively high percentages of sulphur and nitrogen making the preparation of pure hydrocarbon mixtures very difficult indeed. Another contributing factor is the high olefine content of the oil, which causes the formation of large quantities of tarry matter when the oil is treated with sulphuric acid, in a manner which is applicable to flow oils containing a much smaller amount of this hydrocarbon type.

The crude oil possessed the following properties:—

Specific Gravity @ 15°C.	=	0.8540
Refractive Index @ 15°C.	=	1.4684
Water	=	0.34%
Tar Acids	=	4.5%
Tar Bases	=	3.2%
Sulphur	=	2.22%
Nitrogen	=	0.34%
Mercaptan Sulphur	=	0.30%
Diolefines	=	5.7%
Olefines + Aromatics	=	56.1%
Free Sulphur		not present
Hydrogen Sulphide		not present
Acetylenes		present, but not determined
Organic Peroxides		present, but not determined

The above values of the specific gravity and the refractive index; and all proceeding ones in this paper were determined in the following manner:—

The Specific Gravity was measured by means of the Westphal balance standardized against distilled water. If any small correction was thought necessary, the amount of the correction was obtained from the data published by Beale (1937).

The Refractive Index was found using an Abbé refractometer, and the temperature corrections were based on the Eykman equation and the results of Kurtz and Ward (1936). Except where the temperature is given, both of these constants have been corrected to 20°C. All volumes are volume per cent, and all temperatures are given in degrees Centigrade and are not corrected for the emergent stem.

Distillation

The oil was fractionated in an iron drum of five gallons capacity, with an upright fractionating column at the top. This column was lagged with asbestos tape, between two layers of which was wound a helix of nichrome resistance wire, to a point 10 cm. from the top and to 23 cm. from the bottom, and by this means the column was warmed in the later stages, in order to produce a more even distillation. Inside the column, as a packing agent, were hung six one-yard lengths of brass chain. Towards the end of the distillation it was found impossible to get over the last fractions on account of the heat losses at the sides of the drum, and for this reason the last litre or so were distilled in a small apparatus of the normal laboratory type. Seventeen litres of the oil were distilled, with the results shown in the first four columns of Table I. The colour of the fractions varied progressively from colourless, in the first three fractions, through pale and dark yellow to nearly black in the last fractions.

Washing of the Fractions to Determine the Tar Acids and Tar Bases

100 ml. of each fraction were taken and poured into a stoppered separatory funnel, and an equal volume of 10 per cent aqueous sodium hydroxide added, then strongly agitated and the two layers allowed to separate out, the bottom layer run off, and the procedure repeated until the volume of the residual oil remained constant after two consecutive washings. The decrease in volume of the oil was taken as the percentage of *tar acids*. The above treatment was repeated substituting 10 per cent sulphuric acid for the caustic solution, and in this manner the amount of *tar bases* was determined. This treatment was

followed by a light sodium carbonate treat in order to remove traces of acid, then by a water wash, and finally the fractions were dehydrated over calcium chloride. The results of these treatments are shown in the Table I.

The Isolation of m-Cresol in the Tar Acids

The caustic washings from seven litres of the oil were united and the crude phenols liberated by dilute hydrochloric acid. They were redissolved in 4N caustic soda and the phenols—free from naphthenic acids—liberated by means of carbon dioxide. The reddish oily liquid was fractionated using a Young and Thomas column.

<i>Fraction No.</i>	<i>Boiling Range.</i>	<i>Density.</i>	<i>Refractive Index.</i>
1	183-204	0.9811	1.5346
2	204-207	1.0119	1.5330
3	207-217	1.0138	1.5321
4	217-226	1.0216	1.5287
5	226-233	1.0235	1.5253
6	Residues.		

The first and second fractions were united and distilled three times and divided into the following cuts:—

<i>Cut No.</i>	<i>Boiling Range.</i>	<i>Density.</i>	<i>Refractive Index.</i>
I.	200-203	1.021	1.5201
II.	203-208	1.018	1.5220
III.	208-214	1.011	1.5284

All three fractions were water-white when freshly distilled, but developed a reddish tinge after a few days. They possessed the characteristic cresol odour, and were practically sulphur free (all thiocresols possess a boiling point lower than 200°C).

Isolation of m-Cresol from Cut I

This fraction was treated with mercuric chloride in order to remove traces of sulphur compounds, washed with water, and purified by ether extraction. The purified extract was again distilled, when the major portion distilled over at $204^{\circ} \pm 0.4$. This was put aside and its characteristics found; density = 1.027 and refractive index = 1.5527, and on distillation with zinc dust it yielded toluene.

Schotten Baumann reaction with benzoyl chloride produced a benzoate of melting point 53.1° ; this corresponds fairly closely with m-tolyl benzoate of m.p. = 54° (Behal & Choay, 1894), and gave no depression of melting point when mixed with the latter substance. Another portion was nitrated according to the method of Rashig (1900) and the trinitro derivative isolated; this was light yellow in colour and melted at 104.7° ; the melting point of 2:4:6-trinitro-m-cresol = 106° .

According to Darzens (1931), anhydrous sodium acetate forms with m-cresol a complex $5\text{CH}_3\text{COONa} \cdot 2\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, which, on decomposition with water, yields m-cresol in a high degree of purity. This reaction, so the author maintains, is specific to m-cresol. A similar procedure was applied to the purified m-cresol from Tasmanite, with positive results. The m-cresol isolated had a melting point of 10.5° and refractive index of 1.5343 at 20°C , agreeing very closely with the data published by Darzens. All attempts to detect the ortho- and para-isomers were unsuccessful.

THE OLEFINE CONTENT

The determination of the correct olefine content is a matter of great difficulty in an oil such as this. Owing to the colour of the middle and last fractions, methods such as that of Mulliken and Wakeman (1935), involving the use of bromine, could not be used, as even the middle fractions had sufficient yellow colour to mask completely the very similar colour of the bromine. Moreover Thomas, Bloch, and Hoestra (1938) suggest that bromine absorption does not give correct values for the unsaturation when diolefines are present, which is undoubtedly the case in this oil. The use of the Francis bromide-bromate solution (Francis, 1926) was tried in the lower fractions without concordant results, probably due to the presence of cyclic olefines, which, according to Cortese (1929) give anomalous results.

After trying several reagents it was decided to employ sulphuric acid without the addition of boric acid as suggested by Kattwinkle (1927), as this has been shown incorrect by Tropsch and others (1929). It was fully realized that this method possessed many inherent disadvantages, such as the formation of polymerization products, attack on other substances, also the constitution of the saturated hydrocarbons is not necessarily the same before and after the sulphuric acid treatment, as new paraffins and naphthenes may be formed under the influence of the acid (Brochet, 1893).

OPTIMUM ACID STRENGTH FOR OLEFINE DETERMINATION

In order to gain some idea of the action of different strengths of sulphuric acid on the oil, a representative fraction was treated with gradually increasing strength sulphuric acid, in the manner suggested by Fisher and Eisner (1937). The results of this are shown below:

<i>Acid Strength.</i>	<i>Residual Volume.</i>	<i>Refractive Index.</i>
%	ml.	
....	100	1.4812
70	93.0	1.4778
75	88.0	1.4785
80	82.5	1.4796
82.5	80.5	1.4800
85	76.6	1.4820
88	60.5	1.4795
90	58.0	1.4765
96	51.0	1.4583
100	44.5	1.4364
105	39.5	1.4385

From these figures it can be seen that there is incipient attack on the aromatics when the acid strength has reached 88 per cent and that complete removal of aromatics and the commencement of attack on the paraffin-naphthene mixture starts with the 100 per cent acid.

50 ml. of the acid and base-free oil were placed in a stoppered separatory funnel and treated with an equal volume of 85 per cent sulphuric acid for ten minutes with external cooling, the acid layer separated off, and the treatment continued until the volume of the residual oil was constant. The results are given in Table I.

The residual oils were water-white, had practically no odour, and did not decolourize a weak solution of potassium permanganate.

The presence of Diolefines

The presence of appreciable amounts of diolefines in the oil was indicated by the intense yellow colour in some fractions. A certain fraction, in which the presence of diolefines was strongly suspected, was placed in a flask with 20 per cent of its weight of maleic anhydride and kept at a temperature of 100°C. for four hours under reflux. At the end of this period the residual oil was decanted off and the crystals washed free from oil; these crystals were soluble in alcohol and melted at 145°. To prove that ring formation had actually taken place, 1.5 gm. of the maleic anhydride compound was heated with 2 gm. of resorcinol and 1 gm. of zinc chloride for several hours. The product of this reaction was an intense red solid, soluble in alcohol, and had a characteristic colour change from acid to alkaline solution. The formation of this coloured substance (to be assumed of the phthalein type) could only arise from a cyclic structure, necessitating ring closure between the maleic anhydride and the diolefine with the formation of an acid similar to terephthalic acid and the subsequent formation of the anhydride.

The Presence of Terpene-like Olefines

A series of investigations were carried out in order to determine whether terpenes or substances allied to them were present in the oil. It is not intended to give a detailed description of the work done in this direction, but to state briefly that no conclusive evidence for their presence was obtained, although certain lines of research produced promising results, notably halogenation, followed by treatment with mercuric acetate.

THE SULPHUR COMPOUNDS

Sulphur is always present in shale, and, in general, a similarity exists between the sulphur compounds in shale oil and those in petroleum, but it is found that aromatic compounds predominate in the oil from shale in contrast to the usual aliphatic nature of the sulphur compounds in petroleum.

An examination of the more important sulphur compounds occurring in shale oil will serve to show that they are essentially thiophenic in nature and for this reason investigations on the sulphur bodies in shale oil are usually more difficult than the corresponding work on petroleum. This is more easily realized when the unsaturated nature of the former is taken into account.

On an allied oil Morgan and Soule (1923) write, 'There is no concentration of sulphuric acid capable of removing such sulphur compounds without attacking the unsaturates which predominate in the neutral oil. These unsaturated compounds, moreover, interfere with the usual qualitative thiophene identifications, by reacting with the sulphuric acid of the indophenin test and with the nitric acid of the thalline test to give reddish brown shades which mask the colour reactions, even in the presence of added thiophene.'

The presence of sulphur compounds in an oil which is to be used for power purposes has been one of the great disadvantages against the employment of shale oil in this connexion, for not only does the sulphuric acid formed during its combustion have a corrosive effect on the cylinders of the engine, but recently Kruser and Schade (1933) have shown that such compounds can act as accelerators in gum formation.

Challenger (1926) and Schleiber (1915, 1916) have performed important investigations into the nature of the sulphur compounds occurring in shale oil; both of the above investigators have shown that these bodies are mainly derivatives of thiophene, and have succeeded in isolating thiophene itself and certain of the lower alkyl homologues.

EXPERIMENTAL

Mercaptans

Mercaptan sulphur was estimated by a modification of the method proposed by Bond (1933). The results are given in the first table.

The Thiophenes

Five litres of crude Tasmanite gasoline were given a light acid and alkali wash and then distilled with the following results:—

<i>Fraction.</i>	<i>Temperature Range.</i>	<i>Volume mls.</i>	<i>Density @ 18°.</i>	<i>Refractive Index.</i>	<i>Sulphur % by Wt.</i>
1	-50	9.6	0.6934	1.3834	0.20
2	50-70	87	0.7037	1.3972	0.53
3	70-90	457	0.7484	1.4088	1.18
4	90-110	491	0.7641	1.4207	1.51
5	110-130	538	0.7884	1.4364	1.97
6	130-150	593	0.7928	1.4389	2.31
7	150-160	163	0.8049	1.4469	3.06
8	160-170	161	0.8112	1.4496	3.58
9	170-180	115	0.8225	1.4558	3.24
10	180-190	91	0.8377	1.4590	3.22
11	190-200	58	0.8400	1.4654	3.02
12	Residues.				

Fractions 3 and 4 were united and subjected to more exact fractionation, thus:—

<i>Fraction.</i>	<i>Temperature Range.</i>	<i>Density.</i>	<i>Refractive Index.</i>	<i>Sulphur % by Wt.</i>
3a	70-75	0.7179	1.4003	1.02
3b	75-80	0.7295	1.4073	1.18
3c	80-85	0.7583	1.4232	1.48
3d	85-90	0.7667	1.4180	1.54
4a	90-95	0.7548	1.4205	1.48
4b	95-100	0.7585	1.4300	1.49

The Presence of Thiophene in Fractions 3c + 3d

A representative portion of these two fractions was again distilled and cut at 2° intervals. The 83°-85° cut was treated with mercuric chloride in the following manner:—Alcohol was added to the fraction until the solution contained 80 per cent alcohol, and to it was added twice the amount of mercuric chloride required to form the mercurichloride (assuming that all the sulphur was contained in the thiophene), and five times the quantity of sodium acetate necessary to combine with the liberated hydrochloric acid. It was allowed to stand for two days with frequent shaking, and at the end of this period the precipitate was filtered off. A portion of this precipitate after purification gave, on analysis:—

Chloride	11.8% found; 11.1 calculated
Sulphur	9.7% found; 10.0 calculated

The melting point of the compound was rather indefinite near 179°, and at 183° it commenced to blacken. The melting point of thiophene mercurichloride is reported by Steinkopf to be 183°. Another portion of the precipitate on distillation with 6N hydrochloric acid decomposed to produce a liquid which reacted positively to the usual thiophene colorimetric tests.

The Methyl-Thiophenes

Fractions 4b and 5 were united and distilled three times.

<i>Fraction No.</i>	<i>Temperature Range.</i>	<i>Density.</i>	<i>Refractive Index.</i>	<i>Sulphur % by Wt.</i>
MT (i)	105-109	0.7642	1.4246	2.43
MT (ii)	109-117	0.7759	1.4345	2.98
MT (iii)	117-126	0.7808	1.4348	2.27

Lot MT(ii) was fractionated twice, and the final temperature limits taken at 111° to 115°. The volume of this fraction was 67 ml., and it contained 2.99 per cent sulphur. 60 ml. of this were dissolved in a litre and a half of alcohol and agitated with one litre of aqueous sodium acetate (33 per cent) and four litres of saturated aqueous mercuric acetate. After two and a half hours a dirty yellow precipitate formed; this was removed, and further precipitation allowed to take place. At the end of one day the combined precipitates were extracted with boiling alcohol and the solute crystallized and purified. The crystals melted between 202° and 204°. Steinkopf (1914) states that the melting point of 2-methylthiophene-5-mercurichloride is 204° with previous sintering, while the corresponding figure for the 3-methyl isomer is quoted at 138°. The methylthiophene-mercurichloride was decomposed with hydrochloric acid as before, and a portion of the liberated methylthiophene converted into its tribromo derivative. On recrystallization a sharp melting point was obtained at 85.6°. The melting point of tribromomethylthiophene is recorded in the literature at temperatures varying between 87° and 94° but most reliable sources place it at 86°. The melting point of the other isomer is 35°, while Gatterman (1885) states that a mixture of the two isomers cannot be separated by crystallization and melts at 74°. In order to complete the identification a small portion of the purified compound was oxidized to the corresponding acid with potassium permanganate. The melting point of this acid (126°) clearly corresponded to 2-thiophenecarboxylic acid.

Examination of Fraction 6 for Dimethylthiophenes

Fraction 6 was distilled several times and finally cut into two lots:—

6 (a) 130°-135° Density, 0.7854; Refractive Index, 1.4390.

6 (b) 135°-143° Density, 0.8012; Refractive Index, 1.4468.

No thiophene derivatives could be found in the first lot. The other lot, 6(b), gave very peculiar results. 60 ml. were treated with mercuric acetate as before, and, within a half hour, a large amount of white granular precipitate was formed. The mixture was allowed to stand for thirty hours with frequent shaking, after which the precipitated mercury compounds were filtered off. An examination of the filtrate showed that the whole of the fraction had been converted into the mercury compound. The precipitate was washed with petroleum ether, after

which it was distilled with 6N hydrochloric acid, whereupon 57 ml. of a sweet aromatic oil were recovered. The oil burnt with a very smoky flame, and possessed the following properties:—

Density	0.8107
Refractive Index	1.4471
Sulphur	3.0 per cent

It reacted negatively to the usual thiophene tests. On distillation the whole of the distillate came over between 136° and 140°, which immediately precludes other sulphur containing substances, such as thioethers, thiols, thiophanes, &c., none of which have been reported to boil within these limits. In the case of 2:3-dimethylthiophene-mercurichloride, there is a direct covalent link between the mercury and carbon atoms, in contrast to the addition compounds formed when mercury salts act on other sulphur compounds, such as mercaptans. This latter type is split up on treatment with caustic alkalis with the formation of the oxide of the metal. It was proved in the present case that the compound under consideration was essentially aromatic in nature. However, at this juncture it seems inadvisable to assume that dimethylthiophenes are absent, nevertheless it appears that another type of sulphur compound is present in such large quantities that the usual methods used in the isolation of thiophene homologues are not applicable. It is hoped to continue this phase of the research in the future.

These investigations were carried out in the Department of Chemistry in the University of Tasmania during the tenure of a Commonwealth Government Research Scholarship (1938 and 1939).

SUMMARY

Tasmanite shale on gentle pyrolysis produces an unsaturated oil with a relatively high aromatic content. The oil was fractionated and the physical properties of the different fractions found, after which the fractions were washed with sodium hydroxide solution and dilute sulphuric acid, in order to determine the tar acids and tar bases. The isolation of m-cresol from the tar acids is described. The degree of unsaturation, as determined by 85 per cent sulphuric acid, varied between 40 per cent and 47 per cent, including as much as 11 per cent diolefines. It is probable that terpenes, or substances closely allied to them, occur in the oil, although their presence was not confirmed. Tasmanite shale oil contains large quantities of sulphur, the major portion of which is contained in heterocyclic molecules. The cyclic sulphur bodies in the lower fractions were thiophenic in nature and the presence of thiophene and methyl thiophene was confirmed.

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TABLE I.

Fraction.	Temperature Range.	Volume ml.	Specific Gravity @ 20°.	Refractive Index @ 20°.	Tar Acids.	Tar Bases.	After Removal of Acids and Bases.			Mercaptan Sulphur.
							Specific Gravity.	Refractive Index.	Olefines Per cent.	
A	36-60	60	0.6799	1.3857	0.0	0.5	0.6800	1.3858	40	0.000
B	60-70	414	0.6958	1.4038	0.0	0.5	0.6959	1.4039	40	0.029
C	70-80	162	0.7199	1.4046	0.0	1.0	0.7200	1.4048	46	0.044
D	90-100	227	0.7200	1.4060	0.0	1.1	0.7195	1.4063	47	0.074
E	100-110	125	0.7237	1.4097	0.0	1.0	0.7230	1.4098	46	0.105
F	110-120	256	0.7425	1.4130	0.0	1.1	0.7415	1.4130	45	0.082
G	120-130	261	0.7531	1.4205	0.0	1.1	0.7528	1.4200	41	0.115
H	130-140	497	0.7630	1.4242	0.1	1.4	0.7649	1.4254	45	0.126
I	140-150	544	0.7665	1.4284	0.3	1.6	0.7665	1.4286	45	0.164
J	150-160	529	0.7785	1.4329	0.4	2.0	0.7806	1.4330	44	0.232
K	160-170	956	0.7934	1.4418	0.5	2.4	0.7897	1.4380	42	0.273
L	170-180	841	0.8062	1.4468	1.5	2.5	0.8004	1.4419	40	0.282
M	180-200	910	0.8148	1.4523	2.0	2.5	0.8154	1.4494	40	0.226
N	200-220	2022	0.8298	1.4607	3.0	2.7	0.8277	1.4567	41	0.390
O	220-240	1920	0.8461	1.4657	3.5	3.5	0.8396	1.4612	40	0.507
P	240-260	1873	0.8713	1.4805	3.5	4.0	0.8668	1.4758	40	0.224
Q	260-280	822	0.8779	1.4848	4.5	4.0	0.8763	1.4832	40	0.392
R	280-300	864	0.8803	1.4932	5.0	4.5	0.8764	1.4906	41	0.421
S	300-320	778	0.8978	1.4992	5.0	4.5	0.9858	1.4974	41	0.438
T	320-340	843	0.9161	1.5077	5.5	4.5	0.8999	1.5056	40	0.515
U	340-360	705	0.9328	1.5183	5.5	4.0	0.9311	1.5170	40	0.344
V	360-	175	0.9514	1.5227	5.8	4.0	0.9500	1.5213	40	0.445

The subject matter of this paper is taken from a thesis previously submitted for the degree of Master of Science.

THE NITROGEN BASES IN TASMANITE SHALE OIL

By

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FROM PAPERS AND PROCEEDINGS OF THE ROYAL SOCIETY OF TASMANIA, 1941

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The Nitrogen Bases in Tasmanite Shale Oil

By

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INTRODUCTION AND HISTORICAL

The type of nitrogen compounds produced during the retorting of oil shale, although essentially of a heterocyclic nature, depends on several factors, the chief of which are :—

- (i) The rate of heating:
- (ii) The retorting method:
- (iii) The absence or presence of air.

Although these 'tar bases' are mainly derivatives of pyridine and/or quinoline, other compounds of a pyrrole nature have been reported to occur, for instance Petrie (1905) recorded the presence of pyrrole compounds in the oil obtained from the torbanites of New South Wales, and accounts of the shale oil from Colorado giving the same reaction have been reported by McKee (1925).

The first systematic work on the nitrogen compounds in shale oil was that of Williams (1854) on Dorsetshire shale. Williams wrote that they burnt with a smoky flame, possessed a very bad smell, were soluble in alcohol and gave a blue precipitate with cupric nitrate. He isolated pyridine and some of its lower homologues. Garret and Smythe (1902) working on Scottish shale oil succeeded in isolating and identifying seven members of the pyridine series by oxidation to the corresponding acids with potassium permanganate and by the preparation of the aurichlorides of the bases.

Robinson (1879) recorded the presence of nitrogen compounds in Scottish shale oil bases, occurring in the fractions boiling between 270° C. and 390° C. He proved that they were dicyclic compounds of the iso-quinoline series. In reference to the formation of salts, Robinson writes 'attempts were made to get crystalline salts from the mixed bases; the double chlorides of platinum, gold, cadmium, mercury, lead and zinc were tried but without success, only resinous sticky masses being obtained. The same failure in getting crystalline salts was experienced when the bases were treated with sulphuric, hydrochloric, nitric and oxalic acids'.

Kogerman (1931) gives a detailed description of the methods used to obtain the purified bases from Estonian shale oil, and makes the statement that 'The pure bases, separated from the shale oil, formed a reddish liquid with a quinoline-like odour, specific gravity—0.9731 at 15° and n_D^{20} —1.539/19°'. He also states that

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some of the higher bases failed to give crystalline salts, (cp. Robinson's remarks above), and, although he remarks that they belong to the pyridine and quinoline series, their presence was not confirmed. Eguchi (1927) has reported the presence of pyridine compounds in Fushun shale oil and identified methyl, dimethyl, and trimethylpyridines.

From the above brief summary it can be seen that aliphatic nitrogen compounds do not play an important role in the tar bases present in shale oil. These bases are, practically without exception, heterocyclic in structure and consist of alkylated pyridines and quinolines. The bases found in Tasmanite shale oil were typical of the above, members of the monocyclic and dicyclic series having been identified. However, a second type of base was found to be present, apparently belonging to the 'naphthenic base' group already discovered in Californian petroleum.

EXPERIMENTAL

The material used in this investigation was not a representative crude oil in the true sense of the word, because very gentle pyrolysis was used in its production, the temperature being kept at all times below 420° C., a description of the properties of this oil has been given elsewhere by Cane (1941). The amount of tar bases present in the oil as determined by a modification of the Universal Oil Products Laboratory method No. C-78-40 was 3.2 per cent, while an examination of 10° C. cuts showed zero per cent in the lower fractions, with increasing amounts to nearly six per cent in the higher ones. The oil was extracted with successive batches of 10 per cent sulphuric acid, the acid washings removed, bulked, and then made alkaline with caustic soda, the supernatant oily layer allowed to settle on the top and then removed. The united bases were extracted with anhydrous petroleum ether and the ethereal layer concentrated. The bases were again converted into their sulphates and the aqueous layer washed with petroleum ether to remove traces of hydrocarbons, and finally the purified bases liberated with dilute caustic soda solution. The isolated bases were orange in colour with a distinct greenish fluorescence, and possessed the following properties:—

Specific Gravity @ 20° C.	0.9717
Refractive Index @ 20° C.	1.5242
Nitrogen	8.41%
Sulphur	0.27%

Their smell was characteristic of the shale bases; i.e., a mixture of pyridine and quinoline together with a faint peppermint smell. The smell of the bases lingered on the hands, even after several washings, and the physiological action was quite pronounced, the vapour producing the most acute headaches across the eyes and at the nape of the neck.

GENERAL REACTIONS OF THE BASES

- (I.) No carbylamine reaction.
- (II.) No crystalline quaternary ammonium salts with methyl iodide, but after standing for six months in a sealed tube a dark red tarry solid was formed.
- (III.) When diazotised and subsequently coupled with beta-naphol a dark green material was precipitated, and, when this was washed with sodium carbonate solution, a portion of the precipitate dissolved to form a deep red solution which dyed filter-paper orange. The residue from the sodium carbonate treatment was a green powder.
- (IV.) No Rimini's reaction and a very faint and doubtful Liebermann reaction.

- (v.) A deep blue precipitate was formed with cupric nitrate.
 (vi.) When the bases were reduced with sodium amalgam and alcohol for about 150 hours, a white water-soluble crystalline substance was precipitated.

Distillation of the Bases. The purified and dehydrated bases were distilled several times in all glass apparatus of special design, the column was silvered and vacuum jacketed, and the packing consisted of single turn wire helices. The following were the distillation results:—

Fraction No.	Boiling Range ° C.	Density @ 20° C.	Refractive Index @ 20° C.	Average Mol. Wt. (¹).	Nitrogen. %	Vol. %
B1	165-213	0.9270	1.5070	128.3	10.89	5.7
B2	213-238	0.9518	1.5128	158.1	10.07	32.5
B3	238-250	0.9778	1.5299	169.9	9.39	22.0
B4	250-270	0.9803	1.5200	174.9	9.10	13.0
B5	270-290	0.9891	1.5349	171.8	8.89	13.7
B6	Residues and loss	13.1

The first fractions were colourless, but developed a light yellow colour on standing, while the higher fractions varied progressively from light yellow to a deep orange shade. All fractions deepened on standing, and it is interesting to note here the observations of Delaby and Hiron (1930) 'The alkyl quinolines are liquids of strong odour, light yellow in colour, and the colour becomes deeper, according to increasing molecular weight. Ethyl quinoline is nearly colourless when freshly distilled and under the same conditions butyl quinoline is straw yellow, but finally it assumes a brown red colour which deepens according to the time of preservation'.

Fraction B1.—When closely fractionated on a semi-micro scale, the following results were obtained. In this work the criterion for the acceptance of any one substance from the point of view of boiling point was that all of this fraction must distill between the boiling limits of 1° C.

Fraction No.	Boiling Point.	Specific Gravity @ 18° C.	Refractive Index @ 20° C.	M.P. of Picrate.	Nitrogen. %
B1 (i)	173.2	0.9181	1.4984	154	11.33
B1 (ii)	198.4	0.9390	1.5004	N.O. (²)	10.91
B1 (iii)	206.4	0.9503	1.5054	N.O.	10.24

The above picrate and all others in this paper was obtained in the following manner:—The base was dissolved in 35 ml. of acetic acid, and to it was added two grams of picric acid contained in 5 ml. of 50 per cent acetic acid. When the crystals were deposited they were centrifuged from the mother liquor and crystallised from alcohol, washed, dried, and the melting point found.

(¹) The molecular weight was determined by the cryoscopic method, using cyclohexane as the solvent, Muscarelli and Benati (1909).

(²) Not obtainable.

Analysis of the results of Fraction B1 (i) agree closely with reported ones for γ -collidine (2, 4, 6, trimethylpyridine), but it must be kept in mind that different authorities give very divergent values for these constants, and it has been noticed that they even differ by as much as 6° C. in the case of the boiling points of uncommon derivatives.

Portion of this fraction was oxidised with potassium permanganate in a normal laboratory manner, and among the oxidation products the presence of trimesitic acid was confirmed.

Trimethyl pyridine has already been found in Fushun shale oil by Eguchi (1927) and also has been isolated from lignite tar by Krey (1895). No success was obtained in the analysis of the Fraction B1 (ii). The preparation of crystalline precipitates was rendered impossible on account of the formation of thick orange tarry masses when the bases were treated in accordance with the technique described above. Every case resulted in the formation of this resinous mass, no matter how the formation of crystals was promoted, and it is interesting to note that Robinson made the same observation. He tried many inorganic salts, but the only result was 'resinous, sticky masses being obtained'. From later researches it seems probable that Robinson's, and the present, results were due, in part, to insufficient purification, but even Baily (1930), in the last few years, has had the same difficulty in the elucidation of the structure of the tar bases occurring in Californian petroleum. The last fraction, together with Fraction B2, seemed to be a transition stage between, or a mixture of, the mono-cyclic and di-cyclic bases. That the next fraction was of quinolinic nature is indicated by the sudden drop in nitrogen content and rise in molecular weight. An analysis of the boiling points and refractive indices might indicate the presence of hydrogenated quinolines, for as far as could be ascertained from the available literature none of the simpler alkyl pyridines have boiling points approaching any of the above. Even assuming that this fraction was composed of a complex mixture of highly alkylated pyridines, the refractive index is much too high to allow this consideration, e.g., propyl pyridine (b.p. 178° C.) has a refractive index of only 1.4934. Similar statements could be made with regard to the presence of hydro-quinolines. No less than nine alkyl deca- and tetra-hydro quinolines have boiling points approaching the above. It may be assumed that, if these fractions contain hydro-quinolines at all, the refractive index would surely rise as the fraction was reduced, and with this end in view a representative sample was dehydrogenated according to the procedure of Diels and Karstens (1927):—Five gms. of the base and 7 gms. of powdered selenium were heated for 38 hours at a temperature of $185 \pm 1.5^\circ$ C. and the change in refractive index noted.

Refractive index before treatment	1.5126
Refractive index after treatment	1.5128

From a consideration of the hydro-quinolines, it can be calculated that the removal of four hydrogen atoms would cause an increase in the refractive index by an amount varying between 0.038 and 0.032, an increase which could be easily determined by refractometric methods.

Fraction B3.—From this fraction onward it can be seen that there is a drop in nitrogen content, while the refractive index and molecular weight still rise. The per cent of nitrogen in trimethyl quinolines is 8.9 and molecular weight 171.1, which are in the range of the above fraction, but there are two important properties which require explanation, i.e., the low refractive index and density.

From the preliminary work on a bulk sample, the presence of quinolines was confirmed, but members of the series boiling in this range have refractive indices

greater than 1.58. It was shown, by treatment with selenium as before, that hydro-quinolines were not causing this discrepancy.

The work of Baily and his collaborators on the nitrogen-containing bases in Californian petroleum, has shown that another important type of tar base (naphthenic base) may occur, and it seems probable that similar compounds occur in Tasmanite shale oil. They are apparently tri-cyclic in structure and contain a piperidine nucleus. Baily's process of a cumulative extraction was applied to a representative fraction boiling between 240° C. and 290° C. It was dissolved in 1 : 1 aqueous hydrochloric acid and treated with chloroform according to the procedure developed by Baily. The aqueous layer containing the hydrochlorides of the quinolinic bases was washed with decreasing amounts of chloroform; the chloroform layer containing the naphthenic bases with decreasing amounts of water. Under this treatment the refractive index of the 'aromatic section' rose from 1.5321 to 1.5845, and the specific gravity increased to nearly unity after five stages of extraction.

From this it can be seen that we are dealing with exactly the same set of conditions experienced by Baily. Furthermore, the values of the refractive index and density are now within the range of the tri-methyl quinolines.

The extracted bases consisted of a sticky, semi-crystalline mass of light yellow colour with a greenish yellow fluorescence. The chloroform washings of the 'non-aromatic' bases were treated so as to isolate the free bases and their general properties found. They were brownish red in colour, with a blue fluorescence and refractive index of 1.4985. They gave the normal reactions characteristic of pyrrole compounds. It is believed that the structure of these bases is very complex, and no attempt was made to elucidate their structure. The quinolinic bases were converted into their picrates in solution buffered with sodium acetate, purified, and then heated with ammonia, from which the bases separated out as nearly solid masses. The bases were further purified by treatment with acetone, and then very carefully distilled in vacuo.

Fraction No.	Temperature Range.	Refractive Index @ 20° C.	Density @ 15° C.	Molecular Weight.	Nitrogen. %
C1	244-245	1.5983	1.0641	142.0	9.89
C2	271-273	1.5903	0.9953	163.8	8.77
C3	277-279	1.5832	0.9307	177.4	8.01
C4	284-285	1.5742	0.9502	179.7	7.49

Analysing these results it can be seen that the first two fractions appear to contain methyl and di-methyl quinolines respectively, although their presence could not be confirmed. Tri-methyl quinoline was isolated from Fraction C3. This will be discussed later.

Great uncertainty exists with regard to the characteristics of these bases, and widely divergent values have been reported with regard to the higher alkyl quinolines; for example, four different values for the boiling point have been reported recently of 2-3-dimethyl quinoline varying between 261° and 273° C., so that in these analyses it has been attempted to class the quinolines according to the number of alkyl groups rather than to isolate individual compounds.

THE PRESENCE OF THE QUINOLINE RING IN THE HIGHER BASES

A small quantity of the 'non-extracted' bases corresponding to Fraction C2 (no more of the purified substance being available) was oxidised very carefully with 2 per cent aqueous alkaline potassium permanganate solution for 15 hours. Quite an amount of trouble was caused by the bumping of the solution on account of the precipitated manganese dioxide. A small air leak introduced into the solution helped to minimise this difficulty and also served to inject sufficient permanganate solution during the operation. The resulting solution of pale stone colour was filtered and rendered acid. This was slowly distilled and the vapours condensed into aqueous ammonia solution, and the volatile organic acids examined (I.), the non-volatile matter was extracted with benzene in a Soxhlet extraction apparatus (II.), and the residue recrystallised from hot water (III.).

THE VOLATILE ORGANIC ACIDS

The ammonium salts of the volatile organic acids were analysed, only the presence of acetic acid being confirmed in this solution, although a slight reducing action was observed, perhaps indicating the presence of formates, although they could not be confirmed.

THE BENZENE SOLUBLES

The yellowish non-volatile mass was placed in a Soxhlet thimble and extracted with benzene for 38 hours, the residue being left in the thimble and extracted with water (III.). The benzene solution was evaporated in vacuo. All attempts to elucidate the structure of this portion were unsuccessful, but results tended to prove that this was due to the presence of the naphthenic bases, which, according to other investigators, are extremely stable, both to neutral or alkaline permanganate oxidation.

THE WATER SOLUBLES

The water soluble material was concentrated and silver nitrate added; this caused an immediate dirty white precipitate, which was filtered off and purified. The amount of silver in the silver salt amounted to 58.6. Another portion of the silver salt was treated so as to liberate the free acid, no attempt being made to concentrate this on account of the difficulties encountered by Hantzsch (1882). The reaction with ferrous sulphate indicated a carboxylic acid in the α position. When this acid was distilled to dryness with lime, the odour of pyridine was observed.

It has been shown that the nitrogenous base present in the 271°-273° boiling range leads, on oxidation, to the production of pyridine carboxylic acids and, from the percentage of silver in the silver salt and basicity measurements, gives a molecular weight of 231.6 for the acid: this approximates fairly closely with methyl pyridine tri-carboxylic acid. Two of these carboxylic groups can be accounted for by the disintegration of the 'benzene' half of the molecule. This shows that there are two side chains in the 'pyridine' half of the molecule, one of which is obviously a methyl group.

From a study of the molecular weights of the base, it can be seen that we are dealing with either an ethylmethyl or trimethyl quinoline with perhaps a small percentage of higher homologues. However, assuming that trimethylquinoline is the major component, then there must be only one methyl group in the benzene half of the molecule. When the acid was heated and then coupled with resorcinol, a deep red substance was formed which had a distinct colour change from acid to alkaline solution; this compound, assumedly of the phthalein type, could only arise from an acid anhydride, necessitating two carboxyl groups in the ortho position to one another. Further proof of this orientation lies in the fact that it

was found, by using formaldehyde, that two and not three hydrogen atoms were replaced by carbinol, which, according to the results of Königs (1899), will only occur when the ortho position to the methyl radicle is substituted, that is, if the benzene ring is not acting as the ortho substituent.

Phthalone formation, requires a methyl or methylene group in the α or γ position. A small amount of the base was heated with phthalic anhydride and zinc chloride for five hours at 165°; the resulting compound was a fine deep-red solid, which dissolved in boiling alcohol to give a crimson-orange solution.

The lack of formation of quarternary ammonium salts by methyl iodine may well be explained by reference to the results of Decker (1905), who found that ortho substituted quinolines exhibit steric hindrance, in that they do not form quarternary ammonium compounds with iodides. Oxidation of the base with chromic acid gave brownish needles, soluble in hot water, which sintered about 245°. The distillation of the barium salt gave a liquid (n_D^{20} 1.6053), which on oxidation with potassium permanganate, and distillation of the acid thus produced, gave quinoline itself.

SUMMARY OF THE BASIC BODIES

The only base isolated in the lower fraction was trimethylpyridine, the presence of which was confirmed by oxidation to the corresponding acid.

The compounds in the higher fractions consist, in the main part, of tertiary bases of the quinoline series, but results have shown that a second type of basic substance occurs, which possesses a low refractive index and probably contains a pyrrol nucleus in its structure.

The presence of hydrogenated quinolines was shown to be impossible from a study of the refractive indices before and after dehydrogenation experiment with selenium.

The presence of the quinoline ring was confirmed by oxidation, and from this it was shown that the alkyl radicles attached to the nucleus were nearly all methyl radicles.

The orientation of the methyl radicles in one fraction was elucidated, and it was found that one of them was in the 1; position, the other in the 2; position. The remaining radicle was in either the 5; or 8; position.

This investigation was carried out in the Department of Chemistry in the University of Tasmania, during the tenure of a Commonwealth Government Research Scholarship (1938 and 1939).

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[Issued December 21, 1942.]

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Some of the results given in this paper show a slight variation from the results given in the main thesis. This discrepancy is caused by later revised values.

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INTRODUCTION.

The property of oil shale which renders it a valuable and interesting material both to the scientist and to the industrialist is that, on the application of heat, the organic matter decomposes into substances of lower molecular weight; these include all phases, liquids, solids and gases. In order to achieve an effective retorting of the shale it is necessary, in the first place, to have a clear understanding of the reactions which occur during the retorting process, and of the physical and thermochemistry of the shale pyrolysis. Very little is known of the mechanism of the reactions occurring here, chiefly because of the fact that the structural chemistry of the kerogen molecule is practically unknown. The conditions existing during the relatively small temperature interval in which the kerogen molecule decomposes render it absolutely essential to have exact information on the magnitude of the quantities involved during this transformation.

The torbanites occurring in the Upper Coal Measures of Permian age vary in colour from black with a satin-like lustre, in the case of a rich shale, to greyish rock in the inferior quality seams. These two extremes vary in oil yield from 210 gallons per ton (specific gravity 1.04) to 30 gallons per ton (specific gravity 2.31). It is unnecessary to give here a lengthy description of the physical and microscopic structure of the torbanite in this region, as this has already been given excellent treatment by Dulhunty (1941).

The principal changes in the microstructure of these torbanites can be summarised briefly as follows: up to 350° C., no apparent changes are produced in their chemical structure, but the mechanical properties alter to a slight extent, for instance their bending moment decreases, and speaking generally they become "weaker" in strength. As the temperature approaches 400° C., the organic cell structure of the shale begins to disintegrate. This increases with temperature until 450° C. is reached, when the cell structure has completely disappeared.

The Nature of the Thermal Decomposition.

In order to investigate the mechanism of the reactions occurring during the decomposition of oil shale, a small reaction vessel was built, consisting of 1 in. seamless pipe with flanged ends. One end was fitted with a thermocouple well and the other end to a pressure gauge system. The first stage in this phase of the investigation was to find the amount of pressure generated by the shale during the different stages of decomposition and, from the application of the gas laws, to determine whether any appreciable amount of gas was evolved before the true pyrolysis, and so ascertain whether the incipient formation of the precursor to decomposition was purely a molecular rearrangement or the first stage in the breakdown. The vessel was charged with granulated shale and the temperature gradually increased until the pressure reached about 20 lb. per sq. in., whereupon the vessel was cooled, the flanges opened and the

nature of the product investigated. This was a most interesting phase of the work, as whilst still hot, the shale, after having undergone the above treatment, was practically in the liquid phase, resembling a mixture of liquid bitumen and molten rubber.

Following the removal of water vapour and occluded gases, the first stage of the decomposition is marked by the evolution of carbon dioxide and hydrogen sulphide. This occurs at comparatively low temperatures, and denotes the initial steps of the transformation into the intermediate bitumen. It is impossible to state the lowest temperature at which this "depolymerisation" will occur, as results showed at least minute traces at temperatures approaching 300° C. and even oil formation at 360° C., after about three hours' heating. However, at 360° C. it was shown that relatively little gas is generated during the first stages of decomposition and that the large volumes of gas met with during the retorting of shale arise, not from the decomposition of the kerogen, but from the subsequent cracking of the pyrobitumen to oil. This pyrobitumen appears to be the real origin of the crude oil. The physical properties of this substance are entirely in contrast to those of the original oil shale; for example, the shale is tough, rigid and insoluble in most organic solvents, whereas the resulting bitumen was of a rubber-like texture and practically entirely soluble in solvents such as benzene.

It appears that the original organic matter of the shale is not the true oil producing body, but this organic matter changes, at a temperature lower than that necessary to produce oil, into the abovementioned bitumen. Normal shale which has not been treated by heat in any way is solid, hard to fracture, and practically insoluble in the normal organic solvents (some cyclic ketones, such as cyclo-hexanone, appear to be the best solvents), but after it has been heated in the region of 380° C. a remarkable structural change occurs, whereupon the shale changes into a gummy semi-liquid mass.

The decomposition of the kerogen in oil shale is regarded by many as occurring in steps, as in the distillation of crude oil, so that, during pyrolysis, the first oil produced must necessarily be of lower specific gravity than the later fractions. However, results showed that after its formation the bitumen decomposes and yields, simultaneously, the whole series of products varying from the lightest to the heaviest. It has been shown that the crude oil does not vary appreciably in gravity as the retorting process goes on to completion, and it may be assumed that each kerogen molecule acts independently as a potential producer of oil, gas and coke.

A sample of shale was slowly retorted, and samples of the liquid products of decomposition collected over equal intervals of temperature, as measured in the shale mass. A determination of specific gravity was carried out on each sample. A microdistillation showed that all fractions contained "light ends". These results are illustrated in Table I.

TABLE I.

Temperature Range of Retorting ° C.		Specific Gravity of Oil at 20° C.
-450	0.88
450-470	0.89
470-480	0.89
480-490	0.90
490-500	0.90
500-510	0.90
510-520	0.90
520-530	0.90
530-540	0.91
540-550	0.92
550-		

Thus it can be seen that the retorting of shale resolves itself into the conversion of the organic matter into the bitumen, and the subsequent cracking (at atmospheric or slightly subatmospheric pressure) of this bitumen into crude oil, naphtha, gas, etc. Taking this point of view, the lighter fractions may then be regarded as having no origin in the shale at all, but are produced by the cracking of the "nascent" crude oil under the conditions existing in the retort at the time of their formation. This does in some way explain the great variability in the properties of the crude oil produced from the same shale under various retorting conditions. Hence, the retort must be regarded, not as an oil-producer, but as a bitumen former (i.e., the transformation of the organic matter in the shale into the heavy bitumen-like product mentioned above). This having taken place, the retort from then onwards is simply acting as a cracking still. This is emphasised by the fact that shale oils are highly unsaturated, and in this way resemble cracked pressure distillates from flow oils.

The Rate of Pyrolysis.

Rate of pyrolysis of shale is an important factor in determining the kinetics of the removal of gases and vapours from the shale. The rate of pyrolysis was determined experimentally in the apparatus outlined below.

A piece of channel iron 18 by 7 by 3 inches, upon which was welded a bar of iron approximately 15 by $\frac{3}{4}$ inches, served as the base of the apparatus. Between the end lugs was strung a length of piano wire, in which tension was maintained by two end screws. At the mid-point of this wire, and at right angles to each other and to the wire, two cross members were brazed, the horizontal member of which was 8 inches long and served to carry the shale sample. The upright member was 2 inches long and carried a small mirror. From the end of the horizontal member a small balance pan was hung by means of a thin steel wire. The whole set-up resembled a torsion balance. The procedure was as follows.

A tubular furnace, closed at both ends except for a small hole for the suspension wire, was set in an upright position, and into it the shale sample contained on the balance pan was hung, and the maximum torsion produced in the piano wire was determined by measurement of the deflection of an optical beam, reflected from the small mirror attached to the upright. The furnace was preheated to the required temperature and the interior filled with an inert gas, and the rate of decrease of mass of the shale was measured by the decreasing deflection of the optical beam as measured on a scale. The experiment was discontinued when constant deflection denoting complete carbonisation was obtained. The set-up was then calibrated by putting known masses on the pan and calibrating the scale reading. A series of experiments was carried out with the apparatus above described, the results obtained being interpreted by means of graph (see Figs. 1 and 2).

These results showed clearly that the rate of pyrolysis was a function of the particle size.

Two series of determinations were carried out, at 400° C. and 450° C. A series of test blocks were cut from "first quality" shale by means of a rotating aluminium disc fed with carborundum powder; these were, as far as could be maintained, in arithmetical progression as regards linear dimensions, the smallest one being approximately one centimetre cube (see curves 1, 2, 3 and 4 in Figs. 1 and 2).

Qualitative Examination of the Shale Pyrolysis.

In order to determine experimentally whether the shale pyrolysis was an endothermic reaction, as might at first be imagined, several experiments were carried out with this aim in view. Following the work of Hollings and Cobb

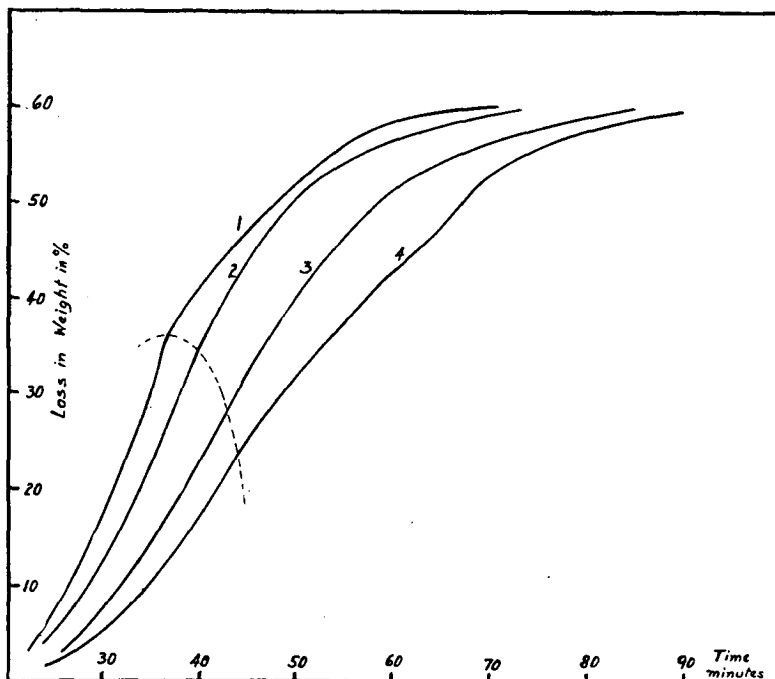


Fig. 1.—Rate of Pyrolysis. Temperature 400° C.

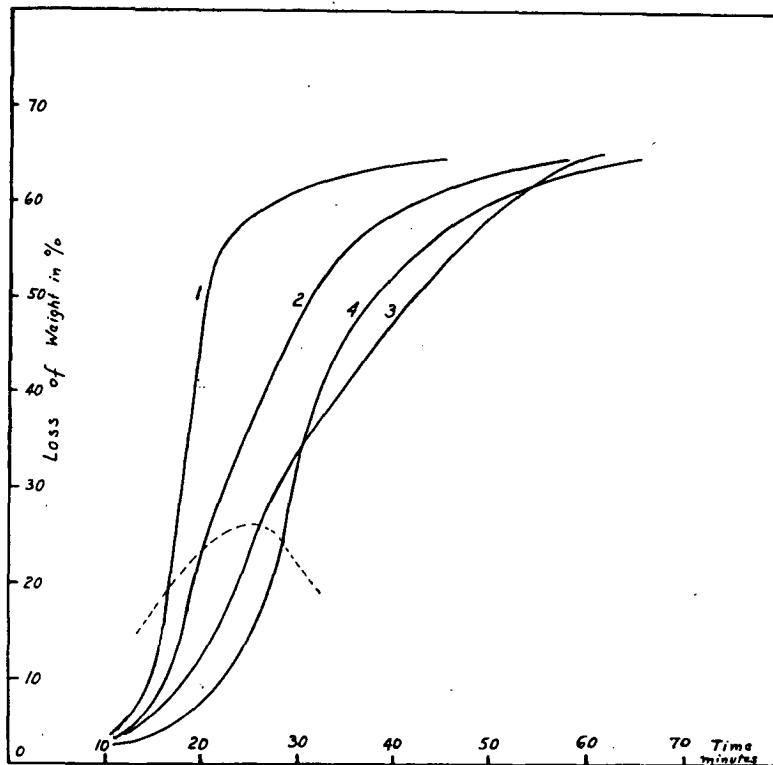


Fig. 2.—Rate of Pyrolysis. Temperature 450° C.

(1915), the following set-up was arranged: An iron tube 1 inch in diameter was clamped concentric to the wall of a furnace and in it two silica tubes were clamped running parallel to one another, resting inside the iron tube. Two thermocouples were placed in the silica tubes, so as to constitute a differential thermocouple. The silica tubes were lightly packed with dehydrated Fuller's earth, the temperature of the furnace gradually raised, and any deflection of the galvanometer connected to the differential thermocouple noted. Two parallel experiments were carried out, in which one of the silica tubes was packed with dry powdered shale. Should the reaction occurring during the pyrolysis of the shale mass be definitely exo- or endo-thermic, such direction of reaction would show up in the galvanometer deflection. Results of this phase of the work are shown in Fig. 3.

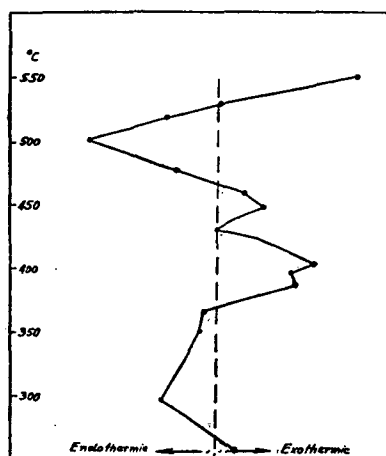


Fig. 3.—Thermal Reactivity of Shale.

It can be seen that the direction of the reaction is by no means regular, and in this respect is similar to other shales, and to coal. [See McKee (1925) and Luts (1935).]

In relation to Fig. 3, the following remarks should be made. The sulphur and oxygen containing compounds are the first to decompose with exothermic reaction, producing carbon dioxide, hydrogen sulphide and water vapour. Apparently the hydrocarbons at once commence to crack with an endothermic reaction. Owing to the low thermal conductivity and high end temperature necessary for the complete decomposition of the contained organic matter, some cracking of the oil vapours to fixed gases will occur, and a certain amount of fixed carbon is to be expected at the end of the pyrolysis. Furthermore, in commercial practice, as it is necessary to raise the temperature of the shale well above this temperature ($380^{\circ}\text{C}.$), we can expect a greatly accelerated rate of cracking even in the most gentle of retorting operations. The relation given by von Strache (1922) between the amount of contained oxygen and the heat of low temperature carbonisation is that heat of reaction increases with the increase of oxygen; but with a very small oxygen content the heat of reaction is negative. The overall direction of the reaction may be found from the difference in heat values of the gas, oil and coke, and the heat of combustion of the shale. From this consideration Constan and Kolbe (1908) have found that the reaction is 7.2% exothermic for ichthyol shales.

Thermal Expansion of Shale Oil.

The coefficient of thermal expansion was determined by measuring the expansion of a known volume of the liquid when raised from one temperature to another under closely controlled conditions. It has been shown that the coefficient of thermal expansion varies inversely as the specific gravity between approximately 0.001 for naphtha and 0.0008 for crude oil. The results obtained gave close agreement with those of the A.S.T.M. specifications for flow oil, and showed that these tables may be used for gravity corrections for shale oil. Table 2 shows the mean coefficient of thermal expansion between 20° C. and 60° C. for oils of different specific gravity.

TABLE 2.

Specific Gravity.		Coefficient of Expansion.
0.781	10.66×10^{-4}
0.794	10.41
0.804	10.07
0.825	9.66
0.843	9.13
0.868	8.60
0.883	8.26
0.895	7.94

From this table a chart may be constructed from which a system of specific gravity correction factors may be obtained.

Viscosity of Shale Oil.

The effect of constitution on viscosity is too complex a subject to be treated here, and no formulæ have been found to be entirely satisfactory in this application. However, broadly speaking it is found that, in the case of complex hydrocarbon mixtures, the viscosity varies with the specific gravity, together with another factor, and several relationships have been put forward connecting viscosity with specific gravity and/or other constitutional properties.

In the case of crude shale oil, it is found that a rough linear relationship exists between viscosity and specific gravity as indicated in Table 3. The results were determined with an Ostwald pipette viscometer under isothermal conditions at 100° F. The individual figures were interpolated from a graph resulting from many determinations over a long period of time. This table also shows the variation in viscosity with change of temperature of a typical crude oil, giving a viscosity index of approximately 150.

TABLE 3.

Specific Gravity at 20° C.	Viscosity. Centistokes at 100° F.	Viscosity Centistokes at t° C.	Temperature t° C.
0.87	5.7	16.0	30
0.88	8.4	10.8	40
0.89	11.1	7.5	50
0.90	13.9	5.5	60
0.91	16.6	4.2	70
0.92	19.3	3.3	80

The Specific Heat of Oil Shale.

The specific heat of oil shale can be determined experimentally by the normal method of mixtures. However, owing to the varying composition of the shale and the varying amount of inorganic matter contained therein, one value will not suffice to cover all samples of shale. Employing the results of Dulong and von Kopp on the additive character of the specific heats, a theoretical approach

may be made and the specific heat of the pure organic and inorganic matter in shale may be determined. The composition of a representative sample of the ash from the Glen Davis deposits is shown in Table 4.

TABLE 4.

Chemical Composition.	Percentage.	Specific Heat.	Product.
SiO ₂	67.3	0.191	12.85
Fe ₂ O ₃	3.9	0.155	0.60
Al ₂ O ₃	22.0	0.184	4.05
CaO	0.9	0.181	0.16
MgO	0.5	0.220	0.11
SO ₃	2.6	0.18	0.47
Alkaline oxides ..	2.8	0.2	0.56
			<hr/> 18.80 <hr/>

Specific heat of the shale ash : 0.19 cal./gram./° C.

The specific heat of the organic matter in oil shale may be approximated in the same manner from the percentage composition of the kerogen and the atomic heats of the constituent atoms (see Table 5).

Percentage Composition :

TABLE 5.

C = 85.1%.	H = 10.6%.	S = 0.5%.	N = 1.3%.	O = 2.3%.
Analysis Percentage.	Atomic Heat.	Atomic Weight.	Percentage × $\frac{\text{Atomic Heat}}{\text{Atomic Weight.}}$	
C : 85.1	1.76	12	12.5	
H : 10.6	2.3	1	24.38	
S : 0.5	5.54	32	0.09	
N : 1.3	3.42	14	0.32	
O : 2.5	3.48	16	0.54	
			<hr/> 37.8 <hr/>	

Specific heat : 0.38 cal./gram.

Thus for dry shale with 50% mineral matter the theoretical specific heat of the sample would be $\frac{0.38 + 0.19}{2} = 0.28$ cal./gram. For American shales, values shown in Table 6 have been found.

TABLE 6.

Shale from De Beque..	0.265	McKee and Lyder (1922).
Shale from Parachute	0.242	U.S. Bureau of Mines (Gavin and Sharp, 1920).
De Beque	0.273	" " " "
Shale residue	0.223	" " " "
De Beque	0.280	McKee and Lyder (1922).

Thus it can be seen that the specific heat increases with increasing "richness" of the shale and varies between the theoretical limits found above.

The specific heat of the moisture-free shale was found experimentally by the usual method of mixtures, using an adiabatic calorimeter. It was found that water was not a good cooling medium because of the fact that there was no effective "wetting" of the surface of the shale. Some organic liquids were found to be more effective in this direction, carbon tetrachloride and nitrobenzene being used. The results obtained are given in Table 7.

TABLE 7.

Sample Number.	Ash Percentage.	Specific Heat. (Observed.)	Specific Heat. (Calculated.)	Temperature Range. ° C.
14	22.2	0.318	0.336	20-50
7	32.3	0.301	0.316	30-80
23	56.4	0.278	0.271	20-50
42	86.2	0.242	0.214	20-50

By interpolation of these results the specific heat of a shale with a known ash content may be found.

The Specific Heat of Shale Oil.

The functional relationship between specific heat and specific gravity has not been satisfactorily determined in the case of complex hydrocarbon mixtures. The specific heat of most crude oils is approximately 0.5 grm. cal./grm./°C. and agree with the general equation

$$C_p = a + bt + ct^2 \dots\dots\dots (1)$$

where $a = 0.5$ and $b = 0.001$.

t = temperature in °C.

The specific heat of petroleum oil has been determined by Kraussold (1932), who suggested the equation $C_p = 0.5 + 0.0011 (t-20)$. From experimental work on crude shale oil from the Glen Davis torbanites it has been shown that Kraussold's formula is only approximate, and a better relationship is

$$C_p = 0.503 + 0.00118 (t-20) \dots\dots\dots (2)$$

Assuming that the variation is linear over a limited temperature range, we may substitute " a " in formula (1) by a function of the specific gravity of the form

$\frac{K}{(\text{Sp. gr.})^n}$, where K is a constant and n is a number less than 1.

A suggested equation is:

$$C_p = \frac{0.4915}{(\text{Sp. gr.}_{20})^{0.1}} + 0.00118 (t-20)$$

It is interesting to compare this equation with that suggested by Kraussold for flow oil,

$$C_p = \frac{0.425}{(\text{Sp. gr.}_{15})^{\frac{1}{2}}} + 0.0011 (t-20)$$

Heat of Combustion of Oil Shale.

Heat of combustion was determined by igniting a known mass of the shale in a Parr oxygen calorimeter, in which the sample is burnt in an atmosphere of oxygen under 20 atm. pressure. The charge is ignited by means of a small fuse wire and the heat generated is absorbed in water in the usual manner. If samples showed traces of free carbon after ignition, the results were discarded. The results obtained are given in Table 8.

TABLE 8.

Sample No.	16A	14	18A	23	20A	51
Heat of combustion (cals./grm.) (corrected) ..	7,804	7,651	5,739	3,818	3,150	2,317
Ash (per cent.) ..	21.1	22.2	24.03 44.0	59.09	61.52	76.2

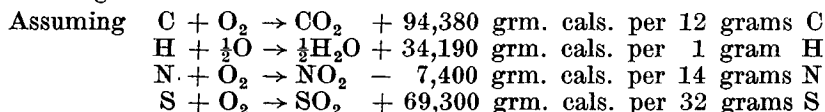
This, by extrapolation, gives a value of 10,680 grms./cals. for the calorific value of pure kerogen.

Corrections for Fuse Wire.

The sample in the bomb is ignited by a fuse wire which is partially consumed during the combustion. The amount of wire taking place in the combustion is determined and a correction of approximately 2.8 calories per centimetre of burned wire is then applied.

Correction for Acid.

Since the combustion in the bomb takes place in an atmosphere of pure oxygen, there is a better chance of complete oxidation than under normal conditions. For example, in the normal oxidation of sulphur compounds sulphur dioxide is produced. However, under the conditions existing in the bomb at the time of the explosion there are appreciable amounts of sulphur trioxide produced which, in the presence of water vapour, form sulphuric acid. As this is an exothermic reaction, some correction must be applied to compensate for it. The calculations are based on the assumption that all the acid is in the form of nitric acid, rather than to attempt to separate the two acids. However, the heat liberated by the formation of sulphuric acid is greater than that liberated by the formation of a corresponding amount of nitric acid, and it becomes necessary to apply another correction for the heat generated above that accounted for in the acid correction. This is the Sulphur Correction. Approaching this, as previously, from the theoretical angle, we may arrive at the following calculation :



and taking the empirical composition of typical torbanite of this deposit as :

$$\begin{array}{l} \text{C} = 85.1\% \\ \text{S} = 0.5\% \\ \text{N} = 1.3\% \\ \text{H} = 10.6\% \end{array}$$

gives a theoretical heat of combustion of 10,003 grm. cals. per grm. for pure kerogen.

Heat of Combustion of Shale Oil.

The heat of combustion of the liquid products of the pyrolysis were determined in a Parr oxygen bomb calorimeter using the same method as with the solid shale. Using different samples of oil, the following results were obtained :

Sample No.	8	17	21	14N	18N
Calorific value, gross (grams/cals.)	10,610	10,904	11,018	10,732	11,091
Mean value for liquid products of decomposition : 10,872 grm./cals.					

This value may be checked approximately either by means of the characteristics of the oil in question or by means of the ultimate composition.

(i) From the characteristics of the oil.

Average values of the combustion characteristics of different oils have been tabulated, and representative values have been assigned to the heat of combustion when such data as gravity and distillation curve are known.

Assuming a specific gravity of 27° A.P.I. and "mean average boiling point" of 630° F., a calorific value of approximately 10,700 cal./grm. is given by tables published by Universal Oil Products Company of Chicago.

(ii) From ultimate composition.

Assuming an average analysis of the oil as

$$\begin{array}{ll} \text{C} = 86.3 & \text{S} = 0.6 \\ \text{H} = 11.3 & \text{O} + \text{N} = 0.4 \end{array}$$

a theoretical value of 10,737 cal./gram. for the gross heat of combustion is obtained.

The Heat Necessary to Decompose a Known Mass of Shale.

The theoretical heat for the low temperature carbonisation of shale may be divided into the following sections :

1. The warming of the shale and contained moisture from room temperature to 100° C.
2. The heat of vapourisation of the water.
3. The heating of the shale from 100° C. to the point of decomposition.
4. The heat to decompose the shale.
5. The heat to volatilise the products of pyrolysis.

Various values have been found for these operations, varying from 190 cal./gram. for Estonian shales to 480 cal./gram. for American shales.

"Heat of Reaction" of the Shale.

By "heat of reaction" it must be understood that this term is not used in its common sense, but is meant to convey "the heat necessary to convert a given mass of shale into oil, gas and coke under standard conditions".

The "heat of reaction" of the shale may be obtained by one of three methods :

1. Direct determination of the heat necessary for the pyrolysis, calculated from the application of the Stefan-Boltzmann Law, allowing for radiation and conduction and convection losses. However, owing to the great complexity of the equations involved, and the many assumptions that have to be made, this method of determining the heat necessary for the decomposition is not satisfactory in the present case.

2. By the use of Hess's Law it follows that, if we determine the heat for the complete oxidation of one gram of shale and subtract from that the heat evolved when the total products of pyrolysis are oxidised completely, the differences should be the amount of heat necessary to cause the above pyrolysis. It is realised that the heats involved on both sides of this equation are comparatively large and are quite large in relation to the difference between them (the quantity which we wish to determine), and consequently some errors may be introduced but this method, although approximate, gave the most reliable results.

3. Measurement of the heat necessary to cause shale pyrolysis by calorimetric methods. A quantity of heat slightly in excess of that needed for the pyrolysis is added to the shale under consideration, and that measured by suitable means.

Gray King Assay of the Shale to Determine the Heat Balance.

Two Gray King assays were carried out on a type sample of shale. The normal condensing system was replaced by a freezing mixture of solid CO₂, in which a U-tube was immersed. Every precaution was observed to see that the weight balance was as accurate as experimental details allowed. The Runs (5 and 6) were carried out under strictly controlled conditions, and the results are set out in Table 9.

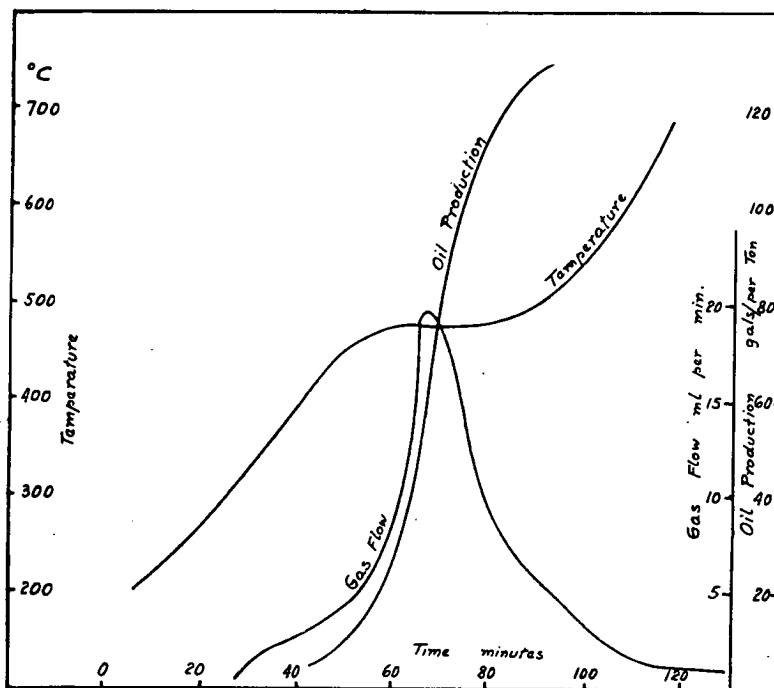


Fig. 4.—Gray King Assay of Shale.

TABLE 9.

Run No.	5	6
Weight of shale	10.314 grms.	11.131 grms.
Weight of coke	4.261 "	4.766 "
Weight of oil	5.510 "	5.595 "
Volume of gas—		
At 25° C. and 712 m.m.	557 ml.	550 ml.
At S.T.P.	478 "	472 "
Weight of gas	0.547 grms.	0.552 grms.
Shale (per cent.) . . .	100	100
Coke (per cent.) . . .	41.31	42.82
Oil (per cent.)	53.42	52.26
Gas (per cent.)	5.30	4.96
	<u>100.03</u>	<u>100.04</u>

Analysis of the gas and coke produced during Run 6 showed the composition given in Table 10.

TABLE 10.

Composition of Gas.				Composition of Coke.			
		%				Run 5.	Run 6.
Acid gases	0.13		Volatile matter	8.14	10.58
Oxygen	0.17		Fixed carbon	29.95	27.12
Olefines	0.36		Ash	61.91	62.30
Ethylene	0.18					
Carbon monoxide	0.18					
Hydrogen	0.45					
Methane	1.70					
Ethane and higher paraffins	..	1.10					
Nitrogen	0.68					
		<u>4.95</u>				<u>100.0</u>	<u>100.0</u>

Heat Balance on Run 6.

Heat of Reactants:

Heat of combustion of the shale = 7211.8 cal./gm. (observed).

Heat of Products:

Coke—

Volatile matter..	..	10.58	4.53	406.6 cal.
Fixed carbon	27.12	11.61	1123.6 ..
Ash	62.30	26.68	
		<u>100.0</u>	<u>42.82</u>	<u>1530.2 cal.</u>

Oil—

Mean of three determinations .. 52.26% 5661 cal.

Gas—

From gas analysis and calculation .. 472 ml. 4.95% 44.6 cal.

Heat Balance.

Shale	Oil + Gas + Coke.
100	52.26 + 4.96 + 42.82 (weight balance)
7212	5669 + 45 + 1530 + R
	24	
	<u>45</u>	

$R = 45$ calories/grm. of shale.
 $= 96$ cal./gm. of oil produced.
~~46~~

From the above results, which must be regarded as approximate only on account of the experimental errors involved, it may be seen that there is only a small quantity of heat transfer in the conversion of the shale into oil. The comparatively large amount of heat which is found to be necessary in the commercial retorting of shale is accounted for by heat losses and the low thermal conductivity of the shale.

The determination of thermal conductivity of shale is a matter of some difficulty in the present case as, owing to the low value of this characteristic, one face of the shale has to be maintained at a relatively high temperature, and this will always cause some decomposition. The thermal conductivity of American oil shale has been determined by McKee and Lyder (1922), for which they report a value of 0.00086 c.g.s. units. Winkler has recorded a result of 0.0005 as the thermal conductivity of Estonian oil shale, but he does not state whether it is air-dried or moisture free. As an interesting comparison, the following equations have been proposed by the International Conference in Pittsburgh in 1931 for the thermal conductivity of coals.

For a coking coal:

$$\text{Thermal conductivity} = 0.003 + 0.0016 \times 10^{-3}t + 0.0016 \times 6 \times 10^{-6}t^2.$$

For a middle gravity coal:

$$\text{Thermal conductivity} = 0.003 + 0.0013 \times 10^{-3}t + 0.0015 \times 10^{-6}t^2.$$

Cp. U.S. Bureau of Mines value = 0.0038 c.g.s. units [Gavin and Sharp (1920)].

SUMMARY.

Several salient features of torbanite pyrolysis have been investigated, and it has been shown that the oil is produced by the decomposition of a semi-solid intermediate phase, and there is no direct conversion of the original organic matter into crude oil and gas. The nature of this reaction is by no means regular—the two controlling factors in the nature of the oil produced are time and temperature. Values have been found for the following properties of the crude oil obtained from Glen Davis torbanite, viz., thermal expansion, viscosity, specific heat and heat of combustion, and in most cases

values have been determined also for the torbanite or oil shale as it is generally known.

ACKNOWLEDGMENT.

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subject matter of this paper does not deal with
Shale and therefore should be considered distinct
m the main scope of the work.

Hydrocarbon Polymerization and a New Method of Determining Catalyst Activity

By R. F. CANE, M.Sc., A.A.C.I.



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HYDROCARBON POLYMERIZATION AND A NEW METHOD OF DETERMINING CATALYST ACTIVITY.

By R. F. CANE, M.Sc., A.A.C.I.*

The process of catalytic polymerization of gaseous hydrocarbon mixtures containing a limited amount of olefins, predominately propene and butenes, consists of the passage of the gases under pressure over certain catalysts at medium temperatures to produce a controlled liquid product boiling within the gasoline range. Under these conditions the paraffins remain unchanged while the olefins polymerize to a liquid product termed "polymer gasoline," or more familiarly, "poly."

In plant practice, the gases, heated to 425 deg. C. and under a pressure of 1,150 lb. per square inch, are passed through reactors containing the catalyst, from top to bottom in cascade series and continuously cooled. The exothermic heat of reaction for polymerization is approximately 0.4 therms per lb. mole, and appears to be constant regardless of the types of molecules which combine.

The rate and nature of the polymerization reaction is influenced by pressure, temperature, and the moisture content of the gaseous charge, and all factors must be kept at optimum conditions in order to obtain maximum yields and catalyst life. Efficient operation will produce about 80 gallons per lb. of catalyst before it becomes non-functional. Loss in catalyst activity is primarily caused by the deposition of coke and high carbon tars on the surface of the catalyst particle. The tendency to form coke is promoted by the presence of higher hydrocarbons and incorrect moisture in the charge. The relationship existing between the liquid yield and the olefin content of the gaseous charge is shown in Fig. 1.

The catalyst itself consists of an active portion, e.g., ortho-phosphoric acid, and inert supporting material which may consist of kieselguhr, or other infusorial earths admixed with inert oxides of the alkaline earths such as alumina or magnesia.

Ortho-phosphoric acid is one of the most active polymerization catalysts, but if its temperature is allowed to exceed 450 deg. C., it tends to form inactive meta-phosphoric acid with loss of water. One form of catalyst consists of white cylindrical pellets, about $\frac{3}{16}$ inch in diameter and $\frac{5}{16}$ inch long, each weighing approximately 182 milligrammes.

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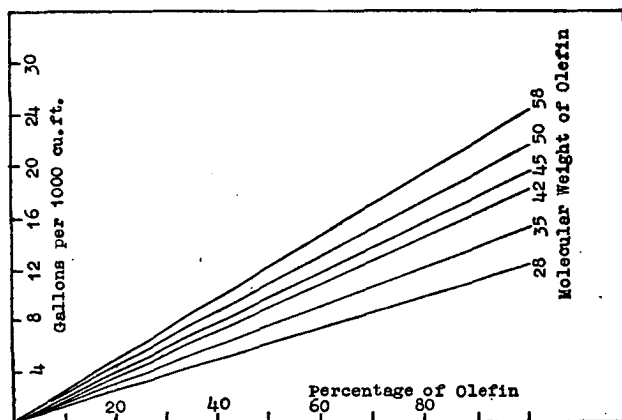
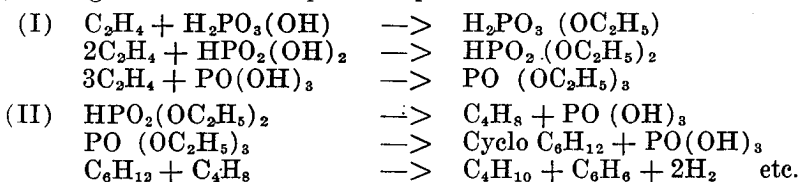


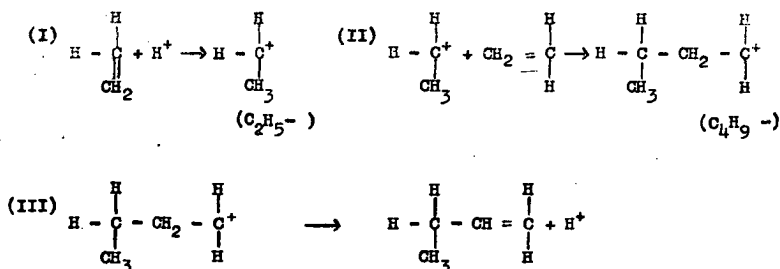
Fig. 1. Theoretical Liquid Yield Polymer Gasoline. (Data ex. U.O.P.)

In order to explain the formation of olefins, paraffins, naphthenes, and aromatics in the products of polymerization, Ipatieff (1) has formulated the following series of reactions as a possible explanation.

Taking ethene as a simple example:—



In contrast to the above, according to Whitmore (2) there is no esterification in which the phosphoric acid takes an active part, but the first reaction is the addition of one hydrogen ion to the molecule to form a free radicle which then combines with another unsaturated molecule to give a higher free radicle which by loss of a proton produces the stable olefin.



Unfortunately, neither of the above hypotheses gives a true picture of the reactions which occur, for 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene are found in the polymerization of isobutene by phosphoric acid, which is not explained by Ipatieff's formulation. Furthermore, polymerization will occur in the presence

of the acid anhydride in which no ionization can occur, proving that Whitmore's mechanism does not give a true explanation.

The rate of polymerization, apart from operational factors, is determined by the nature of reactants and the catalyst. Assuming that the charge and catalyst is of constant chemical composition, the reaction rate depends on the physical configuration of the catalyst particles and the rate of flow of the reactants and products over the active centres. These factors are determined by the size, porosity and surface area of the catalyst. The fundamental factor is the rate at which the reacting molecule leaves the main mass of the liquid and is absorbed on and into the catalyst at the active centres, polymerizes, and is then desorbed back into the liquid mass.

The Determination of Catalyst Activity.

The need for the present investigation arose because there is, as far as is known, no published method for determining the polymerizing power of a given catalyst sample. The test must be easily carried out, reproducible, and not time-consuming. It is impracticable to reproduce plant conditions of temperature, pressure, and other thermodynamical variables. In addition, the lower hydrocarbons are comparatively difficult to handle.

After some preliminary work, it was found that terpenes were readily polymerized by the catalyst at room conditions, and the exothermic heat developed by the reaction could be well correlated with the plant performance of the same batch of catalyst.

Some terpenes were tried and α -phellandrene was selected, although it was not the most active, since ease of purification and supply had to be considered. The phellandrene was purified by repeated distillation; traces of the β -isomer present did not affect the accuracy of the test.

The test was carried out as follows:—

Fifty millilitres of phellandrene were introduced into an efficient thermos bottle, of which the water equivalent and cooling correction were known. A standardized thermometer, reading 1/10 deg. C., fitting through the cork, was read after attaining thermal equilibrium.

Twenty grammes of the catalyst sample were introduced into the bottle, the contents gently agitated, a stop watch started and the temperature taken over one-minute intervals up to five minutes, and every five minutes thereafter to 30 minutes. It was found that the course of the reaction was accurately represented in most cases during the first thirty minutes by the general formula:—

$$\frac{d\theta}{dt} = Kt^{-m} \dots\dots\dots (1)$$

where θ = temperature rise.

K, m = constants

t = time.

In the case of fresh and moist catalysts the formula held up to

150 mins. Assuming that formula (1) is true, it can be seen that it is only necessary to take two readings to determine the curve.

After the reaction, the phellandrene was light yellow in colour; in addition, it was found that the catalyst had changed in colour from homogeneous white to a spotted heterogeneous reddish colour, the discoloration appearing in a few seconds.

Equation (1) may be integrated and rewritten in the form—

$$Q = At^n \quad \dots \dots \dots (2)$$

where Q = heat developed in cal./g.
 A, n = constants
 t = time in mins.

The following terminology is introduced in this paper: The constant A has been termed the *activity constant* and depends on the catalyst activity. The constant n is termed the *slope*; it is more or less independent of the activity and apparently depends on the nature of the poisoning (see Table 1).

It is further suggested that the term *activity number* (N), representing the time necessary for a given amount of heat to be generated (temperature rise in a known vessel), be used to state the catalyst activity. It is to be noted that the higher the catalyst activity, the lower the activity number thus defined, and *vice versa*.

The temperature at which the determination is carried out (within room temperature) was found to have some effect on the activity constant, but not on the slope. Using fresh catalyst it was found that approximately .1 unit correction had to be subtracted for every 1 deg. C. above 20 deg. C. In all the experiments herein described, the initial temperature of the reactants was maintained at 20 deg. C.

Activity of Fresh Catalyst

The relationship between exothermic heat per unit mass and time for fresh catalyst is shown in Fig. 2, curve A. The second curve, B, shows the same experiment taken over 5 hours, using a temperature recorder and thermocouple in place of the thermometer.

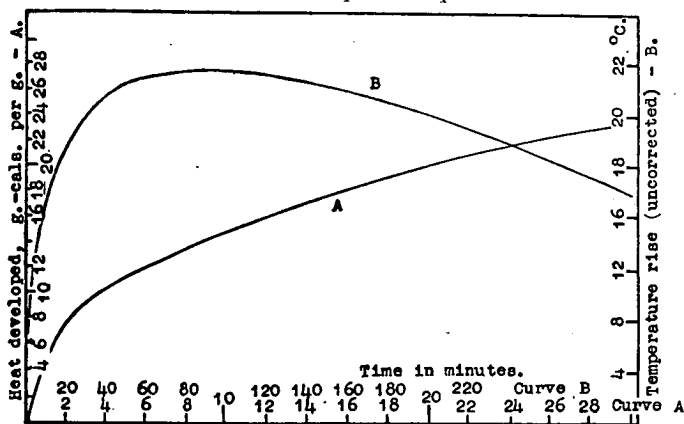


Fig. 2. Heat of Polymerization—Fresh Catalyst.

The plot of the relationship (curve A) on log paper showed a definite linearity; on account of later evidence this was corrected to a straight line with the following equation:—

$$Q = 6.14 t^4 \quad \dots\dots\dots (\text{curve 2; Fig. 3})$$

Activity of Moist Catalyst

The activity of the catalyst after taking up moisture to different degrees of hydration is shown in Fig. 3.

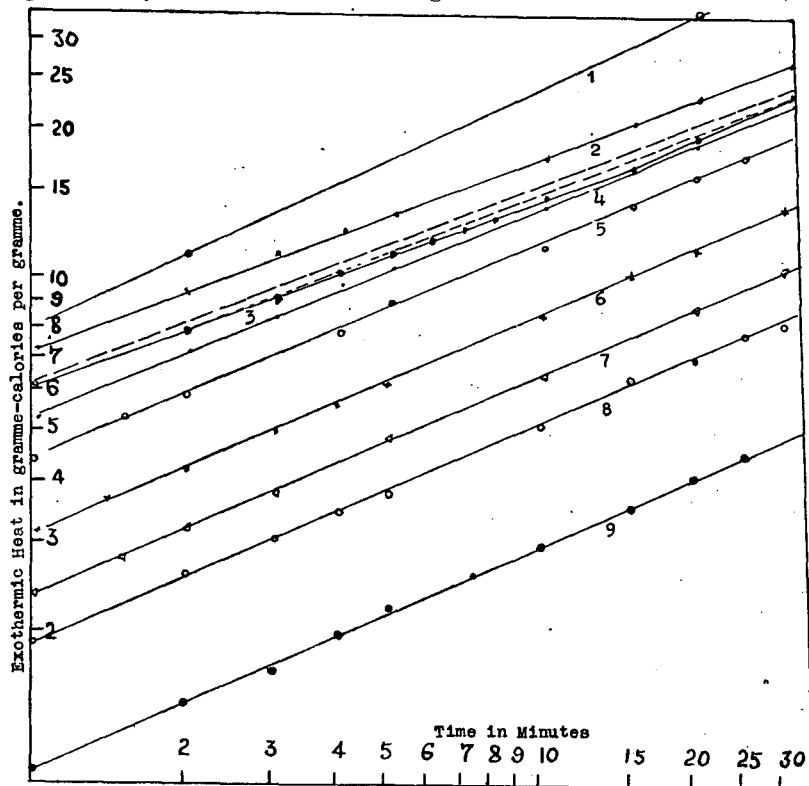


Fig. 3. Heat of Polymerization of Phellandrene with Hydrated Catalyst.

From the figure it may be seen that the plots are linear and nearly parallel. The equations to these lines are shown in Table 1 below.

Table No. 1.

Equation.	Per cent. Moisture	Activity Number (10 cal.)	Curve No. Fig. 3.
$Q = 6.14 t^{.40}$	fresh	3.4	3
$Q = 5.44 t^{.41}$	1.26	4.4	4
$Q = 4.50 t^{.43}$	2.00	6.4	5
$Q = 3.12 t^{.44}$	3.32	14.3	6
$Q = 2.37 t^{.44}$	4.38	26.4	7
$Q = 1.90 t^{.44}$	5.35	43.5	8
$Q = 1.06 t^{.45}$	8.70	147	9
cf. $Q = K \sqrt{t}$	—	—	1

In plant practice, the state of hydration of the catalyst is kept constant by injecting water into the polymer charge. The solubility of water in butane is shown in Table 2.

Table No. 2.

Temperature, deg. C.	Solubility w/w %.
5	0.0034
10	0.0041
15	0.0048
20	0.0054
25	0.0060
30	0.0064
35	0.0068
40	0.0069

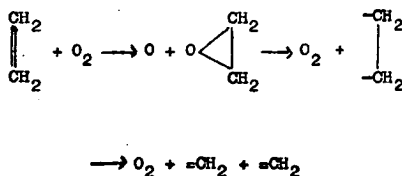
The Effect of Oxygen on Catalyst Activity

The reaction rate, using catalyst with adsorbed oxygen, was initially accelerated, but slowed down after some time.

The equation for the heat developed during the first thirty minutes only may be approximated by the empirical equation:—

$$Q = 7.4 \, t^{.37}$$

The acceleration of catalytic polymerization in the presence of oxygen has been treated by Lehner (3). Lehner postulated the formation of an intermediate oxide which then decomposed to yield a bivalent radical and free oxygen.



The Effect of Nitrogen Compounds on Catalyst Activity

The term "poison" refers to any substance which will decrease the activity of the catalyst, i.e., will reduce the number of active centres. In the catalyst under consideration, any basic body will have this undesirable effect, but under plant conditions only those compounds whose boiling point is less than approximately 20 deg. C. need be considered. This includes ammonia, methyl and ethyl amine. For the purpose of this investigation, under laboratory conditions, n-butylamine and ammonia were used.

The catalyst was poisoned with varying amounts of ammonia and butylamine, and the activity determined in the normal manner. The general form of equation (2) applied only when the introduced compound was not in excess of 0.05 per cent. w/w of the hydrocarbon.

The activity numbers thus measured with partly poisoned catalyst are recorded in Table 3.

Table No. 3.

Per cent. Basic Nitrogen	Activity Number (observed)
.1	11.4
.3	18.7
cf. Fresh Catalyst	3.4

In plant practice it is found necessary to wash the polymer charge with water to remove ammonia; four-tenths per cent. by weight is enough to render the catalyst inert.

Other nitrogen compounds were tried qualitatively; pyridine, secondary and tertiary amines, and nitriles had a depressing action, while nitro-compounds had little or no effect.

The Effect of Mercaptans on Catalyst Activity

The effect of small amounts of mercaptans in the polymer charge has resulted in some diversity of opinion; some workers maintain that the only result of mercaptans in the charge is to produce a "Doctor sour" gasoline, the liquid mercaptans in the polymer having been formed by the interaction of lower mercaptans and olefins. Other authorities are of the opinion that the introduced sulphur compounds have a direct deleterious action on the catalyst. However, it is normal plant practice when recycling butane to give it a caustic wash prior to recharging it to the reactors. Using the test described in this paper, it has been shown that mercaptans considerably increase the activity number of the catalyst. For example, one-half per cent. of mercaptan sulphur introduced into the charge reduced the activity constant by 2.3 units; double this amount reduced it a further 3 units.

Thus it may be seen that information on the state of a catalyst sample may be obtained by the laboratory method outlined above.

Whilst not professing to give exact quantitative data directly interpretable in lb./gallon catalyst life, this method serves to indicate the amount of useful life which may be expected from a given catalyst sample. It is hoped to carry this investigation to a further stage.

Acknowledgment

The writer acknowledges with thanks the permission by National Oil Pty. Ltd. for the publication of this paper.

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- (2) Whitmore, F. C.—*Ibid.* **26**: 94 (1934).
- (3) Lehner, S.—*J. Amer. Chem. Soc.* **53**: 3752 (1931); *Ibid.* **54**: 1830 (1932).

Appendix

Suggested Standard Test for Activity of Polymerization Catalyst.

(i) *Scope:*

This method of test is intended for the determination of the degree of activity of phosphoric acid catalyst when used to polymerize gaseous olefinic hydrocarbons to a liquid product.

(ii) *Definition:*

Activity is defined as the ability per unit mass of a catalyst sample to polymerize a given hydrocarbon compound, and in this test the activity is measured by the time required to produce a certain amount of heat, usually ten gramme-calories, the initial temperature of the reactants being 20 deg. C.

(iii) *Apparatus:*

The apparatus shall consist of the following:—

- (a) An efficient vacuum flask of known water equivalent and cooling characteristics. A small "thermos" bottle is entirely suitable.
- (b) A closely fitting cork with a suitable hole.
- (c) An accurate thermometer, preferably one reading in 1/10 deg. C.
- (d) A stop watch or clock with distinct second markings.

(iv) *Preparation of Sample:*

(a) *Catalyst.* The catalyst sample shall be representative and free from dust and foreign matter. Tarry material firmly adhering to the pellet surface shall remain in place, but individual masses of coke may be removed. The sample shall be stored in an air-tight dry bottle.

(b) *Phellandrene.* The phellandrene shall be purified by distillation until substantially free from the β isomer and other compounds. It shall be protected from standing in contact with air and shall be in an anhydrous condition.

(v) *Procedure:*

- (a) A 50-ml. sample shall be measured into the clean and dry vacuum bottle and brought to 20 deg. C.
- (b) Twenty grammes weighed to the nearest pellet of the prepared catalyst at 20 deg. C. shall be introduced into the flask in as short a time as possible and the stop watch started.
- (c) The contents gently agitated and the temperature recorded after every minute for the first five minutes and every five minutes thereafter until thirty minutes have elapsed.

(vi) *Calculation:*

- (a) A curve shall be drawn connecting the points taken and either by observation or calculation the time necessary to evolve 10 gramme-calories per unit mass of catalyst sample shall be recorded as the *activity number*.