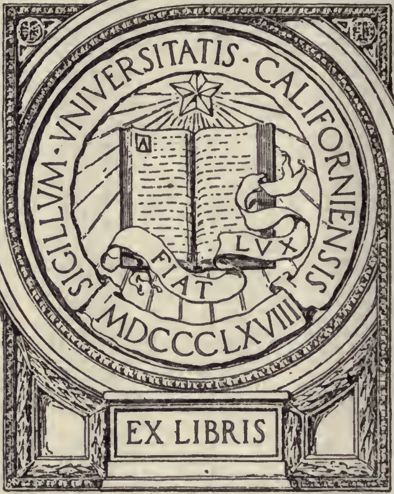
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The Thermal Decomposition of Oil Shales

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY
OF PURE SCIENCE, COLUMBIA UNIVERSITY

BY

Ernest Elmer Lyder, B.S., M.S., A.M.

NEW YORK CITY
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Department of Chemical Engineering
Columbia University

The Thermal Decomposition of Shales. I—Heat Effects

The methods of recovering oil from oil shales are discussed in so many recent articles that they need not be repeated here. Suffice it to say that, at present, the only known methods involve the principle of destructive distillation.[1,2,3,*] This being the case, some of the factors involved in the thermal decomposition of shale have been studied. The results of this research will be published in two papers. The present one deals with the manner in which the shale decomposes under the influence of heat, while the subsequent article describes a method for the determination of the heat of reaction involved when the organic material of the shale decomposes to form oil.

ORIGIN OF OIL SHALES

DEFINITION—Oil shale is defined[4] as an argillaceous or shaley deposit from which petroleum may be obtained by distillation but not by trituration or treatment with solvents. The term is also applied to those shaley deposits which are saturated with asphalt or petroleum and from which the bituminous matter can be removed by such solvents as carbon bisulfide and benzene, but the term, as ordinarily understood and in the sense in which it is used throughout this paper, excludes the oil-bearing shales and applies only to those which contain little or no bitumen soluble in the ordinary organic solvents.

The chemical composition of the oil-forming materials from which the oil is produced is little understood. Professor Crum Brown has given the name "kerogen" to the material in Scottish shale which, on destructive distillation, yields oil.[4] He defines it as neither petroleum nor bitumen, but a substance yielding petroleum and ammonium compounds on distillation.

NOMENCLATURE—Some confusion is apt to arise as a result of the designations of the various products formed one from the other. A bitumen is usually defined as a natural or pyrogenous hydrocarbon which may or may not contain oxygen, nitrogen, or sulfur, and which is largely

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[*] Numbers refer to bibliography on page 18.

soluble in carbon bisulfide. Abraham[5] calls the insoluble compounds, such as are found in shales, pyrobitumens. Engler[6] classifies as bitumens the whole series of products which are formed from the decomposition of vegetable or animal fats, waxes, or residues. This latter definition would include the insoluble substances, such as kerogen and pyrobitumens, as well as the soluble ones. Since the terms "kerogen" and "pyrobitumen" have been used to designate the insoluble substance, the word "bitumen" in this paper will be restricted to the soluble hydrocarbons.

INSPISSATED PETROLEUM—Little is known as to the origin or nature of kerogen or other organic material in the shale. That all of the organic or carbonaceous matter does not produce oil is known.[7] E. H. Cunningham-Craig attributes the origin of kerogen to inspissated or dried-up petroleum. He concludes that the oil shale stratum is a former oil-bearing formation which, under the action of heat, has evaporated and dried up, leaving petroleum residues which have become insoluble by polymerization.[4] Other authorities are not inclined to accept this theory, as they see no substantial evidence of petroleum having passed through the formation.

RESIN THEORY—H. R. J. Conacher,[8] on the basis of microscopic examination, describes the organic matter in the shale as (1) carbonaceous bits of plants with occasional small spores, (2) yellow bodies believed to be algae, spores, or oil globules, (3) shells of minute crustaceans, and bones, teeth, and scales of fish, and (4) sand grains. Shale portions rich in animal remains give small yields of oil. Those rich in vegetable remains give a greater yield of oil. The yellow bodies in the foregoing tests are considered vegetable matter. New Brunswick, Colorado, and Utah shales do not contain many of these yellow bodies. They are thought to be fragments of resins set free by decay and oxidation of materials of which they were once a part. Solubility of resins decreases with age; therefore the theory that failure to extract them by solvents proves that these bodies are not resins is of no value. Resinous materials from coal yield on oxidation the same products as obtained from torbanites.

Jones and Wheeler[9] report that by extraction of common coal with pyridine and reëxtraction of this extract with chloroform, coal can be resolved into cellulosic and resinic parts. On distillation of the former they obtained phenols, while the latter gave paraffins, olefines, and naphthenes.

ANOTHER THEORY—D. R. Stuart[10] is inclined to think that the kerogen may come from different kinds of organic matter, either animal or vegetable, by the action of microbes under special conditions, the product depending upon the microbe and the starting material. The kerogen, on the other hand, may be the remains of certain kinds of vegetable matter, like pine pollen or lycopod spores. He actually prepared oils very similar in properties to shale oil by the distillation of a mixture of 75 per cent fuller's earth and 25 per cent lycopodium spore dust.

ORGANIC REMAINS—Engler[11] chooses to fit the origin of the pyrobitumens of shales into the whole scheme of bitumen and petroleum formation from organic remains, successive polymerization and decomposition playing a very important part both in the character of the petroleum and in the bitumen formed.

By the decay of fats, waxes, and other animal and plant remains there are produced free fatty acids, wax esters, and hydrocarbons of the type of adipocere, montan waxes, and, perhaps, ozokerite. These are soluble in benzene, carbon bisulfide, etc. Part of this material may condense and polymerize to form what Engler chooses to call polybitumens. These are infusible and insoluble, and are found in nature as the insoluble part of the Scottish, Austrian, and Autun shales. These, under the action of heat, may go over to soluble bitumens, small amounts of which are always found in the shale, and which may also be found in nature as malthas, etc. Disintegrating further under the action of heat and pressure, these compounds go over to natural petroleum as we find it in wells, and this, on polymerization, yields the heavy asphalts.

CLASSIFICATION

Shales differ considerably among themselves. Upon destructive distillation, they yield products differing in character even though they be produced under similar conditions. It is estimated that Elko Nevada shales will produce paraffin wax to the weight of 35 per cent of the total oil recovered, whereas the New Brunswick shale oil contains but little paraffin. The oil from the latter resembles California crude. An attempt to classify the various hydrocarbons in these shales leads to some confusion, but a partial classification on the basis of solubility in organic solvents and chemical composition is possible.

The pyrobitumens, which form bitumens on heating, may be further subdivided into one class which contains little or no oxygen and another which does contain oxygen. Those in the first class are called asphaltic pyrobitumens because they resemble asphalts, which contain but little oxygen. They are infusible and insoluble, and include elaterite, wurtzellite, albertite, imposinite, and asphaltic pyrobituminous shales. The New Brunswick, Nova Scotia, and Quebec shales are of this type.

The nonasphaltic pyrobitumens are those which contain oxygen and oxygenated bodies, but are also insoluble and infusible. Into this class fall cannel coals, lignites, torbanites, and shales containing torbanite material. The Scottish shale belongs in this category.

DISTRIBUTION

Oil shales occur in various parts of the world in apparently unlimited quantities. In Scotland the shale oil industry dates back to 1850.[12] France began to develop shales in Autun even before the Scottish industry existed. New Zealand has several times attempted to use them.[13] In Australia several large deposits and some very rich shales occur.[14] In Tasmania there are extensive deposits.[14] In Africa there are shales in the Transvaal and in Portugese East Africa.[15] Spain and Serbia also have oil shales.[13] In the western hemisphere they are to be found in various parts of South America,[13] in Canada,[16, 17, 18] and in the United States.[19] None of these enormous deposits, except the Scottish oil shales, have, as yet, been worked with complete success.

The oil shales of the United States rival in quantity the known coal deposits. There is sufficient oil obtainable from the shales of Colorado, Wyoming, and Utah to supply the United States for several generations.[20] Colorado alone has enough shale to produce 58,000,000,000 barrels of oil.[21] When it is remembered that less than 8,000,000,000 barrels of oil have been taken from wells in this country since the first well was drilled in 1859, the quantity of oil available from these shales begins to be appreciated.

Although attention is, at present, centered on the oil shales of Colorado, Utah, Wyoming, and Nevada, it is only because these are exceptionally rich in oil-forming material. Other deposits exist,[22] and as methods are perfected for working shales the poorer ones will, no doubt, be utilized. In Kentucky there are quite extensive shale beds which, though not quite so rich as the Colorado shales, yield more oil than those being worked in Scotland at present.

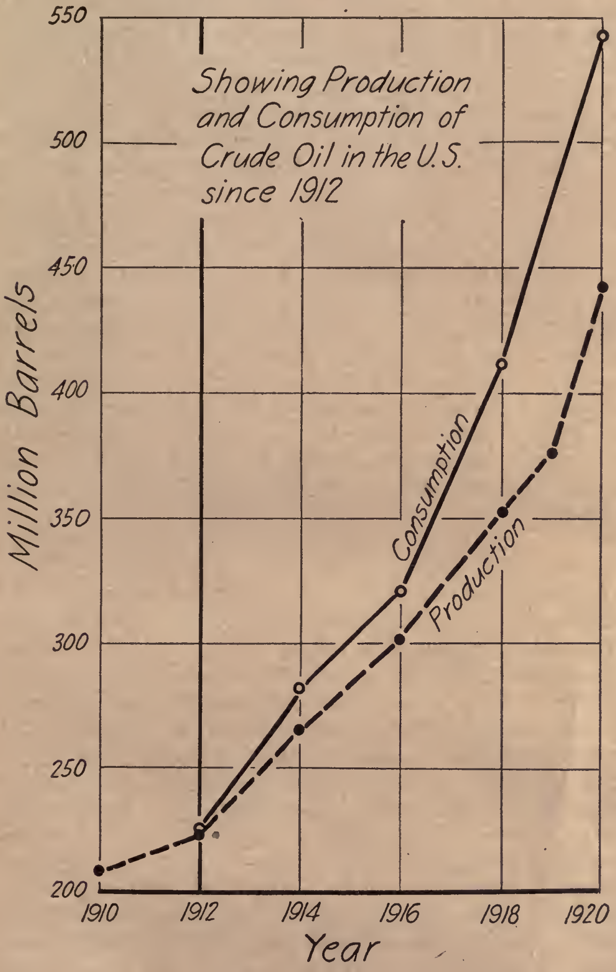
The enormous quantities of shale available for oil production is the factor that continually encourages investigation in the face of all the difficulties surrounding the problem.

THE PETROLEUM SITUATION

In view of present-day statistics it must be admitted that the future of petroleum in the United States is not encouraging. The figures for 1920 show that some 110,000,000 barrels of oil were imported to make up the deficit in home production. Fig. 1 illustrates the situation as it stands.

While as yet the maximum production of petroleum in this country has not been reached, it will be seen that the consumption is much greater than the production, and the consumption is expected to increase. It was in 1895 that the first commercially practical automobile was demonstrated, and at the beginning of 1920 there were 8,000,000 automobiles, 1,000,000 trucks, and 300,000 tractors in use. Further, it is expected that by the end of 1921 there will be 9,000,000 automobiles and trucks, and 450,000 tractors in use. Aerial navigation is yet ahead, but may be expected soon to consume large quantities of particularly high-grade motor spirit.

That oil shale can be utilized to make up the deficiency caused by the increased consumption of petroleum is the opinion of our best authorities on the subject. In this connection we may quote Dr. Dean E. Winchester,[23] formerly of the U. S. Geological Survey:



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After spending nearly five years in studying the oil shales of the western part of the United States, I am thoroughly convinced that the day is not far distant when these very shales that the cattlemen and farmers of the Rocky Mountain region have sworn at so often because they make neither good farm land nor good range, will yield oil in sufficient amounts to prevent the rapid decline on our total production which is imminent if no new source of petroleum is developed. There seems to be every indication that in the near future (perhaps ten years) there will be established in Colorado and Utah an industry for mining and distilling of oil shales which will rival in size any mining or manufacturing industry in the United States.

FIELD OBSERVATION

An inspection trip to the Colorado, Utah, and Nevada districts during the summer of 1920 revealed the fact that considerable work of a certain nature is being done toward the development of these shales. Several retorts have been built in the field, but none of them are operating in any regular way. Some are small one-unit plants operated for demonstration and experimental purposes only. Some of the schemes will probably never work and are intended more for promoting purposes and the sale of stock than for actual production of oil. Others are making every effort to produce a retort which will successfully distil these shales. Almost all of the development seems to be toward the perfecting of a retort which will produce oil, without consideration of the character and quality of the oil produced. None of the oil is, as yet, being refined, and when refining operations are begun it is quite probable that the oil will be found deficient in quality, and some of the retorts that are furthest advanced, at present, may have to be redesigned completely to meet the necessity of producing a marketable oil. Let it be said that this does not apply to all of the plants in the field. Some are studying all of the conditions, each one in its proper relation to the other, and are making definite progress.

THERMAL DECOMPOSITION OF SHALES

Oil shales are but little soluble in organic solvents, as has been pointed out. They are not, therefore, hydrocarbons of the type of gilsonite,[24] grahamite,[24] ozokerite,[24] or asphalt. Shales must be distilled to recover the oil and ammonia products from them. The oil is said to come from a specific pyrobituminous material, and not from the entire organic remains in the shale. From Scottish shale, oil is said to come from kerogen. In any case, upon destructive distillation of a number of different kinds of pyrobituminous substances, hydrocarbons of the nature of paraffins, olefines, and aromatics are produced.[7, 25]

The hydrocarbons, when distilled off and fractionated, yield low-boiling, intermediate, and high-boiling fractions, just as do naturally occurring petroleums. Many retorts have been designed to distil these shales, and each is based on the designer's conception of the manner in which the shales decompose. For the most part the idea seems to be prevalent that, upon breaking down, the kerogen or other pyrobitumens yield, directly, petroleum oils. Many think that they yield, first, gasoline-like products; second, heavier products, such as kerosene; next, gas oil; and so on as the temperature increases. Others believe they yield a wide range of products directly, that is to say, each molecule of kerogen will decompose into gasoline, kerosene, etc., in essentially one step In this case the gravity of the oil should not appreciably increase as the temperature rises. It has been demonstrated in this work that neither of the above conceptions is correct. The first product of decomposition was found to be a heavy semisolid or solid bitumen which is soluble in benzene and carbon bisulfide, and it was found that the formation of the petroleum oil is a result of the cracking of this heavy bitumen. This is in accord with Engler's deduction[26] that certain pyrobitumens, when heated to certain temperatures, become soluble in organic solvents. Table I shows some of the results of the decomposition of materials of this nature.[27]

TABLE I—INCREASE IN SOLUBILITY OF SHALE UPON HEATING

	Soluble in Benzene				
Source	Before Heating Per cent	Temp. °C.	Duration	After Heating Additional Per cent	
Posidonomya shale from Reutlingen	0.6	250	24 hrs.	0.34	3.58
		300	Additional 24 hrs.	3.24	
		400	Additional 24 hrs.	0.00	
Menilite shale from Strzytki, Egst. Glacia	0.85	300	0.5 hr.	1.21	2.31
		350	Additional 24 hrs.	0.70	2.06
		350	Additional 24 hrs.	0.40	
Shale from N. S. Wales, Australia	1.40	250	2 days	1.33	
		250	Additional 8 days	0.73	
Shale from N. S. Wales, Australia	1.40	300	2 days	28.50	36.3
		300	Additional 8 days	7.80	
Shale from N. S. Wales, Australia	1.40	400	1 hr.	4.90	55.2
		400	Additional 2 hrs.	44.90	
		400	Additional 2 hrs.	5.40	
		400	Additional 2 hrs.	0.00	

If this deduction is correct it is of considerable importance, and if proved experimentally would define methods for shale distillation superior to the ones now used. Experimental work was carried out as follows:

EXPERIMENTAL METHODS—The finely ground shale, 60-mesh, was placed in a 2-in. iron tube, 20 in. long. The tube was capped at both ends and fitted with a pressure gage. The whole was placed in a rotary-type, gas-heated furnace in which it was possible to control the temperature very accurately. A base-metal thermocouple was also placed in the tube with the shale. The shale was heated in this apparatus for periods of time ranging from 1 to 8 hrs. It was then taken out and examined, and the amount of soluble material in it was determined. Observations were made on the temperature and pressure as the heating progressed.

It was found that in some cases when the shale was heated for 6 hrs. around 390° C., no apparent change occurred. Little gas was given off, as was indicated by the fact that the pressure remained around 25 or 30 lbs. per sq. in. Slight increase in solubility was noted, but the shale in general maintained its hard, rubber-like texture. In other experiments only a few degrees higher (394° to 398°), and in one case at the same temperature, decided changes were noted. The pressure suddenly rose after the shale became heated up, and remained around 100 lbs. per sq. in. The product was a black tar-like mass with the shale residue suspended in it. Upon extraction with benzene this yielded 30 to 40 per cent of soluble material, as compared to 1.5 to 2.9 per cent on the original shale.

It was not possible in these experiments to keep the tubes entirely tight, and some gas and vapors usually escaped. This rendered the results inconclusive. Although a heavy product was obtained, as was expected, it could easily have been the result of the light vapors having been lost by distillation, but the results did show that a decided change was taking place in the shale, and this at a quite definite temperature.

The pyrometer used in these determinations was of the ordinary base-metal type and was, unfortunately, equipped with a relatively low resistance indicator, which rendered the results somewhat questionable. On this account other means of studying the changes that were taking place were adopted.

The final method was to distil the finely pulverized shale under atmospheric pressure in a small, electrically heated, brass retort, shown in Fig. 2. This apparatus had the advantage that the temperature could be controlled accurately and could be measured to within the experimental error of the mercury thermometer. Also, it was desirable that the distillation be made under atmospheric pressure.

The run was made as follows: About 25 g. of shale were placed in the retort. After the temperature of the metal bath had reached that at which it was desired to make the run, the retort was set in place and allowed to heat for 1 hr. 20 min. The temperature was measured by means of a 500° C. nitrogen-filled mercury thermometer placed in the bath. In one run thermometers were placed both in the retort and in the metal bath in order to determine the temperature lag through the shale. It was found that the center of the retort attained the temperature of the bath within 20 min.; hence, in order that all the shale might stay at the desired temperature for an hour, the heating was continued for 1 hr. 20 min. Preliminary tests had shown that if the shale did not decompose at a given temperature within an hour it could be heated at that same temperature for several hours with no apparent change. During the determination the thermometer was not used in the retort, as shown in the figure, but was placed directly in the bath. It was only the highest temperature that was of interest and, of course, this could be more easily obtained in the bath than elsewhere. The oil that distilled over was caught and measured.

After the shale had been heated for 1 hr. it was removed from the retort and extracted in a Soxhlet extractor with carbon bisulfide to remove the heavy oil or bitumen which had formed but had not distilled over. This bitumen was freed from carbon bisulfide by evaporation, and weighed.

Several runs were made, varying the temperature by small increments each time.

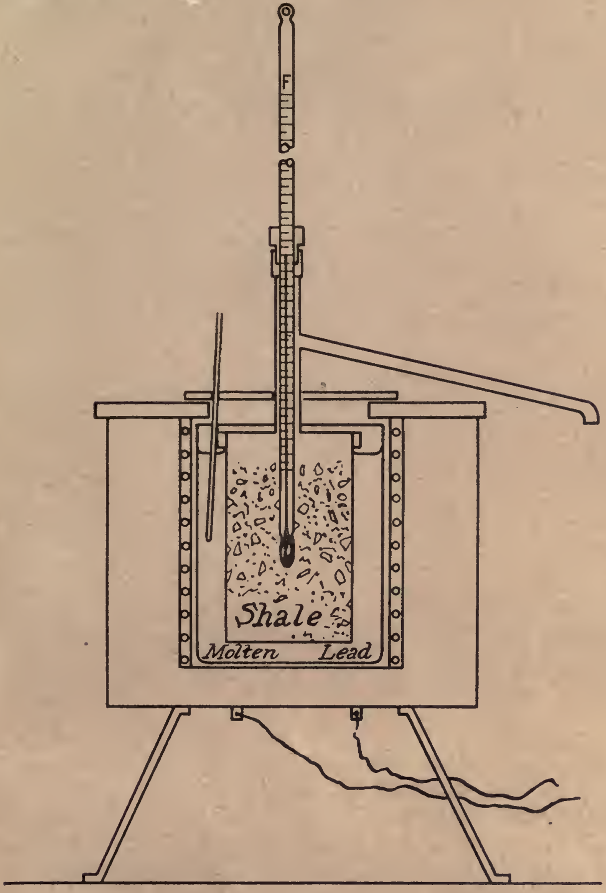

FIG. 2

DETERMINATIONS—The shale used was from the Parachute Creek district near Grand Valley, Colorado. It had the following properties.

MASSIVE TYPE SHALE

Specific gravity	1.60
Specific heat	0.25
Moisture, per cent	0.13
Volatile matter, per cent	53.90
Ash, per cent	47.00
Oil yield per ton, gal.	63.50
Solubility in CS_2, per cent	1.96

Run 1—This run was made as described above, with the bath kept at from 373° to 375° C. Eighty-five hundredths of a gram of oil distilled over and 1.45 g. of heavy bitumen were extracted from the residue. The shale was but slightly changed in appearance, and had not lost its hard massive texture.

Run 2—This run on 24 g. was like the previous one, except that the temperature was kept at 384° to 386° C. One and three-tenths grams of light oil were obtained, with 1.52 g. of heavy bitumen. Little change was seen in the general appearance of the shale; it was, however, slightly darker.

Run 3—This run was made at 398° to 400° C. One and seven-tenths grams of light oil were collected and 1.9 g. of bitumen. No noticeable difference had occurred in the appearance of the shale.

Run 4—A run at 425° C. yielded 4.2 g. of light oil and 4.93 g. of heavy bitumen. The character of the residue was decidedly changed. It was a dry coke-like mass which could be easily pulverized with the fingers to an impalpable powder, the original hardness and general character of the shale having been entirely destroyed. The specific gravity of the bitumen recovered was about 1.

Run 5—This decided change within 25° suggested that valuable information might be gained by taking an intermediate step. In a run made at 410° C., the amount of light oil was 2.55 g., and the amount of bitumen was 6.4 g. This bitumen, when extracted and dried, was of a rather rubber-like texture. The residue left in the retort before extraction was not a dried coke mass as in Run 4, but a sticky, tarry conglomeration which held together quite tenaciously. The following are the tabulated results of the five runs:

	Temp.	Light Oil		Heavy Oil (Bitumen)		Total Oil	
RUN	°C.	G.	Per cent	G.	Per cent	G.	Per cent
1	374	0.85	3.4	1.45	5.7	2.30	9.1
2	385	1.30	5.3	1.52	6.2	2.82	11.5
3	399	1.70	7.0	1.90	7.9	3.80	14.9
4	425	4.20	16.8	4.93	19.6	9.13	36.4
5	410	2.55	10.2	6.40	25.6	8.50	35.8

No correction has been made in these figures for the original 1.96 per cent soluble in carbon bisulfide before heating. The figures would, of course, bear the same relation to each other as is shown above. Fig. 3 is the graph of these various factors.

INTERPRETATION OF RESULTS—The interpretation of the results of the experiments just described is plain and important. As the temperature rises in each successive determination, increasing amounts of oil are produced, but the quantity is rather small. At between 400° and 410° C. the curve suddenly rises, showing a complete destruction of the insoluble kerogen bodies in the shale. The temperature limits are seen to be close. This would indicate that the kerogen has a decomposition temperature which is definite to within 10° C.

Although it is seen from the curves that light oil is always produced, more of the heavy bitumen than light oil is produced at the lower temperatures. At the temperature of decomposition, *i. e.*, where the curve starts abruptly upward, by far the largest part is heavy bitumen, and during decomposition large quantities of heavy oil are produced, with no corresponding increase in light oil. If light oil had been directly produced from the kerogen, its curve would have followed the heavy bitumen curve.

CRACKING OF SHALE OILS

Another item of importance in connection with these decompositions is that the shales decompose at temperatures above the point where cracking will take place to a limited extent. It is seen that even at 375° C., where the decomposition of the kerogen was relatively slow, some light oil was formed, but cracking became rapid at almost the same temperature as that at which the shale decomposes.

The break and descent of the bitumen curve with no change in the total quantity of oil show conclusively that the heavy bitumen is decomposing to form light oils.

Another important point is noted here. Various distillations of this Colorado shale, either in 2-lb. lots or 20-lb. charges, under the most careful conditions, yielded 63 gal. of oil per ton. The oil obtained had a specific gravity of 0.921, which means 480 lbs. of oil. Add to this 20 lbs. of gas obtained, and we have 500 lbs., or 25 per cent of product per ton of shale. The amount of product obtained when the shale was heated just to its decomposition temperature was 36 per cent, or 720 lbs. per ton. If all this could be converted into oil of 0.921 specific gravity, it would yield 91.5 gal. of oil per ton. There would, of course, be a cracking loss if the tar were converted into light oils after its removal by solvents. This calculation is included to show that the maximum hydrocarbon yield is not produced by the present method of distillation and that it is the phenomenon of cracking that produces the light oils with which the industry is familiar.

These deductions place shale oil on the same basis as cracked products from naturally occurring petroleum. It has been shown that little or no gasoline is obtained from shale as a primary product. The gasoline and other light cuts from shale oil are in many respects similar to gasoline obtained by cracking petroleum. They are highly unsaturated; the boiling point is low for a given gravity compared with that of paraffin hydrocarbons; they are a mixture of paraffins, olefines, and aromatics.[7,25] This would indicate that shale oil must compete with cracked products as to supplying gasoline. If these heavy residua can be cracked to produce motor fuels, other heavy residua can also be utilized for the same purpose. Development will be along the lines of improvement of cracking processes adaptable to such oils.

Another phase of the situation is that, although gasoline is the product most in demand and the tendency is to convert other fractions into it, all of the crude cannot be used in this way, because other fractions, such as kerosene, gas oil, lubricating oil, fuel oil, and wax, are also needed. Consequently, it is the shortage in crude, and not that of gasoline, which threatens. As high-grade oils (those containing large percentages of gasoline) decrease, more gasoline will have to be produced by the cracking of heavy fractions of low-grade oils. As cracking processes improve and heavy oils are more in demand, shale oil will compete favorably as a product which can be worked up into motor fuel.

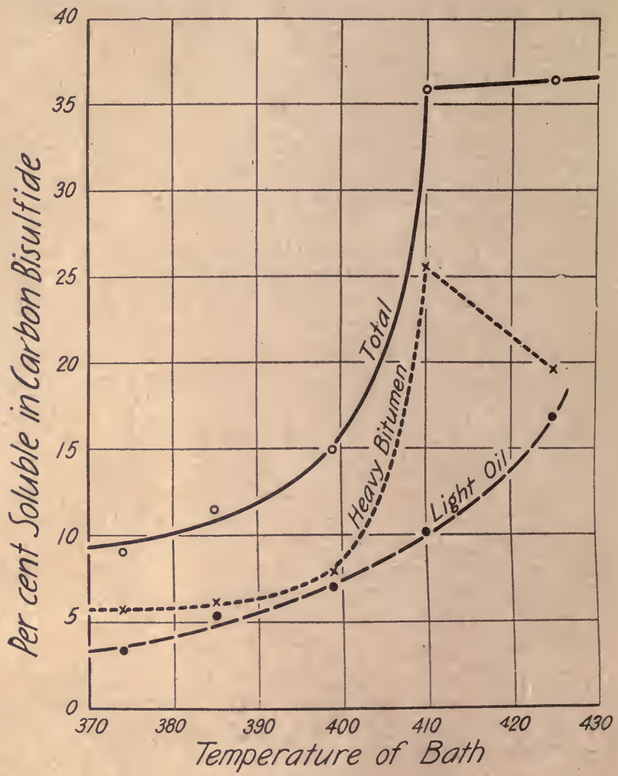

Fig. 3

This conception has an important bearing on the commercial distillation of oil shale. It shows that there is a certain minimum temperature (which will probably vary with each shale) below which it is useless to heat and expect to recover oil at any reasonable rate. Also, when the temperature is held within the decomposition range, no gasoline is produced as a primary product. It is fallacy to say that a certain retort will yield a given amount of gasoline as a primary product. The retort should be looked upon as an apparatus for the production of heavy residua, while its efficiency as a gasoline producer should be based on its adaptability to convert these heavy oils to motor fuel. It is not meant to convey the idea that this bitumen or primary product should be removed by solvents before cracking; in fact, it is more than probable that the most effective way to crack it is while it is yet mixed with the shale residue, but the whole problem of the production of light oils should be approached from the point of view of the cracking of heavy oils.

With this information as a guiding principle, a conclusion may be reached as to the relation that shale oils will bear in making up the shortage due to the increased consumption of petroleum.

It has been shown that the light oil is obtained by the cracking of heavy products which are formed when the shale is heated to a quite definite temperature. This means that the shale retort of to-day which produces light oils is being used as a cracking still. A little consideration will show that it may be made a very efficient one.[28]

Here is a hydrocarbon formed from the decomposition of microscopic particles of material disseminated throughout a mineral mass, and this hydrocarbon is formed near the temperature at which it is subsequently cracked to form light oils. This insures uniform distribution of heat not usually met with in ordinary processes. Further, one of the most difficult problems attending the cracking of oil is the removal of the carbon formed and deposited in the still. In the Rittman process it is continually scraped down by the revolving of chains. In the Burton still it is caught on the false bottoms of the still and thus prevented from caking on the heated zone. In the case of a shale retort such, for instance, as those used in Scotland, it is being continually removed by means of a mass of mineral matter so great that the amount of carbon is insignificant.

Without the use of steam in these retorts a high oil-yielding shale will yield about 12 per cent of carbon, which will remain in a perfectly dry, finely divided condition disseminated throughout an equally dry mineral mass. This moves through the retort without difficulty, and no carbon troubles are encountered.

It is not necessary to limit the amount of bitumen passing through the retort to that which is contained in the shale. Other heavy residua, such as bottoms from previous runs or from petroleum oil, could be injected into the retort and cracked to light oil along with the shale residua. The carbon residue would be materially increased, which is desirable because it could then be used in the production of water gas or as a fuel direct. Shale residues from the straight distillation of shales are, at present, used in a gas producer for the production of fuel for retorting.[21] They are also being used as solid fuels. It need not be emphasized that additional carbon would make them more valuable.

CONCLUSIONS

It has been shown that the pyrobitumens do not decompose to form petroleum oils as a primary product of decomposition, but that the first substance obtained is a heavy solid or semisolid bitumen. This bitumen is formed at a quite definite temperature, the formation taking place between 400° and 410° C., in the case of this particular shale. The petroleum oils formed from the shale are the result of the decomposition or cracking of the heavy bitumen.

BIBLIOGRAPHY

1—Thomas Clarkson, "Facts about the Shale Oil Industry," *Oil and Gas J.*, **17** (1919), 60, No. 52.

2—M. J. Gavin, H. H. Hill and W. E. Perdew, "Notes on the Oil Shale Industry," Bureau of Mines, *Bulletin*, **1919.**

3—Greene, "Oil Shales."

4—E. H. C. Cunningham-Craig, "Kerogen Shales," *Chem. Trade J.*, **58** (1916), 360.

5—Herbert Abraham, "Asphalts and Allied Substances," **1918,** 158.

6—C. Engler, "Das Erdöl," **1** (1917), 35.

7—H. R. J. Conacher, "The Scottish Oil Shales," *Petroleum Rev.*, December **1916,** 509.

8—H. R. J. Conacher, "Oil Shales and Torbanites," *Geol. Soc. Glasgow*, Dec. 14, **1916,** 164; *Geol. Mag.*, **4** (1917), 93.

9—D. T. Jones and R. V. Wheeler, "Composition of Coal," *J. Chem. Soc.*, **109** (1916), 767.

10—D. R. Stuart, "Chemistry of the Oil Shales," "Oil Shales of the Lothians," Part 3. *Scotland Geol. Sur. Mems.*, **1912,** 136.

11—C. Engler, "Formation of the Chief Constituents of Petroleum," *Petroleum*, **7** (1912), 399; *C. A.*, **6** (1912), 1221.

12—H. M. Cadell and Grant Wilson, "Geology of the Oil Shale Fields. The Oil Shales of the Lothians," Part 1. *Scotland Geol. Sur. Mems.*, **1912,** 1–97.

13—Hardy W. Mansfield, "Oil Shales and Their Occurrence," *Petroleum Rev.*, **34** (1916), 159, 199.

14—Hardy W. Mansfield, "Oil Shales," *J. Inst. Petroleum Tech.* (London), **2** (1916), 162.

15—"Transvaal Oil-Shale Deposits," *Min. World*, **34** (1911), 74–75; *Petroleum Rev.*, **24** (1911), 147–148; *C. A.*, **5** (1911), 783.

16—J. W. McGrath, "Oil Shales of Newfoundland," *Petroleum Rev.*, **33** (1915), 209; *Can. Min. J.*, **36** (1915), 493.

17—"Bituminous Oil Shales in Canada," *Min. World*, **37** (1912), 202.

18—R. W. Ells, Can. Dept. Mines Joint Report on the Bituminous Oil Shales of New Brunswick and Nova Scotia; also on the Oil Shale Industry of Scotland, **1909.**

19—Dean E. Winchester, "Oil Shale in Northwestern Colorado and Adjacent Areas," U. S. Geological Survey (Contributions to Economic Geology), *Bulletin*, **641-F** (1916), 139.

20—G. E. Mitchell, "Billions of Barrels of Oil Locked up in Rocks," *Geog. Mag.*, **33** (1918), 194.

21—V. C. Alderson, "The Oil Shale Industry," **1920,** 31.

22—G. H. Ashley, "Oil Resources of the Black Shales of the Eastern United States," U. S. Geological Survey, *Bulletin* **641** (1917), 311.

23—Dean E. Winchester, "Oil Shales," *J. Frank. Inst.*, **87** (1919), 689.

24—C. Bardwell, B. A. Berryman, T. B. Brighton, K. D. Kuhre, "Chemical Properties of Utah Hydrocarbons," *Trans. of Utah Acad. of Sci.*, **1** (1913), 78.

25—A. H. Allen, "On the Relative Proportions of Olefines in Shale and Petroleum Products," *Analyst*, **6** (1881), 177–180.

26—C. Engler, "Formation of the Chief Constituents of Petroleum," *Petroleum*, **7** (1912), 399–403; *C. A.*, **6** (1912), 1221.

27—Herbert Abraham, "Asphalts and Allied Substances," **1918,** 57.

28—R. H. McKee and E. E. Lyder, U. S. Pat., Application No. 381,440.

II. Determination of the Heat of Reaction Involved in Their Thermal Decomposition

The solution of the problem of the recovery of petroleum oils and other products from the so-called oil shales of this country must be based on exact information, such as the values of all the physical constants involved, a knowledge of the manner in which the oil-forming material decomposes, and information as to the character of the product obtained under varying conditions. Also, since it is apparently established that the only way to recover petroleum oils from shales is by thermal decomposition,[1,2,3*] a study of the heats involved and the primary effect of heat on the shale is evidently most essential to the intelligent development of the industry. It has been the object of this research to study these hitherto little known factors in relation to their bearing on commercial retorting.

A method has been devised for the determination of the amount of heat involved in the conversion to oil of the organic material in the shale, and the value has been determined on three quite different types of shale. It was found that these values for the three shales used ranged from 421 to 484 cal. per g. of oil and gas produced.

The heat conductivity of the shale has been determined for this work, and the coefficient of thermal conductivity has been found to be 0.00086, expressed in c. g. s. units.

The specific heat has been determined and found to be around 0.265 for most shales.

Part I of this paper has shown that certain fundamental conceptions as to the manner in which the organic material decomposes are different from those ordinarily accepted. The hitherto generally accepted explanation of the manner in which these shales decompose is that, under the influence of heat, the organic material breaks down from a high-molecular-weight, insoluble substance to form petroleum-like hydrocarbons. These hydrocarbons increase in density and boiling point as the temperature rises, that is to say,

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* Numbers refer to bibliography on page 36.

the first product of destructive distillation of shale is the light hydrocarbon oil corresponding to gasoline in physical properties. The next is a somewhat heavier product like that found in the kerosene fractions, and the next still heavier, and so on until, finally, heavy residuents, such as fuel oil and paraffin, are produced. Part I has also shown that the organic material does not decompose as above outlined, but that its first product of decomposition is a heavy solid or semi-solid bitumen soluble in carbon bisulfide, whereas the original material was but very slightly soluble. The production of petroleum-like oils is, then, the result of the decomposition of these heavy bitumens by cracking.

The importance of this idea is that it places the production of oil, especially gasoline, from shales in the same category as the production of gasoline from the cracking of other oils. It should, therefore, promote the design of a shale retort along this line.

At the beginning of this work little or nothing was known as to the amount of heat required to convert to hydrocarbons the pyrobitumen of the shale. It was not even known whether the reaction was endothermic or exothermic, and, as this could easily be a factor of prime importance in the design of a retort, it was decided to determine it experimentally. The design of the apparatus and the method of determining this constant are described in this paper. Also, there have been included data on other heat factors, such as specific heat and heat of vaporization. Additional information can be obtained on these and other constants by consulting the original articles referred to.

HEAT FACTORS

In the design of a retort it is desirable to know the quantity of heat that must be added to bring the shale to the distillation temperature, to cause a decomposition of the organic matter, and to distil off the products.

SPECIFIC HEAT—The specific heat will vary according to the composition of the shale. It could not be expected that the specific heat of all shales would be the same, when it is considered that the shales are mixtures of mineral constituents of varying proportions, through which an organic material is disseminated, also in varying proportions. The specific heats of certain shales are tabulated below.

SUBSTANCE	Specific Heat	° C. Temperature Range	AUTHORITY
DeBeque Shale	0.265	20–90	Bureau of Mines[4]
Parachute Shale	0.242	20–90	Bureau of Mines
DeBeque Shale	0.273	18–90	McKee and Lyder
DeBeque Shale	0.280	20–90	McKee and Lyder
(Shale Residue)	0.223	20–90	Bureau of Mines

In this work the method used was the simple method of mixtures as ordinarily applied. The average of the raw shale, which is probably as accurate as is necessary, is 0.265.

HEAT CONDUCTIVITY—The heat conductivity of the shale should be expected to vary with composition as does the specific heat. At our request, this constant was determined on four samples of Parachute shale by the Bureau of Standards at Washington, D. C. The method used was one that they have devised for the determination of the heat conductivity of poor conductors, such as asbestos board. It should be quite accurate. Briefly, the method consists of placing a slab of material in the side of a well insulated box, heated from the inside, and comparing the loss of heat, with the sample in place, with that of a sample of material of the same dimensions whose conductivity is known. The samples for the experiment were prepared by having a stonecutter saw them from a large lump of shale. They were cut 7 in. square and 0.75 in. thick. The slabs were so cut that in conducting heat from one face to the other the heat would pass perpendicular to the stratification of the shale. The coefficient of conductivity as determined on the samples was 0.00086 (c. g. s. units). This shows that the shale is four times as good a conductor as paraffin (0.0002), about one-third as good as glass (0.0025), and about one-sixth as good as marble (0.005).

This value is quite different from that obtained on other shales by the Bureau of Mines. Their value is 0.0038.[4]

HEAT OF VAPORIZATION—The heat of vaporization is a factor of considerable uncertainty. It has been shown that these shales decompose into a heavy tar-like substance and that the cracking of this product produces shale oil. The heat required to vaporize this heavy tar-like material must include the heat necessary to form shale oil from it. At present, little can be said as to this value; the best that can be done is to include the true heat of vaporization of similar oils. Gräfe has calculated these values for "Braunkohle" oils.[5] The following are his data:

MATERIAL	Average[1] Boiling Point ° C.	Sp. Gr.	Heat of Vaporization Cal.	Heat to Raise to B. P. Cal.	Total Heat Cal.
Light crude	216	0.883	86.5	82	168.5
Heavy crude	270	0.905	68.8	105	173.7
Paraffin oil	328	0.920	63.3	130	193.3
Heavy paraffin oil	346	0.933	53.8	138	191.8

[1] The average boiling point is the average value of the boiling ranges of all of the 5 per cent cuts of the oil.

The heat of vaporization of Russian petroleums is around 75 cal. per gram.[6] The specific heat of most petroleum oils may be taken as around 0.42.

HEAT OF REACTION—The heat of reaction is, in this case, the heat of decomposition of the kerogen of the shale into oil. Heats of decomposition are usually expressed as the number of calories absorbed or evolved per gram mole of the decomposing substance. In the present case, nothing is known of the molar weights involved, and it is therefore desirable to express the heat of reaction, *i. e.*, the heat of decomposition, either in terms of the number of calories per gram mole of shale decomposed, or, better, in terms of calories per gram of oil (and gas) formed. In this work the use of the heat of reaction, meaning the number of calories per gram of oil and gas formed, has some advantages; for instance, it permits, at once, the comparison of different shales irrespective of the amount of kerogen they contain.

Heat of Combustion Method—In determining the heat of reaction of organic compounds a common method is to determine the heat of combustion of the original material and of the products of the reaction. Hess, in 1840, showed that the amount of heat generated by a chemical reaction is the same whether it takes place in steps or all at once, it being only the initial and final states that count and not the path by which the reaction proceeds. If, then, a given organic substance is burned to carbon dioxide and water, and the heat involved in the reaction is determined by a calorimetric method, a certain value is obtained. If, on the other hand, the substance is changed by heat into one or more other substances, and the heat of combustion of these products is determined in the same manner as above, the difference in the heats of combustion will represent the heat that it took to go from the original substance to its decomposition product. In the case of a material like coal where the products can be collected and the heat of combustion of the original coal, as well as of all of its products of decomposition, determined, one is able to arrive at a value for the heat necessary to decompose the coal. Mahler did this in the case of some coals. In a substance like shale the experimental problem is somewhat difficult. The carbon compound or combustible material is relatively low, ranging from 10 to 50 per cent. This means an exceedingly high residue or ash. If these high residue materials are burned in an ordinary bomb calorimeter the combustion is nearly complete, and constant results are generally obtained; yet in every case the residue is a fused jet-black material in which unburned carbon is in evidence. In order to show the extent of this combustion, runs were made on a shale, and the residue from a bomb calorimeter was burned in a Fleming apparatus of the type ordinarily used for the determination of carbon in steel. The heat value of the shale and the corresponding correction for carbon is shown in the table. In making this calculation, it is assumed that all the organic material left in the ash is there as amorphous carbon and not as a hydrocarbon. This assumption seems fair, in view of the very high temperatures attained in the bomb.

Sample No.	Heat of Combustion Cal. per Gram	Carbon in Residue	Correction	
			Cal. per Gram	Per cent
1	2949	0.0031	6.80	0.23
2	2954	0.0035	7.70	0.26
3	2963	0.0038	8.30	0.28
4	2941	0.0036	8.50	0.29

While this total correction is small on the original shales and, if made in the manner described, is, no doubt, accounted for to within the experimental error, when it comes to making the same correction on the residue of the shale after the oil has been distilled off, it becomes more significant.

Sample No.	Heat of Combustion Cal. per Gram	Carbon in Residue	Correction Cal. per Gram	Correction Per cent
1	1319	0.014	30.2	2.3
2	1318	0.016	35.1	2.5

Here there is an error of 2.5 per cent if left uncorrected, and one somewhat less if it is corrected. Any carbon dioxide remaining in the residue after combustion would appear by this determination as a corresponding amount of carbon, but no evidence of carbonates was found in the residue after it had been heated in a bomb calorimeter.

A further objection to the method as applied to the shale is that there is a large percentage error, owing to the small value of the heat of combustion of the residue after the oil has been distilled off. From the second table it is seen that only 1136 cal. per g. of shale are obtained; this may be in error by 2 per cent. Another disadvantage in this connection is that it is differences of heat which are being considered, and the differences are usually small, which correspondingly increases the percentage of error in the final result.

After making several preliminary runs by this method it was decided that the errors involved were too great and that it would be best to work up an apparatus in which the heat of reaction could be determined experimentally.

Euchéne Method—Euchéne,[7] in his calculations on "Thermo Reactions," has calculated the heat quantities involved in the decomposition of coal. This he did by summing up the heats used and those consumed in the commercial distillation, and striking a balance which showed that, in the ordinary coal-gas process, heat, though it may be small, is liberated. His method, which was somewhat tedious and subject to large error, was briefly as follows:

First, he determined how much fuel it took to distil a given amount of coal, and the heat value of the fuel was calculated from its elemental composition. To this heat he added that which was recovered in the process from the formation of certain gases which are formed with a liberation of heat: carbon dioxide, carbon monoxide, methane, water, hydrogen sulfide, and ammonia are the ones involved. The sum of these two quantities would give him the total amount of heat available for the distillation of coal.

The heat used in the process was then calculated by duly considering the heat used in the formation of such gases as ethylene, benzene, carbon bisulfide, and cyanogen, which are formed with the absorption of heat. To this was added the heat lost in the hot gases, coke, ash, and by radiation. By balancing up these quantities he found that the entire process liberated heat to the extent of from 12.39 to 63.51 cal. per g. in certain English coals.

This value may be considered to fall well within the very large experimental error of such intricate calculations, but the work of Mahler, referred to above, shows also that the heat of combustion of the original coal is greater than that of the products by some 254 cal. per g. This value, while not agreeing with those of Euchéne, is in the same direction and of the same order and shows that, taken as a whole, heat is liberated in the processes.

Qualitative—Some evidence as to the intricacy of the reaction may be gathered from the work of Hollings and Cobb[8] on coal. While their work was purely qualitative, it shows the procedure of such reactions. The method employed by these workers was to place in an ordinary combustion furnace two boats, side by side, one containing the coal to be distilled, and the other, a nonvolatile inert coal which would undergo no change as the distillation of the volatile coal proceeded. As the two were heated up together, the change in temperature was measured by means of placing in each the junction of a differential thermometer, such as is used in metallurgical work in determining the transition point. If the volatile coal absorbed or evolved heat and the other did not, their difference in temperature would be recorded by the instrument, but as long as both rose in temperature by simply heating up with the furnace, no abnormal deflections would be noticed in the recording instrument.

By this method they showed that coal went through several stages of decomposition, some being accompanied by exothermic and others by endothermic reactions.

Up to 410° C.	Reaction endothermic
410° to 470° C.	Reaction exothermic
470° to 610° C.	Reaction endothermic (CH_4 evolved)
610° to 800° C.	Reaction exothermic (H_2 evolved)

There is a definite similarity between these results and some which the present authors have obtained by an entirely different method. A small brass retort (see Part I, Fig. 2) containing the shale and a 1000° F. nitrogen-filled thermometer was placed in an electrically heated bath after the temperature of the bath had reached a rather high value (850° F.). The temperature of the bath was measured by means of a rare metal thermocouple, calibrated in terms of 1000° F. thermometer. As the temperature rose, oil was formed and distilled over, and, within about an hour, the entire 50 g. of shale could be decomposed. After the completion of the run on shale, a residue (the same shale from which the oil had been distilled) was run in the same manner, and the temperature effects in both runs were compared. The results of this experiment are graphically represented in Curves I and II, Fig. 1. The method used in plotting the data was to plot time in minutes as abscissa and the temperature changes as ordinate, and, in order to facilitate plotting, the ΔT was taken as the average for each 5 min. Reference to the curve shows that, with the shale in the retort, the temperature change remained constant until the still reached 745°, showing that no appreciable decomposition was taking place and that the still was simply rising in temperature with the bath. As the temperature increased, however, the temperature changes became smaller, passing to a negative value within the next 10 min. As the heating continued, the temperature change again approached normal and was followed by another drop. It then rose gradually

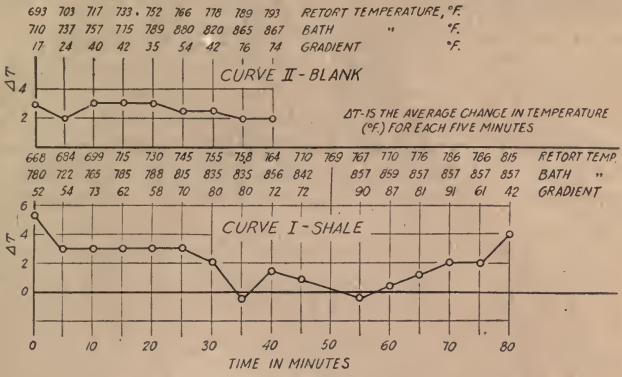

FIG. 1

to the end of the run. This is, of course, a rough measurement, but it indicates at least two distinct stages in the reaction. Attention is here called to the corresponding curve for the run on the residues. It will be noticed that the time required to reach approximately the same temperature (800° F.) in the case of the residue is only about half that in the case of the shale. About 4 g. of oil were obtained, and Curve I must be assumed to represent partly the latent heat of vaporization of this oil; but the large difference must be taken to mean that the heat of reaction over the whole range of the curve is endothermic, and that the rise at 764° is an indication of an exothermic reaction.

DESIGN OF APPARATUS FOR MEASURING HEAT OF REACTION

Inasmuch as these data indicated a measurable heat of reaction, it was determined to design, if possible, an apparatus wherewith its value could be accurately measured. The factors entering into such a determination are as follows:

1—The heat conductivity of the material is very small (0.00086); therefore a considerable temperature gradient must be maintained to decompose a particle of shale at some distance from the source of heat.

2—Unless a very high temperature gradient is maintained the reaction will take place very slowly. (It extended over about an hour in the experiment above described.)

3—The product obtained depends in character upon the manner in which the shale has been decomposed.

The problem was, therefore, to design some sort of calorimeter in which a high temperature could be maintained while the shale was being decomposed, and one to which large amounts of heat could be added without abnormally high calorimeter temperatures being produced; that is, a temperature change of more than 10° C. was not advisable in the calorimeter, and accordingly the calorimeter should be so designed that the total heat added would not raise it more than this. The calorimeter should also be such that the radiation correction, due to the comparatively long time in which it must be run, could be calculated with a fair degree of accuracy.

DECOMPOSITION CHAMBER—The first problem undertaken was the design of a suitable decomposition chamber, and the points to be considered in this connection were (1) to be able to measure the heat energy added with sufficient accuracy, (2) so to design it that a high temperature could be maintained while the decomposition was going on and yet to eliminate conduction and waste heat to the surrounding water, (3) to arrange the apparatus to cool as quickly as possible after the reaction ceased and, thereby, decrease the radiation correction, and (4) to make the parts substantial and rugged enough to stand repeated determinations.

As regards the first requisite, it was decided to use the resistance of an electric current as the source of heat. At the beginning, the assumption was made that the heat of reaction would be relatively large and that it would be sufficiently accurate to measure the energy by means of an ordinary ammeter and voltmeter, and it was believed that the line current in the building was sufficiently steady for use. As work progressed it was found that the apparatus gave only 3 to 5 g. of oil, and that its heat of reaction was so small that more refined methods were necessary. The current had to be taken from sixteen Edison cells, and, in order to reduce further the error in the quantity of heat supplied, a copper voltameter was substituted for the ordinary ammeter, and the voltmeter, which was a Weston instrument, was calibrated* and corrected and read to 0.01 of a volt.

The decomposition chamber was a brass cylinder about 1.5 in. in diameter and about 2 in. long. It was fitted with a center tube sealed up through the bottom and extending nearly to the top. This center tube was to serve as a passage for the oil vapor to leave the retort, to be condensed and collected in a receptacle fitted to the bottom of the center tube. This chamber is shown as A in Fig. 2, with the condensation chamber C attached to the bottom. All joints were hard soldered, so that the apparatus would stand any reasonable temperature. The lid, through which ran the electrical leads, was fastened on by means of a union joint.

HEATING ELEMENT—The heating element of the apparatus proved to be the most delicate part and, at first, required frequent renewal. Great difficulty was experienced in getting a properly insulated heating element so small and yet substantial enough to stand constant use. This was finally accomplished by winding a fine nichrome (22-gage) wire around an ordinary alundum extraction thimble and cementing it in place (the wires properly distanced from one another)

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* This instrument was calibrated by Dr. F. A. Strauss, to whom thanks is extended.

by means of alundum cement. The resistance of this wire was so high that it was found best to wrap two wires and connect them in parallel. This permitted the use of fine wire, making possible ease of wrapping and even distribution, and at the same time sufficient current to effect decomposition.

In the first apparatus made, the coil was large enough just to fit within the walls of the retort, it being the intention to place all of the shale within the alundum thimble and to heat entirely from the outside. After many attempts this was given up because (1) more heat was given off to the walls of the retort than was utilized by the shale, and (2) the extremely low heat conductivity of the shale and the fact that it was all relatively far from the outside of the retort made cooling very slow. To avoid this a smaller heating element was made and placed in the center of the retort, and the shale to be decomposed was placed around it instead of in it, as in the previous case. This improvement, more than any other one thing, made possible the desired decomposition. First, it caused the shale, which is a splendid insulator, to act as its own insulation from the surroundings while the heating was going on, and, second, it placed the shale near the surface of the retort where effective cooling could be accomplished when it was desired to bring the retort to the temperature of the calorimeter.

CALORIMETER—With the retort thus designed and tested as to the amount of oil that could be recovered in a given length of time, etc., the next problem was to find a way to measure the heat recovered during the decomposition. Of course, an ordinary standard calorimeter would suggest itself as the most likely piece of apparatus to use, and it was thought that in this connection a gas calorimeter of the Junker type might be successful. The ordinary bomb type (Mahler, for instance) held only 2000 g. of water, and preliminary experiments showed that heat to the extent of 30,000 to 40,000 cal. would be necessary to effect sufficient decomposition to render measurements accurate. With 2000 g. of water, therefore, the final temperature would be from 15° to 20° C., which was entirely out of the question, but the gas calorimeter, being a constant flow apparatus, seemed to overcome this disadvantage. The method was to insert the decomposition chamber, fitted up as described, into the body of the calorimeter where the combustion ordinarily takes place, to close the bottom tightly and blow a steady current of air through, virtually creating an artificial product of combustion, and to measure in the ordinary way the heat given off to the water. This failed completely because the retort cooled so slowly in the current of air that about 100 lbs. of water had to be put through before the retort came to the temperature of the incoming water. With this large amount of water the small error due to temperature readings would be of the same order as the value of the heat of reaction sought.

The only objection to the use of the bomb type calorimeter was, as has been mentioned, the fact that it did not hold enough water, and it seemed that, if the bucket were removed from that type of apparatus (one of the Emmerson makes), the insulation of which is a large Dewar flask, and the flask simply filled with water, the capacity would be greatly increased and no serious disadvantage would be incurred. By this method 4000 g. of water could be used and. by proper insulation, the retort could be heated and, at the proper time, quenched and cooled down at will.

INSULATION—In order to heat the retort effectively in a body of water it was necessary to insulate it very completely and to be able to quench it quickly when once the run was complete. To accomplish this an outside shell, also made of brass, was made large enough to fit over the retort and leave a 0.5-in. space for insulation. This space was loosely filled with woven asbestos cloth. The jacket was fitted with a screw cover with insulated lead wires through for carrying the current. The jacket was also fitted with a side tube, F in Fig. 2, connected at the top and bottom. In the bottom of this tube was placed a ball valve, and through the tube was fitted a plunger. The object of this arrangement was to allow the apparatus to heat up with the insulating material dry and then, when the run was finished, to pump water from the calorimeter by means of the plunger, thus bringing the retort back to the temperature of the calorimeter as quickly as possible. This pumping arrangement worked very well.

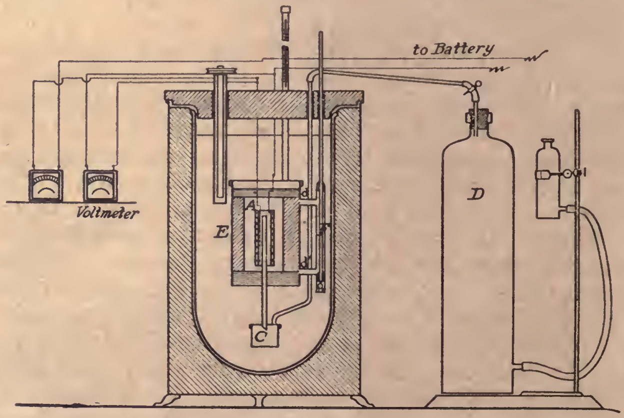

FIG. 2

The complete apparatus consisted of a brass retort A, Fig. 2, fitted with a water-tight cover and insulated plugs through which the electric lead wires were passed. It also had a center tube extending nearly to the top and 3 in. below the bottom of the retort. On the bottom of the center tube was a small brass receptacle fitted with a screw cover, and an outlet through which the permanent gases could escape.

A, the retort proper, was surrounded by a brass jacket large enough to permit the insulating material (asbestos cloth) to be placed between them and leave space for water to circulate. The outer shell or jacket was fitted with a side tube containing a hand-worked piston pump by means of which water was circulated through the apparatus to cool it down to the temperature of the calorimeter. The whole decomposition chamber was suspended from an especially made lid to the calorimeter.

PROCEDURE

The procedure in making the run was as follows: The retort was filled with a weighed amount of shale, and, after all connections were made to prevent the water from getting into the decomposition chamber, the whole was suspended from the lid of the calorimeter, immersed in a weighed amount of water (4000 g.), the thermometer adjusted, and the stirrer started as in a bomb calorimeter determination. At the beginning of the determination the temperature of the water in the calorimeter should be about as much below room temperature as it will be above it when the run is finished. This decreases the radiation corrections. After the decomposition chamber and parts in contact with the water had come to the water temperature the current, which should be adjusted to about 7 or 8 amperes at 16 volts, was turned on. Half-minute readings were taken on the voltage and minute readings on the water temperature. At this rate of supplying heat the current may be left on about 23 min. without raising the temperature of the calorimeter more than 10° C. This will decompose shale sufficient to furnish 2 to 6 g. of oil and gas. At the expiration of this time, the current was turned off and water admitted by raising the pump plunger. Water was pumped through the apparatus continually as long as the temperature rose. The decomposition chamber was then removed, and the oil and water were removed from the distillation chamber C. The shale was taken out of the retort and extracted with benzene. This was necessary because the larger part of the oil had not distilled over, but remained in the shale as a tar-like substance. The gas collected in the bottle D was run into a Bunsen specific gravity bottle and its gravity determined. From its specific gravity and the volume, the weight of the gas may be determined.

WATER EQUIVALENT

On account of the variations in the kind of material used in making the parts of the calorimeter (glass as a container, brass for retort and jacket, alundum heating core, asbestos insulating material, nichrome resistance, and copper leads) it would have been difficult to calculate the water equivalent of the calorimeter from the specific heats of the parts. This was particularly true of the heat taken up by the glass containing vessel. It was a large double-walled vacuum flask holding 4000 g. of water, the whole being permanently fastened into the felt insulation of the calorimeter proper. The entire flask was, therefore, not heated to the temperature of the water, only the inner wall being in contact with it; hence there was no way of weighing the particular portion of the flask heated. The water equivalent could, however, be determined by methods similar to those used in the determination of the water equivalent of an ordinary bomb calorimeter. The method was to heat up the apparatus with all of its parts in place and under the conditions under which an actual run was made, excepting that instead of using the shale on which the heat of reaction was to be determined, a residue from a previous run which contained no volatile matter was placed in the decomposition chamber. Then, knowing the weight of the water present and the energy added, the water equivalent could be calculated. The calculations involved in determining the water equivalent were as follows:

Let H_1 = heat added during the process
V = volts (average at which current is supplied)
m = weight of copper deposited on electrode of voltameter
e = electrochemical equivalent of copper, 0.0003294
f = mechanical equivalent of heat in cal., 4.18

$$\text{Then } H_1 = \frac{(Vm)}{0.0003294 \times 4.18}$$

Also let H_2 = heat recovered by calorimeter
W = weight of water in g.
w = g. water equivalent of calorimeter
t_1 = initial temperature, temperature of calorimeter ° C. (corrected)
t_2 = final temperature of calorimeter ° C. (corrected)
M = weight of oil and gas recovered

Then $H_2 = (W + w)(t_2 - t_1)$

Water equivalent is then found by equating the values of H_1 and H_2 and solving for W

$$w = \frac{(Vm) - W\ (t_2 - t_1)\ 0.0003294 \times 4.18}{0.0003294 \times 4.18\ (t_2 - t_1)}$$

By this method w was found by two determinations to be 157 g. and 163 g., or an average of 160 g. The value of the weight of the water was taken to be 4000 + 160, or 4160 g.

Errors and Corrections

RADIATION LOSSES—In the actual manipulation of the apparatus the time taken to heat the shale to its decomposition temperature and to transfer all of the excess heat to the calorimeter was considerable. On an average it was from 40 to 50 min. and, even though the apparatus was well insulated (by a vacuum jar) and the radiation per minute was relatively small, yet when the operation was extended over such a long time the radiation factor was quite large. It would amount to as much as 0.1° C. This would mean approximately 410 cal. on the total run. This correction could be largely eliminated by starting the experiment as far below room temperature as it would be above room temperature at the finish if the time were the same during which it remained above and below room temperature; but this is not the case. At the start, assuming that the system was 4° or 5° below room temperature, it would heat up with only the normal radiation from the room, but after the operation was finished with the temperature of the water some 4° or 5° above that of the room, the apparatus cools down at a rate which depends upon the rapidity with which the heat is transferred from the inside of the retort to the water. This is exceedingly slow and the instrument may run at a constant maximum temperature for as much as 6 or 7 min. Therefore, the calorimeter may remain at this high temperature for a considerable time.

In order further to eliminate the radiation losses, a correction was applied each time. The method adopted was the graphical one used by the Bureau of Standards in connection with their bomb calorimeters.[9] It is found to work out very well in the latter case, and, inasmuch as the operation is similar in principle to that applied here, the correction is probably the most applicable one to be had.

Let r_1 = Rate of rise (or fall) of temperature at start of experiment
r_2 = Rate of fall (or rise) of temperature at finish after all of heat has been dissipated to the water
t_1 = Time at which current was turned on
t_2 = Time at which temperature begins to fall after operation is complete
t_3 = Such a time that the total heat radiated to the calorimeter from the surroundings while it is below room temperature is exactly equal to that radiated to the room by the calorimeter when it is above room temperature. In other words, it is the time at which the calorimeter ceases to absorb heat and starts to radiate it. For graphical reasons it is taken to be 0.6 of the total rise of the calorimeter.

Then $r_1 \times (t_3 - t_1)$ Heat absorbed by the calorimeter and is, therefore, added to the initial temperature and heat radiated by the calorimeter to the surroundings
$r_2 \times (t_2 - t_3)$ This is added to the maximum temperature

It is seen that these two temperature corrections tend to equalize one another, and if the proper conditions, such as starting at the right temperature and running the proper length of time, could be established, they would cancel each other. A typical set of data on Colorado shale is included to illustrate the manner of this correction.

Thus it is seen that there is an actual correction of 0.20 — 0.13 = 0.07° F.

It will be noticed that the temperature reached a maximum and ran along constant for 8 min. The question might arise as to whether the time t_2 should be taken at the time when the temperature reached a maximum or at the end of the 8 min. It is probably advisable to take it at the end of the 8 min.

	Grams
Wt. of electrode	84.5260
Wt. of electrode + copper	87.2360
Wt. of copper deposited	2.7100

TIME	TEMP. ° F.	VOLTS	AMPS.
3:44.30	64.9		
:45	64.98		
:46	64.99	12.00	
:47	65.00	12.00	6.49
		12.03	
:48	65.10	11.95	
		12.00	
:49	65.20	11.98	6.49
		12.10	
:50	65.35	11.95	
		12.00	
:51	65.55	12.00	7.05
		12.00	
:52	65.80	14.10	7.00
		14.05	
:53	66.05	14.00	
		14.00	
:54	66.40	14.00	
		14.00	
:55	66.70	14.00	7.05
		14.00	
:56	67.20	14.00	
		14.00	
:57	68.70	13.98	7.10
		14.00	
:58	69.00	14.00	
		14.00	
:59	69.60	13.00	
		13.00	
4:00	70.10	12.95	6.90
		12.75	
:01	70.60	12.90	
		12.95	
:02	71.20	13.05	7.00
		12.90	
:03	71.80	12.95	7.00
		13.00	
:04	72.25	Current off	Time 17.5 min.
		Av. 13.08 volts	
:05	73.30		
:06	74.40		
:07	75.20		
:08	76.60		
:09			
:10	77.65		
:11	78.10		
:12	78.35		
:13	78.55		
:14	78.85		
:15	78.89		
:16	78.95		
:17	79.04		
:18	79.10		
:19	79.15		
:20	79.20		
:21	79.24		
:22	79.26		
:23	79.27		
:24	79.28		
:25	79.29		
:26	79.30		
:27	79.30		
:28	79.30		
:29	79.30		
:30	79.30		
:31	79.30		
:32	79.30		
:33	79.30		
:36	79.29		
:42	79.26		

	Ohms
Resistance of voltmeter	180.4
Resistance added	60.0
TOTAL.................	240.4

$$\text{Voltage} = \frac{240.4 \times 13.08}{180.4} = 17.41$$

DATA (*Concluded*)

Weight of electrode = 2.7100 — 0.0271 = 2.6829

Initial temperature	64.99 ° F.
Stem correction	0.00
Calibration correction	—0.07
$r_1 (t_3 - t_1) = 0.01 \times 20 = 0.20°$	0.20
Corrected initial temperature	65.12
Final temperature	79.20
Stem correction	0.00
Calibration correction	—0.07
$r_2 (t_2 - t_3) = 0.005 \times 27 = 0.13$	0.13
Corrected final temperature	79.26

because the retort is still radiating heat to the water, as otherwise the temperature would start to fall.

VOLTMETER RESISTANCE—Another correction became necessary because of the manner in which the determination was made. The voltmeter was kept in the circuit continuously instead of plugging it in when it was desired to make a reading. This was done because the readings were taken every half minute, and it was simpler not to throw the voltmeter out of the circuit between the readings. The resistance of the voltmeter was known, and the current it took could readily be calculated. This amounted to the equivalent of about 1 per cent of the weight of the copper deposited on the electrode. It was, therefore, subtracted each time.

The method was subject to several sources of error which could not be eliminated. These were calculated so far as possible.

ERRORS IN HEAT SUPPLIED—In the heat supplied the first error would be that due to voltage. The readings of the voltmeter were taken every half minute, and the average of these was the voltage used. The readings, when corrected by applying a standardization correction, should be quite accurate, but, unfortunately, the batteries used were not in first-class condition, and the voltage varied somewhat. The readings were made to 0.01 volt, which is approximately 1 in 1600. As a result of this variation, the average was probably not better than 0.02 volt, which is 0.13 per cent.

The second error is that due to the amperage. The use of a copper voltameter upon which 2.7 g. of copper is usually deposited renders the correction extremely low. With customary precautions in weighing, the weight could easily be determined to 3 in 10,000, or an error of 0.03 per cent.

Heat losses due to leads, conductivity of alundum, etc., would probably not exceed 0.05 per cent.

Adopting the principle that the most probable error is represented by the square root of the sum of the squares of the respective errors, the probable error would be 0.14 per cent. On 30,000 cal. produced this would be 42 cal.

THERMOMETER READING—As regards the measurement of the heat recovered by the calorimeter, the largest error is, perhaps, that of reading the thermometer. The thermometer used (calibrated Bureau of Standards, No. 10,482) was graduated to 0.05° F. Readings could be made to within 0.005°

TABLE I

SHALE	Run No.	Temperature ° F.						Rise ° C.	Heat Recovered Cal.	Volts	Weight of Electrode G	Heat Added Cal.	Wt. of Heavy Oil G.	Wt. of Light Oil G.	Wt. of Gas G.	Total Wt. G.	Difference of Heats	Heat of Reaction.Cal. per G.
		Initial	Total Correction	Corrected Initial	Final	Total Final Correction	Corrected Final											
Colorado	1	64.99	0.12	65.11	79.30	0.06	79.36	7.91	32905	17.70	2.693	34641	1.880	0.840	1.63	4.35	1730	398
Colorado	2	66.43	0.03	66.40	80.05	0.12	80.17	7.54	31366	16.90	2.703	33198	2.470	0.648	1.10	4.22	1832	434
Colorado	3	71.31	0.07	67.38	82.81	0.04	82.85	8.60	35776	16.74	3.065	37287	2.310	0.773	0.50	3.59	1542	430
Nevada	4	68.55	0.08	68.63	82.29	0.10	82.39	7.64	31782	16.62	2.707	32696	1.263	0.100	0.64	2.00	914	457
Nevada	5	67.52	0.11	67.63	82.94	0.04	82.98	8.53	35485	18.06	2.820	37012	1.065	0.385	1.78	3.22	1527	474
Canada	6	69.86	0.12	69.98	84.35	0.02	84.37	7.99	33238	16.56	2.480	34195	0.924	0.360	0.70	1.98	957	484

F. at initial and final temperatures, meaning that the error would not exceed 0.01° F. or 0.005° C. If the temperature rise was 70 (about the average), the error was 0.07 per cent.

It has been shown that after calculation for the radiation, the radiation correction is relatively small. There is no definite way of arriving at what the radiation error may be after calculation but it is certainly within 0.005° C. This would make a correction of 0.07 per cent.

The weighing of the water, evaporation losses etc., will not exceed 1.5 g., which on 4000 is equal to 0.03 per cent. Taking the square root of the sum of the squares it gives 0.10 per cent. On 30,000 cal. this would be 30 cal.

The maximum error due to subtraction of the heat recovered from the heat added equals $30 + 42 = 72$ cal. This represents only the maximum actual error due to the subtraction of the heat. The actual value on the heat of reaction as finally obtained will be discussed later.

Table I is a summary of data and results.

The oil recovered was, for the most part, a heavy tar-like mass which was largely left in the retort mixed with the shale and had to be extracted with benzene. This is the character of the material produced during the first stage of decomposition from kerogen to shale oil. In order to produce lighter distillates, etc., from these it is necessary to crack these residua. The heat of reaction is then the heat necessary to change the kerogen into this primary product.

In determining the heat of reaction of these materials three quite different types of shale were used: (1) The Colorado shale which yields products similar in constitution to a mixed base petroleum oil such as is found in the Mid-continent field; (2) the Canadian shale which is more like an asphaltic base oil, such as California crude, and contains but little paraffin; (3) the Nevada shale which is peculiar in that it contains very large percentages of solid paraffin wax.

The average of the results of the Colorado shale is seen to be −421 cal. per g. of oil and gas produced, for the Nevada shale it is −465, and a single run on the Canadian shale shows −484. These results are, within the experimental error, practically the same, showing that this value is quite constant regardless of which shale is used.

SUMMARY—PARTS I AND II

1—An experimental method has been devised for the determination of the heat of reaction involved when these organic materials decompose to form oil and gas. This factor has been determined on three quite different shales and found to range from −421 to −484 cal. per g. of oil and gas produced. So far as is known, this is the first apparatus designed for the direct determination of this factor in shales or similar bituminous materials.

2—It has been generally thought that the organic matter in shales decomposed to form petroleum products as the primary products of decomposition. This research has shown that this is not the case, but that the primary product of decomposition is a heavy solid or semi-solid bitumen.

3—The decomposition temperature of the shale material has been shown to be quite definite and is within a range of 10° C. The decomposition takes place between 400° and 410° C.

4—When petroleum oils are formed from shales they are not formed directly from the pyrobituminous material in the shale, but they are formed by a cracking process from the semi-solid bitumen just mentioned. This cracking process is similar to the well-known phenomenon of the cracking of petroleum oils.

5—New data have been compiled on the heat conductivities of shale. The coefficient of conductivity was found to be 0.00086, expressed in c. g. s. units.

6—The experimental facts determined have shown that it will be possible to design a shale retort to be used simultaneously as a cracking still for shale bitumen and heavy residua from natural petroleum.

BIBLIOGRAPHY

1—Thomas Clarkson, "Facts About the Shale Oil Industry," *Oil and Gas J.*, **17** (1919), 60.

2—M. J. Gavin, H. H. Hill, and W. E. Perdew, "Notes on the Oil Shale Industry," Bureau of Mines *Bulletin* **1919.**

3—Greene, "Oil Shales."

4—M. J. Gavin and L. H. Sharp, "Some Physical and Chemical Data on Shales," *Oil and Gas J.*, **19** (1920), 86.

5—E. Gräfe, "The Heat of Vaporization of Petroleum Oils," *Petroleum*, **5** (1910), 569.

6—C. F. Mabery and A. H. Goldstein, "On the Specific Heat and Heats of Vaporization of Paraffin and Olefine Hydrocarbons," *Am. Chem. J.*, **28** (1902), 66.

7—Euchéne, *Trans. Internat. Gas Cong.*, Paris, **1910.**

8—Hollings and Cobb, *J. Chem. Soc.*, **107** (1915), 1106.

9—Bureau of Standards, *Scientific Paper* **230**, 229.

VITA

Ernest Elmer Lyder was born at Kansas City, Kansas, on September 30, 1886. At the age of nine he moved with his parents to Paola, Kansas, where he received his elementary and high school education.

In September 1909 he entered the University of Kansas and in 1913 received from that institution the degree of Bachelor of Science in Chemical Engineering.

After graduation he was employed by the University in the capacity of research assistant in the department of State Chemical Research. During the first year he made an investigation of the salt deposit of the state. This work is being published by the Kansas State Geological Survey. The following year and one half he, in conjunction with Dr. H. C. Allen, made a chemical survey of the natural gases of Kansas and Oklahoma. This work was published as Bulletin No. 3. of the University of Kansas. During this time at the University sufficient additional graduate work was done for the degree of Master of Science.

In January 1916 he went to Bartlesville, Oklahoma, as Chief Chemist for the Empire Gas and Fuel Company. This position was held until October 1917 when he came to Columbia University to study in the departments of Chemistry and Chemical Engineering. Two and one half years have been spent in graduate work in this institution. The degree of Master of Arts was granted in October 1918.