

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY.]

A CHEMICAL INVESTIGATION OF THE ASPHALT IN THE TAR SANDS OF NORTHERN ALBERTA.BY VERNON K. KRIEBLE AND WILLIAM F. SEYER.¹

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Introduction.

Asphalt is a commodity of continually increasing importance. Its uses are familiar to every one. Although much has been written about it there is very little real information about its chemical composition, principally because there has not been a satisfactory method of isolating any of its constituents. Asphalts are bituminous substances. Their carbon content varies from 75 to 85%, the hydrogen from 7 to 14%, the sulfur from 0.6 to 10%, and the nitrogen from 0.1 to 2%. Few asphalts contain oxygen. Boussingault² in 1837 appears to have been the first to attempt to solve the chemical nature of asphalts. He distilled Pechelbroun asphalt and obtained an oil which he called "petrolene." Its analysis corresponded to the formula C_5H_8 , which he pointed out was isomeric with the oil of turpentine. The non-volatile portion he called "asphaltene." In 1897, Endeman³ claimed to have isolated two acids from asphalts after heating them to 250° for some hours. They were obtained from the non-volatile portion and corresponded in their analysis to the formulas of $C_{26}H_{26}O_4$ and $C_{26}H_{20}O_{12}$. A short time later Richardson,⁴ working with Trinidad asphalt, isolated a brown oil by distillation which he was able to fractionate partially after reducing the pressure to 60 mm. and working in an atmosphere of carbon dioxide. The lowest two fractions contained the compounds $C_{13}H_{26}$ and $C_{14}H_{28}$. He believed that members of the C_nH_{2n-2} and C_nH_{2n-4} series were also present. In 1917, Mabery⁵ distilled in an iron pipe at 400° gilsonite and grahamite, substances supposed to be closely related to asphalts, on one hand, and petroleum, on the other. He obtained a heavy oil which, on being fractionated, yielded compounds belonging to the C_nH_{2n} and C_nH_{2n-2} series.

Object of the Investigation.

One of the greatest fields of bituminous material found in the world is that located in the northern part of Alberta, and lies roughly in a circle having a radius of 50 miles with Fort McMurray as center. Outcrops of varying thickness occur along all the river banks in that region. The

¹ W. F. Seyer held a research fellowship under the auspices of the Honorary Advisory Council for Scientific and Industrial Research for Canada. (V. K. K.)

² Boussingault, *J. chim. phys.*, **64**, 141 (1837); **73**, 442 (1840).

³ Endeman, *J. Soc. Chem. Ind.*, **16**, 122 (1897).

⁴ Richardson, *ibid.*, **17**, 13 (1898).

⁵ Mabery, *THIS JOURNAL*, **39**, 2015 (1917).

asphaltic material is mixed with sand of varying degrees of fineness, and contains from 7 to 20% of bituminous matter, the sample investigated containing 17.85%. The object of this investigation was to gain some insight into the composition of the asphalt, as it was hoped, by gaining this knowledge, the utilization of these immense deposits would be furthered.

Experimental.

The Sample.—The sample upon which the following work has been done was the remnant of a lot used by S. C. Ells,¹ formerly of the Mines Branch, Ottawa, for paving experiments in the city of Edmonton. It was stated by Mr. Ells to have been taken from an exposure on the Hangingstone river, about 3 miles from Fort McMurray.

Physical and Chemical Properties of the Asphalt.—The asphalt, when freed from the sand, is of the semi-liquid variety which is classed by Richardson as malthas; d^{20} , 1.022; penetration at 20°, 0.00.

Solvent.	SOLUBILITY.	
	% Soluble.	Nature of residue.
Carbon disulfide.....	100	
Carbon tetrachloride.....	100	
Chloroform.....	100	
Benzene.....	98	black solid
Ether (hot).....	86.9	brown solid
Acetone (hot).....	70	brown solid
Alcohol (hot).....	33	brown solid
Sulfuric acid, conc.....	100, after several days	
Nitric acid, conc.....	100, after several days	

Application of Marcusson's Method of Analysis.²—The estimation of free acids could not be obtained by the method outlined by Marcusson. Emulsions which could not be broken up were formed in every case, even after standing for several months. The acids are therefore included in the saponifiable matter which was determined by the method of Spitz and Honig.³

The amount of asphaltenes was determined by first dissolving a weighed quantity of the asphalt in 10 cc. of benzene and adding to this 250 cc. of petroleum ether (b. p. below 55°), which caused these substances to separate as black solids. They were filtered out and the petroleum ether filtrate was then run through fuller's earth, which removed the resinous substances. The petroleum ether solution, upon evaporation, left behind a petroleum-like oil. The resins were removed by extracting the fuller's earth with benzene or chloroform.

¹ Ells, "Preliminary Report on the Bituminous Sands of Northern Alberta," No. 281, Mines Branch, Dept. of Mines, Canada, 1914.

² Marcusson, *Z. angew. Chem.*, 29, 346 (1916).

³ Spitz and Honig, "Examination of Hydrocarbon Oils and Saponifiable Fats," Holde Mueller, p. 161.

The table below shows the relation the Alberta asphalt bears to two typical ones, namely, the Trinidad and Bermudez.¹

	Alberta.	Trinidad.	Bermudez.
	%.	%.	%.
Saponifiable.....	2.0	10.3	5.5
Asphaltenes.....	22.5	37.0	35.3
Resins.....	24.0	23.0	14.4
Oily constituents.....	51.5	31.0	39.6

It will be seen that the resins and oily constituents are greater in the Alberta than in the Trinidad or Bermudez asphalts.

ULTIMATE COMPOSITION OF THE ALBERTA ASPHALT IN COMPARISON WITH CERTAIN STANDARDS.²

	Sulfur.	Carbon.	Hydrogen.	Nitrogen.
	%.	%.	%.	%.
Trinidad (Lake).....	6.23	82.33	10.69	0.81
Bermudez.....	5.87	82.88	10.79	0.75
Nevada.....	9.76	79.58	9.31	1.30
Alberta.....	2.73	84.49	11.23	0.04
Mexico.....	1.48	85.65	12.37	0.00
Texas.....	1.13	87.27	11.79	0.23

This shows that the Alberta asphalt stands midway between the hard and the soft asphalts.

Many attempts were made before a satisfactory method for isolating any of the constituents of the asphalt was discovered. One of the first experiments was to try to distil the asphalt with and without the naturally admixed sand, but cracking started before 100° was reached, and the distillates usually became less mobile after standing. They also changed markedly in color, becoming quite black after several weeks. The next attempt was to obtain derivatives of some of the constituents of the asphalt by treating it with nitric acid and with sulfuric acid, but neither method led to any isolable compounds. The former produced a red resin-like substance which could not be crystallized. It dissolved in a number of solvents, including dilute alkalis, but no crystalline material separated from any of them. The treatment with sulfuric acid was equally unsatisfactory. We finally succeeded in dividing the asphalt into 4 different fractions by extracting it with alcohol, acetone and ether in the order named and then boiling off the solvent. These fractions were then treated with nitric acid, sulfuric acid, ozone, etc., but we did not succeed in isolating even one pure compound.

We were, however, much impressed by the few cubic centimeters of the clear, almost colorless, oil which we obtained by the Marcusson method of analysis and felt that if we had 10 to 15 liters of this oil we might be

¹ Marcusson *Z. angew. Chem.*, 29, 346 (1916).

² Richardson *J. Soc. Chem. Ind.*, 17, 29 (1898).

able to fractionate it satisfactorily. We will not describe all the modifications in our procedure before we succeeded in getting a satisfactory method for isolating the oil in fairly large quantities.

Method of Separating Oil on a Large Scale.—The process consisted of extracting the tar sands with petroleum ether, which removed the oil and the resins. This was filtered through fuller's earth, which removed the resins, and the petroleum ether was then distilled on the water-bath, leaving the oil as a residue. The petroleum ether ordinarily purchased contained certain constituents which boiled at over 100° and it was essential to remove these, as they not only would dissolve more of the asphaltenes but also would interfere in the fractional distillation by possibly contaminating the lower fractions. For these reasons, a special gasoline was secured which had a larger amount of low-boiling constituents than ordinary petroleum ether. This was redistilled through a fractionating column 2.1 meters in length and 25 mm. in diameter, filled with glass beads. Only that portion distilling below 55° was used. The fuller's earth was crushed until it passed completely through a 40-mesh sieve. After crushing, the earth was heated in an iron pipe to redness, thereby removing not only the adhering but much of the combined water, and materially increasing the adsorptive power. It was then placed in an iron pipe 90–120 cm. in length and 5 cm. in diameter, which had a reducer at the lower end that connected with an outlet pipe of 12 mm. diameter.

Tar sand to the amount of 2 to 3 kg. was placed in each of several stone jars of about 1.5 liters capacity, fitted tightly with wooden lids. The sand was covered with petroleum ether and allowed to stand for several hours with intermittent stirring, after which the solution was removed by decantation. This extraction was continued until the petroleum ether became only slightly discolored, the decanted portions being put into large bottles to allow the settling of the fine particles of sand, which would otherwise clog the pores in the fuller's earth and hinder filtration.

The treatment with fuller's earth was carried out in such a manner that the concentrated petroleum ether solution first came into contact with earth that was already partially saturated with resins, while solutions partially decolorized always came in contact with fresh earth which removed all the red color and left the solution yellow. It was also observed that temperature had a marked effect on the adsorbing power of the earth; the higher the temperature the greater the efficiency. Further, the efficiency could be increased by using a concentrated petroleum ether solution.

The material retained by the fuller's earth, which Marcusson termed petroleum resins, could be removed by extracting the earth with benzene,

chloroform, carbon tetrachloride, or carbon disulfide. These resins have not been investigated further. It was, however, noticed that crystals separated upon slow evaporation of a benzene solution.

The material insoluble in the petroleum ether, the asphaltenes, were black solid substances, insoluble in acetone, in ether and in alcohol. They decomposed before they reached the melting point. They have not yet been investigated.

After the solvent had been removed as completely as possible from the oil by the aid of suction and by heating on a water-bath, the residue was transparent and had a light red color. It appeared to possess good lubricating properties, for after a week's exposure to the air in thin layers it showed no evidence of resinification. When heated for 4 or 5 days at 180° it became black and of high viscosity, resembling the original asphalt removed from the sand.

PHYSICAL AND CHEMICAL PROPERTIES OF THE OIL.

d^{20}	0.927	Sulfur.....	1.87
n^{20}	1.5000	Carbon.....	85.76
Optical activity....Dextro—	1.5–1.6	Hydrogen.....	12.19
Viscosity at 25°.....	20.0	Iodine no.....	2.1
Molecular weight.....	350.0		

Slightly over 7.5 liters of this oil was obtained by extraction. This was considered to be sufficient for the fractional distillation, as the intention was only to acquire a knowledge of the series of hydrocarbons present without actually isolating any of the constituents.

Fractional Distillation of the Oil at Reduced Pressures.—It was impossible to distil the oil at atmospheric pressure without decomposition. When the distillation apparatus was made air-tight and the pressure reduced to 40 mm. by means of a water suction pump, a small amount of a colorless oil could be removed. When the temperature at which the oil came over reached 150° cracking began, which could be detected by the appearance of a fog in the condensing tube and the rank odor of the distillate, which now possessed a deep red color. The pressure was then reduced to 18 mm. with the result that cracking did not begin until a slightly higher temperature was reached. The oil was then distilled in the presence of carbon dioxide to prevent decomposition if possible, but this was of no avail, for decomposition even under 18 mm. pressure was so great at 165° that no separation could be obtained. The distillate above 100° had a red color and a rank odor; that below 100° was a clear, colorless, limpid oil with a strong turpentine odor.

The only successful way of distilling the oil appeared to be by further reduction of the pressure. This could not be effected by a water pump, and as there were always small amounts of gases given off, Sprengel or

Gaede pumps could not be used. The difficulty was overcome by employing a Maass sulfuric acid pump¹ which is an automatic Töpler pump using sulfuric acid. By means of this pump it was possible to reach and maintain as long as desired a pressure as low as 0.1 mm., even when there was a small evolution of gas. Distillation at such low pressures required the construction of a special distillation apparatus which is described below.

The flask A was of Pyrex glass, the neck being filled with glass beads, and connected with a receiver B. By means of Stopcocks 1, 2 and 3, the bottle C could be entirely separated from the rest of the apparatus and removed. G was a bulb which could be immersed in a Dewar flask and cooled with solid carbon dioxide, to condense and collect the most volatile substances. D was a strong bottle of 5 liters capacity which acted as an equalizer of the pressure. From this led three tubes, X to the distilling flask, Z to the Maass pump, and V to a mercury manometer. The tube S led to a large rotary pump by means of which the pressure in the bottle C could be rapidly reduced to 20 mm., so that when the stopcock connecting the bottle C with the apparatus was opened

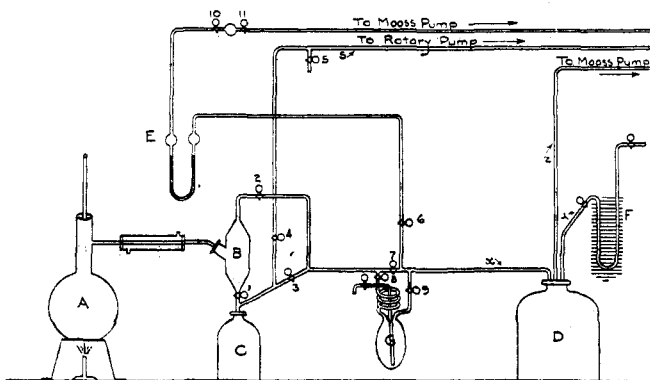


Fig. 1.

there was only a very slight change in the pressure. E was a sulfuric acid manometer. As this was seven times as sensitive as the mercury one, changes in pressure of 0.1 mm. could readily be detected. One arm of the manometer was connected to the sulfuric acid pump through Stopcocks 10 and 11, the other arm was connected to the distilling apparatus. At the start all these stopcocks were open until the pressure throughout the apparatus, as indicated by Manometer F, was that desired for the distillation. Then Stopcocks 10 and 11 were closed but 6 was left open so that small variations of 0.1 mm. could be detected and counteracted by connecting and disconnecting the sulfuric acid pump through a stopcock on Tube Z not indicated in the sketch.

A liter flask was used for the first distillation. It was filled to $\frac{2}{3}$ of its capacity with oil. The pressure during the distillation was reduced by steps, as at the low pressure the first fractions were fairly volatile, even at room temperatures. The fractions were collected at first over 25° intervals then over 10° , then 5° , and finally over 3° or smaller intervals, as

¹ Maass, THIS JOURNAL, 42, 2571 (1920).

the quantity of oil determined. After the first distillation the oil fell into the following fractions:

Temperature. °C.	Pressure. Mm.	Amount. Cc.
0-30	10	160
80-110	10	395
110-135	5	530
135-160	1	300
160-185	0.5	550
185-195	0.4	220
195-213	0.4	400
213-230	0.4	430
	Condensed in carbon dioxide bulb	400
	Total	3385

After the third distillation, the fractions tended to collect in quantity about certain temperatures. These fractions were subjected to two additional distillations.

The fractions were all clear and transparent, the lower boiling ones possessing a strong terpene odor. No attempt was made to fractionate the oil distilling above 230°, although it was possible to heat it up to 300° without any signs of cracking, provided that the pressure was kept below 0.4 mm. An increase of pressure of only 0.2 mm. was sufficient at these temperatures to cause cracking.

Purification of the Distillates.—All previous investigators of heavy hydrocarbon oils used sulfuric acid to purify the distillates, for the removal of the unsaturated, sulfur and nitrogen compounds. The value of sulfuric acid as a purifying agent for hydrocarbon oils has been much questioned. It has long been known that sulfuric acid attacks the higher saturated hydrocarbons with the production of tars. It was found that all the distillates, although they were only slightly unsaturated, would dissolve completely in conc. sulfuric acid even when these oils were dissolved in petroleum ether. Once these oils had been dissolved, they could not be recovered from the acid; it slowly converted them into tar-like substances. Liquid sulfur dioxide at -10° has been used for a number of years in the separation of saturated and unsaturated hydrocarbons on a commercial scale, the saturated compounds being insoluble while the unsaturated compounds dissolve. So far only the very light hydrocarbons have been purified in this manner.¹ However, it has been found that even the heavy hydrocarbons also can be separated by the use of liquid sulfur dioxide. There appears to be only one limiting factor, and that is the viscosity of the heavy hydrocarbons at -10° . This disadvantage

¹ R. J. Morre, J. C. Morrell and S. Egloff, *Met. Chem. Eng.*, 18, 396 (1918).

can be overcome by dissolving the oil in petroleum ether previously treated with sulfur dioxide to remove the unsaturated compounds.

The whole procedure was very simple. The oil to be purified was placed in a buret with stopcocks at each end, immersed in an ice-bath and cooled to -10° . Liquid sulfur dioxide was then run in. After shaking and allowing the buret to remain in the bath for 15 minutes, two layers were observed. The upper one, the oil, was colorless; the lower one, the sulfur dioxide layer, was red. The lower layer was run off and the oil treated again. This was continued until the sulfur dioxide layer remained colorless. It was noticed that upon the first addition of sulfur dioxide, crystals formed in the oil which sank and were redissolved in the lower layer. It was also observed that the sulfur compounds could be removed by this method, as oils which contained almost 1% before treatment contained only a faint trace afterwards.

The amount removed by the sulfur dioxide varied with the different distillates, being on the average about 1%. After purification, the oils distilling below 162° were completely colorless, while those which had become lightly discolored upon standing and distilled above that temperature, possessed a light yellow color and had no longer a disagreeable odor.

The molecular-weight determinations were made by the freezing-point method in benzene. Advantage was taken of a device first used by O. Maass and described in the *Proceeding of the Royal Society of Canada* for 1919. Instead of adding a crystal of benzene from some external source to start crystallization, one simply touches a platinum wire, sealed in the inner freezing tube, with the end of a copper rod which has been cooled in a solid carbon dioxide—ether bath. This causes the formation of crystals about the platinum wire inside the tube. In this manner the degree of supercooling can be accurately controlled. Also the difference between the freezing point of benzene and the temperature of the cooling bath can be reduced, thus decreasing the magnitude of the error from this source. The difference between these two temperatures, it was found, should never be less than 1° nor greater than 1.5° . If the difference is less and the cooled rod is applied there is an immediate supercooling of as much as 0.3° before crystals appear. When, however, it is greater than 1° crystals appear immediately and there is no supercooling. About 0.05° of supercooling should be allowed.

The benzene was regularly stirred by means of a magnetic stirrer. The outer bath was kept constant by means of an electric stirrer, the temperature being lowered to correspond to the depression of the freezing point of the solution as the concentration increased. With care, the determinations would check within 1%. Thus the molecular weights for the lowest fractions were 154, 156, 155, with varying concentrations, while for the highest fraction they were 346, 346, 347.

Physical and Chemical Properties of the Distillates.—All the distillates except the first were optically active. The rotation was not large, being of the same order as that of the petroleums examined and, like them, was dextrorotatory. The activity was slightly increased by purification. The optical activity of petroleums has been questioned by some

authorities, especially Mabery, who examined a number of distillates but found no sign of activity.¹ It is possible that the oils he tested had been racemized during the distillation.

The optical activity proves clearly that the asphalt in its formation has not passed through a temperature above 450°, as it has been found that all activity is destroyed at this temperature.

Molecular weight determinations and combustion analyses indicated the presence of the following hydrocarbons.

HYDROCARBONS FOUND.

	B. p. °C.	Pressure in mm.	Found.			Calculated.		
			H.	C.	M.w.	H.	C.	M.w.
C ₁₁ H ₂₂	75-80	10	14.40	85.20	155	14.30	85.70	154
C ₁₂ H ₂₄	95-99	10	14.58	85.10	167.5	14.30	85.70	168
C ₁₃ H ₂₄	84-87	3	13.90	86.70	178	13.33	86.66	180
C ₁₄ H ₂₆	90-93	2.5	13.92	86.92	192	13.41	86.59	194
C ₁₅ H ₂₈	95-98	2	13.52	86.33	209	13.47	86.53	208
C ₁₆ H ₃₀	107-10	2	13.62	86.33	220	13.51	86.49	222
C ₁₇ H ₃₂	122-25	2	13.42	86.42	237	13.56	86.44	236
C ₁₈ H ₃₄	133-35	1.5	13.57	86.30	249	13.60	86.40	250
C ₁₉ H ₃₆	143-47	1	13.34	86.38	265	13.64	86.36	264
C ₂₀ H ₃₈	153-56	1	13.72	86.09	274	13.68	86.32	278
C ₂₁ H ₃₈	158-62	0.7	13.10	86.00	288	13.10	86.89	290
C ₂₃ H ₄₂	183-84	0.7	13.12	86.69	314	13.21	86.79	318
C ₂₅ H ₄₆	220-25	0.7	13.11	85.70	346	13.30	86.70	346

We feel convinced that, if we had had the time, the hydrocarbons C₂₂H₄₀ and C₂₄H₄₄ could also have been isolated, as repeated fractionation was not completed on some of the higher boiling fractions.

PHYSICAL PROPERTIES OF THE DISTILLATES.

	B. p. °C.	Pressure mm.	Density at 20°.	Ref. index 20.5°.	Rotation 1 dcm. tube
C ₁₁ H ₂₂	75-80	10.0	0.8186	1.4450	0.0
C ₁₂ H ₂₄	95-99	10.0	0.8395	1.4580	0.14
C ₁₃ H ₂₄	81-84	2.5	0.8558	1.4640	0.15
C ₁₄ H ₂₆	90-93	2.5	0.8632	1.4681	0.17
C ₁₅ H ₂₈	95-98	2.0	0.8723	1.4722	0.18
C ₁₆ H ₃₀	107-10	2.0	0.8751	1.4778	0.17
C ₁₇ H ₃₂	122-25	2.0	0.8833	1.4820	0.22
C ₁₈ H ₃₄	133-35	1.5	0.8889	1.4768	0.25
C ₁₉ H ₃₆	143-47	1.0	0.8926	1.4859	0.30
C ₂₀ H ₃₈	153-56	1.0	0.8977	1.4911	0.36
C ₂₁ H ₃₈	158-62	0.7	0.9026	1.4942	0.48
C ₂₃ H ₄₂	183-84	0.7	0.9180	1.5011	0.76
C ₂₅ H ₄₆	220-25	0.7	0.9432	1.5180	1.24

¹ Mabery, THIS JOURNAL, 41, 1690 (1919).

		MOLECULAR REFRACTIVE POWER.		
		Found.	Difference.	Calculated.
C_nH_{2n}	$C_{11}H_{22}$	50.55		50.56
			4.52	
	$C_{12}H_{24}$	55.07		55.15
	<hr/>		2.97	
	$C_{13}H_{26}$	58.04		57.83
			4.47	
C_nH_{2n-2}	$C_{14}H_{26}$	62.51		62.45
			4.56	
	$C_{15}H_{28}$	67.07		67.52
			3.87	
	$C_{16}H_{30}$	70.94		71.68
			4.55	
	$C_{17}H_{32}$	75.49		76.30
			3.94	
	$C_{18}H_{34}$	79.43		80.92
			5.48	
C_nH_{2n-4}	$C_{16}H_{36}$	84.91		85.54
			5.71	
	$C_{20}H_{40}$	90.62		90.16
	<hr/>		2.89	
	$C_{21}H_{42}$	93.51		92.57
			4.25	
C_nH_{2n-4}	$C_{23}H_{42}$	102.0		101.8
			4.5	
	$C_{25}H_{46}$	111.1		111.0

The refractive index was measured on an Abbé instrument at 20.5°. The values in the first column were determined by using the Lorentz-Lorenz formula, $n^2 - 1/n^2 + 2. m/d = M$, where n represents the refractive index measured, d the density and m the molecular weight. We used the theoretical molecular weight for the compound indicated for m . The values in the last column are the summation of the values for the number of carbon and hydrogen atoms in the compound, taking 2.418 for a singly bound carbon atom and 1.100 for hydrogen. The close agreement between the two columns shows that there is no double bond present, which corresponds to their chemical behavior, as the oils do not have any iodine value. The results also seem to substantiate the conclusions from our molecular weight determinations and our combustion analysis, namely, that we have three series of hydrocarbons present, C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} .

Molecular Volume.

We will now point out that the molecular refractive index indicates no unsaturation. The same is true of the molecular volume. The molecular volume of decane is 190.2 at 0° and the average difference for each CH_2 for paraffin hydrocarbons from C_4 to C_{10} is 15.6, so $C_{11}H_{24}$ should

have a molecular volume of 205.8. The first member of our series has a volume of 188.1 at 20.5° or about 184.1 at 0°. The difference between 205.8 and 184.1, a contraction of 21.7, is too great to be accounted for by the loss of 2 hydrogen atoms and the introduction of a double bond. According to Kopp,¹ the value of 2 hydrogen atoms is 11 and the value of a double bond seldom exceeds 8. This clearly indicates ring formation.

MOLECULAR VOLUME AT 20.5°.

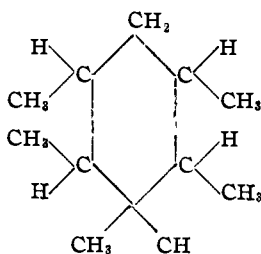
C ₁₁ H ₂₂	188.1
		14.4
C ₁₂ H ₂₄	202.5	7.8
C ₁₃ H ₂₆	210.3	14.5
C ₁₄ H ₂₈	224.8	13.7
C ₁₅ H ₃₀	238.5	14.0
C ₁₆ H ₃₂	252.5	14.7
C ₁₇ H ₃₄	267.2	14.1
C ₁₈ H ₃₆	281.3
C ₁₉ H ₃₈	295.7	14.4
C ₂₀ H ₄₀	309.6	13.9
C ₂₁ H ₄₂	321.3	11.7
C ₂₂ H ₄₄	346.4	25.1 or 12.5 for CH ₂
C ₂₃ H ₄₆	367.0	20.6 or 10.3 for CH ₂
C ₁₉ H ₃₆	295.7	14.4
C ₂₀ H ₃₈	309.6	13.9
C ₂₁ H ₃₈	321.3	11.7
C ₂₂ H ₄₀	346.4	25.1 or 12.5 for CH ₂
C ₂₃ H ₄₂	367.0	20.6 or 10.3 for CH ₂

The molecular volumes also substantiate that the third hydrocarbon belongs to a new series, as the average difference for a CH₂ group in our

¹ F. Eisenlohr, quoted in Nernst, "Theoretical Chemistry," revised in accordance with the seventh German edition by H. T. Tizard, McMillan & Company, London, 1916, p. 339.

values is 14.2 and as 2 hydrogen atoms are equal to 1 carbon atom there should be a difference between the second and the third member of 7.1 while the actual value found is 7.8. The second change in series between the tenth and eleventh member is not so characteristic; in fact, the molecular volumes found for the last three seem to suggest that they are not quite pure.

A hydrocarbon, $C_{11}H_{22}$, has been found by Mabery and Takano¹ in Japanese petroleum, by Mabery and Hudson² and has been obtained by Markownikoff and Oglobin from Apscheron naphtha.³ It was also found by Pictet and Bouvier⁴ in the Loire coal. They showed that this compound was a naphthene having the following structural formula:



The refractive index (1.4231 at 20°) and specific gravity (0.7832 at 20°) of this hydrocarbon corresponded to that one which Mabery and Quagle⁵ found in Canadian petroleum, being lighter than the one found in Californian petroleum. The hydrocarbon found in the Alberta asphalt, as will be seen from the tables, has also a higher refractive index and specific gravity than Pictet's had.

Hydrocarbons similar to the others we obtained have been found by Mabery in Texas petroleum⁶ and in grahamite and gilsonite.⁷ The distinctive feature of the hydrocarbons we have found is their density. The compounds isolated from gilsonite, grahamite, and in fact from most petroleum, are lighter than those of the Alberta asphalt. The hydrocarbons found by Mabery in the Texas petroleum are an exception, being of approximately the same density. This petroleum, like the oil from the Alberta asphalt, contains the series C_nH_{2n-4} , C_nH_{2n-2} , but not the series C_nH_{2n} .

¹ Mabery and Takano, *J. Soc. Chem. Ind.*, **29**, 614 (1900).

² Mabery and Hudson, *Proc. Am. Acad. Arts Sci.*, **35**, 255 (1900).

³ Oglobin, *Ber.*, **16**, 1983 (1873).

⁴ Pictet and Bouvier, *ibid.*, **46**, 3342 (1913).

⁵ Mabery and Quagle, *Proc. Am. Acad.*, **32**, 121 (1897).

⁶ Mabery, *THIS JOURNAL*, **22**, 553 (1900).

⁷ Mabery, *ibid.*, **39**, 2015 (1918).

No attempt has yet been made to determine the structures of these hydrocarbons. As they were all saturated, there can be only two possible structures in the case of the C_nH_{2n-2} series, either two phenyl groups linked together with the appropriate number of methyl or ethyl radicals, or of the saturated naphthalene type. The C_nH_{2n-4} compounds are tricyclic and the two of the C_nH_{2n} simply naphthenes with methyl groups attached.

Summary.

1. The asphalt from the Alberta tar sands has been analyzed by the Marcusson method and compared with the Trinidad and Bermudez asphalts.

2. A laboratory method has been devised to extract the hydrocarbon oil present in asphalts on a sufficiently large scale for fractional distillation. It is the only method so far devised which insures that the oils extracted actually existed as such in the original asphalt. It can, no doubt, be applied to all other asphalts and allied substances. Dr. Ruttan and Mr. McKinney of this university are using it successfully in isolating the hydrocarbons from the acetone extract of oil shale.

3. Our results show that heavy hydrocarbon oils can be distilled at temperatures up to at least 300° , without the aid of carbon dioxide, provided the pressure is kept low enough.

4. Thirteen apparently pure hydrocarbons have been isolated and their physical properties studied. They belong to the C_nH_{2n} , C_nH_{2n-2} , and C_nH_{2n-4} series.

A similar investigation of the Trinidad and Bermuda asphalts is now in progress. In concluding we wish to express our gratitude to Drs. Lehmann and Maass for their valuable help and suggestions.