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**MANUAL OF TESTING METHODS
FOR OIL SHALE AND SHALE OIL**

BY

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MANUAL OF TESTING METHODS FOR OIL SHALE AND SHALE OIL

By LEWIS C. KARRICK

INTRODUCTION

Although the Bureau of Mines has thus far made no large-scale experiments with oil shales, and the feasibility of the commercial manufacture of shale-oil products suited to present market requirements has not been demonstrated, there is ample reason to believe that these products will eventually supplement the more commonly used petroleum products and give equally good service. In 1919 the bureau, in cooperation with the Department of Metallurgical Research, University of Utah, began investigating the oil shales of the United States to obtain detailed information on their value. The States of Colorado and Indiana also cooperated through their State universities, in which research laboratories were organized to assist in carrying on the oil-shale studies planned and directed by the bureau. As a result of these studies much information is now available concerning laboratory methods of producing the greatest yields of the best products from oil shale.

In order to study the principles that govern the retorting of oil shales and to test the oils produced, it has been necessary to develop and standardize reliable apparatus and methods for distilling shale, and to adapt to the testing of shale oils some of the methods the Bureau of Mines uses for testing petroleum. The methods employed by the Scottish shale-oil manufacturers were also studied, but most of them have been superseded by those described in this bulletin, which give more comprehensive and accurate results and employ more convenient apparatus. This paper is presented, therefore, as a manual of apparatus and methods that the bureau has developed for work on oil shale and found satisfactory for routine tests and for research. Explanation and discussion of the principles underlying the methods of testing are included wherever necessary for a clearer understanding.

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Douglas Gould, J. W. Horne, W. L. Finley, and Douglas Fell. E. W. Dean gave valuable advice on apparatus and methods for testing shale oil. Special acknowledgment is made to L. A. Anderson for assistance and suggestions in the development of the oil-shale assay retort, and to Douglas Gould for his efforts throughout the long and detailed investigation required to determine the adaptability and limitations of the testing methods and apparatus.

OIL-SHALE TESTING ¹

OIL SHALE

The term "oil shale" covers a wide variety of solidified mixtures of argillaceous sediments and organic matter. The muds from which the shales were formed came from the erosion of many kinds of rocks within great drainage areas. The eroded materials were transported by streams to their final points of deposition—probably fresh-water lakes. The proportions of the component minerals differ in different parts of the shale beds because of the proximity of these areas to the sources of those minerals. Furthermore, the products of erosion varied as streams altered their courses and changes in the contours of the weathering mountains exposed different rocks to the elements. Therefore oil shales in different parts of the same formation vary in the proportions of their chief mineral constituents, such as quartz, pyrite, gypsum, and the silicates and carbonates of sodium, calcium, and magnesium. The organic matter in the shale is generally accepted to be plant remains derived either from accumulation of vegetation carried by streams into the lakes or from algæ that grew in the lakes. The plant remains became partly decomposed before they were solidified and sealed within the shale deposits. Gavin² has given an excellent summary of the opinions of the best authorities on the origin of oil shales.

Variations in the percentages of the ingredients that form the shale beds and the effects of geochemical and physical processes caused the oil shales as they now exist to differ greatly in color, texture, hardness, and resistance to erosion. The oil-shale measures contain many beds of oil shale, and the yield of oil ranges from a negligibly small quantity in some beds to as high as 80 gallons per ton of shale in others.

The organic substance of true oil shales is only slightly soluble in the common solvents of bitumen. Oil, therefore, is not present as oil in the shale, but must be formed from the organic substances of

¹ Karrick, L. C., *Fundamental Factors in Analyzing and Evaluating Oil Shales*; chapter in *Oil Shale*, pp. 90–105: A. C. S. monograph series, 1925.

² Gavin, M. J., *Oil Shale—An Historical, Technical, and Economic Study*: Bull. 210, Bureau of Mines, 1922, 201 pp.

the shale by the application of heat; that is, by destructive distillation.

PRINCIPLES OF DESTRUCTIVE DISTILLATION AS APPLIED TO THE RETORTING OF OIL SHALE

Knowledge of the chemistry of pyrolysis (the breaking down by heat) and pyrogenesis (the formation by heat) of organic substances is being rapidly extended through the growing use of these principles in the cracking of oils and in the industries of coal distillation and gas manufacture. The thermochemical reactions in the destructive distillation (retorting) of oil shales are similar to those that occur in cracking oil and in carbonizing coal. The retorting of oil shale is similar to the low-temperature distillation of coal in that the products are a carbon residue containing a relatively high percentage of volatile matter, a small yield of gas, and a large yield of oil. High-temperature distillation of oil shale or coal gives a carbon residue having a low proportion of volatile matter, a large quantity of fixed gas, and a small quantity of oil. The oil produced by low-temperature distillation is much more easily refined to yield petroleum substitutes. The fixed carbon that remains in the spent shale corresponds to petroleum still-coke or to the coke from the carbonization of coal; the amount of volatile matter present in the coke is reduced as the temperature of distillation is raised.

The first action of heat on oil shale is the removal of the occluded gases that are present in small quantities. Also, in some shales low temperatures remove traces of light oil that may have been present as such or perhaps, prior to its decomposition, as resin or bitumen. As the temperature is raised, the organic matter of the shale decomposes and produces vapors which condense to form shale oil. Simultaneously, fixed gases are evolved. When the organic matter of a typical shale is heated, it changes first into a soluble bitumen and, as the heating continues, this bituminous substance further breaks down or "cracks" and forms shale oil. Whether all shales yield a bituminous substance of this kind as a primary decomposition product is not definitely known as yet. Some of the rich shales yield less bitumen than leaner shales when both are subjected to the same temperature and period of heating. A possible explanation of this paradox is that these richer shales produce a larger amount of bitumen that is less stable and therefore breaks down quickly into vapors and gases.

Little is known of the ingredients or the chemical composition of the oil-yielding substance in oil shale, but the bureau's investigations have shown that it is complex, that it is composed mainly of

the elements, carbon, hydrogen, oxygen, sulphur, and nitrogen, and that its composition differs in different shales. Since the proportions of these elements are not the same in all shales, it is probable that the chemical composition of most shale oils varies likewise.

The Bureau of Mines has centered its experimental work largely upon the development of retorting conditions that will obtain from shales the largest yields of the desired products. In general, these products are those that can be substituted for petroleum products and can be made and refined with the smallest loss and by the simplest operations. The work done has shown that the conditions which can be controlled easily during retorting—time, temperature, and pressure—influence greatly the chemical and physical properties and the yields of the crude oils obtained from oil shales. The organic matter (kerogen) of the shales breaks down to form oils of higher quality when the retort temperature is low.³ Although most shales apparently begin to give off vapors at 300 to 375° C., these same shales will slowly decompose and yield oil at temperatures as low as 100 to 200° C. To retort the shales completely at such low temperatures, however, would require many hundreds of years.

SHALE OIL

As stated above, shale oil is an extremely variable product. It is also extremely complex in composition. By many retorting tests of the principal oil shales of the United States and of foreign countries, the Bureau of Mines has demonstrated that identical methods of retorting give different oils from different oil shales and also that the same shale yields markedly different oils when the conditions of retorting are changed. Apparently, there is no practical method or manipulation of retorting conditions by which shales that differ widely can be made to produce oils having exactly the same properties. Shale oils may contain paraffin hydrocarbons, the proportion of which is largely influenced by the thermal reactions that took place during retorting. However, in most shale oils other types of hydrocarbons and their derivatives predominate. Olefins may be present in large proportions and aromatics in small proportions. Shale oils probably also contain extremely complex compounds. The nature and complexity of these are due to the oil-producing substance in the shale, the amount of undecomposed bitumen present, and the conditions that existed during the destructive distillation.

³ Karrick, L. C., Effects of Temperature and Time of Reaction in Distilling Oil Shales on the Yields and Properties of the Crude Oils: Reports of Investigations, Serial 2456, Bureau of Mines, March, 1923, 8 pp.

NEED FOR STANDARD TESTING METHODS AND APPARATUS

The results obtained in tests of oil shale and shale oil depend upon the apparatus and methods used, as well as upon the nature of the shale. Many retorts now used in oil-shale assaying, especially by commercial assayers, are unreliable and give misleading results. Furthermore, no comprehensive method for the examination of oil shale or shale oil has yet been adopted by the shale industry. Consequently, to assure convenience and accuracy in rapid assays in the laboratory and in field tests and to provide a basis of comparison between assays made by other methods, a standardized retort and standard methods of testing are necessary. The author hopes that this report will supply the information needed.

SCHEME OF TESTS TO WHICH OIL SHALES AND SHALE OILS MUST BE SUBJECTED

An accurate determination of the oil yield of an oil shale is by no means simple. If the assay involved merely the extraction of a natural oil from associated mineral matter, different analysts could be expected to agree reasonably well as to the quantity and quality of the recovered oil. The determination of the oil yield of shale involves, however, the process of "manufacturing" the oil within the retort through the action of heat on the organic constituents of the shale under carefully controlled conditions, and also the removal, condensation, and recovery of the oil.

The conduct of the retorting is the most important part of the oil-shale assay because the yield and character of the oil obtained depend largely on it. The bureau has carefully investigated how far the yield and the properties of the oil may be varied by changes in retorting conditions, and has adopted a procedure that involves five retorting tests which will give this information accurately for any oil shale. These retorting conditions must be closely followed in testing all shales, otherwise logical comparisons can not be made.

Next the products of the retorting test are examined. The amounts and properties of the oils are determined and compared. Fractional distillations are made, and specific gravity, viscosity, melting point, unsaturation, and carbon residue are determined, usually by the method employed in testing petroleum oils.⁴

The yield and composition of the gas evolved during retorting is determined. From the results of the gas analysis the amount of thermal decomposition of the organic matter can be estimated and the fuel value of the gas determined.

⁴ Dean, E. W., Hill, H. H., Smith, N. A. C., and Jacobs, W. A., *The Analytical Distillation of Petroleum and Its Products*: Bull. 207, Bureau of Mines, 1922, 82 pp.

It is to be emphasized that the application of the tests described in this bulletin makes available information as to the quantity and quality of the different types of crude oils and distillates that may be produced from an oil shale by varied conditions of retorting. In other words, the tests furnish reliable data from which conclusions as to the relative values of different shale oils and oil shales may be drawn. The shale-oil testing methods give results similar to those obtained by the usual methods of testing petroleum. It is obvious that the relative values of different oil-shale deposits can not be determined until the shales have been accurately compared. Then, and then only, should consideration be given other economic factors, such as labor, fuel, power, water, timber, and transportation and markets.

BUREAU OF MINES OIL-SHALE ASSAY RETORT

The assay retort and its accessories, shown in Figure 1, are easily assembled and may be obtained from most dealers in laboratory supplies. The 1-pint retort was selected because a full charge of a lean shale (35 gallons of oil per ton) produces just enough oil for the subsequent small-scale analytical distillation test and other tests. The same volume of a richer shale (although of less weight) yields more oil; therefore a larger retort is not necessary for routine determinations. Furthermore, because of the low heat conductivity of oil shale, rapid retorting in a large retort would require high temperatures which would cause vapor-phase decomposition of the crude oil. In consequence the results would be extremely variable and the yields of oil would be low. In the assay retort the vapors and gases move in the direction of the flow of heat so that little secondary decomposition can take place. This movement of vapors and gases toward the center and the top of the charge of shale helps to equalize temperatures in the retort.

Figure 1 also shows a battery of assay retort burners connected to the gas supply and a manometer in order that the pressure at each burner may be observed. By turning the individual regulating cocks, the gas for each burner can be adjusted at a predetermined pressure to give any desired heat and rate of distillation.

The ease with which destructive distillation can be controlled in the assay retort makes possible the production of oils of good quality from most American oil shales. When Scottish oil shale is retorted in this apparatus the oil produced is of as high quality as that produced from the same shale by commercial Scottish retorts. (See analyses 1 and 2, Table 1.)

EFFECTS OF VARYING RATES OF DISTILLATION OF OIL SHALES

An extended series of tests was made to determine within what limits the quality and the yield of oil from any shale may be changed by changing the rate and the temperature at which the oil is formed.⁵ These tests showed definitely that the quantity of oil obtained from any oil shale depends on the rate of retorting; the large quantity is

FIGURE 1.—Bureau of Mines oil-shale assay retort, gas connections, and manometer heat-control device for a battery of four retorts: 1, Fisher gas burner; 2, mercury retort, pint size; 3, asbestos-lined metal jacket; 4, asbestos cover; 5, ring support and ring stand; 6, $\frac{1}{4}$ -inch street ell; 7, $\frac{1}{4}$ -inch wrought-iron pipe; 8, $\frac{3}{8}$ -inch by $\frac{1}{4}$ -inch by $\frac{1}{4}$ -inch tee; 9, $\frac{1}{4}$ -inch nipple, 45° at plain end; 10, 100-c. c. glass-stoppered graduate; 11, $\frac{3}{8}$ -inch pyrex glass tubing; 12, Liebig condenser; 13, best grade of cork bushings; 14, cut-off clamps for tubing; 15, gas piping; 16, rubber tubing; 17, manometer pressure bulb; 18, main gas valve; 19, individual gas-regulating cocks

obtained by retorting rapidly. When the actual oil-producing period is approximately two hours, the yield of oil from different domestic shales is from 2 to 5 per cent greater (depending on the richness of

⁵ Karrick, L. C., *Effects of Temperature and Time of Reaction in Distilling Oil Shales on the Yields and Properties of the Crude Oils: Reports of Investigations, Serial 2456, Bureau of Mines, March, 1923, 8 pp.*

Finley, W. L., Horne, J. W., Gould, D. W., and Bauer, A. D., *Assay Retort Studies of Ten Typical Shales: Reports of Investigations, Serial 2603, Bureau of Mines, May, 1924.*

the shales) than when the retorting period is eight hours. When retorting is conducted so rapidly that distillation is complete in less than one and one-half hours, there is danger of inaccurate results because the condenser capacity may be exceeded; moreover, the oil vapors may be decomposed into fixed gases and carbon by the excessively high temperatures necessary at this rate.

TABLE 1.—Comparison of shale oils made in testing retorts¹ with Scottish shale oil produced commercially and average-quality petroleum from Pennsylvania and Mid-Continent fields

Source of oil.....	Scottish shale		Shale from Soldier Summit, Utah	Pennsylvania crude	Typical Mid-Continent crude
How produced.....	Scottish commercial retort	Assay retort	Assay retort	Oil well	Oil well
Retorting time (hours).....	6 to 8	2	5		
Yield of oil.....		18.1	40.2		
Specific gravity of oil.....	0.867	.864	.882	0.812	0.835
Setting point of oil, ° C.....	28	32	33	(¹)	(¹)
Distillation, first drop, ° C.....	49	44	40	26	30
Per cent distilled to 200° C.....	12.22	16.63	18.81	31.93	28
Unsaturation, 200° C. fraction per cent.....	28	34.1	40.2	3.6	4
Per cent distilled, 200–275° C.....	23.22	20.47	20.10	20.83	15
Unsaturation, 200–275° C. fraction per cent.....	34	34.1	40.2	3.6	4
Vacuum fraction to 200° C.:					
Per cent.....	9.32	2.10	2.64	3.33	4
Specific gravity.....	.872	.868	(³)	.826	.850
Viscosity.....	38	38	(³)	39	41
Setting point, ° C.....	(¹)	(¹)	(¹)	(¹)	(¹)
Vacuum fraction, 200–225° C.:					
Per cent.....	5.27	4.38	7.80	7.75	6
Specific gravity.....	.881	.872	.880	.832	8.55
Viscosity.....	40	41	42	40	47
Setting point, ° C.....	(¹)	(¹)	(¹)	(¹)	(¹)
Vacuum fraction, 225–250° C.:					
Per cent.....	7.16	5.88	9.20	6.02	7
Specific gravity.....	.892	.874	.889	.841	.865
Viscosity.....	46	43	48	45	60
Setting point, ° C.....	24.5	21.5	18	15.5	15
Vacuum fraction, 250–275° C.:					
Per cent.....	6.13	7.30	14.90	5.37	4
Specific gravity.....	.902	.894	.906	.848	.875
Viscosity.....	52	50	58	51	80
Setting point.....	29	29	31.5	22.5	20
Vacuum fraction, 275–300° C.:					
Per cent.....	6.07	9.45	8.88	5.16	6
Specific gravity.....	.911	.898	.928	.859	.890
Viscosity.....	60	60	72	67	130
Setting point, ° C.....	34	37	40	30	30

¹ Analyses by L. C. Karriek and M. J. Gavin.

² Fixed-gas gasoline not included in crude used for these distillations.

³ Combined with next higher cut.

⁴ Not determined.

Not only does the rate of retorting influence the yield of shale oil but it greatly affects the quality of the oil—so much so that the relative values of oil shales can not be estimated from the yields and qualities of the crude oils unless the rates (temperatures) of retorting are known.

Rapid retorting of shales gives large yields of crude oil having a high specific gravity (low A. P. I. gravity⁶), high melting point, small percentage of light distillate (motor fuel), low degree of saturation of the light distillate, and high carbon residue, as shown by the Conradson test. An oil produced by rapid retorting will usually contain carbon and dust particles in suspension, because of the high temperature and the high velocity at which the vapors escape from the retort.

A slow rate of retorting gives a lower yield of crude oil than fast retorting, but the specific gravity of the crude oil is low (high A. P. I. gravity), the melting point is low, the percentage of light distillate in the crude is high, the light distillate is more highly saturated, and the carbon residue is low. The crude oil produced in this manner is practically free from dust and carbon particles and is superior in odor and general appearance to that produced rapidly. Slow retorting tends to yield oils that are clear and transparent, bright and noticeably green in color, and usually fluorescent.

The curves in Figure 2⁷ show the differences in yield and properties of crude oil that are caused by differences in the rate of retorting. They were plotted from results obtained by retorting a typical shale at many different rates (temperatures). Similar experiments with other samples from the major oil-shale deposits of the United States and foreign countries indicate that curves of the same type with the same relative values (of course not the same absolute values) are applicable to any shale. To facilitate interpretation of the data the curves have been plotted above the same horizontal axis, which is scaled to represent the time required to retort the shale sample at the different rates of retorting. Therefore, the points of intersection of any vertical line—for example, that representing two hours—with the different curves indicate the properties of the oil produced when retorting proceeded at a uniform rate and was just completed in two hours.

TEMPERATURES REQUIRED FOR DIFFERENT RATES OF RETORTING

The temperature necessary to complete the retorting at each of the different rates is of interest. Curve 9 in Figure 2 shows that in rapid retorting the oil is formed at higher temperatures than in slow retorting. The curve indicates the temperature of the shale when retorting was completed—it does not represent the average temperature of the shale during retorting. The temperature of the shale

⁶ The A. P. I. (American Petroleum Institute) gravity scale has been adopted by the oil industry because of the confusion caused by Baumé gravity scales being calculated from different moduli. The A. P. I. gravity is the same as the Baumé with modulus 141.5.

⁷ Karrick, L. C., work cited.

during both rapid and slow retorting and the corresponding progress of retorting is shown in Table 2:

FIGURE 2.—Curves showing changes in properties of crude shale oil resulting from different rates (temperature) of distillation

TABLE 2.—Temperature of shale during rapid and slow retorting

Total oil yield from shale (per cent)	Tempera- ture of shale re- torted rapidly	Tempera- ture of shale re- torted slowly	Difference in tem- peratures for equal progress of retorting
	° C.	° C.	° C.
0 (first oil vapors)	365	360	5
25	425	400	25
50	440	405	35
75	460	420	40
100	525	460	65

These data show that at a fast rate of retorting the temperature of the oil-forming material of the shale may be considerably higher than is necessary. The high temperature required for fast retorting of the shale—that is, retorting in a short interval of time—causes rapid decomposition of the original organic material. Because of the large volume of vapors and the velocity at which they issue from the shale particles, some bitumen, a primary decomposition product, is carried out mechanically before it is sufficiently changed into oil. Thus the conditions which favor both fast retorting and quick removal of vapors from the retort will produce a large yield of crude oil, but this oil will be of poorer quality than that produced slowly and at lower temperature.

FLOW OF HEAT INTO OIL SHALE DURING DISTILLATION

Oil shale is a mixture of minerals and organic substances solidified into a close-grained and compact mass. The rate at which heat flows into a piece of shale depends (1) on the temperature of the atmosphere surrounding the shale and (2) on the thermal conductivities of the mineral and organic components of the shale. Heat flow is retarded by heat being consumed (1) in vaporizing free moisture, (2) in decomposing unstable minerals, such as gypsum, hydrous silicates, and pyrite, and (3) in breaking down the organic substances. In addition, heat is carried out of the piece of shale by the vapors and gases evolved. Obviously, these vapors and gases become increasingly hotter as they pass outward from the inside of a piece of shale in a retort.

Since the distillation of shale necessarily begins on the surfaces of the lumps and progresses toward the center while the volatile products of the retorting flow in an opposite direction, the production of crude oil of the best quality by quick retorting of large lumps of shale is evidently impossible. The well-known Scottish type of shale retort handles shale in lumps the size of building bricks, consequently eight hours is allowed for retorting, so that temperatures within the shale lumps may be fairly even. An atmosphere of superheated steam and water gas surrounding the pieces of shale supplies heat, therefore all faces of the shale lumps are at the same temperature and receive heat at an equal rate. As a result, the crude oil is produced slowly and at moderately low temperatures and is of relatively excellent quality.

If shale is crushed rather fine, it may be heated fairly rapidly in the assay retort without much decomposition of the vapors. Of course, slower heating will produce crude oils that are better, but fine crushing is a means of preventing the oil vapors being over-

heated as they come to the surface of the shale lumps during fast retorting.

The assay retort is so shaped that the paths of flow of the vapors converge toward its center and its outlet. This assists efficient transfer of heat to shale at a distance from the retort walls and thereby helps to reduce at all times the temperature differences between the outside and the interior of the shale mass.

TEMPERATURE RELATIONS WITHIN THE CHARGE

A series of tests was made to determine temperature relations within the retort during both fast and slow retortings. Thermocouples were placed within the charge at four points 1 inch apart on the vertical axis of the retort as shown in Figure 3. Thermocouple No. 1 was near the bottom of the charge but did not touch the retort bottom, No. 2 was 1 inch above No. 1, No. 3 was 1 inch above No. 2, and No. 4 was 1 inch above No. 3, or about 1 inch below

FIGURE 3.—Section of assay retort, showing position of thermocouples

the top of the shale charge. The curves in Figure 4 show the temperature changes at these four positions while the charge is retorted at fast and slow rates. The dotted lines record the production of oil from the beginning to the end of the runs. Therefore the curves show continuous relationships between the temperatures throughout the shale charge and the progress of retorting.

The curves of Figure 5 show the relationship when the shale is distilled at the same rates in a rotary retort (fig. 6) of the same capacity as the assay retort. This rotary retort was designed to insure uniform heating at all points in the charge of shale.

Comparison of the curves for temperature and oil yields in Figures 4 and 5 shows that the average rate of retorting (rate of rise of temperature) of the shale in the cooler parts of the charge of the assay retort is the same as at the surface of the charge, because the temperature curves are generally parallel and also are similar to the curves for the rotary retort. Therefore, as the average rate of distillation is the same throughout the stationary charge, the oils produced by either retort from the same shale retorted at equal rates are equivalent in yield and quality.

EQUIVALENT RATES OF RETORTING

Oil shales are retorted at the same rate when the retortings are completed in the same interval of time. "Equal rates" imply equal

rates of transformation of the kerogen to bitumen and shale oil, not equal rates of accumulation of oil. Two shales of different richness are not retorted at the same rate if oil is caused to accumulate at the same rate. The rates of retorting are equal only when the thermochemical reactions producing the oil take place at equal rates; that is, all shales must pass through the same range of temperature in the same interval of time if the rates of retorting are to be considered

FIGURE 4.—Record of temperature change at four positions in retort, at fast and slow rates of distillation

equal. A 60-gallon shale contains three times as much oil-forming substance as a 20-gallon shale, and therefore the volume and velocity of escape of vapor from the first shale will be three times as great as from the second shale. Nevertheless, equal rates of retorting obtain only when both rich and lean shales are heated at the same rate. Since more of the bitumen of the rich oil shale is carried out of the retort in suspension in the large volume of vapors and gases evolved,

it is well to recognize the fact that the oil produced at a given rate from a rich shale resembles the oil produced at a slightly faster rate from a leaner shale of the same type.

Many experiments show that a shale yields equal quantities of crude oil of the same quality, whether retorted in the assay retort or in the experimental rotary retort (which keeps the charge well mixed and at equal temperature throughout), provided the rate of

FIGURE 5.—Relation of temperature to oil production at fast and slow rates of distillation in rotary retort

retorting is the same. This indicates that the small temperature differences within the charge of shale in the stationary assay retort have no appreciable effect on the yield and quality of the oil produced.

CARE OF ASSAY RETORT

When the assay retort and its accessories are assembled, all pipe threads should be turned up tightly. The cork connections 13 (fig. 1) with the reflux condenser 11 and the graduated cylinder 10 should

FIGURE 6.—Rotary retort for oil-shale assays: 1, Commutator rings; 2, binding posts for heating element; 3, commutator block, mercury cells; 4, binding posts for power connections; 5, variable speed motor; 6, belt driving pulley; 7, worm drive; 8, worm gear; 9, nonfriction rollers; 10, base; 11, transit disk; 12, permanent gasket; 13, aluminum cylinder; 14, retort cylinder for shale; 15, thermocouple junction; 16, thermocouple well; 17, nipple to bring outlet above shale level; 18, el.; 19, vapor outlet; 20, space for graphite packing; 21, sealing flange on brass outlet tube; 22, steel friction washer; 23, asbestos compression disk; 24, retort cap; 25, adjustable plug; 26, vapor tee for condenser and receiver; 27, brass washer; 28, steel compression spring; 29, electrical heating elements; 30, porcelain tubes; 31, steel cylinder incasing heating elements; 32, transit ends; 33, asbestos paper covering; 34, steel drum; 35, drip tube; 36, water-filled manometer tubes; 37, gas measuring meter; 38, air-cooled reflux condenser, pyrex tubing; 39, 100-c. c. graduate; 40, scrubbing towers; 41, water-cooled reflux condenser; 42, annular radiation-equalizing space

be well sealed with a mixture of dry pulverized litharge and glycerin.

The contact surface between the lid and base of the retort must be prepared and maintained with extreme care. The surface will not form a gas-tight fit when new, therefore the two parts must be ground together by hand with 150-mesh carborundum and water; the motion used is the same as that in grinding gas-engine valves. Grinding is facilitated if the lid is clamped in an inverted and level position on a table and the base of the retort is pressed down lightly while it is rotated on the lid. After being ground until the contact surfaces are bright, the parts are cleaned thoroughly with water and the lid is clamped in place. The improved contact is then tested by immersing the retort in water and forcing air from the lungs or from an air supply into the delivery tube. If air bubbles appear and readjustment of the lid does not stop the leakage, the grinding is repeated. The contact between the clamp screw and the retort lid must be perfectly flat and smooth; otherwise tightening the screw will not equalize the pressure between the lid and base of the retort and stop the leakage. When the retort is charged, the test for leakage is again made. Preparation of the contact surfaces may require 30 minutes to an hour when the retort is first used; but if an air-tight contact is once obtained a little grinding, requiring less than one minute, before each run will keep the surfaces in perfect condition. The ground surfaces will form a gas-tight seal if kept perfectly clean and aligned while the clamp is tightened.

The author does not recommend the use of cement or a gasket, as neither is necessary if the contact surfaces have been properly prepared. All of the cements tested for this purpose were unsuitable, either because they failed to seal the joint or, if they made a tight seal, they adhered so tenaciously that cleaning the surfaces for subsequent runs was difficult. Some cements when heated become more or less porous and lose oil by capillarity. A clean, well-prepared, carborundum-ground contact is easily maintained, and when tested as above described the analyst may be certain that no oil has been lost through leakage of vapors during the run. After a little experience each retort can be ground and charged ready for a run in about five minutes.

OPERATION OF ASSAY RETORT

CHARGING THE RETORT

The shale for charging the retort is crushed so that all of it will pass an 8-mesh or finer screen. If the sample of shale is a mixture of rich and lean shales, it must be ground to approximately 10 mesh

to prevent the segregation of rich shale from lean during handling. Rich shale is tougher than lean shale and resists crushing, therefore it will predominate in the larger pieces in the sample. If a bulk sample that has passed through a $\frac{1}{4}$ -inch screen is separated by selective screening and the various sizes retorted, it often happens that the coarser sizes yield 50 per cent more oil than the finest sizes. It is advisable, therefore, to mix the sample thoroughly and then weigh out just enough to fill the retort. The charge may be tamped into the retort without affecting the results, although tamping is seldom necessary. Experience has demonstrated that it is better to permit the charge to rest loosely in the retort, as some rich shales sinter and cake together during retorting and removal of the residue becomes extremely difficult. After the lid is fastened carefully in place and tested for leakage, as described above, the retort is placed in the jacket 3, Figure 1, and closed with the cover 4; the burner 1 is started, then the graduated cylinder 10 and reflux condensers 11 and 12 are fastened tightly in place.

RETORTING THE SHALE

At first a small flame is used so that no oil will appear in the receiver within one hour after starting. An hour is about the minimum time in which the shale charge can be brought to the initial oil-yielding temperature and yet be of fairly even temperature throughout. Some shales begin to yield vapors at approximately 250° C., but others require a temperature of 375° C. Before much oil is distilled the coolest shale in the center of the charge should be at least as hot as the vaporizing temperature of the oil; otherwise some of the vapors will condense in passing through the central or coolest part of the charge toward the outlet. Subsequent redistillation of this condensed oil will cause cracking and resultant losses; it will also influence the properties of the recovered oil.

The manometer 17 (fig. 1), when connected in turn to the different burners, will indicate by the pressure registered the heat supplied to each retort. The same initial supply of heat is suitable for all shales during the preliminary heating. When oil has begun to form, however, the supply of heat must be controlled to retort the particular shale at the desired rate, as shales of different types and richness require slightly different amounts of heat when being retorted at equal rates.

When about 1 c. c. of oil has accumulated, the flame should be increased. If the maximum yield of oil is desired, the shale must be retorted rapidly as soon as oil vapors begin to evolve. If the flame has been so regulated that oil first appears in about 60 minutes and retorting is to be rapid, the size of the flame may be safely doubled;

thereafter every 20 to 40 minutes (the interval to be determined by experiment) the heat should be so increased that the oil will continue to collect at a uniform rate. Retorting may be accurately controlled by frequent use of the gas-pressure manometer.

The oil should accumulate in the graduate at an even rate. The analyst will soon become adept in controlling the rate during rapid retorting so that the capacity of the condenser will not be exceeded by sudden and irregular evolutions of large volumes of vapors.

FIGURE 7.—Rate of oil production and gas burner regulation at fast and slow rates of retorting

Figure 7 shows a convenient way of recording the accumulation of oil during retorting at any given rate. The oil-yield curve should be smooth and straight throughout its major part, as shown by ideal curves. The regulation of the gas burner should also be recorded, as indicated, throughout the progress of retorting.

If retorting has progressed uniformly, the rate of accumulation of oil will decline suddenly as the last oil is being distilled; when this cessation is evident the heat must be increased once more. The final heat should be the same for all shales, as the analyst often

desires comparative information concerning the yield of combustible gas produced from different shales. For a short time after oil production ceases, combustible gas continues to evolve, though its fuel value decreases rapidly due to the evolution of a large percentage of hydrogen and to contamination with carbon dioxide gas pro-

FIGURE 8.—Changes of gas composition during the retorting of a typical oil shale

duced by the dissociation of carbonates. Some shales are composed largely of carbonates and yield a large percentage of carbon dioxide gas if the shale is heated to red heat. Figure 8 shows how the composition of the gas evolved changes during retorting. For uniform practice it is therefore advisable to increase the heat

slightly, immediately after oil production stops, and allow 30 minutes for temperature equilibrium to be reached. This additional heating will suffice to remove most of the volatile constituents in the residual carbon of the spent shale. A white fume may appear at the end of the run, but this carries no condensable oil vapors.

The delivery tube 7, Figure 1, should be kept fairly warm throughout the run in order to prevent oil congealing in it, and also to facilitate drainage at the end of the run. At the end of the final 30-minute heating period the bottom of the retort will be a very dull red; then the analyst can be certain that oil production is complete, as this temperature is well above the final oil-yielding temperature of all oil shales. Heating for the additional half hour also permits the delivery tube and reflux condenser to drain completely.

FIGURE 9.—Ideal curves of oil production at five standard rates

NECESSITY OF TESTS AT SEVERAL RATES OF RETORTING

The value of one oil shale compared with others can be determined only after all the shales in question have been retorted under identical standard conditions. Many oil-shale analyses show that the degree of change in the yield and properties of the crude produced at different rates of retorting varies markedly with different shales. Therefore it is important to retort all shales at several different standardized rates. The Bureau of Mines has adopted as standard practice five rates that are easily applied; these rates provide data on the limits of variation in yields and properties of the crude which might be obtained in actual practice. Less than five retortings ordinarily can not supply the necessary data on how far the yield and the properties of oil are altered by a change in the rate of retorting. The heat supply is so controlled that oil will be produced throughout the five standard retortings at the following rates: 1 c. c. in 1, 2, 3, 4, and 5 minutes, respectively. (See curves, fig. 9.) These rates are such that a shale yielding approximately 42 gallons (1 barrel) of oil per ton requires 1.15, 2.30, 3.45, 4.60, and 5.80 hours, respectively,

to carry through the retortings. These periods do not include the time required to raise the temperature of the shale in the retort to the oil-production point. Distillation tests of the oils obtained in the five rates of retorting of a 42-gallon shale will give data which correspond to those from the curves of Figure 2 above points 1.15, 2.30, 3.45, 4.60, and 5.80 on the horizontal axis. From a set of curves of this type the yield and properties of the crude oil can be conveniently determined by interpolation for any rate of distillation—that is, the time of retorting—within the limits of the curves.

MEASUREMENT OF OIL PRODUCED FROM A RETORTING TEST

VOLUMETRIC METHOD

Inexperience in measuring the accumulated oil often causes a greater error in results than the lack of refinement in retorting technique or the imperfections in the retort. Therefore, the yield of oil must be measured with much care. The following rapid and accurate procedure has been developed:

Warm the stoppered graduate 10 (fig. 1) and contents at 50° C. until the oil is quite fluid. Allow the water in the oil to settle well (some water is given off during the last stages of the shale retorting and may remain suspended in the partly congealed oil). Before the volume of oil and water can be determined accurately, the formation of a perfect meniscus must be aided by the release of any oil and water clinging to the sides of the graduate. This release is accomplished best by rapidly revolving the graduate, while it is still warm, between the palms of the hands.

First read the upper level and then the lower level of the oil, provided the lower level is well defined and not obscured by emulsion, sediment, or clinging oil and water. The following procedure will facilitate accurate reading of the lower meniscus and will also insure that water and sediment have settled out completely: With a pipette draw off all except a few cubic centimeters of the warmed oil and save it for further testing; dilute the remaining oil with 10 to 20 c. c. of clean gasoline and agitate gently until the emulsion disappears. Allow the solution of shale oil and gasoline to settle, then draw it off and discard it; add gasoline as before. Repeat this washing until a clear meniscus results, then make a final reading; the difference will be the yield of oil. From the number of cubic centimeters of oil collected, calculate the oil yield in gallons per ton of shale.

GRAVIMETRIC METHOD

To determine more accurately the amount of oil produced, weigh the graduate and contents (the weight should be expressed in

grams); allow enough time for water and dust to settle well while the graduate is kept warm; then determine the yield of oil by the method described below:

With a large pipette draw off all the oil except 4 or 5 c. c., taking care that no water or sediment is drawn into the pipette. Set this sample aside for use in all determinations to be made, as it will be sufficiently representative of the total oil recovered. Dilute the remaining few cubic centimeters of oil with 20 c. c. of warm gasoline and wash down the inner sides of the graduate with the gasoline. When the shale oil is well mixed with the gasoline and all water and solids have settled, draw off the clear liquid nearly to the level of the water and discard it. Repeat the washing several times until colorless gasoline remains above the water and no shale oil is left clinging to the sides of the graduate.

Remove the gasoline to approximately the level of the water and repeat the washing with petroleum ether. Draw off most of the ether and eliminate the remainder by evaporation. The last traces of ether are quickly removed by tipping the graduate as far as possible to one side without spilling the contents, and then revolving the graduate while air is blown into it; during rotation the ether is picked up on the side walls of the graduate, which provide a large evaporating surface.

As soon as the ether disappears (in about a minute), weigh the graduate, which now contains only the water and sediment. Subtract this weight from that of the graduate before the oil is removed; the difference will be the exact weight of the total oil obtained from the shale. With the Barret, Regnault, or similar type of specific gravity bottle, determine the specific gravity of the oil first removed and divide the total weight of oil obtained by the specific gravity of the oil. The result will be the true volume of oil (in cubic centimeters) recovered at the temperature (preferably 60° F.) at which the specific gravity was determined.

CALCULATION OF YIELD OF OIL

FORMULAS

The following formulas are convenient for calculating yields of oil:

$$\text{Gallons of oil per ton of shale} = \frac{\text{Cubic centimeters of oil} \times 239.66}{\text{Grams of shale used in retort.}} \quad (1)$$

$$\text{Gallons of oil per ton of shale} = \frac{\text{Cubic centimeters of oil} \times 0.52836}{\text{Pounds of shale used in retort.}} \quad (2)$$

Figure 10.—Alignment chart for determining oil yields in assaying oil shale

Duplicate volumetric determinations should agree within 2 per cent and gravimetric determinations within 0.5 per cent.

The factors given in Table 3 facilitate calculations. For any given weight of shale used (column 1 or 2) select the corresponding factor in column 3. Divide the volume of oil collected (expressed in cubic centimeters) by this factor to convert the volume into gallons of oil per ton of shale. For charges of shale whose weights in grams are not even multiples of 10, the proper factor can be quickly determined by interpolation. Example:

400 grams of shale used (column 1), therefore factor=1.669 (column 3).

$$68 \text{ c. c. of oil obtained, therefore oil yield} = \frac{68}{1.669} = 40.8 \text{ gallons.}$$

TABLE 3.—*Factors facilitating calculations*¹

Weight of retort charge			Weight of retort charge			Weight of retort charge		
Grams	Ounces	Factor	Grams	Ounces	Factor	Grams	Ounces	Factor
10	0.35	0.042	210	7.41	.876	410	14.47	1.711
20	.71	.083	220	7.77	.918	420	14.83	1.753
30	1.06	.125	230	8.12	.960	430	15.18	1.794
40	1.41	.167	240	8.47	1.001	440	15.53	1.836
50	1.76	.209	250	8.82	1.043	450	15.88	1.878
60	2.12	.250	260	9.18	1.085	460	16.24	1.919
70	2.47	.292	270	9.53	1.127	470	16.59	1.961
80	2.82	.334	280	9.88	1.168	480	16.94	2.003
90	3.18	.376	290	10.24	1.201	490	17.30	2.045
100	3.53	.417	300	10.59	1.253	500	17.65	2.086
110	3.88	.459	310	10.94	1.294	510	18.00	2.128
120	4.24	.501	320	11.30	1.335	520	18.36	2.170
130	4.59	.542	330	11.64	1.377	530	18.71	2.212
140	4.94	.584	340	12.00	1.419	540	19.06	2.254
150	5.29	.626	350	12.36	1.460	550	19.41	2.295
160	5.65	.668	360	12.71	1.502	560	19.77	2.337
170	6.00	.709	370	13.06	1.544	570	20.12	2.379
180	6.35	.751	380	13.41	1.586	580	20.47	2.420
190	6.71	.793	390	13.77	1.627	590	20.83	2.462
200	7.06	.835	400	14.12	1.669	600	21.18	2.504

¹ The need of making calculations is obviated by using the alignment diagram, Figure 10.

CONDENSATION AND SCRUBBING TO COLLECT VOLATILE HYDROCARBONS

NECESSITY FOR COLLECTING LIGHT HYDROCARBONS

Many analytical distillations of crude shale oil have brought out the important fact that the gasoline fraction of the crude does not contain enough low-boiling fractions to make a satisfactory motor fuel; that is, the crude has a high initial boiling point. If, however, the shale-gas gasoline is added to it, the boiling range of the blended gasoline will usually be similar to that of gasoline from petroleum.

Most shale oils congeal at temperatures between 20 and 35° C. (68 to 95° F.), the exact temperature for any oil depending on the amount and nature of the wax the oil contains. However, the large volume of incondensable gases present with the vapors makes the condensation and recovery of the lightest hydrocarbons difficult.

Because of the high solidifying temperature of the oil, special means must be adopted to insure complete condensation and recovery of products of both high and low volatility without allowing the oil to congeal in the condensers, and to permit the recovery of the condensables from the fixed gases.

The assay retort has a metal delivery tube, 7, Figure 1 (p. 7), which serves as a "hot" condenser for products of low volatility. Thus by fractional condensation the waxy and other heavy constituents are liquefied and delivered into the receiver before they cool enough to congeal. The lighter vapors pass on and rise into the reflux condensers 11 and 12, where most of them condense and are delivered into the common receiver. Thus only one receiver is required for the total condensate, both the delivery tube and the reflux condensers drain quickly and thoroughly, and quantitative determinations are highly accurate.

DESCRIPTION AND USE OF ACTIVATED-CHARCOAL SCRUBBER

Some of the shale-gas gasoline⁸ escapes from the condenser; to prevent its loss, which may amount to several per cent of the total crude oil recovered, a scrubbing tower containing activated charcoal is used (see fig. 11). The gas from the reflux condenser enters at *a* and passes down through the tower *e*; the dry scrubbed gas exhausts to the atmosphere at 5, and the charcoal filling absorbs the shale-gas gasoline. At the end of the retorting run the gasoline is removed by slowly heating the charcoal to 250° C. with the electric heating elements surrounding the charcoal tube, and at the same time passing steam at 250° C. through the tower. Steam generated in the boiler *o* is raised to the desired temperature, as indicated by thermometer *i*, by passing through the superheater *n*. The condensed steam and light hydrocarbons collect and are measured in the ice-jacket receiver *k* at the discharge end of the ice-filled condenser *j*. The tower is large enough to remove all the gasoline from the gases produced from a 40-gallon oil shale by a battery of four retorts. The results obtained with activated charcoal compare favorably with large-scale plant recoveries if the charcoal is not permitted to absorb more than 10 to 12 per cent of its volume of gasoline. When lean shales are retorted, the gas from several charges of shale should be passed together through the tower in order to collect enough gasoline for accurate measurement. A 40-gallon oil shale will yield 2 to 4 c. c. of fixed-gas gasoline per retort charge.

⁸ The term "shale-gas gasoline" has been adopted by the bureau to define the liquid of high volatility in the fixed gas. This light product corresponds to casing-head gasoline recovered from the wet natural gases of oil fields.

REMOVAL OF ADSORBED GASOLINE AND REACTIVATION OF CHARCOAL

The activated-charcoal tower is more accurate and convenient for research-laboratory use than the scrubber using mineral seal oil,

FIGURE 11.—Activated-charcoal gas scrubber: *a*, Gas supply to scrubber; *b*, gas line to gas holder; *c*, *d*, tees; *e*, insulation on charcoal tower; *f*, electric heating elements; *g*, charcoal tube; *h*, charcoal; *i*, thermometer and well; *j*, ice-water condenser; *k*, receiving burette; *l*, ice jacket; *m*, safety valve; *n*, steam superheater; *o*, steam boiler

described in the next section. The apparatus is set permanently in place close to the condensers of the retorts. At the end of the run

the adsorbed gasoline can be removed without preliminary handling. The switch is closed and the temperature of both the heating elements around the charcoal tower and the steam-boiler heater is raised to the desired point. Pinch clamp *2* is closed and *3* is opened, thus connecting the charcoal chamber with the ice condenser *j* (fig. 11). When steam begins to issue at a constant rate from the blow-off *5*, at the top of the boiler, the gas flame is started under the steam superheater *n* and the blow-off *5* is closed; this causes the steam to flow through the superheater and into the tower. The steam carries with it from the tower the last traces of adsorbed gasoline. In practice, when the temperature at the center of the tower reaches 125° C., as indicated by thermometer *i*, nearly all of the gasoline will have been removed. As a standard practice, the temperature is raised to 250° C. to restore the charcoal to its original activity. Steaming at this temperature also removes most of the sulphur which is formed from the gas in the presence of the activated charcoal by reaction between the hydrogen sulphide and traces of air in the gas.

USE OF OIL GAS SCRUBBER

Shale-gas gasoline may be removed from shale gas by bubbling the gas through a 500-c. c. gas-washing bottle containing mineral-seal oil. The oil must be carefully topped to 250° C. before use, in order to remove all traces of light hydrocarbons. After scrubbing the gases from a retorting run, the mineral seal oil is distilled to remove all the gasoline absorbed from the gas. During such a recovery distillation it is customary gradually to raise the temperature of the mineral-seal oil until the thermometer in the neck of the distilling flask suddenly shows a rapid rise of temperature as the last gasoline is distilled. The thermometer bulb should be placed at a point 1 inch below the side arm of the distilling flask in order that the distillation can be stopped when the vapor of the mineral seal oil just reaches the thermometer bulb and causes the sudden rise in temperature, and before any of the heavy oil has escaped into the receiver with the gasoline.

DISPOSAL OF SHALE-GAS GASOLINE AND CALCULATION OF YIELD

The shale-gas gasoline recovered by either method should be measured immediately after collecting and then stored in a glass-stoppered bottle in an ice chest until required for further tests. The shale-gas gasoline is considered as part of the yield of crude oil and therefore should be added to the motor-fuel fraction of the crude. It should not be mixed with the crude oil, as it would be lost by volatilization when the crude is subsequently heated to a

state of fluidity. The yield of shale-gas gasoline is calculated by use of a formula similar to the one used for crude oil:

Gallons of shale-gas gasoline per ton of shale

$$= \frac{\text{Cubic centimeters of shale-gas gasoline} \times 239.66}{\text{Grams of shale used in retort.}}$$

USE OF STEAM IN DISTILLING OIL SHALE

The use of steam is not recommended in the laboratory distillation of oil shales if the yield and properties of the oil are to be determined accurately. Exact control of the temperature and quantity of steam is so difficult that the use is not practicable where careful testing is required and comparable results are important.

In the Scottish oil-shale retorts steam is used of necessity and performs a number of important functions, none of which apply in laboratory retorting of shales. The main functions of steam in the Scottish retort are as follows: (1) Through the heat-carrying capacity of the steam the high temperature of the heat-transmitting walls of the retort is efficiently transmitted to the shale charge; (2) the temperature of the charge at varying distances from the hot walls of the retort is equalized; (3) the heat of the spent shale is carried into the distilling zone of the retort and thereby is recycled or continuously reused; (4) the wiping effect of the steam against the red-hot walls at the base of the retort causes a large transfer of heat to the interior of the retort and thereby greatly increases the thermal and heat-transferring efficiency of the Scottish type of retort; (5) the steam comes in contact with the incandescent fixed carbon of the spent shale near the bottom of the column of shale, and water gas is produced which increases the supply of fuel gas; (6) steam greatly increases the production of ammonia from the shale; and (7) steam lowers somewhat the temperature necessary for distillation of the shale.

Steam will increase the yield of oil, provided its temperature is not much above 500° C. so as to cause losses by cracking. The quality of the oil is impaired by contamination with bitumen which is removed from the shale prior to its dissociation into shale oil. The larger volume of vapors passing through the charge of shale as a result of the presence of steam moves at high velocity and carries more dust into the oil. Dust and water in the oil usually result in the formation of emulsions, and the difficulty in breaking them usually leads to sacrifice of accuracy in laboratory tests.

ROTARY-TYPE TESTING RETORT

A revolving retort is convenient for many studies. The rotary retort shown in Figure 6 (p. 15) has been used extensively by the

Bureau of Mines and has been an excellent means of determining such data as (1) the rate at which oil is produced from different shales at different temperatures; (2) the initial and final oil-yielding temperatures; (3) the effect of the size of the pieces of shale on the yield and character of the oil; (4) the effect that steam and other vapors and gases introduced into the shale charge have on the properties of the oil; (5) the character of the oil produced at different stages of the distillation; (6) the influence of the rate of distillation on the yield and properties of the oil; and (7) the effect of distillations at various pressures. This type of retort is more flexible in operation than the stationary retort. As the charge is continuously mixed during distillation the temperature of the shale mass is uniform. Therefore if the charge is finely ground, all of the shale can be considered as having the same temperature at the same time, and the thermal decomposition becomes almost a surface distillation.

SHALE-OIL TESTING

GENERAL STATEMENT

The crude oils produced by the destructive distillation of oil shales are examined to determine their properties and to ascertain the yields and properties of the products obtained from them by fractional distillation. Complete analytical distillation of a crude shale oil requires a volume of 300 c. c., and with slight modifications follows the procedure used by the Bureau of Mines for the analytical distillation of crude petroleum.⁹ This method of analysis has been adopted for testing large samples of shale oil because it furnishes a convenient basis for comparing shale oils and petroleum oils. A method for the analytical distillation of small (50-c. c.) volumes of shale oil has also been developed because in many instances it is necessary to test small samples.

The analytical distillation of a 300-c. c. sample of shale oil includes fractionating the crude at atmospheric pressure and measuring the percentages of the crude that distills between limits of 25° C. (45° F.) up to 275° C. (527° F.).

The residuum is then distilled under vacuum—that is, at 40 mm. absolute pressure—and similar fractionations are made between limits of 25° C. up to 300° C. (572° F.). The specific and A. P. I. gravities (141.5 modulus) of all fractions are determined. The fractions of the “air” distillation which distilled below 200° C. (392° F.)

⁹ For a complete discussion of Bureau of Mines methods of testing crude petroleum, see the following publications:

Dean, E. W., Hill, H. H., Smith, N. A. C., and Jacobs, W. A., *The Analytical Distillation of Petroleum and Its Products*: Bull. 207, Bureau of Mines, 1922, 82 pp.

Federal Specifications Board, United States Government Specification for Lubricants and Liquid Fuels and Methods for Testing; Standard Specification No. 2c: Tech. Paper 323A, Bureau of Mines, 1924, 89 pp.

are then combined to form the "crude gasoline and naphtha" cut which, after addition of the proportionate amount of shale-gas gasoline, is tested for "unsaturation." The fractions distilling between 200° C. (392° F.) and 275° C. (527° F.) are similarly combined and the percentage of unsaturation is determined. This cut is reported as "crude kerosene." Viscosities of the vacuum fractions are determined at 130° F. with the pipette viscosimeter. The "air" and "vacuum" residuums are used for determining the percentage of carbon residue by the Conradson method.

A laboratory distillation should not be expected to separate a crude oil into fractions precisely like those obtained in practice at a large refinery. Although such a separation is possible it is seldom warranted. Since refining practices differ, a standardized laboratory method can not give the results obtained by all refineries. Some refineries effect much cleaner separations of their products than do others that handle identical crudes. The yields of certain distillation products can be increased by the correct use of oil stills and towers. A laboratory distillation determines the comparative yields of crude gasoline, kerosene, and lubricating-oil distillates from different shale oils under standard conditions. The trade terms "gasoline," "kerosene," etc., are used for convenience in laboratory reports and do not necessarily represent the yields of crude or the finished products to be expected in commercial practice.

The yields of commercial products from crude shale oil can be determined only by actually making these products and refining them. Crude shale oils differ in their properties, and refinery losses will certainly be greater than in refining petroleum products. Therefore, to conclude from distillation analyses that certain yields of finished gasoline or other products may be obtained from a given shale oil is misleading unless the commercial refining loss is actually determined. The refining loss for petroleum products in the United States is between 1 and 5 per cent of the crude oil treated, whereas in Scotland the shrinkage in converting crude shale oil into finished products is 22 per cent. Results of the bureau's tests of many shale oils indicate that the loss in refining American shale products by ordinary refining methods will probably be at least 20 per cent. If motor fuel proves to be the chief product made from oil shale, as is anticipated, retorting methods may be modified to reduce the refining loss considerably below 20 per cent; in that event the yield of crude oil will be less, particularly if colored gasoline is acceptable.

Throughout the investigations of the Bureau of Mines oil shales and shale oils have been evaluated on the basis of the amount and quality of the motor-fuel fraction produced from the oils by the standard retorting methods already described. Consequently, the

procedure described below deals largely with determining the quantity and quality of the motor-fuel fraction distilled from the crude shale oil, and the quantity and quality of the product made by blending the motor-fuel fraction with the shale-gas gasoline recovered by scrubbing the fixed gases of retorting.

DEHYDRATION OF CRUDE OILS

Water is distilled from oil shales during retorting. The water comes from three sources: (1) The free moisture of the shale; (2) the hydrous mineral constituents of the inorganic matter; and (3) the decomposition of the organic substances in the shales. The water evolved collects with the oil in the receiver; part of it remains in suspension with the oil as an emulsion or as drops held in the congealed oil. Several methods are satisfactory for separating the oil and water. The method to be used for any particular oil depends on the tests to which the oil is to be subjected later.

DEHYDRATION BY SETTLING

Allow the crude to stand for one hour at a temperature of 50° C. in a tightly closed flask or cylinder. Then draw off the oil and determine the percentage of water by the method described under "Measurement of quantity of oil produced from a retorting test." Suspended water droplets settle completely from the most waxy shale oil if it is heated to 50° C. (122° F.). If the water is merely to be separated and its volume not determined, the oil may be heated in a stoppered separatory funnel and the water removed by draining after the lapse of enough time to insure complete settling. Oils produced from shales differ from those obtained by low-temperature distillation of bituminous coals, in that they are always lighter than water and can be separated readily by gravity settling.

DEHYDRATION STILL

The water in large samples may be separated quantitatively by distillation. The distillation flask, a short-neck pyrex flask, or the copper still is placed in a drying oven and its temperature held at 120 to 140° C. until all the water is distilled. (See fig. 12.) Between the flask and the bottom of the oven is placed a disk of asbestos board to prevent overheating of the oil in the lower part of the flask. A down-sloping delivery tube of glass passes from the flask through a small hole in the side of the oven and delivers the distillate into a Liebig condenser and a graduated receiver, preferably a burette. Complete separation of water from the oil requires two to three hours. Then the volume of water is read, and the light oil

distilled over with the water is returned to the flask after the dehydrated crude has cooled.

Oils from cannel coals, lignites, and bituminous coals often have about the same specific gravity as water. Frothing takes place when attempt is made to dehydrate such oils by the usual method of distillation, and in consequence the dehydration requires special apparatus. A still running under 20 to 80 pounds pressure is satisfactory for this purpose. Figure 13 shows a convenient apparatus consisting of a short section of pipe with heads welded on; it is provided with a pressure gauge, a thermometer well, a charge and drain opening, and a delivery pipe with a needle valve. A small oxygen cylinder is suitable for a pressure still of this type.

FIGURE 12.—Dehydration still: *a*, Short-neck pyrex flask; *b*, Liebig condenser; *c*, receiving burette; *d*, drying oven

FIGURE 13.—Pressure dehydration still: *a*, Pressure still; *b*, removable bushing and thermometer well; *c*, pressure gauge; *d*, pressure-regulating valve; *e*, Liebig condenser; *f*, receiving burette

When the still is running, the valve is set to maintain a pressure of at least 20 pounds, which is usually required to keep emulsion from rising into the delivery tube. Until all of the water is evaporated, the temperature inside the still remains nearly constant at approximately the temperature of saturated steam for the pressure used. The light oil distilled off with the water must be returned to the sample after the latter has been cooled enough.

DEAN AND STARK METHOD OF DETERMINING WATER

The percentage of water may be determined accurately by the method of Dean and Stark.¹⁰ This method, however, renders the oil sample useless for further work, consequently the method is not used for the small samples of shale oils produced by the assay retort.

Often the crude oil contains both dust and water, therefore the oil is weighed into the dehydrating still and the weight of the water collected is subtracted from this gross weight. Correction is next made for weight of dust in the oil. (See next section, "Dust determination.") Then the percentage of water is calculated on the basis of clean oil. An example of the calculations is given below.

FIGURE 14.—Apparatus for determining sediment: *a*, Extraction flask; *b*, condenser; *c*, extraction thimble; *d*, solvent; *e*, hot plate

DETERMINATION OF DUST

Before dust or sediment can be determined the crude oil must be dehydrated. The apparatus shown in Figure 14 is very satisfactory for determining sediment. Weigh a 10-gram sample of dehydrated oil into the previously extracted and dried alundum thimble. The thimble should be 1 inch in diameter by $2\frac{3}{4}$ inches high and should weigh not less than 15 or more than 17 grams.¹¹ Use benzol to extract the oil from the sediment. Run the test at such a rate that the condensed benzol dripping from the condenser *b* does not overflow the thimble. Continue the extraction for one hour after the solvent dripping from the thimble *c* becomes colorless. Drain the thimble, dry for one hour at 105° C., and weigh. The gain in weight of the thimble is the true weight of the sediment.

Example of calculations of dust and water in oil

	Grams
Gross weight of oil in dehydration still (oil, water, dust)-----	350.10
Cubic centimeters or grams of water distilled (1 c.c.=1 gram)-----	3.50
Weight of oil plus dust-----	346.60

¹⁰ Dean, E. W., and Stark, D. D., "A convenient method for the determination of water in petroleum and other organic emulsions": Jour. Ind. Eng. Chem., vol. 12, 1920, pp. 486-490.

¹¹ Federal Specifications Board, United States Government Specification for Lubricants and Liquid Fuels and Methods for Testing; Specification No. 2c; Tech. Paper 323A, Bureau of Mines, 1924, pp. 70-71. Alundum thimbles listed by the Norton Co., Worcester, Mass., as 5163 RA 98 have proved satisfactory.

	Grams
Weight of thimble, oil (dehydrated), dust-----	26.37
Weight of thimble-----	16.12
Weight of oil plus dust-----	10.25
Weight of thimble plus dust after extracting and drying-----	16.22
Weight of thimble-----	16.12
Weight of dust-----	0.10
Dust in dry oil, $\frac{0.10}{10.25} \times 100$ per cent-----	0.975 per cent
Weight of dust in dehydration-still charge, 346.60×0.00975 -----	3.38
Weight of clean oil in still, $346.60 - 3.38$ -----	343.22
Water in oil, $\frac{3.50}{343.22 + 3.50} \times 100$ per cent-----	1.01 per cent

DETERMINATION OF SPECIFIC GRAVITY

It is obvious that the water and dust-free oil should be used for accurate determinations of gravity. The oil will be sufficiently freed of impurities if it stands for one hour, tightly sealed, at a temperature of 50° C. (122° F.). After it has cooled the container is opened and enough oil for the determination of specific gravity is drawn out with a pipette. Care must be taken to avoid drawing water or sediment into the pipette.

Specific gravities are determined at 15.56° C. (60° F.). Most shale oils congeal above this temperature, and therefore pycnometer bottles are used for specific gravity determinations. The Hubbard, Barrett, and Regnault types of bottles are satisfactory, and bottles of either 50 or 25 c. c. capacity are convenient. Before use weigh the dry empty bottle and determine its volume by weighing it full of air-free distilled water at 15.56° C. (60° F.) and subtracting from this weight the weight of the empty bottle. If the weights are in grams, the difference will be the volume of the bottle in cubic centimeters. Run the fluid oil carefully from the pipette into the bottle, avoiding the formation of air bubbles in the oil. Fill the bottle at least half full and weigh it, then allow the bottle and contents to cool slowly. If the oil (particularly an oil containing much wax) cools rapidly, the solidifying oil will shrink from the walls of the bottle, and a cavity will form at the center. If this happens, remelt the sample before continuing the test. Next, bring the bottle and contents to 15.56° C. (60° F.) in a constant-temperature bath and hold them at that point until the temperature becomes uniform throughout. Then fill the bottle completely with distilled water that has been freed from air by boiling and cooled to 15.56° C. (60° F.). Remove the specific gravity bottle from the bath, dry it thoroughly, and weigh it again. Substitute in the following formula the weights obtained and calculate the specific gravity of the oil as indicated.

$$\text{Specific gravity} = \frac{c-a}{(b-a) - (d-c)}, \text{ where}$$

a =weight of empty bottle clean and dry.

b =weight of bottle full of distilled water at 15.56° C. (60° F.).

c =weight of bottle plus oil sample.

d =weight of bottle plus oil sample plus water at 15.56° C. (60° F.).

The sample of oil may be carefully removed from the pycnometer and returned to the stock sample for other determinations.

Specific gravities of oils that are quite fluid at 15.56° C., such as fractions produced by analytical distillations, are best determined by the Westphal balance. The small samples to be tested should be placed in test tubes supported in the constant-temperature bath, which is maintained at 15.56° C. (60° F.) while the determinations are being made.

DETERMINATION OF MELTING POINTS OF SHALE OILS AND SHALE-OIL DISTILLATES

The temperatures at which different shale oils change from the solid to the liquid state vary widely. Not only do the melting points of crude oils produced from different shales by identical methods of retorting differ, but the melting point of the crude oil obtained from any shale differs with changes in the rates and conditions of retorting. Oils produced by rapid distillations (high temperature, but not above 550° C.) have the higher melting points. Crude oil produced from any given shale or definite mixture of shales by rapid distillation has a higher melting point and yields more paraffin wax than an oil obtained from the same shale or mixture by slow distillation at a lower temperature. The amount of wax that can be obtained from the crude oils made from different oil shales can be determined only by actual test, and it is wrong to assume that yields of wax from various crudes of different origins have a definite relation to the melting points of the oils—that the oil of higher melting point has the larger proportion of recoverable wax. However, this relationship applies in a general way to crude oils of different melting points produced from any one shale or shale mixture by different conditions of retorting. In general, the crude oil that has the highest melting point may be expected to produce the greatest yield of wax. How closely this relationship holds for American shale oils is not known, although in the Scottish shale-oil industry the melting-point determination is of value in estimating the amount of wax obtainable from a given crude shale oil produced from the usual run of shale.

The melting point of crude shale oils should be determined. The test is easily and quickly made and is a simple means of ascertaining the extent of the thermal decomposition during the production of a particular crude oil. Curve 4 of Figure 2 (p. 10) shows the wide

variation in the melting point caused by changing the rate or temperature of retorting. The method of determining melting points described below is a modification of the method generally used for testing petrolatums¹² and is satisfactory for shale oils.

A melting-point thermometer graduated from 0 to 50° C. is used for the test. The sample must truly represent the oil to be tested. If necessary, the sample is kept in a fluid state by heating and is stirred to prevent wax crystals from forming and settling out. Before it is tested the oil is allowed to cool to approximately 10° C. above its melting point. The thermometer bulb is also cooled for a few minutes in ice water, then thoroughly dried and thrust into the oil until the lower half of the bulb is covered. The thermometer is withdrawn immediately and is held vertically in an inverted position while the clinging oil solidifies. The thermometer is kept in this position and heat is applied, so regulated that the temperature will rise at an approximate rate of 2° C. per minute while the thermometer is being rotated about its vertical axis. When the melting-point temperature of the oil is reached an oil film will creep down the bulb. The first evidence of melting is most easily recognized if there is a sharp line of demarcation between the edge of the congealed oil and the glass surface of the thermometer bulb. The temperature at which the oil film first appears is considered the melting temperature of the oil.

At least three melting-point determinations should be made for each sample, and if the variation does not exceed 2° the average of the three most concordant may be reported as the melting point of the sample.

A more rapid and accurate method than the above for determining melting points of shale oils and shale-oil distillates is given in the appendix (p. 61). This method has been used extensively in the shale-oil studies of the Bureau of Mines, but its success depends upon a supply of electric current at constant voltage—a requirement that may seriously limit its general use. A promising method of determining the flow point is given in the appendix (p. 67).

TOPPING DISTILLATION FOR DETERMINING MOTOR-FUEL FRACTION

The topping distillation method previously mentioned was developed for testing small samples of oil. The Bureau of Mines assay retort holds enough shale to produce approximately 60 c. c. of oil from an oil shale of average richness (35 gallons per ton). The richer shales obviously yield somewhat more oil per retort charge.

¹² Federal Specifications Board, United States Government Specification for Lubricants and Liquid Fuels; Standard Specification No. 2c: Tech. Paper 323A, Bureau of Mines, 1924, p. 45.

The topping still described below is a reliable fractionating device and is convenient for testing small samples of oil.

Only one "cut" is made during the distillation of a crude oil with this still—namely, the fraction that distills below 275° C. (527° F.) vapor temperature. This fraction, the "motor-fuel" fraction or "tops," at present serves as a satisfactory basis for estimating the relative values of shale oils. The future demand for motor fuel will probably bring about the development of a shale-oil industry. Although the fraction up to 275° C. has a higher boiling range than petroleum gasoline, the growing demand for gasoline during the past few years has resulted in increasing the boiling range of motor gasoline; that is, the end points of these gasolines have been raised

and their average volatility lowered. It seems probable that in the near future the volatility of motor fuel may gradually decrease so that fractions cut at 275° C. may be taken to indicate the relative yields of motor fuel.

The motor-fuel fraction produced from any crude oil by the topping still described is almost identical with that produced by the Bureau of Mines standard

FIGURE 15.—Apparatus for topping distillation: *a*, Electric power circuit and rheostat; *b*, electric heater; *c*, topping flask and charge of oil; *d*, fractionating column with jack-chain packing; *e*, thermometer; *f*, ice-water condenser; *g*, drain; *h*, receiving graduate

analytical distillation method used for testing 300-c. c. samples of crude petroleum.

DESCRIPTION OF STILL

Figure 15 shows the topping still and its accessories when assembled. The still *c* is a 100-c. c. Engler flask made with the side arm 2 inches from the top of the neck. The fractionating medium *d* in the neck of the flask consists of fine jack chain supported on a wire-gauze carrier which is suspended by a wire hooked into the outlet opening of the side arm. Place the thermometer bulb so that its top is just below the level of the side arm of the flask. The cork through which the thermometer passes and the one connecting the side tube to the condenser should be covered with a paste of glycerin and pulverized litharge, which has been previously calcined at 350° C. (662° F.). During distillation the condenser box *f* is kept full of broken ice with only enough water to cover the vapor tube.

OPERATION OF STILL

For comparable results the flask is always charged with the same volume of oil when measured at the same temperature. The flask is charged most accurately by weighing the oil into it. To calculate the weight of oil necessary, multiply the volume of oil desired for the charge (50 c. c.) by the specific gravity of the oil; the result is the weight of oil required for the standard charge at 15.56° C. (60° F.). Fifty cubic centimeters of oil at 60° F. has been adopted as the standard charge. If, for example, the specific gravity of the oil at 60° F. is 0.880, then $50 \times 0.880 = 44.00$, or the weight in grams of oil to be charged into the still.

The distillation must progress at a uniform rate of 1 c. c. of distillate per minute and must stop at the proper temperature. When the temperature reaches 275° C. (527° F.) blow a stream of air on the neck of the flask and at the same time quickly remove the electric heater from under the still. The blast of air cools the neck of the flask, slightly checks the flow of vapor, and consequently cuts the distillation sharply. Allow the condenser tube to drain well before the receiver is removed. Next weigh the receiver containing the distillate, and from this weight subtract the weight of the empty receiver; the difference is the weight of the motor-fuel distillate or tops. The specific gravity of the distillate at 15.56° C. (60° F.) is determined with the Westphal balance. Divide the weight of distillate by the specific gravity; the result is the exact volume (at 60° F.) of distillate recovered. Divide the volume of distillate obtained by the volume of oil charged, both expressed in cubic centimeters, and multiply by 100; the result is the percentage yield of motor-fuel distillate. (This does not include the shale-gas gasoline.)

CALCULATION OF TOTAL YIELD OF MOTOR FUEL

To determine the total motor-fuel yield of an oil shale, take the "motor-fuel" distillate, obtained as described, express it in terms of gallons per ton of shale, and add to this value the quantity of shale-gas gasoline recovered by scrubbing the gases. The sum is the total motor-fuel yield in gallons per ton of shale. The proper mixture of motor-fuel distillate (tops) and shale-gas gasoline, as obtained from the shale, is tested for specific gravity and degree of unsaturation.

DETERMINATION OF PERCENTAGE OF UNSATURATION

The motor-fuel value of a crude shale oil depends not only on its yield of tops plus shale-gas gasoline, but on its quality as well. For a given volatility range the quality of a crude motor fuel can be

estimated by determining the refining loss. The unsaturation determined is not an exact measure of the proportion of unsaturated hydrocarbons present or of the probable loss in refining, but a comparative analysis of different shale oils on the basis of unsaturation percentages, obtained by the method described, will undoubtedly show that in general the refining loss is directly proportional to the

percentage of unsaturation. For this reason the motor-fuel fractions of all shale oils are tested for unsaturation percentage. The proper mixture of tops (motor-fuel fraction) and shale-gas gasoline is agitated with concentrated sulphuric acid under specified conditions; the proportion soluble in the acid is considered "unsaturated" for the purposes of the test.

FIGURE 16.—Apparatus for determining unsaturation: *a*, Unsaturation bottle; *b*, calibrated pipette; *c*, temperature-regulating water jacket; *d*, suction tube; *e*, jacket drain

DESCRIPTION OF APPARATUS

Figure 16 shows an apparatus that has been successfully used in determining the percentage of unsaturation of shale-oil fractions. The unsaturation bottle *a*, when filled to the zero mark, has a volume of 30 c. c. The neck of the bottle is accurately graduated into 100 equal parts; the volume of the graduated part is exactly 5 c. c.

Pipette *b* is designed to deliver to each bottle enough oil to fill exactly the gradu-

ated part of the neck of the bottle. The stem of the pipette is made of capillary glass tubing; the etched calibration lines are so spaced that the quantity of oil required for any bottle may be delivered. Each number opposite the graduations on the stem corresponds to a numbered bottle.

Water jacket *c* holds the temperature of the pipette and its contents at 15.56° C. (60° F.) during measurements.

PROCEDURE

Percentage of unsaturation is determined as follows: Cool the oil to 15.56°C . (60°F .) and by means of suction tube *d* fill the pipette to the zero mark. Allow the oil to stand in the pipette for a few moments to insure that the temperature of the oil is 15.56°C . (60°F .) and that the oil is properly measured. Then allow it to flow slowly into an unsaturation bottle—careful measurements require that the oil does not run from the pipette too quickly. Close the stopcock when the level of the oil reaches the division on the pipette stem corresponding to the number of the bottle used. If about one minute is allowed for the discharge of the pipette, no oil will drain from the walls of the pipette after the cock has been closed; incomplete drainage will be shown by a rise in the oil level of the lower capillary tube. During slow discharge the surface tension of the oil frees the walls of the pipette of all oil; if the rate of discharge is too rapid, the adhering oil will drain down later.

After the oil has been run into the bottle add 15 c. c. of concentrated sulphuric acid (1.84 sp. gr.); it may be conveniently added from a large burette and should flow gently down the side of the unsaturation bottle while the bottle is rotated, so that the acid will carry any clinging drops of oil into the bottom. If the bottle is of the proper design, the bottom space will now be about three-fourths full, and ample space will be left for efficient agitation while the acid and oil react. As soon as the acid has been added, stopper the bottle tightly with a cork or rubber stopper. Then hold the bottle or bottles, if several determinations are to be made, under very cold water and shake while the reaction progresses. Samples are best run in duplicate and handled together throughout the different steps of the determination.

Carefully conducted experiments indicate that thoroughness of agitation has an important influence on the accuracy of results of the unsaturation test. The base of the bottle must be large enough to allow ample space for violent agitation. The method of agitation should not be changed after a satisfactory method has been adopted. The best results are obtained by shaking the bottles gently 100 times under the surface of cold running water, then violently 300 times. This agitation thoroughly mixes the acid and oil, and additional shaking of the bottles will not affect the results. With less agitation the results usually do not agree and the apparent unsaturation values are lower. The agitation must be the same for all bottles; therefore at equal intervals during the shaking the position of the bottles in the hand should be reversed.

Add more acid until the upper level of the oil rises to the base of the necks of the bottles. Then place the bottles in a centrifuge

and rotate them at approximately 750 revolutions per minute for 10 minutes. Remove the bottles and add more acid until the upper oil surface is near the upper graduation mark on the bottle. Then centrifuge the bottles again for five minutes and set them aside for one hour before reading, or until they have reached a constant and equal temperature. The bottles should be set in subdued light, or the oil may darken enough to make reading difficult.

If correct results are to be obtained, the readings must be made when the bottles and contents are at the same temperature as that of the oil samples when they were measured into the pipette—15.56° C. (60° F.). A magnifying glass like those sold by chemical supply houses for reading thermometers assists in accurate reading of the top and bottom levels of the oil in the bottles. It is important to read carefully and, if possible, to estimate to the nearest one-tenth of the smallest division. The results of duplicate determinations should agree within 0.2 per cent. Typical results obtained with duplicate samples are given below:

Examples of results

	Bottle No. 1	Bottle No. 2
Upper oil level.....	98.6	97.1
Lower oil level.....	38.6	36.9
Difference (per cent of saturated oil).....	60.0	60.2
Per cent of unsaturated oil.....	40.0	39.8
Average per cent of unsaturation.....	39.9	-----

VISCOSITY OF SHALE OILS AND SHALE-OIL DISTILLATES

Viscosities of small samples of crude shale oils and lubricating-oil fractions can be conveniently and accurately determined with a pipette viscosimeter.¹³ The apparatus is well suited for studies of shale oils, because analytical distillation of the crude oil gives only small samples of lubricating cuts. Standard viscosimeters require 75 to 250 c. c. of oil for a determination, but samples as small as 2 c. c. suffice for a determination with the pipette viscosimeter.

DESCRIPTION OF PIPETTE VISCOSIMETER

Figure 17 illustrates the pipette viscosimeter. Pipette *c* is made from a piece of capillary glass tubing of about 1 mm. bore and 6 mm. outside diameter. The bulb has a capacity of 1 to 1.5 c. c. and is 30 mm. from the discharge end. Above the bulb is 12 cm. of tubing that terminates in a glass cock or a short rubber tube with a pinch clamp. Receiver *a* is a test tube that has a glass vent tube to prevent

¹³ Dean, E. W., Hill, H. H., Smith, N. A. C., and Jacobs, W. A., *The Analytical Distillation of Petroleum and Its Products*: Bull. 207, Bureau of Mines, 1922, p. 45.

the development of back pressure as the oil flows into the receiver. A tight rubber stopper seals the pipette into the receiver. Two lines are etched on the pipette, one above the bulb, the other below.

OPERATION OF VISCOSIMETER

Draw the oil to be tested into the pipette until it reaches the upper line, then close the stopcock. Attach the pipette to the receiver and submerge the assembled parts to a point above the upper mark on the pipette in a constant temperature bath held at 130° F. When enough time has elapsed for the temperature of the viscosimeter and oil to rise 130° F., open the stopcock. Start a stop watch as the oil level passes the upper line and stop the watch as the oil passes the lower line; record the time. Obtain the Saybolt viscosity equivalent by the methods described in Bulletin 207, page 45, cited above.

APPLICATION OF CARBON-RESIDUE TEST TO SHALE OILS

Determination of the carbon residue of the residuums from vacuum-distillation analyses of petroleum provides a fairly accurate means of determining the relative value of the residuum as a source of lubricating stock for steam cylinders. Usually residuum of petroleum that gives 3 per cent or less of carbon residue will make a satisfactory cylinder stock when properly steam refined. Cylinder stock can be made from petroleum residuums giving carbon-residue values as high as 6 per cent and over, if special refining methods are used. Scottish shale oils are not suitable for manufacturing into heavy lubricants, and it is not yet definitely known whether heavy lubricating oils or steam-cylinder stocks can be made from American shale oils. It is possible that shale oils capable of yielding heavy lubricants may be produced by use of retorting conditions that prevent excessive cracking or secondary decomposition. For many years the demand for lubricating oils from oil shales will probably not be great enough to make their manufacture profitable, because for a long time to come the United States will have a large supply of petroleum from which lubricants can be produced; much of it is now being consumed as fuel oil. However, the

FIGURE 17.—Pipette viscosimeter: *a*, Receiving test tube with sealed-on pressure-equalizing tube; *b*, cork or rubber stopper; *c*, pipette viscosimeter; *d*, stopcock

carbon-residue test is applied to shale oils, notwithstanding the unlikelihood of shale oils ever being used as sources of heavy lubricants. The carbon-residue value of the oil from any shale can be made to vary materially by changing the retort temperature. The results of the carbon-residue determination¹⁴ therefore indicate the extent to which thermal decomposition has progressed; show the relative amount of asphaltic or pitchy ingredients still remaining in the oil; can undoubtedly be related to the refining loss; and suggest the suitability of the oil for making lubricants.

FIGURE 18.—Conradson carbon-residue apparatus: *a*, Porcelain crucible; *b*, Skidmore crucible; *c*, iron crucible; *d*, asbestos block; *e*, hood; heat-control manometer

CONRADSON APPARATUS

Figure 18 is the Conradson carbon-residue testing apparatus that is used in the petroleum and oil-shale laboratories of the Bureau of Mines. This apparatus may be purchased complete, as illustrated, from dealers in oil-testing apparatus.

¹⁴ Karrick, L. C., Effects of Temperature and Time of Reaction in Distilling Oil Shales on the Yields and Properties of the Crude Oils: Reports of Investigations, Serial 2456, Bureau of Mines, March, 1923, 8 pp.

DETERMINATION OF CARBON RESIDUE

The determination is made on a part of the residue that remains after the topping distillation is finished. The results are reported as the percentage of carbon residue produced from the "air" residue, or if the figure is desired only as a measure of the thermal decomposition, it may be calculated on the basis of the original crude with the shale-gas gasoline added.

The amount of residuum required for the test depends on the amount of carbon residue produced. The residue should not exceed 0.15 gram, so if the oil yields 15 per cent of carbon residue it is best to use only a 1-gram sample. If the oil yields 1.5 per cent carbon residue a 10-gram sample may be used. For greatest accuracy a preliminary test must be made to ascertain the correct weight of oil.

The test is conducted as follows:¹⁵

A sample of the oil to be tested is weighed in a porcelain crucible, *a*, which is placed in a Skidmore crucible, *b*. These two crucibles are set in a larger iron crucible, *c*, being careful to have the Skidmore crucible set in the center of the iron crucible, covers being applied to the Skidmore and iron crucibles. Place on triangle and suitable stand with asbestos block *d*, and cover with a sheet-iron or asbestos hood in order to distribute the heat uniformly during the process.

Heat from a Bunsen or other burner is applied with a high flame surrounding the large crucible *c* until vapors from the oil begin to ignite over the crucible; then the heat is slowed down so that the vapor (flame) will come off at a uniform rate. The flame from the ignited vapors should not extend over 2 inches above the sheet-iron hood. After the vapor ceases to come off the heat is increased as at the start and kept constant for 5 minutes, making the lower part of the large crucible red hot, after which the apparatus is allowed to cool somewhat before the crucible is uncovered. The porcelain crucible is removed, cooled in a desiccator, and weighed.

The entire process should require one-half hour to complete when the heat is properly regulated. The time will depend somewhat upon the kind of oil tested, as a very thin, rather low flash-point oil will not take as long as a heavy, thick, high flash-point oil.

Manometer *f* affords a means of regulating the heat supply and therefore makes uniformity possible in the conduct of tests.

¹⁵ Federal Specifications Board, United States Government Specification for Lubricants and Liquid Fuels and Methods for Testing; Standard Specification No. 2c: Tech. Paper 323A, Bureau of Mines, 1924, 89 pp.

COMPARISON OF SHALE OILS AND OIL SHALES BY INDEX NUMBERS

In order that oil shales and shale oils may be readily classified, a numerical basis of comparison has been developed.¹⁶ Index numbers can be calculated for any sample of shale oil if the yield of tops (motor-fuel distillate) plus shale-gas gasoline and the saturation percentage of the correct mixture have been determined. This method of evaluation takes no account of the value of a shale oil for purposes other than the production of motor-fuel distillate, although the oil remaining after the removal of the light distillate will probably be of value for other purposes than fuel oil. Usually the shale oils that show the higher index values will also yield superior products other than light distillate. The index value of a shale oil is the product of its percentage of tops, including shale-gas gasoline, times the percentage of saturation of the combined tops and shale-gas gasoline. Examples are as follows:

Sample No.	Combined per cent of tops and shale-gas gasoline	Per cent of saturation	Shale-oil index number
Oil A	37.5	60.0	22.5
Oil B	40.3	62.0	25.0

To calculate the index numbers of the shales producing these crude oils, the yield of crude oil, expressed in gallons per ton, is multiplied by the oil index.

Sample No.	Oil yield of shale (gallons per ton)	Shale-oil index number	Oil-shale index number
Shale A	34.8	22.5	873.0
Shale B	45.6	25.0	1,150.0

EFFECTS OF RATE AND TEMPERATURE OF DISTILLATION ON INDEXES

It is obvious that the index number may be greatly influenced by changes in the rate or temperature of retorting; the slower rates (lower temperature) of retorting produce a crude oil containing a larger proportion of tops and a larger proportion of saturated hydrocarbons. Therefore it is of greatest importance that index numbers be used in comparing oil shales and shale oils, but the rate of retorting must be noted. (See section on "Effects of varying rates of distillation of the shale.") Index numbers applicable to the five standard retorting rates are of particular value in determining

¹⁶ Gavin, M. J., Oil Shale: Bull. 210, Bureau of Mines, 1924, pp. 156-159.

the best rate of retorting for any shale. (See curve 8, fig. 2, for an illustration of how rate or temperature of retorting affects the index number of a particular shale.)

ANALYSIS OF SHALE GAS

SHALE GAS—ITS SOURCE AND USE

In the retorting of oil shales, fixed gas is produced largely at the expense of oil. It is theoretically possible to produce all gas and no oil, or all oil and virtually no hydrocarbon gas. Oil, however, is the product sought; therefore the gas yield should be kept at a minimum by eliminating from the process the high-temperature reactions that crack the oil vapors and form permanent gases. The desirable thermal decomposition that takes place at low temperature as the bitumen is converted into oil forms additional gas, but the gas is not necessarily disadvantageous, as in its formation the index value of the oil will be increased.

As industrial considerations require the retorts to have large capacities, relatively large quantities of gases will be produced by the rather high temperatures required for the rapid flow of the heat into the shale. Gas is the chief fuel used at all large oil-shale plants in foreign countries. It may also be the chief fuel used in domestic oil-shale plants, unless there is a near-by market for gas for domestic use, and moderately priced coal is available for the shale plant. In testing oil shales it is therefore of great importance that the yield and fuel value of the fixed gases produced be determined carefully. (See fig. 8 for change in composition of gas at different stages of distillation.)

The Scottish and Australian retorts and some of the oil-shale processes proposed for use in America do not yield gas of the same composition as that produced by the testing retort described in this paper. For a number of reasons these commercial retorts use steam (p. 27). The steam reacts with the highly heated fixed carbon of the spent shale to form water gas which is high in carbon dioxide; because of this water gas the calorific value of the combined gases is much lower than that of the gases produced solely by the destructive distillation of the shale. The volume of gas produced, however, is much greater when steam is used. The incondensable gas made by the Scottish retort averages 9,800 cubic feet per ton of shale and has a fuel value of approximately 300 B. t. u. per cubic foot. When retorted in the bureau's assay retort the same shale yields 760 cubic feet of gas per ton, and this gas has a calorific value of 675 B. t. u. per cubic foot. These differences in yield and in fuel value may be explained by the diluting effect of the water gas and, to a small extent, by gases from the combustion of carbon with air that leaks in at the base of the retort.

As fuel will be such an important item of necessary expense in the operation of an oil-shale plant, accurate data should be obtained on the yield and quality of the gas produced when the shales are distilled at the five standard rates. (See p. 20.)

COLLECTING AND METERING GAS

An assay-retort charge of shale, except shale of low grade, will yield 1 to 2 cubic feet of gas. Use of a gas holder large enough to hold the entire yield of gas from a single retort charge of rich shale is advantageous. The gas holder shown in Figure 19 is satisfactory. It has three principal parts, namely, a sliding drum and two stationary concentric drums. The inner stationary drum is sealed, gas tight, to the floor of the gas holder, and has a gas-tight head. The annular space between the two stationary drums in which the movable drum rises and falls is one-half inch wide; it is filled with concentrated brine, in which the gas is not appreciably soluble.

FIGURE 19.—Gas holder for gas from retort: *a*, Liquid reservoir; *b*, inner bell; *a-b*, annular space filled with liquid; *d*, supports for counterbalancing mechanism

The gas holder is carefully calibrated, and a sliding scale and pointer attached furnish a convenient means of measuring volumes. A manometer filled with water is connected to the inlet of the gas holder so that atmospheric pressure can be held inside the receiver, and therefore inside the retort and gas train, while gas is collected or measured. Weights on the counterbalance are adjusted as may be necessary to regulate the pressure.

A wet test meter is satisfactory for measuring the gas if its interior parts are made of noncorrosive material such as Monel metal. Some oil shales yield gases that quickly attack the interior parts of most meters. If a calibrated gas holder is used, no meter will be required.

CALCULATION OF YIELD

The following formulas are convenient for calculating gas yields:

$$\begin{aligned} \text{Cubic feet of gas per ton of shale} &= \frac{32.037 \times \text{c. c. of gas obtained}}{\text{Grams of shale distilled}} \\ \text{Cubic feet of gas per ton of shale} &= \frac{2000 \times \text{cu. ft. of gas collected}}{\text{Pounds of shale used}} \\ 1 \text{ lb.} &= 453.6 \text{ grams} \end{aligned}$$

COMPLETE GAS ANALYSES

Shale-gas samples contain the following constituent gases: Hydrogen sulphide (H_2S), carbon dioxide (CO_2), unsaturated hydrocarbons (illuminants), oxygen (O_2), hydrogen (H_2), carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), and nitrogen (N_2). If any oxygen is present, it has come from air already in the system or air leaked in when the sample of gas was taken. Table 4 gives analyses of gases from various shales.

The gas is analyzed carefully in order to determine its approximate fuel value and the amount of undesirable constituents to be removed if the gas is to be sold for domestic use. An experienced analyst using well-designed equipment can make a complete analysis in one hour.

TABLE 4.—Analyses of gases (air-free basis)

Type	Source	Volume, cubic feet per ton	Gross B.t.u. ¹	H_2S	CO_2	Illuminants	H_2	CO	CH_4	C_2H_6	N_2
				Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Massive oil shale...	Grand Valley, Colo.	943	957	1.6	14.9	7.7	35.4	5.6	17.7	15.5	1.6
"Mahogany" oil shale.	DeBeque, Colo.	1,423	1,088	3.7	15.7	9.3	32.8	6.3	18.0	14.2	.0
Curly massive oil shale.	do.....	1,221	965	2.1	13.3	7.6	38.4	6.3	20.6	12.5	1.3
Brown oil shale...	Elko, Nev.....	1,214	1,051	14.9	11.7	7.1	30.1	3.7	16.5	13.1	2.9
Massive oil shale...	Soldier Summit, Utah.	1,110	1,102	8.9	10.7	9.5	31.7	3.9	20.0	15.3	.0
Bituminous coal...	Sunnyside, Utah.	972	972	1.1	5.2	4.9	25.8	8.9	46.0	8.3	.0
Brown lignite....	California.....	756	825	.3	28.4	5.8	25.0	8.5	21.1	10.9	.0
Oil sand.....	Athabaska.....	1,206	-----	4.0	14.9	11.0	23.0	4.5	22.2	21.4	1.8
Massive oil shale.	Australia.....	121	1,452	1.0	3.6	13.0	7.0	4.9	33.5	27.0	.0
Do.....	Scotland.....	715	731	3.2	35.1	8.0	26.8	2.9	11.3	9.9	2.8

¹ At 0° C. and 760 mm. This figure was obtained with a gas calorimeter.

EQUIPMENT USED

The Burrell or similar type of Orsat gas analyzer,¹⁷ shown in Figure 20, is admirably suited for testing coal and shale gases. The Tutwiler hydrogen sulphide burette, shown in Figure 21, is used for determining the percentage of H_2S . This determination is separate from the analysis made with the Burrell outfit. If analyses for total sulphur in the gas are required, the referee's method should be used.

¹⁷ The Burrell Technical Supply Co. and the Fisher Scientific Co., of Pittsburgh, Pa., and other chemical supply houses manufacture the analyzers and furnish complete instructions for their operation.

Burrell, G. A., and Seibert, F. M., revised by Jones, G. W., Sampling and Examination of Mine Gases and Natural Gas: Bull. 197, Bureau of Mines, 1925, p. 40.

FIGURE 20.—Burrell precision gas-analysis apparatus

SUGGESTIONS FOR CORRECT SAMPLING OF GAS

If H_2S is present in the gas to be analyzed in the Orsat apparatus, it will be removed by the caustic potash solution and the results will be inaccurate. If the amount of H_2S is not determined separately, the calculated fuel value of the gas will be low because the fuel value of the H_2S will be omitted. It is best to remove H_2S from the gas sample to be used for the complete analysis and to determine the H_2S separately. H_2S reacts with the mercury in the gas analyzer, and leaves a dirty film on the burette walls that makes accurate readings difficult. The gas sample, as it is drawn from the gas holder into the sample tube or gas analyzer, can be washed free of H_2S by passing the gas through a washing bottle filled with a slightly acid 10 per cent solution of cadmium chloride. The bottle must be swept clean of any air or gas remaining from other analyses before the gas for filling the sample tube is drawn through.

Tubes for gas samples are made of heavy glass. (See fig. 22.) A 250-c. c. tube with a glass cock at each end is most satisfactory. The tube can be without glass cocks, if rubber tubes with clamps are provided for sealing. This type is satisfactory if the sample is to be analyzed immediately or at least on the same day. Some gases pass rapidly through rubber, therefore incorrect data may be obtained from analyses of samples that have been stored long in this type of sample tube.

VALUE OF GAS ANALYSIS IN DETERMINING FUEL VALUE

An accurate gas analysis shows the composition of the gas and makes possible the calculations of approximate fuel value. For accurate results the fuel value of the gas should be determined with a gas calorimeter, but where the highest accuracy is not necessary calculations from gas analyses will usually be satisfactory.

The composition of a gas is decidedly changed by scrubbing it to remove shale-gas gasoline. Both scrubbing oil and activated charcoal selectively absorb certain constituent gases, and thus the treated gas has a composition different from that it had before scrubbing. As retorting practice has not been developed on a large scale in America, laboratory studies can not predict exactly the composition of the gases that will be produced. Therefore it is necessary, for the sake of comparison, to adhere to a definite procedure in handling and

FIGURE 21. — Tutwiler hydrogen sulphide burette

testing the gases from all shales brought into the laboratory. The gas is sampled and analyzed as it comes from the condensers, before the fixed-gas gasoline has been extracted. From the results of the analysis the fuel value is calculated, and this is corrected for the amount of condensable hydrocarbons present, as determined by scrubbing. (See p. 23.) Different gas analyses are thereby made comparable and become useful not only for calculating fuel value and comparing composition data, but for showing directly how much the hydrocarbons decomposed in the retort. Effects of time and temperature of distillation are readily shown by changes in percentages of hydrogen, methane, and ethane in the gas. The fuel value of the gas is calculated by multiplying the heats of combustion of the separate constituents by their respective percentages. The sum of the values thus obtained is usually a close approximation to the actual fuel value of the gas.

The following table of gas compositions shows the difference in the character of the gas produced when shale is distilled at a fast and a slow rate; that is, at a high and a low temperature.

Composition of gases produced at two different rates (temperatures) of distillation

Constituent gases	Fast rate	Slow rate
	<i>Per cent</i>	<i>Per cent</i>
Hydrogen sulphide (H ₂ S).....	6.3	6.2
Carbon dioxide (CO ₂).....	11.0	10.2
Illuminants.....	9.7	2.9
Hydrogen (H ₂).....	32.6	44.5
Carbon monoxide (CO).....	4.0	3.7
Methane (CH ₄).....	20.7	24.1
Ethane (C ₂ H ₆).....	15.9	8.1
Time required to distill shale, hours.....	2	8
Highest temperature required, °C.....	525	450

FIGURE 22.—
Gas-sampling
tube

DETERMINATION OF AMMONIUM SULPHATE

BEST CONDITIONS FOR CONVERTING NITROGEN COMPOUNDS INTO AMMONIA

The Bureau of Mines has made a laboratory study of the production of ammonia in retorting oil shales. Factors such as time, temperature, concentration of steam, and presence of other gases and vapors affect the yield of ammonia. Experiments show that there is little conversion of the nitrogen compounds in the shale into ammonia at temperatures below 700° C. Steam is essential in the ammonia-producing reactions, and the conversion becomes larger

as the concentration of steam increases. At temperatures below 700° C. the production of ammonia is slight, and below 500° C. it is almost negligible. As distillations for yield of oil are stopped when the production of oil ends, not more than a small fraction of the total ammonia yield that is theoretically possible can be expected. Oil production ceases at 525° C., and this temperature is far too low to give a worth-while yield of ammonia.

ESTIMATION OF AMMONIA YIELD BY AN ANALYSIS FOR NITROGEN

A satisfactory apparatus for determining ammonia yields of oil shales can be built, but the conversion of the nitrogen compounds into ammonia requires careful control of temperature and steam supply to insure the agreement of duplicate determinations. Large-scale operation may not give the same relative yield as that obtained in the laboratory. It is therefore more satisfactory to determine the nitrogen content of the shale by the Kjeldahl-Gunning method. A plant of the Scottish type converts about 60 per cent of the nitrogen of the shale into ammonia, and other types of shale retorts may be expected to be as efficient. When results of this determination are reported, the total nitrogen (not the yield of ammonia) should be stated, unless the assumed percentage recovery of nitrogen is also given.

CALCULATIONS FOR YIELD OF AMMONIUM SULPHATE

In estimating the possible yield of ammonium sulphate from a shale, a convenient procedure is as follows: Theoretical pounds of ammonium sulphate from shale=percentage of nitrogen in shale $\times$ 94.3. On the assumption that 60 per cent of the total nitrogen is converted into ammonia and collected as ammonium sulphate, then pounds of ammonium sulphate=percentage of nitrogen in shale $\times$ 94.3 $\times$ 0.60.

SUMMARY AND CONCLUSIONS

In the foregoing pages the author has described testing methods, has explained the reasons for their adoption, and discussed the best ways of applying them. For seven years the Bureau of Mines has had chemists and engineers constantly studying oil shales. Their investigations have been confined rather closely to several main lines of investigations, as follows: (1) Chemical study of the oil-yielding materials of shales; (2) the behavior of the oil-yielding material of the shales when subjected to many different interrelated conditions of rate and temperature of distillation; and (3) determinations of the conditions that must exist during thermal decomposition of oil shales in order to insure the highest yield of the best

oils from the important shales of the world, particularly those of the United States.

It was evident at the beginning that no results of value could be obtained from the study of destructive distillation of oil shales and from the factors affecting the yields and properties of the resulting oils, unless analytical methods and testing equipment were available that would invariably give results that could be duplicated. As no such methods existed, they had to be developed. In the necessary effort required to develop accurate and dependable testing procedures, much new information has been accumulated and much knowledge has been obtained as to the mechanism of destructive distillation of oil shales, bituminous coals, lignites, and cannel coals, all of which have been studied as possible future sources of oil supply.

It is not claimed that each testing method described herein is perfect, but the author has investigated the methods carefully and has thoroughly considered the desirability of each. He has given the reasons for the adoption of the methods and believes that the scheme of tests presented should satisfy the demand of the immediate future for routine testing of oil shales, coals to be used in low temperature carbonization, or other oil-yielding materials, and may well be considered as tentative umpire methods. In the event of an "artificial mineral-oil" industry developing in the United States, the operation of plants will require control tests and analyses. When their need arises, the methods of testing described in this paper will, it is believed, prove satisfactory.

APPENDIX

Some data of use to chemists studying oil shale and shale oil are appended. On later pages are described an extraction apparatus and a melting-point bridge devised by the author and his assistants.

CONVENIENT FACTORS FOR USE IN OIL-SHALE CALCULATIONS

FREQUENTLY USED EQUIVALENTS

LENGTH

1 centimeter=0.3937 inch
1 meter=3.281 feet
1 meter=1.0936 yards
1 inch=2.54 centimeters (cm.)
1 foot=0.3048 meter (m.)
1 yard=0.9144 meter (m.)

AREA

1 acre=43,560 square feet
640 acres=1 square mile

VOLUME

1 cubic inch=16.39 cubic centimeters (c. c. or cm.³)
1 cubic foot=1,728 cubic inches (cu. in.)
1 cubic foot=28,352 cubic centimeters (c. c. or cm.³)
1 gallon=231 cubic inches (cu. in.)
1 gallon=3.785 cubic centimeters (c. c.)
1 gallon=0.1357 cubic foot (cu. ft.)
1 gallon=0.004951 cubic yard (cu. yd.)
1,000 cubic centimeters=1.0 liter (l.)
1 liter=0.03531 cubic foot (cu. ft.)
1 cubic meter=35.3 cubic feet (cu. ft.)

MASS

1 gram=weight of 1 cubic centimeter of pure water at 4° C.
28.35 grams (gm.)=1 ounce (oz.)
453.6 grams=1 pound (lb.)=16 ounces
1,000 grams=1 kilogram (kg.)=2.205 pounds

MISCELLANEOUS

- 1 gallon of water (specific gravity, 1.0)=8.328 pounds=3,780 grams
- 1 cubic foot of water (at 40° C.)=62.428 pounds
- 1 cubic foot of water (at 100° C.)=59.830 pounds
- 1 pound of water=0.12 gallon
- 1 pound of oil (specific gravity, 0.9)=0.1334 gallon
- 1 barrel=42 gallons=350 pounds of liquid of specific gravity 1.000
- 1 ton of oil (specific gravity, 0.9)=5.72 barrels
- 1 barrel of liquid=5.6154 cubic feet

TEMPERATURE

Fahrenheit scale (F.): Freezing point of water=32°; boiling point of water=212°.

Centigrade scale (C.): Freezing point of water=0°; boiling point of water=100°.

Absolute scale (A.): Freezing point of water=273° C. (492° F.); boiling point of water=373° C. (672° F.).

To change temperature in °F. to °C.: $(F. \text{ reading} - 32) \times 5/9 = °C.$

To change temperature in °C. to °F.: $(C. \text{ reading} \times 9/5) + 32 = °F.$

To change temperature in °C. to °A.: $C. \text{ reading} + 273 = °A.$

To change temperature in °F. to °A.: $F. \text{ reading} + 460 = °A.$

To change temperature in °A. to °C.: $A. \text{ reading} - 273 = °C.$

To change temperature in °A. to °F.: $A. \text{ reading} - 460 = °F.$

HEAT

The *calorie* (small calorie) is the quantity of heat required to raise the temperature of 1 gram of pure water from 4 to 5° C.

The *kilogram-calorie* (large calorie) is 1,000 times the small calorie.

The *British thermal unit* (B. t. u.) is the quantity of heat required to raise the temperature of 1 pound of pure water 1° F.; precisely, it is one one-hundred-and-eightieth of the heat required to raise the temperature of 1 pound of pure water from 32 to 212° F.

1 B. t. u.=252 calories=0.252 kilogram-calorie.

1 kilogram-calorie=3.968 B. t. u.

To change calories per gram to B. t. u. per pound, multiply by 1.8 or 9/5.

To change B. t. u. per pound to calories per gram, divide by 1.8 (9/5) or multiply by 5/9.

ENERGY

1 kilogram-calorie=426.64 kilogram-meters

1 gram-calorie=4.184 joules

1 horsepower-minute=42.44 B. t. u.

1 horsepower-hour=2546.20 B. t. u.

1 kilowatt-hour=3415.50 B. t. u.

MECHANICAL EQUIVALENT OF HEAT

1 B. t. u.=777.64 foot-pounds

TABLE 5.—*Analytical data on oil shale and shale oil*

Material	Where procured	Oil yield, gallons per ton			Specific gravity			Per cent of unsaturates		Melting point of crude oil	Carbon residue in "air" residuum	Volume of gas, cubic feet per ton ¹	Gross B.t.u. in gas, cubic feet	Spent shale	Water, gallons per ton
		Crude	Sub-ber naphtha	Crude and sub-ber naphtha	Crude	Sub-ber naphtha	Crude and sub-ber naphtha	Crude, distilled to 275° C. tops	Tops	Tops and sub-ber naphtha					
Massive oil shale.....	Grand Valley, Colo.	35.54	1.17	36.71	0.905	0.720	0.899	38.5	43.9	42.8	Per cent	943	957	80.58	4.59
"Mahogany" oil shale.....	Dry Fork, Colo.	34.44	.70	35.14	.90	.753	.901	37.0	41.2	29.0	1.72	791	1,523	81.94	4.04
Coking "mahogany" oil shale.....	De Beque, Colo.	63.32	.99	64.31	.89	.729	.891	36.3	41.4	40.7	1.42	1,423	1,088	66.05	6.74
Curly massive oil shale.....	do.	43.27	2.00	45.27	.907	.683	.897	34.8	42.2	39.8	2.50	1,221	965	76.95	4.59
Black (Wurtzilite).....	do.	59.03	1.76	59.79	.909	.739	.907	36.3	45.3	44.7	2.22	1,522	1,009	69.38	5.66
Oil shale.....	Elko, Nev.	38.39	2.40	40.79	.880	.731	.880	36.18	37.2	34.0	2.22	1,214	1,051	73.21	12.44
Do.....	do.	59.56	3.63	63.19	.877	.700	.866	36.66	34.1	33.3	1.28	2,070	1,020	63.1	12.94
Do.....	Soldier Summit, Utah	48.27	1.41	49.68	.899	.703	.894	37.16	38.2	36.9	1.71	1,110	1,102	74.96	4.43
Bituminous coal.....	Sunnyside, Utah	31.27	2.37	33.64	1.015	.821	1.002	38.00	47.8	47.8	9.41	2,980	972	68.92	20.35
Lignite.....	California	68.29	3.64	71.93	.9095	.725	.900	38.83	45.6	25.6	6.23	756	825	47.2	25.3
Oil shale.....	Illinois	39.61	3.52	43.13	.923	.679	.901	40.9	45.5	21.8	9.79	1,637	1,035	74.5	6.31
Do.....	Kentucky	15.01	1.02	16.03	.948	.730	.934	40.9	45.5	44.2	0	1,931	1,032	87.97	1
Oil sand.....	Alberta, Canada	26.99	.24	27.23	.925			28.33	31.4	5	.73			87.0	1
Do.....	do.	27.45			.928			28.66	31.4			206		87.1	1
Oil shale.....	Brazil	113.84	4.85	118.69	.877	.712	.870	40.5	34.3	33.6	1.51	2,146	967	34.0	22.4
Do.....	Australia	121.01	.80	121.81	.867	.755	.867	40.16	27.5	26.9	1.16	1,121	1,452	48.6	1.01
Do.....	Chile	26.70	1.26	27.96	.901	.698	.891	36.5	33.3	33.3	4.31	615		83.71	6.95
Do.....	Scotland	16.63	1.03	17.66	.883	.703	.872	37.6	24.3	23.8	1.68	715	731	86.7	8.25

¹ Air free at 0° C. and 760 mm.

Temperature conversion tables

[By Albert Sauveur]

0 to 100				100 to 1000			
<i>C.</i>	<i>F.</i>	<i>C.</i>	<i>F.</i>	<i>C.</i>	<i>F.</i>	<i>C.</i>	<i>F.</i>
-17.8	0	32	10.0	50	122.0	38	100
-17.2	1	33.8	10.6	51	123.8	43	110
-16.7	2	35.6	11.1	52	125.6	49	120
-16.1	3	37.4	11.7	53	127.4	54	130
-15.6	4	39.2	12.2	54	129.2	60	140
-15.0	5	41.0	12.8	55	131.0	66	150
-14.4	6	42.8	13.3	56	132.8	71	160
-13.9	7	44.6	13.9	57	134.6	77	170
-13.3	8	46.4	14.4	58	136.4	82	180
-12.8	9	48.2	15.0	59	138.2	88	190
-12.2	10	50.0	15.6	60	140.0	93	200
-11.7	11	51.8	16.1	61	141.8	99	210
-11.1	12	53.6	16.7	62	143.6	100	212
-10.6	13	55.4	17.2	63	145.4	104	220
-10.0	14	57.2	17.8	64	147.2	110	230
-9.44	15	59.0	18.3	65	149.0	116	240
-8.89	16	60.8	18.9	66	150.8	121	250
-8.33	17	62.6	19.4	67	152.6	127	260
-7.78	18	64.4	20.0	68	154.4	132	270
-7.22	19	66.2	20.6	69	156.2	138	280
-6.67	20	68.0	21.1	70	158.0	143	290
-6.11	21	69.8	21.7	71	159.8	149	300
-5.56	22	71.6	22.2	72	161.6	154	310
-5.00	23	73.4	22.8	73	163.4	160	320
-4.44	24	75.2	23.3	74	165.2	166	330
-3.89	25	77.0	23.9	75	167.0	171	340
-3.33	26	78.8	24.4	76	168.8	177	350
-2.78	27	80.6	25.0	77	170.6	182	360
-2.22	28	82.4	25.6	78	172.4	188	370
-1.67	29	84.2	26.1	79	174.2	193	380
-1.11	30	86.0	26.7	80	176.0	199	390
-0.56	31	87.8	27.2	81	177.8	204	400
0	32	89.6	27.8	82	179.6	210	410
0.56	33	91.4	28.3	83	181.4	216	420
1.11	34	93.2	28.9	84	183.2	221	430
1.67	35	95.0	29.4	85	185.0	227	440
2.22	36	96.8	30.0	86	186.8	232	450
2.78	37	98.6	30.6	87	188.6	238	460
3.33	38	100.4	31.1	88	190.4	243	470
3.89	39	102.2	31.7	89	192.2	249	480
4.44	40	104.0	32.2	90	194.0	254	490
5.00	41	105.8	32.8	91	195.8		
5.56	42	107.6	33.3	92	197.6		
6.11	43	109.4	33.9	93	199.4		
6.67	44	111.2	34.4	94	201.2		
7.22	45	113.0	35.0	95	203.0		
7.78	46	114.8	35.6	96	204.8		
8.33	47	116.6	36.1	97	206.6		
8.89	48	118.4	36.7	98	208.4		
9.44	49	120.2	37.2	99	210.2		
			37.8	100	212.0		
						260	500
						266	510
						271	520
						277	530
						282	540
						288	550
						293	560
						299	570
						304	580
						310	590
						316	600
						321	610
						327	620
						332	630
						338	640
						343	650
						349	660
						354	670
						360	680
						366	690
						371	700
						377	710
						382	720
						388	730
						393	740
						399	750
						404	760
						410	770
						416	780
						421	790
						427	800
						432	810
						438	820
						443	830
						449	840
						454	850
						460	860
						466	870
						471	880
						477	890
						482	900
						488	910
						493	920
						499	930
						504	940
						510	950
						516	960
						521	970
						527	980
						532	990
						538	1000

INTERPOLATION
FACTORS

<i>C.</i>		<i>F.</i>	<i>C.</i>		<i>F.</i>
0.56	1	1.8	3.33	6	10.8
1.11	2	3.6	3.89	7	12.6
1.67	3	5.4	4.44	8	14.4
2.22	4	7.2	5.00	9	16.2
2.78	5	9.0	5.56	10	18.0

Table showing equivalent specific gravities and degrees American Petroleum Institute

0.650	86.2	0.700	70.6	0.750	57.2	0.800	45.4	0.850	35.0	0.900	25.7	0.950	17.5
1	85.9	1	70.4	1	56.9	1	45.2	1	34.8	1	25.6	1	17.3
2	85.5	2	70.1	2	56.7	2	44.9	2	34.6	2	25.4	2	17.1
3	85.2	3	69.8	3	56.4	3	44.7	3	34.4	3	25.2	3	17.0
4	84.9	4	69.5	4	56.2	4	44.5	4	34.2	4	25.0	4	16.8
5	84.5	5	69.2	5	55.9	5	44.3	5	34.0	5	24.9	5	16.7
6	84.2	6	68.9	6	55.7	6	44.1	6	33.8	6	24.7	6	16.5
7	83.9	7	68.6	7	55.4	7	43.8	7	33.6	7	24.5	7	16.4
8	83.6	8	68.4	8	55.2	8	43.6	8	33.4	8	24.3	8	16.2
9	83.2	9	68.1	9	54.9	9	43.4	9	33.2	9	24.2	9	16.0
.660	82.9	.710	67.8	.760	54.7	.810	43.2	.860	33.0	.910	24.0	.960	15.9
1	82.6	1	67.5	1	54.4	1	43.0	1	32.8	1	23.8	1	15.7
2	82.2	2	67.2	2	54.2	2	42.8	2	32.7	2	23.7	2	15.6
3	81.9	3	67.0	3	54.0	3	42.6	3	32.5	3	23.5	3	15.4
4	81.6	4	66.7	4	53.7	4	42.3	4	32.3	4	23.3	4	15.3
5	81.3	5	66.4	5	53.5	5	42.1	5	32.1	5	23.1	5	15.1
6	81.0	6	66.1	6	53.2	6	41.9	6	31.9	6	23.0	6	15.0
7	80.6	7	65.9	7	53.0	7	41.7	7	31.7	7	22.8	7	14.8
8	80.3	8	65.6	8	52.7	8	41.5	8	31.5	8	22.6	8	14.7
9	80.0	9	65.3	9	52.5	9	41.3	9	31.3	9	22.5	9	14.5
.670	79.7	.720	65.0	.770	52.3	.820	41.1	.870	31.1	.920	22.3	.970	14.4
1	79.4	1	64.8	1	52.0	1	40.9	1	31.0	1	22.1	1	14.2
2	79.1	2	64.5	2	51.8	2	40.6	2	30.8	2	22.0	2	14.1
3	78.8	3	64.2	3	51.6	3	40.4	3	31.6	3	21.8	3	13.9
4	78.4	4	63.9	4	51.3	4	40.2	4	30.4	4	21.6	4	13.8
5	78.1	5	63.7	5	51.1	5	40.0	5	30.2	5	21.5	5	13.6
6	77.8	6	63.4	6	50.9	6	39.8	6	30.0	6	21.3	6	13.5
7	77.5	7	63.1	7	50.6	7	39.6	7	29.9	7	21.1	7	13.3
8	77.2	8	62.9	8	50.4	8	39.4	8	29.7	8	21.0	8	13.2
9	76.9	9	62.6	9	50.1	9	39.2	9	29.5	9	20.8	9	13.0
.680	76.6	.730	62.3	.780	49.9	.830	39.0	.880	29.3	.930	20.7	.980	12.9
1	76.3	1	62.1	1	49.7	1	38.8	1	29.1	1	20.5	1	12.7
2	76.0	2	61.8	2	49.5	2	38.6	2	28.9	2	20.3	2	12.6
3	75.7	3	61.5	3	49.2	3	38.4	3	28.8	3	20.2	3	12.5
4	75.4	4	61.3	4	49.0	4	38.2	4	28.6	4	20.0	4	12.3
5	75.1	5	61.0	5	48.8	5	38.0	5	28.4	5	19.8	5	12.2
6	74.8	6	60.8	6	48.5	6	37.8	6	28.2	6	19.7	6	12.0
7	74.5	7	60.5	7	48.3	7	37.6	7	28.0	7	19.5	7	11.9
8	74.2	8	60.2	8	48.1	8	37.4	8	27.9	8	19.4	8	11.7
9	73.9	9	60.0	9	47.8	9	37.2	9	27.7	9	19.2	9	11.6
.690	73.6	.740	59.7	.790	47.6	.840	37.0	.890	27.5	.940	19.0	.990	11.4
1	73.3	1	59.5	1	47.4	1	36.8	1	27.3	1	18.9	1	11.3
2	73.0	2	59.2	2	47.2	2	36.6	2	27.1	2	18.7	2	11.1
3	72.7	3	56.9	3	46.9	3	36.4	3	27.0	3	18.6	3	11.0
4	72.4	4	58.7	4	46.7	4	36.2	4	26.8	4	18.4	4	10.9
5	72.1	5	55.4	5	46.5	5	36.0	5	26.6	5	18.2	5	10.7
6	71.8	6	58.2	6	46.3	6	35.8	6	26.4	6	18.1	6	10.6
7	71.5	7	57.9	7	46.0	7	35.6	7	26.3	7	17.9	7	10.4
8	71.2	8	57.7	8	45.8	8	35.4	8	26.1	8	17.8	8	10.3
.699	70.9	.749	57.4	.799	45.6	.849	35.2	.899	25.9	.949	17.6	.999	10.1
												1.000	10.0

Formula: Degrees A. P. I. — $\frac{141.5}{\text{sp. gr.}}$ — 131.5

Table of heats of combustion of gases and vapors

Gas	Formula	Molecular weight	Wt. at 0° C. and 760 mm. Hg.		Authority	Gram calories per gram	B. t. u. per pound	Authority	B. t. u. per cubic foot at 0° C. and 760 mm. Hg.		B. t. u. per cubic foot at 60° F. and 29.92 inches Hg.		Remarks
			Grams per liter	Pounds per cubic foot					Gross	Net	Gross	Net	
Acetylene	C_2H_2	26.02	1.1707	0.07308	Leduc	11,916	21,449	Thomsen	1,567	1,518	1,483	1,437	Mean gram calories used. Gases at 18° C. or 64.8° F. Thomsen's Thermochimischer Unter suchun, 1906.
Benzol	C_6H_6	78.05	3.4859	.21760	Calculated	10,066	18,173	Stohmann	3,954	3,808	3,741	3,603	Same as No. 1.
Butane	C_4H_{10}	58.08	2.5985	.16221	Frankland	11,832	21,298	Thomsen	3,455	3,211	3,269	3,038	D.
Butylene	C_4H_8	56.06	2.5038	.15629	Calculated	11,604	20,891	do	3,265	3,038	3,089	2,875	D.
Isobutylene	C_4H_8	56.06	2.5038	.15629	do	11,624	20,923	do	3,270	3,075	3,094	2,909	D.
Carbon	C	12.00				8,080	14,544	do					
Carbon to CO						2,417	4,325	Fauvre & Silberman					
Carbon monoxide	CO	28.00	1.2503	.07805	Rayleigh	2,427	4,369	Thomsen	341	341	323	323	D.
Ethane	C_2H_6	30.05	1.3567	.08469	Baumé & Perrot	12,328	22,190	do	1,879	1,731	1,778	1,638	D.
Ethylene	C_2H_4	28.03	.07815	.00562	Calculated	11,893	21,407	do	1,673	1,575	1,583	1,491	D.
Hydrogen	H_2	2.016	.08998	.00562	Rayleigh	33,936	61,085	do	343	294	325	279	D.
Hydrogen sulphide	H_2S	34.09	1.5392	.09608	Baumé & Perrot	4,010	7,218	do	694	645	657	610	D.
Methane	CH_4	16.03	.7168	.04475	do	13,221	23,798	do	1,065	967	1,008	916	D.
Pentane	C_5H_{12}	72.10	3.2197	.20098	Calculated	11,751	21,152	do	4,231	3,959	4,022	3,745	D.
Pentylene	C_5H_{10}	70.08	3.1300	.19538	do	11,524	20,743	do	4,053	3,809	3,835	3,604	D.
Propane	C_3H_8	44.06	1.9680	.12285	do	12,011	21,620	do	2,656	2,461	2,513	2,329	D.
Normal propylene	C_3H_6	42.05	1.8781	.11724	do	11,718	21,092	do	2,473	2,327	2,340	2,202	D.
Trimethylene propylene	C_3H_6					11,877	21,379	do	2,506	2,360	2,371	2,233	D.
Sulphur	S	32.06				2,217	3,991	do					
Toluol	C_7H_8	92.06	4.1116	.25665	Calculated	10,270	18,270	Stohmann	4,689	4,494	4,436	4,251	D.
Methyl alcohol	CH_3OH	32.03	1.4305	.08930	do	5,688	10,238	Thomsen	914	816	865	773	D.
Ethyl alcohol	C_2H_5OH	46.05	2.0567	.12839	do	7,394	13,309	do	1,709	1,563	1,617	1,479	D.
Di-isopropyl hexane	C_8H_{18}	86.11	3.8454	.24004	do	11,604	20,887	do	5,014	4,668	4,744	4,417	D.
Heptane	C_7H_{16}	100.13	4.4722	.27917	do	11,374	20,473	Lugnin	5,715	5,325	5,407	5,038	Heating value of the liquid.

Calculated weight of gas per liter = $\frac{\text{molecular weight of gas}}{\text{molecular weight of oxygen} = 32.00} \times 1.4292$.

Pound per cubic foot = $\frac{\text{grams per liter} \times 28.315}{453.598}$

B. t. u. per pound = Gram calories per gram $\times 1.8$. B. t. u. at 60° F. and 29.92 inches Hg = B. t. u. at 0° C. and 760 mm. Net B. t. u. : $2.02 \times \frac{18.02}{\text{molecular weight}} \times H_2 \times 970.4 = A$. B. t. u. per lb. - A = f, gross B. t. u. = net B. t. u. per pound.

B. t. u. per cubic foot = Pound per cubic foot $\times$ B. t. u. per pound. $\frac{491.6}{519.6} = 0.94611$ Hg $\times \frac{491.6}{519.6}$

AN EXTRACTION APPARATUS FOR OIL SHALES, COALS, AND OIL SANDS¹⁸

The more common methods of extraction used in the laboratory are not entirely suitable for certain finely divided substances, largely because the fine particles clog the filter medium during the downward flow of the solvent. The apparatus shown in Figure 23 was designed particularly to eliminate trouble from the clogging of filters. A space above the layer of pulverized material is provided to permit most of the suspended particles to settle before they reach the filter. It was also designed to prevent the compacting of the material under treatment, and to do this the solvent flows upward. The device successfully extracts soluble matter from crushed or pulverized substances.

The drawing shows the essential parts of the apparatus; the course of the solvent in passing through the system is indicated by arrows. The solvent enters the bottom of the extraction tube, passes upward through the sample, and flows out of the

FIGURE 23.—Extraction apparatus with recovery and regenerative devices: A, Leaching tube; B, pulverized sample; C, fiber mat; D, filter; E, settling space; F, extract recovery flask; G, boiler; H, solvent vapor condenser; J, filter-washing and solvent-charging funnel; K, siphon; L, constant-level device

¹⁸ Designed and applied by Lewis C. Karrick and Douglas Gould.

tube by way of the settling space and filter. Then it flows into the extract-recovery flask, in which it is vaporized. The vapors pass to the reflux condenser, from which the condensed solvent returns to the extraction tube.

The extraction tube may be made of glass or iron, but otherwise the entire apparatus is of glass. A 2-inch iron pipe has been used as an extraction chamber and is satisfactory. In the bottom of the tube is placed a mat which may be a layer of glass wool covered with a piece of cloth. This mat is used merely to provide a support for the material to be extracted and to aid the uniform distribution of the solvent through the sample. A suitable filter is a Watman extraction thimble fastened around a one-hole cork stopper through which a glass tube is inserted. The glass tube also passes through a cork stopper in the upper cap of the extraction tube, thus providing a tight joint, and the filter remains inside the extraction tube in contact with the solvent. Glass beads or a wire-gauze form should be placed in the thimble to prevent the collapse of the filter. The solution therefore enters the filter in a direction opposite to that usually employed and passes out through the glass-tube connection.

If, as a result of too rapid circulation of the solvent, the filter should begin to clog, the filter cake may be released by temporarily reversing the flow of the solvent through the filter. This reversal is accomplished by introducing fresh solvent through the funnel *J*, while the cock below the funnel is turned so that the new solvent will flow into the filter and not into the side tube leading to the extract-recovery flask. The solvent in the return pipe leading downward from the condenser must first be drawn off through the drain cock provided. When the drain cock is again turned to the position shown in the drawing, the solvent will flow backward out of the extraction tube and rise in the pipe below the condenser as the fresh solvent is added through the filter and funnel. The filter will seldom clog, and it will rarely be necessary to clean it during an extraction test.

Obviously the entire system should be filled with solvent throughout the run, and enough solvent should be in the recovery flask at all times to keep the extract in perfect solution. Should it be desirable, the collected extract may be removed and the flask replaced by a new one during the test without the loss of solvent. The drain cock at the bottom of the condenser tube must be turned so that the solvent contained in this tube, as well as the solvent in the flask, can pass out of the system and be collected in the new flask. When the extract in the first flask is virtually free from solvent, the new flask containing the recovered solvent may be substituted in its place and extraction resumed. This procedure is convenient when

the extraction nears completion, because it will show by the amount of extract recovered in the flask how nearly complete the extraction is.

The rate of extraction may be varied at will. Since the velocity of circulation of the solvent through the system is dependent on the pressure head $r-s$, the head may be increased or decreased by varying the rate at which the solvent is vaporized from the flask. Therefore the burner flame may be manipulated to give the desired rate of extraction. The bath G containing water or other liquid of a boiling point higher than that of the solvent is placed around the flask to provide ample heating surface for boiling at the desired rate without danger of overheating the flask and damaging the extract in it.

In order that the apparatus may run continuously for several days at a time without attention, a constant-level device is provided which keeps the liquid (water, in the case illustrated) at a definite height in the bath. K is a siphon and is an essential part of the constant-level device. The siphon is provided with a reservoir at its highest point to prevent an accumulation of air from interrupting its operation. This assures the continuous and uniform operation of the apparatus.

When the extraction is finished, the extract accumulated in the flask is freed of solvent by continuing the distillation until the excess solvent is removed and withdrawn from the system through the drain cock below the condenser. Most of the solvent remaining in the extraction tube is drawn off through the cock placed in the side of the extraction tube. A certain amount of solvent will remain in the treated sample, and this may be entirely removed by distillation. By gently heating the sides of the tube with a flame (other means may be used, if desirable) the vaporized solvent may be conducted out through the same cock and condensed by suitable means.

The device was designed and built for use in extracting from pulverized oil shale the bituminous substance produced by heating the shale to its initial temperature of thermal decomposition. It gave excellent results and has proved to be equally satisfactory for leaching oil sands, coals, or salt-laden earths, and for lixiviation purposes in general.

MELTING-POINT BRIDGE FOR PETROLATUMS, SHALE OILS, AND SHALE-OIL DISTILLATES¹⁹

To determine by the cooling-curve method the temperature at which some liquids pass into the crystalline state²⁰ is simple, but to

¹⁹ Designed and applied by Lewis C. Karrick and V. F. Parry.

²⁰ Federal Specifications Board, United States Government Specification for Lubricants and Liquid Fuels and Methods for Testing: Standard Specification No. 2c: Tech. Paper 323A, Bureau of Mines, 1924, 89 pp.

determine a true melting point for petrolatums and some types of greases which harden gradually is difficult. The petrolatums are composed largely of mixtures of hardening and nonhardening paraffins, whereas the greases are made of a mixture of animal and vegetable fats and mineral oils. These substances, however, congeal within fairly narrow temperature limits. On the other hand, substances such as tar or asphalt harden at extremely slow rates, become more and more viscous as they cool, and when "hard" in the practical sense they still possess to a certain degree the properties of true liquids. It is therefore customary for manufacturers and users of those substances of which petrolatum and asphalt are examples to adopt special means of determining softening temperatures. A particular, and usually an arbitrarily chosen, degree of hardness within the softening range of the substance is determined and is considered the melting or softening point of the substance. Descriptions of the most extensively used apparatus and methods for determining the temperatures at which these substances change by setting, congealing, or hardening are to be found in the publications of the American Society for Testing Materials, Bureau of Standards, and various laboratories.

The oils produced by the distillation of shales differ widely in their melting points. This difference is largely due to heavy hydrocarbons which are present in proportions that depend on the type of shale and on the conditions used in producing the oil. Scottish oil-shale operators have found that the melting point of a shale oil or shale-oil fraction has a direct relation to the amount of recoverable paraffin wax in the oil. Throughout their research on oil shale the chemists of the Bureau of Mines have found it important to observe carefully the melting temperatures of the shale oils produced, as this property indicates the degree to which thermal decomposition has taken place within the retort. The testing of shale oils therefore requires a simple, accurate, and rapidly operated method of determining melting point.

The apparatus shown in Figure 24 was designed primarily for testing shale oils and shale-oil distillates, but proved to be suitable for testing petroleum and several grades of paraffin waxes manufactured by refiners of petroleum products. Little effort has been devoted to adapting the apparatus to the testing of greases and bituminous substances, but probably this apparatus or a modification of it can be used successfully for that purpose.

PRINCIPLE OF THE METHOD

The new method depends on the use of a heat-conducting rod (the ends of which can be adjusted quickly to maintain slightly

different temperatures) which will rapidly establish a rectilinear temperature gradient between its ends. In other words, the temper-

FIGURE 24.—Melting-point bridge for shale oils and shale-oil distillates: A, Preheater; B, gradient rod; C, detector; D, interpolator; E, constant head device; F, supports; G, heating wires; H, thermometer; J, rheostat; K, switch; M, air trap; P, sealed plugs; R, current supply, heating wires; S, base; T, stylus; →, flow of water; ←, flow of oil

ature of the gradient rod is so regulated that within its range of temperature from end to end the melting point of the oil under test will

be included. If a line of oil is drawn from end to end of the gradient rod with a stylus, at a certain point on the rod the oil will pass from the solid to the liquid state. The distance in centimeters from the cold end of the rod to the point where the oil changes from the solid to liquid state is a measure of the temperature increment that must be added to the cold-end temperature to obtain the true melting point of the oil.

The flexibility of the apparatus is evident. By reducing the temperature difference between the ends of the gradient rod the precision of the apparatus is increased, if the thermometers are sufficiently accurate. Use of a longer gradient rod which has the same end temperatures is another means of obtaining greater sensibility. A length of 100 cm. will be generally satisfactory as a standard length for the gradient rod, as this length provides an apparatus of ample sensibility and is convenient in calculating results.

DESCRIPTION OF APPARATUS

The gradient rod consists of a thin-walled glass tube, 0.5 inch in diameter and 1 meter long, through which runs a small coil of chromel resistance wire. The diameter of the coil should not be more than one-half the inside diameter of the glass tube, and the wire must be carefully wound so that all turns are equally spaced. Water flowing with constant velocity passes through the glass tube, filling it completely and thereby enveloping the resistance coil. An electric current is passed through the coil and the heat produced is absorbed by the water. Because the water flows at a constant rate, it continues to absorb heat uniformly as it passes through the tube. The resulting temperature of the water is imparted to the glass tube, thus producing a straight-line temperature gradient from end to end.

Two thermometers which are accurate to 0.1° C. are mounted, one at each end of the glass tube, so that the water surrounds them in flowing into and out of the tube. If extreme accuracy is to be attempted, the thermometers should be immersed to the point to which they were immersed when calibrated, though such precision will seldom be found necessary in routine testing.

A preheater for the water is provided. It is of the same design as the gradient tube, is placed directly ahead of the cold-end thermometer, and thus is in series with the gradient tube. The water flows from a constant-head device through the preheater, around the cold-end thermometer, through the temperature-gradient tube, around the hot-end thermometer, and thence to the waste drain. Obviously, if the rheostats regulating the current are shifted, the

temperatures of the heating coils immediately change and the rapidly flowing water quickly imparts its change in temperature to the glass tube. Thus a new temperature gradient is established within a few seconds.

The resistance-wire coils are supplied with current from a 110 or 220 volt line. Each coil should be connected separately through individual regulating rheostats to the line. The current to the pre-heater may be varied between successive melting-point determinations, whereas the current to the gradient tube is varied only occasionally—when the temperature difference between the ends of the tube is to be changed for adjusting or for obtaining closer agreement of results.

The flow of water may be changed when the temperature difference between the ends of the tube is to be changed. The greater the flow of water through the gradient tube the nearer does the temperature gradient become truly rectilinear, as the heat capacity of the gradient tube and its contents is increased with the large flow of water, while the average temperature remains constant. The tendency for radiation to distort the temperature gradient from a straight-line relation, owing to external heat being absorbed at the cold end if below room temperature and to heat being radiated at the hot end of the tube if above room temperature, will be reduced by the greater quantity of water affected by such heat transfer. For economy of power a small amount of water should be used.

The stylus is a piece of $\frac{1}{8}$ -inch glass tube 6 inches long, drawn out to a fine opening at one end, and containing a bulb of about 3 c. c. capacity close to the pointed end. Melted oil to be tested is drawn into the bulb by means of a small rubber suction tube fastened to the upper end of the stylus. The oil is permitted to flow from the point by releasing the suction, while the stylus is simultaneously moved at a uniform rate along the tube, the thumb and first finger acting as guides. If the switch to the power line is open and cold water is flowing through the tube, the oil line will solidify at once as it touches the cold surface of the tube, and the result will be a straight and fine line of uniform dimensions running the full length of the tube.

The detector is a small device which slides along the gradient tube and carries a glass nozzle that directs an air blast on the oil line. This device rests firmly on the tube in such a manner as not to disturb the oil line. The air nozzle inclines at a 45° angle in the direction of the flow of water. The orifice is flat, 1 by 3 mm. in section. The long axis of the orifice is horizontal and at right angles to the direction of the oil line, and is held uniformly 2 mm. above the top surface of the gradient tube. Air is supplied to the

nozzle by a small rubber tube leading to a source of compressed air. The air pressure must be uniform. A manometer is attached near the nozzle and should indicate a pressure of 1 inch of mercury when the air blast is turned on.

The interpolator is a meter stick mounted immediately under and parallel to the gradient tube. The ends of the meter stick must be directly under the gradient-tube thermometers. The interpolator is used for measuring the distance from the cold-end thermometer to the point where the oil melts. It also acts as a guide for the detector by preventing it from tipping from side to side on the tube. As the interpolator is 100 cm. long, the distances from the cold end of the tube to the points where the oils melt are read directly in percentages of the entire length of the tube. The percentage of the temperature difference between the ends of the tube is the temperature increment which must be added to the cold-end temperature to obtain the melting temperature of the oil.

OPERATION

With the switch open and cold water flowing through the tubes the oil line is drawn on the gradient tube with the stylus. Then the switch is closed, and as the temperature of the gradient tube rises the line should start to melt near the hot end of the tube. If melting does not start by the time temperature equilibrium is established, the resistance in the preheater circuit should be reduced to allow more current to flow, thereby causing the oil line to melt a short distance from the hot end of the tube. When equilibrium is established the thermometer readings should be carefully noted, the air blast started, and the detector moved along the tube from hot to cold end at a uniform rate of about 35 cm. per second. The air blast obliterates the melted part of the oil line, while the unmelted part remains undisturbed. The air blast should then be turned off and the detector returned to the "break" in the oil line. The small pointer attached to the detector will indicate on the interpolator the distance of the melting point from the cold end.

The resistance in the preheater circuit should now be reduced slightly by means of the rheostat so that temperature of the gradient tube rises and the oil line melts farther from the hot end. When temperature equilibrium is again established, the detector should be run along the tube and the temperatures and the distance to the break noted. This operation should be repeated once or twice more if enough of the oil line remains. For accurate work it is desirable to make three or four such determinations on the same line of oil, as results can be checked in this manner more rapidly than by using a

new line of oil. Each additional determination made on the same oil line requires about one minute, whereas the time required for the first determination is about three minutes. Calculations are made using the following formula:

$$\frac{(t_h - t_c)d}{100} + t_c = \text{m. p.}$$

in which t_h is the temperature of the hot end of the gradient tube t_c the temperature of the cold end, d the distance in centimeters from the cold end of the tube to the break in the oil line, and m. p. the melting-point result.

Example 1		Example 2	
$t_h = 31.8^\circ \text{ C.}$		$t_h = 33.6^\circ \text{ C.}$	
$t_c = 22.6^\circ \text{ C.}$		$t_c = 24.3^\circ \text{ C.}$	
$d = 62 \text{ cm.}$		$d = 45 \text{ cm.}$	
$(31.8 - 22.6) 62$		$(33.6 - 24.3) 45$	
<hr/>		<hr/>	
100	$+ 22.6 = 28.3^\circ \text{ C.}$	100	$+ 24.3 = 28.5^\circ \text{ C.}$

Three to four determinations made on the same oil line, including calculations, will require not more than 6 minutes. If desired, the determinations may be repeated with a new oil line. However, in tests of oils that give a fairly sharp break, successive determinations made on the same line will agree within 0.3° . When the determinations are repeated with a new oil line the averages of the results obtained by the two lines will agree within 0.1° .

As shale oils and petrolatums have no absolute melting temperatures it is necessary to establish arbitrarily the temperature to be taken as the melting point. For use with the apparatus described above, the author has arbitrarily defined the melting temperature of an oil as the temperature of the hottest point on the line of oil which is not disturbed by the air blast. This position is referred to as the break in the oil line. The same point also applies to paraffin wax. Paraffin becomes transparent near the break and the point is difficult to distinguish. However, if a little dye is added to the sample of melted paraffin this difficulty is overcome.

FLOW-POINT METHOD FOR DETERMINATION OF MELTING POINTS

The flow-point determination is a modification of the pour test used in testing petroleum²¹ and consists in cooling the sample, under a definite procedure, to a point beyond which there is no visible tendency for the oil to flow. The apparatus and the operating technique that give the best results are as follows:

A 4-ounce oil bottle having an etched line $1\frac{1}{4}$ inches from the bottom is used as a container for the sample to be tested. The thermometer has a range of -35° F. to 120° .

The bottle is filled to the etched line with the oil sample. The thermometer is lowered into the center of the oil until the bulb is completely immersed. A one-hole cork holds the thermometer rigidly in place.

²¹ Federal Specifications Board, United States Government Specification for Lubricants and Liquid Fuels and Methods for Testing; Specification No. 2c: Tech. Paper 323A, Bureau of Mines, 1924, 89 pp.

The bottle is now set vertically in an ice-water bath and as the mercury column descends the bottle is tilted slightly every 5° until very little flow of the oil is observed. Removal of the bottle and tilting are now repeated at each degree drop in temperature, and when no flow of the oil nearest the thermometer stem is observed after the bottle has been held in an inclined position for five seconds, the temperature read is considered the flow point. Results of duplicate determination by different analysts will usually agree well enough.

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