discussion of the NBS tabulation by Masi (*30*) has not yet appeared.

OTHER WORK

Since the above computations were completed, extensive tables of thermodynamic properties (*4, 30, 35-37*) have appeared. Some (*4,30*) are revisions of tables (*11,31*) incorporated in the comparisons above, while the data of Price (*35-37*) are based upon volumetric determinations of Kennedy (*13*). Values given by Kennedy do not appear to be sufficiently accurate for comparison of virial coefficients with those of Table V. The newer tabulation (*30*) contains zero pressure values for carbon dioxide (*47*) which differ from the original data (*31*). The second portion of Table III compares the data of Table II and (*30*). Except at the higher pressures and at 150° C. agreement to 1% exists.

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Measurement of the Thermal Properties of Carbonaceous Materials

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The companion article on "Heat Transfer and Thermal Stresses in Carbonization of Briquets" appears in the July issue of *Industrial and Engineering Chemistry*, Vol. 51, page 833.

Many processes for the treatment of coal involve thermal conversion. In process development, thermal data on the materials are desirable. This work was designed to supply such thermal data for carbonaceous materials. Heat capacity measurements were made on a bituminous coal from the Pittsburgh seam and its low-temperature char. Thermal conductivity was measured on a coal-char-pitch briquet. Finally, an estimate was made of the heat transfer film coefficient from a fluidized heating medium to a spherical briquet. This latter work was carried out so that the thermal parameters could be applied to the calculation of heating rates for carbonaceous briquets, an application which is described in an article in the July issue of I/EC on heat transfer in the carbonization of briquets (*17*).

LITERATURE SURVEY

The heat capacity data for coal and coke were reviewed by Clendenin and others (*3*). A correlation equation for the specific heat capacity of moisture-free coal is presented, based on data for 23 American bituminous coals. The equation expresses heat capacity as a linear function of temperature and volatile matter content, but is not expected to hold into the temperature range in which coal becomes plastic. In fact, the very limited data included in the correlation for temperatures above 100° C. make its use above about 150° C. an unjustifiable extrapolation.

The heat capacity of a material undergoing thermal decomposition such as bituminous coal in the plastic range loses its conventional significance. One deals basically with two heat quantities. One, the total "heat of carbonization," is defined to include all the sensible and reaction heats involved in carbonization; the other, often called the "heat of decomposition," refers to the reaction heats only after the sensible heats have been removed by calculation or by the use of a differential calorimetric method. The most notable of the data in the literature are those of Terres and coworkers (*11–15*), Davis and others (*4–6*), Weyman (*16*), and Burke and Parry (*2*). Work has also been reported upon the heat capacity of chars produced from coal by thermal treatment (*13*). In general, the data found in the literature fall short of providing applicable and consistent data for materials typical of Pittsburgh seam bituminous coal.

Published information on the thermal conductivity of briquets is also very meager. Some data by Terres (*11*) cover the whole coking range, but because the values are reported as "mean" conductivities, they probably represent average values over a wide temperature range. Millard (*8*) published conductivity data for beds of granulated coal (and coke, subsequently produced) over a 100° to 900° C. temperature range. Work by Birch and Clark (*1*) on the conductivity of rock samples up to 900° F. provided the basic design for the conductometer used in this work.

Nothing in the literature directly predicts the surface film heat transfer coefficient between fluidized solids and small spheres immersed in the bed. Numerous investigations and correlations are available for heat transfer coefficients between fluidized solids and the walls of the containing vessel and some work is reported for internal tubes. This information has not been critically evaluated, but the range of values for *h* thought to be applicable is from 20 to 50 B.t.u./hr. sq. ft. °F.

HEAT CAPACITY MEASUREMENTS

Method. A variation of the standard calorimetric method of mixtures was used. The bituminous coal samples were known to undergo irreversible changes upon thermal treatment in the temperature range of interest; therefore, a high temperature calorimeter had to be used in which the sample is heated and the calorimeter cooled. The method measured the total heat required to raise the sample from room temperature to the temperature investigated; sensible and reaction heats are thus lumped together. However, this is the important quantity for most practical applications. The term mean specific heat used in the rest of the article applies to this "practical" quantity and should not be interpreted as a true specific heat when the sample decomposes.

The high temperature calorimeter (Figure 1) made it impractical to reduce the thermal losses to a negligible level. Instead, the losses had to be controlled and standardized at a reasonably high level. To keep the unit as simple as possible, an unsteady-state method was used, in which the effect of an added sample on the normal cooling curve of a heated metal block was observed. This method proved adequate and allowed the use of simple equipment; however, considerable care and extensive calculation were needed to produce these satisfactory results.

The heart of the calorimeter was an aluminum block 1-1/2 inches in outside diameter and 2-7/8 inches long with an axially bored hole 3/4 inch in diameter and 2-1/2 inches deep. The block was hung down into a glass Dewar flask, which in turn was placed in a tube furnace. A "seal-ring" of Transite, slightly smaller than the inside diameter of the Dewar flask, was placed between the block and its supporting disk. This seal-ring, which contained an electric heater powered from a constant voltage source, reduced the end losses upward from the block and improved the temperature symmetry of the system. The calorimeter is shown assembled in Figure 1.

The thermocouple circuits for sensitive measure of the temperatures of the system consisted of two four-element thermopiles of iron-constantan. The four hot junctions of one thermopile were placed in holes drilled in the aluminum block, and because of their spacing in the block, yielded a good average temperature directly. The hot junctions of the second thermopile were held near the inner wall of the Dewar flask and were spaced around the block. The sensitivity of each of these thermopiles is of the order of 0.12 mv. per °F., so that the temperatures within the system could be readily measured to the nearest 0.1° F.

In the normal experimental procedure, the outer furnace and the seal ring heater were used to establish an elevated "steady-state" temperature in the calorimeter block. From this level a resistance heater on the block raised the block temperature to a level about 20° F. higher. After conditions were steady at this upper temperature level, the block heater was switched off, and the block allowed to cool toward its lower steady state temperature. After about 3 minutes had elapsed, a powdered solid sample, held in a small aluminum foil cylinder about 5/8 inch in diameter and 1-1/2 inches long, was dropped into the block. The block and external temperatures were read alternately, each on a 30-second schedule, until the cooling rate became relatively small so that less frequent readings were sufficient.

The calculation of the effect of the added sample required that a "normal" cooling curve be determined for each temperature level without any sample addition or other external stimulus. By graphical differentiation of the block temperature curve during normal cooling, the block cooling rate was plotted as a function of the instantaneous temperature difference between the block and its surroundings. At each level a good straight-line relation existed, as predicted by the simple

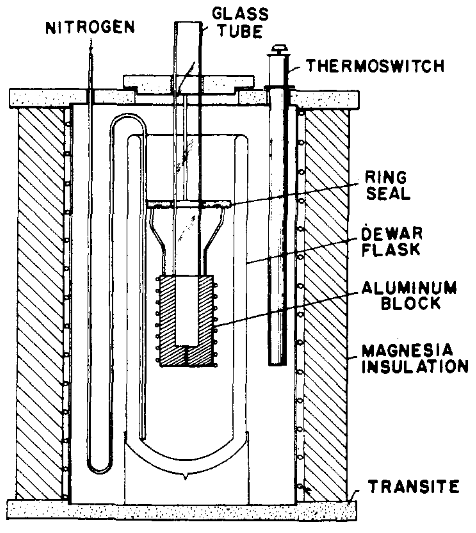
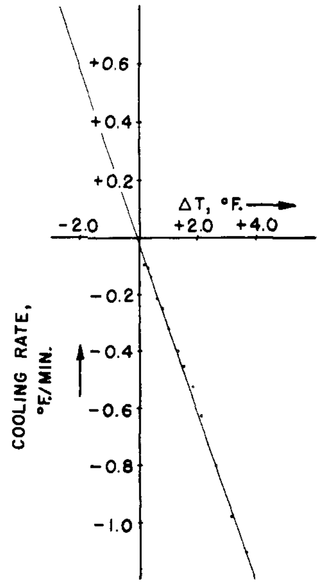


Figure 1. Calorimeter

Figure 2. Normal cooling correction line



Newtonian cooling law; a typical plot is shown in Figure 2. The slope of this line depends on the properties of the system, but the intercept depends, principally, on the input to the seal ring heater. When used as a correction of the observed cooling after a sample has been added to the calorimeter block, this Newtonian plot must be extrapolated into the heating domain where dt block/$d\theta$ is positive and $(t_{\text{block}} - t_{\text{external}})$ is negative. To prove that this extrapolation was reasonably accurate, a dry ice pellet was added at one temperature level to force the block temperature below the external temperature; the observed heating rate for the block was just that predicted by extrapolation.

A typical pair of temperature curves for a run in which a solid sample was added is shown in Figure 3. For selected values of time, the temperature driving force, $(t_{\text{block}} - t_{\text{external}})$, was noted and the normal cooling rate determined from the Newtonian plot. The integral expression,

$$\int \left(\frac{dt\ \text{block}}{d\theta}\right)_{\text{normal}} d\theta$$

was determined graphically for each run, and served as a correction for the observed temperature drop of the block. The corrected temperature effect of the sample was the algebraic difference of the observed temperature drop and this integral normal temperature drop. The corrected temperature effect should approach a steady final value after a reasonable period of time, as shown in Figure 4. When no final steady value was approached, it was necessary to shift the Newtonian cooling plot, holding its slope constant, until the total effect was forced to level off. This forced balance was equivalent to assuming that the seal ring heater input varied while the insulating properties of the system did not. This assumption appeared reasonable because the corrections were random, and no aging trend was noticed during the period spent on measurements at a given temperature level.

After the total corrected effect of a sample on the calorimeter block was found, the remaining calculations were familiar. Powdered aluminum oxide, a substance of known heat capacity, was run to establish a calorimeter constant. The heat capacities of other materials were determined by using this calibration as a reference.

Results. The heat capacity of a Pittsburgh seam coal (38.6% volatile matter and 7.0% ash, from the Arkwright mine in West Virginia) was determined to a maximum temperature of 800° F. Swelling and frothing of the coal made it impossible to use higher temperatures. A char produced from this coal by fluidized carbonization at 950° F. was used for measurements to 890° F. This Arkwright char contained 13.2% volatile matter. Magnesium oxide was used as a secondary standard to check the accuracy of the method by comparison between observed and literature values for heat capacity from 650° to 800° F. The mean specific heat capacities (Figure 5) are averaged from room temperature to the final temperature plotted.

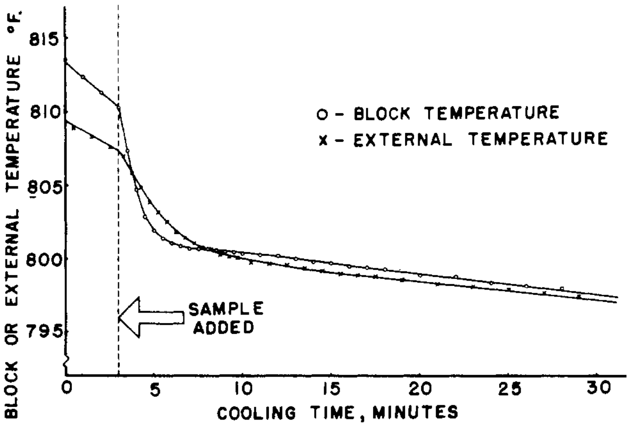


Figure 3. Observed data for a calibration test

Most points on the curves in Figure 5 are the average of two or more determinations. The variability of individual values from the mean was generally less than 2% for the heat-stable materials, but rose as high as 5% in one instance for the coal sample in the middle of the plastic temperature range. The agreement between the observed and literature values for magnesium oxide adds confidence in the method.

For comparison with data found in the literature, two other curves are shown in Figure 5. One represents the values that would be predicted by applying the equation derived by Clendenin and others (*3*); the other curve is from data by Porter and Taylor (*9*), these data being the highest temperature values included in the correlation of Clendenin. No comparable data are available for char.

The data obtained here by use of a high temperature calorimeter apply to the particular case in which the sample is heated very rapidly and the products of carbonization are carried out of the system. This corresponds to the pattern in fluidized low temperature carbonization of coal, the application for which these data were originally determined, but may differ substantially from the heating regime in some other processes. Reaction effects, particularly from extensive secondary reaction of the tar products, may cause some variance in the practical mean specific heat capacity under other treatment conditions.

THERMAL CONDUCTIVITY MEASUREMENTS

Method. Absolute thermal conductivities of a material are best determined by direct measurement of the temperature gradient which exists for a known rate of heat transfer across a unit area of material under steady-state conditions. From the Fourier heat transfer equation, the thermal conductivity can be calculated directly. The thermal conductometer, modeled after one described by Birch and Clark (*1*), allowed these needed factors to be measured for compactions made of char, coal, and pitch.

The location of the lead-in wires was omitted from the cross-sectional view of the conductometer (Figure 6). The apparatus

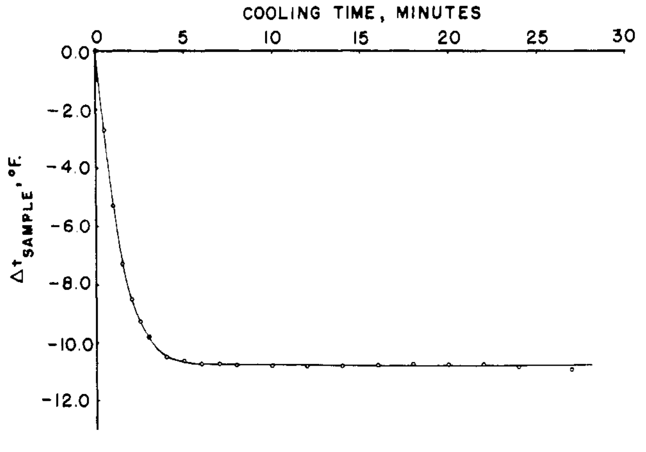


Figure 4. Total corrected effect of alumina in a calibration test

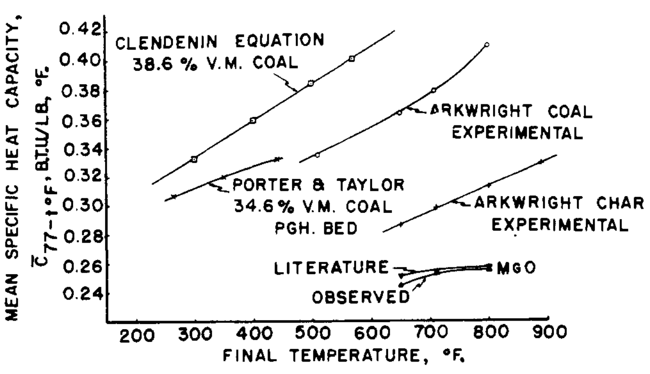


Figure 5. Mean specific heat capacities of coal and char

was symmetrically square about the vertical axis. The specimen was a flat slab approximately 2 inches square and 1/2 inch thick, cut from a single large briquet, or formed of close fitting rectangular sections from small briquets. It was placed between the heater block and cooling plate, both of which are made of copper to assure an even temperature distribution. A 30-gage Nichrome wire heating element in the heater block held its temperature about 10° C. above that of the cooling plate when a steady state was reached. This temperature difference across the specimen was measured with thermocouples placed at positions indicated by the heavy dots. Provided that there is no heat transfer from the heater block other than through the specimen, the conductivity is simply calculated. The condition of no extraneous heat loss from the block was approached as closely as possible by using a thermal guard dome of copper which covered the heater block as shown. The guard dome contained a heating element by which the dome's temperature was adjusted to equal the temperature of the heater block. Heat losses to the surroundings then came from the guard dome and not from the heater block. Lateral heat losses from the specimen were minimized by the guard ring of insulating material (Transite) that surrounds the specimen. Small ceramic spacers prevented accidental metal-to-metal contact between the dome and heater block.

The entire conductometer was enclosed in a steel box which was purged with nitrogen to prevent oxidation of the copper or the specimen at high temperatures. The entire unit was immersed in a fluidized sand bath to control the elevated ambient temperatures.

Stable power for the heater block was provided by two 6-volt storage batteries in series. The current was manually controlled with rheostats to give the desired temperature differential across the specimen. With currents of 100 to 200 ma. in the block heater, there was no discernible drift in the current during the course of a measurement. The less critical power for the guard dome was provided by a Variac with a rheostat for fine control. A Type K Leeds and Northrup potentiometer was used for accurate measurement of the thermocouple potentials and the voltage and current of the heater block. Voltage measurements across a standard 1-ohm resistor in the heater circuit gave direct measurements to the heater current.

Results. Thermal conductivities were determined for sections of briquets made from coal, char, and pitch. The composition was 25% coal (Pittsburgh seam from Montour mine in western Pennsylvania), 63.5% low temperature char produced from this coal by fluidized carbonization at 950° F., and 11.5% pitch. These briquets were precoked at several temperature levels; their conductivity was measured at that temperature and then at lower temperatures. This procedure separately demonstrates both the effect of coking on conductivity at a particular temperature and the temperature dependence of conductivity of specifically coked briquets. These data are plotted in Figure 7.

Trustworthy results could not be obtained at temperatures above 1600° F. on the fully coked briquets because fluidized sand furnace temperature was not adequately controlled. However, the values at other temperatures on this fully coked material allow a reasonable extrapolation of the curve to 1800° F.

Figure 8 shows a comparative plot of the present data with those presented by Millard (*8*) for coal. Millard made no attempt to explain the difference in the conductivities of the two coals, which came from different mines. There is no radical difference in the briquet conductivity as compared to the coals (Figure 8). Both materials show a very large increase in conductivity with temperature and a marked increase with degree of coking.

Estimation of Surface Film Coefficient for Heating with Fluidized Solids. Applying the thermal parameters very often requires the estimation of a surface film heat transfer coefficient pertinent to the thermal system to be used. One of the thermal arrangements of interest for the carbonization of briquets is the heating with circulating, hot fluidized solids. To bring order and predictability to some of the results, and to check further the validity of assumed values of the heat transfer film coefficient used in machine calculations made on this type system (*17*), an experimental method for the estimation of the film coefficient was tested. This experimental method is simple, especially under the special conditions in which it has been applied. The results represent only a cursory examination of the transfer coefficient, but the method deserves description.

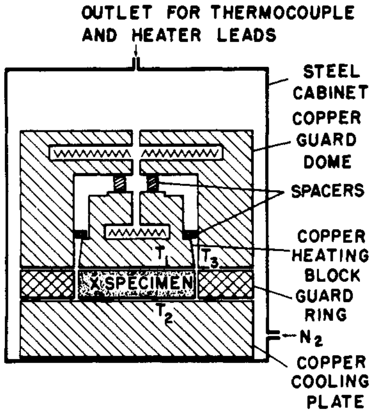


Figure 6. Thermal conductometer

The temperature rise of spherical objects was observed after immersion in a constant temperature, fluidized sand bath. Although, generally speaking, the unsteady-state system lacks precision, these measurements are rapid and may be made in a very simple system, much simpler than would be needed for steady-state measurements.

Mathematical expressions for this system showed that to relate these results to the film coefficient only materials and temperature ranges for which the thermal diffusivity may be treated as a constant could be considered. In these cases, the Fourier equation can be solved analytically. A solution which has been published may then be applied to this problem (*7, 10*). This solution reduced further to a very simple form for the case of objects with a high thermal conductivity such as aluminum or copper ($Nu << 1$).

Under these specific conditions the temperatures of the center and surface, respectively, of a sphere of radius r_0 at initial temperature T_1 which is suddenly surrounded by a medium at a constant temperature T_0 are given by the equations

$$Y_{r=0} \equiv \left(\frac{T_0 - T}{T_0 - T_1}\right)_{r=0} = e^{-3Nu\theta}$$

$$Y_{r=r_0} \equiv \left(\frac{T_0 - T}{T_0 - T_1}\right)_{r=r_0} = \sqrt{3Nu}\, e^{-3Nu\theta}$$

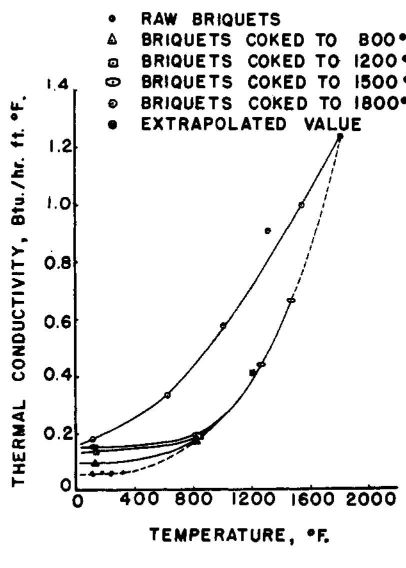


Figure 7. Thermal conductivity of char-coal-pitch briquets

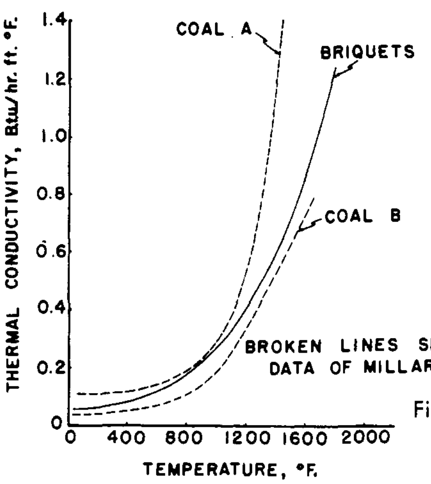


Figure 8. Comparative conductivities of coal and char-coal-pitch briquets

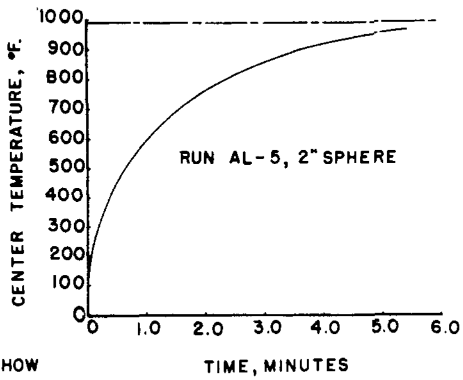


Figure 9. Center temperature of aluminum sphere heated by fluidized sand bed

The Nusselt number, Nu, is defined as

$$Nu = \frac{hr_0}{k}$$

and θ is a dimensionless time $= \dfrac{\alpha\, t}{r_0^2}$ or $\dfrac{kt}{\rho c_p r_0^2}$

The Nusselt number can be determined by plotting experimental values of ln Y versus θ. A straight line whose slope is $-3Nu$ should be obtained for both the center and surface temperatures.

Experimentally, all measurements were made by plunging an aluminum sphere into a fluidized sand bath 8 inches in diameter. The sand bath temperature was maintained constant in the range of 950° to 1000° F. because this corresponds to the process temperature required in practice for initial shock heating of the briquets to manufacture formcoke. An aluminum sphere was chosen so that the simplified form of the Fourier solution equation could be applied—i.e., the thermal conductivity of aluminum is high and almost exactly independent of temperature, and the thermal diffusivity is relatively constant. The nature of the sphere's surface was assumed unimportant to the result, so that calculated values of h would be applicable to carbonaceous briquets.

Two thermocouples were used to sense the temperatures in the sphere, one attached to the surface and one placed in a small hole bored to the specimen center. Small-diameter thermocouple wire (28 gage) was used to minimize error caused by heat conduction down the wire. A third thermocouple in the fluidized sand bath was used to sense and control its temperature. All three temperatures were recorded on a multipoint strip chart recorder. All the tests used a nominal fluidized sand temperature of 1000° F.

Five tests were run using a 2-inch sphere. Four of these tests were made using a fluidization velocity (superficial) of 0.6 to 0.7 foot per second; one test used a reduced linear velocity of 0.34 foot per second. Single tests were made with a 1- and a 3-inch sphere. Figure 9 is a typical plot of the temperature history recorded by the thermocouple placed at the center of the sphere.

A plot of the temperature approach data used for the estimation of some of the film coefficients, h, is shown in Figure 10. Straight lines are obtained as predicted by the special solution for the basic Fourier equation. Similar results may be obtained when the surface temperature is treated similarly, but the surface temperature is more difficult to measure with precision.

The lines in Figure 10 do not show the unit value of y-intercept as predicted by theory. Part of the cause of this discrepancy is thought to be a thermocouple error caused by conduction of heat down the thermocouple wire, thus producing high temperature readings. The total heat conducted down the wire is a negligibly small fraction of that conducted through the aluminum. If the thermocouple error is proportional to the temperature difference between the surroundings and the center of the sphere (a logical assumption), then only the intercept of the Fourier solution equation is shifted, and its slope is unaffected.

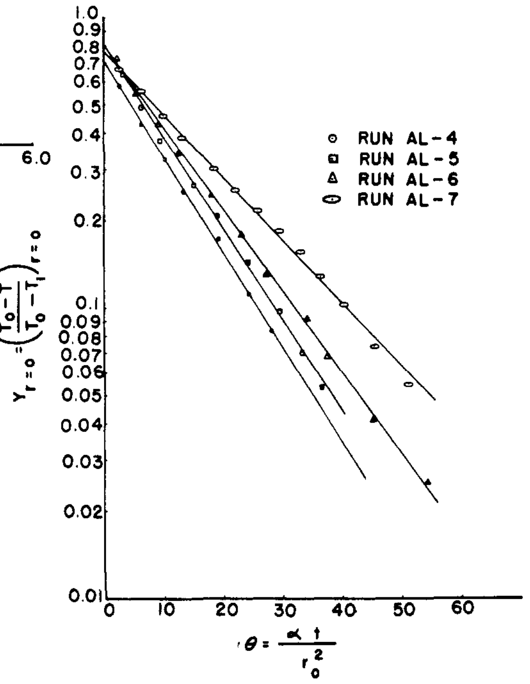


Figure 10. Temperature approach plot for determination of the film coefficient fluidized bed

The calculated values of the film coefficient, h, are listed in Table I. The precision of the replicate tests on the 2-inch sphere is not the best, but the results are consistent and reasonable. The test made at a reduced fluidizing velocity shows a somewhat lower value for h, which is also reasonable.

The values might be expected to lie in the upper range of values reported because of the high density of the fluidized sand; on the other hand, the fluidization velocities used were rather low, especially for a dense solid, and this factor would lower the value of h. The average value of h is about 30 B.t.u./hr. sq. ft. °F., thus well within the range of 20 to 50 B.t.u./hr. sq. ft. °F. chosen for the calculations of heating rates of carbonaceous briquets in fluidized solids systems.

Table I. Experimental Values of Heat Transfer Coefficient between Fluidized Sand and Aluminum Spheres

Thermal parameters for calculations. k = 117 B.t.u./hr. ft. °F.
a = 3.33 sq. ft./hr.

Run No.	Sphere Diameter, In.	Fluidization Velocity, Ft./Sec.	Fluidized Sand Temp., °F.	Calcd. Heat Transfer Coefficient, h, B.t.u./hr.sq.ft.°F.
Al-1	3	0.72	950	38
Al-2	2	0.72	1000	31
Al-3	1	0.72	1050	27
Al-4	2	0.61	985	36
Al-5	2	0.61	990	34
Al-6	2	0.34	980	23
Al-7	2	0.61	950	30

SUMMARY

These thermal data are not entirely comparable in terms of materials and temperature ranges. However, they all bear directly on the problem of heat transfer to carbonaceous briquets containing coal, char, and pitch. The heat capacity data measured for coal and char may be combined with values in the literature for pitch to provide composite values applicable to briquets. The thermal conductivity data were obtained directly on briquet samples. There is no apparent reason why the heat transfer film coefficient, *h*, cannot be applied directly to the heating of carbonaceous shapes of low conductivity.

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Isomerization Equilibria

The C_2H_6S, C_3H_8S, and $C_4H_{10}S$ Alkane Thiols and Sulfides and the Methylthiophenes

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Chemical thermodynamic studies of complete groups of isomeric sulfur compounds are included in the program of American Petroleum Institute Research Project 48A in this laboratory. For four groups of compounds, the C_2H_6S, C_3H_8S, and $C_4H_{10}S$ alkane thiols and sulfides and the methylthiophenes, values of free energy of formation for all isomers have been obtained over the temperature range of practical interest. These values have been calculated by statistical thermodynamic methods from spectral and molecular structure data and are based on experimental determinations of the heat capacity, entropy, and heat of formation.

Values of the standard free energy of isomerization and the corresponding equilibrium concentrations are reported here. To illustrate the utility of the results, the isomerization equilibria are discussed in relation to the concentration of sulfur compounds in petroleum. Possible application in future speculation about the origin of petroleum is suggested. Revisions and extensions of previously published tables of chemical thermodynamic properties are included when necessary.

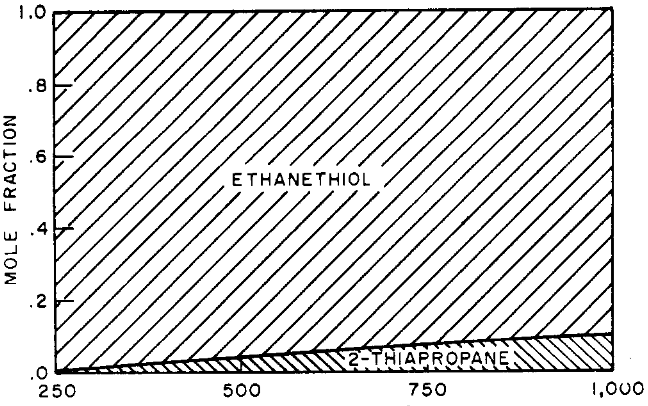


Figure 1. Equilibrium concentrations of C_2H_6S alkane thiols and sulfides

The individual isomers under consideration are:

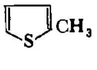
C_2H_6S Compound	
Ethanethiol	CH_3CH_2SH
2-Thiapropane	CH_3SCH_2

C_3H_8S Compounds	
1-Propanethiol	$CH_3CH_2CH_2SH$
2-Propane thiol	$CH_3CH(SH)CH_3$
2-Thiabutane	$CH_3CH_2SCH_3$

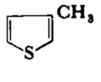
$C_4H_{10}S$ Compounds	
1-Butanethiol	$CH_3CH_2CH_2CH_2SH$
2-Butanethiol	$CH_3CH_2CH(SH)CH_3$
2-Methyl-1-propanethiol	$CH_3CH(CH_3)CH_2SH$
2-Methyl-2-propanethiol	$CH_3C(CH_3)_2SH$
2-Thiapentane	$CH_3CH_2CH_2SCH_3$
3-Thiapentane	$CH_3CH_2SCH_2CH_3$
3-Methyl-2-thiabutane	$CH_3CH(CH_3)SCH_3$

Methylthiophenes

2-Methylthiophene



3-Methylthiophene



RESULTS

The values of $\Delta Fi°$, the standard change of free energy for the isomerization reaction,

Reference compound (gas) = isomeric compound (gas)

and N*i*, the mole fraction of the given isomer when at equilibrium with all of its other isomers in the gas phase, are listed