

The Thermodynamics of Coal Chars;
Correlation of Free Energy of Formation with Reactivity

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INTRODUCTION

A large number of existing and proposed coal conversion technologies yield a char as a by-product or as a process intermediate. These technologies may be classified into the following categories:

1. Coal carbonization procedures, yielding a char by-product.
2. Steam or steam-oxygen gasification. Char is either a gasification intermediate or a by-product.
3. Coal gasification with hydrogen or hydrogen rich gas. The char intermediate is gasified with steam and oxygen or further gasified with hydrogen.
4. Supercritical gas extraction. A char by-product might either be gasified or used as fuel.

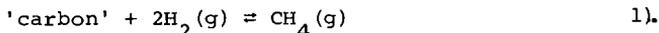
For the proper design of a given process and for the comparison of competing processes, both in the technical and economic sense, an understanding of the gasification reactivity (kinetics) and thermochemistry of the chars is essential.

Broadly speaking, the chemical reactivity of a char (in reference to gasification with steam or carbon dioxide, or hydrogen, or in combustion with oxygen) is its most important property in relation to its subsequent utilization. A traditional test for the measurement of the reactivity of a char is the rate of reaction of the char with carbon dioxide (1). The gasification process can be divided into two distinct stages (2); the first stage due to pyrolysis and the second stage due to the char-gas reaction. The pyrolysis reactivity can be related to volatile matter content of the solid, to the rate of heating and to the pyrolysis temperature. The reactivity of the char in the gasification stage seems to depend on the source of char (nature of the original coal) and the thermal history (heat treatment) of the char (3).

In spite of the efforts of many researchers, kineticists are far from able to make a priori prediction of reaction rates for the gasification of a given coal or char in various devices (processes). Consider the steam gasification process. The situation is highlighted by the fact that an oven coke - resembling blast furnace coke and having intrinsically a low chemical reactivity - gasifies poorly in a steam-oxygen blown gravitating bed gasifier, yet gasifies in a steam fluidized bed with much the same reactivity as an intrinsically reactive char made at low temperatures (4).

In an attempt to correlate the gasification data from steam fluidized beds, Squires (4) proposed that the data be explained by thermodynamic equilibrium considerations. The chemical reaction of

relevance is:



Squires hypothesized that the methane in the effluent stream from a steam fluidized bed stands in a quasi-equilibrium relationship to the hydrogen and carbon material present in the bed. He demonstrated that the calculated "equilibrium" constants for various processes and solid feeds correlated with temperature in the usual manner if the thermal history of the 'carbon' was taken into account. The data for fluidized beds with continuous feed of raw (or lightly pretreated) coals fell on a line indicating higher yields of methane at a given temperature than the data for chars and anthracite coals that had been kept for some time at elevated temperature under nitrogen atmosphere before they were fed to a steam fluidized bed. However, in all cases the methane yields obtained were substantially higher than one would have calculated from thermodynamic equilibrium assuming that the 'carbon' in the feed was graphite. The implications of this observation and hypothesis are that (a) the chars have an excess free energy of formation relative to graphite and (b) the amount of excess energy is a function of the thermal history of the char. Thus, one should be able to correlate the reactivity of a char with its thermodynamic properties. This conjecture is not made to place thermochemical data in competition with structural and kinetic information that has been developed. Indeed, all the information should be regarded as complementary.

To test Squires' hypothesis we may calculate the equilibrium constant, K , for the reaction given by Equation 1 using data for a selected 'carbon', at a given temperature and compare it to the equilibrium constant for the same reaction, at the same conditions, whereas for 'carbon' graphite is assumed to be used. From the standard thermodynamic relationship, the ratio of the equilibrium constants $K^{\text{ch}}/K^{\text{gr}}$ is related to the free energy changes, ΔG , for the reactions by:

$$\ln \frac{K^{\text{ch}}}{K^{\text{gr}}} = \frac{1}{RT} (\Delta G^{\text{gr}} - \Delta G^{\text{ch}}) \quad 2).$$

The symbols have their usual meaning. The superscripts ch and gr indicate that 'carbon' is in the form of char or graphite in the reaction considered (Eq. 1). It is obvious that in the present case

$$\Delta G^{\text{gr}} - \Delta G^{\text{ch}} = G_f^{\text{ch}} - G_f^{\text{gr}} \quad 3).$$

where G_f is the free energy of formation of the species at the reaction temperature. Thus, a test of the hypothesis reduces to the estimation of the free energy of formation of a char relative to that of graphite at a reaction temperature, and comparing the calculated ratio of equilibrium constants to that found experimentally.

The free energy of formation of a substance at a given temperature is usually calculated from the standard heat of formation, the absolute entropy of formation and heat capacity of the substance as a function of temperature. The heat of formation can be calculated

from a measured heat of combustion. Before we proceed to an actual calculation of the free energy formation of a char relative to graphite, a short review of the relevant available data is undertaken.

Standard Heat of Combustion of Chars and Graphite

The API Project 44's value for the heat of combustion of graphite is 7831 calories/gram. Dolch and Rank (5) inferred heats of combustion of chars, prepared from lignite, steam activated charcoal, cellulose and coke from peat as ranging from 8135 to 8277 cal/gram of fixed carbon. The hydrogen content of these materials ranged from 0.5 to 0.8% and carbon contents were above 96.7%. Recently, the heats of combustion of two well characterized chars have been measured (6). These chars were produced in experimental runs on a synthane process test unit and one corresponded to a char heat treated at 400°C and the other to a char heat treated at 900°C. They were produced from an Illinois No. 6 coal feed. The heat of combustion of the 400°C char is 8540 cal/gram carbon and of the 900°C char 8322 cal/gram carbon. The hydrogen-to-carbon ratios as determined from elemental analysis were: 0.73 for the 400°C and 0.20 for the 900°C. Thus the difference in the heats of combustion of chars and graphite ranges from 300 to 700 cal/gram of carbon. The larger heat of combustion of the chars relative to graphite reflects both the energy associated with the residual hydrogen in the chars and the excess heat of formation of the chars. Bronowski (7) reported measurements on the carbonization of bituminous coals. The carbonization process is exothermic and the heat involved is of the order of 500 cal/gram. This is of the same order of magnitude as the excess heat content of the chars as measured by the relative difference between the heats of combustion of chars and graphite on a fixed carbon basis. Thus, in subsequent calculations, the standard heat of formation of a char relative to graphite will be estimated as the difference between the respective heats of combustion on a per gram atom of carbon basis.

The Heat Capacity of Chars and Graphite

The heat capacity of graphite has been measured by numerous investigators. The data available covers the entire temperature range of interest and has been reviewed by Kelly and Taylor (8). It has been noted by many of the investigators that the heat capacity of graphite is dependent on the state of the structural perfection of the graphite specimen. Natural crystalline graphites have the lowest heat capacities at any given temperature. Synthetic graphites prepared by carbonization procedures have excess heat capacities. The amount of excess is mainly a function of the carbonization temperature. Attempts to eliminate the excess heat capacity of the synthetic graphites by heat treatments above 3000°C were unsuccessful. Thus, one should expect that the heat capacity of chars will be in excess of that of graphite.

Heat capacity data on coal chars are extremely scarce. An extensive literature search yielded only three sets of data relevant to the task at hand. The Bartlettville and Albany Laboratories (6) of ERDA measured the heat capacities of the same two synthane process chars for which they measured the heats of combustion. However,

the heat capacities were only measured above 300K. Data in the 50K to 300K region were reported by Kasatochkin, et al., (9) for chars prepared from a fossil carbon, Schungite, and from anthracite coals. These chars were prepared by "heat treatments" (pyrolysis) ranging from 600°C to 2800°C. The third set of data is from the Carbon Research Laboratories, SUNY, Buffalo (10) on chars prepared from resin C pitch by heat treatments ranging from 600°C up. The temperature range for heat capacity measurements was from 1K to 5K.

Some important generalizations can be deduced from the analysis of the above three data sets. First of all, as expected, the chars have an excess heat capacity relative to graphite at all experimental temperatures. The excess heat capacity of the chars is related to the heat treatment temperature. The lower the heat treatment temperatures for a given char the greater is its excess heat capacity relative to graphite.

One may quantify the relation between char heat capacity and heat treatment temperature by noting that the data on the resin-C chars and on Schungite chars can be expressed as:

$$c^{ch}(T) = C_0(T) \exp(a(T)/T_{HT}) \quad 4).$$

Here $c^{ch}(T)$ is the heat capacity of the char at a given temperature (°K) per gram atom of carbon contained in the char, and $C_0(T)$, $a(T)$ are constants and T_{HT} is the heat treatment temperature (°K). We found that this relationship is useful for fitting heat capacity data on all chars as a function of arbitrary heat treatment temperature.

The magnitude of the excess heat capacity is not a function of heat treatment temperature alone. The 900°C synthane process char has more excess heat capacity than the 600°C Schungite char. This difference may be simply due to the structural differences in the coals from which the chars were made. Alternately, it is possible that this difference in excess heat capacities is related to the residual hydrogen content and ash content of the chars. These conjectures should be subjected to experimental verification.

In Table 1 the heat capacity of the 900°C synthane process char is compared to that of graphite as a function of temperature. Entries into this table were obtained as follows: The heat capacity of graphite was taken from literature (11). The heat capacity of the char above 300K is calculated from the Barlettville data (6) directly. Below 300K entries for the char were calculated using the following procedure. We assume that below 300K the synthane char heat capacity has the same kind of functional dependence on temperature as the experimentally determined heat capacities for Schungite (9) and resin-C pitch chars (10). Therefore, if we have the heat capacity of one char as a function of temperature, the values for another may be calculated by assuming that the fractional change in heat capacity between two temperatures is the same. That is, we use a relation of the following form to calculate the heat capacity of the synthane char at a temperature T_2 .

$$\frac{\text{Synthane } C(T_2) - \text{Synthane } C(T_1)}{\text{Synthane } C(T_1)} = \frac{\text{Ref } C(T_2) - \text{Ref } C(T_1)}{\text{Ref } C(T_1)}$$

where C^{Ref} is a reference char of known heat capacity at temperatures T_1 and T_2 , and the C^{Synthane} is known (or has been calculated) at temperature T_1 . For reference char, a char of the same thermal history, i.e., heat treatment temperature is selected. Thus the C^{Ref} versus temperature curve between 50K and 300K was established using Equation 4 to calculate the heat capacities of a Schungite char, hypothetically heat treated at 900°C. The same procedure was used between 1K and 5K using for reference a hypothetical resin-C pitch char.

The reference heat capacity curve was completed between 5K and 50K by smoothly joining the two calculated curves. The accuracy of calculated heat capacities for the Synthane process char is probably of the order of 5 percent.

The Absolute Entropy of Formation of Chars and Graphite

The entropy of formation of carbon in the form of graphite is 1.35 (cal/gram atom-°K) at standard conditions. The entropy of formation of coals at standard conditions have been estimated as 4 to 12 (cal/mole-°K) with the preferred value around 5 (12). Chars are expected to have lower entropies of formation than coals. Since chars are not fully crystalline, structurally ordered materials, they do not follow the third law of thermodynamics. A residual entropy due to structural disorder must be added to the thermal entropy calculable from heat capacity data, in order to have a value of the absolute entropy of formation at a given temperature. Using the data given in Table 1, the standard entropy of formation, S_f^{Std} , for the 900°C synthane process char was calculated as $S_f^{\text{Std}} = S_0 + 2.49$ (cal/gram-atom carbon-°K). Here S_0 is the residual entropy of the char.

The residual entropy for the char could be estimated experimentally. For example, it could be done from the accurate determination of the equilibrium constant for a reaction involving the char. However, due to the lack of data we will arbitrarily assume that S_0 for this char equals one cal/(gram-atom carbon-°K). We feel that this number is of the right order of magnitude.

Test of Squires' Hypothesis

The thermodynamic data assembled in the preceding sections on the 900°C synthane process char are sufficient to test Squires' hypothesis. We expect that the numbers we will get will only be correct to an order of magnitude due to the assumptions we make with regard to the residual entropy of the char, the low temperature heat capacities and heat of formation. The calculation is done considering that the gasification reaction as given by Equation 1 is carried out at 1200K.

As we have indicated, first we must calculate the Gibbs free energy of formation of the char relative to that of graphite at the selected temperature. Then we use Equation 2 to calculate the ratio of the equilibrium constants. The relative free energy of formation at temperature τ may be written in the usual form:

$$G_f^{\text{ch}} - G_f^{\text{gr}} = (H_f - \tau S_f)^{\text{ch}} - (H_f - \tau S_f)^{\text{gr}} = H_f^{\text{ch}} - H_f^{\text{gr}} - \tau (S_f^{\text{ch}} - S_f^{\text{gr}}) \quad 6).$$

Here, all the symbols have their usual meaning, and the superscripts have been defined. All quantities must be evaluated at the reaction temperature τ .

The relative heat of formation at the reaction temperature is given by the expression:

$$H_f^{\text{ch}} - H_f^{\text{gr}} = \Delta H_f^* + \int_{\tau^*}^{\tau} [C^{\text{ch}}(T) - C^{\text{gr}}(T)] dT \quad 7).$$

where τ^* is the standard temperature, and ΔH_f^* equals the difference in the standard heats of formation of the char and graphite. Experimentally determined heats of combustion data can be converted to yield heats of formation. In this case this is not done but ΔH_f^* is estimated as the difference between the measured standard heats of combustion of the char and the graphite. Justification of this procedure has been made in a prior section of this paper. For the 900°C synthane process char ΔH_f^* equals 5.9Kcal/gr atom carbon.

The integral in Equation 7. is evaluated graphically. Data in Table 1 are used to prepare a smooth graph of the heat capacity difference between the char and graphite as a function of temperature. The numerical value of 1.7Kcal/gr atom carbon is obtained by graphical integration for the increase in the relative heat of formation between the standard temperature and the assumed reaction temperature of 1200K. Therefore, $H_f^{\text{ch}} - H_f^{\text{gr}}$ equals 7.6Kcal/gram-atom carbon at 1200K.

The relative entropy of formation can be written as:

$$S_f^{\text{ch}} - S_f^{\text{gr}} = S_0 + \int_0^{\tau} \left[\frac{C^{\text{ch}}(T) - C^{\text{gr}}(T)}{T} \right] dT \quad 8).$$

For S_0 the value of 1 cal/gr-atom carbon-°K is assumed since all the residual entropy is associated with the char. The integral in Equation 8 is again evaluated graphically from a smooth graph of the ratio of the heat capacity difference to the temperature versus temperature. The value of this integral between the indicated limits is 3.82 (cal/gram atom carbon-°K). Thus the relative entropy of formation at 1200K is 4.82 (cal/gram atom carbon-°K).

Substituting the numerical values into Equation 6 we obtain 1.8Kcal/gr atom carbon for the relative Gibbs free energy of formation, $G_f^{\text{ch}} - G_f^{\text{gr}}$, at 1200K. The ratio of the equilibrium constants $K^{\text{ch}}/K^{\text{gr}}$ is calculated with use of Equation 2 and is found to be 2.14 at 1200K. From the experimental data compiled by Squires

(4) for the gasification of pretreated chars in steam fluidized beds the value of 3.5 at 1200K is estimated for K^{ch}/K^{gr} . Considering all the assumptions involved in this calculation the agreement between experimental data and calculation is significant. While this calculation does not provide a clearcut proof of Squires' hypothesis, it does strongly support it.

Conclusions

From the available experimental data one may conclude that coal chars have larger heat capacities and heats of combustion than graphite when these quantities are compared on equivalent amount of carbon content basis. The magnitude of the thermodynamic quantities depends both on the thermal history of the char and on the source of the char. The magnitude of the excess quantities relative to graphite varies with the pyrolysis temperature of the char in an inverse fashion. In case of the heat capacity function a relationship was found (Equation 4) which enables one to estimate the heat capacities of a given char at some assumed pyrolysis (heat treatment) temperature. Chars obtained from a bituminous coal have larger excess heat capacities than chars originating from anthracite coals or fossil carbons. One may speculate that this difference could be related to the amount of residual hydrogen contained in a given char.

Since chars are not fully crystalline ordered solids, they must have some residual entropy of formation. There is no experimental data which allow one to estimate the magnitude of the residual entropy. A value for the residual entropy must be assumed. If one makes the reasonable assumption of one (1) (cal/gram atom carbon-°K) for the value of the residual entropy, then the calculated value of the Gibbs free energy of formation of chars is positive relative to that of graphite. Hence, one concludes that chars should be chemically more reactive than graphite. This conclusion of course is consistent with other experimental data on char reactivity.

In order of magnitude agreement between the numerical values of the equilibrium ratio K^{ch}/K^{gr} as calculated and as inferred from experimental data, tends to support Squires' hypothesis that the observed gasification yield in a steam fluidized bed process depends on equilibrium considerations. For a more quantitative test of the hypothesis more thermodynamic data than presently available are needed.

The available data show the importance of the pyrolysis temperature as a major factor in the thermal history, and consequently in the thermodynamics of the coal chars. However, the thermal history of a char should also depend on the rate of temperature rise to the pyrolysis temperature and on the length of time the char is kept at the pyrolysis temperature (soak time). The effect of these factors on the thermodynamics of the chars should be investigated. For example, one would expect that longer soaking times will reduce the residual entropy.

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Table 1

The Heat Capacities of a 900°C Synthane Process Char and of Graphite

Temperature (°K)	c^{char} (cal/gr-atom carbon-°K)	c^{graphite} (cal/gram atom carbon-°K)
1	0.23×10^{-3}	0.02×10^{-3}
3	1.1×10^{-3}	0.21×10^{-3}
5	4.1×10^{-3}	$.67 \times 10^{-3}$
10	1.4×10^{-2}	3.0×10^{-3}
15	3.2×10^{-2}	1.0×10^{-2}
20	5.4×10^{-2}	1.8×10^{-2}
25	7.7×10^{-2}	2.6×10^{-2}
30	0.103	4.6×10^{-2}
40	0.172	8.3×10^{-2}
50	0.25	0.122
75	0.48	0.253
100	0.73	0.401
125	1.01	0.557
150	1.33	0.730
175	1.65	0.912
200	2.02	1.101
225	2.39	1.291
250	2.73	1.486
275	3.11	1.684
300	3.43	1.96
350	4.03	2.46
400	4.52	2.90
450	4.95	3.24
500	5.33	3.55
600	5.96	4.07
700	6.49	4.49
800	6.90	4.82
900	7.27	5.07
1000	7.57	5.26
1100	7.83	5.41
1200	8.08	5.54