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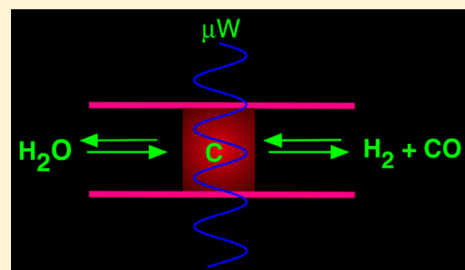
Microwave-Specific Effects on the Equilibrium Constants and Thermodynamics of the Steam–Carbon and Related Reactions

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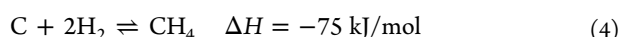
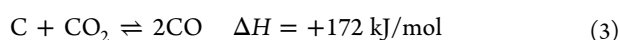
S Supporting Information

ABSTRACT: The steam–carbon reaction, which is the essential reaction of the gasification processes of carbon-based feed stocks (e.g., coal and biomass), produces synthesis gas ($\text{H}_2 + \text{CO}$), a synthetically flexible, environmentally benign energy source. The reaction is very endothermic, which mandates high temperatures and a large expenditure of energy to drive the reaction. We have found that using microwave irradiation to selectively heat the carbon leads to dramatically different observed thermodynamics for the reaction. From measurement of the equilibrium constants as a function of temperature, the enthalpy of the reaction under microwave radiation was found to become significantly more exothermic, dropping from 144.2 kJ/mol at the median reaction temperature of 880 K to 15.2 kJ/mol under microwave irradiation. The reaction conditions under which the steam–carbon reaction was run, and under which the equilibrium measurements were determined, consisted of three other reactions that came to equilibrium. These reactions were the Boudouard reaction, which is the reaction of CO_2 with carbon to form CO ; the water–gas shift reaction, where CO and water react to form H_2 and CO_2 ; and the carbon–hydrogen reaction, which generates methane from the reaction of H_2 with carbon. We determined the equilibrium constants and thermodynamic parameters for all of these reactions. The Boudouard reaction, which is also strongly endothermic, was found to be more exothermic under microwave radiation (180.2 kJ/mol (thermal) and 27.0 kJ/mol (MW)). The water–gas shift reaction became more endothermic (−36.0 kJ/mol (thermal) and −11.4 kJ/mol (MW)). The carbon–hydrogen reaction also underwent an endothermic shift, from −79.7 to −9.1 kJ/mol. From the associated equilibrium expressions and the equilibrium constants for the steam–carbon reaction system, the mole fractions of the system components under thermal and microwave conditions were estimated. The effect of the microwave radiation was to change the position of the equilibrium so that the temperature at which H_2 was at a maximum dropped from 643 °C in the conventional thermal reaction to 213 °C in the microwave. Notwithstanding the predicted temperature shift, there was an observable threshold below which microwaves could not produce products. In our system, the minimum energy at which H_2 appeared was 373 °C (30 W), while the temperature at which equilibrium could be established in a reasonable period of time (100 min) was 491 °C (100 W).



INTRODUCTION

The reaction between superheated steam and carbon to produce synthesis gas (reaction 1) is part of the general category of gasification reactions used to obtain hydrogen from coal and other carbon-rich sources.^{1,2} Gasification reactions typically occur at temperatures ≥ 700 °C depending on the carbon source, while industrial processes, such as coal gasification, run at much higher temperatures (>1000 °C). These high temperatures are required to drive the endothermic components of the primary reactions and to obtain useful reaction velocities.²



Along with production of synthesis gas (reaction 1), the reactions between carbon and high-temperature steam consist

of a complex set of equilibria, which produce not only hydrogen and carbon monoxide but also carbon dioxide through the water–gas shift (WGS) reaction (reaction 2), carbon monoxide through the disproportionation of carbon and carbon dioxide (Boudouard reaction 3), and methane through the reaction of carbon and hydrogen (reaction 4). The complexity of the equilibria, along with the primary steam–carbon reaction (reaction 1) being very endothermic, means that the composition of the gases produced in gasification will depend critically on the temperature and pressure of the reaction.

Because of the industrial importance of these reactions in the production of hydrogen for direct use as a clean alternative fuel or for the production of hydrocarbons through the Fischer–Tropsch process, the development of less energy-intensive methods for driving these reactions is desirable.^{3,4} Recently, we have shown that for the carbon–carbon dioxide (Boudouard)

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reaction (reaction 3), the use of microwave radiation to heat the carbon results in a dramatic change in the observed thermodynamics of the reaction.⁵ These thermodynamic changes result in an increase in the equilibrium constant so that carbon monoxide becomes the favored product at 213 °C, as compared to 643 °C when using conventional convective heating. This is a rather profound effect that potentially allows the remediation of CO₂ to be carried out using the Boudouard reaction at temperatures well below what is possible using conventional heating. Given the importance of the general class of gas–carbon reactions in the overall scenario of energy production, it is useful to determine whether the thermodynamic benefits that microwave heating imparts to the Boudouard reaction are general for the other processes, in particular, the endothermic steam–carbon reaction. We report here a study of the effect of microwave radiation on the observed thermodynamics of the steam–carbon reaction and the other equilibria that take place during the gasification process.

EXPERIMENTAL SECTION

Materials. Graphite (Fisher, grade #38) was the carbon source, and it was used as received. Complete characterization of this material is given in section I of the Supporting Information.

Methods. Reactions were carried out in a commercial CEM Discover microwave reactor in open vessel configuration. The apparatus used for acquiring static measurements was described previously and is also given in the Supporting Information (section IIa). For the equilibrium experiments, the reaction cell was charged with 1 g of graphite powder. The sealed vessel was evacuated to <1 mbar and then charged with approximately 450 mbar (35 mL) of N₂ (g). The sample was irradiated for 10 min at 200 W of microwave power and then evacuated. This cleaning procedure was repeated twice more for a total of three cleaning cycles to remove any adsorbed water or surface oxide species from the graphite. After the final cleaning cycle, the cell was evacuated and brought to room temperature before slowly being vented to atmospheric pressure using N₂.

While the sample cooled, the deionized (DI) water was added to the static cell using the following technique. Using a micropipet, 30 μ L of DI water was pipetted into a small Dewar flask (Lab-line Thermo-Flask) filled with LN₂. The droplet was frozen and weighed for accuracy of the water addition, 29 mg (1.6 mmol). The static cell was placed in the LN₂ bath and the sphere of ice was placed into the cell, all the while being kept at LN₂ temperatures. The cell was quickly reattached to the apparatus and evacuated to <1 mB while submerged in the LN₂ bath. Once evacuated, the cell was allowed to warm to room temperature, giving an initial pressure reading of \sim 30 mbar.

With the apparatus at room temperature and initial pressure, the cell was irradiated at 200 W to initiate the equilibrium. During irradiation, the cavity of the microwave was continually flushed with air to maintain a constant cavity temperature and remove any insulating effect. After about 100 min at 200 W, the surface temperature and total pressure of the cell remained constant and were determined to be at equilibrium. Four aliquots of 50 μ L were taken, after 10 min of constant temperature and pressure, and analyzed by gas chromatography (GC) to determine the gas composition. After the last injection, the microwave power was decreased to 175 W, and after an additional 10 min, it was re-equilibrated to constant temperature and pressure, and then again 4 aliquots of 50 μ L were

taken and analyzed by GC. This procedure was repeated for 150, 125, and 100 W of microwave power. From the determined gas compositions and recorded total pressure, K_p values were calculated for the carbon–steam, homogeneous WGS, Boudouard, and carbon–hydrogen reactions at the five experimental microwave powers (Supporting Information, section IIIa).

Data Analysis. The penetration depth of the microwaves in the carbon at 2.45 GHz was calculated from the values of the real (ϵ') and the imaginary (ϵ'') dielectric constants, taken from the dielectric measurement (Supporting Information, sections IIb and IIc).

The enthalpy (ΔH) was determined from the Van't Hoff equation from a weighted least-squares fit of the natural log of the experimentally determined equilibrium constant versus the reciprocal of the temperature (Supporting Information, section IIId).

Thermochemical Calculations. For the thermal reaction, the thermodynamic parameters, specifically ΔH and ΔS , were calculated using standard thermodynamic tables. The enthalpy and entropy were corrected for temperature using the heat capacities of the reactants and products to better match the temperatures at which the microwave reaction was experimentally determined. The free energy and equilibrium constant were, in turn, computed from ΔH and ΔS , using the standard thermodynamic relationships (Supporting Information, section IIIC).

RESULTS

Penetration Depth of Graphite. The volumetric heating of carbonaceous materials by microwave radiation at 2.45 GHz generally proceeds efficiently, making carbon-based reactions particularly amenable to microwave processing.⁶ Studies of permittivity and dielectric relaxation processes in different kinds of carbon, including graphite, have indicated that heat is produced through space charge (interfacial) polarization, which is typical for solid dielectric materials.^{7,8} The loss mechanism arises primarily from the generation and migration of electron–hole pairs by the incident radiation, which becomes trapped at the surface at defect sites and grain boundaries. The trapping process hinders recombination, thereby dephasing the charge transport from the oscillating electric field, resulting in a loss process. The loss process is measured through the imaginary part of the dielectric constant (ϵ'' in eq 5), with the magnitude of the loss often measured through the loss tangent, which is the ratio of the imaginary (ϵ'') to the real (ϵ') dielectric constant (eq 6).

$$\epsilon = \epsilon' + i\epsilon'' \quad (5)$$

$$\tan \delta = \epsilon''/\epsilon' \quad (6)$$

The real and imaginary parts of the dielectric constant for the graphite used in this study were measured over the relevant frequency range (Figure 1). The largest values for the loss tangent occurred where it peaked around 2.6, 4.5, and 8.5 GHz. At the microwave excitation frequency of 2.45 GHz, the loss tangent was found to be 0.26(\pm 0.01). From the values of the real and imaginary dielectric constants (10.14(\pm 0.29) and 2.62(\pm 0.16), respectively), we calculated a penetration depth of 19.05 mm.

In the CEM microwave used in these experiments, irradiating occurred radially across the 24 mm diameter of the carbon sample, as expected. We also observed relatively uniform

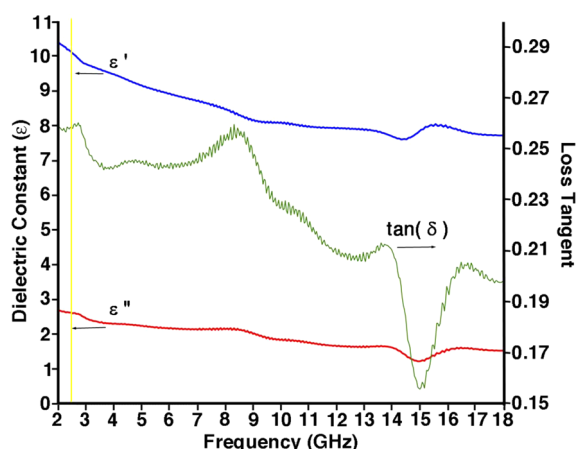


Figure 1. Real (blue) and imaginary (red) components of the dielectric constant and the loss tangent (green) of the graphite used in these experiments. The yellow line indicates the frequency (2.45 GHz) of the incident radiation from the microwave oven.

heating of the material, with no significant attenuation in the center of the sample.

Establishing Equilibrium. Because the results depended upon an accurate determination of the equilibrium constants under microwave radiation, it was necessary to establish that equilibrium had been attained. Using the static reaction vessel, charged with graphite and water, the pressure of the vessel and the temperature of the carbon surface were monitored in situ during the course of the reaction. Samples of the gas were extracted and analyzed by GC over the course of the reaction to determine the amount of H_2 , CO , CO_2 , and CH_4 present as a function of irradiation time. The sample was initially irradiated at 200 W of applied power, yielding a surface temperature of 997 K, with the establishment of equilibrium judged to occur when the pressure, temperature, and composition reached steady-state values. Multiple trials were carried out, and the time to reach a steady state at 200 W was ~ 100 min in all cases. When the steady state was reached, the atmosphere was analyzed four separate times (approximately once every 5 min) with the partial pressures of the constituent species determined. The values of the partial pressures used in calculation of the equilibrium constants were the average of the four steady-state values; a typical data set at 200 W applied power is shown in Figure 2. This whole process was repeated four times with four independent samples. The compositions at lower temperatures were arrived at in the same system by reducing the applied microwave power and allowing the system to reestablish equilibrium, which took approximately 10 min.

To verify that the system was at equilibrium, a separate experiment was performed to show that the equilibrium, once established, would return to the same value of the equilibrium constant when perturbed by the addition of additional reactants or products. In this experiment (Figure 3), the system was brought to equilibrium at 200 W of applied microwave power. As can be seen in Figure 3, the application of microwave radiation resulted in an initial decrease in temperature of the carbon surface as the water was heated and vaporized. Upon achieving constant temperature and pressure, the power was reduced to 100 W, and the system was allowed to re-equilibrate for 30 min prior to analysis by GC. The temperature of the graphite surface was $516^\circ C$ at this power, and a value of $K_p = 2.90 \pm 0.21$ was determined from analysis of the constituent

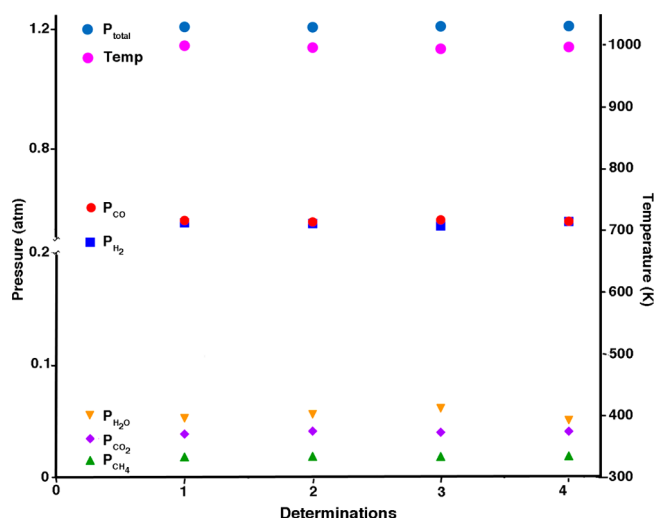


Figure 2. Four independent determinations of temperature, pressure, and composition at approximately 5 min intervals after equilibrium was established in the system (1 g of graphite, 200 W irradiation, 100 min to reach equilibrium).

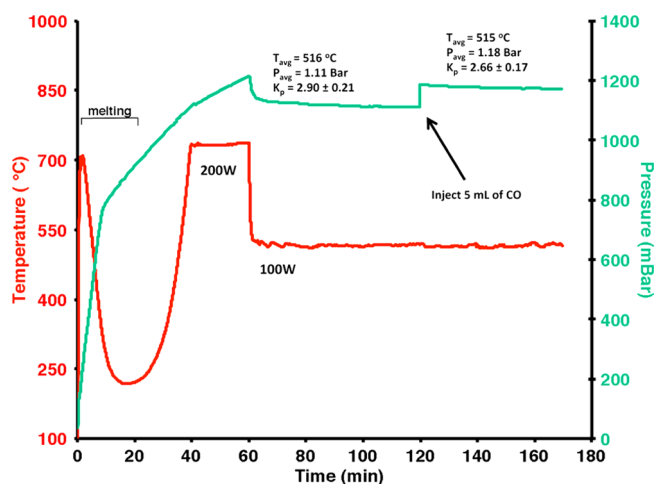


Figure 3. Pressure, temperature, and equilibrium constants show that the equilibrated system returned to the same equilibrium value for the steam–carbon reaction after perturbation by the addition of CO to the system.

gases. After the analyzed products had fully gone through the GC column, the equilibrium constant was determined, and 5 mL of CO (g) was injected into the closed system, leading to an increase in total pressure of ~ 70 mB (from 1110 to 1180 mB). Once the CO (g) was introduced, the system was allowed to re-equilibrate for 30 min, and the composition was analyzed. The temperature was $515^\circ C$, and K_p was determined to be 2.66 ± 0.17 , which was, within experimental error, the same as determined prior to the addition of CO , suggesting that, under the conditions we were using, equilibrium had been established.

Power Threshold for Microwave-Driven Reactivity.

The generation of products from the steam–carbon and related gasification reactions was expected to be dependent on the applied microwave power, and, as we observed previously with the Boudouard reaction, there should be a threshold power below which the reaction would not occur.⁵ In this particular study, which focused only on the thermodynamics of the reaction as a means to assess the magnitude of the microwave

effect, such a threshold was related to whether any products could be produced and whether the equilibrium could be attained in a reasonable period of time, which, in these experiments, was set at 100 min. Because, given enough time, any system will ultimately reach equilibrium, this time period, while somewhat arbitrary, reflected the practical experimental limitations of doing very long-term exposures in the microwave.

To determine this threshold, a sample cell, charged as described above with water and graphite, was systematically irradiated with applied powers, starting at 10 W and moving up in 5-W increments. At each power level, the system was irradiated for 1 h, and the composition of the gas was determined. It was found that no product gases (H_2 or CO) were observed until 30 W of applied power, corresponding to a carbon temperature of 373 °C, where trace amounts of H_2 were detected. While this represented an approximate minimum energy for the production of H_2 and CO, it was well below a practical threshold for the establishment of equilibrium in a reasonable period of time. It was found that at 90 W, while products were readily observed, the system was far from equilibrium, even after 240 min. Upon increasing the power to 100 W (491 °C), equilibrium was attained within 120 min. As such, all equilibrium determinations were carried out at ≥ 100 W, which we viewed as the practical range for the establishment of equilibrium in our system.

Equilibrium and Thermodynamic Properties. The reaction of carbon with steam, which forms the basis of energy production processes such as coal gasification, has been studied experimentally under kinetic conditions using flowing reactor systems.^{2,9–11} In general, the gas mixture produced from the reaction contains all of the possible species, commensurate with the equilibria shown above (reactions 1–4). The dominant species are H_2 and CO, with the H_2 coming from the steam–carbon (reaction 1) and WGS reactions (reaction 2). The reaction of CO_2 with carbon to produce CO (Boudouard reaction) does not contribute appreciably until high temperatures are reached due to its high endothermicity. Similarly, although for the opposite reason, the production of CH_4 through the hydrogenation of carbon (reaction 4) is always a very minor pathway, because at the temperatures at which gasification reactions are typically run, the equilibrium lies to the left. In addition, the primary step in the reaction, which is the hydrogenation of the graphite, is known to be extremely slow.¹²

In our previous studies on the isolated $\text{C} + \text{CO}_2$ (Boudouard) reaction (reaction 3), we observed a strong microwave-specific effect that resulted in a significantly exothermic shift in the enthalpy of reaction.⁵ The changes in the apparent thermodynamics of the reaction were proposed to be the result of specific microwave effects on the mechanism from the interaction of the radiation with the carbon surface. Because the steam–carbon reaction occurs through the same basic mechanism as the Boudouard reaction, it seemed likely that it would also be accelerated due to similar microwave effects.²

Equilibrium constants for the steam–carbon reaction system were determined at five different power settings that produced graphite surface temperatures from 764 to 997 K. The distribution of species at equilibrium, as a percent of the total composition, is shown in Figure 4 for each of the temperatures. As can be seen in the graph, as the temperature increased, the amount of syngas, CO and H_2 , increased steadily at the expense of the minor constituents, CO_2 , CH_4 , and H_2O . This trend was

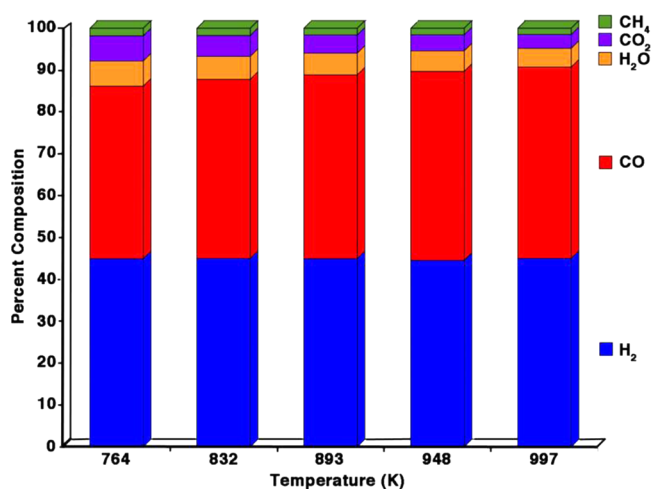


Figure 4. Equilibrium composition as a percent of the total and as a function of temperature under microwave irradiation.

consistent with the known thermodynamics of the various equilibria.

The strongly endothermic reactions, the steam–carbon (reaction 1) and the Boudouard reaction (reaction 3), had their equilibria shifted to the right, generating more CO and H_2 as the temperatures increased. Conversely, the equilibrium of the WGS (reaction 2) and the carbon–hydrogen reaction (reaction 4) shifted to the left with increasing temperature due to the exothermicity of those reactions, thereby contributing to the production of CO and H_2 while depleting CO_2 and CH_4 .

Steam–Carbon Reaction. The steam–carbon reaction is the most technologically important of the gas–carbon reactions, as it is used directly for the production of syngas. As such, it was of interest to determine whether the large microwave-derived thermodynamic advantage we observed for the Boudouard reaction would be realized for the steam–carbon reaction. The equilibrium constants and values for the free energy of the steam–carbon reaction, determined under microwave irradiation as a function of the temperature of the graphite, are shown in Table 1. To provide a quantitative comparison between the thermochemical properties of the microwave and thermal reaction, we calculated the free energy change and the equilibrium constant using contemporary thermodynamic data (ΔH_f° and S°), temperature-corrected using the appropriate heat capacities to match the temperature of the carbon surface measured in the microwave experiments (Supporting Information, section IIIb).¹³

As the data show, under microwave conditions, the equilibrium laid significantly further to the right, favoring the production of synthesis gas at much lower temperatures than those observed under conventional thermal conditions. A plot of the equilibrium constants as a function of temperature for the microwave and thermal reaction is shown in Figure 5. As can be seen, the thermal reaction had a rapid drop in the magnitude of the equilibrium constant as the temperature dropped below ~ 1000 K, while the decrease was much more gradual under microwave irradiation.

Because the enthalpy of gas–carbon reactions tends to vary only slightly with temperature due to the small temperature-dependent heat capacities of the gas-phase reactants, we could estimate the enthalpy of the microwave-driven reaction from a Van't Hoff plot of $\ln(K_p)$ versus $1/T$.¹³ As can be seen in Figure 6, we obtained a good linear relationship for the regression

Table 1. Equilibrium Constants and Thermochemical Parameters for the Steam–Carbon Reaction

| Microwave | | | | | |
|-----------|--------------------------|---------------------|----------------------------------|---------------------|--------------------|
| T (K) | T (K) gas ^a | K_p | ΔG (kJ/mol) ^b | ΔH (kJ/mol) | ΔS (J/mol) |
| 764(±4) | 293 | 3.19(±0.53) | −7.4(±1.0) | 15.2(±0.8) | 29.5(±0.1) |
| 832(±3) | 309 | 3.90(±0.61) | −9.4(±1.0) | | |
| 893(±2) | 321 | 4.39(±0.43) | −11.0(±0.7) | | |
| 949(±2) | 331 | 4.95(±0.50) | −12.6(±0.8) | | |
| 997(±2) | 337 | 5.61(±0.48) | −14.3(±0.7) | | |
| Thermal | | | | | |
| T (K) | K_p ^c | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol) | |
| 764 | 0.03 | 23.5 | 144.2 | 158.1 | |
| 832 | 0.16 | 12.8 | | | |
| 893 | 0.66 | 3.12 | | | |
| 949 | 2.07 | −5.74 | | | |
| 997 | 4.99 | −13.33 | | | |

^aEstimated using the ideal gas equation. ^bCalculated from $\Delta G = -RT \ln K_p$, where R is the ideal gas constant. ^cAll tabulated thermodynamic quantities and equilibrium constants were calculated from standard thermochemical data (see the Supporting Information).

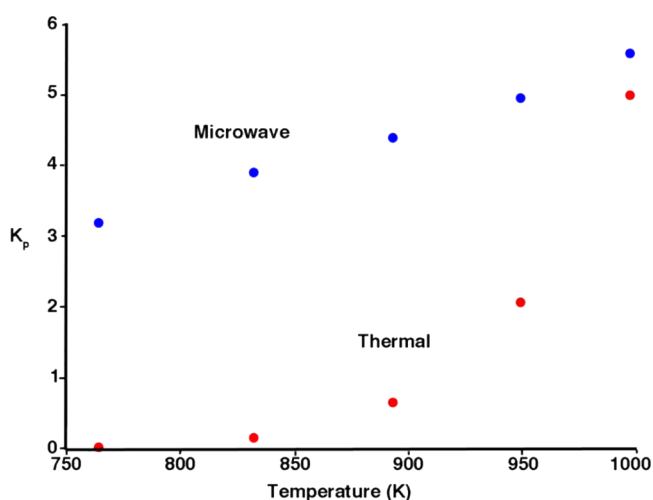


Figure 5. Equilibrium constants as a function of temperature for microwave (blue) and thermal (red) steam–carbon reactions.

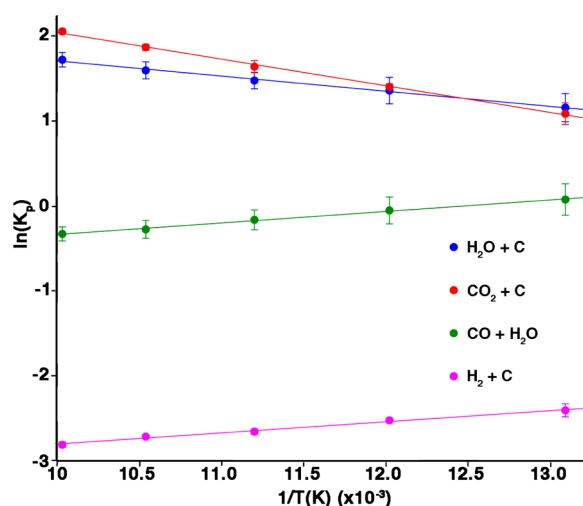


Figure 6. Van't Hoff plots for the microwave-driven equilibria present in the steam–carbon ($H_2O + C$) reactions.

analysis. The value of ΔH obtained from the slope of the plot was 15.2(±0.08) kJ/mol, while the value calculated for the thermal reaction, in this temperature range, was 144.2 kJ/mol

(Table 1) (Supporting Information, section IIIb). Clearly, under microwave irradiation, the apparent thermodynamics of the reaction changed dramatically. The microwave-driven reaction had a negative ΔG at lower temperatures than did the thermal reaction due to its significantly smaller enthalpy, ΔH , which tended to be less than $-T\Delta S$ at lower temperatures. Conversely, the lower entropy meant that as the temperature increased, the thermal process became more favorable much more quickly than did the microwave process, as $-T\Delta S_{\text{therm}} > -T\Delta S_{\text{micro}}$. Equating the thermodynamic relationship, $\Delta G = \Delta H - T\Delta S$, for the two processes, the temperature at which both processes had the same value for ΔG was 1003 K; above that temperature, the thermal process was more favorable for producing CO and H_2 , and below it, the microwave process dominated.

Boudouard Reaction. Because CO is produced as part of the steam–carbon reaction, and CO_2 is rapidly produced from the WGS reaction, the Boudouard reaction is one of the equilibria present in the steam–carbon reaction. Because of its high endothermicity, this reaction only plays a small role in the thermally driven steam–carbon process until very high temperatures were reached. In the microwave, however, it was found to be much more exothermic, so it may play a more significant role by converting CO_2 into CO.⁵

The free energy and associated equilibrium constants for the Boudouard reaction, determined experimentally in the microwave and calculated from the thermodynamic tables over the temperature range probed experimentally, are shown in Table 2. As can be seen, the free energy was negative over the entire temperature range under microwave conditions, while it became negative only at 949 K and above for the thermal reactions.

The equilibrium constants for the two processes over the temperature range investigated are shown in Figure 7.

As with the steam–carbon reaction, the equilibrium under microwave conditions favored the production of CO at significantly lower temperatures than were possible thermally. From the Van't Hoff equation (Figure 6), we estimated the value of the enthalpy for the microwave-driven reaction to be 27.0 kJ/mol, which is more exothermic; from the free energy and enthalpy, the entropy was found to be 43.1 J/mol. Both of these values were significantly less than those determined for the thermal process. Significantly, both the direction and the

Table 2. Equilibrium Constants and Thermochemical Parameters for the Boudouard Reaction

| Microwave | | | | | |
|----------------------|-----------------------------------|----------------------|----------------------------------|---------------------|--------------------|
| <i>T</i> (K) | <i>T</i> (K) gas ^a | <i>K_p</i> | ΔG (kJ/mol) ^b | ΔH (kJ/mol) | ΔS (J/mol) |
| 764(±4) | 293 | 2.97(±0.38) | −6.9(±0.8) | 27.0(±0.7) | 43.1(±1.4) |
| 832(±3) | 309 | 4.08(±0.14) | −9.7(±0.2) | | |
| 893(±2) | 321 | 5.17(±0.37) | −12.2(±0.5) | | |
| 949(±2) | 331 | 6.50(±0.24) | −14.8(±0.3) | | |
| 997(±2) | 337 | 7.83(±0.25) | −17.1(±0.3) | | |
| Thermal ^c | | | | | |
| <i>T</i> (K) | <i>K_p</i> ^c | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol) | |
| 764(±4) | 0.0048 | 34.12 | 180.2 | 191.2 | |
| 832(±3) | 0.050 | 21.12 | | | |
| 893(±2) | 0.29 | 9.458 | | | |
| 949(±2) | 1.2 | −1.249 | | | |
| 997(±2) | 3.6 | −10.43 | | | |

^aEstimated using the ideal gas equation. ^bCalculated from $\Delta G = -RT \ln K_p$, where *R* is the ideal gas constant. ^cAll tabulated thermodynamic quantities and equilibrium constants were calculated from standard thermochemical data (see the Supporting Information).

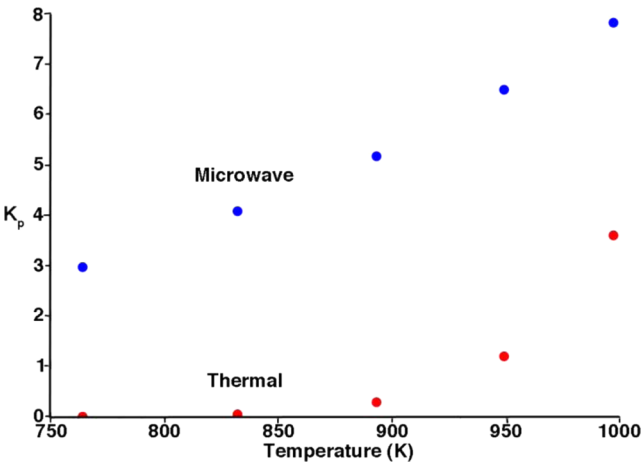


Figure 7. Equilibrium constants as a function of temperature for microwave (blue) and thermal (red) Boudouard reactions.

magnitude of the microwave effect for the Boudouard reaction were similar to that observed for the steam–carbon reaction.

It was important to compare the equilibrium constants and thermochemical parameters for the Boudouard reaction in the

present study, as part of the steam–carbon system, and those determined independently from investigating the isolated reaction to verify that the values obtained in independent measurements were consistent. It must be noted, however, that the current study was carried out over graphite while the prior study used activated charcoal, so some thermodynamic differences were to be expected. The value of ΔH in the current study was 27.0(±0.7) kJ/mol, while a value of 33.4(±3.3) kJ/mol was reported in the prior study.⁵ This small, 6.4 kJ/mol enthalpy difference can be accounted for because the current study was carried out at a lower average temperature than was the prior Boudouard study (887 vs 1192 K). Thermochemical calculations yielded an enthalpy decrease of around 3 kJ/mol between the two average temperatures, bringing the values to within experimental error. The entropy difference between the two studies, however, is more pronounced, with a 43.1(±1.4) J/mol ΔS obtained in the current study and 65.6(±3.1) J/mol in the prior study. Thermochemical calculations yielded an entropy difference of ~3 J/mol between the two average temperatures, which did not completely explain the observed difference. It seems that this difference may well reflect the difference in entropy between

Table 3. Equilibrium Constants and Thermochemical Parameters for the WGS Reaction

| Microwave | | | | | |
|--------------|-----------------------------------|----------------------|----------------------------------|---------------------|--------------------|
| <i>T</i> (K) | <i>T</i> (K) gas ^a | <i>K_p</i> | ΔG (kJ/mol) ^b | ΔH (kJ/mol) | ΔS (J/mol) |
| 764(±4) | 293 | 1.08(±0.2) | −0.47(±1.1) | −11.4(±0.4) | −14.1(±0.2) |
| 832(±3) | 309 | 0.95(±0.15) | 0.35(±1.0) | | |
| 893(±2) | 321 | 0.85(±0.1) | 1.22(±0.9) | | |
| 949(±2) | 331 | 0.76(±0.08) | 2.14(±0.8) | | |
| 997(±2) | 337 | 0.72(±0.06) | 2.8(±0.7) | | |
| Thermal | | | | | |
| <i>T</i> (K) | <i>K_p</i> ^c | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol) | |
| 764 | 0.267 | 8.39 | −36.0 | −58.1 | |
| 832 | 0.168 | 12.34 | | | |
| 893 | 0.118 | 15.88 | | | |
| 949 | 0.089 | 19.14 | | | |
| 997 | 0.071 | 21.92 | | | |

^aEstimated using the ideal gas equation. ^bCalculated from $\Delta G = -RT \ln K_p$, where *R* is the ideal gas constant. ^cAll tabulated thermodynamic quantities and equilibrium constants were calculated from standard thermochemical data (see the Supporting Information).

Table 4. Equilibrium Constants and Thermochemical Parameters for the Carbon–Hydrogen Reaction

| Microwave | | | | | |
|-----------|-----------------------------|----------------|--------------------------|-------------|-------------|
| T (K) | T (K) gas ^a | K _p | ΔG (kJ/mol) ^b | ΔH (kJ/mol) | ΔS (J/mol) |
| 764(±4) | 293 | 0.087(±0.007) | 15.5(±0.52) | −9.1(±0.6) | −32.2(±0.9) |
| 832(±3) | 309 | 0.078(±0.002) | 17.7(±0.13) | | |
| 893(±2) | 321 | 0.070(±0.002) | 19.8(±0.21) | | |
| 949(±2) | 331 | 0.066(±0.001) | 21.4(±0.16) | | |
| 997(±2) | 337 | 0.062(±0.002) | 23.1(±0.25) | | |
| Thermal | | | | | |
| T (K) | K _p ^c | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol) | |
| 764 | 5.332 | −10.63 | −79.7 | −90.4 | |
| 832 | 1.914 | −4.49 | | | |
| 893 | 0.871 | 1.03 | | | |
| 949 | 0.462 | 6.09 | | | |
| 997 | 0.284 | 10.43 | | | |

^aEstimated using the ideal gas equation. ^bCalculated from $\Delta G = -RT \ln K_p$, where R is the ideal gas constant. ^cAll tabulated thermodynamic quantities and equilibrium constants were calculated from standard thermochemical data (see the Supporting Information).

activated charcoal and more highly crystalline graphite, although further studies may be required to fully elucidate this.

WGS Reaction. The WGS reaction is generally considered an integral part of the carbon steam reaction, which accounts for production of CO₂ in the product gas (reaction 2).² The reaction is weakly exothermic, and, unlike the other reactions in the steam–carbon system, carbon is not a reactant. Instead, the reaction is thought to be catalyzed by the carbon, and, under conditions typical of the steam–carbon reaction, equilibrium is rapidly attained.² Among the gas–carbon reactions, however, the WGS reaction is not an independent reaction but can be written as the difference between the steam–carbon and Boudouard reactions (i.e., reactions 1–3) so that the equilibrium constants are simply related, $(K_{sc})(K_{Bou})^{-1} = K_{WGS}$. Thermodynamically, this means that the enthalpy of the reaction is the difference in enthalpies, $\Delta H_{WGS} = \Delta H_{sc} - \Delta H_{Bou}$, and, similarly, the entropy is $\Delta S_{WGS} = \Delta S_{sc} - \Delta S_{Bou}$.

Despite its lack of independence, the WGS reaction is typically (and historically) included in treatments of the steam–carbon system. As such, we determined the values for the equilibrium constants and thermodynamic parameters over the temperature range investigated (Table 3) as we did for the other equilibria (Tables 1 and 2).

As would be expected for an exothermic reaction, the free energy increased with temperature, so the equilibrium constant favored the products at lower temperatures. This trend was observed in both the thermal and the microwave reactions. As can be seen in Table 3, over the temperature range studied, the microwave-driven reaction equilibrium generally laid further to the right, with the free energy becoming negative at the low end of the temperature range studied.

The enthalpy of the reaction under microwave conditions was −11.4 kJ/mol, and the entropy was −14.1 J/mol. Clearly, the presence of the microwaves made the apparent enthalpy of the reaction more endothermic by over 24 kJ/mol and the entropy more positive by 44 J/mol. The thermodynamic advantage provided by the microwaves was only realized at higher temperatures where the small negative entropy caused $T\Delta S < \Delta H$. As the temperature decreased, the free energy of the thermal reaction became more negative per degree temperature change due to the large entropy. Equating the free energy expressions for the thermal and microwave reaction, it was determined that at 559 K, both processes have the same

free energy (−3.51 kJ/mol); below that value, the thermal process dominated.

Carbon–Hydrogen Reaction. The carbon–hydrogen reaction, which initially produces methane, is a minor component of the carbon–gas reaction system. When our system attained equilibrium, small amounts of methane were detected at concentrations that were steady-state over the course of the experiment and decreased with reaction temperature (Figure 4). Values for the equilibrium constant and ΔG for the carbon–hydrogen reaction were calculated (Table 4) and compared to the predicted values of these quantities for the thermal reactions. The data suggest that, under microwave conditions, the free energy is always positive and the equilibrium constant always lies to the reactant side over the temperature range investigated. In contrast, the thermal reaction had negative values of ΔG as the temperature decreased, consistent with the exothermic nature of the reaction.

The enthalpy of the microwave-driven reaction, determined from the Van't Hoff plot (Figure 6), was −9.1 kJ/mol, and the entropy, determined from the free energy and the enthalpy, was −32.2 J/mol. The standard thermodynamic relationship ($\Delta G = \Delta H - T\Delta S$) predicted that, in the microwave, ΔG would remain positive all of the way down to 282.6 K, whereas for the thermal reaction, free energy would be negative below 881 K. This is an interesting result, as it means that the reverse reaction, the dehydrogenation of methane, will be favored. In recent years, this dehydrogenation reaction has been of some interest in the production of clean hydrogen fuel.^{14,15} However, we approached this result with some caution. The forward reaction of hydrogen reacting with carbon is known to be extremely slow, with methane formation rates ranging from 10^{-16} to 10^{-12} mol g^{−1} s^{−1} between 600 and 1100 K.^{12,16,17} As such, we may not have quite attained equilibrium for this reaction. Careful scrutiny of the measured CH₄ concentrations for the data points used to determine the equilibrium constants across the temperature range indicated that, within experimental error, there was no systematic increase in CH₄ generation, suggesting that the system was either at equilibrium or closely approaching it. As such, it is reasonable to suggest that the direction, if not the absolute magnitude, of the microwave effect was likely to be correct.

Discussion. The reaction of primary interest is the steam–carbon reaction, which is highly endothermic and is used commercially to generate synthesis gas. As indicated in the results, there is a clear shift in the equilibrium toward the desired syngas products under microwave irradiation. A more general view of the effect of microwaves on the complex equilibria that make up the gasification reaction system can be estimated from the thermodynamic parameters. In particular, the equilibrium composition in mole fractions of the total reaction system over a broad temperature range can be approximated from the predicted values of the equilibrium constants, written in terms of mole fraction (K_X), with the temperature dependence of the equilibrium expression estimated from the thermodynamic parameters (eq 7) obtained experimentally for the microwave reaction and calculated for the thermal reaction.

$$K_X = e^{-\Delta G/RT} = e^{-\Delta H - T\Delta S/RT} \quad (7)$$

By using eq 7 for the temperature dependence of each of the equilibrium constants in reactions 1–4, the equilibrium expressions can be solved numerically for the mole fractions of each constituent as a function of temperature (Supporting Information, section IIIc). Figure 8 shows the approximate

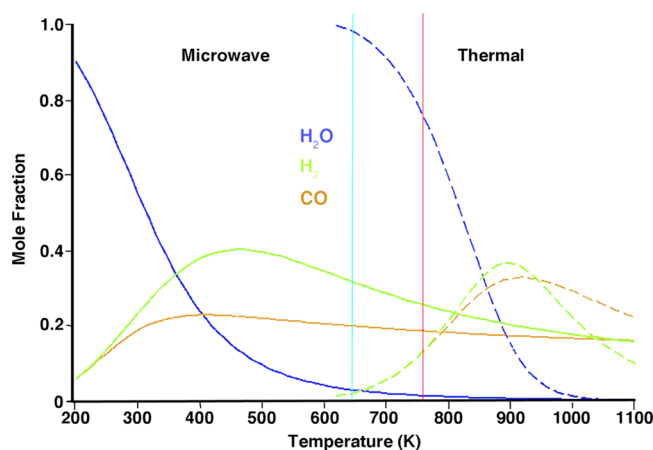


Figure 8. Equilibrium composition of the reactants (H_2O) and products (CO , H_2) of the steam–carbon reaction as a function of temperature under microwave (solid) and thermal (dashed) conditions. The vertical lines represent microwave thresholds for product formation. The cyan line represents the lowest temperature (power) at which any H_2 is observed, and the red line represents the lowest temperature (power) at which equilibrium could be readily established in 100 min.

composition of the reactant (H_2O) and products (CO and H_2) of the steam–carbon reactions as a function of temperature for the microwave and thermal process. As can be seen in the figure, in the microwave, the consumption of water and generation of hydrogen and carbon monoxide occur at significantly lower temperatures than those required by the thermal process, consistent with the more exothermic nature of the reaction. These calculations predict that hydrogen will reach a maximum at 463 K, whereas under thermal conditions it is expected to occur at 890 K. The calculations predict that, in general, less CO will be produced under microwave radiation, with its production slowly decreasing over the temperature range, while under thermal conditions, its production is on par with that of H_2 , peaking at 917 K. The decrease in CO arises

because the lower temperatures lead the exothermic WGS reaction to be more favorable, and CO is consumed. As the temperature goes up, the WGS reaction becomes less favorable; however, the Boudouard reaction, which is thermodynamically more favorable under microwave conditions but still endothermic, begins to produce CO from CO_2 at the higher end of the temperature range, yielding the predicted curve. Consistent with this, CO_2 production is greater at low temperatures in the microwave reaction (Supporting Information, Figure S3).

Obviously, while these plots provide a good graphical comparison of the difference between microwave and thermal reactivities for the steam–carbon system, the low-temperature regions of the graphs are not accessible due to the threshold power limits of the microwave reactions. In short, while the graphs indicate that we should attain the highest equilibrium concentration of H_2 at 463 K, this is below the threshold where any product would be observed in the microwave. The practical threshold temperatures are indicated by the vertical lines in Figure 8; the cyan line represents the lowest temperature (power) at which any H_2 is observed, and the red line represents the lowest temperature (power) at which equilibrium could be established in a reasonable period of time (100 min). All reported equilibrium data were collected at or above the highest threshold. It is important to note, however, that when evaluating the magnitude of any possible advantage of using microwaves to drive the steam–carbon reaction, it will be necessary to perform the reaction under kinetic conditions with flowing reactants. Under those conditions, parameters such as the power, flow rate, and carbon mass (i.e., path length) can be varied to optimize product production.

The equilibrium constants and associated thermochemical parameters that were determined for the steam–carbon process are important for understanding the magnitude and direction (exothermic or endothermic) of the microwave-specific effect. What is indicated by the enthalpy and entropy for the various constituent reactions of the process is that the microwave effect is quite pronounced, in most cases differing significantly from what is predicted for the conventional thermal reaction. However, the magnitude and direction of the apparent effects are reaction-dependent, with both increases and decreases in enthalpy and entropy observed.

We can obtain a useful measure of the magnitude and direction of the microwave-specific effect from thermodynamic consideration. The enthalpy of the gas–carbon reactions can be determined in the standard way from the standard enthalpies of the products and reactants at the reaction temperature, T (eqs 8–10). For the thermal reaction, this is the difference between the product and reactant, including the relevant stoichiometry factors (n).

$$\Delta H_{\text{thermal}} = \left[\sum_i n_i (\Delta H^\circ_T) \right]_{\text{product}} - \left[\sum_i n_i (\Delta H^\circ_T) \right]_{\text{reactants}} - (\Delta H^\circ_T)_C \quad (8)$$

Table 5. Thermodynamic Parameters for Thermal and Microwave Gas–Carbon Reactions

| reaction | thermal | | microwave | | microwave effect | |
|-----------------|---------------------|--------------------|---------------------|--------------------|------------------------|------------------------|
| | ΔH (kJ/mol) | ΔS (J/mol) | ΔH (kJ/mol) | ΔS (J/mol) | $(\Delta H^\circ)_C^a$ | $(\Delta S^\circ)_C^b$ |
| steam–carbon | 144.2 | 158.1 | 15.2 | 29.5 | 129.0 | 128.6 |
| Boudouard | 180.2 | 191.2 | 27.0 | 43.1 | 153.2 | 148.1 |
| WGS | −36.0 | −58.1 | −11.4 | −14.1 | −24.6 | −44.0 |
| carbon–hydrogen | −79.7 | −90.4 | −9.1 | −32.2 | −70.6 | −58.2 |

$$^a \Delta H_{\text{ther}} - \Delta H_{\text{microwave}} \quad ^b \Delta S_{\text{ther}} - \Delta S_{\text{microwave}}$$

$$\Delta H_{\text{microwave}} = \left[\sum_i n_i (\Delta H^\circ_T) \right]_{\text{product}} - \left[\sum_i n_i (\Delta H^\circ_T) \right]_{\text{reactants}} - (\Delta H^\circ_T + \Delta H^\circ_{\text{MW}})_C \quad (9)$$

$$\Delta H_{\text{thermal}} - \Delta H_{\text{microwave}} = (\Delta H^\circ_{\text{MW}})_C \quad (10)$$

For the gas-phase reactants and products, it is assumed that even though the average temperature of the gas in the medium is much lower in the microwave experiment, the temperature of the gas equilibrates rapidly with the carbon surface when the reaction takes place. As such, the enthalpies are the same in both processes. We also assume, because carbon is the only reactant that directly absorbs the microwaves, that the magnitude of the microwave effect can be treated as a change in the apparent enthalpy of the carbon. We write the enthalpy as the sum of the thermal enthalpy and the enthalpy due to the microwave-specific contribution (eq 9). The magnitude of the microwave-specific enthalpy imparted to the carbon is simply the difference between the microwave and thermal reaction enthalpy (eq 10), which for the steam–carbon system is 129.0 kJ/mol. A similar analysis can be carried out for the entropy ($\Delta S_{\text{ther}} - \Delta S_{\text{mw}}$), which for the steam–carbon reaction is 128.6 J/mol. This value constitutes the apparent free entropy induced in the carbon by the microwave radiation. Clearly, from a thermodynamic standpoint, if the value obtained from eq 10 is positive, it appears as though extra heat (or entropy) is being “stored” in the carbon, whereas if it is negative, it appears as though there is an effective heat (or entropy) loss.

The key thermodynamic values for the thermal and microwave reactions and the magnitude and direction of the microwave-specific effect are summarized in Table 5. As discussed, for the steam–carbon and the Boudouard reaction, which are both strongly endothermic, the microwave effectively increases the enthalpy and entropy of the carbon, thereby making the overall reaction more exothermic and reducing the overall entropy.

For the carbon–hydrogen reaction, which is inherently exothermic, the effect of the microwave is very different; it makes the reaction more endothermic and increases the effective entropy. The apparent effect on the carbon is that heat has been “removed” by the microwave.

Obviously, the microwave is not literally adding or subtracting heat (or entropy) to or from the carbon, respectively, due to its being held at certain temperatures that are the same for both the thermal and the microwave reactions. The observed microwave effect on the thermodynamic properties of the reaction must be due to changes in the thermochemical kinetics of the forward and reverse reactions,

which define the position of equilibrium. Because the gas-phase species do not absorb microwaves, these thermodynamic changes must necessarily arise from changes in the reactivity of the carbon surface, or species adsorbed on the surface, through interactions with the radiation. In a simple fashion, the temperature dependence of the equilibrium constant and the forward and reverse rates can be written in terms of the free energy of activation.¹³

$$K_p = e^{-\Delta G^\circ/RT} = \frac{k_1}{k_{-1}} = \frac{a_1 e^{-G_1^*/RT}}{a_{-1} e^{-G_{-1}^*/RT}} \quad (11)$$

$$\Delta G^\circ = (G_1^* - G_{-1}^*) \quad (12)$$

In eq 11, the forward and reverse reactions have a free energy of activation associated with them and a pre-exponential factor, a , which will itself have a temperature dependence.¹⁸ From this relationship, it can be seen that the free energy of the reaction is equal to the difference in the activation free energy of the forward and reverse reaction (eq 12). The effect of microwaves on the positions of the equilibrium can be interpreted as arising from differential changes in the forward and reverse activation parameters: free energy (G^*) and selective heating (T , a). Because these are gas–solid reactions, the kinetics are not described by a pair of elementary opposing reactions but involve adsorption and desorption processes at the surface and reactions with active sites or other reactants on the carbon surface. As such, both the forward and the reverse processes will have thermokinetic parameters associated with each discrete step in the mechanism, many of which can potentially be influenced by the microwave radiation.

In our prior study of the Boudouard reaction, we hypothesized that the enhanced reactivity and exothermic shift of the observed enthalpy under microwave conditions could potentially arise from interaction of the radiation with key mechanistic steps in the reaction. Specifically, we proposed that there were two places where microwave effects could manifest themselves. It is known that one of the primary dielectric loss processes, arising from the interaction of microwaves with carbon, is a space-charge mechanism (Maxwell–Wagner) where electron–hole pairs are generated and can be trapped at the surface.^{7,8}

The electron–hole pairs are reactive and can potentially accelerate the oxidation of the surface by a substrate (CO_2 in the case of the Boudouard reaction) (Figure 9a). As we pointed out in our original study, the strength of this mechanism is that it is consistent with the known physics of microwave heating of carbon; however, given the difficulty of performing in situ analysis of the surface under microwave heating, it is difficult to prove, and other processes can certainly play a role.

Notably, a similar mechanism has been previously proposed to explain the influence of surface groups in the microwave-driven dry reforming of methane.¹⁹ In addition to activation of

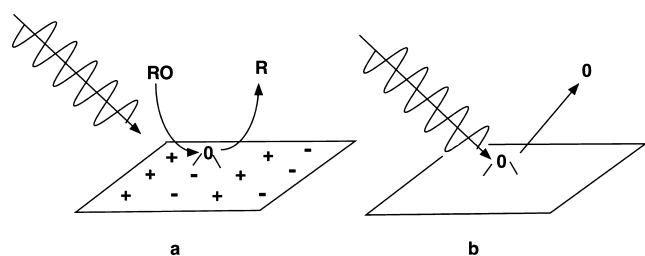


Figure 9. Proposed mechanisms for microwave enhancement of gas-carbon reactions: (a) microwave-induced space charges (electron-hole pairs) react with a substrate, and (b) the dipoles of the surface oxides couple to the microwave and are rapidly ejected from the surface.

the surface, the microwaves can couple strongly with the dipole moments that form on the oxidized surface, thereby selectively heating them and accelerating the ejection of CO from the surface (Figure 9b). The effectiveness of selective interfacial heating of surface-bound species has been well established in recent work by Conner.^{20–22} Because the general mechanisms of the steam-carbon and Boudouard reactions are believed to be essentially the same, the mechanism of microwave enhancement should also be similar (Figure 9).^{2,10,11,23–25} In particular, the first step is the oxidation of the carbon surface by H₂O or CO₂ for the steam-carbon and Boudouard reactions, respectively (Figure 10a, reaction i), which occurs with the concomitant elimination of H₂ and CO (Figure 10a, reaction ii). The rate-determining step is the subsequent elimination of CO from the oxidized carbon surface (Figure 10a, reaction iii). The reverse reaction will involve the H₂ or CO reacting with the oxidized surface to regenerate H₂O or CO₂.

Our hypothesis is that the presence of electron-hole pairs creates a more easily oxidized carbon surface, thus reducing the free energy of activation of the forward oxidation process. This would tend to favor the forward reaction (Figure 10a, reaction i), consistent with the shift of the equilibrium to the right, under microwave irradiation. In the reactions considered here, the selective heating of the surface oxide by the microwave (Figure 9b) could result in both the acceleration of CO ejection from the oxidized surface (Figure 10a, reaction iii), which would enhance the forward reaction, and the enhancement of the reverse reaction, because the hot oxide groups react more readily with CO and H₂ (Figure 10a, reaction ii). In short, it could be argued that the microwaves can accelerate both the forward and the reverse reactions. However, if the most facile process is CO dissociation from the surface (which is a unimolecular process), then the oxide groups will be rapidly depleted, thereby suppressing the reverse reaction (Figure 10a, reaction ii).

For the WGS reaction (Figure 10b-1,2), it is obvious that the selective microwave effect on the equilibrium constant arises from different magnitudes of microwave acceleration of the forward and reverse reactions. As discussed previously, the WGS reaction and its thermodynamic parameters are obtained simply from the difference between the steam-carbon (reaction 1) and Boudouard reaction (reaction 3). Mechanistically, the forward reaction involves initial oxidation of the carbon surface by water (Figure 10b-1) to produce hydrogen, with CO subsequently reacting with the oxidized surface (Figure 10b-2) to yield CO₂.^{2,25} As such, the observed microwave effect, in which the enthalpy of the reaction was found to be more endothermic, arises because the reverse reaction is simply the Boudouard reaction, which has a greater microwave-induced exothermicity ($\Delta H^{\circ}_{\text{MW}}$) than does the forward, steam-carbon reaction, so the magnitude of the microwave effect of the WGS reaction in Table 5 is $(\Delta H^{\circ}_{\text{MW}})_{\text{steam-carbon}} - (\Delta H^{\circ}_{\text{MW}})_{\text{Boudouard}} = -24.6 \text{ kJ/mol}$. An analogous analysis holds for the entropy.

For the carbon-hydrogen reaction (reaction 4), the effect of the microwaves is to induce an endothermic shift in the thermodynamics, which shifts the equilibrium to the left, favoring the formation of H₂ from CH₄. This is potentially useful, as the reverse reaction will produce clean hydrogen fuel from hydrocarbons and, as such, is of significant interest. In fact, the reverse reaction is a key component of the dry reforming of methane ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$) over carbon, which has been found to be accelerated by microwaves.^{19,26} The detailed mechanism of the carbon-hydrogen reaction has not been studied extensively, but the primary gas surface process for the forward reaction is thought to involve sequential hydrogenation of the carbon surface (Figure 10c). For graphite, this takes place primarily at the edges of the basal plane. After a sufficient degree of hydrogenation, methane, the initial product, is eliminated.^{2,17,27} The mechanism of the reverse reaction is not well understood and will depend on the nature of the carbon surface. It would involve dehydrogenation of the methane with the deposition of carbon on the surface followed by elimination of H₂, whether this occurs in a concerted fashion or through the transfer of hydrogen to the carbon surface, from which it is subsequently eliminated.

The effect of microwaves on either of these reactions is difficult to assess. Using our model in which enhanced reactive sites are charge-separated sites on the surface induced by the microwave radiation, it is reasonable to suggest that the hydrogenation step, in both directions, might be accelerated, although possibly to different degrees. Alternatively, the acceleration of the reverse reactions may arise from the interfacial interactions of the C-H group with the microwave

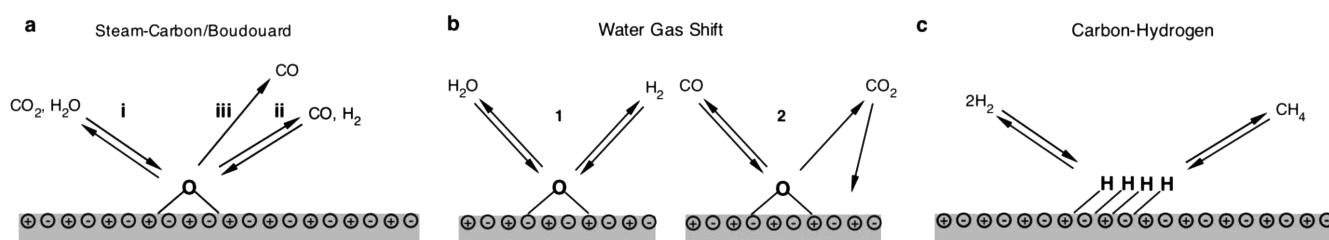


Figure 10. Proposed mechanism of (a) steam-carbon and Boudouard reactions, (b) the WGS, and (c) hydrogen-carbon reactions on a carbon surface. While not shown graphically in the figure, the surfaces depicted are under steady-state microwave irradiation. The alternating charges indicate the steady-state electron-hole pairs in the carbon surface arising from the space-charge mechanism of microwave heating.

radiation, which may preferentially accelerate the elimination of H_2 from the surface in the reverse reaction over CH_4 in the forward reaction. Obviously, many other factors may be at play in such a mechanistically complex reaction.

CONCLUSIONS

This study indicates that there is a significant microwave-specific effect on the apparent thermodynamics of the reactions associated with the steam-carbon gasification process. The net effect of the microwaves is not constant but depends on the specific reaction and on the differential effect that the microwaves have on the forward and reverse reaction. From a practical standpoint, the most significant observation is that, under microwave irradiation, the thermodynamics of the reaction favor the production of synthesis gas from the steam-carbon reactions. In addition, the work also suggests that microwave radiation favors the production of H_2 from the carbon-hydrogen reaction. In both cases, the use of microwaves reduces the temperature required to drive the endothermic reactions that produce environmentally desirable hydrogen as fuel. In terms of fundamental science, the work supports the hypothesis that, for heterogeneous reaction systems, microwaves not only selectively heat the substrate but, beyond that, also affect the primary thermokinetic steps of the process to yield dramatically different equilibrium properties. This latter effect we propose is related to the mechanism by which dielectric loss occurs through microwave interactions with carbon.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, materials, methods and apparatus, dielectric measurements, data analysis, and thermodynamic calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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