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Thermodynamic Equilibrium for Wyoming Coal: New Calculations

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THERMODYNAMIC EQUILIBRIA FOR WYOMING COAL:
NEW CALCULATIONS

ABSTRACT

NOTICE
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Previous work by Stephens in the coal-water-oxygen thermodynamic system is extended. Results with 20% combustion and amorphous carbon are shown to be a good approximation to kinetic data. Experimental Lurgi coal gasification data are closely approximated by a calculated thermodynamic temperature of 1060 K. This temperature is used to show that for underground coal gasification with a constant oxygen/coal ratio, optimum steam/oxygen ratios should be as low as possible. Probably the steam/oxygen ratio should exceed 3.6 to avoid slagging of the ash. At this ratio, about twice as much methane can be obtained in comparison to the Lurgi ratio of 7.7.

INTRODUCTION

Thermodynamic studies are of interest for any chemically reacting system. Thermodynamics constitute the limiting cases for kinetically reacting systems. In many systems, as a result of the exponential nature of most chemical reactions (reaction rate = $k A e^{-\Delta H/RT}$), reactions of interest occur over a fairly narrow temperature region. At lower temperatures, reaction rates are negligible, while at higher temperatures the reaction can be so rapid as to be controlled either by thermodynamics or mass transfer. Thus, thermodynamic equilibrium at a characteristic temperature can often be a close approximation to a kinetic system.

For these reasons, a previous study¹ was initiated to examine the coal-carbon-water-oxygen system with particular reference to the LLL packed-bed process.² Many issues concerning this system were addressed but some questions were left unanswered. In particular, conclusion six of Ref. 1 suggests areas for work, three of which we address here:

- Determining the amount of oxygen (percentage of combustion) needed for the underground reaction system
- Determining the thermodynamic stability of carbon formed in gasification reactions
- Determining the thermodynamic properties of char and tar.

In addition, we consider the effect of steam/oxygen ratios.

In this study we do not calculate adiabatic reaction temperatures. In an actual underground reacting system, temperatures would be distributed in the reaction zone and combined with axial convection, axial conduction, and radial heat losses. In the calculations here we consider only those species stable at a given temperature and pressure under varying systematics of coal, water, and oxygen.

DISCUSSION

Oxygen for *In-Situ* Gasification

Field tests will be required to determine the amount of oxygen required for *in-situ* gasification. The Lurgi high-BTU process³ uses an amount of oxygen very close to 20% combustion,^{*} and for a conservative design, data for 20% combustion probably should be used. Higher values have been reported in previous *in-situ* gasification experiments, albeit in different underground systems and with about 30% gas losses underground.^{4,5} Therefore, at present, 20% combustion is recommended.

Thermodynamic Stability of Char

Thermodynamic properties of two Wyoming chars have been calculated from their ultimate analysis and heat of combustion.⁶ Both were derived from Roland seam coal from the Wyodak mine near Gillette, Wyoming. Carbonization temperatures were 500°C and 625°C (Table 1). These data were used in the TIGER code,⁷ a multicomponent thermodynamic equilibrium code, to determine the significance of equilibria over char and the stability of char with respect to coal or

* Equivalent to 20% of the oxygen required for stoichiometric combustion of the coal.

Table 1. Thermodynamic properties of Wyoming chars of carbonization temperatures of 500 and 625°C.

	500°C char				625°C char			
Molecule	CH	O	N	S	CH	O	N	S
	0.432	0.128	0.0148	0.0049	0.293	0.784	0.0110	0.0036
Molecular weight	14.80				13.83			
Heat of combustion, $-\Delta H_c$	109.79 $\frac{\text{kcal}}{\text{mole}}$				109.91 $\frac{\text{kcal}}{\text{mole}}$			
Enthalpy of formation, $\Delta H_{f,298}^\circ$	+0.982 $\frac{\text{kcal}}{\text{mole}}$				+5.85 $\frac{\text{kcal}}{\text{mole}}$			
S_{298}° (estimates, in cal/mole K)	3.17				2.71			
C_p (estimates, in cal/mole K)	2.63 + 0.0031 T				2.29 + 0.0031 T			

amorphous carbon. Runs were made for 1, 30, and 70 atm for 10% combustion, 30 and 70 atm for 20% combustion. (These runs correspond with Tables A-6, A-8, A-10, A-11, A-13, A-15, A-21, A-23, A-26 and A-28 of Ref. 1.) The results were remarkably simple and are as follows:

- The present temperature-pressure composition calculations verify those in Ref. 1 in regions of applicability as expected. Coal is never computed to co-exist with amorphous carbon.

- Both chars are unstable. Equilibria with either char are equivalent to the case with no solids allowed (for example, Table A-26 in Ref. 1), except at the lowest temperatures: 600 and 700 K for the 625°C char and 600 K for the 500°C char for 20% combustion and 30 atm where some solid was computed to be present. In all other cases, no chars were computed to be present.

For all practical purposes, then, equilibria with these chars are equivalent to the cases in Ref. 1 with no solid phases computed to be present.

Recommended Thermodynamic State of Carbon

We consider four types of carbon: coal, chars, graphite, and amorphous carbon. As noted above, coal and chars are unstable at the temperatures of interest. It remains to examine graphite and amorphous carbon.

Squires⁸ summarized several kinetic studies, and his resulting equilibrium constants at 1100 K can be used to resolve the issue of the thermodynamic state of carbon. For the reaction at 1100 K,

free energy ΔF_R° is given by

$$\Delta F_R^\circ = \Delta F_{f\text{CH}_4}^\circ - \Delta F_{f\text{C}}^\circ, \quad (2)$$

where, by convention, $\Delta F_{f\text{H}_2}^\circ$ is zero. The value of $\Delta F_{f\text{C}}^\circ$ depends on its state; if it is graphite (the stable state at 1100 K and 1 atm), then ΔF_f° will be zero. Equation (2) can be recast in terms of $\Delta F_{f\text{C}}^\circ$:

$$\Delta F_{f\text{C}}^\circ = \Delta F_{f\text{CH}_4}^\circ - \Delta F_R^\circ,$$

where $\Delta F_{f\text{CH}_4}^\circ$ is 7.25 kcal/mole (JANAF Tables). Thus, carbon is in the graphite form, if $\Delta F_{f\text{R}}^\circ = 7.25$ kcal/mole: if not, it must be some other form.

Squire's results for the various equilibria experiments include values of the equilibrium constant K from which we can calculate ΔF_R° using

$$\Delta F_R^\circ = -RT \ln K.$$

Table 2 contains the values of K calculated from the mole fractions and pressure, ΔF_R° calculated from K, and $\Delta F_{f\text{C}}^\circ$ calculated from ΔF_R° . The results from different experiments are scattered, but all imply a form of carbon unstable with respect to graphite (i.e., $\Delta F_{f\text{C}}^\circ > 0$).

Also included in Table 2 are ΔF_f° values for graphite (necessarily 0) and for the amorphous carbon used in the TIGER code. This carbon is taken to have exactly the same properties as graphite with the exception that $\Delta H_{f298}^\circ = 2.6$ kcal/mole. Since the entropy and heat capacity are the same, and since graphite is the standard state, we must have $\Delta F_f^\circ = \Delta H_f^\circ = 2.6$ kcal/mole at all temperatures.

The average of the experimental data is 3.14 kcal/mole, which is reasonably close to the value 2.6 kcal/mole of the TIGER amorphous carbon. On this basis, the amorphous carbon TIGER calculations of Ref. 1 are good approximations to the experimental data.

Table 2. Equilibrium constant and free energies.

Reference	K	$\Delta F_R^{\circ} \frac{\text{kc}}{\text{mole}}$	ΔF_{fC}°
Dent ⁷	0.05	+6.55	0.70
Squires ⁷	0.11	4.82	2.43
May <i>et al.</i> , Graham ⁷	0.20	3.25	3.73
Jolley <i>et al.</i> , McDougall ⁷	0.49	1.56	5.69
Graphite (theoretical)		7.25	0
Amorphous carbon (TIGER)		4.65	2.6

Lurgi Equilibria

In evaluation of the LLL packed-bed process,^{9,10} base-case economics were calculated using Lurgi gasifier data¹¹ for product compositions. It is true that *in-situ* processes will have lower contact efficiencies than the Lurgi; these efficiencies would cause lower gas quality. On the other hand, residence times for the reduction zone in the packed-bed process may be longer than for the Lurgi and may more than compensate for the poorer contact efficiencies. Thus, it was of interest to calculate equilibria for published Lurgi data. Using data from Moe,³ the reactants for New Mexico coal can be simplified to

$$P = 31.6 \text{ atm (450 psig)}.$$

Calculated results are shown in Table 3 and in Fig. 1. No solids were computed to be present. *Experimental Lurgi data are closely fit by assuming an equilibrium temperature of 1060 K: see Table 4.* Although the exit gas temperatures for a Lurgi gasifier are reported to be 700 to 1100°F (640 to 870 K), the temperatures at the end of the gasification zone are about 1450 to 1650°F (1060 to 1170 K).¹¹ The excellent fit of the thermodynamic calculation with the experimental Lurgi data, together with the close fit of the thermodynamic and experimental temperature, is believed to be more than coincidence. The thermodynamic evidence for a temperature of 1060 K is used in the next section as an approximation to reacting coal-steam-oxygen systems.

Fig. 1. Lurgi equilibrium on a water-free basis. New Mexico coal at 31.6 atm ($CH_{0.887}O_{0.149} + 0.2048 O_2 + 1.573 H_2O$).

Table 3. Equilibrium with Lurgi compositions for New Mexico coal ($\text{CH}_{0.887}\text{O}_{0.149}$ + 0.2048 O_2 + 1.573 H_2O) at 31.6 atm without solids.

Species	Mole % by temperature (K)										
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600
H_2	36.51	37.12	37.79	38.28	37.20	31.81	22.74	13.66	6.79	2.65	0.74
H_2O	30.34	29.72	29.01	28.35	28.61	31.49	36.68	42.25	46.85	49.81	51.23
CO	25.96	25.32	24.49	23.30	20.96	15.93	8.94	3.45	0.90	0.15	0.01
CO_2	7.18	7.83	8.64	9.74	11.66	15.41	20.44	24.14	25.54	25.69	25.57
CH_4	0.01	0.02	0.07	0.33	1.57	5.36	11.20	16.49	19.92	21.70	22.44

Species	Mole %, water free										
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600
H_2	52.41	52.82	53.23	53.43	52.11	46.43	35.91	23.65	12.78	5.28	1.52
CO	37.27	36.03	34.50	32.52	29.36	23.25	14.12	5.97	1.69	0.30	0.02
CO_2	10.31	11.14	12.17	13.59	16.33	22.49	32.28	41.80	48.05	51.19	52.43
CH_4	0.01	0.03	0.10	0.46	2.20	7.82	17.69	28.55	37.48	43.24	46.01

Table 4. Comparison at experimental Lurgi gas compositions with TIGER equilibrium calculation at 1060 K.

Species	Experimental Lurgi gas composition	Best-fit equilibrium
H_2	37.89	42.3
CO	20.24	19.9
CO_2	28.6	26.4
CH_4	11.38	11.6

Effect of Steam/Oxygen Ratios

Steam/oxygen ratios have a large effect on product gas quality. A number of calculations were made varying this ratio. The Lurgi uses a very large ratio (steam/oxygen = 7.68, or a feed of 11.5% oxygen) to avoid high temperatures and damage to the grate. This is probably not such an important consideration in underground gasification.

Much less steam has been used in fixed-bed, steam-oxygen gasifiers in the past. For example, during WWII at Leuna, German technologists¹² operated fixed-bed coal and coke gasifiers up to concentrations of 21% oxygen, or steam/oxygen = 3.76.

Calculations were made for 20% combustion, amorphous carbon ($\Delta H_f = 2.6$ kcal/mole) and Wyoming coal as follows:

Results are given in Tables A1 through A16, while Table A17 summarizes the results from Ref. 1 for steam/oxygen = 2.068.

Figure 2 shows the percent of methane in product gas (water-free) vs steam/oxygen at 1060 K, while Fig. 3 is a similar plot for product heating value. High steam/oxygen ratios are undesirable because they lower the methane content and heating value.

The primary effect at high steam/oxygen ratios appears to be the steam-reforming of methane and carbon monoxide to hydrogen and carbon dioxide. For example, compare Table A3 with Table A11. Both tables are for 30 atm; Table A3 shows results for a ratio of 7.68 (the Lurgi ratio) while Table A11 shows results for a ratio of 3.0. Results for 1060 K are plotted in Table 5.

Fig. 2. Percent methane vs steam/oxygen ratio, by pressure. (For 20% combustion, 1060 K equilibrium.)

Fig. 3. Gas heating value vs steam/oxygen ratio, by pressure. (For 20% combustion, 1060 K equilibrium.)

Table 5. A comparison of 30-atm equilibrium data (water-free basis at 1060 K).

Species	$H_2O/O_2 = 7.68$	$H_2O/O_2 = 3.00$
	(%)	(%)
CH ₄	8.83	17.82
CO	19.05	31.48
H ₂	43.86	26.38
CO ₂	28.26	24.32
Heating value (Btu/scf)	285	361

The methane content is doubled for the lower steam/oxygen ratios. These effects, summarized in Table 6, are seen experimentally for the low pressure steam-oxygen gasification runs at Leuna.¹² Little methane was produced because the pressures were low. Note the reversal of the CO/H₂ ratio, apparently as a result of a shift conversion of CO at the high steam/oxygen ratios ($CO + H_2O \rightleftharpoons CO_2 + H_2$).

Table 6. Experimental steam-oxygen gasification data (from Ref. 12).

Species	Gas composition (%) by % oxygen in feed stream	
	10% O ₂	21% O ₂
CO	21.7	40.7
H ₂	52.5	35.4
CO ₂	24.0	22.5

From these data and if gasifier damage is not a severe problem, one might wish to operate at a ratio of 2 or even less. However, at very low ratios, unreacted carbon is computed to be present. A ratio of at least 2 to 3 is preferred, depending on the pressure. However, in our underground system we wish to avoid slagging or even extensive agglomeration of the ash that could limit reactant access to the coal and could even plug the bed in severe cases. Extensive German fixed-bed gasifier work¹² suggests an upper limit of 22% oxygen ($H_2O/O_2 = 3.55$) to prevent slagging.

This ratio is affected by the melting and agglomeration points of the ash, by heat losses from the gasifier, and by the chemical reactivity of the coal.

Lower steam/oxygen ratios can be used for coals of higher reactivity, coals with higher ash agglomeration or fusion temperatures, or for systems with higher heat losses. Experiments should be conducted with Wyoming coals of interest and with heat losses estimated to fix the safe upper limit for *in-situ* coal gasification.

CONCLUSIONS

From these calculations and from the experimental German work, for efficient gasification, one should operate as close to the ash agglomeration point as is safe. A considerable improvement in methane content and heating value can be made by operating at lower steam/oxygen ratios.

EXTENSION TO OTHER COALS

All calculations in this report and Ref. 1 were based on Wyoming coal with a "molecule" of $\text{CH}_{0.858}\text{O}_{0.208}$, neglecting sulfur and nitrogen. These calculations are easily extended to any other coal, providing the moisture and ash-free elemental analysis is known. Simply calculate the atomic ratios of hydrogen and oxygen to carbon, and express the analysis as CH_xO_y , where x is the atomic hydrogen/carbon ratio and y is the corresponding oxygen/carbon ratio. Then for any of the calculations in this report or Ref. 1, simply make the stoichiometric substitution for $\text{CH}_{0.858}\text{O}_{0.208}$ for the coal of interest, as follows:

$$\text{CH}_{0.858}\text{O}_{0.208} = \text{CH}_x\text{O}_y + (0.429 - 0.5x)\text{H}_2\text{O} + (0.25x - 0.5y - 0.1105)\text{O}_2.$$

Then recalculate the steam and oxygen compositions.

For example, consider Illinois #6 coal, whose chemical analysis can be simplified to $\text{CH}_{0.928}\text{O}_{0.171}$. Then,

$$\begin{aligned}\text{CH}_{0.858}\text{O}_{0.208} &= \text{CH}_{0.928}\text{O}_{0.171} + [0.429 - 0.5(0.928)]\text{H}_2\text{O} \\ &\quad + [0.25(0.928) - 0.5(0.171) - 0.1105]\text{O}_2 \\ &= \text{CH}_{0.928}\text{O}_{0.171} - 0.035\text{H}_2\text{O} + 0.036\text{O}_2.\end{aligned}$$

For a calculation of $\text{CH}_{0.858}\text{O}_{0.208} + 0.4594 \text{H}_2\text{O} + 0.2221 \text{O}_2$, the same thermodynamics apply to

$\text{CH}_{0.928}\text{O}_{0.171} + (0.4594 - 0.035)\text{H}_2\text{O} + (0.2221 + 0.036)\text{O}_2$
or

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Table A1. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.706 \text{H}_2\text{O}$ at 1 atm
(Lurgi ratio: $\text{H}_2\text{O}/\text{O}_2 = 7.68$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
H_2O	34.99	34.30	33.47	32.44	31.17	29.59	27.77	27.76	35.20	45.50	52.34	28.86	-
H_2	33.11	33.80	34.63	35.66	36.93	38.50	40.24	39.05	27.37	13.07	4.06	39.19	55.10
CO	23.56	22.88	22.04	21.01	19.74	18.14	16.01	11.86	4.50	0.79	0.07	17.29	24.31
CO_2	8.34	9.022	9.86	10.88	12.16	13.76	15.83	19.31	24.26	25.70	25.19	14.59	20.51
CH_4	0.00	0.00	0.00	0.00	0.00	0.00	0.15	2.00	8.63	14.93	18.33	0.06	0.08

Table A2. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.706 \text{H}_2\text{O}$ at 10 atm
(Lurgi ratio: $\text{H}_2\text{O}/\text{O}_2 = 7.68$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
H_2O	35.00	34.32	33.49	32.49	31.39	30.88	33.64	40.10	46.98	51.95	54.46	31.98	-
H_2	33.10	33.78	34.60	35.58	36.63	36.65	31.67	21.44	11.43	4.65	1.33	34.66	50.96
CO	23.57	22.88	22.04	21.00	19.61	17.26	12.04	5.35	1.45	0.24	0.02	15.17	22.30
CO_2	8.33	9.01	9.85	10.89	12.23	14.31	18.26	22.81	24.93	25.12	24.89	15.89	23.36
CH_4	0.00	0.00	0.00	0.02	0.13	0.90	4.40	10.30	15.20	18.04	19.30	2.30	3.38

Table A3. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.76 \text{H}_2\text{O}$ at 30 atm
(Lurgi ratio: $\text{H}_2\text{O}/\text{O}_2 = 7.68$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Mole % by temperature (K)													
Species	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060 (Water free)	
H_2O	35.04	34.38	33.63	32.88	32.75	34.94	39.88	45.57	50.35	53.43	54.90	36.92	-
H_2	33.06	33.7]	34.45	35.12	34.80	30.90	22.82	13.95	6.99	2.74	0.77	27.67	43.86
CO	23.58	22.88	22.01	20.82	18.77	14.52	8.27	3.22	0.84	0.14	0.01	12.02	19.05
CO_2	8.32	9.01	9.87	11.01	12.78	16.05	20.50	23.77	24.93	24.98	24.83	17.83	28.26
CH_4	0.00	0.01	0.04	0.18	0.90	3.59	8.53	13.49	16.90	18.72	19.49	5.57	8.83

Table A4. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.76 \text{H}_2\text{O}$ at 70 atm
(Lurgi ratio: $\text{H}_2\text{O}/\text{O}_2 = 7.68$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Mole % by temperature (K)													
Species	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060 (Water free)	
H_2O	35.18	34.64	34.18	34.28	35.99	39.79	44.49	48.84	51.96	54.17	55.12	41.67	-
H_2	32.92	33.44	33.81	33.37	30.49	24.30	16.56	9.63	4.67	1.79	0.50	21.20	36.34
CO	23.56	22.18	21.78	20.06	16.74	11.41	5.84	2.14	0.55	0.09	0.01	9.18	15.74
CO_2	8.32	9.05	10.03	11.53	14.14	18.06	21.94	24.22	24.91	24.90	24.80	19.61	33.6
CH_4	0.02	0.05	0.19	0.76	2.64	6.46	11.18	15.17	17.72	19.04	19.58	8.35	14.3

Table A5. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.1105 \text{H}_2\text{O}$ at 1 atm ($\text{H}_2\text{O}/\text{O}_2 = 5.000$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
H_2	37.38	37.99	38.75	39.68	40.85	42.82	43.43	38.87	24.79	11.31	3.45	43.06	52.14
CO	32.59	31.98	31.21	30.28	29.10	27.58	25.27	18.63	7.10	1.27	0.11	26.66	32.28
H_2O	23.24	22.63	21.88	20.94	19.77	18.31	16.80	17.98	24.31	31.94	37.06	17.71	-
CO_2	6.79	7.40	8.16	9.10	10.27	11.79	14.01	19.74	29.18	33.43	33.84	12.68	15.35
CH_4	0.00	0.00	0.00	0.00	0.00	0.04	0.48	4.78	14.63	22.06	25.53	0.19	0.23

Table A6. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.1105 \text{H}_2\text{O}$ at 10 atm ($\text{H}_2\text{O}/\text{O}_2 = 5.000$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
H_2	37.36	37.97	38.70	39.53	40.12	38.30	30.42	19.28	9.90	3.95	1.12	35.15	44.92
CO	32.59	31.98	31.22	30.24	28.77	25.51	17.86	8.23	2.31	0.39	0.04	22.45	28.69
H_2O	23.25	22.65	21.91	21.03	20.18	20.48	23.66	28.52	33.25	36.80	38.66	21.75	-
CO_2	6.78	7.40	8.16	9.14	10.54	13.42	19.84	27.77	32.40	33.64	33.73	15.99	20.43
CH_4	0.00	0.00	0.01	0.06	0.38	2.29	8.21	16.20	22.14	25.21	26.45	4.66	5.95

Table A7. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.1105 \text{H}_2\text{O}$ at 30 atm ($\text{H}_2\text{O}/\text{O}_2 = 5.000$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
H_2	37.31	37.85	38.40	38.52	36.55	30.21	20.93	12.24	5.99	2.32	0.65	26.50	36.01
CO	32.60	31.96	31.14	29.85	27.10	21.10	12.45	5.03	1.34	0.22	.02	17.64	23.97
H_2	23.30	22.73	22.11	21.65	22.22	24.87	28.72	32.50	35.70	37.89	38.99	26.41	-
CO_2	6.78	7.41	8.24	9.48	11.92	17.00	24.22	30.24	33.01	33.68	33.70	19.89	27.03
CH_4	0.01	0.03	0.12	0.51	2.21	6.81	13.68	19.99	23.95	25.88	26.64	9.56	12.99

Table A8. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 1.1105 \text{H}_2\text{O}$ at 70 atm ($\text{H}_2\text{O}/\text{O}_2 = 5.000$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
H_2	37.08	37.37	37.18	35.37	30.43	22.80	14.82	8.35	3.98	1.51	0.42	19.61	28.07
CO	32.59	31.87	30.76	28.58	24.08	16.88	8.98	3.40	0.88	0.15	0.01	13.72	19.64
H_2O	23.47	23.07	22.89	23.55	25.70	28.88	32.02	34.76	36.98	38.44	39.15	30.14	-
CO_2	6.82	7.54	8.62	10.64	14.56	20.65	27.16	31.55	33.32	33.70	33.69	23.25	33.28
CH_4	0.05	0.15	0.54	1.87	5.23	10.79	17.02	21.93	24.83	26.20	26.72	13.28	19.01

Table A9. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 0.663 \text{H}_2\text{O}$ at 1 atm ($\text{H}_2\text{O}/\text{O}_2 = 3.00$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	43.73	43.33	48.25	42.24	41.46	40.41	38.04	29.02	12.87	2.60	0.24	39.46	42.85
H ₂	41.07	41.46	41.95	42.55	43.30	44.06	43.16	33.87	18.53	7.64	2.28	43.70	47.45
H ₂ O	11.20	10.81	10.32	9.72	8.96	8.08	7.62	9.32	11.62	13.75	15.91	7.90	-
CO ₂	4.00	4.39	4.88	5.49	6.26	7.31	9.62	18.29	33.82	43.66	45.87	8.23	8.94
CH ₄	0.00	0.00	0.00	0.00	0.02	0.14	1.53	9.50	23.17	32.36	35.71	0.70	0.76

Table A10. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 0.663 \text{H}_2\text{O}$ at 10 atm ($\text{H}_2\text{O}/\text{O}_2 = 3.00$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	43.73	43.34	42.83	42.12	40.69	36.63	27.29	14.35	4.56	0.81	0.07	32.89	37.34
H ₂	41.05	41.43	41.84	42.13	41.26	36.20	25.80	14.60	6.83	2.63	0.74	32.04	36.38
H ₂ O	11.21	10.83	10.37	9.90	9.80	11.04	13.24	14.45	14.99	15.93	16.74	11.92	-
CO ₂	3.99	4.38	4.90	5.62	7.04	10.99	19.99	32.43	41.80	45.34	46.00	14.59	16.57
CH ₄	0.00	0.01	0.05	0.23	1.21	5.14	13.68	24.16	31.82	35.30	36.45	8.56	9.72

Table A11. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 0.663 \text{H}_2\text{O}$ at 30 atm ($\text{H}_2\text{O}/\text{O}_2 = 3.00$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	43.74	43.32	42.69	41.40	38.16	31.17	20.30	9.32	2.70	0.47	0.04	26.82	31.48
H ₂	40.95	41.18	41.09	39.68	34.96	26.39	16.60	8.83	4.05	1.53	0.43	22.47	26.38
H ₂ O	11.26	10.95	10.71	10.94	12.28	14.32	15.56	15.67	15.81	16.41	16.91	14.82	-
CO ₂	4.01	4.45	5.11	6.45	9.70	16.54	26.98	37.44	43.64	45.68	46.03	20.72	24.32
CH ₄	0.03	0.11	0.40	1.52	4.90	11.59	20.56	28.79	33.80	35.91	36.59	15.18	17.82

Table A12. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.222 \text{O}_2 + 0.663 \text{H}_2\text{O}$ at 70 atm ($\text{H}_2\text{O}/\text{O}_2 = 3.00$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	43.69	43.23	42.19	39.80	34.75	26.20	15.53	6.53	1.77	0.31	0.03	21.93	26.23
H ₂	40.45	40.12	38.51	34.39	27.36	18.86	11.23	5.84	2.69	1.00	0.28	15.81	18.91
H ₂ O	11.46	11.42	11.82	13.08	14.94	16.32	16.51	16.18	16.59	16.65	16.99	16.40	-
CO ₂	4.09	4.71	5.90	8.46	13.58	21.90	31.98	40.29	44.40	45.85	46.05	25.93	31.01
CH ₄	0.17	0.52	1.58	4.27	9.37	16.72	24.77	31.16	34.55	36.20	36.66	19.94	23.85

Table A13. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 0.332 \text{H}_2\text{O}$ at 1 atm ($\text{H}_2\text{O}/\text{O}_2$ = 1.5; ΔH_f carbon = +2.6 kcal/mole).

Species in gas phase	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	56.42	56.43	56.45	56.48	56.47	55.98	52.13	35.89	13.47	2.69	0.27	54.44	55.11
H ₂	43.50	43.43	43.29	42.98	42.28	40.58	36.73	29.31	17.76	7.37	2.02	39.04	39.52
CH ₄	0.07	0.11	0.20	0.39	0.84	1.95	4.82	11.69	22.36	31.04	35.61	3.10	3.14
H ₂ O	0.01	0.02	0.04	0.08	0.21	0.63	2.08	6.07	11.10	13.36	12.98	1.21	-
CO ₂	0.00	0.01	0.02	0.06	0.21	0.86	4.23	17.03	35.30	45.52	49.11	2.21	2.24
Carbon as:													
CO	98.52	98.48	98.40	98.18	97.46	94.58	81.96	46.52	13.93	2.48	0.24		
CH ₄	0.11	0.20	0.35	0.68	1.44	3.29	7.58	15.16	23.14	28.57	31.49		
CO ₂	0.01	0.02	0.04	0.11	0.36	1.45	6.65	22.08	36.55	41.89	43.43		
C(s)	1.34	1.30	1.21	1.03	0.74	0.68	3.80	16.25	26.36	27.08	24.88		

Table A14. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 0.332 \text{H}_2\text{O}$ at 10 atm ($\text{H}_2\text{O}/\text{O}_2 = 1.5$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species in gas phase	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	56.66	56.78	56.71	56.37	55.29	50.36	34.96	16.02	4.73	0.87	0.09	44.20	46.87
H ₂	42.57	41.91	41.08	39.31	35.35	28.86	21.47	13.38	6.59	2.46	0.65	25.90	27.47
CH ₄	0.64	1.04	1.53	2.59	5.13	9.79	16.35	24.17	30.50	34.35	36.44	12.41	13.16
H ₂ O	0.09	0.17	0.41	0.95	1.97	4.04	8.19	12.44	14.57	14.57	13.37	5.70	-
CO ₂	0.04	0.09	0.26	0.77	2.24	6.94	19.03	33.98	43.61	47.75	49.45	11.78	12.49
Carbon as:													
CO	98.25	97.93	96.94	94.37	88.24	72.68	42.42	16.38	4.37	0.77	0.08		
CH ₄	1.11	1.80	2.61	4.34	8.19	14.14	19.83	24.70	28.22	30.51	31.95		
CO ₂	0.07	0.16	0.44	1.29	3.57	10.01	23.09	34.73	40.35	42.41	43.37		
C(s)	0.56	0.11	0.0	0.00	0.00	3.17	14.65	24.19	27.06	26.30	24.60		

Table A15. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 0.332 \text{H}_2\text{O}$ at 30 atm ($\text{H}_2\text{O}/\text{O}_2 = 1.5$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species in gas phase	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	56.77	56.72	56.41	55.54	53.09	41.87	24.39	9.91	2.77	0.50	0.05	34.88	38.36
H ₂	41.24	40.18	38.04	34.01	27.29	21.03	14.43	8.36	3.94	1.44	0.38	18.39	20.22
CH ₄	1.37	1.98	3.22	5.69	10.25	15.34	21.77	27.89	32.26	34.88	36.44	17.91	19.70
H ₂ O	0.36	0.73	1.39	2.47	3.89	7.38	11.60	14.62	15.61	15.10	13.76	9.07	-
CO ₂	0.17	0.40	0.95	2.28	5.48	14.37	27.81	39.22	45.42	48.07	49.37	19.75	21.72
Carbon as:													
CO	97.23	95.76	92.75	87.44	76.99	52.89	26.23	9.49	2.50	0.44	0.04		
CH ₄	2.35	3.35	5.29	8.96	14.86	19.38	23.42	26.69	29.10	30.75	31.91		
CO ₂	0.29	0.67	1.55	3.59	7.95	18.16	29.91	37.54	40.98	42.39	43.22		
C(s)	0.00	0.00	0.00	0.00	0.19	9.57	20.44	26.29	27.42	26.41	24.83		

Table A16. Equilibrium calculations for $\text{CH}_{0.858}^{0.208} + 0.2221 \text{O}_2 + 0.332 \text{H}_2\text{O}$ at 70 atm ($\text{H}_2\text{O}/\text{O}_2 = 1.5$; $\Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole}$).

Species in gas phase	Mole % by temperature (K)												1060 (Water free)
	1600	1500	1400	1300	1200	1100	1000	900	800	700	600	1060	
CO	56.85	56.67	56.12	54.57	47.93	33.46	17.46	6.66	1.81	0.32	0.03	27.06	30.70
H ₂	39.32	37.04	33.21	27.33	21.18	15.59	10.20	5.70	2.63	0.95	0.25	13.43	15.24
CH ₄	2.35	3.59	5.80	9.55	14.04	19.15	24.70	29.60	32.90	34.91	36.22	21.37	24.24
H ₂ O	1.00	1.70	2.75	4.04	6.43	10.35	14.01	16.10	16.50	15.78	14.40	11.81	-
CO ₂	0.48	1.00	2.11	4.51	10.42	21.45	33.54	41.95	46.17	48.04	49.11	26.29	29.82
Carbon as:													
CO	95.26	92.51	87.64	79.51	62.80	38.02	17.46	6.15	1.61	0.28	0.03		
CH ₄	3.94	5.86	9.06	13.92	18.39	21.76	24.79	27.35	29.30	30.67	31.68		
CO ₂	0.80	1.63	3.30	6.57	13.65	24.38	33.54	38.76	41.12	42.20	42.96		
C(s)	0.00	0.00	0.00	0.00	5.16	15.85	24.21	27.73	27.97	26.84	25.33		

Table A17. Equilibrium calculations for $\text{CH}_{0.858}\text{O}_{0.208} + 0.2221 \text{O}_2 + 0.4594 \text{H}_2\text{O}$ at 1060 K by pressure
 $(\text{H}_2\text{O}/\text{O}_2 = 2.068; \Delta H_f \text{ carbon} = +2.6 \text{ kcal/mole})$.

Species in gas phase	1 atm		10 atm		30 atm		50 atm		70 atm	
	Water- free		Water- free		Water- free		Water- free		Water- free	
CO	48.39	49.93	40.04	42.98	32.41	35.79	28.54	31.91	25.45	28.79
H ₂	42.20	43.54	28.18	30.25	19.29	21.30	15.67	17.52	13.79	15.60
H ₂ O	3.08	-	6.84	-	9.43	-	10.54	-	11.61	-
CO ₂	4.67	4.82	13.18	14.15	20.30	22.42	23.76	26.56	26.15	29.59
CH ₄	1.65	1.70	11.75	12.61	18.57	20.50	21.48	24.01	22.99	26.01
Heating value (Btu/scf)	312		357		386		396		400	

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