

~~OFR 494~~



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ERP/ERL 78-111 (TR)

THERMODYNAMICS OF COAL CONVERSION REACTIONS

PART 4. THE SHIFT REACTION

R.A. CAMPBELL
COAL CONVERSION SECTION

DECEMBER, 1978.

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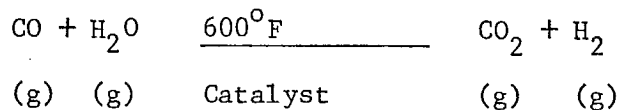
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THERMODYNAMICS OF COAL CONVERSION REACTIONS

PART 4 - THE SHIFT REACTION

This reaction is generally used to alter the composition of the gas produced in a gasifier, by increasing the hydrogen content at the expense of the other component gases.



More CO_2 also is produced but this can be scrubbed out. This report constitutes a brief examination of the thermodynamics of this reaction.

As in previous reports (Parts 1, 2, 3) the free energy change for the reaction can be expressed in the form

$$\Delta F = A + BT \ln T + CT^2 + D/T + ET$$

The information for calculation of the parameters was derived from Ref.(1). The derived parameters are listed at the end, Appendix A. The program was established in the NOVA computer and values for the free energy of the reaction, $\ln K$, and K , were calculated from 100°C to 1400°C . The information is given in Appendix A.

In addition it is sometimes useful to see the relationship set out graphically. A program was established in the Hewlett-Packard calculator-plotter, and the relationship was plotted from 200°C to 1000°C and shown in Fig.1. It appears that the free energy change for the reaction is negative at low temperatures, reaches a value of zero at about 847°C , and is positive at higher temperatures. Evidently though the reaction goes best at about 600°F (316°C) in the presence of a catalyst. At that temperature the free energy of the reaction was calculated to be about 4190 kcal.

The heat of the reaction at 298°K was calculated to be 681 kcal.

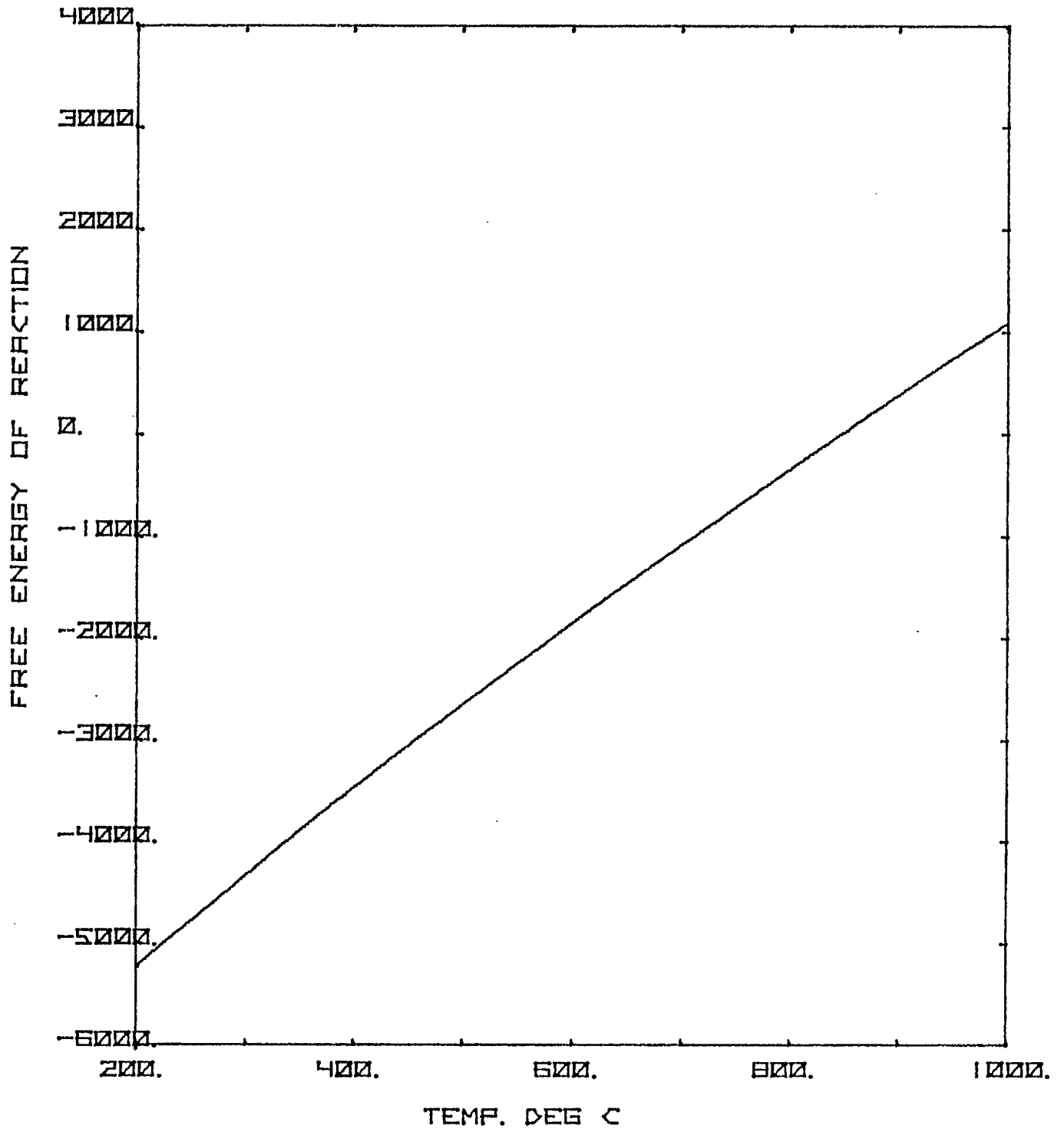


FIGURE 1. FREE ENERGY VERSUS TEMPERATURE FOR THE SHIFT REACTION

APPENDIX A

SHIFT REACTION

TEMP. DEG.C	TEMP. DEG.K	FREE ENERGY KCAL/KG-MOL	LN K	K	
100.	373.	-6150.	8.30	0.402508E	4
105.	378.	-6102.	8.13	0.338474E	4
110.	383.	-6055.	7.95	0.285953E	4
115.	388.	-6007.	7.79	0.242668E	4
120.	393.	-5960.	7.63	0.205824E	4
125.	398.	-5913.	7.48	0.177006E	4
130.	403.	-5866.	7.33	0.152093E	4
135.	408.	-5819.	7.18	0.131191E	4
140.	413.	-5772.	7.04	0.113581E	4
145.	418.	-5725.	6.89	0.986870E	3
150.	423.	-5678.	6.75	0.860424E	3
155.	428.	-5631.	6.62	0.752576E	3
160.	433.	-5585.	6.49	0.660542E	3
165.	438.	-5539.	6.37	0.581488E	3
170.	443.	-5492.	6.24	0.513429E	3
175.	448.	-5446.	6.12	0.454551E	3
180.	453.	-5400.	6.00	0.403731E	3
185.	458.	-5354.	5.88	0.359486E	3
190.	463.	-5308.	5.77	0.320931E	3
195.	468.	-5262.	5.65	0.287238E	3
200.	473.	-5217.	5.55	0.257713E	3
205.	478.	-5171.	5.45	0.231774E	3
210.	483.	-5125.	5.34	0.208927E	3
215.	488.	-5080.	5.24	0.188753E	3
220.	493.	-5035.	5.14	0.170896E	3
225.	498.	-4990.	5.04	0.155054E	3
230.	503.	-4945.	4.95	0.140967E	3
235.	508.	-4900.	4.86	0.128413E	3
240.	513.	-4855.	4.76	0.117202E	3
245.	518.	-4810.	4.67	0.107169E	3
250.	523.	-4765.	4.59	0.981718E	2
255.	528.	-4721.	4.50	0.900879E	2
260.	533.	-4676.	4.42	0.828111E	2
265.	538.	-4632.	4.33	0.762482E	2
270.	543.	-4588.	4.25	0.703189E	2
275.	548.	-4543.	4.17	0.649522E	2
280.	553.	-4499.	4.10	0.600856E	2
285.	558.	-4455.	4.02	0.556580E	2
290.	563.	-4411.	3.94	0.516486E	2
295.	568.	-4368.	3.87	0.479869E	2
300.	573.	-4324.	3.80	0.446458E	2
305.	578.	-4280.	3.73	0.415925E	2
310.	583.	-4237.	3.65	0.387984E	2
315.	588.	-4193.	3.59	0.362377E	2
320.	593.	-4150.	3.52	0.338878E	2
325.	598.	-4107.	3.46	0.317281E	2
330.	603.	-4064.	3.39	0.297409E	2
335.	608.	-4021.	3.33	0.279399E	2
340.	613.	-3978.	3.27	0.262208E	2
345.	618.	-3935.	3.21	0.246606E	2

TEMP. DEG.C	TEMP. DEG.K	FREE ENERGY KCAL/KG-MOL	LN K	K	
350.	623.	-3892.	3.14	0.232178E	2
355.	628.	-3849.	3.09	0.218819E	2
360.	633.	-3807.	3.03	0.205437E	2
365.	638.	-3754.	2.97	0.194947E	2
370.	643.	-3722.	2.91	0.184273E	2
375.	648.	-3680.	2.85	0.174347E	2
380.	653.	-3637.	2.80	0.165107E	2
385.	658.	-3595.	2.75	0.155496E	2
390.	663.	-3553.	2.70	0.148463E	2
395.	668.	-3511.	2.65	0.140964E	2
400.	673.	-3469.	2.59	0.133954E	2
405.	678.	-3427.	2.54	0.127397E	2
410.	683.	-3386.	2.50	0.121258E	2
415.	688.	-3344.	2.45	0.115504E	2
420.	693.	-3302.	2.40	0.110107E	2
425.	698.	-3251.	2.35	0.105340E	2
430.	703.	-3219.	2.31	0.100280E	2
435.	708.	-3178.	2.26	0.958038E	1
440.	713.	-3137.	2.21	0.915911E	1
445.	718.	-3096.	2.17	0.876234E	1
450.	723.	-3055.	2.13	0.838835E	1
455.	728.	-3014.	2.08	0.803550E	1
460.	733.	-2973.	2.04	0.770261E	1
465.	738.	-2932.	2.00	0.738804E	1
470.	743.	-2891.	1.95	0.709067E	1
475.	748.	-2850.	1.92	0.680937E	1
480.	753.	-2810.	1.88	0.654307E	1
485.	758.	-2769.	1.84	0.629082E	1
490.	763.	-2729.	1.80	0.605172E	1
495.	768.	-2688.	1.76	0.582493E	1
500.	773.	-2648.	1.72	0.560968E	1
505.	778.	-2608.	1.69	0.540527E	1
510.	783.	-2568.	1.65	0.521102E	1
515.	788.	-2528.	1.61	0.502633E	1
520.	793.	-2488.	1.58	0.485051E	1
525.	798.	-2448.	1.54	0.468334E	1
530.	803.	-2408.	1.51	0.452401E	1
535.	808.	-2368.	1.48	0.437218E	1
540.	813.	-2328.	1.44	0.422741E	1
545.	818.	-2289.	1.41	0.408929E	1
550.	823.	-2249.	1.38	0.395745E	1
555.	828.	-2209.	1.34	0.383154E	1
560.	833.	-2170.	1.31	0.371124E	1
565.	838.	-2131.	1.28	0.359623E	1
570.	843.	-2091.	1.25	0.348623E	1
575.	848.	-2052.	1.22	0.338097E	1
580.	853.	-2013.	1.19	0.328020E	1
585.	858.	-1974.	1.15	0.318358E	1
590.	863.	-1935.	1.13	0.309120E	1
595.	868.	-1895.	1.10	0.300254E	1

TEMP. DEG.C	TEMP. DEG.K	FREE ENERGY KCAL/KG-MOL	LN K	K	
600.	873.	-1857.	1.07	0.291750E	1
605.	878.	-1818.	1.04	0.283591E	1
610.	883.	-1779.	1.01	0.275759E	1
615.	888.	-1741.	0.99	0.268238E	1
620.	893.	-1702.	0.96	0.261012E	1
625.	898.	-1663.	0.93	0.254068E	1
630.	903.	-1625.	0.91	0.247391E	1
635.	908.	-1586.	0.88	0.240969E	1
640.	913.	-1548.	0.85	0.234789E	1
645.	918.	-1510.	0.83	0.228841E	1
650.	923.	-1471.	0.80	0.223113E	1
655.	928.	-1433.	0.78	0.217595E	1
660.	933.	-1395.	0.75	0.212277E	1
665.	938.	-1357.	0.73	0.207152E	1
670.	943.	-1319.	0.70	0.202209E	1
675.	948.	-1281.	0.68	0.197440E	1
680.	953.	-1243.	0.66	0.192839E	1
685.	958.	-1205.	0.63	0.188397E	1
690.	963.	-1168.	0.61	0.184108E	1
695.	968.	-1130.	0.59	0.179965E	1
700.	973.	-1092.	0.57	0.175961E	1
705.	978.	-1055.	0.54	0.172092E	1
710.	983.	-1017.	0.52	0.168351E	1
715.	988.	-980.	0.50	0.164732E	1
720.	993.	-942.	0.48	0.161232E	1
725.	998.	-905.	0.46	0.157844E	1
730.	1003.	-868.	0.44	0.154565E	1
735.	1008.	-830.	0.41	0.151390E	1
740.	1013.	-793.	0.39	0.148315E	1
745.	1018.	-756.	0.37	0.145335E	1
750.	1023.	-719.	0.35	0.142448E	1
755.	1028.	-682.	0.33	0.139649E	1
760.	1033.	-645.	0.31	0.135935E	1
765.	1038.	-608.	0.29	0.134303E	1
770.	1043.	-571.	0.28	0.131749E	1
775.	1048.	-534.	0.26	0.129271E	1
780.	1053.	-498.	0.24	0.125866E	1
785.	1058.	-461.	0.22	0.124531E	1
790.	1063.	-424.	0.20	0.122263E	1
795.	1068.	-388.	0.18	0.120060E	1
800.	1073.	-351.	0.16	0.117920E	1
805.	1078.	-315.	0.15	0.115841E	1
810.	1083.	-278.	0.13	0.113819E	1
815.	1088.	-242.	0.11	0.111854E	1
820.	1093.	-206.	0.09	0.109942E	1
825.	1098.	-170.	0.07	0.108083E	1
830.	1103.	-133.	0.06	0.106275E	1
835.	1108.	-97.	0.04	0.104515E	1
840.	1113.	-61.	0.03	0.102801E	1
845.	1118.	-25.	0.01	0.101134E	1

TEMP. DEG.C	TEMP. DEG.K	FREE ENERGY KCAL/KG-MOL	LN K	K
850.	1123.	11.	-0.00	0.995096E 0
855.	1128.	47.	-0.02	0.979280E 0
860.	1133.	83.	-0.04	0.963872E 0
865.	1138.	119.	-0.05	0.948851E 0
870.	1143.	154.	-0.06	0.934231E 0
875.	1148.	190.	-0.08	0.919972E 0
880.	1153.	225.	-0.09	0.905071E 0
885.	1158.	262.	-0.11	0.892516E 0
890.	1163.	297.	-0.13	0.879296E 0
895.	1168.	333.	-0.14	0.866401E 0
900.	1173.	368.	-0.16	0.853821E 0
905.	1178.	404.	-0.17	0.841544E 0
910.	1183.	439.	-0.19	0.829562E 0
915.	1188.	474.	-0.20	0.817867E 0
920.	1193.	510.	-0.22	0.806448E 0
925.	1198.	545.	-0.23	0.795298E 0
930.	1203.	580.	-0.24	0.784407E 0
935.	1208.	615.	-0.26	0.773770E 0
940.	1213.	651.	-0.27	0.763377E 0
945.	1218.	686.	-0.28	0.753222E 0
950.	1223.	721.	-0.30	0.743297E 0
955.	1228.	756.	-0.31	0.733595E 0
960.	1233.	791.	-0.32	0.724112E 0
965.	1238.	826.	-0.34	0.714839E 0
970.	1243.	860.	-0.35	0.705770E 0
975.	1248.	895.	-0.36	0.696901E 0
980.	1253.	930.	-0.37	0.688225E 0
985.	1258.	965.	-0.39	0.679736E 0
990.	1263.	999.	-0.40	0.671430E 0
995.	1268.	1034.	-0.41	0.663301E 0
1000.	1273.	1069.	-0.42	0.655345E 0
1005.	1278.	1103.	-0.43	0.647556E 0
1010.	1283.	1138.	-0.45	0.639931E 0
1015.	1288.	1172.	-0.46	0.632464E 0
1020.	1293.	1207.	-0.47	0.625151E 0
1025.	1298.	1241.	-0.48	0.617988E 0
1030.	1303.	1275.	-0.49	0.610972E 0
1035.	1308.	1310.	-0.50	0.604097E 0
1040.	1313.	1344.	-0.52	0.597361E 0
1045.	1318.	1378.	-0.53	0.590760E 0
1050.	1323.	1412.	-0.54	0.584291E 0
1055.	1328.	1446.	-0.55	0.577948E 0
1060.	1333.	1480.	-0.56	0.571731E 0
1065.	1338.	1514.	-0.57	0.565635E 0
1070.	1343.	1548.	-0.58	0.559657E 0
1075.	1348.	1582.	-0.59	0.553794E 0
1080.	1353.	1616.	-0.60	0.548043E 0
1085.	1358.	1650.	-0.61	0.542402E 0
1090.	1363.	1684.	-0.62	0.536868E 0
1095.	1368.	1718.	-0.63	0.531438E 0

TEMP. DEG.C	TEMP. DEG.K	FREE ENERGY KCAL/KG-MOL	LN K	K	
1100.	1373.	1752.	-0.64	0.526109E	0
1105.	1378.	1785.	-0.65	0.520880E	0
1110.	1383.	1819.	-0.66	0.515747E	0
1115.	1388.	1853.	-0.67	0.510708E	0
1120.	1393.	1886.	-0.68	0.505751E	0
1125.	1398.	1920.	-0.69	0.500904E	0
1130.	1403.	1953.	-0.70	0.496135E	0
1135.	1408.	1987.	-0.71	0.491451E	0
1140.	1413.	2020.	-0.72	0.486851E	0
1145.	1418.	2054.	-0.73	0.482332E	0
1150.	1423.	2087.	-0.74	0.477893E	0
1155.	1428.	2121.	-0.75	0.473532E	0
1160.	1433.	2154.	-0.76	0.469246E	0
1165.	1438.	2187.	-0.77	0.465035E	0
1170.	1443.	2220.	-0.77	0.460896E	0
1175.	1448.	2254.	-0.78	0.456829E	0
1180.	1453.	2287.	-0.79	0.452831E	0
1185.	1458.	2320.	-0.80	0.448900E	0
1190.	1463.	2353.	-0.81	0.445036E	0
1195.	1468.	2386.	-0.82	0.441236E	0
1200.	1473.	2419.	-0.83	0.437500E	0
1205.	1478.	2452.	-0.84	0.433825E	0
1210.	1483.	2485.	-0.84	0.430211E	0
1215.	1488.	2518.	-0.85	0.426657E	0
1220.	1493.	2551.	-0.86	0.423160E	0
1225.	1498.	2583.	-0.87	0.419720E	0
1230.	1503.	2616.	-0.88	0.416336E	0
1235.	1508.	2649.	-0.88	0.413005E	0
1240.	1513.	2682.	-0.89	0.409728E	0
1245.	1518.	2714.	-0.90	0.406503E	0
1250.	1523.	2747.	-0.91	0.403329E	0
1255.	1528.	2780.	-0.92	0.400205E	0
1260.	1533.	2812.	-0.92	0.397129E	0
1265.	1538.	2845.	-0.93	0.394102E	0
1270.	1543.	2877.	-0.94	0.391121E	0
1275.	1548.	2910.	-0.95	0.388186E	0
1280.	1553.	2942.	-0.95	0.385296E	0
1285.	1558.	2975.	-0.96	0.382449E	0
1290.	1563.	3007.	-0.97	0.379646E	0
1295.	1568.	3039.	-0.98	0.376886E	0
1300.	1573.	3072.	-0.98	0.374166E	0
1305.	1578.	3104.	-0.99	0.371487E	0
1310.	1583.	3136.	-1.00	0.368848E	0
1315.	1588.	3169.	-1.00	0.366248E	0
1320.	1593.	3201.	-1.01	0.363686E	0
1325.	1598.	3233.	-1.02	0.361162E	0
1330.	1603.	3265.	-1.03	0.358674E	0
1335.	1608.	3297.	-1.03	0.356223E	0
1340.	1613.	3329.	-1.04	0.353806E	0
1345.	1618.	3361.	-1.05	0.351424E	0

TEMP. DEG.C	TEMP. DEG.K	FREE ENERGY KCAL/KG-MOL	LN K	K
1350.	1623.	3393.	-1.05	0.349077E 0
1355.	1628.	3425.	-1.06	0.345762E 0
1360.	1633.	3457.	-1.07	0.344481E 0
1365.	1638.	3489.	-1.07	0.342231E 0
1370.	1643.	3521.	-1.08	0.340013E 0
1375.	1648.	3553.	-1.09	0.337826E 0
1380.	1653.	3585.	-1.09	0.335669E 0
1385.	1658.	3616.	-1.10	0.333542E 0
1390.	1663.	3648.	-1.10	0.331444E 0
1395.	1668.	3680.	-1.11	0.329375E 0
1400.	1673.	3711.	-1.12	0.327334E 0

A= -11330.000000
B= -3.090000
C= 0.000300
D= 95000.000000
E = 31.390000

EQUATION: $F = A + B \cdot T \cdot \ln(T) + C \cdot T \cdot T + D/T + E \cdot T$
STOP
R

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