Supporting Information

Chemical equilibria in methanol synthesis including the water-gas shift reaction: a critical reassessment

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1. Introduction

This document contains further details regarding the collected (pseudo-)experimental equilibrium constants and the calculation methods applied.

- Table S2.1 gives an overview of the collected Kp_1^0- and Kp_2^0-values.
- Table S2.2 presents the experimental equilibrium data as measured by Graaf et al. [1, 2] (pressure, temperature and gas composition).
- The recalculated equilibrium composition data of Liu et al. [26] are presented in Table S2.3.
- Details of the reactor simulations for methanol synthesis experimental results are given in Table S2.4.
- Finally, an overview of the thermochemical basic data as used in this publication is given in Table S2.5 including the derivation of the Kp^0-relationship.

In combination with the information presented in the underlying literature sources (e.g. reactor inlet composition, measured conversions, selectivities, product yields and/or reaction rates) all results can be reproduced, checked or recalculated, if desired.

2. Detail information

Table S2.1 contains the pseudo-experimental Kp_1^0- and Kp_2^0-values. Where no Kp_1^0-values are listed, the experimental results are based on the (reverse) water-gas shift reaction without methanol formation. In several cases no Kp_2^0-values are listed. Here, it is not possible to derive (accurate) Kp_2^0-values from the experimental information, because the reactor feed contains no CO_2 (Hilmen et al. [68]) or the necessary information is either not available or not suitable from an accuracy point of view.

Table S2.1 Collected Kp_1^0- and Kp_2^0-values

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
1	533.15	40	1.209E-03	1.262E-02	An et al.[32]	Figure 4
2	553.15	40	5.521E-04	1.675E-02		
3	521.55	20	2.108E-03	-	Bill [65]	Figure 13 (Cat. A, B)
4	552.55	20	4.991E-04	-		
5	572.35	20	1.940E-04	-		
6	568.04	20	2.483E-04	-		
7	533.91	20	1.064E-03	-		Figure 19 (CO_2/H_2 1/10)
8	552.49	20	4.783E-04	-		
9	570.55	20	2.215E-04	-		
10	571.08	20	2.017E-04	-		
11	509.51	20	3.529E-03	-		
12	524.92	20	1.505E-03	-		
13	550.38	20	6.068E-04	-		
14	575.31	20	2.257E-04	-		
15	523.17	1.013	-	1.215E-02	Brooks et al. [33]	Slide 8
16	548.13	1.013	-	1.789E-02		
17	573.16	1.013	-	2.578E-02		
18	473.15	10	1.725E-02	4.480E-03	Chen & Yuan [34]	Figure 4
19	483.15	10	1.053E-02	5.424E-03		Figure 8
20	491.15	10	7.112E-03	6.216E-03		
21	500.15	10	4.808E-03	7.586E-03		
22	534.33	1.013	-	1.214E-02	Dagle et al. [35]	Figure 3
23	564.00	1.013	-	2.097E-02		
24	589.06	1.013	-	2.793E-02		
25	587.85	1.013	-	2.712E-02		
26	723.15	1.013	-	1.368E-01	Emmett & Shultz [19]	Text p. 1789
27	788.15	1.013	-	2.320E-01		
28	843.15	1.013	-	3.401E-01		
29	873.15	1.013	-	3.799E-01	Emmett & Shultz [20]	Table IX
30	973.15	1.013	-	6.238E-01		
31	1073.15	1.013	-	9.166E-01		
32	1173.15	1.013	-	1.305E+00		
33	1273.15	1.013	-	1.692E+00		
34	923.15	1.013	-	5.330E-01	Emmett & Shultz [21]	Table III
35	973.15	1.013	-	6.570E-01		
36	1023.15	1.013	-	7.868E-01		
37	1073.15	1.013	-	9.183E-01		
38	923.15	1.013	-	4.859E-01		
39	973.15	1.013	-	6.169E-01		
40	1023.15	1.013	-	7.508E-01		
41	1073.15	1.013	-	8.929E-01		
42	723.15	1.1	-	1.380E-01	Galuszka et al. [36]	Figure 4
43	723.15	1.1	-	1.272E-01		
44	723.15	1.1	-	1.383E-01		
45	474.4	10.7	1.599E-02	4.040E-03	Graaf et al. [1, 2]	Table S2 (see below)
46	488.2	19.3	7.657E-03	6.050E-03		
47	489.6	10.6	7.378E-03	5.420E-03		
48	502.3	10.7	4.025E-03	7.400E-03		
49	509.3	9.8	2.915E-03	8.820E-03		
50	530.4	10.8	1.160E-03	1.310E-02		
51	532.3	11.5	1.071E-03	1.330E-02		
52	506.4	26.5	3.258E-03	9.160E-03		
53	509.1	34.6	2.852E-03	8.890E-03		
54	515.2	32.6	2.144E-03	1.000E-02		
55	518.7	25.2	1.849E-03	1.100E-02		
56	534.9	23.8	1.015E-03	1.520E-02		
57	538.1	26.5	8.694E-04	1.510E-02		

Table S2.1 Collected Kp_1^0- and Kp_2^0-values (continued)

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
58	472.4	44.5	1.648E-02	4.190E-03	Graaf et al. [1, 2] (continued)	Table S2 (see below)
59	481.0	63.1	1.031E-02	5.460E-03		
60	487.8	48.7	7.474E-03	6.070E-03		
61	488.1	50.5	7.650E-03	5.760E-03		
62	495.2	72.2	5.078E-03	7.210E-03		
63	502.3	50.5	3.834E-03	7.580E-03		
64	509.3	72.2	2.704E-03	9.400E-03		
65	516.9	44.2	1.973E-03	1.020E-02		
66	530.0	43.4	1.155E-03	1.340E-02		
67	536.2	49.8	9.126E-04	1.440E-02		
68	480.4	49.6	1.247E-02	5.150E-03		
69	491.1	62.1	6.976E-03	6.230E-03		
70	492.5	27.1	6.664E-03	7.310E-03		
71	497.0	72.1	5.314E-03	6.920E-03		
72	503.6	50.3	3.876E-03	7.670E-03		
73	503.9	31.4	3.993E-03	6.990E-03		
74	504.7	30.7	4.009E-03	7.810E-03		
75	507.5	32.9	3.162E-03	7.930E-03		
76	512.7	72.7	2.551E-03	8.560E-03		
77	518.4	52.2	2.077E-03	1.060E-02		
78	519.8	30.7	1.966E-03	1.000E-02		
79	530.4	43.0	1.163E-03	1.340E-02		
80	536.9	49.8	8.974E-04	1.420E-02		
81	538.0	26.6	8.585E-04	1.490E-02		
82	538.8	30.5	9.029E-04	1.710E-02		
83	560.04	45	4.307E-04	-	Hilmen et al. [68]	Figure 1
84	560.04	45	4.663E-04	-		
85	562.97	45	3.982E-04	-		
86	564.00	45	4.277E-04	-		
87	573.97	45	2.809E-04	-		
88	574.89	45	2.198E-04	-		
89	574.89	45	2.288E-04	-		
90	575.97	45	2.669E-04	-		
91	580.89	45	1.751E-04	-		
92	580.89	45	2.032E-04	-		
93	581.97	45	1.938E-04	-		
94	581.97	45	2.069E-04	-		
95	582.89	45	1.725E-04	-		
96	582.89	45	1.788E-04	-		
97	582.89	45	1.975E-04	-		
98	583.97	45	1.788E-04	-		
99	592.82	45	1.189E-04	-		
100	593.21	1.013	-	3.356E-02	Jeong et al. [37]	Figure 4
101	633.08	1.013	-	5.063E-02		
102	593.02	1.013	-	3.398E-02	Jeong et al. [38]	Figure 8
103	593.10	1.013	-	3.163E-02		
104	513.15	20	2.834E-03	1.093E-02	Jingfa et al. [39]	Table 2 (CZA02)
105	793.15	0.1	-	2.301E-01	Kaneko & Oki [22]	Table 5
106	653.15	0.1	-	6.507E-02		
107	648.15	0.1	-	5.307E-02		
108	678.15	0.1	-	8.275E-02	Kaneko & Oki [23]	Tables 1 – 4
109	658.15	0.1	-	6.275E-02		
110	678.15	0.1	-	6.771E-02		
111	659.15	0.1	-	6.235E-02		
112	623.15	1.013	-	4.740E-02	Kodama et al. [24]	Table III
113	673.15	1.013	-	7.960E-02		

Table S2.1 Collected Kp_1^0- and Kp_2^0-values (continued)

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
114	523.15	1.013	1.851E-3	1,219E-2	Kuznetsov et al. [25]	
115	575.15	1.013	2.394E-4	-		
116	493.55	40	5.724E-03	-	Liu et al. [26]	Table S3 (see below)
117	503.35	40	3.762E-03	-		
118	494.25	49	6.653E-03	-		
119	504.35	49	4.059E-03	-		
120	514.05	49	2.343E-03	-		
121	492.75	60	7.638E-03	-		
122	504.15	60	4.306E-03	-		
123	514.25	60	2.598E-03	-		
124	524.65	60	1.426E-03	-		
125	493.45	66	7.651E-03	-		
126	504.45	66	4.446E-03	-		
127	515.15	66	2.796E-03	-		
128	524.75	66	1.554E-03	-		
129	923.00	1.013	-	4.549E-01	Lortie [40]	Figure 4.8 (Pt/SDC)
130	973.15	1.013	-	6.192E-01		
131	573.15	1.20	-	2.576E-02	Mendes [41]	Figure 3
132	1133.15	1.013	-	1.085E+00	Neumann & Köhler [28]	Tables 4 - 10
133	1098.15	1.013	-	1.026E+00		
134	1045.15	1.013	-	8.940E-01		
135	1018.15	1.013	-	7.670E-01		
136	1005.15	1.013	-	7.090E-01		
137	975.15	1.013	-	6.400E-01		
138	956.15	1.013	-	6.180E-01		
139	928.15	1.013	-	5.400E-01		
140	899.15	1.013	-	4.540E-01		
141	874.15	1.013	-	4.230E-01		
142	846.15	1.013	-	3.480E-01		
143	819.15	1.013	-	3.000E-01		
144	788.15	1.013	-	2.410E-01		
145	760.15	1.013	-	1.950E-01		
146	727.15	1.013	-	1.430E-01		
147	698.15	1.013	-	1.140E-01		
148	723.15	1.013	-	1.620E-01		
149	792.15	1.013	-	2.540E-01		
150	862.15	1.013	-	3.840E-01		
151	906.15	1.013	-	4.730E-01		
152	944.15	1.013	-	6.020E-01		
153	991.15	1.013	-	7.140E-01		
154	1044.15	1.013	-	8.500E-01		
155	1083.15	1.013	-	1.050E+00		
156	1132.15	1.013	-	1.170E+00		
157	1172.15	1.013	-	1.290E+00		
158	1216.15	1.013	-	1.454E+00		
159	881.15	1.013	-	4.070E-01		
160	928.15	1.013	-	5.340E-01		
161	977.15	1.013	-	6.710E-01		
162	1031.15	1.013	-	7.700E-01		
163	1081.15	1.013	-	9.430E-01		
164	1117.15	1.013	-	1.092E+00		
165	1170.15	1.013	-	1.338E+00		
166	1213.15	1.013	-	1.425E+00		
167	775.15	1.013	-	2.630E-01		
168	849.15	1.013	-	3.650E-01		
169	903.15	1.013	-	4.470E-01		
170	948.15	1.013	-	5.560E-01		
171	1002.15	1.013	-	7.280E-01		
172	1047.15	1.013	-	8.340E-01		
173	1096.15	1.013	-	9.980E-01		
174	1147.15	1.013	-	1.186E+00		
175	1206.15	1.013	-	1.492E+00		

Table S2.1 Collected Kp_1^0- and Kp_2^0-values (continued)

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
176	788.15	1.013	-	2.410E-01	Neumann & Köhler [28] (continued)	Tables 4 - 10
177	706.15	1.013	-	1.260E-01		
178	1257.15	1.013	-	1.582E+00		
179	1259.15	1.013	-	1.598E+00		
180	1258.15	1.013	-	1.626E+00		
181	1259.15	1.013	-	1.587E+00		
182	1258.15	1.013	-	1.570E+00		
183	1264.15	1.013	-	1.644E+00		
184	1263.15	1.013	-	1.662E+00		
185	1258.15	1.013	-	1.604E+00		
186	1261.15	1.013	-	1.644E+00		
187	1260.15	1.013	-	1.626E+00		
188	1259.15	1.013	-	1.592E+00		
189	1258.15	1.013	-	1.618E+00		
190	1260.15	1.013	-	1.643E+00		
191	1261.15	1.013	-	1.593E+00		
192	1257.15	1.013	-	1.593E+00		
193	1259.15	1.013	-	1.594E+00		
194	1258.15	1.013	-	1.623E+00		
195	1261.15	1.013	-	1.634E+00		
196	1260.15	1.013	-	1.629E+00		
197	1259.15	1.013	-	1.583E+00		
198	553.09	9	4.774E-04	-	Nitta et al. [65]	Figure 3 (CSN-1)
199	740.15	0.1	-	1.898E-01	Oki & Mezaki [29]	Table II
200	762.15	0.1	-	1.824E-01		
201	795.15	0.1	-	2.311E-01		
202	784.15	0.1	-	2.601E-01		
203	512.92	20	3.082E-03	-	Omata et al. [69]	Figure 4
204	685.90	1.013	-	1.010E-01	Panagiotopoulou & Kondarides [42]	Figures 3, 5, 8
205	693.79	1.013	-	9.947E-02		
206	710.06	1.013	-	1.077E-01		
207	722.01	1.013	-	1.261E-01		
208	734.97	1.013	-	1.492E-01		
209	672.03	1.013	-	8.209E-02		
210	725.03	1.013	-	1.386E-01		
211	709.17	1.013	-	1.156E-01	Panagiotopoulou & Kondarides [43]	Figure 8A
212	723.08	1.013	-	1.286E-01		
213	724.11	1.013	-	1.339E-01		
214	728.03	1.013	-	1.377E-01		
215	769.13	1.013	-	1.829E-01		
216	613.07	1.013	-	4.082E-02	Panagiotopoulou & Kondarides [44]	Figure 7A, 7B
217	638.05	1.013	-	5.148E-02		
218	638.16	1.013	-	5.771E-02		
219	650.88	1.013	-	6.114E-02		
220	667.96	1.013	-	7.044E-02		
221	667.06	1.013	-	7.060E-02		
222	693.17	1.013	-	8.506E-02		
223	696.03	1.013	-	9.023E-02		
224	696.03	1.013	-	9.255E-02		
225	725.14	1.013	-	1.097E-01		
226	725.14	1.013	-	1.168E-01		
227	729.03	1.013	-	1.317E-01		
228	660.94	1.013	-	6.812E-02		
229	663.13	1.013	-	7.168E-02		
230	689.02	1.013	-	9.082E-02		
231	692.26	1.013	-	8.815E-02		
232	769.22	1.013	-	1.809E-01		
233	593.15	1.013	-	3.280E-02	Potdar et al. [45]	Figure 5
234	593.15	1.013	-	3.434E-02		

Table S2.1 Collected Kp_1^0- and Kp_2^0-values (continued)

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
235	823.15	1.013	-	3.197E-01	Reddy et al. [46]	Figure 1 (Fe/Ce)
236	518.64	1.013	-	1.024E-02	Reddy et al. [47]	Figures 3, 4, 6
237	525.95	1.013	-	1.124E-02		
238	533.05	1.013	-	1.262E-02		
239	540.56	1.013	-	1.437E-02		
240	547.66	1.013	-	1.617E-02		
241	554.97	1.013	-	1.845E-02		
242	562.27	1.013	-	2.092E-02		
243	569.58	1.013	-	2.342E-02		
244	577.08	1.013	-	2.636E-02		
245	540.86	1.013	-	1.636E-02		
246	548.47	1.013	-	1.759E-02		
247	555.98	1.013	-	2.090E-02		
248	563.08	1.013	-	2.295E-02		
249	570.79	1.013	-	2.693E-02		
250	578.30	1.013	-	2.894E-02		
251	566.13	1.013	-	2.340E-02		
252	558.78	1.013	-	2.102E-02		
253	551.27	1.013	-	1.807E-02		
254	543.59	1.013	-	1.648E-02		
255	536.08	1.013	-	1.415E-02		
256	528.57	1.013	-	1.261E-02		
257	521.05	1.013	-	1.103E-02		
258	513.54	1.013	-	9.740E-03		
259	584.16	1.013	-	2.964E-02		
260	591.47	1.013	-	3.303E-02		
261	598.78	1.013	-	3.671E-02		
262	606.30	1.013	-	4.090E-02		
263	613.22	1.013	-	4.515E-02		
264	621.21	1.013	-	4.998E-02		
265	627.83	1.013	-	5.529E-02		
266	585.89	1.013	-	3.142E-02		
267	593.20	1.013	-	3.475E-02		
268	600.81	1.013	-	3.865E-02		
269	608.13	1.013	-	4.294E-02		
270	622.65	1.013	-	5.143E-02		
271	573.05	1.013	-	2.689E-02	Rosa et al. [48]	Figures 8, 9
272	573.09	1.013	-	2.158E-02		
273	603.18	1.013	-	3.595E-02		
274	523.15	8.106	1.842E-03	1.071E-02	Sakurai et al. [49]	Figures 1, 2, 3 (Cu/ZnO 3/7)
275	573.15	8.106	2.583E-04	2.881E-02		
276	573.15	50.66	1.977E-04	2.702E-02	Sakurai et al. [50]	Table 1 (Cu/ZnO, $Cu/ZnO/Al_2O_3$)
277	573.15	50.66	2.112E-04	3.023E-02		
278	623.15	50.66	4.058E-05	5.200E-02	Sakurai et al. [51]	Figure 2 (Au/ZnO)
279	473.73	50.66	-	5.234E-03	Sakurai et al. [52]	Figure 1
280	473.73	50.66	-	4.739E-03		
281	523.92	50.66	-	1.301E-02		
282	523.92	50.66	-	1.223E-02		
283	573.99	50.66	-	2.555E-02		
284	573.99	50.66	-	2.730E-02		
285	623.92	50.66	-	4.897E-02		
286	623.92	50.66	-	5.015E-02		
287	674.12	50.66	-	8.572E-02		
288	674.12	50.66	-	7.909E-02		

Table S2.1 Collected Kp_1^0- and Kp_2^0-values (continued)

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
289	528.10	1.013	-	1.359E-02	Shakeel [53]	Figure 2 (Cu-Fe-Mn)
290	543.05	1.013	-	1.723E-02		
291	558.65	1.013	-	2.084E-02		
292	573.11	1.013	-	2.363E-02		
293	593.15	105.88	-	3.340E-02	Sorgato & Angelin [30]	Tables 3 - 6
294	593.15	98.29	-	3.250E-02		
295	593.15	151.99	-	3.400E-02		
296	593.15	148.95	-	3.380E-02		
297	593.15	97.37	-	3.570E-02		
298	593.15	88.15	-	3.550E-02		
299	593.15	166.38	-	3.820E-02		
300	593.15	156.14	-	3.850E-02		
301	593.15	201.54	-	3.860E-02		
302	593.15	192.52	-	3.780E-02		
303	653.15	81.36	-	7.200E-02		
304	653.15	66.67	-	7.180E-02		
305	653.15	192.11	-	7.730E-02		
306	653.15	177.42	-	7.440E-02		
307	653.15	273.58	-	7.950E-02		
308	653.15	258.78	-	7.820E-02		
309	653.15	111.76	-	7.090E-02		
310	653.15	100.01	-	7.020E-02		
311	653.15	186.34	-	7.160E-02		
312	653.15	174.58	-	7.150E-02		
313	653.15	271.65	-	7.290E-02		
314	653.15	256.35	-	7.400E-02		
315	653.15	168.71	-	7.310E-02		
316	653.15	20.57	-	7.000E-02		
317	673.15	171.64	-	8.690E-02		
318	673.15	148.04	-	8.730E-02		
319	673.15	246.22	-	8.730E-02		
320	673.15	227.58	-	8.700E-02		
321	673.15	294.15	-	1.010E-01		
322	673.15	280.06	-	1.010E-01		
323	673.15	168.00	-	9.440E-02		
324	673.15	154.01	-	9.340E-02		
325	673.15	157.86	-	9.370E-02		
326	673.15	146.11	-	9.390E-02		
327	673.15	167.69	-	9.510E-02		
328	673.15	157.86	-	9.450E-02		
329	673.15	247.13	-	1.010E-01		
330	673.15	102.95	-	9.230E-02		
331	673.15	97.07	-	9.270E-02		
332	673.15	241.76	-	1.020E-01		
333	673.15	228.59	-	1.040E-01		
334	673.15	49.45	-	8.850E-02		
335	673.15	46.91	-	8.840E-02		
336	473.15	4.3	1.943E-02	-	Struis & Stucki [66]	Figure 4(D)
337	593.22	1.013	-	3.485E-02	Subramanian et al. [54]	Figure 7
338	553.38	20	4.540E-04	-	Sun et al. [70]	Figure 14
339	532.90	20	1.188E-03	-		
340	553.38	20	5.085E-04	-		
341	532.94	20	9.555E-04	-		
342	553.38	20	4.831E-04	-		
343	588.79	1.013	-	2.937E-02	Swartz et al. [55]	Slide 10
344	593.29	1.013	-	3.414E-02	Swartz et al. [56]	Figure 3
345	613.23	1.013	-	4.062E-02		

Table S2.1 Collected Kp_1^0- and Kp_2^0-values (continued)

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
346	823.00	1.013	-	3.476E-01	Tang et al. [57]	Figures 5b, 5c
347	823.59	1.013	-	2.407E-01		
348	493.85	1.013	-	7.049E-03	TeGrotenhuis et al. [58]	Figure 3
349	507.33	1.013	-	8.701E-03		
350	518.24	1.013	-	1.047E-02		
351	535.89	1.013	-	1.441E-02		
352	538.61	1.013	-	1.504E-02		
353	546.68	1.013	-	1.709E-02		
354	547.44	1.013	-	1.693E-02		
355	551.77	1.013	-	1.813E-02		
356	554.98	1.013	-	1.889E-02		
357	562.20	1.013	-	2.116E-02		
358	562.68	1.013	-	2.116E-02		
359	571.18	1.013	-	2.355E-02		
360	581.13	1.013	-	2.642E-02		
361	593.01	1.013	-	3.026E-02		
362	597.50	1.013	-	3.315E-02		
363	629.53	1.013	-	5.376E-02	Tibiletti et al. [59]	Figures 1, 2
364	634.39	1.013	-	5.523E-02		
365	639.25	1.013	-	5.820E-02		
366	644.20	1.013	-	6.089E-02		
367	649.06	1.013	-	6.533E-02		
368	653.92	1.013	-	6.847E-02		
369	659.15	1.013	-	7.309E-02		
370	664.01	1.013	-	7.763E-02		
371	669.24	1.013	-	8.097E-02		
372	674.10	1.013	-	8.568E-02		
373	679.05	1.013	-	8.934E-02		
374	684.00	1.013	-	9.425E-02		
375	689.23	1.013	-	9.927E-02		
376	694.47	1.013	-	1.030E-01		
377	699.42	1.013	-	1.082E-01		
378	704.28	1.013	-	1.139E-01		
379	709.23	1.013	-	1.181E-01		
380	713.99	1.013	-	1.275E-01		
381	629.72	1.013	-	5.456E-02		
382	634.11	1.013	-	5.602E-02		
383	639.67	1.013	-	5.800E-02		
384	644.26	1.013	-	6.034E-02		
385	649.50	1.013	-	6.340E-02		
386	654.52	1.013	-	6.596E-02		
387	659.12	1.013	-	6.929E-02		
388	664.57	1.013	-	7.247E-02		
389	669.28	1.013	-	7.626E-02		
390	674.09	1.013	-	8.016E-02		
391	679.54	1.013	-	8.349E-02		
392	684.13	1.013	-	8.595E-02		
393	689.69	1.013	-	8.999E-02		
394	694.40	1.013	-	9.234E-02		
395	699.95	1.013	-	9.790E-02		
396	704.55	1.013	-	1.078E-01		
397	709.25	1.013	-	1.187E-01		
398	673	1.013	-	7.575E-02	Uemiya et al. [60]	Figure 2
399	673	1.013	-	8.042E-02		
400	673	1.013	-	9.565E-02		

Table S2.1 Collected Kp_1^0- and Kp_2^0-values (continued)

Nr.	T (K)	p (bar)	Kp_1^0 (bar^{-2})	Kp_2^0	Source	Source details
401	493	80	5.739E-03	-	Van Bennekom et al. [71]	Exp. 2
402	518	80	2.083E-03	-	(Appendix B and Table 6.1)	Exp. 3
403	542	81	7.915E-04	-	(Selection of experimental results based	Exp. 4
404	497	155	6.764E-03	-	on the following criteria: average	Exp. 7
405	518	150	1.984E-03	-	C-, H- and O-imbalances <5%; no	Exp. 8
406	543	155	7.115E-04	-	in situ condensation; neglible	Exp. 9
407	519	200	2.194E-03	-	formation of higher alcohols)	Exp. 14
408	543	200	6.805E-04	-		Exp. 15
409	494	195	5.823E-03	-		Exp. 45
410	518	196	1.995E-03	-	Van Bennekom et al. [72]	Exp. 7C
411	543	195	7.442E-04	-	(Supporting Information)	Exp. 8C
412	519	200	2.182E-03	-	(Selection of experimental results based	Exp. 12D
413	543	200	6.781E-04	-	on the above-mentioned criteria)	Exp. 13D
414	675.98	1.013	-	9.758E-02	Xue et al. [61]	Figure 5
415	724.98	1.013	-	1.451E-01		
416	533.12	36	1.068E-03	-	Yin [73]	Figure 5.6 (syngas 2)
417	543.11	36	7.110E-04	-		
418	553.15	40	5.214E-04	-		Figure 5.8 (syngas 4)
419	534.06	36	1.084E-03	-		Figure 5.12 (36 bar)
420	545.08	36	7.106E-04	-		
421	536.01	46	8.438E-04	-		Figure 5.12 (46 bar)
422	548.10	46	6.337E-04	-		
423	553.01	30	4.917E-04	-		Figure 5.15 (30 bar)
424	553.15	40	4.886E-04	-		Figure 5.15 (40 bar)
425	532.90	20	9.327E-04	-	Zhang et al. [74]	Figure 6

Table S2.2 Experimental data Graaf et al. [1, 2]

Nr.	p (bar)	T (K)	y_{CO}	y_{CO2}	y_{H2}	y_{CH3OH}	y_{H2O}	y_{CH4}	y_{C2H6}	y_{C3H8}	y_{DME}
45	10.7	474.4	0.0534	0.0424	0.8324	0.0690	0.0027	0.0000	0.0000	0.0000	0.0001
46	19.3	488.2	0.1066	0.0965	0.6548	0.1379	0.0037	0.0000	0.0000	0.0000	0.0005
47	10.6	489.6	0.0680	0.0444	0.8427	0.0406	0.0030	0.0008	0.0000	0.0001	0.0004
48	10.7	502.3	0.0822	0.0419	0.8438	0.0273	0.0032	0.0006	0.0005	0.0001	0.0004
49	9.8	509.3	0.0869	0.0429	0.8464	0.0176	0.0037	0.0010	0.0008	0.0002	0.0005
50	10.8	530.4	0.0865	0.0456	0.8483	0.0085	0.0059	0.0024	0.0014	0.0005	0.0009
51	11.5	532.3	0.0886	0.0447	0.8473	0.0091	0.0057	0.0018	0.0015	0.0005	0.0008
52	26.5	506.4	0.0545	0.0393	0.8135	0.0861	0.0055	0.0006	0.0000	0.0001	0.0004
53	34.6	509.1	0.0339	0.0449	0.8242	0.0830	0.0100	0.0022	0.0008	0.0002	0.0008
54	32.6	515.2	0.0512	0.0420	0.8162	0.0816	0.0069	0.0014	0.0000	0.0002	0.0005
55	25.2	518.7	0.0709	0.0425	0.8206	0.0579	0.0055	0.0014	0.0004	0.0002	0.0006
56	23.8	534.9	0.0798	0.0469	0.8289	0.0323	0.0075	0.0022	0.0010	0.0005	0.0009
57	26.5	538.1	0.0776	0.0472	0.8285	0.0334	0.0077	0.0030	0.0012	0.0005	0.0009
58	44.5	472.4	0.0063	0.0316	0.7954	0.1468	0.0180	0.0012	0.0000	0.0001	0.0006
59	63.1	481.0	0.0055	0.0253	0.7806	0.1641	0.0219	0.0019	0.0000	0.0001	0.0006
60	48.7	487.8	0.0120	0.0313	0.7918	0.1504	0.0135	0.0005	0.0000	0.0000	0.0005
61	50.7	488.1	0.0097	0.0347	0.7989	0.1372	0.0177	0.0010	0.0000	0.0001	0.0007
62	71.6	495.2	0.0083	0.0264	0.7854	0.1591	0.0201	0.0002	0.0000	0.0000	0.0005
63	50.5	502.3	0.0165	0.0388	0.8103	0.1169	0.0153	0.0012	0.0000	0.0002	0.0008
64	72.2	509.3	0.0139	0.0312	0.7910	0.1428	0.0183	0.0019	0.0000	0.0002	0.0007
65	44.2	516.9	0.0290	0.0468	0.8228	0.0809	0.0141	0.0041	0.0012	0.0001	0.0010
66	43.4	530.0	0.0346	0.0542	0.8273	0.0544	0.0178	0.0068	0.0025	0.0008	0.0016
67	49.8	536.2	0.0312	0.0547	0.8277	0.0514	0.0215	0.0080	0.0029	0.0009	0.0017
68	49.6	480.4	0.0071	0.0295	0.7886	0.1547	0.0183	0.0010	0.0000	0.0001	0.0007
69	62.1	491.1	0.0078	0.0280	0.7897	0.1526	0.0194	0.0017	0.0000	0.0001	0.0007
70	27.1	492.5	0.0287	0.0474	0.8128	0.0977	0.0101	0.0018	0.0007	0.0001	0.0007
71	72.1	497.0	0.0078	0.0268	0.7847	0.1583	0.0208	0.0009	0.0000	0.0001	0.0006
72	50.3	503.6	0.0174	0.0371	0.8068	0.1227	0.0140	0.0012	0.0000	0.0001	0.0007
73	31.4	503.9	0.0122	0.0267	0.9057	0.0408	0.0141	0.0003	0.0000	0.0000	0.0002
74	30.7	504.7	0.0278	0.0263	0.8580	0.0809	0.0065	0.0003	0.0000	0.0000	0.0002
75	32.9	507.5	0.0291	0.0508	0.8305	0.0722	0.0118	0.0029	0.0015	0.0003	0.0009
76	72.7	512.7	0.0117	0.0376	0.8010	0.1162	0.0239	0.0068	0.0011	0.0005	0.0012
77	52.2	518.4	0.0107	0.0218	0.8952	0.0515	0.0200	0.0005	0.0000	0.0000	0.0003
78	30.7	519.8	0.0403	0.0278	0.8668	0.0582	0.0061	0.0006	0.0000	0.0000	0.0002
79	43.0	530.4	0.0413	0.0486	0.8257	0.0640	0.0134	0.0037	0.0016	0.0005	0.0012
80	49.8	536.9	0.0422	0.0459	0.8249	0.0680	0.0132	0.0031	0.0013	0.0004	0.0010
81	26.6	538.0	0.0696	0.0518	0.8312	0.0300	0.0093	0.0043	0.0017	0.0008	0.0013
82	30.5	538.8	0.1396	0.0988	0.6934	0.0591	0.0086	0.0003	0.0000	0.0000	0.0002

Table S2.3 Recalculated experimental data Liu et al. [26]

Run [a]	p (bar)	T (°C)	y_{CO}	y_{CO2}	y_{H2}	y_{CH3OH}	y_{H2O}	y_{N2}	y_{CH4}	Kp_1^0 (bar^{-2})	AAD (%) [b]
1 (116)	40.0	220.4	0.0288	0.1315	0.5312	0.0828	0.0168	0.1702	0.0387	5.724E-03	3.4
2 (117)	40.0	230.2	0.0356	0.1298	0.5438	0.0696	0.0165	0.1663	0.0384	3.762E-03	3.9
3	40.0	240.7	0.0438	0.1267	0.5627	0.0520	0.0163	0.1612	0.0373	*2.163E-03*	*5.1*
4	40.0	251.7	0.0516	0.1233	0.5898	0.0271	0.0170	0.1539	0.0373	*8.841E-04*	*7.3*
5	40.0	260.4	0.0592	0.1204	0.6068	0.0120	0.0172	0.1495	0.0349	*3.252E-04*	*8.6*
6 (118)	49.0	221.1	0.0219	0.1339	0.5033	0.1025	0.0221	0.1759	0.0403	6.653E-03	1.5
7 (119)	49.0	231.2	0.0286	0.1285	0.5249	0.0870	0.0204	0.1714	0.0393	4.059E-03	3.6
8 (120)	49.0	240.9	0.0356	0.1279	0.5455	0.0663	0.0200	0.1654	0.0393	2.343E-03	4.5
9	49.0	250.7	0.0420	0.1260	0.5673	0.0464	0.0205	0.1596	0.0383	*1.306E-03*	*6.0*
10	49.0	259.6	0.0502	0.1242	0.5800	0.0323	0.0199	0.1554	0.0379	*7.357E-04*	*6.4*
11 (121)	60.0	219.6	0.0169	0.1294	0.4752	0.1283	0.0262	0.1835	0.0406	7.638E-03	1.0
12 (122)	60.0	231.0	0.0235	0.1295	0.4978	0.1070	0.0242	0.1772	0.0408	4.306E-03	1.9
13 (123)	60.0	241.1	0.0302	0.1281	0.5184	0.0878	0.0230	0.1716	0.0409	2.598E-03	2.9
14 (124)	60.0	251.5	0.0365	0.1261	0.5463	0.0631	0.0234	0.1644	0.0402	1.426E-03	4.9
15	60.0	259.2	0.0417	0.1252	0.5609	0.0493	0.0236	0.1604	0.0389	*9.373E-04*	*5.7*
16 (125)	66.0	220.3	0.0150	0.1295	0.4636	0.1351	0.0296	0.1854	0.0418	7.651E-03	0.4
17 (126)	66.0	231.3	0.0214	0.1283	0.4843	0.1183	0.0261	0.1805	0.0411	4.446E-03	1.3
18 (127)	66.0	242.0	0.0271	0.1286	0.5040	0.0993	0.0258	0.1750	0.0402	2.796E-03	2.0
19 (128)	66.0	251.6	0.0333	0.1270	0.5332	0.0738	0.0255	0.1675	0.0396	1.554E-03	4.0
20	66.0	260.3	0.0386	0.1260	0.5536	0.0543	0.0260	0.1619	0.0395	*9.328E-04*	*5.3*

a) The numbers between brackets refer to Table S2.1. The numbers 1 – 20 refer to Liu et al.[26, 27].

b) AAD of the C-, H- and O-balance between reactor inlet and outlet. Kp10-values corresponding with AAD > 5% (*italic*) were not used in the analysis.

Liu et al. [26] present the measured dry gas reactor outlet composition. From these experimental results in combination with the reactor inlet composition the outlet composition is calculated als follows.

$$F_{in,i} = \alpha\, y_{in,i} \qquad (\alpha = 1 \text{ mol s}^{-1}\text{; arbitrary choice}) \qquad \text{(S1)}$$

$$F_{out,N_2} = F_{in,N_2} \qquad (N_2 \text{ is inert}) \qquad \text{(S2)}$$

$$F_{out,i} = F_{out,N_2} \frac{y_{out,i}^{dry}}{y_{out,N_2}^{dry}} \qquad (i = CO, CO_2, H_2, CH_4) \qquad \text{(S3)}$$

$$F_{out,H_2O} = Kp_2 \frac{F_{out,CO_2} F_{H_2}}{F_{CO}} \qquad \text{(water-gas shift equilibrium)} \qquad \text{(S4)}$$

$$F_{out,CH_3OH} = \frac{1}{3}\left(F_{in,T} - \sum_{i \neq CH_3OH} F_{out,i} \right) \qquad \text{(total molar balance)} \qquad \text{(S5)}$$

$$y_{out,i} = F_{out,i} / F_{out,T} \qquad \text{(S6)}$$

The calculation procedure is iterative, because Kp_2 is dependent on the gas composition (and p, T). However, convergence is easily obtained starting with ideal gas behaviour as a first guess.

Several Kp_1^0-/ Kp_2^0-values were derived from experimental results close to (but in most cases not completely at) equilibrium. Here, we used a fixed bed catalytic reactor simulation model as described by Graaf et al. [64]. Main assumptions are: plug flow behaviour; isothermal operation; no internal and external mass transfer limitations. The kinetic model of Graaf et al. [62] was used in combination with the kinetic parameters taken from Graaf et al. [63] or taken from Struis & Stucki [66]. The presented simulation results are based on the kinetic parameters that gave the most consistent results. Activity corrections (multiplication factors) for the kinetic rate constants were derived from experimental results at lower temperatures or (in some cases) higher flow rates (constant pressure and reactor inlet composition). These activity corrections were fitted as Arrhenius' relationships.

$$^{10}\log(ACT_k) = a_k - \frac{b_k}{T} \quad \text{with k = A3 or B2} \tag{S7}$$

$$ACT_{C3} = ACT_{A3} \tag{S8}$$

Here, the subscripts A3, B2 and C3 refer to the kinetic rate expressions for the three methanol synthesis reactions (the methanol from CO/H_2 reaction, the water-gas shift reaction and the methanol from CO_2/H_2 reaction, see Graaf et al. [62] for details). Since activity corrections were determined for experimental results obtained at constant pressure and reactor inlet composition, a (meaningful) separate estimation of ACT_{C3} was not possible. Hence we assume that ACT_{A3} and ACT_{C3} are identical. However, this assumption is reasonable, because the results derived from the kinetic parameters of Graaf et al. [63] (comparable reaction rates A en C) and of Struis & Stucki [66] (reaction rate C dominant) turned out to be very comparable.

The approach to equilibrium for each reaction was checked and calculated as follows.

$$\beta_{A3} = \frac{f_{CH_3OH}}{f_{CO} f_{H_2}^2 Kp_1^0} \tag{S9}$$

$$\beta_{B2} = \frac{f_{H_2O} f_{CO}}{f_{CO_2} f_{H_2} Kp_2^0} \tag{S10}$$

$$\beta_{C3} = \frac{f_{CH_3OH}\, f_{H_2O}}{f_{CO_2}\, f_{H_2}^3\, Kp_3^0} \qquad \text{(S11)}$$

We have only collected Kp_1^0-/ Kp_2^0-values with all corresponding β-values lying in a range of 0.9 – 1.1 (most results fall in a range of 0.95 – 1.05).

An overview of the simulation results is given in Table S2.4 as an extension to Table S2.1. The numbers in the first column of Table S2.4 correspond with the numbering in Table S2.1.

Table S2.4 Simulation details methanol synthesis

Nr [a]	**F_{in}/W (mol s^{-1} g^{-1})**	**Kinetic Parameters** [b]	**a_{A3}**	**b_{A3}**	**a_{B2}**	**b_{B2}**	**β_{A3}**	**β_{B2}**	**β_{C3}**
1	$1.210*10^{-4}$	GRA	-5.3729	2982.4	-8.4287	4897.6	0.962	1.007	0.969
2	$1.210*10^{-4}$	GRA	-5.3729	2982.4	-8.4287	4897.6	1	1	1
3	$5.575*10^{-4}$	GRA	-6.4928	3422.7	-5.6860	3422.7	0.950	1.006	0.955
4	$5.575*10^{-4}$	GRA	-6.4928	3422.7	-5.6860	3422.7	1	1	1
5	$5.575*10^{-4}$	GRA	-6.4928	3422.7	-5.6860	3422.7	1	1	1
6	$5.575*10^{-4}$	GRA	-4.3775	2167.1	-3.8614	2167.1	1	1	1
7	$5.575*10^{-4}$	GRA	-6.0218	3110.9	-5.0356	3110.9	0.993	1	0.993
8	$5.575*10^{-4}$	GRA	-6.0218	3110.9	-5.0356	3110.9	1	1	1
9	$5.575*10^{-4}$	GRA	-6.0218	3110.9	-5.0356	3110.9	1	1	1
10	$5.575*10^{-4}$	GRA	-6.0218	3110.9	-5.0356	3110.9	1	1	1
11	$5.575*10^{-4}$	GRA	-3.3302	1847.4	-2.5234	1847.4	0.938	1.009	0.946
12	$5.575*10^{-4}$	GRA	-3.3302	1847.4	-2.5234	1847.4	0.999	1	0.999
13	$5.575*10^{-4}$	GRA	-3.3302	1847.4	-2.5234	1847.4	1	1	1
14	$5.575*10^{-4}$	GRA	-3.3302	1847.4	-2.5234	1847.4	1	1	1
18	$7.232*10^{-6}$	STR	-0.0388	0	-0.0388	0	1.055	0.964	1.018
19	$1.474*10^{-5}$	STR	-0.0388	0	-0.0388	0	1.061	0.963	1.022
20	$1.921*10^{-5}$	STR	-0.0388	0	-0.0388	0	1.024	0.986	1.009
21	$2.562*10^{-5}$	STR	-0.0388	0	-0.0388	0	1.008	0.995	1.003
104	$4.576*10^{-5}$	STR	-0.2828	0	-0.3868	0	1.013	0.993	1.006
198	$5.95*10^{-5}$	GRA	-2.1305	1075.0	0.6459	-169.8	1.009	0.987	0.997
203	$1.852*10^{-5}$	GRA	-1.3109	956.6	-1.3109	956.6	0.985	1.010	0.995
274	$3.718*10^{-5}$	GRA	0.2406	0	1.0884	0	1	1	1
275	$3.718*10^{-5}$	GRA	0.2406	0	1.0884	0	1	1	1
276	$3.718*10^{-5}$	GRA	-0.8912	0	-0.1636	0	1	1	1
277	$3.718*10^{-5}$	GRA	-0.4707	0	0.3278	0	1	1	1
278	$3.718*10^{-5}$	GRA	-2.7737	826.1	-814.3	3844.6	1.018	0.939	0.955
336	$8.097*10^{-6}$	STR	0.0800	0	0.0800	0	1.087	0.939	0.955

Table S2.4 Simulation details methanol synthesis (continued)

Nr [a]	**F_{in}/W (mol s^{-1} g^{-1})**	**Kinetic Parameters** [b]	**a_{A3}**	**b_{A3}**	**a_{B2}**	**b_{B2}**	**β_{A3}**	**β_{B2}**	**β_{C3}**
338	$4.46*10^{-5}$	STR	-0.7788	-241.4	1.5979	-1428.7	1.011	0.998	1.009
339	$4.46*10^{-5}$	STR	-1.2406	183.9	0.8852	-807.7	0.970	1.003	0.974
340	$4.46*10^{-5}$	STR	-1.2406	183.9	0.8852	-807.7	1	1	1
341	$4.46*10^{-5}$	STR	-5.3012	2351.3	-5.2361	2351.3	1.034	0.987	1.020
342	$4.46*10^{-5}$	STR	-5.3012	2351.3	-5.2361	2351.3	1.011	0.997	1.008
416	$8.676*10^{-5}$	GRA	0.4133	0	0.4133	0	0.932	1.045	0.974
417	$8.676*10^{-5}$	GRA	0.4133	0	0.4133	0	0.977	1.002	0.999
418	$8.676*10^{-5}$	GRA	-4.5171	2462.1	-4.5171	2462.1	0.995	1.003	0.998
419	$6.569*10^{-5}$	GRA	0.2126	114.3	0.2126	114.3	0.945	1.035	0.978
420	$8.676*10^{-5}$	GRA	0.2126	114.3	0.2126	114.3	0.999	1.001	1
421	$8.676*10^{-5}$	GRA	0.2589	82.9	0.2589	82.9	0.968	1.021	0.988
422	$8.676*10^{-5}$	GRA	0.2589	82.9	0.2589	82.9	0.999	1	1
423	$6.569*10^{-5}$	GRA	1.0475	-413.3	1.0475	-413.3	1	1	1
424	$6.569*10^{-5}$	GRA	-4.4079	2397.5	-4.4079	2397.5	0.994	1.004	0.998
425	$5.72*10^{-5}$	STR	5.1646	-2316.3	5.1646	-2316.3	1	1	1

a) The numbers in this Table S2.4 correspond with the numbering in Table S2.1.
b) GRA: Graaf et al. [63]; STR: Struis & Stucki [66].

Table S2.5 Thermochemical data (Haynes et al. [8])

i	CO	CO_2	H_2	CH_3OH	H_2O
cpA_i (J mol^{-1} K^{-1})	3.1297E+01	1.9291E+01	2.6782E+01	2.0497E+01	3.3205E+01
cpB_i (J mol^{-1} K^{-2})	-1.6990E-02	7.7562E-02	1.2238E-02	7.2372E-02	-4.4936E-03
cpC_i (J mol^{-1} K^{-3})	4.0535E-05	-6.8177E-05	-2.2989E-05	3.6816E-05	2.2860E-05
cpD_i (J mol^{-1} K^{-4})	-2.8336E-08	3.1746E-08	1.9404E-08	-5.6791E-08	-1.2427E-08
cpE_i (J mol^{-1} K^{-5})	6.6858E-12	-6.1234E-12	-5.2609E-12	1.6851E-11	2.2525E-12
$\Delta H^0(T_{ref})_i$ (J mol^{-1})	-1.10530E+05	-3.93510E+05	0	-2.01000E+05	-2.4183E+05
$\Delta G^0(T_{ref})_i$ (J mol^{-1})	-1.37168E+05	-3.94373E+05	0	-1.62298E+05	-2.2858E+05

$$c_{p,i}^{0}(T) = cpA_i + cpB_i T + cpC_i T^2 + cpD_i T^3 + cpE_i T^4 \qquad \text{(S12)}$$

Haynes et al. [8] present isobaric heat capacity values at several temperatures. These data were fitted with equation S12, yielding a highly accurate description of the original data.

We have used the following relationship for Kp^0, based on these 4th order polynomial functions for the specific heats of the components.

$$\ln Kp^0(T) = \frac{1}{RT}\left[a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 + a_6 T^5 + a_7 T \ln T\right] \qquad \text{(S13)}$$

This relationship is derived as follows, where $\Delta H^0(T)$, $\Delta G^0(T)$ and $\Delta cp^0(T)$ refer to the reaction of interest. First of all, $\Delta H^0(T)$ has to be defined as a function of *T*.

$$\Delta H^0(T) = \Delta H^0(T_{ref}) + \int_{T_{ref}}^{T} \Delta cp^0(T)\,dT \quad \text{(S14)}$$

$$\Delta cp^0(T) = \Delta cpA + \Delta cpBT + \Delta cpCT^2 + \Delta cpDT^3 + \Delta cpET^4 \quad \text{(S15)}$$

Equations S14 and S15 lead to equation S16, where I_H is an integration constant.

$$\Delta H^0(T) = I_H + \Delta cpAT + \frac{1}{2}\Delta cpBT^2 + \frac{1}{3}\Delta cpCT^3 + \frac{1}{4}\Delta cpDT^4 + \frac{1}{5}\Delta cpET^5 \quad \text{(S16)}$$

Here, I_H is defined by equation S17.

$$I_H = \Delta H^0(T_{ref}) - \Delta cpA\,T_{ref} - \frac{1}{2}\Delta cpB\,T_{ref}^2 - \frac{1}{3}\Delta cpC\,T_{ref}^3 - \frac{1}{4}\Delta cpD\,T_{ref}^4 - \frac{1}{5}\Delta cpE\,T_{ref}^5 \quad \text{(S17)}$$

Now, $\Delta G^0(T)$ can be determined as a function of T by implementing S16 and S17 in equation S18 and solving the integral.

$$\frac{-\Delta G^0(T)}{T} = \frac{-\Delta G^0(T_{ref})}{T_{ref}} + \int_{T_{ref}}^{T} \frac{\Delta H^0(T)}{T^2}\,dT \quad \text{(S18)}$$

$$\frac{-\Delta G^0(T)}{T} = I_G - \frac{I_H}{T} + \Delta cpA \ln T + \frac{1}{2}\Delta cpBT + \frac{1}{6}\Delta cpCT^2\ \frac{1}{12}\Delta cpDT^3 + \frac{1}{20}\Delta cpET^4 \quad \text{(S19)}$$

Here, I_G is a second integration constant, which is defined as follows.

$$I_G = \frac{-\Delta G^0(T_{ref})}{T_{ref}} + \frac{I_H}{T_{ref}} - \Delta cpA \ln T_{ref} - \frac{1}{2}\Delta cpB\,T_{ref} - \frac{1}{6}\Delta cpC\,T_{ref}^2 - \frac{1}{12}\Delta cpD\,T_{ref}^3 - \frac{1}{20}\Delta cpE\,T_{ref}^4 \quad \text{(S20)}$$

By implementing S19 and S20 in the well-known equation S21 for $Kp^0(T)$, the parameters a_1 – a_7 can easily be defined by equations S22 to S28.

$$\ln Kp^0(T) = \frac{-\Delta G^0(T)}{RT} \quad \text{(S21)}$$

$$a_1 = -I_H \quad \text{(S22)}$$

$$a_2 = I_G \quad \text{(S23)}$$

$$a_3 = \frac{1}{2}\Delta cpB \quad \text{(S24)}$$

$$a_4 = \frac{1}{6}\Delta cpC \quad \text{(S25)}$$

$$a_5 = \frac{1}{12}\Delta cpD \quad \text{(S26)}$$

$$a_6 = \frac{1}{20}\Delta cpE \quad \text{(S27)}$$

$$a_7 = \Delta cpA \quad \text{(S28)}$$

■ REFERENCES (see main paper)

■ NOMENCLATURE (additional to main paper)

List of symbols

a_k	constant in ACT_k equation S7	-
b_k	constant in ACT_k equation S7	-
cpA_i, cpB_i, cpC_i, cpD_i, cpE_i	parameters c_p^0-equation S12	see Table S2.5
α	molar flow rate (equation S1)	mol s^{-1}
β_k	approach to equilibrium for reaction k	-

-subscripts

k	indicates reaction (A3, B2 or C3)
T	total (molar flow rate)