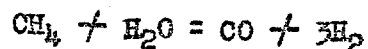


Methane - Steam Reaction
at High Pressure

By E. E. Donath, July 24, 1947

SUMMARY

For the reaction



the equilibrium constants for various temperatures using approximation formulas have been calculated. Approximate equilibrium temperatures for 0.5 and 1% methane content in the dry reaction gas for various pressures are given in the following table. Steam methane ratios of 2 to 1 and 8 to 1 by volume were used. Furthermore, the influence of 0.5 vol. oxygen per 1 vol. methane has been taken in account as a means to deliver the heat of reaction.

Vol. Steam/Vol. CH ₄ %CH ₄ in the dry reaction gas	2/1	8/1	2/1	8/1
	1%		0.5%	
Pressure <u>atm</u>			Temp. °C	
1	670	580	700	610
20	930	790	970	820
200	1240	1040	1310	1070
Pressure <u>psi</u>			Temp. °F	
14	1240	1080	1290	1130
285	1700	1450	1780	1500
2850	2260	1900	2390	1960

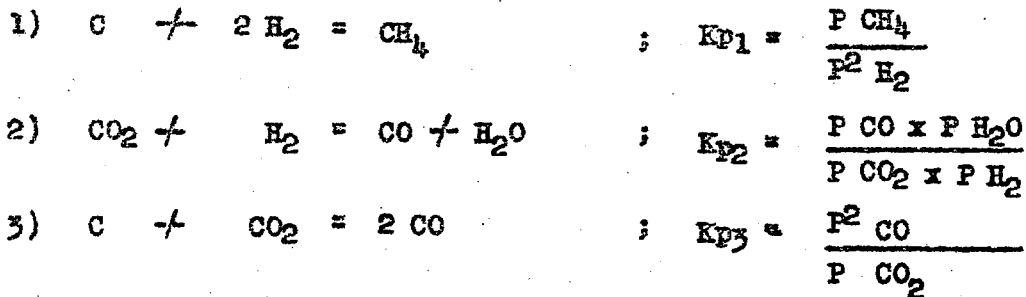
Further engineering calculations could give the heat recovery attainable by heat exchange. With these data, the actual required amount of heat and oxygen respectively could be calculated. If an economic study would then show an advantage of the gasification at elevated pressures, more accurate equilibrium calculations could be made. This is necessary because in the present calculations, no consideration has been given to deviations from the ideal gas law.

Dr. T. E. Warren, Canadian Department of Mines, mentioned during his visit in Torrance, June 19, 1947, the possibility of an elimination of the hydrogen compression by a conversion of the hydrogenation of gases with steam and oxygen at full hydrogenation pressure. It is evident from equilibrium considerations that at higher pressures for this reaction higher temperatures are necessary. For the calculation of the equilibrium constant of the reaction

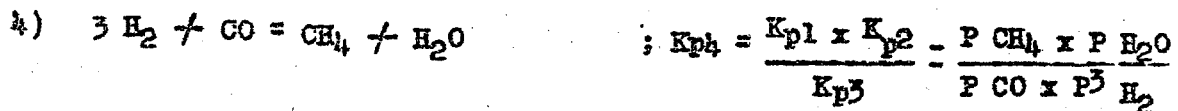


data can be derived from GUMZ, FREIERUNGS-TECHNIK, 1942, P. 264-271.

Then, for the following reactions, formulas for the equilibrium constant are given:



Addition of 1) and 2) and subtraction of 3) gives



The numerical values of K_{p1} , K_{p2} and K_{p3} can be obtained from the following equations:

$$1a) \quad \log K_{p1} = \log \frac{P \text{ CH}_4}{P^2 \text{ H}_2} = \frac{4770}{T} - 5.7345$$

$$2a) \quad K_{p2} = \frac{P \text{ CO} \times P \text{ H}_2\text{O}}{P \text{ CO}_2 \times P \text{ H}_2} = - \frac{9902.7}{T} - 84.304 \times \log T +$$

$$.040967 \times T - 5.631 \times 10^{-6} \times T^2 + 228.197$$

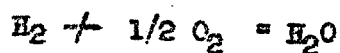
$$3a) \quad \log K_{p3} = \log \frac{P^2 \text{ CO}}{P \text{ CO}_2} = 9.1106 - \frac{8841.7}{T}$$

The numerical values are given in the following table 1:

TABLE 1

T ° K	t ° C	K _{p1}	K _{p2}	K _{p3}	K _{p4} = $\frac{K_{p1} \times K_{p2}}{K_{p3}}$
873	600	0.536	0.39	0.096	2.18
973	700	0.147	0.64	1.15	0.082
1073	800	0.0514	0.95	7.4	0.0066
1173	900	0.0215	1.31	37.4	0.00075
1273	1000	0.0103	1.69	146	0.00012
1373	1100	0.0055	2.1	468	0.000025
1473	1200	0.0032	2.6	1,290	0.0000065
1673	1400	0.00135	3.1	6,610	0.00000063
1873	1600	0.00065	4.0	24,600	0.00000011

From the values for K_{p4} the methane partial pressure according to equation 4) can be calculated. In this calculation for the partial pressure of H₂O a ratio P H₂O/P CH₄ in the initial gas mixture of 2/1 and 8/1 respectively will be used. For the hydrogen partial pressure it will be assumed, that for 1 vol. methane in the initial gas 1/2 vol. oxygen has been used. Thereby according to the equation



the partial pressure of H₂ is decreased and of H₂O increased.

For low percentages of CH₄ in the reaction gas i.e. nearly complete conversion the following figures were obtained from K_{p4} (Table 1):

TABLE 2

Total pressure atm.	1		20		200	
H ₂ O/CH ₄ ratio	2	8	2	8	2	8
Equilibrium partial pressures for low values of P CH ₄						
P CO	0.2	0.09	4	1.8	40	18
P H ₂	0.4	0.18	8	3.6	80	36
P H ₂ O	0.4	0.73	8	14.6	80	146
Corresponding % CH ₄ in dry gas at						
600°C	(11)	0.6				
700°C	0.43	0.02		(8.7)		
800°C	0.04	0.002	(14)	0.7		
900°C	0.004		1.6	0.08		(8)
1000°C			0.26	0.013		1.3
1100°C			0.05		(5.3)	0.26
1200°C					1.4	0.068
1400°C					0.13	
1600°C					0.023	

These data are drawn in Fig. 1 and show the equilibrium methane content for the three mentioned pressures and two H₂O/CH₄ ratios at various temperatures.

/nkj

KATHLEEN & EBERLE CO. NO. 10 30 AM
 MADE IN U.S.A.

METHANE EQUILIBRIUM FUNCTION
At Various Total Pressures

EQUILIBRIUM

Methane content of dry gas according to approximation formulas for the reactions:



Inlet gas composition:



% CH_4

by Vol.

to

dry

gas

20 atm

200 atm

1 atm

600 → 6,700

1100 1200 1300 1400

1600

1800

2000

2200

2400

2600

2800

→ P

