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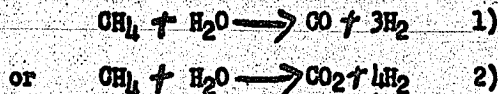
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The Conversion of Methane With Steam and Carbon Dioxide to Synthetic GasPart I: Equilibrium Calculations

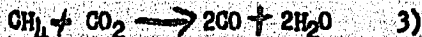
The conversion of methane with steam to carbon monoxide, carbon dioxide and hydrogen is well known as the basis of a technical process for obtaining hydrogen. The methane is converted according to the equations:



to a mixture of CO, CO₂ and H₂. These reactions at high temperatures over catalysts lead to an equilibrium between starting materials and end-products whose position has been variously calculated, for example, by W. Klempt and F. Brodkorb¹, Neumann² and Padovani³. These authors so proceeded in their calculations that they formulated for the partial reactions 1) and 2) the equilibrium constants according to the law of mass action,

$$K_{P'} = \frac{P_{\text{CO}} \cdot P_{\text{H}_2}^3}{P_{\text{CH}_4} \cdot P_{\text{H}_2\text{O}}}, \quad K_{P''} = \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}^4}{P_{\text{CH}_4} \cdot P_{\text{H}_2\text{O}}^2}$$

and reduced the reaction purely schematically to different, well-investigated single reactions. From the experimentally determined constants for the methane dissociation, the "Boudouard" reaction and the water gas equilibrium, the constants $K_{P'}$ and $K_{P''}$ are calculated in known manner. Padovani had calculated, besides, the equilibrium for the reaction



since he had also experimentally proved the possibility to convert methane with H₂O + CO₂ to a mixture of H₂ and CO in the ratio of 2:1 according to the equation



1. W. Klempt and F. Brodkorb, Ber. Ges. Kohlentechn. 3, 211 (1930).
2. Neumann, Z. Elektr. 34, 218 (1928).
3. Padovani, Chim. & Ind. 32, 517 (1934).

In the comparison of the indicated with the experimentally measured values, one must take into consideration that at lower temperatures, below 600°, the methane is mainly converted according to equation 2, at higher temperatures over 1000°, on the other hand, according to equation 1. In the region between 600°-1000°, which is directly technically interesting, both reactions overlap so that a complete conversion of the methane with water, carbon monoxide and carbon dioxide are obtained in parallel exactly as the water gas equilibrium at the concerned temperature expresses. But one is able to raise⁴ the content of exit gas of carbon monoxide to the ratio CO:H₂ = 1:2 by addition of carbon dioxide. The required amount of carbon dioxide is calculated when one introduces in the water-gas formula:

$$K_p = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}}$$

the ratio CO:H₂ = 1:2, for example at about 820°C $P_{H_2O} = 2 (K_p 820^\circ = 1)$

At about 820° the excess amounts of H₂O and CO₂ must behave as 2:1 and the methane conversion then follows the equation



At divergent temperatures the ratio P_{H₂O}:P_{CO₂} displaces in the excess for example, if at 600° one has less water, therefore more CO₂, at 1000° it is just opposite. The conversion equation is then generalized to



For the calculation of the equilibrium constants the present excess of H₂O + CO₂ is immaterial, because it is on both sides of equation and disappears. Owing to this equations 5 and 6 have the same constants as equation 4:

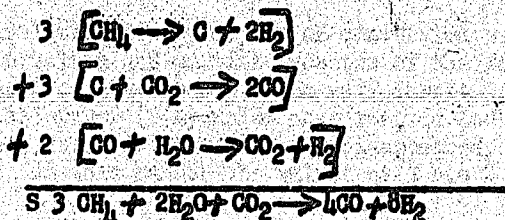
$$K_p = \frac{P_{CO}^4 \cdot P_{H_2}^8}{P_{CH_4}^3 \cdot P_{H_2O}^2 \cdot P_{CO_2}^q}$$

This constant was further calculated in three different ways, namely, (1) on the basis of experimental data of simple reactions (2) with the help

of the Nernst approximate equation, and (3) according to the formula of Einstein-Eucken. In connection with the first calculation the degree of conversion at different temperatures, pressures and excesses was calculated. In the latter case, with excess of $H_2O + CO_2$ a calculation was made** according to equation 5 instead of equation 6 also at higher or lower temperatures than 820° . This brings an error into the calculation but simplifies it essentially. One can easily estimate that the accuracy is large enough, inasmuch as the methane conversion primarily is influenced by the temperature course of methane dissociation.

1. Calculation of K_p from the constants of simpler reactions

Equation 4 can be described as a series of different simple reactions



The single reactions have the following equilibrium constants

$$K_{P1} = \frac{P_{CH_4}}{P_{H_2}^2} \quad K_{P2} = \frac{P_{CO_2}}{P_{CO}^2} \quad K_{P3} = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}}$$

The constant of equation 4 is suitable

$$K_{P4} = \frac{P_{CO}^4 \cdot P_{H_2}^8}{P_{CH_4}^3 \cdot P_{H_2O}^2 \cdot P_{CO_2}} \quad 7)$$

Through combination of these three equations one obtains the sought constant,

$$K_{P4} = K_{P1}^{-3} \cdot K_{P2}^{-3} \cdot K_{P3}^{-2} \quad 8)$$

** (Trans.; Text is not complete at this point)

For K_{p1} , K_{p2} , and K_{p3} we have inserted the values of Mitschmann, Chem. Met. Zeitschrift "Die Metallbörse" 1928 No. 73, 75, 77, Bodmer Schweizer Monatsbulletin 1926, 203, Neumann (loc.cit.). The calculated values of K_{p1} are contained in Table 1, Column I (also see Curve I).

Table 1

Temp.	I	II	III
650°	1.88×10^1	3×10^2	9.55
750°	2.26×10^3	4×10^6	1.55×10^5
850°	9.37×10^8	1×10^{10}	5.50×10^7
900°	1.75×10^{10}	4×10^{11}	6.12×10^9
1000°	8.56×10^{12}	2×10^{14}	2.24×10^{12}

For calculation of the degree of conversion we derive from equation 5 the mole values and partial pressure of the reaction participants, for example, from 3 moles CH_4 which were inserted, X moles are at hand in the equilibrium, $(3-X)$ moles have reacted and $2/3 (3-X)$ moles H_2O and $1/3 (3-X)$ moles CO_2 have thereby disappeared, $4/3 (3-X)$ moles CO are formed. In this manner the values of Table 2 are calculated.

Table 2

Mole Numbers

	Start	in equilibrium
CH_4	3	X
H_2O	$2n$	$2n + 2/3X - 2$
CO_2	n	$n + 1/3X - 1$
CO	0	$4/3 (3-X)$
H_2	0	$8/3 (3-X)$

Total mole value: $M = 3n - 2X + 9$

The partial pressures of the components are single mole number in equilibrium P

wherein P is the total pressure. By introduction of this expression in equation 7 and several transformations one obtains

$$K_{p1} = \frac{2^{30} (1 - 1/3X)^{12} p^6}{X^3 (n + 1/3X - 1)^2 (3n - 2X + 9)^6} \quad 9)$$

This equation we have evaluated for $n=1, 2$ and 6 besides for $P=1$ and 10 atm., in that we take arbitrary values for X from which K_{P_4} is calculated, and the attending temperatures from Table 1 ascertained. The results are contained in Table 3 (see also page of curves).

Table 3

X	CH ₄ Conv.	Equilibrium Temperatures						CH ₄ -content and CO ₂ content of the H ₂ O-free and gases					
		P=1 atm.			P=10 atm.			n=1		2		6	
		n=1	2	6	n=1	2	6	CH ₄ %	CO ₂ %	CH ₄ %	CO ₂ %	CH ₄ %	CO ₂ %
1	66.7	875	570	530	830	720	680	10.7	3.6	8.6	10.4	6.4	29.9
0.6	80.0	730	650	570	890	800	720	6.4	2.1	4.9	9.8	3.7	29.7
0.2	93.3	820	700	640	>1000	870	790	1.7	0.6	1.6	7.9	1.2	29.6
0.1	96.7	885	735	650	>1000	920	800	0.8	0.3	0.8	7.8	0.6	29.4
0.05	98.3	950	760	675	>1000	960	825	0.4	0.1	0.4	7.7	0.3	29.4
0.02	99.2	>1000	835	700	>1000	>1000	870						
0.01	99.7	>1000	865	730	>1000	>1000	900						

2. Calculation of K_{P_4} according to Nernst's Approximate Equation.

About the method and numerical value, see Kuster - Thiel, last edition. The equation reads

$$\log K_{P_4} = \frac{-157900}{4.57 T} + 10.5 \log T + 8.9$$

The results are in Table 1, column II (Curve II)

3. Calculation of K_{P_4} according to the equation of Einstein-Eucken

It is treated by the valuation of the following formula for K_{P_4}

$$\log K_{P_4} = \frac{-H_0}{4.573 T} + \frac{\Delta \sum C_{P_0}}{1.986} \log T$$

$$+ \frac{1}{4.573} \int_0^T \frac{dT}{T^2} \int_0^T \Delta \sum C_s dT + J_K$$

The significance of the singular quantities is the usual. Compare, for example, A. Eucken "Grundriss der phys. Chemie". Table 4 shows the values used by us for heat of formation, chemical constants and specific heat.

Table 4

	<u>Heat of forma- tion at 25°(5)</u>	<u>Chemical Constants(6)</u>	<u>(6) C_p</u>
CH ₄	18.0 K cal.	-1.879	$\frac{8}{2} R + 6S \frac{(2000)}{T} + 3S \frac{(4350)}{T}$
H ₂ O	57.85 K cal.	-1.78	$\frac{8}{2} R + S \frac{(2260)}{T} + S \frac{(5000)}{T}$
CO ₂	94.20 K cal.	+0.83	$\frac{7}{2} R + 2S \frac{(970)}{T} + S \frac{(1720)}{T} + S \frac{(3100)}{T}$
CO	26.5 K cal.	+0.157	$\frac{7}{2} R + S \frac{(3100)}{T}$
H ₂	---	-3.357	$\frac{7}{2} R + S \frac{(6100)}{T}$

5) Landolt-Bornstein

6) A. Eucken "Grundriss d. phys. Chemie", 4th Edition.

The heat of transformation of the reaction $3CH_4 + 2H_2O \rightarrow 4CO + 8H_2$ is calculated from the several heats of formation to

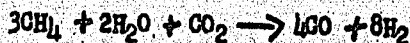
$$W_{250} = 157,900 \text{ cal.}$$

$$\text{or } W_0 = 146,850 \text{ cal.}$$

Table 1, Column III (see also Curve III) shows the calculation.

Summary:

The equilibrium constant for the reaction



was calculated for 650-1000° in which this reaction was reduced to simple, experimentally well-investigated reactions. In addition the equilibrium constant was calculated according to Nernst's approximate equation and according to the equation of Einstein-Eucken. The agreement between the values of the Einstein-Eucken equation and that secured experimentally is good, while the approximate equation gives little satisfactory results. From the constants secured experimentally the degree of conversion was calculated for various excesses of H₂O + CO₂ and for 1 and 10 atmospheres pressure. The results may also be applied to the conversion of methane with oxygen.

/s/ Platz

"Die Umsetzung von Methan mit Wasserdampf und Kohlensäure zu Synthesegas", 7pp. 1 illustration

Requested by J.W. Schustek

Translated Jan. 13, 1947 - Dr. H. Cohen

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