

M. Piar's  
private files.

W. Sternberg  
July 14, 1947

High Pressure Studies  
P/La 558

April 2, 1947

THEORY OF FORMATION OF HIGHER HYDROCARBONS FROM METHANE  
IN THE PRESENCE OF SULFUR OR SULFUR COMPOUNDS

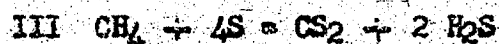
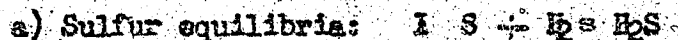
A few theoretical considerations will be shown below regarding the conversion of methane into saturated or unsaturated paraffin hydrocarbons in the presence of sulfur or any sulfur compounds in the catalysts and with a simultaneous use of hydrogen:

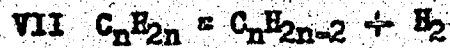
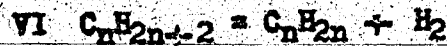
From the position of the thermodynamic equilibria, all conversions of paraffin hydrocarbons alone, at higher temperatures, will result in their splitting up into smaller molecules, and in the last end a breaking down into methane + carbon. If sufficient hydrogen is present, methane alone will result as the hydrocarbon lowest in energy content and therefore the most stable. In the latter case the conversion is not accompanied by a change in the number of mols, and the corresponding equilibria can not therefore be displaced towards the higher hydrocarbons by the application of higher pressures. Such a displacement may however be brought about by the presence of system absorbing hydrogen, if (1) the formation of higher hydrocarbons is occasionally energetically more favorable, and (2) this formation is connected with a reduction of the number of mols, and therefore favored by the use of higher pressures. The knowledge of a series of thermodynamic equilibria is required to answer the question whether or not the addition of sulfur in any form whatsoever (elementary sulfur,  $SO_2$ ,  $CS_2$ ,  $COS$ ) would satisfy these demands. The equilibrium constants were therefore calculated from the thermodynamic data (heats of formation of the compounds from the elements and the normal entropies of formation) using the approximation formula  $4.573 \log K_p = \frac{Q_{2980}}{T} - \Delta S$ , unless taken from data in literature. In that connection the probable required addition of hydrogen in practice was taken into consideration, either for a better mastery of the reaction from the standpoint of heat, or else to avoid the formation of coke and shortening the life of the catalysts.

A knowledge of the following equilibria in the temperature range of interest to us, i.e. between  $300$  and  $750^\circ$  is required in evaluating the different reactions possible from a thermodynamic standpoint for the formation of higher hydrocarbons in a system of



where the S compounds may be  $S_2$ ,  $SO_2$ ,  $CS_2$  or  $COS$ , and z may be = 0.





Among the hydrocarbon equilibria, the case with  $n = 2$  is particularly interesting, because the heat of the reactions of the equilibria V - VII may be considered independent from  $n$  as a first approximation, when calculating per mol  $CH_4$  or  $H_2$ . In a system in which the equilibrium conditions would permit the production of higher hydrocarbons from methane, it would essentially become a matter of catalysts whether only  $C_2H_6$  or a mixture of higher hydrocarbons were to form.

Table 1.  
Equilibrium Constants (v. also curves).

No. of equilibrium	Temperature, °C	log $K_p$	Literature.
I $H_2 + 1/8 S_8$ $H_2 + 1/6 H_6$	below 460	$+503/T + 1.30$	
	460 - 750°	$+225/T + 0.507$	
II	300 - 750°	$+10,830/T - 3.00$	
III $CH_4 + 1/2 S_8$	below 460°	$-10,410/T + 13.70$	Fr. Fromherz
	460 - 750°	$-11,530/T + 12.15$	Ber. vol. 13, p.7151
IV	300 - 750°	$-1,885/T - 1.81$	
V $n = 2$	300 - 750°	$-2,910/T - 0.475$	
VI $n = 2$ $n = 8$	"	$-6,750/T + 0.05$	G.R.Schultze, Oel und Kohle, vol. 12, 1936, p 267; Z. ang. Chem., vol. 49, 1936, p. 284.
	"	$-6,360/T + 7.85$	
VII $n = 2$	"	$-8,440/T + 6.00$	

Table 2.  
Calculation of the Basic Thermodynamic Data.

gaseous compd.	Normal entropy, S cal/degree	Heat of formation Q Kcal.	Remarks.
S6	82.6	22.6	Conventions on the signs: $A + = B + C + \dots$ $K_p = \frac{B \times C \times \dots}{A \times \dots}$ $4.574 \log K_p = \frac{Q}{T} + \Delta S$
S8	95.8	20.00	
SO2	59.4	70.95	
H2S	49.15	4.80	
CS2	56.84	-29.05	
CO2	60.5 (uncertain)	35.7	
H2	31.23	0	
H2O	45.10	57.95	
CH4	44.46	18.2	
C2H6	55.5	22.7	
C2H4	51.90	see under remarks. $C_2H_4 + H_2 = C_2H_6 + 29 - 32.8 \text{ kcal.}$	
C2H2	48.08	-54.8	

The constants for a series of typically composed equilibria have been calculated using table 1, and the total methane conversion found from them for the total pressures of 1 and 1000 atmospheres for the two temperatures 394° and 727° on the assumption that the equilibrium could become established starting with a stoichiometric mixture represented by the left side of the equation (v. table 3). The results of the computations were as follows:

1.) Conversion of methane with sulfur: One may not anticipate on thermodynamic grounds any significant amount of formation of higher paraffinic hydrocarbons by a simple reduction of sulfur to H<sub>2</sub>S, but under extreme conditions (1000 atm, 727° C) appreciable amounts of olefines may form with greater additions of sulfur. V., however, the readily resulting formation of CS<sub>2</sub> from CH<sub>4</sub> + S in Fromherz, Ber., vol. 13, p. 7151.

Table 3.  
Equilibria Between Methane and Sulfur Compounds.

Equilibrium	K <sub>p</sub>	727° C		K <sub>p</sub>	394° C		CH <sub>4</sub> conversion at 1000 atm.
		CH <sub>4</sub> conversion at 1 atm.	1000 atm.		conversion at 1 atm	K <sub>p</sub>	
1. 2 CH <sub>4</sub> + S = C <sub>2</sub> H <sub>6</sub> + H <sub>2</sub> S	5.6x10 <sup>-3</sup>	0.2	10	1.6x10 <sup>-3</sup>	0.1	1.5x10 <sup>-4</sup>	1
2CH <sub>4</sub> + 2S = C <sub>2</sub> H <sub>4</sub> + 2H <sub>2</sub> S	1.5x10 <sup>-2</sup>	6	40	1.5x10 <sup>-5</sup>	1	3.8x10 <sup>-7</sup>	2
2. 6CH <sub>4</sub> + SO <sub>2</sub> = 3C <sub>2</sub> H <sub>6</sub> + H <sub>2</sub> S + 2H <sub>2</sub> O	6.6x10 <sup>-3</sup>	25	50	6.2x10 <sup>-2</sup>	30	6.2x10 <sup>-2</sup>	60
2CH <sub>4</sub> + SO <sub>2</sub> = C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> S + 2H <sub>2</sub> O	22.4	95	80	5.6x10 <sup>-3</sup>	75	5.6x10 <sup>3</sup>	30
2CH <sub>4</sub> + SO <sub>2</sub> + 2H <sub>2</sub> = C <sub>2</sub> H <sub>6</sub> + H <sub>2</sub> S + 2H <sub>2</sub> O	3.1x10 <sup>4</sup>	90	95	3x10 <sup>8</sup>	100	3x10 <sup>8</sup>	100
3. 3CH <sub>4</sub> + CS <sub>2</sub> = 2C <sub>2</sub> H <sub>4</sub> + 2H <sub>2</sub> S	5.4x10 <sup>-5</sup>	10	10	2.2x10 <sup>-8</sup>	1	2.0x10 <sup>-8</sup>	1
CH <sub>4</sub> + CS <sub>2</sub> + 3H <sub>2</sub> = C <sub>2</sub> H <sub>6</sub> + 2H <sub>2</sub> S	3.3	3	85	2.3x10 <sup>5</sup>	60	1.9x10 <sup>5</sup>	99
4. 3CH <sub>4</sub> + COS = 2C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub> S + H <sub>2</sub> O	10 <sup>-8</sup>	1	1	5x10 <sup>-3</sup>	0	4.2	0
CH <sub>4</sub> + COS + 3H <sub>2</sub> = C <sub>2</sub> H <sub>6</sub> + H <sub>2</sub> S + H <sub>2</sub> O	6.7x10 <sup>-4</sup>	0	5	5.2	3	4.5x10 <sup>-13</sup>	70

2.) Conversion of Methane with Sulfur Dioxide: Thermodynamically, the production of the higher paraffines would be possible because of the reduction in the number of mols in this reaction. In the presence of some hydrogen the thermodynamic equilibrium under all the conditions investigated is practically entirely on the higher hydrocarbon side. The production of the strongly unsaturated hydrocarbons is also thermodynamically possible, and the lower pressures are to be preferred because of the reduction in the number of mols. The equilibria with SO<sub>2</sub> are little affected by temperatures, and need not be restricted by temperature considerations in the selection of the experimental temperatures. At rising temperatures, the paraffine equilibria are somewhat displaced towards the methane side, the equilibria of the unsaturated towards acetylene.

- 3.) Conversion of Methane with Carbon Disulfide: The equilibrium is entirely on the methane side in the assumed ethylene formation in the absence of  $H_2$ .
- 4.) Conversion of Methane with Carbon Oxyulfide: Conditions in this case are qualitatively the same as in the use of  $CS_2$ , but appreciably less favorable quantitatively.

Signed: Reitz.

