

# INVESTIGATIONS IN FISCHER-TROPSCH SYNTHESIS REACTIONS BY C-BALANCE

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## PART III

### A. Importance of the Overall Hydrogen to Carbon Monoxide Conversion Ratio ( $H_2:CO$ )

In our previous discussions in Parts I and II,\* we have observed that different hydrogen-activating capacities of a catalyst have a great influence on the run of the reactions and their results. A certain definite  $H_2$  to  $CO$  conversion ratio (usage ratio) is maintained by a catalyst according to its hydrogen-activating capacity. This ratio is characteristic for each catalyst and does not depend upon the ratio offered to the catalyst in the synthesis gas. Further, this conversion ratio regulates the composition and nature of the products formed, and it depends on the catalyst nature and fixes its conversion capacity. The last one is optimum only when  $H_2$  to  $CO$  ratio of the synthesis gas is equal to the conversion ratio maintained by the catalyst. It has also been made clear in our previous discussions that the total converted hydrogen consists of two parts, viz., the reduction hydrogen and the hydrogenation hydrogen, and these should be calculated separately.

Equation (22)

$$(x - f) = 100 - 3(a + b) = 3[33.33 - (a + b)] \quad (22)$$

enables us to obtain a general conversion scheme for all possible  $H_2$  to  $CO$  conversion ratios. In Table III are given some syntheses examples of Cobalt, Iron and Ruthenium catalysts calculated by the C-balance method. In order to make this overall scheme more clear, it is represented in a number of figures (Figs. 3 to 8). Fig. 3 represents a basic picture of a reaction which changes from the pure water reaction on one side to the pure carbon dioxide reaction on the other, within the limiting state where the formation of hydrogenation hydrogen is assumed to be zero. Within the possible conversion ratios of 3:1 to 0.5:1, it is not possible to obtain a straight line for this function. But in order to obtain a clear concept of the matter, we have stretched the curves into straight lines by using a varying multiplication factor.

\* *Jour. Indian Inst. Sci.*, 1955, 37, 215-25.

Beyond the ratio 2:1, the  $\text{CO}_2$  reaction is no more necessary to give hydrogenation hydrogen, as in this region more and more hydrogen is directly available for hydrogenation. This direct hydrogenation will continue, until at the ratio of 3:1 only methane will be formed. The figure for a Ruthenium

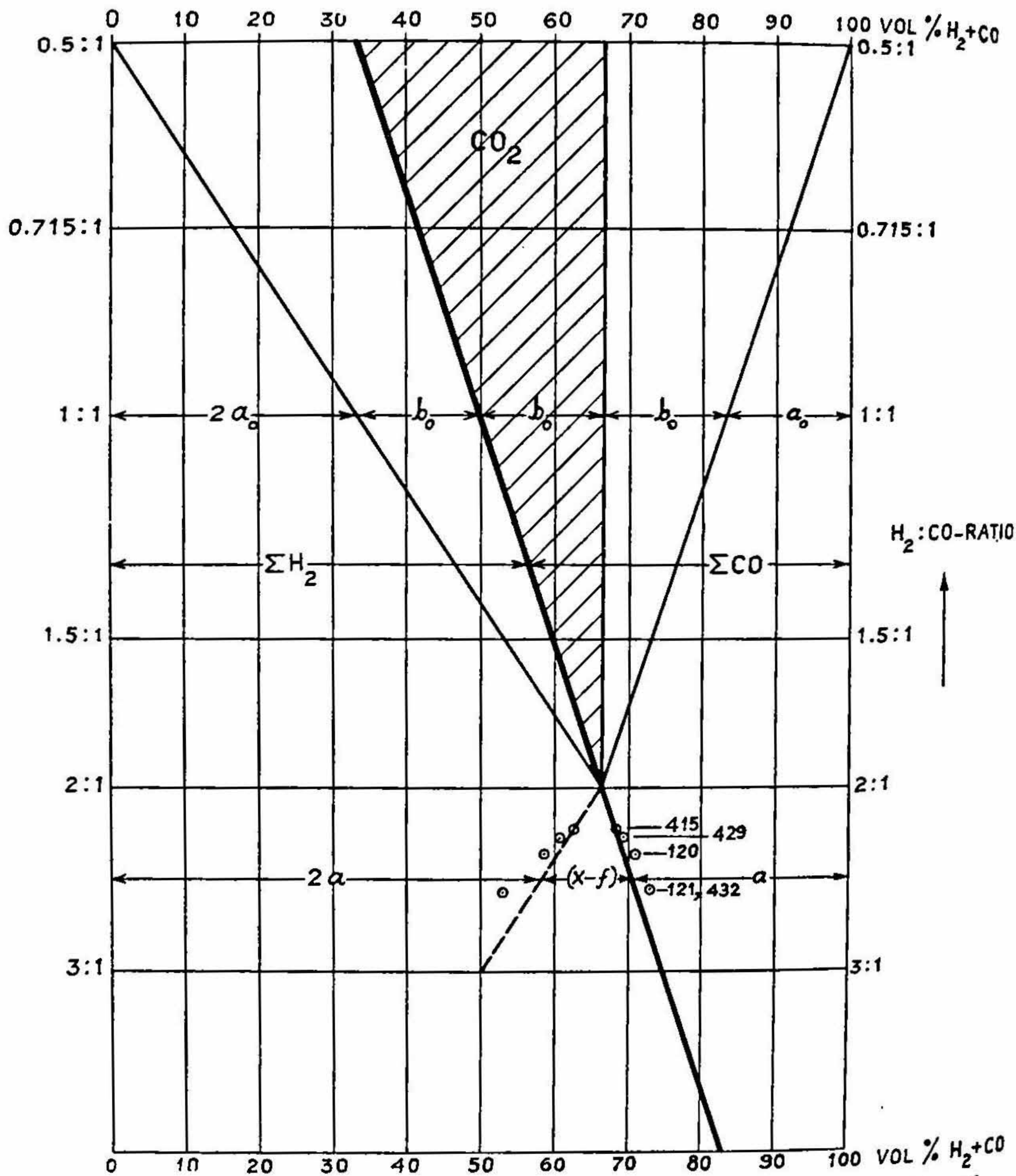


FIG. 3. Possible Distribution of CO Reduction Reaction for Extreme Condition of Hydrogenation Hydrogen Equal to Zero.

catalyst under certain temperature conditions satisfies this argument (see Nos. 415, 429 and 432 of Table III). In fact, the  $\text{CO}_2$  reaction is not completely suppressed but occurs to a very small amount. It is also observed that a Cobalt catalyst at rather low temperatures could also directly activate hydrogenation hydrogen or activate it in some indirect connection with the water reaction, without the

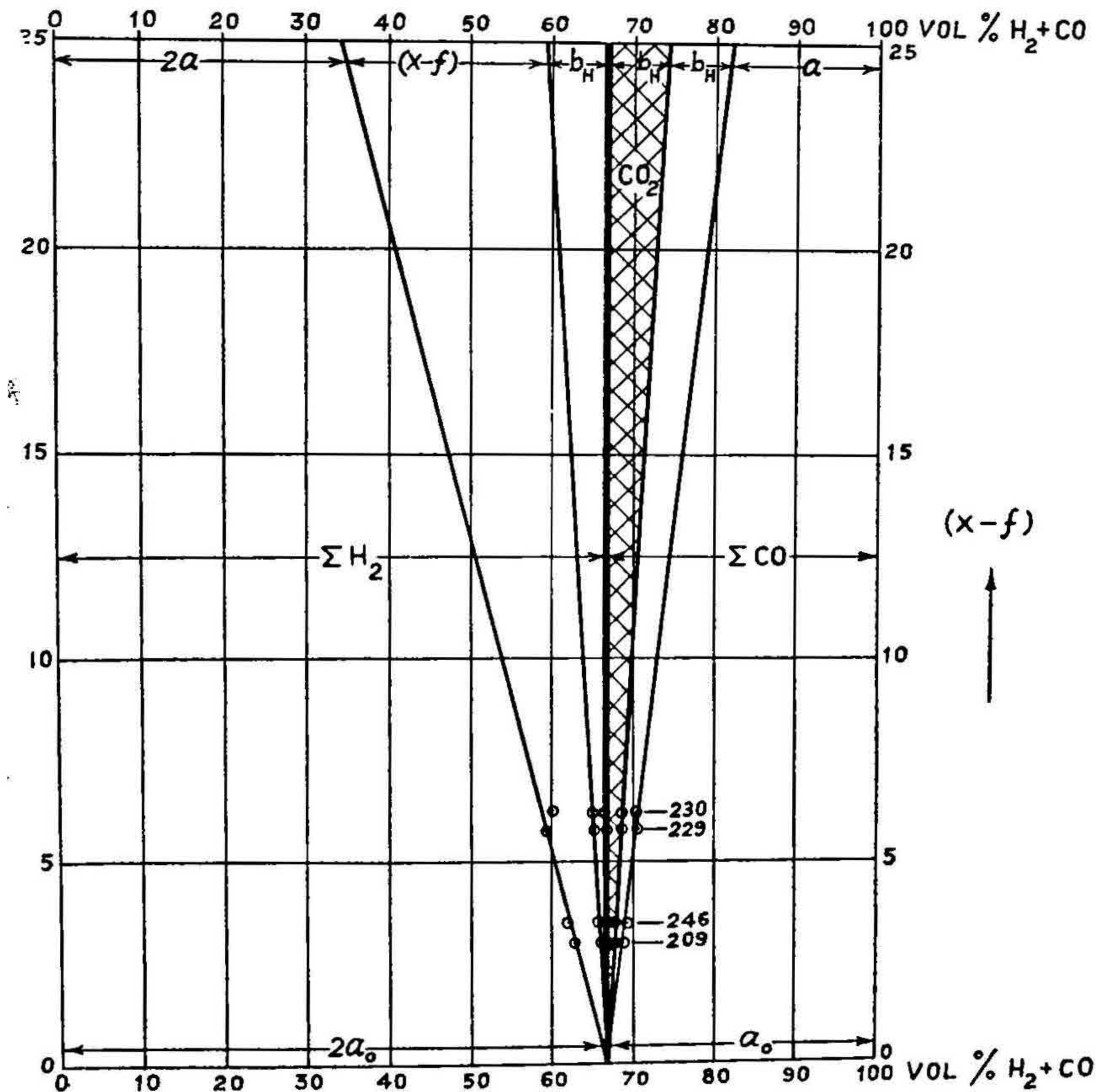


FIG. 4. Possible Distribution Reaction for the Overall Ratio  $\text{H}_2:\text{CO}=2:1$  for all possible Hydrogenation Hydrogen Values.

appreciable occurrence of the  $\text{CO}_2$  reaction. Such an example of Cobalt catalyst (Nos. 121 and 120), contained in Table III, is also indicated in Fig. 3.

All catalysts, having conversion ratios of  $\text{H}_2$  to  $\text{CO}$  less than 2:1, must then follow more towards the  $\text{CO}_2$  reaction as this requires lesser amount of

hydrogen for the reduction than the water reaction. This is also true for a hypothetical case where hydrogenation hydrogen is assumed to be zero. This is shown in Fig. 3 for  $H_2:CO$  ratios from 2:1 to 0.5:1 for zero values of  $(x-f)$ . At the lowest conversion ratio of 0.5:1, the water reaction is absolutely impossible if the reduction of CO to  $CH_2$  radicals shall take place. The

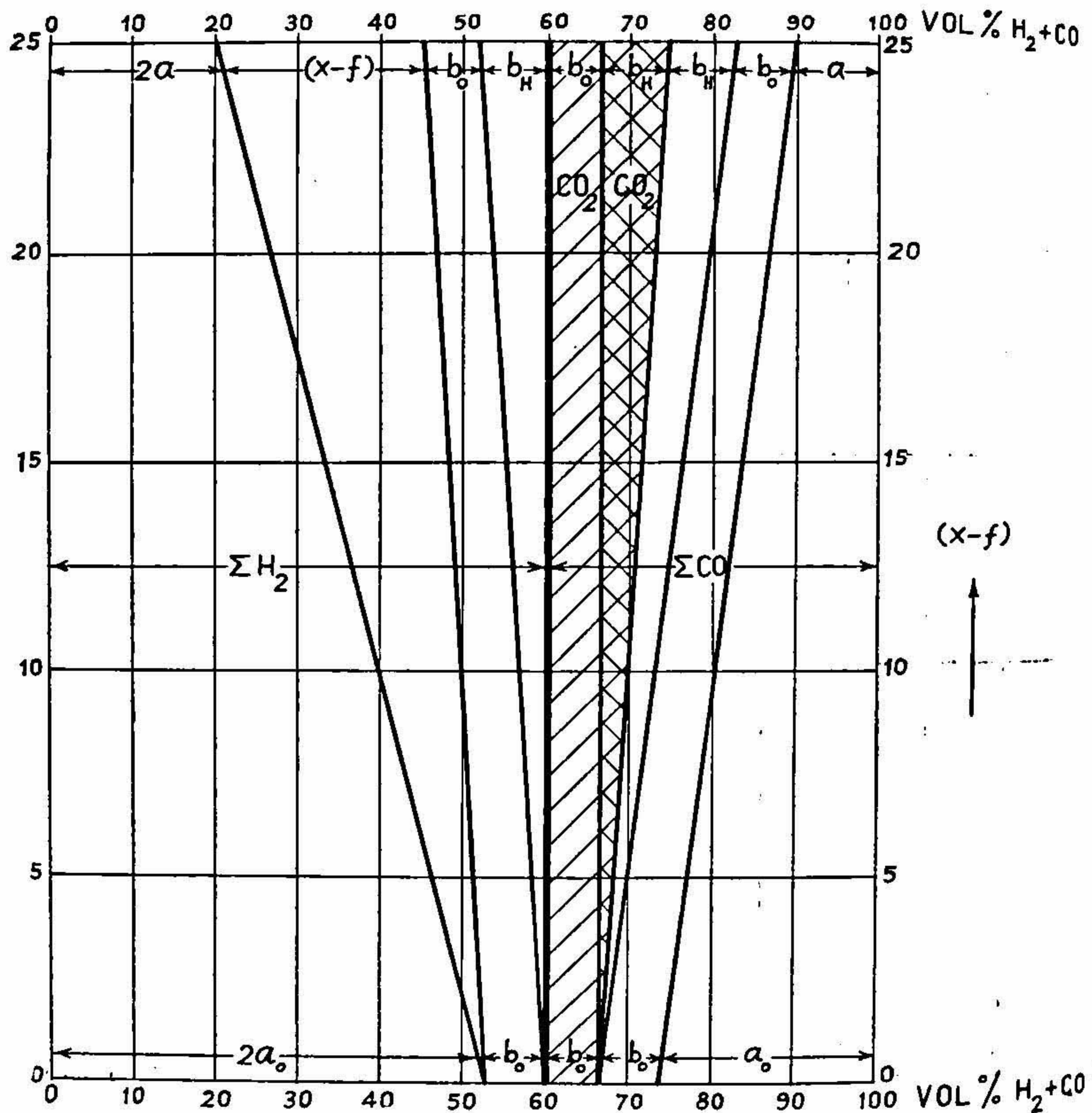


FIG. 5. Possible Distribution Reaction for the Overall Ratio  $H_2:CO=1.5:1$  for all possible Hydrogenation Hydrogen Values,

deposition of stable carbon is mostly a consequence of rather low hydrogen activity of the catalyst.

The conditions for the two extreme limits of all synthesis reactions can then be the total absence of hydrogenation hydrogen on one hand, i.e.,  $(x-f)=0$ ,

and exclusive methane formation on the other. Let us now consider every possible conversion ratio between the limits 2:1 and 0.5:1 of H<sub>2</sub> to CO and try to bring the additional hydrogenation hydrogen within the two above-mentioned extreme conditions. This is then only possible according to equation (22), by an *additional shift* towards the CO<sub>2</sub> reaction, without, however, changing

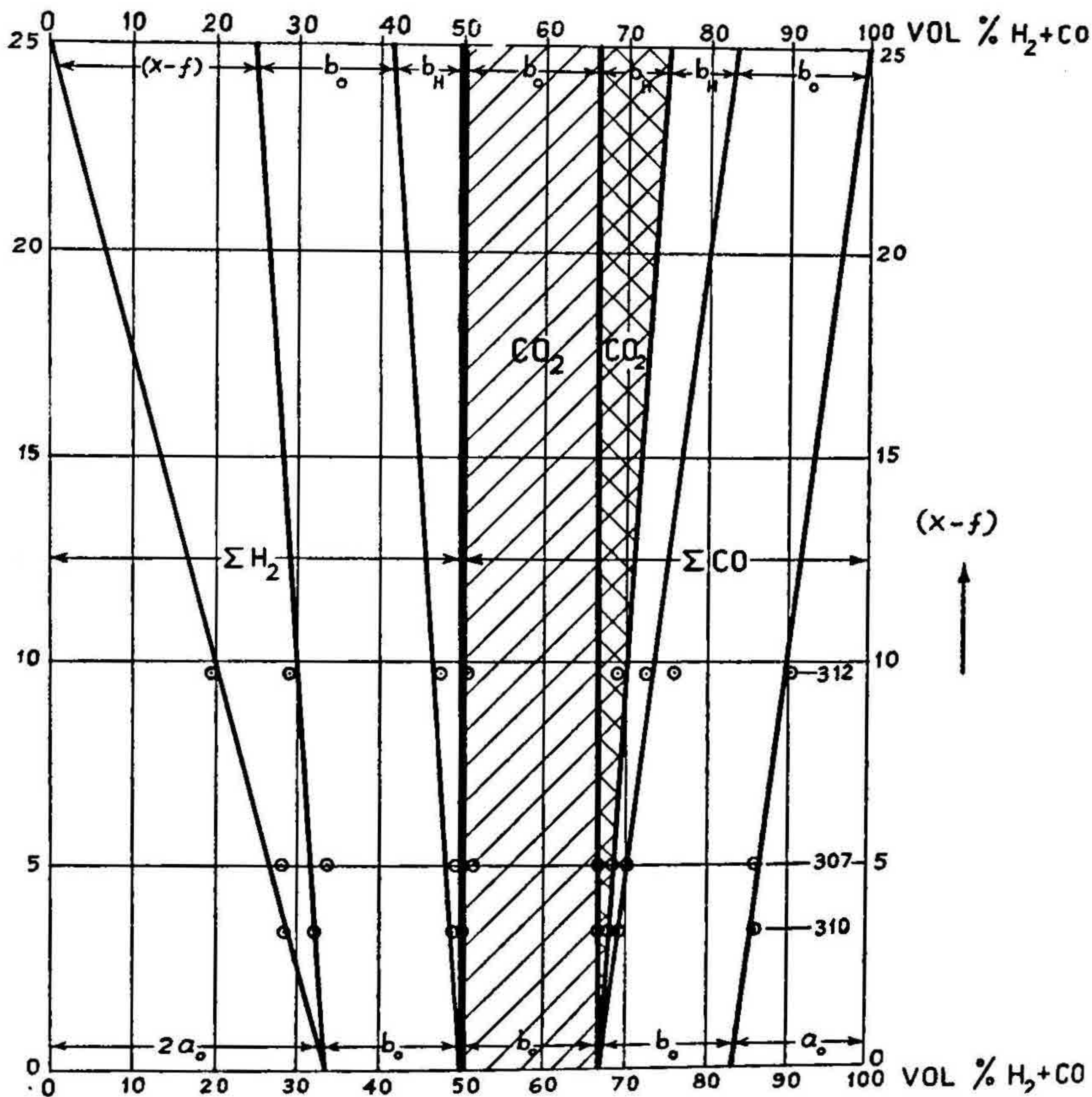


FIG. 6. Possible Distribution Reaction for the Overall Ratio H<sub>2</sub>:CO=1:1 for all possible Hydrogenation Hydrogen Values.

the overall conversion ratio of H<sub>2</sub> to CO. This additional shift towards the CO<sub>2</sub> side for the activation of hydrogenation hydrogen is shown in Figs. 4 to 8 for the H<sub>2</sub>:CO ratios of 2:1, 1.5:1, 1:1, 0.715:1 and 0.5:1 respectively. These cuts may be vertically placed on the respective abscissa of Fig. 3, thus

giving a three-dimensional picture of all possible reaction cases. One can observe from this that whenever hydrogenation hydrogen is made available from a part of the total converted CO by the  $\text{CO}_2$  reaction, which we will call as ' $b_H$ ', there is always a corresponding diminution of CO converted according to the water reaction which figure we had called as ' $a$ '. Therefore, the maximum value

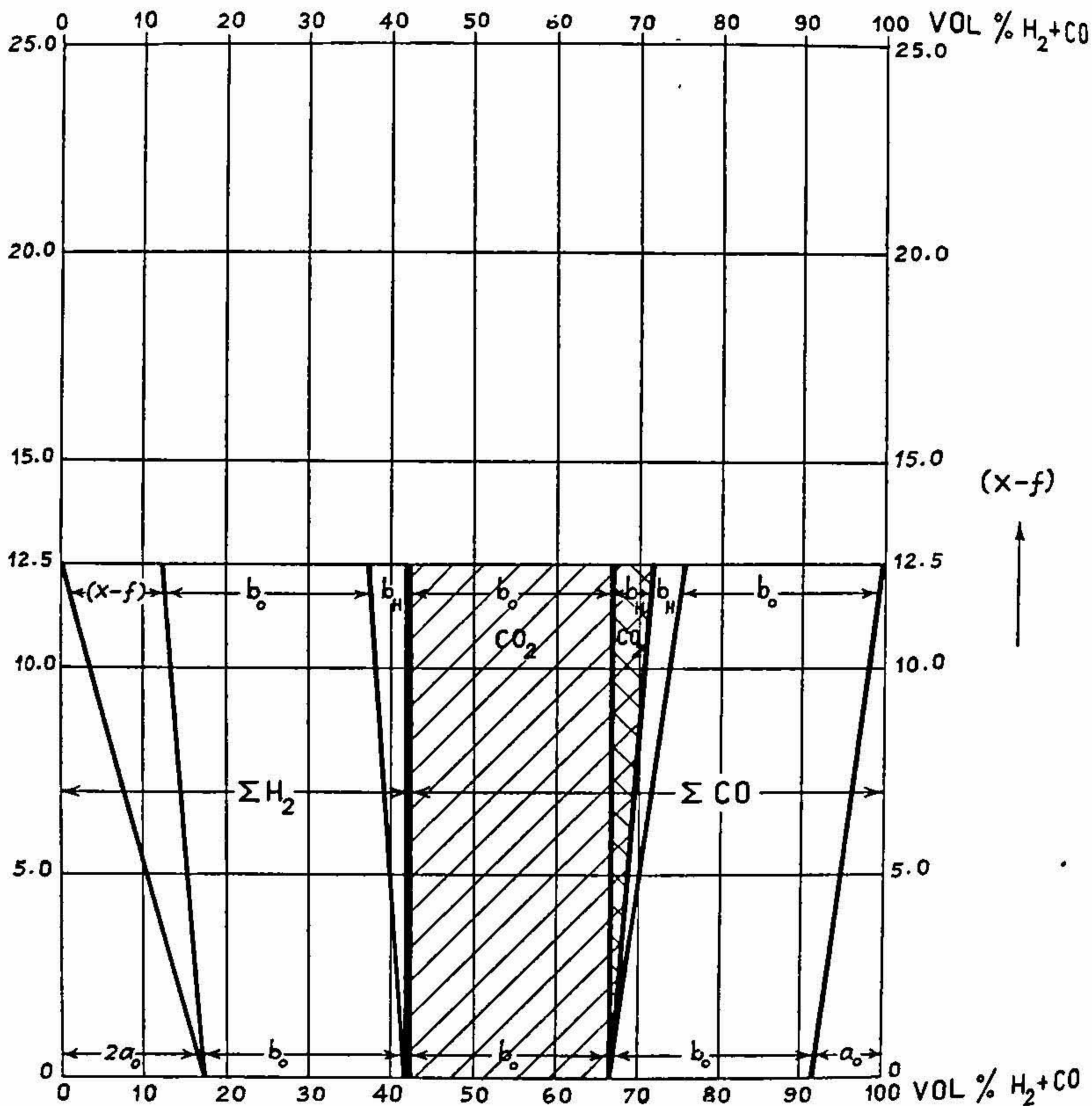


FIG 7. Possible Distribution Reaction for the Overall Ratio  $\text{H}_2:\text{CO}=0.715:1$  for all possible Hydrogenation Hydrogen Values.

for the exclusive methane formation (which is three times the maximum value of ' $b_H$ ', i.e.,  $3 \times 8.33 = 25$ ) will be reached earlier for the higher  $\text{H}_2:\text{CO}$  ratios at lower temperatures and for all other lower ratios at higher temperatures. For the

ratio 0.5:1 the activation of hydrogenation hydrogen without the carbon deposition is no more possible.

As far as the overall ratios of the examples given in Table III correspond, in general, with the chosen ratios, then their values are plotted in the Figs.

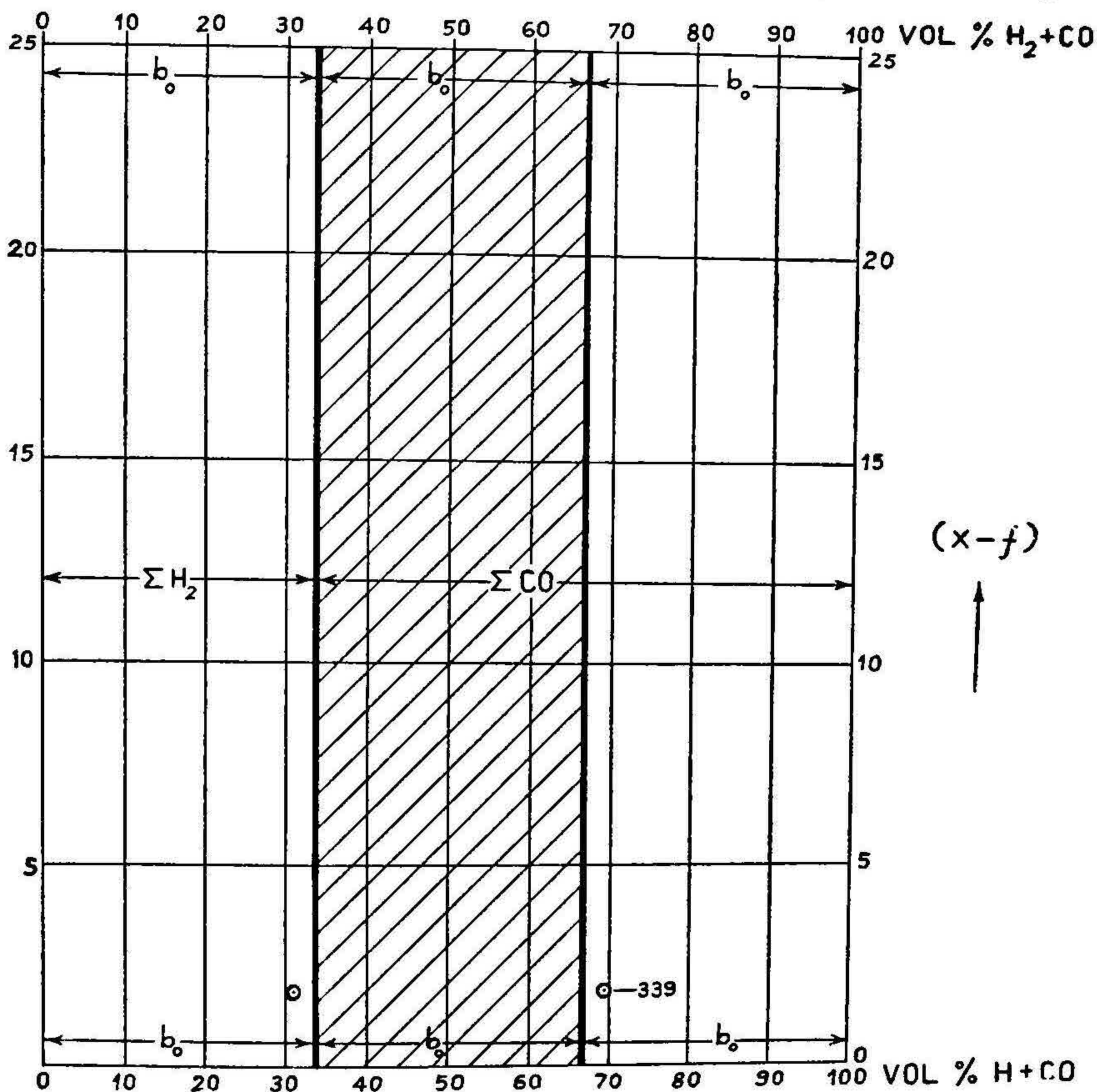


FIG. 8. Possible Distribution Reaction for the Overall Ratio  $H_2:CO = 0.5:1$  for all possible Hydrogenation Hydrogen Values.

3 to 8. One can see that their values fit well in the scheme, and it is found that each catalyst possesses a definite overall ratio independently of whatever amount of hydrogenation hydrogen is to be made available, and this ratio is kept constant inspite of all the different reaction conditions like temperature, gas composition and space velocity, and is changed only when changes in the catalyst composition

and nature occur. As indicated by examples in Table III, Cobalt and Ruthenium catalysts maintain a ratio of about 2.1 to 2.0:1 even if they are forced to produce more hydrogenation hydrogen, with the aid of additional  $\text{CO}_2$  reaction. Iron catalysts, however, keep a characteristic ratio of about 1.2:1 and lower, mostly 1:1, equally independent of absolute heights of  $(x - f)$  values. This means that different types of catalysts possess a definite overall hydrogen activity and arrange for reduction and hydrogenation within these limits by a consecutive shift from  $\text{H}_2\text{O}$  to  $\text{CO}_2$  reaction.

The mathematical formulation of these relations may be added here for further clarification of this overall picture as follows:

Expressing the  $\text{H}_2$  to  $\text{CO}$  overall conversion ratio as

$$\frac{\text{H}_2}{\text{CO}} = \frac{2a + b + (x - f)}{a + 2b} = \rho \quad (24)$$

for instance, for the ratio 2:1 we get

$$2a + b + (x - f) = 2a + 4b$$

*i.e.*,

$$(x - f) = 3b \quad (25)$$

Thus we get the  $(x - f)$ -values for all other  $\text{H}_2$ : $\text{CO}$  ratios in the same manner. If we assume that no  $\text{CO}_2$  reaction takes place, *i.e.*,  $b = 0$ , then with  $\text{H}_2$ : $\text{CO}$  ratio of 2:1 we get the  $(x - f)$  value as zero. For ratios more than 2:1, *positive values* of  $(x - f)$  are obtained, while for ratios less than 2:1, *negative values* of  $(x - f)$  are got. This means that in the latter case  $(x - f)$  can only be obtained as a positive value with the occurrence of a  $\text{CO}_2$  reaction. Such conditional calculations are shown in Table IV. Similarly, we can assume that no hydrogenation hydrogen is available, *i.e.*,  $(x - f) = 0$ , and then calculate the values of ' $b$ ' as given in Table IV, column 1. The values for ' $b$ ' obtained between the ratios 3:1 and 2:1 will then be negative.

Let us call the minimum value of ' $b$ ', when  $(x - f) = 0$  as ' $b_0$ ', and the corresponding value of ' $a$ ' as ' $a_0$ '. As there is no hydrogenation hydrogen available under these conditions, the existing ' $b_0$ ' reaction serves only for getting a part of reduction hydrogen. At the ratio 2:1, ' $b_0$ ' is zero and for higher ratios ' $b_0$ ' is found to be negative. This means that at ratios lower than 2:1 ' $b_0$ ' is always positive and hydrogenation hydrogen can only be obtained by an additional ' $b$ ' amount, apart from ' $b_0$ ' amount. This additional ' $b$ ' value has already been referred to as ' $b_H$ '. Thus the total ' $b$ ' value within this region will always be the sum of ' $b_0$ ' and ' $b_H$ '. At the ratio 2:1, ' $b_0$ ' is zero, and thus, for this ratio any ' $b$ ' reaction serves for obtaining hydrogenation hydrogen. As the ratio is lowered, ' $b_0$ ' increases, indicating thereby the shift of the total reaction towards  $\text{CO}_2$  reaction side. This indicates the increasing disability of the catalysts to activate sufficient quantity of additionally needed hydrogenation



hydrogen. It means that the chances of a 'b<sub>H</sub>' reaction become less and less. As a result of this, the products of synthesis become richer in olefines and alcohol compounds with higher molecular weights, and the deposition of permanent carbon becomes more pronounced, if hydrogenation hydrogen activity is enforced on the catalyst by the increase of temperature.

In equation (24), 'a' represents that amount of CO which has served for the reduction, according to water reaction for any finite values of (x - f), and 'b' represents the respective CO volume which has been converted into hydrocarbons according to the carbon dioxide reaction. The following equations are thus valid:

$$a = a_0 - 2b_H; a_0 = a + 2b_H; a_H = 2b_H; b = b_0 + b_H;$$

$$b_0 = b - b_H; b_H = b - b_0 = \frac{(a_0 - a)}{2}. \quad (26)$$

Further, we get

$$a = a_0 - a_H; a_0 = a + a_H; a_H = a_0 - a; b = b_0 - \frac{a_H}{2};$$

$$b_0 = b - \frac{a_H}{2}; a_H = 2(b - b_0) \text{ and } a - a_0 = 2(b - b_0); a_0 = a + 2(b - b_0) \quad (27)$$

Thus we see that (x - f) is then always equal to 3b<sub>H</sub> for all H<sub>2</sub>:CO ratios of 2:1 and less. We also get this relationship if we introduce the newly formed equation (26) into equation (22). Then we have

$$(x - f) = 100 - 3(a_0 - 2b_H + b_0 + b_H) \quad (28)$$

$$(x - f) = 100 - 3(a_0 + b_0) + 3b_H \quad (29)$$

and as by our definition

$$3(a_0 + b_0) = 100 \quad (30)$$

therefore,

$$(x - f) = 3b_H \quad (31)$$

TABLE IV

Different Possible Values for 'a', 'b' and '(x - f)' for a Number of Characteristic Usage Ratios at Extreme Conditions of (x - f); Equation used:  $2a + b + (x - f)/a + 2b = \rho$  (24)

No.	H <sub>2</sub> /CO →		3:1	2:1	1.5:1	1:1	0.5:1
	Value of	Condition					
1	b	(x - f) = 0	-1/5 a; -1/5 a <sub>0</sub>	0.00	1/4 a; 1/4 a <sub>0</sub>	a; a <sub>0</sub>	∞
		(x - f) = 25	5 - 1/5 a	8.33	12.5 + 1/4 a	25 + a	∞
2	a	(x - f) = 0	-5 b; -5 b <sub>0</sub>	∞	4 b; 4 b <sub>0</sub>	b; b <sub>0</sub>	0.00
		(x - f) = 25	25 - 5 b	∞	4 b - 50	b - 25	-16.66
3	(x - f)	b = 0	a	0.00	-1/2 a	-a	-3/2 a
4	(x - f)	a = 0	5 b	3 b	2 b	b	0.00

This means that all catalysts, working with  $H_2$ :CO ratio higher than 2:1, activate hydrogenation hydrogen directly or with the help of water reaction and not by the carbon dioxide reaction. We will consider at a later stage consequences that would result from the above equations. However, we can notice from some examples of Cobalt and Ruthenium catalysts given in Table III that the carbon dioxide reaction is not completely suppressed in those cases where  $H_2$ :CO ratio is higher than 2:1. We will deal with this phenomenon in a later part.

### *B. Proposal of an Explanation for the Formation of Methane*

The carbon dioxide reaction, although taking place in a limited way even in those cases where it should no more be possible, may be explained as follows: Along with the main  $H_2O$  reaction with simultaneous higher ratios than 2:1, a  $CO_2$  reaction of limited nature and restricted to the hotter spots of the surface is going on, on account of  $(x - f)$ -formation, and the latter reaction is mainly responsible for methane formation. These relations, which will allow a first deeper look into the reaction distribution shall be more closely explained with the help of examples of Ruthenium catalysts in Table III. We can subdivide these experimental runs in the case of Ruthenium catalyst at different temperatures, according to the overall  $H_2$ :CO ratios as follows: examples 415, 429, 432 and 433 with ratios higher than 2:1 form one group and examples 448 and 451 with ratios slightly lower than 2:1 form another group. According to their overall ratios, examples of first group must be plotted, within the area for higher ratios than 2:1 in Fig. 3 and they are found to fit very well, as long as  $CO_2$  reaction remains negligibly small. This is correct for examples 415 and 429. On the other hand, examples of second group with ratios slightly lower than 2:1 at higher temperatures and practically complete methane formation can be plotted in the upper part of the Fig. 4 without any difficulty. Here, an exclusive methane formation is ruling, for which the maximum requirement of hydrogenation hydrogen is made available by the additional  $CO_2$  reaction ( $b_H$ ). One recognises that the exclusive methane formation in connection with ' $b_H$ ' reaction fixes the upper limiting condition for these Ruthenium catalysts at higher temperature. Therefore it can be closely concluded that this limiting reaction condition for exclusive methane formation by ' $b_H$ ' reaction also exists at locally hot spots on the catalyst surface at average low temperatures. Its low percentage indicates that only very small superheating exists. If this observation proves to be correct, then the values of  $CO_2$  and  $b_H$  should stand in a close relationship with each other. Unfortunately, such a relation cannot be confirmed properly enough due to the uncertainty of methane values with regard to its C-No. Still one gets an impression of such a relation as methane values are often multiples of ' $b_H$ ' values, as can be seen from column  $(e/b_H)$  in Table III. A further hint of such a relationship can be obtained by subdividing the different reactions. At low methane formation no significant relationship is obtained, but at higher methane formation we get a definite result, as methane results out of the products of ' $b_H$ ' reaction.

Two examples of such a calculation are given below:—

The above indicated classification can be carried out in the following manner:

$$a + \beta + \gamma + \delta = a + 2b \quad (32)$$

and

$$(\mu + 1) a + (\eta + 1) \beta + (\psi + 1) \gamma + (\tau + 1) \delta = (\rho + 1) (a + 2b) \quad (33)$$

Where

$a$  = CO conversion according to  $\text{CO}_2$  reaction from equation (6)  
=  $2b_{\text{H}}$ ;

$\beta$  = CO conversion according to water reaction connected with  $\text{CO}_2$  reaction for ratios 2:1;

$\beta = a = 2b_{\text{H}}$ ;

$\gamma$  and  $\delta$  are equal to CO conversion of the two remaining reactions which are water reactions;

$\mu$  =  $\text{H}_2$ : CO ratio of the  $\text{CO}_2$  reaction;  
= 0.5 for pure olefine formation, and  
= 1.0 for pure methane formation,

$\eta$  =  $\text{H}_2$ : CO ratio of water reaction connected with  $a$   
= 2.0 for pure olefines, and  $a$   
= 3.0 for pure methane formation;

$\psi, \tau$  =  $\text{H}_2$ : CO ratios of the remaining reactions unknown or partly known, in case the methane formation is higher than  $(a + \beta)$ ;

$\rho$  =  $\text{H}_2$ : CO overall ratio obtained from C-balance;

$(a + 2b)$  = Total converted CO obtained from C-balance.

From equations (32) and (33) we obtain an equation for  $\psi$ , neglecting  $(\tau + 1) \delta$

$$\psi = \frac{(\rho + 1) (a + 2b) - (\mu + 1) a - (\eta + 1) \beta}{(a + 2b) - a - \beta} - 1 \quad (34)$$

If we use this equation and enter in it values for different possibilities of total methane formation either from  $a + \beta$  or from  $\gamma$ , then only those cases are possible where  $\psi$  or  $\tau$  values obtained are equal to or higher than 2:1. The same procedure is also applicable if we include  $\delta$  and  $\gamma$ . This will be shown by a thorough calculation of the following synthesis examples Nos. 432 and 433 of Table III.

*Example No. 432.*

*Condition (a).*—The  $\text{CO}_2$  and additional  $\text{H}_2\text{O}$  reactions form olefines only and all methane is formed by the remaining reactions.

The  $\text{CO}_2$  formation in this example is 2.37 and methane is 8.36. The overall CO conversion is 31.12 and the  $\text{H}_2$ :CO-ratio is 2.213. We find the following value for  $\tau$ :

$$\tau = \left[ \frac{(2.213 + 1) \times 31.12 - (0.5 + 1) \times 2.37 \times 2 - (2 + 1) \times 2.37 \times 2 - (3 + 1) \times 8.36}{31.12 - 2 \times 2.37 - 2 \times 2.37 - 8.36} \right] - 1$$

$$\tau = 2.412$$

This division of methane formation on the remaining reaction and the formation of olefines from  $\text{CO}_2$  and additional  $\text{H}_2\text{O}$  reactions is therefore possible.

*Condition (b).*—The  $\text{CO}_2$  and additional  $\text{H}_2\text{O}$  reactions produce  $\text{CH}_4$  only.

$$\tau = \left[ \frac{(2.213 + 1) \times 31.12 - (1 + 1) \times 2 \times 2.37 - (3 + 1) \times 2 \times 2.37}{31.12 - 2 \times 2.37 - 2 \times 2.37} \right] - 1$$

$$= 2.306.$$

This division of the partial reactions is therefore also possible in this case.

#### Example No. 433

*Condition (a).*—The  $\text{CO}_2$  and additional  $\text{H}_2\text{O}$  reactions produce olefines only and the methane is formed by the remaining water reactions.

The  $\text{CO}_2$  formation in this example is 5.60 and methane is 15.13. The overall CO conversion is 31.79 and  $\text{H}_2$ :CO ratio is 2.145. We get the following expression for  $\tau$ :

$$\tau = \left[ \frac{(2.145 + 1) \times 31.79 - (0.5 + 1) \times 2 \times 5.6 - (2 + 1) \times 2 \times 5.6 - (3 + 1) \times 15.13}{31.79 - 2 \times 5.6 - 2 \times 5.6 - 15.13} \right] - 1$$

$$\tau = 0.904$$

This division, however, is not possible.

*Condition (b).*—The  $\text{CO}_2$  and additional  $\text{H}_2\text{O}$  reaction produce methane only.

For the same example as above we can then write an equation for  $\psi$

$$\psi = \left[ \frac{(2.145 + 1) \times 31.79 - (1 + 1) \times 2 \times 5.6 - (3 + 1) \times 2 \times 5.6}{31.79 - 2 \times 5.6 - 2 \times 5.6} \right] - 1$$

$$= 2.49$$

This division is therefore the only possible one in this case. The small difference in methane formation between the calculated and observed values (17.5 and 15.13) can be easily explained from the uncertainty of pure methane evaluation and it does not change the fundamental results. Division calculations like these can be made for all syntheses examples, and they usually give a clear result with respect

to the cases with higher methane values, but they always give uncertain results for lower methane values. Though these deductions are not absolutely conclusive, due to uncertainty of the CH<sub>4</sub> values, they still show that it is possible to get more information from these calculations.

### C. Conditions for Exclusive Methane Formation

In the course of our discussion we have mentioned about the complete methane formation, which has also been shown in some of our synthesis examples. It is, therefore, necessary to develop equations to describe the conditions for complete methane formation. The general condition for exclusive methane formation is that the hydrogenation hydrogen volume should be equal to the CO volume, which has been converted into hydrocarbons, *i.e.*,

$$(x - f) = (a + b) = 3b_{\text{H}} \quad (35)$$

From this, it follows that

$$\frac{(a + b)}{(x - f)} = n = 1 \quad (36)$$

If we introduce into this equation, figures from our earlier equations (26) and (27), we get

$$(x - f) = a_0 - 2b_{\text{H}} + b_0 + b_{\text{H}} = a_0 + b_0 - b_{\text{H}} \quad (37)$$

$$(x - f) = 3b_{\text{H}}; \quad b_{\text{H}} = \frac{1}{3}(x - f)$$

$$(x - f) = a_0 + b_0 - \frac{1}{3}(x - f) = \frac{2}{3}(a_0 + b_0) \quad (38)$$

This equation is valid for all conversion ratios as  $(a_0 + b_0)$  is always equal to 33.33 (see equation 30), and thus we find that maximum possible methane formation is always 25. Following is an example for the calculation of the maximum possible methane value for an overall conversion ratio H<sub>2</sub>:CO = 1.4. Independently from the internal division of the conversion ratio, the quotient is found as follows:

$$\frac{\text{H}_2}{\text{CO}} = \frac{1.4}{1} = \frac{2a_0 + b_0}{a_0 + 2b_0} = \frac{\frac{1.4}{2.4} \times 100}{\frac{1.0}{2.4} \times 100} = \frac{58.3}{41.7}$$

$$2a_0 + b_0 = 58.3; \quad b_0 = 58.3 - 2a_0; \quad a_0 + 2b_0 = 41.7;$$

$$a_0 = 41.7 - 2b_0; \quad b_0 = 58.3 - 2(41.7 - 2b_0) = 8.33.$$

$$a_0 = 41.7 - 2(8.33) = 25.$$

$$(x - f) = \frac{2}{3}(a_0 + b_0) = \frac{2}{3}(25 + 8.33) = 25.$$

By such calculations, values of  $a_0$ ,  $b_0$ ,  $a$ ,  $b$  and  $(x - f)$  can be calculated for all overall conversion ratios.

*D. Influence of Hydrogenation Hydrogen on the Formation of Synthesis Products*

The knowledge of hydrogenation hydrogen enables us to make some predictions on the formation of the synthesis products. The hydrogenation hydrogen value represents an expression for the sum of the vapour volumes of all the paraffin hydrocarbons, including methane. Thus, if we deduct the methane value 'e' from  $(x - f)$ , we get that amount of hydrogenation hydrogen which has served for converting certain olefines into paraffins:

$$(x - f) - e = (y - f) \quad (39)$$

where 'e' is equal to the methane value from C-balance, and  $(y - f)$  represents the sum of all vapour volumes of paraffins from  $C_2$  upwards. The absolute values of these figures give some idea of the characteristics of molecular distribution of the saturated products. If  $(x - f)$  is relatively high, predominantly lighter paraffins are formed, while with small  $(x - f)$  values high-boiling saturated hydrocarbons are formed. Also with the help of  $(x - f)$  we can predict the amount and character of olefines. Above a certain  $(x - f)$  value, no or very little olefines should form as all the products will then be hydrogenated. At lower  $(x - f)$  values, the synthesis products will be richer in olefines.

The methane formation has also a great influence on the nature of the paraffins and olefines formed, as can be seen from equation (39). Keeping the  $(x - f)$  value fixed, if we increase methane formation, the value of remaining hydrogenation hydrogen  $(y - f)$  is decreased, and consequently higher molecular paraffins can no more be formed. The upper limit of this condition is then reached when methane formation just equals the hydrogenation hydrogen, *i.e.*,  $e = (x - f)$  and  $(y - f) = 0$ . In this case no paraffins higher than methane can possibly be formed, and all the products beyond methane must appear as olefines or as oxygenated compounds. This upper limit, therefore, represents for any fixed  $(x - f)$  value, the optimum condition for olefine formation. In the case of a catalyst with higher hydrogenation hydrogen activity,  $(x - f)$  increases with temperature and ultimately a stage is reached when a complete and maximum methane formation occurs. Other catalysts with lower potentiality of hydrogenation hydrogen, and which under normal operational conditions run at higher temperatures, are often not capable of increasing their  $(x - f)$  values with further increase of temperature. Such catalysts will give much higher olefine formation with simultaneous lower methane formation. As in these cases  $(x - f)$  values are small, the olefines will predominantly be of high molecular weight. The influence of methane formation on the distribution of the other products can be expressed by its ratio with hydrogenation hydrogen

$$\xi = \frac{e}{(x - f)} \quad (40)$$

This ratio can vary between 0 and 1.0 for each  $(x - f)$  value, when  $e = 0$  and  $e = (x - f)$ . If this so-called "relative methane formation" is introduced into equation (39) we get

$$(1 - \xi) = (y - f)/(x - f). \quad (41)$$

This important ( $\xi$ ) value has been calculated for a number of examples and is shown in Table III.

It is clear from the above discussion that methane formation influences in all cases the formation of other products. This means that the specific reaction which leads to methane formation must be in close relation to the nature and formation of other synthesis products. More quantitative data are necessary to throw greater light on the subject which has been discussed here rather qualitatively.

#### SUMMARY

A general reaction scheme for Fischer-Tropsch syntheses reactions has been developed with the help of C-balance calculations. By this scheme one can ultimately find the polymerization function and the hydrogenation hydrogen which has been used to hydrogenate part of the primary olefines into paraffins. With the knowledge of these values one can get some idea about the nature and the distribution of the products. The relationships which govern the formation of methane, olefines and paraffins are discussed here. A general conversion scheme which is valid for all kinds of syntheses is established, and it allows the division of the total reaction into different individual reactions at all possible overall conversion ratios.