

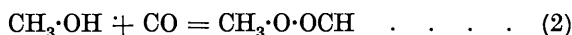
LIV.—*The Equilibrium between Methyl Formate and Methyl Alcohol, and Some Related Equilibria.*

By JENS ANTON CHRISTIANSEN.

THE announcement that the Badische Anilin- und Soda-Fabrik had succeeded in synthesising methyl alcohol from carbon monoxide and hydrogen attracted great interest. Patart (*J. Ind. Eng. Chem.*, 1925, **17**, 430, 859) claimed priority in this invention; but without entering into this discussion it may be mentioned that the process



patented by the author in 1918, combined with the reaction



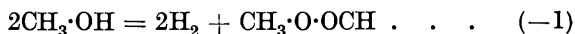
investigated by Stähler (*Ber.*, 1914, **47**, 580), was the first which made it possible to prepare methyl alcohol from water gas, although any process by which the reaction



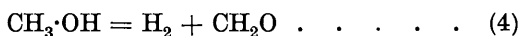
can be carried out without methyl formate as an intermediate product must be of the greatest value.

The author was able to measure the equilibrium constant of reaction (1) by the kind permission of Prof. E. Büilmann, Director of this Laboratory, to whom he wishes to express his thanks. Later, in connexion with a firm in Copenhagen, Mr. Arne Olsen and the author made some measurements of the equilibrium constant of reaction (2). The results of these researches are in this paper: the substance of them was described, with the permission of the firm, in a lecture to the Chemical Society of Copenhagen on October 14, 1924.

Earlier work had shown that when methyl alcohol vapour is passed over reduced copper at 200° it splits up according to the equation



and not, as stated by Sabatier, according to



Before this result was published, Mannich and Geillmann (*Ber.*, 1916, **49**, 585) had drawn the same conclusion. As this reaction (—1) did not appear to be complete, a mixture of measured quantities of hydrogen and methyl formate was passed over reduced copper at about 180°, and a considerable decrease in volume observed, showing the occurrence of reaction (1).

To determine the equilibrium, a stream of electrolytic hydrogen, freed from oxygen by means of palladinised asbestos, and dried, was passed at a constant rate (by the use of a pressure regulator and capillary) through a saturator, containing methyl formate, in a thermostat. It then passed through a pipette containing reduced cuprous oxide on asbestos, which was heated in an electric oven, through two absorption tubes, and into a gas burette. The catalyst was reduced with hydrogen *in situ* before the experiment. The absorption tubes were filled with *N*/10-sodium hydroxide. In each experiment, the gas was allowed to escape before reaching the absorption tubes until the rate of flow and the temperatures of the saturator and the oven had been constant for some time. The escape was then stopped and the reaction products were collected. After a suitable time, the absorption tubes were removed and weighed (the hydrogen in them having been replaced by air free from carbon dioxide), and their contents titrated after addition of barium chloride (Winckler's method), so that both methyl alcohol and carbonic and formic acids were determined. The gas was analysed in an Orsat apparatus with platinum capillary. In this way, the amounts of methyl alcohol, methyl formate, hydrogen, carbon monoxide, and dioxide could be estimated. Allowance was made for water lost by evaporation from the absorption tubes, etc.

The equilibrium was also determined by starting with methyl alcohol. This was admitted directly to the catalyst in the oven from a burette through a capillary which was warmed above the b. p. of the alcohol. The results are in Table I, Nos. 1—10 being experiments on reaction (1), Nos. 11—17 on reaction (—1). The temperature of the oven was measured by a standardised thermometer placed outside the catalyst pipette; the error so produced was small, since the rate of flow was slow. The velocities in column 5 are in millimols. of methyl formate or pairs of millimols. of methyl

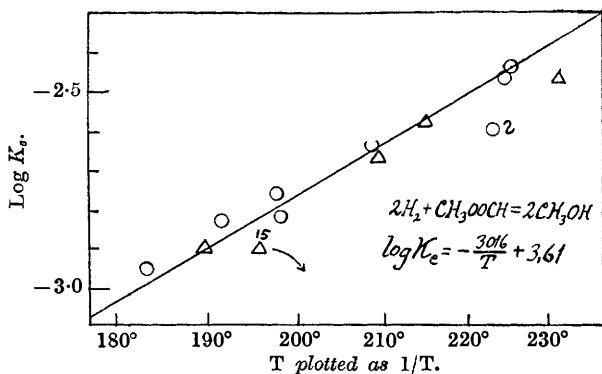
TABLE I.

| No. | Temp. of oven. | Pressure in mm. Hg. | Temp. of water-bath. | Velocity, mmol./hr. | $\text{CH}_3\text{-OH}$, mmol. | $\text{CH}_3\text{-O-CH}_3$, mmol. | CO , mmol. | CO_2 , mmol. | CH_4 , mmol. | H_2 , mmol. | $\text{CH}_3\text{-O-CH}_3$, H_2 v. p. | $K_1 \times 10^3$. |
|-----|----------------|---------------------|----------------------|---------------------|---------------------------------|-------------------------------------|---------------------|-----------------------|-----------------------|----------------------|--|---------------------|
| 1 | 198-9° | 758 | 13-56° | 6-91 | 8-29 | 2-42 | 4-38 | 0-29 | 0-17 | 5-96 | 0-912 | 1-51 |
| 2 | 199-6 | 773 | 13-60 | 8-80 | 11-59 | 3-23 | 6-32 | 0-15 | 0-13 | 8-60 | 0-880 | 1-55 |
| 3 | 198-7 | 773 | 13-64 | 2-79 | 7-51 | 1-54 | 5-08 | 0-22 | 0-12 | 6-64 | 0-882 | 1-50 |
| 4 | 224-8 | 779 | 10-60 | 6-86 | 5-03 | 0-68 | 5-04 | 0-19 | 0-15 | 8-44 | 0-676 | 2-5 |
| 5 | 227-0 | 779 | 10-60 | 1-40 | 2-53 | 0-33 | 3-34 | 0-16 | 0-10 | 5-65 | 0-676 | 3-4 |
| 6 | 197-6 | 765 | 10-60 | 4-16 | 5-53 | 1-145 | 3-16 | 0-13 | 0-10 | 5-25 | 0-697 | 1-75 |
| 7 | 225-5 | 772 | 10-60 | 1-85 | 2-86 | 0-31 | 4-68 | 0-18 | 0-15 | 7-80 | 0-687 | 3-62 |
| 8 | 183-4 | 776 | 10-67 | 5-67 | 12-00 | 3-08 | 3-35 | 0-12 | 0-13 | 6-98 | 0-683 | 1-11 |
| 9 | 192-2 | 785 | 10-71 | 4-29 | 6-93 | 1-48 | 2-96 | 0-11 | 0-11 | 5-49 | 0-672 | 1-47 |
| 10 | 208-3 | 771 | 10-70 | 3-63 | 4-85 | 0-79 | 4-09 | 0-15 | 0-16 | 6-66 | 0-693 | 2-28 |
| 11 | 209-0 | 785 | | 2-07 | 5-46 | 0-785 | 2-64 | 0-16 | 0-12 | 7-12 | 0-500 | 2-15 |
| 12 | 214-2 | 784 | | 6-05 | 6-67 | 1-34 | 2-65 | 0-15 | 0-13 | 8-00 | 0-500 | 2-62 |
| 13 | 231-2 | 785 | | 5-55 | 4-83 | 0-80 | 3-11 | 0-16 | 0-14 | 8-26 | 0-500 | 3-38 |
| 14 | 189-4 | 787 | | 2-26 | 6-00 | 1-08 | 0-76 | 0-08 | 0-05 | 4-38 | 0-500 | 1-27 |
| 15 | 195-3 | 778 | | 2-37 | 6-53 | 1-42 | 0-64 | 0-08 | 0-02 | 4-16 | 0-500 | 1-26 |
| 16 | 198-9 | 779 | | 4-39 | 8-22 | 1-70 | 0-34 | 0-17 | 0-03 | 4-45 | 0-500 | 0-89 |
| 17 | 200-0 | 774 | | 5-30 | 13-8 | 2-67 | 0-52 | 0-19 | 0-04 | 7-01 | 0-500 | 0-74 |

alcohol passing the catalyst per hour. Columns 12 and 13 give the initial ratio in molecules of ester to hydrogen, and are calculated (1) from the vapour pressure of the ester and the total pressure in the saturator, (2) from the analysis of the products; in the decomposition experiments the ratio should obviously be 0.500. These values give a check on the analyses, and show a satisfactory agreement. The values in the last column are those of the constant $K_1 = C_{\text{H}_2}^2 C_{\text{CH}_3\text{OCH}} / C_{\text{CH}_3\text{OH}}^2$.

The values of $\log_{10} K_1$ (expts. 1—15) are plotted in Fig. 1 against $1/T$; they show that the results of association and dissociation experiments lie on the same curve, proving that true equilibrium was reached. The values of K_2 for the reaction $\text{CH}_3\text{OCH} = \text{CO} + \text{CH}_3\text{OH}$ were so discordant as to show that equilibrium had not

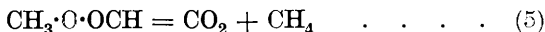
FIG. 1.



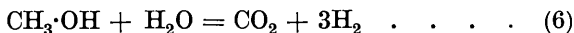
△ (dissociation) refers to experiments starting with CH_3OH [reaction (-1)].
 ○ (association) " " " " " $\text{H}_2 + \text{CH}_3\text{OCH}$ [reaction (1)].

been reached. The values obtained from expt. 15 (Fig. 1) and expts. 16 and 17 (not plotted) lie well below the curve; evidently the catalyst, which was the same in all these experiments, had lost its activity, so that even the equilibrium (± 1) was not now attained.

The values for CO_2 and CH_4 in the table suggest that the reaction



took place to a slight extent. If, however, a trace of water was present, carbon dioxide may have been formed by the reaction



(*J. Amer. Chem. Soc.*, 1921, **43**, 1670); this would explain the excess of carbon dioxide found in some of the experiments.

The equilibrium constant of reaction (2) was determined in a

similar manner and in the same apparatus. The catalyst here was solid sodium methoxide. This absorbed some carbon monoxide, and hence the results are not very trustworthy. The same thing occurred, but to a much smaller extent (about 1 mol. of sodium methoxide disappearing for every 100 mols. of carbon monoxide converted into methyl formate), when the reaction was carried out in solution, and in this case the reaction causing the carbon monoxide to disappear was shown to be $\text{CH}_3\cdot\text{O}\cdot\text{OCH} + \text{NaO}\cdot\text{CH}_3 = \text{CH}_3\cdot\text{O}\cdot\text{CH}_3 + \text{NaO}\cdot\text{OCH}$. Hence the values of the equilibrium constant K_2 are only to be regarded as preliminary, but those of the association and dissociation experiments agree fairly well, as the following table shows.

TABLE II.

| Reaction. | Temp. | Log K_2 by exper. | Log K_2 calc. |
|-----------|-------|------------------------|--------------------|
| (-2) | 102° | 1.82 | 1.81 |
| (2) | 74 | 1.53 | 1.40 |
| (-2) | 74 | 1.40 | 1.40 |
| (-2) | 70 | 1.29 | 1.34 |

$K_2 = C_{\text{CO}} \cdot C_{\text{CH}_3\cdot\text{OH}} / C_{\text{CH}_3\text{OCH}}$ is for the gas mixture leaving the catalyst. The values in column 4 are calculated by the equation $\log_{10} K_2 = -1880/T + 4.82$.

The effect of temperature on equilibrium should be accurately given over a fairly wide range by an expression of the form

$$\log_{10} K = -A/T + B,$$

where A = heat of reaction at constant volume divided by 4.571, and B is a constant (Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 636). Values calculated on this formula are in Table II and are represented by the straight line in Fig. 1. The values given in the literature for the heats of combustion of methyl alcohol and methyl formate are discordant, Stohmann's value for methyl alcohol being about 2 Cals. lower than that of Thomsen. I have preferred to use the latter, since, although Thomsen's "universal burner" is apt to give somewhat high values, the error may be expected to be small when the substances are volatile, whilst, on the other hand, Stohmann's values, according to Roth (*Z. Elektrochem.*, 1911, **17**, 789), may be suspected to be low, especially in the case of volatile liquids.

The heat capacity of methyl alcohol has been calculated from the values in Landolt-Börnstein's tables for the ratio, k , between the two heat capacities. For methyl formate, no direct data seem to be available, but from the value for ethyl formate and those for methyl and ethyl alcohols the heat capacity of methyl formate (at constant volume) has been estimated at 10 cal. per degree.

The following table contains all the numerical values used in the calculation of the reaction heats at the temperatures in question.

| Substance. | Heat of combustion at const. press. | Heat capacity at const. vol. |
|-----------------------|--|---------------------------------|
| Methyl alcohol | 182,230 | 7.8 |
| Methyl formate | 241,210 | 10.0 |
| Carbon monoxide | 67,960 | 5.0 |
| Hydrogen | 68,430 | 4.8 |

By means of this table the heat of reaction (1) at constant volume and about 200° is calculated to be 13,800 cal. and that of reaction (2) at about 100°, 8,600 cal. From these values and the above determinations of the equilibrium constants, the constants, B , of reactions (1) and (2) can be calculated as 3.61 and 4.82, respectively. These two numbers thus contain the results of the above investigation of the two reactions.

It is now possible to obtain from Fig. 1 and Table II a preliminary value of the equilibrium constant $K_3 = C_{\text{CO}} \cdot C_{\text{H}_2}^2 / C_{\text{CH}_3\text{OH}}$ for the reaction (3). Calculation shows that

$$\log K_3 = -4896/T + 8.43 \quad . \quad . \quad . \quad (7)$$

From (7) it can be calculated that at about 200° K_3 is about 10^{-2} , so that at this temperature, if the hydrogen concentration is 1 mol. per litre, only 1% of the carbon monoxide will remain if the reaction $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$ proceeds until equilibrium has been reached, whilst, on the other hand, if the hydrogen concentration is 0.01, only 1% of the carbon monoxide will be transformed into methyl alcohol.

The value of K_3 can also be roughly predicted by means of one of the well-known approximate equations arrived at from Nernst's third law of thermodynamics, for instance, the one given by Nernst himself,

$$\log K_p = -Q_{18}/4.57T + 3.5 \log T + 2i_{\text{H}_2} + i_{\text{CO}} - i_{\text{CH}_3\text{OH}} \quad (8)$$

where the i 's are the so-called conventional chemical constants of the different molecular species.

As shown by Cederberg (*Dissert.*, Upsala, 1916), a close connexion seems to exist between the critical pressure of a substance and its chemical constant and therefore I have used the values $i_{\text{H}_2} = 1.6$; $i_{\text{CO}} = i_{\text{N}_2} = 2.6$; $i_{\text{CH}_3\text{OH}} = i_{\text{SO}_2} = 3.3$ (see Pollitzer, *Ahrens's Sammlung* 17, 1912).

By means of $K_p = (RT)^2 K_c$ and the data just mentioned we thus find

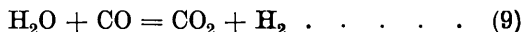
$$\log K_3 = -22700/4.57T + 1.5 \log T + 4.7 \quad . \quad . \quad (8, i)$$

As furthermore $1.5 \log T$ at temperatures about 200° is very nearly equal to 4.0, the equation becomes

$$\log K_3 = -4966/T + 8.7 \quad . \quad . \quad . \quad (8, ii)$$

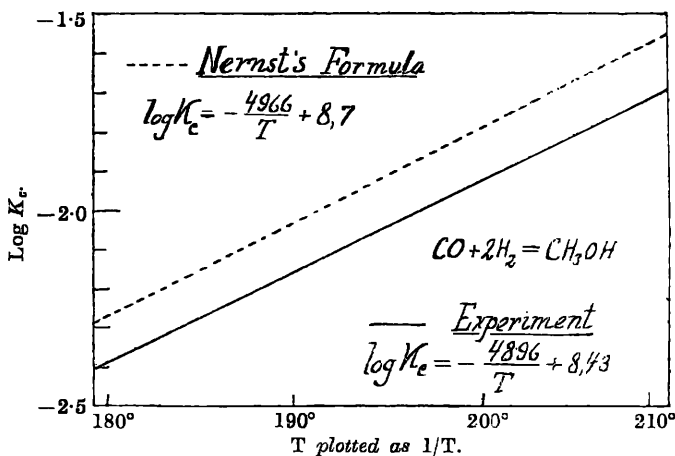
The agreement (see Fig. 2) between (8, ii) and (7) is as good as could be expected, considering the preliminary character of the investigation of reaction (2) and the approximations implied in the use of the Nernst equation (8).

By combining equation (7) with a similar relation derived from earlier experiments on the reaction



it is furthermore possible to calculate the equilibrium constant of the reaction (6). If we define K_9 by means of the equation $K_9 = C_{\text{H}_2\text{O}} \cdot C_{\text{CO}} / C_{\text{CO}_2} \cdot C_{\text{H}_2}$, where the concentrations are those at equi-

FIG. 2.



librium, we get from Hahn's experiments (*Z. physikal. Chem.*, 1903, **44**, 513; 1904, **48**, 735; see Haber, "Thermodynamik technischer Gasreaktionen," Berlin, 1905)

$$\log_{10} K_9 = -1854/T + 1.66 \quad . \quad . \quad (10)$$

When this equation is subtracted from (8, ii) we obtain

$$\log_{10} K_6 = -3042/T + 6.77 \quad . \quad . \quad (11)$$

where K_6 is the equilibrium value of $C_{\text{CO}_2} \cdot C_{\text{H}_2}^2 / C_{\text{CH}_3\text{OH}} \cdot C_{\text{H}_2\text{O}}$.

Finally it should be remarked that by means of existing data on the equilibria



and



and the equations given above, it should also be possible to calculate the value of the equilibrium constant for the reaction (5).

The first of these reactions has been investigated by Mayer and

Alt Mayer (*Ber.*, 1907, **40**, 2134), Coward and Wilson (*J.*, 1919, **115**, 1380), and Pring and Fairlie (*J.*, 1912, **101**, 91). The results of these authors may be represented with sufficient accuracy by means of the equation

$$\log K_p = \log \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} = \frac{5450}{T} - 6.33 \quad . \quad . \quad (14)$$

If we wish to get $K_c = C_{\text{CH}_4}/C_{\text{H}_2}^2$ with the concentrations expressed in mols. per litre, we must add $\log RT = \log T - 1.09$ and consequently

$$\log K_c = 5450/T + \log T - 7.42 \quad . \quad . \quad (14, i)$$

For the reaction (14) a summary of the existing data is to be found in a paper by Jellinek and Diethelm (*Z. anorg. Chem.*, 1922, **124**, 220). From their table of the mean values of K_p found at different temperatures by different authors, the following expression may be calculated :

$$\log K_p = 8620/T - 8.80 \quad . \quad . \quad (15)$$

and transforming into K_c ,

$$\log K_c = \log \frac{C_{\text{CO}_2}}{C_{\text{CO}}^2} = \frac{8620}{T} + \log T - 9.89 \quad . \quad (15, i)$$

By adding these equations we get the equilibrium constant for the reaction $2\text{H}_2 + 2\text{CO} = \text{CH}_4 + \text{CO}_2$, viz.,

$$\log K_p = \log \frac{p_{\text{CH}_4} \cdot p_{\text{CO}_2}}{p_{\text{H}_2}^2 \cdot p_{\text{CO}}^2} = \frac{14070}{T} - 15.13 \quad . \quad . \quad (16)$$

$$\text{or} \quad \log K_c = \log \frac{C_{\text{CH}_4} \cdot C_{\text{CO}_2}}{C_{\text{H}_2}^2 \cdot C_{\text{CO}}^2} = \frac{14070}{T} + 2 \log T - 17.31 \quad (16, i)$$

Adding to this the equation (7), we get the logarithm of the equilibrium constant for the reaction $\text{CH}_3\cdot\text{OH} + \text{CO} = \text{CH}_4 + \text{CO}_2$, viz.,

$$\log K_c = \log \frac{C_{\text{CH}_4} \cdot C_{\text{CO}_2}}{C_{\text{CH}_3\cdot\text{OH}} \cdot C_{\text{CO}}} = \frac{9170}{T} + 2 \log T - 8.88 \quad . \quad (17)$$

from which it is evident that the formation of methyl alcohol from methane and carbon dioxide will take place only at temperatures at which methane is not at all stable, whilst it is possible, according to equations (11) and (7), to obtain reasonable amounts of methyl alcohol from hydrogen and either carbon monoxide or dioxide at not too high temperatures.

It is obvious that the equations given above all contain the uncertainty introduced by the use of the preliminary results for the equilibrium between carbon monoxide, methyl alcohol, and methyl formate.

Summary.

(1) The equilibrium constant of the reaction $\text{CH}_3\cdot\text{O}\cdot\text{OCH} + 2\text{H}_2 = 2\text{CH}_3\cdot\text{OH}$ has been determined with fair accuracy at temperatures in the neighbourhood of 200° .

(2) Preliminary values for the equilibrium constant of the reaction $\text{CH}_3\cdot\text{OH} + \text{CO} = \text{CH}_3\cdot\text{O}\cdot\text{OCH}$ at about 100° have been given.

(3) It is shown that by combination of the found values with existing data the equilibrium constants of the reactions $\text{CO} + 2\text{H}_2 = \text{CH}_3\cdot\text{OH}$; $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\cdot\text{OH} + \text{H}_2\text{O}$; and $\text{CH}_4 + \text{CO}_2 = \text{CH}_3\cdot\text{OH} + \text{CO}$ may be calculated.

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