

## CHEMICAL EQUILIBRIA IN METHANOL SYNTHESIS FROM METHYL FORMATE

Kwang Man KIM, Jae Chang KIM, Minsek CHEONG, Jae Sung LEE and Young Gul KIM

Chemical Engineering Division, Research Institute of Industrial Science and Technology (RIST),

P.O. Box 135, Pohang 790-600, Korea

Department of Chemical Engineering, Pohang Institute of Science and Technology (POSTECH),

P.O. Box 125, Pohang, 790-600, Korea

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**Abstract**—The chemical equilibria of the gas-phase methanol production from methyl formate were studied by analyzing the hydrogenolysis reaction ( $\text{HCOOCH}_3 + 2\text{H}_2 = 2\text{CH}_3\text{OH}$ ) and decarbonylation reaction ( $\text{HCOOCH}_3 = \text{CH}_3\text{OH} + \text{CO}$ ) occurring concurrently. The equilibrium constant, which includes the effects of nonideality, was estimated for each reaction using equations of state. Equilibrium composition for each constituent in this reaction system was evaluated in relation to temperature, pressure, and initial concentration ratio ( $\text{H}_2/\text{HCOOCH}_3$ ), and the effect of CO feed on equilibrium conversion of methyl formate was also discussed. General guidelines to improve the selectivity of hydrogenolysis reaction were proposed.

### INTRODUCTION

Methyl formate (MF;  $\text{HCOOCH}_3$ ) has been reported to undergo a variety of reactions and could serve as a building block molecule in  $\text{C}_1$  chemistry [1-3]. The combination of an efficient synthesis of MF and its facile decomposition allows the molecule to be used as a means for separation, storage, and transport of syngas ( $\text{CO}/\text{H}_2$ ) as well. Among these applications, methanol synthesis from MF has become one of promising indirect syngas conversions in an integrated  $\text{C}_1$  chemical complex involving MF which could come into existence in the future [3].

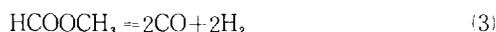
MF can undergo hydrogenolysis to produce two moles of methanol as follows:



This reaction was first described by Christiansen [4] as a two-step methanol synthesis route from syngas. Besides the hydrogenolysis reaction, MF could undergo other reactions under similar conditions. For instance, thermal decomposition or pyrolysis [5] of MF to methanol and CO has been used to obtain high purity CO [6] according to the following reaction.



The methanol could react further to form CO and  $\text{H}_2$  at higher temperatures, and thus yield reaction (3).



Reaction (2) is known to be the reaction producing the major by-product, CO, in the gas-phase reaction (1) over a copper chromite catalyst [7].

As a part of a research program to produce methanol efficiently through the vapor-phase hydrogenolysis of MF over suitable copper-containing catalysts, we investigated the chemical equilibria for the reactions (1) and (2). In this work we calculated vapor-phase fugacity coefficients for the reactions and estimated the equilibrium constants including the correction factors for nonideality from an adequate equation of state (EOS). From these thermodynamic viewpoints, the effects of the initial concentration, temperature, and pressure on the equilibrium conversion of MF were examined and the equilibrium compositions of the constituents for the reaction system were estimated.

### THERMODYNAMIC EVALUATIONS

#### 1. Basic thermodynamics

Prior to the calculation of equilibrium constants, it is necessary to determine the heat of reaction  $\Delta H$  and Gibbs free energy  $\Delta G$  for each reaction as function of temperature ( $T$  in degrees Kelvin) and pressure ( $P$  in atm). Unfortunately, few data for these values, espe-

**Table 1. Thermodynamic properties of the constituent species in this reaction system**

Compound number	1	2	3	4
Compound	HCOOCH <sub>3</sub>	CH <sub>3</sub> OH	CO	H <sub>2</sub>
Specific heat capacity coefficients <sup>a</sup>				
$a_1$	4.456	4.394	6.342	6.947
$a_2 \times 10^3$	42.096	24.274	1.836	-0.199
$a_3 \times 10^7$	-203.4	-68.55	2.80	4.81
Gibbs free energy coefficients <sup>b</sup>				
$A_1$	-350.9	-201.9	-109.9	0
$A_2 \times 10^2$	17.47	12.54	-9.22	0
$A_3 \times 10^6$	16.32	20.34	1.45	0
Critical constants <sup>c</sup>				
$T_c$ (K)	487.2	513.2	133.4	33.3 <sup>d</sup>
$P_c$ (atm)	59.15	78.7	34.5	12.8 <sup>d</sup>
$v_c$ (cm <sup>3</sup> /mol)	172.0	117.9	93.1	65.0 <sup>d</sup>
$Z_c$	0.255	0.224	0.294	0.305 <sup>d</sup>
Acentric factor <sup>e</sup> $\omega$	0.257	0.556	0.066	0

<sup>a</sup>Specific heat capacity  $C_p(T) = a_1 + a_2T + a_3T^2$  (cal/mol·K). Data from Ref. [8].

<sup>b</sup>Gibbs free energy of formation  $\Delta G_f(T) = A_1 + A_2T + A_3T^2$  (kJ/mol). Data from Ref. [9].

<sup>c</sup>Data from Ref. [10].

<sup>d</sup>Data from Ref. [8].

cially for the reactions with MF, have been reported. Therefore,  $\Delta H$  and  $\Delta G$  must be determined using the thermodynamic data for the constituent species of the reaction system (Table 1). The compound numbers in Table 1 (1 for MF, 2 for methanol, 3 for carbon monoxide, and 4 for hydrogen) are assigned for the convenience in computations which will be performed below. The heat of reaction is calculated including the effect of elevated pressures in conjunction with an EOS (here we choose the Berthelot EOS as previously used [11]). Then, for reaction (1)

$$\begin{aligned} \Delta H_1(T, P) = & -8973 + 3706931/T^2 - 9.5624T \\ & + 3.426 \times 10^{-3} T^2 + 18.89 \times 10^{-7} T^3 \\ & - (0.056 + 3706931/T^2)P \text{ (cal/mol)} \end{aligned} \quad (4)$$

and for reaction (2)

$$\begin{aligned} \Delta H_2(T, P) = & 8911 - 424064/T^2 + 6.28T - 7.993 \\ & \times 10^{-3} T^2 + 45.88 \times 10^{-7} T^3 + (0.301 \\ & + 424064/T^2)P \text{ (cal/mol)}. \end{aligned} \quad (5)$$

In order to find the thermodynamically favorable reaction ranges, Gibbs free energy change for each reaction is investigated.

$$\begin{aligned} \Delta G_1(T) = & -52.806 + 7.61 \times 10^{-2} T \\ & + 2.4368 \times 10^{-5} T^2 \text{ (kJ/mol)} \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta G_2(T) = & 39.169 - 1.4154 \times 10^{-1} T \\ & + 5.4777 \times 10^{-6} T^2 \text{ (kJ/mol)}. \end{aligned} \quad (7)$$

Employing the rough criteria for screening chemical reactions (favorable reaction for  $\Delta G < 0$  and possibly favorable one for  $0 < \Delta G < 50$  kJ/mol [9]), thermodynamically favorable temperature range for the reaction system is determined as 280-580 K.

According to the heats of reaction calculated, the hydrogenolysis reaction is highly exothermic [ $\Delta H_1(298 \text{ K}, 1 \text{ atm}) = -11.470$  kcal/mol] while the decarbonylation reaction is highly endothermic [ $\Delta H_2(298 \text{ K}, 1 \text{ atm}) = 10.194$  kcal/mol] and both  $\Delta H$  have nearly same magnitude. In terms of the calculated Gibbs free energy changes, however, the hydrogenolysis reaction [ $\Delta G_1(298 \text{ K}) = -6.62$  kcal/mol] occurs much more favorably than the decarbonylation reaction [ $\Delta G_2(298 \text{ K}) = -0.62$  kcal/mol]. It can be easily noticed from these results that the reaction (1) is dominant at lower temperatures whereas the reaction (2) is dominant at higher temperatures, and that at moderate temperatures the two reactions must be competing with each other.

Additionally, equilibrium constants  $K_a$  as a function of temperature can be conventionally calculated by van't Hoff rule:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H}{RT^2} \quad (8)$$

where  $R$  is the universal gas constant. Substituting eq. (4) or (5) for  $\Delta H$  in eq. (8) and integrating it, the equilibrium constant for each reaction may be determined through the adjustment of integration constants with the known values of  $\Delta G$ : for reaction (1)

$$\begin{aligned} K_{a1} = \exp(5772.5/T - 4.81 \ln T + 1.72 \times 10^{-3} T \\ - 6.79 \times 10^{-7} T^2 + 19.1) \end{aligned} \quad (9)$$

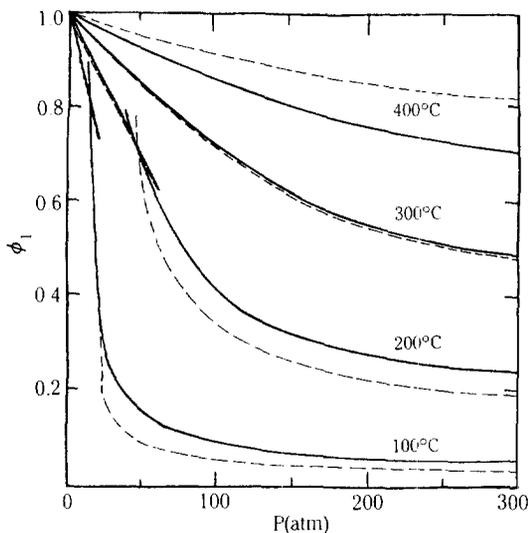
and for reaction (2)

$$\begin{aligned} K_{a2} = \exp(-5130/T + 3.16 \ln T - 4.023 \times 10^{-3} T \\ + 1.55 \times 10^{-6} T^2 - 14.15). \end{aligned} \quad (10)$$

In the gas-phase reaction system, the equilibrium constant for each reaction is

$$K_{a1} = K_{x1} K_{\phi 1} P^{-1} \quad (11)$$

$$K_{a2} = K_{x2} K_{\phi 2} P \quad (12)$$



**Fig. 1.** Fugacity coefficient for MF calculated from the Soave-Redlich-Kwong EOS: (—) for the pure component; (---) for a mixture of 16 mol% MF, 79.5 mol% methanol, and 4.5 mol% H<sub>2</sub>.

where

$$K_{x_1} = (x_2^e)^2 / [(x_1^e) (x_4^e)^2] \quad (13)$$

$$K_{x_2} = (x_2^e) (x_3^e) / x_1^e \quad (14)$$

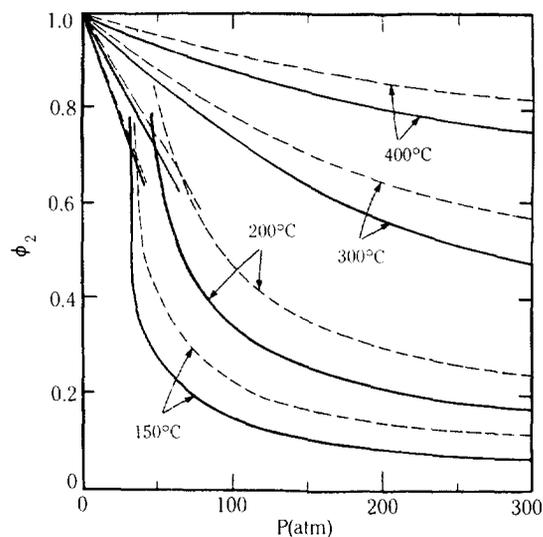
$$K_{\phi_1} = \phi_2^2 / (\phi_1 \phi_4^2) \quad (15)$$

$$K_{\phi_2} = (\phi_2 \phi_3) / \phi_1 \quad (16)$$

Here, the subscripts 1, 2, 3, and 4 in each mole fraction  $x_i$  and in each vapor-phase fugacity coefficient  $\phi_i$  denote the component  $i$  as already defined in Table 1, and the superscript  $e$  represents an equilibrium state.  $K_{\phi_1}$  and  $K_{\phi_2}$  are correction factors for nonideality defined in terms of the vapor-phase fugacity coefficients of  $i$ ,  $\phi_i$ . The computation of  $K_{x_1}$  and  $K_{x_2}$  is related to equilibrium compositions of reaction mixtures and considered in the subsection of equilibrium calculations.

## 2. Fugacity coefficients and correction factors

Fugacity coefficients can be evaluated using an adequate EOS, which indicates the deviations from ideal gas behavior. The choice of EOS is not easy because each component in reaction mixture exhibits different deviation from the ideality. For instance, CO and H<sub>2</sub> represent nearly ideal gas behaviors while MF and methanol are far off from ideality. Therefore the choice of the method to estimate exact  $\phi_i$ 's of MF and methanol becomes important. A number of works [12-14] for the chemical equilibria in methanol syn-



**Fig. 2.** Fugacity coefficient for methanol. Refer to the caption in Fig. 1.

thesis from syngas indicate that the Soave-Redlich-Kwong EOS [15] or Peng-Robinson EOS [16] gives best results in correcting nonideal gas behaviors. In comparing two EOS's applied, the difference in fugacity coefficients is significant for representing the nonideality [13]. In the present work, the values of fugacity coefficients and correction factors are calculated using the Soave-Redlich-Kwong EOS.

Fig. 1 shows fugacity coefficients of MF as a function of temperature and pressure, which are calculated from the Soave-Redlich-Kwong EOS for the pure component (solid curves) and for a mixture that is 16 mol% MF, 79.5 mol% methanol and 4.5 mol% H<sub>2</sub> (dotted curves), which is a composition in that range of that found in methanol synthesis reactions and will be resulted in the next section. Fugacity coefficients of methanol have been calculated previously [12] using Peng-Robinson EOS. Here we have calculated using Soave-Redlich-Kwong EOS as shown in Fig. 2. The discontinuities of the fugacity coefficient curves, as shown in Figs. 1 and 2, represent the saturation conditions between pure liquid and pure vapor phases. The curved segment below and to the right of the intersection corresponds to liquid-phase fugacity coefficient of MF or methanol [12]. The dotted curves in these figures represent vapor-phase fugacity coefficients of MF and methanol, respectively, in the equilibrium mixture of MF, methanol, and H<sub>2</sub>. At low temperature, MF in a vapor-phase mixture rich in methanol (79.5 mol%) behave more like nonideal gas than it does in the pure vapor state. As temperature is increased, however, MF

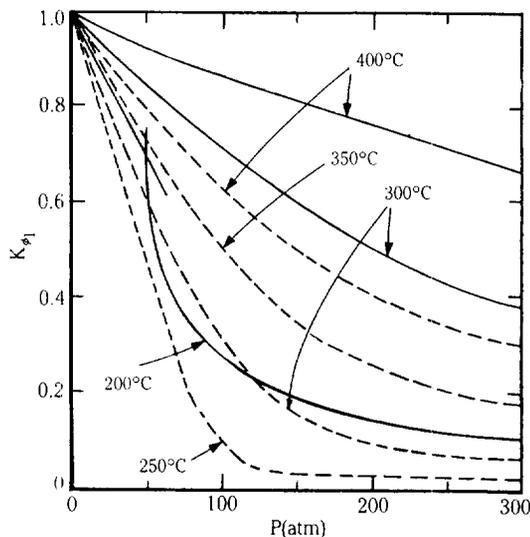


Fig. 3. Correction factor for the vapor-phase hydrogenolysis of MF to methanol. Refer to the caption in Fig. 1.

in the equilibrium mixture appears higher ideality than in its pure state. Contrary to these facts, the fugacity coefficient of methanol (Fig. 2) in the vapor-phase mixture, irrespective of the reaction ranges of temperature and pressure, is higher than in the case of pure state.

The correction factors for each reaction can be calculated from the vapor-phase fugacity coefficients of equilibrium components. Figs. 3 and 4 show the dependence of correction factors  $K_{\phi_1}$  and  $K_{\phi_2}$  on the temperature, pressure, and composition (for Fig. 3 only) of a equilibrium mixture. In terms of pure-component fugacity coefficients, Fig. 3 show that the correction factor of the hydrogenolysis reaction shows more similar pattern to the fugacity coefficient of methanol rather than to that of MF. This observation indicates that the contribution of methanol to  $K_{\phi_1}$  is more significant than that of MF in the equilibrium mixture of the hydrogenolysis reaction. Furtherly, considering the compositional effect  $K_{\phi_1}$  represent much less value than the case of pure state. This behavior is from the dominance of methanol fraction in  $K_{\phi_1}$  formula and the application of a methanol-rich equilibrium mixture (16 mol% MF, 79.5 mol% methanol, and 4.5 mol%  $H_2$ ) in the calculation of the fugacity coefficients. For the decarbonylation reaction whose correction factor is shown in Fig. 4, however,  $K_{\phi_2}$  hardly depends on the reaction pressure since the nonidealities of MF and methanol compensate each other. The compositional effect of a equilibrium mixture of  $K_{\phi_2}$  is not suggested in Fig. 4 because the numerator ( $\phi_2\phi_3$ ) has higher than

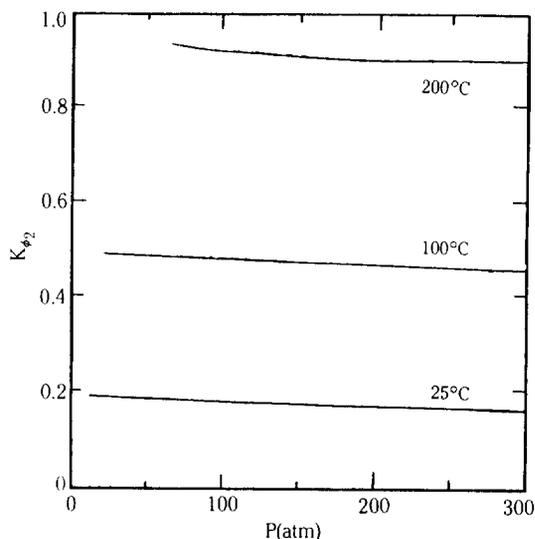


Fig. 4. Correction factor for the decarbonylation of MF to methanol and CO calculated from the Soave-Redlich-Kwong EOS for the pure component.

the denominator ( $\phi$ ) when calculating with the same mixture compositions as the case of  $K_{\phi_1}$ .

### 3. Equilibrium calculations

Defining two equilibrium extent of reaction  $\xi_1$  and  $\xi_2$  for reactions (1) and (2) respectively, the total mole of reaction mixture at equilibrium becomes  $n_{tot}$  ( $= 1 - \xi_1 + \xi_2$ ) by the stoichiometry of the reaction system. Then, the mole fractions of each component at equilibrium can be easily obtained as following expressions.

$$x_1^e = (x_1^o - \xi_1 - \xi_2) / n_{tot} \quad (17)$$

$$x_2^e = (2\xi_1 + \xi_2) / n_{tot} \quad (18)$$

$$x_3^e = (x_3^o + \xi_2) / n_{tot} \quad (19)$$

$$x_4^e = (x_4^o - 2\xi_1) / n_{tot} \quad (20)$$

where the superscript  $o$  denotes the initial state. It should be noted from the above equations that methanol was considered as a product only, and that the initial CO was imposed to evaluate its effect on the equilibrium conversion of MF.

Then, eqs. (13) and (14) can be rewritten as

$$K_{x1} = \frac{(2\xi_1 + \xi_2)^2 (1 - \xi_1 + \xi_2)}{(x_1^o - \xi_1 - \xi_2) (x_4^o - 2\xi_1)^2} \quad (21)$$

$$K_{x2} = \frac{(2\xi_1 + \xi_2) (x_3^o + \xi_2)}{(x_1^o - \xi_1 - \xi_2) (1 - \xi_1 + \xi_2)} \quad (22)$$

$\xi_1$  and  $\xi_2$  can be determined by solving two simultaneous algebraic equations (21) and (22). In this study

we use Taylor expansions of functions for  $K_{x_1}$  and  $K_{x_1}/K_{x_2}$  with respect to  $\xi_1$  and  $\xi_2$ . Restricting the functions up to the terms with first power of  $\xi_1$  and of  $\xi_2$ , it may be obtained as follows.

$$\xi_1 = \{ K_{x_2} x_1^o [K_{x_2} - K_{x_1} (x_4^o)^2] + K_{x_1} x_3^o (x_4^o)^2 [K_{x_2} (x_1^o - 1) - x_3^o] \} / \{ [K_{x_2} - K_{x_1} (x_4^o)^2] [K_{x_2} (x_1^o + 1) + 2x_3^o] + 2(K_{x_2} + 2K_{x_1} x_3^o x_4^o) [K_{x_2} (x_1^o - 1) - x_3^o] \} \quad (23)$$

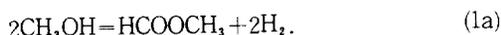
$$\xi_2 = \{ K_{x_1} x_3^o (x_4^o)^2 [K_{x_2} (x_1^o + 1) + 2x_3^o] - 2K_{x_2} x_1^o (K_{x_2} + 2K_{x_1} x_3^o x_4^o) \} / \{ [K_{x_2} - K_{x_1} (x_4^o)^2] [K_{x_2} (x_1^o + 1) + 2x_3^o] + 2(K_{x_2} + 2K_{x_1} x_3^o x_4^o) [K_{x_2} (x_1^o - 1) - x_3^o] \} \quad (24)$$

Prior to the calculation of equilibrium mole fractions [eqs. (17)-(20)], the values of  $K_{x_1}$  and  $K_{x_2}$  should possess the equilibrium constants [eqs. (9) and (10)], the correction factors [eqs. (15) and (16)], and total pressure effects.  $K_{x_1}$  and  $K_{x_2}$  should be determined by the relations such as  $K_{x_1} = K_{a_1} P / K_{\phi_1}$  and  $K_{x_2} = K_{a_2} / K_{\phi_2} P$  [see eqs. (11) and (12)].

### CHEMICAL EQUILIBRIA

From the results of computation according to the above procedures, the extent of each reaction and the composition for each component at equilibrium can be represented as a function of temperature, pressure, and initial composition. Figs. 5 and 6 show the extents of reaction calculated in the coordinates of  $\xi_1$  vs.  $T$  and  $\xi_2$  vs.  $T$ , respectively, emphasizing the effects of pressure and of feed ratio. From these figures it can be seen that both reactions are affected by temperature more sensitively rather than pressure. The increase in pressure does not influence maximal  $\xi_1$  and  $\xi_2$  attainable. Hence, thermodynamically the reaction can be adequately carried out at atmospheric pressure.

The equilibrium extent  $\xi_1$  of the hydrogenolysis reaction decreases with increasing temperature until the reverse reaction, dehydrogenation of methanol, takes place:



At atmospheric pressure, the temperature at which the reaction (1a) starts to show its effect is about 620 K. The dehydrogenation of methanol to MF has been carried out [17] as a step in the synthesis of some organic chemicals [18,19]. Comparing Fig. 5(a) with 5(b), however, MF produced by the reaction (1a) is quickly decarbonylated into methanol and CO since the reaction (2) is dominant around the temperature. This

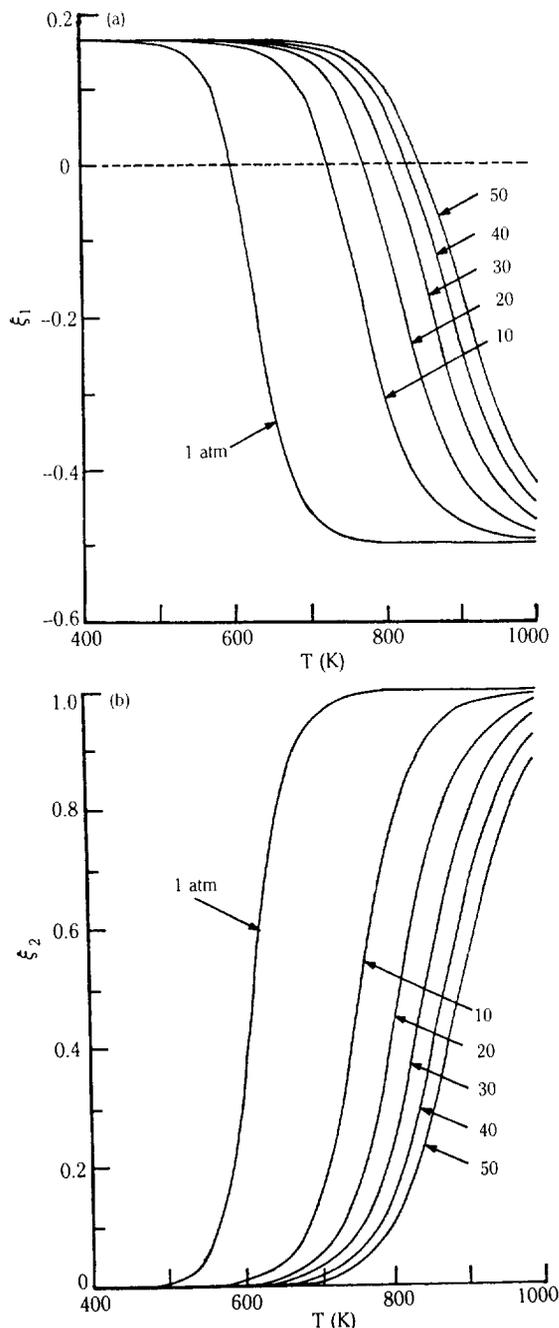
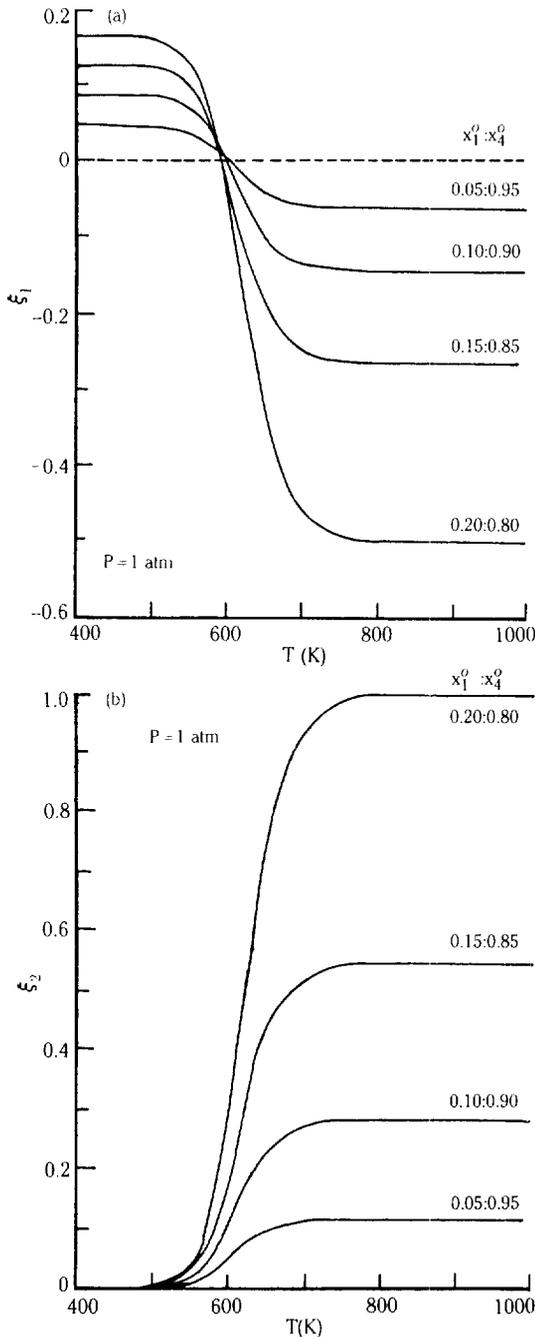


Fig. 5. Dependence of degrees of reaction (a)  $\xi_1$  and (b)  $\xi_2$  on reaction pressure. Initial composition is fixed as  $x_1^o=0.2$ ,  $x_3^o=0.0$ , and  $x_4^o=0.8$ .

fact confirms the qualitative arguments forwarded in the previous section, that as reaction temperature is raised the dominant reaction changes from the reaction (1) to the reaction (2). The effect of initial com-



**Fig. 6. Dependence of degrees of reaction (a)  $\xi_1$  and (b)  $\xi_2$  at atmospheric pressure on the initial feed compositions.**

position without CO on  $\xi_1$  and  $\xi_2$  is shown in Fig. 6. It can be easily noticed from the figure that the increase in initial  $H_2/MF$  ratio ( $x_4^o/x_1^o$ ) lessens the magnitudes of  $\xi_1$  and  $\xi_2$  without change in general shape of the

curves.

Fig. 7 shows the equilibrium mole fractions of each constituent ( $x_i^o$ ) and MF conversion ( $X_{MF}$ ) at various initial compositions without CO. Here the equilibrium conversion of MF is calculated as following;

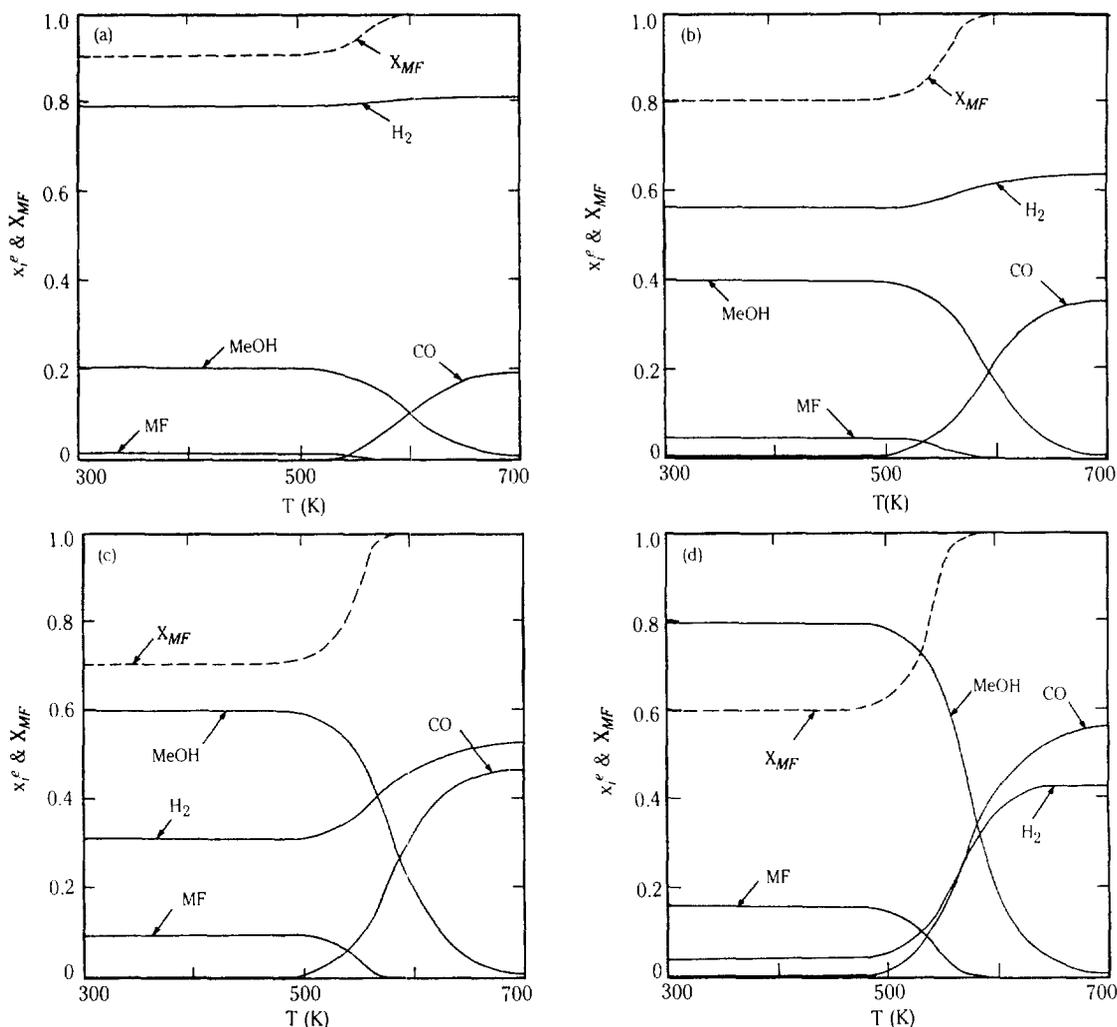
$$X_{MF} = 1 - x_1^o/x_1^e. \quad (25)$$

The sharp variation in equilibrium mole fraction is observed when the temperature exceeds about 500 K at atmospheric pressure irrespective of the  $H_2/MF$  ratio employed. Below 500 K it is easy to understand that each mole fraction is constant since within the temperature range 300-500 K chemical equilibrium is affected by the reaction (1) only. More fractions of MF and methanol decrease with increasing temperature (above 500 K) because the reaction (1a) ( $2 \text{ MeOH} \rightarrow \text{MF} + 2\text{H}_2$ ) and the reaction (2) ( $\text{MF} \rightarrow \text{MeOH} + \text{CO}$ ) are competing with each other. MF is produced by the consumption of two moles of methanol by the reaction (1a) and then this MF is converted to one mole of methanol and of CO by the reaction (2). So the increase in temperature causes the reduction of the amount of methanol from two moles into one mole. MF is completely consumed by the dominant reaction (2) eventually whereas the consumption of  $H_2$  decreases because some  $H_2$  is produced by the reaction (1a). The concentration of CO increases by the reaction (2). However, the actual experimental results [20] show that with the further increase in temperature the amounts of CO and  $H_2$  continuously increases while that of methanol is decreases. This fact is thought to be due to the decomposition of methanol at high temperatures:



The decomposition of methanol has been extensively studied from 1930s [21], and a comprehensive review is available [22].

The conversion of MF also takes the similar tendency to equilibrium mole fraction, which remains constant at lower temperature and then abruptly changes at the transition region of about 500 K. The effect of initial  $H_2/MF$  ratio on the equilibrium conversion of MF is compared in Fig. 8 compared with the result of Evans et al. [7]. Open circles in Fig. 8 are their experimental data from the vapor-phase hydrogenolysis of MF on a commercial copper chromite catalyst at 413 K and atmospheric pressure with 160  $\text{cm}^3/\text{min}$  of total flow rate. At constant temperature and pressure the conversion of MF is increased with increasing  $H_2/MF$  ratio in both cases. Since there is no reason that the calculated thermodynamic conversions and experimental kinetic results should show a similar



**Fig. 7.** Calculated equilibrium compositions of each component (—) and MF conversion (---) at atmospheric pressure where the initial composition ratios ( $x_1^0 : x_2^0$ ) are (a) 0.1:0.9, (b) 0.2:0.8, (c) 0.3:0.7, and (d) 0.4:0.6. All cases are without CO.

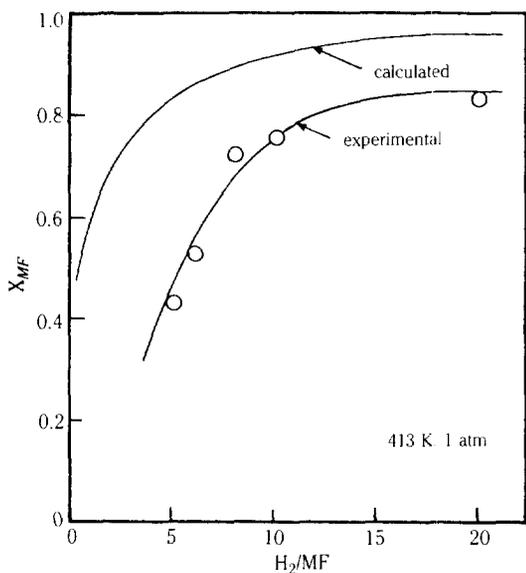
dependency on H<sub>2</sub>/MF ratio, and their data are numerically quite close to our calculated values, it is suspected that their kinetic measurements might have been influenced by thermodynamic equilibrium.

The influence of CO on the hydrogenolysis of MF has been observed by many authors [23-25] but most of the works were based on the reaction kinetics. Hence, the roles of CO have been explained in terms of their effects on catalyst [23-25]. At chemical equilibrium discussed here, the effect of CO is shown in Figs. 9 and 10. It is found that even if a small amount of CO is present in an initial gaseous mixture, the reaction degrees  $\xi_1$  and  $\xi_2$  suffer an inhibition effect by CO;  $\xi_1$  shows a maximum point at a certain

temperature and then decreases in the same pattern as the case of no initial CO, whereas  $\xi_2$  has a negative value at lower temperatures and then increases to a positive value of the same magnitude as the case of no initial CO. From these effects of CO on  $\xi_1$  and  $\xi_2$ , it can be concluded that the carbonylation reaction is easy to take place at low temperatures:

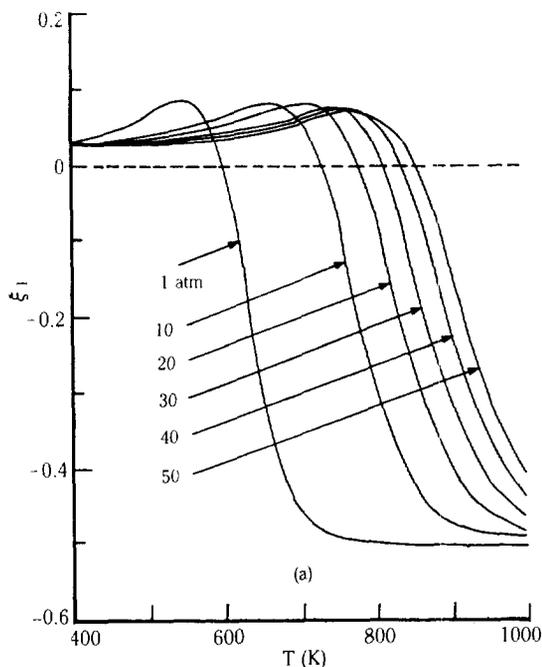


As shown in Fig. 10, initial presence of CO influences the temperature dependence of equilibrium composition and MF conversion in a fairly different way from the case without CO feed. The most distinct behavior with CO feed is that methanol mole fraction shows a



**Fig. 8.** Comparison of MF conversion as a function of initial  $H_2/MF$  ratio. Reaction conditions are 413 K and 1 atm. Open circles are from Evans et al. [7].

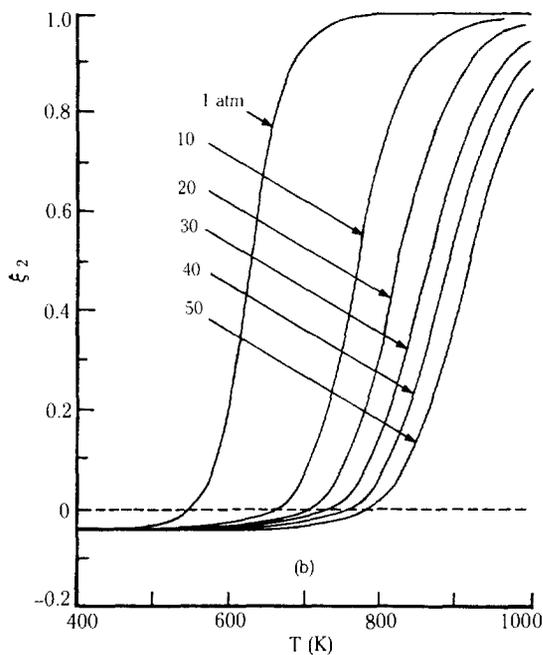
maximum and then decreases with increasing temperatures. This curve must be strongly associated with the curve of  $\xi_1$  in Fig. 9(a), which has a maximum point.



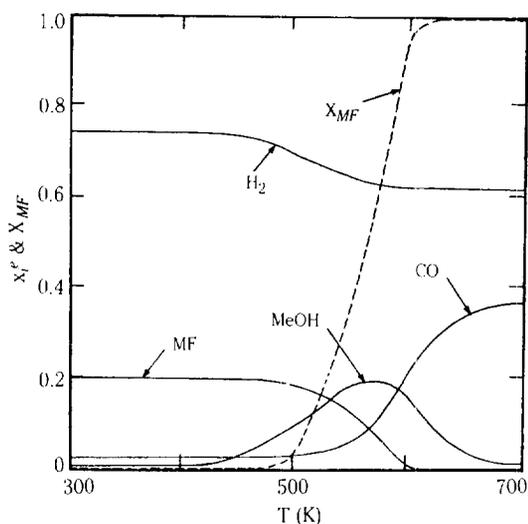
In other words, at lower temperature the forward reaction of the reaction (1) proceeds and one mole of  $MF$  and two moles of  $H_2$  produce two moles of methanol, whereas one mole of methanol reacts with initial  $CO$  to make one mole of  $MF$  via the reaction (2a). As the temperature increases, the amount of methanol increases through the reactions (1) and (2) until its amount decreases by the backward reactions of the reactions (1) and (2) because one mole of methanol is produced [reaction (2)] while two moles of it being consumed [reaction (1a)]. Very low  $MF$  conversion at low temperatures is abruptly increased within the temperature range of the transition where the inhibition of initial  $CO$  feed on the reaction (2) is no longer effective. For other components, the effect of initial  $CO$  was very small except that the mole fraction for  $H_2$  is lowered before the transition of  $MF$  conversion. The reason for this phenomena can be explained once again by the competition between the reaction (1) and (2a), (2b) being inhibited by initial  $CO$  feed at low temperatures.

## CONCLUSION

The chemical equilibria of the gas-phase methanol production from methyl formate has been studied considering the hydrogenolysis and decarbonylation at



**Fig. 9.** Dependence of degrees of reaction (a)  $\xi_1$  and (b)  $\xi_2$  on the reaction pressure. Initial composition is fixed as  $x_1^0=0.2$ ,  $x_3^0=0.05$ ,  $x_4^0=0.75$ .



**Fig. 10. Calculated equilibrium compositions of each component (—) and MF conversion (---) at atmospheric pressure where the initial composition is fixed as  $x_1^0=0.2$ ,  $x_3^0=0.05$ ,  $x_4^0=0.75$ .**

the same time. From the equilibrium constants and compositions calculated, following conclusions have emerged for better yields of methanol:

- (1) At the same pressure, lower the reaction temperature.
- (2) At the same temperature, raise the reaction pressure.
- (3) At the same temperature and pressure,  $H_2$ /MF ratio should be increased.
- (4) CO should be removed in the feed.

These results can help determine reaction conditions before the experiments and modify reaction parameters during experiments. Furthermore, the thermodynamic analysis revealed some characteristics of the reaction which have been considered as kinetic effects. These two effects should be differentiated in order to understand the reaction correctly.

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#### NOMENCLATURE

- $A_1, A_2, A_3$ : coefficients for the Gibbs free energy of formation (Table 1)  
 $a_1, a_2, a_3$ : coefficients for the specific heat capacity (Table 1)

- $C_p$ : temperature-dependent specific heat capacity (Table 1)  
 $i$ : component (1: MF, 2: MeOH, 3: CO, 4:  $H_2$ )  
 $j$ : reaction (1:  $MF+2H_2 \rightarrow 2MeOH$ , 2:  $MF \rightarrow MeOH+CO$ )  
 $K_{aj}$ : equilibrium constant for reaction  $j$   
 $K_{\phi_j}$ : equilibrium correction factor for reaction  $j$   
 $n_{tot}$ : total mole of reaction mixture at equilibrium  
 $P$ : pressure  
 $P_C$ : critical pressure (Table 1)  
 $R$ : universal gas constant  
 $T$ : temperature  
 $T_C$ : critical temperature (Table 1)  
 $v_C$ : critical volume  
 $X_{MF}$ : equilibrium conversion of MF  
 $x_i^e$ : vapor-phase mole fraction of component  $i$  at equilibrium  
 $x_i^0$ : vapor-phase mole fraction of component  $i$  in initial mixture  
 $Z_C$ : critical compressibility factor (Table 1)

#### Greek Letters

- $\Delta H_j$ : heat of reaction  $j$   
 $\Delta G_j$ : Gibbs free energy change of reaction  $j$   
 $\Delta G_f$ : temperature-dependent Gibbs free energy of formation (Table 1)  
 $\xi_j$ : extent of reaction  $j$   
 $\phi_i$ : fugacity coefficient of component  $i$   
 $\omega$ : acentric factor for nonideal component (Table 1)

#### Abbreviations

- EOS : equation of state  
 MeOH: methanol  
 MF : methyl formate

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