

CHAPTER III

THERMODYNAMICS CONSIDERATIONS

It is known that all chemical reactions are governed by thermodynamics (i.e., ΔG , ΔH , ΔS), properties associated with temperature, pressure, and composition. Therefore, thermodynamics is a primary concept in studying the nature of a chemical reaction, such that the feasibility of reaction and equilibrium conversion/yield can be estimated. The equilibrium conversion of a reaction is sometimes a goal for accomplishing the reaction (e.g., WGS), although in many cases one adjusts the relative rates of surface reactions so that the most thermodynamically favored product is minimized (e.g., CH_4). In this study, the feasibility of the methylation of benzene with methane was explored and, moreover, the effects of reaction conditions, such as temperature, pressure, and initial composition, on the equilibrium conversion were also calculated. Both non-oxidative benzene methylation and oxidative benzene methylation reactions were demonstrated. Furthermore, based on the literature, presumed side reactions such as toluene disproportionation, methane coupling, and toluene methylation, were also taken into account in the calculations.

3.1 Definition of the Equilibrium Constant

The general equilibrium constant (Smith et al., 2005):

$$K_a = \prod \left[\frac{\hat{f}_i}{f_i^o} \right]^{v_i} \quad (3.1)$$

Where K_a is the equilibrium constant, \hat{f}_i and f_i^o are the fugacity of a species at state of interest and at standard state, respectively, and v_i is a stoichiometric coefficient of each species in the interested reaction.

At equilibrium, K_a is expressed by thermodynamic terms as following:

$$K_a = \exp\left(\frac{-\Delta G^o}{RT}\right) \quad (3.2)$$

Suppose for gas-phase reaction at 1 bar ($f^o = P = 1 \text{ bar}$).

Thus,
$$\prod \hat{f}_i^{v_i} = \exp\left(\frac{-\Delta G^o}{RT}\right) = K_a \quad (3.3)$$

In gas-phase reaction at low pressure, gas mixture can be simplified as ideal solution,

$$\hat{f}_i^{is} = y_i \varphi_i P.$$

For gas-phase ideal solution, substitution yields,

$$(\prod \varphi_i^{v_i})(\prod y_i^{v_i}) P^{\sum v_i} = \exp\left(\frac{-\Delta G^o}{RT}\right) = K_a \quad (3.4)$$

Note that if ideal gas, $\varphi_i = 1$ for all i, then

$$(\prod y_i^{v_i}) P^{\sum v_i} = \exp\left(\frac{-\Delta G^o}{RT}\right) = K_a \quad (3.5)$$

3.2 Gibbs Free Energy of Reaction

Gibbs free energy is the energy associated with a chemical reaction. Therefore, it must be first evaluated in order to describe the behavior of any species in the reaction at equilibrium condition. The free energy of a system is the sum of its enthalpy (H) subtract the product of the temperature (Kelvin) and the entropy (S) of the system (Smith et al., 2005):

$$G = H - TS \quad (3.6)$$

Free energy change (ΔG) is the change in the enthalpy (ΔH) of the system minus the product of the temperature (Kelvin) and the change in the entropy (ΔS) of the system:

$$\Delta G = \Delta H - T\Delta S \quad (3.7)$$

And the free energy change at standard-state condition is defined by:

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (3.8)$$

The standard-state is based on the temperature and pressure. hence ΔG^o , ΔH^o , and ΔS^o can be varied with the conditions of interest.

The standard heat of reaction related to temperature:

$$\Delta H^o = \Delta H_0^o + R \int_{T_0}^T \frac{\Delta C_p^o}{R} dT \quad (3.9)$$

where ΔH^o and ΔH_0^o are standard enthalpy changes of reaction at temperature T and at reference temperature T_0 (normally at 25 °C, 1 bar), respectively.

The standard entropy of reaction related to temperature:

$$\Delta S^o = \Delta S_0^o + R \int_{T_0}^T \frac{\Delta C_p^o}{R} \frac{dT}{T} \quad (3.10)$$

where ΔS^o and ΔS_0^o are standard enthalpy changes of reaction at temperature T and at reference temperature T_0 respectively.

Combining eq. (3.8), (3.9), and (3.10) to yield:

$$\Delta G^o = \Delta H_0^o + R \int_{T_0}^T \frac{\Delta C_p^o}{R} dT - T \Delta S_0^o - RT \int_{T_0}^T \frac{\Delta C_p^o}{R} \frac{dT}{T}$$

However,
$$\Delta S_0^o = \frac{\Delta H_0^o - \Delta G_0^o}{T_0}$$

Finally, divided by RT yields:

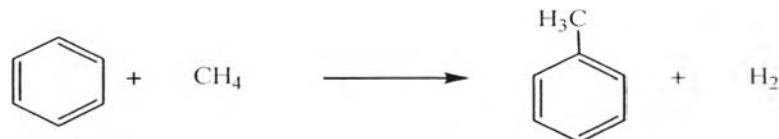
$$\frac{\Delta G^o}{RT} = \frac{\Delta G_0^o - \Delta H_0^o}{RT_0} + \frac{\Delta H_0^o}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^o}{R} dT - \int_{T_0}^T \frac{\Delta C_p^o}{R} \frac{dT}{T} \quad (3.11)$$

3.3 Calculation of Equilibrium Conversion

For methylation of benzene with methane, there are 2 different reaction routes, which are the methylation of benzene with methane in the absence of oxygen (non-oxidative benzene methylation) and the methylation of benzene with methane in the presence of oxygen (oxidative benzene methylation). The calculations were conducted with the conditions (e.g., temperature, pressure, and feed molar ratio) represented in the open literature, so that a comparison between the calculated values and the experimental values could be shown. Moreover, the effects of temperature, pressure, and feed molar ratio on equilibrium constant and conversion were also calculated.

3.3.1 Methylation of Benzene with Methane in the Absence of Oxygen (Non-oxidative Benzene Methylation)

Reaction:



Condition: temperature = 370°C , pressure = 1 bar,

benzene/methane (B/M) feed molar ratio = 1:9

Table 3.1 Thermodynamic properties of all relevant species

Substance	Thermodynamic properties @ 298 K			Heat capacity of gas ($C_p=A+BT+CT^2+DT^3+ET^4$)(J/mol-K)				
	ΔG°_f (kJ/mol)	ΔH°_f (kJ/mol)	ΔS°_f (J/mol-K)	A	B	C	D	E
Methane	-50.84	-74.85	-80.53	3.49E+01	-3.99E-02	1.92E-04	-1.53E-07	3.93E-11
Benzene	129.66	82.93	-156.73	-3.14E+01	4.75E-01	-3.11E-04	8.52E-08	-5.05E-12
Toluene	122.01	50.00	-241.52	-2.41E+01	5.22E-01	-2.98E-04	6.12E-08	1.26E-12
Hydrogen	0	0	0	2.54E+01	2.02E-02	-3.86E-05	3.19E-08	-8.76E-12

Calculation:

- Thermodynamics properties

$$\begin{array}{ccc} \Delta H^\circ_0 \text{ (J/mol)} & \Delta S^\circ_0 \text{ (J/mol}\cdot\text{K)} & \Delta G^\circ_0 \text{ (J/mol)} \\ 43,190 & 4.260 & 41,920 \end{array}$$

- Equilibrium conversions

Basis 1 min of total molar flow rate of 2 mol/min.

Substance	Mole in	Mole react	Mole out	y
Methane	1.8	$-\epsilon$	$1.8 - \epsilon$	$(1.8 - \epsilon)/2$
Benzene	0.2	$-\epsilon$	$0.2 - \epsilon$	$(0.2 - \epsilon)/2$
Toluene	0	ϵ	ϵ	$\epsilon/2$
H ₂	0	ϵ	ϵ	$\epsilon/2$

By assuming the reaction is gas phase ideal solution, recall eq.(3.5)

$$\left(\prod y_i^{v_i}\right)P^{\sum v_i} = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = K_a$$

$$K_a = \left(\prod y_i^{v_i}\right)P^{\sum v_i}$$

where $\sum v_i = 0$,

Then,

$$K_a = \frac{y_{\text{toluene}}y_{\text{hydrogen}}}{y_{\text{benzene}}y_{\text{methane}}}$$

$$K_a = \frac{\epsilon^2}{(0.2-\epsilon)(1.8-\epsilon)} \quad (*)$$

Calculating K_a from

$$K_a = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$$

For $T = 370\text{ }^\circ\text{C} = 643\text{ K}$, the term $\frac{-\Delta G^\circ}{RT}$ is calculated by using eq.(3.11)

$$\frac{-\Delta G^\circ}{RT} = -7.9404$$

Hence,

$$\begin{aligned} K_a &= \exp(-7.9404) \\ &= 3.5608 \times 10^{-4} \end{aligned}$$

Substituting $K_a = 3.5608 \times 10^{-4}$ into eq.(*), so that

$$\begin{aligned} 3.5608 \times 10^{-4} &= \frac{\varepsilon^2}{(0.2-\varepsilon)(1.8-\varepsilon)} \\ \varepsilon &= 0.01097 \end{aligned}$$

$$\begin{aligned} \text{Thus,} \quad \text{So, \% Benzene conversion} &= \frac{0.01097 \times 100}{0.2} \\ &= 5.487\% \end{aligned}$$

$$\text{and} \quad \% \text{ Methane conversion} = 0.61\%$$

This reaction is highly endothermic and non-spontaneous at $25\text{ }^\circ\text{C}$. With the given conditions, the equilibrium conversions of benzene and methane are quite low. The calculation result is in good agreement with that of Lukyanov and Vazhnova, who reported both equilibrium conversions and experimental conversions. Using Pt/H-MFI as a catalyst, the reaction can be achieved with a benzene and methane conversion of 4.5 mol% and 0.53 mol%, respectively, that are close to the equilibrium values; 5.6 mol% and 0.62 mol% conversions of benzene and methane respectively, under the same condition (Lukyanov et al., 2009).

The effects of temperature and feed molar ratio of benzene to methane on the equilibrium conversion of benzene.

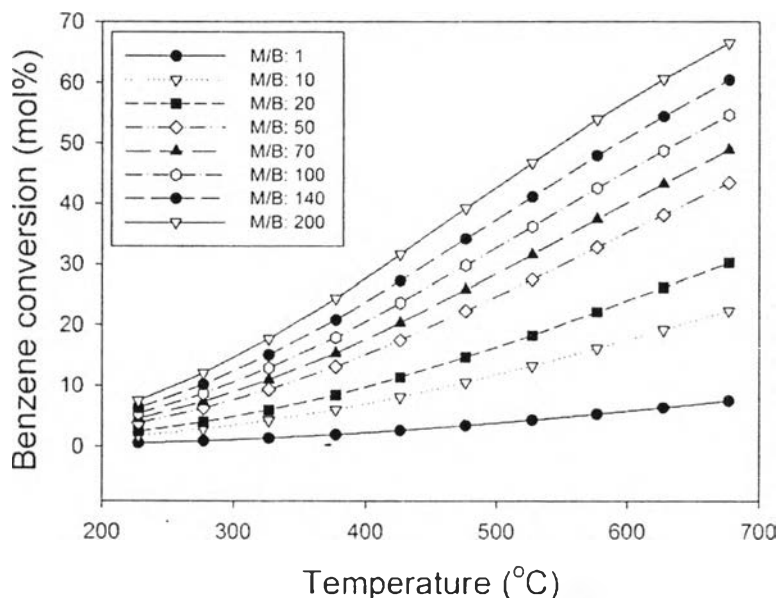


Figure 3.1 Conversion of benzene as a function of temperature at 8 different values of methane to benzene (M/B) feed molar ratio.

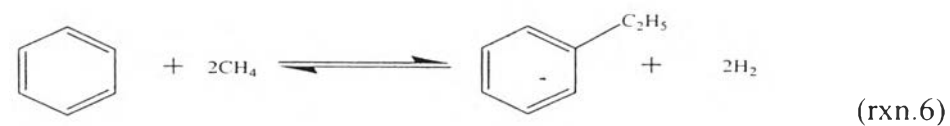
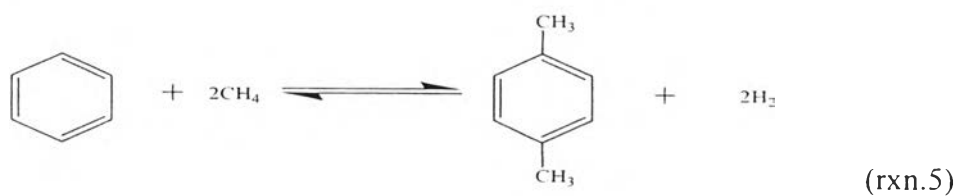
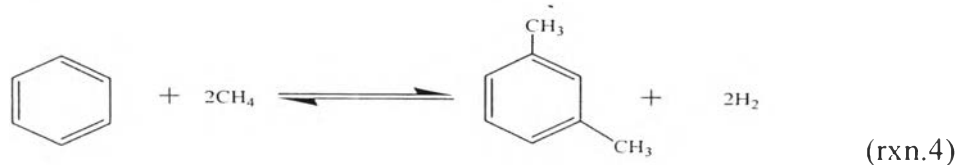
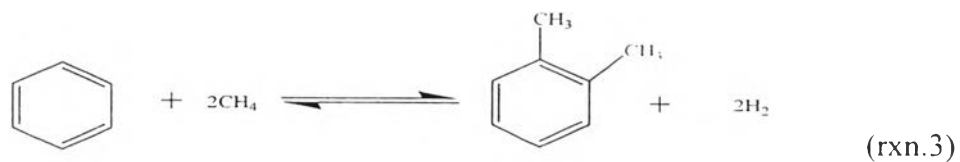
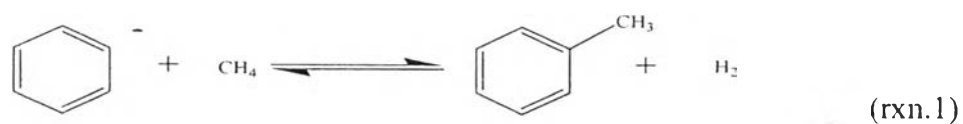
Due to the highly endothermic nature of the reaction, the conversion of benzene increases with increasing temperature as shown in Figure 3.1; however, benzene conversion is still quite low at high temperature. Moreover, Figure 3.1 shows the effect of B/M feed molar ratio that the higher the M/B molar ratio, the higher the benzene conversion. This result can be described by *Le Chatelier's* principle.

- Consideration of side reaction occurring with the methylation of benzene with methane to toluene.

Typically, the desired reaction doesn't take place as a single reaction but is accompanied by other side reactions. However, selectivity to desired product can be controlled by an appropriate catalyst. In the case of using ZSM-5 based catalyst, the most currently appropriate catalyst reported, there are five possible side reactions: toluene disproportionation, toluene methylation, benzene methylation to xylenes, benzene methylation to ethyl benzene, and methane coupling to ethane, as proposed in the literature. In this part, the calculation relied on a couple of research works, including (1) the reaction over Pt/H-MFI suggested by Lukyanov and Vazhnova

(Lukyanov et al., 2009) and (2) the reaction over Ag-exchanged ZSM-5 proposed by Baba and Sawada (Baba et al., 2002).

First, the reaction routes consist of benzene methylation to toluene, xylenes, and ethylbenzene, and methane coupling to ethane, as shown below. These reactions are proposed to occur over Pt/H-MFI catalyst (Lukyanov and Vazhnova).



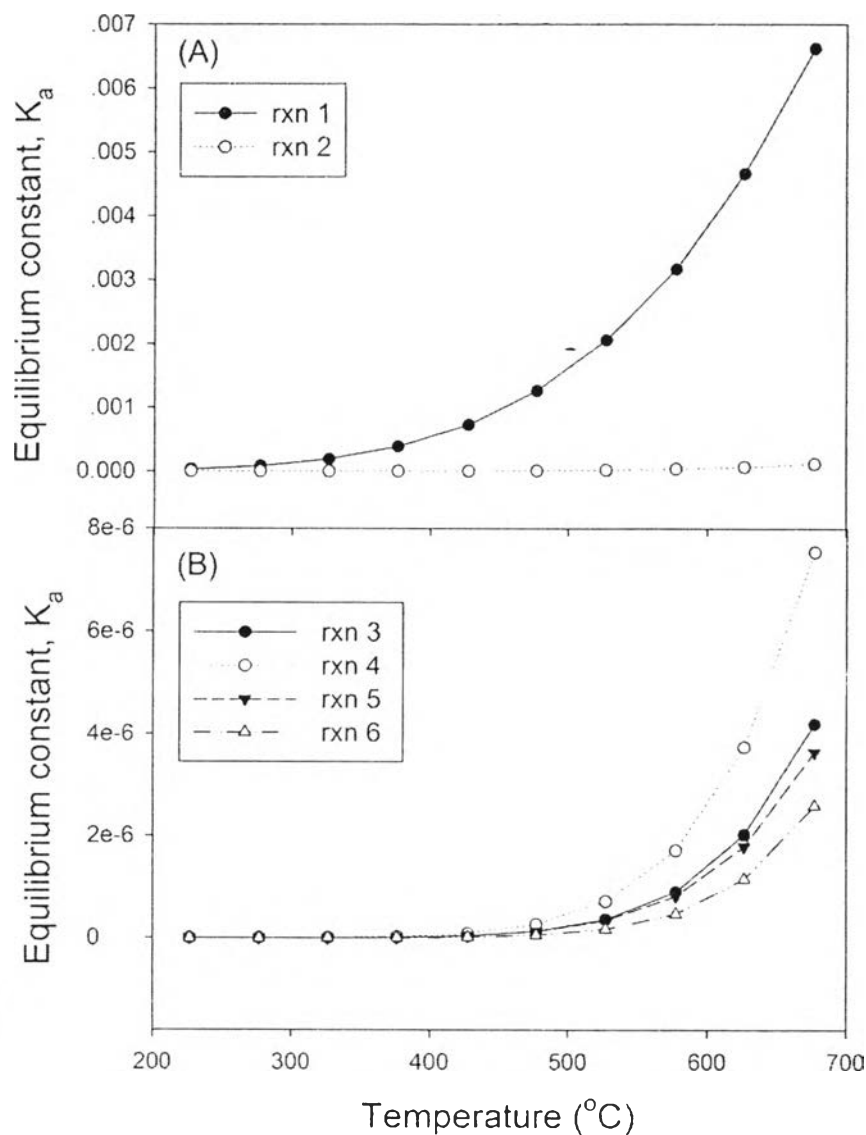
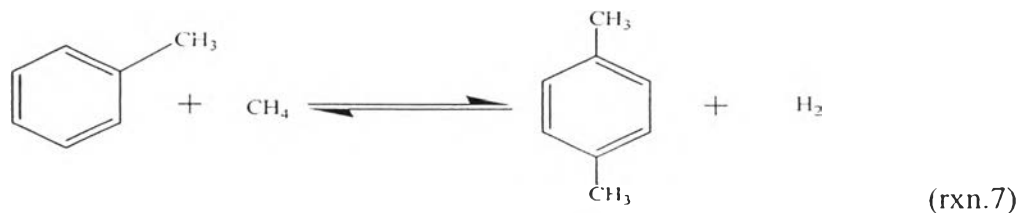
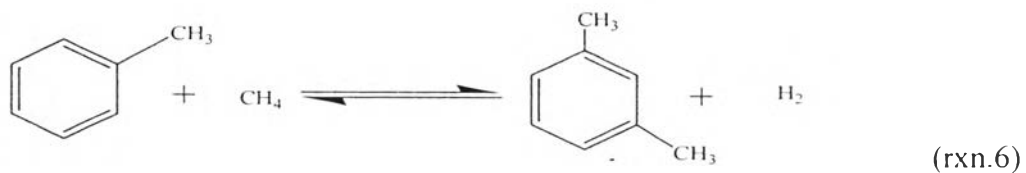
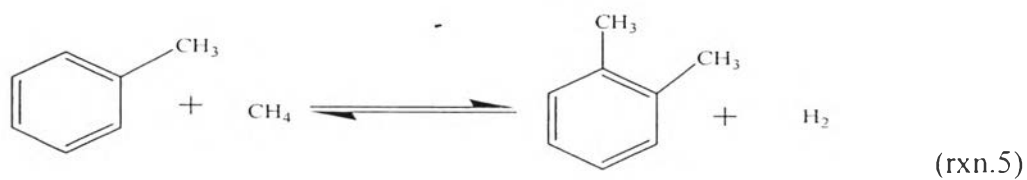
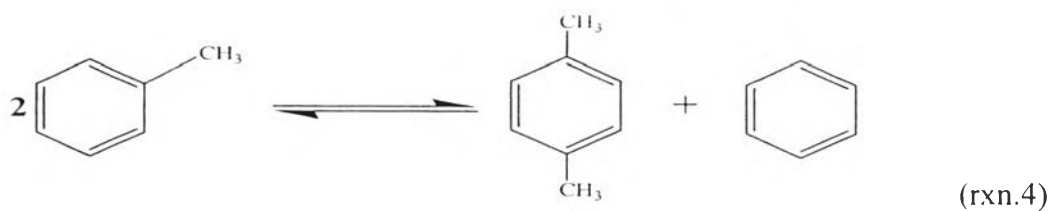
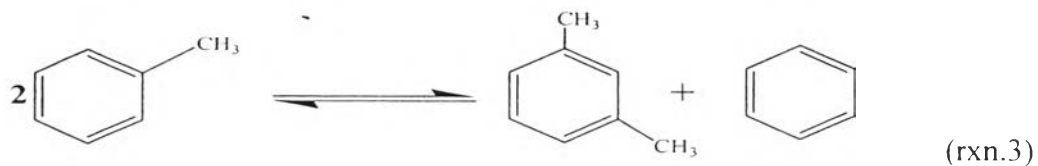
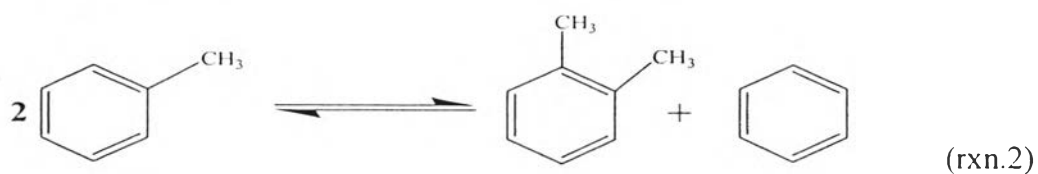
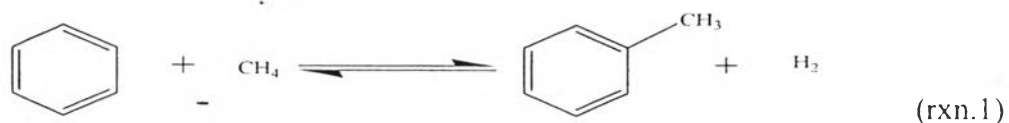


Figure 3.2 Equilibrium constants of all 6 reactions as a function of temperature.

The equilibrium constants, K_a 's, of all six reactions were calculated at different temperatures and the results are illustrated in Figure 3.2. The result shows clearly that K_a of reaction 1 is much higher than those of other reactions and that differences in values can be obviously seen at high temperature. This implies that reaction 1, benzene methylation to toluene, dominates in this reaction system, thus toluene is expected to be a major product with ethane, xylenes, and ethylbenzene as minor products. This is in good agreement with the experimental results of Lukyanov and co-workers (Lukyanov et al., 2009).

Second, the reaction routes consist of benzene methylation to toluene, toluene disproportionation, and toluene methylation to xylenes, as shown below. These reactions are suggested to occur over Ag-exchanged ZSM-5 (Baba and Sawada).



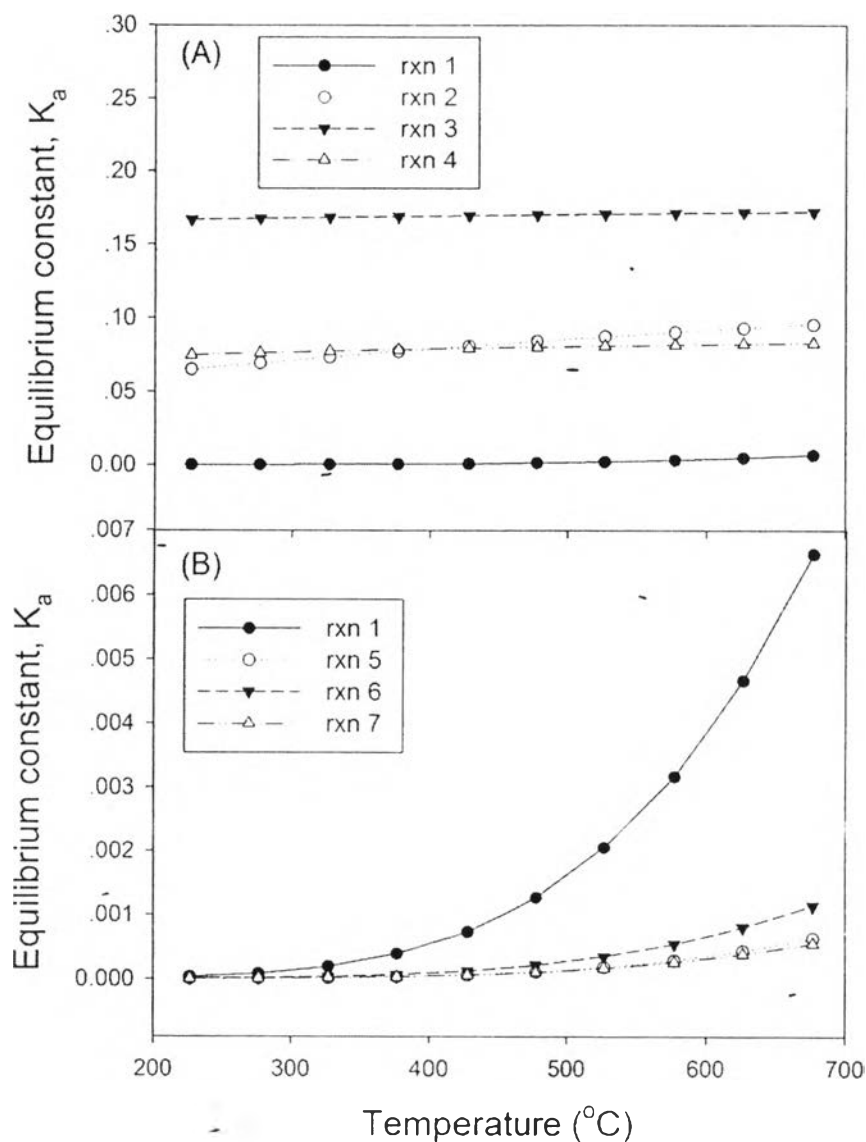


Figure 3.3 Equilibrium constant of all 7 reactions as a function of temperature.

The equilibrium constants, K_a 's, of all seven reactions were calculated as a function of temperature. Figure 3.3(A) shows a comparison between K_a values of the benzene methylation to toluene reaction, and the toluene disproportionation reactions. Figure 3.3(B) presents a comparison between the K_a values of the benzene methylation to toluene reaction and the toluene methylation to xylenes reactions. It indicates that toluene disproportionation reactions (reactions 2, 3, and 4) are thermodynamically favorable compared to other reactions, especially the reaction to *m*-xylene. To achieve these reactions, reaction 1 must have first occurred as a source

of toluene; unfortunately, the reaction to toluene is quite difficult. However, as xylenes can be obtained, Ag-exchanged ZSM-5 is still an interesting catalyst system to study.

3.3.2 Methylation of Benzene with Methane in the Presence of Oxygen (Oxidative Benzene Methylation)

Reaction:



Conditions: temperature = 370°C , pressure = 1 bar,

benzene/methane/oxygen(B/M/O)/ molar feed ratio = 1:1:0.5

Table 3.2 Thermodynamic properties of all relevant species:

Substance	Thermodynamic properties @ 298 K			Heat capacity of gas ($C_p = A + BT + CT^2 + DT^3 + ET^4$) (J/mol-K)				
	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	ΔS_f° (J/mol-K)	A	B	C	D	E
Methane	-50.84	-74.85	-80.53	34.94	-0.040	1.92E-04	-1.53E-07	3.93E-11
Benzene	129.66	82.93	-156.73	-31.37	0.47	-3.11E-04	8.52E-08	-5.05E-12
Toluene	122.01	50.00	-241.52	-24.10	0.52	-2.98E-04	6.12E-08	1.26E-12
H ₂ O	-228.60	-241.80	-44.27	33.93	-0.0084	2.99E-05	-1.78E-08	3.69E-12
O ₂	0	0	0	29.53	-0.0089	3.81E-05	-3.26E-08	8.86E-12

Calculation:

Thermodynamics properties

ΔH_f° (J/mol) ΔS_f° (J/mol-K) ΔG_f° (J/mol)

-199880 -48.53 -185410

Equilibrium conversions

Basis 1 min of total molar flow rate of 2.5 mol/min.

Substance	Mole in	Mole react	Mole out	y
Methane	1.0	- ϵ	1.0 - ϵ	$(1.0 - \epsilon)/(2.5 - 0.5\epsilon)$
Benzene	1.0	- ϵ	1.0 - ϵ	$(1.0 - \epsilon)/(2.5 - 0.5\epsilon)$
Oxygen	0.5	-0.5 ϵ	0.5 - 0.5 ϵ	$(0.5 - 0.5\epsilon)/(2.5 - 0.5\epsilon)$
Toluene	0	+ ϵ	ϵ	$\epsilon/(2.5 - 0.5\epsilon)$
Water	0	+ ϵ	ϵ	$\epsilon/(2.5 - 0.5\epsilon)$

The calculation algorithm is similar to that of previous part.

Finally,

$$K_a = \frac{\epsilon^2(2.5 - 0.5\epsilon)^{1/2}}{(1 - \epsilon)^2(0.5 - 0.5\epsilon)^{1/2}}$$

$$7.2426 \times 10^{14} = \frac{\epsilon^2(2.5 - 0.5\epsilon)^{1/2}}{(1 - \epsilon)^2(0.5 - 0.5\epsilon)^{1/2}}$$

$$\epsilon = 0.9999$$

Thus, So, % Benzene conversion = $\frac{0.9999 \times 100}{1}$
= 99.99%

Although this reaction route can theoretically provide benzene conversion close to 100%, there is no experimental evidence to support such a conversion. The most relevant work is that of Adebajo and co-workers (Adebajo et al., 2005), who devoted themselves to the study of oxidative benzene methylation, but their results are still not practical with high benzene conversion as well as toluene selectivity corresponding to this equilibrium. Moreover, the formations of CO₂ or CO can also take place in a system containing methane and oxygen at high temperature (Miao et al., 2004).