

## RESEARCH NOTE

## The Equilibrium Constant for the Methylcyclohexane–Toluene System

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The equilibrium constant for the methylcyclohexane–toluene system has been experimentally determined due to a lack of fit appearing in kinetic evaluations when using literature values for the equilibrium constant. The most recent literature value of  $K_{\text{eq}(T=650\text{ K})} = 4.61 \pm 0.04 \times 10^9 \text{ kPa}^3$  due to J. Akyurtlu and W. E. Stewart (*J. Catal.* **51**, 101 (1978)) was redetermined to a value of  $K_{\text{eq}(T=650\text{ K})} = 3.60 \pm 0.05 \times 10^9 \text{ kPa}^3$  with isothermal experiments using methylcyclohexane and toluene feeds separately.

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**Key Words:** methylcyclohexane; toluene; equilibrium constant; wall reactors.

## INTRODUCTION

The hydrogenation–dehydrogenation of toluene and methylcyclohexane (MCH) has been studied for seasonal hydrogen energy storage for both mobile (1) and stationary (2) systems. The efficiency of the system is strongly dependent on the kinetics of the endothermic, equilibrium-limited dehydrogenation reaction of methylcyclohexane ( $\text{C}_7\text{H}_{14}$ ) to toluene ( $\text{C}_7\text{H}_8$ )



where  $\Delta H_r^0$  is the endothermic heat of reaction under standard conditions. The equilibrium limitation of the reaction rate can be described as

$$r = k \cdot p_{\text{MCH}} \cdot \left[ 1 - \left( p_{\text{Toluene}} \cdot p_{\text{H}_2}^3 / K_{\text{eq}} \cdot p_{\text{MCH}} \right) \right], \quad [2]$$

where  $r$  means the reaction rate,  $k$  the reaction rate constant,  $p_i$  the different partial pressures, and  $K_{\text{eq}}$  the equilibrium constant, which depends on the temperature:

$$K_{\text{eq}} = K_{\text{eq}(T=650\text{ K})} \cdot \exp \left[ -\Delta H_r^0 / R \cdot (1/T - 1/650\text{ K}) \right]. \quad [3]$$

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In previous kinetic work on the system (3) supported by experimental data, the equilibrium constant determined in the literature (4),  $K_{\text{eq}(T=650\text{ K})} = 4.61 \times 10^9 \text{ kPa}^3$ , was used in preference to an older literature value based on API data (5),  $K_{\text{eq}(T=650\text{ K})} = 2.03 \times 10^9 \text{ kPa}^3$ . Subsequent kinetic measurements in an isothermal microreactor with high nitrogen dilution in the feed still revealed a lack of fit if the equilibrium constant from (4) was used. For example, the value of the activation energy appeared to vary with the nitrogen dilution in the reactants.

The purpose of this Research Note is to experimentally determine the equilibrium constant for the methylcyclohexane–toluene system to resolve this lack of fit.

## METHODS

The experimental setup consisted of a PC-controlled reactor system, allowing continuous operation while varying reaction parameters such as temperature, pressure, concentration of reactants, and residence time. Hydrogen and nitrogen gases (purity > 99.995%) with liquid MCH (>99.75%) and toluene (>99.5%) were monitored and fed to a preheater and reactor system located in a heated, fluidized sand bath. Reaction took place isothermally in three tube reactors in series (length  $3 \times 200$  mm, inner diameter 4 mm). Their inner walls were coated with a 100- $\mu\text{m}$  washcoat layer of alumina (BET area = 197  $\text{m}^2/\text{g}$ ), which was impregnated using the incipient-wetness method, resulting in a 2.75 wt.% platinum catalyst. The preparation of these reactors has been described (6). On-line temperature and concentration measurements (GC-FID) were made with product separation and further analyses (GC-MSD) for byproduct formation and carbon balances over the unit. At different temperatures (578–643 K), pressures (707–742 kPa), and feed inlet hydrogen-to-hydrocarbon ratios between 17 and 27, the residence time was increased from 20 to 66.5 s (MCH feed 1.26–0.44 ml/h or toluene feed 1.56–0.9 ml/h), until no further change in conversion occurred to attain equilibrium in the reactor.

## RESULTS AND DISCUSSION

Typical byproducts were methane, benzene, cyclopentanes, and xylenes, but all in trace quantities (<0.1%) allowing C and H balances for the datapoints between 95 and 104%, which resulted in a data reproducibility of  $\pm 5\%$ , Fig. 1.

With the experimental results measured near equilibrium, a nonlinear regression using Simusolv, a software package (7), gave a maximum likelihood estimate of  $K_{\text{eq}}(T=650 \text{ K}) = 3.60 \times 10^9$  with a standard deviation of  $5.12 \times 10^7 \text{ kPa}^3$ . The correlation matrix, as shown, suggested only a weak correlation between the two parameters of the equilibrium constant:

	$K_{\text{eq}}(T=650 \text{ K})$	$\Delta H_r$
$K_{\text{eq}}(T=650 \text{ K})$	1.0	
$\Delta H_r$	0.529	1.0

The 95% confidence interval for the first parameter was calculated using the Student's distribution, giving limits of  $3.31 \times 10^9$  and  $3.75 \times 10^9 \text{ kPa}^3$ . The parity plot in Fig. 1 confirms the quality of this regression, which is supported by the fact that comparable estimates were reached from the MCH side and from the toluene side.

Several  $F$  tests showed that the differences between the parameter estimates from experiments with MCH feed and those with toluene feed are plausibly consistent with the experimental variance.

As a synopsis, Fig. 2 shows an Arrhenius-type diagram of the experimental points and the correlation determined in this work,

$$K_{\text{eq}} = 3.60 \times 10^9 \text{ kPa}^3 \cdot \exp[-217,650 \text{ J/mol} \cdot R^{-1} \cdot (1/T - 1/650 \text{ K})],$$

three experimental points found by Rimensberger *et al.* (3),

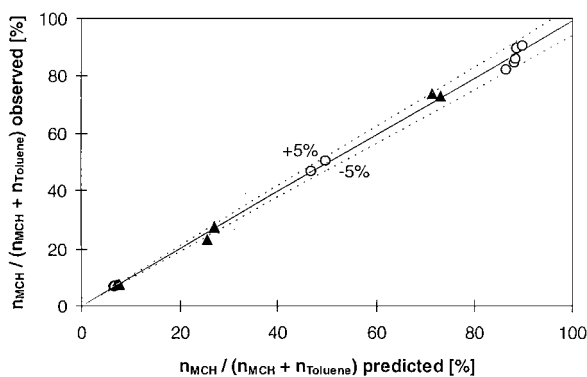


FIG. 1. Parity plot for the predicted and observed molar ratios  $n_{\text{MCH}}/(n_{\text{MCH}} + n_{\text{Toluene}})$  at equilibrium (temperatures 578–643 K, pressures 707–742 kPa, feed inlet  $17 < \text{H}_2/\text{Hydrocarbon} < 27$ ).  $\circ$ , MCH/hydrogen mixtures as feed;  $\blacktriangle$ , toluene/hydrogen mixtures as feed.

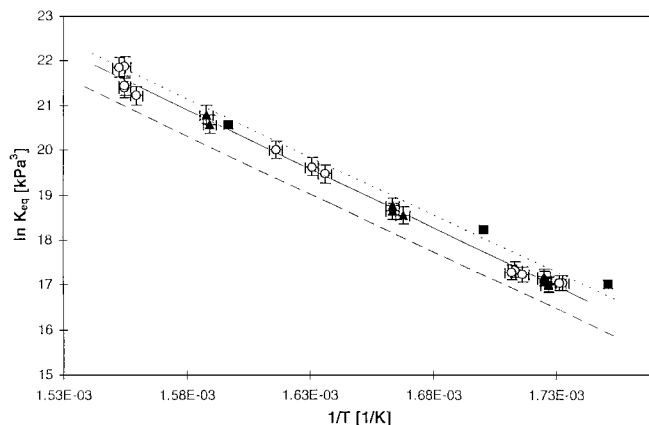


FIG. 2. Synopsis of the experimental points, published data, and correlations for  $K_{\text{eq}}$ : Sultan and Shaw (5), ---; Akyurtlu and Stewart (4),  $\cdots$ ; data from (3), MCH/toluene mixtures as feed,  $\blacksquare$ ; MCH/hydrogen mixtures as feed,  $\blacksquare$ ; toluene/hydrogen mixtures as feed,  $\circ$ ,  $\blacktriangle$ .

the correlations due to Akyurtlu and Stewart (4),

$$K_{\text{eq}} = 4.61 \times 10^9 \text{ kPa}^3 \cdot \exp[-216,350 \text{ J/mol} \cdot R^{-1} \cdot (1/T - 1/650 \text{ K})],$$

and Sultan and Shaw (5),

$$K_{\text{eq}} = 2.03 \times 10^9 \text{ kPa}^3 \cdot \exp[-215,270 \text{ J/mol} \cdot R^{-1} \cdot (1/T - 1/650 \text{ K})].$$

The small differences observed in the exponential term for the reaction enthalpy at 650 K are within the experimental uncertainty of the measurements by the different groups.

Based on the new experimental data, the accurate determination of the equilibrium constant and comparison with literature values (3–5), the conclusion is that the value for the equilibrium constant for the dehydrogenation of methylcyclohexane should be modified from

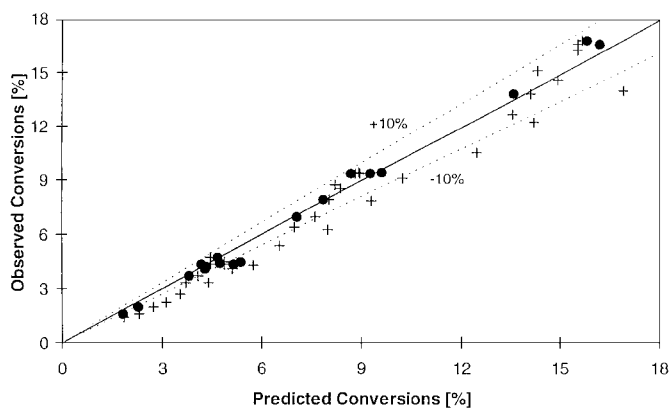


FIG. 3. Parity plot observed/predicted conversions depending on the different values for the equilibrium constant  $K_{\text{eq}}$ : from (4),  $+$ ; this work,  $\bullet$ .

TABLE 1  
Kinetic Data of Müller (8) for the Dehydrogenation of Methylcyclohexane to Toluene

$T(^{\circ}\text{C})$	MCH feed (ml/h)	$\text{H}_2$ feed (ml/min)	He feed (ml/min)	$p_{\text{MCH},0}$ (kPa)	$p_{\text{H}_2,0}$ (kPa)	$p_{\text{He},0}$ (kPa)	% tol	% MCH
282	0.50	14.70	0.00	63.45	636.45	0.00	1.39	98.24
290	0.50	14.70	0.00	63.45	636.45	0.00	2.67	96.95
298	0.50	14.70	0.00	63.45	636.45	0.00	5.36	94.29
309	0.50	14.70	0.00	63.45	636.45	0.00	12.34	87.30
282	1.00	14.70	0.00	116.35	583.48	0.00	1.57	98.08
290	1.00	14.70	0.00	116.35	583.48	0.00	3.35	96.29
298	1.00	14.70	0.00	116.35	583.48	0.00	6.25	93.43
309	1.00	14.70	0.00	116.35	583.48	0.00	14.12	85.53
282	1.50	14.70	0.00	161.11	538.65	0.00	1.95	97.68
290	1.50	14.70	0.00	161.11	538.65	0.00	4.06	95.61
298	1.50	14.70	0.00	161.11	538.65	0.00	7.84	91.89
309	1.50	14.70	0.00	161.11	538.65	0.00	17.83	81.77
282	2.00	14.70	0.00	199.48	500.22	0.00	2.21	97.44
290	2.00	14.70	0.00	199.48	500.22	0.00	4.26	95.39
298	2.00	14.70	0.00	199.48	500.22	0.00	9.13	90.54
281	0.50	9.80	4.90	63.45	424.30	212.15	4.36	95.29
290	0.50	9.80	4.90	63.45	424.30	212.15	8.54	91.13
298	0.50	9.80	4.90	63.45	424.30	212.15	14.66	84.98
282	1.00	9.80	4.90	116.35	388.99	194.49	4.40	95.27
290	1.00	9.80	4.90	116.35	388.99	194.49	9.38	90.31
298	1.00	9.80	4.90	116.35	388.99	194.49	16.36	83.32
282	1.50	9.80	4.90	161.11	359.10	179.55	4.37	95.29
290	1.50	9.80	4.90	161.11	359.10	179.55	9.41	90.20
298	1.50	9.80	4.90	161.11	359.10	179.55	16.87	82.79
282	2.00	9.80	4.90	199.48	333.48	166.74	4.47	95.18
290	2.00	9.80	4.90	199.48	333.48	166.74	9.44	90.25
298	2.00	9.80	4.90	199.48	333.48	166.74	16.67	82.97
282	0.50	11.00	3.70	63.45	476.26	160.20	3.31	96.33
290	0.50	11.00	3.70	63.45	476.26	160.20	6.40	93.27
298	0.50	11.00	3.70	63.45	476.26	160.20	10.62	89.05
282	1.00	11.00	3.70	116.35	436.62	146.86	3.71	95.95
290	1.00	11.00	3.70	116.35	436.62	146.86	6.96	92.73
298	1.00	11.00	3.70	116.35	436.62	146.86	12.77	86.90
282	1.50	11.00	3.70	161.11	403.07	135.58	4.24	95.44
290	1.50	11.00	3.70	161.11	403.07	135.58	7.93	91.77
298	1.50	11.00	3.70	161.11	403.07	135.58	13.89	85.76
282	2.00	11.00	3.70	199.48	374.31	125.90	4.73	94.93
290	2.00	11.00	3.70	199.48	374.31	125.90	8.73	90.95
298	2.00	11.00	3.70	199.48	374.31	125.90	15.20	84.51

$K_{\text{eq}(T=650\text{ K})} = 4.61 \pm 0.04 \times 10^9 \text{ kPa}^3$  to the new value of  $K_{\text{eq}(T=650\text{ K})} = 3.60 \pm 0.05 \times 10^9 \text{ kPa}^3$ .

Finally, Fig. 3 shows the effects of the different equilibrium constants on the representation of the kinetic data of Müller (Table 1), extracted from his Ph.D. Thesis (8). These measurements were carried out using a continuously operated, electrically heated fixed-bed microreactor (inner diameter 4 mm, bed length 9 mm). Isothermal experiments at 700 kPa in the temperature range 555–582 K were performed using 50 mg of a commercial 0.8 wt.% platinum/alumina catalyst (particle diameter 65–125  $\mu\text{m}$ ).

Overprediction of the conversion occurred with both estimates of  $K_{\text{eq}}$ ; it occurred more often with the value

from (4). It is noteworthy that several points, especially those without feed dilution, had to be excluded from the kinetic evaluation since equilibrium was practically reached before the end of the reactor.

#### ACKNOWLEDGMENTS

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