

Heterogenous Data Analysis for Reactor Design

Book: *Elements of Chemical Reaction Engineering*, H.S. Fogler, 4th Edition (Chapter 10)

Review

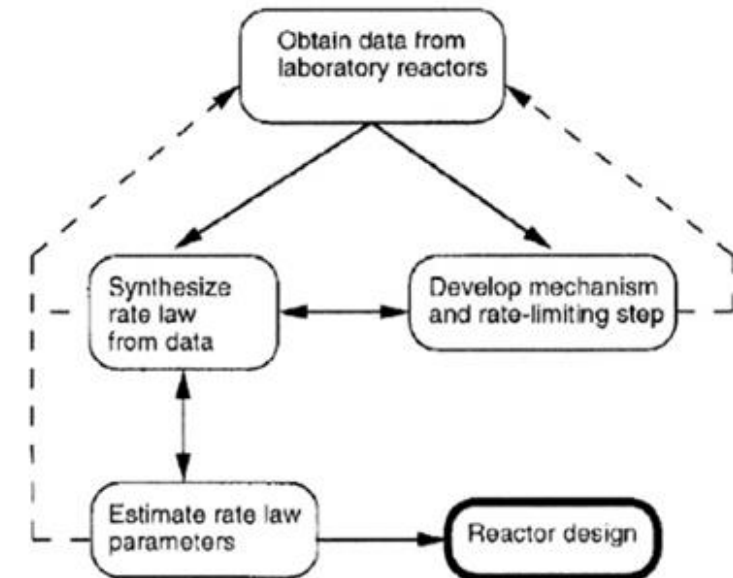
In the previous section, we learnt how to derive a rate law for a heterogeneously catalyzed chemical reaction

- A mechanism was proposed for the reaction - the sequence of steps assumed consisted of an adsorption step, a surface reaction step and a desorption step
- Rate laws are written for the individual steps assuming each one of them as reversible
- A rate limiting step was postulated amongst the individual steps and the rate expression was written for that step
- The non-rate limiting steps were used to eliminate the concentration terms of adsorbed species and vacant sites (terms that cannot be measured) in the rate expression
- Rate equations were derived for different mechanisms in order to list all the possible forms of the rate law one can have in heterogeneous catalysis

In this section, in continuation with what was learnt previously, we will gain the understanding of **how to use experimental data collected from a test reactor to deduce a rate law for a reaction**

- Previously we learnt how to derive the various forms of the rate expression for a reaction, assuming different steps (adsorption, reaction, desorption) to be rate controlling
- The experimental rate data collected from a reactor (with no internal or external diffusion resistances) is analysed, and the trends in the data are used to suggest an algebraic rate law consistent with the data
- A mechanism and rate limiting step is then found that is consistent with the experimental data
- Knowing the form of the rate law, the parameters present in the rate expression (k , K) can be numerically evaluated from the experimental data
- The nature and values of the parameters helps to finalize the reaction mechanism and rate limiting step
- Finally, a catalytic reactor can be designed to achieve a specified conversion using the rate expression just developed

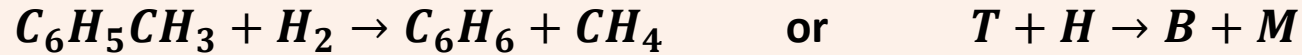
Collecting and Analyzing Data



Collecting information for catalytic reactor design

Design of a packed bed reactor for hydrodemethylation of toluene

The reaction of toluene and hydrogen is carried out over a silica-alumina solid catalyst to form methane and benzene



A packed bed reactor (PBR) and a fluidized CSTR needs to be designed to process a feed consisting of 30% toluene, 45% hydrogen, and 25% inerts. Toluene is fed at a rate of 50 mol/min at a temperature of 640°C and a pressure of 40 atm (4052 kPa). Calculate the catalyst weight necessary to achieve 65% conversion in a CSTR and a PBR (neglect pressure drop)

The experimental data for rate of reaction, r_T (gmol toluene/g cat.s) as a function of partial pressure of hydrogen, toluene, benzene and methane are given below:

Run	$r_T \times 10^{10}$	Partial pressure (atm)			
	gmol/ gcat.s	Toluene (p_T)	Hydrogen (p_H)	Methane (p_M)	Benzene (p_B)
1	71.0	1	1	1	0
2	71.3	1	1	4	0
3	41.6	1	1	0	1
4	19.7	1	1	0	4
5	42.0	1	1	1	1
6	17.1	1	1	0	5
7	71.8	1	1	0	0
8	142.0	1	2	0	0
Run	$r_T \times 10^{10}$	Partial pressure (atm)			
	gmol/ gcat.s	Toluene (p_T)	Hydrogen (p_H)	Methane (p_M)	Benzene (p_B)
9	284.0	1	4	0	0
10	47.0	0.5	1	0	0
11	71.3	1	1	0	0
12	117.0	5	1	0	0
13	127.0	10	1	0	0
14	131.0	15	1	0	0
15	133.0	20	1	0	0
16	41.8	1	1	1	1

The first step of the process is to develop an algebraic rate law consistent with the experimental reactor data

Thermodynamic calculations show large value of $K \left(= \frac{k_S}{k_{-S}} \right)$

- indicates an irreversible reaction

Guidelines for deducing mechanisms –

- More than 70% of heterogeneous reaction mechanisms are surface reaction limited
- If a species appears in the numerator of the rate law, it is probably a reactant
- If a species appears in the denominator of the rate law, it is probably adsorbed in the surface

(i) If the **product CH₄ (M)** was absorbed on the surface, the partial pressure of CH₄ would appear in the denominator of the rate expression and rate would vary inversely with CH₄ concentration

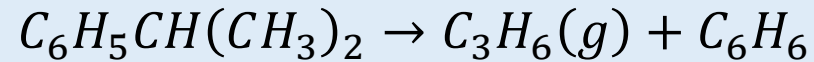
From Run 1 and 2, it is seen that increasing the pressure of CH₄ four times does not have much effect on the rate

Thus it can be concluded that CH₄ is either weakly adsorbed (i.e., $K_M p_M \leq 1$) or goes directly into gas phase

Run	$r_T \times 10^{10}$	Partial pressure (atm)			
		Toluene (p_T)	Hydrogen (p_H)	Methane (p_M)	Benzene (p_B)
1	71.0	1	1	1	0
2	71.3	1	1	4	0
3	41.6	1	1	0	1
4	19.7	1	1	0	4
5	42.0	1	1	1	1
6	17.1	1	1	0	5
7	71.8	1	1	0	0
8	142.0	1	2	0	0
9	284.0	1	4	0	0
10	47.0	0.5	1	0	0
11	71.3	1	1	0	0
12	117.0	5	1	0	0
13	127.0	10	1	0	0
14	131.0	15	1	0	0
15	133.0	20	1	0	0
16	41.8	1	1	1	1

Previous example

Decomposition of cumene to form **benzene and propylene**



(a) Adsorption is rate limiting

$$r_A = \frac{k_A C_t \left[p_C - \frac{p_B p_P}{K} \right]}{1 + K_B p_B + \frac{K_B p_B p_P}{K_S}}$$

(b) Surface reaction is rate limiting

$$r_S = \frac{k_S K_C C_t \left[p_C - \frac{p_B p_P}{K} \right]}{1 + K_B p_B + K_C p_C}$$

(c) Desorption of benzene is rate limiting (controlling)

$$r_D = \frac{k_D K_C K_S C_t \left[p_C - \frac{p_P p_B}{K} \right]}{p_P + K_S K_C p_C + K_C p_C p_P}$$

(ii) In Runs 3, 4 and 6, it is observed that for a fixed concentration of H₂ and toluene, the rate decreases with increasing **partial pressure of benzene**

A rate expression with in which the benzene partial pressure is in the denominator would explain this behaviour

$$-r_T = \frac{[\dots\dots]}{1 + K_B p_B + \dots}$$

(iii) In Runs 10-15, there are no products in the inlet and the hydrogen partial pressure is constant

In Runs 10, 11, the rate increases with **increasing partial pressure of toluene**

In Run 12, 13, it still increases but at a slower rate and in Runs 14, 15, the rate is almost constant (independent of p_T)

The form of rate equation that would describe this behaviour is when p_T appears in both the numerator and denominator of the rate expression

$$-r_T = \frac{p_T}{1 + K_B p_B + K_T p_T}$$

Run	$r_T \times 10^{10}$	Partial pressure (atm)			
		Toluene (p_T)	Hydrogen (p_H)	Methane (p_M)	Benzene (p_B)
1	71.0	1	1	1	0
2	71.3	1	1	4	0
3	41.6	1	1	0	1
4	19.7	1	1	0	4
5	42.0	1	1	1	1
6	17.1	1	1	0	5
7	71.8	1	1	0	0
8	142.0	1	2	0	0
9	284.0	1	4	0	0
10	47.0	0.5	1	0	0
11	71.3	1	1	0	0
12	117.0	5	1	0	0
13	127.0	10	1	0	0
14	131.0	15	1	0	0
15	133.0	20	1	0	0
16	41.8	1	1	1	1

(iv) In Runs 7, 8 and 9, it is observed that the rate increases linearly with increase in **hydrogen concentration**

The reaction is first order with hydrogen concentration

The hydrogen is probably not adsorbed, as adsorption would have led to a dependence similar to the increasing toluene partial pressure (rate of increase is different at low and high partial pressures of toluene)

$$-r_T \propto p_H$$

(v) Runs 5 and 16, has identical amounts of both reactants and products in the inlet, and the rate of reaction is also the same

Combining all the information from the experimental rate data we have,

$$-r_T = \frac{kp_H p_T}{1 + K_B p_B + K_T p_T}$$

Run	$r_T \times 10^{10}$	Partial pressure (atm)			
		Toluene (p_T)	Hydrogen (p_H)	Methane (p_M)	Benzene (p_B)
1	71.0	1	1	1	0
2	71.3	1	1	4	0
3	41.6	1	1	0	1
4	19.7	1	1	0	4
5	42.0	1	1	1	1
6	17.1	1	1	0	5
7	71.8	1	1	0	0
8	142.0	1	2	0	0
9	284.0	1	4	0	0
10	47.0	0.5	1	0	0
11	71.3	1	1	0	0
12	117.0	5	1	0	0
13	127.0	10	1	0	0
14	131.0	15	1	0	0
15	133.0	20	1	0	0
16	41.8	1	1	1	1

The second step is to find a mechanism that agrees with the experimental observations

Steps:



$$r_A = k_A \left[p_T C_v - \frac{C_{T.S}}{K_T} \right]$$



$$r_S = k_S \left[C_{T.S} p_H - \frac{p_M C_{B.S}}{K_S} \right]$$



$$r_D = k_D \left[C_{B.S} - \frac{p_B C_v}{K_{DB}} \right] = k_D [C_{B.S} - K_B p_B C_v]$$

Assuming the surface reaction step to be rate limiting,

$$r_S = k_S \left[C_{T.S} p_H - \frac{p_M C_{B.S}}{K_S} \right] \quad \text{and adsorption and desorption steps are fast, } \frac{r_A}{k_A} \approx 0 \text{ and } \frac{r_D}{k_D} \approx 0$$

$$\therefore C_{T.S} = K_T p_T C_v \quad \text{and} \quad C_{B.S} = K_B p_B C_v$$

$$r_S = k_S \left[K_T p_T C_v p_H - \frac{K_B p_B C_v p_M}{K_S} \right] = k_S K_T C_v \left[p_T p_H - \frac{K_B p_B p_M}{K_T K_S} \right]$$

$$r_S = k_S K_T C_v \left[p_T p_H - \frac{p_B p_M}{K} \right] \quad \text{as} \quad K = \frac{K_T K_S}{K_B}$$

Site balance: $C_t = C_v + C_{B.S} + C_{T.S}$

or, $C_t = C_v + K_B p_B C_v + K_T p_T C_v$

or, $C_t = C_v [1 + K_B p_B + K_T p_T]$

or, $C_v = \frac{C_t}{1 + K_B p_B + K_T p_T}$

Replacing the value of C_v in the rate of surface reaction equation we get,

$$r_S = \frac{k_S K_T C_t \left[p_T p_H - \frac{p_B p_M}{K} \right]}{1 + K_B p_B + K_T p_T}$$

Since K is large, $\frac{1}{K} \approx 0$ and

$$-r_T = r_S = \frac{k [p_T p_H]}{1 + K_B p_B + K_T p_T}$$

The form of the rate equation matches with the one that was suggested from analyzing the experimental data

It is now essential to evaluate the values of the parameters, k, K_B, K_T by regression methods

This is called **parameter estimation**

The third step is parameter estimation - the parameters present in the rate expression (k, K) can be numerically evaluated from the experimental data

The linearized form of the rate equation can be written as,

$$\frac{[p_T p_H]}{(-r_T)} = \frac{1}{k} + \frac{K_B p_B}{k} + \frac{K_T p_T}{k}$$

Or in the generalized form, $y_j = a_0 + a_1 x_{1j} + a_2 x_{2j}$

Linearized least square analysis can be used to obtain the initial estimates of the parameters. This can then be used as initial guesses for non-linear regression

For this particular problem, it is possible to use sections of the experimental data to calculate the parameters through linear equations

In Runs 10-15, the values of p_B and p_M are zero.

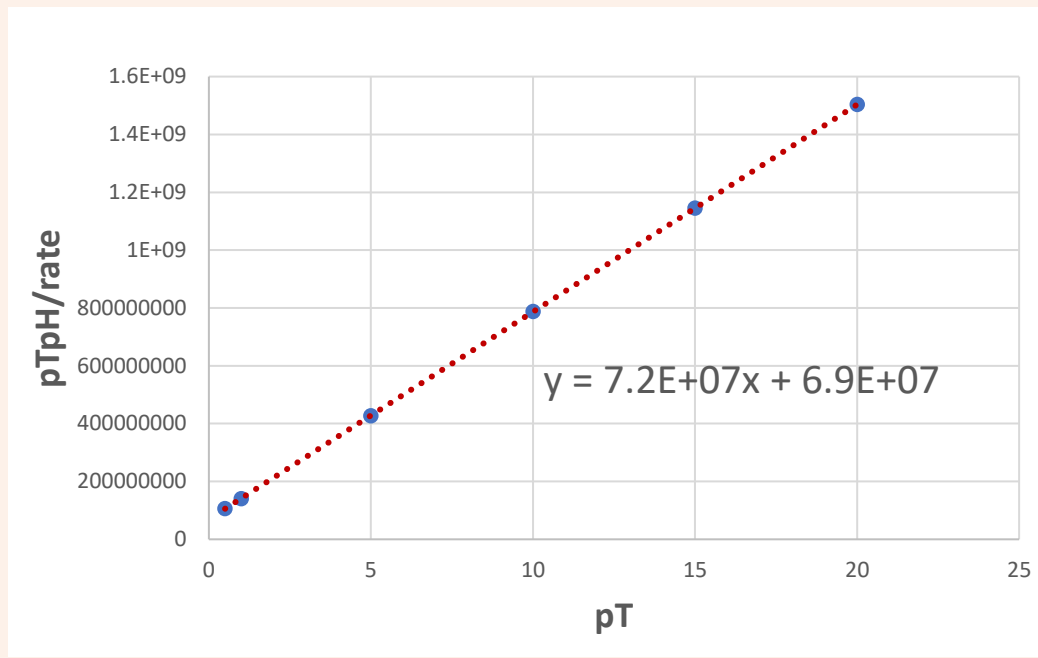
The linear equation becomes,

$$\frac{[p_T p_H]}{(-r_T)} = \frac{1}{k} + \frac{K_T p_T}{k}$$

A plot of $\frac{[p_T p_H]}{(-r_T)}$ versus p_T should yield a straight line and the slope and intercept can help calculate values of k and K_T

Run	$r_T \times 10^{10}$	Partial pressure (atm)			
	gmol/ gcat.s	Toluene (p_T)	Hydrogen (p_H)	Methane (p_M)	Benzene (p_B)
10	47.0	0.5	1	0	0
11	71.3	1	1	0	0
12	117.0	5	1	0	0
13	127.0	10	1	0	0
14	131.0	15	1	0	0
15	133.0	20	1	0	0

Run	$r_T \times 10^{10}$	Partial pressure (atm)		$\frac{[p_T p_H]}{(-r_T)} \times 10^{-10}$
		Toluene (p_T)	Hydrogen (p_H)	
10	47.0	0.5	1	0.01064
11	71.3	1	1	0.01403
12	117.0	5	1	0.04274
13	127.0	10	1	0.07874
14	131.0	15	1	0.11450
15	133.0	20	1	0.15038



$$\frac{1}{k} = 6.9 \times 10^7$$

$$k = 144.93 \times 10^{-10}$$

$$\frac{K_T}{k} = 7.2 \times 10^7$$

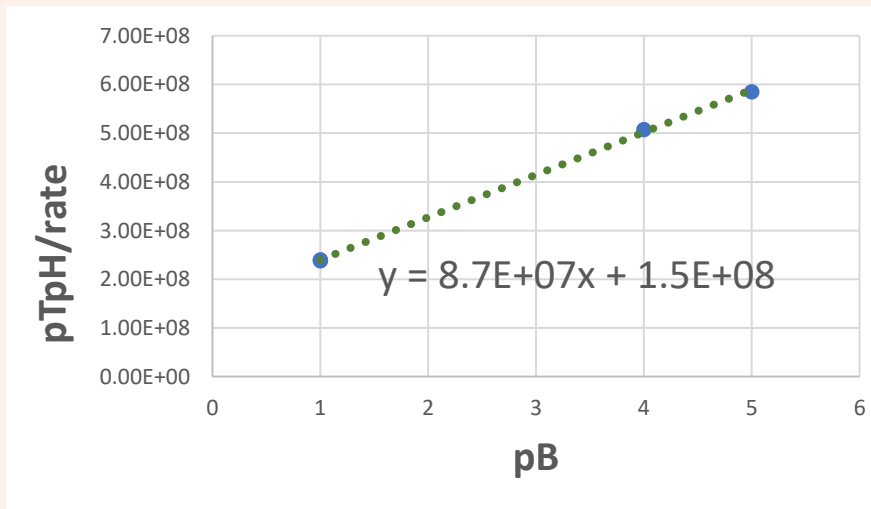
$$K_T = 1.0435$$

In Runs 3-6, the values of p_T is constant, and the linear equation becomes,

$$\frac{[p_T p_H]}{(-r_T)} = \left(\frac{1}{k} + \frac{K_T p_T}{k} \right) + \frac{K_B p_B}{k}$$

A plot of $\frac{[p_T p_H]}{(-r_T)}$ versus p_B should yield a straight line and the value of K_B can be calculated from the slope and value of k

Run	$r_T \times 10^{10}$	Partial pressure (atm)				$\frac{[p_T p_H]}{(-r_T)} \times 10^{-10}$
		Toluene (p_T)	Hydrogen (p_H)	Methane (p_M)	Benzene (p_B)	
3	41.6	1	1	0	1	0.0240
4	19.7	1	1	0	4	0.0508
5	42.0	1	1	1	1	0.0238
6	17.1	1	1	0	5	0.0585



$$\frac{K_B}{k} = 8.7 \times 10^7$$

$$K_B = 1.2609$$

- Regressions can be carried out using the **Polymath 6.1 software**
- Non-linear regressions involves the search for parameter values that minimize the sum of the squares of the differences between the measured values and the calculated values for the data points

$$\sigma^2 = \sum_{i=1}^N \frac{(r_{im} - r_{ic})^2}{N - k}$$

where N = number of runs

k = no. of parameters to be determined

r_{im} = measured reaction rate for run i r_{ic} = calculated reaction rate for run i

- Using the Polymath linear regression $k = 140.47 \times 10^{-10}$ $K_T = 1.0058$ $K_B = 1.2638$
- Using these values as initial guesses for non-linear regression, the actual values come out as,
 $k = 144.77 \times 10^{-10}$ $K_T = 1.0384$ $K_B = 1.3905$

The final rate expression can thus be written as,

$$-r_T = \frac{144.77 \times 10^{-10} [p_T p_H]}{1 + 1.3905 p_B + 1.0384 p_T}$$

This rate expression can then be used for reactor design