A First Course on Kinetics and Reaction Engineering

Class 5 on Unit 5

Where We've Been

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
  - A. Rate Expressions
    - 4. Reaction Rates and Temperature Effects
    - 5. Empirical and Theoretical Rate Expressions
    - 6. Reaction Mechanisms
    - 7. The Steady State Approximation
    - 8. Rate Determining Step
    - 9. Homogeneous and Enzymatic Catalysis
    - 10. Heterogeneous Catalysis
  - B. Kinetics Experiments
  - C. Analysis of Kinetics Data
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors

Empirical and Theoretical Rate Expressions

- Empirical rate expressions are chosen for their mathematical convenience
  - Power law rate expressions: $r_j = k_j \prod_{\substack{i=\text{all}\\ \text{species}}} \left[i\right]^{m_i}$
    - m_i is the reaction order in i
  - Multiplicative term to force proper behavior at equilibrium: $\left\{1 - \frac{\prod_{\substack{i=\text{all}\\ \text{species}}} \left[i\right]^{\nu_{i,j}}}{K_{eq,j}}\right\}^a$
  - Monod equation for cell growth
- Elementary reaction is one where the reaction as written is an exact description of what happens in a single molecular event
- Principle of microscopic reversibility: at the molecular level, every reaction must be reversible
- Collision theory rate expression for a gas phase elementary bimolecular reaction between two different types of reactants
  - $r_{AB,f} = N_{Av}\sigma_{AB}C_AC_B\sqrt{\frac{8k_BT}{\pi\mu}}\exp\left(\frac{-E_j}{RT}\right)$
- Transition state theory rate expression for an elementary reaction
  - $r_{j,f} = \frac{N_{Av}q_{\ddagger}}{q_{AB}q_C}\left\{\frac{k_BT}{h}\right\}\exp\left(\frac{-\Delta E_0^0}{k_BT}\right)\left[AB\right]\left[C\right]$

Theoretical Rate Expressions

- Collision theory and transition state theory give almost the same mathematical form for the net rate of an elementary reaction

$$r_{j,f} = k_{0,j,f} \exp\left(\frac{-E_{j,f}}{RT}\right) \prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{i,j}} - k_{0,j,r} \exp\left(\frac{-E_{j,r}}{RT}\right) \prod_{\substack{i=\text{all}\\ \text{products}}} C_i^{\nu_{ij}}$$

$$r_j = k_{0,j,f} \exp\left(\frac{-E_{j,f}}{RT}\right) \left(\prod_{\substack{i=\text{all}\\ \text{reactants}}} C_i^{-\nu_{ij}}\right) \left(1 - \frac{\prod_{\substack{i=\text{all}\\ \text{species}}} C_i^{\nu_{ij}}}{K_{eq_c - j}}\right)$$

- They differ in the form and temperature dependence of the pre-exponential term

$$k_{0,j,f} = N_{Av} \sigma_{AB} \sqrt{\frac{8 k_B T}{\pi \mu}} \qquad k_{0,j,f} = \left(\frac{q_\ddagger}{N_{Av}}\right) \left(\prod_{\substack{i=\text{all}\\ \text{reactants}}} \left(\frac{q_i}{N_{Av}}\right)^{\nu_{ij}}\right) \left(\frac{k_B T}{h}\right)$$

- Generally the differences in temperature dependence of the pre-exponential terms are almost impossible to detect due to the exponential term
  - We will usually take the pre-exponential terms to be constants
    - Both theories give the exact same mathematical form for the rate expression for an elementary reaction
    - This makes the forward and reverse rate coefficients obey the Arrhenius expression

Questions?

Last Class

The rate coefficient for a particular reaction varies with temperature as follows:

T(°C)	25	35	45	55	65
$10^3 \times k$, min^{-1}	0.8	3.8	15.1	46.7	151

Determine the pre-exponential factor and the activation energy.

Last Class

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10^3 x k, min^{-1}	0.8	3.8	15.1	46.7	151

Determine the pre-exponential factor and the activation energy.

$$k = k_0 \exp\left(\frac{-E}{RT}\right)$$

$$\ln(k) = E\left(\frac{-1}{RT}\right) + \ln(k_0)$$

$$y = mx + b$$

Fitting a Single Response Linear Model to Data

- Models and Data
  - $y = \theta_1 x_1 + \theta_2 x_2 + \cdots + \theta_{n_s} x_{n_s} + \theta_{n_s+1}$ with data points of the form $\left(x_1, x_2, \cdots, x_{n_s}, \hat{y}\right)$
  - y = m*x + b with data points of the form (x,y)
  - y = m*x with data points of the form (x,y)
- Objective function; sum of the squares of the errors
  - $\Phi = \sum_{l=1}^{n_e} \varepsilon_l^2 = \sum_{l=1}^{n_e} \left(\hat{y}_l - y_l\right)^2 = \sum_{l=1}^{n_e} \left(\hat{y}_l - \theta_1 x_{1,l} - \theta_2 x_{2,l} - \cdots - \theta_{n_s} x_{n_s,l} - \theta_{n_s+1}\right)^2$
  - Minimized when $\frac{\partial \Phi}{\partial \theta_k} = 0$
    - Application leads to (n_s + 1) equations that can be solved to find expressions for the best values of the (n_s + 1) parameters
- Quality of the fit can be assessed
  - Statistically, correlation coefficient, r^2
  - Graphically
    - Parity plot and residuals plots for the general linear model
    - Model plot for the simple (single set variable) models
- MATLAB scripts FitLinSR, FitLinmbSR and FitLinmSR perform all tasks
  - Fit, calculation of parameters with uncertainties, calculation of correlation coefficient, plots
  - When using the scripts with a general model, it must have a non-zero intercept

Model: $y = mx + b$

x	$\hat{y}$
0	9.88
1	12.67
2	15.09
3	18.1
4	21.2
5	24.2
6	27.8
7	30.2
8	33.9
9	36.6
10	39.1

- Model to be fit to data at left
  - y = m*x + b
  - Objectives
    - Determine if the fit is acceptable
    - Determine best values and uncertainties for m and b
- The MATLAB script FitLinmbSR.m can be used
  - Import the values of x and ŷ into the MATLAB workspace as column vectors
  - The column vectors must be named x and y_hat
- Then simply run the script
  - Make sure FitLinmbSR.m is in the MATLAB search path
  - Type "FitLinmbSR" at the MATLAB command prompt

Creating the Input

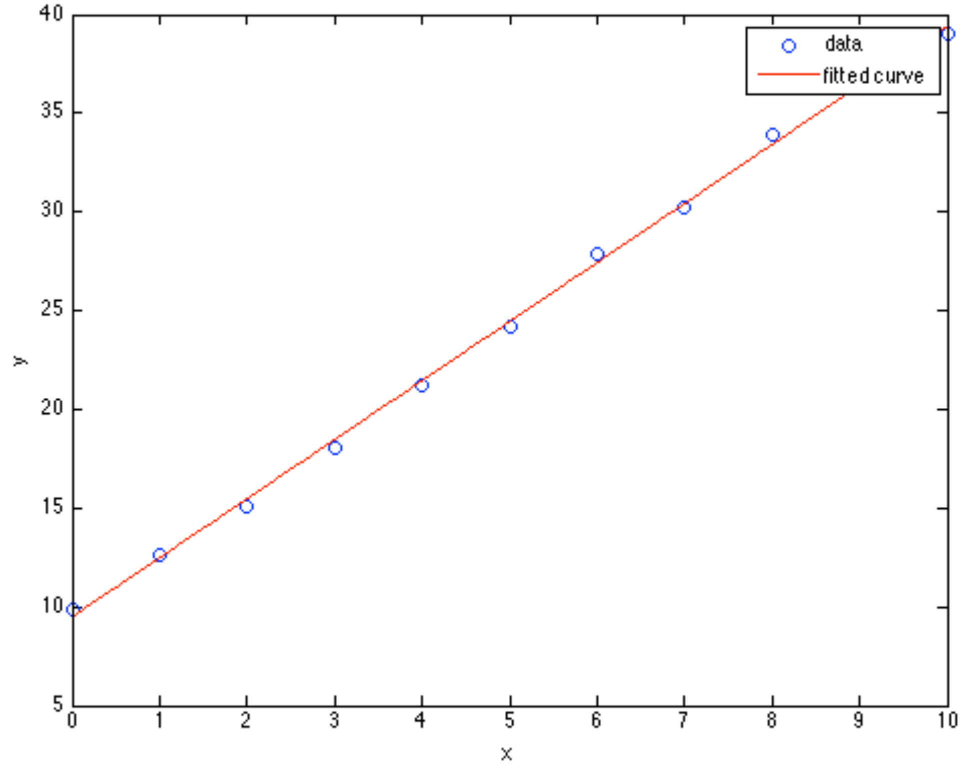
```
x =

     0
     1
     2
     3
     4
     5
     6
     7
     8
     9
    10
```

x	$\hat{y}$
0	9.88
1	12.67
2	15.09
3	18.1
4	21.2
5	24.2
6	27.8
7	30.2
8	33.9
9	36.6
10	39.1

```
y_hat =

    9.8800
   12.6700
   15.0900
   18.1000
   21.2000
   24.2000
   27.8000
   30.2000
   33.9000
   36.6000
   39.1000
```

FitLinmbSR Results

```
>> FitLinmbSR

r_squared =
   0.9989

m =
   2.9914

m_u =
   0.0764

b =
   9.4741

b_u =
   0.4523
```



- Fit is acceptable
  - r^2 close to 1.0
  - little scatter of data from line
  - no systematic variations of data from line
- Best parameter values
  - $m = 2.99 \pm 0.08$
  - $b = 9.47 \pm 0.45$

y = mx

x	*ŷ*
0	-0.74
1	4.31
2	9.76
3	14.14
4	19.31
5	24.6
6	29.8
7	34.2
8	39.6
9	44.1
10	49.6

- Model to be fit to data at left
  - y = m*x
  - Objectives
    - Determine if the fit is acceptable
    - Determine best value and uncertainties for m
- The MATLAB script FitLinmSR.m can be used
  - Import the values of x and ŷ into the MATLAB workspace as column vectors
  - The column vectors must be named x and y_hat
- Then simply run the script
  - Make sure FitLinmSR.m is in the MATLAB search path
  - Type “FitLinmSR” at the MATLAB command prompt

Creating the Input

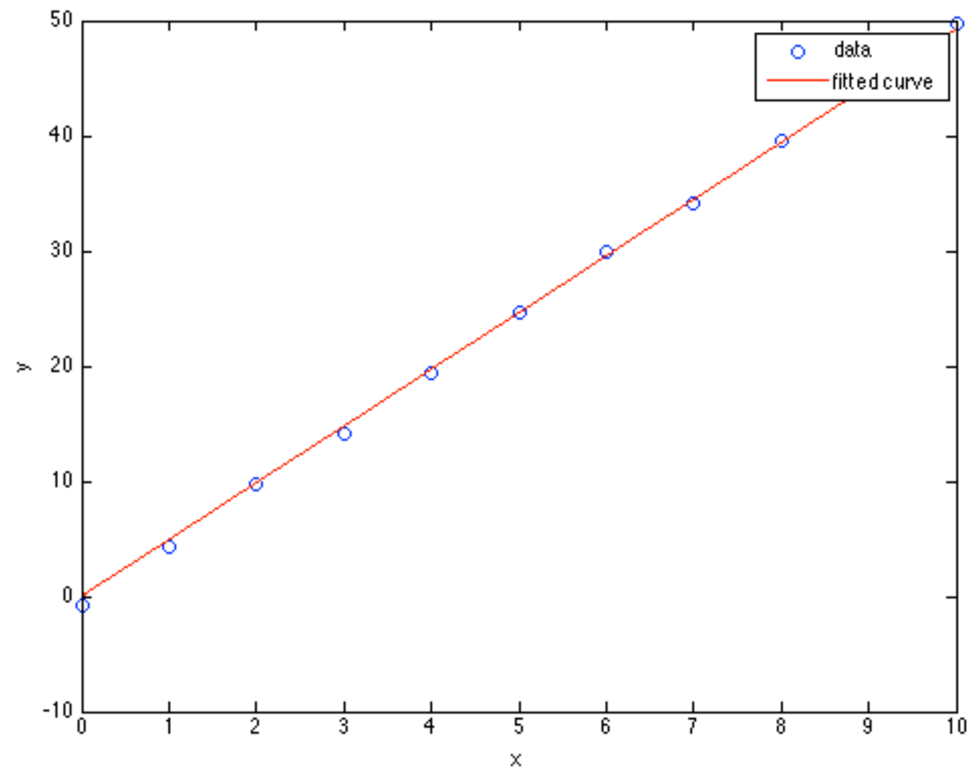
```
x =

     0
     1
     2
     3
     4
     5
     6
     7
     8
     9
    10
```

x	*ŷ*
0	-0.74
1	4.31
2	9.76
3	14.14
4	19.31
5	24.6
6	29.8
7	34.2
8	39.6
9	44.1
10	49.6

```
y_hat =

   -0.7400
    4.3100
    9.7600
   14.1400
   19.3100
   24.6000
   29.8000
   34.2000
   39.6000
   44.1000
   49.6000
```

FitLinmSR Results

```
>> FitLinmSR

r_squared =
   0.9993

m =
   4.9205

m_u =
   0.0486
```



- Fit is acceptable
  - r^2 close to 1.0
  - little scatter of data from line
  - no systematic variations of data from
- Best slope value
  - m = 4.92 ± 0.05

$$y = m_1x_1 + m_2x_2 + m_3x_3 + b$$

x_1	x_2	x_3	$\hat{y}$
0	5	20	12.27
1	4	19	11.15
2	3	18	9.77
3	2	17	8.88
4	1	16	8.21
5	0	15	7.05
6	1	14	15.46
7	2	12	26
8	3	10	36.9
9	4	6	49.4
10	5	4	58.1

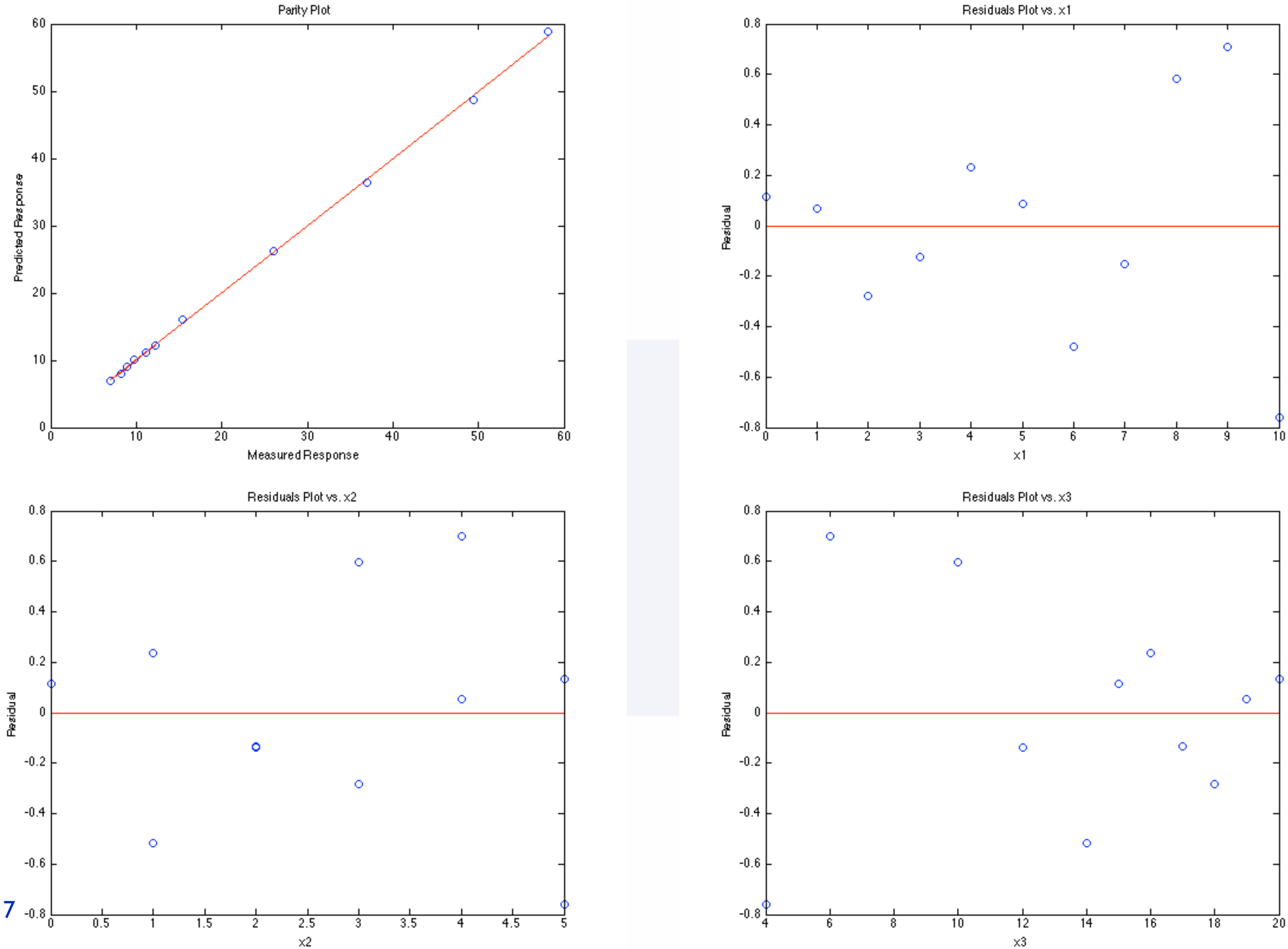
```
x =

    0    5   20    1
    1    4   19    1
    2    3   18    1
    3    2   17    1
    4    1   16    1
    5    0   15    1
    6    1   14    1
    7    2   12    1
    8    3   10    1
    9    4    6    1
   10    5    4    1
```

Using the Script

- Nothing more to do except run the script
  - The matrix x and the column vector y_hat must be in the MATLAB workspace
  - The script file, FitLinSR.m must be in the MATLAB path
- Results shown at right
  - Correlation coefficient $r^2 = 0.9994$
    - Very close to 1.0, indicating this is a very good fit
  - Parameter values
    - $m_1 = 2.88 \pm 0.99$
    - $m_2 = 5.04 \pm 0.51$
    - $m_3 = -1.12 \pm 0.64$
    - $b = 9.29 \pm 15.0$
- Plots are also generated
  - Parity plot
  - Residuals vs. x1
  - Residuals vs. x2
  - Residuals vs. x3

```
>> FitLinSR

r_squared =
  9.9942e-01

m =
  2.8836e+00
  5.0418e+00
 -1.1181e+00

m_u =
  9.9147e-01
  5.0940e-01
  6.4459e-01

b =
  9.2882e+00

b_u =
  1.5037e+01
```

Plots from FitLinSR



Homework Assignment 5

Suppose that for a quick preliminary calculation you need an approximate value for the rate of reaction (1) below for a mixture containing 22 % CO, 46 % H_2, 1 % CH_3OH and 31 % CO_2 at a total pressure of 49.3 atm and a temperature of 327 °C. Suppose further, that you have obtained an old company report which says that the rate expression given in equation (2) below was shown to fit experimental data from reaction (1) at similar compositions and pressure, but at the temperatures given in the table below. Using the data in that table, what is your best estimate for the rate of reaction (1) at the conditions of interest to you. (Note: the rate expression used in this example is made-up and should not be used for any purpose other than answering this question.)

$$CO + 2\,H_2 \rightleftarrows CH_3OH \qquad (1)$$

$$r_1 = k_1 P_{CO}^{0.46} P_{H_2}^{1.37} \qquad (2)$$

Temperature (degrees C)	k (mol min^{-1} L^{-1} atm$^{-1.83}$)
80	0.024
110	0.138
140	0.606
170	2.180

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