

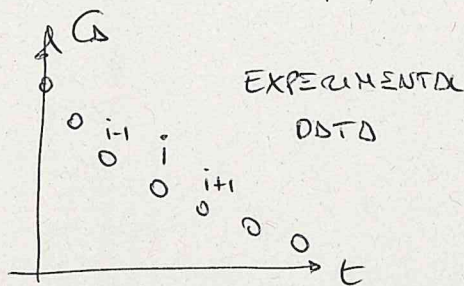
PRACTICAL SESSION 4

EXERCISE 1

$A \rightarrow \text{Products}$

$$\tau = K \cdot C_A^m \quad \left. \begin{array}{l} \text{parameters} \\ K, m \end{array} \right\}$$

Differential method: $\frac{dC_A}{dt} = -\tau = -K C_A^m$



from experimental lab

$$-\left(\frac{dC_A}{dt}\right)_i^{\text{exp}} \approx \frac{C_{A,i-1} - C_{A,i+1}}{t_{i-1} - t_{i+1}} \quad \text{centered differencing scheme}$$

$$-\frac{dC_A}{dt} = K C_A^m \rightarrow \underbrace{\ln\left(-\frac{dC_A}{dt}\right)}_{y_{\text{exp}}} = \underbrace{\ln K}_q + m \underbrace{\ln C_A}_{x_{\text{exp}}}$$

Linear model: $\begin{cases} y_{\text{exp}} = m x_{\text{exp}} + q \\ m = m \\ q = \ln K \end{cases}$

$$\rightarrow y = a_0 + a_1 x_1$$

LINEAR REGRESSION ANALYSIS

$$\underline{X} = \begin{bmatrix} 1 & \ln C_{A,1}^{\text{exp}} \\ 1 & \ln C_{A,2}^{\text{exp}} \\ \vdots & \vdots \\ 1 & \ln C_{A,N}^{\text{exp}} \end{bmatrix} \quad \underline{Y} = \begin{bmatrix} \ln\left(-\frac{dC_A}{dt}\right)_1^{\text{exp}} \\ \ln\left(-\frac{dC_A}{dt}\right)_2^{\text{exp}} \\ \vdots \\ \ln\left(-\frac{dC_A}{dt}\right)_N^{\text{exp}} \end{bmatrix}$$

$$\underline{A} = \underline{X}^T \underline{X} \quad \underline{b} = \underline{X}^T \underline{Y} \rightarrow \underline{A} \underline{a} = \underline{b} \rightarrow \underline{a} = [a_0, a_1] = [\ln K, m]$$

EXERCISE 2

$A \rightarrow \text{Products}$

$$r = k C_A^u$$

Integral method:
$$\begin{cases} \frac{dC_A}{dt} = -k C_A^u \\ C_A(t=0) = C_{A0} \end{cases}$$

$$\rightarrow C_A^{-u+1}(t) - C_{A0}^{-u+1} = -k(u+1)t$$

analytical solution:
$$C_A^{1-u}(t) = C_{A0}^{1-u} - k(1-u)t$$

parameters: $\begin{cases} u \\ k \end{cases}$ it is not possible to get a linear expression with respect to the parameters, i.e. we have a NON-LINEAR REGRESSION problem

However, we can transform it in a iterative linear regression problem, by fixing the u parameter to arbitrary values

Fixed u

$$\underbrace{C_A^{-u+1} - C_{A0}^{-u+1}}_{y_{\text{exp}}} = \underbrace{-k(1-u)}_m \underbrace{t}_{x_{\text{exp}}}$$

linear model: $y_{\text{exp}} = m x_{\text{exp}}$

$$y = a_1 x_1 \quad (a_0 = 0)$$

$$\underline{X} = \begin{bmatrix} [(C_{A1}^{\text{exp}})^{1-u} - C_{A0}^{1-u}] \\ [(C_{A2}^{\text{exp}})^{1-u} - C_{A0}^{1-u}] \\ \vdots \\ [(C_{AN}^{\text{exp}})^{1-u} - C_{A0}^{1-u}] \end{bmatrix}$$

$$\underline{Y} = \begin{bmatrix} t_1 \\ \vdots \\ t_n \end{bmatrix}$$

$$\underline{X}^T \underline{X} a_1 = \underline{X}^T \underline{Y}$$

$$a_1 = -k(1-u)$$

$$k = -\frac{a_1}{1-u} = \frac{a_1}{u-1}$$

We can evaluate the R^2 coefficient to estimate the accuracy of the regression.

In particular, we can consider a range of m values, repeating the linear regression several times. The best model is the one for which the R^2 value is maximum

INPUT M	OUTPUT k	R^2
—	—	—
—	—	—
→ —	—	⊖ maximum
—	—	—
—	—	—

EXERCISE 3

Modified Arrhenius' law : $k(T) = A \cdot T^{\beta} \cdot \exp\left(-\frac{E}{RT}\right)$

Linearization

parameters $\begin{pmatrix} A \\ \beta \\ E \end{pmatrix}$

$$\ln k = \ln A + \beta \ln T - \frac{E}{R} \frac{1}{T}$$

\downarrow

$$y = a_0 + a_1 x_1 + a_2 x_2$$

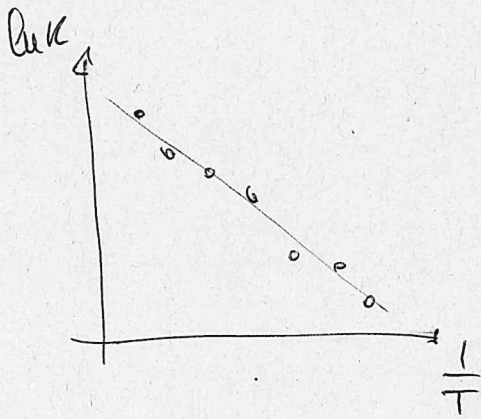
$$\begin{cases} a_0 = \ln A & x_1 = \ln T \\ a_1 = \beta & x_2 = \frac{1}{T} \\ a_2 = -\frac{E}{R} & y = \ln k \end{cases}$$

$$\underline{\underline{X}} = \begin{bmatrix} 1 & \ln T_1 & 1/T_1 \\ 1 & \ln T_2 & 1/T_2 \\ 1 & \ln T_3 & 1/T_3 \\ \vdots & \vdots & \vdots \\ 1 & \ln T_N & 1/T_N \end{bmatrix}$$

$$\underline{\underline{Y}} = \begin{bmatrix} \ln K_1 \\ \ln K_2 \\ \ln K_3 \\ \vdots \\ \ln K_N \end{bmatrix}$$

$$\underline{\underline{X}}^T \underline{\underline{X}} \underline{\underline{a}} = \underline{\underline{X}}^T \underline{\underline{Y}} \longrightarrow \underline{\underline{a}} = (a_0, a_1, a_2)$$

}
t



$$\left\{ \begin{array}{l} A = \exp(a_0) \\ \beta = a_1 \\ E = -R a_2 \end{array} \right.$$

PRACTICAL SESSION 4

EXERCISE 4



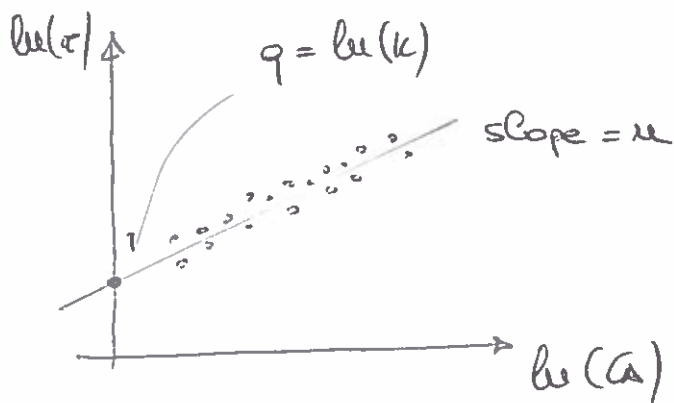
differential method $\frac{dC_A}{dt} = -r \Rightarrow -\frac{dC_A}{dt} = +k C_A^u$

$\ln\left(-\frac{dC_A}{dt}\right) = \ln(k C_A^u) \Rightarrow \ln\left(-\frac{dC_A}{dt}\right) = \ln k + u \ln C_A$

$\ln(r) = \ln(k) + u \ln C_A$

$y = a_0 + a_1 x_1$

$\left\{ \begin{array}{l} y = \ln(r) \\ a_0 = \ln(k) \\ a_1 = u \\ x_1 = \ln(C_A) \end{array} \right.$



$\underline{\underline{Y}} = \begin{bmatrix} \ln(r) \\ \vdots \end{bmatrix}$

$\underline{\underline{X}} = \begin{bmatrix} 1 & \ln C_A^0 \\ 1 & \vdots \\ 1 & \vdots \end{bmatrix} \left\{ \begin{array}{l} \text{Nexp} \end{array} \right.$

$\underline{\underline{X}}' \underline{\underline{X}} \underline{\underline{a}} = \underline{\underline{X}}' \underline{\underline{Y}}$

$\Rightarrow \underline{\underline{A}} \underline{\underline{a}} = \underline{\underline{b}}$

$\left\{ \begin{array}{l} \underline{\underline{A}} = \underline{\underline{X}}' \underline{\underline{X}} \\ \underline{\underline{b}} = \underline{\underline{X}}' \underline{\underline{Y}} \end{array} \right.$

EXERCISE 5



$$r = f(\text{CO}) \cdot g(\text{H}_2)$$

TEST 1 (Hypothesis)

$$r = K C_{\text{CO}}^{\mu_{\text{CO}}} \cdot C_{\text{H}_2}^{\mu_{\text{H}_2}}$$

$$\ln(r) = \ln K + \mu_{\text{CO}} \ln C_{\text{CO}} + \mu_{\text{H}_2} \ln C_{\text{H}_2}$$

$$y = a_0 + a_1 x_1 + a_2 x_2$$

$$\left\{ \begin{array}{l} y = \ln(r) \\ a_0 = \ln(K) \\ a_1 = \mu_{\text{CO}} \\ a_2 = \mu_{\text{H}_2} \\ x_1 = \ln C_{\text{CO}} \\ x_2 = \ln C_{\text{H}_2} \end{array} \right.$$

$$\underline{y} = \begin{bmatrix} \ln(r) \\ \vdots \\ \vdots \end{bmatrix} \quad \mu_{\text{exp}}$$

$$\underline{X} = \begin{bmatrix} 1 & \ln C_{\text{CO}} & \ln C_{\text{H}_2} \\ \vdots & \vdots & \vdots \\ 1 & \vdots & \vdots \end{bmatrix} \quad \mu_{\text{exp}}$$



$$\left\{ \begin{array}{l} K = \exp(a_0) = 6.05 \cdot 10^{-3} \\ \mu_{\text{CO}} = 1.00 \\ \mu_{\text{H}_2} = 0.0168 \end{array} \right.$$

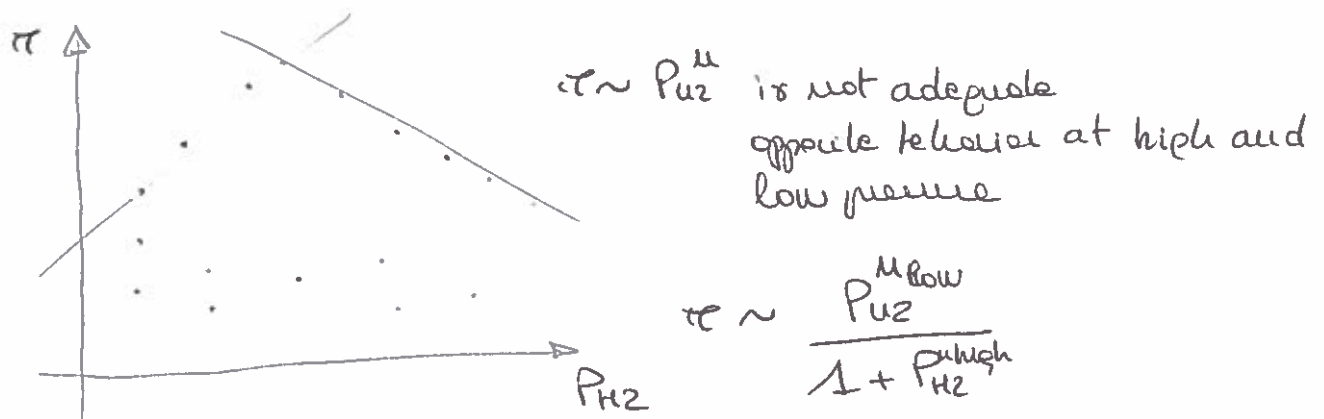
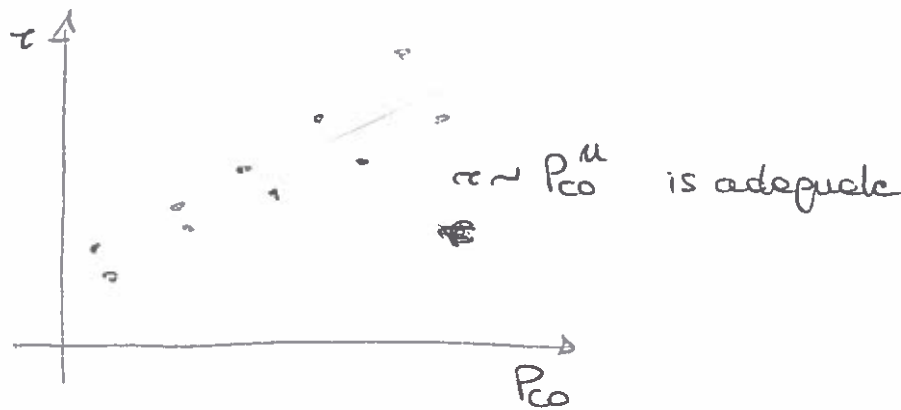
$$R^2 = 0.92$$



very bad

model not adequate

Look at experimental data



Hypothesis:
$$r = \frac{b_1 \cdot P_{CO}^{\mu_{CO}} \cdot P_{H_2}^{\mu_{H_2}^{low}}}{1 + b_2 P_{H_2}^{\mu_{H_2}^{high}}}$$

$$\ln(r) = \ln b_1 + \mu_{CO} \ln P_{CO} + \mu_{H_2}^{low} \ln P_{H_2} - \ln(1 + b_2 P_{H_2}^{\mu_{H_2}^{high}})$$

5 parameters

$$\begin{cases} a_1 = \ln b_1 \\ a_2 = \mu_{CO} \\ a_3 = \mu_{H_2}^{low} \\ a_4 = \mu_{H_2}^{high} \\ a_5 = b_2 \end{cases}$$

~~$\ln(r) = a_1 + a_2$~~

$$\ln(r) = a_1 + a_2 \ln P_{CO} + a_3 \ln P_{H_2} - \ln(1 + a_5 P_{H_2}^{a_4})$$

non linear regression analysis

{	1 dependent variable	$y = \ln(\cdot)$
	2 independent variables	$\begin{cases} x_1 = P_{CO} \\ x_2 = P_{H_2} \end{cases}$
	5 parameters	

$$y = a_1 + a_2 \ln(x_1) + a_3 \ln(x_2) - \ln(1 + a_5 x_2^{a_4})$$