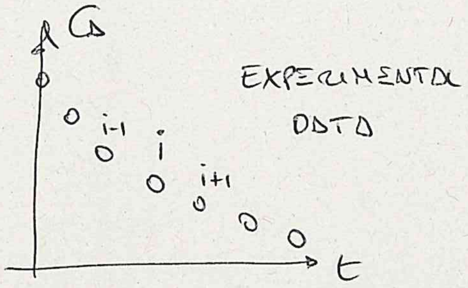
PRACTICAL SESSION 5

EXERCISE 1

$A \rightarrow$ Products

$r = K \cdot C_A^{n}$ $\Big\}$ parameters K, n

Differential method: $\dfrac{dC_A}{dt} = -r = -KC_A^{n}$



from experimental data

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

$$-\frac{dC_A}{dt} = KC_A^{n} \longrightarrow \underbrace{\ln\left(-\frac{dC_A}{dt}\right)}_{y_{exp}} = \underbrace{\ln K}_{q} + \underbrace{n}_{m}\, \underbrace{\ln C_A}_{x_{exp}}$$

linear model: $\begin{cases} y_{exp} = m x_{exp} + q \\ m = n \\ q = \ln K \end{cases} \longrightarrow y = a_0 + a_1 x_1$

LINEAR REGRESSION ANALYSIS

$$\underline{\underline{X}} = \begin{bmatrix} 1 & \ln C_{A1}^{exp} \\ 1 & \ln C_{A2}^{exp} \\ 1 & \vdots \\ \vdots & \vdots \\ 1 & \ln C_{AN}^{exp} \end{bmatrix} \qquad \underline{\underline{Y}} = \begin{bmatrix} \ln\left(-\frac{dC_A}{dt}\Big|_1^{exp}\right) \\ \ln\left(-\frac{dC_A}{dt}\Big|_2^{exp}\right) \\ \vdots \\ \ln\left(-\frac{dC_A}{dt}\Big|_N^{exp}\right) \end{bmatrix}$$

$$\underline{\underline{A}} \stackrel{def}{=} \underline{\underline{X}}^T \underline{\underline{X}} \quad \underline{b} = \underline{\underline{X}}^T \underline{Y} \longrightarrow \underline{\underline{A}}\,\underline{a} = \underline{b} \longrightarrow a = [a_0, a_1] = [\ln K, n]$$

EXERCISE 2

$A \longrightarrow$ Products

$r = k C_A^{n}$

Integral method: $\begin{cases} \dfrac{dC_A}{dt} = -k C_A^{n} \\ C_A(t=0) = C_A^{0} \end{cases}$

$\longrightarrow \quad C_A^{-n+1}(t) - C_{A0}^{-n+1} = -k(-n+1)\,t$

analytical solution: $\quad C_A^{1-n}(t) = C_{A0}^{1-n} - k(1-n)\,t$

parameters: $\begin{cases} n \\ k \end{cases}$ 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 <u>iterative</u> linear regression problem, by fixing the n parameter to arbitrary values

<u>Fixed n</u> $\quad \underbrace{C_A^{-n+1} - C_{A0}^{-n+1}}_{y_{exp}} = \underbrace{-k(1-n)}_{m}\,\underbrace{t}_{x_{exp}}$

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

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

$$\underline{\underline{X}} = \begin{bmatrix} \left[(C_{A1}^{exp})^{1-n} - C_{A0}^{1-n}\right] \\ \left[(C_{A2}^{exp})^{1-n} - C_{A0}^{1-n}\right] \\ \vdots \\ \left[(C_{AN}^{exp})^{1-n} - C_{A0}^{1-n}\right] \end{bmatrix} \qquad \underline{Y} = \begin{bmatrix} t_1 \\ \vdots \\ t_N \end{bmatrix}$$

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

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

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

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

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

INPUT	OUTPUT	
n	k	R^2
—	—	—
—	—	—
—	—	— maximum
—	—	—
—	—	—
	—	—

EXERCISE 3

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

linearization

parameters $\left\{ \begin{array}{l} A \\ \beta \\ E \end{array} \right.$

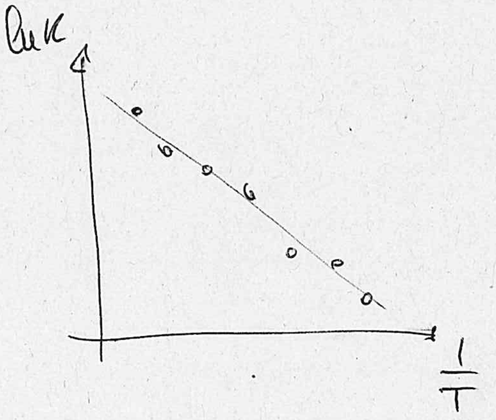
$$\ln K = \ln A + \beta \ln T - \frac{E}{R}\frac{1}{T}$$

$$\Downarrow$$

$$y = a_0 + a_1 x_1 + a_2 x_2 \qquad \left\{ \begin{array}{l} a_0 = \ln A \\ a_1 = \beta \\ a_2 = -\frac{E}{R} \end{array} \right. \qquad \begin{array}{l} x_1 = \ln T \\ x_2 = \frac{1}{T} \\ y = \ln K \end{array}$$

$$\underline{\underline{X}} = \begin{bmatrix} 1 & \ln T_1 & 1/T_1 \\ 1 & \ln T_2 & 1/T_2 \\ 1 & \ln T_3 & 1/T_3 \\ \vdots & & \\ 1 & \ln T_N & 1/T_N \end{bmatrix} \qquad \underline{Y} = \begin{bmatrix} \ln K_1 \\ \ln K_2 \\ \ln K_3 \\ \vdots \\ \ln K_N \end{bmatrix}$$

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



$$\begin{cases} A = \exp(a_0) \\ \beta = a_1 \\ E = -R a_2 \end{cases}$$

PRACTICAL SESSION 5

EXERCISE 4

$A \longrightarrow \text{Products} \qquad r = k C_A^{n}$

differential method

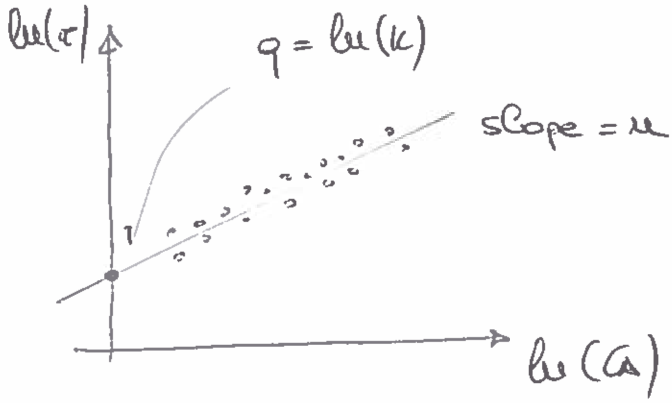
$$\frac{dC_A}{dt} = -r \implies -\frac{dC_A}{dt} = +k C_A^{n}$$

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

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

$$y = a_0 + a_1 x_1$$

$$\begin{cases} y = \ln(r) \\ a_0 = \ln(k) \\ a_1 = n \\ x_1 = \ln(C_A) \end{cases}$$



$$\underline{Y} = \begin{bmatrix} \ln(r) \\ \vdots \\ \vdots \end{bmatrix} \qquad \underline{\underline{X}} = \underbrace{\begin{bmatrix} 1 & \ln C_A^{0} \\ 1 & \vdots \\ \vdots & \vdots \\ 1 & \end{bmatrix}}_{N_{exp}}$$

$$\underbrace{\underline{\underline{X}}'\underline{\underline{X}}}_{\underline{\underline{A}}}\ \underline{a} = \underbrace{\underline{\underline{X}}'\underline{Y}}_{\underline{b}} \implies \underline{\underline{A}}\ \underline{a} = \underline{b} \qquad \begin{cases} \underline{\underline{A}} = \underline{\underline{X}}'\underline{\underline{X}} \\ \underline{b} = \underline{\underline{X}}'\underline{Y} \end{cases}$$

EXERCISE 5

$$3H_2 + CO \longrightarrow CH_4 + 2H_2O$$

$$r = f(CO) \cdot g(H_2)$$

TEST 1 (Hypothesis)

$$r = K\, C_{CO}^{n_{CO}} \cdot C_{H_2}^{n_{H_2}}$$

$$\ln(r) = \ln K + n_{CO} \ln C_{CO} + n_{H_2} \ln C_{H_2}$$

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

$$\begin{cases} y = \ln(r) \\ a_0 = \ln(K) \\ a_1 = n_{CO} \\ a_2 = n_{H_2} \\ x_1 = \ln C_{CO} \\ x_2 = \ln C_{H_2} \end{cases}$$

$$\underline{Y} = \underbrace{\begin{bmatrix} \ln(r) \\ \vdots \\ \vdots \end{bmatrix}}_{n_{exp}}$$

$$\underline{\underline{X}} = \underbrace{\begin{bmatrix} 1 & \ln C_{CO} & \ln C_{H_2} \\ 1 & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ 1 & \vdots & \vdots \end{bmatrix}}_{n_{exp}}$$

$$\Downarrow$$

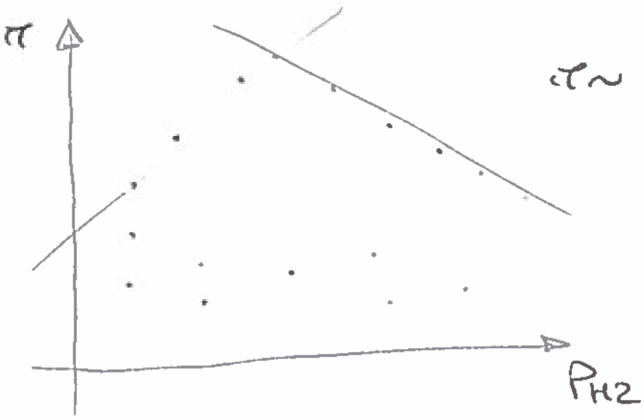
$$\begin{cases} K = \exp(a_0) = 6.05 \cdot 10^{-3} \\ n_{CO} = 1.00 \\ n_{H_2} = 0.0168 \end{cases}$$

$R^2 = 0.92$

very bad   model not adequate

Look at experimental data

$\tau \sim P_{CO}^{u}$ is adequate



$\tau \sim P_{H2}^{u}$ is not adequate
opposite behavior at high and low pressure

$$\tau \sim \frac{P_{H2}^{u_{low}}}{1 + P_{H2}^{u_{high}}}$$

Hypothesis: $$\tau = \frac{b_1 \cdot P_{CO}^{u_{CO}} \cdot P_{H2}^{u_{H2}^{low}}}{1 + b_2 P_{H2}^{u_{high}}}$$

$$\ln(\tau) = \ln b_1 + u_{CO} \ln P_{CO} + u_{H2}^{low} \ln P_{H2} - \ln\left(1 + b_2 P_{H2}^{u_{high}}\right)$$

5 parameters
$$\begin{cases} a_1 = \ln b_1 \\ a_2 = u_{CO} \\ a_3 = u_{H2}^{low} \\ a_4 = u_{H2}^{high} \\ a_5 = b_2 \end{cases}$$

$\cancel{\ln(\tau) = a_1 + \ldots}$

$$\ln(\tau) = a_1 + a_2 \ln P_{CO} + a_3 \ln P_{H2} - \ln\left(1 + a_5 P_{H2}^{a_4}\right)$$

non linear regression analysis

1 dependent variable $y = \ln(r)$

2 independent variables $\begin{cases} x_1 = P_{CO} \\ x_2 = P_{H2} \end{cases}$

5 parameters

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