



Determination of c — t relation

☑ Chemical Analysis Methods

Sample



Termination



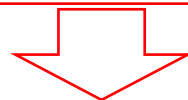
Measurement

Disadvantages:

- Many compounds, especially organic ones, are hardly to be determined quantitatively
- Larger reactors are used because large amount of samples are needed
- Determinations are of very much time consuming

☑ Physicochemical Analysis Methods

——Time dependence of some physical properties of the reaction system

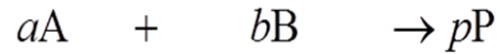


- (1) the contributions of various substances to Y are additive
- (2) the contributions of various substances to Y are proportional to or are linear to their concentrations
- (3) The equilibrium constant is large enough that the reactant A can be regarded as completely consumed if the time is long enough

Electric conductance, optical rotation, absorbance, refractive index, vapor pressure, viscosity, pressure etc.



Physicochemical Analysis Methods



$$t = 0: \quad c_{A0} \quad c_{B0} \quad 0 \quad Y_0$$

$$t = t: \quad c_{A0} - x \quad c_{B0} - \frac{b}{a}x \quad \frac{p}{a}x \quad Y_t$$

$$t = \infty: \quad 0 \quad c_{B0} - \frac{b}{a}c_{A0} \quad \frac{p}{a}c_{A0} \quad Y_\infty$$

M refers to reaction medium

Λ refers to coefficient

$$t = 0: \quad Y_0 = Y_M + \Lambda_A c_{A0} + \Lambda_B c_{B0}$$

$$t = t: \quad Y_t = Y_M + \Lambda_A (c_{A0} - x) + \Lambda_B (c_{B0} - \frac{b}{a}x) + \Lambda_P \frac{p}{a}x$$

$$t = \infty: \quad Y_\infty = Y_M + \Lambda_B (c_{B0} - \frac{b}{a}c_{A0}) + \Lambda_P \frac{p}{a}c_{A0}$$

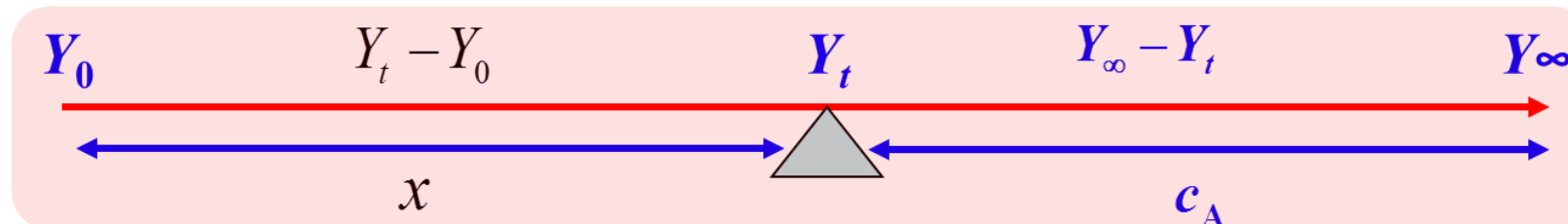
$$\frac{c_{A0}}{c_{A0} - x} = \frac{Y_\infty - Y_0}{Y_\infty - Y_t}; \quad \frac{x}{c_{A0} - x} = \frac{Y_t - Y_0}{Y_\infty - Y_t}; \quad x = c_{A0} \frac{Y_t - Y_0}{Y_\infty - Y_0}$$



$$Y_\infty - Y_0 = (\Lambda_P \frac{p}{a} - \Lambda_B \frac{b}{a} - \Lambda_A) c_{A0} = \Lambda c_{A0}$$

$$Y_t - Y_0 = (\Lambda_P \frac{p}{a} - \Lambda_B \frac{b}{a} - \Lambda_A) x = \Lambda x$$

To use the ratio of physical properties instead that of concentration





Physicochemical Analysis Methods

☑ Zeroth order $c_{A0} - c_A = k_A t$

$$\frac{c_{A0} - c_A}{c_{A0}} = \frac{k_A t}{c_{A0}} = \frac{Y_t - Y_0}{Y_\infty - Y_0}$$

☑ First order $\ln \frac{c_{A0}}{c_A} = k_A t$

$$\ln \frac{c_{A0}}{c_A} = \ln \frac{c_{A0} - c_{A\infty}}{c_A - c_{A\infty}} = \ln \frac{Y_\infty - Y_0}{Y_\infty - Y_t} = k_A t$$

The rate coefficient can be calculated without knowing the initial concentration

☑ Second order $\frac{1}{c_A} - \frac{1}{c_{A0}} = k_A t$

$$\frac{c_{A0} - c_A}{c_{A0} \cdot c_A} = \frac{1}{c_{A0}} \cdot \frac{Y_t - Y_0}{Y_\infty - Y_t} = k_A t$$



Data Processing in Chemical Kinetics

☑ Method one—Integration Method (Trying method)

Exp. Data $(t_1, c_1), (t_2, c_2), (t_3, c_3), \dots$



Substitute into integrated rate equations of various orders



Zeroth

c_A

First

$\ln\{c_A\}$

Second

$1/c_A$

Third

$1/c_A^2$

} Plot against t



From the obtained straight line n, k

Advantage: Simple and convenient when the reaction order is a simple positive integer

Disadvantages:

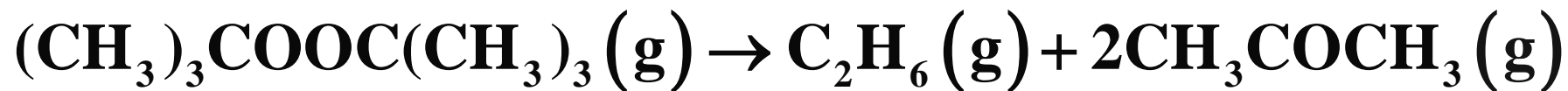
It is not sensitive enough especially for narrower concentration range of experiment resulting in difficulty to distinguish the different orders.

It can not be used when the order is a non-integer including a fraction, or a negative value.



Data Processing in Chemical Kinetics

Example



t/min	0.0	2.5	5.0	10.0	15.0	20.0
p/kPa	1.00	1.40	1.67	2.11	2.39	2.59

$$p_t \sim Y; p_\infty = 3p_0$$

☑ Zeroth

$$\frac{k_A t}{c_{A0}} = \frac{Y_t - Y_0}{Y_\infty - Y_0} = \frac{p_t - p_0}{3p_0 - p_0}$$

$$p_t \text{ --- } t$$

☑ First

$$k_A t = \ln \frac{Y_\infty - Y_0}{Y_\infty - Y_t} = \ln \frac{3p_0 - p_0}{3p_0 - p_t}$$

$$\ln \frac{2p_0}{3p_0 - p_t} \text{ --- } t$$

☑ Second

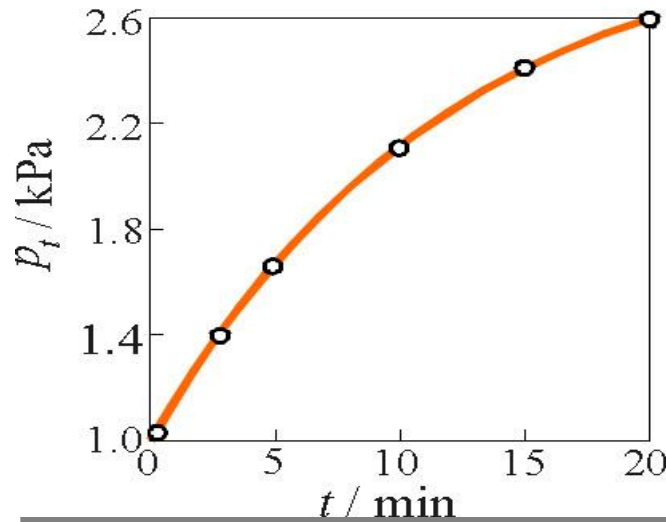
$$k_A t = \frac{1}{c_{A0}} \cdot \frac{Y_t - Y_0}{Y_\infty - Y_t} = \frac{1}{c_{A0}} \cdot \frac{p_t - p_0}{3p_0 - p_t}$$

$$\frac{1}{3p_0 - p_t} \text{ --- } t$$

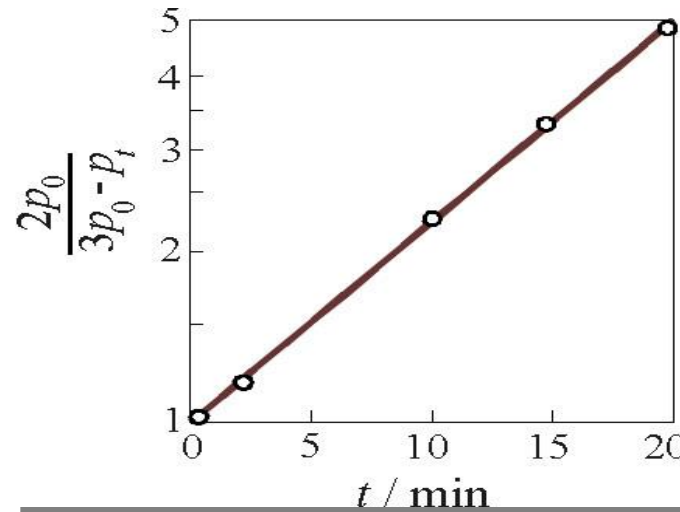


Data Processing in Chemical Kinetics

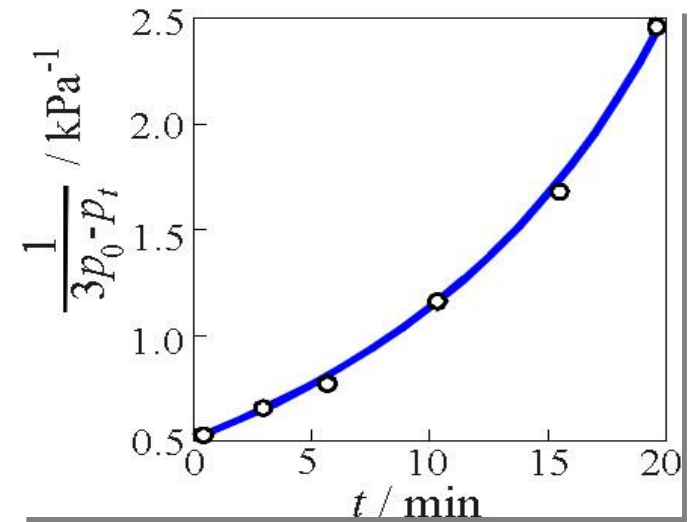
☑ Zeroth



☑ First



☑ Second



$$n = 1$$

$$k_A = 0.08 \text{ min}^{-1}$$



Data Processing in Chemical Kinetics

Example



t/min	a_t / Degree
0	34.50
1435	31.10
4315	25.00
7070	20.16
11360	13.98
14170	10.61
16935	7.57
19815	5.08
29925	-1.65
∞	-10.77

Reaction order and rate coefficient?



Data Processing in Chemical Kinetics

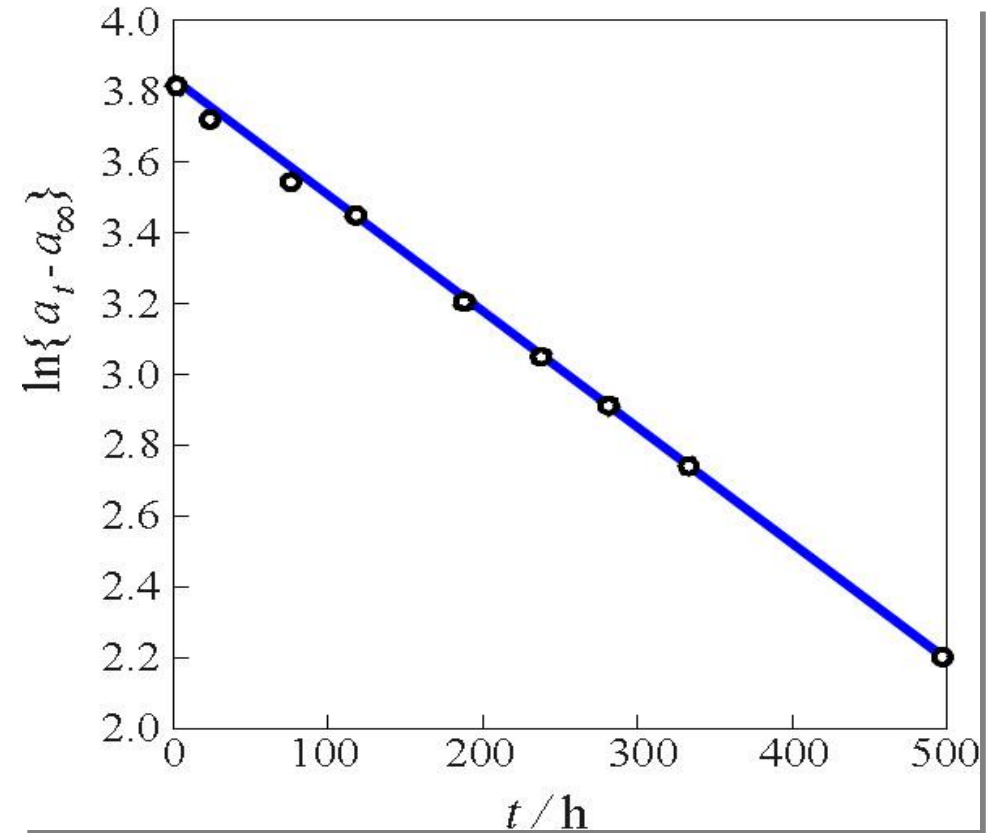
Method one——Plot a straight line

$$k_A = \frac{1}{t} \ln \frac{c_{A0}}{c_{A0} - x} = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

$$\ln(\alpha_t - \alpha_\infty) \text{---} t$$

$$n = 1$$

$$k_A = 5.37 \times 10^{-5} \text{ min}^{-1}$$





Data Processing in Chemical Kinetics

Method two——Calculate k_A at different times

$$k_A = \frac{1}{t} \ln \frac{c_{A0}}{c_{A0} - x}$$
$$= \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

$$n = 1$$

$$k_{A(\text{avg})} = 5.36 \times 10^{-5} \text{ min}^{-1}$$

t/min	a_t / Degree	$(a_t - a_\infty)$	$k_A \times 10^5 / \text{min}^{-1}$
0	34.50	45.27	—
1435	31.10	41.87	5.44
4315	25.00	35.77	5.46
7070	20.16	30.93	5.39
11360	13.98	24.75	5.32
14170	10.61	21.38	5.29
16935	7.57	18.34	5.34
19815	5.08	15.85	5.30
29925	-1.65	9.12	5.35
∞	-10.77	0.00	—



Data Processing in Chemical Kinetics

An ideal gas reaction $A(g) \rightarrow B(g) + 2C(g)$ is carried out in an isothermal and isochoric reactor. The pressure of the reaction system changed with time. Try to calculate the rate coefficient:

Exp. 1 Only A was presented at the initial time

t / min	0	2.5	5.0	10.0	15.0	20.0
p / kPa	1.00	1.40	1.67	2.11	2.39	2.59

Exp. 2 Part of A was decomposed at the initial time

t / min	0	5.0	10.0	15.0	∞
p / kPa	1.67	2.11	2.39	2.59	3.00



Data Processing in Chemical Kinetics

☑ Method two——Differential Method

$$\nu_A = -dc_A / dt = k_A c_A^n$$

$$\lg \{ \nu_A \} = n \lg \{ c_A \} + \lg \{ k_A \}$$

➤ Regression

Experimental data



$$c_A = f(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + \dots$$

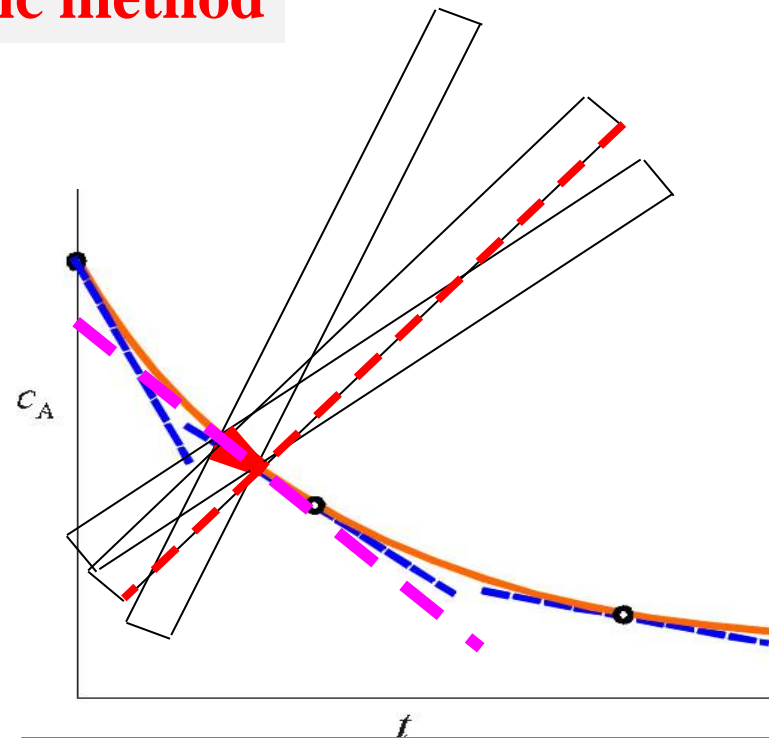
Regression parameters a_0, a_1, a_2, \dots



$$\nu_A = -dc_A / dt = a_1 + 2a_2 t + 3a_3 t^2 + \dots$$

Reaction rate at different time

➤ Graphic method

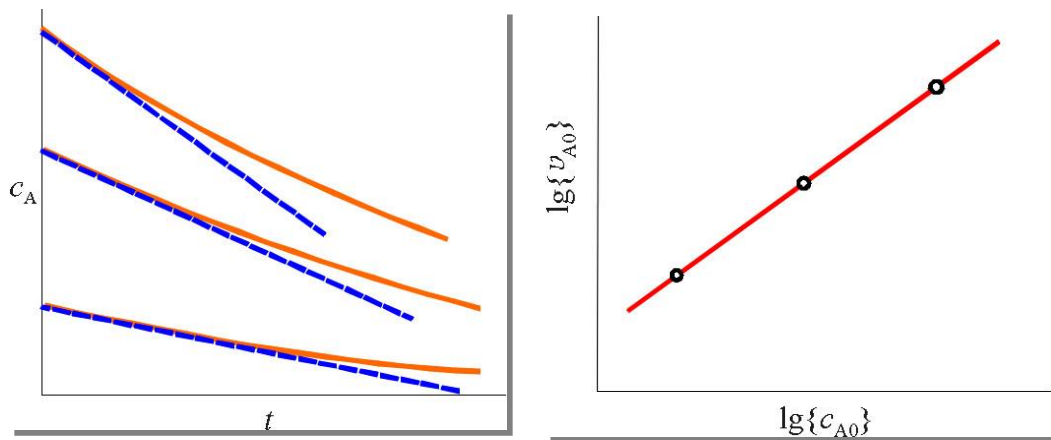




Data Processing in Chemical Kinetics

☑ Method two——Differential Method

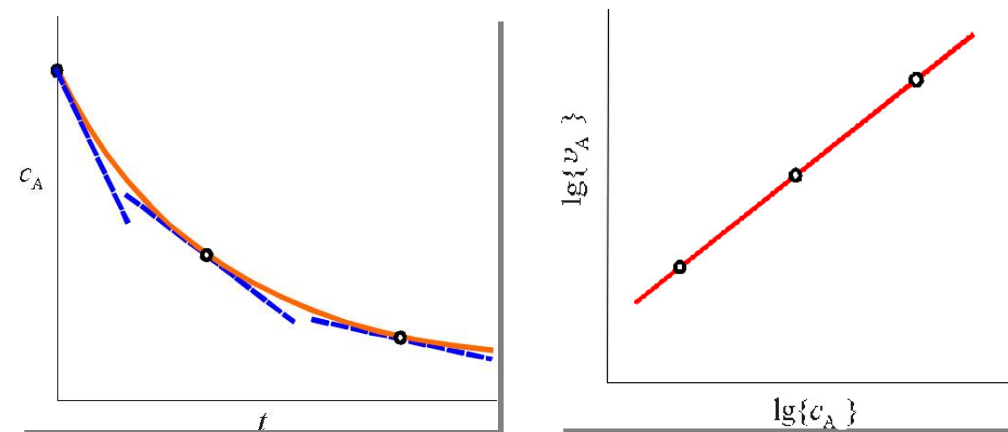
Initial Rate Method



True order n_c

The rate determination will not be disturbed by the products

One Run Method



Reaction order n_t

$n_t > n_c$ the products play **retarding** effect
 $n_t < n_c$ the products play **accelerating** effect



Data Processing in Chemical Kinetics

☑ Method two——Differential Method

Isolating Variables Method

$$\nu_A = k_A c_A^\alpha c_B^\beta \quad \lg\{\nu_A\} = \alpha \lg\{c_A\} + \beta \lg\{c_B\} + \lg k_A$$

Reactant B is in great excess

$$\nu_A = -dc_A / dt = k'_A c_A^\alpha$$

A pseudo α order reaction

Reactant A is in great excess

$$\nu_B = -dc_B / dt = k'_B c_B^\beta$$

A pseudo β order reaction

Advantage: It is applicable when the order is non-integer

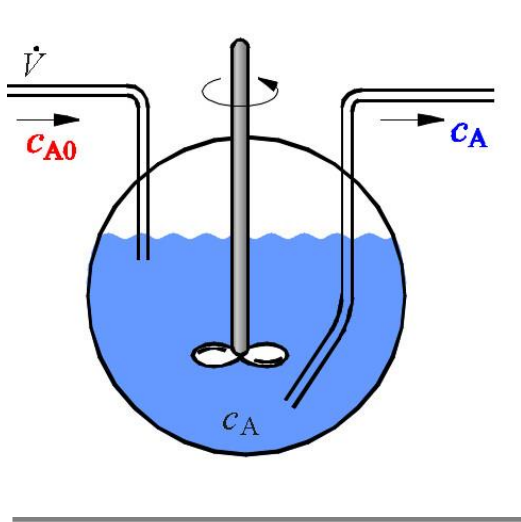
Disadvantage: Large uncertainty



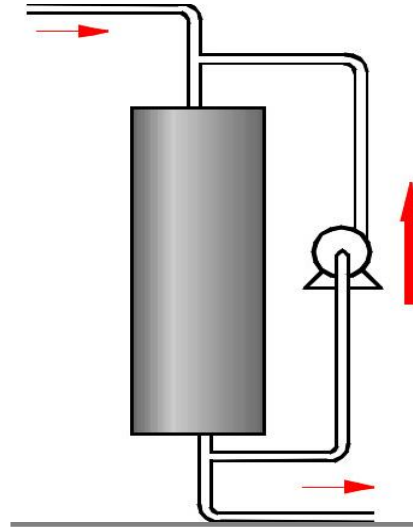
Data Processing in Chemical Kinetics

☑ Method two——Differential Method

Differential Reactors



Continuous Tank Reactor



Continuous Tubular Reactor with a Loop

Concentrations unchanged with time and in space

$$v_A = q_V \frac{c_{A0} - c_A}{V_R}$$



Data Processing in Chemical Kinetics

☑ **Method three——half life**

$$v_A = -dc_A / dt = k_A c_A^n$$

$$k_A = \frac{1}{t(n-1)} \left[\frac{1}{(c_{A0} - x)^{n-1}} - \frac{1}{c_{A0}^{n-1}} \right] \quad (n \neq 1)$$

$$t_{1/2} = (2^{n-1} - 1) / [(n-1)k_A c_{A0}^{n-1}]$$

$$\lg\{t_{1/2}\} = (1-n)\lg\{c_{A0}\} + \lg\left\{\frac{2^{n-1} - 1}{k_A(n-1)}\right\}$$

➤ Plotting $\lg\{t_{1/2}\}$ against $\lg\{c_{A0}\}$ gives a straight line

➤ Half-lives at different initial concentrations $n = \frac{\lg(t_{1/2}/t'_{1/2})}{\lg(c'_{A0}/c_{A0})} + 1$