Combination Reaction

Opposite reaction
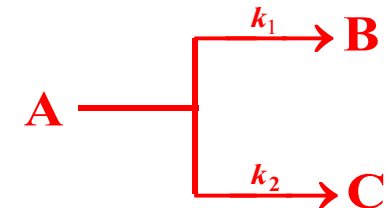
$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$
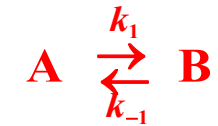
☑ **Complex Reaction**   **Consecutive reactions**

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Parallel Reactions

$$A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$$
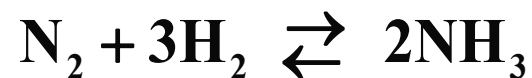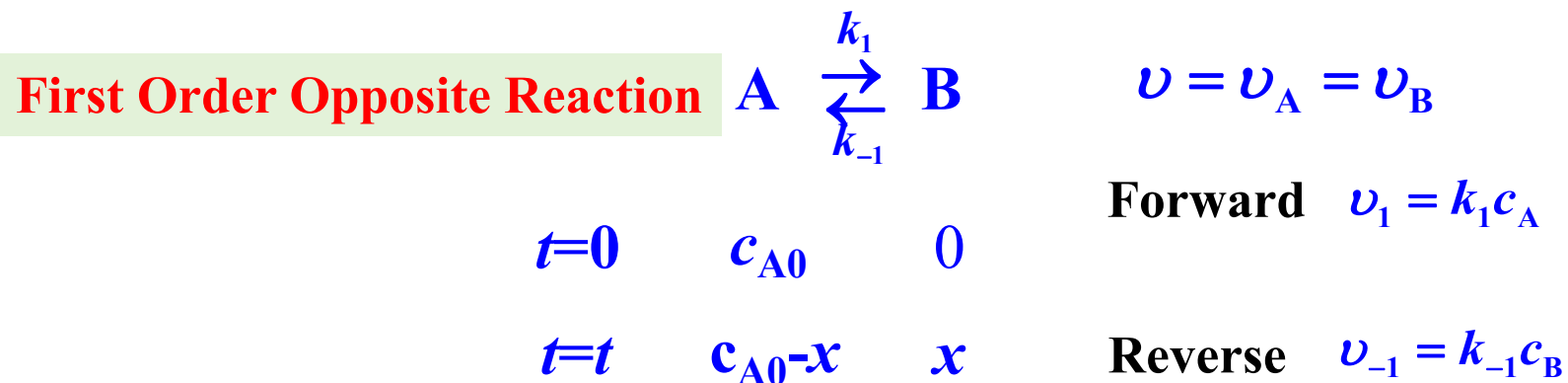
Opposite reaction

When a reaction is the **reverse** to another reaction, the **combination** of the two reactions is called an opposite reaction

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

In principle, all reactions are opposite reactions

First Order Opposite Reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \qquad \upsilon = \upsilon_A = \upsilon_B$$

Forward $\upsilon_1 = k_1 c_A$

$t=0$	c_{A0}	0
$t=t$	$c_{A0}-x$	x

Reverse $\upsilon_{-1} = k_{-1}c_B$

Total rate

$$\upsilon = \upsilon_1 - \upsilon_{-1} = k_1 c_A - k_{-1}c_B$$

Differential

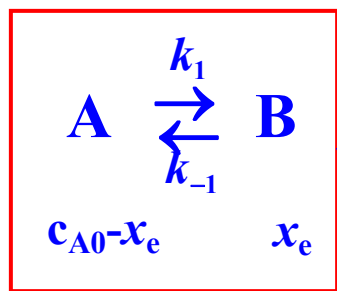$$\upsilon = \upsilon_A = -\frac{dc_A}{dt} = \frac{dx}{dt} = k_1 c_{A0} - (k_1 + k_{-1})x$$

Integrated

$$\ln c_{A0} - \ln\left(c_{A0} - \frac{k_1 + k_{-1}}{k_1}x\right) = (k_1 + k_{-1})t$$

Opposite reaction

Equilibrium

$$\upsilon = k_1 c_{A0} - (k_1 + k_{-1})x_e = 0$$

Kinetics

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$c_{A0} - x_e \qquad x_e$$

Thermodyanmics

$$c_{A0} = \frac{k_1 + k_{-1}}{k_1} x_e$$

$$\ln c_{A0} - \ln\left(c_{A0} - \frac{k_1 + k_{-1}}{k_1}x\right) = (k_1 + k_{-1})t$$
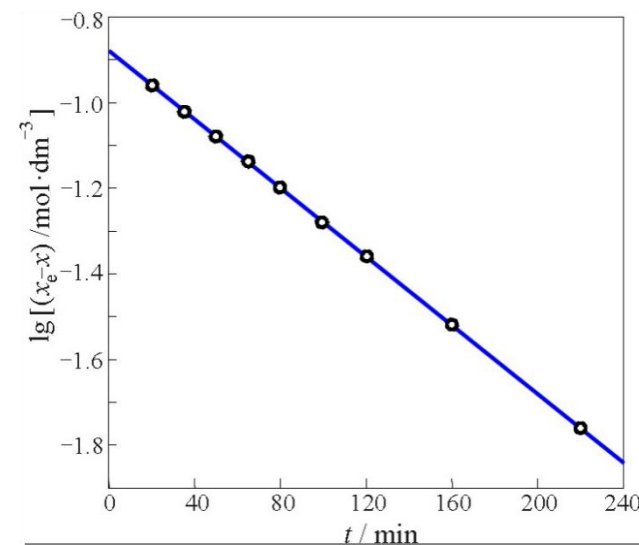
$$K_c = \frac{x_e}{c_{A0} - x_e}$$

$$\ln\{x_e - x\} \quad vs.\ t$$

$$\ln \frac{x_e}{x_e - x} = (k_1 + k_{-1})t$$

$$K_c = \frac{x_e}{c_{A0} - x_e} = \frac{k_1}{k_{-1}}$$

$$Slope = k_1 + k_{-1}$$

$$k_1 \text{ and } k_{-1}$$

The Synergy of Thermodynamics and Kinetics!
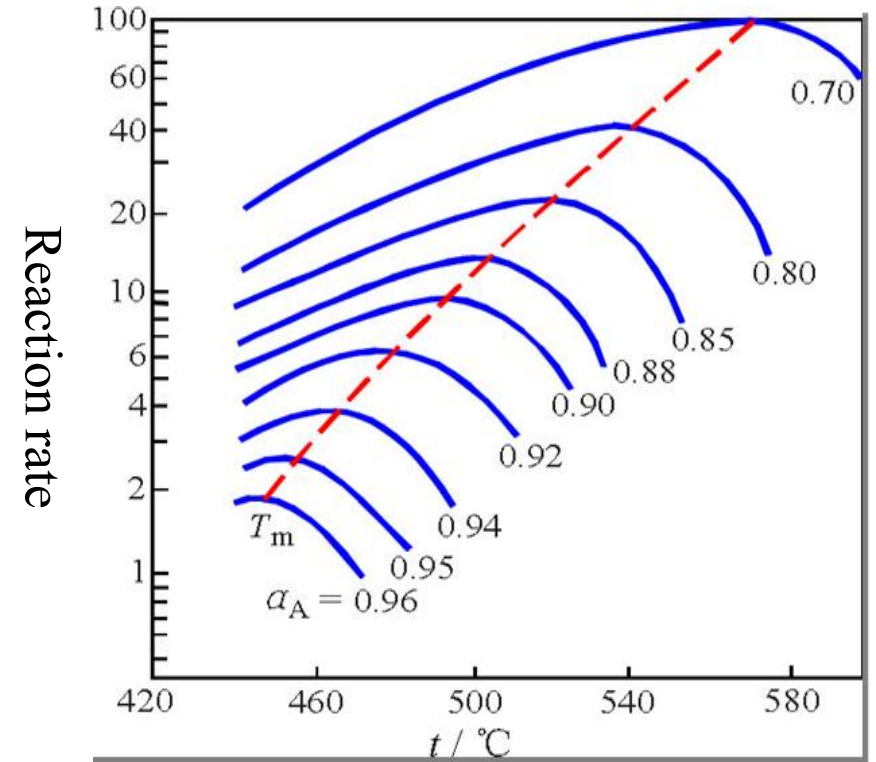
Opposite reaction

$$\upsilon = \upsilon_A = -\frac{dc_A}{dt} = \frac{dx}{dt} = k_1 c_{A0} - (k_1 + k_{-1})x$$

$$K_c = \frac{k_1}{k_{-1}}$$

$$\boxed{\frac{dx}{dt} = k_1(c_{A0} - x) - \frac{k_1}{K_c}x}$$

Exothermic　　　T **increases** ── k_1 **increases**
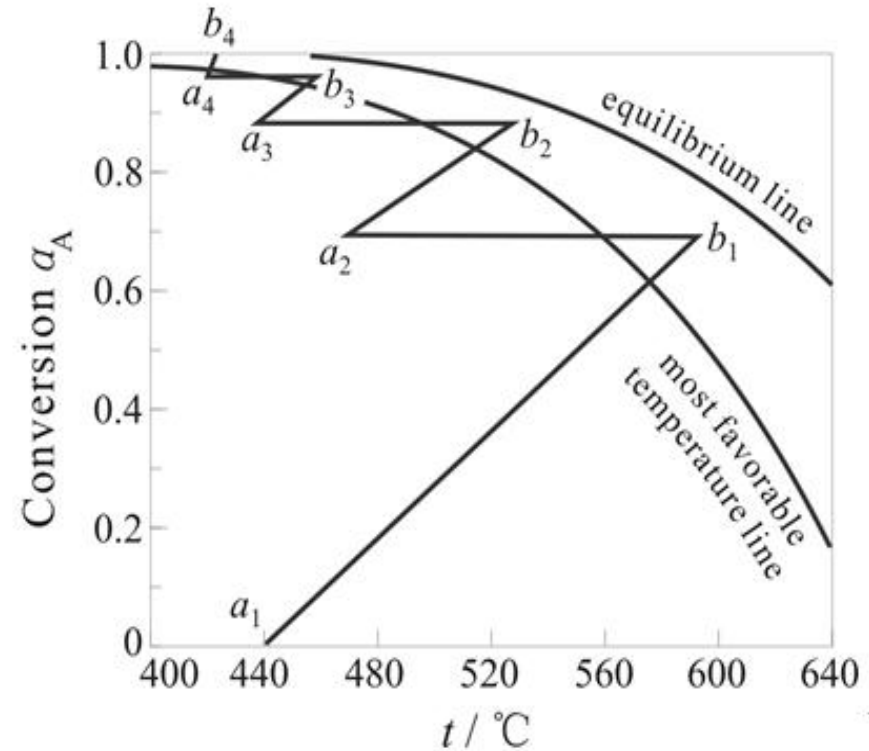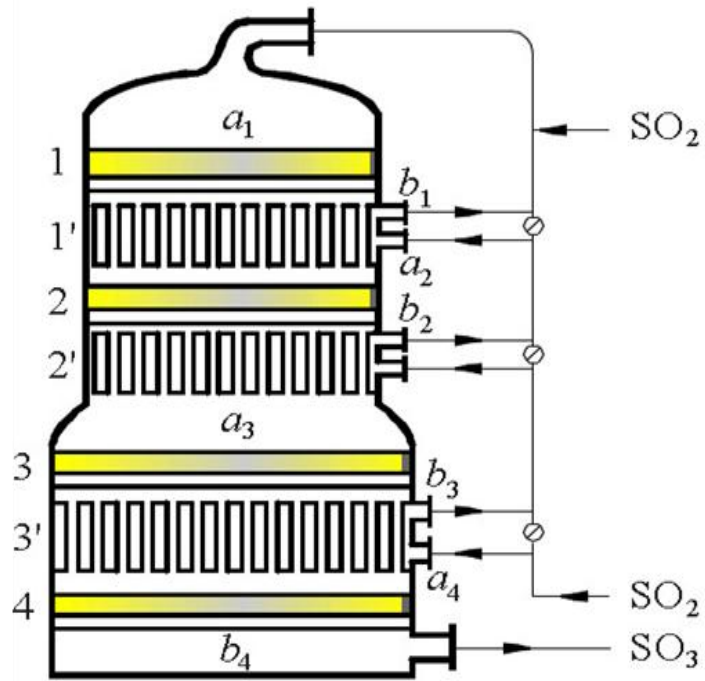
── K_c **decreases**

A maximum for the temperature dependence of the reaction rate at a given conversion would be displayed

☆ Corresponding temperature T_m at the maximum is called the **most favorable temperature**

☆ T_m **decreases with the increasing conversion**
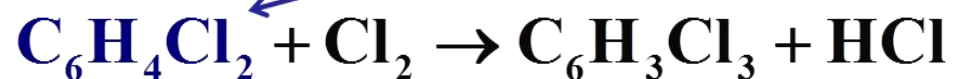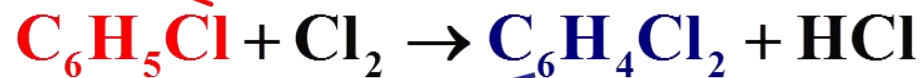
Opposite reaction

A four-stage reactor for the oxidation of SO_2 and the corresponding operation sketch diagram.

1, 2, 3, 4- catalyst layers, 1′, 2′, 3′- heat exchanger

Consecutive reactions

When a certain product of a reaction is a reactant of another reaction (the later is **not the reverse reaction** of the former), the combination of these reactions is called a consecutive reaction.

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$$

$$C_6H_4Cl_2 + Cl_2 \rightarrow C_6H_3Cl_3 + HCl$$

$$A \longrightarrow B \longrightarrow C \longrightarrow ...$$

Consecutive reactions

First Order Consecutive Reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$t=0 \quad c_{A0} \neq 0, \quad c_{B0}=c_{C0}=0$

$$\upsilon_A = -\frac{dc_A}{dt} = k_1 c_A$$

$$\upsilon_C = \frac{dc_C}{dt} = k_2 c_B$$

$$\upsilon_B = \upsilon_A - \upsilon_C$$

$$\upsilon_B = \frac{dc_B}{dt} = k_1 c_A - k_2 c_B$$
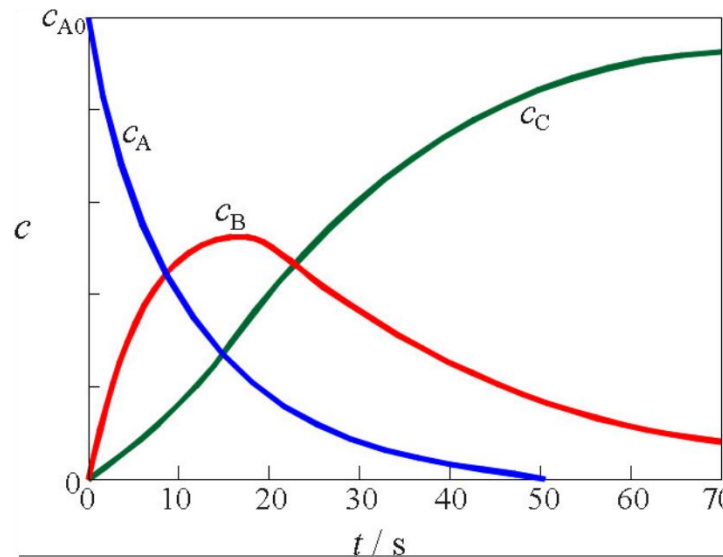
$$c_A = c_{A0} e^{-k_1 t}$$

$$c_B = c_{A0} \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

$$c_C = c_{A0}\left(1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1}\right)$$

$$c_A + c_B + c_C = c_{A0}$$

An appearance of a **maximum** of the concentration of the intermediate B

Consecutive reactions

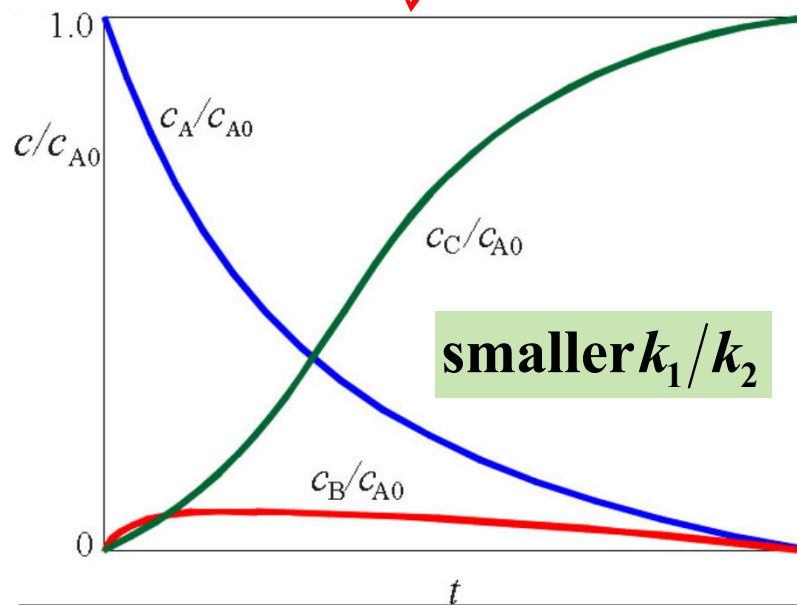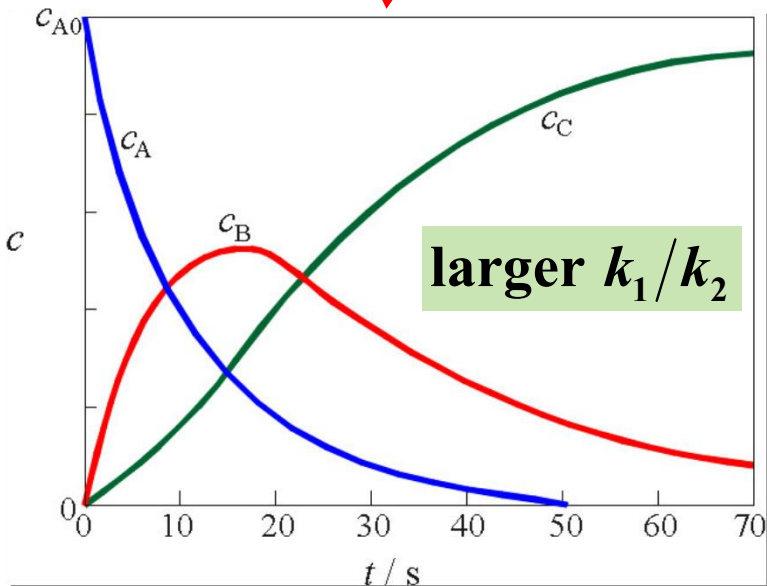$$c_B = c_{A0} \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

At maximum $\quad \dfrac{dc_B}{dt} = c_{A0} k_1 \dfrac{k_2 e^{-k_2 t_{max}} - k_1 e^{-k_1 t_{max}}}{k_2 - k_1} = 0$

$$t_{max} = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1}$$

$$c_{B,max} = c_{A0} \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}$$

$$\frac{k_1}{k_2}$$

Stable intermediate

larger k_1/k_2

smaller k_1/k_2

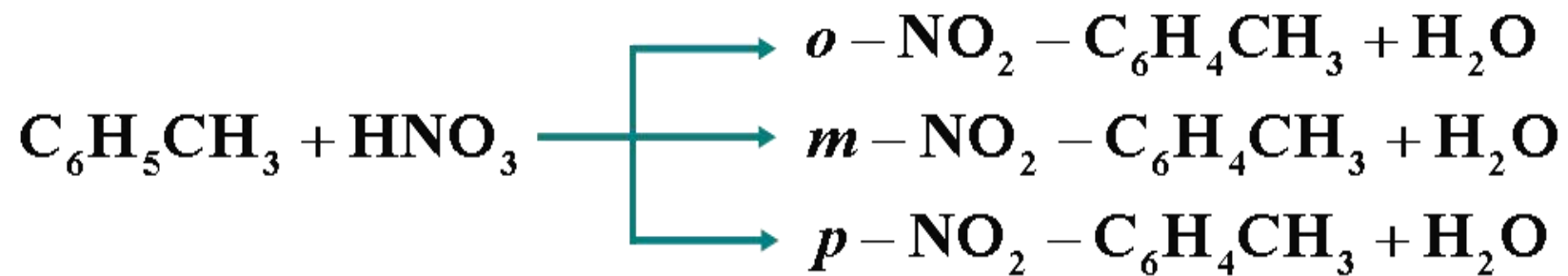**Unstable intermediate**

$$\frac{dc_B}{dt} \approx 0$$

Steady State

$$k_1 c_A = k_2 c_B$$

Parallel Reactions
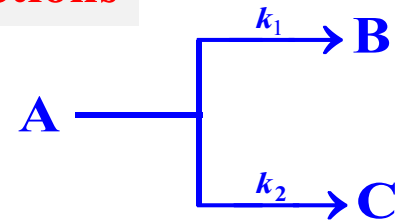
When the reactants participate in two or more reactions independently and simultaneously, the combination of these reactions is called a parallel reaction.

$$C_6H_5CH_3 + HNO_3 \longrightarrow \begin{cases} o - NO_2 - C_6H_4CH_3 + H_2O \\ m - NO_2 - C_6H_4CH_3 + H_2O \\ p - NO_2 - C_6H_4CH_3 + H_2O \end{cases}$$

Parallel Reactions

First Order Parallel Reactions

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

$$\upsilon_B = \frac{dc_B}{dt} = k_1 c_A$$

$$\upsilon_C = \frac{dc_C}{dt} = k_2 c_A$$

$$\upsilon_A = -\frac{dc_A}{dt} = \upsilon_B + \upsilon_C$$
$$= (k_1 + k_2)c_A$$

integrated

$$c_B = c_{A0}(1 - e^{-(k_1+k_2)t})\frac{k_1}{k_1 + k_2}$$

$$c_C = c_{A0}(1 - e^{-(k_1+k_2)t})\frac{k_2}{k_1 + k_2}$$

$$c_A = c_{A0}e^{-(k_1+k_2)t}$$

Plot $\ln c_A$ vs. t

$$F \xleftarrow{k_2} A+B \xrightarrow{k_1} E$$

$$\upsilon_E = k_1 c_A^{\alpha} c_B^{\beta}$$
$$\upsilon_F = k_2 c_A^{\alpha} c_B^{\beta}$$

$$\frac{c_E}{c_F} = \frac{k_1}{k_2}$$

Extension

$$\frac{c_B}{c_C} = \frac{k_1}{k_2}$$

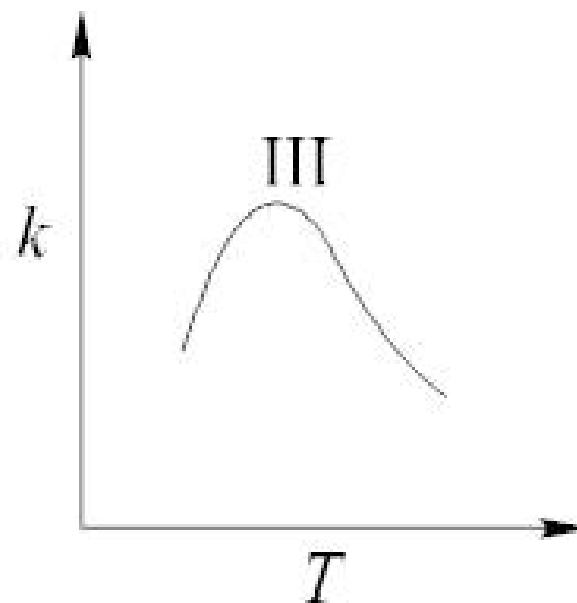$$Slope = k_1 + k_2$$

$$\frac{k_1}{k_2}$$

Effect of Temperature on Reaction Rates
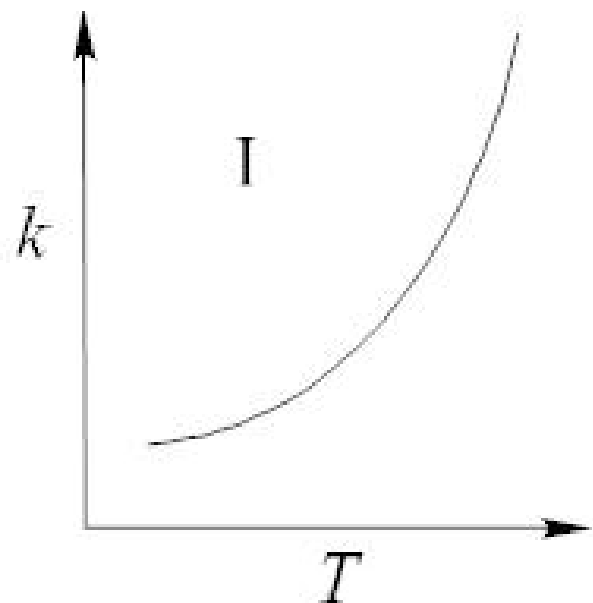
Common reactions
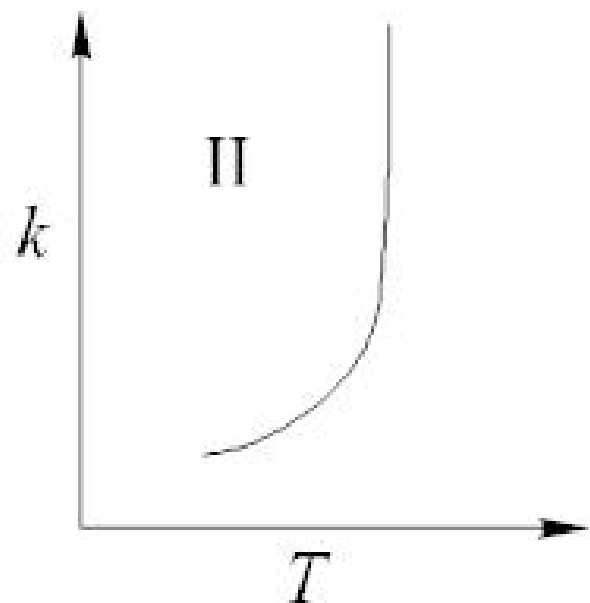
Explosion reactions

Enzyme reactions
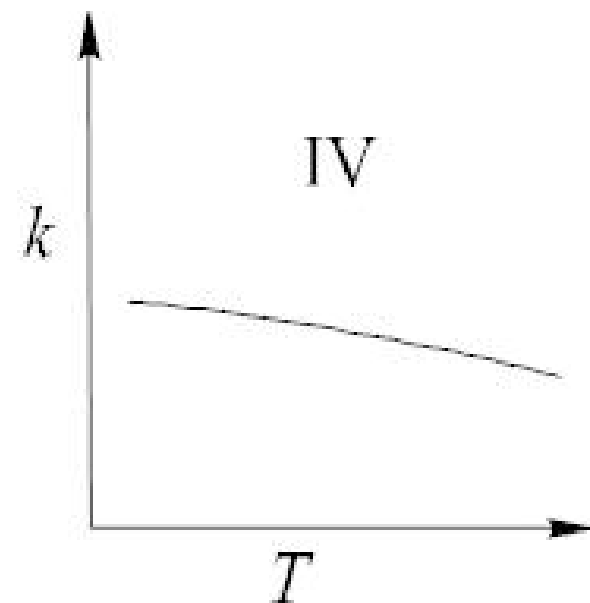
Other reactions

Exponential *T*-dependence

$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$
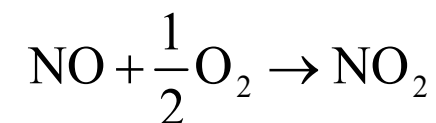
Arduous process of understanding the influence of T

☑ **Ostwald**

Temperature dependence is one of the darkest chapters in chemical mechanics.

—— 《Kinetics》, 1904, Mellor

☑ **van't Hoff**

It is so far impossible to choose between the above equations.

—— 《Physical Chemistry》, 1898

| Differential Form	Integrated Form	Expression for k	Supported by
$\dfrac{d \ln k}{dT} = \dfrac{B + CT + DT^2}{T^2}$	$\ln k = A' - \dfrac{B}{T} + C \ln T + DT$	$k = AT^C e^{-(B - DT^2)/T}$	van't Hoff, 1898; Bodenstein, 1899
$\dfrac{d \ln k}{dT} = \dfrac{B + CT}{T^2}$	$\ln k = A' - \dfrac{B}{T} + C \ln T$	$k = AT^C e^{-B/T}$	Kooij, 1893; Trautz, 1909
$\dfrac{d \ln k}{dT} = \dfrac{B + DT^2}{T^2}$	$\ln k = A' - \dfrac{B}{T} + DT$	$k = A e^{-(B - DT^2)T}$	Schwab, 1883; van't Hoff, 1884; Spohr, 1888; van't Hoff and Reicher, 1889; Buchböck, 1897; Wegscheider, 1899
$\dfrac{d \ln k}{dT} = \dfrac{CT + DT^2}{T^2}$	$\ln k = A' + C \ln T + DT$	$k = AT^C e^{DT}$	. . .
$\dfrac{d \ln k}{dT} = \dfrac{B}{T^2}$	$\ln k = A' - \dfrac{B}{T}$	$k = A e^{-B/T}$	van't Hoff, 1884; Arrhenius, 1889; Kooij, 1893
$\dfrac{d \ln k}{dT} = \dfrac{C}{T}$	$\ln k = A' + C \ln T$	$k = AT^C$	Harcourt and Esson, 1895; Veley, 1908; Harcourt and Esson, 1912
$\dfrac{d \ln k}{dt} = D$	$\ln k = A' + DT$	$k = A e^{DT}$	Berthelot, 1862; Hood, 1885; Spring, 1887; Veley, 1889; Hecht and Conrad, 1889; Pendelbury and Seward, 1889; Tammann, 1897; Remsen and Reid, 1899; Bugarszky, 1904; Perman and Greaves, 1908

Explanation from Arrhenius——Activated molecules

Arrhenius

Only activated molecules participate in the reaction

Activated molecules
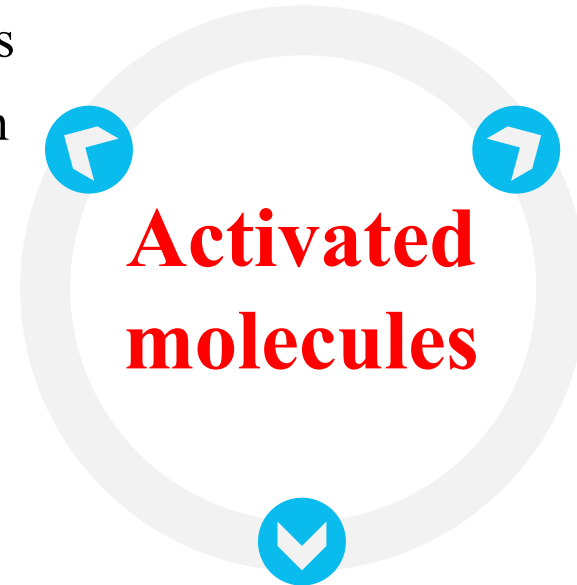
The number of activated molecules increase with T

An equilibrium exists between the activated molecules and those ordinary molecules

1903 Nobel Prize

"Ionization theory"——Success belongs to the persevering!

Explanation from Arrhenius——Activation Energy

Reaction

$$A \rightarrow P$$

$$A \rightleftharpoons A^*$$

Rapid Equilibrium $\qquad K_c = \dfrac{c_A^*}{c_A}$

$$A^* \rightarrow P$$
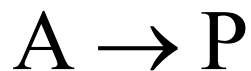
Rate-control step   (Irrelevant with T)

$$v = k'c_A^* = k'K_c c_A = kc_A$$

$$\frac{d\ln k}{dT} = \frac{d\ln K_c}{dT} = \frac{\Delta U_m^{\ominus}}{RT^2}$$

$$E_a = RT^2 \frac{d\ln k}{dT}$$

☑ Elementary Reaction——E_a refers to the difference between the average energy of 1mol activated molecules and 1mol reactant molecules.

☑ Complex reaction——*No physical meaning* Apparent activation energy

Arrhenius Equation

$$E_a = RT^2 \frac{d\ln k}{dT}$$

➡ $$k = Ae^{-E_a/(RT)}$$

A ——— **Frequency factor**

$e^{-Ea/(RT)}$ ——— **Boltzmann factor**

E_a is constant →

$$\ln\{k\} = -\frac{E_a}{RT} + \ln\{A\}$$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

反　　　应	$E_a /(kJ \cdot mol^{-1})$
$2HI \rightarrow H_2 + I_2$	183
$H_2 + I_2 \rightarrow 2HI$	167
$2NH_3 \rightarrow N_2 + 3H_2$	330(近似值)
$2NOCl \rightarrow 2NO + Cl_2$	98.7
$2NO_2 \rightarrow 2NO + O_2$	112
$2H_2O_2 \rightarrow 2H_2O + O_2$	75.3
$CH_3CHO \rightarrow CH_4 + CO$	190
$H_2 + C_2H_4 \rightarrow C_2H_6$	180
$C_2H_5OC_2H_5 \rightarrow C_2H_6 + CO + CH_4$	224
$Cl + NOCl \rightarrow NO + Cl_2$	4.2
$H_2 + Cl_2 \rightarrow 2HCl(光化反应)$	25
$2N_2O \rightarrow 2N_2 + O_2$	245
$CH_2I \cdot COO^- + OH^- \rightarrow CH_2OHCOO^- + I^-$	93.7
$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$	89.5
$CH_3Br + I^- \rightarrow CH_3I + Br^-$	76.1
$CH_3I + OH^- \rightarrow CH_3OH + I^-$	92.9
$C_6H_5N(CH_3)_2 + CH_3I \rightarrow C_6H_5N(CH_3)_3I$	49

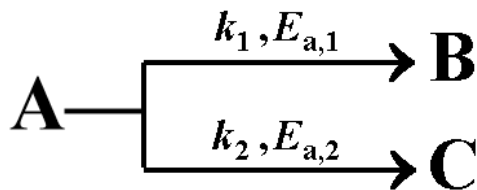**40 ~ 400kJmol^{-1}**

60 ~ 250 kJmol^{-1}

Arrhenius Equation

For a certain reaction, $E_a = 100$ kJ·mol^{-1} try to estimate

    (*a*) *T* increases from 300K to 310K; (*b*) *T* increases from 400K to 410K, the increase times of *k*?

If $E_a = 150$ kJ·mol^{-1}, what about the results?

What's your conclusions from the calcualtions?

$$A \xrightarrow{\ k_1, E_{a,1}\ } B$$
$$A \xrightarrow{\ k_2, E_{a,2}\ } C$$

$$A \xrightarrow{\ k_1, E_{a,1}\ } B \xrightarrow{\ k_2, E_{a,2}\ } C$$

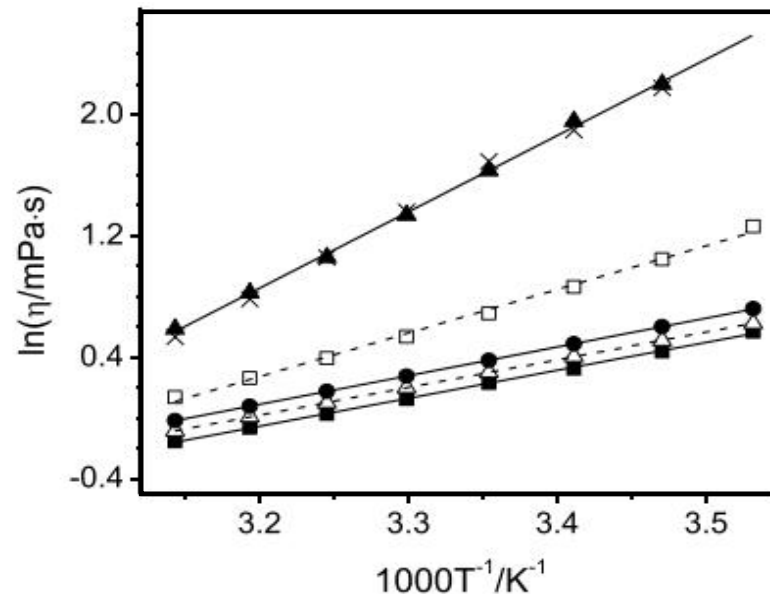**If we want to increase the concentration of B in the final products, how to control the temperature?**

Extension of Arrhenius Equation

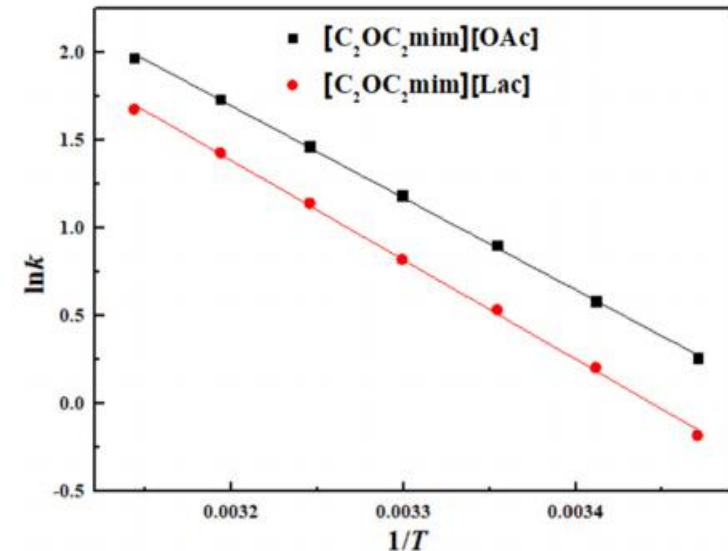☑ Consider the impact of relative humidity (RH)

$$k = Ae^{(-E_a/(RT)+B \times RH)}$$

AAPS PharmSciTech, 2011, 12, 932-937

☑ Calculation of physical properties

J. Phys. Chem. B, 2020, 124, 9115-9125

J. Mol. Liqs., 2022, 351, 118621