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Rate Law :→ Inst. Rate is directly proportional to the product of active masses of reactant raised to the the power some number which are determined experimently.

$$aA + bB \longrightarrow cC$$

$$\text{rate} \propto (a_A)^p (a_B)^q$$

p = order wrt A
q = " " B
$p+q$ = order of reaction

⇒ order may be +ive, -ive, zero or fractional

⇒ for elementry rxn order = stoichiometric coeff

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$$\text{rate} \propto (a_A)^p (a_B)^q$$

$a_A = \gamma [A]$

γ ↑ activity coefficient

active mass can be replaced by

1.) for gases = either by molar conc or by partial pressure

2) for solute = by molar conc only

3) for solid / pure liq / solvent = active mass is constant (independent of amount) and is merged with proportionality constant

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$aA(g) + bB(g) \longrightarrow$ Product

$\text{rate} \propto [A]^p [B]^q$

$\text{rate} \propto P_A^p \cdot P_B^q$

$C(s) + O_2(g) \rightarrow CO_2(g)$

$\text{rate} \propto (a_C)^p (a_{O_2})^q$

$(a_C)^p$ ↑ const

$\text{rate} \propto (a_{O_2})^q$

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$$a\,A + b\,B \longrightarrow c\,C$$

for a given reaction rate constant depends only on temperature

$$\text{rate} \propto [A]^p [B]^q$$

$$\left(-\frac{d[A]}{dt}\right) = k_A [A]^p \cancel{[B]^q}$$

$$-\frac{d[B]}{dt} = k_B [A]^p [B]^q$$

$$\frac{1}{a}\left(-\frac{d[A]}{dt}\right) = k_r [A]^p [B]^q$$

$$\frac{1}{b}\left(-\frac{d[B]}{dt}\right) = k_r [A]^p [B]^q$$

rate constant

$$k_A = a k_r \qquad k_B = b k_r$$

$$\left(\frac{k_A}{a} = \frac{k_B}{b} = k_r = \frac{k_C}{C}\right)$$

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Integrated rate law

① Zero order Rxn

$$a\,A \longrightarrow \text{Product}$$

$$-\frac{d[A]}{dt} = k\,[A]^0 = k$$

$$\int_{[A]_0}^{[A]_t} d[A] = -k\int_0^t dt$$

$$[A]_t - [A]_0 = -kt$$

$$\boxed{[A]_t = [A]_0 - kt}$$

$[A]_0 = a$

$[A]_t = [A] = a - x$

$$\boxed{x = [A]_0 - [A]_t = kt}$$

$$a\,A \longrightarrow \text{Product}$$

a

$a - x$

$$-\frac{d[A]}{dt} = k[A]^0$$

$$-\frac{d(a-x)}{dt} = k(a-x)^0 = k$$

$$\frac{dx}{dt} = k$$

$$\int_0^x dx = k\int_0^t dt$$

$$\boxed{x = kt}$$

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Characteristics of Zero order Rxn :→

① Unit of 'k'

$$\left(\frac{-d[A]}{dt}\right) = k[A]^n$$

$$(\text{mol/lit}) \times \text{time}^{-1} = \text{Unit of } k \times (\text{mol/lit})^n$$

$$(\text{mol/lit})^{1-n} \times \text{time}^{-1} = \text{Unit of } k$$

② Completion time

$$[A]_t = 0$$

$$[A]_t = [A]_0 - kt = 0$$

$$t = \frac{[A]_0}{k}$$

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Kinetics

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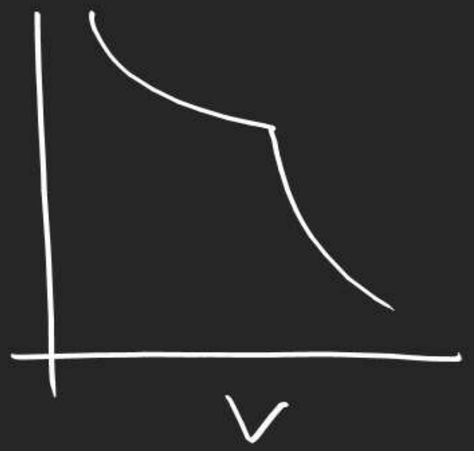
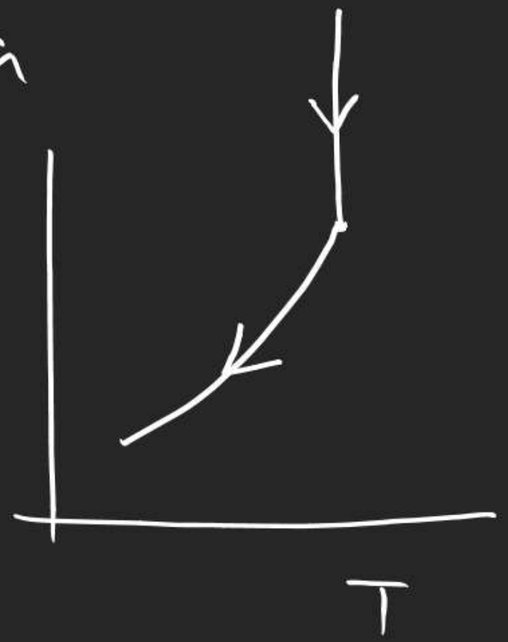
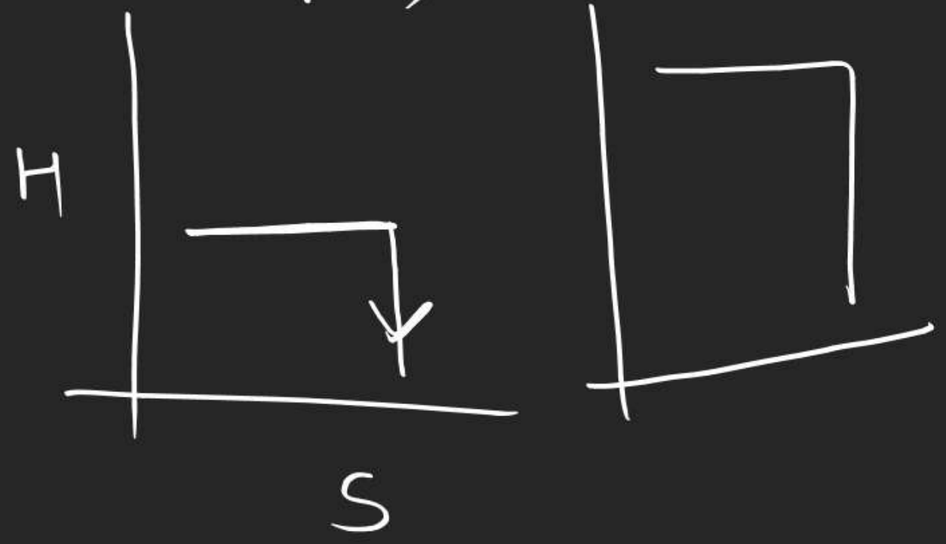
② Iso



Ⓐ Adia



$H = f(T)$



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$$X(s) \rightarrow Y(s) + Z(g)$$

$$K_p = P_Z$$

$$P^\circ = 1\ \text{bar}$$

$$\ln K = \ln P_Z = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right)$$

$$\ln P_Z = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{10^4 \times R} \times \frac{10^4}{T}$$

$$-3 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R \times 10^4} \times 10$$

$$\text{slope} = -\frac{4}{2} = -2$$

$$-\frac{\Delta H^\circ}{10^4 \times R} = -2$$

$$\underline{\Delta H^\circ} = 2R \times 10^4$$

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⑤ [A] < S

[P] > S

$K = \frac{[P]}{[A]} > 1$

$K > 1$

$\Delta G^\circ = -RT \ln K$

$\Delta G^\circ < 0$

$T \uparrow \; K_{eq} \downarrow$ exothermic

$\Delta H^\circ < 0$

$$\frac{\ln k_{T_1}}{\ln k_{T_2}} > \frac{T_2}{T_1}$$

$RT_1 \ln k_{T_1} > RT_2 \ln k_{T_2}$

$-RT \ln k_{T_1} < -RT_2 \ln k_{T_2}$

$\Delta G^\circ_{T_1} < \Delta G^\circ_{T_2}$

$\cancel{\Delta H^\circ} - T_1 \Delta S^\circ < \cancel{\Delta H^\circ} - T_2 \Delta S^\circ$

$(T_2 - T_1)\,\Delta S^\circ < 0$

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exo $T \uparrow$ $K_{eq} \downarrow$

endo $T \uparrow$ $K_{eq} \uparrow$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$