Focus 17: Chemical Kinetics

The rates of chemical reactions

Integrated rate laws

Reactions approaching equilibrium

The Arrhenius equation

Reaction mechanisms

Photochemistry

Integrated Rate Laws

A rate law is a differential equation, and solving it gives the integrated form

 $A \rightarrow P$

 $A \rightarrow P$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}$$

 $A \rightarrow P$

 $\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}$

 $[\mathbf{A}] - [\mathbf{A}]_0 = -k_{\rm r}t$

$$A \rightarrow P$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}$$

$$[\mathbf{A}] - [\mathbf{A}]_0 = -k_{\rm r}t$$

$$[\mathbf{A}] = [\mathbf{A}]_0 - k_{\mathrm{r}} t$$





$$A \rightarrow P$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}]$$

$$A \rightarrow P$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}]$$

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k_{\mathrm{r}}\mathrm{d}t$$

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

$$A \rightarrow P$$

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$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k_{\mathrm{r}}\mathrm{d}t$$

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

LHS =
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]}$$

-

 $A \rightarrow P$

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

LHS =
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \ln [A] - \ln [A]_0$$

 $A \rightarrow P$

LHS =
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \ln [A] - \ln [A]_0 = \ln \frac{[A]}{[A]_0}$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}]$$

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k_{\mathrm{r}}\mathrm{d}t$$

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

 $A \rightarrow P$

 $\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}]$

LHS =
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \ln [A] - \ln [A]_0 = \ln \frac{[A]}{[A]_0}$$

$$\ln \frac{[A]}{[A]_0} = -k_r t, \quad [A] = [A]_0 e^{-k_r t}$$

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k_{\mathrm{r}}\mathrm{d}t$$

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

$A \rightarrow P$

remaining concentration after time t

remaining concentration after time t

$$A \rightarrow P$$
$$[A] = [A]_0 - [P] \qquad [P] = [A]_0 - [A]$$

$$A \to P$$

 $\ln \frac{[A]}{[A]_0} = -k_r t$ [A] = [A]_0 - [P] [P] = [A]_0 - [A]

$$A \rightarrow P$$

$$\ln \frac{[A]}{[A]_0} = -k_r t \qquad [A] = [A]_0 - [P] \qquad [P] = [A]_0 - [A]$$



$$A \rightarrow P$$

$$\ln \frac{[A]}{[A]_0} = -k_r t \qquad [A] = [A]_0 - [P] \qquad [P] = [A]_0 - [A]$$

$$\ln \frac{[A]_0 - [P]}{[A]_0} = -k_r t_r$$

$$[P] = [A]_0 (1 - e^{-k_r t})$$

$$A \rightarrow P$$

 $\ln \frac{[A]}{[A]_0} = -k_r t$ [A] = [A]_0 - [P] [P] = [A]_0 - [A]

- Colores

$$\ln \frac{[A]_0 - [P]}{[A]_0} = -k_r t_1$$

$$[P] = [A]_0 (1 - e^{-k_r t})$$

$$A \to P$$

 $\ln \frac{[A]}{[A]_0} = -k_r t$ [A] = [A]_0 - [P] [P] = [A]_0 - [A]

$$\ln \frac{[A]_0 - [P]}{[A]_0} = -k_r t_1$$

$$[P] = [A]_0 (1 - e^{-k_r t})$$

$$-k_{\rm r}t = \ln \frac{[{\rm A}]}{[{\rm A}]_0}$$
$$k_{\rm r}t_{1/2} = -\ln \frac{\frac{1}{2}[{\rm A}]_0}{[{\rm A}]_0}$$

$$A \rightarrow P$$

 $\ln \frac{[A]}{[A]_0} = -k_r t$ [A] = [A]_0 - [P] [P] = [A]_0 - [A]

$$\ln \frac{[A]_0 - [P]}{[A]_0} = -k_r t_1$$

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$$-k_{\rm r}t = \ln\frac{[{\rm A}]}{[{\rm A}]_0}$$
$$k_{\rm r}t_{1/2} = -\ln\frac{\frac{1}{2}[{\rm A}]_0}{[{\rm A}]_0} = -\ln\frac{1}{2} = \ln 2$$

$$A \to P$$

$$\ln \frac{[A]}{[A]_0} = -k_r t \qquad [A] = [A]_0 - [P] \qquad [P] = [A]_0 - [A]$$

$$\ln \frac{[A]_0 - [P]}{[A]_0} = -k_r t_1$$

$$[P] = [A]_0 (1 - e^{-k_r t})$$

$$-k_{\rm r}t = \ln\frac{[{\rm A}]}{[{\rm A}]_0}$$
$$k_{\rm r}t_{1/2} = -\ln\frac{\frac{1}{2}[{\rm A}]_0}{[{\rm A}]_0} = -\ln\frac{1}{2} = \ln 2$$

$$t_{1/2} = \frac{\ln 2}{k_{\rm r}}$$

$$A \to P$$

$$\ln \frac{[A]}{[A]_0} = -k_r t \qquad [A] = [A]_0 - [P] \qquad [P] = [A]_0 - [A]$$

$$\ln \frac{[A]_0 - [P]}{[A]_0} = -k_r t_1$$

$$[P] = [A]_0 (1 - e^{-k_r t})$$

half-life, $t_{1/2}$, of a substance, the time taken for the concentration of a reactant to fall to half its initial value

$$-k_{\rm r}t = \ln\frac{[{\rm A}]}{[{\rm A}]_0}$$
$$k_{\rm r}t_{1/2} = -\ln\frac{\frac{1}{2}[{\rm A}]_0}{[{\rm A}]_0} = -\ln\frac{1}{2} = \ln 2$$



Independent of initial concentration!

Reaction	Phase	<i>θ</i> /°C	$k_{\rm r}/{\rm s}^{-1}$	<i>t</i> _{1/2}
$2 N_2 O_5 \rightarrow 4 NO_2 + O_2$	g	25	3.38×10^{-5}	5.70 h
	$Br_2(l)$	25	$4.27\times10^{^{-5}}$	4.51 h
$C_2H_6 \rightarrow 2 CH_3$	g	700	5.36×10^{-4}	21.6 min

 $A \rightarrow P$



 $A \rightarrow P$



$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2} = -k_{\mathrm{r}}\mathrm{d}t$$

 $-\int_{[A]_{0}}^{[A]} \frac{d[A]}{[A]^{2}} = k_{r} \int_{0}^{t} dt$

 $A \rightarrow P$



$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2} = -k_{\mathrm{r}}\mathrm{d}t$$



Concentration of A at any time after the start of the reaction



Second-order reaction half-life

For
$$A \rightarrow P$$

$$t_{1/2} = \frac{\ln 2}{k_{\rm r}}$$

Second-order reaction half-life

For
$$A \rightarrow P$$



$$t_{1/2} = \frac{1}{k_{\rm r}[{\rm A}]_0}$$

Second-order reaction half-life

For
$$A \rightarrow P$$



Only first-order reactions have a constant half-life regardless of how much reactant you start with. For higher-order reactions, the half-life shortens or lengthens depending on $[A]_0$.

Half-life

Reaction Order	Dependence of $t_{1/2}$ on $[A]_0$	Behavior of Half-life
Zeroth	$t_{1/2} \propto [A]_0$	Increases with increasing $[A]_0$
First	$t_{1/2} = { m constant}$	Independent of $[A]_0$
Second or higher (n \ge 2)	$t_{1/2} \propto rac{1}{[A]_0^{n-1}}$	Decreases with increasing $[A]_0$

Only first-order reactions have a constant half-life regardless of how much reactant you start with. For higher-order reactions, the half-life shortens or lengthens depending on $[A]_0$.

$A + B \rightarrow P$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]$$

A reaction that is first order in each of the two reactants A and B

 $A + B \rightarrow P$

$$[A]_0 - x \quad [B]_0 - x$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]$$

 $A + B \rightarrow P$

$$[A]_0 - x \quad [B]_0 - x$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]$$

$$\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)k_r t$$

Order	Reaction	Rate law and its integrated form*	t _{1/2}
0	$\mathbf{A} \to \mathbf{P}$	$v = k_r$	$[A]_0/2k_r$
		$k_{\rm r}t = [P] \text{ for } 0 \le [P] \le [A]_0$	
		$[A] = [A]_0 - k_r t \text{ for } 0 \le [A] \le [A]_0$	
1	$\mathbf{A} \to \mathbf{P}$	$\nu = k_r[A]$	$(\ln 2)/k_r$
		$k_r t = \ln \frac{[A]_0}{[A]}, [A] = [A]_0 e^{-k_r t}, [P] = [A]_0 (1 - e^{-k_r t})$	
2	$\mathbf{A} \to \mathbf{P}$	$\nu = k_{\rm r}[{\rm A}]^2$	$1/k_{\rm r}[{\rm A}]_0$
		$k_{r}t = \frac{[P]}{[A]_{0}([A]_{0} - [P])}, [A] = \frac{[A]_{0}}{1 + k_{r}t[A]_{0}}, [P] = \frac{k_{r}t[A]_{0}^{2}}{1 + [A]_{0}k_{r}t}$	
	$A + B \rightarrow P$	$v = k_{\rm r}[{\rm A}][{\rm B}]$	
		$k_{\rm r}t = \frac{1}{[{\rm B}]_0 - [{\rm A}]_0} \ln \frac{[{\rm A}]_0 ([{\rm B}]_0 - [{\rm P}])}{([{\rm A}]_0 - [{\rm P}])[{\rm B}]_0},$	
		$\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)k_r t, [P] = \frac{[A]_0[B]_0(1 - e^{([B]_0 - [A]_0)k_r t})}{[A]_0 - [B]_0 e^{([B]_0 - [A]_0)k_r t}}$	
	$A + 2 B \rightarrow P$	$v = k_r[A][B]$	
		$k_{r}t = \frac{1}{[B]_{0} - 2[A]_{0}} \ln \frac{[A]_{0}([B]_{0} - 2[P])}{([A]_{0} - [P])[B]_{0}}, [P] = \frac{[A]_{0}[B]_{0}(1 - e^{([B]_{0} - 2[A]_{0})k_{r}t})}{2[A]_{0} - [B]_{0}e^{([B]_{0} - 2[A]_{0})k_{r}t}}$	
3	$A + 2B \rightarrow P$	$\nu = k_{\rm r}[{\rm A}][{\rm B}]^2$	
		$k_{\rm r}t = \frac{2[{\rm P}]}{(2[{\rm A}]_0 - [{\rm B}]_0)([{\rm B}]_0 - 2[{\rm P}])[{\rm B}]_0} + \frac{1}{(2[{\rm A}]_0 - [{\rm B}]_0)^2} \ln \frac{[{\rm A}]_0([{\rm B}]_0 - 2[{\rm P}])}{([{\rm A}]_0 - [{\rm P}])[{\rm B}]_0}$	
		[P] must be determined graphically or numerically	
$n \ge 2$	$\mathbf{A} \to \mathbf{P}$	$\nu = k_r[\mathbf{A}]^n$	$\frac{2^{n-1}-1}{(n-1)k [A]^{n-1}}$
		$k_{r}t = \frac{1}{n-1} \left\{ \frac{1}{([A]_{0} - [P])^{n-1}} - \frac{1}{[A]_{0}^{n-1}} \right\}$	/y.,ry0
		No simple general solution for [P] for $n > 3$	



Consider a second-order reaction of the type $A + B \rightarrow P$ carried out in a solution. Initially, the concentrations of reactants are $[A]_0 = 0.075 \text{ mol dm}^{-3}$ and $[B]_0 = 0.050 \text{ mol dm}^{-3}$. After 1.0 h the concentration of B has fallen to $[B] = 0.020 \text{ mol dm}^{-3}$.

Find the second-order rate constant.

$$\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)k_r t$$
Example

Consider a second-order reaction of the type $A + B \rightarrow P$ carried out in a solution. Initially, the concentrations of reactants are $[A]_0 = 0.075 \text{ mol dm}^{-3}$ and $[B]_0 = 0.050 \text{ mol dm}^{-3}$. After 1.0 h the concentration of B has fallen to $[B] = 0.020 \text{ mol dm}^{-3}$. Because the change in the concentration of B is the same as that of A (and equal to *x*), it follows that during this time interval

 $x = (0.050 - 0.020) \text{ mol dm}^{-3} = 0.030 \text{ mol dm}^{-3}$

$$\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)k_r t$$

Example

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$$x = (0.050 - 0.020) \text{ mol dm}^{-3} = 0.030 \text{ mol dm}^{-3}$$

 $[A] = [A]_0 - x = (0.075 - 0.030) \text{ mol } dm^{-3} = 0.045 \text{ mol } dm^{-3}$

$$\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)k_r t$$

Example

Consider a second-order reaction of the type $A + B \rightarrow P$ carried out in a solution. Initially, the concentrations of reactants are $[A]_0 = 0.075 \text{ mol dm}^{-3}$ and $[B]_0 = 0.050 \text{ mol dm}^{-3}$. After 1.0 h the concentration of B has fallen to $[B] = 0.020 \text{ mol dm}^{-3}$. Because the change in the concentration of B is the same as that of A (and equal to *x*), it follows that during this time interval

$$x = (0.050 - 0.020) \text{ mol dm}^{-3} = 0.030 \text{ mol dm}^{-3}$$

 $[A] = [A]_0 - x = (0.075 - 0.030) \text{ mol } dm^{-3} = 0.045 \text{ mol } dm^{-3}$

$$k_{\rm r} = \frac{1}{((0.050 - 0.075) \,\mathrm{mol} \,\mathrm{dm}^{-3}) \times (3600 \,\mathrm{s})} \ln \frac{0.020/0.050}{0.045/0.075}$$
$$= 4.5 \times 10^{-3} \,\mathrm{dm}^{3} \,\mathrm{mol}^{-1} \,\mathrm{s}^{-1}$$

$$\ln \frac{[B]/[B]_0}{[A]/[A]_0} = ([B]_0 - [A]_0)k_r t$$

Focus 17: Chemical Kinetics

- The rates of chemical reactions
- Integrated rate laws
- **Reactions approaching equilibrium**
- The Arrhenius equation
- Reaction mechanisms
- Photochemistry

$$A \xrightarrow{k_r} B \quad \frac{d[A]}{dt} = -k_r[A]$$

$$A \xrightarrow{k_{\rm r}} B \quad \frac{d[A]}{dt} = -k_{\rm r}[A]$$
$$B \xrightarrow{k'_{\rm r}} A \quad \frac{d[A]}{dt} = k'_{\rm r}[B]$$

$$A \xrightarrow{k_{r}} B \qquad \frac{d[A]}{dt} = -k_{r}[A]$$
$$B \xrightarrow{k'_{r}} A \qquad \frac{d[A]}{dt} = k'_{r}[B]$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r}}[\mathrm{A}] + k_{\mathrm{r}}'[\mathrm{B}]$$

$$A \xrightarrow{k_{r}} B \quad \frac{d[A]}{dt} = -k_{r}[A]$$
$$B \xrightarrow{k'_{r}|} A \quad \frac{d[A]}{dt} = k'_{r}[B]$$

$$\frac{d[A]}{dt} = -k_{r}[A] + k'_{r}[B]$$
$$\frac{d[A]}{dt} = -k_{r}[A] + k'_{r}([A]_{0} - [A])$$

at all times $[A] + [B] = [A]_0$.

$$A \xrightarrow{k_{r}} B \quad \frac{d[A]}{dt} = -k_{r}[A]$$
$$B \xrightarrow{k'_{r}|} A \quad \frac{d[A]}{dt} = k'_{r}[B]$$

$$\frac{d[A]}{dt} = -k_r[A] + k'_r[B]$$

$$\frac{d[A]}{dt} = -k_r[A] + k'_r([A]_0 - [A]) = -(k_r + k'_r)[A] + k'_r[A]_0$$

at all times $[A] + [B] = [A]_0$.

$$A \xrightarrow{k_{r}} B \quad \frac{d[A]}{dt} = -k_{r}[A]$$
$$B \xrightarrow{k'_{r}|} A \quad \frac{d[A]}{dt} = k'_{r}[B]$$

$$\frac{d[A]}{dt} = -k_r[A] + k'_r[B]$$

$$\frac{d[A]}{dt} = -k_r[A] + k'_r([A]_0 - [A]) = -(k_r + k'_r)[A] + k'_r[A]_0$$

$$[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$$

at all times $[A] + [B] = [A]_0$.

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$$A \xrightarrow{k_{r}} B \quad \frac{d[A]}{dt} = -k_{r}[A]$$
$$B \xrightarrow{k'_{r}} A \quad \frac{d[A]}{dt} = k'_{r}[B]$$

 $\frac{d[A]}{dt} = -k_r[A] + k'_r[B]$ $\frac{d[A]}{dt} = -k_r[A] + k'_r([A]_0 - [A]) = -(k_r + k'_r)[A] + k'_r[A]_0$

$$[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$$

 $[B] = [A]_0 - [A]$

$$[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$$

 $[B] = [A]_0 - [A]$



As
$$t \to \infty$$
,

$$[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$$

$$[A]_{eq} = \frac{k'_{r}[A]_{0}}{k_{r} + k'_{r}}$$

 $[B] = [A]_0 - [A]$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r [A]_0}{k_r + k'_r}$$

$$[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$$

$$[A]_{eq} = \frac{k'_{r}[A]_{0}}{k_{r} + k'_{r}}$$

As $t \to \infty$,

$$[B] = [A]_0 - [A]$$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r [A]_0}{k_r + k'_r}$$

$$A \rightarrow B$$

K = a_B/a_A

 $[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$

As
$$t \to \infty$$
,
 $[A]_{eq} = \frac{k'_r[A]_0}{k_r + k'_r}$
 $K = a_B/a_A$

$$[B] = [A]_0 - [A]$$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r [A]_0}{k_r + k'_r}$$

$$= \frac{k_{\rm r}[A]_0}{k_{\rm r} + k_{\rm r}'} \qquad \qquad K = \frac{[B]_{\rm eq}}{[A]_{\rm eq}}$$

 $[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$

As
$$t \to \infty$$
,
 $[A]_{eq} = \frac{k'_r[A]_0}{k_r + k'_r}$
 $K = a_B/a_A$

$$[B] = [A]_0 - [A]$$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r [A]_0}{k_r + k'_r}$$

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_r}{k'_r}$$

 $[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$

As
$$t \to \infty$$
,

$$[A]_{eq} = \frac{k'_r[A]_0}{k_r + k'_r}$$

$$K = a_B / a_A$$

$$[P] = t$$

 $[B] = [A]_0 - [A] \qquad [B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r [A]_0}{k_r + k'_r} \qquad K = \frac{[D]_{eq}}{[A]_{eq}} = \frac{k_r}{k'_r}$

$$A \stackrel{k_r}{\rightleftharpoons}_{k'_r} B \qquad \quad K = rac{k_r}{k'_r} \quad ext{is valid only for simple elementary reversible reactions.}$$

$$[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0} \qquad [A]_{eq} = \frac{k'_{r}[A]_{0}}{k_{r} + k'_{r}} \qquad K = a_{B}/a_{A}$$
$$[B] = [A]_{0} - [A] \qquad [B]_{eq} = [A]_{0} - [A]_{eq} = \frac{k_{r}[A]_{0}}{k_{r} + k'_{r}} \qquad K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_{r}}{k'_{r}}$$

At equilibrium, the forward and reverse rates must be the same

 $[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$

 $[B] = [A]_0 - [A]$

As
$$t \to \infty$$
,

$$[A]_{eq} = \frac{k'_r[A]_0}{k_r + k'_r}$$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r[A]_0}{k_r + k'_r}$$

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_r}{k'_r}$$

At equilibrium, the forward and reverse rates must be the same

$$\frac{d[A]}{dt} = -k_{r}[A] + k'_{r}[B] = 0$$

 $[A] = \frac{k'_{r} + k_{r} e^{-(k_{r} + k'_{r})t}}{k_{r} + k'_{r}} [A]_{0}$

As
$$t \to \infty$$
,

$$[A]_{eq} = \frac{k'_r[A]_0}{k_r + k'_r}$$

$$K = a_B/a_A$$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k_r[A]_0}{k_r + k'_r}$$

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_r}{k'_r}$$

 $[B] = [A]_0 - [A]$

$$\frac{d[A]}{dt} = -k_{r}[A] + k'_{r}[B] = 0$$

 $k_{\rm r}[{\rm A}]_{\rm eq} = k_{\rm r}'[{\rm B}]_{\rm eq}$

$$A \xrightarrow{k_{r}} B$$
$$k'_{r}|$$
$$B \xrightarrow{} A$$

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Arrhenius equation

The Arrhenius equation suggests that the rate constant of a reaction increases exponentially with temperature

$$\ln k_{\rm r} = \ln A - \frac{E_{\rm a}}{RT}$$

Arrhenius equation

The Arrhenius equation suggests that the rate constant of a reaction increases exponentially with temperature

activation energy.



frequency factor

accounts for collision frequency and orientation



Reaction coordinate

The activation energy is the minimum energy reactants must have in order to form products.

Arrhenius equation



accounts for collision frequency and orientation

Arrhenius equation



Represents the probability that a molecular collision has enough energy to lead to a reaction

 ${
m Fraction} {
m of molecules with energy} \ \geq E_a \propto e^{-E_a/RT}$

accounts for collision frequency and orientation

Arrhenius equation



Arrhenius equation



A can depend on temperature, although it's often approximated as constant over small temperature ranges.

Arrhenius equation



$$k_{\rm r} = A {\rm e}^{-E_{\rm a}/RT}$$

Question For a reaction with an activation energy of 50 kI mol^{-1} . an increase in the temperature from $25 \,^{\circ}\text{C}$ to $37 \,^{\circ}\text{C}$

What is the change in the rate constant?

Question For a reaction with an activation energy of 50 kI mol^{-1} , an increase in the temperature from $25 \degree \text{C}$ to $37 \degree \text{C}$

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 $k_{\rm r,2} = 2.18k_{\rm r,1}$

Question Which statements are true?

- A high activation energy signifies that the rate constant depends strongly on temperature.
- If a reaction has zero activation energy, its rate is independent of temperature.
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Non-Arrhenius Chemical reactions



- Chemical reactions involving quantum effects
- Reactions with temperature-dependent activation energies
- Thermal degradation

The role of a catalyst

A substance that accelerates a reaction but undergoes no net chemical change

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Provides an alternative path!

Reaction coordinate

Focus 17: Chemical Kinetics

The rates of chemical reactions

Integrated rate laws

- Reactions approaching equilibrium
- The Arrhenius equation

Reaction mechanisms

Photochemistry