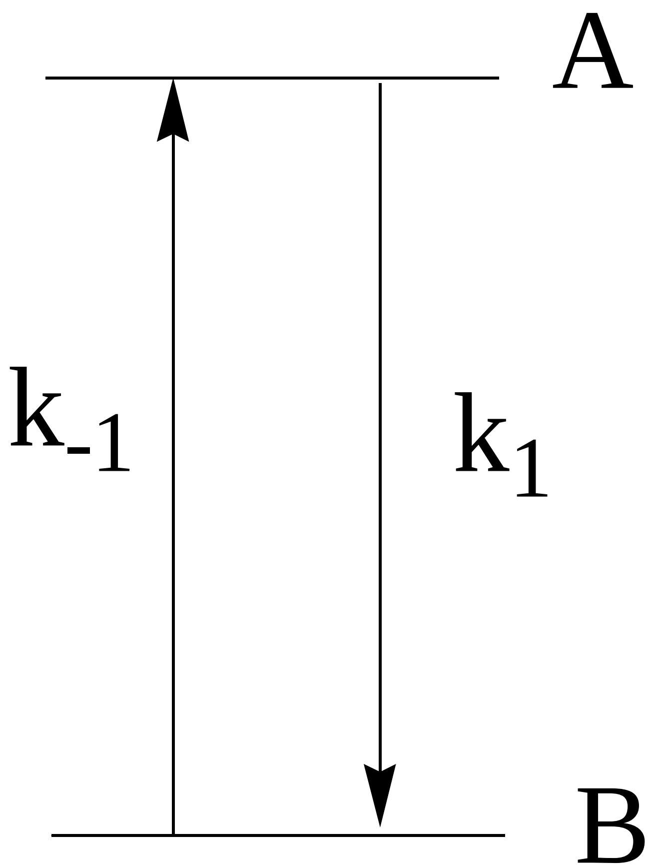
Approach to equilibrium



- A $\rightarrow$ B and B $\rightarrow$ A
- Rate equations are:
- $d[A]/dt = -k_1[A] + k_{-1}[B]$
- $d[B]/dt = k_1[A] - k_{-1}[B]$
- Simultaneous solutions of these equations leads to a rate constant of

  $k_1 + k_{-1}$.
- Equilibrium is approached

  as the sum of the forward

  and reverse rate constants.

Approach to equilibrium

Let x be the deviation from equilibrium

$x = [A] - [A]_{eq} = [B]_{eq} - [B]$

Approach to equilibrium

Let x be the deviation from equilibrium

$x = [A] – [A]_{eq} = [B]_{eq} – [B]$

then $[A] = [A]_{eq} + x$ and $[B] = [B]_{eq} – x$

Rate equations are:

$-d[A]/dt = k_1[A] - k_{-1}[B]$

Approach to equilibrium

Let x be the deviation from equilibrium

$x = [A] - [A]_{eq} = [B]_{eq} - [B]$

then $[A] = [A]_{eq} + x$ and $[B] = [B]_{eq} - x$

Rate equations are:

$-d([A]_{eq} + x)/dt = k_1([A]_{eq} + x) - k_{-1}([B]_{eq} - x)$

and

$-d[A]_{eq}/dt = k_1[A]_{eq} - k_{-1}[B]_{eq} = 0$

We can understand this because $[A]_{eq}$ is a constant. A second point is that

$$K = \frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}}$$

Approach to equilibrium

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then $[A] = [A]_{eq} + x$ and $[B] = [B]_{eq} – x$

Rate equations are:

$-d([A]_{eq} + x)/dt = k_1([A]_{eq} + x) - k_{-1}([B]_{eq} – x)$

and

$-d[A]_{eq}/dt = k_1[A]_{eq} - k_{-1}[B]_{eq} = 0$

Therefore,

$-dx/dt = (k_1 + k_{-1})x$

Approach to equilibrium

Let x be the deviation from equilibrium

$x = [A] – [A]_{eq} = [B]_{eq} – [B]$

then $[A] = [A]_{eq} + x$ and $[B] = [B]_{eq} – x$

Rate equations are:

$-d([A]_{eq} + x)/dt = k_1([A]_{eq} + x) - k_{-1}([B]_{eq} – x)$

and

$-d[A]_{eq}/dt = k_1[A]_{eq} - k_{-1}[B]_{eq} = 0$

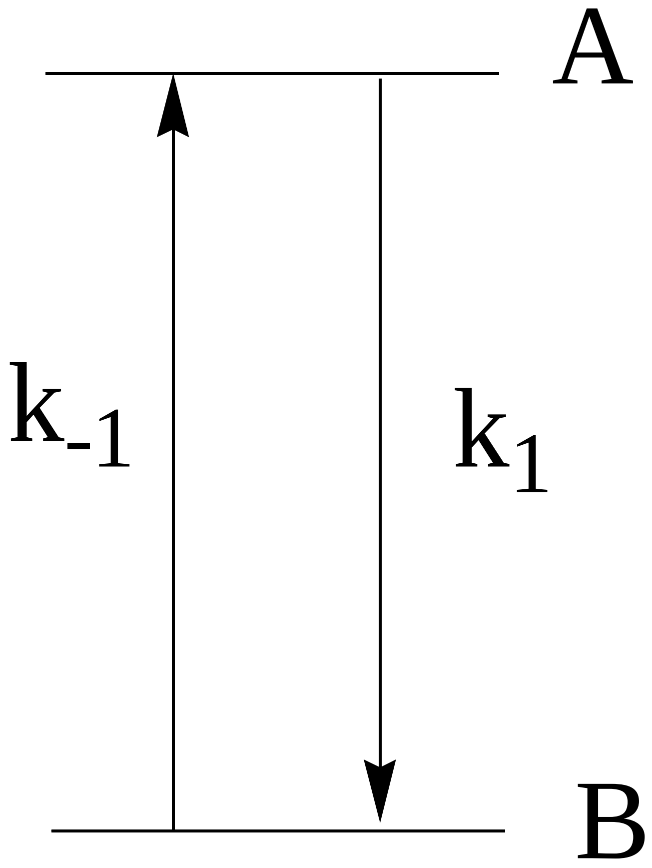
Therefore,

$-dx/dt = (k_1 + k_{-1})x$

$x(t) = x_0 \exp\{ - (k_1 + k_{-1})t \}$

NOTE: This is not intuitive. Return to equilibirum occurs at the sum of the forward and reverse rate constants.

Principle of microscopic reversibility



- A → B and B → A
- The equilibrium constant for such a process can be related for the forward and reverse rate constants.

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

- From before:

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