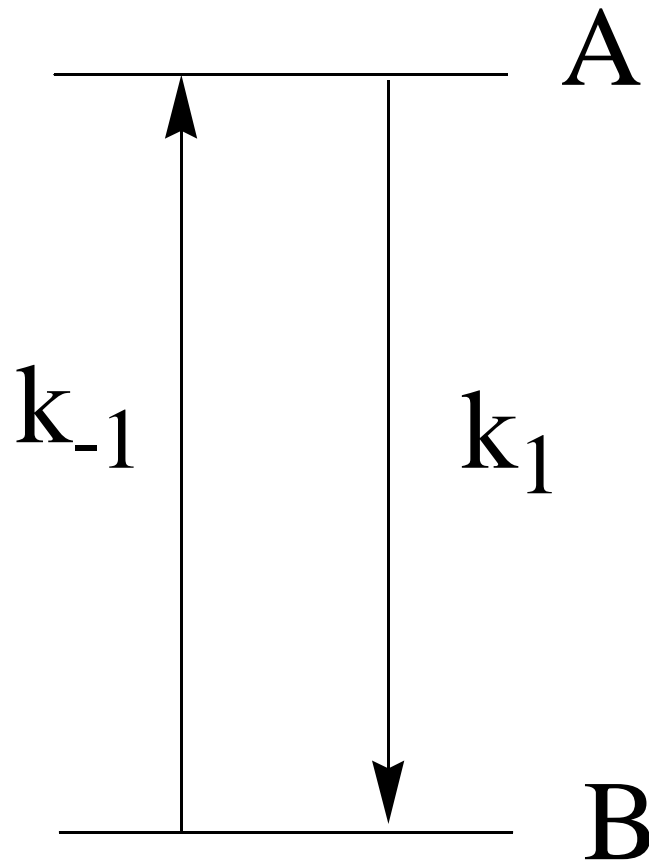


# *Approach to equilibrium*



- $A \rightarrow B$  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*

A decorative graphic consisting of a horizontal bar with a color gradient from dark purple on the left to bright yellow on the right, tapering into a rounded arrowhead pointing to the right.

Let  $x$  be the deviation from equilibrium

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

# *Approach to equilibrium*



Let  $x$  be the deviation from equilibrium

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

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

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*



Let  $x$  be the deviation from equilibrium

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

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

Rate equations are:

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

and

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

Therefore,

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

# *Approach to equilibrium*



Let  $x$  be the deviation from equilibrium

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

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

Rate equations are:

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

and

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

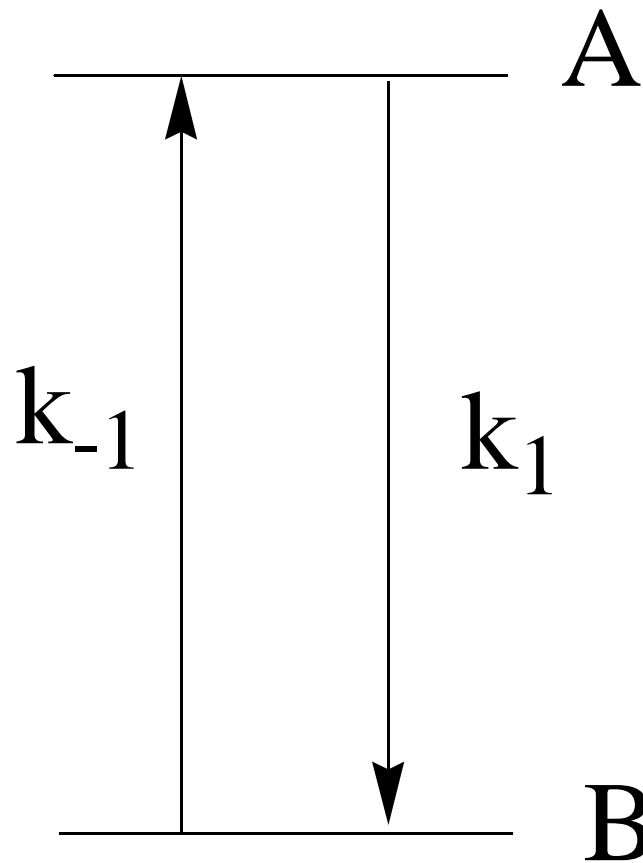
Therefore,

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

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

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

# *Principle of microscopic reversibility*



- $A \rightarrow B$  and  $B \rightarrow A$
- 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:

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