Rate versus temperature: $E_a$ and $A$

Putting it all together: First law, second law, equilibrium, and kinetics.

When $T$ is increased, the rate of every chemical reaction must...

- 1. increase
- 2. stay the same
- 3. decrease
- 4. More information needed

Rate constants depend on $T$ as $k = A \exp \left( \frac{-E_a}{RT} \right)$

The value of $k$ at $T = 0$ is...

- 1. 0
- 2. $A$
- 3. $E_a / (RT)$
- 4. $\infty$
Quiz: Rate constants depend on $T$ as $k = A \exp\left(-\frac{E_a}{RT}\right)$

The value of $k$ at $T = \infty$ is...

1. 0
2. $A$
3. $E_a / (RT)$
4. $\infty$

Rate versus temperature

Arrhenius relation: $k = A \exp[-E_a / (RT)]$

$E_a$ is activation energy

$A$ is frequency factor $A$

How could we use data for $k$ versus $T$ to get $E_a$ and $A$?

$$\ln(k) = (-\frac{E_a}{R}) \left(\frac{1}{T}\right) + \ln(A)$$

Sketch $\ln(k)$ versus $1/T$ for an arbitrary reaction.

$$\ln(k) = (-\frac{E_a}{R}) \left(\frac{1}{T}\right) + \ln(A)$$

Slope = $-E_a/R$

Intercept (at $T = \infty$) = $\ln(A)$
For $A \rightarrow B$, $k_{ar}$ is $0.003/\text{min}$ at $25 \degree C$ and $0.025/\text{min}$ at $35 \degree C$.

For $C \rightarrow D$, $k_{ar}$ is $0.003/\text{min}$ at $25 \degree C$ and $0.035/\text{min}$ at $35 \degree C$.

Compared to the activation energy of $A \rightarrow B$, the activation energy of $C \rightarrow D$ is ...

1. smaller
2. the same
3. larger
4. More information needed

Putting it all together:
First law, second law, equilibrium, and kinetics
First law, second law, equilibrium, and kinetics

Rate constant: \( \ln(k) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A) \), ...

So, at very high \( T \), \( \ln(k) \rightarrow \ln(A) \)

Equilibrium constant: \( \ln(K) = -\left(\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \), ...

so, at very high \( T \), \( \ln(K) \rightarrow \frac{\Delta S^\circ}{R} \)

What's the connection?

\[ \text{[TP]} \text{ What happens to } \ln(K) \text{ as } T \text{ increases to infinity?} \]

- 25% 1. \( \ln(K) = 0 \)
- 25% 2. \( \ln(K) = 1 \)
- 25% 3. \( \ln(K) = \infty \)
- 25% 4. \( \ln(K) = \text{something else} \)

Since \( K = \frac{k_{\text{tar}}}{k_{\text{rev}}} \), we see that at very high \( T \), ...

\( \ln(k) \rightarrow \ln\left(\frac{A_{\text{tar}}}{A_{\text{rev}}}\right) \)
First law, second law, equilibrium, and kinetics

\[ \lim_{T \to \infty} \ln(K) = \frac{\Delta S^o}{R} = \lim_{T \to \infty} \ln \left( \frac{k_{\text{for}}}{k_{\text{rev}}} \right) = \ln \left( \frac{k_{\text{for}}}{k_{\text{rev}}} \right) \]

What is the significance of this result?

**First**, at very high \( T \), \( K \) only depends on \( \Delta S^o = \Delta S^\text{sys} \).

This is because at very high \( T \), heat flow can no longer change entropy of the surroundings:

\[ \Delta S^\text{sur} = -\frac{\Delta H^\text{sys}}{T} = \Delta S^\text{sys} = 0 \]

Second, since the entropy change of the system can be expressed as

\[ \frac{\Delta S^o}{R} = \frac{1}{R} \ln \left( \frac{N_{\text{products}}}{N_{\text{reactants}}} \right) \]

at very high \( T \), the ratio of the Arrhenius factors is related to the ratio of the number arrangements or reactants and products,

\[ \lim_{T \to \infty} \ln(K) = \frac{\Delta S^o}{R} = \frac{1}{R} \ln \left( \frac{N_{\text{products}}}{N_{\text{reactants}}} \right) = \ln \left( \frac{k_{\text{for}}}{k_{\text{rev}}} \right) \]

Rate constant: \( \ln(k) = -(E_a/R)(1/T) + \ln(A) \)

Equilibrium constant: \( \ln(K) = -(\Delta H^o/R)(1/T) + \Delta S^o/R \)

What about when \( T \) is not very high?

What’s the connection between enthalpy change and activation energies?

\[ K = \frac{k_{\text{for}}}{k_{\text{rev}}} \text{ and so } \]

\[ \ln(K) = -\frac{\Delta H^o}{R} \frac{1}{T} + \frac{\Delta S^o}{R} = \ln \left( \frac{k_{\text{for}}}{k_{\text{rev}}} \right) = -\frac{E_a,\text{for} - E_a,\text{rev}}{R} \frac{1}{T} + \ln \left( \frac{k_{\text{for}}}{k_{\text{rev}}} \right) \]

and therefore, ...

\[ \Delta H^o = E_a,\text{for} - E_a,\text{rev} \]
First law, second law, equilibrium, and kinetics

Everything all together ...

\[ \ln(k) = -(E_a/R)(1/T) + \ln(A) \]

\[ \ln(K) = -(\Delta H^\circ / R)(1/T) + \Delta S^\circ / R \]

\[ \ln(K) = -\frac{\Delta H^\circ}{R} + \frac{\Delta S^\circ}{R} = \ln \left( \frac{k_{for}}{k_{rev}} \right) = -\frac{E_{a,for} - E_{a,rev}}{R} \frac{1}{T} + \ln \left( \frac{A_{for}}{A_{rev}} \right) \]

\[ \Delta S^\circ = R \ln \left( \frac{A_{for}}{A_{rev}} \right) \]

\[ \Delta H^\circ = E_{a,for} - E_{a,rev} \]