reaction coordinate diagram— shows the change in energy of a reaction along the most-likely reaction pathway (3D simplification of a multi-dimensional graph)

- R = reactants
- I = intermediates
- P = products
- T = transition state
- \( \Delta H_{\text{act}} \) = activation energy
- \( E_a \) = activation energy

- Only those reagents involved in the rate-limiting step (RLS) are found in the rate law.
- There is no relationship between the overall stoichiometric equation, the rate law, and \# of steps.

Arrhenius expression:

\[ k = A e^{-\frac{E_a}{RT}} \]

- \( A \) = frequency factor
- \( E_a \) = activation energy
- \( T \) = temperature
- \( \Delta H_{\text{act}} \) = energy of activation

- Energy distribution diagrams
  - \# of molecules
  - \# of molecules
  - \# of molecules
  - \# of molecules

- Energy per molecule w/ energy to react
- Energy per molecule w/ energy to react
- Energy per molecule w/ energy to react
- Energy per molecule w/ energy to react
Idealized rxn: \( A \rightleftharpoons B \)
- Assume both forward and reverse rxns are single-step unimolecular reactions
- Assume \( A \rightleftharpoons A \)

\[ \text{Equilibrium } R_s = R_r \]
\[ R_s = K_f [A] \quad ; \quad R_r = K_r [B] \]
\[ K_f [A] = K_r [B] \]

Since \( E_a < E_r \), \( K_f > K_r \)

Although rates are equal at equilibrium, rate constants do not have to be, which will affect the

\[ \text{reactants} \rightleftharpoons \text{products} \]

\[ \text{1,2-addition} \]

\[ \text{1,4-addition} \]

 thermo-dynamically more favorable due to internal \( \text{C} = \text{C} \)

The intermediate is a delocalized carbocation; there are not two distinct carbocations. Any difference of energy that may result occurs once bond

formation w/ \( R_r - \) starts.

\[ \text{1}^\text{o} \delta^+ \]

\[ \text{2}^\text{o} \delta^+ \]
At low enough temp, a rxn can become effectively irreversible, since both reverse Ea's are larger than the forward. In this situation, the forward rxn w/ the lowest $E_a$ will occur, even if it causes a less thermodynamically favorable product to form. kinetic control

• At high $T$, all reaction rates increase (and the rxn is reversible). Although the kinetic product may still initially form, it has the chance to reverse and potentially form B. Since B is the lowest-energy product, it is less likely to reverse and will therefore accumulate over time thermodynamic control

\[ \text{A} + \text{B} \rightarrow \text{semicarbazone} \]

\[ \text{A'} + \text{B'} \rightarrow \text{semicarbazone} \]