Kinetic and Thermodynamic Control

The potential outcome of a reaction is usually influenced by two factors:

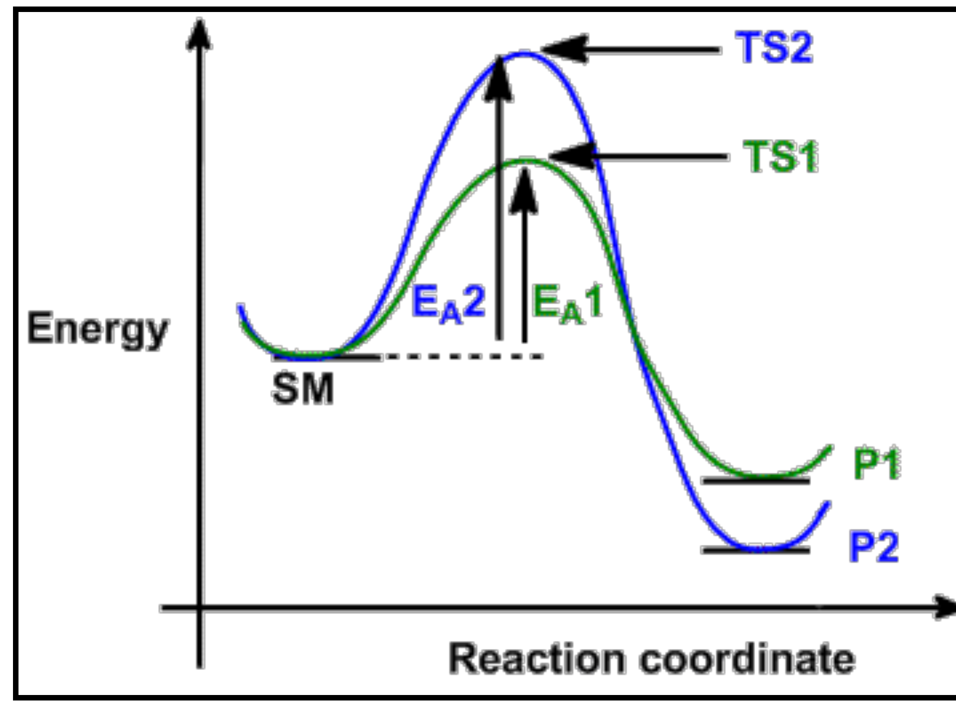
1. the relative stability of the products (*i.e. thermodynamic factors)*
2. the rate of product formation (*i.e. kinetic factors)*

The following simple reaction coordinate diagram provides a basis for the key issues about kinetic and thermodynamic control:

Consider the case where a starting material, **SM**, can react in a similar manner to give two different products, **P1** and **P2** via different (competing) pathways represented by **green** and **blue** curves.

Reaction 1 via pathway 1 (**green**) generates product 1 (**P1**) via transition state 1 (**TS1**).
This will be the *faster reaction* since it has a lower energy (more stable) transition state, and therefore a lower activation barrier. Therefore, product 1, **P1** is the **kinetic product** (the product that forms the fastest).

Reaction 2 via pathway 2 (**blue**) generates product 2 (**P2**) via transition state 2 (**TS2**).
P2 is the more stable product since **P2** is at a lower energy than **P1**.
Therefore, **P2** is the **thermodynamic product** (the more stable product).



We now need to consider how the outcome of this situation changes with the competing reactions of the starting material as we alter the reaction temperature and therefore the *average* energy of the molecules changes.

1. At low temperature, the average energy of the molecules is low and more molecules have enough sufficient energy cross activation energy E_A1 than E_A2. Therefore the reaction preferentially proceeds along the green path to **P1**. The reaction is not reversible since the molecules lack sufficient energy to reverse to **SM**, *i.e. it is irreversible*, so the product ratio of the reaction is dictated by *the rates of formation of* **P1** and **P2**, $k_1 : k_2$.

2. At some slightly higher temperature, reaction 1 will become reversible when sufficient molecules have enough energy to cross the reverse reaction barrier for reaction 1, while reaction 2 remains irreversible. So although **P1** may form initially, over time it will revert to **SM** and react to give the more stable **P2**.

3. At high temperature, both reaction 1 and 2 are reversible and the product ratio of the reaction is dictated by the *equilibrium constants for* **P1** and **P2**, $K_1 : K_2$.

Summary

- At low temperature, the reaction is under **kinetic control** (rate, irreversible conditions) and the major product is that from the fastest reaction.
- At high temperature, the reaction is under **thermodynamic control** (equilibrium, reversible conditions) and the major product is the more stable system