Effect of temperature on enzyme activity.

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Enzyme reaction rate "constant" is a product of the rate constant leading to the product, k_2, and the amount of active enzyme, E_{active}.

$$v = k_2 \cdot E_{active}$$

With enzyme deactivation, active enzyme decreases exponentially with time. Consequently, the enzyme reaction rate too decreases exponentially with time.

$$\frac{d}{dt}E_{active} = -k_d \cdot E_{active} \longrightarrow E_{active} = E_0 \cdot \exp(-k_d \cdot t) \longrightarrow v = k_2 \cdot E_0 \cdot \exp(-k_d \cdot t)$$

where the reaction rate "constants" k_2 and k_d depend on temperature in an Arrhenius fashion, with activation energies of E_a and E_d, or equivalently with activation temperatures of T_a and T_d, respectively.

$$k_2 = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \qquad k_2 = A \cdot \exp\left(-\frac{T_a}{T}\right)$$

$$k_d = B \cdot \exp\left(-\frac{E_d}{R \cdot T}\right) \qquad k_d = B \cdot \exp\left(-\frac{T_d}{T}\right)$$

Thus, reaction rate now depends on both temperature and time.

$$v(T,t) = A \cdot \exp\left(-\frac{T_a}{T}\right) \cdot E_0 \cdot \exp\left(-B \cdot \exp\left(-\frac{T_d}{T}\right) \cdot t\right)$$

To find the temperature at which v is maximum, solve dv/dT=0. Here we mark "T" in the above equation and choose |Symbolic|Differentiate on Variable|.

$$\frac{d}{dT}v(T,t) = A \cdot \frac{T_a}{T^2} \cdot \exp\left(\frac{-T_a}{T}\right) \cdot E_0 \cdot \exp\left(-B \cdot \exp\left(\frac{-T_d}{T}\right) \cdot t\right) - A \cdot \exp\left(\frac{-T_a}{T}\right) \cdot E_0 \cdot B \cdot \frac{T_d}{T^2} \cdot \exp\left(\frac{-T_d}{T}\right) \cdot t \cdot \exp\left(-B \cdot \exp\left(\frac{-T_d}{T}\right) \cdot t\right)$$

We subsequently find dv/dT=0 with "Given-Find". Or, one can first mark T, then choose |Symbolic|Solve for Variable|.

Given

dv/dT=0 $$0 = A \cdot \frac{T_a}{T^2} \cdot \exp\left(\frac{-T_a}{T}\right) \cdot E_0 \cdot \exp\left(-B \cdot \exp\left(\frac{-T_d}{T}\right) \cdot t\right) - A \cdot \exp\left(\frac{-T_a}{T}\right) \cdot E_0 \cdot B \cdot \frac{T_d}{T^2} \cdot \exp\left(\frac{-T_d}{T}\right) \cdot t \cdot \exp\left(-B \cdot \exp\left(\frac{-T_d}{T}\right) \cdot t\right)$$

$$\text{Find}(T) \rightarrow \frac{-T_d}{\ln\left[\frac{T_a}{\left[B \cdot \left(T_d \cdot t\right)\right]}\right]}$$

Thus, the temperature at which v is maximum is:

$$T_{max} = \frac{-T_d}{\ln\left(\frac{T_a}{B \cdot T_d \cdot t}\right)}$$

Note that the temperature of maximum activity does not depend on the pre-exponential factor for k_2 nor E0, but it does depend on the pre-exponential factor for k_d and t, as well as the activation energies.

To find the maximum v, copy the RHS, mark T in the rate expression below, and choose |Symbolic|Substitute for Variable|:

$$v = A\cdot\exp\left(-\frac{T_a}{T}\right)\cdot E_0\cdot\exp\left[-\left(B\cdot\exp\left(-\frac{T_d}{T}\right)\right)\cdot t\right]$$

Maximum v

$$v_{max} = A\cdot\exp\left(\frac{T_a}{T_d}\cdot\ln\left(\frac{T_a}{B\cdot T_d\cdot t}\right)\right)\cdot E_0\cdot\exp\left(\frac{-T_a}{T_d}\right)$$

Plot for specific parameter values (taken from Shuler & Kargi, Figure 3.15) $R := 0.0019872\frac{kcal}{mole\cdot K}$

$E_a := 11\frac{kcal}{mole}$ $A := 10^8\ min^{-1}$ ← chosen to yield activity~O(1) $T_a := \frac{E_a}{R}$ $E_0 := 1$

$E_d := 70\frac{kcal}{mole}$ $B := 10^{49} min^{-1}$ ← chosen to yield T_{max} around ambient. $T_d := \frac{E_d}{R}$

$$v(T,t) := A\cdot\exp\left(-\frac{T_a}{T}\right)\cdot E_0\cdot\exp\left(-B\cdot\exp\left(-\frac{T_d}{T}\right)\cdot t\right) \qquad v_{max}(t) := A\cdot\exp\left(\frac{T_a}{T_d}\cdot\ln\left(\frac{T_a}{B\cdot T_d\cdot t}\right)\right)\cdot E_0\cdot\exp\left(\frac{-T_a}{T_d}\right)$$

$T := 273 .. 323$