Kinetics and Activation Parameters

- In order to probe reaction mechanisms, one must understand the activation parameters: $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$

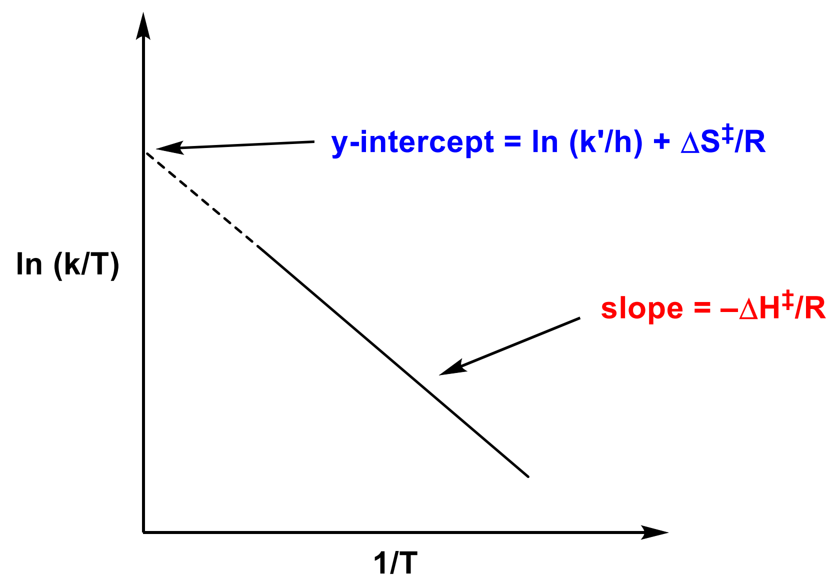
- $\ln (k/t) = -\Delta H^{\ddagger}/RT + \ln (k'/h) + \Delta S^{\ddagger}/R$

- The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can

- The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be obtained by measuring the rate of a reaction at different temperatures. A plot of ln (k/T) vs. 1/T (an Eyring plot) will give a straight line with a slope of $-\Delta H^{\ddagger}R$ and an intercept of $\ln(k'/h) + \Delta S^{\ddagger}R$. Once $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been determined, $\Delta G^{\ddagger}$ can be calculated according to $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

- k = rate constant
- T = temperature (K)
- $\Delta H^{\ddagger}$ = enthalpy of activation (J mol^{-1})
- R = molar gas constant (8.3145 J K^{-1} mol^{-1})
- k' = Boltzmann constant (1.38 x 10^{-23} J K^{-1})
- h = Plank constant (6.626 x 10^{-34} J s)
- $\Delta S^{\ddagger}$ = entropy of activation (J K^{-1} mol^{-1})

Eyring plot:



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- Values of $\Delta S^{\ddagger}$ are particularly useful to distinguish between associative (A) and dissociative (D) substitution mechanisms:

  - Large –ve $\Delta S^{\ddagger}$ (–10 to –15 e.u.) → A or I_a mechanism
    (1 e.u. = 1 cal K^{-1} mol^{-1} = 4.184 J K^{-1} mol^{-1})
  - Large +ve $\Delta S^{\ddagger}$ (+10 to +15 e.u.) → D or I_d mechanism

- The volume of activation ($\Delta V^{\ddagger}$) can also be useful. A reaction in which the transition state has a greater volume than the initial reactants (including changes in the volume of the solvent, which is particularly important if solvated ions are involved) will have a large +ve $\Delta V^{\ddagger}$. $\Delta V^{\ddagger}$ can be determined from the pressure dependence of a reaction:

  - Large –ve $\Delta V^{\ddagger}$ (–5 to –15 cm^3 mol^{-1}) → A or I_a mechanism
  - Large +ve $DV^{\ddagger}$ (+5 to +15 cm^3 mol^{-1}) → D or I_d mechanism

$$\ln (k_{P1}/k_{P2}) = -\Delta V^{\ddagger}/RT\ (P_1 - P_2)$$