TRANSITION STATE THEORY : THE MATHS! (Part 1/2)

TST = this

TST assumes that the transition state, $TS^\ddagger$, is in equilibrium w/ the reactants:

$$\underbrace{A + BC \rightleftharpoons TS^\ddagger}_{①}\overbrace{\,TS^\ddagger \longrightarrow AB + C}^{②}$$

① For this equilibrium, we can write:

$$K^\ddagger = \frac{[TS^\ddagger]/c^\circ}{[A]/c^\circ\,[B]/c^\circ} \qquad \text{and therefore:} \quad [TS^\ddagger] = \frac{1}{c^\circ}K^\ddagger[A][BC]$$

big K = eqm constant

$c^\circ = 1$ mol dm^{-3}, so the [ ] terms are unitless

Put this into this (easy!)

② For the overall rate:

small k = rate constant

$$\text{rate} = v = \frac{d[AB]}{dt} = k^\ddagger[TS^\ddagger] = \frac{1}{c^\circ}k^\ddagger K^\ddagger[A][BC]$$

Collect constants into an observed rate constant, k_{obs}:

units are s^{-1} mol^{-1} dm^3 as expected

$$\text{rate} = \frac{1}{c^\circ}k^\ddagger K^\ddagger[A][BC] = k_{obs}[A][BC], \quad k_{obs} = k^\ddagger K^\ddagger\left(\frac{1}{c^\circ}\right)$$

$\frac{1}{\text{mol dm}^{-3}} = \text{mol}^{-1}\,\text{dm}^3$

1st order rate constant (s^{-1})

dimensionless eqm constant

From statistical mechanics magic (trust me!):

From earlier

$$k^\ddagger\left(\frac{1}{c^\circ}\right)K^\ddagger = \frac{k_BT}{h}\left(\frac{1}{c^\circ}\right)K_c^\ddagger$$

$\frac{\text{boltzmann} \times T}{\text{planck}}$

a "new" equilibrium constant, that can be expressed in terms of ΔG (see part 2/2)

Then: $k_{obs} = \frac{k_BT}{hc^\circ}K_c^\ddagger$ for a bimolecular rxn (bimolecular → 2nd order, so units are mol^{-1} dm^3 s^{-1})

remember this

In general, $\boxed{k_{obs} = \frac{k_BT}{hc^{\circ m-1}}K_c^\ddagger}$, where m = molecularity*. But WHY??

*molecularity = how many molecules collide in a rxn:
m = 1 - 1st order
m = 2 - 2nd order

Do Dimensional Analysis → $k_{obs} = \frac{k_B(JK^{-1})\,T(K)}{h(Js)\,c^{\circ m-1}(\text{mol dm}^{-3})^{m-1}} = \frac{\cancel{J}\cancel{K^{-1}}\cancel{K}}{\cancel{J}s(\text{mol dm}^{-3})^{m-1}} = (\text{mol dm}^{-3})^{m-1}\,s^{-1}$

Molecularity	Rxn order	Units of k_{obs}
m = 1	First	$(\text{mol dm}^{-3})^{1-1}s^{-1} = s^{-1}$ $(\because (\text{mol dm}^{-3})^0 = 1)$
m = 2	Second	$(\text{mol dm}^{-3})^{2-1}s^{-1} = \text{mol}^{-1}\text{dm}^3 s^{-1}$
m = 3	Third	$(\text{mol dm}^{-3})^{3-1}s^{-1} = \text{mol}^{-2}\text{dm}^6 s^{-1}$

⇒ ENTIRELY AS EXPECTED! How pleasant! Tune into Part 2 for ENERGETICS!