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

From part 1 : $k_{obs} = \frac{k_B T}{h c^{\circ m-1}} K_c^{\ddagger}$. Recall that $\Delta G^{\ddagger} = -RT \ln K^{\ddagger}$ ($\Delta G^{\ddagger}$ → Gibbs' Energy of activation. $K^{\ddagger}$ → equ^n constant)

$$\therefore K_c^{\ddagger} = \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) = \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \quad (\because \Delta G = \Delta H - T\Delta S)$$

c from concentration → i.e. solution

So overall; (sol: solution)

$$k_{TST,sol} = k_{obs} = \frac{k_B T}{h c^{\circ m-1}} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)$$

] TST rate constant in solution phase.

In the gas-phase, need $K_p^{\ddagger}$ not $K_c^{\ddagger}$ → equ^n constant with pressure not concentration

Bonus Q: Derive this!

[Generally : $K_c^{\ddagger} = K_p^{\ddagger}\left(\frac{RT c^{\circ}}{p^{\circ}}\right)^{m-1}$ ⇒ $c^{\circ} = 1\,\text{mol dm}^{-3}$, $p^{\circ} = 1\,\text{atm}$

Therefore:

$$k_{TST,gas} = k_{obs} = \frac{k_B T}{h}\left(\frac{RT}{p^{\circ}}\right)^{m-1} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)$$

] TST rate constant in the gas phase.

Now we want to compare to Arrhenius:

$$k = A\exp(-E_a/RT)$$

This is derived separately

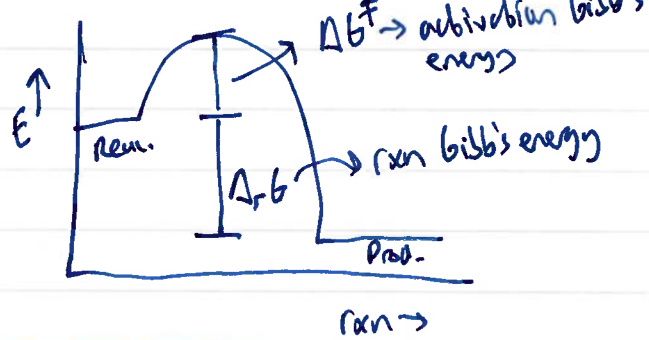
m = molecularity

→ to link E_a and $\Delta H^{\ddagger}$, use:

$$E_a = \Delta H^{\ddagger} + RT \quad \text{(sol. phase)}$$

$$E_a = \Delta H^{\ddagger} + mRT \quad \text{(gas. phase)}$$

Aside: $\Delta G^{\ddagger}$ vs ΔG



Therefore, overall we can write:

Solution Phase:

$$k_{TST,sol} = \frac{k_B T}{h c^{\circ m-1}} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)$$

$$= e^{1}\frac{k_B T}{h c^{\circ m-1}} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{E_a}{RT}\right)$$

] from Arrhenius. $A = e^{1}\frac{k_B T}{h c^{\circ m-1}}\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$

Gas Phase:

$$k_{TST,gas} = \frac{k_B T}{h}\left(\frac{RT}{p^{\circ}}\right)^{m-1} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)$$

$$= e^{m}\frac{k_B T}{h}\left(\frac{RT}{p^{\circ}}\right)^{m-1} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{E_a}{RT}\right)$$

] $A = e^{m}\frac{k_B T}{h}\left(\frac{RT}{p^{\circ}}\right)^{m-1} \times \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$

We can now estimate the Arrhenius factor using both SCT and TST! Nice! (I think it's nice...)