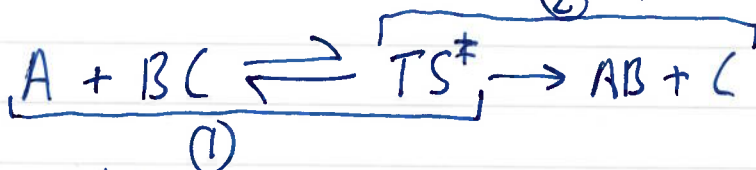


TRANSITION STATE THEORY: THE MATHS! (Part 1/2)

↑ TST = this ↑

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



(1) For this equilibrium, we can write:

big K = eqⁿ constant

$$K^\ddagger = \frac{[TS^\ddagger]/c^\circ}{[A]/c^\circ [B]/c^\circ}$$

and therefore: $[TS^\ddagger] = \frac{1}{c^\circ} K^\ddagger [A][B]$

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

(2) For the overall rate:

small k = rate constant

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

Put this into this (easy!)

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

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

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

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

From statistical mechanics magic (troub me):

From earlier

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

a "new" equilibrium constant, K_c^\ddagger can be expressed in terms of ΔG^\ddagger (see part 2/2)

boltzmann $\times T$ / planck

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

dimensionless eqⁿ constant

Then: $k_{\text{obs}} = \frac{k_B T}{h c^\circ} K_c^\ddagger$ for a bimolecular rxn (bimolecular \rightarrow 2nd order so units are $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)

In general, $k_{\text{obs}} = \frac{k_B T}{h c^{\circ m-1}} K_c^\ddagger$, where $m = \text{molecularity}^*$. But WHY??

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

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

\Rightarrow ENTIRELY AS EXPECTED! How pleasant! Time into Part 2 for ENERGETICS!

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