From Fig-1

Potential energy of precursor complex = potential energy of successor complex

$$\therefore\ G^{o}_{(A^{*}-)} + G^{o}_{(B^{*})} = G^{o}_{(A^{*})} + G^{o}_{(B^{*}-)} \quad \cdots ⑦$$

For self exchange reaction: Fig-2:

$$\Delta G^{*}_{(A^{-}A)} = G^{o}_{(A^{*}-)} + G^{o}_{(A^{*})} - \left\{ G^{o}_{(A-)} + G^{o}_{(A)} \right\} \quad \cdots ⑧$$

$$\Delta G^{*}_{(B^{-}B)} = G^{o}_{(B^{*}-)} + G^{o}_{(B^{*})} - \left\{ G^{o}_{(B-)} + G_{(B)} \right\} \quad \cdots ⑨$$

From eqn-④

$$\Delta G^{*}_{(A^{-}B)} = G^{o}_{(A^{*}-)} + G^{o}_{(B^{*})} - G^{o}_{(A^{-})} - G^{o}_{(B)}$$

Multiply both side by '2'

$$2\Delta G^{*}_{(A^{-}B)} = 2G^{o}_{(A^{*}-)} + 2G^{o}_{(B^{*})} - 2G^{o}_{(A^{-})} - 2G^{o}_{(B)} \quad \cdots ⑩$$

Adding equation ⑥, ⑧ & ⑨

$$\Delta G^{o}_{(A^{-}B)} + \Delta G^{*}_{(A^{-}A)} + \Delta G^{*}_{(B^{-}B)} = \cancel{G^{o}_{(A^{o})}} + \cancel{G^{o}_{(B^{-})}} - G^{o}_{(A^{-})} - G^{o}_{(B)} + G^{o}_{(A^{*}-)}$$
$$+ G^{o}_{(A^{*})} - G^{o}_{(A^{-})} - \cancel{G^{o}_{(A)}} + G^{o}_{(B^{*}-)} + G^{o}_{(B^{*})}$$
$$- \cancel{G^{o}_{(B^{-})}} - G^{o}_{(B)}$$

$$= G^{o}_{(A^{*}-)} + G^{o}_{(A^{*})} + G^{o}_{(B^{*}-)} + G^{o}_{(B^{*})}$$
$$- 2G^{o}_{(A^{-})} - 2G^{o}_{(B)}$$

Considering equation 7

$$G^{o}_{(A^{*-})} + G^{o}_{(B^{*})} = G^{o}_{(A^{*})} + G^{o}_{(B^{*-})}$$

we get.

$$\Delta G^{o}_{(A^{-}B)} + \Delta G^{*}_{(A^{-}A)} + \Delta G^{\neq}_{(B^{-}B)} = 2G^{o}_{(A^{*-})} + 2G^{o}_{(B^{*})} - 2G^{o}_{(A^{-})} - 2G^{o}_{(B)} \quad \text{.....} (11)$$

considering equ^n... 4

$$= 2G^{\#}_{(A^{-}B)}$$

$$\Rightarrow 2\Delta G^{\#}_{(A^{-}B)} = \Delta G^{o}_{(A^{-}B)} + \Delta G^{\neq}_{(A^{-}A)} + \Delta G^{\neq}_{(B^{-}B)} \quad \text{.....} (12)$$

The above reaction is valid, if

(i) Activation process for each reactant is independent of other reactant.

(ii) Activated species are same for both self exchange & cross reaction.

From transition state theory:

$$k_{ij} = Z_{ij}\, e^{-\frac{\Delta G^{*}_{ij}}{RT}} \qquad \left[\text{or } \Delta G^{*}_{ij} = -RT\ln\frac{k_{ij}}{Z_{ij}}\right]$$

$$\Rightarrow \Delta G^{*}_{ij} = -RT\ln\frac{k_{ij}}{Z_{ij}} \quad \text{...} (13)$$

Putting the value of (13) in (12) $i = A^{\circ}, j = B$

$$-2\cancel{RT}\ln\frac{k_{A^{-}B}}{Z_{A^{-}B}} = -\cancel{RT}\ln \underset{\substack{\uparrow \\ \text{equ. const.}}}{K_{A^{-}B}} - \cancel{RT}\ln\frac{k_{A^{-}A}}{Z_{A^{-}A}} - \cancel{RT}\ln\frac{k_{B^{-}B}}{Z_{B^{-}B}}$$

$$\Rightarrow \ln\left(\frac{k_{A^-B}}{Z_{A^-B}}\right)^2 = \ln\left(\frac{k_{A^-A}}{Z_{A^-A}}\right) \times \frac{k_{B^-B}}{Z_{B^-B}} \times K_{A^-B}$$

$$\Rightarrow \frac{k^2_{A^-B}}{Z^2_{A^-B}} = \frac{k_{A^-A} \times k_{B^-B} \times K_{A^-B}}{Z_{A^-A} \times Z_{B^-B}}$$

$$\Rightarrow k^2_{A^-B} = k_{A^-A} \times k_{B^-B} \times K_{A^-B} \times \frac{Z^2_{A^-B}}{Z_{A^-A} \times Z_{B^-B}}$$

$$\Rightarrow k_{A^-B} = \sqrt{k_{A^-A}\, k_{B^-B}\, K_{A^-B}\, f_{AB}}$$

Z = no. of collission/sec.
k = electron exchange rate const.

simplifying by removing A^- & B^-

$$\Rightarrow k_{AB} = \sqrt{k_{AA}\, k_{BB}\, K_{AB}\, f_{AB}}$$

$f_{AB} \simeq 1$

This is Mercus-Hush equation

k = e^- exchange rate const.