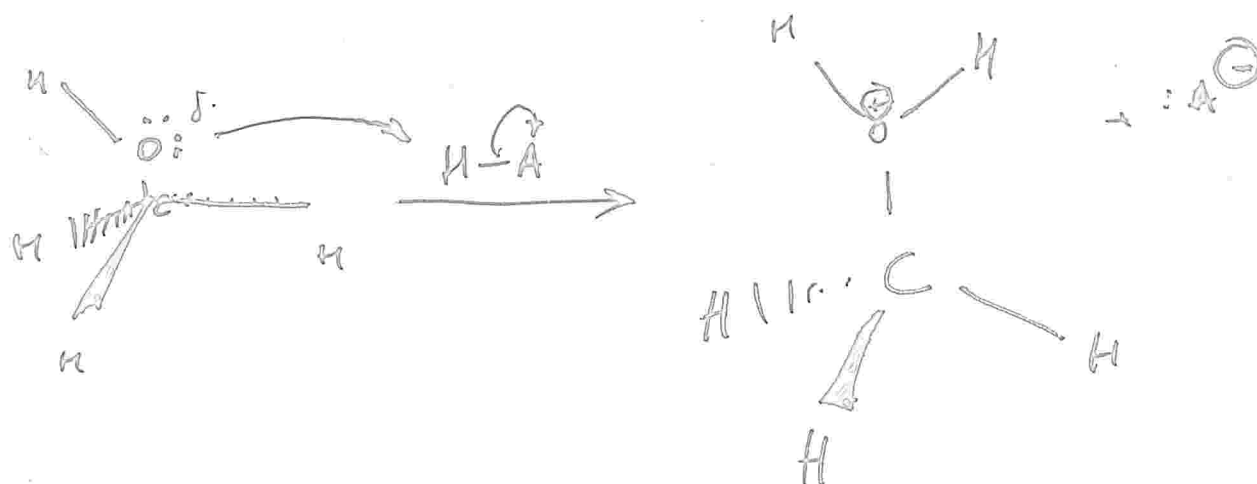


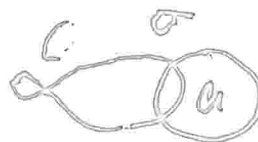
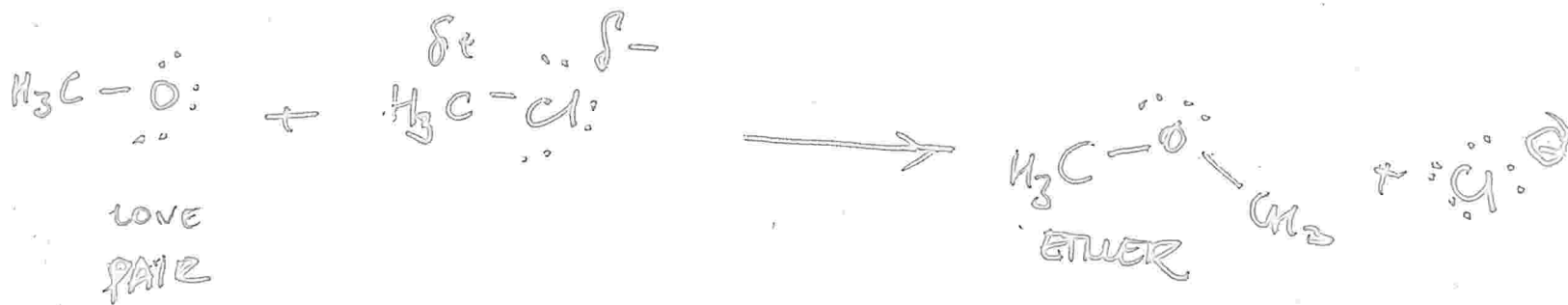
POLARIZABILITY

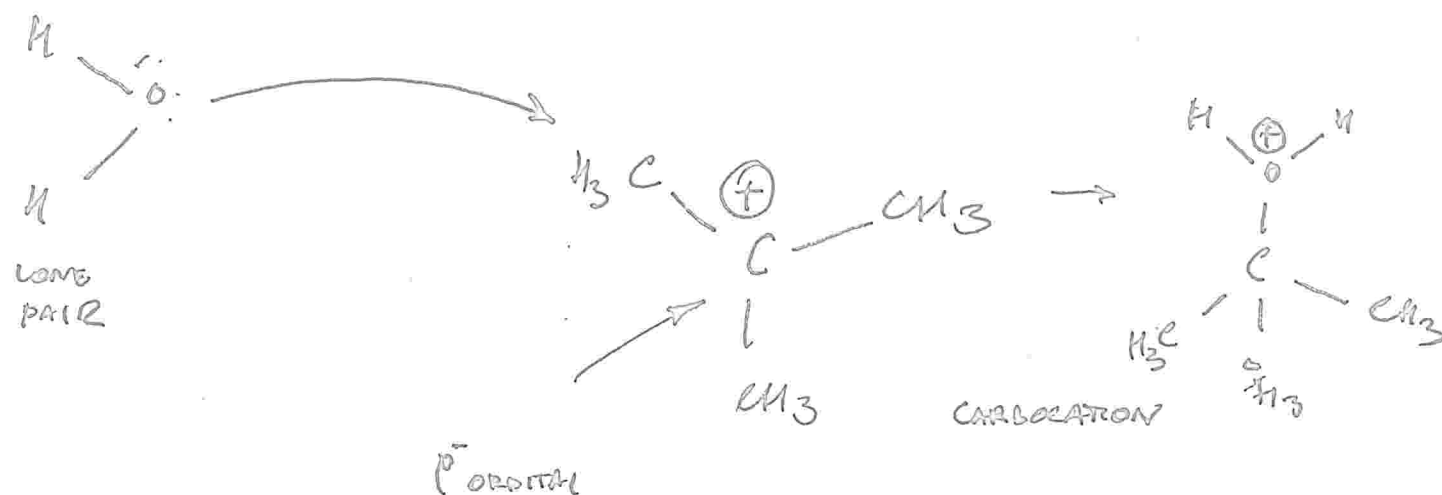
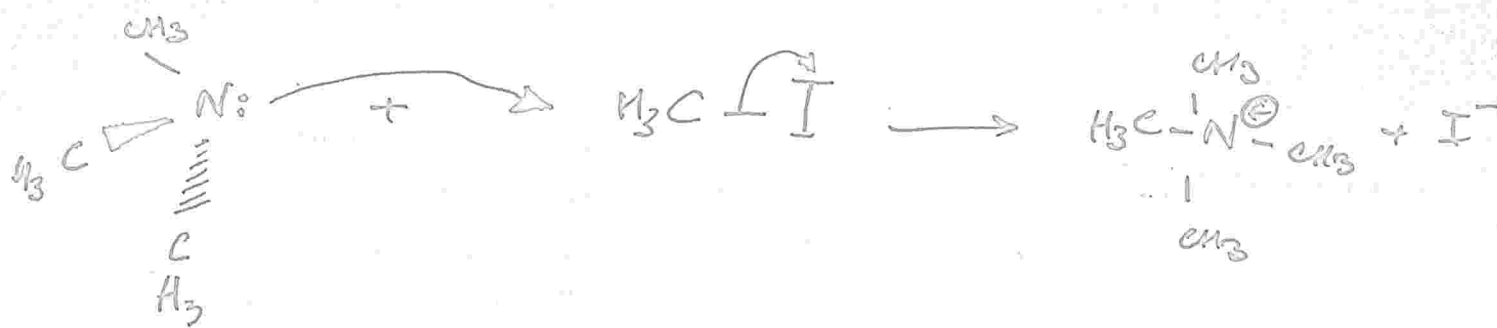
ABILITY TO SHIFT BONDING  
OR NONBONDING ELECTRONS  
IN RESPONSE TO A  
NEIGHB: ELECTROPHILE OR NUCLEOPHILE

GENERATION OF  $\delta^-$ -PHILES /  $\delta^+$ -PHILES



ARROW-PUSHING FOR  $\delta^-$  /  $\delta^+$ -PHILE REACTIONS





## THERMODYNAMICS OF CHEMICAL REACTIVITY

- 1. WHAT DIRECTION DOES THE REACTION PROCEED?  
 WHAT IS THE POSITION OF A GIVEN CHEMICAL EQUILIBRIUM?

### THERMODYNAMICS

- 2. WHAT IS THE RATE OF CHEMICAL REACTIONS?  
 RATE OF CHEMICAL REACTIONS-

## CHEMICAL EQUILIBRIA



$$K_{eq} = \frac{[C]^c [D]^d}{[B]^b [A]^a}$$

## FREE ENERGY AND CHEMICAL EQUILIBRIA

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

✓:  $\Delta G < 0$  ( $G_{\text{products}} < G_{\text{reactants}}$ ) EXERGONIC

✗:  $\Delta G > 0$  ( $G_{\text{products}} > G_{\text{reactants}}$ ) ENDERGONIC

PURE SUBSTANCES, SET PRESS, SET TEMP.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\Delta H^\circ \longrightarrow$  THE STRENGTH OF BONDS FORMED AND BROKEN IN THE REACTION

$\Delta S^\circ \longrightarrow$  RELATED TO CHANGES IN THE DEGREE OF DISORDER (ENTROPY) RESULTING FROM THE REACTION

## ENTHALPY CHANGES

$\Delta H^\circ < 0$  : EXOTHERMIC PROCESS

$\Delta H^\circ > 0$  : ENDOTHERMIC PROCESS.

---

USING BOND DISSOCIATION ENTHALPIES  
TO PREDICT  $\Delta H$

$$\Delta H^\circ_{\text{REACTION}} = \left( \text{SUM OF BDE BROKEN} \right) - \left( \text{SUM OF BDE BONDS FORMED} \right)$$

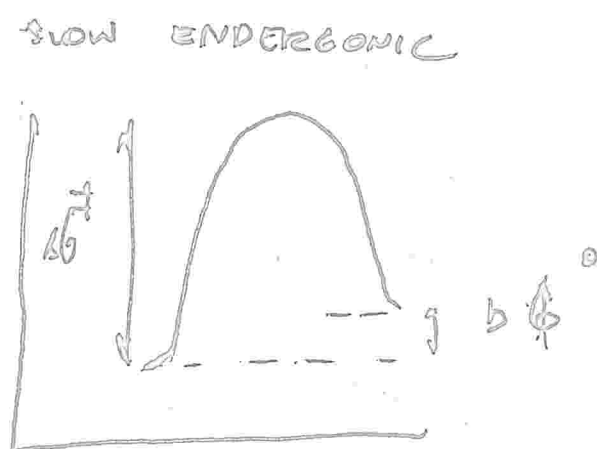
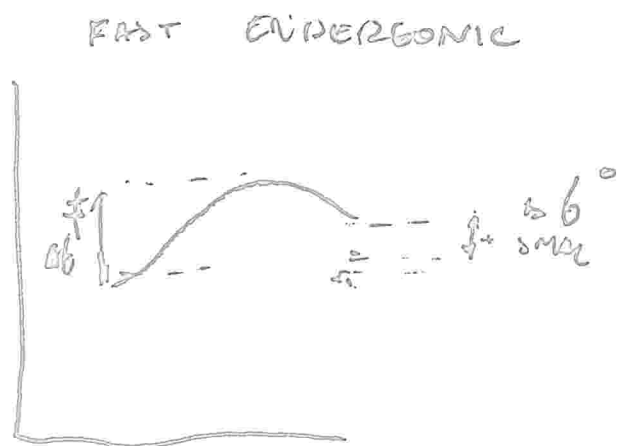
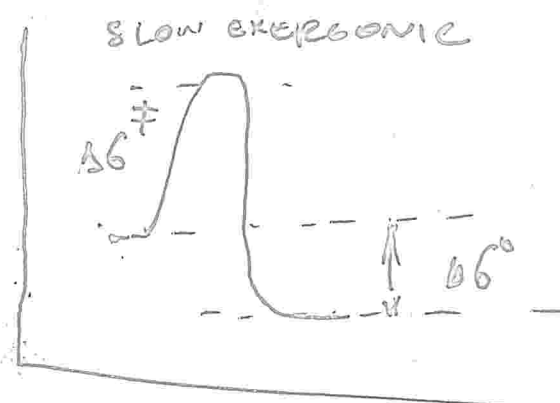
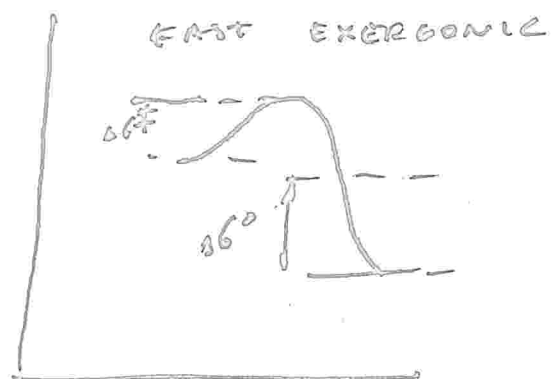
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## ENTROPY CHANGES

$\Delta S^\circ < 0$  : ENTROPICALLY UNFAVOURABLE



EQUILIBRIUM vs RATE:  
FREE ENERGY DIAGRAMS



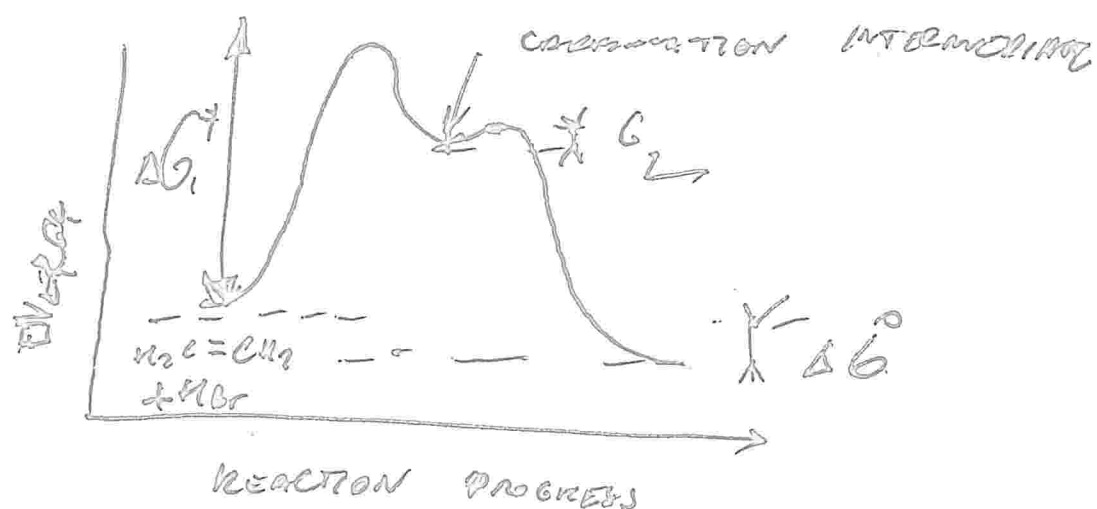
## TRANSITION STATES AND ACTIVATION ENERGIES

ACTIVATION ENERGY  $\Delta G^\ddagger$ :

THE FREE ENERGY DIFFERENCE BETWEEN  
REACTANT AND TRANSITION STATE

INTERMEDIATE: A LOCAL MINIMUM ON A  
POTENTIAL ENERGY SURFACE: INTERMEDIATES  
ARE FORMED TRANSIENTLY IN REACTIONS  
INVOLVING MORE THAN ONE ELEMENTARY  
STEP.

INTERMEDIATES ARE DISTINCT FROM TRANSITION  
STATES.



## CATALYSIS

