

LEC (14)

CHEM 30A

FEB 11th

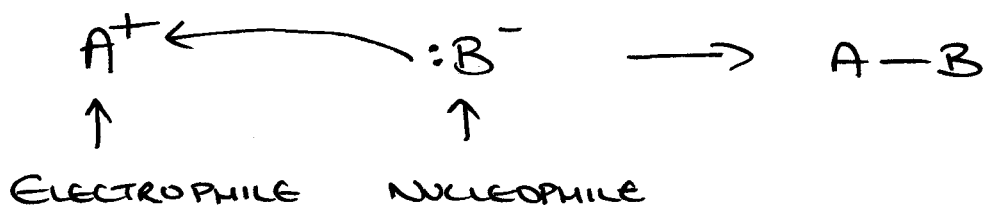
(1)

- ① ELECTROPHILES / NUCLEOPHILES
- ② ENERGY DIAGRAMS
- ③ KINETICS VS THERMODYNAMICS

HWK: READ 6-6.5

---

### ① ELECTROPHILES / NUCLEOPHILES



Nucleophiles : have an  $e^-$  rich atom and are NEUTRAL or -VERY charged

Electrophiles : have an  $e^-$  poor atom and are NEUTRAL or +VERY charged.

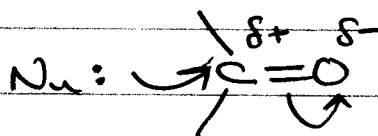
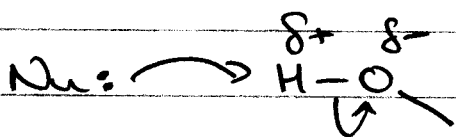
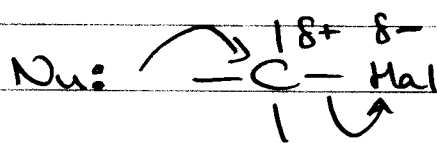
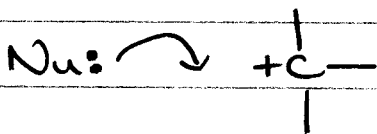
### PATTERNS

Electrons flow FROM nucleophiles



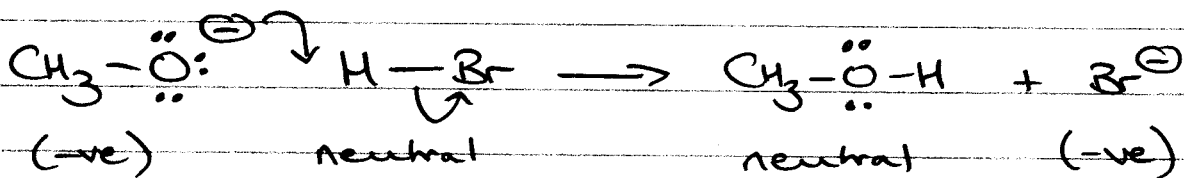


Electrons flow to electrophiles

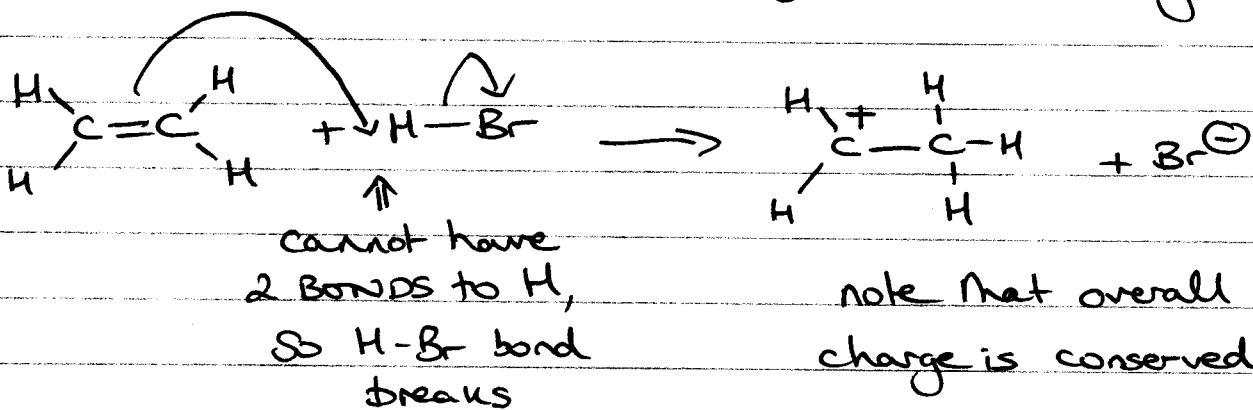


### Rules

- conserve charge

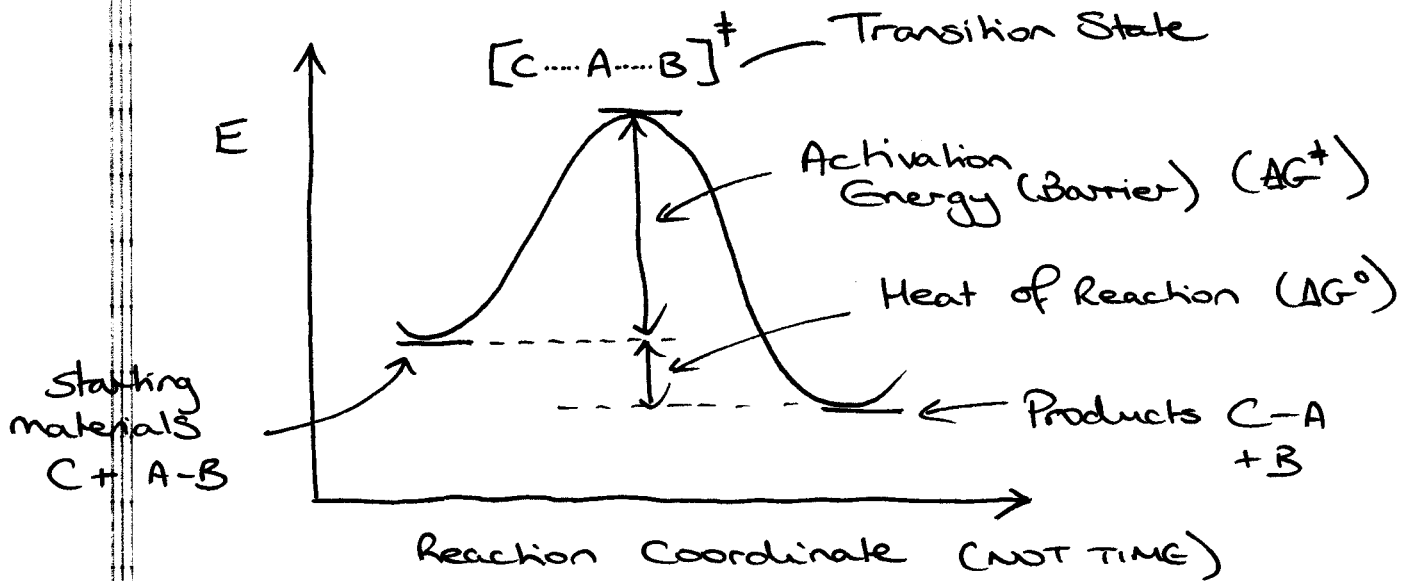
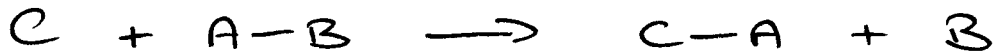


- octet rule must be obeyed (if necessary)



② ENERGY DIAGRAMS

- ONE STEP REACTION



For a reaction to occur as written

$$\Delta G^{\circ} < 0 \quad (\text{proceeds spontaneously})$$

if  $\Delta G^{\circ} > 0$  reaction does not proceed

- Heat of Reaction

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

↑  
change in enthalpy  
(CAN BE MEASURED DIRECTLY)

← change in ENTROPY  
(more significant  
at higher T)

$\Delta H^\circ$  -ve EXOTHERMIC RXN

$\Delta H^\circ$  +ve ENDOTHERMIC RXN

### - TRANSITION STATE

Energy maximum on reaction co-ordinate

$\Rightarrow$  definite geometry and arrangement of atoms but CANNOT BE ISOLATED, STRUCTURE CANNOT BE DETERMINED EXPERIMENTALLY

(sometimes we can infer structure, or use computational techniques)

### - ACTIVATION ENERGY

Difference in energy between starting materials and the transition state

$\Delta G^\ddagger$  or  $E_A$

Arrhenius equation

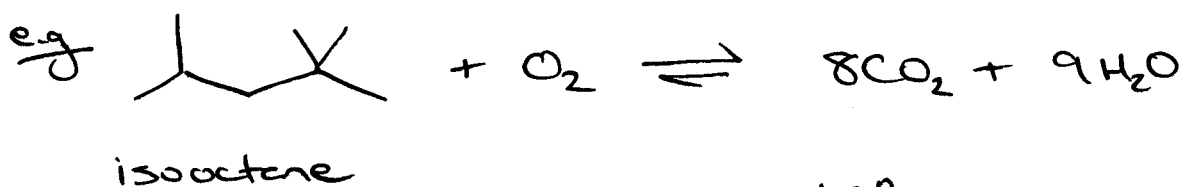
$$k = A e^{(-E_A/RT)}$$

↑  $A$  ← pre-exponential factor  
rate constant of reaction

### ③ KINETICS vs THERMODYNAMICS

↓  
How fast  
will it  
happen

↓  
Will it  
happen

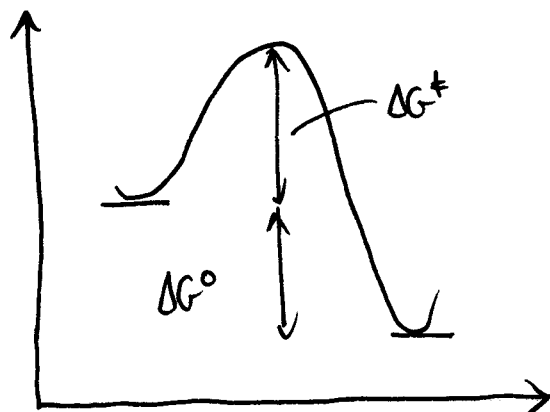


$$\Delta G^\circ = -1000 \text{ kJ mol}^{-1}$$

$k_{\text{eq}} = 10^{17.5}$  at 298K  
(only  $10^{86}$  atoms in the observable universe!)

But isooctane is stable  
(you put it in your car)

Energy is required to start the reaction  
⇒ ACTIVATION ENERGY (spark plug!)



So, isooctane + oxygen

THERMODYNAMICALLY  
UNSTABLE,

BUT  
KINETICALLY  
STABLE!

6

However  $\rightarrow$  apply a burst of energy to a mixture of  $H_2O$  and  $CO_2$ , they will not reconvert to octane and oxygen

### ENERGY BARRIERS and RATE

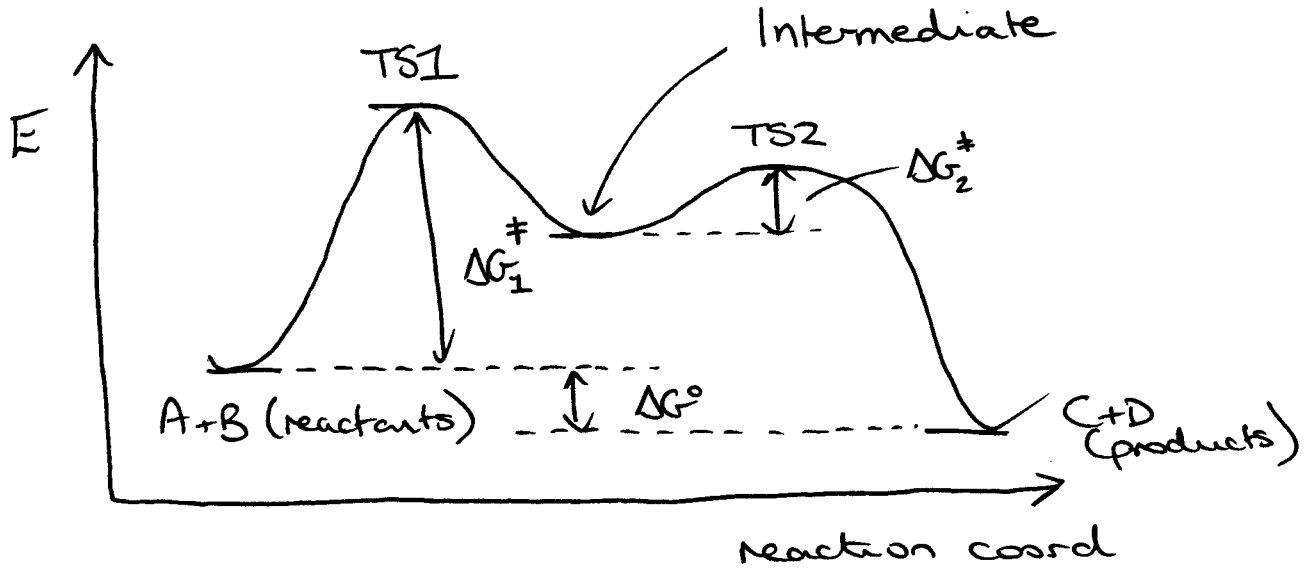
(consider BOND ROTATIONS  $\rightarrow$  some principles apply to reactions)

	$E_A$ (kcal/mol)	$k(s^{-1})$ (298K)	$t_{1/2}$
$H_3C-CH_3$ ↑	3	$5 \times 10^{10}$	0.02 ns
$Cl_3C-CCl_3$ ↑	11	$8 \times 10^4$	10 ns
$Me-\overset{O}{\parallel}-N-H$ ↑ H	17	3	0.2s
$Ph-C=C-Ph$ H H	45	$2 \times 10^{-9}$	$\sim 10^{11}$ years

(AGE of the EARTH  $\sim 4.6 \times 10^9$  years)

### BACK TO ENERGY PROFILES

$\Rightarrow$  TWO STEP REACTION



Reaction Intermediate

⇒ localized energy minimum  
between two transition states

(sometimes possible to isolate)

Slowest step in a MULTISTEP reaction  
(one w/ highest barrier) is called the  
rate determining step (RDS)