

**(31) Today**

Sections 6.5 – 6.11

**Next Class (32)**

Test 3 on Chap 4 and 5

**(33) Second Class from Today**

Chap 7

**Third Class from Today (34)**

Chap 7

Review session Thursday at 7:30 in Wilson 304

The Equilibrium Constant



$$\frac{1}{100} < 1$$

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

lots of product  
 $\frac{100}{1}$   
 not much react

size of K

$1 <$

small K

vs

large K

$< 1$

$> 1$

reaction favors reactants

reaction favors products

How can I get more D if my reaction has a small K?

Add more A or B to push toward product

Remove D as it forms + reaction will make more

Le Chatelier's



Gibbs Free Energy relates to universe reaction temp K

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

$\Delta G$  is related to the entropy of the universe

is a measure of whether a reaction, as written, is spontaneous

$\Delta G > 0$  ... spontaneous ... in the reverse direction

$\Delta G < 0$  spontaneous in the direction that the reaction is written

negative  $\Delta G$  means the products are lower in E than the reactants

$$\Delta G = G_{\text{prod}} - G_{\text{react}}$$

f - i

negative means energy is being released to the universe

endergonic

exergonic

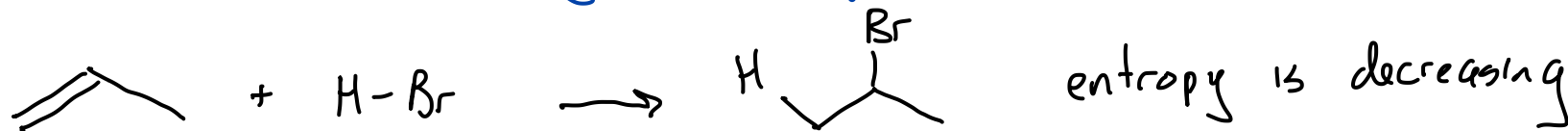
Gibbs Free Energy  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

relates energy associated with the rxn to the entropy of the universe

temp K

$\Delta G$  is related to the entropy of the universe  
 is a measure of whether a reaction, as written, is spontaneous

$S$  is entropy ... a measure of randomness  
 a  $\oplus \Delta S \uparrow$  entropy encourages reaction to proceed



$H$  is enthalpy ... under very specific conditions  $\Delta H$  is heat

releasing heat ... exothermic  $\Delta H = H_{\text{prod}} - H_{\text{react}} < 0$

encourages reaction because the rxn is releasing heat into the universe making the universe more random

endothermic  $\Delta H > 0$

Gibbs Free Energy

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

small  $k$

$$k < 1$$

$\ln k$  when  $k < 1$

$$\ln 1 = \ominus$$

$$\Delta G^\circ = -RT (\ominus)$$

gas constant (+) (+)  $k$

$$\Delta G^\circ = \ominus \oplus \oplus \ominus$$

$$\Delta G^\circ = \oplus$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

equilibrium constant is related to

$\Delta G$

reactions with small  $k$ 's have  $\oplus \Delta G^\circ$

reactions with large  $k$ 's have  $\ominus \Delta G^\circ$

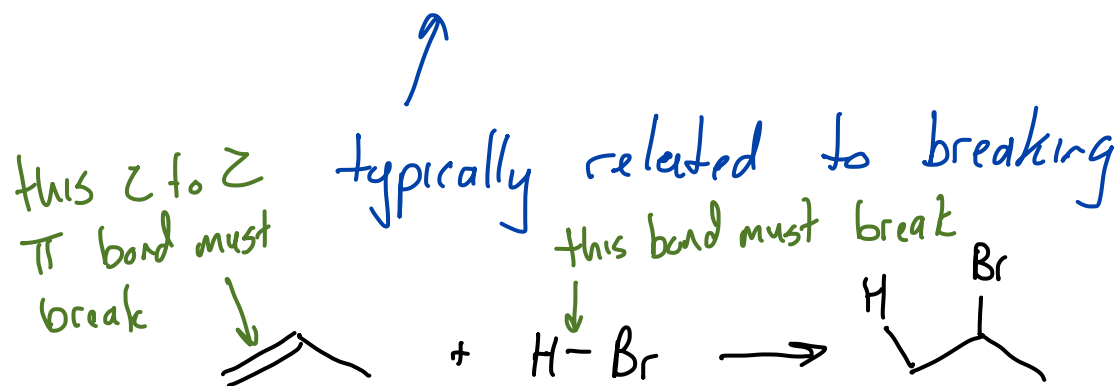
relationship between (equilibria and energy changes) and rates

do reactions with favorable equilibrium constants ( $\ominus \Delta G^\circ$ 's) have high rates? yes... and... no

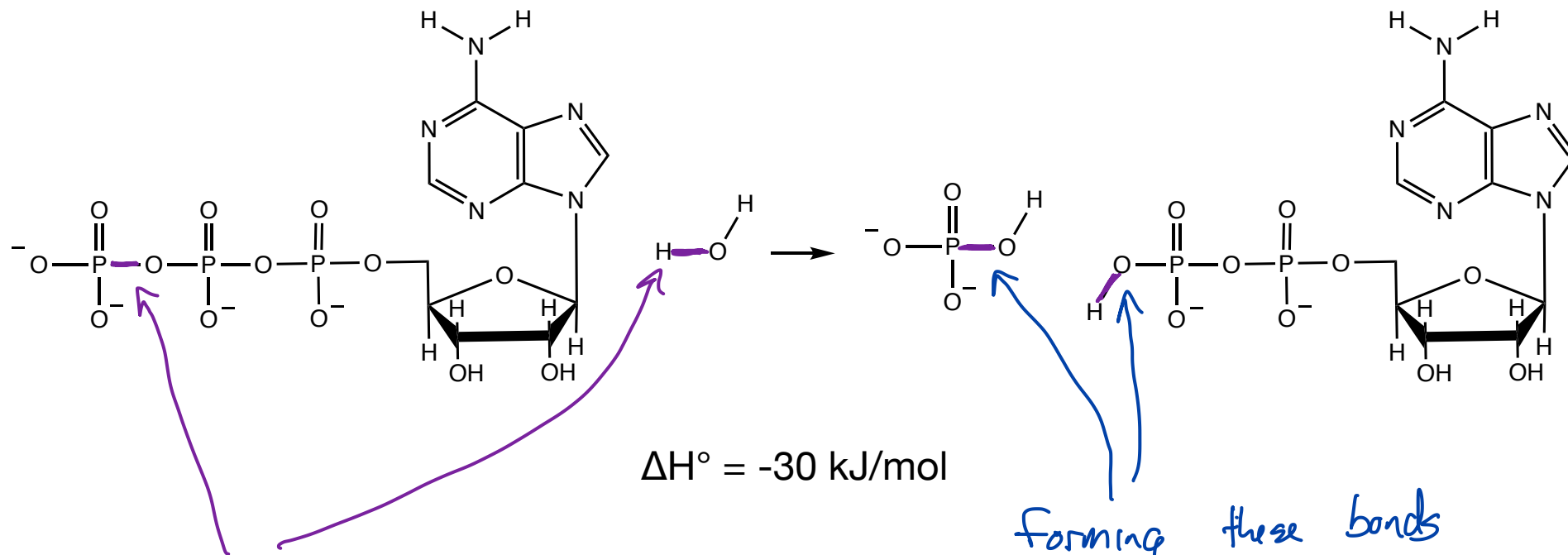
There is no relationship between ( $K + \Delta G$ ) and Rate

Rate is determined by the concentration of the reactants (in the rate determining step) and

the activation energy



energy in to break bonds and overcome activation  $E$  energy is released when bonds form



energy goes in  
to break these  
bonds  
weaker bonds....

why? the O is sharing with 2 p's  
instead of just 1  
lower e<sup>-</sup>-e<sup>-</sup> repulsion

forming these bonds

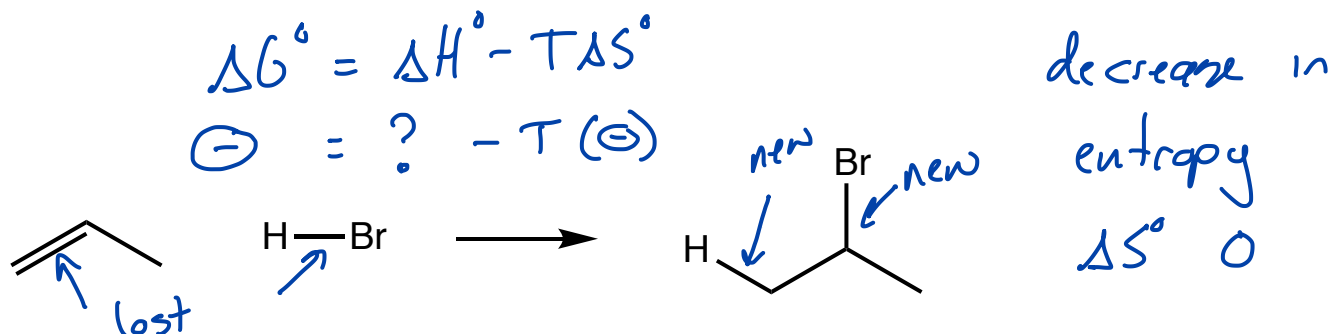
- releases energy
- stronger bonds on this side  
energy was released
- the molecules are lower  
in energy

# Describing a Reaction: Bond Dissociation Energies

$$\Delta G^\circ = -RT \ln K$$

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

$$\ominus = ? - T(\ominus)$$



For the reaction to proceed as written,  $\Delta G^\circ$  must be  $< 0$  or  $\neq 0$

The reaction is not being driven by an increase in entropy in the reaction, so...

It must be driven by a change in enthalpy...  
a release of energy to the universe

$$\Delta H_{\text{rxn}} = (\text{energy in to break bonds}) + (\text{energy out to make bonds})$$

$$(\Delta H_{\text{BDE}} \text{ reactants}) + (-\Delta H_{\text{BDE}} \text{ products})$$

bond dissociation energies is the amount of E required to break the bond

$$(C-C\pi + H-Br) - (C-H + C-Br)$$

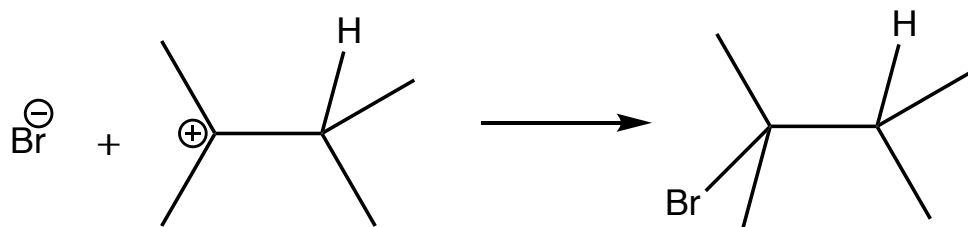
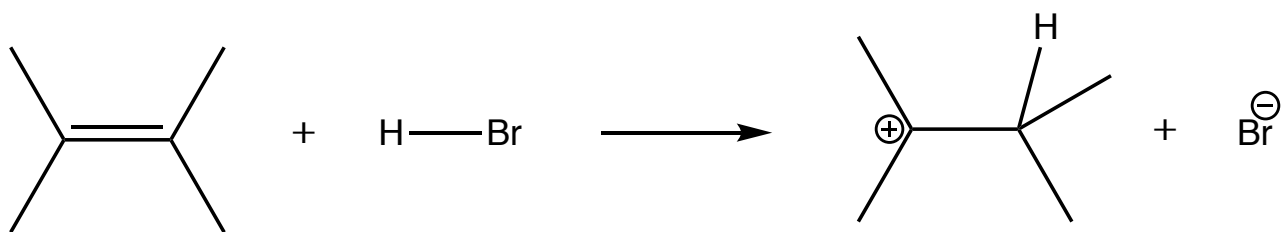
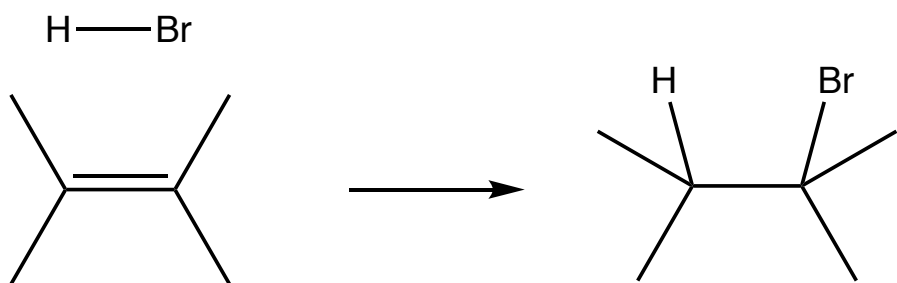
$$(312 + 366) - (421 + 294) = -37 \text{ kcal/mol}$$



Mechanisms: A hypothesis about how the reaction occurs

Section 6.9, 6.10

Mechanisms are like the recipe instructions; mechanisms are how a reaction occurs



# Mechanism and Reaction Coordinate Diagrams

# Section 6.9, 6.10

Reactant(s)

In this reaction the reactants are higher in energy

Product(s)

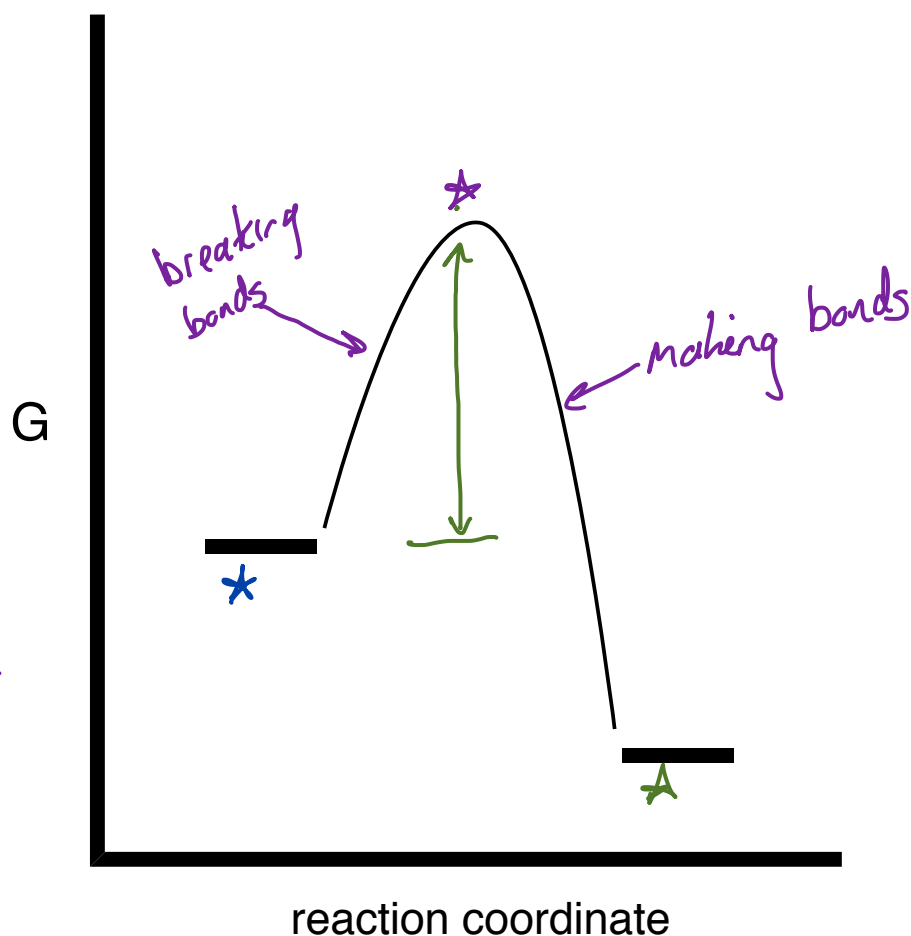
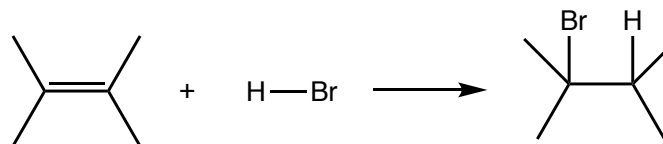
Lower than the products

Transition State

The highest energy point on the path from reactants to products  
- where bond breaking switches over to bond making

Intermediate

in this one step mechanism there is no intermediate



# Reaction Coordinate Diagrams: Thermodynamics

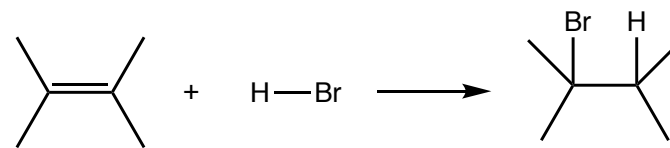
Section 6.9, 6.10

$\Delta G$  is the difference between the reactants + products

$$\Delta G = G_F - G_i$$

$$\Delta G = \text{smaller } \# - \text{larger } \# < 0$$

K will be ... large



Relationship between  $\Delta G$  and K

$$\Delta G = -RT \ln K$$

$$\ominus = \ominus \oplus \oplus \ln K$$

to be  $\oplus$  K must be larger than 1

