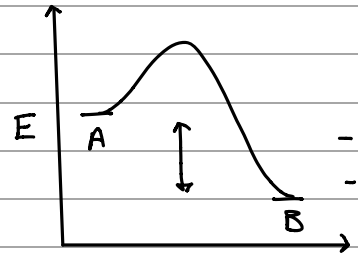
Part I: Energy

Gibbs Free Energy Equation: $\Delta G = \Delta H - T\Delta S$ (enthalpy, entropy)

$\Delta G = -RT \ln K_{eq}$ For: $A \rightleftharpoons B$ $K_{eq} = \frac{[B]}{[A]}$



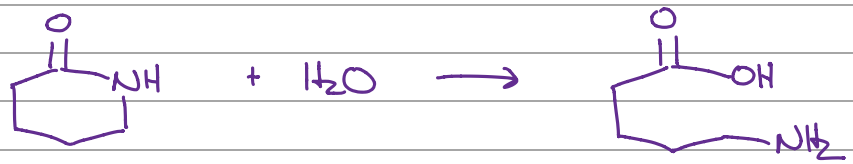
$-\Delta G$ = exergonic $+\Delta G$ = endergonic

$-\Delta H$ = exothermic $+\Delta H$ = exothermic

* Every 1.36 kcal/mol (~1.4) ΔG = factor of 10 in K_{eq}

$A \rightleftharpoons B$	ΔG	A:B	* At 298 K
	0	1:1	
	-1.4	1:10	
	-2.8	1:100	
	-4.2	1:1000	

Ex: What is the max yield of:



$\Delta G = +4.2$ kcal/mol

At best $\frac{1}{1000} \times 100\% = 0.1\%$ yield

Entropy (S)

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

- Disorder of the system
- Often ignored $\Delta G \approx \Delta H$
- Becomes increasingly important with ↑Temp.

Types:
- Translational
- Rotational
- Vibrational

} Degrees of freedom

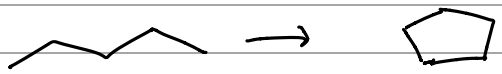
Translational = movement

Solid → low entropy gas → high entropy

A–B → A + B

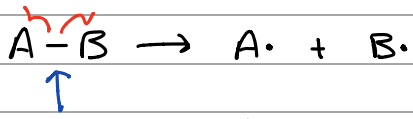
higher entropy

Rotational = number of accessible conformations



Higher Entropy

Enthalpy (H) - change in heat between system & surroundings
- change in temp of rxn vessel

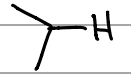
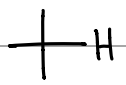


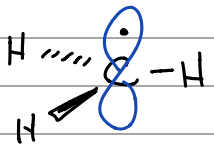
Homolytic Bond Dissociation Energy

Stronger bond = Higher BDE = less stable radicals

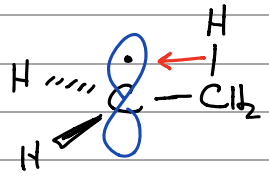
BDE Table
MPOC pg 72

Hydrocarbons:

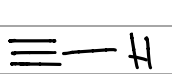
	BDE (kcal/mol)
H_3C-H	105
H_3C-CH_2-H	98
	95
	93



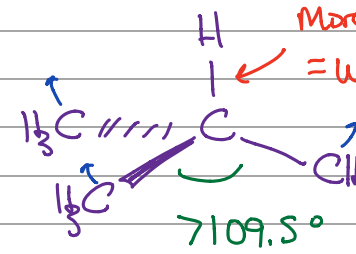
vs



hyperconjugation

Hybridization	BDE (kcal/mol)
	98
	110
	132

Increasing s-character = stronger bond



More p-char = weaker

>109.5°

= more s-char

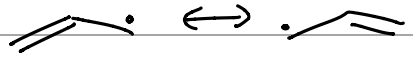
JOC 2006, 71, 1209

Heteroatoms	BDE (kcal/mol)
H_3C-H	104
H_2N-H	107
$HO-H$	119

Increasing e⁻ neg = Stabilized bonds

Resonance:	BDE (kcal/mol)
	98
	86

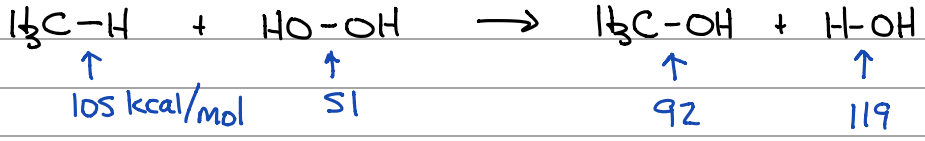
Stabilized radicals = weaker bonds



π-Bonds	BDE (kcal/mol)	
C–C	81	C=C π = 64 kcal/mol
C=C	145	← Breaking both σ + π
C–O	79	
C=O	173	C=O π = 94 kcal/mol

Hess's Law

- Estimation of ΔH from BDE



ΔH = broken − formed

= (105 + 51) − (92 + 119)

= 156 − 211 = **−55 kcal/mol**

But... tells us nothing about how fast this will occur.

Exothermic + enthalpically favored

More accrate measure = Heat of formation

ΔH_f = formation of a molecule from its elements

$3C + 4H_2 \rightarrow C_3H_8 + Heat$

For $A \rightarrow B$

$\Delta H_{rxn} = \Delta H_f(B) - \Delta H_f(A)$



ΔH_f	-29.9	-25.5	+18.8

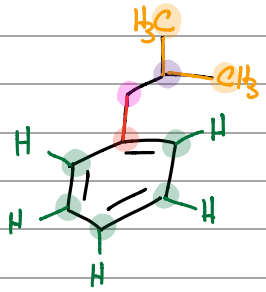
Benson's Additivity Rules (MPOC pg 81 = Chart)

- Predicting ΔH_f using group increments
- Ex: Adding a "CH_2" to a chain ↑ ΔH ~ 5 kcal/mol

$H_3C-CH_3 \longrightarrow$ 

-20 +2(5) -30 kcal/mol

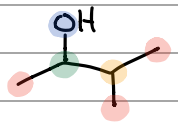
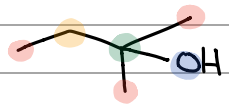
* Learn to use Chart



C type attached

5	$C_B-(H)$	5(3.30)
1	$C_B-(C)$	5.51
1	$C-(C_B)(C)(H)_2$	-4.86
1	$C-(H)(C)_3$	-1.90
2	$C-(H)_3(C)$	-10.20
		-5.15 kcal/mol

There are correction factors
- Steric Strain
- ring Strain
- Cis/trans

Compare:  vs 

3	$C-(H)_3C$	3(-10.20)	3	$C-(H)_3C$	3(-10.20)
1	$O-(C)(H)$	-37.9	1	$O-(C)(H)$	-37.9
1	$C-(C)_2(H)(O)$	-7.2	1	$C-(C)_3O$	-6.6
1	$C-(C)_3(H)$	-1.9	1	$C-(C)_2(H)_2$	-4.93
		-77.6 kcal/mol			-80.03 kcal/mol

* more stable

Chem Rev. 1969, 69 279