# Topic 3: Energy

$$\Delta G^{\circ}_{AB} = -RT \ln \frac{[A]}{[B]}$$

**Skim:** F. A. Carey & R. J. Sundberg *Advanced Organic Chemistry, Part A: Structure and Mechanisms*. 5th Ed. **Ch. 3**

**Reference:**

Bond Dissociation Energies: Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.*, **2003**, *36*, 255.

NIST Webbook has lots of thermochemical enthalpy data (**H**f): http://webbook.nist.gov/cgi/cbook.cgi?Name=toluene&Units=SI

C. J. Walter and J. K. M. Sanders "Diels-Alder Reaction; Influence of Entropy": http://www.ch.ic.ac.uk/motm/porphyrins/introDA.html

## Exponentials and Logarithms are NOT INTUITIVE

- **How much more expensive?**
- **How much faster?**

2017 Huffy Camden Bicycle

vs

2017 Ferrari Aperta

1 kcal/mol  5 kcal/ mol  10 kcal/mol  20 kcal/ mol

- **How man liters of gas will fill your tank?**


$e^4$ vs. $e^6$

## RATIOS are Intuitive: Free Energy is a Predictor of Ratios

■ You'll gain insight into chemical phenomena by converting energy (in kcal/mol or kJ/mol) into numerical ratios. Even a child can think in factors of 10. Recall the Gibbs relationship: $\Delta G° = -RT \ln K_{eq}$:

$$A \rightleftharpoons B \qquad K_{eq} = \frac{[B]}{[A]}$$

| A | : | B | ΔG° |
|---|---|---|---|
| 1 | : | 1000 | -4.2 |
| 1 | : | 100 | -2.8 |
| 1 | : | 10 | -1.4 |
| 1 | : | 1 | 0 kcal/mol |
| 10 | : | 1 | 1.4 |
| 100 | : | 1 | 2.8 |

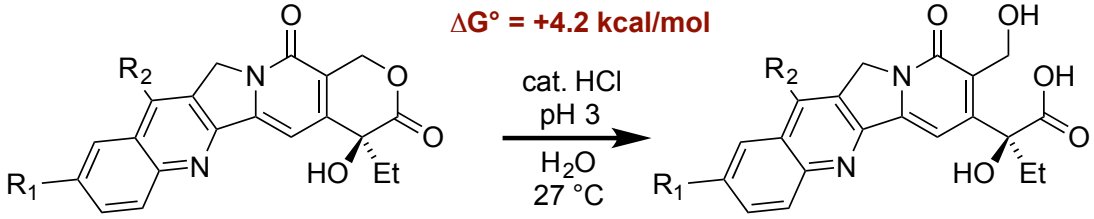
**RULE:**

**1.4 kcal/mol**
**II**
**factor of 10**
**in $K_{eq}$ or k**

**for experts**

**0.4 kcal/mol**
**II**
**factor of 2**
**in $K_{eq}$ or k**

■ Predict the yield for the following (equilibrium) reaction.



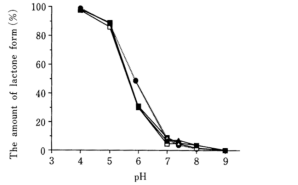
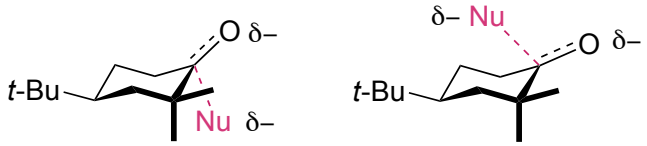




Fig. 6. pH–Amount Profile for Lactone Form of CPT-11
0.2 μg/ml: ○, 32 °C. 2.0 μg/ml: ●, 32 °C. 20.0 μg/ml: □, 27 °C; ■, 32 °C; △, 37 °C; ▲, 42 °C.

Akimoto K, Kawai A, Ohya K
*Chem. Pharm. Bull.* **1994**, *42*, 2138.

■ Estimate the difference in energy of the transition states.

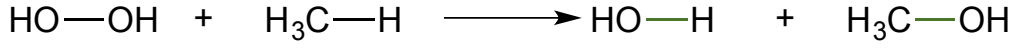

Wu, Y.-D.; Houk, K. N.
*JACS* **1987**, *109*, 908

You don't know how EXACTLY how much of the equatorial product was present, but you do know that it was ≤5%. **Use that information**. Therefore the ratio of products was 95: <5 or >20:1 and $\Delta G^{‡} > 1.8$ kcal/mol.

# Using BDEs to Estimate Enthalpy Differences

■ Drilling for oil often releases $CH_4$. It is cheaper to burn than ship the gas. Why can't we convert $CH_4$ gas into a useful liquid? Is it uphill in energy?

methane flare during oil drilling




■ Hard to calculate $\Delta G = \Delta H - T\Delta S$

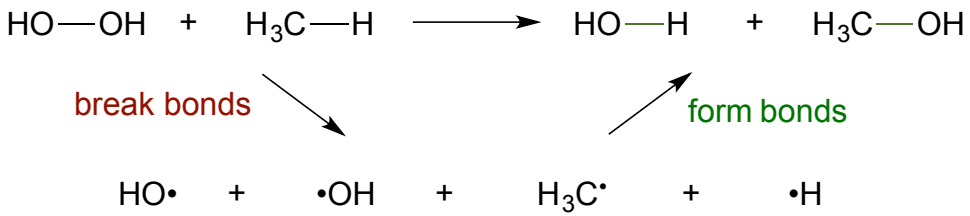
■ Easy to estimate $\Delta H$ but hard to estimate - $T\Delta S$

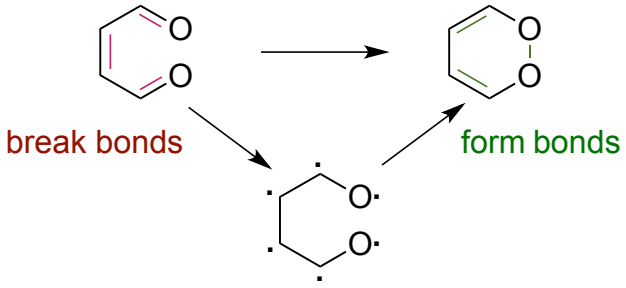
■ $\Delta G \approx \Delta H$ (ignore $T\Delta S$) if we compare similar things:

- 2 reactants vs 2 products
- similar transition states

etc.

■ Applying **Hess' Law**: $\Delta H$ = **E**(bonds broken) - **E**(bonds formed)



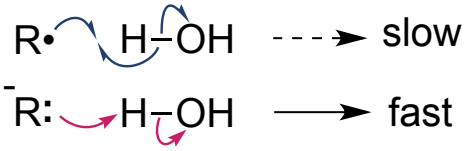




***Hess**: The enthalpy change accompanying a chemical transformation is independent of the mechanism or number of steps.*

■ Reactions are favorable if you **break weak bonds** and/or **form strong bonds**

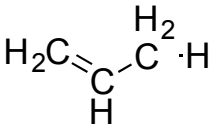
# Bond Dissociation Energies - Memorize

■ **Bond STRENGTH refers to B.DE. = homolysis**


**Memorize:**

**COMMON BONDS**

| | | | | |
|---|---|---|---|---|
| C-C–H | 98 | C–C | 81 | 64 = $\pi_{cc}$ |
| C=C–H | 110 | C=C | 145 | |
| C≡C–H | 131 | C≡C | 198 | |
|  | 87 | C–O | 79 | 94 = $\pi_{co}$ |
| | | C=O | 173 | |

**STRONG SINGLE BONDS (>100 kcal/mol)**

| | |
|---|---|
| RO–H | 110 |
| C≡C–H | 131 |
| Si—F | 141 |
| $Ph_3P^+-O^-$ | 136 |

**WEAK SINGLE BONDS (<70 kcal/mol)**

| | |
|---|---|
| C—Si | 69 |
| C—Br | 67 |
| C——I | 57 |
| O—Br | 53 |
| N—Cl | 48 |

**X-X BONDS = ALWAYS WEAK**

| | | | |
|---|---|---|---|
| $H_3C–CH_3$ | 88 | Cl—Cl | 58 |
| $H_2N–NH_2$ | 65 | Br—Br | 46 |
| HO–OH | 51 | I————I | 36 |
| F–F | 38 | | |

■ Covalent bonds *between* electronegative atoms will be weak.

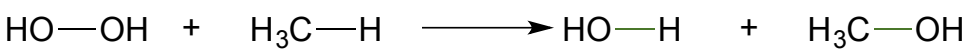
■ BDEs for X-H bonds correlate with X• radical stability

■ Looonger bonds are weeeeaker

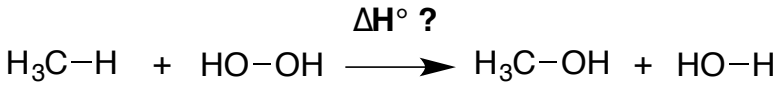
■ $\pi_{C=C}$ is weak … but **$\pi_{C=O}$ is strong**

## Estimating $\Delta H_{rxn}$ using Hess' Law

■ We can't make methanol from methane, but why not? Is it a thermodynamic problem?




■ **Hess' Law**: $\Delta H°_{rxn} \approx \Sigma$ **BDE**(bonds **broken**) – $\Sigma$ **BDE**(bonds **formed**)




Broken:

| | |
|---|---|
| C–H | 98 |
| O–O | 36 |
| | 134 |

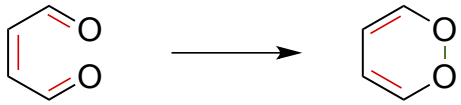
(104 better)

Formed:

| | |
|---|---|
| C–O | 79 |
| O–H | 110 |
| | 189 |

**ΔH** ~ 134 – 189
= - 65 kcal/mol

$\Delta H_f°$(gas) *= - 55 kcal/mol*




Broken

| | |
|---|---|
| πCO | 94 |
| πCO | 94 |
| πCC | 64 |
| | 252 |

Formed

| | |
|---|---|
| σOO | 51 |
| πCC | 64 |
| πCC | 64 |
| | 179 |

**ΔH =** 252 - 179
= +73 kcal/mol UPHILL!

■ **Caveats:**

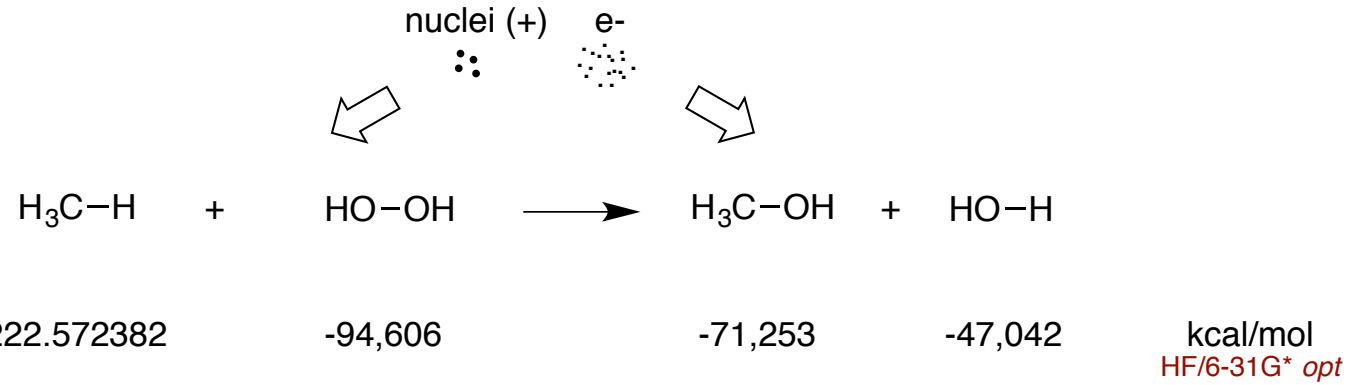
Hess' law is only as good as your BDEs.

Doesn't account for strain & aromaticity

**Doesn't account for entropic costs**; e.g., A+B -> C vs A -> D

## Energies From Computer Calculations ~ Enthalpies

■ *Electronic structure calculations* give you the energey difference between nuclei and electrons and infinite separation versus nuclei at specified positions with electrons in optimized molecular orbital configuraitons. Use ΔE from electronic structure calculations is similar to ΔH°.

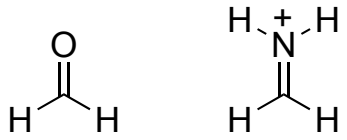



**ΔH°** ≈ **ΔE** (products - reactants) = - 55 kcal/mol

■ Natural gas ($CH_4$) is a by-product of most oil wells. It is usually cheaper to burn $CH_4$ at the well than to transport it somewhere useful. While it is thermally favorable to oxidize methane to methanol, there is no easy way to stop the oxidation from going all the way to $CO_2$.

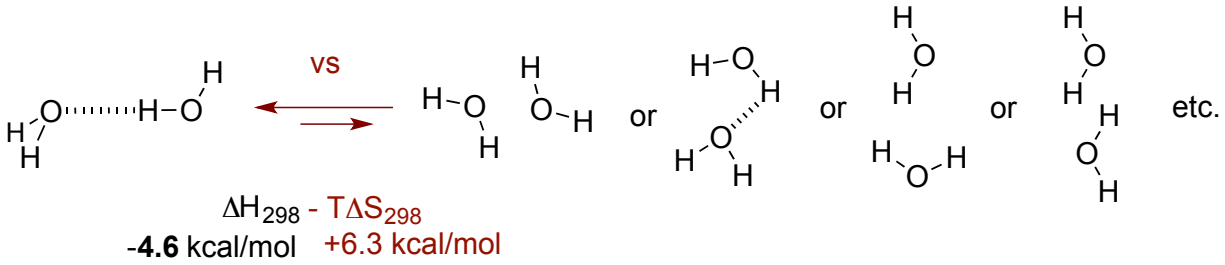
■ **Electronic structure calculations can help you rationalize and predict regiochemistry, stability, etc.**

Which is more stable?



# Entropy: -TΔS

■ In order to conceptualize **entropy**, one must simultaneously visualize **all possible states of a system**:

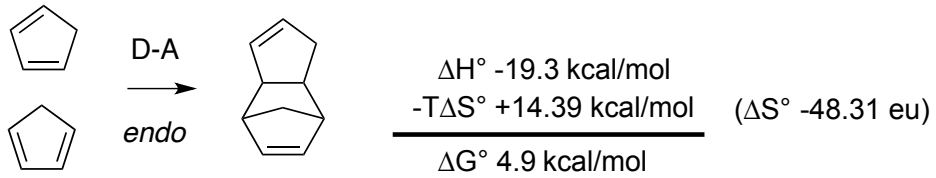



*J. Phys. Chem. A* **2006**, *110*, 5411

Only 1 out of 16 $H_2O$ molecules exists as an ideal H-bond at equilibrium.

■ **Pairing up molecules costs energy, up to 14 kcal/mol** If you take a random solution of two compounds, both at 1 M concentration, and pair the molecules up like ballroom dancers (no bonding) it will cost up to +14 kcal/mol.

A Diels-Alder reaction looks massively favorable, until you consider the entropic cost in the T.S.




**ΔS°**
big for ballroom dancing
small for club dancing

Page, M. I.; Jencks, W. P. *Proc. Nat. Acad. Sci.* **1971**, *68*, 1678

■ The entropy term, -TΔ*S*, is temperature dependent.
As one raises the temp., molecules will begin to adopt less favorable trajectories, positions, and shapes.

■ **Intramolecular reactions involving 5 and 6 membered rings T.S.s are often fast.**