

*Exercise 11***Energies in Perspective**

A Fig. X11-1

B Fig. X11-2

C Fig. X11-3

- A) James Prescott Joule (1818 - 1889)  
<http://www.msu.edu/~brennem2/joule/home.htm>
- B) Hermann Ludwig Ferdinand von Helmholtz (1821 - 1894)  
<http://www-groups.dcs.st-and.ac.uk/~history/Mathematicians/Helmholtz.html>
- C) Josiah Willard Gibbs (1839 - 1903)  
<http://www-groups.dcs.st-and.ac.uk/~history/Mathematicians/Gibbs.html>

It is valuable to have a feel for the magnitudes of the energy changes that accompany physical and chemical changes of organic compounds. Typical energy differences range from the relatively small 8 kJ/mol difference between simple conformers to the approximately 400 kJ/mol required to break carbon to carbon or carbon to hydrogen bonds. The value of the energy required for a process gives you insight regarding how fast a process will occur or where the equilibrium will lie at various temperatures for the process.

Organic chemists commonly invoke inductive, resonance, steric, hyperconjugative and hybridization effects to explain how structural changes influence physical and chemical processes. Strictly speaking, the discussion should focus on how the structural variables affect the energy change of the process. For example, 1-propene undergoes addition of hydrogen bromide to give predominantly 2-bromopropane. Markovnikov's rule is used to explain this observation. Going a step further, we can explain Markovnikov's rule by saying that electrophilic addition of a proton to the primary carbon gives a secondary carbocation which is more stable than the primary carbocation that results from protonation at the secondary carbon. It is then necessary to invoke the Hammond postulate because the rate of formation of the carbocation depends on the energy of the transition state which usually correlates with the energy of the intermediate carbocation. Thus, it would be informative to know the energetics behind the statement that tertiary carbocations are more stable than secondary which are more stable than primaries. The table and exercises below are intended to give you a sense of the magnitudes of energy effects and their relative influence on equilibria and rates.

<u>typical energies</u>	<u>kJ/mol</u>
nmr	$8 \times 10^{-6}$ - $4 \times 10^{-4}$ (depends on field strength, type of nucleus)
microwave	0.0012 - 1.2 (overlaps with ir)
infrared	0.12 - 170 (overlaps with microwave)
fundamental	4.8 - 48
dipole - dipole attractions	0 - 3
dispersion forces	1 - 40
heat of fusion	2 - 25
conformational changes	7 - 30
hydrogen bonds	10 - 40
heat of vaporization	20 - 60
inductive effects	0 - 25 highly dependent on functional group and nature of process
resonance	0 - 60 highly dependent on functional group and nature of process

<u>typical energies</u>	<u>kJ/mol</u>
aromaticity	80 - 150
visible	170 - 300
ultraviolet	300 - 1200
<b>Bonds</b>	
O-O	160 - 220
C-C, H, O	320 - 460
C-Cl	280 - 400
C-Br	230 - 300
O-H	370 - 500
C=C	~720
C≡C	~960

Below, the dependence of the position of equilibrium on the free energy difference between two isomers, the dependence of first order half lives on the free energy of activation and the dependence of rate ratios on activation energy differences will be considered and graphs presented as a basis for discussion.

For the equilibrium  $A = B$ . To determine the %B, it has been assumed that B is less stable than A. The equilibrium constant has been calculated from  $\Delta G = -RT\ln K_{eq}$  and  $\%B = K/(K + 1)$  at two temperatures, 25°C and 200°C. (If B is more stable than A, then the vertical axis can be used to represent the %A and the x axis should be considered to be negative values of  $\Delta G$ .)

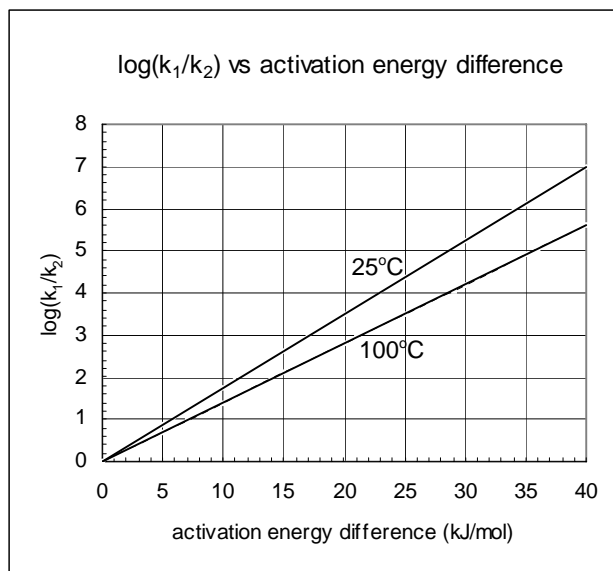
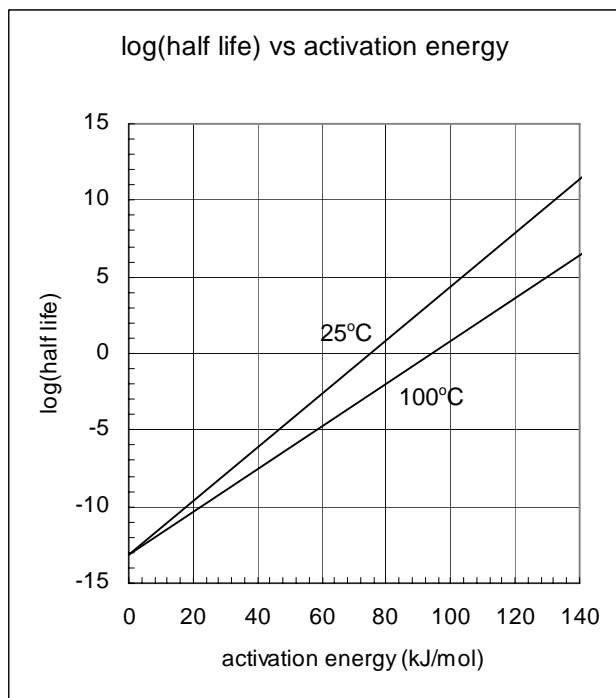
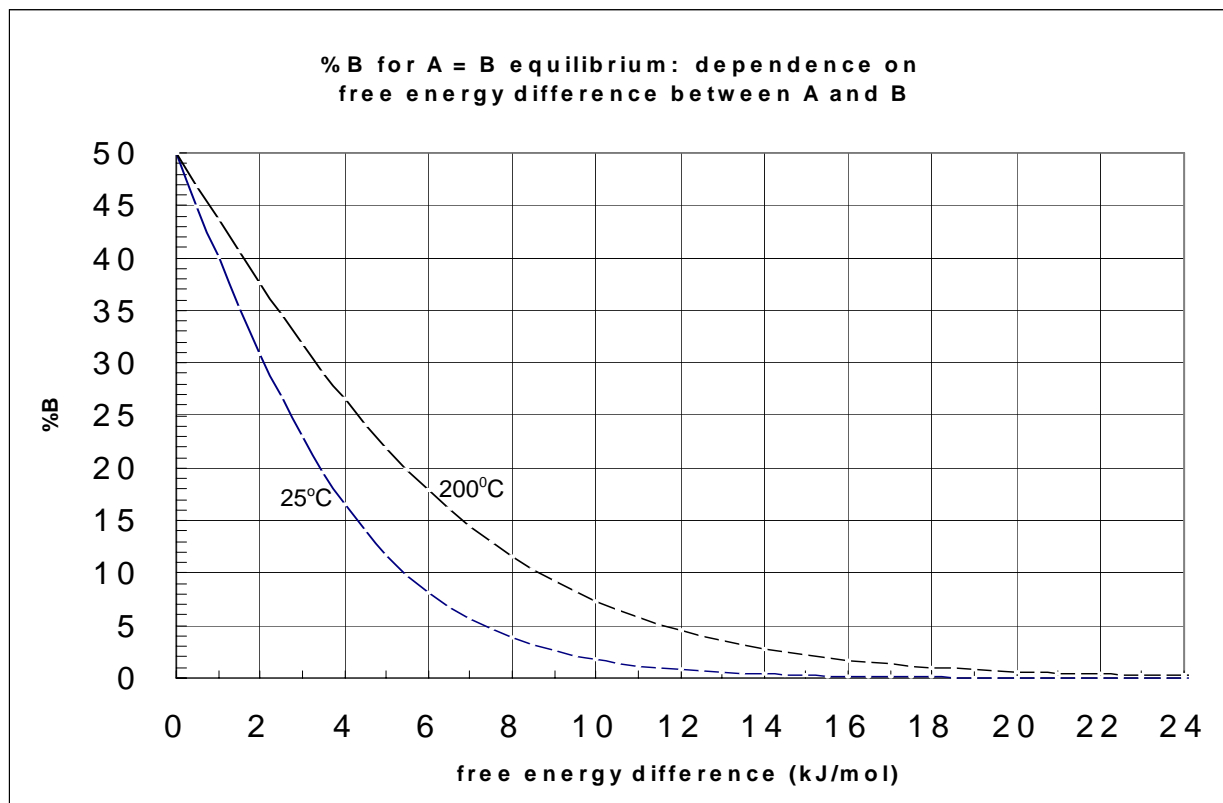
Half life of a first order reaction. The second graph gives the logarithm (log) to the base 10 of the half life as a function of the activation energy. The half life has been calculated from the rate constant k according to  $\tau = 0.693/k$  with  $\tau$  in seconds. The rate constant k has been calculated from  $k = Ae^{-E^*/RT}$ . For the graph included here, it has been assumed that  $A = 1 \times 10^{13}$ . Thus, **the graph is not a general behavior** but probably an average behavior. The two lines represent the values at 25°C and 100°C.

Rate ratio of two first order reactions. The final graph gives the logarithm of the ratio of the rates of two reactions from the same starting material along two different pathways to different products. The assumption has been made that the A values for both pathways are the same. The two lines represent temperatures of 298°C and 373°C.

Use the accompanying graphs and the equations [ $\Delta G = -RT\ln K_{eq}$ ,  $\%B = K/(K + 1)$ ,  $R = 8.314 \times 10^{-3}$  kJ/mol,  $\ln(k_1/k_2) = \Delta E^*/RT$ ] to determine solutions to the following problems.

Equilibrium questions:

1. The eclipsed form of ethane is about 12.6 kJ/mol less stable than the staggered form. As we shall observe later, rotation is very rapid at room temperature. If an equilibrium did exist between the staggered and eclipsed form, what percentage would be in the eclipsed form at 25°C and 200°C?
2. Alkyl substituted cyclohexanes with the alkyl group in the equatorial position are about 7.1, 7.5, 8.8 and 21 kJ/mole more stable respectively for methyl, ethyl, isopropyl and t-butyl than the conformers with the alkyl in the axial position. Approximately what percentage of each of the four alkyl cyclohexanes have the alkyl group in an axial position at 25°C? Explain why the percentage decreases in this series.



- Halogen substituted cyclohexanes with the halide group in the equatorial position are about 0.8, 2.1, and 2.5 kJ/mole respectively for fluoro, chloro and bromo more stable than the conformers with the halide in the axial position. Approximately what percentage of each of the three halo cyclohexanes have the halide group in an axial position at 25°C?
- The chair is about 23 kJ/mole lower in energy than the twisted boat conformation. Approximately what percentage of cyclohexane is in the twisted boat conformation at 25°C?
- If two reaction pathways from the same starting material have an activation energy difference of about 5 kJ/mol, the pathway with the lower activation energy will go about how many times faster than the higher activation energy reaction at 25°C?
- The difference in energy for the nuclear spin states of a hydrogen in a 60 MHz field is  $2.4 \times 10^{-5}$  kJ/mol. In a magnetic field, to 2 significant figures, what percentage of the spins are in the upper state at 25°C?
- Para position bromination of anisole is about  $2 \times 10^9$  times faster for than for benzene at 25°C. Does this rate factor fall within the range presented above for the magnitude of resonance effects? If so, explain why this is a resonance effect.
- The rate of deuterium exchange at the para position of toluene is about 300 times faster than for exchange of a benzene hydrogen at 25°C. Does this rate factor fall within the range presented above for the magnitude of inductive effects? if so, explain how an inductive effect applies to this reaction.
- The carbonyl absorbs at about  $1700 \text{ cm}^{-1}$  (20.3kJ/mol). Approximately what percentage of carbonyl molecules should be in their lowest vibrational state at 25°C, 200°C?
- The energies of activation for the decomposition of hydrogen peroxide and di-*t*-butyl peroxide are about 75 kJ/mol and 159 kJ/mol respectively. What is the half life of hydrogen peroxide at 25°C? Is di-*t*-butyl peroxide stable at 25°C? Explain your answer.
- Carboxylic acids have pKa values around 5 at 25°C. What is the very approximate free energy difference between the left and right sides of the following reaction for a carboxylic acid:  
$$\text{HA} + \text{H}_2\text{O} = \text{A}^- + \text{H}_3\text{O}^+$$
- What is the minimum value for the activation energy of a decomposition if the compound is going to have a half life at 25°C of 1 day? Will there be a problem storing compounds with activation energies less than this amount?
- The twisted boat is 23 kJ/mole less stable than the chair conformation of cyclohexane but the  $E^*$  for the conversion of the chair to the twist boat is 45 kJ/mol. Will the chair undergo a conformational change to the twisted boat at 25°C? What is the half life for this change? How will a temperature increase affect this rate?
- If a compound absorbs ultraviolet energy, is it possible that a (photo)chemical reaction could result?
- The percent of enol present in neat acetone is estimated to be  $2.4 \times 10^{-4}\%$ . What is the energy difference between the carbonyl and enol forms of acetone?

16. The percent of the enol form of 2,4-pentanedione present is solvent dependent and varies from 15% in water to 92% in hexane. What is the energy change in kJ/mole as a result of changing from water to hexane? Explain why the dicarbonyl is favored in water but the enol in hexane.
17. Very approximately, it can be calculated from the spectra in *Exercise 4* that the zero point energy difference between a C-H and a C-D bond is  $400\text{ cm}^{-1}$  (5 kJ/mol). For a reaction in which the C-H bond completely cleaves going from the starting point to the transition state, how much slower should the rate ratio [C-H/C-D] for the bond cleavage be (at 25°C)? Note that the answer to this is the approximate value for the maximum isotope effect observable.
18. The rotational barrier for ethane is about 12 kJ/mol. About how fast is the rotation of the C-C bond of ethane at 25°C? How will a temperature increase affect this rate?