A tray of ice cubes is left out on the counter in a room, and the ice cubes melt. If the room is a closed system, what is the total enthalpy of the system (room + ice)? The entropy of the system? What about the free energy? Is this process thermodynamically favorable? How would the temperature of the ice, now water, and the room compare?
Q27

(a) Using the following bond strengths, calculate the $\Delta H^o$ for each of the reactions.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average Strength (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>83</td>
</tr>
<tr>
<td>C=C</td>
<td>146</td>
</tr>
<tr>
<td>C-H</td>
<td>99</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>57</td>
</tr>
<tr>
<td>H-Cl</td>
<td>102</td>
</tr>
<tr>
<td>C-Cl</td>
<td>78</td>
</tr>
</tbody>
</table>

(i) $\text{CH}_3\text{-CH}=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CH}_3\text{-CHCl-CH}_2\text{Cl}$

(ii) $\text{CH}_3\text{-CH}=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl-CH}=\text{CH}_2 + \text{HCl}$

(b) One of these reactions as a $\Delta S^o < 0$ (-35 cal mol$^{-1}$) and the other has a $\Delta S^o = 0$. Assign the two to the equations, and give your reasoning.

(c) Based on both $\Delta S^o$ and $\Delta H^o$ calculate $\Delta G^o$ for each reaction at $30^\circ\text{C}$ and $800^\circ\text{C}$. Are the reactions favorable at these temperatures?

Q28

I. In each of the following equations label the Brønsted acid and base, on both sides.

II. Also, determine which way the equilibrium lies, left or right.

III. From the given $pK_a$ of each acid calculate the equilibrium constant, $K_{eq}$. ($pK_a \text{ H}_3\text{O}^+ = -1.7$)

$$\text{H}_2\text{O} + \text{HF} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$$

a. $pK_a = 14$ 3.45

$$\text{H}_2\text{O} + \text{HCN} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$$

b. $pK_a = 14$ 9.2
Q29
In problem 28 use electron pushing arrows to show what is occurring, looking from left to right.

Q30
Determine whether each of the following species is a Lewis acid or Lewis base. Demonstrate this ability with an electron arrow pushing mechanism.

(a) AlCl$_3$  (b) H$_2$O  (c) ZnCl$_2$  (d) ScCl$_3$  (e) N$_3^-$  (f) CH$_3$CH$_2$O$^-$

Q31
For each of the following molecules denote the bond polarities, $\delta^+$ or $\delta^-$. 

(a)

(b)

(c)
Q32

Identify whether each species is nucleophilic or electrophilic

(a) Fluoride anion, $F^-$ (b) Hydride anion, $H^-$ (c) acid chloride, $\text{CH}_3\text{COCl}$ (d) $\text{ScCl}_3$ (e) $\text{N},\text{N}'$-diethylcarbodiimide

Q33

Identify the functional groups present in each molecule below.

(a)
Q34

Determine, based on Coulombic interaction, if the following are likely to react. No reaction is a possibility.

(a) ammonia (NH$_3$) and cyclohexanone (b) H$^+$ and ethanol (c) azide (N$_3^-$) and bromoethane (d) nitrogen (N$_2$) and propane (e) triethylamine and H$^+$

Q35

Draw the electron arrow pushing mechanism of the potential interaction in problem 34.
Q36

Name each of the following compounds according to IUPAC.

(a) 

(b) 

(c) 

(d) 

(e)
Q37

Draw the following structures from the name

a. 2,3,4-trimethylpentane  
b. 4-ethyl-3,4,5,5-tetramethylnonane  
c. neopentane  
d. 2,2,4,4-tetramethylpentane  
e. 7-pentyltridecane  
f. 2,3,4,5,6-pentamethylheptane

Q38

Draw the structures that correspond to the following names, correct any names that are not in accord with the rules of systematic nomenclature.

a. 3-methyl-2-fluoropentane  
b. 1-chloro-3-bromo-2,2-dimethylbutane  
c. 2-ethyl-2-chloro-4,5-methylhexane  
d. 3-methylpentane

Q39

Draw all possible isomers of C₆H₁₄

Q40

In each of the following compounds identify each carbon as either primary (1°), secondary (2°), tertiary (3°), or quaternary (4°).

(a) cyclopentane  (b) 3,3,5,5-tetraethylheptane  (c) methylcyclopentane  (d) 2,3,4-trimethylpentane
Q41

Identify each of the following alkyl groups as primary, secondary, tertiary, or quaternary. This is based off of the 1 position in the alkyl group, connected to the dashed bond. Also, give its IUPAC name.

(a)

(b)

(c)

(d)

Q42

Does the molecule in (a) contain a tertiary carbon? Does the molecule in (b)? Explain why.

(a)

(b)
Q43

Based on the following structures, think about the London dispersion forces and how that would affect the boiling point. Rank the following compounds in order from lowest to highest boiling point.

(a) 2,3,4-trimethylhexane (b) nonane (c) 2,3-dimethylpentane (d) 3-methylheptane

Q44

Draw the lowest energy Newman projection of the following:

a. 2,3-dimethylbutane C2-C3  
  b. 2,2-dimethylbutane C2-C3  
  c. 2-methylpentane C2-C3  
  d. 2-methylpropane

Q45

Draw the energy diagram, Energy vs. Torsional angle of the C2-C3 bond of butane, rotating increments of 60° starting at the lowest energy conformation. Also draw the Newman projection of each.

Q46

Given that 85% of all molecules are anti- and 15% of all molecules are eclipsed conformation along a certain C-C bond, take for example C2-C3 of butane, draw the two Newman projections. Calculate the ΔG° value using ΔG°=-RTln(K), at 25°C where R=1.986 cal deg⁻¹ mol⁻¹. Does the given information make sense? If not, in what ways?

Q47

Identify the functional groups in each compound.

(a) 

(b) (aspirin)
Q48

Name the alkyl group as if the dashed line were where it was connect to the rest of the molecule, state whether it is primary, secondary, or tertiary.

(a)

(b)

(c)
Q49
Calculate the new value of k, relative to the initial value, using the Arrhenius equation with increases of 10, 25, and 60°C. Assume the initial temperature is 300°C.

Where $E_a$ is the following:

(a) 10 kcal mol$^{-1}$  (b) 25 kcal mol$^{-1}$  (c) 50 kcal mol$^{-1}$

Q50
An alternate form of the Arrhenius equation involves taking the natural logarithm of the equation giving the following.

$\ln k = \ln A - \left(\frac{E_a}{RT}\right)$

What plot involving both $k$ and $T$ would yield a straight line? Give some characteristics of the line, slope and intercept.

Q51
For question 35 draw the product that would result from the arrow pushing mechanism. Make sure not to draw a pentavalent carbon in (a) (use the oxygen atom) and (b) (substitute the bromine and have it leave).

Q52
Given that the Gibbs free energy is given by the following equation $\Delta G = \Delta H - T\Delta S$, fill in the table that yield a spontaneous process ($\Delta G < 0$)

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than Zero</td>
<td>???</td>
</tr>
</tbody>
</table>
Under certain conditions the two following reactions are second order, proportional to both reactants concentrations. Write the rate law for each reaction, and similar to in problem 35 draw the structures with any electrostatic interactions.

(a) 
\[
\text{Br} + \text{O}^\ominus \rightarrow \text{O} + \text{Br}^\ominus
\]

(b) 
\[
\text{Br} + \text{C} \rightarrow \text{C} + \text{Br}^\ominus
\]

Q54

Which of the following is true about 2,3-dimethylbutane?

a. There are 10 primary H's
b. There are 6 times as many primary H's as there are tertiary H's
c. There are 3 tertiary C's
d. There are no primary C's

Q55

Using \(\Delta G = \Delta H - T\Delta S\), where \(\Delta H = -1000\ \text{cal/mol}\) and \(\Delta S = -2\ \text{cal/mol}\) at \(T = 200\ \text{K}\), which of the following is true.

a. The reaction is endothermic
b. The reaction is not spontaneous
c. The reaction is exergonic
d. It is likely that the reaction involves one reactant and yields two products.
Q56

In 2-methylbutane what bond angles exist?

a. $90^\circ$
b. $120^\circ$
c. $180^\circ$
d. $109.5^\circ$

Q57

Which conformation describes the following Newman projection? Which one would be the lowest in energy?

![Newman projection](image)

a. *anti* eclipsed
b. *anti* gauche
c. *gauche* staggered
d. *anti* staggered

Q58

The following molecule, isatin, has all of the following functional groups except for:

![Isatin](image)

a. aromatic ring
b. ketone
c. aldehyde
d. amide
Solutions

S26

The enthalpy of the system is zero, since the change is cancelled out by the ice gaining heat and the room losing heat. However, the entropy does increase and so the free energy decreases. This process is thermodynamically favorable as the free energy decreases. The end temperature of the ice and water would be equal.

S27

(a) $\Delta H^0 = \text{Bonds Broken} - \text{Bonds Formed}$

(i) $\Delta H^0 = (\text{C}=\text{C} + \text{Cl}-\text{Cl}) - (2\ \text{C}-\text{Cl} + \text{C}-\text{C})$

$= (146 + 57) - (2\times78 + 83) = -36 \text{ kcal mol}^{-1}$

(ii) $\Delta H^0 = (\text{C}-\text{H} + \text{Cl}-\text{Cl}) - (\text{C}-\text{Cl} + \text{H}-\text{Cl})$

$=(99 + 57) - (78 + 102) = -24 \text{ kcal mol}^{-1}$

(b) Reaction (i) involves the combination of two molecules into one. Fewer numbers of products concentrates the energy, and therefore leads to a negative $\Delta S^0$ value. Reaction (ii) starts with two molecules and results in two molecules. There is no change in the entropy, and so $\Delta S^0=0$.

(c) The two above values can be used to find the change in the Gibbs Free Energy using the following equation.

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

(i) at $30^\circ C$, or $(30 + 273.15)=303.15 \text{ K}$

$\Delta G^0 = -36 - 303.15(-35\times10^{-3}) = -25 \text{ kcal mol}^{-1} \text{ Favorable}$

at $800^\circ C$, or $973.15 \text{ K}$

$\Delta G^0 = -36 - 1073.15(-35\times10^{-3}) = +1 \text{ kcal mol}^{-1} \text{ Not Favorable}$

(ii) at $30^\circ C$

$\Delta G^0 = -24 - 303.15(0) = -24 \text{ kcal mol}^{-1} \text{ Favorable}$

at $700^\circ C$

$\Delta G^0 = -24 - 1073.15(0) = -24 \text{ kcal mol}^{-1} \text{ Favorable}$
(a) (i) H₂O=Weaker Base HF= Weaker Acid; H₃O⁺= Stronger Acid F⁻=Stronger Base

(ii) From above, the equilibrium would lie to the left

(iii) Using the pKa we can find the Ka for each acid, Ka=10⁻^pKₐ HF Kₐ=10⁻³.45 and H₃O⁺ Kₐ= 10⁻¹.7

Kₐ HF= [F⁻][H⁺]/[HF] and Kₐ H₃O⁺=[H⁺][H₂O]/[H₃O⁺] and Kₑq=[H₃O⁺][F⁻]/[H₂O][HF], from this we can see that Kₑq= Kₐ HF/Kₐ H₃O⁺ or 10⁻³.45/10⁻¹.7 = 7.08x10⁻⁶. This makes sense because the favors the left, so calculating the equilibrium to the right would mean a very small equilibrium constant.

(b) (i) H₂O=Weaker Base HCN=Weaker Acid; H₃O⁺=Stronger Acid CN⁻=Stronger Base

(ii) From part (i), the equilibrium would lie to the left.

(iii) Kₐ H₃O⁺=[H⁺][H₂O]/[H₃O⁺]= 10⁻¹.7 and Kₐ HCN= [CN⁻][H⁺]/[HCN]= 10⁻⁹.2 and the Kₑq= Kₐ HCN/Kₐ H₃O⁺ = 10⁻⁹.2/10⁻¹.7 = 1.26x10⁻¹¹, the case is the same as the previous problem. The equilibrium constant for the reaction as drawn, left to right, is very small.

(c) (i) CH₃COOH=Weaker Acid F⁻=Weaker Base; CH₃COO⁻=Stronger Base HF=Stronger Acid

(ii) Due to part (i), the equilibrium would lie to the left.

(iii) Kₐ CH₃COOH= [H⁺][CH₃COO⁻]/[CH₃COOH]=10⁻⁴.7 Kₐ HF= [H⁺][F⁻]/[HF]=10⁻³.45 This results in Kₑq=Kₐ CH₃COOH/Kₐ HF= 10⁻⁴.7/10⁻³.45 =5.62x10⁻²

(d) (i) H₃BO₃= Equally Acid NH₃=Equally Basic; H₂BO₃⁻=Equally Basic NH₄⁺=Equally Acidic

(ii) The reaction equilibrium does not lie to either side. H₃BO₃ and NH₄⁺ are equally acidic according to their pKa

(iii) If the Kₑq were calculated it be equal to 1. 10⁻⁹.3/10⁻⁹.3=1.

S29

(a)

(b)
(a) AlCl₃ is a Lewis acid. Aluminum is electron deficient, and with three electronegative halogens attached, the aluminum center is an electron acceptor.

(b) H₂O is a Lewis base. The oxygen has two lone pairs of electrons, and is thus an electron donor.

(c) ZnCl₂ is a Lewis acid. The zinc center is Zn²⁺, losing two electrons from the 4s orbitals leaving it with a full 3d orbital. It is in a positive oxidation state and has two electronegative halogens attached, and so the zinc center is an electron acceptor.

(d) ScCl₃ is a Lewis acid. The scandium center is Sc³⁺, lacking two electrons in the 4s orbitals and one from the 3d orbital, leaving it with a full 3p orbital. It is in a positive oxidation state and has three electronegative halogens attached, and so the scandium center is an electron acceptor.
(e) $\text{N}_3^-$ is a Lewis base. There are two possible resonance structures for this species, and in both there are lone pair electrons on the front nitrogen. It is an electron donor.

\[
\begin{array}{c}
\text{N=N=N} \\
\text{N=N=N}
\end{array}
\xrightarrow{\text{LA}}
\begin{array}{c}
\text{N=N-N} \\
\text{N=N-N}
\end{array}
\]

for simplicity, only one resonance structure was shown as the Lewis acid/base adduct.

(f) $\text{CH}_3\text{CH}_2\text{O}^-$ is a Lewis base. The oxygen has three lone pairs of electrons, it is an electron donor. Even if it was not negatively charged it would still be a Lewis base, with two lone pairs.

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\xrightarrow{\text{LA}}
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

---

S31

(a)

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\xrightarrow{\text{δ+}}
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

(b)

(c)
(a) The fluoride anion is negatively charged, and it is nucleophilic. (b) The hydride anion is negatively charged, and it is nucleophilic. (c) Acid chlorides are similar to esters and ketones in that there is an electrophilic carbon double bonded to the oxygen, but acid chlorides are typically much more reactive. (d) ScCl₃ was seen earlier to be Lewis acidic, and it is electrophilic. (e) The central carbon in N,N'-diethylcarbodiimide is electrophilic due to the bond polarizations between the two nitrogen atoms.

(a) An aromatic ring and a carboxylic acid are present. (b) Alcohol (c) ester (d) haloalkane (e) anhydride, this is similar to an ester, but the difference is the oxygen atom placement. (f) amide

a. The ketone provides an electrophilic carbon.
b. The alcohol has two lone pairs of electrons, and with a positive charge there is a Coulombic attraction.
c. The important thing here is the polarization of the C-Br bond, making the carbon electrophilic. The azide has an overall negative charge, and a Coulombic attraction is present.
d. There is no large polarization in bonds present. Both of these gases are not known for being nucleophilic or electrophilic.
e. This is a standard acid base reaction, but it can be explained by the Coulombic attraction between the positively charged hydrogen ion and the lone pair on the nitrogen.

**S35**

(a)

(b)

(c)

(d) No reaction (e)

**S36**

(a)

3-ethyl-2-methylpentane
(b) 5,7-diisopropyl-2,6,10-trimethylundecane

(c) 2,2-dimethylpentane

(d) 4-ethyl-2,2-dimethylhexane

(e) 3-ethyl-2,4,5-trimethylhexane

(f) 2,3,6-trimethylheptane
(a)

2-fluoro-3-methylpentane

(b)

3-bromo-1-chloro-2,2-dimethylbutane

(c)

5-chloro-2,3,5-trimethylheptane
isopentane
or 2-methylpentane

S39

(a)

S40

(b) All 2° Carbons

(c)
(a) primary, 2,2-dimethylbutyl (b) tertiary, 1-ethyl-1-methylbutyl (c) secondary, 1,3-dimethylbutyl (d) tertiary, 1,1,2,2-tetramethylethyl

Molecule (a) does not contain a tertiary carbon, it is only bonded to two other carbon atoms. An oxygen atom does not affect this. Compound (b) does contain a tertiary carbon, as it is bonded to three other carbon atoms.

2,3,4-trimethylpentane<2,3-dimethylhexane<3-methylheptane<nonane

This is a combination of both molecular weight and how branched the molecule is (affect the strength of the London dispersion forces). The higher the molecular weight the higher the boiling point, but also the more branched a molecule is the lower the boiling point.

(a)
\[ \Delta G^0 = -(1.986)(273+25)\ln\left(\frac{15}{85}\right) = -1027 \text{ cal or } -1.027 \text{ kcal} \]

The given information makes sense in that a larger percentage of the molecules are present in the Anti conformation due to its lower energy. However, other conformations are not included, some lower in energy than the eclipsed form such as staggered. These are likely to also make a contribution.
(a) 1,6,6-trimethylhexyl, secondary  
(b) 1,1,2,2-tetramethylbutyl, tertiary  
(c) 2,2-dimethylbutyl, primary  
(d) 2-methylethyl or isopropyl, primary

The Arrhenius equation is $k = Ae^{-\frac{E_a}{RT}}$ where $A$ is a constant. To calculate the new $k$ value use the following

\[ \frac{k_2}{k_1} = \frac{Ae^{-\frac{E_a}{RT_2}}}{Ae^{-\frac{E_a}{RT_1}}} \]

and the constant, $A$, cancels.

\[ k_2 = \left[ e^{-\frac{E_a}{RT_2}} / e^{-\frac{E_a}{RT_1}} \right] k_1 \]

Also remember to convert the $E_a$ from kcal to cal.
(a) \[10^\circ C - k_2 = \frac{e^{-\frac{10,000}{1.986}(310)}}{e^{-\frac{10,000}{1.986}(300)}}k_1 = 1.71k_1\]

\[25^\circ C - k_2 = 3.64k_1\]

\[60^\circ C - k_2 = 16.4k_1\]

(b) \[10^\circ C - k_2 = 3.87k_1\]

\[25^\circ C - k_2 = 25.2k_1\]

\[60^\circ C - k_2 = 1090k_1\]

(c) \[10^\circ C - k_2 = 15.0k_1\]

\[25^\circ C - k_2 = 636k_1\]

\[60^\circ C - k_2 = 1.19 \times 10^6k_1\]

Note the increase in affect of the temperature the larger the activation energy.

---

\[\text{S50}\]

\[\ln k = \ln A - \frac{E_a}{RT}\]

A plot of \(\ln k\) vs. \(1/T\) would yield a straight line. The slope of this line would be \(-\frac{E_a}{R}\) with an x-intercept of \(\frac{E_a}{R(\ln A)}\) and a y-intercept of \(\ln A\).

---

\[\text{S51}\]

(a)

(b)

\[\text{OH}_2\]
(c) This is an example of a substitution reaction, which you'll learn about later.

(d) No Reaction

\[ \Delta G = \Delta H - T\Delta S \]

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than Zero</td>
<td>$\Delta S$ can either be any positive value, or a negative value such that $</td>
</tr>
<tr>
<td>$\Delta H$ can either be any negative value, or a positive value such that $</td>
<td>\Delta H</td>
</tr>
</tbody>
</table>

S53

(a) Rate = $k[\text{CH}_3\text{CH}_2\text{O}^-][\text{alkyl bromide}]$

(b) Rate = $k[\text{CHC}^-][\text{alkyl bromide}]$
(b) is correct, there are 12 primary H's and 2 tertiary H's.

(a) There are 10 primary H's - incorrect, there are 12 primary H's

(c) There are 3 tertiary C's - incorrect, there are 2 tertiary C's

(d) There are no primary C's - There are 4 primary C's

ΔG=ΔH-TΔS=-1000-(200)(-2)=-600 cal/mol, so (c) is true. exergonic means that ΔG<0.

(a) The reaction is endothermic - incorrect, ΔH<0

(b) The reaction is not spontaneous - incorrect, ΔG<0

(d) It is likely that the reaction involves one reactant and yields two products. - incorrect, with a negative change in entropy, it is more likely that two reactants yielded one product.

This molecule is entirely sp\(^3\) hybridized, so all angles are 109.5°, (d).

(c) *gauche* staggered is the conformation. The two CH\(_3\) groups are separated by 60° and no group is eclipsed. The lowest energy conformation would be (d) *anti* staggered, where the larger CH\(_3\) groups are anti and there is no eclipsed group.
(c), aldehyde is not in the molecule. There is a ketone, but no aldehyde.