

AME599 Combustion Chemistry and Physics

Lecture 2

2. CHEMICAL, PHYSICAL, AND THERMOCHEMICAL PROPERTIES OF HYDROCARBONS

We learned from Lecture 1 that there are three important thermochemical properties for combustion analysis. These are specific heat (or sensible enthalpy), enthalpy of formation, and entropy. In this lecture, we will learn the methods with which these properties may be estimated. To do this we will have to understand a bit of organic chemistry, and specifically the structure of organic molecules.

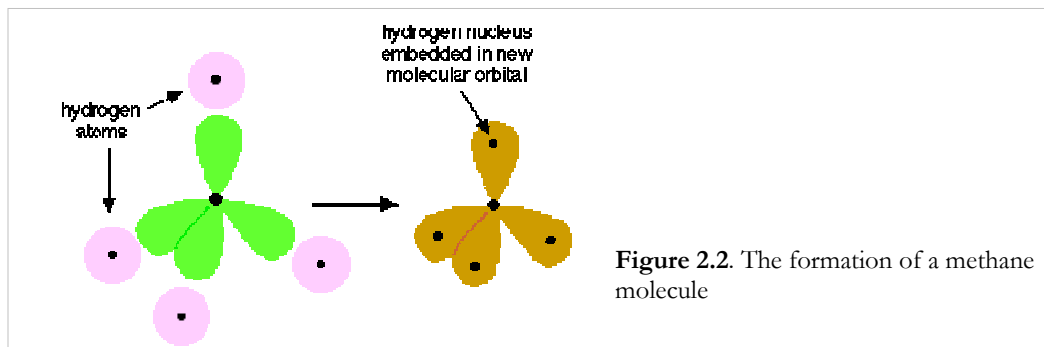
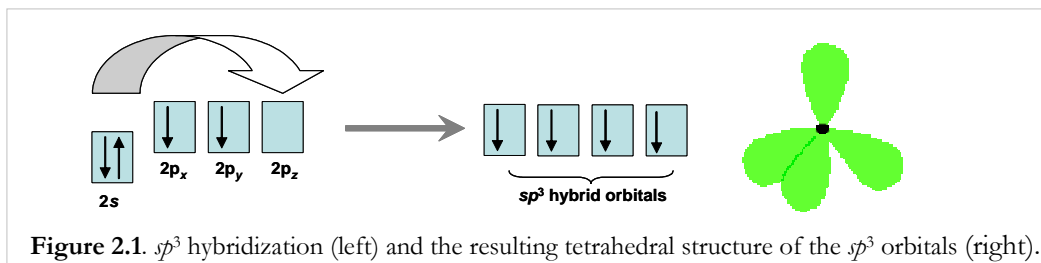
2.1. Chemical Bonds in Organic Molecules

Fossil fuels are basically hydrocarbons. While some of them are oxygenated (e.g., methanol and ethanol), others are pure hydrocarbons composed of only carbon and hydrogen atoms. The structure and chemical make-up of hydrocarbons are closely related to the electronic structures of carbon.

2.1.1 Alkanes

A carbon atom has 6 electrons distributed into several atomic orbitals. These are termed as $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ etc. The Pauli exclusion principle says that each orbital can have a maximum of 2 electrons in opposite spin. Therefore we expect that 2 electrons will fill the $1s$ orbital, 2 electrons for the $2s$ orbital, and 1 electron each for the $2p_x$ and $2p_y$ orbitals (i.e., $1s^2 2s^2 2p_x^1 2p_y^1$). For a C-H bond to form, the electron in the $2p_x$ or $2p_y$ orbital will have to be shared, and with the unpaired electron in an H atom the two electrons form a molecular orbital or a covalent bond that again satisfies Pauli's exclusion principle. The trouble is that if the electronic structure of a carbon atom is indeed $1s^2 2s^2 2p_x^1 2p_y^1$, we would expect that the stable form of a C_1 hydrocarbon is CH_2 since there are only two unpaired electrons in carbon. Of course, we know that the most stable form of C_1 hydrocarbon is methane, CH_4 .

It turns out that the four electrons in the $2s$, $2p_x$ and $2p_y$ orbitals like to undergo hybridization to promote bond formation, since in general the formation of a chemical bond releases energy and gives more stability to the molecule resulting from bond formation. The sp^3 hybridization is the result of promotion of an electron from the $2s$ orbital to the $2p_z$ orbital and in doing so it produces four identical orbitals organized in a tetrahedral fashion (see, Figure 2.1). Of course, each of these orbitals has an unpaired electron, ready for chemical or covalent bonding. Paired with four unpaired electrons in four H atoms, a methane molecule is formed (see, Figure 2.2). The covalent bonds formed in this process are known as the σ bonds. Because the four sp^3 orbitals are identical, the four C-H bonds have the same bond length (1.09 Å) and all H-C-H angles are equal (109°).



Of course, 2 carbon atoms and 6 hydrogen atoms can produce an ethane (C_2H_6) molecule by forming 1 C–C σ bond and 6 C–H σ bonds. Continuing molecular building in this fashion, we obtain normal, straight-chain *alkane* molecules of arbitrary sizes (C_nH_{2n+2}). These are propane (C_3H_8 or $CH_3-CH_2-CH_3$), normal butane ($n-C_4H_{10}$, $CH_3-CH_2-CH_2-CH_3$) and so on. In general, groups connected by the C–C σ bond can rotate about the bond axis.

Branched-chain alkanes are formed when a carbon atom has more than 2 C–C σ bond. Examples include *iso*-butane and *iso*-octane (or 2,2,4-trimethylpentane).



Figure 2.3 shows the molecular structures of some typical alkane compounds. Alkanes can also form cyclic structures. The resulting compounds are known as *cycloalkanes* (C_nH_{2n}). Cyclopentane ($c-C_5H_{10}$) and cyclohexane ($c-C_6H_{12}$) are typical example. Because the preferred C–C–C bond angle in the sp^3 hybridization angle is fixed at 109° , there is some degree of *strain* in almost all cycloalkane molecules.

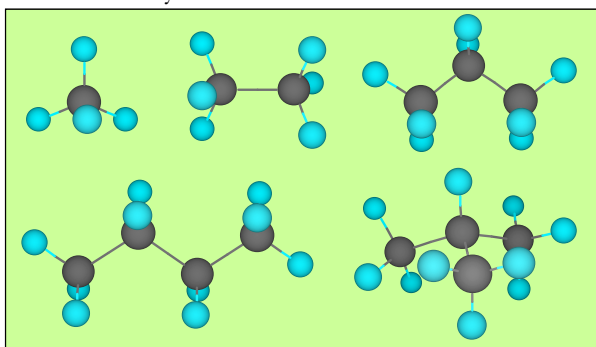
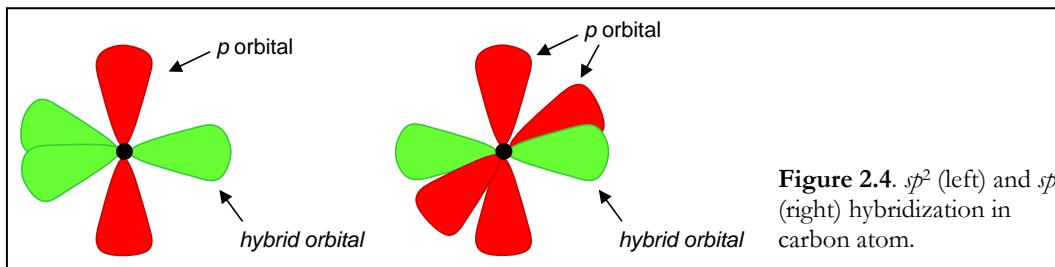


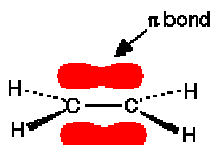
Figure 2.3. Structures of typical alkane molecules. Top row (from left): methane, ethane, propane; bottom row: normal butane, iso-butane.

2.1.2 Alkenes and Alkynes

Other types of atomic orbital hybridization exist. These are sp^2 and sp hybridization. The sp^2 hybridization uses two $2s$ electrons and one $2p$ electron, but it leaves the other $2p$ electron unchanged. The sp hybridization uses the two $2s$ electrons only, promoting one of the electrons to the third $2p$ orbital but leaves the two $2p$ electrons unchanged. These hybridizations are illustrated in Figure 2.4.



The hybrid orbitals can form σ bonds with hydrogen or other carbon atoms. The unpaired electron in the p orbital inevitably form a different type of bonds known as the π bond, as illustrated below for ethylene (C_2H_4 , $H_2C=CH_2$). Therefore the double C-C bond in ethylene is the result of one σ C-C bond and one π C-C bond, as illustrated below:



Hydrocarbons containing one or more double C=C bonds are known as alkenes. Examples are allene (C_3H_4 , $H_2C=C=CH_2$), propene (C_3H_6 , $CH_3-CH=CH_2$), 1-butene (C_4H_8 , $CH_2=CH-CH_2-CH_3$) and 1,3-butadiene (C_4H_6 , $H_2C=CH-CH=CH_2$).

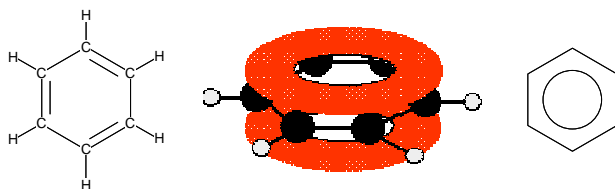
Because of the rigidity of the p orbital (i.e., it always like to stay perpendicular to the plane of the hybrid orbitals), the π bond remains rigid towards rotation. Therefore, a C=C bond does not allow rotation about its bond axis.

Under sp hybridization, a triple C-C bond forms because of the pair of perpendicular p orbitals as shown in Figure 2.4. A typical example is acetylene (C_2H_2 , $HC\equiv CH$), in which the two carbon atoms are bonded by a triple bond consisting of one σ and two π C-C bonds. Acetylene is a linear molecule because the hybrid orbitals in the carbon atom lie on a straight line. Hydrocarbons containing one or more triple C \equiv C bond are known as alkynes. Examples are propyne (C_3H_4 , $CH_3-C\equiv CH$) and diacetylene (C_4H_2 , $HC\equiv C-C\equiv CH$).

2.1.3 Aromatics

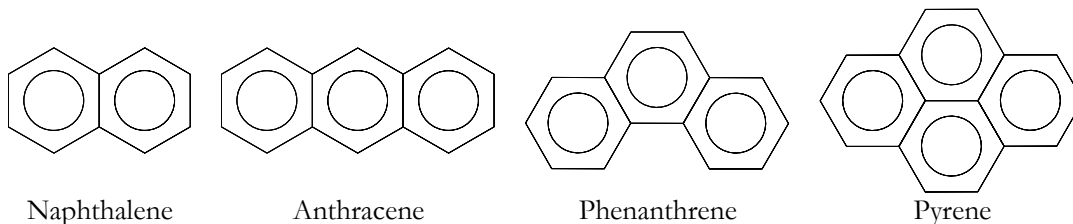
Kekule structure is important to aromatics. Benzene (C_6H_6), naphthalene ($C_{10}H_8$), bucky balls (C_{60} etc), perfect graphite, and carbon nanotubes are a few examples. These compounds or substances have very low potential energies owing to the delocalization of the π bonds

and the resonance of the π electrons. For example, a benzene molecule may be viewed as three ethylene molecules connected in a circular fashion:



The alternating π bonds cause the electrons in these bonds to completely delocalized and undergo electron resonance. In doing so they become evenly distributed in a ring-like fashion, above the beneath the hexagon. It is for this reason that the aromatic structure is often denoted by a hexagon with a ring in the middle. The six C–C bonds are identical to each other, and so are the six C–H bonds.

Of course, one or more hydrogen atoms in benzene may be replaced by other hydrocarbon groups, known as *functional* groups. If a functional group is derived from alkane by removing one hydrogen atom, this group is called the alkyl group. Likewise, the ethenyl and ethynyl groups are derived from alkene and alkyne, respectively. Examples include toluene and styrene in which a hydrogen atom in benzene is replaced by a methyl (CH_3) group (derived from methane) and a vinyl (C_2H_3) group (derived from ethylene), respectively. Aromatic rings can also fuse together, leading to a class of organic compounds known as the polycyclic aromatic hydrocarbons (PAHs). Examples are



2.1.4 Oxygenated Hydrocarbons

There are several types of oxygenated hydrocarbons that are relevant to combustion, including

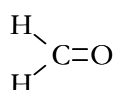
Group name	Examples
alcohols	methanol: CH_3OH ethanol: $\text{CH}_3\text{--CH}_2\text{--OH}$ (or $\text{C}_2\text{H}_5\text{OH}$)
aldehydes	formaldehyde: CH_2O acetaldehyde: $\text{CH}_3\text{--CHO}$ (or $\text{C}_2\text{H}_4\text{O}$)
peroxides	methylperoxide: $\text{CH}_3\text{--O--O--H}$ ($\text{CH}_3\text{O}_2\text{H}$)

The oxygen atom has two unpaired electrons. The electronic structure may be given by $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. In general there are two ways for oxygen to bond with other atoms. In alcohols, for example, the oxygen atom forms a σ bond with a carbon atom, using one of the two unpaired electrons in the p orbitals. The second unpaired electrons forms the second

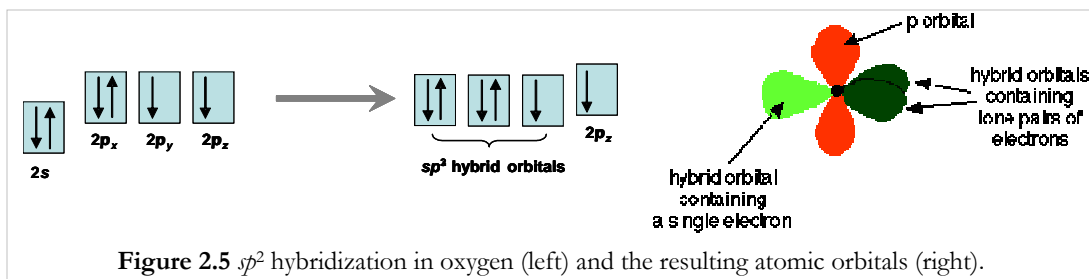
σ bond with a hydrogen atom. Because two p orbitals do not lie on a straight line, the resulting C–O–H angle is not 180° .

Aldehydes, on the other hand, have a double C=O bond. In this case, the oxygen atom undergoes sp^2 hybridization leading to three sp^2 orbitals, two of which contain lone pairs of electrons, while the third has an unpaired electron (see, Figure 2.5). The unaltered $2p_z$ orbital also has an unpaired electron and lies perpendicular to the sp^2 orbitals. Therefore the oxygen atom and carbon atom may bond in much the same way as the two carbons do in ethylene, i.e., a σ bond and a π bond.

Formaldehyde is symmetric about the double C=O bond, i.e.,



where one or both H atoms may be replaced by any functional groups. For example, acetaldehyde (CH_3CHO) is derived by replacing one hydrogen atom in formaldehyde by a methyl (CH_3) group.



2.1.5 Free Radical Species

Free radicals are usually abundant in hydrocarbon flames. At high temperatures, the hydrocarbon oxidation chemistry is largely dictated by the presence of such radical species as the H atom ($\text{H}\bullet$), the O atom ($\text{O}\bullet$) and the hydroxyl radical ($\text{OH}\bullet$). We will discuss the role of these highly reactive species in the next several weeks.

Free radicals are derived from breaking a covalent chemical bond, leading to molecular fragments that contain one or more unpaired electrons. Common hydrocarbon free radicals include methyl ($\text{CH}_3\bullet$), ethyl ($\text{C}_2\text{H}_5\bullet$), vinyl ($\text{C}_2\text{H}_3\bullet$), formyl ($\text{HCO}\bullet$), allyl ($\text{C}_3\text{H}_5\bullet$), phenyl ($\text{C}_6\text{H}_5\bullet$ -derived from benzene), benzyl ($\text{C}_6\text{H}_5\text{CH}_2\bullet$ -derived from toluene) etc.

2.2 Physical Properties of Hydrocarbon Fuels

Natural gas, petroleum and petroleum-derived products, including gasoline, diesel and jet fuels contain a large amount of alkanes. The practical use of a fuel is often dictated by its physical properties along with a consideration of fuel cost. For example, natural gas is used in home gas stove, simply because it is easy to design an efficient gas stove than an oil-fired stove. Automobiles and airplanes use liquid fuels largely because of ease with which the fuel is transported and stored.

Figure 2.6 shows the normal boiling and melting points and mass density of straight-chain alkane compounds. In general, these physical property values increase as the size of the molecule increases. The normal boiling points may be expressed as a function of the number of carbon atoms N_C as

$$b.p. (\text{°C}) = -225.5 + 74.68N_C - 5.552N_C^2 + 0.2518N_C^3 - 0.00449N_C^4 \quad (N_C \leq 20). \quad (2.1)$$

The boiling points of methane and ethane are far below the freezing point of water. They are present under the room temperature almost invariably as a gas. Propane and butane, on the other hand, have boiling points of -42 and -1 °C at the ambient pressure. Therefore they are easily compressed into the liquid state and can evaporate without external heating source. It is for these reasons they are used as the fuel for cooking (grills) and as a lighter fluid. Normal alkanes larger than butane are generally liquid under the ambient pressure. Their volatility, however, decrease as the carbon atom number increases. Gasoline fuel is octane-like and has boiling point roughly around 100 °C. Its vapor pressure, however, is sufficiently large to allow for evaporation without the need of external heating. For example, at 20°C iso-octane (2,2,4-trimethylpentane, C_8H_{18}) has a vapor pressure of 0.0514 Bar, which is larger than the partial pressure of iso-octane in a stoichiometric fuel-air mixture (0.0165 Bar). Diesel fuel, on the other hand, contains a larger number of carbon atoms ($\sim C_{12}$) in each fuel molecule, because compression ignition along with the high compression ratio requires it to remain in the liquid-droplet state when it is injected into the engine.

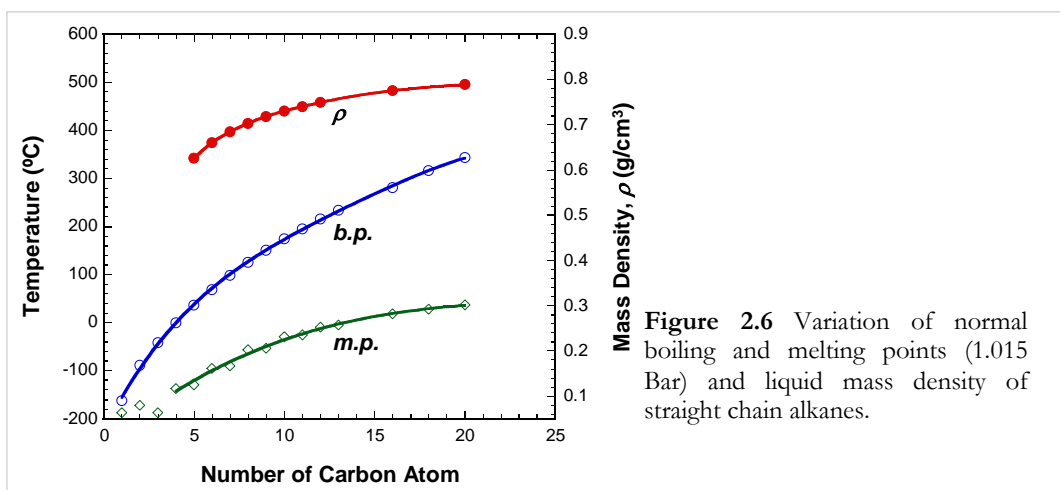


Figure 2.6 Variation of normal boiling and melting points (1.015 Bar) and liquid mass density of straight chain alkanes.

2.3 Thermochemical Properties

2.3.1 Group Additivity

Group additivity is a simple yet powerful empirical method used for estimation of thermochemical properties. The development of the method and its application were largely due to the pioneering work of Professor Sydney Benson of USC almost a half of century ago.¹ The method has been fine tuned over the years by a large number of researchers. The latest advancements came from the work of J. Bozzelli.²

The fundamental basis of group additivity (GA) is that the thermochemical properties of a species are additive with respect to the functional groups that makes up the molecule. Consider the straight-chain alkane compounds. Figure 2.7 shows the variation of their enthalpy of formation $\bar{h}_{f,298}^\circ$ and specific heat $\bar{c}_{p,298}^\circ$ as a function of the number of carbon atom N_C in the molecules. Clearly, for $N_C \geq 3$ the values of these properties exhibit a linear relationship with N_C . It follows that the contributions of each CH_3- and $-\text{CH}_2-$ group to the total $\bar{h}_{f,298}^\circ$ and $\bar{c}_{p,298}^\circ$ of the compound are constants. Therefore, the $\bar{h}_{f,298}^\circ$ and $\bar{c}_{p,298}^\circ$ values may be partitioned into group values. For a straight-chain $\text{C}_n\text{H}_{2n+2}$ alkane compound, we have

$$\bar{h}_{f,298}^\circ = 2\bar{h}_{f,298}^\circ [\text{C}-(\text{C},\text{H}_3)] + (n-2)\bar{h}_{f,298}^\circ [\text{C}-(\text{C}_2,\text{H}_2)] + \varepsilon_{\bar{h}_f}, \quad (2.2)$$

$$\bar{c}_{p,298}^\circ = 2\bar{c}_{p,298}^\circ [\text{C}-(\text{C},\text{H}_3)] + (n-2)\bar{c}_{p,298}^\circ [\text{C}-(\text{C}_2,\text{H}_2)] + \varepsilon_{\bar{c}_p}, \quad (2.3)$$

where $[\text{C}-(\text{C},\text{H}_3)]$ and $[\text{C}-(\text{C}_2,\text{H}_2)]$ represent the functional groups, defined by the center atom as well as the atoms bonded to the center atom, and ε 's account for higher-order effects of molecular structures not accounted for by the linear additivity. For the straight-chain alkane series, a fit to available $\bar{h}_{f,298}^\circ$ and $\bar{c}_{p,298}^\circ$ data gives

$$\begin{aligned} \bar{h}_{f,298}^\circ [\text{C}-(\text{C},\text{H}_3)] &= -42.02 \text{ (kJ/mol)} \\ \bar{h}_{f,298}^\circ [\text{C}-(\text{C}_2,\text{H}_2)] &= -20.73 \text{ (kJ/mol)} \\ \bar{c}_{p,298}^\circ [\text{C}-(\text{C},\text{H}_3)] &= 25.78 \text{ (J/mol-K)} \\ \bar{c}_{p,298}^\circ [\text{C}-(\text{C}_2,\text{H}_2)] &= 22.75 \text{ (J/mol-K)} \end{aligned}$$

and the higher-order terms ε are negligible. Table 2.1 shows the experimental $\bar{h}_{f,298}^\circ$ and $\bar{c}_{p,298}^\circ$ values and the group-additivity predictions. In general the error is well within 2%, and in the case of $\bar{h}_{f,298}^\circ$, the error is much smaller than 1%.

¹ S. W. Benson *Thermochemical Kinetics*, Second Edition, Wiley, New York, 1976.

² Ritter, E. R. & Bozzelli, J. W. THERM: Thermodynamic Property Estimation for Gas Phase Radicals and Molecules, *Int. J. Chem. Kin.*, vol. 23, pp. 767-778 (1991).

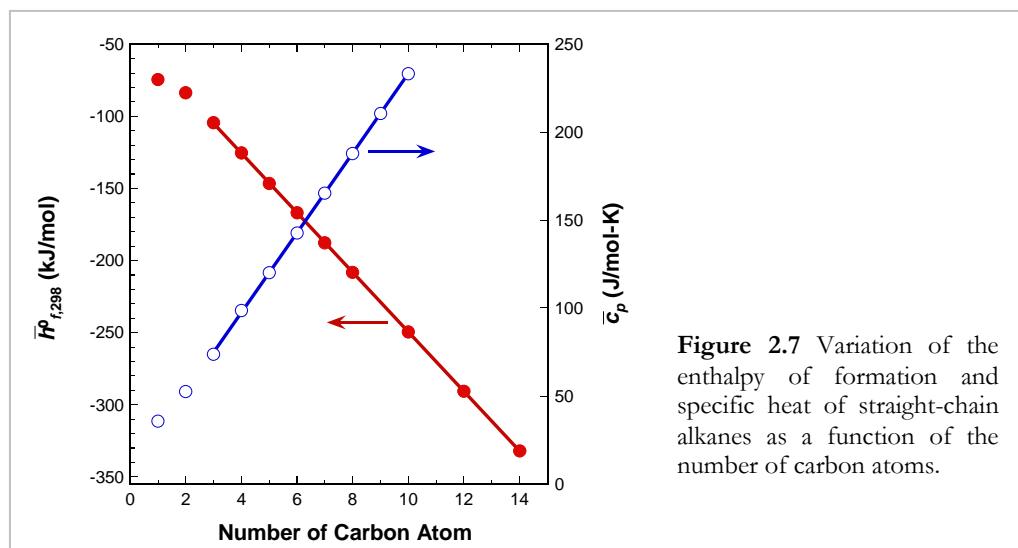


Figure 2.7 Variation of the enthalpy of formation and specific heat of straight-chain alkanes as a function of the number of carbon atoms.

Table 2.1 Experimental $\bar{h}_{f,298}^\circ$, $\bar{c}_{p,298}$ and \bar{s}_{298}° values of straight-chain alkanes and group additivity predictions.

Species	$\bar{h}_{f,298}^\circ$ (kJ/mol)			$\bar{c}_{p,298}$ (J/mol-K)			\bar{s}_{298}° (J/mol-K)		
	Expt.	GA	%Error	Expt.	GA	%Error	Expt.	GA	%Error
C ₂ H ₆	-83.8	-84.0	-0.2	52.5	51.6	-1.8	229	235	2.7
C ₃ H ₈	-104.7	-104.8	-0.1	73.6	74.3	1.0	270	270	0.1
C ₄ H ₁₀	-125.6	-125.5	0.1	98.5	97.1	-1.5	310	310	0.0
C ₅ H ₁₂	-146.8	-146.2	0.4	120.1	119.8	-0.2	348	349	0.3
C ₆ H ₁₄	-167.2	-166.9	0.2	142.6	142.6	-0.0	389	388	-0.2
C ₇ H ₁₆	-187.8	-187.7	0.1	165.2	165.3	0.1		427	
C ₈ H ₁₈	-208.4	-208.4	0.0	187.8	188.1	0.2	467	466	-0.2
C ₉ H ₂₀		-229.1		210.5	210.8	0.2	507	506	-0.2
C ₁₀ H ₂₂	-249.7	-249.9	-0.1	233.0	233.6	0.2	546	545	-0.2
C ₁₁ H ₂₄		-270.6						584	
C ₁₂ H ₂₆	-290.9	-291.3	-0.2				623	623	0.1
C ₁₃ H ₂₈		-312.0						662	
C ₁₄ H ₃₀	-332.1	-332.8	-0.2				700	701	0.1
C ₁₅ H ₃₂		-353.5						741	
C ₁₆ H ₃₄	-83.8	-374.2					778	780	0.2

The standard entropy \bar{s}_{298}° of a compound may also be partitioned into group contributions. However, before the group additivity rule may be applied, we need to discuss the symmetry number associated with each molecule and its influence on entropy. Recall that entropy is a measure of randomness. A symmetric molecule is associated with a smaller entropy since through rotation the molecules can assume two or more indistinguishable configurations. This leads to an increase in the predictivity of the spatial orientation of the molecule. The symmetric number or rotational symmetry number σ is defined as the number of ways a molecule can rotate itself to obtain indistinguishable spatial orientations. The σ values for methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄) and benzene (C₆H₆) are 12, 6, 4 and 12, respectively. All straight-chain alkanes with $N_C > 2$ have σ values equal to 2.

For reasons to be discussed later, the influence of molecular symmetry on entropy may be quantified by $-R_u \ln(\sigma)$. It follows that for straight-chain alkanes the group-additivity entropy is given by

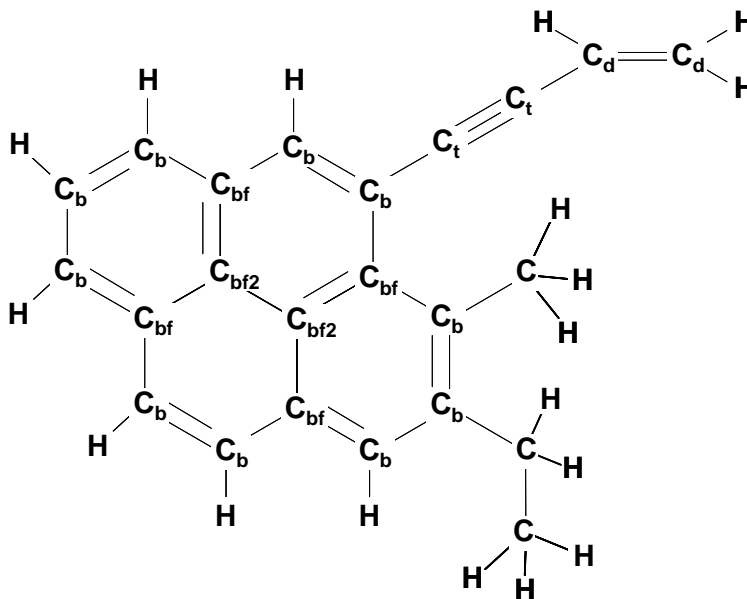
$$\bar{s}_{298}^{\circ} = 2\bar{s}_{298}^{\circ} [C-(C,H_3)] + (n-2)\bar{s}_{298}^{\circ} [C-(C_2,H_2)] - R_u \ln(\sigma) + \varepsilon_{\bar{s}^{\circ}}, \quad (2.4)$$

where

$$\begin{aligned} \bar{s}_{298}^{\circ} [C-(C,H_3)] &= 114.61 \text{ (J/mol-K)} \\ \bar{s}_{298}^{\circ} [C-(C_2,H_2)] &= 39.18 \text{ (J/mol-K)} \end{aligned}$$

Table 2.1 provides a comparison of the experimental \bar{s}_{298}° values with the group-additivity predictions for straight-chain alkanes. Again, the agreement is quite good.

Obviously all group values need to be “trained” against available experimental data. Selected group values for hydrocarbons are presented in Table 2A. In this table the nomenclature of the functional groups is quite straightforward to understand. The following scheme shows the atom nomenclature commonly used by the group additivity method:

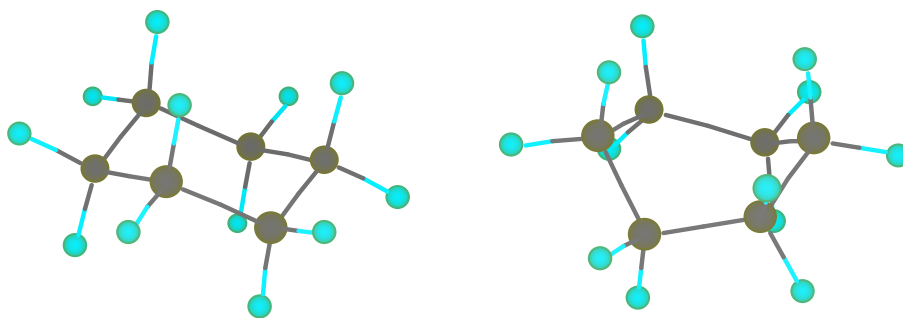


For example, the non-aromatic, double C=C bond atoms are denoted by C_d; the triple C≡C bond atoms are given by C_t.

For estimation of thermochemical properties an online program is available at <http://webbook.nist.gov/chemistry/grp-add/>.

While the group additivity method is intuitively simple, it has its drawbacks stemming from the need to consider higher-order correction terms for a large number of molecules. Take cyclopentane as an example, the addition of group contributions yields $\bar{h}_{f,298}^{\circ} = -103$ kJ/mol, yet the experimental value is -76 kJ/mol. The difference is caused by the strain in cyclopentane discussed earlier, which is not accounted for in the group value of C-(C₂H₂) obtained from unstrained, straight-chain alkane molecules. For this reason, the group additivity method is not quite a useful approach when higher-order correction is required, since these corrections are usually specific to each molecule.

Other corrections include the molecular conformers. For example, cyclohexane can assume two structures known as the chair (left) and boat (right) conformations:



In general, the chair conformer has a lower energy [O(5 kJ/mol)] than the boat conformer, because on average the carbon atoms are further apart in the chair conformer, leading to smaller electron-electron repulsion.

Here it is important to note that the group additivity method is useful to quantify the effect of special molecular configuration on the molecular potential energy. For example, we learned from the cyclopentane example that the strain energy in this cyclic alkane is $-76 - (-103) = 27$ kJ/mol. In the case of hexane, the strain energy drops to an insignificant 0.5 kJ/mol. Consider the benzene molecule. The extent of stabilization by the π electron resonance is characterized by the resonance energy. If we sum the contributions of 6 C_d-(C,H), we find that without resonance benzene should have $\bar{h}_{f,298}^{\circ} = 216$ kJ/mol. Its actual $\bar{h}_{f,298}^{\circ}$ value is 83 kJ/mol. Therefore the difference is attributable to resonance, though the actual difference here (134 kJ/mol) is smaller than the accepted value of 152 kJ/mol.

2.3.2 Bond Energy

A knowledge of bond energy is important to the prediction of enthalpy of formation for free radical species. The *bond dissociation energy* or *bond energy* is the energy required to break a chemical bond. While the bond energy is quite easy to understand, let us dwell for a moment at this concept, since this is relevant to stretch vibration in a molecule—a topic we shall discuss later.

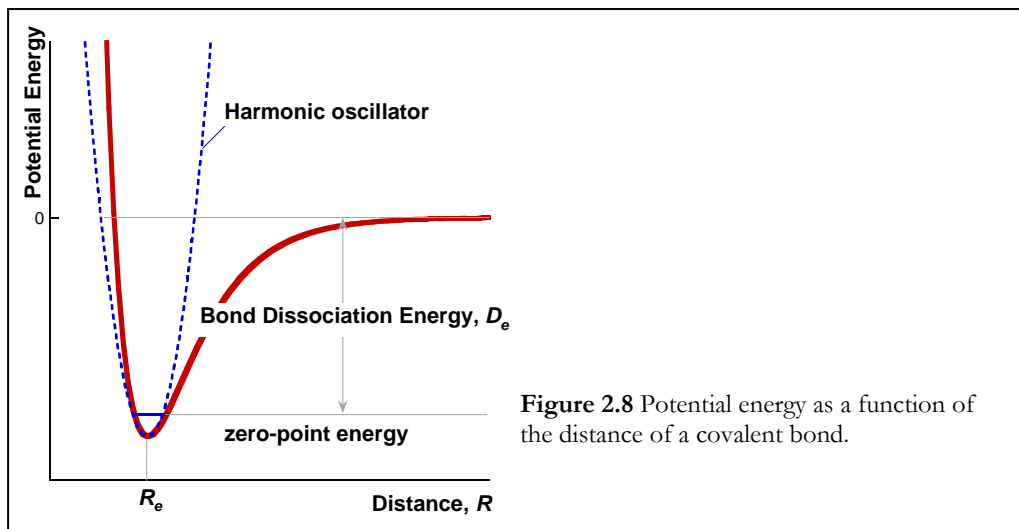


Figure 2.8 Potential energy as a function of the distance of a covalent bond.

Earlier, we briefly discussed that the formation of a covalent bond is generally associated with a release of energy and lowering the potential energy of the resulting molecule. Conceptually, the formation of a covalent bond may be viewed on a potential energy diagram as shown in Figure 2.8. We set the potential energy to be zero for two free radical fragments at infinite separation, $R \rightarrow \infty$. As the two fragments approach each other, the two fragments begin to attract each other because the molecular electron configuration favors two unpaired electrons to form a molecular orbital of opposite spin. The attractive force is translated into a negative potential energy (recall that force is the spatial derivative of potential energy). Eventually the two fragments are brought close to each and the dominant force of interactions is replaced by nucleus-nucleus repulsion. Therefore at short separation distance the potential energy rises. The minimum energy distance is known as the equilibrium distance R_e which is equal to the bond distance. The potential energy difference between that of infinite separation and the *zero-point energy* at $R = R_e$ is equal to the bond dissociation energy or bond energy \bar{D}_e . The origin of the zero-point is derived from quantum mechanics description of a harmonic oscillator, which will be discussed in section 2.4.3.4.

Since this potential energy difference is the same as the internal energy difference, we find, for example, the C–C bond energy in ethane is equal to the enthalpy of reaction³



with

³ For an ideal gas at a constant temperature we have $\Delta \bar{h} = \Delta \bar{u} + \Delta p\bar{v} = \Delta \bar{u} + R_u \Delta T = \Delta \bar{u}$.

Table 2.2 Typical C-C and C-H bond energies ($D_{\epsilon,298K}$, kJ/mol).

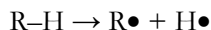
atom or group	methyl CH ₃	ethyl C ₂ H ₅	<i>i</i> -propyl (CH ₃) ₂ CH	<i>t</i> -butyl (CH ₃) ₃ C	phenyl C ₆ H ₅	benzyl C ₆ H ₅ CH ₂	allyl C ₃ H ₅	acetyl CH ₃ CO	vinyl C ₂ H ₃	ethynyl C ₂ H
H	439	420	413	400	474	375	369	377	465	547
OH	384	392	400	398	473	339	332		464	552
CH ₃	375	369	370	362	435	323	317	352	424	516
C ₂ H ₅	369	364	363	353	428	318		346	419	510
(CH ₃) ₂ CH	370	363	358	343	425	319		341		510
(CH ₃) ₃ C	362	353	343	322	410			327		498
C ₆ H ₅	435	428	425	410	496	381		414	491	588
C ₆ H ₅ CH ₂	323	318	319		381	278		290		

$$\begin{aligned}
 \bar{D}_{\epsilon,0K} &= \Delta \bar{H}_{r,0K}^0 \\
 &= 2\bar{h}_{f,0K}^\circ(\text{CH}_3\bullet) - \bar{h}_{f,0K}^\circ(\text{C}_2\text{H}_6) \\
 &= 2\bar{h}_{f,298K}^\circ(\text{CH}_3\bullet) - \bar{h}_{f,298K}^\circ(\text{C}_2\text{H}_6) \\
 &\quad + 2[\bar{h}(0K) - \bar{h}(298K)]_{\text{CH}_3\bullet} - [\bar{h}(0K) - \bar{h}(298K)]_{\text{C}_2\text{H}_6}
 \end{aligned}$$

Of course, the bond energy at the standard temperature of 298.15 K may be calculated as

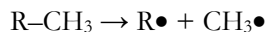
$$\begin{aligned}
 \bar{D}_{\epsilon,298K} &= \Delta H_{r,298K}^0 \\
 &= 2\bar{h}_{f,298K}^\circ(\text{CH}_3\bullet) - \bar{h}_{f,298K}^\circ(\text{C}_2\text{H}_6) \\
 &= \bar{D}_{\epsilon,0K} - 2[\bar{h}(0K) - \bar{h}(298K)]_{\text{CH}_3\bullet} + [\bar{h}(0K) - \bar{h}(298K)]_{\text{C}_2\text{H}_6}
 \end{aligned}$$

Typical C–C and C–H bond energies may be found in Table 2.2. Since the enthalpy of formation values of typical radical species, e.g., H• and CH₃•, are well known,⁴ we may estimate the enthalpy of formation of a radical species, denoted by R•, by



$$\bar{h}_{f,298K}^\circ(\text{R}\bullet) = \bar{D}_{\epsilon,298K}(\text{R-H}) + \bar{h}_{f,298K}^\circ(\text{R-H}) - \bar{h}_{f,298K}^\circ(\text{H}\bullet).$$

Alternatively, the enthalpy of formation of the same species may be estimated by



as

$$\bar{h}_{f,298K}^\circ(\text{R}\bullet) = \bar{D}_{\epsilon,298K}(\text{R-CH}_3) + \bar{h}_{f,298K}^\circ(\text{R-CH}_3) - \bar{h}_{f,298K}^\circ(\text{CH}_3\bullet).$$

In both cases, the bond dissociation energy should be chosen such that the corresponding bond mimics the nature of the real R-H and R-CH₃ bond. For example, the $\bar{h}_{f,298}^\circ$ value of *n*-propyl (*n*-C₃H₇•, CH₃–CH₂–CH₂•) may be estimated by

⁴ See, for example, <http://webbook.nist.gov/chemistry/>.

$$\begin{aligned}\bar{b}_{f,298K}^{\circ}(n\text{-C}_3\text{H}_7\bullet) &= \bar{D}_{e,298}^{\circ}(\text{C}_2\text{H}_5\text{-H}) + \bar{b}_{f,298K}^{\circ}(\text{C}_3\text{H}_8) - \bar{b}_{f,298K}^{\circ}(\text{H}\bullet) \\ &= 420 + (-104.7) - 218.0 = 97 \text{ (kJ/mol)}\end{aligned}$$

The above estimate compares quite well with the experimental value at 100 ± 2 kJ/mol. The alternative estimation yields a similar value, i.e.,

$$\begin{aligned}\bar{b}_{f,298K}^{\circ}(n\text{-C}_3\text{H}_7\bullet) &= \bar{D}_{e,298}^{\circ}(\text{C}_2\text{H}_5\text{-CH}_3) + \bar{b}_{f,298K}^{\circ}(n\text{-C}_4\text{H}_{10}) - \bar{b}_{f,298K}^{\circ}(\text{CH}_3\bullet) \\ &= 369 + (-125.6) - 145.7 = 98 \text{ (kJ/mol)}\end{aligned}$$

2.3.4 Statistical Mechanics Description of Thermochemical Properties

Our goal here is to calculate macroscopic thermochemical properties in terms of molecular properties, including molecular mass, rotational constants, and molecular vibrations. These molecular properties may be measured by spectroscopic methods and perhaps more importantly, by quantum chemistry codes now widely available to us.

2.3.4.1 Molecular degrees of freedom

A N_a -atom molecule has $3N_a$ degrees of freedom. Attaching the coordinate system to the mass center of the molecule leads to a classification of 3 degrees for translational motions. For a linear molecule (all diatomic molecules, CO_2 , acetylene etc) the remaining $3N_a - 3$ degrees of freedom is partitioned into 2 rotational and $3N_a - 5$ vibrational degrees of freedom, and for a nonlinear molecule we have 3 rotational and $3N_a - 6$ vibrational degrees of freedom. In separating the rotational degrees of freedoms from the internal vibrational degrees of freedom, we have intrinsically assumed that the centrifugal force of rotation does not exert any influence on the vibration. This is generally a good assumption since molecular vibration usually has frequencies far larger than that of rotation. In other words, the force acting on an oscillator, such as the stretch of a chemical bond, is far larger than the centrifugal force. Conversely, the amplitude of vibration is so small that the bond length may be approximated as a constant. Hence the rotation may be approximated as a rigid rotor. This approximation is known as the rigid rotor-harmonic oscillator approximation.

Here we note that the potential energy near the equilibrium distance for a bond stretch process (Figure 2.8) may be approximated by a symmetric potential energy well given by the Hooke's law of harmonic oscillation, i.e., $V(r-r_e) = (r-r_e)^2/2$. Thus to calculate the thermochemical properties, we are interested in the energy and its distribution for the following three problems: the translational motion of a particle in a box, a rigid rotor, and a harmonic oscillator.

Below, we shall briefly review the principles of quantum and statistical mechanics theories. We will introduce the equations that relate the thermochemical properties, such as specific heat and entropy, with the molecular properties of vibration and rotation. Although the

materials to be discussed are not required for this course, the student is nonetheless encouraged to go over the notes and establish a basic understanding of the origins of energy quantization and partition function.

2.3.4.2 Quantum mechanics

In classical mechanics a knowledge of initial coordinates and velocities of a system of particles is sufficient to predict the future course of the system if the equations of motion and the potential field are known. At the atomic and sub-atomic scale, the Heisenberg uncertainty principle states that it is impossible to specify the momentum and coordinate of a particle simultaneously, since the measurement of one of these two quantities would inevitably perturb the other. Therefore the classical mechanics treatment will have to be modified to include the principle of uncertainty. This modification led to the development of quantum mechanics.

The basic premise of quantum mechanics is the existence of the so-called wave function $\Psi(\mathbf{r}, t)$, where \mathbf{r} is the set of coordinate necessary to describe the system of particles, and t is the time. Thus the quantity

$$\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)dr_1dr_2\cdots dr_{3N}$$

gives the probability at time t the system of particles is found between r_1 and r_1+dr_1 , r_2 and r_2+dr_2 , and so on. The normalization condition is

$$\int \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\mathbf{r} = 1 . \quad (2.5)$$

The solution of the problem is provided by the Schrödinger equation, which is given for a one particle system by

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} , \quad (2.6)$$

where $\hbar = h/2\pi$, h is the Planck constant ($h = 6.626068 \times 10^{-34}$ m²kg/s), m is the particle mass and $V(x)$ is the potential function. This differential equation is linear so it satisfies any linear superposition of wave functions. The operator on the left-hand side of equation is known as the Hamiltonian operator, which in classical mechanics expresses the total energy or a sum of the kinetic energy K and potential energy V

$$H = K + V = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \rightarrow \tilde{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) , \quad (2.7)$$

where \mathbf{p} is the momentum vector. Here we make the identification that $\mathbf{p} \rightarrow i\hbar\nabla$. Therefore $-\hbar^2/2m\nabla^2$ is the kinetic energy operator and the Hamiltonian operator \tilde{H} is the total energy operator.

A separation of variable $\Psi(x,t) = \psi(x)T(t)$ led us to obtain

$$\frac{1}{\psi} \left[-\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r})\psi \right] = \frac{i\hbar \frac{dT}{dt}}{T} = E, \quad (2.8)$$

where E is the eigenvalue of the eigenfunction ψ or the total energy of the system. The time independent Schrödinger equation is thus obtained as

$$\tilde{H}\psi = \psi E. \quad (2.9)$$

2.4.3.3 Particle-in-a-one-dimensional box

A one-dimensional box of length L may be described by a square potential energy well given by

$$V(x) = \begin{cases} \infty & \text{for } x < 0 \text{ and } x > L \\ 0 & \text{for } 0 \leq x \leq L \end{cases}. \quad (2.10)$$

Therefore, the wavefunction of the particle satisfies

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi. \quad (2.11)$$

Since the probability of finding a particle outside the box is zero, the wave function must go to zero at the walls, i.e., the boundary conditions are

$$\begin{aligned} \psi(0) &= 0 \\ \psi(L) &= 0 \end{aligned}. \quad (2.12)$$

The solution is given by

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x, \quad (2.13)$$

and the energy eigenvalue is

$$E_n = \frac{(hn)^2}{8mL} \quad n = 1, 2, \dots. \quad (2.14)$$

Extending the above solution to the motion of a particle in a three-dimensional box and recognizing that the underlying problem describes the translational motions of a particle, we write the translational energy as

$$E_{trans(n_x, n_y, n_z)} = \frac{\hbar^2}{8mL} (n_x + n_y + n_z)^2 \quad n_x, n_y, n_z = 1, 2, \dots, \quad (2.15)$$

An important consequence of Eq. (2.15) is that it shows the energy of a particle in motion to be quantized. Here n is the quantum number.⁵

2.4.3.4 A simple harmonic oscillator

The potential function of a simple harmonic oscillator is given by

$$V(x) = \frac{1}{2} kx^2 = \frac{1}{2} m\omega x^2, \quad (2.16)$$

where k is the spring constant, x is the displacement from the equilibrium, and $\omega = k/m$ is the angular frequency (the natural vibrational frequency of the system). Putting Eq. (2.16) into Eq. (2.9) and non-dimensionalizing it by letting $x = \sqrt{\hbar/m\omega} \chi$, we obtain

$$\left(\frac{d^2}{d\chi^2} - \chi^2 \right) \psi = -\frac{2E}{\omega\hbar} \psi. \quad (2.17)$$

Letting $\varepsilon = 2E/\omega\hbar$, we simplify the above equation to

$$\frac{d^2\psi}{d\chi^2} = (\chi^2 - \varepsilon) \psi. \quad (2.18)$$

Although there are several ways to solve the above equation, we shall obtain the solution using a simpler approach. Considering the form of Eq. (2.18) and that the wave function ψ must be zero for $\chi \rightarrow \infty$, we find that the following form of function satisfies these condition,

$$\psi_n = c_n x_n e^{-\alpha_n \chi^2} \quad n = 0, 1, \dots. \quad (2.19)$$

For $n = 0$, we differentiate the above expression twice to give

$$\frac{d\psi_0}{d\chi} = -2\alpha_0 \chi \psi_0. \quad (2.20)$$

⁵ Note that $n=0$ is the trivial solution of the problem, and physically it represents a particle with zero momentum.

$$\frac{d^2\psi_0}{d\chi^2} = (4\alpha_0^2\chi^2 - 2\alpha_0)\psi_0 \quad (2.21)$$

Comparing Eq. (2.21) with Eq. (2.18), we obtain

$$\alpha_0 = \frac{1}{2} \quad \text{and} \quad \varepsilon_0 = 1 \quad , \quad (2.22)$$

It follows that

$$E_0 = \frac{1}{2}\hbar\omega \quad . \quad (2.23)$$

For $n = 1$ we have

$$\frac{d^2\psi_1}{d\chi^2} = (4\alpha_1^2\chi - 6\alpha_1)\psi_1 \quad , \quad (2.24)$$

$$\varepsilon_1 = 3 \quad , \quad (2.25)$$

and

$$E_1 = \frac{3}{2}\hbar\omega \quad . \quad (2.26)$$

The general solution is

$$E_{vib,n} = \left(n + \frac{1}{2}\right)\hbar\omega \quad n = 0, 1, \dots \quad , \quad (2.27a)$$

where n is the vibrational quantum number and the subscript “*vib*” is added to denote vibrational energy. Here we see that with $n = 0$, $E_0 = \hbar\omega/2 > 0$. Therefore, the energy of oscillator is greater than zero at the lowest quantum state. This gives rise to the *zero-point energy* of a molecule (see, Figure 2.8). The angular frequency ω may be converted to the vibration frequency, $\nu = \omega/2\pi$. Thus the vibrational energies are

$$E_{vib,n} = \left(n + \frac{1}{2}\right)h\nu \quad n = 0, 1, \dots \quad , \quad (2.27b)$$

2.4.3.5 A rigid rotor

In the center of mass reference frame, the moment of inertia of a diatomic molecule is given by

$$I = \mu R_e^2 \quad . \quad (2.28)$$

where μ is the reduced mass of the two atoms, $\mu = m_1 m_2 / (m_1 + m_2)$, and R_e is the distance of separation between the two atoms. The classical mechanics description of the kinetic energy of a rigid rotor is

$$\begin{aligned} K &= \frac{\mu}{2} (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \\ &= \frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) \end{aligned} \quad (2.29)$$

We make the transformation that $p_x \rightarrow i\hbar \partial / \partial x$ and write the rotational Hamiltonian as

$$\tilde{H} = -\frac{\hbar^2}{2\mu} \nabla^2, \quad (2.30)$$

which may be transformed to the spherical polar coordinate form⁶ to give

$$\tilde{H} = -\frac{\hbar^2}{2\mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \varphi} \right]. \quad (2.31)$$

Since this is a rigid rotor, $r = R_e$ is fixed, the first term disappears. We have $I = \mu R_e^2 = \mu r^2$ and

$$\tilde{H} = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \varphi} \right]. \quad (2.32)$$

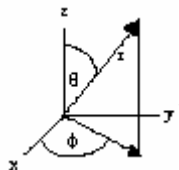
Using the approach of separation of variables by letting $\psi(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$, we obtain

$$\begin{aligned} -\frac{1}{\Phi} \frac{d^2 \Phi}{d\varphi^2} &= \alpha \\ \left(\frac{d^2 \Theta}{d\theta^2} + \frac{\cos \theta}{\sin \theta} \frac{d\Theta}{d\theta} + \frac{2IE\Theta}{\hbar^2} \right) \frac{\sin^2 \theta}{\Theta} &= \alpha \end{aligned} \quad (2.33)$$

where α must be a constant. The first equation has the solution of the form

$$\Phi = A e^{im\varphi}, \quad (2.34)$$

⁶ The spherical coordinate is given by



where normalization gives $\mathcal{A} = (2\pi)^{-1/2}$. In addition, it may be shown that $\alpha = m^2$ by differentiating Eq. (2.34) twice and comparing it with Eq. (2.33). The periodicity of Φ requires that $\Phi(\phi) = \Phi(\phi + 2\pi)$. It follows that the acceptable values for m are $0, \pm 1, \pm 2, \dots$. The second equation may now be re-written as

$$\frac{d^2\Theta}{d\theta^2} + \frac{\cos\theta}{\sin\theta} \frac{d\Theta}{d\theta} + \left(\frac{2IE}{\hbar^2} - \frac{m^2}{\sin^2\theta} \right) \Theta = 0 . \quad (2.35)$$

This is, in fact, the Legendre differential equation. The energy may be found by recognizing the cyclic boundary condition. The final result for rotational energy is

$$E_{rot,J} = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, \dots , \quad (2.36)$$

where J is the rotation quantum number. The lowest energy state is $E_{rot,0} = 0$, so there is no zero-point rotational energy. In units of wave numbers (cm^{-1}), Eq. (2.36) may be written as

$$E_{rot,J} = BJ(J+1) \quad J = 0, 1, \dots , \quad (2.37)$$

where B is known as the rotational constant

$$B = \frac{h^2}{8\pi^2 cI} , \quad (2.38)$$

and c is the speed of light.

There is a small complication here. The eigenfunctions are known to be spherical harmonics $Y_{J,m_j}(\theta, \phi)$

$$\psi_{J,m_j}(\theta, \phi) \equiv Y_{J,m_j}(\theta, \phi) = P_J^{|m_j|}(\cos\theta) \exp(im\phi) , \quad (2.39)$$

with

$$m_j = -J, -J+1, \dots, 0, 1, \dots, J-1, J , \quad (2.40)$$

where $P_J^{|m_j|}$ is the associated Legendre functions. We see that the energy eigenvalue is dependent on J only. Yet for each J we can have $2J+1$ m 's. In other words, there are $2J+1$ eigenfunctions that give identical energy or *degenerate* energy levels for a given J value. The energy degeneracy of a rotor is therefore $2J+1$.

2.4.3.6 The molecular partition function

The partition function is the primary quantity of statistical mechanics. In the next section, we shall develop the relationships between the partition function and macroscopic thermochemical properties. Here, we shall develop the expression for molecular partition functions.

We first note that the partition function measures the *total number of possible energy states* a molecule can be in at an equilibrium temperature T . The partition function is related to the Maxwell-Boltzmann distribution of energy, which in a discrete form is expressed by

$$\rho(E_i) = \frac{e^{-E_i/k_B T}}{\sum_j e^{-E_j/k_B T}} , \quad (2.41)$$

where $\rho(E_i)$ is the density of energy states between E_i and $E_i + dE_i$, and k_B is the Boltzmann constant ($k_B = 1.3806503 \times 10^{-23}$ J/K).

The denominator on the right-hand side of Eq. (2.41) is in fact the one-molecule partition function $q(T, V)$, since it is the sum of all possible energy states at temperature T .

$$q(V, T) = \sum_j e^{-E_j/k_B T} . \quad (2.42)$$

The total Hamiltonian of a molecule may be written as the sum of translational, rotational, vibrational, and electronic contributions

$$\tilde{H} = \tilde{H}_{trans} + \tilde{H}_{rot} + \tilde{H}_{vib} + \tilde{H}_{elec} . \quad (2.43)$$

Since these degrees of freedoms are decoupled, the total energy of a molecule is

$$E = E_{trans} + E_{rot} + E_{vib} + E_{elec} , \quad (2.44)$$

where the expressions for the translational, rotational and vibrational energies have been obtained previously.

Because the one-molecule partition function gives the total number of possible energy states, this partition function is calculated as the product of partition functions for separate degrees of freedom and the contributions from various electronic states,⁷ i.e.,

$$q = q_{trans} q_{rot} q_{vib} q_{elec} , \quad (2.45)$$

⁷ Consider that we have 2 quarters and 2 dimes. The number of ways that the 2 quarters can be organized are head/head, head/tail, tail/head, tail/tail. That is, a total of 4 configurations. Likewise the 2 dimes can also have 4 configurations. The total number of configurations when we count the quarts and dimes together is $4 \times 4 = 16$.

Translational partition function

The translational partition function may be obtained by combining Eqs. (2.15) and (2.42), i.e.,

$$q_{trans}(V, T) = \sum_j e^{-\frac{h^2}{8mL}(n_x+n_y+n_z)^2/k_B T} . \quad (2.46)$$

The summation cannot be performed in closed form but since the energy levels are closely spaced compared with $k_B T$ it can be approximated by an integral

$$\begin{aligned} q_{trans}(V, T) &= \int_0^\infty \int_0^\infty \int_0^\infty e^{-\frac{h^2}{8mL}(n_x+n_y+n_z)^2/k_B T} dn_x dn_y dn_z \\ &= \left(\int_0^\infty e^{-\frac{h^2 n^2}{8mL}/k_B T} dn \right)^3 , \\ &\approx \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} V \end{aligned} \quad (2.47)$$

where $V = L^3$ is the volume.

Rotational partition function

The rotational partition function may be obtained by combining Eqs. (2.37) and (2.42)

$$q_{rot}(V, T) = \sum_J (2J+1) e^{-BJ(J+1)/k_B T} , \quad (2.48)$$

where the $(2J+1)$ term accounts for energy degeneracy (statistical weight). We again recognize that the energy spacing is small compared to $k_B T$ and approximate the infinite sum by an integral

$$\begin{aligned} q_{rot}(V, T) &= \int_0^\infty (2J+1) e^{-BJ(J+1)/k_B T} dJ \\ &= \frac{k_B T}{B} . \end{aligned} \quad (2.49)$$

Since the rotational constant has units of wave number (cm^{-1}), the Boltzmann constant must have the units $\text{cm}^{-1}\text{K}^{-1}$. Here we must recognize that for symmetric molecules like N_2 , H_2 , and CO_2 , the molecule would need to rotate 180° to come back to the same state, yet an asymmetric molecule has passed only one state by going around 360° . Therefore Eq. (2.49) must have overcounted the energy states by a factor of 2 for a symmetric molecule. We therefore introduce a rotational symmetry number σ and re-write Eq. (2.49) as

$$q_{rot}(V, T) = \frac{k_B T}{\sigma B} . \quad (2.50)$$

Alternatively, the rotational partition function may be written in terms of the moment of inertia

$$q_{rot}(V, T) = \frac{8\pi^2 I k_B T}{\sigma h^2} . \quad (2.51)$$

Vibrational partition function

Combining Eqs. (2.27b) and (2.42) gives the vibrational partition function for one mode of vibration

$$\begin{aligned} q_{vib}(V, T) &= \sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)h\nu/k_B T} \\ &= e^{-h\nu/2k_B T} \sum_{n=0}^{\infty} e^{-nh\nu/k_B T} . \end{aligned} \quad (2.52)$$

The summation of Eq. (2.52) can be performed in closed form to give

$$q_{vib}(V, T) = \frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}} , \quad (2.53)$$

Electronic partition function

The partition function of electronic states q_{elec} quantifies electronic degeneracies for the molecule at the ground and electronically excited states. We select the ground state energy to be zero and the partition function is written as

$$q_{elec}(V, T) = g_1 + g_2 e^{-\frac{E_2}{k_B T}} + \dots , \quad (2.54)$$

where g_i is the degeneracy of the i^{th} electronic state. For $i = 1$, we have the ground state. For $i > 1$, we have excited electronic states, which are important only at extremely high temperatures.

The general rule of thumb is that the degeneracy value $g = 1$ for a molecule (all electrons are paired and therefore there is only one arrangement for electron spin). This type of molecule is sometime called a singlet molecule. For a free radical species with only one unpaired electron, $g = 2$ since the unpaired electron can have up or down spin. This type of molecule is referred to as doublet. A triplet molecule or free radical would have two unpaired electrons,⁸ and $g = 3$.

⁸ Guess what? The ground-state molecular oxygen (O_2) is triplet. Perhaps that's why it's so reactive.

2.4.3.7 The canonical ensemble and its partition function

The *canonical* (N, V, T) *ensemble* defines a system of N molecules with fixed volume V and temperature T . The molecular partition function, discussed in the previous section, is a special case of the canonical partition function, i.e., $q(V, T) = Q(1, V, T)$. For a diluted gas of N molecules which are non-interacting (where the energy states of one molecule has no impact on the energy states of another molecule), the ensemble partition function is

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}, \quad (2.55)$$

where the $N!$ accounts for the fact that molecules are indistinguishable.⁹ We are now ready to develop the expressions for the canonical partition function,

$$\begin{aligned} Q(N, V, T) &= \frac{(q_{\text{tran}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}})^N}{N!}, \\ &= \frac{q_{\text{tran}}^N}{N!} (q_{\text{rot}} q_{\text{vib}} q_{\text{elec}})^N, \end{aligned} \quad (2.56)$$

The Stirling approximation comes handy here since for large N values

$$\ln N! \approx N \ln N - N, \quad (2.57)$$

or

$$N! \approx N^N e^{-N}. \quad (2.58)$$

The translational part of the partition function is then

⁹ Consider that we have 3 coins being tossed. For each coin, we have $q = 2$ possible outcomes. If the coins are distinguishable, we have $2^3 = 8$ possible outcomes. These are

outcome #	coin #		
	1	2	3
1	head	head	head
2	head	head	tail
3	head	tail	head
4	head	tail	tail
5	tail	head	head
6	tail	head	tail
7	tail	tail	head
8	tail	tail	tail

If the coins are indistinguishable, some of outcomes would be identical to each other, as seen by the outcome that are shaded in the same color. We see that the number of outcomes for indistinguishable coins is $2^3/(3-1)!$ or $q^N/(N-1)!$. Of course, if N is very larger (e.g., number of gas molecules in 1 m³ at 1 atm pressure), $q^N/(N-1)! \approx q^N/N!$

$$Q_{\text{trans}} = \left(\frac{q_{\text{trans}}^e}{N} \right)^N . \quad (2.59)$$

Internal Energy

Now we have the entire suite of expressions for the partition function and are ready to obtain the expressions for calculating macroscopic thermochemical properties. In the canonical ensemble (N, V, T), the ensemble average of energy may be expressed by

$$\langle E \rangle = \frac{\sum_{i=1}^N E_i e^{-E_i/k_B T}}{Q} , \quad (2.60)$$

where E_i is the energy of the i^{th} molecule at a given time and temperature. It is easily shown that the right-hand side of the above equation is $-\partial \ln Q / \partial (1/k_B T)$. Hence, we have

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} . \quad (2.61)$$

The energy expressed above is in fact the internal energy U of the system, which is the sum of internal energies for N number of molecules.

Considering that a monoatomic molecule has only translational degrees of freedom, the total internal energy of a monoatomic gas is

$$\begin{aligned} U = \langle E_{\text{trans}} \rangle &= k_B T^2 \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} \\ &= k_B T^2 \left(\frac{3N}{2T} \right) \\ &= \frac{3}{2} N k_B T \end{aligned} . \quad (2.62)$$

This result is expected since the mean internal translational energy of each molecule is $3k_B T/2$. Note that Eq. (2.62) is completely valid for a monoatomic molecule if the contributions of higher electronic energy state can be neglected. Take the H• atom as an example. Eq. (2.62) gives $\bar{c}_v = (\partial u / \partial T)_v = 3R_u/2$ and for an ideal gas $\bar{c}_p = \bar{c}_v + R_u = 5R_u/2 = 20.785 \text{ J/mol}$,¹⁰ which agrees exactly with the \bar{c}_p values given on p. 47 of Lecture 1 notes.

Pressure

For a canonical (N, V, T) ensemble, suppose the first n_1 molecules have the same energy state ($\epsilon_1 = \epsilon_2 = \dots = \epsilon_{n_1} = E_1$), the second n_2 molecules have the same energy state ($\epsilon_{n_1+1} = \epsilon_{n_1+2} = \dots = \epsilon_{n_1+n_2} = E_2$), and so on. The molecules of each energy states therefore belong

¹⁰ Note that for 1 mole of molecule, $\bar{u} = \frac{3}{2} N_{\text{avg}} k_B T = \frac{3}{2} R_u T$ where N_{avg} is Avogadro's number.

to a separate *microcanonical* (n_i, V, E_i) ensemble, and the (N, V, T) ensemble is a collection of many microcanonical ensembles. Of course, $N = \sum n_i$.

We now examine the statistical mechanical expression for pressure. The first law of thermodynamics states that for an adiabatic, constant pressure process $dE_j = -p_j dV$ is the work done by expanding the system volume by dV . Thus the pressure of that state is given by

$$p_j = -\left(\frac{\partial E_j}{\partial V}\right)_n = -\left(\frac{\partial E_j}{\partial V}\right)_N. \quad (2.63)$$

In the above equation, since all n 's are fixed, $N = \sum n_i$ must be fixed. The canonical ensemble average of pressure at a given temperature T is therefore

$$\begin{aligned} p &= -\frac{\sum_j \left(\frac{\partial E_j}{\partial V}\right)_N e^{-E_j/k_B T}}{Q} \\ &= k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}. \end{aligned} \quad (2.64)$$

Again, for a monoatomic gas, we have

$$\begin{aligned} p &= k_B T \left(\frac{\partial \ln Q_{\text{trans}}}{\partial V}\right)_{N,T}, \\ &= k_B T \left(\frac{N}{V}\right), \end{aligned} \quad (2.65)$$

where is the equation of state for an ideal gas. Additionally, a comparison of Eq. (2.69) with the well known $p\bar{v} = R_u T$ gives $k_B = R_u N_{\text{avg}}$, where N_{avg} is Avogadro's number ($N_{\text{avg}} = 6.022 \times 10^{23}$ molecules/mol).

Entropy

Recall that entropy is a measure of the randomness of the system. Here we quantify what this randomness means. For a canonical (N, V, T) , the number of ways to place the N molecules into the microcanonical (n, V, E) ensembles is¹¹

$$\Omega_N = \frac{N!}{n_1! n_2! \dots}. \quad (2.66)$$

¹¹ Suppose we have 4 coins and two bags, one colored yellow and the other green. Each bag is to hold two coins. We can have the following arrangements: (1,2) and (3,4), (1,3) and (2,4), (1,4) and (2,3), (2,3) and (1,4), (2,4) and (1,3), and lastly (3,4) and (1,2), or a total of 6 ways to do this. Here $N = 4$, $n_1 = 1$, $n_2 = 2$ and $\Omega_N = 4!/(2!2!) = 6$

We can imagine that the larger the Ω_N is, the larger the entropy S . Statistical mechanics define the entropy to be

$$S = k_B (\ln \Omega_N) . \quad (2.67)$$

Using the Stirling approximation, we have

$$\begin{aligned} \ln \Omega_N &= N \ln N - N - \sum_i (n_i \ln n_i - n_i) \\ &= -N \sum_i \frac{n_i}{N} \ln \frac{n_i}{N} , \end{aligned} \quad (2.68)$$

where, of course, $n_i/N = e^{-E_i/k_B T} / Q$. It follows that

$$\begin{aligned} S &= -N k_B \sum_i \frac{e^{-E_i/k_B T}}{Q} \ln \frac{e^{-E_i/k_B T}}{Q} \\ &= k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q \\ &= k_B \left(\frac{\langle E \rangle}{k_B T} + \ln Q \right) \end{aligned} \quad (2.69)$$

It may be shown¹² that for $T \rightarrow 0$ K, $S \rightarrow N k_B \ln g_1$. Since most crystal materials have the ground-state degeneracy of 1, we see that Eq. (2.69) satisfies the thermodynamic third law. That is, entropy of a substance approaches zero at the temperature approaches absolute zero.

Without considering the electronic partition function, the entropy of an ideal, monoatomic gas can be derived from Eq. (2.69) as

$$S = N k_B \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right]. \quad (2.70)$$

The standard molar entropy ($p = 1$ atm, $N = N_{\text{avg}} = 6.023 \times 10^{23}$) may be given by (see note 10 on p. 24 for the conversion of absolute total entropy to molar entropy),

$$\bar{s}^\circ = R_u \ln \left[\left(\frac{2\pi m}{h^2} \right)^{3/2} \frac{(k_B T e)^{5/2}}{(1.013 \times 10^5 \text{ Pa})} \right].$$

For one mole of H• atoms at 298.15 K, we have¹³

¹² McQuarrie, D. A. *Statistical Mechanics*, Happer & Row, New York, 1973.

¹³ Note that the molecular mass of the H• atom is 1 amu, or $1/N_{\text{avg}} = 1.6605 \times 10^{-24}$ g or 1.6605×10^{-27} kg.

$$\begin{aligned} \bar{s}^\circ(298.15 \text{ K}) &= 8.3144 \ln \left[\left(\frac{2\pi \times 1.6605 \times 10^{-27}}{(6.626068 \times 10^{-34})^2} \right)^{\frac{3}{2}} \times \frac{(1.3806503 \times 10^{-23} \times 298.15 \times e)^{\frac{5}{2}}}{1.013 \times 10^5} \right] \\ &= 108.8 \text{ (J/mol-K)} \end{aligned}$$

A similar calculation at 1000 K gives $\bar{s}^\circ(1000 \text{ K}) = 134.0 \text{ (J/mol-K)}$. Comparing these values with those listed on p. 47 of Lecture 1 notes [i.e., $\bar{s}^\circ(298.15 \text{ K}) = 114.7 \text{ (J/mol-K)}$, and $\bar{s}^\circ(1000 \text{ K}) = 139.9 \text{ (J/mol-K)}$], we see that the calculated values are smaller by a constant factor of 5.9 (J/mol-K).

Obviously we are missing something here. Recall that the ground-state hydrogen atom is a doublet because it has an unpaired electron, which give rise to a non-unity electronic degeneracy number. Here, $g_1 = 2$. Neglecting excited electronic states, we have the electronic partition function $q_{elec} = 2$ (see, Eq. 2.54). It follows that there must be an extra $k_B \ln q_{elec} = k_B \ln(2)$ term in the entropy equation. In the form of molar entropy, this extra term is $R_u \ln(2) = 5.8 \text{ (J/mol-K)}$, which largely explains the difference in the entropy value given above.

2.4.3.8 Polyatomic molecules and summary of statistical mechanics expressions

So far, we have discussed the partition functions of a rigid rotor and a single harmonic oscillator. For polyatomic molecules, we need to consider that there are up to three rigid rotors and a bunch of harmonic oscillators. The translational partition function of polyatomic molecules, on the other hand, is completely identical to that of monoatomic and diatomic molecules.

Rotational partition function of a polyatomic molecule

If a molecule is linear, the problem is identical to a diatomic molecule. The moment of inertia I is

$$I = \sum_{j=1}^{N_a} m_j d_j^2, \quad (2.71)$$

where d_j is the distance of the j^{th} atom from the center of mass of the molecule. The coordinates of the center of mass are given by

$$\begin{aligned} x_{cm} &= \frac{1}{M} \sum_{j=1}^{N_a} m_j x_j \\ y_{cm} &= \frac{1}{M} \sum_{j=1}^{N_a} m_j y_j, \\ z_{cm} &= \frac{1}{M} \sum_{j=1}^{N_a} m_j z_j \end{aligned} \quad (2.72)$$

where $x_j, y_j,$ and z_j are the Cartesian coordinates of the j^{th} atom, and $M = \sum_{j=1}^{N_a} m_j$.

For a rigid, nonlinear molecule, the rotational properties may be characterized by the principal moments of the body. That is, among all possible sets of Cartesian axes with origin at the center of mass of the molecule, there always exist a particular set of coordinates $X, Y,$ and Z such that all the products of inertia vanishes, e.g.,

$$I_{xy} = \sum_{j=1}^{N_a} m_j (x_j - x_{cm})(y_j - y_{cm}) = 0. \quad (2.73)$$

The rotations of a molecule defined by this particular set of coordinates are completely decoupled from each other. The moments of inertia along this specific set of coordinates are known as the principal moments of inertia. They may be calculated from

$$\begin{aligned} I_X &= \sum_{j=1}^{N_a} m_j \left[(Y_j - Y_{cm})^2 + (Z_j - Z_{cm})^2 \right] \\ I_Y &= \sum_{j=1}^{N_a} m_j \left[(X_j - X_{cm})^2 + (Z_j - Z_{cm})^2 \right]. \\ I_Z &= \sum_{j=1}^{N_a} m_j \left[(X_j - X_{cm})^2 + (Y_j - Y_{cm})^2 \right] \end{aligned} \quad (2.74)$$

Likewise three rotational constants may be defined for each principal axis of rotation,

$$B_{(X,Y,Z)} = \frac{h^2}{8\pi^2 I_{(X,Y,Z)}}. \quad (2.75)$$

Let's start with an easy case in which $I_X = I_Y = I_Z$ ($B_X = B_Y = B_Z = B$). Such case is known as a spherical top. Because the three rotors are identical (or degenerate), we only need to specify one rotational quantum number J with rotational energy levels given by $E_J = BJ(J+1)$, and the rotational degeneracy is $(2J+1)^2$ ($J = 0, 1, 2, \dots$). As in the derivation of Eq. (2.49), the partition function at sufficiently high temperature may be approximated by the integral

$$\begin{aligned} q_{rot} &= \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{-BJ(J+1)/k_B T} dJ \\ &\approx \frac{1}{\sigma} \int_0^{\infty} 4J^2 e^{-BJ(J+1)/k_B T} dJ \\ &= \frac{\pi^{1/2}}{\sigma} \left(\frac{k_B T}{B} \right)^{3/2} \end{aligned} \quad (2.76)$$

In the case of a symmetric top $I_X = I_Y \neq I_Z$, the problem is a bit involved but the solution at the end is nearly identical to Eq. (2.76). Specifically, the expression of rotational energy levels of a symmetric top is $E_{JK} = B_X J(J+1) + K^2 (B_Z - B_X)$ with the degeneracy $(2J+1)$,

where $J = 0, 1, 2, \dots$; $K = J, J-1, \dots, -J$. Putting these expressions into the partition function equation and carrying out double integration, we obtain

$$q_{rot} = \frac{1}{\sigma} \int_0^\infty \int_{-J}^J (2J+1) e^{-[B_x J(J+1) + K^2(B_z - B_x)]/k_B T} dJ dK$$

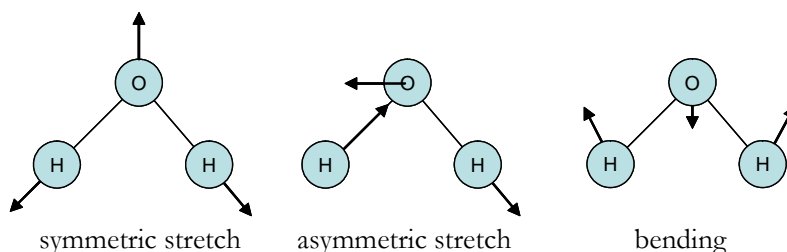
$$\approx \frac{\pi^{1/2}}{\sigma} \left(\frac{k_B T}{B_x} \right) \left(\frac{k_B T}{B_z} \right)^{1/2} \quad (2.77)$$

We may now extend the problem to the case where $I_x \neq I_y \neq I_z$ by noting the similarity of Eqs. (2.76) and (2.77). The general equation of rotational partition function may be given by

$$q_{rot} \approx \frac{\pi^{1/2}}{\sigma} \left(\frac{k_B T}{B_x} \right)^{1/2} \left(\frac{k_B T}{B_y} \right)^{1/2} \left(\frac{k_B T}{B_z} \right)^{1/2} \quad (2.78)$$

Vibrational partition function of a polyatomic molecule

For a nonlinear polyatomic molecule, we have $3N_a - 6$ internal vibrational degrees of freedom. These degrees of freedom represent the number of independent coordinates in which the nuclei vibrate. It is possible to define $3N_a - 6$ coordinates such that the vibrational motions along these coordinates are completely independent of each other, i.e., these coordinates are orthogonal. These vibrational modes are known as the *normal mode vibration*. Take the water molecule as an example. The 3 normal modes are illustrated in the following diagram:



Each of these normal mode vibrations has its own normal frequency ν_i . Since these vibrations are independent of each other, the total vibrational partition function is a product of the partition functions for the α number of harmonic oscillators,

$$q_{vib} \approx \prod_{i=1}^{\alpha} q_{vib,i} = \prod_{i=1}^{\alpha} \frac{e^{-h\nu_i/2k_B T}}{1 - e^{-h\nu_i/k_B T}}, \quad (2.79)$$

where $\alpha = 3N_a - 6$ for a nonlinear molecule and $3N_a - 5$ for a linear molecule.

Summary of statistical mechanics equations of thermochemical data

In summary, we have the following expressions developed for diatomic gases at the ground electronic state:

$$Q = \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V \right] \left[\frac{k_B T}{\sigma B} \right] \left[\frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}} \right] g_1,$$

$$\frac{\bar{u}}{R_u T} = \frac{5}{2} + \frac{h\nu}{2k_B T} + \frac{h\nu/k_B T}{e^{h\nu/k_B T} - 1},$$

$$\frac{\bar{c}_v}{R_u} = \frac{5}{2} + \left(\frac{h\nu}{k_B T} \right)^2 \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2},$$

$$\frac{\bar{s}^\circ}{R_u} = \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right] + \ln \left[\frac{k_B T e}{\sigma B} \right] + \left[\frac{h\nu/k_B T}{e^{h\nu/k_B T} - 1} - \ln(1 - e^{-h\nu/k_B T}) \right] + \ln g_1.$$

For a linear polyatomic gas, we have

$$Q = \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V \right] \left[\frac{k_B T}{\sigma B} \right] \left[\prod_{i=1}^{3N_a-5} \frac{e^{-h\nu_i/2k_B T}}{1 - e^{-h\nu_i/k_B T}} \right] g_1,$$

$$\frac{\bar{u}}{R_u T} = \frac{5}{2} + \left[\sum_{i=1}^{3N_a-5} \left(\frac{h\nu_i}{2k_B T} + \frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} \right) \right],$$

$$\frac{\bar{c}_v}{R_u} = \frac{5}{2} + \sum_{i=1}^{3N_a-5} \left(\frac{h\nu_i}{k_B T} \right)^2 \frac{e^{h\nu_i/k_B T}}{(e^{h\nu_i/k_B T} - 1)^2},$$

$$\frac{\bar{s}^\circ}{R_u} = \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right] + \ln \left[\frac{k_B T e}{\sigma B} \right] + \sum_{i=1}^{3N_a-5} \left[\frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} - \ln(1 - e^{-h\nu_i/k_B T}) \right] + \ln g_1,$$

and for a nonlinear polyatomic gas,

$$Q = \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V \right] \left[\frac{\pi^{1/2} \left(\frac{k_B T}{B_X} \right)^{1/2} \left(\frac{k_B T}{B_Y} \right)^{1/2} \left(\frac{k_B T}{B_Z} \right)^{1/2}}{\sigma} \right] \left[\prod_{i=1}^{3N_a-6} \frac{e^{-h\nu_i/2k_B T}}{1 - e^{-h\nu_i/k_B T}} \right] g_1,$$

$$\frac{\bar{u}}{R_u T} = 3 + \left[\sum_{i=1}^{3N_a-6} \left(\frac{h\nu_i}{2k_B T} + \frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} \right) \right],$$

$$\frac{\bar{c}_v}{R_u} = 3 + \sum_{i=1}^{3N_a-6} \left(\frac{h\nu_i}{k_B T} \right)^2 \frac{e^{h\nu_i/k_B T}}{(e^{h\nu_i/k_B T} - 1)^2},$$

$$\frac{\bar{s}^\circ}{R_u} = \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right] + \ln \left[\frac{\pi^{1/2} e^{3/2} \left(\frac{k_B T}{B_X} \right)^{1/2} \left(\frac{k_B T}{B_Y} \right)^{1/2} \left(\frac{k_B T}{B_Z} \right)^{1/2}}{\sigma} \right]$$

$$+ \sum_{i=1}^{3N_a-6} \left[\frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} - \ln(1 - e^{-h\nu_i/k_B T}) \right] + \ln g_1$$

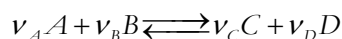
2.4.3.9 Final remarks

There are several key points that one may derive from the above discussion.

- (a) The sensible enthalpy, specific, and entropy of a substance may be accurately determined if its molecular properties of rotational constants and vibrational frequencies are known. Until recently, these molecular properties were usually determined by various spectroscopy techniques. The advances made in recent years in quantum chemistry tools have allowed these molecular properties be determined from *ab initio* theory. Therefore, the calculation of the thermochemical properties of a given substance is no longer a scientific challenge.
- (b) Many equations presented in the proceeding sections are also critically to a basic understanding of combustion reaction kinetics. Therefore, we shall revisit some of these equations in a few weeks.

Homework #2

1. Using the group additivity method, estimate the enthalpy of formation, specific heat (\bar{c}_p) and standard entropy for vapor-phase normal octane (C_8H_{18}) at 298 K (300 K).
2. Show that for a polyatomic gas, the contribution of molecular rotations to the total internal energy is equal to $3/2R_uT$.
3. Obtain an expression for the equilibrium constant K_p for an arbitrary reaction give by



in terms of the partition functions for substances A , B , C , and D .

4. The molecular properties of water H_2O are known. These are, molecular mass: 18.01528 amu, rotational constants: 27.87, 14.53, and 9.31 cm^{-1} , and normal vibrational frequencies: 1592, 3587, and 3726 cm^{-1} . Determine the specific heat (\bar{c}_p), standard entropy, and sensible enthalpy as a function of temperature, and tabulate these thermochemical values in the form of the JANAF table (the first four columns only). Compare your values with those shown on p. 35 of Lecture 1 notes.

APPENDIX

Table 2A. Group additivity values taken from Ritter and Bozzelli²

Groups	$\bar{h}_{f,298}^{\circ}$ (kJ/mol)	\bar{s}_{298}° (J/mol-K)	$\bar{c}_p(T)$ (J/mol)						
			300	400	500	600	800	1000	1500
C-(C,H ₃)	-42.68	127.24	25.90	32.80	39.33	45.15	54.48	61.80	73.55
C-(C _b ,H ₃)	-42.68	127.24	25.90	32.80	39.33	45.15	54.48	61.80	73.55
C-(C _d ,H ₃)	-42.68	127.24	25.90	32.80	39.33	45.15	54.48	61.80	73.55
C-(C _t ,H ₃)	-42.68	127.24	25.90	32.80	39.33	45.15	54.48	61.80	73.55
C-(C ₂ ,H ₂)	-20.63	39.41	23.01	29.08	34.52	39.12	46.32	51.63	59.41
C-(C ₃ ,H)	-7.95	-50.50	19.00	25.10	30.00	33.68	38.95	42.05	46.78
C-(C ₄)	2.09	-146.86	18.28	25.65	30.79	33.97	36.69	36.65	33.97
C _d -(H ₂)	26.19	115.52	21.34	26.61	31.42	35.56	42.13	47.15	55.19
C _d -(C,H)	35.94	33.35	17.41	21.05	24.31	27.20	32.01	35.35	40.25
C _d -(C ₂)	43.26	-53.14	17.15	19.29	20.88	22.01	24.27	25.44	26.61
C _d -(C _d ,H)	28.37	26.69	18.66	24.23	28.24	31.05	34.94	38.12	42.22
C _d -(C,C _d)	37.15	-61.09	18.41	22.47	24.81	25.86	27.20	27.70	28.12
C _d -(C _b ,H)	28.37	26.69	18.66	24.23	28.24	31.05	34.94	38.12	42.22
C _d -(C,C _b)	36.15	-61.09	18.41	22.47	24.81	25.86	27.20	27.70	28.12
C _d -(C _b ,C _d)	30.04	-69.04	19.66	25.65	28.74	29.71	30.12	29.96	29.54
C _d -(C _d ,C _t)	29.04	-69.04	19.66	25.65	28.74	29.71	30.12	29.96	29.54
C _d -(C _b ,C _t)	28.03	-69.04	19.66	25.65	28.74	29.71	30.12	29.96	29.54
C _d -(C _{d2})	19.25	-69.04	19.66	25.65	28.74	29.71	30.12	29.96	29.54
C _d -(C _{t2})	27.03	-69.04	19.66	25.65	28.74	29.71	30.12	29.96	29.54
C _d -(C _{b2})	33.47	-69.04	19.66	25.65	28.74	29.71	30.12	29.96	29.54
C _d -(C _t ,H)	28.37	33.60	18.66	24.23	28.24	31.05	34.94	38.12	42.22
C _d -(C,C _t)	35.69	-61.09	18.41	22.47	24.81	25.86	27.20	27.70	28.12
C-(C,C _d ,H ₂)	-19.92	41.00	21.42	28.70	34.81	39.71	46.94	52.22	60.08
C-(C _{d2} ,H ₂)	-17.95	42.68	19.66	28.45	35.15	40.17	47.28	52.72	60.25
C-(C _b ,C _d ,H ₂)	-22.13	42.68	19.66	28.45	35.15	40.17	47.28	52.72	60.25
C-(C,C _t ,H ₂)	-19.79	43.10	20.71	27.45	33.18	37.99	45.44	51.00	59.41
C-(C,C _b ,H ₂)	-20.33	39.08	24.43	31.84	37.57	41.88	48.07	52.47	57.57
C-(C ₂ ,C _d ,H)	-6.19	-48.91	17.41	24.73	30.71	34.27	39.58	42.63	47.20
C-(C ₂ ,C _t ,H)	-7.20	-46.82	16.69	23.47	28.66	32.55	38.07	41.42	46.53
C-(C ₂ ,C _b ,H)	-4.10	-50.84	20.42	27.87	33.05	36.61	40.71	42.89	44.69
C-(C,C _b ,C _t ,H)	-6.49	-48.74	18.12	26.23	31.71	35.48	39.83	42.26	44.48
C-(C,C _b ,C _d ,H)	-6.53	-49.25	18.83	27.49	33.76	37.20	41.34	43.47	45.15
C-(C,C _d ,C _t ,H)	-9.87	-46.82	15.10	23.10	29.37	33.14	38.70	41.42	46.99
C-(C,C _{d2} ,H)	-9.67	-47.32	15.82	24.48	31.42	34.73	40.21	43.22	47.66
C-(C,C _{t2} ,H)	-10.63	-44.73	14.39	21.84	27.32	31.42	37.20	40.79	46.32
C-(C,C _{b2} ,H)	-4.44	-51.17	21.84	30.63	36.11	35.35	42.47	43.72	42.63
C-(C _b ,C _{d2} ,H)	-5.82	-47.66	17.24	27.24	34.48	37.66	41.97	44.06	45.56
C-(C _{d3} ,H)	-8.95	-45.73	14.23	24.10	32.13	35.31	40.84	43.81	48.12
C-(C _{b3} ,H)	-1.42	-51.51	23.26	33.39	39.16	42.47	44.22	44.56	40.58
C-(C ₃ ,C _d)	7.03	-145.27	16.69	25.27	31.09	34.56	37.32	37.49	34.43
C-(C ₃ ,C _b)	11.76	-147.19	18.28	28.41	33.85	36.74	38.45	37.49	31.92
C-(C ₃ ,C _t)	11.76	-147.19	18.28	28.41	33.85	36.74	38.45	37.49	31.92
C-(C ₂ ,C _{d2})	6.74	-143.68	15.10	25.02	31.42	35.02	37.66	37.74	34.89
C-(C,C _{d3})	10.63	-142.09	13.89	24.52	31.67	35.73	38.58	39.16	35.35
C-(C ₂ ,C _b ,C _d)	12.51	-145.60	16.69	28.03	34.14	37.32	39.08	38.33	32.38
C-(C ₂ ,C _d ,C _t)	12.51	-145.60	16.69	28.03	34.14	37.32	39.08	38.33	32.38

Table 2A. Group additivity values taken from Ritter and Bozzelli² (continued)

Groups	$\bar{h}_{f,298}^{\circ}$ (kJ/mol)	\bar{s}_{298}° (J/mol-K)	$\bar{c}_p(T)$ (J/mol)						
			300	400	500	600	800	1000	1500
C ₋ (C,C _{b2} ,C _d)	21.34	-145.94	16.69	30.79	37.20	40.08	40.84	38.33	30.33
C ₋ (C,C _b ,C _d ,C _t)	21.34	-145.94	16.69	30.79	37.20	40.08	40.84	38.33	30.33
C ₋ (C,C _d ,C _{t2})	21.34	-145.94	16.69	30.79	37.20	40.08	40.84	38.33	30.33
C ₋ (C ₂ ,C _{b2})	4.85	-147.53	14.94	25.02	31.42	35.02	37.66	37.74	34.89
C ₋ (C ₂ ,C _b ,C _t)	4.85	-147.53	14.94	25.02	31.42	35.02	37.66	37.74	34.89
C ₋ (C ₂ ,C _{t2})	4.85	-147.53	14.94	25.02	31.42	35.02	37.66	37.74	34.89
C ₋ (C,C _{b3})	26.07	-147.86	18.28	33.93	39.96	42.26	41.97	39.16	27.82
C ₋ (C,C _{b2} ,C _t)	26.90	-147.86	18.28	33.93	39.96	42.26	41.97	39.16	27.82
C ₋ (C,C _b ,C _{t2})	26.07	-147.86	18.28	33.93	39.96	42.26	41.97	39.16	27.82
C ₋ (C,C _{t3})	26.07	-147.86	18.28	33.93	39.96	42.26	41.97	39.16	27.82
C ₋ (C _{b2} ,C _{d2})	22.93	-144.35	15.10	30.54	37.53	40.54	41.17	39.41	30.79
C ₋ (C _b ,C _{d2} ,C _t)	22.93	-144.35	15.10	30.54	37.53	40.54	41.17	39.41	30.79
C ₋ (C _{d2} ,C _{t2})	22.93	-144.35	15.10	30.54	37.53	40.54	41.17	39.41	30.79
C _r -(H)	112.68	103.34	22.09	25.06	27.15	28.74	31.25	33.30	37.03
C _r -(C)	115.27	26.57	13.10	14.56	15.94	17.11	19.25	20.59	26.57
C _r -(C _d)	117.99	26.90	10.75	14.81	14.64	20.59	22.34	23.01	24.27
C _r -(C _b)	103.22	26.90	10.75	14.81	14.64	20.59	22.34	23.01	24.27
C _r -(C _t)	119.24	24.60	14.81	16.99	18.41	19.41	20.92	21.88	23.30
C _b -(H)	13.81	48.24	13.56	18.58	22.84	26.36	31.55	35.19	40.71
C _b -(C)	23.05	-32.17	11.17	13.14	15.40	17.36	20.75	22.76	25.02
C _b -(C _d)	23.81	-32.64	15.02	16.61	18.33	19.75	22.09	23.47	24.06
C _b -(C _t)	23.81	-32.64	15.02	16.61	18.33	19.75	22.09	23.47	24.06
C _b -(C _b)	20.75	-36.15	13.93	17.66	20.46	22.05	24.10	24.89	25.31
C _b f-(C _{b2} ,C _b f)	20.08	-20.92	15.40	15.40	17.57	19.29	21.76	23.85	25.94
C _b f-(C _b ,C _b f ₂)	15.48	-20.92	15.40	15.40	17.57	19.29	21.76	23.85	25.94
C ₋ (C _d ,C _t ,H ₂)	-17.82	44.77	18.95	27.07	33.47	38.79	46.07	51.59	59.87
C ₋ (C _{b2} ,H ₂)	-23.18	38.74	25.86	34.60	40.63	44.64	49.83	53.30	55.52
C ₋ (C _b ,C _t ,H ₂)	-23.68	42.76	22.13	30.21	36.23	40.75	47.20	51.84	57.36
C ₋ (C _{t2} ,H ₂)	-23.14	46.78	18.41	25.82	31.84	36.86	44.56	50.38	59.20
C _{tb}	207.82	47.61	10.00	11.72	13.10	14.39	16.11	17.28	19.08