

Chapter 8: Thermochemistry

Except for nuclear energy, chemical fuels are the densest sources of energy for transportation, space heating, cooking, and industrial production. Alcohols are possible choices for large scale energy storage. Determine the enthalpy of combustion and formation of methanol.

The First Law of thermodynamics provides a careful accounting of the transfers of heat and work for a system. Energy is conserved; energy is neither created nor destroyed. However, energy can be converted from one form to another: among heat, work, and internal energy. At times we are interested in obtaining the maximum amount of heat from a process, and we wish to minimize the PV work that is done. Space heating, cooking, and many industrial processes require large amounts of heat. At other times we are interested in obtaining the maximum amount of work from a process, and we wish to minimize the heat produced. For batteries, fuel cells, and chemical synthesis we wish to waste as little energy as possible as heat. Thermochemistry is the study of heat transfer in phase transitions and chemical reactions.

The experimental branch of thermochemistry is calorimetry. Calorimetry plays a fundamental role in the understanding of chemical transformations, ecology, and energy technology. Millions of chemical compounds are known. We need to be able to assess the potential of every substance for fulfilling new uses. The experimental determination of thermodynamic parameters is a time consuming process. Computational techniques have been developed to estimate the internal energy and enthalpy changes for chemical processes when the experimental parameters are unknown.

Organisms need energy to provide warmth, shelter, and food. Energy production and consumption are central aspects of the functioning of society. The efficient production of energy provides independence and minimizes global pollution and climate change. Thermochemistry shows the interrelationships that govern what we can do to insure energy independence and responsible stewardship of the environment.

8.1 The Internal Energy and Enthalpy Changes for Phase Transitions

For a phase transition in a closed system at constant pressure, the heat transfer is given by the enthalpy change. For example, the heat transfer per mole for the constant pressure vaporization of water at one bar pressure and 298.15 K is given by the enthalpy of vaporization:



The internal energy change for the phase transition can be calculated using the definition of the enthalpy, Eq. 7.8.16, $\Delta H = \Delta U + \Delta(PV)$. Specifically for vaporization at constant pressure:

$$\Delta_{\text{vap}}H = H_{\text{vap}} - H_{\text{liq}} \quad \Delta_{\text{vap}}U = U_{\text{vap}} - U_{\text{liq}} \quad \Delta_{\text{vap}}(PV) = P(V_{\text{vap}} - V_{\text{liq}}) \quad (\text{cst. } P) \quad 8.1.2$$

For calculating $\Delta_{\text{vap}}(PV)$, the molar volume of the vapor is much larger than the molar volume of the liquid, so the volume of the liquid can be neglected. In addition, treating the vapor as an ideal gas is usually sufficiently accurate for most purposes (see Problem 7.6). Assuming the phase transition takes place at constant temperature with these approximations gives:

$$\Delta_{\text{vap}}(PV) = PV_{\text{vap}} = n_g RT \quad (\text{ideal gas, cst. T\&P}) \quad 8.1.3^\circ$$

where n_g is the number of moles of vapor in the balanced equation. Combining Eqs. 7.8.16, 8.1.2, and 8.1.3° relates $\Delta_{\text{vap}}H$ and $\Delta_{\text{vap}}U$:

$$\Delta_{\text{vap}}H = \Delta_{\text{vap}}U + n_g RT \quad (\text{ideal gas, cst. T\&P}) \quad 8.1.4^\circ$$

Phase transitions that have a non-zero enthalpy are called first-order phase transitions. Eqs. 8.1.2-8.1.4° apply to all first-order phase transitions, $\Delta_{\text{tr}}H = \Delta_{\text{tr}}U + n_g RT$, which include:

General transition:	$\alpha \rightarrow \beta$	$\Delta_{\text{tr}}H = H_\beta - H_\alpha$	
Melting or fusion:	solid \rightarrow liquid	$\Delta_{\text{fus}}H = H_{\text{liq}} - H_{\text{solid}}$	
Sublimation:	solid \rightarrow vapor	$\Delta_{\text{sub}}H = H_{\text{vap}} - H_{\text{solid}}$	
Vaporization:	liquid \rightarrow vapor	$\Delta_{\text{vap}}H = H_{\text{vap}} - H_{\text{liq}}$	8.1.5

Tabulations of transition enthalpies are in Appendix Data Section Table 8.1.1. For melting transitions the change in volume is determined by the change in density from the solid to the liquid, which is quite small. Except for very high pressures, $\Delta_{\text{tr}}(PV) = P\Delta V(1/d_{\text{liq}} - 1/d_{\text{solid}})$ is negligible for melting transitions. Notice that phase transitions can also be considered as chemical reactions. The reactant for Eq. 8.1.1 is liquid water and the product is water vapor. The relationships that we derive for chemical reactions and phase transitions are interchangeable.

Example 8.1.1:

The molar enthalpy of vaporization of water at 298.15 K is $\Delta_{\text{vap}}H = 44.01 \text{ kJ mol}^{-1}$. Calculate the molar internal energy of vaporization, assuming a constant pressure of 1.00 bar.

Answer: Using Eq. 8.1.4 gives:

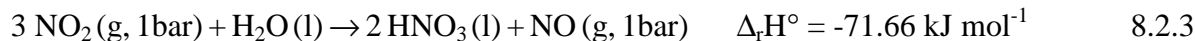
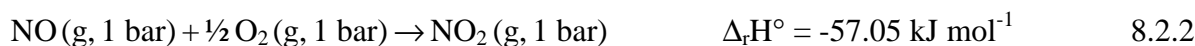
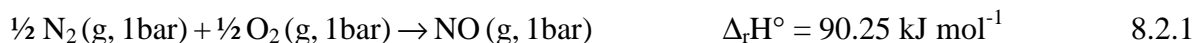
$$\begin{aligned} \Delta_{\text{vap}}U &= \Delta_{\text{vap}}H - n_g RT \\ &= 1 \text{ mol}(44.01 \text{ kJ mol}^{-1}) - 1 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \\ &= 44.01 \text{ kJ} - 2.48 \text{ kJ} = 41.53 \text{ kJ} \end{aligned}$$

Since this result is for one mole, we can also write the units as $\Delta_{\text{vap}}U_m = 41.53 \text{ kJ mol}^{-1}$. Why is the internal energy of vaporization less than the enthalpy change? At constant pressure $\Delta H = \Delta U + P\Delta V$. The system expands, pushing back the atmosphere upon vaporization. The work done is given by $w = -P\Delta V$, assuming the pressure is held constant by maintaining contact of the system with the surroundings. So the enthalpy change exceeds the internal energy change by the negative of the work against the surroundings. Since the process is at constant temperature, the extra energy must be supplied by the surroundings: $q_p = \Delta_{\text{vap}}H = \Delta_{\text{vap}}U + P\Delta V$.

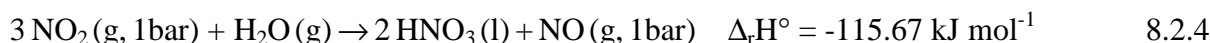
8.2 The Conditions for the Reaction Must Be Specified

Standard States for Constituents in Chemical Reactions: For a chemical reaction in a closed system at constant pressure, the heat transfer is given by the enthalpy change, assuming no non-PV work exchange with the surroundings. For example, in Eqs. 1.4.2, we discussed the formation of nitric acid and the role of nitric acid in acid deposition. Nitric oxide is formed during high temperature combustion processes, principally in internal combustion engines. Nitric

oxide is rapidly oxidized in air to form an equilibrium mixture with NO_2 , and the reaction of NO_2 with water gives nitric acid:



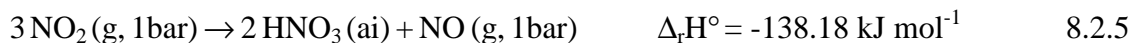
The reaction enthalpies are at 298.15 K. The oxidation of N_2 in air is endothermic, while the oxidation of NO and the reaction of NO_2 with water are exothermic. The internal energy or enthalpy change for a chemical reaction is symbolized as $\Delta_r U$ and $\Delta_r H$ to highlight the connection between the heat transfer and the specific reaction process. As we discuss the thermochemistry of these reactions, we must be careful to specify the state of each reactant and product. The state of aggregation, solid, liquid, or gas, must be specified. The reaction enthalpy for Eq. 8.2.3 is different if the water reacts as a gas:



The difference between Eqs. 8.2.3 and 8.2.4 is the enthalpy of vaporization of water, Eq. 8.1.1. For solids, the crystalline form is also important; reactions of $\text{C}(\text{graphite})$ and $\text{C}(\text{diamond})$ have different enthalpies.

The internal energy and enthalpy changes for gases are strong functions of pressure; so the pressure must be specified for all gaseous species. The standard state pressure is defined as: $P^\circ = 1 \text{ bar}$. Internal energies and enthalpies under standard conditions are listed as $\Delta_r U^\circ$ and $\Delta_r H^\circ$. The pressure of liquids and solids need not be specified if the pressures are near 1 bar. The weak pressure dependence of the enthalpy for condensed phases was discussed in Example 7.8.2. Note that there is no standard temperature. The internal energy and enthalpy changes for chemical reactions can be strong functions of temperature.

The reaction in Eq. 8.2.3 gives pure liquid nitric acid. However, the reaction to give an aqueous solution is even more exothermic:



The reaction enthalpy quoted is for all reactants and products in their standard states. The standard state for species in solution is unit concentration. For electrolytes, the “ai” standard state corresponds to complete dissociation.¹ We use the “aq” designation for aqueous species that are not at standard state. In solution, the thermodynamic contribution of a substance to the enthalpy is determined by the activity of the substance. The activity of a species in solution is the “chemically effective concentration.” We will discuss the relationship between concentration, activity, and activity based standard states in Chapter 19.

With the conditions of the reaction carefully specified, we are now ready to consider the reaction internal energy and enthalpy.

8.3 Relating Internal Energy and Enthalpy Changes for Chemical Reactions

Internal energy and enthalpy changes for a chemical reaction can be related using the definition of the enthalpy, Eq. 7.8.16, $\Delta H = \Delta U + \Delta(PV)$. The derivation parallels the steps for phase transitions, Eqs. 8.1.1-8.1.4°. Consider oxidation of NO , Eq. 8.2.2:



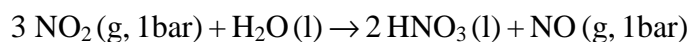
Once again, treating any gases involved in the reaction as ideal is usually sufficiently accurate for most purposes. The change in the (PV) product at constant temperature is given by:

$$\Delta_r(PV) = \Delta_r(n_g RT) = \Delta_r n_g RT \quad (\text{ideal gas, cst. T\&P}) \quad 8.3.1^\circ$$

where $\Delta_r n_g$ is the number of moles of gaseous products minus the number of moles of gaseous reactants. For Eq. 8.2.2, the difference is $\Delta_r n_g = [1] - [1 + 1/2] = -1/2$. Combining Eqs. 7.8.16 and 8.3.1° gives:

$$\Delta_r H = \Delta_r U + \Delta_r n_g RT \quad (\text{ideal gas, cst. T\&P}) \quad 8.3.2^\circ$$

For reactions involving liquids and solids, the volume of the gaseous reactants and products is much larger than the corresponding volume of the condensed phases, so the volume of any liquids and solids can be neglected (see Problem 7.6). Consider Eq. 8.2.3:



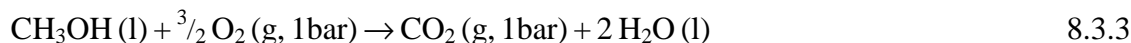
The difference in moles of gases is $\Delta_r n_g = [1] - [3] = -2$, giving $\Delta_r H = \Delta_r U - 2 RT$.

With the conditions of the reaction carefully specified and the reaction internal energy and enthalpy in hand, we can now ask if relationships exist among the heat transfers for different coupled chemical reactions.

Example 8.3.1:

The internal energy of combustion of methanol can be determined using bomb calorimetry, $\Delta_{\text{comb}}U^\circ = -725.27 \text{ kJ mol}^{-1}$ at 298.2 K. Calculate the enthalpy of combustion of methanol at 298.2 K.

Answer: The balanced reaction for the combustion of methanol is:



Eq. 8.3.2° gives the relationship between the reaction internal energy and enthalpy. The change in the number of moles of gases is $\Delta_r n_g = [1 \text{ mol}] - [3/2 \text{ mol}] = -1/2 \text{ mol}$. Note that the liquids are not included. The result for one mole is:

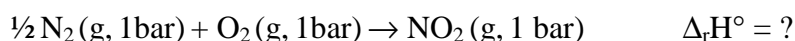
$$\begin{aligned} \Delta_{\text{comb}}H^\circ &= \Delta_{\text{comb}}U^\circ + \Delta_r n_g RT \\ &= -725.27 \text{ kJ} - 1/2 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})(298.2 \text{ K}) \\ &= -725.27 \text{ kJ} - 1.240 \text{ kJ} \\ \Delta_{\text{comb}}H^\circ &= -726.51 \text{ kJ} \end{aligned}$$

Since the reaction is for one mole, the units are also $\Delta_{\text{comb}}H^\circ = -726.51 \text{ kJ mol}^{-1}$. Why is the enthalpy of combustion more negative than the internal energy change? Consider the reaction run at constant pressure. Since there are fewer moles of product gases than reactant gases, the system contracts during the reaction. The surroundings therefore does PV work on the system, $w = -P\Delta V > 0$, giving $P\Delta V < 0$. At constant pressure $\Delta H = \Delta U + P\Delta V$. So the enthalpy change is more negative than the internal energy change by the negative of the work. This example shows

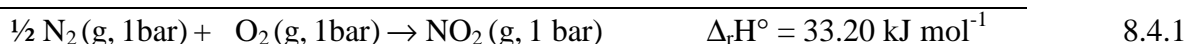
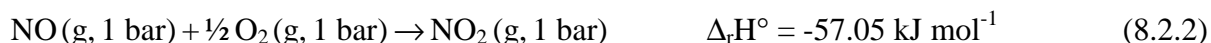
that if we are interested in the heat transferred for a chemical reaction at constant pressure, we also need to keep track of the PV work.

8.4 Hess's Law is a Result of the First Law

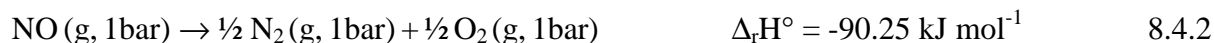
Consider the direct formation of NO₂ from N₂:



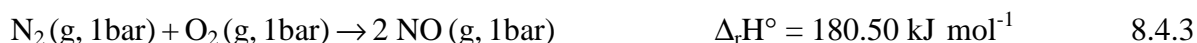
Can we combine the reaction enthalpies from Eqs. 8.2.1 and 8.2.2 to find the reaction enthalpy for this reaction? Reaction internal energies and enthalpies are state functions, by the First Law of thermodynamics. The changes are independent of the path. Therefore, the change in enthalpy for the two-step production of NO₂, with NO as an intermediate, should give the same enthalpy change as the direct, one-step process:



If two chemical reactions are added the enthalpies also add. This observation was first made by Germain Henri Hess in about 1840, before the general form of the First Law had been proposed. But, we now realize that Hess's Law is a consequence of the path independence of thermodynamic state functions. Another ramification of the path independence is if a reaction is reversed, the sign of the internal energy and enthalpy also reverses; reversing Eq. 8.2.1 gives:



Since internal energy and enthalpy are extensive, if we multiply a reaction by a constant, the internal energy and enthalpy are also multiplied by the same value:



The internal energy and enthalpy changes for chemical reactions are useful information for many purposes. The value of Hess's Law is that we can predict the energy changes for reactions that may not be possible in the laboratory. We can combine the enthalpy changes for known reactions to give the values for reactions that can't be studied directly. An important question then arises as to how to tabulate information on reactions in the most efficient way. One approach might be to tabulate the absolute internal energy or enthalpy of each pure substance. In each of the previous examples, however, note that we only determine the change in enthalpy for each process. The First Law pertains only to internal energy changes: $\Delta U = q + w$. The heat and work transfers are inherently changes in energy. There is no experimental way to establish an absolute internal energy or enthalpy of a substance. How do we tabulate thermochemical information in the most useful and efficient manner?

The Enthalpy of Formation is for a Specific Reaction: In practical applications, we always determine the change in internal energy and enthalpy for a chemical reaction; the absolute parameters are never necessary. Therefore, we are free to establish by convention any arbitrary reference point that is convenient, Figure 8.4.1.

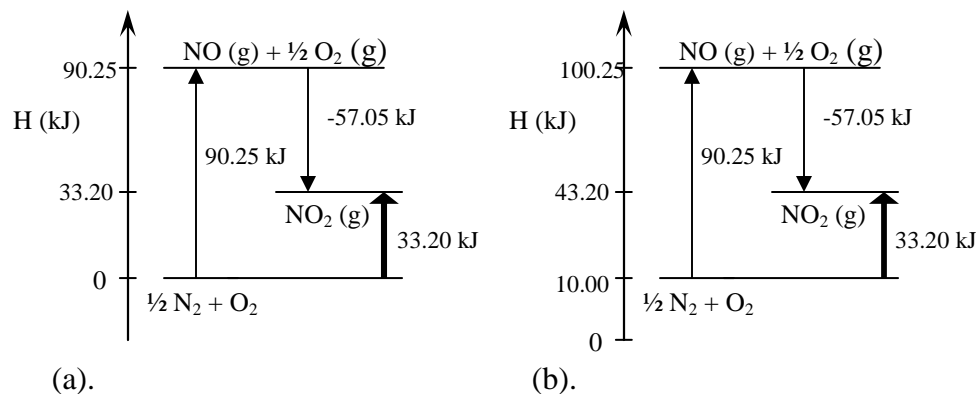
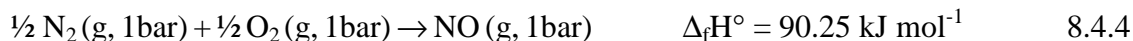
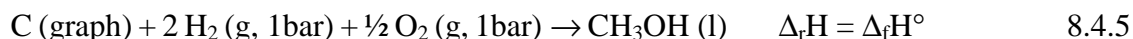


Figure 8.4.1: An arbitrary reference point may be chosen if only energy differences are needed. (a) The reference point is arbitrarily chosen as the elements in their standard states. (b). A different reference point is chosen, but the enthalpy differences remain the same.

The **enthalpy of formation** for a substance is defined as the reaction enthalpy for the formation of one mole of substance from the constituent elements in their standard states. For example Eq. 8.2.1 is just such a reaction:

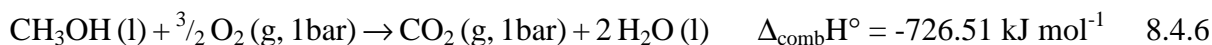


while Eqs. 8.2.2 and 8.2.3 are not. The reaction enthalpy that corresponds to the formation reaction is symbolized as $\Delta_f H$, and if the reaction is run under standard conditions, at 1 bar, then the value is $\Delta_f H^\circ$. If the state of aggregation of a reactant or product is not specified, the most stable state at the given temperature and pressure is assumed. For example, near atmospheric pressure the most stable state for water is liquid and for carbon is graphite. It is important to realize that a $\Delta_f H^\circ$ relates to a specific reaction. For another example, the standard state enthalpy of formation of methanol is the reaction enthalpy for the formation reaction:



The implication of this choice for the reference is that the standard state enthalpy of formation of any element is defined as zero. Tabulations are in Appendix Data Section Tables 8.4.1-8.4.3.¹⁻⁴

Enthalpies of Combustion can be Accurately Determined: It is usually not possible to measure enthalpies of formation directly. Rather, for many substances, the enthalpy of combustion is the most accurate experimental measurement that can be made. Combustion of organic compounds gives $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{N}_2(\text{g})$, and $\text{SO}_2(\text{g})$ as products. Tabulated values are in Data Section Table 8.4.3. For example, the enthalpy of combustion of methanol is given by Example 8.3.1:

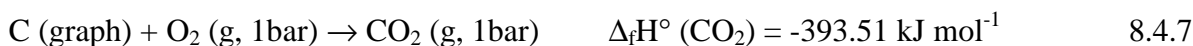


This large exothermic enthalpy of combustion would make methanol a good transportation fuel, if methanol could be made without fossil fuels. The combustion of methanol can be used to calculate the enthalpy of formation of methanol using Hess's Law.

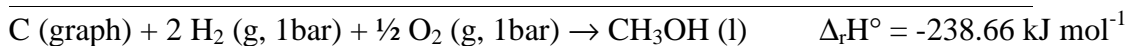
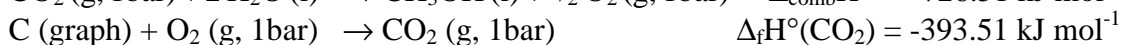
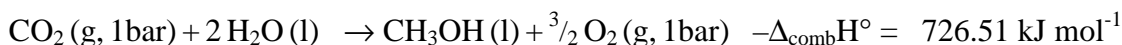
Example 8.4.1:

Calculate the enthalpy of formation of methanol from the enthalpy of combustion for methanol, $\Delta_{\text{comb}}H^\circ = -726.51 \text{ kJ mol}^{-1}$. The enthalpy of formation of CO_2 (g) is $\Delta_f H^\circ (\text{CO}_2) = -393.51 \text{ kJ mol}^{-1}$ and for H_2O (l) is $\Delta_f H^\circ (\text{H}_2\text{O}) = -285.83 \text{ kJ mol}^{-1}$.

Answer: The reactions that correspond to the enthalpy of formation of CO_2 (g) and H_2O (l) are:



The goal is to find the enthalpy change for the formation reaction, Eq. 8.4.10. Reversing Eq. 8.4.6 for one mole, adding in the formation reaction for CO_2 , and adding in twice the formation reaction for H_2O gives:



The final reaction is the formation reaction: $\Delta_r H^\circ = \Delta_f H^\circ$

The addition and subtraction of chemical reactions becomes cumbersome for complex processes. An equivalent and computationally efficient approach for finding the reaction enthalpy is to use:

$$\Delta_r H = \sum_{i=1}^{n_s} \nu_i \Delta_f H_i \quad 8.4.9$$

where ν_i are the stoichiometric coefficients for the reaction and the $\Delta_f H_i$ values are the molar enthalpies of formation for each reactant and product. The sum extends over the n_s constituents for the reaction. Remember that the stoichiometric coefficients are positive for products and negative for reactants, Section 3.1. If the reaction is run under standard state conditions then Eq. 8.4.9 can be written:

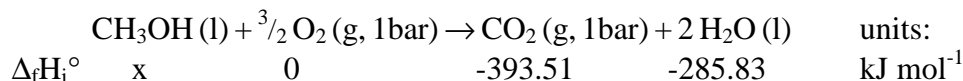
$$\Delta_r H^\circ = \sum_{i=1}^{n_s} \nu_i \Delta_f H_i^\circ \quad (P^\circ = 1 \text{ bar}) \quad 8.4.10$$

A colloquial way of presenting this equation is $\Delta_r H = [\Sigma \text{products}] - [\Sigma \text{reactants}]$, which highlights that we always take the enthalpies of the products minus the reactants.

Example 8.4.2:

Calculate the enthalpy of formation from the enthalpy of combustion for methanol, $\Delta_{\text{comb}}H^\circ = -726.51 \text{ kJ mol}^{-1}$. The enthalpy of formation of CO_2 (g) is $\Delta_f H^\circ (\text{CO}_2) = -393.51 \text{ kJ mol}^{-1}$ and for H_2O (l) is $\Delta_f H^\circ (\text{H}_2\text{O}) = -285.83 \text{ kJ mol}^{-1}$ (*Additional values in the Appendix Data Section*).

Answer: An efficient way to work problems of this type is to set up a table of enthalpies of formation. The enthalpy of combustion of methanol corresponds to Eq. 8.4.6:



The enthalpy of formation of $\text{O}_2(\text{g})$ at 1 bar is zero, because it is an element in its standard state. For this particular reaction $\Delta_r H^\circ = \Delta_{\text{comb}} H^\circ = -726.51 \text{ kJ mol}^{-1}$. Using Eq. 8.4.10 for the combustion of methanol, $\Delta_r H = [\Sigma \text{products}] - [\Sigma \text{reactants}]$:

$$-726.51 \text{ kJ mol}^{-1} = [-393.51 \text{ kJ mol}^{-1} + 2(-285.83 \text{ kJ mol}^{-1})] - [x + \frac{3}{2}(0)]$$

Solving for x gives the enthalpy of formation of methanol: $x = \Delta_f H^\circ = -238.66 \text{ kJ mol}^{-1}$. Remember to use the stoichiometric coefficients for each participant; enthalpies are extensive.

The Internal Energy and Enthalpy Changes for Chemical Reactions The general form for Eq. 8.4.9 occurs so often, we should explore the relationships involved. If we could establish an absolute reference point for the enthalpy of a substance, the enthalpy change for a reaction would simply be:

$$\Delta_r H = \sum_{i=1}^{n_s} \nu_i H_i \quad 8.4.11$$

where the H_i are the absolute molar enthalpies for each reactant and product. This last equation is theoretically allowable, but for practical circumstances we need to choose a reference point. For example consider the reaction enthalpy for the oxidation of nitric oxide, Eq. 8.2.2. Using the absolute form in Eq. 8.4.11 for this reaction gives:



$$\Delta_r H = H_{\text{NO}_2} - H_{\text{NO}} - \frac{1}{2} H_{\text{O}_2} \quad 8.4.12$$

However, using Eq. 8.4.9, which references the enthalpies of formation to the elements in their standard states, gives instead:

$$\Delta_r H = \Delta_f H_{\text{NO}_2} - \Delta_f H_{\text{NO}} - \frac{1}{2} \Delta_f H_{\text{O}_2} \quad 8.4.13$$

We need to show that Eqs. 8.4.12 and 8.4.13 are equivalent. First, we can write the formation reactions in absolute form. Applying Eq. 8.4.11 to the formation of NO_2 , Eq. 8.2.2, and NO , Eq. 8.2.1, gives:

$$\Delta_f H_{\text{NO}_2} = H_{\text{NO}_2} - \frac{1}{2} H_{\text{N}_2} - H_{\text{O}_2} \quad 8.4.14$$

$$\Delta_f H_{\text{NO}} = H_{\text{NO}} - \frac{1}{2} H_{\text{N}_2} - \frac{1}{2} H_{\text{O}_2} \quad 8.4.15$$

Note also that by definition $\Delta_f H_{\text{O}_2} = 0$. Substituting Eqs. 8.4.14-8.4.15 into the relative version, Eq. 8.4.13, gives:

$$\Delta_r H = \Delta_f H_{\text{NO}_2} - \Delta_f H_{\text{NO}} - \frac{1}{2} \Delta_f H_{\text{O}_2} \quad (8.4.13)$$

$$\Delta_r H = [H_{\text{NO}_2} - \frac{1}{2} H_{\text{N}_2} - H_{\text{O}_2}] - [(H_{\text{NO}} - \frac{1}{2} H_{\text{N}_2} - \frac{1}{2} H_{\text{O}_2}) - 0] \quad 8.4.16$$

$$\Delta_r H = H_{\text{NO}_2} - H_{\text{NO}} - \frac{1}{2} H_{\text{O}_2}$$

The terms for the elements cancelled giving Eq. 8.4.17. We gave a proof for a particular example, but it can be shown generally that Eqs. 8.4.9 and 8.4.11 are equivalent. We can choose any arbitrary reference point, as long as we are consistent. The diagram in Figure 8.4.2 will help to depict the relationships in Eq. 8.4.13. We set up an indirect path that gives the same change in enthalpy as the direct reaction. In the indirect path, each reactant is decomposed into its elements in their standard states. The elements from each reactant are combined and then reformed into the products of the reaction. The net change is given by Eq. 8.4.13.

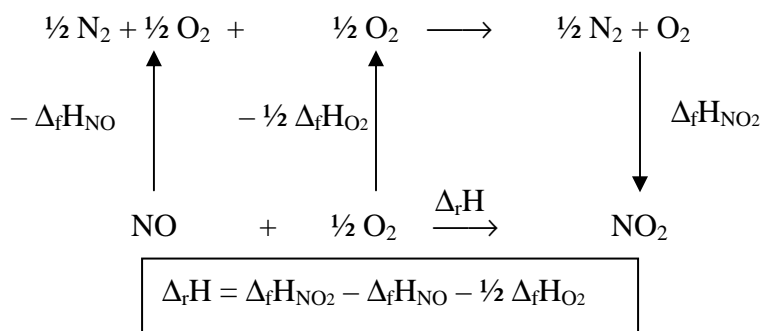


Figure 8.4.2: Since enthalpy is a state function, the change for the reaction is independent of the path.

Note that when we calculate the enthalpy change for a reaction, the conditions for each reactant and product are kept constant. How can we run a reaction with constant partial pressures? For the example reaction, $\text{NO}(\text{g}, 1 \text{ bar}) + \frac{1}{2} \text{O}_2(\text{g}, 0.2 \text{ bar}) \rightarrow \text{NO}_2(\text{g}, 1 \text{ bar})$, the $\Delta_r H$ is the reaction enthalpy with all partial pressures held constant. Consider a large flask with many moles each of NO, O₂, and NO₂, Figure 8.4.3. The reaction enthalpy, $\Delta_r H$, corresponds to the change in enthalpy when one mole of NO reacts with a half mole of O₂ to give one mole of NO₂. However, since the mole change is such a small fraction of the total amounts, the partial pressure of each constituent remains constant.

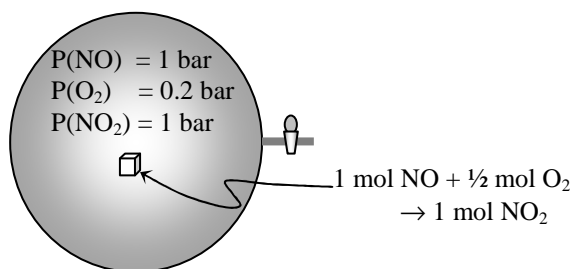


Figure 8.4.3: The reaction enthalpy, $\Delta_r H$, corresponds to constant partial pressures.

The reaction enthalpy, $\Delta_r H$, is the change in enthalpy for unit extent in so large an amount of the reaction that the partial pressures of the constituents remain unchanged.

An alternate and equivalent perspective is to consider the change in enthalpy for a small change in extent of the reaction, say 0.0001 mole, and then divide the resulting change in enthalpy by the number of moles, $\Delta H / 0.0001 \text{ mol} = \Delta_r H$. The result is a per mol quantity, and since the change in extent of the reaction is so small, the partial pressures of the constituents

remain constant, in the limit of infinitesimal changes. Mathematically, the change in enthalpy for infinitesimal changes in the amounts of reactants and products is:

$$dH = \sum_{i=1}^{n_s} H_i dn_i \quad (\text{cst. T\&P}) \quad 8.4.17$$

or in terms of the extent of the reaction, Eq. 3.1.4, with $dn_i = \nu_i d\xi$:

$$dH = \sum_{i=1}^{n_s} \nu_i H_i d\xi \quad (\text{cst. T\&P}) \quad 8.4.18$$

The change in extent for the reaction enthalpy is one mole by convention. Since the H_i are constant, the integral of this last equation from $\xi = 0$ to 1 mol gives Eq. 8.4.11. The change in extent in Eq. 8.4.18, $d\xi$, is a common factor for each term in the sum. Dividing both sides of the equation by $d\xi$ gives:

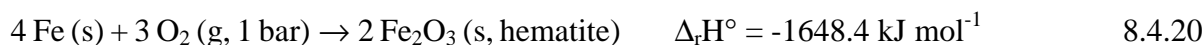
$$\left(\frac{\partial H}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{n_s} \nu_i H_i = \Delta_r H \quad (\text{cst. T\&P}) \quad 8.4.19$$

where the last equality is from Eq. 8.4.11. Dividing dH by $d\xi$ puts the reaction enthalpy on a per mole basis, even though the change in extent of the reaction is infinitesimal.

The reaction enthalpy is the derivative of the enthalpy with respect to the extent of the reaction.

The approaches in Figure 8.4.3 and in Eq. 8.4.19 are equivalent ways of understanding the meaning of the derivative. We will use similar reasoning often.

The reaction enthalpy as defined by Eq. 8.4.9 or 8.4.11 corresponds to unit extent, $\xi = 1$ mol, for the reaction as written. The units of the reaction enthalpy are kJ mol^{-1} . These units hold even if none of the stoichiometric coefficients are unity. For example, for $\xi = 1$ mol:



where four moles of iron react with three moles of oxygen to give two moles of iron oxide. The reaction enthalpy is specific to a given specific reaction stoichiometry.

Standard state reaction enthalpies are at a specific constant pressure of 1 bar. However, standard state reaction enthalpies and reactions in general still depend on temperature. We often control the outcome of chemical reactions by changing the temperature.

8.5 Reaction Internal Energies and Enthalpies Depend on Temperature

The enthalpy changes for phase transitions and chemical reactions depend on temperature. The temperature variation depends on the heat capacities of the products and reactants. We can determine the temperature dependence by using a thermodynamic cycle. Thermodynamic cycles exploit the path independence of the underlying state function. For example, consider the simple reaction $R \rightarrow P$. Assume that we know the reaction enthalpy at temperature T_1 . We require the reaction enthalpy at some new temperature T_2 . For example, T_1 is often 298.2 K, and the corresponding reaction enthalpy, $\Delta_r H_{T_1}$, is often calculated from enthalpies of formation obtained from standard tables. To calculate the new reaction enthalpy at T_2 , we start with the reactant at T_2 and then heat or cool the reactant to T_1 , Figure 8.5.1. The change in enthalpy for this heating or cooling step is given by $\Delta H = C_p^{\text{rc}} (T_1 - T_2)$, assuming a constant heat capacity for the reactant,

C_p^{re} . The temperature difference is $(T_1 - T_2)$, because we start at T_2 and change the temperature to T_1 , where we know the reaction enthalpy. The reaction is then run at T_1 , giving the known enthalpy change $\Delta_r H_{T_1}$. Then the product of the reaction is cooled or heated back to the desired final temperature T_2 with the corresponding enthalpy change $\Delta H = C_p^{\text{pr}} (T_2 - T_1)$, where C_p^{pr} is the heat capacity for the product.

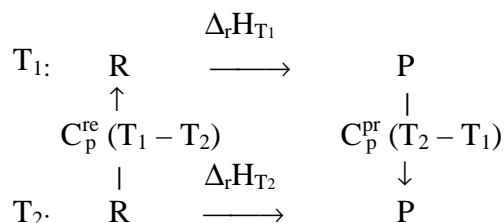


Figure 8.5.1: Enthalpy is a state function, and is therefore independent of the path. A three-step process with the reaction run at T_1 is equivalent to the direct process at T_2 .

The overall change is given by the sum for the three processes:

$$\Delta_r H_{T_2} = C_p^{\text{re}} (T_1 - T_2) + \Delta_r H_{T_1} + C_p^{\text{pr}} (T_2 - T_1) \quad (\text{cst. } C_p^{\text{re}} \text{ \& } C_p^{\text{pr}}) \quad 8.5.1$$

Because the enthalpy change is independent of the path, the indirect, three-step process gives the same result as the direct reaction at T_2 . To highlight the relationship of Figure 8.5.1 to cyclic processes we can start with the reactant at T_2 and run the processes around a cycle, Figure 8.5.2. To complete the cycle, we run the reaction at T_2 backwards.

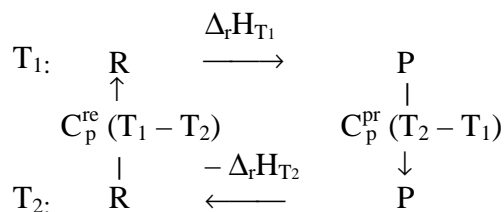


Figure 8.5.2: Thermodynamic cycle to determine the reaction enthalpy at T_2 from the reaction enthalpy at T_1 . The change in enthalpy around the cycle is zero.

Summing the enthalpy changes around the cycle gives $\oint dH = 0$:

$$C_p^{\text{re}} (T_1 - T_2) + \Delta_r H_{T_1} + C_p^{\text{pr}} (T_2 - T_1) - \Delta_r H_{T_2} = 0 \quad (\text{cst. } C_p^{\text{re}} \text{ \& } C_p^{\text{pr}}) \quad 8.5.2$$

This last equation can be solved for $\Delta_r H_{T_2}$ to give Eq. 8.5.1. Either approach, Figure 8.5.1 or Figure 8.5.2, can be considered a thermodynamic cycle.

Eq. 8.5.1 is often rearranged to factor out a common term of $(T_2 - T_1)$:

$$\Delta_r H_{T_2} = \Delta_r H_{T_1} + (C_p^{\text{pr}} - C_p^{\text{re}}) (T_2 - T_1) \quad (\text{cst. } C_p^{\text{re}} \text{ \& } C_p^{\text{pr}}) \quad 8.5.3$$

The difference in the heat capacities, with products minus reactants, is defined as:

$$\Delta_r C_p \equiv C_p^{\text{pr}} - C_p^{\text{re}} \quad 8.5.4$$

Substitution of this definition into Eq. 8.5.3 gives:

$$\Delta_r H_{T_2} - \Delta_r H_{T_1} = \Delta_r C_p \Delta T \quad (\text{cst. } C_p^{\text{re}} \& C_p^{\text{pr}}) \quad 8.5.5$$

The term on the left side of the equals sign is the change in reaction enthalpy for the temperature change ΔT . If the change in temperature is infinitesimal, Eq. 8.5.5 becomes:

$$d\Delta_r H = \Delta_r C_p dT \quad 8.5.6$$

The integral of this equation from T_1 to T_2 gives Eq. 8.5.5. This result is called Kirchoff's Law, which was established in 1858. So far we have worked with a simple stoichiometry. What happens in the general case?

Consider the general reaction, $\nu_a A + \nu_b B \rightarrow \nu_c C + \nu_d D$. The reaction enthalpy is given by:

$$\Delta_r H = \nu_c H_C + \nu_d H_D - \nu_a H_A - \nu_b H_B \quad 8.5.7$$

The temperature derivative of the reaction enthalpy is then given by:

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_P = \nu_c \left(\frac{\partial H_C}{\partial T}\right)_P + \nu_d \left(\frac{\partial H_D}{\partial T}\right)_P - \nu_a \left(\frac{\partial H_A}{\partial T}\right)_P - \nu_b \left(\frac{\partial H_B}{\partial T}\right)_P \quad 8.5.8$$

The partial derivatives in this last equation are just the molar constant pressure heat capacities for each product and reactant:

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_P = \nu_c C_{p,m}(C) + \nu_d C_{p,m}(D) - \nu_a C_{p,m}(A) - \nu_b C_{p,m}(B) \quad 8.5.9$$

The differences, products minus reactants, for the heat capacities is the general version of Eq. 8.5.4, giving:

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_P = \Delta_r C_p \quad 8.5.10$$

This last equation rearranges to Eq. 8.5.6, which shows that Eq. 8.5.6 also holds for the general case. For the most general case, using the notation from Eq. 8.4.11:

$$\Delta_r C_p = \sum_{i=1}^{n_s} \nu_i C_{p,i} \quad 8.5.11$$

The integrated form of Eq. 8.5.10 is Eq. 8.5.5, assuming constant heat capacities. For practical problems we sometimes need to know the reaction enthalpy for very high or low temperatures. For example, we might be studying reactions in the stratosphere, or in high temperature geological systems, or high temperature processes in the chemical industry. For extreme temperature differences, we can no longer assume constant heat capacities.

To integrate Eq. 8.5.10 for large temperature differences, we need to keep track of the heat capacity terms on a substance-by-substance basis. For example, for reactants A and B we use the power series expansions of the heat capacities from Eq. 7.2.10, keeping just three terms for convenience:

$$C_p(A) = a(A) + b(A) T + c(A) T^2 \quad 8.5.12$$

and $C_p(B) = a(B) + b(B) T + c(B) T^2 \quad 8.5.13$

where, for example, $a(A)$ is the power series expansion coefficient for reactant A from Table 7.2.3. Similar heat capacity expansions hold for the products. The change in the heat capacity for the reaction is:

$$\Delta_r C_p = \Delta_r a + \Delta_r b T + \Delta_r c T^2 \quad 8.5.14$$

with:

$$\Delta_r a = \nu_c a(C) + \nu_d a(D) - \nu_a a(A) - \nu_b a(B) \quad 8.5.15$$

$$\Delta_r b = \nu_c b(C) + \nu_d b(D) - \nu_a b(A) - \nu_b b(B) \quad 8.5.16$$

$$\Delta_r c = \nu_c c(C) + \nu_d c(D) - \nu_a c(A) - \nu_b c(B) \quad 8.5.17$$

$$\Delta_r d = \nu_c d(C) + \nu_d d(D) - \nu_a d(A) - \nu_b d(B) \quad 8.5.18$$

Substitution of Eq. 8.5.14 into Eq. 8.5.6 gives:

$$d\Delta_r H = (\Delta_r a + \Delta_r b T + \Delta_r c T^2) dT \quad 8.5.19$$

Integrating between T_1 and T_2 gives:

$$\Delta_r H_{T_2} - \Delta_r H_{T_1} = \int_{T_1}^{T_2} (\Delta_r a + \Delta_r b T + \Delta_r c T^2) dT \quad 8.5.20$$

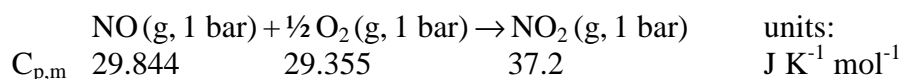
Solving for the new reaction enthalpy in terms of the reference reaction enthalpy gives:

$$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r a (T_2 - T_1) + \frac{\Delta_r b}{2} (T_2^2 - T_1^2) + \frac{\Delta_r c}{3} (T_2^3 - T_1^3) \quad 8.5.21$$

Example 8.5.1:

The oxidation of NO and the subsequent conversion of NO₂ to nitric acid, Eqs. 8.2.2-8.2.3, are important steps in the cyclic destruction of ozone in the stratosphere, see Chapter 5 Problem 10. Nitric acid forms hydrates at the low temperatures during the Antarctic winter. The surfaces of nitric acid hydrates are possible catalysts that accelerate the formation of the Antarctic ozone hole, Eq. 1.4.3. The temperature in the stratosphere ranges from about 190. K to 270. K. The reaction enthalpy for Eq. 8.2.2 is given at 298.15 K. Calculate the reaction enthalpy for the oxidation of NO at 220. K.

Answer: The reaction is:



The difference in heat capacity for the reaction is $\Delta_r C_p = [\Sigma \text{products}] - [\Sigma \text{reactants}]$:

$$\begin{aligned} \Delta_r C_p &= [37.2 \text{ J K}^{-1} \text{ mol}^{-1}] - [29.844 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{1}{2} 29.355 \text{ J K}^{-1} \text{ mol}^{-1}] \\ &= -7.32 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Eq. 8.5.5 gives:

$$\begin{aligned} \Delta_r H_{T_2} &= \Delta_r H_{T_1} + \Delta_r C_p \Delta T \\ \Delta_r H_{T_2} &= -57.05 \text{ kJ mol}^{-1} + (-7.32 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})(220. \text{ K} - 298.2 \text{ K}) \\ \Delta_r H_{T_2} &= -57.05 \text{ kJ mol}^{-1} - 0.573 \text{ kJ mol}^{-1} = -56.50 \text{ kJ mol}^{-1} \end{aligned}$$

The sensitivity of chemical reactions to changes in temperature varies greatly with reaction stoichiometry. Often the heat capacities of the reactants and products roughly cancel giving weak temperature dependence. However, the approximate cancellation of heat capacities, as in this example, doesn't always occur.

Eqs. 8.5.6 and 8.5.10 are examples of a general pattern that we will use repeatedly. These equations show that it is easy to convert a thermodynamic relationship that applies to a pure substance to an equivalent relationship for a chemical reaction.

General Pattern §8 Thermodynamic Relationships for Reactions ($\Delta_r X = \sum v_i X_i$)

The heat capacity of a pure substance is defined by Eq. 7.8.24. Comparison of the relationship for a pure substance to the result for a chemical reaction, Eq. 8.5.10, shows the correspondence:

<p style="text-align: center;">pure substance:</p> $\left(\frac{\partial H}{\partial T}\right)_P = C_p$	<p style="text-align: center;">chemical reaction:</p> $\left(\frac{\partial \Delta_r H}{\partial T}\right)_P = \Delta_r C_p \quad 8.5.22$
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The derivation in Eqs. 8.5.7-8.5.10 establishes this relationship. Going forward, we can use this general pattern to establish the thermodynamic relationships for other partial derivatives. In effect, we start with the result for a pure substance and then simply insert the Δ_r to convert to a relationship for a chemical reaction. For example, the temperature dependence of the change in internal energy for a chemical reaction at constant volume can be determined from Eq. 7.8.7:

<p style="text-align: center;">pure substance:</p> $\begin{array}{c} \Delta_r \\ \downarrow \\ \left(\frac{\partial U}{\partial T}\right)_V = C_v \end{array}$	<p style="text-align: center;">chemical reaction:</p> $\left(\frac{\partial \Delta_r U}{\partial T}\right)_V = \Delta_r C_v \quad 8.5.23$
--	---

The reaction changes for any function can be expressed in general form, analogous to Eq. 8.4.11:

$$\Delta_r X = \sum_{i=1}^{n_s} v_i X_i \quad 8.5.24$$

where X_i is the molar value of the parameter for each of the n_s constituents in the reaction. For example, the reaction internal energy can be written as:

$$\Delta_r U = \sum_{i=1}^{n_s} v_i U_i \quad 8.5.25$$

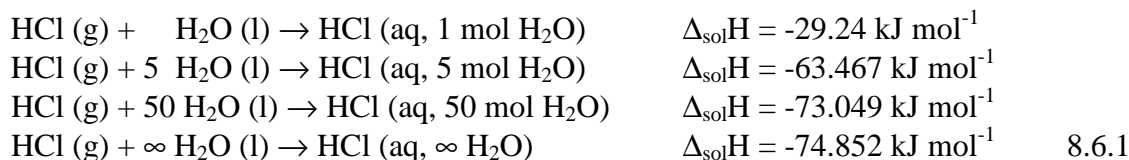
and the corresponding heat capacity difference for the reaction is given by:

$$\Delta_r C_v = \sum_{i=1}^{n_s} v_i C_{v,i} \quad 8.5.26$$

Many of the applications of thermodynamics are for processes in solution. We next discuss how to determine the enthalpy of formation of substances in solution.

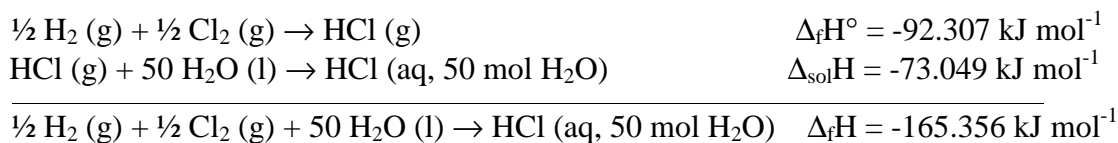
8.6 Enthalpy of Solution

The formation of a solution can be written as a chemical reaction. The heat evolved or absorbed when making a solution depends on the concentration of the final solution. Standard reference tables give the enthalpies for the solution when one mole of solute is added to a given number of moles of solvent. For example, the enthalpy of solution for HCl in water is given as:¹

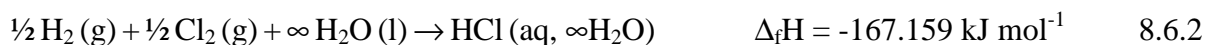


The last value corresponds to the enthalpy of solution extrapolated to infinite dilution. For non-electrolytes at infinite dilution, there are no interactions between the molecules of the solute. For electrolytes at infinite dilution, there are no interactions among the anions and cations. The mole amounts can be converted to concentrations. For example, for 50 mol of H₂O, $x_{\text{HCl}} = 0.01961$ and $m_{\text{HCl}} = 1.110 \text{ M}$. These enthalpies of solution are commonly called integral enthalpies of solution, because they are the total heat transfer for making the solution at the given concentration.

The Enthalpy of Formation of Species in Solution: To calculate the enthalpy of formation of a substance in solution, the enthalpy of solution is added to the enthalpy of formation of the pure substance using Hess's Law:



and at infinite dilution:

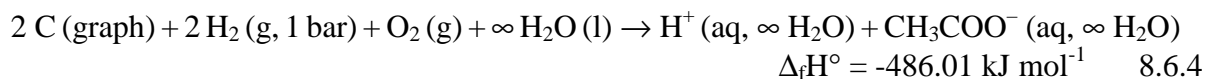


The standard state enthalpy of formation of a substance in solution corresponds to unit concentration. For strong electrolytes the standard state is listed as the "ai" value in reference tables and is numerically equal to the infinite dilution enthalpy change, Eq. 8.6.2:¹

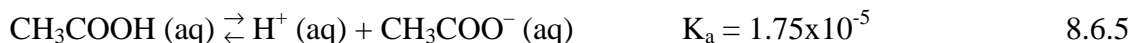


For electrolytes, the products are the ions that exist at infinite dilution. The "ai" standard state assumes the electrolyte is completely dissociated and there are no interactions among the cations and anions. We will discuss standard states in more detail in Chapter 19. For weak electrolytes a distinction must be made. At infinite dilution, a weak electrolyte is completely dissociated.

Consider acetic acid:



However, for a solution at unit concentration (actually activity), acetic acid is only 0.4% dissociated:



The predominant form of 1.0 m acetic acid is as undissociated CH_3COOH . The standard state for undissociated weak electrolytes is at unit concentration with “no further dissociation,” and is signified as “ao”. In other words, the “ao” enthalpy of formation is for undissociated CH_3COOH , not 0.4% dissociated acetic acid nor dissociated ions:



Conversely, the infinite dilution standard state enthalpy for acetic acid is $\Delta_f H^\circ(\text{CH}_3\text{COOH, ai}) = \Delta_f H^\circ(\text{H}^+, \text{ao}) + \Delta_f H^\circ(\text{CH}_3\text{COO}^-, \text{ao})$ and is numerically equal to the infinite dilution enthalpy change, Eq. 8.6.4, given $\text{CH}_3\text{COOH (ai)} = \text{H}^+ \text{(ao)} + \text{CH}_3\text{COO}^- \text{(ao)}$:



The standard state enthalpy change of dissociation, Eq. 8.6.5, is then $\Delta_r H^\circ = \Delta_f H^\circ(\text{ai}) - \Delta_f H^\circ(\text{ao}) = 0.25 \text{ kJ mol}^{-1}$. As another example, H_2S is a diprotic acid:



The “ao” standard states are for undissociated H_2S , undissociated HS^- , and unhydrolyzed S^{2-} . The “ai” standard state for H_2S is for the ions that exist at infinite dilution: $\Delta_f H^\circ(\text{H}_2\text{S, ai}) = 2\Delta_f H^\circ(\text{H}^+, \text{ao}) + \Delta_f H^\circ(\text{S}^{2-}, \text{ao})$. For strong electrolyte ions, the “ai” and “ao” standard states are equivalent, $\Delta_f H^\circ(\text{K}^+, \text{ao}) = \Delta_f H^\circ(\text{K}^+, \text{ai})$ and $\Delta_f H^\circ(\text{Cl}^-, \text{ao}) = \Delta_f H^\circ(\text{Cl}^-, \text{ai})$.

The Enthalpies of Formation of Ionic Species are Independent At Infinite Dilution: For electrolytes, you might wonder if enthalpies of formation for ions can be tabulated. In general, the enthalpies of ions in solution are dependent on the interactions between all the ions in solution. Therefore, the enthalpies of formation for ions depend on the identities of the counter ions and cannot be separated. However, at infinite dilution no interactions occur between ions because the ions are so far apart. For the specific case of infinite dilution, the individual ionic enthalpies of formation can be tabulated, Table 8.6.1. These values are commonly found in standard reference sources and in the appendix data section.¹⁻⁴ However, it is impossible to make a solution containing just cations or just anions. Such a solution would not be electrically neutral. In addition, the enthalpy of formation for electrolytes is always given as a change in enthalpy, based on the formation reaction from the constituent elements in their standard states. Therefore, there is no experimental way of determining the absolute enthalpy of formation of an ion, only changes in enthalpy can be measured for electrically neutral solutions. However, as we noted before, since we only need changes in enthalpy in practical problems, we are free to choose an arbitrary reference point.

$\Delta_f H^\circ(\text{H}^+)$ is Defined as 0: To determine the enthalpy of formation of an ion in solution, we choose to define the enthalpy of formation of H^+ as zero: $\Delta_f H^\circ(\text{H}^+, \text{ao}) \equiv 0$. For example, using this definition, the reaction in Eq. 8.6.3 gives the enthalpy of formation of chloride ions:



Table 8.6.1^(DS): Enthalpy of formation of ionic species.¹ $\Delta_f H^\circ(\text{H}^+, \text{ao}) \equiv 0$

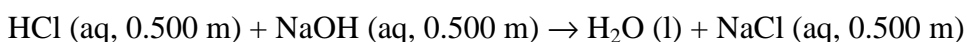
species	$\Delta_f H^\circ(\text{ao})$	species	$\Delta_f H^\circ(\text{ao})$
Na^+	-240.12	NO_3^-	-207.36
K^+	-252.38	Cl^-	-167.159
Ca^{2+}	-542.83	S^{2-}	33.1
Fe^{2+}	-89.1	CH_3COO^-	-486.01
Fe^{3+}	-48.5	OH^-	-229.994

(DS): Additional Values in the Appendix Data Section

Table 8.6.1 lists additional values. Though the enthalpy of formation of electrolyte solutions at moderate concentrations depend on the specific cations present and the concentration, the infinite dilution values are often a good starting approximation for calculating reaction enthalpies.

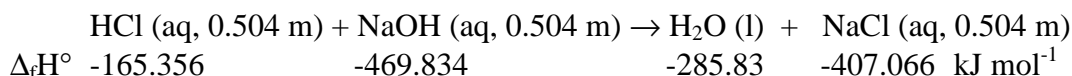
Example 8.6.2

Use the values in standard reference tables¹ to calculate the reaction enthalpy for the neutralization reaction:



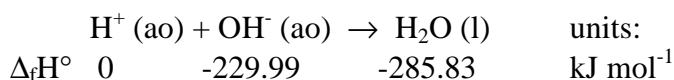
Use the values specific to the given concentrations and also estimate the reaction enthalpy from ionic enthalpies of formation.

Answer: The tabular values in Ref. 1 at 110 moles of H_2O correspond to 0.504 m, which is close enough to the given conditions:



Using Eq. 8.4.10, $\Delta_r H^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}] = -57.71 \text{ kJ mol}^{-1}$.

Alternatively, using the infinite dilution enthalpies of formation for the individual ions, the contributions of the spectator ions cancel leaving, Table 8.6.1:



Once again using Eq. 8.4.10: $\Delta_r H^\circ = -55.84 \text{ kJ mol}^{-1}$.

This result is called the enthalpy of neutralization of water. The estimated enthalpy of neutralization from the ionic contributions at infinite dilution differs from the more accurate value by 3.2%. The ionic contributions give a reasonable first approximation.

8.7 Calorimetry

There are many different types of calorimeters. We will focus on oxygen bomb calorimeters. Each type shares some common characteristics. All calorimetry experiments have two basic steps: the first is to determine the heat capacity of the calorimeter and the second is to use this heat

capacity to determine the heat of reaction for the compound of interest. A general outline of a calorimetric experiment is:

1. Determine the heat capacity of the calorimeter: $C_{\text{cal}} = q_{\text{cal}}/\Delta T_{\text{cal}}$
 - a. with q_{cal} from a known reaction: $q_{\text{cal}} = -q_v = -\Delta U$ or $q_{\text{cal}} = -q_p = -\Delta H$
 - b. or with q_{cal} from Joule heating: $q_{\text{cal}} = \int V I dt$
2. Determine the internal energy or enthalpy for the reaction in the calorimeter:
 - a. with $q_{\text{cal}} = C_{\text{cal}} \Delta T_{\text{react}}$ and $q_{\text{react}} = -q_{\text{cal}}$
 - b. giving $q_{\text{react}} = q_v = \Delta U$ or $q_{\text{react}} = q_p = \Delta H$
3. Convert to molar terms for unit extent: $\Delta_r U = \Delta U/n$ or $\Delta_r H = \Delta H/n$
4. Relate $\Delta_r U$ and $\Delta_r H$: $\Delta_r H = \Delta_r U + \Delta_r n_g RT$
5. Calculate $\Delta_f H^\circ$ from $\Delta_r H$.

Step 5 is not necessary for many purposes. There are three general classes of reaction calorimeters: insulated, isoperibol, and adiabatic. Insulated calorimeters isolate the reaction vessel from the surroundings using just an insulating barrier. The static-jacket style bomb calorimeters used in many undergraduate physical chemistry labs is of this type. **Isoperibol** calorimeters provide a jacket surrounding the reaction vessel that is held at constant temperature. This constant temperature environment decreases thermal fluctuations and noise in the measurements allowing higher sensitivity. In some isoperibol calorimeters the constant temperature is maintained by a large constant temperature bath, regulated at $\pm 0.001^\circ\text{C}$ or better. In isoperibol bomb calorimeters, the jacket is maintained at constant temperature by circulating water. To maintain constant temperature, the heating rate of the circulating bath is adjusted to account for the heat flux from the reaction vessel during the combustion reaction. **Adiabatic** calorimeters use a temperature controlled shield surrounding the reaction vessel that is heated or cooled electronically to match the temperature of the reaction vessel. Adiabatic shields are discussed in Section 7.2. Isothermal titration calorimeters for use in biochemical reaction studies are often based on adiabatic calorimeters, which give the highest sensitivity.

Oxygen Bomb Calorimeters are at Constant Volume: The enthalpy of combustion of a compound is determined in an oxygen bomb calorimeter, Figure 8.7.1. Bomb calorimeters are also used to find the "caloric" content of foods. Biologists use bomb calorimeters to determine the energy content of foods and feces for ecological field studies. Bomb calorimeters are also widely used in energy industries. The combustion process is initiated by passing a brief electrical current through a fuse wire that is in contact with the sample. The bomb is charged with 30 atm of oxygen to ensure complete combustion. The bomb sits in a calorimeter pail that is filled with water. The temperature of the water is measured by an electronic thermometer with 0.0001°C resolution.

Bomb calorimeters are constant volume systems; therefore the direct result of bomb calorimetry experiments is the internal energy change of the reaction: $\Delta U = q_v$. In most bomb calorimeters, a substance with a known internal energy of combustion is used to determine the heat capacity of the calorimeter. The internal energy of combustion of benzoic acid is precisely known. The heat transferred to the calorimeter from the combustion of benzoic acid is

$$q_{\text{cal}} = n_{\text{bz}} \Delta_{\text{comb}} U = w_{\text{bz}} \Delta_{\text{comb}} U_s \quad (\text{cst. } V) \quad 8.7.1$$

where n_{bz} is the number of moles, $\Delta_{\text{comb}}U$ is the molar internal energy of combustion, w_{bz} is the mass, and $\Delta_{\text{comb}}U_s$ is the internal energy of combustion per gram of benzoic acid. $\Delta_{\text{comb}}U_s$ for benzoic acid¹ is $-26.436 \text{ kJ g}^{-1}$. If the change in temperature of the calorimeter is ΔT_{cal} for the combustion of benzoic acid, the heat capacity of the calorimeter, C_{cal} , is:

$$C_{\text{cal}} = \frac{q_{\text{cal}}}{\Delta T_{\text{cal}}} \quad (\text{cst. V}) \quad 8.7.2$$

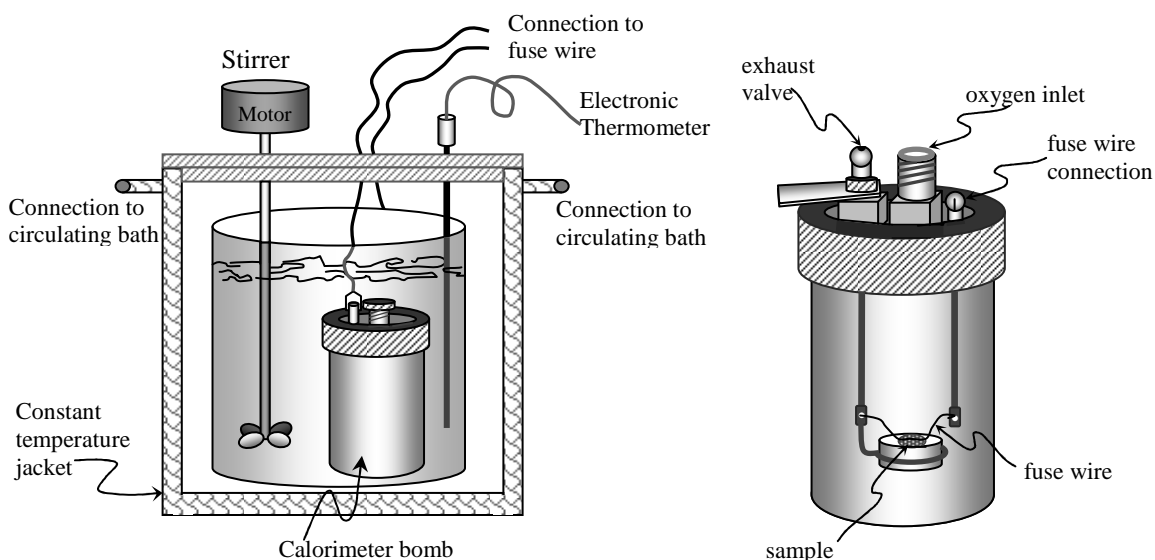


Figure 8.7.1: Isoperibol oxygen bomb calorimeter. The bomb is filled with oxygen at 30 atm to ensure complete combustion. One side of the fuse wire is connected to the body of the bomb.

The calorimeter consists of the bomb, thermometer, stirrer, calorimeter pail, and water in addition to the products of the combustion, which are CO_2 (g) and H_2O (l). In other words, the calorimeter includes everything that is heated by the combustion reaction. Having calculated the heat capacity of the calorimeter, the reaction of interest can be studied.

If the change in temperature for the combustion of n_{sample} moles of compound is ΔT_{react} then the heat transferred to the calorimeter during the reaction is:

$$q_{\text{cal}} = C_{\text{cal}} \Delta T_{\text{react}} \quad (\text{cst. V}) \quad 8.7.3$$

The heat lost by the reaction is given by the heat gained by the calorimeter, $q_{\text{react}} = -q_{\text{cal}}$. Then since the reaction is at constant volume, $q_{\text{react}} = q_v$:

$$\Delta_{\text{comb}}U = \frac{q_v}{n_{\text{sample}}} \quad (\text{cst. V}) \quad 8.7.4$$

The internal energy of combustion from Eq. 8.7.4 is at the temperature and pressure of the calorimeter. The internal energy of combustion at 298.2 K can be calculated using Eq. 8.5.23. The corrections to 298.2 K and the corrections to 1 bar pressure are often less than the experimental uncertainty.⁵⁻⁷ For nitrogen containing compounds in actual experiments a mixture

of N_2 and aqueous nitric acid are produced and for sulfur containing compounds a mixture of SO_2 and aqueous sulfuric acid are produced in the bomb. The data is corrected to give the value for the production of only $\text{N}_2(\text{g})$ and $\text{SO}_2(\text{g})$.⁵⁻⁷

The standard state enthalpy of combustion is then calculated from the standard state internal energy of combustion, as in Example 8.3.1. The enthalpy of formation of the compound is finally calculated using Hess's Law, as in Example 8.4.2.

A typical plot of the temperature as a function of time for an insulated or isoperibol calorimeter is shown in Figure 8.7.2. The temperature before ignition of the bomb is usually not constant. The temperature will decrease if the calorimeter is warmer than the surroundings, and the temperature will increase if the calorimeter is colder than the surroundings. The temperature drift is linear for short time intervals and small temperature differences. Under these conditions, Newton's Law of Cooling, Eq. 7.2.18, can be expanded in a power series and only the first two terms retained. The result gives a linear drift of the temperature (see Problem 10). The calorimeter also has a stirrer in the pail surrounding the bomb. The stirrer does work, and in the process heats the water in the pail. After ignition the temperature increases approximately exponentially, according to Newton's Law of Cooling. The temperature usually doesn't reach a constant value, because the temperature slowly drifts towards the temperature of the surroundings after the reaction is complete. If the temperature after the reaction is higher than the surroundings the temperature decreases, and vice versa.

The errors in the determination of ΔT caused by temperature drift before and after the reaction can be minimized by an extrapolation procedure. Least squares fits are done for the interval of linear drift before ignition and the interval of linear drift after the maximum temperature is attained. The line before ignition is extrapolated forwards and the line after the reaction is complete is extrapolated backwards. The ΔT is then the difference between these two extrapolated lines. However, at what time should the temperature difference be measured? Experiments at the National Institute of Standards and Technology (NIST) show that the most accurate time is when the temperature reaches 63% of its final value, Figure 8.7.2.⁸ The factor of 63% is approximate and results from Eq. 7.2.18 and $(1 - e^{-1}) = 0.63$. Let T_0 be the temperature at the time of ignition, t_0 , and T_{max} be the maximum temperature. The time, t_e , is selected when the temperature is $T_0 + 0.63*(T_{\text{max}} - T_0)$.

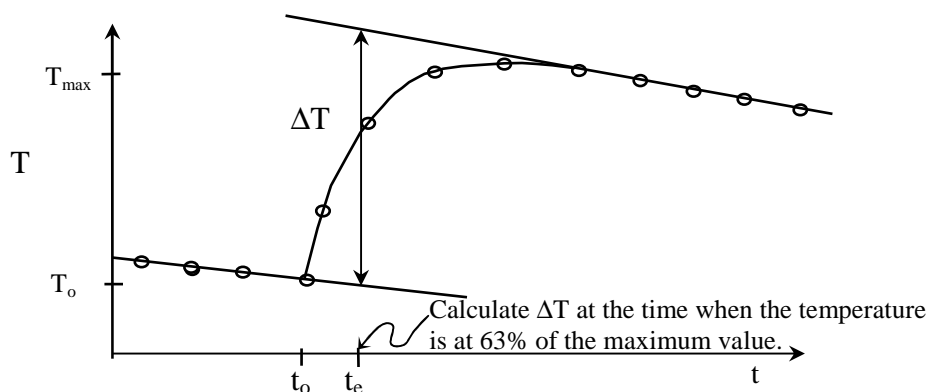


Figure 8.7.2. A typical thermogram for bomb calorimetry. The extrapolation minimizes errors caused by temperature drift before and after the reaction.

There are over 100 million substances registered in Chemical Abstracts. The accurate experimental thermodynamic characterization of each of these compounds is impossible. However, as we search for solutions to challenges in human health, energy production, and environmental issues, we need to know as much as possible about every known compound and compounds yet to be synthesized. The prediction of the internal energy, enthalpy, and heat capacities for substances is a central goal of physical chemistry.

8.8 Predicting Internal Energy, Enthalpy, and Heat Capacities

Thermodynamics is said to be “**model free**,” thermodynamic theories hold independently of how we interpret the underlying structure and properties of matter. Thermodynamics was developed largely before the concepts of atoms and molecules were widely accepted by the scientific community. However, taking a molecular view helps us to understand the meaning of internal energy and allows us to predict the thermodynamic properties of substances that have not been studied in the laboratory.

We will focus first on an ideal gas. In an ideal gas the molecules are independent of each other because there are no intermolecular forces. We will add molecular interactions in later chapters so that we can discuss real gases and condensed phases. The energy of a mole of an ideal gas is the energy of a single molecule multiplied by Avogadro’s number. We need to build the system containing one mole of molecules from the ground up. We start first with the ground state electronic structure to predict the internal energy of the molecule at absolute zero, $U(0)$. The contribution of the ground state is temperature independent. We then add temperature dependent terms for the motional degrees of freedom of the molecule, which are translation, rotation, and vibration, and contributions from any accessible excited electronic states:

$$U = U(0) + \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elect}} \quad (\text{ideal gas}) \quad 8.8.1^\circ$$

The temperature dependent electronic term, ϵ_{elect} , is zero for molecules lacking low lying electronic excited states. Few molecules have low lying electronic excited states. The $U(0)$ term is determined subject to the chosen reference point. As noted in Sec. 8.4, only differences in the internal energy may be measured and not absolute values, so an arbitrary reference is chosen as the energy of the elements in their standard states. The relationship between the enthalpy and internal energy is given by Eq. 8.1.4° with $n_g = 1$ mol, $H = U + RT$. The enthalpy is then determined using Eq. 8.8.1°:

$$H = U(0) + \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elect}} + RT \quad (\text{ideal gas}) \quad 8.8.2^\circ$$

Note also at absolute zero, $RT = 0$, giving $H(0) = U(0)$. The ground state electronic energy of a molecule is best determined using quantum mechanical techniques, however an empirical method based on the concept of bond enthalpies is easy and useful. Bond enthalpies are based solely on atom-atom connectivity. The ground state electronic energy is the sum of the prediction based on bond enthalpies, ϵ_{bond} , and the **steric energy**, which takes the conformation of the molecule into account:

$$H(0) = U(0) = \epsilon_{\text{bond}} + \epsilon_{\text{steric}} \quad 8.8.3^\circ$$

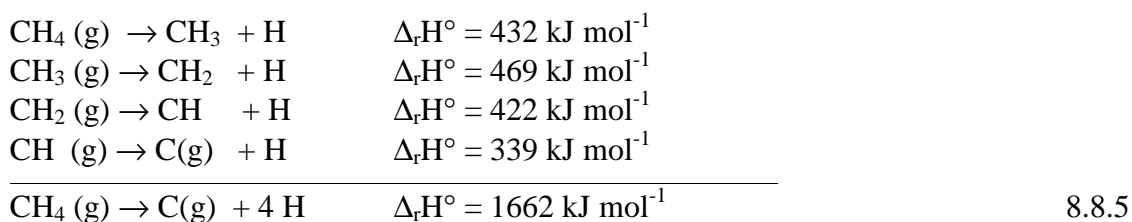
The Ground State Electronic Energy can be Approximated as the Sum of the Bond Energies:

One empirical way of determining the ground state electronic energy is to use bond enthalpy calculations. The internal energy or enthalpy of a molecule is assumed to be an additive function

of the energy of individual bonds, Table 8.8.1. For example, the assumption is that a C–H bond in methane has the same energy as in an aldehyde, $-(O=)C-H$, or an olefin $-C=C-H$. Bond energies can be calculated from spectroscopic gas-phase dissociation energies. The general process is:



The bond enthalpy at 0 K, $\Delta_r H^\circ(0)$, is also called the bond dissociation energy, $D_o(A-B)$. For example, for methane the experimental successive bond dissociation enthalpies are:



The four C–H bonds in methane must be equivalent, which gives the bond dissociation enthalpy for a C–H bond in methane as $\Delta_r H^\circ = 1662/4 = 416 \text{ kJ mol}^{-1}$. The average value over many types of compounds for the bond dissociation enthalpies for several types of bonds is given in Table 8.8.1. In general triple bonds are stronger than double bonds, which in turn are stronger than single bonds. The $\Delta_r H^\circ$ for a reaction is given by $\sum \Delta_r H^\circ(\text{bonds broken}) - \sum \Delta_r H^\circ(\text{bonds formed})$. Bond enthalpies pertain to reactions where all species are in the gas phase. One difficulty is that the enthalpy of sublimation for graphite to give gas phase carbon atoms is not experimentally measurable. This important parameter is calculated indirectly and has a large uncertainty; however, the uncertainty is negligible relative to the assumption of the additivity of the bond enthalpies over many different chemical environments.

Table 8.8.1. Bond Enthalpies, $\Delta_r H^\circ(A-B)$ (kJ mol^{-1}).⁹

	H	C	N	O
H	436			
C	412	348 – 518 ∴ ^a 614 = 839 ≡		
N	391	305 – 615 = 891 ≡	163 – 418 = 945 ≡	
O	463	358 – 745 = 1070 ≡	201 – 607 =	146 – 498 =
C (graph) \rightarrow C (g)		$\Delta_r H^\circ = 716.7 \text{ kJ mol}^{-1}$		

(a). ∴ aromatic

For example, the enthalpy of formation of acetaldehyde, $CH_3-CH=O$, is calculated as:



# Bonds Broken		# Bonds Formed	
2 C (graph)	2 (716.7 kJ mol ⁻¹)	1 C=O	745 kJ mol ⁻¹
2 H-H	2 (436 kJ mol ⁻¹)	4 C-H	4(412 kJ mol ⁻¹)
$\frac{1}{2}$ O=O	$\frac{1}{2}$ (498 kJ mol ⁻¹)	1 C-C	348 kJ mol ⁻¹
total	2554.4 kJ mol ⁻¹	total	2741 kJ mol ⁻¹

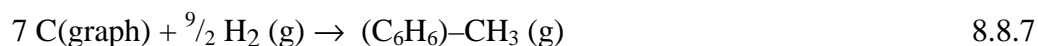
$= -187. \text{ kJ mol}^{-1}$

The experimental value for the $\Delta_f H^\circ$ of acetaldehyde is $-166.19 \text{ kJ mol}^{-1}$, so the value derived from bond dissociation enthalpies is not accurate, but a useful starting point none-the-less.

Example 8.8.1:

Calculate the molar enthalpy of formation of toluene (methylbenzene) using bond dissociation enthalpies and compare with the literature experimental values.

Answer: The enthalpy of formation of toluene, $(\text{C}_6\text{H}_6)\text{-CH}_3$, is calculated as:



# Bonds Broken		# Bonds Formed	
7 C (graph)	7(716.7 kJ mol ⁻¹)	6 C \equiv C	6(518 kJ mol ⁻¹)
$\frac{9}{2}$ H-H	$\frac{9}{2}$ (436. kJ mol ⁻¹)	1 C-C	348 kJ mol ⁻¹
		9 C-H	9(412 kJ mol ⁻¹)
total	6978.9 kJ mol ⁻¹	total	7164 kJ mol ⁻¹

$= 185. \text{ kJ mol}^{-1}$

The experimental value in the gas phase is $+50.0 \text{ kJ mol}^{-1}$. Bond energy predictions for conjugated molecules are particularly inaccurate, unless bond energies for appropriate partial-order bonds are known.

To improve on predictions based on bond dissociation energies, the chemical environment of a given bond needs to be taken into account. Quantum mechanical calculations are the best way to predict ground state electronic energies, but a number of extensions of the bond energy concept have also been developed. One approach is based on **bond increments** that are additive parameters for specific types of bonds and chemical environments.¹⁰ Bond increments are easy to implement in computational algorithms. This approach is taken in the MM2/MM3/MM4 series of molecular mechanics programs.^{11,12} The MM3 bond increments for saturated hydrocarbons are given in Table 8.8.2. The bond increments are optimized to reproduce the enthalpy of formation for a wide variety of compounds when used in conjunction with steric energy calculations (see below). This listing is a small subset of the necessary parameters. Notice that two different values for the C-C bond energy are used, depending on the chemical environment, $\text{sp}^3\text{-sp}^3$ or $\text{sp}^3\text{-sp}^2$. Some increments, such as the C-H terms, are for a given bond enthalpy contribution and some increments are corrections for environment effects, such as the RCH_3 methyl correction.

Table 8.8.2: MM3 bond increments for hydrocarbons, kJ mol⁻¹.¹³

Bond contributions:			
C-H	C-C (sp ³ -sp ³)	C-C (sp ³ -sp ²)	C=C (sp ² -sp ²)
-19.205	10.238	-0.753	110.583
Environment contributions:			
RCH ₃ (methyl)	R ₃ CH (iso)	R ₄ C (neo)	R ₂ C=C (iso alkene)
4.37	-10.99	-27.79	-8.414

The bond energy calculation for acetaldehyde from MM3 with energies in kJ mol⁻¹ is:

#	Bond or Structure	Each	Total
1	C-C sp ³ -sp ² C=O	-15.452	-15.452
3	C-H Aliphatic	-19.205	-57.614
1	C-H Aldehyde	-19.205	-19.205
1	C=O	-90.793	-90.793
1	Me-Carbonyl	3.615	3.615
		$\epsilon_{\text{bond}} = -179.45 \text{ kJ mol}^{-1}$	8.8.8

The enthalpy of formation based on bond energies provides an estimate of U(0) and H(0). Bond energies alone are not accurate predictions for enthalpies of formation. The conformation of the molecule and associated steric energy has an important contribution to the ground state energy.

Molecular Mechanics Steric Energies and Bond Increments Provide Better Estimates for Enthalpies of Formation: The **steric energy** is the energy due to the three-dimensional conformation of the molecule. Steric interactions change the ground state energy, Eq. 8.8.3°.

Molecular mechanics provides a method to estimate the steric energy. The interactions comprising the steric energy include the stretching or compressing of bonds from their equilibrium lengths and angles, torsional effects of twisting about single bonds, Van der Waals attractions or repulsions, and electrostatic interactions between partial charges.^{11,12} The steric energy of a molecule is the sum of the energies of the interactions:

$$\epsilon_{\text{steric}} = \epsilon_{\text{str}} + \epsilon_{\text{bend}} + \epsilon_{\text{str-bend}} + \epsilon_{\text{oop}} + \epsilon_{\text{tor}} + \epsilon_{\text{vdW}} + \epsilon_{\text{ele}} \quad 8.8.9$$

The bond stretching, bending, stretch-bend, out-of-plane, and torsion interactions are called **bonded interactions** because the interactions result from distortions of chemical bonds. The Van der Waals and electrostatic (qq) interactions are between non-bonded atoms. The sum of all the interactions is called the **force field** for the molecule. We consider first the bonded interactions.

Bonded Interactions Use Hookean Potentials: The potential energy term ϵ_{str} represents the energy required to stretch or compress a bond between two atoms, i and j, Figure 8.8.1. A bond can be modeled as a spring with equilibrium length, r_0 , and the energy required to stretch or compress the bond can be approximated by using the **Hooke's Law** potential:

$$\epsilon_{\text{str}} = \frac{1}{2} k_{\text{str},ij} (r_{ij} - r_0)^2 \quad 8.8.10$$

where $k_{\text{str},ij}$ is the stretching force constant for the bond and r_{ij} is the distance between the two atoms. The stronger the bond the larger the force constant.

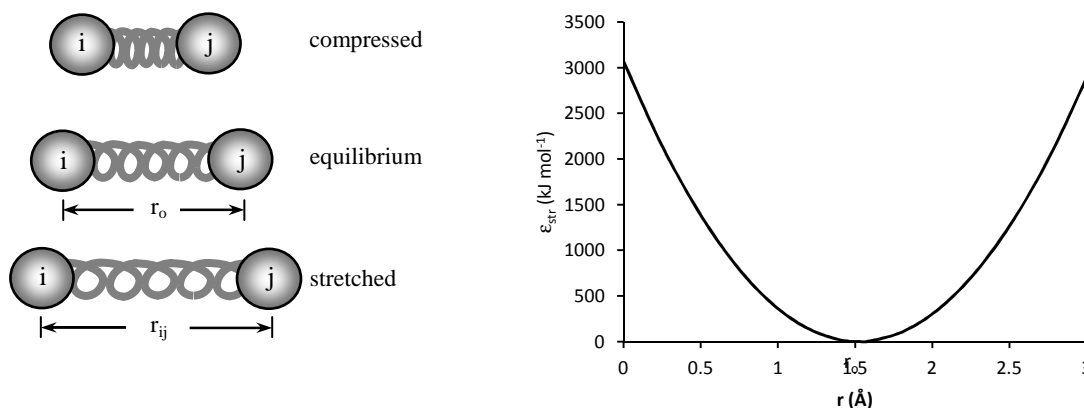
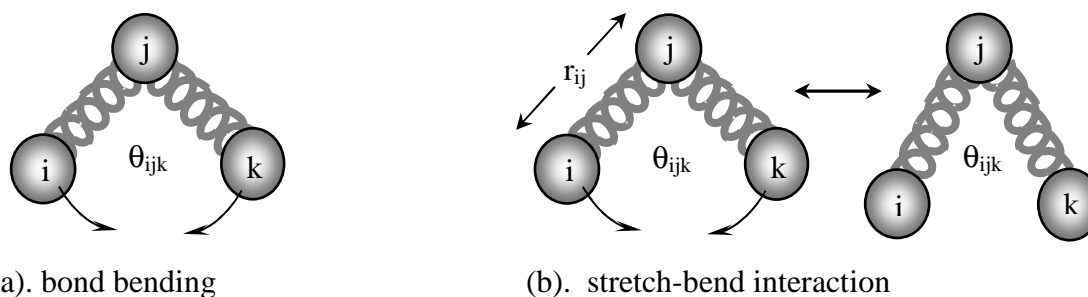


Figure 8.8.1. Bond stretch quadratic potential.

The potential energy term ϵ_{bend} is the energy required to bend a bond from its equilibrium angle, θ_o . Again this distortion can be modeled by a spring, and the energy is given by the Hookean potential with respect to angle:

$$\epsilon_{\text{bend}} = \frac{1}{2} k_{\text{bend},ijk} (\theta_{ijk} - \theta_o)^2 \quad 8.8.11$$

where $k_{\text{bend},ijk}$ is the bending force constant and θ_{ijk} is the bond angle, Figure 8.8.2a.



(a). bond bending

(b). stretch-bend interaction

Figure 8.8.2. (a). Bond bending, (b). Stretch-bend interaction: as the bond bends to smaller angle, the lowest energy bond length increases.

The stretch and bend are not independent; the stretching and bending motions interact. The stretch-bend interaction potential, $\epsilon_{\text{str-bend}}$, accordingly takes into account the observation that when a bond is bent to smaller angles, the two associated lowest energy bond lengths increase, Figure 8.8.2b:

$$\epsilon_{\text{str-bend}} = \frac{1}{2} k_{\text{sb},ijk} (r_{ij} - r_o) (\theta_{ijk} - \theta_o) \quad 8.8.12$$

where $k_{\text{sb},ijk}$ is the stretch-bend force constant for the bond between atoms i and j with the bend between atoms i, j, and k.

The potential energy term ϵ_{oop} is the energy required to deform a planar group of atoms from its equilibrium angle, ω_o , which is usually equal to zero.¹³ This out-of-plane force field term is

necessary for sp^2 hybridized atoms, and some small ring systems. The energy is given by the Hookean potential with respect to planar angle:

$$\epsilon_{oop} = \frac{1}{2} k_{oop,ijkl} (\omega_{ijkl} - \omega_0)^2 \quad 8.8.13$$

where $k_{oop,ijkl}$ is the bending force constant and ω_{ijkl} is the bond angle, Figure 8.8.3. The out-of-plane term is also called the improper torsion in some force fields. Most force fields use oop terms for the carbonyl carbon and the amide nitrogen in peptide bonds in proteins, which are planar, Figure 8.8.4.¹⁴

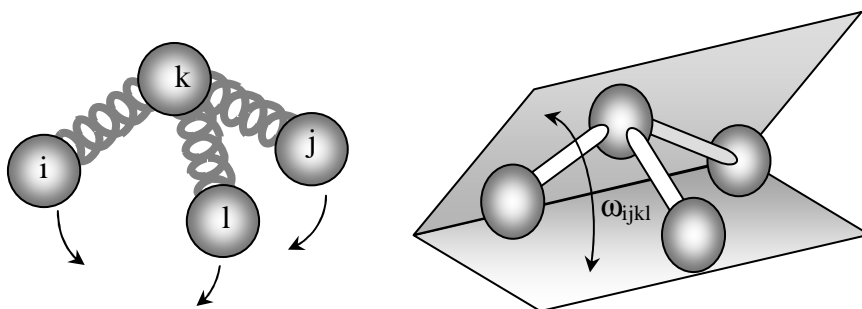


Figure 8.8.3. Out-of-plane bending.

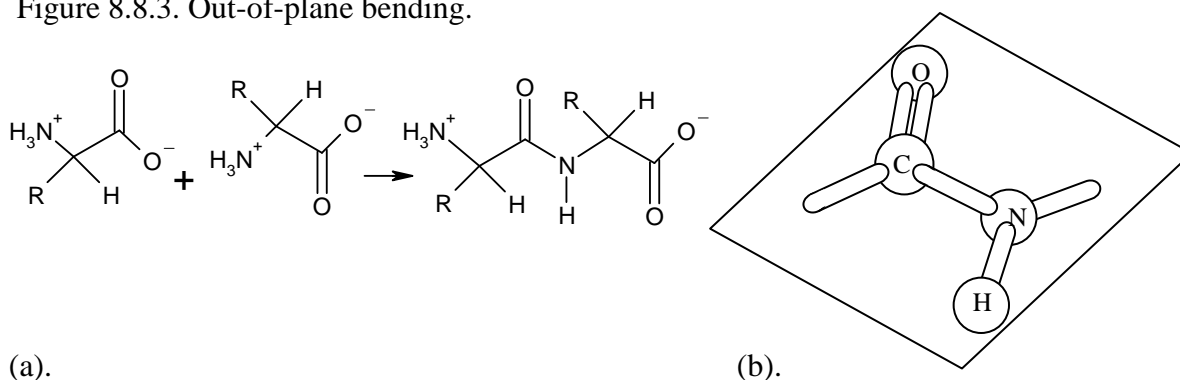


Figure 8.8.4: (a). The amino acids in proteins are attached through peptide bonds. (b). The peptide bond is planar and requires out-of-plane bending terms.

The term ϵ_{tor} is the potential energy of rotation about bonds. Torsional energies are usually important only for single bonds because double bonds are too rigid to permit rotation. Torsional interactions are modeled by the potential:

$$\epsilon_{tor} = \frac{1}{2} k_{tor,1} (1 + \cos \phi) + \frac{1}{2} k_{tor,2} (1 + \cos 2\phi) + \frac{1}{2} k_{tor,3} (1 + \cos 3\phi) \quad 8.8.14$$

The angle ϕ is the dihedral angle about the bond, Figure 8.8.5a. The constants $k_{tor,1}$, $k_{tor,2}$, and $k_{tor,3}$ are the torsional force constants for one-fold, two-fold, and three-fold rotational barriers, respectively. The torsional potential for $H-C(sp^3)-C(sp^3)-H$ from the commonly used Merck Molecular Force Field, MMFF, is:¹⁵⁻¹⁷

$$\epsilon_{tor} = 0.594 (1 + \cos \phi) - 2.900 (1 + \cos 2\phi) + 0.657 (1 + \cos 3\phi) \text{ kJ mol}^{-1} \quad 8.8.15$$

The three-fold term, which is the last term in 3ϕ , is important for sp^3 hybridized systems.¹¹ The two-fold term, in 2ϕ , is the lower curve in Figure 8.8.5b and is the dominant torsional interaction

for H–C–C–H. The torsional interaction summed over all pairs of H-atoms for ethane gives a symmetric three-fold potential, Figure 8.8.5c.

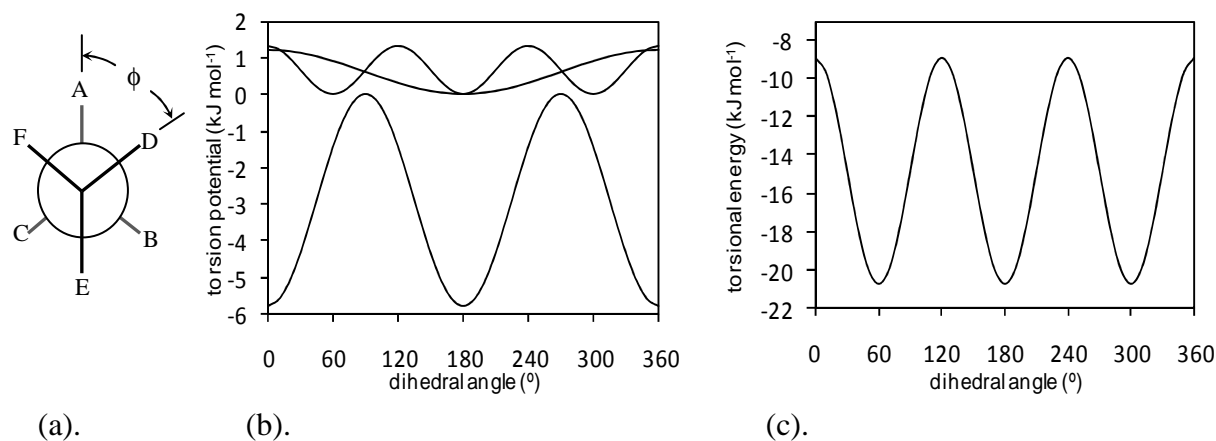


Figure 8.8.5: (a). Definition of the dihedral angle, ϕ . (b). Torsional potential for H–C–C–H for the separate one, two, and three-fold terms. (c). Total torsional interaction for ethane.

To summarize the bonded force field terms, when molecular interactions stretch, compress, or bend bonds from the equilibrium lengths and angles, the bonds resist the change with an energy given by the potential functions, Eqs. 8.8.10-8.8.15, summed over all bonds. When the bonds cannot relax back to their equilibrium positions, the steric energy increases. When the different units of distance and angle are considered, the force constants have relative sizes:

$$\text{Stretch} \gg \text{bend} > \text{stretch-bend} \sim \text{out-of-plane} > \text{torsion}$$

It is difficult to stretch, easier to bend, and very easy to twist a single bond.

Non-bonded Interactions include Van der Waals and Coulomb Interactions: **Van der Waals** interactions, which are responsible for the liquefaction of non-polar gases like O₂ and N₂, also govern the energy of interaction of non-bonded atoms within a molecule. These interactions contribute to the steric interactions and are often the most important factors in determining the overall molecular conformation. Such interactions are extremely important in determining the three-dimensional structure of many biomolecules, especially proteins. The Van der Waals interaction between closed-shell atoms and non-polar molecules is called the **induced dipole-induced dipole interaction** or the **dispersion interaction**.

A plot of the Van der Waals energy as a function of distance between two hydrogen atoms is shown in Figure 8.8.6. When two atoms are far apart, an attraction is felt. When two atoms are very close together, a strong repulsion is present. Although both attractive and repulsive forces exist, the repulsions are often the most important for determining the conformations of molecules. One expression for the Van der Waals dispersion energy is:

$$\epsilon_{\text{vdW},ij} = -\frac{A}{r_{ij}^6} + \frac{B}{r_{ij}^{12}} \quad 8.8.16$$

where A and B are constants dependent upon the two atoms and r_{ij} is the distance separating the two nuclei. This equation is also called the Lennard-Jones potential or the 6-12 potential, referring to the exponents for r_{ij} . Since, by definition, lower energy is more favorable, the $-A/r^6$ term is the attractive part and the $+B/r^{12}$ term is the repulsive part of the interaction. For two hydrogen atoms in a molecule:¹²

$$A = 294.5 \text{ kJ mol}^{-1} \text{ \AA}^6 \quad B = 2.63 \times 10^4 \text{ kJ mol}^{-1} \text{ \AA}^{12}$$

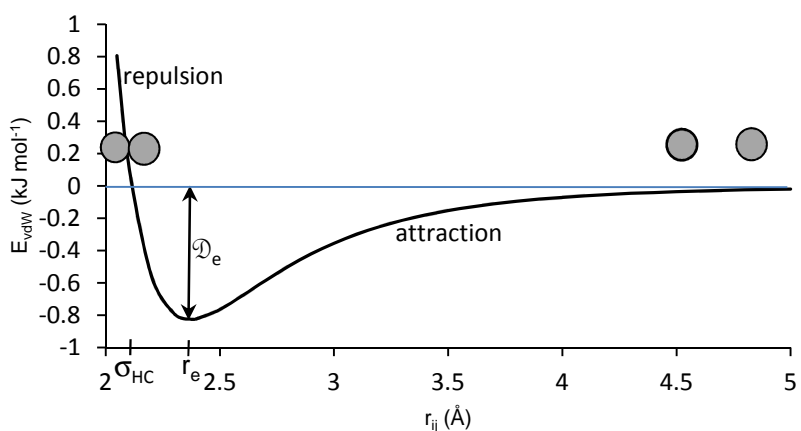


Figure 8.8.6: Van der Waals dispersion interactions between two hydrogen atoms in a molecule, such as H_2O_2 or $\text{CH}_3\text{-CH}_3$, $\mathcal{D}_e = 0.8146 \text{ kJ mol}^{-1}$, $r_e = 2.376 \text{ \AA}$, and $\sigma_{\text{HC}} = 2.117 \text{ \AA}$.

Two additional equivalent and commonly used forms of the Lennard-Jones potential are:

$$\epsilon_{\text{vdW},ij} = \mathcal{D}_e \left[-2 \left(\frac{r_e}{r_{ij}} \right)^6 + \left(\frac{r_e}{r_{ij}} \right)^{12} \right] = 4\mathcal{D}_e \left[- \left(\frac{\sigma_{\text{HC}}}{r_{ij}} \right)^6 + \left(\frac{\sigma_{\text{HC}}}{r_{ij}} \right)^{12} \right] \quad 8.8.17$$

Where \mathcal{D}_e is the minimum energy, r_e is the minimum energy distance, and σ_{HC} is the sum of the hard-core Van der Waals radii of the two atoms. When looking for close contacts between atoms, it is best to use the hard-core Van der Waals diameter, σ_{HC} . This distance is the point where the Van der Waals potential is zero. When two atoms are closer than σ_{HC} , strong repulsions are present. The hard core diameter and the minimum energy distance are related by $\sigma_{\text{HC}} = 2^{-1/6} r_e$.

Electrostatic Interactions: If bonds in the molecule are polar, the atoms carry partial electrostatic charges. The electrostatic interactions are represented by the Coulomb potential:

$$\epsilon_{\text{ele},ij} = \frac{c Q_i Q_j}{4\pi\epsilon_r r_{ij}} \quad 8.8.18$$

where Q_i and Q_j are the unitless partial atomic charges for atoms i and j separated by a distance r_{ij} , and ϵ_r is the relative dielectric constant. The constant c is a units conversion constant; $c = N_A e^2 / \epsilon_0 / 1000 \text{ J kJ}^{-1} / 1 \times 10^{-10} \text{ m \AA}^{-1} = 17459.2 \text{ kJ mol}^{-1} \text{ \AA}$. The Coulomb potential for a unit positive and negative charge is shown in Figure 8.8.7a and the Coulomb potential for the hydrogens in H_2O_2 is shown in Figure 8.8.7b.

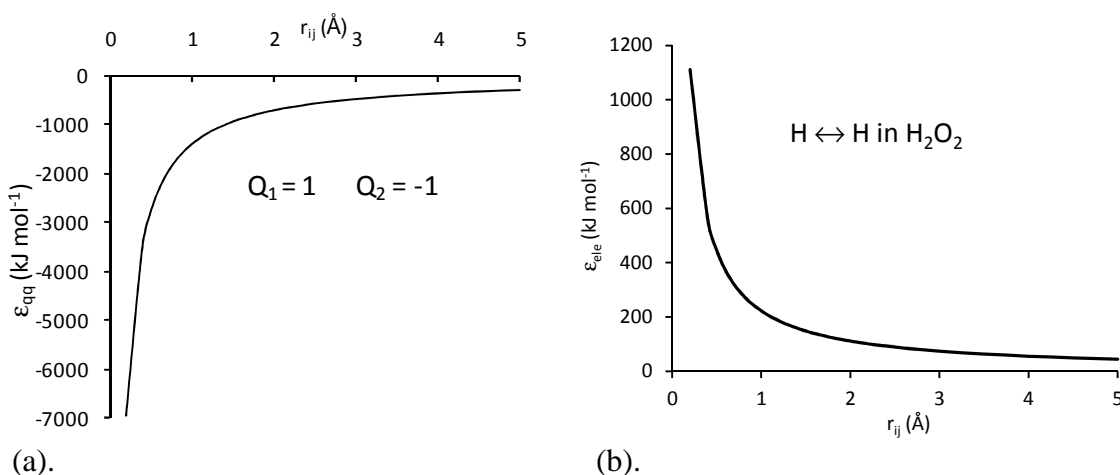


Figure 8.8.7: (a) Coulomb attraction of a positive and a negative charge. (b) Coulomb repulsion of the two hydrogens in H_2O_2 , with the charge on the hydrogens $Q_1 = Q_2 = 0.40$.

Like charges raise the steric energy, while opposite charges lower the energy. For gas phase calculations ϵ_r is set to 1. Larger values of ϵ_r are used to approximate the dielectric effect of intervening solute or solvent atoms in solution. For water ϵ_r is 78.54. For the interior of a protein ϵ_r is often taken as 4.

To summarize the non-bonded force field terms, the Van der Waals and electrostatic potential functions represent the non-bonded interactions between pairs of atoms i and j . The non-bonded interactions also govern the intermolecular interactions in complexes. A full force field determines the steric energy by summing these potentials over all non-bonded pairs of atoms in the molecule. Finally, the full steric energy including bonded and non-bonded terms is given by the sum over all atoms:

$$\begin{aligned} \epsilon_{\text{steric}} = & \sum_r \frac{1}{2} k_{\text{str},ij} (r_{ij} - r_o)^2 + \sum_{\theta} \frac{1}{2} k_{\text{bend},ijk} (\theta_{ijk} - \theta_o)^2 + \sum_r \sum_{\theta} \frac{1}{2} k_{\text{sb},ijk} (r_{ij} - r_o) (\theta_{ijk} - \theta_o) \\ & + \sum_{\omega} \frac{1}{2} k_{\text{oop},ijkl} (\omega_{ijkl} - \omega_o)^2 + \sum_{\phi} \sum_{n=1}^3 \frac{1}{2} k_{\text{tor},n} (1 + \cos n\phi) + \sum_i \sum_{j>i} \left[-\frac{A}{r_{ij}^6} + \frac{B}{r_{ij}^{12}} + \frac{c Q_i Q_j}{4\pi\epsilon_r r_{ij}} \right] \end{aligned} \quad 8.8.19$$

where the sum over r symbolizes all bonded pairs of atoms i, j . The sum over θ symbolizes all bends for atoms i, j , and k . The sum over ω symbolizes all out-of-plane angles, and the sum over ϕ symbolizes all torsions for atoms $i-j-k-l$.

One of the major goals of molecular mechanics is to determine the low energy conformations of a molecule or complex. **Geometry optimization** is the process of varying each bond length and angle to minimize the steric energy of the molecule. The minimum steric energy conformation is the most stable conformation, which is called the **global minimum**.

All the potential functions involve a force constant or interaction constant. These constants are derived empirically. That is, the constants are adjusted by trial-and-error so that the geometry of a number of well-known compounds is properly predicted. These constants are then used to calculate the structures of new compounds. The accuracy of these constants is critical to molecular mechanics calculations. Unfortunately, no single best set of force constants is

available because of the diversity of types of compounds and uses for molecular mechanics. Many force fields are in current use; each force field uses a different set of force constants.

Different force fields also use additional terms. For example, force fields add terms to the bonded interactions to better approximate the real potential function of a chemical bond, Figure 8.8.8a. These additional terms take into account anharmonicity, which is a result of the fact that given enough vibrational energy, bonds break. Purely quadratic potentials have steep "walls" that prevent bond dissociation, Figure 8.8.1. Cubic terms are added to purely quadratic potentials, as in Eq.8.8.7, to adjust for anharmonicity:¹¹

$$\epsilon_{\text{str}} = \frac{1}{2} k_{\text{str},ij} (r_{ij} - r_o)^2 - \frac{1}{2} k_{\text{str},ij} C_s (r_{ij} - r_o)^3 \quad (\text{anharmonic}) \quad 8.8.20$$

where C_s is the cubic stretch constant. For example, in MM2 for a $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ bond, k_{str} is 1325 kJ mol^{-1} and the cubic stretch constant is 2.00 \AA^{-1} , Figure 8.8.8b. Some force fields, including MMFF, add a quartic term, $\frac{7}{12} (\frac{1}{2} k_{\text{str},ij} C_s^2) (r_{ij} - r_o)^4$, to help improve the potential for large r_{ij} .^{14,15}

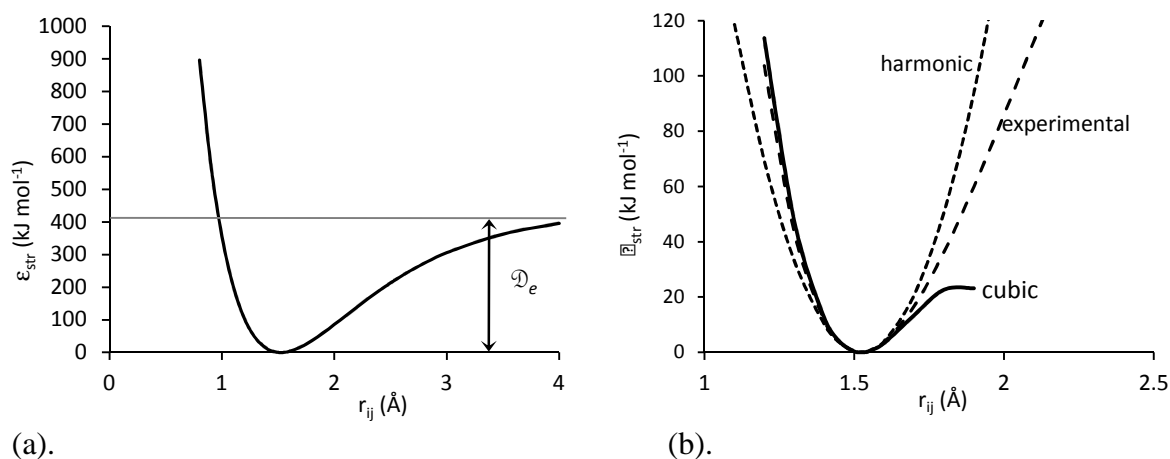


Figure 8.8.8: (a). Realistic potential energy curve for C–C bond stretching, which shows anharmonicity. The asymptotic limit at the dissociation energy, \mathcal{D}_e , corresponds to breaking the C–C bond. (b). Comparison of the harmonic potential, Eq. 8.8.10, for short distances with Eq. 8.8.20, which includes the $(r - r_o)^3$ cubic term to correct for anharmonicity.

Another example of the differences between force fields is that MM3 uses the Buckingham potential instead of the Lennard-Jones equation for the Van der Waals interaction. The general form of the Buckingham potential for the dispersion interaction is:

$$\epsilon_{\text{vdw},ij} = \mathcal{D}_e \left\{ \frac{6}{\alpha - 6} e^{-\alpha(r_{ij} - r_o)/r_o} - \frac{\alpha}{\alpha - 6} \left(\frac{r_o}{r_{ij}} \right)^6 \right\} \quad 8.8.21$$

This potential uses the r^6 attractive part of the Lennard-Jones functional form, Eq. 8.8.16. The exponential part of the Buckingham potential matches the repulsive part of the Lennard-Jones 6-12 potential best with an α of 14-15. However, MM3 uses a "softer" more realistic repulsion with $\alpha = 12.5$.

Protein Structure: Alpha Helices and Beta-Pleated Sheets: One important use of molecular mechanics is the determination of the secondary and tertiary structure of proteins. Two examples of **secondary** structural motifs are the alpha-helix and the beta-pleated sheet, Figure 8.8.9. The secondary structure of proteins is stabilized by a network of hydrogen bonds. The network of hydrogen bonds in the alpha-helix are between the C=O carbonyl oxygen on one amino acid and the NH hydrogen on the amino acid four residues further along the backbone. The hydrogen bonds in the beta-pleated sheet structure are between the parallel chains. The **tertiary structure** of a protein is determined by the spatial relationships of the secondary elements. In other words, the tertiary structure describes the spatial relationships of the alpha-helices, beta-pleated sheets, and peptide turn regions of the protein. The proper functioning of a protein is dependent on folding the protein into the proper secondary and tertiary conformation. A typical protein has tens of millions of possible low energy conformations, but only one or a few conformations correspond to the active, native protein. Structural biology is the study of protein and nucleic acid structure and function. Molecular mechanics plays a central role in structural biology and biochemistry in predicting the proper folding of proteins and refining experimental structures from X-ray crystallography and NMR.

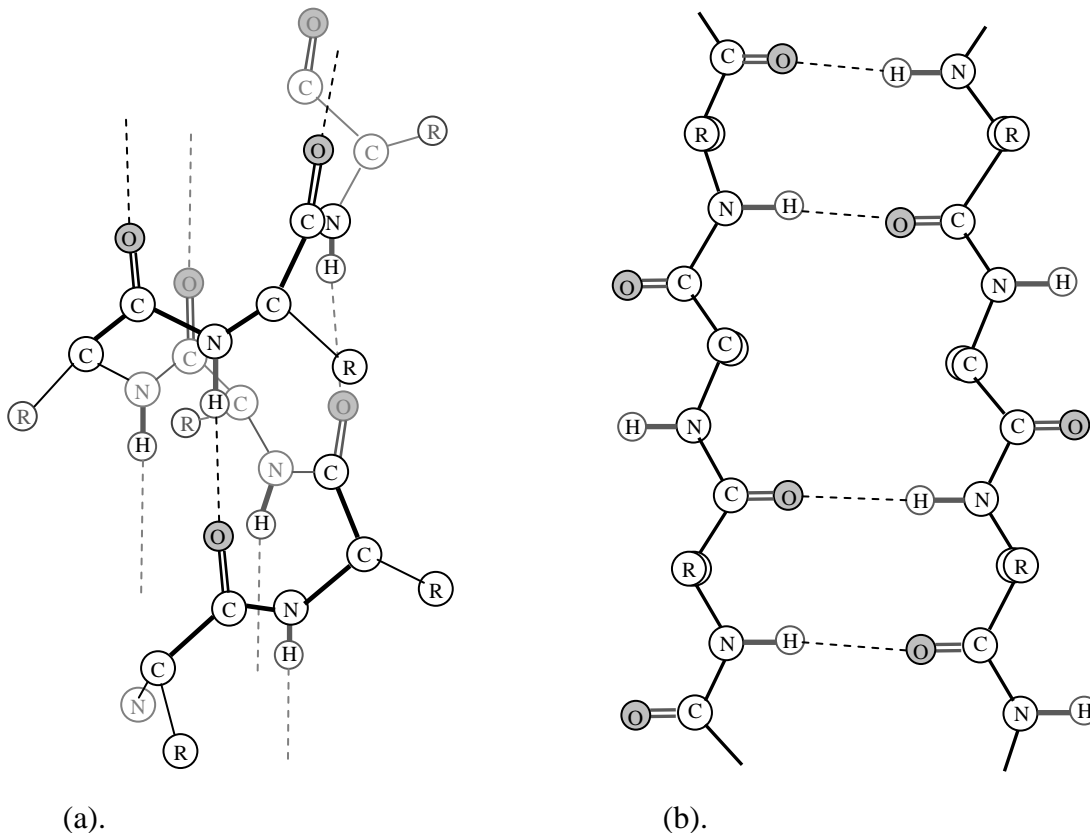
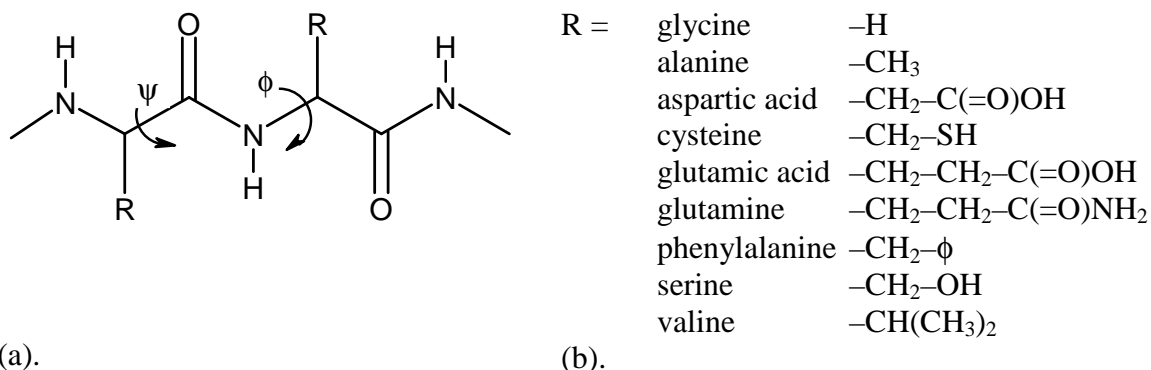


Figure 8.8.9: (a). In the alpha-helix secondary structure, hydrogen bonds between amino acid (i) and (i+4) stabilize the structure. (b). In the beta-pleated sheet secondary structure, inter-strand hydrogen bonds stabilize the sheet. See Sec. 10.3 for another view of the alpha-helix.

The secondary structure of a protein is determined by the dihedral angles in the backbone of the protein, Figure 8.8.10. The C-alpha carbon is the backbone carbon with the amino acid side

chain. ψ is defined by the N-C(α)-C-N dihedral and ϕ is defined between the carbonyl carbons in the dihedral C-N-C(α)-C.



(a).

(b).

Figure 8.8.10: (a). The backbone dihedral angles in a peptide. The peptide is shown in the all-*trans* conformation, $\psi = 180^\circ$ and $\phi = 180^\circ$. (b). Several side-chains for common amino acids. There are 20 commonly occurring amino acids in proteins.

The average values in the alpha helix are $\psi = -47^\circ$ and $\phi = -57^\circ$ and for beta-pleated sheet structures the backbone angles are near $\psi = 135^\circ$ and $\phi = -140^\circ$.

Is the alpha-helix stable without the hydrogen bonding network? The conformational energy of the alanylalanine dipetide as a function of the backbone dihedral angles is shown in Figure 8.8.11. This plot is called a Ramachandran plot.¹⁸

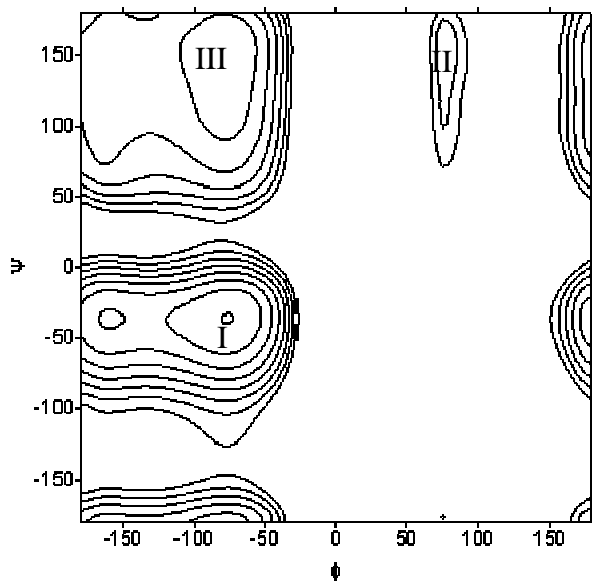


Figure 8.8.11: Ramachandran plot for alanylalanine dipetide. Region I is near the typical angles for an alpha-helix, region II is an alternate helical structure, region III is near the typical dihedrals for a beta-pleated sheet secondary structure.

The plot was constructed using molecular mechanics steric energies for the complete ranges of the backbone dihedral angles. The region labeled I corresponds to low energy conformations near the expected angles for an alpha-helix. Therefore, the hydrogen bond network is not necessary to stabilize the alpha-helix. The region labeled III is near the expected angles for the beta-pleated sheet. So the beta-pleated sheet secondary structure conformation is also intrinsically stable without the aid the hydrogen bond network. These observations have important implications for the early stages of protein folding, before the hydrogen bond network is formed. The region labeled II corresponds to an alternate helical structure.

The structure of proteins is far from static. Molecules are in constant motion and motions play a critical role in chemical reactivity. The molecular mechanics based steric energy and the bond increments give an estimate of $U(0)$ and $H(0)$, which are at absolute zero K. The temperature dependent terms for the thermally excited motional degrees of freedom in Eq. 8.8.1° are added to bring the molecules to room temperature.

8.9 The Equipartition Theorem Predicts the Internal Energy and Heat Capacity of Gases

The **Equipartition Theorem** was the historical basis for the first attempts to theoretically predict the thermodynamic properties of substances. The basis for the Equipartition theorem is the observation that the internal energy of monatomic gases is $^{3/2} nRT$, except at temperatures near absolute zero. Near room temperature, monatomic gases have only translational energy, and the translational kinetic energy has three components, in the x, y, and z directions. The three components of the kinetic energy of translation are:

$$\epsilon_{\text{trans},x} = \frac{1}{2} m v_x^2 = p_x^2/2m \quad \epsilon_{\text{trans},y} = \frac{1}{2} m v_y^2 = p_y^2/2m \quad \epsilon_{\text{trans},z} = \frac{1}{2} m v_z^2 = p_z^2/2m \quad 8.9.1$$

where v is the velocity and p is the momentum in the x, y and z directions. The mass of the molecule is m . The total translational kinetic energy of the gas is $\epsilon_{\text{trans}} = \epsilon_{\text{trans},x} + \epsilon_{\text{trans},y} + \epsilon_{\text{trans},z}$. Each quadratic term in the total energy of a substance is called a **degree of freedom**. Monatomic gases have three translational degrees of freedom. Comparison with the experimental internal energy of $^{3/2} nRT$ suggests that each degree of freedom contributes $\frac{1}{2} nRT$ to the internal energy of the gas. In addition, from Eq. 7.8.7, the heat capacity of a monatomic gas is $C_v = (\partial U/\partial T)_v = ^{3/2} nR$. The Equipartition theorem then predicts that each degree of freedom contributes $\frac{1}{2} RT$ to the molar internal energy and $\frac{1}{2} R$ to the molar heat capacity, Table 8.9.1.

Table 8.9.1: Molar Heat Capacity Predictions from Equipartition, C_v ($\text{J K}^{-1} \text{ mol}^{-1}$).

Species	translation	rotation	vibration	total	total – vib	experiment	experiment
Ar	$^{3/2} R$			$^{3/2} R$	$^{3/2} R$	12.5 J K^{-1}	$^{3/2} R$
N_2	$^{3/2} R$	$^{2/2} R$	$^{2/2} R$	$^{7/2} R$	$^{5/2} R$	20.8	$^{5/2} R$
Cl_2	$^{3/2} R$	$^{2/2} R$	$^{2/2} R$	$^{7/2} R$	$^{5/2} R$	25.6	$^{6/2} R$
CO_2	$^{3/2} R$	$^{2/2} R$	$4(^{2/2} R)$	$^{13/2} R$	$^{5/2} R$	28.5	$^{6.9/2} R$
O_3	$^{3/2} R$	$^{3/2} R$	$3(^{2/2} R)$	$^{12/2} R$	$^{6/2} R$	30.9	$^{7.4/2} R$
H_2O	$^{3/2} R$	$^{3/2} R$	$3(^{2/2} R)$	$^{12/2} R$	$^{6/2} R$	25.3	$^{6.1/2} R$

Polyatomic molecules have energy in translation, rotation, and vibration. Consider rotation first. Linear molecules have two degrees of freedom in rotation, because there are two non-zero

moments of inertia. The rotational energy is quadratic in the angular velocity about each axis; for rotation about the x-axis:

$$\epsilon_{\text{rot},x} = J_x^2/2I_x = \frac{1}{2} I_x \omega_x^2 \quad \epsilon_{\text{rot},y} = J_y^2/2I_y = \frac{1}{2} I_y \omega_y^2 \quad (\text{linear}) \quad 8.9.2$$

where $J_x = I_x \omega_x$ is the angular momentum around the x-axis, ω_x is the angular velocity about the x-axis, and I_x is the moment of inertia about the x-axis. Non-linear molecules have three degrees of freedom in rotation, because there are three non-zero moments of inertia. For a linear molecule, the third moment of inertia is zero because rotation about the internuclear axis does not move the nuclei, Figure 8.9.1.

Each vibration corresponds to two degrees of freedom, one for the kinetic energy and one for the potential energy. The potential energy of vibration is approximated using Hooke's Law, Eq. 8.8.10. Hooke's Law potentials are also called **quadratic potentials** because of the dependence on r^2 . The kinetic and potential energy of vibration are each a quadratic degree of freedom. The contribution of each vibration to the internal energy is therefore $2/2 RT$.

For a diatomic molecule, with two rotational axes and one vibration, the predicted temperature dependent contribution to the internal energy is the sum for translation, rotation, and vibration:

$$U - U(0) = \underbrace{3/2 RT}_{\text{translation}} + \underbrace{2/2 RT}_{\text{rotation}} + \underbrace{2/2 RT}_{\text{vibration}} = 7/2 RT \quad (\text{diatomic, equipartition}) \quad 8.9.3$$

The translational, rotational, and vibrational contributions to the internal energy are the energy of motion above the energy at 0 K. The corresponding heat capacity is C_v (diatomic) = $7/2 R$.

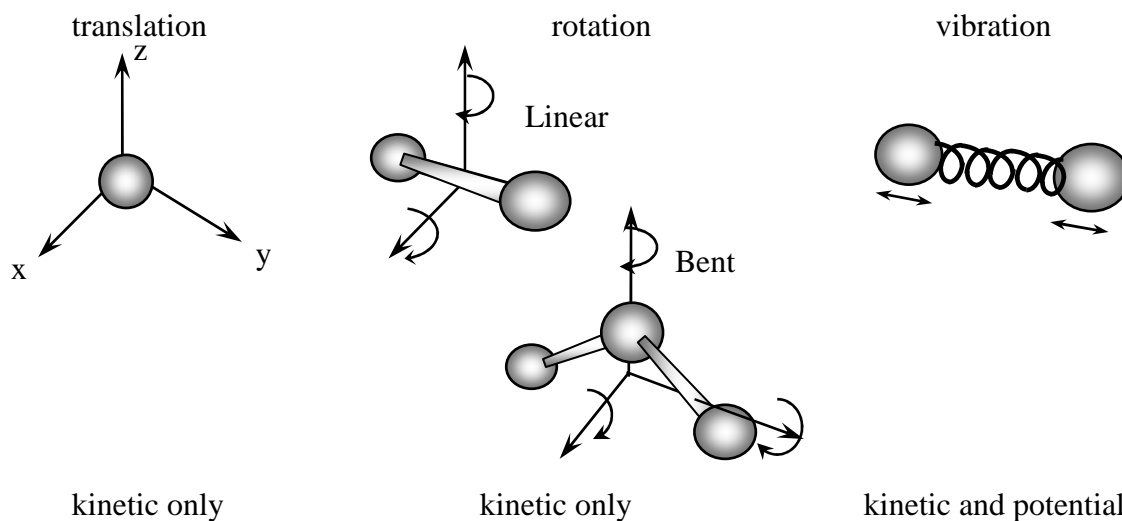


Figure 8.9.1: Each quadratic term in the total energy of a molecule is called a degree of freedom. Each degree of freedom contributes $1/2 RT$ to the total molar internal energy.

For molecules larger than diatomics, we need to find the total number of vibrations. To calculate the energy of a molecule with N atoms we must specify $3N$ coordinates; we need to find the x, y, and z position of each atom in the molecule. Rather than specifying the x, y, and z coordinates of each atom, an equivalent approach is to specify the x, y, z coordinates of the center of mass of the molecule, the rotational angles around the x, y, and z axis, and the progress of each vibration. The translational energy of the molecule is determined by the motion of the

center of mass and therefore requires three coordinates. The rotational energy requires two coordinates, as angles, for a linear molecule and three coordinates for a non-linear molecule. The number of coordinates remaining gives the number of vibrations. Each vibration of a molecule is called a **normal mode**. The number of normal modes, n , for a linear molecule is given as:

$$n = \underset{\text{total}}{3N} - \underset{\text{translation}}{3} - \underset{\text{rotation}}{2} = \underset{\text{vibration}}{3N - 5} \quad (\text{linear}) \quad 8.9.4$$

and for a non-linear molecule as:

$$n = \underset{\text{total}}{3N} - \underset{\text{translation}}{3} - \underset{\text{rotation}}{3} = \underset{\text{vibration}}{3N - 6} \quad (\text{non-linear}) \quad 8.9.5$$

Normal modes will be discussed in more detail in Section 8.10. In particular, each normal mode acts as an independent harmonic oscillator. Carbon dioxide is a linear molecular and has $3(3) - 5 = 4$ normal modes. Ozone and water are bent triatomics and each has $3(3) - 6 = 3$ normal modes, Table 8.9.1. The normal modes for a bent triatomic are shown in Figure 8.9.2.

The experimental values for the molar heat capacities of several substances are given in Table 8.9.1. For ease of comparison the experimental value is also listed in multiples of $\frac{1}{2} R$ in the last column. Note that the predictions based on the equipartition theorem, as shown in the column labeled “total,” are often too large. If the prediction is based on only translation and rotation, as shown in the column labeled “total-vib,” better agreement with the experimental values is found. The prediction based only on translation and rotation provides a lower bound and the prediction with vibration gives the limit at high temperature. The comparison shows that while translation and rotation obey the Equipartition predictions, the contributions from vibrations are less and often much less than expected. Why don’t vibrations contribute the full contribution expected from equipartition?

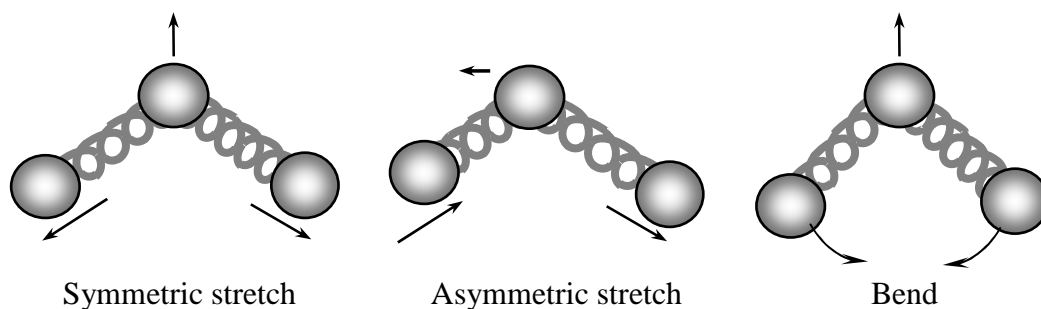


Figure 8.9.2: Normal modes of vibration for a bent triatomic; $n = 3N - 6 = 3$.

8.10 The Boltzmann Distribution-The Energy Difference Between Vibrational States is Usually Large Compared to the Available Thermal Kinetic Energy

The energy states for translation, rotation, and vibration are not continuous. The energy states are **quantized**. Molecules may not have energies between the allowed energy states. An analogy is the steps on a ladder. You can stand on each successive step, but you can’t stand between the steps. For example, for vibration the allowed energy states are equally spaced, in the harmonic approximation, Figure 8.10.1. How much do vibrations contribute to the internal energy of molecules? Molecules gain energy through collisions. The energy available through collisions

increases with temperature and is given roughly by RT . The term RT is often called the **available thermal kinetic energy**, which at room temperature is:

$$RT = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} (298.2 \text{ K}) = 2.48 \text{ kJ mol}^{-1} \quad (T = 298.2 \text{ K}) \quad 8.10.1$$

It is often convenient to work with the energy in **wavenumbers**, cm^{-1} , since vibrational transitions are easily expressed in these units. The horizontal axis of IR spectrophotometers for the mid-infrared is $4000 \text{ cm}^{-1} - 400 \text{ cm}^{-1}$. The wavenumber of a transition is given as $\tilde{\nu} = 1/\lambda$ and the energy of the transition is $\Delta E = hc/\lambda = hc\tilde{\nu}$ per molecule, where h is Planck's constant. On a per mole basis the energy is:

$$\Delta E = N_A hc\tilde{\nu} = (0.011963 \text{ kJ mol}^{-1} \text{ cm}) \tilde{\nu} \quad 8.10.2$$

where N_A is Avogadro's number. Then RT in cm^{-1} is:

$$RT = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (298.2 \text{ K})}{N_A hc} = 207.2 \text{ cm}^{-1} \quad (T = 298.2 \text{ K}) \quad 8.10.3$$

As the available thermal kinetic energy approaches the difference in energy between the states, some molecules gain sufficient energy to be excited to the next energy state. As the temperature increases, the available thermal kinetic energy increases, and the populations of higher energy states increase.

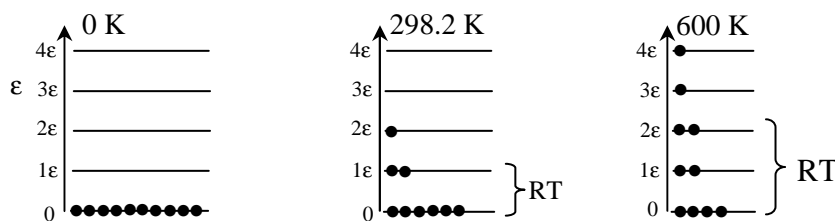


Figure 8.10.1: Boltzmann occupations for harmonic oscillator energy states at various temperatures. The energy spacing is 200 cm^{-1} or 2.39 kJ mol^{-1} . $RT = 207.2 \text{ cm}^{-1}$ at 298.2 K .

The Boltzmann Distribution Determines the Distribution of Energy: The probability of a molecule occupying energy state i is given by the number of molecules in energy state i , n_i , divided by the total number of molecules, N :

$$p_i = \frac{n_i}{N} \quad 8.10.4$$

The probability of occupying energy state i is determined by the **Boltzmann distribution**:

$$p_i = \frac{n_i}{N} = \frac{e^{-\varepsilon_i/kT}}{q} = \frac{e^{-\varepsilon_i/RT}}{q} \quad (kT \text{ per molecule, } RT \text{ per mole}) \quad 8.10.5$$

where ε_i is the energy of state i , k is **Boltzmann's constant**, and T is the absolute temperature. Boltzmann's constant is just the gas constant on a per molecule basis instead of per mole, $k = R/N_A = 1.38066 \times 10^{-23} \text{ J K}^{-1}$. If the energy is given in J, then kT is used. If the energy is given in J mol^{-1} then RT is used to match the units. The q in the denominator is called the **partition function**. The partition function is the normalization constant, which ensures that the

probabilities sum over all the possible energy states to give one, $\sum p_i = 1$. Summing Eq. 8.10.5 over all possible energy states gives:

$$\sum_i p_i = \frac{\sum_i e^{-\epsilon_i/kT}}{q} = 1 \quad 8.10.6$$

Solving for q gives the definition of the partition function:

$$q \equiv \sum_i e^{-\epsilon_i/kT} \quad 8.10.7$$

The $e^{-\epsilon_i/kT}$ or $e^{-\epsilon_i/RT}$ terms are called the Boltzmann weighting factors. This general form for the temperature dependence is outlined in *General Pattern* §4, Sec. 3.5. The probability of a molecule occupying a given energy state is directly proportional to the Boltzmann weighting factor. The partition function is the sum of the Boltzmann weighting factors over all energy states. Low energy states have a higher occupation than high energy states. The Boltzmann distribution for the harmonic oscillator at several different temperatures using Eq. 8.10.5 and 8.10.7 is shown in Figure 8.10.1 for an energy spacing of 200 cm^{-1} . The ratio of the number of molecules in two energy states is determined by the ratio of the Boltzmann weighting factors for the two states; dividing Eq. 8.10.4 for state j by Eq. 8.10.4 for state i gives:

$$\frac{n_j}{n_i} = \frac{e^{-\epsilon_j/kT}}{e^{-\epsilon_i/kT}} = e^{\frac{-\Delta\epsilon}{kT}} \quad 8.10.8$$

where n_j is the number of molecules in state j , n_i is the number of molecules in state i , and the energy difference is $\Delta\epsilon = \epsilon_j - \epsilon_i$. In effect, the argument of the exponential compares the energy difference to RT . If $\Delta\epsilon \gg RT$ all the molecules will be in the lower energy state. The population of the two energy states is equalized if $RT \gg \Delta\epsilon$. Note that there may be more than one state with a given energy; Eqs. 8.10.4-8.10.8 apply to each individual state. We will derive the Boltzmann distribution in Chapter 12. However, the principles behind the Boltzmann distribution are useful in understanding many phenomena, so we will use the result without proof for now.

The Boltzmann distribution can also be applied to the case where the temperature is held constant and systems with different energy spacing are compared. The Boltzmann distribution at 298.2 K for the vibrational energy states of a harmonic oscillator are shown in Figure 8.10.2 for several values of the fundamental vibration frequency.

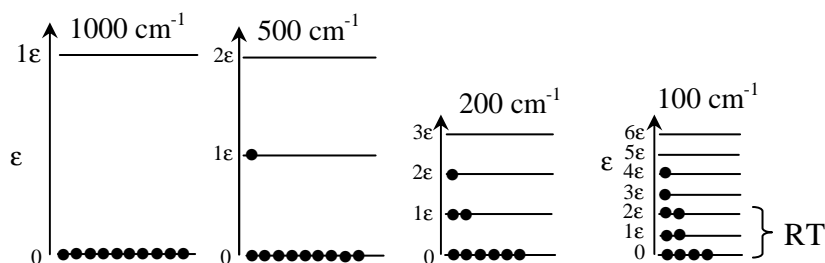


Figure 8.10.2: Boltzmann occupations for harmonic oscillator energy states at 298.2 K. $RT = 207.2 \text{ cm}^{-1}$ at 298.2 K.

If the energy spacing is much bigger than RT all molecules remain in the lowest energy state. If the energy state spacing is small compared to RT , many molecules occupy excited energy states.

The Boltzmann distribution provides a useful interpretation for the contribution of a degree of freedom to the internal energy and heat capacity. Thermal excitation of a molecule from one state to the next is “all or nothing.” A molecule can’t jump half-way. If the available thermal kinetic energy is much less than the energy state spacing, a small increase in temperature doesn’t provide sufficient energy for the molecule to change energy states and $(\partial U/\partial T)_v = 0$. However, if the energy states are very close together a small change in temperature is readily absorbed as molecules are excited to higher energy states and then $(\partial U/\partial T)_v$ is large. If $\Delta\epsilon \gg RT$, the degree of freedom contributes little to the internal energy and heat capacity. If $\Delta\epsilon \ll RT$, even a small change in available thermal energy resulting from a small temperature increase results in an increase in internal energy, which is the classical result $(\partial U/\partial T)_v = \frac{1}{2} R$ per degree of freedom.

Only Low Energy Vibrations Contribute to the Heat Capacity: The energy state spacing for translation and rotation is much smaller than RT at room temperature. Under these circumstances, translation and rotation behave essentially as if they had continuous energy states and then classical physics is applicable. The essentially classical behavior of degrees of freedom with small energy state spacing is the reason that the Equipartition theorem holds for translation and rotation. However, the typically large energy spacing for vibration results in only a partial contribution to the internal energy of the system. We will show in Chapt. 32 that the contribution of a vibration to the enthalpy is given by:¹⁹

$$H_{\text{vib}} - H_{\text{vib}}(0) = U_{\text{vib}} - U_{\text{vib}}(0) = \epsilon_{\text{vib}} = \frac{N_A h\nu e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} \quad 8.10.9$$

where ν is the frequency of the vibration. Eq. 8.10.9 is summed for each vibration in the molecule. This contribution to the enthalpy is plotted as a function of vibration frequency in Figure 8.10.3.

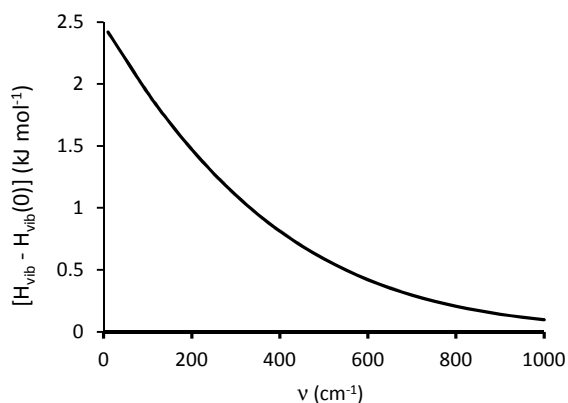


Figure 8.10.3. Contribution of a vibration to the enthalpy of formation of a molecule, above $U(0)$, at 298.2 K.

Vibrations with energy state spacing greater than 500 cm^{-1} are too energetic compared to RT to make a significant contribution to the internal energy, enthalpy, and heat capacity. One effective

way to predict the vibrational contribution to the heat capacity of a substance is to count only the normal modes with vibrational energies less than 500 cm^{-1} .

Internal rotations, that is torsional motions around freely rotating bonds, are the most common low frequency vibrations in molecules. The contribution of internal rotations to the enthalpy of formation is called the **torsional increment** and is estimated to be $0.36\text{ kcal mol}^{-1}$ or 1.51 kJ mol^{-1} for each internal rotation, taking into account anharmonicity.²⁰ Counting the number of internal rotations then gives a quick, approximate estimate of the contribution of vibrations to the internal energy and enthalpy of formation. However by convention, the internal rotation of the methyl group is included in the bond increment calculation for the methyl group, so methyl rotations are not included in the count. For example, butane, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$, has one additional internal rotation, other than the methyl group rotations; so the torsional increment for butane is 1.51 kJ mol^{-1} .

In summary, the enthalpy of formation for a non-linear molecule, using Eqs. 8.8.2° and 8.8.3 and the Equipartition contributions for translation and rotation, is then:

$$\Delta_f H^\circ = \epsilon_{\text{bond}} + \epsilon_{\text{steric}} + \underbrace{RT}_{\Delta(\text{PV}) \text{ translation}} + \underbrace{\frac{3}{2}RT}_{\text{rotation}} + \underbrace{\frac{3}{2}RT}_{\tilde{\nu} < 500\text{ cm}^{-1}} + \epsilon_{\text{vib}} \quad (\text{non-linear}) \quad 8.10.10$$

This formula also assumes that there is only one low energy conformation of the molecule. If there are several low energy conformations then each must be added, weighted by the Boltzmann probability relative to the lowest energy conformation. This last equation is easy to apply if the frequencies of the normal modes are known. In the next section we develop the technique of normal mode analysis to predict the frequencies for the normal modes of vibration.

Example 8.10.2:

Use MM2 or MM3 to estimate the enthalpy of formation of acetaldehyde.

Answer: The bond energy calculation is in Eq. 8.8.6. The MM3 steric energy is calculated to be:

FINAL STERIC ENERGY IS	0.4521	KCAL/MOL.
COMPRESSION	0.0052	
BENDING	0.0821	
BEND-BEND	-0.0105	
STRETCH-BEND	0.0046	
VANDERWAALS		
1,4 ENERGY	0.5805	
TORSIONAL	-0.2099	
TORSION-STRETCH	0.0000	
DIPOLE-DIPOLE	0.0000	
CHARGE-DIPOLE	0.0000	
CHARGE-CHARGE	0.0000	

No torsional increments are required, since the methyl torsion is included in the bond increment calculation. The methyl torsion is the only low frequency vibration below 500 cm^{-1} . Note that MM2/MM3 do not automatically add the torsional increments; torsional increments must be added to the final printed results. The final enthalpy of formation is $-40.04\text{ kcal mol}^{-1}$ or $-167.53\text{ kJ mol}^{-1}$, which is a significant improvement over the bond energy calculation in Eq. 8.8.6. The experimental value is $-166.19\text{ kJ mol}^{-1}$.

8.11 Normal Mode Analysis: The Harmonic Approximation

The vibrations of a molecule are given by its normal modes. Each absorption in a vibrational spectrum corresponds to a normal mode. The normal modes for a bent triatomic are shown in Figure 8.9.2. The four normal modes of carbon dioxide, Figure 8.11.1, are the symmetric stretch, the asymmetric stretch and two bending modes.

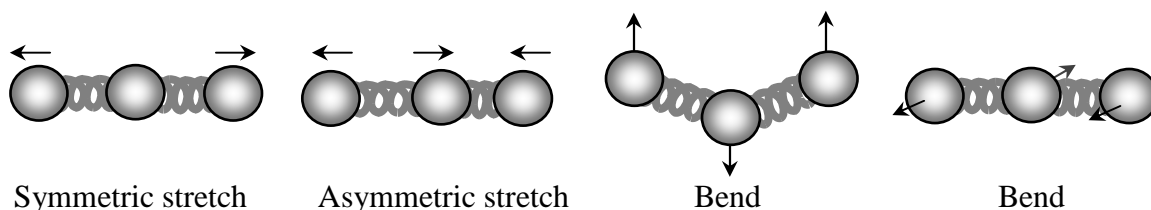


Figure 8.11.1. Normal Modes for a linear triatomic molecule. In the last bending vibration, the motion of the atoms is in and out of the plane of the paper.

The two bending modes have the same energy and differ only in the direction of the bending motion. Modes that have the same energy are called **degenerate**. In the classical treatment of molecular vibrations, each normal mode is treated as a simple harmonic oscillator.

The characteristics of normal modes are:

1. Each normal mode acts like a simple harmonic oscillator.
2. A normal mode is a concerted motion of many atoms.
3. The center of mass doesn't move.
4. All atoms pass through their equilibrium positions at the same time.
5. Normal modes are independent in the harmonic approximation.

The concerted motion of many of the atoms is a characteristic of normal modes; however, symmetry may require that a few atoms remain stationary for some normal modes. In the asymmetric stretch and the two bending vibrations for CO_2 , all the atoms move. However, in the symmetric stretch, to keep the center of mass constant, the center atom is stationary. The independence of normal modes means that normal modes don't exchange energy. For example, if the symmetric stretch is excited, the energy stays in the symmetric stretch.

The background spectrum of air, Figure 8.11.2, shows the asymmetric and symmetric stretches and the bending vibration for water, and the asymmetric stretch and bending vibrations for CO_2 . These absorptions are responsible for the vast majority of the greenhouse effect. The symmetric stretch for CO_2 doesn't appear in the infrared; a Raman spectrum is needed to measure the frequency of the symmetric stretch (see Chapt. 27).

The normal modes are calculated using Newton's equations of motion.²¹⁻²⁴ Molecular mechanics and molecular orbital programs use the same normal mode calculation method.

The Harmonic Oscillator—Oscillatory Motion at the Fundamental Vibration Frequency:

Consider a mass m , supported on a spring with force constant k . Hooke's Law for the restoring force for an extension, $x = r - r_0$, is $F = -kx$. In other words, if the spring is stretched a distance $x > 0$, the restoring force is negative, which acts to pull the mass back to its equilibrium position. The potential energy for Hooke's Law is obtained by integrating:

$$F = -\frac{dV}{dx} = -kx \quad 8.11.1$$

to give $V = \frac{1}{2} kx^2 = \frac{1}{2} k(r - r_0)^2$, Eq. 8.8.11. In molecular mechanics and molecular orbital calculations, the force constant is not known directly. However, the force constant can be calculated from the second derivative of the potential energy:

$$k = \frac{d^2 V}{dx^2} \quad 8.11.2$$

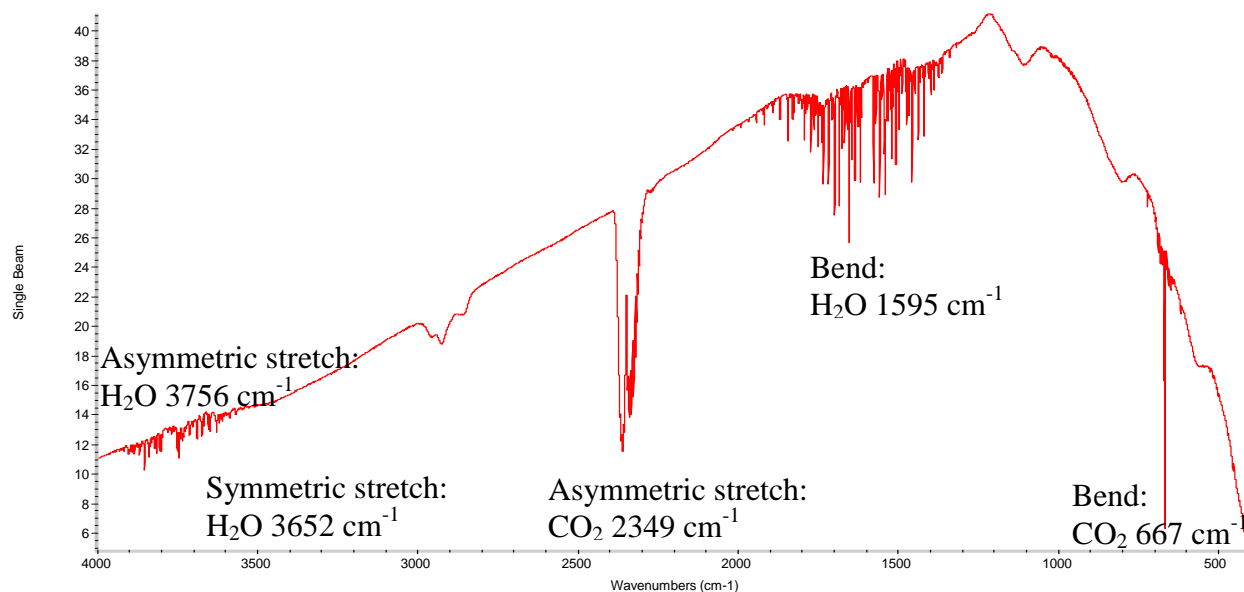


Figure 8.11.2. The infrared spectrum of air. This spectrum is the background scan from an FT-IR spectrometer.

The Hooke's Law force is substituted into Newton's Law:

$$F = ma \quad \text{or} \quad m \frac{d^2x}{dt^2} = -kx \quad 8.11.3$$

and solved to obtain the extension as a function of time (Addendum Sec. 8.12):

$$x(t) = A \sin(2\pi\nu_0 t) \quad 8.11.4$$

where ν_0 is the fundamental vibration frequency and A is the amplitude of the vibration. Taking the second derivative of the extension gives:

$$\frac{d^2x}{dt^2} = -4\pi^2\nu_0^2 x \quad 8.11.5$$

Substituting Eq. 8.11.5 back into Eq 8.11.3 gives:

$$-4\pi^2\nu_0^2 m x = -kx \quad 8.11.6$$

which is the basis for the classical calculation of the normal modes of a molecule.

Normal Mode Analysis Determines the Frequencies of Molecular Vibrations: For molecules the x, y, z coordinates of each atom must be specified. The coordinates are:

Atom 1: $X_1, Y_1, Z_1,$ Atom 2: $X_2, Y_2, Z_2,$ for each atom.....

The extensions are the differences in the positions and the equilibrium positions for that atom:

$$\text{Atom } i: \quad x_i = X_i - X_{i,\text{eq}} \quad y_i = Y_i - Y_{i,\text{eq}} \quad z_i = Z_i - Z_{i,\text{eq}} \quad 8.11.7$$

Where $X_{i,\text{eq}}, Y_{i,\text{eq}},$ and $Z_{i,\text{eq}}$ are the equilibrium (energy minimized) positions for atom i. Molecular mechanics or molecular orbital calculations are used to find the potential energy of the molecule as a function of the position of each atom, $V(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3, \dots, x_N, y_N, z_N).$ The second derivative of the potential energy can then be used to calculate the force constants using Eq. 8.11.2. However, there are now $3N \times 3N$ possible second derivatives and their corresponding force constants. For example,

$$\frac{\partial^2 V}{\partial x_1^2} = k_{xx}^{11} \quad 8.11.8$$

is the change of the force on atom 1 in the x-direction when you move atom 1 in the x-direction. Similarly,

$$\frac{\partial^2 V}{\partial x_1 \partial y_2} = k_{xy}^{12} \quad 8.11.9$$

is the change of the force on atom 1 in the x-direction when you move atom 2 in the y-direction. The various types of force constants are shown in Figure 8.11.3.

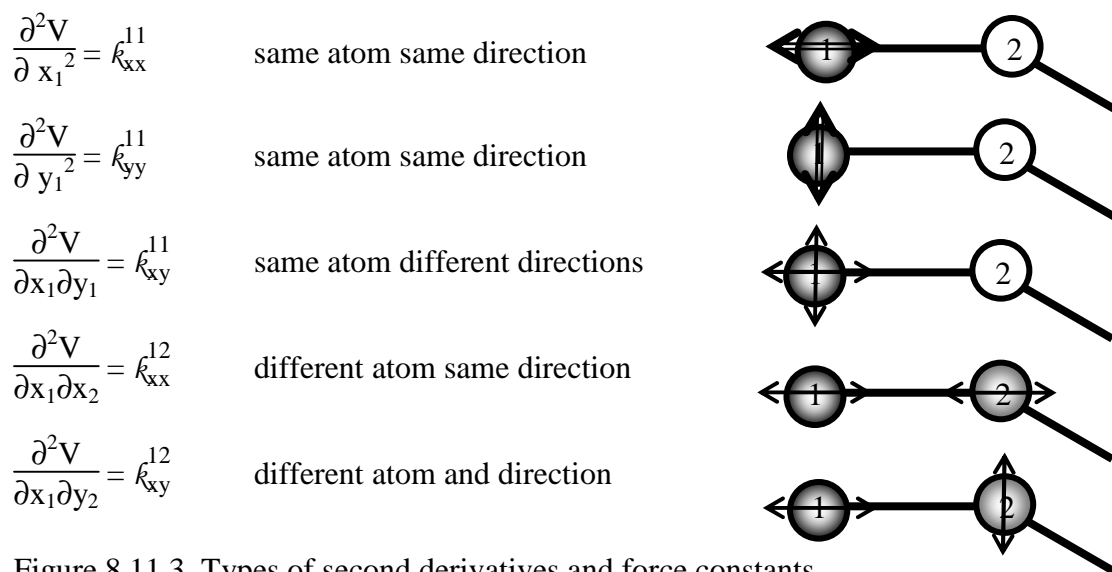


Figure 8.11.3. Types of second derivatives and force constants

These force constants are not the force constants for individual bonds, they are force constants for the motion of a single atom subject to all its neighbors, whether directly bonded or not. The

complete list of these force constants is called the Hessian, which is a $3N \times 3N$ matrix. The Hessian also plays a central role in energy minimization techniques. Eq. 8.11.6 is then applied for each force constant.^{21,23}

$$\begin{aligned}
 -4\pi^2\nu_0^2 m_1x_1 &= -k_{xx}^{11} x_1 - k_{xy}^{11} y_1 - k_{xz}^{11} z_1 - k_{xx}^{12} x_2 - k_{xy}^{12} y_2 - \dots - k_{xz}^{1N} z_N & 8.11.10 \\
 -4\pi^2\nu_0^2 m_1y_1 &= -k_{yx}^{11} x_1 - k_{yy}^{11} y_1 - k_{yz}^{11} z_1 - k_{yx}^{12} x_2 - k_{yy}^{12} y_2 - \dots - k_{yz}^{1N} z_N \\
 &\vdots \\
 -4\pi^2\nu_0^2 m_2x_2 &= -k_{xx}^{21} x_1 - k_{xy}^{21} y_1 - k_{xz}^{21} z_1 - k_{xx}^{22} x_2 - k_{xy}^{22} y_2 - \dots - k_{xz}^{2N} z_N \\
 &\vdots \\
 -4\pi^2\nu_0^2 m_Nz_N &= -k_{zx}^{N1} x_1 - k_{zy}^{N1} y_1 - k_{zz}^{N1} z_1 - k_{zx}^{N2} x_2 - k_{zy}^{N2} y_2 - \dots - k_{zz}^{NN} z_N
 \end{aligned}$$

In words, the right-hand sides of the above equations simply state that the total force on atom i is the sum of the forces of all the atoms on atom i , keeping track of the x , y , and z directions for each atom. There are a total of $3N \times 3N$ terms on the right. All these terms are confusing. A simple example will help at this point.

Consider a symmetrical linear triatomic molecule that can only vibrate along the x -axis, Figure 8.11.4. CO_2 is a good environmentally significant example.

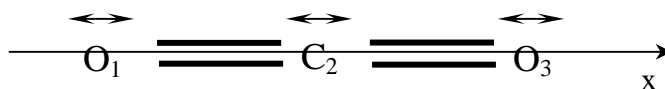


Figure 8.11.4: A symmetrical triatomic molecule with vibrations limited along the internuclear axis.

Because we have limited the vibrations to the x -axis, which is the internuclear axis, this model will provide the symmetric and asymmetric stretching modes, only. Eqs. 8.11.10 then reduce to:

$$-4\pi^2\nu_0^2 m_1x_1 = -k_{xx}^{11} x_1 - k_{xx}^{12} x_2 - k_{xx}^{13} x_3 \quad 8.11.11$$

$$-4\pi^2\nu_0^2 m_2x_2 = -k_{xx}^{21} x_1 - k_{xx}^{22} x_2 - k_{xx}^{23} x_3 \quad 8.11.12$$

$$-4\pi^2\nu_0^2 m_3x_3 = -k_{xx}^{31} x_1 - k_{xx}^{32} x_2 - k_{xx}^{33} x_3 \quad 8.11.13$$

since we only need to keep the x -terms. Several numerical techniques are available to solve linear sets of simultaneous equations. Conventionally, however, the problem is simplified by converting to mass-weighted coordinates:

$$\tilde{x}_1 = \sqrt{m_1} x_1 \quad \tilde{x}_2 = \sqrt{m_2} x_2 \quad , \text{ etc.} \quad 8.11.14$$

and mass-weighted force constants:

$$\tilde{k}_{xx}^{12} = \frac{k_{xx}^{12}}{\sqrt{m_1}\sqrt{m_2}} \quad 8.11.15$$

In the new mass weighted coordinates, Eqs. 8.11.11-8.11.13 become:

$$-4\pi^2\nu_o^2 \tilde{x}_1 = -\tilde{k}_{xx}^{11} \tilde{x}_1 - \tilde{k}_{xx}^{12} \tilde{x}_2 - \tilde{k}_{xx}^{13} \tilde{x}_3 \quad 8.11.16$$

$$-4\pi^2\nu_o^2 \tilde{x}_2 = -\tilde{k}_{xx}^{21} \tilde{x}_1 - \tilde{k}_{xx}^{22} \tilde{x}_2 - \tilde{k}_{xx}^{23} \tilde{x}_3 \quad 8.11.17$$

$$-4\pi^2\nu_o^2 \tilde{x}_3 = -\tilde{k}_{xx}^{31} \tilde{x}_1 - \tilde{k}_{xx}^{32} \tilde{x}_2 - \tilde{k}_{xx}^{33} \tilde{x}_3 \quad 8.11.18$$

For example, we can show that Eq 8.11.16 is equivalent to Eq 8.11.11 by substituting Eqs. 8.11.14 and 8.11.15 into Eq 8.11.16:

$$-4\pi^2\nu_o^2 \sqrt{m_1} x_1 = -\frac{\tilde{k}_{xx}^{11}}{\sqrt{m_1}\sqrt{m_1}} \sqrt{m_1} x_1 - \frac{\tilde{k}_{xx}^{12}}{\sqrt{m_1}\sqrt{m_2}} \sqrt{m_2} x_2 - \frac{\tilde{k}_{xx}^{13}}{\sqrt{m_1}\sqrt{m_3}} \sqrt{m_3} x_3 \quad 8.11.19$$

Multiplying both sides by $\sqrt{m_1}$ and canceling mass terms gives Eq 8.11.11.

Eqs. 8.11.16-8.11.18 are most easily written in the equivalent matrix form:

$$-\begin{pmatrix} \frac{\tilde{k}_{xx}^{11}}{\sqrt{m_1}\sqrt{m_1}} & \frac{\tilde{k}_{xx}^{12}}{\sqrt{m_1}\sqrt{m_2}} & \frac{\tilde{k}_{xx}^{13}}{\sqrt{m_1}\sqrt{m_3}} \\ \frac{\tilde{k}_{xx}^{21}}{\sqrt{m_2}\sqrt{m_1}} & \frac{\tilde{k}_{xx}^{22}}{\sqrt{m_2}\sqrt{m_2}} & \frac{\tilde{k}_{xx}^{23}}{\sqrt{m_2}\sqrt{m_3}} \\ \frac{\tilde{k}_{xx}^{31}}{\sqrt{m_3}\sqrt{m_1}} & \frac{\tilde{k}_{xx}^{32}}{\sqrt{m_3}\sqrt{m_2}} & \frac{\tilde{k}_{xx}^{33}}{\sqrt{m_3}\sqrt{m_3}} \end{pmatrix} \begin{pmatrix} \tilde{x}_1 \\ \tilde{x}_2 \\ \tilde{x}_3 \end{pmatrix} = -4\pi^2\nu_o^2 \begin{pmatrix} \tilde{x}_1 \\ \tilde{x}_2 \\ \tilde{x}_3 \end{pmatrix} \quad 8.11.20$$

The mass-weighted force constants give a symmetric matrix; the corresponding off-diagonal elements are equal. Eq. 8.11.20 is an eigenvalue-eigenvector equation, see *General Pattern* § 6, Sec. 6.3. The eigenvalues are the negative of the squared normal mode frequencies. The eigenvectors are the mass-weighted normal coordinate displacements (Addendum Sec. 8.12).

Example 8.11.1:

Find the normal mode frequencies for the symmetric and asymmetric stretch for CO₂ using approximate force constants and Eq. 8.11.20. The experimental values are 1340 cm⁻¹ for the symmetric stretch and 2349 cm⁻¹ for the asymmetric stretch, Fig. 8.11.2.

Answer: First, consider the units for the fundamental vibration frequency. The fundamental vibration frequency for a harmonic oscillator is:

$$\nu_o = \frac{1}{2\pi} \sqrt{\frac{\tilde{k}}{m}} \quad \text{or} \quad 4\pi^2\nu_o^2 = \frac{\tilde{k}}{m} \quad 8.11.21$$

with \tilde{k} in N m⁻¹ and m in kg molecule⁻¹. Normally, vibrational spectra are plotted versus wavenumber, instead of frequency. To convert to wavenumbers remember that $\nu\lambda = c$:

$$\tilde{\nu} = \frac{1}{\lambda} \quad \text{or} \quad \nu = \frac{c}{\lambda} = c\tilde{\nu} \quad 8.11.22$$

Using $\tilde{\nu}_o$ in cm⁻¹ and m in g mol⁻¹, Eq. 8.11.21 becomes:

$$\frac{4\pi^2 c^2 \tilde{\nu}_0^2}{1000 \text{ g/kg N}_A} = \frac{k}{\text{m}} \quad 8.11.23$$

or solving for the frequency squared in wavenumbers gives a convenient conversion factor:

$$\tilde{\nu}_0^2 = \frac{k/\text{m}}{5.8921 \times 10^{-5}} \quad 8.11.24$$

Next, we need all the force constants for Eq. 8.11.20. Some force constants are related by symmetry; since the left and right-hand sides of the CO₂ molecule are the same:

$$\text{By symmetry : } \quad k_{xx}^{11} = k_{xx}^{33} \quad k_{xx}^{12} = k_{xx}^{23} \quad 8.11.25$$

The terms that exchange the atom labels are also equivalent, since atom 1 interacting with atom 2 gives the same result as atom 2 interacting with atom 1. In matrix terms, these corresponding off-diagonal terms are equal for a symmetric matrix:

$$\text{Symmetric matrix: } \quad k_{xx}^{12} = k_{xx}^{21} \quad k_{xx}^{23} = k_{xx}^{32} \quad 8.11.26$$

These equivalences leave four force constants that we need to guess. First, focus on atom 1. By trial and error, a good guess for the force constant for moving atom 1 by stretching the C=O bond is:

$$k_{xx}^{11} = 1600 \text{ N m}^{-1} \quad 8.11.27$$

This force constant gives the restoring force, $F = -kx$, as atom 1 is moved. For moving atom 1 to the right, $x > 0$ in Figure 8.11.4, the restoring force is negative, pulling the atom back to its equilibrium position. That is, if atom 1 is forced forward to shorten the bond then atom 1 will try to move back to keep the bond length constant. Next, a reasonable guess for the force constant for atom 1 while moving atom 2 is:

$$k_{xx}^{12} = -k_{xx}^{11} \quad 8.11.28$$

Here the “12”-force constant is negative, and the restoring force, $F = -kx$, is positive. This positive force results because as you move atom 1’s neighbor, atom 2, atom 1 will try to follow along in the same direction to keep the bond length constant. The absolute value of the two force constants is the same since moving either atom 1 or atom 2 has the same effect on the bond length and, therefore, the force on atom 1. Now focus on atom 2. We can guess that it is twice as hard to move atom 2 as it is to move atom 1, since moving atom 2 effects both bonds, on the left and on the right:

$$k_{xx}^{22} \approx 2 k_{xx}^{11} = 3200 \text{ N m}^{-1} \quad 8.11.29$$

Finally, we will assume that atom 3 doesn’t affect atom 1 significantly because the two atoms aren’t directly bonded:

$$k_{xx}^{13} = 0 \quad 8.11.30$$

Substituting Eqs 8.11.25-8.11.30 into Eq. 8.11.20 gives the mass-weighted force constant matrix. The row and columns correspond to the three different atoms, O₁, C₂, and O₃, respectively.

$$\begin{matrix} & \text{O}_1 & \text{C}_2 & \text{O}_3 & & \\ & \left(\begin{array}{ccc} \frac{1600}{\sqrt{16}\sqrt{16}} & -\frac{1600}{\sqrt{16}\sqrt{12}} & 0 \\ -\frac{1600}{\sqrt{12}\sqrt{16}} & \frac{3200}{\sqrt{12}\sqrt{12}} & -\frac{1600}{\sqrt{12}\sqrt{16}} \\ 0 & -\frac{1600}{\sqrt{16}\sqrt{12}} & \frac{1600}{\sqrt{16}\sqrt{16}} \end{array} \right) & = & \left(\begin{array}{ccc} -100 & 115.47 & 0 \\ 115.47 & -266.67 & 115.47 \\ 0 & 115.47 & -100 \end{array} \right) & 8.11.31
 \end{matrix}$$

The “eigen” Web applet on the companion CD is available to solve the eigenvalue problem. Computer algebra programs like Maple and Mathematica are also handy for solving eigenvalue problems. The output of the “eigen” applet is shown below. The eigenvalues are listed with “E=.” The first eigenvector corresponds to the motion of the center of mass in the x-direction. The normal mode frequencies are calculated using the units conversion from Eq. 8.11.24.

Eigenvector 1: E= -0.0009769 \approx 0 \rightarrow	Center of mass motion in x-direction
0.603024	
0.522229	
0.603024	
Eigenvector 2: E= -100 \rightarrow	Symmetric stretch:
-0.707107	$\tilde{\nu}_o = \sqrt{\frac{100}{5.892 \times 10^{-5}}} = 1303 \text{ cm}^{-1}$
0	
0.707107	
Eigenvector 3: E= -366.669 \rightarrow	Asymmetric stretch:
-0.369272	$\tilde{\nu}_o = \sqrt{\frac{366.67}{5.892 \times 10^{-5}}} = 2495 \text{ cm}^{-1}$
0.852805	
-0.369272	

The three numbers below each eigenvalue are the normal coordinates. For example, the normal coordinates for the second eigenvector show atom 1 (-0.707) moving in the opposite direction as atom 3 (0.707), while atom 2 remains stationary (0). This normal mode is the symmetric stretch, since the oxygen atoms are moving in the opposite direction. In the asymmetric stretch, eigenvector 3, the oxygen atoms move backward while the carbon atom moves forward. For this example we have motion only in the x-direction, so there are only three coordinates listed, x for each atom. To display the motion of the atoms during the vibration, the atom coordinates are calculated for atom i in normal mode j as:

$$X_i = X_{i,\text{eq}} + \frac{\tilde{x}_{ij}}{\sqrt{m_i}} q \quad Y_i = Y_{i,\text{eq}} + \frac{\tilde{y}_{ij}}{\sqrt{m_i}} q \quad Z_i = Z_{i,\text{eq}} + \frac{\tilde{z}_{ij}}{\sqrt{m_i}} q \quad 8.11.32$$

where $q = \sin(2\pi\nu_j t)$ and \tilde{x}_{ij} is the x-component of the normal coordinate for atom i and mode j. For example, for the asymmetric stretch for CO₂ for the first O atom:

$$X_1 = X_{1,\text{eq}} + \frac{-0.369}{\sqrt{16}} \sin(2\pi\nu_o t) \quad 8.11.33$$

You can tell that the first eigenvector is for the motion of the molecule as a whole because all the normal coordinates have the same sign, that is all the atoms are traveling in the same

direction. For fully three-dimensional problems, the first 5 eigenvalues, for linear molecules, or 6 eigenvalues, for nonlinear molecules, correspond to translation and rotation. Some molecular orbital programs don't list these first 5 or 6 eigenvalues.

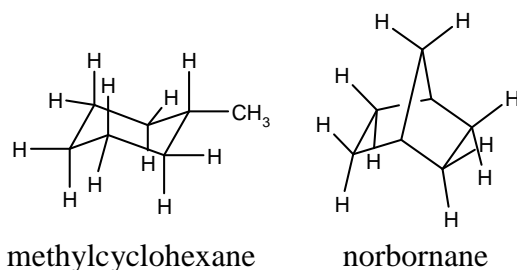
How good is our simplified model? The symmetric stretch is low and the asymmetric stretch is high, for a combined error of about 5%. It doesn't make sense to try to get the results to agree any better. Using a molecular mechanics or molecular orbital program is more accurate.

Anharmonicity Decreases the Fundamental Vibration Frequency: The preceding normal mode analysis assumes all the vibrations are purely harmonic. Our treatment of molecular mechanics force fields shows that anharmonic corrections are often important. What is the effect of anharmonicity on vibrational spectra and normal mode calculations? For anharmonic vibrations, vibrational spectra include the fundamental transitions and also show overtones, sum, and difference bands. Overtones are at integer multiples of the fundamental frequency, $n\tilde{\nu}_A$. Sum and difference bands occur at $\tilde{\nu}_A + \tilde{\nu}_B$ and $\tilde{\nu}_A - \tilde{\nu}_B$, respectively. Considering normal mode calculations, frequencies from *ab initio* molecular orbital calculations are normally multiplied by 0.9 to correct for anharmonicity. For strong anharmonicity, including bond torsions that have low energy barriers, ring vibrations in large ring systems, and vibrations in hydrogen-bonded systems, a refined treatment is necessary.²⁰ Unfortunately, such vibrations are often the most interesting, especially in studies of proteins and nucleic acids. Treating very flexible, low energy vibrations in biomolecules is an active area of current study.²⁵⁻²⁹ Vibrations play a central role in protein folding and protein flexibility.²⁷⁻²⁹

Bond Energy, Steric Energy, Translation, Rotation, and Normal Mode Contributions Estimate the Internal Energy and Enthalpy of Formation: In principle, every vibration, including internal rotations, contribute to the enthalpy. Following a normal mode analysis, it is very easy to calculate the enthalpy of formation of a substance using Eq. 8.10.9. Molecular mechanics and molecular orbital programs routinely do these calculations. For our present purposes, simply noting the low frequency vibrations and the internal rotations, in particular, are sufficient to understand the relative enthalpies of formation for substances.

Example 8.11.2:

Use normal mode analysis to decide if methylcyclohexane or norbornane has a higher contribution of vibrations toward the enthalpy of formation. Molecular mechanics or AM1 or PM3 molecular orbital calculations are sufficiently accurate for this qualitative analysis.



Answer: Using PM3 level molecular orbital calculations, the vibrational normal modes less than 500 cm^{-1} are:

methylcyclohexane: 153, 214, 230, 317, 343, 428, 471, 476, 476 cm^{-1}
 norbornane: 201, 366, 436, 477 cm^{-1}

The rigid framework of the bicyclic form provides fewer low frequency normal modes giving norbornane a small contribution from vibrations towards the enthalpy of formation and heat capacity. However, norbornane is highly strained giving an overall higher steric energy and bond energy. The literature gas phase enthalpies of formation are -155 kJ mol^{-1} for methylcyclohexane and -55 kJ mol^{-1} for norbornane.³

8.12 Summary—Looking Ahead

The experimental measurement of the heat transfer of phase transitions and chemical reactions is a central component in the application of thermodynamics to practical problems. The internal energy change is the heat transfer at constant volume and the enthalpy change is the heat transfer at constant pressure. If experimental measurements are unavailable, then predictions are made.

The conformation of a molecule often has a great effect on its reactivity. The effect of structure on reactivity is particularly important for large molecules, such as proteins and nucleic acids. Structure-function relationships are the heart of chemistry. Steric interactions include through-bond distortions of the bond lengths and angles in the molecule and through-space Van der Waals and electrostatic interactions. Distortions from the equilibrium bond lengths and angles are always unfavorable, adding to the overall ground state energy. Through-space, non-bonded interactions can be favorable or unfavorable. Geometry optimization predicts the low energy conformations. The ground state energy at 0 K of the molecule is the sum of the bond energy and the steric energy. Equipartition provides the contributions of the thermal motions of translation and rotation. Normal mode analysis determines the low frequency vibrations that contribute to the internal energy and the enthalpy.

Reaction enthalpies are necessary for understanding the interrelationships that govern processes in energy technology, living cells, and ecosystems. Ecologists, nutritionists, and chemical engineers use calorimetry to monitor the flow of energy through an ecosystem, an organism, or through a society. The production and use of energy are governed by the First Law of Thermodynamics in any circumstance; energy in an isolated system is conserved. Except for nuclear energy, chemical fuels are the densest sources of energy for transportation, space heating, cooking, and industrial production. Glucose is the primary chemical fuel for organisms. Coal, oil, and natural gas are the primary chemical fuels for current societies.

We have not completed our development of the First Law and the theoretical methods that enable the use of the powerful idea of energy conservation. In the next chapter, we develop further the mathematical manipulations that allow us to solve problems in a general and useful way. We also apply the First Law to some additional practical problems that will lead to the criteria for spontaneous processes. In Chapter 15 we will consider work transfer.

8.13 Addendum

The Classical Harmonic Oscillator: The Hooke's Law force for a harmonic oscillator is $F = -kx$, where x is the displacement of the mass, m . To find the motion of an oscillator we need to integrate Newton's second law for x as a function of time, $x(t)$, Figure 8.13.1.

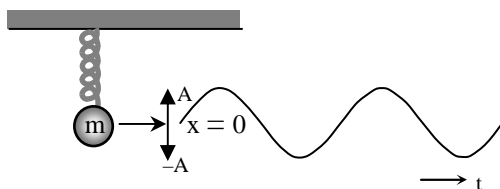


Figure 8.13.1: A mass suspended by a spring undergoes sinusoidal motion with amplitude A .

Newton's second law relates the force and the acceleration, $F = ma$. Substituting the second derivative of the position for the acceleration and Hooke's law for the force gives:

$$m \frac{d^2x(t)}{dt^2} = -\kappa x(t) \quad 8.13.1$$

There are many ways to solve differential equations; however, the easiest is to try to guess a solution. Experimental observation suggests that the mass will oscillate about its equilibrium position, $x = 0$, as a sinusoidal function of frequency ν . We therefore guess the functional form:

$$x(t) = A \sin ct \quad 8.13.2$$

where A is the amplitude and c is a constant. The general approach for verifying our guess is to substitute the guess into the left-hand side of the differential equation and then the right-hand side of the differential equation and then check to see if the two sides agree (see Sec. 6.1).

Beginning with the left-hand side, the first and second derivatives of the guessed solution are:

$$\frac{dx(t)}{dt} = A (\cos ct) c \quad 8.13.3$$

$$\frac{d^2x(t)}{dt^2} = -c^2 A \sin ct \quad 8.13.4$$

Substituting the second derivative into the left-hand side of Eq. 8.13.1 gives:

$$m \frac{d^2x(t)}{dt^2} = -m c^2 A \sin ct \quad (\text{lhs}) \quad 8.13.5$$

Now consider the right-hand side of Eq. 8.13.1. All we need do is multiply $x(t)$ by $-\kappa$:

$$-\kappa x(t) = -\kappa A \sin ct \quad (\text{rhs}) \quad 8.13.6$$

Now we check to see if the left and right-hand sides can be made equal. Equating Eqs. 8.13.5 and 8.13.6 gives:

$$-m c^2 A \sin ct = -\kappa A \sin ct \quad (\text{lhs} \stackrel{?}{=} \text{rhs}) \quad 8.13.7$$

Cancelling the common factors gives:

$$m c^2 = \kappa \quad (\text{lhs} \stackrel{?}{=} \text{rhs}) \quad 8.13.8$$

This last equation fixes the value of the constant that gives a valid solution:

$$c = (\kappa/m)^{1/2} \quad \text{giving} \quad x(t) = A \sin((\kappa/m)^{1/2} t) \quad 8.13.9$$

The frequency of the oscillation can be determined by comparing this last equation with the general form for a sinusoidal oscillation with frequency ν :

$$x(t) = A \sin(2\pi\nu t) \quad 8.13.10$$

Comparison of Eqs. 8.13.9 and 8.13.10 gives the fundamental vibration frequency of the harmonic oscillator:

$$\nu_0 = \frac{1}{2\pi} \left(\frac{k}{m} \right)^{1/2} \quad 8.13.11$$

The force and the potential energy of the harmonic oscillator are related by:

$$\left(\frac{\partial V}{\partial x} \right) = -F \quad \text{and integration gives} \quad V = - \int F dx \quad 8.13.12$$

In words, the force is the negative of the gradient of the potential energy. Substituting Hooke's law force into this last equation gives the potential energy for the harmonic oscillator:

$$V = \int kx dx = \frac{1}{2} kx^2 \quad 8.13.13$$

The total energy of the harmonic oscillator is the sum of the kinetic and the potential energy:

$$\epsilon = \epsilon_K + V = \frac{1}{2} m v_x^2 + \frac{1}{2} kx^2 \quad 8.13.14$$

which results in two quadratic terms, or in other words two degrees of freedom. To find the total energy of the harmonic oscillator we can determine the energy at any point in the oscillation, since the total energy is constant. Choosing the time when the oscillator is at its maximum extension, $x(t) = A$, gives zero kinetic energy and total energy:

$$\epsilon = \frac{1}{2} kA^2 \quad 8.13.15$$

The energy of a classical harmonic oscillator is proportional to the amplitude squared. For a diatomic molecule the extension is given by $x = (r_{ij} - r_0)$, giving Eq. 8.8.10, and the mass of the object on the spring, m , is replaced by the reduced mass for the molecule:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad 8.13.16$$

where m_1 and m_2 are the masses of the two bonded atoms.

Normal Coordinates Show the Progression of the Vibration: We wish to show more clearly the relationship between Eqs. 8.11.16-8.11.18 and the normal coordinates, for the curious. First note that substituting Eq. 8.11.4 into Eq. 8.11.6 gives:

$$-4\pi^2 \nu_0^2 m A \sin(2\pi\nu_0 t) = -k A \sin(2\pi\nu_0 t) \quad 8.13.17$$

Dividing both sides by the $\sin(2\pi\nu_0 t)$ gives:

$$-4\pi^2 \nu_0^2 m A = -k A \quad 8.13.18$$

In other words, the Eq. 8.11.6 applies equally to the time dependence of the vibration and just the amplitude of the vibration. Therefore Eqs. 8.11.11-8.11.13 and 8.11.16-8.11.18 allow us to solve

for the amplitudes of the vibrations, where x_i , y_i , z_i can be read as the amplitudes of the oscillation in the x , y , and z directions for atom i . Similarly, \tilde{x}_{ij} , \tilde{y}_{ij} , \tilde{z}_{ij} are the corresponding mass weighted amplitudes for mode j . The time dependent values are then:

$$\tilde{x}_{ij}(t) = \tilde{x}_{ij} \sin(2\pi\nu_0 t) \quad \tilde{y}_{ij}(t) = \tilde{y}_{ij} \sin(2\pi\nu_0 t) \quad \tilde{z}_{ij}(t) = \tilde{z}_{ij} \sin(2\pi\nu_0 t) \quad 8.13.19$$

Dropping the “(t)” for convenience and converting back into non-mass weighted coordinates:

$$x_{ij} = \frac{\tilde{x}_{ij}}{\sqrt{m_i}} \sin(2\pi\nu_0 t) \quad y_{ij} = \frac{\tilde{y}_{ij}}{\sqrt{m_i}} \sin(2\pi\nu_0 t) \quad z_{ij} = \frac{\tilde{z}_{ij}}{\sqrt{m_i}} \sin(2\pi\nu_0 t) \quad 8.13.20$$

Converting from extensions into final coordinates using Eq. 8.11.7 gives Eq. 8.11.32.

Note that Eqs 8.11.16-8.11.18 involve four unknowns (ν , \tilde{x}_i , \tilde{y}_i , and \tilde{z}_i) but only three equations. To obtain unique solutions, some more information is necessary. We must add the requirement that the center of mass can't move:

$$m_1 x_1 + m_2 x_2 + m_3 x_3 = 0 \quad 8.13.21$$

or equivalently in mass-weighted coordinates:

$$\sqrt{m_1} \tilde{x}_{1j} + \sqrt{m_2} \tilde{x}_{2j} + \sqrt{m_3} \tilde{x}_{3j} = 0 \quad 8.13.22$$

As we solve for each successive normal mode we also need to ensure that the vibrations don't interact. Mathematically this requires that the normal modes are orthogonal. For each pair of normal modes p and q , with normal coordinates \tilde{x}_{ip} and \tilde{x}_{iq} , respectively, the orthogonality condition is:

$$\tilde{x}_{1p} \tilde{x}_{1q} + \tilde{x}_{2p} \tilde{x}_{2q} + \tilde{x}_{3p} \tilde{x}_{3q} = 0 \quad 8.13.23$$

Taken together, Eqs 8.11.16-8.11.18 and Eqs. 8.13.22 and 8.13.23 provide the unique set of normal modes satisfying the desired characteristics set out in the introduction to Sec. 8.11. Solving these equations as an eigenvalue-eigenvector equation using Eq 8.11.20 automatically satisfies the requirement for orthogonality, Eq. 8.13.23.

Chapter Summary

1. Phase transitions and the formation of solutions can be considered as chemical reactions:
 $\Delta_r H = \Delta_{tr} H$ or $\Delta_r H = \Delta_{soln} H$.
2. For a phase transition, formation of a solution, or a chemical reaction in a closed system at constant pressure, the heat transfer is given by the enthalpy change.
3. The reaction enthalpy and internal energy are related by:
 $\Delta_r H = \Delta_r U + \Delta_r n_g RT$ $\Delta_r n_g = \sum \nu_i(g)$ for all gas phase reactants and products
4. The reaction internal energy and enthalpy depend on the reaction conditions:
 The state of aggregation, solid, liquid, or gas.
 For solids, the crystalline form.
 For gases, the pressure.
 For species in mixtures, the concentration.
 The pressure of liquids and solids need not be specified for pressures near 1 bar.

5. The standard states are $P^\circ = 1$ bar and in solution unit concentration. If the state of aggregation is not specified, the most stable state at the given temperature and pressure is assumed.
6. There is no standard temperature.
7. Hess's Law is a consequence of the path independence of thermodynamic state functions:
If chemical reactions are added, the internal energies and enthalpies add.
If the direction for a reaction is reversed, the sign of the internal energy and enthalpy reverse.
If a reaction is multiplied by a constant, the internal energy and enthalpy are also multiplied by the same constant, because internal energy and enthalpy are extensive.
8. There are no experimental methods to establish an absolute internal energy or enthalpy of a substance. Since only the changes in internal energy and enthalpy for a chemical reaction are needed, the reference point is arbitrary.
9. The enthalpy of formation for a substance is the reaction enthalpy for the formation of one mole of substance from the constituent elements in their standard states. The standard state enthalpy of formation of any element is defined as zero.
10. The reaction enthalpy in terms of the molar enthalpies of formation, $\Delta_f H_i$, is:

$$\Delta_r H = \sum_{i=1}^{n_s} \nu_i \Delta_f H_i$$

where ν_i are the stoichiometric coefficients and the sum extends over the n_s constituents.

11. The enthalpy change for a reaction in terms of the absolute molar enthalpies for each reactant and product, H_i , is:

$$\Delta_r H = \sum_{i=1}^{n_s} \nu_i H_i$$

12. The reaction enthalpy, $\Delta_r H$, is the change in enthalpy for unit extent in so large an amount of the reaction that the partial pressures of the constituents remain unchanged.
13. The reaction enthalpy, $\Delta_r H$, is the derivative of the enthalpy with respect to the extent of the reaction.
14. The dependence of the reaction enthalpy on temperature is given by:

$$\left(\frac{\partial \Delta_r H}{\partial T} \right)_P = \Delta_r C_p \quad \text{with} \quad \Delta_r C_p = \sum_{i=1}^{n_s} \nu_i C_{p,i}$$

15. For temperature independent heat capacities: $\Delta_r H_{T_2} - \Delta_r H_{T_1} = \Delta_r C_p \Delta T$. In general:

$$\Delta_r H_{T_2} = \Delta_r H_{T_1} + \Delta_r a (T_2 - T_1) + \frac{\Delta_r b}{2} (T_2^2 - T_1^2) + \frac{\Delta_r c}{3} (T_2^3 - T_1^3) + \frac{\Delta_r d}{4} (T_2^4 - T_1^4)$$

16. At infinite dilution, for non-electrolytes there are no interactions between the molecules of the solute, for electrolytes there are no interactions among the anions and cations.
17. To calculate the enthalpy of formation of a substance in solution, the enthalpy of solution is added to the enthalpy of formation of the pure substance.
18. For electrolytes, the "ai" standard state corresponds to complete dissociation. The "ao" standard state for weak electrolytes is at unit concentration with no further dissociation; the weak electrolytes are completely undissociated or hydrolyzed.

28. An alternative expression for the dispersion interaction is the Buckingham potential:

$$\epsilon_{\text{vdw},ij} = \mathcal{D}_e \left\{ \frac{6}{\alpha-6} e^{-\alpha(r_{ij}-r_o)/r_o} - \frac{\alpha}{\alpha-6} \left(\frac{r_o}{r_{ij}} \right)^6 \right\}$$

The value of α controls the steepness of the repulsion, for MM3 $\alpha = 12.5$.

29. The secondary structure of a protein is determined by the dihedral angles in the backbone of the protein. Typical values in the alpha helix are $\psi = -47^\circ$ and $\phi = -57^\circ$ and for beta-pleated sheets, $\psi = 135^\circ$ and $\phi = -140^\circ$.

30. Each quadratic term in the total energy is called a degree of freedom. The Equipartition theorem predicts that each degree of freedom contributes $\frac{1}{2} RT$ to the molar internal energy and $\frac{1}{2} R$ to the molar constant volume heat capacity.

31. For a diatomic molecule, which have two rotational axes, the predicted temperature dependent contribution to the internal energy is: $U - U(0) = \frac{3}{2} RT + \frac{2}{2} RT + \frac{2}{2} RT = \frac{7}{2} RT$ with vibration and $\frac{5}{2} RT$ neglecting vibration, giving a lower bound.

32. The number of normal modes, n , for a linear molecule is $n = 3N - 5$ and for a non-linear molecule is $n = 3N - 6$.

33. The available thermal kinetic energy is $RT = 2.48 \text{ kJ mol}^{-1} = 207.2 \text{ cm}^{-1}$ at 298.2 K.

34. The wavenumber of a transition is given as $\tilde{\nu} = 1/\lambda$ and the energy of the transition is:

$$\Delta E = hc\tilde{\nu} \text{ per molecule} \quad \text{or} \quad \Delta E = N_A hc\tilde{\nu} = (0.011963 \text{ kJ mol}^{-1} \text{ cm}^{-1}) \tilde{\nu} \text{ per mole.}$$

35. The probability of occupying energy state i is determined by the Boltzmann distribution:

$$p_i = \frac{n_i}{N} = \frac{e^{-\epsilon_i/kT}}{q} = \frac{e^{-\epsilon_i/RT}}{q} \quad \text{with } kT \text{ per molecule and } RT \text{ per mole}$$

where ϵ_i is the energy of state i , $k = R/N_A$ is Boltzmann's constant, and T in kelvins.

36. The partition function is the sum of the Boltzmann weighting factors over all energy states. The partition function is the probability normalization: $q \equiv \sum e^{-\epsilon_i/kT}$

37. Low energy states have a higher occupation than high energy states. The ratio of the number of molecules in two states with energy difference $\Delta\epsilon = \epsilon_j - \epsilon_i$ is:

$$\frac{n_j}{n_i} = \frac{e^{-\epsilon_j/kT}}{e^{-\epsilon_i/kT}} = e^{\frac{-\Delta\epsilon}{kT}}$$

38. The Equipartition theorem holds for degrees of freedom with essentially continuous energy states. The typically large energy spacing for vibration results in only a partial contribution to the internal energy and heat capacity of the system.

39. The enthalpy of formation for a non-linear molecule near 298. K is:

$$\Delta_f H^\circ = \epsilon_{\text{bond}} + \epsilon_{\text{steric}} + RT + \frac{3}{2} RT + \frac{3}{2} RT + \epsilon_{\text{vib}} \quad \text{counting vibrations with } \tilde{\nu} \lesssim 500 \text{ cm}^{-1}.$$

40. The characteristics of normal modes are:

Each normal mode acts like a simple harmonic oscillator.

A normal mode is a concerted motion of many atoms.

The center of mass doesn't move.

All atoms pass through their equilibrium positions at the same time.

Normal modes are independent in the harmonic approximation.

41. The classical equation of motion for a harmonic oscillator is: $-4\pi^2\nu^2 m x = -kx$, with the displacement $x = r - r_0 = A \sin(2\pi\nu_0 t)$, where ν_0 is the fundamental vibration frequency and A is the amplitude of the vibration.
42. The Hessian is the matrix of the second derivatives of the potential energy with respect to motion in the x , y , and z directions. For atoms i and j :

$$\frac{\partial^2 V}{\partial x_i \partial x_j} = k_{xx}^{ij} \quad \frac{\partial^2 V}{\partial x_i \partial y_j} = k_{xy}^{ij} \quad \text{for all combinations of } x, y, \text{ and } z$$

43. The mass-weighted coordinates are: $\tilde{x}_i = \sqrt{m_i} x_i$, $\tilde{y}_i = \sqrt{m_i} y_i$, and $\tilde{z}_i = \sqrt{m_i} z_i$, for each atom i and the mass-weighted force constants for atoms i and j are in the form:

$$\tilde{k}_{xy}^{ij} = \frac{k_{xy}^{ij}}{\sqrt{m_i} \sqrt{m_j}}$$

44. The equations of motion in terms of mass weighted coordinates are:

$$\begin{aligned} -4\pi^2\nu^2 \tilde{x}_1 &= -\tilde{k}_{xx}^{11} \tilde{x}_1 - \tilde{k}_{xy}^{11} \tilde{y}_1 - \tilde{k}_{xz}^{11} \tilde{z}_1 - \tilde{k}_{xx}^{12} \tilde{x}_2 - \tilde{k}_{xy}^{12} \tilde{y}_2 - \dots - \tilde{k}_{xz}^{1N} \tilde{z}_N \\ -4\pi^2\nu^2 \tilde{y}_1 &= -\tilde{k}_{yx}^{11} \tilde{x}_1 - \tilde{k}_{yy}^{11} \tilde{y}_1 - \tilde{k}_{yz}^{11} \tilde{z}_1 - \tilde{k}_{yx}^{12} \tilde{x}_2 - \tilde{k}_{yy}^{12} \tilde{y}_2 - \dots - \tilde{k}_{yz}^{1N} \tilde{z}_N \\ &\vdots \\ -4\pi^2\nu^2 \tilde{x}_2 &= -\tilde{k}_{xx}^{21} \tilde{x}_1 - \tilde{k}_{xy}^{21} \tilde{y}_1 - \tilde{k}_{xz}^{21} \tilde{z}_1 - \tilde{k}_{xx}^{22} \tilde{x}_2 - \tilde{k}_{xy}^{22} \tilde{y}_2 - \dots - \tilde{k}_{xz}^{2N} \tilde{z}_N \\ &\vdots \\ -4\pi^2\nu^2 \tilde{z}_N &= -\tilde{k}_{zx}^{N1} \tilde{x}_1 - \tilde{k}_{zy}^{N1} \tilde{y}_1 - \tilde{k}_{zx}^{N1} \tilde{z}_1 - \tilde{k}_{zx}^{N2} \tilde{x}_2 - \tilde{k}_{zy}^{N2} \tilde{y}_2 - \dots - \tilde{k}_{zz}^{NN} \tilde{z}_N \end{aligned}$$

These equations are solved for the normal mode frequencies as an eigenvalue-eigenvector equation: $-\underline{\tilde{k}} \underline{\tilde{x}} = -4\pi^2\nu^2 \underline{\tilde{x}}$, with $\underline{\tilde{x}} = (\tilde{x}_1, \tilde{y}_1, \tilde{z}_1, \tilde{x}_2, \tilde{y}_2, \tilde{z}_2, \dots, \tilde{x}_N, \tilde{y}_N, \tilde{z}_N)^T$.

45. For anharmonic vibrations, vibrational spectra include the fundamental transitions and also overtones, sum, and difference bands.

§8 General Pattern 8: Thermodynamic Relationships for Reactions: The reaction changes for any function can be expressed in the general form:

$$\Delta_r X = \sum_{i=1}^{n_s} \nu_i X_i$$

A relationship for a pure substance can be converted to a relationship for a chemical reaction by inserting Δ_r before each extensive variable.

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Problems: Thermochemistry

- Verify the statement from Sec. 8.2 that the difference between Eqs. 8.2.3 and 8.2.4 is the enthalpy of vaporization of water, Eq. 8.1.1.
- (a). Write the chemical reaction that corresponds to the enthalpy of formation of urea, $(\text{NH}_2)_2\text{CO}$. (b). The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide. Using the data in the appendix, calculate the reaction enthalpy for the hydrolysis of urea to give gaseous ammonia and carbon dioxide, at standard state and at 298.15 K.
- NaCl aerosols are created when bubbles burst at the surface of the ocean. However, NaCl in marine aerosols has a short lifetime. A natural source of sulfur in the atmosphere above the ocean is the production of H_2S (g) from bacteria. H_2S is oxidized by atmospheric oxygen to give sulfur trioxide, which then dissolves in water droplets to form highly concentrated sulfuric acid. The sulfuric acid reacts with NaCl to give HCl gas and aqueous NaHSO_4 . (a). Using the data in the appendix, calculate the reaction enthalpy for the reaction of NaCl (s), H_2S (g), and atmospheric O_2 through the following reactions, under standard conditions and at 298.15 K.

$$\begin{aligned} \text{H}_2\text{S} (\text{g}, 1\text{bar}) + 2 \text{O}_2 (\text{g}, 1\text{bar}) &\rightarrow \text{SO}_3 (\text{g}, 1\text{bar}) + \text{H}_2\text{O} (\text{g}, 1\text{bar}) \\ \text{SO}_3 (\text{g}, 1\text{bar}) + \text{H}_2\text{O} (\text{l}) &\rightarrow \text{H}_2\text{SO}_4 (\text{l}) \\ \text{NaCl} (\text{s}) + \text{H}_2\text{SO}_4 (\text{l}) &\rightarrow \text{HCl} (\text{g}, 1\text{bar}) + \text{Na}^+ (\text{ao}) + \text{HSO}_4^- (\text{ao}) \end{aligned}$$
 (b). Combine the three reactions to show the overall process. Use the combined reaction to calculate the overall reaction enthalpy. Compare with the result in part (a).
- Components of perfumes must be in the gas phase to be smelled. Monoterpenes are common ingredients in perfumes and "essential oils," Figure P8.1. Monoterpenes are also found in health-care products and the air in forests. Determine the enthalpy of formation for each listed monoterpene in the gas phase. The literature values for the enthalpy of formation of the solids or liquids are available from Lange's Handbook, the CRC, or Data Section Table 8.4.2. The enthalpies of vaporization or sublimation are in Data Section Table 8.1.1.

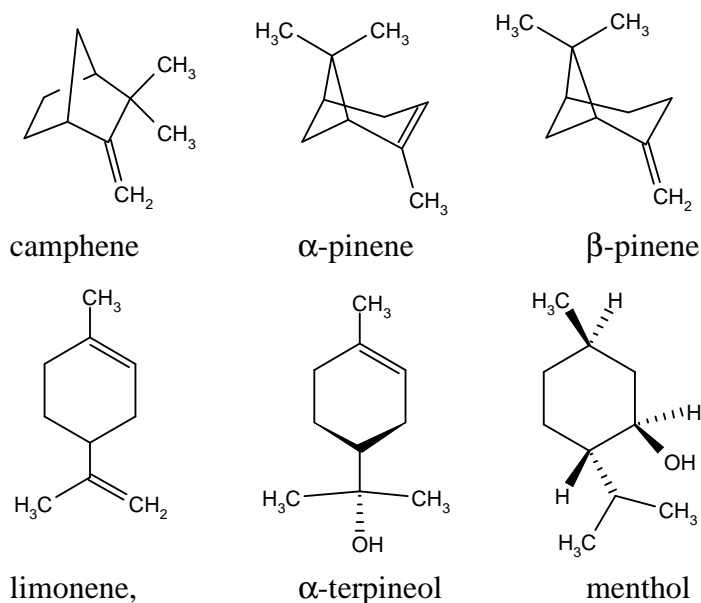
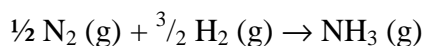


Figure P8.1: Some monoterpene natural products.

- Calculate the standard internal energy of formation at 298.2 K of liquid methyl acetate, $\text{C}_3\text{H}_6\text{O}_2$, from its standard enthalpy of formation, which is $-442.0 \text{ kJ mol}^{-1}$ at 298.2 K.
- The enthalpy of combustion of cyclopropane, C_3H_6 , is $-2091. \text{ kJ mol}^{-1}$ at 298.2 K and 1.00 bar. Given that $\Delta_f H^\circ$ for $\text{CO}_2 = -393.509 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ$ for $\text{H}_2\text{O}(l) = -285.830 \text{ kJ mol}^{-1}$, calculate the enthalpy of formation of cyclopropane.
- The enthalpy of combustion at 298.2 K and 1.000 bar pressure for cyclohexane is $-3953.0 \text{ kJ mol}^{-1}$. Calculate the standard state enthalpy of formation at 298.2 K.
- The Haber process is central to the production of fertilizers and many commodity chemicals:



The kinetics for the reaction are unfavorable at room temperature. Calculate the enthalpy change for the reaction at 500. K. Use Table 7.2.3 to express the heat capacities as a cubic polynomial.

- Yeasts convert glucose to ethanol. Calculate the change in enthalpy if one mole of glucose is converted to ethanol at 298.2 K:



$[\Delta_f H^\circ(\text{glucose}) = -1274. \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{ethanol}) = -277.69 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{CO}_2) = -393.51 \text{ kJ mol}^{-1}$] (For comparison the oxidation all the way to CO_2 and H_2O provides much more energy for the organism, but requires O_2 .)

- The molar enthalpy of vaporization of water at 298.2 K is $\Delta_{\text{vap}} H^\circ = 44.01 \text{ kJ mol}^{-1}$. Calculate the molar enthalpy of vaporization of water at the boiling point of water, 373.2 K. The $C_{p,m}$ of water liquid is $75.29 \text{ J K}^{-1} \text{ mol}^{-1}$ and of water vapor is $33.58 \text{ J K}^{-1} \text{ mol}^{-1}$.

11. Thermophilic bacteria operate at 80.0°C. Calculate the change in enthalpy for the reaction in the Problem 9 at 80.0°C. C_p for glucose is 209. J K⁻¹mol⁻¹, C_p for ethanol is 111.5 J K⁻¹mol⁻¹, and C_p for CO₂ is 37.11 J K⁻¹mol⁻¹.

12. Show that the temperature drift in a calorimetry experiment, before and after the reaction is complete, for short times and small temperature differences with the surroundings, is approximately linear. [Hint use Newton's Law of Cooling.]

13. In Sec. 8.4 we used two different perspectives for envisioning a partial derivative. The first was based on making a very small change in the extent of a reaction and then normalizing the change in enthalpy to place the result on a per mole basis, $\Delta_r H = (\partial H / \partial \xi)_P = \Delta H / \Delta \xi$. The second model was to make a one mole change in the extent of the reaction, but in such a large quantity of reactants and products that the partial pressures remained essentially constant, Figure 8.4.3. In either perspective the constancy of the pressures was maintained for the partial derivative. Consider a solution containing n_A moles of A and n_B moles of B. The partial molar volume with respect to changes in the number of moles of A while keeping the number of moles of B constant is given as $(\partial V / \partial n_A)_{n_B}$. The resulting partial derivative is at constant concentration in the same way that the reaction enthalpy is at constant pressure for each reactant and product. Use both of the perspectives for envisioning partial derivatives to describe the meaning of the partial molar volume.

14. In Sec. 8.4 we used two different perspectives for envisioning a partial derivative. The first was based on making a very small change in the extent of a reaction and then normalizing the change in enthalpy to place the result on a per mole basis, $\Delta_r H = (\partial H / \partial \xi)_P = \Delta H / \Delta \xi$. The second model was to make a one mole change in the extent of the reaction, but in such a large quantity of reactants and products that the partial pressures remained essentially constant, Figure 8.4.3. In either perspective the constancy of the pressures was maintained for the partial derivative. Use both of the perspectives for envisioning partial derivatives to describe the meaning of the reaction heat capacity $\Delta_r C_p$.

15. Octane is often taken as being representative of the fuel value for gasoline. When 0.7908 g of benzoic acid was burned in a bomb calorimeter the temperature of the calorimeter increased 2.0252°C. When 0.5458 g of octane was burned in the same calorimeter under the same conditions, the temperature increase was 2.5272°C. Assume the calorimeter was at an average temperature of 298.15 K. Calculate the enthalpy of combustion and the enthalpy of formation of octane at 298.15 K.

16. This problem explores the difference between bond enthalpies, Table 8.8.1, and bond increments, Table 8.8.2. Use the bond enthalpies in Table 8.8.1 to estimate the enthalpy of formation for methane. Calculate the bond increment for the C–H bond as ¼ of the estimated enthalpy of formation of methane. Compare your results with the bond increments in Table 8.8.2.

17. In Table 8.9.1 note that the constant volume heat capacity for CO₂ exceeds the prediction based on translation and rotation alone by a larger margin than does O₃. (a). Why? Answer qualitatively, no calculations are needed. (b). Why does rotation contribute only $\frac{2}{2}$ RT to the heat capacity for CO₂, while the contribution for O₃ and H₂O is $\frac{3}{2}$ RT?

18. The general form for the Coulomb potential is:

$$\epsilon_{\text{ele}} = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}}$$

where q_i and q_j are the charges on the two atoms in coulombs, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant, and r_{ij} is the distance between the two charges in meters. Eq. 8.8.18 is written in terms of the partial charges Q_i , where $q_i = Q_i e$, with e the fundamental unit of charge in coulombs. For example, for an electron, $Q_i = -1$ and for a proton $Q_i = 1$. If the partial charge on an atom is given as $Q_i = 0.210$ then the charge in coulombs is $q_i = 0.210 e$. Q_i and ϵ_r are unitless. The vacuum permittivity is the dielectric constant of vacuum, $\epsilon_0 = 8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$. Verify the units conversion constant in Eq. 8.8.18.

19. Calculate the electrostatic potential energy of two partial charges with $Q_i = Q_j = 0.40$ at a distance corresponding to the H atom distance in H_2O_2 assuming the relative dielectric constant for vacuum and also the relative dielectric constant for water. The dihedral angle for H_2O_2 is near 118° giving the H atom distance as 2.37 \AA . Does the higher dielectric constant of water increase or decrease the magnitude of the electrostatic interaction?

20. The Merck Molecular Force Field, MMFF, uses a “buffered” electrostatic interaction. MMFF is optimized for work on small molecules and proteins in aqueous solution, for use in medicinal chemistry. In addition, MMFF and some other force fields scale electrostatic interactions for atoms that are separated by three bonds by a factor of 0.75. Interactions for atoms separated by more than three bonds and atoms in different molecules are not scaled. The buffered Coulomb potential is:¹

$$\epsilon_{\text{ele}} = \frac{c Q_i Q_j}{4\pi\epsilon_r (r_{ij} + 0.05 \text{ \AA})}$$

The distance between the two oxygen atoms in hydrogen peroxide, H_2O_2 , is near 2.37 \AA and the partial charges are 0.40. The H-atoms are three bonds apart, H–O–O–H. Calculate the electrostatic potential energy term using Eq. 8.8.18 and also the buffered and scaled version.

21. The calculated equilibrium bond length for the C–H bond in ethane is $r_e = 1.0856 \text{ \AA}$. The potential energy for the C–H stretch is $0.1917 \text{ kJ mol}^{-1}$ higher when the bond is compressed to 1.0750 \AA . Calculate the stretching force constant.

22. The calculated equilibrium bond length for the C–H bond in ethane is $r_e = 1.0856 \text{ \AA}$. The potential energy for the C–H stretch is listed as a function of bond length in the following table. Calculate the stretching force constant using a quadratic potential. (Don’t bother to calculate uncertainties.)

$r_{\text{C-H}} (\text{\AA})$	$\epsilon_{\text{str}} (\text{kJ mol}^{-1})$
1	15.136
1.05	2.3630
1.075	0.1917
1.0856	0
1.1	0.3439
1.15	6.414

23. Use the data in the last problem to determine the C–H stretching force constant and the cubic stretch constant.
24. The geometry optimized bond angle for water is 105.50° . The potential energy for the bend is $0.305 \text{ kJ mol}^{-1}$ higher when the bond angle is expanded to 107.50° , keeping the same bond lengths. Calculate the bending force constant.
25. Build and geometry optimize water using a molecular orbital calculation at the HF 6-31G* level (a fairly quick level with only moderate accuracy). Determine the equilibrium bond length. Then constrain the bond angle in several steps between 95° and 110° and geometry optimize at each new bond angle. (Make sure to measure the bond angle each time to verify that you constrained the bond angle properly.) Plot the geometry optimum bond length versus the bond angle. In our discussion of the stretch-bend interaction, Eq. 8.8.12, we argued that when a bond is bent to smaller angles, the two associated lowest energy bond lengths increase. Does your plot agree with this observation?
26. Determine the enthalpy of formation for the monoterpenes listed in Problem 4 using the MM2, MM3, or MM4 molecular mechanics program. Compare the results with the literature values from Problem 4.
27. Estimate the contribution of vibration to the enthalpy of formation for the monoterpenes in Problem 4. Use the approximate torsional increments described in Sec. 8.10.
28. Calculate the partition function for a harmonic oscillator with fundamental vibration frequency 200 cm^{-1} at 298.2 K , by explicit summation. (Use the lowest energy state as the reference energy, $\epsilon_0 = 0$). Then calculate the probability of occupation for the states with population greater than $\sim 1\%$. Plot the probability as a function of the energy of the states.
29. A good example of the use of the Boltzmann distribution is the derivation of the barometric formula, Eq. 1.3.16°. The potential energy of a molecule of mass m at an elevation h is $\epsilon = mgh$, with g the acceleration of gravity. The ratio of the number of molecules at height h to height h_0 is then given by Eq. 8.10.8 with $\Delta\epsilon = mg(h - h_0)$. Let the number of molecules at sea level, $h_0 = 0$, be n_0 . Then note that the molar mass is given by $\mathcal{M} = N_A m$, and the pressure of the gas is $P = nRT/V$ for a given fixed volume of gas. In other words, the pressure is proportional to the number of molecules. Derive the barometric formula from the Boltzmann distribution assuming a constant temperature.
30. The energy between the ground electronic state and the first excited state in typical molecules is on the order of $30,000. \text{ cm}^{-1}$. Find the ratio of the number of molecules in the first excited state and the ground state at 298.2 K . Find the temperature that gives a ratio of 0.001. (Assume the ground and excited states are non-degenerate.)
31. Calculate the energy difference in J, kJ mol^{-1} , and cm^{-1} for transitions with the wavelength of maximum absorbance at 500.00 nm and $50,000. \text{ nm}$. The transition at 500 nm corresponds to the blue-green portion of the visible spectrum. The transition at $50,000 \text{ nm}$ or equivalently $50 \mu\text{m}$ is in the infrared. Calculate the ratio of the number of molecules in two states separated by these

energy differences at 298.2 K. Do this calculation with $\Delta\epsilon/kT$ or $\Delta\epsilon/RT$ with the energy in J, kJ mol^{-1} , and cm^{-1} (three separate calculations, to get used to the units).

32. Use the Equipartition theorem to predict the heat capacity of N_2O and HCN . Constant pressure heat capacities are more commonly tabulated than constant volume heat capacities. For an ideal gas $C_p = C_v + nR$. Compare your predictions to literature values for C_p .

33. Molecular shape plays an important role in determining the properties of a substance. Of sulfur dioxide and carbon dioxide, which molecule is predicted to have the greater heat capacity? Constant pressure heat capacities are more commonly tabulated than constant volume heat capacities. For an ideal gas $C_p = C_v + nR$. Compare your predictions to literature values for C_p .

34. The amino acid valine has three possible conformations for the side chain $-\text{CH}(\text{CH}_3)_2$ group. Calculate the probabilities of the side chain being in each of these three conformations at 298 K. Use molecular mechanics with the MMFF force field in the gas phase for the zwitter-ionic form to determine the low energy side chain conformations and the corresponding energies.

35. Nitrous oxide, N_2O , can act as a ligand in transition metal complexes. The infrared stretching frequencies for N_2O are used to judge the strength of coordination to the metal.² Nitrous oxide is also an important component of the atmosphere.³ The isotopic composition of nitrous oxide is a useful marker in atmospheric photochemistry.⁴ Nitrous oxide can be thought of as a resonance hybrid among: $\text{N}^-\text{N}^+=\text{O} \leftrightarrow \text{N}\equiv\text{N}^+-\text{O}^- \leftrightarrow \text{N}-\text{N}^-\equiv\text{O}^+$. N_2O is isoelectronic with carbon dioxide. As such N_2O is linear and has a symmetric ($\tilde{\nu}_1 = 1285 \text{ cm}^{-1}$) and an asymmetric ($\tilde{\nu}_3 = 2223.5 \text{ cm}^{-1}$) stretching mode and two degenerate bending modes ($\tilde{\nu}_2 = 588 \text{ cm}^{-1}$). Using valence force field techniques, the force constants for the NN and NO bonds in nitrous oxide have been estimated to be 1790 N m^{-1} and 1140 N m^{-1} , respectively.⁵ (a). Use these bond force constant estimates and MatLab, Mathematica, or the “eigen” Web applet from the companion CD or the text Web site to calculate the frequencies for the symmetric and asymmetric stretches for nitrous oxide. Your calculation will be very similar to the CO_2 example in Sec. 8.11. For example, restrict the motions to just the x-axis (e.g. neglect the bending vibrations) and estimate the force constants in a similar way. You should end up, again, with a 3×3 mass weighted force constant matrix. [Hint: k_{xx}^{22} won't be equal to $2k_{\text{xx}}^{11}$ in this case because there is a nitrogen on one side and an oxygen on the other side of the central atom, atom 2] (b). Which of the three resonance structures is most representative of the true bonding in N_2O , based on the NN and NO force constants?

36. Acetylene is a linear hydrocarbon with a carbon-carbon triple bond, $\text{H}-\text{C}\equiv\text{C}-\text{H}$, with stretching modes at 1973.8 cm^{-1} , 3287.0 cm^{-1} , and 3373.7 cm^{-1} . Using valence force field techniques, the force constants for the C-H and $\text{C}\equiv\text{C}$ bonds in acetylene have been estimated to be $592. \text{ N m}^{-1}$ and $1580. \text{ N m}^{-1}$, respectively. Use these bond force constant estimates and MatLab, Mathematica, or the “eigen” Web applet, from the text Web site, to calculate the frequencies for the three linear stretch normal modes for acetylene. Your calculation will be similar to the CO_2 example in Sec. 8.11. For example, restrict the motions to just the x-axis (e.g. neglect the bending vibrations) and estimate the force constants in a similar way. You should end up with a 4×4 mass weighted force constant matrix. [Hint: k_{xx}^{22} won't be equal to $2k_{\text{xx}}^{11}$ in this case

because there is a hydrogen on one side and a carbon on the other side of atom 2]. Sketch the normal modes.

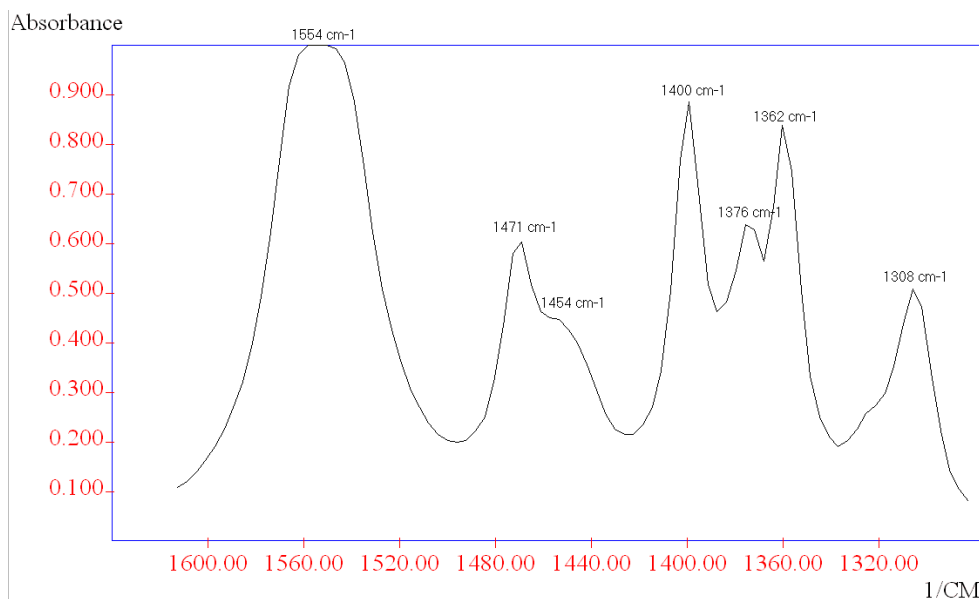
37. Infrared spectroscopy is a useful tool for functional group determination in organic molecules. The correlation chart from your Organic Chemistry text lists typical values for infrared frequencies for different functional groups.⁶ Do a normal mode analysis for acetone and dimethylether using molecular mechanics or molecular orbital methods and compare the C–H, C=O, and C–O stretching frequencies to the typical values. These absorptions are typically easy to find because they are intense or in uncluttered regions of the spectrum.

Characteristic Infrared Absorption Frequencies.⁷

bond	Compound type	Frequency range (cm ⁻¹)
C–H	Alkanes	2850-2960
C–H	Alkenes	3020-3080(<i>m</i>)
C–H	Aromatic	3000-3100(<i>m</i>)
C=C	Alkenes	1640-1680(<i>v</i>)
C \equiv C	Aromatic	1500, 1600(<i>v</i>)
C–O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
C \equiv N	Nitriles	2210-2260(<i>v</i>)
–NO ₂	Nitro	1515-1560, 1345-1385

All absorptions are strong except: *m* moderate, *v* variable

38. The infrared spectrum for 2-nitropropane is shown below. Do a normal mode analysis using B3LYP/6-31G* molecular orbital calculations to assign the –NO₂ asymmetric and symmetric stretches. You will need to use a visualization environment that displays the normal mode displacements or animates the vibrations.



P 8.2: The infrared spectrum of 2-nitropropane, presented in absorbance mode.

39. The energy density of fuels differs greatly. At times optimizing the energy density per unit weight is most important. For practical purposes the low energy density per unit volume for gases or biomass are an issue. Calculate the enthalpy of combustion on a kJ kg^{-1} and a kJ L^{-1} basis for the following fuels, and plot the enthalpy of combustion in kJ L^{-1} versus kJ kg^{-1} . Note that $1 \text{ Btu lb}^{-1} = 2.326 \text{ kJ kg}^{-1}$. For the gases, assume ideal gas behavior at a pressure of 10 bar at 298 K. The octanes are commonly used to represent gasoline and methane is the major component in natural gas.

Enthalpy of formation or combustion for common fuels.⁸⁻¹⁰

Fuels	$\Delta_f H^\circ$ kJ mol^{-1}	$\Delta_{\text{comb}} H$ kJ g^{-1}	$\Delta_{\text{comb}} H$ Btu lb^{-1}	density g mL^{-1}
graphite	0			2.25
methanol (l)	-238.66			0.7914
ethanol (l)	-277.69			0.7893
octane	-249.9			0.7025
isooctane	-255.1			0.6918
glucose	-1274			1.526
wood			-4480	0.55
biodeisel		-41.2		0.87
coal (lignite)			-8000	0.75
coal (anthracite)			-14000	0.88
H_2 (g)	0			
CH_4 (g)	-74.81			

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