# Chapter 13.   Thermodynamics

## 13.1.  Heat

All natural energy on Earth ultimately comes from the stars; the sun provides solar energy and super novae processes store nuclear energy in radioactive elements. Chemical bonds store energy in the attractions of subatomic particles. Chemical reactions, which are rearrangements of bonds, are accompanied by energy changes. **Thermochemistry** deals with the heat consumed or produced in chemical processes.

We would like to put the flow of energy to use, but there are limitations to how much we can control. The subject of **thermodynamics** indicates how much useful work can be obtained from processes, among other things. It is the fundamental theoretical model for large groups of particles similar to the role mechanics plays for individual particles. The term *thermo*dynamics originally referred to dynamical processes involving *heat*, such as automobile or rocket engines. However, the subject of thermodynamics is much more fundamental, and governs all processes taking place in the universe, from biological metabolism to stellar evolution.

As classical mechanical descriptions of objects have been refined through consideration of their component parts, so classical thermodynamic descriptions of systems have been placed on the firmer foundation of statistical mechanics. In this chapter we will introduce the concepts and laws of these important fields of science.

## 13.2.  The First Law

Among the most fundamental laws of the universe are *conservation laws*, laws describing what remains constant when other things are changing. The atomic theory explanation of chemical reactions is based on an understanding of the law of conservation of matter. Not too long before Dalton's time, chemists did not understand that matter was conserved during chemical transformations. Consider a burning candle. As it burns, it diminishes in size, until it appears entirely "consumed." Where did the candle go? Only when the combustion reaction was contained and the gaseous products (carbon dioxide and water vapor) captured did chemists realize that matter had not disappeared. Experiments such as these were performed

by Lavoisier, Dalton's immediate predecessor, to demonstrate the critical roll of gases in chemical reactions and the conservation of matter when it undergoes transformation. Although the law of conservation of matter may seem only logical from our vantage point, it certainly wasn't so obvious before the carefully controlled analytical experiments of the 18th Century.[1]

Similarly, one may have an intuitive feeling that *energy* should be conserved. After all, don't we eat food for calories to replace the energy we expend during exercise? In fact the idea that *energy may change form but is neither created nor destroyed* (conservation of energy) was fundamental to the kinetic and potential energies of the mechanics of classical isolated bodies (cf Section 5.2). Since heat is commonly a product of chemical processes, some subscribed to the notion that heat is a substance.[2] However, heat is not conserved like matter. This was observed by Benjamin Thompson (Count Rumford) in 1789 using dull canon boring tools to generate unlimited amounts of heat through friction. In 1842 a ship physician, Julius R. Mayer, noted that the amount of work sea men could do in the tropics was more than in the arctic, suggesting a connection between heat and work.[3] James Joule[4] performed the first careful experiments generating heat from a variety of sources and found an equivalence between the amount of work done on a system and the amount of heat generated. Joule found that the temperature of a substance such as water could be increased a

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[1] Lavoisier, using analytical balances barely fit for a freshman laboratory, consistently reported his experimental results to seven or eight significant figures. He would have loved hand-held calculators.

[2] Lavoisier included a nonmaterial "element" *caloric* in his table of the elements of 1789.

[3] He also noted sailor's blood from blood-letting treatment was redder in the tropics. "A force (energy) once in existence cannot be annihilated; it can only change form." Mayer's article was rejected by the *Annalen der Physik* as being too radical.

Helmholtz' paper on the subject at age 27 in 1847 was likewise rejected by the *Annalen*. It contains the now classic statment "the quantity of energy in nature is just as eternal and unalterable as the quantity of matter."

[4] James Prescott Joule (British, 1818-1889), son of a Manchester Brewer who, at age nineteen, took an interest in the source of the heat attending fermentation. Joule's paper "On the Mechanical Equivalent of Heat" was rejected for publication, in part because of his age (19 years). Only after Michael Faraday endorsed his paper to the Royal Society eleven years later in 1849 was it accepted for publication. His (correct) proposition that friction consists in the conversion of mechanical energy into heat was edited out by the review committee, and his deduction from the thermal expansion of gases that there should be an absolute zero of temperature failed to provoke comment. The SI unit of energy (one kg m$^2$/s$^2$) is named in his honor.

given amount either by direct heating *or indirectly* by stirring, or by a combination of the two processes. The amount of heat was measured through the heat capacity, Eq. (2.26). The amount of work was measured with Eq. (5.15) using a falling weight connected through pulleys to a stirring paddle wheel. An important insight is that the change in the system (water) is brought about by processes *external* to the system (heater, stirrer). This may not seem obvious at first since the heater and stirrer are in contact with the system (and are part of a larger system). But conceptually at least, the system can be isolated from its surroundings. Now, the *state* of a system is determined by specifying the values of the quantities that can vary without changing the identity of the system itself (the variables which distinguish this system from all others). A state measuring instrument (thermometer) indicates the values of a state variable (temperature) defining the internal states of the system. Although there is a change in the state of the system according to the measuring instrument, the system has no memory of how it arrived at its final state. All that can be detected internally in the system is that the system has changed states. Since heat and work are different manifestations of a common state variable (temperature) and work was already identified with as energy through classical mechanics, Joule's experiments showed that the *sum* of heat (q) and work (w), or total change in energy ($\Delta E = E_{final} - E_{initial}$), is conserved (constant):

$$\Delta E = q + w \qquad (13.1)$$

This is the mathematical statement of the **First Law of Thermodynamics**. Note that only *changes* in energy are measured. Energy is not an absolute quantity, but must be referred to the value at some state by convention accepted as the "standard state".[5] An immediate

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[5] One might imagine that there is no energy at absolute zero temperature. According to the kinetic molecular theory, there is zero *thermal* energy at zero absolute temperature. But there may still be energy stored in the bonds between atoms and molecules. Separating the atoms to infinity at absolute zero does not result in zero energy because there is energy stored in the bonds between the electrons and nuclei, etc. So how about separated protons, neutrons, and electrons at rest? Well, that ignores the relativistic rest mass energy (not a small quantity, considering thermonuclear energies). And what about the more fundamental particles that make up protons and neutrons, quarks? Unfortunately, they cannot be isolated to establish a state of zero energy.

consequence of the fi rst law is that if a system has no energy contact with its surroundings, its total energy must remain constant. This is the *law of conservation of energy*, $E_{isolated}$ = constant and

$$\Delta E_{isolated} = 0 \qquad (13.2)$$

According to Einstein's theory of relativity, matter and energy are manifestations of each other and interconvertible (Eq. (5.24)). The First Law then becomes a statement of the conservation of mass-energy. In chemical and physical transformations, energy changes involve mass changes, although the conversion factor ($c^2$) is weighted so heavily in favor of mass that mass changes are negligible for ordinary energy transformations.

**Example 13.1** Calculate the mass change accompanying an energy change of 1000 kJ.

According to Eq. 5.21

$$\Delta E = \frac{1000 kJ \times (\frac{10^3 \text{ J}}{1 \text{ kJ}}) \times (\frac{1 \text{ kg m}^2 / \text{s}^2}{1 \text{ J}}) \times (\frac{10^3 \text{ g}}{1 \text{ kg}})}{(3 \times 10^8 \text{ m/s})^2} = 1 \times 10^{-8} \text{ g}$$

A useful analogy is the potential energy of gravity (see Example 5.7). We all are familiar with climbing up and rolling down hills. During these processes work is converted into potential energy, and *vice versa*. The *sum* of work and gravitational potential energy equal to the total energy, however, is conserved. Alternative statements of the First Law of Thermodynamics, equivalent to Eq. (13.1), are that *energy is a "state" function* (depends only on the current state of the system), and that *changes in energy are independent of the path leading from initial to final states*. A direct consequence of independence of path is the fact that the total change ($\Delta$) in energy for a *cyclic* process (one that ends up in the same state in which it started), is zero:

$$\Delta E_{cyclic} = 0 \qquad (13.3)$$

Stating that the energy change of a cyclic process is zero is analogous to pumping a bicycle

up a hill and rolling back down to the starting point. Of course we know that some energy *appears* to be lost in this process, because we may still feel the fatigue of the climb on our return to the starting point. Similar considerations apply to related oscillating systems, such as people on swings, or bouncing balls. The processes do not proceed indefinitely without additional energy input. At the end of each cycle, a little energy appears to be lost. However, closer examination shows that *some* of the energy is converted into other forms, such as sound and heat, which are not easily recoverable. *Taking all the forms of energy into account, the total energy is indeed conserved in all processes.* In fact, had there not been some loss of *useful* energy (potential energy in these examples), the laws of thermodynamics would have been violated, and we could create out of such a process a *perpetual motion machine*, one that provides an infinite source of energy perpetually at no cost.

### 13.3. The Kinetic Molecular Theory

The kinetic molecular theory adds to the atomic theory of matter the notion that molecules are in constant motion, obeying the same laws of mechanics as macroscopic objects. The essential concept is that *heat is the macroscopic manifestation of molecular motion*.[6] This establishes links between classical physics and thermodynamics. The kinetic and potential energies of mechanics become heat and work in thermodynamic transformations. The work done on the falling weight in Joule's experiment is converted into kinetic energy of the weight (motion) if the weight is isolated, but if connected to the paddle wheel, the weight comes to rest and the work is manifested as an increase in kinetic energy of the molecules of the water.

> **Example 13.2** Estimate the difference in temperature of the water between the top and the bottom of Niagara Falls, 160 ft.
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> When an object falls a height $\Delta h$ in the gravitational field of the earth, the potential energy decreases by $mg\Delta h$, where m is the mass of the object, and g is the gravitational constant, 9.80665 m/s$^2$ on Earth (Eq. (5.15)). Assuming the water to be an isolated

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[6] Heat as motion is not a new idea. Plato said, "heat and fire ... are themselves begotten by impact and friction, but this is motion." Francis Bacon in 1602 said, "heat is motion and nothing else."

It may be helpful to think of a drop of water sizzling on a hot stove burner. The idea of molecules buzzing around and bumping into each other was not considered essential by John Dalton, and he rejected it in favor of a derivation of the Ideal Gas Law based on a model of static, but expandable molecules.

system, its decrease in potential energy is converted into an increase in thermal (heat) energy. The change in heat of an object is proportional to its mass and the temperature change, Δt; the proportionality constant is the specific heat capacity of the object (Eq. (2.26)). The specific heat capacity of water is $\dfrac{4.184 \text{ J}}{°C} = \dfrac{4.184 \text{ kg m}^2}{s^2 °C}$. As the water falls, potential energy is released that was stored when the water was lifted to the top of the falls (through evaporation and heating by the sun). The released potential energy can be converted into kinetic energy of the water (increase in speed), relative kinetic energy (motion) of the water molecules, or transferred to the surroundings. If the water reaches a relatively slow terminal (constant) velocity, yet falls quickly enough to hinder transfer of energy to the surroundings (air), the bulk of the released potential energy is converted into heating the falling water. From the first law, the net change in energy of the system (water) is zero:

$$\Delta E = q + w = mSH\Delta t + mg\Delta h = 0$$

Solving for Δt,

$$\Delta t = \frac{-g\Delta h}{SH} = \frac{(-9.81 \, \frac{m}{s^2})(-160 \text{ ft})(\dfrac{0.3048 \text{ m}}{1 \text{ ft}})}{(4.1844 \text{ kg} \, \dfrac{m^2}{s^2 °C})(\dfrac{10^3 \text{ g}}{1 \text{ kg}})} = 0.11 \; °C$$

a small, but interesting result, first predicted by Joule, and later confirmed by observation.[7] Lord Kelvin records that when he vacationed at Mont Blanc, "whom should I meet walking up but Joule, with a long thermometer in his hand, and a carriage with a lady in it not far off. He told me that he had been married since we parted at Oxford! and he was going to try for the elevation of temperature in waterfalls." This is how real scientists spend their honeymoons.

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### 13.4.  Enthalpy

Work commonly appears in chemical reactions as the expansion or contraction of gases at constant P (a common circumstance in the laboratory open to the atmosphere), with the amount being measured by the change in the product of pressure and change in volume: w = $-P\Delta V$.[8] For reactions in solution the $P\Delta V$ work is usually negligible, and for ideal gases $P\Delta V$ = $\Delta nRT$, where $\Delta n$ is the change in number of mols of gas between reactants and products (Chapter 15).  For constant volume processes no expansion work is done and Eq. (13.1) shows that change in energy is equivalent to heat.

$$\Delta E = q_V \qquad (13.4)$$

Chemical reactions involve heat production and consumption as well as matter transformations.  **Enthalpy** is a measure of reaction heat at constant pressure and is related to energy by

$$H = E + PV \qquad (13.5)$$

Enthalpy is a thermodynamic state function of the state variables entropy, pressure and number of particles, H(S,P,N).  At constant pressure, $w = -P\Delta V$ and $\Delta H = \Delta E + P\Delta V = q - P\Delta V + P\Delta V = q$, or

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[8]  Pressure is force divided by area.  From classical mechanics, work is the integral of force across a distance (Eq. (5.10)).  For constant pressure sweeping out a volume equal to area times distance, the work done is $w = \int f dr = \int PA dr = P \int dV = P\Delta V$.

Doing work on a system by squeezing it decreases its volume ($\Delta V < 0$) and increases its energy (capacity to do work), so $\Delta E = -P\Delta V > 0$.

$$\Delta H = q_P \qquad (13.6)$$

In the case of chemical reactions involving ideal gases $P\Delta V = \Delta nRT$, Eq. (13.5) shows at zero kelvin, $\Delta H = \Delta E$, and at room temperature (300 K) they differ by $2.5\Delta n$ kJ/mol, a rather insignifi cant amount compared with the hundreds of kilojoules commonly associated with chemical reactions. Enthalpy is thus a measure of energy in the common situation of a reaction taking place in solution open to the atmosphere (which maintains constant pressure on the solution). For these reasons, the heat, enthalpy change and energy change of a chemical reaction are often not distinguished.

Reaction heats are measured in "calorimeters" based on the First Law. If a reaction takes place in a thermally isolated system containing water, the temperature change in the water indicates the heat change of the reaction. From Eq. (13.2)

$$\Delta E_{isolated} = 0 = \Delta E_{reaction} + \Delta E_{products} + \Delta E_{H_2O} + \Delta E_{calorimeter}$$

where $\Delta E_{isolated}$ is the total energy change for the isolated system of reactants, products, water and calorimeter. $\Delta E_{reaction}$ is the desired quantity, $\Delta E_{products}$ represents the energy absorbed by the products of reaction, equal to $m_{products} \times SH_{products} \times \Delta T$ (usually neglected if the products are gases or small in amount), $\Delta E_{H_2O}$ is the energy absorbed by the water and equal to $m_{H_2O} \times SH_{H_2O} \times \Delta T$, and $\Delta E_{calorimeter}$ equals $m_{calorimeter} \times SH_{calorimeter} \times \Delta T$, either assumed negligible or determined in accurate experiments by measurements with a reaction of known reaction energy. Knowledge of $m_{calorimeter} \times SH_{calorimeter}$, called the calorimeter constant, the mass of the water (and its specifi c heat, 4.1840 J/g-°C) allows one to determine the energy of reaction from the measured temperature change:

$$\Delta E_{reaction} = -[(m \times SH \times \Delta T)_{H_2O} + (m \times SH \times \Delta T)_{products} + (m \times SH \times \Delta T)_{calorimeter}] (13.7)$$

The determination of $\Delta E_{reaction}$ assumes the experiment is carried out at constant volume (a "bomb" calorimeter). Since the enthalpy is a thermodynamic state function as well, a calorimetry experiment carried out at constant pressure (such as open to the atmosphere) yields $\Delta H_{reaction}$.

**Example 13.3** Combustion of 1 mol of methane at 25 °C in a calorimeter open to the atmosphere and containing 10 kg water raises the temperature by 19.176 °C. What is the

molar heat of combustion of methane?

Assuming the calorimeter absorbs little heat (i.e. that the calorimeter constant is negligible) and that the products (carbon dioxide and water) absorb little heat, Eq. (13.7) written in terms of $\Delta H$ gives

$$\Delta H_{reaction} = -10,000 \text{ g} \times (\frac{4.1840 \text{ J}}{1 \text{ g } °C}) \times (19.176°C) \times (\frac{1 \text{ kJ}}{1000 \text{ J}}) = -802.3 \text{ kJ/mol methane}$$

$\Delta E_{combustion}$ differs from $\Delta H_{combustion}$ by $RT\Delta n_g$. For $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g)$, $\Delta n_g = 0$ and $\Delta E_{combustion} = \Delta H_{combustion} - RT\Delta n_g = \Delta H$
If the product is liquid water, then $\Delta n = -2$ and $\Delta E$ differs from $\Delta H$ by 5.0 kJ. It is appropriate that $\Delta H$ is negative, since burning methane (natural gas) produces heat (is exothermic).

The idea from the First Law that energy is independent of path (Section 13.2) suggests an algorithm for deriving equations describing the heat changes of chemical transformations. Consider the following figure with enthalpy plotted as a function of the progress of a reaction:
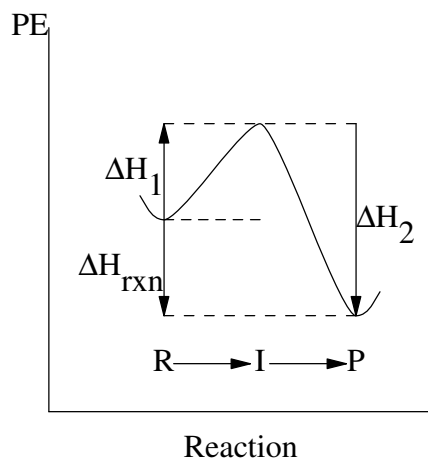


**Fig. 13.1** Potential Energy Change During Reaction

For chemical reactions, the initial state is the reactant state (R) and the final state is the product state (P). Going directly from the initial state to the final state involves a reaction enthalpy change, $\Delta H_{rxn}$. The indirect path going through intermediates (I) involves the sum of the enthalpy change in going from the reactants to intermediates, $\Delta H_1$, and the enthalpy change in going from the intermediates to products, $\Delta H_2$. Note the direction of the arrows in the figure indicate the direction from initial to final states.

The form of the First Law in terms of the enthalpy change for a process independent of path leads to the general relation:

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 \tag{13.8}$$

Eq. (13.8) can be generalized further to include more than two intermediate states, if necessary.

$$\Delta H_{rxn} = \sum_i^{\text{intermediates}} n_i \Delta \tilde{H}_i \tag{13.9}$$

where the tilde denotes enthalpy per one mol, or *molar enthalpy*.

One application of Eq (13.9) is to reactions that take place in several steps. Chemists are rarely able to produce the product they want in a single synthetic step. Direct paths between simple starting materials and complex products are not usually known. Similar to the multiple steps of a conversion factor process, the algorithms of chemical synthesis can involve many steps. Eq. (13.9) says that the heat of reaction of a process which takes place in a number of steps equals the sum of the heats of reaction of the intermediate steps. This relation was first demonstrated by Germain Hess in 1840, and is referred to as **Hess's Law**. If the steps of the reaction do not algebraically add up to the total reaction, the steps may be multiplied by factors causing intermediates to cancel and the resulting reactants and products to match the total reaction. This is similar to algebraic manipulations used to eliminate variables in systems of simultaneous linear equations (Section 3.9). Because heats attending reactions are proportional to the amounts of reaction, multiplying reactions by factors will multiply their heats by the same factors.

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**The Hess Law Algorithm**

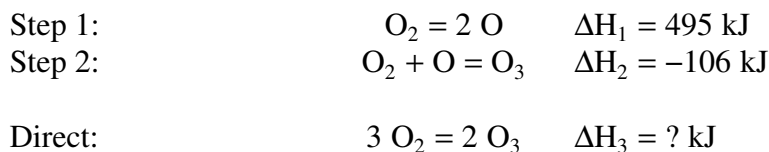Purpose: To determine the heat of a chemical reaction which is a combination of other reactions.

Procedure:

1. Write down balanced chemical equations for the direct and indirect processes of interest, including the heats of reaction for each reaction.

2. Multiply the indirect reaction equations and their heats by factors such that their sum equals that of the direct chemical equation.

3. The total heat for the direct reaction then equals the algebraic sum of the heats of the indirect reaction equations, multiplied by the factors needed in step 2.
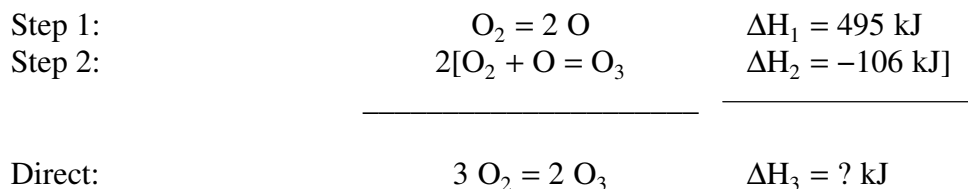
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One may use the resulting heat equation to solve for one unknown given values of all the remaining variables.

**Example 13.4** Dioxygen is converted in the atmosphere into ozone, $O_3$, by an indirect process in two steps that involves oxygen atoms as intermediate species. Given the heats of the intermediate steps, calculate the heat of direct conversion.

1.  The intermediate and direct steps and their heats are:

|          |                        |                          |
|----------|------------------------|--------------------------|
| Step 1:  | $O_2 = 2\,O$           | $\Delta H_1 = 495$ kJ    |
| Step 2:  | $O_2 + O = O_3$        | $\Delta H_2 = -106$ kJ   |
|          |                        |                          |
| Direct:  | $3\,O_2 = 2\,O_3$      | $\Delta H_3 = ?$ kJ      |

2.  The direct reaction has 3 $O_2$ molecules. There are several ways to combine the $O_2$ in Step 1 and Step 2 to add up to 3 $O_2$. But there is only one way (with smallest integers) which adds up to 3 $O_2$ and *eliminates* O atoms (intermediates), which don't appear in the direct equation.

|          |                         |                          |
|----------|-------------------------|--------------------------|
| Step 1:  | $O_2 = 2\,O$            | $\Delta H_1 = 495$ kJ    |
| Step 2:  | $2[O_2 + O = O_3$       | $\Delta H_2 = -106$ kJ]  |
|          | _____     | _____         |
|          |                         |                          |
| Direct:  | $3\,O_2 = 2\,O_3$       | $\Delta H_3 = ?$ kJ      |

3.  From the relation between the three reactions, we have

$$\Delta H_3 = \Delta H_1 + 2\,\Delta H_2 = 495 \text{ kJ} + 2\,(-106 \text{ kJ}) = 283 \text{ kJ}$$

## 13.5.  Heat and Stoichiometry

The sign of $\Delta H$ in the last example is positive. Since $\Delta$ signifies change from initial to final, $H_{final} - H_{initial} > 0$ or $H_{final} > H_{initial}$. In such a process, the enthalpy of the system increases and the change is said to be *endothermic* (heat goes in). The opposite case is *exothermic* (heat goes out or exits). There is an intuitive understanding about process which go "up hill" in energy (or enthalpy). They are not spontaneous. The example is consistent with the observation that ozone production is not spontaneous (lucky for us). On the other

hand, objects tend to roll down hill spontaneously, and chemical reactions which are exothermic are expected to be favorable (consider explosions). However, this is only half the story, the rest of which will be told in the section on reactions and thermodynamics (Section 13.10 below). You may wonder where the heat comes from and where it goes. Heat changes in chemical reactions are the result of breaking and forming *chemical bonds*, the forces which hold atoms together in molecules. Heat is absorbed from the surroundings or transferred to the surroundings by changing the kinetic energy of the molecules in the surroundings.

It is possible to include the heat (or energy) of reaction as a participant,

$$\text{Reactants} + \Delta H_{rxn} = \text{Products} \qquad (13.10)$$

where the sign has been chosen to be consistent with the notions of endo- and exothermicity. Because thermodynamic quantities are proportional to the amounts of substances they are associated with (*extensive* quantities), they can be treated like reactants or products in stoichiometry calculations. This suggests another extension to the Stoichiometry Mol Map with energy change or enthalpy change as an additional conversion factor.

**Example 13.5** How much enthalpy is consumed per mol of dioxygen in the conversion to ozone?

From example 13.4

$$1 \text{ mol } O_2 \times (\frac{283 \text{ kJ}}{3 \text{ mol } O_2}) = 94.3 \text{ kJ/mol } O_2$$

### 13.6. Reaction Heat from Heats of Formation

Conceivably, one can imagine breaking reactant molecules into smaller parts, such as elements, and then reforming the elements into products. The separated elements may be thought of as an *intermediate* state between the initial (reactant) and final (product) states. The intermediate state is analogous to a mountain pass. The analogy with gravity helps the understanding of chemical reactions in terms of the familiar. Chemists often refer to reacting molecules as "surmounting the reaction barrier".

Referring to Fig. 13.1 with intermediates as elements, Eq. (13.9) becomes:[9]

$$\Delta H_{rxn} = \sum_{i}^{products} n_i \Delta \tilde{H}_f(i) - \sum_{i}^{reactants} n_i \Delta \tilde{H}_f(i) \qquad (13.11)$$

where $n_i$ is the stoichiometric (balancing) coefficient of the i-th molecule in the chemical reaction, and $\Delta \tilde{H}_f$ is the **molar heat of formation** of reactant or product molecule. That is, $\Delta \tilde{H}_f$ *is the heat energy absorbed or released when one mol of molecules is formed from its elements*. Here the initial state is that of the elements and the final state is that of the compound. Consistent with the definition of $\Delta$ being the difference between initial and final states, $\Delta \tilde{H}_f$ is positive for molecular formations which absorb heat, and negative for those which release heat (and zero for "formation" of elements from themselves). Eq. (13.11) is quite useful, because the reaction energies of a multitude of chemical reactions can be calculated from a relatively small table of molar formation heats. An entry in the table for a molecule may be applied to any reaction involving that molecule.

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[9] It helps to recognize that the several reactants and several products are bridged by a single set of elements. Also note the signs of the terms, a result making the definition of heat of formation consistent with the direction of the arrows of Fig. 13.1.

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**Reaction Heats from Formation Heats Algorithm**

Purpose: To determine the heat of chemical reaction from heats of formation.

Procedure:

1. Write down the balanced chemical reaction for the process of interest.

2. The heat contribution of each substance in the reaction is the product of the molar heat of formation and the number of mols of that substance in the balanced reaction.

3. The reaction heat is the difference between the sum of heat contributions from step 2 for products, and the sum of heat contributions terms from step 2 for reactants (Eq. 13.11).

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**Example 13.6** Given the molar heats of formation at 298.15 K of methane, $CH_4$ (−74.81 kJ/mol), carbon dioxide, $CO_2$ (−393.51 kJ/mol) and water, $H_2O$ (−241.82 kJ/mol), calculate the heat of *combustion* of methane (to produce gaseous water at 298.15 K).

1. Combustion is reaction with oxygen:

$$CH_4 + 2\, O_2 = CO_2 + 2\, H_2O$$
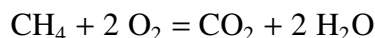
2. Step 2 can be combined with step 3 since reaction heat of the total reaction is sought.

3. From Eq. (13.11):

$$\Delta H_{combustion} = \Delta\tilde{H}_f(CO_2) + 2\, \Delta\tilde{H}_f(H_2O) - \Delta\tilde{H}_f(CH_4) - 2\, \Delta\tilde{H}_f(O_2)$$

$$\Delta H_{combustion} = (-393.51) + 2\,(-241.82) - (-74.81) - 2\,(0)\ kJ = -802.34\ kJ$$

in agreement with the calorimetric value of Example 13.3

## 13.7. Reaction Heats from Bond Energies

Heats of reaction involving covalent molecules can be estimated using Lewis structures of the participating molecules. Lewis structures give a description of the covalent bonds in a molecule. (See the Lewis Structure Algorithm in Section 12.5.) Each bond is isolated from

the remaining bonds. This picture of bonding suggests that a given bond between to atoms might have the same properties independent of the rest of the molecular environment. One of these properties is the bond dissociation energy, the energy required to *break* the bond.[10] Tables 12.1 and 12.2 and Fig. 12.12 in Section 12.10 on Bonding Strengths give selected diatomic and polyatomic molecule bond energies.

From bond energy values it is possible to estimate the energies of the participating molecules in a chemical reaction, and thus the energy change of the reaction. As discussed above, the heat of reaction can be estimated from $\Delta H = \Delta E + \Delta PV \approx \Delta E + RT\Delta n_{gas}$.

To compute the energy of a reaction from bond energy values, one adds up all the bond dissociation energies of reactants and products and takes the difference between total energy of products and reactants.[11]

$$\Delta E_{rxn} \approx \sum(\text{reactant bond energies}) - \sum(\text{product bond energies}) \qquad (13.12)$$

Note that this is an approximate equation (estimation) whereas Eq. (13.11) is exact.

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[10]  The energy to *form* a bond is the *negative* of the bond dissociation energy.

[11]  One may imagine breaking all the bonds of reactants and reforming the atoms into products. Since energy difference is independent of path according to the first law of thermodynamics, the energy for the direct conversion of reactants into products equals the energy to go from reactants to atoms (sum of bond dissociation energies or reactants) plus the energy to go from atoms to products (sum of *negative* bond dissociation energies).

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**Reaction Heats from Bond Energies Algorithm**

Purpose: To estimate the reaction energy of a given reaction from bond energies.

Procedure:

1. Write the Lewis structure for each molecule in the balanced reaction using the Lewis Structure Algorithm in Section 12.5.

2. Look up the molar bond dissociation energy for each type of diatom bond in each molecule (Tables 12.1 and 12.2).

3. Estimate the reaction energy as the difference between the sum of bond dissociation energies of all bonds among reactants and the sum of bond dissociation energies of all bonds among products (Eq. 13.12). Since bond energies are per mole of bond, multiply the number of bonds of each type in a molecule by the stoichiometric coefficients of the balanced reaction.

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**Example 13.7** Estimate the heat of formation of water.

1. Water is formed from its elements according to the reaction $H_2 + (1/2)O_2 = H_2O$. In terms of Lewis structures the reaction is $H{-}H + (1/2)\ O{=}O\ =\ H{-}O{-}H$.

2. From a table of bond energies, the molar bond dissociation energies are: $BE(H{-}H) = 436$ kJ, $BE(O{=}O) = 498$ kJ, $BE(O{-}H) = 467$ kJ.

3. Recognizing that there is one-half mole of dioxygen and one mole of water containing two moles of OH bonds,

$$\Delta E_{rxn} = [BE(H{-}H) + (1/2)BE(O = O)] - 2[BE(O{-}H)] = -249 \text{ kJ},$$

which is close to the experimentally measured heat of formation, $-242$ kJ. (The heat of formation adds only $-(1/2)RT = -(1/2)(2.5\ KJ) = -1.2$ kJ to the energy of formation.)

### 13.8.  The Second Law

A first law of thermodynamics suggests there might be a second law, and indeed there is. Historically, it was announced before the First Law in a little memoir by Sadi Carnot[12] at age 27 in 1823 titled "On the Motive Power of Heat." Joule's work showed that a great amount of energy is stored in "hidden" internal heat. For example, the equivalent of 430 kg (about half a ton) falling in the gravitational field for one meter raises the temperature of one gram of water one degree Celsius. If the process could be reversed (and it was in steam engines), hot water could produce large amounts of work. However, the conversion is never complete and some energy is dissipated. This is a consequence of the Second Law of Thermodynamics, one form of which says that it is impossible to convert a given amount of heat energy totally into work energy.

The second law of thermodynamics relates to a property of systems called the *entropy* (Greek *trope* for transformation), given the symbol S. The natural state variables for which entropy is a state function are energy, volume and number: S(E,V,N). The Second Law states that whenever any change occurs in an isolated system, the entropy of the system increases. Entropy changes are determined from experiments as accumulations of heat changes divided by (absolute) temperature.

$$\Delta S \equiv \int \frac{dq}{T} \qquad (13.13)$$

Two common changes are phase changes (such as melting) and heating (at constant temperature). The corresponding entropy changes attending these processes are

$$\Delta S_{\text{phase change}} = \frac{q_{\text{phase change}}}{T_{\text{phase change}}} \qquad (13.14)$$

$$\Delta S_{\text{heating}} = \int_{T_i}^{T_f} \frac{C_p}{T}\, dT = \int_{T_i}^{T_f} C_p\, d\ln T \approx C_p \ln\left(\frac{T_f}{T_i}\right) \qquad (13.15)$$

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[12] Said Carnot (French, 1796-1832), the son of Napoleon's Minister of War (L.M.N. Carnot who found relation expressing the work needed to raise an object in the gravitational field, mgΔh), was in a good position to consider practical applications of heat energy. Since his memoir was expressed in terms of the caloric (sub-

where $C_p$ is the molar heat capacity (Eq. (2.26b)), assumed to be constant over the temperature range, and

**Example 13.8** Calculate the change in entropy accompanying the heating of 1 mol of ice at 0 °C to steam at 100 °C. The heat of melting ice at 0 °C is 6.01 kJ/mol, the heat of vaporizing water at 100 °C is 40.67 kJ/mol. The molar heat capacity of liquid water varies with temperature, but can be assumed constant and equal to the value at 25 °C of 75.3 J/mol-K.

According to Eqs. 13.14 and 13.15

$$\Delta S_{total} = \Delta S_{melting} + \Delta S_{heating} + \Delta S_{vaporization}$$

$$= \frac{6,010 \text{ J/mol}}{273.15 \text{ K}} + \frac{75.3 \text{ J}}{\text{mol} - \text{K}} \ln\left(\frac{373.15 \text{ K}}{273.15 \text{ K}}\right) + \frac{40,600 \text{ J/mol}}{373.15 \text{ K}}$$

$$= 22.0 + 23.5 + 109.0 \text{ J/mol} - \text{K} = 154.5 \text{ J/mol} - \text{K}$$

This illustrates the magnitudes of entropy changes for various processes. Water is exceptional, however, as the entropy of vaporization of most substances is about 85 J/mol-K (Trouton's rule).

Absolute values of molar entropy are tabulated for a variety of substances. These values may be combined to calculate the change in entropy in chemical reactions according to a formula similar to Eq. 13.11:

$$\Delta s_{rxn} = \sum_{i}^{products} n_i \tilde{S}_f(i) - \sum_{i}^{reactants} n_i \tilde{S}_f(i) \qquad (13.16)$$

**Example 13.9** Given the molar entropies at 298.15 K of methane, $CH_4$ (186.26 J/mol-K), dioxygen, $O_2$ (205.14 J/mol-K), carbon dioxide, $CO_2$ (213.74 J/mol-K) and water, $H_2O$ (188.83 J/mol-K), calculate the entropy of *combustion* of methane (to produce gaseous water at 298.15 K).

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stance) theory of heat (which he himself subsequently rejected), it was largely ignored.

Combustion is reaction with oxygen:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$
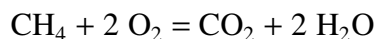
From Eq. (13.16):

$$\Delta S_{combustion} = \tilde{S}(CO_2) + 2\ \tilde{S}(H_2O) - \tilde{S}(CH_4) - 2\ \tilde{S}(O_2)$$

$$\Delta S_{combustion} = (213.74) + 2\ (188.83) - (186.26) - 2\ (205.14)\ J/mol - K = -5.14\ J/mol - K$$

This is not a very large value, as would be expected since there are equal numbers of mols of reactant and product gases (3 mols) and there should not be much difference in the disorder of the system as it passes from reactants to products.

## 13.9.  Boltzmann Distributions

Both laws of thermodynamics were given sound theoretical explanations in the last quarter of the nineteenth Century by Clerk Maxwell (of electromagnetic theory fame) and Ludwig Boltzmann,[13] in terms of the kinetic molecular theory.

The kinetic molecular theory provided a mechanical explanation for heat in terms of molecular motion, thus establishing a link between the energy of the first law of thermodynamics and the energy of dynamics. Boltzmann subsequently sought a mechanical explanation for entropy (the fundamental state variable of the second law of thermodynamics) and determined that *entropy is a measure of disorder*, by quantitatively expressed the relation which bears his name:[14]

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[13] Ludwig Eduard Boltzmann (Austrian, 1844-1906) made a goal to find a mechanical explanation for entropy as Maxwell had for energy through the kinetic-molecular theory. After years of labor he finally arrived at his the relation between disorder and entropy. Boltzmann stood alone against the physics community in defending the atomic theory when it came into question at the end of the Nineteenth Century. Despondent over the loss of his sister to leukemia and depressed with his defense of the atomic theory, he committed suicide just as Albert Einstein was reaffirming the atomic theory through his work on Brownian motion. Boltzmann's relation is engraved on his tomb in Vienna.

[14] Boltzmann's equation is another relationship dealing with the transport or flux of matter and energy.

$$S = k \ln \Omega \qquad (13.17)$$

where $\Omega$ (omega) represents the number of possible arrangements of the system for a given macroscopic state, and the proportionality constant k is a universal constant, called Boltzmann's constant, equal to $1.38066 \times 10^{-23}$ J/molecule-K. For systems composed of N independent subsystems (such as independent molecules in the gas phase), the number of possible arrangements of the total system is a product of the number of possible arrangements of each subsystem, and $S = Nk \ln \Omega$. Since the number of mols $n = N/N_A$, where $N_A$ is Avogadro's number, $Nk = nN_A k \equiv nR$ (Sec. 2.2), where R has the value 8.314510 J/mol-K.[15]

$$S = nR \ln \Omega_{\text{independent subsystem}} \qquad (13.18)$$

As the number of states available to a system increases, the number of possible arrangements increases and the *disorder* increases. Entropy can thus be thought of as a measure of the disorder of a system. Note that, unlike energy, entropy is an absolute quantity, with value zero for perfectly ordered systems ($\Omega = 1$).

According to Boltzmann's interpretation, the **Second Law of Thermodynamics** states that *isolated systems spontaneously become more disorganized*.

$$\Delta S_{\text{isolated}} > 0 \qquad (13.19)$$

Entropy has an intuitive meaning in common occurrences of gases escaping from containers by diffusion, erosion, rusting and other natural processes.[16] One might argue that growing organisms become spontaneously more organized, but Erwin Schrödinger showed

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[15] This is the value of R in heat energy units. An alternative value may be obtained in work energy units of R = 0.082057 L-atm/mol-K, using conversion factors. Since R was first discovered in connection with gas properties, it is called the molar gas constant.

[16] Ashes to ashes and dust to dust. Imagine what happens when a small child is placed before a pile of neatly stacked blocks.

that when the source of energy is included (the sun), the net entropy of the *total* system increases. In fact, organizing systems are the *exception* rather than the rule in nature. Humans do refine ores and manufacture plastics from petroleum, but from a larger perspective, more randomness is produced in the environment than organization is gained in the products. On a grand scale, the second law of thermodynamics says that the universe (which is an isolated system by definition) is always running down, leading eventually to a "heat death"![17]

**Example 13.10** Gas molecules are mobile and their number of arrangements is proportional to their available volume. The entropy of expansion into a larger volume of n mols of a gas from $V_{initial}$ to $V_{final}$ may be seen from Eq. (13.18) to be

$$\Delta S_{expansion} = nR \ln(\frac{V_{final}}{V_{initial}}) \tag{13.20}$$

Numerically, doubling the volume of one mole of gas increases the entropy by 8.31441 ln (2) = 5.763 J/mol-K.

**Example 13.11** Mixing substances together increases their disorder. Using the fact that the disorder increases with the number of molecules, the entropy of mixing can be derived from Eq. (13.17)

$$\Delta S_{mixing} = S_{mixed} - S_{unmixed} = (n_1 + n_2 + \dots)R \ln(n_1 + n_2 + \dots) - [n_1 R \ln(n_1) + n_2 R \ln(n_2) + \cdots]$$

$$\Delta S_{mixing} = - \sum_i n_i R \ln(\frac{n_i}{n}) \tag{13.21}$$

where $n_i$ is the mols of substance i, and n is the total mols, $n = \sum_i n_i$. Thus the mixing of one mol each of two substances increases their entropy by 2R ln(2) = 11.526 J/mol-K.

Temperature is defined in thermodynamics as the ratio of change in energy to change in entropy at constant volume and amount of matter.

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[17] This pessimistic notion inspired the ending to H. G. Well's science fiction classic, *The Time Machine*, and the nihilistic (Latin *nihil* for nothing) suicide movement of the late Nineteenth Century. General relativity allows for three scenarios of the fate of the universe, continual expansion, oscillation between expansion and contraction, and steady state. So far, observations have not provided definitive evidence in favor of any of the scenarios.

$$T \equiv \frac{\Delta E}{\Delta S} \qquad (13.\,22)$$

According to the kinetic molecular theory, *molecules distribute their energy via encounters with their neighbors (collisions).* **Boltzmann's distribution function** (Eq. 13.23) can be derived from the thermodynamic defi nition of temperature and Boltzmann's equation for entropy. The distribution of thermal energy follows a very simple, but general law, derived for kinetic energy by Clerk Maxwell and more generally by Ludwig Boltzmann. The law states that *the fraction of a population of molecules possessing energy E above some ground state is a decreasing exponential function of the ratio of the energy to absolute temperature T.* It may be derived from Eqs. (13.17) and (13.22) by noting that the fraction f of molecules in a given state is inversely proportional to the number of possible arrangements. Hence (with A representing the proportionality constant)

$$\Delta S = k \ln(A/f) = \frac{\Delta E}{T}$$

which gives, on rearrangement, with E measured relative to E = 0

$$f(E) = Ae^{-E/kT} \qquad (13.\,23)$$

where e is the base of natural logarithms. The proportionality constant A can be determined from the fact that the the sum of a discrete distribution function (or integral of a continuous distribution) over all possible states must equal unity (i.e. the distribution is *normalized*). Thus, $\sum f = A \sum e^{-E/kT} = 1$, and

$$A = \frac{1}{\sum e^{-E_i/kT}} \rightarrow \frac{1}{\int e^{-E/kT}}$$

Therefore

$$f(E_i) = \frac{e^{-E_i/kT}}{\sum e^{-E_i/kT}} \rightarrow f(E) = \frac{e^{-E/kT}}{\int e^{-E/kT}} \qquad (13.24)$$

where the arrow indicates the transition from a discrete (quantum) distribution to a continuous (classical) distribution. Boltzmann's distribution law applies to a wide range of phenomena, as we shall see. For example, it is the basis of the distribution of intensities of spectroscopic lines based on state populations discussed in Section 12.13. Note that the Boltzmann distribution function is a proper fraction (<1) for positive E (k and T are always nonnegative), meaning smaller population at higher energy.

**Example 13.12** The pressure of the atmosphere, due to molecular density, is known to fall off exponentially with altitude:

$$p(h) = p_0 e^{-(\frac{mgh}{kT})} \qquad (13.25)$$

$p_0$ is the pressure at sea level, defined to be one atmosphere unit (76 cm of mercury barometric pressure). The gravitational potential energy is mgh, where m is the mass of an object at height h, and g is the gravitational proportionality constant, 9.80665 $m/s^2$ (Cf. the discussion of Newton's law of gravitation in Section 5.2). The average molecular mass m of Earth's atmosphere (80% $N_2$ and 20% $O_2$) is 29.

## 13.10.  Chemical Thermodynamics

Building on the foundation laid by Maxwell and Boltzmann, the American mathematician Josiah Willard Gibbs[18] developed a thermodynamic quantity that is more appropriate to chemistry than either energy or entropy. It is called the **free energy**, and given the symbol G in honor of Gibbs. Free energy combines energy and entropy into a single term related to the direction of reactions:

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[18] Josiah Willard Gibbs (American, 1839-1903), considered to be the greatest native-born American scientist, a recluse at Yale University who published in an obscure Connecticut Journal. His work went largely unnoticed, but today he is considered to have addressed every major problem in statistical mechanics, the modern form of the kinetic molecular theory.

$$G \equiv H - TS \qquad (13.26)$$

At a given temperature T, the change in free energy is

$$\Delta G = \Delta H - T\Delta S \qquad (13.27)$$

G is a state function of the state variables temperature, pressure and number, G(T,P,N), which makes it appropriate to chemical reactions taking place under the common conditions of fixed temperature and pressure.

Free energies of reaction can be obtained from tables of molar formation free energies in the same way as enthalpies.

$$\Delta G_{rxn} = \sum_{i}^{products} n_i \Delta \tilde{G}_f(i) - \sum_{i}^{reactants} n_i \Delta \tilde{G}_f(i) \qquad (13.28)$$

**Example 13.13** Given the molar free energies of formation at 298.15 K of methane, $CH_4$ (−50.72 kJ/mol), carbon dioxide, $CO_2$ (−394.36 kJ/mol) and water, $H_2O$ (−228.72 kJ/mol), calculate the free energy of *combustion* of methane (to produce gaseous water at 298.15 K).

Combustion is reaction with oxygen:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$
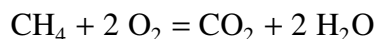
From Eq. (13.28):

$$\Delta S_{combustion} = \Delta \tilde{G}_f(CO_2) + 2\ \Delta \tilde{G}_f(H_2O) - \Delta \tilde{G}_f(CH_4) - 2\ \Delta \tilde{G}_f(O_2)$$

$$\Delta G_{combustion} = (-394.36) + 2\ (-228.72) - (-50.72) - 2\ (0)\ kJ = -801.08\ kJ$$

From Eq. (13.27) and the result of Example 13.8 (noting that entropy is measures in Joules whereas energy is measured in kJ)

$$\Delta G = \Delta H - T\Delta S = -802.34 - 298.15 \times 5.14 \times 10^{-3} = -803.87$$

The discrepancy indicates the uncertainty in the reported experimental values.

A consequence of the *combined first and second laws* is that *favorable processes are accompanied by negative changes in free energy*. Free energy is appropriate to chemical processes taking place under constant temperature and pressure. The combination of exothermicity ($\Delta H < 0$) and increased entropy ($\Delta S > 0$) yields negative $\Delta G = \Delta H - T\Delta S$ at all temperatures. Conversely, endothermic processes ($\Delta H > 0$) accompanied by increased entropy ($\Delta S > 0$) require the temperature to be high enough for the $T\Delta S$ term to dominate over the $\Delta H$ term to be favorable ($\Delta G < 0$). This is displayed graphically in Fig. 13.2.
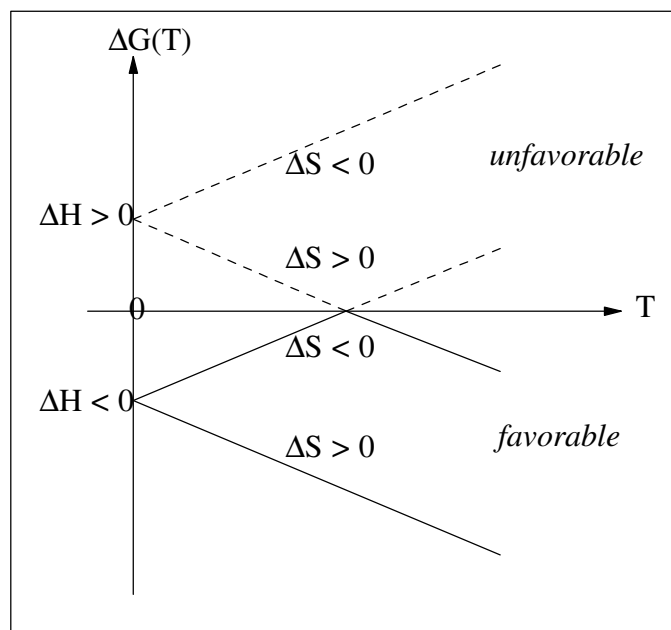


**Fig. 13.2** Conditions for Favorable ($\Delta G < 0$) and Unfavorable ($\Delta G < 0$) Processes

**Example 13.14** Discuss the solubility of dioxygen ($O_2$) in water.

Dioxygen is a non-polar molecule while water is polar. By the Solubility Heuristic of Chapter 17, dioxygen is not expected to be very soluble in water.

From a thermodynamic point of view, one expects the heat of solution of dioxygen in water to be negative due to intermolecular attractions. However the attractions are due to dispersion only (see Chapter 14) and not expected to be very large. Dissolved dioxygen is expected to have a smaller entropy than gaseous dioxygen because the solution is more ordered, so $\Delta S_{solution}$ is a negative quantity, and $-T\Delta S_{solution}$ is a positive quantity. Thus the two contributions to the free energy of solution of dioxygen in water are of opposite sign. Solubility is aided by the enthalpy of solution but hindered by the entropy of solution.

At room temperature, $\Delta H_{solution}$ = −12 kJ/mol, $T\Delta S_{solution}$ = +28 kJ/mol for the dissolution of dioxygen in water, and the net $\Delta G_{solution}$ = +16 kJ/mol. Since the enthalpy of solution is a relatively small quantity, entropy dominates the situation as the temperature increases. Solution is not very favorable. The measured solubility of dioxygen in water is $3 \times 10^{-4}$ M at room temperature, which is 5 parts per million (ppm).[19] This is all there is to support aquatic life. Heated water has even less dissolved dioxygen, leading to *thermal pollution*.

## 13.11. Statistical Thermodynamics

Mathematical statistics deals with *distributions*, or collections which can be grouped into subcollections. For example the age distribution of a population of humans would be expressed in terms of the number of people (or equally well the fraction of people in the population) in each increment of age. The size of the increments could be narrow, such as each second of age, or broad, such as each decade of years. Narrow increments tend to produce larger fluctuations in measured distributions than broader increments. The *distribution function* is a representation of the number (or the fraction) of items in the collection as a function of the independent variable(s). As with most numerical relationships a distribution may be represented equivalently as a table, a graph, or a formula. Note that it is typical that

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[19] Since the solution is dilute, its density is close to that of water:

$$\frac{3 \times 10^{-4} \text{ mol O}_2}{1 \text{ L solution}} \left(\frac{1 \text{ L}}{10^3 \text{ mL}}\right)\left(\frac{1 \text{ mL}}{1 \text{ g H}_2\text{O}}\right)\left(\frac{18 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}\right) = \frac{5 \times 10^{-6} \text{ mol O}_2}{1 \text{ mol H}_2\text{O}} = \frac{5 \text{ mol O}_2}{1 \times 10^6 \text{ mol H}_2\text{O}}$$

distributions apply to large numbers of members in the collection. The fraction of a population in some range is equivalent to the probability of selecting a member at random from the population and finding that it belongs to that range.

Probability theory can be used to model distributions. Consider a coin having two sides, labeled heads (H) and tails (T). If the coin is perfectly symmetrical ("fair"), the probability of a thrown coin landing with the heads face up is the same as landing tails up. After many (N) tosses, one would expect heads to appear about half the time (N/2 times) and tails half the time (N/2 times). As the number of tosses (N) increases, one would expect the observed fractions to approach the theoretical values. In general, the probability of a given outcome may be thought of as the fraction of ways that outcome can be realized out the total number of possible arrangements, and the sum of the probabilities of all arrangements is unity. This suggests that theoretical probabilities can be calculated by counting possibilities. In the case of the coin, heads or tails are the only possibilities considered. Thus the total number of arrangements is two and the number of ways heads or tails can be realized is one, so the probability of heads is 1/2 and the probability of tails is 1/2.

Now consider tossing two coins. The total possible outcomes are four: HH, HT, TH, TT with a probability of 1/4 for each possibility. Note that the probability of two events that are independent of each other is the product of the probabilities of the component events.[20] This is a general rule: *mutually independent probabilities multiply*. Also note that independence means that tossing two coins simultaneously produces the same results as tossing one coin two times.[21] Grouping the collection into similar subgroups generates various distribution functions. If the coins are distinguishable (colored or numbered, say), the distribution is uniform (constant), with four equal fractions of 1/4. If the coins are indistinguishable the TH outcome is equivalent to the HT outcome and the distribution of probabilities as fractions of the possible outcomes is 1/4 for two heads, 2/4 for one head and one tail, and 1/4 for two tails. Note the example of another general rule: *indistinguishable probabilities add*. The principles of the coin example can be extended to a larger number of coins, and to other systems as well.

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[20] E.g. if p represents probability, $p(HT) = p(H) \times p(T) = 1/2 \times 1/2 = 1/4$.

[21] The general idea of time averages being equivalent to space averages is called *ergodicity*, and plays an important role in modern science.

Application of the methods of statistics to thermodynamic systems leads to the field of *statistical thermodynamics* (or more broadly, statistical mechanics). This powerful field of science was invented by Boltzmann and Willard Gibbs around the turn of the Twentieth Century. We will derive some of the fundamental formulas of statistical thermodynamics. First let us derive Boltzmann's relation (Eqn. 13.17). Consider a system made of a number of subsystems, numbered 1 and 2, ... having entropies $S_1$ etc. Let $\Omega_1$, $\Omega_2$, etc. represent the number of ways each subsystem can be rearranged without altering its macroscopic state. The entropy is considered to be some function of the number of arrangements consistent with the state of the system, $S_1 = f(\Omega_1)$, etc. If the subsystems are independent, the number of arrangements of the total system is the product of the number of arrangements of each independent subsystem, while the entropy of the combined system is the sum of the entropies of the separate subsystems.

$$\Omega = \Omega_1 \Omega_2 \cdots$$

$$S = S_1 + S_2 + \cdots$$

Since entropy is a function of arrangements, we seek that functional form for which the product of the arguments produces a sum of functional values. The logarithm function has just that property (the logarithm of a product is the sum of the logarithms of the multiplicands). Thus

$$S = k \ln(\Omega) + b$$

is the general expression. By definition, the entropy of a perfectly arranged system is zero, so $S = k \ln(1) + b = 0 + b = 0$ and $b = 0$. This is consistent with a "third" law of thermodynamics which states that the entropy of a system at absolute zero of temperature (where presumably all motion ceases) has a value of zero.

A modern interpretation of entropy developed from the field of *information science*, founded by Claude Shannon at Bell Laboratories in 1947. Shannon was interested in understanding corruption of communications signals during transmission. The resulting model, called *information theory*, like thermodynamics, is very general and finds significant applications in computer science, economics and probability theory. Here is a brief treatment.

Consider a situation, or system with two states. It could be a question which could be answered *yes* or *no*, a coin with *heads* and *tails*, a statement which is *true* or *false*, a digital computer memory bit with state *on* or *off*, etc. If the system is known to be in one of the

possible states, then one has gained some information about the system, exactly one *bit* of information. Note that the information gained, $I_{gained}$, can be expressed as

$$I_{gained} = I_{final} - I_{initial} = \lg(2^1) - \lg(2^0) = 1 \text{ bit}$$

where lg stands for the logarithm in the base 2 (i.e. the set of digits {0,1}). (Recall that the logarithm of a number in any base is the power of the number in that base.) In terms of the probability, the system is in one state half the time, so the probability of being in one state is 1/2. The information gained can be expressed in terms of this probability as

$$I_{gained} = -[\frac{1}{2} \lg(\frac{1}{2}) + \frac{1}{2} \lg(\frac{1}{2})] = -[\frac{1}{2}(-1) + \frac{1}{2}(-1)] = 1 \text{ bit}$$

Now consider a four-state system, perhaps one whose state is determined by answering two yes/no questions, two coins, two true/false statements, a two-bit computer word, etc. If the system is known to be in just one of the possible states, then one has gained some information about the system, namely two bits of information. Note that the information gained can now be expressed in terms of possible arrangements and in terms of probabilities as

$$I_{gained} = \lg(2^2) - \lg(2^0) = -[\frac{1}{4} \lg(\frac{1}{4}) + \frac{1}{4} \lg(\frac{1}{4}) + \frac{1}{4} \lg(\frac{1}{4}) + \frac{1}{4} \lg(\frac{1}{4})] = 2 \text{ bits}$$

Extending the situation to an N-state system,

$$I_{gained} = \lg(2^N) = -\sum^{2^N} \frac{1}{2^N} \lg(\frac{1}{2^N}) = N \text{ bits} \tag{13.29}$$

that is, N bits of information are gained by knowing the system is in a particular state out of $2^N$ possibilities. Note the similarity with Boltzmann's relation Eq. (13.17) where $2^N$ would be the number of possible states of a thermodynamic system.

In probability theory, one identifies the probability p of a state as the number of favorable realizations of the state out of the total possibilities. Probabilities are fractions summing to unity (something must be probable). In the previous examples each state is equally probable, equal to $1/2^N$. When there is a range of probable states for a system, with $p_i$ being the probability that the system is in state i, the average information gained is defined to be

$$I_{gained} \equiv - \sum_i p_i \ln(p_i) \qquad (13.30)$$

where the sum is over all the probability possibilities.[22]

The connection between information theory and thermodynamics is made by identifying entropy S with the *lost* information $I_{lost}$ as a system randomizes. But the information *lost* when a a system *randomizes* is identical to the information *gained* when a system when a system *organizes*. Thus $S = I_{lost} = I_{gained}$ and

$$S = - \sum_i p_i \ln(p_i) \qquad (13.31)$$

The Boltzmann distribution, Eq. (13.24), gives the probability $p_i$ of being in energy state $E_i$. In statistical mechanics it is customary to call the inverse of the normalization factor in Eq. (13.24) the *partition function*, Q, as it describes how the energy is partitioned among the possible energy states.

$$Q = \sum e^{-E_i/kT} \rightarrow Q = \int e^{-E/kT} \qquad (13.32)$$

First we note that the average energy of the system, E, can be obtained from the general defi - nition in probability theory of the average value <x> of a set of x values $\{x_i\}$ in terms of a distribution $f(x_i)$ of the values,[23]

$$< x > \equiv \frac{\sum_i x_i f(x_i)}{\sum_i f(x_i)} \qquad (13.33)$$

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[22] The base of the logarithm is not important becauses a change of logarithm base only introduces a constant conversion factor.

Noting that (cf. Section 3.11 on calculus)

$$\frac{d\ln(Q)}{dT} = \frac{1}{Q}\frac{dQ}{dT} = \frac{1}{Q}\frac{d}{dT}(\sum_i e^{-E_i/kT}) = \frac{1}{Q}\sum_i \frac{E_i}{kT^2} e^{-E_i/kT} \tag{13.34}$$

$$E = \sum_i E_i e^{\frac{-E_i}{kT}} = kT^2[\frac{\partial\ln(Q)}{\partial T}]_{N,V} \tag{13.35}$$

Applying the distribution $p_i = e^{E_i/kT}/q$ to $S = -k\sum p_i \ln(p_i)$ gives the fundamental relationship of statistical thermodynamics:[24]

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[23]  Consider a class average of grades $g_i$ or a grade point average

$$<\text{grade}> = \frac{\sum\limits_i g_i f(g_i)}{\sum\limits_i f(g_i)} = \sum_i g_i f(g_i)$$

where $g_i$ is the grade of each person in a class and $f(g_i)$ is the fraction of the class membership in the case of a class average, or the numerical value of a grade and $f(g_i)$ is the fractional number of each grade in the case of a GPA.

[24]

$$S = -k\sum_i p_i \ln(p_i) = -k\sum_i \frac{e^{-E_i/kT}}{Q}\ln(\frac{e^{-E_i/kT}}{Q})$$

Expanding the logarithm term and bringing constant (unsubscripted) terms outside the summation

$$S = -\frac{k}{Q}\sum_i e^{-E_i/kT}(-E_i/kT - \ln(Q)) = \frac{1}{QT}\sum_i E_i e^{-E_i/kT} + \frac{k\ln(Q)}{Q}\sum_i e^{E_i/kT}$$

we can see from Eq. (13.34) that

$$S = kT(\frac{d\ln(Q)}{dT}) + k\ln(Q)$$

$$S = k \ln(Q) + kT[\frac{\partial \ln(Q)}{\partial T}]_{N,V} \qquad (13.36)$$

The $\partial$ (partial derivative) symbol simply means the derivative is taken with respect to T only (i.e. holding N and V constant). This rather formidable equation holds the key to calculating all the properties of a thermodynamic system, given an expression for the partition function.

To apply these expressions to molecular systems we note that for independent subsystems, energies are essentially additive (Eq. (12.10)) and partition functions are multiplicative over the subsystems.[25] Thus a solid containing N independent vibrations has a total partition function

$$Q_{solid} = q_{molecule}^{N}$$

and an ideal gas containing N molecules has a total partition function[26]

$$Q_{gas} = \frac{q_{molecule}^{N}}{N!} \approx (q_{molecule} \frac{e}{N})^{N}$$

(The approximation is called Stirling's approximation for the factorial.) Non-ideal gases and liquids have intermolecular interactions and do not behave as independent particles, making their study more difficult.

The energy states of a molecule can be partitioned into translational, rotational and vibrational motions (called *degrees of freedom*). Since the energy contributions to the total energy of a molecule are additive, the partition function becomes the product

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[25] This follows from the definition of Q as a summation over all possible states:

$$Q = \sum_{i} e^{E_i/kT} = \sum_{i} e^{(\varepsilon_{i1} + \varepsilon_{i2} + \cdots)/kT} = \sum_{i} \prod_{j} e^{\varepsilon_{ij}/kT} = \prod_{j} \sum_{i} e^{\varepsilon_{ij}/kT} = \prod_{j} q_i$$

[26] The N! term takes into account the fact that exchanging all N (identical) molecules should produce the same state as if they weren't exchanged, so the summation over states in the partition function overcounts the states by the number of ways N objects can be permuted (the first can be placed in N positions, the second in N-1 positions left, ... = N(N-1)... = N!).

$$q_{molecule} = q_{translation}q_{rotation}q_{vibration}q_{electronic}$$

For a molecule containing a atoms, there are 3 degrees of translational freedom (for motion in 3D space), and depending on whether the molecule is linear or non-linear, there are 2 or 3 rotational degrees of freedom and 3a−5 or 3a−6 degrees of vibrational freedom. Molecules can have any number of electronic states but unusually only the lowest is occupied at temperatures less than thousands of degrees.[27] Starting with energy expressions from quantum mechanics given in Section 12.11, it is possible to derive the following results

**Table 13.1 Statistical Thermodynamical Functions**

| Degrees of Freedom | $q$ | $\Theta$ | $E = kT^2[\frac{\partial \ln(Q)}{\partial T}]_{N,V}$ | $S = k\ln(Q) + \frac{E}{T}$ |
|---|---|---|---|---|
| t = 1−3 translation | $(\frac{T}{\Theta_t})^{t/2}L^t$ | $\frac{h^2}{2\pi mk}$ | $\frac{t}{2}RT$ | $R\ln\left[(\frac{T}{\Theta_t})^{t/2}e^{5/2}\frac{V}{N}\right]$ |
| r = 2,3 rotation | $\frac{1}{\pi\sigma}\prod^r(\sqrt{\pi}\frac{T}{\Theta_r})^{1/2}$ | $\frac{h^2}{8\pi^2 kI_i}$ | $\frac{r}{2}RT$ | $R\ln[\frac{e^{r/2}}{\pi\sigma}\prod^r(\sqrt{\pi}\frac{T}{\Theta_r})^{1/2}$ |
| v = 3a−5,6 vibration | $\prod^v\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}$ | $\frac{h\nu}{k}$ | $RT\sum^v[\Theta_v/2T + \frac{\Theta_v/T}{e^{\Theta_v/T}-1}]$ | $R\sum^v[\frac{\Theta_v/T}{e^{-\Theta_v/T}-1} - \ln(1-e^{-}$ |
| e > 0 electronic | $\sum^e g_e e^{-\Theta_e/T}$ | $-\frac{D_e}{k}$ | $-D_e$ | $R\ln(g_e)$ |

where the molecular parameters are: $\sigma$ is the number of equivalent orientations of the molecule (symmetry), L is the length of the container, I is the rotational molecular moment of inertia, m is the molecular mass, $\nu$ is the molecular vibrational frequency, and $g_e$ is the electronic degeneracy (number of equivalent energy states). The remaining parameters are universal constants: k (Boltzmann's constant), and h (Planck's constant). There are two

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[27] Molecules absorb photons which elevate them to excited electronic levels. Colored molecules (like elemental purple iodine) absorb visible photons suggesting low-lying excited electronic levels according to the Planck-Einstein equation, Eq. (7.5) (cf. Example 7.5).

variables on which the quantities depends, absolute temperature T and V ($d^3$), where $V = \dfrac{NkT}{P}$ for an ideal gas. $\Theta$ is a "thermodynamic temperature" indicating the temperature at which the motion is activated (except in the case of translation, the only external motion degree of freedom, for which $\Theta$ depends has units of temperature times length$^{t/6}$). Typical values are $\Theta_{translation} = 10^{-15}$ cm$^2$K, $\Theta_{rotation} = 10^1$ K, $\Theta_{vibration} = 10^3$ K, $\Theta_{electronic} = 10^5$ K, $\Theta_{nuclear} = 10^7$ K. Thus molecules are in thermal translation at essentially all temperatures, rotating at room temperature (300 K), vibrating in flames (1,000 K), electronically excited and possibly ionized at the surface of the sun (6,000 K) and their elements undergoing thermonuclear reactions in the interior of the sun ($10^7$ K).

Values of the parameters needed to evaluate the statistical mechanical expressions in Table 13.1 can be derived from optical spectroscopy (microwave for rotational parameters, infrared for vibrational parameters, ultraviolet for electronic parameters). See Section 12.13. Table 13.2 lists typical values for gases. Note that homonuclear diatomics and water have a symmetry number of 2 (2 equivalent orientations), and that systems with paired electrons have singlet ground electronic states while dioxygen with unpaired electrons has a triplet electronic ground state. In the case of carbon dioxide, the product of the three $\theta_r$ values is listed (all that is needed for the equations in Table 13.1), and for methane the number of degenerate vibrational $\theta_v$ values are given in parentheses (note there are 3a−6 = 9 vibrational degrees of freedom). Finally, it is easy to see that electronically excited states are going to contribute negligibly to the thermodynamic properties of most molecules at room temperature.

**Table 13.2 Statistical Thermodynamical Parameters**

| Species | $D_0$(kJ/mol) | $\sigma$ | $\theta_r$/K | $\theta_v$/K | $g_e$ | $\theta_e$/K |
|---------|--------------|----------|----------|----------|-------|----------|
| $H_2$ | 432.07 | 2 | 87.547 | 6338.3 | 1 | 179,000 |
| $N_2$ | 941.1 | 2 | 2.875 | 3392.01 | 1 | 180,800 |
| $O_2$ | 491.89 | 2 | 2.079 | 2273.64 | 3 | 140,100 |
| $Cl_2$ | 239.216 | 2 | 0.3456 | 807.3 | 1 | 133,300 |
| HCl | 427.77 | 1 | 15.2344 | 4301.38 | 1 | 136,700 |
| $CO_2$ | 1596.23 | 2 | 0.56167 | 960.10 | 1 | 112,400 |
| $H_2O$ | 917.77 | 2 | 13.4 | 2294.27 | 1 | 117,300 |
| | | | 20.9 | 5261.71 | | |
| | | | 40.1 | 5403.78 | | |
| $CH_4$ | 1640.57 | 12 | 435.6 | 1957.0(3) | 1 | 136,300 |
| | | | | 2207.1(2) | | |
| | | | | 4196.2(1) | | |
| | | | | 4343.3(3) | | |

These statistical thermodynamic results are justified by comparing calculated thermodynamic quantities with experimental values.

**Example 13.15** Calculate the statistical thermodynamic entropy of water at 300 K and one atmosphere pressure and compare with the experimental value of 188.83 J/mol-K.

Water has the parameter values $\Theta_{t=3} = 1.6933 \times 10^{-15}$ cm$^2$ K, $\Theta_{r=3} = 13.4$, 20.9, 40.1 K, $\Theta_{v=3} = 2290$, 5160, 5360 K, $\sigma = 2$ (two equivalent orientations in space), $\omega_e = 1$ (no electronic degeneracy in the ground state), $g_e = 1$. Applying the formulas in Table 13.1, and noting that $V = d^3 = 22{,}414 \times \dfrac{300}{273}$ cm$^3$ (the molar volume of an ideal gas at 300 K), the contributions are

$$S = S_{translation} + S_{rotation} + S_{vibration} + S_{electronic} = 144.93 + 43.83 + 0.031 + 0 = 188.79 \text{ J/mol} - \text{K}$$

which compares very favorably with the experimental value.

There is enough information in Tables like 13.1 and 13.2 to calculate quantities of chemical experimental interest, such as the heat of combustion of methane. In fact, thermodynamic quantities calculated from statistical thermodynamics were considered so accurate that the U.S. military decided in the 1960s that developing computers to calculate theoretical values would be cheaper than building instruments to obtain experimental values. The resulting classic JANAF (Joint Army, Navy, Air Force) Thermodynamic Tables became another example of theory replacing experiment.[28]

*Summary*

The laws of thermodynamics state that energy is conserved, or independent of path, and that entropy (disorder) always increases for isolated processes. Thermodynamic energy, entropy and temperature have microscopic interpretations in terms of the mechanics of motion and disorder.

Thermochemistry deals with two derivatives of the laws of thermodynamics, enthalpy and free energy. Tables of thermodynamic formation values can be combined to give thermodynamic values for process, including chemical reactions. The thermodynamic free energy, which is a combination of energy and entropy gives a quantitative measure how far a reaction proceeds to completion.

Statistical thermodynamics provides an accurate micro model of macro phenomena.

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[28]  Other examples include historical ballistic trajectories (which stimulated development of mechanical computing machines in the Eighteenth Century), chemical stoichiometry and more recently astronomical ephemeral (satellite) orbits and molecular spectra.

**THERMODYNAMICS EXERCISES**

1. Is the energy of the universe limited?

2. Explain how a "super ball" can bounce higher and higher.

3. Given the heats of incomplete and complete combustion of carbon (to one mol carbon monoxide and one mol carbon dioxide, respectively), what is the heat of combustion of carbon monoxide?

4. Derive an algebraic formula for determining the *heat of combustion of saturated hydrocarbons* in terms of the number of carbon atoms (n), and the molar heats of formation for the hydrocarbon (h), water (w) and carbon dioxide (c).

5. Estimate the heat of combustion of methane from bond energies.

6. What causes gases to mix?

7. What happens to the entropy of the universe when water is heated?

8. What happens to the entropy of a gas which is compressed?

9. Estimate the pressure of the atmosphere at the top on Mt. Everest, 29,028 ft above sea level, where the temperature is −43 °C.

10. Given that the energy of vaporization of water at the boiling point is 44.0 kJ/mol and that the entropy of vaporization is 119 J/mol-K, estimate the boiling temperature of water.

11. Discuss the solubility of sugar in water.

12. Discuss the solubility of methyl alcohol $CH_3CHOH$ in water.

13. Compute the probability distribution of the sum of the pips (numbers on the faces) of two six-sided dice.

14. How much possible information can be obtained in the game of twenty questions?

15. Compare the entropies at a given temperature for a) the solid, liquid and gas forms of a given substance, b) two monatomic gas atoms of different mass, c) a monatomic and polyatomic gas of the same mass.

16. Calculate the statistical thermodynamic entropy of dihydrogen at 300 K.

**THERMODYNAMICS EXERCISE HINTS**

1. This could be an open-ended question.
2. This can't be an example of perpetual motion.
3. First write down the balanced equations for the three combustions.
4. Saturated hydrocarbons have the general molecular formula $C_nH_{2n+2}$. Combustion is reaction with oxygen. Balance the general combustion reaction in terms of n.
5. Methane is $CH_4$. Combustion is reaction with $O_2$. Assume complete combustion to $CO_2$.
6. If ideal, there is no intermolecular energy.
7. Consider the universe divided into two parts, the water, and everything else.
8. Consider what happens when it expands.
9. The atmospheric pressure at sea level is by definition 1 atm.
10. Vaporization is a change from liquid to gas at the boiling temperature.
11. Sugar has OH groups on a hydrocarbon backbone.
12. Alcohols have OH groups on a hydrocarbon backbone.
13. Count can categorize the possible outcomes.
14. The object of the game of twenty questions is to identify an object known to one player by asking a maximum of twenty questions which have only yes or no answers.
15. Think about which state would be more random in each case.
16. Table 12.1 lists the spectroscopic parameters of $H_2$. The ground electronic state is non-degenerate.