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Chapter 2. Thermodynamics, Work and Energy

A mathematician may say anything he pleases, but a physicist must be at least partially sane.

Josiah Willard Gibbs

The Scientific Monthly, December 1944

The playful statement written by Josiah Gibbs, who claimed identity as both a mathematician and physicist, provides some truth in jest. Mathematical descriptions of the earth-atmosphere system must be anchored within the allowable states and state transitions defined by physics. Thus, as we begin to focus on the specific processes that drive ecosystem-atmosphere fluxes, we will return to the discussion we presented in the last chapter on the nature of fluxes as thermodynamic processes; now, taking a bit more time to understand the principles of physics within which our mathematical models are framed. We have already established that fluxes between two coupled, open thermodynamic systems are driven by states of disequilibrium sustained by the flow of solar energy and the continuous exchange of energy and mass between the systems and their surroundings. In this chapter we will develop these principles in more formal terms. Transformations between energy and work are required for fluxes to exist; a flux is work done by a system on its surroundings as the system moves toward equilibrium; this is a fundamental theme that will permeate this chapter. The chapter begins with a discussion of the laws of thermodynamics. We then take up the topic of energy transfer through heat and electromagnetic radiation, the two forms of energy transfer that drive most ecosystem-atmosphere fluxes.

Following our discussion of on these biophysical topics, we will move to consideration of chemistry. Organisms can be viewed as vessels within which thousands of biochemical reactions are organized and integrated to enable the processing of mass and energy. Biochemical reactions lie at the foundation of biogeochemical cycling. It is through biochemistry that organic molecules are processed as they carry elements from one biogeochemical pool to another, elements are chemically reduced or oxidized, and metabolic products are released to the atmosphere. Biochemical fluxes reflect the speed at which molecules are converted from one form to another – i.e., the rates of chemical reaction. In this chapter, we will delve into the

fundamental thermodynamic relations of chemical reactions. In the case of biochemistry, we will also consider the role of protein enzymes, the catalysts of biochemical reactions. Without enzyme catalysts, life could not be sustained at the temperatures that exist on the Earth's surface.

2.A Thermodynamics, work and fluxes

Two of the most fundamental concepts that we will consider in describing biophysical and biogeochemical fluxes are *energy* and *work*. Energy is a fundamental scalar quantity that describes the amount of work that can be done in response to a specific force. A number of theoretical treatments have attempted to categorize all forms of energy into two fundamental, root categories – potential energy and kinetic energy. *Potential energy* is the internal energy stored within a system that has the potential to do work. Potential energy can be converted to kinetic energy as work is done; in essence, work expends energy. *Kinetic energy* is the work required to accelerate a unit of mass to a given speed. Kinetic energy is the source of mass movement, and as such, the source of biogeochemical transport involving the flow of mass.

Relations involving energy and work are derived from the *laws of thermodynamics*. We will not go into great detail about these laws, as this is the topic for an entire book all unto itself. However, we do need to put into place some general principles that will carry us through the more advanced topics of future chapters. Thermodynamics refers to the energy relations of a *thermodynamic system*, where system is defined as the three-dimensional space under analysis. A thermodynamic system has boundaries which separate the system from its surroundings. The system can be described in terms of *equilibrium*, in which the system is not capable of a change in the partitioning of its internal energy. Equilibrium is the most stable state that a thermodynamic system can attain. Equilibrium is defined according to the *state properties* of the system; e.g., temperature, pressure, volume and mass. A system at equilibrium cannot do work. A system at equilibrium, however, can be disturbed when energy is transferred or work is done to the system from the surroundings. In that case, the system is pushed to a state of *disequilibrium*. A system at disequilibrium can do work on its surroundings, or within its boundaries, as it spontaneously moves in a thermodynamic direction toward equilibrium.

In considering the thermodynamic nature of biophysical and biogeochemical systems we can describe different types of equilibrium. In the case of homogeneous systems, or pure systems, in which only one physical and chemical phase is present (e.g., a volume of pure gas),

mechanical equilibrium (involving pressure and volume) and *thermal equilibrium* (involving temperature and entropy) are the most relevant thermodynamic variables. In heterogeneous systems, wherein different elements and/or compounds exist simultaneously, chemistry can occur and mass can be transported along abundance gradients; in these systems, *chemical equilibrium* (which is also dependent on pressure and temperature) also becomes relevant. As was discussed in the previous chapter, ecosystems and the atmosphere can be considered as separate, open thermodynamic systems. They are maintained in a perennial state of disequilibrium by the flow of solar energy, which also drives the fluxes of elements and compounds within and between the systems, and by inequities in the distribution of mass and energy within the system, which creates abundance gradients. Thus, biogeochemical fluxes must be constrained by the laws of thermodynamics. In this section we will first discuss the various 'laws' of thermodynamics that govern how we view energetics and equilibrium in natural systems. We will then progress to a discussion of the thermodynamics of gases, a topic that must be central in our minds as we consider topics specific to ecosystem atmosphere exchanges.

The *Zeroth Law of Thermodynamics* (or the Law of Thermal Equilibrium) states that 'two systems in thermal equilibrium with a third system are also in equilibrium with each other'. Using the Zeroth Law we can infer that two systems in contact with each other tend toward the same temperature and reach equilibrium at the same temperature. It's the Zeroth Law that explains the measurement of surface temperature using a mercury-bulb thermometer. If, for example, the bulb of a mercury-in-glass thermometer is allowed to reach thermal equilibrium with your body temperature by placing it under your tongue, then the temperature we read from the thermometer will accurately reflect the temperature of your tongue, and by further inference the temperature of your body. The Zeroth Law establishes the concept of thermal equilibrium between conjoined systems. While the earth and atmosphere are indeed conjoined systems, they never reach thermal equilibrium because of the continual and unequal flow of solar energy to them; they are maintained at different thermal states. The Zeroth Law however, establishes a thermodynamic baseline in the concept of equilibrium; it is by comparison with this baseline that we can gauge the degree of thermal disequilibrium that exists within the earth system.

The *First law of Thermodynamics* states: 'the change in internal energy of a system (dU) is a function of the amount of heat absorbed (δQ) and the amount of work done (δW) by the system'. Stated mathematically:

$$dU = \delta Q - \delta W \quad (2.1)$$

where δ notation is used for inexact differentials in the right-hand terms because Q and W cannot be defined exactly by differentiable functions. The First Law establishes that thermodynamic systems can absorb and store energy from work that is done to the system by outside forces and this internal energy is conserved. The First Law will be especially relevant to our discussions of atmospheric transport. Theoretical descriptions of atmospheric transport are best derived within the context of small (relative to the entire volume of the atmosphere) '*parcels of air*', or volume elements, that move within, and interact with, the fluid atmosphere that surrounds them. The parcel concept accommodates treatments of conservation of mass and permits the development of buoyancy as a driver of atmospheric motions. Using the concept of air parcels we can begin to describe many aspects of atmospheric dynamics within the context of the First law. We can, for example, develop the concept of thermodynamic work within the context of pressure and volume changes in atmospheric parcels. We can state more exactly that: $dW = PdV$. In other words, work can be done by a thermodynamic system (in this case parcels of air) only at the expense of pressure and volume; alternatively, work can be done to the system by increasing its pressure and volume at the expense of energy transferred from the system's surroundings. These interactions are clear in the units used to measure these various quantities. The units of work are joules, the same as those of energy. Work is formally defined as a force (mass times acceleration) applied across a linear distance (m). Given the units of mass (kg) and acceleration ($m\ s^{-2}$), a *joule* can be defined as a 'Newton-meter' of work, or more formally as $kg\ m^2\ s^{-2}$. The units of pressure are $N\ m^{-2}$, and those of V are m^3 . Thus, the product between pressure and volume transform to units of work, or energy. Two corollaries that emerge from the First Law are: (1) energy cannot be created, nor destroyed, but it can be transferred from one state to another, and (2) the total amount of energy in a closed system is constant. It is important to note that the First Law says nothing about how much internal energy exists; *only how much it changes* as work is done or as a system interacts with its surroundings.

The First Law can be used to develop a thermodynamic foundation for the driving forces that sustain biophysical fluxes. A flux is an example of *work* being performed on a system. Within the context of the First Law, the capacity to do work is measured in terms of the change

in Gibbs free energy (G):

$$dG = dH - T dS \quad (2.2)$$

where H is the enthalpy of the system, T is absolute temperature and S is entropy. The enthalpy of the system is a state variable defined as the sum of the internal energy (U) and the product between pressure and volume (PV) of the system (i.e., $H = U + PV$). In essence, enthalpy defines the total energy required to synthesize the system. It takes into account that some energy is required to 'create space for the system' by expanding the system (requiring volume and pressure). Entropy refers to the degree of disorder in the system. A system with higher entropy has more disorder. Entropy is essentially a measure of a quantity of heat. Entropy provides the thermodynamic link between heat and work, in that it provides the means by which heat is converted into work. Thus, we can state $dS = \delta Q/T$. From Equation 2.2, we begin to understand that the capacity to drive fluxes, or conduct biogeochemical work, within the earth system is linked to the total energy contained within the system and the state of disorder that exists within components of the system.

The Second Law of Thermodynamics takes up the issue of irreversibility in closed systems and states that: the entropy of a closed system that is not in a state of equilibrium will increase over time and eventually reach a maximum at equilibrium. That is, left without energy input from the surroundings, a march toward greater disorder is inevitable in thermodynamic systems. Stated mathematically:

$$\frac{dS}{dt} \geq 0 \quad (2.3)$$

Given what we learned from the First Law, the conditions of the Second Law make clear that free energy in a closed thermodynamic system will decrease as entropy increases, and thus work will have to be done on the system in order to resist the inevitable progression toward greater entropy. Viewed from another perspective, work can be done to the surroundings as a system moves to states of greater entropy, and thus lower free energy. One common misconception is that the existence of life on Earth violates the Second Law because living organisms are highly

ordered 'systems' with low entropy compared to their surroundings. In fact, the Second Law only pertains to changes in the total entropy in a closed thermodynamic system. It does not pertain to changes in the entropy of individual components within a system, which may exhibit a decrease in entropy at the expense of an increase in entropy from another, linked, component. In considering the Earth's universe as one closed thermodynamic system, the overall entropy of the universe must increase over time. However, one component of the universe, such as the sun, can exhibit an increase in entropy, while transferring energy to the Earth, where it can be used to reduce the entropy of another component of the system. This is what happens through the process of photosynthesis on Earth. Solar energy is transferred to the Earth, where photosynthetic organisms are able to capture a small portion of the energy and use it to synthesize biomass. Production of biomass represents a decrease in entropy, which in this case has occurred at the expense of a small portion of the increase in solar entropy. Overall, entropy in the universe has increased; but locally, on the Earth, molecular entropy has decreased. Organisms on the surface of the earth must be connected through food webs back to the photosynthetic primary producers (except for those groups of chemoautotrophs capable of extracting energy from reduced inorganic compounds); otherwise, the energy required to decrease entropy and drive growth and biological maintenance is not available. When an organism dies, and ceases assimilating the products of photosynthesis, the inevitable march toward greater entropy will ensue, resulting in bodily decay – a harsh reality, indeed; but one based on physics. The requirements of the Second Law will be further evident as we talk about biological redox reactions that involve the transfer of electrons up or down free energy gradients. They will also be evident as we discuss reversible and irreversible metabolic reactions.

In describing the internal energy of thermodynamic systems, we rely on pairs of *conjugate variables*; variables that when combined can be used to calculate thermodynamic displacement from equilibrium. Examples of conjugate variable pairs are temperature and entropy (which together define energy transfer due to heating), or pressure and volume (which together define stress and strain in a system). One way to visualize conjugate variables is to think of them as working together to produce a generalized 'force' on a system, that in turn displaces the system from equilibrium. For example, temperature gradients can be viewed as a generalized 'force' that create thermodynamic disequilibrium and cause energy to flow; the flow of energy represents an increase in the entropy of the system. As a second example, pressure gradients can be viewed as

a generalized 'force' that permits changes in volume. A decrease in the pressure surrounding a sample of gas will create thermodynamic disequilibrium and cause the gas to expand against its surroundings. The product between the change in pressure and volume can be taken as the mechanical work done by the air against its surroundings. Thus, conjugate variable pairs provide both theoretical context and mathematical convenience when describing changes to thermodynamic systems and the capacity of such changes to conduct work.

2.B Free energy and chemical potential

We can develop the connection between work and energy more formally by stating that the minimum amount of work needed to change a system from one state to another is *free energy*. If we restrict the discussion of free energy change to systems at constant pressure and temperature, which approximately applies to many biological processes, we refer to the free energy as *Gibbs energy* (or Gibbs free energy), after Josiah Gibbs an American mathematician who developed the concept in 1873. Gibbs energy is a measure of the potential to conduct work not associated with volumetric expansion; what is sometimes called 'useful' work. If work is done by a system, at the expense of its internal energy, then free energy has been expended and we refer to the process underlying the work as an *exergonic process*. Exergonic processes can occur spontaneously (i.e., without additional energy from the surroundings). An example of an exergonic process is the progressive combustion of biomass (fire), that after crossing a threshold of activation energy (through a spark or match) is capable of burning spontaneously until the fuel is expended. If work is done to a system, such that its internal energy content is increased, we refer to the process underlying the work as an *endergonic process*. Endergonic processes cannot be driven spontaneously by a system, but rather require energy be added from the surroundings. According to mathematical convention, positive work conducted by a system must be accompanied by negative free energy expenditure, such that exergonic processes are associated with negative free energy change. Conversely, endergonic processes are associated with positive free energy changes. Free energy can exist as either potential or kinetic energy.

As an example of free energy change, we will draw from a lesson in biology. Sugar molecules are produced from CO₂ and H₂O extracted from the atmosphere, after molecules of these compounds are combined through the biochemical reactions of photosynthesis. Molecules of CO₂ and H₂O have low potential energy, compared to sugar molecules. Overall, the process

of photosynthesis is endergonic; it requires energy from the surroundings and the free energy change in going from CO₂ and H₂O to sugars is positive. Once the sugars are made, they contain stored potential energy, which can then be used to conduct further chemical work. In fact, aerobic respiration in living cells is an exergonic biochemical process that converts the potential energy of sugars to a form capable of supporting metabolic work – e.g., moving ions across membranes, synthesizing other high energy biomolecules, and producing metabolic heat. During aerobic respiration sugar molecules are converted back to CO₂ and H₂O; a process involving negative free energy change.

We define *chemical potential* as free energy per mole of a substance. Thus, chemical potential is a measure of the capacity for the chemical constituents of a system to do work. The chemical potential of a substance depends in part on properties of chemical composition, such as atomic structure and bond strength. However, other properties also contribute to chemical free energy as evident in the following quantitative definition:

$$\mu = \mu^* + RT \ln c + \bar{V}P + zFE + mgh \quad (2.4)$$

where μ is chemical potential (J mol⁻¹), μ^* is the standard chemical potential (a reference potential determined under standardized conditions of temperature and pressure) (J mol⁻¹), R is the universal gas constant (J K⁻¹ mol⁻¹), T is temperature (K), c is concentration in mole fraction, \bar{V} is the partial molal volume (m³ mol⁻¹), P is pressure (Pa, where 1 Pa = 1 kg m⁻¹ s⁻²), z is the electrical charge (if any), F is Faraday's constant (coulomb mol⁻¹), E is electrical potential (J coulomb⁻¹), m is mass (kg), g is gravitational acceleration (~9.8 m s⁻²), and h is height (m). Thus, properties such as electrical charge, concentration and position relative to the Earth's surface can also affect chemical potential.

The additional factors in Equation 2.4 allow us to expand the use of chemical potential to evaluate the free energy changes associated with fluxes. For example, the diffusive transport of a substance from a region of high concentration to a region of low concentration can be represented as a thermodynamic flux from a region of high chemical potential to a region of low chemical potential. The flux of water vapor from a region of high vapor pressure to a region low vapor pressure, or from a point further from the Earth's surface to a point closer to the Earth's

surface, can be represented as thermodynamic fluxes from regions of high chemical potential to regions of low chemical potential. In all of these cases, the flux of mass requires work (to oppose the frictional forces of the medium through which the mass is moving), and the process of moving mass from one point to another is accompanied by a loss of free energy.

2.C Heat and temperature

Heat is a form of energy. The heat of a thermodynamic system refers to the sum of the kinetic energy of the atoms and, ultimately subatomic particles, that make up the mass of a system. Heat is a state property of a system, which means it can be used to define the state of equilibrium in a system. For example, connection at the boundary between two systems, each at their own internal state of equilibrium, but with different heat quantities, will cause heat to flow from the system with higher heat content to the system with lower heat content, as defined according to the Zeroth Law of Thermodynamics. In that case, heat will be transferred when molecules or atoms from the system with higher heat content collide at the boundary with molecules or atoms from the system at lower heat content, and thus transfer energy through direct contact, or conduction. In thermodynamic terms, the boundary between the systems defines a zone of disequilibrium. If allowed to interact, energy flow between the two systems will act to eliminate the zone of disequilibrium and establish a state of equilibrium between the systems.

Temperature is a measure of the average kinetic energy of the molecules or atoms in a system. Temperature is ultimately a measure of heat content. In the example described above, as heat is transferred through collision at the boundary of two systems, the temperature of the system that initially had lower heat content will increase. Temperature is measured on various scales – e.g., Celsius, Fahrenheit. In this book, we will use the Celsius scale when justified by traditional uses in the literature, or more frequently, the Kelvin scale (symbolized as K), which is the most thermodynamically-consistent measure of temperature. The Kelvin scale is referenced to the thermal state of a system at which there is no internal energy (taken as $0\text{ K} = -273.2\text{ }^{\circ}\text{C}$ and $-459.7\text{ }^{\circ}\text{F}$).

2.D Pressure, volume and the ideal gas law

Pressure is a force exerted on a surface. Gas pressure results from mass particles (atoms

and molecules) with kinetic energy suspended in air, and the resultant collisions that occur as the moving mass collides with the surface. Pressure is described as force per unit area and has units of *pascals* (Pa) ($1 \text{ Pa} = 1 \text{ N m}^{-2}$). As discussed above, pressure is the thermodynamic conjugate pair of volume. Volume is defined as the three-dimensional space occupied by a system. Clearly pressure, with its nature as a force, has the potential to cause changes in volume. In the case of gases, pressure and volume are often described in relation to one another according to the *ideal gas law*:

$$P V = n R T \quad (2.5)$$

where P is pressure (Pa), V is volume (m^3), n is the number of moles of gas constituents, R is the gas constant ($8.31 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$), and T is temperature (K). The ideal gas law is an example of an *equation of state*, which provides quantitative relations among the *state variables* used to describe matter. The ideal gas law governs the distribution of internal energy of a gas as it interacts with its surroundings. For example, Equation 2.5 makes it clear that any decrease in the pressure of a gas, not accompanied by a proportional decrease in volume or increase in molar abundance, must be accompanied by a proportional decrease in temperature. Equation 2.5 can be rearranged to show that pressure is proportionally related to the density of gas molecules (n/V).

2.E Adiabatic and diabatic processes

Work can be done by a thermodynamic system at the expense of its own internal energy, isolated from its surroundings, or at the expense of energy transferred from the surroundings. An *adiabatic process* is one in which work is done without exchange of energy between the system and its surroundings. A *diabatic process* is one in which energy is exchanged with the surroundings. Biogeochemical fluxes between ecosystems and the atmosphere can be driven by either adiabatic or diabatic processes, or a combination of both.

In order to illustrate the nature of adiabatic and diabatic processes, we will start by considering a classic experiment conducted by James Prescott Joule in 1845, called Joule's Expansion Experiment. Joule constructed an apparatus with two glass bulbs connected by a closed stopcock. One of the bulbs was filled with gas and the other was evacuated. Using the

apparatus, Joule tested the hypothesis that expansion of a gas causes it to cool. He insulated the experimental apparatus such that it could not exchange heat with the surroundings; in other words $\delta Q = 0$. By definition, this is an adiabatic system. Upon opening the stopcock, gas from the gas-filled bulb expanded into the evacuated bulb, but because there was no pressure to resist the expansion, no work was done; in other words $\delta W = 0$. (Recall that $dW = PdV$; in this case, P represents the pressure that resists volumetric expansion; because $P = 0$, $dW = 0$.) Given that $dU = \delta Q - \delta W$, the internal energy of the system was constant during the experiment. Given that the internal energy was constant, but the volume of the gas increased, Joule was able to conclude that internal energy is not a function of V , and therefore must be only a function of temperature, T .

Now, let's consider the case whereby an adiabatic system is allowed to do work against its surroundings. Imagine a parcel of air sealed off from the surrounding atmosphere by a boundary across which no heat can be exchanged, but which also offers no resistance to volumetric expansion; i.e., an ideal balloon. If the parcel is allowed to rise in the atmosphere, accompanied by a decrease in the external pressure of its surroundings, the air parcel will expand (Fig. 2.1). In this case, however, unlike Joule's experiment, an external pressure exists that resists the parcel's expansion. Work must be done by the parcel to the surrounding atmosphere in order to permit expansion; in this case, $\delta W \neq 0$, but $\delta Q = 0$. The internal energy of the parcel will decrease, and as internal energy is a function of T , the temperature of the parcel will also decrease. This explains why buoyant air parcels cool as they rise. It also explains why air parcels that are heated at the earth's surface, rise in the first place. As the temperature of the parcel increases near the surface, its pressure and volume increase; this in turn decreases the density (n/V) of the air in the parcel. A parcel with lower density compared to its surroundings will rise in the atmosphere. By definition, all of the change in internal energy that occurs in an adiabatic system that expands or contracts must be accounted for in work that is done.

A diabatic process is one involving energy transfer. An example of a diabatic process is the evaporation of water from a wet surface driven by the transfer of solar energy. In this case, we can consider the wet surface to be an open thermodynamic system. As the surface absorbs energy from the sun, some of that energy is channeled into increasing the kinetic energy of water molecules. With the increased energy, a fraction of the water molecules will break free of the

cohesive electrostatic interactions (hydrogen bonds) that hold them to other water molecules at the surface, and enter the vapor phase in the overlying air. Not all of the molecules that escape will remain in the vapor phase; some will lose energy through multiple collisions and rejoin the liquid phase. Thus, there is net evaporative flux from the surface.

2.F Electromagnetic radiation

All these fifty years of conscious brooding have brought me no nearer to the answer to the question: 'What are light quanta?' Nowadays every Tom, Dick and Harry thinks he knows it, but he is mistaken.

Albert Einstein

The Born-Einstein Letters , 1954 (translated by Irene Born, 1971)

The physical nature of radiant energy has challenged description since Max Planck first took up the topic in 1894 and Albert Einstein tried to clarify the matter with his Photoelectric Theory in 1905. This form of energy, commonly quantified according to a measure of 'quanta' referred to in Einstein's quote, exhibits properties that can be described by both wave and quantum mechanics. It's this dichotomous nature of electromagnetic radiation that eludes simple quantitative description. *Electromagnetic radiation* is defined as the energy emitted from mass when the vibrational motions of its charged subatomic particles create alternating electric and magnetic fields. These fields give rise to self-propagating waves that travel through space. The energy of the waves is called electromagnetic energy or often, *radiant energy*. Electromagnetic energy is quantized; that is, it is delivered to an absorbing surface in discrete amounts, depending on the wavelength of the propagated wave. These discrete amounts, or 'packets' of energy delivered to a surface are defined in terms of quanta, or *photons*. The quantized nature of electromagnetic radiation originates in the quantized vibrational motions of electrons in the emitting matter. The energy of a photon is dependent on the wavelength of electromagnetic radiation, which illustrates an enigmatic property of electromagnetic radiation: *it displays both wave-like and particle-like properties*. Electromagnetic radiation is propagated as a wave, but it strikes a surface like a particle. In other words, it imparts energy to an absorbing mass in quantized fashion. The energy of a photon can be defined as:

$$E = \frac{hc}{\lambda} \quad (2.6)$$

where E is energy (J), h is Planck's constant (J s), c is the speed of electromagnetic radiation propagation (or speed of 'light') (m s^{-1}), and λ is wavelength (m).

Any system of matter that exists above 0 K will have vibrational motion in its subatomic particles, and will thus emit electromagnetic radiation. A *black body* is defined as a system of mass that ideally exchanges electromagnetic radiation with its surroundings, meaning that it totally absorbs all radiant energy it receives (i.e., none passes through it or is reflected from it), and re-emits all energy that is absorbed (i.e., none is stored in its mass). By definition, a black-body emitter will emit radiant energy as a function of wavelength according to *Planck's radiation distribution law*:

$$\frac{dR}{d\lambda} = k_1 \frac{\lambda^{-5}}{(e^{k_2/\lambda T} - 1)} \quad (2.7)$$

where $dR/d\lambda$ is the radiant energy flux per unit wavelength ($\text{W m}^{-2} \text{m}^{-1}$, or W m^{-3}), λ represents wavelength (m), k_1 is a constant ($3.74 \times 10^{-8} \text{ W m}^{-2}$), k_2 is a constant (143.9 m K), and T is the temperature (K) of the emitting body. A watt is a unit of power, and is equivalent to a J s^{-1} .

Power is formally defined as the rate at which energy is expended, or in other words, the rate at which work is performed. In the case of Equation 2.7, the radiant power is calculated as the rate at which radiant energy is emitted from a black-body surface per unit of wavelength. This is also the rate at which radiant energy can be transferred to an absorbing surface, or the 'photon power'.

Written in its differentiated form, as in Equation 2.7, Planck's law is defined in the limit as $\Delta\lambda \rightarrow 0$. If we set the derivative to 0, we can evaluate the fundamental relation between radiative power and wavelength. In other words, we can ask: what is the wavelength of maximum radiative power? Mathematically, we state the condition as:

$$\frac{\partial R(T, \lambda)}{\partial \lambda} = 0 \quad (2.8)$$

The solution to this maximization yields:

$$\lambda_{\max} = \frac{2897}{T} \quad (2.9)$$

where T is the black-body temperature (K). Equation 2.9 is known as *Wien's displacement law*. Using Wien's displacement law, for example, we can calculate the wavelength of maximum radiative emission from the sun. The surface temperature of the sun is estimated to be 5500 K, which translates to a wavelength of maximum emission at 527 nm. This wavelength also happens to be in the middle of the range of wavelengths most active in driving the photosynthetic systems of plants and in the utilization of 'light' for vision processes in many animals. Thus, biological systems have evolved in a way that matches the wavelengths of light required to drive their energy transduction systems with the wavelength domain of greatest energy transfer from the sun. In this book, we will refer to photons in the wavelength band from 400-700 nm as *photosynthetically-active radiation* (PAR), and the photon energy flux in this waveband will be referred to as *photosynthetic photon flux density* (PPFD).

As radiant energy is transferred through the earth's atmosphere it is partially absorbed by suspended molecules. Absorption occurs within specific bands of wavelengths, depending on the oscillation frequency of atoms within the molecule as they stretch and contract within the constraint of the molecular bonds holding them in position (Box 2.1). In the atmosphere, O₃ and O₂ attenuate solar energy at relatively short wavebands, whereas H₂O and CO₂ attenuate energy at longer wavebands (Figure 2.2). Solar absorption by CO₂ is relatively minor, compared to O₃, O₂ and H₂O. The principal CO₂ absorption bands are at wavelengths longer than 2,000 nm, placing them well within the spectrum of earth-emitted radiation, but beyond most of the solar spectrum. Thus, recent perturbations to the atmospheric greenhouse effect, which have largely been attributed to the emission of CO₂ from anthropogenic energy use, are not due to attenuation of solar energy, but rather the energy emitted by the earth.

The absorption of electromagnetic radiation as it penetrates a medium (such as the atmosphere or a solution of molecules) is typically described quantitatively according to the *Beer-Lambert Law* (or *Beer's Law*). Beer's Law relates the absorption of a photon flux to the quantity and nature of matter suspended in a medium. As photons travel through a medium, the

suspended molecules will absorb some fraction of that photon flux according to the total cross-sectional area the molecules display perpendicular to the flux (which can be related to concentration) and to the inherent capacity of each molecule to absorb photons at the wavelengths represented in the flux:

$$I/I_0 = e^{-kc}, \quad (2.10)$$

where I is the photon flux exiting the medium, I_0 is the photon flux entering the medium, k is the absorption coefficient of the molecule (absorption per unit concentration) and c is the concentration of the molecule. The exponential extinction of the photon flux as a function of distance traveled through the medium falls out of the derivation of the relation. The Beer-Lambert Law takes a central role in many aspects of earth systems sciences, including the foundation for radiative transfer models in the atmosphere and through canopies, and the basis for detecting the concentration of molecules in many trace gas detectors.

The transfer of radiant energy often occurs after a mass has absorbed incident radiant energy, and thus involves the re-emission of energy at longer wavelengths. The total amount of radiant energy emitted by a molecule or surface can be calculated by integrating Equation 2.7 across all wavelengths. When this is done, we obtain the Stefan-Boltzmann law, which relates radiant emissions from a black-body to the fourth power of its temperature [i.e. ($R = \sigma T^4$, where σ is the Stefan-Boltzmann constant ($5.673 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$)). For objects other than blackbody emitters, the Stefan-Boltzmann law is modified according to the object's emittance (ϵ ; the fractional emission of a non-blackbody relative to a blackbody). The modified Stefan-Boltzmann law is represented as $R = \epsilon \sigma T^4$.

Solar energy occurs as short, higher-energy wavelengths that are referred to generically as short-wave radiation. [By convention, radiant energy of wavelengths less than $2.5 \mu\text{m}$ is defined as short-wave radiation and that greater than $2.5 \mu\text{m}$ is defined as long-wave radiation.] Often, the term near infrared radiation is used for that part of the solar spectrum incident on the earth at wavelengths greater than $0.7 \mu\text{m}$. The earth's surface emits radiant energy with an emission maximum near $9.6 \mu\text{m}$, fully within the long-wave portion of the spectrum. The energy emitted by the earth's surface is also referred to as "re-radiated" energy, since it represents short-wave

energy that was originally emitted by the sun, absorbed by the earth's surface and re-radiated back to space as long-wave energy. The *net radiation* (R_n) incident on a surface is defined as the sum of the short-wave (R_s) and long-wave (R_L) radiation absorbed by a surface, minus the re-radiated radiation:

$$R_n = R_s a_s + R_L a_L - \varepsilon \sigma T_s^4 \quad (2.11)$$

where a_s and a_L are the fractional absorptances (absorbed radiation relative to that of a true blackbody) of the surface for short- and long-wave radiation, respectively (Fig. 2.3).

Energy that is absorbed by a surface sustains the surface in a state of thermodynamic disequilibrium. Absorbed energy will be dissipated through a variety of mechanisms, including conduction as heat to deeper layers of the surface or to the molecules of an overlying fluid (such as air or water), which can then carry the heat away in the fluid flow, and loss as latent heat when water changes state from liquid to vapor and evaporates from the surface. Energy can be transferred to a surface through a variety of sources. In the case of the Earth's surface, solar radiation is the primary source of radiant energy. However, other sources can be important, including the advection of heat from a warm wind and the addition of latent heat during dew formation. At steady-state, the fluxes that move energy away from the surface will equal the fluxes that bring it to the surface, and the surface will be in *energy balance*. Perturbation to the flux of incoming or outgoing energy will disrupt the energy balance, and cause the temperature of the surface to increase or decrease. Ultimately, surface temperature is the transducer that connects energy gain and energy loss, and allows the surface to maintain energy balance in the face of variable energy loads. In future chapters, we will consider the energy balance of various surfaces in the earth system, including leaves, canopies and the planet, and ultimately link the energy balance of these surfaces to the fluxes of energy to and from the surface, and the surface temperature.

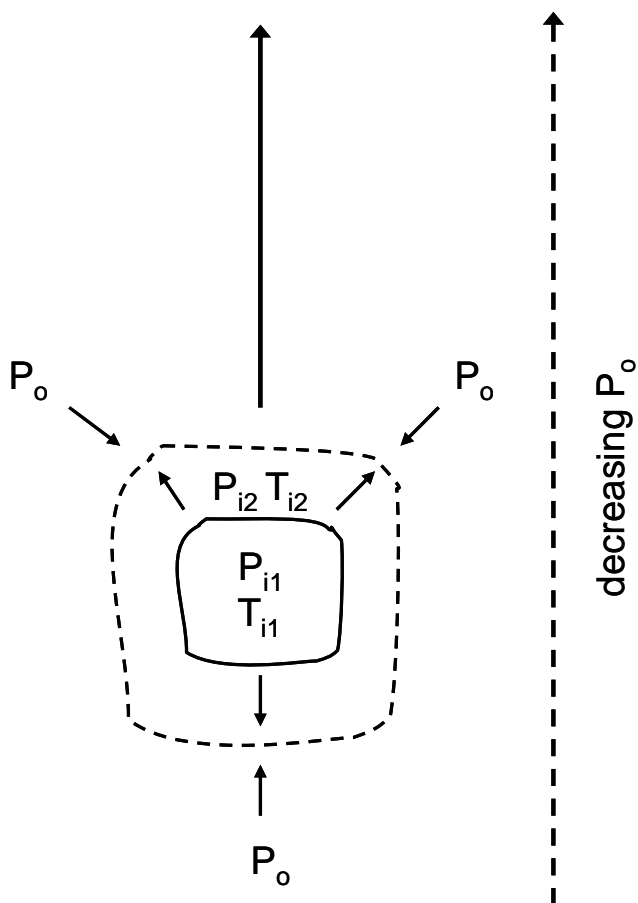


Figure 2.1. Schematic of rising air parcel exhibiting adiabatic expansion in the face of decreasing atmospheric pressure (P_o). The internal pressure of the parcel (P_i) is greater than P_o , allowing the parcel to expand. Two states are presented for the parcel – state 1 and state 2, with P_{i1} and T_{i1} representing the internal pressure and temperature of state 1 and P_{i2} and T_{i2} representing the internal pressure and temperature of state 2. Because work is done as the parcel expands and works against the resistance of the external pressure, the internal energy of the parcel (U) decreases, and because the mass contained within the parcel remains constant, the internal pressure must decrease as the volume increases. Thus, $P_{i1} > P_{i2}$ and $T_{i1} > T_{i2}$.

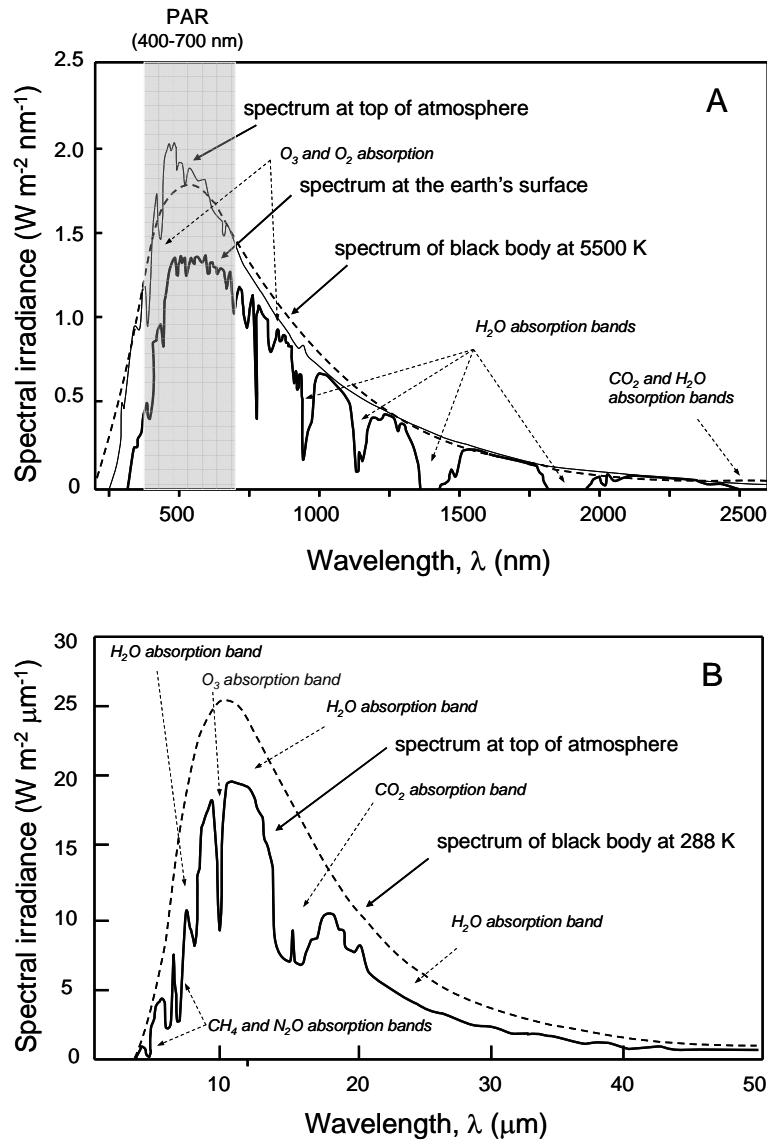
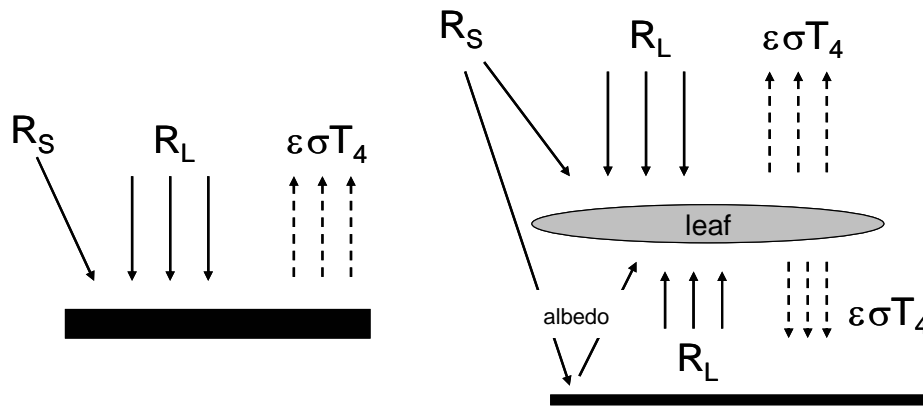


Figure 2.2. A. The solar spectrum at the top of the atmosphere and at the earth's surface showing peak energy emission in the domain of photosynthetically active radiation (PAR) and attenuation due to atmospheric constituents. The spectrum of an ideal 5500 K (estimated temperature of sun) black body is shown for comparison. **B.** The long-wave radiation spectrum at the top of the atmosphere and the spectrum of an ideal 288 K (mean earth surface temperature) black body showing alteration of radiation in certain wavebands due to absorption by atmospheric constituents. Figure 2.2 A redrawn from a figure produced by Robert A. Rohde, for the Global Warming Art project and distributed under the GNU Free Documentation License. Figure 2.2 B is redrawn from data originally presented in Gates (1980).



$$R_n = R_s a_s + R_L a_L - \epsilon\sigma T^4$$

Figure 2.3. Net radiation with respect to two surfaces. **Left.** The solid ground surface intercepts short-wave radiation (R_s) from the sun and long-wave radiation from the sky R_L , and emits long-wave radiation according to the Stefan-Boltzmann relation. **Right.** A leaf that is elevated above the ground receives radiation inputs from both above and below. The net radiation budget of a leaf must take into account exchanges at both surfaces.

Box 2.1. What makes a greenhouse gas radiatively active?

The so-called *greenhouse gases* in the earth's atmosphere trap radiant energy emitted from the earth, in the long-wave (infrared) part of the electromagnetic spectrum; part of the trapped energy is transmitted back to earth, creating the greenhouse effect (see Section 1.A.1). Not all atmospheric molecules are radiatively active in the infrared part of the spectrum. For example, N₂ and O₂, the two most abundant gases in the atmosphere, do not contribute to the greenhouse effect. Here, we first consider the properties of a molecule that permit it to absorb radiant energy, and in a particular waveband. Then, we will consider the properties of greenhouse gases that determine their radiative activity in the atmosphere.

In order for a molecule to absorb radiant energy, the frequency of oscillation in the electromagnetic field of emitted radiation must match the frequency of atomic oscillation within the molecule. Atomic oscillations occur within covalent bonds. The covalent bonds that allow two neighboring atoms to share electrons do not exist at a static length and angle. Rather the length of the bond can extend and shorten, and the angle of the bond can oscillate between alternative states, as centers of positive charge (nuclei) and negative charge (electron clouds) are alternately repelled and attracted by electrostatic forces (Fig. B.2.1). As charged domains of a molecule oscillate asymmetrically a dipole moment is created. *Dipole moment* refers to the degree of polarity that exists within a molecule as a result of asymmetric charge distribution. An oscillating dipole moment creates an electromagnetic field capable of matching the resonant frequency in the electromagnetic field of emitted radiation; thus, permitting energy absorption.

In the case of the CO₂ molecule, a linear structure is predicted on the basis of optimal separation of shared electron clouds, with two pairs of shared electrons in each double bond between carbon and oxygen (Figure B.2.1). Asymmetric extension and contraction of the double bonds on each side of the molecule creates an oscillating dipole capable of absorbing electromagnetic energy; symmetric extension and contraction leads to electrical balance within the molecule, and no potential for absorption of electromagnetic energy. A water molecule is predicted to take the shape of a tetrahedron. In this case, angular oscillation occurs as the bonded hydrogen atoms move back and forth in relation to each other, creating a dynamic dipole capable of energy absorption. There is a range of possible oscillating frequencies in molecules with dipoles, meaning that a range of wavelengths (within a waveband) can be absorbed. The most probable absorption frequencies lie in the center of the waveband, with lower absorption

probabilities at the 'wings'. Diatomic molecules composed of atoms of the same element (e.g., N_2 and O_2) do not exhibit asymmetry as the component atoms stretch and bend about their bonds; thus, they don't function as atmospheric greenhouse gases. One interesting example to demonstrate the concepts of molecular asymmetry and dipole in producing radiatively-active compounds involves ozone (O_3). This compound is composed of atoms of the same element, but they are bonded asymmetrically with respect to one another (Figure B.2.1); thus, a polar dipole is created as the component atoms move about their bonds, and as electrons move from atom to atom to form fluctuating double bonds within the molecule (forming a so-called resonance hybrid molecule). Ozone is a radiatively-active component of the troposphere.

Different types of greenhouse gases cause different amounts of global warming when added to the earth's atmosphere. One metric used to characterize warming impact is the *global warming potential* (GWP). The GWP provides an estimate of the warming caused by the emission of a unit mass of a trace gas, compared to CO_2 . For example, CH_4 is estimated to have a GWP of 72 for a 20-year time horizon and 25 for a 100-year time horizon; meaning that it is 72 and 25 times more potent as a greenhouse gas compared to CO_2 when calculated over 20-year and 100-year spans, respectively. Differences in the warming potential of CO_2 and CH_4 can be traced in large part to existing atmospheric concentrations of these gases, and the existing degree to which they absorb emitted energy. For example, CO_2 exists at a concentration several orders of magnitude higher than that of CH_4 ($\sim 380 \mu\text{mol mol}^{-1}$ for CO_2 versus $\sim 1.7 \mu\text{mol mol}^{-1}$ for CH_4). The concentration of CO_2 is high enough that the absorption of long-wave radiation is saturated near the center of its principal absorption bands. This means that additional CO_2 will only cause warming through energy absorption near the wings of the wavebands. Thus, as CO_2 is progressively added to the atmosphere, its potential to induce warming, on a per mole basis, decreases non-linearly. Methane also exists at an atmospheric concentration that saturates the center of its primary absorption bands. However, more of the overall absorption spectrum is available for enhanced energy absorption in the case of CH_4 , compared to CO_2 . The reason that the GWP for CH_4 decreases between the 20-year and 100-year estimates, is that the effective atmospheric lifetime of CH_4 is shorter than that of CO_2 (8-10 years for CH_4 versus > 100 years for CO_2). Thus, relative to CO_2 , the GWP of a pulse of CH_4 added to the atmosphere will decline over the time scale of a decade or more due to its removal from the atmosphere. (For the

convenience of calculating GWPs, the reference GWP accorded to CO₂ is kept constant at 1 for all considered time spans.)

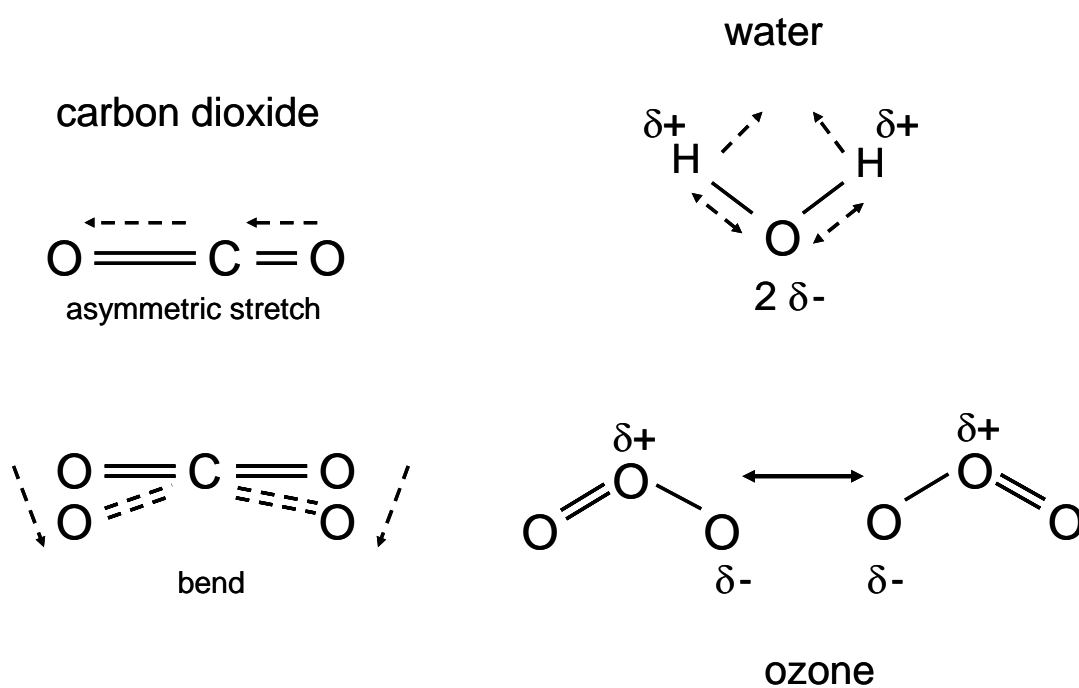


Figure B.2.1. Molecular structures and oscillations in carbon dioxide, water and ozone showing the potential for dipole development, and thus absorption of electromagnetic radiation. The δ symbol is used to indicate partial charges resulting from the asymmetric distribution of electron clouds. The interconversion of O_3 between two molecular forms represents the 'resonance hybrid structure' of compounds in which no single theory of bonding conformation can account for stability in the molecular structure; thus, the double bond is considered to alternate across both forms presented here. These drawings were derived from concepts presented in Archer (2006).