Lectures 11 Temperature and Thermodynamics, Part 1, Concepts

Instructor: Dennis Baldocchi Professor of Biometeorology Ecosystem Science Division Department of Environmental Science, Policy and Management 345 Hilgard Hall University of California, Berkeley Berkeley, CA 94720

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Topics to be Covered

A. Why is temperature important?

- 1. Kinetics of photosynthesis, respiration, isoprene emission.
- 2. Growth, phenology on temperature summation units.

B. Thermodynamics

1st Law 2nd Law

L11.1 Introduction

Temperature is a meteorological variable of general interest. On waking up in the morning we often listen to the radio to determine if it will be hot or cold, so we can decide whether to wear shorts or a parka to work or school.

Numerous factors affect the temperature we sense. Some relate to the conditions of the surface over which we stand. The amount of sunlight overhead and how much of it is reflected by the surface is one factor. And this will change is you are standing under a forest or in a clearing, over a snow field, grass or parking lot. The air temperature will be cooler if there is freely available water to evaporate, or will warm, ever so slightly, if the vapor in the air condensates. The temperature you sense will also be altered by how much the air and surface temperature differ and by how fast the wind is blowing.

Another set of temperature moderating factors is imposed upon us. The most obvious factor is associated with the type and temperature of the air mass overhead or the advection of hot or cold as you may be standing beside a lake, irrigated field or desert. The depth to which the boundary layer grows will also affect the diurnal swing in air temperature, as it is easier to warm a small box than a deep one.

A biometeorologist is interested in an array of temperatures [*Norman and Becker*, 1995; *Porter and Semenov*, 2005]. These include:

- a) leaf temperature
- b) soil temperature
- c) air temperature
- d) radiative temperature
- e) aerodynamic temperature
- f) virtual temperature
- g) potential temperature
- h) wet bulb temperature.

We are interested in temperatures that happened to be averaged over specific time scales. Daily **maximum** and **minimum**, daily **average** temperature, annual mean, and mean **growing season** temperature are examples of temperatures used to describe links between biology and meteorology.

Temperature is important to biological systems because it sets growth limit, it affects the kinetic rates of enzymatic reactions and phenological development of plants. Temperature affects biological processes, primarily through enzyme kinetics.

It affects the life stages of plants. Seed germination, budburst and leaf expansion, flowering and maturity, vernalization, dormancy, leaf abscission all respond to thermal summation.

In some instances we want annual temperature, and in others average temperature during the growing season, to characterize biological activity and the distribution of plants, as with the distribution of C_3 and C_4 species.

Temperature also plays a role on various aspects of environmental biology including low temperature **chilling injury**, **frost injury**, temperature **adaptation**, **acclimation**, and **hardening**. Chilling injury is suffered by tropical and subtropical plants. It occurs when T is below 10 C. It is manifested by wilting, inhibited growth. Freezing injury occurs in plants that are not acclimated to cold. They die at -1 to -3 C. On the other hand, acclimated plants can survive to -40 C and seeds to -196 C. The formation of ice crystals in cells and cytoplasm is the major form of damage.

Through these concerted interactions, temperature sets the limits of where plants can exist and grow. Plants can live in the range of -89 and 58 C, but they only grow only in the 0 to 40 C range.

Classic microclimatology is concerned with the classification of temperature and microclimates. We, however, cannot divorce temperature from heat transfer. This set of lectures will involve an overview of thermodynamics and heat transfer and definition of various types of temperature.

L11.2 Temperature and Biology

The response of plants to temperature is highly non-linear, so evaluation of temperature is critical to assess the proper response. For instance, the rates of many processes like growth and photosynthesis may double with a 5 C rise when T is 10 C, will have no effect when temperature is near 25 C and will cause catastrophic behavior, death at 40 C.

The impact of temperature chemical kinetics is generally evaluated with the Arrenhius Equation:

$$f(T) = A \exp(-\frac{E_a}{RT})$$

 E_a is the activation energy, R is the universal gas constant and A is a constant. Manipulation of this relation can derive a parameter called the Q_{10} , the relative change in the rate of a reaction (k_1/k_2) with a 10 C increase in temperature.

$$\frac{k_2}{k_1} = \frac{\exp(-\frac{E_a}{RT_2})}{\exp(-\frac{E_a}{RT_1})} = \exp(\frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})) = \exp(\frac{E_a}{R}(\frac{T_2 - T_1}{T_2T_1}))$$

We can manipulate this relation and define a quantity that defines the fractional change in reaction rates with a 10 degree increase in temperature.

$$Q_{10} = \frac{k_2 : f\{T+10\}}{k_1 : f\{T\}} = \exp(\frac{10E_a}{RT(T+10)})$$

A Q₁₀ of 2 tells us that the rate of reaction has doubled with a 10 C rise, which is a typical value for enzyme kinetics studies performed in the laboratory. At 20 C, E_a is 51 kJ mol⁻¹.

$$k_2 / k_1 = Q_{10}^{(\frac{T_2 - T_1}{10})}$$

We can solve for Q10 with the log transform

$$\log(k_2 / k_1) / \frac{T - T_r}{10} = \log(Q_{10})$$

The Q_{10} concept is used with both disdain and convenience. Do note that its value, for a specific activation energy, **is temperature dependent**.



Figure 1The relationship between Ea and T for a constant Q_{10} of 2.

There are many practical problems with applying the Q_{10} relation. In many circumstances, the range of temperature may not be broad enough to derive a significant relation. In this case, many investigators choose to use data from a longer period. But this introduces new problems, as new factors may start controlling respiration. We know plant respiration is a function of maintenance and growth respiration. Using data from 0 to 30 C may lead to periods with different forcings of respiration. In the semi-arid west, dry periods have a different impact on respiration than to dry. There is also the issue of which depth to use if one is assessing soil respiration. Shallow sunny and dry soils experience wide daily swings (from 0 to 50 C, during our recent Oregon experiment), while deeper soils experience a shallower range. The point to be made is that one needs to chose the biologically representative temperature and one that occurs where there is biological activity, as where most of the microbes and roots exist if one is explaining soil respiration.

In nature, rate equations for biochemical reactions do not to increase until infinity, as would be implied by extension of the Arrenhius equation. Ultimately, rate limiting processes kick in at higher temperatures, such as enzyme denaturization. Forty degrees C is a critical level for many biochemical processes. Protein synthesis stops, enzymes denature, cell lose membrane integrity at or near this temperature. One function used is a form of the Boltzmann distribution [*Bernacchi et al.*, 2003; *Harley and Tenhunen* 1991]

$$f(T) = \frac{\exp\left(E_a \cdot (T_l - T_{opt}) / (R \cdot T_l \cdot T_{opt})\right)}{1 + \exp\left(\frac{\Delta S \cdot T_l - \Delta H}{R \cdot T_l}\right)}$$

 E_a is the activation energy, *R* is the universal gas constant, T_l is leaf temperature and T_{opt} is the optimum temperature. The terms ΔH and ΔS represent changes in enthalpy and entropy.



f(T)=exp(c - H₄/(R T))/(1+exp(S T- H₄/(R T)))

L11.3 Defining Temperature

What is temperature?

The dictionary defines it as a degree of hotness or coldness of a body or environment. A basic physics textbook on my desk states that **temperature is a reading of a thermometer.**

A conceptual understanding of the concept temperature is difficult to grasp for it cannot be defined in terms of *mass*, *length* and *time*. Essentially, elementary physics books state that the definition and measurement of temperature are inseparable.

We know from our chemistry and physics classes that there are several ways to measure temperature. We know that metals, liquids and gases expand when they are warmer. So one possible definition of temperature can be the reading of a thermometer. We can thereby derive a scale for certain forms of matter have distinct behavior at different temperatures, such as **freezing**, **boiling** and **igniting**.

As a gas is heated its pressure rises (in a fixed volume). We can define a gas thermometer at fixed volume using the gas law, a function of pressure, P, volume, V, the number of moles, n, and R, the universal gas constant, $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$:

$$PV = nRT ::$$

$$P = \frac{\rho RT}{m} ::$$

$$P\alpha = \frac{RT}{m} ::$$

$$T = \frac{Pm}{\rho R}$$

Definitions: Physics textbooks define thermodynamic and kinetic temperatures. Though equal fundamentally, they are defined differently.

A kinetic definition of temperature can be derived from a form of the Ideal Gas Law

$$PV = nRT = nkN_{avogadro}T$$

N is the number of molecules in the sample, n is the number of moles, $N_{avogardo}$ is the number of molecules per mole

Translational Kinetic Temperature is defined as:

$$E = \frac{1}{2}mv^2 = \frac{3}{2}kT$$

k is the Boltzmann constant (1.380662 x 10^{-23} J K⁻¹), v is the molecular velocity.

Finally, a **thermodynamic temperature** is defined by the derivative of entropy (S), with respect to energy (Q) [*Norman and Becker*, 1995]:

$$\frac{\partial S}{\partial Q} = \frac{1}{T}$$

The absolute temperature scale has units of Kelvin. Several set points are defined on this scale. At 0 K matter has no motion. The **triple point of water** (where the temperature, pressure at which ice, liquid and vapor are in equilibrium with each other in the absence of air) is defined at 273.16 K. **Ice point** is 273.15 K.

L11.4 Heat and Thermodynamics

Temperature, heat, energy and thermodynamics are inseparable. To understand temperature in the natural environment, it is best to start with an understanding of fundamentals of heat, energy and thermodynamics.

For background, remember:

- Temperature gradients drive fluxes of heat energy
- Work equals Energy (Joule = $1 \text{ N m} = \text{kg m}^2 \text{ s}^{-2}$)
- Work equals Force <u>times</u> distance that an object is displaced (kg $m^2 s^{-2}$)

$$E = W = \int F dx = \int madx = \int mvdv = \frac{1}{2}mv^{2}$$

$$adx = \frac{dv}{dt}dx = \frac{dx}{dt}dv = vdv$$

• Energy has units equivalent to mass times velocity squared, $\sim mv^2$ (kg m² s⁻²)

Two formal Laws of Thermodynamics exist. They were derived from classic heat and work experiments in the 18th Century by Joule and others thermodynamicists.

One experiment involved using a calorimeter to measure changes in internal energy of a closed system by performing working on it. Work could be done several ways, such as stirring the water with a paddle wheel or egg beater or by rubbing objects together the water reservoir of the calorimeter. A conclusion drawn from the experiments was that the **change in internal energy** (U) of a closed system equaled the **work** (W) performed on the system:

$$U_2 - U_1 = \Delta U = W_2 - W_1 = \Delta W$$

Work has a **positive** sign when work done by an **external force** on the system. It is **negative** when the system does work on its surrounds, as when a cylinder expands.

Internal energy is associated with **sub microscopic** and **disordered energy**. It is the energy contained in the motion of molecules (e.g. translational kinetic energy), the rotation and vibration of individual molecules, electronic and nuclear states of atoms, chemical bonding of molecules and energy associated with intermolecular forces. In many circumstances, the **internal energy** of the system is associated with energy used to change the temperature of the system or over come the attractive forces of molecules. Internal energy is distinct from heat, which is a mode of energy exchange. One can also define the bulk or macroscopic energy of a system, such as potential and kinetic energy.

In describing thermodynamics these terms are considered to be negligible when considering changes in internal energy.

A second experiment involved examining what happens when hot and cold objects are placed in contact with one another. For example, take a frozen steak or tofu patty out of the freezer and place it on a plate. After time elapses the steak will have warmed and the plate on which it sits will have become cold, until both are at the same temperature; assuming they are in a closed insulated system. This example is defined by the:

'The Law of Equilibrium or the Zeroth' Law of Thermodynamics:

Two systems in thermal contact tend toward the same temperature and reach equilibrium at the same temperature.

It is this principle enables us to apply a thermometer to measure temperature.

If **no work** is done on the system then the **change in internal energy** equals the heat **absorbed or released** by the system

$$\boldsymbol{U}_2-\boldsymbol{U}_1=\boldsymbol{\Delta}\boldsymbol{U}=\boldsymbol{Q}_2-\boldsymbol{Q}_1=\boldsymbol{\Delta}\boldsymbol{Q}$$

For reference, the change in heat, ΔQ , is positive in sign if the system absorbs it from its surroundings; it is negative if a system loses heat to its surrounding.

In the real world, systems experience work and hot and cold objects within them come in contact with one another.

Changes of internal energy of such a closed system is explained by the **First Law of Thermodynamics**:

The change in internal energy ΔU is a function of the amount of heat absorbed or lost (ΔQ) and the amount of work done on the system (ΔW)

$$U_2 - U_1 = \Delta U = \Delta Q + \Delta W$$

Two corollaries can be deduced from the First Law of Thermodynamics.

- 1) Energy cannot be created, nor destroyed; it can only be transferred from one state to another.
- 2) The total amount of energy in a system is constant

It is important to note that **the First Law of Thermodynamics** does not say anything about how much internal energy exists. It only gives us information on how it **changes**.

In biometeorology we are concerned with gas transfer, so we examine work associated with the incremental expansion in the volume of the gas, V. This change in work, dW, is defined as pressure, P, times and incremental change in volume, dV. Because of our sign convention, incremental changes in work are related to:

$$dW = -PdV$$

Conceptually the relation between incremental changes in work, force, pressure and volume comes from the following relations, where a change in volume, dV, is equal to area, A, times a change in x, dx:

$$dW = -Fdx = -PAdx = -PdV$$

Work at constant pressure can be envisioned by considering a piston of known mass and cross-sectional area. It is suspended in a cylinder at a given height by a gas of a known temperature. If we put heat into the system the gas will expand, pushing the piston upward. Obviously pressure will not change because the force per unit area on the gas will not change. Work however will be performed as the pushing of the piston upward increases the volume of the gas.

With algebraic substitutions we can redefine incremental changes in heat, internal energy and work as:

$$dQ = dU - dW = dU + PdV$$

An example of this equation in operation can be seen by what happens when one opens a compressed gas cylinder. Feel the regulator. Note how cold it gets. The expansion of the air is accompanied by its cooling.

From calculus **the total derivative** is a function of the **sum of the partial derivatives**. We, therefore, can break the internal energy into partial derivative components associated with changes due to temperature and volume, while keeping V and T constant, respectively.

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Thereby the incremental change in heat can be re-expressed as:

$$dQ = dU + PdV =$$

$$(\frac{\partial U}{\partial T})_V dT + (P + (\frac{\partial U}{\partial V})_T) dV$$

If the **volume** of a system is held **constant**, then the following are true:

dV=0 and
$$\frac{\partial U}{\partial V} = 0$$

This allows us to define the heat capacity of the system at constant volume as:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Units of heat capacity at constant volume are J K⁻¹ mole⁻¹

$$dQ = C_v dT + P dV$$

For meteorological applications it is often convenient to express the **heat capacity of air at constant pressure**. This relation is defined as:

$$C_p = \frac{dQ}{dT}|_P$$

By relating C_v with C_p , and algebraic substitution we product an representation for dQ that is a function of C_p . Its derivation will be explained in Lecture 13.

Heat Capacities at Constant Volume and Pressure

If you like to cook, you already know it takes a modest amount of time to bring a pot of water under a gas flame to boil. This is because water has a significant heat capacity. If we used another liquid with a different 'heat' capacity it would take a different amount of time for its temperature to raise to 100 °C.

If we place two different masses in contact, one will lose heat $-\Delta Q = C_a(T_f - T_1)$ and the other will gain it $\Delta Q = C_b(T_f - T_2)$ at a rate proportional to the temperature difference and a constant, C. The proportionalities, C_a and C_b , are defined as heat capacities, defined as:

$$C \sim \frac{\Delta Q}{\Delta T};$$
$$C \sim \frac{dQ}{dT}$$

Note that the temperature differences may not be the same between T_1 and T_f and T_2 and T_f . It is heat transfer that is conserved, not the temperature differences.

In principle the heat capacity at constant pressure will be **greater** than that at constant volume (see Alberty and Daniel, 1978). To explain, let's start again with the First Law of Thermodynamics and express dQ as:

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right) dV$$

Next, we divide dQ by dT and substitute a new term for dV

$$dV = \frac{\partial V}{\partial T}|_P \, dT$$

$$\frac{dQ}{dT}|_{p} = C_{p} = \left(\frac{\partial U}{\partial T}\right)_{V} + \left(P + \left(\frac{\partial U}{\partial V}\right)_{T}\right)\frac{\partial V}{\partial T}|_{p}$$
$$\frac{dQ}{dT}|_{p} = C_{p} = C_{V} + \left(P + \left(\frac{\partial U}{\partial V}\right)_{T}\right)\frac{\partial V}{\partial T}|_{p}$$

For perfect gas at constant pressure, dP=0, this does not imply that the change in volume is zero. At constant pressure we can also define the change in volume with change in temperature

$$\frac{\partial V}{\partial T}|_{P} = \frac{R}{P}$$
 because $V = \frac{nRT}{P}$

$$\frac{dQ}{dT}\Big|_{p} = C_{p} = C_{V} + (P + (\frac{\partial U}{\partial V})_{T})\frac{R}{P}$$

$$\frac{dQ}{dT}\Big|_{p} = C_{p} = C_{V} + R + \left(\frac{\partial U}{\partial V}\right)_{T} \frac{R}{P}$$

This leaves us with defining $(\frac{\partial U}{\partial V})_T$

If a gas expands with no change in temperature, there is no work or exchange of heat so

$$dU(T,V) = \left(\frac{\partial U}{\partial V}\right)_T dV = dQ + dW = 0$$
 (Joule experiment)

and since $dV \neq 0$ then it is implied that

$$\frac{\partial U}{\partial V}|_{T} = 0$$

So with final rearrangement of the above equation for heat capacity at constant pressure we arrive at:

$$C_P = C_V + R$$

We conclude that the specific heat of a gas at **constant pressure** is **greater** than its value at **constant volume**. This can be envisioned by that fact that heat added to a system at constant pressure causes it to expand, against which work is consumed and energy is expended.

The specific heat capacities at constant pressure and volume are important as they can be measured directly and represent intrinsic information on the property of the gas or material.

Specific Heats of Materials at constant pressure (cp), [Jones, 1992]

Air	1010 (J kg ⁻¹ K ⁻¹)
Water	4182
Leaves	3500-4000
Cellulose	2500
Glucose	1260
Dry clay soil	890
Dry peat	300

Second Law of Thermodynamics

The first law of thermodynamics is concerned only with the conservation of energy. It says nothing about the direction towards which the processes proceed.

The second Law of Thermodynamics states that once energy is converted to heat it is partially unavailable. Entropy describes the amount of energy that is unavailable when it is transformed. In a closed system entropy either is constant or increases.

Several terms are needed to understand the second law. Two terms are reversible and irreversible processes. The third term is entropy. In a reversible process, each state of the system is in equilibrium. If we reverse a process it goes back to its equilibrium state. So does its environment. In an irreversible system we may return a system to its original state, but its environment will have changed.

To obtain a relation for entropy we divide the first law of thermodynamics by temperature:

$$\frac{dh}{T} = \frac{C_p dT}{T} - \frac{R dp}{mp}$$

$$\frac{dh}{T} = c_p d(\ln T) - \frac{R}{m} d(\ln p)$$

dh/T is dS, the change in entropy. This equation arises solely from mathematical argument.

But its implications are important for it forms an exact differential $(\int_{a}^{b} dS = S_{b} - S_{a})$. The

change of entropy does not depend on the path taken.

In contrast work is not an exact differential $(\int_{a}^{b} dw = w)$. How much work is done does

depend on its path. Think about pushing a cart up and down a hill. The total amount of work is different if you push it directly up and down or whether you traverse the hill on switch backs (w=Fdx).

An infinitesimal change in heat is an inexact differential. Just consider the case:

$$\oint \delta h = \oint p d\alpha = w \neq 0$$
$$\oint \delta h \neq 0$$

We consider the second law of Thermodynamics in order to understand how solar energy drives our climate system and life. Schodordinger in 1944 argued that *'life depletes energy and creates high entropy waste to maintain internal order'*. Over time this transfer of energy also holds for dissipative systems and non-equilibrium like the earth's atmosphere. It is also contended that such systems attempt to maximize entropy production, theories advocated by Paltridge and Kleidon [*Kleidon*, 2004a]. Consider the conversion of solar energy to terrestrial energy:

$$dS = \frac{Q_{out}}{T_{earth}} - \frac{Q_{in}}{T_{sun}} = 342(1-\alpha)(\frac{1}{255} - \frac{1}{5770})$$



Examples of maximum entropy production can be gleaned from atmospheric circulation, the surface energy balance and the carbon cycle. [*Kleidon*, 2004b]

Consider global circulation. There is maximum heating at the equator and minimum at the poles. We know that there is heat transfer, and we also find it is associated with maximum entropy production. Extreme cases are no heat transfer and infinite heat transfer, both produce no entropy. In reality the intermediate case occurs.

Kleidon shows how the presence of life alters albedo and the surface Bowen ratio to maximize the production of entropy, as opposed to a 'desert-world' without life affecting surface energy fluxes [*Kleidon et al.*, 2000].



From Kleidon, 2005



From Kleidon

SUPPLEMENTAL INFORMATION FOR GRADUATE STUDENTS

3. Boussinesq approximation

Air is incompressible so air density as a function of x, y, z and t ($\rho(x,y,z,t)$) is constant. Air density is a function of temperature Take log transformation of

$$P = \frac{\rho RT}{m}$$
$$\ln P = \ln \rho + \ln \frac{R}{m} + \ln T$$
$$\frac{dP}{P} = \frac{d\rho}{\rho} + \frac{dT}{T}$$

dP/P is essentially zero so fluctuations in density can be presented by fluctuations in temperature.

$$\frac{d\rho}{\rho} = -\frac{dT}{T}$$

When air is moist we use the virtual temperature rather than air temperature

Conservation Equation for Heat

Using the concepts used to derive the conservation of mass, one can derive equations for the conservation of heat for conduction and turbulent transfer (this topic will be covered in full detail later in the course; the equations are presented here for reference and background).

Conduction

$$\frac{\partial T}{\partial t} = -\frac{k_t}{\rho C_p} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right)$$

Turbulent transfer

$$\frac{\partial \overline{T}}{\partial t} + \overline{u}_j \frac{\partial \overline{T}}{\partial x_j} + \frac{\partial \overline{u_j'T'}}{\partial x_j} = -\frac{\partial}{\partial x_j} \left[\frac{k_t}{\rho C_p} \frac{\partial \overline{T}}{\partial x_j}\right]$$

The turbulent flux density of sensible heat is defined as :

$$H = \rho c_p \overline{w'T'}$$

The product, ρc_p , must be weighted for the effects of moist air.

 c_p dry air is 1010 J kg⁻¹ K⁻¹ c_p water vapor is 4182 J kg⁻¹ K⁻¹

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