ATMOSPHERIC THERMODYNAMICS

1. Introduction

1.1 The field of thermodynamics

Classical thermodynamics deals with energy and the transformations of the nature of energy. To a certain extent, it classifies the forms of energy. It does not ask "why" in terms of the fundamental principles of atomic and molecular structure and the energetics of the interactions between atoms and molecules. Rather, it deals with the observables (bulk properties, e.g., pressure, temperature) and is thus more empirical in nature. The First Law of Thermodynamics, for example, classifies energy into thermal and non-thermal forms. From the energetics of physical and chemical changes, thermodynamics provides a means of calculating the equilibrium state of a process as well as defining the conditions for constrained equilibrium.

Thermodynamics is the study of the inter-relation between heat, work and internal energy of a system. Consequently, classical thermodynamics is based on three empirical laws:

- 1. the equation of state (ideal gas law),
- 2. the first law of thermodynamics (conservation of energy),
- 3. the second law of thermodynamics (degradation of energy, i.e., entropy increases).

There is also a branch of thermodynamics, which we will also utilize to a limited extent in this course that deals with models and infers from these models a set of thermodynamic properties. This branch is termed statistical thermodynamics. The statistical treatment must, of necessity, deal with large numbers of atoms or molecules and then deduce their average properties. We will use the statistical approach in considerations of the equation of state and the concept of entropy, and in the development of classical nucleation theory.

Before we proceed, two examples (posed as questions) are used to illustrate how thermodynamics fits into the big picture.

Question 1: How does thermodynamics and cloud physics relate to atmospheric science?

Answer 1: Consider the generalized primitive equations and note the "presence" of thermodynamics. Dynamics/kinematics (momentum equations for u, v; continuity equation)

$$\begin{split} \frac{\partial u}{\partial t} &= -u \frac{\partial u}{\partial x} - v \frac{\partial u}{\partial y} - \omega \frac{\partial u}{\partial p} - \frac{\partial \phi}{\partial x} + fv + F_x \\ \frac{\partial v}{\partial t} &= -u \frac{\partial v}{\partial x} - v \frac{\partial v}{\partial y} - \omega \frac{\partial v}{\partial p} - \frac{\partial \phi}{\partial y} - fu + F_y \\ \frac{\partial \omega}{\partial p} &= -\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right) \end{split}$$

Thermodynamics (equation of state, hydrostatic equation, thermodynamic equation or First Law):

$$\begin{aligned} \frac{\partial \phi}{\partial p} &= -\frac{RT}{p} \\ \frac{\partial T}{\partial t} &= -u\frac{\partial T}{\partial x} - v\frac{\partial T}{\partial y} + \omega \left(\frac{\kappa T}{p} - \frac{\partial T}{\partial p}\right) + \frac{\dot{H}}{c_p} \end{aligned}$$

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Question 2: What about more complicated atmospheric systems, such as fog and clouds?

Answer 2: Consider the following set of equations, which are used in a more sophisticated and detailed model to understand the development and evolution of ice fog, thin stratus, etc. This illustrates the dependence among atmospheric dynamics, thermodynamics, cloud physics (including aerosols), and radiation.

Girard, Eric, Blanchet, Jean-Pierre. 2001: Simulation of Arctic Diamond Dust, Ice Fog, and Thin Stratus Using an Explicit Aerosol–Cloud–Radiation Model. *Journal of the Atmospheric Sciences*: Vol. 58, No. 10, pp. 1199–1221.

- m_A mass of aerosols
- m_I mass of ice particles

m_W - mass of water droplets

- q specific humidity
- T temperature
- δ saturation ratio

$$\frac{\partial}{\partial t}m_A(r) = K \frac{\partial^2}{\partial z^2} m_A(r) + S_{A_{\text{cond}}} + S_{A_{\text{depo}}} + S_{A_{\text{coag}}} + S_{A_{\text{coag}}} + S_{A_{\text{coag}}} + S_{A_{\text{coag}}}, \qquad (1)$$

$$\frac{\partial}{\partial t}m_{I}(r) = K \frac{\partial^{2}}{\partial z^{2}}m_{I}(r) + S_{I_{depo}} + S_{I_{aggr}} + S_{I_{sedi}} + S_{I_{nucl}} + S_{I_{phas}}, \qquad (2)$$

$$\frac{\partial}{\partial t}m_{W}(r) = K \frac{\partial^{2}}{\partial z^{2}}m_{W}(r) + S_{W_{\text{cond}}} + S_{W_{\text{coal}}} + S_{W_{\text{sedi}}} + S_{W_{\text{nucl}}} + S_{W_{\text{phas}}}, \qquad (3)$$

$$\frac{\partial q}{\partial t} = K \frac{\partial^2 q}{\partial z^2} + S_{I_{depo}} + S_{W_{cond}} + S_{A_{cond}} + S_{A_{depo}},$$
(4)

$$\frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial z^2} + \frac{Q_{\text{rad}}}{C_p} + \frac{Q_{\text{cond}}}{C_p} + \frac{Q_{\text{depo}}}{C_p}, \tag{5}$$

$$\frac{d\delta}{dt} = -\left(\frac{L_{\nu}}{R_{\nu}T^{2}}\right)\frac{\partial T}{\partial t} - \left(\frac{p}{\varepsilon e_{s}}\right) \times [S_{W_{\text{cond}}} + S_{I_{\text{depo}}} + S_{A_{\text{cond}}} + S_{A_{\text{depo}}}], \quad (6)$$

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1.2 Definitions

In this section some of the basic definitions of thermodynamic variables and processes are defined. We will also include at this time definitions of some of the moisture variables. The terminology will follow that commonly used by the atmospheric science community and may thus depart from that used in physics, chemistry and engineering. A (nearly) complete list of symbols used in this course is provided in Appendix A.

<u>Energy</u>: This is almost impossible to define precisely. It is not the "ability to do work" unless some conditions are carefully defined. Energy is a property and is defined as such by the First Law.

<u>System</u>: A system is some portion of the universe selected for study. Strictly speaking a system may, or may not, contain matter or energy. For atmospheric applications, systems will always contain both matter and energy. The remainder of the universe is defined as the "surroundings" of the system. Selection of the system is primarily a matter of convenience. Systems may be classified as *isolated, closed* or *open*.

Isolated system: A system which cannot exchange either matter or energy with its surroundings. The universe is defined by the First Law as an isolated system.

<u>Closed system</u>: A system which can exchange energy, but not matter, with its surroundings.

Open system: A system which can exchange both matter and energy with its surroundings.

The systems in Atmospheric Thermodynamics will be "globs" of air undergoing transformations in the atmosphere. Thus, these are really open systems, but for the sake of simplicity, they will often be treated as closed systems.

<u>*Parcel*</u>: We will often use the concept of a parcel (which is a *closed system*) in our discussions of atmospheric thermodynamic processes. A parcel is often defined as a volume of air which does not interact with its environment, i.e., (a) no compensating motions occur in the environment as a consequence of the parcel motions, and (b) the parcel does not exchange mass with the environment. A parcel can do work on the environment. A parcel is therefore an example of a closed system.

<u>*Property*</u>: A property is an observable. It results from a physical or chemical measurement. A system is characterized by a set of properties. Typical examples are mass, volume, temperature, pressure, moisture content, chemical composition, energy, etc. Properties may be classified as *intensive* or *extensive*.

<u>Intensive property</u>: A property that characterizes the system as a whole, and is not given as the sum of the property for portions of the system. Pressure, temperature, density, water vapor mixing ratio, and specific heat are examples of intensive properties.

<u>Extensive property</u>: A property which is dependent on the extent or physical size of the system, and which is given by the sum of the extensive properties of portions of the system. Examples are mass, volume and energy. [We will avoid this to a large extent by defining *specific volume* and *specific energy*, which have units per unit volume or mass, respectively.]

<u>State of a system</u>: The state of a system is defined by a set of system properties. A certain minimum number of such properties are required to specify the state. Thus in an ideal gas, any three of the four properties -- pressure, volume, number of moles, and temperature -- define the state of the system. The *equation of state* defines the relation among these properties.

Process: A description in the manner in which a change in state occurs. Four examples are:

- a) <u>isothermal process</u>: a change in state occurring at constant temperature;
- b) <u>adiabatic process</u>: a change in state involving no transfer of energy between the system and its surroundings;
- c) isochoric process: a change in state occurring at constant volume;
- d) <u>cyclic process</u>: a change occurring when the system (but not necessarily its surroundings) is returned to its initial state after one or more processes.

Are there more?

Equilibrium: A necessary, but insufficient, condition for a system to be in equilibrium is that the system *state* must be constant with time. In addition, if the system is perturbed by a small amount, then in an

equilibrium state the system would retain its initial properties. We will later further distinguish among, stable, unstable and metastable equilibria.

Scale and units: We will generally adhere to the SI (System Internationale) or MKS (meter/kilogram/second) units, but for convenience we will depart from MKS at times. (After all, we can't avoid using calories in a course like this.) The appropriate temperature scale will be either Celsius or Kelvin, and pressure will be expressed in both mb and Pa (or hPa which is numerically identical to mb). Other relevant physical quantities and their units are given below.

| <u>Quantity</u> | Unit | | | |
|-----------------|---|--|--|--|
| Length | m (or cm, mm, μm) | | | |
| Mass | kg (g) | | | |
| Acceleration | m s ⁻² | | | |
| Density | kg m ⁻³ | | | |
| Force | newton (N), $N = kg m s^{-2}$ | | | |
| Temperature | Kelvin (K) or Celsius (C) - K = $^{\circ}$ C+273.15 | | | |
| | °F = 1.8 °C + 32 | | | |
| Pressure | pascal (Pa) $[1 \text{ mb} = 10^3 \text{ dyne cm}^{-2} = 10^2 \text{ Pa}]$ | | | |
| | Pressure is force per unit area, so the unit of Pa is | | | |
| | $Pa = N m^{-2} = kg m^{-1} s^{-2}$ (1 mb = 10 ² Pa = 1 hPa) | | | |
| | Also: $1 \text{ atm} = 1013.25 \text{ mb} = 101.325 \text{ kPa}$ | | | |
| | $= 14.696 \text{ PSI} (\text{lb in}^{-2}) = 760 \text{ mm Hg} (29.92 \text{ in})$ | | | |
| | | | | |
| Energy | joule (J), $J = N m = kg m^2 s^{-2}$ [1 cal = 4.1868 J] | | | |

Another commonly-used unit for energy is the *calorie* or the gram-calorie (cal). This is defined as the heat necessary to raise by 1 K the temperature of one gram of water at a temperature of 15 $^{\circ}$ C. In terms of the MKS units, 1 cal = 4.1868 J. The international calorie was introduced in Engineering, in relation to characteristics of water. The thermochemical calorie was formulated by physical chemists and is defined as above. We will at times use the IT cal in this course.

Finally, the kilogram molecular weight, or kilomole (kmol) is defined as the molecular weight (M) of a material in kg. Thus, one kmol of water is 18.016 kg. The number of kmol n in a mass m is given by

n = m/M.

The number of molecules in one kmol of any material is constant and equal to 10^3 x Avogadro's number $(6.022 \times 10^{23}).$

1.3 Atmospheric Composition

We will consider the atmosphere to be composed of:

- a) a mixture of gases as defined in Tables 1 and 2;
- b) water substance in the gaseous, liquid, or ice phase;
- c) and liquid (aerosol) particles of very small size $(10^{-7} \text{ to } 10^{-4} \text{ m})$.

Water in all phases is highly variable in both space and time. The phase changes associated with water represent some of the key thermodynamic processes (e.g., latent heating) that we will consider. The particles mentioned in (c) above represent the family of atmospheric aerosols, both natural and anthropogenic (man-made). Such particles play key roles in cloud physics (cloud nucleation), air pollution, atmospheric optics and atmospheric radiation.

Except for H_2O (in all phases), CO_2 and some of the trace gases, the air composition is quite constant in space and time up to an altitude of ~100 km.

| Gas | Molecular Weight | Molar (or volume) | Mass fraction | Specific gas constant | m _i R _i /m |
|----------------|------------------|--------------------|-------------------|---------------------------|----------------------------------|
| | | fraction | (m _i) | $(R_i, J kg^{-1} K^{-1})$ | |
| N ₂ | 28.013 | 0.78084 | 0.7552 | 296.80 | 224.15 |
| O ₂ | 31.999 | 0.20948 | 0.2315 | 259.83 | 60.15 |
| Ar | 39.948 | 0.00934 | 0.0128 | 208.13 | 2.66 |
| CO_2 | 44.010 | 0.00033 (variable) | 0.0005 | 188.92 | 0.09 |
| H_2O | 18.016 | 0 - 0.07 | | | |
| Sum | Avg = 28.964 | Sum = 1.00000 | Sum = 1.0000 | | 287.05 |

 Table 1.1 Main gas components of the dry atmosphere (U.S. Standard Atmosphere, 1976)

Table 1.2 Minor gas components of the dry atmosphere (U.S. Standard Atmosphere, 1976)

| Gas | Abbreviation | Molar (volume) fraction |
|------------------|------------------|-----------------------------|
| Neon | Ne | 18.18 x 10 ⁻⁶ |
| Helium | Не | 5.24 x 10 ⁻⁶ (?) |
| Methane | CH ₄ | 2 x 10 ⁻⁶ |
| Krypton | Kr | 1.14 x 10 ⁻⁶ |
| Nitrous Oxide | N ₂ O | 2.5 x 10 ⁻⁷ |
| Hydrogen | H ₂ | 0.5 x 10 ⁻⁶ |
| Xenon | Xe | 0.087 x 10 ⁻⁶ |
| Ozone | O ₃ | $0 - 10^{-4}$ |
| Sulfur dioxide | SO ₂ | variable |
| Nitrogen dioxide | NO ₂ | 0-2 x 10 ⁻⁶ |
| Carbon monoxide | СО | |

1.4 Vertical profiles of pressure, density and temperature

The earth's atmosphere is often divided into distinct layers that are defined in Fig. 1a. This structure represents the so-called idealized U.S. Standard Atmosphere and consists of the troposphere, stratosphere, mesosphere and thermosphere. It represents a globally- and seasonally-averaged temperature profile. As we shall see, the atmosphere can show appreciable deviations from this standard at any location and time.

Fig. 1b shows profiles of pressure, density and mean free path, again for a standard atmosphere. Note that both pressure and density can be well approximated by the simple relation

$$p(z) = p(0) \exp(-z/H),$$
 (1.1)

where H is the atmospheric scale height (H \sim 7-8 km), to be defined later on.

A standard atmosphere calculator can be found at the web site <u>http://www.digitaldutch.com/atmoscalc/</u>. It calculates the relationships among height, pressure, density, temperature, and the speed of sound for a dry atmosphere (more on this later).



Figure 1.1a. Vertical temperature profile for the U.S. Standard Atmosphere. From Wallace and Hobbs (1977).



Figure 1.1b. Verical profile of pressure in mb (dashed), density in g m⁻³ (solid) and mean free path in m (dot-dashed) for the U.S. Extension to International Civil Aviation Organization (ICAO) Standard Atmospere. From CRC Press, Cleveland, 1973.



Figure 1.1c (preceding page). Global mean pressure (bold), temperature (shaded), mean molar weight (solid) and number densities of atmospheric constituents, as functions of altitude. Source: U.S. Standard Atmosphere. Taken from Salby (1996).

Problems

- Find the average molecular weight M and the specific gas constant for air saturated with water vapor at 273 K and 1 atm of pressure. The (saturation) vapor pressure at 273 K is 6.11 mb. [Ans.: M=28.90 g mol⁻¹, R=287.71 J kg⁻¹ K⁻¹] Hint: See Tsonis, p. 19.
- 2. Determine the apparent molecular weight of the Venusian atmosphere, assuming that it consists of 95% of CO₂ and 5% N₂ by volume. What is the gas constant for 1 kg of such an atmosphere? (Atomic weights of C,O, and N are 12, 16, and 14, respectively.)
- 3. Derive an expression for the volume mixing ratio of the *i*th species in terms of its mass mixing ratio. (The mass mixing ratio is defined as $r_i = m_i/m_d$; the volume mixing ratio is defined as V_i/V_d). [Ans: $V_i/V_d = r_i/\epsilon_i$, where $\epsilon_i = M_i/M_d$]
- 4. Given that pressure is defined as a force per unit area, find the mass of the entire atmosphere. State all necessary assumptions.

Notes and References