

1 Basic Concepts of Thermodynamics

.1 Thermodynamic system

A specified collection of matter is called a **system**, which is defined by the mass and the composition.

- a. **Open system:** mass is exchanged with its surroundings;
- b. **Closed system:** NO mass is exchanged with its surroundings.

What type of system does atmospheric thermodynamics deal with?

The systems that atmospheric thermodynamics deal with include

- 1) an air parcel;
- 2) a cloud;
- 3) the atmosphere;
- 4) an air mass etc.

Precisely speaking, they are open systems because mass can be changed by the entrainment and mixing processes.

But, we will treat them as a closed system in this course.

Assumptions:

- 1) the volume is large that mixing at the edges is negligible; or
- 2) the system is imbedded in a much larger mass which has the same properties.

2 Thermodynamic properties

The properties define the thermodynamic **state** of a system.

- a. **Intensive property**: does not depend on the mass (m) or does not change with subdivision of the system, denoted by lowercase letters, e.g., z .

- b. **Extensive property**: does depend on the mass (m) or does change with subdivision of the system, denoted by uppercase letters, e.g., Z .

Exception to the convention: T for temperature and m for mass

* An intensive property is also called a **specific property** if

$$z = \frac{Z}{m}$$

For example, volume V is an extensive property, so $v=V/m$ (i.e., volume per unit mass) is a specific property and an intensive property.

* Homogeneous vs heterogeneous

- a. A system is considered to be **homogeneous** if every intensive property has the same value for every point of the system.

$$Z = mz$$

- b. A system is said to be **heterogeneous** if the intensive property of one portion is different from the property of another portion.

$$Z = \sum_i m_i z_i$$

* A system can exchange energy with its surroundings through two mechanisms:

1) Mechanical exchange (Expansion work)

performing work on the surroundings

2) Thermal exchange (Heat transfer)

transferring heat across the boundary

- * A system is in thermodynamic equilibrium if it is in mechanical and thermal equilibrium.

Mechanical equilibrium: the pressure difference between the system and its surroundings is infinitesimal;

Thermal equilibrium: the temperature difference between the system and its surroundings is infinitesimal.

2.3 Expansion work

If a system is not in mechanical equilibrium with its surrounding it will expand or contract.

The incremental expansion work:

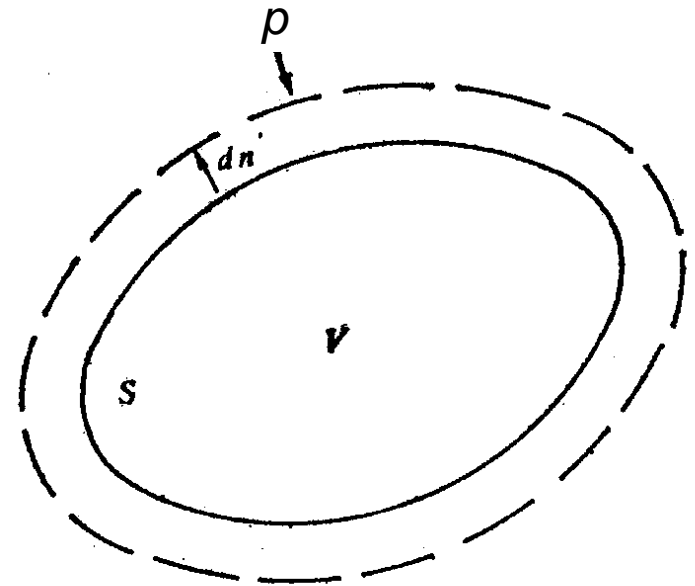
$$\delta W = p dS dn = p dV$$

p : the pressure exerted by the surroundings over the system

dV : the incremental volume

dS : the displaced section of surface

dn : the normal distance between original and expanded surface



2.4 Heat transfer

Adiabatic process: no heat is exchanged between the system and the environment.

Diabatic process: heat is exchanged between the system and the environment.

Which one will we use the most? Why?

2.5 State variables and equation of state

- * A system, if its thermodynamic state is uniquely determined by any two intensive properties, is defined as a **pure substance**. The two properties are referred to as ***state variables***.
- * From any two state variables, a third can be determined by an ***equation of state***,

$$f(z_1, z_2, z_3) = 0.$$

A pure substance only has two degrees of freedom. Any two state variables fix the thermodynamic state,

- * Any third state variable as a function of the two independent state variables forms a **state surface** of the thermodynamic states, i.e.,

$$z_3 = g(z_1, z_2).$$

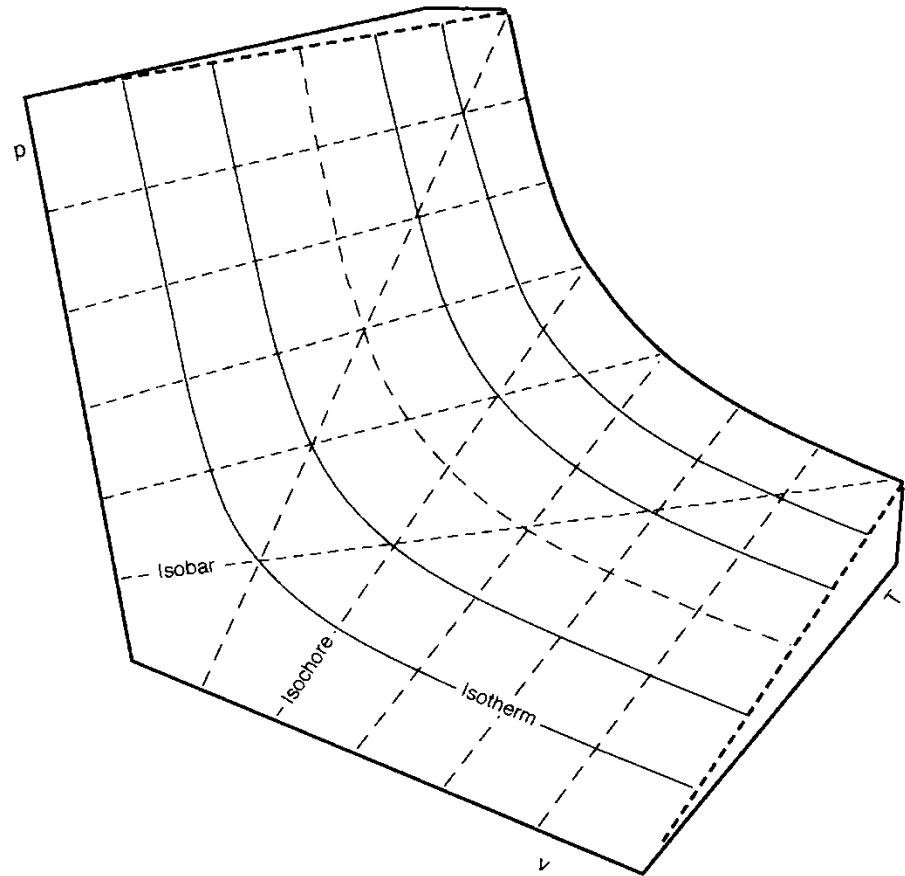


Figure 2.3 State space of an ideal gas, illustrated in terms of p as a function of the state variables v and T . Superposed are contours of constant pressure (*isobars*), constant temperature (*isotherms*), and constant volume (*isochores*).

2.6 Thermodynamic process

- * The transformation of a system between two states describes a path, which is called a **thermodynamic process**.
- * There are infinite paths to connect two states.

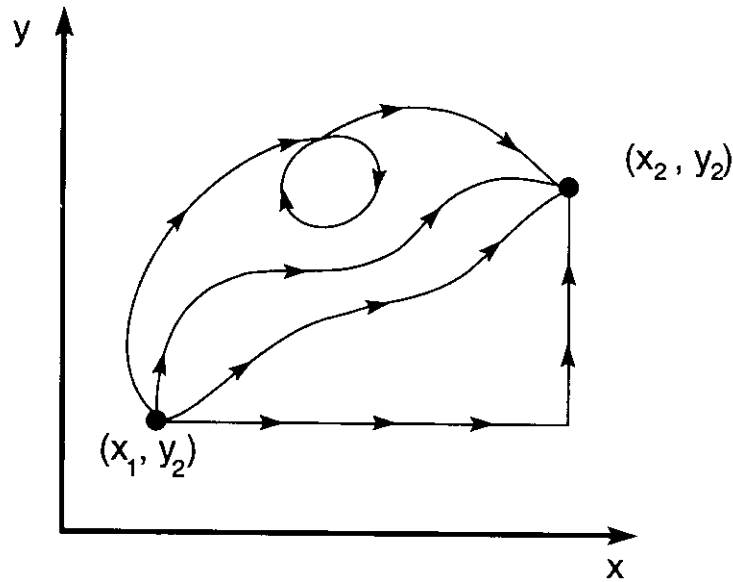


Figure 2.4 Possible thermodynamic processes between two states: (x_1, y_1) and (x_2, y_2) .

* Exact differentials

Consider

$$\delta z = M(x, y)dx + N(x, y)dy .$$

If

$$M(x, y) = \frac{\partial z}{\partial x}, \quad N(x, y) = \frac{\partial z}{\partial y},$$

which is the same as

$$\frac{\partial M(x, y)}{\partial y} = \frac{\partial N(x, y)}{\partial x} ,$$

we have

$$\delta z = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy = dz ,$$

dz is an exact differential, $z(x, y)$ is a point function which is **path independent**,

$$\oint dz = 0 .$$

2.7 Equation of state for ideal gases

2.7.1 How to obtain the ideal gas equation?

The most common way to deduce fundamental equations is to observe controlled experiments.

- * Based on Boyle's observation, if the temperature of a fixed mass of gas is constant, the volume of the gas (V) is inversely proportional to its pressure (p), i.e.,

$$pV = \text{const} \quad (1)$$

- * From Charles' observation, for a fixed mass of gas at constant pressure, the volume of the gas is directly proportional to its absolute temperature (T), i.e.,

$$\frac{V}{T} = \text{const} \quad (2)$$

- * For a fixed mass of gas, consider three different equilibrium states that have (p, V, T) , (p_s, V_s, T) , and (p_s, V_{0s}, T_0) , respectively.
- * From (1) and (2), we have

$$pV = p_s V_s, \quad \frac{V_s}{T} = \frac{V_{0s}}{T_0}$$

Combine them,

$$\frac{pV}{T} = \frac{p_s V_{0s}}{T_0} \quad (3)$$

Divide (3) by the **molar abundance (or number of moles)**

$$n = \frac{m}{M}$$

which is constant since the **mass (m)** and **molecular weight (M)** are constant, we have

$$\frac{pV}{Tn} = \frac{p_s V_{0s}}{T_0 n} \quad (4)$$

* For a standard condition,

$$T_0 = 273.15 \text{ K}, \quad p_s = 1 \text{ atm} = 101325 \text{ mb} = 1.01325 \times 10^5 \text{ kgm}^{-1} \text{ s}^{-2}$$

$$V_{0s} / n = 22.4 \times 10^{-3} \text{ m}^3 / \text{mol}$$

$$R^* = \frac{p_s V_{0s}}{T_0 n} = 8.3143 \text{ Jmol}^{-1} \text{ K}^{-1}$$

is called the **universal gas constant**.

Now, (4) can be rearranged to get the equation of state for the ideal gas

$$pV = nR^* T \quad (5)$$

2.7.2 Equivalent forms of ideal gas equation

Ideal gas equation (5) can be written in several forms,

$$pV = \frac{m}{M} R^* T = mRT \quad (6)$$

$R = \frac{R^*}{M}$ is the **specific gas constant**.

Since the specific volume

$$v = \frac{V}{m} = \frac{1}{\rho}, \quad \rho \text{ is the density,}$$

(6) can be also written as

$$pv = RT, \quad \text{or} \quad p = \rho RT \quad (7)$$

2.7.3 Equation of state for mixture of ideal gases

Each gas obeys its own state equation, for the i th gas

$$p_i V_i = m_i R_i T_i \quad (8)$$

Since in a mixture of gases,

- * The partial pressure p_i is:
the pressure the i th gas would have if the same mass existed alone at the same temperature and occupied the same volume as the mixture;
- * The partial volume V_i is:
the volume the i th gas would occupy if the same mass existed alone at the same temperature and pressure.

(8) can be written in form,

$$p_i V = m_i R_i T \quad (9)$$

Sum (9) over all gases in the mixture, and apply Dalton's law,

$$p = \sum_i p_i$$

we get the equation of state for the mixture,

$$pV = m \bar{R} T \quad (10)$$

which is similar to the ideal gas equation (6).

$$m = \sum_i m_i$$

$$\bar{R} = \frac{\sum_i m_i R_i}{m} \quad \text{is the **mean specific gas constant**}$$

The **mean molecular weight** of the mixture is defined by

$$\bar{M} = \frac{\sum_i n_i M_i}{n} = \frac{\sum_i m_i}{n} = \frac{m}{n} \quad (11)$$

Since

$$n = \sum_i n_i = \sum_i \frac{m_i}{M_i}$$

(11) can be written as

$$\bar{M} = \frac{R^* m}{\sum_i m_i (R^* / M_i)} = \frac{R^* m}{\sum_i m_i R_i} = \frac{R^*}{R}$$

The *absolute concentration* of the i th gas is measured by its **density** ρ_i .

The **molar fraction** is used to measure the *relative concentration* of the i th gas over the *total abundance air* in the mixture,

$$N_i = \frac{n_i}{n}$$

Using the state equations for the i th gas and the mixture of gases, we can also have

$$N_i = \frac{n_i}{n} = \frac{p_i}{p} = \frac{V_i}{V} \quad (12)$$

The **mass fraction** is also used to measure the relative concentration.

Using $n = m / \overline{M}$, and $n_i = m_i / M_i$ in (12), we can get

$$\frac{m_i}{m} = \frac{n_i}{n} \frac{M_i}{\overline{M}} = N_i \frac{M_i}{\overline{M}}$$