

THERMODYNAMICS

LECTURE 6 MACROSCOPIC DESCRIPTIONS OF SYSTEMS

Topics

- Surroundings, State (thermodynamic) Variables, Boundaries
- Classification of state variables
- Extensive and intensive variables
- Conjugate pairs of thermodynamic variables



OBJECTIVES

At the end of this lecture you should be able to

1. Define the following terminologies:
Thermodynamics, thermodynamic system, phase, closed system and isolated system, rigid and diathermal walls, adiabatic and adiabatic changes, equilibrium state, state variables, intensive and extensive variables
2. Distinguish between: closed and isolated systems, adiabatic and diathermal walls, intensive and extensive variables
3. Explain the concept of conjugate pairs of thermodynamic variables

6.1 Introduction

In the next few lectures we shall be dealing with introductory thermodynamics (A detailed course of thermodynamics in your next year of study). **Thermodynamics** is defined as a science concerned with the relationships between the large-scale bulk (*macroscopic*) properties of a system, which are measurable, such as volume, elastic moduli, temperature, pressure and specific heat. For this reason thermodynamics belongs to *classical physics*. It is important to note that thermodynamics by itself cannot give us fine microscopic details, but can only tell us about the bulk properties of the system. The branch of physics that relates the macroscopic properties of matter to the underlying microscopic processes (behaviour of the constituent atoms or molecules) is called **statistical mechanics**. In this lecture we shall familiarize ourselves with terminologies that are often used when dealing with the subject of thermodynamics. It is therefore very important that these terminologies become part and parcel of your vocabulary.

6.2 Systems, Surroundings, State variables and Walls

A *thermodynamic system* is that portion of the universe which we select for investigation, e.g., a gas in a cylinder is a simple system, whereas a mixture of water and alcohol is a more complicated system as it contains two different substances or *components*.

A *phase* is a system or part of a system which is homogeneous and has definite boundaries.

Outside the system is known as the *surrounding*. The *system* and the *surrounding* are separated by a *boundary* or *wall*, as depicted in Fig. 6.1. The system and the surrounding in general, may exchange energy and matter, depending on the nature of the wall. The system is said to be *closed* if the wall allows the exchange of energy but not matter.

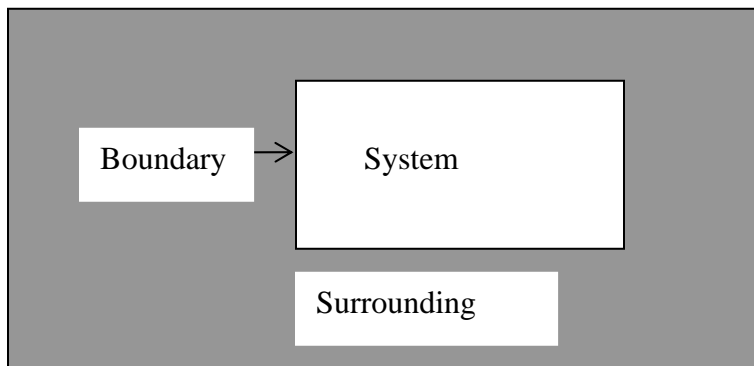


Figure 6.1. System, boundary and surrounding

The system can be influenced either thermally, or by doing work on it. For example, heating is a thermal process, and compression is a work-like process.

If the boundary inhibits the system from changing its volume or shape so that no mechanical work is performed on it, the wall is said to be *rigid*. Walls that prevent thermal interactions are called *adiabatic*, and a system enclosed by an adiabatic wall is called an *isolated system*. An isolated system cannot exchange heat with its surroundings, though work may be done on it. Such changes it will undergo are called *adiabatic changes*.

Walls that allow some interactions between the system and the surrounding are called *diathermal*, and two systems separated by a diathermal wall are said to be in *contact*. In other words, two systems are in thermal contact if heating one of them results in macroscopic changes in the other. For example, you are aware that if we place two metal containers of water in physical contact, and heat one container, the water in both containers becomes hotter. We say that the two containers are in thermal contact.

6.3 Equilibrium state

This is one state in which all the bulk physical properties of a system are uniform throughout the system and do not change with time.

It is important to realize that we require two variables to specify the equilibrium state of a simple system. These measurable variables are called *state variables* (or thermodynamic variables or thermodynamic coordinates). For example, for a gas, specifying the equilibrium values of a pair of independent variables P and V , and mass, fixes all the macroscopic (bulk) properties of the gas.

The state variables may be classified into two groups: the *intensive variables* and the *extensive variables*. **Intensive variables** are those that are discrete (local) in nature, i.e., are size independent. Examples include pressure, electric field, force, and density. **Extensive variables** are proportional to the mass of the system if the intensive variables are kept constant, that is, they correspond to some measure of the system as a whole. Examples include volume, internal energy and length.

If the extensive variables are expressed per unit mass of the system they are then known as *specific variables*.

System	Intensive variable	Extensive variable
Gas/fluid	Pressure (P)	Volume (V)
Film	Surface tension (γ)	Area (A)
Cell	E.m.f (E)	Charge (Z)



Questions

1. Two identical-looking physical systems are in the same macroscopic state. Must they be in the same microscopic state? Explain.
2. Two identical-looking physical systems are in the same microscopic state. Must they be in the same macroscopic state? Explain.

LECTURE 7 TEMPERATURE AND ZEROth LAW OF THERMODYNAMICS

Topics

- Thermal equilibrium (Zeroth law)
- Thermodynamic and other types of equilibrium
- Temperature, isotherms, Equations of State
- Scales of Temperature
- Concepts of Zeroth law and Temperature



OBJECTIVES

At the end of this lecture you should be able to

- 1 Define thermodynamic equilibrium and distinguish between the various types of equilibrium
- 2 State the Zeroth law and explain its importance in temperature measurements
- 3 Draw indicator diagrams for an ideal gas
- 4 State and apply correctly the various equations defining the different scales of temperature

7.1 Equilibrium States

We now define the different categories of equilibrium.

1. *Thermal equilibrium*: Two systems are in thermal equilibrium when they have the same temperature.
2. *Mechanical equilibrium*: This occurs when the system experiences no unbalanced forces.
3. *Chemical equilibrium*: Occurs when no chemical reaction occurs
4. *Thermodynamic (complete) equilibrium*: Attained when the system experiences thermal, mechanical and chemical equilibria.



Exercise

Think of and name examples of systems that fall in the categories of equilibria defined in section 7.1

7.2 Zeroth Law of thermodynamics

Consider three systems A, B, and C as shown in Fig. 7.1. If system A and system B are brought into thermal contact and thereafter achieve thermal equilibrium, and the same holds for systems A and system C, then the same will also hold true for systems B and system C. This experimental observation is surmised in Zeroth law, which states that

If each of two systems is in thermal equilibrium with a third, they are in equilibrium with one another.



Note:

This experimental observation is the basis of our concept of temperature.

All the systems referred to the above and any other in equilibrium with them possess a common property called **temperature** (T).

The temperature of a system is a property that determines whether or not that system is in thermal equilibrium with other systems.

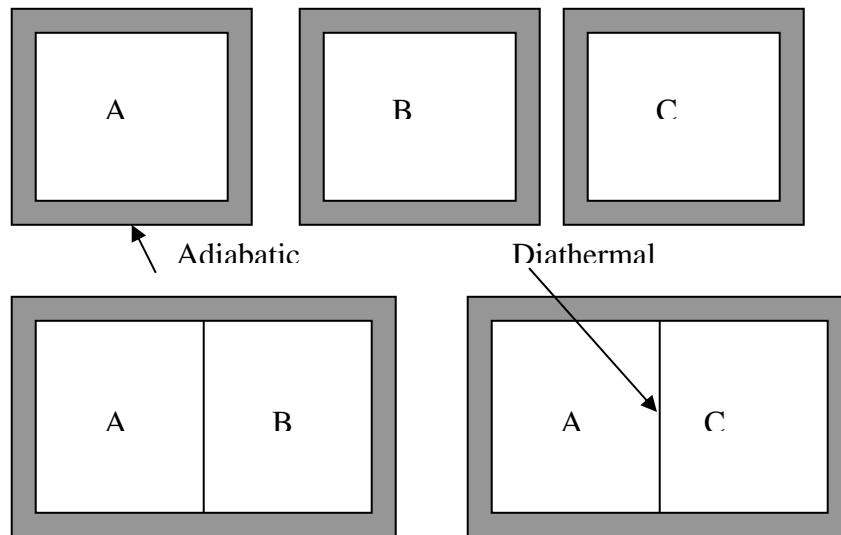


Figure 7.1. Systems in thermal equilibrium

7.3 Measurement of temperature

We can rephrase the zeroth law in terms of temperature thus: If system A has the same temperature as system B, and system B has same temperature as system C, then systems A and C have the same temperature. We are now in a position to quantitatively measure temperature.



Question

Explain, using the mercury-in-glass thermometer as an example, how the Zeroth law concept is used to determine temperature.

A thermometer is a device with which we can conveniently observe macroscopic property that changes as temperature change. You are familiar with the change of the length of the mercury column in a mercury thermometer.



Question

What are other macroscopic properties of a substance that can be used to measure temperature?

To employ a thermometer we bring it in thermal contact with the system whose temperature we wish to determine and allow the two systems reach thermal equilibrium. The extent of change of the macroscopic property of interest gives a quantitative indication of temperature. This is in conformity with the zeroth law.

7.4 Isotherms

An isotherm is defined as the locus of (line joining all) points with same temperature. The isotherms for an ideal gas are shown in Fig. 7.2.

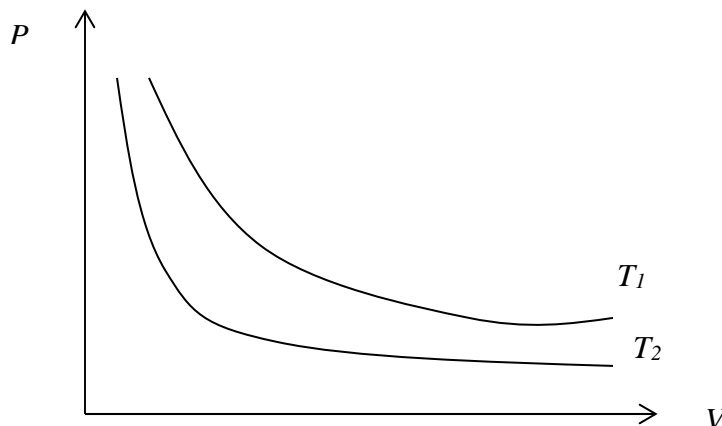


Fig. 7.2. Isotherms for an ideal gas.

Such a (P, V) diagram of the gas in equilibrium state is known as an *indicator diagram*. Remember that an equilibrium state corresponds to specific values of the system parameters. In effect, indicator diagrams are obtained for *quasi-static processes*, i.e., processes that are carried out so slowly that at every state the system may be considered an equilibrium state.

7.5 Scales of temperature

We have defined temperature as that property that determines whether or not a system is in thermal equilibrium with other systems. We now need to construct a scale of temperature. This can be achieved if for the system we chose an appropriate thermometric property and adopt away of assigning numerical values for its isotherms. Let the thermometric property chosen be X . The simplest procedure is to let X and the scale be linearly related; i.e.,

$$X = aT_x \quad (7.1)$$

where a is a constant, whose value is fixed either by choosing the value of the temperature at one reference point, or by choosing the unit so that a given number of units lie between two fixed points. The customarily chosen reference point is the triple point of water (**TP**), i.e., the point at which ice, water and water vapour coexist in equilibrium. The value given to T_x at this point is 273.16. We thus have

$$T_x = 273.16 \left(\frac{X}{X_{TP}} \right) \quad (7.2).$$

Equation (7.2) implies that T_x equal zero at X equals zero. In practice, this may not occur if the thermometric property chosen does not vanish as the temperature is continually lowered.

We can now apply equation (7.2) to several thermometers depending on the thermometric property chosen. For a liquid-in-glass thermometer, X is the length (L) of the liquid column, so equation (7.2) gives

$$T_x = 273.16 \left(\frac{X}{X_{TP}} \right)$$

For a gas at constant pressure, X is the volume (V) of the gas, and

$$T_V = 273.16 \left(\frac{V}{V_{TP}} \right)$$

For a platinum resistance thermometer, X is, the electrical resistance (R),

$$T_R = 273.16 \left(\frac{R}{R_{TP}} \right)$$

7.6 The perfect gas scale

The perfect gas scale has been found, not to depend on the particular properties of a particular gas, and using either pressure or volume of a gas to indicate temperature quite wide temperature range can be covered. In this scale

$$T_{gas} = 273.16 \left(\frac{P}{P_{TP}} \right) \quad K \quad (7.3)$$

where K , the Kelvin, is the unit of temperature on the ideal gas scale. On the Kelvin scale the temperature between ice point and steam point is 100 K .

Example: A certain platinum resistance thermometer has a resistance R of $90.35 \, \Omega$ when its bulb is placed in a triple point cell. What is temperature when the bulb is placed in an environment where its resistance is $96.28 \, \Omega$?

Solution From the equation $T_R = 273.16 \left(\frac{R}{R_{TP}} \right)$ we get

$$T_R = 273.16 \left(\frac{96.28}{90.35} \right) K = 280.6 K$$

A constant-volume gas thermometer is shown in Fig. 7.3. The temperature and the gas pressure are taken to be linearly related as shown in Fig. 7.4. The two points required to define this linear relationship are the zero temperature corresponding to zero pressure and the triple point of water ($\text{TP} = 273.16 \text{ K}$)



Question:

1. Why do you think it is better to define temperature scales in terms of a physical state, like the triple point of water, rather than having an official, standard thermometer stored at the International Bureau of Weights and Measures?
2. Does a vacuum have temperature? Explain.

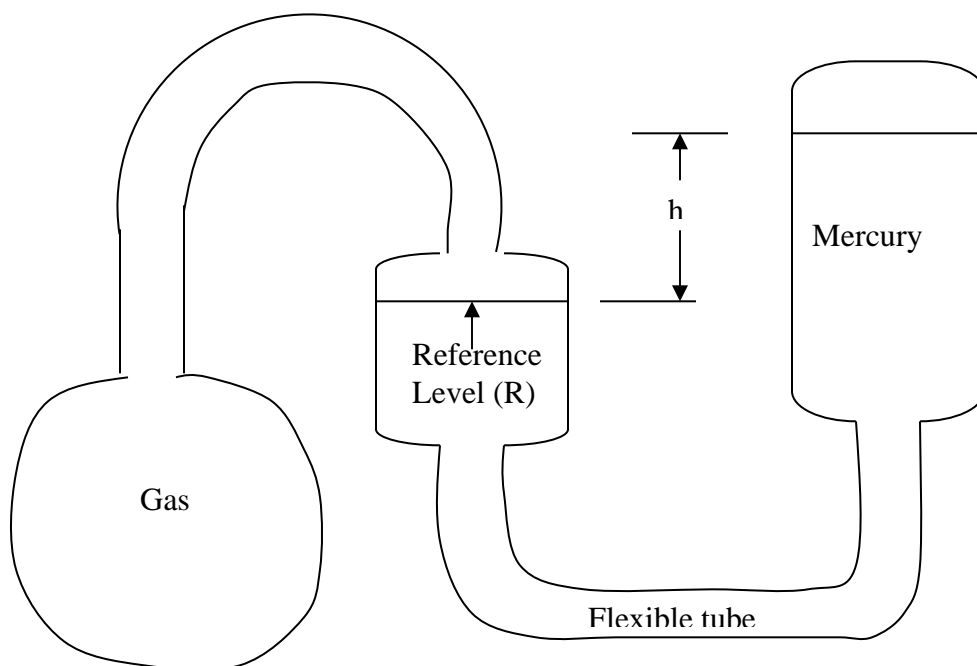


Figure 7.3 A constant-volume gas thermometer. As the gas pressure increases with temperature, the closed tube on the right is raised to keep the mercury level at R , hence maintaining a constant gas volume. h is thus a measure of gas pressure and hence of temperature.

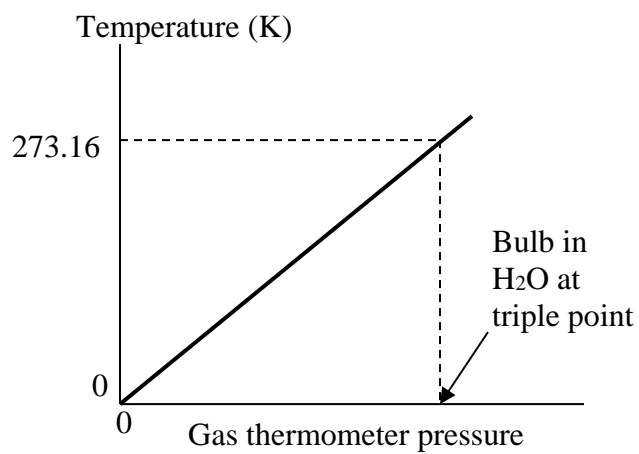


Fig. 7.4 Kelvin temperature scale defined using a constant-volume gas thermometer

7.6.1 The Celcius scale

$$t(^{\circ}C) = T(K) - 273.15 \quad (7.4)$$

In this scale the triple point (**TP**) is $0.01^{\circ}C$.

Since the gas thermometers are cumbersome to use, they are used to calibrate other secondary thermometers.

7.7 Equation of state

Recall that specifying two independent state variables specifies all the bulk physical properties of a system in thermal equilibrium state, and these properties must include temperature. In the case of a gas, then there must be a functional relationship between P , V , and T :

$$\Theta(P,V) = T \quad (7.5)$$

Such a relationship is called the **equation of state**. *It shows that of the three measurable parameters P , V , and T , only two are independent and any one of them may be expressed in terms of the other two.* For example the state of a gas may be specified by stating (P,V) , (P,T) or (V,T) . The equation of state of an ideal gas takes the form

$$PV = nRT \quad (7.6)$$

where n is the number of moles present, R is the universal gas constant.

LECTURE 8 REVERSIBLE, IRREVERSIBLE, QUASISTATIC AND ADIABATIC PROCESSES

Topics

- Thermodynamic processes
- Reversible processes
- Bulk modulus and expansivity



OBJECTIVES

At the end of the lecture you should be able to:

1. Define thermodynamic process
2. Distinguish between a reversible, and irreversible thermodynamic process.
3. Derive the expression for the work done on a system under (a) isothermal condition (b) isobaric condition.
4. Define coefficient of expansivity, coefficient of volume expansivity, Young's modulus, and bulk modulus.

8.1 Thermodynamic reversibility

A process is said to be thermodynamically reversible if and only if, its direction can be reversed by an infinitesimal change in the conditions. This requires two conditions: (i) the process must be quasi-static (the process is very slow that the equilibrium state is always maintained) and (2) there must be no hysteresis (i.e., no dissipation of energy). If hysteresis occurs, the system does not retrace its previous path if the process is reversed. Hysteresis is caused by dissipative forces such as friction.

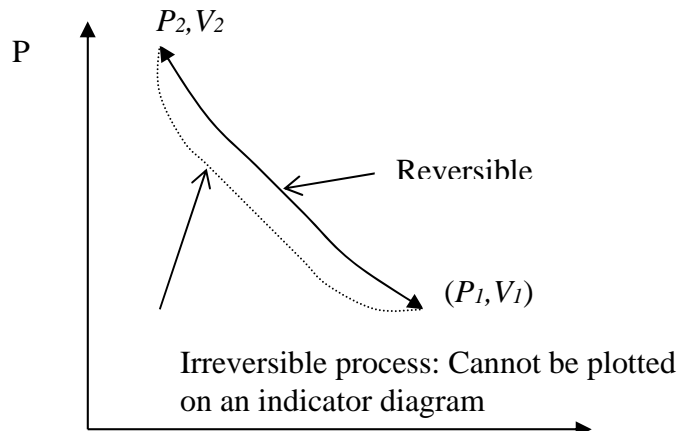


Figure 8.1. Reversible and irreversible processes.



A **process** is the mechanism of bringing about changes in the different state functions when the system moves from an equilibrium state to another.



Question:

1. Why is it not possible to plot an irreversible process on a PV diagram?
2. A process may be irreversible even though it returns a system to its original state. Explain.

In irreversible processes, the equation of state does not hold for the intermediate stages.

8.2 Work and volume changes

We now consider a gas in the initial equilibrium state (P_1, V_1) that is allowed to expand to a new to a new equilibrium state (P_2, V_2) .

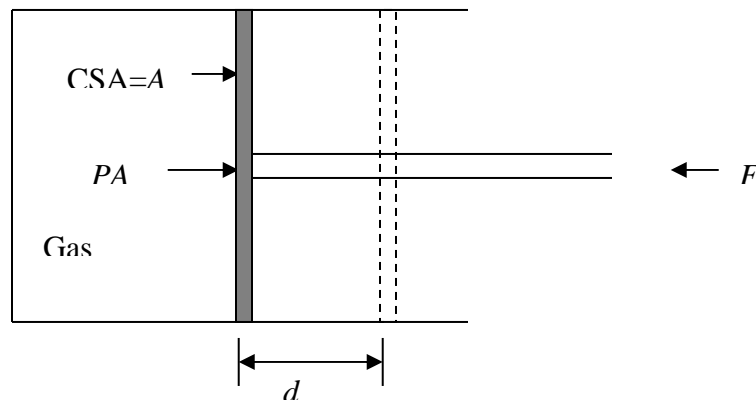


Figure 8.2 Work done an expanding gas

If there are no dissipative forces all the work done goes in performing work on the surrounding (pushing the piston back). Thus for a reversible process (assumed above) we can proceed to determine the work done as follows:

At any intermediate equilibrium state the force on the gas is given by

$$\text{Force } (F) = PA$$

Where P is the pressure, and A is the cross-sectional area (CSA) of the piston. If the piston moves a distance dx (F decreased infinitesimally) the work done is

$$dW = PAdx = PdV \quad (8.1)$$

where $V = Adx$ is the gas volume. Therefore the total work done is

$$W = \int_{V_1}^{V_2} PdV \quad (8.2)$$

Now consider the indicator diagram

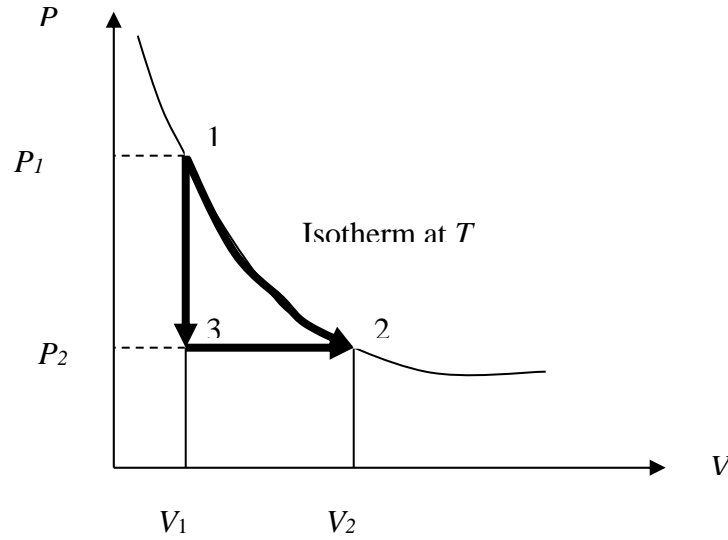


Figure 8.3. The indicator diagram for Fig.8.2.

From equation (8.2) the work done in a reversible process is the area under the curve or path of the process. There are an infinite number of ways of reaching point 2 from point 1. Thus the work done depends on the actual path taken, that is, the way P varies with V .

If the expansion was isothermal (i.e., takes place at constant temperature), that is, along the path 1-2 (i.e., the cylinder wall are diathermal and are in contact with a thermal reservoir at T), then

$$W_{1-2} = \int_{V_1}^{V_2} PdV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \left(\frac{V_2}{V_1} \right) \quad (8.3)$$

since $PV = nRT$.

Along the path 1-3-2, i.e., an isochoric (constant volume) decrease of pressure (1-3) followed by an isobaric expansion (3-2), the work done is just

$$W_{1-3-2} = P(V_2 - V_1) \quad (8.4)$$

We thus conclude that in general work done is path dependent and cannot be expressed simply as the difference between the end points of some state functions. There are however, some cases, for example in adiabatic work where the work is path independent.

Sign convention for work

Herein we adopt the convention that

- Work is positive when the surroundings do work on the system (in our example above, work is positive when the volume increases, showing that the gas does work on the piston, but is negative if work is done on the gas by the piston, i.e., when the volume decreases)
- Work is negative when the system does work on the surrounding.

NB: Different sign conventions are used by different authors, so take care to note the sign convention used.

8.3 Bulk modulus and the expansivity

These are among the important physical properties in thermodynamics that are easy to measure.

The volume expansivity (β) is the fractional change in volume divided by the temperature rise, that is,

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (8.5)$$

where the subscript P denotes that the measurement is at constant pressure.

In one-dimension (e.g. a wire) we have linear expansion coefficient (α) given by

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_F \quad (8.6)$$

$$\beta \approx 3\alpha \quad (8.7)$$

For a solid or fluid the bulk modulus (K) is given by

$$K = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{1}{\kappa} \quad (8.8)$$

where κ is the compressibility.

In the case of a stretched wire of cross-sectional area A , the appropriate modulus of elasticity is Young's modulus

$$E = \frac{L}{A} \left(\frac{\partial F}{\partial L} \right)_T \quad (8.9).$$

It is worthy of note that these important physical quantities, like other thermodynamic coefficients are partial differentials since their values depend on the conditions under which they are measured.



SUMMARY (Lectures 7 & 8)

1. Two systems are said to be **Thermodynamic equilibrium** if all their macroscopic properties remain invariant when they are brought in thermal contact. Such systems possess the same **temperature**.
2. The zeroth law of thermodynamics states that *if each of two systems is in thermal equilibrium with a third, they are in equilibrium with one another*.
3. A thermometer is a device or system where an appropriate macroscopic property acts to indicate temperature. The SI unit of temperature is the **Kelvin**.
4. A thermodynamic **process** is the mechanism of taking a system from one equilibrium state to another.
5. A **quasi-static process** is one that occurs so slowly that the system moves through successive equilibrium states thus enabling the process to be represented in the PV diagram. The work done by a system undergoing a quasi-static process resulting volume change from V_1 to V_2 is

$$W = \int_{V_1}^{V_2} P dV$$

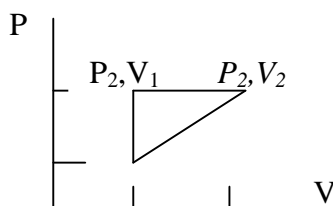
6. Four basic thermodynamic processes are: **Isothermal** (constant temperature), **Isochoric** (constant volume), **Isobaric** (constant pressure), and **Adiabatic** (no heat transfer).
7. The coefficient of volume expansivity (β) and coefficient of thermal expansivity (α) are related by the expression

$$\beta \approx 3\alpha$$



PROBLEMS (Lectures 7 & 8)

1. The length of the mercury column in a mercury-in-glass thermometer is 5 cm when the bulb is immersed in water at its triple point. What is the temperature on the mercury-in-glass scale when the length of the column is 6.0 cm? What will the length of the column be when the bulb is immersed in a liquid at 100 degrees, as measured on the mercury-in-glass scale, above the ice point? You may take the temperature of the ice point, as measured on the mercury-in-glass scale, as 273.15 degrees. (**Ans:** 327.79 degrees, 6.83 cm).
2. The resistance of a wire is given by $R = R_0(1 + \alpha t + \beta t^2)$ where t is the temperature in degrees Celsius on the ideal gas scale and so R_0 is the resistance at ice point. The constant α and β are $3.8 \times 10^{-3} \text{ K}^{-1}$ and $-3.0 \times 10^{-6} \text{ K}^{-2}$ respectively. Calculate the temperature on the resistance scale at temperature of 70°C on the ideal gas scale. (**Ans:** 341.79 degrees).
3. A constant-volume gas thermometer is filled with air whose pressure is 101 kPa at the normal melting point of ice. What would be its pressure at (a) the normal boiling point of water, (b) the normal boiling point of oxygen (90.2 K)? (**Ans:** 138 kPa, 33.4 kPa).
4. A constant-volume gas thermometer supports a 72.5-mm high mercury column when it is immersed in liquid nitrogen at -196°C . What will be the column height when the thermometer is in molten lead at 350°C ? (**Ans:** 586 mm)
5. 10 moles of an ideal gas are compressed isothermally and reversibly from a pressure of 1 atmosphere to 10 atmospheres at 300 K. How much work is done? (**Ans:** $5.7 \times 10^4 \text{ J}$).
6. A balloon contains 0.30 mol of helium. It rises, while maintaining a constant 300 K temperature, to an altitude where its volume has expanded 5 times. How much work is done by the gas during this isothermal expansion? (**Ans:** 1.2 kJ).
7. An ideal gas expands from the state (P_1, V_1) to the state (P_2, V_2) , where $P_2 = 2P_1$. The expansion proceeds along the path ACB as shown. Find an expression for the work done by the gas during this process. (**Ans:** $2P_1V_1$).



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