University of Science
Department of Materials science

Chapter 1
Introduction and Definition of Terms

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Outline

- Introduction of Course
- Chapter 1: Introduction and definition of Terms

1.1The Concept of System, State
1.2 Simple Equilibrium
1.3 The Equation of State of an Ideal Gas
1.4 The Units of Energy and Work
1.5 Extensive and Intensive Properties
1.6 Phase Diagrams and Thermodynamic Components

Introduction of Course
Thermodynamics of Materials

Course Description

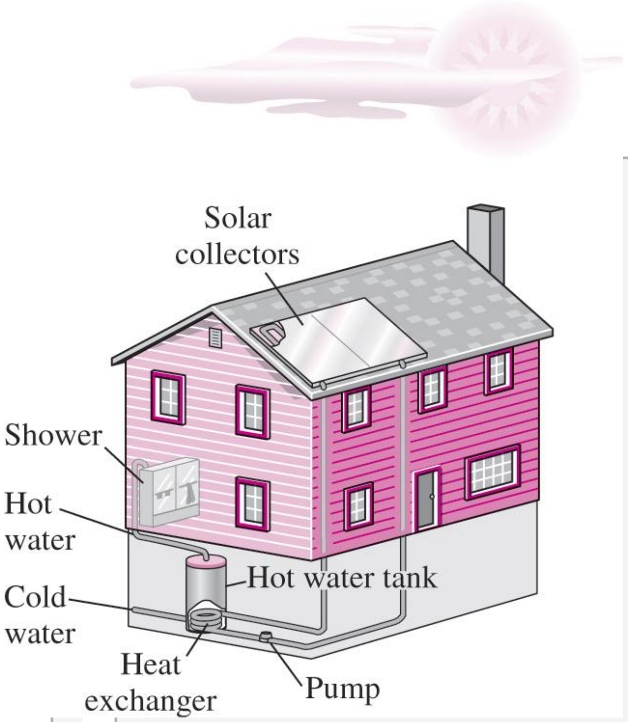
◆ Nhiệt động lực học cho vật liệu là một môn học lý thuyết cơ bản cho ngành Khoa học và kỹ thuật vật liệu.

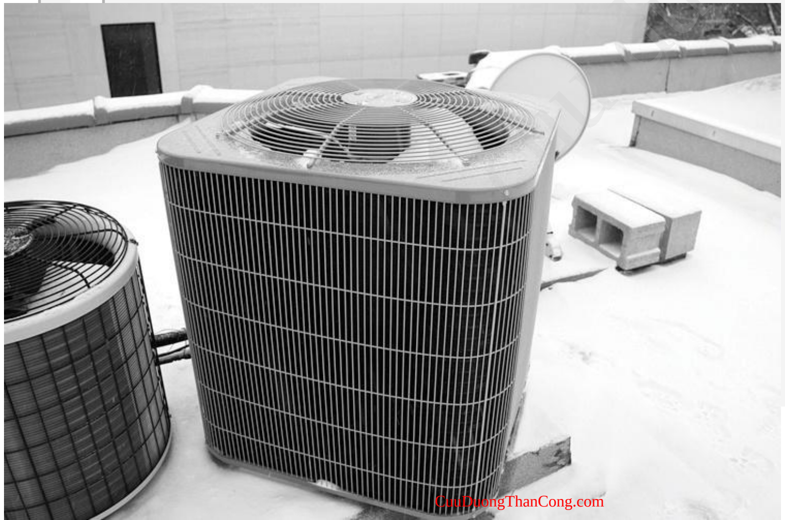
◆ Nó hỗ trợ để phân tích các tính chất vật liệu cơ bản và quá trình cho các điều kiện gần cân bằng.

◆ Các khái niệm và các ứng dụng chung của nhiệt động lực học là giúp sinh viên hiểu được các tính chất nhiệt của vật liệu trong các chương đầu của môn học.

◆ Hiện tượng cân bằng pha và chuyển pha các hệ đơn và đa thành thần cũng được chú ý đến trong môn học này.

Application Areas of Thermodynamics





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Text Book

- David R. Gaskell, Introduction to The Thermodynamics of Materials, Fourth Edition, Taylor & Francis Books, Inc. 2003. (Tài liệu tham khảo chính)

References

- Richard A. Swalin, Thermodynamics of Solids, 2nd ed., John Wiley & Sons, 1972.
- David V. Ragone, Thermodynamics of Materials, Vol. I and II, John Wiley & Sons, The MIT Series, 1995.
- Robert T. DeHoff, Thermodynamics in Materials Science, McGraw-Hill, Inc. 1993.

Introduction of Course
Thermodynamics of Materials

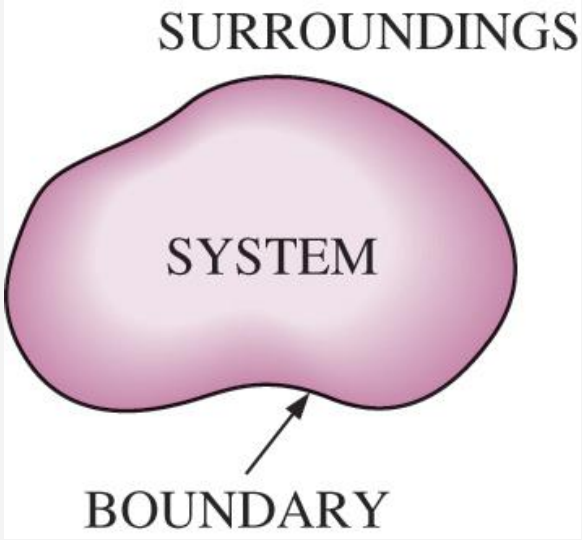
Syllabus

- 1. Introduction and Definition of Terms
- 2. The First and Second Laws of Thermodynamics
- 3. Entropy - the Statistical Interpretation
- 4. Auxiliary Functions
- 5. Heat Capacity, Enthalpy, Entropy, and The Third Law of Thermodynamics
- 6. Phase Equilibrium in a One-Component System
- 7. The Behavior of Gases
- 8. The Behavior of Solutions
- 9. Gibbs Free Energy Composition and Phase Diagrams of Binary Systems
- 10. Reaction Involving Gases
- 11. Reaction Involving Pure Condensed Phases and a Gaseous Phase
- 12. Reaction Equilibria

Chapter 1 Introduction and Definition of Terms

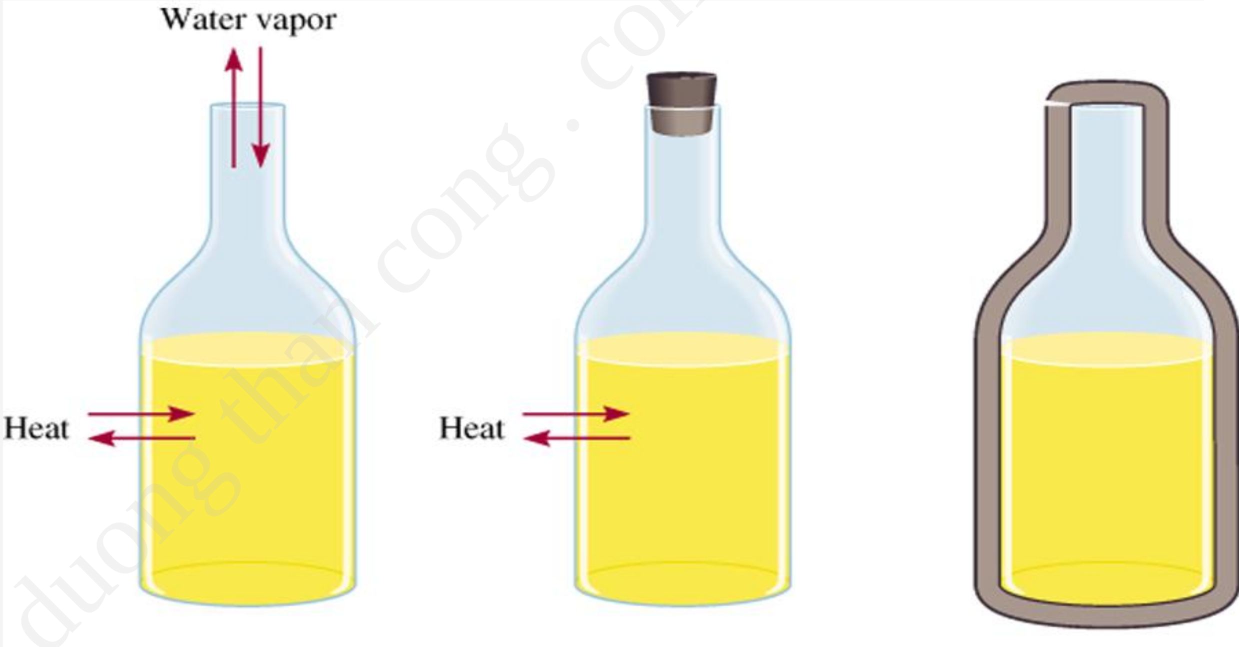
◆ 1.1THE CONCEPT OF SYSTEM, STATE

✓A system is a part of the world which is isolated from the rest of the world by definite boundaries.
✓The world outside the system is called Surrounding.
✓In materials science and engineering, the systems to which thermodynamics principles are applied are usually chemical reaction systems.



Chapter 1 Introduction and Definition of Terms

* **Types of System**



(1) Isolated system

No possibility of transfer either of energy or matter across the boundaries.

(2) Closed system

Possibility of energy exchanged with the environment. No transfer of matter across the boundaries.

(3) Open system

Exchange of both energy and matter with the environment is possible.

Chapter 1 Introduction and Definition of Terms

◆ **State**

Microscopic state: If it is possible to know the masses, velocities, positions, and all modes of all of the constituent particles in a system, this mass of knowledge would serve to describe the state of the system, which would determine all of the properties of the system.

Macroscopic state: A specific condition of a system, which is completely and precisely described through its properties.

Generally, only the minimum number of properties necessary to completely describe the state.

Chapter 1 Introduction and Definition of Terms

- **State Function (State Variable)**

A variable which depends only on the state of the system. If a change in the system occurs, the change in such a function depends only on the initial and final state, and is independent of the path of the change. e.g. ***T, V, P, U, H, S, G***.

- **Equation of State**

A mathematical relationship between the state functions.

Example: Consider the volume *V* of a fixed quantity of a pure gas as a property, the value of which is dependent on the values of *P* and *T*. The relationship between the dependent variable *V* and the independent variables *P* and *T* can be expressed as

$$V = V(P,T)$$

This is called an equation of state.

Chapter 1 Introduction and Definition of Terms

In a three-dimensional diagram, the coordinates of which are volume, temperature, and pressure, the points in *P*-*V*-*T* space which represent the equilibrium states of existence of the system lie on a surface.

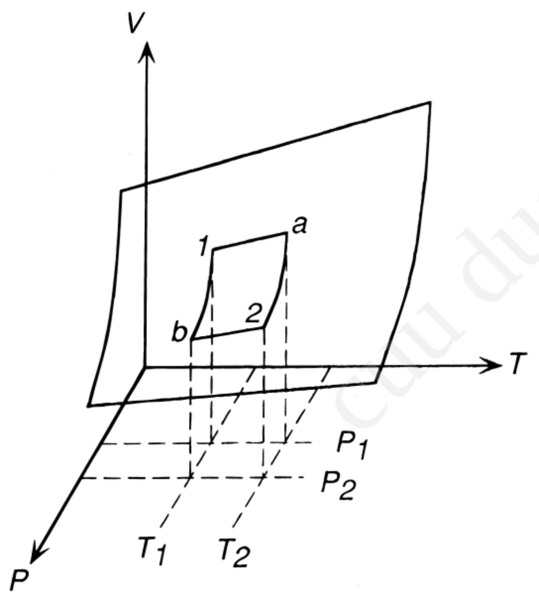


Figure 1.1 The Equilibrium States of existence of a Fixed Quantity of gas in P-V-T space.

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Fixing the values of any two of the three variables fixes the value of the third variable. Consider a process which moves the gas from state 1 to state 2. This process causes the volume of the gas to change by

$$\Delta V = V_2 - V_1$$

This process could proceed along an infinite number of paths on the *P*-*V*-*T* surface, two of which, 1→a→2 and 1→b→2, are shown in Fig. 1.1.

Considering the path 1→a→2, the change in volume is

$$\Delta V = V_2 - V_1 = (V_a - V_1) + (V_2 - V_a) = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$$

Similarly for the path 1→b→2,

$$\Delta V = (V_b - V_1) + (V_2 - V_b) = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_2} dT$$

The change in volume caused by moving the state of the gas from state 1 to state 2 depends only on the volume at state 1 and the volume at state 2 and is independent of the path.

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- **Zero Law of Thermodynamics**

If body A and B are each in thermal equilibrium with a third body C, they are also in thermal equilibrium with each other.

$$T_A = T_C \text{ and } T_B = T_C \Rightarrow T_A = T_B$$

The aim of classical thermodynamics is to establish the relationships which exist between equilibrium state of a given system and the influences which are brought to bear on the system.

Chapter 1 Introduction and Definition of Terms

- **Phase**

  A phase is defined as being a finite volume in the physical system within which the properties are uniformly constant.

  i.e. It does not experience any abrupt change in passing from one point to another.

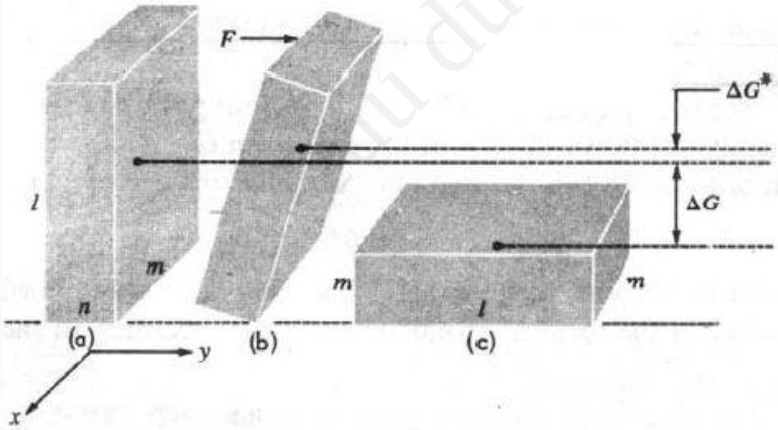
Chapter 1 Introduction and Definition of Terms

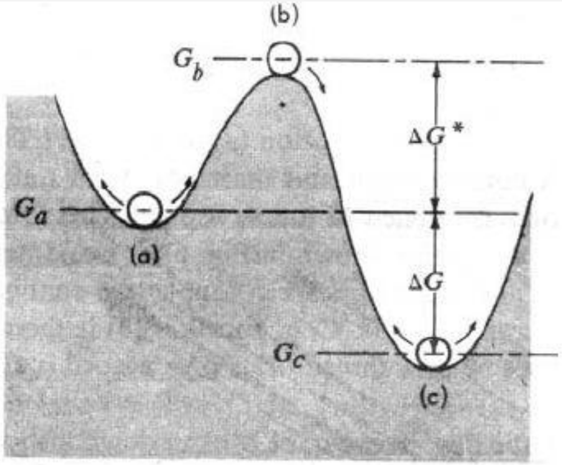
1.2 SIMPLE EQUILIBRIUM

A system shows no further tendency to change its properties with time.

(1) Stable equilibrium

(2) Meta-stable equilibrium





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1.2 SIMPLE EQUILIBRIUM

A particularly simple system is illustrated in Fig. 1.2. This is a fixed quantity of gas contained in a cylinder by a movable piston. The system is at rest, i.e. is at equilibrium, when:

1. The pressure exerted by the gas on the piston equals the pressure exerted by the piston on the gas, and
2. The temperature of the gas is the same as the temperature of the surroundings (provided that heat can be transported through the wall).

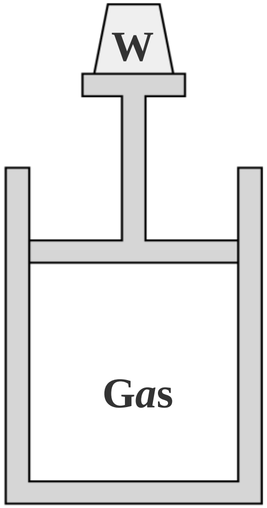


Figure 1.2 A quantity of gas contained in a cylinder by a piston.

Chapter 1 Introduction and Definition of Terms

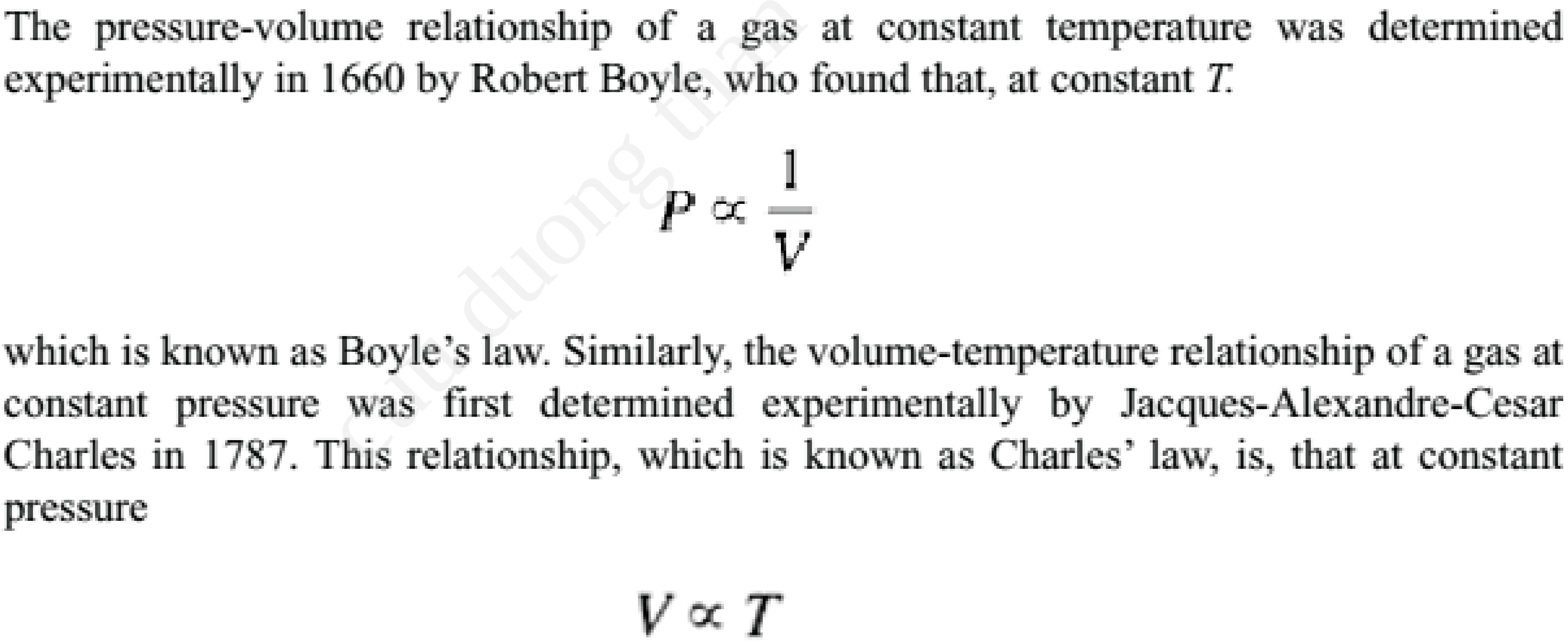
1.2 SIMPLE EQUILIBRIUM

Equilibrium occurs as a result of the establishment of a balance between the tendency of the external influences acting on the system to cause a change in the system and the tendency of the system to resist change.

The fixing of the pressure of the gas at P_1 and the temperature T_1 determines the state of the system and hence fixes the volume at the value V_1. If, by suitable decrease in the weight placed on the piston, the pressure exerted on the gas is decreased to P_2, the resulting imbalance between the pressure exerted by the gas and the pressure exerted on the gas causes the piston to move out of the cylinder. This process increases the volume of the gas and hence decreases the pressure which it exerts on the piston until equalization of the pressure is restored.

Chapter 1 Introduction and Definition of Terms

1.3 THE EQUATION OF STATE OF AN IDEAL GAS



The pressure-volume relationship of a gas at constant temperature was determined experimentally in 1660 by Robert Boyle, who found that, at constant *T*.

$$P \propto \frac{1}{V}$$

which is known as Boyle's law. Similarly, the volume-temperature relationship of a gas at constant pressure was first determined experimentally by Jacques-Alexandre-Cesar Charles in 1787. This relationship, which is known as Charles' law, is, that at constant pressure

$$V \propto T$$

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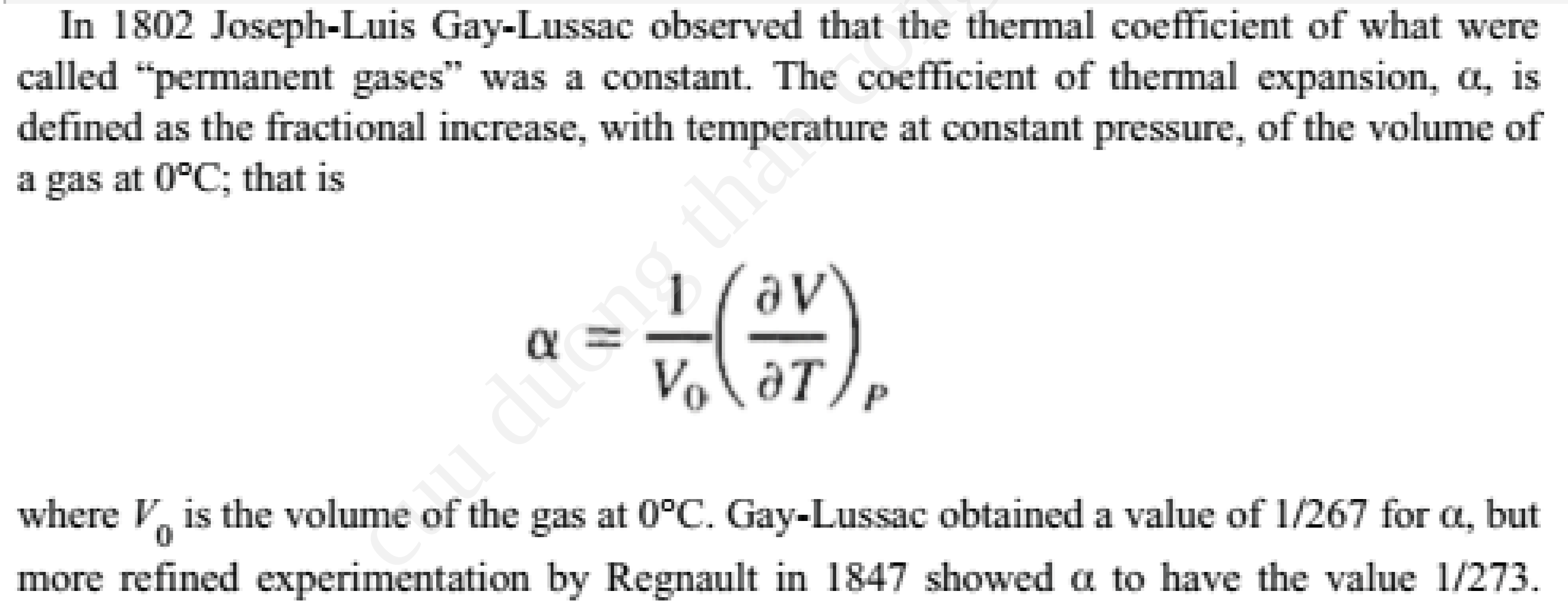
1.3 THE EQUATION OF STATE OF AN IDEAL GAS



In 1802 Joseph-Luis Gay-Lussac observed that the thermal coefficient of what were called "permanent gases" was a constant. The coefficient of thermal expansion, α, is defined as the fractional increase, with temperature at constant pressure, of the volume of a gas at 0°C; that is

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$$

where V_0 is the volume of the gas at 0°C. Gay-Lussac obtained a value of 1/267 for α, but more refined experimentation by Regnault in 1847 showed α to have the value 1/273.

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1.3 THE EQUATION OF STATE OF AN IDEAL GAS

combination of Boyle's law

$$P_0V(T,P_0) = PV(T,P)$$

and Charles' law

$$\frac{V(P_0,T_0)}{T_0} = \frac{V(P_0,T)}{T}$$

where

P_0=standard pressure (1 atm)
T_0=standard temperature (273.15 degrees absolute)
$V(T,P)$=volume at temperature T and pressure P

gives

$$\frac{PV}{T} = \frac{P_0V_0}{T_0} = \text{constant} \qquad (1.5)$$

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1.3 THE EQUATION OF STATE OF AN IDEAL GAS

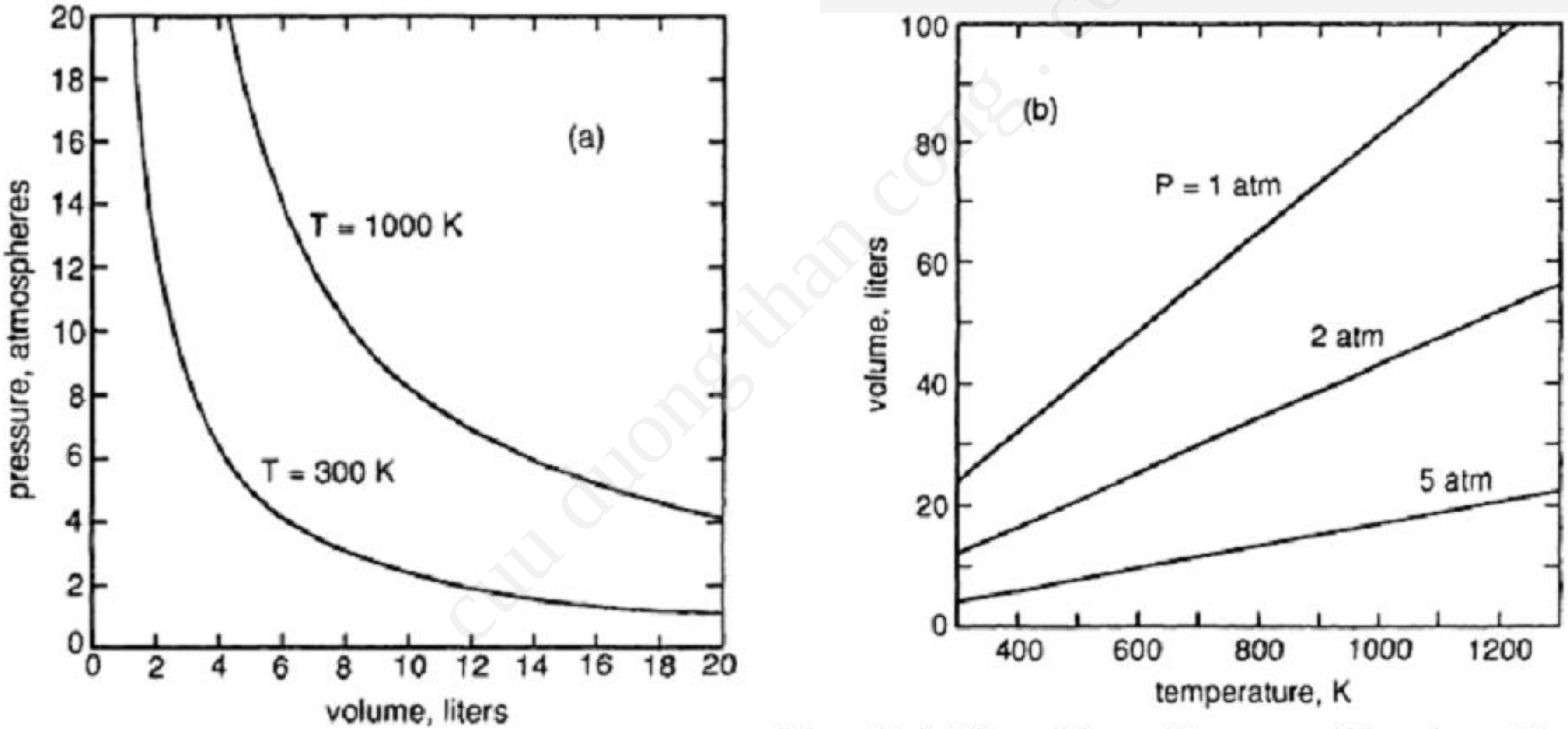

Figure 1.3 *(a)* The variations, with pressure, of the volume of 1 mole of ideal gas at 300 and 1000 K. *(b)* The variations, with temperature, of the volume of 1 mole of ideal gas at 1, 2, and 5 atm.

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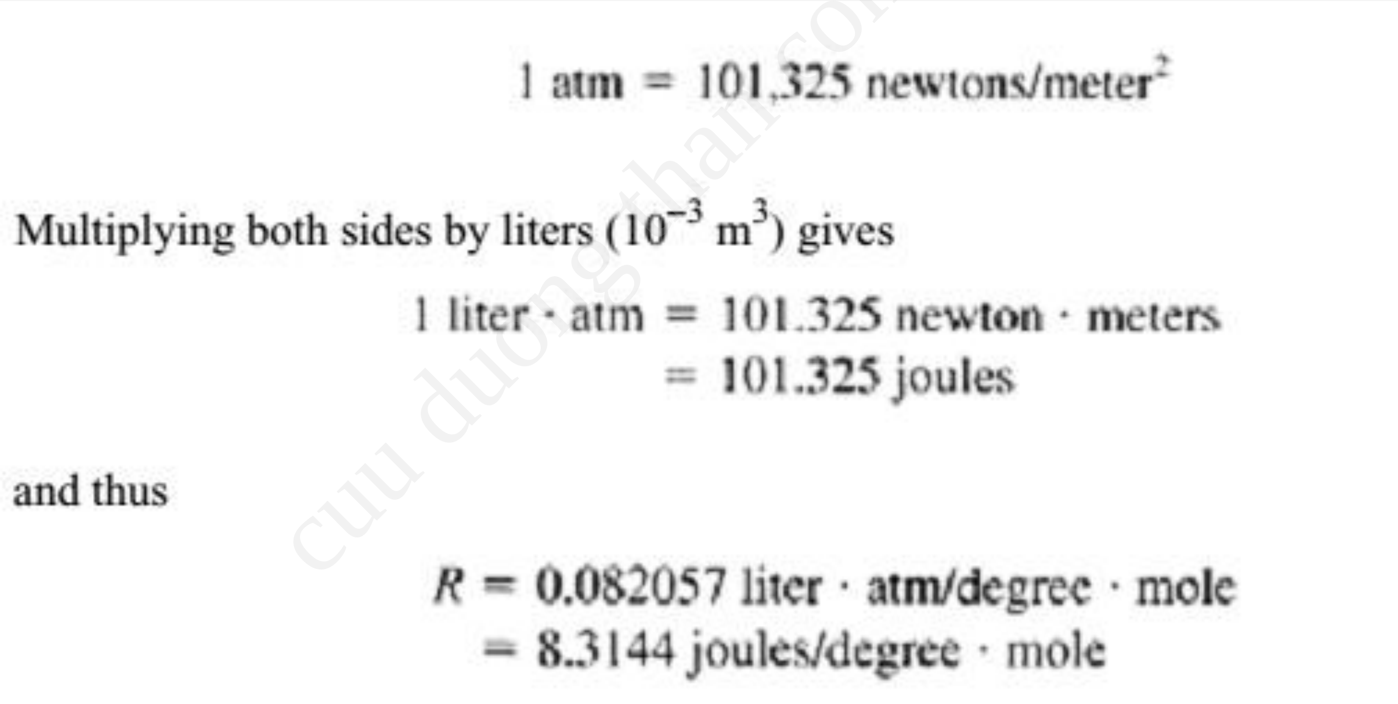
1.4 THE UNITS OF ENERGY, WORK, TEMPERATURE AND PRESSURE



$$1 \text{ atm} = 101{,}325 \text{ newtons/meter}^2$$

Multiplying both sides by liters (10^{-3} m^3) gives

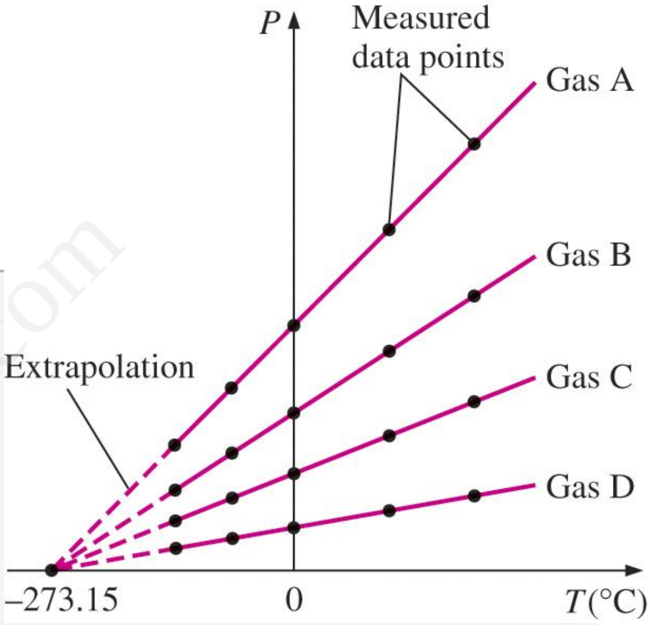
$$\begin{aligned} 1 \text{ liter} \cdot \text{atm} &= 101.325 \text{ newton} \cdot \text{meters} \\ &= 101.325 \text{ joules} \end{aligned}$$

and thus

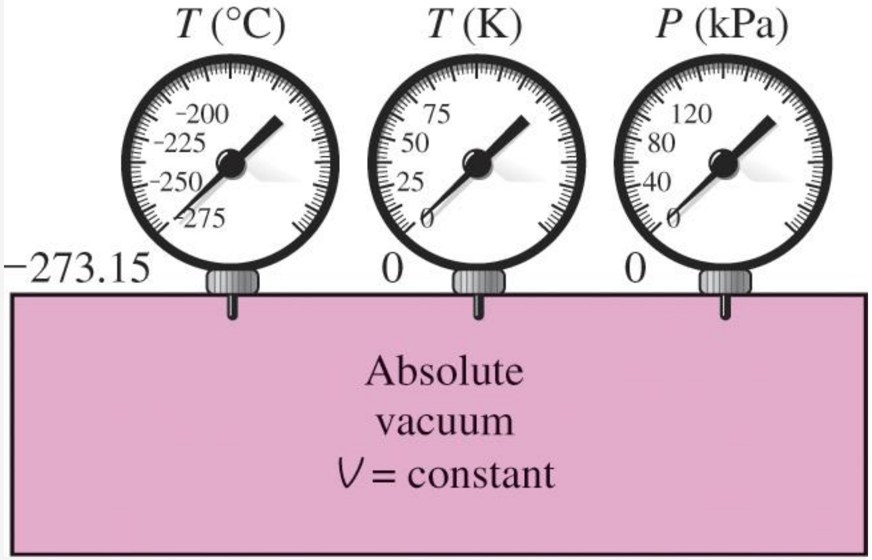
$$\begin{aligned} R &= 0.082057 \text{ liter} \cdot \text{atm/degree} \cdot \text{mole} \\ &= 8.3144 \text{ joules/degree} \cdot \text{mole} \end{aligned}$$

Temperature Scales

- All temperature scales are based on some easily reproducible states such as the freezing and boiling points of water: the *ice point* and the *steam point.*
- **Ice point**: A mixture of ice and water that is in equilibrium with air saturated with vapor at 1 atm pressure (0°C or 32°F).
- **Steam point**: A mixture of liquid water and water vapor (with no air) in equilibrium at 1 atm pressure (100°C or 212°F).
- **Celsius scale**: in SI unit system
- **Fahrenheit scale**: in English unit system
- **Thermodynamic temperature scale**: A temperature scale that is independent of the properties of any substance.
- **Kelvin scale** (SI) **Rankine scale** (E)
- A temperature scale nearly identical to the Kelvin scale is the **ideal-gas temperature scale**. The temperatures on this scale are measured using a constant-volume gas thermometer.



P versus T plots of the experimental data obtained from a constant-volume gas thermometer using four different gases at different (but low) pressures.



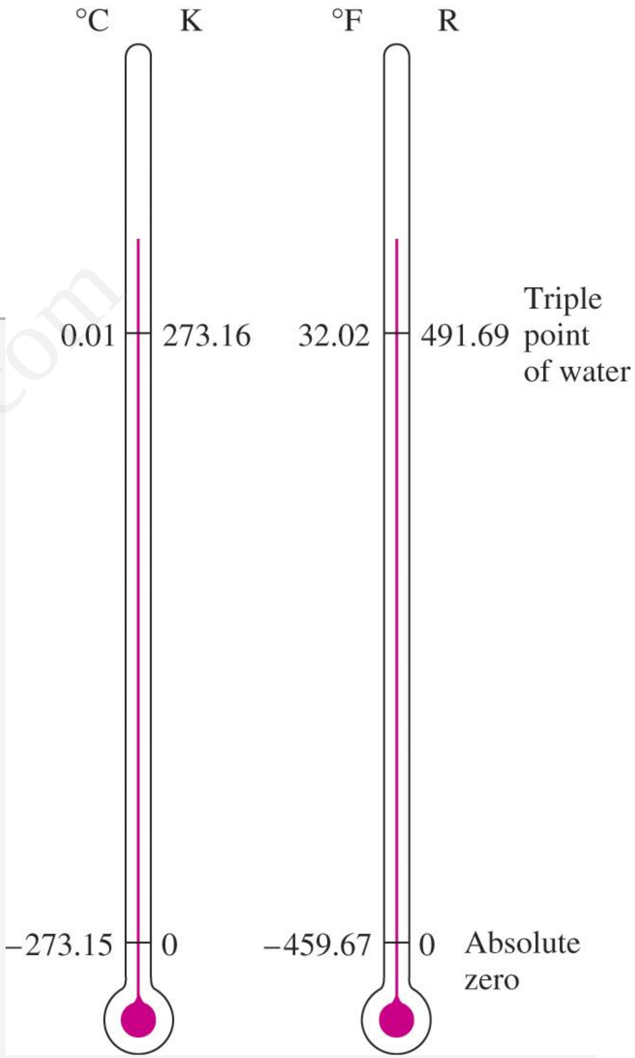
A constant-volume gas thermometer would read -273.15°C at absolute zero pressure.

$$T(\mathrm{K}) = T(^\circ\mathrm{C}) + 273.15$$

$$T(\mathrm{R}) = T(^\circ\mathrm{F}) + 459.67$$

$$T(\mathrm{R}) = 1.8T(\mathrm{K})$$

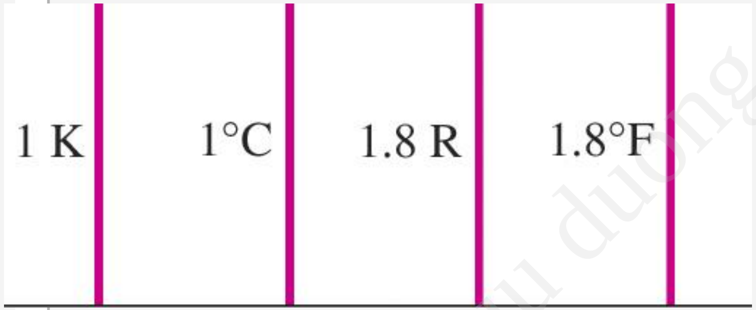
$$T(^\circ\mathrm{F}) = 1.8T(^\circ\mathrm{C}) + 32$$



Comparison of temperature scales.

$$\Delta T(\mathrm{K}) = \Delta T(^\circ\mathrm{C})$$

$$\Delta T(\mathrm{R}) = \Delta T(^\circ\mathrm{F})$$



Comparison of magnitudes of various temperature units.

- The reference temperature in the original Kelvin scale was the ***ice point***, 273.15 K, which is the temperature at which water freezes (or ice melts).
- The reference point was changed to a much more precisely reproducible point, the ***triple point*** of water (the state at which all three phases of water coexist in equilibrium), which is assigned the value 273.16 K.

PRESSURE

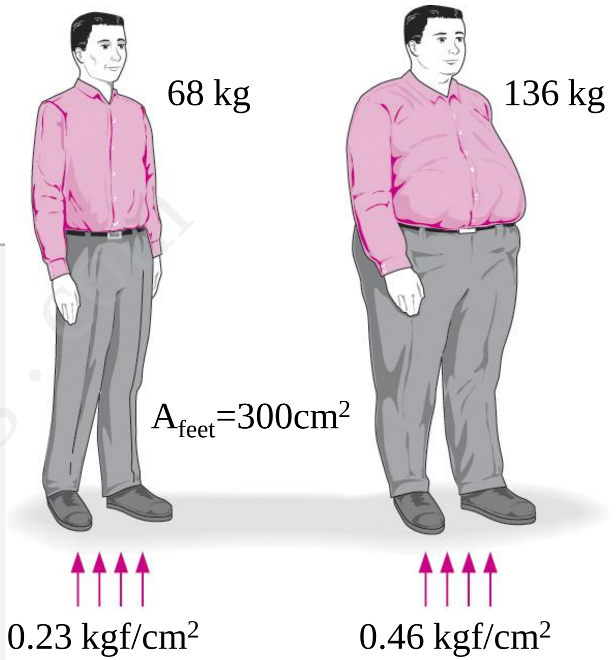
Pressure: A normal force exerted by a fluid per unit area

$$1\ \text{Pa} = 1\ \text{N/m}^2$$

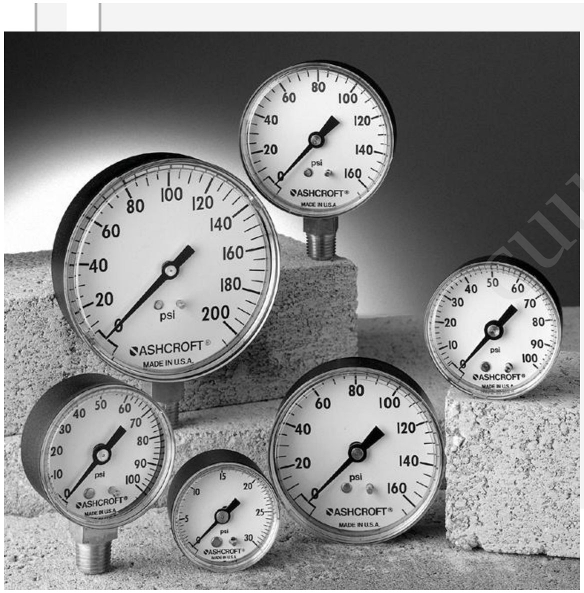
$$1\ \text{bar} = 10^5\ \text{Pa} = 0.1\ \text{MPa} = 100\ \text{kPa}$$

$$1\ \text{atm} = 101{,}325\ \text{Pa} = 101.325\ \text{kPa} = 1.01325\ \text{bars}$$

$$\begin{aligned} 1\ \text{kgf/cm}^2 &= 9.807\ \text{N/cm}^2 = 9.807 \times 10^4\ \text{N/m}^2 = 9.807 \times 10^4\ \text{Pa} \\ &= 0.9807\ \text{bar} \\ &= 0.9679\ \text{atm} \end{aligned}$$



P=68/300=0.23 kgf/cm²



Some basic pressure gages.

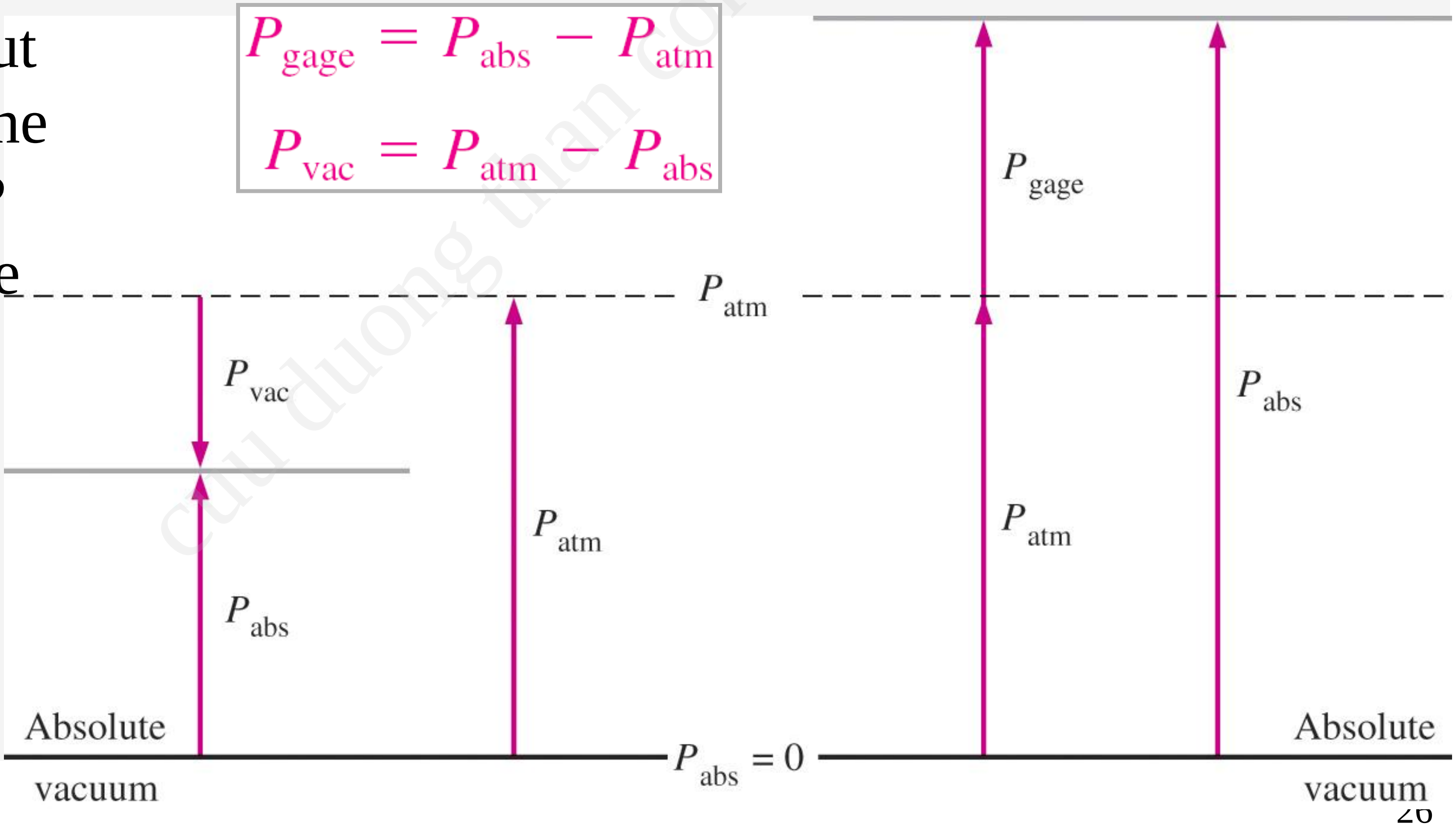
The normal stress (or "pressure") on the feet of a chubby person is much greater than on the feet of a slim person.

- **Absolute pressure**: The actual pressure at a given position. It is measured relative to absolute vacuum (i.e., absolute zero pressure).
- **Gage pressure**: The difference between the absolute pressure and the local atmospheric pressure. Most pressure-measuring devices are calibrated to read zero in the atmosphere, and so they indicate gage pressure.
- **Vacuum pressures**: Pressures below atmospheric pressure.

Throughout this text, the pressure ***P*** will denote ***absolute pressure*** unless specified otherwise.

$$P_{\text{gage}} = P_{\text{abs}} - P_{\text{atm}}$$

$$P_{\text{vac}} = P_{\text{atm}} - P_{\text{abs}}$$



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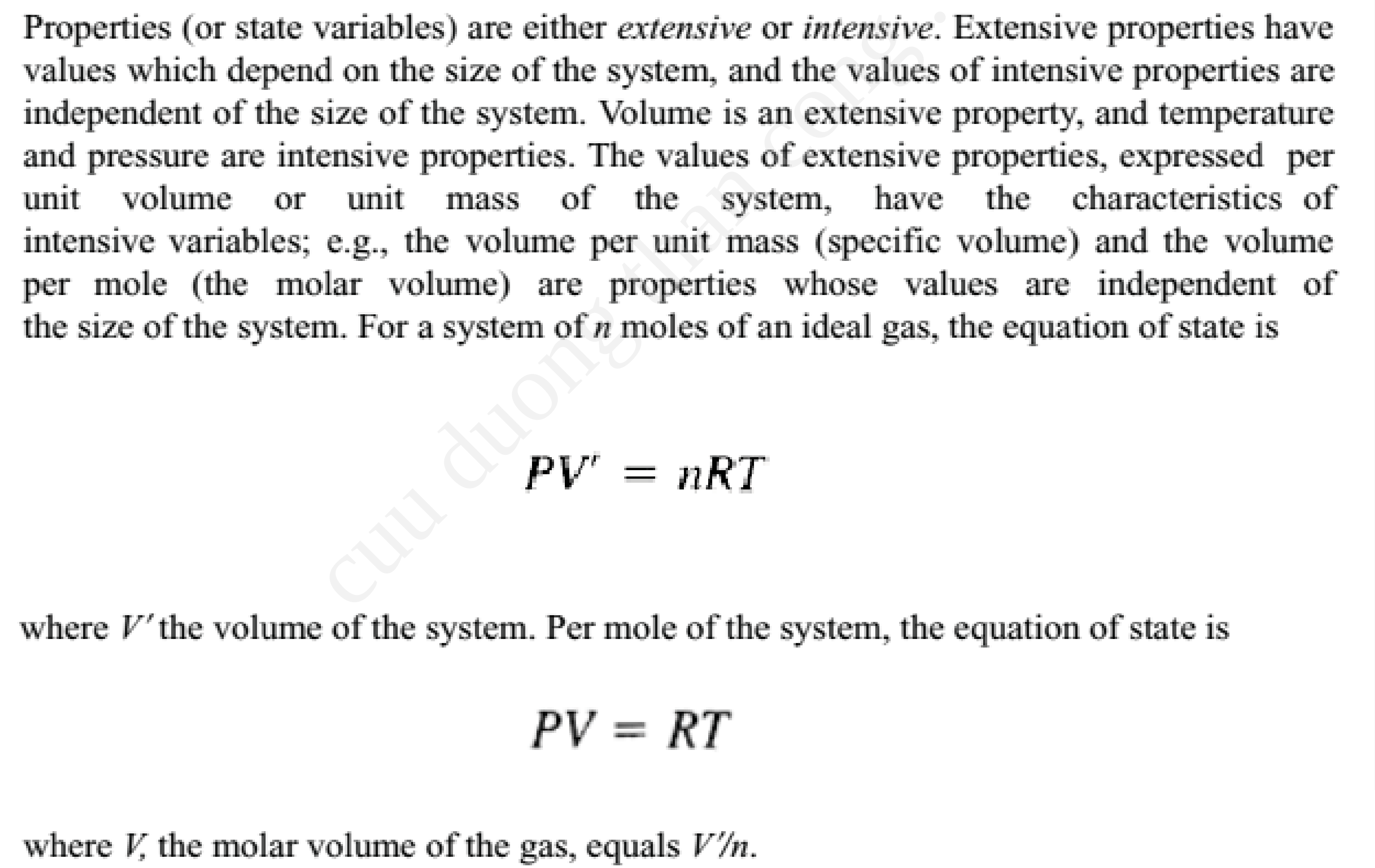
1.5 INTENSIVE AND EXTENSIVE PROPERTIES



Properties (or state variables) are either *extensive* or *intensive*. Extensive properties have values which depend on the size of the system, and the values of intensive properties are independent of the size of the system. Volume is an extensive property, and temperature and pressure are intensive properties. The values of extensive properties, expressed per unit volume or unit mass of the system, have the characteristics of intensive variables; e.g., the volume per unit mass (specific volume) and the volume per mole (the molar volume) are properties whose values are independent of the size of the system. For a system of n moles of an ideal gas, the equation of state is

$$PV' = nRT$$

where V' the volume of the system. Per mole of the system, the equation of state is

$$PV = RT$$

where V, the molar volume of the gas, equals V'/n.

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1.5 INTENSIVE AND EXTENSIVE PROPERTIES

Quantities which can be used to describe a system, e.g. density, volume, …

(1) Intensive properties

not additive, independent of size or mass of the system. e.g. temperature, pressure, density, …

(2) Extensive properties

additive, dependent of the size of the system. e.g. volume, no. of moles, …

extensive/extensive = intensive

e.g. density = mass/volume, pressure = force/area.

Chapter 1 Introduction and Definition of Terms

1.6 PHASE DIAGRAMS AND THERMODYNAMIC COMPONENTS

The phase diagram of a one-component system (i.e. a system of fixed composition) is a two-dimensional representation of the dependence of the equilibrium state of existence of the system on the two independent variables. *T* and *P* are normally chosen as the two independent variables. Fig. 1.4 shows a schematic of part of the phase diagram for H_2O.

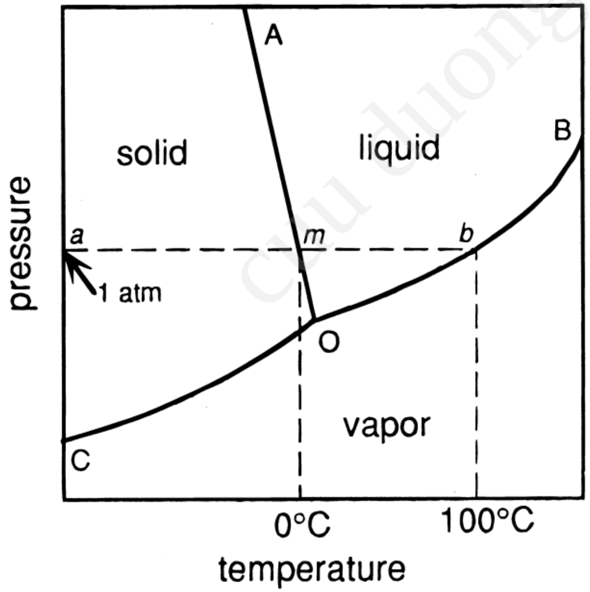

Figure 1.4 Schematic representation of part of the phase diagram for H_2O.

1.6 PHASE DIAGRAMS AND THERMODYNAMIC COMPONENTS

If the system contains two components, a composition axis must be included and the complete diagram is three-dimensional with the coordinates composition, temperature, and pressure. In most cases, however, it is sufficient to present a binary phase diagram as a constant pressure section of the three-dimensional diagram. The constant pressure chosen is normally 1 atm. Figure 1.5 shows the phase relationships occurring in the system Al_2O_3-Cr_2O_3 at 1 atm pressure.

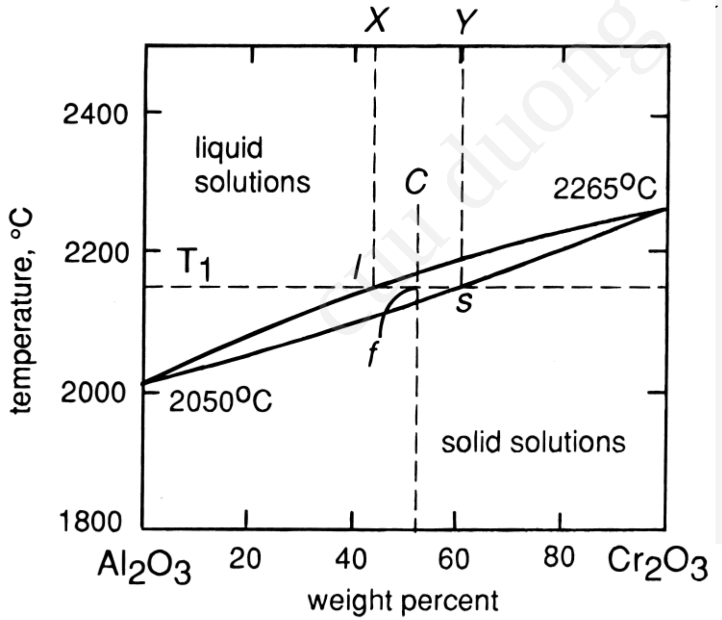

Figure 1.5 The phase diagram for the system Al_2O_3–Cr_2O_3.

The end!

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