الثرموداينمك
المرحلة الثانية

Thermodynamic

- الفصل الأول - الخواص العامة للغازات :

The perfect gas

1.1 The states of gases

(a) Pressure

(b) The measurement of pressure

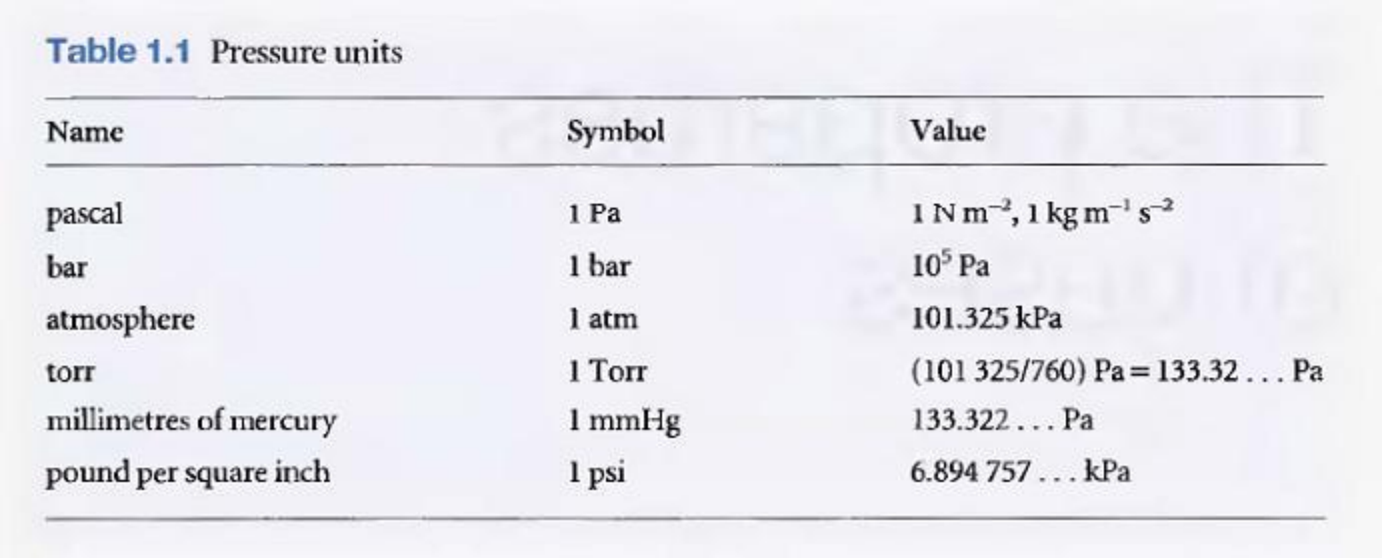


Table 1.1 Pressure units

Name	Symbol	Value
pascal	1 Pa	$1\ \mathrm{N\ m^{-2}}$, $1\ \mathrm{kg\ m^{-1}\ s^{-2}}$
bar	1 bar	10^5 Pa
atmosphere	1 atm	101.325 kPa
torr	1 Torr	(101 325/760) Pa = 133.32 . . . Pa
millimetres of mercury	1 mmHg	133.322 . . . Pa
pound per square inch	1 psi	6.894 757 . . . kPa

درجة الحرارة C) Temperature

- القانون الصفري للثرموداينمك و التوازن الحراري\
- قوانين الغازات:
- قوانين الغاز المثالي:

1.2 The gas laws

(a) The perfect gas law

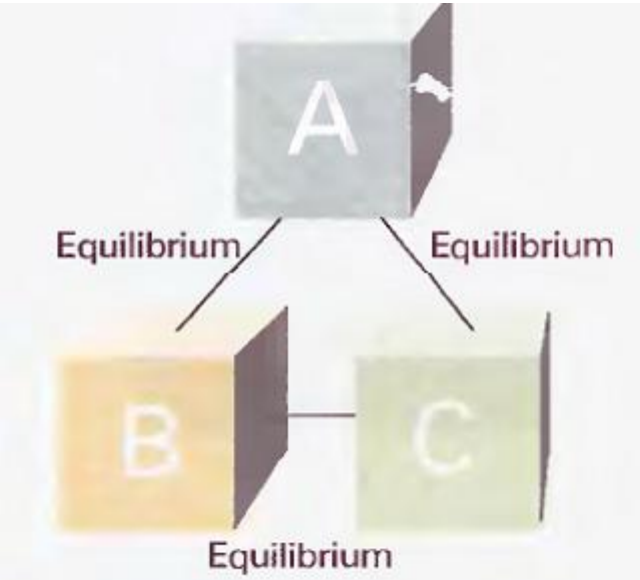


Fig. 1.3 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

- سنتطرق خلالها بدراسة علاقة T
- مع , V , P ثم اشتقاق القانون:

$$pV = nRT$$

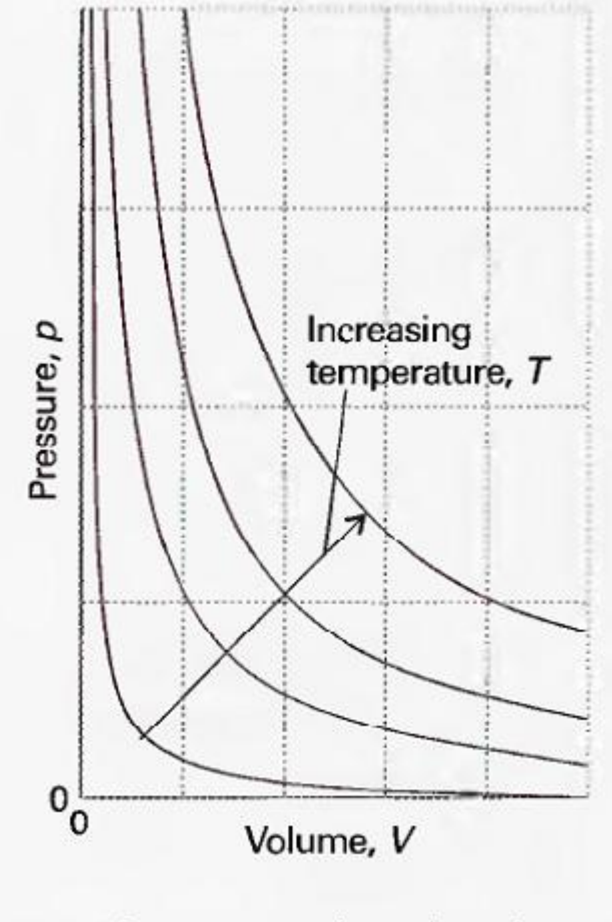


Fig. 1.4 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola (pV = constant) and is called an *isotherm*.

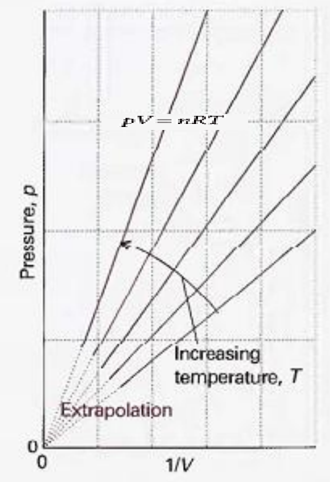


Fig. 1.5 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

Exploration Repeat *Exploration 1.4*, but plot the data as p against $1/V$.

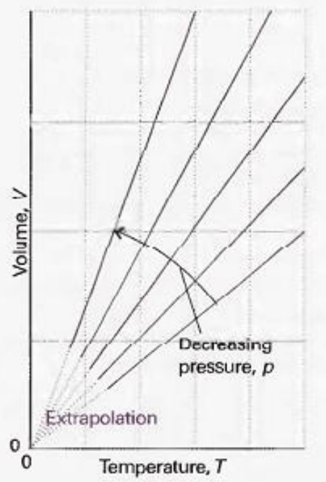


Fig. 1.6 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, or $\theta = -273°C$.

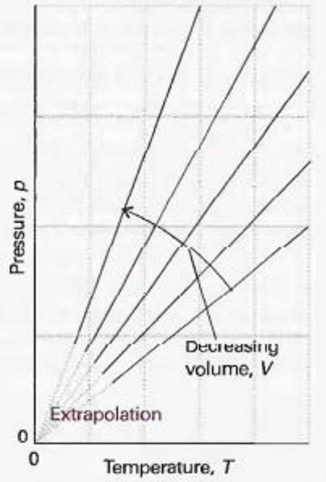


Fig. 1.7 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (−273°C).

Exploration Explore how the pressure of 1.5 mol $CO_2(g)$ in a container of

- الغازات الحقيقية

Real gases

1.3 Molecular interactions

(a) The compression factor

(b) Virial coefficients

(c) Condensation

(d) Critical constants

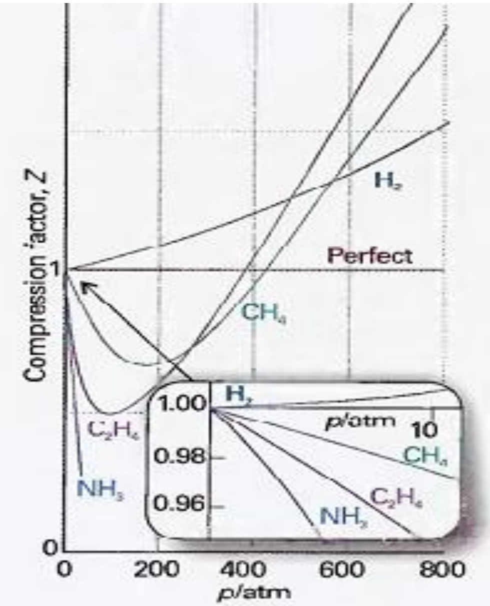


Fig. 1.14 The variation of the compression factor, Z, with pressure for several gases at 0°C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \to 0$, they do so with different slopes.

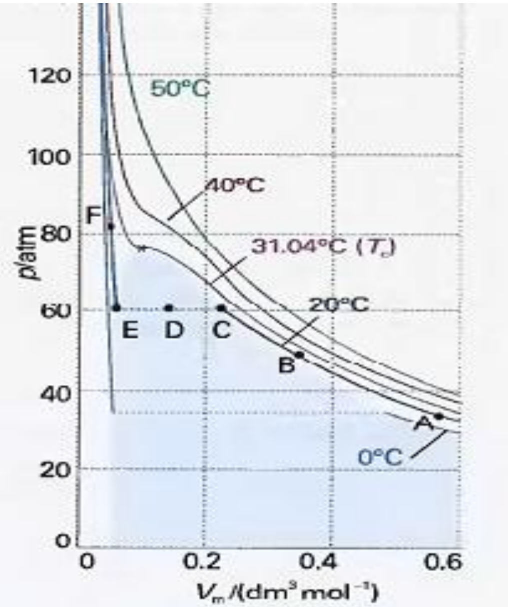


Fig. 1.15 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.04°C. The critical point is marked with a star.

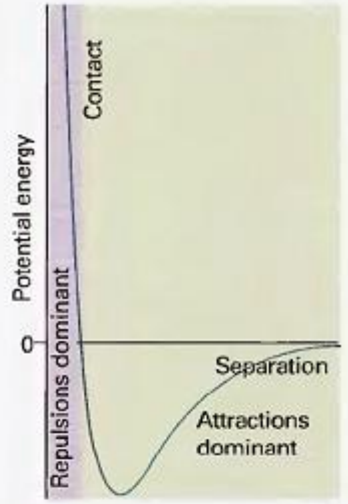


Fig. 1.13 The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.

- معادلة فاندرفالز:

1.4 The van der Waals equation

- الفصل الثاني - القانون الأول للثرموداينمك:

The basic concepts

2.1 Work, heat, and energy
2.2 The internal energy
2.3 Expansion work
2.4 Heat transactions
2.5 Enthalpy
I2.1 Impact on biochemistry and materials science: Differential scanning calorimetry
2.6 Adiabatic changes

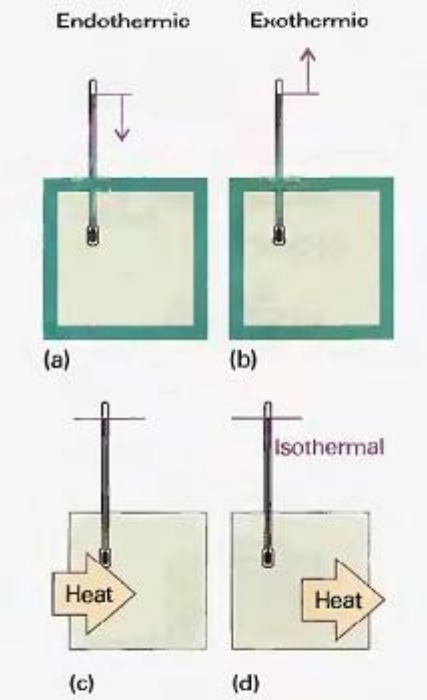


Fig. 2.2 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.

- الفصل الثالث - الكيمياء الحرارية
- الكيمياء الحرارية

Thermochemistry

2.7 Standard enthalpy changes

I2.2 Impact on biology: Food and energy reserves

2.8 Standard enthalpies of formation

2.9 The temperature-dependence of reaction enthalpies

State functions and exact differentials

2.10 Exact and inexact differentials

2.11 Changes in internal energy

2.12 The Joule–Thomson effect

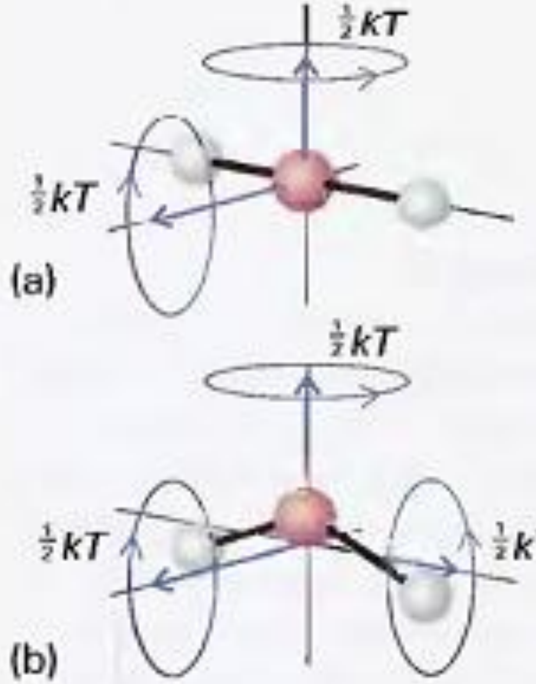


Fig. 2.5 The rotational modes of molecules and the corresponding average energies at a temperature T. (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

2.3 Expansion work

- الشغل او توسع الشغل
- مبداء التبريد و تحول الطاقة من ضغط
- الى شغل، .....
-

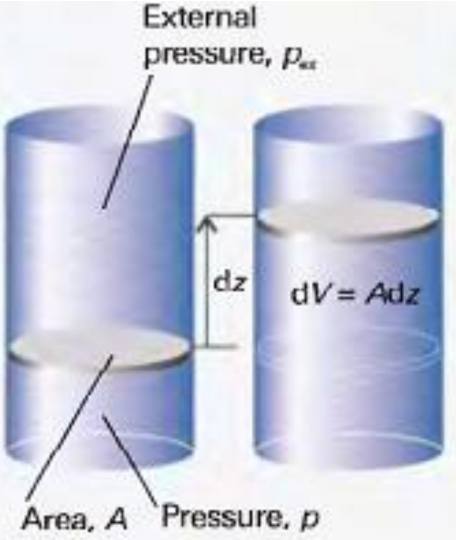


Fig. 2.6 When a piston of area A moves out through a distance dz, it sweeps out a volume $dV = Adz$. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.

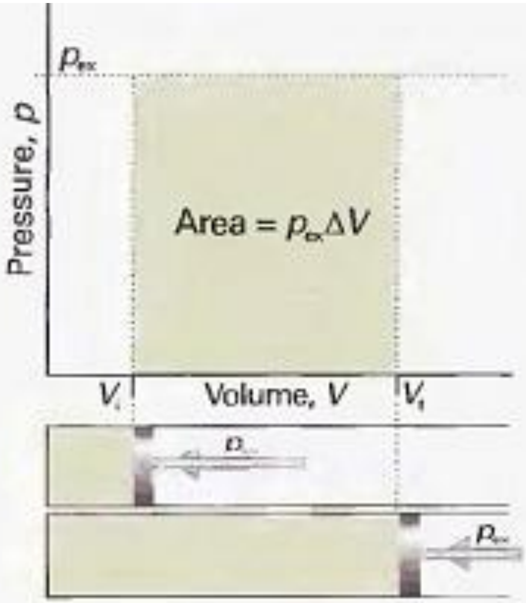


Fig. 2.7 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

- التحولات الحرارية

2.4 Heat transactions

(a) Calorimetry

(b) Heat capacity

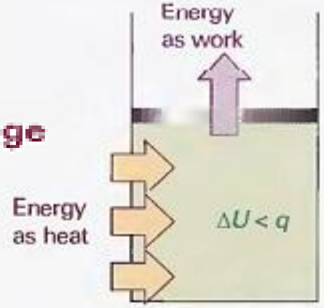
2.5 Enthalpy

(a) The definition of enthalpy

The enthalpy, H, is defined as

$$H = U + pV$$

(b) The measurement of an enthalpy change



(c) The variation of enthalpy with temperature

heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

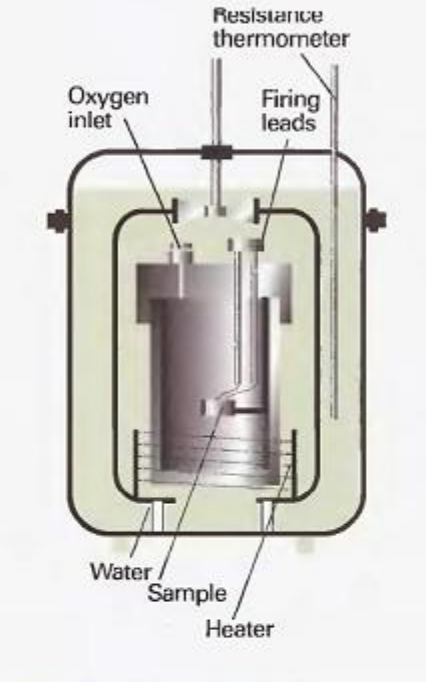
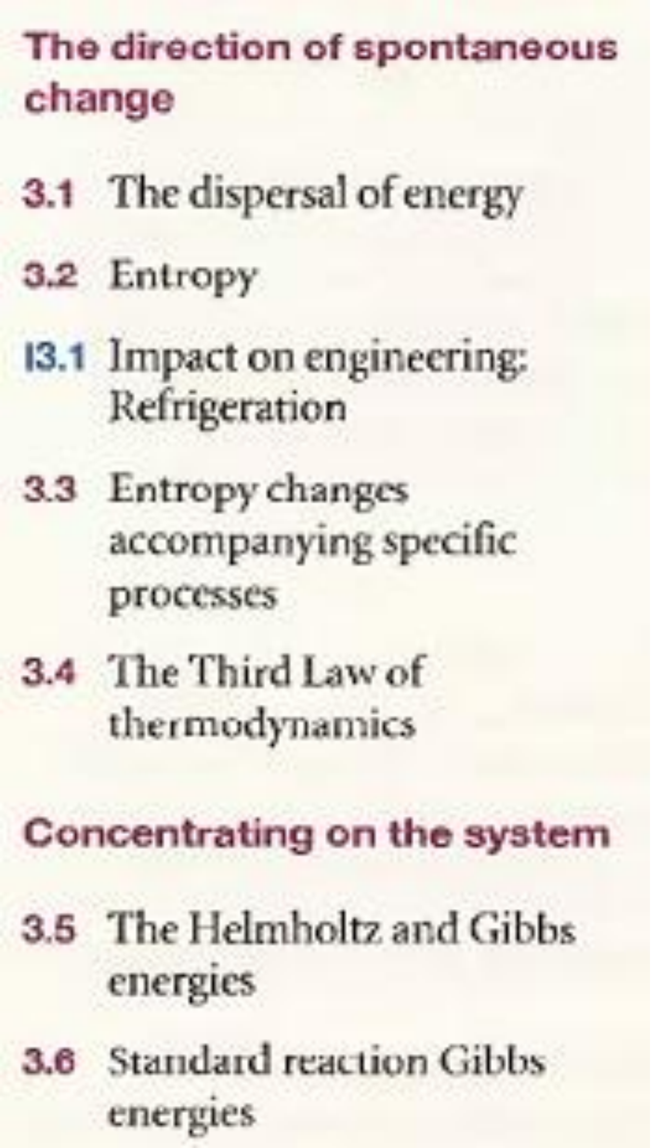


Fig. 2.9 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

- الفصل الرابع - القانون الثاني والثالث للثرموداينمك:



The direction of spontaneous change

3.1 The dispersal of energy

3.2 Entropy

I3.1 Impact on engineering: Refrigeration

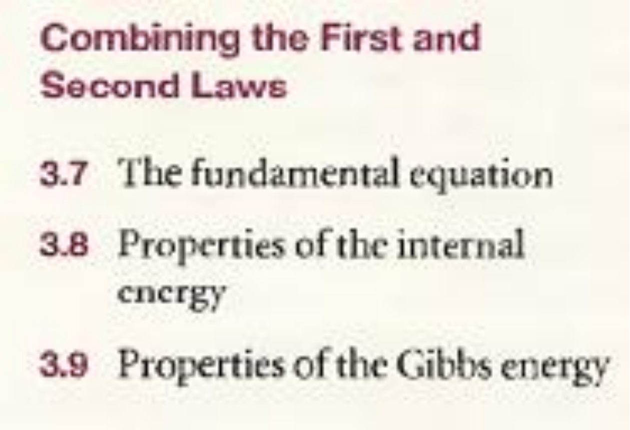
3.3 Entropy changes accompanying specific processes

3.4 The Third Law of thermodynamics

Concentrating on the system

3.5 The Helmholtz and Gibbs energies

3.6 Standard reaction Gibbs energies



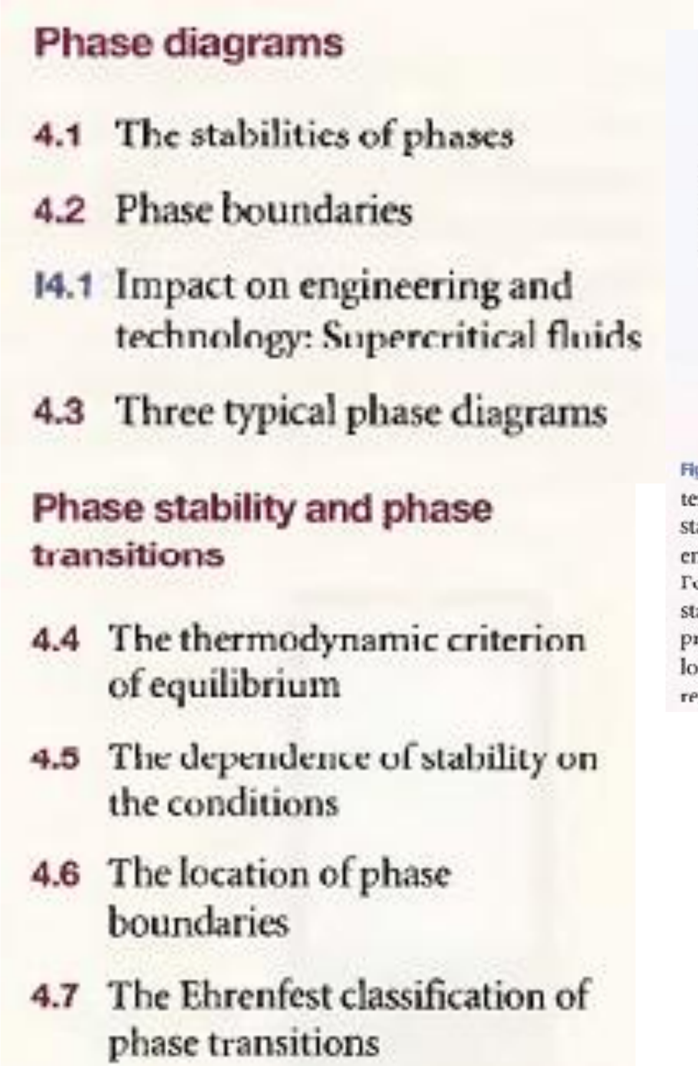
Combining the First and Second Laws

3.7 The fundamental equation

3.8 Properties of the internal energy

3.9 Properties of the Gibbs energy

- الفصل الخامس - مقدمة في العلاقة بين الطاقة الحرة والاتزان الكيميائي
- الفصل السادس - الأتزان الكيميائي



Phase diagrams

4.1 The stabilities of phases
4.2 Phase boundaries
I4.1 Impact on engineering and technology: Supercritical fluids
4.3 Three typical phase diagrams

Phase stability and phase transitions

4.4 The thermodynamic criterion of equilibrium
4.5 The dependence of stability on the conditions
4.6 The location of phase boundaries
4.7 The Ehrenfest classification of phase transitions

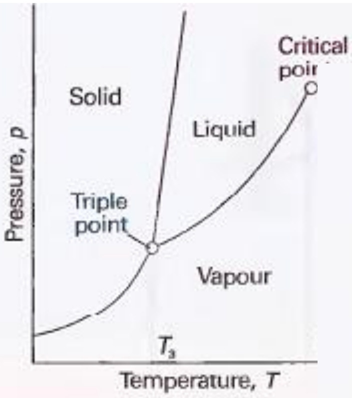


Fig. 4.1 The general regions of pressu
temperature where solid, liquid, or g
stable (that is, has minimum molar (
energy) are shown on this phase diag
For example, the solid phase is the m
stable phase at low temperatures and
pressures. In the following paragrapl
locate the precise boundaries betwee
regions.

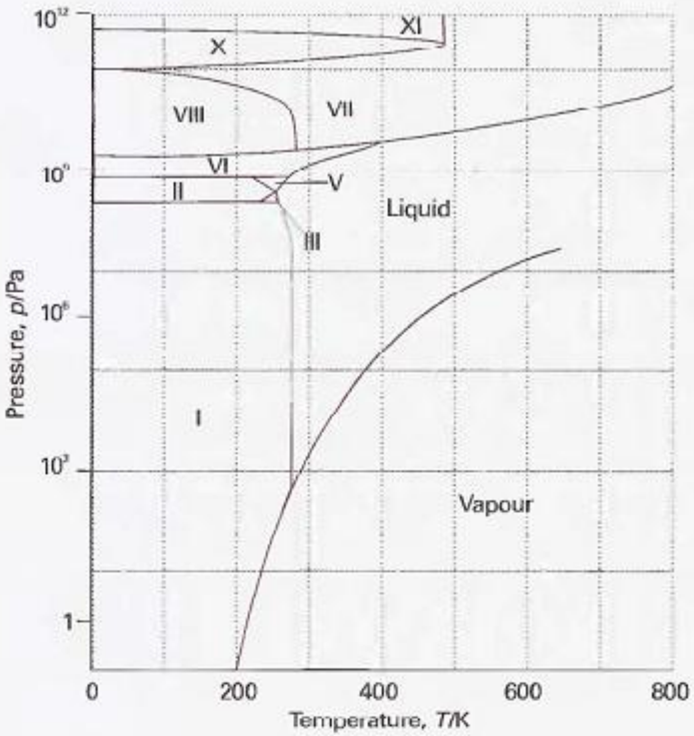


Fig. 4.5 The experimental phase diagram for water showing the different solid phases.

- من الاتزانات الاخرى:

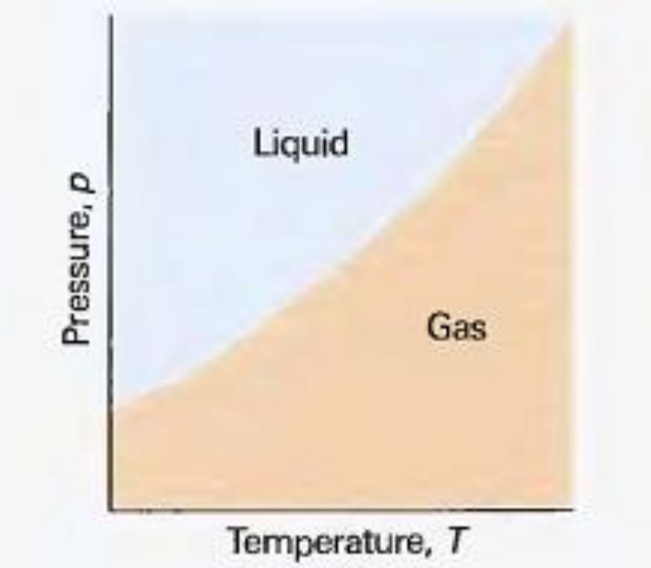


Fig. 4.14 A typical liquid–vapour phase boundary. The boundary can be regarded as a plot of the vapour pressure against the temperature. Note that, in some depictions of phase diagrams in which a logarithmic pressure scale is used, the phase boundary has the opposite curvature (see Fig. 4.7). This phase boundary terminates at the critical point (not shown).

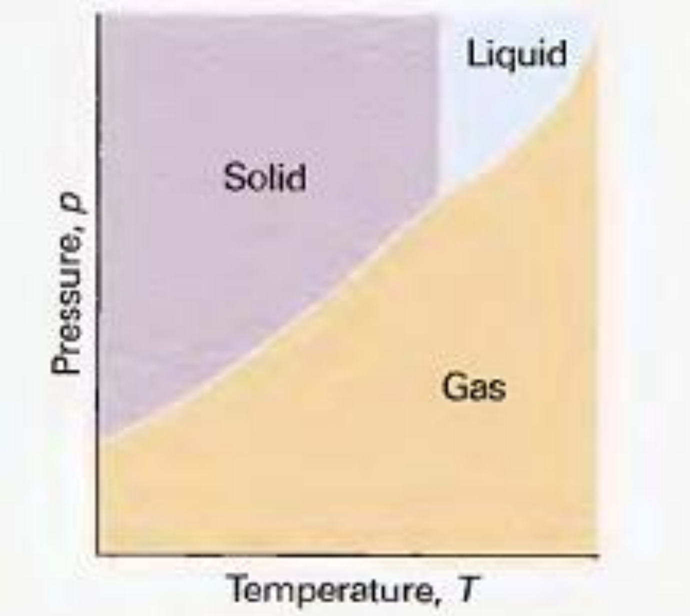


Fig. 4.15 Near the point where they coincide (at the triple point), the solid–gas boundary has a steeper slope than the liquid–gas boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization and the temperatures that occur in the Clausius–Clapeyron equation for the slope have similar values.

The thermodynamic description of mixtures

The thermodynamic description of mixtures

5.1 Partial molar quantities

5.2 The thermodynamics of mixing

5.3 The chemical potentials of liquids

I5.1 Impact on biology: Gas solubility and breathing

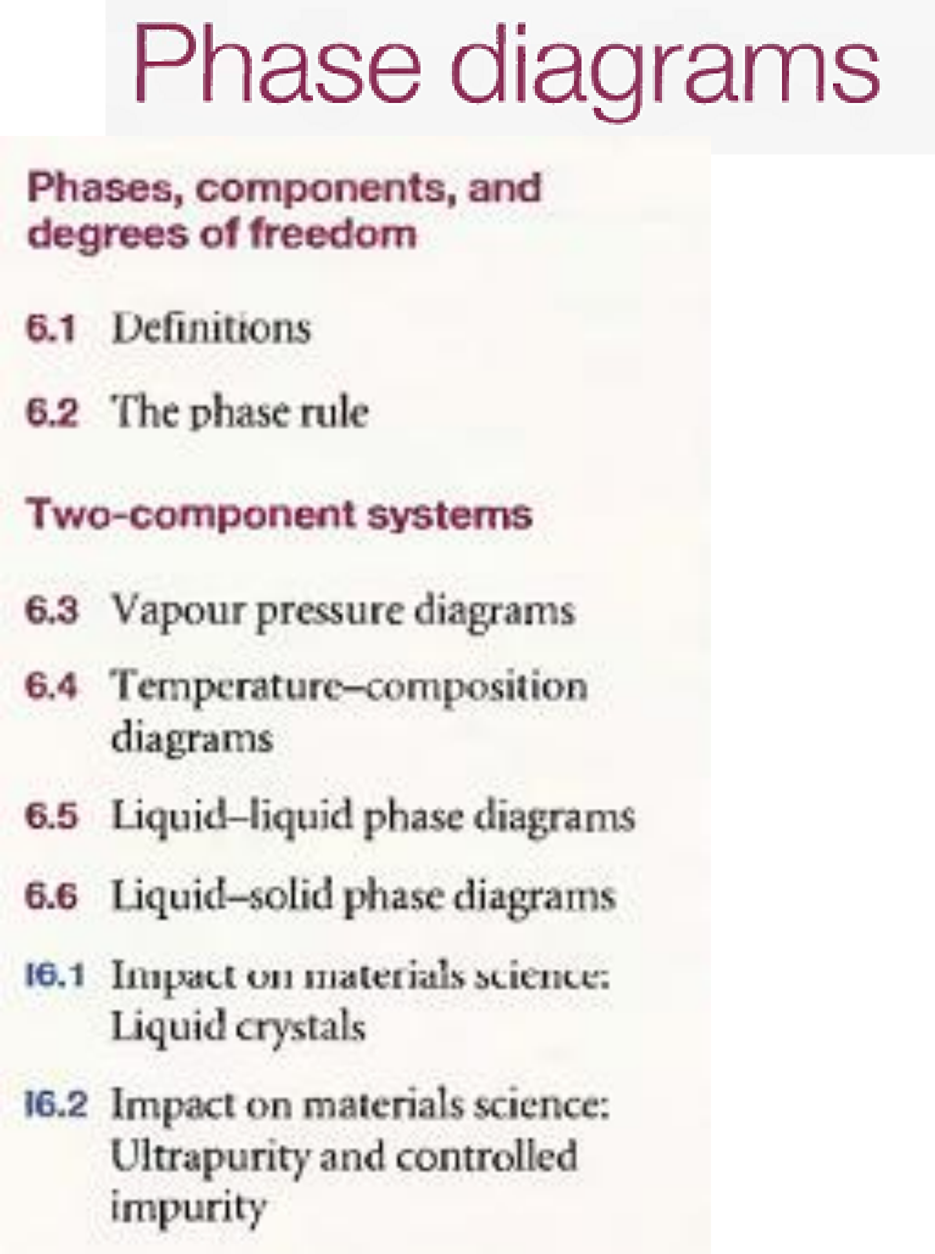
The properties of solutions

5.4 Liquid mixtures

5.5 Colligative properties

I5.2 Impact on biology: Osmosis in physiology and biochemistry

- تغيرات الطور:



Phase diagrams

Phases, components, and degrees of freedom

Two-component systems

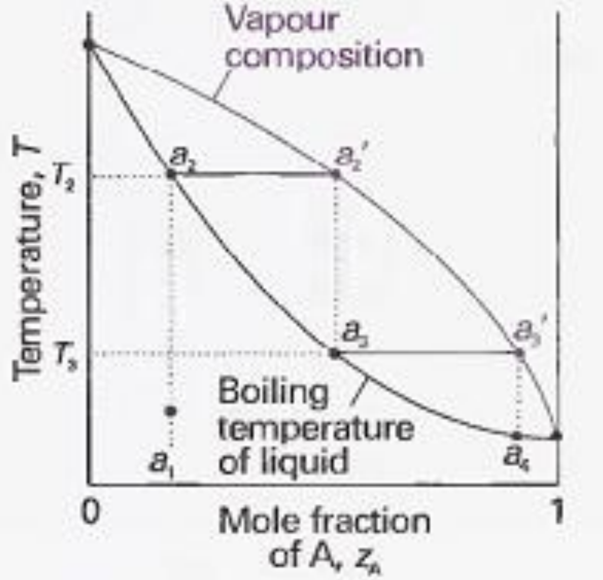


Fig. 6.14 The temperature–composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation technique is called fractional distillation.

- مخططات حرارة-مكونات:

6.4 Temperature–composition diagrams

(a) The distillation of mixtures

(b) Azeotropes

(c) Immiscible liquids

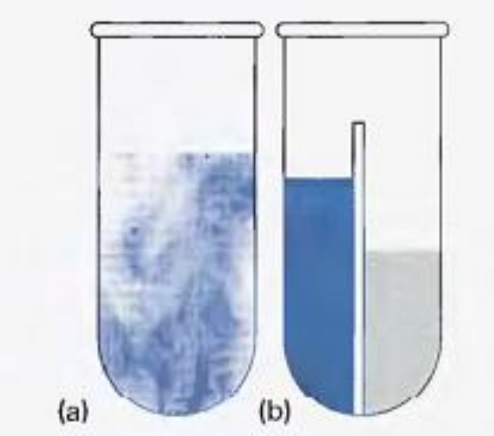


Fig. 6.18 The distillation of (a) two immiscible liquids can be regarded as (b) the joint distillation of the separated components, and boiling occurs when the sum of the partial pressures equals the external pressure.

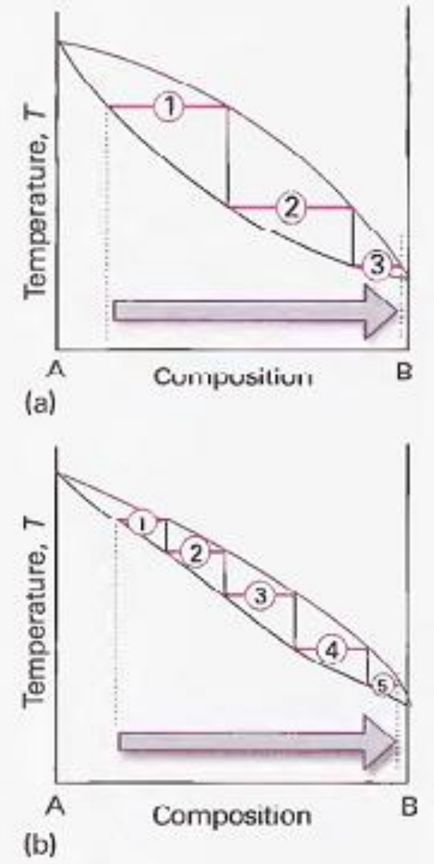


Fig. 6.15 The number of theoretical plates is the number of steps needed to bring about a specified degree of separation of two components in a mixture. The two systems shown correspond to (a) 3, (b) 5 theoretical plates.

6.5 Liquid–liquid phase diagrams

Thermodynamics

Lecture 2

- خصائص الغازات

- **The perfect gas الغاز المثالي**

- We shall find it helpful to picture a gas as a collection of molecules (or atoms) in continuous random motion, with average speeds that increase as the temperature is raised.

- A gas differs from a liquid in that, except during collisions, the molecules of a gas are widely separated from one another and move in paths that are largely unaffected by intermolecular forces.

1.1 **The states of gases**

The physical state of a sample of a substance,

its physical condition, is defined by its physical properties. Two samples of a substance that have the same physical properties are in the same state.

The state of a pure gas, for example, is specified by giving its volume, *V, and amount of substance (number of moles), n, pressure, p, temperature, T*

However, it has been established experimentally that it is sufficient to specify only three of these variables, for then the fourth variable is fixed. That is, it is an experimental fact that each substance is described by an ***equation of state, an equation that***

interrelates these four variables. The general form of an equation of state is

- معادلة الحالة: تلك المعادلة التي تربط المتغيرات الاربعة لوصف الحالة لتلك المادة.

$$p = f(T, v, n) \qquad (1.1)$$

This equation tells us that, if we فالمعادلة تلك تخبرنا :
of *T, V, and n for a particular* know the values
*subst*ance, then the pressure has a fixed value.

Each substance is described by its own equation of state, but we know the explicit form of the equation in only a few special cases.

One very important example is the equation of state of **a 'perfect gas',** which has the form:

$$p = nRT/V$$

where R is a constant. •

Much of the rest of this chapter will examine the origin of this equation of state and its applications.

- وحدات الضغط:

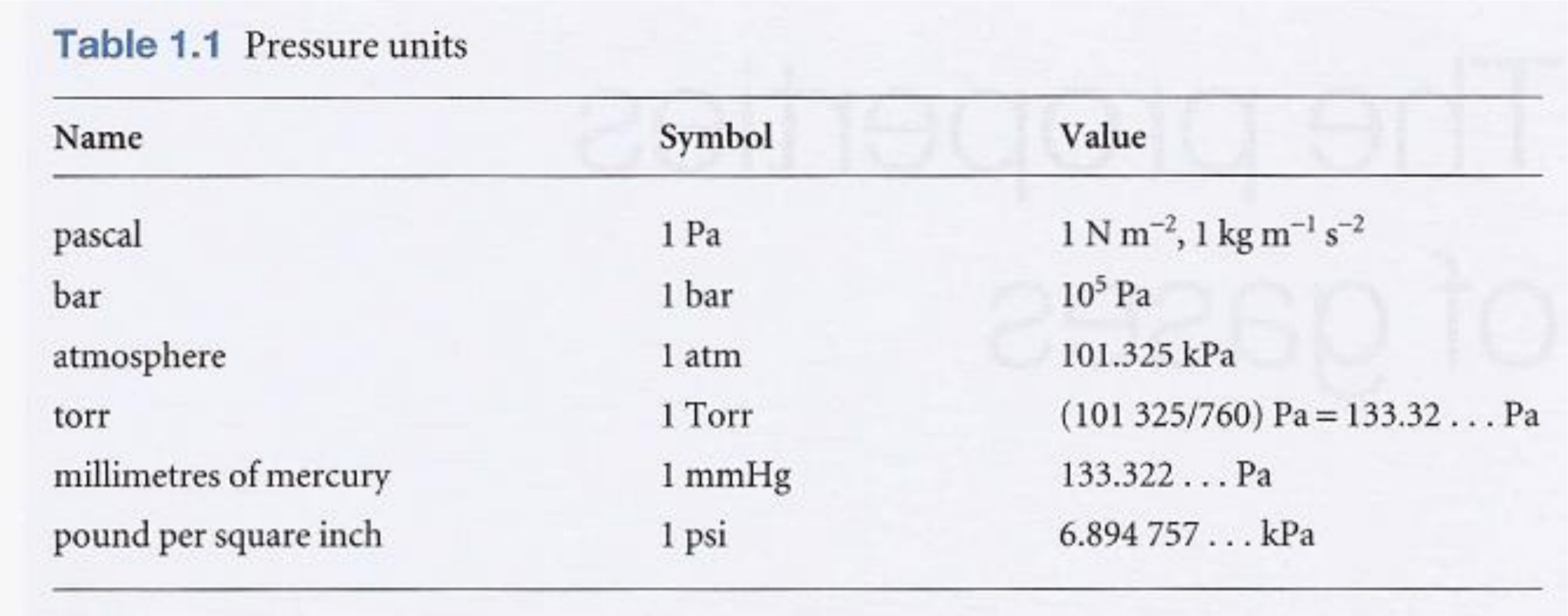


Table 1.1 Pressure units

Name	Symbol	Value
pascal	1 Pa	1 N m^{-2}, 1 kg m^{-1} s^{-2}
bar	1 bar	10^5 Pa
atmosphere	1 atm	101.325 kPa
torr	1 Torr	(101 325/760) Pa = 133.32 . . . Pa
millimetres of mercury	1 mmHg	133.322 . . . Pa
pound per square inch	1 psi	6.894 757 . . . kPa

- الضغط و وحداته:

(a) Pressure

[1,2a] In terms of base units,

- Pressure is defined as force divided by the area to which the force is applied. The greater the force acting on a given area, the greater the pressure. The origin of the force exerted by a gas is the incessant battering of the molecules on the walls of its container. The collisions are so numerous that they exert an effectively steady force, which is experienced as a steady pressure.
- The SI unit of pressure, the *pascal (Pa), is defined as 1 newton per metre-squared: 1 Pa= 1* Nm^{-2}

- وهناك عدد اخر من الوحدات مازال يستخدم كما في الجدول السابق

Several other units are still widely used (Table 1.1); of these units, the most commonly

used are atmosphere (1 atm = 1.013 25 x 105 Pa exactly) and bar (1 bar = 105 Pal. A pressure of 1 bar is the standard pressure

for reporting data; we denote it $p^{\ominus}$.

قياس الضغط:

(b) The measurement of pressure

The pressure exerted by the atmosphere is measured with a barometer. The original version of a barometer (which was invented by Torricelli, a student of Galileo) was an inverted tube of mercury sealed at the upper end. When the column of mercury is in mechanical equilibrium with the atmosphere, the pressure at its base is equal to that exerted by the atmosphere. It follows that the height of the mercury column is proportional to the external pressure.

- قياس الضغط:

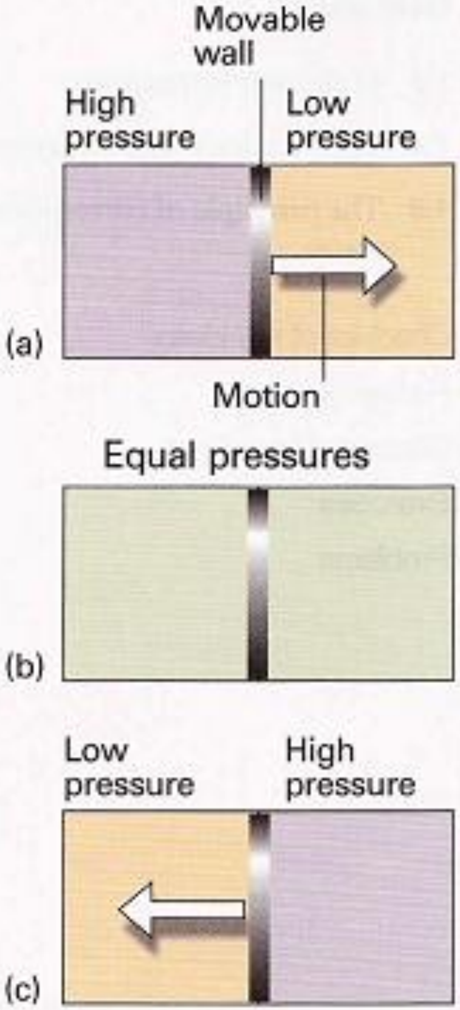
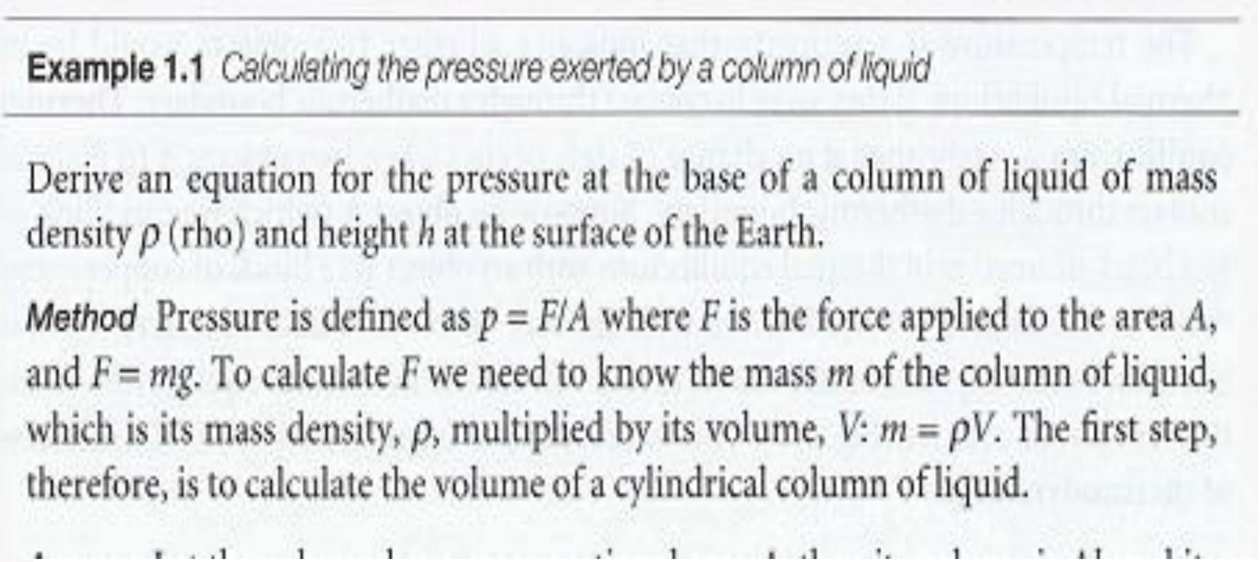


Fig. 1.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium between the two regions.

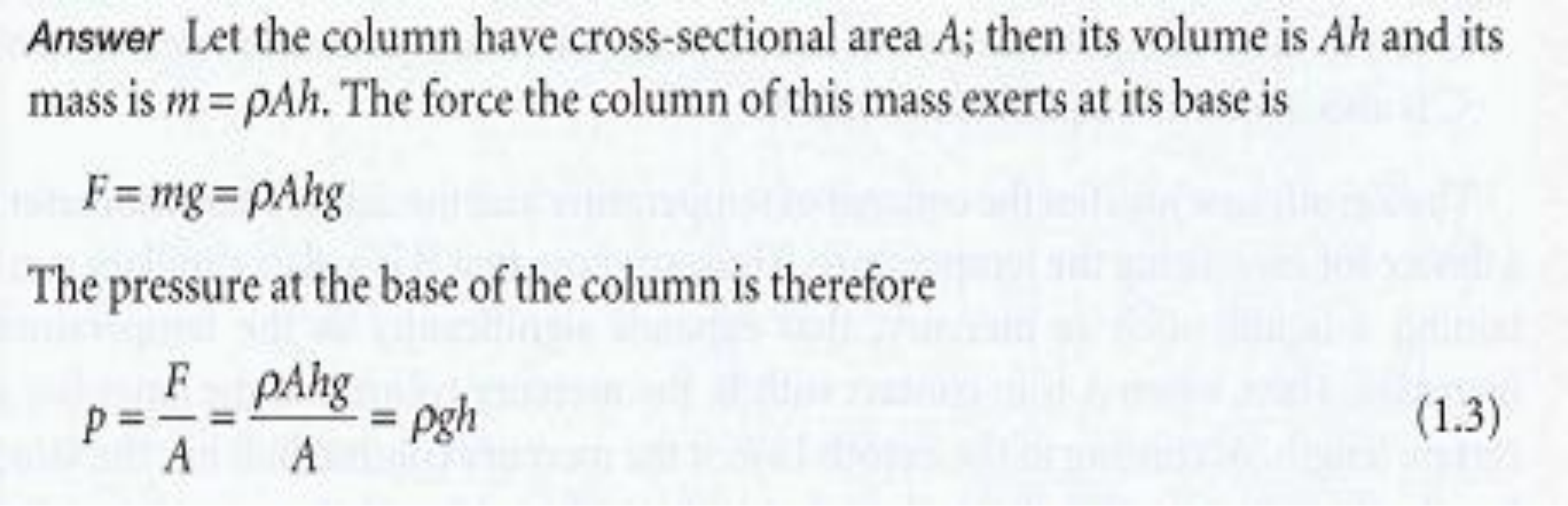


Example 1.1 *Calculating the pressure exerted by a column of liquid*

Derive an equation for the pressure at the base of a column of liquid of mass density ρ (rho) and height h at the surface of the Earth.

Method Pressure is defined as $p = F/A$ where F is the force applied to the area A, and $F = mg$. To calculate F we need to know the mass m of the column of liquid, which is its mass density, ρ, multiplied by its volume, V: $m = \rho V$. The first step, therefore, is to calculate the volume of a cylindrical column of liquid.

- الجواب :



Answer Let the column have cross-sectional area A; then its volume is Ah and its mass is $m = \rho Ah$. The force the column of this mass exerts at its base is

$$F = mg = \rho Ahg$$

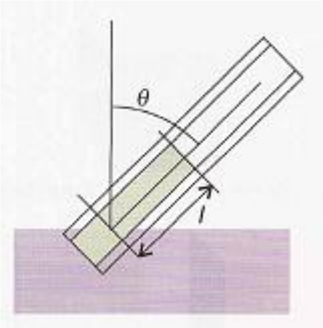
The pressure at the base of the column is therefore

$$p = \frac{F}{A} = \frac{\rho Ahg}{A} = \rho gh \qquad (1.3)$$

- وإذا كان السطح مائلا او محدبا او مقعرا فيحسب كمايلي:

Derive an expression for the pressure at the base of a column of liquid of length l held at an angle e(theta) to the vertical (1).

$$p = \rho\, g\, \ell\, \cos\ \theta$$



- انواع مقاييس الضغط:

The pressure of a sample of gas inside a container is measured by using a pressure gauge, which is a device with electrical properties that depend on the pressure. For instance, a *Bayard-Alpert pressure gauge* is *based on the ionization of the molecules present in the gas and the resulting current of ions is interpreted in terms of the pressure.*

In a capacitance manometer, the deflection of a diaphragm relative to a fixed electrode is monitored through its effect on the capacitance of the arrangement.

Certain semiconductors also respond to pressure and are used as transducers in solid-state pressure gauges.

- درجة الحرارة:

(c) Temperature

The concept of temperature springs from the observation that a change in physical state (for example, a change of volume) can occur when two objects are in contact with one another, as when a red-hot metal is plunged into water. Later (Section 2.1) we shall see that the change in state can be interpreted as arising from a flow of energy as heat from one object to another. The temperature, *T*, *is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall. If energy flows from A to B when they are in contact, then we say that A has a higher* temperature than B (Fig. 1.2).

It will prove useful to distinguish between two types of boundary that can separate the objects. A boundary is **diathermic** (thermally conducting) if a change of state is observed when two objects at different temperatures are brought into contact. A metal container has diathermic walls. A boundary is **adiabatic** (thermally insulating) if no change occurs even though the two objects have different temperatures. A vacuum flask is an approximation container.

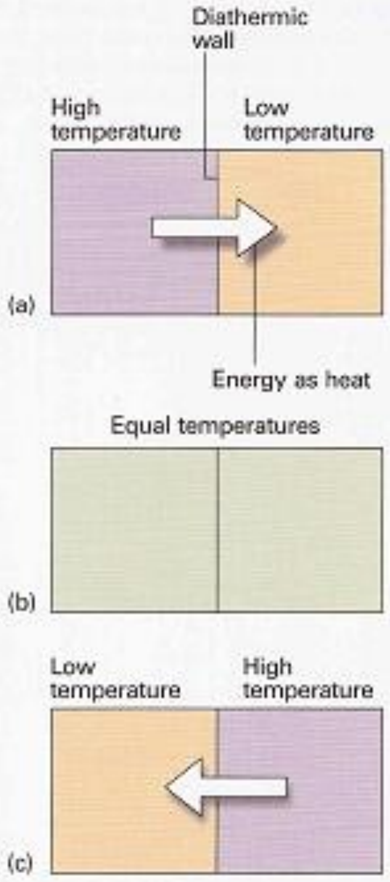


Fig. 1.2 Energy flows as heat from a region at a higher temperature to one at a lower temperature if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are separated by a diathermic wall (b). The latter condition corresponds to the two regions being at thermal equilibrium.

The temperature is a property that indicates whether two objects would be in

thermal equilibrium' if they were in contact through a diathermic boundary**.**

Thermal equilibrium is established if no change of state occurs when two objects A to B are in contact through a diathermic boundary. Suppose an object A (which we can think of as a block of iron) is in thermal equilibrium with

- uppose an object A (which we can think of as a block of iron) is in thermal equilibrium with an object B (a block of copper), and
- that B is also in thermal equilibrium with another object C (a flask of water). Then it has been found experimentally that A and C will also be in thermal equilibrium when they are put in contact (Fig. 1.3).
- This observation is summarized by the Zeroth Law of thermodynamics:
- If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A

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Zeroth Law of thermodynamics:

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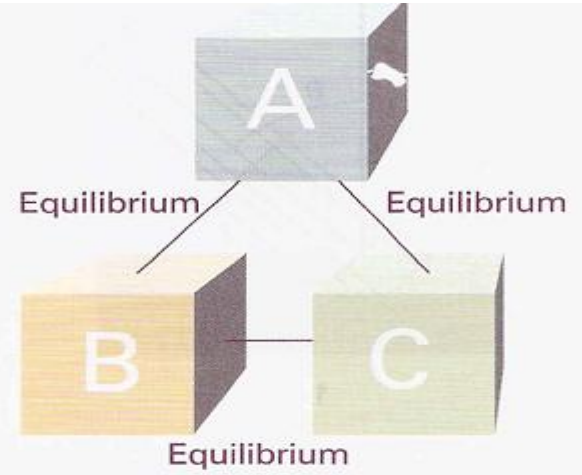


Fig. 1.3 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

- In the early days of thermometry (and still in laboratory practice today), temperatures were related to the length of a column of liquid, and the difference in lengths shown when the thermometer was first in contact ice and then with boiling water was divided into 100 steps with melting called' degrees', the lower point being labelled 0.This procedure led to the Celsius scale of temperature. In this text, temperatures *ϴ.*

- hermodynamic and Celsius temperatures are related by the exact expression

$$T/K= \Theta/ {}^{o} C + 273.1 \quad .... (1.\ 4\ )$$

This relation, in the form $\Theta/ {}^{o} C = T/K - 273.15$, *is the current definition of the Celsius* scale in terms of the more fundamental Kelvin scale. It implies that a difference in temperature of 1°C is equivalent to a difference of 1 K.

A note on good practice We write

***T* = 0, not *T* = 0 K** *for the zero temperature on the thermodynamic temperature scale. This scale is absolute, and the lowest* temperature is 0 regardless of the size of the divisions on the scale (just as we write

p = 0 for zero pressure,

regardless of the size of the units we adopt, such as bar or pascal). However, we write O°C because the Celsius scale is not *absolute*.

To express 25.00°C as a temperature in Kelvins, we use eqn. 1.4 to write

$$TIK = (25.00°C)\ /\ {}^{o}C + 273.15 = 25.00 + 273.15 = 298.15$$

Note *how the units (in this case, ^{o} C) are cancelled like numbers. This is the procedure* called **'quantity calculus'** in which a physical quantity (such as the temperature) is the product of a numerical value (25.00) and a unit (1 ^{o} *C*).

Multiplication of both sides by the unit K then gives *T = 298.15 K*.

1.2 The gas laws

The equation of state of a gas at low pressure was established by combining a series of empirical laws.

(a) The perfect gas law

We assume that the following individual gas laws are familiar:

Boyle's law: *pV = constant, at constant n, T* .....*(1.5*)°

Charles's law: *V = constant X T, at constant n, p* ....*(1.6* a)°

p = constant X T, at constant n, V ....(1.6b)°

Boyle's and Charles's laws are examples of a limiting law, a law that is strictly true only

Avogadro's principler *V = constant X n at constant p,T* ....(1.7)°

- Boyle's and Charles's laws are examples of a limiting law, a law that is strictly true only in a certain limit, in this case $p \rightarrow 0$.

- Boyle's law: $pV = \text{constant}$, at constant n, T

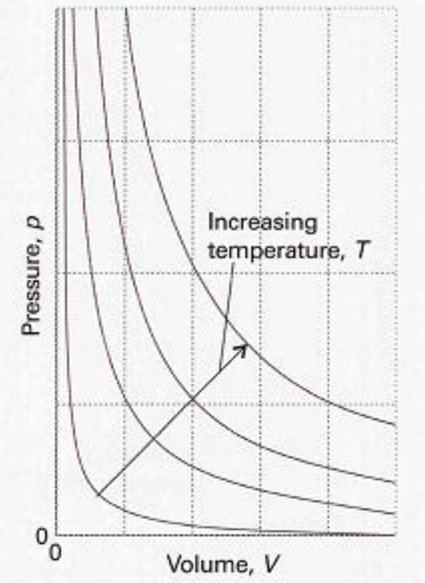


Fig. 1.4 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola (pV = constant) and is called an *isotherm*.

Exploration[3] Explore how the pressure of 1.5 mol $CO_2(g)$ varies with volume as it is compressed at (a) 273 K, (b) 373 K from 30 dm^3 to 15 dm^3.

Charles's law: $V = \text{constant X } T$, at constant n, p … ……(1.6a)

$p = \text{constant X } T$, at constant n, V …………(1.6b)

Avogadro's principler' $V = \text{constant X } n$ at constant p, T ….(1.7)

ccording to Boyle's law, the isotherms of gases are hyperbolas. An alternative depiction, a plot of pressure against l/volume, is shown in Fig. 1.5

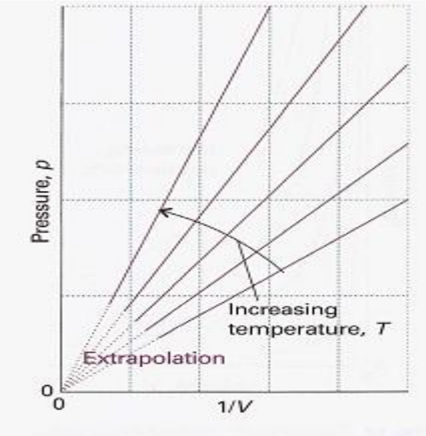


Fig. 1.5 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

Exploration Repeat *Exploration 1.4*, but plot the data as p against $1/V$.

- An alternative depiction, a plot of pressure against l/volume, is shown in Fig. 1.5. The linear variation of volume with temperature summarized by Charles's law is illustrated in Fig. 1.6

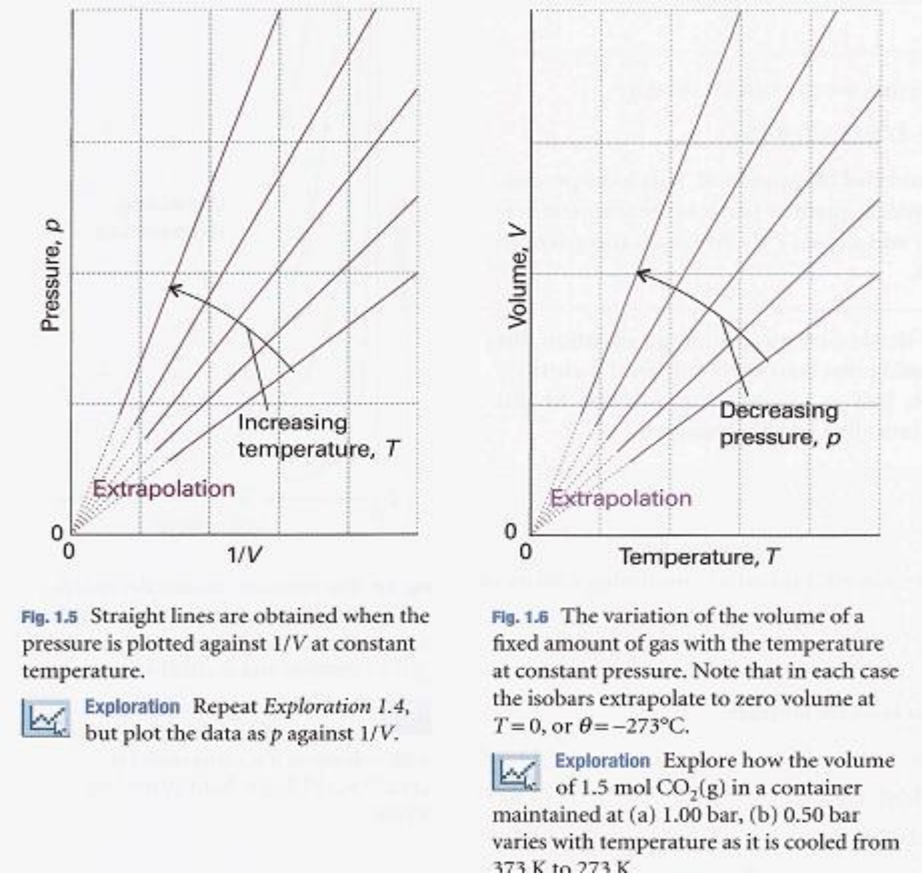


Fig. 1.5 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

Exploration Repeat *Exploration 1.4*, but plot the data as p against $1/V$.

Fig. 1.6 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, or $\theta = -273°C$.

Exploration Explore how the volume of 1.5 mol $CO_2(g)$ in a container maintained at (a) 1.00 bar, (b) 0.50 bar varies with temperature as it is cooled from 373 K to 273 K.

- Figure 1.7: illustrates the linear variation of pressure with temperature.
- The lines in this diagram are isochores, or lines showing the variation of properties at constant volume

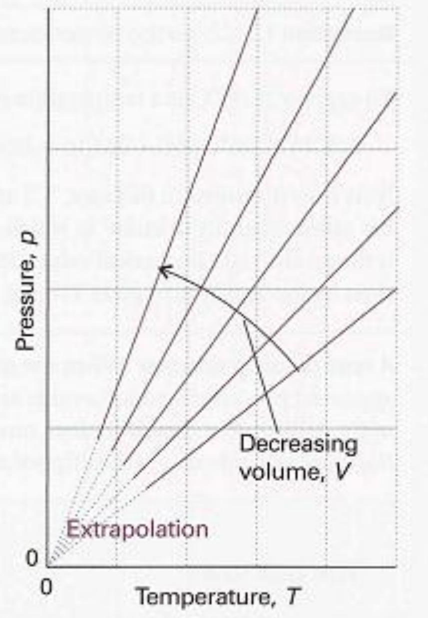


Fig. 1.7 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (−273°C).

Exploration Explore how the pressure of 1.5 mol $CO_2(g)$ in a container of volume (a) 30 dm^3, (b) 15 dm^3 varies with temperature as it is cooled from 373 K to 273 K.

The empirical observations summarized by eqns 1.5-7 • can be combined into a single expression:

$p V = \text{constant x } nT$

This expression is consistent with

Boyle's law (*$p V = \text{constant}$*) *when n and T are constant,* with both forms of

Charles's law ($p \alpha T$, $V \alpha T$) *when n and either V or p are held constant, and with Avogadro's principle ($V \alpha n$) when p and T are constant.*

The constant of proportionality, which is found experimentally to be the same for all gases, is denoted R and called the gas constant. The resulting expression

$$pV=nRT$$

is the perfect gas equation •

Molecular interpretation 1.1 *Thekinetic model of gases*

Lecture 3

Molecular interpretation 1.1

Thekinetic model of gases

التوضيح الجزيئي

النموذج الحركي للغازات

- ان التوضيح الجزيئي لقانون بويل هو اذا ضُغطت عينة من الغاز الى نصف حجمه فانه سيتضاعف عدد الجزيئات التي تصطدم بالجدار بمرتين خلال الفترة الزمنية قبل اجراء عملية الضغط
- As a result, the average force exerted on the walls is doubled. Hence, when the volume is halved the pressure of the gas is doubled, and *p x V is a constant.*
- ***Boyle's law applies*** to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently.

- The molecular explanation of Charles's law lies in the fact that raising the temperature of a gas increases the average speed of its molecules collide with the walls more frequently and with greater impact. Therefore they exert a greater pressure on the walls of the container molecules.

فالخصائص النوعية لخصت كميا بشروط النموذج الحركي للغازات
و الذي يستند على ثلاث فرضيات:

These qualitative concepts are expressed quantitatively in terms of the kinetic model of gases, which is described more fully in Chapter 21. Briefly, the kinetic model is based on three assumptions:

1. The gas consists of molecules of mass *m in ceaseless random motion.*

2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions.

3. The molecules interact only through brief, infrequent, and elastic collisions.

An *elastic collision is a collision in which the total translational kinetic energy of the* molecules is conserved.

From the very economical assumptions of the kinetic model, it can be deduced (as we shall show in detail in Chapter 21) that the pressure and volume of the gas are related by

$$pV = \frac{1}{3} nMC^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.9)°}$$

where $M = mN_A$ *the molar mass of the molecules, and c is the root mean square speed of the molecules, the square root of the*

mean of the squares of the speeds, υ,

$$c = \langle \upsilon^2 \rangle^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.10)$$

- We see that, if the root mean square speed of the molecules depends only on the temperature, then at constant temperature

p V =constant

which is the content of Boyle's law وهذا هو قانون بويل

$pV = ⅓\, nMc^2$ ………………………… *(1.9)°*

Moreover, for eqn 1.9 to be the equation of state of a perfect gas, its right-hand side must be equal to *nRT. It follows that the root mean square speed of the molecules in a gas at a temperature T must be*

$$c = \left(\frac{3RT}{M}\right)^{1/2} \qquad (1.11)°$$

<u>We can conclude </u>that *the root mean square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass.*

The root mean square speed of N_2 molecules, for instance, is found from eqn 1.11 to be 515 m S^{-1} at 298 K

The surface in Fig. 1.8 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 1.8.

The surface depicts the only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface.

The graphs in Figs. 1.4 and 1.6 correspond to the sections through the surface (Fig. 1.9)

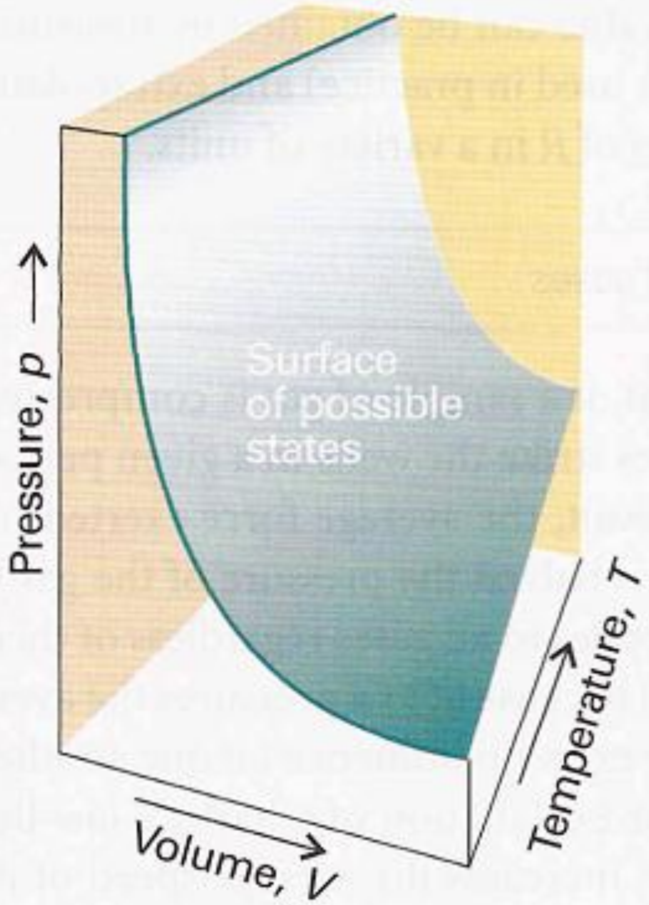


Fig. 1.8 A region of the p,V,T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

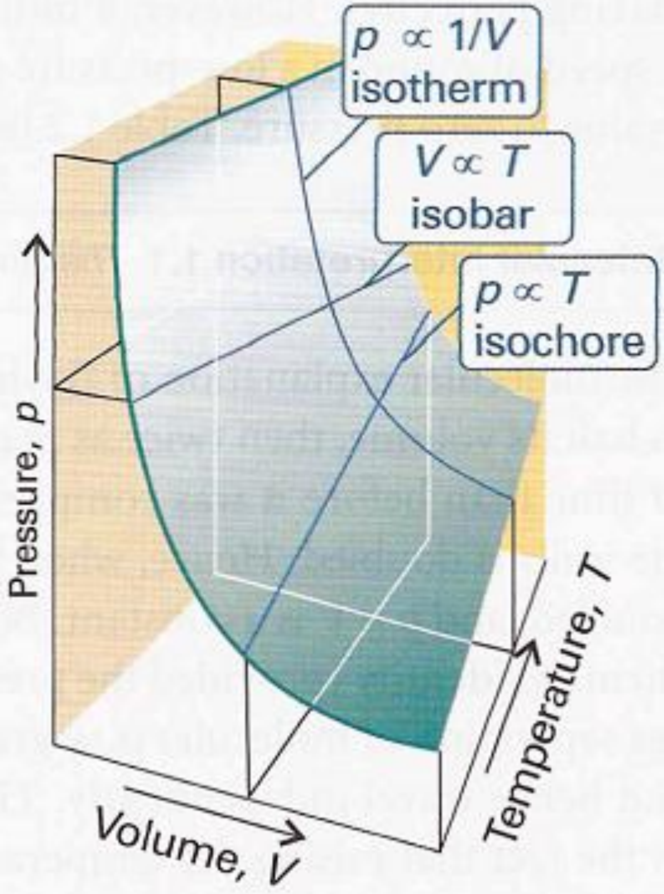


Fig. 1.9 Sections through the surface shown in Fig. 1.8 at constant temperature give the isotherms shown in Fig. 1.4 and the isobars shown in Fig. 1.6.

Example 1.2 *Using the perfect gas equation*

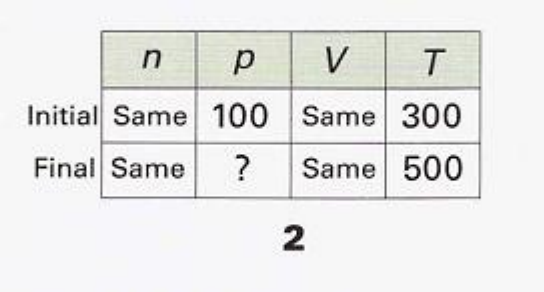
In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas?

Method We expect the pressure to be greater on account of the increase in temperature. The perfect gas law in the form PV/ nT = R implies that, if the conditions are changed from one set of values to another, then because *PV/nT is equal to a constant, the two sets of values are related by*

The combined gas law

$$\frac{p_1V_1}{n_1T_1} = \frac{p_2V_2}{n_2T_2} \qquad (1.12)^{\circ}$$

The known and unknown data are summarized in (2)



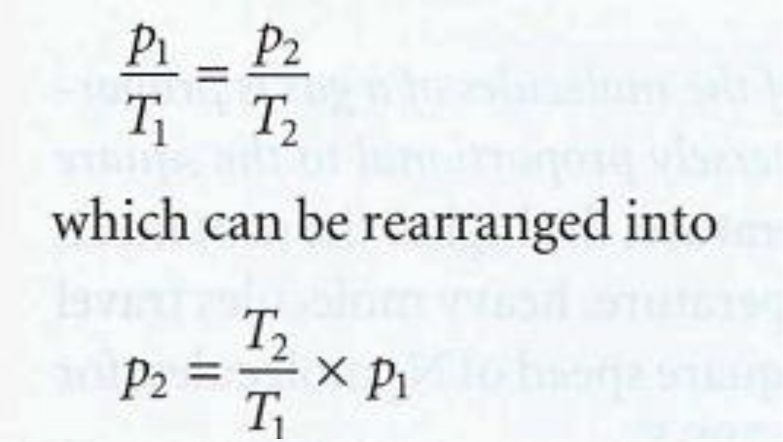
	n	p	V	T
Initial	Same	100	Same	300
Final	Same	?	Same	500

2

Answer

Cancellation of the volumes (because $V_1 = V_2$*) and amounts (because* $n_1 = n_2$*) on each side of the*

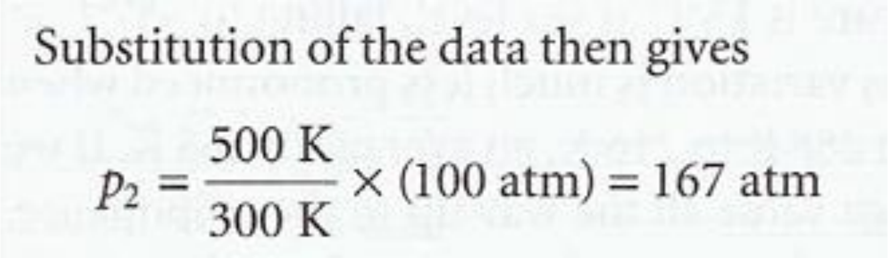
combined gas law results in



$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

which can be rearranged into

$$p_2 = \frac{T_2}{T_1} \times p_1$$



Substitution of the data then gives

$$p_2 = \frac{500\ \text{K}}{300\ \text{K}} \times (100\ \text{atm}) = 167\ \text{atm}$$

Experiment shows that the pressure is actually 183 atm under these conditions, so the assumption that the gas is perfect leads to a 10 per cent error

what temperature would result in the same sample exerting a pressure of300 atm? [900 K]

11

MPACT ON ENVIRONMENTAL SCIENCE

11.1 *The gas laws and the weather*

The biggest sample of gas readily accessible to us is the atmosphere, a mixture of gases with the composition summarized in Table 1.3. The composition is maintained moderately constant by diffusion and convection (winds, particularly the local turbulence called *eddies*) *but the pressure and temperature vary with altitude and with the local conditions, particularly in the troposphere (the 'sphere of change'), the layer extending up to about 11 km.*

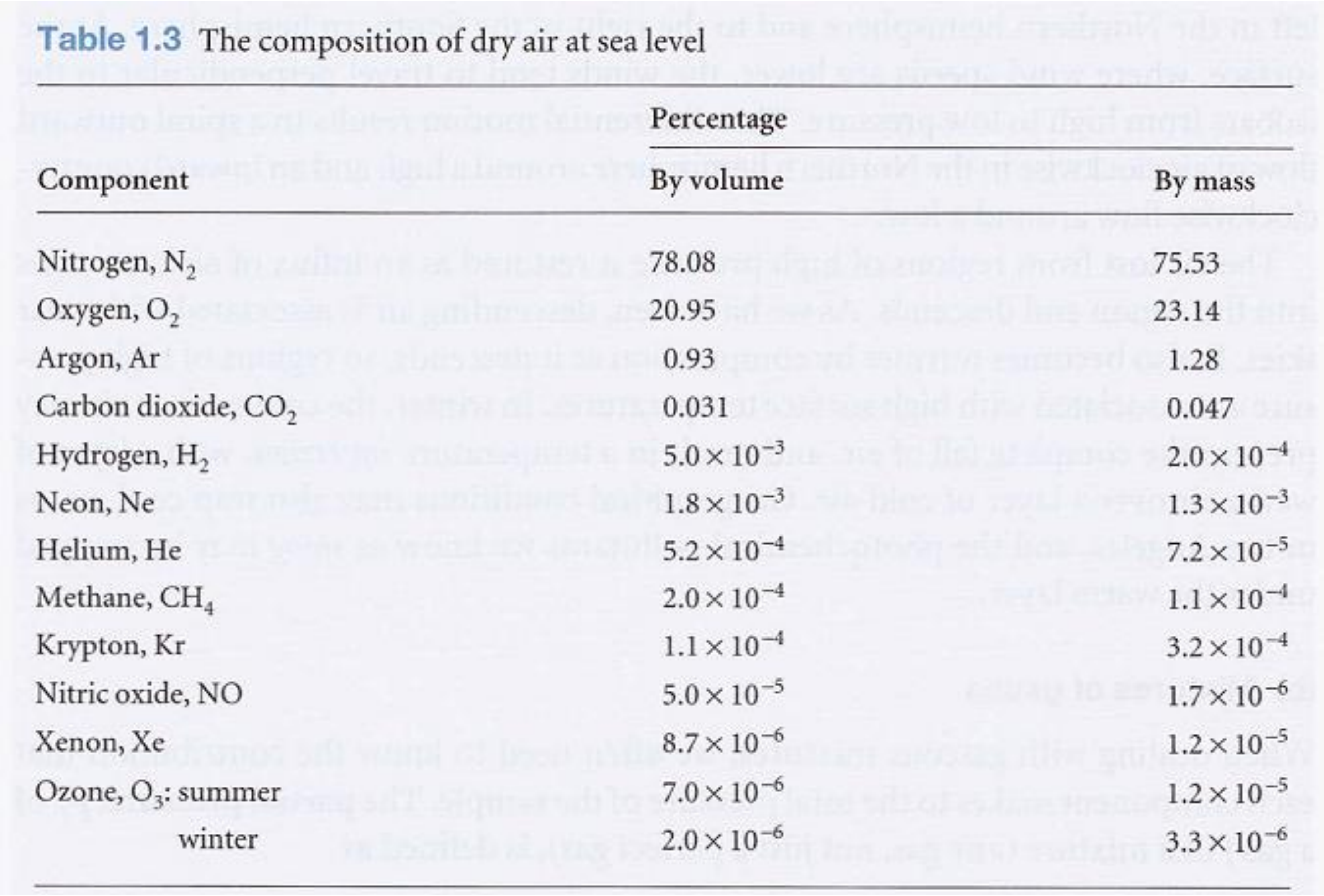


Table 1.3 The composition of dry air at sea level

Component	Percentage By volume	Percentage By mass
Nitrogen, N_2	78.08	75.53
Oxygen, O_2	20.95	23.14
Argon, Ar	0.93	1.28
Carbon dioxide, CO_2	0.031	0.047
Hydrogen, H_2	5.0×10^{-3}	2.0×10^{-4}
Neon, Ne	1.8×10^{-3}	1.3×10^{-3}
Helium, He	5.2×10^{-4}	7.2×10^{-5}
Methane, CH_4	2.0×10^{-4}	1.1×10^{-4}
Krypton, Kr	1.1×10^{-4}	3.2×10^{-4}
Nitric oxide, NO	5.0×10^{-5}	1.7×10^{-6}
Xenon, Xe	8.7×10^{-6}	1.2×10^{-5}
Ozone, O_3: summer	7.0×10^{-6}	1.2×10^{-5}
winter	2.0×10^{-6}	3.3×10^{-6}

- In the troposphere the average temperature is 15°C at sea level, falling to -57°C at the bottom of the tropopause at 11km. This variation is much less pronounced when expressed on the Kelvin scale, ranging from 288 K to 216 K, an average of268 K. If we suppose that the temperature has its average value all the way up to the tropopause, then the pressure varies with altitude, *h, according to*

the barometric formula

$$p = p_0 e^{-h/H}$$

where p_o *is the pressure at sea level and H is a constant approximately equal to 8 km.*

More specifically,

H = RTIMg,

where M is the average molar mass of air and T is the temperature. The barometric formula fits the observed pressure distribution quite well even for regions well above the troposphere (see Fig. 1.10).

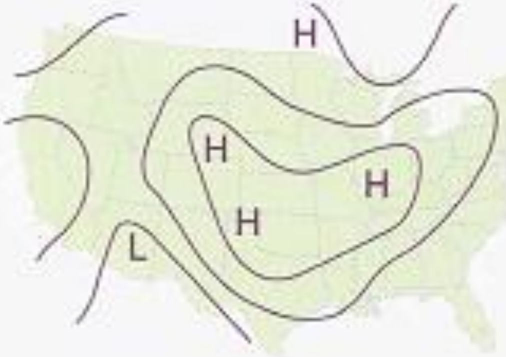


Fig. 1.11 A typical weather map; in this case, for the United States on 1 January 2000.

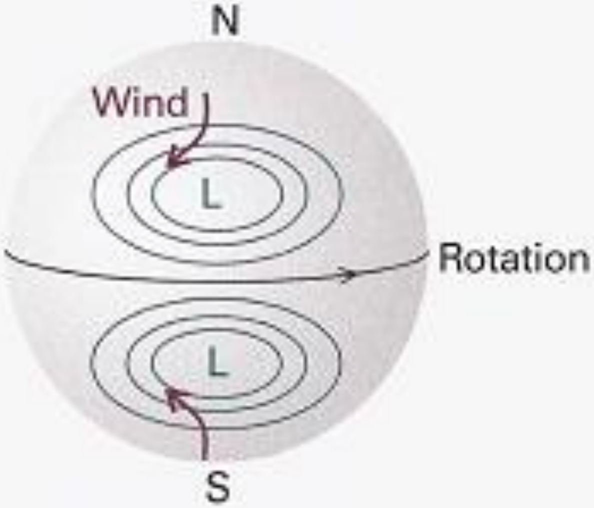


Fig. 1.12 The flow of air ('wind') around regions of high and low pressure in the Northern and Southern hemispheres.

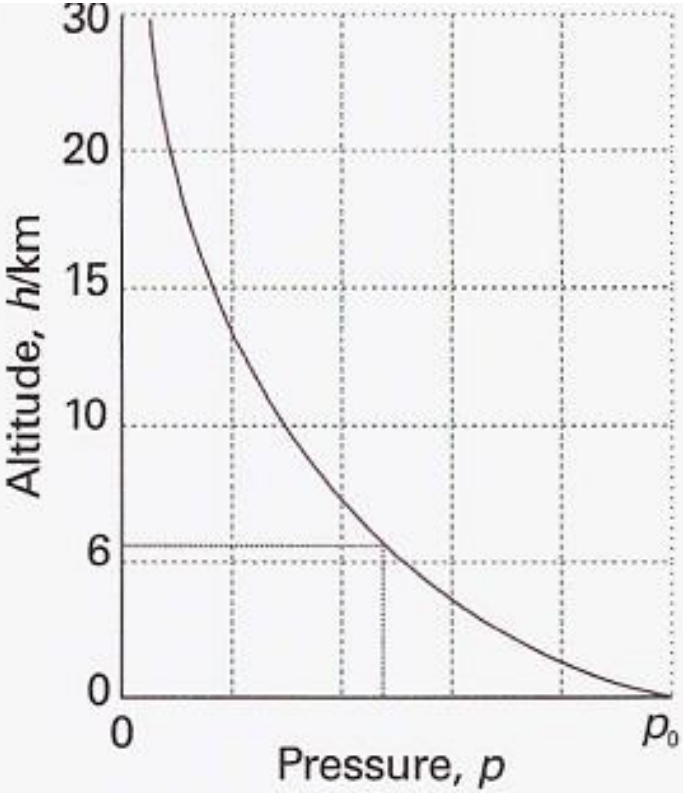


Fig. 1.10 The variation of atmospheric pressure with altitude, as predicted by the barometric formula and as suggested by the 'US Standard Atmosphere', which takes into account the variation of temperature with altitude.

(b) Mixtures of gases

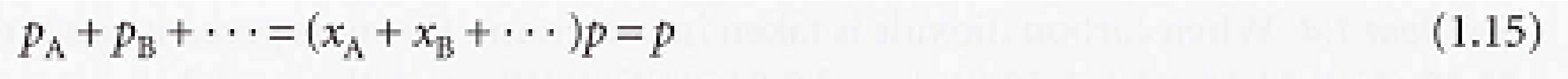
When dealing with gaseous mixtures, we often need to know the contribution that each component makes to the total pressure of the sample. The **partial pressure,** P_J **of a** gas J in a mixture (any gas, not just a perfect gas), is defined as

$$p_J = x_J p \qquad [1.13]$$

where X_J *is* ***<u>the mole fraction</u> of the component J, the amount of J expressed as a fraction of the total amount of molecules, n, in the sample:***

$$x_J = \frac{n_J}{n} \qquad n = n_A + n_B + \cdots \qquad [1.14]$$

When no J molecules are present, x_J *=0; when only J molecules are present,* x_J *= 1. It follows from the definition of* x_J *that, whatever the composition of the mixture,* $x_A + x_B + ... = 1$ *and therefore that the sum of the partial pressures is equal to the total pressure:*



$$p_A + p_B + \cdots = (x_A + x_B + \cdots)p = p \qquad (1.15)$$

This relation is true for both real and perfect gases. When all the gases are perfect, the partial pressure as defined in eqn 1.13 is also the pressure that each gas would occupy if it occupied the same container alone at the same temperature. The latter is the original meaning of 'partial pressure'. That identification was the basis of the original formulation of

Dalton's law:

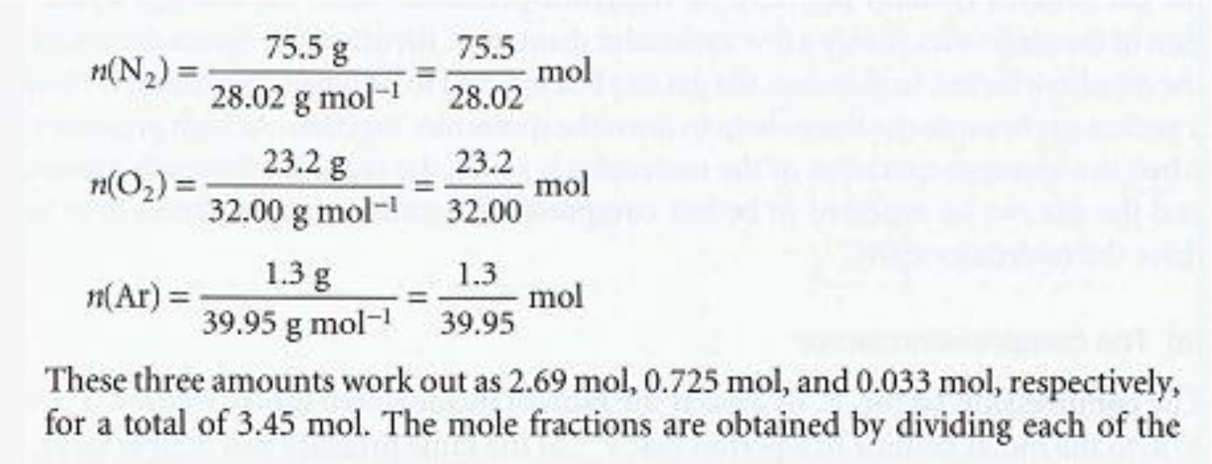
The pressure exerted by a mixture of gases is the sum of the pressures that each one would exist if it occupied the container alone

Example 1.3 *Calculating partial pressures*

The mass percentage composition of dry air at sea level is approximately *N_2: 75.5; O_2: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.00 atm?*

Method We expect species with a high mole fraction to have a proportionally high partial pressure. Partial pressures are defined by eqn 1.13. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 1.14, we use the fact that the amount of molecules J of molar mass MJ in a sample of mass m_J *is* $n_J = m/ M_J$ *• The mole fractions are independent of the total mass of the sample, so we can choose the latter to be 100 g (which makes the conversion from mass percentages very easy). Thus, the mass of N, present is 75.5 per cent of 100 g, which is 75.5 g.*

Answer The amounts of each type of molecule present in 100 g of air, in which the masses of N_2, 0_2' and Ar are 75.5 g, 23.2 g, and 1.3 g, respectively, ar

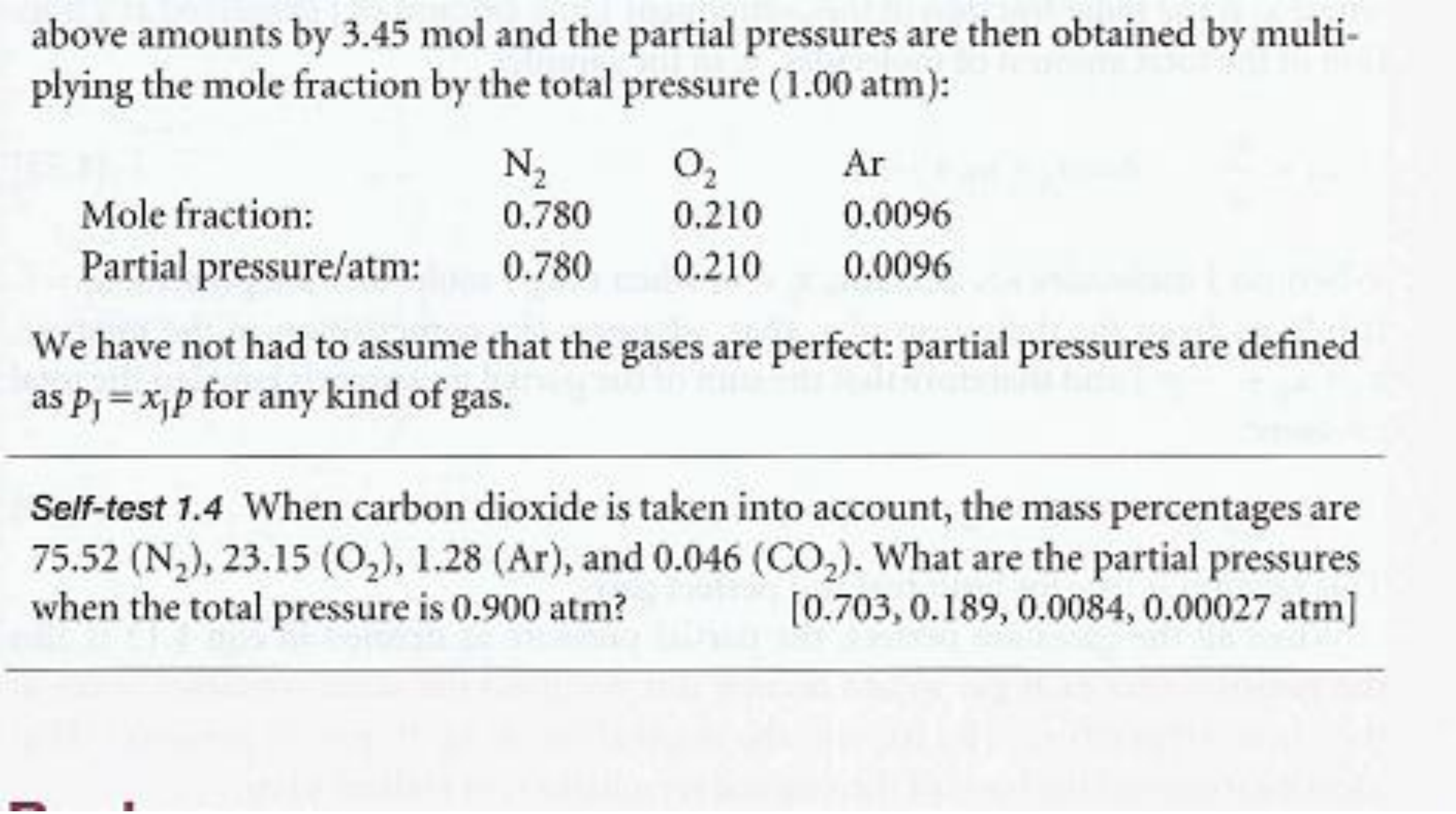


$$n(\mathrm{N_2}) = \frac{75.5\ \mathrm{g}}{28.02\ \mathrm{g\ mol^{-1}}} = \frac{75.5}{28.02}\ \mathrm{mol}$$

$$n(\mathrm{O_2}) = \frac{23.2\ \mathrm{g}}{32.00\ \mathrm{g\ mol^{-1}}} = \frac{23.2}{32.00}\ \mathrm{mol}$$

$$n(\mathrm{Ar}) = \frac{1.3\ \mathrm{g}}{39.95\ \mathrm{g\ mol^{-1}}} = \frac{1.3}{39.95}\ \mathrm{mol}$$

These three amounts work out as 2.69 mol, 0.725 mol, and 0.033 mol, respectively, for a total of 3.45 mol. The mole fractions are obtained by dividing each of the



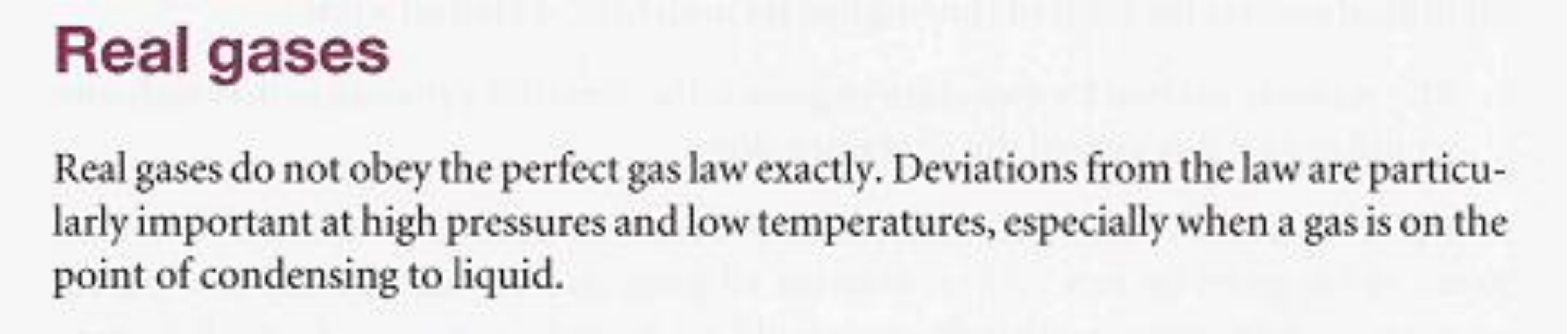
above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.00 atm):

	N_2	O_2	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.780	0.210	0.0096

We have not had to assume that the gases are perfect: partial pressures are defined as $p_J = x_J p$ for any kind of gas.

Self-test 1.4 When carbon dioxide is taken into account, the mass percentages are 75.52 (N_2), 23.15 (O_2), 1.28 (Ar), and 0.046 (CO_2). What are the partial pressures when the total pressure is 0.900 atm? [0.703, 0.189, 0.0084, 0.00027 atm]

الغازات الحقيقية



Real gases

Real gases do not obey the perfect gas law exactly. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid.

Lecture 4

Realgases

الغازات الحقيقية

Real gases

Real gases do not obey the perfect gas law exactly. Deviations from the law are particularly important at **high pressures** and ***low temperatures***, especially **when a gas is on the point of condensing to liquid**

1.3 **Molecular interactions**

Real gases show deviations from the perfect gas law because molecules interact with one another. Repulsive forces between molecules assist expansion and attractive forces assist compression

ان سبب حيود الغازات عن السلوك المثالي يعود لتحاث الجزيئات مع بعضها فهناك قوى تنافر تعمل على تمدد الغاز و قوى تجاذب تعمل على تضاغط الجزيئات

- Repulsive forces are significant only when molecules are almost in contact: they are short -range interactions, even on a scale measured in molecular diameters (Fig. 1.13). Because they are short-range interactions,
- Repulsions can be expected to be important only when the average separation of the molecules is small. This is the case at high pressure, when many molecules occupy a small volume. On the other hand, **attractive intermolecular forces** have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching (at the intermediate separations in Fig. 1.13).

- الشكل 1.13 :
- التغير في طاقة الجهد بتغير المسافة الفاصلة بين جزيئين. اذ تنشاء طاقة جهد عالية و موجبة عند مسافة قصيرة بين الجزيئات لتبين ان التحاث بينهما هو تنافر قوي عند تلك المسافات. و عند مسافات متوسطة عندما تكون عندها طاقة الجهد سالبة فإن التحاث هو تجاذب و تكون هذه القوى هي السائدة او المسيطرة.
- و عند مسافات كبيرة فإن طاقة الجهد تساوي صفر ومن ثم فلا وجود لتحاث بين الجزيأت

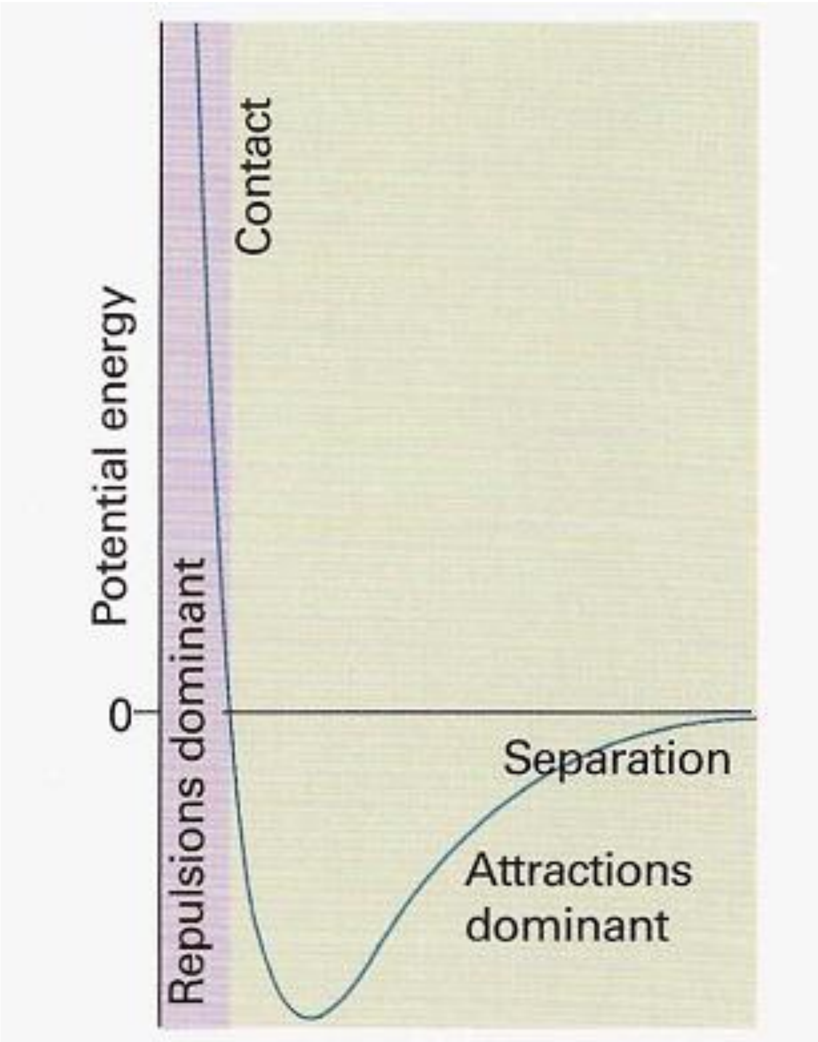


Fig. 1.13 The variation of the potential

(a) The compression factor

The compression factor, Z, of a gas is the ratio of its measured molar volume, $V_m = V/n$

to the molar volume of a perfect gas, V°_{m} *at the same pressure and temperature:*

$$Z = \frac{V_m}{V^{\circ}_{m}} \qquad [1.16]$$

Because the molar volume of a perfect gas is **equal** to *RT/p, an equivalent expression is:*

$$Z = RT/p\,V^{\circ}_{m}\ ,$$

which we can write as:

$$pV_m = RTZ \qquad (1.17)$$

Because for a perfect gas *Z = 1 under all conditions*, *deviation of Z a measure* of departure from perfect behavior.

ان حيود قيمة Z عن 1 تكون دليل على حيود الغاز عن السلوك المثالي

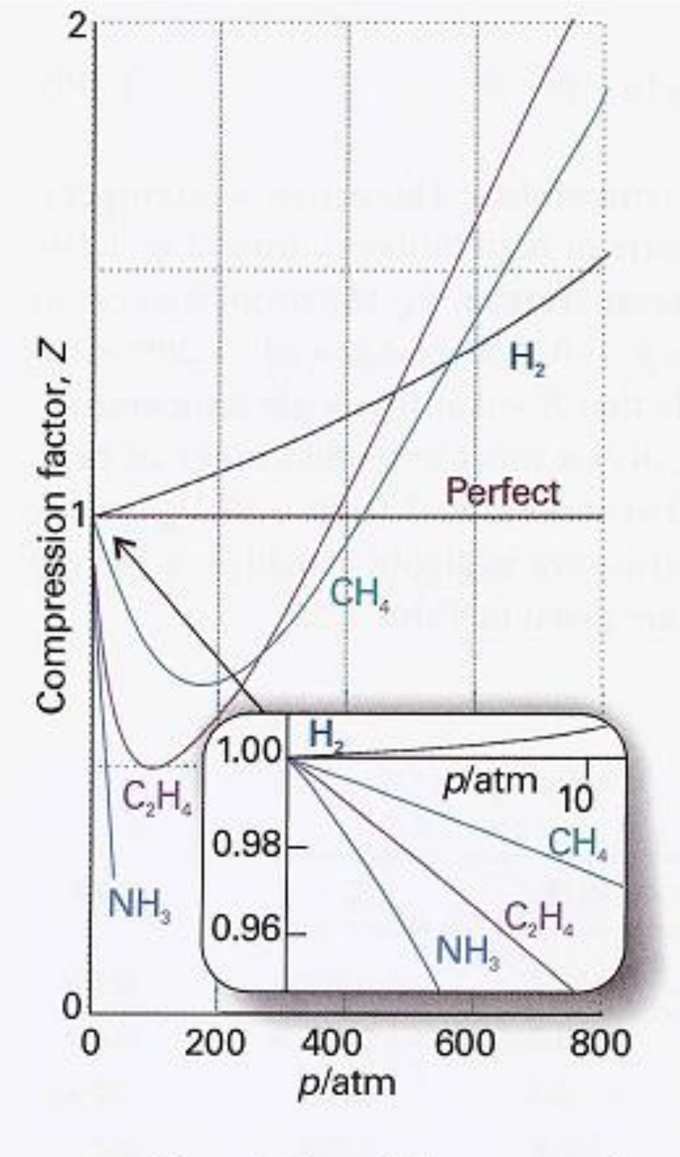


Fig. 1.14 The variation of the compression

Some experimental values of Z *are plotted in Fig. 1.14.*

At very low pressures, *all* the gases shown have $Z \approx 1$ *and behave nearly perfectly.*

At high pressures, all the gases have $Z > 1$, signifying that they have a larger molar volume than a perfect gas.

Repulsive forces are now dominant. ***At intermediate pressures****, most gases have $Z < 1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.*

لاحظ: في الشكل المجاور الاختلاف في عامل التضاغط Z مع الضغط و لغازات عدة .

فعند درجة $0\ ^{o}C$ فإن الغاز المثالي يملك $Z=1$ عند جميع الضغوط و لكن على الرغم من ذلك من ان المنحنيات تقترب من الـ 1 كلما $p \rightarrow 0$ فلها قيم ميل مختلفة .

b) Virial coefficients معاملات فيريال

Figure 1.15 shows the experimental isotherms for carbon dioxide.

At large molar volumes and high temperatures the real-gas isotherms do not differ greatly from perfect-gas isotherms.

The small differences suggest that the perfect gas law is in fact the first term in an expression of the form

$$pV_m = RT(1 + B'p + C'p^2 + \cdots) \qquad (1.18)$$

This expression is an example of a common procedure in physical chemistry, in which a simple law that is known to be a good first approximation (in this case *pV = nRT)*

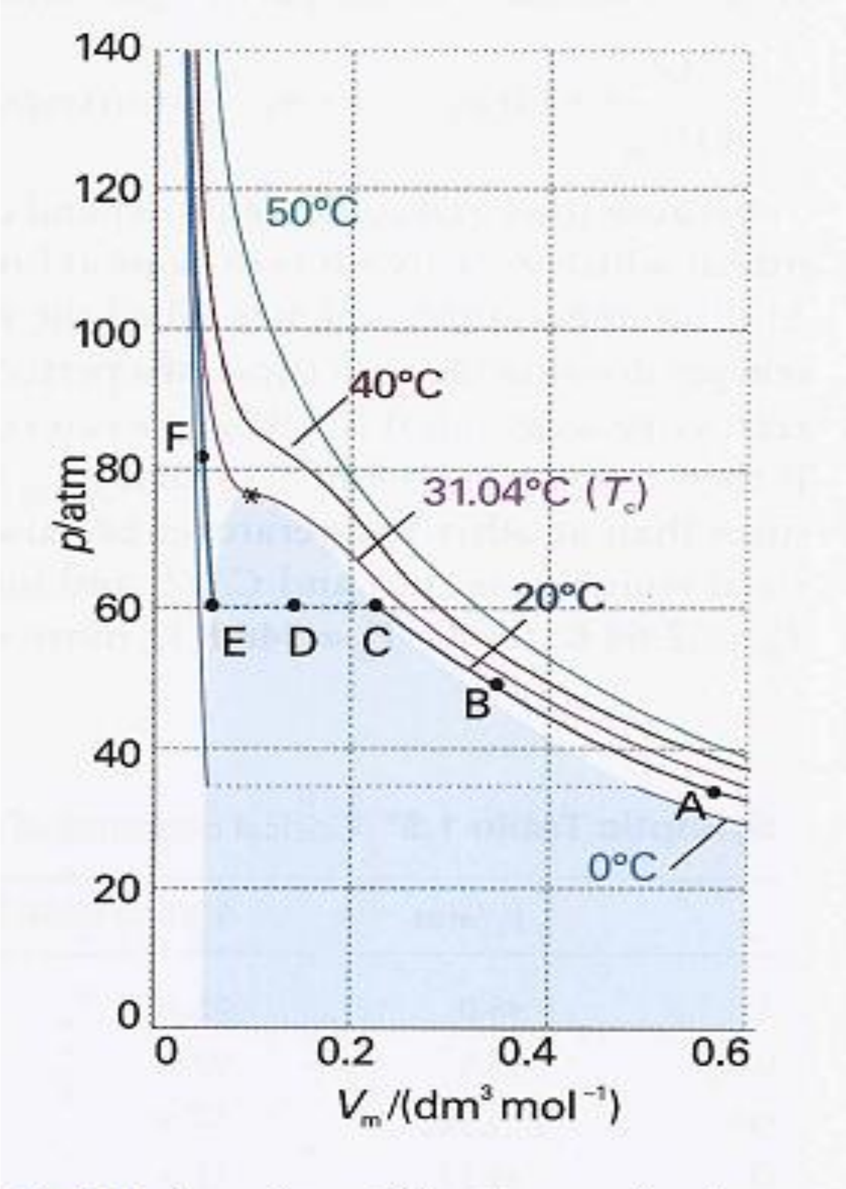


Fig. 1.15 Experimental isotherms of carbon

- في الشكل المجاور : تمثيل بياني ايزوثيرمي لثاتي اوكسيد الكاربون و لعدد من الدرجات الحرارية. المخطط الايزوثيرمي الحرج هو الذي تقع عليه
- الدرجة الحرارية الحرجة كانت عند 31.04^{o}C
- و النقطة الحرجة قد أُشرت بنجمة على المخطط

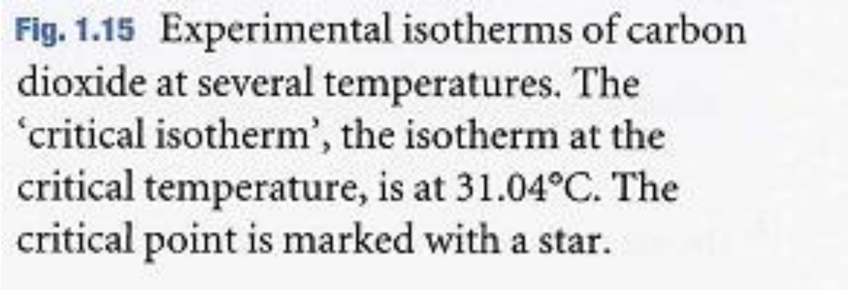


Fig. 1.15 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.04°C. The critical point is marked with a star.

reated as the first term in a series in powers of a variable (in this case *p). A more convenient expansion for many applications is*

$$pV_{\mathrm{m}} = RT\left(1 + \frac{B}{V_{\mathrm{m}}} + \frac{C}{V_{\mathrm{m}}^{2}} + \cdots\right) \qquad (1.19)$$

These two expressions are two versions of the virial equation of state. By comparing the expression with eqn 1.17 we see that the term in parentheses can be identified with the compression factor, Z.

The coefficients *B, C,* ... , *which depend on the temperature, are the second, third, ... virial coefficients*

(Table lA); the first virial coefficient is 1.

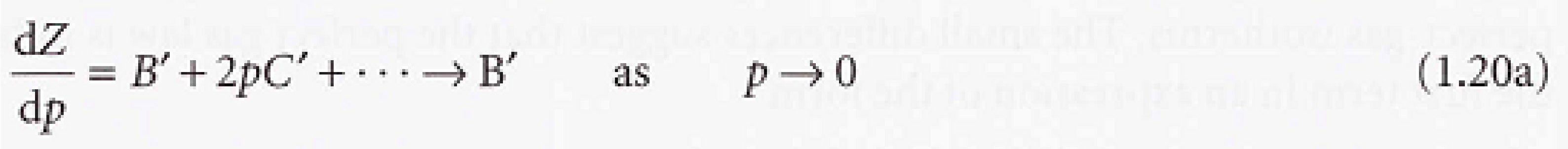
***The third virial* coefficient, C,** is usually less important than the second coefficient, *B,*

in the sense that at typical molar volumes $C/V^2_{\mathrm{m}} \ll B/V_{\mathrm{m}}$

We can use the virial equation to demonstrate the important point that, although the equation of state of a real gas may coincide with the perfect gas law as *p →0 , not all its properties necessarily coincide with those of a perfect gas in that limit.*

Consider, for example, the value of dZ/dp, the slope of the graph of compression factor against pressure.

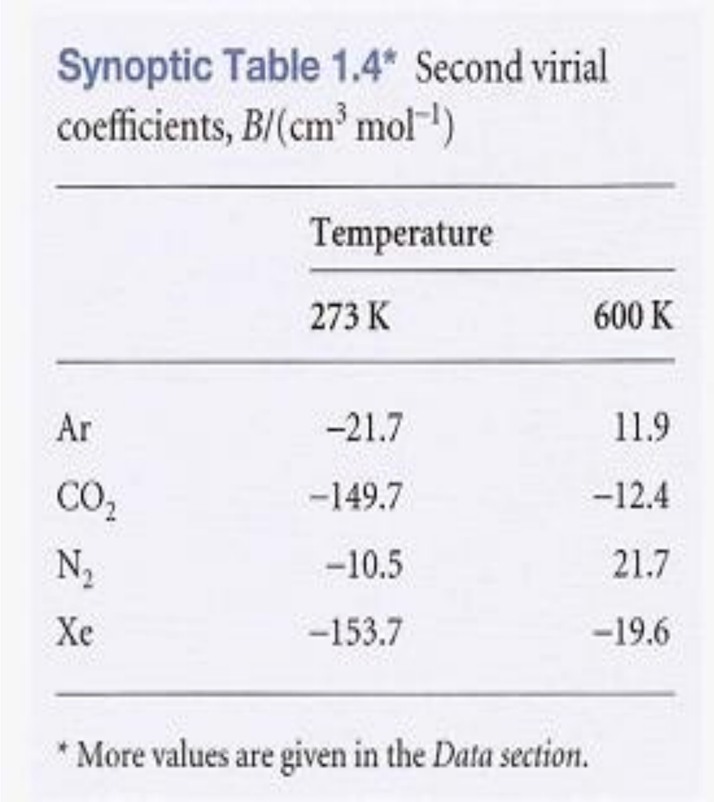
For a perfect gas dZ/dp = 0 (because Z =1 at all pressures), but for a real gas from eqn 1.18 we obtain



$$\frac{dZ}{dp} = B' + 2pC' + \cdots \rightarrow B' \quad \text{as} \quad p \rightarrow 0 \qquad (1.20a)$$

However, *B' is not necessarily zero,* ***so the slope of Z with respect to p does not necessarily approach 0 (the perfect gas value), as we can see in Fig. 1.14.*** *Because several physical properties of gases depend on derivatives, the properties of real gases do not always coincide with the perfect gas values at low pressures.*

$$\frac{dZ}{d(1/V_m)} \rightarrow B \text{ as } V_m \rightarrow \infty, \qquad \text{corresponding to} \quad p \rightarrow 0 \qquad (1.20b)$$



Synoptic Table 1.4* Second virial coefficients, $B/(\mathrm{cm^3\,mol^{-1}})$

	Temperature	
	273 K	600 K
Ar	−21.7	11.9
CO_2	−149.7	−12.4
N_2	−10.5	21.7
Xe	−153.7	−19.6

* More values are given in the *Data section*.

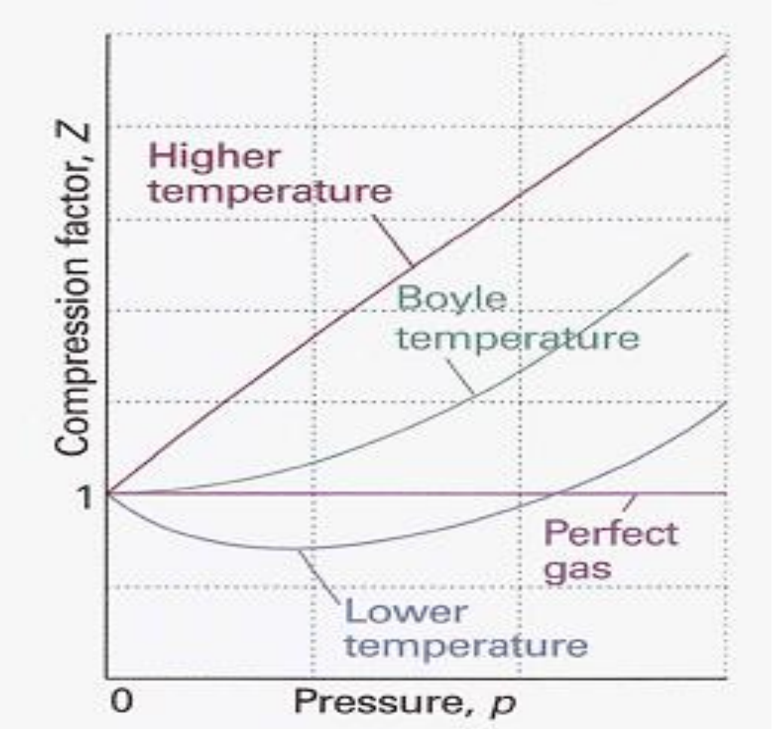


Fig. 1.16 The compression factor, Z,

شكل 1.16 عامل التضاغط Z يقترب من 1 عند ضغوط واطئة و لكنها بقيم ميل مختلفة و بالنسبة للغازات الحقيقية قد يكونا كلاهما ميلا موجبا او سالبا و قد تتغير القيم بتغير درجات الحرارة. و عند درجة بويل يكون الميل يساوي صفر و الغاز سيسلك مثاليا ضمن مدى واسع من الشروط مقارنتا بدرجات الحرارة الاخرى.

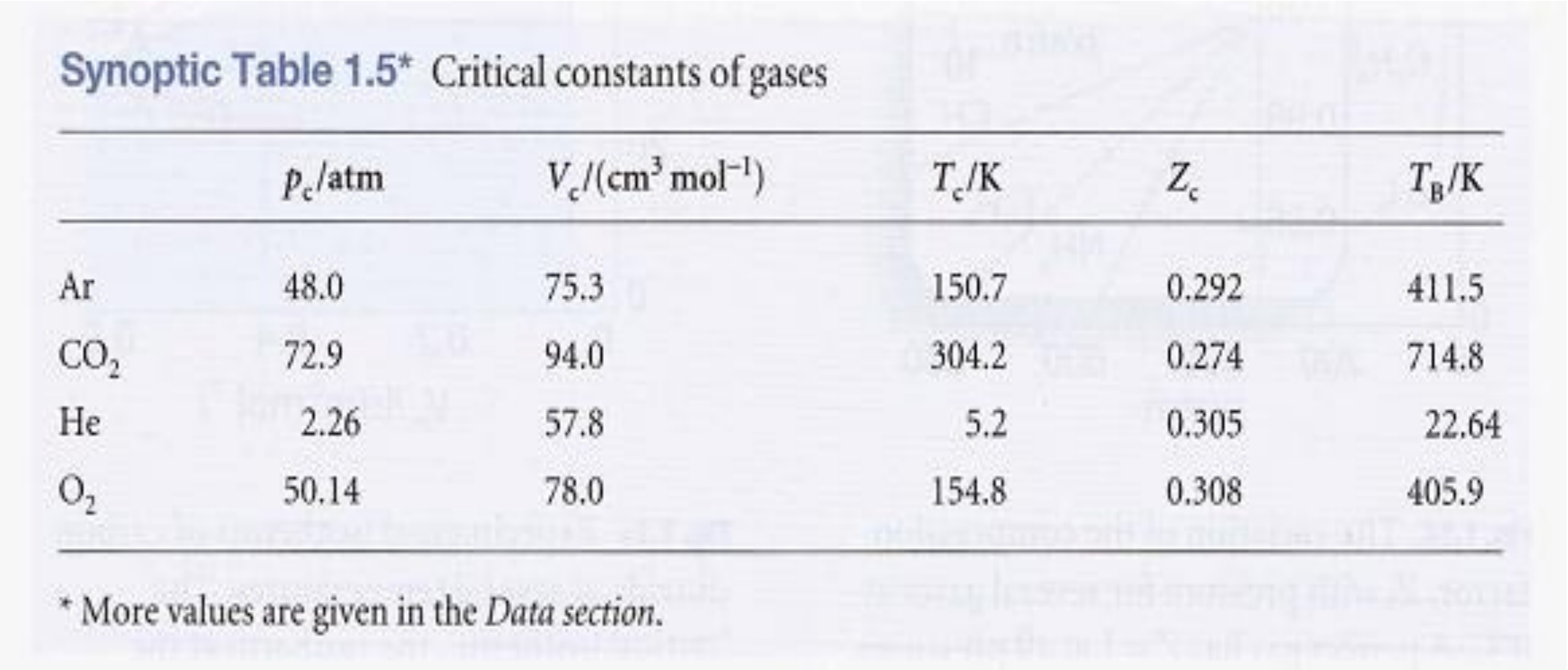
Boyle temperature, *T_B' the properties of the real gas do coincide with those of a perfect gas as p →0.*

According to eqn 1.20b, Z has zero slope as *p →0 if B = 0,*

so we can conclude that B = 0 at the Boyle temperature*. It then follows from eqn 1.19 that $pV_m \approx RT_B$ over a more extended range of pressures than at other temperatures because the first term after 1 (that is, B/V_m) in the*

virial equation is zero and *C/V_m and higher terms are negligibly small. For helium T_B=22.64 K; for air T_B=346.8 K; more values are given in Table 1.5*

- الجدول



Synoptic Table 1.5* Critical constants of gases

	p_c/atm	V_c/(cm^3 mol^{-1})	T_c/K	Z_c	T_B/K
Ar	48.0	75.3	150.7	0.292	411.5
CO_2	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O_2	50.14	78.0	154.8	0.308	405.9

* More values are given in the *Data section*.

(c) Condensation

Now consider what happens when we compress a sample of gas initially in the state marked A in Fig. 1.15 at constant temperature (by pushing in a piston). Near A, the pressure of the gas rises in approximate agreement with Boyle's law. Serious deviations from that law begin to appear when the volume has been reduced to B.

At C (which corresponds to about 60 atm for carbon dioxide), all similarity to perfect behavior is lost,

for suddenly the piston slides in without **any further rise in pressure**: this stage is represented by the horizontal line CDE. Examination of the contents of the vessel shows that just to the left of C a liquid appears, and there are two phases separated by a sharply defined surface.

As the volume is decreased from C through D to E, the amount of liquid increases. **There is no additional resistance to the piston because the gas can respond by condensing.** The pressure corresponding to the line CDE, when both liquid and vapour are present in equilibrium, **is called the vapour pressure of the liquid at the temperature of the experiment**.

At E, the sample is entirely liquid and the piston rests on its surface. Any further reduction of volume requires the exertion of considerable pressure, as is indicated by the sharply rising line to the left ofE. Even a small reduction of volume from E to F requires a great increase in pressure

(d) Critical constants

The isotherm at the temperature T_c; *(304.19 K, or 31.04 °C for* CO_2*) plays a special role in the theory of the states of matter.*

An isotherm slightly below T_c, *behaves as we have already described: at a certain pressure, a liquid condenses from the gas and is distinguishable from it by the presence of a visible surface.*

The critical point of the gas. The temperature, pressure, and molar volume at the critical point **are called the critical temperature,** T_c, ***critical pressure,*** P_c ***, and*** **critical molar volume,** V_c ***, of the substance.*** *Collectively,* P_c, V_c, *and* T_c *are the critical constants of a substance (Table 1.5).*

At and above T_c *the sample has* ***a single phase*** *that occupies the entire volume of the container. Such a phase is,* ***by definition, a gas.***

The critical temperature of oxygen, for instance, signifies that it is impossible to produce liquid oxygen by compression alone if its temperature is greater than 155 K: to liquefy oxygen-to obtain a fluid phase that does not occupy the entire volume-the temperature must first be lowered to below 155 K, and then the gas compressed isothermally. The single phase that fills the entire volume when $T > T_c$*; may be much denser than we normally consider typical of gases, and the name supercritical fluid is preferred*

Lecture 5

1.4 **The van der Waals equation**

1.4 **The van der Waals equation:**

We can draw conclusions from the virial equations of state only by inserting specific values of the coefficients. It is often useful to have a broader, if less precise, view of all gases. Therefore, we introduce the approximate equation of state suggested by J.D. van der Waals in 1873. This equation is an excellent example of an expression that can be obtained by thinking scientifically about a mathematically complicated but physically simple problem, that is, it is a good example of 'model building'.

The van der Waals equation is:

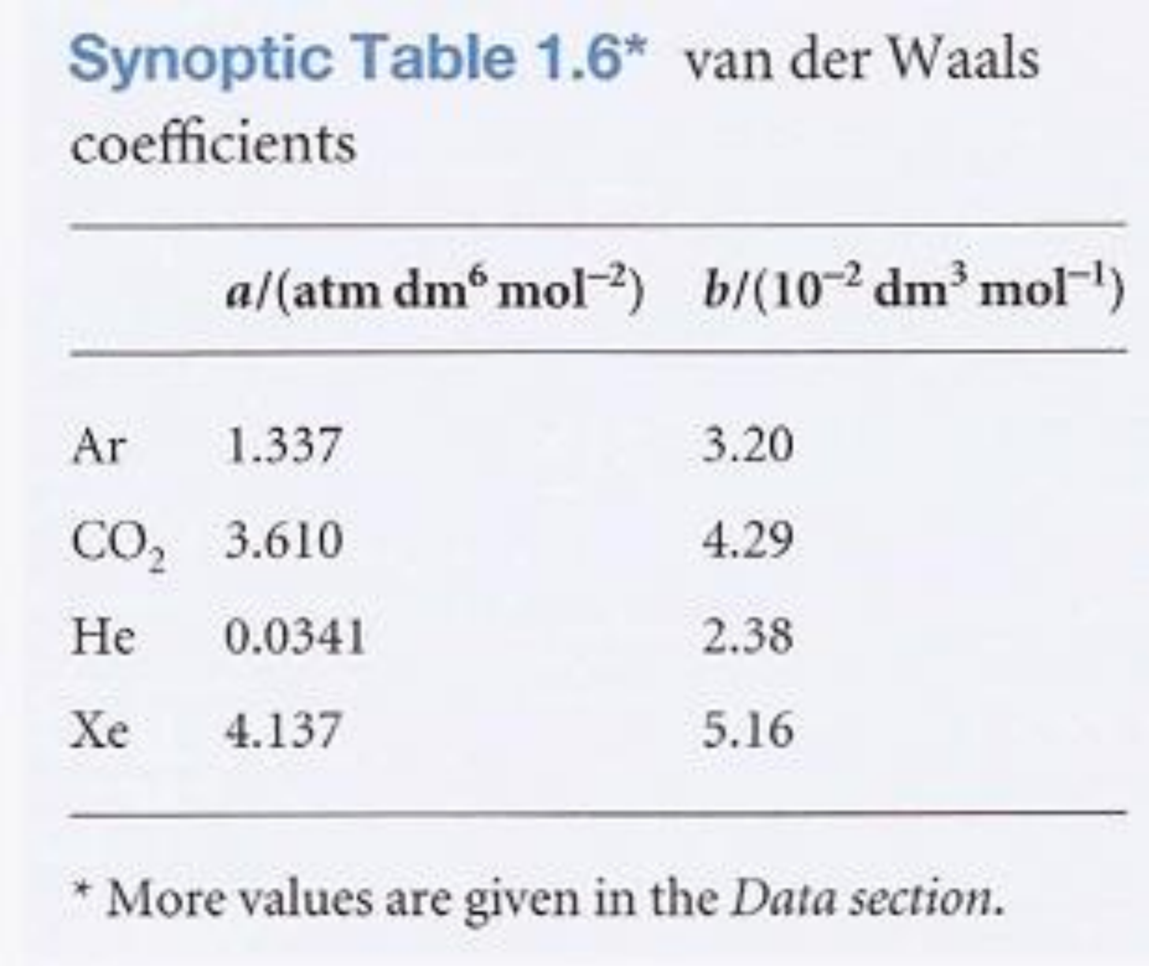
$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \qquad (1.21a)$$

and a derivation is given in *Justification 1.1. The equation is often written in terms of the molar volume $V_m = V/n$ as:*

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad (1.21b)$$

The constants ***a*** *and* ***b*** *are called* ***the van der Waals coefficients. They are characteristic of each gas but independent of the temperature (Table 1.6).***

الثابتان a و b يدعيان بمعاملات فاندرفالز و هما مميزان لذلك الغاز و لايعتمدان على درجة الحرارة.



Synoptic Table 1.6* van der Waals coefficients

	a/(atm dm^6 mol^{-2})	b/(10^{-2} dm^3 mol^{-1})
Ar	1.337	3.20
CO_2	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

* More values are given in the *Data section.*

- ايضاح : 1.1 : معادلة فاندر فالز كمعادلة حالة :

ان تأثير التنافر بين الجزيئات يؤخذ بالحسبان وعلى الرغم من ان الجزيئات تسلك كسلوك كرات صغيرة وغير قابلة للاختراق أي صلدة . كما ان الحجم اللاصفري للجزيئات يفترض انه بدلاً من ان الجزيئات تتحرك في الحجم V انها سوف تستقر في ذلك الحجم الصغير nb - V حيث ان nb يمثل تقريباً الحجم الكلي الذي تشغله الجزيئات .

ان الافتراضات هذه تفترض انه لابد من استبدال قانون الغاز المثالي P= nRT/V بالعلاقة :

$$P = \frac{nRT}{V - nb}$$

ذلك عندما يكون التنافر مؤثر .

كما ان اقرب مسافة لكرتين صلدتين ذات نصف قطر r وحجم

$$V_{molecule} = \frac{4}{3}\pi r^3$$

تكون المسافة هي 2r لذى فان الحجم الذي يُشغل هو: $\frac{4}{3}\pi(2r)^3$

او $8V_{molecule}$ اي ثمانية حجوم جزيئية او الحجم الذي يشغله الجزيء الواحد هو نصف ذلك الحجم $4V_{molecule}$ وعليه فان :

$$b \approx 4V_{molecule}\, N_A$$

والضغط يعتمد على كلٍ من عدد التصادمات على الجدران وقوتها والتي تقللها او تُضعف من قوتها هي قوى الجذب والتي تعمل بشكل نسبي اي نسبة التركيز المولاري $\frac{n}{V}$ من الجزيأت في النموذج .

اذن بسبب كل من التردد (عدد التصادمات) وقوة التصادمات مطروحاً منها قوى التجاذب ،اذن الضغط سينخفض نسبيا الي مربع ذلك التركيز فاذا كُتب مقدار الانخفاض في الضغط يساوي المقدار $-a\left(\frac{n}{V}\right)^2$ حيث ان a هو ثابت موجب وهو صفة مميزة لكل غاز وبتوحيد تاثير قوى التنافر والتجاذب ستعطي معادلة الحالة لفاندر فالز المعادلة (1.21)

ففي هذا الايضاح قد كوّنا مفهوماً للحجوم الجزيئية وتاثير القوى.

والمعادلة يمكن اشتقاقها بطرق اخرى ولكن الطريقة الحالية لها فائدة اذ تبين كيف يمكن اشتقاق الهيئة الرياضية وتحويلها الى معادلة رياضية من الافكار الازمة . كما وان الاشتقاق له فائدة ابقاء عدم دقة المعاملان a , b : وفي الحقيقة يعتبران متغيران وضعيان او افتراضيان من انهما خاصيتان جزيئتان دقيقتان .

- <u>مثال 1.4</u>
- قدر الحجم المولي (CO2 بدرجة 500K وضغط 100 atm بعد معالجة الحسابات بقوى فاندرفالز .
- <u>طريقة الحل Method</u>
- لغرض استخدام تعبير نسحب منه الحجم المولي سنستخدم العلاقة . (1.21b) وسوف نضرب طرفي المعادلة بالمقدار $(V_m - b)V_m^2$ للحصول على :

$$(V_m - b)V_m^2 P = RT\, V_m^2 - (V_m - b)a$$

- وبالقسمة بالمقدار p وجمع الاسس لـ V_m سنحصل على:

$$V_m^3 - \left(b + \frac{RT}{P}\right) V_m^2 + \left(\frac{a}{b}\right) V_m - \frac{ab}{P} = 0$$

- بارغم من انه يمكن الحصول على تعبير رياضي دقيق لمعادلة الدرجة الثالثة الاّ انها معقدة جداً في الحل . ولكن يمكن حلها باستخدام البرامج الحاسوبية التجارية في الحل.

8

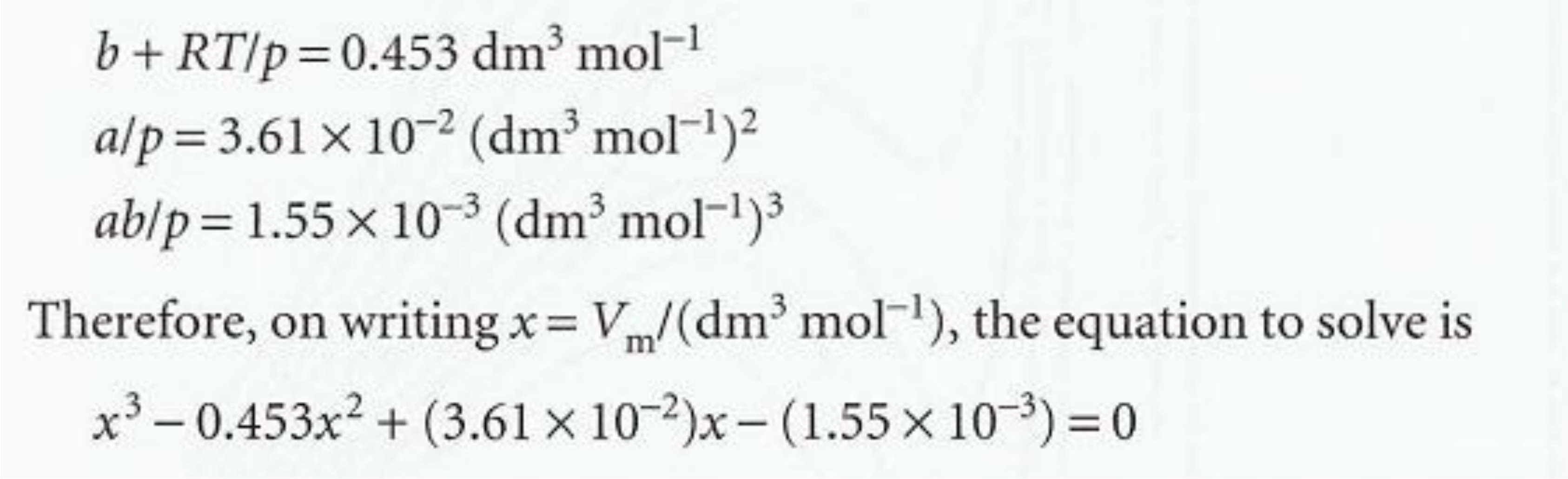
الحل Answer

حسب الجدول (1.6) فان $a = 3.592$ و $b = 4.267 \times 10^{-2}$ dm^3 moℓ$^{-1}$

فتحت الظروف المعطاة نجد ان :

$RT/p = 0.410$ dm^3 mol^{-1}.

فالمعاملان في المعادلة بالنسبة V_m يكون اذن :



$$b + RT/p = 0.453 \text{ dm}^3 \text{ mol}^{-1}$$
$$a/p = 3.61 \times 10^{-2} \text{ (dm}^3 \text{ mol}^{-1})^2$$
$$ab/p = 1.55 \times 10^{-3} \text{ (dm}^3 \text{ mol}^{-1})^3$$

Therefore, on writing $x = V_m/(\text{dm}^3 \text{ mol}^{-1})$, the equation to solve is

$$x^3 - 0.453x^2 + (3.61 \times 10^{-2})x - (1.55 \times 10^{-3}) = 0$$

فالجذر المقبول لـ $X = 0.366$ وهذا يعطي حجماً مولياً V_m =0.366 dm^3 moℓ$^{-1}$ وبالنسبة للغاز المثالي تحت هذه الظروف سيكون الحجم المولي 0.410 dm^{3}moℓ$^{-1}$

9

Reliability of the equation اعتمادية المعادلة (a)

- والان سنختبر الى اي مدى ان معادلة فاندر فالز تستطيع استنتاج سلوك الغاز الحقيقي . وقد تكون وحده جداً في توقع تجير مفرد وبسيط لمعادلة الحالة للمادة الحقيقية وانه يمكن الحصول على قيم دقيقة بعد تطبيقها على علاقة فيريال وباستخدام القيم المجدولة للمعاملان لدرجات حرارة مختلفة وتحليل الانظمة عددياً ان ميزة مادلة فاندفال انها تطي تحليل (وقد عُبِّر عنه رمزياً) يسمح لنا من ان نكوِّن خلاصة عامة عن الغازات الحقيقية . وعندما تفشل المعادلة علينا استخدام احد المعادلات الحالة الاخرى والتي افترضت في الجدول (1.7) وذلك باشتقاق معادلة حالة جديدة او الرجوع الى معادلة فيريال .

اي نريد ان نقول علينا ان نحكِّم **انطقة المعادلة** بمقدار مع المخططات الايزوثيرميّة المستنتجة نظريا مع تلك المستنتجة عملياً في الشكل (1.15)

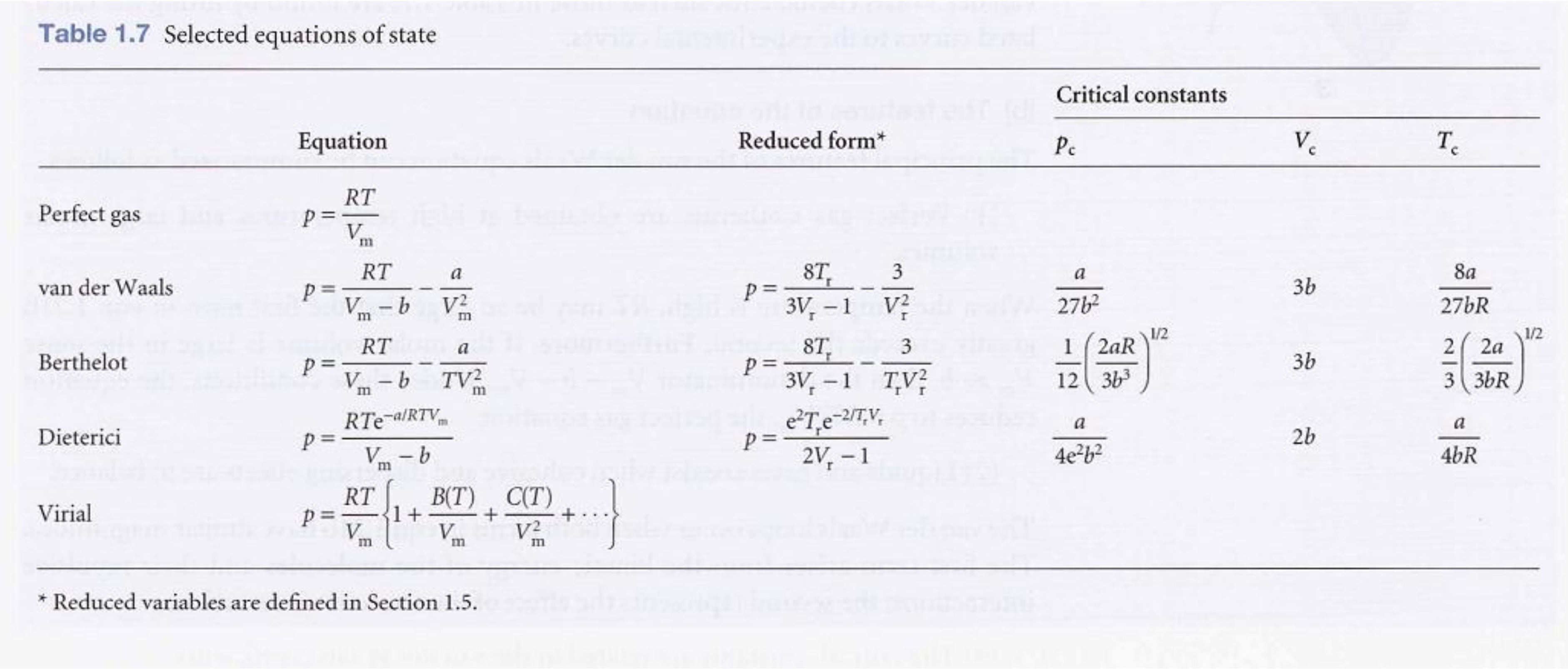


Table 1.7 Selected equations of state

	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p=\dfrac{RT}{V_m}$				
van der Waals	$p=\dfrac{RT}{V_m-b}-\dfrac{a}{V_m^2}$	$p=\dfrac{8T_r}{3V_r-1}-\dfrac{3}{V_r^2}$	$\dfrac{a}{27b^2}$	$3b$	$\dfrac{8a}{27bR}$
Berthelot	$p=\dfrac{RT}{V_m-b}-\dfrac{a}{TV_m^2}$	$p=\dfrac{8T_r}{3V_r-1}-\dfrac{3}{T_rV_r^2}$	$\dfrac{1}{12}\left(\dfrac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2}$
Dieterici	$p=\dfrac{RTe^{-a/RTV_m}}{V_m-b}$	$p=\dfrac{e^2T_re^{-2/T_rV_r}}{2V_r-1}$	$\dfrac{a}{4e^2b^2}$	$2b$	$\dfrac{a}{4bR}$
Virial	$p=\dfrac{RT}{V_m}\left\{1+\dfrac{B(T)}{V_m}+\dfrac{C(T)}{V_m^2}+\cdots\right\}$				

* Reduced variables are defined in Section 1.5.

- وادناه مجموعة من المخططات الايزوثيرمية كما في الشكل (1.17) والشكل (1.18) . وبغض النظر عن التذبذب في المناطق اسفل درجة الحرارة الحرجة ، الا انها اعطت مخططات آيزوثيرميّة بشكل ممتاز . ان خطوط فاندر فالز Vander Waals loops هي غير واقعية بسبب انها تفترض انها تحت شروط معينة هناك زيادة في الضغط تحدث هذه تؤدي الى زيادة في الحجم ومن ثم استبدلت برسم خطوط مستقيمة افقية وعليه فان الانشوطات او المخططات الجزيئية انها تحدد مساحات متساوية فوق وتحت الخطوط هذه الطريقة تدعى بتركيب ماكس ويل Maxwell (3) construction فمعاملان فاندر فالز مثل تلك المذكورة في الجدول (1.7) قد وجدت من مطابقة المنحنات المحسوبة والمنحنات المحصل عليها تجريبياً .

12

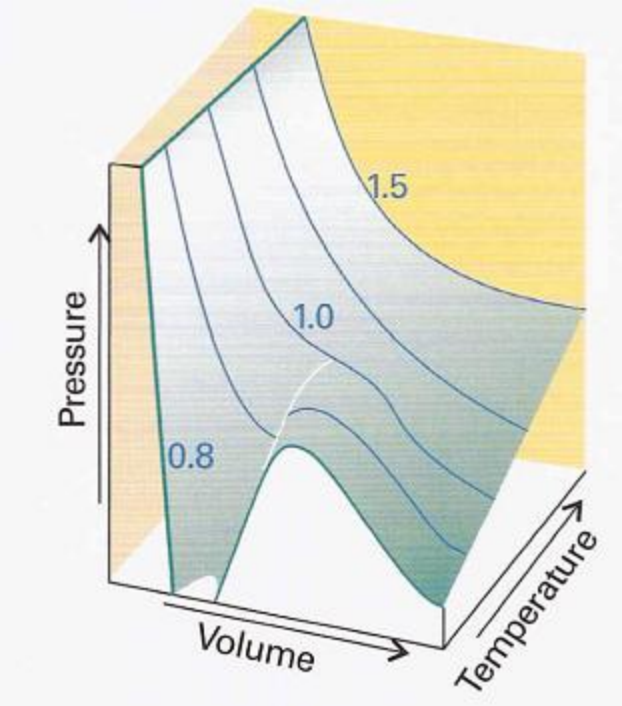


Fig. 1.17 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.

- الشكل 1.17:
- السطح المحتمل للحالات المسموح بمعادلة فاندرفالز
- قارن هذا السطح مع الشكل 1.8.

- شكل 1.8:

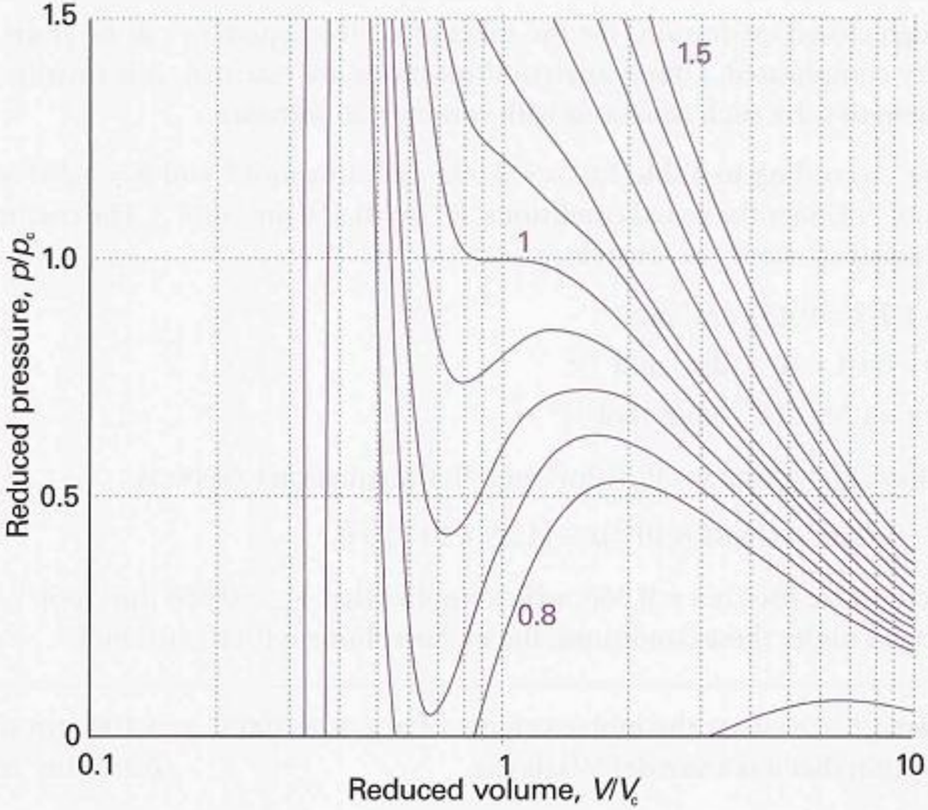


Fig. 1.18 Van der Waals isotherms at several values of T/T_c. Compare these curves with those in Fig. 1.15. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$.

(b) The features of the equation

The principal features of the van der Waals equation can be summarized as follows.

(1) Perfect gas isotherms are obtained at high temperatures and large molar volumes. When the temperature is high, *RT may be so large that the first term in eqn 1.21b* greatly exceeds the second.

Furthermore, if the molar volume is large in the sense *$V_m \gg b$, then the denominator $V_m - b \approx V_m$. Under these conditions, the equation reduces to $p = RT/V_m$, the perfect gas equation.*

(2) Liquids and gases coexist when cohesive and dispersing effects are in balance. The van der Waals loops occur when both terms in eqn 1.21b have similar magnitudes.

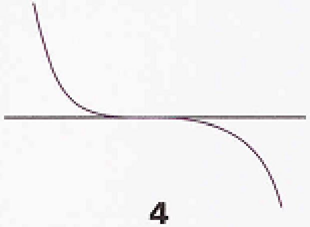
The first term arises from the kinetic energy of the molecules and their repulsive interactions; the second represents the effect of the attractive interactions.

(3) The critical constants are related to the van der Waals coefficients.

For *$T < T_c$, the calculated isotherms oscillate, and each one passes through a minimum followed by a maximum. These extrema converge as $T \rightarrow T_c$; and coincide at $T = T_c$; at the critical point the curve has a* ***flat inflexion (4).*** *From the properties of curves, we know that an inflexion of this type occurs when both the first and second derivatives are zero. Hence, we can find the critical constants by calculating these derivatives and setting them equal to zero:*

$$\frac{\mathrm{d}p}{\mathrm{d}V_\mathrm{m}} = -\frac{RT}{(V_\mathrm{m} - b)^2} + \frac{2a}{V_\mathrm{m}^3} = 0$$

$$\frac{\mathrm{d}^2p}{\mathrm{d}V_\mathrm{m}^2} = \frac{2RT}{(V_\mathrm{m} - b)^3} - \frac{6a}{V_\mathrm{m}^4} = 0$$



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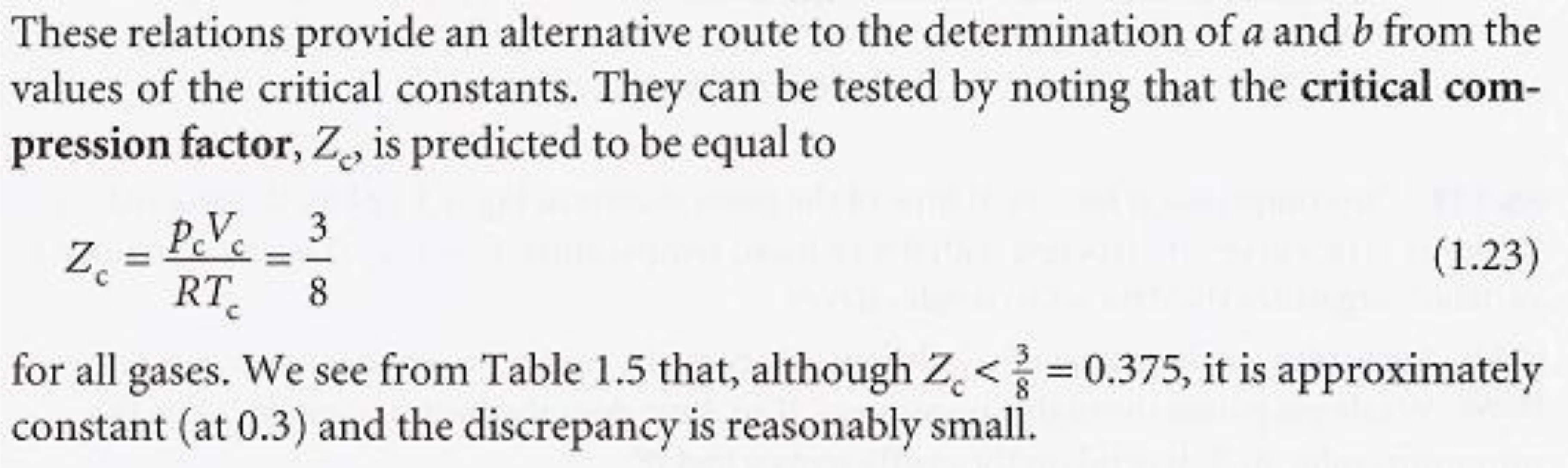
at the critical point. The solutions of these two equations (and using eqn 1.21b to calculate p_c from V_c and T_c) are

$$V_\mathrm{c} = 3b \qquad p_\mathrm{c} = \frac{a}{27b^2} \qquad T_\mathrm{c} = \frac{8a}{27Rb} \tag{1.22}$$

عامل الانضغاطية الحرج Z_c

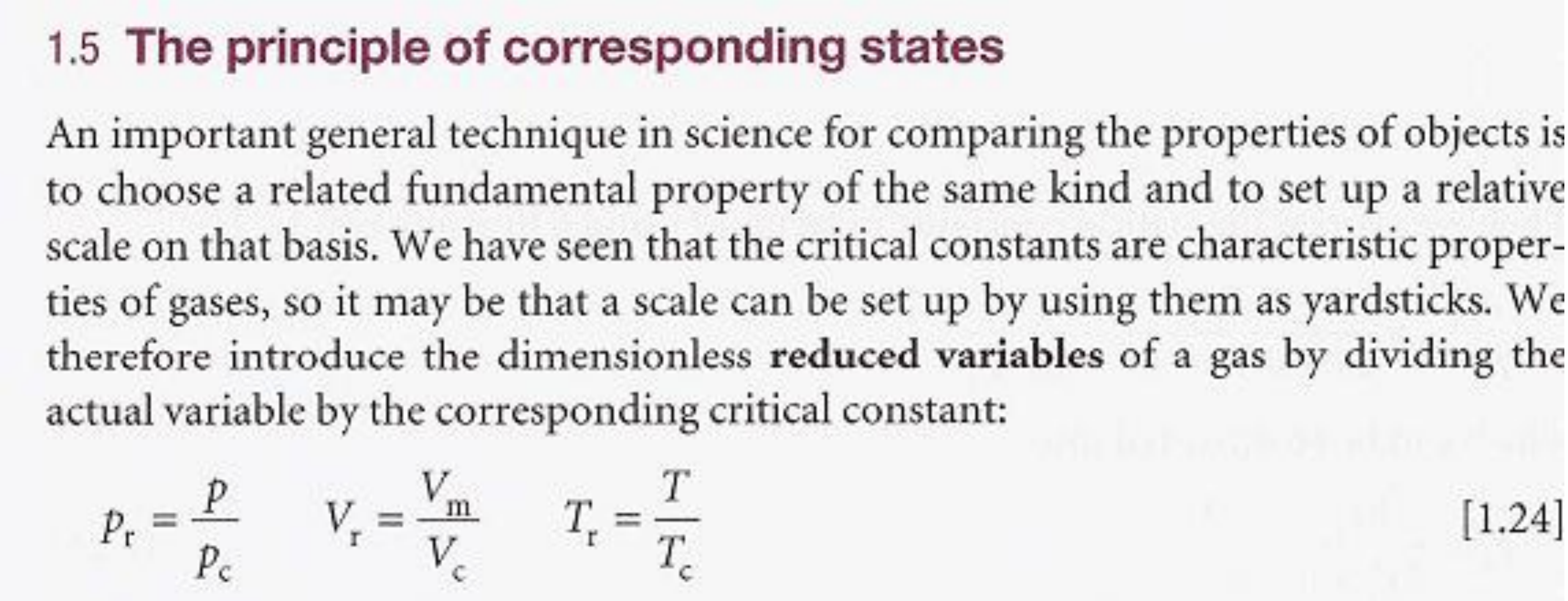


These relations provide an alternative route to the determination of *a* and *b* from the values of the critical constants. They can be tested by noting that the **critical compression factor**, Z_c, is predicted to be equal to

$$Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8} \qquad (1.23)$$

for all gases. We see from Table 1.5 that, although $Z_c < \frac{3}{8} = 0.375$, it is approximately constant (at 0.3) and the discrepancy is reasonably small.

- مبداء تلاقي الحالات:



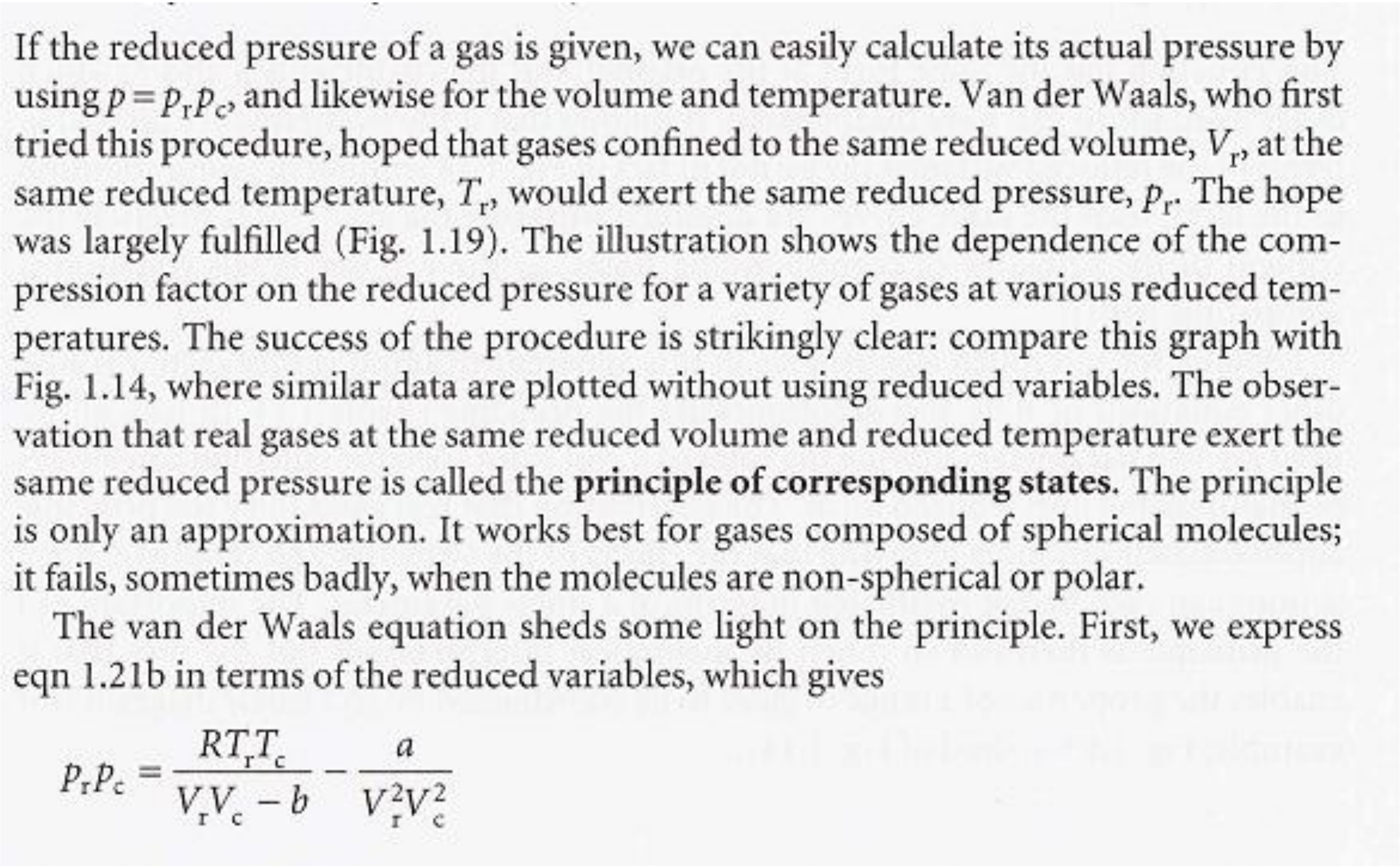
1.5 The principle of corresponding states

An important general technique in science for comparing the properties of objects is to choose a related fundamental property of the same kind and to set up a relative scale on that basis. We have seen that the critical constants are characteristic properties of gases, so it may be that a scale can be set up by using them as yardsticks. We therefore introduce the dimensionless **reduced variables** of a gas by dividing the actual variable by the corresponding critical constant:

$$p_r = \frac{p}{p_c} \qquad V_r = \frac{V_m}{V_c} \qquad T_r = \frac{T}{T_c} \qquad [1.24]$$

حيث ان P_r هو الضغط المختزل V_r الحجم المختزل و T_r درجة الحرارة المختزلة.

- فاذا اعطينا الضغط المختزل فاننا يمكن ايجاد الضغط الحقيقي للغاز



If the reduced pressure of a gas is given, we can easily calculate its actual pressure by using $p = p_r p_c$, and likewise for the volume and temperature. Van der Waals, who first tried this procedure, hoped that gases confined to the same reduced volume, V_r, at the same reduced temperature, T_r, would exert the same reduced pressure, p_r. The hope was largely fulfilled (Fig. 1.19). The illustration shows the dependence of the compression factor on the reduced pressure for a variety of gases at various reduced temperatures. The success of the procedure is strikingly clear: compare this graph with Fig. 1.14, where similar data are plotted without using reduced variables. The observation that real gases at the same reduced volume and reduced temperature exert the same reduced pressure is called the **principle of corresponding states**. The principle is only an approximation. It works best for gases composed of spherical molecules; it fails, sometimes badly, when the molecules are non-spherical or polar.

The van der Waals equation sheds some light on the principle. First, we express eqn 1.21b in terms of the reduced variables, which gives

$$p_r p_c = \frac{RT_rT_c}{V_rV_c - b} - \frac{a}{V_r^2V_c^2}$$

- اثبتت المشاهدات التجريبية بان الغازات الحقيقية و لنفس الحجم المختزل و درجة الحرارة المختزلة فانها سوف تسلط الضغط المختزل هذه الحالة تدعى بمبداء تلاقي الحالات. و هذا المبداء هو تقريبي و تطيعه الغازات المكونة من جزيئات كروية و تفشل احيانا عندما لاتكون الجزيئات كروية او مستقطبة و معادلة فاندرفالز يمكن ان تكتب بصورة المتغيرات المختزلة و كمايلي:

$$p_r p_c = \frac{R T_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2}$$

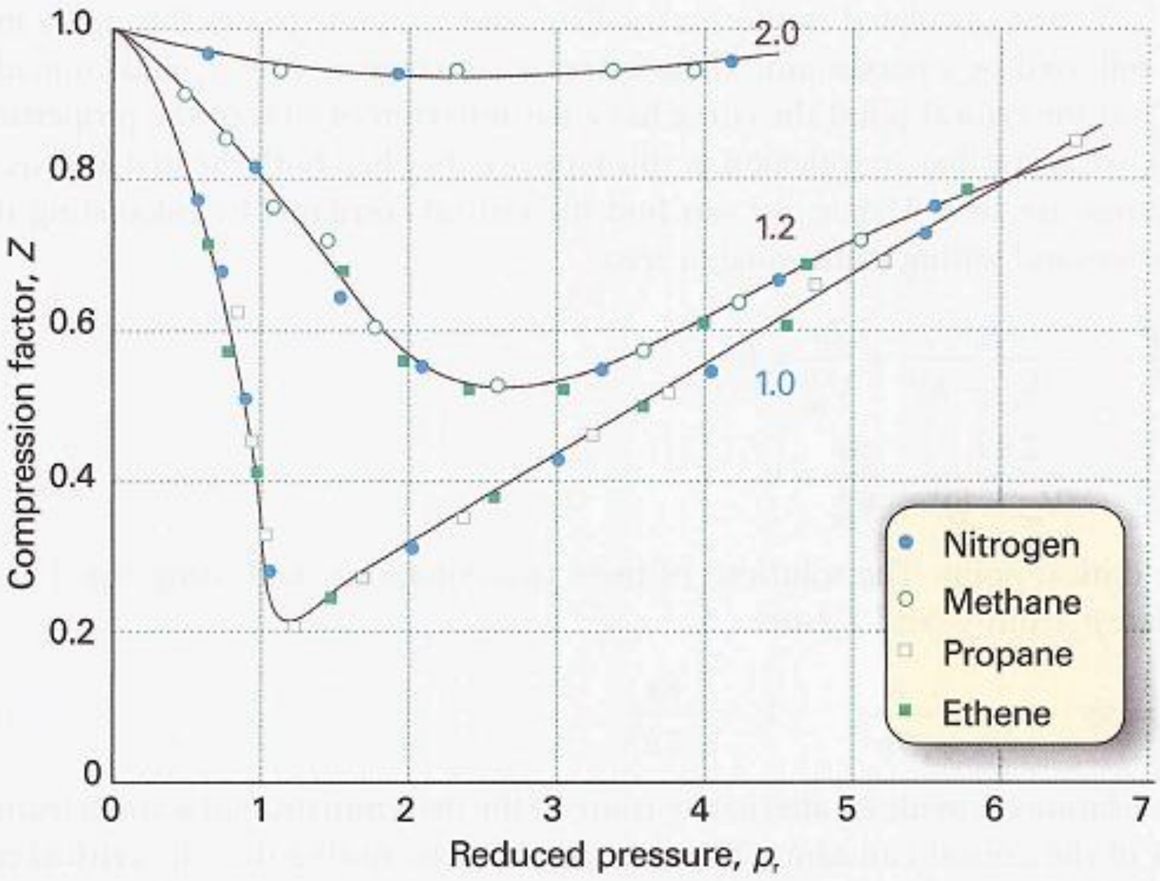
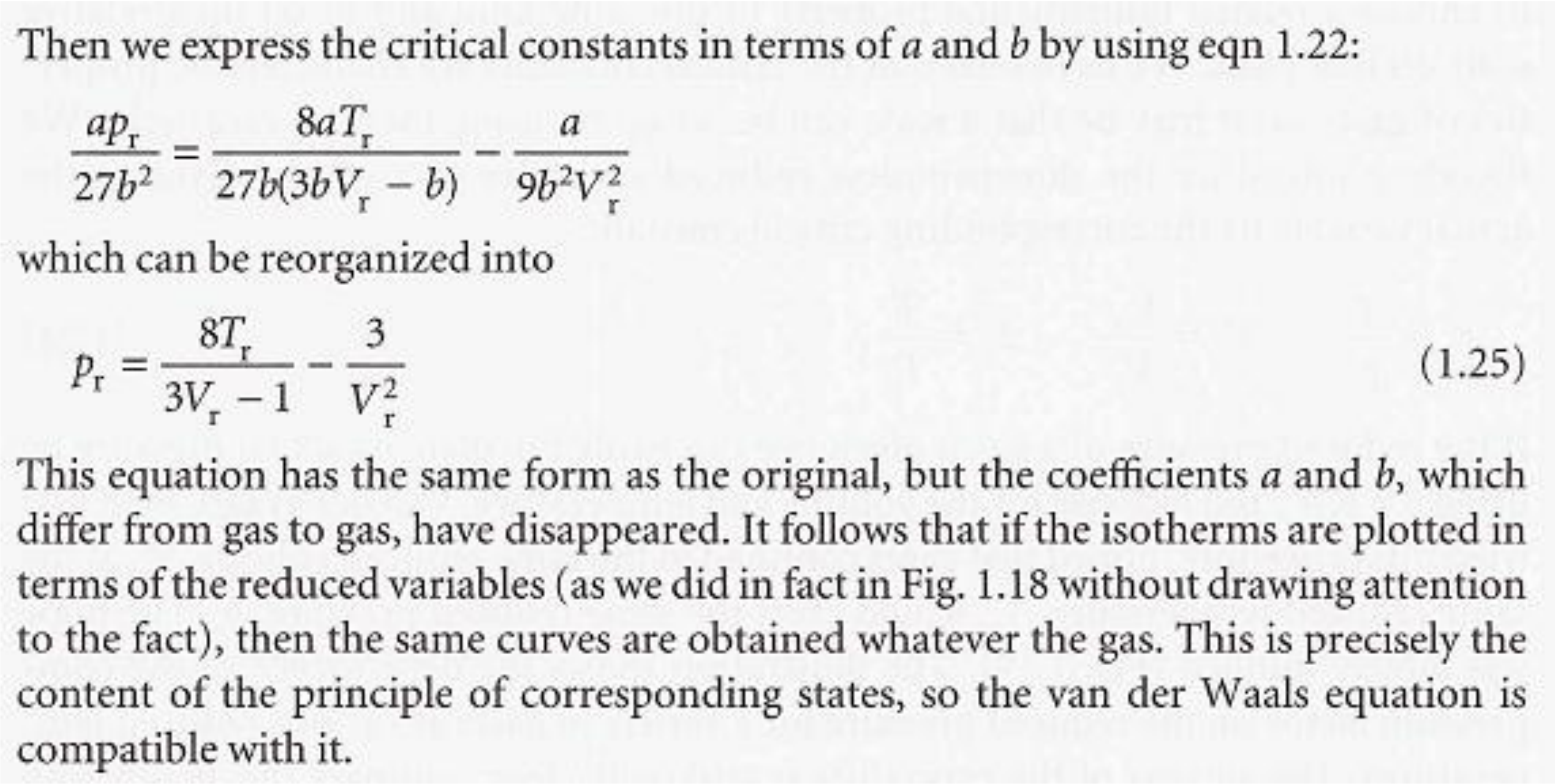


Fig. 1.19 The compression factors of four of the gases shown in Fig. 1.14 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.



Then we express the critical constants in terms of *a* and *b* by using eqn 1.22:

$$\frac{ap_r}{27b^2} = \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2V_r^2}$$

which can be reorganized into

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \qquad (1.25)$$

This equation has the same form as the original, but the coefficients *a* and *b*, which differ from gas to gas, have disappeared. It follows that if the isotherms are plotted in terms of the reduced variables (as we did in fact in Fig. 1.18 without drawing attention to the fact), then the same curves are obtained whatever the gas. This is precisely the content of the principle of corresponding states, so the van der Waals equation is compatible with it.

Lecture 6

The First Law

- **The First Law** القانون الاول للثرموداينمك
- **الخصائص العامة للثرموداينمك:**

For the purposes of physical chemistry, the universe is divided into two parts, the system and its surroundings.

The system is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on.

The surroundings comprise the region outside the system and are where we make our measurements.

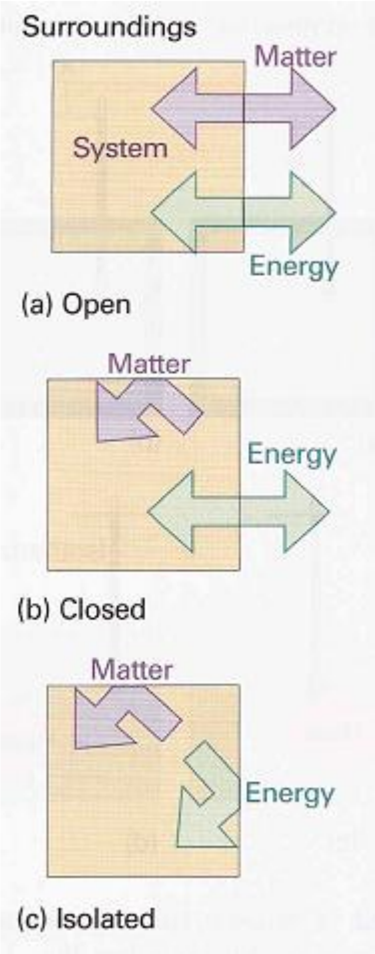
The type of system depends on the characteristics of the boundary that divides it from the surroundings (Fig. 2.1).

If matter can be transferred through the boundary between the system and its surroundings the system is classified as open.

If matter cannot pass through the boundary the system is **classified as closed**. Both open and closed systems can exchange energy with their surroundings.

For example, a closed system can expand and thereby raise a weight in the surroundings; it may also transfer energy to them if they are at a lower temperature.

An isolated system is a closed system that has neither mechanical nor thermal contact with its surroundings.



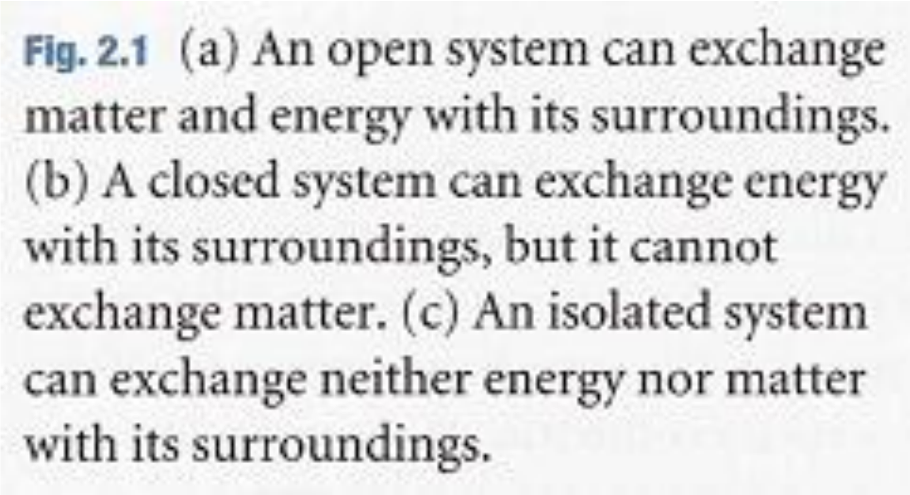


Fig. 2.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

2.1. **Work, heat, and energy:**

The fundamental physical property in thermodynamics is work:

work is motion against an opposing force.

An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

The energy of a system is its capacity to do work.

اضهرت التجارب ان طاقة اللنظام يمكن تغييرها بطرق اخرى غير الشغل كنتيجة للفرق بين النظام و المحيط فيمكننا القول بان الطاقة قد انتقلت كحرارة.

Experiments have shown that the energy of a system may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between the system and its surroundings we say that energy has been transferred as heat. When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than the same amount of cold water. Not all boundaries permit the transfer of energy even though there is a temperature difference between the system and its surroundings

An exothermic process is a process that releases energy as heat into its surroundings. All combustion reactions are exothermic.

An endothermic process is a process in which energy is acquired from its surroundings as heat.

An example of an endothermic process is the vaporization of water.

An endothermic process energy is transferred 'as heat' from

the surroundings into the system.

Molecular interpretation 2.1 *Heat and work*

In molecular terms, heating is the transfer of energy that makes use of *disorderly molecular motion.*

In contrast, *work is the transfer of energy that makes use of organized motion (Fig. 2.4). When a weight is raised or lowered, its atoms move in an organized way (up or down). The*

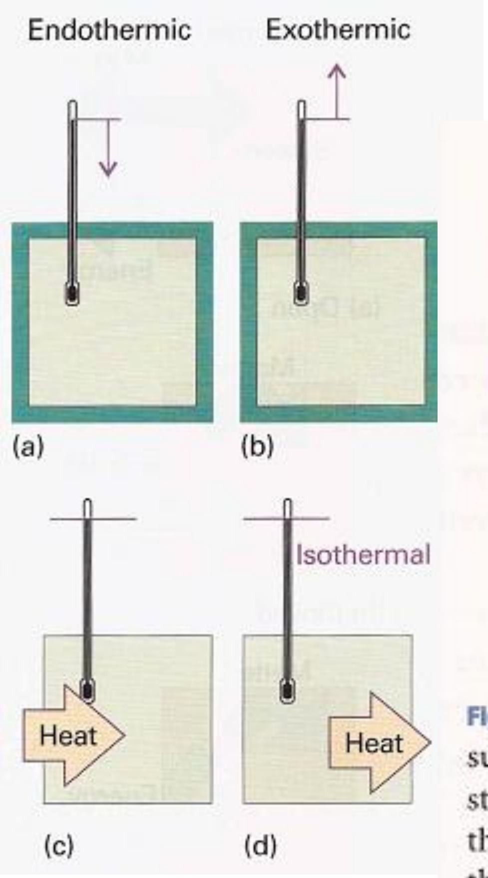


Fig. 2.2 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.

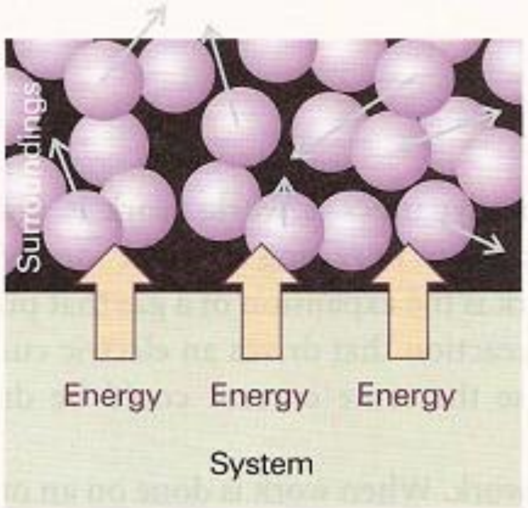


Fig. 2.3 When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

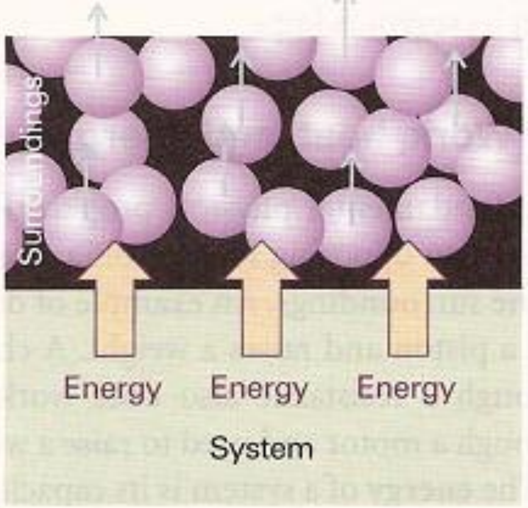


Fig. 2.4 When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

- للتمييز بين الشغل و الحرارة المسلطة على النظام

The distinction between work and heat is made in the surroundings: The fact that a falling weight may stimulate thermal motion in the system is irrelevant to the distinction between heat and work:

work is identified as energy transfer making use of the organized motion of atoms in the surroundings, and

heat is identified as energy transfer making use of thermal motion in the surroundings. I

2.2 **The internal energy**

In thermodynamics, the total energy of a system is called its internal energy, *U.*

***The internal energy** is **the total kinetic** and **potential energy** of the molecules in the system (see Comment 1.3 for the definitions of kinetic and potential energy).'*

*We denote by **ΔU the change in internal energy** when a system changes from an initial state $\dot{i}$ with internal energy **U_i** to a final state **f** of internal energy U_f:*

$$\Delta U = U_f - U_i \qquad \text{......................................(2 .1)}$$

The internal energy is a state function in the sense that its value depends only on the current state of the system and is **independent of how that state has been prepared.**

In other words, it is a function of the properties that determine the current state of the system. Changing

فالطاقة الداخلية هي دالة حالة أي بمعنى ان قيمتها تعتمد فقط على الحالة الحالية للنظام ولا تعتمد على كيفية تحضير تلك الحالة.

Changing any one of the state variables, such as the pressure, results in a change in internal energy.

The internal energy is an extensive property. That the internal energy is a state function has consequences of the greatest importance, as we start to unfold in Section 2.10

فالطاقة الداخلية هي خاصية شاملة و هي دالة حالة ايظا و لها اهمية كبرى كما سنرى في العناوين اللاحقة.

heat, Internal energy, and work are all measured in the same units, the joule (J). The joule, which is named after the nineteenth-century scientist J.P. Joule, is defined as

$$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ S^{-2}}$$

A joule is quite a small unit of energy: for instance, **each beat of the human heart consumes about 1 J.**

Changes in molar internal energy, ***ΔU_m*** *are typically expressed in kilojoules per mole (kJ mol $^{-1}$). Certain other energy units are also used, but are more* common in fields other than thermodynamics.

Thus, 1 electronvolt (1 eV) is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1 V; the relation between **electronvolts** and joules is 1 eV ≈ 0.16 aj (where 1 aj = **10^{-18}** J). Many processes in chemistry have an energy of several electronvolts. Thus, the energy to remove an electron from a sodium atom is close to 5 eV. Calories (cal) and kilocalories (kcal) are still encountered. The current definition of the calorie in terms of joules is

1 cal = 4.184 J exactly An energy of 1 cal is enough to raise the temperature of 1 g of water by 1°C

Lecture 7

Molecular interpretation

2.2 . *The internal energy of a gas*

التفسير الجزيئي للطاقة الداخلية للغاز

Molecular interpretation 2.2 *The internal energy of a gas* :

A molecule has a certain number of degrees of freedom, such as the ability to **translate** (the motion of its centre of mass through space), **rotate** around its centre of mass, or vibrate (as its bond lengths and angles change). **Many physical and chemical properties depend on the energy associated with each of these modes of motion.** For example, a chemical bond might break if a lot of energy becomes concentrated in it.

. **The *equipartition theorem*** *of classical mechanics is a useful guide to the average energy associated with each degree of freedom when the sample is at a temperature T. First, we need to know that a*

*'**quadratic contribution**' to the energy means a contribution that can be expressed as the square of a variable, such as the position or the velocity. For example, the kinetic energy an atom of mass m as it moves through space l*

الاسهام التربيعي *و يعني الاسهام الذي يعبَّر عنه بمربع ذلك المتغيّر كالسرعة او الموقع مثلا الطاقة الحركية لذرة ذات كتلة m و تتحرك في الفضاء l فستكون هناك ثلاثة اسهامات تربيعية في تلك الطاقة.*

$$E_K = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$$

There are three quadratic contributions to its energy. **الاسهام التربيعي للطاقة**

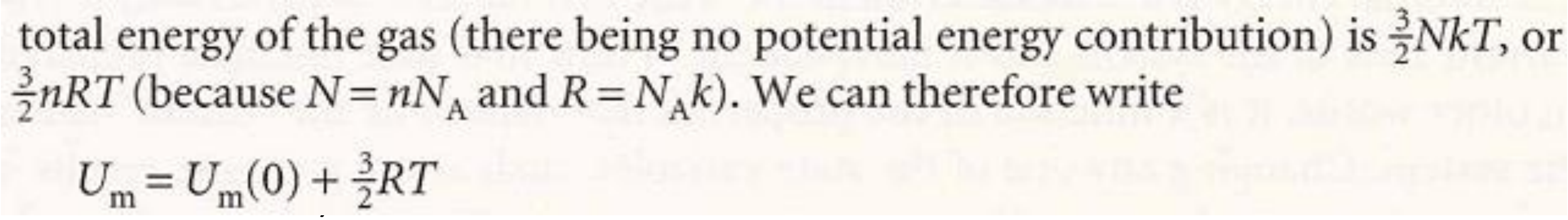
وتنص نظرية الاسهام المتساوي لعدد من الجسيمات بحالة توازن حراري بدرجة حرارة T ، ان معدل قيمة كل اسهام تربيعي للطاقة يكون نفسه و يكون مساوي الى 1kT حيث k يمثل ثابت بولتزمان وله القيمة:

$$k=1.381 \times 10^{-23}\ JK^{-1}$$

The equipartition theorem then states that, for a collection of particles at thermal equilibrium at a temperature *T, the average value of each quadratic contribution to the energy is the same and equal to 1kT, where k is Boltzrnann's constant (k = 1.381 x* 10^{-23} *J* K^{-1}*).*

i**The equipartition theorem :** is a conclusion from classical mechanics and is applicable only when the effects of quantization can be ignored (see Chapters 16 and 17). In practice, it can be used for molecular translation and rotation **but not vibration**.

At 25°C, $\frac{1}{2}kT = 2$ zJ (where 1 zJ = 10^{-21} J), or about 13 meV.



total energy of the gas (there being no potential energy contribution) is $\frac{3}{2}NkT$, or $\frac{3}{2}nRT$ (because $N = nN_A$ and $R = N_Ak$). We can therefore write

$$U_m = U_m(0) + \frac{3}{2}RT$$

where $U_m(0)$ is the molar internal energy at T = 0, when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. This equation shows that the internal energy **of a perfect gas increases linearly with temperature**.

At 25°C, (3/2)*RT = 3.7 kl mol* $^{-1}$*,*

***so translational motion** contributes about 4 kJ mol* $^{-1}$ *to the molar internal energy of a gaseous sample of atoms or molecules (the remaining contribution arises from the internal structure of the atoms and molecules).*

When the gas consists of polyatomic molecules, we need to take into account the effect of rotation and vibration.

A linear molecule, such as N_2 and CO_2, can rotate around two axes perpendicular to the line of the atoms (Fig. 2.5), so it has two rotational modes of motion, each contributing a term *tkT to the internal energy. Therefore, the mean rotational energy is kT and the rotational contribution to the molar internal energy is RT. By adding the translational and rotational contributions, we obtain*

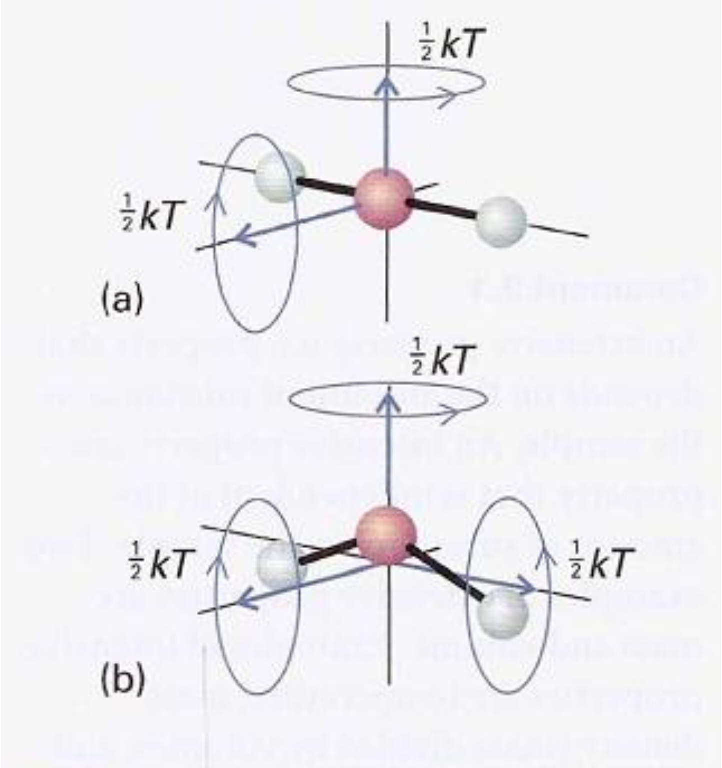
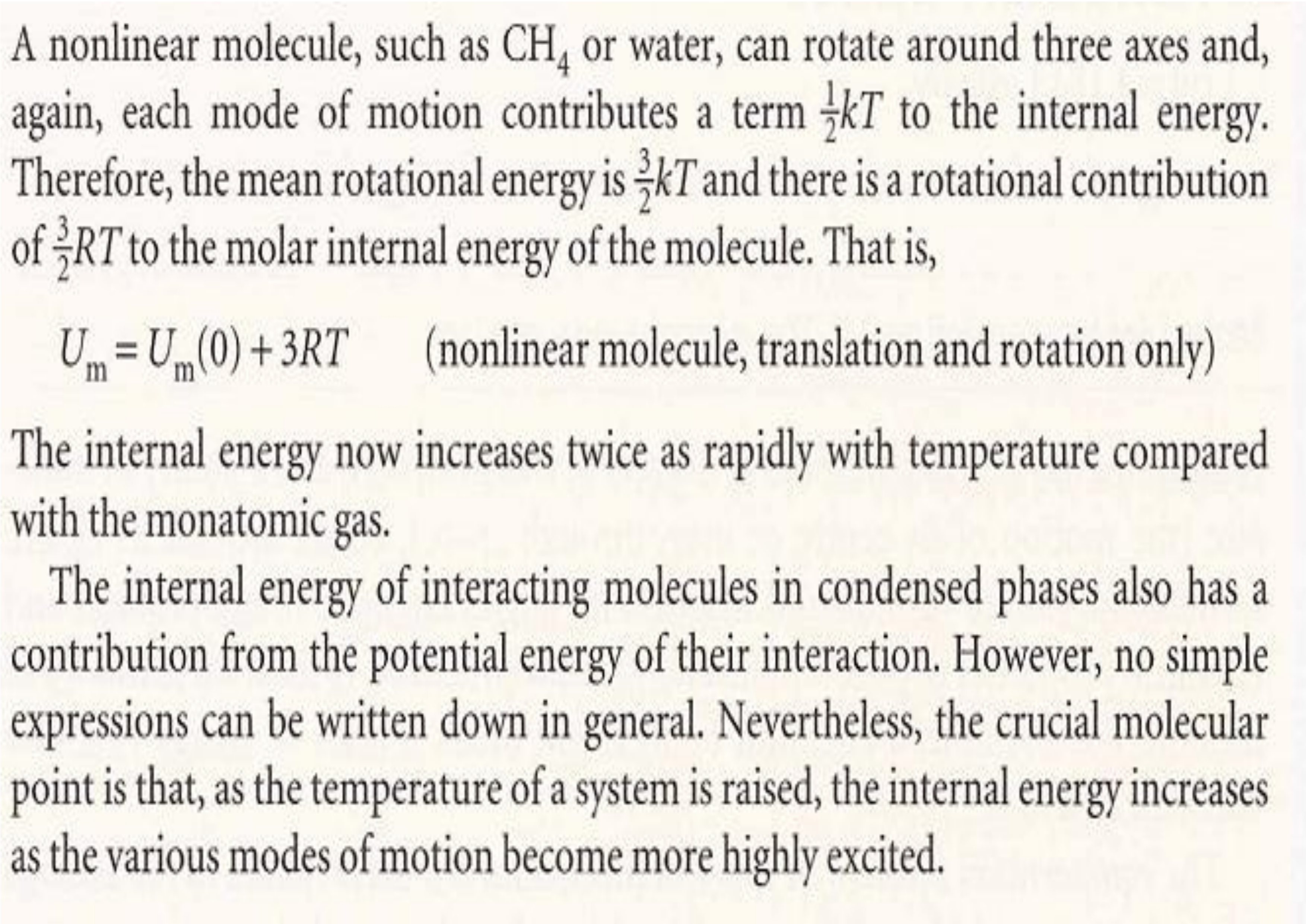


Fig. 2.5 The rotational modes of molecules and the corresponding average energies at a temperature T. (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

$$U_m = U_m(0) + \tfrac{5}{2}RT \qquad \text{(linear molecule, translation and rotation only)}$$



A nonlinear molecule, such as CH_4 or water, can rotate around three axes and, again, each mode of motion contributes a term $\frac{1}{2}kT$ to the internal energy. Therefore, the mean rotational energy is $\frac{3}{2}kT$ and there is a rotational contribution of $\frac{3}{2}RT$ to the molar internal energy of the molecule. That is,

$$U_m = U_m(0) + 3RT \qquad \text{(nonlinear molecule, translation and rotation only)}$$

The internal energy now increases twice as rapidly with temperature compared with the monatomic gas.

The internal energy of interacting molecules in condensed phases also has a contribution from the potential energy of their interaction. However, no simple expressions can be written down in general. Nevertheless, the crucial molecular point is that, as the temperature of a system is raised, the internal energy increases as the various modes of motion become more highly excited.

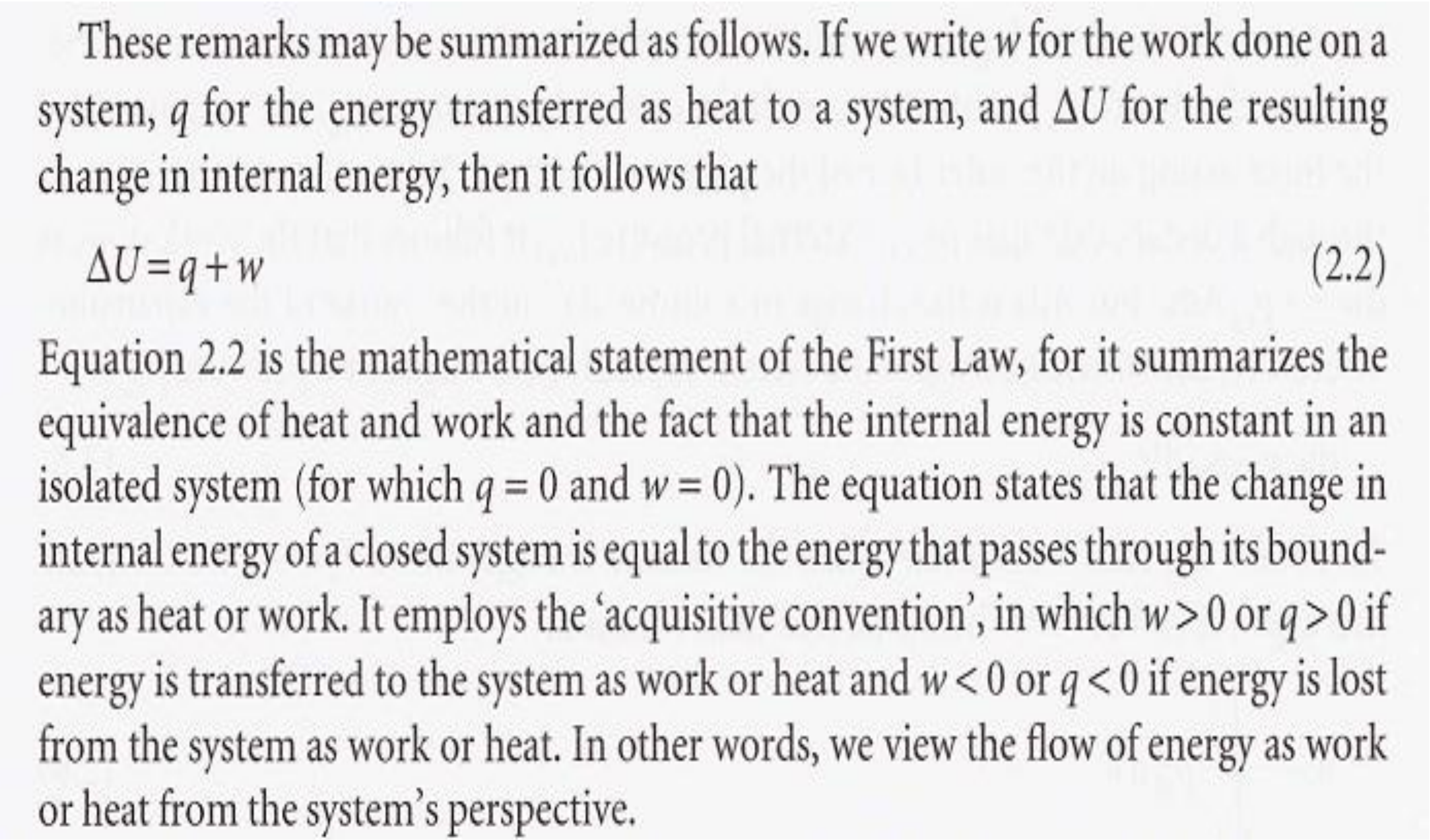
It has been found experimentally that **the internal energy of a system** may **be changed either by doing work on the system or by heating it**.

Whereas we may know how the energy transfer has occurred (because we can see if a weight has been raised or lowered in the surroundings, indicating transfer of energy by doing work, or **if ice isolated from its surroundings, then no change in internal energy takes place.**

This summary of observations is now known as the First Law **of thermodynamics and** expressed as follows:

The internal energy of an isolated system is constant.

- We cannot use a system to do work, leave it isolated for a month, and then come back expecting to find it restored to its original state and ready to do the same work again. The evidence for this property is that no 'perpetual motion machine' (**a machine that does work without consuming fuel or some other source of energy)** has ever been built.



These remarks may be summarized as follows. If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that

$$\Delta U = q + w \tag{2.2}$$

Equation 2.2 is the mathematical statement of the First Law, for it summarizes the equivalence of heat and work and the fact that the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$). The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work. It employs the 'acquisitive convention', in which $w > 0$ or $q > 0$ if energy is transferred to the system as work or heat and $w < 0$ or $q < 0$ if energy is lost from the system as work or heat. In other words, we view the flow of energy as work or heat from the system's perspective.

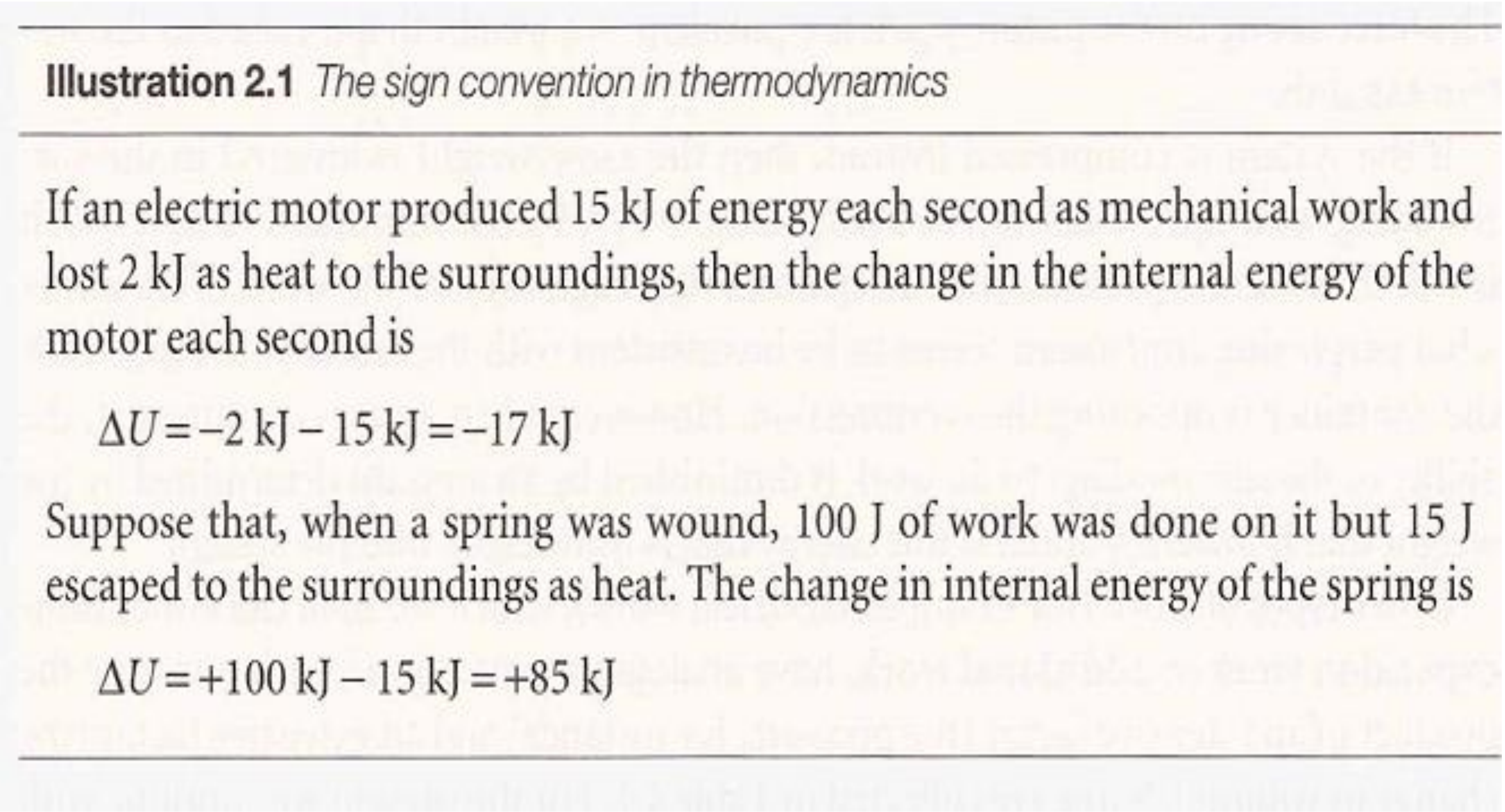


Illustration 2.1 *The sign convention in thermodynamics*

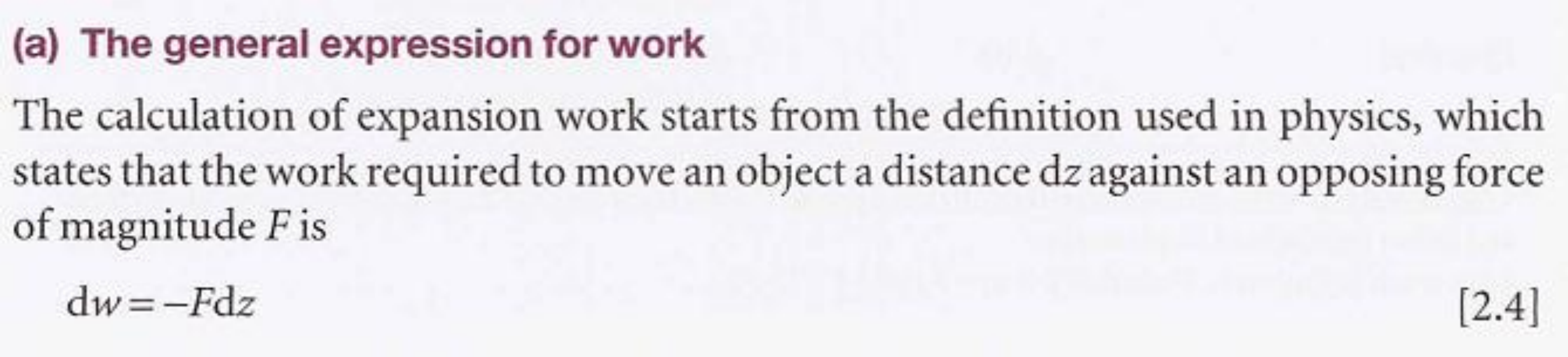
If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2\text{ kJ} - 15\text{ kJ} = -17\text{ kJ}$$

Suppose that, when a spring was wound, 100 J of work was done on it but 15 J escaped to the surroundings as heat. The change in internal energy of the spring is

$$\Delta U = +100\text{ kJ} - 15\text{ kJ} = +85\text{ kJ}$$

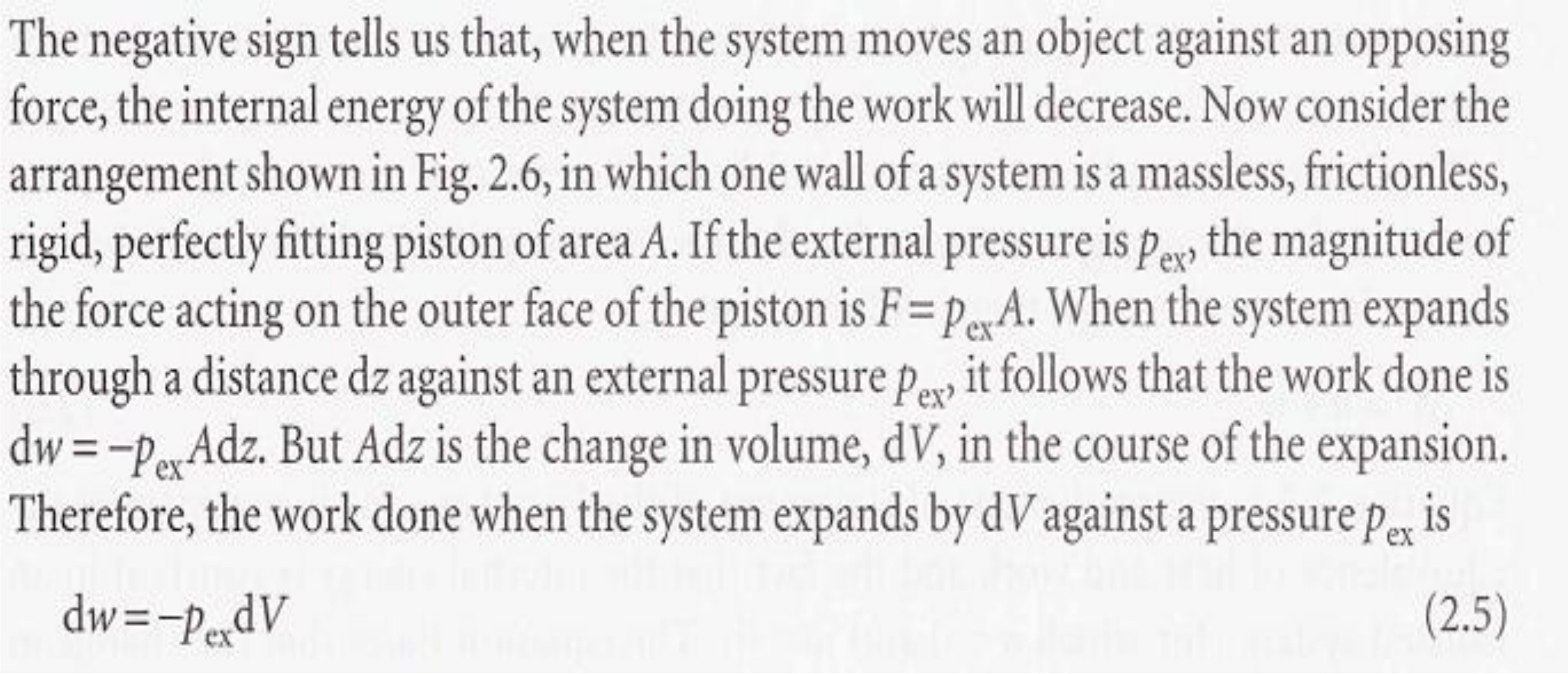
- **التعبير الرياضى العام للشغل**



(a) The general expression for work

The calculation of expansion work starts from the definition used in physics, which states that the work required to move an object a distance dz against an opposing force of magnitude *F* is

$$\mathrm{d}w = -F\mathrm{d}z \qquad [2.4]$$



The negative sign tells us that, when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease. Now consider the arrangement shown in Fig. 2.6, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area *A*. If the external pressure is p_{ex}, the magnitude of the force acting on the outer face of the piston is $F = p_{ex}A$. When the system expands through a distance dz against an external pressure p_{ex}, it follows that the work done is $\mathrm{d}w = -p_{ex}A\mathrm{d}z$. But $A\mathrm{d}z$ is the change in volume, $\mathrm{d}V$, in the course of the expansion. Therefore, the work done when the system expands by $\mathrm{d}V$ against a pressure p_{ex} is

$$\mathrm{d}w = -p_{ex}\mathrm{d}V \qquad (2.5)$$

To obtain the total work done when the volume changes from V_i *to* V_f *we integrate this expression between the initial and final volumes:*

The force acting on the piston, $P_{ex}A$*, is equivalent to a weight that is raised as the system expands.*

If the system is compressed instead, then the same weight is lowered in the sur-

$$w = -\int_{V_i}^{V_f} p_{ex}\mathrm{d}V \quad 00000000000\ (2.6)$$

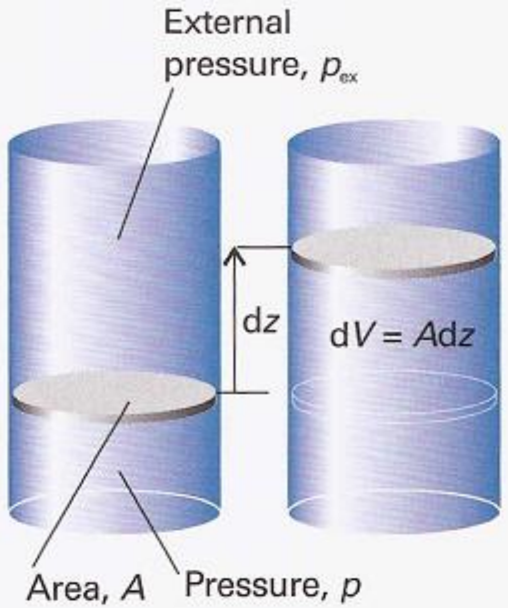


Fig. 2.6 When a piston of area A moves out through a distance $\mathrm{d}z$, it sweeps out a volume $\mathrm{d}V = A\mathrm{d}z$. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.

التوسع الحر

(b) Free expansion

By free expansion we mean expansion against zero opposing force. It occurs when

P_{ex}=O. According to eqn 2.5, ***dw = 0*** *for each stage of the expansion. Hence overall:*

$$\text{Free expansion:} \quad w = 0 \qquad (2.7)$$

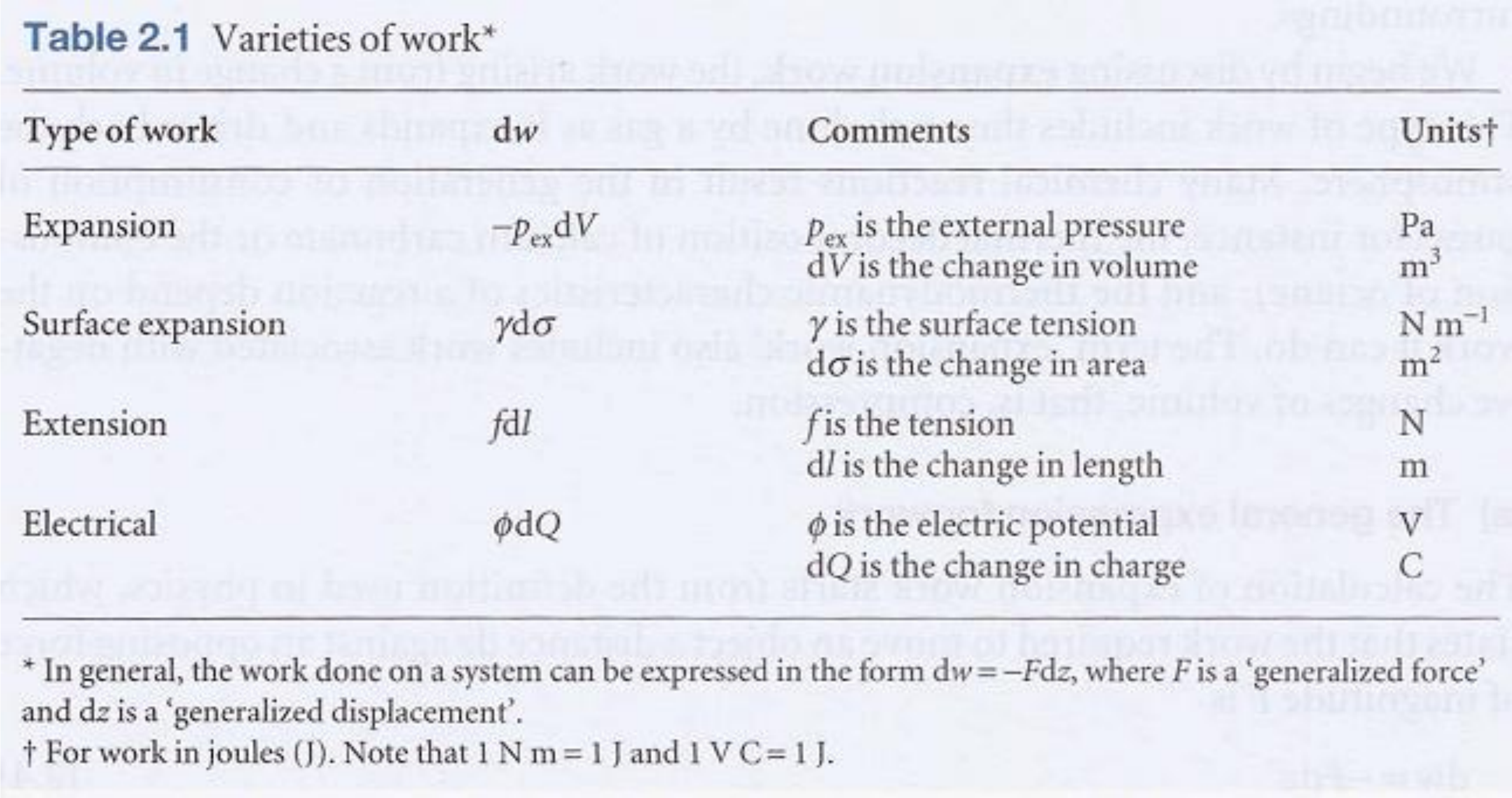


Table 2.1 Varieties of work*

Type of work	dw	Comments	Units†
Expansion	$-p_{ex}dV$	p_{ex} is the external pressure dV is the change in volume	Pa m^3
Surface expansion	$\gamma d\sigma$	γ is the surface tension $d\sigma$ is the change in area	$N\,m^{-1}$ m^2
Extension	$f dl$	f is the tension dl is the change in length	N m
Electrical	ϕdQ	ϕ is the electric potential dQ is the change in charge	V C

* In general, the work done on a system can be expressed in the form $dw = -Fdz$, where F is a 'generalized force' and dz is a 'generalized displacement'.

† For work in joules (J). Note that 1 N m = 1 J and 1 V C = 1 J.

(c) Expansion against constant pressure

Now suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion. A chemical example of this condition is the expansion of a gas formed in a chemical reaction. We can evaluate eqn 2.6 by taking the constant p_{ex} outside the integral:

$$w = -p_{ex}\int_{V_i}^{V_f} dV = -p_{ex}(V_f - V_i)$$

Therefore, if we write the change in volume as $\Delta V = V_f - V_i$,

$$w = -p_{ex}\Delta V \qquad (2.8)$$

This result is illustrated graphically in Fig. 2.7, which makes use of the fact that an integral can be interpreted as an area. The magnitude of w, denoted $|w|$, is equal to the area beneath the horizontal line at $p = p_{ex}$ lying between the initial and final volumes. A p,V-graph used to compute expansion work is called an **indicator diagram**; James Watt first used one to indicate aspects of the operation of his steam engine.

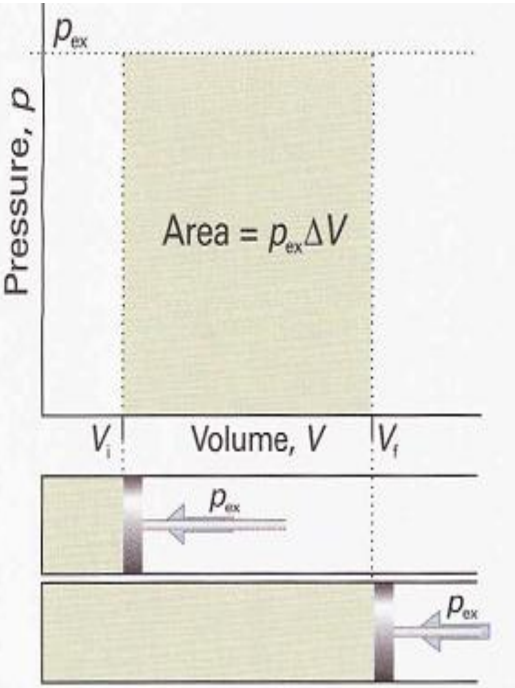


Fig. 2.7 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

(d) Reversible expansion

Lecture 8

(d) Reversible expansion

(d) Reversible expansion:

A reversible change in thermodynamics is a change that can be reversed by an **infinitesimal modification** of a variable.

Suppose a gas is confined by a piston and that the external pressure, *P_{ex}'is set equal to the pressure, p, of the confined gas. Such a system is in mechanical equilibrium with its surroundings (as illustrated in Section 1.1)* ***because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions.*** *If the external pressure is reduced infinitesimally, then the gas expands slightly. If the external pressure is increased infinitesimally, then the gas contracts slightly.* ***In either case the change is reversible in the thermodynamic sense****. If, on the other hand, the external pressure differs measurably from the internal pressure, then changing p., infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process. Such a system is not in mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible.*

To achieve reversible expansion **we set** ***P_{ex} equal*** *to P at each stage of the expansion.*

To achieve reversible expansion we set ***P_{ex} equal to P*** *at each stage of the expansion. In practice, this equalization could be achieved by gradually removing weights from the piston so that the downward force due to the weights always matched the changing upward force due to the pressure of the gas. When we set Pex = p, eqn 2.5 becomes*

$$dW=-P_{ex}\,dV=-pdV \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.9)_{rev}$$

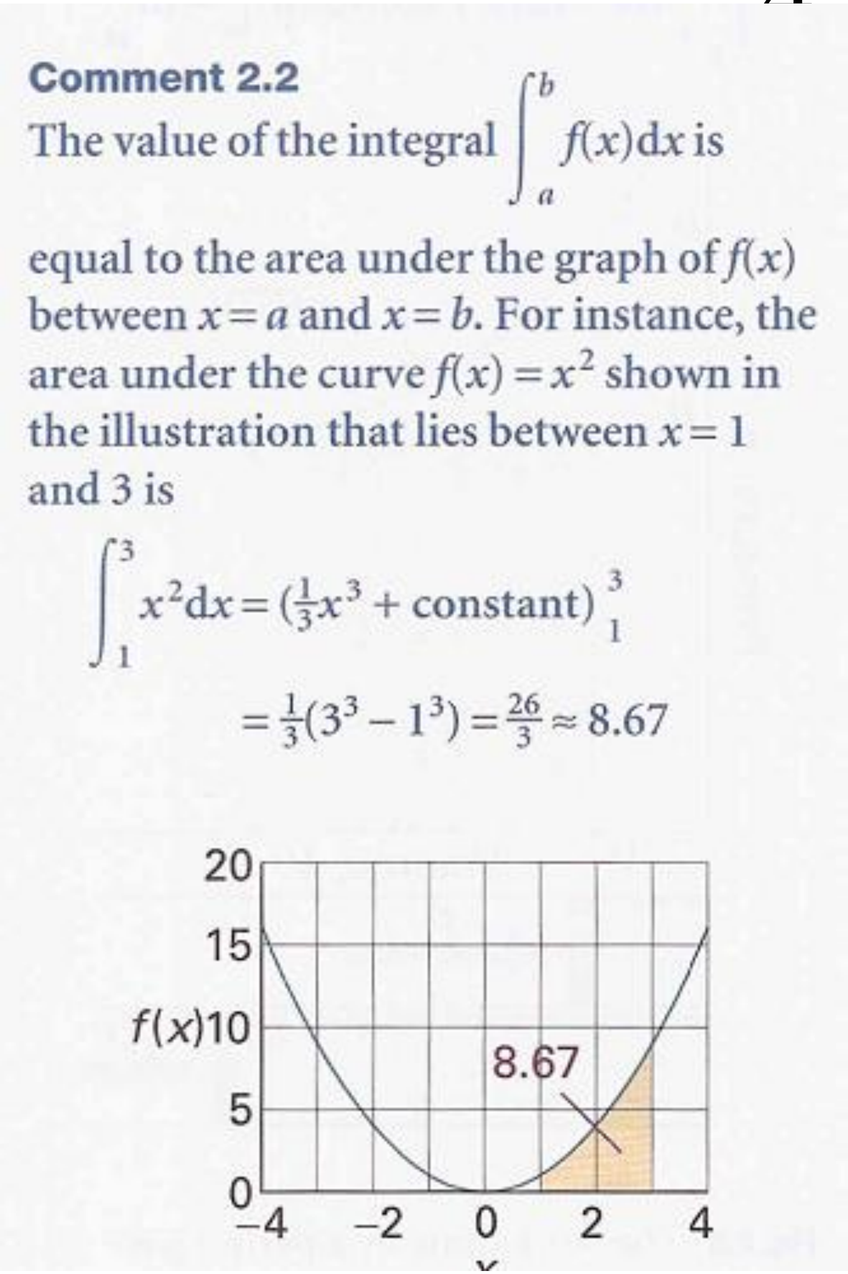
(Equations valid only for reversible processes are labelled with a subscript rev.)

Although the pressure inside the system appears in this expression for the work, it does so only because P_{ex} *has been set equal to P to ensure reversibility.* The total work of reversible expansion *is therefore*

$$w=-\int_{V_i}^{V_f} p\,dV \qquad (2.10)_{rev}$$

We can evaluate the integral once we know how the pressure of the confined gas depends on its volume. Equation 2.10 is the link with the material covered in Chapter 1 for, if we know the equation of state of the gas, then we can express *p in terms of V and evaluate the integral.*

- توضيح رياضي:



Comment 2.2

The value of the integral $\int_a^b f(x)\mathrm{d}x$ is equal to the area under the graph of $f(x)$ between $x = a$ and $x = b$. For instance, the area under the curve $f(x) = x^2$ shown in the illustration that lies between $x = 1$ and 3 is

$$\int_1^3 x^2\mathrm{d}x = \left(\tfrac{1}{3}x^3 + \text{constant}\right)_1^3$$

$$= \tfrac{1}{3}(3^3 - 1^3) = \tfrac{26}{3} \approx 8.67$$

(e) Isothermal reversible expansion التوسع المعزول حراريا

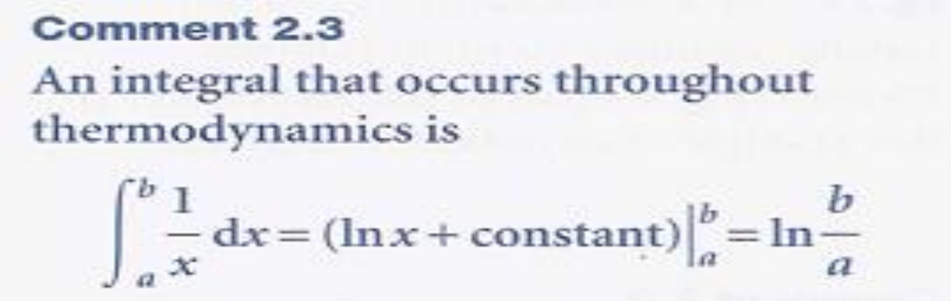
Consider the isothermal, reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with its surroundings (which may be a constant-temperature bath). **Because the equation of state is *$pV = nRT$, we know that at each stage $p = nRT/V$, with V the volume at that stage of the expansion.*** *The temperature T is constant in an isothermal expansion, so (together with n and R)*

it may be taken outside the integral. **It follows that the work of reversible isothermal expansion of a perfect gas from *V_i to V_f at a temperature T is***

$$w = -nRT\int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{\mathrm{d}V}{V} = -nRT\ln\frac{V_\mathrm{f}}{V_\mathrm{i}} \qquad (2.11)^{\circ}_{\mathrm{rev}}$$

We can express the result of the calculation as an indicator diagram, for the magnitude of the work done is equal to the area under the isotherm *P = nRTIV (Fig. 2.8). Superimposed on the diagram is the rectangular area obtained for irreversible expansion against constant external pressure fixed at the same final value as that reached in the reversible expansion. More work is obtained when the expansion is reversible (the area is greater) because matching the external pressure to the internal pressure at each stage of the process ensures that none of the system's pushing power is wasted. We cannot obtain more work than for the reversible process because increasing the external pressure even infinitesimally at any stage results in compression. We may infer from this discussion that, because some pushing power is wasted when* $p > P_{ex}$' *the maximum work available from a system operating between specified initial and final states and passing along a specified path is obtained when the change takes place reversibly.*

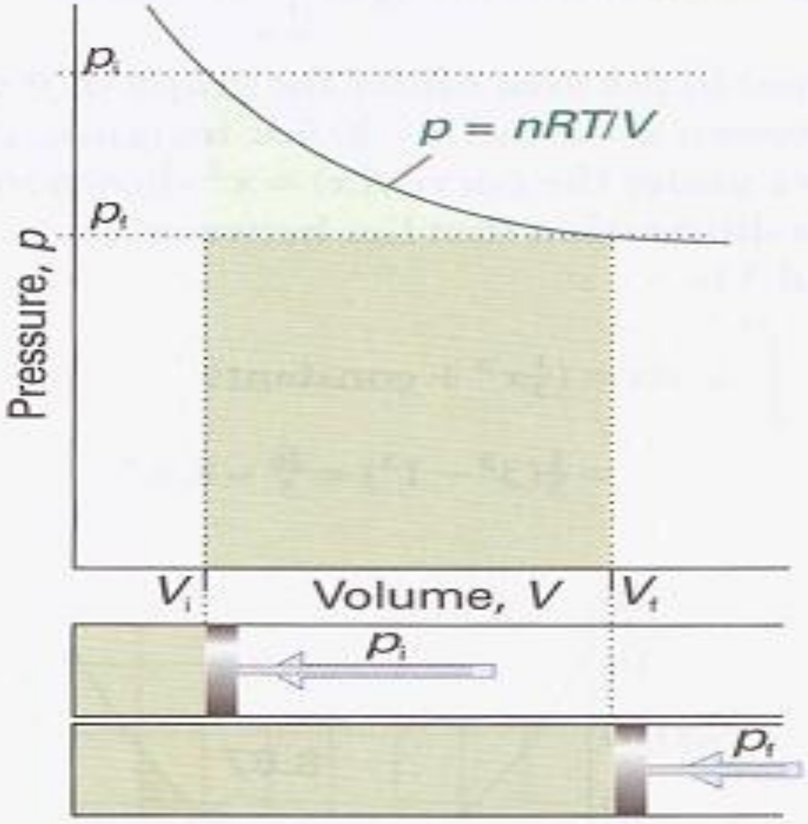
We have introduced the connection between reversibility and maximum work for the special case of a perfect gas undergoing expansion. Later (in Section 3.5) we shall see that it applies to all substances and to all kinds of work.



Comment 2.3

An integral that occurs throughout thermodynamics is

$$\int_a^b \frac{1}{x}\,dx = (\ln x + \text{constant})\Big|_a^b = \ln\frac{b}{a}$$



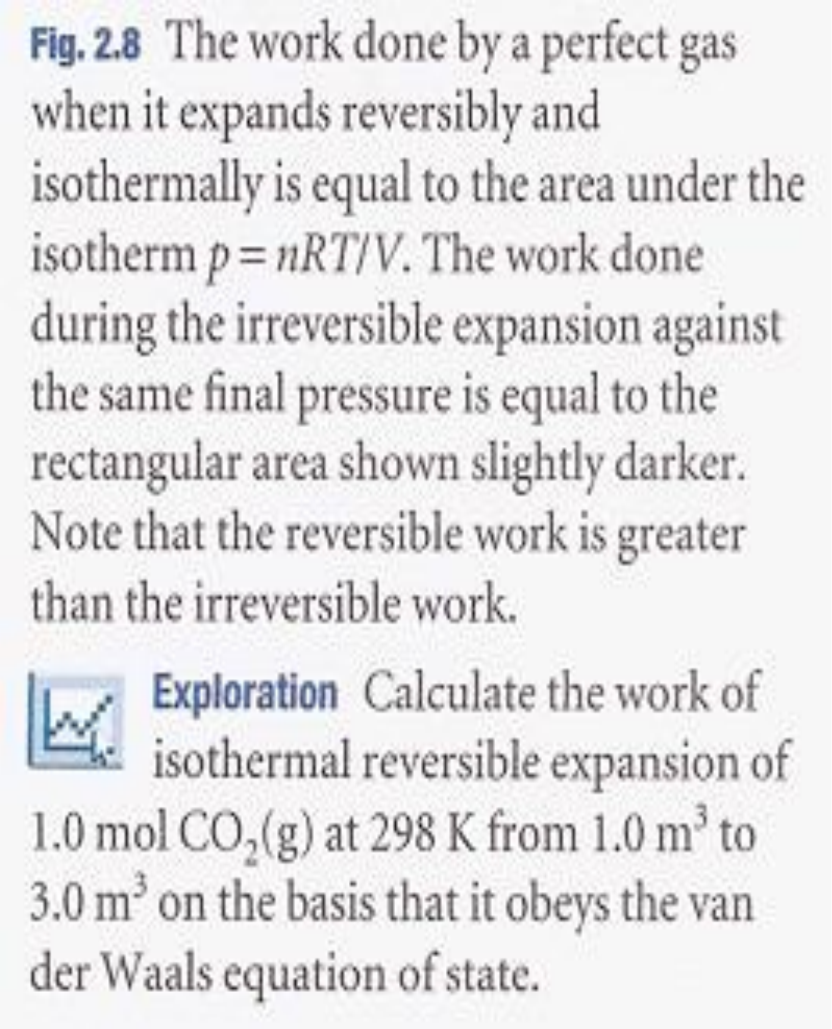


Fig. 2.8 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.

Exploration Calculate the work of isothermal reversible expansion of 1.0 mol $CO_2(g)$ at 298 K from 1.0 m^3 to 3.0 m^3 on the basis that it obeys the van der Waals equation of state.

Example 2.1 ***Calculating the work of gas production***

Calculate the work done when 50 g of iron reacts with hydrochloric acid in

(a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

Method

We need to judge the magnitude of the volume change and then to decide how the process occurs. If there is no change in volume, there is no expansion work however the process takes place. If the system expands against a constant external pressure, the work can be *calculated from eqn 2.8. A general feature of processes in which a condensed phase changes into a gas is that the volume of the former may usually be neglected relative to that of the gas it forms.*

Answer

In (a) the volume cannot change, so no expansion work is done and w = O.

In (b) the gas drives back the atmosphere and therefore $W = -P_{ex}\Delta V$. *We can* neglect the initial volume because the final volume (after the production of gas) is so much larger and $\Delta V = V_f - V_i \approx V_f = nRT/P_{ex}$, *where n is the amount of H, produced.*

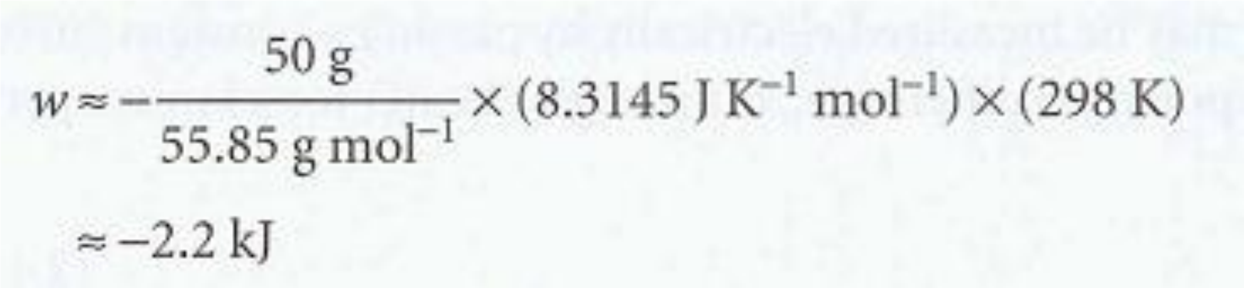
Therefore,

$$w = -p_{ex}\Delta V \approx -p_{ex} \times \frac{nRT}{p_{ex}} = -nRT$$

Because the reaction is :

$Fe(s) + 2\,HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$,

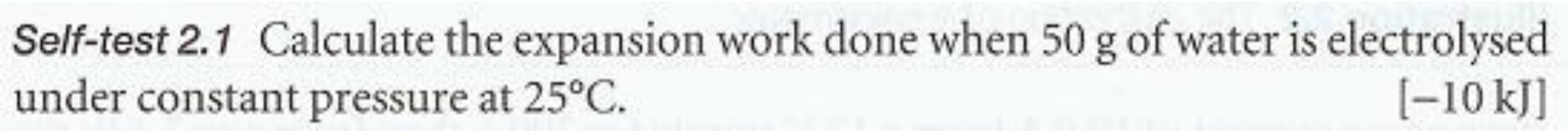
we know that 1mol H_2 is generated when 1 mol Fe is consumed, and *n can be taken as the amount of Fe atoms that react. Because the molar mass of Fe is 55.85 g mol $^{-1}$, it follows that:*



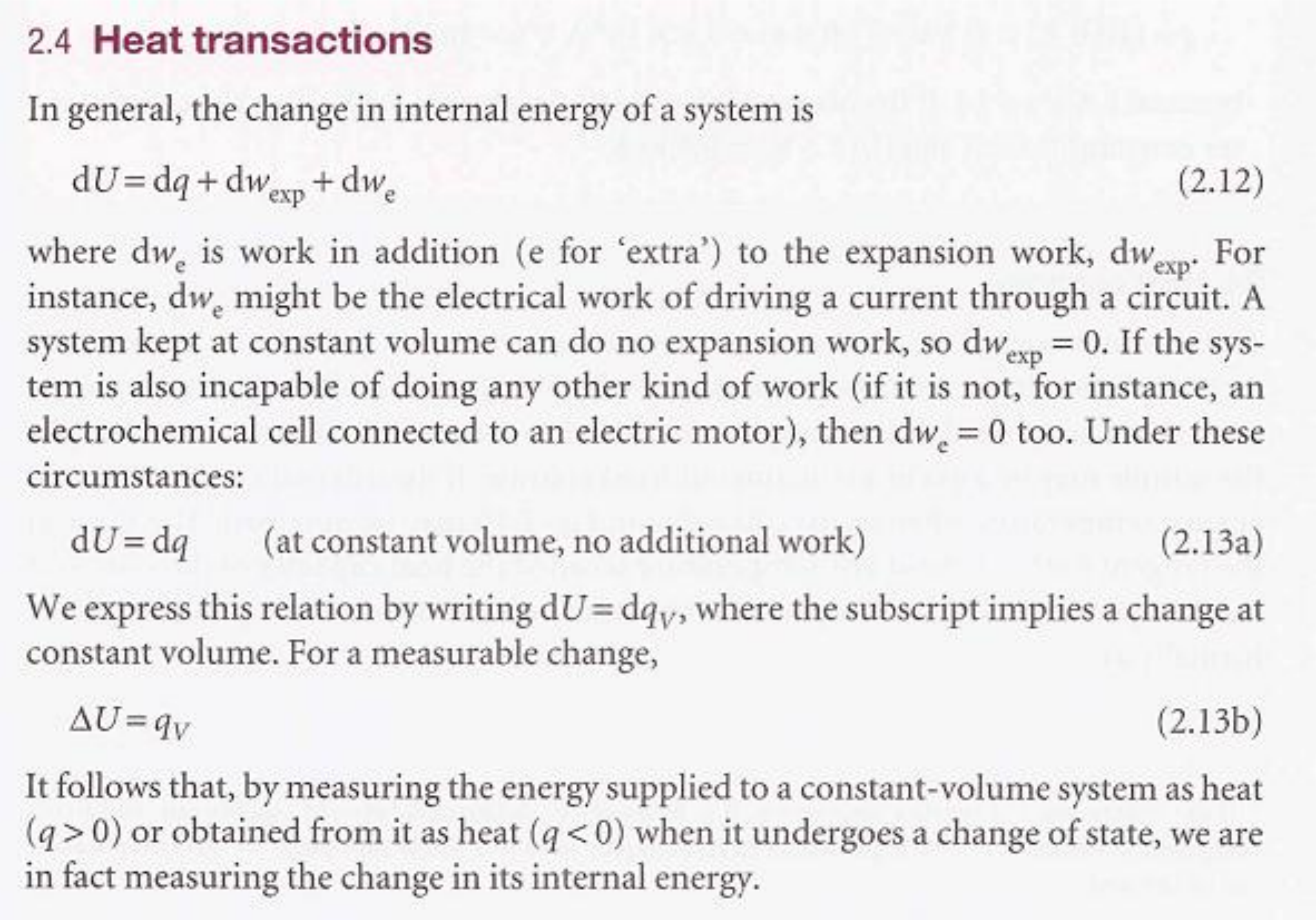
$$w \approx -\frac{50\ \text{g}}{55.85\ \text{g mol}^{-1}} \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})$$
$$\approx -2.2\ \text{kJ}$$

The system (the reaction mixture) does 2.2 kJ of work driving back the atmosphere.

Note that (for this perfect gas system) the magnitude of the external pressure does not affect the final result: the lower the pressure, the larger the volume occupied by the gas, so the effects cancel.



Self-test 2.1 Calculate the expansion work done when 50 g of water is electrolysed under constant pressure at 25°C. [−10 kJ]



2.4 Heat transactions

In general, the change in internal energy of a system is

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w_{\mathrm{exp}} + \mathrm{d}w_{\mathrm{e}} \qquad (2.12)$$

where $\mathrm{d}w_{\mathrm{e}}$ is work in addition (e for 'extra') to the expansion work, $\mathrm{d}w_{\mathrm{exp}}$. For instance, $\mathrm{d}w_{\mathrm{e}}$ might be the electrical work of driving a current through a circuit. A system kept at constant volume can do no expansion work, so $\mathrm{d}w_{\mathrm{exp}} = 0$. If the system is also incapable of doing any other kind of work (if it is not, for instance, an electrochemical cell connected to an electric motor), then $\mathrm{d}w_{\mathrm{e}} = 0$ too. Under these circumstances:

$$\mathrm{d}U = \mathrm{d}q \qquad \text{(at constant volume, no additional work)} \qquad (2.13\mathrm{a})$$

We express this relation by writing $\mathrm{d}U = \mathrm{d}q_V$, where the subscript implies a change at constant volume. For a measurable change,

$$\Delta U = q_V \qquad (2.13\mathrm{b})$$

It follows that, by measuring the energy supplied to a constant-volume system as heat ($q > 0$) or obtained from it as heat ($q < 0$) when it undergoes a change of state, we are in fact measuring the change in its internal energy.

11

Lecture 9

Heat Transactions

تحولات الحرارة

2.4 Heat transactions

In general, the change in internal energy of a system is:

$dU = dq + dw_{exp} + dw_{e}$ ………………………………………….(2.12)

where dw_e is work in addition (e for 'extra') to the expansion work, dw_{exp}' For instance, dw, might be the electrical work of driving a current through a circuit. A system kept at constant volume can do no expansion work, so $dw_{exp} = 0$. If the system is also incapable of doing any other kind of work (if it is not, for instance, electrochemical cell connected to an electric motor), then $dW_e = 0$ too. Under these circumstances:

$dU = dq$ (at constant volume, no additional work) *--------- (2.13a)*

We express this relation by writing

$dU = dq_v$ *where the subscript implies a change at* constant volume. For a measurable change:

$\Delta U = q_v$ ………………………………………………………………..(2.13b)

It follows that, by measuring the energy supplied to a constant-volume system as heat *($q > 0$) or obtained from it as heat ($q < 0$) when it undergoes a change of state, we are in fact measuring the change in its internal energy.*

(a) Calorimetry

Calorimetry is the study of heat transfer during physical and chemical processes.

A calorimeter is a device for measuring energy transferred as heat. The most common device for measuring *ΔU is an adiabatic bomb calorimeter (Fig. 2.9).*

The process we wish to study-which may be a chemical reaction-is initiated inside a constant volume container, the 'bomb'. The bomb is immersed in a stirred water bath, and the whole device is the calorimeter. The calorimeter is also immersed in an outer water bath. The water in the calorimeter and of the outer bath are both monitored and adjusted to the same temperature. This arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the calorimeter is adiabatic.

$$q = C\Delta T \quad \text{.......................} \quad (2.14a)$$

The calorimeter constant C *may be measured electrically by passing a constant current, I, from a source of known potential difference, V, through a heater for a known period of time, t, for then*

$$q = IVt \quad \text{.................................} \quad (2.14b)$$

$$q = I\mathcal{V}t$$

Alternatively, ***C may be determined by burning a known mass of substance*** *(benzoic* acid is often used) that has a known heat output. With C known, it is simple to interpret an observed temperature rise as a release of heat.

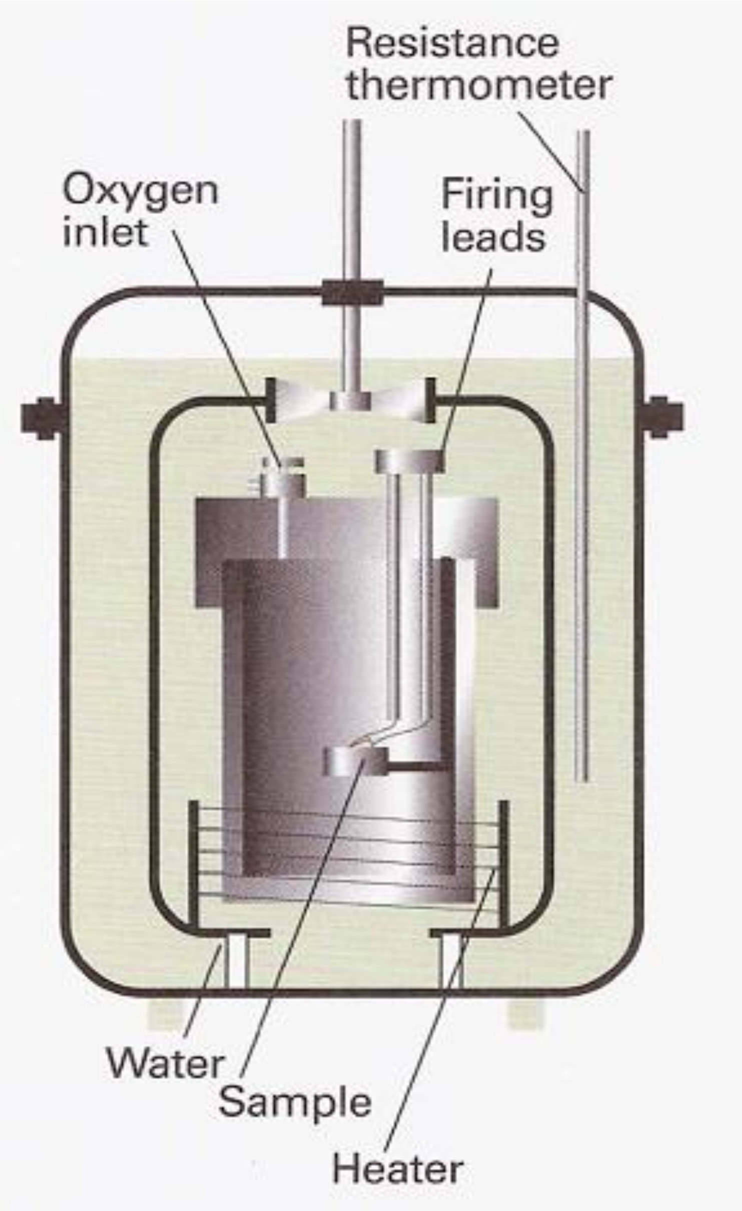
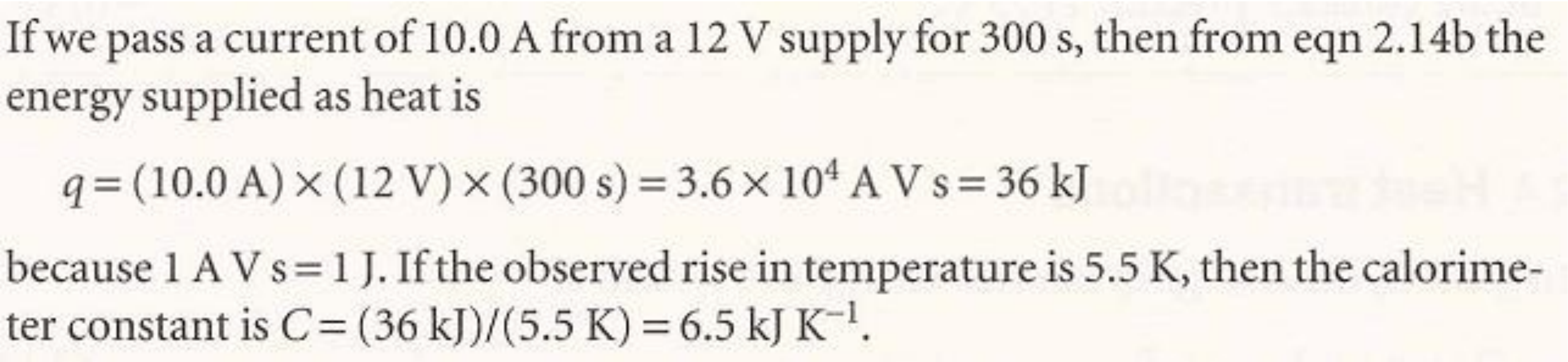


Fig. 2.9 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

Illustration 2.2

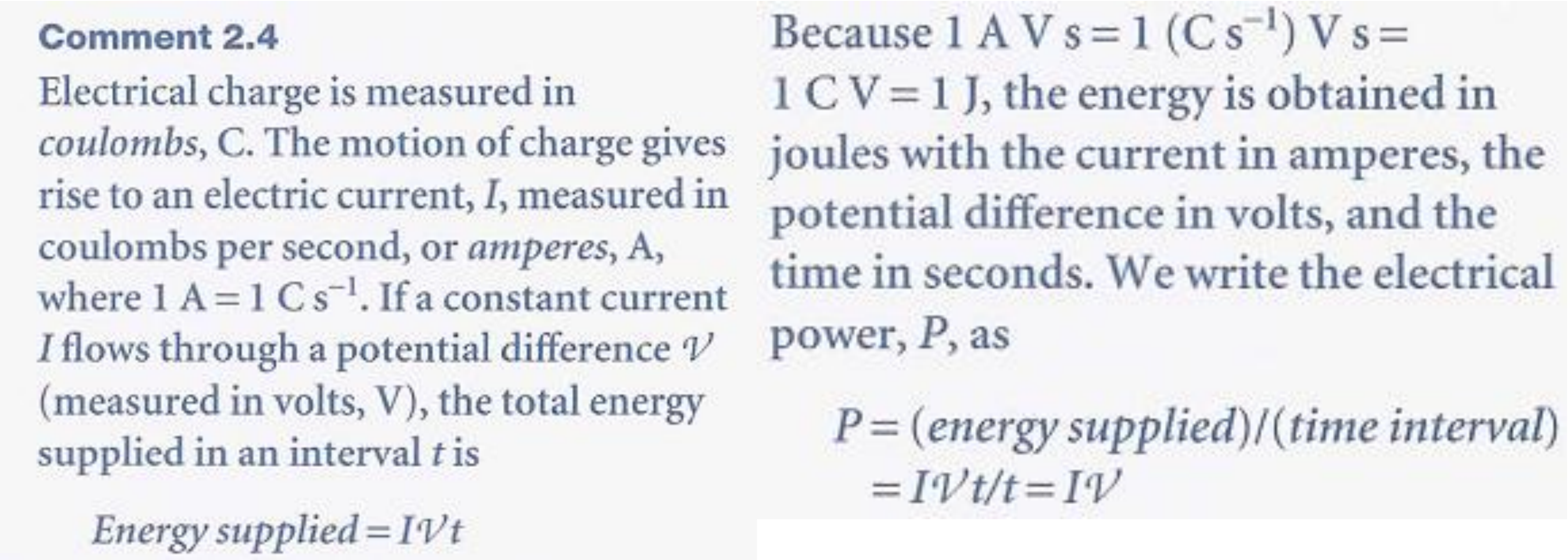
The calibration of a calorimeter معايرة المسعر



If we pass a current of 10.0 A from a 12 V supply for 300 s, then from eqn 2.14b the energy supplied as heat is

$$q = (10.0\ \mathrm{A}) \times (12\ \mathrm{V}) \times (300\ \mathrm{s}) = 3.6 \times 10^4\ \mathrm{A\ V\ s} = 36\ \mathrm{kJ}$$

because $1\ \mathrm{A\ V\ s} = 1\ \mathrm{J}$. If the observed rise in temperature is 5.5 K, then the calorimeter constant is $C = (36\ \mathrm{kJ})/(5.5\ \mathrm{K}) = 6.5\ \mathrm{kJ\ K^{-1}}$.



Comment 2.4

Electrical charge is measured in *coulombs*, C. The motion of charge gives rise to an electric current, I, measured in coulombs per second, or *amperes*, A, where $1\ \mathrm{A} = 1\ \mathrm{C\ s^{-1}}$. If a constant current I flows through a potential difference $\mathcal{V}$ (measured in volts, V), the total energy supplied in an interval t is

$$\textit{Energy supplied} = I\mathcal{V}t$$

Because $1\ \mathrm{A\ V\ s} = 1\ (\mathrm{C\ s^{-1}})\ \mathrm{V\ s} = 1\ \mathrm{C\ V} = 1\ \mathrm{J}$, the energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds. We write the electrical power, P, as

$$P = (\textit{energy supplied})/(\textit{time interval}) = I\mathcal{V}t/t = I\mathcal{V}$$

(b) Heat capacity

The internal energy of a substance increases when its temperature is raised. **The increase depends on the conditions under which the heating takes place and for the present we suppose that the sample is confined to a constant volume**. For example, the sample may be a gas in a container of fixed volume. If the internal energy is plotted against temperature, then a curve like that in Fig. 2.10 may be obtained. The slope of the tangent to the curve at any temperature is called the heat capacity of the system at that temperature. The heat capacity at constant volume is denoted C_V *and is defined formally as*

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad [2.15]$$

In this case, the internal energy varies with the temperature and the volume of the sample, but we are interested only in its variation with the temperature, the volume being held constant (Fig. 2.1l).

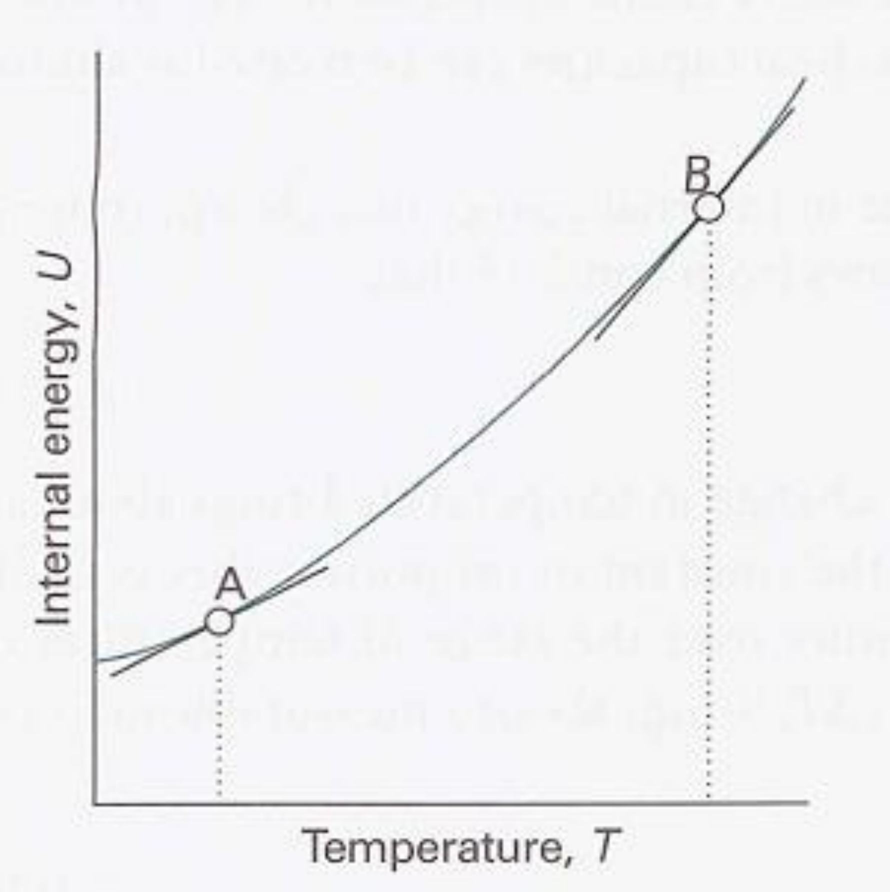
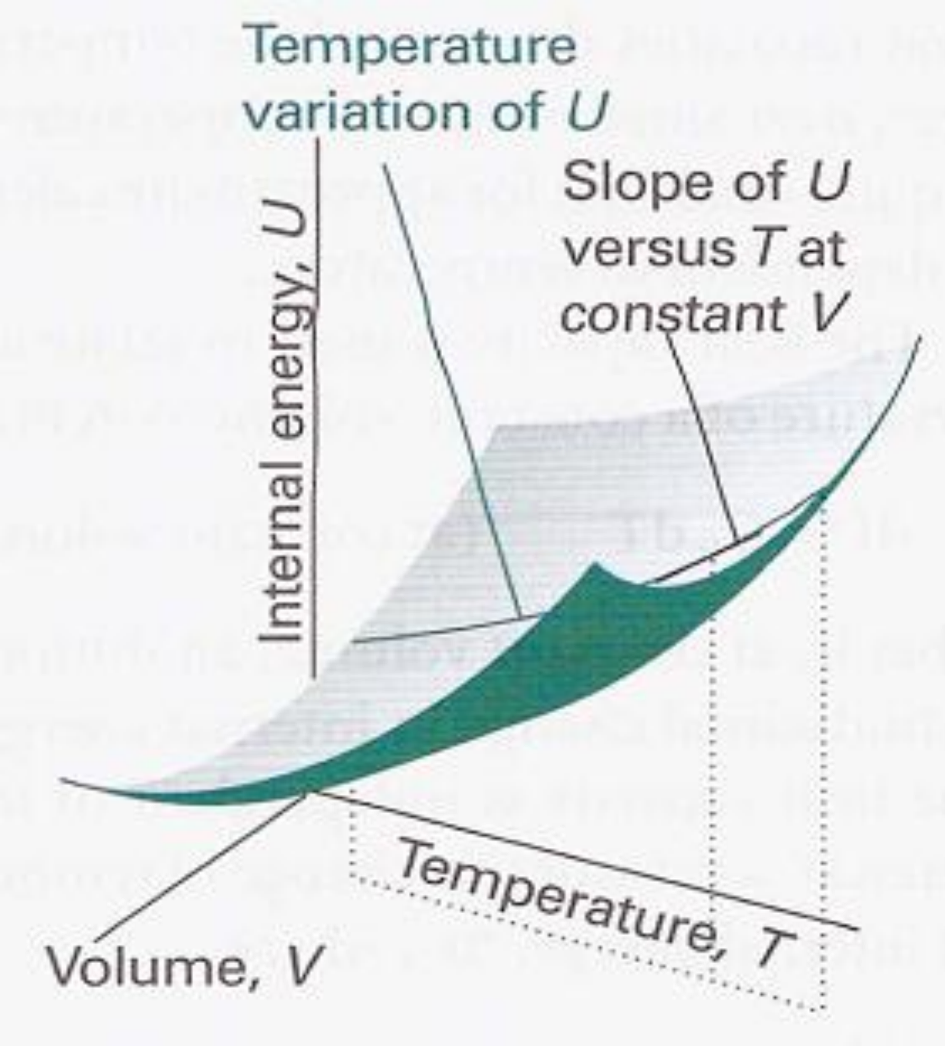


Fig. 2.10 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.



- تتغير الطاقة الداخلية للنظام بتغير الحجم و درجة الحرارة و كما موضح في السطح البياني. و قد وضحنا التغير في الطاقة الداخلية و لحجم ثابت قد أُشير له بالخط المنحني المرسوم بشكل موازي لمحور الحرارةT. و الميل لهذا المنحنى عند أي نقطة عليه سيمثل المشتقة الجزئية للطاقة الداخلية:

$$(\partial U/ \partial T)_v$$

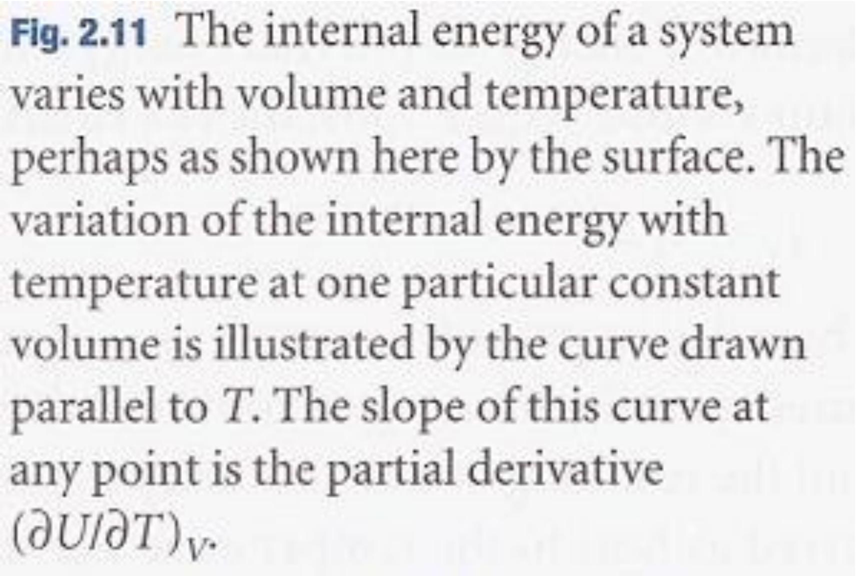
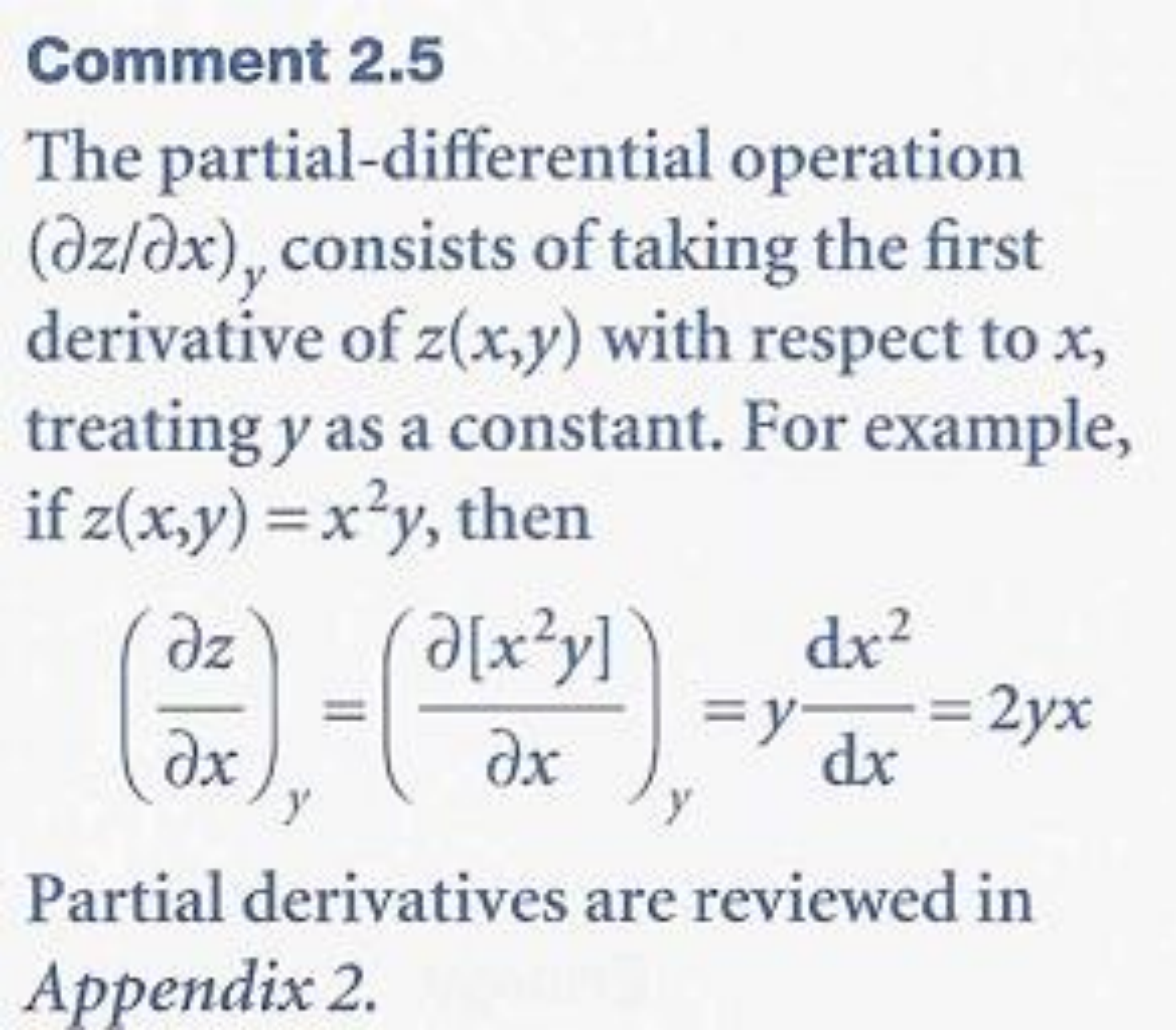


Fig. 2.11 The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to T. The slope of this curve at any point is the partial derivative $(\partial U/\partial T)_V$.



Comment 2.5

The partial-differential operation $(\partial z/\partial x)_y$ consists of taking the first derivative of $z(x,y)$ with respect to x, treating y as a constant. For example, if $z(x,y) = x^2y$, then

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial [x^2y]}{\partial x}\right)_y = y\frac{\mathrm{d}x^2}{\mathrm{d}x} = 2yx$$

Partial derivatives are reviewed in *Appendix 2.*

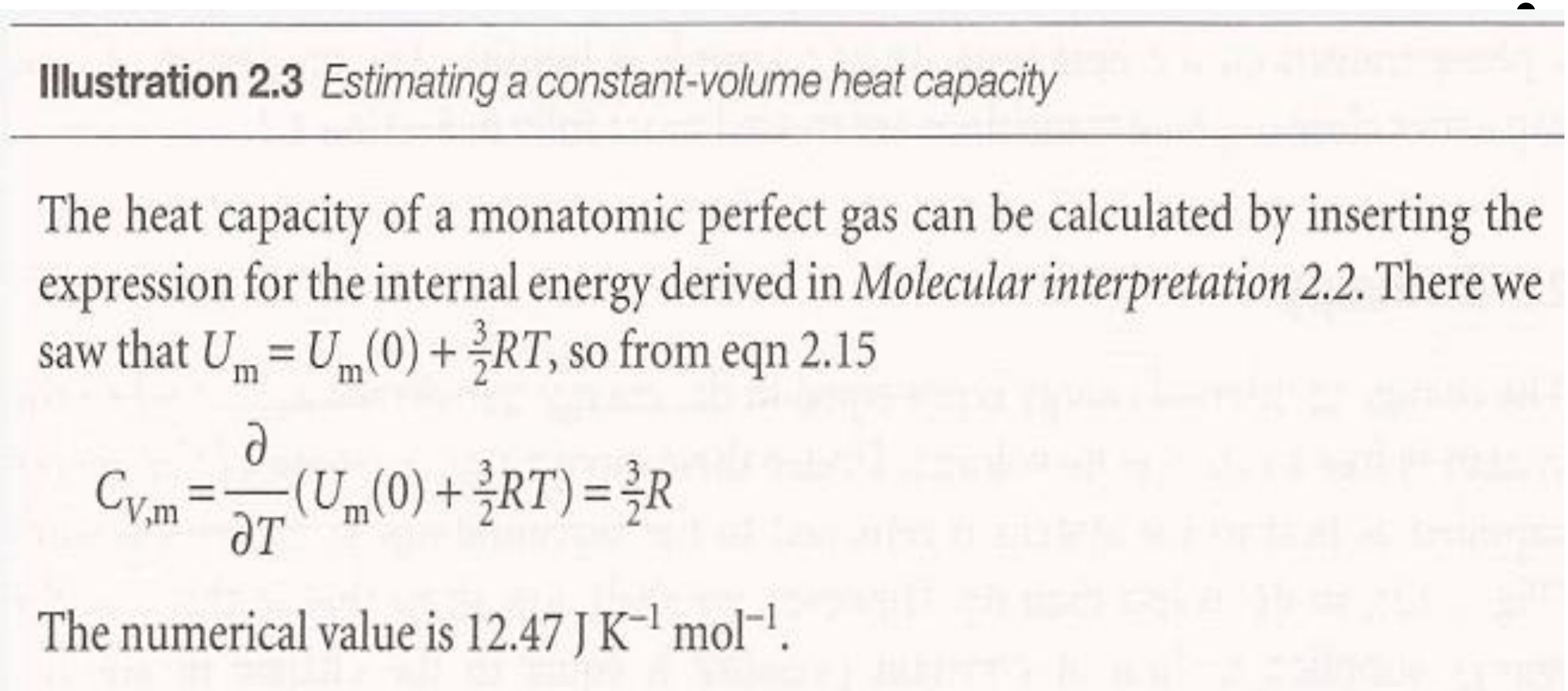


Illustration 2.3 *Estimating a constant-volume heat capacity*

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy derived in *Molecular interpretation 2.2*. There we saw that $U_m = U_m(0) + \frac{3}{2}RT$, so from eqn 2.15

$$C_{V,m} = \frac{\partial}{\partial T}(U_m(0) + \tfrac{3}{2}RT) = \tfrac{3}{2}R$$

The numerical value is 12.47 J K^{-1} mol^{-1}.

Heat capacities are extensive properties

السعات الحرارية تعتبر خصائص شاملة

: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature).

The molar heat capacity at constant volume, $C_{V,m} = C_V/n$, *is the heat capacity per mole of material, and* ***is an intensive property*** **خاصية مركزة**

(***all molar quantities are intensive***)*. Typical values of* $C_{V,m}$ *for polyatomic* gases are close to 25 J k^{-1} mol^{-1} . For certain applications it is useful to know the specific heat capacity (more informally, the 'specific heat') of a substance, which is the **heat capacity of the sample divided by the mass**, usually in grams:

$C_{V,s} = C_V/m$.

The specific heat capacity of water at room temperature is close to 4 J K^{-1} g^{-1}.

In general, **heat capacities** depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and **for approximate calculations heat capacities can be treated as almost independent of temperature.**

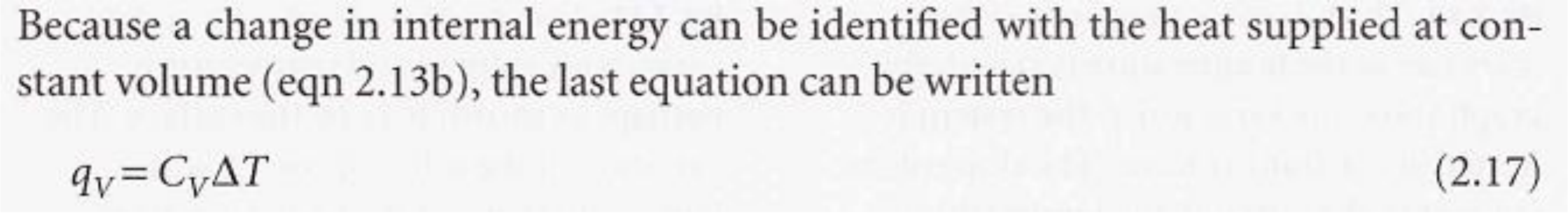
** **The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system.** It follows from eqn 2.15 that:

$$dU = C_V dT \qquad \text{(at constant volume)} \qquad (2.16a)$$

That is, at constant volume, an infinitesimal change in temperature brings about an infinitesimal change in internal energy, and the constant of proportionality is Cv. *If the heat capacity is independent of temperature over the range of temperatures of interest, a measurable change of temperature, ΔT, brings about a measurable increase in internal energy,*

ΔU, where

$$\Delta U = C_V \Delta T \qquad \text{(at constant volume)} \qquad (2.16b)$$



Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 2.13b), the last equation can be written

$$q_V = C_V \Delta T \qquad (2.17)$$

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of energy is transferred as heat to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the energy transferred as heat to the temperature rise it causes ($q_V/\Delta T$) is the constant-volume heat capacity of the sample.

A large heat capacity implies that, for a given quantity of energy transferred as heat, there will be only a small increase in temperature (the sample has a large capacity for heat). An infinite heat capacity implies that there will be no increase in temperature however much energy is supplied as heat. At a phase transition, such as at the boiling point of water, the temperature of a substance does not rise as energy is supplied as heat: the energy is used to drive the endothermic transition, in this case to vaporize the water, rather than to increase its temperature. Therefore, at the temperature of a phase transition, the heat capacity of a sample is infinite. The properties of heat capacities close to phase transitions are treated more fully in Section 4.7.

2.5 **Enthalpy**

Lecture 10

Enthalpy

2.5 **Enthalpy**

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work (Fig. 2.12),

so:

dU is less than *dq.*

However, we shall now show that in this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy.

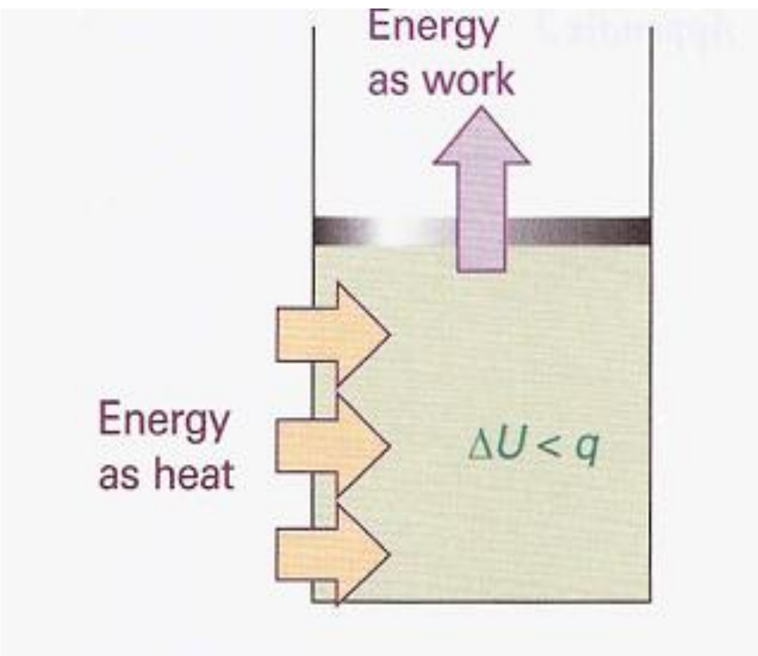


Fig. 2.12 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

(a) The definition of enthalpy

The enthalpy, ***H***, *is defined as:*

$H = U + pV$ *……………………………… [2.18]*

where ***p*** *is the pressure of the system and* ***V*** *is its volume.* ***Because U, p, and V are all state functions****,* ***the enthalpy is a state function too****.*

As is true of any state function, the change in enthalpy, ΔH, between any pair of initial and final states is independent of the path between them.

Although the definition of enthalpy may appear arbitrary, it has important implications for thermochemisty.

For instance, we show in the following *Justification that eqn 2.18 implies that the change in enthalpy is:*

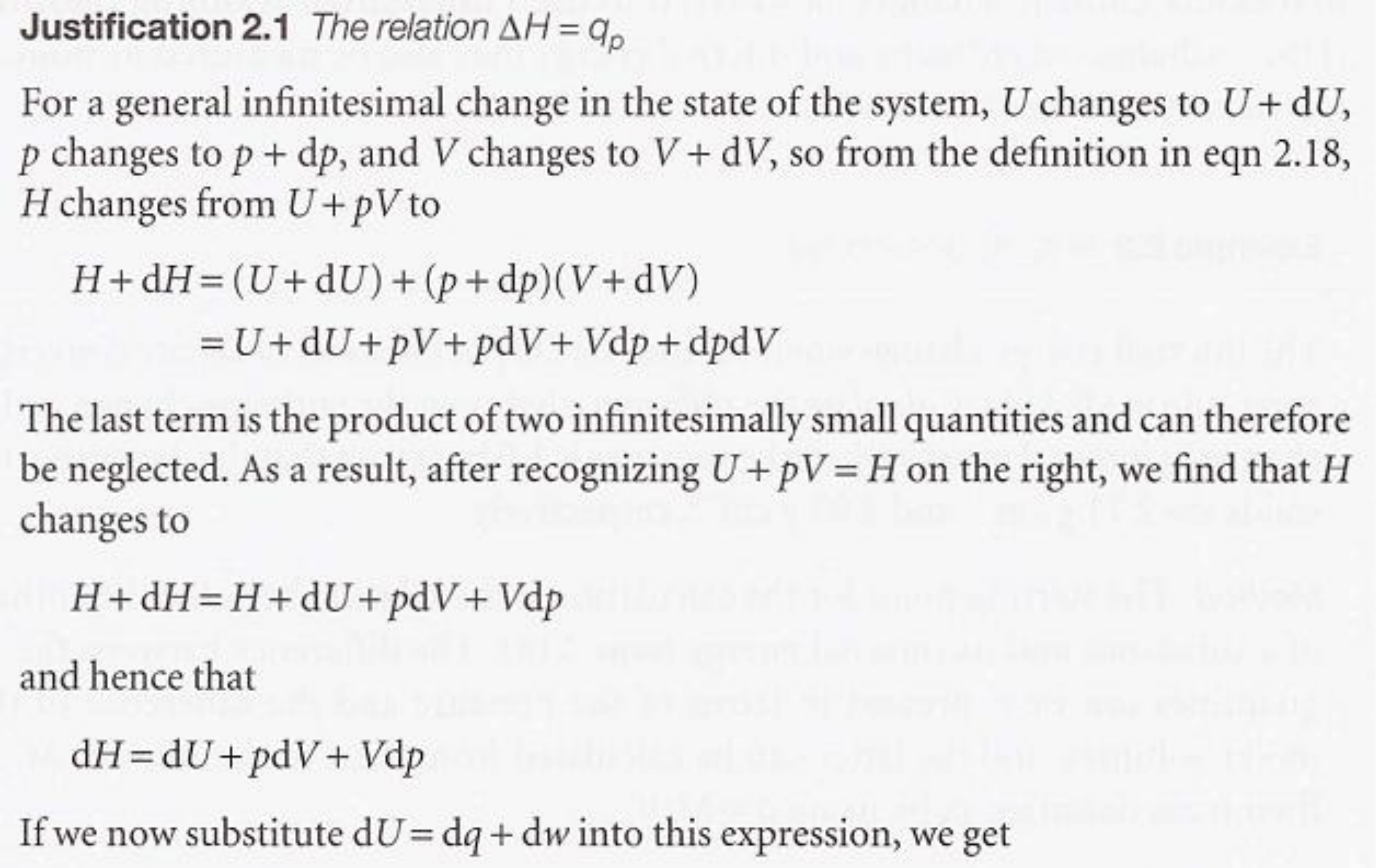
equal to the energy supplied as heat at constant pressure (provided the system does no additional work):

$$\mathrm{d}H = \mathrm{d}q \qquad \text{(at constant pressure, no additional work)} \qquad (2.19a)$$

dH = dq (at constant pressure, no additional work) -------------------- (2.19a)

For a measurable change,

$$\Delta H = q_p \qquad (2.19b)$$



Justification 2.1 *The relation $\Delta H = q_p$*

For a general infinitesimal change in the state of the system, U changes to $U + \mathrm{d}U$, p changes to $p + \mathrm{d}p$, and V changes to $V + \mathrm{d}V$, so from the definition in eqn 2.18, H changes from $U + pV$ to

$$\begin{aligned} H + \mathrm{d}H &= (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V) \\ &= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V \end{aligned}$$

The last term is the product of two infinitesimally small quantities and can therefore be neglected. As a result, after recognizing $U + pV = H$ on the right, we find that H changes to

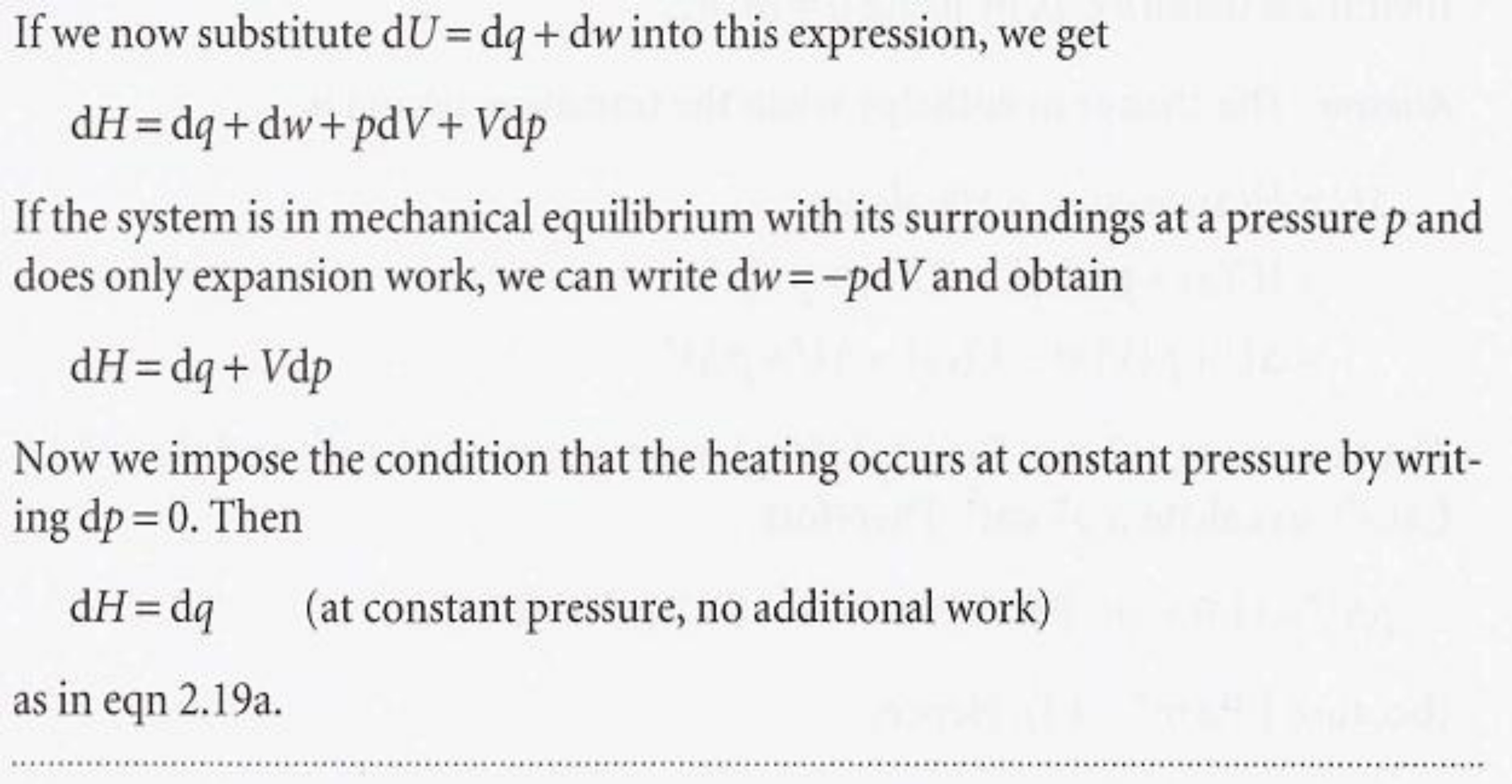
$$H + \mathrm{d}H = H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

and hence that

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

If we now substitute $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$ into this expression, we get

- تتمت الايضاح



If we now substitute $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$ into this expression, we get

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work, we can write $\mathrm{d}w = -p\mathrm{d}V$ and obtain

$$\mathrm{d}H = \mathrm{d}q + V\mathrm{d}p$$

Now we impose the condition that the heating occurs at constant pressure by writing $\mathrm{d}p = 0$. Then

$$\mathrm{d}H = \mathrm{d}q \qquad \text{(at constant pressure, no additional work)}$$

as in eqn 2.19a.

The result expressed in eqn 2.19 states that, **when a system is subjected to a constant pressure, and only expansion work can occur, the change in enthalpy is equal to the energy supplied as heat.**

For example, if we supply 36 kJ of energy through an electric heater immersed in an open beaker of water, then the enthalpy of the water increases by 36 kJ and we write

$\Delta H = +36$ kJ.

(b) The measurement of an enthalpy change

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change occurring at constant pressure. A calorimeter for studying processes at constant pressure is called an **isobaric calorimeter. A simple example is a thermally insulated vessel open to the atmosphere:**

the heat released in the reaction is monitored by measuring the change in temperature of the contents.

For a combustion reaction an adiabatic flame calorimeter may be used to measure ΔT *when a given amount of substance burns in a supply of oxygen (Fig. 2.13).*

Another route to ΔH is to measure the internal energy change by using a bomb calorimeter, and then to convert ΔU to ΔH.

Because solids and liquids have small molar volumes, **for them** pV_m ***is so small that the molar enthalpy and molar*** **internal energy** are **almost identical**

$$(H_m = U_m + pV_m \approx U_m)$$ للمواد الصلبة و السوائل

Consequently, if a process involves only solids or liquids, the values of ΔH and *ΔU are almost identical.*

Physically, *such processes are accompanied by a very small change in volume, the* system does negligible work on the surroundings

when the process occurs, so the energy supplied **as heat stays entirely within the system.**

The most sophisticated way to measure enthalpy changes, however, is to use a differential scanning calorimeter (DSC). Changes in enthalpy and internal energy may also be measured by noncalorimetric methods (see Chapter 7)0op

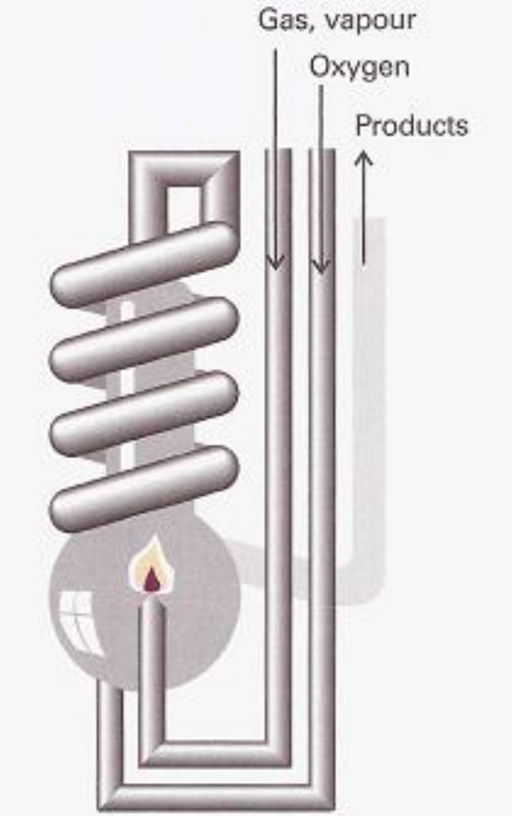
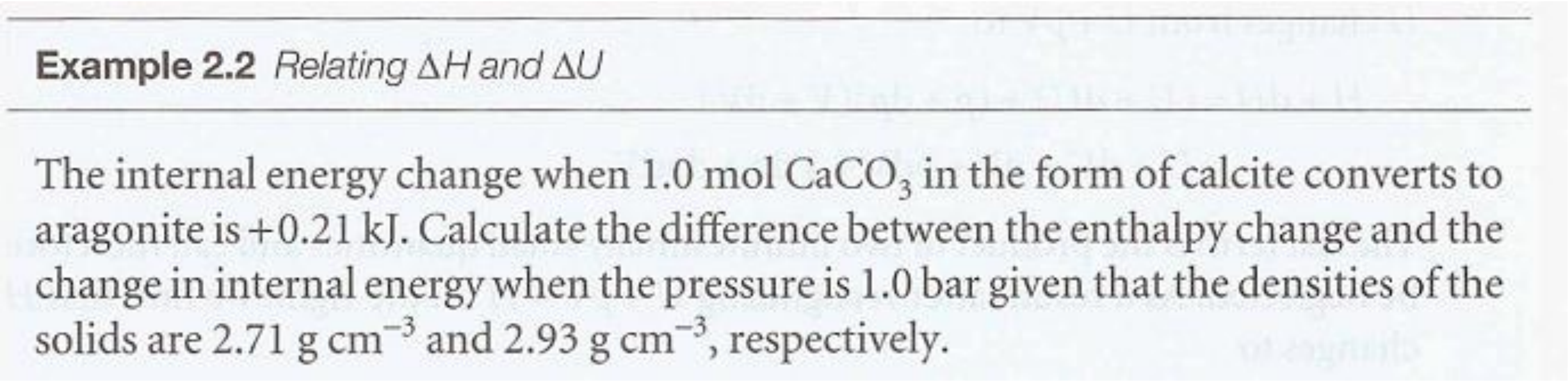


Fig. 2.13 A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath. Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

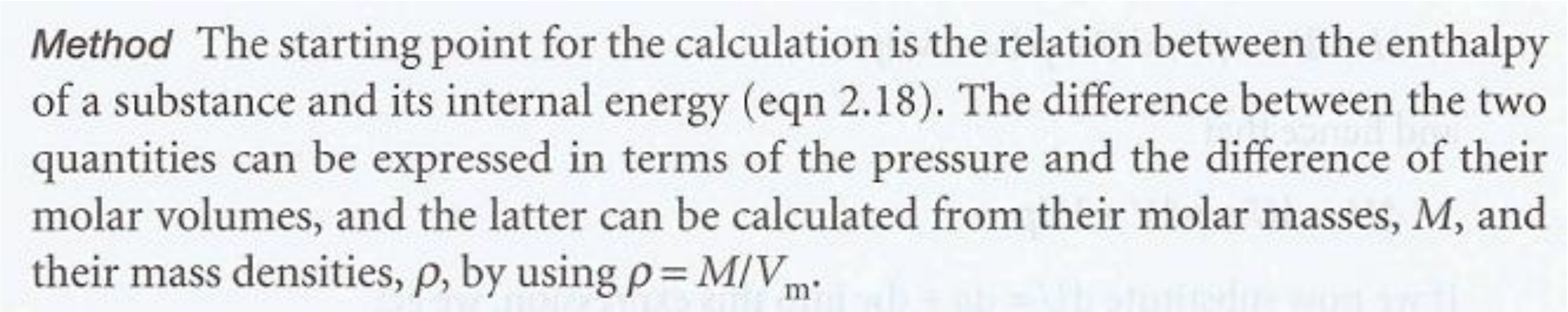
- مثال العلاقة بين الانثالبية و الطاقة الداخلية



Example 2.2 *Relating ΔH and ΔU*

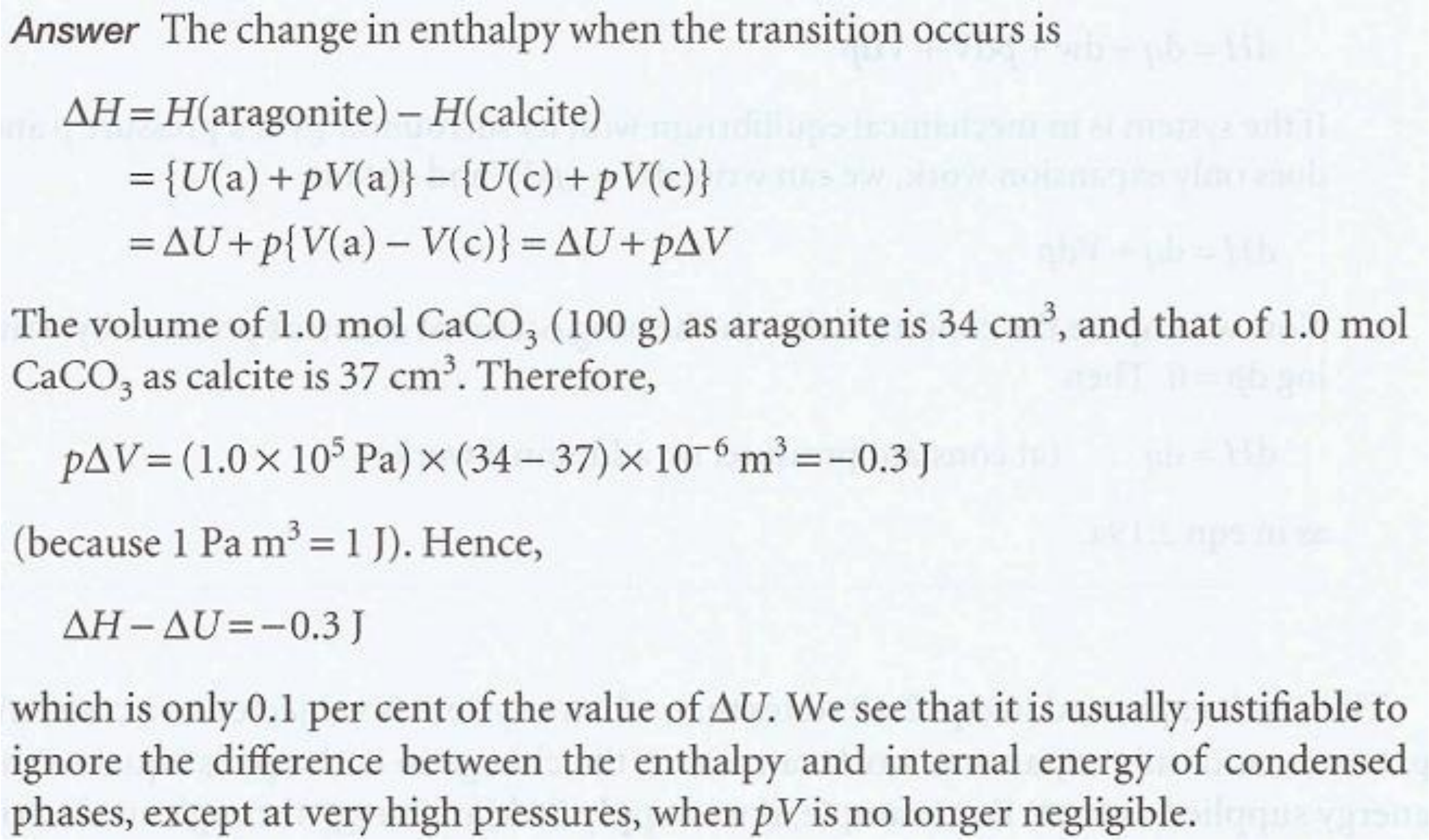
The internal energy change when 1.0 mol $CaCO_3$ in the form of calcite converts to aragonite is +0.21 kJ. Calculate the difference between the enthalpy change and the change in internal energy when the pressure is 1.0 bar given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3}, respectively.

- طريقة الحل



Method The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy (eqn 2.18). The difference between the two quantities can be expressed in terms of the pressure and the difference of their molar volumes, and the latter can be calculated from their molar masses, M, and their mass densities, ρ, by using $\rho = M/V_m$.

- الحل



Answer The change in enthalpy when the transition occurs is

$$\begin{aligned}\Delta H &= H(\text{aragonite}) - H(\text{calcite}) \\ &= \{U(\text{a}) + pV(\text{a})\} - \{U(\text{c}) + pV(\text{c})\} \\ &= \Delta U + p\{V(\text{a}) - V(\text{c})\} = \Delta U + p\Delta V\end{aligned}$$

The volume of 1.0 mol $CaCO_3$ (100 g) as aragonite is 34 cm^3, and that of 1.0 mol $CaCO_3$ as calcite is 37 cm^3. Therefore,

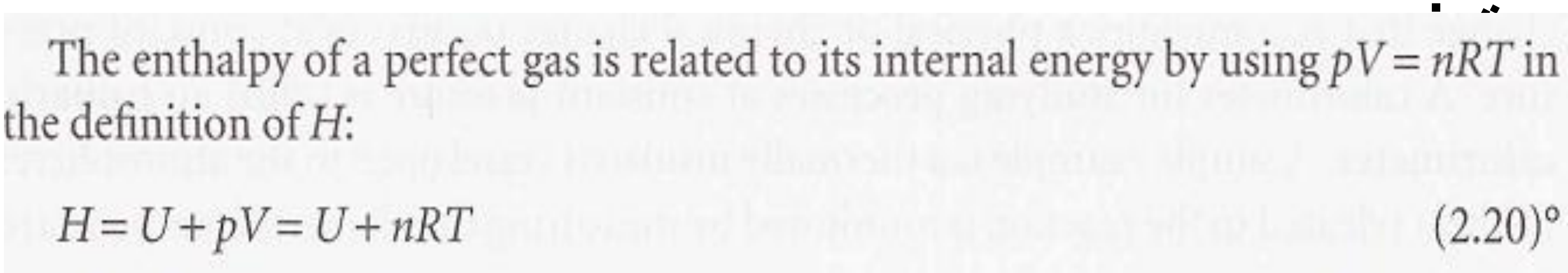
$$p\Delta V = (1.0 \times 10^5\ \text{Pa}) \times (34 - 37) \times 10^{-6}\ \text{m}^3 = -0.3\ \text{J}$$

(because 1 Pa m^3 = 1 J). Hence,

$$\Delta H - \Delta U = -0.3\ \text{J}$$

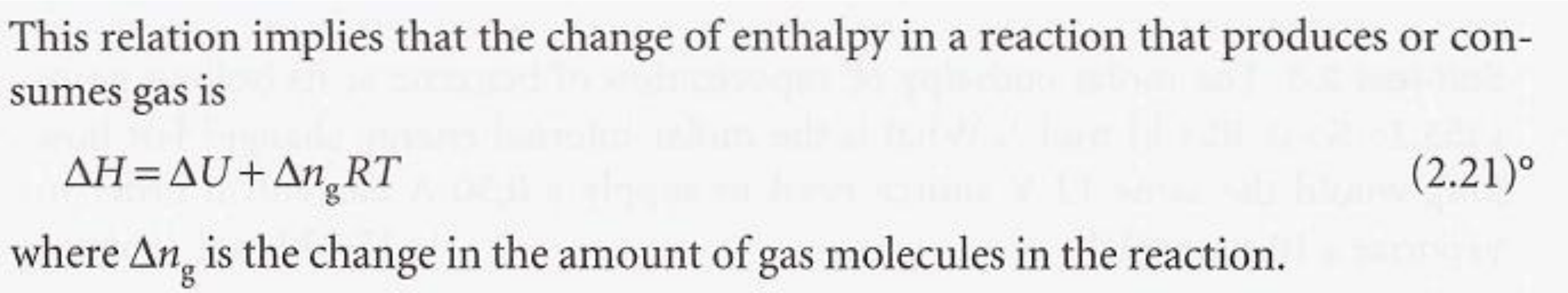
which is only 0.1 per cent of the value of ΔU. We see that it is usually justifiable to ignore the difference between the enthalpy and internal energy of condensed phases, except at very high pressures, when pV is no longer negligible.

- ترتبط الانثالبية للغاز المثالي بالطاقة الداخلية حسب العلاقة التالية:



The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H:

$$H = U + pV = U + nRT \qquad (2.20)^\circ$$



This relation implies that the change of enthalpy in a reaction that produces or consumes gas is

$$\Delta H = \Delta U + \Delta n_g RT \qquad (2.21)^\circ$$

where Δn_g is the change in the amount of gas molecules in the reaction.

- ألعلاقة الرياضية اعلاه تطبق على حساب التغير في الانثالبية للتفاعل الذي يحرر غاز او يستهلك غاز.

- توضيح

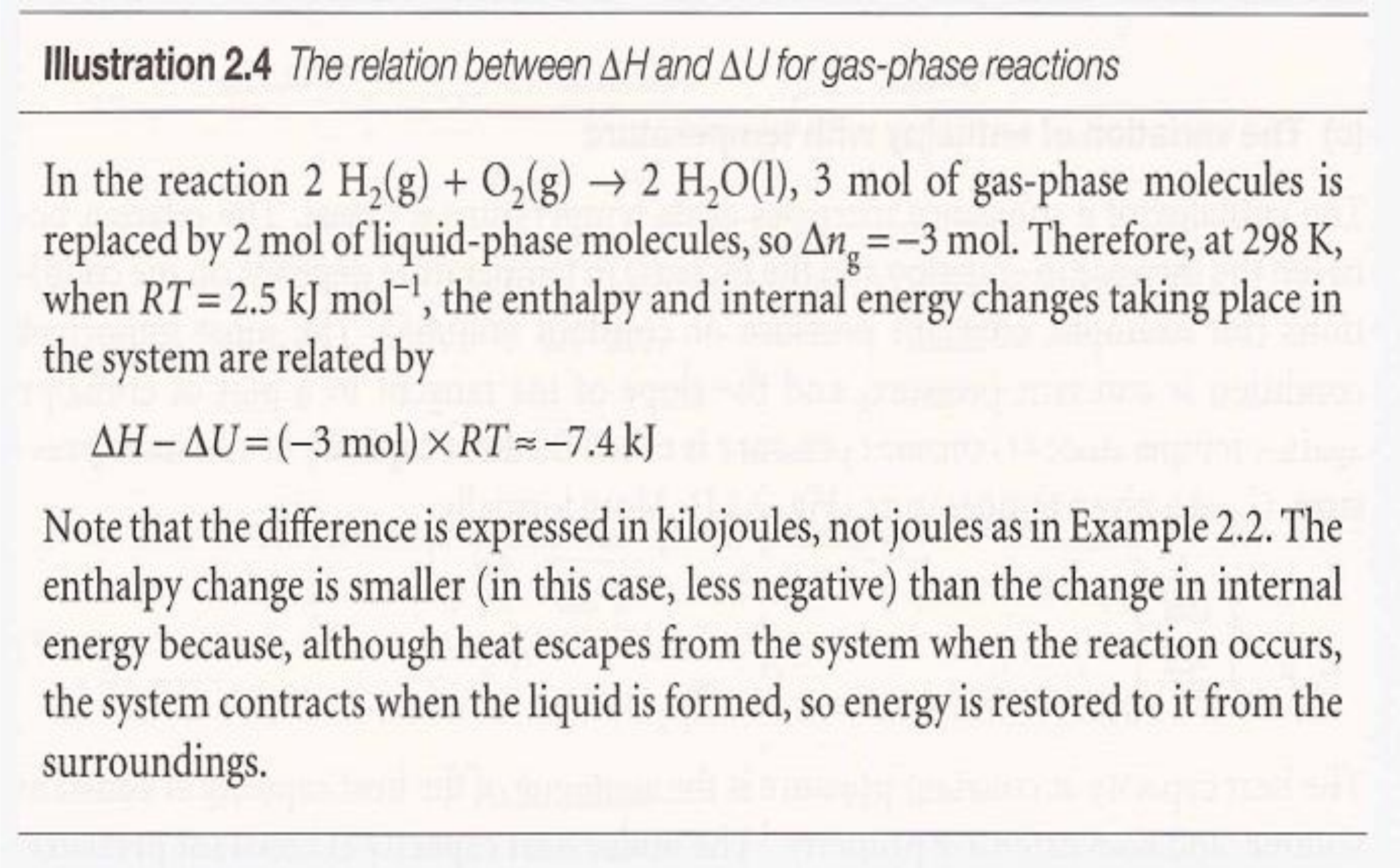


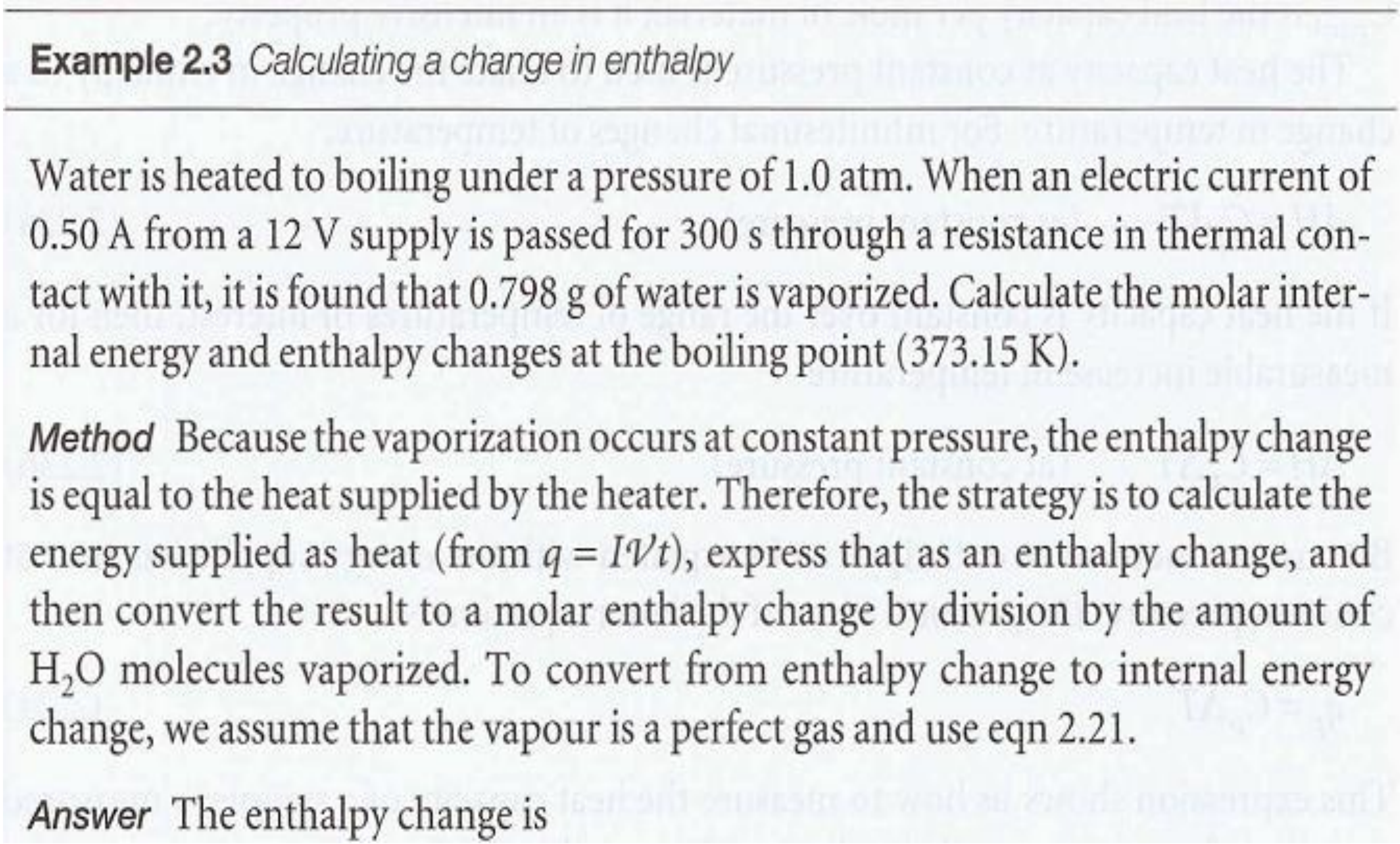
Illustration 2.4 *The relation between ΔH and ΔU for gas-phase reactions*

In the reaction $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$, 3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules, so $\Delta n_g = -3$ mol. Therefore, at 298 K, when $RT = 2.5\ \mathrm{kJ\ mol^{-1}}$, the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H - \Delta U = (-3\ \mathrm{mol}) \times RT \approx -7.4\ \mathrm{kJ}$$

Note that the difference is expressed in kilojoules, not joules as in Example 2.2. The enthalpy change is smaller (in this case, less negative) than the change in internal energy because, although heat escapes from the system when the reaction occurs, the system contracts when the liquid is formed, so energy is restored to it from the surroundings.

- مثال



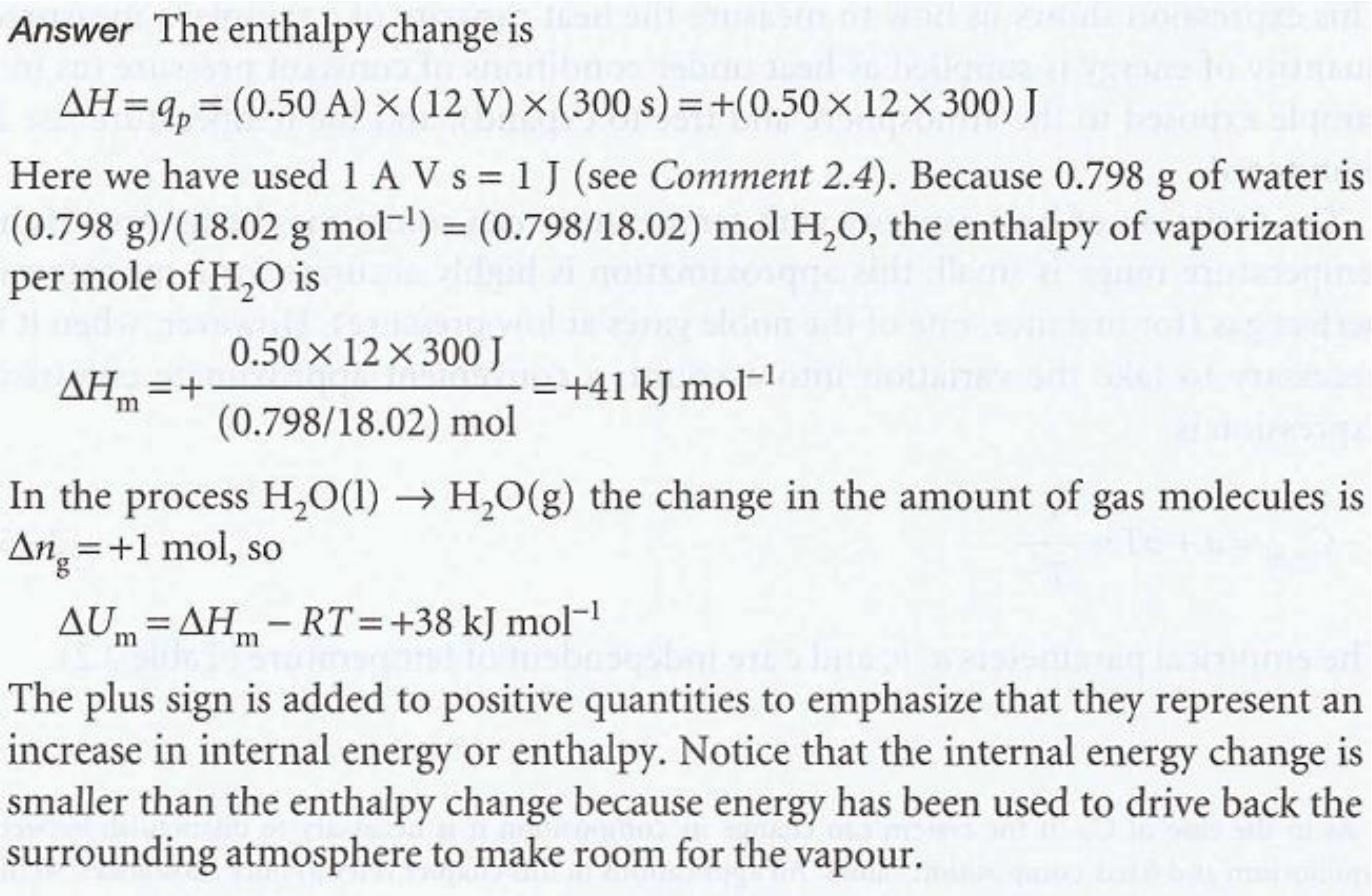
Example 2.3 *Calculating a change in enthalpy*

Water is heated to boiling under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

Method Because the vaporization occurs at constant pressure, the enthalpy change is equal to the heat supplied by the heater. Therefore, the strategy is to calculate the energy supplied as heat (from $q = I\mathcal{V}t$), express that as an enthalpy change, and then convert the result to a molar enthalpy change by division by the amount of H_2O molecules vaporized. To convert from enthalpy change to internal energy change, we assume that the vapour is a perfect gas and use eqn 2.21.

Answer The enthalpy change is

- الحل



Answer The enthalpy change is

$$\Delta H = q_p = (0.50\ \text{A}) \times (12\ \text{V}) \times (300\ \text{s}) = +(0.50 \times 12 \times 300)\ \text{J}$$

Here we have used 1 A V s = 1 J (see *Comment 2.4*). Because 0.798 g of water is (0.798 g)/(18.02 g mol^{-1}) = (0.798/18.02) mol H_2O, the enthalpy of vaporization per mole of H_2O is

$$\Delta H_\text{m} = +\frac{0.50 \times 12 \times 300\ \text{J}}{(0.798/18.02)\ \text{mol}} = +41\ \text{kJ mol}^{-1}$$

In the process $H_2O(l) \rightarrow H_2O(g)$ the change in the amount of gas molecules is $\Delta n_\text{g} = +1$ mol, so

$$\Delta U_\text{m} = \Delta H_\text{m} - RT = +38\ \text{kJ mol}^{-1}$$

The plus sign is added to positive quantities to emphasize that they represent an increase in internal energy or enthalpy. Notice that the internal energy change is smaller than the enthalpy change because energy has been used to drive back the surrounding atmosphere to make room for the vapour.