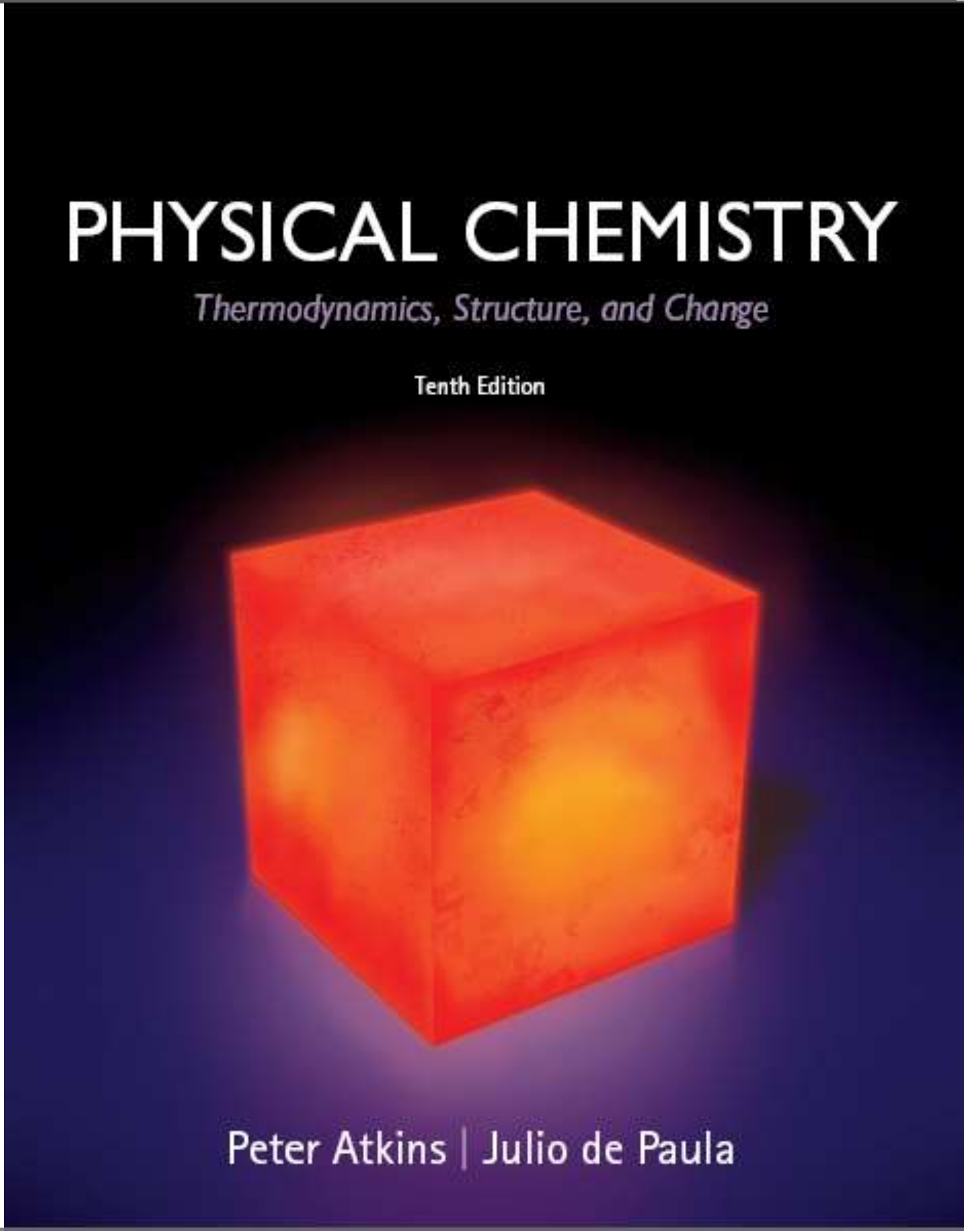
Physical Chemistry: Thermodynamics, Structure, and Change
Tenth Edition

ART
POWERPOINT
PRESENTATIONS

Chapter 1



CHAPTER 1: TABLE 1A.1

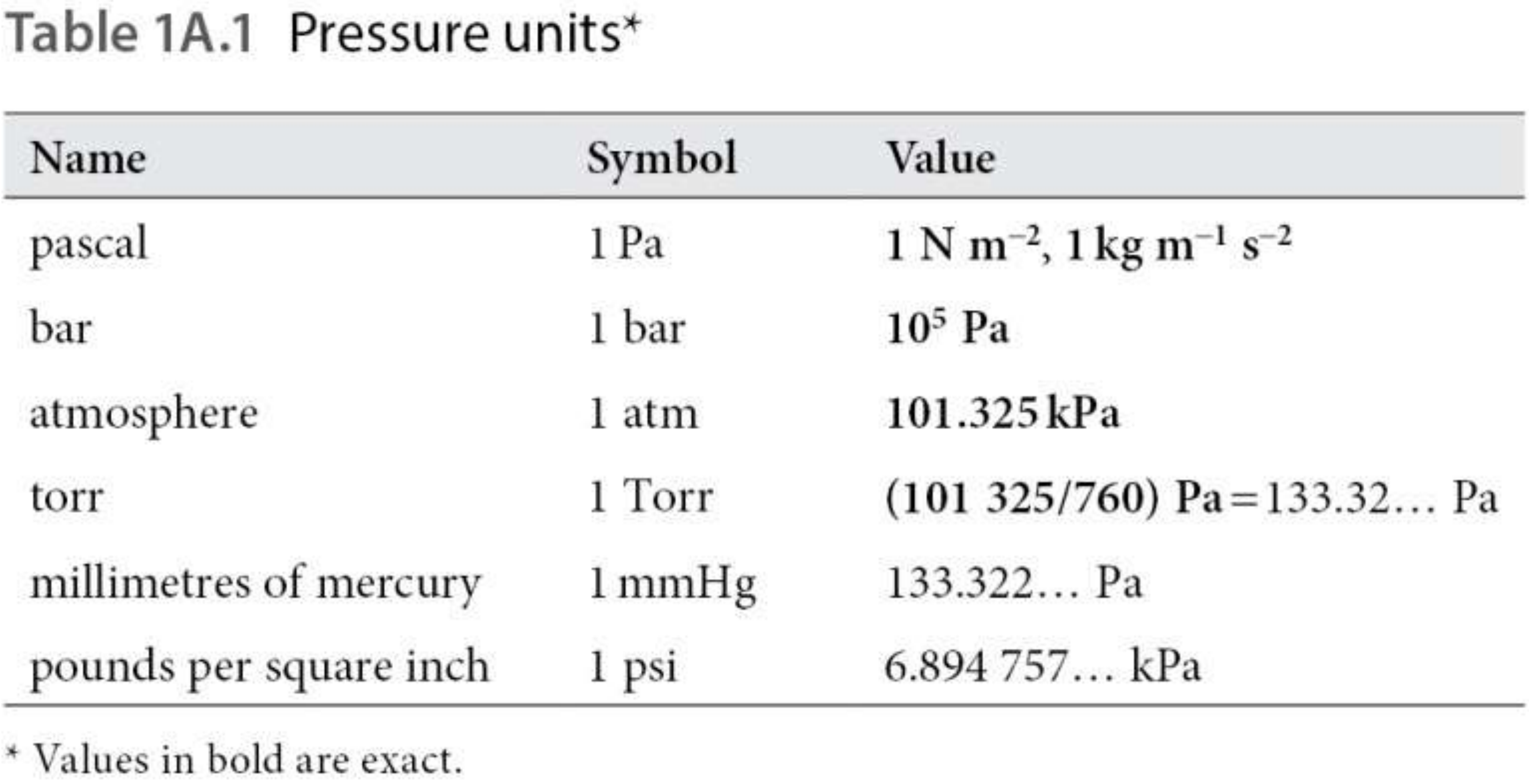


Table 1A.1 Pressure units*

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
pounds per square inch	1 psi	6.894 757… kPa

* Values in bold are exact.

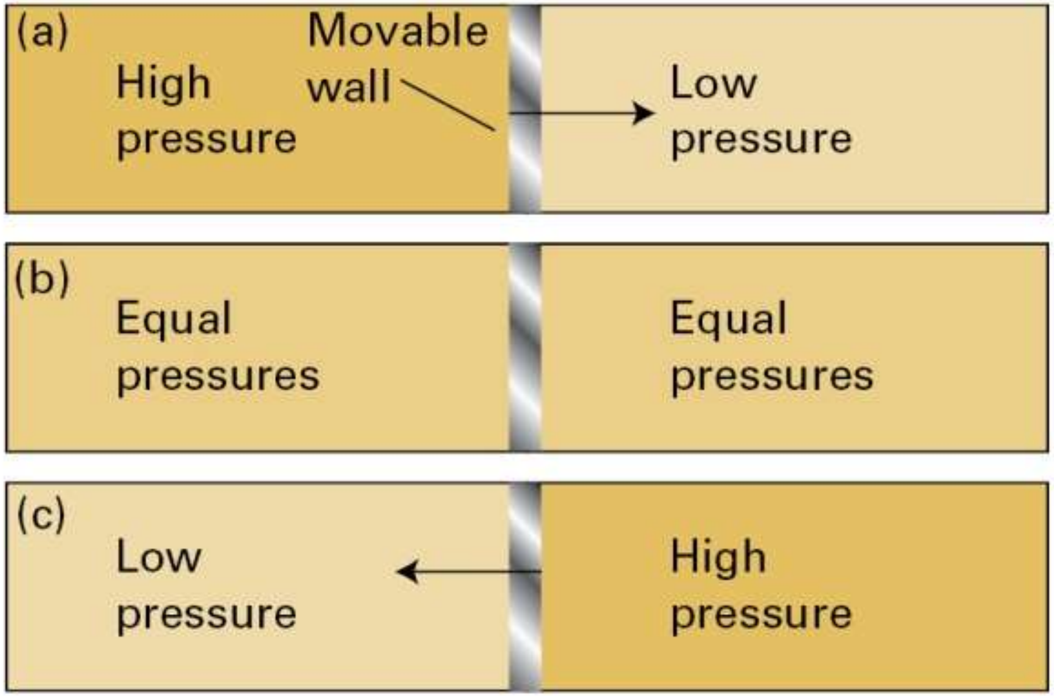


Figure 1A.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium between the two regions.

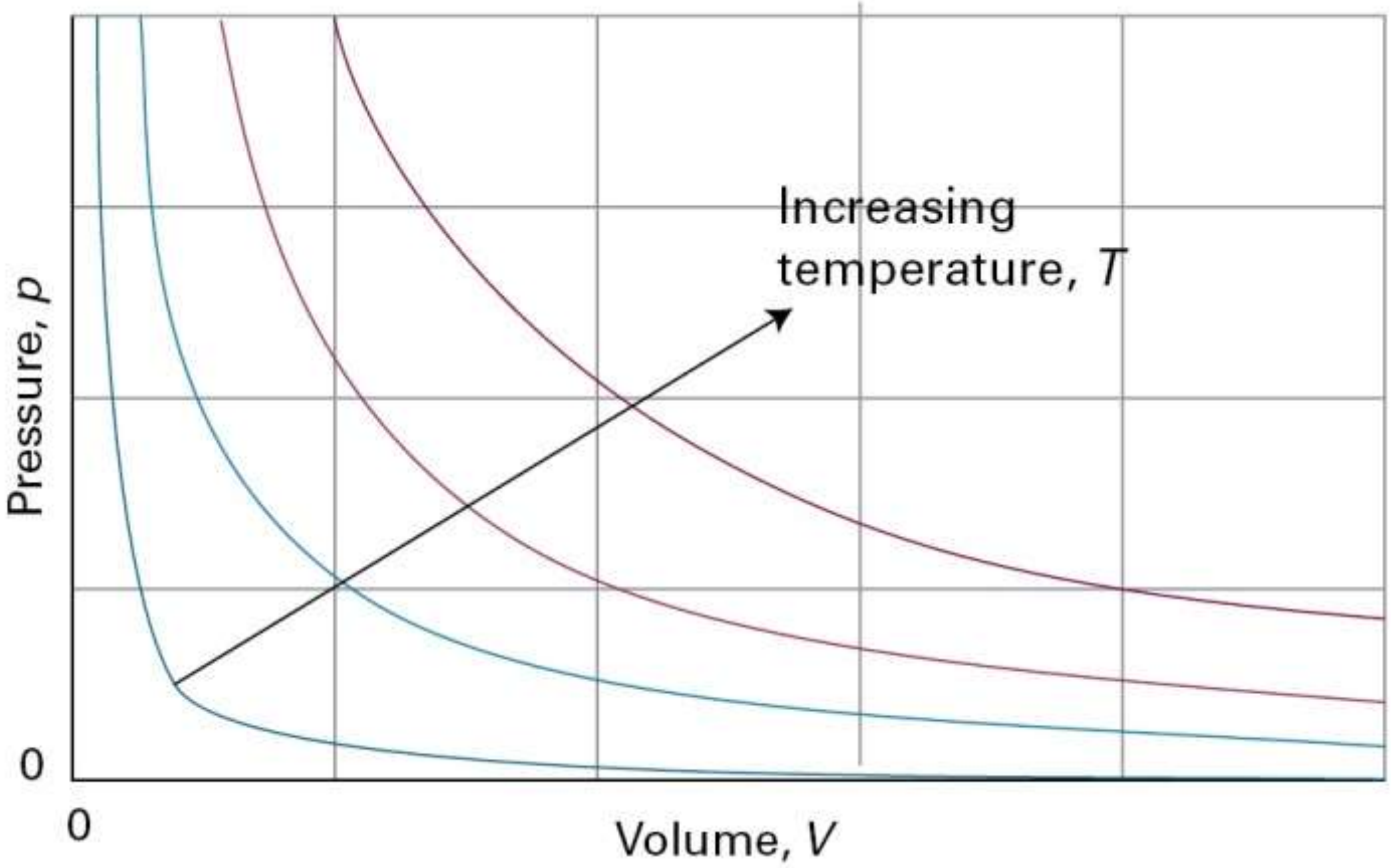


Figure 1A.2 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola (pV=constant) and is called an isotherm.

CHAPTER 1: FIGURE 1A.3

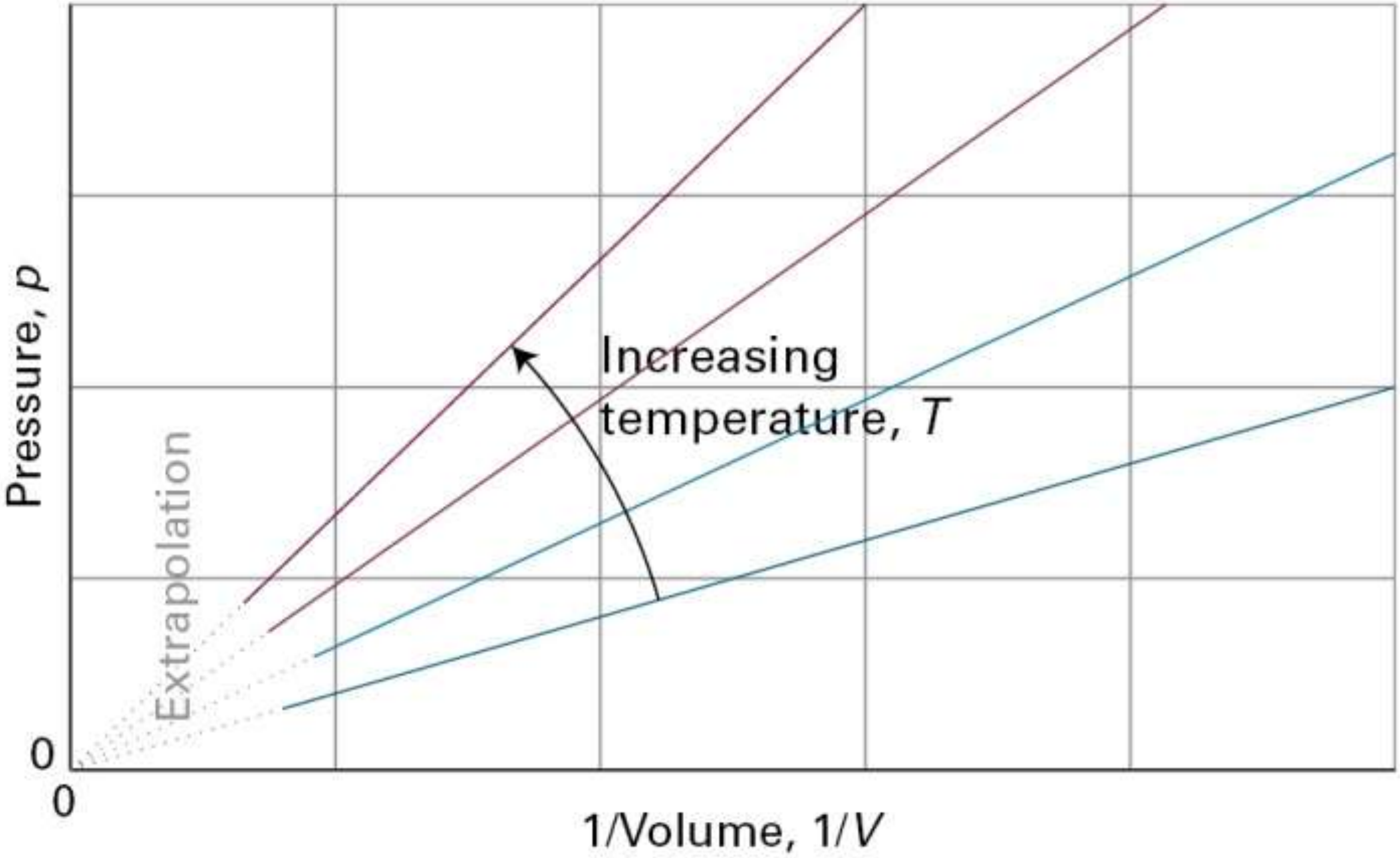


Figure 1A.3 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

CHAPTER 1: FIGURE 1A.4

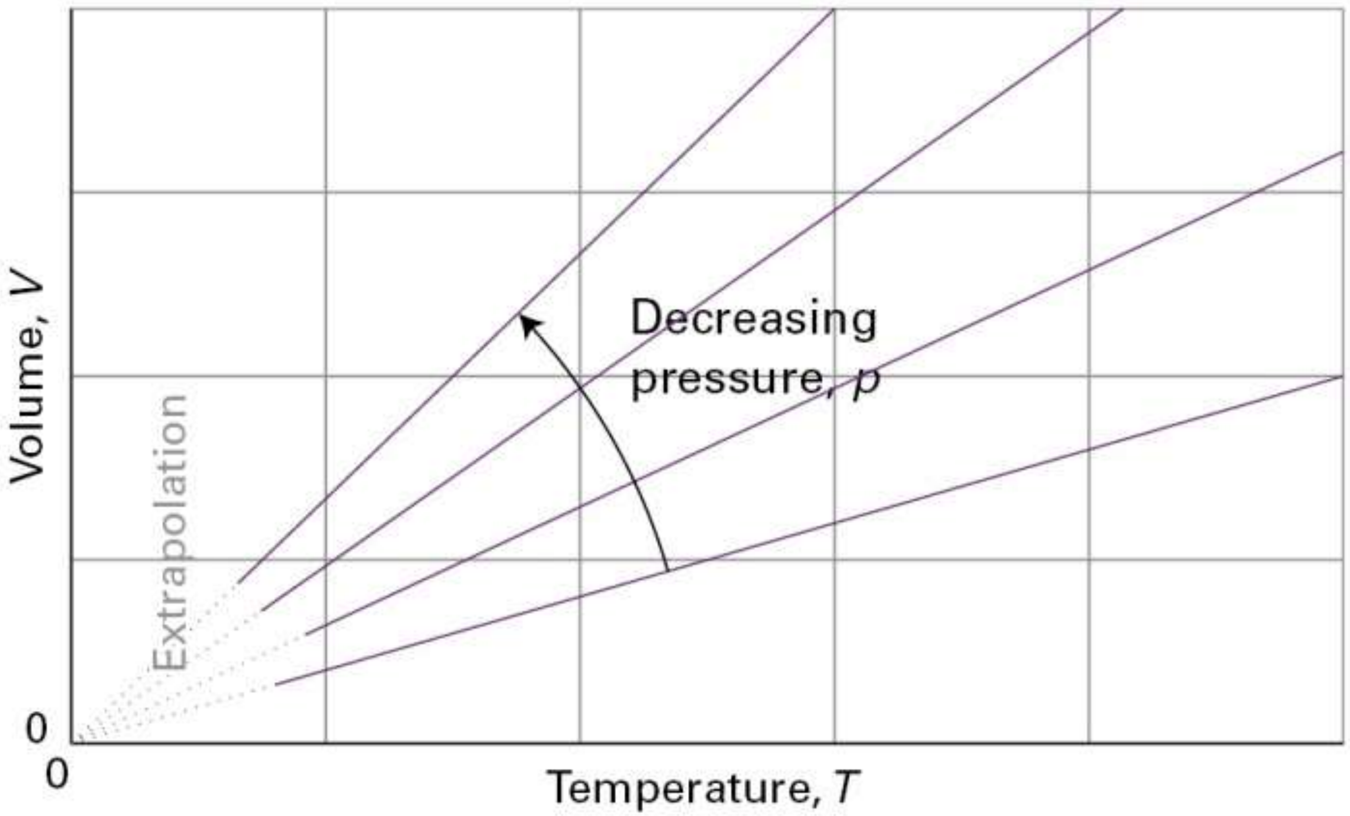


Figure 1A.4 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T=0$, or $\theta=-273\,°\mathrm{C}$.

CHAPTER 1: FIGURE 1A.5

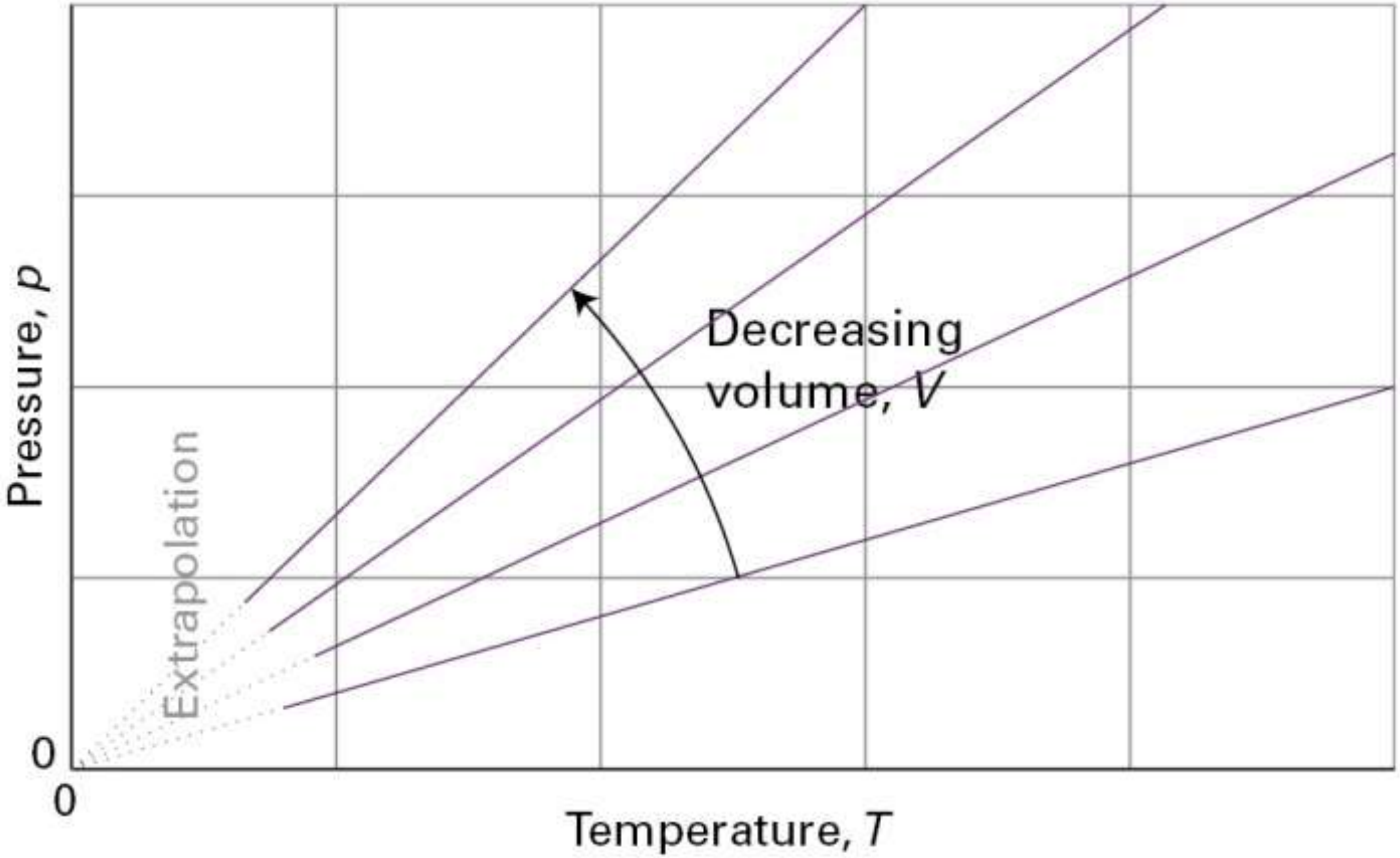
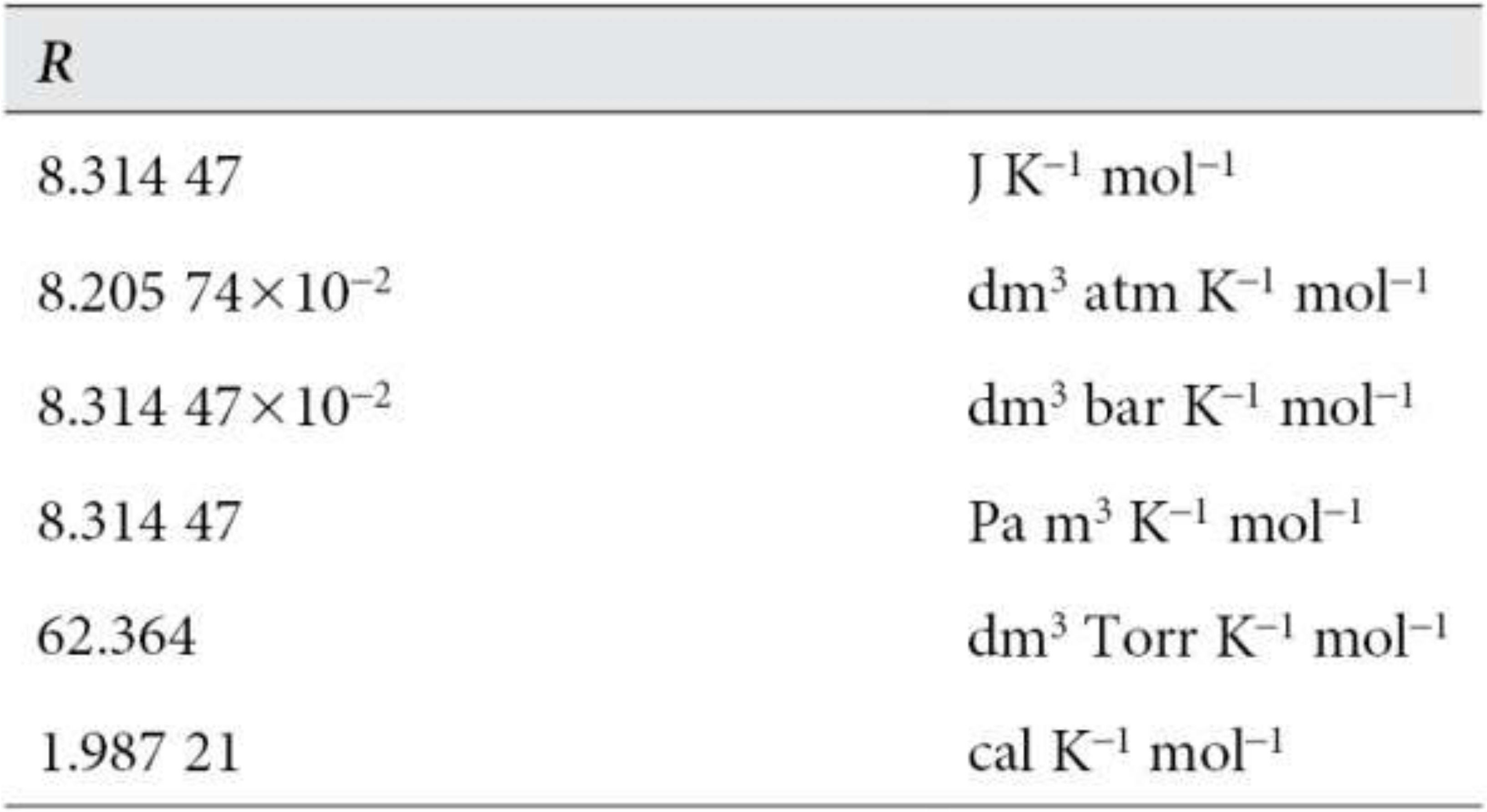


Figure 1A.5 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (−273 °C).

CHAPTER 1: TABLE 1A.2

Table 1A.2 The gas constant ($R = N_A k$)



R	
8.314 47	$J\ K^{-1}\ mol^{-1}$
$8.205\ 74 \times 10^{-2}$	$dm^3\ atm\ K^{-1}\ mol^{-1}$
$8.314\ 47 \times 10^{-2}$	$dm^3\ bar\ K^{-1}\ mol^{-1}$
8.314 47	$Pa\ m^3\ K^{-1}\ mol^{-1}$
62.364	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
1.987 21	$cal\ K^{-1}\ mol^{-1}$

CHAPTER 1: FIGURE 1A.6

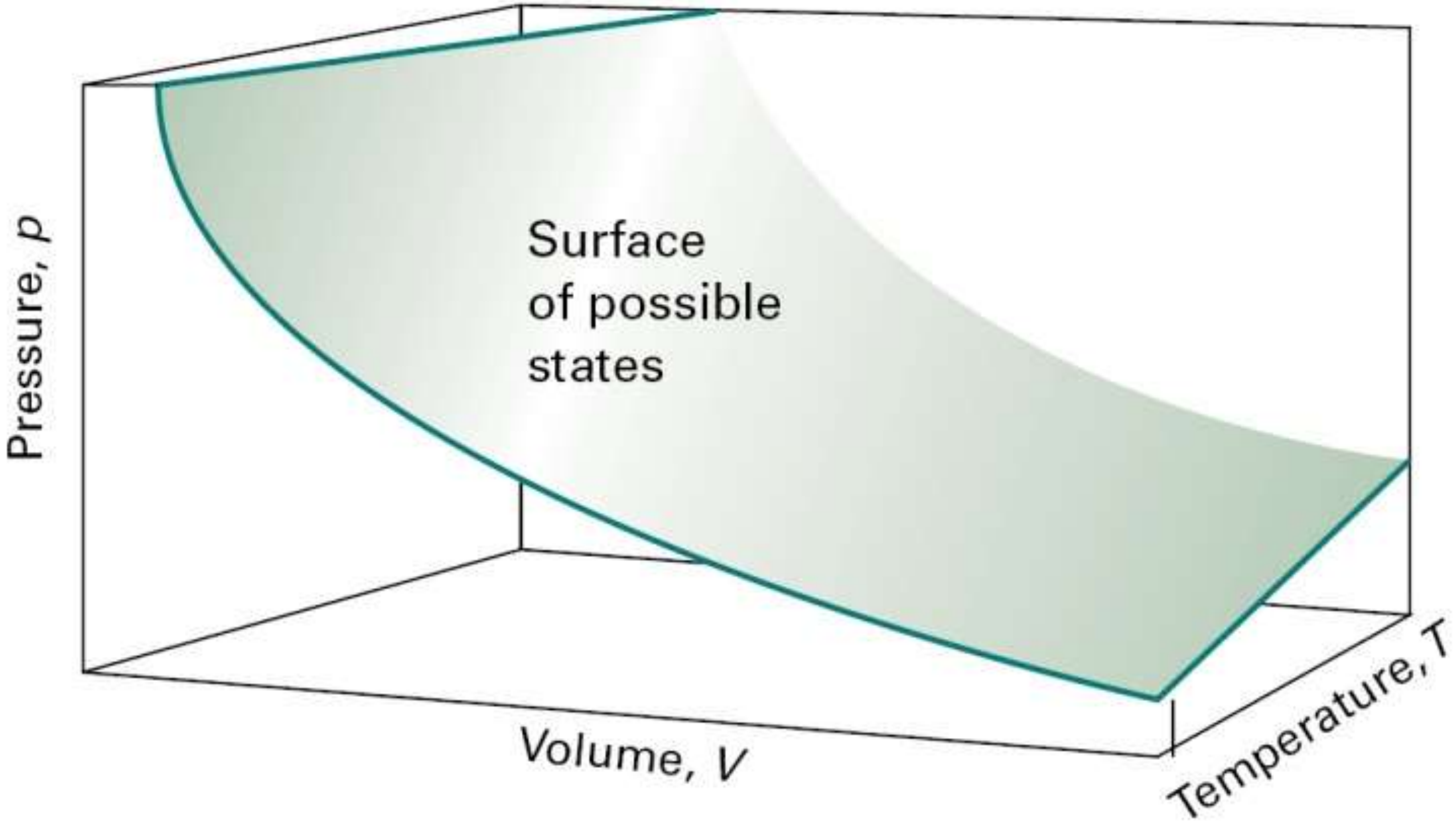


Figure 1A.6 A region of the p,V,T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

CHAPTER 1: FIGURE 1A.7

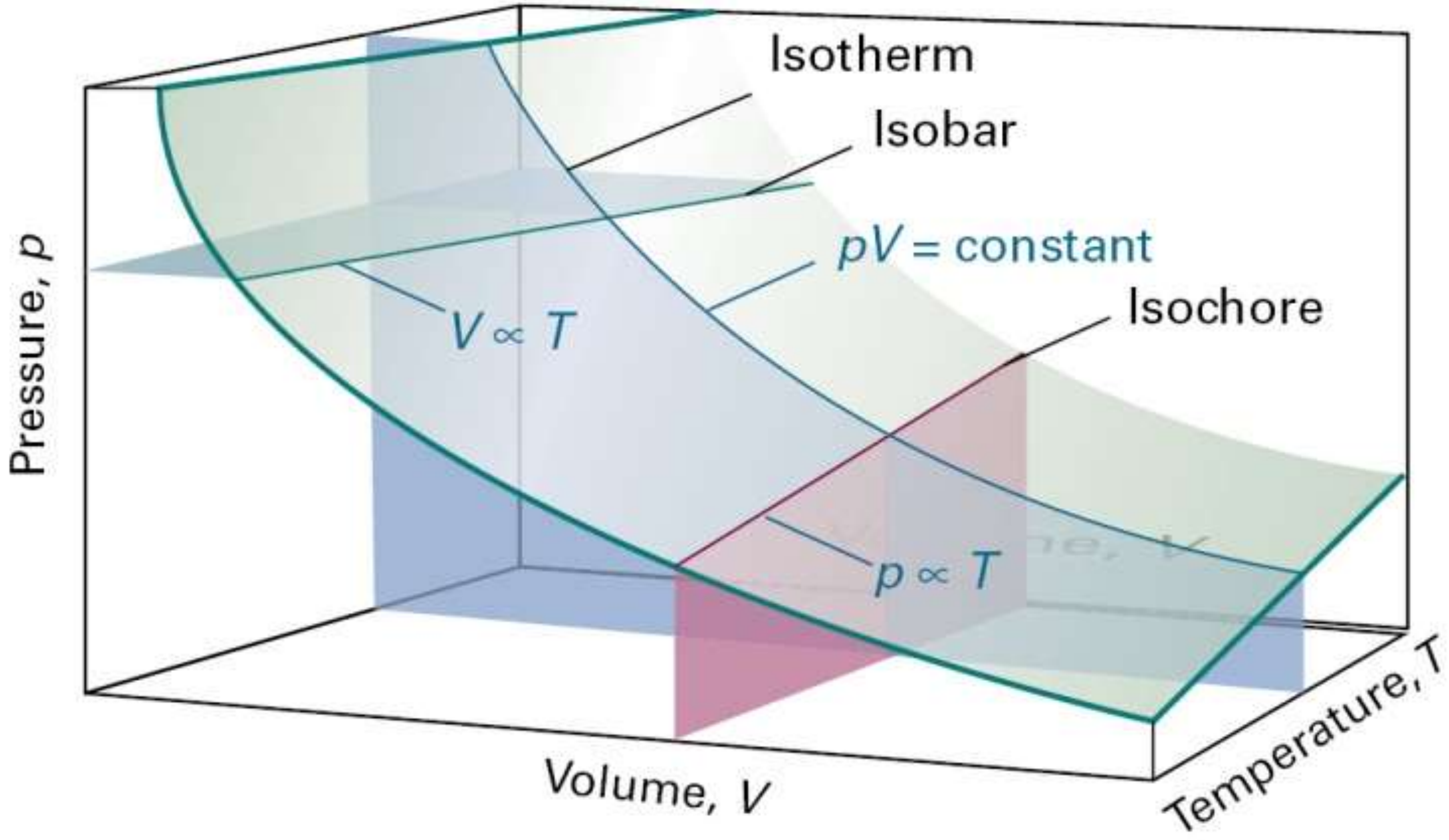


Figure 1A.7 Sections through the surface shown in Fig. 1A.6 at constant temperature give the isotherms shown in Fig. 1A.2, the isobars shown in Fig. 1A.4, and the isochores shown in Fig. 1A.5.

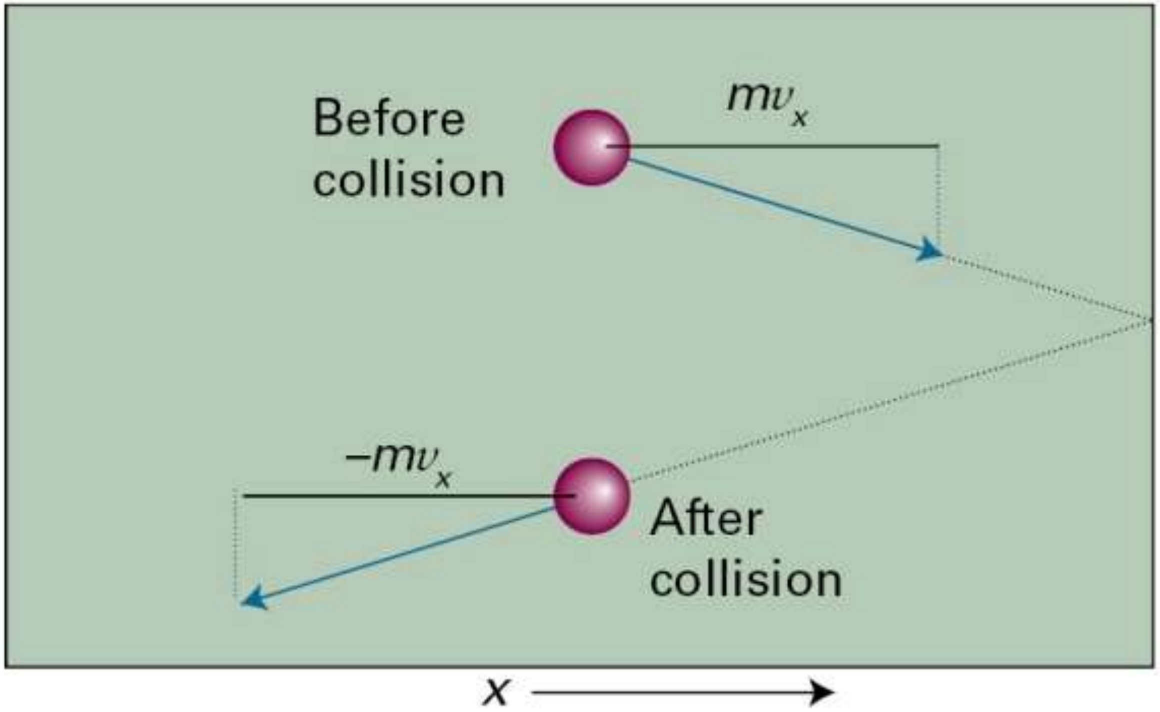


Figure 1B.1 The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x-axis, the x-component of velocity is reversed but the y- and z-components are unchanged.

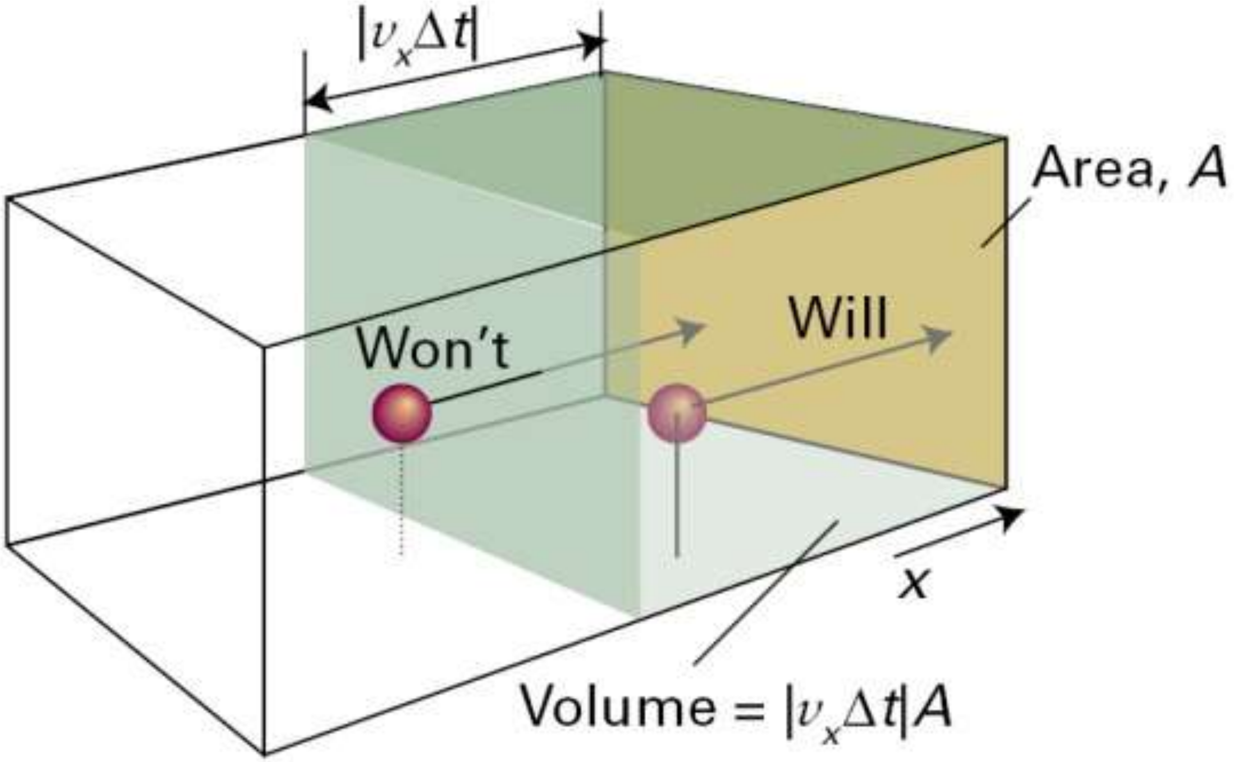


Figure 1B.2 A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x\Delta t$ of the wall and travelling to the right.

CHAPTER 1: FIGURE 1B.3

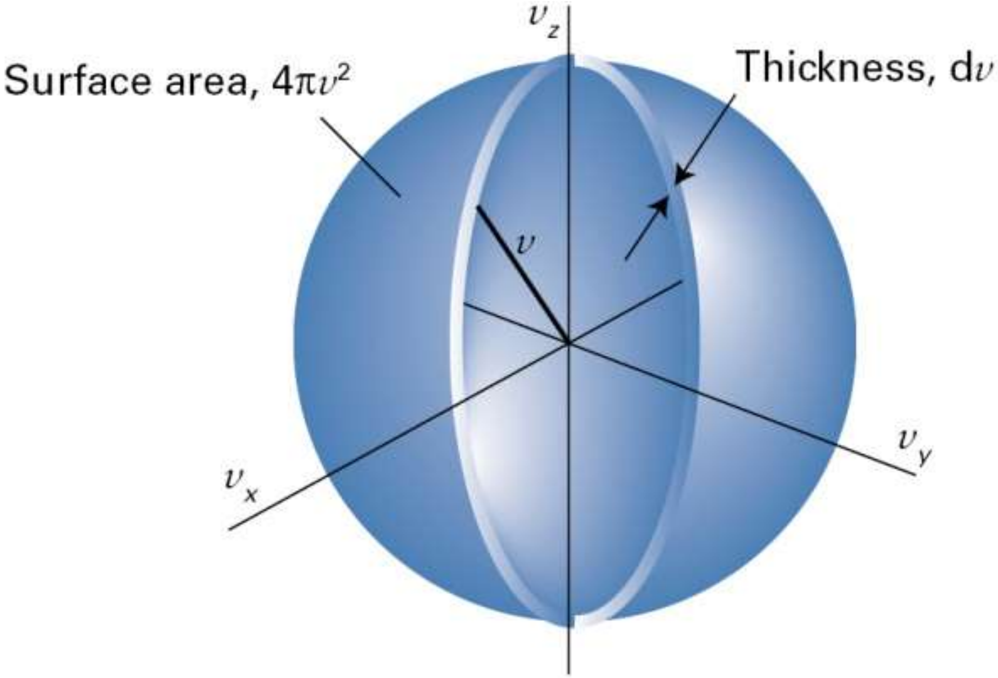


Figure 1B.3 To evaluate the probability that a molecule has a speed in the range v to $v+\mathrm{d}v$, we evaluate the total probability that the molecule will have a speed that is anywhere on the surface of a sphere of radius $v=(v_x^2+v_y^2+v_z^2)^{1/2}$ by summing the probabilities that it is in a volume element $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ at a distance v from the origin.

CHAPTER 1: FIGURE 1B.4

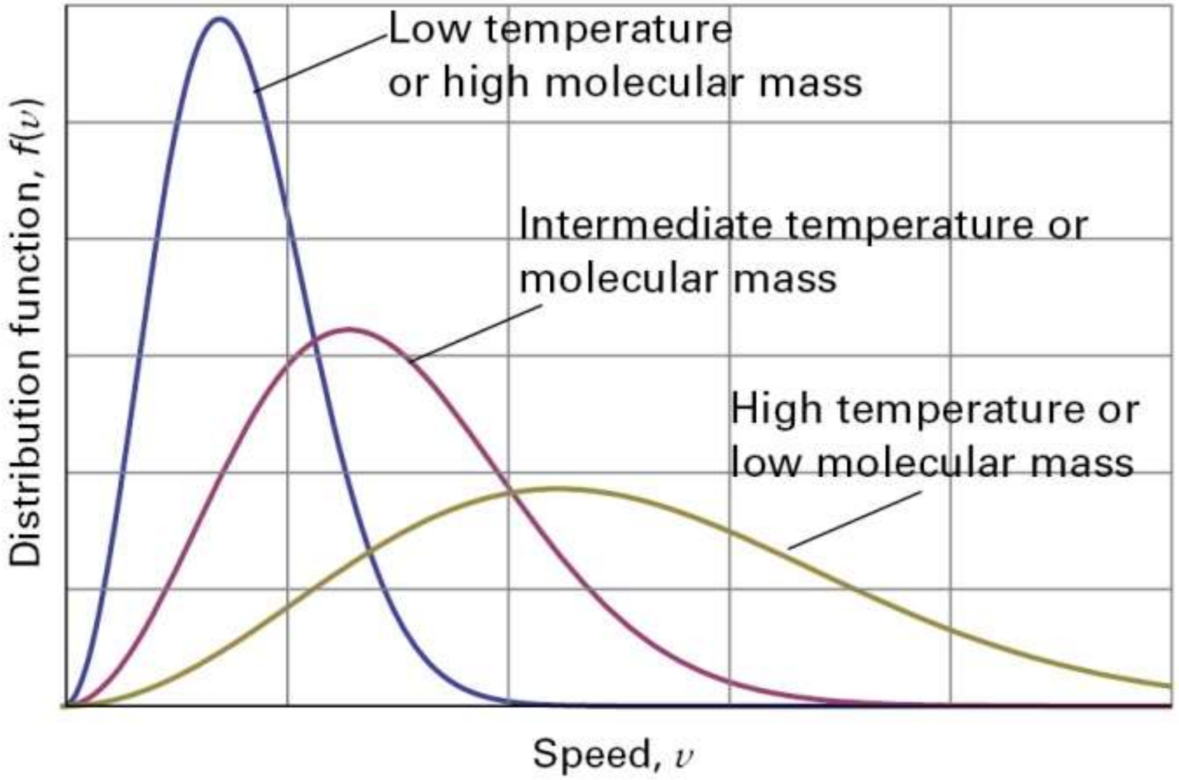


Figure 1B.4 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

CHAPTER 1: FIGURE 1B.5

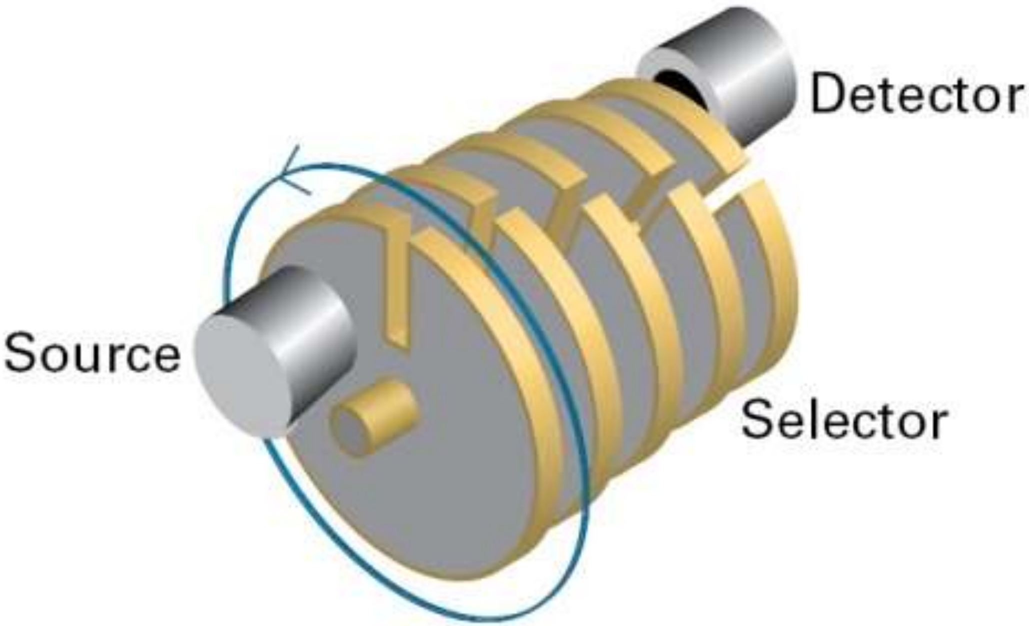


Figure 1B.5 A velocity selector. Only molecules travelling at speeds within a narrow range pass through the succession of slits as they rotate into position.

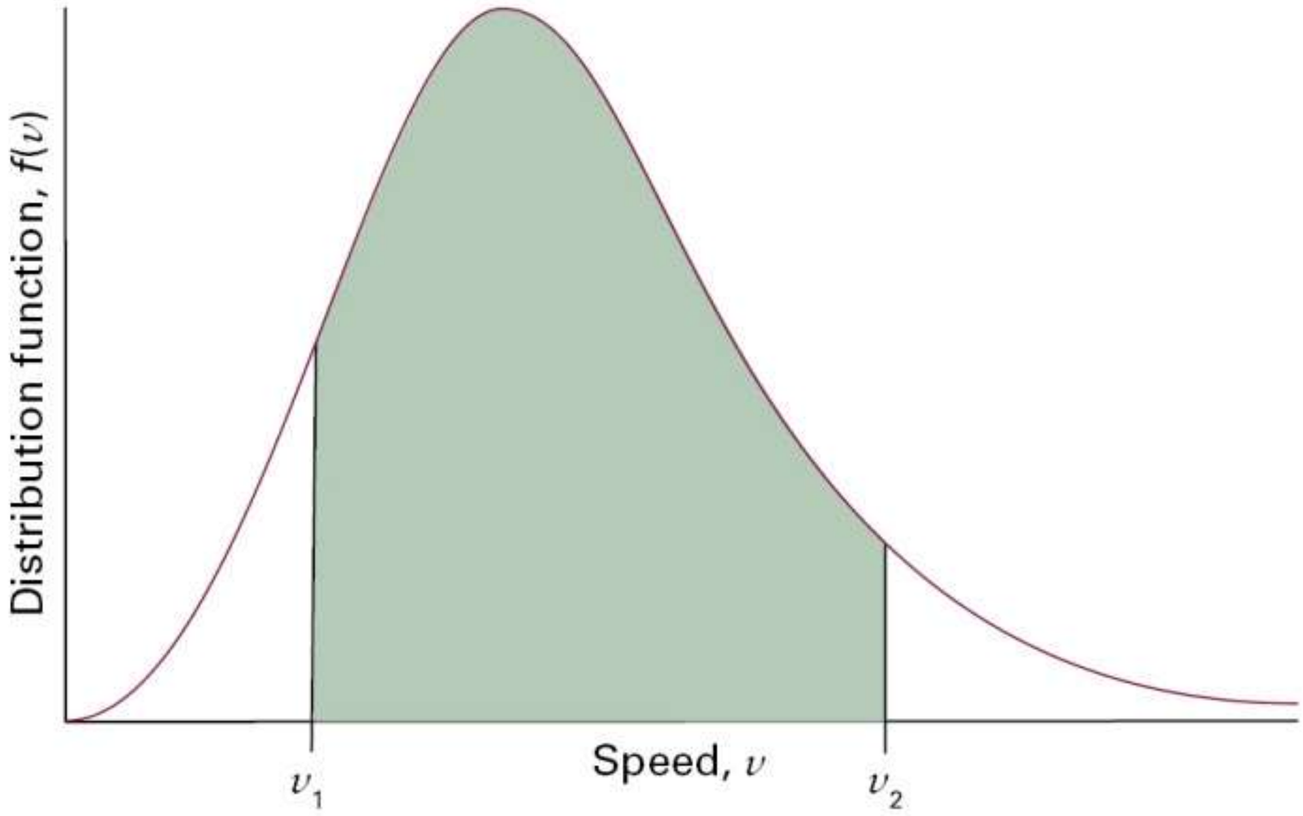


Figure 1B.6 To calculate the probability that a molecule will have a speed in the range v_1 to v_2, we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.

CHAPTER 1: FIGURE 1B.7

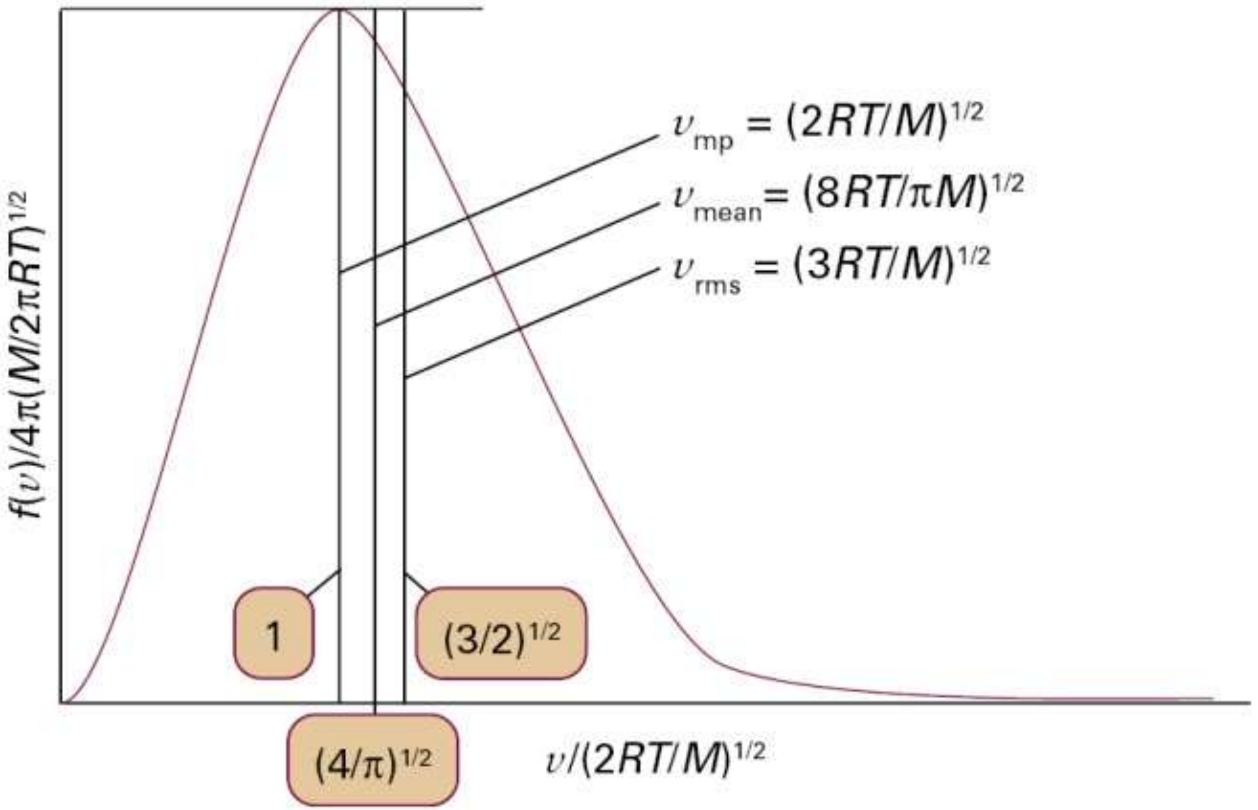


Figure 1B.7 A summary of the conclusions that can be deduced form the Maxwell distribution for molecules of molar mass *M* at a temperature *T*: v_{mp} is the most probable speed, v_{mean} is the mean speed, and v_{rms} is the root-mean-square speed.

CHAPTER 1: FIGURE 1B.8

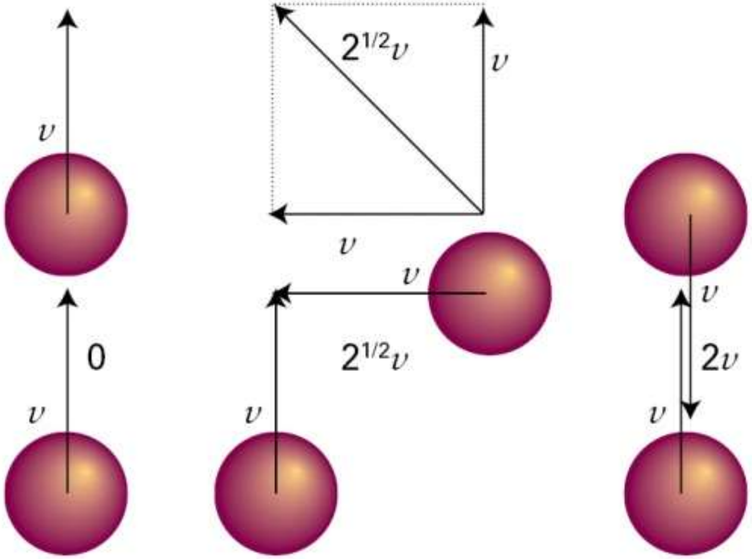


Figure 1B.8 A simplified version of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the mean relative speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the mean speed of approach is then $2^{1/2}v$. The last direction of approach is the most characteristic, so the mean speed of approach can be expected to be about $2^{1/2}v$. This value is confirmed by more detailed calculation.

CHAPTER 1: TABLE 1B.1

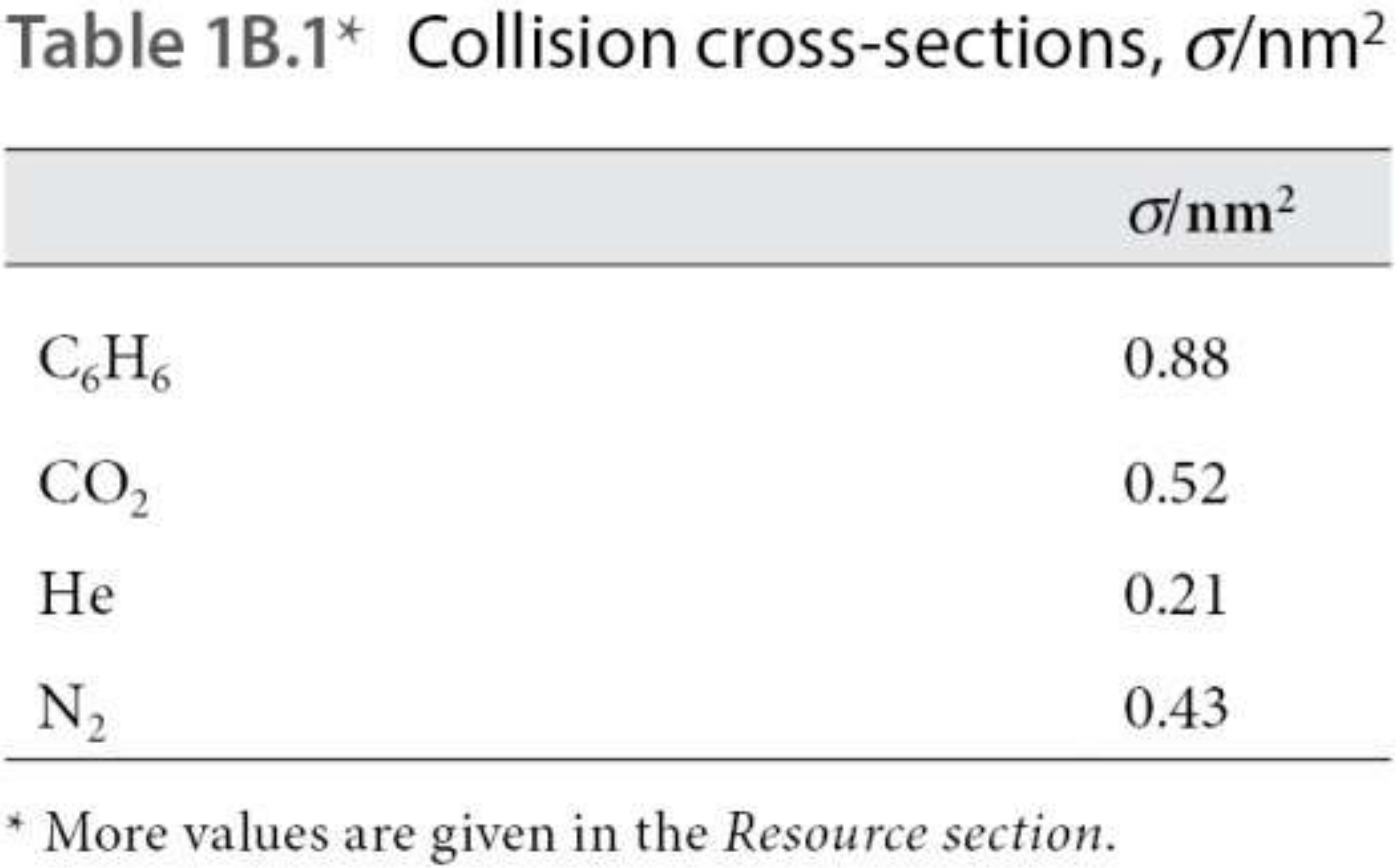


Table 1B.1* Collision cross-sections, σ/nm^2

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

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

CHAPTER 1: FIGURE 1B.9

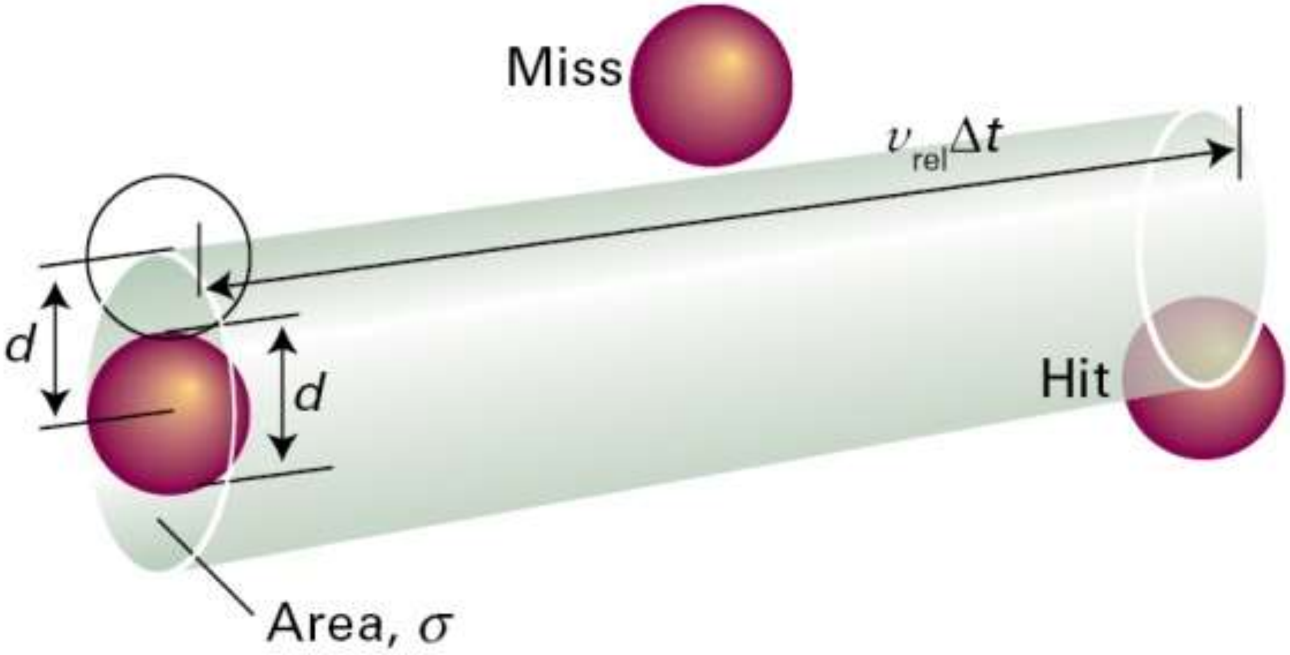


Figure 1B.9 The calculation of the collision frequency and the mean free path in the kinetic theory of gases.

CHAPTER 1: FIGURE 1C.1

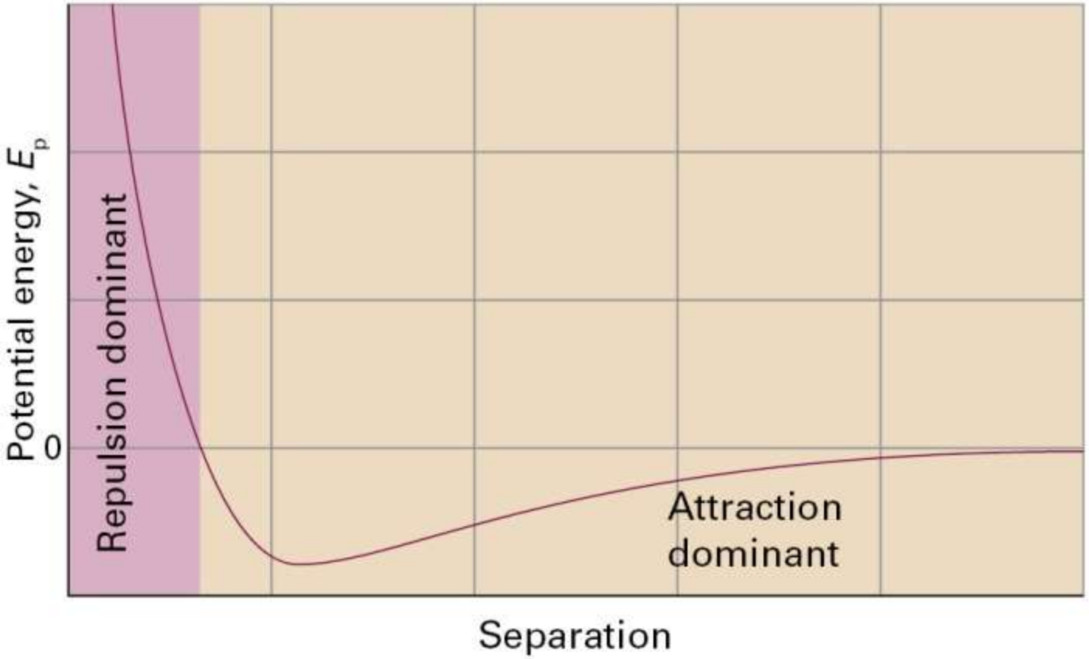


Figure 1C.1 The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.

CHAPTER 1: FIGURE 1C.2

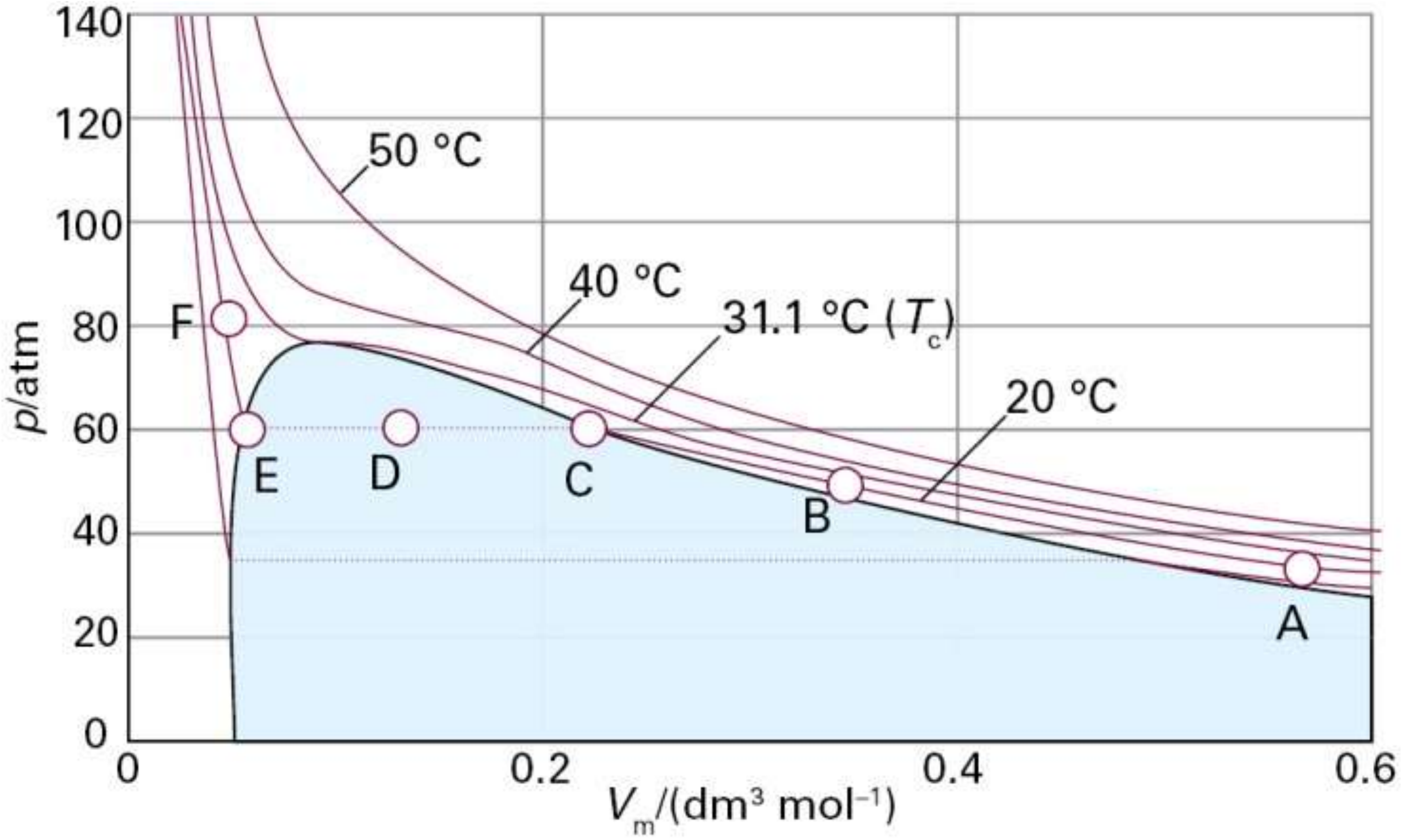


Figure 1C.2 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.1 °C.

CHAPTER 1: FIGURE 1C.3

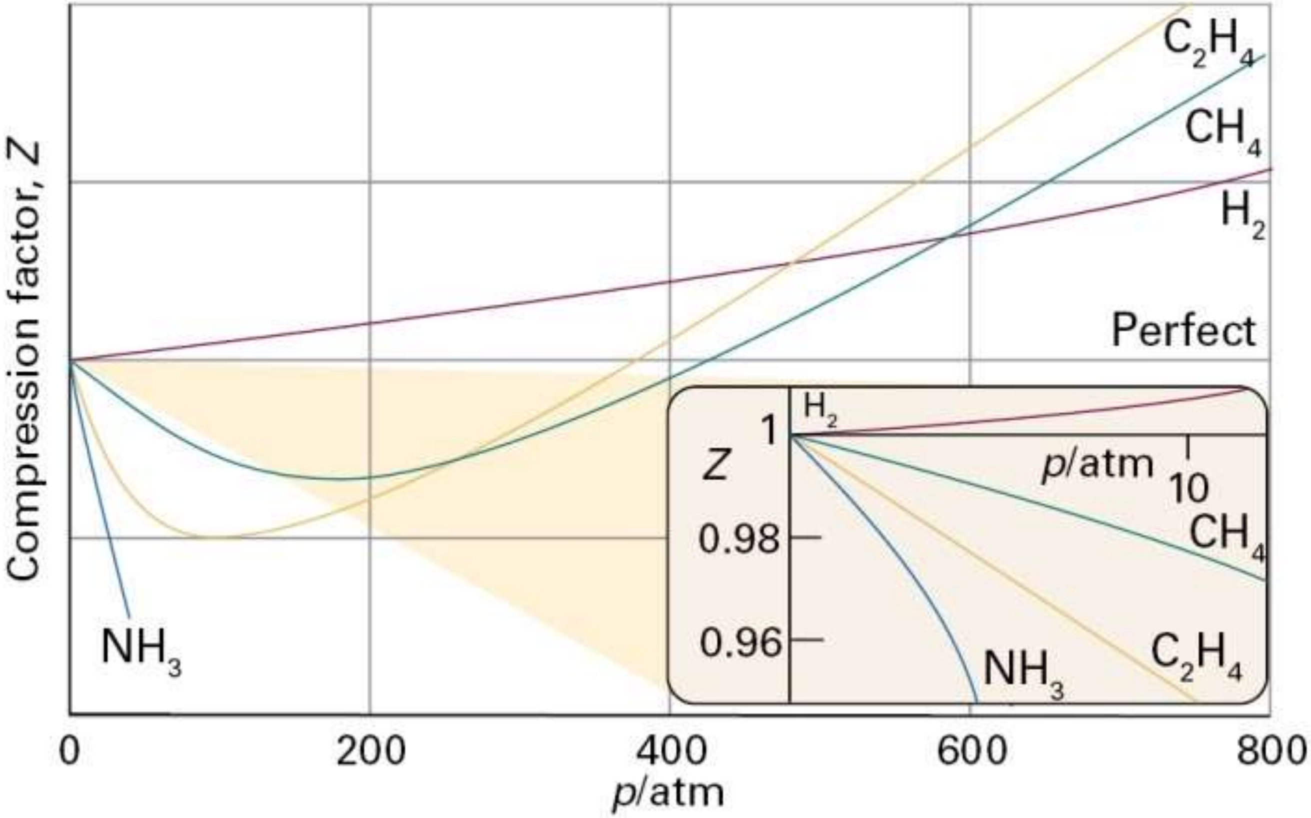


Figure 1C.3 The variation of the compression factor, Z, with pressure for several gases at 0 °C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

CHAPTER 1: TABLE 1C.1

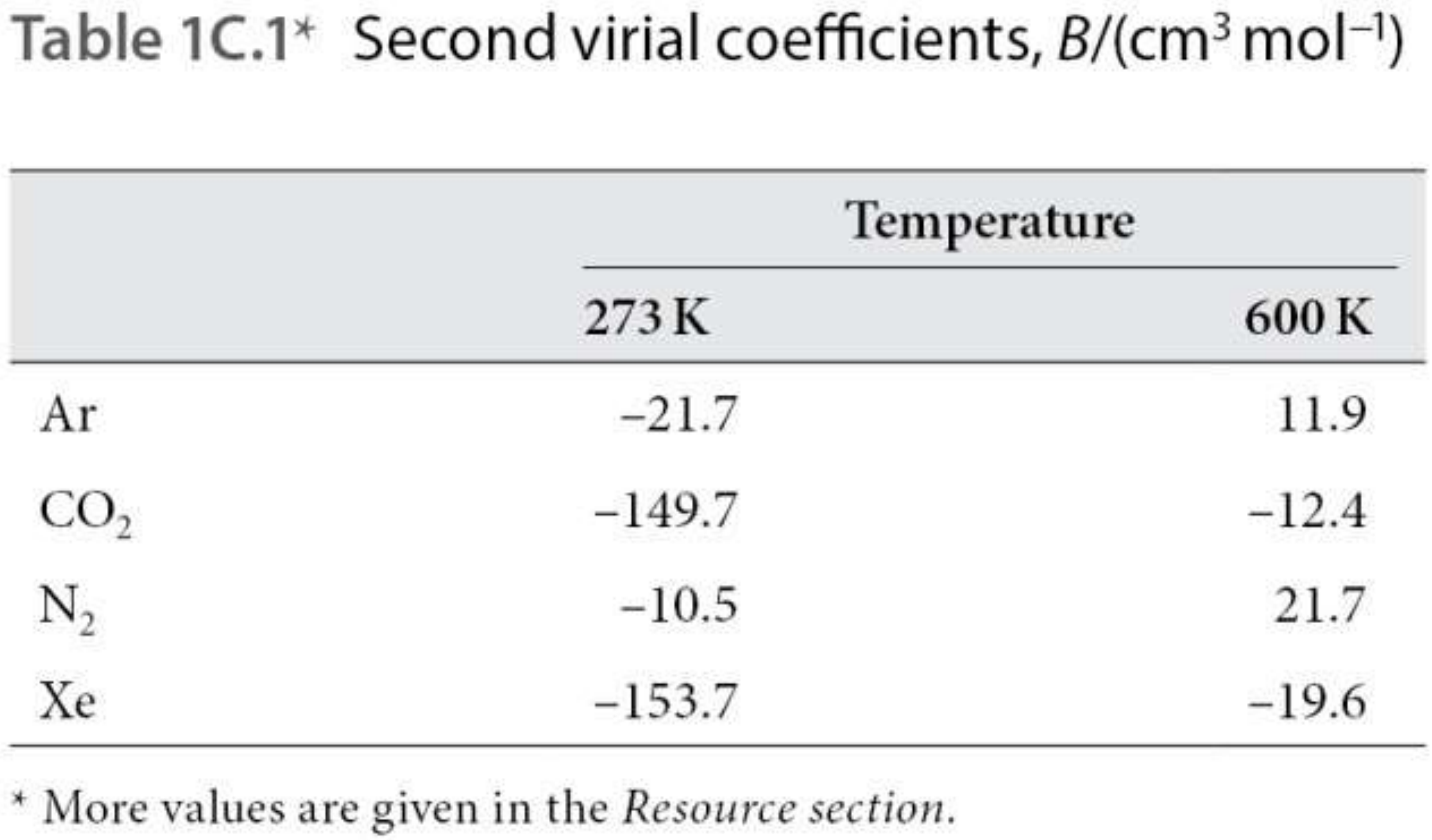


Table 1C.1* Second virial coefficients, $B/(\mathrm{cm^3\,mol^{-1}})$

	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 *Resource section*.

CHAPTER 1: FIGURE 1C.4

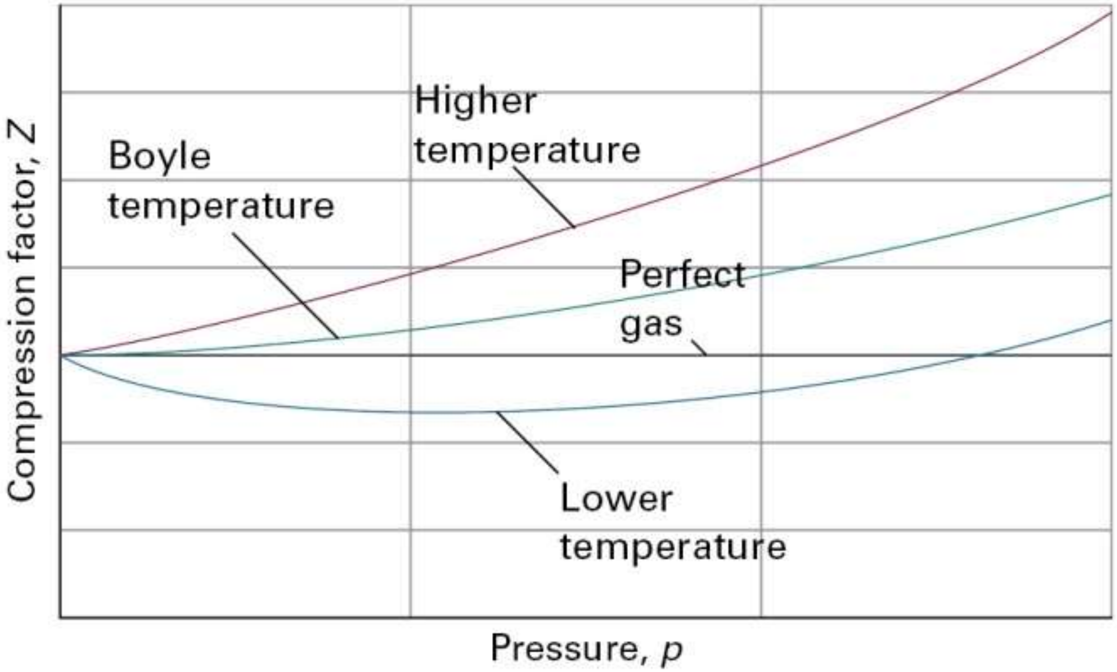


Figure 1C.4 The compression factor, Z, approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

CHAPTER 1: TABLE 1C.2

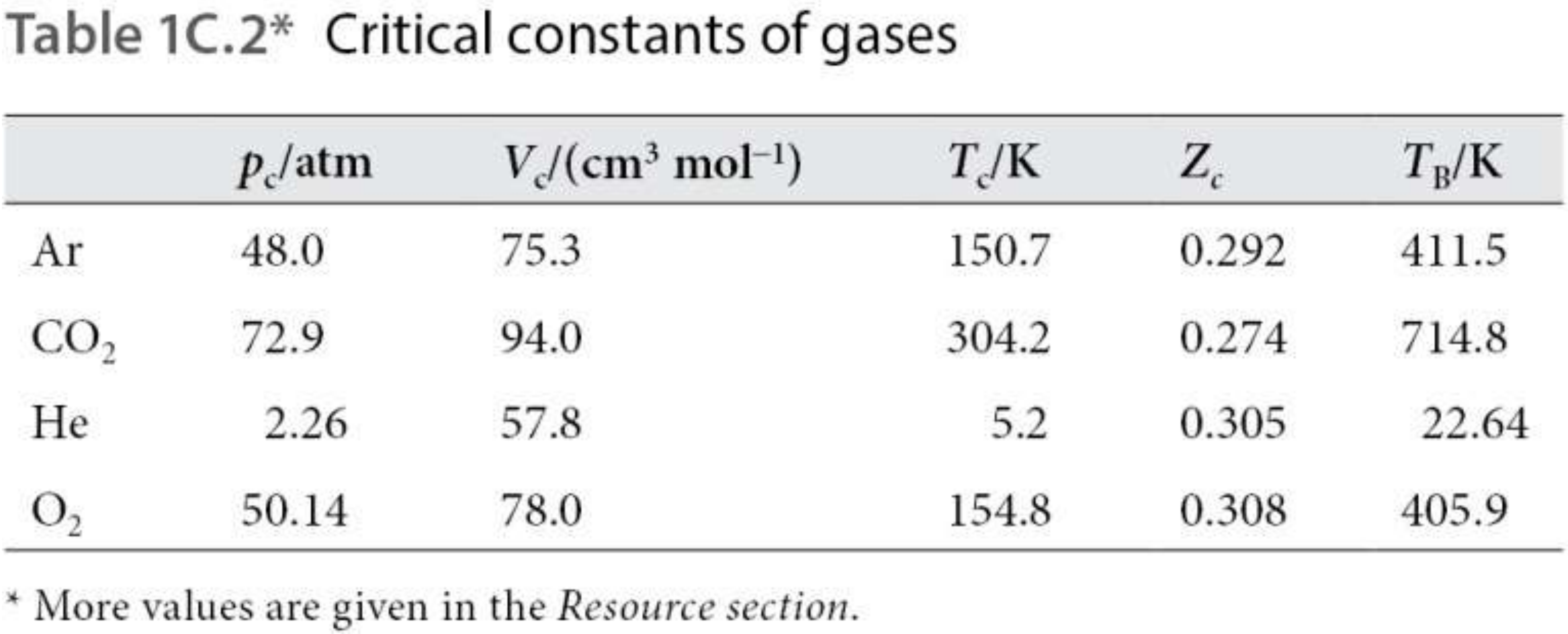


Table 1C.2* Critical constants of gases

	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 *Resource section*.

CHAPTER 1: TABLE 1C.3

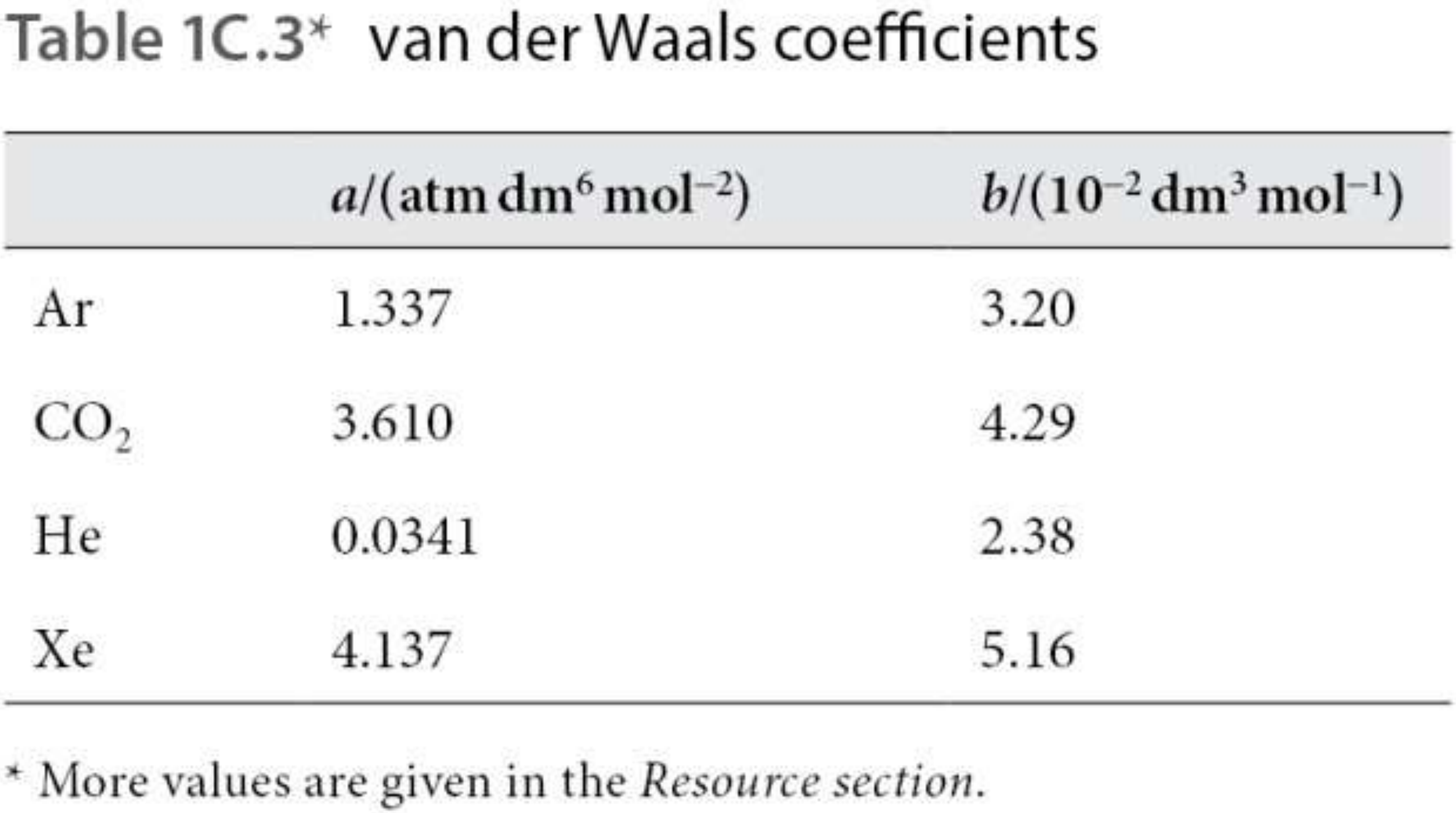


Table 1C.3* van der Waals coefficients

	$a/(\mathrm{atm\ dm^6\ mol^{-2}})$	$b/(10^{-2}\ \mathrm{dm^3\ mol^{-1}})$
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 *Resource section*.

CHAPTER 1: FIGURE 1C.5

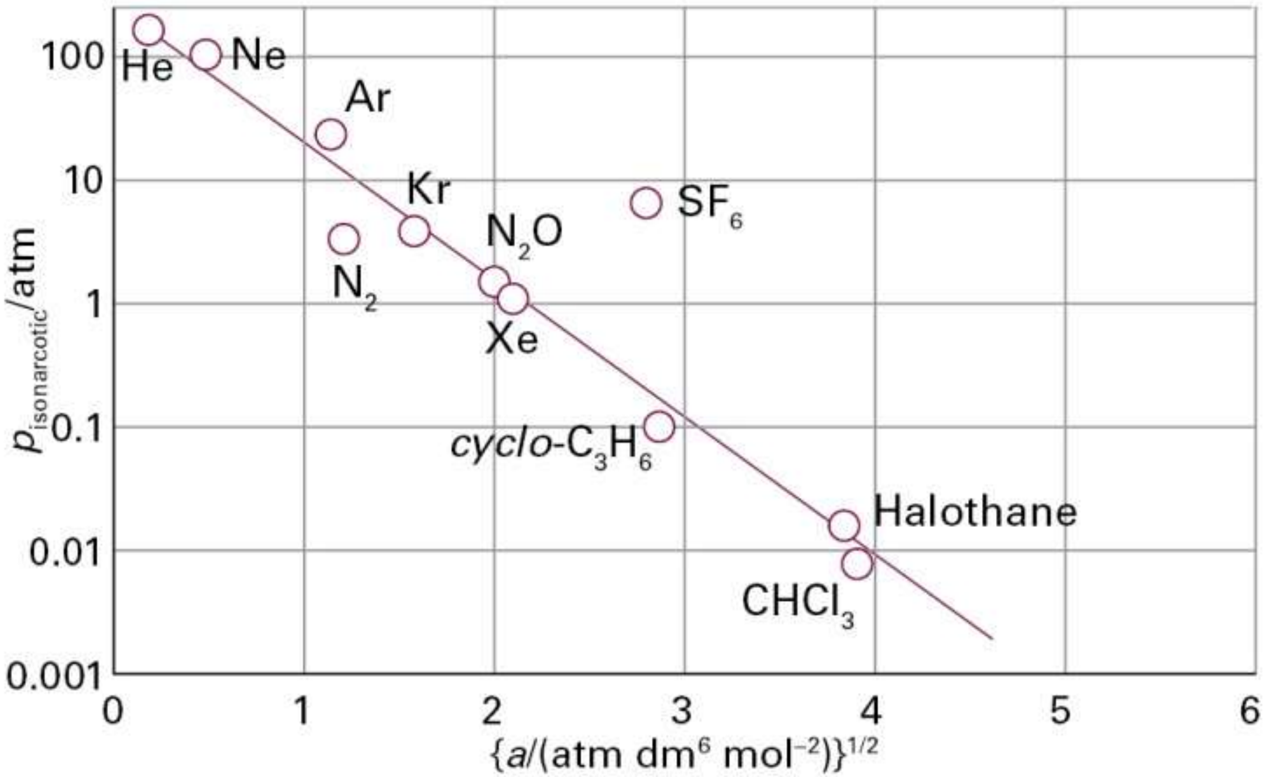


Figure 1C.5 The correlation of the effectiveness of a gas as an anaesthetic and the van der Waals parameter *a*. (Based on R.J. Wulf and R.M. Featherstone, *Anesthesiology* **18**, 97 (1957).) The isonarcotic pressure is the pressure required to bring about the same degree of anaesthesia.

CHAPTER 1: FIGURE 1C.6

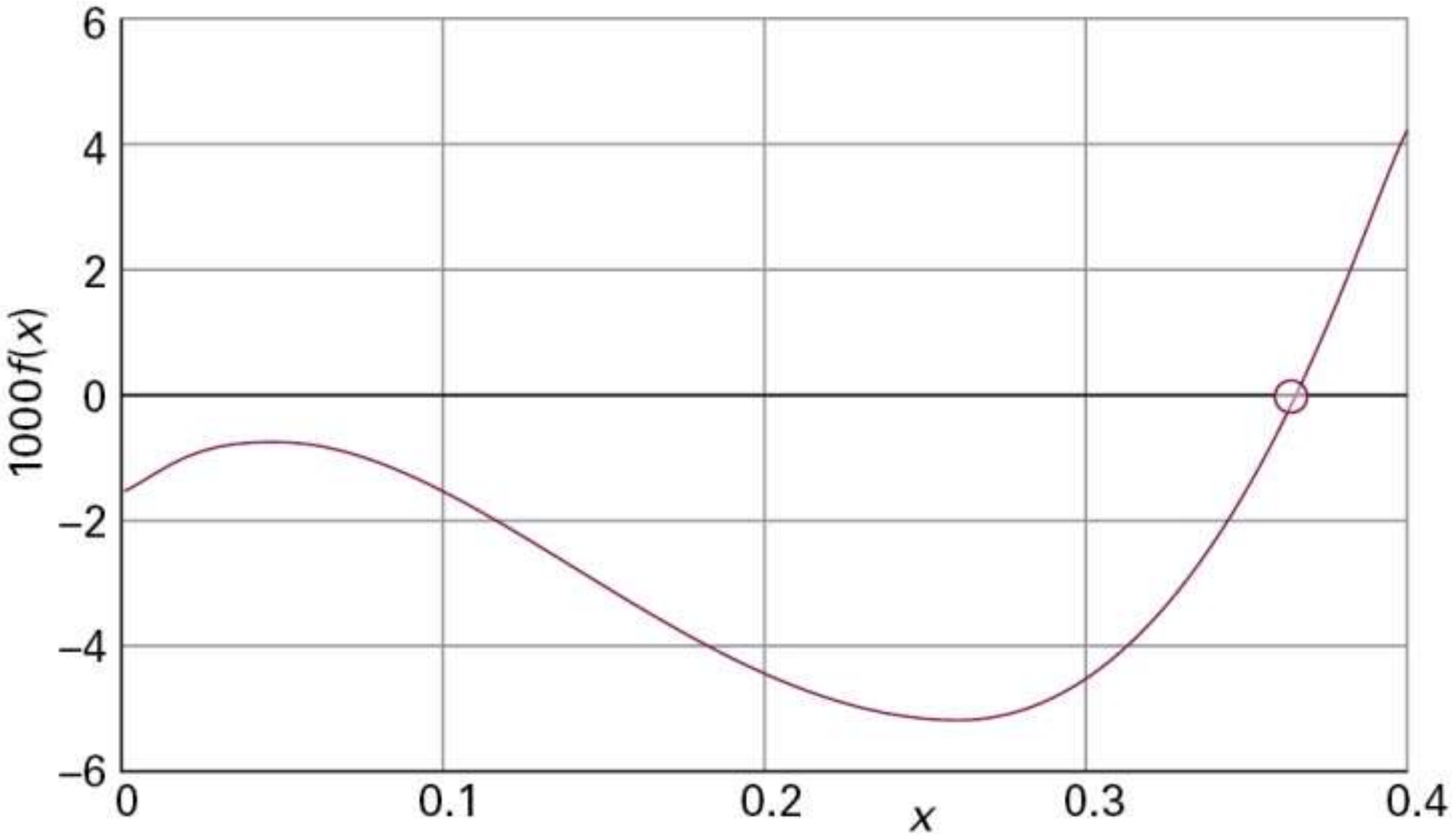


Figure 1C.6 The graphical solution of the cubic equation for V in *Example* 1C.1.

CHAPTER 1: TABLE 1C.4

Table 1C.4 Selected equations of state

			Critical constants		
	Equation	**Reduced form***	p_c	V_c	T_c
Perfect gas	$p=\frac{nRT}{V}$				
van der Waals	$p=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}$	$p_r=\frac{8T_r}{3V_r-1}-\frac{3}{V_r^2}$	$\frac{a}{27b^2}$	$3b$	$\frac{8a}{27bR}$
Berthelot	$p=\frac{nRT}{V-nb}-\frac{n^2a}{TV^2}$	$p_r=\frac{8T_r}{3V_r-1}-\frac{3}{T_rV_r^2}$	$\frac{1}{12}\left(\frac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\frac{2}{3}\left(\frac{2a}{3bR}\right)^{1/2}$
Dieterici	$p=\frac{nRTe^{-aRTV/n}}{V-nb}$	$p_r=\frac{T_re^{2(1-1/T_rV_r)}}{2V_r-1}$	$\frac{a}{4e^2b^2}$	$2b$	$\frac{a}{4bR}$
Virial	$p=\frac{nRT}{V}\left\{1+\frac{nB(T)}{V}+\frac{n^2C(T)}{V^2}+\cdots\right\}$				

* Reduced variables are defined in Section 1C.2(c). Equations of state are sometimes expressed in terms of the molar volume, $V_m=V/n$.

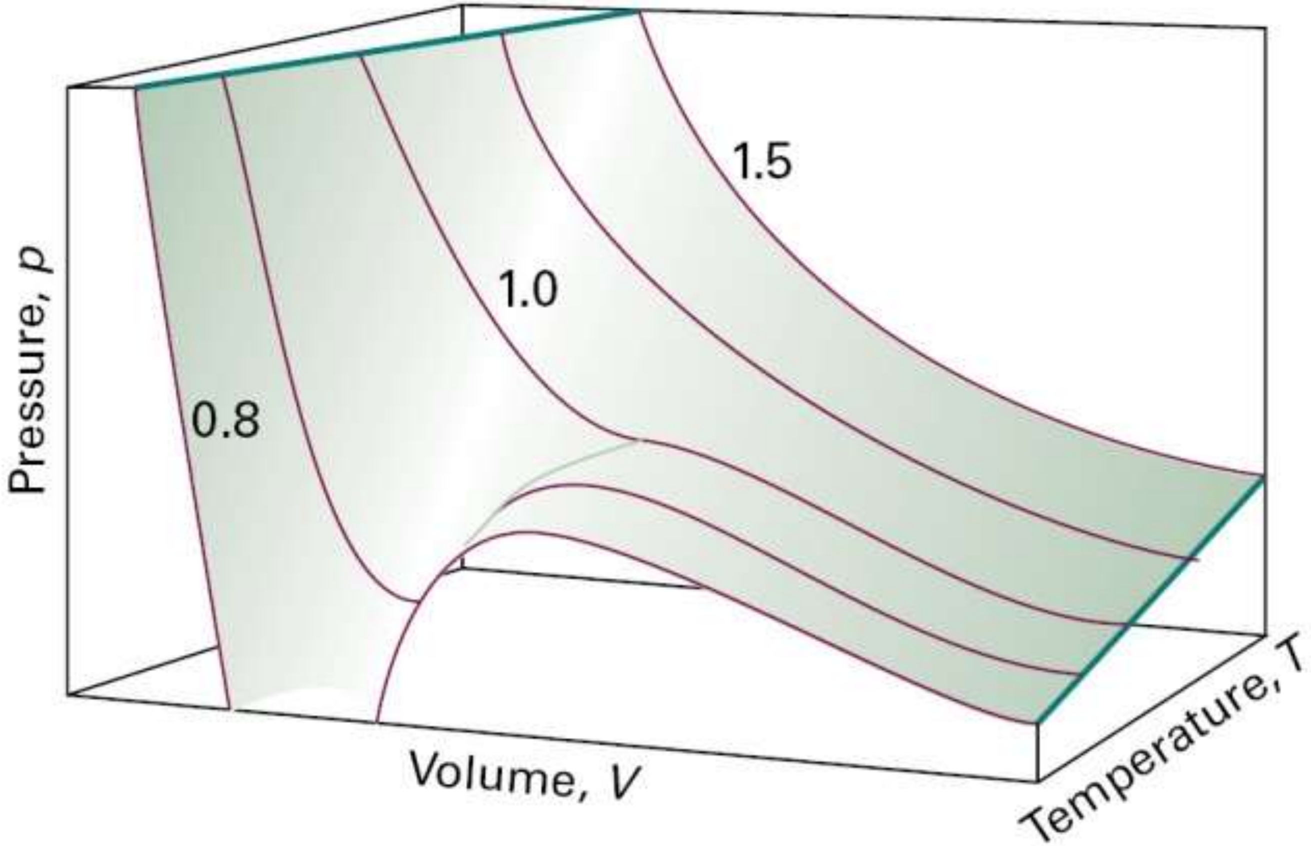


Figure 1C.7 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1C.8.

CHAPTER 1: FIGURE 1C.8

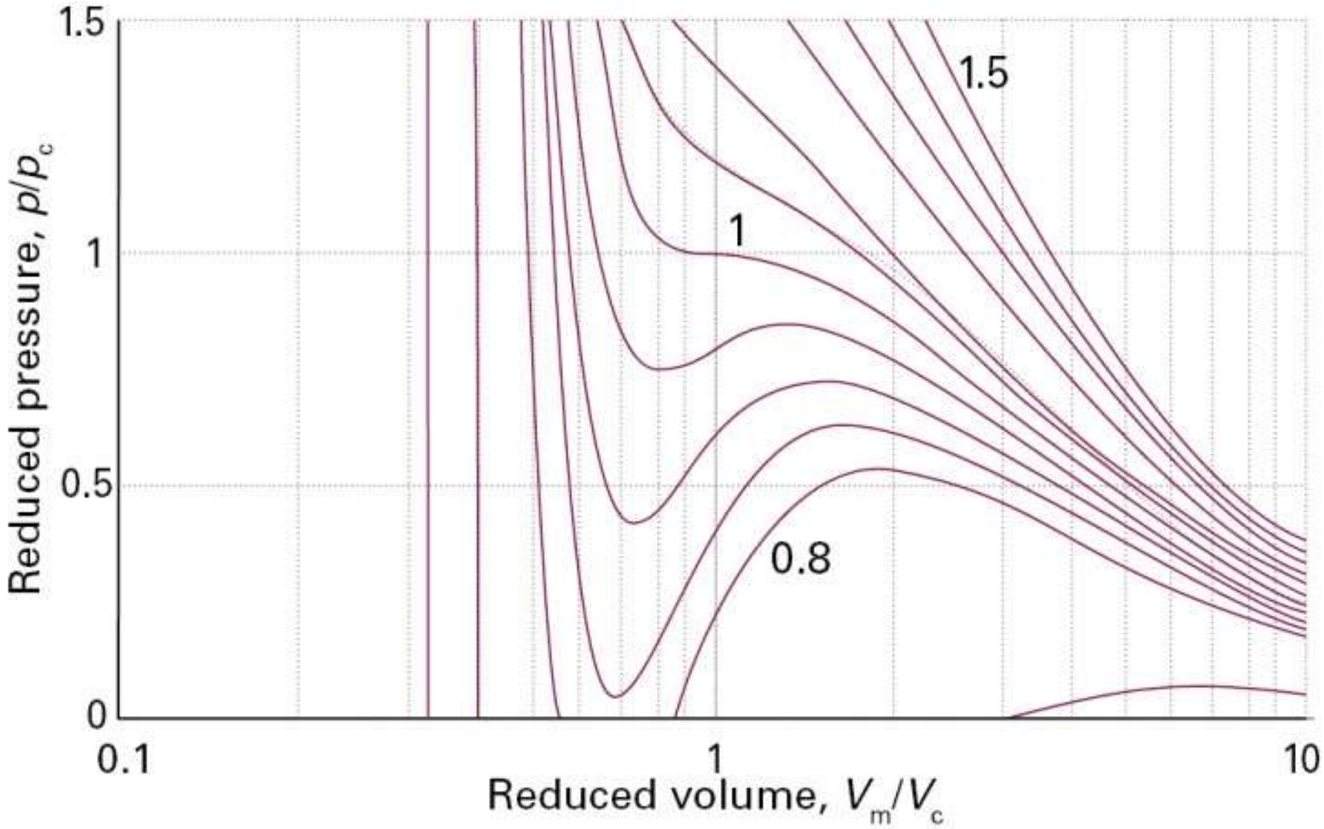


Figure 1C.8 van der Waals isotherms at several values of T/T_c. Compare these curves with those in Fig. 1C.2. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$.

CHAPTER 1: FIGURE 1C.9

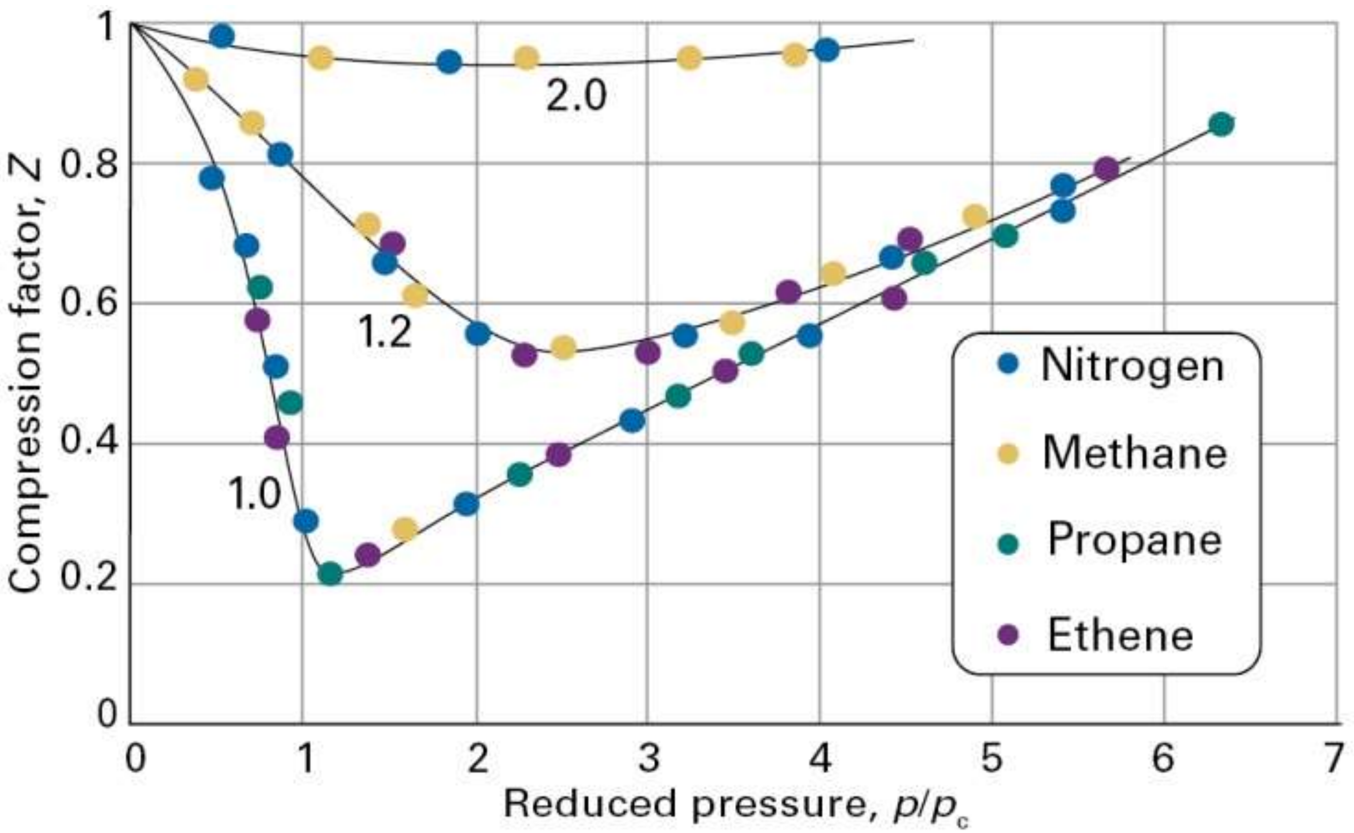


Figure 1C.9 The compression factors of four of the gases shown in Fig. 1C.3 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.

CHAPTER 1: FIGURE MB1.1

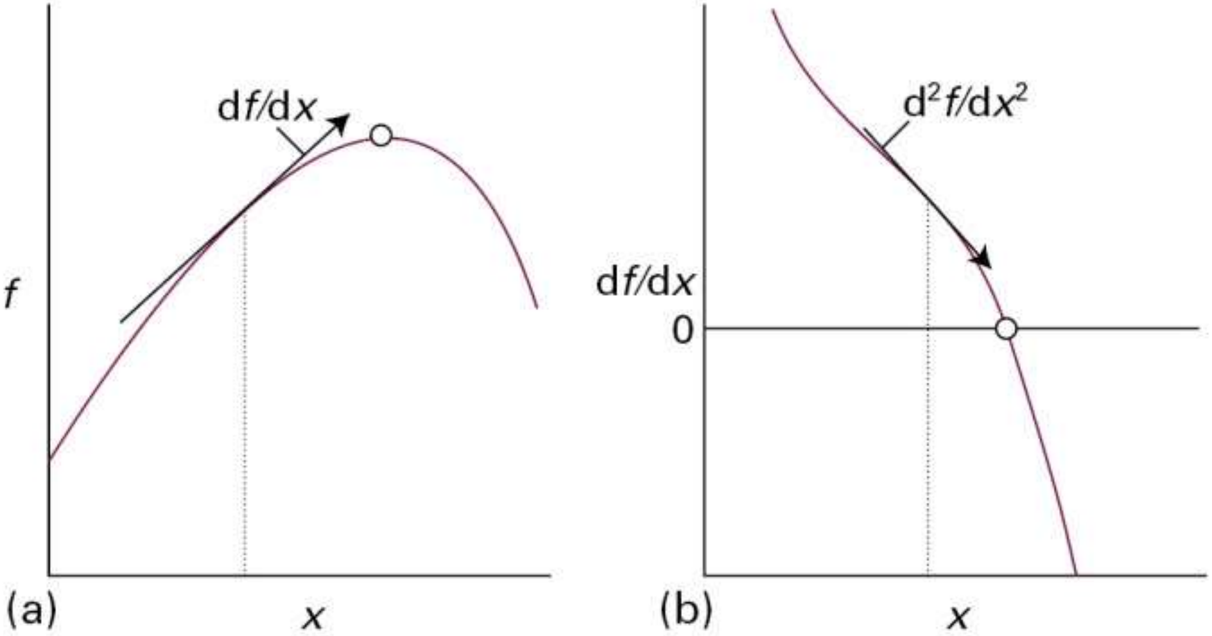


Figure MB1.1 (a) The first derivative of a function is equal to the slope of the tangent to the graph of the function at that point. The small circle indicates the extremum (in this case, maximum) of the function, where the slope is zero. (b) The second derivative of the same function is the slope of the tangent to a graph of the first derivative of the function. It can be interpreted as an indication of the curvature of the function at that point.

CHAPTER 1: FIGURE MB1.2

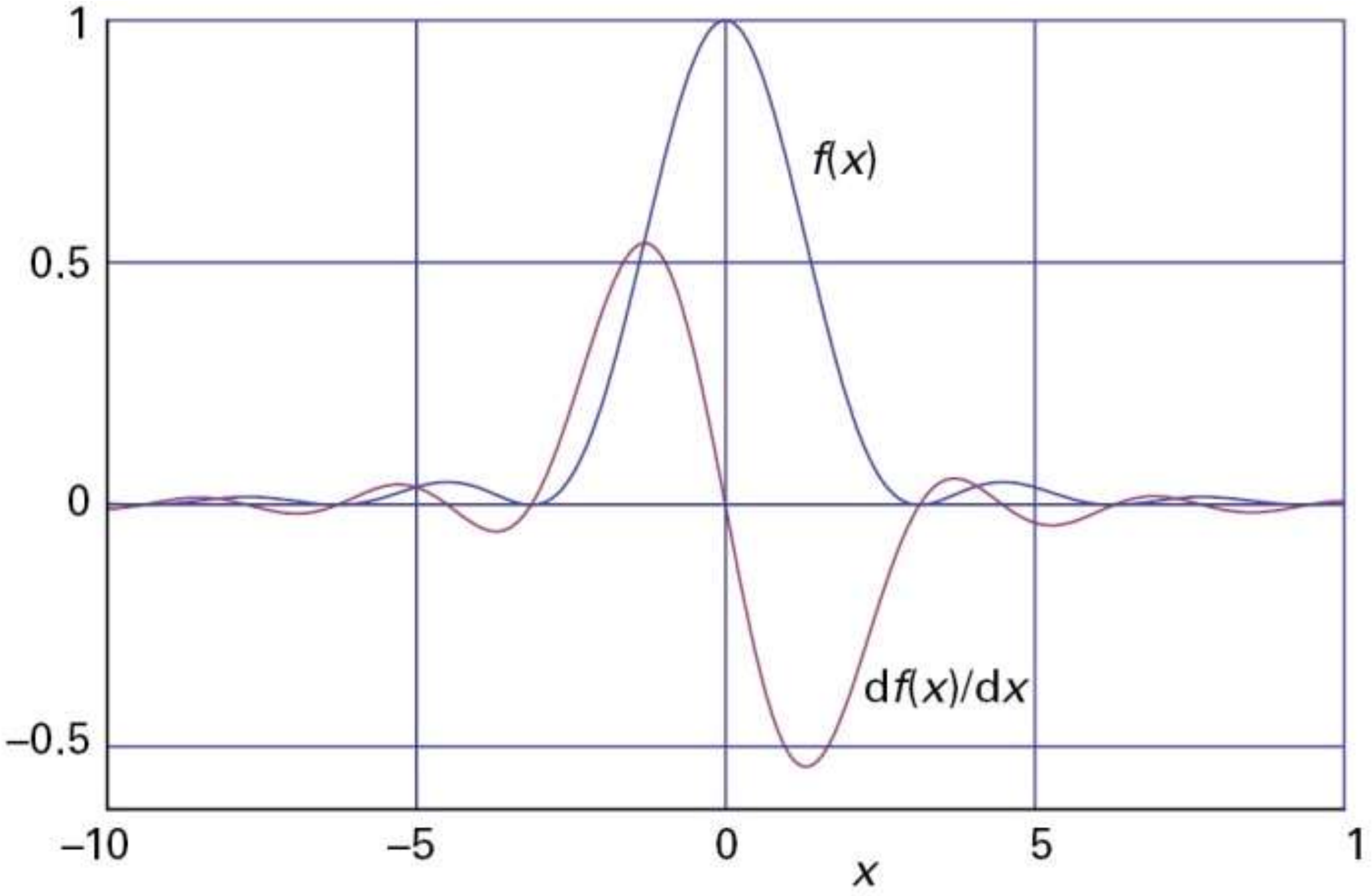


Figure MB1.2 The function considered in *Brief illustration* MB1.2 and its first derivative.

CHAPTER 1: FIGURE MB1.3

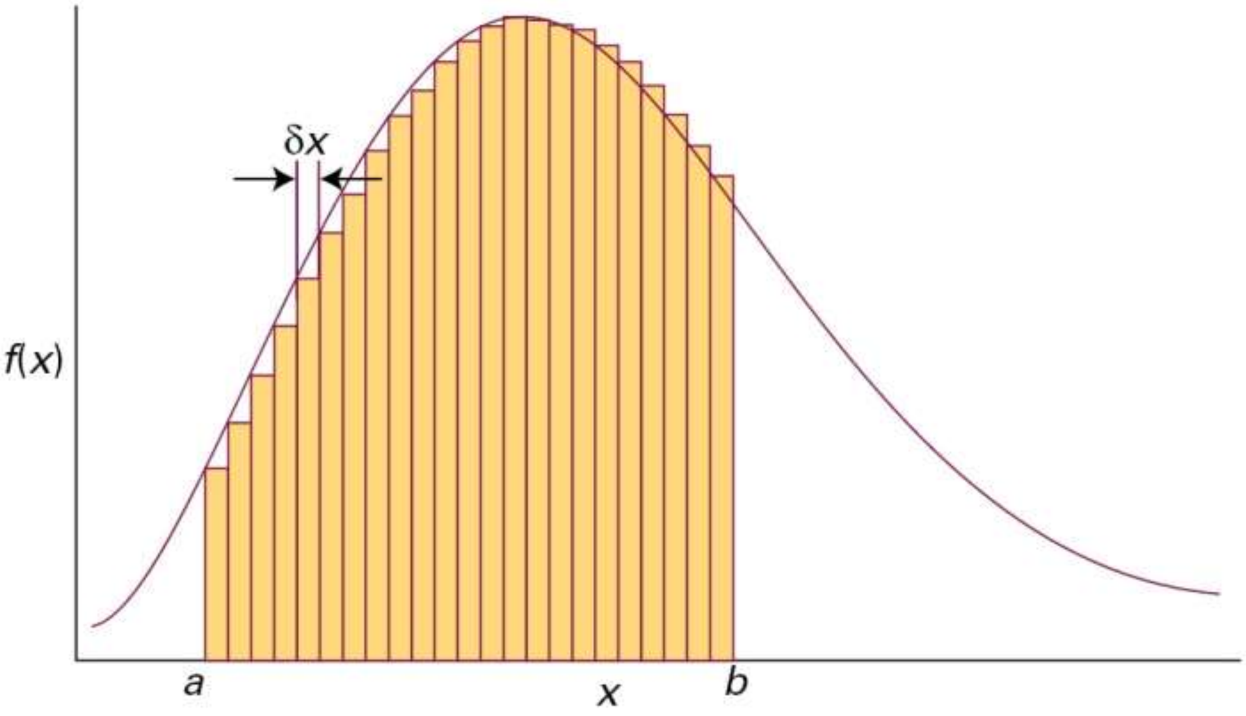


Figure MB1.3 A definite integral is evaluated by forming the product of the value of the function at each point and the increment δx, with $\delta x \rightarrow 0$, and then summing the products $f(x)\delta x$ for all values of x between the limits a and b. It follows that the value of the integral is the area under the curve between the two limits.