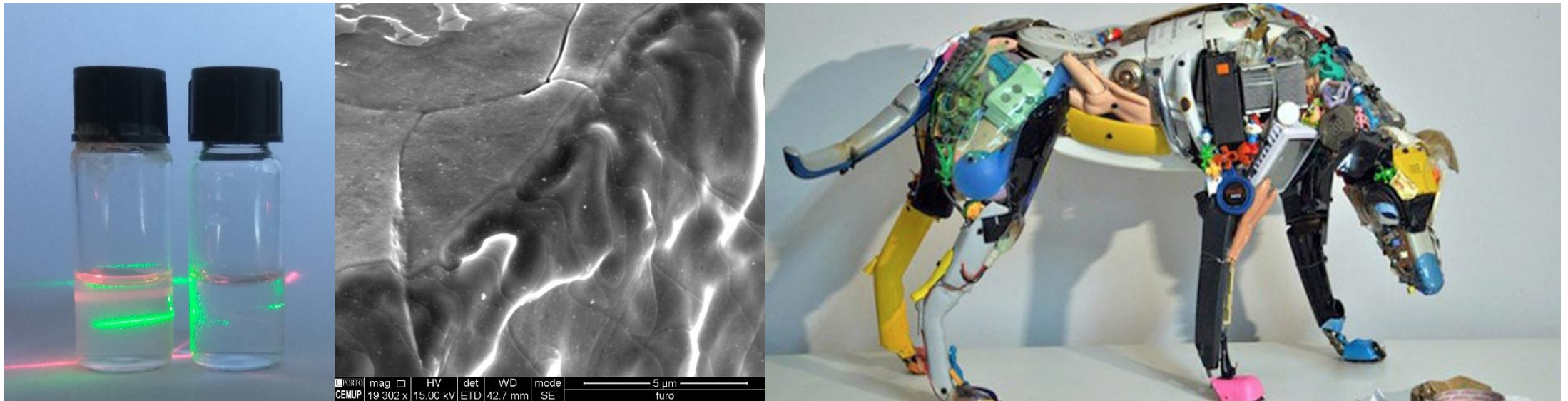


Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.



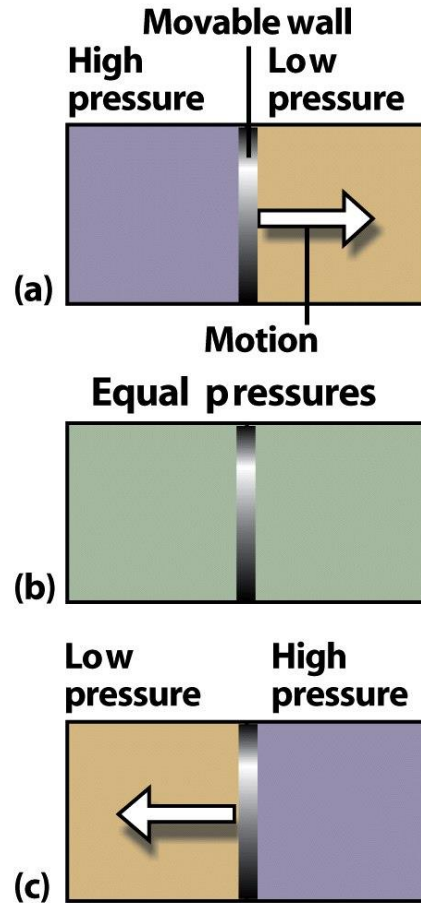


Figure 1-1
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Table 1.1 Pressure units

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

Table 1-1
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van der Waals ..equation

The van der Waals equation is

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

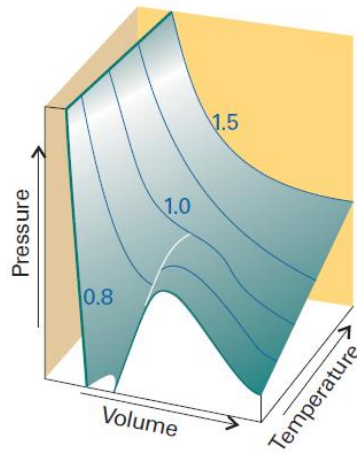


Fig. 1.17 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.

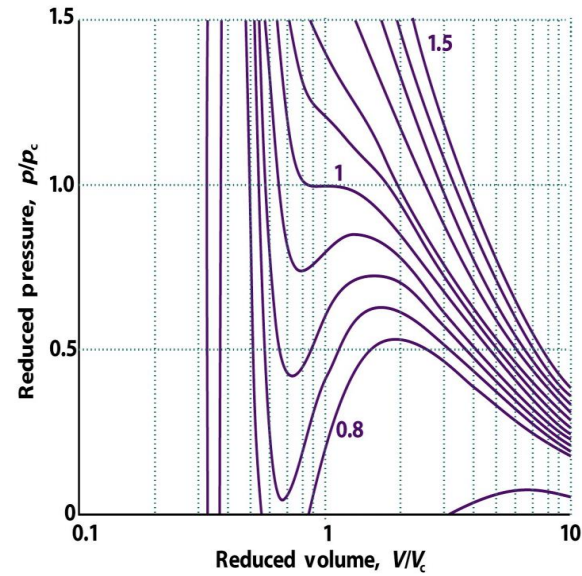


Figure 1-18
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Properties of Gases (EoS: p, V, T)

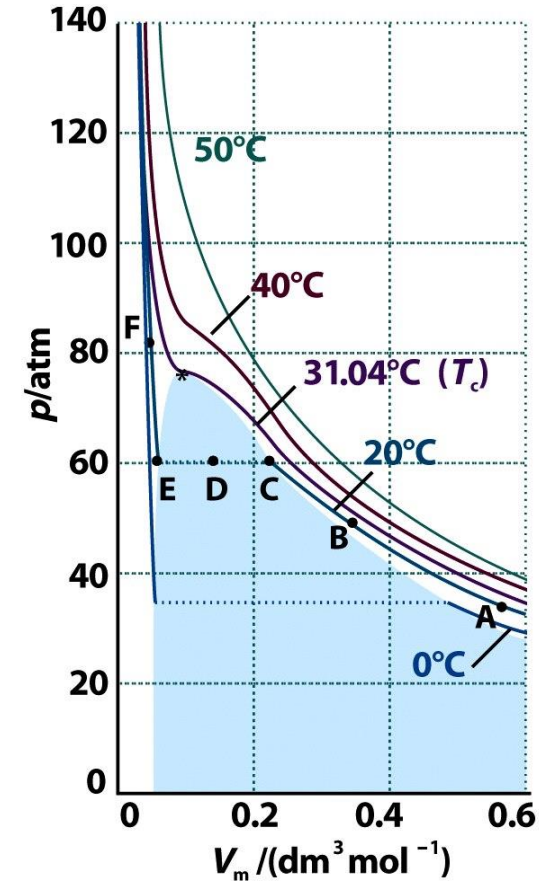


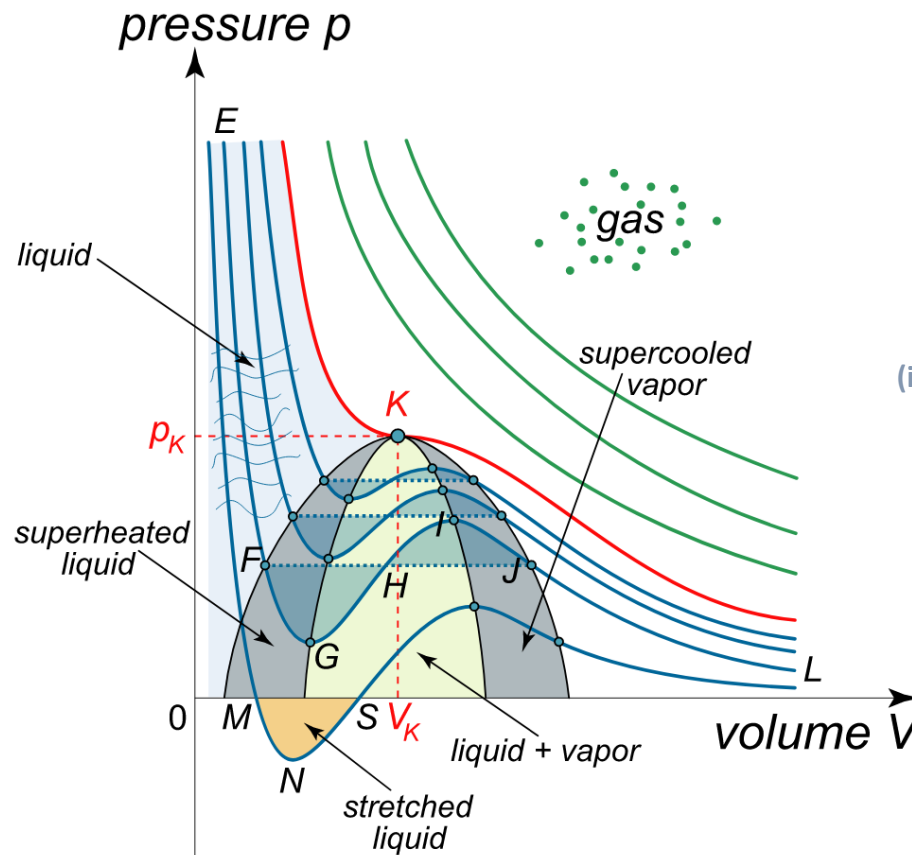
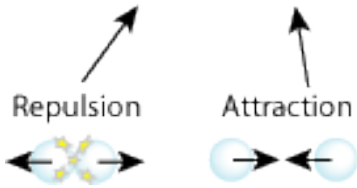
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van der Waals ..equation

Properties of Gases (EoS: p, V, T)

van der Waals ...equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$



$$Z = \frac{V_m}{V_m^0}$$

$$Z = \frac{RT/p}{V_m^0}$$

(ideal vol) $V_m = RT/p$

$$pV_m = RT \cdot Z$$

(Real gas)

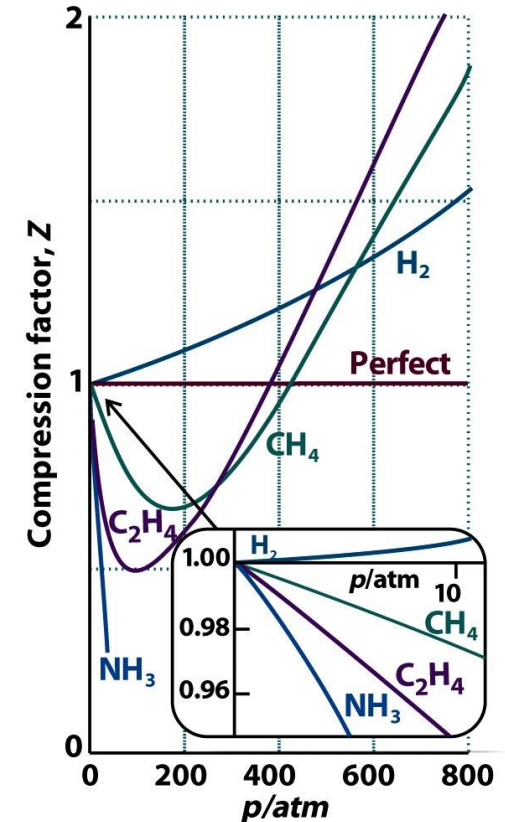


Figure 1-14
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van der Waals ..equation

Properties of Gases (EoS: p, V, T)

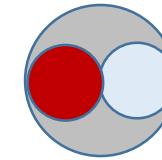
Approximate equation of state **EoS**

J.D. van der Waals in 1873

moving in a **volume V** ...they are restricted to a smaller volume $V - nb$

$$p = \frac{RT}{V_m - b} \longrightarrow b \approx 4V_{\text{molecule}}N_A$$

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



Restriction
 $2 \times r$ (molecular)

Volume:
 $4V = 2^2 \times V$ (molecular)

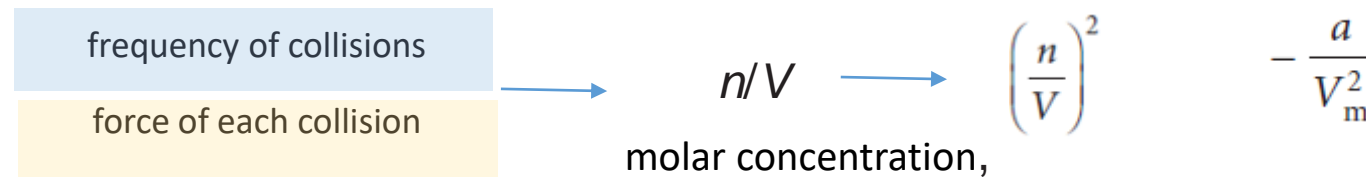
volume excluded is $\frac{4}{3}\pi(2r)^3$

$8V_{\text{molecule}}$

The van der Waals equation is

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

attractive forces, the pressure is reduced in proportion to the **square** of this concentration



van der Waals ..equation

Properties of Gases (EoS: p, V, T)

The van der Waals equation is

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

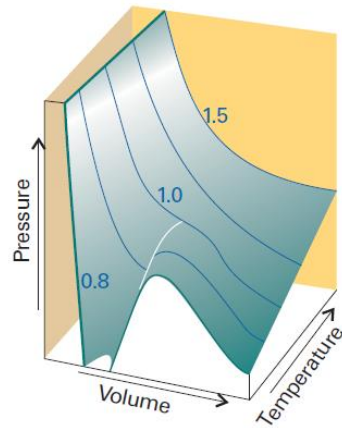
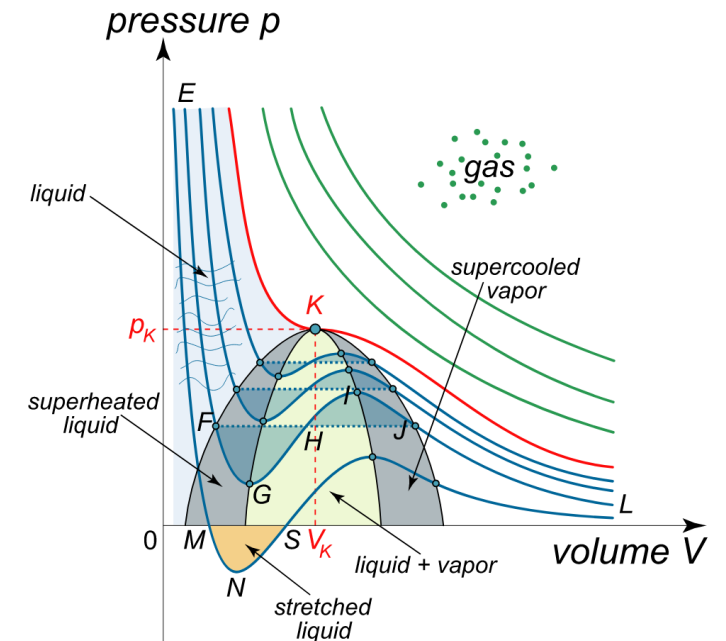
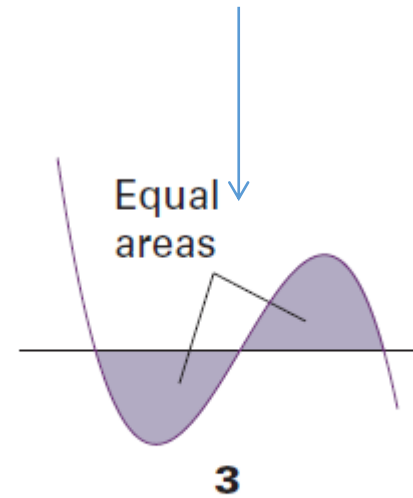


Fig. 1.17 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.

The oscillations, the **van der Waals loops**, are unrealistic because they suggest that under some conditions an increase of pressure results in an increase of volume



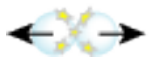
van der Waals ..equation

Properties of Gases (EoS: p, V, T)


van der Waals ...equation

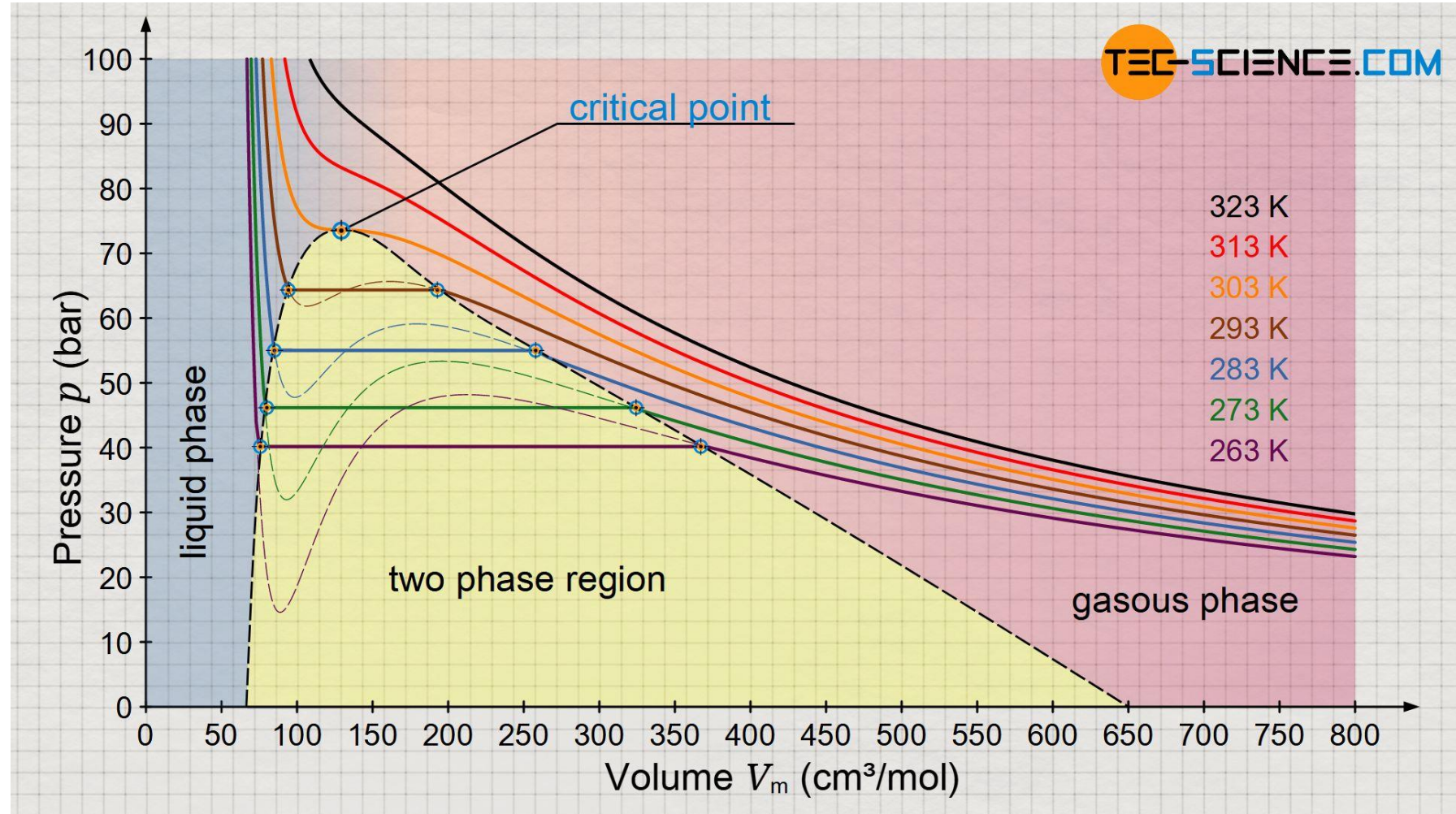
$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Repulsion



Attraction





Critical point

T_c = Critical temperature

p_c = Critical pressure

V_c = Critical Volume

Critical point

T_c, p_c, V_c

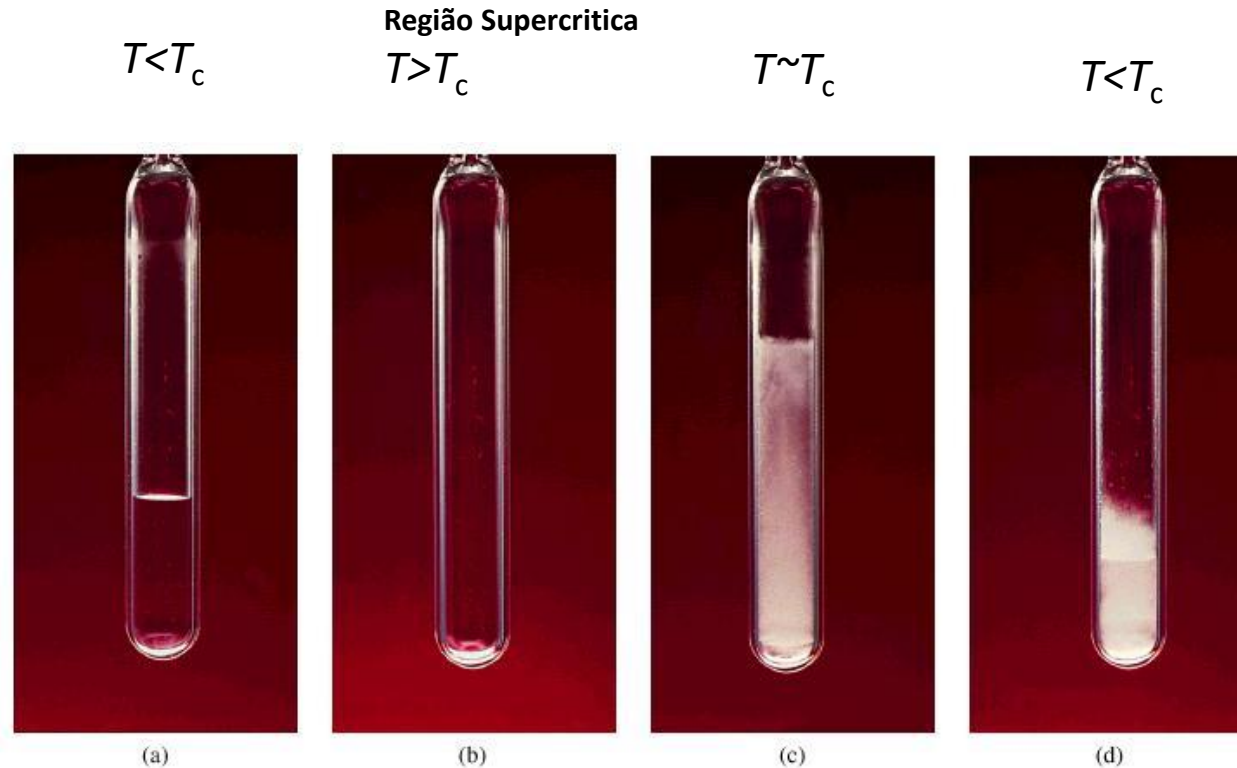


FIGURE 11.37 The critical phenomenon of sulfur hexafluoride. (a) Below the critical temperature the clear liquid phase is visible. (b) Above the critical temperature the liquid phase has disappeared. (c) The substance is cooled just below its critical temperature. The fog represents the condensation of vapor. (d) Finally, the liquid phase reappears.

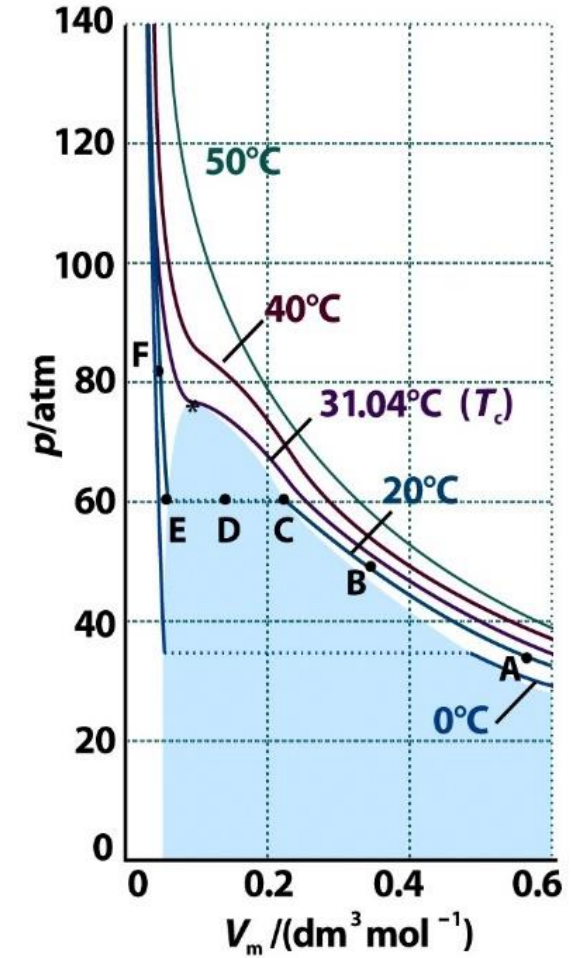


Figure 1-15
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van der Waals ..equation

Properties of Gases (EoS: p, V, T)

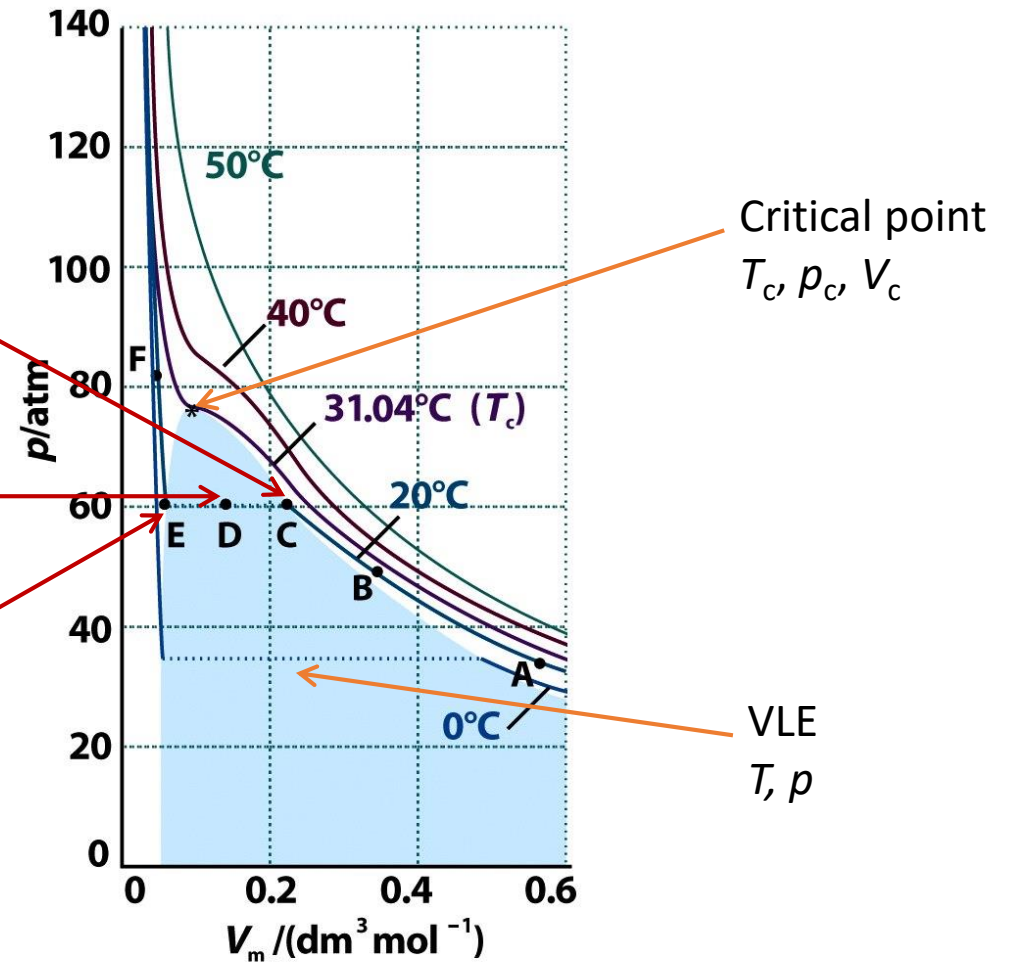
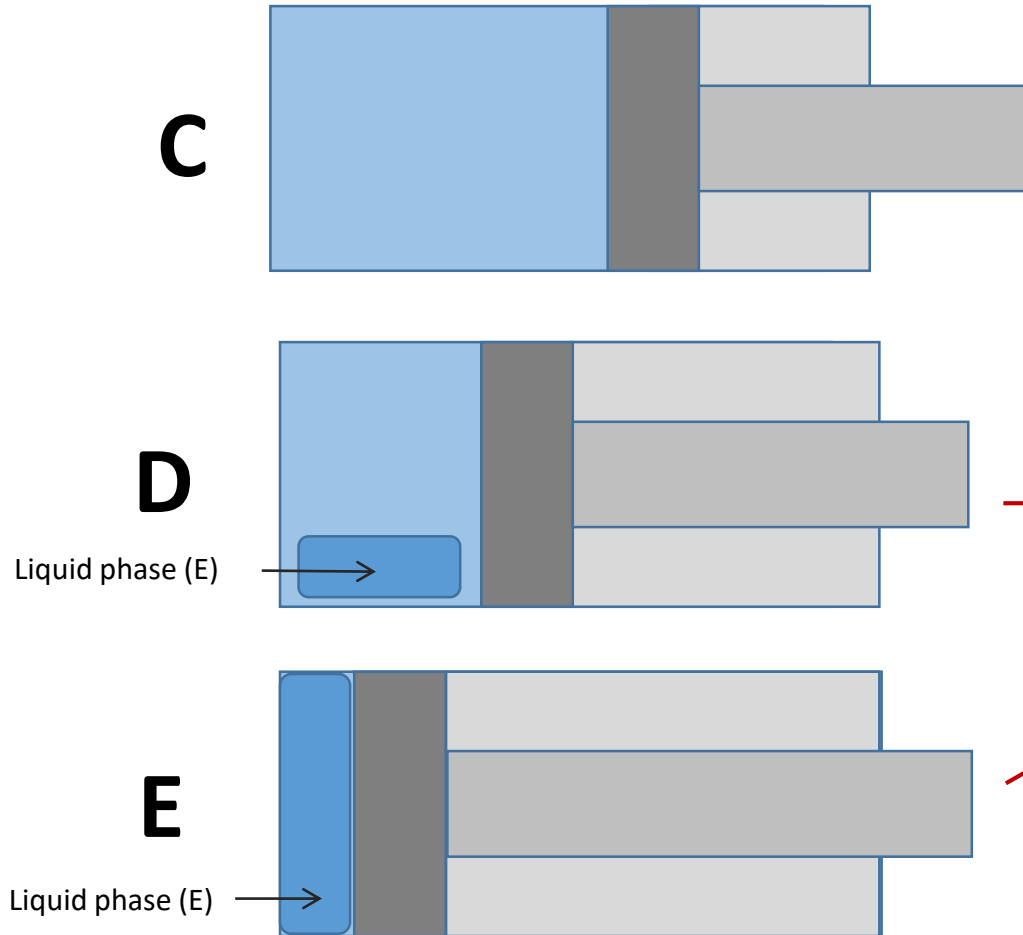


Figure 1-15
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reduced pressure

$$p_r = \frac{p}{p_c}$$

reduced volume

$$V_r = \frac{V_m}{V_c}$$

reduced temperature

$$T_r = \frac{T}{T_c}$$

The principle of corresponding states

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**.

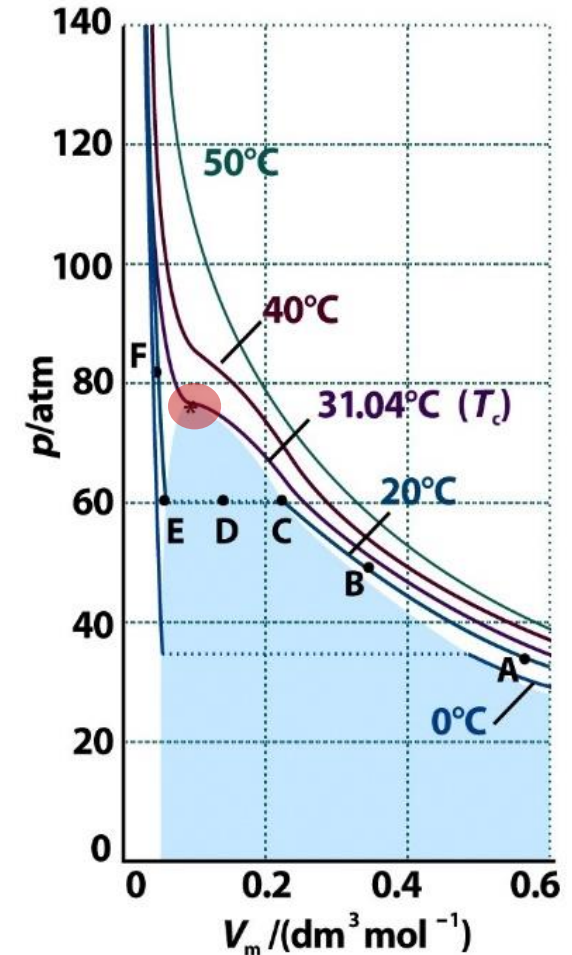


Figure 1-15
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The principle of corresponding states

$$p_r = \frac{p}{p_c} \quad V_r = \frac{V_m}{V_c} \quad T_r = \frac{T}{T_c}$$

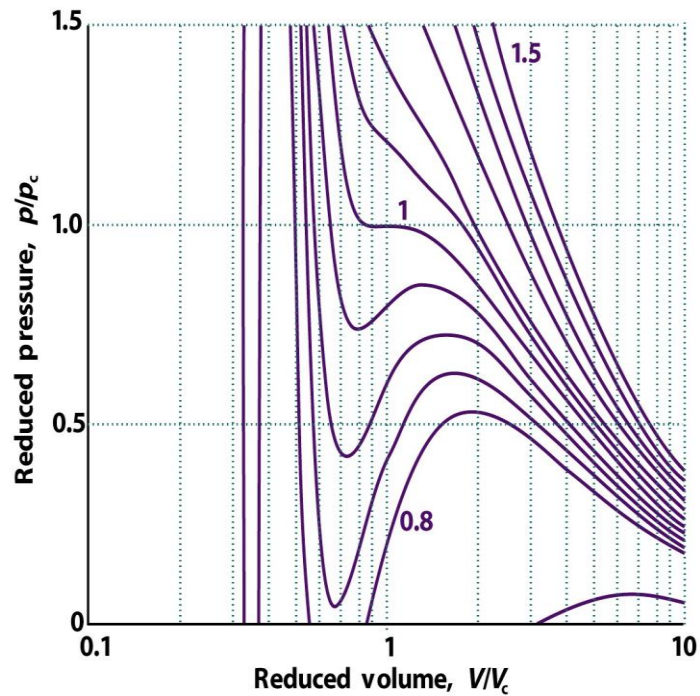
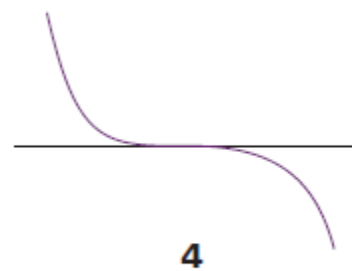


Figure 1-18
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T_c = Critical temperature



The van der Waals equation is

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

$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$$

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

$$V_c = 3b \quad p_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb}$$

The principle of corresponding states

$$p_r = \frac{p}{p_c} \quad V_r = \frac{V_m}{V_c} \quad T_r = \frac{T}{T_c}$$

The van der Waals equation is

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

$$V_c = 3b \quad p_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb}$$

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

SAME FOR ALL GASES!

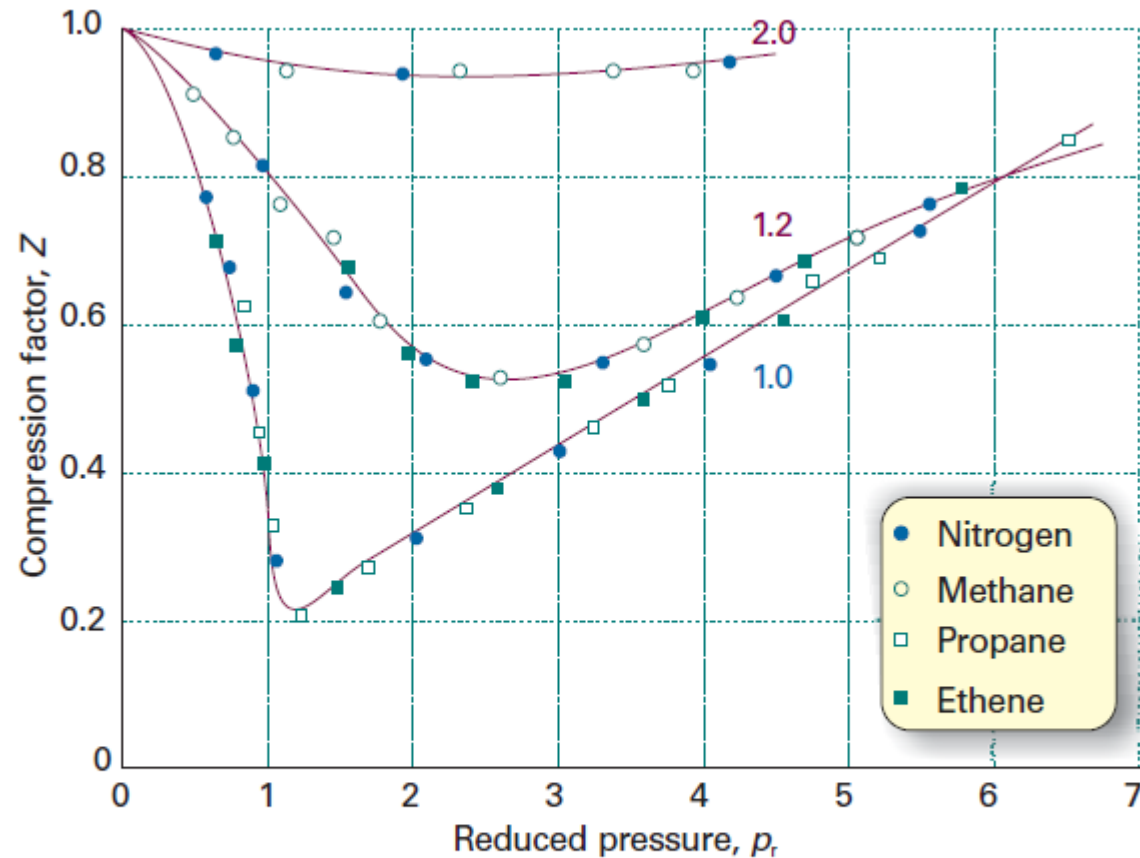


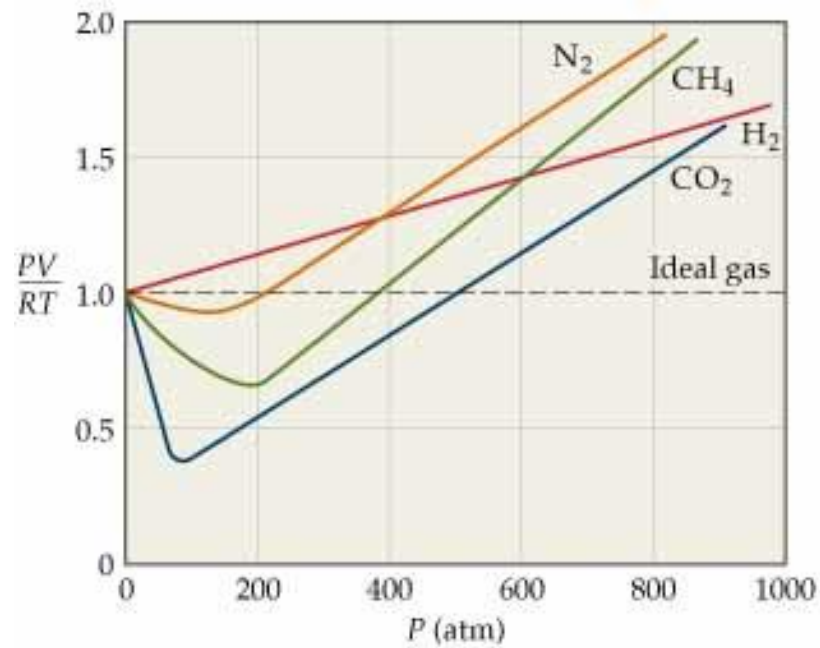
Fig. 1.19 The compression factors of four of the gases shown in Fig. 1.14 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.

van der Waals ..equation

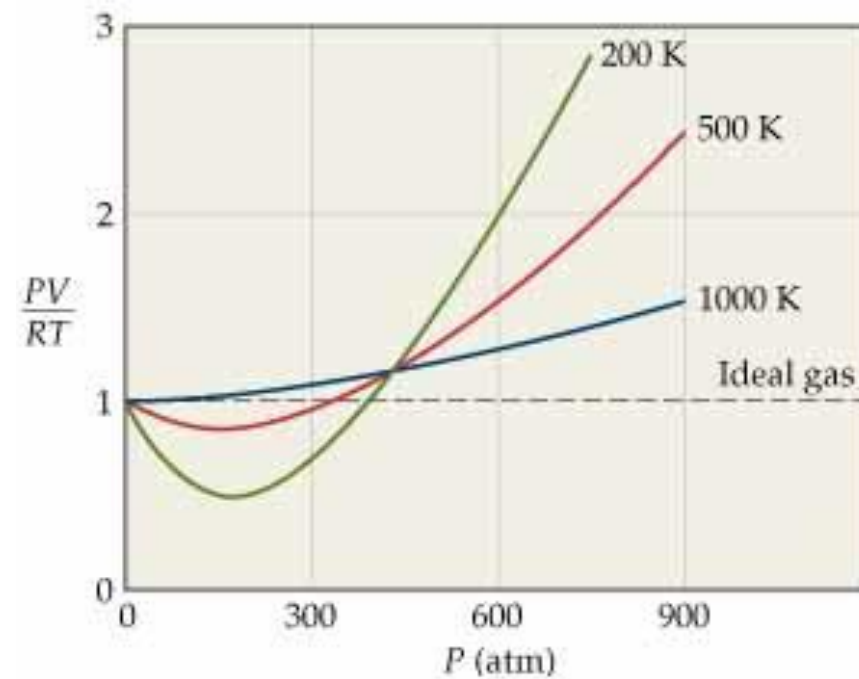
Properties of Gases (EoS: p, V, T)

van der Waals ...equation

Deviation from ideal behavior



1 mol of N_2



Virial coefficients

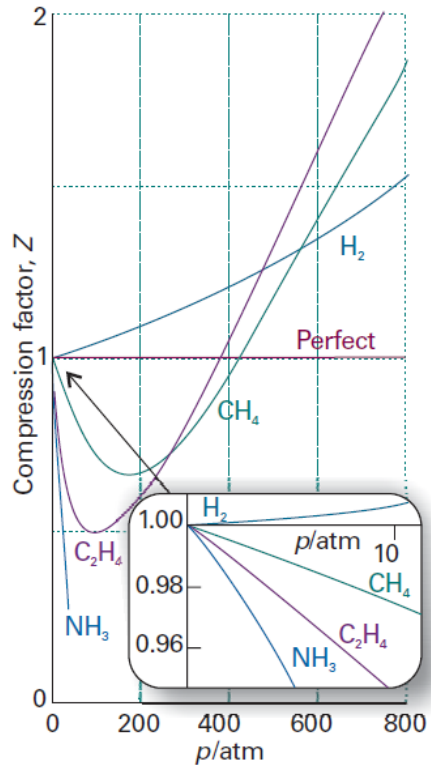


Fig. 1.14 The variation of the compression factor, Z , with pressure for several gases at 0°C . A perfect gas has $Z=1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

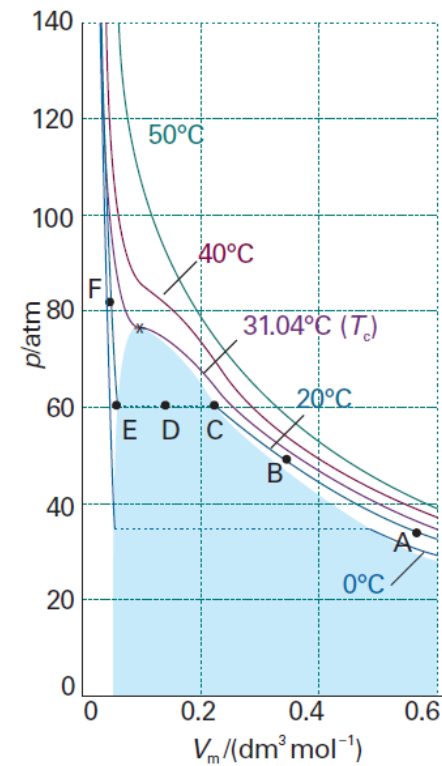


Fig. 1.15 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.04°C . The critical point is marked with a star.

Virial equations of state

$$pV_m = RT(1 + B'p + C'p^2 + \dots)$$

$$pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

$$pV_m = RT \cdot Z \quad \leftarrow \quad Z = \frac{V_m}{V_m^0} \quad V_m^0 = RT/p$$

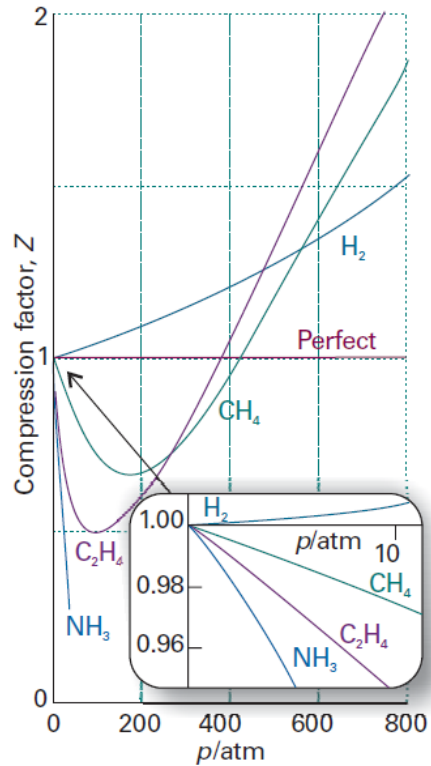


Fig. 1.14 The variation of the compression factor, Z , with pressure for several gases at 0°C . A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

Virial equations of state

$$pV_m = RT(1 + B'p + C'p^2 + \dots)$$

$$\frac{dZ}{dp} = B' + 2pC' + \dots \rightarrow B' \quad \text{as} \quad p \rightarrow 0$$

$$pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

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

Virial coefficients

TEMPERATURE DEPENDENCE

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

	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*.

$$pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

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

Fig. 1.16 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.

Synoptic Table 1.5* Critical constants of gases

	p_c/atm	$V_c/(\text{cm}^3 \text{ mol}^{-1})$	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*.

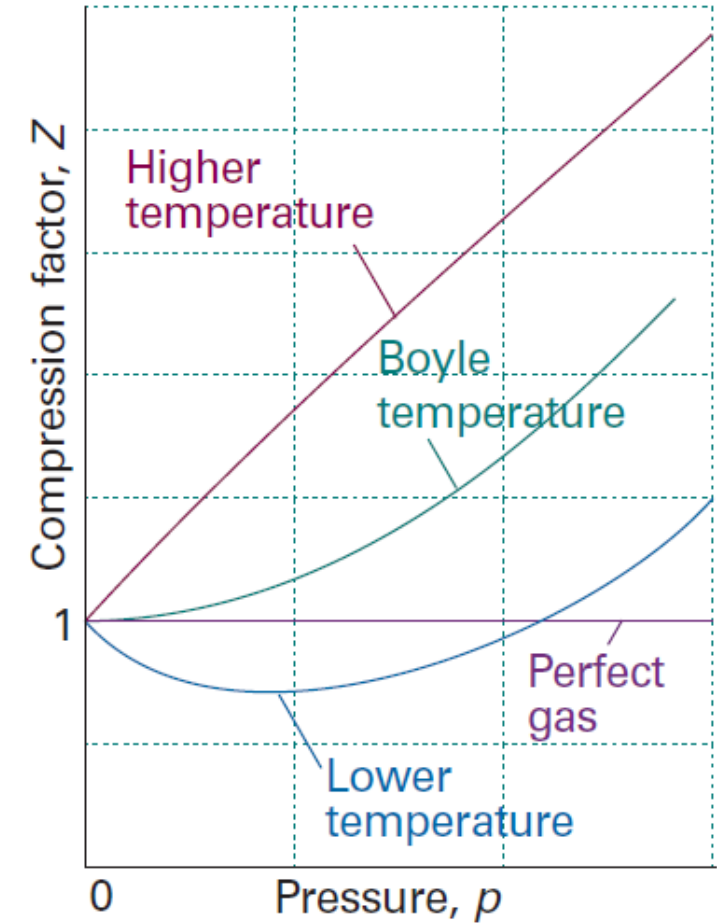
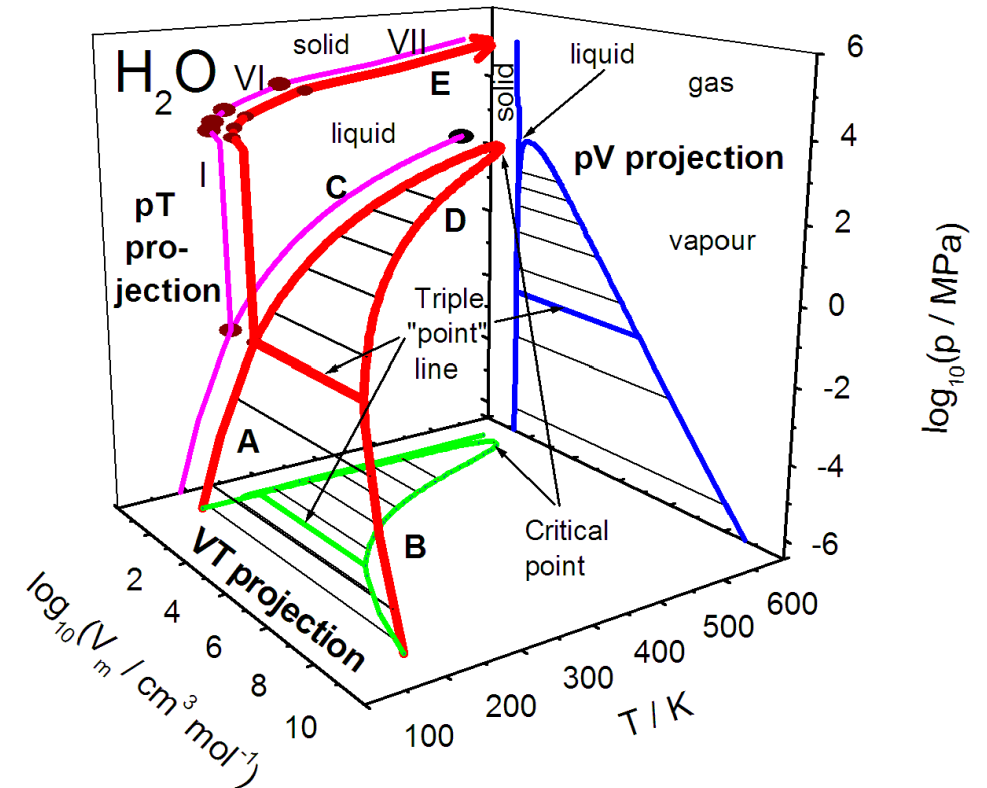
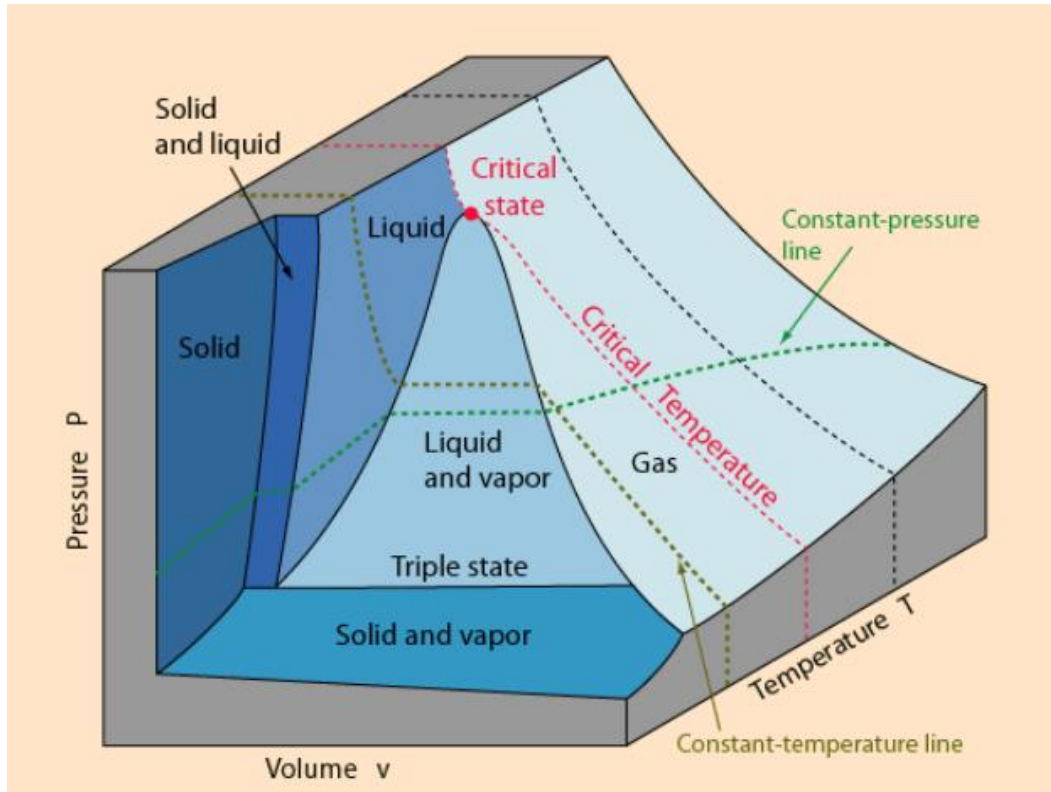


Table 1.7 Selected equations of state

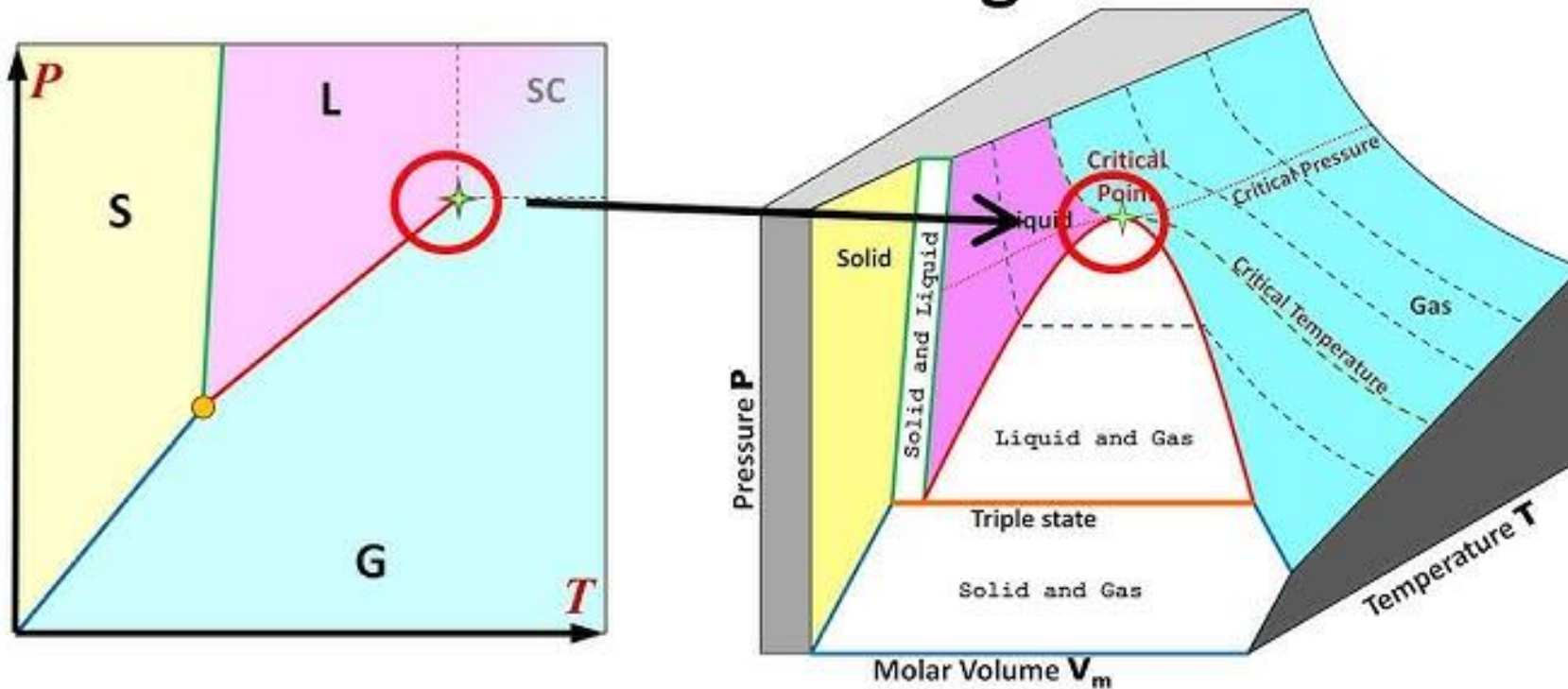
	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p = \frac{RT}{V_m}$				
van der Waals	$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$	$p = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$	$\frac{a}{27b^2}$	$3b$	$\frac{8a}{27bR}$
Berthelot	$p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$	$p = \frac{8T_r}{3V_r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

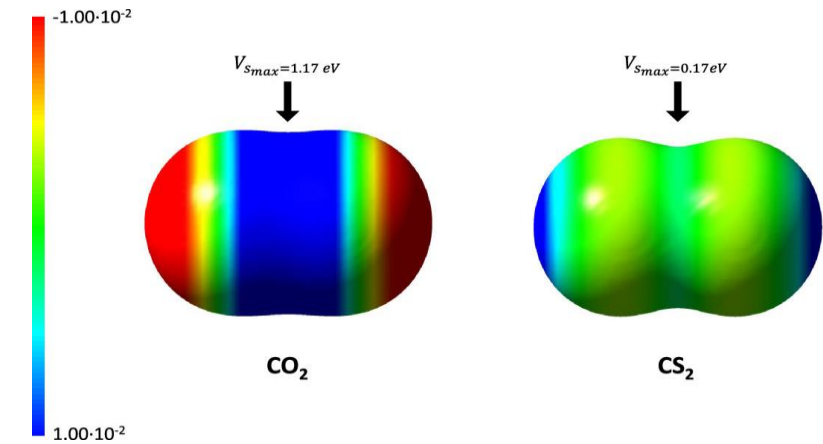
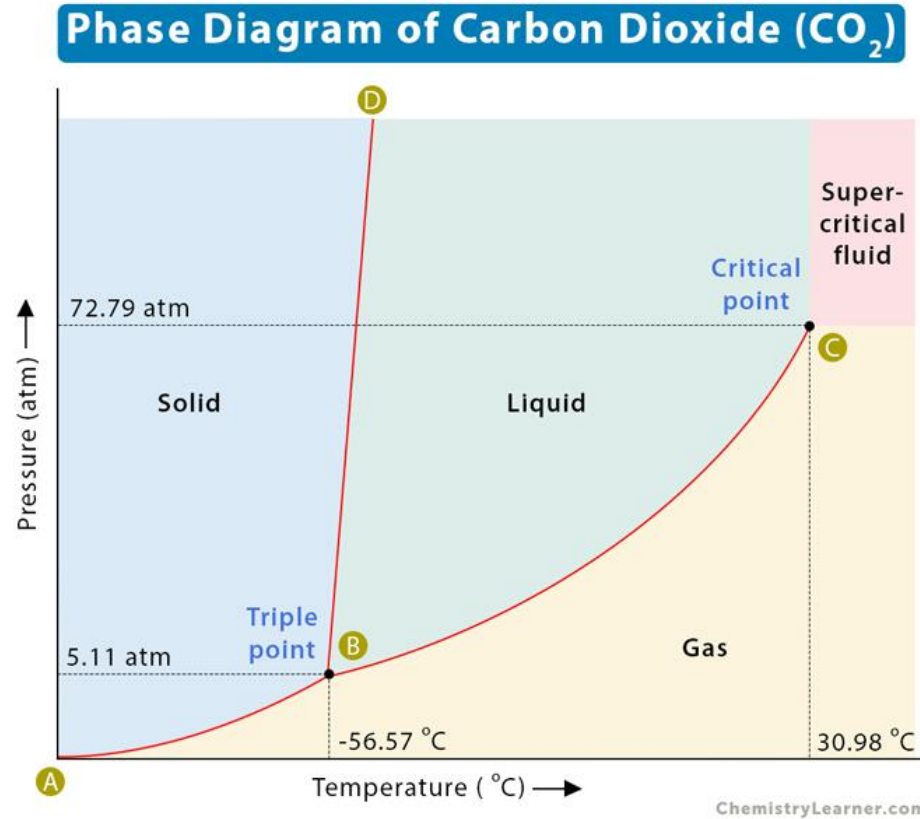
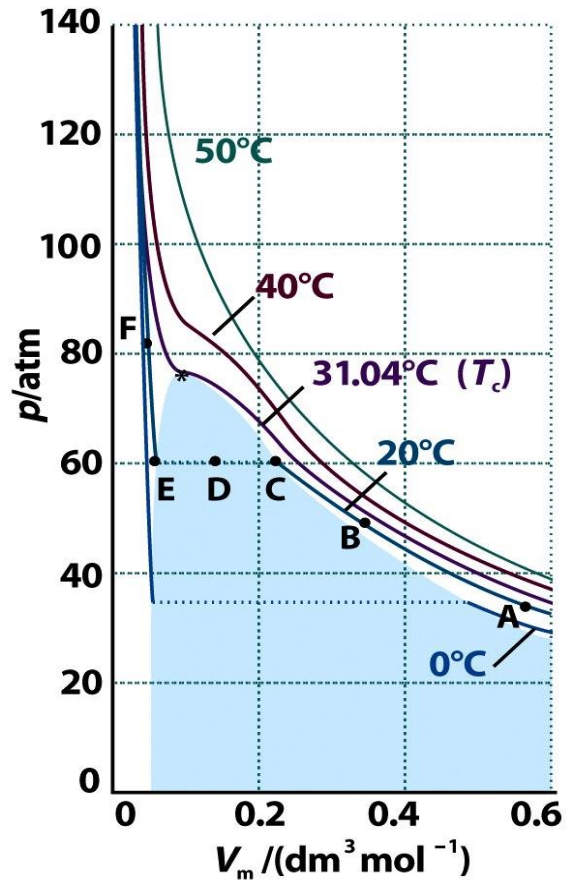
* Reduced variables are defined in Section 1.5.

Properties of Gases (EoS: p, V, T)



The Critical Point and 3D PVT Phase Diagrams





molecular electrostatic potential (MEP) of CO_2 (left) and CS_2 (right)

van der Waals ..equation

Properties of Gases (EoS: p, V, T)

The van der Waals equation is

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

Synoptic Table 1.6* van der Waals coefficients

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

Example 1.4 Using the van der Waals equation to estimate a molar volume

Estimate the molar volume of CO₂ at 500 K and 100 atm by treating it as a van der Waals gas.

Method To express eqn 1.21b as an equation for the molar volume, we multiply both sides by $(V_m - b)V_m^2$, to obtain

$$(V_m - b)V_m^2 p = RTV_m^2 - (V_m - b)a$$

and, after division by p , collect powers of V_m to obtain

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

Cubic equation !!

$$a X^3 + b X^2 + c X + d = 0$$

van der Waals ..equation

Properties of Gases (EoS: p, V, T)

The van der Waals equation is

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

Synoptic Table 1.6* van der Waals coefficients

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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*.

Although closed expressions for the roots of a cubic equation can be given, they are very complicated. Unless analytical solutions are essential, it is usually more expedient to solve such equations with commercial software.

Answer According to Table 1.6, $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2}$ and $b = 4.267 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$. Under the stated conditions, $RT/p = 0.410 \text{ dm}^3 \text{ mol}^{-1}$. The coefficients in the equation for V_m are therefore

$$b + RT/p = 0.453 \text{ dm}^3 \text{ mol}^{-1}$$

$$a/p = 3.61 \times 10^{-2} (\text{dm}^3 \text{ mol}^{-1})^2$$

$$ab/p = 1.55 \times 10^{-3} (\text{dm}^3 \text{ mol}^{-1})^3$$

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

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

The acceptable root is $x = 0.366$, which implies that $V_m = 0.366 \text{ dm}^3 \text{ mol}^{-1}$. For a perfect gas under these conditions, the molar volume is $0.410 \text{ dm}^3 \text{ mol}^{-1}$.

Self-test 1.5 Calculate the molar volume of argon at 100°C and 100 atm on the assumption that it is a van der Waals gas. [0.298 dm³ mol⁻¹]