재료 물리화학
Physical Chemistry of Materials

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Lecture contents

The perfect gas

Real gases

The perfect gas

1.1 The states of gases

General form for an equation of state

: $p = f(T, V, n)$

Four variables specifying the state

: V (volume), n (amount of substance or number of moles),
p (pressure), T (temperature)

The perfect gas

< Pressure ; *p* >

- **Definition : A force divided by the area to which the force is applied**

- **The origin of the force exerted by a gas : the incessant battering of the molecules on the walls of its container**

- **Unit (Table 1)**
  1 Pa = 1Nm^{-2} (in SI) = 1 kgm^{-1}s^{-2} in (mks),
  Standard pressure: 1 bar = 10^5 Pa

- **Mechanical equilibrium (Fig. 1.1)**

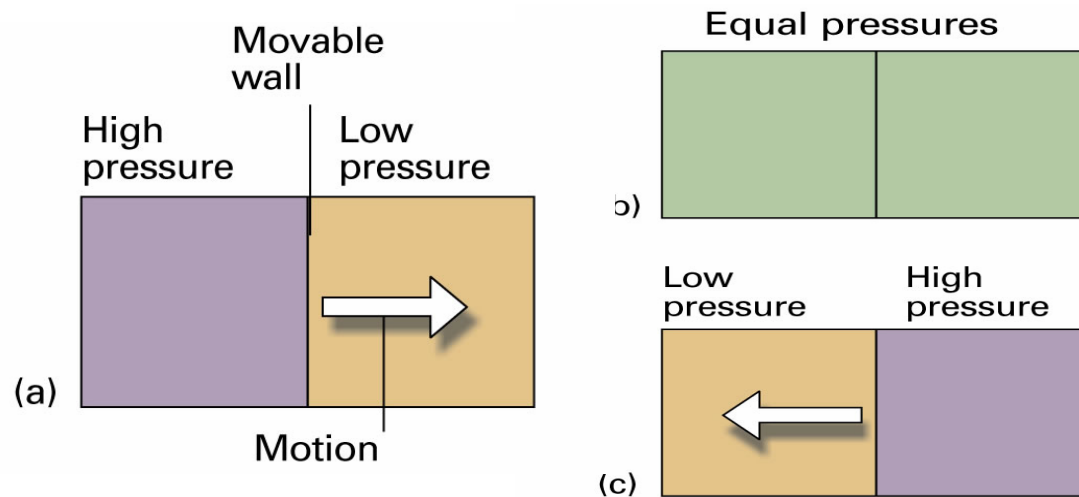| Symbol	Value
1 Pa	1 N m^{-2}, 1 kg m^{-1} s^{-2}
1 bar	10^5 Pa
1 atm	101.325 kPa
1 Torr	(101 325/760) Pa = 133.32 . . . Pa
1 mmHg	133.322 . . . Pa
1 psi	6.894 757 . . . kPa

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.

The perfect gas

<Temperature ; _T_>

- **Definition** : **The property that indicates the direction of the flow of energy through a thermally conducting, rigid wall**

- **Two types of boundary separating the objects: diathermic and adiabatic**

- **Thermal equilibrium : No change occurs even though the two objects are in contact through a diathermal boundary**

- **Zeroth(0_{th}) Law of thermodyanamics : 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**
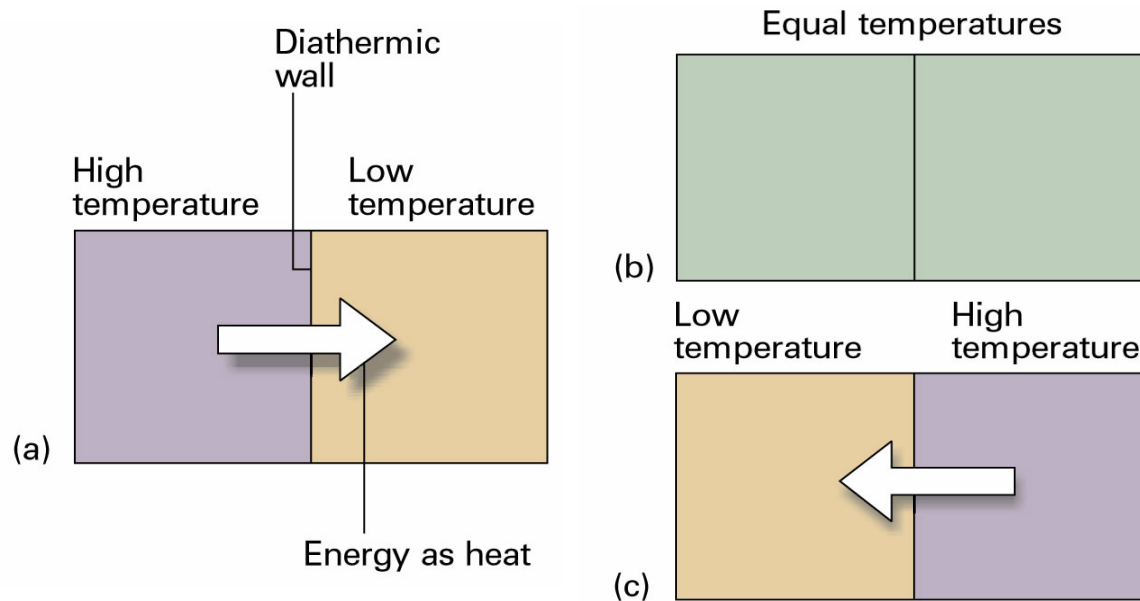

Fig. 1.2 Energy flows as heat from a region at a higher temperature to one at a lower temperature if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are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

The perfect gas

1.2 The gas laws

(a) The perfect gas law

Boyle's law : pV = constant (at constant n, T)

Charles's law (or Gay-Lussac's law) : V = constant $\times T$ (at constant n, p)

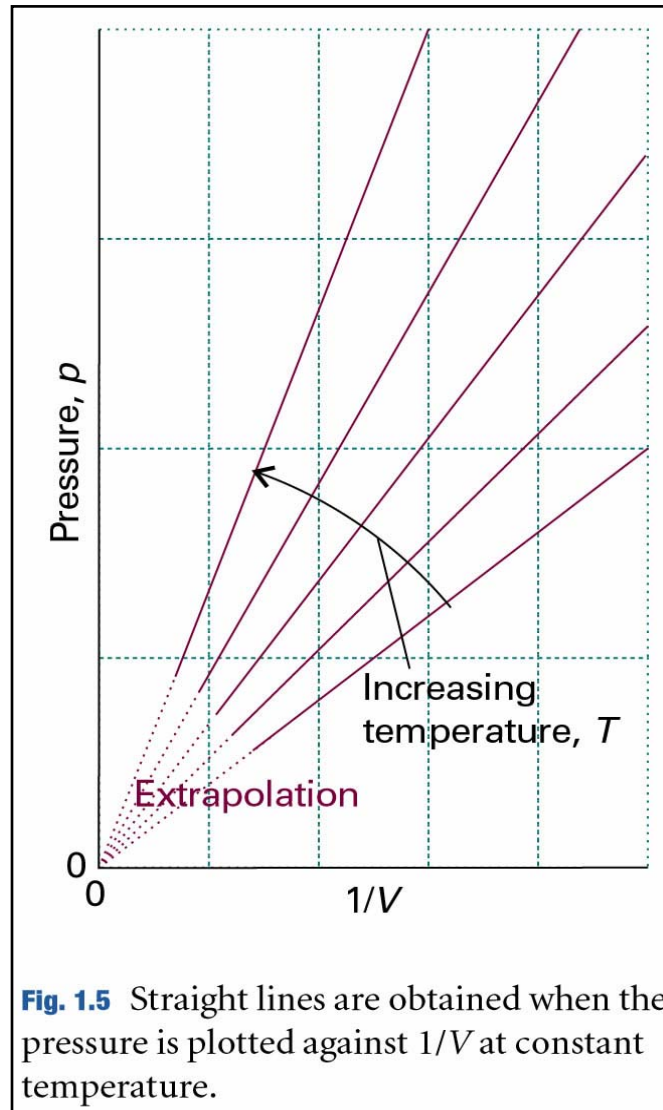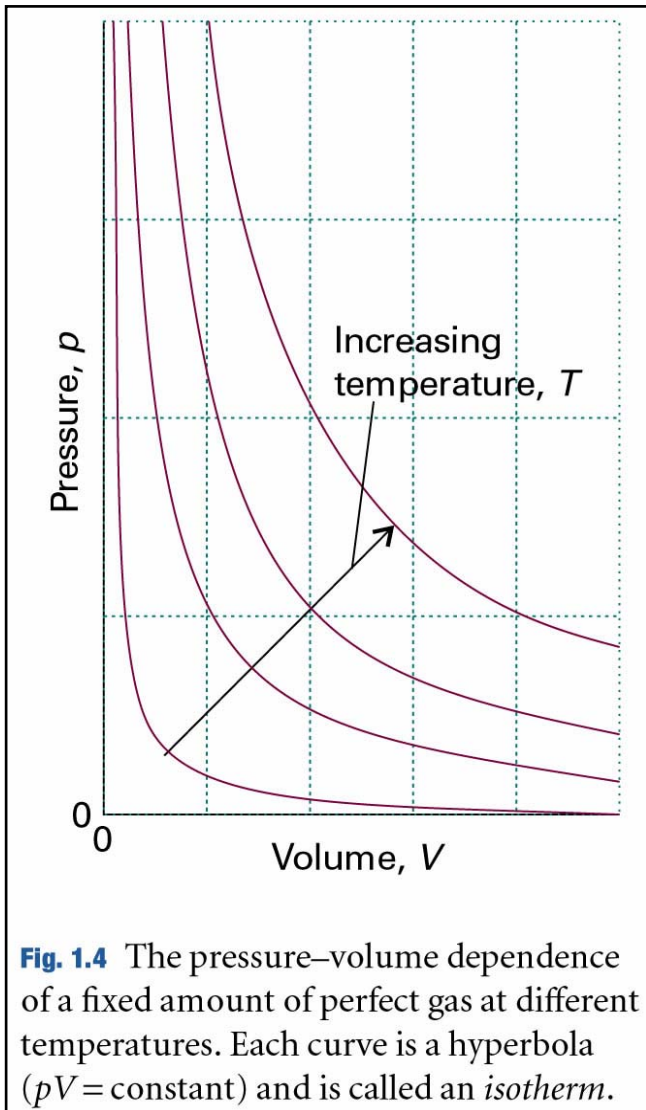p = constant $\times T$ (at constant n, V)

Examples of a **limiting law**
: Valid only at low pressures in real gases, i.e., $p \rightarrow 0$

Avogadro's principle : V = constant $\times n$ (at constant p and T)

The volume of a gas is proportional to n and the proportionality constant is independent of the gas species.

The perfect gas

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.

Boyle's law :

$$pV = \text{constant}$$
$$(\text{ at constant T})$$

The perfect gas

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 $T = 0$ ($-273°C$).
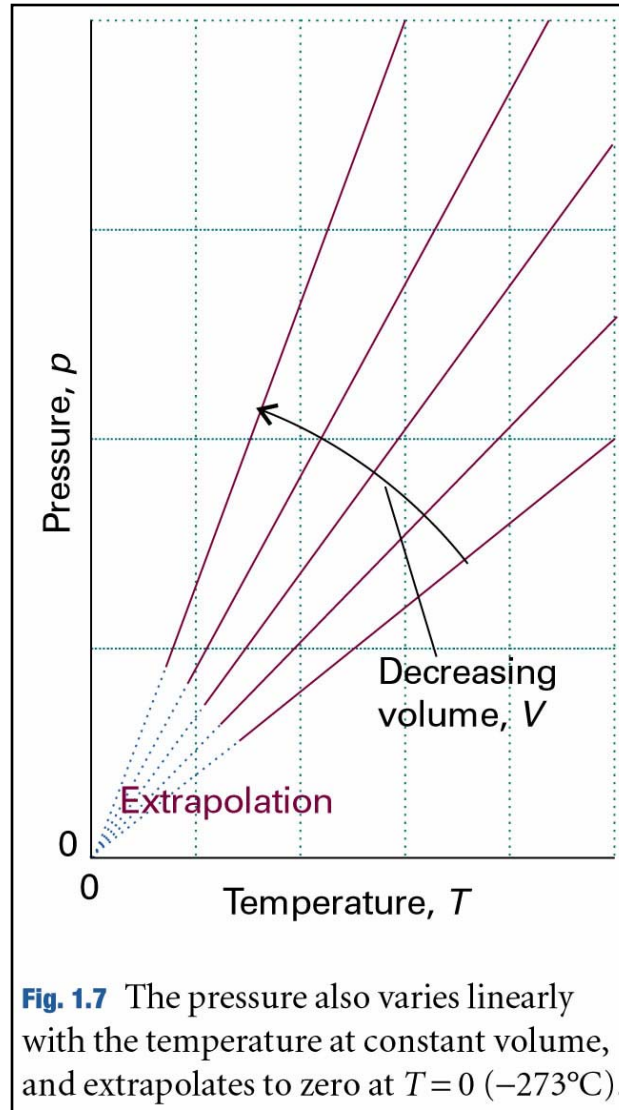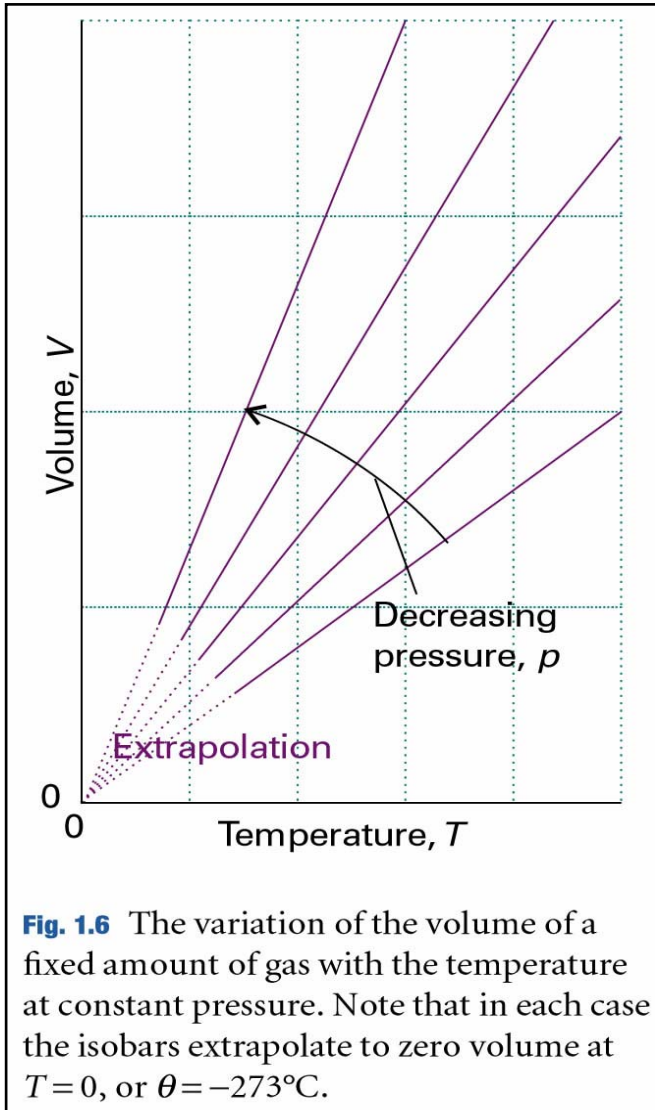
Charles's law (or Gay-Lussac's law):

$$V = \text{constant} \times T$$
(at constant p)

or

$$p = \text{constant} \times T$$
(at constant V)

The perfect gas

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.

$p \propto 1/V$
isotherm

$V \propto T$
isobar

$p \propto T$
isochore

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.
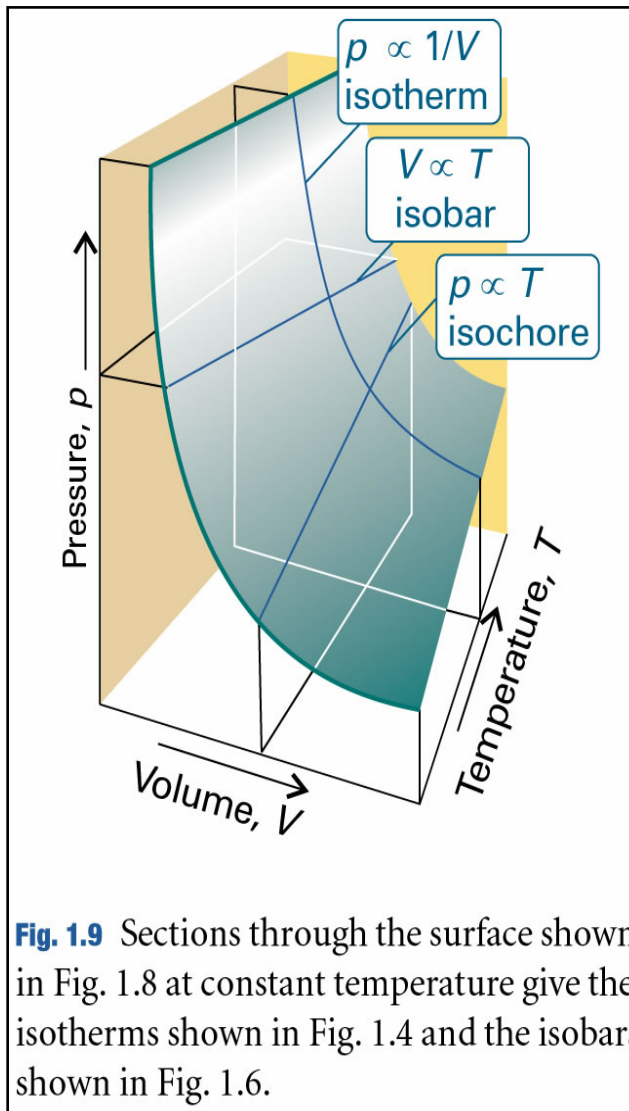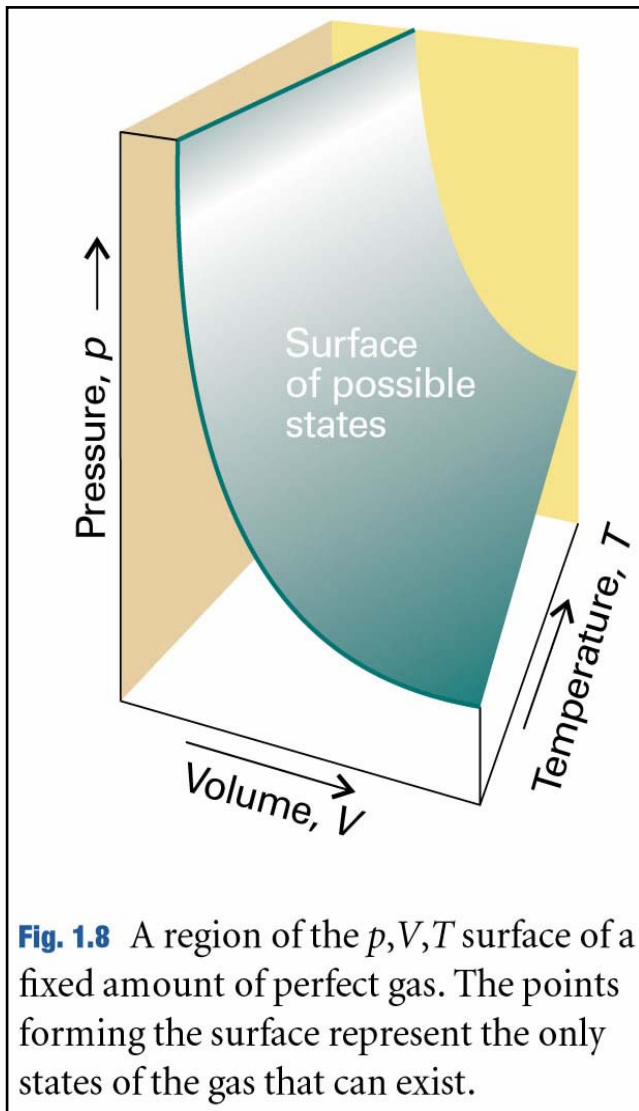
$$pV = \text{constant} \times nT$$
$$= nRT$$

R	: The gas constant
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}
1 62.364	dm^3 Torr K^{-1} mol^{-1}
1.987 21	cal K^{-1} mol^{-1}

The perfect gas

(b) Mixtures of gases

Dalton's law : The pressure exerted by a mixture of gases is the sum of the partial pressures of the gases

The partial pressure of a perfect gas : The pressure that would exert if it occupied the container alone at the same temperature

Total pressure, $p = p_A + p_B + ...$ where, for each gas J, $p_J = n_J RT/V$

Partial pressure, $p_J = x_J p$, true for any gas (not just a perfect gas)

Mole fraction of the component J, $x_J = n_J/n$, $n = n_A + n_B + ...$

$p_A + p_B + ... = (x_A + x_B + ...)p = p$, true for both real and perfect gases

Real gases

Real gases show deviations from the perfect gas law particularly at high pressures and low temperatures especially when a gas is on the point of condensing to liquid.

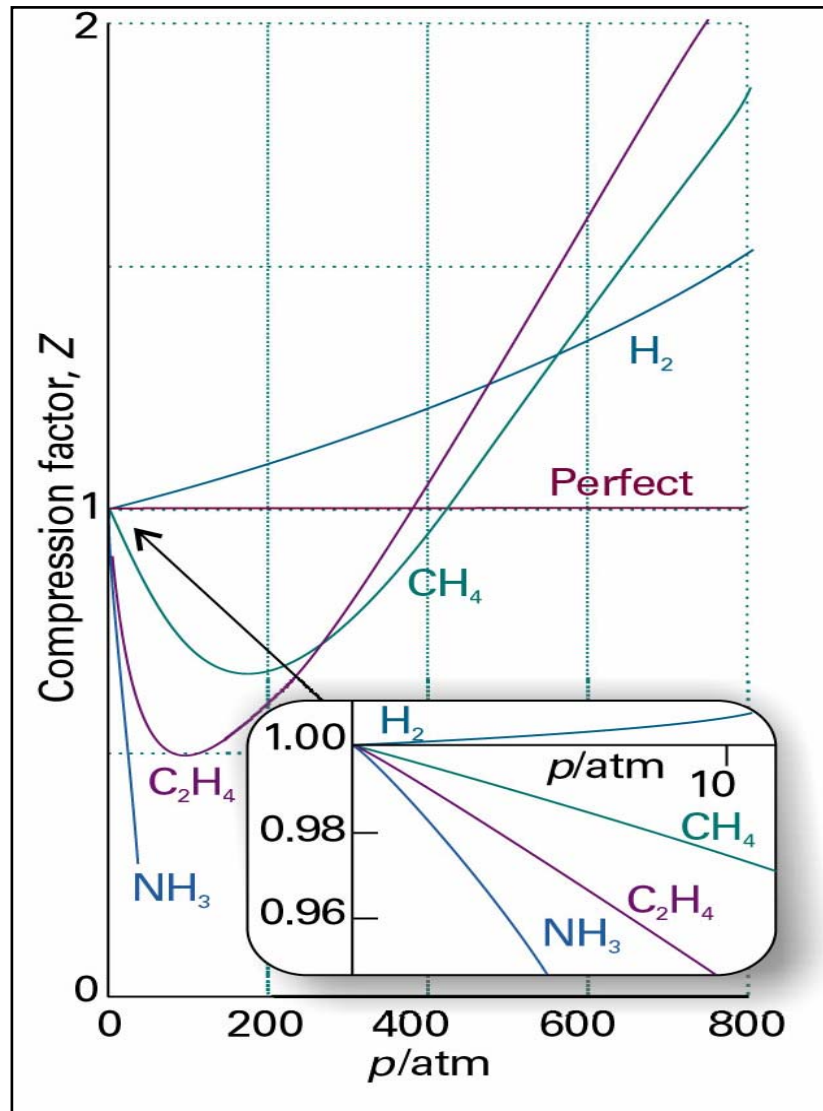**Why? Due to an interaction between molecules**

1.3 Molecular Interactions

(a) The compression factor, *Z*

$$Z = V_m/V_m^o,$$

$$pV_m = RTZ$$

$Z = 1$ for a perfect gas : at very low pressures (V_m^o: molecular volume of a perfect gas)
$Z > 1$ at high pressures : repulsive pressures are dominant ($V_m > V_m^o$)
$Z < 1$ at intermediate pressures : attractive forces are reducing the molar volume
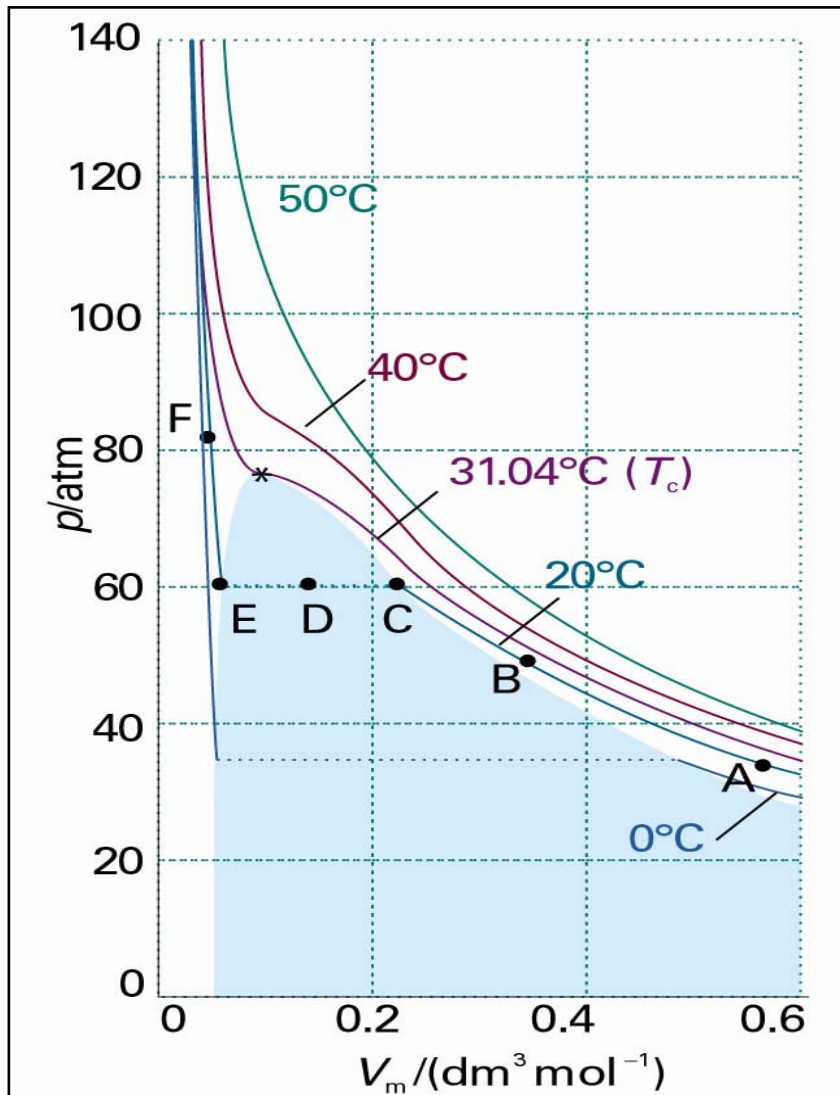relative to that of a perfect gas

Real gases

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.

Compression factor

$$Z = V_m/V_m^o$$
$$pV_m = RTZ$$

for a real gas of 1 mole

Real gases

(b) Virial coefficients

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

$$= RT(1 + B/V_m + C/V_m^2 + \ldots)$$

: **Virial equation of state**

$$dZ/dp = B' + 2\,pC' + \ldots \rightarrow B'$$

as $\ p \rightarrow 0$

$$dZ/d(1/V_m) \rightarrow B$$

as $V_m \rightarrow \infty$, corresponding to $p \rightarrow 0$

$B = 0$ at Boyle temp., T_B

$pV_m = RT$ over an extended range of pressures

(c) Condensation

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.

Real gases

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

	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

(d) Critical constants

At the critical point,

$$P_c,\ T_c,\ V_c,\ Z_c$$

Supercritical fluid

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

Real gases

1.4 The van der Waals equation

The approximate equation of state

$$p = nRT/(V - nb) - a(n/V)^2$$

$$= RT/(V_m - b) - a/V_m^2$$

or $(p + an^2/V^2)(V - nb) = nRT$

where, a, b : **van der Waals coefficients**

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

Real gases

(a) The reliability of the equation

Table 1.7 Selected equations of state

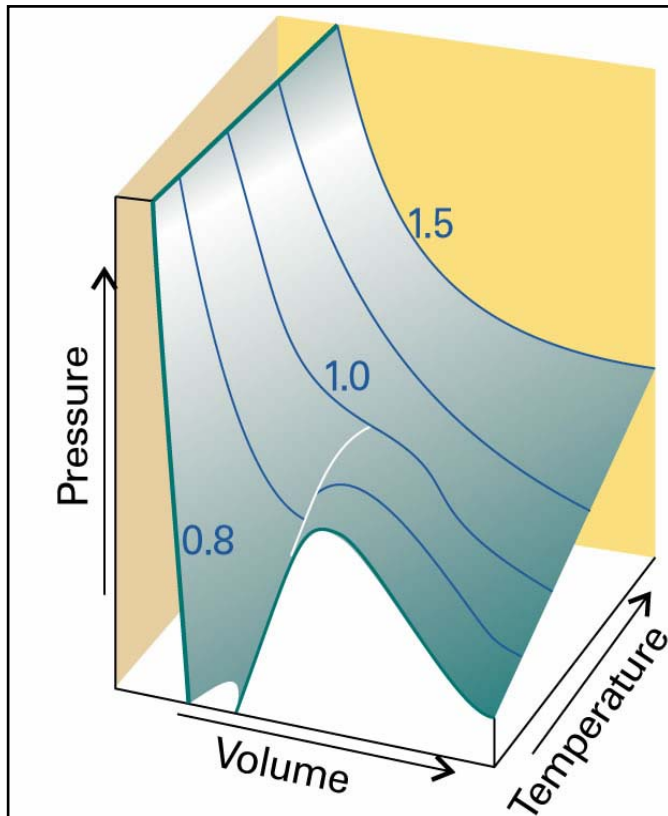|	Equation	Reduced form*	Critical constants p_c	V_c	T_c
Perfect gas	$p = \dfrac{RT}{V_m}$				
van der Waals	$p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$	$p = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{V_r^2}$	$\dfrac{a}{27b^2}$	$3b$	$\dfrac{8a}{27bR}$
Berthelot	$p = \dfrac{RT}{V_m - b} - \dfrac{a}{TV_m^2}$	$p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

Real gases

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.
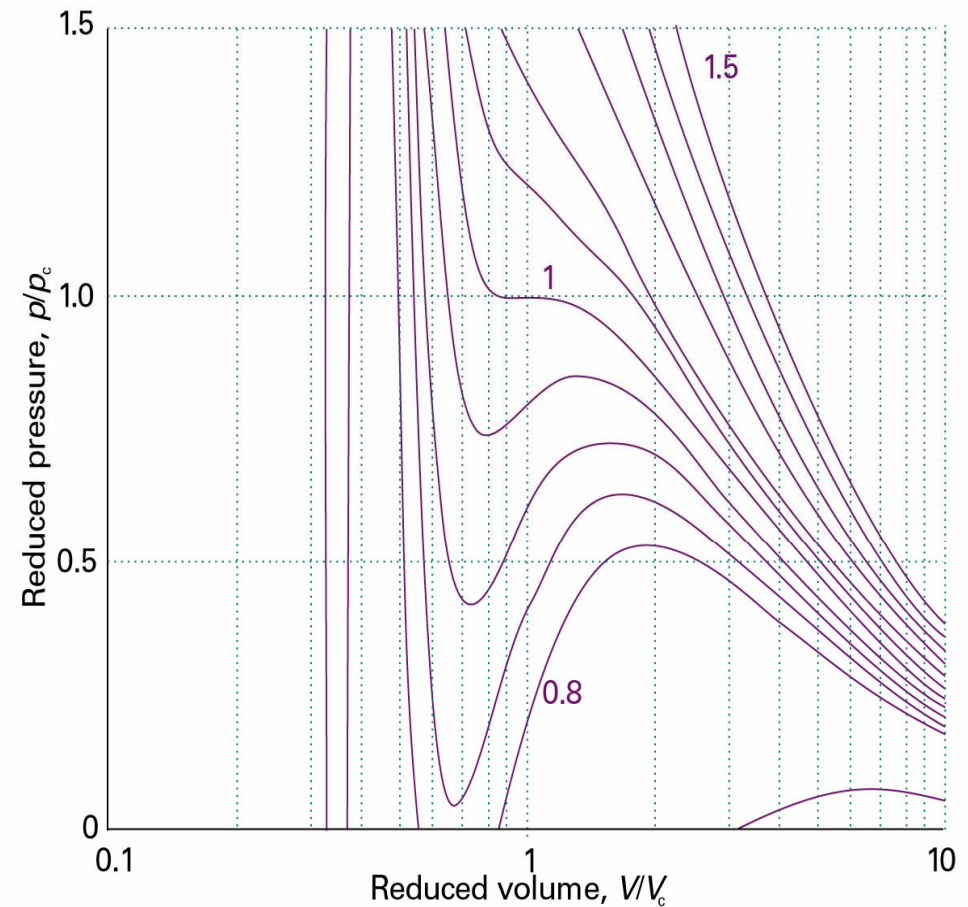

Fig. 1.18 Van der Waals isotherms at several values of T/T_c. Compare these curves with those in Fig. 1.15. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$.

Real gases

(b) The features of the van der Waals equation

(1) Perfect gas isotherms are obtained at high T and large V_m

(2) Liquids and gases coexist when cohesive and dispersing effects are in balance

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

- The critical point is located at an inflection of van der Waals loops

- $dp/dV_m = 0$, $d^2p / dV_m^2 = 0 \rightarrow V_c = 3b$, $p_c = a/27b^2$, $T_c = 8a/27Rb$

- **Then Z_c** (critical compression factor) $= p_c V_c / RT_c = 3/8$ ($= 0.375$)

Equal areas

3

4
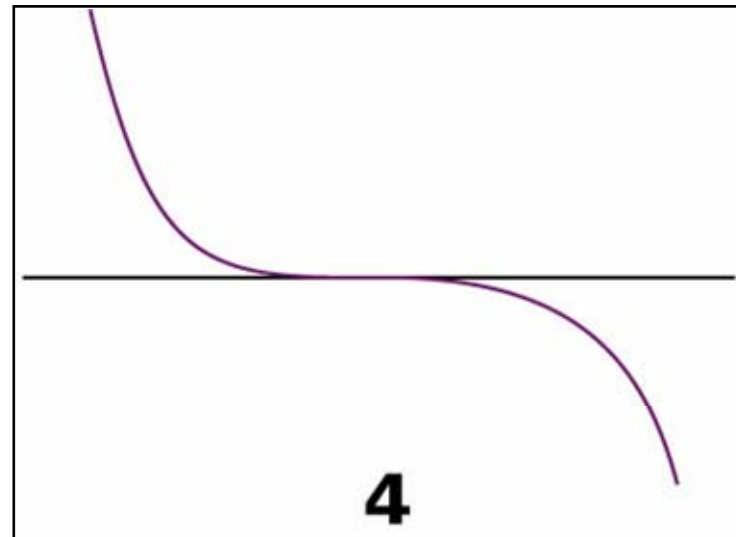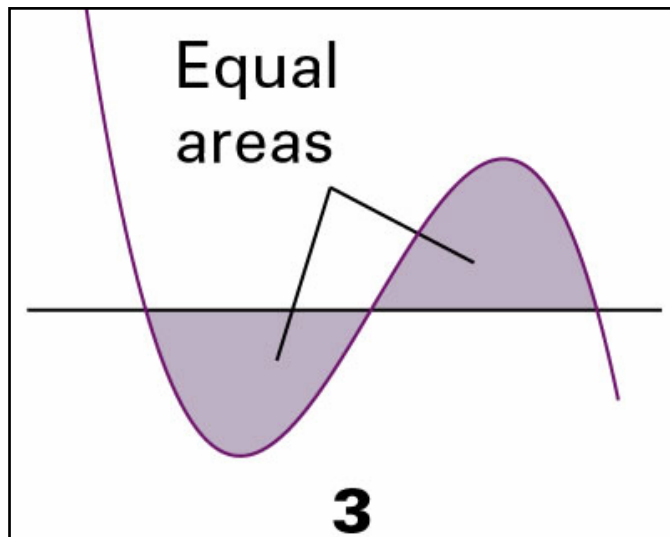
Real gases

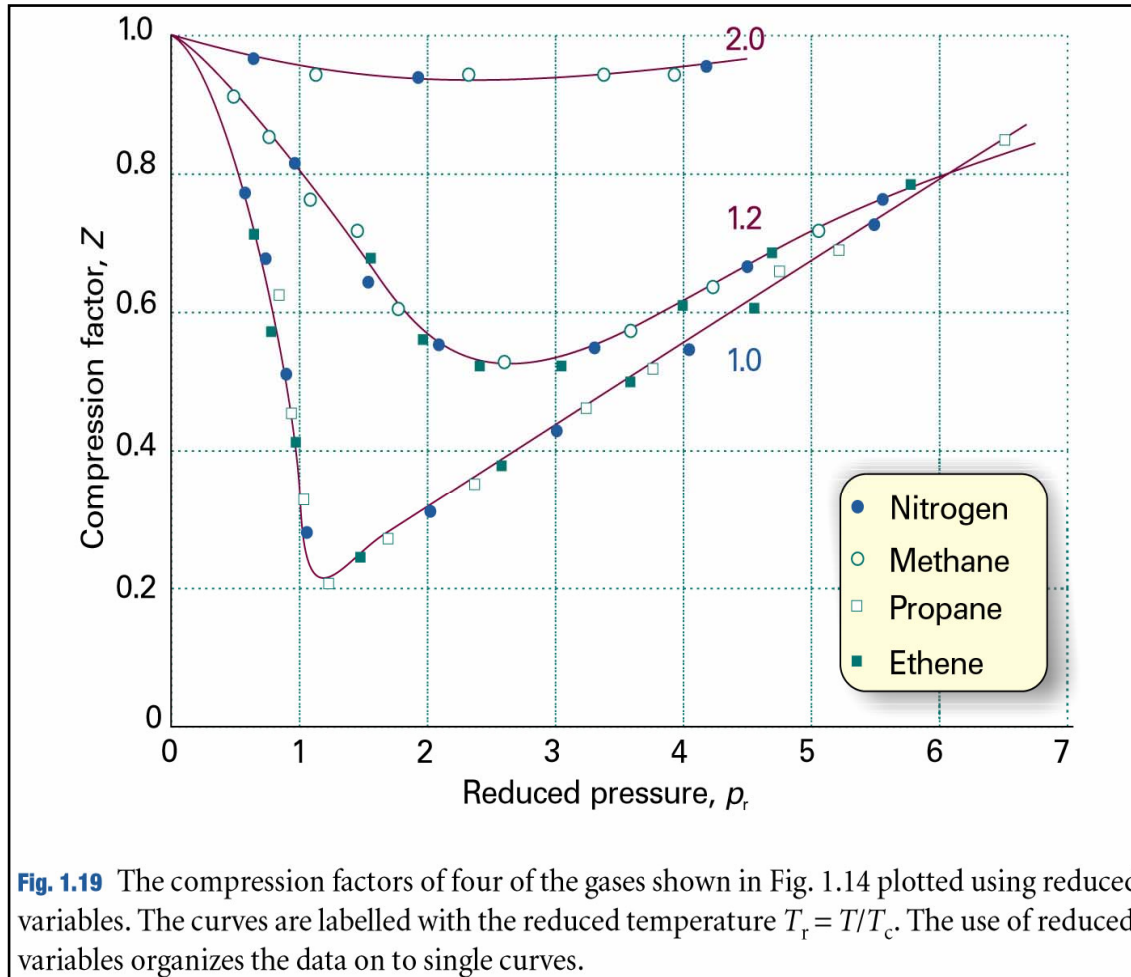## 1.5 The principle of corresponding states

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.

The observation that real gases at the same reduced volume and reduced temperature exert the same reduced pressure
→ works for spherical molecules, but fails for non-spherical or polar molecules

Reduced variables

$$P_r = p/p_c$$

$$V_r = V_m/V_c$$

$$T_r = T/T_c$$