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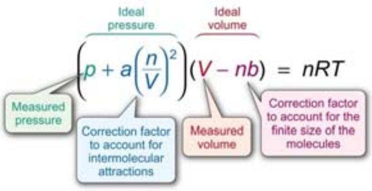
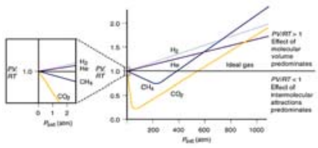


Lecture 4

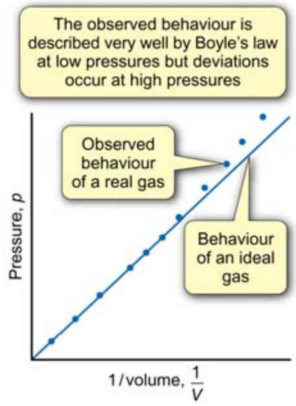
Real Gases

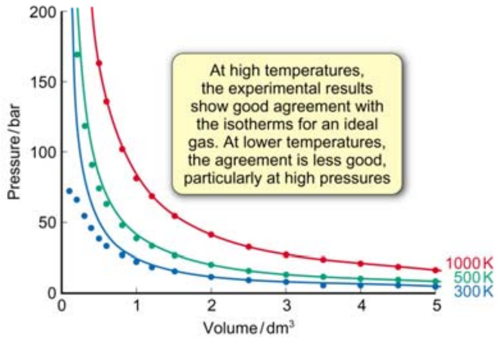


Ideal Gas behaviour: summary

- We recall the conditions under which the ideal gas equation of state PV=nRT is valid:
  - Volume of individual gas molecules is neglected
  - No interactions (either attractive or repulsive) exist amongst the molecules.
- These are not very reasonable assumptions. However the ideal gas approximation is useful for many gases at high temperatures or moderately low (< 10 atm) pressures, i.e. dilute gases.
- In the context of the kinetic molecular theory an ideal gas is one for which the mean free path λ (the distance over which the gas molecules travel before they experience collision) of the molecules is much greater than the collision diameter d.
- Also in an ideal gas the only contribution to the internal energy comes from the translational kinetic energy of the gas molecules. There is no contribution from the potential energy arising from interactions of gas molecules with each other.
- We now examine the behaviour of real gases.

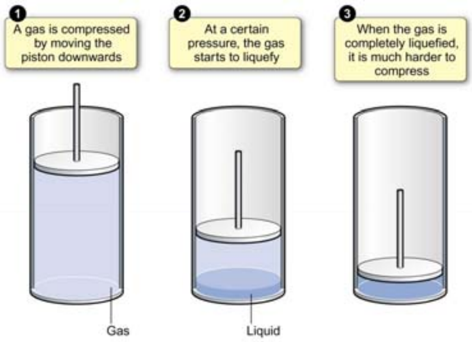
Breakdown of ideal gas behaviour : Low temperature and high pressure.

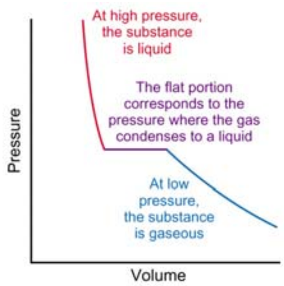


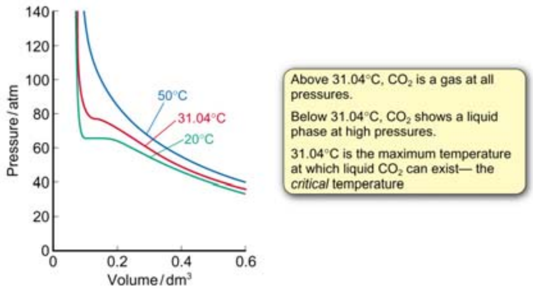


Gases cannot be subjected to an infinite compression.
Gases liquefy at low temperatures and at high pressures.

Chemistry[3] Section 7.6, pp.330-335.
Kotz, Section 11.9, pp.542-543.







Real Gases

Assume that a gas sample is compressed using a piston.
As the gas undergoes compression the individual molecules are brought closer together : the finite volume of the individual molecules will become important and these molecules will interact with one another.
Hence finite molecular size and intermolecular interactions will be important in the description of real gases.
Deviations from ideal gas behaviour will therefore be observed as the gas becomes more dense.

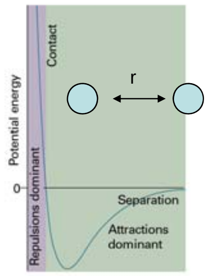
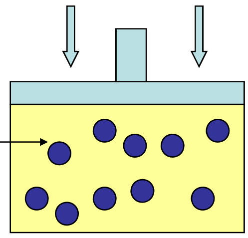


Fig. 1.13 The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative,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

Molecular interactions may be neglected. Volume of individual gas molecules << overall gas volume.

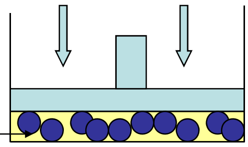


Dilute gas

Intermolecular forces may be either *attractive* or *repulsive*.

Repulsive forces assist expansion of gas : significant when molecules are close together (within single molecular diameter) and operative at high pressure.

Attractive forces assist compression of gases : can have influence over a long distance (close but not touching). Operative at modrerate pressures.



Dense Gas

Significant molecular interactions present. Volume of individual gas molecules cannot be neglected compared with overall volume of gas.

Compressibility (Compression) Factor

We can express the extent of deviation from ideal behaviour as a function of pressure (which is related to the density of the gas) by introducing a quantity called the *Compressibility* or *Compression factor* Z.

$$Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$$

Foe an ideal gas Z = 1, and real gases exhibit Z values different from unity. Z values may be explained in terms of the operation of *intermolecular forces*.

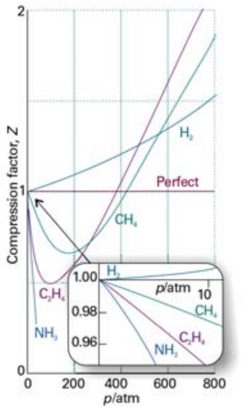
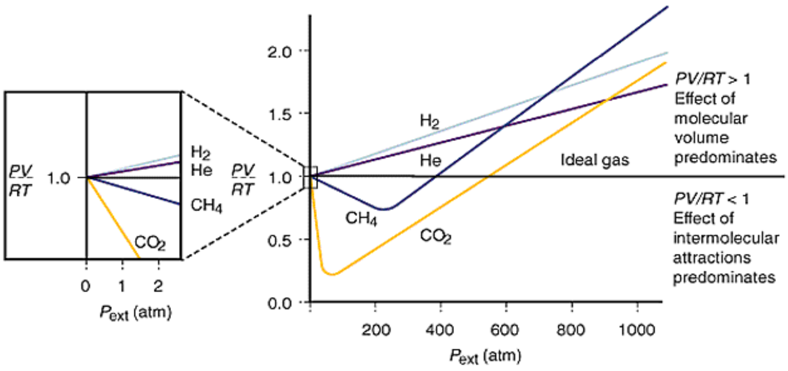


Fig. 1.14 The variation of the compression factor, Z, with pressure for several gases at 0°C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \to 0$, they do so with different slopes.

At low pressures the molecules are far apart and the predominant intermolecular interaction is attraction. The molar volume V_m is less than that expected for an ideal gas : intermolecular forces tend to draw the molecules together and so reduce the space which they occupy. Under such conditions we expect that Z < 1.

As the pressure is increased the average distance of separation between molecules decreases and repulsive interactions between molecules become more important. Under such conditions we expect that Z > 1. When Z > 1, the molar volume is greater than that exhibited by an ideal gas: repulsive forces tend to drive the molecules apart.



Virial equation of state

The observation of a Z factor different from unity can be used to construct an empirical or observation based equation of state, by supposing that the ideal gas equation of state is only the first term of a more complex expression which can be expressed in terms of a mathematical power series. This is called the Virial equation of state.

$$Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ... = 1 + B'P + C'P^2$$

$$\frac{PV_m}{RT} \to 1 \quad V_m \to \infty \quad P \to 0$$

p = 0: Close to ideal gas law, but not exact
p increases: *B* contributes, linear relation between *Z* and *P*
p higher: *C* and higher order terms contribute, deviation from linearity

Note that the virial coefficients B, C, B' and C' are obtained by fitting the experimental Z vs P data to the virial equation of state. Their values depend on the identity of the gas and Reflect the presence of intermolecular forces and interactions.
When the pressure P is small the molar volume V_m will be very large and so the second and third terms in the virial series will be very small and to a good approximation the virial equation of state reduces to the ideal gas equation of state.

Virial: comes from that Latin word *vis*, *viris*, meaning force - the coefficients in the **virial equation** depend on the forces of interaction between molecules of the gas

Boyle Temperature

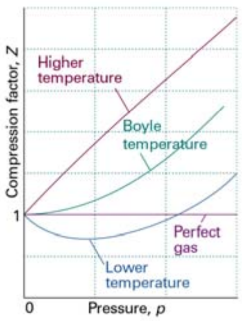


Fig. 1.16 The compression factor, Z, approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

In a perfect gas dZ/dP = 0 (since Z = 1).
In a real gas the result is different.

$$\frac{dZ}{dP} = B' + 2PC' + ... \cong B' \text{ as } P \to 0$$

$$\frac{dZ}{d(1/V_m)} \cong B \text{ as } V_m \to \infty$$

At low T the initial dZ/dP < 0, B is negative.
At high T the initial dZ/dP > 0 and B is positive.
The temperature at which the initial slope is zero is
Termed the Boyle Temperature T_B where B = 0.
Here the real gas behaves as an ideal gas.

Van der Waals (VdW) equation of State

Johannes D Van der Waals
1837-1923

The virial equation of state (VES) can make sense of the experimentally observed Z versus P data but it is empirical and does not directly tell us how the ideal gas equation of state is modified due to the operation of intermolecular interactions.

The Van der Waals equation of state, although approximate, is based on a very simple physical model of intermolecular interactions.

Repulsive Interactions.

The operation of repulsive intermolecular interactions implies that two gas molecules cannot come closer than a certain distance of each other. Instead of being free to travel anywhere in a volume V, the actual volume in which the molecule can travel is reduced by an amount which is proportional to the number of molecules present and the volume which they exclude. The volume excluding repulsive forces are modelled by changing the volume term V in the ideal gas equation to V-nb, where b represents the proportionality constant between the reduction in volume and the amount of molecules present in the container: it is the excluded volume per mole.

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

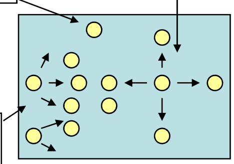
Finite molecular Size: excluded Volume correction

Attractive Interactions.

The presence of attractive interactions between molecules is to reduce the pressure that the gas exerts. The attraction experienced by a given molecule is proportional to the concentration n/V of molecules in the container. Attractive forces slow the molecules down: molecules strike the walls less frequently and with less impact.
Pressure determined by impact of molecules on container walls and is proportional to rate of impact times average strength of impact. Both of these quantities are proportional to the concentration.

Molecules have finite size. Hence occupy space.

Molecules in interior of gas volume experience a uniform force field



Molecules near container wall experience net attractive force towards body of gas.

Reduction in pressure proportional to $(n/V)^2 = a(n/V)^2$ where a denotes a constant of proportionality which takes account of attractive interactions.
Hence this correction factor should be added to the pressure P to make up for this deficit, and the Pressure term in the ideal gas equation of state is changed from P to $P + a(n/V)^2$.

Measured pressure → $$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$ ← Correction factor to account for Intermolecular attractions

Measured volume

Correction factor to Account for finite molecular size

VdW equation of state

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

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

$$V_m = \frac{V}{n}$$

Useful limits of the VdW equation of state.

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

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

When P is very low then V is very large since P is proportional to 1/V. Then $b \ll V_m$ and $a/V_m^2 \ll P$ and the VdW expression reduces to $PV_m = RT$, the ideal gas equation as it should.
At slightly higher pressures the following pertains.

$$\left(P + \frac{a}{V_m^2}\right)V_m = RT$$

$$PV_m = RT - \frac{a}{V_m}$$

$$Z = \frac{PV_m}{RT} = 1 - \frac{a}{RTV_m}$$

Hence $PV_m < RT$ and decreases with increasing pressure P.
The dip observed in the curve of Z versus P is attributed to the a/RTV_m term and is due to attractive forces which will predominate when molecules are far apart at low pressures.

$$P(V_m - b) + \frac{a}{V_m^2}(V_m - b) = RT$$

$$P(V_m - b) + a\left(\frac{1}{V_m} - \frac{b}{V_m^2}\right) = RT$$

The VdW expression may be recast in another manner which proves useful at higher pressures.

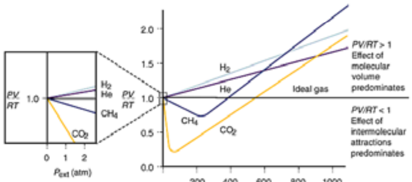
$$P(V_m - b) \cong RT$$

$$PV_m = RT + bP$$

$$Z = \frac{PV_m}{RT} \cong 1 + \frac{bP}{RT}$$

Now when P is large, the term $1/V_m - b/V_m^2$ is small and can be neglected.

Now Z > 1 and increases with increasing pressure P. This rise in Z with P is due to the b term which arises from the operation of repulsive interactions since the latter forces kick in when molecules are close together at high pressure.



At the Boyle temperature T_B $dZ/dP = 0$ and we can show that $T_B = a/bR$.

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

	100 K	273 K	373 K	600 K
Air	−167.3	−13.5	3.4	19.0
Ar	−187.0	−21.7	−4.2	11.9
CH_4		−53.6	−21.2	8.1
CO_2		−142	−72.2	−12.4
H_2	−2.0	13.7	15.6	
He	11.4	12.0	11.3	10.4
Kr		−62.9	−28.7	1.7
N_2	−160.0	−10.5	6.2	21.7
Ne	−6.0	10.4	12.3	13.8
O_2	−197.5	−22.0	−3.7	12.9
Xe		−153.7	−81.7	−19.6

Data: AIP, JL. The values relate to the expansion in eqn 1.22 of Section 1.3b; convert to eqn 1.21 using $B' = B/RT$.
For Ar at 273 K, $C = 1200\ \text{cm}^6\ \text{mol}^{-1}$.

Table 1.6 van der Waals coefficients

	$a/(\text{atm dm}^6\ \text{mol}^{-2})$	$b/(10^{-2}\ \text{dm}^3\ \text{mol}^{-1})$		$a/(\text{atm dm}^6\ \text{mol}^{-2})$	$b/(10^{-2}\ \text{dm}^3\ \text{mol}^{-1})$
Ar	1.337	3.20	H_2S	4.484	4.34
C_2H_4	4.552	5.82	He	0.0341	2.38
C_2H_6	5.507	6.51	Kr	5.125	1.06
C_6H_6	18.57	11.93	N_2	1.352	3.87
CH_4	2.273	4.31	Ne	0.205	1.67
Cl_2	6.260	5.42	NH_3	4.169	3.71
CO	1.453	3.95	O_2	1.364	3.19
CO_2	3.610	4.29	SO_2	6.775	5.68
H_2	0.2420	2.65	Xe	4.137	5.16
H_2O	5.464	3.05			

Data: HCP.

Relating the Virial and VdW equations of state.

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

VdW equation of state

$$\frac{1}{1-x}\cong 1+x+x^3 \qquad x<<1$$

$$\frac{1}{1-\frac{b}{V_m}}\cong 1+\frac{b}{V_m}+\left(\frac{b}{V_m}\right)^2$$

Valid for moderate pressure where $b/V_m << 1$

Compressibility factor VdW gas

$$Z=\frac{PV_m}{RT}=\frac{V_m}{V_m-b}-\frac{a}{V_mRT}=\frac{1}{1-\frac{b}{V_m}}-\frac{a}{V_mRT}$$

$$Z\cong 1+\frac{b}{V_m}+\frac{b^2}{V_m^2}-\frac{a}{V_mRT}=1+\left(b-\frac{a}{RT}\right)\frac{1}{V_m}+\frac{b^2}{V_m^2}$$

Virial equation of state

$$Z=1+\frac{B}{V_m}+\frac{C}{V_m^2}+\ldots$$

$$B=b-\frac{a}{RT}$$

$$C=b^2$$

Hence the second virial coefficient B incorporates terms arising from repulsive and attractive forces. At high temperature when bRT >> a then repulsive forces predominate, whereas at low temperature when bRT << a, attractive forces predominate (gases condense to liquids at low temperature due to attractive forces).
When bRT = a, T = T_B the Boyle temperature of the gas.