

• Thermal & Statistical Physics

Thermal & Statistical Physics PHYS 343

Dr.Salwa Alsaleh

Salwams@ksu.edu.sa

fac.ksu.edu.sa/salwams



LECTURE 7



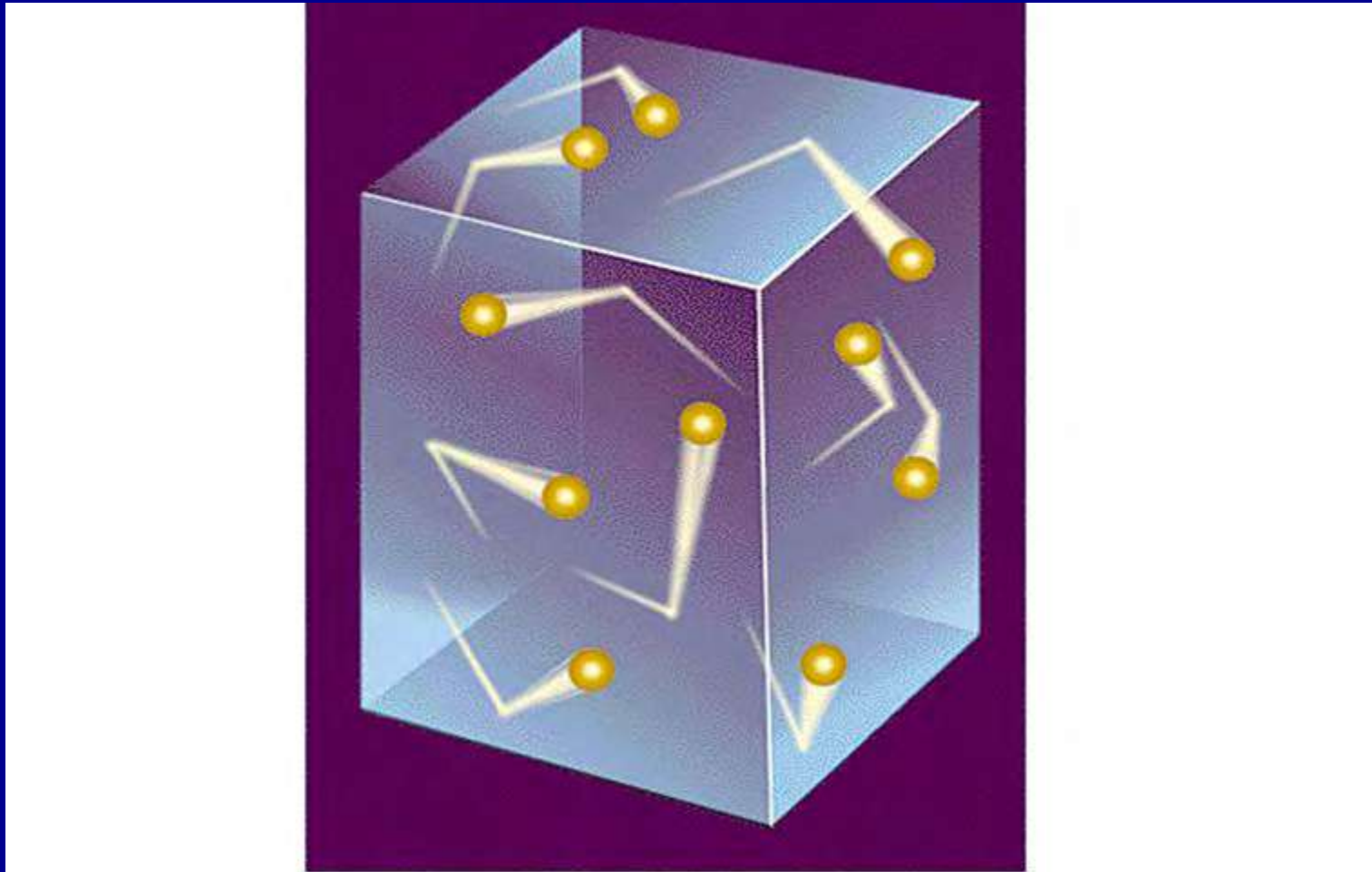
Deviations from Ideality

Van Der Waals Equation

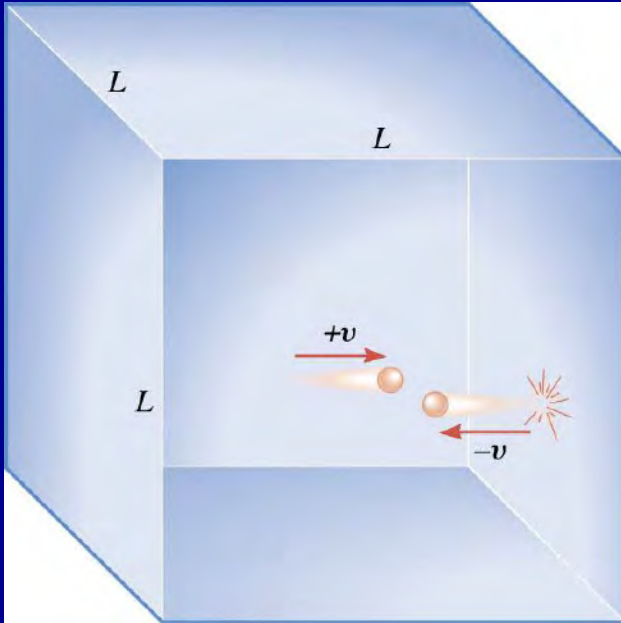
Virial equations of state

Compressibility factor

*Derivation of some laws from
kinetic theory of gases*



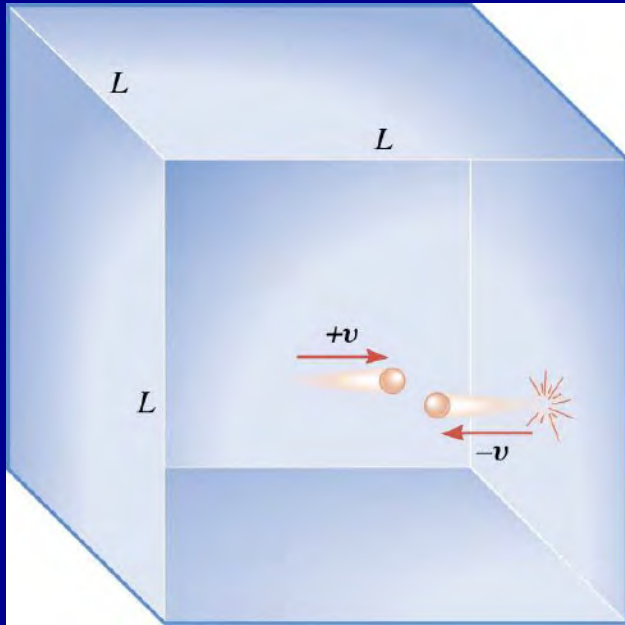
KINETIC THEORY



$$\sum F = ma = m \frac{\Delta v}{\Delta t} = \frac{\Delta(mv)}{\Delta t}$$

$$\text{Average force} = \frac{\text{Final momentum} - \text{Initial momentum}}{\text{Time between successive collisions}}$$

$$= \frac{(-mv) - (+mv)}{2L/v} = \frac{-mv^2}{L}$$



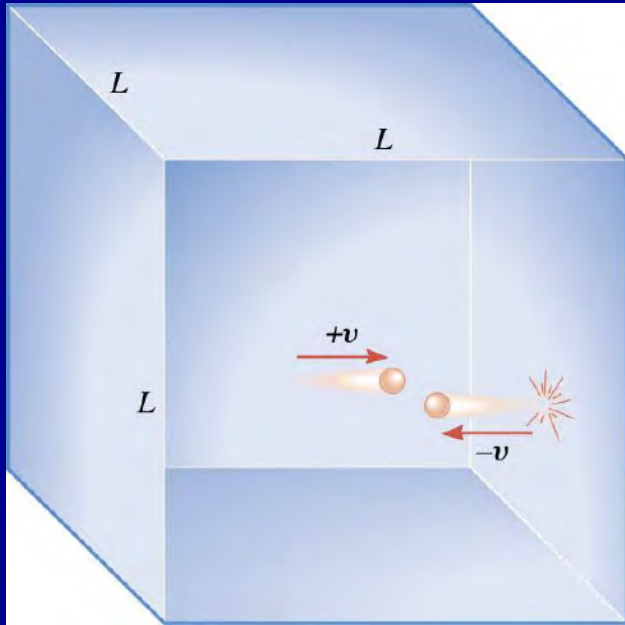
$$F = \frac{mv^2}{L}$$

$$F = \left(\frac{N}{3}\right) \left(\frac{\overline{mv^2}}{L}\right)$$

An orange arrow points from the $\overline{mv^2}$ term in the equation above to the mv^2 term in the equation above.

$$P = \frac{F}{A} = \frac{F}{L^2} = \left(\frac{N}{3}\right) \left(\frac{\overline{mv^2}}{L^3}\right)$$

An orange arrow points from the $\overline{mv^2}$ term in the equation above to the $\overline{mv^2}$ term in the equation above.



$$P = \left(\frac{N}{3} \right) \left(\frac{m \overline{v^2}}{V} \right)$$

NkT

$\overline{\text{KE}}$

$$PV = \frac{1}{3} N (m v_{rms}^2) = \frac{2}{3} N \left(\frac{1}{2} m v_{rms}^2 \right)$$

$$\overline{\text{KE}} = \frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT$$

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT$$

$$v_{rms} = \sqrt{\frac{3 kT}{m}}$$

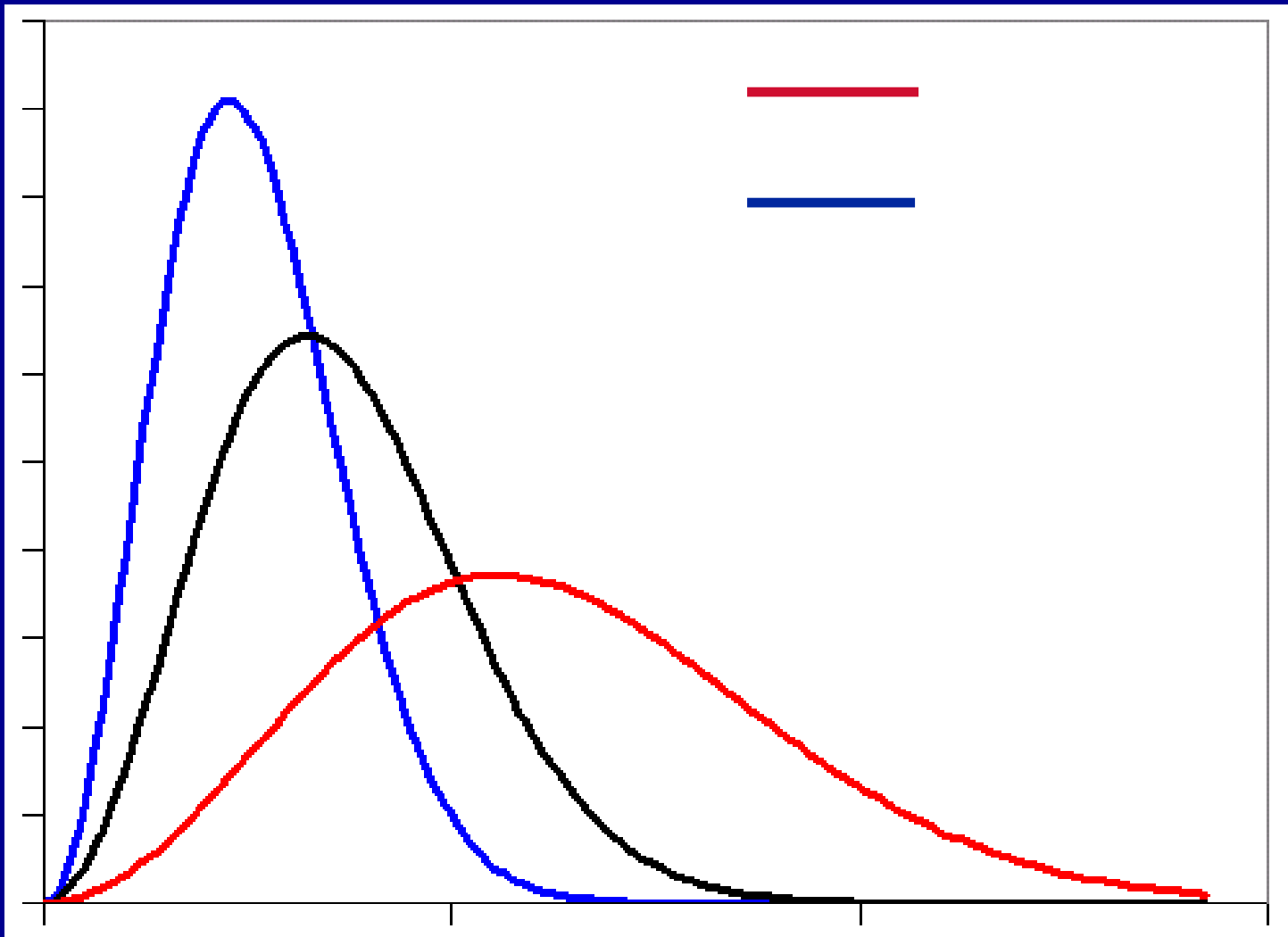
$$m = \frac{28.0 \text{ g/mol}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 4.65 \times 10^{-23} \text{ g} = 4.65 \times 10^{-26} \text{ kg}$$

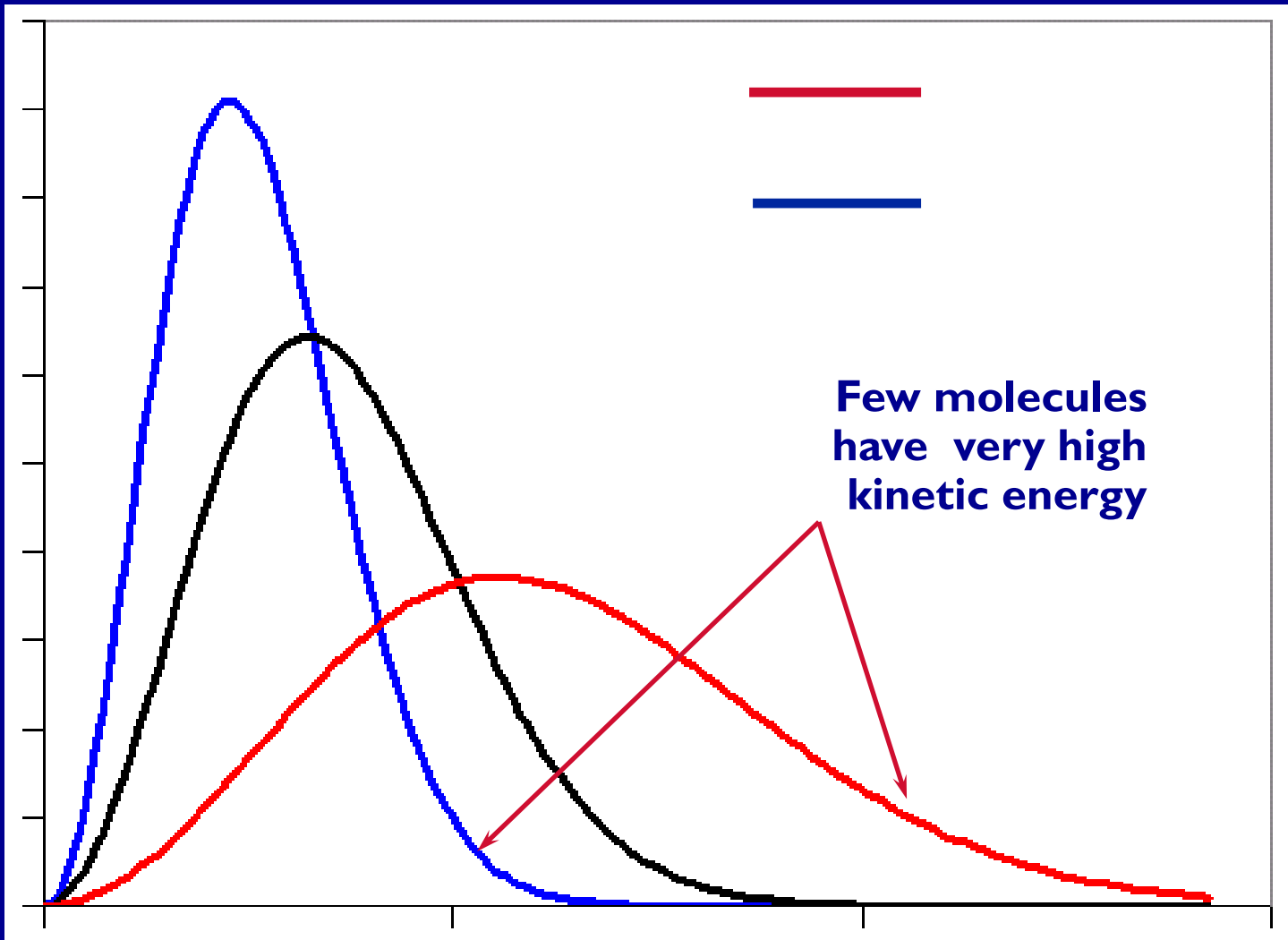
$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{4.65 \times 10^{-26} \text{ kg}}} = 511 \text{ m/s}$$

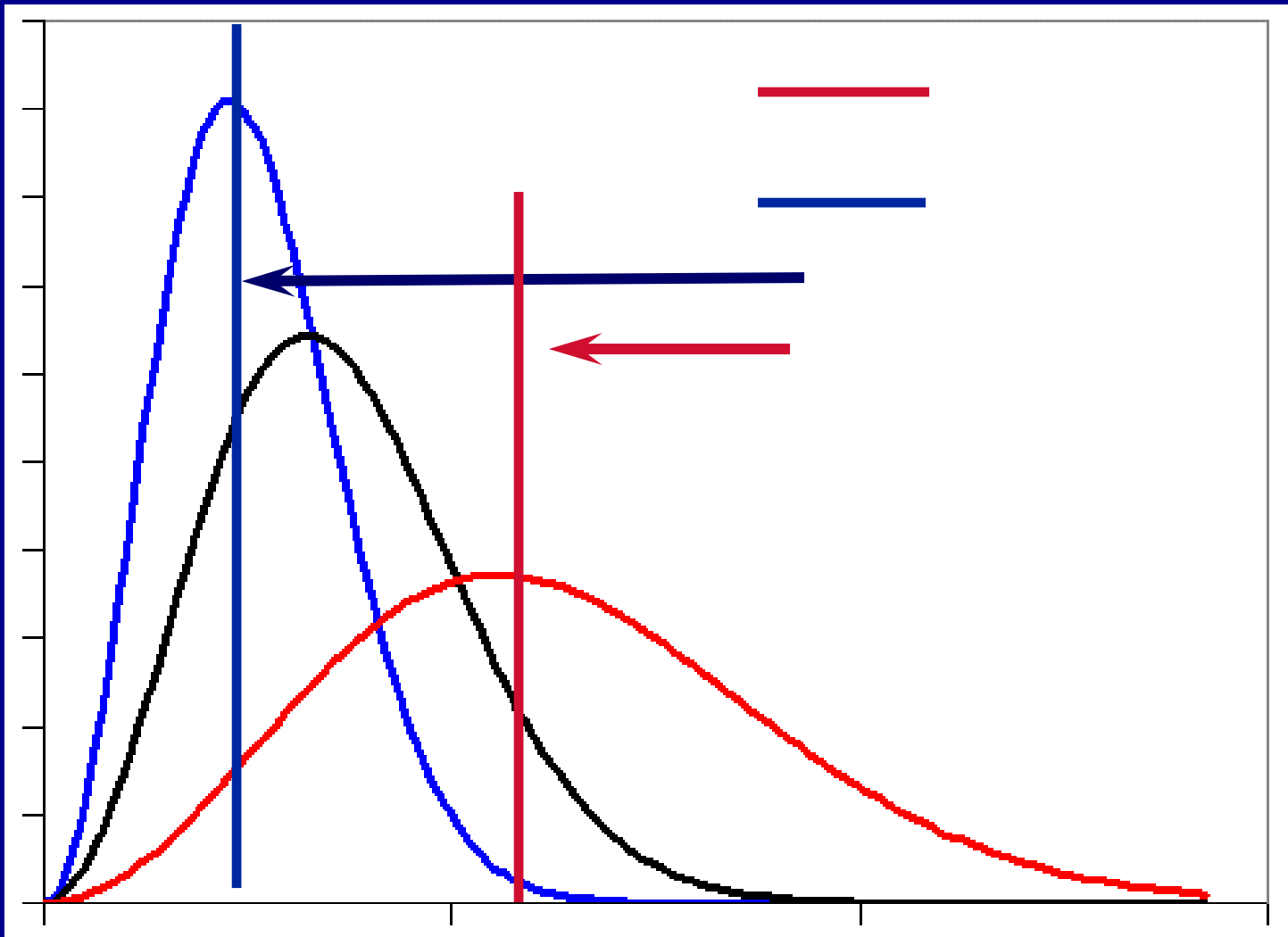
The internal energy of monatomic ideal gas

$$\overline{\text{KE}} = \frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT$$

$$U = N \frac{3}{2} kT = \frac{3}{2} nRT$$







Kinetic Theory – Summary

Using Newtonian mechanics we have established:

- the relationship between p , N/V , T ;
- the universality of the gas constant;
- the relationship between temperature and K.E.
- the internal energy of a monatomic ideal gas

Real Gases



J. van der Waals, 1837-1923,
Professor of Physics,
Amsterdam. Nobel Prize 1910.

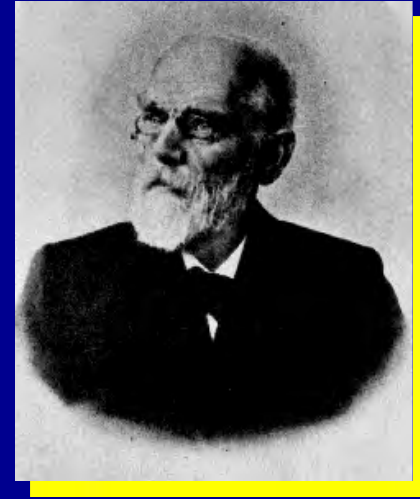
Real Gases

General Observations

- Deviations from ideal gas law are particularly important at high pressures and low temperatures
- Real gases differ from ideal gases in that there can be interactions between molecules in the gas state
 - **Repulsive forces** important only when molecules are nearly in contact, i.e. very high pressures
 - Gases at high pressures , gases less compressible
 - **Attractive forces** operate at relatively long range (several molecular diameters)
 - Gases at moderate pressures are more compressible since attractive forces dominate
 - At low pressures, neither repulsive or attractive forces dominate **ideal behavior**

Real Gases

Deviations from Ideality



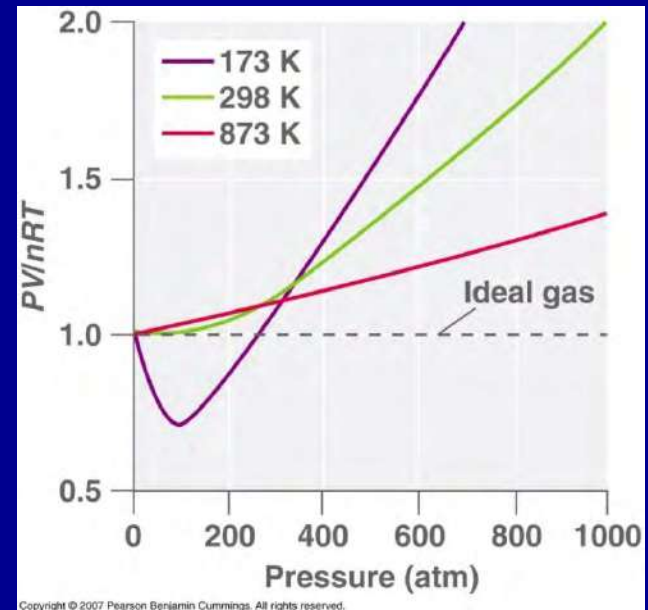
J. van der Waals, 1837-1923,
Professor of Physics, Amsterdam.
Nobel Prize 1910.

Real Gases

Deviations from Ideality

- For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis.
- Real gases behave ideally at ordinary temperatures and pressures. At low temperatures and high pressures real gases do not behave ideally.
- The reasons for the deviations from ideality are:

The molecules are very close to one another, thus their volume is important.
The molecular interactions also become important.



Copyright © 2007 Pearson Benjamin Cummings. All rights reserved.

Real Gases

Van Der Waals Equation

Real gases do not follow $PV = nRT$ perfectly. The *van der Waals equation* corrects for the nonideal nature of real gases.

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

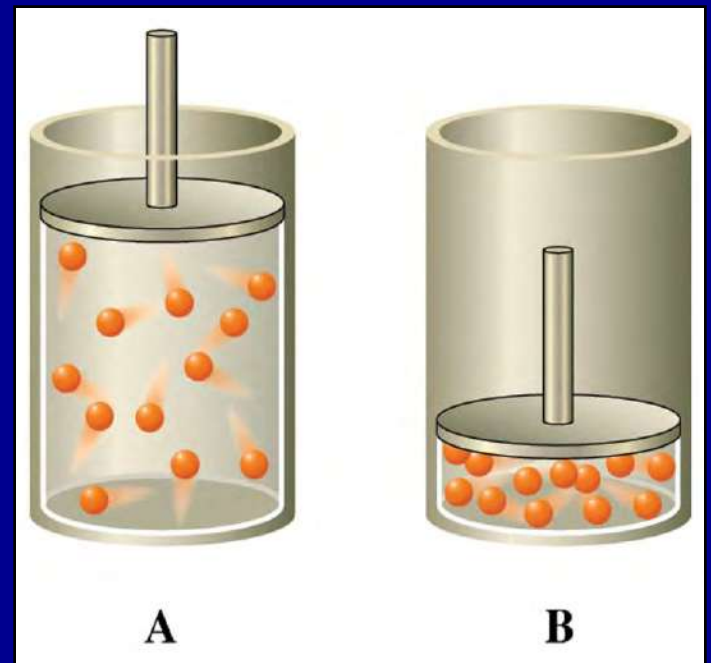
Real Gases

Van Der Waals Equation

- A non-zero volume of molecules = b (b is a constant depending on the type of gas, the 'excluded volume'). The molecules have less free space to move around in, so replace V in the ideal gas equation by $V - b$
- Very roughly, $b \approx \frac{4}{3} n r^3$ where r is the molecular radius.

the van der Waals equation,

V becomes $(V - nb)$



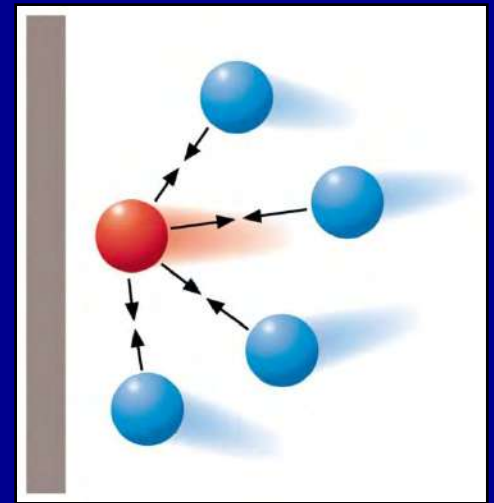
Real Gases

Van Der Waals Equation

- **The attractive forces between real molecules, which reduce the pressure:**
 - p wall collision frequency *and*
 - p change in momentum at each collision.
- **Both factors are proportional to concentration, n/V , and p is reduced by an amount $a(n/V)^2$, where a depends on the type of gas.**
- **[Note: a/V^2 is called the internal pressure of the gas].**

Also, in the van der Waals equation,

P becomes $(P + \frac{n^2 a}{V^2})$



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

V.D.W Cubic equations of state

- Simple equation capable of representing both liquid and vapor behavior.

- The van del Waals equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

- a and b are positive constants
- unrealistic behavior in the two-phase region. In reality, two, within the two-phase region, saturated liquid and saturated vapor coexist in varying proportions at the saturation or vapor pressure.
- Three volume roots, of which two may be complex.
- Physically meaningful values of V are always real, positive, and greater than constant b .

Real Gases

Deviations from Ideality

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

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

Real Gases

Nonideal Conditions when gas gets close to conditions where it will liquify

- Lower Temperature
- Higher Pressure

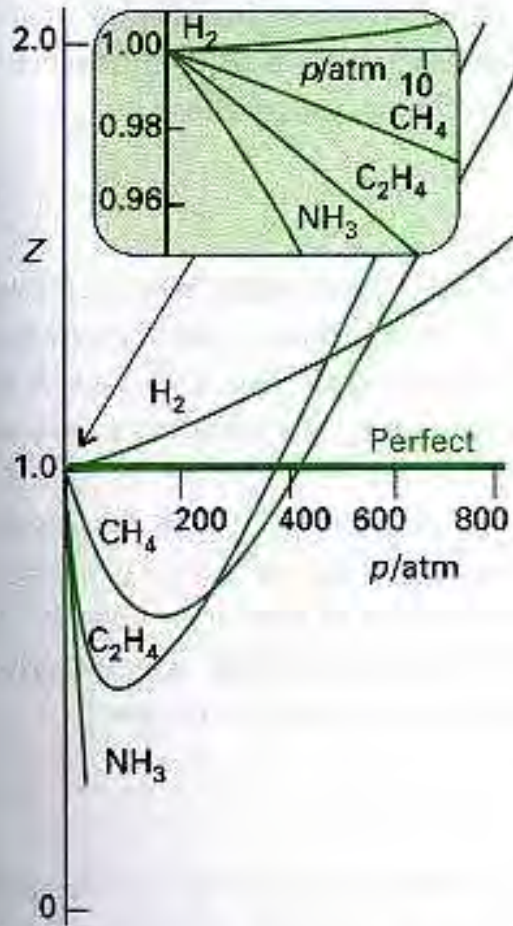
$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Table 5.3 Van der Waals Constants of Some Common Gases

Gas	a $\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \right)$	b $\left(\frac{\text{L}}{\text{mol}} \right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CO ₂	3.59	0.0427
CH ₄	2.25	0.0428
CCl ₄	20.4	0.138
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

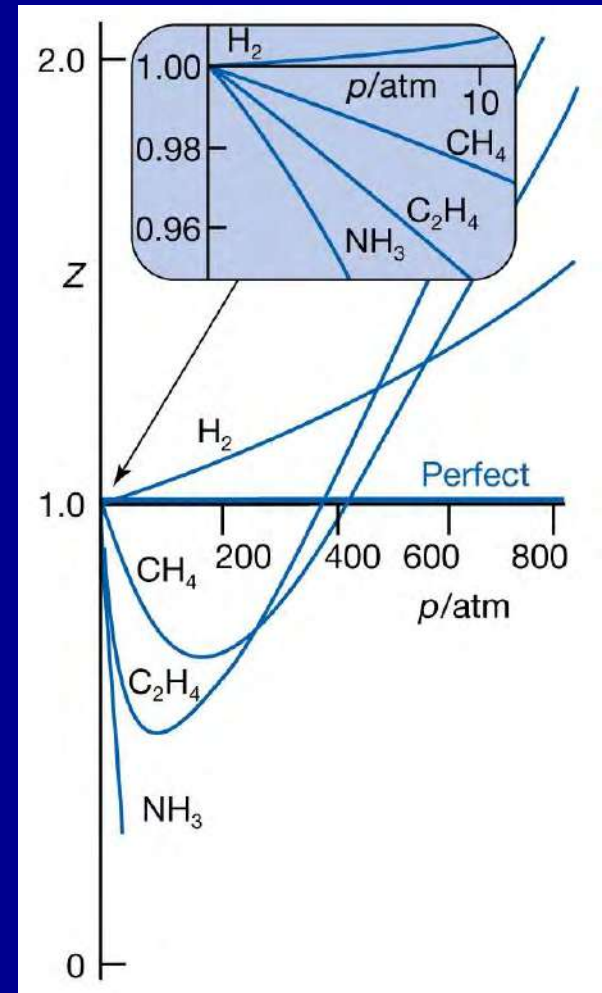
Real Gases

Compressibility factor, Z



1.22 The variation of the compression factor $Z = pV_m/RT$ 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.

Compressibility factor, Z



Compressibility factor, Z ...

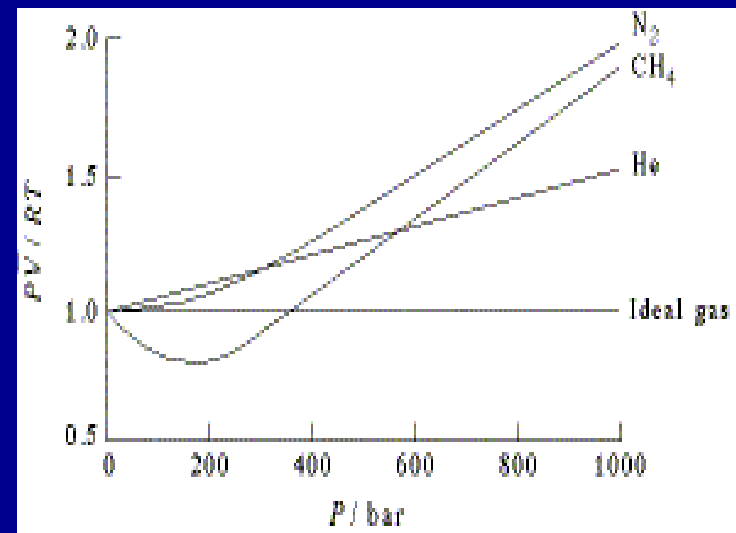
$$Z \equiv \frac{PV}{RT}$$

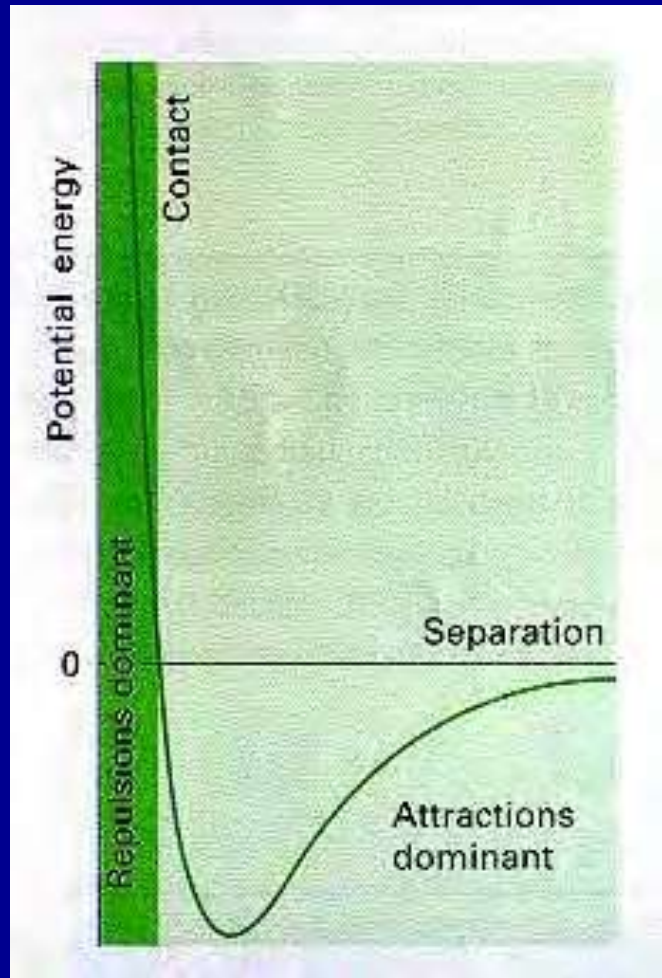
“compressibility factor”:

Ideal gas: $z = 1$

$z < 1$: attractive intermolecular forces dominate

$z > 1$: repulsive intermolecular forces dominate





Critical point of Van Der Waals Equation

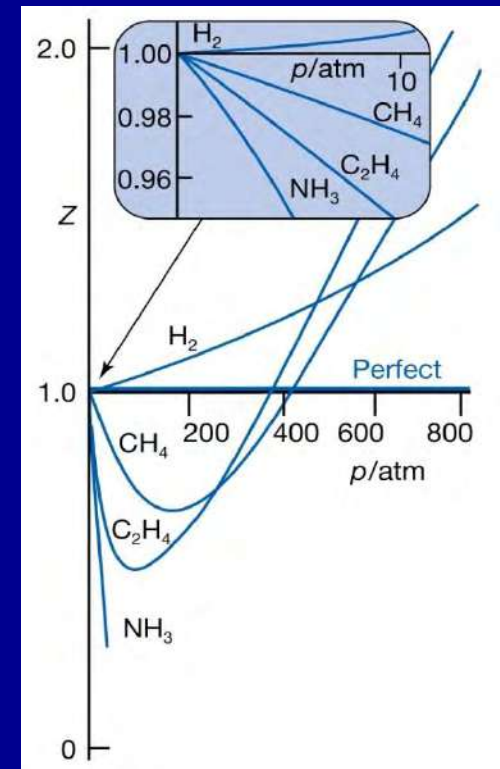
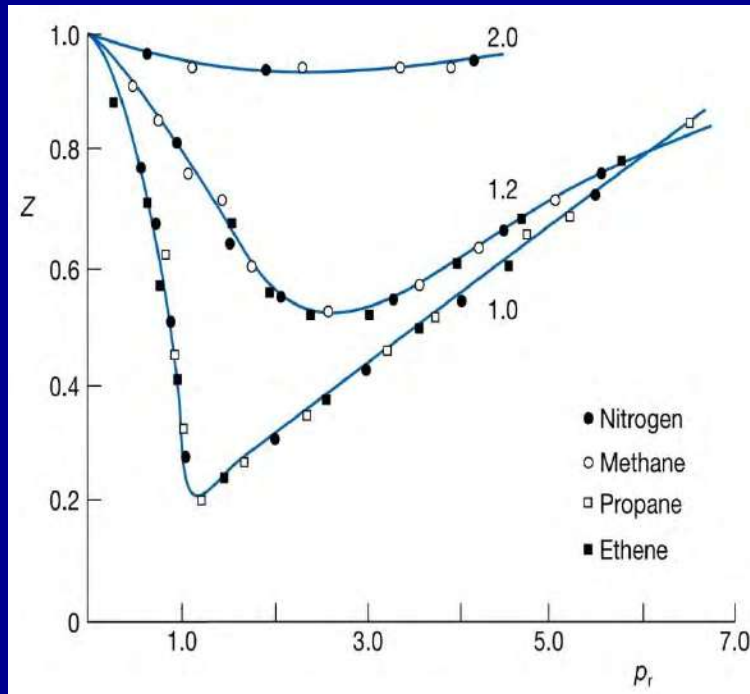
$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

At fixed P and T , \bar{V} is the solution of a cubic equation. There may be one or three real-valued solutions.

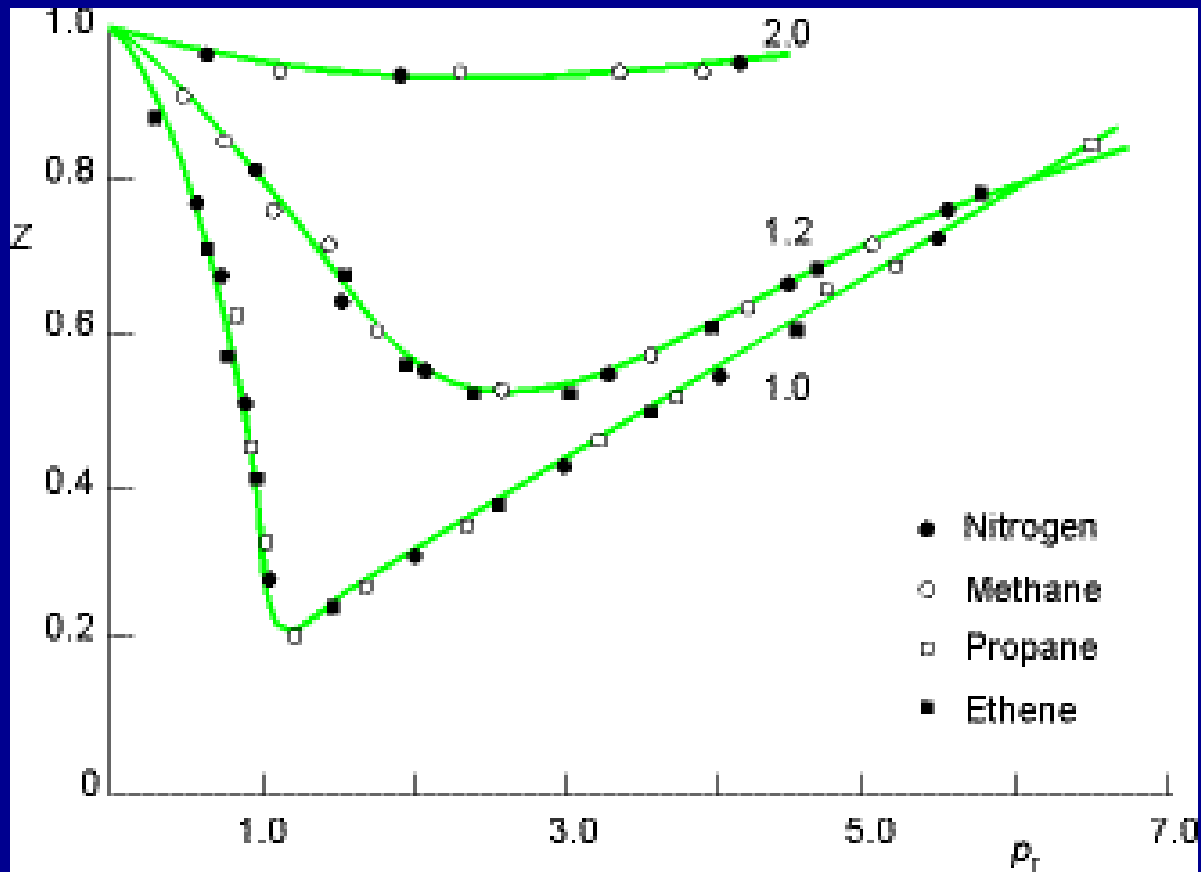
The set of parameters P_c , V_c , T_c for which the number of solutions changes from one to three, is called the **critical point**. The van der Waals equation has an inflection point at T_c .

Critical point of Van Der Waals Equation

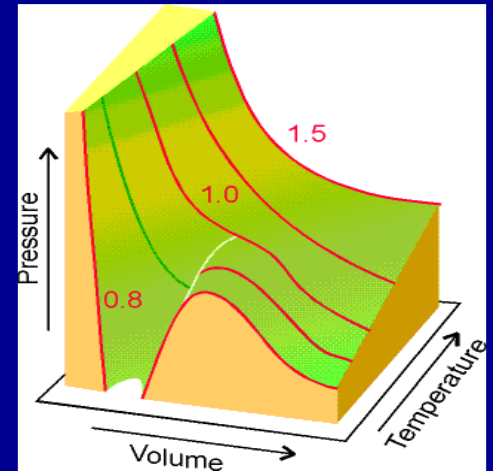
Different gases have different values of p , V and T at their critical point



Comparing different gases



Critical point of *Van Der Waals Equation*

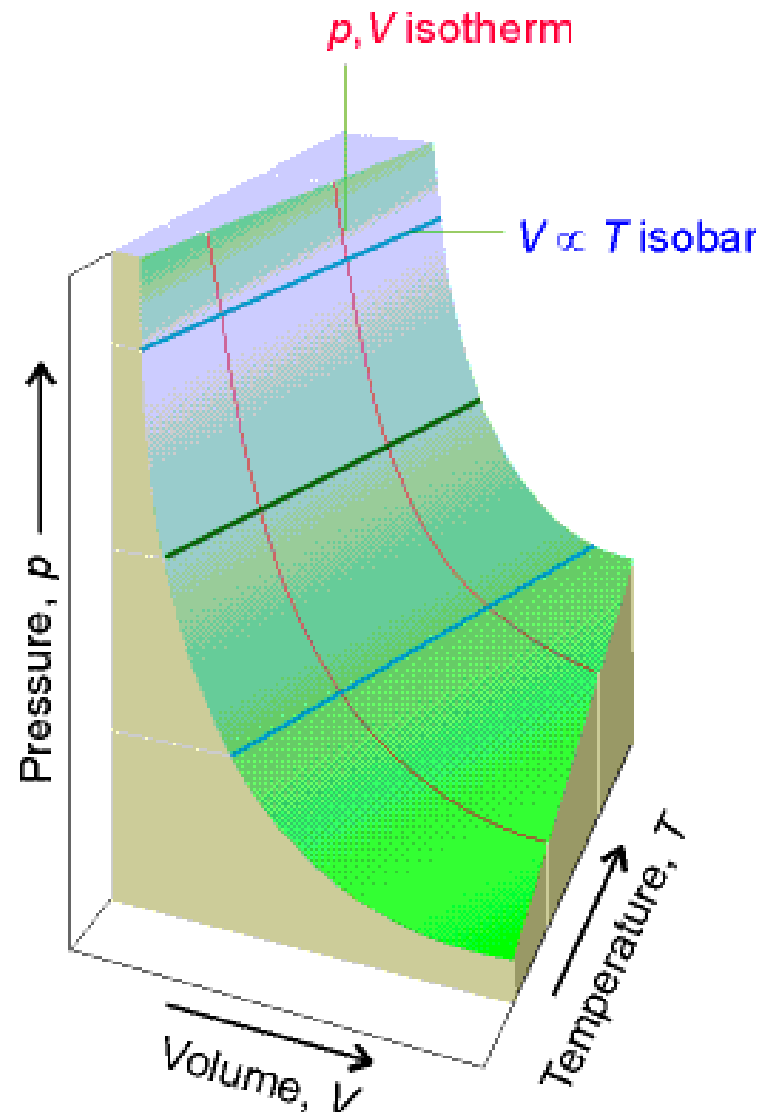
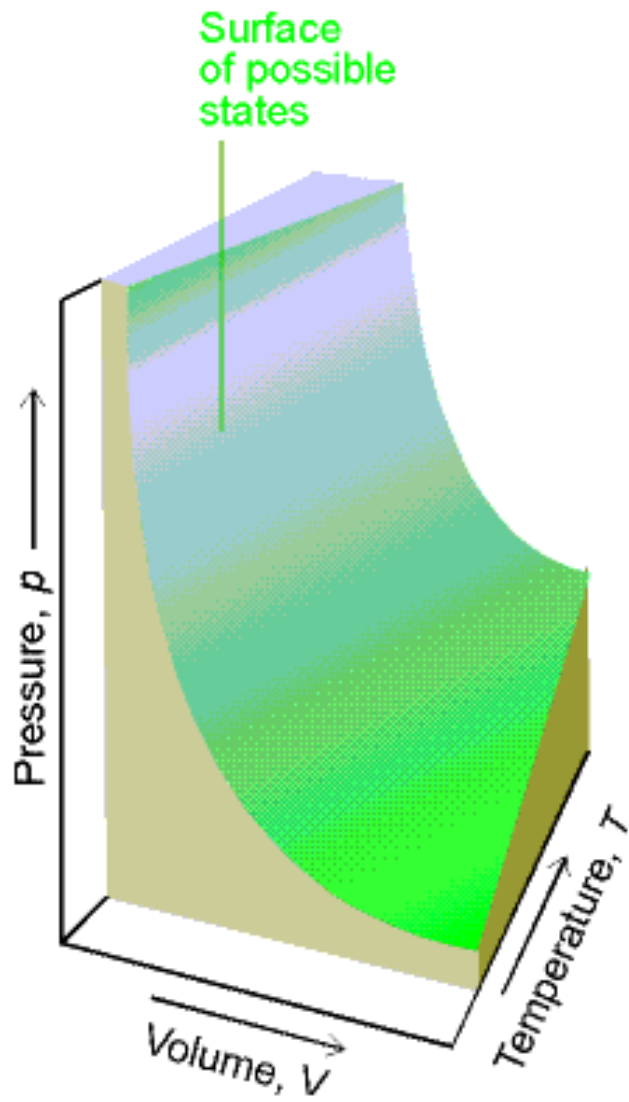


Both are satisfied at the critical (inflection) point, so...

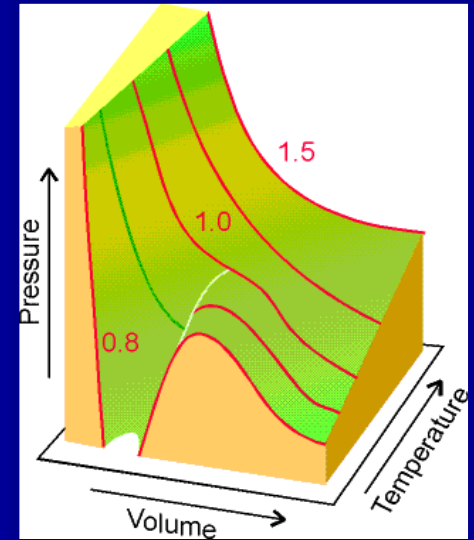
$$p_r p_c = \frac{RT_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2}$$

$$\frac{p_r a}{27b^2} = \frac{RT_r 8a}{27Rb(V_r 3b - b)} - \frac{a}{V_r^2 9b^2}$$

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



Problem



Problem

If sulfur dioxide were an "ideal" gas, the pressure at 0°C exerted by 1.000 mol occupying 22.41 L would be 1.000 atm. Use the van der Waals equation to estimate the "real" pressure.

Solution

First, let's rearrange the van der Waals equation to solve for pressure.

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

$$R = 0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$$

$$T = 273.2 \text{ K}$$

$$V = 22.41 \text{ L}$$

$$a = 6.865 \text{ L}^2 \cdot \text{atm/mol}^2$$

$$b = 0.05679 \text{ L/mol}$$

Problem

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

$$P = \frac{(1.000 \text{ mol})(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(273.2\text{K})}{22.41 \text{ L} - (1.000 \text{ mol})(0.05679 \text{ L/mol})} - \frac{(1.000 \text{ mol})^2 (6.865 \frac{\text{L}^2\cdot\text{atm}}{\text{mol}^2})}{(22.41 \text{ L})^2}$$

$$P = 0.989 \text{ atm}$$

The “real” pressure exerted by 1.00 mol of SO₂ at STP is slightly less than the “ideal” pressure.

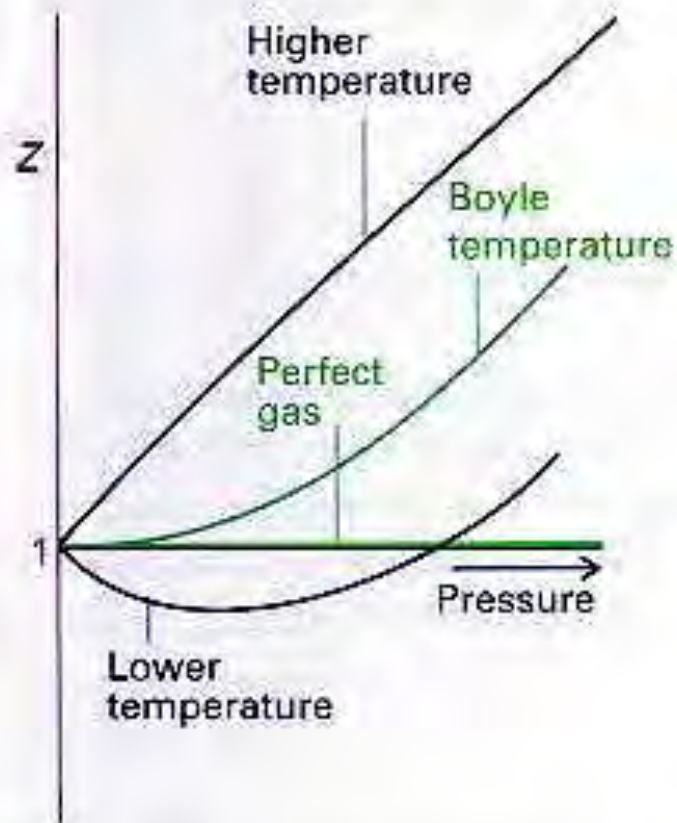
Virial equations of state

- PV along an isotherm:
- $PV = a + bP + cP^2 = a(1 + B'P + C'P^2 + D'P^3 + \dots)$
 - The limiting value of PV as $P \rightarrow 0$ for all the gases:
 - $(PV)^* = a = f(T)$
 - $(PV)^* = a = RT$, with R as the proportionally constant.
 - Assign the value of 273.16 K to the temperature of the triple point of water: $(PV)_t^* = R \times 273.16$
- **Ideal gas:**
 - the pressure ~ 0 ; the molecules are separated by infinite distance; the intermolecular forces approaches zero.

$$R = \frac{(PV)_t^*}{273.16} = 83.1447 \frac{\text{cm}^3 \text{ bar}}{\text{mol K}}$$

◦

VIRIAL COEFFICIENTS and



1.24 The compression factor 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.

Real Gases - Other Equations of State

- Virial equation is phenomenological, i.e., constants depend on the particular gas and must be determined experimentally
- Other equations of state based on models for real gases as well as cumulative data on gases
 - Berthelot (1898)
 - Better than van der Waals at pressures not much above 1 atm

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

- a is a constant

- Dieterici (1899)

$$p = \frac{RTe^{-a/RTV_m}}{V_m - b}$$

Question time!

Question

- Consider a fixed volume of gas. When N or T is doubled the pressure doubles since $pV=NkT$
 - T is doubled: what happens to the rate at which a molecule hits a wall?
(a) 1 (b) 2 (c) 2
 - N is doubled: what happens to the rate at which a molecule hits a wall?
(a) 1 (b) 2 (c) 2

Question 2

- Container A contains 1 l of helium at 10 °C, container B contains 1 l of argon at 10 °C.
 - a) A and B have the same internal energy
 - b) A has more internal energy than B
 - c) A has less internal energy

Question 3

- Container A contains 1 l of helium at 10 °C, container B contains 1 l of argon at 10 °C.
 - a) The argon and helium atoms have the same average velocity
 - b) The argon atoms are on average faster than the helium atoms
 - c) The argon atoms are on average slower than the helium atoms

Question 4

- **Container A contains 1 l of helium at 10 °C, container B contains 1 l of helium at 20 °C.**
 - a) The average speeds are the same**
 - b) The average speed in A is only a little higher**
 - c) The average speed in A is about 2 higher**
 - d) The average speed in A is about twice as high**