

# Chapter 1. The properties of gases

## Major Concepts

- Ideal gas
  - Equations of State
- Real Gases
  - Virial Series
  - Vdw
  - Critical Behavior
- Kinetic Model of Gases
  - Velocity and speed distribution
  - Types of average speed
  - Collision of gases and pressure

## You should review

- Definition of a mole
- SI Units
- Ideal gas law
- Critical point definition

Force

$$F = ma = m \left( \frac{dv}{dt} \right) = m \left( \frac{d^2r}{dt^2} \right) = \frac{dp}{dt}$$

Momentum

$$p = mv = m \frac{dr}{dt}$$

Pressure

$$P = F / A = \left( \frac{dp}{dt} \right) / A$$

## Mathematical tools

- Power series [https://en.wikipedia.org/wiki/Power\\_series](https://en.wikipedia.org/wiki/Power_series)
- MacLaurin series

<http://mathworld.wolfram.com/MaclaurinSeries.html>

- Inflection point

<https://www.khanacademy.org/math/differential-calculus/analyzing-functions-with-calculus/points-of-inflection-dc/v/inflection-points>

- Simple derivatives

<https://www.mathsisfun.com/calculus/derivatives-rules.html>

- Solving cubic equations

[https://en.wikipedia.org/wiki/Cubic\\_function](https://en.wikipedia.org/wiki/Cubic_function)

- Spherical Polar coordinates
- Center of Mass Coordinates
- Using Tables of Integrals

# Pressure and Temperature

**Variables of state:** specify the state of a system

n, amount of substance

P, pressure

V, volume it occupies

T, temperature

$$P = F/A$$

$$T/K = \theta/^{\circ}\text{C} + 273.15$$

Table 1A.1 Pressure units\*

Name	Symbol	Value
pascal	1 Pa	$1 \text{ N m}^{-2}, 1 \text{ kg m}^{-1} \text{ s}^{-2}$
bar	1 bar	$10^5 \text{ Pa}$
atmosphere	1 atm	101.325 kPa
torr	1 Torr	$(101\,325/760) \text{ Pa} = 133.32\dots \text{ Pa}$
millimetres of mercury	1 mmHg	133.322... Pa
pounds per square inch	1 psi	6.894 757... kPa

\* Values in bold are exact.

# Equations of State

## Equation of state

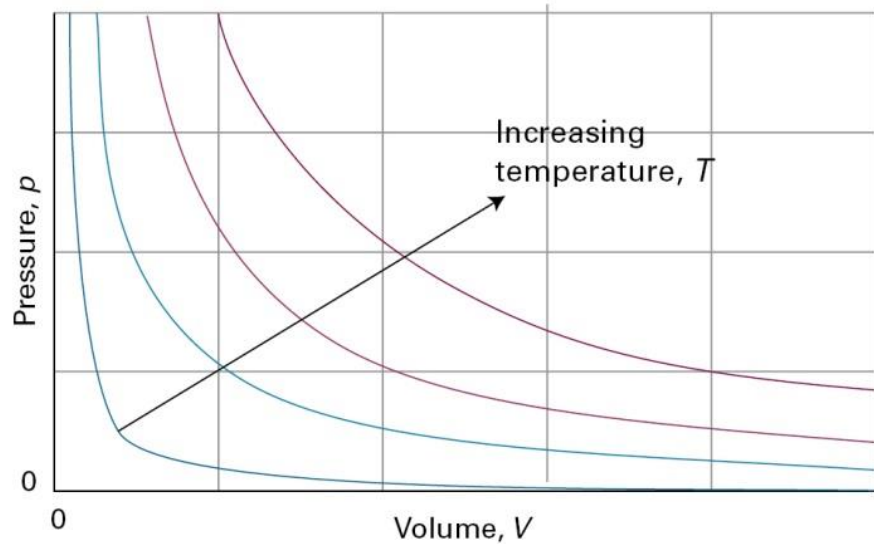


Figure 1A.2 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ( $pV = \text{constant}$ ) and is called an isotherm.

$$P = f(n, V, T)$$

### Empirical Laws:

**Boyle's Law:**

$$PV = \text{constant}$$

constant  $n$ ,  $T$

**Charles Law:**

$$V = \text{constant} \times T$$

constant  $n$ ,  $P$

$$P = \text{constant} \times T$$

constant  $n$ ,  $V$

**Avogadro's Principle:**

$$V = \text{constant} \times n$$

constant  $P$ ,  $T$

Limiting Laws— strictly true only at  $P \rightarrow 0$

### Ideal Gas Law (Perfect Gas Law)

$$PV = nRT$$

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

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

# PVT Surface

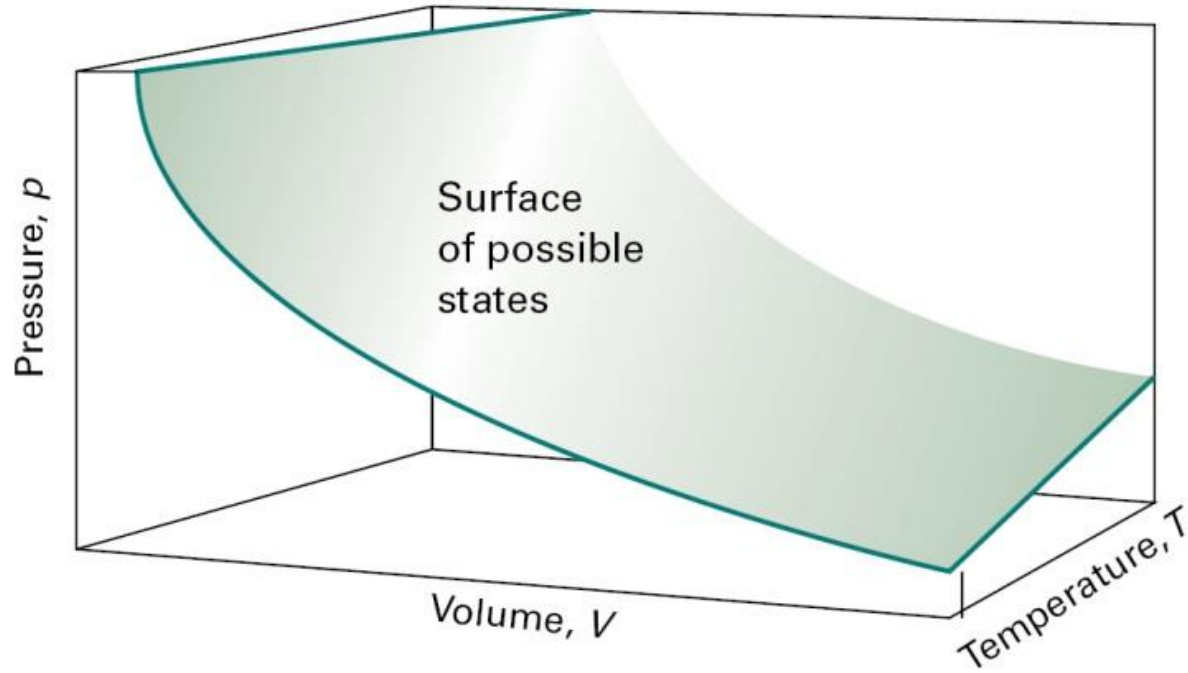


Figure 1A.6 A region of the  $p, V, T$  surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

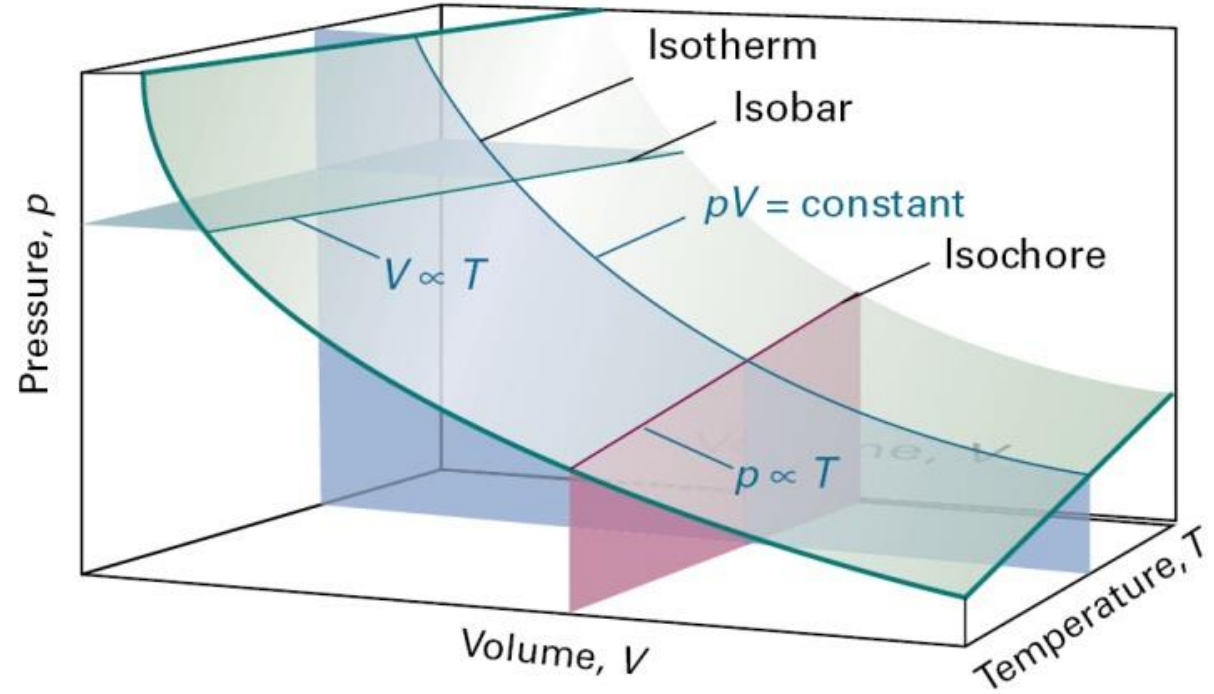


Figure 1A.7 Sections through the surface shown in Fig. 1A.6 at constant temperature give the isotherms shown in Fig. 1A.2, the isobars shown in Fig. 1A.4, and the isochores shown in Fig. 1A.5.

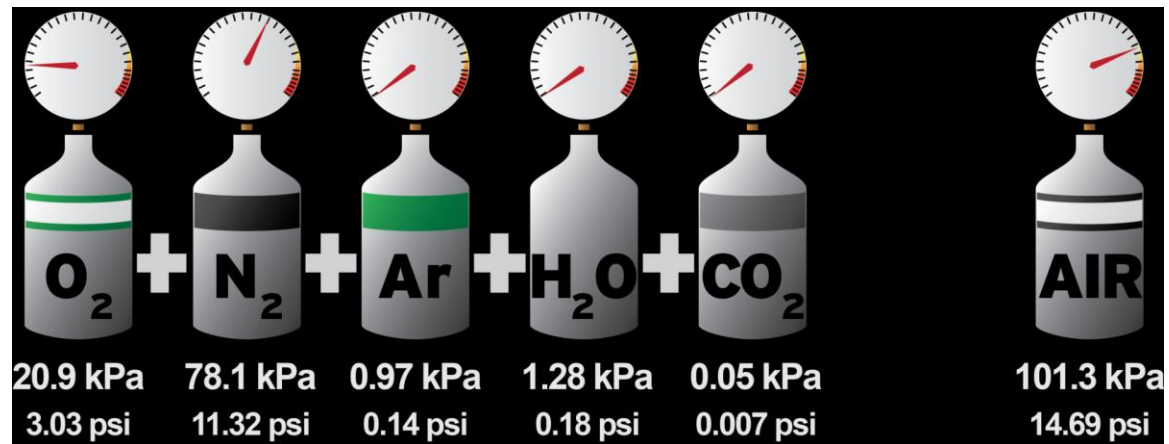
# Partial pressure of mixture of gases, Dalton's Law

- Total pressure of gas mixture = sum of partial pressures of the gases
- Partial pressure of the gas is proportion to the **mole fraction** ( $x_i$ )

$$P_i = x_i \cdot P$$

$$P = \sum P_i, \quad P_i V = n_i RT$$

$P_i$ : partial press of gas  $i$ ,  $n_i$ : amount of gas  $i$  in moles



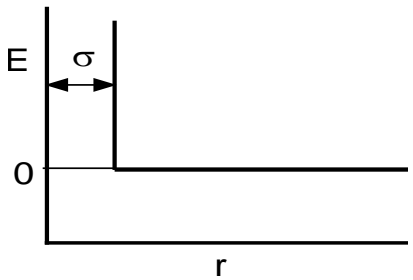
# Real gases

- Real gases have molecular interactions, both attractive and repulsive.
- Short range – strongly repulsive
- Long range – weakly attractive

**Pairwise potential function**  $U(r)$  gives potential energy between a pair of molecules as a function of distance between them,  $r$ .

We'll ignore orientation dependence (bad for polar molecules; ok for spherical)

$U = 0$	$r > \sigma$	$U = 0$	$R\sigma < r < \infty$	$U = -\varepsilon \left(\frac{\sigma}{r}\right)^n$	$\sigma < r < \infty$
$U = \infty$	$r \leq \sigma$	$U = -\varepsilon$	$\sigma < r < R\sigma$	$U = \infty$	$0 < r < \sigma$
		$U = \infty$	$0 < r < \sigma$		

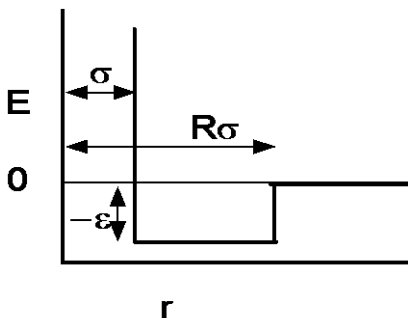


### Hard Sphere

Simplest model

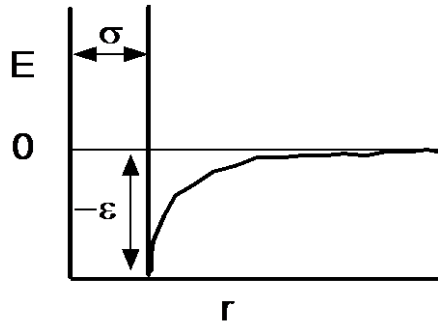
Parameters

- Well depth  $\varepsilon$
- diameter  $\sigma$  (hard sphere)



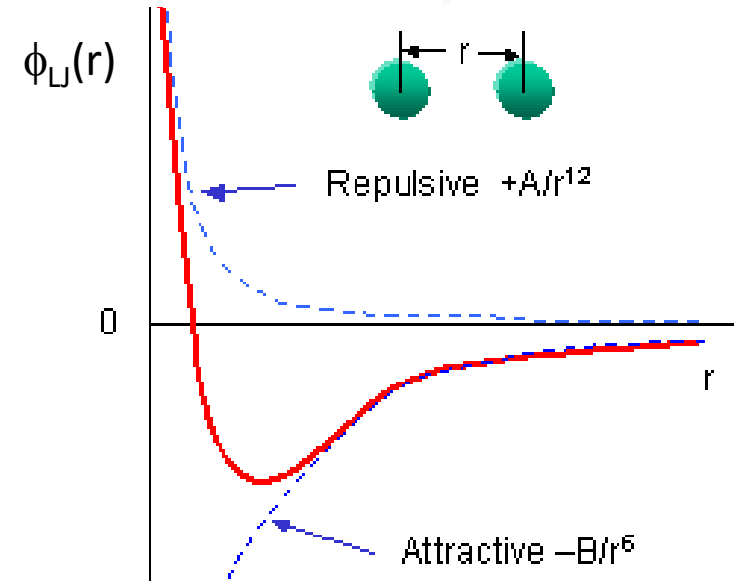
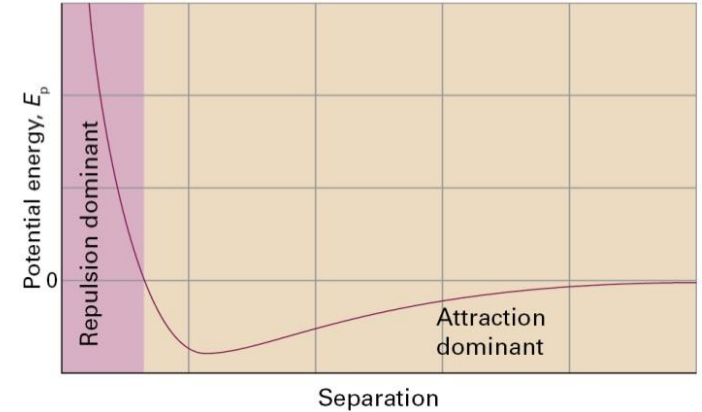
### Square Well

has a potential well



### Sutherland

Better represents long-term attraction



$$U(r) = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

Lennard-Jones Potential

# Perfect vs. Real Gas Behavior

At critical point, phase boundary between liquid and gas disappears and satisfies:

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

ideal gas isotherms do not predict critical behavior

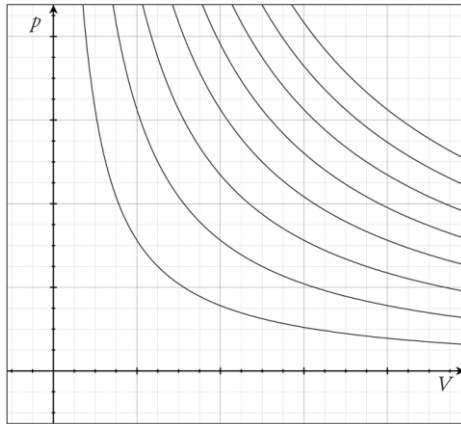


Table 1C.2\* Critical constants of gases

	$p_c/\text{atm}$	$V_c/(\text{cm}^3 \text{ mol}^{-1})$	$T_c/\text{K}$	$Z_c$	$T_B/\text{K}$
Ar	48.0	75.3	150.7	0.292	411.5
CO <sub>2</sub>	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O <sub>2</sub>	50.14	78.0	154.8	0.308	405.9

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

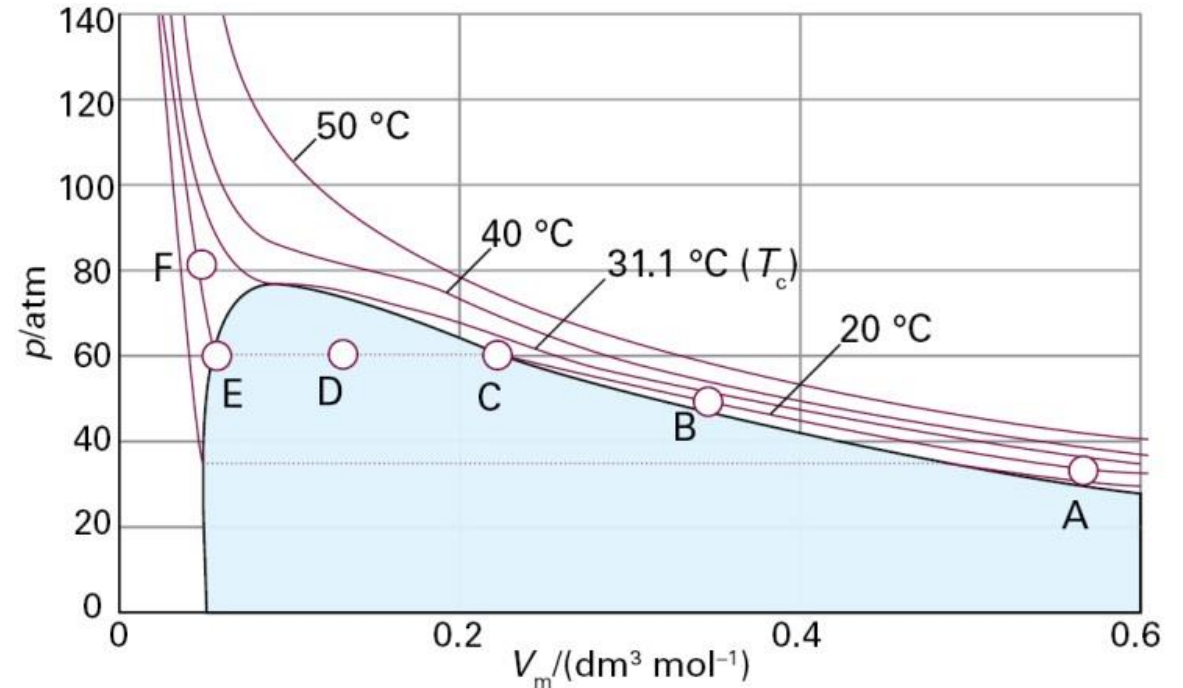


Figure 1C.2 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.1 °C.

# Compressibility Factor

Need to modify ideal gas equation of state to accommodate non-ideality of the real gas.

$$z \equiv \frac{PV_m}{RT}$$

Compressibility

For ideal gas,  $z = 1$

Deviation from 1 is measure of non-ideality

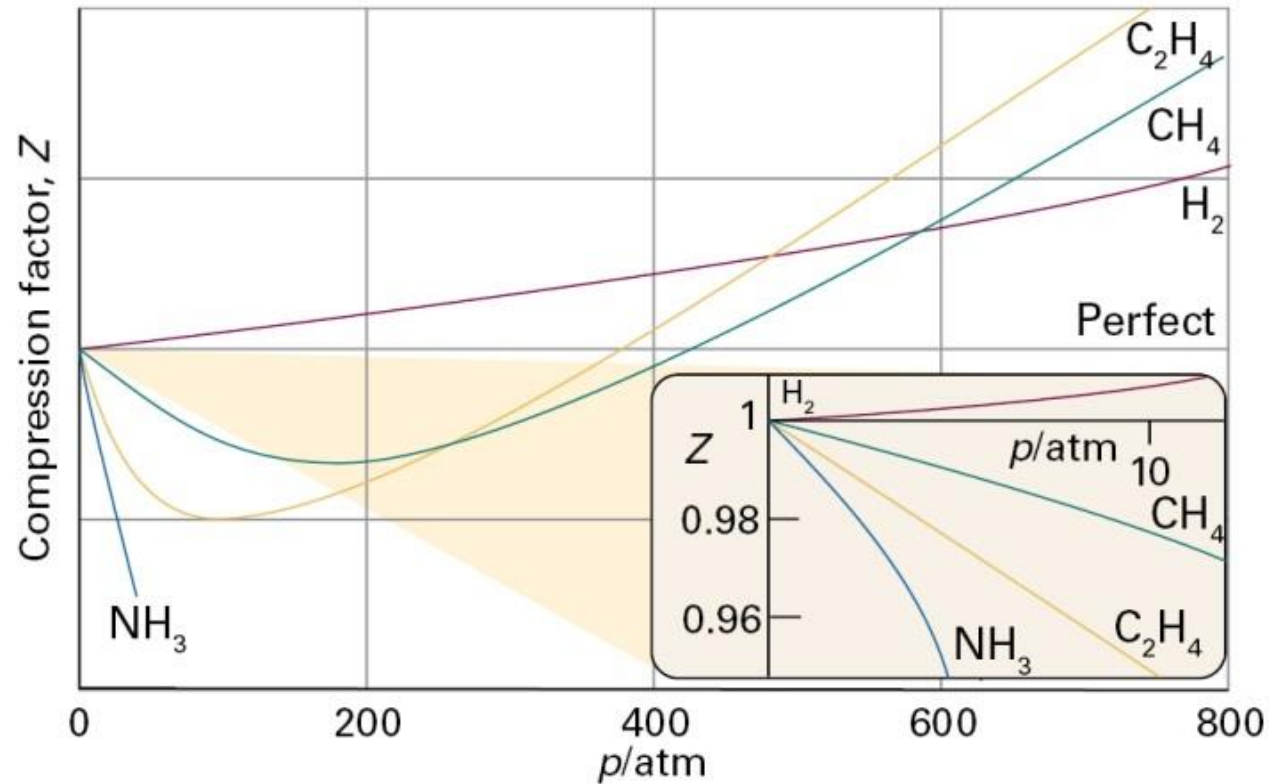


Figure 1C.3 The variation of the compression factor,  $Z$ , with pressure for several gases at  $0^\circ\text{C}$ . A perfect gas has  $Z = 1$  at all pressures. Notice that, although the curves approach 1 as  $p \rightarrow 0$ , they do so with different slopes.



# Virial Coefficients

**Virial equation of state:** one way to discuss real gases with moderate deviation from ideality

$$PV_m = RT(1 + B'P + C'P^2 \dots)$$

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

Coefficients used to calculate intermolecular interactions

1st term (1) represents non-interacting particles

2nd term (B) represents *pairs* of molecules

3rd term (C) represents *trios* of molecules (usually less important than B)

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

	Temperature	
	273 K	600 K
Ar	-21.7	11.9
CO <sub>2</sub>	-149.7	-12.4
N <sub>2</sub>	-10.5	21.7
Xe	-153.7	-19.6

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

----- Math Sidebar -----

Any analytic function can be fit by an infinite power series

$$f(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + \dots$$

Only useful if series can be truncated after a few terms i.e.  $a_{n+1} \ll a_n$  or  $x \ll 1$

## Boyle Temperature, $T_B$

$B(T)$  can be +, - or 0

T when  $B(T)=0$  is called Boyle temperature.

Gas behaves ideally at this temp.

# van der Waals equation of state

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

or

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

Accounts for  
intermolecular attraction

Accounts for volume of  
molecule

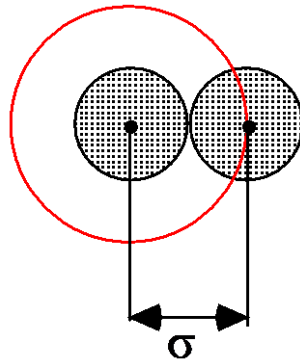
a, b constants depend on gas.

a (Pa.m<sup>6</sup>.mol<sup>-2</sup>) -- accounts for attractive force which effectively reduce pressure.

b (m<sup>3</sup>.mole<sup>-1</sup>) -- accounts for the fact that molecules occupy space (repulsive forces)

Volume available = container vol. - volume of molecules  
excluded volume:

$$b = \frac{2\pi L\sigma^3}{3}$$



$2\sigma$  -- diameter of spheres of excluded volume

$\sigma$  -- diameter of molecules

L -- number of molecules (L/2 pairs)

Excluded volume per pair of atoms:

$$V = \frac{4\pi\sigma^3}{3}$$

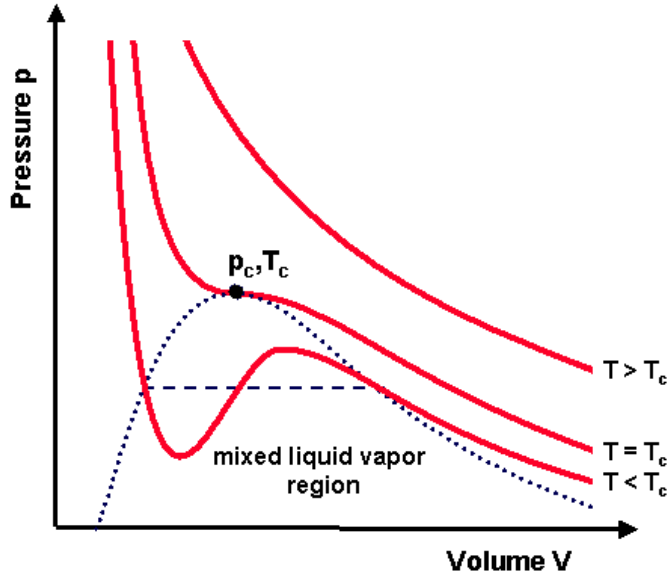
Table 1C.3\* van der Waals coefficients

	$a/(\text{atm dm}^6 \text{ mol}^{-2})$	$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$
Ar	1.337	3.20
CO <sub>2</sub>	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

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

# Van der Waals and Critical Constants

vdw gas isotherms qualitatively predict critical behavior.  $P_c$ ,  $V_c$ ,  $T_c$  can be expressed in terms of vdw constants



(c) C. Rose-Patruck, Brown University, 7-Jan-99, Chem 201 #1

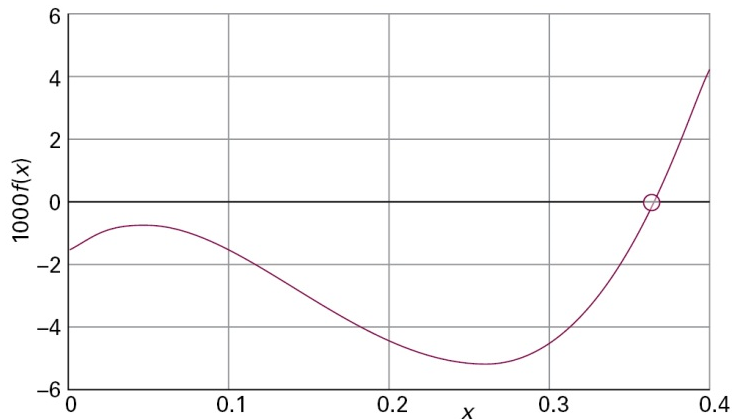


Figure 1C.6 The graphical solution of the cubic equation for  $V$  in Example 1C.1.

At tie-line,  $P = \text{Vapor Pressure}$   
Liq. & Gas in Equilibrium

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

vdw is cubic in volume, so has 3 roots

2 of the roots account for volumes of two phases

1 -- large volume (gas)

2 -- small volume (liquid)

3 -- not a stable root ( $dP/dV$  is positive)

better for *qualitative* information than *quantitative*

e.g.  $\text{NH}_3$  at 350 K vdw predicts vp of 61 atm; actual is 38.4 atm

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

# Law of Corresponding States

- *Law of Corresponding States* -- properties of different gases are similar at their respective critical points.
- Scaling properties to critical parameters produces universal behavior.

## Reduced Constants

$$T_r = \frac{T}{T_c} \quad P_r = \frac{P}{P_c} \quad V_r = \frac{V}{V_c}$$

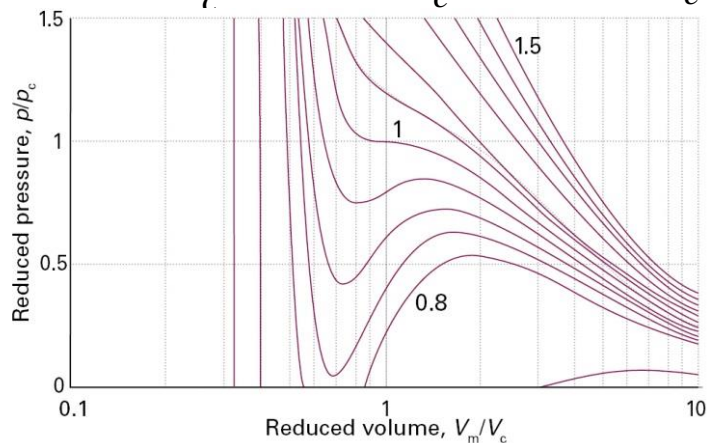


Figure 1C.8 van der Waals isotherms at several values of  $T/T_c$ . Compare these curves with those in Fig. 1C.2. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for  $T/T_c=1$ .

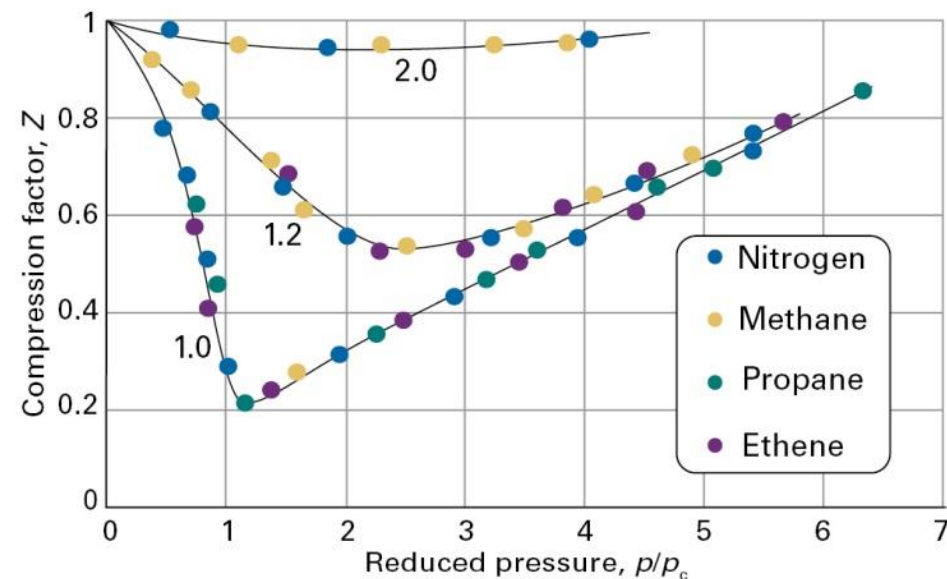
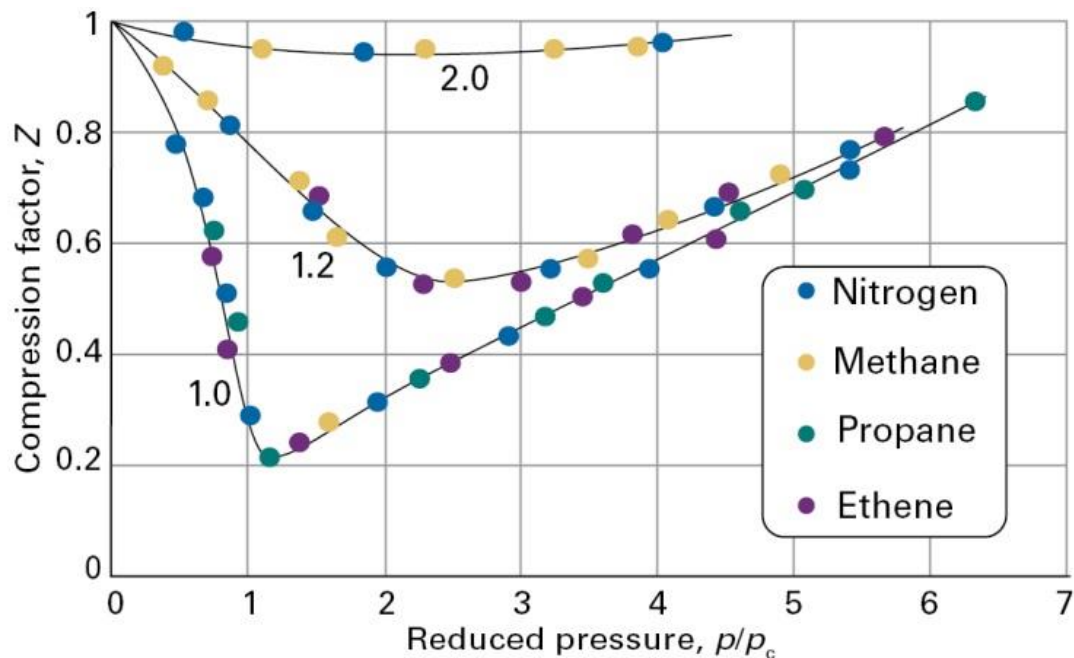


Figure 1C.9 The compression factors of four of the gases shown in Fig. 1C.3 plotted using reduced variables. The curves are labelled with the reduced temperature  $T_r = T/T_c$ . The use of reduced variables organizes the data on to single curves.



**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.

**Table 1C.2\*** Critical constants of gases

	$p_c/\text{atm}$	$V_c/(\text{cm}^3 \text{ mol}^{-1})$	$T_c/\text{K}$	$Z_c$	$T_B/\text{K}$
Ar	48.0	75.3	150.7	0.292	411.5
CO <sub>2</sub>	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O <sub>2</sub>	50.14	78.0	154.8	0.308	405.9

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

# Other Equations of State

Table 1C.4 Selected equations of state

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

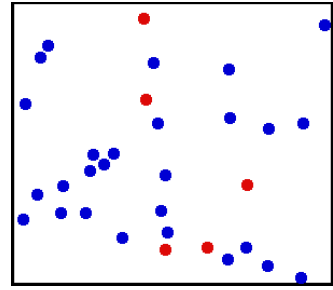
\* Reduced variables are defined in Section 1C.2(c). Equations of state are sometimes expressed in terms of the molar volume,  $V_m = V/n$ .

Vdw and other gas law constants can be related to Virial Coefficients B, C, and D

e.g. vdw:  $B = b - \frac{a}{RT}$      $C = b^2$      $D = b^3$

# Kinetic Theory of Gases

**Kinetic Theory of Gases** - assumes that the only contribution to the energy of gas is from kinetic energy of molecules (i.e. - potential energy of interactions is negligible)



Based on 3 assumptions:

1. **Molecules have mass,  $m$ , and diameter,  $d$**

Characterized by velocity\*,  $v$ , and momentum ( $p = mv$ ) or kinetic energy ( $KE = 1/2mv^2$ )

Important quantity: Number density:  $n^* = N/V$  [Using ideal gas law  $n^* = PN_A/RT$  ( $n = N/N_A$ )]

2. **Size of molecules is negligible** (diameters much smaller than average distance travelled between collisions)

3. **Molecules do not interact other than perfectly elastic collisions** when separation of their centers is equal to  $d$ .

Will use kinetic theory to find energy and speed of molecules.

\***velocity** - vector quantity; has direction ( $\theta, \phi$ ) and magnitude ( $|v|$ )  $v_x = \frac{dx}{dt}$   $v_y = \frac{dy}{dt}$   $v_z = \frac{dz}{dt}$   
can be positive or negative

**speed** -- always positive  $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$   $v_x = v \sin \theta \cos \phi$   $v_y = v \sin \theta \sin \phi$   $v_z = v \cos \theta$

# Collisions with Wall

Consider that you have a wall in the  $yz$  plane.

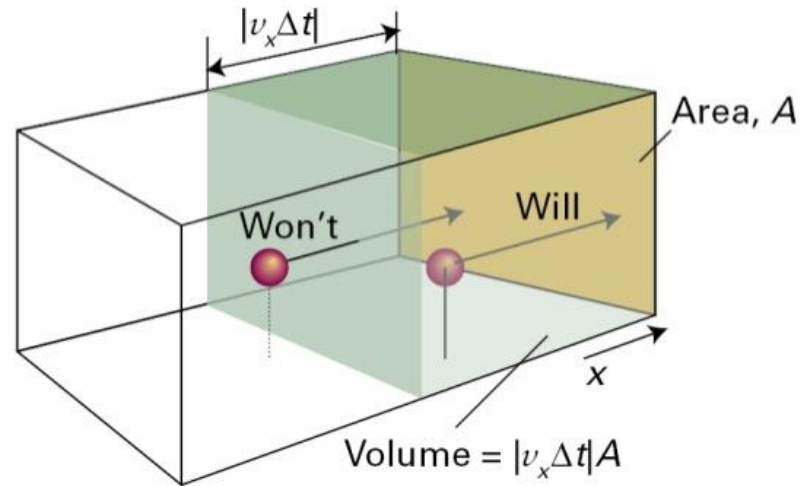
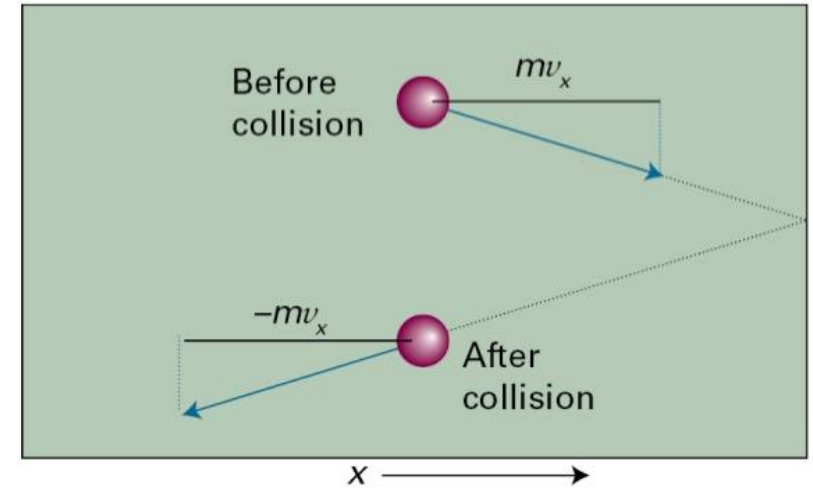
Molecules with a velocity in  $x$  direction will collide with wall.

A molecule with  $v_x$  will collide w/ wall w/in time  $\Delta t$ .

Will molecule collide with wall?

"Construct" a box with height =  $|v_x| \Delta t$  and cross-sectional area =  $A$

Volume =  $A|v_x| \Delta t$





# Collisions & Momentum

- So *# collisions with velocity  $v_x$*  =  $n^* A |v_x| \Delta t f(v_x)$  (Remember,  $n^*$  is molecules/unit volume) where  $f(v_x)$  is the fraction of molecules having  $v_x$
- *Total collisions* =  $n^* A \Delta t \sum |v_x| f(v_x)$  summed over positive velocities; must know  $f(v_x)$  to find  
But, can find P and speed of gas without  $f(v_x)$

Consider momentum: Molecule heading toward wall

- *momentum before collision:*  $p_x = mv_x$        $p_y = mv_y$        $p_z = mv_z$   
*after collision:*  $p_x = -m|v_x|$        $p_y = mv_y$        $p_z = m|v_z|$

• *Difference in momenta for each collision:*  $\Delta p = 2m|v_x|$

• *Momenta of all collisions of  $v_x$*  =  $\Delta p / \text{collision} \cdot \# \text{ collisions} = 2m|v_x| n^* A \Delta t |v_x| f(v_x) = 2mn^* A \Delta t |v_x|^2 f(v_x)$

• *Momenta for all collisions* =  $2mn^* A \Delta t \sum |v_x|^2 f(v_x)$  summed over positive velocities

## Using Change in Momentum to find Pressure of a Gas

$$\sum_{\text{positive}} v_x^2 f(v_x) = \frac{1}{2} \sum_{\text{all}} v_x^2 f(v_x) \text{ b/c on average, as many molecules have positive as negative velocity}$$

- Define *average squared velocity*  $\langle v_x^2 \rangle = \sum_{\text{all}} v_x^2 f(v_x)$  (angle brackets used to denote an average)

$$\sum_{\text{positive}} v_x^2 f(v_x) = \frac{1}{2} \langle v_x^2 \rangle$$

- Change in momenta for all collisions  $2mn^*A \Delta t \Sigma |v_x|^2 f(v_x)$ :  $\Delta p = mn^*A \Delta t \langle v_x^2 \rangle$

- Pressure of a Gas Pressure = Force/unit Area

$$\text{Force (F) = mass (m) \cdot acceleration (a) = m \cdot dv/dt = dp/dt \sim \Delta p / \Delta t}$$

$$\text{Therefore, } P \sim \Delta p / \Delta t A \quad P = mn^* \langle v_x^2 \rangle$$

- Pressure in terms of velocity  $PV = mnN_A \langle v_x^2 \rangle = nM \langle v_x^2 \rangle$

Use ideal gas  $nRT = PV = nM \langle v_x^2 \rangle$ . So,  $\langle v_x^2 \rangle = \frac{RT}{M}$

relates a microscopic quantity (velocity) to macroscopic quantity (temperature)

Choose other walls would get same result for  $v_y$  and  $v_z$   $v^2 = v_x^2 + v_y^2 + v_z^2$

Average:  $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \frac{3RT}{M}$  • *root-mean-square speed*

$$u = \sqrt{\frac{3RT}{M}}$$

$$\langle v^2 \rangle^{1/2} \equiv u$$

# Recap & Reminders

- **Virial Series and virial coefficients used to describe real gases**

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

- ***Van der Waals equation of state corrects for non-idealities with constants a and b***

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

- ***Reduced parameters ( $T_r$ ,  $V_r$ ,  $P_r$ ) can be used to compare different gases since many properties scale as a ratio of their critical points. Principle of Corresponding States***

$$T_r = \frac{T}{T_c} \quad P_r = \frac{P}{P_c} \quad V_r = \frac{V}{V_c}$$

- ***Other equations of states are used. These models of gas laws can be related to each other.***
- ***Kinetic theory of gases assumes gases have mass  $m$ , diameter,  $d$  and velocity  $v$ .***

## Kinetic Energy

$$KE = \frac{1}{2}mv^2$$

$$\text{Average } KE = \frac{m\langle v^2 \rangle}{2} = \frac{m(3RT)}{2M}$$

$$\text{Average } KE = \frac{3}{2}k_bT$$

m - mass per atom

M - mass per mole

Boltzmann's constant

$$M = mL$$

$$k_b = R / L$$

Only accounts for translational energy

Now, to determine number of collisions, need to know  $f(v_x)$  -- the probability distribution function

# Probability Distribution Function

Start by considering an average  $\langle x \rangle = \frac{\sum n_i x_i}{\sum n_i}$

$\langle x \rangle$  --average property -- will use this notation often!

$n_i$  -number of molecules having property

$n_T = \sum n_i$  -- total number of molecules

Probability of finding a certain property is  $f_i = \frac{n_i}{n_T}$

average:  $\langle x \rangle = \sum f_i x_i$       mean square:  $\langle x^2 \rangle = \sum f_i x_i^2$

$\langle x^2 \rangle^{1/2}$  (**root-mean-square**) is different from  $\langle x \rangle$  (**average**).

Mean square is related to degree which numbers differ from average.

- If  $x$  is continuous: convert sum to integral

$dn = n_T f(x) dx$        $dn$  -- number of items having property between  $x$  and  $x+dx$

$n_T$  -- total number of particles

$f(x)$  probability distribution function

$$f(x) dx = \frac{dn}{n_T}$$

Example:

$$f(x) = \frac{1}{2\sqrt{\pi}} \exp\left[\frac{-(x-21)^2}{4}\right]$$

## Rules for Distribution Functions

1) The sum of all fractions is 1.  
Such a function is said to be *normalized*.  $\int_{-\infty}^{\infty} f(x)dx = 1$

2) Average value of x is given by  $\langle x \rangle = \int_{-\infty}^{\infty} xf(x)dx$   
Compare to  $\langle x \rangle = \sum f_i x_i$

3) Mean Square of x is given by  $\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 f(x)dx$   
Compare to  $\langle x^2 \rangle = \sum f_i x_i^2$

4) To find the probability that a particle has a property between  $x_1$  and  $x_2$

$$P(x_1, x_2) = \int_{x_1}^{x_2} f(x)dx$$

# Maxwell – Boltzmann Distribution of Speeds

Velocity distribution function

$$f(v_x)dv_x = \sqrt{\frac{m}{2\pi k_b T}} \exp\left(-\frac{mv_x^2}{2k_b T}\right) dv_x$$

Speed distribution function  
Justification 1B.2

$$F(v)dv = 4\pi\left(\frac{m}{2\pi k_b T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_b T}\right) v^2 dv$$

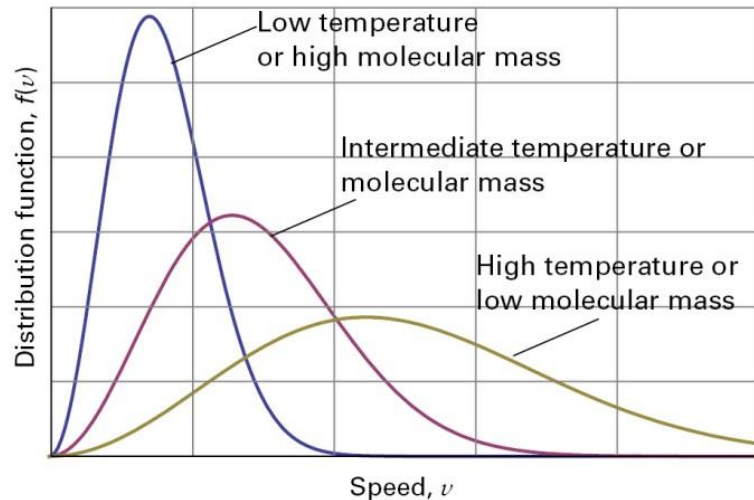
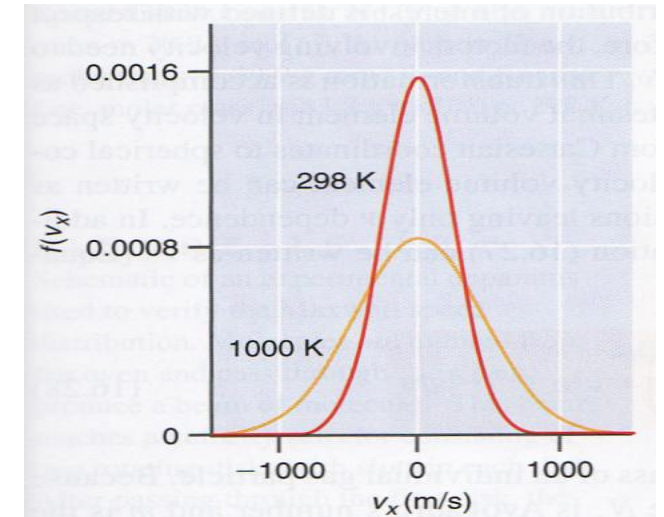
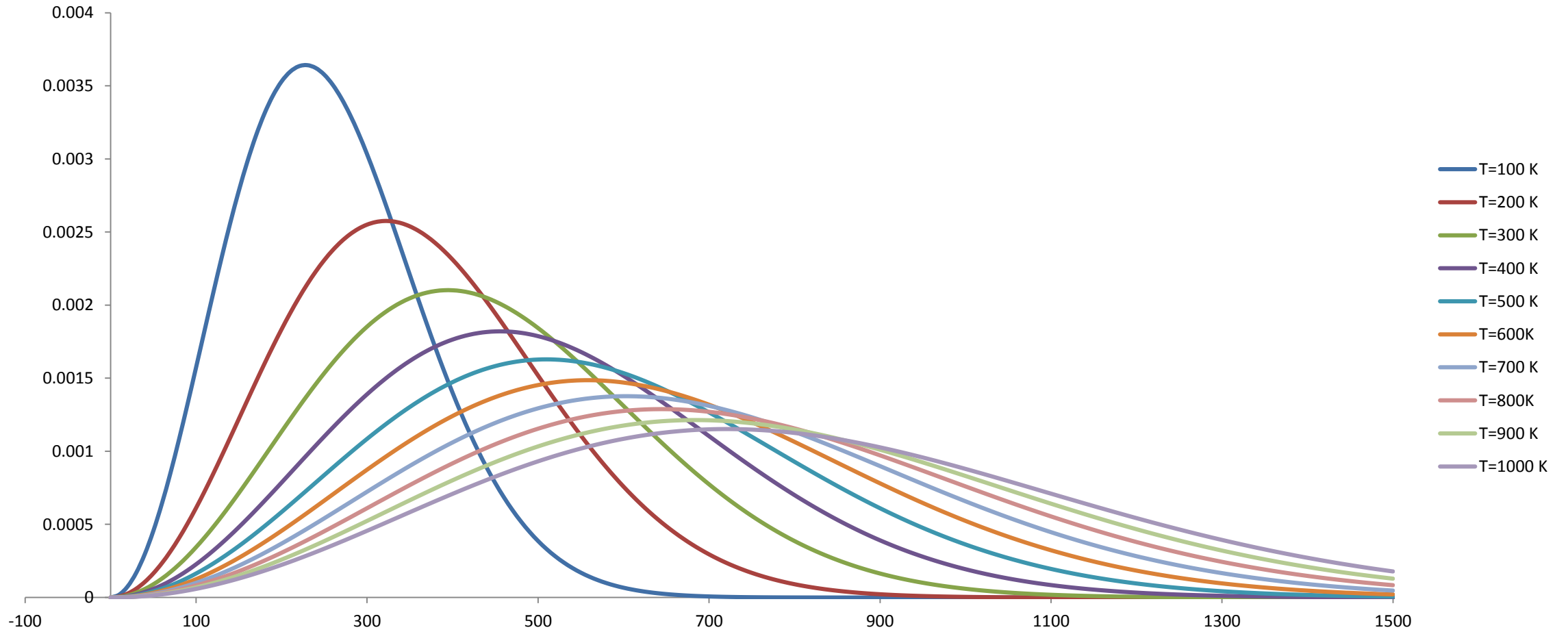


Figure 1B.4 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

- Decaying exponential
  - fraction of molecules with high speeds is small
- Mass factor in exponential
  - heavy molecules unlikely to be found at high speeds
- Inverse T in exponential
  - greater fraction of molecules at high speeds at high T
- Factor of  $v^2$ 
  - Fraction of molecules with low speeds will be small

# Distribution of speeds for O<sub>2</sub>





# Probable and Average Speeds

$$F(v)dv = 4\pi \left( \frac{m}{2\pi k_b T} \right)^{3/2} \exp\left(-\frac{mv^2}{2k_b T}\right) v^2 dv$$

↓ m or ↑ T, maxima occur at higher v.

- **Most Probable Speed** -- take derivative of  $F(v)dv$  and set equal to 0. (Do this!)

$$v_p = \sqrt{\frac{2k_b T}{m}}$$

- **Average speed**  $\bar{v} = \langle v \rangle = \sqrt{\frac{8RT}{\pi M}}$

From  $\langle v \rangle = \int_0^{\infty} v F(v) dv$  -- starts at 0, because there are no negative speeds (Do this!)

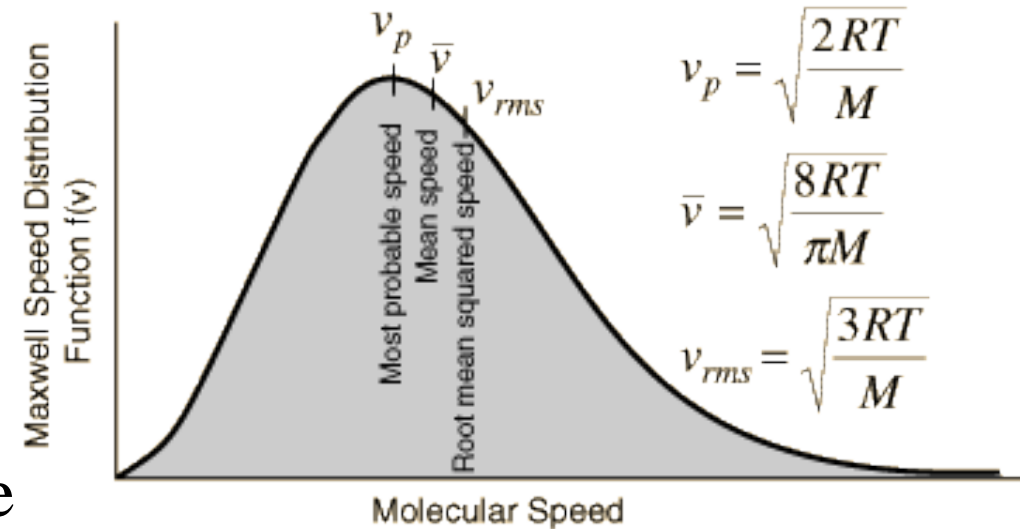
- Fraction of molecules having speeds between  $v_1$  and  $v_2$

$$P(v_1, v_2) = \int_{v_1}^{v_2} F(v) dv = 4\pi \left( \frac{m}{2\pi k_b T} \right)^{3/2} \int_{v_1}^{v_2} \exp\left(-\frac{mv^2}{2k_b T}\right) v^2 dv$$

Must evaluate numerically—can use unitless equation with  $w \equiv v/\sqrt{2k_b T/m}$  (m in kg)

$$P(v_1, v_2) = \frac{4}{\sqrt{\pi}} \int_{w_1}^{w_2} \exp(-w^2) w^2 dw$$

$$f(v) = 4\pi \left[ \frac{M}{2\pi RT} \right]^{3/2} v^2 \exp\left[ \frac{-Mv^2}{2RT} \right]$$



# Molecular Collisions

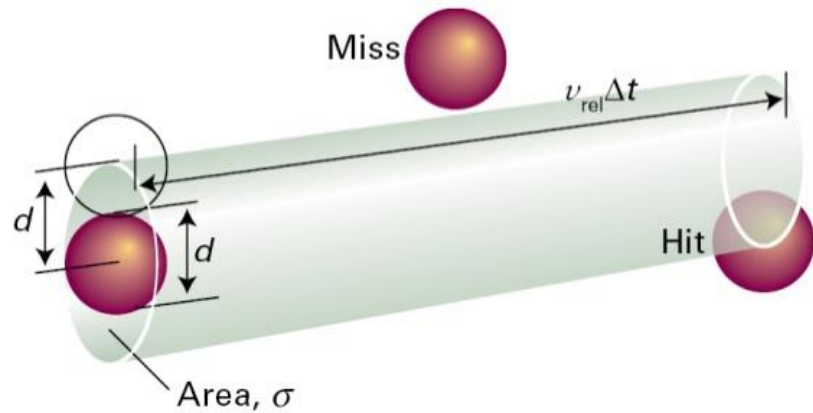
Want to determine the **collision frequency** and **total number of collisions** between gas molecules.

Assume molecules are hard spheres with *diameters* of  $d$ .

Two molecules will collide if they approach w/in distance  $d$ .

A molecule moving through space at speed  $v$  will sweep out cylinder of volume  $V$  in  $\Delta t$ .

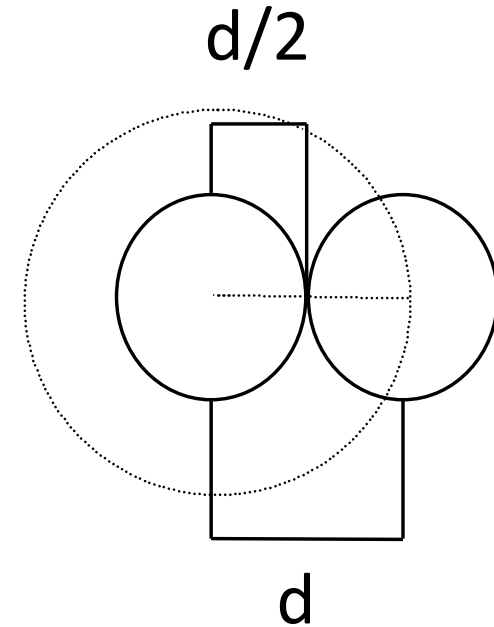
Any molecule whose center is in this volume will be hit.



$$V = \pi d^2 v \Delta t$$

$$\text{Area : } \sigma = \pi d^2$$

$$\text{Length: } v \Delta t \text{ (m/s)s=m}$$



**collision cross section:**  $\sigma = \pi d^2$   
cross-sectional area of an imaginary sphere  
surrounding molecule into which the center of  
another molecule cannot penetrate

Table 1B.1\* Collision cross-sections,  $\sigma/\text{nm}^2$

	$\sigma/\text{nm}^2$
$\text{C}_6\text{H}_6$	0.88
$\text{CO}_2$	0.52
He	0.21
$\text{N}_2$	0.43

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

# Molecular Collisions, Continued

Collision frequency,  $Z$ , depends on molecule's **collisional cross-section**, **speed**, & **density of targets**.  $Z = \sigma v n^*$

density of targets in cylinder depends on **number density** (molecules / unit volume),  $n^*$

Using ideal gas (and  $n = N/N_A$ ),  $n^* = \frac{N}{V} = \frac{PN_A}{RT}$

Not all molecules moving at same  $v$ .

$$\bar{v} = \int_0^{\infty} v F(v) dv = \sqrt{\frac{8RT}{\pi M}}$$

**The average speed:**

Really want **average relative velocity** b/c molecule is hitting a moving target (another molecule) not a fixed target (e.g. wall) (See Figure 1B.8)

$$v_{rel} = \left( \frac{8kT}{\pi\mu} \right)^{1/2} \quad \mu = \frac{m_A m_B}{m_A + m_B} \quad v_{rel} = \sqrt{2} \bar{v} \quad \text{For identical molecules}$$

$$Z = \sigma v_{rel} n^* \quad z = \frac{\sigma v_{rel} P}{kT}$$

# Mean Free Path

**Mean free path** ( $\lambda$ ) is the average distance traveled by a molecule between collisions

$$\lambda = \frac{v_{rel}}{Z}$$

Using  $z$ ,  $\lambda = \frac{k_b T}{\sigma P}$

Get  $\sigma$  from Table 1B.1 or resource section

Table 1B.1\* Collision cross-sections,  $\sigma/\text{nm}^2$

	$\sigma/\text{nm}^2$
$\text{C}_6\text{H}_6$	0.88
$\text{CO}_2$	0.52
He	0.21
$\text{N}_2$	0.43

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

Compare  $\lambda$  to  $\sigma$ : Gas is mostly empty space!

# Major Concept Review

Ideal Gas,  $PV = nRT$

- Compressibility ( $z$ ), Virial Series, and Coefficients
- How used; Boyle Temperature

Gas Mixtures

Critical Behavior and Law of Corresponding States

Modeling of Intermolecular Interactions in Real Gases

Real Gas Laws: vdw, others

Relationship between intermolecular forces, gas constants, critical constants, and virial coefficients

Kinetic Molecular Theory

Molecular Speeds

Maxwell-Boltzmann distribution

Collision Frequency

Mean Free Path