Part 1: Equilibrium

1. The properties of gases

Bilingual

Program

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This chapter establishes the properties of gases that will be used throughout the text. It begins with an account of an idealized version of a gas, a perfect gas, and shows how its equation of state may be assembled experimentally. We then see how this relation between the properties of the gas can be explained in terms of the kinetic model, in which the gas is represented by a collection of point masses in continuous random motion. Finally, we see how the properties of real gases differ from those of a perfect gas, d C 0 n s t a 1 r 11 an equation of state that describes their properties.



The perfect gas **1.1 The states of gases 1.2 The gas laws 1.3 The kinetic model of gases Real gases 1.4 Molecular interactions 1.5 The van de Waals equation 1.6 The principle of corresponding states**

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The perfect gas

The simplest state of matter is a gas, a form of matter that fills any container it occupies. A gas may be pictured as a collection of molecules in continuous random motion, with speeds that increase as the temperature is raised. A gas differs from a liquid in that the molecules of a gas are widely separated from one another and move in paths t h a t a r e l a r g e l yunaffected by intermolecular forces.



1.1 The states of gases

The physical state of a sample of a substance is defined by its physical properties, and two samples of a substance that have the same physical properties are in the same state. The state of a pure gas is specified by giving the values of its volume, V, amount of substance, *n*, pressure, *p*, and temp-erature, *T*. However, it has been established experimentally that it is sufficient to specify only three of these variables, for then the fourth variable is fixed. That is, it is an experimental fact that each substance is described by an equation of state, an equation that interrelates these four variables.

The general form of an equation of state is: p = f(T, V, n)



The general form of an equation of state is: p=f(T,V,n)

1). Pressure, *p*

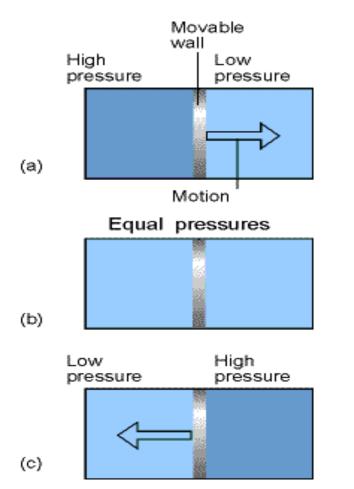
Definition: Pressure is defined as force divided by the area to which the force is applied.

Unit: Pascal (Pa), 1 Pa= 1 Nm⁻²; the SI unit. It is defined as 1 newton per meter squared;

Standard pressure: $p^{\circ} = 10^5 \text{ Pa}$



Mechanical equilibrium



Two gases are in separate containers that share a common movable wall The stage when the two pressures are equal and the wall has no further tendency to move. This condition of equality of pressure on either side of a movable wall is a state of mechanical equilibrium between the two gases.

*p*₁=*p*₂



2). Temperature, T

The temperature is the property that tells us the direction of the flow of energy,

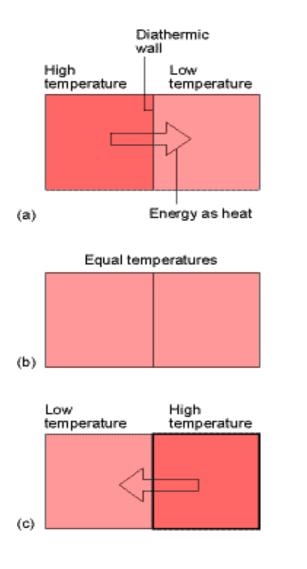
Temperature scales:

- The Celsius scale of temperature, θ , $^{\circ}$ C
- The thermodynamic temperature scale, *T*, K

T / K= *θ*, / °C+273.15



1.1 The states of gases



Thermal equilibrium

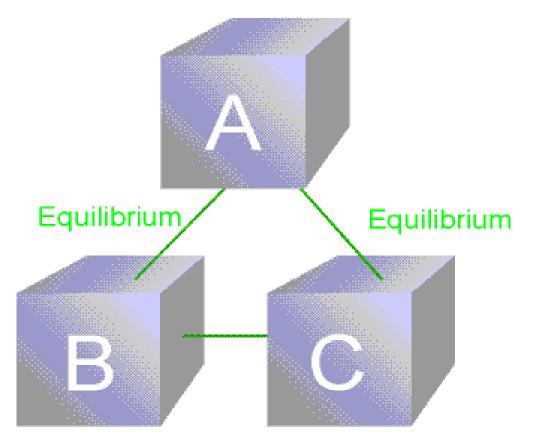
Energy flows as heat from a region at a higher T to one at a lower T if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are separated by a diathermic wall (b). The latter condition corresponds to the two regions being at thermal equilibrium: $T_1 = T_2$



1.1 The states of gases

Zeroth Law of thermodynamics

If an object A is in thermal equilibrium with B and if B is in thermal equilibrium with C, then C is in thermal equilibrium with A.



Equilibrium

The Zeroth Law of thermodynamics



3). Volume, V, m³

4). The amount of substance

n, mole (mol)





1). Three important gas Laws

2). The combined gas Law

3). Mixtures of gases

4). Mole fractions and partial pressures

1.2 The gas laws — 1).Three important gas Laws

a). Boyle's Law- at constant T

Bressing temperature, T

Volume, V

The *p*-*V* dependence of a fixed amount of perfect gas at different *T*.

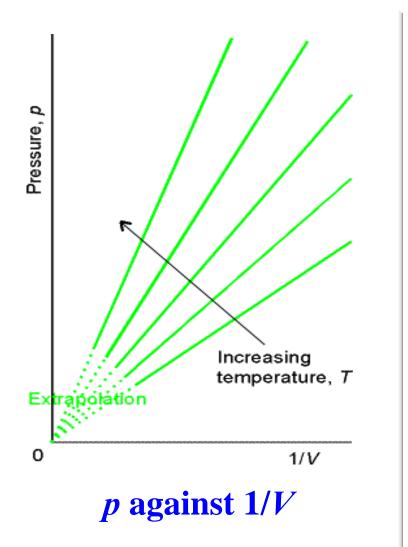
At constant *T*, *p* and *V* of a fixed amount of gas are related by

pV = constant

Each of the curves in the graph corresponds to a single *T* and is called an isotherm.

According to Boyle's law, each of the isotherms is hyperbola.





$$p \propto \frac{1}{V} \qquad V \propto \frac{1}{p}$$

At constant *T*, the pressure of a sample of gas is inversely proportional to its volume, and the volume it occupies is inversely proportional to its pressure.



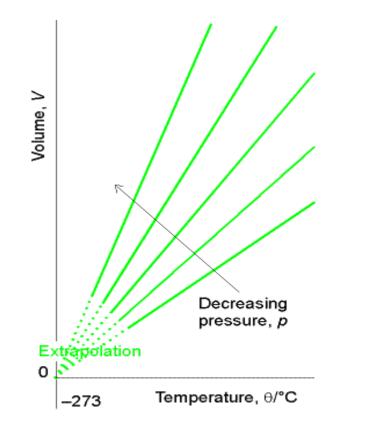
The limiting law

Boyle's law is valid only at low pressures; and that real gases obey it only in the limit of the pressure approaching zero ($p \rightarrow 0$).

Equations that are valid in this limiting sense will be signaled by a ^o on the equation number in our text book.

1.2 The gas laws — 1).Three important gas Laws

b). Charls's Law- at constant p



The variation of V with T

V/T = constant

The volume of any gas should extrapolate to zero at $\theta = -273$ °C or T = 0 K. **1.2 The gas laws** — 1). Three important gas Laws

- c). Avogadro's Principle at constant *T* and *p*:
 - $V = \text{constant} \times n \qquad V_m = V/n$

At a given pressure and temperature, the molar volume of a gas is approximately the same; the volume of a sample of gas is proportional to the amount of molecules present.

Avogadro's principle: The equal volumes of gases at the same pressure and temperature contain the same numbers of molecules.

1.2 The gas laws — 1).Three important gas Laws

b). Charls's Law

Pressure, p Decreasing volume, V Extrapolation 0 o Temperature, T/K The variation of p with T

p/T = constant

The pressure varies linearly with the temperature, and extrapolates to zero at T=0



2). The combined gas Law ______ the perfect gas equation

When combine the Boyle's Law, Charle's Law and Avogadro's Principle, then:

 $pV = \text{constant} \times nT$ pV = nRT $pV = \frac{m}{M}RT \qquad pV_{\text{m}} = RT$



2). The combined gas Law — the perfect gas equation pV = nRT

A gas that obeys this Equation exactly under all conditions is called a perfect gas. A real gas behaves more like a perfect gas the lower the pressure, and is described exactly by this equation in the limit $p \rightarrow 0$.



2). The combined gas Law — the perfect gas equation

When combine the Boyle's Law, Charle's Law and Avogadro's Principle, then:

$$R = \frac{1 \text{atm} \times 22.414 \text{ L}}{1 \text{mol} \times 273.15 \text{ K}} = 8.20578 \times 10^{-2} \text{ L atm} \text{ mol}^{-1} \text{ K}^{-1}$$
$$= 8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$$

The constant, *R*, is called gas constant, and is the same for all gases.

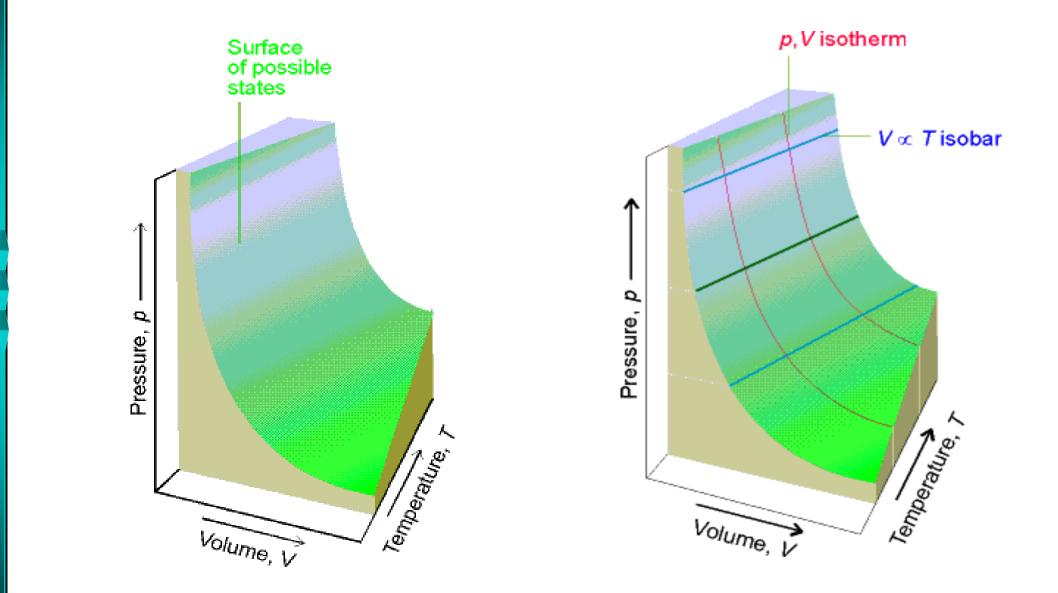


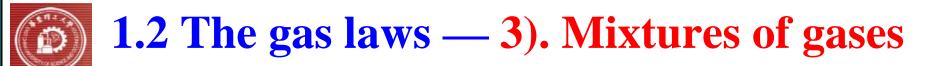
The perfect gas equation

R, The gas constant 8.31451 JK⁻¹mol⁻¹ $8.20578 \times 10^{-2} Latm K^{-1} mol^{-1}$ 8.31451 $\times 10^{-2}$ LbarK⁻¹mol⁻¹ $1.98722 \text{ cal } \text{K}^{-1} \text{mol}^{-1}$



2). The combined gas Law





Dalton's Law

The pressure exerted by a mixture of perfect gases is the sum of the partial pressures of the gases.

 $p = p_A + p_B + \cdots$

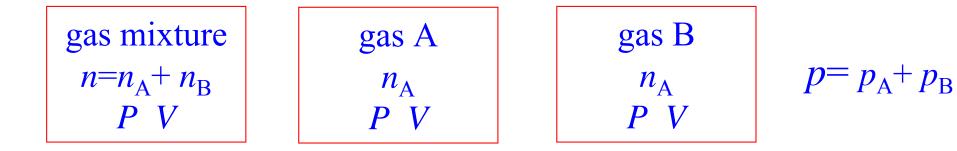
Generally $p = \sum p_i$

for each substance J: $p_J = \frac{n_J RT}{V}$



a). Dalton's Law

The partial pressure of a perfect gas is the pressure that it would exert if it occupied the container alone.



$$p = (n_{\mathrm{A}} + n_{\mathrm{B}})\frac{RT}{V} = n_{\mathrm{A}}\frac{RT}{V} + n_{\mathrm{B}}\frac{RT}{V} = p_{\mathrm{A}} + p_{\mathrm{B}}$$



A container of volume 10.0 L holds 1.00 mol N_2 and 3.00 mol H_2 at 298 K. What is the total pressure in atmospheres if each component behaves as a perfect gas?

Since

 $\boldsymbol{p} = \boldsymbol{p}_{\mathrm{A}} + \boldsymbol{p}_{\mathrm{B}} + \cdots;$

 $p_{\rm J} = \frac{n_{\rm J} RT}{V}$



We have

$$\boldsymbol{p} = \boldsymbol{p}_{\mathrm{A}} + \boldsymbol{p}_{\mathrm{B}} = (\boldsymbol{n}_{\mathrm{A}} + \boldsymbol{n}_{\mathrm{B}}) \frac{\boldsymbol{R}\boldsymbol{T}}{\boldsymbol{V}}$$

= $(1.00 \text{mol} + 3.00 \text{mol}) \times \frac{(8.206 \times 10^{-2} \text{ LatmK}^{-1} \text{mol}^{-1}) \times 298 \text{K}}{10.0 \text{L}}$

 $= 9.87 \, \text{atm}$





4). Mole fractions and partial pressures

The mole fraction, x_J , is the amount of component J expressed as a fraction of the total amount of molecules, *n*, in the sample:

$$x_{\rm J} = n_{\rm J}/n$$
 $n = n_{\rm A} + n_{\rm B} + \cdots$



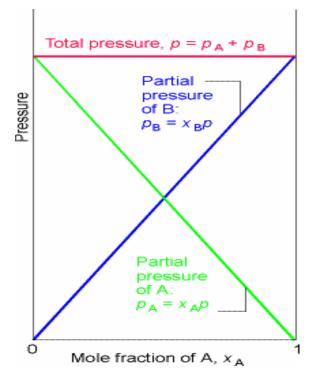
 $x_J = 0$: no J molecules are present; $x_J = 1$: only J molecules are present

For example, a mixture of 1.0 mol N₂ and 3.0 mol H₂, and therefore of 4.0 mol molecules in all, consists of mole fractions 0.25 of N₂ and 0.75 of H₂. It follows from the definition $p_{\rm J}$, that, whatever the composition of the mixture

$$x_A + x_A + \cdots = 1$$



4). Mole fractions and partial pressures



The partial pressures p_A and p_B of a binary mixture of gases of total pressure p as the composition changes from pure A to pure B. The partial pressure of a gas J in a mixture is defined as:

 $p_{\rm J} = x_{\rm J} p$

It follows that:

 $p_{A} + p_{B} + \cdots$ $= (x_{A} + x_{B} + \cdots) p$ = p



The perfect gas

1.1 The states of gases
1.2 The gas laws
1.3 The kinetic model of gases
Real gases
1.4 Molecular interactions
1.5 The van de Waals equation
1.6 The principle of corresponding states



Three assumptions for the kinetic model :

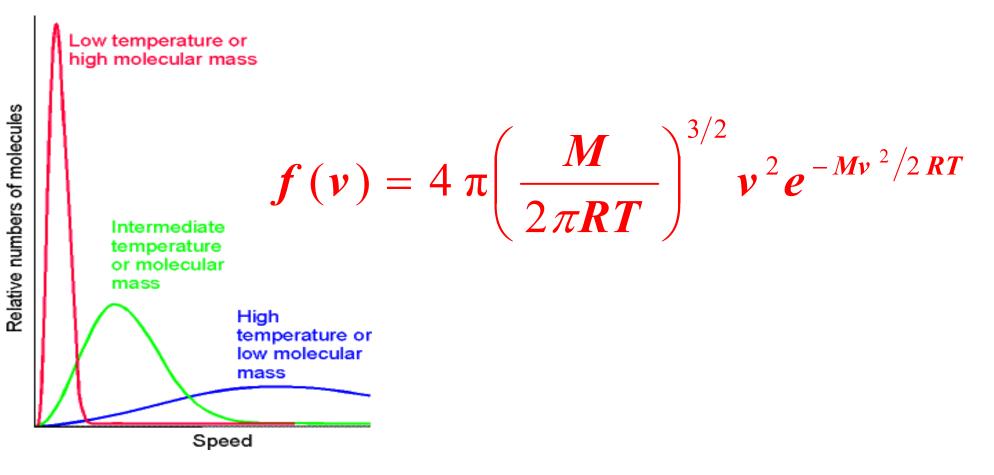
- 1). The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions.
- 2). The molecules do not interact, except that they make perfectly elastic collisions.
- 3). The gas consists of molecules of mass *m* in ceaseless random motion.



1.3 The kinetic model of gases

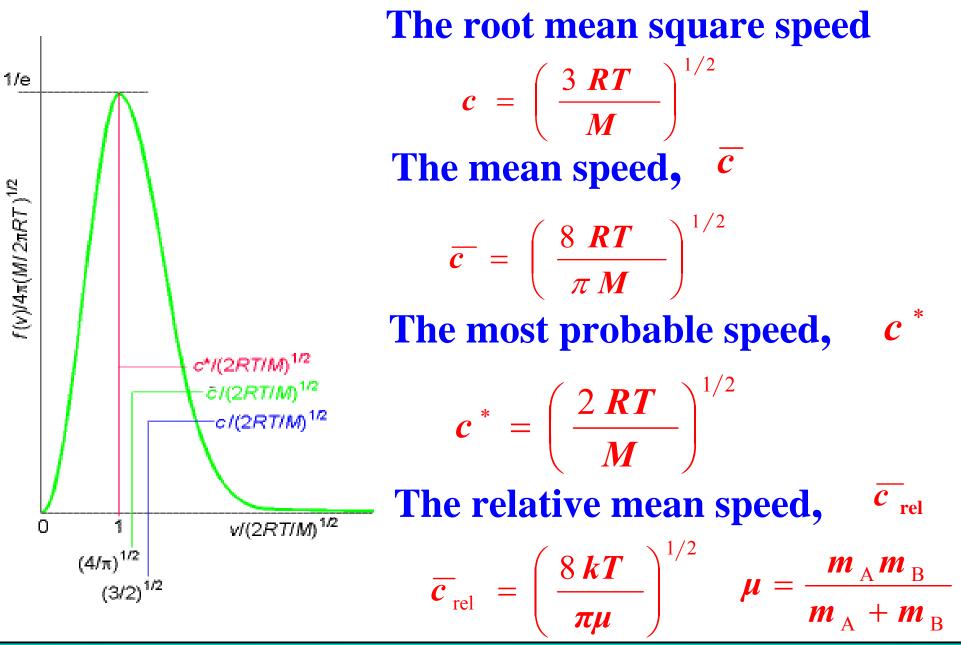
1) Molecular speeds

Maxwell distribution of speeds:





1.3 The kinetic model of gases





2). The collision frequency, z

When there are N molecules in a volume V, The collision frequency, z, the number of collisions made by one molecule divided by the time interval during which the collisions are counted, is expressed as

$$z = \sigma \,\overline{c}_{\rm rel} \,\mathcal{N} \qquad \sigma = \pi d^{-2}$$

where $\mathcal{N} = N/\mathcal{V}$, \mathcal{O} s collision cross-section and d is the collision diameter.

$$\boldsymbol{d} = (\boldsymbol{d}_{\mathrm{A}} + \boldsymbol{d}_{\mathrm{B}})/2$$



In terms of pressure

$$z = \frac{\sigma \ \overline{c}_{rel} \ p}{kT}$$

The equations tell us that the collision frequency increases with increasing temperature in a sample held at constant volume. The reason is that the mean relative speed increases with temperature. And at constant temperature, the collision frequency is proportional to the pressure.



3). The mea free path, λ

The mean free path is the average distance a molecule travels between collisions. If a molecule collides with a frequency z, it spends a time 1/z in free flight between collisions, and therefore travels a distance (l/z)c. The mean free path is:

$$\lambda = \overline{c}/z$$

Since
$$z = \frac{\sigma \overline{c_{rel}} p}{kT}$$
 and $\overline{c_{rel}} = 2^{1/2}, \overline{c}$



3). The mea free path, λ

then:
$$\lambda = \frac{kT}{2^{1/2} \sigma p}$$

In a sample of constant volume, the pressure is proportional to T, so T/p remains constant when the temperature is increased. So the mean free path is independent of the temperature.The distance between collisions is determined by the number of molecules present in the given volume, not by the speed at which they travel.



The perfect gas

1.1 The states of gases1.2 The gas laws1.3 The kinetic model of gases

Real gases
1.4 Molecular interactions
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1.6 The principle of corresponding states



Real gases do not obey the perfect gas law exactly because molecules interact with each other. Two important inter-molecular forces exist: repulsive forces attractive forces.

1.4 Molecular interactions



- **1.5 The van de Waals equation**
- **1.6 The principle of corresponding states**



Repulsive forces between molecules assist expansion and attractive forces assist compression. They are significant only when molecules are almost in contact: short-range interactions.

Attractive forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching. Attractive forces are ineffective when the molecules are far apart.



1). The compression factor

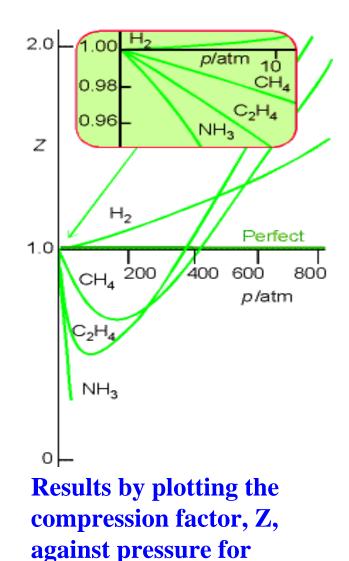
The compression factor, Z, is defined as

$$pV_m = ZRT$$
 $Z = \frac{pV_m}{RT}$

For a perfect gas, Z = 1 under all conditions; the deviation of Z from 1 is a measure of departure from perfect behaviour.



1.4 Molecular interactions



At very low pressures: $Z \approx 1$.

At high pressures: Z> 1. Repulsive forces are now dominant.

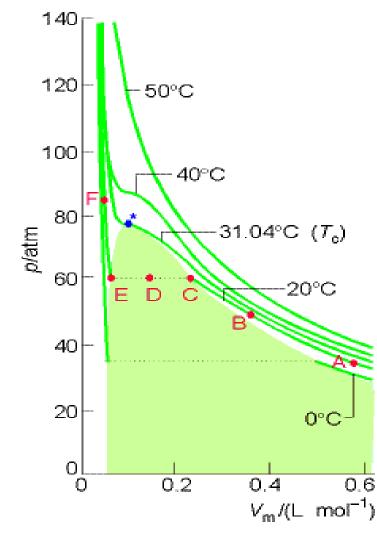
At intermediate pressures: Z<1 For most gases have, the attractive forces are dominant. .

A perfect gas has Z = 1 at all pressures.

several gases at 0 °C.

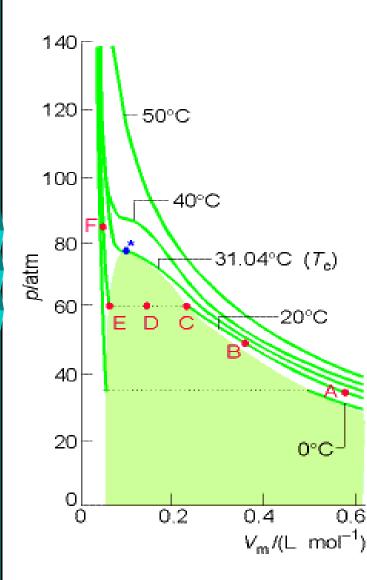


2). Virial coefficients



At large molar volumes and high temperatures the real isotherms do not differ greatly from perfect isotherms. The small differences suggest that the perfect gas law is in fact the first term in the expression of the form:





$$pV_{\rm m} = RT (1 + B'p + C'p^2 + \cdots)$$

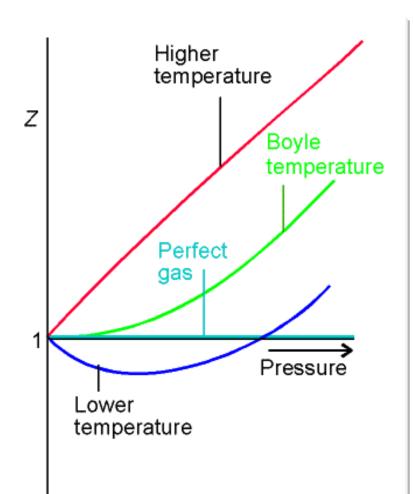
 $pV_{\rm m} = RT (1 + \frac{B}{V_{\rm m}} + \frac{C}{V_{\rm m}^2} + \cdots)$

These are two versions of the virial equation of state. The coefficients B, C,..., which depend on the T, are the second, third,... virial c o e f f i c i e n t s ; t h e first virial coefficient is 1.



1.4 Molecular interactions

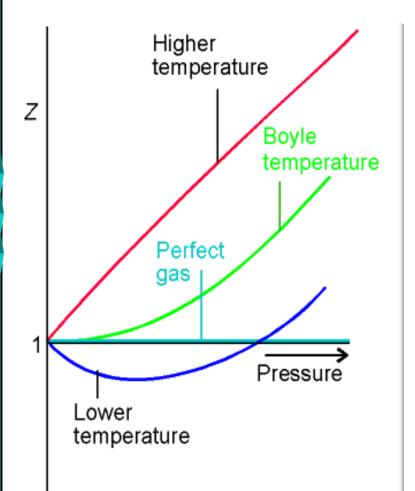
Boyle Temperature, *T*_B



 $(\partial Z/\partial p)_{T, p \to 0} > 0$ At higher T $(\partial Z/\partial p)_{T,P} < 0$ At lower T $(\partial Z/\partial p)_{T,P\to 0}=0$ At $T_{\mathbf{R}}$ $(\partial \boldsymbol{p} \boldsymbol{V}_{\mathrm{m}} / \partial \boldsymbol{p})_{T, \boldsymbol{p} \to 0} = 0$ At $T_{\rm R}$ $T_{\rm R}$ is so called the Boyle **Temperature**



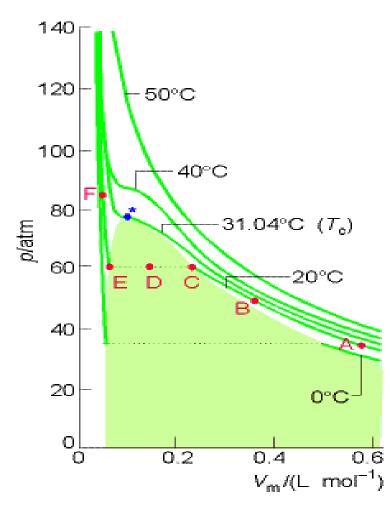
Boyle Temperature, *T*_B



At Boyle temperature, $T_{\rm B}$ the properties of the real gas coincide with those of a perfect gas as $p \rightarrow 0$; and $pV_{\rm m} \approx$ $R T_{\rm B}$

1.4 Molecular interactions

3). Condensation



Experimental isotherms of carbon dioxide at several temperatures

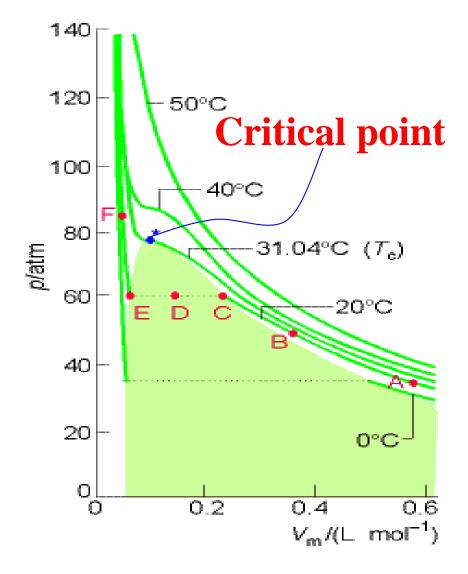
At C, all similarity to perfect behaviour is lost. This stage is represented by the horizontal line CDE. At the point just to the left of C, a liquid appears, and there are two phases in the system in this stage.

The pressure corresponding to the line CDE, when both liquid and vapour are present in equilibrium, is called the vapour pressure of the liquid at thetemperature of the experiment.

At E, the sample is entirely liquid.



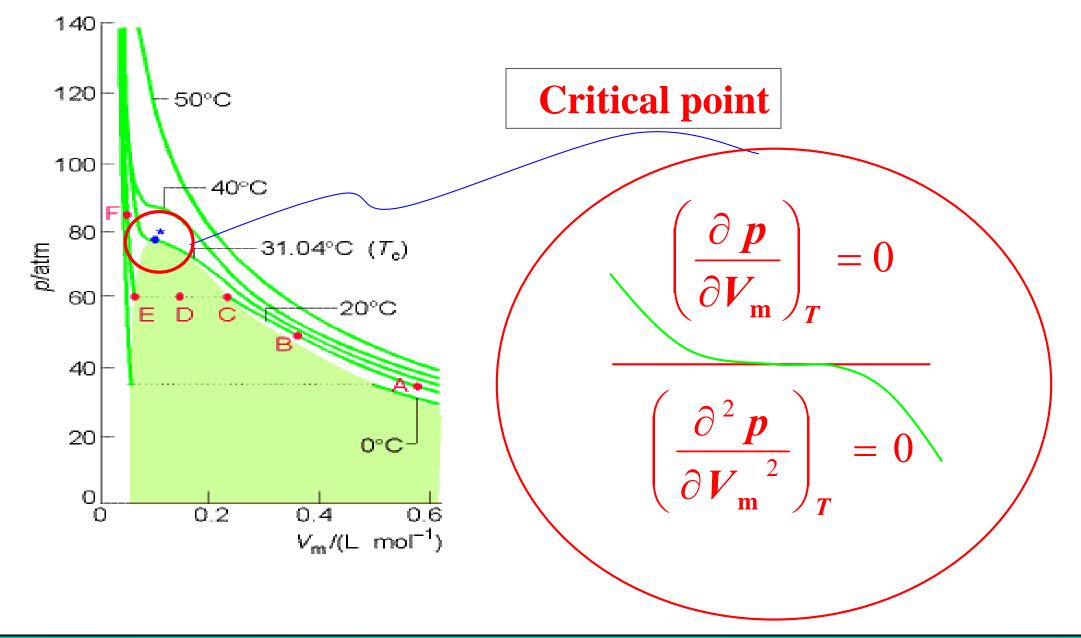
4). Critical constants



At and above T_c , the sample has a single phase. The liquid phase of a substance does not form a b o v e t h e c r i t i c a l temperature.

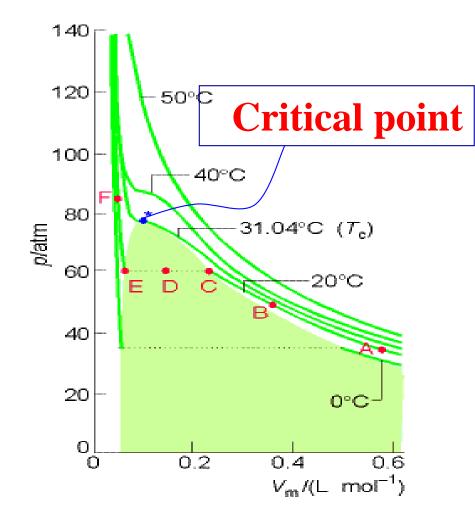
 $T_{\rm c}$, the critical point of the gas. Critical constants are different from gas to gas.

1.4 Molecular interactions





4). Critical constants



The temperature, pressure, and molar volume at the critical point are called:

Critical temperature, $T_{\rm c}$

Critical pressure, p_{c}

Critical molar volume, $V_{\rm c}$

 $T_{\rm c}, p_{\rm c}, V_{\rm c}$ -critical constants



1.5 The van der Waals equation

For the perfect gas:

- 1). The size of molecules is negligible;
- 2). Molecules do not interact;

pV=nRT

For real gases:

- 1). The molecule itself occupies a volume;
- 2). There are interactions among molecules;

$(p + \triangle p) (V - \triangle V) = nRT$



1). Expressions the van der Waals equation

 $(p + \triangle p) (V - \triangle V) = nRT$

$$\left(\begin{array}{c} \boldsymbol{p} + \frac{\boldsymbol{a}}{V_{\rm m}^2} \right) (V_{\rm m} - \boldsymbol{b}) = \boldsymbol{R}\boldsymbol{T}$$

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

$$p = \frac{RT}{V_{\rm m} - b} - \frac{a}{V_{\rm m}^2}$$

 $\Delta p = \frac{a}{V_{\rm m}^2}$

 $\Delta V = \boldsymbol{b}$



1). Expressions the van der Waals equation

 $\frac{a}{V_{\rm m}^2}$, the internal pressure due to intermolecular forces.

The constants *a* and *b* are the van der Waals coefficients. They are characteristic of each gas but independent of the temperature.



- 2). The features of the equation
- (1) Perfect gas isotherms are obtained at high temperatures and large molar volumes.

$$p = \frac{RT}{V_{\rm m} - b} - \frac{a}{V_{\rm m}^2}$$

$$T^{\uparrow} \Rightarrow RT^{\uparrow}$$

$$V^{\uparrow} \Rightarrow V_{\rm m} \gg b \Rightarrow V_{\rm m} - b \approx V_{\rm m}$$

$$\Rightarrow a/V_{\rm m}^2 \downarrow$$

$$p V_{\rm m} = RT$$

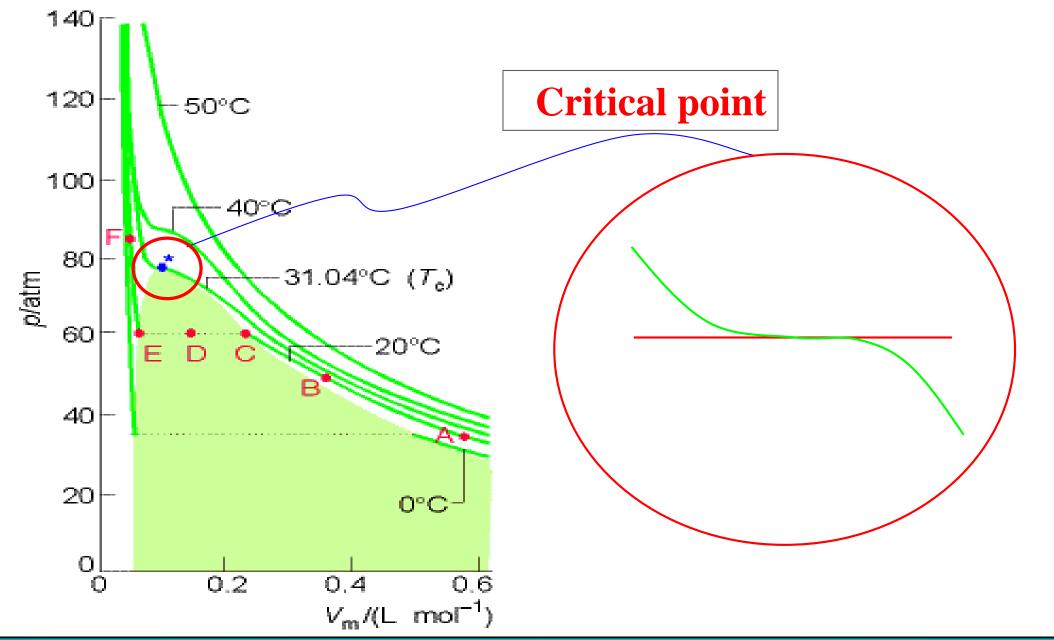


2). The features of the equation

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

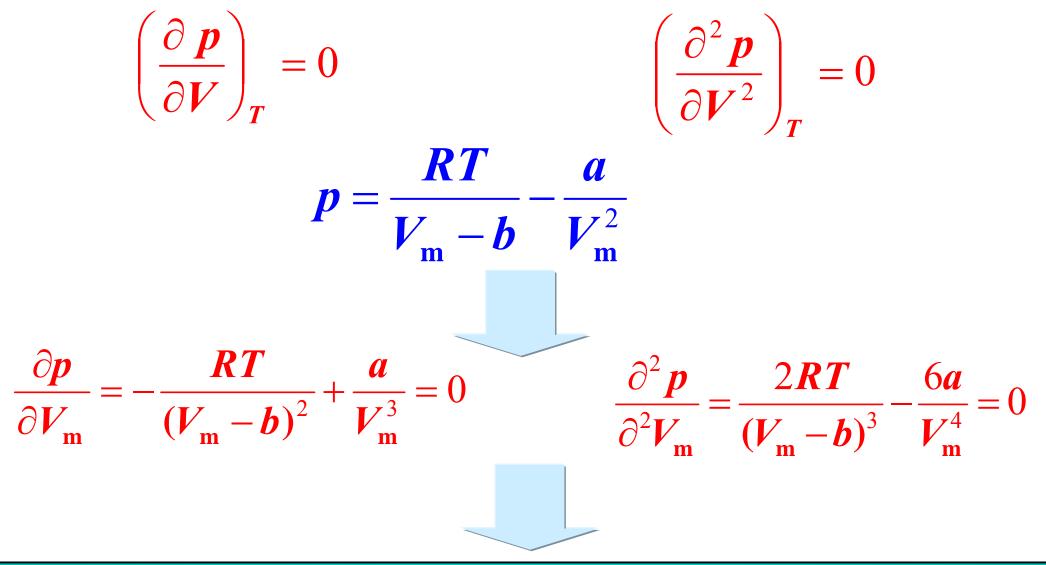
At the critical point:

1.5 The van der Waals equation





2). The features of the equation



1.5 The van der Waals equation

$$\frac{V_{c}}{V_{c}} = 3b \qquad p_{c} = \frac{a}{27b^{2}} \qquad T_{c} = \frac{8a}{27Rb} \qquad R = \frac{8p_{c}V_{c}}{3T_{c}}$$

The critical compression factor

$$Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8} = 0.375$$

For all gases. the critical compression factor, Z_c , is constant.



Example

Using the van der Waals equation to estimate a molar volume: the molar volume of CO_2 at 500K and 100 atm by treating it as van der Waals gas.

Method: To rearrange the van der Waals equation as a form for the molar volume, multiplying the both sides of the van der Waals equation by $V_m^3(V_m - b)$

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



The van der Waals's coefficients, *a* and *b* are as following $a = 3.640 \text{ atm} \text{L}^2 \text{ mol}^{-2}$, $b = 4.267 \times 10^{-2} \text{ L mol}^{-1}$, and $RT/p = 0.410 \text{ L mol}^{-1}$.

Answer:

$$V_{\rm m}^3 - 0.4523 V_{\rm m}^2 + (3.64 \times 10^{-2}) V_{\rm m} - (1.55 \times 10^{-3}) = 0$$

The acceptable root is $V_{\rm m} = 0.370 \,\mathrm{mol^{-1}}$.

An important general technique in science for comparing the properties of objects is to choose a related fundamental property of the same kind and to set up a relative scale on that basis. The critical constants are characteristic properties of gases, so a scale can be set up by using them as yardsticks.

- 1). Relative variables
- **2). The corresponding states**

1). Reduced variables

The reduced variables of a gas may be obtained by dividing the actual variable by the corresponding critical constant:

The reduced pressure: $p_r = p/p_c$ The reduced temperature: $T_r = T/T_c$ The reduced volume: $V_r = V_m/V_c$

2). The generalized van der Waals equation

The van der Waals Equation:

$$p = \frac{RT}{V_{\rm m} - b} - \frac{a}{V_{\rm m}^2}$$

The corresponding form in reduced variables:

$$p = p_{r} p_{c} \qquad V_{m} = V_{r} V_{c} \qquad T = T_{r} T_{c}$$

$$p_{r} p_{c} = \frac{RT_{r} T_{c}}{V_{r} V_{c} - b} - \frac{a}{V_{r}^{2} V_{c}^{2}}$$

$$p_{r} p_{c} = \frac{RT_{r} T_{c}}{V_{r} V_{c} - b} - \frac{a}{V_{r}^{2} V_{c}^{2}}$$

Substitute the following critical constants for the above equation

$$V_{\rm c} = 3b$$
 $p_{\rm c} = \frac{a}{27b^2}$ $T_{\rm c} = \frac{8a}{27Rb}$

then

$$\frac{ap_{\rm r}}{27 b^{2}} = \frac{8 aT_{\rm r}}{27 b(3 bV_{\rm r} - b)} - \frac{a}{9 b^{2} V_{\rm r}^{2}}$$



$$p_{\rm r} = \frac{8T_{\rm r}}{3V_{\rm r}-1} - \frac{3}{V_{\rm r}^2}$$

$$p = \frac{RT}{V_{\rm m} - b} - \frac{a}{V_{\rm m}^2}$$

 $p = \frac{RT}{V_{\rm m}}$

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Part 1: Equilibrium

- **1.** The properties of gases
- 2. The First Law: the concepts
- 3. The First Law: the machinery
- 4. The Second Law: the concepts
- 5. The Second Law: the machinery
- **6.** Physical transformations of pure substances
- 7. Simple mixtures
- 8. Phase diagrams
- 9. Chemical equilibrium
- **10. Electrochemistry**