COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
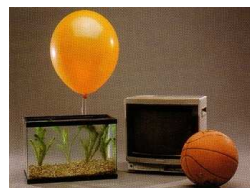Ollscoil Átha Cliath | The University of Dublin

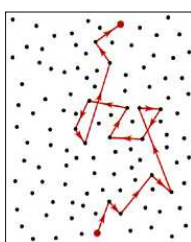# JF Chemistry CH 1101
Introduction to Physical Chemistry
2011-2012

**Properties of Gases,
Basic Thermodynamics,**

Dr Mike Lyons

School of Chemistry
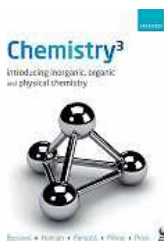Trinity College
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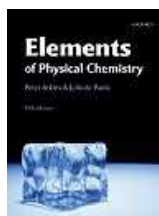Trinity College
Dublin 2.

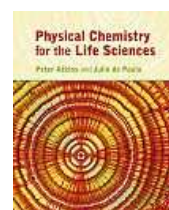email: melyons@tcd.ie

JF

SF

SF-SS

16 lectures. **8** tutorials
Lecture slides/problem sheets
sent via class email before
each lecture.
Also available on Chem. School
web site and on Web CT after module finishes.

Recommended reading

- Peter Atkins & Julio de Paula (AdP E5), *Elements of Physical Chemistry, OUP, 5th Edition,* 2009, Chapter 0, pp.1-14 and Chapter 1, pp.15-40.
- Burrows, Holman, Parsons, Pilling, Price, Chemistry[3], OUP, 2009, Chapter 7, pp.301-315.
- Kotz, Treichel, Townsend, Chemistry and Chemical Reactivity, 7th Edition, Brooks Cole C Engage Learning, Chapter 11, pp.514-553.
- Peter Atkins & Julio De Paula (AdP PC8), Physical Chemistry, 8th Edition, OUP 2006.

Robert Boyle 1627-1691   Jacques Charles 1746-1823   Amedeo Avogadro 1776-1856   John Dalton 1766-1844

'Thermodynamics is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never be overthrown'. - Albert Einstein.

'The law that entropy always increases- the Second Law of Thermodynamics- holds, I think, the supreme position among the laws of Physics. If someone points out to you that your pet theory of the universe is in disagreement with maxwells equations- then so much the worse for maxwell's equations. If it is found to be contradicted by observation- well, these experimentalists do bungle things from time to time. But if your theory is found to be against the Second law of Thermodynamics I can give you no hope: there is nothing for it but to collapse in deepest humiliation.' -Sir Arthur Eddington.

'Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it , except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it it doesn't bother you anymore.' - Arnold Sommerfeld.
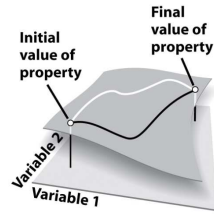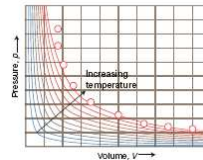
COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
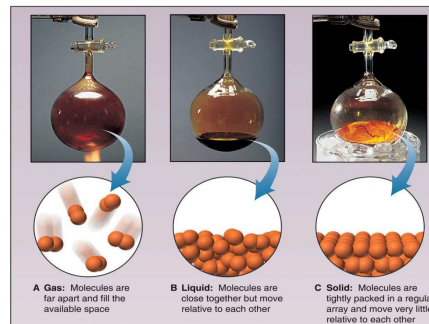Ollscoil Átha Cliath | The University of Dublin

Lecture 1

## Gas Laws and the ideal gas equation.

The three states of matter.

Phases of Matter *

Three basic phases of matter:

Gas: Fills a container, taking on the shape of the container. Similar to a liquid, except that particles are very widely spaced from one another, and interparticle interactions are minimal.

Liquid: Does not fill a container, but takes on the shape of the container. Similar to gases, except particles very closely spaced.

Solid: Does not fill a container, and do not conform to the shape of the container. Particles are very closely packed - still much dynamic motion in a solid, which increases with heating.

A **Gas:** Molecules are far apart and fill the available space

B **Liquid:** Molecules are close together but move relative to each other

C **Solid:** Molecules are tightly packed in a regular array and move very little relative to each other

General properties of gases

- A gas is a state of matter which fills any container it occupies.
- Molecular picture of gas:
  - Collection of widely separated molecules in random chaotic motion. Hence molecules move through space freely to fill any volume.
- Gases are highly compressible hence readily confined to smaller volume.
- Gases respond readily to changes in temperature and occupy a larger volume when heated and a smaller volume when cooled.
- Fundamental properties of gases described in terms of pressure P (units: Nm^{-2}, atm etc), Volume V (units: L (or dm^3), m^3 etc), temperature T (unit: K) and amount (unit: mol).
- General properties of gases are described in terms of three empirical laws developed by Boyle, Charles and Avogadro which may be used to predict the behaviour of a gas under given conditions of temperature, pressure and volume.
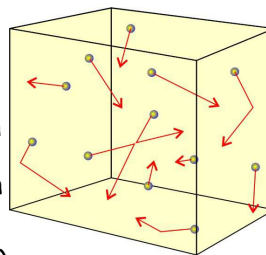
Perfect Gases *

We shall consider a hypothetical **perfect** or **ideal** gas, which is a form of matter that completely fills any container.

A *perfect gas* is pictured as a collection of molecules or atoms which undergo continuous random motion (or Brownian motion):

- The speeds of the particles increase as the temperature is increased

- The molecules are widely separated from one another, with the only interactions being with the side of the container and other molecules during infrequent collisions

- The molecules are unaffected by intermolecular forces (e.g., dipole-dipole, van der Waals, etc.)

Pressure †

Pressure is the amount of equal force applied (measured in N) to a specific area (measured in m^2):

$$p \; = \; F/A$$

Pressure from a gas is the result of countless collisions of rapidly moving molecules with the walls of the container.

Units of pressure:

Name	*Symbol*	*Value*
pascal	1 Pa	1 N m^{-2}, $1 \text{ kg m}^{-1} \text{ s}^{-2}$
bar	1 bar	10^5 Pa
atmosphere	1 atm	101325 Pa
torr	1 Torr	101325/760 Pa = 133.32 Pa
mm of mercury	1 mm Hg	133.322 Pa
pound per sq inch	1 psi	6.894 757 kPa

Table 1.1 Pressure units

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

Table F.1 Pressure units and conversion factors*

pascal, Pa	**1 Pa = 1 N m^{-2}**
bar	**1 bar = 10^5 Pa**
atmosphere, atm	**1 atm = 101.325 kPa = 1.013 25 bar**
torr, Torr†	**760 Torr = 1 atm**
	1 Torr = 133.32 Pa

$$P = \lim_{\Delta A \to 0} \frac{|\Delta F|}{\Delta A} = \frac{dF}{dA}$$

*Values in bold are exact.

†The name of the unit is torr; its symbol is Torr.

Pressure P defined as Force per unit area.

Unit	Atmospheric Pressure	Scientific Field
pascal(Pa); kilopascal(kPa)	1.01325×10^5 Pa; 101.325 kPa	SI unit; physics, chemistry
atmosphere(atm)	1 atm*	chemistry
millimeters of mercury(Hg)	760 mm Hg*	chemistry, medicine, biology
torr	760 torr*	chemistry
pounds per square inch (psi or lb/in²)	$14.7 \, lb/in^2$	engineering
bar	1.01325 bar	meteorology, chemistry, physics

This is an exact quantity; in calculations, we use as many significant figures as necessary.

Some basic Physics

liquid   dF

ρ h

dA
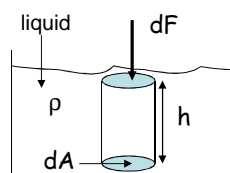
Volume V of liquid cylinder = h dA
Mass m of cylinder = ρh dA
Weight of cylinder = mg = ρhg dA
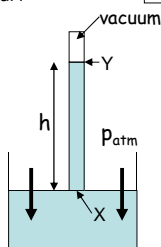Force acting downwards dF = ρhg dA

Pressure P = dF/dA = ρgh

$P_X - P_y = \rho gh$

$P_y = 0$ (Vacuum)
$P_X = P_{atm}$ (P_{atm} acts on same Plane as point X)

$P_{atm} = \rho gh$

$\rho_{Hg} = 13.6 \times 10^3$ kg m^{-3}
h = 760 mm

Measuring Pressure

One device used to measure pressure is a **barometer** (by Torricelli). When the column of mercury is in equilibrium with the atmosphere, the pressure at the base is equal to that from the atmosphere - so the height of the mercury is a measure of the external pressure.

A simple pressure measuring device is a **manometer**, in which a non-volatile viscous fluid is contained in a U-tube

The pressure in the apparatus (a) or from atmosphere (b) is directly proportional to the height difference of the two columns, *h*:

$$p = \rho gh$$

ρ = density of viscous fluid
g = gravitational acceleration, 9.8 m s^{-2}

vacuum

Y

h P_{atm}

X

See AdP 5th ed. Fig. 0.3 and Derivation 0.1 p.6.

6
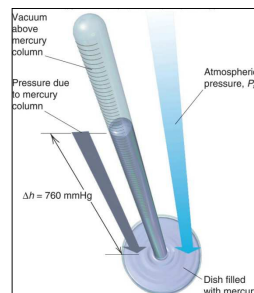
Temperature

Temperature is a property that describes the flow of energy. Energy will flow between two objects in contact, resulting in **change of state** of these two objects. If objects A and B are touching, and A has a higher temperature than B, energy flows from A to B until some equilibrium condition is established.
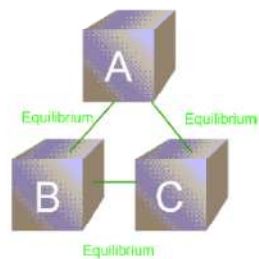
Separatory boundaries:

Diathermic - if a change of state is observed when two bodies are brought into contact with one another (e.g., metal)

Adiabatic - if no energy flow is permitted between the two objects in contact (e.g., styrofoam)
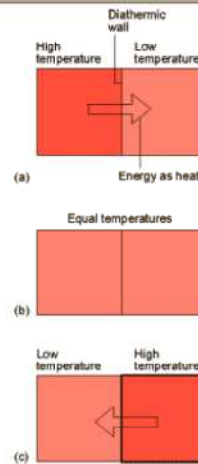
Thermal Equilibrium

Two objects are said to be in **thermal equilibrium** if no change in state occurs when they are in contact with one another.

A: Block of iron
B: Block of copper
C: Flask of water

Zeroth Law of Thermodynamics:
If A is in thermal equilibrium with B, and B is in thermal equilbrium with C, then C is also in thermal equilibrium with A

If B is a **thermometer** (glass capillary with Hg), in contact with A the Hg column has a certain length. If B is placed in contact with another object C, one can predict the change of state when A and C are put in contact. Thus, the Hg column is used to measure the temperatures of A and C.

Thermodynamic temperature scale (Kelvin): $T/K = q/^oC + 273.15$

Thermometers & Temperature

A system that changes in a regular and observable manner with changes in temperature has the potential to be used as a thermometer.

Examples:
- Height of liquid in a narrow tube (mercury or alcohol)
- Change in gas volume (argon)
- Variation in electrical resistance in a wire (platinum)

Thermometers are **calibrated** by comparison to systems in reproducible states: e.g., H_2O at its **triple point** or Ag at its **melting point**.

> **Calibration**: determination of a base point and graduated scale by comparison to systems with reproducible base points

Temperature is not heat! Temperature is a relative measure of heat between multiple systems - in fact, if you touch a system, and it feels hot, temperature can be defined as the tendency of that system to lose heat! We will make a formal definition of heat later...
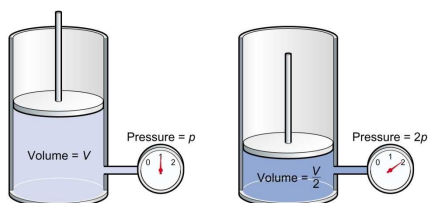

Boyle's Law

Robert Boyle, (1627-91), who was an "experimental philosopher" in the early years of the Royal Society, made a very important contribution in developing a description of the **ideal gas** (also developed ideas about vacuum, atomic nature of matter, etc.)
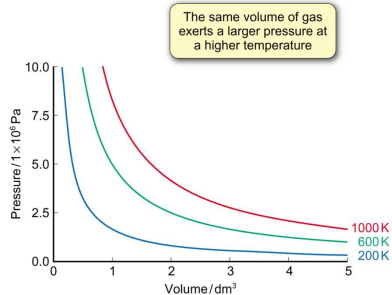
In 1661, he showed that to a very good approximation that for a constant amount of gas at a fixed temperature:

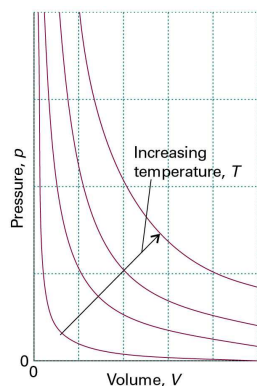$$pV = \text{constant} \qquad p \propto \frac{1}{V}, \quad V \propto \frac{1}{p}$$

The pressure of a sample is inversely proportional to its volume, and the volume of a sample is inversely proportional to pressure
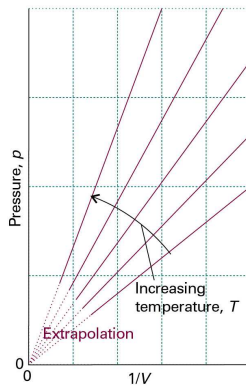
Volume = V, Pressure = p

Volume = $\frac{V}{2}$, Pressure = 2p

> The same volume of gas exerts a larger pressure at a higher temperature
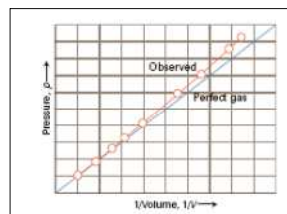
1000 K
600 K
200 K

Pressure / 1×10^6 Pa
Volume / dm^3

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.

The volume of a gas decreases as the Pressure on it is increased.
For a sample which obeys Boyle's Law and that is kept at constant temperature the P-V relationship is hyperbolic.

A good test of Boyle's Law is to plot the pressure P against 1/V at constant temperature where a straight line should be obtained.
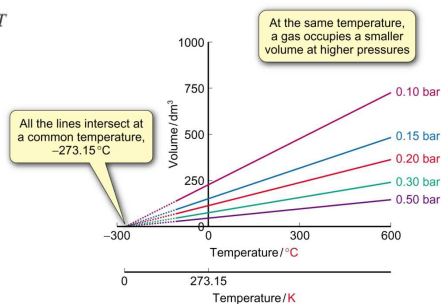
Charles' (Gay-Lussac's) Law

Charles (1746-1823), a French physicist, constructed the first hydrogen balloons, making an ascent to over 3000 meters (1.9 mi) in 1783. His name is chiefly remembered, however, for the discovery of Charles's law, which states that the volume of a fixed quantity of gas at constant pressure is proportional to its temperature. Hence all gases, at the same pressure, expand equally for the same rise in temperature. He communicated his early results to Joseph-Louis Gay-Lussac, who published his own experimental results in 1802, six months after Dalton had also deduced the law.
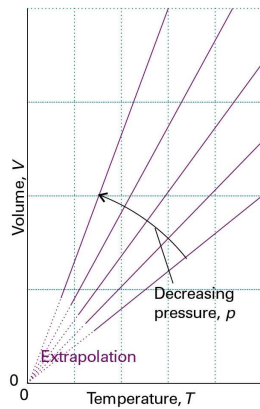
At constant pressure: $\quad V = \text{constant} \times (\theta + 273 \ ^\circ C)$

Or, on the **thermodynamic temperature scale** devised by Kelvin:

$$V = \text{constant} \times T \ , \quad p = \text{constant} \times T$$

Chemistry[3] pp.304-305.
Kotz, Ch.11, pp.519-521.

All the lines intersect at a common temperature, −273.15°C

At the same temperature, a gas occupies a smaller volume at higher pressures
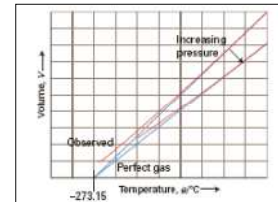
Fig. 1.6 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, or $\theta = -273°C$.
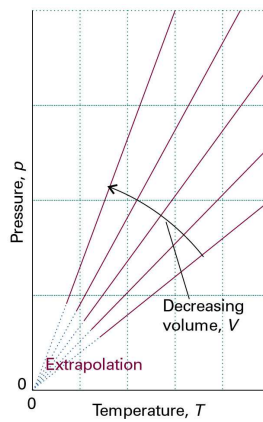
Fig. 1.7 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ ($-273°C$).
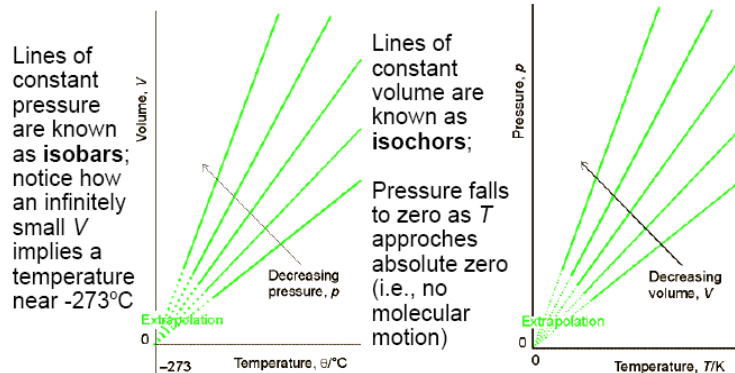
Note that the V versus T curves all
Intersect at a single point termed
The absolute zero of temperature.
This is the lowest attainable temperature
And has the value – 273.15 °C.

From this observation we define the Thermodynamic Temperature (Absolute) Scale as follows:
T (K) = θ (°C) +273.15
where T denotes the thermodynamic temperature in degrees Kelvin (K) and θ represents the temperature in degrees Celsius (°C).

Effects of Changing Temperature

The volume of a gas should extrapolate to zero near -273°C. Plots of volume and pressure as a function of temperature, at constant pressure and volume, respectively, are shown below:

Lines of constant pressure are known as **isobars**; notice how an infinitely small V implies a temperature near -273°C

Lines of constant volume are known as **isochors**;

Pressure falls to zero as T approches absolute zero (i.e., no molecular motion)

Avogadro's Principle.

- Under conditions of constant temperature and pressure, equal volumes of gases contain the same number of molecules.
- In simple terms doubling the amount (unit: mol) of molecules in a gas sample results in a doubling of the volume of the gas, if the pressure and temperature are held constant.

$$V \propto n$$ ← Amount of gas (mol)

$$\frac{V}{n} = K = \text{constant}$$

Table 1.2
The molar volumes of gases at standard ambient temperature and pressure (SATP: 298.15 K and 1 bar)

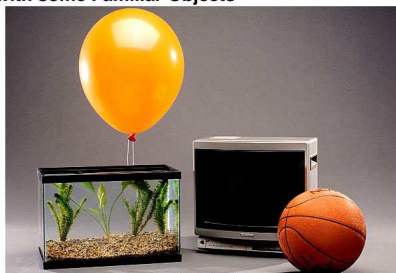| Gas	V_m/(dm³ mol⁻¹)
Perfect gas	24.7896*
Ammonia	24.8
Argon	24.4
Carbon dioxide	24.6
Nitrogen	24.8
Oxygen	24.8
Hydrogen	24.8
Helium	24.8

* At STP (0°C, 1 atm), V_m = 24.4140 dm³ mol⁻¹.

The quantity V/n is termed the molar volume V_M.
Hence Avogadro's Law states that a gas containing 1 mole of X molecules occupies the same volume (molar Volume) as one consisting of 1 mole of Y molecules, Whatever the identity of the substances X and Y.
Hence Avogadro's principle implies that *the molar volume of a gas should be the same for all gases at the same Pressure and temperature*.

Reference: AdP5: p.19.

Molar volume of a perfect gas at Standard Ambient Temperature and Pressure (SATP: 298.15 K and P = 1 bar) Is V_M = 24.7896 dm³mol⁻¹ and at Standard Temperature and Pressure (STP: T = 0°C, P = 1 atm) V_M = 24.414 dm³mol⁻¹ .

The Volume of 1 mol of an Ideal Gas Compared with some Familiar Objects

Standard Molar Volume

22.4 L   22.4 L   22.4 L

He   N₂   O₂

He	N₂	O₂
n = 1 mol	*n* = 1 mol	*n* = 1 mol
P = 1 atm (760 torr)	*P* = 1 atm (760 torr)	*P* = 1 atm (760 torr)
T = 0°C (273 K)	*T* = 0°C (273 K)	*T* = 0°C (273 K)
V = 22.4 L	*V* = 22.4 L	*V* = 22.4 L
Number of gas particles = 6.022 × 10²³	Number of gas particles = 6.022 × 10²³	Number of gas particles = 6.022 × 10²³
Mass = 4.003 g	Mass = 28.02 g	Mass = 32.00 g
d = 0.179 g/L	*d* = 1.25 g/L	*d* = 1.43 g/L

Ideal Gas equation of State.

Constant T,n

Constant P,n

Constant T,P

$$V \propto \frac{1}{P}$$

$$V \propto T$$

$$V \propto n$$

$$V \propto \frac{nT}{P}$$

$$V = R\left\{\frac{nT}{P}\right\}$$

$$PV = nRT$$

Ideal Gas Equation of State

R = Universal Gas Constant
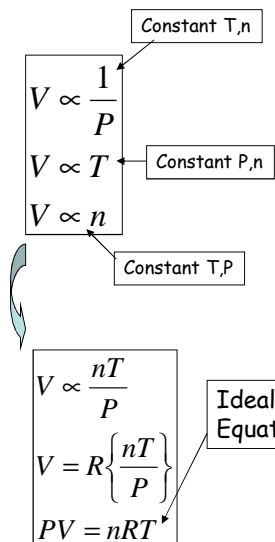
Table 1.2 The gas constant

R	
8.314 47	J K⁻¹ mol⁻¹
8.205 74 × 10⁻²	dm³ atm K⁻¹ mol⁻¹
8.314 47 × 10⁻²	dm³ bar K⁻¹ mol⁻¹
8.314 47	Pa m³ K⁻¹ mol⁻¹
1 62.364	dm³ Torr K⁻¹ mol⁻¹
1.987 21	cal K⁻¹ mol⁻¹

Table 1-2
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

$$R = \frac{PV}{nT} = \frac{PV_M}{T}$$

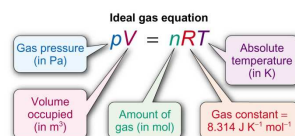The numerical value of R will depend On the units adopted for P, V and T.

Determination of Universal Gas Constant R.

$$R = \frac{PV}{nT} = \frac{PV_M}{T}$$

Boyle's law	Charles's law	Avogadro's law
$V \propto \frac{1}{P}$	$V \propto T$	$V \propto n$
constant T, n	constant p, n	constant T, p

Ideal gas equation

$$pV = nRT$$

Gas pressure (in Pa) — Volume occupied (in m³) — Amount of gas (in mol) — Gas constant = 8.314 J K⁻¹ mol⁻¹ — Absolute temperature (in K)

Assume 1 mol gas (n = 1). At STP, P = 1 atm, T = 273.15 K, V_M = 22.414 dm³.

$$R = \frac{(1\,atm)\times(22.414\,dm^3)}{(1\,mol)\times(273.15\,K)} = 0.0821\,dm^3 atm K^{-1} mol^{-1}$$

In SI units: n = 1, P = 1 atm = 1.013 x 10⁵ N m⁻², V_M = 22.414 x 10⁻³ m³ since 1 dm³ = 1 L = 10⁻³ m³.

1 Nm = 1 J

$$R = \frac{(1.013\times10^5\,Nm^{-2})\times(22.414\times10^{-3}\,m^3)}{(1\,mol)\times(273.15\,K)} = 8.314\,Nm\,mol^{-1}K^{-1} = 8.314\,J\,mol^{-1}K^{-1}$$
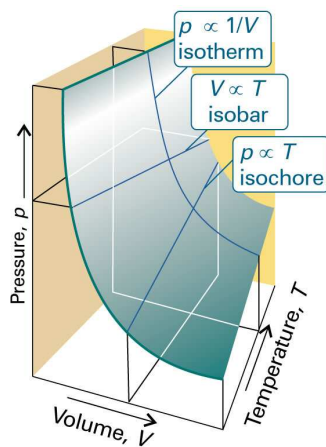
Initial State P_i, V_i, T_i, n

Final State P_f, V_f, T_f, n

$$\frac{PV_i}{T_i} = nR \qquad \frac{P_f V_f}{T_f} = nR$$

$$\frac{PV_i}{T_i} = \frac{P_f V_f}{T_f}$$

Can re-arrange equation to express any one of the six quantities in terms of the other five.

Ideal Gas Equation of State (IGEOS)

$$PV = nRT$$

The expression PV = nRT is termed the ideal gas equation of state (IGEOS). This defines an ideal gas.

An equation of state is a mathematical Expression relating the pressure P, volume V and Temperature T and amount of substance n present in a sample.

Equations of state are very useful because they Make it possible to calculate one particular property (either P,V,T or n) once we have values assigned to the other three.

Most gases obey the IGEOS approximately under normal lab conditions.

All gases obey IGEOS more and more closely as the gas pressure is _reduced_ and the gas becomes more _dilute_.

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.

Equation of state of gases

- The state of a gas sample can be specified by giving the values of the pressure P, volume V, temperature T and amount n.
- P,V,T and n are not independent of one another.
- Any gaseous substance will be described by an equation of state which describes the relationship between pressure P and the other variables V,T and n.
- Mathematically the equation of state is expressed as:

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

Figure 1-8
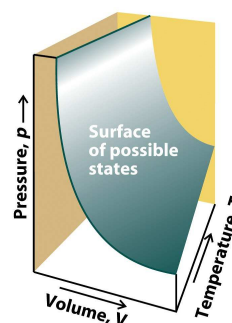Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Ideal Gas equation of state

$$PV = nRT$$

Van der Waals equation of state

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

Takes molecular interactions into account

Density of an ideal gas.

We can easily calculate the density ρ of an ideal gas.
Mass of gas m =amount (mol) of molecules in sample X mass per mole (g/mol)

$$m = n\,M$$

Gas density ρ = mass of sample / volume of sample.

$$\rho = \frac{m}{V} = \frac{nM}{V}$$

From Ideal Gas equation

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

Hence gas density ρ is

$$\rho = \frac{n}{V} M = \frac{PM}{RT}$$

For a given type of gas (fixed M) the density ρ is directly
proportional to the pressure P at constant temperature T.
Furthermore if the pressure P is constant the density is inversely
proportional to the temperature T. Hence as the temperature
is increased, the density of the gas decreases (secret
behind operation of hot air balloon).
For a fixed temperature T and pressure P the density of a gas is
Directly proportional to the molar mass M of the gas.
Hence gas molecules of high molar mass are more dense than
gas molecules of low molar mass.
Note that _many sensible predictions can be extracted from_
mathematical formulae.

Kotz, Ch.11, pp.525-526.
See also Kotz section 11.4
on gas laws & chemical
Reactions, pp.527-530.

John Dalton

John Dalton (1766-1844), an English chemist
and physicist, was the first to provide a
scientific description of color blindness (1794),
a condition from which he suffered and which
was long called "Daltonism."

Dalton recorded over 200,000 observations of
the atmosphere in his notebooks, and studied
mixed gases and the expansion of gases
under heat. **Dalton's Law** is still used to
describe the law of partial pressures in
chemistry.

This work led him to his most important theoretical contribution to
chemistry, a scientifically grounded atomic theory of matter. He lectured
on his discoveries in 1803, and published them at greater length in _A
New System of Chemical Philosophy_ in 1808.

Kotz, Section 11.5, pp.530-532.

Mixtures of Ideal Gases : Daltons Law of Partial Pressures.

We can extend our discussion to mixtures of ideal gases. We can expect that a mixture of gases that do not react with each other will behave like a single pure gas.
Hence we introduce the _partial pressure_ p of a gas in a gas mixture as follows:
this is the pressure which the gas component would exert if it alone occupied the container.

Daltons Law: For a system containing two or more different gases, the total pressure P is the sum of the individual partial pressures p that each gas would exert if it alone occupied the container.

The total pressure P of a gas mixture containing k component gases each of partial pressure p_k is:

We consider a system of two ideal gases A,B contained in a volume V at a temperature T.
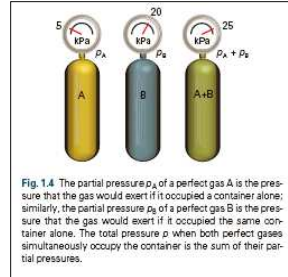gas partial pressures are p_A, p_B and amounts are n_A, n_B.

Fig. 1.4 The partial pressure p_A of a perfect gas A is the pressure that the gas would exert if it occupied a container alone; similarly, the partial pressure p_B of a perfect gas B is the pressure that the gas would exert if it occupied the same container alone. The total pressure p when both perfect gases simultaneously occupy the container is the sum of their partial pressures.

$$P = p_1 + p_2 + p_3 + \dots + p_k = \sum_{i=1}^{k} p_i$$

$$p_A V = n_A RT \quad \Rightarrow \quad p_A = \frac{n_A RT}{V}$$

$$p_B V = n_B RT \quad \Rightarrow \quad p_B = \frac{n_B RT}{V}$$

$$P = p_A + p_B = \frac{n_A RT}{V} + \frac{n_B RT}{V} = (n_A + n_B)\frac{RT}{V}$$

$$\frac{p_A}{P} = \frac{n_A RT}{V} \left\{ \frac{V}{(n_A + n_B)RT} \right\} = \frac{n_A}{n_A + n_B} = \frac{n_A}{n}$$

$$\frac{p_B}{P} = \frac{n_B RT}{V} \left\{ \frac{V}{(n_A + n_B)RT} \right\} = \frac{n_B}{n_A + n_B} = \frac{n_B}{n}$$

We define the mole fraction X of gases A and B as

$$X_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n}$$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n}$$

$$n = n_A + n_B$$

Hence we arrive at expressions for the partial Pressures of each component gas in terms of the Mole fraction and the total pressure.

We note that the sum of the mole fractions in a mixture must equal unity.

$$p_A = X_A P$$
$$p_B = X_B P$$

$$X_A + X_B = \frac{p_A}{P} + \frac{p_B}{P} = \frac{p_A + p_B}{P} = \frac{P}{P} = 1$$

$$X_A + X_B = 1$$

If only A is present then $X_A = 1$ and $X_B = 0$. When only B is present $X_A = 0$ and $X_B = 1$. When both are present in equal Amounts then $X_A = X_B = 0.5$.

General case for a k component mixture.

$$p_i = X_i P$$
$$P = \sum_{i=1}^{k} p_i$$
$$\sum_{i=1}^{k} X_i = 1$$

$x_A = 0.708$
$x_B = 0.292$

$x_A = 0.375$
$x_B = 0.625$

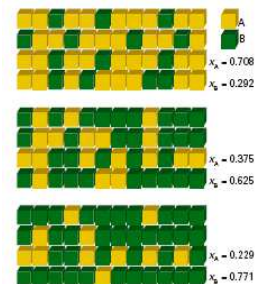$x_A = 0.229$
$x_B = 0.771$

Fig. 1.5 A representation of the meaning of mole fraction. In each case, a small square represents one molecule of A (yellow squares) or B (green squares). There are 48 squares in each sample.