

Chapter 1. The properties of gases

Gas - a form of matter that fills any container it occupies

Physical state - the state of physical properties of a sample such as

volume, mole, pressure, and temperature

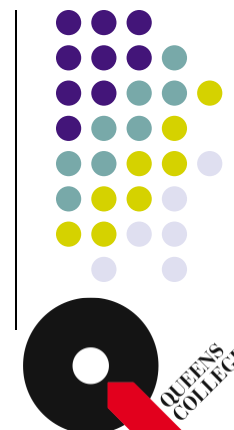
Mole - the number of atoms or molecules equal to Avogadro's number $N_A = 6.022137 \times 10^{23}$, which is defined as the number of atoms in exactly 12 grams of ^{12}C .

Pressure - the amount of force applied to a surface of unit area

SI unit of force : Newton (N) = 1 kgms⁻²

SI unit of pressure : Pascal (Pa) = 1 N m⁻²

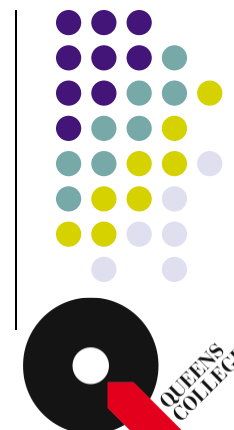
1 bar = 100,000 Pa, 1 atm = 101,325 Pa



Temperature

- (1) The **degree of hotness** or coldness (general chemistry)
- (2) The property that indicates the **direction of flow of energy through a thermally conducting, rigid wall** (Atkins and de Paula)
- (3) Unique physical property that determines the **direction of heat flow** between two objects placed in thermal contact (macroscopic definition, wikipedia)
- (4) **Average energy** of microscopic motions of a single particle in the system **per degree of freedom** (microscopic definition, wikipedia)
- (5) A universal measure that determines the **capability of a system to give out or take in heat energy**

Heat - a form of non-mechanical energy due to the **random or uncontrollable** motion of atoms and molecules



Temperature scale

Celsius scale θ : expressed in $^{\circ}\text{C}$

Thermodynamic temperature scale: expressed in K, kelvins

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

Fahrenheit scale f : expressed in $^{\circ}\text{F}$

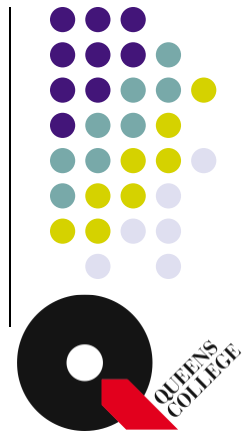
$$f = 9 \theta/5 + 32$$

Standard ambient temperature and pressure (SATP) : 298.15 K and 1 bar

Standard temperature and pressure (STP): 273.15 K and 1 atm

Diathermic - transfer heat, Adiabatic - do not transfer heat

Zeroth law of thermodynamics - If systems A and B are in thermal equilibrium and systems B and C are also in thermal equilibrium, then A and C should be in thermal equilibrium when brought into thermal contact.



Ideal (perfect) gas law

$$pV = nRT \quad \text{or} \quad pV_m = RT, V_m = V/n$$

$$R = 8.31447 \text{ JK}^{-1} \text{ mol}^{-1}$$

Joule (J): Unit of energy, $1\text{J} = 1\text{kg m}^2 \text{ s}^{-2}$

Real gas law -Virial equation of state

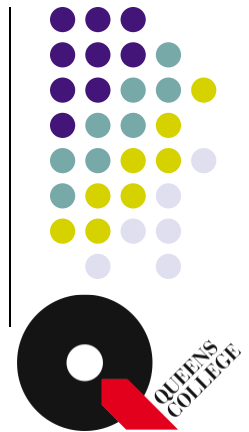
$$pV_m = RT(1 + B'p + C'p^2 + \dots)$$

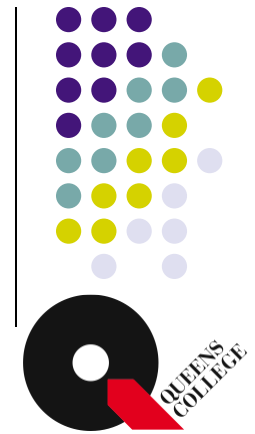
, or equivalently

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

B', C', B, C, \dots are temperature dependent parameters

Compression factor: $Z = \frac{pV_m}{RT}$





Boyle Temperature, T_B

The second virial coefficient $B(T_B)=0$.

Condensation - transformation of real gas to liquid at high pressure or low temperature

Critical Temperature, T_c

If $T > T_c$, no condensation, supercritical fluid

Critical pressure and volume, p_c and V_c - the pressure and volume where condensation starts to occur just below $T=T_c$

van Der Waals equation

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



**Decrease of volume
due to finite size of
molecules or atoms**



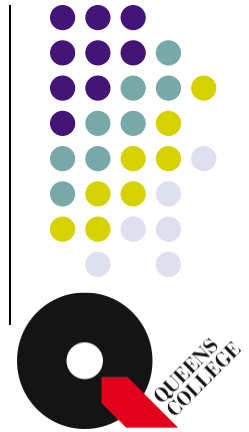
**Decrease of pressure
due to attractive
interactions between
molecules or atoms**

Can explain condensation - need Maxwell construction

$$V_c = 3b, T_c = \frac{8a}{27bR}, p_c = \frac{a}{27b^2}, Z_c = \frac{3}{8} = \mathbf{0.375}$$

Compression factors of actual gases:

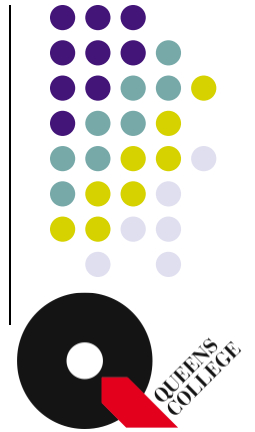
Ar - 0.292, CO₂ - 0.274, He - 0.305, O₂ - 0.308



Principle of corresponding states (PCS) - Real gases at the same reduced volume and reduced temperature exert the same reduced pressure. See Fig. 1.19

Reduced variables

$$p_r = \frac{p}{p_c}, V_r = \frac{V_m}{V_c}, T_r = \frac{T}{T_c}$$



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van der Waals equation:

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



$$p_r \frac{a}{27b^2} = \frac{T_r}{(3V_r - 1)} \frac{8a}{27b^2} - \frac{a}{V_r^2} \frac{1}{9b^2}$$



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

Consistent with the PCS.

True for any equation with two parameters.

