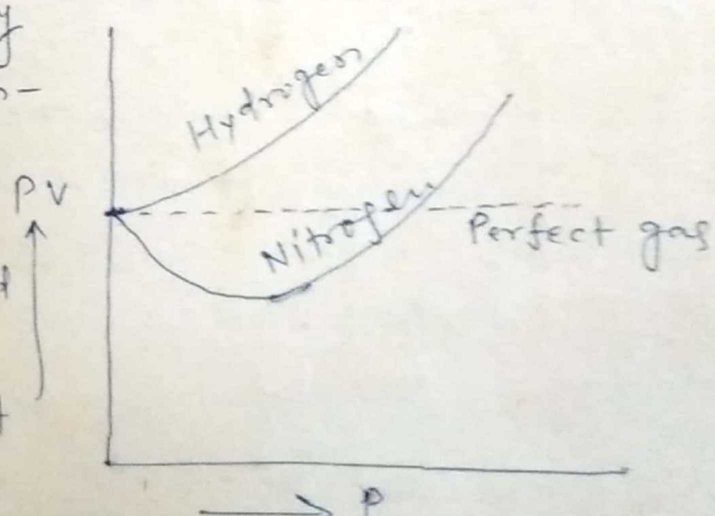
Boyle temperature.

According to Boyle and Charles the equation of state for a perfect gas is, $PV = RT$ ——— (1)

where R is a gas Constant for 1 gm. mole.

According to this relation, for a given quantity of gas at a given temperature, the value of the product PV determined over a wide range of pressure should be Constant i.e Boyle's law. But it was found experimentally by Amagat that for air, Oxygen, nitrogen and Carbon-dioxide, the value of the product PV decreases intially with increasing pressure, becomes a minimum at a particular pressure and then increases with increase in pressure, but for hydrogen the product PV increases steadily with increase in pressure as shown in fig.



Thus the Boyle's law is obeyed only under ideal Conditions i.e at high-temperature and low pressure.

K. Onnes after investigating the behaviour of various gases suggested that the behaviour of all actual gases on Compression at Constant temperature Can be represented by an equation of the type

$$PV = A + BP + CP^2 + DP^3 + \dots \quad (2)$$

where A, B, C, D, .. are Constants for a given temp depending on the nature of the gas and are Called Virial Coefficients.

this suggests the existence of inter-molecular attract

A is simply equal to RT because as $P \to 0$, equation (2) reduces to equation (1). The second, third and fourth terms become negligible in comparision to first at very low pressure and then gases obey Boyle's law accurately.

The coefficient B has a special importance. For all the gases it varies in a similar manner. Its value is negative at low temperatures but gradually increases to zero and becomes positive as the temperature is increased. The temperature at which coefficient B is zero is called the Boyle temperature represented by T_B, because at this temperature, Boyle's law holds over a wide range of pressures provided the constants C, D, ------ are negligible. Thus at Boyle's temperature

$$B = \frac{d}{dP}(PV) = 0$$

and $PV = A$ = Constant.

Now, Vander Waal's equations of state for a real gas is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{——} \quad (3)$$

where a and b are called Vander Waal's Constants.

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

or in the form of equation (2)

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \quad \text{——} \quad (4)$$

Approximately, it is written as

$$V = \frac{RT}{P} \quad \text{——} \quad (5)$$

Putting the value of (5) in (4)

$$PV = RT + Pb - \frac{a}{RT}P + \frac{ab}{R^2T^2}P^2.$$

$$PV = RT + \left(b - \frac{a}{RT}\right)P + \frac{ab}{R^2T^2}P^2. \quad \text{——} \quad (6)$$

(14) Comparing this equation with equation (2), we get

$$A = RT, \quad B = b - \frac{a}{RT}, \quad C = \frac{ab}{R^2T^2} \quad ; \text{———} (7)$$

At Boyle temperature, $T = T_B$ and $B = 0$

therefore,

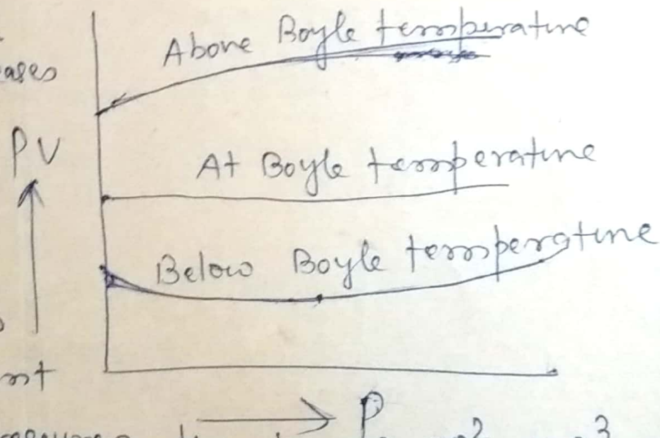
$$0 = b - \frac{a}{RT_B}$$

$$\boxed{T_B = \frac{a}{Rb}} \quad ; \text{———} (8)$$

This equation gives the value of Boyle's temperature for all gases obeying Vander waal's equation of state. clearly Boyle temperature depends upon a and b which are different for different gases. Hence Boyle-temperature is different for different gases. For nitrogen its value is $50^\circ C$, for hydrogen it is $-164^\circ C$ while for helium, $-250^\circ C$.

(i) Below Boyle temperature

The value of PV first decreases (as B is negative) with increase in P, reaches a minimum at a particular pressure and then begins to increase. It is on account



of the fact that at high pressures the terms cP^2, DP^3 etc of equation (2) become more effective and are positive and thus PV increases with increase in P after reaching a minimum. It indicates that, below the Boyle's temperature, the gases are highly compressible and this suggests the existence of inter-molecular attraction

(ii) Above Boyle temperature

The product pv increases with increase in p from the begining. Coefficient B is positive above Boyle temperature and thus the terms on the right hand side of equation (2) are positive. As a result value of pv increases with increase in p. It indicates that inter-molecular attractions are now less significant.

(iii) At Boyle temperature

The product pv is practically constant for a long range of pressure but at very high pressure it begins to increase. Thus Boyle's law is obeyed over a wide range of pressures.

Temperature of Inversion:

When a gas is allowed to escape adiabatically through a porous plug from the region of constant high pressur to the region at constant low pressure, it undergoes a change of temperature. This phenomenon is Called Joule Thomson effect and the process is called the Joule Thomson or adiabatic throttling. The change i temperature depends upon the nature of the gas and the initial temperature.

On suffering Joule Thomson expansion all gases undergo a change in temperature.

There are some points ~~based~~ related to Joule Thomson expansion:

1. At ordinary temperatures, most of the gases show a cooling effect while hydrogen and helium show heating effect. However at sufficiently low temperature all gases show a Cooling effect on suffering Joule-Thomson expansion.
2. The fall in temperature is directly proportional to the difference of pressure on the two sides of the porous plug.
3. The fall in temperature per atmosphere difference of pressure decreases as the initial temperature of the gas increases.
4. The fall of temperature becomes zero at a particular temperature Called the temperatur of inversion. At this temperature, the gas

show neither cooling nor heating effect. Above this temperature, the gases show heating effect.

The fall in temperature δT for a gas obeying vander-Waals equation of state is given by

$$\delta T = \left(\frac{P_1 - P_2}{JMC_p}\right) \times \left(\frac{2a}{RT} - b\right)$$

Here δT will be zero, if $\frac{2a}{RT} - b = 0$

$$\text{i.e. } T = \frac{2a}{Rb}$$

Therefore, the fall in temperature will be zero, if the temperature of the gas is equal to $\frac{2a}{Rb}$. This is called the temperature of inversion and is represented by T_i.

$$\therefore \boxed{T_i = \frac{2a}{Rb}}.$$

Critical temperature (T_c)

The temperature below which the gas can be liquefied by the application of pressure alone is called the critical temperature. Above this temperature the gas can not be liquefied howsoever high the applied pressure may be.

$$\boxed{T_c = \frac{8a}{27Rb}}.$$

Relation among Boyle temperature, Temperature of inversion and critical temperature.

From ① and ② ④
$T_i = 2T_B$
From ① and ③
$\frac{T_i}{T_c} = \frac{2a}{Rb} \times \frac{27Rb}{8a}$
$= \frac{27}{4} = 6.75$

Temperature of inversion,

$$T_i = \frac{2a}{Rb} \quad \text{———} \ (1)$$

Boyle temperature,

$$T_B = \frac{a}{Rb} \quad \text{———} \ (2)$$

Critical temp.

$$T_c = \frac{8a}{27Rb} \quad \text{———} \ (3)$$

From (1) and (5)

$$T_i = 2T_B \quad \text{——} \quad (11)$$

From (1) and (3)

$$\frac{T_i}{T_c} = \frac{2a}{Rb} \cdot \frac{27Rb}{8a}$$

$$= \frac{27}{4} = 6.75$$

The experimental value of $\frac{T_i}{T_c}$ for actual gases is just less than 6.

It means that the temperature of inversion is very much higher than the critical temperature.

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