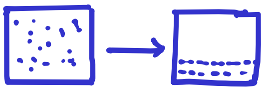
Common observations

for ⓝ moles, of an ideal gas, $pV = nRT$ → no interaction between the gas molecules
→ molecules are treated as point masses.
point ↓ no dimension

p, V, T

* liquefaction of gases.



$pV = nRT$: obeyed only when the p is very low, or the T is very high or both.

Deviations from ideal behaviour

$\boxed{p, V, T}$ for n moles, $pV = nRT$ → equation of state

$$p\left(\frac{V}{n}\right) = RT \qquad \boxed{p\bar{V} = RT} \rightarrow \bar{V}_i = RT/p$$

H_2 C_2H_6 CH_4 CO_2

Z : compressibility factor, $\bar{V}$ = molar vol. of the gas.

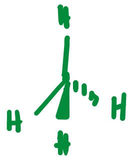
* gas molecules have a finite dimension, $\bar{V}_i$ = molar vol. of the ideal gas.

$$Z = \frac{\bar{V}}{\bar{V}_i} = \frac{\bar{V}}{RT/p} = \frac{p\bar{V}}{RT}$$

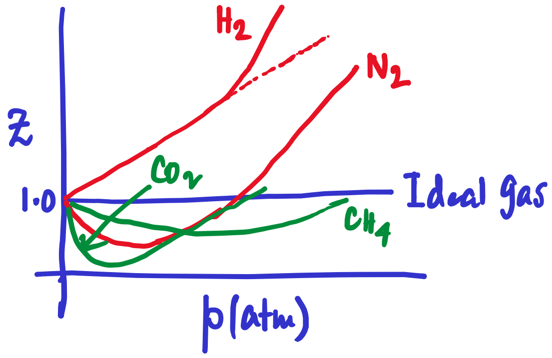
For any gas which behaves ideally, Z = 1

$Z = Z(p, T)$

N≡N H–H



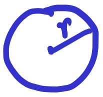
O=C=O



* for H_2, $Z > 1$ at all values of p.
* for N_2, $Z < 1$ when the p is low, but $Z > 1$ when the p is high

Defects of the ideal gas equation ↗ neglect of vol. of gas molecules
↘ neglect of intermolecular interactions

$\bar{V} - \bar{V}_i \neq 0$ $\quad \bar{V} - \bar{V}_i = b \Rightarrow \boxed{\bar{V} = b + (RT/p)}$



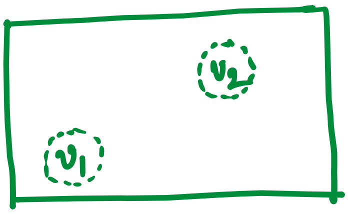
When T = 0 K, $\bar{V} = b$ ↙ multiply by p and divide by RT $\quad N_A \frac{4}{3}\pi r^3$

$$\frac{p\bar{V}}{RT} = \frac{bp}{RT} + 1 \Rightarrow \boxed{Z = 1 + \frac{bp}{RT}}$$

$\boxed{(\bar{V} - b)}\ \bar{V}$

for 1 mole, the space occupied by the gas molecules = b
for n moles, " " " " " " " = nb

$\boxed{p(\bar{V} - b) = RT}$ → better than the ideal gas equation, but it is not a true representation of the actual behaviour; does not explain liquefaction.



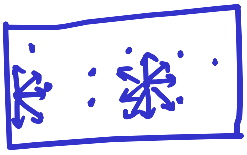
v_1, v_2 : volume elements

the magnitude of force between v_1 and $v_2 = f$

(when both v_1 and v_2 contain one molecule each)

when v_1 contains one molecule, v_2 contains two molecules, the magnitude of attractive force = 2f.

the force of attraction between two vol. elements is proportional to the concentration (C_2) of molecules in v_2.



∴ force acting between the two vol. elements ∝ C_1C_2

Gases are homogeneous, $C_1 = C_2 = C$, $C = n/V$

force ∝ $C_1C_2 = C^2 = n^2/V^2$ ⇒ $\boxed{\text{force} \propto n^2/V^2}$

for one mole, force ∝ $\frac{1}{\bar{V}^2} = \frac{a}{\bar{V}^2}$

$p(\bar{V} - b) = RT$ or, $\boxed{p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}}$

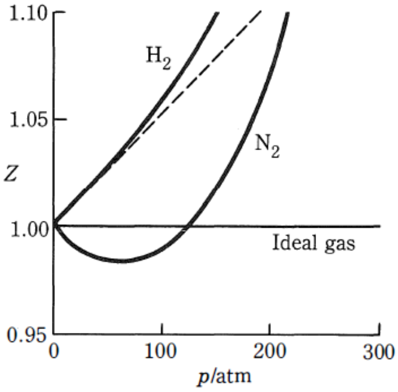
$\boxed{\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT}$ van der Waals equation of state

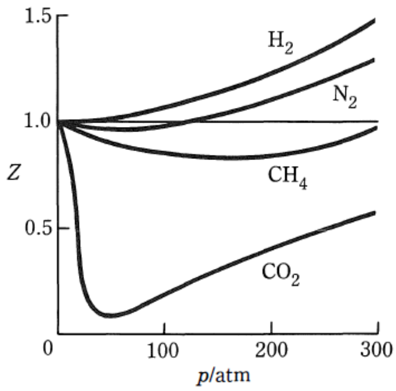
Deviations from Ideal Behavior

The ideal gas law does not accurately represent the behavior of real gases. Formulation of more realistic equations of state for gases and exploring the implications of these equations is important. If measurements of pressure (p), molar volume ($\bar{V}$), and temperature (T) of a gas do not confirm the relation $p\bar{V} = RT$, within the precision of the measurements, the gas is said to deviate from ideality or to exhibit nonideal behavior. To display the deviations clearly, the ratio of the observed molar volume $\bar{V}$ to the ideal molar volume $\bar{V}_{ideal}$ (note that $\bar{V}_{ideal} = RT/p$) is plotted as a function of p at constant T. This ratio,

$$Z = \frac{\bar{V}}{\bar{V}_{ideal}} = \frac{\bar{V}}{RT/p} = \frac{p\bar{V}}{RT}$$

is called the **compressibility factor**. The compressibility factor, $Z = 1$ for a system of an ideal gas, since $\bar{V} = \bar{V}_{ideal}$, and is independent of p and T. For real gases $Z = Z(T, p)$, a function of both temperature and pressure.





For hydrogen, Z is greater than unity (the ideal value) at all pressures. For nitrogen, Z is less than unity in the lower part of the pressure range, but is greater than unity at very high pressures. Note that for those gases that are easily liquefied, Z dips sharply below the ideal line in the low-pressure region.

How can the ideal gas law be modified to yield an equation that will represent the experimental data more accurately?

We begin by correcting an obvious defect in the ideal gas law, namely the prediction that under any finite pressure the volume of the gas is zero at the absolute zero of temperature: $\bar{V} = RT/p$. On cooling, real gases liquefy and ultimately solidify. After liquefaction the volume does not change very much. We can arrange the new equation so that it predicts a finite, positive volume for the gas at $0\ \mathrm{K}$ by adding a positive constant b to the ideal volume

$$\bar{V} = b + (RT/p)$$

∴ The molar volume at $0\ \mathrm{K}$ is b, and we expect that b will be roughly comparable with the molar volume of the liquid or solid. The last equation also predicts that as the pressure becomes infinite the molar volume approaches the limiting value b. This prediction is more in accord with experience than the prediction of the ideal gas law that the molar volume approaches zero at very high pressures. Since by definition $Z = p\bar{V}/RT$, multiplying the equation $\bar{V} = b + (RT/p)$ by p/RT gives

$$\frac{p\bar{V}}{RT} = \frac{bp}{RT} + 1 \Rightarrow Z = 1 + \frac{bp}{RT}$$

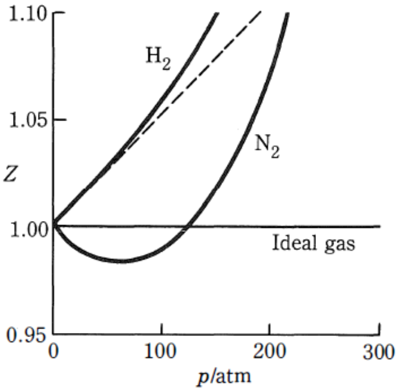
The equation

$$Z = 1 + \frac{bp}{RT}$$

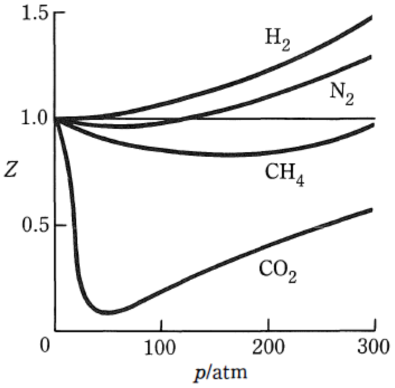
requires Z to be a linear function of p with a positive slope b/RT. The equation

$$Z = 1 + \frac{bp}{RT}$$

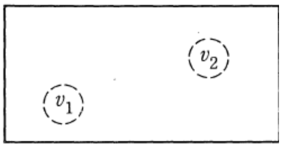
cannot possibly fit the curve for nitrogen, which starts from the origin with a negative slope. But it can represent the behavior of hydrogen. From the equation $Z = 1 + (bp/RT)$ we can conclude that the assumption that the molecules of a gas have finite size is sufficient to explain values of Z greater than unity.



Apparently, this size effect is the dominating one in producing deviations from ideality in hydrogen at 0°C. It is also clear that some other effect must produce the deviations from ideality in gases such as nitrogen and methane, since the size effect cannot explain their behavior in the low p range. We must search the other effect.



We have already noted that the worst offenders in the matter of having values of Z less than unity are CH_4 and CO_2, which are easily liquefied. Thus, we begin to suspect a connection between ease of liquefaction and Z, and to ask why a gas liquefies. First of all, energy, the heat of vaporization, must be supplied to take a molecule out of the liquid and put it into the vapor. This energy is required because of the forces of attraction acting between the molecule and its neighbors in the liquid. The force of attraction is strong if the molecules are close together, as they are in a liquid, and very weak if the molecules are far apart, as they are in a gas. The problem is to find an appropriate way of modifying the gas equation to take account of the effect of these weak attractive forces. The pressure exerted by a gas on the walls of a container acts in an outward direction. Attractive forces between the molecules tend to pull them together, thus diminishing the outward thrust against the wall and reducing the pressure below that exerted by the ideal gas. This reduction in pressure should be proportional to the force of attraction between the molecules of the gas.



Consider two small volume elements v_1 and v_2 in a container of gas. Suppose that each volume element contains one molecule. The attractive force between the two volume elements is some small value f. If another molecule is added to v_2 , keeping one molecule in v_1, the force acting between the two elements should be $2f$. Addition of a third molecule to v_2 should increase the force to $3f$, and so on. The force of attraction between the two volume elements is proportional to the concentration (c_2) of molecules in v_2. If at any point in the argument, the number of molecules in v_2 is kept constant and molecules are added to v_1 then the force should double and triple, etc.

∴ The force acting between the two elements can be written as: $\text{force} \propto c_1 c_2$.

Since the gas is homogeneous, concentration in a gas is everywhere the same, so that, $c_1 = c_2 = c$, and therefore,

$$\text{force} \propto c^2$$

But, $c = n/V = 1/\bar{V}$, $\text{force} \propto 1/\bar{V}^2$.

∴ The equation, $\bar{V} = b + (RT/p)$ can be alternatively written as,

$$p = \frac{RT}{\bar{V} - b}.$$

Because of the attractive forces between the molecules, the pressure is less than that given by the above equation by an amount proportional to $1/\bar{V}^2$, so a term is subtracted from the RHS of the above equation to yield,

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

where a is a positive constant roughly proportional to the energy of vaporization of the liquid. Two things should be noted about the introduction of the term $a/\bar{V}^2$:

- Forces acting on any volume element in the interior of the gas balance out to zero; only those elements of volume near the wall of the container experience an unbalanced force that tends to pull them toward the center. Thus, the effect of the attractive forces is felt only at the walls of the vessel.
- The derivation assumed an effective range of action of the attractive forces of the order of centimeters; in fact, the range of these forces is of the order of nanometers.

The last equation is known as the **van der Waals equation** for a mole of a real gas.

From the last class $\left(p+\frac{a}{\bar{v}^2}\right)(\bar{v}-b) = RT$

For n moles of gas: $\left(p+\frac{n^2a}{v^2}\right)(v-nb) = nRT$

$$\left(p+\frac{a}{\bar{v}^2}\right)(\bar{v}-b) = RT$$

$$p\bar{v} - pb + \frac{a}{\bar{v}} - \frac{ab}{\bar{v}^2} = RT$$

$$p\bar{v}^3 - pb\bar{v}^2 + a\bar{v} - ab = RT\bar{v}^2$$

$$\rightarrow p\bar{v}^3 - (pb+RT)\bar{v}^2 + a\bar{v} - ab = 0$$

$$\boxed{\bar{v}^3 - \left(b+\frac{RT}{p}\right)\bar{v}^2 + \frac{a}{p}\bar{v} - \frac{ab}{p} = 0}$$

$ax^3+bx^2+cx+d=0$

van der Waals equ. is cubic in $\bar{v}$

$ax^2+bx+c=0$, $x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$

⇒ $\boxed{\text{for a single value of } p\text{, there can be three values of } \bar{v}.}$

$$p = \frac{RT}{\bar{v}-b} - \frac{a}{\bar{v}^2}$$

$\boxed{(\bar{v}-b)}$ → vol. for free motion

$\bar{v}$

Multiplying by $\bar{v}$ and dividing by RT

$$\frac{p\bar{v}}{RT} = \frac{\cancel{RT}}{\bar{v}-b}\times\frac{\bar{v}}{\cancel{RT}} - \frac{a}{\bar{v}^{\cancel{2}}}\times\frac{\cancel{\bar{v}}}{RT} \quad \text{or,}\quad z = \frac{1}{1-(b/\bar{v})} - \frac{a}{RT\bar{v}}$$

$b \ll \bar{v} \Rightarrow (b/\bar{v}) \ll 1$ Say, $b/\bar{v} = x$

$\therefore \frac{1}{1-(b/\bar{v})} = \frac{1}{1-x} = 1+x+x^2+x^3+\dots$ (valid only when $x \ll 1$)

$$z = 1 + \frac{\overset{w}{b}}{\bar{v}} + \left(\frac{b}{\bar{v}}\right)^2 + \left(\frac{b}{\bar{v}}\right)^3 + \dots - \frac{\overset{w}{a}}{RT\bar{v}} = 1 + \left(b-\frac{a}{RT}\right)\frac{1}{\bar{v}} + \left(\frac{b}{\bar{v}}\right)^2 + \left(\frac{b}{\bar{v}}\right)^3 + \dots$$

$$z = 1 + \left(b-\frac{a}{RT}\right)\frac{1}{\bar{v}} + \left(\frac{b}{\bar{v}}\right)^2 + \dots$$

all experimental data expresses z as a function of p and T

$z = z(T,p)$?

$z = z(T,\bar{v})$

power series : Series of powers

$$y = f(x,\alpha) = 1 + a_1x + a_2x^2 + a_3x^3 + \dots + a_nx^n + \dots \checkmark$$

$\boxed{a_1, a_2, \dots, a_n, \dots}$

$a_1(\alpha), a_2(\alpha), \dots, a_n(\alpha), \dots$ $y = 1 + b_1(x)\alpha + b_2(x)\alpha^2 + \dots \checkmark$

$$z = 1 + A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \dots$$

$$Z = \frac{p\bar{V}}{RT} \Rightarrow \frac{1}{\bar{V}} = \frac{p}{RTZ}$$

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \cdots$$

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RT}\right)^2\frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^3}{Z^3} + \cdots$$

$$Z = 1 + A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots$$

The LHS of these eqns. are equal.

$$\cancel{1} + A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots = \cancel{1} + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RT}\right)^2\frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^3}{Z^3} + \cdots$$

or, $A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots = \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RT}\right)^2\frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^3}{Z^3} + \cdots$

Dividing throughout by p

$$A_1(T) + A_2(T)p + A_3(T)p^2 + \cdots = \overset{A_1(T)}{\boxed{\left(b - \frac{a}{RT}\right)\frac{1}{RT}}}\frac{1}{Z} + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

When $p \to 0$, $Z \to 1$

$$\boxed{A_1(T) = \left(b - \frac{a}{RT}\right)\frac{1}{RT}} \quad \text{——} \quad ①$$

$$A_1(T) + A_2(T)p + A_3(T)p^2 + \cdots = A_1(T)\frac{1}{Z} + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

$$A_2(T)p + A_3(T)p^2 + \cdots = \left(\frac{1}{Z} - 1\right)A_1(T) + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

$$= \left(\frac{1-Z}{Z}\right)A_1(T) + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \cdots$$

Dividing throughout by p

$$A_2(T) + A_3(T)p + \cdots = -\left(\frac{Z-1}{p}\right)\frac{A_1(T)}{Z} + \left(\frac{b}{RT}\right)^2\frac{1}{Z^2} + \cdots$$

$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \cdots$ or, $\frac{Z-1}{p} = \left(b - \frac{a}{RT}\right)\frac{1}{p\bar{V}} + \frac{1}{p}\left(\frac{b}{\bar{V}}\right)^2 + \cdots$

When the p is low, $p\bar{V} = RT$

$$\therefore \frac{Z-1}{p} = \left(b - \frac{a}{RT}\right)\frac{1}{RT} + \frac{\bar{V}}{RT}\left(\frac{b}{\bar{V}}\right)^2 + \cdots \approx \left(b - \frac{a}{RT}\right)\frac{1}{RT} = A_1(T)$$

$$A_2(T) + A_3(T)p + \cdots = -\left(\frac{Z-1}{p}\right)\frac{A_1(T)}{Z} + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} + \cdots$$

$$A_2(T) + A_3(T)p + \cdots = -A_1(T)\,\frac{A_1(T)}{Z} + \left(\frac{b}{RT}\right)^2 \cdot \frac{1}{Z^2} + \cdots$$

When $p \to 0,\ Z \to 1$

$$Z = 1 + A_1(T)p + A_2(T)p^2 + \cdots$$

$$A_2(T) = \left(\frac{b}{RT}\right)^2 - [A_1(T)]^2$$

We have seen that the **van der Waals equation** for a mole of a real gas is given by,

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

where a is a positive constant roughly proportional to the energy of vaporization of the liquid. Thus, the van der Waals equation for a mole of a real gas may be written in the form,

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

The same equation for n moles will be,

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

where $V = n\bar{V}$ has been used. The van der Waals equation takes two effects into account. First, the effect of molecular size,

$$p = \frac{RT}{\bar{V} - b}$$

Since the denominator in the above equation is smaller than the denominator in the ideal gas equation, the size effect by itself increases the pressure above the ideal value. According to this equation it is the empty space between the molecules, the "free" volume, that follows the ideal gas law. Second, the effect of intermolecular forces is taken into account,

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

The effect of attractive forces by itself reduces the pressure below the ideal value and is taken into account by subtracting a term from the pressure. Multiplying the van der Waals equation,

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

by $\bar{V}/RT$, we get,

$$\frac{p\bar{V}}{RT} = \frac{RT}{\bar{V} - b} \times \frac{\bar{V}}{RT} - \frac{a}{\bar{V}^2} \times \frac{\bar{V}}{RT}$$

$$\text{or, } Z = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}}$$

$$\text{or, } Z = \frac{1}{1 - (b/\bar{V})} - \frac{a}{RT\bar{V}}$$

At low pressures, $b/\bar{V}$ is small compared with unity.

$$\therefore \frac{1}{1 - (b/\bar{V})} = \frac{1}{1 - x} = 1 + x + x^2 + \cdots = 1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \cdots$$

Thus,

$$Z = 1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \cdots - \frac{a}{RT\bar{V}} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \cdots$$

which expresses Z as a function of T and $\bar{V}$. It would be preferable to have Z as a function of T and p, since all the experimental plots are Z versus p graphs. Thus,

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 + \left(\frac{b}{\overline{V}}\right)^3 + \cdots$$

has to be expressed as a function of T and p, and to achieve this we perform a "trick". At low pressures we can expand Z as a power series in the pressure.

$$Z = 1 + A_1 p + A_2 p^2 + A_3 p^3 + \cdots$$

in which the coefficients $A_1, A_2, A_3,$ ... are functions of T only. That is,

$$Z = 1 + A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots$$

To determine these coefficients, we use the definition of Z in

$$Z = \frac{p\overline{V}}{RT}$$

to write

$$\frac{1}{\overline{V}} = \frac{p}{RTZ}$$

Using this value of $1/\overline{V}$ in

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 + \left(\frac{b}{\overline{V}}\right)^3 + \cdots$$

we get,

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RT}\right)^2\frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^3}{Z^3} + \cdots$$

Therefore, we have two expressions for Z, namely,

$$Z = 1 + A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots$$

and,

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RT}\right)^2\frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^3}{Z^3} + \cdots$$

Comparing the right-hand sides of the two equations, we get,

$$1 + A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RT}\right)^2\frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^3}{Z^3} + \cdots$$

We subtract 1 from each side of this equation, to get

$$A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots = \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RT}\right)^2\frac{p^2}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^3}{Z^3} + \cdots$$

and divide the result by p to obtain,

$$A_1(T) + A_2(T)p + A_3(T)p^2 + \cdots = \frac{1}{RT}\left(b - \frac{a}{RT}\right)\frac{1}{Z} + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

When $p \to 0,\ \mathrm{Z} \to 1$, and in this limit,

$$A_1(T) = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$$

which is the required value of $A_1(T)$. We will repeatedly use the equation in red to determine the other coefficients. Therefore, we have,

$$A_1(T) + A_2(T)p + A_3(T)p^2 + \cdots = \frac{1}{RT}\left(b - \frac{a}{RT}\right)\frac{1}{Z} + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

and at $p \to 0,\ \mathrm{Z} \to 1$, and in this limit,

$$A_1(T) = \frac{1}{RT}\left(b - \frac{a}{RT}\right).$$

Substituting the above value of $A_1(T)$ in the equation written in red, we obtain,

$$A_1(T) + A_2(T)p + A_3(T)p^2 + \cdots = A_1(T)\frac{1}{Z} + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

We repeat the procedure by subtracting $A_1(T)$ from both sides of this equation

$$A_2(T)p + A_3(T)p^2 + \cdots = \left(\frac{1}{Z} - 1\right)A_1(T) + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

$$\text{or,} A_2(T)p + A_3(T)p^2 + \cdots = \left(\frac{1 - Z}{Z}\right)A_1(T) + \left(\frac{b}{RT}\right)^2\frac{p}{Z^2} + \left(\frac{b}{RT}\right)^3\frac{p^2}{Z^3} + \cdots$$

Dividing throughout by p, we get

$$\text{or,} A_2(T) + A_3(T)p + \cdots = -\left(\frac{Z-1}{p}\right)\frac{A_1(T)}{Z} + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p}{Z^3} + \cdots$$

From,

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \cdots$$

From,

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \cdots,$$

we have,

$$Z - 1 = \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \cdots$$

$$\therefore \frac{Z-1}{p} = \left(b - \frac{a}{RT}\right)\frac{1}{p\bar{V}} + \frac{1}{p}\left(\frac{b}{\bar{V}}\right)^2 + \frac{1}{p}\left(\frac{b}{\bar{V}}\right)^3 + \cdots$$

Under the limit of low p, $p\bar{V} \approx RT$, so that,

$$\frac{Z-1}{p} = \left(b - \frac{a}{RT}\right)\frac{1}{RT} + \frac{\bar{V}}{RT}\left(\frac{b}{\bar{V}}\right)^2 + \frac{\bar{V}}{RT}\left(\frac{b}{\bar{V}}\right)^3 + \cdots \approx \left(b - \frac{a}{RT}\right)\frac{1}{RT} = A_1(T)$$

Therefore, from

$$A_2(T) + A_3(T)p + \cdots = -\left(\frac{Z-1}{p}\right)\frac{A_1(T)}{Z} + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p}{Z^3} + \cdots$$

we have,

$$A_2(T) + A_3(T)p + \cdots = -A_1(T)\frac{A_1(T)}{Z} + \left(\frac{b}{RT}\right)^2 \frac{1}{Z^2} + \left(\frac{b}{RT}\right)^3 \frac{p}{Z^3} + \cdots$$

When $p \to 0,\ \mathrm{Z} \to 1$, we have,

$$A_2(T) = \left(\frac{b}{RT}\right)^2 - [A_1(T)]^2 = \left(\frac{b}{RT}\right)^2 - \left[\frac{1}{RT}\left(b - \frac{a}{RT}\right)\right]^2 = \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)$$

Thus, we have,

$$A_1(T) = \frac{1}{RT}\left(b - \frac{a}{RT}\right) \text{ and } A_2(T) = \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)$$

Hence,

$$Z = 1 + A_1(T)p + A_2(T)p^2 + A_3(T)p^3 + \cdots$$

may now be presented as,

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)p + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p^2 + \cdots$$

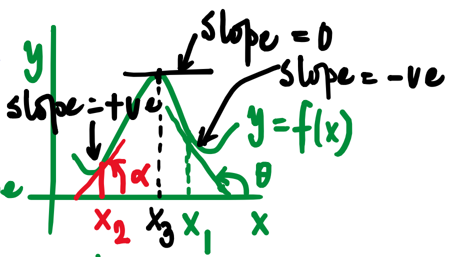
which is the desired form of $Z = Z(p, T)$.

From the last class

$$Z(p,T) = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right) p + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right) p^2 + \cdots$$

for a situation, $p \to 0$
for a situation, $T \to \infty$ } $Z(p,T) = 1$

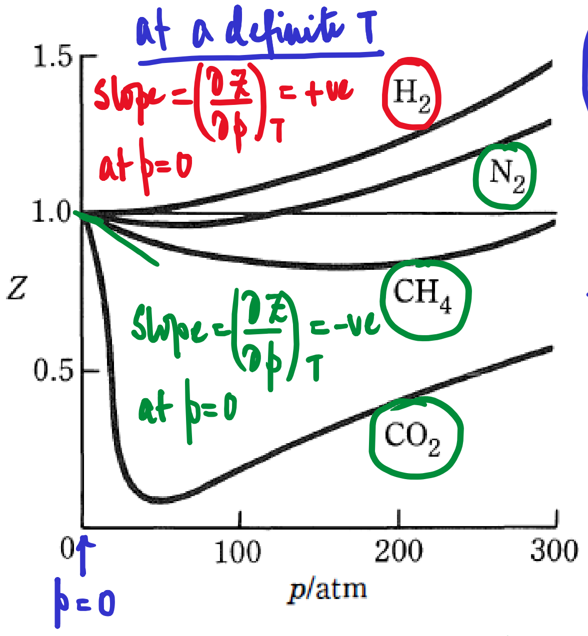
$$\left.\frac{dy}{dx}\right|_{x=x_1} = \text{slope}$$



slope = tan θ

$Z = Z(p,T)$ ↓ Complete derivative

$\left(\frac{dZ}{dp}\right)$ ✗ → $\left(\frac{\partial Z}{\partial p}\right)_T$ = partial derivative of Z with respect to p at constant T



$$\therefore \left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right) + \frac{2a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p + \cdots$$

when $p=0$, all higher terms do not contribute

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right), \text{ at } p=0$$

* for very small H_2 molecules: $(\partial Z/\partial p)_T$ = +ve at $p=0$: $b > a/RT$.

* for relatively larger N_2, CH_4 or CO_2 : $(\partial Z/\partial p)_T$ = -ve at $p=0$: $b < a/RT$.

b → excluded vol. per mole of gas (size effect of molecules)

a → accounts for intermolecular forces

* for smaller molecules the size effect dominates the effect due to the intermolecular forces

* for larger molecules the effect due to intermolecular forces dominate the size effect.

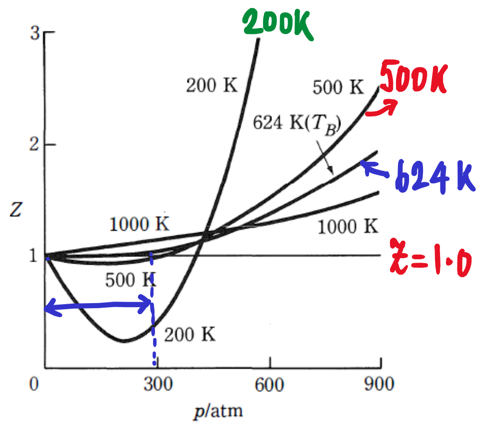
at T = 624 K, for a wide range of p, the plot runs along the Z=1 line.

at 200 K, at $p=0$, $(\partial Z/\partial p)_T$ = -ve

at 500 K, at $p=0$, $(\partial Z/\partial p)_T$ = -ve

at 624 K, at $p=0$, $(\partial Z/\partial p)_T = 0$

at 1000 K, at $p=0$, $(\partial Z/\partial p)_T$ = +ve



∵ the slope is controlled by $(b - a/RT)$, then there must a temp. at which

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

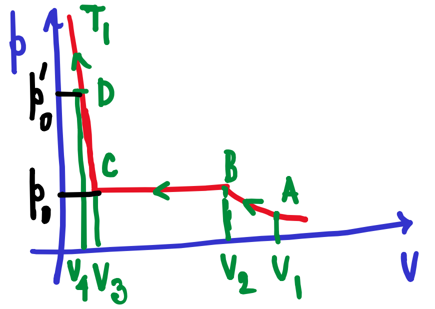
Boyle temp., T_B

$$\boxed{T_B = a/Rb}$$

iso- : same

p-V isotherms of real gases : plot/graphical representation of p versus V of a gas at a constant T

Constant T



AB: as the v decreases, p increases   Why?

BC: as the v decreases, there is no change in p.

CD: the p increases abruptly for a very small decrease in v.   Why?

We have seen,

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)p + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p^2 + \cdots$$

which is the desired form of $Z = Z(p, T)$. The terms responsible for nonideal behavior vanish

- not only as the $p \to 0$,
- but also, as the $T \to \infty$.

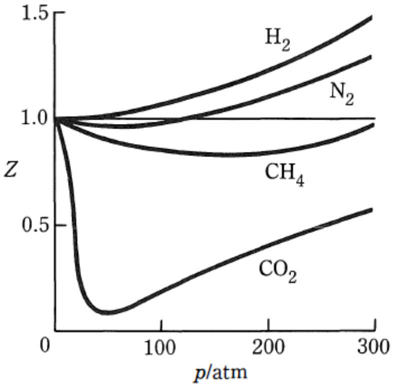
Thus, as a general rule, real gases are more nearly ideal when the pressure is lower and the temperature is higher. The slope of the Z versus p curve is obtained by differentiating the above equation with respect to p, keeping T constant.

$$\therefore \left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right) + \frac{2a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p + \cdots$$

At $p = 0$, all of the higher terms drop out and this derivative reduces simply to

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right),\ p = 0$$

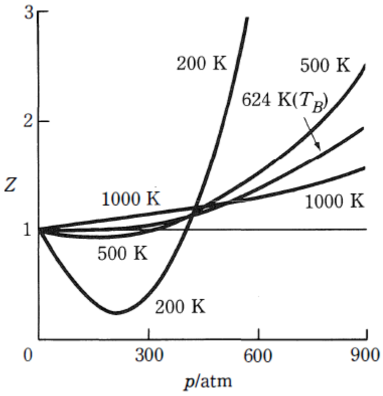
where the derivative is the initial slope of the Z versus p curve. If $b > a/RT$, the initial slope is positive. The size effect dominates the behavior of the gas. If $b < a/RT$, the initial slope is negative. The effect of the attractive forces dominates the behavior of the gas. Thus, the van der Waals equation, which includes both the effects of size and of the intermolecular forces, can interpret either positive or negative slopes of the Z versus p curve. Thus, the effect of the attractive forces dominates the behavior of CH_4 and CO_2, while the molecular size effect dominates the behavior of H_2. We now focus our attention on the Z versus p curves for a single gas at different temperatures.



Thus, at $p = 0$,

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right) \text{ at } p = 0$$

if the temperature is low enough, the term a/RT will be larger than b and so the initial slope of Z versus p will be negative. As the temperature increases, a/RT becomes smaller and smaller; if the temperature is high enough, a/RT becomes less than b, and the initial slope of the Z versus p curve becomes positive.



Finally, if the temperature is extremely high, the slope of Z versus p must approach zero. At some intermediate temperature T_B, the Boyle temperature, the initial slope must be zero. The condition for this is given by,

$$\left(b - \frac{a}{RT_B}\right) = 0 \Rightarrow T_B = \frac{a}{Rb}.$$

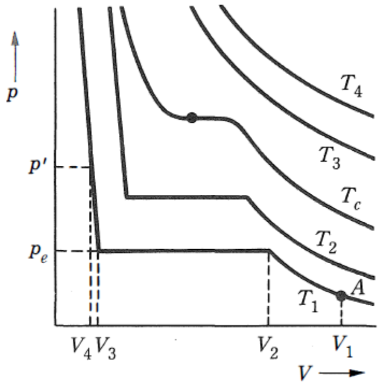
At T_B the Z versus p curve is tangent to the curve for the ideal gas at $p = 0$ and rises above the ideal gas curve only very slowly.

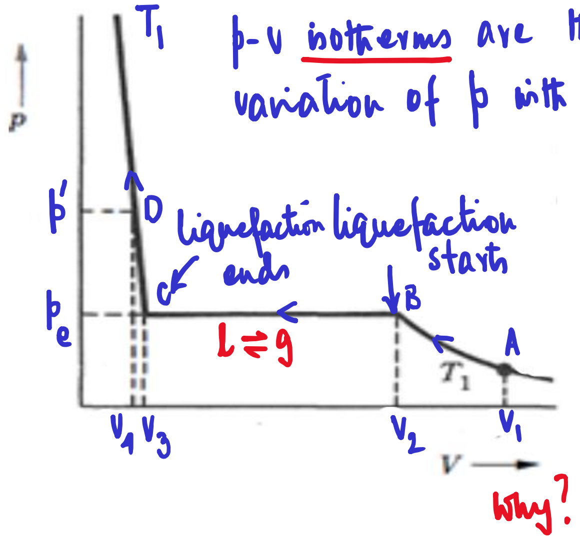
The Real Gas $p - V$ Isotherms

If the $p - V$ relations for a real gas are measured at various temperatures ($T_1 < T_2 < T_c < T_3 < T_4$), a set of isotherms are obtained.

- At high temperatures the isotherms look much like those of an ideal gas.
- At low temperatures the curves have quite a different appearance.
- The horizontal portion of the low-temperature curves is particularly striking.

Consider a container of gas in a state described by point A. Imagine one wall of the container to be movable (a piston). Keeping the temperature at T_1, we slowly push in this wall thus decreasing the volume. As the V becomes smaller, p rises slowly along the curve until the volume V_2 is reached. Reduction of V beyond V_2 produces no change in pressure until V_3 is reached. The small reduction in V from V_3 to V_4 produces a large increase in pressure from p_e to p'. This is a rather remarkable sequence of events, particularly the decrease in volume over a wide range in which p remains at the constant value p_e. If we look into the container while all this is going on, we observe that at V_2 the first drops of liquid appear. As the volume goes from V_2 to V_3 more and more liquid forms. The constant pressure p_e is the equilibrium vapor pressure of the liquid at the temperature T_1. At V_3 the last trace of gas disappears. Further reduction in volume simply compresses the liquid. The pressure rises very steeply, since the liquid is almost incompressible.





p-V isotherms are the graphical representations/plots of the variation of p with the v for a gas at constant T.

Observations:

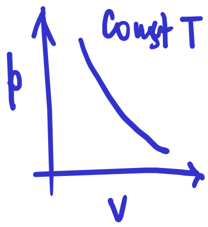
along AB: as the v decreases, p increases, as expected for a system of gas at constant T (Boyle's law)

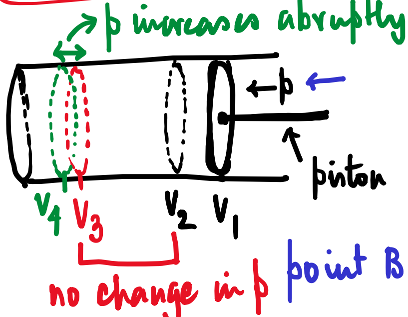
along BC: the volume decreases from V_2 to V_3, but there is no observable change in the p of the gas.

along CD: for a small reduction in vol. (from V_3 to V_4) there is a huge increase in pressure (from p_0 to p_0'); such an abrupt change is unexpected for a gas. Why?

$$\left(p+\frac{a}{\bar{v}^2}\right)(\bar{v}-b)=RT$$

$$ax^3+bx^2+cx+d=0$$





Boyle's law

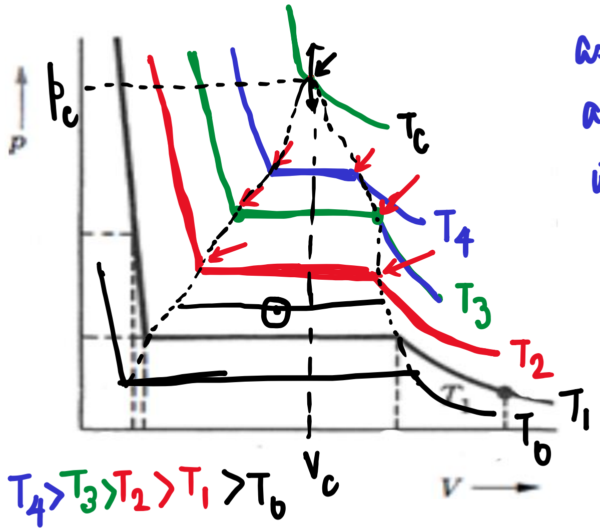
Rectangular hyperbola

point B: liquefaction starts

along the path BC: liquefaction continues

point C: liquefaction ends

along the path CD: compression of the corresponding liquid takes place. → a huge change of p is required



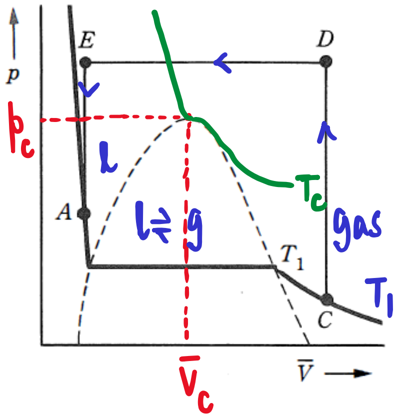
$T_4 > T_3 > T_2 > T_1 > T_0$

As the temp. is increased and the isotherms are drawn, the horizontal portion decreases in length.

T_c = critical temperature
p_c = " pressure
v_c = " volume

} critical state

Google Meet Link: https://meet.google.com/vpf-xufp-ykj



principle of continuity of states

$$\left(p+\frac{a}{\bar{v}^2}\right)(\bar{v}-b)=RT$$

$$p\bar{v}-pb+\frac{a}{\bar{v}}-\frac{ab}{\bar{v}^2}=RT$$

$$p\bar{v}^3-pb\bar{v}^2+a\bar{v}-ab=RT\bar{v}^2$$

$$p\bar{v}^3-(pb+RT)\bar{v}^2+a\bar{v}-ab=0$$

$$\bar{v}^3-\left(b+\frac{RT}{p}\right)\bar{v}^2+\frac{a}{p}\bar{v}-\frac{ab}{p}=0 \qquad ax^3+bx^2+cx+d=0$$

The Real Gas $p-V$ Isotherms

If the $p-V$ relations for a real gas are measured at various temperatures ($T_1 < T_2 < T_c < T_3 < T_4$), a set of isotherms are obtained.

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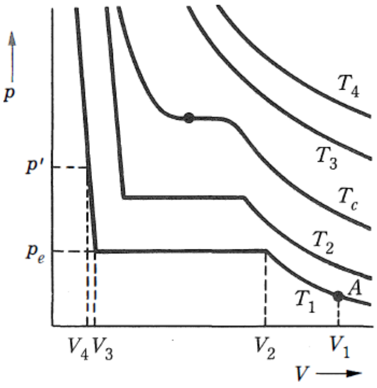
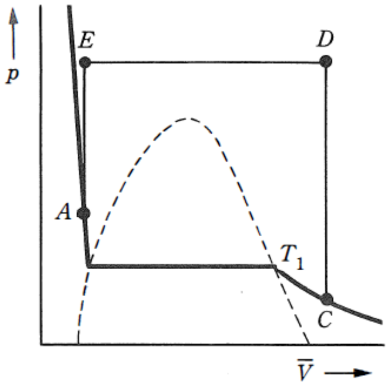
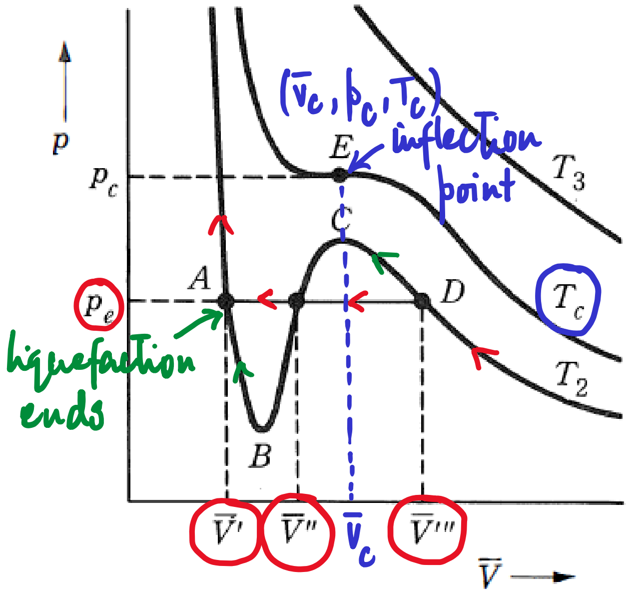


The steep lines at the left of the diagram are therefore isotherms of the liquid. At a somewhat higher temperature the behavior is qualitatively the same, but the range of volume over which condensation occurs is smaller and the vapor pressure is larger. In going to still higher temperatures, the plateau finally shrinks to a point at a temperature T_c, the **critical temperature**. As the temperature is increased above T_c the isotherms approach more and more closely those of the ideal gas. No plateau appears above T_c. The endpoints of the plateaus are connected with a dashed line.



Just as in any $p - V$ diagram every point represents a state of the system. Such as A, on the extreme left of the diagram represents a liquid state of the substance. A point, such as C, on the right side of the diagram represents a gaseous state of the substance. Points under the "dome" formed by the dashed line represent states of the system in which liquid and vapor coexist in equilibrium. It is always possible to make a sharp distinction between states of the system in which one phase is present and states in which two phases coexist in equilibrium, that is, between those points on and under the "dome" and those outside the "dome". A phase is a region of uniformity in a system. This means a region of uniform chemical composition and uniform physical properties. Thus, a system containing liquid and vapor has two regions of uniformity. In the vapor phase, the density is uniform throughout. In the liquid phase, the density is uniform throughout, but has a value different from that in the vapor phase. However, it should be noted that there is no dividing line between the liquid states and the gaseous states. The fact that it is not always possible to distinguish between a liquid and a gas is the **principle of continuity of states**. The points A and C lie on the same isotherm, T_1. Point C clearly represents a gaseous state, and point A clearly represents the liquid obtained by compressing the gas isothermally. Suppose that we begin at C and increase the T of the gas, keeping the V constant. The pressure rises along the line CD. Having arrived at point D, the p is kept constant and the gas is cooled. This decreases the V along the line DE. Having arrived at point E, the V is again kept constant and the gas is cooled. This decreases the p until the point A is reached. At no time in this series of changes did the state point pass through the two-phase region. Condensation in the usual sense of the term did not occur. Point A could reasonably be said to represent a highly compressed gaseous state of the substance. The statement that point A clearly represented a liquid state must be modified. The distinction between liquid and gas is not always clear at all. As this demonstration shows, these two states of matter can be transformed into one another continuously. Whether we refer to states in the region of point A as liquid states or as highly compressed gaseous states depends purely upon which viewpoint happens to be convenient at the moment. If the state point of the system lies under the dome, the liquid and gas can be distinguished, since both are present in equilibrium and there is a surface of discontinuity separating them. In the absence of this surface of discontinuity there is no fundamental way of distinguishing between liquid and gas.

p-V isotherms of van der Waals gases



$$\left(p+\frac{a}{\bar v^2}\right)(\bar v - b) = RT$$

$$p\bar v - pb + \frac{a}{\bar v} - \frac{ab}{\bar v^2} = RT$$

$$p\bar v^3 - pb\bar v^2 + a\bar v - ab = RT\bar v^2$$

$$p\bar v^3 - (pb+RT)\bar v^2 + a\bar v - ab = 0$$

$$\boxed{\bar v^3 - \left(b + \frac{RT}{p}\right)\bar v^2 + \frac{a}{p}\bar v - \frac{ab}{p} = 0}$$

$$\boxed{ax^3 + bx^2 + cx + d = 0}$$

$ax^2 + bx + c = 0$; $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x_1, x_2 \rightarrow (x - x_1)(x - x_2) = 0$

along CD: no liquefaction; supersaturated/supercooled vapour

along AB: superheated vapour

along CB: Something unusual happens; both p and $\bar v$ decrease simultaneously.... no explanation!

has three roots: $x_1, x_2, x_3 \rightarrow (x - x_1)(x - x_2)(x - x_3) = 0$

for the van der Waals equation:

$$(\bar v - \bar v')(\bar v - \bar v'')(\bar v - \bar v''') = 0$$

at the critical point: $\bar v' = \bar v'' = \bar v''' = \bar v_c$

$$(\bar v - \bar v_c)^3 = 0 \quad \text{or,} \quad \bar v^3 - 3\bar v^2 \bar v_c + 3\bar v \bar v_c^2 - \bar v_c^3 = 0$$

$$\text{or, } \boxed{\bar v^3 - 3\bar v_c \bar v^2 + 3\bar v_c^2 \bar v - \bar v_c^3 = 0}$$

van der Waals equ. at the critical point

$$\boxed{\bar v^3 - \left(b + \frac{RT_c}{p_c}\right)\bar v^2 + \frac{a}{p_c}\bar v - \frac{ab}{p_c} = 0}$$

Comparing the coefficients of the last two equations

$$3\bar v_c = b + \frac{RT_c}{p_c}; \quad 3\bar v_c^2 = \frac{a}{p_c}; \quad \bar v_c^3 = \frac{ab}{p_c}$$

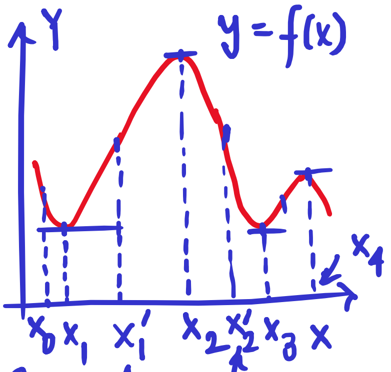
$$\frac{\bar{V}_c^{\cancel{3}}}{3\cancel{\bar{V}_c^{2}}} = \frac{\cancel{a}b}{\cancel{p_c}} \cdot \frac{\cancel{p_c}}{\cancel{a}}$$

$$\boxed{\bar{V}_c = 3b}$$

$$3\times 9b^2 = \frac{a}{p_c} \longrightarrow \boxed{p_c = \frac{a}{27b^2}}$$

$$3\times 3b = b + \frac{RT_c}{a}\cdot 27b^2 \quad \text{or, } 9b = b + \frac{RT_c}{a}\cdot 27b^2$$

$$8\cancel{b} = \frac{RT_c}{a}\cdot 27b^{\cancel{2}} \qquad \boxed{T_c = \frac{8a}{27Rb}}$$



$$\left[\frac{dy}{dx}\right]_{x=x_1} = 0$$

+ve slope

-ve slope

point of inflection ≡ inflection point.

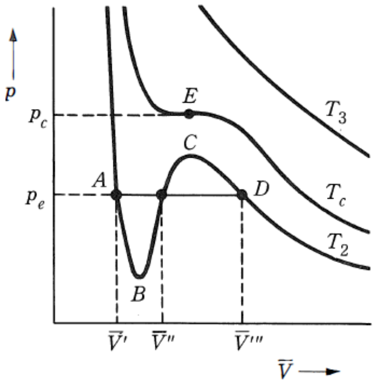
$$\left(\frac{dy}{dx}\right)_{x_i} = 0, \quad \left(\frac{d^2y}{dx^2}\right)_{x_i} = 0 \qquad \left(\frac{\partial p}{\partial \bar{V}}\right)_{T=T_c} = 0, \quad \left(\frac{\partial^2 p}{\partial \bar{V}^2}\right)_{T=T_c} = 0$$

The $p-V$ Isotherms of a van der Waals Gas

Consider the van der Waals equation in the form

$$p = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

When $\bar{V}$ is very large this equation approximates the ideal gas law, since $\bar{V}$ is very large compared with b and $a/\bar{V}^2$ is very small compared with the first term. This is true at all temperatures. At high temperatures, the term $a/\bar{V}^2$ can be ignored, since it is small compared with $RT/(\bar{V}-b)$.



A plot of the isotherms, p versus $\bar{V}$, calculated from the van der Waals equation is shown. It is apparent from the figure that in the high-volume region the isotherms look much like the isotherms for the ideal gas, as does the isotherm at high temperature T_3. At lower temperatures and smaller volumes, none of the terms in the equation may be neglected. At the temperature T_c the isotherm develops a point of inflection, point E. At still lower temperatures, the isotherms exhibit a maximum and a minimum. The curve at T_2 predicts three values of the volume, $\bar{V}'$, $\bar{V}''$, and $\bar{V}'''$, at the pressure p_e. The corresponding plateau in the experimental isotherm predicts infinitely many volumes of the system at the pressure p_e.

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V}-b) = RT \Rightarrow p\bar{V} - pb + \frac{a}{\bar{V}} - \frac{ab}{\bar{V}^2} = RT$$
$$\therefore p\bar{V}^3 - pb\bar{V}^2 + a\bar{V} - ab = RT\bar{V}^2$$
$$\text{or}, p\bar{V}^3 - (pb + RT)\bar{V}^2 + a\bar{V} - ab = 0$$

Thus, van der Waals equation is cubic in $\bar{V}$. It is worthwhile to realize that even if a very complicated function had been written down, it would not exhibit a plateau such as that in the experimental isotherm. The oscillation of the van der Waals equation in this region is as much as can be expected of a simple continuous function. The sections AB and DC of the van der Waals curve at T_2 can be realized experimentally. If the volume of a gas at temperature T_2 is gradually reduced, the pressure rises along the isotherm until the point

D, at pressure p_e is reached. At this point, condensation should occur, however, it may happen that liquid does not form, so that further reduction in volume produces an increase in pressure along the line DC. In this region (DC) the pressure of the gas exceeds the equilibrium vapor pressure of the liquid, p_e at the temperature T_2. These points are therefore state points of a supersaturated (or supercooled) vapor. Similarly, if the volume of a liquid at temperature T_2 is increased, the pressure falls until point A, at pressure p_e is reached. At this point vapor should form; however, it may happen that vapor does not form, so that further increase in the volume produces a reduction of pressure along the line AB. Along the line AB the liquid exists under pressures that correspond to equilibrium vapor pressures of the liquid at temperatures below T_2. The liquid is at T_2 and so these points are state points of a superheated liquid. The states of the superheated liquid and those of the supercooled vapor are metastable states. They are unstable in the sense that slight disturbances are sufficient to cause the system to revert spontaneously into the stable state with the two phases present in equilibrium. The section BC of the van der Waals isotherm cannot be realized experimentally. In this region the slope of the $p - V$ curve is positive, increasing the volume of such a system would increase the pressure, and decreasing the volume would decrease the pressure! States in the region BC are unstable; slight disturbances of a system in such states as B to C would produce either explosion or collapse of the system. Although it is, in practice, impossible to carry out a process along the entire S-shaped isotherm, this curve has some theoretical significance. Maxwell showed by a thermodynamic argument that the line AD must intersect the curve $ABCD$ in such a way that,

$$\oint p dV = 0,$$

otherwise, it would be possible, conceptually, to produce an overall work in a cyclic isothermal process, in violation of the second law of thermodynamics.

The Critical State

We have already seen that the van der Waals equation can be written as,

$$p\bar{V}^3 - (pb + RT)\bar{V}^2 + a\bar{V} - ab = 0,$$

so that,

$$\bar{V}^3 - \left(b + \frac{RT}{p}\right)\bar{V}^2 + \frac{a}{p}\bar{V} - \frac{ab}{p} = 0,$$

and since it is a cubic equation, it may have three real roots for certain values of p and T. These three roots for T_2 and p_e are the intersections of the horizontal line at p_e with the isotherm at T_2. All three roots lie on the boundary of or within the two-phase region. The two-phase region narrows and finally closes at the top. This means that there is a certain maximum pressure p_c and a certain maximum temperature T_c, at which liquid and vapor can coexist. This condition of temperature and pressure is the critical point and the corresponding volume is the critical volume $\bar{V}_c$. As the two-phase region narrows, the three roots of the van der Waals equation approach one another, since they must lie on the boundary or in the region. At the critical point the three roots are all equal to $\bar{V}_c$. The cubic equation can be written in terms of its roots $\bar{V}'$, $\bar{V}''$, and $\bar{V}'''$:

$$(\bar{V} - \bar{V}')(\bar{V} - \bar{V}'')(\bar{V} - \bar{V}''') = 0.$$

At the critical point, $\bar{V}' = \bar{V}'' = \bar{V}''' = \bar{V}_c$, so that the equation becomes $(\bar{V} - \bar{V}_c)^3 = 0$. Expanding, we obtain,

$$\bar{V}^3 - 3\bar{V}^2\bar{V}_c + 3\bar{V}\bar{V}_c^2 - \bar{V}_c^3 = 0.$$

At the critical temperature and pressure $(p = p_c, T = T_c)$, van der Waals equation takes the form

$$\bar{V}^3 - \left(b + \frac{RT_c}{p_c}\right)\bar{V}^2 + \frac{a}{p_c}\bar{V} - \frac{ab}{p_c} = 0$$

The last two equations (in red) are simply different ways of writing the same equations. Thus, the coefficients of the individual powers of $\bar{V}$ must be the same in both equations.

$$3\bar{V}_c = b + \frac{RT_c}{p_c},\ 3\bar{V}_c^2 = \frac{a}{p_c},\ \bar{V}_c^3 = \frac{ab}{p_c}$$

The set of equations can be solved for $\bar{V}_c$, p_c and T_c, the critical constants of the gas.

$$\bar{V}_c = 3b,\ p_c = \frac{a}{27b^2},\ T_c = \frac{8a}{27Rb}$$

If the values of a and b are known, the above expressions may be used to calculate $\bar{V}_c$, p_c and T_c. Alternatively, one might use the equations,

$$3\bar{V}_c = b + \frac{RT_c}{p_c},\ 3\bar{V}_c^2 = \frac{a}{p_c},\ \bar{V}_c^3 = \frac{ab}{p_c}$$

to calculate a, b and R, in terms of $\bar{V}_c$, p_c and T_c:

$$b = \frac{\bar{V}_c}{3},\ a = 3p_c\bar{V}_c^2,\ R = \frac{8p_c\bar{V}_c}{3T_c}$$

However, the value of R so obtained does not agree well at all with the known value of R. There is an alternative way to calculate the critical constants. At any T, along the linear segment the p remains constant as the $\bar{V}$ changes.

$$\therefore \left(\frac{\partial p}{\partial \bar{V}}\right)_T = 0$$

The critical point is the limiting case of a linear segment.

$$\therefore \left(\frac{\partial p}{\partial \bar{V}}\right)_{T=T_c} = 0$$

Below T_c, the slope of each isotherm goes through the sequence negative-zero-negative. The slope also goes through a discontinuity at both boundaries of the two-phase region. As T_c is approached, the isotherms become smoother, less discontinuous in slope, until the critical isotherm itself, which is perfectly smooth. Clearly, the slope, $(\partial p/\partial \bar{V})_T$, thereby goes through a maximum at the critical point. But a necessary condition for a maximum in $(\partial p/\partial \bar{V})_T$ is that its derivative vanish, that is,

$$\left(\frac{\partial^2 p}{\partial \bar{V}^2}\right)_{T=T_c} = 0$$

Thus, at the critical point, $T = T_c$, $p = p_c, \bar{V} = \bar{V}_c$,

$$\left(\frac{\partial p}{\partial \bar{V}}\right)_{T=T_c} = 0,\ \left(\frac{\partial^2 p}{\partial \bar{V}^2}\right)_{T=T_c} = 0$$

From our last class:

- The slope of the p vs. $\bar{v}$ plot, at constant T, $(\partial p/\partial \bar{v})_T$ for a van der Waals gas passes through a max. at the critical point $(T=T_c, p=p_c, \bar{v}=\bar{v}_c)$
- a necessary condition for a max. in $(\partial p/\partial \bar{v})_T$ is that its derivative vanish, that is, $(\partial^2 p/\partial \bar{v}^2)_{T=T_c} = 0$

$$\text{Slope} = \left(\frac{\partial p}{\partial \bar{v}}\right)_T$$

$$\text{Curvature} = \left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T$$

$\therefore$ at the critical point, $T=T_c, p=p_c, \bar{v}=\bar{v}_c$

$$\left(\frac{\partial p}{\partial \bar{v}}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_{T=T_c} = 0$$

From the van der Waals equation of state for a mole of gas

$$p = \frac{RT}{\bar{v}-b} - \frac{a}{\bar{v}^2} \qquad \left(\frac{\partial p}{\partial \bar{v}}\right)_T = -\frac{RT}{(\bar{v}-b)^2} + \frac{2a}{\bar{v}^3}$$

$$\left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_T = \frac{2RT}{(\bar{v}-b)^3} - \frac{6a}{\bar{v}^4}$$

at the critical point, $p=p_c, T=T_c, \bar{v}=\bar{v}_c$

$$\left(\frac{\partial p}{\partial \bar{v}}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial \bar{v}^2}\right)_{T=T_c} = 0$$

$$0 = -\frac{RT_c}{(\bar{v}_c-b)^2} + \frac{2a}{\bar{v}_c^3} \quad \text{and} \quad 0 = \frac{2RT_c}{(\bar{v}_c-b)^3} - \frac{6a}{\bar{v}_c^4}$$

$$\frac{2a}{\bar{v}_c^3} = \frac{RT_c}{(\bar{v}_c-b)^2} \quad \text{and} \quad \frac{6a}{\bar{v}_c^4} = \frac{2RT_c}{(\bar{v}_c-b)^3}$$

$$\frac{6a/\bar{v}_c^4}{2a/\bar{v}_c^3} = \frac{2RT_c/(\bar{v}_c-b)^3}{RT_c/(\bar{v}_c-b)^2}$$

or, $$\frac{\overset{3}{\cancel{6}}\cancel{a}}{\bar{v}_c^{\cancel{4}}} \times \frac{\cancel{\bar{v}_c^3}}{\cancel{2}\cancel{a}} = \frac{2\cancel{RT_c}}{(\bar{v}_c-b)^{\cancel{3}}} \times \frac{\cancel{(\bar{v}_c-b)^2}}{\cancel{RT_c}}$$

$$\boxed{\bar{v}_c = 3b}$$

$$\frac{2a}{\bar{v}_c^3} = \frac{RT_c}{(\bar{v}_c-b)^2} \quad \text{or,} \quad \frac{2a}{27b^{\cancel{3}}} = \frac{RT_c}{4\cancel{b^2}}$$

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

Writing the van der Waals equation at the critical point

$$p_c = \frac{RT_c}{\bar{v}_c-b} - \frac{a}{\bar{v}_c^2} = R\,\frac{8a}{27Rb}\cdot\frac{1}{2b} - \frac{a}{9b^2} \quad \text{or,} \quad \boxed{p_c = \frac{a}{27b^2}}$$

We can experimentally measure the critical constants of a gas.

$\bar{V}_c = 3b,\ p_c = \frac{a}{27b^2},\ T_c = \frac{8a}{27Rb}$

$b = \bar{V}_c/3,\ a = 3p_c\bar{V}_c^2,\ R = \frac{8p_c\bar{V}_c}{3T_c}$

Critical ratio = $\frac{RT_c}{p_c\bar{V}_c}$

the average experimental value of the critical ratio = 3.75

Critical ratio (calculat) = $\frac{RT_c}{p_c\bar{V}_c} = \cancel{R}\,\frac{8\cancel{a}}{\cancel{27}\cancel{R}\cancel{b}}\cdot\frac{\cancel{27}\cancel{b^2}}{\cancel{a}}\cdot\frac{1}{3\cancel{b}} = \frac{8}{3} = 2.67$

Reduced form of van der Waals equation: law of corresponding states

$$p = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

Substituting: $b = \bar{V}_c/3,\ a = 3p_c\bar{V}_c^2,\ R = \frac{8p_c\bar{V}_c}{3T_c}$

$$\therefore p = \frac{8p_c\bar{V}_c}{3T_c}\cdot T\cdot\frac{1}{\bar{V}-(\bar{V}_c/3)} - \frac{3p_c\bar{V}_c^2}{\bar{V}^2}$$

$$\frac{p}{p_c} = \frac{8}{3}\left(\frac{T}{T_c}\right)\frac{1}{(\bar{V}/\bar{V}_c)-(1/3)} - \frac{3}{(\bar{V}/\bar{V}_c)^2}$$

We define: $\frac{p}{p_c} = \pi,\ \frac{\bar{V}}{\bar{V}_c} = \phi$ (phi), $\frac{T}{T_c} = \tau$ (tau)

π, ϕ and τ are dimensionless pressure, volume and temperature, respectively; π, ϕ, and τ are called reduced pressure, reduced vol. and reduced temp., respectively

$$\pi = \frac{8}{3}\tau\cdot\frac{1}{\phi-\frac{1}{3}} - \frac{3}{\phi^2}$$

or, $\boxed{\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\tau}$

van der Waals reduced equation of state

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

Should be capable of describing all gases.

"Two gases at the same reduced temp. and under the same reduced pressure should occupy the same reduced vol."

– law of corresponding states

There is an alternative way to calculate the critical constants. At any T, along the linear segment the p remains constant as the $\bar{V}$ changes.

$$\therefore \left(\frac{\partial p}{\partial \bar{V}}\right)_T = 0$$

The critical point is the limiting case of a linear segment.

$$\therefore \left(\frac{\partial p}{\partial \bar{V}}\right)_{T=T_c} = 0$$

Below T_c, the slope of each isotherm goes through the sequence negative-zero-negative. The slope also goes through a discontinuity at both boundaries of the two-phase region. As T_c is approached, the isotherms become smoother, less discontinuous in slope, until the critical isotherm itself, which is perfectly smooth. Clearly, the slope, $(\partial p/\partial \bar{V})_T$, thereby goes through a maximum at the critical point. But a necessary condition for a maximum in $(\partial p/\partial \bar{V})_T$ is that its derivative vanish, that is,

$$\left(\frac{\partial^2 p}{\partial \bar{V}^2}\right)_{T=T_c} = 0$$

Thus, at the critical point, $T = T_c,\ p = p_c, \bar{V} = \bar{V}_c$,

$$\left(\frac{\partial p}{\partial \bar{V}}\right)_{T=T_c} = 0,\ \left(\frac{\partial^2 p}{\partial \bar{V}^2}\right)_{T=T_c} = 0$$

From van der Waals equation,

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2},$$

$$\left(\frac{\partial p}{\partial \bar{V}}\right)_T = -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3},$$

and

$$\left(\frac{\partial^2 p}{\partial \bar{V}^2}\right)_T = \frac{2RT}{(\bar{V} - b)^3} - \frac{6a}{\bar{V}^4}$$

At the critical point, $T = T_c,\ p = p_c, \bar{V} = \bar{V}_c$,

$$0 = -\frac{RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{\bar{V}_c^3},\ 0 = \frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4}$$

Thus, the two equations,

$$0 = -\frac{RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{\bar{V}_c^3}, \qquad \text{or}, \frac{2a}{\bar{V}_c^3} = \frac{RT_c}{(\bar{V}_c - b)^2}$$

and

$$0 = \frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} \qquad \text{or}, \frac{6a}{\bar{V}_c^4} = \frac{2RT_c}{(\bar{V}_c - b)^3}$$

will together lead to,

$$\frac{2a}{\bar{V}_c^3} \times \frac{\bar{V}_c^4}{6a} = \frac{RT_c}{(\bar{V}_c - b)^2} \times \frac{(\bar{V}_c - b)^3}{2RT_c} \qquad \text{or}, \bar{V}_c = 3b$$

and,

$$\frac{2a}{\bar{V}_c^3} = \frac{RT_c}{(\bar{V}_c - b)^2} \Rightarrow \frac{2a}{27b^3} = \frac{RT_c}{(3b - b)^2} \Rightarrow T_c = \frac{8a}{27Rb}$$

Together with the van der Waals equation at the critical point, we have,

$$p_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2} \Rightarrow p_c = \frac{a}{27b^2}$$

From van der Waals equation, $\bar{V}_c$, p_c and T_c, the critical constants of the gas were found:

$$\bar{V}_c = 3b,\ p_c = \frac{a}{27b^2},\ T_c = \frac{8a}{27Rb}$$

Alternatively, one can calculate a, b and R, in terms of $\bar{V}_c$, p_c and T_c:

$$b = \frac{\bar{V}_c}{3},\ a = 3p_c\bar{V}_c^2,\ R = \frac{8p_c\bar{V}_c}{3T_c}$$

Using these values, the critical ratio, $RT_c/p_c\,\bar{V}_c$, may be calculated to be

$$RT_c/p_c\,\bar{V}_c = 8/3 = 2.67$$

Note that, for an ideal gas, this ratio is unity. The average experimental value of the critical ratio is 3.75.
∴ There is a considerable improvement:

$$\text{Ideal gas }(1.00) \rightarrow \text{van der Waals gas }(2.67) \rightarrow \text{Experimental value }(3.75)$$

Reduced form of the van der Waals equation: The law of corresponding states

The van der Waals equation of state for a mole of gas is,

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Substituting the values of a, b and R, from

$$b = \frac{\bar{V}_c}{3},\ a = 3p_c\bar{V}_c^2,\ R = \frac{8p_c\bar{V}_c}{3T_c}$$

we get,

$$p = \frac{8p_c\bar{V}_c}{3T_c} \times T \times \frac{1}{\bar{V} - (\bar{V}_c/3)} - \frac{3p_c\bar{V}_c^2}{\bar{V}^2}$$

We divide the above equation throughout by p_c and rearrange slightly to get

$$\frac{p}{p_c} = \frac{8}{3} \times \frac{T}{T_c} \times \frac{1}{(\bar{V}/\bar{V}_c) - (1/3)} - \frac{3}{\bar{V}^2/\bar{V}_c^2}$$

We define a set of new (dimensionless) variables as:

$$\pi = \frac{p}{p_c}; \qquad \phi = \frac{\bar{V}}{\bar{V}_c}; \qquad \tau = \frac{T}{T_c}$$

With these variables, we can rewrite the last equation as,

$$\pi = \frac{8}{3}\tau\frac{1}{\phi - 1/3} - \frac{3}{\phi^2}$$

$$\text{or, } \pi = \frac{8}{3}\tau\frac{1}{\phi - 1/3} - \frac{3}{\phi^2}$$

$$\therefore \left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\tau$$

This equation is known as the **van der Waals reduced equation of state**. The variables π, ϕ, and τ are known as the reduced pressure, reduced volume and reduced temperature, respectively. They are collectively termed as the reduced variables. The important thing about the above equation is that it does not contain any constants that are peculiar to the individual gas.
∴ It should be capable of describing all gases.
The loss of generality that appeared with the van der Waals equation, compared with the ideal gas equation, is regained. Thus, in terms of the reduced variables, there exists a universally valid approximation to the equation of state for all substances. This statement is known as the **law of corresponding states**.
∴ Two gases at the same reduced temperature and under the same reduced pressure are in corresponding states.
By the law of corresponding states, they should both occupy the same reduced volume. For example, argon at 302 K and under 16 atm pressure, and ethane at 381 K and under 18 atm are in corresponding states, since each has $\tau = 2$ and $\pi = 1/3$.

Liquids: Surface tension

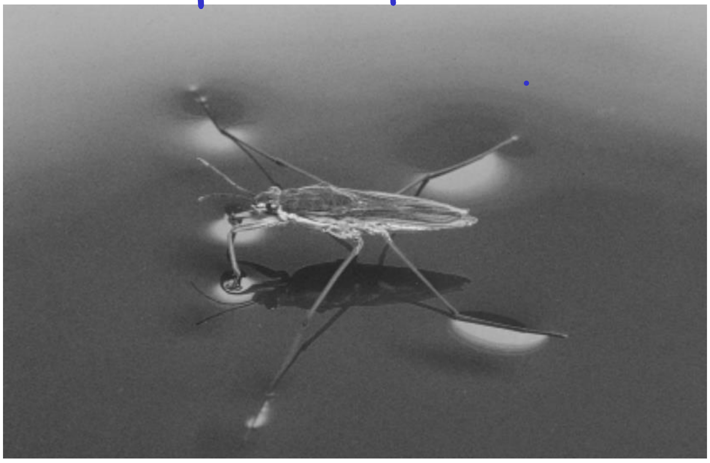
liquids are denser than gases ... typically liquids are ~10^3 times denser

For example, density of $O_2(g)$ at room temp .... 1.4×10^{-3} g/cm^3

density of $O_2(l)$ at room temp ..... 1.1 g/cm^3

Higher density ≡ higher possibility of intermolecular interactions.

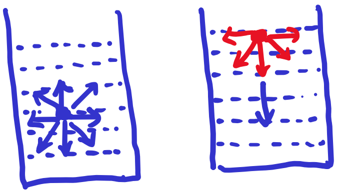
Surface tension (ST) is the tendency of liquid surfaces to shrink into the min. surface area possible.



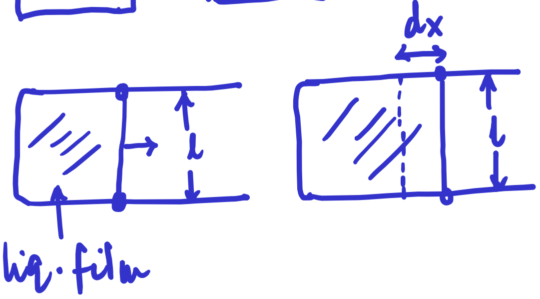
ST is the phenomenon that occurs when the surface of a liq. is in contact with another phase.

The surface of the liquid behaves like an elastic sheet.

* a liquid molecule in the interior of the liquid does not feel any net force of attraction



* a liquid molecule at the surface of the liquid faces a net downward force of attraction.



to increase the area of the film by dA, a proportionate amount of work must be done.

Increase in free energy of the film, γdA, γ is the free energy per unit area.

free energy increase implies that the motion of the wire is opposed by a force f.

If the wire moves a distance dx, the work done is fdx.

$\therefore fdx = \gamma dA$

the film has two sides

If l is the length of the movable wire, increase in area $= \boxed{2}(ldx)$

$\therefore\ f\,dx = \gamma\, 2l\, dx \Rightarrow f = (\underbrace{2l}_{l \text{ on each side}})\gamma$

$\therefore\ \gamma = \frac{f}{2l} \rightarrow$ force acting per unit length of the wire in contact with the film is the surface tension (ST)

$\therefore$ ST acts as a force that opposes the increase in the area of the liq.

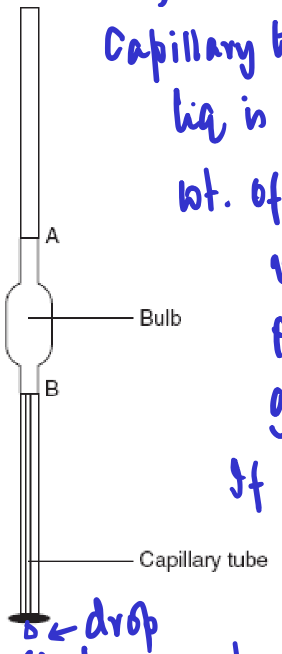
units of ST : N/m ≡ J/m^2

dynes/cm ≡ ergs/cm^2

ST → force per unit length
ST → energy per unit area

$\therefore$ Surface tension of a liq. is defined as the tangential force that acts along the surface of the liq. at right angles to a line of unit length on the surface.

Measurement of surface tension: drop weight method (drop counting method) : stalagmometry



Stalagmometer

Capillary tube ensures a streamline flow.

liq. is allowed to flow through a capillary tube.

wt. of the liq. drop, $w = v\rho g$

v = vol. of the liq. drop

ρ = density of the liq.

g = acceleration due to gravity

If r is the radius of the drop, and if

γ = surface tension acting on the drop

$\therefore$ force on the drop due to surface tension $= 2\pi r\gamma$, $2\pi r$ = circumference of the drop

Say a total of V vol. of the liq. is allowed to flow

$V = nv$, n = total no. of drops falling

$v = V/n$

$\therefore\ 2\pi r\gamma = v\rho g$ or, $2\pi r\gamma = \frac{V\rho g}{n}$

Say, we have two liquids — A, B

ρ_A, ρ_B : densities of A and B

γ_A, γ_B : surface tension of A and B

} A and B are allowed to flow in equal volumes V through the same stalagmometer

n_A, n_B : no. of drops that make up vol. V for A and B

$$\therefore \quad 2\pi r \gamma_A = \frac{V\rho_A g}{n_A} \quad \text{and} \quad 2\pi r \gamma_B = \frac{V\rho_B g}{n_B}$$

$$\text{or,} \quad \frac{\gamma_A}{\gamma_B} = \frac{\rho_A}{\rho_B} \cdot \frac{n_B}{n_A}$$

(Relative surface tension)

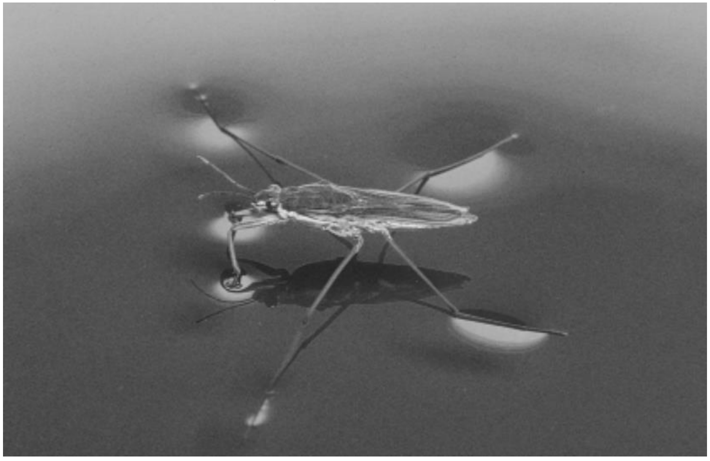
unknown liq. X

reference liq. H_2O }

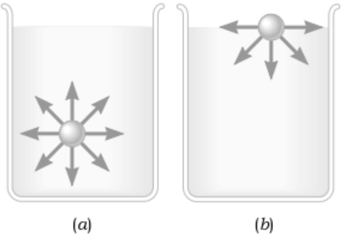
$$\boxed{\frac{\gamma_X}{\gamma_{H_2O}} = \frac{\rho_X}{\rho_{H_2O}} \cdot \frac{n_{H_2O}}{n_X}}$$

Surface Energy and Surface Tension

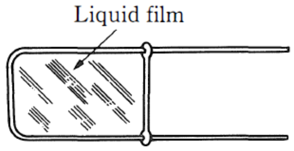
In the fall a fisherman's boat is often surrounded by fallen leaves that are lying on the water. The boat floats, because it is partially immersed in the water and the resulting buoyant force balances its weight. The leaves, however, float for a different reason. They are not immersed in the water, so the weight of a leaf is not balanced by a buoyant force. Instead, the force balancing a leaf's weight arises because of the surface tension of the water. Surface tension is a property that allows the surface of a liquid to behave somewhat as a trampoline does. When a person stands on a trampoline, the trampoline stretches downward a bit and, in so doing, exerts an upward elastic force on the person. This upward force balances the person's weight. The surface of the water behaves in a similar way. In the figure below, for instance, you can see the indentations in the water surface made by the feet of an insect known as a water strider, because it can stride or walk on the surface just as a person can walk on a trampoline.

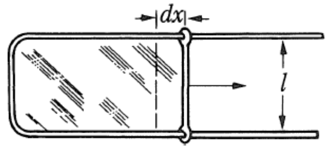


The molecular basis for surface tension can be understood by considering the attractive forces that molecules in a liquid exert on one another.



Part (a) shows a molecule within the bulk liquid, so that it is surrounded on all sides by other molecules. The surrounding molecules attract the central molecule equally in all directions, leading to a zero net force. In contrast, part (b) shows a molecule in the surface. Since there are no molecules of the liquid above the surface, this molecule experiences a net attractive force pointing toward the liquid interior. This net attractive force causes the liquid surface to contract toward the interior until repulsive collisional forces from the other molecules halt the contraction at the point when the surface area is a minimum. If the liquid is not acted upon by external forces, a liquid sample forms a sphere, which has the minimum surface area for a given volume. Nearly spherical drops of water are a familiar sight, for example, when the external forces are negligible. The energy of a surface molecule is therefore higher than that of a molecule in the interior of the solid and energy must be expended to move a molecule from the interior to the surface of a solid. This is also true of liquids. Suppose that a film of liquid is stretched on a wire frame having a movable member.





To increase the area of the film by dA, a proportionate amount of work must be done. The Gibbs energy of the film increases by γdA, where γ is the surface Gibbs energy per unit area. The Gibbs energy increase implies that the motion of the wire is opposed by a force f. If the wire moves a distance dx, the work expended is fdx. These two energy increments are equal, so that

$$fdx = \gamma dA$$

If l is the length of the movable member, the increase in area is $2(ldx)$. The factor 2 appears because the film has two sides. Thus,

$$fdx = \gamma(2l)dx$$

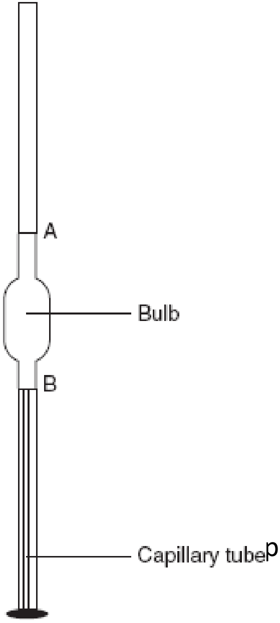
so that,

$$f = 2l\gamma.$$

The length of the film in contact with the wire is l on each side, or a total length is $2l$. The force acting per unit length of the wire in contact with the film is the surface tension of the liquid, $f/2l = \gamma$. The surface tension acts as a force that opposes the increase in area of the liquid. The SI unit for surface tension is the $\mathrm{N \cdot m^{-1}}$, which is numerically equal to the rate of increase of the surface Gibbs energy with area, in $\mathrm{J \cdot m^{-2}}$. The magnitude of the surface tension of common liquids is of the order of tens of $\mathrm{mN \cdot m^{-1}}$. Hence, **the surface tension of a liquid is defined as the tangential force, in dynes, that acts along the surface of the liquid at right angles to a line of 1 cm length on the surface.**

Measurement of Surface Tension

The surface tension of a pure liquid/solution can be measured either by using the drop-weight or the capillary rise method. Here we implement the drop-weight (equivalent to the drop-counting) method to determine the surface tension of the supplied solution or liquid. The principle of the drop-weight method is based on the fact that when a liquid is allowed to flow through a capillary tube (thus ensuring almost streamline flow) and fall in drops from its end, the drop first remains sticking at the end of the capillary tube, but it falls down when its weight becomes just equal to the force of surface tension, acting on it.



The weight w of a drop of liquid of density ρ and volume v is given by

$$w = v\rho g.$$

If the radius of the drop be r, and if γ be the surface tension acting on it, then the force due to surface tension is $2\pi r\gamma$, where $2\pi r$ is the circumference of the liquid drop. If there are n drops in a finite volume V, then the volume of a single drop, $v = V/n$. Therefore, under the condition of equilibrium

$$2\pi r\gamma = \frac{V\rho g}{n}$$

If two different liquids of densities ρ_A and ρ_B and surface tensions γ_A and γ_B are allowed to flow in equal volumes V through the same stalagmometer, and if n_A and n_B be the number of drops that make up for the volume V, then we must have

$$2\pi r\gamma_A = \frac{V\rho_A g}{n_A} \quad \text{and} \quad 2\pi r\gamma_B = \frac{V\rho_B g}{n_B},$$

so that

$$\frac{\gamma_A}{\gamma_B} = \frac{\rho_A}{\rho_B}\cdot\frac{n_B}{n_A}$$

Thus, if the surface tension and the density of one of the liquids be known, n_A and n_B can be experimentally found out, the density be determined and the unknown surface tension can be evaluated. Generally, water is used as the reference liquid and the last equation modifies to

$$\frac{\gamma_X}{\gamma_{H_2O}} = \frac{\rho_X}{\rho_{H_2O}}\cdot\frac{n_{H_2O}}{n_X},$$

where X stands for the unknown liquid. The surface tension obtained in accordance of the aforesaid method is the *relative* surface tension, and not the absolute surface tension, since it is determined relative to the surface tension of the reference liquid.

Variation of surface tension with temperature

Observation: surface tension decreases as T increases.

R. von Eötvös: 1886: relationship between molar surface energy and T.

Say, v = specific vol. of a liquid (vol. per unit mass; reciprocal of density)

M = mol. wt. of the liq. (say, 18 for H_2O; 60 for CH_3COOH, etc.)

$\therefore Mv$ = vol. of one mole of the liq. ≡ molar vol. of the liq.

This vol. of the liq. will try to assume a spherical shape.
(for a given vol. a sphere has the minimum surface area)

$\therefore Mv = \frac{4}{3}\pi r^3$ or, $r = \frac{3}{4\pi}(Mv)^{1/3} \Rightarrow r \propto (Mv)^{1/3}$

molar surface area: surface area of molar vol. amount of liq.

$\therefore$ molar surface area $\propto (Mv)^{2/3}$

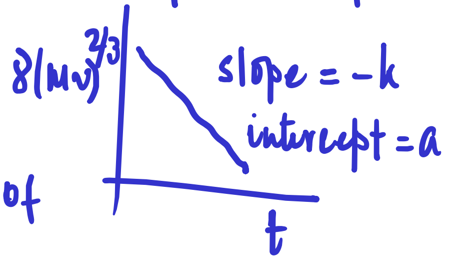
molar surface energy = (molar surface area) × (surface tension)

a force per unit length
or
energy per unit area

$= \gamma (Mv)^{2/3}$

Eötvös: molar surface energy is a linear function of T

$$\gamma (Mv)^{2/3} = a - kt$$



t = temp. in °C

When $t = t_c$, the surface tension of the liquid vanishes, $\gamma = 0$

$0 = a - kt_c$ or, $a = kt_c$

Eötvös equation

$\therefore \gamma(Mv)^{2/3} = kt_c - kt$ or, $\boxed{\gamma(Mv)^{2/3} = k(t_c - t)}$

Ramsay and Shields: surface tension vanishes at a temp. that is 6° below t_c.

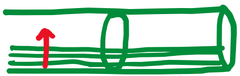
$$\boxed{\gamma(Mv)^{2/3} = k(t_c - 6 - t)}$$

Viscosity of fluids (gases and liquids)

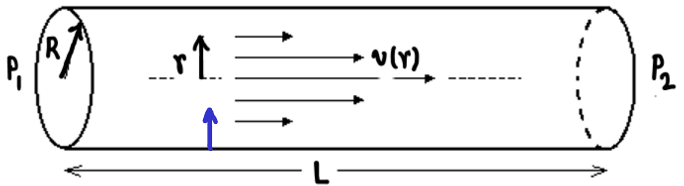
viscosity is a transport property
related to flow

measurement of viscosity of fluids

laminar/streamline flow



laminar/streamline flow ⇒ fluid flows in "layers", such that each layer moves at a velocity infinitesimally different than the layers adjacent to it.



as the radial distance from the centre of the tube changes, the velocities of the corresponding layers change.

for a change dr in the radial distance, there is a change dv in velocity.

$\frac{dv}{dr}$ = rate of change of velocity with the radial distance
= velocity gradient.

if dr is +ve, dv is -ve

viscosity is the frictional resistance to fluid flow

Newton's law of viscous force;
frictional force is proportional to ↗ area of contact, S
↘ velocity gradient, dv/dr

magnitude of the frictional force, $F \propto S \frac{dv}{dr}$

or, $F = \eta S \frac{dv}{dr}$ (η : eta) $\qquad \eta = \frac{F}{S} \cdot \frac{dr}{dv}$

η = coefficient of viscosity

η is defined as the force per unit area required to move a layer of fluid with a velocity difference of 1 cm s^{-1} past another parallel layer 1 cm away.

$$\eta = F S^{-1} \frac{dr}{dv} = \left(\frac{g\ cm}{s^2}\right)(cm^{-2}) \frac{cm}{cm\ s^{-1}} = \boxed{g\ cm^{-1}\ s^{-1} = poise}$$

$$\boxed{kg\ m^{-1}\ s^{-1}}$$

Temperature Dependence of Surface Tension

The surface tension of a pure liquid/solution almost invariably decreases with an increase in the temperature. R. von Eötvös (1886) proposed a relationship between molar surface energy and T. Say, v be the specific volume (volume per unit mass, that is, the reciprocal of density), of a liquid and M be its molecular weight. $\therefore Mv =$ the molar volume of the liquid. If this (molar) volume is assumed to be spherical, which is the stable form (since for a given volume of a liquid, a sphere has the least surface area, and hence the lowest value if surface energy/surface tension), then,

$$Mv = \frac{4}{3}\pi r^3$$

where, r is the radius of the corresponding sphere.

$$\therefore r \propto (Mv)^{1/3}$$

The surface area of this sphere (which will be the molar surface area) will be proportional to $(Mv)^{2/3}$.

A product of the molar surface area, $(Mv)^{2/3}$, and the surface tension, γ, will be the molar surface energy, since γ can also be expressed as energy per unit area.

$\therefore$ The molar surface energy $= \gamma(Mv)^{2/3}$.

Eötvös proposed that the molar surface energy varies as a linear function of temperature in the Celsius scale (t),

$$\gamma(Mv)^{2/3} = a - kt$$

In the equation,

$$\gamma(Mv)^{2/3} = a - kt$$

a and k are constants. Note that, at the critical temperature, t_c, the surface of a liquid vanishes $(\gamma = 0)$, and the law of corresponding states holds true.

$\therefore$ At $t = t_c$, $\gamma = 0$, so that, $0 = a - kt_c$, or, $a = kt_c$.

Hence, Eötvös equation takes the form,

$$\gamma(Mv)^{2/3} = kt_c - kt = k(t_c - t)$$

Ramsay and Shields studied Eötvös equation further and showed that the surface of a liquid vanishes about 6°C ahead of the critical temperature, and based on this fact, corrected the Eötvös equation to write,

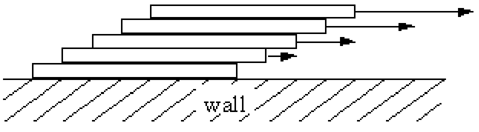
$$\gamma(Mv)^{2/3} = k(t_c - 6 - t)$$

The above equation (often called the Eötvös-Ramsay-Shields equation) depicts the variation of γ with temperature. The constant k may be determined from the slope of $\gamma(Mv)^{2/3}$ versus t plot, and k is called the temperature coefficient of the molar surface energy.

VISCOSITY OF FLUIDS (GASES AND FLUIDS)

Fluid flow through pipes is of immense importance to chemical engineers, who must design appropriate methods for transporting chemicals to and from reaction vessels. Viscosity is a transport property. Transport properties are molecular properties of a substance that indicate the rate at which specific (per unit volume) momentum, heat, or mass are transferred. Science of the study of these processes is called transport phenomenon. Viscosity of fluids is the key physical property that dictates the design of pipelines to transport material. Thus, an understanding of fluid and gas viscosity is essential for engineering a chemical process. Gas viscosity experiments validate the kinetic theory of gases and provide access to microscopic information from macroscopic measurements. The viscosity of a gas provides a means for determining molecular diameters, as viscosity arises from collisions among molecules.

In order to measure fluid viscosities, **laminar/streamline** flow is assumed in the capillary. Laminar flow implies that the fluid flows in "layers" such that each layer moves at a velocity infinitesimally different than the layers adjacent to it.



Since the wall is stationary, the layer along the wall has a velocity of zero. The fluid flows more quickly the further away it is from the stationary wall. Laminar flow is commonly experienced in smooth streams and rivers, where water flows slowly along the banks and rapidly in the centre.

The concept of viscosity is usually met in problems of fluid flow, treated by hydrodynamics, as a measure of the fractional resistance that a fluid in motion offers to an applied shearing force. If a fluid is flowing past a stationary plane surface, the layer of fluid adjacent to the plane boundary is stagnant; successive layers have increasingly higher velocities. The frictional force, F, resisting the relative motion of any two adjacent layers, is proportional to the area of interface, S between them and to the velocity gradient, dv/dr between them. This is known as the **Newton's law of viscous flow**. Thus,

$$F \propto S\frac{dv}{dr} \Rightarrow F = \eta S\frac{dv}{dr} \tag{1}$$

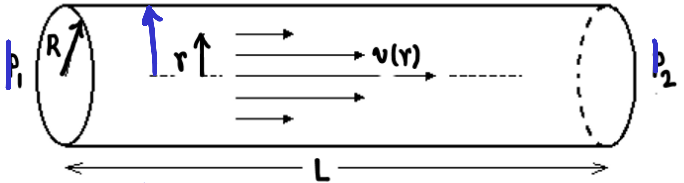
The proportionality constant η is known as the **coefficient of viscosity**, and is the quantity of interest. Thus η may be defined as the force per unit area required to move a layer of fluid with a velocity difference of 1 cm per second past another parallel layer 1 cm away. It is evident that the dimensions of η is $\mathrm{mass} \times \mathrm{length}^{-1} \times \mathrm{time}^{-1}$. The SI unit of η is $\mathrm{kg} \cdot \mathrm{m}^{-1} \cdot \mathrm{sec}^{-1}$, and the CGS unit is $\mathrm{gm} \cdot \mathrm{cm}^{-1} \cdot \mathrm{sec}^{-1}$ or poise (denoted by P), and is equal to one-tenth the SI unit.

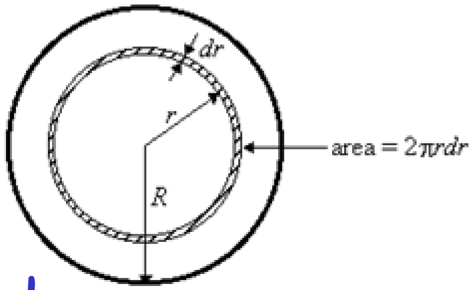
Newton's law of viscous flow, $F = \eta S \frac{dv}{dr}$

η = coefficient of viscosity

Laminar/Streamline flow

$v_1 < v_2 < v_3 < v_4$





viscous drag

Magnitude of the resistive force, $F_r = -\eta \frac{dv}{dr}(2\pi r L)$

(when dr is +ve, dv is -ve)

$2\pi r L = S$ = area of contact along which the force of resistance acts.

Magnitude of the driving force, $F_d = \pi r^2(p_1 - p_2)$

$\therefore$ to maintain a steady flow, $F_r = F_d$

$$\therefore -\eta \frac{dv}{dr}(2\pi r L) = \pi r^2(p_1 - p_2) \quad \text{or, } dv = -\frac{r}{2\eta L}(p_1 - p_2)dr$$

On integration, $v = -\frac{(p_1 - p_2)r^2}{4\eta L} + \text{constant}$

According to our hypothesis, when $r = R$, $v = 0$

$$0 = -\frac{(p_1-p_2)R^2}{4\eta L} + \text{constant} \qquad \therefore \text{constant} = \frac{(p_1-p_2)R^2}{4\eta L}$$

$$\therefore v = \frac{(p_1-p_2)}{4\eta L}(R^2 - r^2)$$

→ velocity of a layer of fluid at a radial distance of r from the axis of the tube.

total vol. of fluid flowing through the tube per second = dV/dt

$$\frac{dV}{dt} = \int_0^R (2\pi r dr)v = \int_0^R 2\pi r v dr = \int_0^R 2\pi r \frac{(p_1-p_2)}{4\eta L}(R^2 - r^2)dr$$

$$= \frac{2\pi(p_1-p_2)}{4\eta L}\int_0^R (R^2 - r^2) r dr = \frac{2\pi(p_1-p_2)}{4\eta L}\left[\int_0^R R^2 r dr - \int_0^R r^3 dr\right]$$

$$= \frac{2\pi(p_1-p_2)}{4\eta L}\left[R^2\int_0^R r dr - \int_0^R r^3 dr\right] = \frac{2\pi(p_1-p_2)}{4\eta L}\left[R^2 \cdot \frac{R^2}{2} - \frac{R^4}{4}\right]$$

$$= \frac{\cancel{2}\pi(p_1-p_2)}{4\eta L}\frac{R^4}{\cancel{4}2} \qquad \therefore \frac{dV}{dt} = \frac{\pi(p_1-p_2)R^4}{8\eta L}$$

∴ the vol. of fluid flowing through the tube per second

$$\frac{dV}{dt} = \frac{\pi (p_1 - p_2) R^4}{8 \eta L}$$: Poisellille's equation

valid for both liquids and gases.

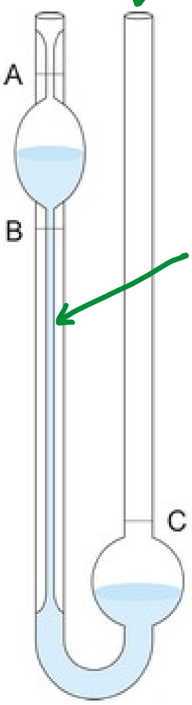
Origin of viscosity in liquids is different from the origin of viscosity in gases.

(a) for liquids

under a constant pressure difference, $p_1 - p_2 = p$ (pressure head)

say V vol. of a liq. is allowed to flow through a fine capillary tube of known radius R; the length of the capillary is L and the liq. is allowed to flow for a time t

$$V = \frac{\pi p R^4 t}{8 \eta L} \Rightarrow \boxed{\eta = \frac{\pi p R^4 t}{8 L V}}$$



Capillary tube

Ostwald viscometer

Say, we have two liquids — H_2O, x

$$\eta_{H_2O} = \frac{\pi p_{H_2O} R^4 t_{H_2O}}{8 L V}$$

$$\frac{\eta_x}{\eta_{H_2O}} = \frac{\pi p_x R^4 t_x / 8LV}{\pi p_{H_2O} R^4 t_{H_2O} / 8LV}$$

$$\eta_x = \frac{\pi p_x R^4 t_x}{8 L V}$$

$$\therefore \frac{\eta_x}{\eta_{H_2O}} = \frac{p_x t_x}{p_{H_2O} t_{H_2O}}$$

$p = h\rho g$

g = acceleration due to gravity

ρ = density

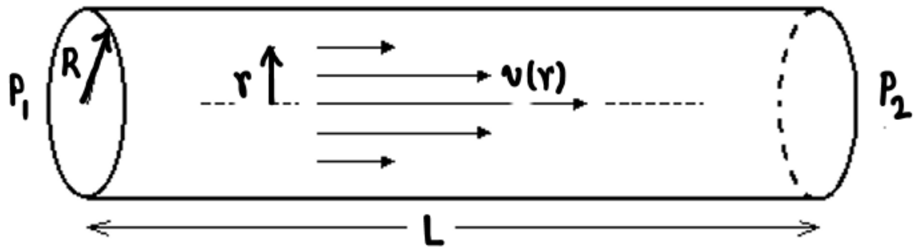
h = height

$$\frac{\eta_x}{\eta_{H_2O}} = \frac{h \rho_x g t_x}{h \rho_{H_2O} g t_{H_2O}}$$

$$\boxed{\frac{\eta_x}{\eta_{H_2O}} = \frac{\rho_x t_x}{\rho_{H_2O} t_{H_2O}}}$$

H_2O : reference liq.

VISCOSITY OF FLUIDS (GASES AND FLUIDS) [Continued from the previous class]



The theory of the process was first worked out by J. L. Poiseuille in 1844. Consider a fluid flowing through a tube of circular cross-section with radius R and length L. The fluid layer in the closest proximity of the walls is assumed to be stagnant, and the rate of flow increases to a maximum at the centre of the tube. Let v be the linear velocity at any distance r from the axis of the tube. A cylinder of fluid of radius r experiences a viscous drag given by Eq.(1) as

$$F_r = -\eta \frac{dv}{dr} \cdot 2\pi r L \tag{2}$$

For a steady flow, this force must be exactly balanced by the force driving the fluid in this cylinder through the tube. Since the pressure is the force per unit area, the driving force is

$$F_d = \pi r^2 (P_1 - P_2) \tag{3}$$

where P_1 and P_2 are fore and back pressures, respectively. Therefore, for steady flow, $F_r = F_d$, that is

$$-\eta \frac{dv}{dr} \cdot 2\pi r L = \pi r^2 (P_1 - P_2)$$

so that,

$$dv = -\frac{r}{2\eta L}(P_1 - P_2)dr \tag{4}$$

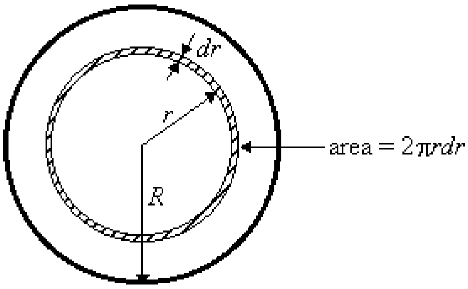
On integration of Eq.(4) we get

$$v = -\frac{(P_1 - P_2)r^2}{4\eta L} + \text{constant of integration} \tag{5}$$

According our hypothesis, $v = 0$, when $r = R$; this boundary condition determines the integration constant, so that

$$v = \frac{(P_1 - P_2)}{4\eta L}(R^2 - r^2) \tag{6}$$

The total volume of fluid flowing through the tube per second dV/dt is calculated by integrating the fluid velocity v over each element of cross-sectional area $2\pi r dr$.



Thus,

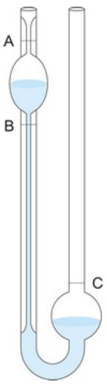
$$\frac{dV}{dt} = \int_0^R 2\pi r v dr = \frac{\pi (P_1 - P_2) R^4}{8\eta L} \tag{7}$$

This is Poiseuille's equation which applies to incompressible fluids undergoing laminar flow. Poiseuille's equation may be satisfactorily applied to liquids but not to gases, as volume is a strong function of pressure for gases.

(a) For Liquids

Under a constant pressure head $P = P_1 - P_2$, V volume of a liquid is allowed to flow through a fine capillary tube of known radius R. The length L and the time t for the flow are noted. The equation would thus be

$$\eta = \frac{\pi P R^4 t}{8LV} \tag{8}$$



Using the Ostwald viscometer one can measure the relative viscosity of a liquid, relative to the viscosity (known) of another liquid, referred to as the reference liquid. Therefore,

$$\frac{\eta_X}{\eta_{\mathrm{H_2O}}} = \frac{\pi P_X R^4 t_X / 8LV}{\pi P_{\mathrm{H_2O}} R^4 t_{\mathrm{H_2O}} / 8LV} = \frac{P_X t_X}{P_{\mathrm{H_2O}} t_{\mathrm{H_2O}}} = \frac{hg\rho_X t_x}{hg\rho_{\mathrm{H_2O}} t_{\mathrm{H_2O}}}$$

Upon cancellation, we have

$$\frac{\eta_X}{\eta_{\mathrm{H_2O}}} = \frac{\rho_X t_x}{\rho_{\mathrm{H_2O}} t_{\mathrm{H_2O}}} \tag{9}$$

If $\eta_{\mathrm{H_2O}}$ is known, a measurement of the densities and times of flow of the two would yield η_X, the coefficient viscosity of the unknown liquid.

MI-1T

Practice Questions on Real Gases (Set-1)

1. What will be the real gas equation if the pressure is extremely high?
2. Comment on the statement: “Higher the critical temperature of a gas easier is to liquefy it.”
3. What is meant by the term “excluded volume”? Explain its significance.
4. The highest allowed pressure of a 20-litre flask containing 1.6 kg of oxygen is 150 atm. To what temperature can it be heated? Assume that oxygen obeys van der Waals equation with a and b values 1.36 $\mathrm{litre}^2 \cdot \mathrm{atm} \cdot \mathrm{mol}^{-2}$ and 31.83 $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, respectively.
5. Draw the Andrews’ curves for a real gas depicting the point of critical temperature T_c. Discuss the principle of continuity of states from the plots. How is the nature of PV isotherm for van der Waals gas? Does it show any region which can never be experienced experimentally?
6. The compressibility factor of a real gas obeys the equation $Z = a_1 + a_2P + a_3P^2$. The Z versus P plot shows a minimum at some pressure P_0 and temperature T_1. Find the value of a_1, the signs of a_2 and a_3, and an expression for P_0 in terms of a_1, a_2 and a_3. If the temperature variation of a_2 is given by $a_2 = C_1 + (C_2/T)$, and the Boyle temperature T_B obeys $T_B > T_1$, remark on the signs of C_1 and C_2 and express T_B in terms of C_1 and C_2.
7. What is meant by compressibility factor? State, without derivation, its value for a van der Waals gas at its critical point.
8. Derive the reduced equation of state for a van der Waals gas assuming the expressions for the critical constants.
9. What is Maxwell’s equal area construction? Why is it necessary?
10. A gas obeys the equation $P(V - b) = RT$. Calculate the compressibility factor and (dZ/dP) at constant T of the gas at 300 K and 10 atm pressure. Given, $b = 0.0266\ \mathrm{lit} \cdot \mathrm{mol}^{-1}$.
11. Explain the physical significance of van der Waals constant a and b. What are SI the units and dimensions of van der Waals constants a and b?
12. If the compressibility factor, Z of a gas is expressed as, $Z = \alpha_0 + \alpha_1 P$, what can you predict about the magnitude of α_0, and the signs of α_1 for different values of P?
13. Will the pressure of a gas on the walls be greater or less than the ideal pressure if we take into account only the finite dimension of the molecules?
14. Comment on the statement: Higher the critical temperature of a gas easier is to liquefy it.
15. Comment on the statement: Rise in compressibility factor with increasing pressure for a van der Waals gas is due to a or b.
16. Draw a set of $P - V$ isotherms below the critical temperature obtained experimentally and for a van der Waals gas. Explain the curves.
17. For a given number of moles of gas, show that the van der Waals equation predicts greater deviation from ideal behaviour (a) at high pressure rather than low pressure at a given temperature, and (b) at low temperature rather than high temperature at a given pressure.
18. Justify or criticize the statement: A gas can be liquefied at $T = T_C$ and $P < P_C$.
19. Express the constants a and b in terms of critical constants P_C, V_C and T_C of a van der Waals gas.
20. Find out the critical constants in terms of α and β and the critical compressibility factor of a gas that obeys the equation of state
$$P = \frac{RT}{V} - \frac{\alpha}{\overline{V}^2} + \frac{\beta}{\overline{V}^3}$$
21. Calculate critical compressibility factor (Z_C) for van der Waals gas. From the value of Z_C, how can you predict which gas behaves more like a van der Waals gas?
22. Write down the major limitations of van der Waals equation of state?
23. What is meant by reduced equation of state? Deduce the reduced equation of state for a van der Waals gas. In the reduced equation of state, are the parameters characteristic of the gas completely removed or just hidden? Explain whether such an equation is possible for an ideal gas.
24. Show that the excluded volume b is approximately four times the actual volume occupied by the molecules in one mole of a van der Waals gas.
25. What is Boyle temperature? A gas obeys the equation of state, $P(V - nb) = RT$. Is it possible to liquefy the gas? Justify your answer. Show that the gas does not have the Boyle temperature.
26. Do you think that the van der Waals constant b depends on temperature? Explain.
27. “The critical temperature must always be less than the Boyle temperature”. Comment on the statement.
28. Two separate bulbs are filled with an ideal gas A and a non-ideal gas B respectively in such a way that PV remains same. B is below its Boyle temperature. Which gas has greater temperature? Give reasons.
29. What do you mean by internal pressure? Assuming a fluid obeying van der Waals equation of state derive the expression for internal pressure.
30. Show that at the corresponding states two van der Waals gases must have the same compressibility factors.