

Equation of State.

Using the potential energy of separation between molecules in a gas, it can be shown that the states of real gases can be modelled by the equation:

$$\frac{PV}{nRT} - 1 \propto \left(\frac{nRT}{PV}\right)^2 \left[\left(\frac{nRT}{PV}\right)^2 - 1\right]$$

With critical temperature:

$$T_c = \frac{\varepsilon}{k \ln 2}$$

And Boyle temperature:

$$T_B = \frac{\varepsilon}{k \ln \frac{4}{3}}$$

Where ε is the potential energy of separation well depth.

All real gases can be described exactly by the equation of state:

$$PV_m = RTZ$$

Where Z is the compression factor, a measure of departure from ideal behaviour.

$$Z = \frac{PV_m}{RT}$$

The behaviour of Z can be explained by the potential energy of separation between the molecules of the gas, $U(r)$.

1. When $U(r) > 0$, repulsive forces between the molecules dominate. V_m and hence Z is greater than the ideal value as a result, i.e. $Z > 1$.
2. When $U(r) = 0$, there are no forces acting between the molecules thus V_m is the same as the ideal value and $Z = 1$.
3. When $U(r) < 0$, attractive forces dominate which make V_m smaller than the ideal value. $Z < 1$.

From these explanations it can be said that:

$$Z - 1 \propto U(r)$$

$U(r)$ is modelled by the Lennard-Jones potential,

$$U(r) \propto \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6$$

Therefore;

$$Z - 1 \propto \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6$$

r is the average separation between gas molecules equal to;

$$\left(\frac{V}{N}\right)^{\frac{1}{3}}$$

σ is the average separation between the gas molecules when $U(r)=0$. At $U(r)=0$ the gas is behaving ideally meaning that the relation $PV=NkT$ becomes valid. Therefore;

$$\left(\frac{V}{N}\right)^{\frac{1}{3}} = \left(\frac{kT}{P}\right)^{\frac{1}{3}}$$

At $r = \sigma$. The expression can now be written purely in terms of state functions of the gas.

$$\frac{PV}{NkT} - 1 \propto \left[\frac{\left(\frac{kT}{P}\right)^{\frac{1}{3}}}{\left(\frac{V}{N}\right)^{\frac{1}{3}}} \right]^{12} - \left[\frac{\left(\frac{kT}{P}\right)^{\frac{1}{3}}}{\left(\frac{V}{N}\right)^{\frac{1}{3}}} \right]^6$$

$$\frac{PV}{NkT} - 1 \propto \left[\left(\frac{NkT}{PV}\right)^{\frac{1}{3}} \right]^{12} - \left[\left(\frac{NkT}{PV}\right)^{\frac{1}{3}} \right]^6$$

$$\frac{PV}{NkT} - 1 \propto \left(\frac{NkT}{PV}\right)^4 - \left(\frac{NkT}{PV}\right)^2$$

$$\frac{PV}{NkT} - 1 \propto \left(\frac{NkT}{PV}\right)^2 \left[\left(\frac{NkT}{PV}\right)^2 - 1 \right]$$

$$\frac{PV}{NkT} - 1 \propto \left(\frac{NkT}{PV}\right)^2 \left[\left(\frac{NkT}{PV}\right)^2 - 1 \right]$$

Or,

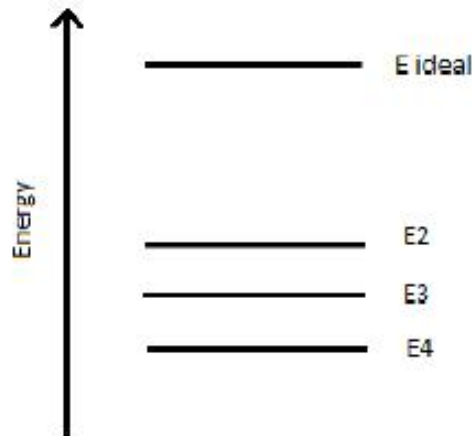
$$\frac{PV}{nRT} - 1 \propto \left(\frac{nRT}{PV}\right)^2 \left[\left(\frac{nRT}{PV}\right)^2 - 1 \right]$$

Solving the above equation for V gives 4 solutions (3 real + 2 complex);

$$V = V_i \quad i = 1,2,3 \text{ or } 4$$

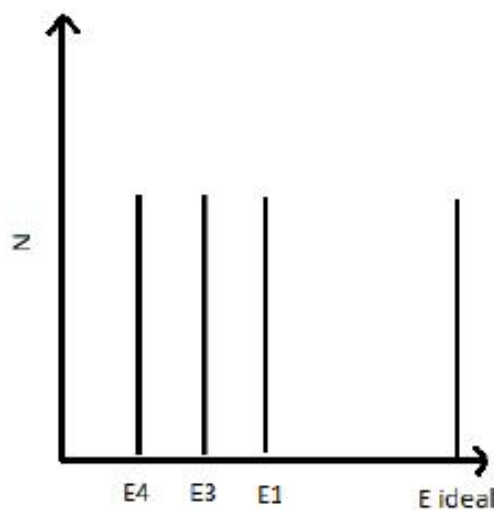
Each volume corresponds to an intermolecular separation which in turn corresponds to a potential energy level. In this case there are 4 potential energy levels that the

intermolecular separations between the molecules are allowed to occupy. The physical interpretation of this is that rather than there being just one distance between all molecules, or even a continuous range of distances, the nature of the equation constrains the allowed distance between any two molecules to just 4 allowed values at each pressure and temperature. The ideal volume, P/nRT is always a solution of the equation and is always the solution that corresponds to the highest energy level in the gas phase. This is because completely ignoring the intermolecular forces puts the potential energy at a very high level.

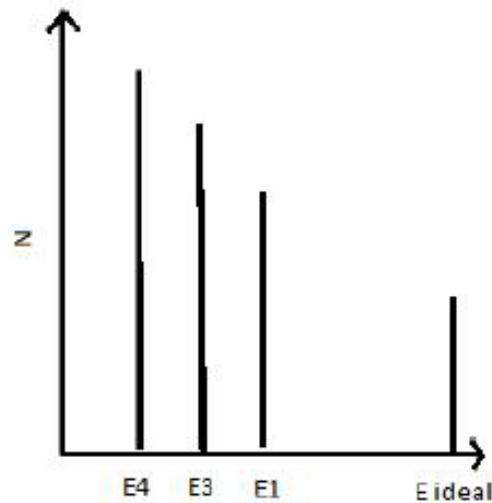


Gas phase potential energy levels

These energy levels start out all filled equally. Because E_{ideal} is at a much higher energy than all other levels, if the levels are filled equally the E_{ideal} energy level will dominate thus giving the gas overall ideal character. It is important to note that as a result of the lower energy levels still being full, although a gas can start to behave *mostly* ideally in the limit of $P \rightarrow 0$ it will never behave *completely* ideally.



As the gas is compressed, the highest energy levels gradually depopulate and the lowest levels populate by an equivalent amount. This causes the gas to lose ideal behaviour and gain real behaviour; real behaviour can either mean $V > V_{ideal}$ or $V < V_{ideal}$ depending on whether the values of V on the energy levels below V_{ideal} are larger or smaller than V_{ideal} .



This continues until only 2 energy levels are filled. At this point the gas is now also allowed to satisfy another relation;

$$U(r) = constant$$

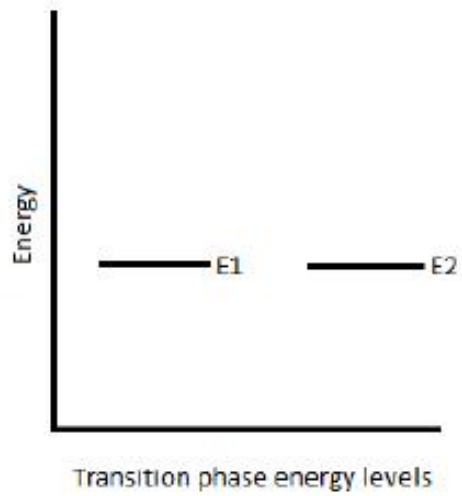
Or,

$$\left(\frac{nRT}{PV}\right)^2 \left[\left(\frac{nRT}{PV}\right)^2 - 1 \right] \propto constant$$

The gas is now allowed to satisfy this equation in addition to the other because this equation is a quadratic. Therefore it only allows for a maximum of 2 degenerate energy levels, which is what the gas can now have. If the gas *does* start obeying the new relation, since;

$$F = -\frac{dU(r)}{dr}$$

If $U(r) = constant$, $F = 0$. When this occurs there is no force acting between the molecules; the volume of the gas decreases without any increase in pressure. Therefore it follows that when all energy levels except the last 2 are depopulated the gas has the option to condense to a liquid.



At any given temperature a proportion p_i of volumes V_i occupy each of the 4 energy levels within the gas.

This gives an average volume, V of;

$$V = \sum_i^4 p_i V_i$$

p_i is given by the Boltzmann Distribution;

$$p_i = \frac{e^{\frac{-E_i}{kT}}}{q}$$

E_i is given by the Lennard-Jones Potential;

$$E_i = 4\varepsilon \left[\sigma^{12} \left(\frac{N}{V_i} \right)^4 - \sigma^6 \left(\frac{N}{V_i} \right)^2 \right]$$

Putting all three equations together gives;

$$V = \sum_i \frac{V_i}{q} e^{\frac{-4\varepsilon}{kT} \left[\sigma^{12} \left(\frac{N}{V_i} \right)^4 - \sigma^6 \left(\frac{N}{V_i} \right)^2 \right]}$$

This is the overall macroscopic (average) volume of the gas.

According to this equation, when $T \rightarrow 0$ the exponential function goes to 0 and $V \rightarrow 0$. This is verified by Charles' Law which states that the volume of a gas goes to zero as its temperature goes to zero. When $T \rightarrow \infty$ the exponential function goes to 1 and $V \rightarrow V_i/4$. As explained earlier, when each energy level is equally filled to 25% the gas behaves mostly ideally; the gas behaves more ideally as T increases. The physical explanation is that molecules at higher temperatures have higher speeds which in turn make them harder to capture by intermolecular forces.

At the Boyle temperature, T_B the gas continues to behave mostly ideally over a much more extended range of pressures than usual. In this model T_B is the minimum temperature at which E_{ideal} never depopulates completely no matter how much the pressure is increased.

In order to find this temperature the number of energy levels populated must be analysed. This information is given by the partition function;

$$q = \sum_i e^{\frac{-4\varepsilon}{kT} \left[\sigma^{12} \left(\frac{N}{V_i} \right)^4 - \sigma^6 \left(\frac{N}{V_i} \right)^2 \right]}$$

If E_{ideal} has reached the point of complete depopulation the number of energy levels left occupied are 3. Therefore below T_B the partition function can equal 3 or less.

$$q = 3$$

As there are 4 energy levels the partition function equals 3 if and only if;

$$e^{\frac{-4\varepsilon}{kT} \left[\sigma^{12} \left(\frac{N}{V_i} \right)^4 - \sigma^6 \left(\frac{N}{V_i} \right)^2 \right]} = \frac{3}{4}$$

Taking logs of each side,

$$\frac{-4\varepsilon}{kT} \left[\sigma^{12} \left(\frac{N}{V_i} \right)^4 - \sigma^6 \left(\frac{N}{V_i} \right)^2 \right] = \ln \frac{3}{4}$$

This can then be rearranged to,

$$\sigma^{12}N^4 \left(\frac{1}{V_i}\right)^4 - \sigma^6N^2 \left(\frac{1}{V_i}\right)^2 + \frac{kT \ln \frac{3}{4}}{4\varepsilon} = 0$$

$$\frac{1}{V_i^2} = \frac{\sigma^6N^2 \pm \sqrt{\sigma^{12}N^4 - \frac{\sigma^{12}N^4 kT \ln \frac{3}{4}}{\varepsilon}}}{2\sigma^{12}N^4}$$

$$\frac{1}{V_i^2} = \frac{\sigma^6N^2 \pm \sqrt{\sigma^{12}N^4 \left(1 - \frac{kT \ln \frac{3}{4}}{\varepsilon}\right)}}{2\sigma^{12}N^4}$$

$$\frac{1}{V_i^2} = \frac{\sigma^6N^2 \pm \sigma^6N^2 \sqrt{1 - \frac{kT \ln \frac{3}{4}}{\varepsilon}}}{2\sigma^{12}N^4}$$

$$\frac{1}{V_i^2} = \frac{\sigma^6N^2 \left(1 \pm \sqrt{1 - \frac{kT \ln \frac{3}{4}}{\varepsilon}}\right)}{2\sigma^{12}N^4}$$

$$\frac{1}{V_i^2} = \frac{\left(1 \pm \sqrt{1 - \frac{kT \ln \frac{3}{4}}{\varepsilon}}\right)}{2\sigma^6N^2}$$

$$V_i = \frac{N\sigma^3\sqrt{2}}{\sqrt{1 \pm \sqrt{1 - \frac{kT \ln \frac{3}{4}}{\varepsilon}}}}$$

The minimum temperature at which there is a value of V_i that does not allow $q \leq 3$ is the Boyle temperature. This temperature occurs when

$$\frac{kT \ln \frac{3}{4}}{\varepsilon} > 1$$

Therefore;

$$T_B < -\frac{\varepsilon}{k \ln \frac{4}{3}}$$

Taking the modulus of T_B and ignoring any infinitesimal increase that is required for the above equation to result in the number of states occupied never going to 3 or below,

$$T_B = \frac{\varepsilon}{k \ln \frac{4}{3}}$$

Above this temperature there is no gas volume that allows the ideal energy level to be completely empty and the gas always behaves perfectly to some extent. The following table contains theoretical and experimental values of T_B for comparison.

Gas	Theoretical Boyle temperature/K	Experimental Boyle temperature/K
Nitrogen	319.3	327.2
Carbon dioxide	701.2	714.8
Krypton	538.3	575
Argon	388.8	411.5
Oxygen	405.9	393.7
Xenon	743.7	768

The critical temperature, T_c is the maximum temperature at which the gas can be condensed into a liquid via compression alone. In this model because gases can only condense to a liquid if no more than 2 energy states are occupied, T_c is the minimum temperature at which E_2 is never completely depopulated no matter how much the pressure is increased.

If E_2 has reached the point of complete depopulation the number of energy levels left occupied are 2. Therefore below T_c the partition function can equal 2 or less.

$$q = 2$$

As there are 4 energy levels the partition function equals 2 if and only if;

$$e^{\frac{-4\varepsilon}{kT} \left[\sigma^{12} \left(\frac{N}{V_L} \right)^4 - \sigma^6 \left(\frac{N}{V_L} \right)^2 \right]} = \frac{1}{2}$$

Similar algebraic manipulations to what was used in order to find the Boyle temperature yields the result

$$T_c < -\frac{\varepsilon}{k \ln 2}$$

Again, taking the modulus and ignoring any infinitesimal increase that is required for the above equation to result in the number of states occupied never going to 2 or below gives;

$$T_c = \frac{\varepsilon}{k \ln 2}$$

Above this temperature the requirement that no more than 2 energy levels must be filled in order for the gas to condense cannot be met, thus the gas never condenses whatever the pressure. Below is a table with theoretical and experimental values of the critical temperature for comparison.

Gas	Theoretical critical temperature/K	Experimental critical temperature/K
Argon	161.4	150.7
Ethylene	289.7	283.1
Ethane	311.8	305.4
Benzene	544.6	562.7
Chlorine	427.4	417.2
Carbon dioxide	291	304.2
Krypton	223.4	209.4
Nitrogen	132.5	126.3
Oxygen	163.4	154.8
Xenon	308.7	289.8

For an ideal gas there is no potential well, resulting in $\varepsilon = 0$. It follows that the experimental critical temperature for an ideal gas is zero Kelvin. This means that an ideal gas cannot condense at any temperature, which is what is observed in ideal gas isotherms.

Also note that,

$$\frac{T_B}{T_c} = \frac{\ln 2}{\ln 4 - \ln 3}$$

i.e. the ratio of the Boyle temperature to the critical temperature of any gas is constant.