Activation Energy and Boltzmann Factor

11 March 2020 16:33

Every wondered how come a puddle can evaporate (ie liquid becomes a gas) at say 20 centigrade?

Average thermal energy = kT

Energy need to break bonds = E_A

Activation Energy

$\frac{E_A}{kT}$ is an important ratio - its

is $\frac{\text{Activation energy}}{\text{Thermal energy}}$. If this is high, nothing much happens.

If $\frac{E_A}{kT}$ is 15 - 30 processes start to happen. How come?

Should should it? E_A is 15 to 30 times kT (energy). Not enough to break those bonds is it?

Random Collisions

Comes down to the fact that when two particles collide there is a chance that one of the pair will gain more than the average kT from the collision. This can happen several times in a row - leading to a particle with more energy (considerably more) than the kT.

Let f = fraction of particles with extra energy E (its a fraction - so less than 1 - lets say f = 0.1 ie 1 in 10)

How many particles will have extra energy 2E.... Well its f x f or f^2
How many will have extra energy 3E .... f^3
You will be surprised to learn for 4E its f^4
Etc...

Here's the important point...
We need 15kT to 30kT - so that's f^{15} to f^{30} - ie a tiny, tiny, tiny fraction
But because we have such huge numbers of particles (like 1 mole is 6×10^{23} remember) - we do in fact end up with quite a few particles with 15kT.

The Boltzmann Factor

You can find the ratio of particles in different energy states from the Boltzmann Factor $e^{-\frac{E}{kT}}$

The BF (as we call it) is also an approx measure of the probability that a particle has an energy at least E (remember E is the energy above the average kT)

For $\frac{E_A}{kT} = 15$ the BF $= e^{-15} \approx 10^{-7}$

For $\frac{E_A}{kT} = 30$ the BF $= e^{-30} \approx 10^{-13}$

So about 1 in every 10^{13} to 10^7 will have enough energy to overcome the E_A - eg break the bonds and leave the puddle - evaporate

So not very many then - - - except that apparently the average particle in an ideal gas makes about 10^9 collisions per second.

Here's an example of how to use this:

A liquid has E_A binding each molecule of 0.4eV
a) What is the average energy of the molecules at T=75K?

Approx energy $= kT = 1.38 \times 10^{-23} \times 75 = 1 \times 10^{-21}$ J

b) Find $\frac{E_A}{kT}$ for 1 escaping molecule?

convert a) → eV $\frac{1 \times 10^{-21}}{1.6 \times 10^{-19}} = 6.5 \times 10^{-3}$ eV

$\frac{E_A}{kT} = \frac{0.4}{6.5 \times 10^{-3}} = 62$ (ish) ↑ good & high

c) Find Boltzmann factor

$e^{-\frac{E_A}{kT}} = e^{-62} = 1.2 \times 10^{-27}$

like the probability ... E

like the probability
particle has energy > E_A

so pretty unlikely!!!

d) Will this liquid evaporate?

You'd think no.... but why

We need BF between 15-30 & its 62!!

So it will evaporate.... just v. v.v. slowly