Revision Guide for Chapter 14

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Student's Checklist

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I can show my understanding of effects, ideas and relationships by describing and explaining cases involving:

the ratio of the numbers of particles in a body that exist in states at different energy, and the change in the ratio when the temperature changes Revision Notes: Boltzmann factor Summary Diagrams: Climbing a ladder by chance; Temperature and average energy per particle; Average energy per particle for various processes; Variation of Boltzmann factor with temperature	
the idea of activation energy, and link this idea to what happens in various processes when the temperature changes (e.g. changes of state, thermionic emission, ionisation, conduction in semiconductors) Revision Notes: Activation processes Summary Diagrams: Variation of Boltzmann factor with temperature; Examples of activation processes	

I can use the following words and phrases accurately when describing effects and observations:

Boltzmann factor Revision Notes: Boltzmann factor	
activation energy Revision Notes: Activation processes Summary Diagrams: Examples of activation processes	

I can sketch, plot and interpret:

graphs showing how the Boltzmann factor varies with energy and temperature Revision Notes: Activation processes Summary Diagrams: Average energy per particle for various processes; Variation of Boltzmann factor with temperature	

I can make calculations and estimates involving:

ratios of characteristic energies (energies of a particle at which changes might occur) to the approximate mean energy per particle kT Revision Notes: Values of the energy kT Summary Diagrams: Temperature and average energy per particle; Average energy per particle for various processes	

the Boltzmann factor exp(– ε / *kT*) Revision Notes: Boltzmann factor; Activation processes Summary Diagrams: Variation of Boltzmann factor with temperature; Examples of activation processes	

Revision Notes

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Boltzmann factor

For a large number of particles in thermal equilibrium at temperature T, the ratio of numbers of particles occupying distinct states which differ by energy ε is given by the Boltzmann factor $e^{-\varepsilon/kT}$, where k is the Boltzmann constant.

The value of the Boltzmann constant is $k = 1.38 \times 10^{-23}$ J mol^{-1} K^{-1}.

The Boltzmann factor is important in cases where particles require a large amount of energy for a process to occur. The Boltzmann factor gives an approximate estimate of the fraction of particles with an excess of energy of at least ε. Thus the value of the Boltzmann factor plays an important role in determining the rate of many physical processes.

Typically, processes proceed at an appreciable rate when the ratio ε/kT is about 20 to 30. The value of $e^{-\varepsilon/kT}$, for $\varepsilon/kT = 20$ is about 10^{-9}. That is, about 1 particle in 10^{9} has energy ε or greater. Since a particle in a gas collides with another about 10^{9} times per second, a reaction in a gas may proceed on a time scale of seconds when ε/kT is about 20.

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Thermal activation processes

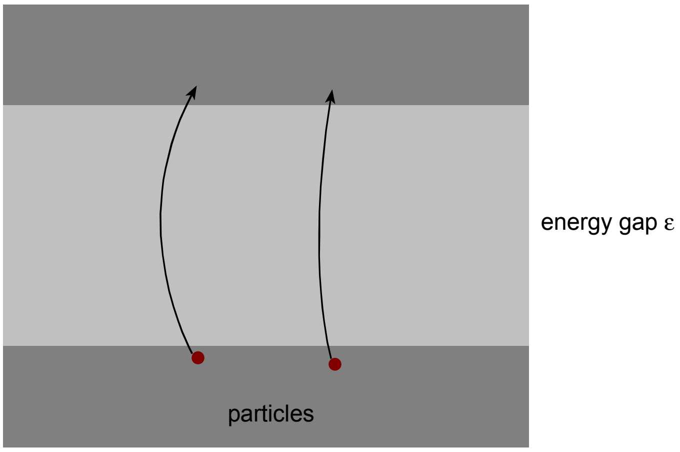
The random thermal energy of a particle is a small multiple of the energy kT. As the temperature increases more particles can cross the energy gap characteristic of activation processes.

Thermal activation processes include:

1. The decrease of resistance of a semiconductor with temperature.
2. The increase of pressure of a vapour with temperature.
3. The increase in the rate of a chemical reaction with temperature.
4. Thermionic emission of electrons.
5. Viscous flow of some liquids.

Many processes require particles to have sufficient energy to cross an energy barrier if the process is to occur. For example, molecules in a liquid can escape from the surface to enter the vapour state by breaking apart from other liquid molecules. Particles with sufficient energy can overcome the barrier. Such a process is known as an **activation process**. The energy needed to cross the gap or barrier is referred to as the **activation energy**.

Activation



The Boltzmann factor $e^{-\varepsilon / kT}$ is an approximation to the fraction of particles in a large system at temperature T having a larger than average energy of at least ε. If the temperature is increased, the number of energetic particles increases, and the process occurs more rapidly.

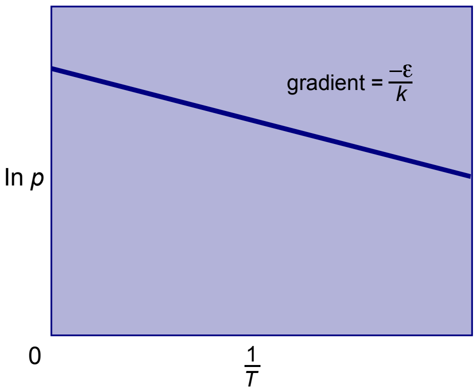
Thermionic emission

To escape from a metal surface, a conduction electron must cross an energy barrier: the work function of the surface. The number of electrons with energy in excess of the work function ϕ is approximately proportional to $e^{-\phi/kT}$. If the temperature increases, then $e^{-\phi/kT}$ increases and more electrons per second are emitted from the surface. This is the process of thermionic emission. Typically, ϕ is of the order of 10^{-19} J or about 1 eV, which gives a negligible value for $e^{-\phi/kT}$ at T = 300 K (ϕ is 40 or 50 times kT). However, at 3000 K, $e^{-\phi/kT}$ is larger and there is significant thermionic emission.

Evaporation

To escape from a liquid, a molecule must have enough energy to overcome the attraction of the other molecules in the surface. The fraction of molecules on the surface that have sufficient energy to escape is approximately proportional to the Boltzmann factor $e^{-\varepsilon / kT}$, where ε is the energy needed by a molecule to escape. Thus at temperature T, the number of molecules in the vapour state is approximately proportional to $e^{-\varepsilon / kT}$. The vapour pressure varies as $p = p_0\, e^{-\varepsilon / kT}$. Thus a graph of ln p against $1/T$ will be a straight line of gradient $-\varepsilon / k$.

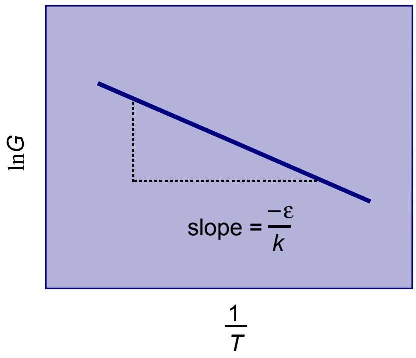
Vapour pressure



Intrinsic semiconductors

Conduction in an intrinsic semiconductor is due to electrons which have broken free from the atoms and move about inside the semiconductor. The higher the temperature, the greater the number of free electrons. At temperature T, the number of free electrons is approximately proportional to the Boltzmann factor $e^{-\varepsilon / kT}$, where ε is the energy needed to free an electron. Hence the conductivity σ of an intrinsic semiconductor is approximately proportional to $e^{-\varepsilon / kT}$: $\sigma = \sigma_0 e^{-\varepsilon / kT}$.

Conductance variation with temperature for an intrinsic semiconductor



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Values of the energy *kT*

The average energy of a particle in matter at absolute temperature *T* is often of the order of magnitude *kT*, where *k* is the Boltzmann constant.

A table of order of magnitude values of temperature, energy *kT* and photon wavelength

Temperature *T* / K	Energy *kT* / eV	Energy *kT* / kJ mol^{-1}	photon wavelength for *E* = *hf* = *kT*
1	0.0001	0.01	10 mm
10	0.001	0.1	1 mm
100	0.01	1	0.1 mm
1000	**0.1**	**10**	**0.01 mm**
10 000	1	100	1 μm
100 000	10	1000	100 nm
1 million	100	10 000	10 nm
10 million	1000	100 000	1 nm

These values involve two large approximations, each of about 20%. So the values are an order of magnitude guide only. The row in bold may be worth memorising. Other values can then be got by multiplying or dividing by 10.

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Summary Diagrams (OHTs)

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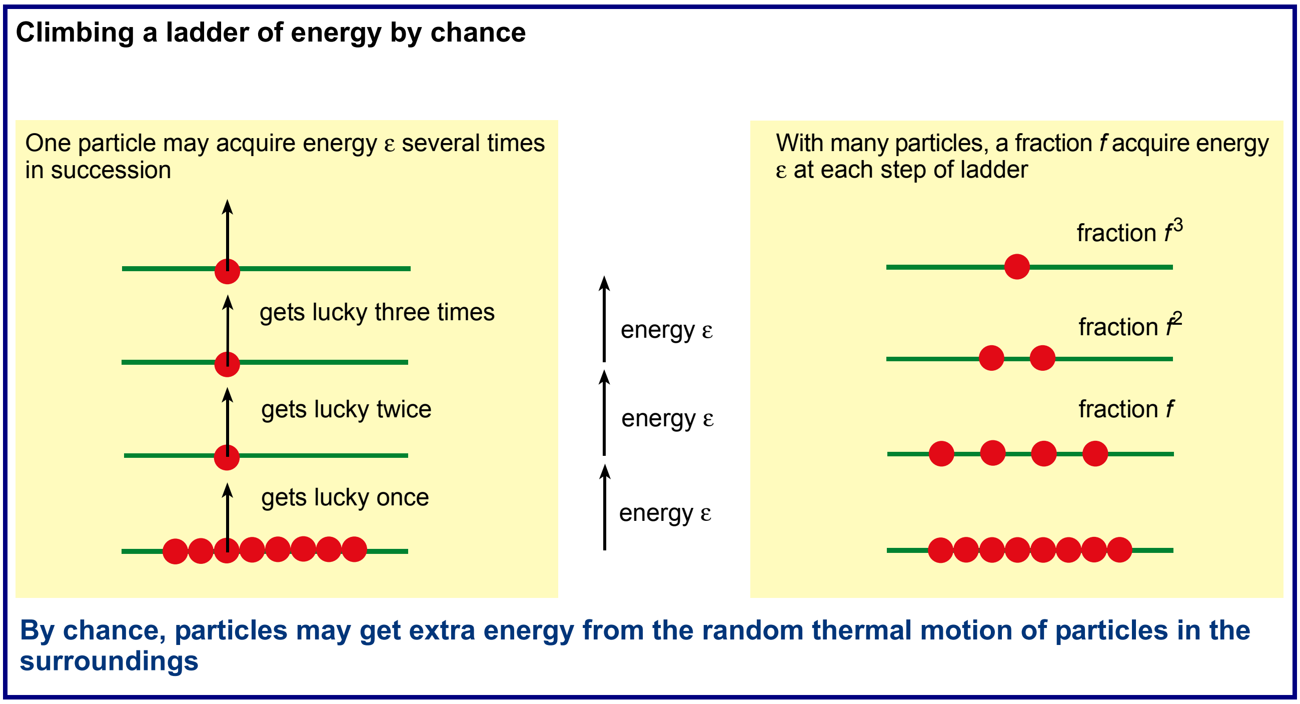
Climbing a ladder by chance



This diagram shows why only a small fraction of particles acquire energy much larger than average, through random collisions.

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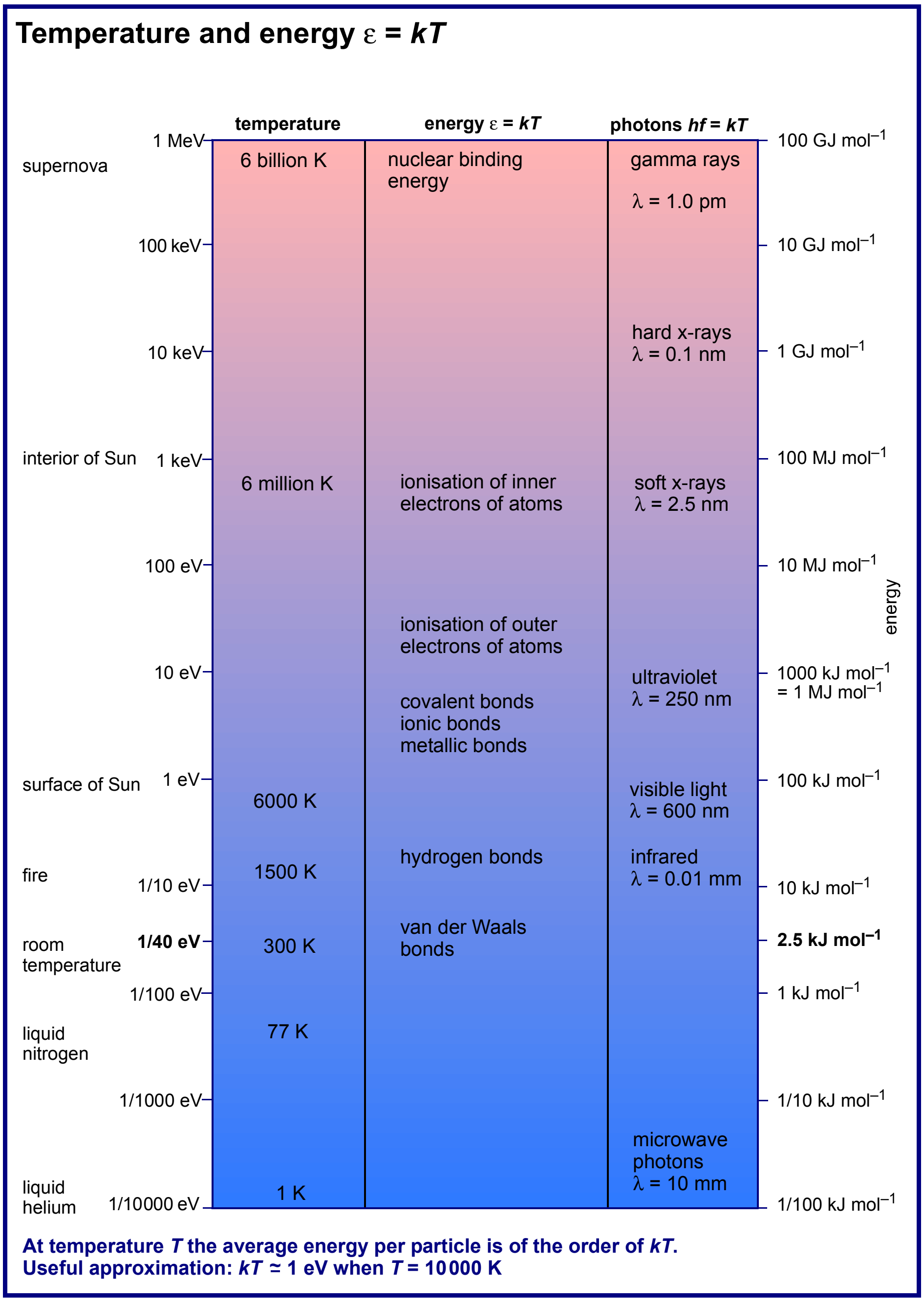
Temperature and average energy per particle



This diagram shows how temperature and the average energy per particle are related, across a very wide range of temperatures.

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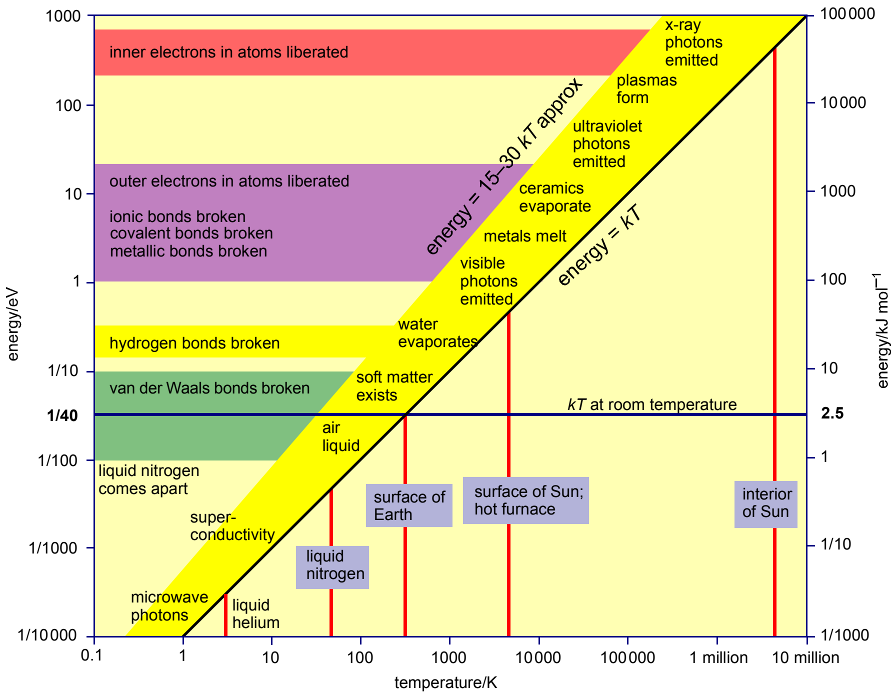
Average energy per particle for various processes

Processes and energy ≈ *kT* per particle



Many processes requiring energy ≈ 15–30 *kT* happen at an appreciable rate

This diagram emphasises the range 15–30 times *kT*, where the average energy per particle is enough for a process to begin to happen at an appreciable rate.

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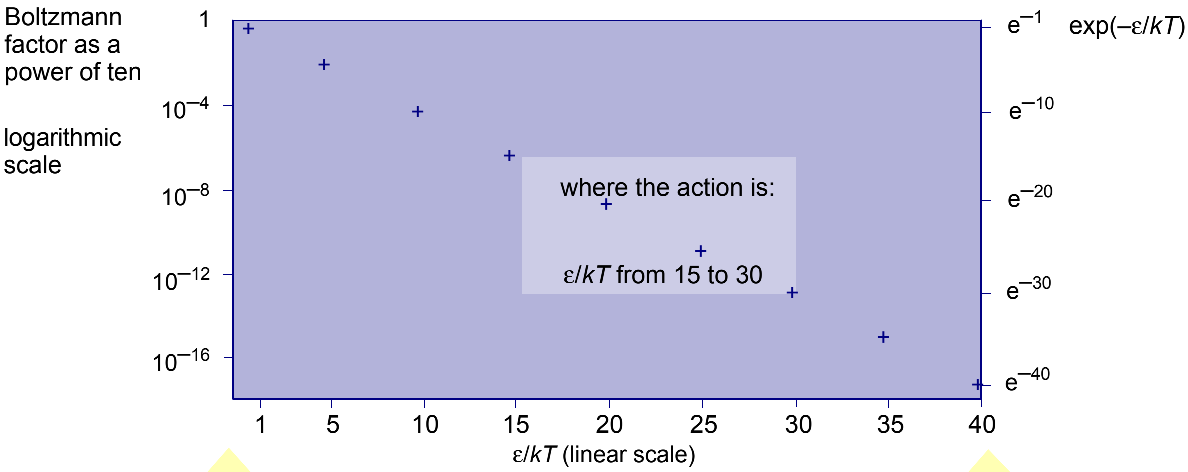
Variation of Boltzmann factor with temperature

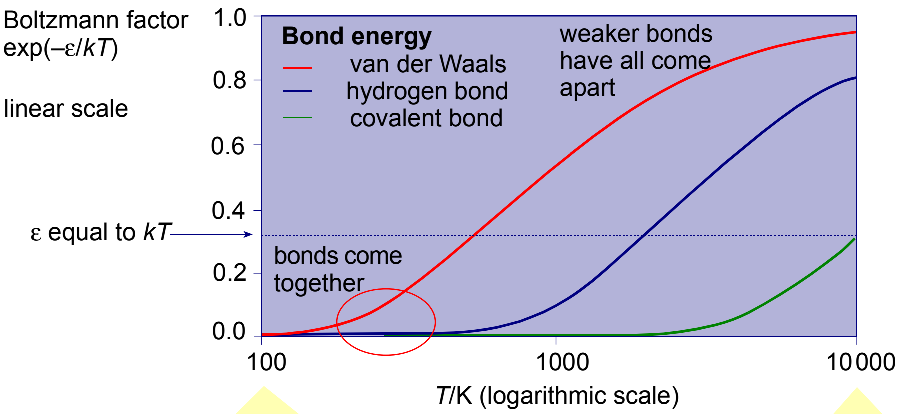
Boltzmann factor: the minority with energy ε/*kT*



Hot at this end of the scale
The temperature *T* is high
The ratio ε/*kT* is small
The fraction exp(–ε/*kT*) is large and approaches 1

Cold at this end of the scale
The temperature *T* is low
The ratio ε/*kT* is large
The fraction exp(–ε/*kT*) is small and approaches 0

Boltzmann factor plotted against temperature

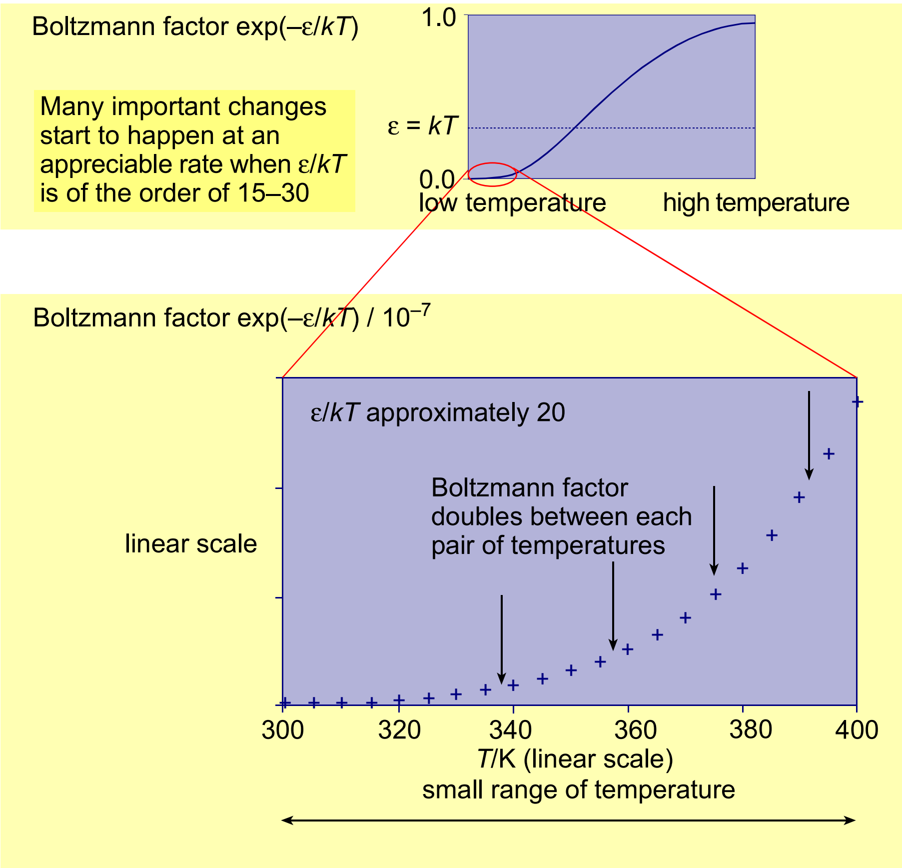


Cold at this end of the scale
The temperature *T* is low
The ratio ε/*kT* is large
The fraction exp(–ε/*kT*) is small and approaches 0

Hot at this end of the scale
The temperature *T* is high
The ratio ε/*kT* is small
The fraction exp(–ε/*kT*) is large and approaches 1

The Boltzmann factor is the ratio of numbers of particles in states separated by energy ε. It depends on temperature and the energy needed to get from one state to the other.

Change in Boltzmann factor with temperature



When ε > *kT* the Boltzmann factor increases very rapidly with temperature

The Boltzmann factor changes very rapidly with temperature. This is why the rates at which various processes proceed often increase very rapidly with temperature.

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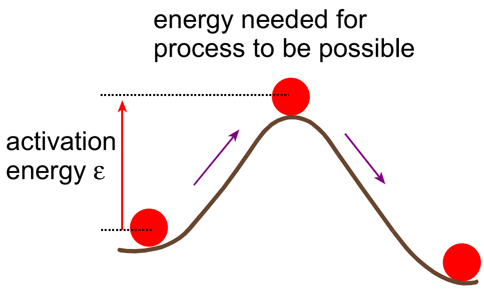
Examples of activation processes

Activation processes

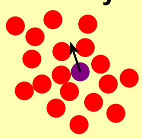
An energy hill has to be climbed before the process can happen

The energy needed has to be acquired by chance from random thermal agitation of the surroundings



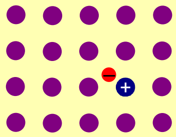
Examples of activation processes

Viscosity of liquids



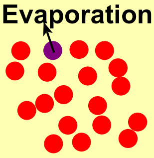
particles need enough energy to break out of 'cage' formed by their neighbours, so liquid can flow

Ionisation of semiconductor



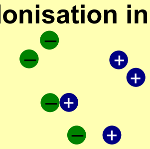
atoms need enough energy to become ionised, freeing electrons which can conduct

Evaporation of liquids



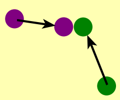
particles need enough energy to break away from attractions of particles at surface, and leave the liquid

Ionisation in a flame



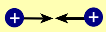
molecules need enough energy to dissociate into ions, which can conduct a current

Many chemical reactions



particles must collide with enough energy to get close enough to bond to make a new molecule

Nuclear fusion in the Sun



protons must have enough energy to get close enough to fuse into deuterium

An activation process is one in which the particles have to overcome an energy barrier before the reaction or change can occur.

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