

**A Hitch-Hiker's  
Guide  
To  
Molecular  
Thermodynamics**

*... DON'T PANIC!!*

In which the most probable things generally happen,  
and we explore the mysteries of entropy, free energy  
and the ultimate secrets of the molecular universe.

by

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**(with apologies to Douglas Adams)**

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*“A theory is the more impressive the greater the simplicity of its premises... therefore...  
...thermodynamics is the only physical theory of universal content which I am  
convinced  
that, within the framework of the applicability of its basic concepts, will never be  
overthrown.”*

A. Einstein (1946)

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Stray thoughts....

Thermodynamics is a magnificent accomplishment of 19th century science - logically complete and irrefutably correct in every detail - but, like many 19th century novels, boring and impenetrable to students brought up in the latter part of the 20th century. Thermodynamics can be, and was, derived without any knowledge of or reference to the atomic or molecular nature of matter. Armed with a few basic axioms and the desire to improve the efficiency of steam engines, it is perfectly feasible to derive the whole of thermodynamics without ever mentioning atoms or molecules. It's a fantastic achievement.

But, just 'cos you can derive thermodynamics that way doesn't mean that you must. We are products of the 20th century. We can't unthink molecules. Heat engines and Carnot cycles are as foreign to us now as molecules would have been to late Victorians. There is an alternative...

Remember: science in general, and thermodynamics in particular, is about asking silly questions. Why is water wet? Why doesn't it burn? -- that sort of thing. Sometimes the answers look pretty silly too - at first.

User's instructions:

Read and enjoy, in conjunction with your recommended text. The first half of the Guide may be read, more or less, at one go - and will take you far enough along the road to get you started. The remaining bits and pieces may help along the way. And, when you have finished the Guide, throw it away or pass it on to a friend, 'cos it's like riding a bike: once you've mastered the technique, you'll always be able to think this way.

Start here...



## IN THE BEGINNING ...

A long, long time ago there was one almighty big bang, and the universe was created. Matter (particles, atoms, molecules) was formed together with an awful lot of energy. Everything that has happened since is the result of the gradual redistribution (evolution) of this matter and energy to form the world as we know it today. The process continues, and controls everything we do and everything that happens around us.

Energy seems to come in various forms, but really boils down to just two: kinetic energy due to motion of objects, and potential energy due to forces between objects.

If the objects are large (stars, planets, motor cars, bricks, footballs...) then there is no problem: we can see them moving and we can feel the forces (gravity, springs etc.). We can even calculate pretty exactly how they are going to move, using Newton's laws of motion or Quantum Mechanics (if we're really clever).

But what if the objects are very small - atoms & molecules? We believe they are there, but we can't see them nor perceive, directly their motion or the forces between them. But we feel the effects! HEAT is what we feel if atoms and molecules are moving fast, COLD if they're not. And the forces between them are what we call "bonds" or "interactions".

Chemical processes involve atoms and molecules, and - just like the universe as a whole - involve the redistribution of matter and energy.

Hence:-

$$HEAT \Rightarrow \text{THERMO - DYNAMICS} \Leftarrow MOTION$$

Molecular thermodynamics is the attempt to understand chemical processes in objects that we can see (test-tubes, reaction flasks) in terms of things we can't (atoms, molecules).

So why can't we just calculate the motions of all the molecules in the same way as we do for large objects? The problem is that there are just too many of them.

A typical thimbleful of water contains about  $10^{23}$  molecules. That is, approximately:-

100,000,000,000,000,000,000,000 molecules.

and that's really too many to handle, even with the biggest and fastest computers.

What's more, we don't even care about the exact motion of every single one of those  $10^{23}$  molecules - we can't see them any way.

More interesting is the mean or average behaviour of the molecules most of the time, and that turns out to be much easier to think about - though you may not agree, at first. This means that we are going to have to look at some basic ideas about probability and statistics - and it is for this reason that the subject of Molecular Thermodynamics is also referred to as Statistical Thermodynamics.

Before we go on, just a reminder about energy & some definitions:

**NO FREE LUNCHES ...** ... the First Law

Energy is conserved: it can be changed from one form to another, but it can never be created or destroyed.

(Well - you knew that all along, but why is it true ?)

*(Einstein modified this a little bit by showing that matter can be converted into energy, and vice versa:  $E = mc^2$ , and all that. This is usually only important in nuclear reactions. Please consult your demonstrator before attempting this experiment).*

Definitions:- Internal Energy: U  
Enthalpy: H = U + PV

As the name implies, "internal" energy is the energy tied up inside any object in the form of molecular motions and molecular forces. We can usually consider this separately from the other kinds of energy an object may also have. For instance, a beaker of water sitting on the table has gravitational potential energy (it will fall to the floor, given half a chance) - but it also has internal energy made up of the kinetic energy of motion of the individual water molecules and potential energy from the forces between them.

*(In many books you will find the symbol "E" used for internal energy. However, "U" is now the internationally agreed symbol. We will later use "E" to mean energy in general, wherever we don't need to be too specific about what kind of energy we are talking about).*

"Work" is a form of energy, and Enthalpy is the appropriate energy term to use to take account of PV work in situations when volumes can change.

Reminder: Work = Force × Distance moved  
= Pressure × Volume change

Hess's Law - which you use to calculate heats of reaction or combustion - is just one application of the First Law.

**NOTHING IS CERTAIN ...** - a reminder concerning the laws of probability.

There are many areas of life where we can't make exact predictions - for example: general elections, Rangers vs. Celtic matches, how long we shall live, what our exam results will be, ... and so on. There are just too many variables, things to take into account. But we can try to estimate the "probability" of some particular event.

Suppose, for example, we roll some dice. Each dice has six sides, numbered 1 to 6, and unless someone has cheated, there is an equal chance of any particular number coming up. There are

six possibilities, so the probability of throwing a particular number (a 4 say) is just 1/6. That is to say, the probability of this particular event:

$$p(4) = 1/6 \quad \underline{\text{or}} \quad 0.16667 \quad \underline{\text{or}} \quad 16.667\%$$

(If somebody has cheated and the dice were loaded, we could not predict this probability. But we could estimate it experimentally by throwing the dice lots of times and calculate what proportion of the time each number came up. Clearly, the larger number of throws the better the estimate).

Let's throw the dice again and ask what is the chance of getting either a 4 or a 6 say. The answer is just the sum of the two probabilities:

$$p(4 \underline{\text{or}} 6) = p(4) + p(6) = 1/3 \quad \text{in this case.}$$

Now for a daft question ...

What is the probability of throwing any number?

$$p(1 \underline{\text{or}} 2 \underline{\text{or}} 3 \dots \underline{\text{or}} 6) = p(1) + p(2) + p(3) \dots + p(6) = 1$$

which is obvious since there is always a 100% chance that some number will turn up.

This is a general rule: The sum of all probabilities must be one.

$$\text{i.e. } \Sigma p(N) = 1$$

where  $\Sigma$  ("sigma") is just a shorthand way of saying "the sum over all possibilities".

It follows that the probability of throwing any number except N is:  $1 - p(N)$ .

(For example: If you think you have a 90% chance of passing the Chemistry exam,  $p(\text{Pass}) = 0.9$ . The chance of that not happening,  $p(\text{Fail}) = 1 - p(\text{Pass}) = 0.1$ , or 10%. Does that make you feel any better?)

### Means & Averages

Let's make the game a bit more interesting. Suppose every time you throw the dice I give you £3.00, cash, and for each particular number N that turns up you give me £N in return. Who makes a profit, in the long run? In other words, what is the average amount you pay per throw?

A certain fraction of the time,  $p(1)$ , you pay £1.00; another fraction,  $p(2)$ , of the time you pay £2.00; and so on. On average you will pay me:

$$1.p(1) + 2.p(2) + 3.p(3) + \dots + 6.p(6) \quad \text{pounds.}$$

This works out to £3.50 per throw - prove it. Or, if you don't believe me, you are welcome to play the game with me anytime. (All major credit cards accepted.)

In other words, the mean or average value is given by:

.... *Don't Panic !!*

$$\langle N \rangle = \sum N.p(N)$$

and this is another general rule. (The funny brackets  $\langle \rangle$  mean the average value over all possibilities).

*Just one more thing before we go on ...*

What if we make the game a little bit more complicated and throw the dice twice each time? What is the probability of throwing a particular sequence of numbers - a "3" followed by a "5", say?

On the first throw we have a probability  $p(3)$  of getting it right. Of these successful throws we have a further probability  $p(5)$  of getting it right again. So the combined probability of throwing a 3 followed by a 5 is just the product:  $p(3) \times p(5)$ .

This again illustrates a general rule:

If two events,  $E_1$  and  $E_2$ , can occur independently with probabilities  $p(E_1)$  and  $p(E_2)$ , respectively, then the probability of getting  $E_1$  and  $E_2$  together, in that order, is just the product:

$$p(E_1 + E_2) = p(E_1).p(E_2)$$

(If the order doesn't matter then the combined probability is  $2 \times p(E_1).p(E_2)$  - think about it).

**IGNORANCE IS BLISS ...**      So what's the point of all this?

Earlier in this guide we discussed the impossibility of ever being able to calculate the precise motions of all the molecules in a typical object. We wouldn't even want to if we could, because that's not what we see.

And another thing...      Where do quantities like "temperature" appear in Newton's laws ?

Instead of trying to calculate *exactly* what happens, let's do it by statistics and see if we can estimate *what probably happens* most of the time.

Imagine two physical objects, A and B. These can be anything you like - blocks of wood, lumps of metal, reaction flasks containing nasty smelling mixtures, etc. We can't work out, nor even measure, the energies of these objects in terms of their molecular motions. They're not even constant - molecules of the air are constantly battering into them, or bouncing off them, so that the energy fluctuates all the time. But we suspect that things tend to average out.

What is the probability that any object has a certain amount of energy at any one time?

Suppose that:      the *probability* that object A has energy  $E_A$  =  $p(E_A)$

and that:      the *probability* that object B has energy  $E_B$  =  $p(E_B)$

Now bring the two objects together. What is the combined probability?

We could consider A and B together as yet another object, with energy  $E_A + E_B$ , and say that:

$$\text{the probability that object (A+B) has energy } (E_A+E_B) = p(E_A+E_B)$$

But we know from the rules of combined probabilities (above) that this must be the product of the two separate probabilities:

$$p(E_A+E_B) = p(E_A) \times p(E_B)$$

Now comes the tricky bit:

What mathematical functions do we know that have this property? i.e. that the function of a sum of parameters is equal to the two separate functions multiplied together:  $f(x+y) = f(x).f(y)$  ?

There is only one, and that is the “*exponential*” function.

Remember:  $\exp(x+y) = \exp(x).\exp(y)$   
or:  $e^{x+y} = e^x.e^y$

So, we can say straight away that the probability of anything having an energy  $E$  is proportional to some exponential function of this energy:

$$p(E) \propto \exp(\beta E)$$

where  $\beta$  is some quantity we don't know yet.

Now, we could go through some long complicated mathematics to find out what  $\beta$  is. But instead, think about the following:

(i) Things normally fall to as low an energy as possible, so we expect lower energies to be more probable than high energies. This suggests that  $\beta$  should be a negative number.

(ii) Hot things tend to have more molecular energy than cold things, so temperature must come into it somehow.

The answer turns out to be:

$$\beta = -1/kT$$

where  $T$  is the absolute temperature (Kelvin) and  $k$  is a universal constant, known as Boltzmann's constant after the man who discovered this rule.

From experiments:  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

Also, it turns out:  $k \times \text{Avogadro's number} = R$  (the gas constant).

So, the Boltzmann probability rule is:

$$p(E) = w.\exp(-E/kT)$$

where  $w$  is some proportionality constant which we shall come back to later.

### **BOLTZMANN PROBABLY RULES, O.K. ...**

Let's look at an example.....      ....and another daft question:-

Have you ever wondered what keeps the atmosphere up? Why don't all the molecules in the air just fall to the ground like any other object?

The reason is, of course, that the molecules are small, light objects being kicked around all the time by thermal agitation, so that they spend a lot of their time off the ground. Can we calculate this?

Think about some object, with mass  $m$ , either on the ground or at some height,  $h$ .

On the ground it will have an energy  $E_1$ , say, with a Boltzmann probability:

$$p(E_1) = w \cdot \exp(-E_1/kT)$$

At height  $h$  it will have energy  $E_2$  with probability:

$$p(E_2) = w \cdot \exp(-E_2/kT)$$

so that the relative probability of being at either height is just the ratio:

$$p(E_2)/p(E_1) = \exp(-(E_2-E_1)/kT)$$

But this difference in energies,  $E_2-E_1$ , is just the gravitational energy difference between the two heights:

$$E_2 - E_1 = m \times g \times h$$

Furthermore, if we think about lots of molecules at a time, the average number of objects at any height,  $n(h)$ , is simply proportional to the probability. So that:

$$n(h)/n(0) = \exp(-mgh/kT)$$

meaning that the number, or density of objects, falls off exponentially with height.

Numerical Examples:       $g = 9.81 \text{ m.s}^{-2}$  ;       $T = 300 \text{ K}$  ;       $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

(a) If  $m = 1$  gram (0.001 kg), and  $h = 1$  metre :

*{Remember! SI units: mass should always be in kg}*

$$\begin{aligned}n(h)/n(0) &= \exp(-0.001 \times 9.81 \times 1/1.38 \times 10^{-23} \times 300) \\ &= \exp(-2.37 \times 10^{18}) \\ &= 0 \quad \text{(as near as makes no difference)}\end{aligned}$$

(b) But, if  $m = 5 \times 10^{-23}$  g ( $5 \times 10^{-26}$  kg), i.e. about the mass of an oxygen or nitrogen molecule:

$$n(h)/n(0) = \exp(-1.18 \times 10^{-4}) = 0.9999$$

i.e. the molecule is equally likely to be found 1 metre above the ground.

(Exercise: show that  $n(h)/n(0) = 1/2$  for molecules of air when  $h = 5.8$  km approx. In other words, the density of molecules in the atmosphere, or the atmospheric pressure, falls to half its value at sea level at about 3.6 miles high).

Interestingly, this decrease in atmospheric pressure with height provided one of the earlier methods for measuring the heights of mountains. It also explains why climbers at high altitudes require oxygen, and why boiling an egg or making a hot cup of tea on top of a mountain is a difficult task. (Why?)

### **KEEPING THE PRESSURE UP ...**

What we have said so far is true for energy in whatever form it comes. It is especially true for the internal, molecular energy  $U$ .

Many chemicals and physical processes involve changes in volume, so that some energy is involved in PV work (unless we deliberately keep the volume constant). Normally we don't bother to fix the volume and, since we generally work under the constant pressure of the Earth's atmosphere, it is more convenient to think about processes at constant  $P$ .

Therefore, to keep the energy accounting straight, it is more appropriate to talk in terms of Enthalpy ( $H$ ) rather than internal energy ( $U$ ).

*Remember:-*

Use  $U$  (or  $E$ ) whenever the VOLUME is kept constant (not normally the case).

Use  $H = U + PV$  whenever the PRESSURE is kept constant (i.e. most of the time in normal circumstances).

The Boltzmann probability rule still has the same form, i.e. :-

$$p(U) = w \cdot \exp(-U/kT) \quad \dots \text{ at CONSTANT VOLUME}$$

$$p(H) = w \cdot \exp(-H/kT) \quad \dots \text{ at CONSTANT PRESSURE}$$

### **COUNTING THE WAYS ...**

Now we must tackle that factor "w" in the Boltzmann rule.

So far the probability of something happening seems to depend only on the energy of that "something". But, as you know, energy can come in lots of different forms, and there may be lots of "somethings" which have the same energy (or, of course, enthalpy if at constant pressure).

For instance, a molecule might have a certain energy, E, simply in the form of kinetic energy. Alternatively the molecule might be rotating or vibrating, with the same total energy E but made up in different ways. Similarly, there may be several different geometrical isomers (i.e. different shapes) with the same energy.

Now, if we ask ourselves what is the probability of a certain energy occurring, the answer must depend not only on the particular energy value but also on how many ways there are of getting that energy value.

Think of a simple example: let's go back to throwing dice and make the game even more trivial. Instead of having numbers on each face, let's just paint five of the sides black and the other one white. Since there are 5 ways in which a black can turn up, and only one white, it is 5 times more likely to throw a black than a white.

This is what "w" is.

w = the "number of ways" in which a particular E (or H or U) can occur.

so that if there are w ways in which a particular energy can arise, then it is w-times more probable that it will occur. Hence the need to multiply the exponential Boltzmann probability term by this factor.

### **SO WHAT KEEPS IT ALL UP? ...**

Those among you who know about these things will have realised that there is something paradoxical about the exponential Boltzmann factor.

That is: the exponential function,  $\exp(-E/kT)$ , is biggest when  $E = 0$ .

This should mean that zero energy is the most probable state, and that everything we see and touch - even ourselves - should most probably be at the lowest possible energy. We know this is not true. But why?

As usual, there are at least two answers to this question:

(1) *the total energy of the Universe is not zero.* At the instant of the Big Bang (or whatever) the world was endowed with a large amount of energy. This energy will never go away, no matter how hard we try. So it must be around here somewhere.

Now, it could be that all this energy is locked away in some black hole in the remoter regions of Alpha Centauri, and the rest of us are at zero energy. But it isn't.

More likely is that the energy is spread around in some fashion, so that we all get a share. But how would that square with the exponential Boltzmann rule?

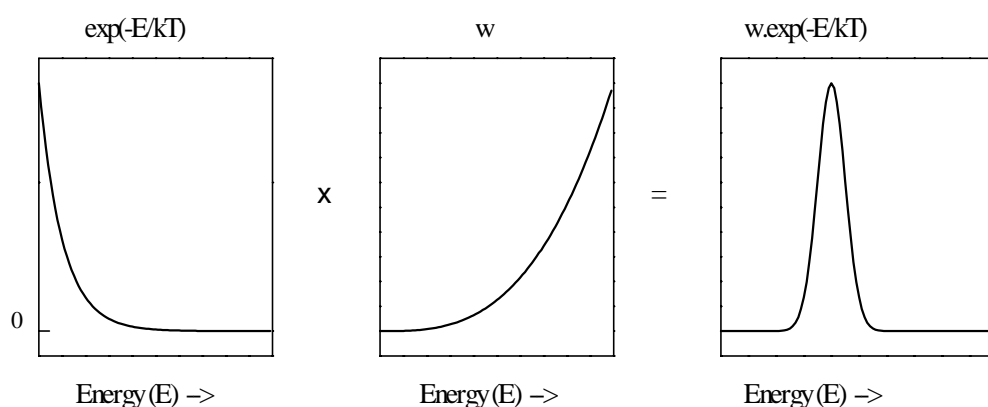
Here's how ...

(2) *It's all to do with "w"*

There aren't many ways you can get low energies. At very low energies things don't move very much, molecules tend to crystallise and everything is nice and ordered. "w" is small.

But at higher energies things are much more exciting. Molecules move around a lot, or rotate or vibrate - lots of things happening at once. So there are lots of different ways of getting the same energies. "w" is big.

The combination of these two effects:



"w" increasing with energy  $\times$  the exponential decreasing with energy, means that most objects spend most of their time at some average energy away from zero.

.... *Don't Panic !!*

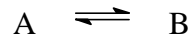
... *end of paradox.*

## AND NOW ... THE INFINITE IMPROBABILITY DRIVE?

### --- Chemical Equilibrium ---

Think about a molecule (or a collection of molecules) given the choice of being in one of two states (or chemical forms) : A or B

In chemical terms we would write this as an equilibrium:



What is the relative probability of finding molecules in either state A or state B ?

Using the Boltzmann rule, and assuming constant pressure, since that's how we normally do chemical reactions:-

$$\text{Probability of state A, } p(A) = w_A \cdot \exp(-H_A/kT)$$

$$\text{Probability of state B, } p(B) = w_B \cdot \exp(-H_B/kT)$$

where  $w_A$  and  $w_B$  are the “numbers of ways” for each molecular form with enthalpies  $H_A$  and  $H_B$ , respectively.

So, combining these two equations, the relative probabilities of the two chemical forms is:-

$$p(B)/p(A) = \exp(-\Delta H/kT) \times w_B/w_A \quad ; \quad \text{where } \Delta H = H_B - H_A$$

Now, instead of thinking about a single molecule, think about the large number of molecules we usually have to handle in a chemical experiment. We can see two things:

(i) The probability of a molecule being in one form or the other is proportional to the concentration of that particular species in the mixture. That is:

$$p(B)/p(A) = [B]/[A]$$

But this is also what we would call the Equilibrium Constant,  $K$ , for the reaction (provided the reaction has actually reached equilibrium). So that:

$$K = [B]/[A] = p(B)/p(A)$$

(ii)  $H_A$  and  $H_B$  are the enthalpies PER MOLECULE, but that's not how we usually talk about energies or enthalpies.

Look at that term in the exponential:  $-\Delta H/kT$

.... Don't Panic !!

Multiply top and bottom by Avogadro's number, and it becomes:  $-\Delta H^0/RT$   
where  $\Delta H^0$  is now the enthalpy difference PER MOLE ( $\text{kJ mole}^{-1}$ , for instance), and the gas constant, R, has replaced k (since  $R = k \times \text{Avogadro's no.}$ , remember?)

So now we can write down the equilibrium constant for this simple reaction:

$$K = \exp(-\Delta H^0/RT) \times w_B/w_A$$

... and remember, this all came from probabilities.

## ENTROPY, FREE ENERGY, AND ALL THAT ...

As if by magic... ...take logs of both sides of that last equation:

$$\ln K = -\Delta H^0/RT + \ln(w_B/w_A) \quad (\text{"ln" means natural log to base "e"})$$

Now shuffle the equation around a bit (multiply both sides by -RT) to get:

$$-RT \cdot \ln K = \Delta H^0 - RT \cdot \ln(w_B/w_A) \quad \text{----} \otimes$$

Things are finally beginning to look familiar, are they? ...

That thing on the left hand side is what we traditionally call "the STANDARD FREE ENERGY" of the reaction:

$$\Delta G^0 = -RT \cdot \ln K \quad (\text{Remember ?})$$

The last thing on the right hand side of  $\otimes$  still looks a bit odd. But you can't stop me calling it something different!

How about:  $\Delta S^0 = R \cdot \ln(w_B/w_A) \quad ?$

'cos that will give us:  $\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$

... a familiar friend (perhaps?) at last.

The mystery is finally revealed.

The entropy difference between two objects is related to the number of ways in which each object can be arranged with a particular energy.

$$\Delta S^0 = S_B - S_A = R \cdot \ln(w_B/w_A)$$

... *Don't Panic !!*

If  $w_B$  is greater than  $w_A$  (that is : B is “more disordered” than A) then  $\Delta S$  is positive, an increase in entropy. And *vice versa*.

The absolute entropy of any object is given by:

$$S = k \cdot \ln(w) \quad \text{per object (e.g. per molecule)}$$

or

$$S = R \cdot \ln(w) \quad \text{per mole of objects}$$

This fundamental equation was discovered in 1877 by Ludwig Boltzmann (yes, him again). He committed suicide in 1906 and had this equation carved on his tombstone in Vienna (not necessarily in that order).

## THE SECOND LAW ...

**... the most probable things generally happen.**

We mustn't forget that entropy was actually discovered experimentally way before Boltzmann - even before our modern notions of atoms and molecules were fully established.

What was found (by Clausius, originally) was that for changes taking place in an isolated system, that is in a system where energy can't get in or out, entropy always increases or stays the same:

$$\Delta S \geq 0$$

and once the entropy stops increasing ( $\Delta S = 0$ ) the system is said to have reached equilibrium.

We can now see what this means in molecular terms.

Increasing  $S$  means increasing “ $w$ ”. So that, left to itself, the most probable things begin to happen in the system. The molecules in the system get as mixed up as they can possibly be, within the constraints of conservation of energy, and “ $w$ ” reaches a maximum.

*{An aside ... You may be worried that this does not seem to fit with common sense or everyday experience. After all, the most improbable things seem to be going on around us all the time, and Life itself seems a pretty unlikely process. But we have to remember that the Universe itself has not yet reached thermodynamic equilibrium. What we are seeing are all sorts of unlikely events in the gradual equilibration (“Heat Death”) of the Universe. The rules of equilibrium thermodynamics only apply when we can take a little bit of the universe and isolate it, in an experiment on the laboratory bench for instance.}*

## PHYSICAL EQUILIBRIUM ...

... changing the phase.

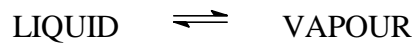
Chemical changes in molecules involve the making, breaking or rearrangement of covalent bonds.

.... *Don't Panic !!*

But matter can exist in different physical forms as well (solid, liquid, gas, etc.) - called "phases" - that are frequently interchangeable, and which frequently co-exist in equilibrium with each other.

We can treat any phase equilibrium in exactly the same way as we did chemical equilibrium above.

For example : think about liquid-vapour equilibrium.



(Imagine a closed flask, half full of some liquid. The "empty" half of the flask isn't really empty - it contains molecules from the liquid running around like crazy as a gas or vapour. This gas will have a pressure (the "vapour pressure") and molecules will be continually jumping in and out of the liquid phase.)

What is the relative probability of finding a molecule in the vapour or liquid phase?  
The argument goes just as before, to give:

$$p(\text{vapour})/p(\text{liquid}) = \exp(-\Delta H/RT) \times w_{\text{vap}}/w_{\text{liq}}$$

where in this case:  $\Delta H = H_{\text{vapour}} - H_{\text{liquid}}$  per mole.  
 $=$  molar heat of vaporization of the liquid.

We can now recognise that:

$$\Delta S(\text{liquid} \rightarrow \text{vapour}) = R \cdot \ln(w_{\text{vap}}/w_{\text{liq}})$$

so that:  $p(\text{vap})/p(\text{liq}) = \exp(-\Delta G/RT)$

where  $\Delta G = \Delta H - T \cdot \Delta S =$  molar free energy of vaporization.

### ***What is the situation at equilibrium ?***

There are various ways of looking at this.

One way is to say that, when equilibrium is reached, the rate at which molecules leave the liquid is just balanced by the rate at which they are returning from the vapour phase.

Alternatively, we could say that at equilibrium it is equally likely for any one molecule to be in either the gas or the liquid phase.

This means that:  $p(\text{vap})/p(\text{liq}) = 1$  AT EQUILIBRIUM

In other words:  $\Delta G = 0$

and this is a general rule for ANY equilibrium situation.

O.K. SO WE CHEATED ...

**... Activity & Activity Coefficient.**

Earlier on, in the section on chemical equilibrium and equilibrium constants, we rather glossed over some important assumptions. It was simpler to do that at that stage because you were probably confused enough already. But we now have to be a bit more honest.

We have assumed that the concentrations (or partial pressures) of a particular molecular form (or phase) are proportional to the probabilities. That is, for example:

$$[A] \propto p(A) = w_A \cdot \exp(-E_A/RT)$$

where  $E_A$  is the energy of molecule A (or we could use  $U_A$  or  $H_A$  for the energy or enthalpy of 1 mole of such molecules).

The important thing we have taken for granted is that  $E_A$  is a property only of the molecule, regardless of what its neighbours are or what physical state (gas, liquid, solid, solution) it is in.

In reality this is unreasonable. For example, the energy of a molecule in a solution mixture will depend not just on its chemical form, but also on what interactions - attractions, repulsions and so on - it experiences from other molecules in the mixture. This will depend both on what kind of molecules are present in the mixture and on their concentrations.

This means that, in general, the energy  $E_A$  can be imagined to be made up of two parts:

$$\begin{aligned} E_A &= E + \delta E \\ &= (\text{molecular energy in some "standard state"}) \\ &\quad \text{PLUS (an extra bit due to interactions with other molecules).} \end{aligned}$$

This second contribution ( $\delta E$ ) depends on how many molecules are there (the concentration), what kind they are, and what physical form they are in. It is usually unknown and extremely difficult to calculate - even with advanced theories and modern powerful computers.

What this means in practise is that we have to introduce some kind of "fudge factor" to correct for molecular interactions.

Look at it this way:



.... *Don't Panic !!*

There now follows some.... ODDS & ENDS ...

*(These are some extra bits and pieces that might help a little bit now, or in later parts of your course, or when reading your textbook. They don't follow any particular sequence - just dip into the parts you fancy, when you need them.)*

## EXPONENTIALS & LOGARITHMS ...

... a brief refresher course for those who are a bit hazy about all this.

Any quantitative science requires us to be able to handle numbers - frequently numbers that are incredibly big or infinitesimally small. Maths/algebra is designed to make this easier (believe it or not).

Any number (x) can be written as any other number (a) raised to some power (b):

$$x = a^b$$

For instance, if the "base" (a) is 10 (try these on your calculator):

$$\begin{aligned} 1000 &= 10^3 \\ 157 &= 10^{2.196} \\ 0.032 &= 10^{-1.495} = 1/10^{1.495} \end{aligned}$$

Certain general rules apply (and should be obvious if you think about them). For example:

If:  $x = a^b$  and  $y = a^c$

Then:  $xy = a^b \cdot a^c = a^{(b+c)}$

$$x/y = a^b \cdot a^{-c} = a^{(b-c)}$$

....and so on (try some examples on your calculator).

These "powers" or "exponents" are also known as "logarithms".

In other words: the logarithm of a number -  $\log(x)$  - is the power to which some other number (the "base", a) must be raised to equal the number you first thought of (x).

It follows that:  $\log(xy) = \log(x) + \log(y)$

$$\log(x/y) = \log(x) - \log(y)$$

...and so on.

Now, there's nothing special about the number 10 as a base - except that that's the number of fingers, or toes, that most of us have to count on. We can choose any base we like.

But there is a "natural" base - called "e" - which turns up in all sorts of mathematical places and which has several useful additional properties which make it convenient to use in most cases.

.... *Don't Panic !!*

Numerically,  $e = 2.71828 \dots$  (no, you don't have to remember it!)

and expressions of the form  $e^b$  or  $\exp(b)$  are called "*exponential functions*".

Logarithms using "e" as base are called "*natural logs*" or " $\log_e$ " or " $\ln$ ", for short.

All the general properties of powers and logs (above) apply equally well when the base is "e".

### **IMPORTANT !!**

NOW is the time to find out how your calculator does natural logs and exponentials. Try the following examples:

$$10 = \exp(2.3026) \quad : \quad 157 = \exp(5.0562) \quad : \quad 0.032 = \exp(-3.4420)$$

$$\ln(10) = 2.3026 \quad : \quad \ln(157) = 5.0562 \quad : \quad \ln(0.032) = -3.4420$$

.... and any more you can think up for yourself.

## WHY DOES $dS = dQ/T$ ?

Thermodynamics developed in the nineteenth century, when people were more concerned about the efficiency of steam engines than the esoteric properties of atoms & molecules. They couldn't manage this without inventing this strange quantity called "entropy".

They found that by adding a small amount of heat energy,  $dQ$ , to an object (a lump of iron, a steam boiler, ... anything) the entropy of the system increases by an amount:

$$dS = dQ/T$$

Can we get the same thing from a molecular point of view?

Imagine any object. We don't know what its energy is, but we know that the probability that it has some internal energy,  $U$ , is given by:

$$p_1 = w_1 \times \exp(-U/RT)$$

Now, let's take this object and add a known amount of heat energy,  $dQ$ , using a Bunsen burner or electric heater, for instance. The internal energy is now  $U + dQ$ .

We still don't know for certain what the internal energy is, since we didn't know  $U$  to start with, but we can again write down the probability:

$$p_2 = w_2 \times \exp\{-(U+dQ)/RT\}$$

Now we have to think a bit!

Since *we know for certain* that we have added  $dQ$  to the system (since we can measure it as we do it), the only uncertainty is in the original energy  $U$ . So the probability that the object now has energy  $U+dQ$  is the same as the probability that it had  $U$  to start with.

In other words:  $p_1 = p_2$

So, taking the two Boltzmann expressions and rearranging a bit, we get:

$$w_2/w_1 = \exp(dQ/RT)$$

or, taking logs of both sides:  $R \cdot \ln(w_2/w_1) = dQ/T$

That thing on the left hand side is what we now recognise, in molecular terms, as the change in entropy,  $dS$ , of the object during whatever change has taken place (a little bit of heating, in this case), so that:

$$dS = dQ/T \qquad \text{Q.E.D.}$$

So, adding heat to anything increases the entropy by giving the molecules more energy to explore many more different ways of arranging themselves.

### HEAT CAPACITIES ...

When we add heat energy to something its temperature rises, and the amount it goes up depends on the "heat capacity",  $C$ , of the object. The definition is:

$$dQ = C.dT$$

where  $dT$  is the temperature rise due to addition of a small amount of heat,  $dQ$ .

In words, the heat capacity can be thought of as: *the amount of energy required to raise the temperature of the object by one degree.*

(The actual numerical value of  $C$  depends on the size, state, chemistry and temperature of the object - and on whether the heat is added at constant pressure or volume - but you'll probably hear more about that elsewhere.)

We can relate this to the entropy change when we heat something up:

$$dS = dQ/T = C.dT/T$$

... but that's only accurate for very small temperature changes.

To get the entropy change during large temperature changes, involving lots of heat energy, we simply imagine the process going in lots of very small steps, and add up -or "*integrate*" - all the little bits of  $dS$ :

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} (C/T).dT$$

to give the change in entropy in going from one temperature ( $T_1$ ) to another ( $T_2$ ).

We can do similar things to get the enthalpy change from heat capacity, by adding up all the small amounts of heat energy required to reach a certain temperature:

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} dQ = \int_{T_1}^{T_2} C.dT$$

(Life gets a little bit more complicated if the object undergoes some phase change - melts, evaporates, or something - during the process, but again you'll learn more about this from your textbook).

**IDEAL (or PERFECT) GASES : ENTROPY - VOLUME - PRESSURE**

Ideal gases don't exist - they are a figment of our warped imagination. Try telling your dear old granny about molecules which have no size or shape, and which can pass through each other as if they weren't there!

But, most gases under normal conditions behave as if they were almost ideal - close enough to be a reasonable approximation most of the time.

Imagine what happens if we take some ideal gas in a box and change the volume. What happens to the entropy?

The ideal molecules don't stick to each other and can go anywhere they like in the box. The only internal energy they have is kinetic, and that won't change if we keep the temperature constant.

So, since the molecules can go anywhere and the energy doesn't change, the "number of ways" is simply the number of different places the molecules can be in the box. In other words,  $w$  is proportional to the volume. (Imagine, if you double the volume, there are twice as many places the molecules might be: there are twice as many "ways").

This means that if we change the volume from  $V_1$  to  $V_2$ :

$$w_2/w_1 = V_2/V_1 = P_1/P_2$$

(... since the pressure will go in the opposite direction:  $PV = nRT$  remember).

And the entropy change is:

$$\Delta S(V_1 \rightarrow V_2) = R \cdot \ln(V_2/V_1) = R \cdot \ln(P_1/P_2)$$

... for 1 mole of gas.

(Remember: this is only true for ideal gases. In solids and liquids the molecules stick to each other, if they can, and can't go anywhere they like if we change the size of their box).

-----

## **Crisis, What Energy Crisis.... ??**

A paradox: if "energy cannot be created or destroyed" (first law), why do we worry about wasting it ? The total amount of energy in the Universe is constant - nothing we can do will make it more or less - so why don't we just squander it recklessly ? (Well, maybe we do just that - but we shouldn't !)

To answer this question we need to think about what we need/use energy for. Apart from keeping ourselves warm (or cool, in hotter climates), we need energy to do the work to make the things that make civilised life more comfortable: mechanical work to make and drive machines; electrical work to power motors, computers, communication systems; chemical work to extract raw materials (metals) from their ores, to synthesize drugs, cosmetics, plastics, and so on....

Energy comes in two basic forms:

HEAT = disorganized, random, uncoordinated motion of atoms and molecules.

WORK = organized, collective motion of atoms and molecules - levers, pulleys, engines, electrochemical cells ("batteries"), information systems, and in a more generalized sense, chemical synthesis: making some specific molecule out of the disorganized mess of molecules around us.

And this is where the second law comes in... "The most probable things generally happen" - remember ? - and this generally means that molecules tend to be as disorganized as they can be.

... and that's just the opposite of what we would like.

It's not that energy is going away, it's just that it tends to be in the wrong form - and anything we do tends to make it worse.

Any attempt to organize molecules ("do useful work") must always be at the expense of more disorder (heat dissipation) somewhere else in the system/Universe - and that can't go on for ever - leading eventually to the "Heat Death" of the Universe ? (see also Free Energy, below).

**Why is energy conserved ?** (for deep thinkers only)

What a silly question..... it just **is** conserved, isn't it ? Everyone knows that ! It just happens to be a property of the Universe we live in.

But is there a deeper reason ? Well, there is, for what it's worth...

.... *Don't Panic !!*

It just so happens that, for purely mathematical reasons, in any system (universe) where the laws of motion (Newton's, quantum, whatever) *do not change with time*, then the quantity we call "energy" is a constant.

It would be a funny old world indeed if the laws of physics and chemistry changed with time - hard to imagine, really, how we would cope if the laws were different today from what they were last week, and different yet again next week. But (fortunately ?) our universe isn't like that. So, as a purely mathematical consequence, energy is conserved.

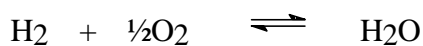
This is just one example of a whole set of constant quantities that arise because our laws are "invariant" under certain symmetry operations. Here the fact that the laws of motion are invariant under translations in time leads to energy conservation. Similarly, the fact that the laws are invariant under translations in space (i.e. are the same in different places in the Universe) means that momentum is conserved. The fact that the laws are the same no matter which direction we point in ("invariant under rotation") leads to conservation of angular momentum. The laws look the same in a mirror (reflection symmetry), so some funny stuff called "parity" is conserved (usually).. and so forth.

- just thought you might like to know that.

### **How to predict an equilibrium constant: An easy way, and another way !**

If statistical thermodynamics is as good as it claims to be, then it should be able to predict important things about chemical processes, such as the equilibrium constant of a chemical reaction.

The equilibrium constant of a reaction is a number that tells us how far that reaction might possibly go under particular conditions, given a chance. Equilibrium constants can vary enormously. For example, for the following familiar example:



the equilibrium constant is roughly:  $K = [\text{H}_2\text{O}]/[\text{H}_2][\text{O}_2]^{1/2} \approx 10^{40}$

which means that, given half a chance, that reaction will proceed - quite explosively and possibly dangerously in this case - to an equilibrium in which products are vastly favoured over reactants.

Compare this with a superficially similar reaction (just change one of the letters, H to N):-



for which the equilibrium constant is roughly:  $K = [\text{N}_2\text{O}]/[\text{N}_2][\text{O}_2]^{1/2} \approx 10^{-18}$

... *Don't Panic !!*

This reaction hardly goes at all - perhaps just as well since the atmosphere we breath is made up predominantly of N<sub>2</sub> and O<sub>2</sub>, and N<sub>2</sub>O (nitrous oxide) is the strangely narcotic "laughing gas" {as used in Victorian/Edwardian laughing gas parties ?}

Can we possibly predict (or, at least, understand) this enormous range of K values ?  
These particular examples are a bit hard at this stage, but let's try something a little bit easier.

Possibly the simplest chemical reaction in the world:



- take some hydrogen gas (H<sub>2</sub>) and mix it with some of its heavier isotope ("heavy hydrogen" or deuterium, D<sub>2</sub>), after a while we see formation of some hybrid molecules HD. (How might you detect this experimentally ?)

The equilibrium constant for this reaction:

$$K = \frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]} \approx 4 \quad \text{experimentally.}$$

To a reasonable approximation, hydrogen (H) and deuterium (D) atoms are chemically identical - being isotopes, they differ only in the number of neutrons in the nucleus. Their electron configurations (which determine chemical properties, by and large) are identical - just one electron each in this case.

This means that the H-H, D-D, and H-D bonds in H<sub>2</sub>, D<sub>2</sub>, and HD molecules, respectively, are essentially identical and of the same bond energy. In fact, from a chemical point of view, it is hard to tell the difference between D and H.

Why, then, do these molecules react with each other at all ?

Well, from time to time, an H-H or D-D bond might break spontaneously (if it gets enough energy from a collision, for example), giving highly reactive H and D atoms that will scurry around desperate to re-form a bond with anything. This could be with another free H atom, or with any D atom that happens to be available - they don't care, they can't even tell the difference. Eventually, therefore, everything gets totally scrambled, with H and D atoms appearing randomly in pairs in H<sub>2</sub>, D<sub>2</sub>, or HD molecules.

The "most probable thing.." in this context is that H and D atoms will pair totally at random, and we should be able to predict the outcome.

Now this is where you come in....

**The easy way:**

Lecture Demonstration - A Class/Group Exercise in which students are the reagents.

.... Don't Panic !!

[This group activity requires coordination of the whole class - the more the merrier -probably best done under the direction of the lecturer, or somebody else who can count...]

OK kids - it's playtime !

Your chance to be an atom - form a bond, make a molecule.

Instructions:

1. Hold hands with the person nearest you.  
Congratulations ! - you are now a diatomic molecule.

You have now formed pairs - perhaps at random, perhaps not - it doesn't matter 'cos you don't yet know whether you are an H atom or a D atom.

2. Exchange telephone numbers (or birthdates, or i.d. numbers...)

These will (usually) be either odd numbers or even numbers. We can now proclaim, quite arbitrarily, that ODD numbers are Deuterium atoms, and that EVEN numbers are Hydrogen atoms. Consequently, each pair may now...

3. Decide whether you are a:  
D<sub>2</sub> molecule (odd-odd)  
H<sub>2</sub> molecule (even-even)  
HD molecule (even-odd)

We now have a standard volume (room/lecture theatre) containing "diatomic molecules" formed at random, simply by chance, with no apparent bias towards one kind of "bond" or another.

4. Count up the total numbers of each  
 $n_{D_2}$  = number of D<sub>2</sub> molecules (odd-odd)  
 $n_{H_2}$  = number of H<sub>2</sub> molecules (even-even)  
 $n_{HD}$  = number of HD molecules (even-odd)

5. Calculate the "equilibrium constant":

$$K = \frac{[HD]^2}{[H_2][D_2]} = \frac{n_{HD}^2}{n_{H_2} \cdot n_{D_2}}$$

This should be a number close to 4.

OK - so maybe it was not exactly 4 - perhaps you got 2.3 or 6.7, or something of that order. The important thing is that it was not  $10^{-18}$  or  $10^{40}$  (nor even 42). Try it again on a different day, with a different class and you'll probably get a different answer, but still in this same ballpark. And, the bigger the class, the closer you are likely to get to the "real" answer. (Computer nerds might like to write a simple program using random numbers to prove this.)

This illustrates a couple of fundamental points:

- (i) The bigger the sample size, the more likely we are to get consistent answers - and for atoms and molecules the "class size" is in the region of  $10^{23}$  - plenty big enough for reliable statistics.
- (ii) Even so, we might expect to see random fluctuations in thermodynamic properties - certainly for systems containing relatively few atoms or molecules (see later).

You can also do this mathematically....

**Another way:** A thought experiment....

*You can do this by yourself, and works well if you don't have anyone to hold hands with. It's harder, but the answer is more accurate (usually).*

Imagine what would happen if we were to make H<sub>2</sub>, D<sub>2</sub>, or HD molecules by picking atoms at random.

Suppose you have a bag containing  $n_H$  hydrogen atoms and  $n_D$  deuterium atoms. ( $n_H$  and  $n_D$  can be as large as you like.) Close your eyes, shake the bag, dip in and pick an atom at random...

Probability of picking an H atom:  $p_H = n_H / (n_H + n_D)$

Probability of picking a D atom:  $p_D = n_D / (n_H + n_D)$

(It follows that the chance of picking any atom regardless of type,  $p_H + p_D = 1$ , obviously. We shall use that shortly.)

To make each molecule, we have to pick the appropriate two atoms, one after the other. Consequently...

The probability of making an H<sub>2</sub> molecule:  $p_{H_2} = p_H \times p_H = p_H^2$

The probability of making a D<sub>2</sub> molecule:  $p_{D_2} = p_D \times p_D = p_D^2$

At first sight, the probability of making an HD molecule might seem to be:

$$p_{HD} = p_H \times p_D$$

But - and here comes an important tricky bit - we could also make an HD molecule the other way round - that is, pick a D followed by an H. So there are actually twice as many ways of making an HD molecule:

$$p_{HD} = 2 \times p_H \times p_D$$

.... *Don't Panic !!*

To check that we've accounted for everything, the sum of all these probabilities must be one:

$$\begin{aligned}\Sigma p &= p_{H_2} + p_{D_2} + p_{HD} \\ &= p_{H_2} + p_{D_2} + 2 \cdot p_H \cdot p_D \\ &= (p_H + p_D)^2 \\ &= 1 \qquad \text{since } p_H + p_D = 1\end{aligned}$$

Now, if we do this thought experiment enough times, and make a large enough collection of molecules, the number (or concentration) of each kind of molecule is simply proportional to the probabilities of making each molecule. So the equilibrium constant is:

$$\begin{aligned}K &= \frac{[HD]^2}{[H_2][D_2]} \\ &= \frac{p_{HD}^2}{p_{H_2} \cdot p_{D_2}} \\ &= \frac{(2 \cdot p_H \cdot p_D)^2}{p_H^2 \cdot p_D^2} \\ &= 4 \\ &\qquad \dots\text{exactly !}\end{aligned}$$

Now that's quite a remarkable result. We have shown that the equilibrium constant of this particular reaction can be calculated simply on the basis of pure chance alone, without any regard for the chemical bonding involved.

It works here because we have been able to assume that all the bonds are the same between the various isotope pairs.

That will rarely be the case with other chemical reactions, where different bond energies will bias the statistics and make certain molecules more or less likely than they would have been by pure chance alone.

(It's not even exactly true here !)

Even though H-H, H-D, and D-D bonds are chemically identical, the different masses of the H and D nuclei mean that the molecules have different rotational, kinetic and vibrational energies - the rotational energy being the most important at normal temperatures. These slight energy differences affect the statistics a little bit and make  $K \approx 3.8$ , rather than exactly 4, both experimentally and theoretically.

... why is nothing ever simple ?)

## Free Energy and Chemical Potential

We met “standard Gibbs free energy change” ( $\Delta G^{\circ}$ ) above as just another way of expressing the equilibrium constant (K) of a physical or chemical process:

$$\Delta G^{\circ} = -RT \ln K$$

but is there anything more to it than this ?

We've now agreed that the basic rule (2nd. Law) at the molecular level is that “the most probable things generally happen”. We also know that the probability of something happening is related to the Boltzmann expression:

$$p = w \cdot e^{-H/RT} \quad (\text{or one of its variants})$$

We can't usually measure this probability directly, still less calculate it for anything but the most trivial examples, but we could rearrange it in some other way.

1. Take (natural) logs of both sides:  $\ln(p) = \ln(w) - H/RT$
2. Multiply by -RT:  $-RT \ln(p) = H - RT \ln(w)$   
 $= H - TS$

[since we know that the absolute entropy  $S = R \ln(w)$  (per mole) ]

We could define the absolute Gibbs free energy as just another way of expressing the probability:

$$G = -RT \ln(p)$$

One advantage of this is that it almost begins to look like common sense. Because of that minus sign, low probability states correspond to a higher free energy than high probability.

So, if the most probable thing generally happens:-

Low probability ---> Higher probability

which is equivalent to:

High free energy ---> Lower free energy

In other words, just like everyday objects which tend to fall to their lowest available (potential) energy, molecules or molecular systems will tend to fall to their lowest available Gibbs free energy (G).

The change in Gibbs free energy ( $\Delta G$ ) just represents the relative probabilities.

For any change, A ---> B

$$\Delta G = G_B - G_A = -RT \ln(p_B) + RT \ln(p_A) = -RT \ln(p_B/p_A)$$

So, for a spontaneous process (i.e. A goes to B of its own accord), state B is more probable than state A:

$$p_B > p_A \quad \text{so} \quad \Delta G \text{ is negative}$$

Alternatively, for a process which is relatively unlikely to go of its own accord:

$$p_B < p_A \quad \text{so} \quad \Delta G \text{ is positive}$$

Finally, for a situation in which A or B are equally likely:

$$p_B = p_A \quad \text{so} \quad \Delta G = 0$$

This corresponds to an equilibrium situation in which the process has no further tendency to go one way or the other.

For mixture of molecules it is sometimes convenient to think about the “partial Gibbs free energy per mole” of the individual molecular species, otherwise known as **the “chemical potential”** and usually given the symbol  $\mu$ . You can think of this as the molecular probability expressed as an energy in the same way as above. And, in the same way, molecules will tend to move to states of lower chemical potential (higher probability) as they approach equilibrium.

### So What's "Free" about Free Energy ?

Is there yet more still to “Free Energy” than just another way of expressing probability ?

$$\text{Free Energy} = \text{Work}$$

Because of the 2nd. Law, not all the heat energy ( $\Delta H$ ) liberated in a chemical reaction can be used to do useful work. Some must be used to increase the overall entropy of the Universe. It turns out that the best we can do - the maximum amount of useful work that we might get out of a spontaneous reaction - is  $\Delta G$ . In other words, this is the amount of energy “free” for us to do what we like with, as opposed to that which must go to the surroundings.

### Population of vibrational levels (a numerical example)

A “typical” exam question:-

*The normal mode frequency for C-I stretching vibrations is about  $500 \text{ cm}^{-1}$ . Estimate what fraction of  $\text{CH}_3\text{I}$  molecules in a sample at room temperature might be undergoing such vibrations.*

This question is concerned with the relative probabilities of finding a molecule in its first excited vibrational state (with energy  $\epsilon_1$ ) compared to the ground state (with energy  $\epsilon_0$ ).

$$p_1 = w_1 \cdot \exp(-\epsilon_1/kT) \quad \text{and} \quad p_2 = w_2 \cdot \exp(-\epsilon_0/kt)$$

so that the ratio:  $p_1/p_0 = (w_1/w_0) \cdot \exp(-[\epsilon_1 - \epsilon_0]/kT)$

Now, in this case, the number of ways in which the molecule can vibrate - the “degeneracy” -  $w_1$  is one, and the degeneracy of the ground state ( $w_0$ ) is also one, so the ratio  $w_1/w_0 = 1$  and we may ignore it. (This may not always be the case, but you will always be given such information when required.)

The energy difference between these two states (*c.f.* spectroscopy course ?) is related to the frequency of vibration:-

$$\begin{aligned}\epsilon_1 - \epsilon_0 &= hc/\lambda \\ &= (6.626 \times 10^{-34}) \times (2.998 \times 10^8) \times (50000) \\ &= 9.9 \times 10^{-21} \text{ J}\end{aligned}$$

[**Remember !** SI units - lengths must be in metres:  $1/\lambda = 500\text{cm}^{-1} = 50000\text{m}^{-1}$  ]

so:  $p_1/p_0 = \exp(-9.9 \times 10^{-21} / 1.381 \times 10^{-23} \times 300) = e^{-2.4} = 0.091$

In other words, roughly 1/10th of these molecules will be vibrating at room temperature.

Ignoring higher vibrational levels, the fraction found in the first vibrational level will be given by:

$$\begin{aligned}\text{Fraction} &= p_1/(p_1 + p_0) = (p_1/p_0)/(1 + p_1/p_0) \\ &= 0.091/1.091 = 0.083 \text{ (or 8.3\%)}\end{aligned}$$

### Average thermal energies...

Heat is molecular motion. That motion is made up movement of atoms or molecules through space (“translation”) together with the rotation of entire molecules and the vibrations of atoms within molecules or in crystal lattices (for example). All this motion is rather chaotic. Molecules move, rotate, vibrate at all sorts of different rates, and bounce around colliding off things as they go.

So, how much “motion” corresponds to how much “heat” ?

As always, we cannot work out exactly how much energy any one molecule has, but only the average it might have over time in a very large population of similar molecules.

We won't bother with the calculation here, but it turns out that the average thermal kinetic energy of any object  $= 3kT/2$  .

(Similar values are obtained for rotational and vibrational motions, provided the energies involved are relatively small - but quantization of vibrational and rotational levels usually makes things more complicated.)

For simple gas molecules this allows us to estimate roughly how fast they are travelling.

Example: What is the average thermal velocity of a nitrogen molecule in the air at room temperature (300 K) ?

$$\text{Kinetic energy: } \frac{1}{2}mv^2 = 3kT/2$$

$$\text{Mass of one N}_2 \text{ molecule, } m = 0.028/6 \times 10^{23} = 4.67 \times 10^{-26} \text{ kg}$$

$$\text{Hence: } v^2 = 3 \times 1.381 \times 10^{-23} \times 300 / 4.67 \times 10^{-26} = 266000$$

$$\text{and } v = 516 \text{ m s}^{-1}$$

(i.e. about 300 mph - so fast ? You'd think we might feel it ! We do. Think about it.)

### **Fluctuations...**

In any statistical process we expect to see fluctuations. So, if our theory is correct, we should expect to see fluctuations in thermodynamic properties of things around us... and we do, if we look hard enough. But normally these fluctuations are too small to be noticeable under normal conditions.

For large, everyday objects containing very large numbers of molecules, the statistical fluctuations are relatively tiny and usually go unnoticed.

However, for very small objects containing just a few molecules, the fluctuations are much more apparent.

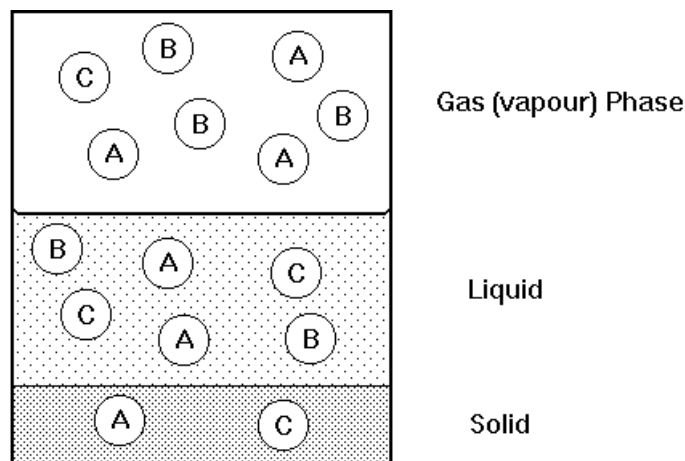
Brownian Motion is one such effect. Seen under a microscope, tiny particle of dust or smoke seem to be in perpetual, chaotic motion - fluctuating in position and velocity all the time. This was first described in 1827 by the Scottish botanist, Robert Brown, but it was not until 1905 that Albert Einstein showed that it was due to fluctuations arising from atomic and molecular motions - essentially pressure fluctuations on small particles due to collisions of molecules from the surrounding solvent.

When we look up at the sky we also see consequences of thermodynamic fluctuations. On the Moon the sky is black, because there is no atmosphere. But on Earth, even though air is quite transparent to light, we see a (usually) blue sky. Why ? Tiny pressure/density fluctuations in the atmosphere cause small changes in refractive index of the air that scatter light from the sun. The fluctuations are greater for smaller volume elements of the atmosphere, so short wavelength light (blue) is scattered more than longer (red) wavelengths. Looking directly at the sun at dusk or dawn, for example, we see the opposite effect as the shorter wavelengths are scattered out of the direct line of sight to give a reddish tinge to the sunlight. This is accentuated in the presence of cloud or dust pollution, giving rise to red sunsets, etc.

Chemical reaction rates also depend on fluctuations. In order for a chemical reaction to proceed, molecules must (normally) collide with sufficient energy to overcome some activation energy barrier. If all molecules had the same average energy this would never happen. Only when particularly energetic collisions occur by chance energy fluctuations will reaction proceed. The higher the temperature the more likely it will be that molecules might have this energy (Boltzmann), so reactions tend to go faster at higher temperature. (Note that the Arrhenius equation for reaction rate constants includes a Boltzmann-like exponential energy term.)

Critical Point fluctuations sometimes occur in certain materials under certain conditions, and this can be used as a graphic demonstration of thermodynamic fluctuations. Under particular conditions of temperature and pressure (the “critical point”) the distinction between liquid and vapour state for some substances disappears. At this point, enormous fluctuations in density of the material give rise to light scattering (“critical opalescence”) that can be seen even in large volumes of the material.

Thermodynamics of Complex Mixtures: “Chemical Potential”



Molecules may be in many different chemical (A, B, C...) or physical (gas, liquid, solid...) states.

How might we write down the probability of a particular state of this mixture ?

For each mole of molecules we will have molecular probabilities:  $p_A, p_B, p_C...$  etc.

where each  $p_A = w_A \cdot \exp(-E_A/RT)$  ...and so on.

But in the mixture we don't just have one mole.

$$\begin{aligned} \text{For } n_A \text{ moles of A, probability} &= p_A^{n_A} \\ \text{For } n_B \text{ moles of B, probability} &= p_B^{n_B} \\ \text{For } n_C \text{ moles of C, probability} &= p_C^{n_C} \end{aligned}$$

... and so on for each component in each phase in the mixture.

[This follows from rules of probability: for combined events, simply multiply together the separate probabilities.]

So, for the entire mixture:

$$\text{Probability } p(\text{mixture}) = p_A^{n_A} \times p_B^{n_B} \times p_C^{n_C} \times \dots$$

To simplify, take natural logs (ln) of both sides...

$$\ln p(\text{mixture}) = n_A \cdot \ln p_A + n_B \cdot \ln p_B + n_C \cdot \ln p_C + \dots$$

Multiply both sides by -RT

$$-RT \cdot \ln p(\text{mixture}) = -n_A RT \cdot \ln p_A - n_B RT \cdot \ln p_B - n_C RT \cdot \ln p_C - \dots$$

↑

↑

$$\text{Total free energy of the mixture} = \text{sum of the "molecular free energies"}$$

[Remember:  $G = -RT \cdot \ln p$  is just another way of expressing probabilities]

"Molecular free energy" are also known classically as "Chemical Potential",  $\mu$

defined as:

$$\begin{aligned} \mu_A &= -RT \cdot \ln p_A \\ &= \text{chemical potential of species A} \\ &= \text{Gibbs free energy per mole of A in the mixture} \end{aligned}$$

(and similarly for all other components of the mixture)

Consequently, instead of thinking in terms of molecular probabilities (unless we wish to), we can work with just chemical potentials, and the total Gibbs free energy of any mixture is given by:

$$G = \sum_i n_i \mu_i$$

In terms of probabilities....

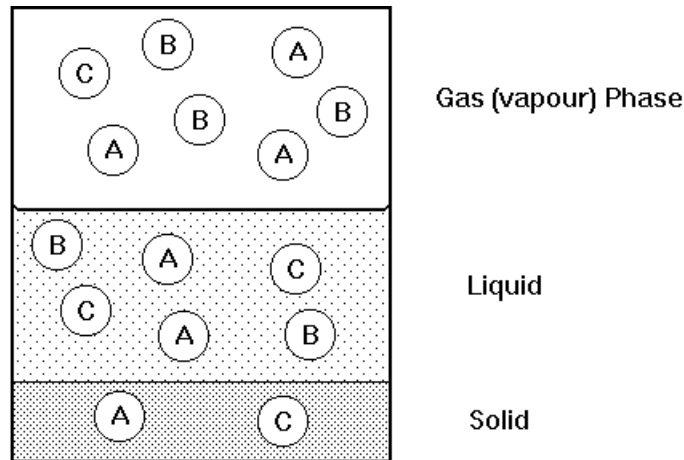
$$\text{HIGH } \mu \equiv \text{LOW probability}$$

.... *Don't Panic !!*

LOW  $\mu$        $\equiv$       HIGH probability

... hence the name “Chemical Potential” since, by analogy with mechanical potential, given the chance, any molecule will tend to move from a state of high  $\mu$  (low  $p$ ) to lower  $\mu$  (higher  $p$ ).

Phase Equilibrium



What is the situation at equilibrium ??

Molecules of any particular species (A say) will tend to move from regions (phases) of high chemical potential to lower  $\mu$  (low probability to high), until an equilibrium situation is reached in which the chemical potential of A is the same in all phases...

i.e. at equilibrium

$$\begin{array}{lcl} \mu_A(\text{in phase 1}) & = & \mu_A(\text{in phase 2}) \\ \mu_B(\text{in phase 1}) & = & \mu_B(\text{in phase 2}) \\ \dots & & \dots \\ & & \dots \text{ and so on.} \end{array}$$

(Important note: This does not mean that  $\mu_A = \mu_B$  , etc...)

Chemical Potentials Vary with Concentration, etc.

In general:  $\mu_i = \mu_i^\circ + RT \ln a_i$

where  $\mu_i$  is the actual chemical potential of species i

$\mu_i^\circ$  is the chemical potential of i under chosen standard conditions

$a_i = \gamma_i[i] = \text{activity of i}$

and the term  $RT \ln a_i$  takes account of the effects of concentration and intermolecular forces.

Chemical Potentials.....

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$a_i = \gamma_i[i] =$  activity of i

In specific circumstances....

(a) For solutions:-

Chemical potential of component A in solution =

$$\begin{aligned}\mu_A &= \mu_A^\circ + RT \ln \gamma_A[A] \\ &\approx \mu_A^\circ + RT \ln [A]\end{aligned}$$

if interaction effects can be ignored (i.e. if  $\gamma_A \approx 1$ ). This is often the case in dilute solutions.

$\mu_A^\circ =$  chemical potential of A when  $[A] = 1 \text{ M}$

So the "standard state" for solutions is a concentration of 1 M.

(b) For liquid mixtures:-

Composition of liquid mixtures is usually expressed in mole fractions ( $x_i$ )

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i$$

Standard state is the pure liquid, for which  $x_i = 1$  and  $\gamma_i = 1$

(c) For gases:-

Composition of gas mixtures is usually expressed in terms of the partial pressures ( $P_i$ , in atm), and we can usually ignore activity corrections since the molecules are too far apart to interact (ideal gas assumption,  $\gamma = 1$ ).

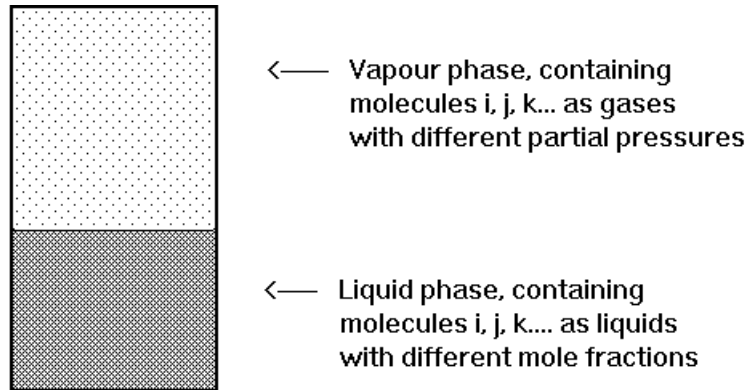
$$\mu_i = \mu_i^\circ + RT \ln P_i$$

Standard state is when  $P_i = 1 \text{ atm}$ .

Example of use of chemical potentials....

### Liquid-Vapour Equilibrium

Imagine a mixture of liquids (e.g. ethanol + water) in a closed container, with a vapour space above.



What is the situation at equilibrium ?

What is the partial pressure (“vapour pressure”) of each of the components in the vapour space ?

At equilibrium, for any component i:

$$\mu_i(\text{liquid}) = \mu_i(\text{vapour})$$

For i in the liquid:  $\mu_i(\text{liquid}) = \mu_i^\circ(\text{liquid}) + RT \cdot \ln \gamma_i x_i$

For i in the vapour:  $\mu_i(\text{vapour}) = \mu_i^\circ(\text{vapour}) + RT \cdot \ln P_i$

So, overall:

$$\mu_i^\circ(\text{liquid}) + RT \cdot \ln \gamma_i x_i = \mu_i^\circ(\text{vapour}) + RT \cdot \ln P_i$$

Re-arrange to give:

$$\begin{aligned} \ln P_i &= \{ \mu_i^\circ(\text{liquid}) - \mu_i^\circ(\text{vapour}) \} / RT + \ln \gamma_i x_i \\ &= - \Delta G^\circ_{\text{vap}} / RT + \ln \gamma_i x_i \end{aligned}$$

since  $\Delta G^\circ_{\text{vap}} =$  standard free energy of vapourization

$$= \mu_i^\circ(\text{vapour}) - \mu_i^\circ(\text{liquid})$$

SPECIAL CASE: What if there is only one liquid ?

Vapour pressure of a pure liquid  $P_i^*$

For a pure liquid:  $x_i = 1$       and       $\gamma_i = 1$  ;       $\ln \gamma_i x_i = 0$

So...

$$\ln P_i^* = - \Delta G_{\text{vap}}^\circ / RT = - \Delta H_{\text{vap}}^\circ / RT + \Delta S_{\text{vap}}^\circ / R$$

This tells us how the vapour pressure of a pure liquid varies with temperature.

If we plot a graph of  $\ln P_i^*$  versus  $1/T$  (lab experiment ?) we get a straight line with slope  $= - \Delta H_{\text{vap}}^\circ / R$  , and can use this to measure heats of vaporization.

A liquid will boil its vapour pressure is equal to (or greater than) the surrounding pressure. Normally this would be 1 atmosphere - though it might be less (e.g. vacuum distillation) or more (e.g. pressure cooker).

The normal boiling point ( $T_b$ ) of a liquid is the temperature when  $P_i^* = 1$  atm.

i.e at the normal b.p.       $P_i^* = 1$  atm

$$\ln P_i^* = 0$$

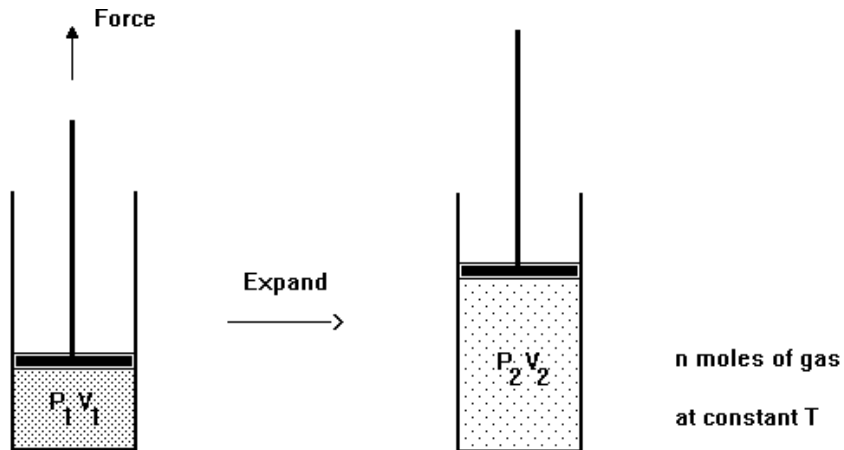
$$\therefore \Delta G_{\text{vap}}^\circ = \Delta H_{\text{vap}}^\circ - T_b \cdot \Delta S_{\text{vap}}^\circ = 0$$

$$T_b = \Delta H_{\text{vap}}^\circ / \Delta S_{\text{vap}}^\circ$$

Why does the Gibbs Free Energy change ( $\Delta G$ ) = maximum work available ?

Examples....

(1) Work done by expansion of an ideal (perfect) gas in a frictionless piston.



Questions; (a) What is the mechanical work done ?  
 (b) What is the change in Gibbs Free energy ?

(a) Mechanical work done during expansion from  $V_1$  to  $V_2$

$$\text{Work} = \text{Force} \times \text{Distance} = \text{Pressure} \times \text{Volume}$$

For a small volume change ( $\delta V$ ), the work done  $\delta W = P \cdot \delta V$

Add up (integrate) all these small increments to give total work done

$$\begin{aligned}
 W &= \int_{V_1}^{V_2} P \cdot dV && \left\{ \begin{array}{l} \text{Ideal gas equation: } PV = nRT \\ \text{so } P = nRT/V \end{array} \right\} \\
 &= nRT \int_{V_1}^{V_2} dV/V \\
 &= nRT \cdot \ln(V_2/V_1)
 \end{aligned}$$

(b) Change in Gibbs Free Energy for the same process

For any process:  $\Delta G = \Delta H - T.\Delta S$

Firstly:  $\Delta H = H_2 - H_1$  (Reminder:  $H = U + PV$ )

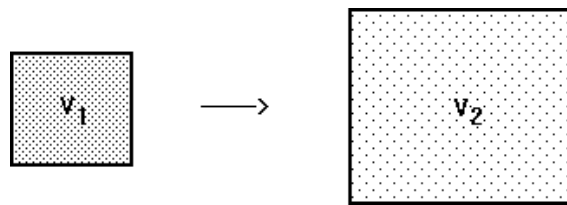
$$= U_2 + P_2V_2 - U_1 - P_1V_1$$

$$= U_2 - U_1 \quad (\text{since } P_1V_1 = P_2V_2 \text{ for ideal gas})$$

$$= 0 \quad \text{for an ideal gas}$$

because: (i) there are no intermolecular forces between molecules in the ideal gas approximation, so no change in potential energy, and (ii) the temperature is constant, so the total kinetic energy of the molecules remains the same.

What is the entropy change ( $\Delta S$ ) for an ideal gas expansion ?



$$\Delta S = R.\ln (w_2/w_1) \quad (\text{per mole})$$

For an ideal gas  $= R.\ln (V_2/V_1)$  since the number of ways the molecules can occupy the space is simply proportional to the available volume.

(True only for an ideal gas - otherwise, intermolecular forces affect the ways the molecules can be distributed. For example, liquids or solids do not expand to fill the space available because intermolecular forces tend to hold the molecules together.)

So, for n moles of ideal gas;  $\Delta S = nR.\ln (V_2/V_1)$

Consequently:  $\Delta G = \Delta H - T.\Delta S$

$$= 0 - nRT. \ln (V_2/V_1)$$

$$= - nRT. \ln (V_2/V_1)$$

$$= - W$$

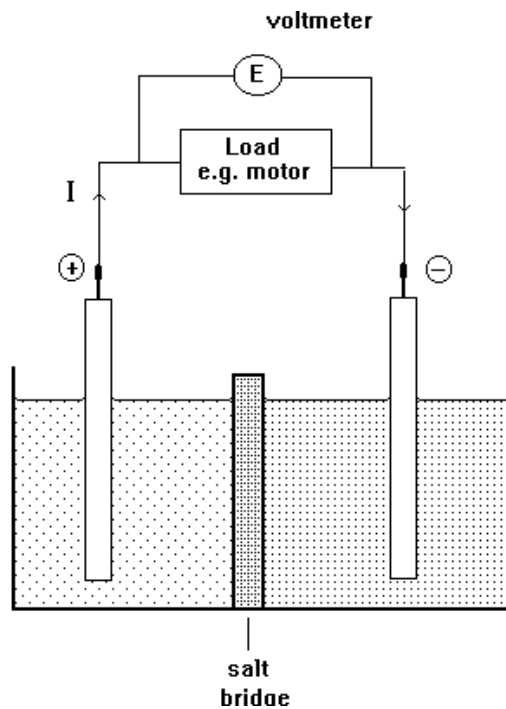
i.e. total useful work gained = total Gibbs Free Energy lost

[QUESTION: Where does this energy come from ??]

(2) Gibbs Free Energy and Electrical Work - the electrochemical cell

An electrochemical cell is a device in which a redox reaction, involving electron transfer, is done in such a way that the electrons are transferred externally (via wires) as an electric current (I), so can do electrical work.

For example: (e.g. Daniell cell -  $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$ )



In general....

$$\text{Electrical work done} = \text{current} \times \text{voltage} \times \text{time}$$

$$\text{current} \times \text{time} = \text{total charge flow}$$

$$\text{charge on 1 mole of electrons} = 1 \text{ Faraday (F)} = 96,500 \text{ Coulomb}$$

For any redox reaction, transferring  $n$  moles of electrons per mole of reaction....

$$\text{in 1 mole of reaction, total charge flow} = nF$$

$$\text{Voltage} = \text{cell potential} = E$$

$$\text{So, electrical work done} = nFE \quad (\text{per mole})$$

From classical thermodynamics (electrochemistry) the change in free energy of the system undergoing this reaction,  $\Delta G = -nFE$

$$\text{So (again), work done} = \text{free energy lost}$$

**Physical constants:**

Quantity	Symbol	Value and units
speed of light	$c$	$2.998 \times 10^8 \text{ m s}^{-1}$
elementary charge	$e$	$1.602 \times 10^{-19} \text{ C}$
Planck constant	$h$	$6.626 \times 10^{-34} \text{ J s}$
Avogadro constant	$N_A$	$6.022 \times 10^{23} \text{ mol}^{-1}$
gas constant	$R$	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Boltzmann constant	$k$	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Faraday constant	$F$	$9.649 \times 10^4 \text{ C mol}^{-1}$
Bohr magneton	$\mu_B$	$9.274 \times 10^{-24} \text{ J T}^{-1}$
nuclear magneton	$\mu_N$	$5.051 \times 10^{-27} \text{ J T}^{-1}$
standard atmosphere	atm	$1.013 \times 10^5 \text{ Pa}$
mass of electron	$m_e$	$9.110 \times 10^{-31} \text{ kg}$
mass of proton	$m_p$	$1.673 \times 10^{-27} \text{ kg}$
Bohr radius	$a_0$	$5.292 \times 10^{-11} \text{ m}$
atomic mass unit	$u$	$1.661 \times 10^{-27} \text{ kg}$
Zero of the Celsius scale		273.15 K
gravitational acceleration	$g$	$9.81 \text{ m s}^{-2}$

**Suggestions for further reading (apart from standard textbooks !)**

Douglas Adams books.

"Engines, Energy and Entropy", J.B. Fenn, W.H. Freeman (1982).

"Maxwell's Demon: Entropy, Information, Computing", H.S. Leff & A.F. Rex (eds.), Adam Hilger, Bristol (1990).

More advanced Stat.Mech. ? (e.g. McQuarrie ?)

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And that really is: **THE END**