

Note 109 : Une approche simple du second principe de la thermodynamique

BOOHAN R. & OGBORN J. (1997) ont construit un programme d'enseignement fort pertinent sur ce thème, pour des élèves du secondaire : Differences, energy and change: a simple approach through pictures (1996) *School Science Review*, **78** (283).



Differences, energy and change: a simple approach through pictures

Richard Boohan and Jon Ogborn

The project 'Energy and Change' has led to a range of teaching materials for use in secondary schools. These provide new ways of teaching about energy and about chemical and physical changes, in the light of the Second Law of Thermodynamics.

Pupils thinking about differences: a scenario

Let us begin with some examples showing what might go on in the science classroom, over several years, using a new way of thinking about physical and chemical change. The examples are based on what we have seen happening in trial classes, but they are compressed and idealised for the sake of illustration. And at the end they look forward to the future.

Some eleven year-olds are working on making pure substances. The subject matter is quite orthodox: filtration, dissolving, distillation, crystallisation. Some activities are less instantly recognisable.

In one activity the pupils are given half a dozen abstract-looking pictures such as those in figure 1 which represent a solid and a liquid becoming a solution, and a liquid evaporating. Other such pictures show solids mixing, liquids mixing and so on. Pupils are asked to match a number of processes, such as a

puddle in the street drying up, wet washing hanging out to dry, 'instant' coffee being made, and dirty plates being washed up after lunch, each to the picture that best represents it. Of course, in doing so they practise using various scientific terms: 'solution', 'vapour' and so on. But one can also overhear them using less familiar terms:

The coffee spreads out into the hot water until it's all the same.

There's a lot of water in the wet washing and not much in the air, so the water spreads out into the air.

The teacher occasionally asks unfamiliar-sounding questions, for example, 'What could be an example of

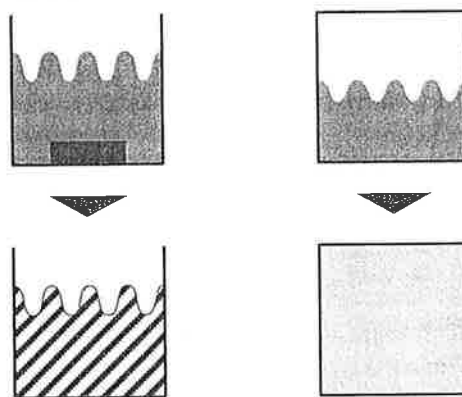


Figure 1

Two abstract pictures: a solid and a liquid turn into a different liquid; a liquid turns into a vapour.

ABSTRACT

New materials, published by the ASE this year from a Nuffield Foundation Project 'Energy and Change', suggest simple and effective ways of going about the seemingly impossible task of teaching about the direction of physical and chemical changes from an early age. The National Curriculum includes many processes, from pollution to respiration, which need to be understood from the point of view of the Second Law of Thermodynamics. The article describes how to get started on such processes, in a simple way with help from pictures.

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that picture, but going backwards?' and for the evaporation picture may, after some discussion and argument, get answers such as water drops condensing on a cold can of coke taken out of the refrigerator. The class might then talk of water 'bunching together' instead of 'spreading out'. Another unfamiliar question might be, 'When does that tend to happen, all by itself?', with a reminder of earlier activities on processes, like dirt spreading out into water or smells spreading out in the air, which 'happen all by themselves'. Answers, for the wet washing drying, might be that it happens all by itself on warm days, dry days or windy days. A pupil, remembering previous activities and the knowledge-slogans learnt from them, claims that 'matter goes by itself from where there's a lot to where there's not'. The talk is in essence about differences of concentration of matter, with matter spreading from higher concentrations to lower.

A year later

The same class now has a different teacher, but one who knows what has gone before. They are discussing central heating systems and refrigerators, after some traditional work on temperature and thermometers during which pupils display all the usual confusions of heat and temperature, and the belief that insulation makes things warm.

This time they are discussing which of the abstract pictures (see figure 2) best represents a room heated by radiators. They know that darker shading means hotter and lighter shading means cooler; that arrows in or out are flows of energy, and that 'happens by itself' is represented by a triangular arrow 'downhill'

on the bottom of the box (as in *a* and *b*) while 'has to be made to happen' has an 'uphill' arrow on the top of the box (as in *e* and *f*). Each box, as in figure 1, shows a 'before' and an 'after' state of affairs, with the small black triangle indicating the direction of time.

Some argue for picture *a*: 'The hot room loses energy through the windows, and will get cooler', or, 'The hot radiator gives energy to the room and gets colder'. Others favour picture *e*: 'Energy comes from the radiator and makes the room hot'. After agreeing that there is something in all these ideas, the class mostly settles on picture *c*: 'The room is kept hotter than outdoors, losing energy through the windows and getting it from the radiator'.

Several pupils still think in absolute terms, saying such things as 'Hot things lose energy'. Others focus more clearly on differences: 'Energy goes from the hotter one to the cooler one', helped by noticing that energy goes from the radiator to the room, but from the room to outdoors.

Later, a discussion of refrigerators gradually identifies picture *f* as showing the refrigerator just after it has been turned on, and picture *b* as showing what happens when it is turned off. The class agree that cold things in warmer surroundings warm up just as hot things cool down, 'all by themselves', but that something has to be done to make the inside of the refrigerator colder than the room. There is surprise at how similar the best picture – picture *d* – is to that for a heated room. The teacher says something about 'running hard to stay in the same place' and 'steady states' and reminds them that their bodies stay warmer than the surroundings.

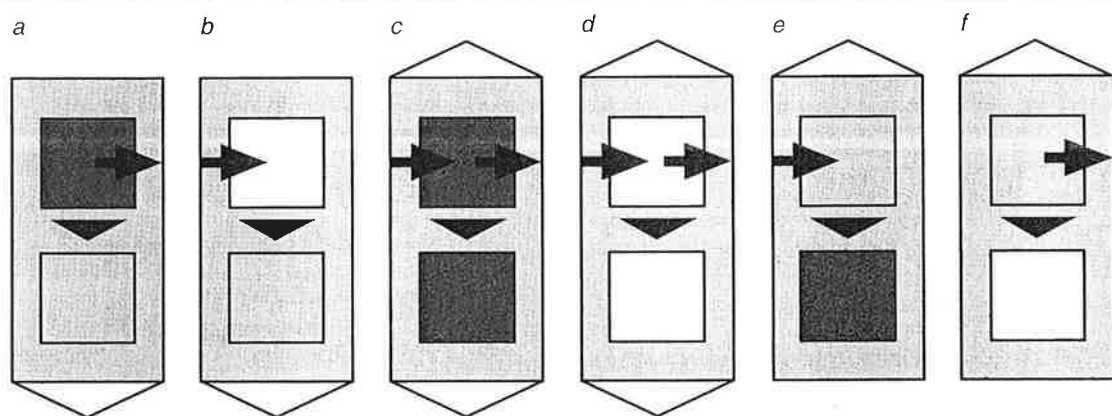


Figure 2
Abstract pictures of cooling, warming and keeping warm.

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The talk is again of differences; this time of differences of hotness, coldness or temperature. The teacher remarks that something hot is quite like matter squeezed in a small space; it has a large concentration of energy, in place of a large concentration of matter. *Energy goes by itself from where it's hot to where it's not*, becomes a new piece of slogan-knowledge. It is becoming clear, little by little, that the distribution of both matter and energy is driven by differences; that in doing so these differences are liable to disappear; but that differences can be created and maintained as well, although this won't happen 'all by itself'.

Mention is being made of matter being made of particles (molecules, atoms or ions) fairly early, around age 12. Our class sees computer simulations, such as that suggested by figure 3, of particles moving at random, always destroying any initial pattern and in particular evening out concentration differences. They also see a simple model of the spreading of energy from hotter to colder, using a simulation like that in figure 4, in which particles are imagined to have just two states of energy ('high' and 'low'), so that energy 'diffuses' from regions where it is most concentrated to regions where it is not. And they are told that there is nothing difficult about this; that really it is just obvious. Matter or energy spontaneously goes from the 'haves' to the 'have-nots' just because the 'haves' have it to give and the 'have-nots' haven't. Translating this into the language of increasing numbers of micro-states is for much later – for the moment it is just an obvious and necessary consequence of matter being made of very many tiny particles whose behaviour is random.

Some years later

The class is tackling aspects of chemical equilibrium. In between they have thought about potential energy stored in stretched springs, and in the 'spring' of the Earth's gravitational field when objects are lifted. The losing of potential energy, when springs collapse or objects run down hill, has become yet another of those events which 'happen all by themselves', the reason being that the energy gets spread out amongst lots of particles so that there is no way it will return just by chance. Potential energy differences are now yet another kind of difference which can drive changes, is liable to be destroyed, but can be created or maintained.

Let us suppose pupils are studying smelting metals. An easy example is the production of mercury from its sulphide ore, cinnabar, just by heating it, a process known for over 3000 years. The bonds between

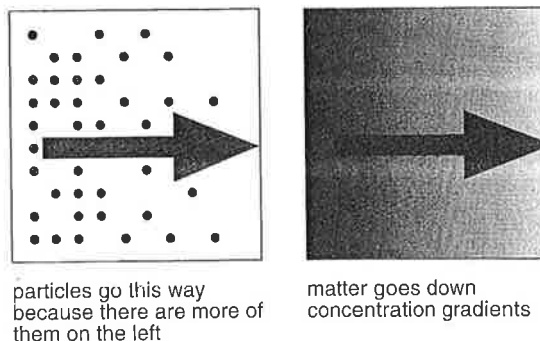


Figure 3
Simulation of diffusion of matter.

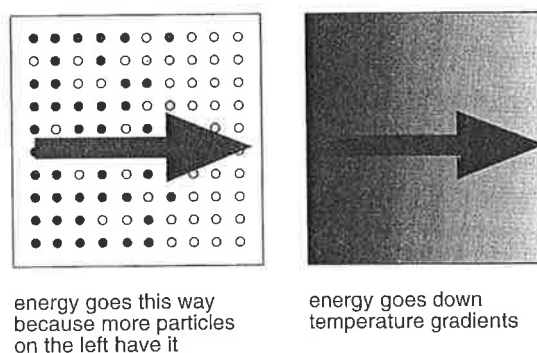


Figure 4
Simulation of flow of energy (an 'on' particle can turn an 'off' one next to it 'on' and itself go 'off').

mercury and sulphur have to be broken, with an increase in potential energy at the expense of the thermal surroundings. Such an increase doesn't happen all by itself. But the sulphur (and mercury) can evaporate, spreading out, and this can be enough to drive the process if the surroundings are hot enough. There are also more particles at the end of the process than there were at the start, another kind of difference which helps drive any process. Figure 5 shows a triplet of icons which represent the competing tendencies. In some earlier work the students probably used the first two icons – breaking bonds and spreading out – to represent the evaporation of water.

A different case is the recovery of iron from iron oxide using magnesium, in the thermite process. Magnesium bonds so strongly to oxygen that the net effect of tearing apart the bonds between iron and

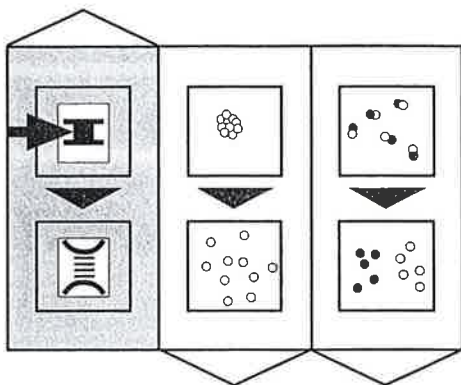
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Figure 5
Smelting cinnabar: bonds broken; particles spreading out; more particles made.

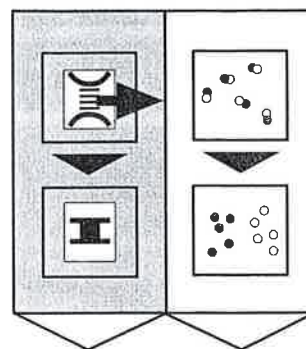


Figure 6
Thermite process: net bond formation; more particles made.

oxygen and making new ones between magnesium and oxygen is to go downhill in potential energy. The number of particles increases a little, too (one Fe_2O_3 and three Mg become three MgO and two Fe). Figure 6 shows that on both these counts the process is downhill, going 'all by itself' once started off.

Finally, the conventional method of smelting iron using carbon is discussed. Unlike magnesium, carbon bonds less strongly to oxygen than does iron, so the net effect, as before in figure 5, is that bonds must be broken and potential energy stored, going uphill. What makes this process work at all is that carbon dioxide – despite the efforts of humanity in the past two hundred years – is still very dilute indeed in the atmosphere, so that the spreading out of carbon dioxide gas into the atmosphere helps the process to happen, by going strongly downhill. The number of particles increases too (two Fe_2O_3 and three C become four Fe and three CO_2). Thus figure 5 serves for both processes.

In biology lessons the class will have seen how oxygen attaches itself to haemoglobin in the oxygen-rich environment of the lungs, and detaches itself again in the oxygen-poorer environment of muscle tissue, another example of differences driving changes, this time in both directions. They may be about to hear how ATP molecules 'fall downhill' when one phosphate group is grabbed strongly by water in the tissues, making possible other 'uphill' changes which create a difference such as increasing the concentration of ions in nerve cells.

Later still...

Those students who study science at a more advanced level will start attaching numbers and sometimes formulae to these and other pictures (for example, pictures showing particles mixing). These numbers may be entropy changes due to various parts of a process. Or they may be Gibbs free energies per mole, which some may learn to call 'chemical potential difference' and expect to see traded against potential energy differences. They will learn to calculate the voltage of an electrochemical cell, by seeing it as the electrical potential difference caused by electron transport under a chemical potential difference, which has grown just large enough to balance that chemical potential difference.

Those who stop studying more science after age 16 may meet little or no quantitative Second Law thinking. But they will have met, over these years, quite a lot of *qualitative* Second Law thinking. They will know that there are spontaneous processes, and that parts of processes which are not spontaneous must be driven by others which are ('at least one must go downhill', we may say, as the qualitative version of the Second Law). And they will know that what makes a process happen all by itself is some kind of 'spreading out', of matter and/or energy. They will know that differences drive changes; that you need a difference to make a difference; that somewhere in every process a difference must be destroyed. If their science teachers collaborate well enough they will have seen that photosynthesis can be thought of as combustion in reverse. They will have compared the steady state of

their own bodies to that of a heated room. And, if their teachers found time, they will have heard stories about the vast differences in the Universe, created by its expansion, which are the source of all the processes which sustain life itself.

The project 'Energy and Change'

The scenario above represents thinking developed in the project 'Energy and Change' which was supported by the Nuffield Foundation. A range of teaching materials were developed in a school and tried out as they were produced, both in that school and in a variety of other schools. A set of three booklets is available from the ASE (Boohan and Ogborn, 1996) and a pack of about eighty classroom activities together with an INSET pack is also available (Boohan, 1996).

The project developed out of an urgent need and an awkward dissatisfaction. The urgent need was that very desirable changes in the science curriculum, giving important and highly relevant processes such as pollution, energy production and conservation, and the maintenance of life a proper prominence in the science curriculum, had not been accompanied by the development of a language adequate to talk about or understand them other than superficially. All of these processes, together with many other matters always central to the curriculum from respiration to combustion, need to be understood in the light of the Second Law of Thermodynamics. And yet, this seemed hopeless. How many teachers would themselves claim to understand thermodynamics, let alone have any clear and simple ways of talking about it with younger secondary pupils?

The awkward dissatisfaction was with the current state of discussion about the teaching of energy. Teachers, we felt, were becoming paralysed by a series of prohibitions: 'Don't speak of heat as a kind of energy'; 'Don't speak about transforming energy, talk about transferring it'; 'Don't say that energy causes change'; and so on. We did not think that any more prohibitions, however well-meant, would do any good. What was needed instead was something positive; some new things that one *could* say, with confidence and with a good chance of being understood. Ideally, any new ways of talking about energy and change should carry on smoothly into later work, where they would develop rather than be jettisoned as over-simplifications. And lastly, they had better be right!

Differences

From the outset, we had the idea that, instead of trying to talk about entropy changes, we could talk about *differences*. Any state of low entropy is one in which differences exist – the distribution of matter and energy is in some way uneven. So instead of saying that the entropy tends to increase we could say that differences drive changes which tend to diminish those differences. An obvious place to start would be differences of concentration, and then of temperature (seen as concentration of energy), as well as pressure differences, followed by potential energy differences of various kinds, gravitational and electrical. This suggested likening potential energy stores to stretched springs, so that gravitational potential energy became that of the 'gravity spring' and the energy stored when chemical bonds were pulled apart became that of 'chemical springs'. By this stage, the value of the metaphor of 'going downhill' for spontaneous changes had become obvious.

The idea of relating changes to the destruction (and creation) of differences seemed to have several advantages. Human beings notice differences – light and dark, loud or quiet – rather readily. That the cause of a change gets used up in the process seems a natural thought, and one that can be usefully related later to the idea of using up fuels. It seemed easy to understand that differences vanish all by themselves just because of the random behaviour of molecules 'going nowhere in particular'. And it meant that we could try to bring potential energy differences, which were there in the curriculum in any case, into the same scheme.

Looking ahead, we could see that these ideas could develop fairly smoothly into the conventional more advanced ways of describing changes, especially in chemistry and biology, and could in particular exploit the notion of chemical potential difference, if required. Because not all our readers will be comfortable with this notion we will illustrate its meaning and use through an example, the equilibrium of the Earth's atmosphere.

Figure 7 suggests a way of thinking about the atmosphere. The gravity hill sloping downwards is 9.8 J per kg per metre. For one mole of nitrogen this amounts to 0.28 kJ per mole per kilometre (not very much, which is why there is still plenty of air on mountains 1000 m high). Gravity pulls the air down towards the Earth. But the air does not end up all lying around our feet, because that would produce a large concentration gradient upwards, and the air would

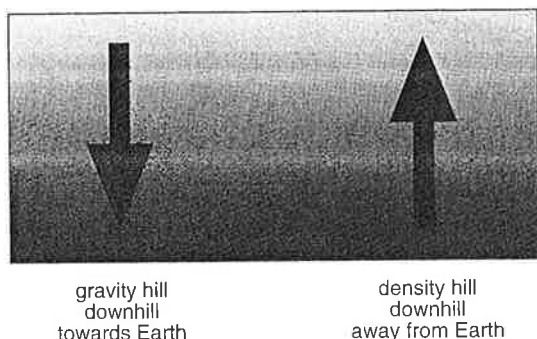
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Figure 7
The Earth's atmosphere, with a gravity hill running down towards the Earth and a density hill running down away from the Earth.

spontaneously diffuse back up again. Therefore the atmosphere ends up with two equal sloping hills, a gravity hill running downwards towards the Earth and a concentration (or density, or pressure) hill running downwards *away* from the Earth. When the two hills slope equally, the atmosphere is in equilibrium.

The concentration slope can also be expressed as an energy difference: the potential energy difference which would produce the same driving effect as the difference in concentration. It is, for N particles of an ideal gas moving from one concentration to another, given by:

$$\mu = NkT \ln(\text{ratio of concentrations})$$

where T is the temperature and k is the Boltzmann constant. μ is called the *chemical potential difference*. A concentration (density, pressure) ratio of about 4 to 1 gives an energy of 2.8 kJ, enough to raise a mole of nitrogen by 10 kilometres. So at the height at which jet aircraft fly, the air is about four times thinner. The gravity slope for nitrogen is 0.28 kJ per mole per kilometre *downwards*, and the chemical potential slope is 0.28 kJ per mole per kilometre *upwards*.

The chemical potential difference is the same as the Gibbs free energy per mole. So the chemists' rule that the Gibbs free energy per mole decreases in any spontaneous reaction is the same as saying that reactions go down chemical potential hills.

All this suggests how our story about 'differences' can develop into a respectable scientific account.

Abstract pictures

A key, but fundamental, difficulty with thermodynamic thinking is that it applies very generally, requiring one to see very different-seeming things – such as a heated room and a person's warm body – as basically similar. When we started work, we had an idea about how to handle this which did not survive exposure to pupils for very long. It was to invent 'prototypes' for crucial kinds of process – for example, hot tea cooling for thermal flow of energy, or smells spreading for diffusion. As we should have guessed, pupils saw these as particular cases, not as cases of something more general. Words to describe the general case were too clumsy, so we were driven to making abstract pictures like those used in the scenarios above.

We found that these were easier to use than anyone expected, and the more shorn of detail the better. One teacher said, after using them for a while:

I've been very surprised at the number of times some of the less able children have come up with the right answer... I'm convinced they are able to follow those pictures and apply them to new situations.

A way to think about them is as an inventory of the kinds of thing which may be going on in any process, which will help or hinder it to happen (aspects which happen 'all by themselves' or 'need to be made to happen'). Take combustion, for example.

- ☐ Are particles spreading out into a larger volume?
Yes.
- ☐ Are more particles being made?
Probably, if a complex molecule is being burnt.
- ☐ Are chemical bonds being sprung shut?
Yes.
- ☐ Are any being torn apart?
Yes, again.

Each picture corresponds to some term in an equation for the total entropy change, or, equivalently, for the change in Gibbs free energy per mole. Thus the entropy of an ideal gas contains a term proportional to the logarithm of the volume, because particles tend to spread out into larger volumes (lower concentrations).

That, of course, is the way to think about the pictures in the end. But how to get started? Our idea is that, over time, in a large number of contexts which naturally occur in the curriculum, from purification, through heat and temperature, to discussions of respiration or of the weather, there are opportunities to identify component aspects of processes, which by 'happening all by themselves' or not, help or hinder

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that process from happening. And each time, with a picture to remind one of it another time, a crucial bit of thermodynamic thinking has been identified.

We very much hope that these pictures will not settle into a new orthodoxy – yet one more thing to learn and repeat back. We see their value as provoking useful discussion with and between pupils about what is or may be going on in a change, whether it be perspiring or the building up of a storm. No doubt teachers can improve on them for their own purposes, preferably in discussion with pupils about what one might want to represent. What the pictures must do is to represent the essential mechanics of part of a physical process, including where energy is going, and they must indicate which way round the event is happening together with whether it is spontaneous or not. We look forward to seeing your ideas for how to do better!

Where are we now?

The scenario with which we began owes something to experience of trying these ideas out with pupils in years 7 to 9, in which a beginning could be made. But there was not time to follow through to later years, nor to

have pupils experience the work in several successive years. Thus it also wishfully projects beyond what we know can be done to what we hope can be done.

With this very partial basis of evidence to go on, we believe we have found a constructive way forward from the current situation, in which because it seems 'obviously' impossible to use any Second Law thinking the poor old 'energy concept' is variously mangled and distorted to do the job. Energy can now be seen as that which limits the magnitude of possible changes, and which plays a part – but only a part – in deciding if a change can happen by whether it is getting more widely spread around or is needing to be concentrated, often in torn apart bonds. With a bit of luck, in place of a variety of prohibitions against badly-understood so-called confusions, we may have a simple language for talking about what's going on when things happen.

If this is right, then it is no objection that these ideas are 'not part of the National Curriculum'. In fact they are, because the National Curriculum requires us to discuss important processes from pollution to digestion which require these ideas. All that remains is to make sure that examiners can recognise correct answers to their questions!

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