Introducing logic in chemical thermodynamics courses

Introduciendo lógica en los cursos de termodinámica química

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Abstract

The introduction to an alternative, logic-based course of chemical thermodynamics is presented. The author trying to combine logic and thermodynamics in a way attractive to students.

***Key words**: logic**,** chemical thermodynamics, active method of teaching*

Resumen

Este artículo presenta la introducción de un curso alternativo y lógico de termodinámica química. El autor trata de combinar estos aspectos del curso con métodos de aprendizaje atractivos para los estudiantes.

Palabras clave: termodinámica química, lógica, métodos activos de enseñanza

INTRODUCTION

When Pooh, Piglet and Rabbit decided to steal Baby Roo and hide him, Rabbit wrote a plan. Here is how it began:

1. General remarks. Kanga runs faster than any of Us, even Me.
2. More general remarks. Kanga never takes her eye off Baby Roo, except when he´s safely buttonerd up in her pocket.
3. Therefore. If we are to capture Baby Roo, we must get a Long Start, because Kanga runs faster than any of Us, even Me. (See 1.).
4. …

Rabbit may have been mistaken about Kanga's abilities. Let us assume he was - his assumption or premise "Kanga runs faster than any of Us, even Me" was false. Then did his conclusions make any sense? Some would say: "If a premise is false just ignore it - look for true premises only". This advice is generated by a type of reasoning called *induction*. Inductivity look for reliably established facts (true premises) and the conclusions they draw are essentially generalizations of those facts. On seeing the 101st white swan, they conclude: "All swans are white". It is as if whiteness entered inductivity's minds, took the shape of a conclusion and remained there. The etymology of "induction" reflects this inward movement. No outward movement seems to take place.

Then the 102nd swan proves black and a revolution in science occurs. Surprised and excited, inductivity draw another conclusion: "Most swans are white. Some are black". Again, no outward movement is detectable.

Before discovering the black swan, a scientist wrote:

All swans are white.

Therefore, no black bird is a swan.

Here an outward movement can be seen - the conclusion goes from the scientist's mind to any black bird and endows it with the quality of not being a swan. In the same way, Rabbit's conclusion went from his mind to future actions accompanying the abduction. In Latin, an outward direction is expressed by the prefix "de-" so this type of reasoning is known as *deduction*. Another name for deduction is *logic*. Note, however, that deduction (logic) is not independent of induction - before getting out you must get in.

The curious thing about deduction (logic) is that it is not very interested in whether the premises and the conclusion are actually true or false. After the discovery of the black swan, the scientist who had proclaimed that no black bird was a swan commented: "My argument is still valid. True, swans are not all white, but if they *were*, no black bird *would* be a swan". This is typical of logicians. The premise "All swans are white" proved false. Then the conclusion "No black bird is a swan" proved false as well. Yet the logician continued to call the argument *valid* and even gave a reason for that: If the premises *were* true, the truth of the conclusion *would* be guaranteed. This understanding of "validity" sounds strange but perhaps it is useful. It allows us to immediately start building some science, although based on uncertain premises, rather than just waiting for the premises to become established facts.

Logic is the study of valid arguments. In other words, logicians try to distinguish valid arguments from invalid arguments. We have just seen what validity means in logic, but then what is an argument? The above examples suggest that an argument has one or more premises and a conclusion. In advancing an argument one assumes that the premises support the conclusion - the relation of support is signalled by such terms as "therefore", "thus", "consequently" etc. Consider the argument:

Initially, the water in the glass is in equilibrium.

Then it undergoes a change (e.g. someone drinks it).

Therefore, the surroundings of the water have also undergone a change.

The premises are "Initially, the water in the glass is in equilibrium" and "Then it undergoes a change". "Therefore" is the sign of the argument and "The surroundings have also undergone a change" is the conclusion. Is the argument valid? Obviously yes - the water will remain in equilibrium until some change in the surroundings disturbs this equilibrium.

Consider another argument:

Friction is a force.

All forces produce acceleration.

Therefore, friction produces acceleration.

The premises are "Friction is a force" and "All forces produce an acceleration". "Therefore" is the sign of the argument and "Friction produces an acceleration" is the conclusion. There is something in the *form* of the argument which convinces us that the argument is valid, although non-physicists may not be able to imagine the acceleration caused by friction and may even not know what acceleration is. So an argument may be valid even if nobody knows what the premises and the conclusion really assert.

The last two arguments differ. The former (about the system in equilibrium) owes its validity to an observed regularity in nature - if something is disturbed, something else disturbs it. The latter argument (about friction) is valid because its *form* is recognizable as valid by our minds, independently of the content of the premises and the conclusion. It makes sense to call the former type of argument *content-argument* and the latter *form-argument*. Traditional logic deals with form-arguments whereas in natural sciences content-arguments are predominant.

One often advances arguments without stating all the premises. This is unavoidable - some premises may be so obvious that it would be too tedious to spell them out. Let us try to find the suppressed premise in the following argument:

If enzymes can shift chemical equilibrium, the second law is false.

Therefore, enzymes cannot shift chemical equilibrium.

Here I must digress and explain what it is like for an enzyme to shift or not to shift chemical equilibrium. It is well known that chemical reactions are bidirectional - reactants are converted into products, in the forward direction, but at the same time products are converted into reactants, in the backward direction. (To account for this, chemists place the sign $\leftrightarrows$ between reactants and products as in $A+B \leftrightarrows C+D$, where A and B are reactants and C and D are products). At equilibrium, the rate of the forward process is equal to that of the backward - for that reason the amounts of all participants in the reaction do not change with time. Then you add an enzyme which is a highly effective catalyst - it accelerates the forward process, say, 1387 times. In other words, the rate of formation of products increases 1387 times. Now if your enzyme is not to disturb the equilibrium, it must accelerate the backward process by the same factor, i.e. 1387 times again! Then you declare that the enzyme *does not shift the equilibrium*. However you may assume that the enzyme does not accelerate the backward process at all - for some reason it refuses to convert products into reactants. Then you say that the enzyme *shifts the equilibrium* towards products.

Now the (explicit) premise in the above argument says that an enzyme which shifts the equilibrium would make something called "the second law" false. Then the conclusion is straightforward: enzymes cannot shift chemical equilibrium. Why does the conclusion sound so confident? Because there is a suppressed premise that nobody doubts: the second law *cannot* be false. The law referred to is the second law of thermodynamics - scientists believe that what it states is absolutely true. Even if all enzymes were observed to be able to shift the equilibrium, scientists would simply ignore the observation - absolute truths always win. The situation is curious because almost all of the countless enzymes in our body accelerate only the forward process whereas the backward one does not take place at all.

Let us see if the following argument is valid.

A liquid powers an engine.

The engine lifts, one by one, ten weights to an elevated platform.

Therefore, the liquid is a fuel (undergoes a transformation in the engine).

Assume the premises are true - the liquid does power the engine and the engine does lift the weights. Can we be sure that the conclusion is true? Remember one-time waterwheels. Water powered them and they were able, if properly harnessed, to lift any number of weights. Yet the water was not a fuel - it bumped into the wheel and then left unchanged. The wheel did not transform it into anything else.

The waterwheel example forces us to say that the argument is invalid. Even if the premises are true, the truth of the conclusion is not guaranteed. An argument is valid when, if the premises are true, the truth of the conclusion is guaranteed.

Now I am going to construct a more complex argument by adding a new premise to the original two:

A liquid powers an engine.

The engine lifts, one by one, ten weights to an elevated platform.

The liquid is not a fuel (undergoes no transformation in the engine).

Therefore, the liquid flows from a high to a low site.

This argument is valid - unless some intricate exception is meant, the engine is a waterwheel. Now let us advance an argument identical in any respect except that "liquid" is replaced by "heat":

Heat powers an engine.

The engine lifts, one by one, ten weights to an elevated platform.

The heat is not a fuel (undergoes no transformation in the engine).

Therefore, the heat flows from a hot to a cold site.

"The heat undergoes no transformation" implies that the amount of heat that enters the engine is equal to the amount of heat that leaves it (just as water behaves as it interacts with the waterwheel). I replaced "high" and "low" with "hot" and "cold" for obvious reasons - water flows from high to low whereas heat flows from hot to cold.

Despite the changes, the two arguments are identical in form. Accordingly, since the liquid argument is valid, so must be the heat argument. Note the formal identity of the two arguments - if it had not been for *this* identity, thermodynamics would have undergone a different development (we shall discuss this soon). The conclusion of the last argument is in fact one of the most famous principles in science - the second law of thermodynamics. Let us state it in this way:

A heat engine would not work unless the heat flows from a hot to a coldsite.

It is *this* law that enzymes would falsify if they ventured to shift the equilibrium.

Let us reconsider the premise "The heat undergoes no transformation". It is false. In heat engines, the heat acts like a fuel - the engine transforms heat into another energy and the process of transformation is called production of work. If, for instance, the engine lifts a weight, some heat disappears and then one finds it transformed into the potential energy of the lifted weight. This does not happen to falling water, so "the liquid undergoes no transformation" is a true premise. The situation is curious. We have two premises identical in form and yet "the liquid undergoes no transformation" is true whereas "the heat undergoes no transformation" is false. The *contents* of the premises make one of them true and the other false. Then how about the conclusions? Are we right to suspect that the true premise (about water) generates a true conclusion whereas the false premise (about heat) generates a false conclusion? Remember that the conclusion we are inclined to suspect as false is the famous second law of thermodynamics (see above).

This is an extremely important but also extremely difficult problem. I would call it the fundamental problem of thermodynamics. We shall have to resolve it somehow. For a start, we could try to resolve the symmetrical problem for the liquid. Assume the premise "The liquid is not a fuel" is false - replace it with the premise "The liquid is a fuel, e.g. gasoline":

A liquid powers an engine.

The engine lifts, one by one, ten weights to an elevated platform.

The liquid is a fuel, e.g. gasoline.

Therefore, the liquid does not have to flow from a high to a low site.

The conclusion changed in accordance with the new premise. Yet the second law does not allow us to modify the heat argument in a symmetrical way. The following argument is *forbidden*:

Heat powers an engine.

The engine lifts, one by one, ten weights to an elevated platform.

The heat acts like a fuel (undergoes transformation in the engine).

Therefore, the heat does not have to flow from a hot to a cold site.

In fact, the second law says: "Although the heat acts like a fuel, it still has to flow from a hot to a cold site. Otherwise the engine would not work".

So far I have failed to mention any particular heat engine. The next argument will fill the gap.

A spring in equilibrium contracts and then restores its initial equilibrium length.

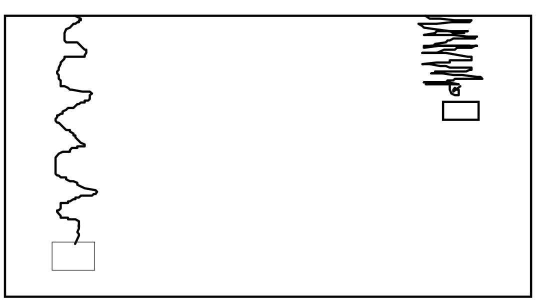
No force has been applied to the spring.

Therefore: ?

Inductivity may find the premises contradictory - if you don't push the spring, how could it contract? Logicians may also find the premises contradictory but they always imagine a world where all the premises are true. In this imaginary world anything but a force is allowed to contract the spring. Logicians pick out "heating" and "chemical action" and write:

Therefore, contraction may have been caused by heating or some chemical agent.

This type of contraction exists in the real world as well. Look at the suspended spring drawn in fig. 6A in a paper with the fearful title "Physical Chemistry of Biological Free Energy Transduction as Demonstrated by Elastic Protein-Based Polymers" (D. Urry, J. Phys. Chem. B 1997, 101, 11007-11028). Here is the essence of the picture:



Temperature increases →

On the left, the temperature is low and the spring (rather, this is a spring-like protein) stretches up to the ground. We see large pockets between the rings - they are filled with water according to the text. Curiously, someone has hooked a weight into the lower end of the spring.

As we move to the right, along the abscissa, the temperature rises and the spring gradually contracts. At 60 ^{0}C the contraction is complete and the weight is lifted. No pockets anymore - water must have been expelled from them.

Let us repeat the process. We unhook the lifted weight, leave it on some elevated platform (not shown in the picture) and remove the heater. The spring cools and stretches to the ground again. Then we hook another weight, fetch the heater etc. - the spring will lift as many weights as we wish. (Of course this is an idealization - we ignore the long-term process of wearing out). We do have some idea of a heat engine now, although this particular "crane" does not seem very useful for the moment.

From where to where does the heat flow? In order to make the spring contract, we warm it - in this step the heat obviously flows from the heater to the spring. Then the spring stretches as it cools - the heat flows from the spring the surroundings. Ultimately, the heat flows along the following route:

Heater → spring → surroundings

Remember the second law - in this case it takes the form

The spring would not work unless the heat flows from the heater (hot site) To the surroundings (cold site).

Strangely, the second law may prove true although it is based on a false premise. But we shall have to test other heat engines. At least 101 heat engines should be tested. Remember the swan story. And the 102nd heat engine may not need a heater - e.g. the temperature is the same everywhere and yet the engine is working. Then the second law would instantly die, just as the wisdom "All swans are white" died. Such things do happen in science.

The spring is a protein, and proteins are synthesized by living cells. How could a cell use a protein which contracts on heating and stretches on cooling? Let us turn the hands of time all the way back to the beginning of life, about four billion years ago. We see our spring - rather, a microscopic snippet of it, with only two rings and one pocket - inside a primitive cell mooning around in a little pond. It is hot during the day and the snippet keeps a compact, pocket less form. At night, as it gets colder, the snippet relaxes - the pocket opens and swells while water invades it.

All the cells in the pond - those which synthesize snippets and those which don't - badly need ATP. This substance (ATP is an acronym - the full name is adenosine triphosphate) is very precious and can be obtained as two molecules precursors, ADP (adenosine diphosphate) and P (inorganic phosphate), combine. That would be an ordinary chemical reaction (ADP + P→ATP) if both ADP and P were not enclosed in shells of water molecules - so thick and stable that ADP and P simply cannot approach one another. In order for ADP and P to be able to combine, something must strip them of the water shells.

This something is in fact the snippet's pocket where a host of growths are greedily waiting for an incidental ADP (or P) molecule to enter. As soon as this happens, the growths destroy the visitor's water shell and use the material for tiling themselves. The denuded ADP molecule remains stuck between the growths.

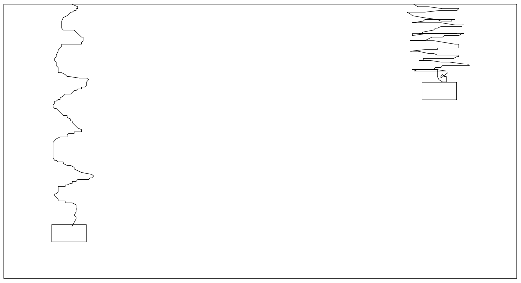
The same could happen to a P molecule and if the two dehydrated particles are close to one another, they easily react and form ATP. But the precious product remains stuck between the growths.

Not forever. In the morning, as it gets warmer, the pocket begins to shrink and eventually expels water together with any alien substances. The cell obtains one invaluable ATP molecule. So cells which synthesize snippets can also synthesize ATP. They survive. The rest suffer and get extinct in the end. Biologists call this natural selection.

Let us skip a billion years and examine a younger pond, only 3 billion years old. (Volcanic eruptions, comets and asteroids have obliterated the previous one). Some of the cells are similar but in others our snippet works differently. Small modifications in its structure have made it able to contract even in the absence of heating. We see pockets squeezing out ATP several times per minute! That is a great advantage. Cells of this type have more ATP at their disposal and survive while others get extinct. Natural selection never stops.

What makes the modified snippet contract? Remember the conclusion: "Therefore, contraction may have been caused by heating or some chemical agent". It seems that the latter prophecy has been fulfilled.

To learn more about this, see fig. 16A in the same J. Phys. Chem. paper. Again, the spring is stretched on the left but gets shorter as we move to the right along the abscissa. The temperature remains constant all along but the solution surrounding the spring becomes more and more sour:



acidity increases →

Someone is pouring, in small portions, hydrochloric acid onto the spring. In fact he/she is adding positively-charged protons and negatively-charged chlorine particles. Only the protons are essential - they react with the spring and cause contraction. (The mechanism is quite interesting - we shall discuss it in detail later).

If the spring from fig. 16A is the right analogy, the chemical agents that cause our snippet to contract and synthesize ATP are protons. But who pours protons into the cell? Who removes them afterwards so that the snippet can stretch again and accommodate other ADP and P molecules?

We shall need some more knowledge to be able to reply to these questions "comme il fault". Still I can give an anticipating answer: Nobody. The spring is very large and we must add half a glass of acid to invoke contraction. The snippet is much smaller and can contract as only one or two protons incidentally bump into it. Then the protons incidentally leave the area and the snippet stretches again. No pouring is needed.

If somebody asked you to explain the difference between "macroscopic" and "microscopic", you could say this: "For instance, you need to pour half of glass of acid onto the macroscopic spring in order to make it contract. But you don't need to pour acid onto the microscopic snippet".

I am boldly skipping another billion of years and am offering a scene of 2 billion years ago. Amazingly, now the snippet is much larger, with three pockets and a number of bizarre annexes. You could hardly call it "microscopic". But you cannot call it "macroscopic" either. Perhaps "nanomachine" is a good name - it suggests that the dimensions can suitably be given in nanometers.

The immediate suspicion is that one or two protons bumping into such a particle would produce no effect. Rather, a large group of protons must simultaneously attack the nanomachine if the latter is to contract and liberate ATP. Protons in the cell are too few and rare to be able to form the desired group. Nevertheless, as soon as three ATP molecules get synthesized (but remain stuck in the pockets), the large group of protons does come from somewhere and liberates them. The synchronization is quite perfect.

I forgot to say that the nanomachine is permanently attached to the inner side of the cell membrane. Let us list this and two other premises and try to draw a conclusion:

Protons in the cell are rare and cannot form a group.
The nanomachine is attached to the inner side of the membrane.
As soon as 3 ATP molecules get synthesized a group of protons comes from somewhere and iberates them.
Therefore, the "somewhere" can only be the external vicinity of the cell where the amount of protons is high.

The argument is valid - the conclusion cannot be false. If you disagree, try another conclusion. In any event you will have to suggest a place where the group of protons could come from.

I have to finish this introduction, although additional questions may have emerged. For instance: How do protons accumulate in the external vicinity of the cell? Does proton-driven ATP synthesis violate the second law of thermodynamics? In fact, the snippet story was a possible (but not necessarily true) evolutionary biography of perhaps the most intriguing enzyme, ATP syntheses. It will be paid a lot of attention in our next discussions. So far my only purposes were, first, to present thermodynamics as an interesting science (it usually presents itself as a dull science) and, second, to invoke types of reasoning that I believe are fruitful. From now on our journey through thermodynamics will be more systematic and rigorous. Yet I promise to try to make the rest of the course more interesting and less difficult than this introduction.

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