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ANOTHER SCIENTIFIC PRACTICE SEPARATING CHEMISTRY FROM PHYSICS: THOUGHT EXPERIMENTS

ABSTRACT. Thought experiments in the history of science display a striking asymmetry between chemistry and physics, namely that chemistry seems to lack well-known examples, whereas physics presents many famous examples. This asymmetry, I argue, is not independent data concerning the chemistry/physics distinction. The laws of chemistry such as the periodic table are incurably *special*, in that they make testable predictions only for a very restricted range of physical conditions in the universe which are necessarily conditioned by the contingences of chemical investigation. The argument depends on how 'thought experiment' is construed. Here, several recent accounts of thought experiments are surveyed to help formulate what I call 'crucial' thought experiments. These have a historical role in helping to judge between hypotheses in physics, but are not helpful in chemistry past or present.

INTRODUCTION

Perhaps there are some thought experiments in the history or practice of chemistry. If so, there don't seem to be any well-known ones. In this, chemistry contrasts strongly with physics and biology, whose most famous historical turns are accompanied by famous thought experiments still remembered today. The lack of famous thought experiments in chemistry can help us to articulate principled differences between physics and chemistry. I claim that there is a relatively well-defined class of thought experiments, which I call 'crucial' thought experiments, that are to be found in the history of physics, but which are of no help for chemistry past or present. This asymmetry is not independent data concerning the chemistry/physics distinction,

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but rather is a manifestation of the incurably special nature of chemical laws and hypotheses in contrast to some of those of physics.

CHEMISTRY AND PHYSICS: FUNDAMENTAL DIFFERENCE?

It has been a common theme of recent philosophy of chemistry that there is such a fundamental difference. Among others, Vančik (1999) notes the existence of distinctly chemical concepts. In particular, those of molecular shape, geometry of bonding, and valence have no use in physics, and moreover neither are reductions, extensions, nor approximations to physical concepts. Moreover, recent work from Scerri (2004, and numerous other articles) and others argue that the concepts of quantum chemistry cannot (completely) be explained by or reduced to quantum mechanics. They argue that this is entailed by the fact that quantum chemistry employs mathematical constructs designed to allow interpretation in terms of more traditional chemical notions. While there continue to be sceptics (see Friedrich, 2004) my sympathies are with Scerri's creed; the critics seem not to have taken in the significance of quantum-chemical concepts with *no* extra-chemical motivation.

Taking the chemistry/physics distinction for granted from here on, I argue that this difference is manifested in the differing situations of thought experiments applied to physics and to chemistry. I suggest that this is owing to the nature of chemistry as a discipline: it does not exhibit laws in the form of universal assertions and it does not lend itself to advancement by *a priori* reasoning. We will see, finally, that the motivations for some recent accounts of scientific thought experiments lie in addressing just those features of scientific activity I claim are lacking in chemistry.

MANY CONSTRUALS OF 'THOUGHT EXPERIMENT'

Every intellectual activity involves reasoning and consideration of hypothetical situations. The phrase 'thought experiment' is used often, yet there seems to be a relative dearth of literature on the subject (Brown, 1991, p. viii). It is difficult to give an account of thought experiments that agrees with everyone's pre-theoretic intuitions concerning what one is. The phrase is used variously for hypothetical or counterfactual reasoning, projected or hypothetical histories, imaginary experiments, and likely other mental exercises that could be named.

We also can inquire into what it might mean for thought experiments actually to be proper to some science or other. It probably is safe to say that journal articles in either physics or chemistry tend not to include self-identified thought experiments. Thought experimentation is not a codified practice, either in science where they are the exception or in philosophy where they are ubiquitous. Thus unlike the case of, say, experiments, we do not even have a positivistic model available for assessing our arguments.

The question as to whether or not there are thought experiments in chemistry or another particular science is meaningless on its own. If 'thought experiment' is construed broadly enough, certainly there are. Consider the use of fictitious processes in chemical thermodynamics. These allow thermodynamic quantities that are not easy to measure to be calculated from ones that are. For example, the enthalpy of solution can be written as the sum of the enthalpies of separating solute apart, separating solvent, then mixing them together (Silberberg, 2000):

$$\Delta H_{\text{solution}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mixing}}$$

This is an imaginary process. Solutions do not form by complete separation of the separate components of a mixture, followed by mixture. The theorems of thermodynamics allow this imaginary process to be assumed however. Thus, it might be said, this use of chemical thermodynamics and other related ones constitute thought experiments.

Now, this sort of procedure does not seem to me a thought experiment, because there does not seem to be associated with it an 'experiment' in any sense, but simply a hypothetical process. Moreover, there does not seem to be anything distinctly scientific about this mode of reasoning. But this is a matter of stipulation: others will not agree. If anything useful can be said regarding the place of thought experiments in the various sciences, we need to be more specific about what will count as one. Pre-theoretic terminology won't do. So let us examine some construals of 'thought experiment'.

Roy Sorensen (1992) tries to favour the specifically experimental aspect of thought experiments. Hence thought experiments are a 'limiting' case of actually performed experiments (p. 186), ones not physically executed for various reasons he catalogues (pp. 197–202). Moreover, Sorensen's aim seems to be the classification of the class of thought experiments along a limited number of spectra; thus he views philosophical and scientific thought experiments as differing only in degree (p. 198). Sorensen seeks to "rule out many cases that casual definitions lack" (p. 206) but his criteria are nonetheless decidedly liberal. It might be said, without too much violence to the word, that the hypothetical separation of solvent and solute molecules is an experiment in thought – we work out the consequences of imagined processes.

Clearly the word 'experiment' is itself up for grabs. The word will not help us to separate thought experiments from broader sorts of hypothetical reasoning. And as the construal of 'experiment' is perhaps discipline-specific, this kind of definition is not going to help us describe what might be the nature of thought experiments in particular sciences.

If there is anything interesting to say about this, we need a sharper construal of 'thought experiment'. Necessarily such a construal will be stipulative; we need to examine its consequences before we can decide if it is worthwhile. Let us look to two recent attempts, not to define 'thought experiment', but to identify how thought experiments can have normative import for scientific thinking. James Robert Brown (1991) and John Norton (1996) agree that thought experiments have been important in the history of science, delivering normative conclusions allowing for theory choice. Neither view is fully satisfactory, but I won't be concerned with a full critique here. I wish to suggest that the considerations that lend each account its plausibility can help us further to delineate the scientific spaces belonging respectively to chemistry and physics. Examination of them followed by analysis of some historical cases allows the articulation of a specific class of thought experiments that I'll call 'crucial' thought experiments, because they typically are designed to adjudicate between rival hypotheses.

Brown (1991) offers a taxonomy of thought experiments, but we need not engage with the entirety here. The most interesting sort for the present purpose is his platonic thought experiments, in which category he includes the Galileo's falling balls and EPR thought experiments. In these cases, Brown contends, we gain *a priori* knowledge of laws of nature without a logically valid argument (1992, pp. 77, 78). This, in brief but not oversimplified outline, is the source of Brown's conceptual platonism (lowercase 'p' because it is a fallibilist version). The construal of laws of nature as a relation between abstract entities (universals) facilitates some description of the contents of the platonic realm (pp. 82–87). His argumentative strategy is abductive: his platonism, he argues, has more explanatory power than do rival hypotheses (pp. 87–90).[1]

Now, in terms of his abductive strategy, it is not clear that Brown has exhausted all alternatives to his views. One might agree with Brown that some thought experiments exhibit evidence beyond that we can get from arguments. In fact, as shown by Gendler (1998), the argument for the conclusion of Galileo's falling balls experiment requires a choice between numerous auxiliary hypotheses, and it is the virtue of that thought experiment to make those that seek to save Aristolean physics seem to require egregiously implausible ones. Nonetheless, there seem to be lots of 'remainder' games available among philosophical options; perhaps a phenomenological account could capture the same remainder as does Brown's.

Norton is led to an opposing view more or less by respect for parsimony (1996, pp. 358–365). Thought experiments, insofar as they have any normative force, are arguments because there is nothing else for them to be. Thought experiments, offering no new data, cannot support any inferences beyond previous knowledge (p. 335). Norton argues for the formal thesis that any thought experiment can be reproduced as an explicit argument such that these arguments exhaust the normative force of the thought experiment (p. 339).

There perhaps is something a little queer in this sort of view, in that we do not typically think of real experiments as arguments. There are syntheses of new chemical compounds, measurements of physical quantities, psychological questionnaires: if these experiments or their reports are indeed arguments then they are highly enthymematic. The rhetoric of science certainly does not represent experiments as arguments, and there is much in every experiment never conveyed to readers: any 'reconstruction' of arguments from experimental reports would be a difficult business if indeed it is possible. Moreover, the normative force of experimental results does not seem usually to lie with an associated argument. Pragmatically, experimental results often are treated as standing on their own, as more or less 'raw' data. So perhaps Norton thinks that thought experiments are of an entirely different kind than real ones.

It obtains that imaginary experiments associated with theory development in physics conform to the standards of Brown's platonic thought experiments. Theory development in history of chemistry often exhibits hypothetical reasoning, but not of a sort conforming to these standards. The assessment according to Norton's thought experiments as arguments is more ambiguous. Let us look at the features of reasoning in each case to find what made them valuable.

DALTON AND KEKULÉ: NO THOUGHT EXPERIMENTS?

John Dalton's atomic theory gave retrodictions of the laws of definite and variable proportions. Dalton proceeded by introspection from the hypothesis that elements are made of identical tiny particles to the conclusion that compounds are made of collections of identical physical combinations of those particles. Then, whereas each such combination consists of a definite number of sub-particles of each element, each macroscopic compound consists of the macroscopic elements in the same proportions. Similarly, whereas different numbers of particles of several elements can combine in various proportions, so there are differing compounds of the same elements in different proportions. The introspection part arises from the extrapolation from the micro to macro. Specifically, scaling the compounds up from single particles to macroscopic compounds should save the proportions unchanged, based upon our instinctive knowledge of physical collections. This sort of reasoning was very valuable for Dalton and his contemporaries, and remains valuable for students of chemistry today. In our modern theory, molecules do not *simply* consist of physical combinations of atoms; for example, the electronic distributions of bonded atoms differ from those in free atoms. Nonetheless, this reasoning still gives the right answer, and not by accident.

But this mode of reasoning seems not to be thought experiment. To begin with, though Dalton did consider some ideas as to the reasons for the empirically obtained proportions for compounds, these ideas were embryonic and untestable in his times; he was ahead of the time in which meaningful hypotheses for the source of molecular structure could be struck. This is to say, there are no *real* experiments in Dalton's time that can be modelled here. Nor was Dalton able to describe imaginary experiments having a bearing on his hypothesis. Surely a scientific thought experiment should to a reasonable degree resemble a scientific experiment that for whatever reason remains imaginary. Now, Dalton's theory does have a testable consequence in its predicted chemical proportion laws, but these already were known independently of his theory.

Similar comments can be made concerning August Kekulé's positing of a ring structure for benzene. Here the possibility of referring to Kekulé's conclusions as the result of thought experimentation might be encouraged by the legend of his dream of the head-to-tail snakes. The ring structure allows us to understand both why the carbon atoms are equivalent in benzene, and also why the number of possible substitution isomers is what it is. The hypothetical reasoning here is of much the same character as Dalton's, and the scientific problem situations also strongly resemble one another. Both chemists offer ingenious abductions that appeal to our pre-theoretic sense of spatial distinctions, and which have stood the test of time. The chemists of Kekulé's time had many more pieces of the puzzle put together, but still lacked a basis for meaningful tests of specific hypotheses of molecular bonding. Hence, as with Dalton's, there is no experiment on offer from Kekulé's hypothesis, and there were no practically testable consequences beyond those motivating the theory. Just the same considerations apply to the explanation of optical isomerism by van't Hoff and Le Bel.

The reasoning employed by Dalton et al. is abductive: a hypothesis is inferred because its consequences agree with observations. This reasoning involves hypothetical reasoning but does not seem to resemble thought experiment in a non-trivial sense.

FALLING BALLS AND REMOTE DETECTORS

Consider Galileo's famed falling bodies thought experiment. It is a reductio of Aristotle's physics. According to Aristotle, heavier bodies fall faster than lighter ones. But a lighter body strapped to a heavier one will slow down the motion of the heavier one. Taking any heavier body H and a lighter one L, the combination of the two H + L got by strapping them together will therefore fall faster than H, being heavier than H, but also slower by the drag effect. Hence these theses of Aristotelian physics are inconsistent.

There are important differences between Galileo's thought experiment and those of the chemists cited. The most obvious is that the former cites an experiment. Also, the inference that is drawn is not an abduction; it is what we might call a 'quasi-deductive' argument. Its extraordinarily conclusive nature may make us forget that the argument is not deductively valid as it stands; as Gendler (1998, p. 405) points out, there is a countermodel to the argument: a world in which regularities of motion do not apply to strapped-together bodies. This is not plausible; it could scarcely be anything but an *ad hoc* attempt to defend a discredited theory. The argument associated with this thought experiment, therefore, is an enthymeme; the deleted premises in this case are too obvious to require mentioning.

It is striking that one leaves the falling balls example with something approaching certainty for its outcome, particularly after considering Gendler's alternative reconstructions of desperate defences for Aristotle. With very little background knowledge, a student today is able to get real insight into how falling must work.

Consider another well-known thought experiment, the Einstein–Podolsky–Rosen (EPR) experiment (Einstein et al., 1935), more recently performed for real (Aspect et al., 1982). Assume that there can be only local influence,[2] and assume special relativity is true. Then capture the two particles produced by a radioactive decay at oppositely placed detectors that allow the particle spins to be determined. The quantum formalism and conservation of angular momentum require that if one spin is measured at a detector, the oppositely-placed detector's reading is determined to be the opposite regardless of the distance of separation of the detectors. Thus, it seems, restriction of influence to the local and the quantum formalism are inconsistent. Famously, EPR conclude that the standard quantum formalism lacks sufficient variables to make all required distinctions.

The argument that accompanies the description of the EPR experiment is considerably more involved than that for the falling balls example. But even a person not trained in physics can understand that its conclusion forces modification either of well-established scientific theory or else some very plausible metaphysical assumption.

LAWS AND ARGUMENTS

Consider Brown's platonic thought experiments in light of these examples. The falling balls and EPR thought experiments are paradigm cases of these (1991, p. 43). At least according to Brown's analysis, these confer *a priori* knowledge of laws of nature. As noted particularly by Brown, thought experiments of physics allow us to engage with laws of nature in a way in which their consequences are very clear. The most famous of past thought experiments typically do this, to compare rival systematic theories or to present the metaphysical commitments of theories. Perhaps this is only because the thought experiments that the tradition has bothered to remember are of this sort. But let us be charitable to our tradition and assume that there is a principled reason that the thought experiments we remember most vividly are reasonably representative of the worthwhile ones of the past.

Now Brown analyses 'laws of nature' as relations among universals (p. 82). Then it appears that there may be no place in Brown's heaven for the laws peculiar to chemistry. First, they don't seem to be relations between universals. Perhaps someone could develop an account of the periodic table as such. But for now I would place the burden of proof on its advocate. Even if this is done, it is difficult to see how periodic relations could be justified with thought experiments.

I suggest that there is a key difference between the periodic law and laws of physics such as energy conservation. It is not *simply* that the laws of chemistry are less general. There are various laws of varying degrees of generality; as with 'thought experiments' it is controversial just what is a 'law of nature'. But the laws of chemistry are incurably *special* in several senses.

First, consider their status alongside the laws of physics. While, as noted earlier, the quantum-chemical descriptions of atoms and molecules cannot be reduced to physical laws in full, those descriptions are nonetheless bounded by those laws. Our descriptions of chemical species must cohere with quantum mechanics. Quantum chemists provide an account of serviceably recognisable chemical concepts, introducing constructs not strictly consistent with quantum mechanics, in a way that appears empirically adequate for chemical purposes. Likewise, our modern understanding of the periodic table must conform in a general way to the requirements of quantum mechanics.

Chemical laws also are special in the sense that they are highly conditioned by empirical contingencies of chemical life. Chemical phenomena, we now know, occur in what is by the universe's standard very special circumstances. Thus chemical laws apply not at all to stellar interiors, for there are no atoms there. But we have every reason to think, for example, that energy conservation will apply in every circumstance. Looking in the opposite direction, we can continue to assume conservation of mass for chemical changes, for mass changes in chemical reactions are undetectable. There probably are branches of physics with laws similarly special, but the significant difference is that physics features a theoretical branch in which laws are *not* special.

Characteristically chemical laws appear not to be testable by thought experiment.[3] We can seek a broader construal than Brown's, taking thought experiments to be ones that can in some way or other *test* laws of nature, without requiring *a priori* knowledge to obtain. But the hypotheses offered by Dalton and Kekulé (or more correctly, our reconstructions of them) are lacking in the specific detail needed to precisely obtain macroscopic results. It is, I suggest, a good-making feature of a thought experiment that it should do exactly this. There standardly is little point in doing an experiment unless the results can be interpreted relatively sharply. We want to see a repeatable qualitative phenomenon or a measurement of numerical data having a meaningfully narrow range. Similarly, for a thought experiment of real interest, the results must be predictable within a reasonable range, narrow enough to be suggestive of something worthwhile. The range need not be as narrow as the exactitude that obtains in the case of the falling balls thought experiment. But the hypotheses of Dalton and of Kekulé are in their times unable to provide any specific macroscopically observable result.

Perhaps, someone might think that while in their own time these men were unable to devise specific experimental results from their hypotheses, we as their modern successors can apply them more specifically. But chemists know this is not so. Firstly, calculations on molecules do not proceed straightforwardly from theory, as pointed out by Scerri. More to the point, though, on a practical level macroscopic accuracy is not in general achievable from theory. There *might* be some macroscopic substances for which many specific predictions could be got from theory, quantum fluids perhaps, or specific properties of substances such as conductivity of certain alloys, that might be accurately predicted from theory. But those are not regarded by Dalton and Kekulé's ideas. Finally, even if very accurate calculations were available for macroscopic properties of substances, we would lose the characteristic simplicity of thought experiments. On any reasonable construal, a thought experiment is not a 1000-page computer printout.

Let us turn to Norton's construal of thought experiments as simply arguments. It is not wholly clear whether the falling balls thought experiment qualifies in light of its unspecified auxiliary hypotheses, as explored by Gentler (1998). It is not clear that a deductive argument can be made for its conclusion that excludes every crazy hypothesis that could be devised. But perhaps we can allow a more lenient standard of argument in which those 'crazy' hypotheses are all too obviously false to consider. By 'too obvious', we mean that the sort of premises needed to make the argument go through deductively are quite basic, the sorts of things that really could not be subverted by any remotely likely scientific theory. Or, to put it more pragmatically: things that we have less reason to doubt than scientific theories at issue. As Kathleen Wilkes puts it:

> We are asked to suspend belief in one feature, and to suppose *that* Einstein could travel at the speed of light, or *that* Stevin has found perfectly frictionless planes and chains. That is all; everything else remains as it was, conforming to the laws we know and trust (1988, pp. 7, 8).[4]

As to the chemical cases, they are abductions, and might therefore conform to Norton's view. But if arguments from chemistry are plausibly to express thought experiments on this construal, they must take us by either deductive or some other sort of reasoning less doubtful than the chemical theories on offer, to a specific conclusion of chemistry. Now certainly there is deductive reasoning in chemistry. Dalton and Kekulé use it. And chemists use special sorts of reasoning like the arrow-pushing diagrams used to illustrate chemical reactions, which include formal elements but are not deductive. For reasons similar to those rehearsed for Dalton's and Kekulé's work, we should not count these arrow-pushing exercises as thought experiments. Characteristically, chemical generalisations of the simplicity and scope of thought experiments like EPR cannot be got this way; the best that can be said from surveying these diagrams is that class A of conditions for species B likely will produce derivative type C.

More generally, competing hypotheses for chemical reaction mechanisms are unlikely to be resolved by single arguments. Instead coherence of various sorts of evidence is likely to be the deciding factor in practice. This coherence is the source of plausibility arguments for one mechanism over another, and reaction kinetics, that most fallible of chemical sub-disciplines, exhibits numerous reversals of fortune over time for various hypotheses for chemical reaction mechanisms.

CRUCIAL THOUGHT EXPERIMENTS

While, as noted before, Brown's and Norton's accounts seem not fully satisfactory, examining them in relation to some historical episodes helps us to see the way to a formulation that can be seen to separate chemistry from physics: crucial thought experiments.

The hypotheses of Dalton and others cited from nineteenth-century chemistry ought not to be considered thought experiments. In each case, there is no experiment on offer resembling scientific experiments in the usual sense. The sort of reasoning involved appeals to our experience with macroscopic things in a way no different than the reasoning involved with putting together modern molecular models – a practice made possible, of course, to a large degree because of these very achievements. We can imagine making lots molecular models of benzene and see how the properties of one model are preserved in arbitrarily large collections of them. Thus there is no purpose served in regarding this cognitive activity as different from simple hypothetical-deductive and spatial-causal reasoning. And this distinction must be maintained in order for 'thought experiments' to denote any interesting category of reasoning.

There are two features that we should demand from a good scientific thought experiment. It should resemble an experiment that there would be some point in performing, and the results should be predictable within an interesting range. The cited experiment should not involve outlandish extensions of the ability to measure: extending the lifetime of scientists is all right, the ability to be in two places at once is not. The thought experiment should be relatively simple, so that interesting results easily can be obtained, and auxiliary assumptions very weak ones, ones we have less reason to doubt than scientific theory at issue. This characterisation seems intuitively plausible. It is weak enough not to exclude clear thought experiments (such as the falling balls, obviously my exemplar), but strong enough to exclude some initially doubtful cases, such as the hypothesis and associated reasoning of Kekulé.

I call this formulation ‘crucial’ thought experiments because they can be used, as in the case of Galileo, to compare the theses of one theory to another. Whether or not *a priori* knowledge is thereby gained, I decline to speculate. Similarly we can consider the metaphysical consequences of a theory, as with the EPR experiment.

No such simple thought experiment was available for the resolution of the chemical revolution. The phlogistinists believed that phlogiston was a principle of matter, capable of transfer from one bit of matter to another. Lavoisier and his supporters in the overthrow of phlogiston theory agreed that burning and heat transfer involves emanation of a physically embodied theory but disagreed about its nature: it was of a massless principle that flowed in the opposite direction. Under these conditions, it was not plausible that there could be a simple mental exercise that would show that one view was better than the other. It would be difficult to imagine a thought experiment that could demonstrate the difference in the theories in terms of observable conditions. Regarding the ultimate victory of Lavoisier’s side, historians will continue to disagree about its ultimate cause, but it seems clear that in the end, part of the answer is that Lavoisier’s view was more adaptable to a productive research program. Competing theories that are, as I term them, 'incurably special', only can be judged by practical value, not by obvious theoretical superiority.

So it is generally for competing chemical generalisations, past and present. Owing to their incurably special nature, it is not possible to design a meaningful thought experiment producing a definite conclusion. Owing to their reference to the unobservable as explanatory source, they cannot be used to argue for specific and characteristically chemical conclusions without real laboratory work. There are deductive reasoning and laws in chemistry, but there is no way to marshal them to produce a convincing thought experiment exhibiting the rather weak requirements outlined above. Thought experiments, and *a priori* reasoning generally, could not have helped in past cases of chemical controversy, and do not seem helpful now.

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NOTES

1. Here, too, I disagree with Brown in that he seems to acknowledge Kekulé's dream as a thought experiment (1992, p. 89).
2. The specific sort of localisation is not important for our present purposes but it is spelled out in the original paper. It is fair to say that it encompasses our intuitive sense of the localised nature of influence.
3. Readers may note that theses of biology tend be very particular and so the laws of biology might be special also. But in biology there is a space for testability by thought experiments because evolution is an abstract theory from which one can reason without reference to the particular circumstances of specific organisms.
4. But Stevin's famous chain on a double inclined plane thought experiment goes through even without the assumption of zero friction; if in the presence of friction the chain is moving one way or the other, an indefinite amount of heat can be produced.

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