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## Prediction and the Periodic Table

# Eric R. Scerri\* and John Worrall\*\*

The debate about the relative epistemic weights carried in favour of a theory by predictions of new phenomena as opposed to accommodations of already known phenomena has a long history. We readdress the issue through a detailed re-examination of a particular historical case that has often been discussed in connection with it—that of Mendeleev and the prediction by his periodic law of the three 'new' elements, gallium, scandium and germanium. We find little support for the standard story that these predictive successes were outstandingly important in the success of Mendeleev's scheme. Accommodations played an equal role—notably that of argon, the first of the 'noble gases' to be discovered; and the methodological situation in this chemical example turns out to be in interesting ways different from that in other cases—invariably from physics—that have been discussed in this connection. The historical episode when accurately analysed provides support for a different account of the relative weight of prediction and accommodation—one that is further articulated here. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mendeleev; Prediction; Periodic Table; Weight of Evidence.

#### 1. Introduction

A scientific theory T (in conjunction with accepted auxiliary assumptions) deductively entails some empirical sentence e; e is, moreover, true (or, rather, accepted as true on the basis of experiment or observation). Does the extent to which this success lends confirmation or support to T depend on whether e describes some state of affairs that was unknown at the time of T's articulation or instead on whether it describes some already well known state of affairs? The methodological issue of whether, roughly speaking, successful prediction 'counts more' for a theory than successful accommodation formed a celebrated part of the debate between William Whewell and John Stuart Mill. The latter, while allowing that successful predictions were 'well calculated' to impress the 'ignorant vulgar', expressed utter

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amazement that 'persons of scientific attainments' (such as Whewell) should believe that such predictions carry extra evidential weight. The issue has subsequently been raised time and again in the philosophy of science literature and remains live and controversial. Not only is there disagreement over whether predictions 'count more', there is great disagreement (on both sides) over why they do (or do not).<sup>1</sup>

The direct focus of the present paper, however, is not this general issue, but rather a famous particular case from the history of science that has become embroiled in it. The episode involves Mendeleev and the 'prediction' of the existence of hitherto unknown elements on the basis of his celebrated periodic table. According to an account that has widespread currency, Mendeleev's table was given little or no general credit by his contemporary scientists in virtue of its 'accommodation' of the already known elements. What really told with Mendeleev's peers, according to this account, was the fact that 'gaps' in the table were used as the basis of predictions of the existence of hitherto unrecognised elements, that turned out really to exist. So, for example, Isaac Asimov writes:

... in the January 7, 1871, issue of the *Journal of the Russian Chemical Society*, [Mendeleev] advanced the crucial notion for which he truly deserves all the credit he gets for the discovery of the periodic table, to the exclusion of his contemporaries and predecessors who also contributed to it. He left gaps in the table in order to make the elements fit into proper columns, and announced that the gaps represented elements not yet discovered ... This prediction ... was met with considerable scepticism ... However, in 1875 Lecoq de Boisbaudran ... discovered an element which matched, to the last property, Mendeleev's prediction for one of the gaps. In 1879, Nilson and Cleve produced another ... and in 1885 Winkler produced still another ... Mendeleev and his periodic table were vindicated in the most dramatic manner possible ... Mendeleev was suddenly the most famous chemist in the world. (Asimov, 1975, p. 410)

This popular account has been endorsed in the recent philosophical literature by Patrick Maher, and, following him, Peter Lipton. Maher writes:

By the middle of the nineteenth century more than 60 elements were known with new ones continuing to be discovered. For each of these elements, chemists attempted to determine its atomic weight, density, specific heat, and other properties. The result was a collection of facts, which lacked rational order. Mendeleev noticed that if the elements were arranged by their atomic weights, then valencies and other properties tended to recur periodically. However, there were gaps in the pattern and in a paper of 1871 Mendeleev asserted that these corresponded to elements that existed but had not yet been discovered. He named three of these elements eka-aluminium, eka-boron and eka-silicon and gave detailed descriptions of their properties. The reaction of the scientific world was sceptical. But then in 1874 Lecoq de Boisbaudran found an

<sup>&</sup>lt;sup>1</sup>Mill's remark is from Mill (1843). For the more recent controversy see, for example, Campbell and Vinci (1983), Howson (1984), Giere (1984), Redhead (1986) and Mayo (1996). Bayesians in particular have been divided on the issue—the debate within the Bayesian camp revolving round the so-called 'Problem of Old Evidence' (see Earman and Glymour, 1980).

element which corresponded to Mendeleev's description of eka-aluminium which he called gallium. This was regarded as a remarkable event; it was the first time in history that a person had correctly foreseen the existence and properties of an undiscovered element. Confidence that Mendeleev's other predictions would be confirmed increased markedly. Four years later, Nilsson discovered an element which corresponded to Mendeleev's description of eka-boron, and which he named scandium. Now chemists were expecting to find Mendeleev's third element, though the Royal Society did not wait for that discovery, awarding Mendeleev its Davy Medal in 1882. Mendeleev's eka-silicon was discovered by Winkler in 1886 and named germanium (Maher, 1988, p. 274).

And Maher goes on explicitly to underline the conclusions about confirmatory weight that he sees as illustrated by this episode. He claims that Mendeleev's prediction of the existence of the third of the new elements, eka-silicon (aka germanium), was initially regarded as quite unlikely to be true; but then later, with the discovery of the first two new elements (gallium and scandium), confidence in the prediction of the existence of the third new element became so high that its eventual empirical confirmation was widely regarded as a matter of course. Maher writes:

If scientists accord no special confirmatory value to predictions, then it is quite inexplicable why their confidence in Mendeleev's predictions should have increased substantially after one or two of these predictions had been verified. There were 62 elements in Mendeleev's periodic table of 1871, so we could say that Mendeleev's prediction of [germanium] was initially made on the basis of evidence concerning 62 elements. After the discovery of gallium, the prediction concerning [germanium] was now backed by evidence concerning 63 elements and after the discovery of scandium, it was backed by evidence concerning 64 elements. But the difference between these bodies of evidence is much too small by itself to account for the dramatically altered attitude to Mendeleev's prediction of [germanium]. The only plausible explanation is that scientists were impressed by the fact that these latter pieces of evidence [the 63rd and 64th] were verified predictions rather than accommodated evidence. (Maher, 1988, p. 275)

### In similar vein, and citing Maher, Peter Lipton asserts:

Successful theories typically both accommodate and predict. Most people, however, are more impressed by predictions than by accommodations. When Mendeleev produced a theory of the periodic table that accounted for all sixty [really sixty-two] known elements, the scientific community was only mildly impressed. When he went on to use his theory to predict the existence of two unknown elements that were then independently detected, the Royal Society awarded him its Davy Medal . . . Sixty accommodations paled next to two predictions. (Lipton, 1991, p. 134)

This particular passage from Lipton is ambiguous. It might simply be making the descriptive claim that, *rightly or wrongly*, 'most people' are, as a matter of psychological fact, more impressed by predictions. But Lipton goes on to endorse a version of the *normative* pro-predictivist thesis, in other words, to assert that what

was allegedly most people's reaction was in fact the methodologically correct one.<sup>2</sup> Maher too uses the episode as support for his preferred version of predictivism—claiming that the episode shows that sometimes *temporal* novelty (the mere fact that the evidence was unknown at the time the theory predicted it) is of special methodological significance.

However, any philosophical conclusions from this case must be based on a fuller and more accurate understanding of the history than anything cited by Maher or Lipton. We seek to supply this here. We argue that there are features of the history which, to say the least, do not sit well with the Maher-Lipton view. Of course, no one could sensibly deny that the successful prediction of the new elements played an important role in the reception of Mendeleev's work; nor can it be denied, perhaps, that successful (temporal) predictions have a special psychological effect and that their impact can easily be felt by a wider audience than just specialists in the field.<sup>3</sup> We shall argue however that the real evidential situation, so far as the experts were concerned, was altogether more cumulative and multi-faceted. There is no real sign of a 'dramatically altered attitude' towards Mendeleev's table and its underpinnings between, say, 1871 and 1874; there seems instead to have been a gradual process of diffusion and 'acceptance' (though this term too hides important complexities)—a process in which certain 'corrections' of previously accepted 'data' (about atomic weights of known elements) and certain 'accommodations' of already known evidence played equally significant roles alongside the predictive successes. Moreover there are, we shall argue, special features of this case that make it materially different from others—such as the general theory of relativity and the star-shift observations,<sup>4</sup> or Fresnel's wave theory and the 'white spot'5—that have previously been analysed in the attempt to shed light on the general issue of prediction and theory-confirmation.

Some of the material we shall use in arguing against the Maher-Lipton claim

<sup>&</sup>lt;sup>2</sup>Lipton does not connect his specific remarks about the Mendeleev case in any detailed way with his general normative account about prediction and accommodation (Lipton, 1991). This general account seems to us a mixture of insight and error. Despite the impression given in his remarks about Mendeleev, his considered view seems to be that the important difference is not in fact that between prediction and accommodation per se but that between prediction and 'fudged' accommodation. Although it is not clear exactly what he has in mind by 'fudging', it may well be that much of his view is in the end broadly consistent with our own general view as explained below in Section 2.5. But then, in order to link this general view with the particular example of Mendeleev, it is not enough to remark that Mendeleev 'accommodated' the known elements; Lipton needs to consider whether or not this was a case of 'fudged' accommodation. This is precisely the issue that we shall treat-based, of course, on our own preferred version of the general account. (One source of divergence is that Lipton, in our view, confuses matters by bringing suspicions into the account: scientists cannot suspect predictive successes of having been produced by 'fudging', but accommodations may have been fudged; hence predictions are prima facie more telling than any accommodation, fudged or not. But suspicions can, surely, play no role in objective accounts of evidential support; and nor, we suggest, would they play any role in the thoughts at least of expert scientists, who would be able to resolve any suspicion one way or the other by recognising whether or not the accommodations were indeed 'fudged'.)

<sup>&</sup>lt;sup>3</sup>See particularly the quote from Ne'eman in note 18, below.

<sup>&</sup>lt;sup>4</sup>See, for example, Earman and Glymour (1980).

<sup>&</sup>lt;sup>5</sup>See, for example, Worrall (1989).

has also been analysed in a recent paper by Stephen Brush (1996). Brush gives an altogether more detailed and scholarly treatment, but arrives at a view that, while much more measured, is none the less similarly pro-predictivist. Indeed he states that this Mendeleev episode is:

the first case [he has] found in which scientists give substantial weight to evidence predicted in advance rather than treating such evidence as being no more important than similar evidence already known and deduced from or accommodated by the new theory. (Brush, 1996, p. 596)

As this indicates, Brush's view of *other* historical cases (see for example Brush, 1989) has been that, whatever philosophers of science may claim about the relative merits of prediction and accommodation, there is no historical evidence that the scientists concerned in these cases gave any special weight to predictive success. But he feels forced by the evidence in the case of Mendeleev to conclude that there—perhaps uniquely—special weight was indeed given to predictions. We will argue that the historical evidence that Brush himself alludes to in fact, on careful analysis, fails to support this conclusion.

We begin with some detailed worries about Lipton's and Maher's accounts and a brief account of our basic methodological thesis about the value of prediction (Section 2). Next (in Section 3) comes our detailed analysis of Brush's treatment of the episode. Then we draw attention to a difference between the Mendeleev case and others that have been analysed from the point of view of the relative weight of prediction and accommodation that has not previously been highlighted and yet which is of fundamental significance (Section 4). These all form necessary preliminaries for our own positive account (in Section 5) of this historical episode and the relative weights accorded to various predictions and various accommodations in it. We argue in particular that certain 'accommodations' within Mendeleev's table were at least as significant as any predictive success—notably the accommodation of argon, the first of the 'noble gases' to be identified.

#### 2. Some Preliminary Clarifications and Counterarguments

#### 2.1. Publication and Prediction

Any claim of the kind endorsed by Maher and Lipton (and, as we already pointed out, the claim has, in one form or another, widespread currency) seems implicitly committed to the existence of two stages in the reception of Mendeleev's ideas. At stage one the scientific community was, as Peter Lipton puts it, 'only mildly impressed', whereas at stage two there was a 'dramatic alteration' (Maher) and Mendeleev became a bemedalled scientific star. According to Lipton, the first stage occurred when Mendeleev produced 'a theory of the periodic table that accounted for all [sixty-two] known elements'. One interpretation of this (though we do not suggest that this is what Lipton really meant) would be that, at stage one, Mendeleev's 'theory' made (or was perceived as making) no predictions, while stage two

then consisted of the recognition that the theory (or some further development of it) did indeed make predictions—ones that proved successful on experimental test.

But this characterisation is difficult to reconcile with the historical record. Inde, the only historian of chemistry quoted by either Maher or Lipton, identifies Mendeleev's famous paper of 1871 as the major turning-point:

Mendeleev's real insight was revealed in his 1871 paper in connection with vacant spaces in the periodic table. He gave the provisional names eka-aluminium, eka-boron and eka-silicon [to the elements he expected to fill these gaps]. (Ihde, 1964, p. 283)

Assuming, then, that 1871 marks stage two, where, in the historical record, lies stage one? It is true that Mendeleev published an account of the periodic table before the one contained in his 1871 paper—in fact in 1869. However, if the claim were that his 1869 paper attracted scarcely any attention at the time because it contained no predictions of hitherto unknown elements, whereas the tide began to turn with the 1871 paper which did predict 'new' elements, then the claim is unsustainable. Mendeleev's first paper of 1869 is just as celebrated as the 1871 piece (and seems to have attracted no less attention at the time). Moreover, the 1869 paper already contained predictions of the unknown elements. Mendeleev there concluded, 'We must expect many yet unknown elements e.g. elements analogous to aluminium and silicon with atomic weights 65-75' (Mendeleev, 1958, p. 31). The periodic tables published in that 1869 paper contain entries for unknown elements in the form of '?=68' and '?=70' in the rows containing Al and Si respectively. (The atomic weights of these new elements turned out to be gallium=69.2 and germanium=72 respectively.) Moreover, Mendeleev's 'attempt at a system' of 1869 contains an entry '?=45'. This turned out to correspond to scandium with an atomic weight of 44.6.

Not only did Mendeleev predict the atomic weights of the famous three new elements already in 1869, he also made predictions of some of their other properties. In a talk to a Moscow Congress in that same year he suggested that two elements missing from the system, which show resemblances to aluminium and silicon, would have atomic volumes of 10 or 15 and specific gravities of about 6 (Mendeleev, 1959, p. 42). In the following year, 1870, he listed the expected atomic volumes of the elements that would become known as scandium, gallium and germanium as 15, 11.5 and 13 respectively.<sup>6</sup>

Nor, finally, can it plausibly be argued that what distinguishes the 1871 paper was that there were no details about the predictions in 1869 and these details were published only in 1871. Certainly there are *more* details about some predicted elements in the 1871 paper—as one would expect given that Mendeleev had done two more years' work—but this was very much a gradual process, with nothing of a qualitatively new kind being provided in 1871 that was not already there in

<sup>6</sup>Mendeleev, Manuscript Table 19 (M13), dating from summer/early autumn of 1870 (the numbering denotes the 13th manuscript table and the 19th table in the overall sequence of 65 tables of all forms).

1869. Surely no one could believe that the 1871 predictions were more definitive than those of 1869 just on the basis that Mendeleev was prepared to give the elements names (eka-silicon, *etc.*) in the 1871 paper, while he had been content with question marks in the relevant positions in 1869! But aside from this, it is difficult to discern any qualitative difference between the two papers that might count as significant in this regard.<sup>7</sup>

Of course, a defender of this account might react to these points by simply repositioning stage two at 1869. After all, Lipton himself makes no particular claim about Mendeleev's 1871 paper being the one that turned the tide. But then it is difficult to identify a stage one: Mendeleev's paper of 1869 contains his first ever published periodic table and hence the first candidate for 'mild scepticism'.

Another possibility for the 'two-stage theorist' is to identify stage one as the stage at which predictions—then of course unverified—were made, and stage two as that at which some of those predictions began to be experimentally verified. It would not, then, matter much whether stage one is taken as starting in 1869 or in 1871, since stage two then begins in 1874, with the discovery of the first new element, gallium. Maher seems to have been unaware of the 1869 paper (or at least he never mentions it), so he seems clearly committed to this version of the view with stage one in 1871 and stage two in 1874. And it seems likely that Lipton too was implicitly assuming that the change in attitude arose from the *verification* of the predictions beginning in 1874 rather than their simply being made on the basis of Mendeleev's table—whether in 1871 or 1869.

No one could deny, of course, that it is one thing for a theory to make predictions of the existence of hitherto unknown elements and quite another for it to make *successful*, empirically verified predictions. But neither Maher nor Lipton—nor, so far as we can see, anyone else—cites any substantial evidence for the 'sceptical' attitude of Mendeleev's fellow scientists in 1869 or 1871; and the only evidence they cite for the 'increased confidence' in the theory as a result of the successful predictions is the award to Mendeleev of the Davy Medal in 1882—and this, as we show in the next sub-section, turns out to be (worse than) unconvincing.

Of course there were *some* scientists who were sceptical of the value of Mendeleev's classification in 1869/1871 (and indeed some who remained sceptical *after* the new elements began to be discovered). However, at least two historical facts seem to us to speak unambiguously against any general scepticism about the value

<sup>7</sup>Certainly Mendeleev himself consistently described 1869 as the starting point of the crucial part of his investigations—the time at which he 'saw the periodic law', began to 'regard it as a new, strictly-established law of nature' and hence 'deduced such logical consequences from it as could show whether it were true or not' (see Mendeleev, 1891, p. 24, n. 13). Mendeleev insisted several times that what principally distinguished him from others who claimed priority over the table was his treatment of the 'periodic law' as a definite theory rather than a mere working hypothesis and hence his expectation right from the start that predictions from it would be borne out. Since he quite explicitly states that 'from the start' means 'from 1869', this also scotches any possible suggestion that the question marks in Mendeleev's 1869 account compared with the names in the 1871 account betoken an increased confidence and increased definiteness about the predictions.

of Mendeleev's work even when it was first published. *First*, his 1869 paper—quite unlike other Russian scientific publications of the time—was immediately translated into German and thereby made readily available to the scholarly world. *Second*, very similar ideas were being developed independently by others in 1869 and indeed earlier—Lothar Meyer, for example, had essentially the same table; and other periodic tables with some differences to Mendeleev's but with much overlap, were, as is well known, developed by Hinrich, Odling, de Chancourtois and Newlands. These facts surely show that Mendeleev's ideas were, right from 1869, accorded enough credibility to at least not be dismissed out of hand.

But this in turn adds to the implausibility of Maher's story about the impact of the predictive success. So long as Mendeleev's scheme was not regarded as beyond the pale of credibility in the period around 1869 to 1871, then *if* the success of the predictions it made was going to prove the crucial evidence that greatly increased its rational believability and gave the scientific community high confidence in further predictions from it, what would be the expected attitude amongst that community towards the scheme in 1869/71? Surely it would be one not of scepticism but rather of 'everything (or at any rate an awful lot) is going to depend on whether or not these bold predictions are verified'. One would have expected the opinion-making scientists interested in the issue to encourage immediate work to see if these bold predictions could be verified experimentally.<sup>8</sup>

Quite aside, then, from the cogency of the cited historical evidence, Patrick Maher's story does not seem to us to stand up in terms of internal coherence. But what of the historical evidence?

### 2.2. Why was the Davy Medal Awarded to Mendeleev?

The Royal Society awarded its Davy Medal to Mendeleev in 1882—three years after the discovery of scandium, the second 'new' element, and three years before the discovery of germanium. Both Maher and Lipton see this award as an important marker of the change from the initial 'mild scepticism' concerning Mendeleev's scheme to much greater enthusiasm. Indeed this is the only evidence that either of them cites for a marked change in attitude within the scientific community. But then if, as each alleges, Mendeleev's predictive success was the principal cause of this changed attitude, one would surely expect the citation accompanying the award

<sup>8</sup>This was certainly the attitude of William Crookes writing in 1877, after the discovery of gallium but *before* those of scandium and germanium. Crookes commented on these latter predictions as follows: 'M. Mendeleeff has also announced the probable existence of another metal, to which he gives the name of "eka-silicium", ES=72, forming an oxide EsO<sub>2</sub>. Its properties ought to be intermediate between those of of silicium and tin, and it is to be especially sought for among arseniferous and titaniferous minerals or residues. To the discovery of this metal . . . we must look forward with anxious interest, not so much for its own sake as for the light which it must throw upon the theory in question' (Crookes, 1877, p. 298; emphasis added).

<sup>9</sup>This again follows several popular accounts. For example, Asimov (1975) immediately follows his remark that 'Mendeleev was suddenly the most famous chemist in the world' with (what we are presumably to take as evidence for this) 'The Royal Society awarded him the Davy medal in 1882 and other honors were showered on him.'

of the Davy medal to at least lay some substantial emphasis on the successful predictions. Let us see if this meta-level prediction is verified.

In order to obviate any suggestion of 'fudging' the historical data to fit our favoured interpretation, it seems best to quote the citation in full:

The Davy Medal has been awarded to Dimitri Ivanovich Mendeleeff and Lothar Meyer.

The attention of the chemists had for many years been directed to the relations between the atomic weights of the elements and their respective physical and chemical properties; and a considerable number of remarkable facts had been established by previous workers in this field of enquiry.

The labours of Mendeleeff and Lothar Meyer have generalised and extended our knowledge of those relations, and have laid the foundation of a general system of classification of the elements. They arrange the elements in the empirical order of their atomic weights, beginning with the lightest and proceeding step by step to the heaviest known elementary atom. After hydrogen the first fifteen terms of this series are the following, viz:—

Lithium	7	Sodium	23
Beryllium	9.4	Magnesium	24
Boron	11	Aluminium	27.4
Carbon	12	Silicon	28
Nitrogen	14	Phosphorous	31
Oxygen	16	Sulphur	31
Fluorine	19	Chlorine	35.5
		Potassium	39

No one who is acquainted with the most fundamental properties of these elements can fail to recognise the marvellous regularity with which the differences of property, distinguishing each of the first seven terms in the series from the next term, are reproduced in the next seven terms.

Such periodic re-appearance of analogous properties in the series of elements has been graphically illustrated in a very striking manner with respect to their physical properties, such as the melting points and atomic volumes. In the curve which represents the relations of atomic volumes and atomic weights analogous elements occupy very similar positions, and the same thing holds good in a striking manner with respect to the curve representing the relations of melting-points and atomic weights.

Like every great step in our knowledge of the order of nature, this periodic series not only enables us to see clearly much that we could not see before; it also raises new difficulties, and points to many problems which need investigation. It is certainly a most important extension to the science of chemistry.<sup>10</sup>

<sup>&</sup>lt;sup>10</sup>Spottiswode (1883), p. 392.

The first striking fact here is that medal was awarded *not* to Mendeleev alone, but rather jointly to him and the German chemist Lothar Meyer. This already poses a problem for the predictivist thesis. Although Lothar Meyer's scheme was, as he himself pointed out, 'essentially identical' to Mendeleev's, Meyer failed to draw attention to the existence of 'gaps' in the periodicities displayed by the table and hence failed to predict new elements. Only Mendeleev explicitly derived the consequence that the scheme must be regarded as containing 'gaps' and therefore only Mendeleev explicitly predicted the 'new' elements.<sup>11</sup>

It might, of course, be argued that the true locus of scientific achievement lies not in which aspects of a theory the inventor of a theory highlights, but rather in the objective logical characteristics of the theory itself (in Frege and Popper's logical 'world 3' rather than the psychological 'world 2'); and that therefore it was reasonable to honour the two jointly in so far as their schemes (as opposed to the features of the schemes they happened to emphasise and draw logical consequences from) were 'essentially identical'.

The issue is somewhat clouded in this case by a feature that we shall eventually need to comment on at some length—that 'the' periodic table is not itself a theory and therefore directly underwrites no prediction. It is the 'periodic law' lurking in the background, underpinning the table, that makes the predictions if anything does. We shall shortly show that there are important problems here. But certainly Mendeleev himself was quite insistent that the periodic law was 'a new, strictly-established law of nature'. Indeed, he repeatedly insisted that it was precisely the fact that only he viewed the 'periodic law' in this way, and hence that only he was ready, for example, to overturn previously accepted values of atomic weights of certain already known elements so that they fitted the table better, that gave him priority over others, like Meyer, who had considered similar classifications of the elements to his own. Mendeleev explicitly contrasted his own attitude of standing ready to 'correct' atomic weight assignments in view of the law, with that of Meyer, whom he quotes as cautioning that 'it would be rash to change the accepted atomic weights on the basis of so uncertain a starting-point'. 12 It seems that Mendeleev was ready to assert 'the' periodic law and therefore to assert what he saw as its consequences concerning both revised atomic weights and hitherto undiscovered

<sup>11</sup>On the other hand, predictions of new elements were made by other periodic table constructors. For example, in his system of 1864 (and hence 5 years before Mendeleev) William Odling left spaces and used the symbol '" to indicate elements still to be discovered. These spaces included ones that would eventually be filled by gallium and germanium; though Odling did not leave a space for scandium (see Odling, 1864). Also Newlands made several predictions of atomic weights of then unknown elements. One especially successful prediction was that of an element of atomic weight 73—lying very close to Mendeleev's prediction of an atomic weight of 72 for eka-silicon (germanium). See Newlands (1865). The fact that others made predictions, and successful ones too, surely makes still more implausible the story that the acceptance of Mendeleev's scheme and the recognition he received were crucially dependent on his predictive successes.

<sup>12</sup>See Mendeleev (1891), p. 24, n. 13. Brush (1996) used the apt term 'contraprediction' for these corrections of hitherto accepted values of atomic weights of known elements. For more on these contrapredictions and their role see below.

elements, while Meyer treated the law more as a working hypothesis or perhaps a codification scheme and drew no predictions from it.

This makes it all the more mysterious why, if those making the award had been specially impressed by predictive success, they made no reference whatsoever in the citation to the fact that only Mendeleev pointed out, and explicitly stood ready to be judged by, the success or failure of these predictive 'consequences'.

Indeed, and more embarrassingly still for those defending the story about the crucial role of the new elements, not only does the Davy citation fail to mention Mendeleev's exclusive role in articulating the predictions of further elements, it makes no explicit mention of any new elements whatsoever. Its emphasis is very much on the 'marvellous regularity' revealed in the recurrence of the properties in two series each consisting of seven already known elements. There is a reference to 'seeing clearly much that we could not see before', but this too seems, in the context, to refer to hitherto unthought—of relations between known elements (at any rate no explicit mention is made of new elements). The only remark that unmistakably refers to hitherto unconsidered matters talks not about successful predictions but about 'new difficulties, and ... problems which need investigation' (emphases added).

#### 2.3. Mendeleev and the Discovery of Gallium

Maher draws attention to the 1874 paper of Lecoq de Boisbaudran in which he announced the discovery of gallium, the first of Mendeleev's predictions to be confirmed. And this is, indeed, an important paper. One possible misconception should, however, be quashed immediately. De Boisbaudran did *not* discover gallium as a result of testing Mendeleev's prediction. Instead he operated quite independently by empirical means in ignorance of Mendeleev's prediction and he proceeded to characterise the new element spectroscopically. De Boisbaudran's findings were published in the *Comptes Rendus*.

Mendeleev later read a Russian translation of this paper, and sent a note to *Comptes Rendus* claiming that this was the element which he had predicted and provisionally named eka-aluminium. De Boisbaudran at first reacted suspiciously to this claim—seeming to believe that Mendeleev was asserting priority over the discovery of the element. Indeed he initially maintained that his own element had significantly different properties from those of the element predicted by Mendeleev (perhaps motivated by a desire to support his priority claims), although he did later change his mind on this score.<sup>13</sup> He did, however, continue to insist that his discovery of gallium involved empirical techniques quite separate from anything related to Mendeleev's work and that prior knowledge of that work would, if anything, have hindered the discovery of the new element.

This raises an important point. Since no one disputes that de Boisbaudran disco-

<sup>&</sup>lt;sup>13</sup>As reported in Brock (1992), p. 324.

vered gallium by pursuing considerations quite independent of Mendeleev's periodic table, it is, relative to Mendeleev's work, surely nothing more than a historical accident that gallium had not been discovered, say, six years earlier—in which case this would have been, historically speaking, a question of accommodation within the table rather than prediction. Can it seriously be held that gallium gives significantly greater support to Mendeleev's table because of having only been discovered in 1874 than it would have done had it been discovered in 1868? It certainly appears that, so far as any consideration connected with Mendeleev goes, it perfectly well might have been discovered at the earlier date.

Admittedly, some question might arise concerning de Boisbaudran's eventual 'concession' over the properties of gallium—might he perhaps have 'fudged' his results here to agree with Mendeleev's predictions in view of the Russian's growing authority?<sup>14</sup> Given de Boisbaudran's independent nature, evinced by his continuing insistence that Mendeleev's prediction had played no role, this seems to us extremely unlikely. But in any event, it is simply a question of independent testability: were there independent reasons (coming from the independent confirmation of the theoretical assumptions underlying the experimental techniques) for accepting the values of the atomic weight, atomic volume, valency and so on at issue? We believe that there were, but shall not argue this here. It is enough for us that no one disputes that the actual identification of the new element was quite independent of any consideration associated with Mendeleev's views, from which it follows that, so far as those views are concerned, the new element might just have well have been identified in 1868. Given that, as a matter of fact, Mendeleev's views were developed in ignorance of the existence of gallium (necessary ignorance since it had not yet been discovered), and hence that there was a heuristic path to those views that did not presuppose its existence, it follows that no detail of those views could have been 'read off' the facts about gallium had they been known and that no detail of those views needed to be read off such facts. Given these circumstances, the counterfactual claim that had gallium been discovered in 1868 it would have counted significantly less strongly in favour of Mendeleev's claims strikes us as frankly bizarre.

#### 2.4. Grounded Confidence about Germanium?

Lipton talks of the predictive successes with gallium and scandium as giving greater credence to Mendeleev's 'theory' (a troublesome notion as already noted and as we shall see later in more detail) and only thence to the further prediction of germanium from that general theory. But Maher talks more directly of the impact of the successes with the first two new elements on the confidence that chemists

<sup>&</sup>lt;sup>14</sup>Similar questions have been raised, for example, about Eddington's confirmation of Einstein's star shift predictions. See Earman and Glymour (1980).

of the time had concerning the prediction of the existence of the third new element, later found and called germanium. Maher's claim is, in effect, that while the chemical community had been quite sceptical about Mendeleev's predictions of the existence of gallium and scandium, once those two elements had been identified, the community was *very* confident that the prediction of (what turned out to be) germanium would pan out. We are given the impression that his fellow chemists regarded the success with germanium as being more or less a matter of course: their degree of confidence had been 'dramatically altered' and 'now chemists were expecting to find Mendeleev's third element, though the Royal Society did not wait for that discovery, awarding Mendeleev its Davy Medal in 1882' (Maher, 1988, p. 274).

We have already pointed out that Maher cites no historical evidence for this dramatically increased confidence beyond the award of the Davy Medal; and we have shown that the citation for that award tells against his claim rather than for it. But what if—for all the lack of evidence—chemists at the time *did* regard the eventual discovery of germanium as a matter of course? Would they have been wise to do so?

The answer is patently 'no'—not because of any general sceptical-philosophical scruples about induction, but because of the particular fact that the impression of consistent predictive success for Mendeleev's scheme is a complete misrepresentation of history: a classic example of an 'effect' (Mendeleev's 'predictive success') created by selection-bias. Mendeleev made any number of predictions on the basis of his scheme (or rather schemes—there are at least 65 versions of Mendeleev's table, published and unpublished). Many of these predictions (depending on how exactly they are individuated)—perhaps a majority—were *unsuccessful*.

For example, if we consider the list of what Brock (1992) calls Mendeleev's 'later predictions', then alongside the five successes—eka-manganese (technetium, discovered in 1939), tri-manganese (rhenium, 1925), dvi-tellurium (polonium, 1898), dvi-caesium (francium, 1939), eka-tantalum (protactinium, 1917)—there were four failures—'coronium' (which turned out to be ionised iron), ether, ekaniobium and eka-caesium. (Since many of these predictions were made in the 1871 paper, Brock's reason for calling them the '*later* predictions' was presumably that they were the ones whose empirical fate was *settled* only later.)

Ether constitutes an especially interesting case. Several of Mendeleev's published tables, postdating the discovery and subsequent accommodation of the noble gases, contain predictions of elements lighter than hydrogen, including the constituent of the optical ether, which Mendeleev named 'newtonium'. Mendeleev (initially at least quite reasonably) took the existence of the ether to have been established by the current success of theories of light based on it. The fact that newtonium, if it existed at all, must permeate all transparent bodies without chemically interacting with any of their constituents had initially been perceived as a problem. But this was made unproblematic by the discovery of the nonreactive noble gases. After

this discovery, Mendeleev became fully confident that newtonium and at least one other element lighter than hydrogen existed. Indeed, in 1904 Mendeleev claimed:

At the present time, when there remains not the slightest doubt that group I, which contains hydrogen, is preceded by a zero group containing elements of lesser atomic weights than the elements of group I, it seems to me impossible to deny the existence of elements lighter than hydrogen. (Mendeleev, 1958, p. 316)

### And, in that same paper (p. 27):

As a consequence of this [satisfactory placing of the inert gases in a zero group preceding group  $I]\ldots$  we can  $\ldots$  expect elements of a zero series with atomic weights much smaller than that of hydrogen.

Needless to say, these predictions were entirely unsuccessful. There can be no doubt that Mendeleev took them very seriously however—just as seriously as the successful ones concerning gallium and the rest. There *are* admittedly various predictions scattered round Mendeleev's published and, especially, unpublished versions of his tables that might be thought of as rather half-hearted: for example, alongside those for the three famous successful predictions, question marks are also associated with the atomic weights 8 and 22 in an unpublished precursor of the 1869 paper. No such elements exist, of course, but then these predictive question marks did not make it to the published 1869 or later 1871 papers, and so Mendeleev may have been, for some never-divulged reason, relatively uncommitted to them. But in the case of elements lighter than hydrogen, Mendeleev not only claimed that it was 'impossible to deny' their existence, he put a good deal of effort into detailed prediction of their properties—just as much effort as in the cases of gallium, scandium and germanium.

Calling two such elements x and y—both lighter than hydrogen and x being the element that consituted the optical ether—Mendeleev based his predictions of their properties on numerical relations between atomic weight ratios in the following periodic table which he devised in 1904:

$$x$$
 $y$ 
 $H = 1.008$ 
 $He = 4.0$ 
 $Li = 7.03$ 
 $Ne = 19.9$ 
 $Na = 23.05$ 
 $Ar = 38$ 
 $K = 39.1$ 
 $Cu = 63.3$ 
 $Kr = 81.8$ 
 $Rb = 85.4$ 

Fig. 1. Fragment of Mendeleev's periodic table of 1904 showing the positions of predicted elements x and y which were not found.

In order to predict the atomic weight of element x—'newtonium'—he considered the atomic mass ratios of the known noble gas elements:

$$Xe/Kr=1.56$$
,  $Kr/Ar=2.15$ ,  $Ar/He=9.5$ 

From these figures he extrapolated the ratio

$$He/Newt=23.6$$

thus giving an atomic mass of 0.17 for newtonium.<sup>15</sup>

In order to estimate the atomic weight for the element which he designated as y Mendeleev considered the ratios of atomic weights for the first two members of adjacent groups in the periodic tables. He noted that the value for this ratio decreased smoothly from left to right:

Extrapolating from this atomic weight and the additional ratio of *Li/H*=6.97 Mendeleev estimated that the ratio of He/y should be at least 10, from which he deduced a value of at least 0.4 for element y.

The discovery of the noble gases also suggested to Mendeleev the possible presence of six new elements *between* the elements hydrogen and lithium. These six empty spaces were indicated in Mendeleev's periodic table of 1904. In one of these cases Mendeleev was more specific, namely in predicting a possible homologue of the halogen fluorine. This alleged new element would serve to restore symmetry to the table by making the number of halogens five thus coinciding with the five known alkali metals. Again these predictions were entirely unsuccessful.

Finally, Mendeleev's failures were not restricted to predicting non-existent new elements; he was, quite contrary to the frequently given impression, often wrong—sometimes quite badly wrong—about the properties of the elements whose existence he *did* successfully predict. For example,

1. Mendeleev predicted that the melting point of gallium would fall between those of aluminium (660°C) and indium (115°C). In fact gallium has an anomalously low melting point of 30°C.

<sup>&</sup>lt;sup>15</sup>The interest of the case of the ether, or newtonium, is given a further twist by the fact that it resists straightforward categorisation in terms of prediction or accommodation. So far as Mendeleev was concerned this was an element whose existence was already known. So in that sense its existence was not predicted but rather accommodated within Mendeleev's tables from 1904 onward. But in fact Maxwell's electromagnetic theory and persistent failures to reduce the electromagnetic field to a material ether had, in the minds of experts in these areas, made the existence of the material ether at least highly problematic—and, for many, in fact unlikely. Mendeleev's post-1904 schemes are left, therefore, logically speaking now *predicting* the existence (and indeed some of the properties such as atomic weight) of the material ether. From this point of view, this now is indeed a bold prediction—since it is certainly not (any longer) already known to be true. And of course it became bolder still in the light of Einstein's 1905 Special Theory of Relativity, which definitely expelled the material ether from 'already accepted background knowledge'.

- 2. Mendeleev predicted that salts of germanium are less stable than those of aluminium. In fact aluminium salts are the more readily hydrolysed.
- 3. Mendeleev predicted that scandium would be precipitated by hydrogen sulphide. This is not the case.
- 4. Mendeleev predicted that eka-boron sulphate is less soluble than aluminium sulphate. This is not the case.
- 5. Mendeleev predicted that eka-silicon is a refractory substance as predicted by Mendeleev. In fact it melts at the relatively low temperature of 950°C.<sup>16</sup>

If, in line with Maher's account, Mendeleev's fellow chemists were very confident about germanium ahead of its actual discovery on account of his previous successes (and we have seen no evidence that they were), then they were right only by serendipity. But there was surely enough clearsightedness—at any rate amongst experts—about the total picture regarding Mendeleev and prediction to make it very doubtful that his fellow chemists would in fact have had the unconstrained confidence attributed to them by Maher.

Since many of these unsuccessful predictions were indeed settled only after in some cases long after—1871, their fate is not directly relevant to the dispute between ourselves and Maher, Lipton and others. However, Maher—following the popular account—gives the impression that once the first two predictions had proved successful, the success of the 'remaining' third prediction was regarded by the scientific community as something of a foregone conclusion—this in turn indicating just how major an evidential impact those two successful predictions had. But there was not one remaining prediction, there were many—and of these several were eventually empirically refuted. There is no historical evidence, so far as we can tell, that the prediction of the existence of germanium was regarded in 1871 as in any way outstandingly important compared to the many other predictions. It is, of course, possible that chemists at the time were highly confident both about the germanium prediction and about the others—in which case they happened (by pure serendipity) to be right about the first such prediction that turned out to be empirically checkable. However the existence of these other predictions and their decidedly mixed empirical fates, together with the complete lack of historical evidence for it, makes the claim about the high confidence concerning the 'third' prediction in our view highly dubious.

<sup>&</sup>lt;sup>16</sup>Notice that we do *not* claim that all of these predictive failures stand on a par. The whole business of assessing the relative success rate of Mendeleev's predictions is itself a complex and tricky one. This is why we have avoided any straightforward count of successes *vs* failures. It is, for instance, clear that there were reasons to be more confident about predictions made about elements in certain areas of the tables than in others. And perhaps there are reasons to be more confident of interpolation as compared with extrapolation regarding trends in the periodic table. Nonetheless Mendeleev was entirely successful in no area and this seems enough to undermine Maher's claim.

### 2.5. A Methodological Preliminary: Prediction and Prediction

Having clarified, and attempted to counter misunderstandings of, some particular aspects of the history, we need also to clarify the general methodological view of the evidential impact of prediction that we endorse—a view that, again, could easily be misunderstood. We shall be brief and rather dogmatic—arguments are developed in more detail elsewhere (see Worrall, 1985b, and, especially, Worrall, 2001).

Our view is that *of course* the time-order of theory and evidence is of no significance *in itself*. The phenomena of planetary stations and retrogressions, for example, provide strong support for Copernicus's heliocentric theory of the solar system irrespective of the fact that those phenomena had been known for centuries before Copernicus articulated his theory. Newton's account of the (already known) precession of the equinoxes provides at least as much support for his theory as the theory's prediction of the (of course, at the time Newton first formulated his theory, unobserved) return of Halley's comet in 1758. On the other hand, the planetary stations and retrogressions provide little or no support for the Ptolemaic geocentric theory. And, similarly, the details of the fossil record provide no support for 'scient-ific' creationism, as supplemented by 'the Gosse dodge'—according to which pretty pictures in the rocks and bone-*like* structures in desert sands just happened to be parts of God's creation. 'Old evidence' for a theory—evidence that was, in the purely temporal sense, accommodated by that theory—sometimes supports the theory and sometimes does not.

The difference between the two types of case cannot, therefore, concern what was or was not known when theory was produced. Instead the crucial difference is the fact that, in the cases of little or no support, certain aspects of the theory concerned were fixed precisely to yield the phenomena at issue. The relative velocities around the deferent and epicyclic circles in Ptolemy's theory had to be 'read off' the phenomena of stations and retrogressions in order for that theory to yield those phenomena. The details of the fossil-accommodating version of creationism had to be read off the already known fossil record—which *particular* pretty pictures God chose to draw and what *particular* features the 'bone-like' structures have can *only* be determined by observation.

On the other hand, although the planetary stations and retrogressions had of course been observed long before Copernicus (indeed, as we just remarked, long before Ptolemy), Copernicus's theory committed him *directly* to their existence quite independently of their observation. The fact that the planets occasionally *seem* to stand still and then, for a while, move backwards before resuming their steady eastward progression round the ecliptic is a direct consequence of the Copernican theory's claim that we are on a moving observatory that will therefore periodically overtake certain planets and be overtaken by others as all move round the sun at different rates.<sup>17</sup>

<sup>&</sup>lt;sup>17</sup>Of course, even here, Duhem is strictly correct. The 'direct' consequence in fact presupposes auxiliary assumptions— but ones that are 'natural' within the Copernican framework and not themselves dependent on the phenomena that they then play a part in explaining.

In other words, the position we favour distinguishes two senses of 'accommodation'. A theory might be said to accommodate a fact merely on the grounds that the fact was already known at the time it was articulated. Or, a fact might be accommodated in the stronger sense that special assumptions need to be made within the theory on the basis of the fact so as to provide an account of it—in such a case, the fact must already have been known. Clearly a fact accommodated in this second sense must then have been accommodated in the first sense; but the converse implication does not hold. For ease of later exposition, call a case in which the fact happened to be already known before a theory entailed it, but in which no feature of the theory was 'read off' the fact, a case of accommodation<sub>1</sub>. And call cases in which, on the contrary, the fact was both known and used in the construction of the theory that entails it, cases of accommodation<sub>2</sub>. Our position can then be put very simply: accommodation, stands on a par with prediction so far as evidential support is concerned (other things, of course—such as the logical strength of the empirical statements concerned—being equal), and only accommodation<sub>2</sub> carries less weight.

There is no reason why a successful accommodation<sub>1</sub> should not count just as highly for a theory as a predictive success—nothing prevents the former being just as severe a test for the theory as the latter. So planetary stations and retrogressions and the precession of the equinoxes—which Copernican theory and Newtonian theory, respectively, accommodated<sub>1</sub>—fully supported those theories. Or, to take another example, the precession of Mercury's perihelion, which had been known about for decades beforehand, fully supported the general theory of relativity.

The accommodation<sub>2</sub> of some piece of evidence e by some theory T undoubtedly tells us something positive about T—namely that it is at least consistent with e. When, as sometimes happens, it begins to seem as if there is no possible explanation for some evidence within some theory, then even finding an accommodation<sub>2</sub> of that evidence may give scientists more confidence in the theory. Something like this happened, for example, with Darwinian evolutionary theory and the widespread phenomenon of apparently altruistic behaviour—the consistency proof in that case coming in the form of the theories of kin selection and reciprocal altruism.

Something else should be said about the impact of accommodation<sub>2</sub>. When the (general) theory concerned is strongly supported *independently of the fact at issue*, the accommodation<sub>2</sub> of some fact, even in this *ad hoc* way, may well still supply the best explanation that science can currently supply for that fact. So, for example, the best explanation in, say, 1700 for the observation of no stellar parallax was surely the Copernican one—that there must in fact be an apparent parallactic motion but that even the nearest stars are so far away as to make the effect too small to be detected by even the best available telescopes. (Here, as before with Ptolemy and with scientific creationism, we use the phenomenon—no observed parallax—to fix (in this case in a rather loose way) an otherwise free parameter in the theory (distance to the nearest star).)

Not only can accommodations, have this sort of impact, but it is standard scientific practice to use empirical data to fix parameter-values left free by general theoretical considerations. (Why conjecture when you can measure?) So, for example, the classical wave theory of light leaves the values of the wavelength of monochromatic light from various sources, such as a sodium arc, entirely free. However, that general theory has various consequences that characterise that wavelength as a (one-to-one) function of a set of measurable quantities—fringe distances and slit distances in some interference experiment, for example. Data from such an experiment then allow the deduction of a specific version of the wave theory, complete with a value for the theoretical parameter of wavelength of light from a sodium arc. Of course such data in a sense provide support—indeed maximum support for that specific theory, because given the general theory they deductively entail it. But notice that this support judgement is ineliminably conditional—for someone who already accepts the general wave theory (with free parameter for the wavelength of light from the sodium arc), the fringe and slit distance data provide conclusive reason for accepting the specific version of the wave theory with the particular wavelength value; but those data alone give no extra reason at all for accepting that general wave framework. This is underlined by the fact that, in the case of creationism, the 'fossil' data similarly give a (near) conclusive reason for holding the gossefied version to anyone who ahead of that data holds the general creationist view. Given that you already accept that God created the universe essentially as it presently is in 4004BC, then in the light of the 'fossil' data you had better hold the specific version of the theory that has God painting pictures in the rocks and so on at the time of creation. But obviously the right judgement is that this data only gives you good reason for accepting the specific gossefied version of creationism if you already accept creationism in general—it gives no reason whatsoever for being a creationist in the first place. By contrast, the data about planetary stations and retrogressions support not just the specific Copernican models that entail that data, but also the basic general Copernican framework.

Notice one final wrinkle. Very often, once some data has been used to fix an initially free parameter, the specific theory concerned goes on to entail some further independent data. Thus, having used, for example, data from the two-slit experiment to fix the value of the wavelength of light from a sodium arc, the more specific theory will then entail results about fringe distances in other interference or diffraction experiments (for example, the one-slit experiment). Of course this further data—if it is indeed data, if the theory gets the further results correct—fully supports both the specific theory that entails it and the general framework. Such further independent data may be either predicted in the temporal sense or accommodated<sub>1</sub>. This again distinguishes the wave theory case from that of creationism. In the latter, gossefying relative to particular data *D* produces a theory that is not testable *independently* of *D*. It might seem to make no difference in cases where independent testability holds whether we say that the data used to fix

some parameter supports the general theory or not. But clarity and even-handedness surely require that we say that in neither the wave theory nor the creationist case does the data used in fixing parameters support the theories concerned in the unconditional sense. However there is in the wave theory, but not the creationist, case *other* data that do provide such support.

The general methodological judgements we endorse are, then, the following. Support within a given theoretical framework must be distinguished from support for a general framework (obtained via some specific version of it). If some general theory is already accepted for independent reasons (in particular for independent empirical reasons), then the specific version of it that allows the accommodation<sub>2</sub> of some evidence *e* is (perhaps maximally) supported by *e*. But such a piece of evidence *e* supplies no extra reason in favour of the general theory in the first place. On the other hand, if *e* is either predicted as new evidence or accommodated<sub>1</sub>—that is, it just happens to be already known evidence but was not used to fix any feature of the specific theory at issue—then it supplies support, not only for the specific version that entails it, but also for the underlying general theory. There is no distinction at all in this regard between prediction and accommodation<sub>1</sub>.

Our account is, of course, a normative one—an account of how evidential support ought to be measured. Linking it to actual judgements by scientists and others is, then, a further matter. As several commentators have pointed out, there may, for example, be a special psychological factor about the prediction of hitherto unsuspected effects. These predictions have a special 'newsworthy' character and can perhaps be more readily and more widely appreciated amongst the educated public as important indicators of the value of the theory than simple accommodations<sub>1</sub> (the identification of which requires more knowledge of the theoretical structure of the scientific field concerned). But this psychological effect can easily be 'controlled for'—mainly by concentrating on the judgements of real experts who are actively researching in the relevant field. We would expect such judgements in fact made by experts to be in line with our normative account.<sup>18</sup>

So, in the Mendeleev case we would expect to find historically the following attitude—at any rate amongst the experts. Insofar as scientists were interested in applying Mendeleev's scheme or simply thinking of it as a codification of the phenomena, it should make no difference at all whether some phenomenon of interest was predicted or accommodated in either sense. However, in so far as

<sup>&</sup>lt;sup>18</sup>See, for example, the discussion between Brush, Achinstein and Shimony in Forbes, Hull and Burian (1995). The eminent physicist Yuval Ne'eman, involved in the discovery of the 'eightfold way' makes the following very insightful comment about the prediction of the Ω- particle by the eightfold way:

the importance attached to a successful prediction is associated with human psychology rather than with scientific methodology. It would not have detracted at all from the effectiveness of the eightfold way if the  $\Omega$  had been discovered *before* the theory was proposed. But human nature stands in great awe when a prophecy comes true, and regards the realizations of a theoretical prediction as irrefutable proof of the validity of the theory. (Ne'eman and Kirsch, 1986, p. 202)

scientists were interested in support for the underlying ideas behind the scheme—in confirming the idea that Mendeleev had discovered some real periodicities in nature—it *does* make a difference. Here we would expect *firstly* that successful predictions are of course taken as important indicators of the value of Mendeleev's ideas. But, *secondly*, we would expect such predictions to be regarded as no more important indicators than the successful, non-*ad hoc* explanation or accommodation (that is, accommodation<sub>1</sub>) of any relevant already known phenomenon. And, *thirdly*, we would expect that the only known evidence whose 'explanation' might be regarded as of doubtful value in confirming Mendeleev's underlying views will be evidence which was accommodated<sub>2</sub>. This consists of phenomena which could be given a place in Mendeleev's detailed scheme only by tailoring the details of that scheme to them, in a way that yielded no independent tests.

We shall see, in Section 5, that these expectations are broadly fulfilled by the history—though they are overlaid not only with the usual uncertainties about interpreting historical data, but also with a number of interesting complications which differentiate this case from other cases (taken almost exclusively from physics) that have been analysed in this regard.

Another way in which the general message that we endorse might be expressed is through clarification not of the notion of 'accommodation' but instead of that of 'prediction'. In fact scientists often use the notion of prediction in an atemporal sense—that is, one which carries no implicit requirement that 'predicted' events have been hitherto unobserved. Here, for example, is a comment on Newton's theory from French's excellent textbook on Newtonian Mechanics (French, 1971, pp. 5–6; emphases added):

like every other good theory in physics [Newton's theory] had predictive value; that is, it could be applied to situations *beside the ones from which it was deduced*. Investigating the predictions of a theory may involve looking for hitherto unsuspected phenomena, or it may involve *recognising that an already existing phenomenon must fit into the new framework*.

This idea is by no means unknown to philosophers. The same idea is at the heart of Whewell's notion of consilience, for example; and it was explicitly spelled out by Moritz Schlick:

the confirmation of a prediction means nothing else but the corroboration of a formula for those data which were not used in setting up the formula. Whether these data had already been observed or whether they were subsequently ascertained makes no difference at all.<sup>19</sup>

Given this explication of prediction, the general message we endorse could equally well be formulated by reserving the term 'accommodation' for cases of what we have been calling accommodation<sub>2</sub>, as by insisting that all predictions, if suc-

<sup>&</sup>lt;sup>19</sup>Quoted from Popper (1979), p. 112.

cessful, count—other (logical) things being equal—equally in favour of a theory whether or not they are (temporal) *pre*dictions.

### 3. Brush's Account of the Reception of Mendeleev's Ideas

Stephen Brush has, in several papers (for example Brush, 1989), examined different episodes from the history of science and argued that the scientists involved in them did not in fact regard (temporal) predictive success as carrying an epistemic premium. However, in a recent paper (Brush, 1996) on the reception of Mendeleev's ideas, he claims that this case is exceptional—here temporal novelty of predictions really did count.

Brush's account can hardly be accused of being unaccompanied by serious historical data and research. He analysed much of the chemical periodical *and* chemical textbook literature from the latter part of the nineteenth century in America and Britain, and also some of the literature from France and Germany in the same period. Brush came to a conclusion that is apparently straightforwardly 'propredictivist':

After spending considerable time perusing the crumbling pages of late nineteenth-century chemistry journals and textbooks, I have confirmed the traditional account: Mendeleev's periodic law attracted little attention . . . until chemists started to discover some of the elements needed to fill the gaps in his table and found that their properties were remarkably similar to those he had predicted. The frequency with which the periodic law was mentioned in journals increased sharply after the discovery of gallium, most of that increase was clearly associated with Mendeleev's prediction of the properties of the new element. (p. 617)<sup>20</sup>

Since we shall need to refer back to this claim quite often, let us call it (propredictivist) 'claim 1'.

Although critical of the precise claims of Maher and Lipton, and especially of the evidential basis they provide for their claims, Brush nonetheless holds that they may be 'broadly' correct:

My survey of chemistry textbooks and articles ... suggests that many chemists did give some credit for novelty; they considered that, other things being equal, the prediction of a new element and its properties counted more than fitting a known element into the table. But not thirty-one times as much! (p. 609)

(Remember that, on Maher's view, the successful prediction of two new elements counted for more than the prior successful accommodation of the then known sixty-two elements—because the two successes dispelled the scepticism that had existed despite the sixty-two successful accommodations.) Since we shall again need to

<sup>&</sup>lt;sup>20</sup>Unadorned page references throughout Section 3 are to Brush (1996).

refer later to the claim made in this passage, let us call it (pro-predictivist) 'claim 2'. So claim 1 is that little attention was paid to Mendeleev's scheme before the predictive successes were achieved; while claim 2 is that these predictive successes counted (considerably) more with the scientific community of the time than did the scheme's accommodational success.

Against this, we will argue

- (a) *both* that Brush's claims 1 and 2, although individually clear, are not clearly mutually consistent *and* that he adds various concessions and details in the course of his article that make it difficult to know in the end what *precise* thesis is being propounded; and
- (b) that the evidence he himself supplies, on further analysis, fails to support propredictivist claims 1 and 2.
- 3.1. Some Complications and Tensions in Brush's Analysis

In a section of his paper entitled 'The Limited Value of Novel Prediction', Brush asserts, pro-predictivist claims 1 and 2 notwithstanding, that:

almost every discussion of the periodic law in nineteenth-century chemistry textbooks, including Mendeleev's, gives much more attention to the correlations of properties of the known elements with their atomic weights than to the prediction of new ones. (p. 612)

He also points out several times the important evidential role played by the success of Mendeleev's 'contrapredictions'—the 'corrections' of atomic weight values previously assigned to already known elements—such as beryllium, uranium and tellurium—so that they fitted into his table smoothly. And indeed the most elaborate statement of Brush's general conclusion seems to be the following:

While chemists differed on the relative importance of prediction and accommodation, it seems fair to approximate the consensus as follows. The reasons for accepting the periodic law are, *in order of importance*, [1] it accurately describes the correlation between physicochemical properties and atomic weights of nearly all *known* elements; [2] it has led to useful corrections in the atomic weights of several elements . . . ; and [3] it has yielded successful predictions of the existence and properties of new elements. (p. 612; emphases added)

But is this new claim really consistent with claims 1 and 2? Clearly this needs further investigation and we begin with the 'contrapredictions'.

First it is surely important to emphasise (as Brush does not) that there turned out to be *independent* empirical evidence for the new values assigned to these atomic weights (this re-evaluation relied, of course, on already accepted auxiliary theories—atomic weights of elements are highly theory-laden facts). It was not that chemists simply came to accept the new values because those values made those elements fit Mendeleev's table better (that would be a classic case of an *ad hoc* accommodation<sub>2</sub>). For example, the corrected value of the atomic weight of

beryllium was confirmed independently of any consideration of its place in any table by Nilson and Petterson's discovery of one of its gaseous compounds—beryllium chloride. This discovery meant that an evaluation of beryllium's atomic weight could be made using already accepted 'background knowledge'—concerning the properties of chlorine and Avogadro's number. (Brush does mention this discovery but does not underline its significance.)

As Brush himself agrees, there is surely no general methodological reason why the empirical success of these aptly named contrapredictions should count any less in favour of Mendeleev's scheme than the success of his predictions of new elements. This becomes, we hold, uncontestable in view of the just emphasised fact that the corrections of atomic weights were independently supported rather than made simply so as to fit the table. Indeed Brush suggests that from the (correct, if only intuitive) point of view of what counts as a severe test of a theory, it might even be argued that such successful contrapredictions should count even more than successful novel predictions (since they are inconsistent with hitherto accepted 'background knowledge' rather than simply independent of it). Be that as it may, Brush certainly thinks that they count at least equally, and finds nothing in his historical researches to suggest that this intuitive methodological judgement failed to be reflected in the particular judgements of late nineteenth-century chemists.

But what, then, of the claims about the greater impact of novel predictions? Brush attempts to glide over any difficulty here by suggesting that contrapredictions should themselves count as 'novel predictions': '[Mendeleev] proposed changes in the accepted atomic weights of several elements in order to fit them into his table ... All of these may be called "novel predictions" (p. 599). But this surely only obscures the issue. We have, of course, no complaint against the thesis that all genuine tests of a theory, if passed by that theory, count in its favour (and, other logical—things being equal, count equally). Indeed this is an outline, pre-analytic version of precisely the general methodological thesis we endorsed in Section 2.5. This thesis entails that successful contrapredictions count fully in favour of the theory that makes them; but it also entails that accommodations—in the sense simply of explanations by the theory of already known evidence—may also count fully in a theory's favour, since they too may be genuine tests. The only evidence that counts less is evidence accommodated in the sense that it was not only already known in advance but was also bound, because of the way in which the theory was developed, to be entailed by that theory (that is, 'accommodation<sub>2</sub>'). The dispute is over the issue of whether Mendeleev's prediction of new elements played a historically special role compared to other kinds of evidence—that is, whether novel facts here in the precise sense of temporally new evidence were especially weighty supports for Mendeleev's scheme. Brush is—we should again stress, in our view correctly—going against this thesis by admitting that successful contrapredictions counted at least as much.

We turn next to Brush's still more telling concession that the ability of Mende-

leev's periodic 'law' to yield an accurate description of 'the correlation between physicochemical properties and atomic weights of nearly all *known* elements' counted even more highly—in the aggregated consensus—than either the predictions of the new elements or the contrapredictions. (He states, remember, that his historical research shows that the reasons for accepting the periodic law were, in order of importance, first, its 'accommodation' of the known elements; second, its 'contrapredictive' success; and (only) third, its success in predicting new elements.) He points (as we have done) to the citation of the Davy Medal Award as showing that this award seems to have been made largely on the basis of the successful 'accommodations'. He also states at one point 'Frequently the reader of [nineteenth-century textbooks] is given the impression that the periodic law is *established* by these correlations [of "properties of the known elements with their atomic weights"] and then *applied* to make predictions' (p. 612; emphases in original).

But all this is surely in direct conflict with the first of the pro-predictivist assertions (claim 1) quoted earlier: if the successful accommodation of the correlation between properties and atomic weights of known elements was to be the single most important factor in the acceptance of Mendeleev's periodic law after, say, 1874, then it is difficult to see why it should be true—as Brush asserts (p. 617)—that 'Mendeleev's periodic law attracted little attention . . . until chemists started to discover some of the elements needed to fill the gaps in his table'. One would, on the contrary, have expected it to attract a great deal of attention at the stage when it just explained the properties of the known elements, and then attract some more once the predictions of new elements proved successful. If it were true that, as a matter of descriptive historical fact, Mendeleev's periodic law attracted little attention and hence very little adherence before 1874, then Brush would have supplied no explanation for it.

He does mention that there was a strong pragmatic reason for a chemist to be less interested in the new elements than in the already known ones—namely their relative scarcity:

The reason why the predicted elements were less important to chemists than the known elements that were initially correlated by the periodic law is the same reason why they had not been discovered before 1869: their abundance at the earth's surface is very small. (p. 612)

This may indeed be true of the judgments of importance made by writers of chemical textbooks (well known, after all, for a tendency towards the pragmatic and the prosaic!). But it can hardly be used to resolve the apparent conflict in Brush's account, since he explicitly states that the explanation of the properties of the known elements was chief amongst the 'reasons for accepting' the periodic law. The relative abundance of the known elements might account for some chemists being more concerned with the sections of the periodic table involving those elements, but it surely cannot account for their thinking of the explanation of the

properties of those elements as the chief reason for holding the periodic law to be some sort of general truth.

Brush's acceptance that, in the aggregate, the accommodation of the properties of the known elements was the single most important factor in the acceptance of Mendeleev's periodic law in the late nineteenth century, while inconsistent with claim 1 *above*, might seem to be vindicated by claim 2 (thus showing that these two apparently complementary pro-predictivist claims are themselves in some tension). In claim 2, Brush modifies—albeit in rather jocular fashion—Maher and Lipton's attempt to quantify the relative impacts of accommodations and predictions: 'other things being equal, the prediction of a new element and its properties counted more than fitting a known element into the table. But not thirty-one times as much!'

Brush then needs to do some work to bring claims 1 and 2, together with the various additional concessions and modifications, into a fully coherent overall view. So far as we can tell, that view would have to amount to something like the following. (i) There were, of course, marked individual differences in the support judgements of individual scientists reacting to Mendeleev's work. (ii) These individual judgements can nonetheless be aggregated to form a 'consensus' view according to which the total evidential support provided for Mendeleev's periodic 'law' by the accommodation of the properties of known elements was higher than the total evidential support provided by the success of the predictions of new elements. However, (iii) what might be called the perceived 'empirical support per single experimental/observational item' was much higher for predictions than it was for accommodations (the fact that the aggregated degree of support from accommodations was higher than the aggregated degree of support from predictions then being explained by the fact that there were, at that time, sixty-two accommodations and only two predictions).

If this is a correct analysis of it, then the chief problem with Brush's overall account—aside from any issue about the historical evidence in its favour—is that, by agreeing with Maher and Lipton that the novel predictions counted more while denying that they counted sufficiently more to outweigh the total effect of the accommodations, it ends up in no man's land. Brush may have an explanation for why special attention should have been paid to the predictive successes (they carried a lot of 'impact per unit', as it were); but this does not, despite his claims and despite, perhaps, first appearances, translate into an explanation for what he accepts is the historical fact that Mendeleev's periodic law attracted little attention before 1874—that is, before the initial success of the predictions. What his account would lead us to expect is, on the contrary, a high rate of credit for, and interest in, Mendeleev's scheme before 1874 and a somewhat higher rate afterwards.

But aside from its explanatory power is there any historical evidence for the truth of this account? And, in particular, is there evidence for the precise propredictivist claims 1 and 2 on which it is—somewhat shakily—built?

3.2. Does Brush's Evidence Really Show that the Predictive Successes Carried More Impact?

First, we concentrate on Brush's precise claim (the essence of 'claim 1') that his historical research

confirm[s] the traditional account: Mendeleev's periodic law attracted little attention . . . until chemists started to discover some of the elements needed to fill the gaps in his table and found that their properties were remarkably similar to those he had predicted. The frequency with which the periodic law was mentioned in journals increased sharply after the discovery of gallium, most of that increase was clearly associated with Mendeleev's prediction of the properties of the new element. (p. 617)

Remarkably enough, Brush immediately adds to this claim the admission that 'in many cases it is difficult to prove a causal relation [between the success of the predictions and the frequency with which the periodic law is mentioned] since the authors do not mention the prediction' (*ibid.*). Two points should be made:

- (a) The whole issue here is, of course, exactly about causality—no one disputes that Mendeleev's scheme attracted somewhat more attention after 1874 than before, the issue is partly over the extent of the increase but, more significantly, over what exactly underlay that increased attention. The inference simply from the premise that there was greater interest in Mendeleev's scheme after the predictive successes to the conclusion that it was the predictive successes that caused the increased interest would be, as it stands (that is, without invoking further evidence), a classic instance of the *post hoc ergo propter hoc* fallacy.
- (b) The acknowledged absence 'in many cases' of any mention of the prediction of gallium is not simply an impediment to drawing a causal conclusion about the role of that prediction, it surely gives at least some *prima facie* support to the causal claim that the prediction played no significant role: it would be strange indeed for an author who had been drawn to Mendeleev's scheme in large part by its predictive success to make no mention of that success at all.

And, indeed, Brush's evidence on this issue (given in his table 1) is striking: no less than 132 of the 197 journal articles 'mentioning' the periodic law in the period 1871–1890 fail to mention the confirmed predictions of new elements.

Perhaps this is why, despite the (just quoted) claim that the evidence from frequency of mention of the periodic law in journals was 'clearly associated with Mendeleev's prediction of the properties of the new element', Brush elsewhere states that the evidence from journals is of little value one way or the other:

The number of explicit references to the periodic law to be found in late nineteenth-century journals is small and fluctuates irregularly. From these data alone it would be difficult to judge whether the periodic law was actually accepted by the entire chemical community or was merely an exotic concept, of interest only to a few specialists. (p. 600)

And he goes on to claim that the really telling evidence comes not from journals, but from textbooks:

If a majority of chemistry textbooks published in a country present the periodic law—as is the case for the United States and Britain by 1890—it is reasonable to conclude that the law was generally accepted in that country. (*ibid*.)<sup>21</sup>

But, to repeat, the extent of the diffusion of Mendeleev's scheme is not the issue here—no one disputes that this was widely (though not universally) 'accepted' by 1890 in the scientifically advanced countries. The question at issue is the relative strength of the roles played in this diffusion by evidence of various sorts and in particular by the successful predictions of new elements.

Looked at from the point of view of this question, even Brush's most vaunted evidence seems to us remarkably underwhelming. Of the total of 244 chemistry textbooks published in the period 1871 to 1890 in the USA, Britain, Germany and France that Brush examined, 76 are recorded as 'mentioning' the periodic law (that is, 168 do not mention it!). Of those 76, 43 mention the successful predictions (that is, 33 do not!); and, while it is true that there is some trend towards a higher rate of citation of the successful predictions later in the period, it is still true that 5 of the 25 textbooks published in the period 1886–1890 in the US and Britain, and 3 of the 7 published in Germany or France which mention the periodic law do not mention the successful predictions. Remember once again that what is at issue here is not whether the successful predictions carried important weight, but whether they carried an especially heavy weight relative to other confirmatory evidence. Brush's own historical evidence hardly seems to be telling for the propredictivist view. Indeed it seems to us, if anything, to tell in the opposite direction. If the single most weighty pieces of evidence in favour of Mendeleev's scheme were the predictions of new elements and their properties, then it surely seems very strange that, overall, more than 43% of those textbooks writers who are taken as evidence for the 'acceptance' of the scheme fail to mention the predictions. And, even allowing for the reasonable suggestion that word of the success of these predictions may take some time to get around, it seems strange, on that same supposition, that more than 25% of even the textbooks published in the period 1886–90 (that is more than twelve years after the discovery of gallium) that present Mendeleev's 'law' still fail to mention the successful predictions.

The only remaining evidence in Brush's paper is a series of isolated quotations from chemists of the time—such as Pattison Muir, Hell, Crookes, Cooke and others (pp. 610–611). It is unclear just how much weight Brush puts on these himself; but objectively they can surely carry very little.

Many of them are uncontroversial: for example, the Stuttgart chemist Carl Hell

<sup>&</sup>lt;sup>21</sup>There are surely difficulties even with this claim. Would not the most telling evidence in fact be instances in *research articles* of explicit assertions by scientists that what especially recommended Mendeleev's scheme to its author as a basis for further research was that scheme's success in predicting the properties of new elements?

is quoted (p. 610) as holding that the agreement of gallium's properties with those predicted by Mendeleev 'has contributed to the recognition and confirmation of the periodic law'. Only someone who inclined to the strange view that successful prediction carried no confirmatory weight at all could find this any sort of telling remark.

Perhaps the two most striking passages quoted by Brush are from William Crookes and from Mendeleev himself. Brush claims that the latter 'stressed the importance of predictions when he reviewed the status of his periodic law in 1879' (*ibid.*) in the following remark (to which we have added the emphasis):

No natural law acquires any scientific importance unless it introduces, so to speak, some practical conclusions, or, in other words, unless it admits of logical conclusions capable of *explaining what has before remained unexplained*, and, above all, unless it raises questions which can be confirmed by experience.<sup>22</sup>

But Mendeleev's talk of 'explaining what has before remained unexplained' is perfectly consistent with the phenomena at issue being already known phenomena—such as the similarities between the known elements in corresponding positions in the table. Thus Mendeleev certainly allows that the fact that known valency relationships, for example, 'follow' from his scheme can count significantly in its favour. It is true that 'raising questions' might refer to making predictions about initially unknown matters, and also true that he does say that these count 'above all'. Notice, however, that, even then, his message seems to be that it is the fact that the 'natural law' makes predictions ('raises questions') at all that is its really significant virtue and not whether these predictions turn out to be empirically confirmed. After all, if a theory makes predictions about matters that scientists had not even thought about hitherto, then science learns something significant from their investigation either way—that is, whether or not the predictions turn out to be correct. Moreover, 'raising questions' could at least equally plausibly refer to the 'contrapredictions'—'does beryllium really have the atomic weight that chemists have hitherto believed it has?' Finally, there is no explicit mention of the specific role of the newly predicted elements.<sup>23</sup>

The other apparently telling quotation comes from William Crookes (1877, p. 292):

The prevision of phenomena not yet observed has been rightly declared by methodologists to be one of the principal distinctions between science, in the strict sense of the term, and a mere accumulation of unorganised knowledge; the discovery of gallium thus shows the value of Mendeleev's theory.

But, once again, no one denies that successful prediction 'shows the value' of Mendeleev's theory, the issue is whether *only* such evidence shows its value or

<sup>&</sup>lt;sup>22</sup>Mendeleev (1879a), p. 292 (quoted from Brush, 1996, p. 610).

<sup>&</sup>lt;sup>23</sup>We would not, however, want to deny that Mendeleev elsewhere does make fairly unambiguous claims about the special power of these predictive successes—but then of course he had his own personal reasons for doing so.

whether, at any rate, such evidence is much more telling than the systematic explanation (not of course the 'unorganised' 'accumulation') of known phenomena. Crookes in fact expressed a definite view on this issue, apparently unnoticed by Brush:

Mendeleeff considers that all the functions by which the dependencies of the elements on the atomic weights are expressed are periodic. The properties change in accordance with the increasing atomic weights, and are then repeated in a new period with the same regularity as in the former. If we examine his scheme we must admit that it brings admitted relations into a very prominent light. Such groups as fluorine, chlorine, bromine, and iodine; as sulphur, selenium, and tellurium; as nitrogen, phosphorus, arsenic, and antimony . . . fall into positions which well agree with their respective analogies . . . A further study of Table II [a version of Mendeleeff's table] will bring to light many more curious instances of such representation, which we submit, lend a powerful support to M. Mendeleeff's arrangement. (Crookes, 1877, p. 303; emphasis added)

Notice that Crookes is here talking about already known ('admitted') relations between *already known* elements—fluorine, chlorine, nitrogen, and so on.

#### 4. The Periodic Table and the 'Periodic Law'

Having argued that neither Peter Lipton nor Patrick Maher nor Stephen Brush supplies any convincing evidence that the successful predictions were the, or even a, major factor in changing attitudes towards Mendeleev's table, nor indeed much in the way of evidence for the existence of any radically changed attitudes, the next stage is clearly to provide our own analysis of the evidential situation and its evolution from 1869 onwards. We shall provide this in the following, final section. However, one further preliminary clarification is necessary. There is at least one sense in which the Mendeleev case is indeed significantly different from others that have been analysed from the point of view of the general prediction versus accommodation debate—though not the sense indicated by Brush.

As already mentioned, the Periodic Table is patently not itself a theory and therefore does not in itself have any logical consequences. Mendeleev saw his Table (indeed, significantly, Tables—he produced a total of sixty-five different ones through the course of his career) as embodying, or as underpinned by, something he called the 'periodic law'. The predictions of the existence of the new elements are, then, if logical consequences of any general claim, presumably logical consequences of this periodic law. Mendeleev himself wrote:

if all the elements be arranged in the order of their atomic weights a periodic repetition of properties is obtained. This is expressed by the law of periodicity; the properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence or, expressing ourselves algebraically, form a periodic function of the atomic weights of the elements. (Mendeleev, 1891, p. 16)

The rows and columns of Mendeleev's table are meant to reflect the 'periodic function' asserted to exist by this periodic law.

It is no surprise that Mendeleev never gave precise mathematical expression to this 'periodic function'. In fact, it would be impossible, we claim, to state at all precisely the content of Mendeleev's 'periodic law'. (We are, of course, referring here to the law as articulated by Mendeleev himself and as understood by his contemporaries. There is no doubt that the subsequent development of chemistry has seen at least great progress toward the articulation of a precise version of the periodic law, based ultimately on quantum mechanics.<sup>24</sup>)

Mendeleev clearly believed (along with others) that there is a whole set of dependencies of chemical properties on atomic weight and that some of these properties recur at regular intervals. The 'periodic law' amounts, essentially, to a commitment to look for such dependencies and recurrences, and the suggestion that something of importance will emerge from this search.

Mendeleev admitted that the basic idea of two elements having 'analogous' properties was a difficult and 'relative' one:

it is easy to fall into error in the formation of the groups because the notions of the degree of analogy will always be relative, and will not present any accuracy or distinctness. Thus lithium is analogous in some respects to potassium and in others to magnesium; or beryllium is analogous to both aluminium and magnesium. (Mendeleev, 1891, p. 15)

His argument seems to have been that the fact that one could make a case for periodic dependencies of properties of elements on the basis of such a natural ordering principle as that of atomic weight lent objectivity to the analogies thus revealed. That is, Mendeleev was so inclined to regard the ordering by atomic weights as natural that he took this as evidence for 'lower level' claims about real similarities between elements, rather than following the usual methodological process whereby lower level empirical results, usually thought of as relatively more certain, are taken as evidence for higher level laws and theories.

Notice that the lack of specificity of the 'periodic law' as then conceived does not entail that Mendeleev failed to operate in a precise way *locally*. For example, he himself gave a clear account of his approach to working out some of the main relationships between the properties of the elements in his textbook *The Principles of Chemistry*. The method consists of simultaneous interpolation within groups or columns as well as within periods or rows of the periodic table. The average of the values of the numerical properties of the four elements flanking the element in question are taken to determine the latter's properties. So Mendeleev wrote:

<sup>&</sup>lt;sup>24</sup>See Scerri (1998), where it is argued that, while still no one has succeeded in giving a mathematically precise version of the periodic law, and while the law has not *exactly* been reduced to quantum mechanics, sufficient progress has been made to suggest that a precise version of the law *may* eventually be possible (if only 'in the limit'). (See also Scerri, 1999, where further clarification is provided.)

If in a certain group there occur elements, R1, R2, R3, and if in that series which contains one of the elements, for instance R2, an element Q2 precedes it and an element T2 succeeds it, then the properties of R2 are determined by the mean of the properties of R1, R3, Q2 and T2. (Mendeleev, 1891, p. 692)

In the various editions of his textbook, and in the publications dealing specifically with his predictions, Mendeleev repeatedly gives the example of calculating the atomic weight of the element selenium, a value that was known at the time and which could thus be used to test the reliability of his method.

(32+75+80+127.5)/4=78.65, which is approximately the correct value for the atomic weight of Se (79).

But there are two points to stress. The first is that Mendeleev did not always operate according to this clear procedure. This is true—surprisingly enough—even in the case of some of his famous predictions. For example, if his method is applied to predict the atomic weights, atomic volumes, densities and other properties of gallium, germanium and scandium, it produces values which differ significantly from those that Mendeleev actually published. Employing Mendeleev's stated method of taking an average of the four flanking elements around gallium, for instance (using, of course, the atomic weights available at the time), gives a prediction of 70.9. Mendeleev modifies this value to 'about 69' without any form of explanation. The accepted value of the atomic weight of gallium at the time of its discovery was 69.35. Since Mendeleev did not of course know this value when he produced his table, and assuming he did not simply make a crude calculational error, this suggests that he had some further theories which operated on some occasions to 'correct' what the above method would otherwise yield. But he never divulged these extra assumptions—he seems, in other words, not to have found it necessary to specify how and why he departed from the simple method of interpolation.

The second point to be stressed about this 'simple' method is that it in fact hides a good deal of vagueness (or rather, theoretical *Spielraum*). Which other elements 'flank' a particular one depends, of course, on (i) which other elements exist, (ii) what properties (in particular, atomic weights) they possess, and (iii) how the table is constructed (in particular, when a new row was begun).

Concerning (iii): Mendeleev, as is well known, produced different tables at different times. In fact, and as already mentioned, approximately sixty-five periodic tables were devised by Mendeleev not including partial tables and simple lists of elements. These sixty-five tables consist of published as well as unpublished manu-

script forms and tables devised by Mendeleev for the purposes of giving public lectures. They show considerable variation indicating the gradual evolution of the periodic system.<sup>25</sup> This again shows that Mendeleev was groping his way towards the best form of the periodic table and that his method, although based, importantly, on the atomic weight ordering, was augmented by numerous, probably rather vague and certainly never fully articulated, heuristic devices.

As for (ii), Mendeleev was, as indicated, quite ready to change atomic weight assignments from those accepted at his time to avoid significant discrepancies in his tables. This may sound *ad hoc*, but in fact, and as we already pointed out, some of these 'contra-predictions' could be independently tested and their success in independent tests played an important evidential role—one which, as Brush allows, there is no reason (either historical or methodological) to suggest was any less significant than that played by the prediction of new elements.

There were more difficulties. In hindsight, Mendeleev was, of course, operating with the 'wrong' ordering principle. The 'correct' ordering principle from the point of view of later science is that based on atomic number, first shown by Moseley in 1914. The atomic weights of the various elements simply reflect purely contingent truths about the relative amounts of various isotopes of those elements in 'typical' samples from the earth. This explains why Mendeleev and his contemporaries met various difficulties. (Notice that we do not need hindsight to identify the difficulties, but only to understand the explanation of them.)

First, the sequence of non-integer atomic weights, consisting of weighted averages over all the isotopes of any particular element, is highly irregular. As a result it was not clear whether any gaps or indeed how many gaps existed between any two consecutive values of known atomic weights. This sort of problem may be illustrated by reference to any of the periods or series in the periodic table. The following data is taken from a periodic table produced by Mendeleev in 1904 and corresponds to series 4 in his scheme:

The gaps between the values of atomic weights are irregular, thus giving no clear indication as to whether one should expect any missing elements within this or other sequences of elements.

Hence, although Mendeleev in particular was committed to ordering the elements according to increasing atomic weights, the use of this 'incorrect' ordering principle (along with various other difficulties) produced much ambiguity in the prediction of missing elements—which resulted, as we already pointed out, in a whole series of failed predictions by Mendeleev about unknown elements and their properties.

One of the problems that further compounded these difficulties was the fact that many of the atomic weights with which Mendeleev was operating—that is, aside

<sup>&</sup>lt;sup>25</sup>See Smith (1975), pp. 199–202 for a complete list of Mendeleev's 65 documented periodic tables.

from those that he 'corrected'—were incorrect (because of mistaken techniques and auxiliary assumptions used by his predecessors). Still further difficulties in this regard were produced by the existence of so-called 'pair reversals'. As we can see with hindsight, there are, scattered throughout the periodic table, pairs of elements E and E' (iodine and tellurium form one such pair) such that E has lower atomic weight than E' (that is, lower atomic weight when measured correctly) but, because E' has the lower atomic number (that is, the lower number of protons in its nucleus), it 'ought' to come before E in the table. As before, although hindsight is needed to identify the anomalous cases as ones of 'pair reversals' and also needed in order to explain why they appeared anomalous, no hindsight was needed to identify them as problems for Mendeleev's scheme. These cases can indeed be regarded as cases of failed 'contrapredictions'—that is, cases where Mendeleev's table would have been better served, given that he was ordering by atomic weight, if the then accepted values for atomic weights of, say, iodine and tellurium were wrong; but they were not: the problem was rather that the concept being used that of atomic weight—is not the fundamental one that Mendeleev and his contemporaries took it to be.

In sum, there is a clear and methodologically highly significant difference between, say, Fresnel's prediction of the 'white spot' at the centre of the shadow of an opaque disc held in light diverging from a point source, and Mendeleev's prediction of the existence of new elements. In the Fresnel case (see Worrall, 1989) and others like it from physics, there is a very definite mathematically derived entailment from a precise theory. Mendeleev, on the contrary, was operating within a general and rather loose framework, underpinned by no very definite theory, and was feeling his way towards making particular predictions rather than being in possession of a theory that makes them willy nilly. This may indeed be a distinguishing mark between physics and chemistry more generally.

A further important aspect of this difference between the case of Mendeleev and the cases from physics should also be noted. While Fresnel's theory (and the general theory of relativity and so on) make precise conditional predictions—to the effect that if certain conditions are instantiated, then a certain effect will be observed—Mendeleev at best made a direct non-conditional prophecy: that there are other elements to be found; though without directing the search for them (or at any rate not directing the search in anything like such a precise way). It is true that in the Fresnel and similar cases, auxiliary assumptions are always involved in underwriting the claim that some particular experiment instantiates the relevant conditions and still further auxiliary assumptions are involved in underwriting the claim that the predicted outcome has indeed occurred. (These are aspects of the 'Duhem Problem'.) But in these cases, the theory certainly directs us quite straightforwardly towards an experiment that will—subject to these further auxiliary assumptions—be decisive as to whether or not its prediction is fulfilled. The 'predictions' made by Mendeleev, aside from the fact that they are not the logical

consequences of any well defined theory, are not of conditional form and hence involve no *direct* indications as to how they are to be verified or falsified. Mendeleev tells us that some element with a certain atomic weight and bearing certain analogies to already known elements exists—is out there to be found. The atomic weight prediction and the analogies, of course, provided investigators with important guidance;<sup>26</sup> but, quite unlike the normal 'predictive case' from physics there is nothing in Mendeleev's 'theory' that entails anything like as precise a statement as that if an experimenter instantiates certain conditions then the relevant element will appear. (Notice that further developments in chemistry moved the field towards the physics case. Once it is understood that what differentiates the elements is atomic number—that is, the number of protons in a nucleus—then the prediction is that there are elements (not necessarily long-lived ones) for all integer atomic numbers, and hence that new elements will be found whenever a certain number of protons, a different number from any known element, are stuck together to form a (perhaps *very* temporarily) stable configuration.)

#### 5. Evidence and the Periodic Table

We have now assembled all the material that allows us finally to outline our own positive view of the role of evidence in the reception of Mendeleev's work.

Firstly, although we have said it several times already, it may be as well to emphasise yet again that of course we agree that the predictive successes played an important role. As we indicated earlier, Mendeleev's prediction played no part in the actual discovery of gallium, the first 'new' element. But in the case of scandium, the second new element, its discoverer, Cleve, remarked:

The great interest of scandium is that its existence had been predicted. Mendeleef, in his memoir on the law of periodicity, had foreseen the existence of a metal which he named ekabor, and whose characteristics agree fairly well with those of scandium. (Cleve, 1879, p. 419)

Secondly, we agree with Brush that there is no doubt that the success of what he calls the 'contrapredictions'—corrections of hitherto assigned atomic weights to known elements—played an important role. We can find nothing in the historical record that suggests that the impact of the contrapredictions, amongst the relevant experts, was any less than that of the prediction of new elements. Had these contrapredictions been a question of assigning a different atomic weight to certain elements simply so that they fitted more neatly into Mendeleev's scheme, then the historical fact that they seem to have counted just as strongly for that scheme as did the novel predictions would, of course, be a counterexample to our own thesis

<sup>&</sup>lt;sup>26</sup>And other heuristic guides could kick in to give plausible, but never deductively derived, 'predictions'. (So, for example, Paneth in the 1920s used simple reasoning based on the Periodic Table to predict that then undiscovered hafnium would occur in the same ores as zirconium. This is nonetheless a considerably looser notion of prediction than applies to standard cases from physics. See Scerri, 1994).

about empirical support. However, this was not the case. It was recognised, for instance, that beryllium's assigned atomic weight made it somewhat anomalous for Mendeleev's scheme. However, far from the fact of it fitting better being the only evidence for the newly assigned value, the discovery of one of beryllium's gaseous compounds—beryllium chloride—made a recalculation of its atomic weight possible using standard methods (essentially using Avogadro's number and the known properties of chlorine). This recalculation confirmed the new value independently of any consideration connected with Mendeleev's table.

But, *thirdly*, and contrary both to Maher and Lipton's story of scepticism giving way to general credence and to Brush's more sophisticated account, the real story of the reception of Mendeleev's ideas was a complicated affair with at least the following aspects:

- (a) There were elements not predicted by Mendeleev whose successful accommodation into his tables played as big a role in the reception of his ideas as the successful predictions—these included the rare earths and the noble gases; and
- (b) The imprecise nature of the underlying ideas, and the highly tentative nature of the details of at least some parts of Mendeleev's table meant that there was no real sense in which the table or the ideas were 'accepted' at any stage: rather there was a tentativity about, and an evolving character to, the tables and the underlying ideas quite different from anything in the standard cases from physics; and these features clearly informed the reaction to various pieces of evidence.

#### 5.1. Accommodation and the Periodic Table

There is strong historical counterevidence to the predictivist thesis in the form of elements—indeed two whole 'families' of them—whose existence neither Mendeleev nor anyone else had predicted and yet whose eventual 'accommodation' within his scheme provided strong evidence for it. These families are the 'rare earths' and the 'noble gases'. We can again find no suggestion in the historical sources that the impact of these successes was in any way lessened on the grounds that the elements concerned were known before being found a place in Mendeleev's scheme. Since we believe that the same methodological lessons could be drawn from the accommodation of either family of elements, and since the story of the 'noble gases' is less complex, we concentrate on it here.

The story of argon—the first of the noble gases to be identified—begins with some work by Rayleigh and Ramsay in 1894 (reported in Rayleigh and Ramsay, 1895). A specially convened meeting was held at the Royal Society on 31st January 1895 at which Rayleigh and Ramsay presented their findings and responded to criticisms and comments from a variety of major scientists at the time. The record of this meeting provides a fascinating insight into the uncertainties surrounding the evidence about argon and the periodic table.

As always, and as Mendeleev had continually stressed, the crucial quantity in placing argon in his table was its atomic weight. Atomic weight determinations, of course, require an assumption about the atomicity of the element. The molecular weight of (standard samples of) argon was fairly readily determined to be close to 40, and this would make its atomic weight 40 if argon is monatomic, 20 if it is diatomic etc. Since all gases discovered up that point—N<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub> and so on—were diatomic and since the only example of monatomicity then known was vaporised mercury, chemists were naturally initially inclined towards the diatomic option for argon, but in any case an atomic weight of either 20 or 40 failed to fit Mendeleev's table. There seemed to be no conceivable gaps in the early part of the table for argon to fill.

One obvious suggestion was that the way that argon was standardly prepared might in fact be producing a *mixture* of gases of different atomic (or molecular) weights so that the measured molecular weight of around 40 represented merely an average. Ramsay and Rayleigh tried to investigate these issues systematically in the following way.

Clausius had shown in 1857 that if K is the translational energy of molecules of a gas and H is the total kinetic energy, then

$$K/H = 3(C_p - C_v)/2C_v$$

where  $C_v$  is the specific heat capacity of the gas at constant volume and  $C_p$  its specific heat capacity at constant volume. Rayleigh and Ramsay had arrived at values for  $C_v$  and  $C_p$  for argon based on measurements of the speed of sound through it under various conditions (Rayleigh and Ramsay, 1895).

Notice that it straightforwardly follows from Clausius's equation that if the ratio  $C_p/C_v$  is 1.66 then K/H=1, that is, K=H: all the kinetic energy of the molecules is taken up by the translation movement. Hence, such a ratio, to say the least, strongly suggests monoatomicity—since some of the energy in a polyatomic molecule would surely be taken up by rotation of the molecules about their common centre of mass. Ramsay and Rayleigh's measurements produced a value of 1.66 for the ratio  $C_p/C_v$  for argon. They—somewhat cautiously—inferred that the gas was monatomic and therefore consisted either of a single element or a mixture of elements. The caution was due to the *logical possibility* that the molecules of a polyatomic molecule might—mysteriously—never acquire any relative motion, either vibrational or rotational.

As for the issue of purity of the sample, Rayleigh and Ramsay again discuss the possibilities and the evidence rather than taking a very definite position. At the same meeting, Crookes had produced spectral evidence that was consistent with the gas being a mixture, but Rayleigh and Ramsay also reminded the meeting of Olszewski's results, which indicated sharp boiling and melting points, as well as constant pressure during boiling—all strong evidence for a single pure substance.

Rayleigh and Ramsay decided that overall 'the balance of evidence seemed to

point to simplicity'—that is, towards the ideas that their samples of argon were pure and that argon is monatomic. They explicitly pointed to the conclusion that, since this assigns a value of around 40 (in fact they gave 39.9) for the atomic weight of argon, the element cannot be fitted into the periodic table:

If argon be a single element then there is reason to doubt whether the periodic classification of elements is complete; whether in fact elements may not exist that cannot be fitted among those of which it is composed. (Rayleigh and Ramsay, 1895, p. 58)

There were certainly commentators at the Royal Society meeting who were ready to contemplate a polyatomic structure for the gas: Armstrong (1985) suggested, for example, that the gas might consist of (individually reactive) atoms so firmly bonded into molecules that it appeared inert—the atoms being 'so firmly locked in each other's embrace' that they are 'perfectly content to roll on together without taking up any of the energy that is put into the molecules'. Rucker and Kelvin (1895) and Fitzgerald (1895) were both also ready to at least contemplate this possibility (though both also saw massive difficulties), while Lord Kelvin (1895) categorically dismissed it.

It seems clear that Armstrong's motivation for taking the polyatomic structure hypothesis seriously was indeed to defend the periodic table. Even on this score, however, there is nothing of the feeling of a Kuhnian 'commitment' to a paradigm. For example, Rucker, the President of the Royal Society, while ready to consider non-rotating polyatomic molecules, was, like Rayleigh and Ramsay themselves, also ready to see the periodic table rejected if necessary:

whatever the effect may be on the great generalisation by Mendeleef, that is, after all, an empirical law which is based at present on no dynamical foundation. If it holds its own in this case, it will, of course, strengthen our belief in it, but, on the other hand, I do not think that it stands on the footing of those great mechanical generalisations which could not be upset without upsetting the whole of our fundamental notions of science. (Rucker and Kelvin, 1895, p. 62)

Notice, then, two points in Rucker's perceptive remark: first, the successful accommodation of argon 'will, of course, strengthen our belief in' Mendeleev's scheme; second, the whole spirit is very much investigative rather than committed to Mendeleev's scheme, whose lack of a 'dynamical foundation' and therefore whose tentativity and eminent revisability are emphasised.

Unsurprisingly, Mendeleev (1895, p. 543) himself was more committed: Rayleigh and Ramsay's gas had to fit in the table somehow, and an atomic weight of 40 meant it did not fit—his favoured hypothesis was that the gas consists of triatomic nitrogen,  $N_3$ , with the hypothesis of an hexatomic element the runner-up.

The eventual resolution of the issue was that argon was fitted into a *new group* within the table, between the halogens and the alkali metals. In the meantime, the properties were being investigated of a gas first detected in 1868 by Frankland and Lockyer by spectroscopic analysis of solar radiation. Shortly after the argon episode, it was discovered that this gas, appropriately named 'helium', could be

evolved terrestrially by heating certain minerals, notably those containing uranium. This allowed empirical investigation of its properties, and it was decided, for evidential reasons unconnected with the periodic table, that it is an inert, monoatomic element with atomic weight 4—an inert 'noble gas' like argon. Helium too had to fit into the new section of the Periodic Table.

The idea of a new group within the table was suggested to Mendeleev by Ramsay during a meeting in Berlin in the spring of 1900. The suggestion was warmly welcomed by Mendeleev and was soon regarded as the solution of the argon problem and very much another feather in the Periodic Table's cap. As Mendeleev himself commented two years later:

This was extremely important for [Ramsay] as an affirmation of the position of the newly discovered elements, and for me as a glorious confirmation of the general applicability of the periodic law.<sup>27</sup>

He elsewhere spoke of the 'magnificent survival' of the periodic system in what had been a 'critical test'.

Mendeleev had personal reasons for indulging in hyperbole, of course, but the general response of the chemical community does indeed seem to have been that this accommodation of argon within Mendeleev's scheme was a major feather in its cap—no less major than any other empirical success, whether predictive in the temporally novel sense or not.

The evidential weight that seems to have been accorded to the 'accommodation' of argon (and then of helium) within the Periodic Table undermines the straightforwardly pro-predictivist view that accommodations always count less than (otherwise equal) predictions. (Notice that helium in particular was first discovered in 1868—before even Mendeleev's first published paper on the Periodic Table.) But the weight accorded to this accommodation might seem equally to undermine the more nuanced view we endorsed earlier. At first sight, the accommodation of argon and helium by inventing a new group looks exactly like the sort of *ad hoc* accommodation<sub>2</sub> that we insisted ought to carry less evidential weight. Surely inventing a new group for these elements is exactly a case of 'writing already known phenomena into' a pre-accepted theory without any independent testiblity?

This may indeed appear true at first sight, but appearances are deceptive. It is not simply a question of inventing a new section of the table to fit the noble gases into; it must then also be checked that the periodicities previously noted in terms of valencies, 'analogous' properties and the like among the already accommodated elements are preserved. The atomic weights of the four newly discovered noble gases have to be such that each one would fit into a particular space in each successive period of the table. That is, each of these atomic weights had to be intermediate between two other elements in each period. In addition, this insertion of the four new elements had to result in all of them lying vertically below one another in

<sup>&</sup>lt;sup>27</sup>Mendeleev (1879a); quoted from Smith (1975), p. 460.

the newly created group. These are stringent (and ultimately empirically based) constraints: it is perfectly conceivable that there was no way of placing the noble gases into the table that simultaneously satisfied all those constraints. In effect, creating a new group for the noble gases leads to a new series of predictions (in the atemporal sense) about already known analogies between elements.<sup>28</sup>

Indeed, as well as 'predicting' already known analogies between already known elements, this invention of a new group turned out to lead to a further temporally novel prediction—that of the existence of a third 'noble gas', neon. As Ramsay explained in his (1897) address to the British Association for the Advancement of Science (published in *Nature*), the periodicities amongst the properties of the known elements would be restored in more convincing fashion after the introduction of the new group if there were a further inert gas with atomic weight 20.<sup>29</sup> Neon, which indeed has an atomic weight of 20, was identified in the following year, 1898, by Ramsay himself and his co-worker Travers. There is, so far as we

<sup>28</sup>In a comment on a distant relative of the present paper, an anonymous referee suggested that 'the "accommodation" within the periodic table of the newly discovered facts about rare earths, noble gases ... are actually grist to the predictivist mill'. According to this referee, accommodation 'for the purposes of the predictivist/anti-predictivist debate concerns the devising of a theory to accommodate *known* facts. It does not concern the "accommodation" of *newly-discovered* facts (whether they have been explicitly predicted or not)' (italics in original). The reason why accommodation of newly [later] discovered facts, as opposed to the accommodation of already known facts, should involve no evidential discount seems to be that 'the periodic table "predicts", or rather, logically implies, that future discoveries will be found to fit with it, find "accommodation" in it', and it therefore deserves credit when this turns out to be the case.

It is easy to see that the referee's claim must be wrong. To take the example of Creationism again, many of the facts—about so-called fossils, for example—that are relevant to its rivalry with Darwinian theory were of course discovered only (long) after the basic Creationist hypothesis had been formulated. It then follows from the position advocated that, since the Creationist hypothesis in effect predicted that these future discoveries would find accommodation within it, and they indeed did via the 'Gosse dodge', that hypothesis is confirmed by those discoveries. But this is of course absurd. In general, the correctness of the Duhem thesis implies that this so-called prediction on behalf of a 'core' theory that future discoveries will be accommodatable is trivially satisfied. Given that the core theory makes no direct empirical predictions, there is always *some way* of accommodating any relevant fact that is discovered within a theoretical framework based on that core idea—that's the whole problem.

Research programmes, paradigms, theoretical frameworks—call them what you will—of course develop over time. The basic ('paradigm-forming' 'hard core') theory makes no predictions (Duhem). The issue of when some evidence was produced relative to when the hard core theory was first articulated is quite irrelevant to any confirmational question—hence the fact that argon was discovered only after Mendeleev's underlying ideas were formulated while sulphur, say, had long been known is of no significance at all. What needs to be asked at each stage in the development of a programme is whether the latest specific theory produced within it is, or is not, supported by various bits of evidence. The temporal view can only sensibly be understood to entail that the chief question is whether some evidence was known, not when the hard core was articulated, but rather when the specific theory that entails that evidence was first articulated. Argon had already been discovered when the specific version of the 'periodic law' that accommodates it was first produced. It nonetheless supports that 'law', not of course because it was still undiscovered when the first version of the 'periodic law' was articulated, but instead because the particular accommodating move, leading to the particular version of the periodic law at issue was independently testable.

<sup>29</sup>This article is reprinted in Knight (1970). It gives further insight into the tentative, probing nature of prediction in this area compared to the clear-cut predictions often made by theories in physics. It is also interesting to note Ramsay's remark in this paper that 'to the general public . . . novelty is often more of an attraction than truth [and consequently for them it is] the prophetic aspect [of science that] excites most interest.' (See above note 18.)

can tell, again no support in the historical record for the idea that the prediction of neon played any particularly 'crucial' role here or that it counted for any more than the 'accommodation' of argon—if anything, the contrary. In fact the whole episode of the 'accommodation of the noble gases' seems to us to underline the lack of any serious distinction between accommodation (accommodation<sub>1</sub>, of course!) and prediction.

This episode did involve proposed shifts in the table and in associated theoretical ideas that indeed amount simply to writing evidence into the table—that is, to cases of accommodation<sub>2</sub>. And just as we would expect, these shifts were, precisely on this account, not taken to be well supported—there was no independent evidence in their favour. For example, Rayleigh and Ramsay (1895) suggested that the gas they investigated might consist not of a single element but of a 93.3% to 6.7% mixture of elements with atomic weights 37 and 82. Needless to say the 93.3% to 6.7% split was exactly designed to give atomic weights that might fit into the table—a classic case of parameter-adjustment. (These atomic weights would in fact place the proposed two elements in the eighth group, one after chlorine and the other after bromine.) This suggestion was never taken up—precisely because the *only* evidence in its favour was accommodated<sub>2</sub> evidence.

Similarly, the hypothesis about argon that Mendeleev originally favoured—that it consists of 'superbonded' triatomic nitrogen—together with the various other 'superbonded', non-rotational polyatomic hypotheses, were not taken seriously because all that they did was save the existing periodic table from *prima facie* negative evidence: the *only* reason to think that there might be such polyatomic molecules all of whose energy was translational was that this might reconcile Rayleigh and Ramsay's data with Mendeleev's table.

Another case—quite separate from the argon affair—in which Mendeleev produced an entirely *ad hoc* non-independently testable response to an initial difficulty concerns one of his failed predictions about the properties of gallium that we mentioned briefly earlier. In his paper of 1871 Mendeleev predicted that eka-aluminium, subsequently known as gallium, would in all respects have properties intermediate between those of the elements above and below it, namely aluminium and indium. However, the melting point of gallium (30°C) is nowhere close to being intermediate between those of aluminium (660°C) and indium (155°C). In 1879 Mendeleev gave the following *ad hoc* rationalisation of the anomalously low value for gallium:

we should pay heed to the fact that the melting-point of gallium is so low that it melts at the temperature of the hand. It might appear that this property is unexpected; but this is not so. It suffices to look at the following series—

Mg Al Si P S Cl Zn Ga ... As Se Br Cd In Sn Sb Te J

It is evident that in the group Mg, Zn, Cd, the most refractory metal has the lowest atomic weight; but in the groups beginning with S and Cl, the most difficultly fusible

simple bodies are, on the contrary, the heaviest. In a transitory group such as Al, Ga, In, we must expect an intermediate phenomenon; the heaviest (In) and the lightest (Al), should be less fusible than the middle one, which is as it is in reality. I turn attention to the fact that properties such as the melting-point of bodies depend chiefly upon molecular weight, and not on atomic weight. If we were to have a variety of solid sulphur not in the form of  $S_6$  (or, perhaps, of still heavier molecules  $S_n$ ), but in the form  $S_2$ , which it assumes at  $800^{\circ}$ C, then its temperature of melting and of boiling would undoubtedly be much lower. In just the same way, ozone,  $O_3$ , condenses and solidifies much more readily than does ordinary oxygen,  $O_2$ . (Mendeleev, 1879b, p, 62)

Not only had such an argument never been given before by Mendeleev as a means of predicting trends in properties, but it also runs contrary to the spirit of his method of simple interpolation used so successfully in many other instances. Finally, the completely *ad hoc* nature of the argument is compounded by the fact that it is by no means clear that it truly represents an intermediate phenomenon to those in the other groups mentioned; nor is it clear why this contrived trend should begin at this particular place in the periodic table. In spite of his use of the word 'must' there is nothing in the least bit compelling about Mendeleev's argument. And, unsurprisingly and in agreement with the methodological thesis we defend, there is absolutely no evidence that this piece of accommodation<sub>2</sub> was considered satisfactory or as supplying any support for the periodic law.

### 5.2. Exploring Periodicity

We have already commented at some length on the lack of any precise version of the periodic law (the lack of a 'dynamical foundation' for the periodic classification, as Rucker put it) and indicated that this had a major impact on the way in which the relevant evidence was treated. The whole notion of the 'acceptance' of theories, even in physics, although often taken for granted by philosophers, is a complex and difficult one. But usually there is, in physics, a set of basic theories that are relatively sharp and that are taken, for some period, as relatively inviolable or at any rate as the last theories to be questioned in case the whole theoretical framework in which they are embedded runs into empirical difficulties (see, for example, Worrall, 1985a). In the case of Mendeleev's table, however, largely because of the vagueness of the underlying theoretical claims, the attitude seems always to have been more questioning and exploratory. There was some commitment to the idea that there are underlying periodicities to be found, but no commitment to any particular set of periodicities: rather these were to be discovered as a result of investigation. Hence we find a rather different attitude to evidence here than we generally do in physics.

Some indication of the differences can be found by analysing some 'criticisms . . . upon the periodic classification' solicited in 1881 by the editor of the *Chemical News* from Adolphe Wurtz, a celebrated Parisian chemist of the time. (Wurtz's note follows notes from Mendeleev and from Lothar Meyer forming their famous priority dispute.)

Wurtz (1881, p. 16) allowed that Mendeleev's system forms a 'powerful generalisation and must in future be taken into account whenever we regard the facts of chemistry from a lofty and comprehensive point of view'. However, he pointed out that the system still contained many imperfections—the rare earths in particular at that time had no satisfactory home in the system. He also pointed out a problem with tellurium and iodine, whose atomic weight ordering is inconsistent with their chemical properties (one of the problems caused, as we can see in hindsight, by the fact that atomic number rather than atomic weight yields the important ordering principle). Moreover, cobalt and nickel have almost identical atomic weights and so their properties ought, on Mendeleev's scheme, to coincide—quite contrary to the truth. He added that the alleged gradations in properties did not in fact progress smoothly or regularly as Mendeleev would have had us believe.

Wurtz then turned specifically to an analysis of the famous predictions:

In Mendelejeff's table we are chiefly struck with the gaps between two elements, the atomic weights of which show a greater difference than two or three units, thus marking an interruption in the progression of the atomic weights. Between zinc (64.9) and arsenic (74.9) there are two, one of which has been lately filled up by the discovery of gallium. But the considerations by which Lecoq de Boisbaudran was led in the search for gallium have nothing in common with the conception of Mendelejeff. Though gallium has filled up a gap between zinc and arsenic, and though other intervals may be filled up in future, it does not follow that the atomic weights of such new elements will be those assigned to them by this principle of classification. The atomic weight of gallium is sensibly different from that predicted by Mendelejeff. It is also possible that the future may have in reserve for us the discovery of a new element whose atomic weight will closely coincide with that of a known element, as do the atomic weights of nickel and cobalt. Such a discovery would not fill any foreseen gap. If cobalt were unknown it would not be discovered in consequence of Mendelejeff's classification. (Wurtz, 1881, p. 16)

Wurtz's point about cobalt and nickel is well taken: given that classification was by atomic weight there would have been no basis for the prediction of two elements between iron and copper, had neither cobalt or nickel been known, and no basis for predicting the existence of the other had only one of them been known.

His whole attitude is also, it seems to us, well justified and reflects quite well a general view: Mendeleev is 'on the right track' at a very general level, but the details are unreliable. Given this, all predictions are to some extent 'shots in the dark'—in this situation neither predictive successes nor predictive failures (as we noted, there were many of these) are as significant as they might otherwise be and as they generally are in science. And indeed, the historian Brock (1992, p. 325) refers to Mendeleev's vaunted predictive successes as 'fortuitous guesses'; while his failures, 'like astrologers' failures are commonly forgotten'. Perhaps they did tend to be forgotten later by some historians—hagiography makes for gripping, if scarcely accurate, history; but there is no evidence that they were not noted and taken into account at the time.

In sum,

- (i) there is no support from this episode for any temporal version of predictivism: we saw earlier that the famous three predictions of new elements, while certainly important, were very much only part of the story and we have seen now that the successful accommodation of the noble gases (and also the rare earths) also formed important evidence for the ideas underlying Mendeleev's scheme;
- (ii) there *is* support for the important distinction being between accommodation<sub>2</sub>, on the one hand, and *either* accommodation<sub>1</sub> *or* prediction on the other: the successful prediction of the new elements, the 'contrapredictions' of revised atomic weights, and the accommodation<sub>1</sub> of the noble gases and rare earths were all treated as definite successes for the scheme—more or less on a par, so far as we can see; while various non-independently testable accommodations—such as the suggestion that argon might be a mixture of two gases each of which individually fitted the original Mendeleev table—were correspondingly downgraded; and
- (iii) there are interesting differences in the impact of evidence in this case compared with the standard cases from the history of physics that have previously been analysed in the attempt to shed light on the predictivism issue: these result from the relative vagueness of the 'periodic law' underlying Mendeleev's table and involve, amongst other things, greater tentativity and greater tolerance of predictive failure than in those other cases, and a corresponding (relative) downgrading of predictive success.

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