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Chemical Laws, Idealization and Approximation

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Abstract This paper examines the notion of laws in chemistry. Vihalemm (*Found Chem* 5(1):7–22, 2003) argues that the laws of chemistry are fundamentally the same as the laws of physics they are all ceteris paribus laws which are true "in ideal conditions". In contrast, Scerri (2000) contends that the laws of chemistry are fundamentally different to the laws of physics, because they involve approximations. Christie (*Stud Hist Philos Sci* 25:613–629, 1994) and Christie and Christie (*Of minds and molecules*. Oxford University Press, New York, pp. 34–50, 2000) agree that the laws of chemistry are operationally different to the laws of physics, but claim that the distinction between exact and approximate laws is too simplistic to taxonomise them. Approximations in chemistry involve diverse kinds of activity and often what counts as a scientific law in chemistry is dictated by the context of its use in scientific practice. This paper addresses the question of what makes chemical laws distinctive independently of the separate question as to how they are related to the laws of physics. From an analysis of some candidate *ceteris paribus* laws in chemistry, this paper argues that there are two distinct kinds of *ceteris paribus* laws in chemistry; idealized and approximate chemical laws. Thus, while Christie (*Stud Hist Philos Sci* 25:613–629, 1994) and Christie and Christie (*Of minds and molecules*. Oxford University Press, New York, pp. 34–50, 2000) are correct to point out that the candidate generalisations in chemistry are diverse and heterogeneous, a distinction between idealizations and approximations can nevertheless be used to successfully taxonomise them.

Despite interest in the philosophy of chemistry over the past decade, the issue of chemical laws has remained relatively under explored, with the exception of a couple of articles, which discuss the topic (e.g. Christie and Christie 2000, 2003; Scerri 2000; Vihalemm 2003). Discussions of the topic have remained squarely within the background discussion of laws of nature in the philosophy of science literature; namely do the laws of chemistry fulfil the criteria for laws of nature more generally? If not, should the laws of chemistry be treated as laws at all? In this paper, I will argue that they should be.

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The philosophical problem of laws of nature is how we should distinguish between those regularities in nature that are merely accidental as opposed to those that are lawful. Indeed, Van Fraassen (1989: 27) pointed out the problem of universal accidentals with a distinctly chemical example. Consider the following two universal generalisations:

(1) All gold spheres are less than one mile in diameter.
(2) All uranium spheres are less than one mile in diameter.

The latter is a law, but the former is a universal accidental. The reason why (2) is a law is because the critical mass of uranium is such that it is impossible for a large sphere to exist. In contrast, large gold spheres do not exist because of the scarcity of the resource, a contingent fact about our world's resources. The philosophical problem is that these two universal generalisations appear to be epistemically on a par, they are both universally true and our evidence for them is the same. Thus, on what grounds do we know that (2) is a law and (1) is not? This is the crux of the philosophical problem of laws of nature.

The general problem of laws of nature can be particularly applied in the philosophy of chemistry; namely what is the nature of chemical laws and how do we distinguish chemical laws and universal chemical generalisations? Physics is often championed as the paramount science and often the philosophical approach has been to inform a general account of laws of nature from a consideration of the most obvious candidates for laws; namely, the fundamental laws of physics (e.g. the conservation laws, the laws of thermodynamics etc). Mitchell (1997: 469) calls this approach to laws "the normative approach",[1] where it is assumed that one size fits all. Thus, if there are laws in chemistry or biology, then they must fulfill the same criteria as the laws of physics. When discussing biological generalisations she states:

> The normative approach is the most familiar one begins with a norm or *definition* of lawfulness and then each candidate generalisation in biology is reviewed to see if the specified conditions are met. If yes, then there are laws in biology, if no, then there are not laws in biology (Mitchell 1997: 469).

In other words, there is an assumption in the laws literature that one size fits all. The naïve normative approach motivates the claim that a genuine law *should have* the following characteristics: it should be formulated syntactically as a universally quantified conditional generalisation in the first order predicate calculus (e.g. $\forall x\ (Fx \rightarrow Gx)$), it should support counterfactuals, have wide scope and not be restricted to spatio-temporal domains.[2] Moreover, a law statement should also support our inductive inferences and have explanatory and predictive power. Broadly speaking, laws of nature are different from accidents in that they have modal force, which is constitutive of their lawfulness. A theoretical account of what laws *ought* to be is provided on the normative approach and then all generalisations are squeezed into this uniform analysis.

The normative approach applied to chemical laws is the same: we should begin with a theoretical definition of lawfulness (most probably extrapolated from thinking about the laws of physics) and then each candidate generalisation in chemistry is reviewed to see if the theoretical definition is met. If these conditions are met, then chemical generalisations are chemical laws. This methodology is limiting and prevents a proper consideration of

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[1] See next section for a discussion.

[2] This is the classic view taken by Hempel and Oppenheim (1948) For example "All Metals Conduct Electricity" is a law because it is expressed in an unproblematic way as a universally quantified conditional. So let F stand for the metal and G the conduction of electricity, then this law can be expressed straightforwardly as $\forall x\ (Fx \rightarrow Gx)$. Importantly, this statement has wide scope is not restricted to spatio-temporal domains and it entails the counterfactual statement that if x were a metal then x would conduct electricity.

chemical generalisations. This point has likewise, been made by Cartwright (1999), but in relation to the laws of physics:

> The pernicious effects of the belief in the single universal rule of law and the single scientific system are spread across the sciences.[…] The theory consumes resources and efforts that could go into the hundreds of other enterprises in physics that ask different kinds of questions and solve different kinds of problems. (Cartwright 1999: 16)

One thing that chemical generalisations have in common is that they require a *cp* proviso. They only hold for the most part or 'all other things being equal'. This is because the theoretical definitions that we use to express these generalisations are often idealizations and approximations. They are removed from the context of complex chemical reactions in the process of chemical practice, where they would be inapplicable because of interfering factors. Thus, in order to make chemical laws suitable to the normative approach any chemical generalisation construed as a universally quantified conditional requires a *ceteris paribus* proviso (e.g. $\forall x\ (Fx \rightarrow Gx)\ cp$).

An early example of the normative approach can be seen in Molnar's (1969) Humean account of laws. A law statement had to fulfil the following criteria: (1) be universally quantified, (2) be true, (3) be contingent and (4) contain only nonlocal empirical predicates. One of the chief problems with this kind of approach is that only a very small subset of scientific laws would count as lawful under these rigid criteria. Likewise, most of the chemical laws would not count as laws of nature at all, since they clearly defy some if not all of the criteria. For example, they are not universally quantified since they have *ipso facto* exceptions and for this reason the formal description of the law is strictly speaking false or if true vacuous.

The standard objection to the use of ceteris paribus provisos in laws of nature is a semantic one; namely that we literally do not know what it is that the ceteris paribus (henceforth *cp*) appendage is introduced to replace, and so cannot give it a determinate meaning (Schiffer 1991; Earman et al. 1999, 2002). The problem then is that "all else being equal" appears to be a catchall phrase for all the possible exceptional cases that might contravene the law, so, 'All *F*'s are *G*'s *cp*' could be read as 'All *F*'s are *G*'s unless they are not', or 'All *F*'s are *G*'s *iff* All F's are *G*'s' or indeed as 'All *F*'s & {…} are *G*'s' and thus, the statements that express *cp* laws are vacuous. The fact that there are *ipso facto* counterexamples to any given *cp* law means that there is no prior stable and statable way of expressing what *cp* means in advance of applying it in specific contexts. The *cp* appendage has no determinate content. This is the standard so-called vacuity objection to *cp* laws.

However, this objection to *cp* laws can be seen as a direct result of the normative approach to laws. The *cp* proviso appears vacuous because vastly heterogenous generalisations are squeezed into a single theoretical account of laws. In the case of chemistry, it's no surprise that the given proviso has no content since it is masking very different kinds of chemical generalisations, where the "all else being equal" functions differently in different kinds of chemical generalisations. Thus, the claim that laws of nature are exact and universal does not apply for a large proportion of the generalisations that are deemed lawful in science.

In fact, Cartwright (1999) has argued that *all* laws are inexact (even those in physics). Interestingly, even though Cartwright's analysis is in direct opposition to the normative approach, nevertheless the normative approach still enters the picture. She still assumes that one size fits all; for Cartwright the laws of nature are all *ceteris paribus* laws. The construal of all chemical laws as *ceteris paribus* laws masks important differences between them. In contrast, this paper takes the heterogeneity of chemical generalisations as proposed by Christie (1994) and Christie and Christie (2000) as a starting point for enquiry. Despite the heterogeneity of chemical generalisations this paper suggests an important way of taxonomising them, in terms of those that involve idealizations and those that involve approximations.

1 The Problems of Laws in Chemistry

Chemistry is a good place to start for analysing this more general discussion of laws of nature in philosophy and the particular problem of laws that have exceptions. Chemistry is generally considered to be the closest companion to physics and the most likely to be grouped together with physics in its treatment. More recently, philosophers of chemistry have discussed the particular case of chemical laws (Christie 1994; Christie and Christie 2000; Scerri 2000; Vihalemm 2003).

There are two ways in which the normative approach can lead to an over simplistic account of chemical generalisations. The first is to presume a reductive analysis of the laws of chemistry; namely our analysis of the laws of chemistry will have the laws of physics as their fundamental bedrock. The laws of chemistry are merely heuristic devices, which pick out the more fundamental generalisations discoverable at the physical level. The fact that chemical laws have exceptions is not a problem, since they are really only placeholders for the real laws of nature, the laws of physics.

The second way is to take the claim that chemical laws have exceptions seriously and try to argue that they are nevertheless lawful. Vihalemm (2003) argues that all laws should be treated homogeneously, once it is understood that laws are not merely statements (e.g. universal conditionals), but rather all laws are idealizations. Similarly, Cartwright (1983, 1999) argues that all laws even the fundamental ones work in this way, because all laws involve *ceteris paribus* conditions, which explicitly cite that the law only holds "in ideal circumstances". Thus, even the laws of physics involve idealizations and thus, what needs to be understood for an analysis of laws more generally is what is meant by idealization in science.

However, the normative approach is not universally accepted in the philosophy of chemistry literature. For example, Scerri (2000) argues that the laws of chemistry are fundamentally different to physical laws. In particular, Scerri claims that the laws of chemistry are distinctive because they involve an *implicit* approximation. Taking the periodic law as an example, Scerri claims that the recurrence of elements in accordance with the periodic law is merely an approximation. He states:

> The periodic law of the elements, for example, differs from typical laws in physics in that the recurrence of elements after certain intervals is only approximate. In addition, the repeat period varies as one progresses through the periodic system. These features do not render the periodic law any less lawlike, but they do suggest that the nature of laws may differ from one area of science to another. (Scerri 2000: 2)

For Scerri then, it is the fact that chemical laws involve approximations, which makes them distinctive.

Christie and Christie (2000) similarly argue that the laws of chemistry are fundamentally different to the laws of physics because they describe fundamentally different kinds of physical systems. In particular, the laws of physics are strict statements about the world, which are universally true, but the same cannot be said for their counterparts in chemistry. They argue that the laws of chemistry appear to be operationally different. When a chemist uses the ideal gas law to deduce values for real gases, the answer is an approximation—the margin of error is about 1% but much larger at higher temperatures and pressures. In contrast, the principle of the conservation of energy is expected to be exact (see Christie 1994 for a discussion). Thus, one of the distinctive characters of chemical laws is that their formal description involves an implicit *approximation*. This marks a difference in kind between the approximations we find in chemistry and the more exact laws we find in physics.

However, Christie (1994) and Christie and Christie (2000) reject the view that approximation alone is the chief characteristic of all chemical laws. "Approximation" stands for very different kinds of approaches in the context of chemical practice. They argue for a more pluralistic and less rigid account of chemical laws where the heterogeneity of chemical laws is acknowledged.

> One thing that all philosophers of science tend to do is to consider laws as a class. Specific laws are cited as examples, and often several rather diverse laws are introduced to show how they all fit into the author's favoured pattern (as we have already seen with Duhem's conventionalism). But there is little or no exploration of the possibility that family resemblances between different individual laws might not extend to the issues discussed by the authors. It is possible, and seems likely, that some laws are merely formal and conventional, while others have a genuinely contingent status. It is possible, and seems likely, that some laws are obeyed exactly, while others are framed in terms of ideals which may only be approached and approximated, but never actually achieved by natural systems. It is possible, and seems likely, that some laws have definite exceptions, while others have some sort of claim to universality - whether as ideals, conventions or accurate and contingent dicta. Christie (1994: 622)

Thus, Christie (1994) argues that there has been a universal failure even to recognize the possibility of diversity among laws in different domains, but also within a single domain like that of Chemistry. In contrast, a more liberal and pluralistic view of what a law of nature is must be provided. Moreover, Christie claims that a pluralistic account is more consistent with scientific practice. In Chemistry, for example she claims: "chemists have recognized this diversity for at least a 100 years. In many ways the differences between the characters of laws are more interesting than the similarities" (Christie 1994: 613).

What is meant by approximation in chemistry, according to Christie (1994), covers at least three different kinds of approaches; those that involve an idealization, (e.g. Boyle's Gas Law) those that do not (Dulong and Petit's Law) and those that involve a purely formal taxonomic statement, namely an exact law, but nevertheless which have exceptions (e.g. The Law of Definite Proportions). Thus, Christie and Christie (2000) and Scerri (2000) agree that the laws of chemistry are distinctive, but their distinctive character cannot be accommodated by a singular conceptual account.

Two important questions in the philosophy of chemistry emerge from this discussion: (1) How are chemical laws related to the laws of physics[3] and (2) what is distinctive about chemical laws? If the first question is put to one side, and the normative approach is rejected then, we can ask (2) which is a more interesting question about chemical generalisations. Christie (1994) has claimed that chemical laws cannot be taxonomised into a single class, since the term chemical law covers a diverse group of chemical generalisations in chemical practice. However, I will argue that while Christie is correct to expose

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[3] This is not the only cross-disciplinary question. Indeed, how the laws of chemistry relate to the laws of biology is also an interesting question. My aim in (1) and (2) is to try to show that we can ask the question as to what makes the laws of chemistry distinctive, in a domain specific way. It is a distinct question from how the laws of chemistry are distinctive to laws in other sciences (e.g. physics and biology).

the diversity of chemical generalisations, nevertheless a simple taxonomy for chemical laws is possible, once idealization and approximation are properly distinguished.

2 Chemical Laws: Chemical Idealization and Chemical Approximation

Vihalemm (2003) argues that all laws should be treated homogeneously, once it is understood that all laws are idealizations. Chemical idealization is certainly an important epistemological tool in chemistry. This can be seen from the fact that chemical idealization is used extensively across chemistry. For example, even the concept of chemical substance is itself arguably a theoretical construct involving an implicit idealization. As Pauling suggested:

> The concept "substance" is of course an idealization: all actual substances are more of less impure. It is a useful concept however, because we have learned through experiment that the properties of various specimens of impure substances with the same major component and different impurities are usually nearly the same if the impurities are present in only small amounts. These properties are accepted as the properties of the ideal substances. (Pauling 1947:12)

However, simply calling all chemical laws *ceteris paribus* laws, masks important differences in what is meant by idealisation. This becomes obvious when we consider the heterogeneous generalisations that can be construed as *ceteris paribus* laws in chemistry. The *ceteris paribus* proviso is often used to mask the differences between distinct species of chemical idealization.

Consider Proust's law of definite proportions which states that:

(1) In a chemical compound, the masses of the elements are in the same proportions *cp*.

For example, oxygen makes up $^8/_9$ of the mass of any sample of pure water, while hydrogen makes up the remaining $^1/_9$ of the mass. Importantly, we can project that in future samples of water that the masses of the elements will be of the ratio 8:1 (Oxygen:Water). However, this law requires a *cp* proviso. This because of the existence of some compounds which are nonstoichiometric, in other words, where the masses of the elements can vary from sample to sample.[4] So, we can predict that "all else being equal" the masses of the elements will be in the same proportions.

How should we interpret this case? The problem is that if we read (1) literally without the *ceteris paribus* proviso it is in fact false. The reason why this is false is because there are cases of nonstoichiometric chemical compounds where the masses of the elements are not in the same proportions. The composition of a non-stoichiometric compound usually varies in a continuous manner over a narrow range.

For example, to represent this fact, the formula for wüstite (a mineral form of iron oxide), is written as $Fe_{1-x}O$, where x is a small number representing the deviation from the "ideal" formula. Thus, the law of definite proportions applies to the ideal formula, but in chemical reality, the law does not apply because the ideal is never instantiated. Moreover, it is not projectible because there is not a consistency across samples, due to the variation in samples of the compound. Thus, taking the law at face value (as a universal generalisation) and being guided by it would be misleading in chemical contexts. The *cp* clause is a reminder that this is the case. The ideal formula distorts the characteristics of non-stoichiometric compounds so as to make them fit into the theoretical description

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[4] Examples of nonstoichiometric compounds are magnetite and iron oxide.

expressed in the law. The *cp* proviso functions as a warning that the theoretical simplicity of the law involves this distortion.

These generalisations function in chemistry by using idealization as a way of abstracting relevant features of the physical systems and incorporating these in the idealized theoretical description, e.g. ignoring relevant features for the purposes of simplicity. This is often the case in chemical modelling for example. Consider the Lewis dot structure description of chemical bonding. This is not a complete description of the molecules because it ignores both the kinetic energies of the particles involved and also relevant coulombic interactions.

Sometimes, idealization is necessary because the causal context is too complex. Idealizations function to delimit a certain describable cause or set of causes and assert that these will bring about an effect if the process occurs *in an idealised setting*. Therefore, the law makes a claim about the effects these causes would bring about in isolation or given the proviso that there are no other interfering causes. The *cp* clause in this proviso means “in the absence of interfering factors”. This is the case, for example in Boyle’s gas law, where normal temperatures and pressures are assumed. Causal complexity (like a rise in temperature) would make Boyle’s law no longer applicable. However, the same principle applies as in (1) above, where, the law makes a claim about the effects these causes would bring about in isolation or given the proviso that there are no other interfering causes.

Other generalisations, describe a regularity that holds comparatively between two variables, where an increase (decrease) in one property x will lead to an increase (or decrease) in another property y. An example is Gay-Lussac’s gas law, which states that:

(2) An increase of gas temperature leads to a proportional increase of gas volume *cp*.

This type of generalisation describes the relationship between two functional variables, once underlying variables remain constant. The *cp* clause in (2) ought to be read as “all else being constant”. However, again the same principle applies as in (1) above, where, the law makes a claim about the effects these causes would bring about in isolation or given the proviso that there are no other interfering causes.

However, there is a different species of chemical law that involves approximation rather than idealization. Consider Scerri’s (2000) example of Mendeleev’s Periodic Law, which states that:

(3) The chemical properties of the elements vary periodically according to their atomic weights *cp*.

In Mendeleev’s early construction of the periodic table of the elements based on his periodic law, he encountered several counterexamples to his own principles. The properties of some of the elements that were discovered empirically were incompatible with the positions they should have occupied according to the theoretical principle of increasing atomic weight. Mendeleev (though he believed in the theoretical principle) assumed that the empirical anomalies were the result of incorrect atomic measurements, since it was very difficult to accurately measure atomic weight in the 1870s. The valence of Potassium (K) would suggest that it should follow argon (Ar) on the periodic table. But, it was discovered empirically that it had a smaller atomic weight than argon. This was not an anomaly that Mendeleev could have seen since argon has yet to be empirically discovered.[5]

In fact, accurate weight determinations did not turn out to validate Mendeleev’s theoretical positioning. Moreover, on consideration of the valency of these two elements;

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[5] See Scerri and Worrall (2001) for a discussion.

atomic weight still predicts the incorrect place for Potassium and Argon. Thus, the periodic law is not an idealization. It is just patently incorrect for certain elements. This is why Scerri (2000), for example, states that the law should be understood to be an approximation; because organising the elements by the periodic law is an inexact chemical representation, even if it is nevertheless close enough to be useful for the majority of elements.[6] In this case, the idealization is stronger than the law of definite proportions, because the theoretical expression of the law is more than a distortion, it is in fact erroneous and misleading, when considered in chemical practice.

A more extreme example of chemical approximation is exhibited by applications of Dulong–Petit's law. Dulong Petit's Law states that:

(4) The molar specific heat of every solid is a constant (six calories per gram atom), for nearly all known solid elements.

However, this law is just an approximation in that it breaks down at various temperatures. It is also dependent on the nature of the material, so it only applies to simple crystal structures. For example, it does not apply to carbon, (which is only 1.8 calories per gram atom). It also does not apply to compounds. These constitute actual exceptions to the law. It is really only correct to express the law in the following terms: for *most* solid elements, the molar specific heat of every solid is a constant (six calories per gram atom) *cp*.

However, in both these cases the fact that these laws are approximations is of great importance to the research that follows. Subsequent research aims at making better approximations or at least explaining away exceptions by other successful generalisations. So, for example, Lothar Meyer articulated a generalisation to deal with exceptions to Dulong–Petit's law, which said that Dulong–Petit's law applied least to elements of low atomic weight and low atomic volume.

Similarly, Neumann attempted to solve the problem of applying Dulong–Petit's law to compounds. Thus, in this example, chemical approximation is taken as a signal for future research. The exceptions and anomalies need to be explained and are epistemically significant. In contrast, in the idealization cases, the chemical laws are considered true "in an idealized setting" and this is useful for epistemic purposes and for scientific practice. The interfering factors are less significant in the idealization cases, whereas in the approximation cases they present an interesting programme for future research. Thus, from an analysis of some different candidates for chemical laws, are distinct important kinds of chemical law emerge: those that involve chemical idealization (e.g. the law of definite proportions and Gay lussac's law) and those that involve chemical approximation (e.g. the periodic law and Dulong Petit's Law).

Idealized chemical laws are those where the *ceteris paribus* clause is introduced to signal that the regularity specified between the antecedent and consequent only happens in isolation. Thus, it is a deliberate distortion, the kind that emerges when a simplified scenario is modelled so that causal relationships can be studied outside of the causal complexity of the target system. To put it in the lingo of the semantic view of theories, it is a partial representation (covering only some aspects of the target system), in a fictional setting. The model is constructed in such a way as to differ from the systems we take to be

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[6] It certainly was useful since prior to Mendeleev's formulation there was no systematic way of organising the chemical elements in a pedagogically significant way. Thus, chemistry textbooks were fast becoming unwieldy and so detailed that they lacked any overall theoretical framework that would sytematically reflect a useful way of organising the elements for chemistry students.

their subject matter, not merely by excluding certain parameters, but by employing assumptions that could *never* obtain. Other parameters that are potentially relevant to the phenomena are ignored. This can be for merely pragmatic reasons, in that it is impractical to consider all the relevant factors. But, it can also be a deliberate distortion, because of the known exceptions in reality, we can learn more about some phenomena by considering them in isolation or in simple systems.

Thus, the *cp* proviso here is specifically stipulating the lack of context (or that the only context is the regularity described by the law, which is itself a fiction). This conception should make us think of *cp* generalisations as *idealised cp* laws. Idealised *cp* laws can be formulated in the following way:

(5) "All *F*'s are *G*'s *cp*" is an *idealised* chemical law just in case all *F*'s would be *G* in an idealized setting.

For example, Boyle's gas law is a deliberate fiction, because it assumes normal temperatures and pressures. Causal complexity (like a rise in temperature) would make Boyle's law no longer applicable. Thus, we model gases as if they were ideal in order to unveil their fundamental properties.

In contrast, in cases of approximation certain variables are either included, excluded or held constant in order for the law to hold *ceteris paribus.* Adding the *cp* clause specifically stipulates that the context will affect whether or not a putative law holds. Thus, it is an approximation, because the context will dictate genuine exceptions to the law. Conceived in this way, we should think of *cp* generalisations as *approximate cp laws.* More specifically, we might say that:

(6) "All *F*'s are *G*'s *cp*" is an *approximate* chemical law just in case most *F*'s are G's in chemical context *C* (*C* = the domain where certain variables are included, excluded or held constant).

However, we know that there are empirical exceptions to the law. Consider again Dulong–Petit's law: The molar specific heat of every solid is a constant (six calories per gram atom), for nearly all known solid elements. We saw above that this law is just an approximation in that it breaks down at various temperatures, it is also dependent on the nature of the material, so it only applies to simple crystal structures and it also does not apply to compounds. Nevertheless, articulation of the law is a useful approximation and moreover, the exceptions to the law become important for future research.

It is important at this point to note that the terminology I am employing is different to that employed in some of the philosophy of chemistry literature to date. For example, my construal of "approximate" laws corresponds to the Christies' "exceptioned" laws, while the "idealized" laws correspond to the Christies' "approximate" laws (Christie 1994; Christie and Christie 2000).[7]

One potential objection relates to whether an idealization can be converted into or read as an approximation and vice versa. For example, take Boyle's gas law as an example of an idealized *cp* law above. Can Boyle's law be read as an approximate *cp* law in the following way:

> The volume of a gas is inversely proportional to the pressure of the gas for most gases in the context *c* where temperature and pressure are held constant.

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[7] I am very grateful to an anonymous referee for pointing this ambiguity out.

The problem with construing the law this way is that in chemical reality for most gases Boyle's law is inapplicable it is simply not applicable to most gases. It is false to say that it applies to most gases. It is only applicable in the highly idealized context.

In contrast, take the approximate law Dulong–Petit's law: The molar specific heat of every solid is a constant (six calories per gram atom), for nearly all known solid elements. The molar specific hear of every solid is a constant in an idealized setting. This is false, since there are certain exceptional cases for which the law does not apply even in an idealized setting. Thus, in the context that the solid being studied is a crystal, the law is simply inapplicable. There is no idealized setting where the crystal obeys the law it is an exception to it. This is why Dulong–Petit's law only applies for "most" solids and is better considered an approximation rather than an idealization.

Another possible objection is to ask whether chemical laws really are laws of nature. Are chemical laws then merely epistemic tools, where idealization and approximation are used because they have an explanatory and epistemic value? If so, is this sufficient for them to be given the honorific "law"? In the last section, we have seen that idealized chemical laws are epistemically useful because they provide a theoretical framework from which predictions and explanations can be given. In the presence of interfering factors, this would be impossible. Similarly, approximate chemical laws at the very least are epistemically useful in so far as they guide future practice, they highlight anomalies and problems and exceptional cases become interesting subject matter for future research. Thus, in the practice of chemistry it is clearly true that both idealized and approximate laws should be considered to be scientific laws.

Another possible objection to the distinction would be to claim that in fact only the idealized laws are laws of nature. Thus, the approximate chemical laws discussed have either been replaced by better alternatives or were merely heuristic tools that have had an epistemic value, in so far as they have led future research programmes and agendas. In other words, are approximate chemical laws just placeholders for more fundamental laws?

This leads back to the first question namely: how are chemical laws related to the laws of physics? Given the distinction in place between idealized and approximate chemical laws, it is now possible to ask more interesting and informative questions about the relationship between chemical and physical laws and indeed between the laws of chemistry themselves. For example, do physical laws or biological laws use idealisation and approximation in the same way as chemical laws do? These are certainly important questions, which go beyond the scope of this paper. Nevertheless, rejecting the normative approach and beginning with an analysis of the heterogeneous kinds of chemical generalisations that function as *ceteris paribus* laws in chemistry allows us to provide a more fine-grained theoretical account of scientific laws in chemistry.

At the beginning, two questions were separated in relation to chemical laws: 1) how are chemical laws related to the laws of physics and (2) what is distinctive about chemical laws. I urged that the second question be put to one side, so that the first question (1) be properly analysed. A domain specific analysis of different kinds of chemical generalisation reveals that there are two distinct theoretical kinds of chemical law; idealized chemical laws and approximate chemical laws.

3 Why is this an Important Question for Chemical Education?

The question of laws of nature has real implications for the epistemology of chemistry. This needs to be taken seriously by chemists and chemical educators. Thus, the philosophical debate has implications for chemical education. Firstly, there is a marked difference in the role of the term law of nature in physics and chemistry textbooks. There are not nearly as many laws in chemistry textbooks as there are in physics textbooks. There are many reasons that might explain this disparity. The most obvious includes a presumed reductive bias in favour of physics as the paramount science. In contrast, chemistry textbooks use the term law much more loosely, when often a chemical law is named a law for merely historical reasons, e.g. the celebrity of the person who discovered it.

A systematic study of chemical generalisations can make the student aware of the role of these generalisations in the broader body of chemical knowledge. This awareness opens up the possibility that some very important generalisations in chemistry play the role of laws, even though they may not be called laws in the chemistry textbook. Conversely, some laws that for historical reasons may be presented as chemical laws in the textbook may not play enough of an epistemic role in broader chemical theory to be considered a law of nature at all. An example of the latter would be the replacement of a historical law associated with a leading chemist with a newer generalisation that is more accurate.

Chemistry educators will do well to make their students aware of the philosophical puzzle of laws of nature, since in doing so they reveal how the body of knowledge presented to them in chemistry teaching is often presented in a historically biased and contingent way. This has implications for how we think about chemical knowledge itself. Chemists equipped with these complications would present their chemical research and teaching materials and resources in a more nuanced way.

Moreover, looking at the conceptual differences between kinds of chemical generalisations, we can see the way in which chemists use different epistemic methods like idealization and approximation to generate chemical knowledge. In this context, it is obvious that laws play an important epistemic role in the generation of chemical knowledge. Chemists and chemical educators need to pay more attention to the use of the honorific "law" in textbooks and chemical research, since it is a catchall phrase for significantly different means for producing knowledge in scientific inquiry.

On the other hand, philosophers of science have been too rigid in their classification of laws of nature, which has been detrimental to the analysis of chemical laws. This paper might suggest a reconciliation of philosophers of science on the one hand and chemists on the other, allowing a theoretical account of chemical laws, which is less rigid and thus, accommodates the diversity of chemical generalisations, which confront the chemist in chemical practice.

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