

# Chapter 2

## Reduction for a Dappled World: Connecting Chemical and Physical Theories

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### 2.1 Introduction

The matter of how theories in science relate to each other is a key aspect of the unity of science. For the philosophy of chemistry, this problem is of paramount importance: chemistry and physics are entwined to a degree where it is sometimes difficult, if not impossible, to imagine chemistry with the physics removed. Yet the widespread use of physical theories in chemistry is often not representative of how these theories are used in physics.<sup>1</sup>

This situation raises the question of how these two sciences are related. In the ‘received view’ on the philosophy of science, the primary connection mechanism between theories is a variety of inter-theory reduction, even while the interpretation of the term reduction could span a range from the relatively liberal scheme advocated by Nagel (1961) to an eliminative scheme advocated by Kemeny and Oppenheim (1956).

In the philosophy of chemistry, it is commonly assumed that the prospects of reduction are rather bleak.<sup>2</sup> The main motivation for this assessment is that the use that chemists make of physical notions quite often violates the uses of these same notions in physics. Yet one of the challenges facing this assessment is the specification of what sort of inter-theory relationships might exist between chemistry and physics in a non-reductive sense.

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<sup>1</sup> The resulting disconnects have led some to question the role of physics and theory in chemistry, for instance, in the paper by Hoffmann (2007).

<sup>2</sup> See for instance Woody (2000), Scerri (1998) and Needham (2010) as examples.

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One potential answer is pluralism. Non-reductive, pluralist positions on science have been defended by Cartwright (1983) and Dupré (1993); in the philosophy of chemistry a variety of such a pluralist model is defended by Lombardi and Labarca (2005) and to some degree in Hettema (2012a). Another potential answer is emergence, a point of view that has been defended by Hendry (2006). In addition, alternative notions of the unity of science have been developed, harking back to Neurath's 'encyclopedic project' (see for instance Cartwright et al. (1996) and Potochnik (2011)) on the one hand, or Duhem's notion of 'incorporation' on the other (see for instance Needham (2010)). In addition, Bokulich (2008) has developed a notion of 'interstructuralism'.

A key motivation for these alternatives is that the project of reduction fails because of a fundamental incompatibility – or logical inconsistency – between the theories of chemistry and the theories of physics, which cannot be overcome even by a liberal reading of the Nagelian reduction postulates.

Yet scientific structures can be inconsistent – that is a fact already noticed by Lakatos (1970) and reinforced, though gently, in Priest (2008) (p. 75). The premise of this chapter is that we take such inconsistency as a feature of the inter-theory connection.

The two main questions posed by this stance are of course how we describe such inconsistent structures as part of an overall whole, as well as how science did end up that way. The first one is a descriptive, the latter a 'generative' question. This distinction in descriptive and generative aspects of the problem of inconsistency in science closely mirrors Reichenbach's 1937 distinction between 'context of discovery' and 'context of justification'. We may conclude that as philosophers of science, we have to be capable of dealing with such inconsistent structures from both points of view.

In this chapter, I will develop an approach to solve the generative question, based on belief revision, which may assist in drawing out the inter-theory relations in operation. This essay is motivated by the contention that a revision of Nagelian reduction may rehabilitate the notion of reduction, incorporate a dynamic structure of belief revision in scientific development, and in doing so largely dissolve the distinction between reductionism and pluralism. To be precise, I will argue that Nagelian reductionism is to a significant degree compatible with the pluralist model, and both models can be based on logics that are capable of specifying the intertheory relationships rather precisely.

To be applicable to the reduction of chemistry to physics, I claim that such a revision must on the one hand go back to Nagel's original intention for heterogeneous reduction, and on the other it must draw on fairly recent logical apparatus to stake its claim. My aim in this paper is to rehabilitate the concept of reduction in this sense and argue that the concept is capable, much more capable than was previously thought, of dealing with sciences that are largely autonomous and even inconsistent. I will moreover argue that such cases do not necessarily destroy the unity of science, provided they satisfy some overall criteria regarding how revisions are done. The interesting outcome of this project is that the scope of pluralism is thus limited, and there is a large degree of overlap between reductionist and pluralist positions in the philosophy of chemistry.

The key to my proposed rehabilitation of the reduction relation is twofold. In the first place I argue that a reduction relation is best conceived as a logical *regimentation* or *paraphrase* of what happens when we claim that one theory explains another. Such a position has recently also been defended, from different points of view, by Klein (2009), Fazekas (2009), Dizadji-Bahmani et al. (2010), and van Riel (2011). A more detailed discussion is given in Hettema (2012a).

Secondly, I argue that such a regimentation must be capable of specifying the sort of connections that obtain in the actual practice of science. I argue that there are several formal mechanisms compatible with the two criteria of the Nagelian scheme.

Belief revision is based on an outright relaxation of the notion of ‘derivation’, and argues that the ‘logical consequence’ of which Nagel speaks in his description of the derivation criterion may be satisfied by a relaxed notion of ‘consequence’. In this paper I will use a structuralist characterisation of the belief revision relation in terms of the structuralist characterisation of ‘conceptual spaces’ as advanced by Gärdenfors and Zenker (2011).

I conclude that with these logical moves a notion of Nagelian reductionism is to a significant degree compatible with a pluralist model and a ‘dappled world’, though not with a world without any unity of science. My conclusion is that it is possible to develop a notion of reduction that is sympathetic to chemistry on the one hand and logically robust on the other. The lesson we may draw from this is that there is not that much that divides reductionist and pluralist approaches in the philosophy of chemistry. This conclusion, I believe, opens up the prospect of fruitful new avenues of research in the philosophy of chemistry.

This paper is structured as follows. In Sect. 2.2 I briefly summarise the important aspects of the Nagelian approach to reduction and some of the recent commentary on this scheme. This development assists in setting the scene for the discussion to follow. In Sect. 2.3 I develop my specific proposals and outline their consequences for a conception of the unity of science. To provide an example of how this might work in practice, I discuss how the proposed structure of reduction *qua* belief revision fits Eyring’s theory of absolute reaction rates in Sect. 2.4. Section 2.5 is a conclusion.

## 2.2 How Liberal Can Nagelian Reduction Be?

As is well known, Nagel (1961) formulates two formal conditions on inter-theory reduction, which can be summarised as the criterion of connectivity and the criterion of derivability. The idea is that terms in the languages of the reducing and reduced theory are connected, and that the laws of the reduced theory can be seen, under a correct connection scheme, to be the logical consequences of the laws of the reducing theory.

However, while Nagel calls these conditions *formal*<sup>3</sup> there is no formal logical ‘scheme’ to be found in his description. As Dizadji-Bahmani et al. note, the Nagelian model is not committed to a specific regimentation, but rather,

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<sup>3</sup> And separates them from a number of informal conditions which he also specifies in great detail.

Where first order logic is too weak, we can replace it with any formal system that is strong enough to do what we need it to do. The bifurcation of the vocabulary plays no role at all. (Dizadji-Bahmani et al. 2010, p. 403)

Usually, the Nagelian requirements are read as requirements of a first-order logic. On this basis, emendations of Nagel's scheme have been proposed by Schaffner (1967) and Sklar (1967). Causey (1977) argued that reduction postulates must necessarily be *identities*. However, the detailed investigation of *actual* cases of reduction<sup>4</sup> has highlighted that reductions based on identities and derivation which fit this particular logical straitjacket are the exception rather than the rule.

The condition of derivability is formulated in terms of *three* formal requirements for reduction. The three conditions that Nagel mentions in the formal section of the chapter on reduction are that (1) the theories involved can be explicitly stated, (2) the meanings used in the terms are fixed by common convention or by the respective theories, and (3) the statements of the reduced theory are logical consequences of the reducing theory and the reduction postulates.

In combination, the derivability conditions establish the unit of reduction as a scientific *theory* which can be appropriately *paraphrased* (through linguistic formulation in some formal language followed by axiomatisation) so that the right sort of *formal connections* (i.e. logical consequence) can be established.

These conditions do not specify connectibility. To introduce connectibility, Nagel introduces, in addition to the formal requirements, the notion of *coordinating definitions* (which, for clarity, we will call 'reduction postulates' in the remainder of this paper) as an additional assumption. The reduction postulates stipulate a sort of translation manual through

[...] suitable relations between whatever is signified by 'A' and traits represented by the theoretical terms already present in the primary science (Nagel 1961, pp. 353–354)

The reduction postulates themselves, however, are far from simple.<sup>5</sup> They allow the language of the theory to be reduced to be connected to the language of the

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<sup>4</sup> See for instance Kuipers (1990) for an example of reductions from many sciences, most of which are not based on strict identities.

<sup>5</sup> For instance, Nagel (1961) discussed three kinds of linkages postulated by reduction postulates

1. The links are logical connections, such that the meaning of 'A' as 'fixed by the rules or habits of usage' is explicable in terms of the established meanings of the theoretical primitives in the primary discipline.
2. The links are conventions or coordinating definitions, created by 'deliberate fiat', which assigns a meaning to the term 'A' in terms of the primary science, subject to a criterion of consistency with other assignments.
3. The links are factual or material, or physical hypotheses, and assert that existence of a state 'B' in the primary science is sufficient (or necessary and sufficient) condition for the state of affairs designated by 'A'. In this scenario, the meanings of 'A' and 'B' are not related analytically.

reducing theory, or, more interestingly, the language and concepts of the reducing theory to be recast in the language and concepts of the reduced theory.

From here, Nagel's two famous conditions can be formulated as follows:

1. A condition of 'connectability' which stipulates the reduction postulates
2. A condition of 'derivability' which states that the laws or theories of the reduced science are logical consequences of the theoretical premises and coordinating definitions of the reducing science.

The liberal reading of Nagel that I am proposing here depends on the idea that we read Nagel's condition of 'derivability' in the sense of a largely unspecified consequence relation based on a suitable paraphrase of the theories under consideration in some formal language.

The recent reassessments of the Nagelian position (especially the one by Klein (2009) and Dizadji-Bahmani et al. (2010)) read this consequence relation largely in terms of a 'representation' relation, in which the reducing theory can be modified in such a way that it *represents* the concepts of the reduced theory. So, for instance, in the summary by Dizadji-Bahmani et al. (2010), a 'generalised Nagel-Schaffner model' in which the reduction postulates are *factual* claims, is alive and well. They defend the generalised Nagel-Schaffner model against seven specific objections, concluding that none of them apply. In the terminology of Dizadji-Bahmani et al. the generalised Nagel-Schaffner model consists of a theory  $T_P$  reducing to a theory  $T_F$  through the following steps:

1. The theory  $T_F$  is applied to a system and supplied with a number of auxiliary assumptions, which are typically idealisations and boundary conditions.
2. Subsequently, the terms in the specialised theory  $T_F^*$  are replaced with their 'correspondents' via bridge laws, generating a theory  $T_p^*$ .
3. A successful reduction requires that the laws of theory  $T_p^*$  are *approximately* the same as the laws of the reduced theory  $T_P$ , hence between  $T_P$  and  $T_p^*$  there exists an analogy relation.

Two features of this generalised Nagel-Schaffner model are worth noting. The first one of these is that the reduction postulates are part of the *reducing* theory, rather than some auxiliary statements that have a primarily metaphysical import.<sup>6</sup> Secondly, of the three types of linkages that may be expressed by reduction postulates, the first two can be discarded and reduction postulates express *matters of fact*. This is so, because the aim of scientific explanation is, in their words, neither 'metaphysical parsimony' nor 'the defence of physicalism' (p. 405). Thus the Nagelian reading they favor is a naturalised one, in which the aim of reduction is *representability* between the reduced and reducing theory, and confirmation of  $T_F$  entails confirmation of  $T_P$  for domains where there is significant overlap. In this manner reductions have a high likelihood of occurring where theories have an overlapping target domain.

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<sup>6</sup> A similar point was made in a somewhat neglected paper by Horgan (1978), who argues that the reduction postulates supervene on the reducing theory.

The ‘idealisations and assumptions’ introduced in this model can take on the role of beliefs in a belief revision scheme. This situation reflects actual scientific practice in the (trivial) sense that approximations and idealisations to a complex theory can be seen as various additional beliefs that play a role in the overall scheme.

It is interesting to note that from this point of view we consider the entire reduction *schema* as a key element of the activity of scientific reduction, as opposed to individual *theories* featuring as elements in an abstract reduction scheme which is largely removed from actual scientific practice.

## 2.3 Structures and Beliefs: Reduction for a Dappled World

In this section, I will consider reduction in the context of a structuralist approach to belief revision based on conceptual spaces. In general, adaptive logics such as belief revision adapt themselves to the situation at the moment of inference. In this, they represent the dynamics of reasoning – a Reichenbachian ‘context of discovery’ – in which, to save overall consistency, some beliefs are dropped from the overall scheme. I will first briefly characterise the structuralist approach to theories before proceeding with my proposal.

### 2.3.1 Structuralism Characterised

The structuralist theory approach to scientific theories originates in the work of Suppes (1957) and was given most of its present form in the work of Sneed (1971). It was discussed in detail in Balzer et al. (1987). The key elements of the structuralist theory are summarised in Table 2.1. In the structuralist approach, a scientific theory is characterised as a structure  $\langle K, I \rangle$  where  $K$  is a structure that characterises the theory ‘core’ at both the theoretical and non-theoretical level in terms of its (potential) models and partial potential models.

In the structuralist approach, reduction is characterised as a (structural) similarity between structures.

A (specialisation) theory net is a set of structures that are connected through the specialisation relation  $\sigma$ .<sup>7</sup> The specialisation relation connects a (general) theory to a specialised instance of that theory, which is applicable to a particular situation through the introduction of a special set of limiting constraints. Technically, the specialisation relation can be reconstructed as a constraint condition on the models.

It is interesting to note a strong relationship between the (partial) potential models of a theory and the *conceptual space* of that theory. The (partial) potential models specify the ‘language’ that is used in the theory, together with some rules for

<sup>7</sup> See Balzer and Sneed (1977, 1978) for an introduction of this relation and the corresponding notion of a theory net.

**Table 2.1** Specification of the components of the structuralist conception of theories, cf. Kuipers (2007)

Component	Description
$\mathbf{M}_p$	The potential models, defined as structures of the type $\langle D_1, \dots, D_k, n_1, \dots, n_p, t_1, \dots, t_q \rangle$ or $\langle D_1, \dots, D_k, x_1 \dots x_{p+q} \rangle$
$\mathbf{M}_{pp}$	The partial potential models $\langle D_1, \dots, D_k, n_1 \dots n_p \rangle$
$\mathbf{M} \subset \mathbf{M}_p$	The models of the theory, which satisfy all the laws of the theory
$r: \mathbf{M}_p \rightarrow \mathbf{M}_{pp}$	The ‘restriction’ relation which connects the potential models to the partial potential models
$C \subset \mathcal{P}(\mathbf{M}_p)$	The ‘constraint’ relation (which will be taken as implicitly present in most of what follows)
$r(\mathbf{M})$	The projected models, i.e. the restriction of the models to the level of partial potential models
$\mathbf{K}$	The theory ‘core’, defined as $\langle M_p, M, M_{pp}, r, C \rangle$
$I \subseteq r(\mathbf{M})$	Weak empirical claim (note that constraints are implicitly assumed)
$I = r(\mathbf{M})$	Strong empirical claim (constraints are implicitly assumed)

its use. This similarity between conceptual spaces and potential models led Kuhn to argue that the structuralist approach was to a high degree compatible with his notion of a paradigm (see Kuhn (1976)) and also forms part of the discussion in Kuipers (2007) on research programmes.

### 2.3.2 *Belief Revision as Regimentation of Reduction*

As I have outlined in Hettema (2012a), the notion of reduction in the structuralist conception of theories is extraordinarily weak, a weakness which can be turned to strength in cases where we wish to consider the sort of liberal interpretation of Nagel required in the reduction of chemistry and physics. The leading idea in the structuralist conception of reduction is a notion of isomorphism between structures. Beyond that, a number of additional conditions may be imposed, as discussed in Balzer et al. (1987), but the majority of these depend on the *kind* of reduction relation that one wants to defend.

For the purposes of this paper, I will focus on the relationship between AGM theory and the development of conceptual spaces as discussed by Gärdenfors and Zenker (2011).<sup>8</sup> Gärdenfors and Zenker note that the framework of conceptual spaces allows for four types of theory change:

<sup>8</sup> In addition, belief revision has been introduced into the structuralist model by Enqvist (2011). Enqvist develops a highly specific alternative to the notion of ‘reduction postulates’ qua ‘linking commitments’ which I developed in Hettema (2012a). Enqvist’s construction relies on a construction of specialisation theory nets, to which he applies the AGM belief revision strategies. Enqvist does not fully develop the AGM theory in a structuralist model, and ignores the stratification between theoretical / non-theoretical levels of the theory. In general, developing complex notions in the stratified model adds complications which are usually ignored in the first ‘step’ of the development of such models, see for instance the development of truthlikeness developed by Kuipers (1992).

1. addition and deletion of special laws (e.g. the creation different models of the theory or the creation of specialisation theory nets);
2. change of scale or metrics as well as the salience of dimensions;
3. change in the separability of dimensions;
4. addition and deletion of dimensions which make up the space

In this context, ‘dimensions’ refers to the terms in the general structure  $\langle D_1, \dots, D_k, x_1 \dots x_{p+q} \rangle$  rather than to physical dimensions. In other words, the belief-revision strategies for theory change may involve limited changes of the theoretical cores as modelled in the structures  $\mathbf{M}$ .

In Hettema (2012a) I proposed that we view reduction relationships as an instance of an interstructural *link*, sufficient to establish a global unity of science, but also capable of dropping local ‘context’. Belief revision is a stronger theory in the sense that it provides additional specification of how such a link might work.

*Abstract* links are simply relationships between two sets of potential models (or the ‘conceptual spaces’) of two theories. An abstract link is defined as (Balzer et al. (1987), p. 61):

**Definition 1 (Abstract link)**  $L$  is an abstract link from  $\mathbf{M}_p$  to  $\mathbf{M}'_p$  iff  $L \subseteq \mathbf{M}_p \times \mathbf{M}'_p$

The leading idea of the abstract link is that it provides a relationship between two different types of potential models, but does little else. In practice, links are instantiated as connection pairs between terms of the ‘conceptual space’ of one theory to those of another; e.g.  $\langle \langle x'_i, x'_j, \dots \rangle, \langle x_p, x_q, \dots \rangle \rangle$  that may have some additional restrictions in terms of either values that the quantities can take in the link, or a (law-like) relation between these concepts. The machinery for links can become cumbersome, but the concept is not conceptually complex: it expresses that some terms in one ‘conceptual’ space can be connected to (a number of) terms in the other conceptual space.

It is possible to define additional properties on links, and in this way develop a concept of interpreting links, reducing links, and so on. Of particular interest is that in the structuralist approach, the unity of science is formulated in terms of theory *holons*, which are large-scale global structures connected by inter-theoretic links. In Hettema (2012a) I have argued that reduction postulates can fruitfully be interpreted in terms of links, and the concept of links can be made to fit the three criteria for reduction postulates that were originally developed by Nagel.

In the remainder I wish to forego many of the details of the structuralist approach by focusing on links as connections between conceptual spaces. The analysis by Gärdenfors and Zenker adds structural precision to the generative strategies that are available to establish links. The main import of treating conceptual disconnects in this way, as Gärdenfors and Zenker argue, is that the scope of *incommensurability* between a predecessor and successor theory, or between a reduced and reducing theory, is limited significantly.

From the viewpoint of reduction, this approach is capable of formalising, and subsequently de-fanging, the discontinuity between concepts in the theories of chemistry and the theories of physics. In the next section I will discuss this with the help of a practical example: the theory of absolute reaction rates.

## 2.4 The Unity of Chemistry and Physics: Belief Revision in the Theory of Absolute Reaction Rates

In this section, I will focus on an example from the chemistry: the theory of absolute chemical reaction rates.<sup>9</sup> This theory is a typical ‘chemical’ theory in the sense that it draws on many underlying theories to synthesise a new theory. Another motivation is that it can be argued that many of the current problems that plague current philosophers of chemistry – such as the problem of molecular structure<sup>10</sup> and the problem of inconsistent use of quantum theoretical notions – were introduced to accommodate this theory.<sup>11</sup> A brief overview and philosophical evaluation of the theory was given in Hetteima (2012b), which I refer to for some of the details.

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<sup>9</sup> As the book by Nye (2011) illustrates, this theory was sometimes jokingly referred to as the ‘absolute’ theory of reaction rates. Many of his contemporaries found Eyring’s ideas too radical, as the proceedings of the 1937 workshop at the University of Manchester illustrate. In my earlier paper (Hetteima (2012b)) I had this wrong, and used the designation of ‘absolute theory’ throughout. At the time I was unaware of the earlier ironic use, and thought that ‘absolute theory of reaction rates’ was a neater choice to designate the theory than the somewhat more clumsy sounding ‘theory of absolute reaction rates’. Of course, I now see the error of my ways.

<sup>10</sup> The notion of a (reactive) potential energy surface for the nuclear motion is key to the development of the theory. While the idea was introduced by Born and Heisenberg (1924) and Born and Oppenheimer (1927) it may be argued that the idea of a potential energy surface only reached its full fruition with the development of a theory of chemical reaction rates. The idea of a potential energy surface is part of Wigner’s ‘three threes’ (see below).

<sup>11</sup> Especially illustrative for this is the motivation Eyring (1938) gave for his introduction of various ‘semi-empirical’ methods in quantum chemistry, which lead to various inconsistencies between these semi-empirical theories and quantum theory.

For the purposes of calculating the potential energy surface for a chemical reaction, Eyring first classifies theories as ‘semi-empirical’ when they have the following characteristics:

- (a) that each electron can be assigned a separate eigenfunction which involves the coordinates of only this one electron.
- (b) Multiple exchange integrals are negligible,
- (c) Normalising integrals for overlapping orbitals are negligible in comparison with unity.
- (d) The exchange and coulombic integrals for a complicated molecular system may be estimated from a potential curve for the isolated pair of atoms.
- (e) For distances involved in activation energy calculations this percentage is around 20 per cent. coulombic and 80 per cent. exchange binding, and this varies but little from atom pair to atom pair. (Eyring 1938, p. 8)

Eyring then remarks that more detailed calculations, as well as principled considerations, give no support for the construction of these theories:

None of these assumptions have been rigorously derived from theory, and, as has been emphasised by Coolidge and James, if one assumes for  $H_3$ , the approximate eigenfunctions used by Heitler and London and Sugiura for  $H_2$ , the assumptions can all be shown to fail badly. (Eyring 1938, p. 8)

Thus stated, these sort of theories seem to be counterexamples to a theory of reduction: the sort of reduction that derives chemical ‘laws’ directly from basic quantum theory can only be achieved on the basis of theoretical assumptions that are unjustified from the viewpoint of basic theory and which can moreover be shown up as factually wrong in a large number of practical cases.

A robust and contemporary overview of the theory is given in the book by Glasstone et al. (1941).

The theory of absolute reaction rates was independently developed by Eyring (1935) and Evans and Polanyi (1935), and was the subject of heated debate during the 1930s. In the introduction to the 1937 conference about the theory held at the University of Manchester, the president of the conference in his address remarked that the jury on the ‘absolute’ theory was still out:

As to whether these methods are fundamentally sound or unsound is a question the consideration of which belongs rather to the domain of philosophy than to that of chemistry, and it may be necessary to call in an expert in that branch of science to advise us in the matter. (Travers 1938, p. 1)

Somewhat belatedly, it is my opinion that the philosophers of science are, at this point at least, likely to disappoint the scientist, and provide no such advice. Instead, it is the purpose of this last section to use the theory as an illustration of how the theory – whether fundamentally sound or unsound – is a good illustration of how a typical chemical theory functions, and to use it to illustrate the ideas developed in the previous sections.

### 2.4.1 Overview of the Theory

Glasstone et al. (1941) gives a book-length treatment of the theory. Eyring et al. (1944) discuss the theory in a single chapter, adding a quantum mechanical formulation of the theory. The historical development of the theory is discussed in Laidler and King (1983) as well as in Miller (1998).

Let us now briefly summarise the theory. If we consider a chemical reaction



the rate of the reaction is given by Arrhenius law. Arrhenius’ law is the main explanatory target of absolute reaction rate theory. Arrhenius’ law was developed 1889<sup>12</sup> and writes the rate constants  $k$

$$k = A \exp(-E/RT) \quad (2.2)$$

expressing the rate constant for a chemical reaction in terms of a ‘frequency’ factor  $A$  and an ‘activation’ energy  $E$ . Several candidate theories were developed to explain Arrhenius’ law.

One of those candidate theories was the *collision theory*. In this theory, the ‘frequency factor’  $A$  in Arrhenius’ equation is interpreted as equal to the frequency

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<sup>12</sup>The article appears in translated form in Back and Laidler (1967).

of collisions between the reactants. The collision theory assumes that all the reactants are hard spheres, and that any collision that has sufficient energy to reach the activated state will proceed to complete the reaction.<sup>13</sup>

Another candidate was the *thermodynamic* formulation, in which the reaction rate constant is expressed in thermodynamic quantities as

$$k = \frac{kT}{h} K^\ddagger \quad (2.4)$$

Since the equilibrium between the activated state and the reactants is a normal chemical equilibrium it can be related to the thermodynamic theory of chemical reactions, and hence, it can be related to the normal thermodynamic entities free energy, enthalpy ('heat content'), entropy and so forth. This yields a measure of the entropy changes associated with the reaction.

Absolute reaction rate theory is a theory that aims to provide explanations for both the 'activation energy' and the pre-exponential factor  $A$  (the 'frequency factor') in the rate equation from first principles. The underlying theories that it uses are quantum mechanics and statistical mechanics. The rate formula of the absolute theory of reaction rates is given in terms of the partition functions  $Z$  of the reactants and the transition state by

$$k = \frac{kT}{h} \frac{Z_\ddagger''}{Z_A Z_B Z \dots} \exp\left(-E_\ddagger^0/RT\right) \quad (2.5)$$

The advantage of this formulation is that the partition functions for all compounds featuring in the reaction can be calculated using statistical mechanics for vibrational and rotational motion of mechanical systems. While this is still a difficult problem, a detailed consideration of different reacting systems yields a mechanistic insight in how the reaction occurs on a molecular level.

A detailed summary of absolute reaction rate theory was given in Wigner's (1938) presentation at the 1937 Faraday conference, where he summarised the

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<sup>13</sup>A modified collision theory often introduces a 'probability factor'  $P$  which measures the probability that a collision will lead to a completed chemical reaction. Hence, in the modified collision theory

$$k = PZ \exp\left(\frac{-E}{RT}\right) \quad (2.3)$$

The 'fudge factor'  $P$  is introduced since the collision cross section of a molecule bears no clear relationship to the probability for a chemical reaction. While the collision theory works well for reactions between mono-atomic gases, it breaks down for reactions between more complex molecules. In this respect, the collision theory is not capable of clarifying the internal mechanisms of chemical reactions in the necessary detail.

**Table 2.2** Wigner's 'three threes' that characterise transition state theory Wigner (1938)

Three steps in theory of kinetics:	
(WS1)	Determine potential energy surfaces
(WS2)	Determine elementary reaction rates
(WS3)	Solve rate equations for complex reaction mechanism
Three groups of elementary reactions:	
(WE1)	Vibrationally/rotationally inelastic collisions (not a chemical reaction)
(WE2)	Reactive collisions on a single potential energy surface
(WE3)	Electronically non-adiabatic reactive collisions
Three assumptions:	
(WA1)	Electronic adiabaticity: the electronic configuration is in the lowest quantum state for each configuration of the nuclei
(WA2)	The validity of classical mechanics for the nuclear motion
(WA3)	Existence of a dividing surface that trajectories do not re-cross

After Miller (1998)

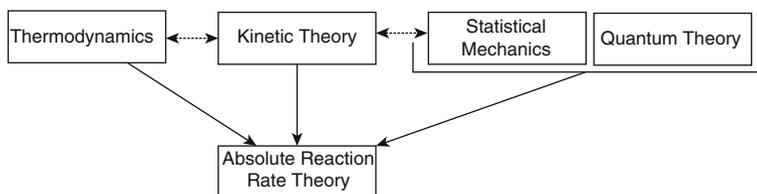
challenges, types of reactions and assumptions of the theory as a set of 'three threes'.<sup>14</sup> The three threes are summarised in Table 2.2, and translated into a specific set of steps (WS), groups (WG) and assumptions (WA).

Wigner's three steps are: (WS1) The determination of potential energy surfaces, which gives, in the words of Wigner, 'the behaviour of all molecules present in the system during the reaction, how they will move, and which products they will yield when colliding with definite velocities, etc.' (p. 29). The solution of this problem requires the calculation of a potential energy surface, which is a quantum chemistry problem that was solved, somewhat unsatisfactorily, by Born and Oppenheimer (1927).

Wigner classifies the elementary reactions in three groups. Only the second type of elementary reactions can be treated with transition state theory, hence, only (WE2) is considered in the theory.

Finally, Wigner discusses three assumptions (WA). The first specific assumption is the adiabatic assumption (WA1), which assumes that during the reaction the molecular system 'stays' on the lowest possible potential energy surface, and there is no change of electronic configuration. The second assumption, (WA2) is that the motion of the nuclei can be described with classical mechanics, and hence entails the Born-Oppenheimer separation between electronic and nuclear motion. The third assumption, (WA3), is that the reaction does not go 'backwards', i.e. all systems crossing the barrier are reacting systems. The consequence of this is that the step from the reactants to the transition state is the rate determining step for the equation. Once a set of reactants form a transition state, this transition state will fall apart to form the end products of the reaction.

<sup>14</sup> Wigner refers to the theory in this paper as 'The Transition State Method'. The paper by Laidler and King (1983) contains a brief discussion of this conference and the role it played in the subsequent adoption of the theory.



**Fig. 2.1** The conceptual structure of the absolute reaction rate theory

As this discussion shows, the theory has two aspects of interest to the philosopher of science:

1. The introduction and specification of a special chemical state, the ‘transition state’ in terms of a specific location on the potential energy surface of the reaction;
2. The degree to which explanation depends on *comparison* between the collision, thermodynamic, and quantum mechanical/statistical mechanical formulations of molecular quantities.

Hence, the theory of absolute reaction rates has a complex structure which given in Fig. 2.1. The purpose of the theory was to provide exact expressions for the two constants  $A$  and  $EA$ . From the viewpoint of *quantitative* explanations for these quantities the theory has been moderately successful, but has, in the words of Laidler and King (1983), ‘its difficulties’.

The most interesting aspect of the absolute reaction rate theory is that, again in the words of Laidler and King, it provided a

[...] conceptual framework with the aid of which experimental chemists (and others) can gain some insight into how chemical processes occur. On this score the theory must receive the highest marks; for nearly half a century it has been a valuable working tool for those who are not concerned with the calculation of absolute rates but are helped by gaining some insight into chemical and physical processes. The theory provides both a statistical-mechanical and a thermodynamic insight – one can take one’s choice or use both formulations. (Laidler and King 1983, p. 2664)

In this sense, the theory of absolute reaction rates is a very strong example for the unity of science – it is precisely one of those examples where it is hard to imagine a chemistry with the physics removed, but at the same time it is a ‘chemical’ theory in that it focuses on molecules, molecular structures, and transformations.

## 2.4.2 *Structuralist Characterisation*

I have presented a structuralist characterisation of quantum chemistry in Hettema (2012a) and will, for the purposes of this section, draw extensively on the structuralist framework developed there. Since in what follows we will focus on the changes in conceptual space as outlined by Gärdenfors and Zenker (2011) we

only have to focus on the (broad) set of structures  $M_p$ , and can ignore many of the finer points of structuralist theorising.

The question is now whether a ‘conceptual spaces’ approach to the theory of absolute reaction rates is capable of characterising the inter-theory relationships appearing in Fig. 2.1. I will now briefly, and largely informally, discuss the sort of relationships that are at play.

1. The simplest relationship exists between the ‘statistical mechanics’ ‘quantum mechanics’ boxes and the theory of absolute reaction rates.

A ‘simple’ quantum mechanics (of the type I argued that was used in quantum chemistry) is characterised by a Hilbert space and a set of operators as a structure  $2_s$ ,

**Definition 2 (QM-S)**  $x$  is a characterisation of a simple quantum mechanics, ( $x \in 2_s$ ) if

1.  $x = \langle \mathbf{S}, \mathcal{H}, \hat{A}, \sigma(\hat{A}) \rangle$ ;
2.  $\mathcal{I}$  is a system of particles;
3.  $\mathcal{H}$  is a separable Hilbert space;
4.  $\hat{A}$  is an operator on  $\mathcal{H}$ ;
5.  $\sigma(\hat{A})$  is the spectrum of  $\hat{A}$ .

As was argued by Muller (1998, 2003), quantum mechanics is not easily characterisable in terms of a structuralist model, and, in fact, ‘all quantum-mechanical set-structures float in a sea of stories’ (Muller 2003, p. 198). As Muller argues, many of the practical applications of quantum mechanics rely on specifications of ‘systems’, ‘measurement’ and the like which are fluidly adapted to the situation at hand. All of these adaptations make up the ‘sea of stories’.

One such story is quantum chemistry. In Hettema (2012a) I characterised ab initio quantum chemistry as a structure of structures, comprising of a molecular frame, an electronic structure and an atomic basis set. The simple definition is as follows:

**Definition 3**  $x$  is a potential model for ab initio quantum chemistry ( $x \in \mathbf{M}_p(\text{QCAI})$ ) if there are (sub)structures F, E and B, such that

1.  $x = (F, E, B)$ ;
2. F represents the molecular frame of the form  $\langle \overline{\mathbf{R}}, \mathbf{Z} \rangle$ ;
3. E represents the electronic structure of the form  $\langle \mathcal{P}_e, \mathbf{r}, \sigma, \Psi, \hat{A}, M \rangle$ ;
4. B represents an atomic basis set of the form  $\langle \overline{\mathbf{R}}_B, \chi, \alpha \rangle$ ;

For now, it is sufficient to recognise that the connections between a generic (‘simple’) quantum mechanics and an ab initio quantum mechanics depend on the moves discussed by Gärdenfors and Zenker (2011) in the following sense.

The specification of a molecular ‘frame’ depends, in the terminology of Gärdenfors and Zenker, on a change of scale or metrics as well as the salience of dimensions as well as on a change in the separability of dimensions. The ‘frame’

realises that atomic nuclei are heavier than electrons, and hence have an equation of motion that is to a significant degree separable from the motion of the electrons. From the viewpoint of ‘principled’ quantum mechanics this makes no difference – all particles form part of the system which must be treated quantum mechanically.

The remainder of the structures, E and B are more specifications of the remainder of the system in the language of simple quantum mechanics – one specifying that the electrons will be treated with the machinery of quantum mechanics, the other specifying the basis in which the quantum mechanical wavefunction will be expanded – they are not overly interesting from a conceptual space point of view.

The links, which I present in detail in Hettema (2012a), express the necessary relationships in relatively complex looking set-theoretic language. The conceptual spaces approach, which I have utilised here, allows for a more intuitive, non-formal characterisation of the same issues.

Eyring’s notion of ‘semi-empirical’ quantum chemistry adds further revisions onto *ab initio* quantum chemistry by specifying a distinction between ‘core’ and ‘valence’ electrons which is unprincipled from the viewpoint of *ab initio* quantum mechanics, but necessary from the viewpoint of practically implementing the theory without the help of a computer.

2. The connection between statistical mechanics and transition state theory is made by eliminating, from the partition function of the activated complex, the translational component due to the motion along the reaction coordinate (see (Glasstone et al. 1941, p. 189)).<sup>15</sup> This step, however, is captured through the addition of a ‘special law’ on statistical mechanics, and moreover, this ‘special law’ characterises the ‘transition state’ precisely in terms of its degrees of freedom.

Through this specification, the notion of ‘transition state’, the ‘saddle’ point on the reactive potential energy surface, can be specified as a ‘special law’ on top of ‘*ab initio*’ quantum chemistry.

3. The comparisons between the thermodynamic, collision and ‘absolute’ theories are at this stage difficult to determine, since detailed structuralist characterisations of these theories are not readily available. However, one would expect that these characterisations will yield similar insights.

### ***2.4.3 Reduction Postulates and Belief Revision***

The characterisations in terms of ‘conceptual spaces’ can be seen, in the traditional theory of reduction, as reduction postulates which tie the formal paraphrases of the reduced and reducing theory to each other. In particular, the analysis in terms of conceptual spaces allows for a precise characterisation of some of the terminology

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<sup>15</sup> A detailed discussion of why this is so falls outside the scope of this paper, but can easily be determined by stepping through the mathematics.

in the generalised Nagel-Schaffner model. Specifically, we can put more precision on the notions of ‘typical idealisations’, ‘boundary conditions’, ‘*approximately the same*’ and ‘analogy relation’, all of which enter into the formulation of the generalised Nagel-Schaffner model.

As a sidenote, the characterisation in terms of this formal framework has additional benefits: it opens the theories of chemistry up to formal treatments in the philosophy of science that focus on other formal aspects of theories such as verisimilitude.

It thus appears that a practical theory of chemistry can, with a little formal help, be reconstructed in terms of philosophical notions such as set theoretic structures and conceptual spaces that are fruitful starting points for the general philosophy of science, and that may have further import for discussions about pluralism and the unity of science.

This result forms a strong motivation for a further study of the theories of chemistry by philosophers of science, and also illustrates that chemistry as a science has interesting philosophical dimensions. Finally, in an attempt to answer the question as to whether ‘these methods’ are ‘fundamentally sound’, it may be concluded that they are indeed, though probably not with the methods available to philosophers of science in 1937.

## 2.5 Conclusion

I have argued that the Nagelian theory of reduction can well be retrofitted to a belief revision approach based on set theoretic structures and conceptual spaces. Doing so leads to a picture of reduction that has interesting consequences for our notions of unity of science. The unity of science under this reconstruction is reconstructed in a ‘dappled’ sense as a set of specific reasoning strategies that transform ‘quantum theory’, a generic theory without a firm set-theoretic formulation, into a highly specific theory of chemistry.

It is important to recognise that the belief revision approach is a generative theory, and has a descriptive counterpart – that is, belief revision lets us determine the sort of reasoning that led to a particular model, but is perhaps less capable of describing the end-result with the necessary level of detail. That latter step, however, falls outside the scope of this paper.

It would seem that this approach is capable of reconciling both our intuitions about how reduction should work in practice with actual examples from science, and show that a number of confusing debates in the philosophy of chemistry could have been avoided altogether.

This reconstruction of the notion of reduction fulfills a number of interesting desiderata: it supports the unity of science as an overall epistemic structure, and can make sense of some actual problematic cases of reduction from the philosophy of chemistry. The limitation on incommensurability inherent in this approach also limits the scope of feasible pluralisms in the philosophy of chemistry, and focuses our attention instead on a more precise formal characterisation of the resulting epistemic structures.

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