

## KINETIC VERSUS THERMODYNAMIC CONTROL: SOME HISTORICAL LANDMARKS

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The study of chemical reactivity may be broadly divided into the subject areas of reaction stoichiometry, reaction kinetics, and reaction thermodynamics. The first deals with the classification of chemical reactions, their expression as properly balanced net chemical equations, and the various quantitative calculations that are based upon these balanced equations. The second deals with the determination of rate laws and the deduction of reaction mechanisms, while the third deals with reaction efficiency and chemical equilibrium as a function of the relative stabilities of the various reactants and products, their concentrations, and the ambient temperature and pressure. In more colloquial terms, these three subject areas deal with the theoretical answers to the questions of “What changes in a chemical reaction?,” “How fast does it change?,” and “How complete is the change?”

Obviously the proper differentiation of these three questions and their resulting areas of specialization only gradually evolved over time. Thus the distinction between questions two and three was probably not complete until the 1880s with the rise of chemical kinetics and chemical thermodynamics as distinct subdisciplines, as personified by the publication of van't Hoff's classic monograph, *Études du dynamique chimique*, in 1884 (1). The key steps in this differentiation are at least implicitly covered in most standard histories of chemistry and it is not our intent to repeat them here. Rather our goal is to trace the subtle manner in which these questions once more became entangled with one another when dealing with the pervasive problem of competing

chemical reactions, only to gradually separate once more under the rubrics of kinetic versus thermodynamically controlled chemical reactivity. As we will see, this pertinent distinction was independently discovered at least three times—each time within a different field of chemistry—thereby also providing us with a cautionary tale concerning the importance of the role played by textbooks and university curricula in the preservation and transmission of chemical knowledge, not to mention the perils of overspecialization.

### The Laws of Chemical Affinity

Though there are scattered precedents in the 17th century, the first attempts to systematically study and classify chemical reactivity really date from the 18th century and came to constitute what became known as the study of “chemical affinity.” This same century also saw the famous chemical revolution of Antoine Lavoisier and his collaborators, which focused instead on the subjects of chemical composition and changes of state. Though Lavoisier fully recognized that the study of chemical affinity was a legitimate and important field of chemical investigation as well, he also felt that it was still too immature and imperfectly developed for coverage in an elementary textbook and, for this reason, purposely chose not to include a discussion of its results in his famous *Traité* of 1789 (2).

So significant was the impact of Lavoisier's revolution for the subsequent development of chemistry that



on a similarity in the properties of the reactants (law 2) and that the properties of the reaction products were an average or blending of those of the starting materials (law 3)—ideas which he had, in turn, probably absorbed from Georg Ernst Stahl's *Fundamenta chymiae* of 1723.

Some indication of the progress made in the study of chemical affinity during the century may be gleaned by comparing Macquer's seven laws of 1749 with the eight laws of chemical affinity given by the French chemist, Antoine-François de Fourcroy (Figure 3), 33 years later in his own textbook of 1782, where the second and third of Macquer's laws are directly contradicted by the first and sixth of Fourcroy's new laws (10):

1. The attraction, or affinity of composition, cannot act but between bodies of different natures.
6. Two or more bodies united by the attraction of composition, form a substance, the properties of which are different from those which each of the bodies possessed before their union.

—versions which the modern chemist hopefully will recognize as being far closer to our current views on the nature of chemical change than those of Macquer.



Figure 3. Antoine-François de Fourcroy (1755-1809).

But what is far more pertinent to our present inquiry is Fourcroy's seventh law of chemical affinity, which reads (10):

7. The attraction of composition is measurable by the difficulty of destroying the combination formed between two or more bodies.

At first glance this may seem irrelevant to the question of kinetic versus thermodynamic control, but on reading Fourcroy's commentary on this law we quickly discover the following statement (10):

We find it as particularly necessary to insist upon this law because beginners are apt to fall into mistakes when estimating the differences of the attraction which unites the principles of different combinations. From the rapidity with which some substances combine, we are ready to imagine that their mutual attraction must be very considerable. But long experience shows that the eagerness to enter into combination, instead of indicating a perfect composition, is rather proof that the attraction between the bodies is extremely weak, and can produce but a very imperfect compound. In order, therefore, to determine accurately the degree of affinity with which bodies unite and remain in union, we must consider the ease or difficulty with which they are separated.

Both the identical law and a similar commentary appear in the discussion of affinity found in Fourcroy's more elaborate, 11-volume, chemical treatise of 1801, in which his list of affinity laws has been expanded from eight to ten (11):

By attention too immediate to the first appearances, chemists have supposed that those bodies which combine the most speedily or with the greatest quantity of motion, have the strongest affinity for each other; with these chemists the speed of combination became the measure of affinity. It has long been ascertained that this is a source of error and delusion. It often happens, on the contrary, that such substances as are with the most difficulty brought into combination are those which adhere the most strongly to each other. Whence it results that the true and only exact method of determining the force of chemical attraction between bodies is to measure the force we are obliged to employ to separate the constituent parts of a compound.

These two statements are, to the best of my knowledge, the first explicit recognition that there is an important distinction to be made between the speed of a chemical reaction and the stability of the resulting products or, in modern terms, between chemical kinetics, on the one hand, and chemical thermodynamics on the other. And it further implies that there is often, but not always, an inverse relationship between the two.

Though none of the modern historical studies of affinity theory mentioned earlier seem to have called attention to the importance of this observation, several of Fourcroy's contemporaries did and dutifully reproduced versions of it in their own textbooks. Thus the 1819 edi-

tion of John Murray's four-volume *System of Chemistry*, which was published nearly a decade after Fourcroy's death, contains the statement (12):

The facility or rapidity of combination depends not on the force of affinity, but on that modified by the cohesion, elasticity, and other qualities of bodies; and we have many examples in which a combination takes place slowly where the attraction from which it arises is strong, or where it is affected with facility, where the attraction is comparatively weak.

Similarly, 23 years later we find a related statement in an 1842 paper by the French chemist, Joseph Louis Gay-Lussac (Figure 4), on the complex aqueous solution chemistry of the oxosalts of chlorine (13):

It is a general rule that, if one is able to form, at the same time and with the same elements, various compounds that are unequally stable, but capable of existing under the same circumstances, then it is the least stable that is formed first. If the circumstances change or are impossible to maintain, the compound of intermediate stability succeeds it and so on until one has arrived at the most stable compound or the component elements are separated.

Note that this statement actually goes one step beyond Fourcroy's original law by applying it, not just to the formation of single products, but to a reaction system capable of forming several distinct sets of competing products. Though Gay-Lussac makes no mention of Fourcroy, it is not improbable that he was fully aware of Fourcroy's law from a reading of his treatise of 1801 since Gay-Lussac was only 23 years old at the time and in the midst of his formative student years when it was first published.



Figure 4. Joseph Louis Gay-Lussac (1778-1850).

## The Demise of Affinity Theory

By the late 1850s the original outlines of classical affinity theory had begun to fade. The first facet to go was the affinity table, whose underlying assumptions had been severely undermined by the work of the French chemist, Claude Berthollet, at the turn of the century, on the influences of both changes of state and mass action effects in modifying the outcomes of the displacement reactions which had formed the basis of such tables in the first place (14). By 1819 the value of these tables was already being seriously questioned by the ever-thoughtful Murray in his masterful textbook (12):

From the preceding observations it must be apparent that the common tables of elective attractions do not represent the relative forces of affinity, but only a series of decompositions, which arise as much from the operation of circumstances which influence attraction, as from differences in the strength of the power itself. Nor do they even express the order of these decompositions accurately, since the influence of quantity, which undoubtedly modifies the results to a certain extent, has been neglected in the experiments on which they are founded. They are therefore of less utility than has been believed.

The second facet to disappear was the affinity diagram. Despite the rule set down by Fourcroy in his seventh law, chemists had in fact never agreed on the proper method for measuring chemical affinity, let alone on how to relate such measurements to the hypothetical numerical interparticle force values given in the typical affinity diagram. Thus, for example, the French chemist, Guyton de Morveau, attempted to correlate the affinities of various metals with the force required to separate a disk of the metal in question from a mercury surface; whereas the German chemist, Carl Wenzel, attempted to correlate them with the time required to dissolve a cylinder of the metal in acid; and the Irish chemist, Richard Kirwin, with the weight of an alkali or metal required to saturate a given amount of acid.

With the gift of hindsight, we now know that all of these attempts were fundamentally flawed. Guyton was actually measuring intermolecular forces (called "attractions of aggregation" by 18th-century chemists) rather than the interatomic forces (or "attractions of composition") actually responsible for compound formation; Kirwin was conflating chemical composition with chemical affinity and was actually measuring combining weights; whereas Wenzel was conflating kinetics with questions of stability. Indeed, there is little doubt that Fourcroy's commentary on the inverse relationship between speed of

reaction and chemical stability was specifically intended as a criticism of the work of Wenzel, as summarized in his 1777 monograph *Lehre von der Verwandtschaft der Körper* (15).

Nevertheless, it should be noted, that, while the use of hypothetical force values had largely disappeared from reaction diagrams by the 1820s (only to be replaced in many cases with stoichiometric equivalent weight values instead), chemists continued to use these diagrams, now reinterpreted to show only which components had interchanged places in a reaction, well into the 1860s, when they were finally fully displaced by the use of balanced linear equations (8).

Of the three original affinity formats, it was the so-called laws of chemical affinity that managed to survive the longest in the textbook literature. Thus, in his popular textbook of 1858, the American chemist, David Wells, was still listing nine laws of chemical affinity, several of which echoed the more significant innovations found in Fourcroy's original list, including both Wells' third and fourth laws (16):

3. Generally speaking, the greater the difference in the properties of bodies, the greater is their tendency to enter into chemical combination. Between bodies of similar character, the tendency to union is feeble.
4. Chemical affinity occasions an entire change in the properties of the substances acted upon.

However, no trace can be found of Fourcroy's seventh law or of its concomitant observations on the inverse relationship sometimes found between speed of reaction and product stability nor of Gay-Lussac's later elaboration. The reasons for this disappearance are not hard to surmise. With the demise of the affinity table and the temporary abandonment of the experimental program to measure affinity values, there was no longer any need for a rule to govern their measurement. As for the still valid observations on the distinction between speed of reaction and product stability, the baby was simply thrown out with the bath water and became an artifact of an outdated literature that most chemists no longer read.

### The Study of Phase Transitions

One of the defects of Fourcroy's original statements of his rule concerning speed of reaction and product stability was his failure to provide concrete examples of its application to actual reaction systems, and much the same may be said of Murray's later discussion as well, though he did provide a physical example involving the separation of solids from cooled liquids and solutions (12):

When attraction of aggregation is exerted, the particles are sometimes united indiscriminately, so as to form irregular masses; sometimes they pass into arrangements, whence masses of regular figures arise. The former happens generally when attraction is exerted suddenly, and with considerable force. If a liquid be suddenly cooled to a sufficient extent, a mass is formed altogether irregular. Or if a substance be produced by chemical action, the particles of which have a strong mutual attraction, this is exerted at the moment of its production, and it is separated in the form of a powder. This latter case is named in chemical language Precipitation, and the substance is said to be precipitated. The other result occurs when aggregation, previously weakened either by the operation of heat or of chemical attraction, resumes its force more slowly. The particles then assume a particular arrangement so as to form masses of regular figures, or bounded by plane surfaces and determinant angles. The result is named Crystallization, and such regular figured masses are denominated Crystals.

Of course there seems to be only a tenuous relationship at best between the issue of crystal size and the issue of product stability required by a literal reading of the original law, and we must now move forward another 70 years, and switch from the study of chemical affinity to the newly emerging field of phase science, in order to reestablish the necessary connection, as found in a paper published in 1897 by the German physical chemist, Wilhelm Ostwald (Figure 5), entitled "Studies on the Formation and Transformation of Solid Bodies" (17).

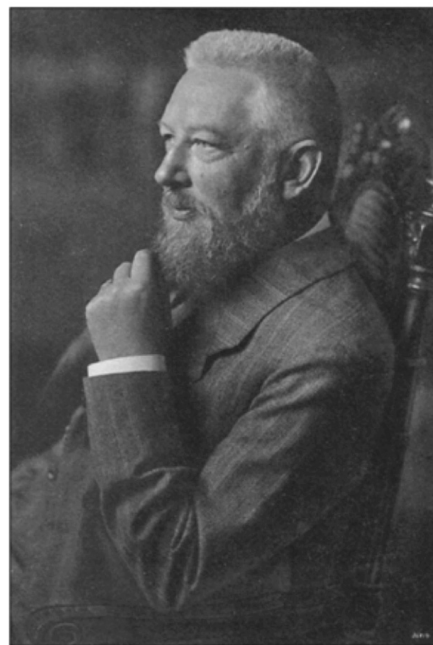


Figure 5. Wilhelm Ostwald (1853-1932).

As suggested by the paper's subtitle, "Supersaturation and Supercooling," Ostwald was interested in the phenomenon that rapidly cooled gases, liquids, and solutions often persisted long after they had ceased to be thermodynamically stable and, when finally transformed into a more stable solid capable of existing in two or more polymorphic modifications, often initially selected the least energetically stable of these possible alternatives rather than the most stable. Halfway through his lengthy 42-page article, Ostwald paused and attempted to generalize—albeit rather awkwardly—these observations in the form of a tentative law:

... I would like to summarize our experiences so far concerning this subject with the general law that, on leaving any state and passing into a more stable one, that which is selected is not the most stable one under existing conditions, but the nearest.

Known sometimes as Ostwald's "law of successive reactions" or "successive transformations" and sometimes as the "Stufenregel" or "rule of stages," it was far more clearly articulated several years later in the 1912 edition of his popular textbook, *Outlines of General Chemistry* (18):

If the metastable region has been exceeded, and a new phase appears spontaneously, it is remarkable that the phase which appears is not the most stable phase under the conditions, but is the least stable, i.e., the next in stability to the phase undergoing the transformation.

A second by-product of Ostwald's work in this area was the establishment of much of our current terminology for dealing with such phenomena. In the 1895 edition of *Outlines of General Chemistry* he had explicitly complained of the absence of a suitable vocabulary (19):

Such phenomena have been mostly considered as being to a certain extent unnatural, and the corresponding states have received the names of superheating and overcooling or supersaturation. They are nevertheless very common, and appear whenever, from a substance or mixture of substances in a homogenous state, a part may separate out; thus, for example, gases, solids, or immiscible liquids from liquids, or, on the other hand, liquids or solids from gases. The name "states of instability," which has also been applied in such cases, is equally unsuitable. For the states are not really unstable, since they by no means pass into others on the smallest change. This must rather be compared to the stable equilibrium of a rather tall cylinder standing on one end; the system is certainly stable, but when it suffers a somewhat large displacement it easily assumes another state which is much more stable than the first. It must be

admitted, however, that here there is no analogy to the special action exercised by a small quantity of the heterogeneous substance [i.e. a seed crystal] in all the cases above mentioned.

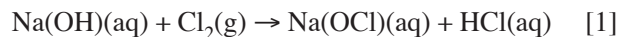
The term "false equilibria," favored by the French physicist, Pierre Duhem, was not much better (20). However, in his 1897 paper Ostwald finally suggested use of the term kinetically "labile" to describe systems that rapidly underwent the necessary phase change upon reaching their thermodynamically proscribed limits, versus use of the term kinetically "metastable" to describe those that persisted beyond that point and which, in the words of Findlay, exhibited the phenomenon of "suspended transformations" (21).

Though exceptions to Ostwald's rule are known, both it and Ostwald's proposed terminology soon found a place in the first generation of physical chemistry texts (22)—perhaps not surprisingly given that many of them were written by Ostwald's former students—as well as in the advanced monograph literature dealing with both the phase rule (21, 23) and with polymorphism (24-26), though neither of these topics have ever loomed large in the education of the average chemist.

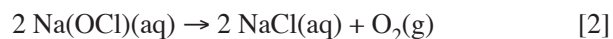
In his later account of 1912 Ostwald also went one step further (no pun intended) and asserted that his rule applied not just to phase transitions but to chemical reactions in general (18):

... This phenomenon is quite general in character, and is not limited to equilibrium of the first order, but holds in all changes of state, and especially in chemical reactions in the strict sense.

This assertion he further illustrated in the 1908 edition of his textbook, *Principles of Inorganic Chemistry*, using the reaction between aqueous sodium hydroxide and dichlorine gas (27). This initially produces the compound known as sodium hypochlorite or Na(OCl):



However, if this is allowed sufficient time, it will eventually decompose into the thermodynamically more stable products of sodium chloride and dioxygen gas:

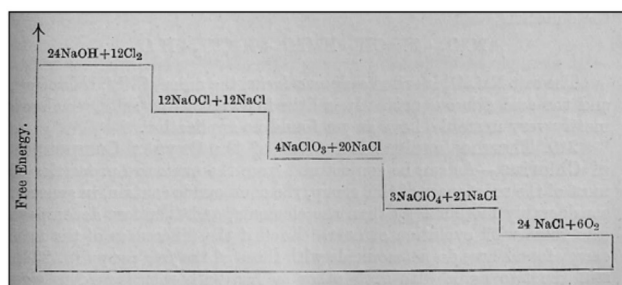


thereby illustrating the rule of stages (27):

It might now be asked why hypochlorite is formed at all, and why the whole amount of the substances doesn't straightway pass into the most stable condition, chloride and oxygen ... The answer to this question is again afforded by a general law, which states that in all reactions the most stable state is not

straightway reached, but the next less stable or that state which is the least stable of the possible states. Starting from this, the more stable states are reached one after the other, and the process of transformation comes to a stop only when a state is finally attained which cannot further change and is, therefore, the most stable.

Indeed, Ostwald was quick to point out that the situation was even more complex than this, since in actual fact several additional transient reactions intervened between reaction 1 and reaction 2, leading to the formation of such products as sodium chlorate or  $\text{Na}(\text{ClO}_3)$  and sodium perchlorate or  $\text{Na}(\text{ClO}_4)$ —a situation which he illustrated by means of the free-energy diagram shown in Figure 6.



**Figure 6.** Ostwald's diagram of 1908 illustrating the successive stages in the reaction between  $\text{Na}(\text{OH})(\text{aq})$  and  $\text{Cl}_2$  as a function of free energy content (27).

I have been unable to uncover any evidence that Ostwald was aware of Gay-Lussac's earlier statement of 1842. By the 1880s the traditional field of chemical affinity had clearly bifurcated into the newer fields of chemical kinetics versus chemical thermodynamics and there was little motivation for the new generation to consult the outdated paradigms of the older affinity literature. Yet it is certainly curious that Ostwald chose to illustrate the application of his rule to chemical reactions proper using the exact same reaction system as Gay-Lussac had used 66 years earlier!

### Transition States and Potential Energy Surfaces

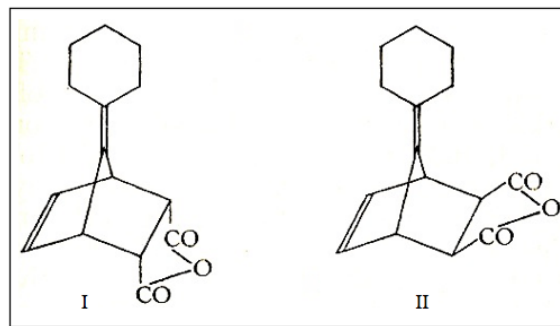
We now fast forward yet another half century and switch from the field of phase science to the field of physical organic chemistry and to a paper published in 1944 by R. B. Woodward (Figure 7) and H. Baer on diene-addition reactions (28). In studying the Diels-Alder addition between 6,6-pentamethylenefulvene and maleic anhydride, they found that a mixture of both the *endo*-

and *exo*- isomers was obtained for the resulting addition product (Figure 8). Initially labelled as the *α-adduct* and *β-adduct*, respectively, these two isomers were found to have quite distinctive physical and chemical properties and to be preferentially favored or disfavored by certain changes in the reaction conditions (28):

... allowed to react in benzene solution, at room temperature, an *α*-adduct,  $\text{C}_{15}\text{H}_{16}\text{O}_3$ , m.p.  $132^\circ$ , is obtained. If, however, the mother liquor from the recovery of this product is allowed to stand for several weeks, very large beautiful crystals of a new, *β*-adduct,  $\text{C}_{15}\text{H}_{16}\text{O}_3$ , m.p.  $93^\circ$ , gradually separate. Further, as the initial condensation is carried out at higher temperatures, the formation of the *β*-adduct takes place more rapidly, and less of the *α*-adduct is obtained.

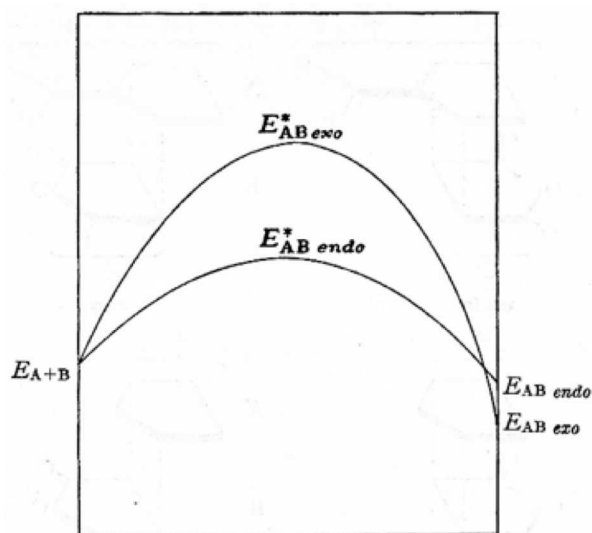


**Figure 7.** Robert Burns Woodward (1917-1979).



**Figure 8.** The structures of the *endo*- (I) and *exo*- (II) isomers for the product formed on reacting 6,6-pentamethylenefulvene with maleic anhydride (28).

With the development of absolute rate theory in the 1930s by Eyring in the United States and by Evans and Polanyi in Great Britain (29, 30), Woodward and Baer had access to a new set of theoretical concepts for the rationalization of reactivity—such as potential energy surfaces, activation barriers, and transition states—that were largely unavailable to Ostwald in 1897. In order to rationalize their results Woodward and Baer made use of these newer tools by postulating the potential energy surfaces shown in Figure 9 in which the rapidly formed *endo*-isomer was assigned a lower activation energy and hence faster kinetics than the *exo*-isomer, but in which the two surfaces crossed before reaching final equilibrium, thereby ultimately making the *exo*-isomer the thermodynamically favored product. Most of the rest of the paper was devoted to experimentally establishing which adduct corresponded to the *exo*- and which to the *endo*-isomer and to electronically and stereochemically rationalizing why the *endo*-isomer might be expected to have a lower activation barrier than the *exo*-isomer.

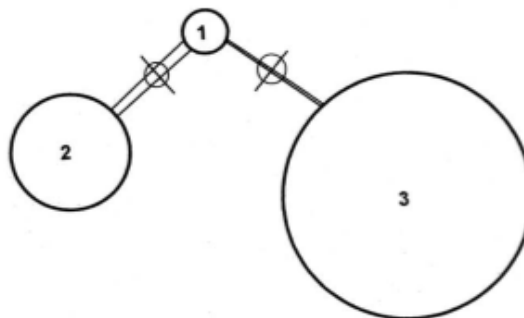


**Figure 9.** Potential energy diagram used by Woodward and Baer to rationalize kinetic versus thermodynamic control in diene-addition reactions (28).

Though Woodward and Baer did not use the terms kinetic control versus thermodynamic control in their paper, this is still, to the best of my knowledge, the first implicit use of these concepts in the field of organic chemistry, and their experimental observations may be generalized using this terminology by the general rule that:

Low temperatures and/or short reaction times favor kinetically controlled reactivity, whereas high temperatures and/or prolonged reaction times favor thermodynamically controlled reactivity.

As for the terms themselves, they appear to have been first used in the 1956 edition of Jack Hine's textbook, *Physical Organic Chemistry* (31), though it would take another three decades for them to become standard textbook fare. Thus, no mention of them is to be found in an index search of the physical organic texts by Wiberg (1964), Wheeler (1966), Kosower (1968), Hammett (1970), Ritchie (1975) or Jones (1984) and their coverage in the text by Hirsch (1974) is incidental (32). On the other hand, they are employed in the later texts by Lowry and Richardson (1981), Klumpp (1982), Maskill (1985) and Isaacs (1987) (33). Likewise, a computer search of the index for *the Journal of Chemical Education* using the search term "kinetic control" revealed roughly 55 entries, starting very sporadically in 1965 and rapidly increasing only during the last two decades, dealing with laboratory experiments, lecture demonstrations, clever teaching analogies (see Figure 10), and popular overview articles related to this topic.

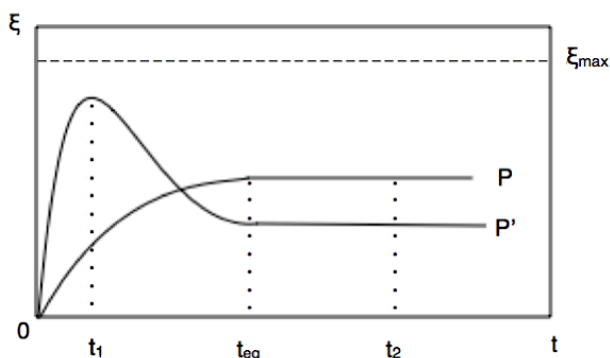


**Figure 10.** An ideal gas analogy for kinetic versus thermodynamic control proposed by Macomber in 1994 (34). Two evacuated flasks (2 and 3) of unequal volumes are connected to the smaller flask 1 containing an ideal gas. The tube connecting 1 and 2 is 10 times the diameter of that connecting 1 and 3. On quickly opening and closing the two stopcocks the quantity of gas in flask 2 is found to be greater than that in flask 3. This is kinetic control. On reopening the stopcocks permanently, the pressures in all three finally equalize, such that the quantity of gas in 3 is now greater than that in 2. This is thermodynamic control. The volumes of the flasks are analogous to the inverse of their free energy content and hence to their positions on an energy-reaction coordinate plot.

The expected time evolution for the system shown in the potential energy plot in Figure 9 is shown in the extent of reaction ( $\xi$ ) - time ( $t$ ) plot in Figure 11, where, if the reaction is terminated at time  $t_1 < t_{eq}$ , where  $t_{eq}$  is the time required to reach equilibrium, the major product (P') is kinetically controlled, whereas, if it is terminated at  $t_2 > t_{eq}$ , the major product (P) is thermodynamically



controlled.  $\xi_{\max}$  denotes the stoichiometrically allowed maximum for the extent of reaction parameter as determined by the concentration of the limiting reagent. Of course, the phrase “terminate the reaction” implies that it is possible to alter the reaction conditions such that any further conversion of the kinetic product into the thermodynamic product is completely inhibited, and it becomes possible to isolate the kinetically metastable product and store it in a bottle indefinitely. In the case of the room temperature Diels-Alder addition studied by Woodward and Baer, this was accomplished simply by eliminating contact with the solvent, whereas in high-temperature reactions it is usually accomplished by the act of rapidly cooling the kinetic product to room temperature.



**Figure 11.** An extent of reaction - time plot for the competitive formation of a kinetically controlled product ( $P'$ ) versus a thermodynamically controlled product ( $P$ ).

### From Isomers to Polymorphs

In sharp contrast to the situation in the field of physical organic chemistry, it took a surprisingly long time to arrive at a satisfactory theoretical rationale for Ostwald's law of stages in the field of phase science—a situation not helped by Ostwald's well-known disdain for the atomic-molecular theory. One such early attempt was made in 1913 by the Dutch phase scientist, Andreas Smits, using his ill-fated theory of allotropy (35). This postulated that the homogeneous phases of all pure substances, including crystalline solids, were in fact homogenous mixtures of rapidly interconverting molecular clusters of various sizes, known as “pseudo-components.” As long as the rate of these interconversions was greater than that for a particular phase change, they had no effect on phase behavior and the substance in question continued to behave thermodynamically as though it had only one component. However, if for some reason, one or more of these cluster interconversions was kinetically inhibited

or slowed down in some way, then the substance would begin to display complex phase behavior more typical of multicomponent systems.

In applying his theory to the question of which of several alternative product phases was selected in a polymorphic phase change, Smits assumed that the situation was in fact competitive. Each possible product phase was determined by a particular cluster present in the reactant phase and the question of which product formed first was reduced to the question of which of these competitive alternatives was present in the greatest concentration at the transition point.

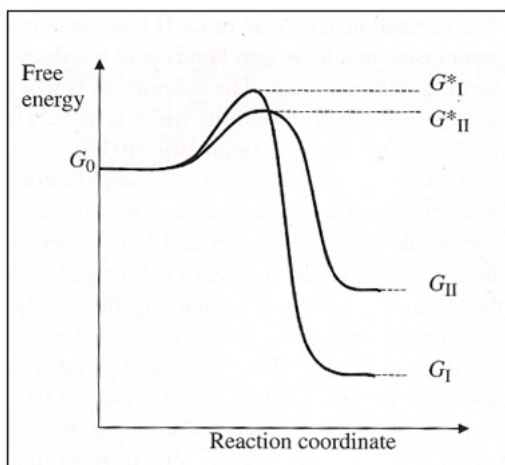
By 1925 the German phase scientist, Gustav Tammann, building on work extending back to the 1890s (36), was advocating a related picture based instead upon the formation of centers of nucleation or crystallization in the liquid or gas phases rather than on hypothetical fluctuating molecular clusters. Once again the process was envisioned as being competitive, with the reactant phase at the moment of actual transition containing nuclei for all of the possible solid product phases and the actual solid phase selected being, in turn, determined by their relative concentrations and/or rates of formation (21):

Inasmuch as the process of spontaneous transitions is an atomic one it will be subject to the laws of probability. Therefore, only the probability of formation of crystal centers, the forms of which have different stability, may properly be discussed ... Ordinarily grains of the forms with different stability appear simultaneously.

In 1933 Stranski and Totomanow attempted to test this hypothesis by calculating the relative numbers of different nuclei present in the melts for two example dimorphic systems as a function of temperature and various structural parameters for the product phases using an equation that had been recently proposed by Volmer (37, 38). For the  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  system the more stable polymorph had the greatest nuclei abundance and thus violated Ostwald's rule upon solidification, whereas for the  $\text{HgI}_2$  system the less stable yellow polymorph had the greatest nuclei abundance and thus obeyed Ostwald's rule upon solidification.

It was, however, not until the 1990s that the concepts of kinetic versus thermodynamic control and a potential energy surface (Figure 12) similar to that originally proposed by Woodward and Baer in 1944 to rationalize competitive isomers were finally applied to Ostwald's *Stufenregel* and the rationalization of competitive polymorphs, allowing the rule to be reformulated as:

When a solid capable of polymorphic modifications separates from a liquid or gas, the polymorph which is initially deposited is metastable relative to the other potential products and is therefore kinetically rather than thermodynamically controlled.



**Figure 12.** The free-energy surfaces used by Bernstein (26) to rationalize Ostwald's law of stages in terms of kinetic versus thermodynamically controlled reactivity.

Furthermore, any apparent exceptions could now be rationalized as cases for which the existence domain for the initial metastable product is so narrow that it is passed through without detection in favor of the more stable product.

It is important to remember that the competitive situation assumed by all of these models applies to the gas or liquid at the point when the first solid phase separates and not necessarily to the subsequent transformation of that solid into more stable modifications. Unlike the competitive formation of isomers dealt with in organic chemistry, in which the various alternative products are simultaneously formed and only their ratios change on moving from the realm of kinetic control to the realm of thermodynamic control, in the case of the competitive formation of polymorphs dealt with in phase science, the winner usually takes all. Indeed, as the names "law of successive reactions" or "rule of stages" strongly imply, the formation of successive solid phases is probably more aptly viewed as a series of consecutive reactions in which each product or stage acts as a metastable reaction intermediate for the production of the next product in the sequence rather than as the competitive situation envisioned for the initial liquid or gas, and the same may be equally true of the  $\text{NaOH}(\text{aq})\text{-Cl}_2(\text{g})$  reaction system discussed earlier.

It should also be noted that Ostwald's rule probably applies to situations other than just the competitive formation of crystalline polymorphs. Thus Walker suggested as early as 1899 that the initial formation of metastable plastic sulfur rather than crystalline rhombic sulfur upon rapidly cooling molten sulfur or the initial formation of oils and tars in organic chemistry prior to final crystallization of the desired product were all examples of Ostwald's rule in action (22), and the same is probably true of the initial formation of colloidal precipitates and their subsequent aging in the field of traditional wet chemical analysis (39).

Walker also suggested that Ostwald's rule was really a rule of least change—in other words, that the initial product corresponded to whichever phase deviated the least from the structure of the reactant phase (22). More recently Isaacs has suggested a molecular version of this idea in the field of organic chemistry based on the "principle of least motion," first suggested by Rice and Teller in 1938 (33, 40):

... those elementary reactions are favored which involve the least change in atomic positions and electronic configurations.

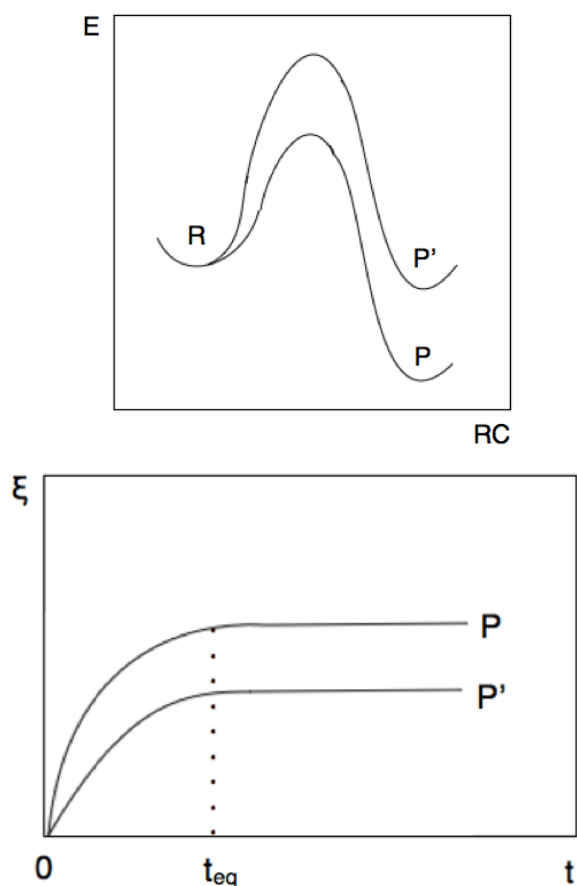
In short, the less structural and electronic rearrangement required, the lower the activation energy for the product in question, and the faster its rate of formation.

Last, but not least, the physical organic textbook by Klumpp has suggested that kinetic control automatically implies that the competitive reactions in question are irreversible, whereas thermodynamic control automatically implies that they are reversible (33). While the second of these statements is true by definition, the first statement is not (41), as demonstrated by the ability of many systems to switch from the domain of kinetic control to the domain of thermodynamic control as a function of reaction time and/or temperature and by our earlier analysis of figures 9, 11 and 12.

Indeed, the situation is even more complex than suggested by the above discussion since yet other possible potential energy surfaces are also conceivable, such as that given in Figure 13. For systems of this type both the kinetics and thermodynamics lead to an identical result and the potential energy surfaces are said to obey the so-called "noncrossing rule" (42). This situation is one of the fundamental, albeit often unarticulated, assumptions underlying the application of so-called linear free-energy correlations, as well as most of the approximate electronic reactivity indices much beloved of the modern-day organic chemist. This is especially true of those based on

the use of perturbation theory, though, as admitted by at least one leading theoretician, its validity appears to have been most often assumed after the fact rather than rigorously proven up front (42):

Such a procedure makes use of a rule known as the noncrossing rule, which states that for similar reactants the ratio of the energy necessary to reach any particular (but common) point on the respective reaction path curves is proportional to the ratio of the activation energies ... Although there is neither proof nor reason for such behavior, it has reasonably been verified experimentally and serves as a basis for most attempts to correlate chemical reactivity, particularly aromatic reactivity.



**Figure 13.** A potential energy plot and the corresponding extent of reaction - time plot for a competitive reaction obeying the noncrossing rule showing that kinetics and thermodynamics both predict the same dominant product (P).

### The Ubiquity of Kinetic Metastability

Though first formulated by Gibbs in 1876, the phase rule did not begin to truly impact on chemistry until the

1890s (43). But once chemists realized that application of the rule held out the promise of definitively characterizing each known reaction system in the form of a summary phase diagram, their enthusiasm knew no bounds. Beginning with the work of the Dutch phase chemist, Bakhuis Roozeboom, in the period 1901-1910 (44), massive collections of experimentally measured phase diagrams began to appear in the literature, especially in those fields dealing with the high-temperature chemistry of metallic alloys and ceramics (45-47) and, with the introduction of the alternative predominance or Pourbaix equilibrium plots in the 1940s, in the field of room-temperature aqueous solution chemistry as well (48-50). Though these latter plots are not identical to phase diagrams, they also deal with equilibrium conditions, albeit with respect to reaction equilibria rather than phase equilibria.

Indeed, so enthusiastic was Ostwald about these developments that in 1907 he wrote a book entitled, in English translation, *The Fundamental Principles of Chemistry: An Introduction to All Textbooks of Chemistry*, in which he attempted to eliminate the atomic-molecular theory from chemistry and to instead operationally derive its most fundamental concepts on the basis of the phase rule and the use of experimentally measured phase diagrams (51). However, about a third of the way through the book, one gets the impression that Ostwald had begun to slowly realize that such an approach failed to capture many essential aspects of chemistry. As we have already seen, he was fully aware of the phenomenon of kinetic metastability in connection with the study of both phase transitions and homogenous reaction systems and dutifully mentioned both, as well as his *Stufenregel*, thus forcing himself to admit, as the book proceeded, the existence of an increasing number of exceptions to his program to base chemistry solely on the study of phase diagrams.

For example, someone who goes to the stock room to get a bottle of phosphorus will have a choice of either solid white (yellow) or amorphous red phosphorus, both of which are kinetically metastable relative to the thermodynamically stable black form and neither of which appear on the phase diagram for this element (52). Likewise, one may read an extensive literature on the role of ozone in protecting the environment from excessive UV radiation and its significance for the evolution of life on earth, or read of its properties in older descriptive inorganic textbooks, or even demonstrate its preparation for an introductory chemistry class, yet once again no trace of its existence will be found on the phase diagram for the element oxygen (52). Entire classes of chemical

compounds, such as the boron hydrides or the nitrogen oxides, also owe their existence to kinetic metastability and are missing from phase diagrams.

As noted by Ostwald near the end of his book, even more significant problems result when one looks at the phenomenon of isomerism and the chemistry of organic carbon compounds (51):

Cases of isomerism are found in very great numbers among carbon compounds, and this is because of two reasons: first, carbon compounds are very numerous and varied; second, they almost always exhibit an extremely small reaction velocity. This means that we are able to prepare and observe forms which could not be characterized as individual substances if other conditions held. The result of this condition has been that investigators have studied these individual substances, unstable of themselves, but easy of isolation because of their very small reaction velocities.

Thus in a few sentences Ostwald managed to dismiss the entire science of organic chemistry as the study of transient metastable reaction intermediates, and it must be admitted that this characterization is not far off the mark, since, with the possible exception of the aqueous phase chemistry of organic species with ionizable functional groups, very few phase studies are known for typical organic systems (53).

The point here is that both phase and Pourbaix diagrams are *equilibrium* diagrams and, as such, display only thermodynamically controlled reactivity. Though they sometimes attempt to incorporate information on kinetically controlled metastability in the form of dotted lines to indicate curves for supercooling or crosshatching to indicate regions of kinetic passivation due to surface precipitation, they, by and large, ignore the rich field of kinetically controlled reactivity with its many metastable compounds and allotropes—a world which gives chemistry much of its variety and fascination. While the information they contain on the equilibrium interactions within a chemical system is extremely valuable, they should never be mistaken for a complete picture of the system's known chemistry as unintentionally implied by the title of at least one such recent compilation (50).

### Forgetting Once Again?

I first became interested in the subject of kinetic versus thermodynamic control of competitive chemical reactions when, as a young assistant professor at the Rochester Institute of Technology, I was assigned the task of developing a laboratory course in inorganic

synthesis. Among the preparations selected for use were several that involved the synthesis of various coordination isomers and it occurred to me that it would make an interesting exercise for the students to deduce which isomer was the thermodynamic product and which the kinetic product and how manipulation of the reaction conditions favored one over the other. Though this distinction lies at the very foundations of chemical theory and is one of the most fundamental questions that can be asked about a chemical reaction, I quickly discovered that the inorganic synthesis literature was all but silent on this issue. The various preparations given in typical lab manuals were presented as rote recipes to be followed, with little or no rationale as to how they were originally discovered or optimized or how they illustrated the application of the theoretical principles presumably learned in an earlier course on physical chemistry.

I had much the same experience several years later when writing a history of chemistry. In tracing the history of photochemistry, I discovered that much of the early theory in this field was based on supposed analogies with the process of electrolysis (54). In this latter process the applied electrical energy is being used to drive an otherwise thermodynamically unfavorable reaction uphill. Yet in many photochemical processes the applied light energy is obviously acting as a source of activation energy to initiate a thermodynamically favorable but otherwise kinetically inert reaction, such as that between dihydrogen and dichlorine gas. Just what was going on in the newer field of organic photochemistry was not so obvious, so I asked a colleague, who was an expert in the field, whether the majority of the reactions he worked with were thermodynamically allowed, but kinetically inert, and thus being photochemically activated, or whether they were thermodynamically unfavorable and were being photochemically driven uphill. The response was a blank look, as though the question made no sense, and an eventual admission that he had never thought about it one way or another as his focus was totally on the nature of the photochemically excited state and the details of the subsequent reaction mechanism.

Even more disturbing was a more recent incident involving the supposed preparation of  $\text{HgF}_4(\text{g})$  using matrix isolation (55). I had previously written a paper pointing out that Zn, Cd and Hg were really main-block, rather than transition-block, elements since they never made use of either d-electrons or empty d-orbitals in their bonding (56), and the possible existence of mercury in a IV oxidation state obviously contradicted this conclusion. This was once again a case of competitive reactions, this

time involving the formation of  $\text{HgF}_2$  versus  $\text{HgF}_4$  rather than alternative isomers or polymorphs, and in my subsequent commentary I pointed out that the latter species, if it actually existed, must be a kinetically metastable reaction intermediate whose detection was made possible only by the fact that the extremely low temperature used ( $4^\circ\text{K}$ ) kinetically inhibited its dissociation (and isomerization when relevant) and the surrounding rare-gas matrix provided a diffusion barrier which kinetically inhibited molecular collisions among the various reactants and products and thus prevented polymerization (and disproportionation when relevant) (57). In this case inhibition of polymerization was key, as the supposed preparation theoretically depended on the favorable competitive formation of a monomeric  $\text{HgF}_4(\text{g})$  molecule versus that of an isolated monomeric  $\text{HgF}_2(\text{g})$  molecule and rapidly became unfavorable once the  $\text{HgF}_2$  monomer was allowed to polymerize into the far more stable 8/4 infinite framework structure that  $\text{HgF}_2$  normally adopts at all temperatures below  $919^\circ\text{K}$ .

All of this raised the further fundamental question of whether such transient species represented typical chemical behavior and whether they should be taken into account when classifying elements in the periodic table. However, when discussing the manuscript of the commentary with a colleague who specialized in matrix isolation, and in a subsequent e-mail correspondence with one of the coauthors of the original paper, both expressed great surprise that I had characterized the reported product as a transient kinetically metastable species and had interpreted the rare-gas matrix as a device for kinetically inhibiting polymerization. Though subsequent work failed to reproduce the reported species, the puzzlement that I encountered once again illustrated a widespread failure to explicitly think in terms of kinetic versus thermodynamic factors when dealing with chemical reactivity—a failure all the more disturbing as it involved specialists using a technique explicitly designed to optimize kinetic control.

Although admittedly anecdotal, such incidents would appear to bode ill for the prospect of making the concepts of kinetic versus thermodynamic control an inherent part of every chemist's thinking about competitive chemical reactions, whether they lead to alternative isomers, alternative polymorphs, or alternative oxidation states, and suggests that, once physical organic chemistry ceases to be a cutting-edge field and fades from the curriculum, its textbooks and lessons, like those of both affinity theory and phase science before it, will also fade from the chemical consciousness only to be rediscovered once again in some future context.

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### 2014 HIST Election Results

Congratulations to the winners of 2014 HIST division elections.

- Chair-Elect (Term 2015-2016): Ronald Brashear
- Secretary/Treasurer (Term 2015-2016): Vera Mainz
- Councilor (Term 2015-2017): Mary Virginia Orna
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As 2014 comes to an end, Ned Heindel ends his term as HIST Chair, replacing E. Thomas Strom in the Past Chair seat on the Executive Committee. Gary Patterson succeeds Heindel as Chair, and Brashear succeeds Patterson as Chair-Elect.