The Importance of Kinetic Metastability:
Some Common Everyday Examples

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The chapter on thermodynamics in the typical freshman textbook is likely to leave students with the erroneous impression that the only requirement for a spontaneous chemical reaction to occur is a negative value for the resulting free-energy (ΔG_{rx}) change. While this is certainly a necessary requirement for a favorable reaction, it is not a sufficient requirement, since the reaction in question may also happen to be kinetically metastable or inert – a condition which, unlike thermodynamic stability, cannot be predicted using a simple pen and paper calculation suitable for an introductory chemistry course.

Unfortunately, this misconception is reenforced by the widespread use of the phrase "thermodynamically spontaneous" as a synonym for "thermodynamically favorable." While it is true that the word "spontaneous" does not mean the same thing as "instantaneous," it does imply that the process in question is self-initiating or, in the words of Webster, that it "arises without external constraint or stimulus." This is not the case for thermodynamically favored but kinetically metastable reactions, since they require, by definition, an "external stimulus" in the form of either an external source of activation energy or the addition of a suitable catalyst before proceeding.

Kinetic metastability is neither rare nor unusual. In fact, an incredible number of chemical compounds and allotropic modifications of simple substances owe their continued existence to this phenomenon. Of course, it is meaningless to talk of a species as being either inherently thermodynamically stable or kinetically metastable. These terms must always be used with reference to a specific chemical reaction and set of reaction conditions. When evaluating whether a given species can be prepared and stored in bulk under normal laboratory conditions, at least five such reactions must be evaluated with respect to their thermodynamic feasibility at room temperature and pressure (RTP): oxidation, hydrolysis, internal decomposition, polymerization, and isomerization (1). If the species in question is found to be thermodynamically unstable with respect to one or more of these, but can still be prepared and stored in bulk, then it may be safely inferred that it is kinetically metastable with respect to the process or processes in question.

In what follows, we will first provide a brief discussion, with examples, of the relevance of kinetic metastability to each of the above five processes, followed by a more detailed discussion of three common household chemicals that owe both their existence and/or commercial use to this often neglected phenomenon. We will conclude with a brief discussion of the status of the metastability concept in the typical chemistry textbook. In all cases, whether dealing with pure substances or solutions, we will assume that we can evaluate the sign of ΔG using the sign of the corresponding standard-state free energy change ($\Delta G°$), since we are only interested its sign and not necessarily in its precise numerical value (2, 3).

Oxidation

Essentially all organic compounds that can be stored and/or manipulated in the presence of air are thermodynamically unstable, but kinetically metastable, with respect to oxidation at RTP – the simplest example being the combustion of methane or natural gas (2):

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta G° = \text{-817.95 kJ/mol rx} \quad [1]$$
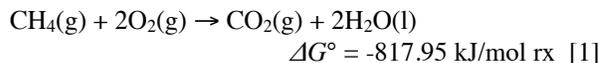
Though such materials are said to be to be flammable, they usually require an external source of activation energy in the form of either a flame or spark before oxidation can commence.

The same is also true of virtually all of the metals from which we fabricate so many everyday items – the most obvious example being the rusting of iron:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$
$$\Delta G° = \text{-1487.22 kJ/mol rx} \quad [2]$$
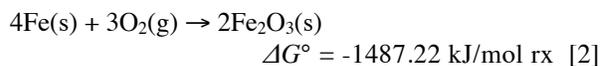
Though this reaction does occur at RTP, it does so quite slowly and then only in the presence of moisture.

For most metals this kinetic metastability is a function of the low surface to volume ratio found in everyday metal objects but rapidly disappears when the metals are finely powdered, in which case they frequently become pyrophoric.

Less often appreciated is the fact that many halide and chalcide salts are also thermodynamically unstable, but kinetically metastable, with respect to oxidation at RTP, though chemists manipulate them with impunity in the air – typical examples being the oxidation of either copper iodide or zinc sulfide:

$$2CuI(s) + O_2(g) \rightarrow 2CuO(s) + I_2(s)$$
$$\Delta G° = -128.8 \text{ kJ/mol rx} \quad [3]$$

$$2ZnS(s) + O_2(g) \rightarrow 2ZnO(s) + 2S(s)$$
$$\Delta G° = -274.64 \text{ kJ/mol rx} \quad [4]$$
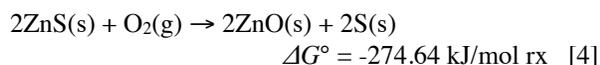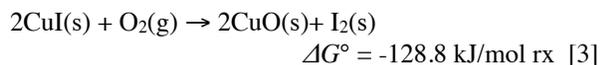
Hydrolysis

Exposure to the air means contact not only with dioxygen gas but also with water vapor. Indeed, water, as both a vapor and liquid, is ubiquitous in both nature and most laboratory settings. Yet, once again, we encounter many substances which, though thermodynamically unstable at RTP with respect to hydrolysis or reaction with water, may be handled with impunity in its presence due to kinetic metastability. A typical example is the liquid, carbon tetrachloride, which can be used to extract organic materials from aqueous solutions in a separatory funnel and which was once sold as a common household spot remover:

$$CCl_4(l) + 2H_2O(l) \rightarrow CO_2(g) + 4HCl(g)$$
$$\Delta G° = -236.48 \text{ kJ/mol rx} \quad [5]$$
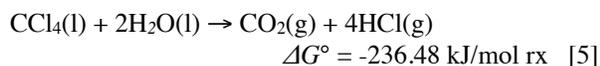
A more spectacular example is metallic aluminum, which is even more thermodynamically unstable with respect to reaction with water at RTP than are the alkali metals:

$$2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 3H_2(g)$$
$$\Delta G° = -870.77 \text{ kJ/mol rx} \quad [6]$$
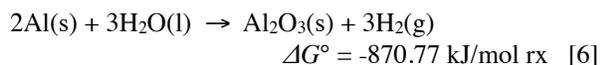
Here kinetic metastability is the result of the formation of a coherent microfilm of $Al_2O_3(s)$ on the surface of the metal that protects it from further reaction with water and air, thus allowing us to use it for the manufacture of everything from beer cans to airplanes.

Internal Decomposition

Substance that are both thermodynamically allowed and kinetically reactive with respect to oxidation and/ or hydrolysis at RTP can, of course, alway be prepared on a vacuum line or in a glove box and stored in evacuated and hermetically sealed glass containers. But even then, these materials may still be thermodynamically unstable with respect to internal decomposition of some sort and can thus exist only if they also happened to be kinetically metastable with respect to these processes.

A good example is the compound, diborane, which must be protected from contact with both dioxygen gas and water, but which is also thermodynamically unstable, but kinetically metastable, with respect to dissociation into its component simple substances at RTP:

$$B_2H_6(g) \rightarrow 2B(s) + 3H_2(g)$$
$$\Delta G° = -173.2 \text{ kJ/mol rx} \quad [7]$$
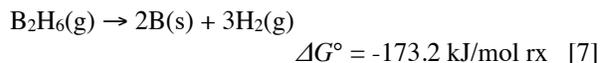
Even more common than decomposition via dissociation is decomposition via disproportion, a process in which a compound having an intermediate oxidation state decomposes into two products – one having a lower oxidation state and the other a higher oxidation state – as illustrated by the kinetically metastable compound titanium triiodide:

$$2TiI_3(s) \rightarrow TiI_2(s) + TiI_4(s)$$
$$\Delta G° = -44.3 \text{ kJ/mol rx} \quad [8]$$
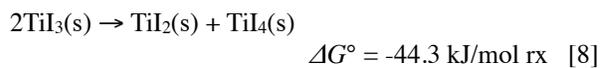
in which half of the Ti(III) is reduced to Ti(II) and half is oxidized to Ti(IV).

Polymerization

Even when a substance is kinetically and/or thermodynamically protected from internal decomposition, yet other processes may still be capable of compromising its existence. Thus white tetraphosphorus is thermodynamic unstable, but kinetically metastable, with respect to polymerization to red phosphorus at RTP:

$$xP_4(s) \rightarrow (P_4)_x(s)$$
$$\Delta G° = -12.12 \text{ kJ/mol rx} \quad [9]$$

Though red phosphorus is amorphous, and hence lacking a crystal structure, it has long been assumed to be composed of infinite chains of some sort produced by linking the discrete tetrahedral molecules of white phosphorus together via the opening of one or more of their edge bonds.

Both white and red phosphorus are also thermodynamically unstable with respect to oxidation at RTP, but whereas white phosphorus is kinetically labile and must be stored under water to protect it from contact with air, red phosphorus is kinetically metastable and

may be handled and stored in its presence. Ironically, the use of water to protect white phosphorus from air oxidation is yet another instance of kinetic metastability, since white phosphorus is also thermodynamically unstable with respect to hydrolysis:

$$P_4(s) + 16H_2O(l) \rightarrow 4H_3(PO_4)(aq) + 10H_2(g)$$
$$\Delta G° = \text{-677.55 kJ/mol rx} \quad [10]$$
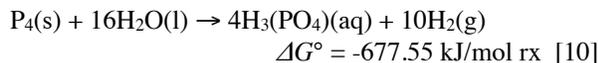
Isomerization

The fifth and last method of compromising the existence of a species is the possibility of internal rearrangement or isomerization. A particularly striking example is the kinetic metastability of diamond, which is thermodynamically unstable at RTP with respect to rearrangement to graphite:

$$C \text{ (diamond)} \rightarrow C \text{ (graphite)}$$
$$\Delta G° = \text{-2.83 kJ/mol rx} \quad [11]$$

a situation that has caused more than one chemical wag to comment on the irony of using diamond engagement and wedding rings as symbols of eternal love. Even more numerous examples are found among the thousands of isomers that have been prepared by the organic chemist since, within any given set of isomers, one of them must be thermodynamically more stable than the others (3).

Hydrogen Peroxide Solution

Moving on to our everyday household examples, we begin with a product found in most bathroom medicine cabinets – a bottle of a 3% aqueous solution of hydrogen peroxide, $H_2(O_2)$ (figure 1), commonly used for cleaning cuts and scraps (4). This compound is already oxidized, is thermodynamically stable with respect to reaction with water, and neither polymerizes nor isomerizes. Since it has a negative free-energy of formation, it is also thermodynamically stable with respect to dissociation into its component simple substances:

$$H_2(O_2)(l) \rightarrow H_2(g) + O_2(g)$$
$$\Delta G° = \text{+120.41 kJ/mol rx} \quad [12]$$
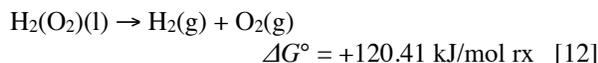
Nevertheless, it turns out that it is thermodynamically unstable with respect to disproportionation into water and dioxygen gas :

$$2H_2(O_2)(l) \rightarrow 2H_2O(l) + O_2(g)$$
$$\Delta G° = \text{-233.54 kJ/mol rx} \quad [13]$$
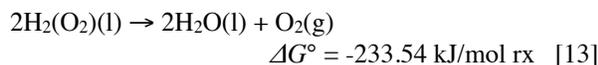
Figure 1. A typical bottle of 3% hydrogen peroxide.

a process in which half of the oxygen in the peroxide anion is oxidized from O(-I) to O(0) and half is reduced from O(-I) to O(-II).

Since it is possible to purchase a bottle of a 3% aqueous solution of hydrogen peroxide at your local drug store and keep it for some time in your medicine cabinet, reaction 13, though thermodynamically allowed, must be kinetically inhibited. In other words, hydrogen peroxide must be kinetically metastable with respect to disproportionation into water and dioxygen gas at RTP. Here, as mentioned earlier, we are assuming that, though the value of ΔG for the decomposition of a dilute solution of hydrogen peroxide will differ numerically from the value of $\Delta G°$ in equation 13, which applies to the pure substance in its standard state, the sign of the free energy change will still be negative (3).

As already noted, when talking about metastability one must specify not only the nature of the reaction under consideration, but the reaction conditions as well. If the latter are altered so as to enhance the rate of reaction, the species in question may well disappear in accord with the dictates of its thermodynamics. In general, at least four factors must be considered when attempting to preserve a kinetically metastable chemical, all of which are relevant when it comes to working with hydrogen peroxide (6):

1. Sensitivity to concentration
2. Increases in temperature
3. Contact with catalysts
4. Exposure to light

The first of these factors is only relevant when dealing with gases and solutions, rather than pure substances (7), but this is precisely the case with hydrogen peroxide which is almost always in the form of an aqueous solution of some sort, ranging from the 3% solution found in drug stores, to the 30% solution normally used in chemical laboratories, to various industrial grades approaching concentrations of 90% and greater. As might be anticipated from the basic principles of chemical kinetics, the more dilute the solution, the slower the rate of reaction 13, thus making the dilute solution in your medicine cabinet less susceptible to disproportionation than the more concentrated laboratory and industrial grades.

An increase in temperature almost always increases the rate of a chemical reaction and reaction 13 is no exception. Indeed, it almost perfectly follows the traditional rule of thumb that the rate of a reaction will double with each 10° C increase in temperature (6). For the dilute solution in your medicine cabinet, storage at room temperature is generally sufficient, but for the preservation of more concentrated solutions refrigeration is recommended.

Figure 2. A typical bottle of household bleach.

Many substances are able catalyze reaction 13, including hemoglobin, transition metal ions, halide ions, many enzymes, and even rough surfaces that can provide nucleation sites for the formation of dioxygen gas bubbles. Protection of hydrogen peroxide solutions from contamination with trace amounts of these catalytic agents is perhaps the greatest challenge when it comes to prolonging its existence. With this in mind, most hydrogen peroxide solutions contain small amounts of other chemicals called "stabilizers" that have been added on purpose. These may range from organic additives, such 8-hydroxyquinoline and acetanilide, to inorganic additives, such as sodium stannate and sodium pyrophosphate. The assumption seems to be that these materials are somehow able to deactivate potential trace catalysts, through there seems to be little consensus concerning their mode of operation or even over the question of whether they are truly effective (6). Both laboratory experiments and classroom demonstrations illustrating the catalytic decomposition of hydrogen peroxide by such materials as $MnO_2(s)$, activated charcoal, or saturated KI solutions are relatively easy to locate on the internet.

The fourth and final factor listed above is seldom discussed in freshman chemistry treatments of chemical kinetics, since not all reactions are photochemically sensitive. However, reaction 13 is, and especially to UV light. For this reason the hydrogen peroxide in your medicine cabinet traditionally came in a dark brown glass bottle, though this has now been largely replaced with opaque plastic containers instead.

If all of the above precautions are followed, at least one commercial manufacturer of hydrogen peroxide was willing to claim on its website that "the losses of hydrogen peroxide will be very slight even during extended periods (years) of storage."

Household Bleach

For our second everyday household example, we move to the laundry room and examine the bottle of so-called chlorine bleach (figure 2). Its label indicates that it actually contains a 8.25% solution of sodium hypochlorite, Na(OCl), as the active ingredient (8). In addition, it also contains some sodium chloride and sodium hydroxide. These are in fact the remnants of its mode of manufacture, since it is not made by directly dissolving pure solid sodium hypochlorite in water but rather by bubbling dichlorine gas through an aqueous solution of sodium hydroxide (9):

$$2Na(OH)(aq) + Cl_2(g) \rightarrow$$
$$Na(ClO)(aq) + NaCl(aq) + H_2O(l)$$
$$\Delta G° = -90.45 \text{ kJ/mol rx} \quad [14]$$
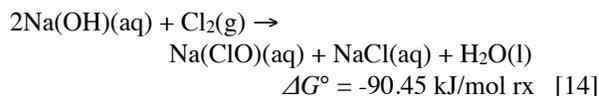
Though pure Na(OCl)(s) can also be prepared, it is presumably completely ionized in aqueous solution, so that our concern here is rather with the stability of the ClO^-(aq) anion instead. This is thermodynamically stable with respect to direct reaction with the dioxygen gas in air:

$$ClO^-(aq) + O_2(g) \rightarrow ClO_3^-(aq)$$
$$\Delta G° = +33.5 \text{ kJ/mol rx} \quad [15]$$
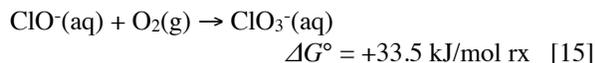
as well as with respect to hydrolysis:

$$ClO^-(aq) + H_2O(l) \rightarrow H(ClO)(aq) + OH^-(aq)$$
$$\Delta G° = +36.79 \text{ kJ/mol rx} \quad [16]$$

and, in any case, the high pH of the commercial solution, due to the slight excess of Na(OH)(aq) present, further guarantees that this equilibrium will be displaced far to the left, though the reverse will happen if the bleach is diluted with large amounts of water.

Nor are there issues with polymerization and isomerization. Rather it is two thermodynamically favorable modes of decomposition at RTP that are of most concern. The first of these involves disproportionation to the chloride and chlorate anions:

$$3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-(aq)$$
$$\Delta G° = -155.01 \text{ kJ/mol rx} \quad [17]$$
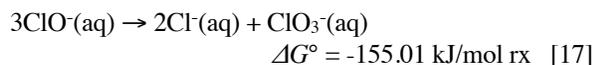
in which two-thirds of the Cl(I) is reduced to Cl(-I) and one third is oxidized to Cl(V). The second reaction involves decomposition into chloride ion and dioxygen gas:

$$2ClO^-(aq) \rightarrow 2Cl^-(aq) + O_2(g)$$
$$\Delta G° = -184.51 \text{ kJ/mol rx} \quad [18]$$
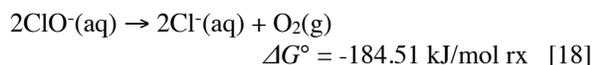
in which Cl(I) is reduced to Cl(-I) and O(-II) is oxidized to O(0). Though reaction 18 is thermodynamically more favorable than reaction 17, the latter reaction is less kinetically metastable at RTP and accounts for over 90% of the decomposition observed over time in commercial bleach solutions at RTP (10). As with the earlier hydrogen peroxide solution, in the above analysis we are assuming that the sign of the actual ΔG values for corresponding reactions of the dilute bleach solution are the same as the sign of the $\Delta G°$ values for a standard state solution (3).

The same four factors that affected the metastability of hydrogen peroxide with respect to reaction 13 also affect the metastability of our hypochlorite solution with respect to reactions 17 and 18. Thus the more concentrated the solution and the higher the temperature, the greater the rate of decomposition. Likewise,

these reactions are sensitive to UV light and for this reason bleach was originally sold in dark brown glass bottles, though it now comes in opaque plastic containers. In keeping with these factors, the label on the bleach bottle instructs the user to "store this product in a cool, dry area, away from direct sunlight and heat to avoid deterioration." Reaction 18 in particular is also catalyzed by various transition metal ions and several laboratory experiments illustrating this phenomenon are available on line, though this problem doesn't seem to be as serious a concern as was the case with hydrogen peroxide (11).

Carbonated Water

For our third and final everyday example we move to the kitchen refrigerator and examine a bottle of soda. In order to avoid any complications due to coloring, flavoring, or sweetening agents, we will select a bottle of seltzer water (figure 3), which is a simple solution of carbon dioxide in water (12). Though there are also small amounts of carbonic acid, bicarbonate anion, and H^+(aq) present due to hydrolysis:

$$CO_2(aq) + H_2O(l) \rightarrow H_2(CO_3)(aq) \rightarrow$$
$$H^+(aq) + HCO_3^-(aq) \quad [19]$$
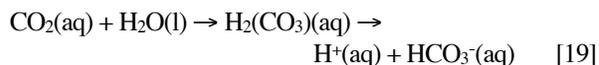
CO_2(aq) is by far the dominant species in solution and

Figure 3. Typical bottles of carbonated water or seltzer.

is the only one of interest to us as it is primarily responsible for the fizz that we associate with carbonated beverages. In other words, when considering the level of carbonation, we are primarily concerned with the simple equilibrium:

$$CO_2(aq) \rightarrow CO_2(g) \qquad \Delta G° = \text{-8.18 kJ/mol rx} \quad [20]$$
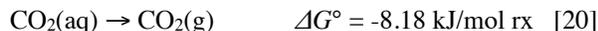
where once again we are assuming that the sign of the actual ΔG value for corresponding reaction of the commercial carbon dioxide solution is the same as the sign of the $\Delta G°$ value for a standard state solution (3).

At room temperature the dissolved carbon dioxide in a sealed can or bottle of carbonated water is in equilibrium with the small volume of gaseous carbon dioxide above the liquid, which is usually set at an average pressure of roughly 2.5 atm, and is thus thermodynamically stable. When the can or bottle is opened, however, this is no longer true as the ambient carbon dioxide pressure rapidly falls to the value of the partial pressure of carbon dioxide in the surrounding air. This is approximately 3.9×10^{-4} atm or roughly 10,000 times less than that in the sealed container (13). Thus, on opening the container, the equilibrium in equation 20 is subjected to a massive Le Chatelier perturbation, which shifts it far to the right, with the result that, when it finally reequilibrates, it has lost most of its detectable fizz.

Indeed, carbonated water approximately obeys Henry's law for the solubility of gases in liquids, which states that, at constant temperature, the concentration of the dissolved gas (C_g) is directly proportional to the partial pressure (P_g) of the gas above the liquid:

$$P_g = kC_g \qquad\qquad [21]$$

This means, of course, that once the carbonated water equilibrates with the atmosphere, the concentration of the dissolved carbon dioxide will also be roughly 10^{-4} or 10,000 times less than that in the unopened can or bottle.

Luckily the rate at which reaction 20 re-equilibrates is relatively slow so that, despite the initial release of dissolved carbon dioxide on opening the container, it takes roughly a half hour or so for the level of carbonation, on exposure to the atmosphere, to fall to a level where the liquid has lost sufficient fizz so as to be declared "flat" and several hours more before it finally comes to equilibrium with the ambient carbon dioxide pressure. Thus, strongly carbonated beverages in an open container or glass are in effect metastable and, if not for the intervention of sluggish kinetics, we would not have the pleasure of drinkable carbonated beverages.

In keeping with this, anything that increases the rate of re-equilibration will also increase the rate at which the carbonation is lost and thus diminish the period of metastability – whence the well-known fact that the warmer the beverage the quicker it loses its fizz. Likewise, rough surfaces that can act as nucleation sites for the formation of carbon dioxide gas bubbles are able to catalyze the rate of decarbonation, as may be demonstrated by dropping some activated charcoal or, better still, a "Mentos" candy mint into a bottle of seltzer water. As may be inferred from the fact that carbonated beverages often come in clear glass or plastic bottles, reaction 20 is fortunately not particularly sensitive to either visible or UV light.

There are, however, some significant differences between this example and our earlier examples, not the least of which is the much shorter time frame. Nevertheless it serves to further underscore the necessity of tempering purely thermodynamic considerations with a knowledge of the relevant kinetic factors, as well as calling attention to the fact that the metastability concept is both time dependent and the subject of a ongoing debate over how to best define it.

The definition problem was already discussed by Lewin many years ago (14). After first noting that use of the term had become broader and broader with the passage of time, this author advocated limiting it to its original usage in the phase literature to describe phases no longer in equilibrium with their environment but which could be induced to transform into the proper equilibrium phase only by addition of an appropriate seed crystal. To deal with yet other kinds of what he called "nonstability," Lewin proposed a five-category classification, which, besides metastable states in this very limited sense, also included unstable states, pseudo-stable states, quasi-stable states and meso-stable states. According to this classification – which to the best of my knowledge has never gained widespread acceptance – the re-equilibrating carbonated water is actually an example of an unstable system and the hydrogen peroxide and bleach solutions are examples of a pseudo-stable system. However, in keeping with the above comment on the role of time, the sole difference between these two classes, according to Lewin, was their rate of transformation, with unstable states "undergoing continuous transformation into states possessing lower free energy content," and pseudo-stable states only appearing to be in equilibrium, but "nevertheless slowly, or very slowly, changing continuously into lower free energy states."

In contrast, Luisi, in a study of the formation of micelles and vesicles, concluded that "metastable states are kinetic traps" which, once surmounted, need not necessarily lead to a true equilibrium state (15).

This definition is much broader than that of Lewin and is much closer to the concept of metastability used in this paper, where we have used the term to denote any thermodynamically unstable substance that persists, for kinetic reasons, for a sufficiently long time period so as to have practical commercial applications. Nevertheless, because of the difference in the time frame and lack of external stimulus, some readers may feel that the example of the re-equilibrating carbonated water is better thought of as a case of simple thermodynamic instability coupled with relatively sluggish kinetics.

Metastability in the Textbook Literature

The concept of kinetic metastability was first introduced by Wilhelm Ostwald in 1897 in connection with his studies of kinetically inhibited phase changes and by 1909 he had extended it to the case of conventional chemical reactions as well (16). Both the topic and term were mentioned in most monographs on the phase rule and in most chemical dictionaries written prior to the 1960s, but references to these traditional applications have since become increasingly rare. To the extent that the terms "metastable and/or metastability" appear in current physical chemistry textbooks, they are used instead to describe either excited spectroscopic states or reaction intermediates with prolonged lifetimes. In no case could I find the terms listed in the indices of introductory chemistry textbooks or in more recent chemical dictionaries.

In their chapters on chemical thermodynamics, some of the more detailed freshman textbooks, after first defining spontaneous as a process that proceeds without external assistance, do admit that many so-called spontaneous reactions actually require an external source of activation energy before proceeding, and at least one gave an example of a thermodynamically allowed process (the dissociation of benzene into its component simple substances) for which the activation barrier was so high that it essentially never occurred. But these few explicit examples are isolated and never generalized under the rubric of kinetic metastability, thus leaving the student with the false impression that they are relatively uncommon.

However, as has hopefully been demonstrated in this paper, such examples are anything but rare and every introductory textbook discussion of chemical thermodynamics should include a cautionary section dealing with the phenomenon of kinetic metastability and its role in creating chemical diversity in both the laboratory and the world at large. Though we have limited ourselves to examples of metastable molecules and ions, the phenomenon is actually more widespread. Thus Everett has emphasized the importance of meta-

stability in preparing colloidal dispersions that are thermodynamically unstable with respect to coalescence into their component bulk phases (17), and Cahn has singled out its importance in the field of materials science with respect to the preparation of unusual alloy phases with unique properties (18). The same is equally true of various glasses, all of which are metastable relative to the corresponding crystalline solids (19).

In keeping with this, use of the misleading descriptors "thermodynamically spontaneous and non-spontaneous" should be eliminated and replaced by a less suggestive terminology, such as "thermodynamically allowed and disallowed" or "thermodynamically feasible and unfeasible" (20). I am hardly the first to object to the restricted thermodynamic use of the word spontaneous. Ochs, for example, has presented a detailed list of reasons for why the term should be eliminated, not only from thermodynamics, but from chemical discourse in general (21). In contrast, Luisi has argued for retaining it in chemical discourse but decoupling it from its restricted thermodynamic sense by adding a kinetic component as well so as to describe a reaction that is both thermodynamically and kinetically favored – a usage that would more closely match its everyday meaning (15). Lastly, Earl has argued for retaining the word in its restricted thermodynamic sense but always coupling it with the qualifier "thermodynamic" in order to explicitly indicate that it is being used in a special way (22).

Personally, I have come to prefer the descriptors "thermodynamically favored and disfavored" and have used them throughout this paper. This is because the condition $\Delta G > 0$ does not mean – at least in the case of reversible reactions – that absolutely no reaction will occur in the direction indicated but only that the reaction as written is not favored by the thermodynamics of the situation and therefore will not be as extensive as the reverse reaction. For example, the phase change:

$$Hg(l) \rightarrow Hg(g) \qquad \Delta G° = +31.9 \text{ kJ/mol rx} \qquad [21]$$

is thermodynamically disfavored at RTP, yet sufficient Hg evaporates so as to constitute a potential health hazard in the case of laboratory mercury spills. In short, a terminology based on the word "favored" is less rigid in its unintended implications than is one based on such words as "spontaneous," "allowed" or "feasible."

As for the term "kinetically metastable," I have chosen to use it because of historical precedent. The only alternative I am aware of are the descriptors "kinetically labile and kinetically inert," first introduced in 1952 by Henry Taube in connection with the study of

substitution reactions in transition-metal complexes (23). While I find the term "labile" useful, the term "inert" seems a bit extreme save for the most intractable cases of kinetic metastability, and the more neutral term "kinetically inhibited" may be a better alternative.

References and Notes

1. Standard-state thermodynamic data is usually listed at 25°C and 1 atm. I have chosen to abbreviate this as room temperature and pressure or RTP to differentiate from it from standard temperature and pressure or STP (0°C and 1 atm) normally used when working gas law problems.

2. Unless otherwise stated, all thermodynamic data is from A. J. Bard, R. Parsons, J. Jordan, Eds., *Standard Potentials in Aqueous Solutions*, Deker: New York, NY, 1984.

3. The only circumstance under which the signs of ΔG and $\Delta G°$ would differ would be if the $RTlnQ$ term in the equation $\Delta G = \Delta G° + RTlnQ$ is positive and sufficiently large to off set a negative value for $\Delta G°$ or vice versa. Since each ten fold increase in Q corresponds to only +5.7 kJ/mol at RTP, a many fold increase in Q, and thus a many fold decrease in the activities of the reactants, would be required to affect a reversal in the sign of ΔG versus that of $\Delta G°$. Given the observed behavior of the solutions discussed in this paper, this is obviously not the case. In addition, $\Delta G°$ values have the advantage that they can be unambiguously calculated from free energies of formation, whereas proper ΔG calculations for solution-gas reactions would rapidly mire one in issues of activities and fugacities versus concentrations and pressures, let alone experimental proof that the reactions in question are truly reversible – topics which are glossed over in the typical freshman text. Finally, since at equilibrium $\Delta G°$ equals $-RTlnK$, it also has the advantage of being a direct measure of the equilibrium constant, which tells us, in turn, how complete the reaction in question will be at equilibrium irrespective of its initial state.

4. M. L. Frenkel, G. Y. Kabo, G. N. Roganov, *Thermodynamic Properties of Isomerization Reactions*, Hemisphere Publishing: Washington, DC, 1993.

5. A more systematic name for this compound would be dihydrogen peroxide or, better still, dihydrogen polydioxide, which makes explicit the fact that the oxygen atoms are dimerized or bonded to one another. In keeping with this, the peroxide anion in the compound's molecular formula has also been enclosed in parentheses in order to emphasize that it is a distinct entity within the molecule and not two separate oxide anions.

6. An excellent summary of the older literature on this compound may be found in W. C. Scumb, C. N. Satterfield, R. L. Wentworth, *Hydrogen Peroxide*, Reinhold: New York, NY, 1955.

7. The concentration of gases and solutions may be varied at constant temperature and pressure whereas that of a pure solid or liquid substance at RTP cannot. However, application of high pressures can alter the mole to volume ratio of pure substances as well and raises the question of its potential effects on metastability, though this factor is not discussed here.

8. A more systematic name for this compound would be sodium oxochlorate. As with the peroxide anion, the discrete hypochlorite anion in the compound's formula has been enclosed in parentheses to emphasize that it is a distinct entity in which the chlorine and oxygen are bound to one another, thus differentiating it from a formula like that for gallium oxide chloride, GaOCl, in which they are not.

9. An excellent summary of the older industrial literature on this compound may be found in J. S. Sconce, Ed., *Chlorine: Its Manufacture, Properties and Uses*, Reinhold: New York, NY, 1962, Chapter 17.

10. *Sodium Hypochlorite – Stability*, PCH-1400-0007, Solvay Chemicals International: Brussels, 2005. Document available on line.

11. *Sodium Hypochlorite: General Information Handbook*, Powell Fabrication and Manufacturing: St. Louis, MI, 2002. Document available on line.

12. For background on carbonated beverages see M. B. Morris, *Manufacture and Analysis of Carbonated Beverages*, Chemical Publishing Co: New York, NY, 1959; and D. P. Steen, P. R. Ashurst, Eds., *Carbonated Soft Drinks: Formulation and Manufacture*, Blackwell: Oxford, 2006.

13. The atmosphere is roughly 3.9×10^{-2} percent carbon dioxide by volume. For gas mixtures at constant temperature and total pressure the volume fraction of a component is equal to its mole fraction, and this, in turn, is equal to its partial pressure when the total pressure is fixed at 1 atm.

14. S. Lewin, "Nonstable States," *J. Chem. Educ.*, **1953**, *30*, 136-138.

15. P. L. Luisi, "Are Micelles and Vesicles Chemical Equilibrium Systems?," *J. Chem. Educ.*, **2001**, *78*, 380-384.

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18. R. W. Cahn, *The Coming of Material Science*, Pergamon: Amsterdam, 2000, pp. 82-83.

19. See, for example, the popular account F. J. T. Maloney, *Glass in the Modern World: A Study in Materials Development*, Doubleday: Garden City, NY, 1968, pp. 13-18.

20. W. B. Jensen, "Reaction Feasibility and the Planck Function," *J. Chem. Educ.*, **2000**, *77*, 1411.

21. R. S. Ochs, "Thermodynamics and Spontaneity," *J. Chem. Educ.*, **1996**, *73*, 952-954.

22. B. L. Earl, "Thermodynamics and Spontaneity," *J. Chem. Educ.*, **1998**, *75*, 658-659.

23.   H. Taube, "Rates and Mechanisms of Substitution in Inorganic Complexes in Solution," *Chem. Rev.*, **1952**, *50*, 69-126. Ostwald also used the term labile as early as 1897.

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